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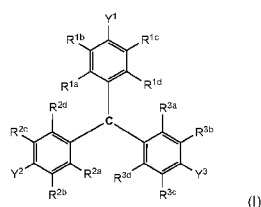
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(54) Title: MULTICYCLIC CARBOCATION AND CARBORADICAL COMPOUNDS AND METHODS OF USE



(I)

(57) Abstract: The present invention provides a compound comprising a moiety of the formula: (I) where said moiety of formula I is a radical, a cation, or a radical dication; Y^1 , Y^2 , Y^3 , R^{1a} , R^{1b} , R^{1c} , R^{1d} , R^{2a} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , R^{3c} , and R^{3d} are as defined herein. Compounds containing a moiety of Formula I are useful in a wide variety of applications including, but not limited to, as photocatalysts, use in OLEDs, in electronic components, etc. As an organic-based photocatalysts, compounds containing a moiety of Formula I are activated by a relatively low energy electromagnetic wavelength, e.g., wavelength of 600 nm or greater. Furthermore, compounds of the invention can be used as both photoreduction catalysts and photooxidation catalysts.

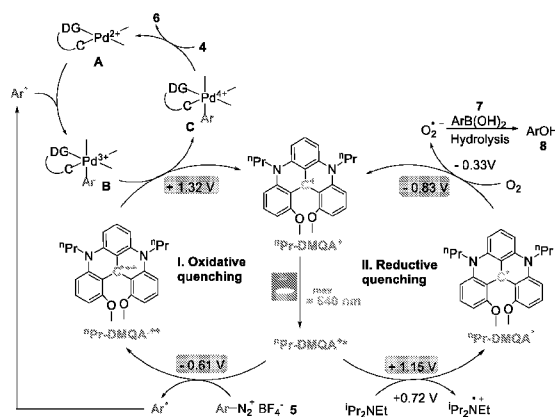


FIG. 5

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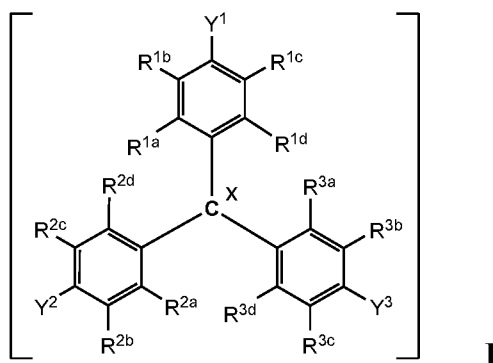
MULTICYCLIC CARBOCATION AND CARBORADICAL COMPOUNDS AND METHODS OF USE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the priority benefit of U.S. Provisional Application Nos. 62/968,880, filed January 31, 2020, and 63/025,915, filed May 15, 2020 which are incorporated herein by reference in their entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to multicyclic carbocation and carboradical compounds and methods of use. In particular, the present invention relates to a compound comprising a moiety of the formula:



where said moiety of Formula **I** is a radical, a cation, or a radical dication; “C^X” denotes central carbon; Y¹, Y², Y³, R^{1a}, R^{1b}, R^{1c}, R^{1d}, R^{2a}, R^{2b}, R^{2c}, R^{2d}, R^{3a}, R^{3b}, R^{3c}, and R^{3d} are as defined herein. Compounds containing a moiety of Formula **I** are useful in a wide variety of applications including, but not limited to, as photocatalysts. In particular, compounds containing a moiety of Formula **I** are activated by a relatively low energy electromagnetic wavelength, e.g., wavelength of 600 nm or greater.

BACKGROUND OF THE INVENTION

[0003] Molecular catalysis plays an important role in a wide variety of applications including, but not limited to, chemical reactions, photosynthesis, electron transfer (e.g., in photovoltaic cells), etc. Catalyst may be classified as either homogeneous or heterogeneous depending on whether the catalyst is dispersed in the same phase (usually gaseous or liquid) as the reactant's molecules or solvent. A heterogeneous catalyst is typically used as a solid catalyst that are often adsorbed onto the surface of a solid material.

[0004] Molecular metal-based photocatalysts (“PCs”) have many advantages as well as disadvantages. Some of the advantages of metal-based PCs include long half-life time, wide range of oxidation and reduction potential, ability to provide both oxidative quenching

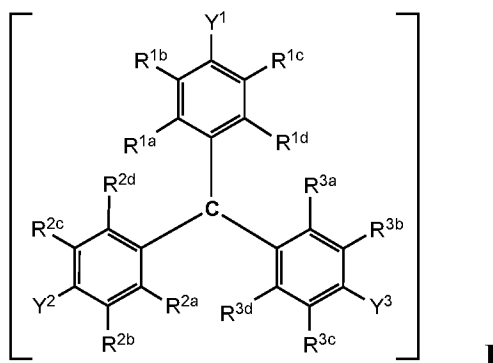
and reductive quenching. Unfortunately, many metal-based PCs are expensive, toxic, environmentally unfriendly, and require high energy electromagnetic radiation, typically in the blue-light region or higher energy (e.g., $h\nu$ of less than about 460 nm).

[0005] To overcome some of the disadvantages of metal-based PCs, organic-based PCs have recently been developed. These organic-based PCs have advantages of being less expensive and more environmentally friendly relative to metal-based PCs. Unfortunately, however, conventional organic-based PCs suffer from short-half life. Moreover, unlike metal-based PCs, organic-based PCs cannot be used to provide both oxidative quenching and reductive quenching. In addition, majority of organic PCs also require blue light or higher energy electromagnetic radiation for activation. While few organic PCs can use lower energy electromagnetic radiation for activation, such organic PCs are relatively difficult to synthesize and/or tune electromagnetic radiation wavelength for activation.

[0006] Therefore, there is a continuing need for organic-based PCs that can be activated with a relative low energy electromagnetic radiation, have a relatively longer half-life, environmentally friendly, and/or readily synthesized.

SUMMARY OF THE INVENTION

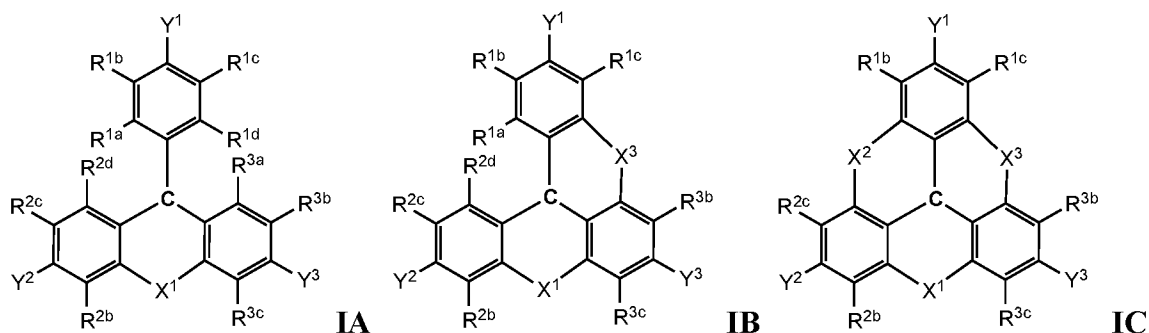
[0007] The present invention provides a radical, a cation, and a radical dication moieties that are useful in a wide variety of applications including, but not limited to, as photocatalysts and components in various electrochemical processes. One aspect of the invention provides a compound comprising a moiety of the formula I:



where said moiety is a radical, a cation, or a radical dication; each of R^{1a} , R^{1b} , R^{1c} , R^{1d} , R^{2a} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , R^{3c} , and R^{3d} is independently H, halide, haloalkyl (e.g., CF_3), $-NR^aR^b$ (each of R^a and R^b is independently H or C_1 - C_4 alkyl), C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, $-NO_2$, $-CN$, $-CO_2R$ (wherein R is H or C_1 - C_4 alkyl), or Ar^1 ; or R^{2a} and R^{3d} together form $-X^1-$; or R^{1a} and R^{2d} together form $-X^2-$; or R^{1d} and R^{3a} together form $-X^3-$; each of X^1 , X^2 and X^3 is independently O, NR^{4a} , PR^{4a} , $CR^{4a}R^{4b}$, or $SiR^{4a}R^{4b}$; or R^{1a} and R^{1b} together with atoms to which they are attached to form an optionally substituted aromatic ring (e.g., optionally

substituted phenyl); or R^{2c} and R^{2d} together with atoms to which they are attached to form an optionally substituted aromatic ring (e.g., optionally substituted phenyl); each of Y^1 , Y^2 , and Y^3 is independently H, OR^{5a} , $CR^{5a}R^{5b}R^{5b}$, $NR^{5a}R^{5b}$, $PR^{5a}R^{5b}$, NO_2 , CN, haloalkyl (e.g., CF_3), CO_2R , N_3 , or Ar^1 ; each of R^{4a} , R^{4b} , R^{5a} , and R^{5b} is independently H, halide, haloalkyl (e.g., CF_3), C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, $-NR^aR^b$ (provided at least one of R^a and R^b is C_1 - C_4 alkyl), Ar^1 , or a moiety of the formula $-L-Z$, where L is a linker; and Z is a heterocyclic species of Formula I (i.e., dimer, trimer, or other oligomers of formula I), a coordinating group able to bind or complex to a metal ion, or a water-soluble group such as phosphate, phosphite, sulfate or sulfite; and Ar^1 is optionally substituted aryl (e.g., optionally substituted phenyl) having from 0 to 5 substituents, each of which is independently selected from the group consisting of X^1 , haloalkyl (e.g., CF_3), NR^aR^b , C_1 - C_4 alkyl, and C_1 - C_4 alkoxy, heteroaryl, fused aryl or Ar^1 , provided when said Formula I is a cation then (i) when R^{2a} and R^{3d} together form $-X^1-$; R^{1a} and R^{2d} together form $-X^2-$; and R^{1d} and R^{3a} together form $-X^3-$, then no more than one of X^1 , X^2 , and X^3 is O; (ii) when R^{2a} and R^{3d} together form $-X^1-$, and R^{1a} and R^{2d} together does not form $-X^2-$; and R^{1d} and R^{3a} together does not form $-X^3-$, then at least one of R^{1a} , R^{1b} , R^{1c} , R^{1d} , or Y^1 is not H, halogen, or C_1 - C_{12} alkyl; (iii) at least one of (a) R^{2a} and R^{3d} together form $-X^1-$; (b) R^{1a} and R^{2d} together form $-X^2-$; or (c) R^{1d} and R^{3a} together form $-X^3-$; and (iv) when R^{2a} and R^{3d} together form $-X^1-$; R^{1a} and R^{2d} together form $-X^2-$; and R^{1d} and R^{3a} together form $-X^3-$, then none of X^1 , X^2 , and X^3 is NR^{4a} .

[0008] In some embodiments, Y^1 is $NR^{5a}R^{5b}$, $PR^{5a}R^{5b}$, haloalkyl (e.g., CF_3), N_3 , or Ar^1 . Yet in other embodiments, said moiety of Formula I is selected from the group consisting of:



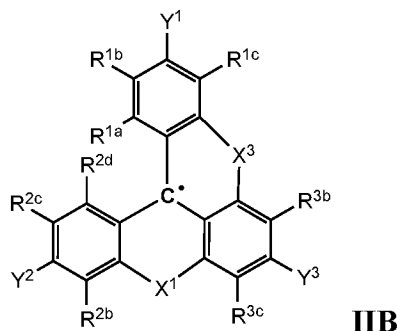
where Y^1 , Y^2 , Y^3 , X^1 , X^2 , X^3 , R^{1a} , R^{1b} , R^{1c} , R^{1d} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , and R^{3c} are those defined herein. Still in some embodiments, said moiety of Formula IB or IC is a radical or a radical dication. In further embodiments, X^1 is NR^{4a} .

[0009] In other embodiments, R^{4a} is a moiety of the formula $L-Z$. Yet in some embodiments, Z is a coordinating group selected from the group consisting of bipyridinyl,

pyridinyl, $-\text{PR}_2$, $-\text{OPR}_2$, $-\text{NHC}$, $-\text{NR}_2$, diimine, imine, $-\text{OH}$, $-\text{OR}$, $-\text{SR}$, $-\text{SH}$, diphosphines, $-\text{RNC}$, $-\text{CO}_2\text{H}$, and carboiimine, where each R is independently C_1 - C_{12} alkyl or Aryl. Still in other embodiments, L is C_1 - C_{10} alkylene, alkynylene, alkenylene, arylene, or heteroarylene.

[0010] Still in another embodiment, each of R^{1c} , R^{2c} , and R^{3c} is independently C_1 - C_4 alkoxy. Yet in another embodiment, Y, R^{1a} , R^{1b} , R^{2a} , R^{2b} , R^{3a} , and R^{3b} are H.

[0011] Another aspect of the invention provides a radical or a diradical cation moiety of the formula:



where each of R^{1a} , R^{1b} , R^{1c} , R^{2b} , R^{2c} , R^{2d} , R^{3b} , and R^{3c} is independently H, halide, haloalkyl (e.g., CF_3), $-\text{NR}^a\text{R}^b$, C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, $-\text{NO}_2$, $-\text{CN}$, $-\text{CO}_2\text{R}$ (wherein R is H or C_1 - C_4 alkyl), or Ar^1 ; or R^{1a} and R^{2d} together form $-\text{X}^2-$; each of R^a and R^b is independently H or C_1 - C_4 alkyl; each of X^1 , X^2 and X^3 is independently O, NR^{4a} , PR^{4a} , $\text{CR}^{4a}\text{R}^{4b}$, or $\text{SiR}^{4a}\text{R}^{4b}$; or R^{1a} and R^{1b} together with atoms to which they are attached to form an optionally substituted aromatic ring (e.g., optionally substituted phenyl); or R^{2c} and R^{2d} together with atoms to which they are attached to form an optionally substituted aromatic ring (e.g., optionally substituted phenyl); each of Y^1 , Y^2 , and Y^3 is independently H, OR^{5a} , $\text{NR}^{5a}\text{R}^{5b}$, $\text{PR}^{5a}\text{R}^{5b}$, NO_2 , CN , CF_3 , CO_2R , N_3 , or Ar^1 ; each of R^{4a} , R^{4b} , R^{5a} , and R^{5b} is independently H, halide, haloalkyl (e.g., CF_3), C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, $-\text{NR}^a\text{R}^b$ (provided at least one of R^a and R^b is C_1 - C_4 alkyl and provided R^{4a} is not attached to N), Ar^1 , or a moiety of the formula $-\text{L}-\text{Z}$, where L is a linker; and Z is a coordinating group able to bind or complex to a metal ion; and Ar^1 is optionally substituted phenyl having from 0 to 5 substituents, each of which is independently selected from the group consisting of X^1 , haloalkyl (e.g., CF_3), NR^aR^b , C_1 - C_4 alkyl, and C_1 - C_4 alkoxy.

[0012] In further embodiments, X^1 and X^3 are NR^{4a} , wherein R^{4a} is as defined herein. In some instances, each R^{4a} is independently C_1 - C_{12} alkyl or a moiety of the formula $-\text{L}-\text{Z}$. Yet in other instances, Z is selected from the group consisting of a heteroaryl, heterocyclyl, and a heteroatom functional group (e.g., NH_2 , etc.). In still other instances, Y^1 , Y^2 , and Y^3 are $\text{NR}^{5a}\text{R}^{5b}$, where each of R^{5a} and R^{5b} is independently H, haloalkyl (e.g., CF_3) or C_1 - C_{12}

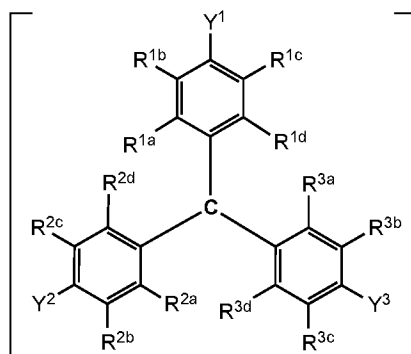
alkyl, provided at least one of R^{5a} and R^{5b} is not H. In other embodiments, R^{1a} and R^{2d} are C₁-C₄ alkoxy.

[0013] Yet another aspect of the invention provides a photocatalytic compound that for capable of catalyzing an oxidative reaction and a reductive reaction, said photocatalytic compound comprising a compound comprising a moiety of Formula I. In some embodiments, said photocatalytic compound is activated by an electromagnetic radiation having wavelength of 390 nm or greater.

[0014] Still another aspect of the invention provides a method for producing an oxidative product from a reaction substrate, said method comprising: contacting said reaction substrate with an oxidizing reagent, and a photocatalytic compound comprising a moiety of Formula I to produce a reaction mixture; and irradiating said reaction mixture with an electromagnetic radiation having a wavelength of 390 nm or greater under conditions sufficient to produce said oxidative product from said reaction substrate. In some embodiments, said method comprises an aerobic oxidative hydroxylation or aerobic oxygenation. In some instances, said aerobic oxygenation comprises oxygenation of benzylic carbon.

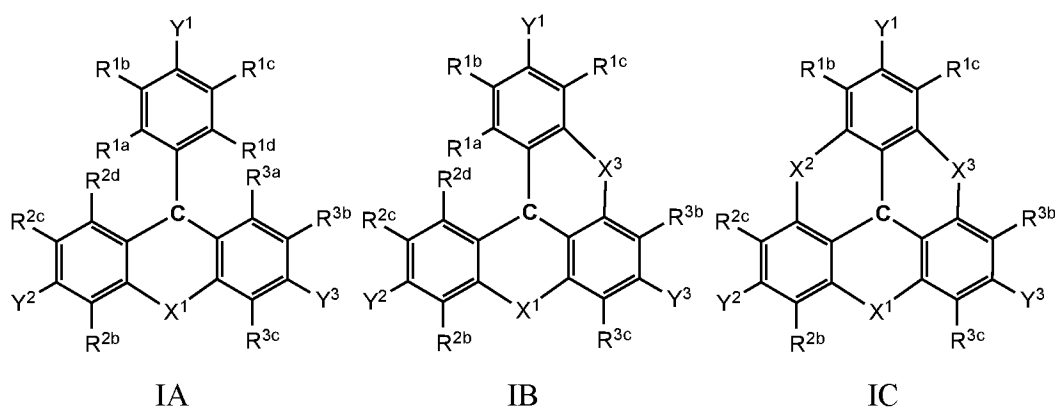
[0015] Another aspect of the invention provides a method for producing a reductive coupling product from a reaction substrate, said method comprising: contacting said reaction substrate with an oxidizing reagent, and a photocatalytic compound comprising a moiety of Formula I to produce a reaction mixture; and irradiating said reaction mixture with an electromagnetic radiation having a wavelength of 390 nm or greater under conditions sufficient to produce said reductive coupling product from said reaction substrate. In some embodiments, said method comprises dual catalysis arylation reaction of an sp²-carbon atom or atom transfer radical reaction (ATRA).

[0016] Still another aspect of the invention provides solid substrate having a surface, wherein said surface comprises a compound comprising a moiety of the formula:



where said moiety is a radical, a cation, or a radical dication; each of R^{1a} , R^{1b} , R^{1c} , R^{1d} , R^{2a} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , R^{3c} , and R^{3d} is independently H, halide, haloalkyl (e.g., CF_3), $-NR^aR^b$, C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, $-NO_2$, $-CN$, $-CO_2R$ (wherein R is H or C_1 - C_4 alkyl), or Ar^1 ; or R^{2a} and R^{3d} together form $-X^1-$; or R^{1a} and R^{2d} together form $-X^2-$; or R^{1d} and R^{3a} together form $-X^3-$; each of R^a and R^b is independently H or C_1 - C_4 alkyl; each of X^1 , X^2 and X^3 is independently O, NR^{4a} , PR^{4a} , $CR^{4a}R^{4b}$, or $SiR^{4a}R^{4b}$; or R^{1a} and R^{1b} together with atoms to which they are attached to form an optionally substituted aromatic ring (e.g., optionally substituted phenyl); or R^{2c} and R^{2d} together with atoms to which they are attached to form an optionally substituted aromatic ring (e.g., optionally substituted phenyl); each of Y^1 , Y^2 , and Y^3 is independently H, OR^{5a} , $CR^{5a}R^{5b}R^{5c}$, $NR^{5a}R^{5b}$, $PR^{5a}R^{5b}$, NO_2 , CN , CF_3 , CO_2R , N_3 , or Ar^1 ; each of R^{4a} , R^{4b} , R^{5a} , and R^{5b} is independently H, halide, haloalkyl (e.g., CF_3), C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, $-NR^aR^b$ (provided at least one of R^a and R^b is C_1 - C_4 alkyl), Ar^1 , or a moiety of the formula $-L-Z$, wherein L is a linker; and Z is a heterocyclic species of formula I (i.e., dimer, trimer, or other oligomers of formula I), a coordinating group able to bind or complex to a metal ion, or a water-soluble group such as phosphate, phosphite, sulfate or sulfite; and Ar^1 is optionally substituted aryl (e.g., phenyl) having from 0 to 5 substituents, each of which is independently selected from the group consisting of X^1 , haloalkyl (e.g., CF_3), NR^aR^b , C_1 - C_4 alkyl, and C_1 - C_4 alkoxy, heteroaryl, fused aryl or Ar^1 .

[0017] Yet in other embodiments, said moiety of Formula I is selected from the group consisting of:



wherein Y^1 , Y^2 , Y^3 , X^1 , X^2 , X^3 , R^{1a} , R^{1b} , R^{1c} , R^{1d} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , and R^{3c} are as defined herein. In some instances, said moiety of Formula IB or IC is a radical or a radical dication.

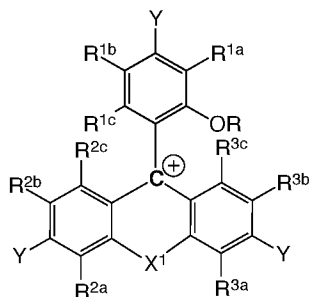
[0018] Still in other embodiments, when said moiety of Formula I is a cation then (i) when R^{2a} and R^{3d} together form $-X^1-$; R^{1a} and R^{2d} together form $-X^2-$; and R^{1d} and R^{3a} together form $-X^3-$, then no more than one of X^1 , X^2 , and X^3 is O; (ii) when R^{2a} and R^{3d}

together form $-X^1-$, and R^{1a} and R^{2d} together does not form $-X^2-$; and R^{1d} and R^{3a} together does not form $-X^3-$, then Y^1 is $NR^{5a}R^{5b}$, $PR^{5a}R^{5b}$, haloalkyl (e.g., CF_3), N_3 , or Ar^1 ; (iii) at least one of (a) R^{2a} and R^{3d} together form $-X^1-$; (b) R^{1a} and R^{2d} together form $-X^2-$; or (c) R^{1d} and R^{3a} together form $-X^3-$; and (iv) when R^{2a} and R^{3d} together form $-X^1-$; R^{1a} and R^{2d} together form $-X^2-$; and R^{1d} and R^{3a} together form $-X^3-$, then none of X^1 , X^2 , and X^3 is NR^{4a} .

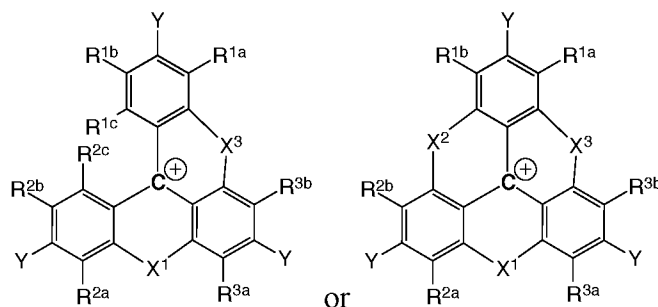
[0019] Yet another aspect of the invention provides a method for conducting a photocatalytic reaction, said method comprising contacting two or more reagents in the presence of a photocatalyst compound under conditions sufficient to produce a photooxidative product or a photoreductive product, wherein said photocatalyst compound comprises a moiety of Formula I, where said moiety of formula I is a radical, a cation, or a radical dication; each of R^{1a} , R^{1b} , R^{1c} , R^{1d} , R^{2a} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , R^{3c} , and R^{3d} is independently H, halide, haloalkyl (e.g., CF_3), $-NR^aR^b$, C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, $-NO_2$, $-CN$, $-CO_2R$ (wherein R is H or C_1 - C_4 alkyl), or Ar^1 ; or R^{2a} and R^{3d} together form $-X^1-$; or R^{1a} and R^{2d} together form $-X^2-$; or R^{1d} and R^{3a} together form $-X^3-$; each of R^a and R^b is independently H or C_1 - C_4 alkyl; each of X^1 , X^2 and X^3 is independently O, NR^{4a} , PR^{4a} , $CR^{4a}R^{4b}$, or $SiR^{4a}R^{4b}$; or R^{1a} and R^{1b} together with atoms to which they are attached to form an optionally substituted aromatic ring (e.g., optionally substituted phenyl); or R^{2c} and R^{2d} together with atoms to which they are attached to form an optionally substituted aromatic ring (e.g., optionally substituted phenyl); each of Y^1 , Y^2 , and Y^3 is independently H, OR^{5a} , $CR^{5a}R^{5b}R^{5c}$, $NR^{5a}R^{5b}$, $PR^{5a}R^{5b}$, NO_2 , CN , CF_3 , CO_2R , N_3 , or Ar^1 ; each of R^{4a} , R^{4b} , R^{5a} , and R^{5b} is independently H, halide, haloalkyl (e.g., CF_3), C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, $-NR^aR^b$ (provided at least one of R^a and R^b is C_1 - C_4 alkyl), Ar^1 , or a moiety of the formula $-L-Z$, where L is a linker; and Z is a heterocyclic species of formula I (i.e., dimer, trimer, or other oligomers of formula I), a coordinating group able to bind or complex to a metal ion, or a water-soluble group such as phosphate, phosphite, sulfate or sulfite; and Ar^1 is optionally substituted aryl (e.g., optionally substituted phenyl) having from 0 to 5 substituents, each of which is independently selected from the group consisting of X^1 , haloalkyl (e.g., CF_3), NR^aR^b , C_1 - C_4 alkyl, and C_1 - C_4 alkoxy, heteroaryl, fused aryl or Ar^1 , provided when said formula I is a cation when R^{2a} and R^{3d} together form $-X^1-$, and R^{1a} and R^{2d} together does not form $-X^2-$; and R^{1d} and R^{3a} together does not form $-X^3-$, then at least one of R^{1a} , R^{1b} , R^{1c} , R^{1d} , Y^1 is OR^{5a} , $NR^{5a}R^{5b}$, $PR^{5a}R^{5b}$, haloalkyl (e.g., CF_3), N_3 , or Ar^1 .

[0020] In some embodiments, said photocatalytic reaction is conducted using a red light. In some instances, said photocatalytic reaction is conducted using an electromagnetic radiation having a wavelength of 500 nm or greater.

[0021] In yet another aspect of the invention, a compound is provided that comprises a carbocation of the formula:



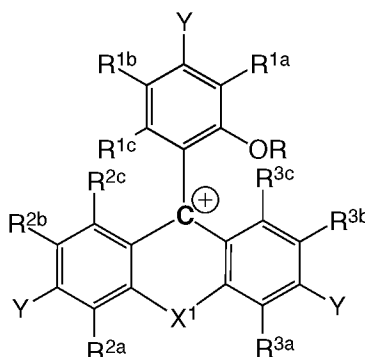
where R is C₁-C₁₂ alkyl or Aryl; X¹ is O, NR^{4a}, PR^{4a}, CR^{4a}R^{4b}, or SiR^{4a}R^{4b}; each of Y is independently H, OR^{5a}, NR^{5a}R^{5b}, PR^{5a}R^{5b}, NO₂, CN, haloalkyl, N₃, CO₂R, or Ar¹; each of R^{1a}, R^{1b}, R^{1c}, R^{2a}, R^{2b}, R^{2c}, R^{3a}, R^{3b}, and R^{3c}, is independently H, halide, CF₃, NH₂, C₁-C₁₂ alkyl, C₁-C₄ alkoxy, C₁-C₄ alkylamino, C₁-C₄ dialkyl amino, NO₂, CN, CO₂R, or Ar¹; each of each of R^{4a}, R^{4b}, R^{5a}, and R^{5b} is independently H, halide, CF₃, C₁-C₁₂ alkyl, C₁-C₄ alkoxy, C₁-C₄ alkylamino, C₁-C₄ dialkyl amino, or Ar¹; or R^{1c} and R^{2c} together form -X²-; or OR and R^{3c} together form -X³-; each of X² and X³ is independently O, NR^{4a}, PR^{4a}, CR^{4a}R^{4b}, or SiR^{4a}R^{4b}; or R^{1b} and R^{1c} together with atoms to which they are attached to form a phenyl; or R^{2b} and R^{2c} together with atoms to which they are attached to form a phenyl; and Ar¹ is optionally substituted phenyl having from 0 to 5 substituents, each of which is independently selected from the group consisting of X¹, CF₃, NH₂, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₁-C₄ alkylamino, and C₁-C₄ dialkyl amino; or at least one of R^{1a}, R^{1b}, R^{1c}, R^{2a}, R^{2b}, R^{2c}, R^{3a}, R^{3b}, R^{3c}, R^{4a}, R^{4b}, R^{5a}, and R^{5b} is a moiety of the formula -L-Z, wherein L is a linker; and Z is a coordinating group that is capable of coordinating to a metal complex. In some embodiments, at least one of R^{1a}, R^{1b}, R^{1c}, R^{2a}, R^{2b}, R^{2c}, R^{3a}, R^{3b}, R^{3c}, R^{4a}, R^{4b}, R^{5a}, and R^{5b} is a moiety of the formula -L-Z, wherein L is a linker; and Z is a coordinating group that is capable of coordinating to a metal complex. Yet in another embodiment, the carbocation is of the formula:



[0022] Still in some embodiments, X^1 is NR^{4a} . In another embodiment, R^{4a} is said moiety of the formula $L-Z$. In some instances, Z is said coordinating group selected from the group consisting of bipyridinyl, pyridinyl, $-PR_2$, $-OPR_2$, $-NHC$, $-NR_2$, diimine, imine, $-OH$, $-OR$, $-SR$, $-SH$, diphosphines, $-RNC$, $-CO_2H$, and carboimine, and wherein each R is independently C_1 - C_{12} alkyl or Aryl. Still in other embodiments, Z is coordinated or complexed to a metal complex. In some instances, said metal ion is a transition metal ion. Still in other instances, said metal ion is a first row transition metal ion. Yet in other instances, said metal ion is selected from the group consisting of Sc(III), Ti(IV), V(III), V(V), Cr(III), Cr(IV), Mn(II), Co (II), Co(I), Ni (II), Fe (II), Fe(III), Cu(II), Cu(I), and Zn(I).

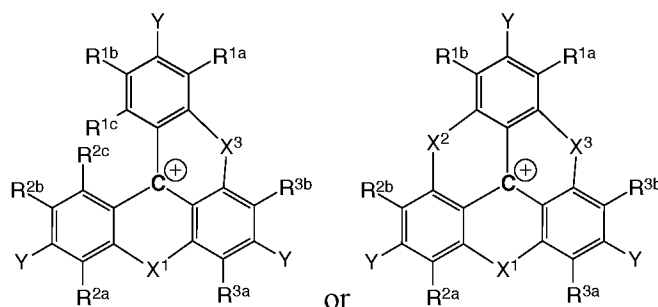
[0023] In further embodiments, L is C_1 - C_{10} alkylene, alkynylene, alkenylene, arylene, or heteroarylene. Yet in other embodiments, each of R^{1c} , R^{2c} , and R^{3c} is independently C_1 - C_4 alkoxy. In one particular embodiment, Y , R^{1a} , R^{1b} , R^{2a} , R^{2b} , R^{3a} , and R^{3b} are H.

[0024] Yet another aspect of the invention provides a photocatalyst composition comprising a conjugated heterocyclic carbenium-metal complex of the formula:



where R is C_1 - C_{12} alkyl or Aryl; X^1 is O , NR^{4a} , PR^{4a} , $CR^{4a}R^{4b}$, or $SiR^{4a}R^{4b}$; each of Y is independently H , OR^{5a} , $NR^{5a}R^{5b}$, $PR^{5a}R^{5b}$, NO_2 , CN , haloalkyl, N_3 , CO_2R , or Ar^1 ; each of R^{1a} , R^{1b} , R^{1c} , R^{2a} , R^{2b} , R^{2c} , R^{3a} , R^{3b} , and R^{3c} is independently H , halide, CF_3 , NH_2 , C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylamino, C_1 - C_4 dialkyl amino, NO_2 , CN , CO_2R , or Ar^1 ; each of each of R^{4a} , R^{4b} , R^{5a} , and R^{5b} is independently H , halide, CF_3 , C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylamino, C_1 - C_4 dialkyl amino, or Ar^1 ; or R^{1c} and R^{2c} together form $-X^2-$; or OR and R^{3c} together form $-X^3-$; each of X^2 and X^3 is independently O , NR^{4a} , PR^{4a} , $CR^{4a}R^{4b}$, or $SiR^{4a}R^{4b}$; or R^{1b} and R^{1c} together with atoms to which they are attached to form an optionally substituted phenyl; or R^{2b} and R^{2c} together with atoms to which they are attached to form an optionally substituted phenyl; and Ar^1 is optionally substituted phenyl having from 0 to 5 substituents, each of which is independently selected from the group consisting of X^1 , CF_3 , NH_2 , C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylamino, and C_1 - C_4 dialkyl amino; or at least one of R^{1a} , R^{1b} , R^{1c} , R^{2a} , R^{2b} , R^{2c} , R^{3a} , R^{3b} , R^{3c} , R^{4a} , R^{4b} , R^{5a} , and R^{5b} is a moiety of the formula

–L–Z, where L is a linker; and Z is a coordinating group that is coordinated to a metal complex. In some embodiments, said conjugated heterocyclic carbenium-metal complex is of the formula:

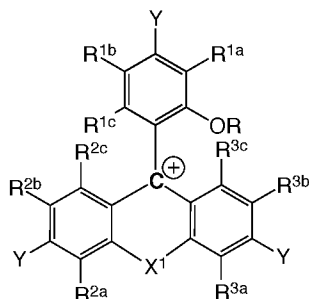


[0025] In other embodiments, X^1 is NR^{4a} , and R^{4a} is said moiety of the formula –L–Z.

[0026] Still in other embodiments, L has from 1 to about 10 chain of atoms. In some instances, L is C_1 – C_{10} alkylene or C_1 – C_{10} heteroalkylene.

[0027] Yet in other embodiments, said metal ion is a transition metal ion. In other embodiments, said metal ion is a first row transition metal ion. Still in other embodiments, said metal ion is selected from the group consisting of Co (II), Ni (II), and Fe (II).

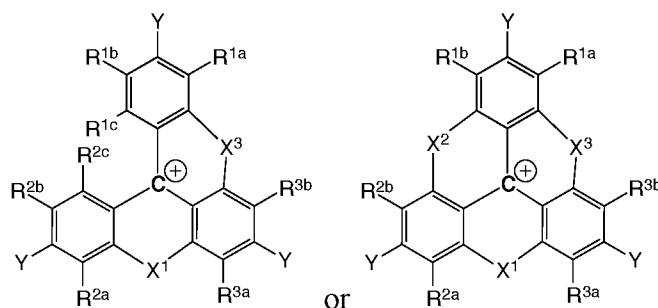
[0028] Another aspect of the invention provides a solid substrate having a surface, wherein said surface comprises a compound comprising a carbocation of the formula:



where R is C_1 – C_{12} alkyl or Aryl; X^1 is O, NR^{4a} , PR^{4a} , $CR^{4a}R^{4b}$, or $SiR^{4a}R^{4b}$; each of Y is independently H, OR^{5a} , $NR^{5a}R^{5b}$, $PR^{5a}R^{5b}$, NO_2 , CN, CO_2R , or Ar^1 ; each of R^{1a} , R^{1b} , R^{1c} , R^{2a} , R^{2b} , R^{2c} , R^{3a} , R^{3b} , and R^{3c} is independently H, halide, CF_3 , NH_2 , C_1 – C_{12} alkyl, C_1 – C_4 alkoxy, C_1 – C_4 alkylamino, C_1 – C_4 dialkyl amino, NO_2 , CN, CO_2R , or Ar^1 ; each of each of R^{4a} , R^{4b} , R^{5a} , and R^{5b} is independently H, halide, CF_3 , C_1 – C_{12} alkyl, C_1 – C_4 alkoxy, C_1 – C_4 alkylamino, C_1 – C_4 dialkyl amino, or Ar^1 ; or R^{1c} and R^{2c} together form $-X^2-$; or OR and R^{3c} together form $-X^3-$; each of X^2 and X^3 is independently O, NR^{4a} , PR^{4a} , $CR^{4a}R^{4b}$, or $SiR^{4a}R^{4b}$; or R^{1b} and R^{1c} together with atoms to which they are attached to form an optionally substituted phenyl; or R^{2b} and R^{2c} together with atoms to which they are attached to form an optionally substituted phenyl; and Ar^1 is optionally substituted phenyl having from 0 to 5 substituents, each of which is independently selected from the group consisting of X^1 , CF_3 , NH_2 , C_1 – C_4 alkyl, C_1 –

C₄ alkoxy, C₁-C₄ alkylamino, and C₁-C₄ dialkyl amino; or at least one of R^{1a}, R^{1b}, R^{1c}, R^{2a}, R^{2b}, R^{2c}, R^{3a}, R^{3b}, R^{3c}, R^{4a}, R^{4b}, R^{5a}, and R^{5b} is a moiety of the formula -L-Z, wherein L is a linker; and Z is a functional group attached to a surface of a solid substrate; or optionally at least one of R^{1a}, R^{1b}, R^{1c}, R^{2a}, R^{2b}, R^{2c}, R^{3a}, R^{3b}, R^{3c}, R^{4a}, R^{4b}, R^{5a}, and R^{5b} is a moiety of the formula -L'-Z', wherein L' is a linker and Z' is a metal complex.

[0029] In some embodiments, said carbocation is of the formula:



[0030] Yet in other embodiments, at least one of R^{1a}, R^{1b}, R^{1c}, R^{2a}, R^{2b}, R^{2c}, R^{3a}, R^{3b}, R^{3c}, R^{4a}, R^{4b}, R^{5a}, and R^{5b} is a moiety of the formula -L'-Z'.

BRIEF DESCRIPTION OF THE DRAWINGS

[0031] FIG. 1 shows a synthetic scheme for producing some of the cations and radicals of the invention.

[0032] FIG. 2 is cyclic voltammograms of compounds **2**⁺-**5**⁺ (2 mM) in DCM ([TBA][PF₆] 0.1 M) solutions recorded at a platinum working electrode (n = 0.1 V/s) and Ag/Ag⁺ as internal reference electrode, with Fc/Fc⁺ used as secondary reference by setting its E_{1/2} = 0.

[0033] FIG. 3 shows results of photoreduction of aryl halides using a helicinium radical of the invention as a photoredox catalyst.

[0034] FIG. 4 shows photophysical and electrochemical properties of compound **3**.

[0035] FIG. 5 illustrates catalytic cycles for (I) C(sp²)-H arylation, and (II) aerobic oxidative hydroxylation.

[0036] FIG. 6 illustrates a possible mechanism for red-light-induced ¹²⁹Pr-DMQA⁺-catalyzed ATRA.

[0037] FIG. 7 is cyclic voltammograms curves of **L1-L3** (3mM) in DCM ([TBA][PF₆] 0.1 M) solutions recorded at a glassy carbon working electrode (n = 0.02 V/s).

[0038] FIG. 8 shows oxidation and reduction half-wave potential values [V] measured by CV for **L1-L3**, E, versus the ferrocene/ferrocenium redox couple (Fc/Fc⁺). Red_n and Ox_n represent the n successive reduction and oxidation events observed in the tested electrochemical window, respectively.

[0039] FIG. 9 shows overlapped absorption spectra and photophysical properties of ligands **L1-L3** in acetonitrile.

[0040] FIG. 10 shows selected bond lengths/distances (Å) and torsion angles (°) of ligand **L1** and complexes **2** as well as bond lengths (Å) of the ring A of **L1** and **2a**.

[0041] FIG. 11 is CV curves of **L1** (3 mM) and complexes **2** (1 mM) in DCM ([TBA][PF₆] 0.1 M) solutions recorded at a glassy carbon working electrode ($n = 0.02$ V/s) along with a table of oxidation and reduction half-wave potential values [V] measured by CV for **L1** and **2**, E, versus the ferrocene/ferrocenium redox couple (Fc/Fc⁺).

[0042] FIG. 12 is CV curves of **L3** (3 mM) and complexes **4** (1 mM) in DCM ([TBA][PF₆] 0.1 M) solutions recorded at a glassy carbon working electrode ($n = 0.02$ V/s) along with a table of oxidation and reduction half-wave potential values [V] measured by CV for **L3** and **4**, E, versus the ferrocene/ferrocenium redox couple (Fc/Fc⁺).

[0043] FIG. 13 shows electrochemical response curve of NiCl₂(DME) (1 mM), **L1** (1 mM), **2b** (1 mM) with acetic acid (50 mM) in CH₃CN ([TBA][PF₆] 0.1 M) solutions recorded at a glassy carbon working electrode ($n = 0.1$ V/s). E, versus the ferrocene/ferrocenium redox couple (Fc/Fc⁺).

[0044] FIG. 14 shows electrochemical response curve of NiCl₂(DME) (1 mM), **4b** (1 mM) with acetic acid (50 mM) in CH₃CN ([TBA][PF₆] 0.1 M) solutions recorded at a glassy carbon working electrode ($n = 0.1$ V/s). E, versus the ferrocene/ferrocenium redox couple (Fc/Fc⁺).

[0045] FIG. 15 shows electrochemical response curve of **2b** (1mM) at various acetic acid concentration (x mM) in CH₃CN ([TBA][PF₆] 0.1 M) solutions recorded at a glassy carbon working electrode ($n = 0.1$ V/s). E, versus the ferrocene/ferrocenium redox couple (Fc/Fc⁺).

[0046] FIG. 16 shows electrochemical response curve of **4b** (1mM) at various acetic acid concentration (x mM) in CH₃CN ([TBA][PF₆] 0.1 M) solutions recorded at a glassy carbon working electrode ($n = 0.1$ V/s). E, versus the ferrocene/ferrocenium redox couple (Fc/Fc⁺).

[0047] FIG. 17 is overlapped absorption spectra in acetonitrile of ligand **L1** and complexe **2**.

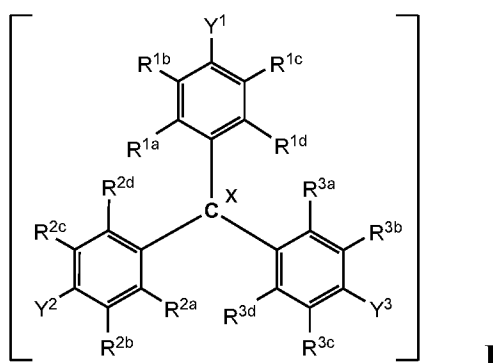
[0048] FIG. 18 is overlapped absorption spectra in acetonitrile of ligand **L3** and complex **4**.

[0049] FIG. 19 is a table showing photophysical properties of ligands **L1**, **L3** and complexes **2,4** in acetonitrile.

DESCRIPTION OF THE INVENTION

[0050] The present invention provides a new class of organic-based photocatalysts, such as those can be activated using a low energy electromagnetic radiation. In particular, organic-based PCs of the invention can be activated using electromagnetic radiation wavelength of about 390 nm or greater, typically about 500 nm or greater, and often about 600 nm or greater. As used herein, the terms “about” and “approximately” when referring to a numerical value are used interchangeably herein and refer to being within an acceptable error range for the particular value as determined by one of ordinary skill in the art. Such a value determination will depend at least in part on how the value is measured or determined, e.g., the limitations of the measurement system, i.e., the degree of precision required for a particular purpose. For example, the term “about” can mean within 1 or more than 1 standard deviation, per the practice in the art. Alternatively, the term “about” when referring to a numerical value can mean $\pm 20\%$, typically $\pm 10\%$, often $\pm 5\%$ and more often $\pm 1\%$ of the numerical value. In general, however, where particular values are described in the application and claims, unless otherwise stated, the term “about” means within an acceptable error range for the particular value, typically within one standard deviation.

[0051] Some aspects of the invention provide a compound comprising a moiety of the formula:



where the moiety of Formula **I** is a radical, a cation, or a radical dication and “x” indicates “central carbon atom”. With respect to the moiety of Formula **I**: each of R^{1a} , R^{1b} , R^{1c} , R^{1d} , R^{2a} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , R^{3c} , and R^{3d} is independently H, halide, haloalkyl (e.g., CF_3), $-NR^aR^b$ (each of R^a and R^b is independently H or C_1 - C_4 alkyl), C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, $-NO_2$, $-CN$, $-CO_2R$ (where R is H or C_1 - C_4 alkyl), or Ar^1 ;

or R^{2a} and R^{3d} together form $-X^1-$;

or R^{1a} and R^{2d} together form $-X^2-$;

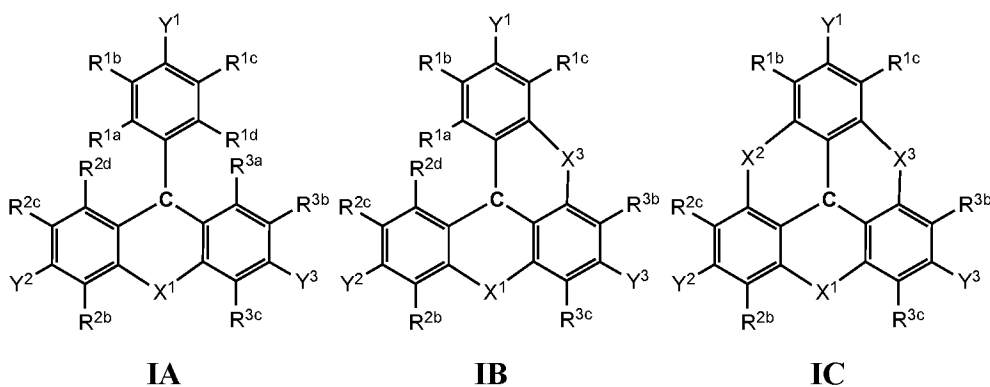
or R^{1d} and R^{3a} together form $-X^3-$;

each of X^1 , X^2 and X^3 is independently O, NR^{4a} , PR^{4a} , $CR^{4a}R^{4b}$, or $SiR^{4a}R^{4b}$;
 or R^{1a} and R^{1b} together with atoms to which they are attached to form an optionally substituted aromatic ring (e.g., optionally substituted phenyl);
 or R^{2c} and R^{2d} together with atoms to which they are attached to form an optionally substituted aromatic ring (e.g., optionally substituted phenyl);
 each of Y^1 , Y^2 , and Y^3 is independently H, OR^{5a} , $CR^{5a}R^{5b}R^{5b}$, $NR^{5a}R^{5b}$, $PR^{5a}R^{5b}$, NO_2 , CN, CF_3 , CO_2R , N_3 , or Ar^1 ;
 each of R^{4a} , R^{4b} , R^{5a} , and R^{5b} is independently H, halide, haloalkyl (e.g., CF_3), C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, $-NR^aR^b$ (provided at least one of R^a and R^b is C_1 - C_4 alkyl), Ar^1 , or a moiety of the formula $-L-Z$,
 where L is a linker (such as an alkylene, ethylene glycol or other glycols, (e.g., propylene glycol) of 2-20 monomeric units); and Z is a heterocyclic species of Formula I (i.e., dimer, trimer, or other oligomers of Formula I), a coordinating group able to bind or complex to a metal ion, or a water-soluble group such as phosphate, phosphite, sulfate or sulfite; and Ar^1 is optionally substituted aryl (e.g., optionally substituted phenyl) having from 0 to 5 substituents, each of which is independently selected from the group consisting of X^1 , haloalkyl (e.g., CF_3), NR^aR^b , C_1 - C_4 alkyl, and C_1 - C_4 alkoxy, heteroaryl, fused aryl or Ar^1 ,

provided when said Formula I is a cation then

- (i) when R^{2a} and R^{3d} together form $-X^1-$; R^{1a} and R^{2d} together form $-X^2-$; and R^{1d} and R^{3a} together form $-X^3-$, then no more than one of X^1 , X^2 , and X^3 is O;
- (ii) when R^{2a} and R^{3d} together form $-X^1-$, and R^{1a} and R^{2d} together does not form $-X^2-$; and R^{1d} and R^{3a} together does not form $-X^3-$, then at least one of R^{1a} , R^{1b} , R^{1c} , R^{1d} , or Y^1 is not H, halogen, or C_1 - C_{12} alkyl; in some embodiments, Y^1 is $NR^{5a}R^{5b}$, $PR^{5a}R^{5b}$, haloalkyl (e.g., CF_3), N_3 , or Ar^1 ;
- (iii) at least one of (a) R^{2a} and R^{3d} together form $-X^1-$; (b) R^{1a} and R^{2d} together form $-X^2-$; or (c) R^{1d} and R^{3a} together form $-X^3-$; and
- (iv) when R^{2a} and R^{3d} together form $-X^1-$; R^{1a} and R^{2d} together form $-X^2-$; and R^{1d} and R^{3a} together form $-X^3-$, then none of X^1 , X^2 , and X^3 is NR^{4a} .

[0052] In some embodiments, the moiety of Formula I is selected from the group consisting of:



where the moiety of Formulas **IA**, **IB**, and **IC** are radical, cation, or radical dication; and Y^1 , Y^2 , Y^3 , X^1 , X^2 , X^3 , R^{1a} , R^{1b} , R^{1c} , R^{1d} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , and R^{3c} are those defined herein. As used herein, the terms “those defined above” and “those defined herein” when referring to a variable incorporates by reference the broad definition of the variable as well as any narrower definitions.

[0053] In some embodiments, when moiety of Formula **I**, **IA**, **IB**, or **IC** is a cation. Still in other embodiments, the moiety of Formula **I**, **IA**, **IB** or **IC** is a radical or a radical dication.

[0054] The compounds of the invention can be used in a wide variety of applications including, but not limited to, as efficient photocatalyst using light. Unlike other conventional organic-based PCs, compounds of the invention can be activated using a low energy electromagnetic radiation. Compounds of the invention are also useful in electronic equipment or as solid phase catalysts in organic reactions. Some of the advantages of compounds of the invention are believed to be due at least in part because: (i) they are among the most stable carbocations, radicals, and diradical cations known to date, including under mild acidic or basic aqueous conditions; (ii) the stepwise and temperature dependence of the synthesis allows versatility of using a wide variety of starting materials for synthesis (e.g., by using aliphatic or aromatic amines) and allows formation of unsymmetrical ions; (iii) they can be readily functionalized, e.g., via C-H metal-catalyzed cross-coupling; and (iv) the negative counterions can be exchanged to affect the physical and chemical properties of the salts. Additionally, compounds of the invention are redox active compounds, thereby allowing them to be used in various electronic equipment.

[0055] Referring to Formula **I**, the term “alkyl” refers to a saturated linear monovalent hydrocarbon moiety. Unless the number of carbon atoms is specified, the term “alkyl” typically refers to hydrocarbon moiety having one to twelve, typically one to six, carbon atoms or a saturated branched monovalent hydrocarbon moiety of three to twelve,

typically three to six, carbon atoms. Exemplary alkyl group include, but are not limited to, methyl, ethyl, *n*-propyl, 2-propyl, *tert*-butyl, pentyl, and the like. The term “alkoxy” refers to a moiety of the formula $-OR^a$, wherein R^a is alkyl as defined herein. The term “alkylamino” refers to a moiety of the formula $-NHR^a$, where R^a is alkyl as defined herein. The term “dialkyl amino” refers to a moiety of the formula $-NR^aR^b$, wherein R^a and R^b are independently alkyl as defined herein. The terms “aryl” and “aromatic ring” are used interchangeably herein and refer to a monovalent mono-, bi- or tricyclic aromatic hydrocarbon moiety of 6 to 15 ring atoms. Exemplary aryl groups include phenyl, naphthyl, and anthracene. Aryl may optionally be substituted with one or more substituents. When substituted, aryl comprises from one to five, typically, one to four, often one to three, more often one or two, and most often one substituent. Suitable substituent(s) for an aryl group include, but are not limited to, halogen (e.g., Cl, F, I, Br, typically Cl or F), alkyl, haloalkyl, hydroxy, alkoxy, heteroalkyl, cyano, nitro, nitroso, carboxylic acid or esters, etc. When more than one substituent is present in the aryl group, each substituent is independently selected. The term “linker” refers to a moiety having from 1 to 20 atoms in the chain. Typically, the chain atoms include carbon, oxygen, nitrogen, sulfur, and phosphorous, provided oxygen-oxygen bond or nitrogen-nitrogen bond is not present in the chain. Often the linker is a hydrocarbon moiety or an ether moiety. The term “heteroaryl” means a monovalent monocyclic or bicyclic aromatic moiety of 5 to 12 ring atoms containing one, two, or three ring heteroatoms selected from N, O, or S, the remaining ring atoms being C. Exemplary heteroaryl includes, but is not limited to, pyridyl, furanyl, thiophenyl, thiazolyl, isothiazolyl, triazolyl, imidazolyl, oxazolyl, isoxazolyl, pyrrolyl, pyrazolyl, pyrazinyl, pyrimidinyl, benzofuranyl, isobenzofuranyl, benzothiazolyl, benzoisothiazolyl, benzotriazolyl, indolyl, isoindolyl, benzoxazolyl, thiazolyl, isothiazolyl, quinolyl, isoquinolyl, benzimidazolyl, benzisoxazolyl, benzothiophenyl, dibenzofuran, and benzodiazepin-2-one-5-yl, and the like. The term “heteroalkyl” means a branched or unbranched, alkyl moiety as defined herein but where one or more carbon or hydrogen is replaced with a heteroatom (e.g., O, N, S) or where one or more heteroatom-containing substituents is present such as $=O$, $-OR^a$, $-C(O)R^a$, $-NR^bR^c$, $-C(O)NR^bR^c$ and $-S(O)_nR^d$ (where n is an integer from 0 to 2, and each of R^a , R^b , R^c , R^d is independently hydrogen or alkyl). “Haloalkyl” refers to an alkyl group as defined herein in which one or more hydrogen atom is replaced by same or different halo atoms. The term “haloalkyl” also includes perhalogenated alkyl groups in which all alkyl hydrogen atoms are replaced by halogen atoms. Exemplary haloalkyl groups include, but are not limited to, $-CH_2Cl$, $-CF_3$, $-CH_2CF_3$, $-CH_2CCl_3$, and the like.

[0056] It should be appreciated moieties of Formulas **I**, **IA**, **IB**, and **IC** themselves do not necessarily comprise chemical compounds. Indeed, in an isolable compound, corresponding cations, radicals, dication radicals must be paired with a corresponding moiety that provides electroneutrality and overall non-radical compound. Thus, compounds of the present invention include corresponding anion, radical, or dication radical that provides overall non-radical electroneutral compound (i.e., “corresponding moiety”). The nature of the corresponding moiety is not as important as the carbocation, radical, or dication radical of Formulas **I**, **IA**, **IB**, and **IC** (collectively simply referred herein as “Formula **I**”) since the electronic property of compounds of the invention is primarily due to the carbocation, radical, or radical dication of Formula **I**. Exemplary counter moiety of Formula **I** include, but are not limited to, any anion including, but not limited to, anionic or radical metal salts, halides (e.g., Cl, F, I, and Br), an anion or a radical derived from organic compounds such as carboxylates, phosphates, sulfates, etc.

[0057] In some embodiments, the moiety of Formula **I** (as well as other compounds disclosed herein) do not require the moiety of the formula $-L-Z$. In these embodiments, the metal complex can be present in solution as a separate entity to provide catalytic and/or photovoltaic activity. Accordingly, in some embodiments, the moiety of Formula **I** lacks a moiety of the formula $-L-Z$ altogether.

[0058] Yet in other embodiments, Z is a coordinating group. Generally, a coordinating group refers to a moiety that has one or more heteroatoms that is capable of coordinating to a metal complex. Exemplary coordinating groups include heteroaryl, heteroatom functional groups such as phosphates, sulfates, carbonates, hydroxyl group and ethers, thiol and thiol ethers, amines, imines, carboimides, carbamides, etc.

[0059] In one particular embodiment, Z is selected from the group consisting of bipyridinyl, pyridinyl, $-PR_2$, $-OPR_2$, $-NHC$, $-NR_2$, diimine, imine, $-OR$, $-SR$, diphosphines, $-RNC$, $-CO_2H$, and carboimine, where each R is independently H, C_1 - C_{12} alkyl or Aryl.

[0060] Still in other embodiments, Z is coordinated (i.e., complexed) to a metal complex. As used herein, “metal complex” refers to a central atom or ion (i.e., coordination center) that is a metal or metal ion and has a surrounding array of bound molecules or ions, which are often called ligands or complexing agents. Exemplary metals in a metal complex include, but not limited to, transition metals, lanthanide metals, actinide metals, alkaline metals, and alkaline earth metals. In one particular embodiment, the metal in a metal complex is a transition metal. Still in another embodiment, the metal is a first-row transition metal. In yet another embodiment, the metal is ones which are known to one skilled in the art

as being useful in a catalytic reaction, such as but not limited to, Fe, Ni, Pd, Pt, Rh, Co, Au, Cu, Zn, Ru, etc. It should be appreciated that unless the oxidation state of the metal is explicitly stated, the term “metal” includes metal ions. For example, the term metal referring to iron or Fe includes ferric ion (Fe^{+3}) and ferrous ion (Fe^{+2}). Similarly, the term metal referring to nickel or Ni includes Ni(I) and Ni(II). In one specific embodiment, the metal is selected from the group consisting of Co (II), Ni (II), Fe (II), Au(I), Pd(II), and Rh(I).

[0061] As stated herein, the term “metal complex” also includes ligands or complexing agents. Typically, when the metal is a metal ion, the ligand is a corresponding anionic ligand such as, but not limited to, a halide (e.g., Cl^- , Br^- , I^- , F^-), a carboxylate (e.g., acetate, oxalate, etc.), hydroxide ($-\text{OH}$), an alkoxide, thiolate, cyclopentadiene (“Cp”), alkyl, oxo, as well as other metal counter ion that is known to one skilled in the art. The ligand or complexing agent can also be a neutral specie such as, but not limited to, naphthalene, phosphine, diphosphine, amine, imine, diamine, diimine, NHC (i.e., N-Heterocyclic Carbene), CO, isocyanides, olefins, alkynes, ethers, pyridines, bipyridines, arenes, etc.

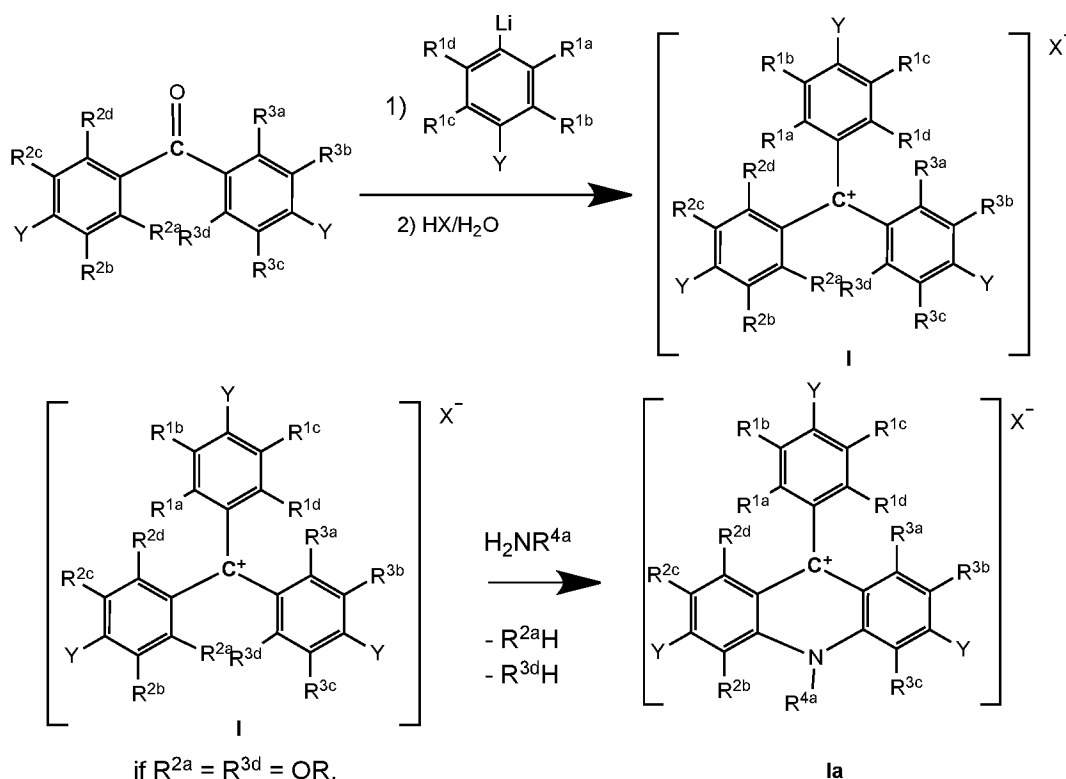
[0062] When present, the linker L should be of sufficient length to allow the metal complex that is attached to the moiety of Formula I to interact with the central carbon atom (e.g., carbocation or carbo-radical). As used herein, the central carbon atom refers to the carbon atom that is attached to the three aromatic ring moieties in Formula I that is indicated with an “x”. Accordingly, in some embodiments, L is C_1 - C_{10} alkylene, typically C_2 - C_8 alkylene, often C_2 - C_6 alkylene, more often C_2 - C_5 alkylene, and most often C_2 or C_3 alkylene. It should be appreciated that the linkers are not limited to these specific alkylene ranges and examples given herein. In general, the length of L (including alkylene) can vary in length in order to affect the desired interaction between the metal complex and the central carbon. The term “alkylene” refers to a saturated linear divalent hydrocarbon moiety or a branched saturated divalent hydrocarbon moiety. Exemplary alkylene groups include, but are not limited to, methylene, ethylene, propylene, butylene, pentylene, 2-methylpropylene, and the like.

[0063] Linkers can also be a C_1 - C_{10} heteroalkylene such as ethers, etc. The term “heteroalkylene” refers to an alkylene group as defined herein in which one or more chain atoms or hydrogen atoms are replaced with a heteroatom such as O, N, P, or S. Exemplary heteroalkylenes include, but are not limited to, polyethylene glycol derived heteroalkylenes such as PEG2 (i.e., 2 molecules of ethylene glycol linker), PEG3, 2-methoxyethylene, 2-hydroxyethyl, 2,3-dihydroxypropyl, etc.

[0064] Compounds of the invention can be used in a wide variety of applications including, but not limited to, as photocatalysts, as photovoltaic cells, as artificial photosynthesis materials, as organic light-emitting diodes, (“OLEDs”), etc.

[0065] Some of the advantages of compounds of the invention include activation of compounds using a much lower energy electromagnetic radiation compared to conventional photocatalysts. In particular, surprisingly and unexpectedly the present inventors have found that compounds of the invention can be activated by wavelength of 390 nm or longer, often 500 nm or longer, and most often 600 nm or longer. In some embodiments, catalytic activity can be observed with electromagnetic radiation having wavelength from about 600 nm to about 1,000 nm, often from about 600 nm to about 800 nm, and more often from about 600 nm to about 700 nm.

[0066] Compounds of the invention can be prepared as shown in FIG. 1, or using the following general synthetic method with appropriately substituted reagents and reaction conditions known to one skilled in the art:



[0067] Surprisingly and unexpectedly, the present inventors have discovered that stable radicals and radical dications can also be prepared. Stable radicals are of particular interest to the scientific community for their applications in catalysis, OLEDs and other material applications. In recent years, organic radicals have enjoyed increasing interest due to their involvement in the fast growing field of photocatalysis. During the photoinduced

electron transfer (PET) process, an electron transfer occurs between the excited state of an organic photocatalyst and an electrochemically matched substrate, resulting in the formation of an organic radical. In almost all systems, the radical moiety remains an unisolable transient intermediate. Interestingly, it has recently been reported that organic radicals formed *in situ* by light-induced reduction of their closed-shell photocatalysts counterpart (i.e., perylenediimine PDI and mesityl acridinium salt (i.e., Mes-Acr⁺), respectively) can further absorb light and efficiently catalyze the photoreduction of aryl halide. Despite early reports showing that transient organic radicals such as diarylketyl and diphenylmethyl can undergo photoinduced electron transfer (PET), PDI[•] and Mes-Acr[•] are the only organic radical photocatalyst reported to date.

[0068] It was discovered by the present inventors that compounds of the invention are efficient photoinduced electron acceptors and can form helicene radicals as well as radical dications during the photocatalysis of organic transformation using a red light-emitting diode (LED) as a light source. To date, only a few examples of [*n*]helicene (*n* = 4, 5, 6, 7 indicates the number of fused aromatic rings) radicals have been reported in the literature. Without being bound by any theory, it is believed that the unpaired electron in these systems is stabilized through delocalization over the π -conjugated substituents, and the molecules with a higher number of fused aromatic rings show a higher stability. Thus, helicenes represent the least stable and least studied radicals of this class. To date, only four examples of helicene radicals have been reported, two of which showed limited stability, and one other was never isolated. It is also of note that no X-ray crystallographic structure of any helicene-based neutral radical has been reported to date.

[0069] Methods of the invention for producing compounds containing a moiety of formula I provide isolation, single crystal structure, and full characterization of a family of helicene radicals, including, but not limited to, methoxyquinacridine (DMQA[•]), by ¹H NMR, continuous wave (CW) EPR, electron-nuclear double resonance (ENDOR), cyclic voltammetry, UV-vis absorption spectroscopy, as well as density functional theory (DFT) calculations.

[0070] Moreover, the invention provides a wide variety of photocatalytic reactions that can be achieved using compounds of the invention including, but not limited to, the reductive dehalogenation of aryl halides, including a less reactive aryl chloride, under photocatalytic condition using an isolated organic radical of the invention.

[0071] Another aspect of the invention provides a method of conducting a photocatalytic reaction, such as those disclosed herein. The method generally includes reacting a two or more substrates in the presence of a photocatalyst compound comprising a moiety of the Formula I. In this aspect of the invention, said moiety of Formula I is a radical, a cation, or a radical dication; each of R^{1a} , R^{1b} , R^{1c} , R^{1d} , R^{2a} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , R^{3c} , and R^{3d} is independently H, halide, haloalkyl, $-NR^aR^b$ (each of R^a and R^b is independently H or C₁-C₄ alkyl), C₁-C₁₂ alkyl, C₁-C₄ alkoxy, $-NO_2$, $-CN$, $-CO_2R$ (where R is H or C₁-C₄ alkyl), or Ar^1 ; or R^{2a} and R^{3d} together form $-X^1-$; or R^{1a} and R^{2d} together form $-X^2-$; or R^{1d} and R^{3a} together form $-X^3-$; each of X^1 , X^2 and X^3 is independently O, NR^{4a} , PR^{4a} , $CR^{4a}R^{4b}$, or $SiR^{4a}R^{4b}$; or R^{1a} and R^{1b} together with atoms to which they are attached to form an optionally substituted aromatic ring (e.g., optionally substituted phenyl); or R^{2c} and R^{2d} together with atoms to which they are attached to form an optionally substituted aromatic ring (e.g., optionally substituted phenyl); each of Y^1 , Y^2 , and Y^3 is independently H, OR^{5a} , $CR^{5a}R^{5b}R^{5b}$, $NR^{5a}R^{5b}$, $PR^{5a}R^{5b}$, NO_2 , CN , CF_3 , CO_2R , N_3 , or Ar^1 ; each of R^{4a} , R^{4b} , R^{5a} , and R^{5b} is independently H, halide, haloalkyl (e.g., CF_3), C₁-C₁₂ alkyl, C₁-C₄ alkoxy, $-NR^aR^b$ (provided at least one of R^a and R^b is C₁-C₄ alkyl), Ar^1 , or a moiety of the formula $-L-Z$, where L is a linker (such as a alkylene, ethylene glycol or other glycols, (e.g., propylene glycol) of 2-20 units); and Z is a heterocyclic species of formula I (i.e., dimer, trimer, or other oligomers of formula I), a coordinating group able to bind or complex to a metal ion, or a water-soluble group such as phosphate, phosphite, sulfate or sulfite; and Ar^1 is optionally substituted aryl (e.g., optionally substituted phenyl) having from 0 to 5 substituents, each of which is independently selected from the group consisting of X^1 , haloalkyl (e.g., CF_3), NR^aR^b , C₁-C₄ alkyl, C₁-C₄ alkoxy, heteroaryl, fused aryl, or another Ar^1 .

[0072] In some embodiments, when said formula I is a cation and (i) when R^{2a} and R^{3d} together form $-X^1-$; R^{1a} and R^{2d} together form $-X^2-$; and R^{1d} and R^{3a} together form $-X^3-$, then no more than one of X^1 , X^2 , and X^3 is O; (ii) when R^{2a} and R^{3d} together form $-X^1-$, then Y^1 is $NR^{5a}R^{5b}$, $PR^{5a}R^{5b}$, haloalkyl (e.g., CF_3), N_3 , or Ar^1 ; (iii) at least one of (a) R^{2a} and R^{3d} together form $-X^1-$; (b) R^{1a} and R^{2d} together form $-X^2-$; or (c) R^{1d} and R^{3a} together form $-X^3-$; and (iv) when R^{2a} and R^{3d} together form $-X^1-$; R^{1a} and R^{2d} together form $-X^2-$; and R^{1d} and R^{3a} together form $-X^3-$, then none of X^1 , X^2 , and X^3 is NR^{4a} .

[0073] Compounds of the invention can be used in a wide variety of photocatalytic processes including those disclosed herein as well as those processes disclosed in DOI:

10.1021/acs.chemrev.9b00045; Chem. Rev. 2019, 119, 6769–6787;

doi.org/10.1021/acscatal.8b03050: *ACS Catal.* 2018, 8, 12, 12046-12055; doi.org/10.1002/ejoc.201700420: DOI: 10.1021/acs.chemrev.6b00057: *Chem. Rev.* 2016, 116, 10075–10166; DOI: 10.1021/acs.joc.6b01449 *J. Org. Chem.* 2016, 81, 6898–6926; and dx.doi.org/10.1021/cr300503r: *Chem. Rev.* 2013, 113, 5322–5363, all of which are incorporated herein by reference in their entirety.

[0074] Stable organic radicals are useful species for developing applications in catalysis as well as material sciences. In particular, helical molecules are of great interest to development and application of novel organic radicals in optoelectronic and spintronic materials. The present inventors have discovered that highly stable neutral quinolinoacridine radicals can be produced by chemical reduction of their quinolinoacridinium cation analogs. These radicals can be used in a wide variety of photocatalysis reactions including, but not limited to, photoreductive dehalogenation of aryl halide under irradiation with a relatively low energy electromagnetic radiation.

[0075] **Synthesis.** The helicenium cations (2^+-5^+) were synthesized, for example, using the general procedure shown in FIG. 1. The room temperature ^1H NMR spectra of the carbocations 2-H^+ and 3^+-5^+ are well resolved and sharp. However, the ^1H NMR spectrum of 2-NO_2^+ shows broad and poorly resolved resonances, suggesting a dynamic exchange. Variable temperature (VT) ^1H NMR spectroscopy analysis of 2-NO_2^+ was conducted over a temperature range of 333 – 193 K confirming the presence of an equilibrium between two conformers. At 193 K, the two $^i\text{Pr-NMe}_2$ arms are inequivalent, and the assignment of the six methylenic protons was successfully carried out using low-temperature ^1H - ^1H COSY NMR sequence. These data support the presence of a $\text{NMe}_2\text{-C}^+$ interaction with an interconversion activation energy of $\Delta G^\ddagger = 12.2$ kcal/mol.

[0076] Referring again to FIG. 1, the radicals $2^\bullet\text{-}5^\bullet$ were obtained by reduction of 2^+-5^+ , respectively, with potassium metal in THF at room temperature overnight. The reaction mixture turned from dark green suspension to a dark magenta solution. The insoluble KBF_4 salt that formed in the process was removed by filtration. THF was removed under vacuum, and the resultant solids were extracted with toluene. Crystallization from a toluene/hexane mixture at -35°C afforded $2^\bullet\text{-}5^\bullet$ as dark brown crystals in good yields. The formation of radicals $2^\bullet\text{-}5^\bullet$ was confirmed by EPR spectroscopy. The resultant radicals are remarkably stable under inert atmosphere at room temperature in both the solid and solution, retaining their color and crystallinity indefinitely (at least, over several months). As used herein, the

term “stable” refers to having about 10% or less, typically about 5% or less, and often about 1% or less decomposition under standard conditions (i.e., 25 °C at 1 atm pressure) over at least one (1) month period. The analysis of ^1H NMR suggests that the unpaired electron is delocalized onto the fused heterocyclic rings and that the nature of the chosen pendant arms has little influence on the radical character of the compounds **2** $\cdot$ -**5** $\cdot$.

[0077] **X-ray diffraction.** Slow DCM/hexane layering afforded suitable crystals of the cationic precursors **2-H** $^+$ and **2-NO₂** $^+$ for X-ray diffraction (XRD) analysis. In both structures, the steric clash between the MeO groups results in a significant twist between the *o*-(MeO)-phenyl moieties (**2-H** $^+$: 41.93°, **2-NO₂** $^+$: 38.37°). These differences in torsion angle between **2-H** $^+$ and **2-NO₂** $^+$ are also underlined by the O1-O2 distances, 2.743 Å and 2.659 Å, respectively. As deduced from the VT ^1H NMR results, one of the *n*Pr-NMe₂ arms in **2-NO₂** $^+$ is folded over the carbocation center with a C1-N3 distance of 3.194 Å.

[0078] The neutral radicals **2-H** $\cdot$ and **2-NO₂** $\cdot$ were isolated from a concentrated toluene solution by slow diffusion of hexane and analyzed by XRD. The distortion of the *o*-(MeO)-phenyl groups is more accentuated than for the cationic precursors in **2-H** $\cdot$ (45.92°, +3.99°), and particularly in **2-NO₂** $\cdot$ (52.05°, +13.68°), resulting in similar O1-O2 distances for both complexes (**2-H** $\cdot$: 2.772 Å and **2-NO₂** $\cdot$: 2.773 Å). The increase in C1-C2, C1-C3 and C1-C4 interatomic distances in **2-H** $\cdot$ (1.439, 1.444, and 1.446 Å, respectively) relative to the cation **2-H** $^+$ (1.406, 1.435 and 1.431 Å), indicates an antibonding interaction between C1 and its surrounding atoms. Similarly, the C1-C3 distance in **2-NO₂** $\cdot$ (1.429 Å) was elongated when compared to **2-NO₂** $^+$ (1.413 Å). In contrast, bond distances in **2-NO₂** $\cdot$ were shortened compared to **2-NO₂** $^+$ C1-C2 (1.423 vs 1.431 Å) and C1-C4 (1.438 vs 1.440 Å). This phenomenon is assigned to the electron withdrawing ability of NO₂ resulting in a higher delocalization of the electronic charge.

[0079] **DFT calculations.** Computational models of the radicals **2** $\cdot$ -**5** $\cdot$ were studied using DFT to determine their electronic structure. The calculations revealed a considerable spin population on the central carbon in all radicals. Analysis of the frontier molecular orbitals shows that considerable amount of the normalized wavefunction was located on the central carbon in **2** $\cdot$ - **5** $\cdot$, where about 27% of the SOMO's wavefunction is located in this atom regardless of the nature of alkyl groups in the amino substituent or the addition of the electron withdrawing group NO₂. A significant change, however, was observed in comparing

the SOMO energy where **2-NO₂•** appear significantly stabilized by the electron withdrawing nitro group compare to **2-H•**.

[0080] EPR, ENDOR, Measurements: The EPR spectra of **2-H•** and **3•-5•** in liquid toluene solutions represent a Gaussian line centered at $g \approx 2.003$, with the width of about 0.76 mT and a poorly resolved hyperfine structure with the splitting of 0.088 mT. The EPR spectrum of **2-NO₂•** has the same g-factor and width, but the hyperfine structure is unresolved. The ¹H ENDOR spectra of **2-H•** and **3•-5•** show three pairs of lines ((*a,a'*), (*b,b'*), and (*c,c'*)), located at the frequencies of $\nu_H \pm a_H/2$, where ν_H is the proton Zeeman frequency and a_H is the hyperfine interaction (hfi) constant. The hfi constants estimated for each pair of ENDOR lines are: $|a_{Ha}| \approx 7.1$ MHz (for *a,a'* lines), $|a_{Hb}| \approx 2.3$ MHz (for *b,b'* lines), and $|a_{Hc}| \approx 0.65$ MHz (for *c,c'* lines).

[0081] For **2-NO₂•**, the hydrogen atom is substituted by the NO₂ group, which results in a significant conformational distortion of the aromatic ring structure and a reorientation of the CH₂ group in the vicinity of NO₂. The accompanying changes in the ENDOR spectrum are a ~ 30% decrease of the relative intensity of (*b,b'*) lines and appearance of (*d,d'*) and (*e,e'*) lines corresponding to $a_H = 6.05$ and 5.37 MHz, respectively. Since the DFT calculation for **2-NO₂•** results in essentially the same distribution of spin populations as in **2-H•** and **3•-5•**, these hfi constants were tentatively assigned to the protons of the reoriented CH₂ group.

[0082] Electrochemistry: As shown in FIG. 2, the electrochemical behavior of **2⁺-5⁺** was investigated by cyclic voltammetry. Under reductive conditions, a fully reversible event is observed around $E_{1/2} = -1.25$ V in **2⁺-5⁺**, which corresponds to the reduction of DMQA⁺ to DMQA•. This event is observed at a lower potential for **2-NO₂⁺** (-1.0 V), consistent with a more electron deficient scaffold due to the presence of the NO₂ group. For **2-NO₂⁺**, a second reversible reduction was observed at $E_{1/2} = -1.8$ V, while for **2-H⁺, 3⁺-5⁺**, an irreversible reduction event is found at $E_{1/2} = -2.3$ V, corresponds to reduction of DMQA• to DMQA⁻.

[0083] UV-Vis spectroscopy. The UV-visible spectra of the cations and radicals (**2-5**) were studied to understand the electronic transitions. All compounds, cations and radicals, possess three distinct absorption features in the visible regions, with the radical absorption being blue shifted from their cation analogs. The blue shift indicates a reduced involvement of the heteroatoms in the molecular framework as well as a remarkably decreased

conjugation. The introduction of the electron withdrawing NO₂ group induces a moderate hypsochromic shift of the lower energy transition and an increase of molar extinction coefficient for the high energy transition in both **2-NO₂⁺** and **2-NO₂[•]** compare to **2-H⁺** and **2-H[•]** respectively.

[0084] Upon exposure to air, the absorption spectrum of the radical **2-H[•]** and **3[•]-5[•]** slowly (within hours) evolves to that of the cationic analog. Unlike most organic radicals, these DMQA radicals do not appear to undergo oxygen insertion or dimer formation. Instead, a clean reversible oxidation to DMQA⁺ is observed. The **2-H[•]** showed the half-life time ($t_{1/2}$) of about 26 min, 51 min for **3[•]**, 54 min for **4[•]**, and 44 min for **5[•]**. The **2-NO₂[•]** radical, however, shows a less selective oxidation and a significantly longer $t_{1/2}$ of about 210 min. The reduced reactivity of **2-NO₂[•]** is assigned to the inductive effect of the electron-withdrawing –NO₂ groups.

[0085] **Photocatalysis.** The photocatalytic potential of **2-H[•]** was investigated using photo reductive dehalogenation of aryl halides at room temperature in the presence of 10 mol % **2-H[•]** and DIPEA (3.0 eq.) under blue (FIG. 3) or green LED light. The desired reductive dehalogenation of aryl iodides were obtain with high yield. Photoreductive debromination and dechlorination were also successful and provided a moderate to good yield. Photoreduction of 4-iodoaniline using the cationic analog **2-H⁺** was successful, yet with significantly lower yield (42% vs 83%).

[0086] **Low energy electromagnetic mediated photoredox catalytic reactions.** Compounds of the invention can be used as organic-based photoredox catalyst. Unlike conventional organic-based PCs, compounds of the invention can be used as both photoreduction and photooxidation catalysts. Furthermore, compounds of the invention can be activated in the presence of low-energy electromagnetic radiation. In some embodiments, compounds of the invention are used as photocatalysts using a low-energy electromagnetic radiation, e.g., red light. In one particular embodiment, compounds of the invention are used as PCs using electromagnetic radiation having wavelength of about 500 nm or higher, typically about 550 nm or higher, and often about 600 nm or higher. In one specific embodiment, red light (e.g., $\lambda_{\text{max}} = 640 \text{ nm}$) is used to activate photocatalytic activity of compounds of the invention.

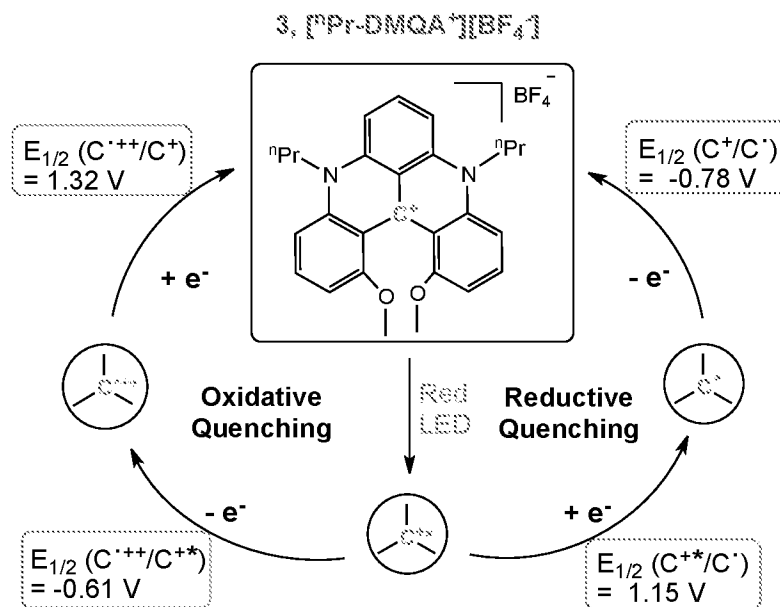
[0087] It has been discovered that compounds of the invention can catalyze different red-light-mediated reactions including, but not limited to, dual transition-metal/photoredox-

catalyzed C-H arylation and intermolecular atom transfer radical addition (ATRA) through oxidative quenching, affording the desired products in up to 93% yield. Moreover, photooxidation properties of compounds of the invention have been demonstrated in the successful applications including, but not limited to, in red-light-induced aerobic oxidative hydroxylation of arylboronic acids and benzylic C(sp³)-H oxygenation through reductive quenching. In some cases, the product yield in the range of 41-92% can be achieved. As used herein, the term “red-light” refers to electromagnetic radiation having the wavelength of from about 600 nm to about 750 nm, typically from about 600 nm to about 700 nm, and often from about 620 nm to about 700 nm.

[0088] Photoredox catalysts can be used in a wide variety of chemical reactions. Given the intrinsic disadvantages of transition-metal (TM) catalysts such as high cost, low sustainability and potential toxicity, there has been a large effort in developing organic-based PCs that are inexpensive and environmentally friendly alternatives to TM catalysts. Despite tremendous research, conventional organic-based PCs have many disadvantages, such as being only useful in reductive quenching, having a narrow redox window, being pH dependent, being susceptible to bleaching, and/or requiring high-energy blue, green or white light for their activity. Use of high-energy blue, green or white light is particular problematic in photocatalyst reactions as these high-energy electromagnetic radiations are potentially hazardous to health (e.g., photooxidative damage to retina) and are also more prone to induce undesired products due to their high energy nature.

[0089] Compounds of the invention overcomes many of these disadvantages of the conventional organic-based PCs. In particular, compounds of the invention can be activated by red light (e.g., 600-700 nm), which has a significantly low energy thereby causing less side reactions, low health risks and is naturally abundant from sunlight. More importantly, unlike high-energy blue or green lights, red light can also penetrate turbid media.

[0090] As an illustrative example, Scheme 1 below shows the photoredox properties of [Pr-DMQA⁺][BF₄⁻] (**3**) under low-energy red light, and its reactivity in a wide range of red-light-mediated reactions including both reductive and oxidative quenching.



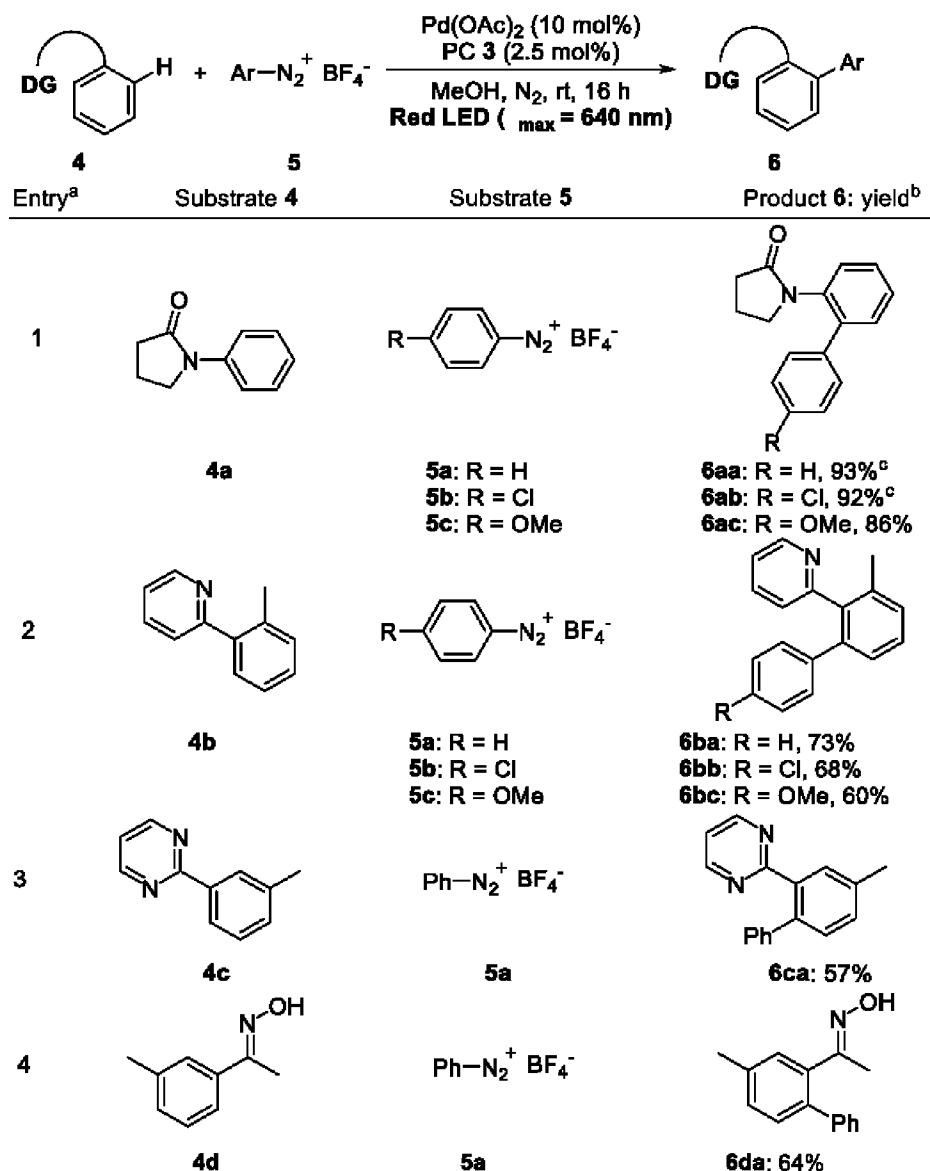
Absorption: $\lambda = 616 \text{ nm}$ (Red light). For photoreduction: I. Dual Catalysis. II. ATRA. For photooxidation: I. Aerobic Oxidative Hydroxylation. II. Aerobic Oxygenation.

Scheme 1.

[0091] Calculation of the excitation energy ($E_{0,0}$), excited state oxidation ($E_{1/2}(\text{C}^{\bullet+}/\text{C}^{\bullet+})$) and reduction potentials ($E_{1/2}(\text{C}^{\bullet-}/\text{C}^{\bullet-})$) based on the absorption and emission spectra and cyclic voltammetry data for compound **3** are shown in FIG. 4. As illustrated in Scheme 1, compound **3** possesses moderate ground state oxidation and reduction potentials $E_{1/2}(\text{C}^{\bullet+}/\text{C}^*) = +1.32 \text{ V}$ and $E_{1/2}(\text{C}^*/\text{C}^{\bullet-}) = -0.78 \text{ V}$ vs. the saturated calomel electrode (SCE), as well as moderate excited state oxidation and reduction potentials $E_{1/2}(\text{C}^{\bullet+}/\text{C}^{\bullet+}) = -0.61 \text{ V}$ and $E_{1/2}(\text{C}^{\bullet-}/\text{C}^{\bullet-}) = +1.15 \text{ V}$. These features render **3** a mild reductant and oxidant whether a reductive or oxidative quenching is involved during photocatalysis. Moreover, the excited state lifetime ($\tau = 5.5 \text{ ns}$) is also comparable to other commonly used organic PCs. In particular, the peak absorption (λ_{max}) is 616 nm, which shows compound **3** can be readily activated using a low-energy red light.

[0092] Given $E_{1/2}(\text{C}^{\bullet+}/\text{C}^{\bullet+}) = -0.61 \text{ V}$ and $E_{1/2}(\text{C}^{\bullet+}/\text{C}^*) = +1.32 \text{ V}$ for **3**, a red-light-mediated dual $\text{Pd}/\text{Pr-DMQA}^+$ -catalyzed $\text{C}(\text{sp}^2)\text{-H}$ arylation using aryldiazonium salts was conducted. The reaction between 1-([1,1'-biphenyl]-2-yl)pyrrolidin-2-one (**4a**) and benzenediazonium tetrafluoroborate (**5a**) proceeded smoothly in the presence of $\text{Pd}(\text{OAc})_2$ and **3** under red LED ($\lambda_{\text{max}} = 640 \text{ nm}$), affording the desired product **6aa** in 95% NMR yield after 4 hours. In the absence of **3**, red light, or $\text{Pd}(\text{OAc})_2$, significantly lower yields ($\leq 25\%$) of **6aa** was observed.

Table 1. Red-Light-Mediated Dual $\text{Pd}/\text{Pr-DMQA}^+$ -Catalyzed $\text{C}(\text{sp}^2)\text{-H}$ Arylation



^a The reaction was conducted with **4** (0.2 mmol), **5** (0.8 mmol), Pd(OAc)₂ (10 mol%), and **PC 3** (2.5 mol%) in MeOH (2.0 mL). ^b Isolated yield. ^c The reaction was ran for 4 h.

[0093] Table 1 shows this red-light-mediated dual Pd/ⁿPr-DMQA⁺-catalyzed C(sp²)-H arylation is applicable to a wide variety of substrates. By using **4a** as the model substrate, different electron-neutral, electron-deficient and electron-rich aryldiazonium salts **5a-5c** were examined. The reactions proceeded smoothly, delivering the desired products **6aa-6ac** in 86-93% (Table 1, entry 1). Substrate **4b** containing pyridine as the directing group (DG) was well-tolerated as well, furnishing the corresponding coupling products **6ba-6bc** in 60-73% yields by reacting with **5a-5c** (Table 1, entry 2). In addition, the desired C-H arylated product **6ca** could also be obtained in 57% yield when **4c** with pyrimidine as the DG reacted with **5a** (Table 1, entry 3). The oxime derivative **6da** was isolated in 64% yield when substrate **4d** was tested with **5a** (Table 1, entry 4). Notably, all the products **6** were obtained in relatively high isolated yields. Furthermore, experiments in the absence of **3**, red light or Pd(OAc)₂

were also conducted, affording **6** in much lower yields for all substrates. The successful application of **3** in this red-light-mediated C-H arylation shows that it is capable of use in oxidative quenching during photocatalysis.

[0094] Compounds of the invention can also be used in red-light-mediated reductive quenching. As an illustrative example, the same compound **3** was used in photo-induced aerobic oxidative hydroxylation of arylboronic acids. A representative reaction involves the oxidation of $^i\text{Pr}_2\text{NEt}$ (DIPEA) by an excited state PC^* to form the radical cation $^i\text{Pr}_2\text{NEt}^{\bullet+}$ ($^i\text{Pr}_2\text{NEt}/^i\text{Pr}_2\text{NEt}^{\bullet+} = +0.72 \text{ V vs. SCE}$) and the reduction of O_2 by the PC^* to generate the superoxide radical anion $\text{O}_2^{\bullet-}$ ($\text{O}_2/\text{O}_2^{\bullet-} = -0.33 \text{ V}$). With the excited state reduction potential ($E_{1/2}(\text{C}^{+*}/\text{C}^{\bullet})$) at +1.15 V and ground state reduction potential ($E_{1/2}(\text{C}^+/\text{C}^{\bullet})$) at -0.78 V, the present inventors believed that compound **3** would be competent to serve as an efficient PC for this reaction. Experiments with phenol **8a** was achieved in 87% NMR and 83% isolated yield when phenylboronic acid **7a** was treated with DIPEA and **3** in the presence of air and red light for 24 hours in DMF (Table 2). In the absence of PC or red light, little or no conversion was observed (Table 2).

Table 2. Optimization and control experiments of ^nPr -DMQA⁺-catalyzed aerobic oxidative hydroxylation of arylboronic acids

Entry ^a	PC	PhB(OH)_2 7a $\xrightarrow[\text{DMF, air, rt, Time}]{\text{DIPEA, PC (2 mol\%)}}$ PhOH 8a		
		Light Source	Time (h)	Yield (%) ^b
1	3	Red LED (640 nm)	18	77
2	3	Red LED (640 nm)	24	87 (83) ^c
3	3	Red LED (640 nm)	28	88
4	—	Red LED (640 nm)	28	9
5	3	—	28	n.d.

^a The reaction was conducted with **7a** (0.5 mmol), DIPEA (1.0 mmol), and **3** (2 mol%) in DMF (5.0 mL) under air at rt.

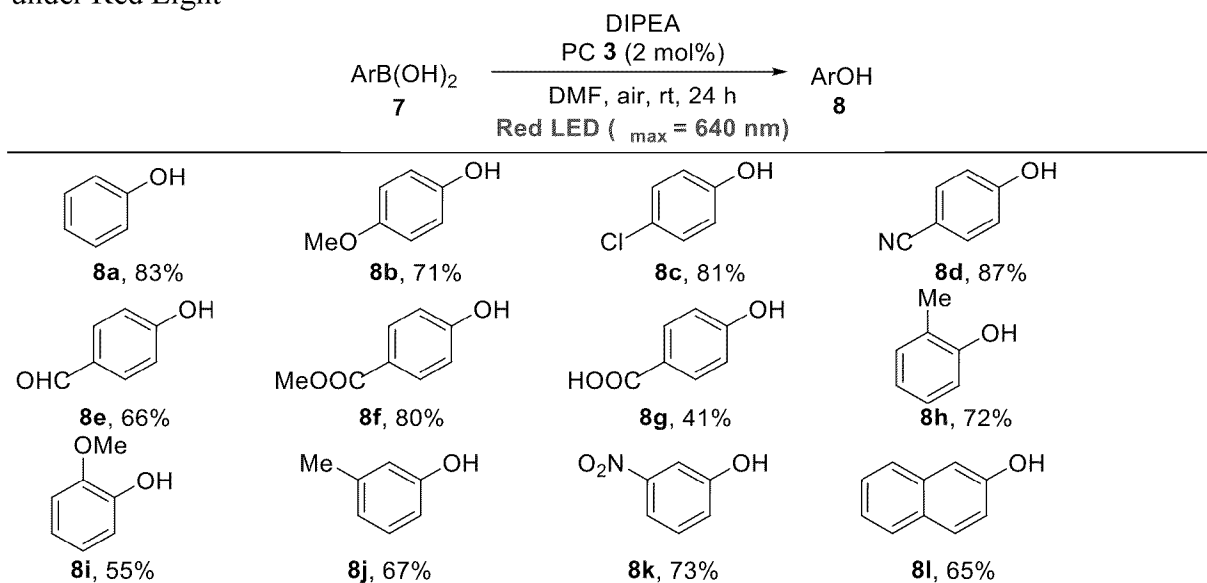
^b NMR yield by using 1,3,5-trimethoxybenzene as internal standard.

^c isolated yield.

[0095] Under the standard reaction conditions, the substrate scope was explored, and the results are presented in Table 3. A wide range of arylboronic acids **7** with diverse useful functional groups such as halide (**7c**), nitrile (**7d**), aldehyde (**7e**), ester (**7f**), carboxylic acid (**7g**) and nitro (**7k**) were well-tolerated, producing the desired phenols **8a-8l**. The substitution pattern on the phenyl ring or electronic properties of **7** didn't have much influence over the reaction outcome. For example, **8b-8g** was isolated in 41-87% yield when **7b-7g** with different electron-donating groups (EDG) or electron-withdrawing groups (EWG) at *para*

position were examined. Substrates **7h-7k** with diverse substituents at *ortho* or *meta* position also provided the corresponding phenols **8h-8k** in 55-73% yields. 2-Naphthylboronic acid **7l** was also suitable for this oxidative hydroxylation, providing naphthalen-2-ol **8l** in 65% yield. This red-light-induced $^{\text{III}}\text{Pr-DMQA}^+$ -catalyzed aerobic oxidative hydroxylation shows that **3** is an efficient PC for photocatalysis involving reductive quenching.

Table 3. $^{\text{III}}\text{Pr-DMQA}^+$ -Catalyzed Aerobic Oxidative Hydroxylation of Arylboronic Acids under Red Light



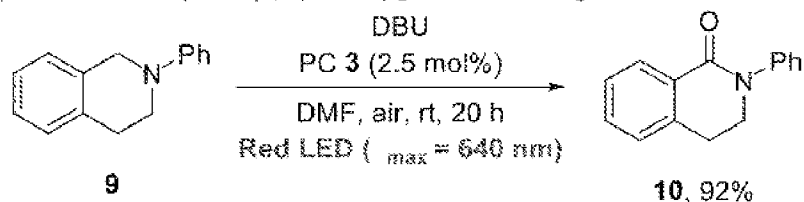
^a The reaction was conducted with **7** (0.5 mmol), DIPEA (1.0 mmol), and **3** (2 mol%) in DMF (5.0 mL) under red LED (640 nm) in the presence of air at rt for 24 h. Isolated yields were shown.

[0096] To further illustrate the generality of **3** as a PC, several other red-light-induced transformations were investigated (Scheme 2). As another example of photocatalysis involving in reductive quenching and $\text{O}_2^{\cdot-}$, visible-light-mediated aerobic benzylic $\text{C}(\text{sp}^3)\text{-H}$ oxygenation using oxygen as the oxidant was extensively studied. When a tertiary amine **9** was treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and **3** in the presence of air and red light for 20 hours in DMF, the amide **10** was isolated in 92% yield (Scheme 2a). Atom transfer radical addition (ATRA) of organic halides to olefins serves as an atom-economical approach of simultaneously forming C-C and C-X bonds, and one of the most effective way to accomplish it is photocatalysis through oxidative quenching. As shown in Scheme 2b, in the presence of LiBr and **3a**, a red-light-induced intermolecular ATRA between 4-nitrobenzyl bromide **11** and styrene **12** was realized, affording the desired adduct **13** in 59% yield. Compound **3** could also act as a dual gold/photoredox-catalyzed $\text{C}(\text{sp})\text{-H}$ arylation of terminal alkyne **14** with **5a**, providing the desired product **15** in 62% yield (Scheme 2). Control experiments in the absence of **3**, red light, or other reagents such as DBU, LiBr or

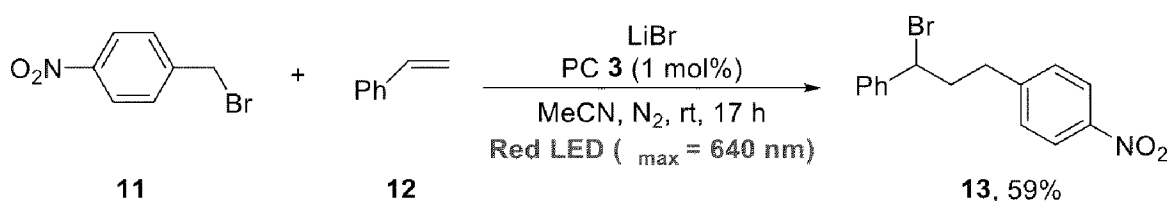
Au(PPh₃)Cl were also performed. The reduced yields of **10**, **13**, and **15** further supports the photocatalytic roles of PC **3** and red light for these reactions.

Scheme 2. Other Red-Light-Induced ¹Pr-DMQA⁺-Catalyzed Reactions

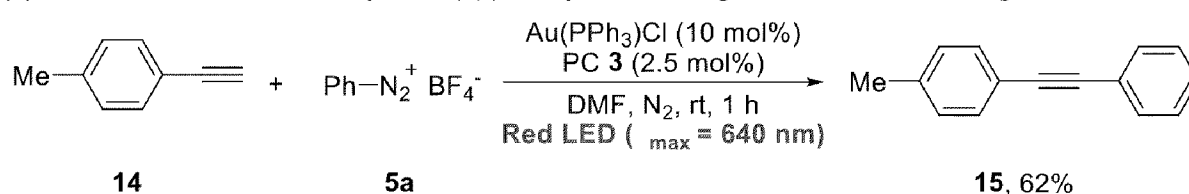
(a) Aerobic Benzylic C(sp³)-H Oxygenation through Reductive Quenching



(b) Intermolecular Atom Transfer Radical Addition (ATRA) through Oxidative Quenching



(c) Dual Au/¹Pr-DMQA⁺-Catalyzed C(sp)-H Arylation through Oxidative Quenching



^a Reactions were conducted on 0.2 mmol scale. Isolated yields were shown.

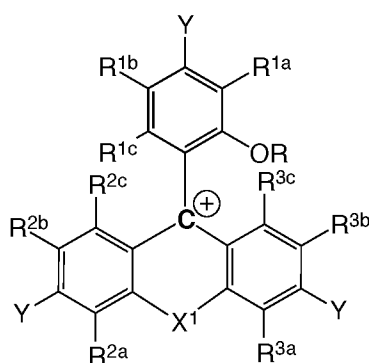
[0097] Without being bound by any theory, two representative catalytic cycles involving in oxidative or reductive quenching are illustrated in FIG. 5. Route I in FIG. 5 shows the possible mechanism for dual Pd/¹Pr-DMQA⁺-catalyzed C(sp²)-H arylation. Firstly, photoexcitation of **3** generates ¹Pr-DMQA⁺⁺, which reduces aryldiazonium **5** to form an aryl radical and ¹Pr-DMQA⁺⁺ through oxidative quenching. Then, addition of the aryl radical to the Pd(II) intermediate **A** (generated by C-H activation of substrate **4**) affords the Pd(III) species **B**, followed by an one-electron oxidation with ¹Pr-DMQA⁺⁺ to regenerate ¹Pr-DMQA⁺ and form a Pd(IV) intermediate **C**. Reductive elimination of the intermediate **C** then produces the arylated product **6**. Mechanism for ¹Pr-DMQA⁺-catalyzed aerobic oxidative hydroxylation is illustrated in route II. ¹Pr₂NEt is first oxidized to an ammonium radical cation by the excited state of **3**, along with a helicene radical ¹Pr-DMQA[•] through reductive quenching. Then, the helicene radical further reacts with oxygen to regenerate **3** and form an O₂^{•-}. Follow-up oxidative attack onto substrates **7** and hydrolysis afford phenols **8**.

[0098] Compounds of the invention, e.g., a helical carbenium organic PC – [¹Pr-DMQA⁺][BF₄⁻] (**3**), features both photoreductions and photooxidations in the presence of low-energy red light. The role of compounds of the invention as an efficient PC in oxidative and reductive quenching were assessed on a wide range of photoredox reactions, including

TM/ⁿPr-DMQA⁺-catalyzed C-H arylations and intermolecular ATRA (oxidative quenching), as well as aerobic oxidative hydroxylation of arylboronic acids and benzylic C(sp³)-H oxygenation (reductive quenching). Many diverse substrates with different DGs have been well-tolerated for the red-light-mediated dual Pd/ⁿPr-DMQA⁺-catalyzed C(sp²)-H arylation, delivering the desired products **6** in up to 93% yield. Red-light-induced ⁿPr-DMQA⁺-catalyzed aerobic oxidative hydroxylation has also been examined with many different arylboronic acids, furnishing the corresponding phenols **8** in 41-87% yields. The success in catalyzing these reactions under red light have proven the role of compounds of the invention as a versatile organic PC.

[0099] One particular aspect of the invention provides a carbenium comprising a coordinating group that is capable of coordinating to a metal complex. Such a compound can be used in a wide variety of applications including, but not limited to, as homogeneous catalysts (e.g., photocatalysts) in chemical reactions, as redox compounds in photovoltaic cells, as compounds in artificial photosynthesis applications, etc. In one particular embodiment, compounds of the invention comprise a conjugated heterocyclic carbenium ion that is suitable to bind to or is bound to a metal complex.

[0100] Compounds of the invention are useful in electronic equipment as well as catalysts in various organic reactions. One particular aspect of the invention provides a compound comprising a carbocation of the formula:



Carbocation A

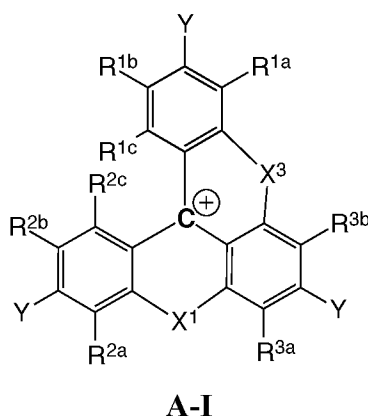
where R is C₁-C₁₂ alkyl or Aryl; X¹ is O, NR^{4a}, PR^{4a}, CR^{4a}R^{4b}, or SiR^{4a}R^{4b}; each of Y is independently H, OR^{5a}, NR^{5a}R^{5b}, PR^{5a}R^{5b}, NO₂, CN, haloalkyl (e.g., CF₃), N₃, CO₂R, or Ar¹; each of R^{1a}, R^{1b}, R^{1c}, R^{2a}, R^{2b}, R^{2c}, R^{3a}, R^{3b}, and R^{3c}, is independently H, halide, CF₃, NH₂, C₁-C₁₂ alkyl, C₁-C₄ alkoxy, C₁-C₄ alkylamino, C₁-C₄ dialkyl amino, NO₂, CN, CO₂R, or Ar¹; each of each of R^{4a}, R^{4b}, R^{5a}, and R^{5b} is independently H, halide, CF₃, C₁-C₁₂ alkyl, C₁-C₄ alkoxy, C₁-C₄ alkylamino, C₁-C₄ dialkyl amino, or Ar¹; or R^{1c} and R^{2c} together form -X²-; or OR and R^{3c} together form -X³-; each of X² and X³ is independently O, NR^{4a}, PR^{4a}, CR^{4a}R^{4b},

or $\text{SiR}^{4a}\text{R}^{4b}$; or R^{1b} and R^{1c} together with atoms to which they are attached to form a phenyl; or R^{2b} and R^{2c} together with atoms to which they are attached to form a phenyl; Ar^1 is optionally substituted phenyl having from 0 to 5 substituents, each of which is independently selected from the group consisting of X^1 , CF_3 , NH_2 , $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ alkoxy, $\text{C}_1\text{-C}_4$ alkylamino, and $\text{C}_1\text{-C}_4$ dialkyl amino; and wherein at least one of R^{1a} , R^{1b} , R^{1c} , R^{2a} , R^{2b} , R^{2c} , R^{3a} , R^{3b} , R^{3c} , R^{4a} , R^{4b} , R^{5a} , and R^{5b} is a moiety of the formula $-\text{L}-\text{Z}$, wherein L is a linker; and Z is a coordinating group that is capable of coordinating to a metal complex or is coordinated to a metal complex. Z can also be a functional group that can be used to attached to a surface of a solid substrate.

[0101] Some of the advantages of compounds of the invention comprising carbocation **A** are believed to be due at least in part because: (i) they are among the most stable carbocations to date, including under mild acidic or basic aqueous conditions; (ii) the stepwise and temperature dependence of the synthesis allows versatility of using a wide variety of starting materials for synthesis (e.g., by using aliphatic or aromatic amines) and allows formation of unsymmetrical ions; (iii) they can be readily functionalized, e.g., via C-H metal-catalyzed cross-coupling; and (iv) the negative counterions can be exchanged to affect the physical and chemical properties of the salts. Additionally, compounds comprising carbocation **A** are redox active compounds, thereby allowing them to be used in various electronic equipment.

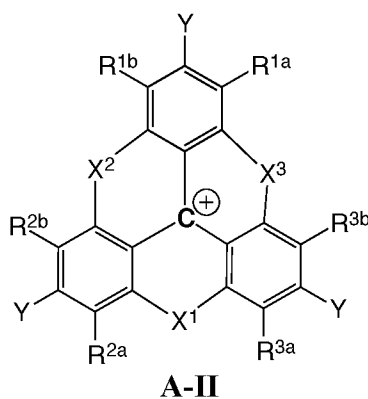
[0102] In some embodiments, carbocations of Formula **A** do not require the moiety of the formula $-\text{L}-\text{Z}$. In these embodiments, the metal complex can be present in solution as a separate entity to provide catalytic and/or photovoltaic activity. Still in other embodiments, carbocation of Formula **A** lacks a moiety of the formula $-\text{L}-\text{Z}$ altogether.

[0103] In some embodiments, the carbocation or carbenium is of the formula:



wherein Y, X^1 , X^3 , R^{1a} , R^{1b} , R^{1c} , R^{2a} , R^{2b} , R^{2c} , R^{3a} , and R^{3b} are as defined herein.

[0104] Yet in another embodiment, the carbenium is of the formula:



wherein Y, X¹, X², X³, R^{1a}, R^{1b}, R^{2a}, R^{2b}, R^{3a}, and R^{3b} are as defined herein.

[0105] Still in another embodiment, X¹ is NR^{4a}. In some instances within this embodiment, R^{4a} is the moiety of the formula –L–Z.

[0106] Still in other embodiments, Z is a coordinating group. Generally, a coordinating group refers to a moiety that has one or more heteroatoms that is capable of coordinating to a metal complex. Exemplary coordinating groups include heteroaryl, heteroatom functional groups such as phosphates, sulfates, carbonates, hydroxyl group and ethers, thiol and thiol ethers, amines, imines, carboimides, carbamides, etc. “Heteroaryl” refers to a monovalent monocyclic or bicyclic aromatic moiety of 5 to 12 ring atoms containing one, two, or three ring heteroatoms selected from N, O, or S, the remaining ring atoms being C. The heteroaryl ring can optionally be substituted with one or more substituents. More specifically the term heteroaryl includes, but is not limited to, pyridyl, furanyl, thiophenyl, thiazolyl, isothiazolyl, triazolyl, imidazolyl, isoxazolyl, pyrrolyl, pyrazolyl, pyrazinyl, pyrimidinyl, benzofuranyl, isobenzofuranyl, benzothiazolyl, benzoisothiazolyl, benzotriazolyl, indolyl, isoindolyl, benzoxazolyl, quinolyl, isoquinolyl, benzimidazolyl, benzisoxazolyl, benzothiophenyl, dibenzofuran, and benzodiazepin-2-one-5-yl, and the like.

[0107] In one particular embodiment, Z is selected from the group consisting of bipyridinyl, pyridinyl, –PR₂, –OPR₂, –NHC, –NR₂, diimine, imine, –OR, –SR, diphosphines, –RNC, –CO₂H, and carboimine, where each R is independently H, C₁–C₁₂ alkyl or Aryl.

[0108] Yet in other embodiments, each of R^{1c}, R^{2c}, and R^{3c} is independently C₁–C₄ alkoxy. In one particular embodiment, R^{1c}, R^{2c}, and R^{3c} are methoxy.

[0109] Still in other embodiments, Y, R^{1a}, R^{1b}, R^{2a}, R^{2b}, R^{3a}, and R^{3b} are H.

[0110] Another aspect of the invention provides a photocatalyst composition comprising a conjugated heterocyclic carbenium-metal complex of Formula **A** in which Z is a coordinating group that is coordinated to a metal complex.

[0111] In one particular embodiment, the conjugated heterocyclic carbenium-metal complex is of the formula **A-I**.

[0112] Still in another embodiment, the conjugated heterocyclic carbenium-metal complex is of the formula **A-II**.

[0113] In another aspect of the invention, Z in compound of Formula I is a functional group that is attached to a surface of a solid substrate. In this manner, a solid substrate comprising a carbocation of Formula **A** is provided. Functional groups that can be used to attach to a surface of a solid substrate depends on the solid substrate material. For example, for Au, often thiol group is used to attach to gold surface, and for silica based solid substrate (e.g., a glass substrate), often amine or silane groups are typically used. Other suitable functional groups that can be used in other solid substrates are well known to one skilled in the art.

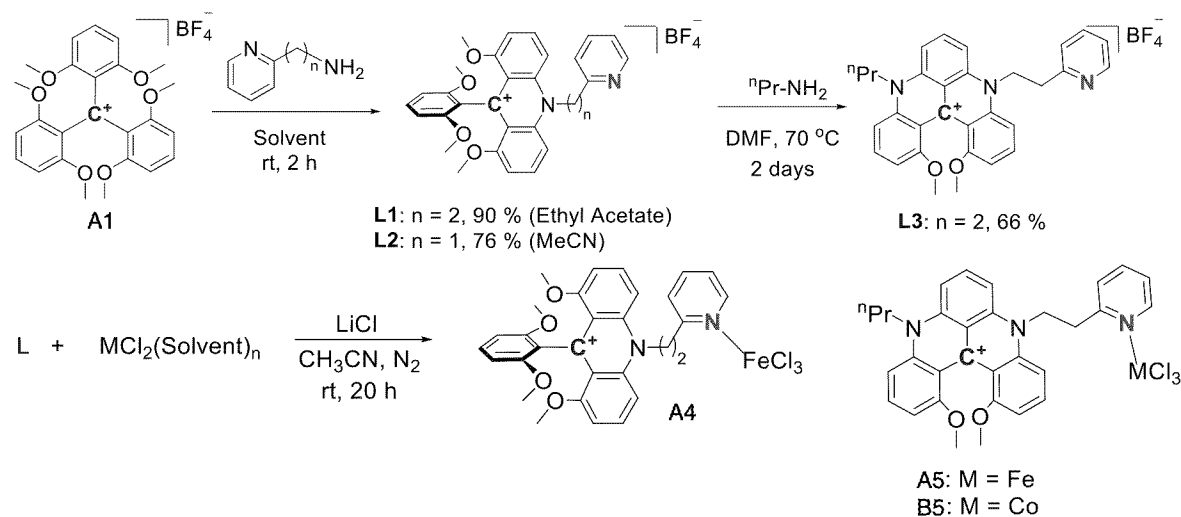
[0114] In some embodiments, the carbocation attached to a solid substrate surface is of the formula **A-I** with Z being the coordinating group that is coordinated to a metal complex. Still in other embodiments, the carbocation is of the formula **A-II** with Z being the functional group that is used to attach to the solid substrate surface.

[0115] Still in other embodiments, the carbocation that is attached to a solid substrate surface can also include a linker and a metal complex. In particular, the carbocation can include a moiety of the formula $-L'-Z'$, where L' is linker as defined for L and Z' is a metal complex as defined for Z. In this manner, the carbocation is attached to a solid substrate via $-L-Z$ moiety and also has at least one linker that is coordinated to a metal complex via $-L'-Z'$ moiety.

[0116] Compounds of the invention can be used in a wide variety of applications including, but not limited to, as photocatalysts, as photovoltaic cells, as artificial photosynthesis materials, etc.

[0117] Compounds of the invention comprising a carbocation of Formula **A** can be prepared as illustrated in scheme **A** below. By using different starting materials with different substituents on the phenyl ring(s), one can readily prepare a wide variety of different carbocation of Formula **A**. While not specifically shown in Scheme **A** below, a further

reaction with additional $n\text{Pr-NH}_2$ or other $-\text{L}-\text{Z}$ moiety with provide an angulanium compound (i.e., compound of Formula **A-II**). Thus, scheme A illustrates a general method for producing acridiniums (e.g., carbocation of Formula **A** where neither R^{1c} and R^{2c} together nor $-\text{OR}$ and R^{3c} together form $-\text{X}^{2-}$ or $-\text{X}^{3-}$, respectively), heliceniums (carbocation of Formula **A-I**) as well as angulaniums (carbocation of Formula **A-II**).



Scheme A

[0118] In some embodiments, catalysts of the invention are activated by wavelength of 450 nm or less.

[0119] Compounds of the invention can be used as photocatalysts in various organic reactions. The type of organic reaction that can be achieved depends on the metal complex that is attached to the compound of the invention. For example, as shown in Table A, using iron metal complex allows 1,2-radical addition.

[0120] The photocatalysis reaction was conducted in a glove box by adding to a Schlenk flask compound 1 (0.2 mmol), compound 2 (1.0 mmol), catalyst (0.006 mmol) and MeCN (2 mL). After the addition of reagents in to the Schlenk flask, the reaction was removed from the glove box and stirred under an inert atmosphere in the presence of blue LEDs (467 nm). When 2.0 equivalent of LiBr was added to the reaction, the yield increased from 12% to 81%. Thus, in some embodiments, an additional reaction enhancing reagent can be added.

[0121] As can be seen in Table A, without photoactivation (e.g., no blue LED), no reaction was observed, while ligand L3 and Co-complex 5b gave ~30% and 8%, respectively. For $\text{FeCl}_2 \cdot (\text{THF})_{1.5}$ (entry 10, Table 1) and FeCl_3 (entry 12) no product was observed in the absence of LED. With LEDs, yield of ~28% and 23%, respectively, was observed. As can be

clearly seen in Table A, at best only a trace product was observed when no catalyst was added.

Table A. Photocatalysis Reaction

Entry ^a	Catalyst	Time [h]	Yield [%] ^b
1	A5	13	~81
2	A5(No LiBr)	13	~12
3	A5(No LED)	13	N. R.
4	A5(No LED) ^c	13	N. R.
5	L3	18	~30
6	B5 (Co)	18	~8
7	No catalyst	24	trace
8	A4 (Acridinium)	24	~3
9	FeCl ₂ (THF) _{1.5}	13	~28
10	FeCl ₂ (THF) _{1.5} (No LED)	13	0
11	FeCl ₃	13	~23
12	FeCl ₃ (No LED)	13	0
15	A5	15	> 95
16	FeCl ₂ (THF) _{1.5} + L3	15	~95
17	FeCl ₃ (H ₂ O) ₆ + L3 ^d	18	>95
18	FeCl ₃ (H ₂ O) ₆ + L2 ^d	18	~3

a) The reaction was ran with **1** (0.2 mmol), **2** (1.0 mmol), **2** (1.0 mmol) and catalyst (0.006 mmol) in MeCN (2 mL). b) NMR yield by using 1,3,5-trimethoxybenzene as internal standard.

c) Ran outside at 19 °C. d) Weighed all compounds outside, and degassed solvent for 15 mins then the Schlenk tube for 15 mins without any Schlenk technique.

[0122] As can be seen, in some instances only a minor trace of product was observed with acridinium complex (e.g., compound of Formula **A-I**) while use of helicenium compounds of the invention (e.g., compound of Formula **A-II**) gave a much higher yield. Furthermore, it should be noted that when all compounds were weighted including FeCl₃•(H₂O)₆ and solvent without using a Schlenck flask, and the combined reaction mixture was degassed for 15 mins, the reaction gave a high yield of the product with helicenium ligand **L3** as a photocatalyst was used (>95% yield), while only 3% yield of product was observed with acridinium ligand **L2**. Accordingly, some embodiments of the invention

include a method of photocatalyst reaction using compound of Formula **A-II** optionally without a need for inert atmosphere during combination of reagents.

Table B. Catalyst loading

Entry ^a	Catalyst	x mol%	Time [h]	Yield [%] ^b
1	A5	3	13	~81
2	A5	3	3	~18
3	A5	3	6	~36
4	A5	3	15	>95
5	A5	3	20	>95
6	A5	1	15	>95
7	A5	0.5	15	>95
8	A5	0.2	15	~67
9	A5	0.1	15	~42
10	A5	0.2	20	~82
11	A5	0.1	20	~55
12	A5	0.1	24	~57
13	FeCl ₂ (THF) _{1.5} + L3	0.1	24	~55
14	A5 (1.2 equiv. 2)	0.5	15	~30
15	A5 (2.0 equiv. 2)	0.5	20	~50

a) The reaction was ran with **1** (0.2 mmol), **2** (1.0 mmol), LiBr (0.4 mmol) and catalyst (X mmol) in MeCN (2 mL). b) NMR yield by using 1,3,5-trimethoxybenzene as internal standard.

[0123] Table B shows the results of using different amounts of photocatalyst of the invention in addition reaction. Based on these results, the present inventors have discovered that for addition reaction (such as those illustrated in Table A and B), the amount of catalyst of the invention used in methods of the invention is about 5 mol% or less, typically about 3 mol% or less, often about 1 mol% or less, and most often about 0.5 mol% or less.

[0124] The reaction temperature can vary depending on a variety of factors, such as but not limited to, reagents used, the amount of reagents used, a particular reaction desired (e.g., addition reaction, radical cyclization reaction, hydrogenation, etc.), reaction solvent, etc. However, in general a photocatalyst reaction using compounds of the invention will range in temperature from about 0 °C to about 140 °C or the boiling point of the solvent,

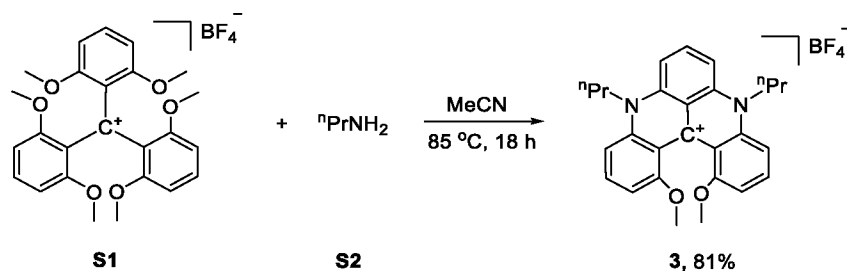
whichever is lower, typically the reaction temperature of a photocatalyst reaction is from about 0 °C to about 100 °C, often from about 5 °C to about 80 °C, more often from about 10 °C to about 50 °C, and most often from about 20 °C to about 30 °C.

[0125] Additional objects, advantages, and novel features of this invention will become apparent to those skilled in the art upon examination of the following examples thereof, which are not intended to be limiting. In the Examples, procedures that are constructively reduced to practice are described in the present tense, and procedures that have been carried out in the laboratory are set forth in the past tense.

EXAMPLES

[0126] Unless otherwise specified, all reactions were carried out in oven-dried (overnight) vials or Schlenk tubes with magnetic stirring in a glove box. ¹H, ¹³C and ¹⁹F NMR spectra were recorded on Bruker Avance III-400 MHz or DRX-500 MHz spectrometers in appropriate solvents using TMS as internal standard or the solvent signals as secondary standards. The chemical shifts are shown in δ scales. Multiplicities of ¹H NMR signals are designated as s (singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet), t (triplet), quin (quintet), m (multiplet), etc.. Compounds were named using ChemDraw and assignments of NMR spectra were done using MestReNova. All chemicals and solvents were purchased from Sigma Aldrich, Fisher Scientific, or VWR. Organic solvents used were dried by a standard solvent purification system (J. C. Meyer or Vigor Solvent Systems). Commercially obtained reagents were used without further purification. All reactions were monitored by TLC silica gel 60 F₂₅₄ (EMD Millipore). Flash column chromatography was carried out using SiliaFlash silica gels F60, 40-63 μm, 60 Å (SiliCycle) at increased pressure. All reactions were performed under N₂ using standard Schlenk techniques or in a glove box (Mbraun glove box).

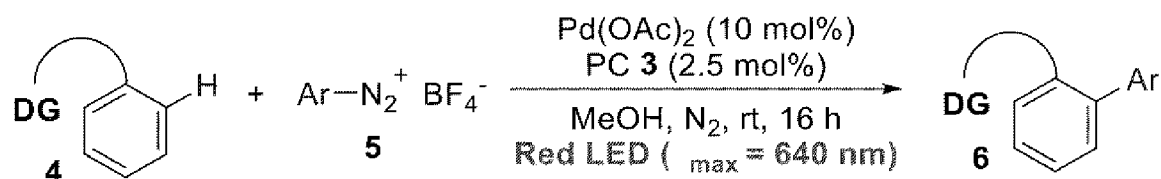
[0127] Synthesis and characterization of dimethoxyquinacridinium (DMQA⁺) tetrafluoroborate **3**.



[0128] A solution of **S1** (1.02 g, 2 mmol, 1.0 equiv.) and **S2** (2.95 g, 50 mmol, 25.0 equiv.) in MeCN (20 mL) was stirred at 85 °C for 18 hours. The mixture was cooled to room temperature, transferred to a 250 mL round bottom flask and a large excess of Et₂O (200 mL) was added to crash out the crude product **3** as a dark green solid (924 mg). After layering in DCM/MeCN/MeOH/Et₂O for 2 days, 811 mg of pure product **3** was obtained as a dark green solid after filtration.

[0129] **Reaction setup for photocatalysis.** Two 25 mL Schlenk tubes were placed in a water bath (Pyrex crystallizing dish, 125 x 65mm, No. 3140) at the center of a stir plate. Two parallel Red LED lamps (KSPR160L-640-C Red LED 640nm Photoredox Light customized wavelength) were placed perpendicular to the sidewall of Schlenk tubes, so that the two tubes can be equally exposed to the LEDs. The stir plate/water bath/LEDs were surrounded by an open-top cardboard box covered with aluminum foil to increase the light reflections. A fan (Honeywell, TurboForce Power HT900) over the water bath was turned on when the reaction was running. The combination of an overhead fan and a water bath was to offset the heat generated from the LED lights and stabilize reaction temperature for reproducible results. The water bath was refilled with room temperature deionized water every 12-18 hours. With the above setup, the reaction temperature was maintained at 21-23 °C during the reaction.

[0130] **General procedure for red-light-mediated dual Pd⁰/Pr-DMQA⁺-catalyzed C-H arylation.**



[0131] In a N₂ glove box, Pd(OAc)₂ (4.5 mg, 0.02 mmol, 10 mol%), **3** (2.5 mg, 0.005 mmol, 2.5 mol%), the substrate **4** (0.2 mmol, 1.0 equiv.) and the aryldiazonium salt **5** (0.8 mmol, 4.0 equiv.) were added to an oven-dried (overnight) Schlenk tube containing a stirring bar, followed by adding degassed anhydrous MeOH (2.0 mL, 0.1 M). The Schlenk tube was then sealed, removed from the glove box and stirred at room temperature under red LED ($\lambda_{\text{max}} = 640 \text{ nm}$) irradiation. After 16 hours, the mixture was quenched with a saturated solution of NaHCO₃ (2 mL), followed by adding deionized water (2 mL). The crude reaction mixture was then extracted with ethyl acetate, and the combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. After filtration, the solvent was removed under

reduced pressure. The crude product was purified by flash chromatography (FC) on silica gel (eluent: Hexanes/EtOAc = 20/1 ~ 1/1) to yield the desired product **6**.

[0132] 1-([1,1'-biphenyl]-2-yl)pyrrolidin-2-one (**6aa**): Yield (44 mg, 93%). A clear viscous oil. R_f = 0.2 (Hexanes/EtOAc = 1/2). FC (Hexanes/EtOAc = 1/1). ^1H NMR (400 MHz, C_6D_6) δ 7.39-7.35 (m, 2H, ArH), 7.33 (dd, J = 8.0, 1.6 Hz, 1H, ArH), 7.21 (dd, J = 7.6, 1.6 Hz, 1H, ArH), 7.17-7.04 (m, 5H, ArH), 2.78 (t, J = 6.8 Hz, 2H, CH_2), 2.04 (t, J = 8.0 Hz, 2H, CH_2), 1.19 (tt, J = 6.8, 8.0 Hz, 2H, CH_2). ^{13}C NMR (101 MHz, C_6D_6) δ 174.18, 140.13, 140.08, 137.67, 130.98, 129.18, 128.82, 128.63, 128.48, 127.74, 127.64, 49.70, 31.11, 19.06. ^1H NMR (400 MHz, CDCl_3) δ 7.43-7.31 (m, 9H, ArH), 3.21 (t, J = 6.8 Hz, 2H, CH_2), 2.42 (t, J = 8.0 Hz, 2H, CH_2), 1.87 (tt, J = 6.8, 8.0 Hz, 2H, CH_2). ^{13}C NMR (101 MHz, CDCl_3) δ 175.70, 139.73, 139.22, 136.43, 130.92, 128.65, 128.51, 128.49, 128.45, 128.12, 127.67, 50.26, 31.30, 19.08.

[0133] 1-(4'-chloro-[1,1'-biphenyl]-2-yl)pyrrolidin-2-one (**6ab**): Yield (50 mg, 92%). A light yellow solid. R_f = 0.2 (Hexanes/EtOAc = 1/2). FC (Hexanes/EtOAc = 1/1). ^1H NMR (400 MHz, C_6D_6) δ 7.24 (dd, J = 8.0, 1.2 Hz, 1H, ArH), 7.15-7.04 (m, 7H, ArH), 2.73 (t, J = 6.8 Hz, 2H, CH_2), 2.00 (t, J = 8.0 Hz, 2H, CH_2), 1.18 (tt, J = 6.8, 8.0 Hz, 2H, CH_2). ^{13}C NMR (101 MHz, C_6D_6) δ 174.18, 138.86, 138.46, 137.53, 133.78, 130.79, 130.21, 129.01, 128.82, 128.81, 49.77, 31.03, 19.01. ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.30 (m, 8H, ArH), 3.26 (t, J = 6.8 Hz, 2H, CH_2), 2.43 (t, J = 8.0 Hz, 2H, CH_2), 1.92 (tt, J = 6.8, 8.0 Hz, 2H, CH_2). ^{13}C NMR (126 MHz, CDCl_3) δ 175.83, 138.71, 137.78, 136.49, 133.87, 130.85, 129.88, 129.10, 128.79, 128.58, 128.34, 128.33, 50.33, 31.13, 18.95.

[0134] 1-(4'-methoxy-[1,1'-biphenyl]-2-yl)pyrrolidin-2-one (**6ac**): Yield (46 mg, 86%). An orange viscous oil. R_f = 0.2 (Hexanes/EtOAc = 1/2). FC (Hexanes/EtOAc = 1/1). ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.34 (m, 3H, ArH), 7.32-7.28 (m, 3H, ArH), 6.94-6.92 (m, 2H, ArH), 3.84 (s, 3H), 3.22 (t, J = 6.8 Hz, 2H, CH_2), 2.44 (t, J = 8.0 Hz, 2H, CH_2), 1.89 (tt, J = 6.8, 8.0 Hz, 2H, CH_2). ^{13}C NMR (101 MHz, CDCl_3) δ 175.76, 159.25, 139.37, 136.42, 131.58, 130.94, 129.59, 128.49, 128.30, 128.12, 113.96, 55.37, 50.18, 31.35, 19.11.

[0135] 2-(3-methyl-[1,1'-biphenyl]-2-yl)pyridine (**6ba**): Yield (36 mg, 73%). A clear viscous oil. R_f = 0.4 (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 20/1). ^1H NMR (500 MHz, CDCl_3) δ 8.63 (ddd, J = 5.0, 2.0, 1.0 Hz, 1H, ArH), 7.44 (ddd, J = 7.5, 7.5, 1.5 Hz, 1H, ArH), 7.36 (dd, J = 7.5, 7.5 Hz, 1H, ArH), 7.31-7.26 (m, 2H, ArH), 7.16-7.11 (m, 3H, ArH), 7.10-7.06 (m, 3H, ArH), 6.88 (ddd, J = 7.5, 7.5, 1.5 Hz, 1H, ArH), 2.19 (s, 3H, Me). ^{13}C

NMR (101 MHz, CDCl₃) δ 159.69, 148.92, 141.77, 141.36, 139.41, 136.80, 135.81, 129.75, 129.71, 129.52, 128.15, 127.70, 127.69, 126.32, 125.74, 121.40, 20.59.

[0136] 2-(4'-chloro-3-methyl-[1,1'-biphenyl]-2-yl)pyridine (**6bb**): Yield (38 mg, 68%). A pale yellow viscous oil. R_f = 0.4 (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 20/1). ¹H NMR (400 MHz, CDCl₃) δ 8.62 (ddd, J = 4.8, 4.8, 1.2 Hz, 1H, ArH), 7.48 (ddd, J = 7.6, 7.6, 2.0 Hz, 1H, ArH), 7.38-7.28 (m, 2H, ArH), 7.23 (dd, J = 7.6, 1.2 Hz, 1H, ArH), 7.13-7.09 (m, 3H, ArH), 7.03-6.99 (m, 2H, ArH), 6.89 (ddd, J = 7.6, 7.6, 1.2 Hz, 1H, ArH), 2.18 (s, 3H, Me). ¹³C NMR (101 MHz, CDCl₃) δ 159.40, 149.11, 140.26, 140.07, 139.42, 136.97, 136.00, 132.46, 130.99, 129.83, 128.24, 127.91, 127.53, 125.64, 121.58, 20.55.

[0137] 2-(4'-methoxy-3-methyl-[1,1'-biphenyl]-2-yl)pyridine (**6bc**): Yield (33 mg, 60%). A clear viscous oil. R_f = 0.4 (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 20/1). ¹H NMR (400 MHz, CDCl₃) δ 8.63 (ddd, J = 4.8, 4.8, 1.2 Hz, 1H, ArH), 7.46 (ddd, J = 7.6, 7.6, 2.0 Hz, 1H, ArH), 7.34 (dd, J = 7.6, 7.6 Hz, 1H, ArH), 7.28-7.23 (m, 2H, ArH), 7.09 (ddd, J = 7.6, 4.8, 1.2 Hz, 1H, ArH), 7.02-6.97 (m, 2H, ArH), 6.88 (d, J = 8.0 Hz, 1H, ArH), 6.70-6.66 (m, 2H, ArH), 3.73 (s, 3H, OMe), 2.18 (s, 3H, Me). ¹³C NMR (101 MHz, CDCl₃) δ 159.93, 158.17, 148.98, 140.90, 139.45, 136.78, 135.86, 134.22, 130.78, 129.18, 128.11, 127.69, 125.71, 121.33, 113.18, 55.20, 20.60.

[0138] 2-(4-methyl-[1,1'-biphenyl]-2-yl)pyrimidine (**6ca**): Yield (28 mg, 57%). A clear viscous oil. R_f = 0.3 (Hexanes/EtOAc = 3/1). FC (Hexanes/EtOAc = 15/1). ¹H NMR (400 MHz, CDCl₃) δ 8.63 (d, J = 4.8 Hz, 2H, ArH), 7.61 (d, J = 1.6 Hz, 1H, ArH), 7.37 (d, J = 7.6 Hz, 1H, ArH), 7.32 (dd, J = 7.6, 1.6 Hz, 1H, ArH), 7.24-7.18 (m, 3H, ArH), 7.14-7.10 (m, 2H, ArH), 7.08 (dd, J = 4.8, 4.8 Hz, 1H, ArH), 2.46 (s, 3H, Me). ¹³C NMR (101 MHz, CDCl₃) δ 168.37, 156.83, 141.67, 138.76, 138.12, 137.28, 131.19, 130.79, 130.29, 129.28, 128.05, 126.39, 118.50, 21.18.

[0139] 1-(4-methyl-[1,1'-biphenyl]-2-yl)ethan-1-one oxime (**6da**): Yield (29 mg, 64%). A white solid. R_f = 0.4 (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 20/1). ¹H NMR (400 MHz, C₆D₆) δ 8.69 (s, 1H, OH), 7.40-7.37 (m, 2H, ArH), 7.32 (d, J = 2.0 Hz, 1H, ArH), 7.13-7.03 (m, 3H, ArH), 6.96 (dd, J = 7.6, 2.0 Hz, 1H, ArH), 2.09 (s, 3H, Me), 1.78 (s, 3H, Me). ¹³C NMR (101 MHz, C₆D₆) δ 159.07, 141.64, 138.32, 137.39, 137.27, 130.55, 130.44, 129.86, 129.37, 128.69, 127.31, 20.85, 16.30. ¹H NMR (500 MHz, CDCl₃) δ 8.15 (s, 1H, OH), 7.42-7.37 (m, 4H, ArH), 7.35-7.31 (m, 1H, ArH), 7.30-7.28 (m, 1H, ArH), 7.27-7.24 (m, 2H, ArH), 2.41 (s, 3H, Me), 1.69 (s, 3H, Me). ¹³C NMR (101 MHz, CDCl₃) δ 159.50,

141.10, 137.89, 137.31, 136.73, 130.38, 129.90, 129.84, 129.09, 128.54, 127.25, 21.12, 16.12.

[0140] Red-light-mediated dual Pd/¹²⁹Pr-DMQA⁺-catalyzed C-H arylation. Using 1-([1,1'-biphenyl]-2-yl)pyrrolidin-2-one (**4a**) and benzenediazonium tetrafluoroborate (**5a**) as the model substrates, Pd(OAc)₂ as the catalyst, **3** as the PC, MeOH as the solvent, the reaction time was screened and the results are outlined in Table S2. Under red LED (λ_{max} = 640 nm), the reaction proceeded smoothly to afford the desired product **6aa** in 95% NMR yield after 8 hours (Table S2, entry 1). By decreasing the reaction time to 6 h, 4 h and 2 h, the desired product **6aa** was obtained in 95%, 95% and 85% NMR yield, respectively. To test the background reactions, several control experiments have also been performed. In the absence of PC **3**, red light or Pd(OAc)₂, significantly lower yields ($\leq 25\%$) of **6aa** was observed for all the conditions.

[0141] NMR results for control reactions. To further demonstrate the essential roles of red light, PC **3** and Pd catalyst, control experiments to determine the background reaction yields for all substrates have been conducted and the NMR results were determined. In general, in the absence of red light, $\leq 15\%$ NMR yield was observed for all the substrates, except for 36% NMR yield for the reaction of **4a** and 4-chlorobenzenediazonium tetrafluoroborate **5b**. In the absence of **3**, $\leq 40\%$ NMR yield was observed for all the substrates, except for 45% NMR yield for the reaction of **4a** and **5b**. The lower background observed in the present system highlights the great potential of low-energy red light towards reaction selectivity. At last, in the absence of Pd catalyst, trace amount of products **6** was observed for all the substrates, which supports the essential role of palladium for activating the substrate **4** during the catalytic cycle.

[0142] General procedure for ¹²⁹Pr-DMQA⁺-catalyzed aerobic oxidative hydroxylation of arylboronic acids under red light. To a mixture of arylboronic acid **7** (0.50 mmol, 1.0 equiv.) and PC **3** (5.0 mg, 0.01 mmol, 2 mol%) in DMF (5.0 mL, 0.1 M) was added DIPEA (129 mg, 1.0 mmol, 2.0 equiv.) in a Schlenk tube. The solution was stirred at room temperature under red LED (λ_{max} = 640 nm) irradiation in open to air (without bubbling air). After 24 hours, the reaction mixture was cooled to 0 °C and quenched by adding aqueous solution of HCl slowly, followed by extracting with Et₂O. The combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. After filtration, the solvent was

removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (eluent: Hexanes/EtOAc = 20/1 ~ 1/2) to furnish the desired product **8**.

[0143] Phenol (**8a**): Yield (39 mg, 83%). A colorless solid. R_f = 0.4 (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 15/1). ^1H NMR (500 MHz, CDCl_3) δ 7.27-7.23 (m, 2H, ArH), 6.96-6.92 (m, 1H, ArH), 6.87-6.83 (m, 2H, ArH), 5.10 (s, 1H, OH). ^{13}C NMR (126 MHz, CDCl_3) δ 155.75, 129.89, 120.97, 115.50.

[0144] 4-Methoxyphenol (**8b**): Yield (44 mg, 71%). A colorless solid. R_f = 0.2 (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ 6.84-6.77 (m, 4H, ArH), 4.76 (s, 1H, OH), 3.80 (s, 3H, OMe). ^{13}C NMR (101 MHz, CDCl_3) δ 153.89, 149.59, 116.19, 115.02, 55.96.

[0145] 4-Chlorophenol (**8c**): Yield (52 mg, 81%). A colorless oil. R_f = 0.4 (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ 7.21-7.18 (m, 2H, ArH), 6.78-6.75 (m, 2H, ArH), 4.86 (s, 1H, OH). ^{13}C NMR (101 MHz, CDCl_3) δ 154.22, 129.67, 125.83, 116.80.

[0146] 4-Cyanophenol (**8d**): Yield (52 mg, 87%). A light yellow solid. R_f = 0.1 (Hexanes/EtOAc = 3/1). FC (Hexanes/EtOAc = 5/1). ^1H NMR (400 MHz, CDCl_3) δ 7.57-7.54 (m, 2H, ArH), 6.96-6.93 (m, 2H, ArH), 6.69 (s, 1H, OH). ^{13}C NMR (101 MHz, CDCl_3) δ 160.34, 134.47, 119.37, 116.61, 103.16.

[0147] 4-Hydroxybenzaldehyde (**8e**): Yield (40 mg, 66%). A white solid. R_f = 0.3 (Hexanes/EtOAc = 3/1). FC (Hexanes/EtOAc = 5/1). ^1H NMR (400 MHz, Methanol- d_4) δ 9.76 (s, 1H, CHO), 7.78-7.75 (m, 2H, ArH), 6.93-6.90 (m, 2H, ArH). ^{13}C NMR (101 MHz, Methanol- d_4) δ 192.81, 165.15, 133.42, 130.30, 116.85.

[0148] Methyl 4-hydroxybenzoate (**8f**): Yield (61 mg, 80%). A white solid. R_f = 0.3 (Hexanes/EtOAc = 3/1). FC (Hexanes/EtOAc = 5/1). ^1H NMR (400 MHz, CDCl_3) δ 7.97-7.93 (m, 2H, ArH), 6.91-6.87 (m, 2H, ArH), 6.46 (s, 1H, OH), 3.90 (s, 3H, OMe). ^{13}C NMR (101 MHz, CDCl_3) δ 167.65, 160.44, 132.11, 122.39, 115.45, 52.26.

[0149] 4-Hydroxybenzoic acid (**8g**): Yield (28 mg, 41%). A white solid. R_f = 0.2 (Hexanes/EtOAc = 1/1). FC (Hexanes/EtOAc = 1/1). ^1H NMR (400 MHz, Methanol- d_4) δ 7.89-7.86 (m, 2H, ArH), 6.83-6.80 (m, 2H, ArH). ^{13}C NMR (126 MHz, Methanol- d_4) δ 170.26, 163.54, 133.13, 122.81, 116.13.

[0150] *o*-Cresol (**8h**): Yield (39 mg, 72%). A light yellow oil. $R_f = 0.5$ (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 20/1). ^1H NMR (500 MHz, CDCl_3) δ 7.14-7.11 (m, 1H, ArH), 7.11-7.06 (m, 1H, ArH), 7.14-7.11 (m, 1H, ArH), 6.77 (dd, $J = 8.0, 1.5$ Hz, 1H, ArH), 4.65 (s, 1H, OH), 2.26 (s, 3H, Me). ^{13}C NMR (101 MHz, CDCl_3) δ 153.89, 131.16, 127.27, 123.80, 120.89, 115.01, 15.84.

[0151] 2-Methoxyphenol (**8i**): Yield (34 mg, 55%). A white solid. $R_f = 0.5$ (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 20/1). ^1H NMR (500 MHz, CDCl_3) δ 6.94-6.91 (m, 1H, ArH), 6.90-6.84 (m, 3H, ArH), 5.60 (s, 1H, OH), 3.89 (s, 3H, OMe). ^{13}C NMR (126 MHz, CDCl_3) δ 146.82, 145.92, 121.66, 120.34, 114.72, 110.90, 55.97.

[0152] *m*-Cresol (**8j**): Yield (36 mg, 67%). A colorless oil. $R_f = 0.5$ (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 20/1). ^1H NMR (400 MHz, CDCl_3) δ 7.13 (dd, $J = 7.6, 8.0$ Hz, 1H, ArH), 6.76 (d, $J = 7.6$ Hz, 1H, ArH), 6.68-6.62 (m, 2H, ArH), 4.76 (s, 1H, OH), 2.32 (s, 3H, Me). ^{13}C NMR (101 MHz, CDCl_3) δ 155.53, 139.97, 129.56, 121.77, 116.15, 112.40, 21.48.

[0153] 3-Nitrophenol (**8k**): Yield (51 mg, 73%). A white solid. $R_f = 0.4$ (Hexanes/EtOAc = 3/1). FC (Hexanes/EtOAc = 10/1). ^1H NMR (400 MHz, CDCl_3) δ 7.81 (dd, $J = 8.4, 2.0$ Hz, 1H, ArH), 7.71 (dd, $J = 2.4, 2.0$ Hz, 1H, ArH), 7.41 (dd, $J = 8.4, 8.4$ Hz, 1H, ArH), 7.19 (dd, $J = 8.4, 2.4$ Hz, 1H, ArH), 5.63 (s, 1H, OH). ^{13}C NMR (101 MHz, CDCl_3) δ 156.39, 149.25, 130.46, 122.16, 116.08, 110.70.

[0154] Naphthalen-2-ol (**8l**): Yield (47 mg, 65%). A light yellow solid. $R_f = 0.3$ (Hexanes/EtOAc = 5/1). FC (Hexanes/EtOAc = 15/1). ^1H NMR (400 MHz, CDCl_3) δ 7.78 (dd, $J = 8.4, 8.4$ Hz, 2H, ArH), 7.69 (d, $J = 8.4$ Hz, 1H, ArH), 7.48-7.43 (m, 1H, ArH), 7.38-7.33 (m, 1H, ArH), 7.16 (d, $J = 2.4$ Hz, 1H, ArH), 7.12 (dd, $J = 8.8, 2.4$ Hz, 1H, ArH), 5.16 (s, 1H, OH). ^{13}C NMR (101 MHz, CDCl_3) δ 153.36, 134.70, 130.01, 129.09, 127.90, 126.68, 126.51, 123.79, 117.84, 109.67.

[0155] **Optimization of ^nPr -DMQA $^+$ -catalyzed aerobic oxidative hydroxylation.** Using phenylboronic acid **7a** as the model substrate, DIPEA as the base, **3** as the PC, air as the oxidant, DMF as the solvent, the reaction time was screened. Under red LED ($\lambda_{\text{max}} = 640$ nm), the reaction proceeded smoothly to afford phenol **8a** in 77% NMR yield after 18 hours. By increasing the reaction time to 24 hours, **8a** was obtained in 87% NMR yield, along with 83% isolated yield. Running the reaction for 28 h did not improve the result. Several control

experiments have also been performed. In the absence of **3** or red light, little or no conversion was observed.

[0156] Red-light-induced ¹²⁹Pr-DMQA⁺-catalyzed oxygenation. To a mixture of tertiary amine **9** (42 mg, 0.20 mmol, 1.0 equiv.) and PC **3** (2.5 mg, 0.005 mmol, 2.5 mol%) in DMF (2.0 mL, 0.1 M) was added DBU (46 mg, 0.3 mmol, 1.5 equiv.) in a Schlenk tube. The solution was stirred at room temperature under red LED ($\lambda_{\text{max}} = 640 \text{ nm}$) irradiation in open to air (without bubbling air) for 20 hours. The mixture was concentrated in vacuo to yield the crude product, which was purified by flash chromatography on silica gel (eluent: Hexanes/EtOAc = 10/1 ~ 5/1) to yield the desired amide **10** as a white solid.

[0157] 2-phenyl-3,4-dihydroisoquinolin-1(2H)-one (10**):** Yield (41 mg, 92%). A white solid. $R_f = 0.3$ (Hexanes/EtOAc = 3/1). FC (Hexanes/EtOAc = 10/1 ~ 5/1). ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, $J = 7.6 \text{ Hz}$, 1H, ArH), 7.55-7.36 (m, 6H, ArH), 7.29-7.24 (m, 2H, ArH), 4.01 (t, $J = 6.4 \text{ Hz}$, 2H, CH₂), 3.16 (t, $J = 6.4 \text{ Hz}$, 2H, CH₂). ¹³C NMR (101 MHz, CDCl₃) δ 164.29, 143.24, 138.42, 132.13, 129.85, 129.02, 128.86, 127.30, 127.05, 126.34, 125.43, 49.53, 28.75.

[0158] Red-light-induced ¹²⁹Pr-DMQA⁺-catalyzed ATRA. In a N₂ glove box, **3** (1.0 mg, 0.002 mmol, 1 mol%), 4-nitrobenzyl bromide **11** (43 mg, 0.2 mmol, 1.0 equiv.) and LiBr (35 mg, 0.4 mmol, 2.0 equiv.) were added to an oven-dried (overnight) Schlenk tube containing a stirring bar, followed by adding dry MeCN (1.0 mL, 0.2 M) and styrene **12** (208 mg, 2.0 mmol, 10.0 equiv.). The Schlenk tube was then sealed, removed from the glove box and stirred at room temperature under red LED ($\lambda_{\text{max}} = 640 \text{ nm}$) irradiation for 17 hours. The mixture was concentrated in vacuo to yield the crude product, which was purified by flash chromatography (FC) on silica gel (eluent: Hexanes/EtOAc = 200/1) to yield the desired product **13** as a colorless oil.

[0159] 1-(3-bromo-3-phenylpropyl)-4-nitrobenzene (13**):** Yield (38 mg, 59%). A colorless oil. $R_f = 0.4$ (Hexanes/EtOAc = 10/1). FC (Hexanes/EtOAc = 200/1). ¹H NMR (400 MHz, CDCl₃) δ 8.18-8.14 (m, 2H, ArH), 7.40-7.28 (m, 7H, ArH), 4.88 (dd, $J = 8.4, 6.0 \text{ Hz}$, 1H, CH), 2.95 (ddd, $J = 14.4, 9.2, 5.6 \text{ Hz}$, 1H, CH₂), 2.82 (ddd, $J = 14.4, 8.8, 6.4 \text{ Hz}$, 1H, CH₂), 2.69-2.59 (m, 1H, CH₂), 2.50-2.41 (m, 1H, CH₂). ¹³C NMR (101 MHz, CDCl₃) δ 148.37, 146.77, 141.53, 129.47, 128.99, 128.78, 127.34, 123.94, 54.09, 40.90, 34.30.

[0160] Red-light-induced ¹²⁹Pr-DMQA⁺-catalyzed intermolecular ATRA. Initial examination of ATRA reaction was tested by reacting 4-nitrobenzyl bromide **11** (1.0 equiv.)

with styrene **12** (5.0 equiv.) in the presence of LiBr (2.0 equiv.) and PC **3** in MeCN under red LED ($\lambda_{\text{max}} = 640 \text{ nm}$). Running the reaction with 1 mol% of **3** at rt for 20 hours delivered the desired adduct **13** in 40% NMR yield, along with 50% starting material **11** (“**SM-11**”). Increasing the PC loading of **3** to 2.5 mol% gave lower yield of **13**, along with more byproducts, which could be the dimer, polymers or other side-products from the radical intermediates. Thus, 1 mol% the PC loading was chosen for all the follow-up screenings. When the reaction was run at 50 °C for 24 hours, only 25% of desired product **13** was observed, along with a lot of byproducts and no **SM-11**. Two control experiments have also been performed, and no reaction occurred at 50 °C in the absence of red light or PC **3**. Performing the reaction at 35 °C didn't improve any reaction result. When the reaction was conducted in a higher concentration (0.2 M), the reaction yield was improved from 40% to 54%. Moreover, when the reaction was performed with 10.0 equiv. of styrene **12** in a higher concentration (0.2 M), **13** was achieved in 65% yield, along with 12% **SM-11**. Further increasing the reaction concentration (0.4 M) did not increase the reaction yield.

[0161] Based on the above results, further screening the solvents and reaction times were carried out. The examination of solvent effects revealed that the reaction in MeCN provided a higher yield than those in DMF/H₂O (1/4), MeOH and DMSO. Increasing the reaction time from 17 to 24 hours in MeCN gave the product **13** in 59% yield along with trace amount of **SM-11**. Several control experiments have also been conducted. No reaction occurred in the absence of **3** or red light, which is consistent with the results at 50 °C. In the absence of LiBr, **13** was obtained in 14% yield along with 75% of **SM-11**.

[0162] Mechanism for red-light-induced ¹²⁵Pr-DMQA⁺-catalyzed intermolecular ATRA. Without being bound by any theory, one possible reaction mechanism for the red-light-induced ¹²⁵Pr-DMQA⁺-catalyzed intermolecular ATRA illustrated in FIG. 6. Firstly, oxidative quenching of the red light-induced excited state of ¹²⁵Pr-DMQA⁺, by 4-nitrobenzyl bromide (**11**) generates a 4-nitrobenzyl radical, along with bromide anion. Then, addition of the 4-nitrobenzyl radical to styrene (**12**) forms another benzyl radical intermediate S3, which undergoes a single electron transfer (SET) process with ¹²⁵Pr-DMQA⁺⁺ to regenerate the PC ¹²⁵Pr-DMQA⁺ and form the carbocation species S4 (PhCH₂⁺/PhCH₂[•] = +0.73 V vs SCE). Final product **13** is formed by the nucleophilic attack of bromide anion to carbocation species S4. Alternatively, **13** could be also obtained through a radical chain transfer mechanism. **14**.

[0163] Red-light-mediated dual Au/ⁿPr-DMQA⁺-catalyzed C(sp)-H arylation. In a N₂ glove box, Au(PPh₃)Cl (9.9 mg, 0.02 mmol, 10 mol%), **3** (2.5 mg, 0.005 mmol, 2.5 mol%), 1-ethynyl-4-methylbenzene **14** (24 mg, 0.2 mmol, 1.0 equiv.) and benzenediazonium tetrafluoroborate **5a** (154 mg, 0.8 mmol, 4.0 equiv.) were added to an oven-dried (overnight) Schlenk tube containing a stirring bar, followed by adding dry DMF (2.0 mL, 0.1 M). The Schlenk tube was then sealed, removed from the glove box and stirred at room temperature under red LED ($\lambda_{\text{max}} = 640 \text{ nm}$) irradiation. After 1 hour, the mixture was quenched with a saturated solution of NaHCO₃, followed by adding deionized water. The crude reaction mixture was then extracted with ethyl acetate, and the combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. After filtration, the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (eluent: Hexanes/EtOAc = Hexanes ~ 200/1) to yield the desired product **15** as a white solid.

[0164] 1-methyl-4-(phenylethynyl)benzene (15**):** Yield (24 mg, 62%). A white solid. $R_f = 0.45$ (Hexanes). FC (Hexanes/EtOAc = Hexanes ~ 200/1). ¹H NMR (400 MHz, CDCl₃) δ 7.56-7.53 (m, 2H, ArH), 7.45 (d, $J = 7.6 \text{ Hz}$, 2H, ArH), 7.38-7.31 (m, 3H, ArH), 7.17 (d, $J = 7.6 \text{ Hz}$, 2H, ArH), 2.39 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 138.51, 131.68, 131.63, 129.25, 128.45, 128.20, 123.63, 120.33, 89.70, 88.86, 21.65.

[0165] Red-light-mediated dual Au/ⁿPr-DMQA⁺-catalyzed C(sp)-H arylation. Optimization of C(sp)-H arylation by screening the solvents were performed. The examination of solvent effects showed that the reaction in DMF gave a higher yield than those in DMSO and MeOH. Control experiments have also been conducted. In the absence of **3** or red light, and the desired product **15** was obtained in 24% and 5% yield, respectively, while the reaction was messy in the absence of Au(PPh₃)Cl.

[0166] NMR results for control reactions for Scheme 2. Several control experiments have also been performed for the red-light-induced aerobic benzylic C(sp³)-H oxygenation, intermolecular ATRA and dual Au/ⁿPr-DMQA⁺-catalyzed C(sp)-H arylation (Scheme 2). For aerobic benzylic C(sp³)-H oxygenation, no conversion was observed in the absence of PC **3** or red light, while the reaction was messy in the absence of DBU. For intermolecular ATRA, no reaction occurred in the absence of PC **3** or red light, while the desired adduct **13** was obtained in 14% yield along with 75% of **SM-11** in the absence of LiBr. For dual Au/ⁿPr-DMQA⁺-catalyzed C(sp)-H arylation, in the absence of PC **3** or red

light, the desired product **15** was formed in 24% and 5% yield, respectively, while the reaction was messy in the absence of Au(PPh₃)Cl.

[0167] General procedure of the preparation of the carbocation-based pyridine-containing ligands L1-L3.

[0168] 2-(2-Aminoethyl)pyridine (0.58 mL, 4.8 mmol, 1.2 equiv.) was added to a suspension of **1** (2.04 g, 4.0 mmol, 1.0 equiv.) in ethyl acetate (100 mL). The solution was stirred at rt for 2 hours. Then 150 mL ethyl ether was added and stirred at rt for 30 mins. The red solid was filtered and further purified by recrystallization in DCM/hexane to yield large dark red crystals (2.04 g, 90%).

[0169] L1: Yield: (2.04 g, 90%). A dark red solid. M.P.: 220-222 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.58 (ddd, J = 4.8, 2.0, 0.8 Hz, 1H, Py), 8.26 (dd, J = 9.2, 8.0 Hz, 2H, ArH), 8.19 (d, J = 9.2 Hz, 2H, ArH), 7.70 (ddd, J = 7.6, 7.6, 2.0 Hz, 1H, Py), 7.57 (ddd, J = 7.6, 0.8, 0.8 Hz, 1H, Py), 7.37 (dd, J = 8.4, 8.4 Hz, 1H, ArH), 7.21 (ddd, J = 7.6, 4.8, 0.8 Hz, 1H, Py), 7.02 (d, J = 8.0 Hz, 2H, ArH), 6.66 (d, J = 8.4 Hz, 2H, ArH), 5.53 (t, J = 8.0 Hz, 2H, NCH₂CH₂Py), 3.69 (t, J = 8.0 Hz, 2H, NCH₂CH₂Py), 3.56 (s, 6H, OMe), 3.58 (s, 6H, OMe). ¹³C NMR (101 MHz, CDCl₃) δ 160.90, 157.83, 156.23, 149.55, 141.67, 140.84, 137.53, 129.62, 124.60, 122.66, 119.91, 119.50, 109.15, 106.62, 103.54, 57.04, 56.08, 52.03, 35.66. ¹⁹F NMR (376 MHz, CDCl₃) δ -153.42, -153.48. HRMS (ESI) Calcd. for C₃₀H₂₉N₂O₄⁺(M⁺+1) requires 481.2122, Found: 481.2119.

[0170] 2-(2-Aminomethyl)pyridine (0.13 mL, 1.2 mmol, 1.2 equiv.) was added to a suspension of **1** (0.51 g, 1.0 mmol, 1.0 equiv.) in MeCN (15 mL). The solution was stirred at rt for 1 hours. MeCN was reduced to 5 mL on RotaVap. Then 100 mL Et₂O was added and stirred at rt for 2 hs. The red solid was filtered and further purified by recrystallization in DCM/Et₂O to yield large dark red crystals (419 mg, 76%).

[0171] L2: Yield: (419 mg, 76%). A dark red solid. M.P.: 280-282 °C. ¹H NMR (500 MHz, DMSO-d₆) δ 8.34 (ddd, J = 5.0, 2.0, 1.0 Hz, 1H, Py), 8.17 (dd, J = 9.0, 8.0 Hz, 2H, ArH), 7.99 (Py, J = 8.0, 8.0 2.0 Hz, 1H, ArH), 7.89 (d, J = 9.0 Hz, 2H, ArH), 7.81 (Py, J = 8.0, 1.0, 1.0 Hz, 1H, ArH), 7.46 (dd, J = 8.5 Hz, 1H, ArH), 7.38 (Py, J = 8.0, 5.0, 1.0 Hz, 1H, ArH), 7.20 (d, J = 8.0 Hz, 2H, ArH), 6.84 (d, J = 8.5 Hz, 2H, ArH), 6.70 (s, 2H, CH₂), 3.57 (s, 6H, OMe), 3.54 (s, 6H, OMe). ¹³C NMR (126 MHz, DMSO-d₆) δ 160.06, 157.06, 153.49, 149.53, 142.26, 140.22, 137.73, 129.53, 123.54, 122.43, 119.35, 119.13, 110.36, 106.97,

103.83, 57.21, 56.16, 55.89. ^{19}F NMR (376 MHz, DMSO- d_6) δ -148.25, -148.31. HRMS (ESI) Calcd. for $\text{C}_{29}\text{H}_{27}\text{N}_2\text{O}_4^{+1}(\text{M}^{+1})$ requires 467.1965, Found: 467.1965.

[0172] A solution of **L1** (1.14 g, 2.0 mmol, 1.0 equiv.) and n-propylamine (1.49 mL, 20.0 mmol, 10.0 equiv.) in 20 mL DMF in a pressure flask was stirred at 70 °C for 2 days. A dark green solution was formed. After cooling to rt, DMF was reduced to 4 mL on RotaVap. 20 mL MeCN was added, followed by adding a large excess of Et₂O (200 mL) and stirring vigorously at rt for 1 h. A lot of dark green solids crashed out, filtered to yield crude product, which was further purified by recrystallization in DCM/Et₂O to yield dark green crystals (742 mg, 66%).

[0173] L3: Yield: (742 mg, 66%). A dark green solid. M.P.: 214-216 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 8.61-8.58 (m, 1H, Py), 8.24 (dd, J = 8.4, 8.4 Hz, 1H, ArH), 7.98-7.92 (m, 2H, ArH), 7.82 (d, J = 8.4 Hz, 1H, ArH), 7.77 (ddd, J = 7.6, 7.6, 2.0 Hz, 1H, Py), 7.71 (d, J = 8.4 Hz, 1H, ArH), 7.68 (d, J = 8.4 Hz, 1H, ArH), 7.62 (d, J = 8.4 Hz, 1H, ArH), 7.50-7.47 (m, 1H, Py), 7.33-7.29 (m, 1H, Py), 7.03-7.00 (m, 1H, ArH), 5.17-5.08 (m, 1H, CH₂), 4.91-4.83 (m, 1H, CH₂), 4.77-4.68 (m, 1H, CH₂), 4.51-4.42 (m, 1H, CH₂), 3.73 (s, 6H, OMe), 3.44-3.39 (m, 2H, CH₂), 2.05-1.90 (m, 2H, CH₂), 1.17 (t, J = 7.2 Hz, 3H, CH₃). ^{13}C NMR (126 MHz, DMSO- d_6) δ 159.62, 157.85, 149.90, 142.31, 142.12, 142.02, 138.64, 137.71, 137.68, 137.37, 137.20, 124.44, 122.67, 118.98, 112.74, 108.11, 107.92, 105.61, 105.34, 103.54, 103.47, 56.02, 56.01, 50.91, 49.32, 33.93, 19.71, 11.07. ^{19}F NMR (376 MHz, DMSO- d_6) δ -148.25, -148.31. HRMS (ESI) Calcd. for $\text{C}_{31}\text{H}_{30}\text{N}_3\text{O}_2^{+1}(\text{M}^{+1})$ requires 476.2333, Found: 476.2331.

[0174] Exemplary procedure of the synthesis of Co(II) and Ni (II) complexes 2-4

[0175] A solution of **L** (0.2 mmol, 1.0 equiv.), CoCl₂(THF)_{1.5} or NiCl₂(glyme) (0.2 mmol, 1.0 equiv.) and LiCl (0.4 mmol, 2.0 equiv.) in MeCN (8 mL) was stirred in the glove box at rt for 20 hours. A cloudy solution was formed. The solid was filtered, washed with MeCN, THF and Et₂O, and dried under vacuum to give the final complex **2-4**.

[0176] **2a** Co(**L1**)Cl₃: Yield: (108 mg, 84%). A dark red solid. M.P.: 262-264 °C. Elementary Analysis (0.886 mg) requires: C, 55.70; H, 4.52; Cl, 16.44; Co, 9.11; N, 4.33; O, 9.89, Found: C, 55.62; H, 4.41; N, 4.56. μ_{eff} = 4.4 (0.1). X-ray crystals were obtained by layering the solution of ligand **L1** in MeCN to the solution of CoCl₂(THF)_{1.5} and LiCl in acetonitrile without stirring at rt in the glove.

[0177] **2b** Ni(**L1**)Cl₃: Yield: (116 mg, 90%). A dark red solid. M.P.: 292-294 °C (Decomposition). Elementary Analysis (0.974 mg) requires: C, 55.73; H, 4.52; Cl, 16.45; N, 4.33; Ni, 9.08; O, 9.90, Found: C, 55.84; H, 4.52; N, 4.50. $\mu_{\text{eff}} = 3.3$ (0.1). X-ray crystals were obtained by layering THF into solutions of **2b** in DMF.

[0178] **3a** Co(**L2**)Cl₃: Yield: (87 mg, 69%). A dark red solid. M.P.: 298-300 °C. Elementary Analysis (1.080 mg) requires: C, 55.04; H, 4.30; Cl, 16.81; Co, 9.31; N, 4.43; O, 10.11, Found: C, 55.24; H, 4.31; N, 4.59. $\mu_{\text{eff}} = 4.3$ (0.1). 4 mL MeCN was used for the reaction, only washed with THF and Et₂O. X-ray crystals were obtained by layering the solution of ligand **L1** in MeCN to the solution of CoCl₂(THF)_{1.5} and LiCl in acetonitrile without stirring at rt in the glove box.

[0179] **3b** Ni(**L2**)Cl₃: Yield: (89 mg, 70%). A dark red solid. M.P.: 222-224 °C. ¹H NMR (500 MHz, Acetonitrile-d₃, 40 °C) δ 14.90 (br, 1H, Py), 10.26 (br, 1H, Py), 9.39 (br, 1H, Py), 8.93 (br, 1H, Py), 8.00 (dd, J = 8.5, 9.5 Hz, 2H, ArH), 7.67 (d, J = 9.5 Hz, 2H, ArH), 7.47 (dd, J = 8.5, 8.5 Hz, 1H, ArH), 7.07 (d, J = 8.5 Hz, 2H, ArH), 6.82 (d, J = 8.5 Hz, 2H, ArH), 5.05 (br, 2H, CH₂), 3.60 (s, 6H, OMe), 3.56 (s, 6H, OMe). Elementary Analysis (0.905 mg) requires: C, 55.06; H, 4.30; Cl, 16.81; N, 4.43; Ni, 9.28; O, 10.12, Found: C, 55.23; H, 4.59; N, 4.32. $\mu_{\text{eff}} = 2.9$ (0.1). 4 mL MeCN was used for the reaction, only washed with THF and Et₂O. X-ray crystals were obtained by layering THF into solutions of **3b** in MeCN.

[0180] **4a** Co(**L3**)Cl₃: Yield: (118 mg, 92%). A dark green solid. M.P.: 218-220 °C. Elementary Analysis (1.011 mg) requires: C, 58.01; H, 4.71; Cl, 16.57; Co, 9.18; N, 6.55; O, 4.99, Found: C, 57.98; H, 4.88; N, 8.18. $\mu_{\text{eff}} = 4.3$ (0.1). X-ray crystals were obtained by layering the solution of ligand **L1** in MeCN to the solution of CoCl₂(THF)_{1.5} and LiCl in acetonitrile without stirring at rt in the glove box.

[0181] **4b** Ni(**L3**)Cl₃: Yield: (99 mg, 77%). A dark green solid. M.P.: 216-218 °C. Elementary Analysis (0.847 mg) requires: C, 58.03; H, 4.71; Cl, 16.57; N, 6.55; Ni, 9.15; O, 4.99, Found: C, 58.13; H, 4.82; N, 8.18. $\mu_{\text{eff}} = 3.3$ (0.1).

[0182] **Crystallography**

[0183] All data were collected on an Agilent supernova dual source diffractometer equipped with an Atlas detector, by using CuK α radiation. Data reduction was carried out in the CrysAlis Pro software. Structure solution was made by using direct methods (sir2004),

dual-space methods (SHELXT), or charge-flipping (OLEX2). Refinements were carried out in SHELXL within the OLEX2 software.

[0184] Cyclic Voltammetry

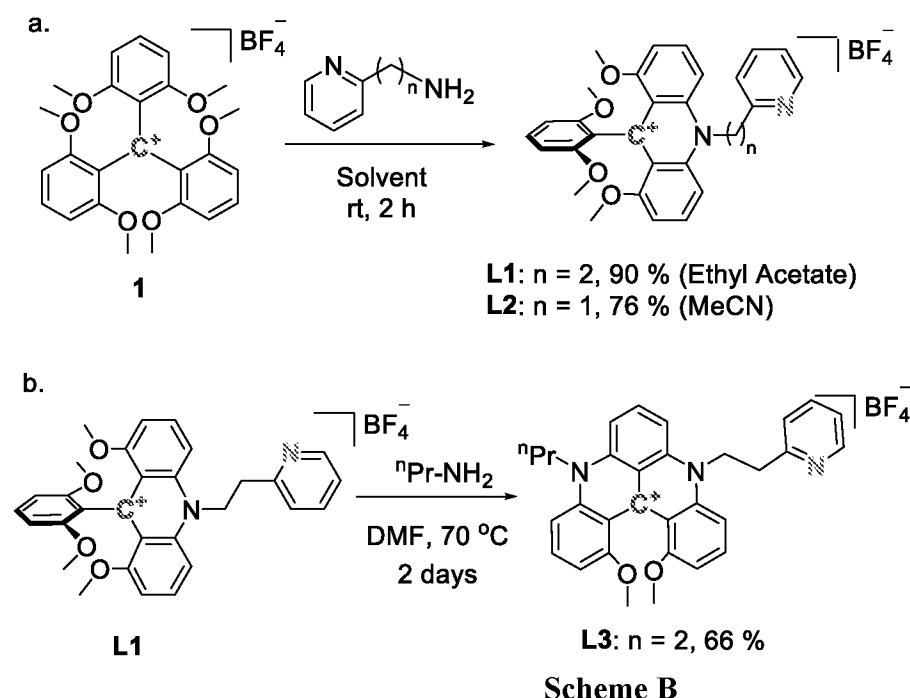
[0185] Voltammetric experiments were performed with a Biologic SP 200 potentiostat connected to a traditional three-electrode cell, which is consisted of an Ag/Ag⁺ reference electrode, a platinum wire counter electrode, and a glassy carbon working electrode. Prior to measurements, the glassy carbon working electrode was polished with alumina slurry (0.05 μ m), rinsed thoroughly with NERL reagent grade water (Thermo Scientific) between each polishing step, and sonicated in water, followed by a final rinse with acetone, and dried with air or a stream of N₂. All solvents were collected from solvent purification system and solutions were degassed for 5 min before measurements. The cyclic voltammograms curves of **L1–L3** (3 mM) and **2-4** (1 mM) in DCM ([TBA][PF₆] 0.1 M) solutions are recorded at a glassy carbon working electrode ($\nu = 0.02$ V/s).

[0186] DFT calculations

[0187] Density functional theory (DFT) calculations were done using the unrestricted hybrid 1993 Becke three-parameter hybrid functional^{4–6} with the non-local correlation Lee-Yang-Par (B3LYP).⁷ The triple- ζ quality basis set LANL2TZ and its correspondent effective core potential was employed for the first row transition metal atoms. The following Gaussian09 internal basis sets were used for non-metal atoms: 6-31G for H, 6-31G(d') for C, O, and N, and 6-31G(d',p') for Cl. The crystal structure of the available complexes were used as starting point for the geometry optimization calculations. The initial structures for complexes XYZ were built using the Spartan modeling software where the C–C bonds in the pyridine alkyl chain were rotated to obtain the desired structure, retaining all the crystallographic bond metrics. Frequency calculations were done to confirm the absence of imaginary frequencies in the geometry optimized structures. The polarizable continuum model (PCM) was employed using the SCRF=PCM keyword and ace-tonitrile as solvent at 298 K. Grimme's empirical dispersion with D3 damping functions were employed for all calculations. Molecular orbitals (MOs) and SCF spin density surfaces were obtained using the standard cubegen utility implemented in Gaussian. The resultant structures and Gaussian cube files were visualized using the Chimera modeling software. All calculations were executed on the Ocelote supercomputer cluster located at the University of Ari-zona High Performance Computing (HPC) center.

[0188] **Results and Discussion**

[0189] Carbocation acridinium-based pyridine-containing ligands **L1-L2** were synthesized by reacting tris(2,6-dimethoxyphenyl)carbenium tetrafluoroborate **1** with the desired primary amine at room temperature for 2 hours (Scheme B-a). **L1** was isolated in 90% yield by reacting **1** and 2-(2-aminoethyl)pyridine in ethyl acetate, and **L2** was obtained in 76% yield from the reaction between **1** and 2-(2-aminomethyl)pyridine in acetonitrile.



[0190] The helicenium **L3** was isolated in 66% yield by reacting **L1** with an excess of *n*-propylamine in dimethylformamide (DMF) at 70 °C for 2 days (Scheme B-b). Single crystals of ligand **L1-L3** were obtained by layering hexane or Et₂O into solutions of ligands in dichloromethane confirming the formation of the desired product. The pyridine rings in all the three ligands are stretched away from the carbenium scaffolds. No interaction between the pyridine and the carbocation center was observed. However, for **L1** and **L2**, the 2,6-dimethoxyphenyl substituents distort to a small degree against the acridine plan suggesting a weak interaction between the methoxy group and the carbenium center.

[0191] The electrochemical behavior of ligands **L1-L3** have been studied by cyclic voltammetry (CV) experiments, which were performed using degassed anhydrous DCM solutions with tetrabutylammonium hexafluorophosphate, [TBA][PF₆], as the supporting electrolyte. The reversibility and quasi-reversibility properties of the electrochemical event are supported by the analysis of current density with the square root of the scan rate.

[0192] The voltammograms of **L1-L3**, as well as their electrochemical data versus Fc/Fc^+ are shown in FIGS. 7 and 8, respectively. In the acridinium cations, an irreversible oxidation of C^+ to C^{++} occurred at 1.08 V for **L1** (1.19 V for **L2**), followed by a characteristic reversible reduction of C^+ to $\text{C}^\cdot$ at $E^{\text{red}}_{1/2} = -1.17$ V (-1.07 V for **L2**), along with a second irreversible reduction to form C^- at -2.18 V (-2.19 V for **L2**). The difference in redox potential reveals that the acridinium scaffold in **L2** is slightly more electron deficient than **L1**. This observation is consistent with the electron withdrawing effect of the pyridine group being alpha (**L2**) or beta (**L1**) to the heterocyclic ring. The helicenium scaffold **L3** displays the same three electrochemical events but at lower potential. Two reductions at $E^{\text{red}}_{1/2} = -1.33$ V (reversible C^+ to $\text{C}^\cdot$) and -2.28 V (irreversible $\text{C}^\cdot$ to form C^-), and one oxidation at 0.90 V (quasi-reversible C^+ to C^{++}). Some small events are observed for **L1-L3**, which were assigned from products generated from C^{++} or C^- . The large difference between the $E^{\text{red}}_{1/2}$ of ligand **L3** compared to **L1** further support that acridinium cations are significantly more electron-poor than their helicenium counterpart.

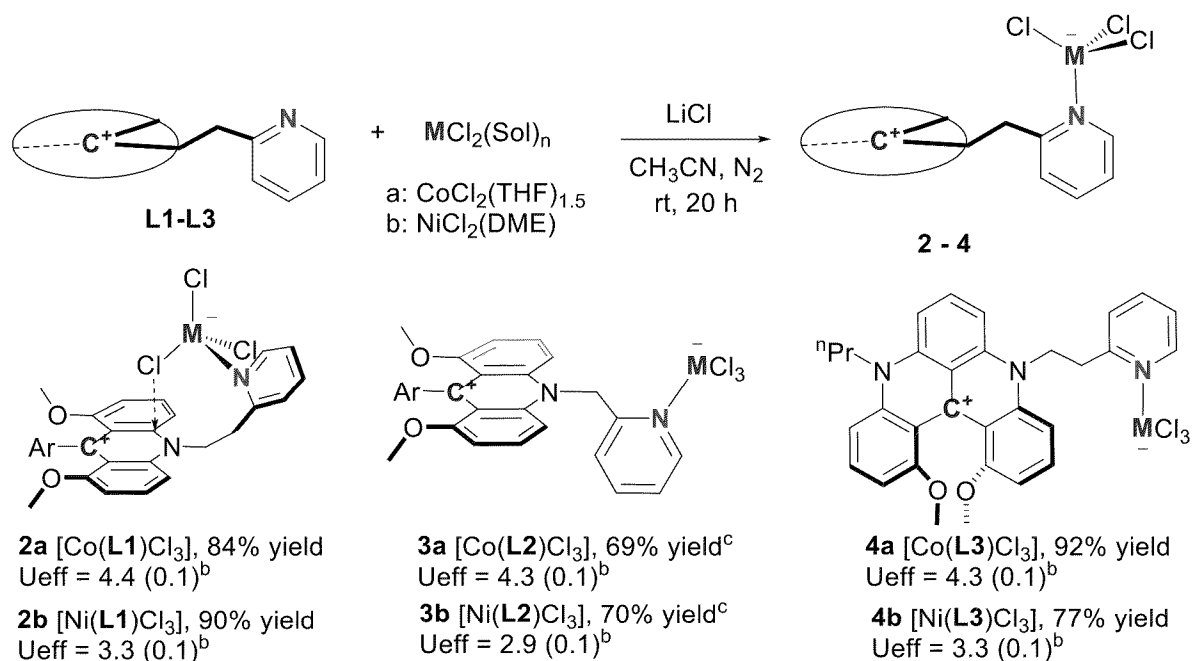
[0193] The electronic absorption spectra of **L1-L3** were recorded in acetonitrile at r.t. The overlapped spectra as well as a summary of the data are presented in Figure 5. As can be seen, **L1** and **L2** have a main absorption band around 400 nm assigned to the local $\pi-\pi^*$ transition of this scaffold. **L1** and **L2** also exhibit two absorptions around 500 and 530 nm which consist on an electron transfer from the orthogonal methoxy-substituted aromatic rings to the conjugated cationic systems. Ligand **L3** also shows three absorption bands, at 426, 582 and 618 nm, assigned to both localized and delocalized transitions. The two low-energy bands, related to the entire conjugated system, undergo a 120 nm bathochromic shift compared to **L1**. Without being bound by any theory, it is believed that this indicates a smaller HOMO-LUMO gap consistent with the more electron-rich conjugated helicenium system. These redshifted bands also have dramatical increase of extinction coefficient from 5789 and 4669 $\text{M}^{-1} \text{cm}^{-1}$ in **L1** to 11648 and 15226 $\text{M}^{-1} \text{cm}^{-1}$ in **L3**. The increased of extinction coefficient can be due to the enlargement and twisting of the chromophoric system.

[0194] Spectroscopic and electrochemical data show similarities in ligands **L1** and **L2**. Though similar features can be observed in **L3**, higher electronic density and a decrease in Lewis acid character can be attributed to their lower-energy absorption bands and redox events. Moreover, the intrinsic rigidity in **L2** compared to **L1** and **L3** (methyl- vs ethyl-pyridine), along with the different electronic properties offered by the acridinium and

helocenium scaffolds, result in coordination complexes with different coordination modes to the carbenium (Lewis acid) center.

[0195] Coordination to Ni and Co

[0196] The coordination chemistry of **L1-L3** with simple first-row transition-metal halides MCl_2 ($M = Co, Ni$) was studied. Reacting equimolar amount of ligand **L1** and $CoCl_2 \cdot (THF)_{1.5}$ in acetonitrile at r.t. under N_2 resulted in a mixture of two paramagnetic species, a dark red compound poorly soluble in acetonitrile and an orange solid soluble in THF. The orange solid was identified as $Co(MeCN)_6][BF_4]_2$, suggesting an anionic salt exchange with the ligand scaffold. The limited solubility of the obtained red powder in acetonitrile- d_3 and $CDCl_3$ was insufficient to confirm the paramagnetic nature due to hampering of proper NMR spectroscopy analysis. However, when dissolved in protic or strongly coordinating solvent, such as $MeOH-d_4$, D_2O or $DMSO-d_6$, free ligand **L1** was observed via 1H NMR spectroscopy, with no signal for $[BF_4]^-$ observed in the ^{19}F NMR spectrum. These observations suggest the successful formation of a metal complex containing **L1** and the Cl/BF_4 anion exchange. In order to optimize the reaction and prevent the formation of side product, 2.0 molar equivalents of $LiCl$ were added to the reaction mixture. Under this condition, the reaction proceeded to completion, affording the desired $Co(II)$ complex (**2a**) in 84% yield (Scheme C). Following the same procedure, the corresponding $Co(II)$ complexes **3a** and **4a** were obtained upon coordination of **L2** and **L3**, respectively. Similarly, $Ni(II)$ complexes **2b**, **3b** and **4b** were synthesized by reacting $NiCl_2(glyme)$ with the corresponding ligands **L1-L3**. Complexes **2-4** have poor solubility in acetonitrile and crashed out from the solution. The resulting powders were filtered and washed with $MeCN$, THF and Et_2O to remove residual $LiCl$, $LiBF_4$ and unreacted starting material. Due to a relatively higher solubility in $MeCN$, **3a,b** were only washed with THF and Et_2O . Isolation of the microcrystalline powder afforded the desired complexes **2-4** in moderate to good yields (Scheme 3). Sample purities have been confirmed by elemental analysis. Magnetic susceptibility measurements in the solid state at r.t. are consistent with: i) $Co(II)$ d^7 and $Ni(II)$ d^8 metallates in a tetrahedral environment and a positively charged carbocation ligand, or ii) $Co(III)$ d^6 and $Ni(III)$ d^7 in a tetrahedral environment and a neutral carboradical ligand with antiferromagnetic coupling between the metal and the unpair electron centered on the ligand.



- a) A solution of **L** (0.2 mmol, 1.0 equiv.), $MCl_2(solvent)_n$ (0.2 mmol, 1.0 equiv.) and LiCl (0.4 mmol, 2.0 equiv.) in MeCN (8 mL) was stirred in the glove box at rt for 20 hours.
- b) Average value and the standard deviation of 3 different tests.
- c) 4 mL of MeCN was used as the solvent.

Scheme C

[0197] Due to a relatively better solubility in CD_3CN , **3b** was analyzed by 1H NMR spectroscopy. Compared to the free ligand **L2**, the protons near the paramagnetic Ni center exhibits broader signals and small but significant chemical shifts changes. The four pyridinic protons are shifted from 7.4-8.3 ppm to 8.9-14.9 ppm, and the methylene protons from 6.70 ppm to 5.05 ppm. However, the protons from the heterocyclic fused aromatic system were not significantly affected, suggesting that spin density is localized at the metal center.

[0198] **Solid state structural analysis.** X-ray quality single crystals of cobalt(II) complexes **2a-4a** were obtained by slow diffusion of a solution of MeCN containing **L1-L3** into a mixture of $CoCl_2(THF)_{1.5}$ and LiCl in acetonitrile. Nickel complexes **2b** and **3b** were crystallized by diffusion of a THF layer into a solution of the complexes in DMF.

[0199] X-ray diffraction analysis confirmed the formation of zwitterion metallate trichloride complexes bound to the cationic ligand via the pyridine anchor in which the metal center adopts a canonical tetrahedral geometry. Due to the difference in rigidity and Lewis acidity between the ligands **L1-L3**, different modes of coordination are observed in the solid state. The flexible and relatively electron poor carbenium **L1** favored a coordination mode of complexes **2** in which one of the chloride resides above the heteroaromatic carbenium ring (ring A) (FIG. 10). Bond distances between the centroid of this ring and Cl(1) are 3.005 Å

and 3.481 Å for complexes **2a** and **2b**, respectively. Additionally, large torsion angles can be found for N(1)–C(24)–C(25)–C(26) in metal complexes **2**. However, despite the close proximity of Cl(1) with C(13) (3.414 Å and 3.439 for **2a** and **2b** respectively) compare to the rest of the elements of the ring A, no significant elongation of the bond lengths between C(13) and the rest of the scaffold was observed between **L1** and **2**. It is believed that this coordination environment suggests the presence of a Cl–C⁺ interaction strong enough to overcome the geometrical strain imposed by the folding of the metallate scaffold above the heterocyclic carbenium rings. However, this interaction between the metallate core and the positively charged scaffold is best described as an ionic Van-der-Waals interaction. Complex **2** can be best described with the coordination Mode II - Lewis acid coordinates with a co-ligand.

[0200] On the other hand, with a shorter linker (**L2**) or more electron rich scaffold (**L3**), no intramolecular interaction is observed and the metallate core sits away from the carbenium scaffold. In complexes **3** and **4** no distortion or changes of bond lengths are observed compare to **L2** and **L3**, respectively. Complexes **3-4** are therefore best described with the coordination Mode I in Figure 1–Lewis acid remains as a pendant part, in which no interaction between the carbocation with the metallate core. Finally, complexes **2-4** have similar structural metrics around the metal centers compare to each other and to reported LMCl₃ (L = Pyridine or amine) further supporting that the interaction in **2** is weak and non-covalent (means values of Co–Cl = 2.26, Ni–Cl = 2.24, Co–N = 2.09 and Ni–N = 2.04 Å).

[0201] **Electrochemical properties.** The electrochemical behavior of the metal complexes **2-4** have been studied by cyclic voltammetry (FIGS. 11 and 12). Complexes **2a** and **2b** featured similar redox events with **L1**: a reversible reduction around -1.1 V, an irreversible reduction around -2.2 V, along with an irreversible oxidation around 1.2 V, which are assigned as ligand-based processes. A second fully irreversible oxidation is observed for **2a** at 1.60 V, which is believed to be result from generation of C⁺⁺⁺ from C⁺⁺. Due to a smaller window for ligand **L1** and complex **2b**, no such event is observed, but similar process occurs at 1.61 V for complex **3b** as well. In addition, a new irreversible reduction is observed for complexes **2a** at -2.09 V and **2b** at -1.54 V, which can be assigned to metal-based reduction from M(II) to M(I). Complexes **3** exhibited a similar behavior as **2**. Similarly, for complexes **4** all the ligand-based redox events were observed, as well as, the irreversible reduction event of M(II) to M(I) at -1.94 V (**4a**) and -1.63 V (**4b**). However, an additional new irreversible oxidation was observed at 0.98 V for the cobalt complex **4a** and

0.91 V for the nickel complex **4b**, which may be assigned as the metal base oxidation of M(II) to M(III).

[0202] Overall, these metal complexes show the three characteristic ligand-based redox events: i) irreversible (**L1,L2**) or quasi-reversible (**L3**) oxidation of C^+ to C^{++} , ii) reversible reduction of C^+ to $C^\cdot$, and iii) an irreversible reduction of $C^\cdot$ to C^- . The reversible reduction of C^+ to $C^\cdot$ and oxidation C^+/C^{++} of **2-4** happen at a more positive potential compared to the free ligands ($\Delta E \sim 50$ mV for $C^+ / C^\cdot$ and $\Delta E \sim 150$ mV for C^+/C^{++}). In addition, for cobalt complexes **2a**, **3a** and **4a**, a reduction event of Co(II) to Co(I) is observed between -1.88 to -2.09 V, while the reduction of Ni(II) to Ni(I) occurs between -1.54 to -1.62 V complexes **2b**, **3b** and **4b**. The reduction potentials are more negative compared to reported neutral Co(II)/Co(I) and Ni(II)/Ni(I), consistent with the metallate form of **2-4**. The irreversible oxidation event assigned to M(II)/M(III) couple is only observed with the electron rich helicenium complexes **4a** and **4b**.

[0203] **Electrocatalytic studies with acetic acid.** The reduction potential of the Ni(II)/Ni(I) couple at around -1.5 V offer the opportunity to evaluate the electrocatalytic properties of **2b-4b** toward proton reduction. Cyclic voltammetry of **2b** and **4b** in presence of various amount of acidic acid showed a catalytic current response. FIGS 15 and 16, respectively. The bare glassy carbon electrode, $NiCl_2(DME)$, complexes **2b** and **4b** and ligands alone were run under the similar conditions and compared. FIGS. 13 and 14, respectively. All three complexes as well as $NiCl_2(DME)$ exhibited catalytic activity. A significant shift of the overpotential was observed for some compounds (e.g., up to 370 mV for **4b**). The catalytic peak reduction of acetic acid occurred at - 2.35 V for $NiCl_2(DME)$ and at around -2.18, -2.24 and -2.02 V, for **2b**, **3b** and **4b** respectively. The lower overpotential observed in **2b-4b** compared to $NiCl_2(DME)$ suggest that the amphiphilic ligand scaffold facilitate electron transfer from the metal center.

[0204] **Spectroscopic properties.** Electronic absorption spectra of the metal complexes **2** and **4** (con. 10^{-5} M) were recorded in acetonitrile at RT. The overlapped spectra with the corresponding ligands **L1-L3** as well as a summary of the data are shown in FIGS 17-19. The cobalt and Ni complexes **2** have similar absorption properties with the free ligand **L1**, with three main absorptions at 400, 501 and 533 nm for **2a** and 402, 498 and 533 nm for **2b**, albeit slightly lower extinction coefficients (FIG. 19). In addition, broad peaks with low extinction coefficient were observed between 600-700nm for both Co(II) complex **2a** and **3a**

(FIG. 17). These Laporte relaxed transitions are characteristic e to t_2 transition for tetrahedral cobalt trichloride species and are in agreement with analog complex such as the $\text{Co}(\text{pyridine})\text{Cl}_3^-$, which supports the formation of zwitterion metallate trichloride $\text{M}(\text{II})$ bound to cationic ligand. Complexes **4** show very slight changes on the spectrum compared to ligand **L3**, regarding to either main absorption peaks or extinction coefficients. As can be seen, the Co and Ni complexes **2-4** display similar absorption properties to the corresponding carbenium free ligand. Without being bound by any theory, this suggests: i) no electron transfer from the metal center to the heterocyclic system occurs and ii) the ionic Van-der-Walls interactions observed in the solid state is not present in the solution at RT.

[0205] DTF calculations. Density functional theory (DFT) calculations were performed on complexes **2a** and **2b** to better understand the interaction of the carbenium center with the transition metal halide observed in the solid state (ionic interaction or crystal packing). Solvated and gas-phase models were calculated to obtain a better representation of the intramolecular forces present during the structural characterization process. Isoelectronic models were calculated with the metal-halide fragment in-plane and out-of plane of the carbenium center. First, calculation was performed without empirical dispersion. Under this condition, the out of plane was found to be more thermodynamically stable in both solution and gas phase by 8.6 and 4.7 Kcal mol⁻¹ respectively. When the Grimme's empirical dispersion with D3 damping functions were employed, the solvated model shows a thermoneutral equilibrium between the in and out of plane conformation, with the out of plane being more thermodynamically stable ($\Delta E = 1.02$ Kcal mol⁻¹). In the gas-phase, this energy difference increases to 4.81 Kcal mol⁻¹, with the in-plane configuration being favoured. Similar trends in the energy difference between solvated and gas-phase models were observed for the Ni complex **2b**, showing no effect on the nature of the first-row transition metal center for a preferred in/out of plane structural configurations.

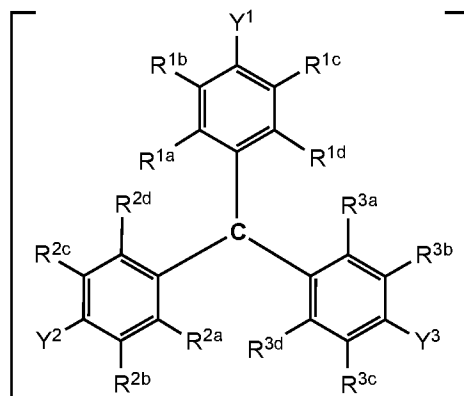
[0206] The thermoneutral equilibrium in solution and the slightly favoured in-plane configuration in the gas phase are both in agreement the experimental observations: i) the lack of interaction observed in solution by UV spectroscopy, ii) the crystallization of the in-plane configuration observed by X-ray diffraction analysis.

[0207] The foregoing discussion of the invention has been presented for purposes of illustration and description. The foregoing is not intended to limit the invention to the form or forms disclosed herein. Although the description of the invention has included description

of one or more embodiments and certain variations and modifications, other variations and modifications are within the scope of the invention, e.g., as may be within the skill and knowledge of those in the art, after understanding the present disclosure. It is intended to obtain rights which include alternative embodiments to the extent permitted, including alternate, interchangeable and/or equivalent structures, functions, ranges or steps to those claimed, whether or not such alternate, interchangeable and/or equivalent structures, functions, ranges or steps are disclosed herein, and without intending to publicly dedicate any patentable subject matter. All references cited herein are incorporated by reference in their entirety.

What is Claimed is:

1. A compound comprising a moiety of the formula:



I

wherein

said moiety of formula I is a radical, a cation, or a radical dication;

each of R^{1a} , R^{1b} , R^{1c} , R^{1d} , R^{2a} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , R^{3c} , and R^{3d} is independently H, halide, haloalkyl (e.g., CF_3), $-NR^aR^b$, C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, $-NO_2$, $-CN$, $-CO_2R$ (wherein R is H or C_1 - C_4 alkyl), or Ar^1 ;

or R^{2a} and R^{3d} together form $-X^1-$;

or R^{1a} and R^{2d} together form $-X^2-$;

or R^{1d} and R^{3a} together form $-X^3-$;

each of R^a and R^b is independently H or C_1 - C_4 alkyl;

each of X^1 , X^2 and X^3 is independently O, NR^{4a} , PR^{4a} , $CR^{4a}R^{4b}$, or $SiR^{4a}R^{4b}$;

or R^{1a} and R^{1b} together with atoms to which they are attached to form an optionally substituted aromatic ring;

or R^{2c} and R^{2d} together with atoms to which they are attached to form an optionally substituted aromatic ring;

each of Y^1 , Y^2 , and Y^3 is independently H, OR^{5a} , $CR^{5a}R^{5b}R^{5b}$, $NR^{5a}R^{5b}$, $PR^{5a}R^{5b}$, NO_2 , CN , haloalkyl, CO_2R , N_3 , or Ar^1 ;

each of R^{4a} , R^{4b} , R^{5a} , and R^{5b} is independently H, halide, haloalkyl, C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, $-NR^aR^b$ (provided at least one of R^a and R^b is C_1 - C_4 alkyl), Ar^1 , or a moiety of the formula $-L-Z$,

wherein

L is a linker; and

Z is a heterocyclic species of Formula **I**, a coordinating group able to bind or complex to a metal ion, or a water-soluble group such as phosphate, phosphite, sulfate or sulfite; and

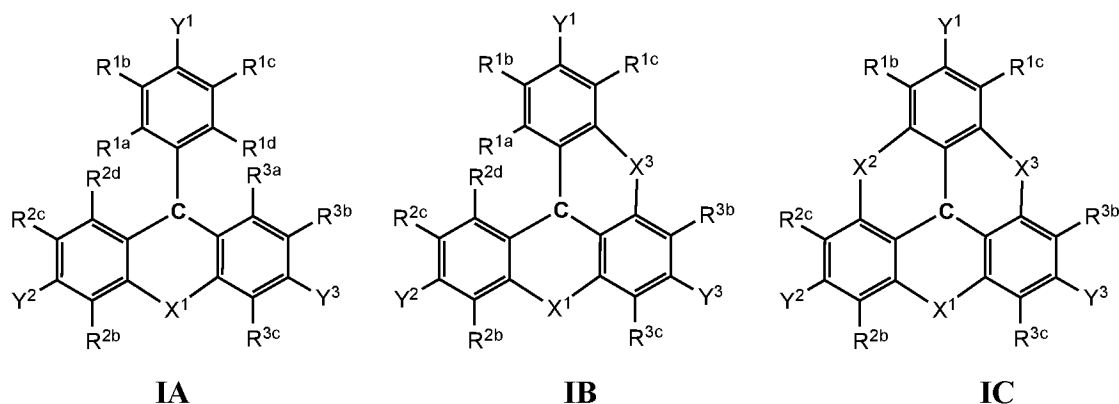
Ar¹ is optionally substituted aryl having from 0 to 5 substituents, each of which is independently selected from the group consisting of X¹, haloalkyl, NR^aR^b, C₁-C₄ alkyl, and C₁-C₄ alkoxy, heteroaryl, fused aryl or Ar¹,

provided when said Formula **I** is a cation then

- (i) when R^{2a} and R^{3d} together form -X¹-; R^{1a} and R^{2d} together form -X²-; and R^{1d} and R^{3a} together form -X³-, then no more than one of X¹, X², and X³ is O;
- (ii) when R^{2a} and R^{3d} together form -X¹-, and R^{1a} and R^{2d} together does not form -X²-; and R^{1d} and R^{3a} together does not form -X³-, then at least one of R^{1a}, R^{1b}, R^{1c}, R^{1d}, or Y¹ is not H, halogen, or C₁-C₁₂ alkyl;
- (iii) at least one of (a) R^{2a} and R^{3d} together form -X¹-; (b) R^{1a} and R^{2d} together form -X²-; or (c) R^{1d} and R^{3a} together form -X³-; and
- (iv) when R^{2a} and R^{3d} together form -X¹-; R^{1a} and R^{2d} together form -X²-; and R^{1d} and R^{3a} together form -X³-, then none of X¹, X², and X³ is NR^{4a}.

2. The compound of claim 1, wherein Y¹ is NR^{5a}R^{5b}, PR^{5a}R^{5b}, haloalkyl (e.g., CF₃), N₃, or Ar¹.

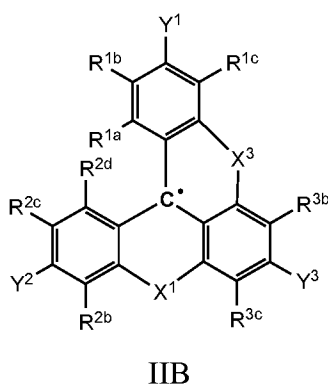
3. The compound of claim 1, wherein said moiety of Formula **I** is selected from the group consisting of:



wherein Y¹, Y², Y³, X¹, X², X³, R^{1a}, R^{1b}, R^{1c}, R^{1d}, R^{2b}, R^{2c}, R^{2d}, R^{3a}, R^{3b}, and R^{3c} are as defined in claim 1.

4. The compound of claim 3, wherein said moiety of Formula **IB** or **IC** is a radical or a radical dication.

5. The compound of claim 3, wherein X^1 is NR^{4a} , wherein R^{4a} is as defined in claim 1.
6. The compound of claim 5, wherein R^{4a} is said moiety of the formula $L-Z$, and wherein L and Z are as defined in claim 1.
7. The compound of claim 1, wherein Z is said coordinating group selected from the group consisting of bipyridinyl, pyridinyl, $-PR_2$, $-OPR_2$, $-NHC$, $-NR_2$, diimine, imine, $-OH$, $-OR$, $-SR$, $-SH$, diphosphines, $-RNC$, $-CO_2H$, and carboiimine, and wherein each R is independently C_1 - C_{12} alkyl or Aryl.
8. The compound of claim 1, wherein L is C_1 - C_{10} alkylene, alkynylene, alkenylene, arylene, or heteroarylene.
9. The compound of claim 1, wherein each of R^{1c} , R^{2c} , and R^{3c} is independently C_1 - C_4 alkoxy.
10. The compound of claim 1, wherein Y , R^{1a} , R^{1b} , R^{2a} , R^{2b} , R^{3a} , and R^{3b} are H.
11. A compound comprising a radical or a diradical cation moiety of the formula:



wherein

- each of R^{1a} , R^{1b} , R^{1c} , R^{2b} , R^{2c} , R^{2d} , R^{3b} , and R^{3c} is independently H, halide, haloalkyl, $-NR^aR^b$, C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, $-NO_2$, $-CN$, $-CO_2R$ (wherein R is H or C_1 - C_4 alkyl), or Ar^1 ;
- or R^{1a} and R^{2d} together form $-X^2-$;
- each of R^a and R^b is independently H or C_1 - C_4 alkyl;
- each of X^1 , X^2 and X^3 is independently O, NR^{4a} , PR^{4a} , $CR^{4a}R^{4b}$, or $SiR^{4a}R^{4b}$;
- or R^{1a} and R^{1b} together with atoms to which they are attached to form an optionally substituted aromatic ring;

or R^{2c} and R^{2d} together with atoms to which they are attached to form an optionally substituted aromatic ring;

each of Y¹, Y², and Y³ is independently H, OR^{5a}, NR^{5a}R^{5b}, PR^{5a}R^{5b}, NO₂, CN, CF₃, CO₂R, N₃, or Ar¹;

each of R^{4a}, R^{4b}, R^{5a}, and R^{5b} is independently H, halide, haloalkyl, C₁-C₁₂ alkyl, C₁-C₄ alkoxy, -NR^aR^b (provided at least one of R^a and R^b is C₁-C₄ alkyl and provided R^{4a} is not attached to N), Ar¹, or a moiety of the formula -L-Z, wherein

L is a linker; and

Z is a coordinating group able to bind or complex to a metal ion; and

Ar¹ is optionally substituted phenyl having from 0 to 5 substituents, each of which is independently selected from the group consisting of X¹, haloalkyl, NR^aR^b, C₁-C₄ alkyl, and C₁-C₄ alkoxy.

12. The radical moiety of claim 11, wherein X¹ and X³ are NR^{4a}, wherein R^{4a} is as defined in claim 11.

13. The radical moiety of claim 11, wherein each R^{4a} is independently C₁-C₁₂ alkyl or a moiety of the formula -L-Z, wherein L and Z are as defined in claim 11.

14. The radical moiety of claim 13, wherein Z is selected from the group consisting of a heteroaryl, heterocyclyl, and a heteroatom functional group.

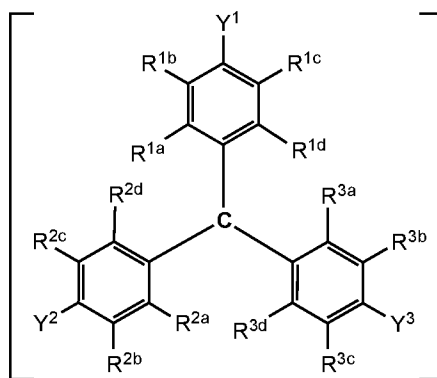
15. The radical moiety of claim 11 wherein Y¹, Y², and Y³ are NR^{5a}R^{5b}, wherein each of R^{5a} and R^{5b} is independently H, haloalkyl, or C₁-C₁₂ alkyl, provided at least one of R^{5a} and R^{5b} is not H.

16. The radical moiety of claim 11, wherein R^{1a} and R^{2d} are C₁-C₄ alkoxy.

17. A photocatalytic compound that for capable of catalyzing an oxidative reaction and/or a reductive reaction, said photocatalytic compound comprising a compound of claim 1.

18. The photocatalytic compound of claim 17, wherein said photocatalytic compound is activated by an electromagnetic radiation having wavelength of 390 nm or greater.

19. A method for producing an oxidative product from a reaction substrate, said method comprising:
- contacting said reaction substrate with an oxidizing reagent, and a photocatalytic compound of claim 1 to produce a reaction mixture; and
- irradiating said reaction mixture with an electromagnetic radiation having a wavelength of 390 nm or greater under conditions sufficient to produce said oxidative product from said reaction substrate.
20. The method of claim 19, wherein said method comprises an aerobic oxidative hydroxylation or aerobic oxygenation.
21. The method of claim 20, wherein said aerobic oxygenation comprises oxygenation of benzylic carbon.
22. A method for producing a reductive coupling product from a reaction substrate, said method comprising:
- contacting said reaction substrate with an oxidizing reagent, and a photocatalytic compound of claim 1 to produce a reaction mixture; and
- irradiating said reaction mixture with an electromagnetic radiation having a wavelength of 390 nm or greater under conditions sufficient to produce said reductive coupling product from said reaction substrate.
23. The method of claim 22, wherein said method comprises dual catalysis arylation reaction of an sp^2 -carbon atom or atom transfer radical reaction (ATRA).
24. A solid substrate having a surface, wherein said surface comprises a compound comprising a moiety of the formula:

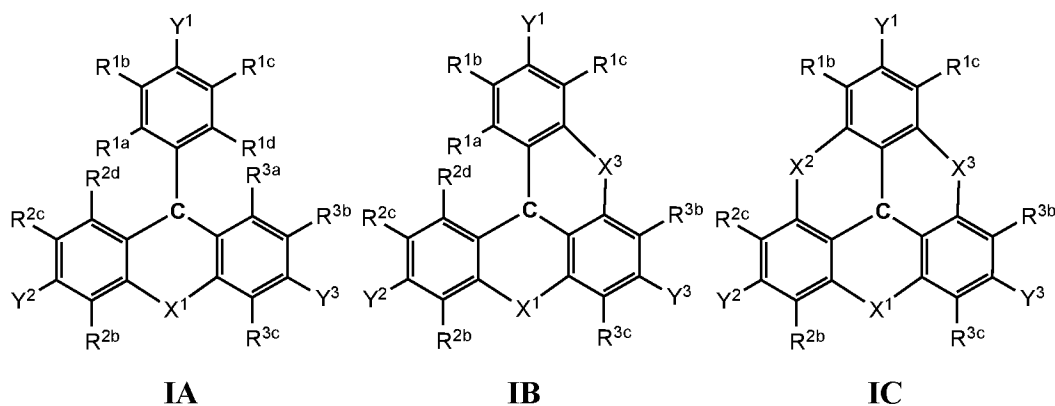


I

wherein

said moiety of formula I is a radical, a cation, or a radical dication;
 each of R^{1a} , R^{1b} , R^{1c} , R^{1d} , R^{2a} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , R^{3c} , and R^{3d} is independently H, halide, haloalkyl, $-NR^aR^b$, C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, $-NO_2$, $-CN$, $-CO_2R$ (wherein R is H or C_1 - C_4 alkyl), or Ar^1 ;
 or R^{2a} and R^{3d} together form $-X^1-$;
 or R^{1a} and R^{2d} together form $-X^2-$;
 or R^{1d} and R^{3a} together form $-X^3-$;
 each of R^a and R^b is independently H or C_1 - C_4 alkyl;
 each of X^1 , X^2 and X^3 is independently O, NR^{4a} , PR^{4a} , $CR^{4a}R^{4b}$, or $SiR^{4a}R^{4b}$;
 or R^{1a} and R^{1b} together with atoms to which they are attached to form an optionally substituted aromatic ring;
 or R^{2c} and R^{2d} together with atoms to which they are attached to form an optionally substituted aromatic ring;
 each of Y^1 , Y^2 , and Y^3 is independently H, OR^{5a} , $CR^{5a}R^{5b}R^{5c}$, $NR^{5a}R^{5b}$, $PR^{5a}R^{5b}$, NO_2 , CN , CF_3 , CO_2R , N_3 , or Ar^1 ;
 each of R^{4a} , R^{4b} , R^{5a} , and R^{5b} is independently H, halide, haloalkyl (e.g., CF_3), C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, $-NR^aR^b$ (provided at least one of R^a and R^b is C_1 - C_4 alkyl), Ar^1 , or a moiety of the formula $-L-Z$,
 wherein
 L is a linker; and
 Z is a heterocyclic species of Formula I, a coordinating group able to bind or complex to a metal ion, or a water-soluble group; and
 Ar^1 is optionally substituted aryl having from 0 to 5 substituents, each of which is independently selected from the group consisting of X^1 , haloalkyl, NR^aR^b , C_1 - C_4 alkyl, and C_1 - C_4 alkoxy, heteroaryl, fused aryl or Ar^1 .

25. The solid substrate of claim 24, wherein said moiety of Formula I is selected from the group consisting of:

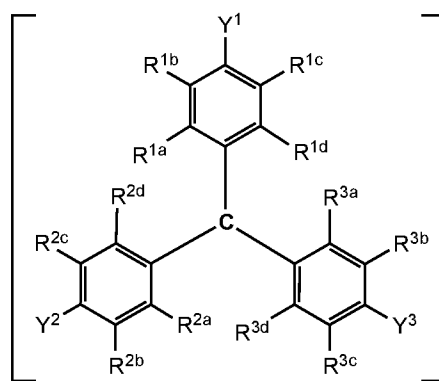


wherein Y^1 , Y^2 , Y^3 , X^1 , X^2 , X^3 , R^{1a} , R^{1b} , R^{1c} , R^{1d} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , and R^{3c} are as defined in claim 24.

26. The solid substrate of claim 25, wherein said moiety of Formula IB or IC is a radical or a radical dication.

27. The solid substrate of claim 24, wherein when said formula I is a cation then
- (i) when R^{2a} and R^{3d} together form $-X^1-$; R^{1a} and R^{2d} together form $-X^2-$; and R^{1d} and R^{3a} together form $-X^3-$, then no more than one of X^1 , X^2 , and X^3 is O;
 - (ii) when R^{2a} and R^{3d} together form $-X^1-$, and R^{1a} and R^{2d} together does not form $-X^2-$; and R^{1d} and R^{3a} together does not form $-X^3-$, then Y^1 is $NR^{5a}R^{5b}$, $PR^{5a}R^{5b}$, haloalkyl, N_3 , or Ar^1 ;
 - (iii) at least one of (a) R^{2a} and R^{3d} together form $-X^1-$; (b) R^{1a} and R^{2d} together form $-X^2-$; or (c) R^{1d} and R^{3a} together form $-X^3-$; and
 - (iv) when R^{2a} and R^{3d} together form $-X^1-$; R^{1a} and R^{2d} together form $-X^2-$; and R^{1d} and R^{3a} together form $-X^3-$, then none of X^1 , X^2 , and X^3 is NR^{4a} .

28. A method for conducting a photocatalytic reaction, said method comprising contacting two or more reagents in the presence of a photocatalyst compound under conditions sufficient to produce a photooxidative product or a photoreductive product, wherein said photocatalyst compound comprises a moiety of the formula:



I

wherein

said moiety of formula I is a radical, a cation, or a radical dication;

each of R^{1a} , R^{1b} , R^{1c} , R^{1d} , R^{2a} , R^{2b} , R^{2c} , R^{2d} , R^{3a} , R^{3b} , R^{3c} , and R^{3d} is independently H, halide, haloalkyl, $-NR^aR^b$, C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, $-NO_2$, $-CN$, $-CO_2R$ (wherein R is H or C_1 - C_4 alkyl), or Ar^1 ;

or R^{2a} and R^{3d} together form $-X^1-$;

or R^{1a} and R^{2d} together form $-X^2-$;

or R^{1d} and R^{3a} together form $-X^3-$;

each of R^a and R^b is independently H or C_1 - C_4 alkyl;

each of X^1 , X^2 and X^3 is independently O, NR^{4a} , PR^{4a} , $CR^{4a}R^{4b}$, or $SiR^{4a}R^{4b}$;

or R^{1a} and R^{1b} together with atoms to which they are attached to form an optionally substituted aromatic ring;

or R^{2c} and R^{2d} together with atoms to which they are attached to form an optionally substituted aromatic ring;

each of Y^1 , Y^2 , and Y^3 is independently H, OR^{5a} , $CR^{5a}R^{5b}R^{5c}$, $NR^{5a}R^{5b}$, $PR^{5a}R^{5b}$, NO_2 , CN , CF_3 , CO_2R , N_3 , or Ar^1 ;

each of R^{4a} , R^{4b} , R^{5a} , and R^{5b} is independently H, halide, haloalkyl (e.g., CF_3), C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, $-NR^aR^b$ (provided at least one of R^a and R^b is C_1 - C_4 alkyl), Ar^1 , or a moiety of the formula $-L-Z$,

wherein

L is a linker; and

Z is a heterocyclic species of Formula I, a coordinating group able to bind or complex to a metal ion, or a water-soluble group; and

Ar^1 is optionally substituted aryl having from 0 to 5 substituents, each of which is independently selected from the group consisting of X^1 ,

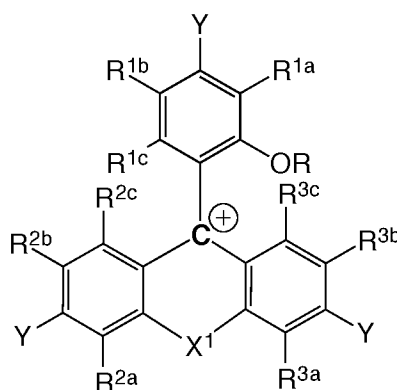
haloalkyl, NR^aR^b , $\text{C}_1\text{-C}_4$ alkyl, and $\text{C}_1\text{-C}_4$ alkoxy, heteroaryl, fused aryl or Ar^1 ,

provided when said formula I is a cation when R^{2a} and R^{3d} together form $-\text{X}^1-$, and R^{1a} and R^{2d} together does not form $-\text{X}^2-$; and R^{1d} and R^{3a} together does not form $-\text{X}^3-$, then at least one of R^{1a} , R^{1b} , R^{1c} , R^{1d} , Y^1 is OR^{5a} , $\text{NR}^{5a}\text{R}^{5b}$, $\text{PR}^{5a}\text{R}^{5b}$, haloalkyl, N_3 , or Ar^1 .

29. The method of claim 28, wherein said photocatalytic reaction is conducted using a red light.

30. The method of claim 28, wherein said photocatalytic reaction is conducted using an electromagnetic radiation having a wavelength of 500 nm or greater.

31. A compound comprising a carbocation of the formula:



wherein

R is $\text{C}_1\text{-C}_{12}$ alkyl or Aryl;

X^1 is O , NR^{4a} , PR^{4a} , $\text{CR}^{4a}\text{R}^{4b}$, or $\text{SiR}^{4a}\text{R}^{4b}$;

each of Y is independently H , OR^{5a} , $\text{NR}^{5a}\text{R}^{5b}$, $\text{PR}^{5a}\text{R}^{5b}$, NO_2 , CN , haloalkyl, N_3 , CO_2R , or Ar^1 ;

each of R^{1a} , R^{1b} , R^{1c} , R^{2a} , R^{2b} , R^{2c} , R^{3a} , R^{3b} , and R^{3c} , is independently H , halide, CF_3 , NH_2 , $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_1\text{-C}_4$ alkoxy, $\text{C}_1\text{-C}_4$ alkylamino, $\text{C}_1\text{-C}_4$ dialkyl amino, NO_2 , CN , CO_2R , or Ar^1 ;

each of each of R^{4a} , R^{4b} , R^{5a} , and R^{5b} is independently H , halide, CF_3 , $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_1\text{-C}_4$ alkoxy, $\text{C}_1\text{-C}_4$ alkylamino, $\text{C}_1\text{-C}_4$ dialkyl amino, or Ar^1 ;

or R^{1c} and R^{2c} together form $-\text{X}^2-$;

or OR and R^{3c} together form $-\text{X}^3-$;

each of X^2 and X^3 is independently O , NR^{4a} , PR^{4a} , $\text{CR}^{4a}\text{R}^{4b}$, or $\text{SiR}^{4a}\text{R}^{4b}$;

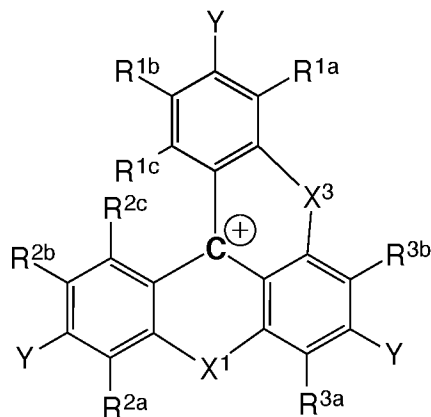
or R^{1b} and R^{1c} together with atoms to which they are attached to form an optionally substituted phenyl;

or R^{2b} and R^{2c} together with atoms to which they are attached to form an optionally substituted phenyl; and

Ar^1 is optionally substituted phenyl having from 0 to 5 substituents, each of which is independently selected from the group consisting of X^1 , CF_3 , NH_2 , C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylamino, and C_1 - C_4 dialkyl amino; or at least one of R^{1a} , R^{1b} , R^{1c} , R^{2a} , R^{2b} , R^{2c} , R^{3a} , R^{3b} , R^{3c} , R^{4a} , R^{4b} , R^{5a} , and R^{5b} is a moiety of the formula $-L-Z$, wherein L is a linker; and Z is a coordinating group that is capable of coordinating to a metal complex.

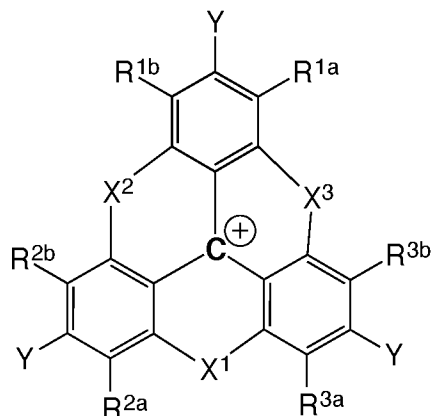
32. The compound of claim 31, wherein at least one of R^{1a} , R^{1b} , R^{1c} , R^{2a} , R^{2b} , R^{2c} , R^{3a} , R^{3b} , R^{3c} , R^{4a} , R^{4b} , R^{5a} , and R^{5b} is a moiety of the formula $-L-Z$, wherein L is a linker; and Z is a coordinating group that is capable of coordinating to a metal complex.

33. The compound of claim 31, wherein said compound is of the formula:



wherein Y , X^1 , X^3 , R^{1a} , R^{1b} , R^{1c} , R^{2a} , R^{2b} , R^{2c} , R^{3a} , and R^{3b} are as defined in claim 31.

34. The compound of claim 31, wherein said compound is of the formula:



wherein Y , X^1 , X^2 , X^3 , R^{1a} , R^{1b} , R^{2a} , R^{2b} , R^{3a} , and R^{3b} are as defined in claim 31.

35. The compound of claim 31, wherein X^1 is NR^{4a} , wherein R^{4a} is as defined in claim 31.

36. The compound of claim 34, wherein R^{4a} is said moiety of the formula L-Z, and wherein L and Z are as defined in claim 31.

37. The compound of claim 31, wherein Z is said coordinating group selected from the group consisting of bipyridinyl, pyridinyl, $-PR_2$, $-OPR_2$, $-NHC$, $-NR_2$, diimine, imine, $-OH$, $-OR$, $-SR$, $-SH$, diphosphines, $-RNC$, $-CO_2H$, and carboimine, and wherein each R is independently C_1 - C_{12} alkyl or Aryl.

38. The compound of claim 37, wherein Z is coordinated or complexed to a metal complex.

39. The compound of claim 38, wherein said metal ion is a transition metal ion.

40. The compound of claim 39, wherein said metal ion is a first row transition metal ion.

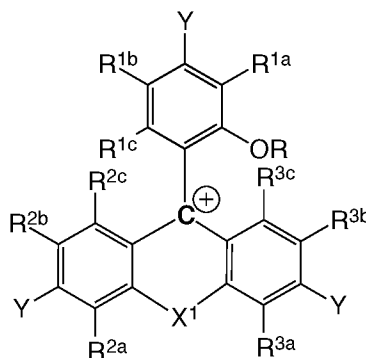
41. The compound of claim 40, wherein said metal ion is selected from the group consisting of Sc(III), Ti(IV), V(III), V(V), Cr(III), Cr(IV), Mn(II), Co (II), Co(I), Ni (II), Fe (II), Fe(III), Cu(II), Cu(I), and Zn(I).

42. The compound of claim 31, wherein L is C_1 - C_{10} alkylene, alkynylene, alkenylene, arylene, or heteroarylene.

43. The compound of claim 31 wherein each of R^{1c} , R^{2c} , and R^{3c} is independently C_1 - C_4 alkoxy.

44. The compound of claim 31, wherein Y, R^{1a} , R^{1b} , R^{2a} , R^{2b} , R^{3a} , and R^{3b} are H.

45. A photocatalyst composition comprising a conjugated heterocyclic carbenium-metal complex of the formula:



wherein

R is C_1 - C_{12} alkyl or optionally substituted Aryl;

X^1 is O, NR^{4a} , PR^{4a} , $CR^{4a}R^{4b}$, or $SiR^{4a}R^{4b}$;

each of Y is independently H, OR^{5a} , $NR^{5a}R^{5b}$, $PR^{5a}R^{5b}$, NO_2 , CN, haloalkyl, N_3 , CO_2R , or Ar^1 ;

each of R^{1a} , R^{1b} , R^{1c} , R^{2a} , R^{2b} , R^{2c} , R^{3a} , R^{3b} , and R^{3c} , is independently H, halide, CF_3 , NH_2 , C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylamino, C_1 - C_4 dialkyl amino, NO_2 , CN, CO_2R , or Ar^1 ;

each of each of R^{4a} , R^{4b} , R^{5a} , and R^{5b} is independently H, halide, CF_3 , C_1 - C_{12} alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylamino, C_1 - C_4 dialkyl amino, or Ar^1 ;

or R^{1c} and R^{2c} together form $-X^2-$;

or OR and R^{3c} together form $-X^3-$;

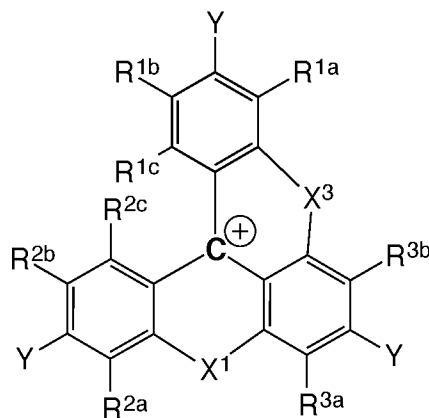
each of X^2 and X^3 is independently O, NR^{4a} , PR^{4a} , $CR^{4a}R^{4b}$, or $SiR^{4a}R^{4b}$;

or R^{1b} and R^{1c} together with atoms to which they are attached to form an optionally substituted phenyl;

or R^{2b} and R^{2c} together with atoms to which they are attached to form an optionally substituted phenyl; and

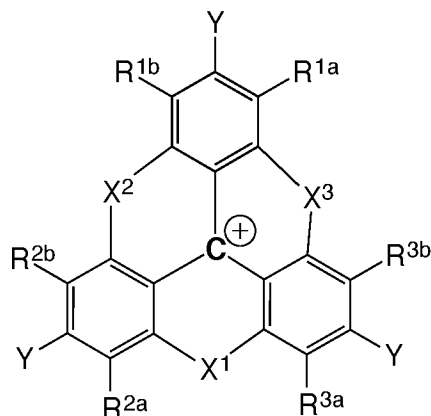
Ar^1 is optionally substituted phenyl having from 0 to 5 substituents, each of which is independently selected from the group consisting of X^1 , CF_3 , NH_2 , C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylamino, and C_1 - C_4 dialkyl amino; or at least one of R^{1a} , R^{1b} , R^{1c} , R^{2a} , R^{2b} , R^{2c} , R^{3a} , R^{3b} , R^{3c} , R^{4a} , R^{4b} , R^{5a} , and R^{5b} is a moiety of the formula $-L-Z$, wherein L is a linker; and Z is a coordinating group that is coordinated to a metal complex.

46. The photocatalyst composition of claim 45, wherein said conjugated heterocyclic carbenium-metal complex is of the formula:



wherein Y, X^1 , X^3 , R^{1a} , R^{1b} , R^{1c} , R^{2a} , R^{2b} , R^{2c} , R^{3a} , and R^{3b} are as defined in claim 45.

47. The photocatalyst composition of claim 45, wherein said conjugated heterocyclic carbenium-metal complex is of the formula:



wherein Y, X¹, X², X³, R^{1a}, R^{1b}, R^{2a}, R^{2b}, R^{3a}, and R^{3b} are as defined in claim 45.

48. The photocatalyst composition according to any one of claims 45-47, wherein X¹ is NR^{4a}, and wherein R^{4a} is said moiety of the formula -L-Z.

49. The photocatalyst composition according to any one of claims 48, wherein L has from 1 to about 10 chain of atoms.

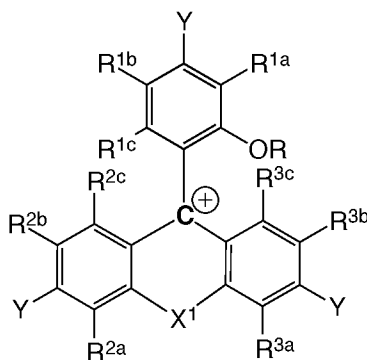
50. The photocatalyst composition according to claim 49, wherein L is C₁-C₁₀ alkylene or C₁-C₁₀ heteroalkylene.

51. The photocatalyst composition of claim 45, wherein said metal ion is a transition metal ion.

52. The photocatalyst composition of claim 51, wherein said metal ion is a first row transition metal ion.

53. The photocatalyst composition of claim 52, wherein said metal ion is selected from the group consisting of Co (II), Ni (II), and Fe (II).

54. A solid substrate having a surface, wherein said surface comprises a compound comprising a carbocation of the formula:



wherein

R is C₁-C₁₂ alkyl or an optionally substituted aryl;

X¹ is O, NR^{4a}, PR^{4a}, CR^{4a}R^{4b}, or SiR^{4a}R^{4b};

each of Y is independently H, OR^{5a}, NR^{5a}R^{5b}, PR^{5a}R^{5b}, NO₂, CN, CO₂R, or Ar¹;

each of R^{1a}, R^{1b}, R^{1c}, R^{2a}, R^{2b}, R^{2c}, R^{3a}, R^{3b}, and R^{3c}, is independently H, halide, CF₃,

NH₂, C₁-C₁₂ alkyl, C₁-C₄ alkoxy, C₁-C₄ alkylamino, C₁-C₄ dialkyl amino,

NO₂, CN, CO₂R, or Ar¹;

each of each of R^{4a}, R^{4b}, R^{5a}, and R^{5b} is independently H, halide, haloalkyl, C₁-C₁₂

alkyl, C₁-C₄ alkoxy, C₁-C₄ alkylamino, C₁-C₄ dialkyl amino, or Ar¹;

or R^{1c} and R^{2c} together form -X²-;

or OR and R^{3c} together form -X³-;

each of X² and X³ is independently O, NR^{4a}, PR^{4a}, CR^{4a}R^{4b}, or SiR^{4a}R^{4b};

or R^{1b} and R^{1c} together with atoms to which they are attached to form an optionally substituted phenyl;

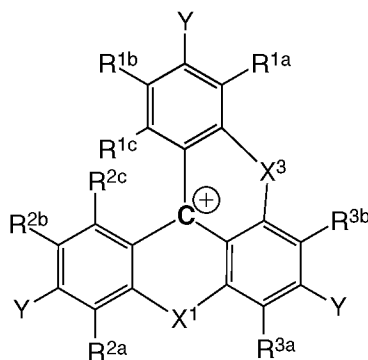
or R^{2b} and R^{2c} together with atoms to which they are attached to form an optionally substituted phenyl; and

Ar¹ is optionally substituted phenyl having from 0 to 5 substituents, each of which is independently selected from the group consisting of X¹, CF₃, NH₂, C₁-C₄ alkyl, C₁-C₄ alkoxy, C₁-C₄ alkylamino, and C₁-C₄ dialkyl amino; or

at least one of R^{1a}, R^{1b}, R^{1c}, R^{2a}, R^{2b}, R^{2c}, R^{3a}, R^{3b}, R^{3c}, R^{4a}, R^{4b}, R^{5a}, and R^{5b} is a moiety of the formula -L-Z, wherein L is a linker; and Z is a functional group attached to a surface of a solid substrate; or

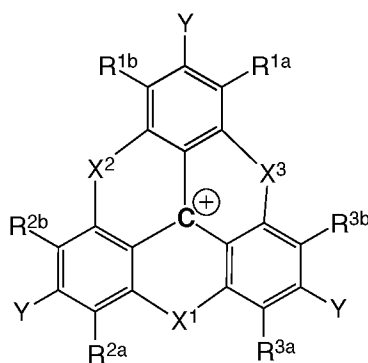
optionally at least one of R^{1a}, R^{1b}, R^{1c}, R^{2a}, R^{2b}, R^{2c}, R^{3a}, R^{3b}, R^{3c}, R^{4a}, R^{4b}, R^{5a}, and R^{5b} is a moiety of the formula -L'-Z', wherein L' is a linker and Z' is a metal complex.

55. The solid substrate of claim 54, wherein said carbocation is of the formula:



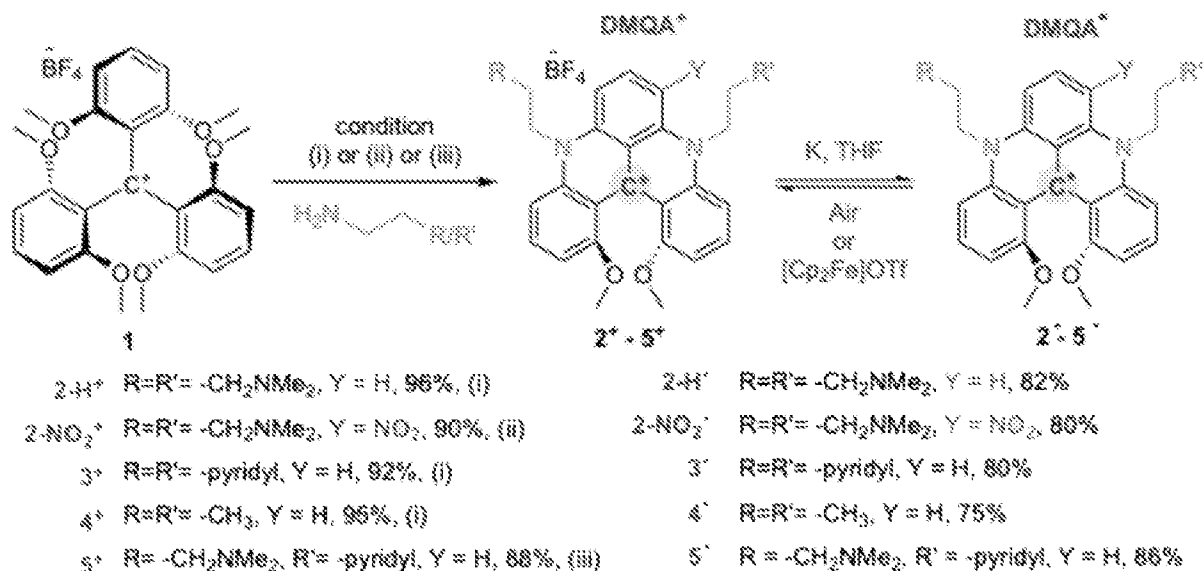
wherein Y, X^1 , X^3 , R^{1a} , R^{1b} , R^{1c} , R^{2a} , R^{2b} , R^{2c} , R^{3a} , and R^{3b} are as defined in claim 54.

56. The solid substrate of claim 54, wherein said carbocation is of the formula:



wherein Y, X^1 , X^2 , X^3 , R^{1a} , R^{1b} , R^{2a} , R^{2b} , R^{3a} , and R^{3b} are as defined in claim 54.

57. The solid substrate of claim 54, wherein at least one of R^{1a} , R^{1b} , R^{1c} , R^{2a} , R^{2b} , R^{2c} , R^{3a} , R^{3b} , R^{3c} , R^{4a} , R^{4b} , R^{5a} , and R^{5b} is a moiety of the formula $-L'-Z'$.



Synthesis of cations: (i) Synthetic route for 2-H⁺, 3⁺ and 4⁺: 1.0 eq. of (1), 25.0 eq. of amine, CH₃CN, 85 °C, 12 h; (ii) Synthetic route for 2-NO₂⁺: 1.0 eq. of (2⁺), HNO₃ (60%, 0.05 M), 30 min; (iii) Synthetic route for 5⁺: 1.0 eq. of (1), 1.2 eq. of 2-(2-dimethylaminoethyl)-pyridine, EtOAc, rt, 1.5 h; followed by 15.0 eq. of 3-(Dimethylamino)-1-propylamine, CH₃CN, 85 °C, 12 h. **Synthesis of radicals:** 2[·]-5[·]: 1.0 eq. of (2⁺ - 5⁺), 1.1 eq. of K or KC₈ in THF, rt, o/n.

FIG. 1

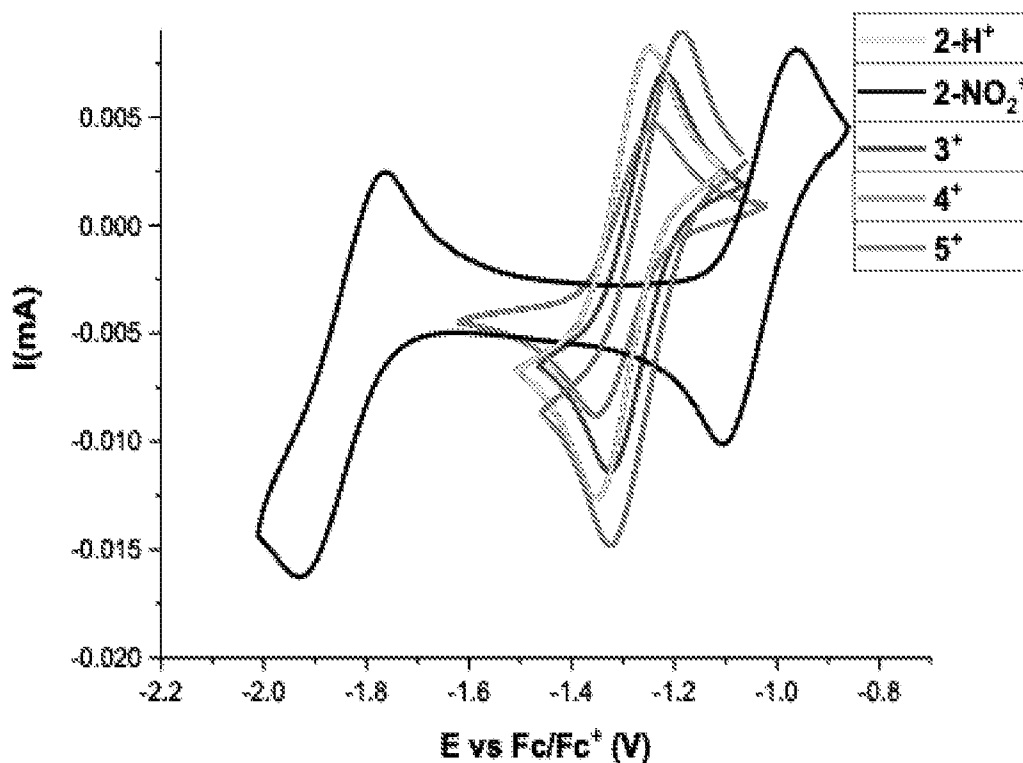


FIG. 2

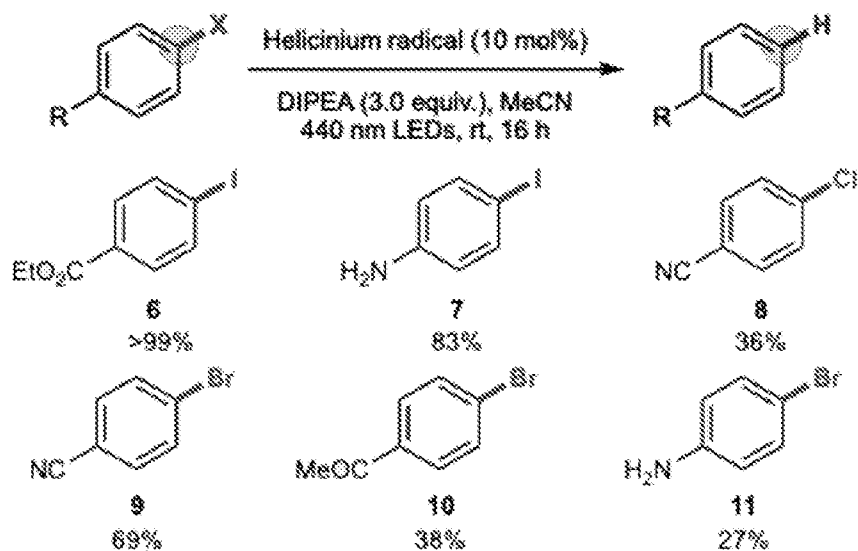


FIG. 3

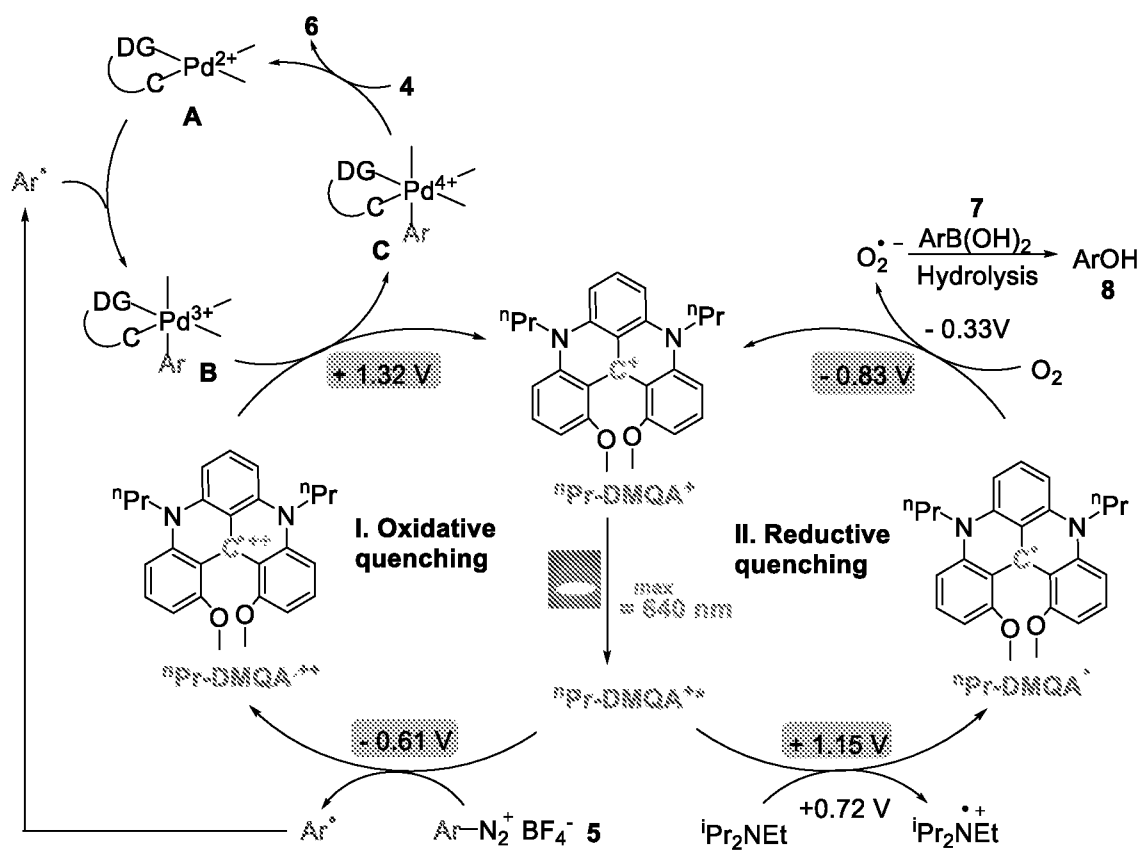


FIG. 5

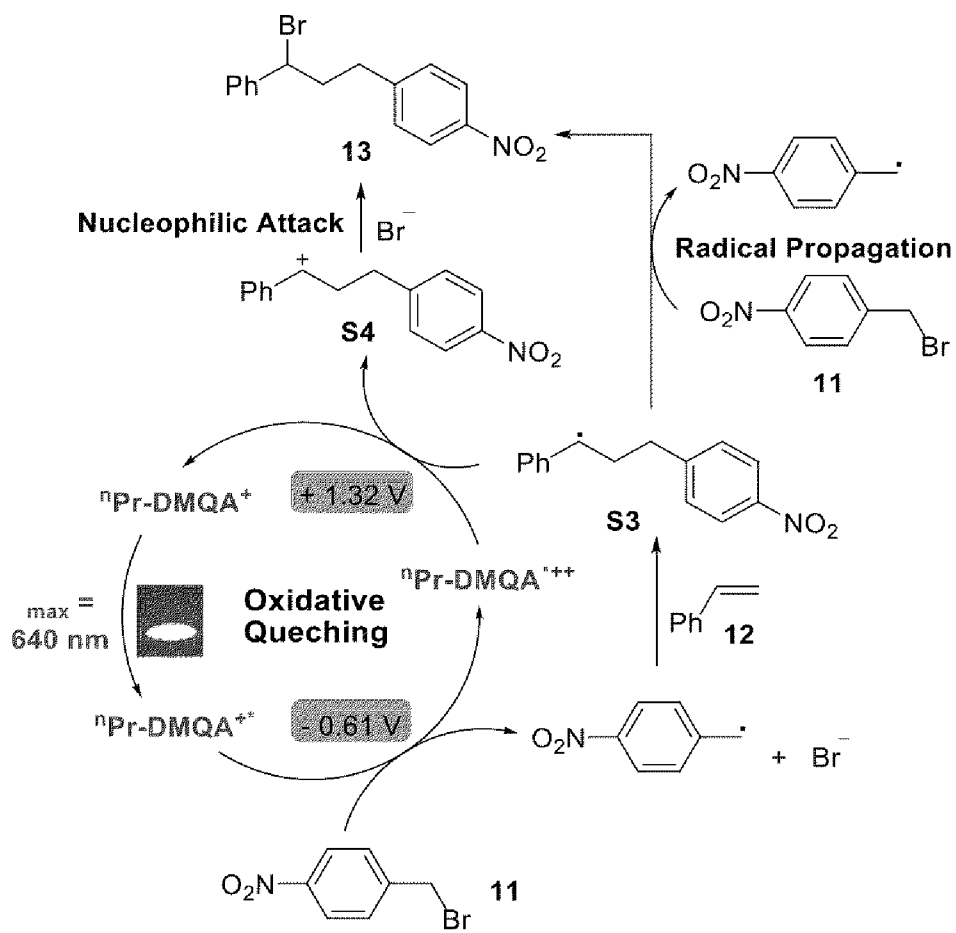


FIG. 6

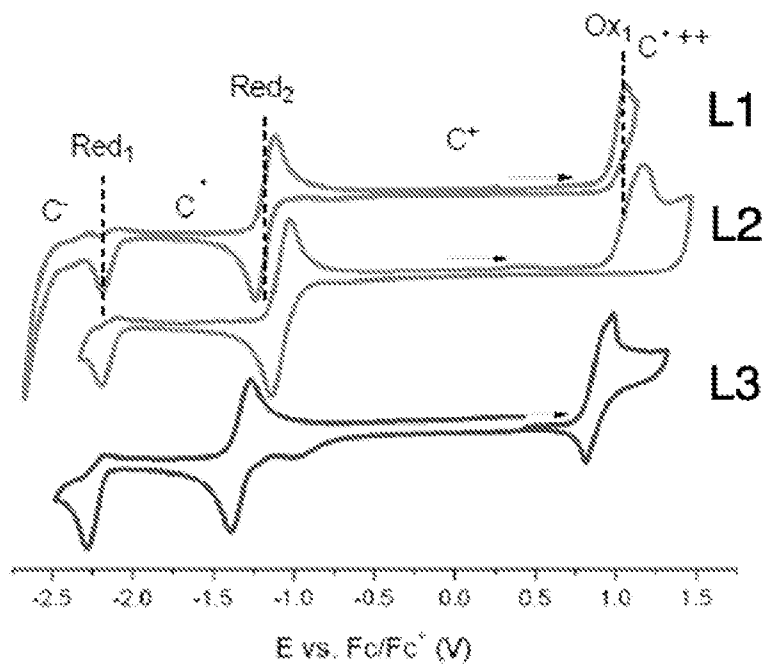
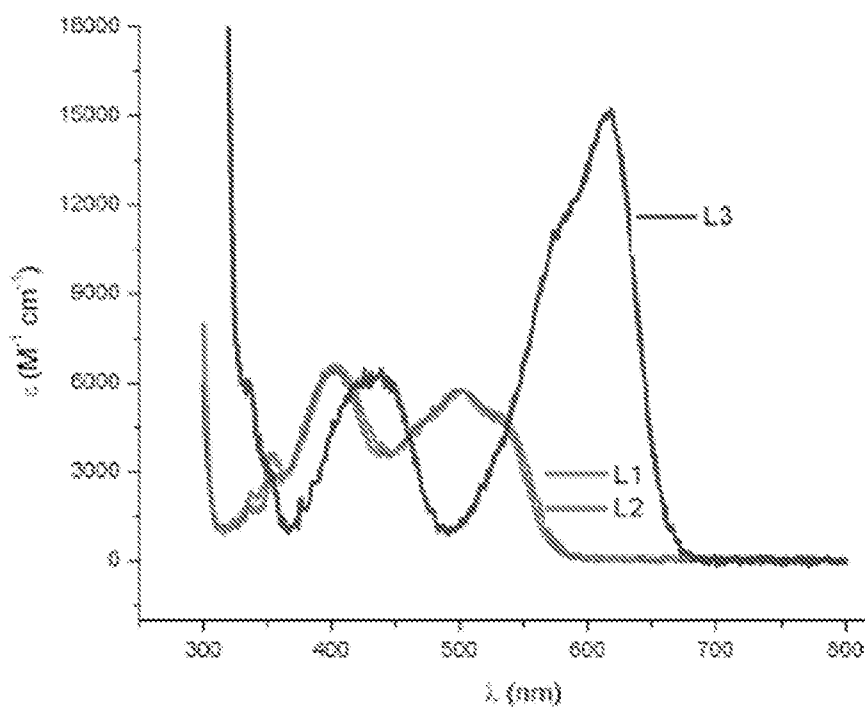


FIG. 7

Compound	Red ₁	Reduction ΔE (Red L1) ^a	Red ₂	Ox ₁
L1	-1.168	0	-2.178 ^b	1.075 ^b
L2	-1.073	0.093	-2.187 ^b	1.186 ^b
L3	-1.328	-0.162	-2.284 ^b	0.898

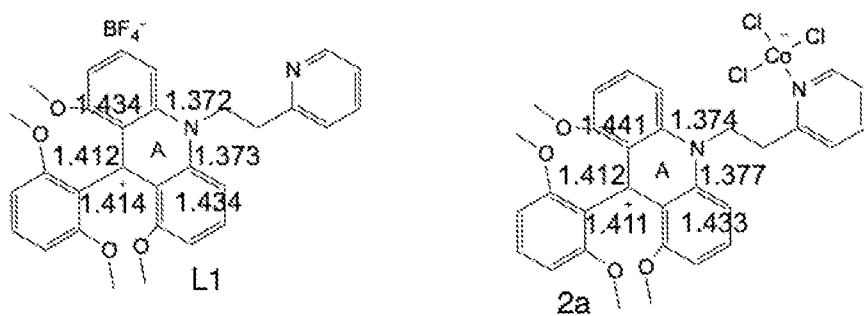
a Half-wave potential difference compared to the first reduction waves of ligand **L1**. b Irreversible process.

FIG. 8



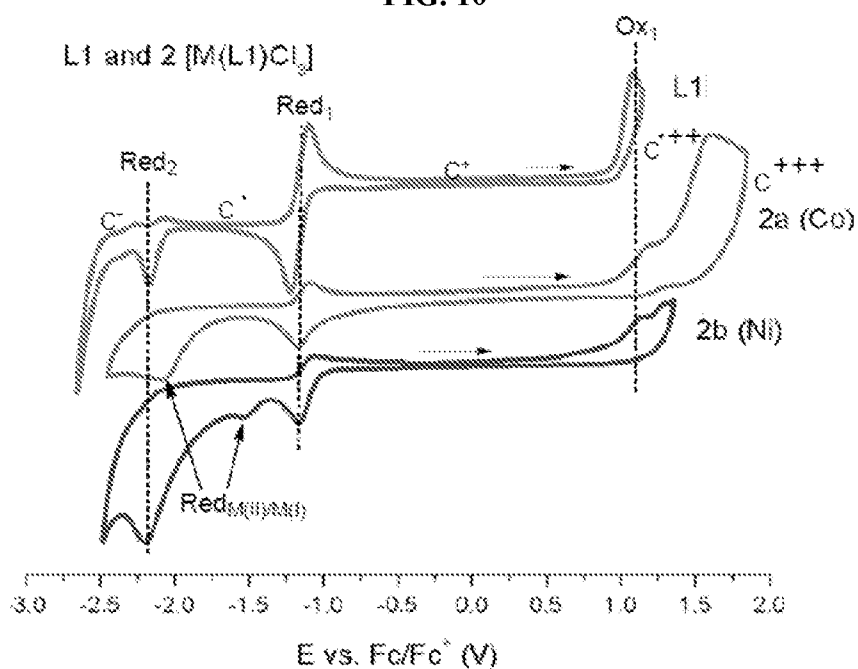
Compound	λ (nm)	ϵ ($M^{-1} cm^{-1}$)
L1	402, 498, 533	6597, 5789, 4669
L2	406, 501, 534	6588, 5751, 4872
L3	426, 582, 618	6488, 11648, 15226

FIG. 9



Compound	C13-N1	Cl1-C13	Cl1-N1	Cl1-centroid of ring A	N1-C24-C25-C26
L1	1.3723 (18)	-	-	-	155.817
2a (Co)	1.374 (3)	3.414	3.556	3.005	87.230
2b (Ni)	1.376 (2)	3.439	3.521	3.481	87.773

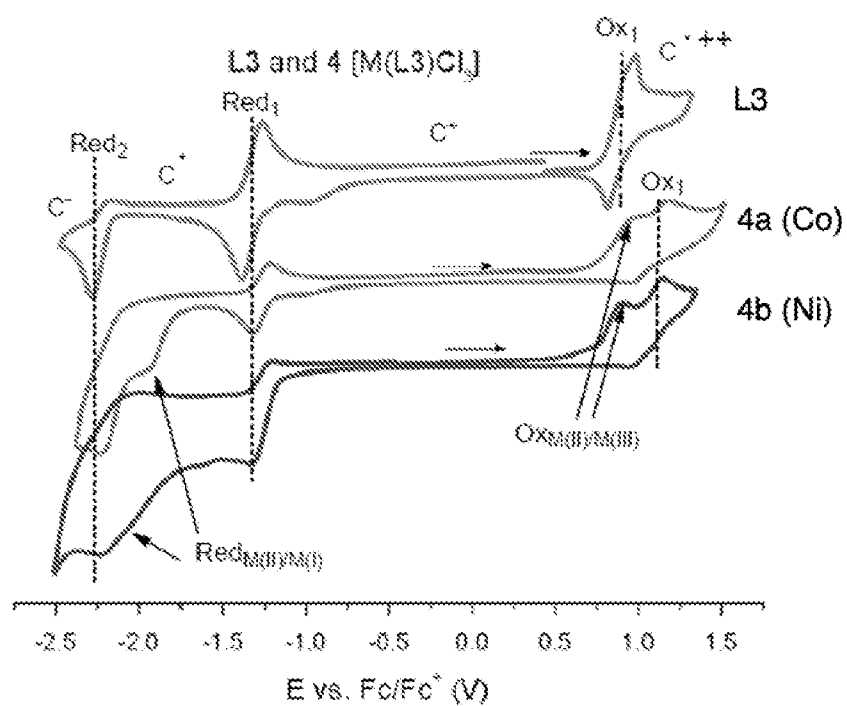
FIG. 10



Compound	Red_1	Reduction ΔE (Red L1) ^a	Red_2	$\text{Red}_{\text{M(II)/M(I)}}$	Ox_1	Ox_2
L1	-1.166	0	-2.178 ^b	-	1.075 ^b	-
2a	-1.136	0.030	-2.197 ^b	-2.088 ^b	1.222 ^b	1.596 ^b
2b	-1.112	0.054	-2.203 ^b	-1.541 ^b	1.178 ^b	-

^a Half-wave potential difference compared to the first reduction waves of ligand **L1**. ^b Irreversible process.

FIG. 11



Compound	Red ₁	Reduction ΔE (Red L3) ^a	Red ₂	Red _{M(II)/M(I)}	Ox ₁	Ox _{M(II)/M(III)}
L3	-1.328	0	-2.284 ^b	-	0.898	-
4a	-1.274	0.054	-2.236 ^b	-1.936 ^b	1.059	0.981 ^b
4b	-1.267	0.061	-2.228 ^b	-1.630 ^b	1.042	0.910 ^b

a Half-wave potential difference compared to the first reduction waves of ligand **L3**. b Irreversible process.

FIG. 12

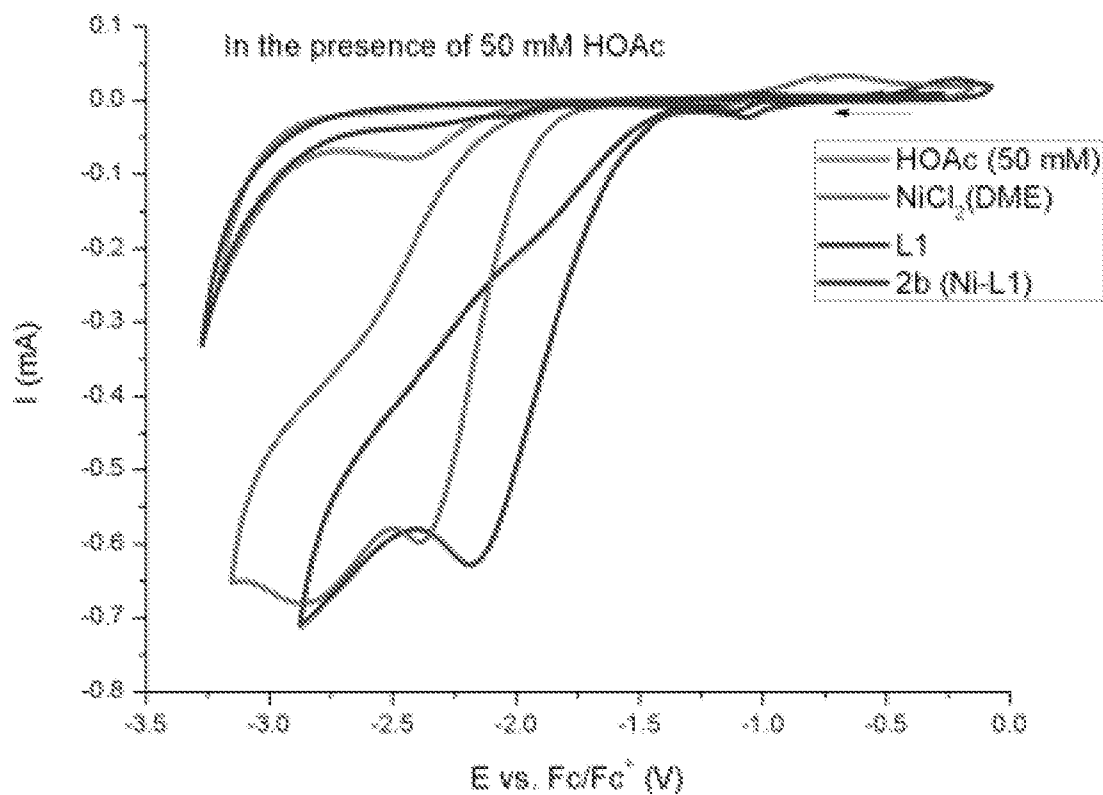


FIG. 13

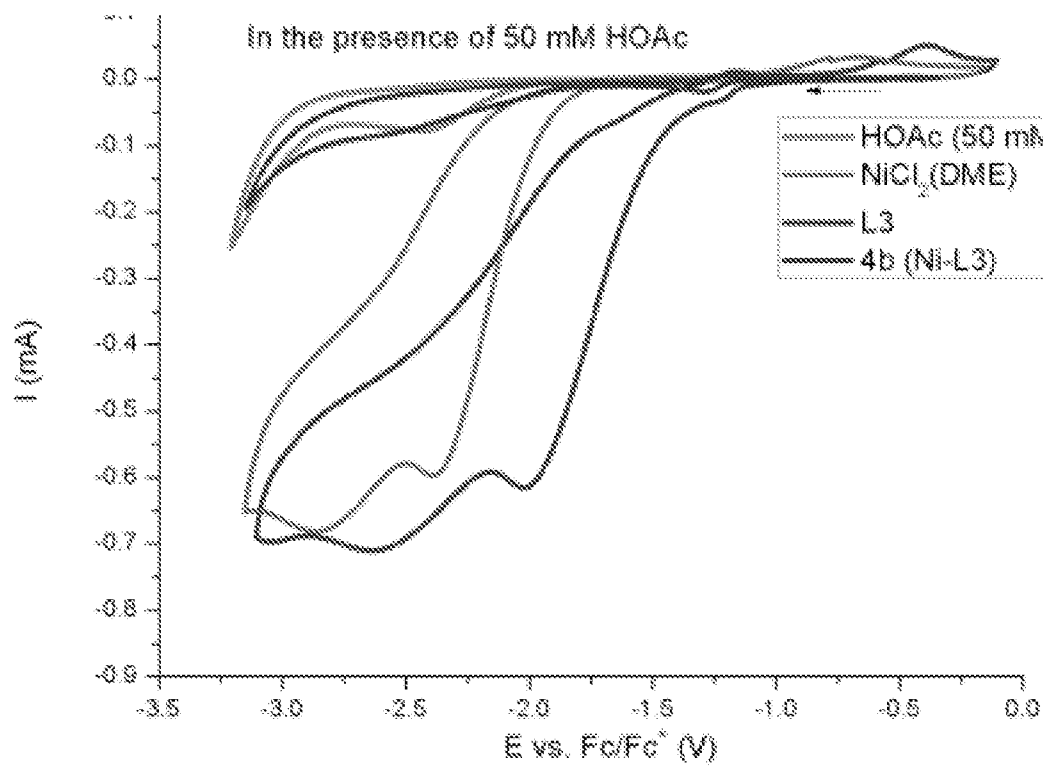


FIG. 14

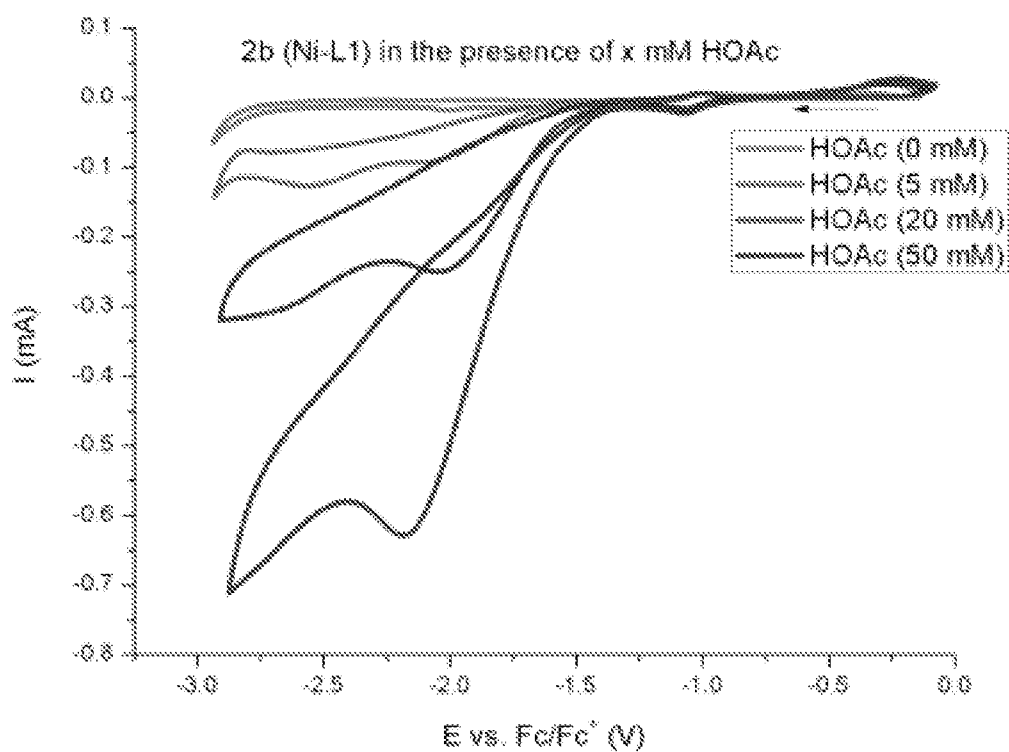


FIG. 15

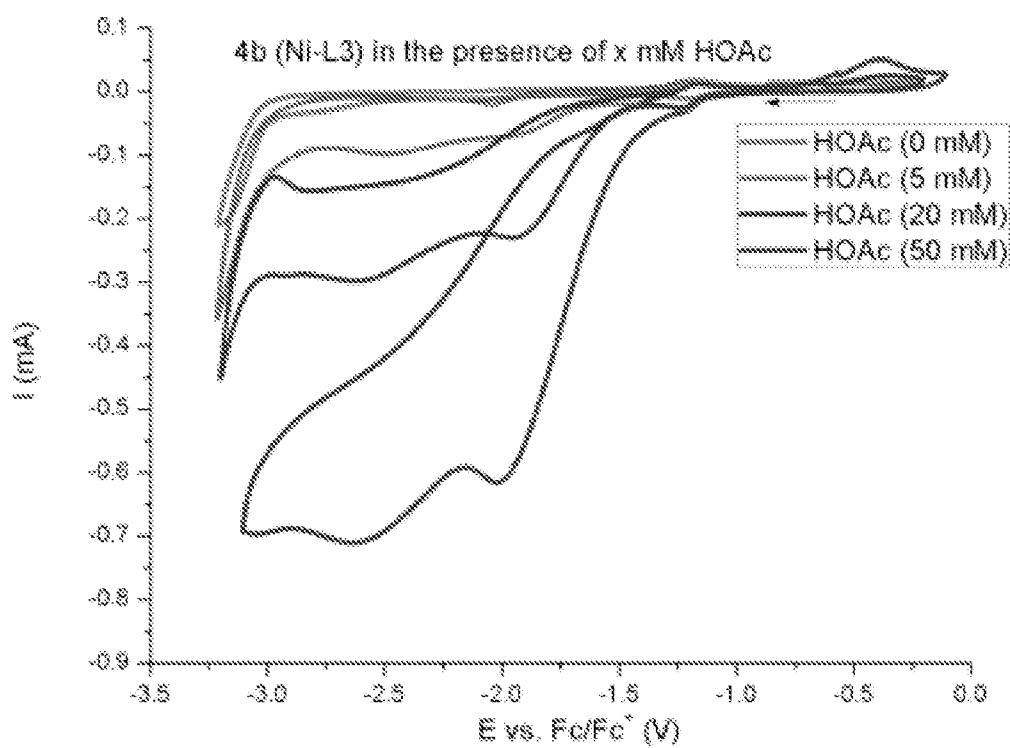


FIG. 16

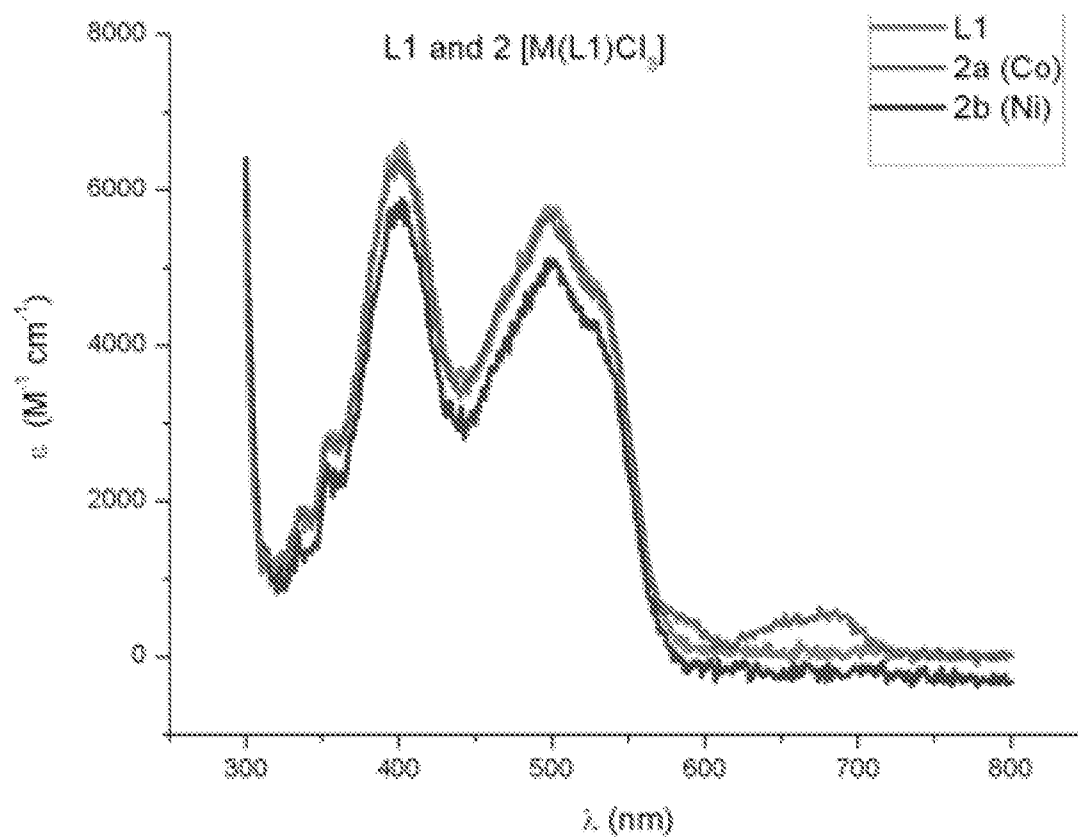


FIG. 17

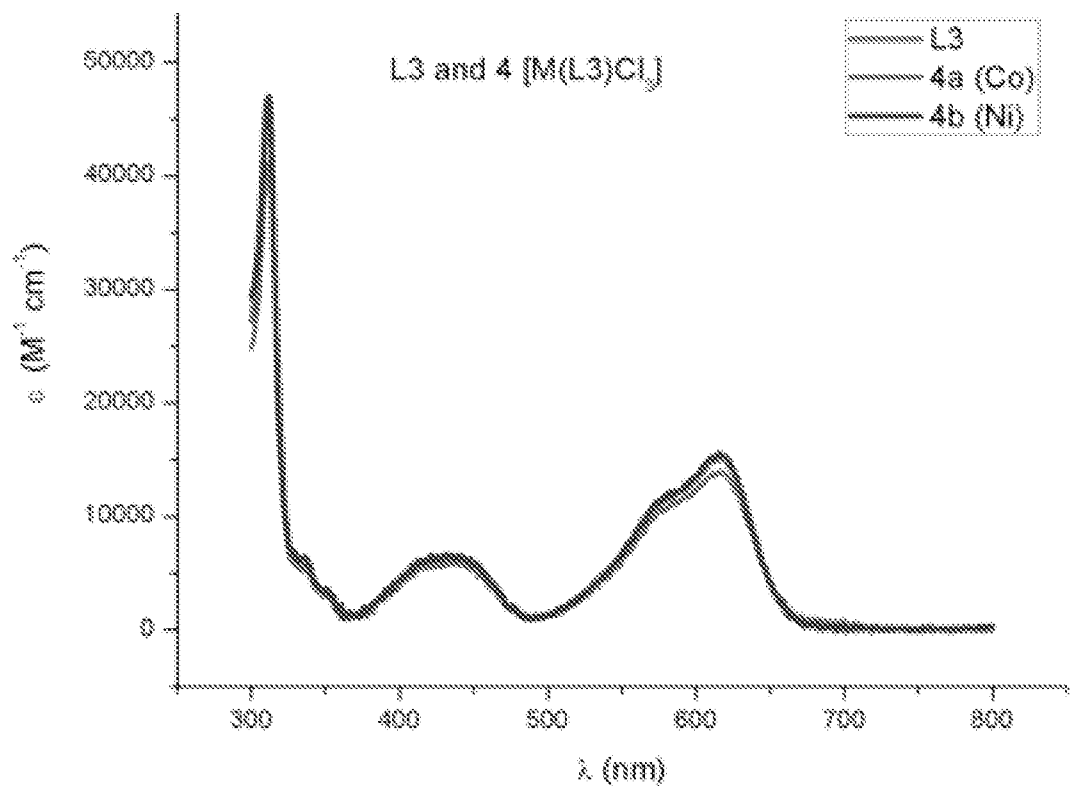


FIG. 18

Compound	λ (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)
L1	402/ 498/ 533	6597/ 5789/ 4669
2a	400/ 501/ 533	6367/ 5668/ 4610
2b	402/ 498/ 533	5880/ 5116/ 4062
L3	426/ 582/ 618	6488/ 11648/ 15226
4a	431/ 583/ 617	6133/ 11007/ 13960
4b	432/ 583/ 616	6677/ 12214/ 15685

FIG. 19

PC	$E_{0,0}$ (eV) ^a	$E_{1/2}$ (C ⁺⁺ /C ⁺) (V) ^b	$E_{1/2}$ (C ⁺ /C [·]) (V) ^b	$E_{1/2}$ (C ⁺⁺ /C ^{++·}) (V) ^c	$E_{1/2}$ (C [·] /C ^{·-}) (V) ^c	excited state lifetime τ (ns) ^d	absorption λ_{max} (nm)	emission λ_{max} (nm)
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3 1.93 +1.32 -0.78 -0.61 +1.15 5.5 616 667

^a Measured in MeCN (10⁻⁵ M). ^b Determined by cyclic voltammetry in MeCN versus SCE. See ref 9.

^c Excited state potentials were estimated from ground state redox potentials and the midpoint of the absorption and emission maxima. ^d Excitation at 470 nm. See ref 8.

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 21/15961

A. CLASSIFICATION OF SUBJECT MATTER

IPC - C08F 110/02; C08F 110/06; C08F 10/00 (2021.01)

CPC - C08F 10/00; C08F 110/02; C08F 110/06; C08F 4/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KRAEUTLER et al. "Direct Observation of Radical Intermediates in the Photo-Kolbe Reaction-Heterogeneous Photocatalytic Radical Formation by Electron Spin Resonance", J. Am. Chem. Soc. 1978. Vol. 100(15), pp 4903-4905, especially: pg 4903, col 2, para 1; pg 4904, col 1, para 2; pg 4904, col 1, para 3; pg 4904, col 2, para 2; pg 4905, col 1, para 2.	1,10,17-18,24
A	ROMERO et al. "Radicals in natural product synthesis", Chem. Soc. Rev. 2018. Vol. 47, pp 7851-7866, especially: pg 1, col 1, para 1; pg 1, Scheme 1, formula 4.	1,10,17-18,24
A	SORENSEN et al. "Synthesis and Structures of N-Alkyl-1,13-dimethoxychromeno-[2,3,4-kl]acridinium Salts: The Missing Azaoxa[4]helicenium", Chem. Eur. J. 2014. Vol. 20, pp 6391-6400, especially: pg 6392, Scheme 1, formula 3+, a.	1,10,17-18,24

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

17 May 2021

Date of mailing of the international search report

JUN 03 2021

Name and mailing address of the ISA/US

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US 21/15961

-BOX III - LACK OF UNITY-

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I+: Claims 1-18, 24-27, 31-35, and 37-57 directed to a compound or a solid substrate or a photocatalyst composition having a surface comprising a moiety of the formula I, wherein said moiety of formula I is a radical, a cation, or a radical dication. The compound of Formula I will be searched to the extent that it encompasses the first species of claim 1, wherein said moiety of formula I is a radical, wherein R1a, R1b, R1c, R1d, R2a, R2b, R2c, R2d, R3a, R3b, R3c and R3d are H; Y1, Y2 and Y3 are H; provided when said Formula I is a cation then (i) when R2a and R3d together form -X1-; R1a and R2d together form -X2-; and R1d and R3a together form -X3-, then no more than one of X1, X2, and X3 is O; (ii) when R2a and R3d together form -X1-, and R1a and R2d together does not form -X2-; and R1d and R3a together does not form -X3-, then at least one of R1a, R1b, R1c, R1d, or Y1 is not H, halogen, or C1-C12 alkyl; (iii) at least one of (a) R2a and R3d together form -X1-; (b) R1a and R2d together form -X2-; or (c) R1d and R3a together form -X3-; and (iv) when R2a and R3d together form -X1-; R1a and R2d together form -X2-; and R1d and R3a together form -X3-, then none of X1, X2, and X3 is NR4a. It is believed that claims 1, 10, 17-18 and 24 encompass this first named invention, and thus these claims will be searched without fee to the extent that they encompass the first species of claim 1. Applicant is invited to elect additional compounds of Formula I, wherein each additional compound elected will require one additional invention fee. Applicants must specify the claims that encompass any additionally elected compound. Applicants must further indicate, if applicable, the claims which encompass the first named invention, if different than what was indicated above for this group. Failure to clearly identify how any paid additional invention fees are to be applied to the "+" group(s) will result in only the first claimed invention to be searched. Additionally, an exemplary election wherein different actual variables are selected is suggested. An exemplary election would be a compound of claim 1, wherein said moiety of formula I is a radical, wherein R1a is halide; R1b, R1c, R1d, R2a, R2b, R2c, R2d, R3a, R3b, R3c and R3d are H; Y1, Y2 and Y3 are H; provided when said Formula I is a cation then (i) when R2a and R3d together form -X1-; R1a and R2d together form -X2-; and R1d and R3a together form -X3-, then no more than one of X1, X2, and X3 is O; (ii) when R2a and R3d together form -X1-, and R1a and R2d together does not form -X2-; and R1d and R3a together does not form -X3-, then at least one of R1a, R1b, R1c, R1d, or Y1 is not H, halogen, or C1-C12 alkyl; (iii) at least one of (a) R2a and R3d together form -X1-; (b) R1a and R2d together form -X2-; or (c) R1d and R3a together form -X3-; and (iv) when R2a and R3d together form -X1-; R1a and R2d together form -X2-; and R1d and R3a together form -X3-, then none of X1, X2, and X3 is Ncontinued in R4a (i.e. claims 1, 17-18 and 24).

Group II: Claims 19-23, directed to a method for producing an oxidative product or a reductive coupling product from a reaction substrate, said method comprising: contacting said reaction substrate with an oxidizing reagent, and a photocatalytic compound of claim 1 to produce a reaction mixture; and irradiating said reaction mixture with an electromagnetic radiation having a wavelength of 390 nm or greater under conditions sufficient to produce said oxidative product from said reaction substrate.

Group III: Claims 28-30, directed to a method for conducting a photocatalytic reaction, said method comprising contacting two or more reagents in the presence of a photocatalyst compound under conditions sufficient to produce a photooxidative product or a photoreductive product, wherein said photocatalyst compound comprises a moiety of the formula I.

The groups of inventions listed above do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features:

Group I+ includes the technical feature of a unique compound of Formula I, which is not required by any other invention of Group I+.

Group II requires a method for producing an oxidative product or a reductive coupling product from a reaction substrate, which is not required by Group I+ or Group III.

Group III requires a method for conducting a photocatalytic reaction, said method comprising contacting two or more reagents in the presence of a photocatalyst compound under conditions sufficient to produce a photooxidative product or a photoreductive product, which is not required by Group I+ or Group II.

Common technical features:

The inventions of Groups I+ and Group III share the technical feature of a compound having the structure of Formula I wherein said moiety of formula I is a radical, a cation, or a radical dication.

These shared technical features, however, do not provide a contribution over the prior art, as being anticipated by the article entitled "Synthesis and Structures of N-Alkyl-1,13-dimethoxychromeno-[2,3,4-kl]acridinium Salts: The Missing Azaoxa[4]helicinium" by Sorensen et al. (hereinafter 'SORENSEN').

Sorensen teaches a compound having the structure of Formula I wherein said moiety of formula I is a cation; wherein R1b, R1c, R2b, R2c, R3b, R3c, Y1, Y2 and Y3 are H; R1a and R2d together form -X2-; R1d and R3a together form -X3-; R2a and R3d are both C1 alkoxy; X2 is O; X3 is NR4a, R4a is C1 alkyl (pg 6392, Scheme 1, formula 3+,a).

As said compound was known in the art at the time of the invention, this cannot be considered a special technical feature that would otherwise unify the inventions of Group I+, Group II and Group III.

The inventions of Group I+, Group II and Group III thus lack unity under PCT Rule 13.

Note:

Claim 36 is unsearchable because it is a dependent claim and is not drafted in accordance with the second and third sentences of Rule 6.4(a).

-continued on next page-

INTERNATIONAL SEARCH REPORT

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—from previous page—

Claim 10 lacks clarity. Claim 10 is "the compound of claim 1, wherein Y, R1a, Rib, R2a, R2b, R3a, and R3b are H." However, Y does not seem to be in claim 1. For the purposes of the search and opinion, it was assumed that the intent of the applicant was that claim 10 should refer to Y1, so that claim 10 would actually read:

The compound of claim 1, wherein Y1, R1a, Rib, R2a, R2b, R3a, and R3b are H.

INTERNATIONAL SEARCH REPORT

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Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 36
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
(see extra sheet)

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1, 10, 17-18 and 24

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.