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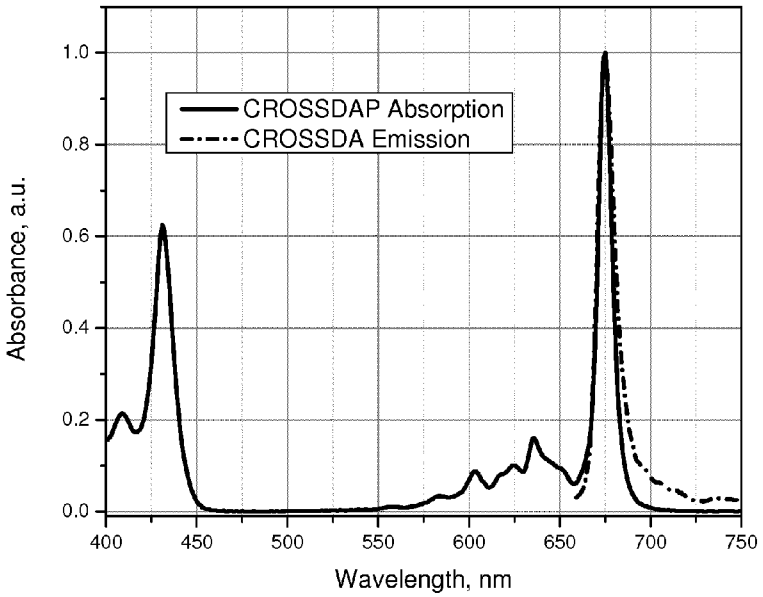

Figure 3

(57) Abstract: This invention relates to dye-sensitive light absorbing species and, more particularly, to trans-disubstituted benzodiazaporphyrins useful in dye-sensitive light absorbing applications especially active in the long wavelength spectrum range.

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TRANS-DISUBSTITUTED BENZODIAZAPORPHYRINS AS SENSITIZERS FOR SOLAR CELLS

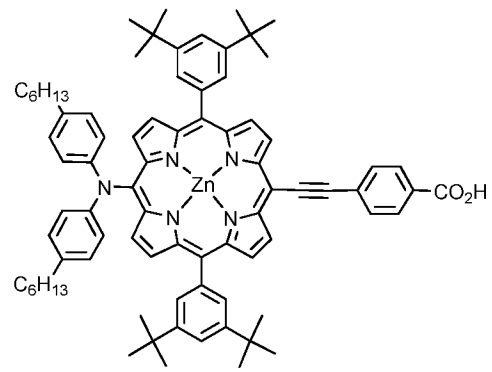
This invention relates to dye-sensitive light absorbing species and, more particularly, to *trans*-disubstituted benzodiazaporphyrins useful in dye-sensitive light absorbing applications especially active in the long wavelength spectrum range.

STATE OF THE ART

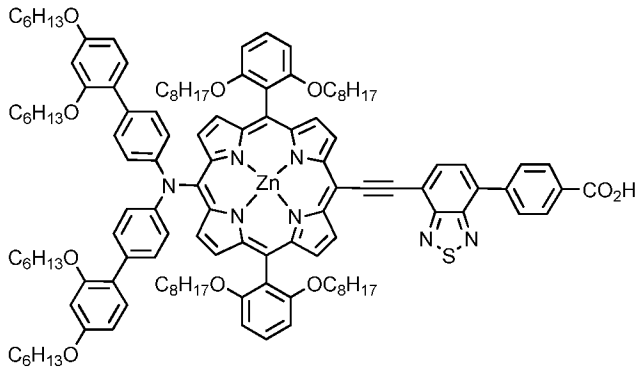
Dye-sensitized solar cells (DSSCs) and organic solar cells (OSCs) have the potential to provide photovoltaic energy at competitive price with a clean and sustainable technology. In the area of DSSCs, ruthenium polypyridine complexes have been the most efficient sensitizers for several decades (photoconversion efficiencies in the range of 10-11%), while in the OSC the development of small photoactive molecules is gaining an increase in attention.

Early 2000, in the field of DSSCs, new organic dyes were synthesized to get rid of the costly and noxious ruthenium element. It was discovered that push-pull systems, comprising a π-conjugated spacer functionalized by an electron donating group and an electron withdrawing group, are particularly efficient sensitizers in DSSCs.

More recently, zinc porphyrin sensitizers have attracted a strong interest in DSSCs because cells with such sensitizers attained the record efficiency of 13%.The most performing porphyrins are YD2 and SM315, as disclosed in Yella, A. et al., *Science*, **2011**, *334,* 629-634 and Mathew, S. et al., *Nat. Chem.*, **2014**, *6*, 242-247. YD2 and SM315 are push-pull systems, containing namely a diaryl amino unit as electron donating group and a benzoic acid or a benzothiadiazole unit as electron withdrawing group, as shown below.



YD2

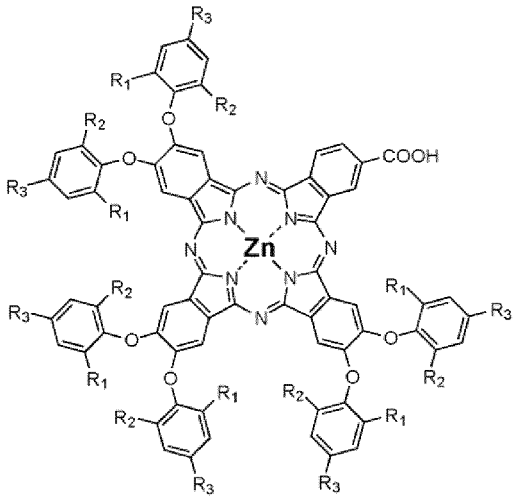


SM315

However, a strong drawback of porphyrin dyes is their weak absorbance both at around 450 nm, and above 750 nm where the incoming solar flux is still significant. Zinc porphyrin absorption spectrum features a strong absorption band around 420 nm (Soret band) and two weaker absorption bands between 500-600 nm (Q-bands) with an almost transparent region around 450-500 nm. This weak light harvesting efficiency in this region certainly limits the overall photovoltaic performances of this class of dyes.

Phthalocyanines are π-conjugated macrocycles related to porphyrins which have also been thoroughly investigated as sensitizers in DSSCs and OSCs. Today, the highest power conversion efficiency (PCE)

obtained with a phthalocyanine in DSSCs is 6.4% and can be obtained with PcS20 represented below, wherein R_1 and R_2 are butoxy and R_3 is H, as disclosed in Ikeuchi, T. et al., *Chem. Commun.*, **2014**, *50*, 1941-1943.



PcS20

A valuable property of phthalocyanines is their strong absorption band located around 670 nm, which enables to obtain a high photoactivity (IPCE around 80%) in a low energy region of the visible spectrum. On the other hand, the higher energy region (between 420-600 nm) is poorly exploited by phthalocyanine dyes owing to the low absorption coefficient in this region. Moreover, the preparation of *trans* disubtituted phtalocyanines is an extremely tedious and challenging synthetic task, which limits the possibility to develop push-pull dyes for solar cell applications.

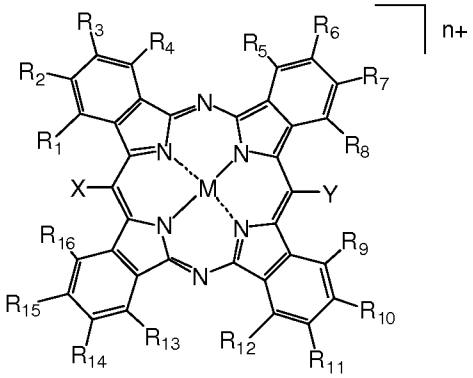
Benzodiazaporphyrins can be considered as hybrid dyes between porphyrins and phthalocyanines since two of the bridging *meso* positions are occupied by nitrogen like phthalocyanines, while the two other *meso* positions are regular methene moieties which can carry substituents. The two interesting and valuable features of benzodiazaporphyrins is first, the presence of an intense and long wavelength absorption band like phthalocyanines, and the possibility to envision the preparation of push-pull or quadrupolar systems by *trans* functionalization of the two adjacent carbon *meso* positions.

The straightforward and efficient synthesis of *trans* disubstituted benzodiazaporphyrins was recently disclosed in Andrianov, D. S. et al., *Chem. Commun.* **2014,** *50*, 7953-7955. However, the structures of the benzodiazaporphyrins disclosed in said reference are not suited for solar cell applications.

The Applicant has now found *trans* disubstituted benzodiazaporphyrins that are highly efficient dye sensitizers for solar cells, particularly for DSSCs or OSCs because they have a strong absorption band in the NIR region and can be used to produce solar cells with interesting power conversion efficiencies (PCEs).

SUMMARY OF THE INVENTION

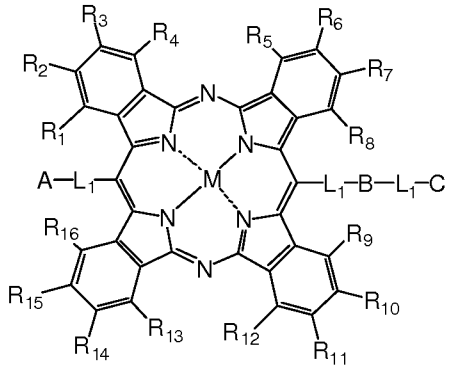
A first object of the present invention is a compound of general formula (I):



(I)

wherein R_1-R_{16}, X, Y and n are as defined herein.

Another object of the present invention is a dye-sensitized solar cell comprising an anode, a counter-electrode, a nanocrystalline semiconductor, a sensitizer and an electrolyte, wherein the sensitizer is a compound of general formula (II):

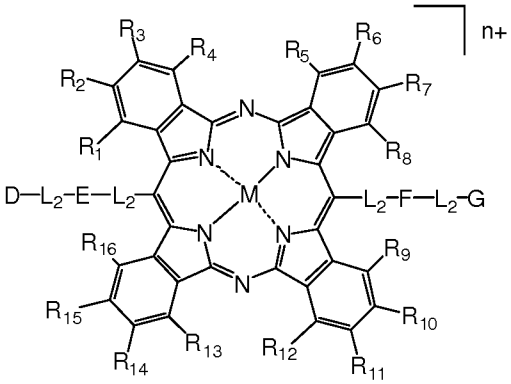


(II)

wherein R_1-R_{16}, A, B,C, L_1 and M are as defined herein.

Yet another object of the present invention is the use of a compound of general formula (II) as a sensitizer for a dye-sensitized solar cell.

Another object of the present invention is an organic solar cell comprising an anode, a cathode and a sensitizer, wherein said sensitizer is a compound of general formula (V):



(V)

wherein R_1-R_{16}, D, E,F, G, L_2, M and n are as defined herein.

Yet another object of the present invention is the use of a compound of general formula (V) as a sensitizer for an organic solar cell.

DESCRIPTION OF FIGURES

Figure 1 shows the synthetic route for the preparation of **CROSSDAP**.

Figure 2 shows the synthetic route for the preparation of **TPA-CROSSDAP**.

Figure 3 shows the electronic absorption (straight line) and emission spectra (dashed line) of **CROSSDAP** recorded in dimethylformamide.

Figure 4 shows the electronic absorption (straight line) and emission spectra (dashed line) of a precursor of **TPA-CROSSDAP** recorded in dichloromethane.

Figure 5 shows the current/voltage characteristics of a DSSC sensitized with **CROSSDAP** recorded in the dark (dashed line) and under AM 1.5 illumination (straight line).

Figure 6 shows the photoaction spectra (Incident photon-to-current efficiency (IPCE) as a function of the incident wavelength) of a DSSC sensitized with **CROSSDAP**.

DEFINITIONS

Unless mentioned otherwise, the groups and radicals listed for X, Y, R_1-R_{16}, A, B, C, D, E, F, G, L_1 and L_2 may be substituted or unsubstituted. By "substituted" it is meant that one of the hydrogen atoms of said group or radical is replaced with a substituent other than H. Examples of suitable substituents are halogen atoms, such as Cl, Br, I and F; and groups selected from alkyl, cycloalkyl, alkoxy, aryl, heteroaryl, cyano, amino, dialkylamino, diarylamino, triarylamino, dialkylarylamino, thioether, a carboxylic group, a sulfonic group.

The term "alkyl" means any monovalent radical of a linear or branched hydrocarbon chain comprising 1 to 18 carbon atoms. The expression "C_1-C_6 alkyl" represents an alkyl having 1 to 6 carbon atoms. Examples of alkyl groups include methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *s*-butyl or *t*-butyl, *n*-pentyl, *n*-hexyl, *n*-heptyl, *n*-octyl, 2-ethylhexyl, *n*-nonyl, 3,5,5-trimethylhexyl, *n*-decyl, *n*-undecyl, *n*-dodecyl or *n*-octadecyl. Preferred alkyls are methyl, ethyl, isopropyl and *t*-butyl.

The term "alkoxy" means an -O-alkyl group wherein the term alkyl is as defined above. The expression "C_1-C_6 alkoxy" represents an alkoxy having 1 to 6 carbon atoms. Examples of alkoxy groups include methoxy, ethoxy, *n*-propoxy, *i*-propoxy, *n*-butoxy, *i*-butoxy, *s*-butoxy or *t*-butoxy, *n*-pentoxy, *n*-hexoxy. Preferred alkoxys are methoxy, ethoxy, isopropoxy and *t*-butoxy.

The term "aryl" means any monovalent radical of an aromatic hydrocarbon ring comprising 6 to 12 carbon atoms. The expression "C_6-aryl" represents an aryl having 6 carbon atoms. Examples of aryls include phenyl, naphthyl and biphenyl. Preferred aryls are phenyl and naphthyl.

The term "phenoxy" means an -O-phenyl group.

The term “thioether” means an -S-alkyl group or -S-aryl group wherein the terms alkyl and aryl are as defined above. The expression “C_1-C_6 thioether” represents a thioether having 1 to 6 carbon atoms. Examples of thioether groups include thiomethyl and thiophenyl (-S-Ph).

The term “heteroaryl” means any monovalent radical of an aromatic 5 to 6 membered monocyclic ring or 9 to 20 membered bicyclic ring which can comprise 1, 2 or 3 heteroatoms selected from nitrogen, oxygen and/or sulphur. The expression “5- to 10-membered heteroaryl” means a heteroaryl with 5 to 10 ring atoms. Examples of heteroaryls include furyl, pyridinyl, pyridazinyl, pyrimidinyl, pyrazinyl, thienyl, isoxazolyl, oxazolyl, oxadiazolyl, imidazolyl, pyrrolyl, pyrazolyl, triazolyl, tetrazolyl, thiazolyl, isothiazolyl, thiadiazolyl, benzoimidazolyl, indolyl, indanyl, indazolyl, benzothiazolyl, benzoisothiazolyl, benzoxazolyl, benzoisoxazolyl, benzothiadiazolyl, benzotriazolyl, quinolinyl, isoquinolinyl, a monovalent pyridinium radical, a monovalent diketopyrrolopyrrole radical and a monovalent isoindigo radical. Preferred heteroaryls are thienyl, benzothiadiazolyl, benzotriazolyl, pyridinyl, triazolyl, a monovalent pyridinium radical, a monovalent diketopyrrolopyrrole radical and a monovalent isoindigo radical.

When the suffixes "ene" or "diyl" are used in conjunction with an alkyl, aryl or heteroaryl group, this means that the alkyl, aryl or heteroaryl group defined above is a divalent radical, i.e. it has two points of attachment to other groups.

The term “cycloalkyl” means a non-aromatic cyclic hydrocarbon chain comprising 5 to 7 carbon atoms.

The term “alkendiyl” means any divalent radical of a hydrocarbon chain comprising 2 carbon atoms and 1 carbon-carbon double bond or 4 carbon atoms and two conjugated carbon-carbon double bonds or 6 carbon atoms and three conjugated carbon-carbon double bonds.

The term “alkyndiyl” means any divalent radical of a hydrocarbon chain comprising 2 carbon atoms and 1 triple carbon-carbon bond or 4 carbon atoms and two conjugated triple carbon-carbon bonds or 6 carbon atoms and three conjugated triple carbon-carbon bonds.

The term “amino” means a $–NH_2$ group.

The term “dialkyl amino” means an amino group wherein each hydrogen has been replaced with an alkyl group.

The term “diaryl amino” means an amino group wherein each hydrogen has been replaced with an aryl group.

The term “triaryl amino” means an aryl group wherein one H has been substituted by a diaryl amino group.

The term “dialkylaryl amino” means an aryl group wherein one H has been substituted by a dialkyl amino group.

The term “oligothienyl” means a monovalent radical of an oligomer of thiophene monomers linked together in positions 2 and 5 by a single bond.

The term “carboxylic group” means a group of general formula $-COOR_c$ wherein R_c is H, a metallic cation or an alkyl group as defined above.

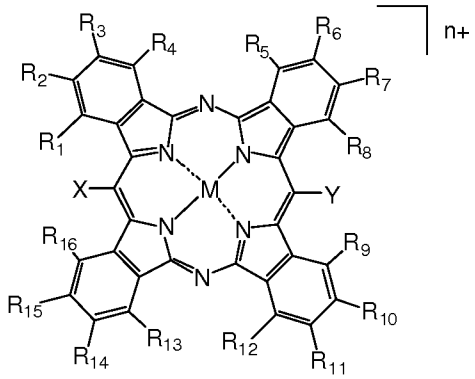
The term "sulfonic group" means a group of general formula $-S(=O)_2OR_d$ wherein R_d is H, a metallic cation or an alkyl group as defined above.

DETAILED DESCRIPTION OF THE INVENTION

Sensitizer Compounds

The compounds of the present invention have a central benzodiazaporphyrin core onto which are branched two groups X and Y in *trans* position.

As such, compounds of the present invention are represented by general formula (I):



(I)

wherein

R_1-R_{16} are each independently selected from H, alkyl and aryl; or two adjacent R_1-R_{16} groups optionally form, together with the carbon atoms to which they are attached, a ring selected from cycloalkyl and aryl, and the remaining R_1-R_{16} groups are each independently selected from H, alkyl and aryl;

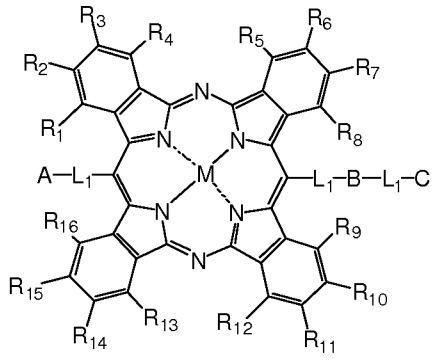
X and Y, similar or different, each comprise at least one group selected from H, alkyl, aryl, arylene, heteroaryl, heteroarylene, alkendiyl, alkyndiyl, dialkyl amino, diaryl amino, triaryl amino and dialkylaryl amino;

M represents 2 hydrogen atoms; or M is selected from Zn, Mg, Al, Si, Cu, Ru, Au, Sn, Pd, Pt, Ir and Ni; or M is selected from $Sn(IV)(L)_2$, $P(V)(L)_2$, Au(III), Ru(II)LL', Ir(III) wherein L and L' represent axial ligands selected from halogeno, hydroxo, alkoxide, carboxylato, CO, and pyridine;

n is 0 or 1;

with the proviso that X and Y are not both H, or both alkyl or both aryl.

In a first embodiment, compounds of the present invention correspond to general formula (II):



(II)

wherein

R_1-R_{16} are each independently selected from H, alkyl and aryl; or two adjacent R_1-R_{16} groups optionally form, together with the carbon atoms to which they are attached, a ring selected from cycloalkyl and aryl, and the remaining R_1-R_{16} groups are each independently selected from H, alkyl and aryl;

A is selected from H, alkyl, aryl, dialkyl amino, diaryl amino, triaryl amino, dialkylaryl amino, thienyl, oligothienyl, and combinations thereof;

B is selected from arylene, heteroarylene, alkendiyl, alkyndiyl and combinations thereof;

C is selected from $-COOR_a$, $-COO^-$, $-PO_3H_2$, $-PO(OH)R_b$, $-CH=C(COOH)_2$, $-CH=C(CN)(COOH)$, $-Si(OR_b)_3$, and $-C(O)-CH_2-C(O)-CH_3$, wherein R_a is H, alkyl, amino, dialkylamino, diaryl amino or $-C(O)-R_b$ and wherein R_b is alkyl;

L_1 are each independently selected from a single bond, $-(C\equiv C)_m-$, and $-(CH=CH)_o-$, wherein m and o are integers independently equal to 1, 2 or 3;

M represents 2 hydrogen atoms; or M is selected from Zn, Mg, Al, Si, Cu, Ru, Au, Sn, Pd, Pt, Ir and Ni.

In particular, R_1, R_4, R_5, R_8, R_9, R_{12}, R_{13} and R_{16} may be H; and R_2 with R_3; R_6 with R_7; R_{10} with R_{11}; and R_{14} with R_{15}; may, together with the carbon atoms to which they are attached, form a ring selected from cycloalkyl and aryl, more particularly a ring selected from C_6-cycloalkyl and C_6-aryl; even more particularly a ring selected from phenyl, cyclohexyl and cyclohexyl substituted with 1 to 4 methyl groups.

In particular, the R_1-R_{16} groups of the compounds of general formula (II) may each be independently selected from H, C_1-C_6-alkyl and C_6-aryl. More particularly, R_1-R_{16} may all be H; or R_1-R_{16} may each be independently selected from H and C_1-C_6-alkyl; or R_1-R_{16} may each be independently selected from H and C_6-aryl. Even more particularly, R_1-R_{16} may each be independently selected from H, methyl, ethyl, isopropyl, tert-butyl and hexyl; or R_1-R_{16} may each be independently selected from H and phenyl optionally substituted by one or two substituents independently selected from alkyl, alkoxy, phenoxy, dialkylamino, diphenylamino, thioether, carboxylic group and sulfonic group.

In particular, the A group of the compounds of general formula (II) may be selected from H, C_1-C_6-alkyl, C_6-aryl, di-C_1-C_6-alkyl amino, di-C_6-aryl amino, tri-C_6-aryl amino, di-C_1-C_6-alkyl-C_6-aryl amino, thienyl, oligothienyl, and combinations thereof. More particularly, A may be selected from phenyl, diphenylamino, triphenylamino wherein said groups may optionally be substituted by one or two substituents selected from alkyl, alkoxy and thioether. Even more particularly A may be di(*t*-butyl)phenyl, diphenylamino, bis(4-methoxyphenyl)amino, bis(4-hexylphenyl)amino, diphenylamino wherein each phenyl is substituted with a dihexyloxyphenyl, phenyl substituted with diphenylamino, phenyl substituted with bis(4-methoxyphenyl)amino, and phenyl substituted with diphenylamino wherein each phenyl group of the diphenylamino substituent are further substituted with a dihexyloxyphenyl.

In particular, the B group of the compounds of general formula (II) may be selected from C_6-arylene, 5- to 10-membered heteroarylene, -CH=CH-, $-C\equiv C-$, and combinations thereof. More particularly, B may be selected from phenylene, thiendiyl, benzothiadiazoldiyl, benzotriazoldiyl, pyridindiyl, triazoldiyl, -CH=CH-, $-C\equiv C-$, and combinations thereof. Even more particularly, B may be a 1,4-phenylene optionally substituted by one or two substituents selected from fluoro and cyano.

In particular, the C group of the compounds of general formula (II) may be selected from -COOH, $-PO_3H_2$, -CH=C(CN)(COOH), $-Si(OMe)_3$, $-Si(OEt)_3$ and $-C(O)-CH_2-C(O)-CH_3$. More particularly, C may be selected from -COOH and CH=C(CN)(COOH). Even more particularly, C may be -COOH.

In particular, the L_1 groups of the compounds of general formula (II) may each be independently selected from a single bond, -C≡C- and -CH=CH-. More particularly each L_1 may independently be selected from a single bond and -C≡C-. Even more particularly, each L_1 may be a single bond.

In particular, the M group of the compounds of general formula (II) may represent 2 hydrogen atoms or M may be selected from Zn, Mg, Al, Si, Cu, Ru and Ni. More particularly M may be selected from Zn, Mg and Cu. Even more particularly, M may be Zn.

As such, the compounds of the first embodiment of the present invention may correspond to general formula (II) wherein

R_1-R_{16} are each independently selected from H, C_1-C_6-alkyl and C_6-aryl;

A is selected from H, C_1-C_6-alkyl, C_6-aryl, di-C_1-C_6-alkyl amino, di-C_6-aryl amino, tri-C_6-aryl amino, di-C_1-C_6-alkyl-C_6-aryl amino, thienyl, oligothienyl, and combinations thereof;

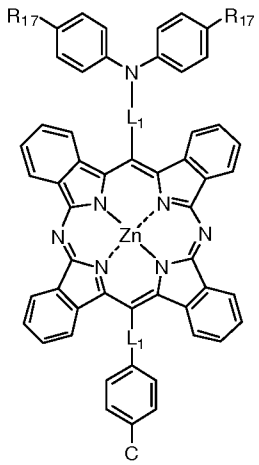
B is selected from C_6-arylene, 5- to 10-membered heteroarylene, -C≡C-, -CH=CH- and combinations thereof; in particular B is selected from phenylene, thiendiyl, benzothiadiazoldiyl, benzotriazoldiyl, pyridindiyl, triazoldiyl, -C≡C-, -CH=CH-, and combinations thereof;

C is selected from -COOH, $-PO_3H_2$, -CH=C(CN)(COOH), $-Si(OMe)_3$, $-Si(OEt)_3$ and $-C(O)-CH_2-C(O)-CH_3$;

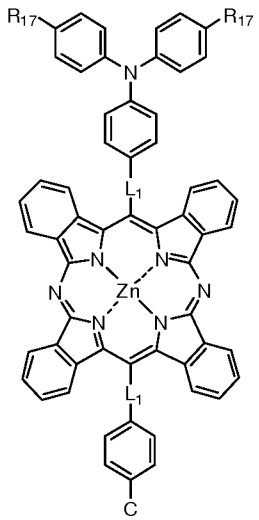
L_1 are each independently selected from a single bond, -C≡C- and -CH=CH-;

M represents 2 hydrogen atoms; or M is selected from Zn, Mg, Al, Si, Cu, Ru and Ni; in particular Zn, Mg and Cu; preferably Zn.

In a preferred embodiment, the compounds of general formula (II) may correspond to general formula (III) or (IV)



(III)



(IV)

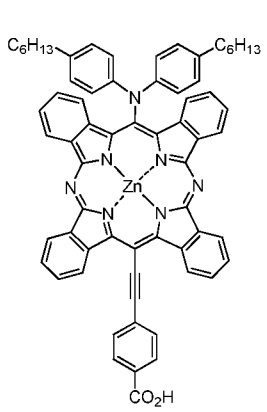
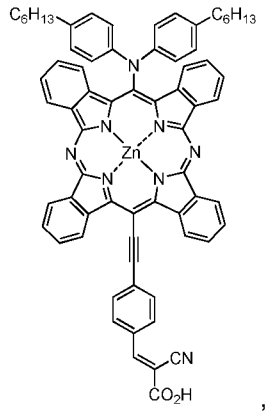
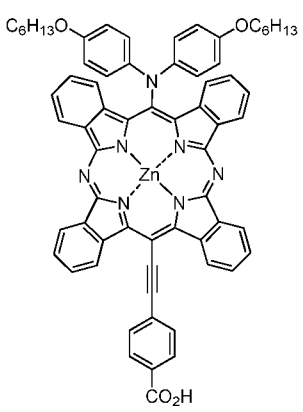
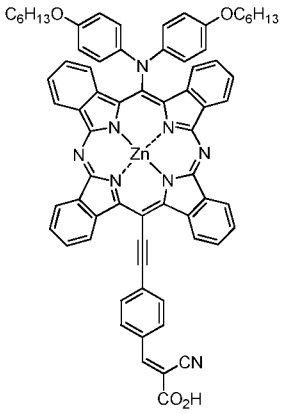
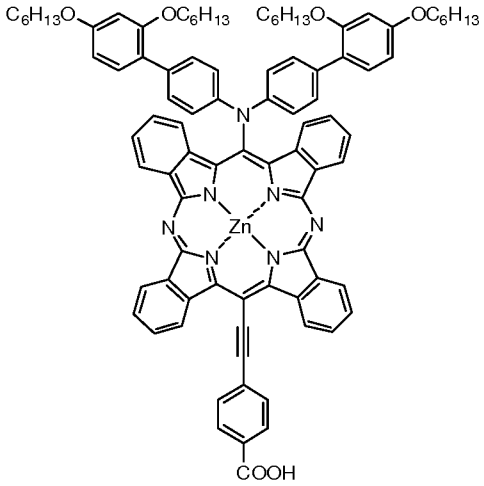
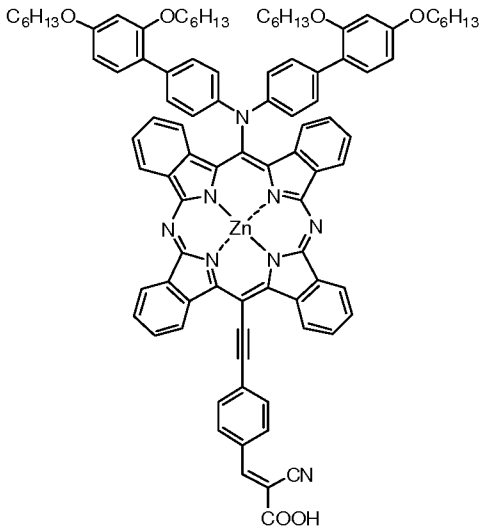
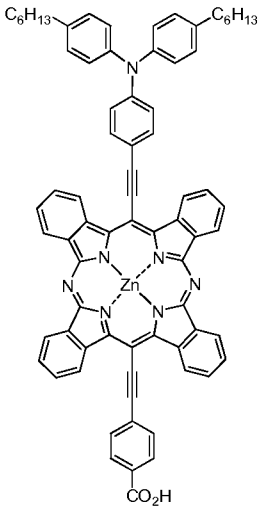
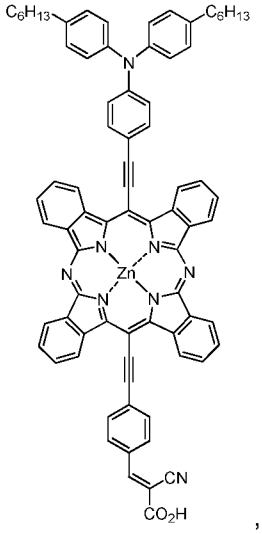
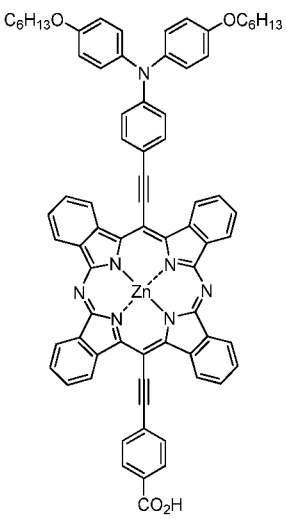
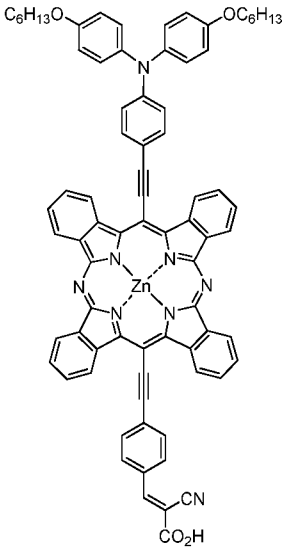
wherein

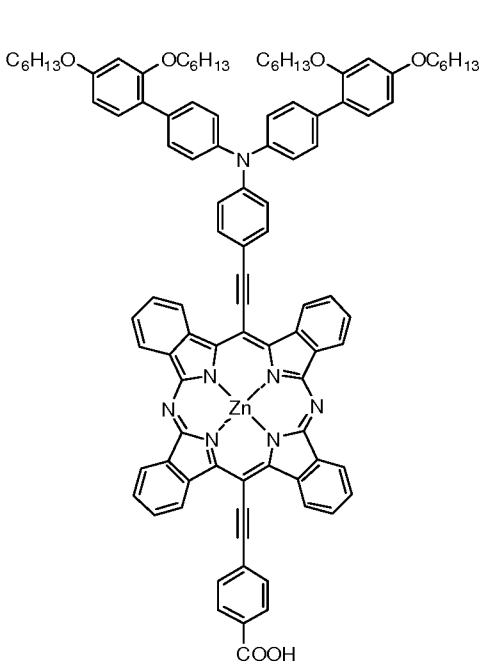
R_{17} is independently selected from H, alkoxy and phenyl substituted by one or two alkoxy groups;

L_1 is independently selected from single bond and -C≡C-; and

C is independently selected from -COOH and -CH=C(CN)(COOH).

More preferably, the compounds of formula (II), (III) and (IV) are selected from:



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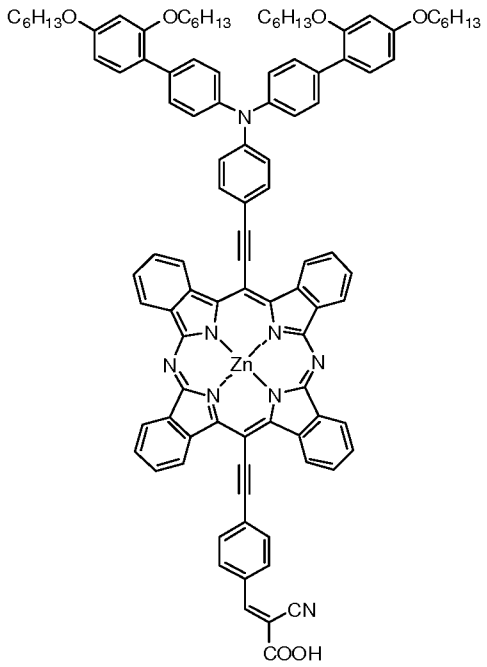

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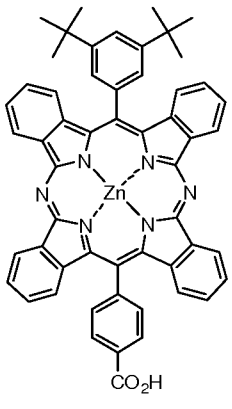
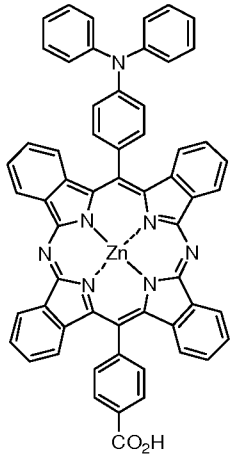
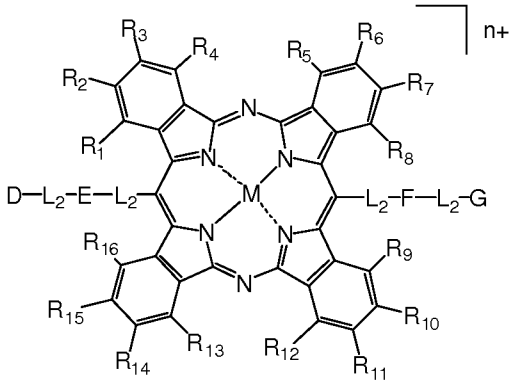




CROSSDAP , **TPA-CROSSDAP** .

In a second embodiment, compounds of the present invention correspond to general formula (V):



(V)

wherein

R_1-R_{16} are each independently selected from H, alkyl and aryl; or two adjacent R_1-R_{16} groups optionally form, together with the carbon atoms to which they are attached, a ring selected from cycloalkyl and aryl, and the remaining R_1-R_{16} groups are each independently selected from H, alkyl and aryl;

D and G are each independently selected from H, alkyl, aryl, heteroaryl, oligothienyl, dialkyl amino, diaryl amino, triaryl amino, dialkylaryl amino, alkenyl, and combinations thereof;

E and F are each independently selected from arylene, heteroarylene, alkendiyl, alkyndiyl, and combinations thereof;

L_2 are each independently selected from a single bond, $-(C\equiv C)_p-$ and $-(CR=CR)_q-$, wherein R is H or -CN and wherein p and q are integers independently equal to 1, 2 or 3;

M represents 2 hydrogen atoms; or M is selected from Zn, Mg, Al, Si, Cu, Ru, Au, Sn, Pd, Pt, Ir and Ni; or M is selected from $Sn(IV)(L)_2$, $P(V)(L)_2$, Au(III), Ru(II)LL', Ir(III) wherein L and L' represent axial ligands selected from halogeno, hydroxo, alkoxide, carboxylato, CO and pyridine; and

n is 0 or 1.

In a preferred embodiment, the compounds of the second embodiment of the present invention may correspond to general formula (V) wherein the sequence D-L_2-E-L_2- is identical to the sequence -L_2-F-L_2-G. Indeed, the synthesis of such compounds is easy and convergent.

In particular, R_1, R_4, R_5, R_8, R_9, R_{12}, R_{13} and R_{16} may be H; and R_2 with R_3; R_6 with R_7; R_{10} with R_{11}; and R_{14} with R_{15}; may, together with the carbon atoms to which they are attached, form a ring selected from cycloalkyl and aryl, more particularly a ring selected from C_6-cycloalkyl and C_6-aryl; even more particularly a ring selected from phenyl, cyclohexyl and cyclohexyl substituted with 1 to 4 methyl groups.

In particular, the R_1-R_{16} groups of the compounds of general formula (V) may each be independently selected from H, C_1-C_6-alkyl and C_6-aryl. More particularly, R_1-R_{16} may all be H; or R_1-R_{16} may each be independently selected from H and C_1-C_6-alkyl; or R_1-R_{16} may each be independently selected from H and C_6-aryl. Even more particularly, R_1-R_{16} may each be independently selected from H, methyl, ethyl, isopropyl, tert-butyl and hexyl; or R_1-R_{16} may each be independently selected from H and phenyl optionally substituted by one or two substituents selected from alkyl, alkoxy, phenoxy, dialkylamino, diphenylamino, thioether, carboxylic group and sulfonic group.

In particular, the D and G groups of the compounds of general formula (V) may each be independently selected from H, C_1-C_6-alkyl, C_6-aryl, 5- to 20-membered heteroaryl, oligothienyl, di-C_1-C_6-alkyl amino, di-C_6-aryl amino, tri-C_6-aryl amino, di-C_1-C_6-alkyl-C_6-aryl amino, alkenyl, and combinations thereof. More particularly, D and G may be independently selected from H, C_1-C_6-alkyl, C_6-aryl, di-C_1-C_6-alkyl amino, di-C_6-aryl amino, tri-C_6-aryl amino, di-C_1-C_6-alkyl-C_6-aryl amino, thienyl, oligothienyl, and combinations thereof; or D and G may be independently selected from H, C_6-aryl, 5- to 20-membered heteroaryl, alkenyl, and combinations thereof. Even more particularly, D and G may be independently selected from phenyl, diphenyl amino and triphenylamino; wherein said groups may optionally be substituted by one or two substituents selected from alkyl, alkoxy, phenoxy, dialkylamino, diphenylamino, thioether, carboxylic group and sulfonic group; or D and G may be independently selected from phenyl, thienyl optionally fused with an *N*-alkyl pyrrolidine-2,5-dione, benzothiadiazolyl optionally fused with a 2-alkyl triazole,

benzotriazolyl, pyridinyl, triazolyl, phthalimidyl, a pyridinium radical, a diketopyrrolopyrrole radical, an isoindigo radical, a *N*-alkyl-2,2′-bithiophene-3,3′-dicarboximide radical, dicyanovinyl, tricyanovinyl, and combinations thereof.

In particular, the E and F groups of the compounds of general formula (V) may be independently selected from C_6-arylene, 5- to 10-membered heteroarylene, -C≡C-, -CR=CR-, and combinations thereof, wherein R is H or -CN. More particularly, E and F may be independently selected from phenylene, thiendiyl, benzothiadiazoldiyl, benzotriazoldiyl, pyridindiyl, triazoldiyl, -C≡C-, -CH=CH-, and combinations thereof. Even more particularly, E and F may be selected from 1,4-phenylene and 2,5-thiendiyl.

In particular, the L_2 groups of the compounds of general formula (V) may each be independently selected from a single bond, -C≡C- and -CR=CR-, wherein R is H or -CN. More particularly, each L_2 may independently be selected from a single bond and -C≡C-. Even more particularly, each L_2 may be a single bond.

In particular, the M group of the compounds of general formula (V) may represent 2 hydrogen atoms; or M may be selected from Zn, Mg, Al, Si, Cu, Ru and Ni; or M may be selected from $Sn(IV)(L)_2$, $P(V)(L)_2$, Au(III), Ru(II)LL', Ir(III) wherein L and L' represent axial ligands selected from halogeno, for example Cl^-, Br^- or I^-; hydroxo (OH^-); alkoxide, for example $R'O^-$ wherein R' is alkyl or phenyl; carboxylato, for example $R'COO^-$ wherein R' is alkyl or phenyl; CO; and pyridine. More particularly, M may be selected from Zn, Mg and Cu; or M may be seleced from $Sn(IV)(L)_2$, $P(V)(L)_2$ and Au(III).

In particular, n is 0 or 1 and depends on the nature of M. As such, n is 1 when M is Au(III) or Ir(III). Otherwise, n is 0.

As such, the compounds of the second embodiment of the present invention may correspond to general formula (V) wherein

R_1-R_{16} are each independently selected from H, C_1-C_6-alkyl and C_6-aryl;

D and G are each independently selected from H, C_1-C_6-alkyl, C_6-aryl, di-C_1-C_6-alkyl amino, di-C_6-aryl amino, tri-C_6-aryl amino and di-C_1-C_6-alkyl-C_6-aryl amino, thienyl, oligothienyl, and combinations thereof; in particular phenyl, diphenyl amino and triphenylamino; wherein said groups may optionally be substituted by one or two substituents selected from alkyl, alkoxy, phenoxy, dialkylamino, diphenylamino, thioether, carboxylic group and sulfonic group;

E and F are each independently selected from C_6-arylene, 5- to 20-membered heteroarylene, -C≡C-, -CH=CH-, and combinations thereof; in particular phenylene, thiendiyl, benzothiadiazoldiyl, benzotriazoldiyl, pyridindiyl, triazoldiyl, -C≡C-, -CH=CH-, and combinations thereof;

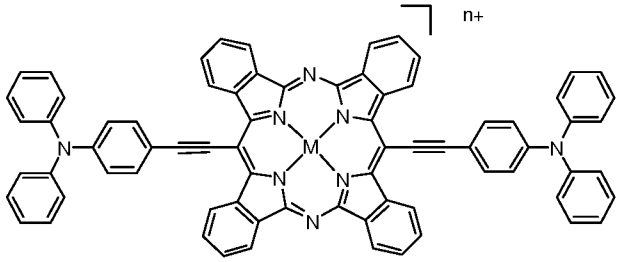
L_2 are each independently selected from a single bond, -C≡C- and -CR=CR-, wherein R is H or -CN;

M represents 2 hydrogen atoms; or M is selected from $Sn(IV)(L)_2$, $P(V)(L)_2$, Au(III), Ru(II)LL', Ir(III) wherein L and L' represent axial ligands selected from halogeno, for example Cl^-, Br^- or I^-; hydroxo (OH^-); alkoxide, for example $R'O^-$ wherein R' is alkyl or phenyl; carboxylato, for example $R'COO^-$ wherein R' is alkyl or phenyl; CO; and pyridine; in particular $Sn(IV)(L)_2$, $P(V)(L)_2$, Au(III);

n is 0 or 1.

Such compounds are considered as Donor-Acceptor-Donor compounds (D-A-D) wherein the central diazaporphyrin core is an electron acceptor and the D and G groups are electron donors.

In a particularly preferred embodiment of the present invention, the D-A-D compound of formula (V) is:

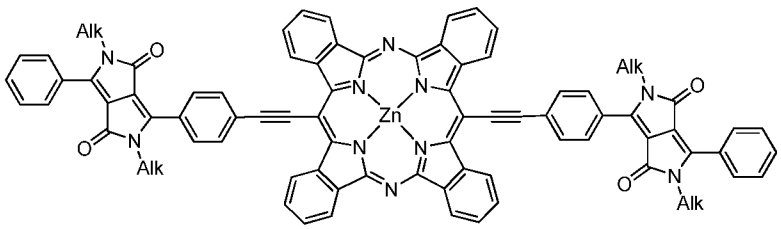


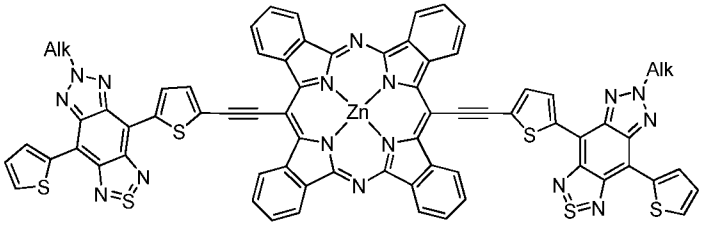
wherein M is Sn(IV)$(L)_2$ and n is 0, or M is P(V)$(L)_2$ and n is 0, or M is Au(III) and n is 1, or M is Ru(II)LL' and n is 0, or M is Ir(III) and n is 1;
wherein L is selected from Cl^-, Br^-, I^-, OH^-, $R'O^-$ and $R'COO^-$ with R' is alkyl or phenyl; and
wherein L' is selected from CO and pyridine.

Compounds of the second embodiment of the present invention may also correspond to general formula (V) wherein
R_1-R_{16} are each independently selected from H, C_1-C_6-alkyl and C_6-aryl;
D and G are each independently selected from H, C_6-aryl, 5- to 20-membered heteroaryl, alkenyl, and combinations thereof; in particular phenyl, thienyl optionally fused with an *N*-alkyl pyrrolidine-2,5-dione, benzothiadiazolyl optionally fused with a 2-alkyl triazole, benzotriazolyl, pyridinyl, triazolyl, phthalimidyl, a pyridinium radical, a diketopyrrolopyrrole radical, an isoindigo radical, a *N*-alkyl-2,2′-bithiophene-3,3′-dicarboximide radical, dicyanovinyl, tricyanovinyl, and combinations thereof;
E and F are each independently selected from C_6-arylene, 5- to 20-membered heteroarylene, -C≡C-, -CH=CH-, and combinations thereof; in particular phenylene, thiendiyl, benzothiadiazoldiyl, benzotriazoldiyl, pyridindiyl, triazoldiyl, -C≡C-, -CH=CH-, and combinations thereof;
L_2 are each independently selected from a single bond, -C≡C- and -CR=CR-, wherein R is H or -CN;
M represents 2 hydrogen atoms; or M is selected from Zn, Mg, Al, Si, Cu, Ru and Ni; in particular Zn, Mg and Cu; preferably Zn; and
n is 0.

Such compounds are considered as Acceptor-Donor-Acceptor compounds (A-D-A) wherein the central diazaporphyrin core is an electron donor and the D and G groups are electron acceptors.

In a particularly preferred embodiment of the present invention, the A-D-A compound of formula (V) is:





Compounds represented by formula (I) may be prepared according to various methods well known in the art. For example, said compounds may be prepared according to the synthetic route detailed in Figures 1 and 2.

Dye-sensitized solar cell (DSSC)

The present invention also relates to a dye-sensitized solar cell (DSSC) comprising a compound of general formula (II) as defined herein.

The DSSC of the present invention comprises an anode, a counter-electrode, a nanocrystalline semiconductor, a sensitizer and an electrolyte.

In a preferred embodiment, the DSSC comprises an anode onto which is deposited a nanocrystalline semiconductor. The sensitizer is adsorbed on said nanocrystalline semiconductor. The DSSC further comprise a counter-electrode onto which is spread the electrolyte. The anode and counter-electrode are joined and sealed together to prevent the electrolyte from leaking.

The anode of the DSSC of the present invention may be a transparent material, for example glass or a transparent polymer such as polyethylene terephthalate or polyethersulfone, doped with a semiconductor, for example indium tin oxide (ITO), tin oxide (SnO_2), fluoride-doped tin dioxide (FTO) and mixtures thereof. For example, the substrate may be a glass plate coated with one or two layers of semiconductor selected from IOT, SnO_2, FTO and mixtures thereof.

The nanocrystalline semiconductor of the DSSC of the present invention may comprise a metal oxide. In particular, said metal oxide may be selected from titanium dioxide, tin oxide, zinc oxide, tungsten oxide, zirconium oxide, gallium oxide, indium oxide, yttrium oxide, niobium oxide, tantalum oxide, vanadium oxide, and mixtures thereof. More particularly, said metal oxide may be selected from titanium dioxide, tin oxide, zinc oxide, indium oxide, and mixtures thereof, preferably titanium dioxide.

Said nanocrystalline semiconductor can be in the form of a nanostructured film. By "nanostructured film" it is meant a film of nanoparticles having a diameter from 1 to 500 nm. As such, in a particularly preferred embodiment, the nanocrystalline semiconductor is a nanostructured TiO_2 film.

For example, the nanocrystalline semiconductor can be a nanostructured TiO_2 film comprising TiO_2 nanoparticles that exhibit a diameter of 10 to 30 nm; in particular 15 to 25 nm; more particularly 20 nm. Said nanostructured TiO_2 film can exhibit a thickness of 7 to 25 µm; in particular 10 to 20 µm; more particularly 12 to 15 µm.

According to an embodiment, the nanocrystalline semiconductor of the DSSC can comprise a plurality of nanostructured TiO_2 layers. In particular, the DSSC can comprise a plurality of TiO_2 layers that do not exhibit the same particle diameter. More particularly, the DSSC can comprise a first layer of TiO_2 on the substrate and a second layer of TiO_2 on said first layer, wherein the diameter of the TiO_2 nanoparticles of the second layer is higher than the diameter of the TiO_2 nanoparticles of the first layer. Indeed, adding a second TiO_2 layer with larger particle size on the first TiO_2 layer can increase the solar efficiency of the DSSC because the second layer with larger particle size increases the light scattering of the semiconductor.

For example, the first TiO_2 layer can be a nanostructured TiO_2 film comprising TiO_2 nanoparticles that exhibit a diameter of 10 to 30 nm; in particular 15 to 25 nm; more particularly 20 nm; and the second TiO_2 layer can be a nanostructured TiO_2 film comprising TiO_2 nanoparticles that exhibit a diameter of 100 to 300 nm; in particular 150 to 250 nm; more particularly 200 nm.

The thickness of the second TiO_2 layer may be lower than the thickness of the first TiO_2 layer. For example, the first TiO_2 lay can exhibit a thickness of 7 to 25 µm, in particular 10 to 20 µm, more particularly 12 to 15 µm and the second TiO_2 layer can exhibit a thickness of 1 to 6 µm, in particular 2 to 5 µm, more particularly 3 to 4 µm.

Said nanocrystalline semiconductor can be formed on the anode by any means known in the art, for example by spraying metal oxide nanoparticles to form a film thereof directly on the anode; by electrically depositing a film of metal oxide nanoparticles on the anode; by applying a slurry or paste comprising metal oxide nanoparticles in a dispersion medium, for example with the "doctor-blade" technique, and drying, curing and/or sintering.

The sensitizer of the DSSC of the present invention is adsorbed onto the nanocrystalline semiconductor. Said sensitizer comprises a compound of general formula (II) as defined herein.

The sensitizer may further optionally comprise an additional organic dye or a metal complex dye. Indeed, combining the compound of general formula (II) with an additional dye can advantageously broaden the absorption spectra of the resulting DSSC. In particular, said metal complex dye may be selected from a ruthenium complex or quaternary salt thereof, a phthalocyanine, a porphyrin. Furthermore, said organic dye may include metal-free phthalocyanine, porphyrin, cyanine, merocyanine, oxonol, or triphenylmethane dye, methyne dye such as acrylate dyes described in European Patent Application n°1,311,001, xanthenes, azo, anthraquinone and perylene dye.

The sensitizer may further optionally comprise a co-adsorbate. Said co-adsorbate advantageously prevents aggregation of the compound of general formula (II) which results in an increase of the injection quantum yield. The co-adsorbate may be selected from deoxycholic acid, dehydrodeoxycholic acid, chenodeoxycholic acid, cholic acid methyl ester, cholic acid sodium, polyethyleneoxides, crown ethers, cyclodextrins, calixarenes, polyethyleneoxides, and mixtures thereof. In particular, said co-adsorbate may be chenodesoxycholic acid.

The sensitizer may be adsorbed on the nanocrystalline semiconductor by any known method in the art. For example, the sensitizer may be chemisorbed on the nanocrystalline semiconductor by immersing

said nanocrystalline semiconductor in a liquid comprising the sensitizer solubilized or dispersed in a suitable medium. Said medium may be selected from water, methanol, ethanol, toluene, acetonitrile, dichloromethane, dimethylsulfoxide, dimethylformamide, acetone, tert-butanol, and mixtures thereof. In particular, said medium may be a mixture of water and toluene. In case the sensitizer comprises a compound of general formula (II) and an additional organic dye or a metal complex dye, they may be sequentially absorbed on the nanocrystalline semiconductor, or mixed and absorbed conjunctively.

The counter-electrode of the DSSC of the present invention may comprise a material selected from platinum, poly(3,4-ethylenedioxythiophene) (PEDOT) and glassy carbon (GC).

The electrolyte may comprise an organic solvent and a redox couple. In particular, the solvent of the electrolyte may be selected from acetonitrile, propylene carbonate, ethylene carbonate, 3-methoxypropionitrile, methoxy acetonitrile, valeronitrile, ethylene glycol, propylene glycol, diethylene glycol, triéthylène glycol, butyrolactone, dimethoxyethane, dimethyl carbonate, 1,3-dioxolane, methylformate, 2-methyltetrahydrofurane, 3-methoxy-oxazolidin-2-one, sulforane, tetrahydrofurane, water, and mixtures thereof. In particular, said solvent may be acetonitrile.

The redox couple of the electrolyte may comprise a halide source and a halogen molecule, preferably an iodide source and iodine. The iodide source may be selected from an iodide metal salt, a tetraalkylammonium iodide, an imidazolium iodide, a pyridinium iodide, and mixtures thereof. In particular, said iodide source may be LiI, NaI, KI, CaI_2, MgI_2, CuI, tetramethylammonium iodide (TMAI), tetrabutylammonium iodide (TBAI), 1-methyl-3-propylimidazolium iodide, 1,2-dimethyl-3-butylimidazolinium iodide (DMBIM), and mixtures thereof. More particularly said halide source may be selected from LiI, 1,2-dimethyl-3-butylimidazolinium iodide, and mixtures thereof.

The electrolyte may further optionally comprise an additive selected from tert-butyl pyridine (TBP), bis(trifluoromethane)sulfonimide lithium (LiTFSI), and mixtures thereof.

Organic solar cell (OSC)

The present invention also relates to an organic solar cell (OSC) comprising a compound of general formula (V) as defined herein.

The OSC of the present invention comprises an anode, a cathode and a sensitizer.

In a preferred embodiment, the OSC comprises a layer of sensitizer sandwiched between the cathode and the anode.

The cathode of the OSC of the present invention may comprise a material selected from indium tin oxide (ITO), fluorine tin oxide (FTO), graphene, and mixtures thereof; said material optionally comprising a thin layer of selective hole extracting material such as, for example, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), molybdenum oxide (MoO_x), tungsten oxide (WO_x), nickel oxide (NiO_x) or vanadium oxide (V_2O_x), for direct solar cells.

The anode of the OSC of the present invention may comprise a material selected from Al, Ag, Cu, Au, and mixtures thereof, said material optionally comprising a thin layer of selective electron extracting

material such as bathocuproine or lithium fluoride (LiF) for direct cells or ITO or FTO transparent conducting electrode coated with a layer of TiO_x or ZnO for inverted solar cells.

The sensitizer of the OSC of the present invention comprises a compound of general formula (V) as defined herein.

The sensitizer may further optionally comprise an additional organic dye or a metal complex dye. Indeed, combining the compound of general formula (II) with an additional dye can advantageously broaden the absorption spectra of the resulting OSC. In particular, said metal complex dye may be selected from a ruthenium complex or quaternary salt thereof, a phthalocyanine, a porphyrin. Furthermore, said organic dye may include metal-free phthalocyanine, porphyrin, cyanine, merocyanine, oxonol, or triphenylmethane dye, methyne dye such as acrylate dyes described in European Patent Application EP 1,311,001, xanthenes, azo, anthraquinone, perylene dye (as described, for example by Nazeeruddin M. K., in Journal of the American Chemical Society (1993), Vol. 115, p. 6382-6390) or a triphenylamine based dye such as D35 ((E)-3-(5-(4-(bis(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)amino)phenyl)thiophen-2-yl)-2-cyanoacrylic acid).

The sensitizer may further optionally comprise a co-adsorbate. Said co-adsorbate advantageously prevents aggregation of the compound of general formula (II) which results in an increase of the injection quantum yield. The co-adsorbate may be selected from deoxycholic acid, dehydrodeoxycholic acid, chenodeoxycholic acid, cholic acid methyl ester, cholic acid sodium, polyethyleneoxides, crown ethers, cyclodextrins, calixarenes, polyethyleneoxides, and mixtures thereof. In particular, said co-adsorbate may be chenodesoxycholic acid.

The OSC may be made by coating the anode or the cathode with the sensitizer, for example by spin-coating, and by combining the anode and cathode.

Use of sensitizers in solar cells

The compounds of general formula (I) may be used in solar cells.

In particular, the compounds of general formula (II) may be used as a sensitizer in a dye-sensitized solar cell as disclosed herein.

In another embodiment, the compounds of general formula (V) may be used as a sensitizer in an organic solar cell as disclosed herein.

This invention will be further illustrated by the following non-limiting examples which are given for illustrative purposes only and should not restrict the scope of the appended claims.

EXAMPLES

Example 1: Synthesis of CROSSDAP

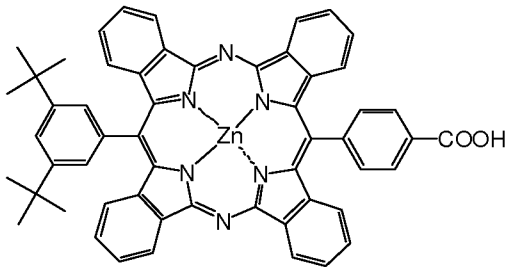


Figure 1 shows the synthetic route for the preparation of **CROSSDAP**.

The starting dihydroisoindole *tert*-butyl ester **1** was prepared according to the procedure described in Cheprakov, A.V. and M.A. Filatov, *The dihydroisoindole approach to linearly annelated π-extended porphyrins*. Journal of Porphyrins and Phthalocyanines, 2009. **13**(03): p. 291-303.

General procedure for preparation of *meso*-aryl substituted dibenzodipyrromethenes 4 and 9

Two equivalents of 4,7-dihydroisoindole **1** and one equivalent of a corresponding aryl aldehyde **2** or **7** were dissolved in dry dichloromethane. *Para*-toluene sulfonic acid (TsOH) (0.1 equivalent) and tetrabutylammonium bromide (Bu_4NBr) (10 equivalents) were then added to the solution and stirred for 24 h at room temperature. Saturated aqueous $NaHCO_3$ was added to the solution and stirred vigorously for 10 min. The organic layer was separated, washed with water, dried and evaporated to afford an orange solid.

The solid residue was dissolved in toluene, 3 equivalents of 2,3-dichloro-5,6-dicyanoquinone (DDQ) was added and the solution was stirred for 2 hours at ambient temperature. 10% aqueous solution of Na_2SO_3 was added and stirred vigorously for 10 min. Most toluene was removed under reduced pressure, the residue was diluted by dichloromethane, organic layer was extracted, washed with water, dried and concentrated *in vacuo*. The residual solution was applied to a column silica gel column, eluted with dichloromethane, a deep-violet fraction was collected and solvent removed under reduced pressure.

***Meso*-(3,5-di-*tert*-butylphenyl)-dibenzodipyrromethene 4**:

Were used 0.4 g of 4,7-dihydroisoindole **1**, 0.2 g of 3,5-di-*tert*-butyl benzaldehyde **2** and 0.6 g of DDQ during the oxidation stage.

Yield 0.42 g (73%) of a dark solid.

M.p. 200°C with decomposition.

^{1}H NMR ($CDCl_3$, 400 MHz): 14.74 (br. s., 1H), 8.15 (d., J = 8.08 Hz, 2H), 7.24 (t., J = 7.43 Hz, 2H), 7.04 (t., J=7.43 Hz, 2H), 6.78 (br. s., 1H), 6.69 (br. s., 2H), 6.39 (d., J=8.08 Hz, 2H), 1.57 (s. 18H) 1.76 (s., 18H).

^{13}C NMR ($CDCl_3$): 161.63, 149.71, 147.87, 142.44, 141.33, 138.97, 135.64, 131.33, 125.67, 123.53, 122.70, 122.42, 107.56, 101.73, 81.10, 55.62, 27.82.

MALDI-TOF (1,8-bis(diphenylamino)-naphthalene , negative ion), *m/z* 631.54 $(M-H)^-$.

***Meso*-(4-methoxycarbonylphenyl)-dibenzodipyrromethene 9**:

Were used 0.5 g of a 4,7-dihydroisoindole **1**, 0.19 g of *p*-methoxycarbonyl benzaldehyde **7** and 0.75 g of DDQ at the oxidation stage.

Yield 0.58 g (87%) of a dark solid.

M.p. 147°C with decomposition.

^{1}H NMR ($CDCl_3$, 400 MHz): 14.79 (br. s., 1H), 8.36 (d., *J* = 8.08 Hz, 2H), 8.16 (d., *J* = 8.08 Hz, 2H), 7.66 (d., *J* = 8.08 Hz, 2H), 7.23 (t., *J* = 7.33 Hz, 2H), 6.97 (t., *J*=7.33 Hz, 2H), 6.09 (d., *J*=8.08 Hz, 2H), 4.08 (s., 3H) 1.78 (s., 18H).

^{13}C NMR ($CDCl_3$): 166.71, 161.00, 141.38, 139.56, 137.50, 135.48, 133.98, 131.38, 131.14, 130.68, 129.63, 126.93, 125.92, 123.07, 121.73, 82.55, 52.54, 28.39.

MALDI-TOF (1,8-bis(diphenylamino)-naphthalene , negative ion), *m/z* 577.86 $(M-H)^-$.

General procedure for preparation of azides 6 and 11:

Dipyrromethene **4** or **9** (0.35 g) was dissolved in trifluoroacetic acid (TFA), stirred for 30 min at room temperature and the solvent was evaporated. The corresponding dibenzodepirromethene acid **5** or **10** was precipitated from diethyl ether and dried.

Excess of thionyl chloride ($SOCl_2$) was added to the dry dibenzodipyrrin acid **5** or **10**, stirred for 30 min at 30°C and evaporated under reduced pressure. The solid residue was dissolved in dry dichloromethane and excess of tetrabutylammonium azide (Bu_4NN_3) was added to the solution. The mixture was stirred for 1 h, washed with water, dried and concentrated *in vacuo*. The residue was passed through a column with silica, collecting a blue fraction and evaporated to dryness.

Azide 6:

Yield 0.25 g (70%) of a dark solid.

M.p. 120°C with decomposition.

^{1}H NMR ($CDCl_3$, 400 MHz): 14.72 (s, 1H), 8.23 (d, *J*=8.08 Hz, 2H), 7.74 (t, *J*=1.77 Hz, 1H) 7.39 (d, *J*=1.77 Hz, 2H), 7.29 (ddd, *J*=7.53, 1.01 Hz, 2H), 7.01 (ddd, *J*=7.71, 1.01 Hz, 2H), 6.17 (d, *J*=8.34 Hz, 2H), 1.37 (s, 18H).

^{13}C NMR ($CDCl_3$) 166.2, 152.4, 138.1, 137.1, 135.9, 134.7, 131.9, 127.3, 126.9, 123.4, 122.7, 122.5, 35.2, 31.4.

MALDI-TOF (dithranol), *m/z* 514.3 $(M-2N_2)^+$, 515.3 $(MH-2N_2)^+$.

Azide 11:

Yield 0.25 g (65%) of a dark solid.

M.p. 120°C with decomposition.

MALDI-TOF (dithranol), *m/z* 460.2 $(M-2N_2)^+$, 461.2 $(MH-2N_2)^+$.

5,15-diaryl-10,20-diazaterabenzoporphrin 12:

An equimolar mixture of azide **11** (0.042 g) and **6** (0.053 g) was refluxed in DMF for 15 min. Dichloromethane was then added and the reaction mixture was washed with water and evaporated to dryness. Porphyrinoid **12** was isolated as an intermediate green fraction by column chromatography on silica.

Yield 0.012 g (15%) of a deep-green crystalline solid.

M.p >300°C.

^{1}H NMR ($CDCl_3$, 400 MHz): 9.69 (d., *J*=7.58 Hz, 2H), 9.62 (d., *J*=7.58 Hz, 2H), 8.59 (d., *J*=8.19 Hz, 2H), 8.20 (m., 4H), 8.14 (s., 1H), 8.05 (d., *J*=7.34 Hz, 2H), 7.93 (t., *J*=7.34 Hz, 2H), 7.73 (t., *J*=7.82 Hz, 2H), 7.60 (t., *J*=7.82 Hz, 2H), 7.29 (d., *J*=6.48 Hz, 2H), 7.00 (d., *J*=7.95 Hz, 2H), 7.24 (s., 3H), 1.62 (s., 18H), -1.25 (br. s., 1H), -1.37 (br. s., 1H).

MALDI-TOF (1,8-bis(diphenylamino)-naphthalene), *m/z* 834.72 $(M-H)^-$.

CROSSDAP:

The mixture of diaryldiazatetrabenzoporphyrin **12** (0.02 g) with excess of $Zn(OAc)_2$ dihydrate was refluxed in DMF for 2 h. The reaction mixture was diluted with dichloromethane, washed with water, dried and evaporated to dryness. The residue was dissolved in concentrated solution of potassium hydroxide in methanol and stirred for 30 min at room temperature. The reaction mixture was diluted by water, precipitate was centrifuged, washed by 0.5M HCl, water and centrifuged again to afford deep-green crystalline solid.

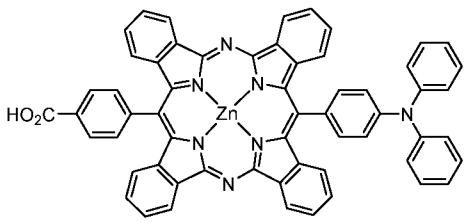
Yield 0.02 g (95%).

^{1}H NMR ($THFd^8$+5%CD_3OD, 300 MHz): 9.72 (d., *J*=6 Hz, 2H), 9.70 (d., *J*=6 Hz, 2H), 8.72 (br. s., 2H), 8.33 (d., *J*=6Hz, 2H), 8.18 (t., *J*=3 Hz, 1H), 8.11 (d., *J*=3 Hz, 2H), 7.97 (t., *J*=7.34 Hz, 4H), 7.63 (m., 4H), 7.21 (d., *J*=6 Hz, 2H), 1.55 (s., 18H).

MALDI-TOF (1,8-bis(diphenylamino)-naphthalene, negative ion), *m/z* 881.6 $(M-H)^-$.

High resolution ESI-MS: calculated for $C_{55}H_{42}N_6O_2Zn$ 882.26552, found 882.26392.

Example 2: Synthesis of TPA-CROSSDAP



TPA-CROSSDAP

Figure 2 shows the synthetic route for the preparation of **TPA-CROSSDAP**.

***Meso*-(4-diphenylamino-phenyl)-dibenzodipyrromethene 16:**

Dibenzodipyrromethene **16** was prepared following the general procedure for preparation of *meso*-aryl substituted dibenzodipyrromethenes **4** and **9** of example 1.

Were used 0.35 g of a dihydroisoindole **1**, 0.22 g of 4-diphenylaminobenzaldehyde **14** and 0.6 g of DDQ during the oxidation stage.

Yield 0.35 g (71%) of a dark solid.

M.p. 200°C with decomposition.

^{1}H NMR ($CDCl_3$, 400 MHz): 8.64 (d., *J*=8.07 Hz, 2H), 7.40-7.28 (m., 14H), 7.15 (m., 4H), 6.57 (d., *J*=8.19 Hz, 2H), 4.13 (s., 6H).

MALDI-TOF (1,8-bis(diphenylamino)-naphthalene, negative ion), *m/z* 602.44 $(M-H)^-$.

Azide 18:

Azide **18** was prepared following the general procedure for preparation of azides **6** and **11** of example 1.

Yield 0.25 g (70%) of a dark solid.

M.p. 120°C with decomposition.

MALDI-TOF (dithranol), *m/z* 569.3 $(M-2N_2)^+$, 570.3 $(MH-2N_2)^+$.

5,15-diaryl-10,20-diazatetrabenzoporphyrin 19:

An equimolar mixture of azides **18** (0.042 g) and **11** (0.053 g) was refluxed in propylene glycol for 20 min. Dichloromethane was then added and the reaction mixture was washed with water and evaporated to dryness. Porphyrinoid **19** was isolated as an intermediate green fraction by column chromatography on silica.

Yield 0.001 g (1%) of a deep-green crystalline solid.

M.p >250°C.

MALDI-TOF (1,8-bis(diphenylamino)-naphthalene), *m/z* 888.53 $(M-H)^-$.

TPA-CROSSDAP:

The mixture of diaryldiazatetrabenzoporphyrin **19** (0.004 g) with excess of $Zn(OAc)_2$ dihydrate was refluxed in DMF for 30 min. The reaction mixture was diluted with dichloromethane, washed with water, dried and evaporated to dryness. The residue was dissolved in concentrated solution of potassium hydroxide in methanol and stirred for 30 min at room temperature. The reaction mixture was diluted by water, precipitate was centrifuged, washed by 0.5M HCl, water and centrifuged again to afford deep-green crystalline solid.

MALDI-TOF (1,8-bis(diphenylamino)-naphthalene, negative ion), *m/z* 936.7 $(M-H)^-$.

Example 3: Evaluation of electronic absorption and emission spectra of CROSSDAP and a precursor of TPA-CROSSDAP

The electronic absorption and emission spectra of **CROSSDAP** are measured with a solution comprising 10 µM of **CROSSDAP**, in dimethylformamide as solvent.

The electronic absorption and emission spectra of the precursor of **TPA-CROSSDAP** are measured with a solution comprising 10 µM of 5,15-diaryl-10,20-diazatetrabenzoporphyrin **19**, in dichloromethane as solvent.

This solution is introduced into a quartz cell. The electronic absorption and emission spectra of **CROSSDAP** and the precursor of **TPA-CROSSDAP** in the wavelength domain were measured by a spectrophotometer and fluorimeter respectively.

Figure 3 shows the electronic absorption (straight line) and emission (dashed line) spectra of **CROSSDAP**, which clearly exhibits the intense absorption band at 685 nm with a high extinction coefficient ($\varepsilon = 9.3 \times 10^4\ M^{-1}cm^{-1}$).

Figure 4 shows the electronic (straight line) and emission (dashed line) spectra of the precursor of **TPA-CROSSDAP**, which clearly exhibits the intense absorption band at 685 nm with a high extinction coefficient ($\varepsilon = 9.33 \times 10^4\ M^{-1}cm^{-1}$).

Example 4: Evaluation of the redox potential of CROSSDAP

The redox potential of **CROSSDAP** was measured by cyclic voltammetry using 3 electrodes.

The 3 electrodes used are:

- 1 Platinum working electrode
- 1 Platinum auxiliary or counter electrode
- 1 saturated calomel electrode (SCE) as reference electrode.

The scan rate of the potential is fixed to 100mV/s.

The analysed solution comprises 0.001 M of **CROSSDAP** in acetonitrile as solvent and with 0.1 M of Bu_4NPF_6 as supporting electrolyte.

The indicated potential values are the first oxidation potentials for the compounds, with respect to the reference electrode (SCE).

It was found that:

$E_{Ox1}(D^+/D) = 0.84$ V, and

$E_{Ox2}(D^{++}/D^+) = 1.05$ V

wherein

$E_{Ox1}(D^+/D)$ corresponds to the first oxidation potential of **CROSSDAP**.

$E_{Ox2}(D^{++}/D^+)$ corresponds to the second oxidation potential of **CROSSDAP**.

Example 5: Evaluation of the electron injection and the dye regeneration of CROSSDAP

By combining the emission wavelength of **CROSSDAP** as determined in example 2 and the redox potential of **CROSSDAP** as determined in example 3, the injection (ΔG_{inj}) and the regeneration driving (ΔG_{reg}) forces can be calculated according to the following equations:

$\Delta G_{inj} = E_{Ox1}(D^+/D) - E_{00}(D^*) + 0.70 = 0.84 - 1.84 + 0.70 = -0.30$ eV

$\Delta G_{reg} = E_{Ox}(I_2^{-\bullet}/I^-) - E_{Ox1}(D^+/D) = 0.55 - 0.84 = -0.29$ eV

wherein

$E_{Ox1}(D^+/D)$ corresponds to the first oxidation potential of **CROSSDAP** as determined in example 3;

$E_{00}(D^*)$ corresponds to the oxidation potential of **CROSSDAP** singlet excited state as determined by $E_{Ox1}(D^+/D^*) = E_{Ox1}(D^+/D) - E_{00}(D^*)$ with $E_{00}(D^*)$ determined by the wavelength at the intersection of the absorption and emission spectra (Figure 1).

$E_{Ox}(I_2^{-\bullet}/I^-)$ corresponds to the oxidation potential of $I_2^{-\bullet}/I^-$ taken as 0.55 V vs SCE as disclosed in G. Boschloo, E. A. Gibson and A. Hagfeldt *J. Phys. Chem. Lett.* **2011**, 2, 3016–3020.

These calculations support that both electron injection and dye regeneration processes are very exergonic.

Example 6: DSSC comprising CROSSDAP

DSSCs were prepared according to the FTO conductive glass substrates (F-doped SnO_2) were purchased from Pilkington (TEC8). The plates were cleaned by successive sonication in soapy water, then an ethanolic solution of HCl (0.1 M) for 10 minutes, and finally dried in air. TiO_2 films were prepared

in three steps. A first treatment is applied by immersion for 30 min in an aqueous $TiCl_4$ solution at 80°C. Three successive layers of mesoporous TiO_2 were then screen printed using a transparent colloidal paste (Dyesol DSL 18NR-T) and a final light scattering layer (Dyesol DSL 18NR-AO) was affixed, with 20-minute long drying steps at 150°C between each layer. The obtained substrates were then sintered at 450°C, following a progressive heating ramp (325°C for 5 min, 375°C for 5 min, 450°C for 30 min). A second $TiCl_4$ treatment was immediately conducted afterwards and the electrodes were fired one last time at 450°C for 30 minutes. Thicknesses (16 µm) were measured by a Sloan Dektak 3 profilometer. The prepared TiO_2 electrodes were soaked while still hot (ca. 80°C) in a 0.2 mM solution of **CROSSDAP** and chenodeoxycholic acid (5 mM) in a 1:1 mixture (v:v) of toluene and ethanol. After one night of dyeing at room temperature, the electrodes were rinsed in ethanol and dried in air, in the dark. Platinum based counter electrodes were prepared by drop casting two drops of hexachloroplatinic acid in distilled isopropanol (2 mg per mL) on FTO plates, and subsequent firing at 380°C for 30 minutes. The photoelectrode and the counter electrode were placed on top of each other and sealed using a thin transparent film of Surlyn polymer (DuPont, 60 µm) as a spacer. The resulting chamber was filled with an iodine-based electrolyte (30 mM I_2, 0.1 M LiI, 0.1 M guanidinium thiocyanate, 0.6 M 1-ethyl-2,3-dimethylimidazolium iodide and 0.6 M 4-tertbutylpyridine when mentioned, in dry distilled acetonitrile) by vacuum back filling through a predrilled hole in the counter electrode, and the photovoltaic device was sealed afterwards with Surlyn and a cover glass. The cell had an active area of 0.25 cm^2. Photovoltaic measurements were performed with a calibrated AM 1.5 artificial solar light simulator (Oriel) and a Keithley 2400 digital source-meter; data were collected with a local software designed by Synervia (labview).

The photovoltaic characteristics of the DSSCs were recorded under calibrated Air mass 1.5 spectrum (AM1.5) simulator at 1000 W/m^2 and are depicted in Figure 5. The mean metrics of at least 3 independent solar cells are: Jsc= 7.73 mA/cm^2; Voc= 597 mV, ff= 74% leading to a PCE of 3.45%, wherein:

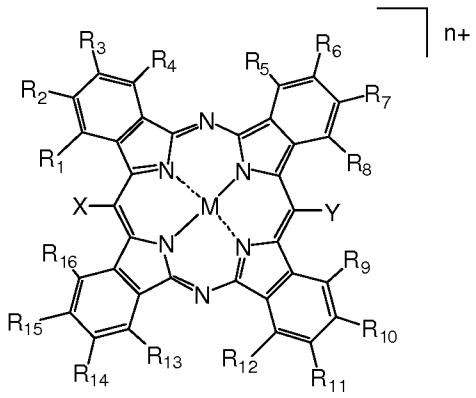
Jsc is the short-circuit current density;
Voc is the open-circuit voltage
ff is fill factor; and
PCE is the photoconversion efficiency.

Figure 5 shows the current/voltage characteristic of the solar cell sensitized with **CROSSDAP** recorded under the dark (dashed line) and under AM 1.5 illumination (straight line). The demonstrated efficiency of 3.45% in a non-optimized solar cell underscores the great potential of compounds of general formula (I) as sensitizers in solar cells.

The photoaction spectrum of the DSSC cell sensitized with **CROSSDAP** is given in Figure 6 and underscores the great photoactivity of this sensitizer in the near infrared region.

CLAIMS

1. Compound of general formula (I):



(I)

wherein

R_1-R_{16} are each independently selected from H, alkyl and aryl; or two adjacent R_1-R_{16} groups optionally form, together with the carbon atoms to which they are attached, a ring selected from cycloalkyl and aryl, and the remaining R_1-R_{16} groups are each independently selected from H, alkyl and aryl;

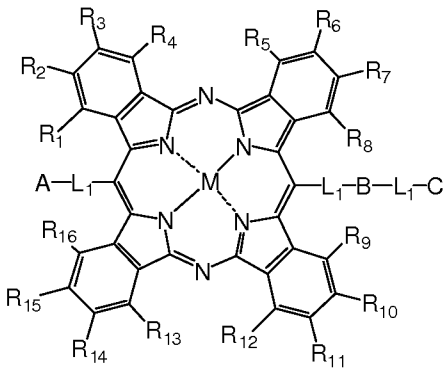
X and Y, similar or different, each comprise at least one group selected from H, alkyl, aryl, arylene, heteroaryl, heteroarylene, alkendiyl, alkyndiyl, dialkyl amino, diaryl amino, triaryl amino and dialkylaryl amino;

M represents 2 hydrogen atoms; or M is selected from Zn, Mg, Al, Si, Cu, Ru, Au, Sn, Pd, Pt, Ir and Ni; or M is selected from $Sn(IV)(L)_2$, $P(V)(L)_2$, Au(III), Ru(II)LL', Ir(III) wherein L and L' represent axial ligands selected from halogeno, hydroxo, alkoxide, carboxylato, CO and pyridine; and

n is 0 or 1;

with the proviso that X and Y are not both H, or both alkyl or both aryl.

2. Compound according to claim 1, wherein said compound corresponds to general formula (II):



(II)

wherein

R_1-R_{16} are each independently selected from H, alkyl and aryl; or two adjacent R_1-R_{16} groups optionally form, together with the carbon atoms to which they are attached, a ring selected from cycloalkyl and aryl, and the remaining R_1-R_{16} groups are each independently selected from H, alkyl and aryl;

A is selected from H, alkyl, aryl, dialkyl amino, diaryl amino, triaryl amino, dialkylaryl amino, thienyl, oligothienyl, and combinations thereof;

B is selected from arylene, heteroarylene, alkendiyl, alkyndiyl and combinations thereof;

C is selected from $-COOR_a$, $-COO^-$, $-PO_3H_2$, $-PO(OH)R_b$, $-CH=C(COOH)_2$, $-CH=C(CN)(COOH)$, $-Si(OR_b)_3$, and $-C(O)-CH_2-C(O)-CH_3$, wherein R_a is H, alkyl, amino, dialkylamino, diaryl amino or $-C(O)-R_b$ and wherein R_b is alkyl;

L_1 are each independently selected from a single bond, $-(C\equiv C)_m-$, and $-(CH=CH)_o-$, wherein m and o are integers independently equal to 1, 2 or 3;

M represents 2 hydrogen atoms; or M is selected from Zn, Mg, Al, Si, Cu, Ru, Au, Sn, Pd, Pt, Ir and Ni.

3. Compound according to claim 2, wherein

R_1-R_{16} are each independently selected from H, C_1-C_6-alkyl and C_6-aryl;

A is selected from H, C_1-C_6-alkyl, C_6-aryl, di-C_1-C_6-alkyl amino, di-C_6-aryl amino, tri-C_6-aryl amino, di-C_1-C_6-alkyl-C_6-aryl amino, thienyl, oligothienyl, and combinations thereof;

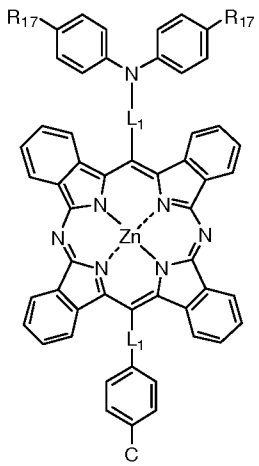
B is selected from C_6-arylene, 5- to 10-membered heteroarylene, $-C\equiv C-$, $-CH=CH-$ and combinations thereof; in particular B is selected from phenylene, thiendiyl, benzothiadiazoldiyl, benzotriazoldiyl, pyridindiyl, triazoldiyl, $-C\equiv C-$, $-CH=CH-$, and combinations thereof;

C is selected from $-COOH$, $-PO_3H_2$, $-CH=C(CN)(COOH)$, $-Si(OMe)_3$, $-Si(OEt)_3$ and $-C(O)-CH_2-C(O)-CH_3$;

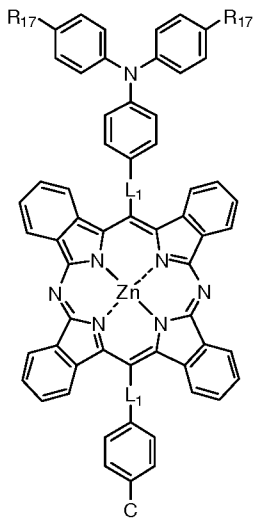
L_1 are each independently selected from a single bond, $-C\equiv C-$ and $-CH=CH-$;

M represents 2 hydrogen atoms; or M is selected from Zn, Mg, Al, Si, Cu, Ru and Ni; in particular Zn, Mg and Cu; preferably Zn.

4. Compound according to any one of claims 1 to 3, wherein said compound corresponds to general formula (III) or (IV):



(III)



(IV)

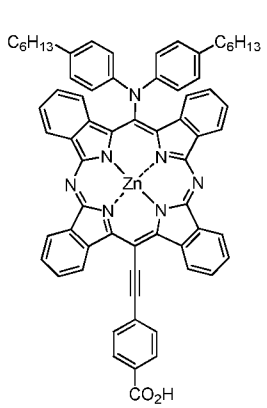
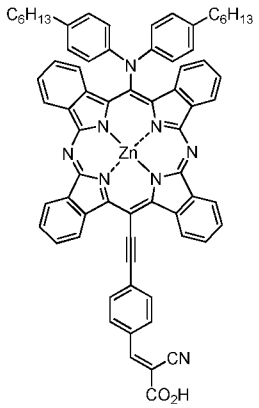
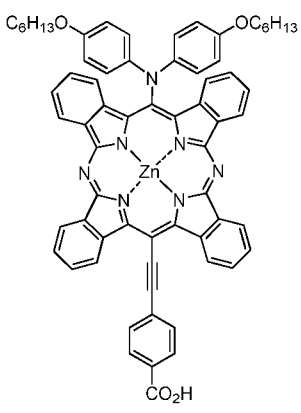
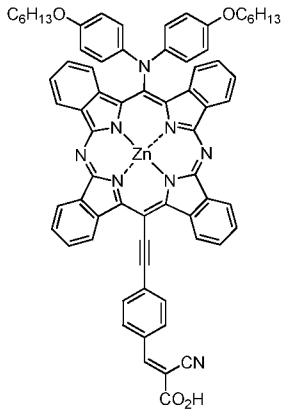
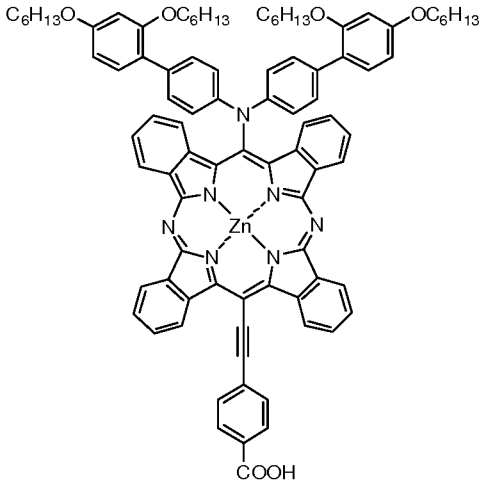
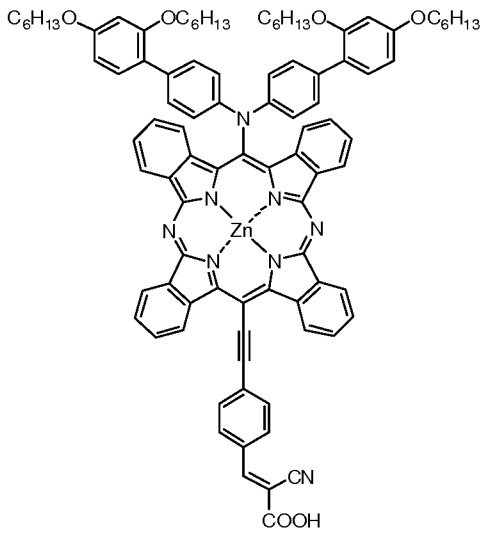
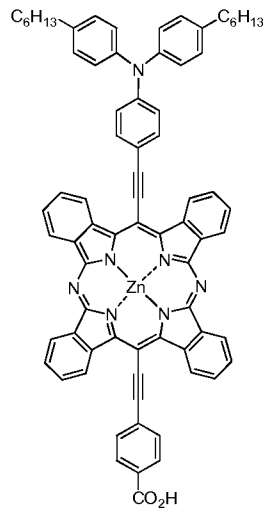
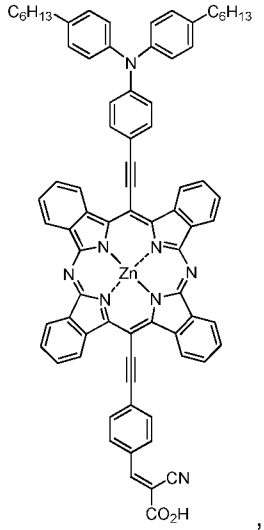
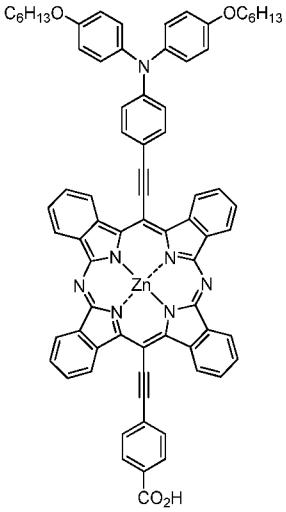
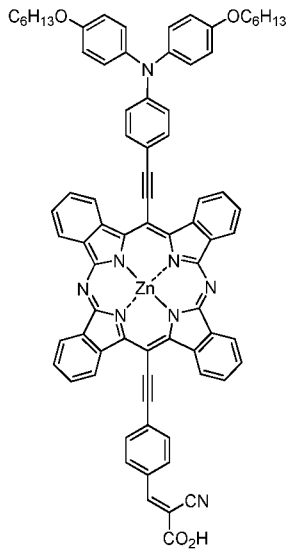
wherein

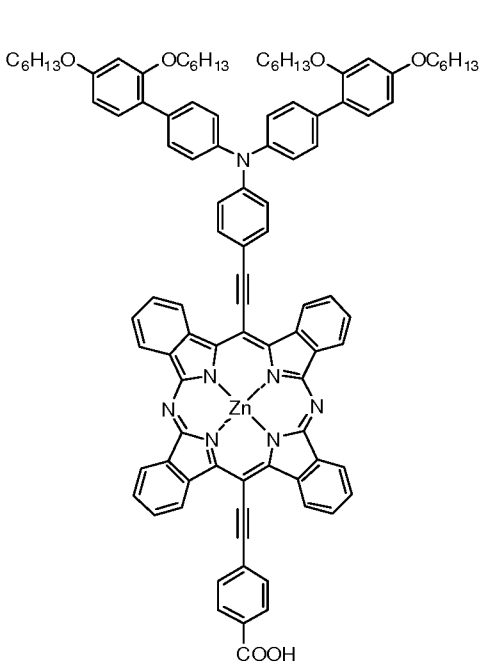
R_{17} is independently selected from H, alkoxy and phenyl substituted by one or two alkoxy groups;

L_1 is independently selected from bond and -C≡C-; and

C is independently selected from -COOH and -CH=C(CN)(COOH).

5. Compound according to any one of claims 1 to 4, wherein said compound is selected from the following compounds:



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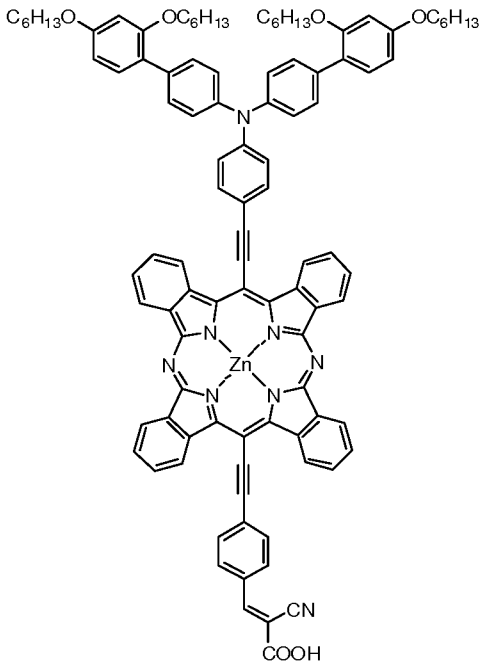

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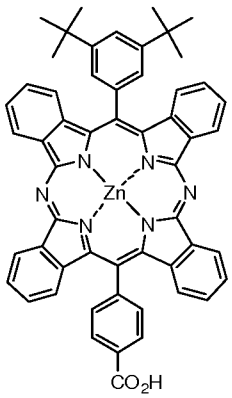
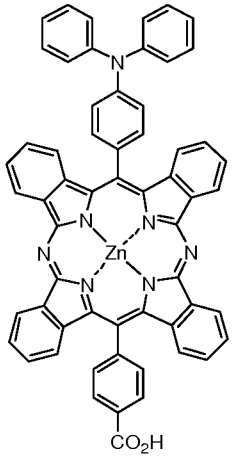


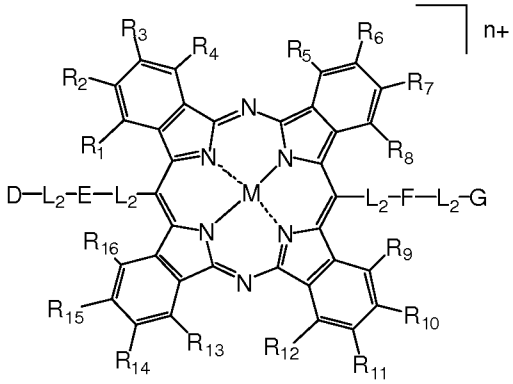


CROSSDAP , **TPA-CROSSDAP** .

6. Dye-sensitized solar cell comprising an anode, a counter-electrode, a nanocrystalline semiconductor, a sensitizer and an electrolyte, wherein the sensitizer comprises a compound as defined in any one of claims 2 to 5.

7. Use of a compound as defined any one of claims 2 to 4 as a sensitizer for a dye-sensitized solar cell.

8. Compound according to claim 1, wherein said compound corresponds to general formula (V):



(V)

wherein

R_1-R_{16} are each independently selected from H, alkyl and aryl; or two adjacent R_1-R_{16} groups optionally form, together with the carbon atoms to which they are attached, a ring selected from cycloalkyl and aryl, and the remaining R_1-R_{16} groups are each independently selected from H, alkyl and aryl;

D and G are each independently selected from H, alkyl, aryl, heteroaryl, oligothienyl, dialkyl amino, diaryl amino, triaryl amino, dialkylaryl amino, alkenyl, and combinations thereof;

E and F are each independently selected from arylene, heteroarylene, alkendiyl, alkyndiyl, and combinations thereof;

L_2 are each independently selected from a single bond, $-(C\equiv C)_p-$ and $-(CR=CR)_q-$, wherein R is H or -CN and wherein p and q are integers independently equal to 1, 2 or 3;

M represents 2 hydrogen atoms; or M is selected from Zn, Mg, Al, Si, Cu, Ru, Au, Sn, Pd, Pt, Ir and Ni; or M is selected from Sn(IV)$(L)_2$, P(V)$(L)_2$, Au(III), Ru(II)LL', Ir(III) wherein L and L' represent axial ligands selected from halogeno, hydroxo, alkoxide, carboxylato, CO and pyridine; and

n is 0 or 1.

9. Compound according to claim 8, wherein

R_1-R_{16} are each independently selected from H, C_1-C_6-alkyl and C_6-aryl;

D and G are each independently selected from H, C_1-C_6-alkyl, C_6-aryl, di-C_1-C_6-alkyl amino, di-C_6-aryl amino, tri-C_6-aryl amino and di-C_1-C_6-alkyl-C_6-aryl amino, thienyl, oligothienyl, and combinations thereof; in particular phenyl, diphenyl amino and triphenylamino; wherein said groups may optionally be substituted by one or two substituents selected from alkyl, alkoxy, phenoxy, dialkylamino, diphenylamino, thioether, carboxylic group and sulfonic group;

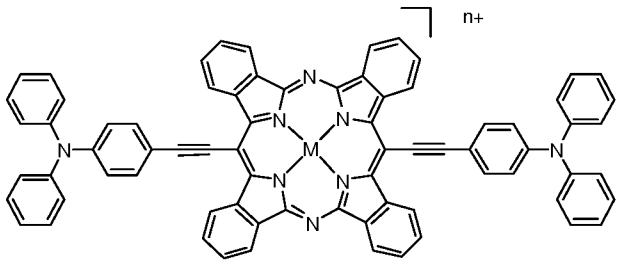
E and F are each independently selected from C_6-arylene, 5- to 20-membered heteroarylene, -C≡C-, -CH=CH-, and combinations thereof; in particular phenylene, thiendiyl, benzothiadiazoldiyl, benzotriazoldiyl, pyridindiyl, triazoldiyl, -C≡C-, -CH=CH-, and combinations thereof;

L_2 are each independently selected from a single bond, -C≡C- and -CR=CR-, wherein R is H or -CN;

M represents 2 hydrogen atoms; or M is selected from Sn(IV)$(L)_2$, P(V)$(L)_2$, Au(III), Ru(II)LL', Ir(III) wherein L and L' represent axial ligands selected from halogeno, for example Cl^-, Br^- or I^-; hydroxo (OH^-); alkoxide, for example $R'O^-$ wherein R' is alkyl or phenyl; carboxylato, for example $R'COO^-$ wherein R' is alkyl or phenyl; CO; and pyridine; in particular Sn(IV)$(L)_2$, P(V)$(L)_2$, Au(III);

n is 0 or 1.

10. Compound according to claim 9, wherein said compound is



wherein M is Sn(IV)$(L)_2$ and n is 0, or M is P(V)$(L)_2$ and n is 0, or M is Au(III) and n is 1, or M is Ru(II)LL' and n is 0, or M is Ir(III) and n is 1;

wherein L is selected from Cl^-, Br^-, I^-, OH^-, $R'O^-$ and $R'COO^-$ with R' is alkyl or phenyl; and

wherein L' is selected from CO and pyridine.

11. Compound according to claim 8, wherein

R_1-R_{16} are each independently selected from H, C_1-C_6-alkyl and C_6-aryl;

D and G are each independently selected from H, C_6-aryl, 5- to 20-membered heteroaryl, alkenyl, and combinations thereof; in particular phenyl, thienyl optionally fused with an *N*-alkyl pyrrolidine-2,5-dione, benzothiadiazolyl optionally fused with a 2-alkyl triazole, benzotriazolyl, pyridinyl, triazolyl, phthalimidyl, a pyridinium radical, a diketopyrrolopyrrole radical, an isoindigo radical, a *N*-alkyl-2,2′-bithiophene-3,3′-dicarboximide radical, dicyanovinyl, tricyanovinyl, and combinations thereof;

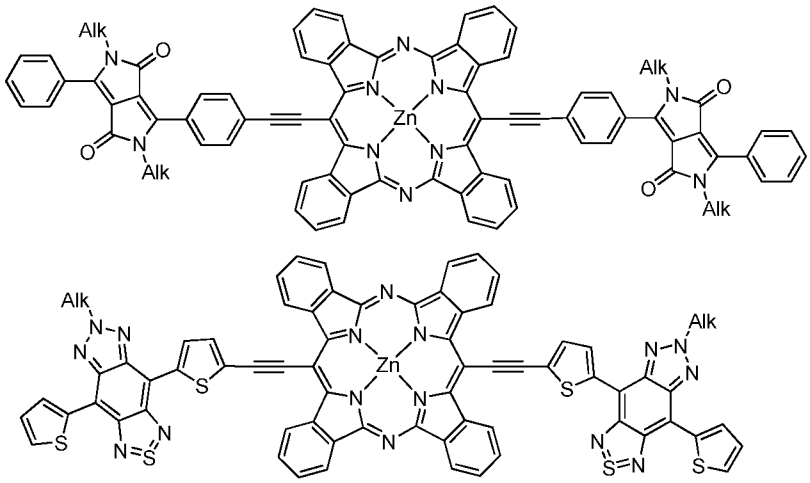
E and F are each independently selected from C_6-arylene, 5- to 20-membered heteroarylene, -C≡C-, -CH=CH-, and combinations thereof; in particular phenylene, thiendiyl, benzothiadiazoldiyl, benzotriazoldiyl, pyridindiyl, triazoldiyl, -C≡C-, -CH=CH-, and combinations thereof;

L_2 are each independently selected from a single bond, -C≡C- and -CR=CR-, wherein R is H or -CN;

M represents 2 hydrogen atoms; or M is selected from Zn, Mg, Al, Si, Cu, Ru and Ni; in particular Zn, Mg and Cu; preferably Zn; and

n is 0.

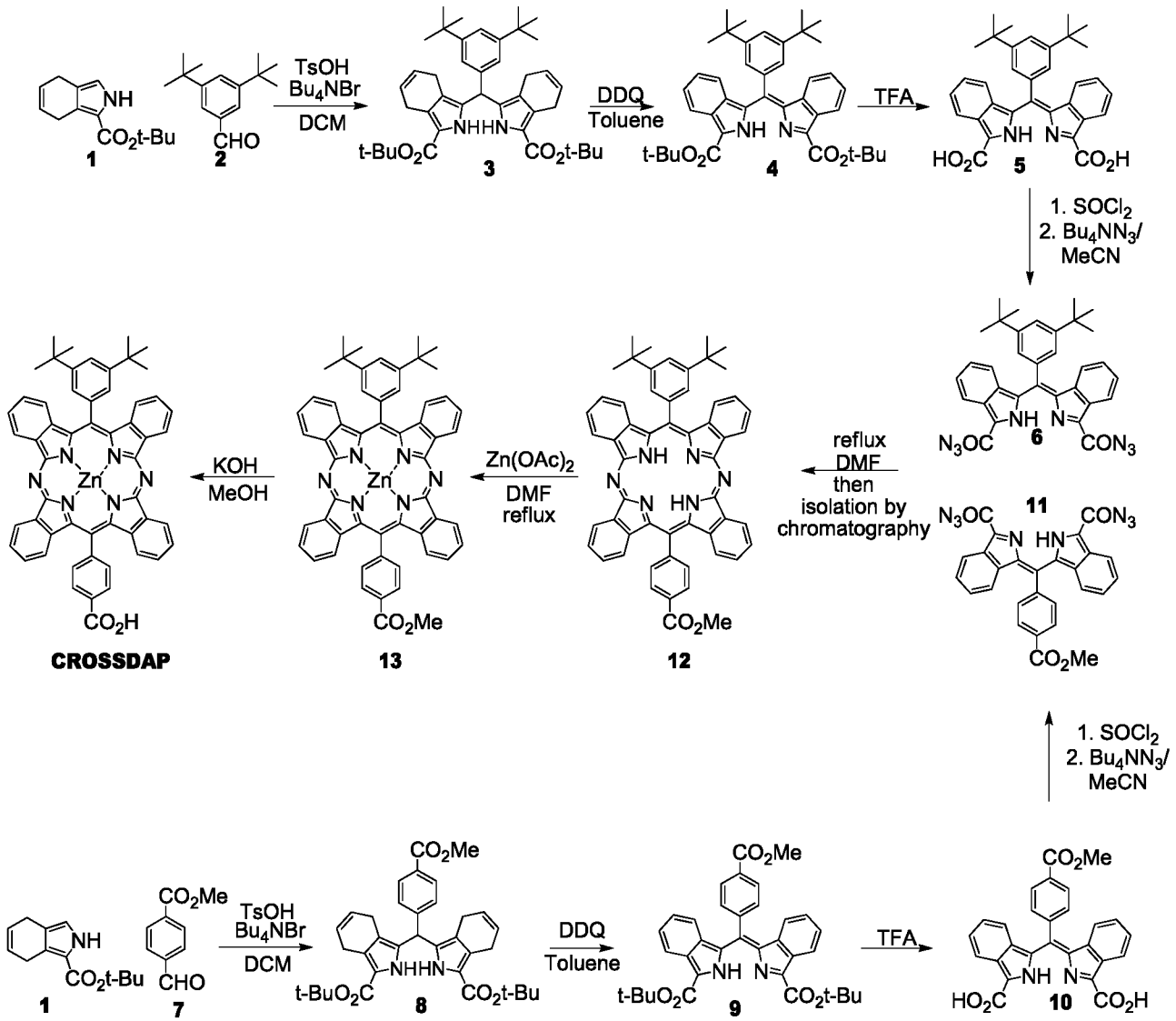
12. Compound according to claim 11, wherein said compound is:



13. Organic solar cell comprising an anode, a cathode and a sensitizer, wherein the sensitizer is a compound as defined in any one of claims 8 to 12.

14. Organic solar cell according to claim 13, wherein the anode comprises a material selected from indium tin oxide and graphene and wherein the cathode comprises a metal selected from Al, Ag, Cu, or Au.

15. Use of a compound as defined in any one of claims 8 to 12 as a sensitizer for an organic solar cell.


TsOH
Bu4NBr
DCM
DDQ
Toluene
TFA
1. SOCl2
2. Bu4NN3/
MeCN
reflux
DMF
then
isolation by
chromatography
Zn(OAc)2
DMF
reflux
KOH
MeOH
1. SOCl2
2. Bu4NN3/
MeCN
CROSSDAP
13
12
11
6
5
4
3
2
1
7
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10

Figure 1

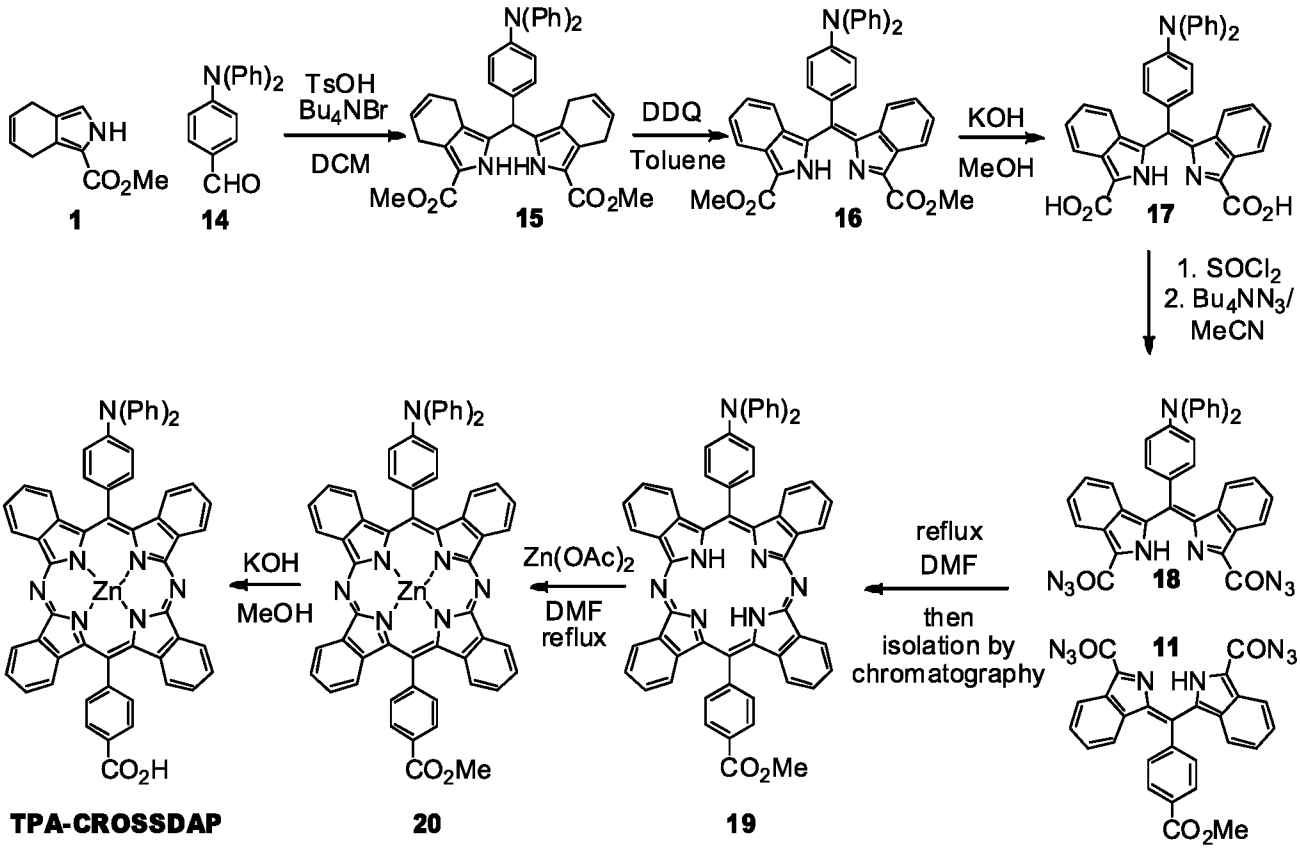


Figure 2

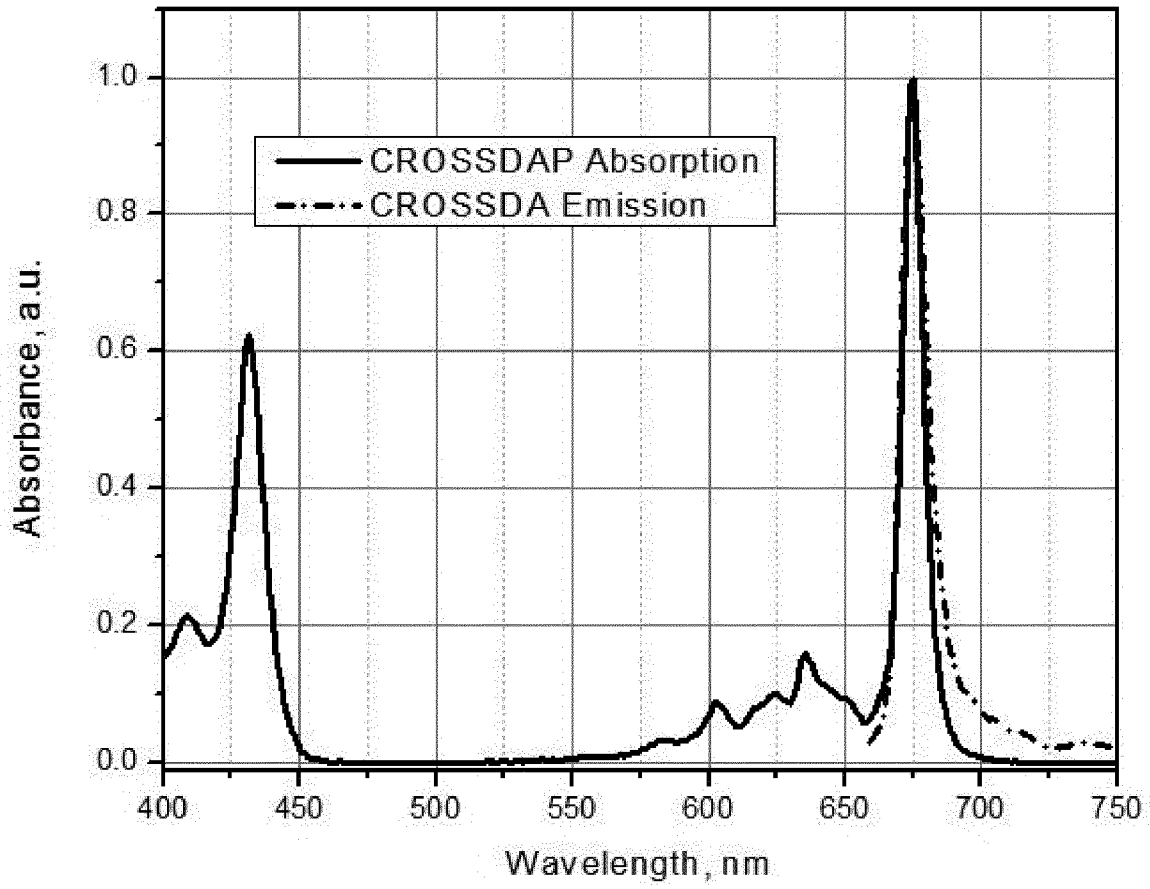


Figure 3

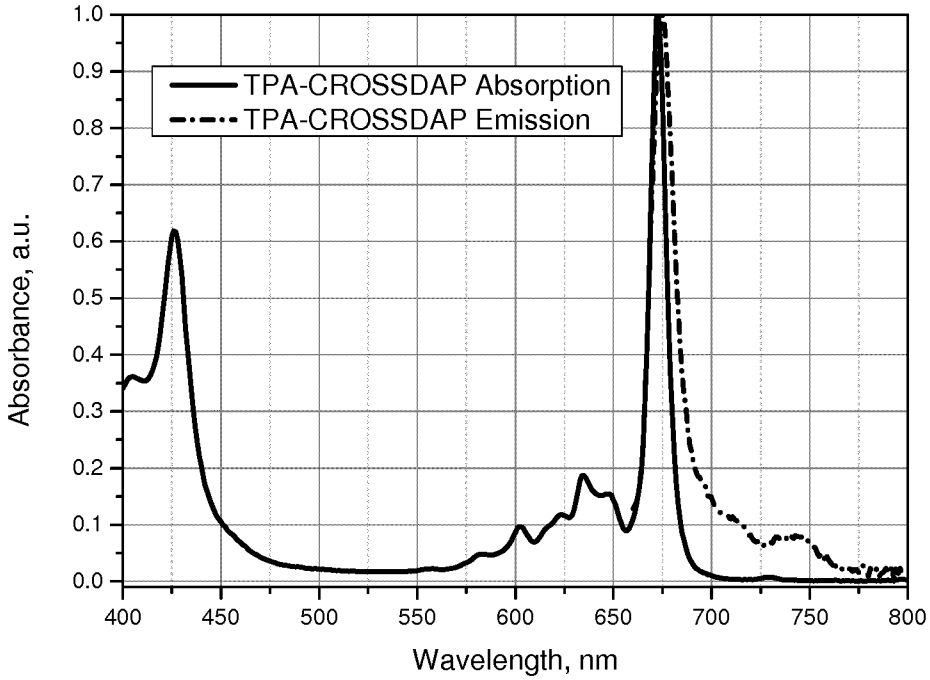


Figure 4

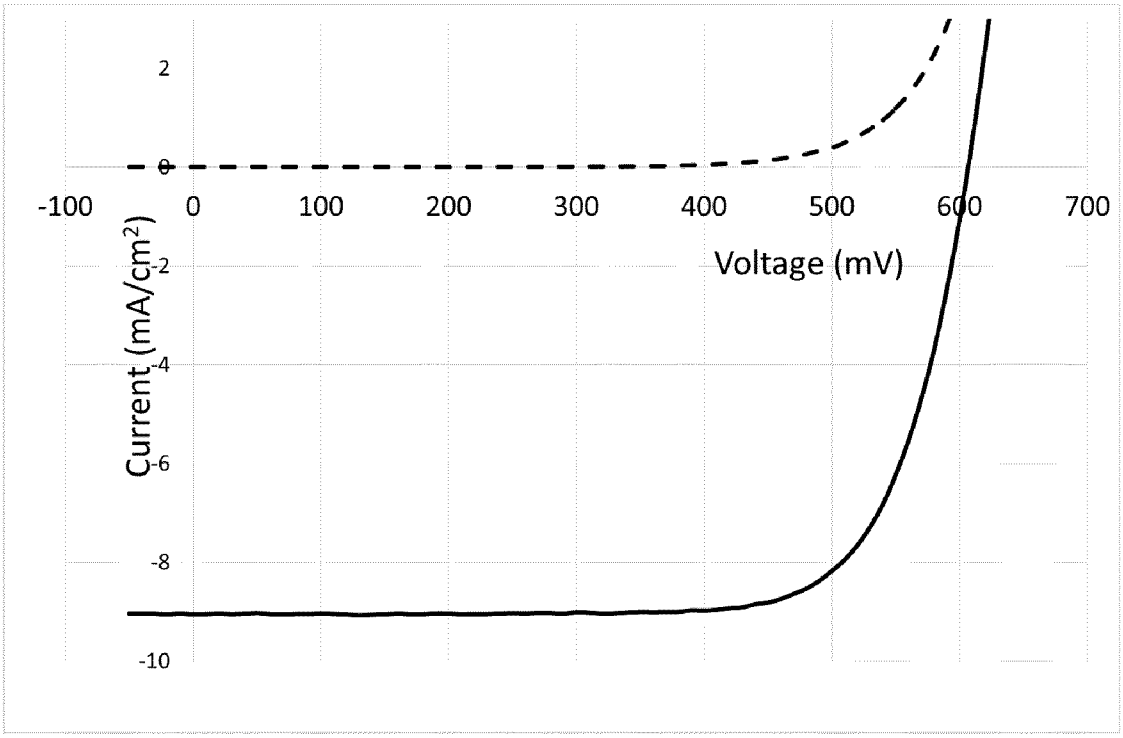
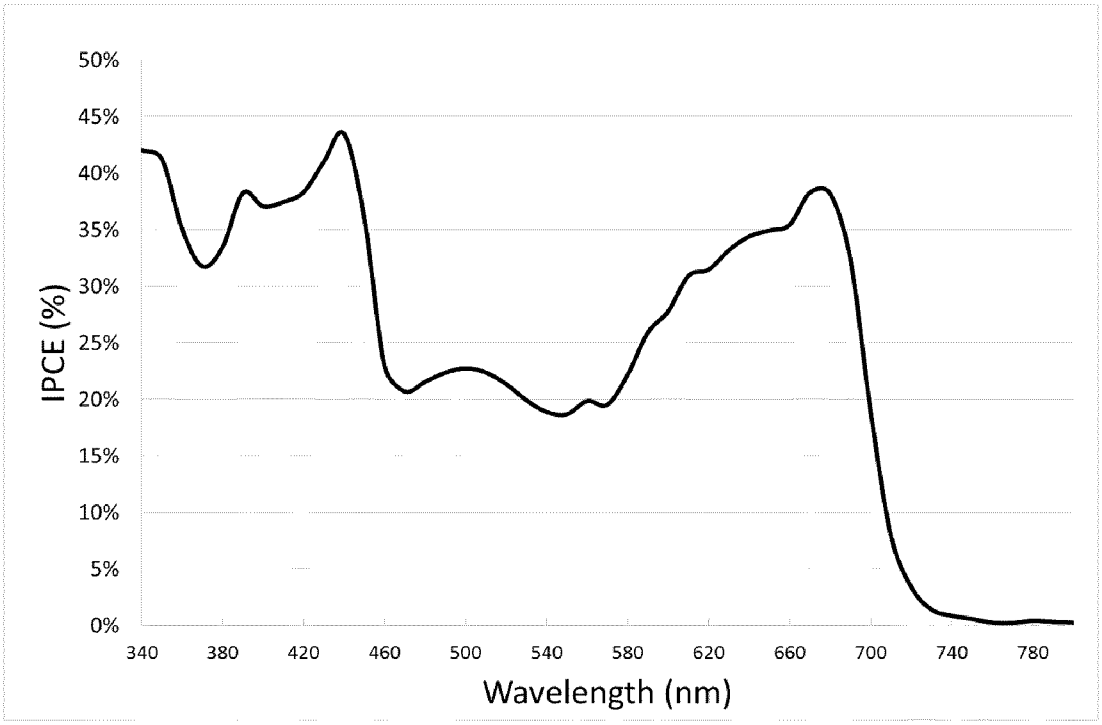


Figure 5


50%
45%
40%
35%
30%
25%
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15%
10%
5%
0%
IPCE (%)
340
380
420
460
500
540
580
620
660
700
740
780
Wavelength (nm)

Figure 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/067848

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09B47/04 C09B47/32
ADD.

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)
C09B

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Rebekah Theisen ET AL: "Theoretical Characterization of Zinc Phthalocyanine and Porphyrin Analogs for Organic Solar Cell Absorption", , 1 January 2014 (2014-01-01), XP055232149, ISBN: 978-1-321-32800-4 Retrieved from the Internet: URL:http://repository.asu.edu/attachments/140796/content/Theisen_asu_0010E_14304.pdf [retrieved on 2015-11-30] page 8 - page 13 page 129 - page 134 ----- -/--	1-15

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents :

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"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	Date of mailing of the international search report
13 September 2016	21/09/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Butkowskyj-Walkiw, T

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ANDREW N. CAMMIDGE ET AL: "Phthalocyanine Analogues: Unexpectedly Facile Access to Non-Peripherally Substituted Octaalkyl Tetrabenzotriazaporphyrins, Tetrabenzodiazaporphyrins, Tetrabenzomonoazaporphyrins and Tetrabenzoporphyrins", CHEMISTRY - A EUROPEAN JOURNAL., vol. 17, no. 11, 7 March 2011 (2011-03-07) , pages 3136-3146, XP055232141, WEINHEIM, DE ISSN: 0947-6539, DOI: 10.1002/chem.201002176 the whole document -----	1-15

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