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(54) Title: LONG WAVELENGTH ABSORBING PORPHYRIN PHOTOSENSITIZERS FOR DYE-SENSITIZED SOLAR CELLS

(57) **Abstract**: A long wavelength absorbing porphyrin/metalloporphyrin molecule is provided, made up of a porphyrin macrocycle and an anchor group for attachment to a substrate. A molecular linking element is interposed between the porphyrin macrocycle and the anchor group. The porphyrin/metalloporphyrin molecule also includes an (aminophenyl)amine group, either N,N-(4-aminophenyl)amine or N-phenyl-N-(4-aminophenyl)amine, where an amino moiety of the 4-aminophenyl group is derivatized by an element such as hydrogen, alkanes, haloalkanes, aromatic hydrocarbons, halogenated aromatic hydrocarbons, heteroarenes, halogenated heteroarenes, or combinations of the above-mentioned elements.

DESCRIPTION

TITLE OF INVENTION: LONG WAVELENGTH ABSORBING PORPHYRIN PHOTOSENSITIZERS FOR DYE-SENSITIZED SOLAR CELLS

TECHNICAL FIELD

This invention generally relates to dye-sensitive light absorbing chemistry and, more particularly, to a porphyrin molecule useful in dye-sensitive light absorbing applications.

BACKGROUND ART

Although chlorophyll, chlorophyll derivatives, and synthetic porphyrins have diverse chemical structures, they exhibit similar absorption characteristics over comparable wavelength ranges (typically λ=350-700 nm). Synthetic porphyrins (and their corresponding metalloporphyrins) consist of a conjugated 22π electron system, 18 of which are effectively delocalized to fit the Huckel requirement for aromaticity. In addition to their structural resemblance to natural chromophores such as chlorophyll, synthetic porphyrins are attractive candidates as light-harvesting materials due to their high structural stability, light absorption capabilities in the visible region, redox properties, and synthetic accessibility as compared to naturally occurring chromophores. Photoexcited processes involving porphyrins are facilitated by the highly delocalized π-system, which is capable of resisting major structural changes upon oxidation. Most importantly, the redox properties of porphyrins and metalloporphyrins are dramatically altered upon photoexcitation, which leads to the generation of porphyrin excited states that can be advantageous in photovoltaic (PV) cell applications.

The ability of porphyrins to efficiently harvest light over broad wavelength ranges has generated significant interest in their potential for solar applications over the last few decades. As a result, synthetic protocols towards the fabrication of “customized” porphyrin architectures have become well-established and have been widely adopted as conventional methods. In general, the electronic properties of porphyrins can be readily altered using a number of strategies including the following: functionalization and/or modification along the porphyrin periphery, insertion of transition metals into the macrocyclic core, complexation of metalloporphyrins with various ligands, etc. The strategic manipulation of porphyrin properties (optical absorption characteristics, photoexcited behaviors, etc.) through rational synthetic design has resulted in numerous publications, an overwhelming majority of which are academic in nature.

Most often, the desired enhancements accessible through chemical modification of porphyrins involve manipulation of light-harvesting (absorption) capabilities and/or excited-state behaviors (electron transfer, for example). For example, it is well- known that increasing the pi-conjugation extending from the porphyrin core can lead to enhanced absorption properties which may include (1) increased absorption over a particular wavelength range, (2) a broadening of optical absorption over wider wavelength ranges and/or (3) (bathochromic) shifting of absorption towards longer wavelengths. Furthermore, forward electron transfer processes from photoexcited porphyrin (donor) to acceptor moieties (metal oxides, fullerenes, carbon nanotubes, etc.) can be dramatically enhanced through the strategic introduction of electron transfer facilitating groups into the appropriate locations along the porphyrin core structure. In addition to exerting a favorable influence on electron transfer kinetics, some classes of functional groups can also dramatically improve the overall light harvesting capabilities of the porphyrin, whether it is in terms of increased absorption intensity over particular wavelengths, bathochromic shifting of absorption to longer wavelengths, or both.

At the present, ruthenium(II) bi- and polypyridyl complexes have proven to be the most efficient TiO_2

sensitizers in dye-sensitized solar cells (DSSC). However, only incremental improvements in the highest power efficiencies have been achieved within the past decade. Considering the facts that ruthenium(II) pyridyl dyes are expensive and ruthenium itself is a rare metal, there exists significant motivation to develop novel photosensitizers that either contain abundant, inexpensive metals or no metals at all. In response to this, several different classes of photosensitizer molecules have led to appreciably high efficiencies in dye-sensitized solar cells (DSSCs) including indoline (9%), coumarin (5.2%), hemicyanine (5.2%), squarine (4.5%), phthalocyanine (3.5%) and porphyrins (from <1% to as high as 11%). See, respectively, D. L. Officer et al., Coordination Chemistry Reviews 2004, 248, 1363, D. L. Officer et al., J. Phys. Chem. C 2007, 111, 11760, E. W-G. Diau and C-Y. Yeh et al., Chem. Eur. J. 2009, 15, 1403, C-Y. Yeh and E. W-G. Diau et al., Phys. Chem. Chem. Phys. 2009, 11, 10270, and M. Gratzel et al., Angew. Chem., Int. Ed. 2010, 49, 6646.

Figs. 1A and 1B are graphs depicting, respectively, the optical absorption spectrum for zinc tetraphenylporphyrin, and quantum efficiency (IPCE) values (%) for zinc tetraphenylporphyrin-TiO_2 as a function of optical absorption (prior art). As illustrated, extended π-conjugation in a zinc tetraphenylporphyrin-TiO_2 DSSC has previously shown to give rise to high internal photon to current efficiencies (IPCEs) at wavelengths in the 400-700 nm range, see D. L. Officer et al., J. Phys. Chem. C 2007, 111, 11760. Although chlorophyll and its derivatives have lower absorption at λ=500-600 nm (Fig. 1A) relative to λ=450 nm, DSSCs made with zinc tetraphenylporphyrin derivatives still exhibit high IPCE values at λ=500-600 nm (Fig, 1B). In this case, the appreciably high %IPCE between λ=400-700 nm can be attributed to broadened absorption for the zinc porphyrin and a favorable electronic communication between the zinc tetraphenylporphyrin and TiO_2, both of which benefit from extended conjugation between the donor and acceptor moieties. Based upon this, it is reasonable to assert the fact that the peak width and absorption edge(s) are the critical parameters when considering the optical absorption spectrum of a potential photosensitizer for DSSC applications. Under standard global AM 1.5 solar conditions, a short circuit photocurrent density (Jsc) of 14.0 ± 0.20 mA/cm^2, an open circuit voltage (Voc) of 680 ±30 mV, and a fill factor (FF) of 0.74, corresponding to an overall conversion efficiency of 7.1%, was achieved using this porphyrin photosensitizer. In spite of this, the IPCE values for zinc tetraphenylporphyrin (~70% at λ=480 and 580-640 nm, respectively) are still lower than that of ruthenium(II) pyridyl complexes. In addition, there is a decrease in IPCE values (~55%) at λ~480 nm. Clearly, there exists the potential to improve IPCE values (possibly to ~80% or beyond).

Fig. 2 is a drawing depicting the molecular structure of a zinc porphyrin photosensitizer (YD1) that exhibits high efficiency (6%) in DSSC when co-adsorbed with chenodeoxycholic acid (CDCA) at ratios of 1:1 and 1:2 (ZnP:CDCA) (prior art). As reported by E. W-G. Diau and C-Y. Yeh et al., Chem. Eur. J. 2009, 15, 1403, this strategy takes advantage of (1) increased conjugation to both broaden and red-shift the absorption characteristics of the photosensitizer and (2) incorporation of a secondary electron transfer "facilitating" group (electron donor) to enhance the electron injection kinetics.

The photosensitizer design (D-P-B-A) takes advantage of a strongly absorbing porphyrin core (P), a conjugated bridge that broadens (red-shifts) the absorption capabilities of the photosensitizer while providing strong electronic coupling (B), a secondary electron transfer "facilitating" group (electron donor) to enhance the electron injection kinetics from the photoexcited porphyrin (D) and an anchoring group for strong attachment to TiO_2 (A).

Figs. 3A, 3B, and 3C are three analogous porphyrin photosensitizer designs, respectively YD11, YD12, and YD13, based upon the architecture of Fig. 2 (prior art). As reported in the literature by C-Y. Yeh and E. W-G. Diau et al., Phys. Chem. Chem. Phys. 2009, 11, 10270, efficiencies between 6 to <7% were achieved in DSSCs using liquid electrolyte (I^-/I_3^-). Noteworthy is the fact that a DSSC utilizing YD12 as photosensitizer afforded an impressive efficiency of 6.91% versus 7.27% for ruthenium 719 dye (with added scattering layer) within the same cell configuration. The poor performance of YD13 can be reasonably attributed to rapid aggregate-induced energy transfer phenomena due to the presence of the anthracene group in the bridge.

Fig. 4 is a graph depicting the optical absorption spectra for YD11, YD12 and YD13 in ethanol (prior art). Zinc porphyrin photosensitizers YD11-YD13 exhibit the characteristic absorption features for both the Soret Band (400-520 nm) and the lower energy Q-Bands (580-700 nm) with significantly decreased absorption along the regions in between. The broadened and red-shifted absorption for YD11-YD13 is rationalized in terms of the structural design described above, which is a widely known strategy for enhancing absorption characteristics of porphyrins relative to “simple” porphyrins such as pristine zinc tetraphenylporphyrin.

Fig. 5 is the molecular structure of zinc porphyrin photosensitizer YD-2 (prior art). Most recently, M. Gratzel et al., Angew. Chem., Int. Ed. 2010, 49, 6646, have reported an exceptionally high efficiency of 11% for a member of the YD class (YD-2) in a double layer TiO_2 film, which is unprecedented for zinc porphyrin photosensitizers in DSSC. To increase the light-harvesting capacity of the devices, an 11 mm (transparent) TiO_2 film was coated with a 5 mm thin layer of 400 nm reflecting particles. The IPCE spectrum of the YD-2 device exhibits a broad absorption from 400 nm to 750 nm with an IPCE peak maximum greater than 90% at 675 nm. Jsc (18.6 mA/cm^2), Voc (0.77 V) and FF (0.764) were derived from the J-V curve, thus giving an overall power conversion efficiency of ~11% under illumination with standard AM 1.5G simulated sunlight.

In light of the recent success using zinc porphyrin-based photosensitizers to achieve high efficiency, it is reasonable to assert that zinc porphyrins have the potential to rival the ruthenium-based dyes traditionally used in conventional DSSCs. In light of this, the rational design of novel porphyrin architectures for DSSC qualifies as an extremely valuable initiative.

Although the strategic introduction of strongly electron-donating di-aryl amine groups at the meso-position of a porphyrin is of interest, the application of aromatic amines to DSSC as co-sensitizers in general, as well the favorable photophysical behaviors obtained by incorporating aromatic amines into photosensitizer core structures, are well established.

Experimental results, reported by Guadiana et al., J. Macromol. Sci. Part A Pure Appl. Chem. 2003, A40, 1295, indicate that electron-donating (aromatic) amines that are anchored to the surface of TiO_2 as co-sensitizers effectively enhance the overall photovoltaic performances of DSSCs. Furthermore, they concluded that electron transfer from the amine to the photosensitizer dye is a key step in the photoexcited process.

Figs. 6A and 6B are, respectively, the molecular structure and optical absorption spectra in dichloromethane of 2TPA, TPA-R and 2TPA-R (prior art). X. Yang, A. Hagfeldt and L. Sun et al., Adv. Funct. Mater. 2008, 18, 3461, report a dye (2TPA-R) containing two triphenylamine (TPA) units connected by a vinyl group and rhodanine-3-acetic acid as the electron acceptor. The experimental results suggest that intramolecular energy transfer processes contributed to the overall light-harvesting abilities of the donor-acceptor (D-A) dye in DSSC. Overall, 2TPA-R exhibited improved photovoltaic performance relative to TPA-R, which is indicative of the favorable enhancements accessible through the careful design of photosensitizers appended with an appropriate aromatic amine containing moiety. In this case, the enhanced performance most likely arises from both a combination of increased optical absorption and enhanced intramolecular electronics.

Although aromatic amines are widely-known to enhance the absorption and/or photoexcited behaviors of photosensitizer dyes, this is by no means a universal generalization. In fact, some ruthenium-based dyes covalently modified with aromatic amines (both conjugatively and non-conjugatively) have failed to produce any real improvements in photovoltaic performance relative to the original dyes (without aromatic amine).

In spite of the strong and broadened absorption for the zinc porphyrin photosensitizers described above, there still exists an overall deficiency in the ability of porphyrins to effectively harvest broad regions of the solar spectrum, especially at wavelengths exceeding 700 nm. Nevertheless, the more recently established potential for porphyrin photosensitizers has positioned this class of materials as a legitimate rival to traditional ruthenium-based dyes for DSSC applications.

It would be advantageous if a porphyrin photosensitizer could be synthesized that performs efficiently in DSSC due to contributions from absorption at wavelengths of 700 nm and beyond.

SUMMARY OF INVENTION

The rational design of photosensitizers that can effectively harvest long wavelengths of light is critical for achieving highly efficient DSSCs. Although there exist a number of strategies for increasing photosenstizer absorption and manipulating electron injection kinetics/pathways, there are often drawbacks that arise from structural implications. For example, the synthesis of large, highly-conjugated photosensitizers is synthetically challenging (sometimes impossible) and often affords materials that are, at least for the most part, intractable. In general, these materials are impractical since they lack sufficient solubility for application and ultimately decrease the number of molecular photosensitizer units that can be employed due to the finite amount of space available for binding along the metal oxide surface (DSSC). In the case of porphyrins and metalloporphyrins, the core structure dominates the absorption and photoexcited-state behaviors of its derivatives although the strategic (covalent) introduction of the appropriate groups can provide a favorable (additive) effect in terms of optical absorption, forward electron transfer kinetics, and/or suppression of charge recombination. Unfortunately, the incorporation of photoactive moieties often leads to additional (unpredictable) photoexcited deactivation pathways which can be detrimental to photosensitizer performance in DSSC.

In light of this, a class of porphyrin-based photosensitizer architectures is presented for which molecular simulations have calculated optical absorption capabilities far greater than those reported for the YD class of materials discussed in the Background Section, above.

As previously mentioned, the concept of incorporating aromatic amines in photosensitizer core structures in order to enhance performance is widely known. In addition, the fact that the existence of a high degree of conjugation between the photosensitizer and metal oxide surface (DSSCs) is critical for providing effective communication through the bridging element is common knowledge in photosensitizer and DSSC development. However, a critical consideration towards the design of highly efficient photosensitizers for DSSC applications involves the concept of orbital partitioning, which is characterized by both high HOMO coefficients on the donor moiety and high LUMO coefficients on the acceptor group within the same molecule. In fact, the high efficiency for ruthenium-based photosensitizers in DSSC can reasonably be attributed to HOMO and LUMO localization on the thiocyanate ligands and pyridyl anchor groups, respectively. In general, high degrees of orbital partitioning can increase the driving force (rates) for electron injection to TiO_2 from the photoexcited dye (LUMO) and may lead to lower rates for charge recombination between photoexcited dye (cations) and electrons in TiO_2 following charge separation.

Accordingly, a long wavelength absorbing porphyrin/metalloporphyrin molecule is provided made up of a porphyrin macrocycle, and an anchor group for attachment to a substrate. A molecular linking element is interposed between the porphyrin macrocycle and the anchor group. The porphyrin/metalloporphyrin molecule also includes an (aminophenyl)amine group, either N,N-(4-aminophenyl)amine or N-phenyl-N-(4-aminophenyl)amine, where an amino moiety of the 4-aminophenyl group is derivatized by an element such as hydrogen, alkanes, haloalkanes, aromatic hydrocarbons, halogenated aromatic hydrocarbons, heteroarenes, halogenated heteroarenes, or combinations of the above-mentioned elements.

Additional details of the above-described porphyrin/metalloporphyrin molecule are presented below.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1A and 1B are graphs depicting, respectively, the optical absorption spectrum for zinc tetraphenylporphyrin, and quantum efficiency (IPCE) values (%) for zinc tetraphenylporphyrin-TiO_2 as a function of optical absorption (prior art).

Fig. 2 is a drawing depicting the molecular structure of a zinc porphyrin photosensitizer (YD1) that exhibits high efficiency (6%) in DSSC when co-adsorbed with chenodeoxycholic acid (CDCA) at ratios of 1:1 and 1:2 (ZnP:CDCA) (prior art).

Figs. 3A, 3B, and 3C are three analogous porphyrin photosensitizer designs, respectively YD11, YD12, and YD13, based upon the architecture of Fig. 2 (prior art).

Fig. 4 is a graph depicting the optical absorption spectra for YD11, YD12 and YD13 in ethanol (prior art).

Fig. 5 is the molecular structure of zinc porphyrin photosensitizer YD-2 (prior art).

Figs. 6A and 6B are, respectively, the molecular structure and optical absorption spectra in dichloromethane of 2TPA, TPA-R and 2TPA-R (prior art).

Fig. 7 is a diagram depicting a long wavelength absorbing porphyrin/metalloporphyrin molecule.

Fig. 8 is a schematic of a molecular structure of porphyrin-based photosensitizer using N,N-(4-aminophenyl)amine as the electron-donating group on the porphyrin meso position.

Fig. 9 is a schematic of a molecular structure of porphyrin-based photosensitizer using N-Phenyl-N-(4-aminophenyl)amine as the electron-donating group on the porphyrin meso position.

Fig. 10 is a simulated optical absorption spectrum for the YD class of porphyrin photosensitizers, which utilize meso-N,N-diphenylamine as the electron-donating group.

Fig. 11 is a simulated optical absorption spectrum for the class of porphyrin photosensitizers which utilizes meso-N,N-(4-aminophenyl)amine as the electron-donating group.

Fig. 12 is a simulated optical absorption spectrum for the class of porphyrin photosensitizers which utilizes meso-N-Phenyl-N-(4-aminophenyl)amine as the electron-donating group.

Figure 13 shows the synthetic reaction pathway towards the preparation of zinc porphyrin photosensitizer (Compound A).

Figure 14 is an optical absorption spectrum of Zinc porphyrin(Znp3) in dichloromethane from 250 nm to 900 nm at various concentrations.

Figure 15 is an optical absorption spectrum of Compound A in dichloromethane from 250 nm to 900 nm at various concentrations.

Figure 16 is an optical absorption spectrum of ZnP3 and Compound A in dichloromethane from 250 nm to 880 nm.

DESCRIPTION OF EMBODIMENTS

Fig. 7 is a diagram depicting a long wavelength absorbing porphyrin/metalloporphyrin molecule. The porphyrin/metalloporphyrin molecule 700 comprises a porphyrin macrocycle 702, and an anchor group 704 for attachment to a substrate. In one aspect, the porphyrin macrocycle 702 includes an "M" moiety such as H_2 or a metal (e.c. Zn, Ti, Mg, Pd). A molecular linking element 706 is interposed between the porphyrin macrocycle 702 and the anchor group 704. The porphyrin/metalloporphyrin molecule 700 also comprises an (aminophenyl)amine group 708 that may be either N,N-(4-aminophenyl)amine 708a or N-phenyl-N-(4-aminophenyl)amine 708b, where the amino moiety of the 4-aminophenyl group is derivatized by an element such as hydrogen, alkanes, haloalkanes, aromatic hydrocarbons, halogenated aromatic hydrocarbons, heteroarenes, halogenated heteroarenes, or combinations of the above-mentioned elements. As used herein, the term "element" is not defined as only an element of the periodic table, but may also refer to a molecule, combination of molecules, or combination of elements from the periodic table.

In one aspect, the molecular linking element 706 is a conjugated, nonconjugated, or combination of conjugated and nonconjugated classes of molecules. For example, the molecular linking element may be one of the following elements: linear alkanes, branched alkanes, cycloalkanes, (poly)cycloalkanes, cis- and trans-linear alkenes, cis- and trans-branched alkenes, linear alkynes, branched alkynes, (poly)alkynes, aromatic hydrocarbons, (poly)aromatic hydrocarbons, heteroarenes, (poly)heteroarenes, thiophenes, (poly)thiophenes, (poly)anilines, or combinations of the above-mentioned elements.

In another aspect, the porphyrin macrocycle 702 has four meso positions. With respect to nomenclature, these 4 meso positions are designated (or commonly referred to as) 5, 10, 15 and 20. Therefore, the four meso positions are labeled 710-5, 710-10, 710-15, and 710-20. The (aminophenyl)amine group 708 originates on one meso position of the porphyrin macrocycle (as shown, 710-20). The molecular linking element 706 originates on a second meso position of the porphyrin macrocycle (as shown, 710-10). For example, the (aminophenyl)amine group 708 and molecular linking element 706 may originate on opposite meso positions of the porphyrin macrocycle 702, as shown in Fig. 7.

In one aspect, the anchor group 704 is a chemical group capable of interacting with a substrate via chemical bonding, complexation, coordination, and any mode of interaction promoting communication between the porphyrin macrocycle 702 and a substrate, through the molecular linking element 706. For example, the anchor group 704 may be one of the following chemical groups: carboxylic acids, carboxylates, sulfonic acids, sulfonates, phosphonic acids, phosphonates, malonic acids, malonates, carboxylic acid anhydrides, lactones, cyanoacrylic acids, silanes, or combinations of the above-mentioned chemical groups.

In one aspect, as shown in Fig. 8, the (aminophenyl)amine group 708 is N,N-(4-aminophenyl)amine 708a, with atoms D1-D4, where D1-D4 is a chemical moiety such as hydrogen, alkanes, haloalkanes, aromatic hydrocarbons, halogenated aromatic hydrocarbons, heteroarenes, halogenated heteroarenes, or combinations of the above-mentioned chemical moieties. Then, the porphyrin macrocycle 702 includes an "M" moiety such as H_2 or a metal (e.c. Zn, Ti, Mg, Pd), a first group A1-A5, and a second group B1-B5, where A1-A5 and B1-B5 are chemical moieties such as hydrogen, halogen, amino, alkyl, haloalkyl, alkoxy, haloalkoxy, aryl, haloaryl, aryloxy, haloaryloxy, heteroaryl, haloheteroaryl, heteroaryloxy, haloheteroaryloxy, or combinations of the above-mentioned chemical moieties.

In a different aspect, as shown in Fig. 9, the (aminophenyl)amine 708 is N-phenyl-N-(4-aminophenyl)amine 708b, with D1-D2, where D1-D2 is a chemical moiety such as hydrogen, alkanes, haloalkanes, aromatic hydrocarbons, halogenated aromatic hydrocarbons, heteroarenes, halogenated heteroarenes, or combinations of the above-mentioned chemical moieties. N-phenyl-N-(4-aminophenyl)amine 708b also includes C1-C5, where C1-C5 is a chemical moiety such as hydrogen, halogen, amino, alkyl, haloalkyl, alkoxy, haloalkoxy, aryl, haloaryl, aryloxy, haloaryloxy, heteroaryl, haloheteroaryl, heteroaryloxy, haloheteroarloxy, or combinations of the above-mentioned chemical moieties. Then, the porphyrin macrocycle 702 includes an "M" moiety such as H_2 or a metal (e.c. Zn, Ti, Mg, Pd), a first group A1-A5, and a second group B1-B5, where A1-A5 and B1-B5 are chemical moieties such as hydrogen, halogen, amino, alkyl, haloalkyl, alkoxy, haloalkoxy, aryl, haloaryl, aryloxy, haloaryloxy, heteroaryl, haloheteroaryl, heteroaryloxy, haloheteroaryloxy, and combinations of the above-mentioned chemical moieties.

In one aspect, the anchor group 704 interacts with a substrate 712 such as a metallic, organic, inorganic, organic-inorganic hybrid material, or combinations of the above-mentioned materials.

(Functional Description)

Molecular simulations have been used to calculate absorption/electronic properties for the above-described porphyrin architectures which exhibit unprecedented optical absorption characteristics (up to ~1150 nm).

Fig. 8 is a schematic of a molecular structure of porphyrin-based photosensitizer using N,N-(4-aminophenyl)amine 708a as the electron-donating group on the porphyrin meso position. In this aspect, A1-A5 = hydrogen, halogen, amino, alkyl, haloalkyl, alkoxy, haloalkoxy, aryl, haloaryl, aryloxy, haloaryloxy, heteroaryl, haloheteroaryl, heteroaryloxy, haloheteroaryloxy, or combinations of the above-mentioned chemical moieties, B1-B5= hydrogen, halogen, amino, alkyl, haloalkyl, alkoxy, haloalkoxy, aryl, haloaryl, aryloxy, haloaryloxy, heteroaryl, haloheteroaryl, heteroaryloxy, haloheteroaryloxy, or combinations of the above-mentioned chemical moieties, D1-D4 = hydrogen, alkanes, haloalkanes, aromatic hydrocarbons, halogenated aromatic hydrocarbons, heteroarenes, halogenated heteroarenes, or combinations of the above-mentioned chemical moieties, and M=H_2 or metal (e.c. Zn, Ti, Mg, Pd). The types of materials identified for the molecular linking element 706 and anchor 704 have been described above.

Fig. 9 is a schematic of a molecular structure of porphyrin-based photosensitizer using N-Phenyl-N-(4-aminophenyl)amine 708b as the electron-donating group on the porphyrin meso position. In this aspect, A1-A5 = hydrogen, halogen, amino, alkyl, haloalkyl, alkoxy, haloalkoxy, aryl, haloaryl, aryloxy, haloaryloxy, heteroaryl, haloheteroaryl, heteroaryloxy, haloheteroaryloxy, or combinations of the above-mentioned chemical moieties, B1-B5= hydrogen, halogen, amino, alkyl, haloalkyl, alkoxy, haloalkoxy, aryl, haloaryl, aryloxy, haloaryloxy, heteroaryl, haloheteroaryl, heteroaryloxy, haloheteroaryloxy, or combinations of the above-mentioned chemical moieties, C1-C5= hydrogen, halogen, amino, alkyl, haloalkyl, alkoxy, haloalkoxy, aryl, haloaryl, aryloxy, haloaryloxy, heteroaryl, haloheteroaryl, heteroaryloxy, haloheteroaryloxy, or combinations of the above-mentioned chemical moieties, D1-D2 = hydrogen, alkanes, haloalkanes, aromatic hydrocarbons, halogenated aromatic hydrocarbons, heteroarenes, halogenated heteroarenes, or combinations of the above-mentioned chemical moieties, and M=H_2 or metal (e.c. Zn, Ti, Mg, Pd). The types of materials identified for the molecular linking element 706 and anchor 704 have been described above.

Molecular simulations were carried out using a zinc diphenylporphyrin core with para-ethynylbenzoic acid as the molecular linking element and anchor group with programs of Gaussian and/or GAMESS known in the art. Oscillator strengths were calculated with time dependent density functional theory (TDDFT) using a gradient corrected Becke-Lee-Yang-Parr (BLYP) functional. Calculated oscillator strengths were used to simulate absolute absorption (solid dark curve) and absorption spectra assuming a 5250K blackbody source (solid lighter curve). In all three cases, the blackbody source is represented by the dotted curve. Simulated spectra assuming a 50 nm Gaussian broadening for three different electron-donating groups are shown in Figs. 10-12.

Fig. 10 is a simulated optical absorption spectrum for the YD class of porphyrin photosensitizers, which utilize meso-N,N-diphenylamine as the electron-donating group. In order to simplify the calculations, the tert-butyl groups and n-hexyl groups were omitted from the structure of YD-2 (see Fig. 5). Although the alkyl groups enhance the solubility of the porphyrin in organic solvents and may aid in the suppression of molecular aggregation, the overall contribution of these groups to the optical absorption properties of the porphyrin is negligible.

Fig. 11 is a simulated optical absorption spectrum for the class of porphyrin photosensitizers which utilizes meso-N,N-(4-aminophenyl)amine as the electron-donating group. Using the molecular diagram in Fig. 8 as a guide, the structure is consistent with the following: A1-A5=H, B1-B5=H, D1-D4=H and M=zinc.

Fig. 12 is a simulated optical absorption spectrum for the class of porphyrin photosensitizers which utilizes meso-N-Phenyl-N-(4-aminophenyl)amine as the electron-donating group. Using the molecular diagram in Fig. 9 as a guide, the structure is consistent with the following: A1-A5=H, B1-B5=H, C1-C5=H, D1-D2=H and M=zinc.

Based upon the molecular simulations, it is evident that the porphyrin Soret Band (~450 nm) is essentially unaffected by changes in the nature of the electron-donating (meso-diphenylamine) group for the classes of YD, N,N-(4-aminophenyl)amine and N-phenyl-N-(4-aminophenyl)amine porphyrin photosensitizers respectively. In contrast, there is a dramatically red-shifted Q-band absorption along the series from the YD porphyrin (850 nm for meso-N,N-diphenylamine, Fig. 10) to N,N-(4-aminophenyl)amine (1150 nm for meso-N,N-(4-aminophenyl)amine, Fig. 11). N-phenyl-N-(4-aminophenyl)amine, which may be considered to be an “intermediate” between YD and N,N-(4-aminophenyl)amine, also shows significant red-shifted Q-band absorption (1050 nm for meso-N-Phenyl-N-(4-aminophenyl)amine, Fig. 12) relative to YD reference although to a lower extent than N,N-(4-aminophenyl)amine. Based upon the experimental optical absorption spectra for YD compounds reported in the literature, the simulation results may overestimate the bathochromic shift for the porphyrin Q-Band to some extent; however, the general trend indicated by meso-N,N-(4-aminophenyl)amine and meso-N-Phenyl-N-(4-aminophenyl)amine substitution is realistic. Therefore, the expected red-shifted absorption due to the meso-N,N-(4-aminophenyl)amine electron-donating group in N,N-(4-aminophenyl)amine can be conservatively estimated to be greater than 800 nm, thus, rendering this class of compounds appropriate as long wavelength absorber materials (400 to >800 nm) for DSSCs. In addition, similar calculations were made using a zinc metallated phthalocyanine core rather than diphenylporphyrin and a similar bathochromic shift was indicated. Therefore, it is likely that such bathochromic shifts are characteristic of these electron-donating groups when suitably attached to a highly delocalized π-system core.

In one aspect, the porphyrin photosensitizer architectures exhibit 2 major characteristics. First, the design imparts a high degree of orbital partitioning (HOMO-LUMO energy distribution). Second, the absorption of a porphyrin material has been pushed towards longer wavelengths in order to more efficiently harvest broader and longer wavelength regions of the spectrum. To some extent, this is facilitated by the orbital partitioning described above, although there are some additional contributing factors which are linked in many ways to the structures. In general, porphyrins exhibit absorption in 2 discrete wavelength regions: strong absorption ~400-450 nm (Soret Band) and considerably weaker absorption at longer wavelengths (550-

700 nm or Q-Band region). In almost all cases, the absorption in the 450-550 nm region (or along an even broader range of this intermittent region) approaches zero. In general, it is quite rare to find a porphyrin material that absorbs light to any significant extent beyond 700 nm and which, at the same time, meets the structural requirements to be promising as an efficient photosensitizer in DSSC. In fact, the "best" performing porphyrin-based photosensitizer in DSSC to date (~11% efficiency, 2010) demonstrates negligible absorption beyond 700 nm, although some residual absorption remains up to ~725 nm or perhaps slightly beyond.

A long wavelength absorbing porphyrin/metalloporphyrin molecule has been provided.

Another example

The synthesis of zinc porphyrin photosensitizer (Compound A) proceeded in 9 synthetic steps including purification, characterization and optimization following each individual reaction.

Figure 13 shows the synthetic reaction pathway towards the preparation of Compound A.

Step 1-3: Synthesis of dipyrrylmethane precursor [Step 1], porphyrin cyclization reaction [Step 2], and zinc metallation [Step 3].

Step 4-6: Meso-bromination with N-bromosuccinimide(NBS) [Step 4], meso-coupling with (triisopropylsilyl)acetylene using tetrakis(triphenylphosphine)palladium(0) and copper(1) iodide [Step 5] followed by meso-bromination with NBS [Step 6].

Step 7-9: modified Buchwald Hartwig cross-coupling with bis(4-dimethylaminophenyl)amine using tris(dibenzylideneacetone)dipalladium(0), sodium tert-butoxide and tri-tert-butylphosphine [Step 7]: deprotection of triisopropylsilyl group using tetrabutylammonium fluoride in tetrahydrofuran [Step 8] and coupling of terminal acetylene to 4-iodobenzoic acid using tris(dibenzylideneacetone) dipalladium(0) and triphenylarsine [Step 9].

The consequences of meso-substitution on the zinc porphyrin core by bis(4-dimethylaminophenyl)amine and (triisopropylsilyl)acetylene are evident in the optical absorption spectrum for ZnP3, which is a synthetic precursor to Compound A (see Figure 14). The optical absorption spectrum of 3 exhibits classical porphyrin features including strong absorption for the Soret band (~425nm) and weaker absorption for the lower energy Q-Bands. The absorption band centered around 300 nm is attributed to the bis(4-dimethylaminophenyl)amine group on the porphyrin periphery. Noteworthy is the fact that absorption extends beyond 800 nm for Znp3, which is generally uncommon for porphyrin-based photosensitizer arrays.

Figure 14 shows optical absorption spectrum of Zinc porphyrin(Znp3) in dichloromethane from 250 nm to 900 nm at high(upper line) and dilute(lower line) concentrations. Y-axis shows absorbance in arbitrary units (au). X-axis shows wavelength in nanometers (nm).

The optical absorption spectra of Compound A at higher, lower and dilute concentrations in dichloromethane are presented in Figure 15. Compound A exhibits strong and broad absorption for the porphyrin Soret bands along with moderate absorption at those wavelengths corresponding to the lower energy Q-bands. As in the case of 3, optical absorption for the porphyrin extends well beyond the 700 nm range and approaches zero at approximately 900 nm.

Figure 15 shows optical absorption spectrum of Compound A in dichloromethane from 250 nm to 900 nm at high(upper line), lower(middle line) and dilute(lower line) concentrations. Y-axis shows absorbance in arbitrary units (au). X-axis shows wavelength in nanometers (nm).

For comparison, the optical absorption spectra of Compound A and synthetic precursor ZnP3 are plotted on the same graph in Figure 16. Although no significant bathochromic shift is observed for the porphyrin Q-band region following installation of the parabenzoic acid anchor group onto 3(to afford Compound A), a slight broadening and red-shifted absorption for the Soret band does indeed occur. This phenomenon arises from both an increased molecular conjugation and orbital partitioning due to the presence of the carboxylic acid group, which functions as an electron accepting moiety.

Figure 16 shows optical absorption spectrum of ZnP3 and Compound A in dichloromethane from 250 nm to 880 nm, for which absorbance has been normalized at the Soret band. Y-axis shows absorbance in arbitrary units (au). X-axis shows wavelength in nanometers (nm).

Examples of particular derivatives have been presented to illustrate the invention. However, the invention is not limited to merely these examples. Other variations and embodiments of the invention will occur to those skilled in the art.

CLAIMS

1. A long wavelength absorbing porphyrin/metalloporphyrin molecule comprising:

a porphyrin macrocycle;

an anchor group for attachment to a substrate;

a molecular linking element interposed between the porphyrin macrocycle and the anchor group; and,

an (aminophenyl)amine group selected from a group consisting of N,N-(4-aminophenyl)amine and N-phenyl-N-(4-aminophenyl)amine, where an amino moiety of the 4-aminophenyl group is derivatized by an element selected from a group consisting of hydrogen, alkanes, haloalkanes, aromatic hydrocarbons, halogenated aromatic hydrocarbons, heteroarenes, halogenated heteroarenes, and combinations of the above-mentioned elements.

2. The porphyrin/metalloporphyrin molecule of claim 1 wherein the molecular linking element is selected from a group consisting of conjugated, nonconjugated, and combinations of conjugated and nonconjugated classes of molecules.

3. The porphyrin/metalloporphyrin molecule of claim 1 wherein the porphyrin macrocycle has four meso positions;

wherein the (aminophenyl)amine group originates on one meso position of the porphyrin macrocycle; and,

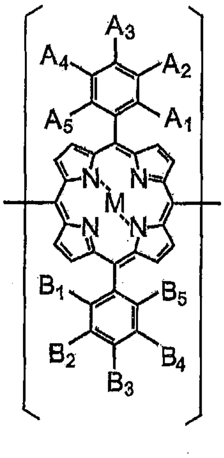
wherein the molecular linking element originates on a second meso position of the porphyrin macrocycle.

4. The porphyrin/metalloporphyrin molecule of claim 3 wherein the (aminophenyl)amine group and the molecular linking element originate on opposite meso positions of the porphyrin macrocycle.

5. The porphyrin/metalloporphyrin molecule of claim 1 wherein

the porphyrin macrocycle includes an "M" moiety selected from a group consisting of H_2 and a metal, and

the porphyrin macrocycle is represented by formula I.



: formula I

6. The porphyrin/metalloporphyrin molecule of claim 1 wherein the molecular linking element is selected from a group of elements consisting of linear alkanes, branched alkanes, cycloalkanes, (poly)cycloalkanes, cis- and trans-linear alkenes, cis- and trans-branched alkenes, linear alkynes, branched alkynes, (poly)alkynes, aromatic hydrocarbons, (poly)aromatic hydrocarbons, heteroarenes, (poly)heteroarenes, thiophenes, (poly)thiophenes, (poly)anilines, and combinations of the above-mentioned elements.

7. The porphyrin/metalloporphyrin molecule of claim 1 wherein the anchor group is a chemical group capable of interacting with a substrate via chemical bonding, complexation, coordination, and any mode of interaction promoting communication between the porphyrin macrocycle and a substrate, through the molecular linking element.

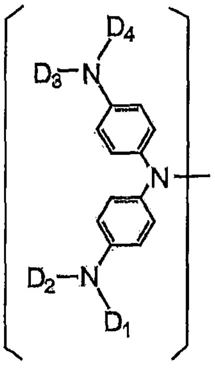
8. The porphyrin/metalloporphyrin molecule of claim 1 wherein the anchor group is selected from a chemical group consisting of carboxylic acids, carboxylates, sulfonic acids, sulfonates, phosphonic acids, phosphonates, malonic acids, malonates, carboxylic acid anhydrides,

lactones, cyanoacrylic acids, silanes, and combinations of the above-mentioned chemical groups.

9. The porphyrin/metalloporphyrin molecule of claim 1 wherein the (aminophenyl)amine group is N,N-(4-aminophenyl)amine, with atoms D1-D4, where D1-D4 is selected from a group of chemical moieties consisting of hydrogen, alkanes, haloalkanes, aromatic hydrocarbons, halogenated aromatic hydrocarbons, heteroarenes, halogenated heteroarenes, and combinations of the above-mentioned chemical moieties;

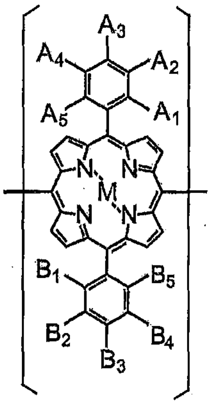
wherein the porphyrin macrocycle includes an “M” moiety selected from a group consisting of H_2 and a metal, a first group A1-A5, and a second group B1-B5, where A1-A5 and B1-B5 are selected from a group of chemical moieties consisting of hydrogen, halogen, amino, alkyl, haloalkyl, alkoxy, haloalkoxy, aryl, haloaryl, aryloxy, haloaryloxy, heteroaryl, haloheteroaryl, heteroaryloxy, haloheteroaryloxy, and combinations of the above-mentioned chemical moieties, and

wherein the (aminophenyl)amine group is represented by formula II, and



: formula II

the porphyrin macrocycle is represented by formula III.



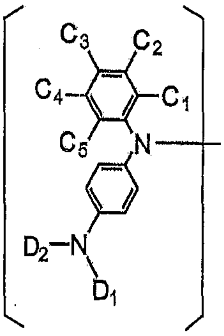
: formula III

10. The porphyrin/metalloporphyrin molecule of claim 1 wherein the (aminophenyl)amine is N-phenyl-N-(4-aminophenyl)amine, with D1-D2, where D1-D2 is selected from a group of chemical moieties consisting of hydrogen, alkanes, haloalkanes, aromatic hydrocarbons, halogenated aromatic hydrocarbons, heteroarenes, halogenated heteroarenes, and combinations of the above-mentioned chemical moieties, and with C1-C5, where C1-C5 is selected from a group of chemical moieties consisting of hydrogen, halogen, amino, alkyl, haloalkyl, alkoxy, haloalkoxy, aryl, haloaryl, aryloxy, haloaryloxy, heteroaryl, haloheteroaryl,

heteroaryloxy, haloheteroarloxy, and combinations of the above-mentioned chemical moieties;

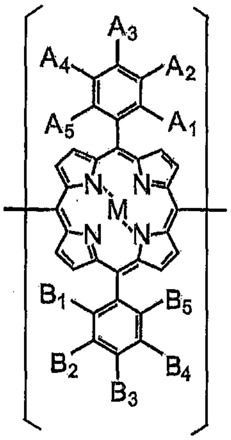
wherein the porphyrin macrocycle includes an "M" moiety selected from a group consisting of H_2 and a metal, a first group A1-A5, and a second group B1-B5, where A1-A5 and B1-B5 are selected from a group of chemical moieties consisting of hydrogen, halogen, amino, alkyl, haloalkyl, alkoxy, haloalkoxy, aryl, haloaryl, aryloxy, haloaryloxy, heteroaryl, haloheteroaryl, heteroaryloxy, haloheteroaryloxy, and combinations of the above-mentioned chemical moieties, and

wherein the (aminophenyl)amine is represented by formula IV, and



: formula IV

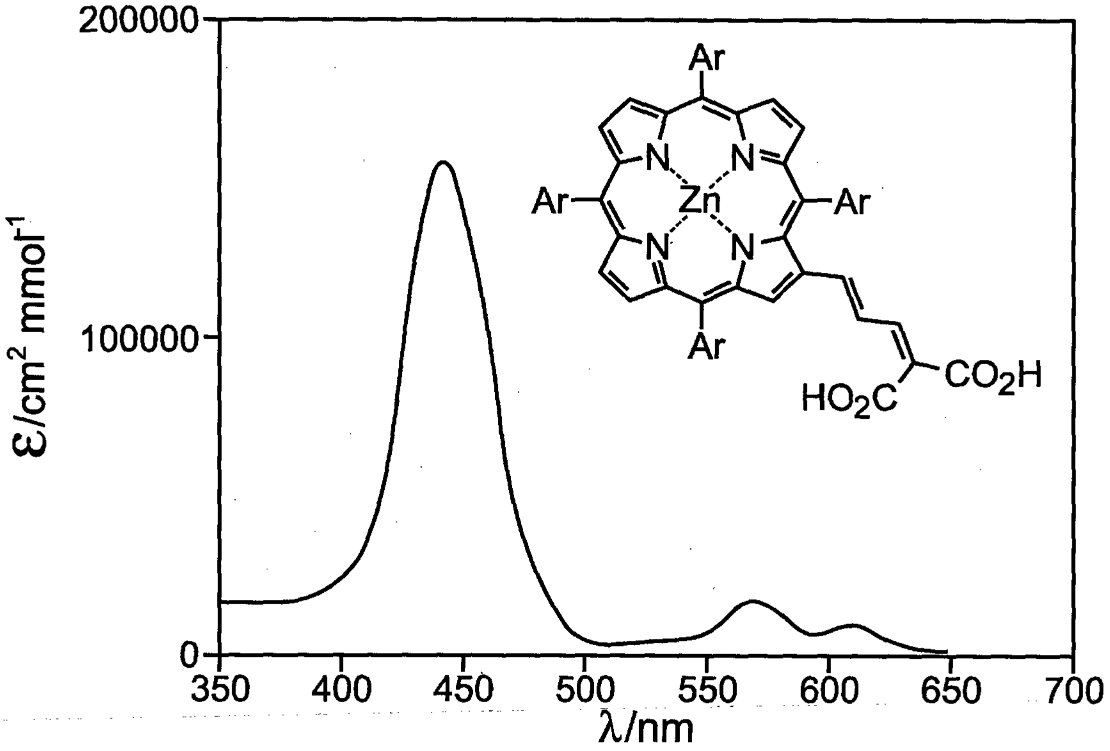
the porphyrin macrocycle is represented by formula V.



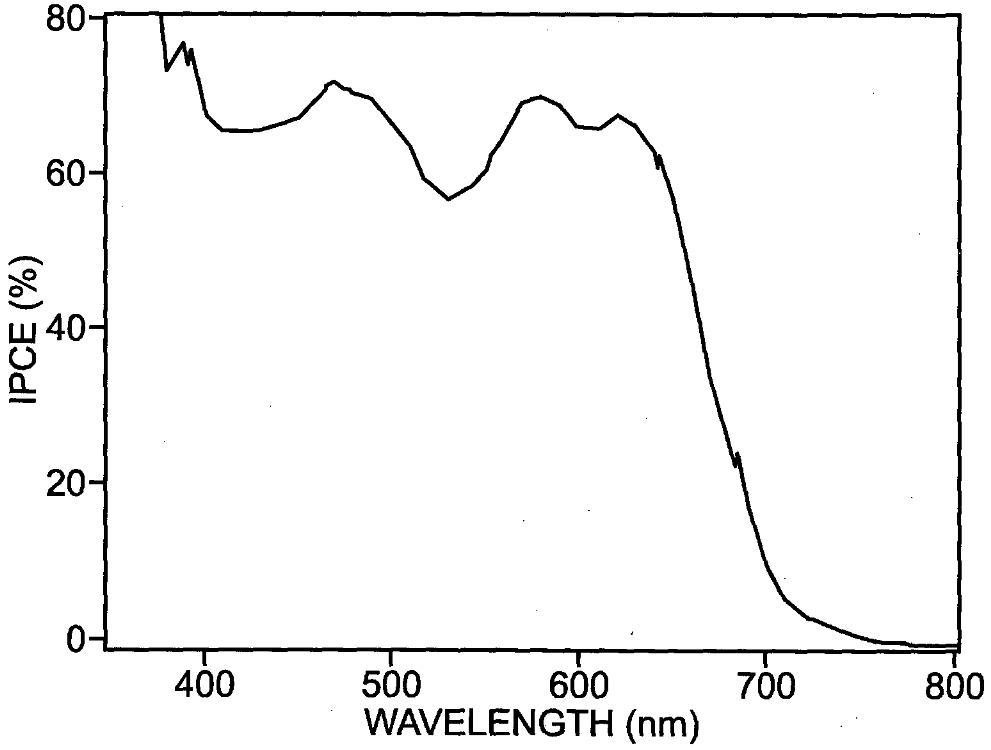
: formula V

11. The porphyrin/metalloporphyrin molecule of claim 1 wherein the anchor group interacts with a substrate selected from a group consisting of metallic, organic, inorganic, organic-inorganic hybrid material, and combinations of the above-mentioned materials.

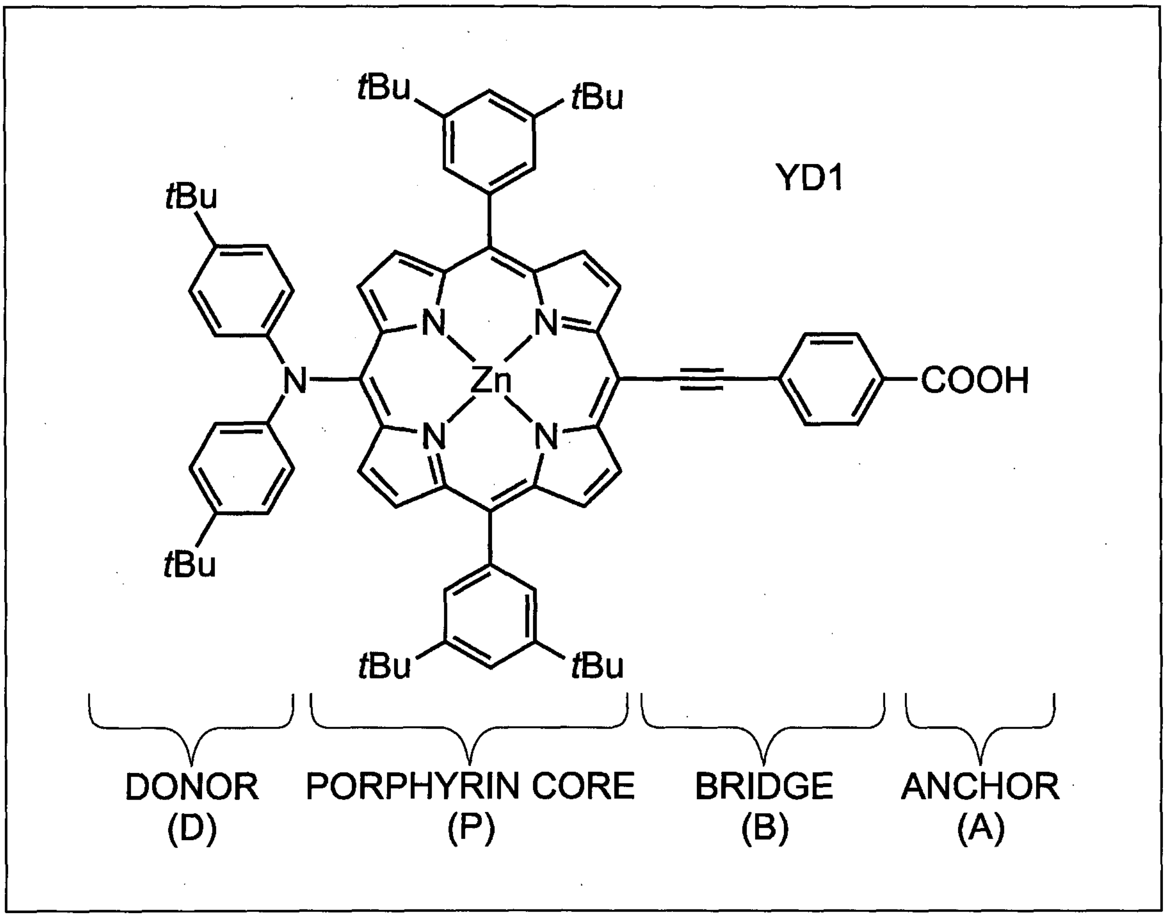
F I G. 1 A


200000
100000
0
ε/cm² mmol⁻¹
350
400
450
500
550
600
650
700
λ/nm
Ar
Ar
Ar
Ar
N
N
N
N
Zn
HO₂C
CO₂H

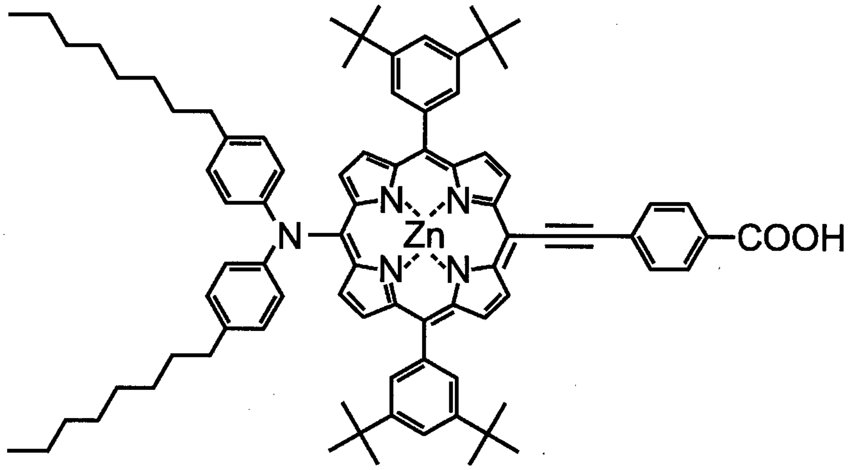
F I G. 1 B


80
60
40
20
0
IPCE (%)
400
500
600
700
800
WAVELENGTH (nm)

F I G. 2

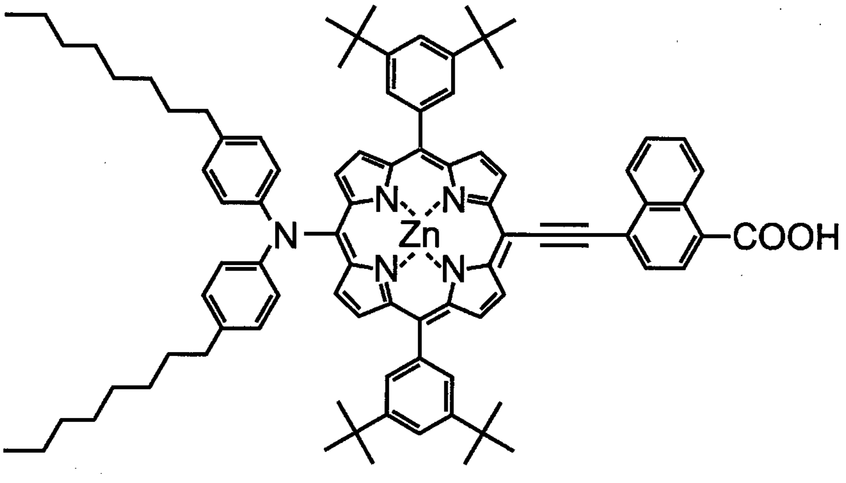

YD1
tBu
tBu
tBu
tBu
tBu
tBu
N
Zn
N
COOH
DONOR
(D)
PORPHYRIN CORE
(P)
BRIDGE
(B)
ANCHOR
(A)

ＦＩＧ．３Ａ



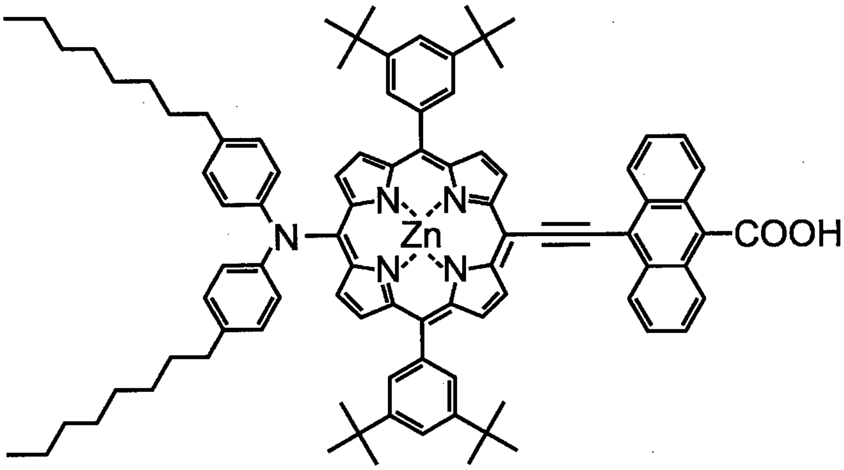
YD11

ＦＩＧ．３Ｂ



YD12

F I G. 3 C



YD13

F I G. 4

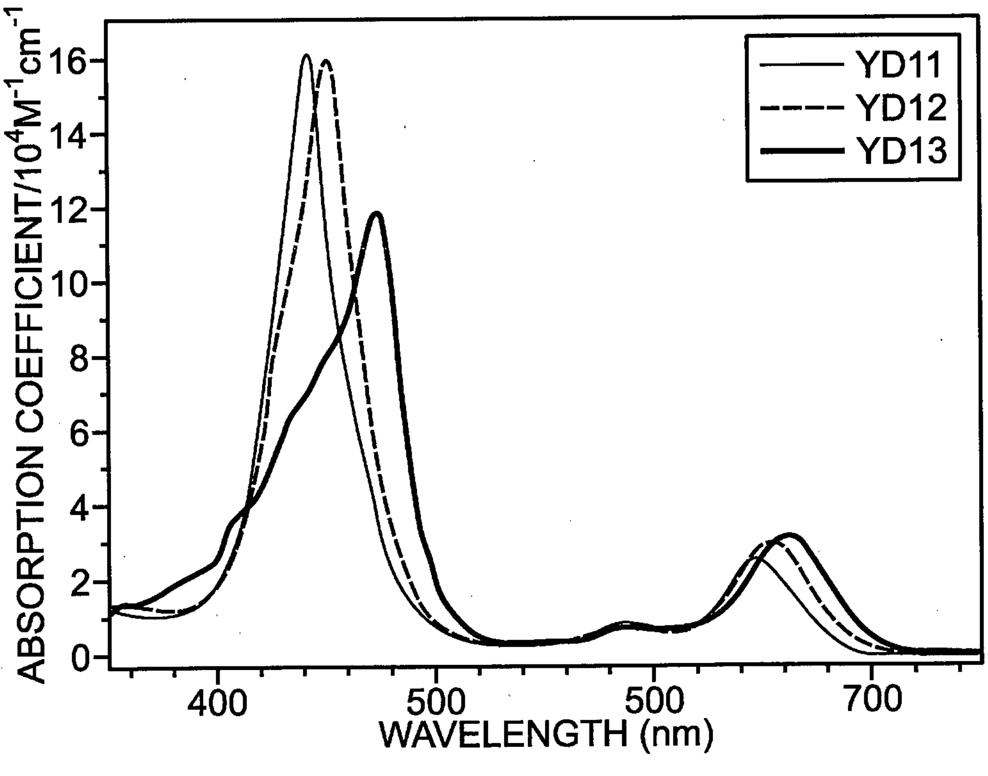


FIG. 5

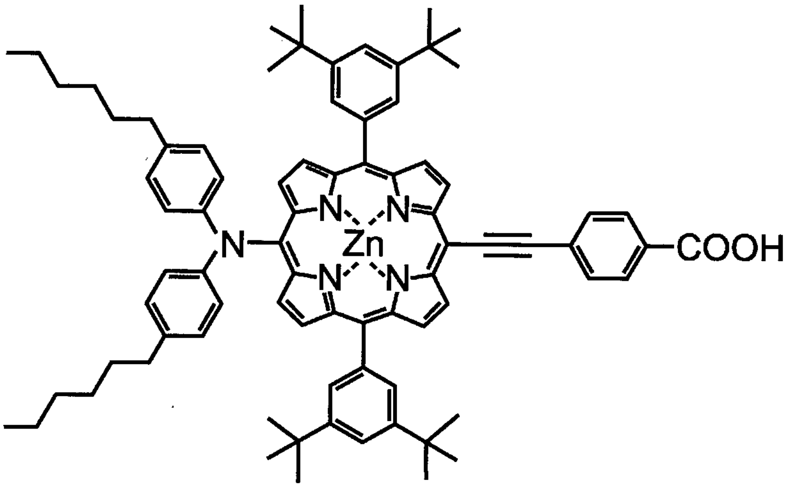
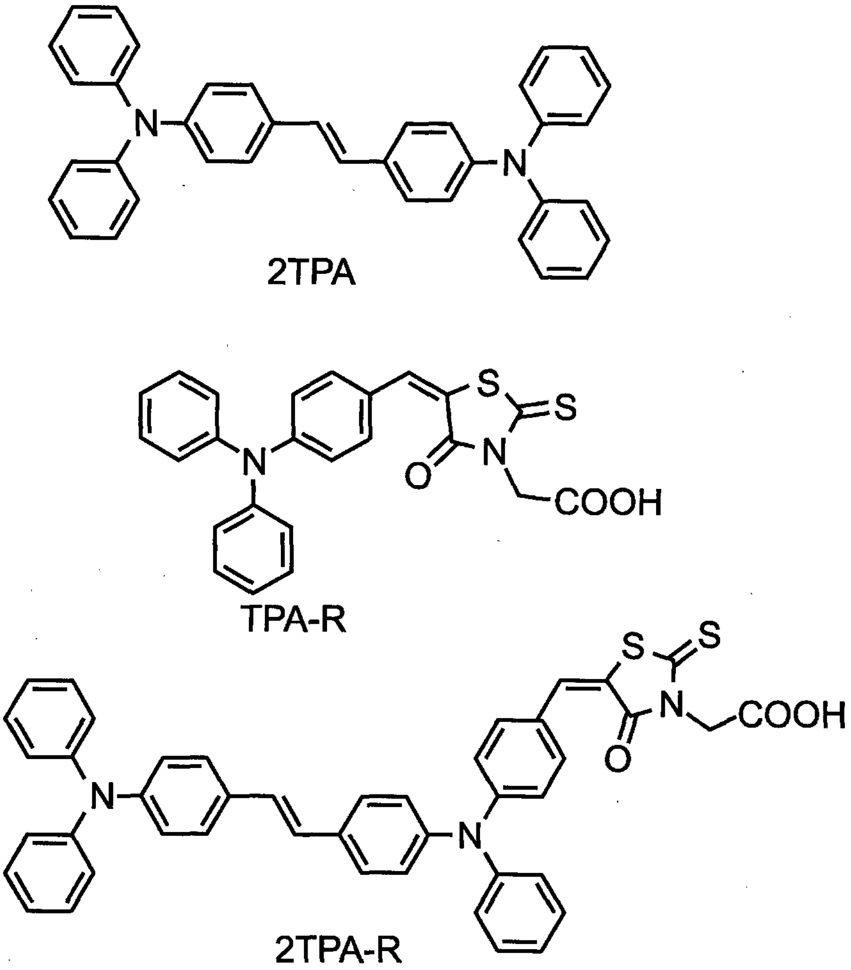
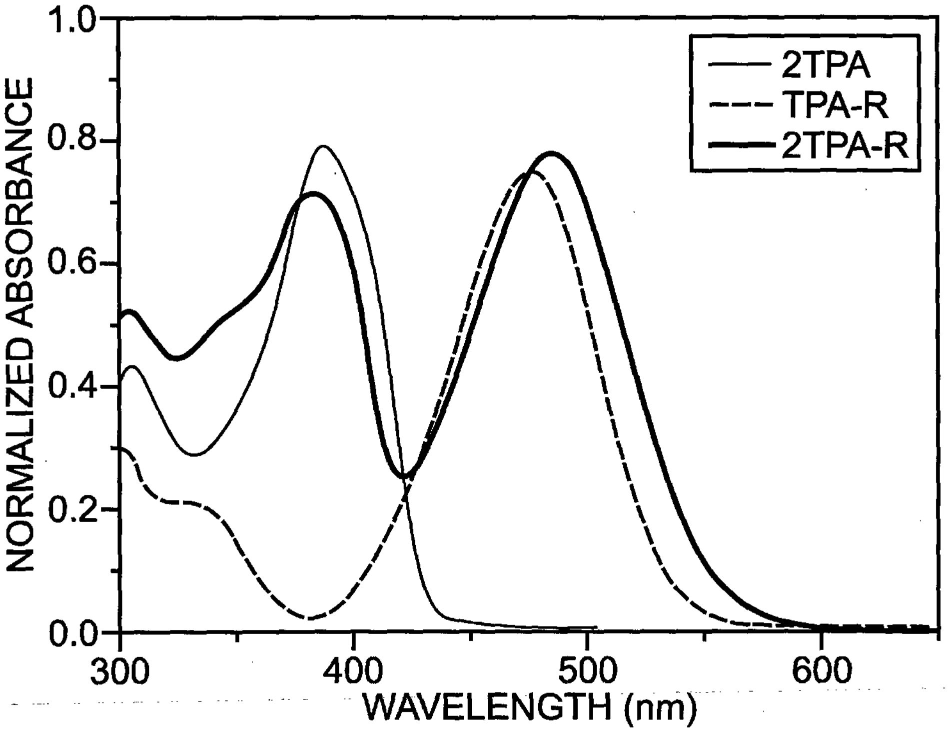


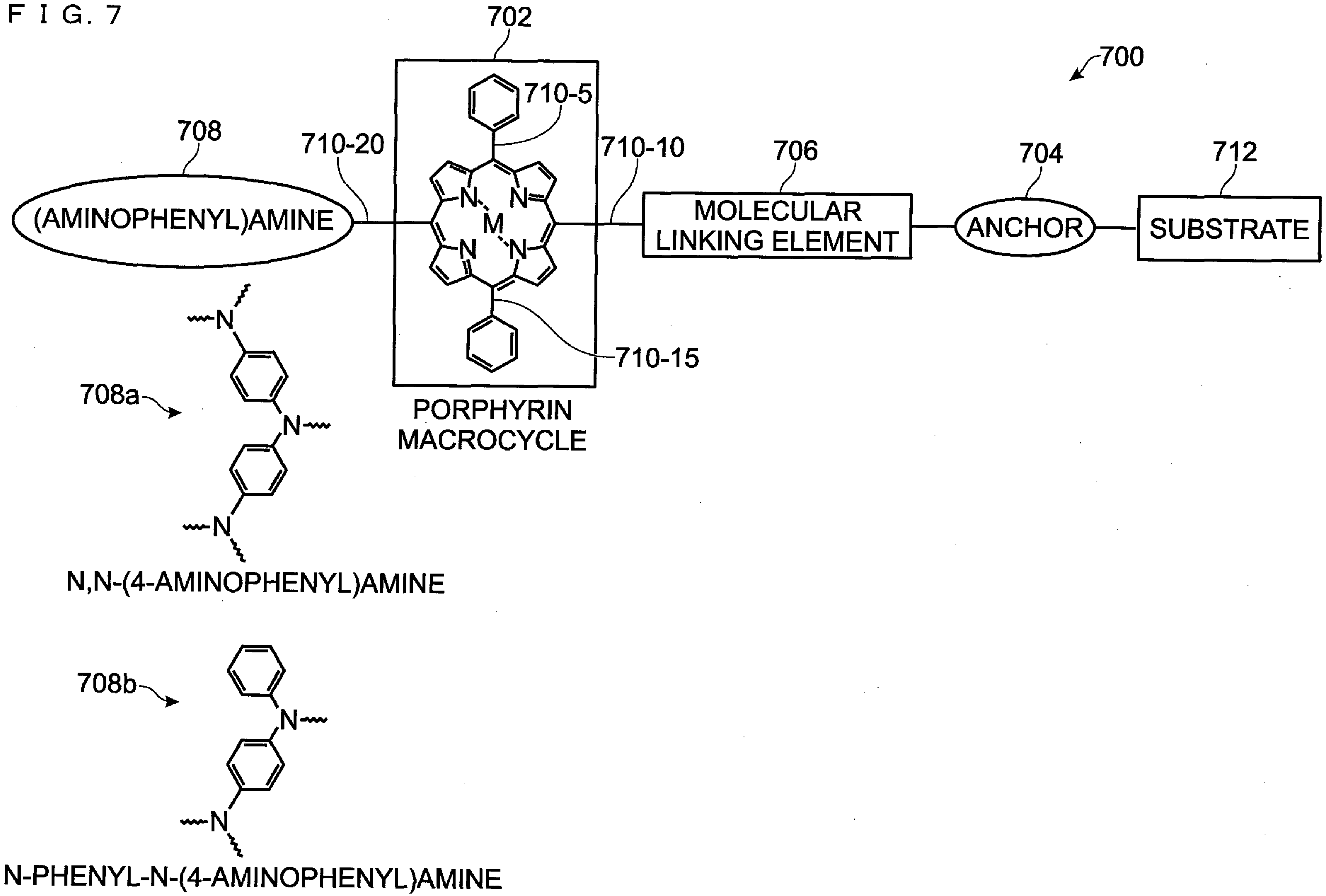
FIG. 6A



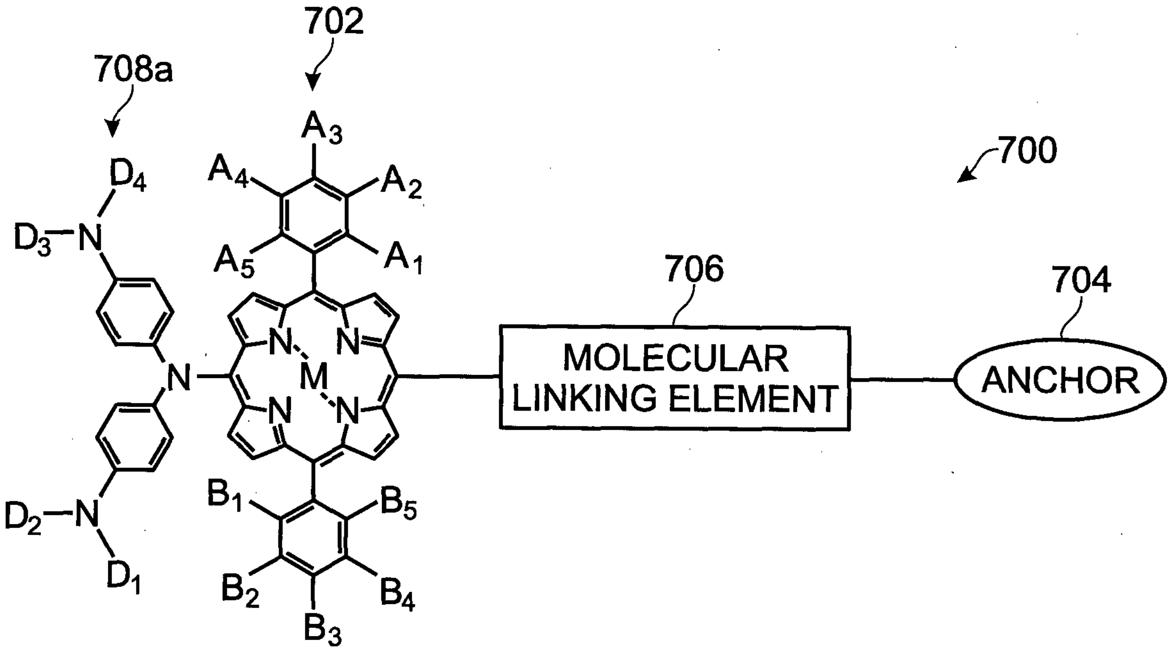
F I G. 6 B


1.0
0.8
0.6
0.4
0.2
0.0
NORMALIZED ABSORBANCE
300
400
500
600
WAVELENGTH (nm)
2TPA
TPA-R
2TPA-R

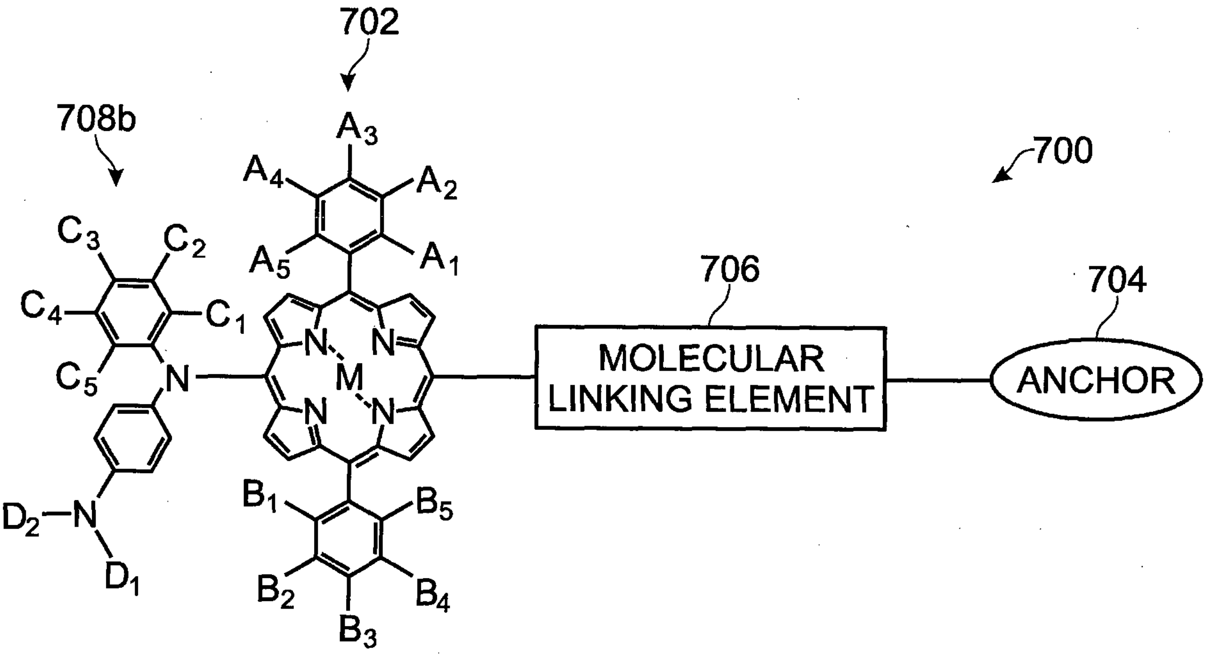
F I G. 7


702
700
708
710-20
710-5
710-10
706
704
712
(AMINOPHENYL)AMINE
M
N
MOLECULAR LINKING ELEMENT
ANCHOR
SUBSTRATE
710-15
708a
PORPHYRIN MACROCYCLE
N,N-(4-AMINOPHENYL)AMINE
708b
N-PHENYL-N-(4-AMINOPHENYL)AMINE

F I G. 8


702
708a
700
A3
A4
A2
A5
A1
D4
D3
D2
D1
N
M
706
MOLECULAR LINKING ELEMENT
704
ANCHOR
B1
B5
B2
B4
B3

F I G. 9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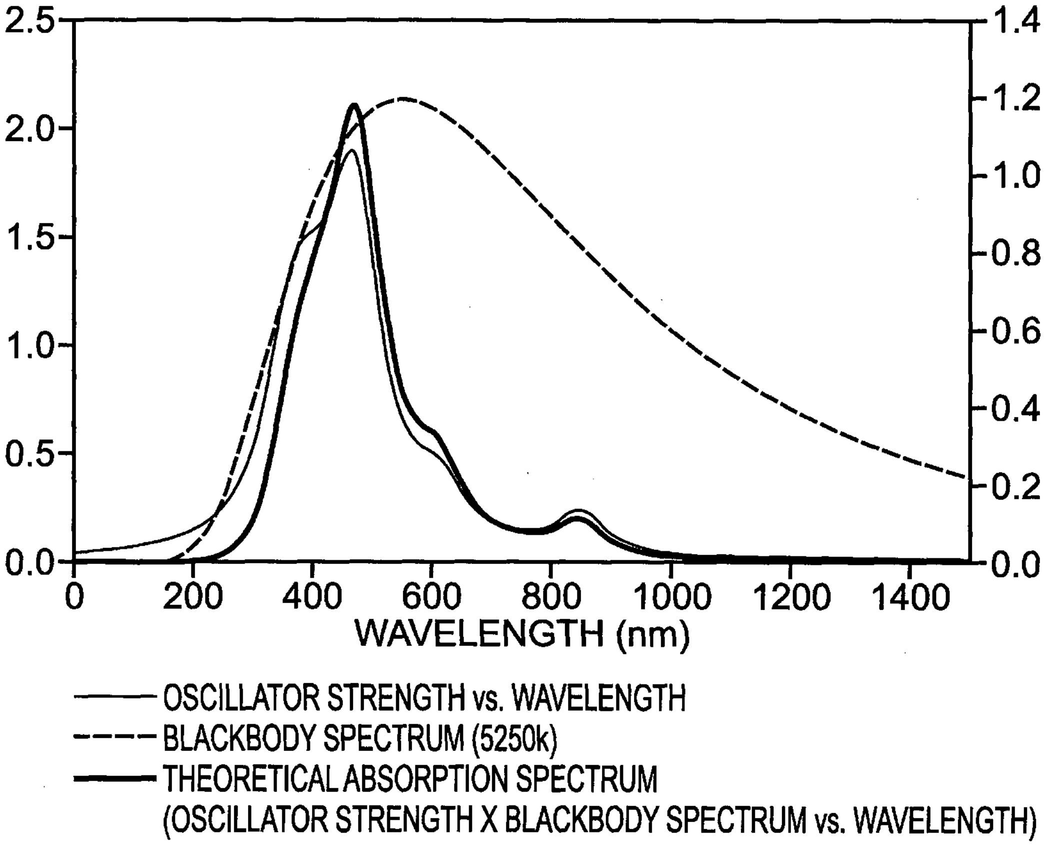
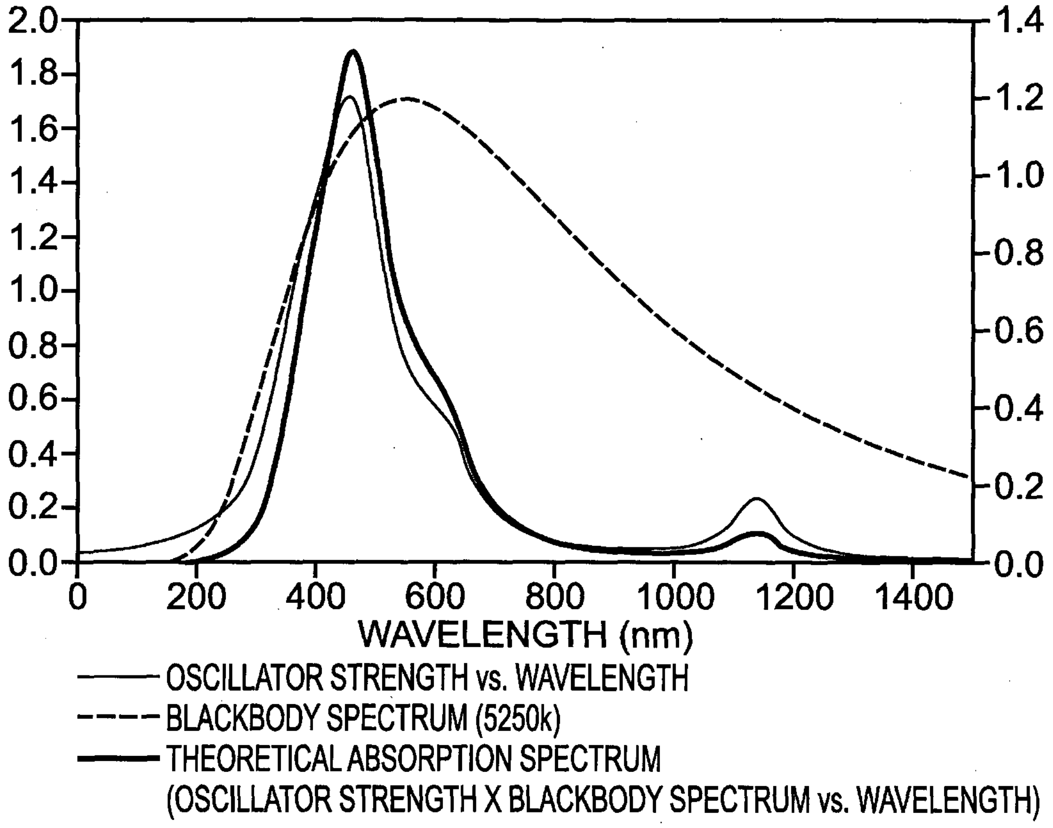
700
A3
A4
A2
A5
A1
C3
C2
C4
C1
C5
N
M
D2
D1
706
MOLECULAR LINKING ELEMENT
704
ANCHOR
B1
B5
B2
B4
B3

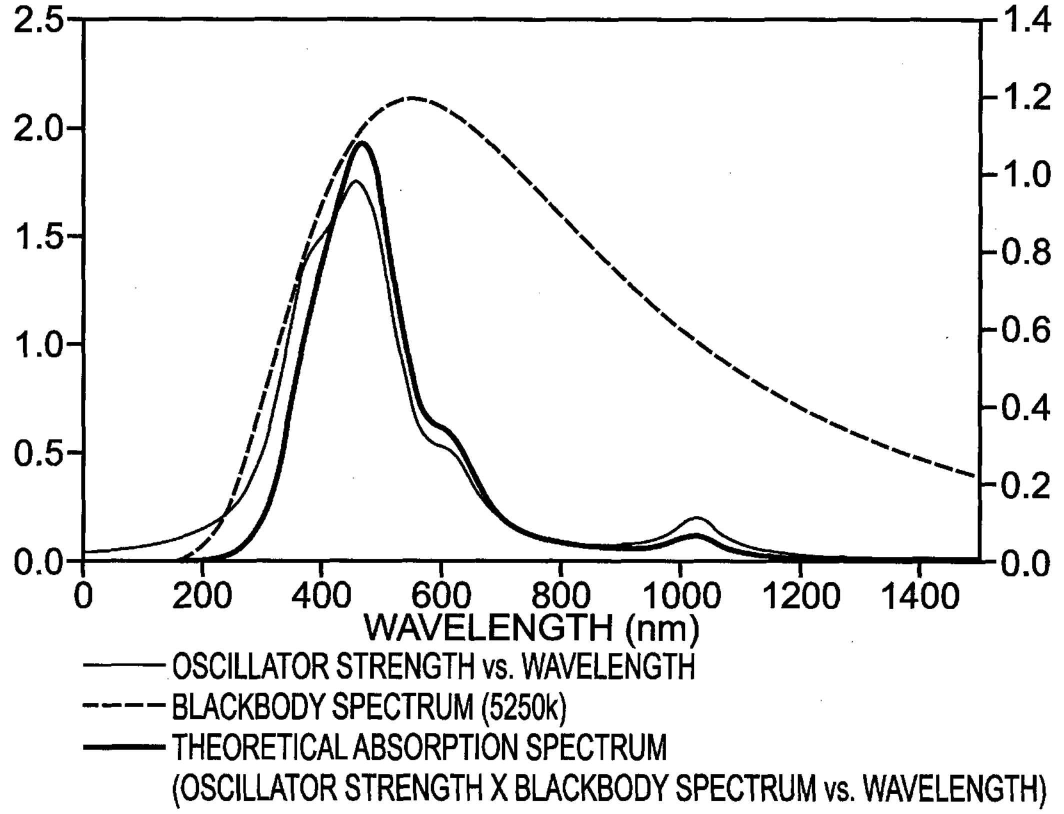
FIG. 10


2.5
2.0
1.5
1.0
0.5
0.0
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
WAVELENGTH (nm)
OSCILLATOR STRENGTH vs. WAVELENGTH
BLACKBODY SPECTRUM (5250k)
THEORETICAL ABSORPTION SPECTRUM
(OSCILLATOR STRENGTH X BLACKBODY SPECTRUM vs. WAVELENGTH)

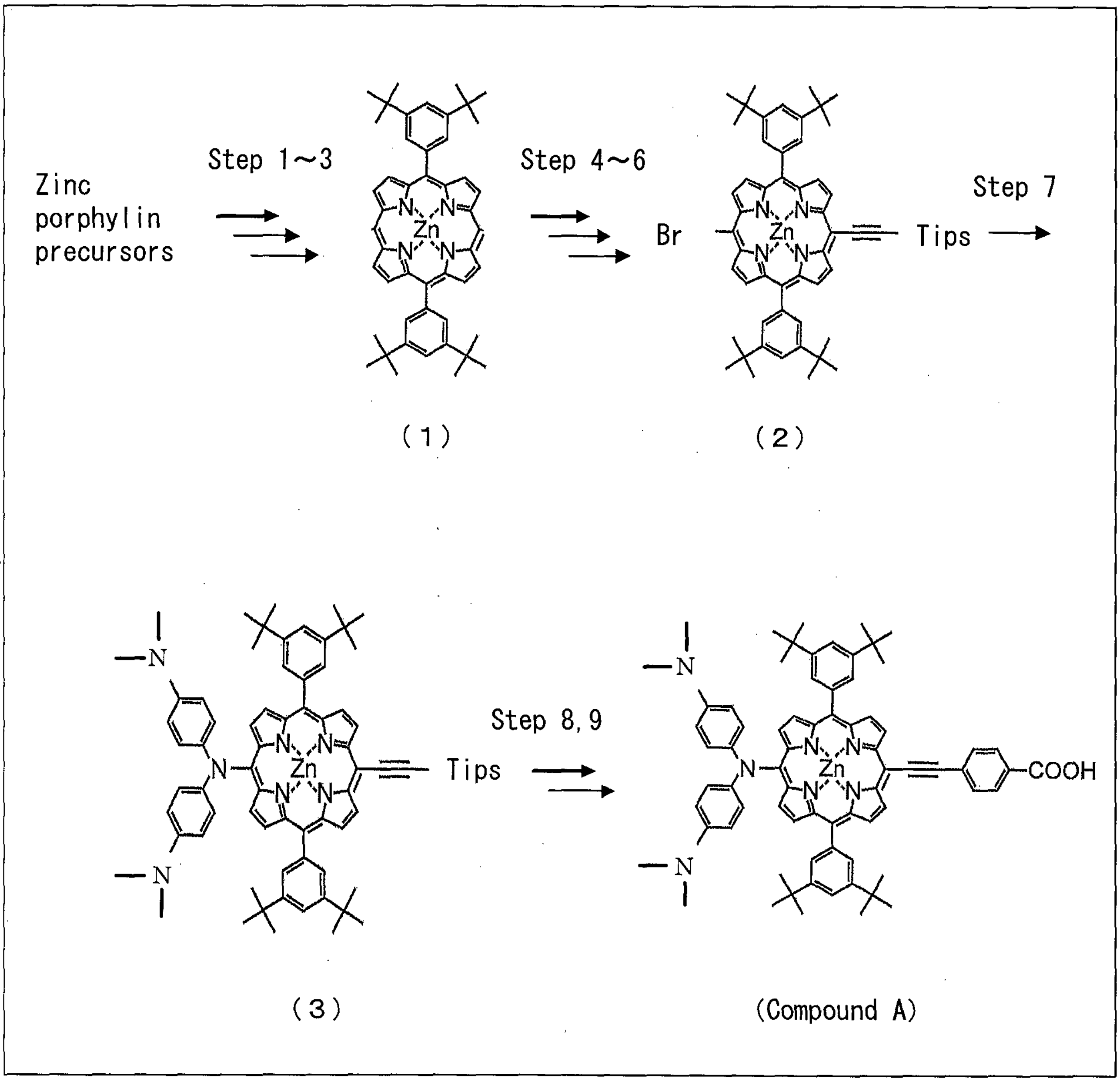
F I G. 1 1


2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
WAVELENGTH (nm)
OSCILLATOR STRENGTH vs. WAVELENGTH
BLACKBODY SPECTRUM (5250k)
THEORETICAL ABSORPTION SPECTRUM
(OSCILLATOR STRENGTH X BLACKBODY SPECTRUM vs. WAVELENGTH)

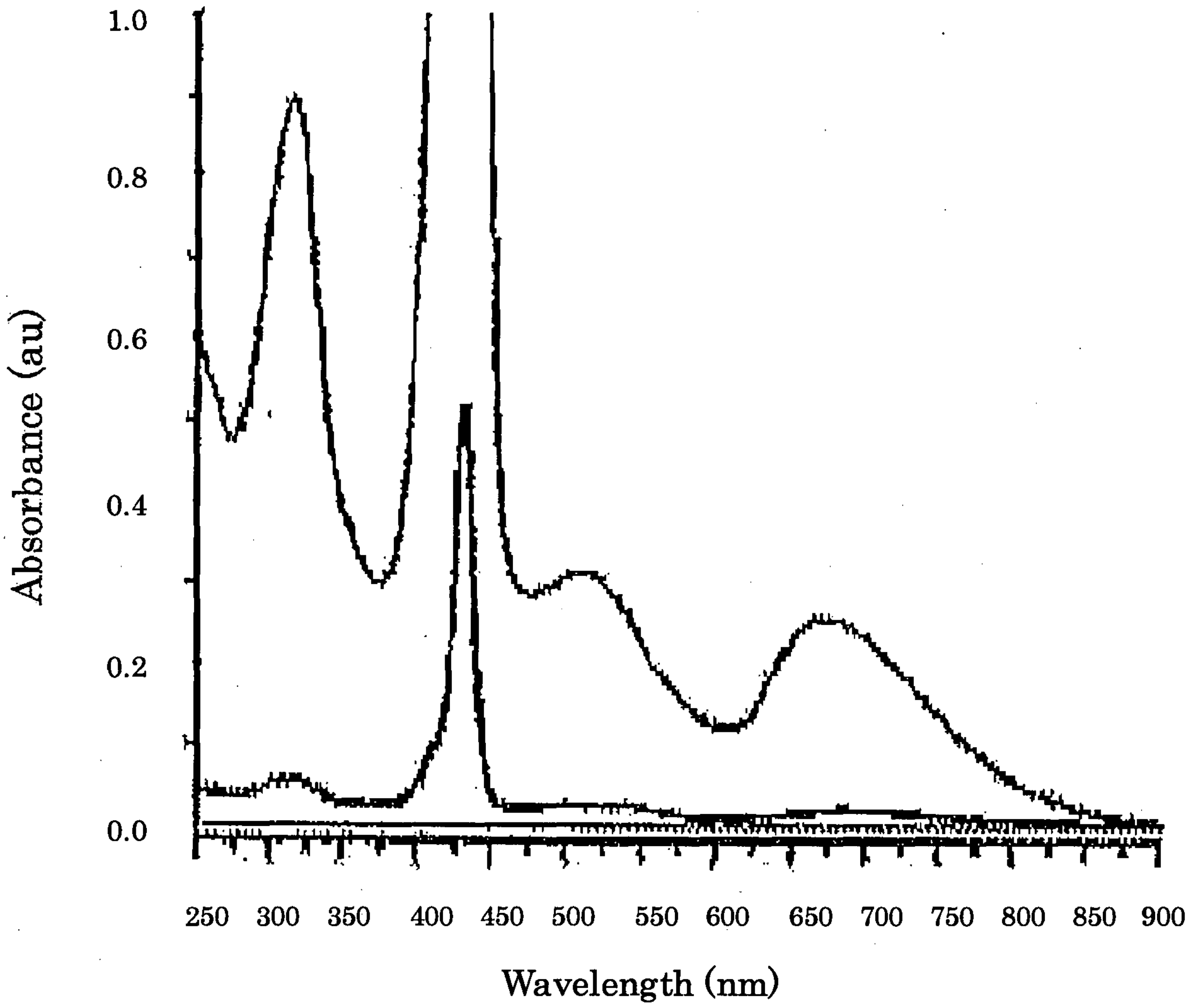
F I G. 1 2


2.5
2.0
1.5
1.0
0.5
0.0
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
WAVELENGTH (nm)
OSCILLATOR STRENGTH vs. WAVELENGTH
BLACKBODY SPECTRUM (5250k)
THEORETICAL ABSORPTION SPECTRUM
(OSCILLATOR STRENGTH X BLACKBODY SPECTRUM vs. WAVELENGTH)

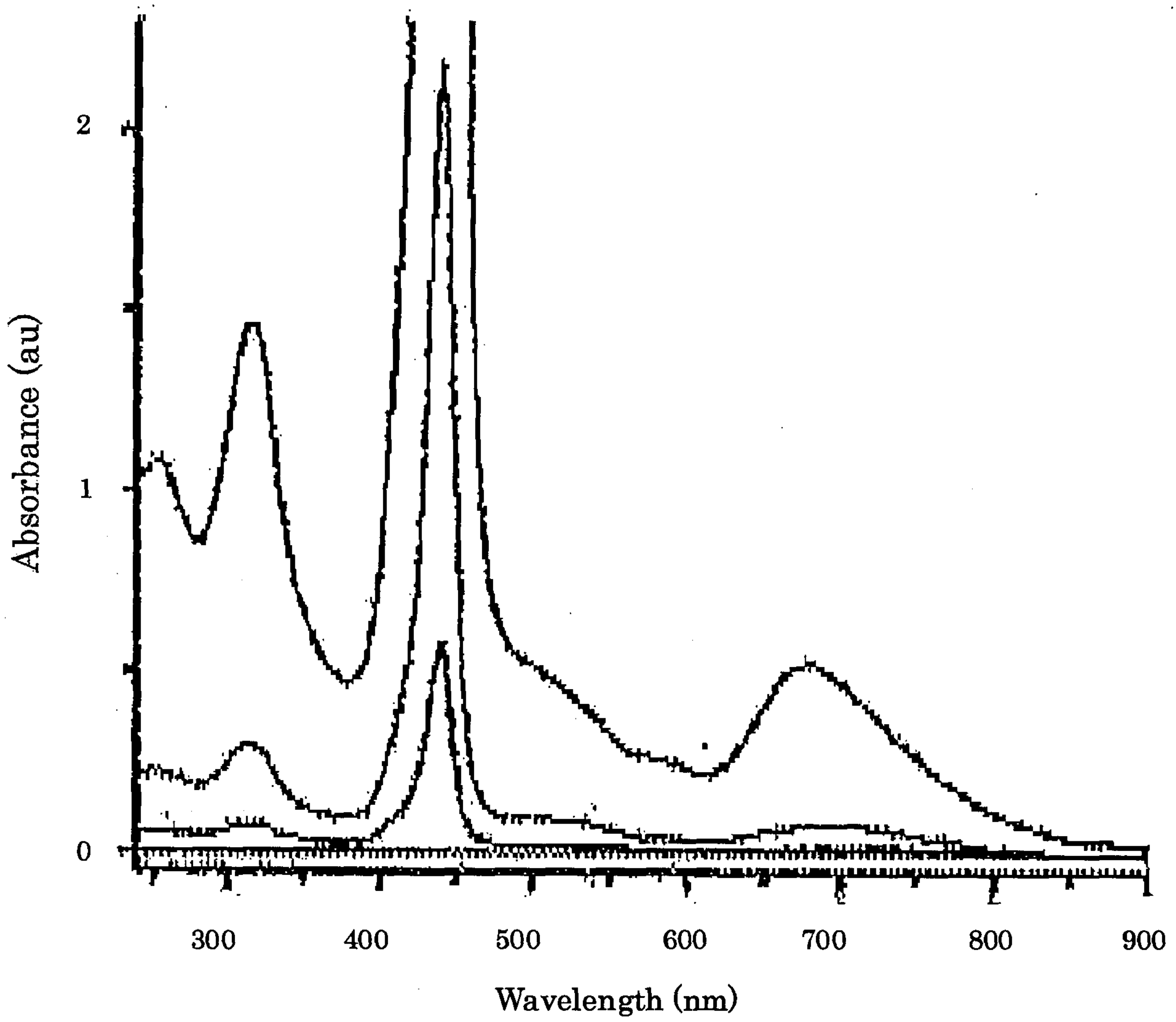
F I G. 1 3


Zinc
porphylin
precursors
Step 1~3
Zn
N
(1)
Step 4~6
Br
Tips
(2)
Step 7
(3)
Step 8, 9
COOH
(Compound A)

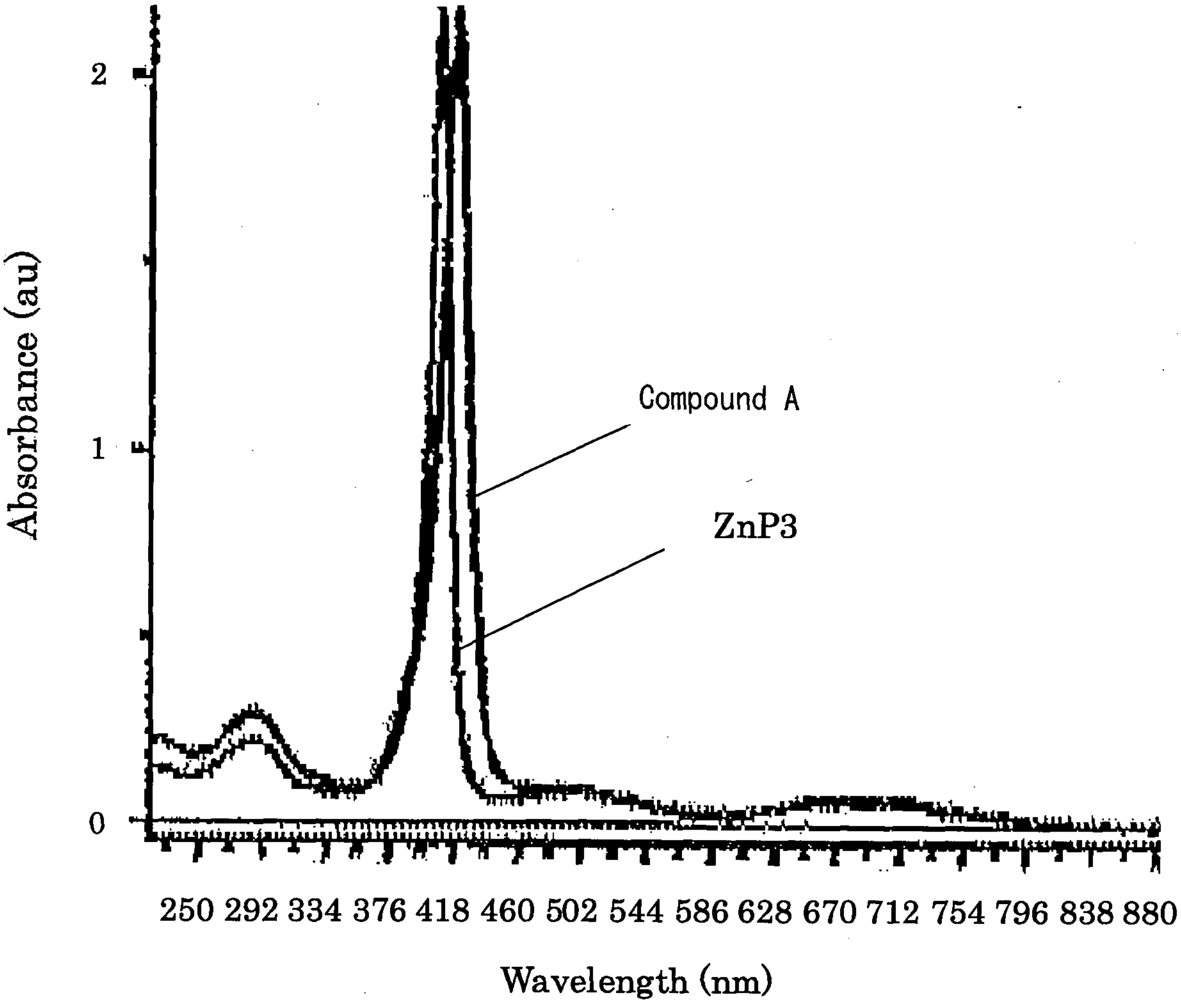
F I G. 1 4


1.0
0.8
0.6
0.4
0.2
0.0
Absorbance (au)
250
300
350
400
450
500
550
600
650
700
750
800
850
900
Wavelength (nm)

F I G. 1 5



F I G. 1 6


Absorbance (au)
2
1
0
Compound A
ZnP3
250 292 334 376 418 460 502 544 586 628 670 712 754 796 838 880
Wavelength (nm)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/064338

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C07D487/22(2006.01)i, H01L31/04(2006.01)i, H01M14/00(2006.01)i

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)

Int.Cl. C07D487/22, H01L31/04, H01M14/00

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2012
Registered utility model specifications of Japan 1996-2012
Published registered utility model applications of Japan 1994-2012

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

CA/REGISTRY(STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LEE, M. J., Novel D-π-A system based on zinc-porphyrin derivatives for highly efficient dye-sensitised solar cells, Tetrahedron Letters, 2011.05.23, Vol.52, No.30, p.3879-3882	1-8,11
X	HUANG, C., Spectral and redox properties of zinc porphyrin core dendrimers with triarylamines as dendron, Dalton Transactions, 2010, Vol.39, No.35, p.8306-8312	1-7,9-11
X	RUBIO-PONS, O., Effects of conjugation length, electron donor and acceptor strengths on two-photon absorption cross sections of asymmetric zinc-porphyrin derivatives, Journal of Chemical Physics, 2006, Vol.124, No.9, p.094310/1-094310/5	1-7,9-11

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

* Special categories of cited documents:

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	AMAYA, T., Coordination-induced branched self-assembly of porphyrins bearing two redox-active phenylenediamine chains, Tetrahedron Letters, 2010, Vol.51, No.26, p.3376-3379	1-7,11
X	AMAYA, T., Transition metal-directed self-assembly of porphyrins bearing redox-active phenylenediamine pendant, Tetrahedron Letters, 2010, Vol.51, No.18, p.2416-2419	1-7,11
X	HIRAO, T., Sandwich dimer complexes of zinc porphyrins bearing three-dimensionally oriented redox-active π-conjugated pendant groups, Synlett, 2002, No.3, p.415-418	1-7,11
X	SAITO, K., Synthesis and characterization of porphyrins bearing four redox-active phenylenediamine pendant groups as a dimensionally oriented π-conjugated system, Tetrahedron, 2002, Vol.58, No.37, p.7491-7501	1-7,11
X	HIRAO, T., A three-dimensionally oriented π-conjugated system; synthesis and characterization of porphyrins bearing π-conjugated pendant strands, Tetrahedron Letters, 2000, Vol.41, No.9, p.1413-1417	1-7,11
A	LU, H., Design and characterization of highly efficient porphyrin sensitizers for green see-through dye-sensitized solar cells, Physical Chemistry Chemical Physics, 2009, Vol.11, No.44,p.10270-10274	1-11