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Yeh et al.

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(54) **PORPHYRIN-BASED PHOTSENSITIZER
DYES FOR DYE-SENSITIZED SOLAR CELLS**

(75) Inventors: **Chen-Yu Yeh**, Tainan (TW); **Eric
Wei-Guang Diau**, Hsinchu (TW);
Cheng-Wei Lee, Changhua (TW);
Hsueh-Pei Lu, Taipei (TW); **Chi-Ming
Lan**, Taoyuan (TW)

(73) Assignees: **National Chiao Tung University**,
Hsinchu (TW); **National Chung Hsing
University**, Taichung (TW)

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(22) Filed: **Jun. 16, 2009**

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(30) **Foreign Application Priority Data**

Nov. 17, 2008 (TW) 97144426

(51) **Int. Cl.**

C09D 11/00 (2006.01)

C07B 47/00 (2006.01)

C07D 487/22 (2006.01)

(52) **U.S. Cl.** **540/145**; 106/31.27

(58) **Field of Classification Search** 540/145,
540/140; 106/31.27

See application file for complete search history.

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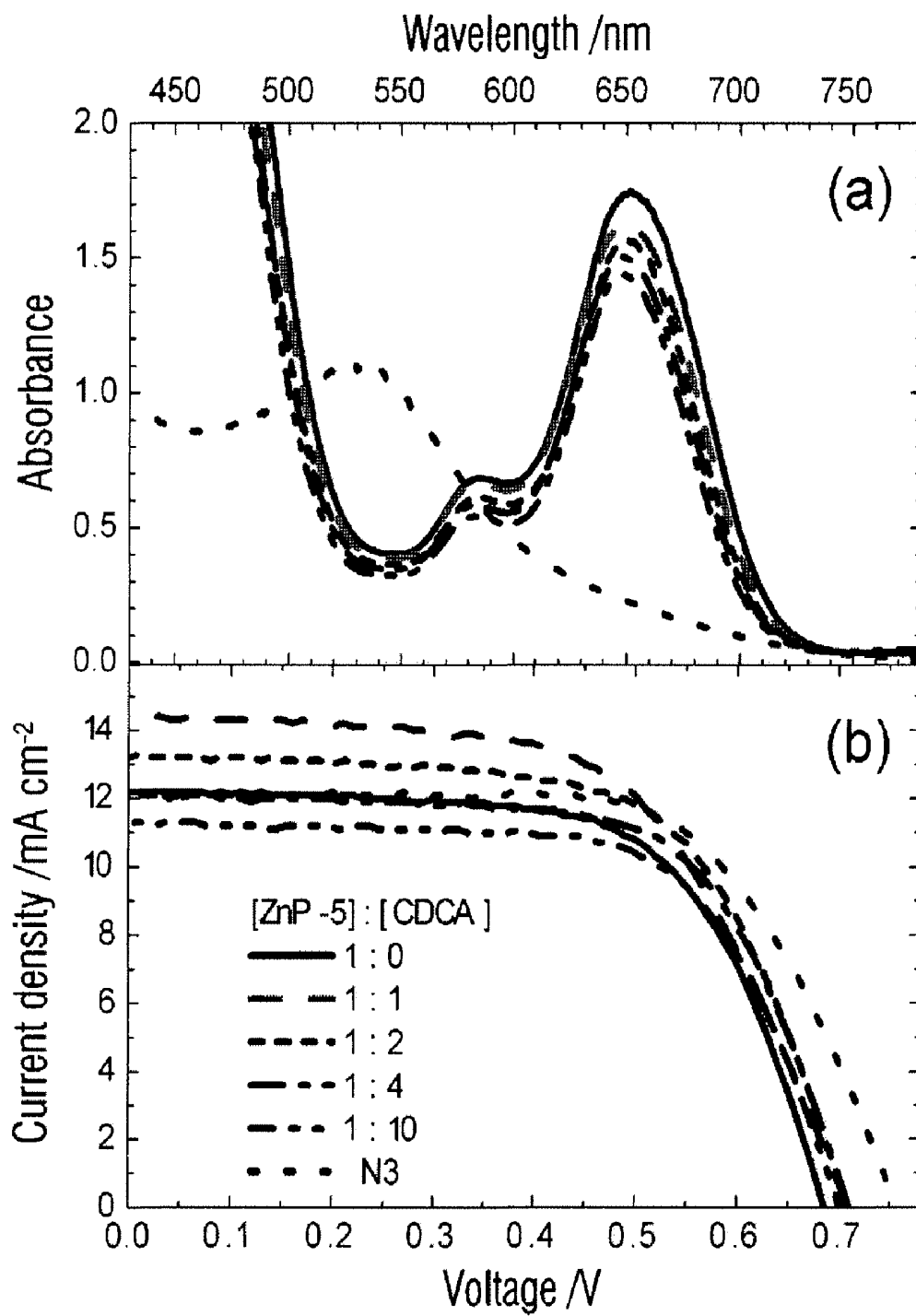
Primary Examiner — Paul V. Ward

(74) *Attorney, Agent, or Firm* — Muncy, Geissler, Olds &
Lowe, PLLC

(57) **ABSTRACT**

The embodiments described herein relate to photosensitizer
dyes for dye-sensitized solar cell (DSSC) devices. In one
example, a series of photosensitizer dyes for DSSC devices
that have a high absorption coefficient and conversion effi-
ciency, lower cost and better safety, are provided. The photo-
sensitizer dyes are porphyrin-based zinc (Zn) complexes.

24 Claims, 1 Drawing Sheet



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**PORPHYRIN-BASED PHOTSENSITIZER
DYES FOR DYE-SENSITIZED SOLAR CELLS**

CROSS-REFERENCE TO RELATED
APPLICATION

This application claims the priority benefit of Taiwan application serial no. 97144426, filed on Nov. 17, 2008. All disclosure thereof is incorporated herein by reference.

BACKGROUND OF THE INVENTION

The present invention relates to a solar cell material. More specifically, the present invention relates to a porphyrin-based photosensitizer dye for dye-sensitized solar cells.

Various research studies have been carried out in an attempt to develop alternative energy sources that can replace conventional fossil fuels and solve an approaching energy crisis. Virtually inexhaustible solar energy has attracted a great deal of notice among the alternative energy sources such as wind power, atomic power, and solar power. Solar cells, or photovoltaic cells (PV cells), are considered as a major candidate for obtaining energy from the sun, since they can convert sunlight directly to electricity, provide long term power at a low operation cost, and be free of pollution associated with energy generation.

Recently, Grätzel and O'Regan have proposed a new type of solar cells known as dye-sensitized solar cells (DSSC), which have drawn much attention because they present a highly promising alternative to conventional silicon based solar cells. In nanocrystalline TiO₂ solar cells sensitized with a dye, poly-pyridyl ruthenium (Ru) complexes are used as photosensitizer dyes. The advantages of using such Ru complexes are that they have broad absorption in the near UV/visible regions, and appropriate excited-state oxidation potential for electron injection into the conduction band of TiO₂. However, on one hand, in the visible region, the absorption coefficient of poly-pyridyl Ru complexes is not large enough; on the other hand, the cost, rarity, and environmental issues of Ru complexes also limit their wide application.

It is known that in the photosynthetic cores of bacteria and plants, solar energy is collected by porphyrin-based chromophores and the captured radiant energy is efficiently converted to chemical energy. In view of such inspiration, porphyrin and phthalocyanine derivatives have been synthesized and used for photovoltaic solar cells. Thus, various porphyrin derivatives can be used to develop cheaper and safer photosensitizer dyes with a high absorption coefficient in the visible region.

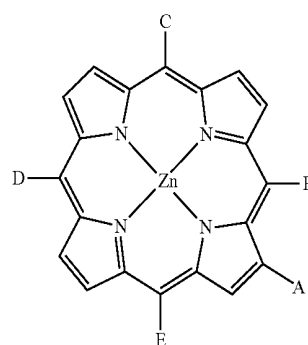
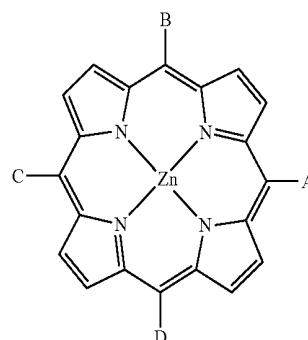
SUMMARY OF THE INVENTION

An objective of the present invention is to provide a series of photosensitizer dyes for DSSC devices that have a high absorption coefficient and conversion efficiency, lower cost, and better safety.

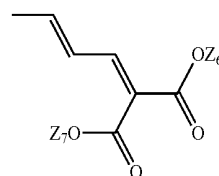
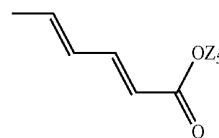
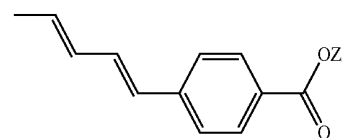
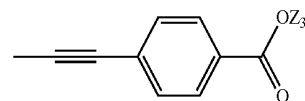
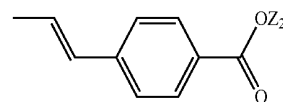
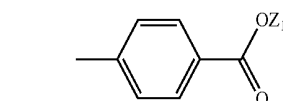
To achieve the objective mentioned above, the present invention provides a series of photosensitizer dyes for DSSC devices, wherein the photosensitizer dyes are porphyrin-based zinc (Zn) complexes represented by the following general formulae (100) and (200):

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wherein A represents one of the following general formulae (111)~(118),



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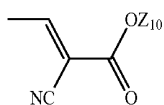
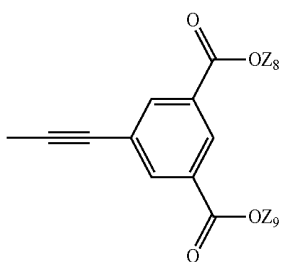
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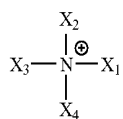
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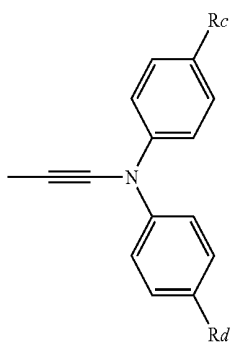
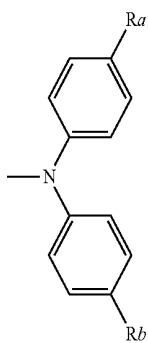
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wherein $Z_1 \sim Z_{10}$ independently represent a hydrogen atom (H), lithium (Li), sodium (Na), or tetra-alkyl ammonium group represented by the following general formula (120),

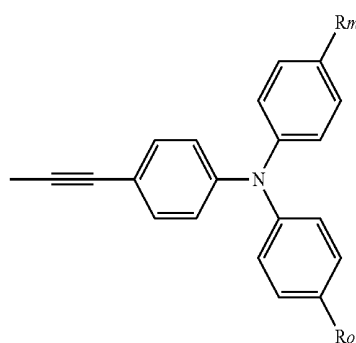
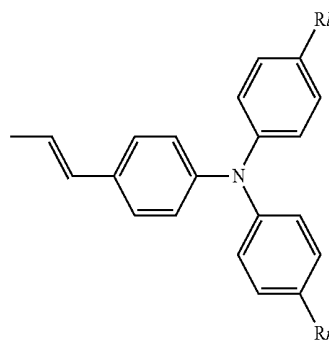
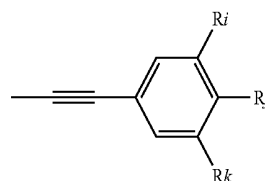
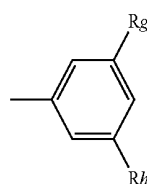
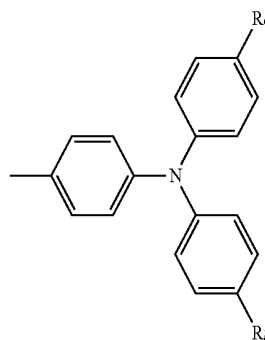


wherein $X_1 \sim X_4$ independently represent $C_m H_{2m+1}$ ($m=1 \sim 6$), and B, C, D, and E are the same or different, and independently represented by one of the following general formulae (131)~(140):



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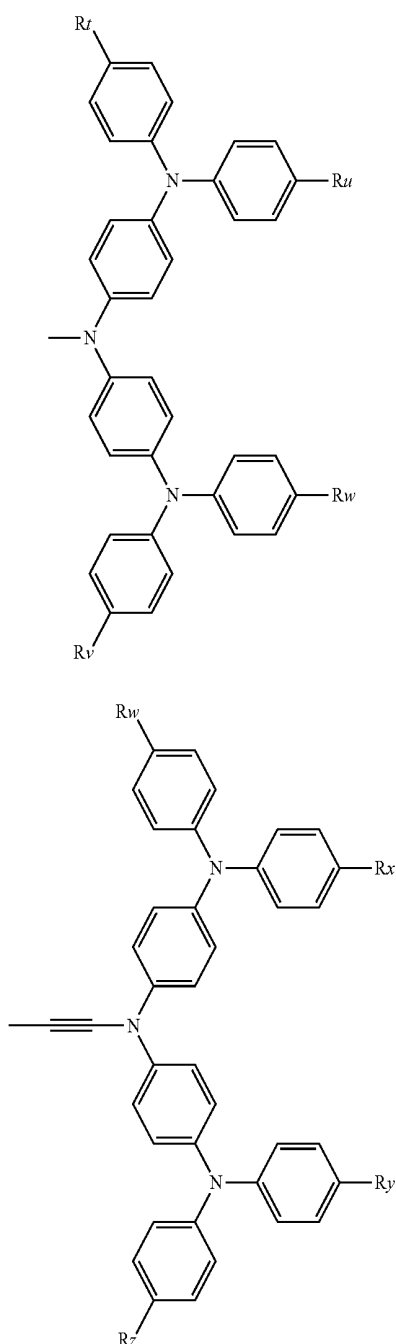
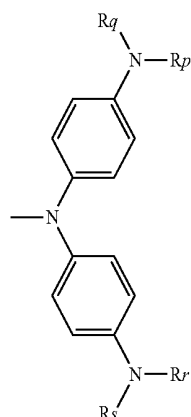
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138 wherein $R_a \sim R_z$ are independently selected from the group
 consisting of H, $C_m H_{2m+1}$ ($m=1 \sim 15$), $OC_p H_{2p+1}$ ($p=1 \sim 15$),
 $CH_2[OC_2H_4]_n OCH_3$ ($n=1 \sim 30$), and $[OC_2H_4]_q OCH_3$
 5 ($q=1 \sim 30$).

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1(a) is the visible absorption spectra of the ZnP-5/
 10 TiO_2 films and N3/ TiO_2 film.

FIG. 1(b) is the IV curves of the corresponding DSSC
 devices in FIG. 1(a).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

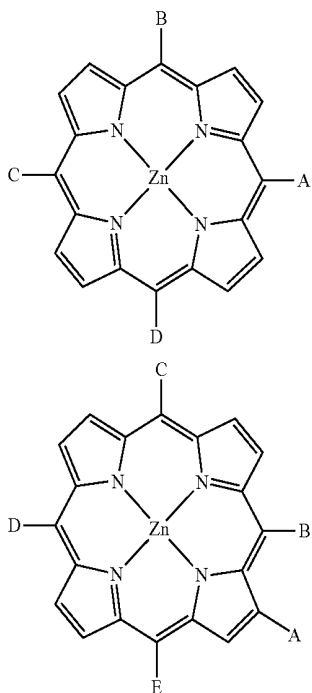
139 The technical contents, features, and effect of the present
 20 invention will be presented in more detail with reference to
 the following preferred embodiments thereof. In the follow-
 ing description, numerous specific details are set forth in
 order to provide a thorough understanding of the present
 25 invention. It will be apparent, however, to one skilled in the
 art, that the present invention may be practiced without some
 or all of these specific details. In other instances, well known
 chemical reactions and/or chemical structures have not been
 30 described in detail in order to not unnecessarily obscure the
 present invention.

For DSSC devices, the efficiency of photoelectric conver-
 sion depends upon the structure of the photosensitizer dyes
 and how the photosensitizer dyes are attached to the surface
 of a semiconductor such as titanium oxide (TiO_2). The
 35 present invention provides numerous porphyrin-based pho-
 tosensitizer dyes, in which the porphyrin rings have anchoring
 groups for attaching to the semiconductor surface. In one
 embodiment, the anchoring group comprises a carboxyl
 40 group $-COOH$ or a carboxylate anion $-COO-$. In order to
 increase the absorption of the porphyrin rings in the visible
 region, several substituents may be attached thereto for
 expanding the π -conjugation system, which causes a red shift
 45 and broadening of both Soret and Q bands in the absorption
 spectra. In one embodiment, the substituents are electron-
 donating groups.

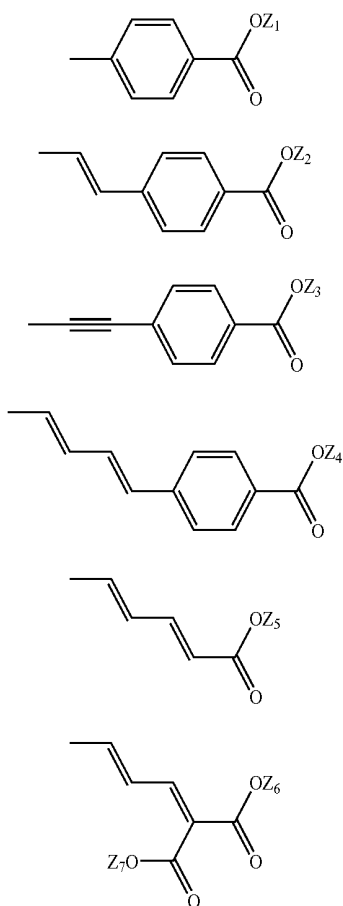
The efficiency of sensitized photocurrent generation
 decreases due to the formation of dye aggregates on the
 semiconductor surface. To inhibit that aggregation, bulky
 50 substituents are introduced into the porphyrin rings, such as
 3,5-di-tert-butylphenyl groups. However, the steric hindrance
 of the bulky substituents can impede adsorption of photosen-
 sitizer dyes onto the semiconductor surface. Thus, the por-
 55 phyrin ring and the anchoring group are connected with a
 proper bridging unit, which provides a longer anchoring
 group promoting the adsorption onto the semiconductor sur-
 face and facilitates electron transfer from the excited dye
 molecules to the semiconductor surface. In one embodiment,
 60 the bridging unit is an ethyne linker. Besides, a co-adsorbate
 for the dye loading can be used to prevent aggregation of the
 photosensitizer dyes. In one embodiment, the co-adsorbate is
 chenodeoxycholic acid (CDCA).

In view of the above, the present invention provides a series
 65 of photosensitizer dyes for DSSC devices, in which the pho-
 tosensitizer dyes are porphyrin-based Zn complexes repre-
 sented by the following general formula (100) or (200):

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wherein A is used as the anchoring group and selected from the group represented by general formulae (111)~(118),



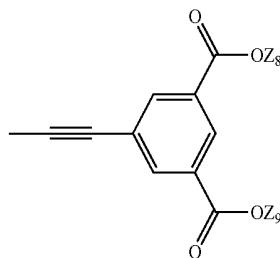
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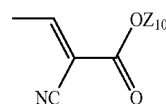
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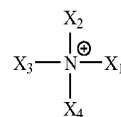
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wherein $Z_1 \sim Z_{10}$ independently represent a hydrogen atom (H), lithium (Li), sodium (Na), or tetra-alkyl ammonium group represented by the following general formula (120),

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wherein $X_1 \sim X_4$ independently represent C_mH_{2m+1} ($m=1 \sim 6$), and B, C, D, and E which can be the same or different are independently represented by one of the following general formulae (131)~(140):

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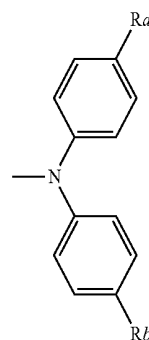
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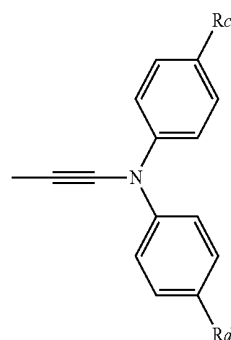
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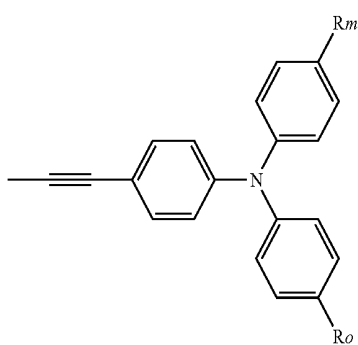
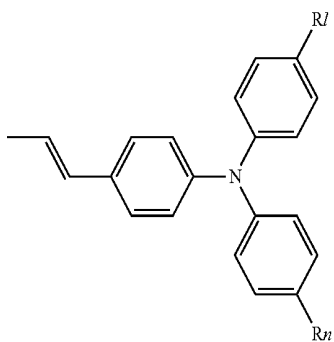
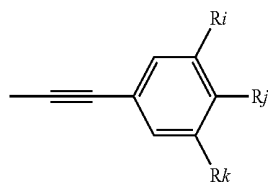
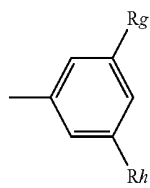
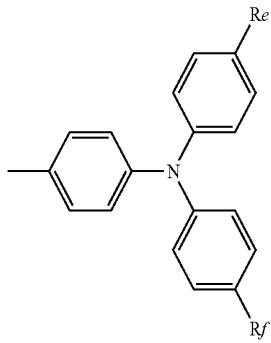
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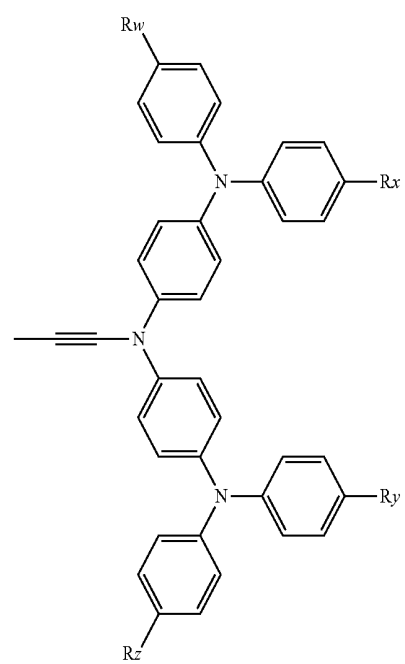
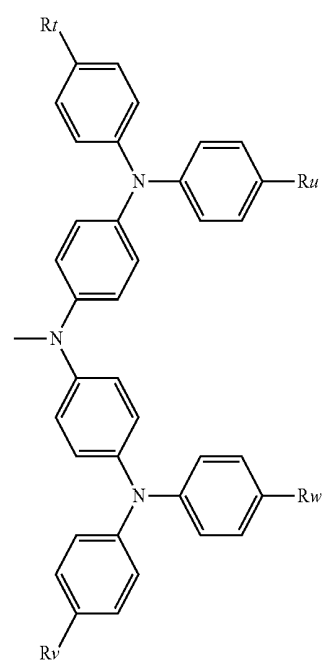
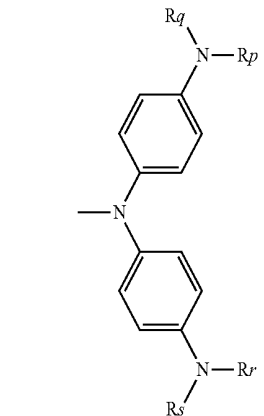
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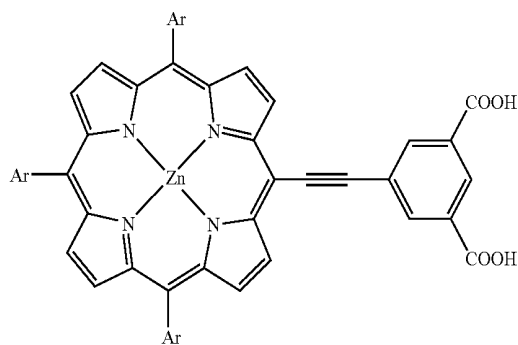
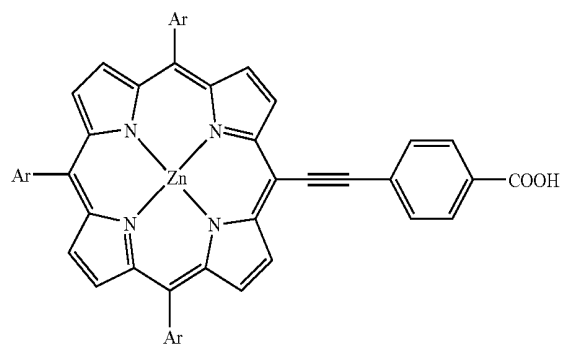
wherein $R_a \sim R_z$ are independently selected from the group consisting of H, C_mH_{2m+1} ($m=1 \sim 15$), OC_pH_{2p+1} ($p=1 \sim 15$), $CH_2[OC_2H_4]_nOCH_3$ ($n=1 \sim 30$), and $[OC_2H_4]_qOCH_3$ ($q=1 \sim 30$).

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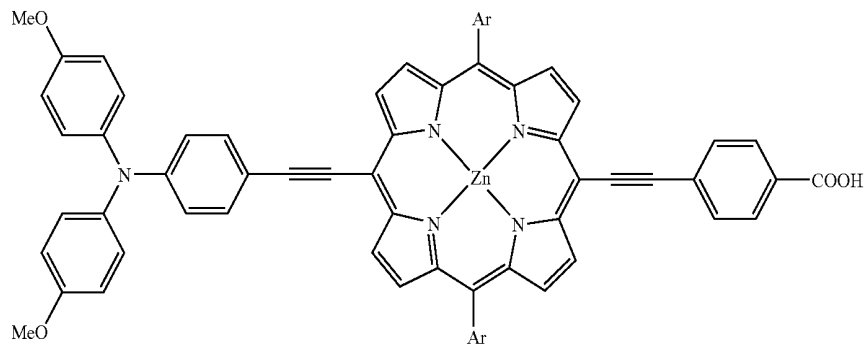
The synthesis of porphyrin-based photosensitizer dyes 1~12 of the present invention will be described in the following embodiments. It is to be noted that the following description should be regarded as illustrative rather than restrictive.

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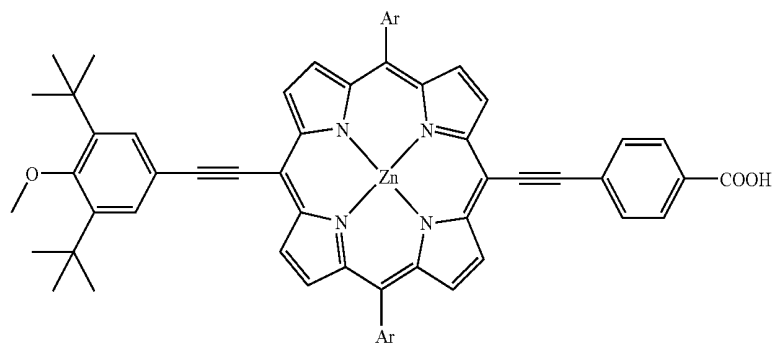
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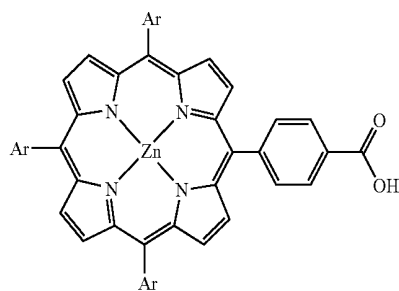
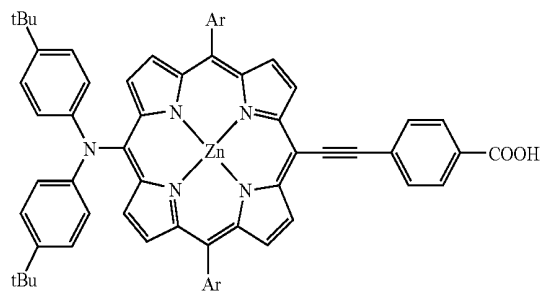


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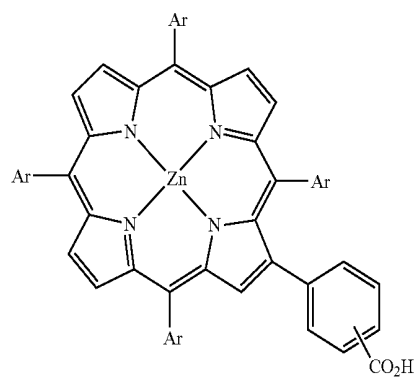
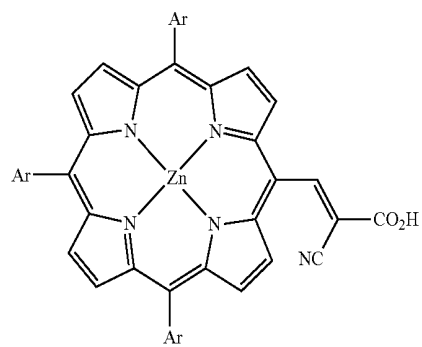


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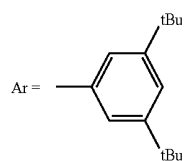
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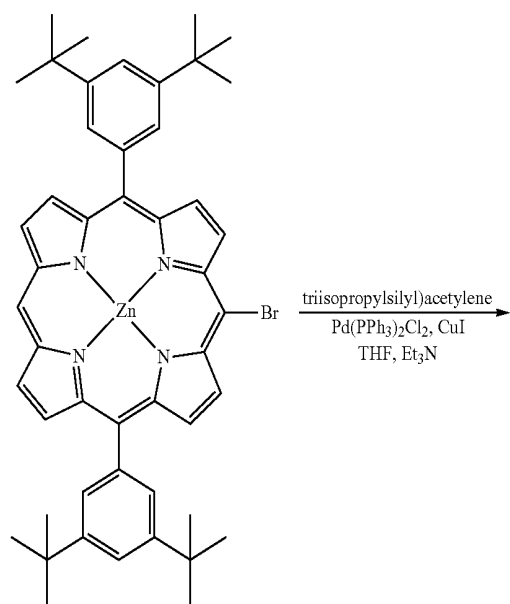


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First Embodiment

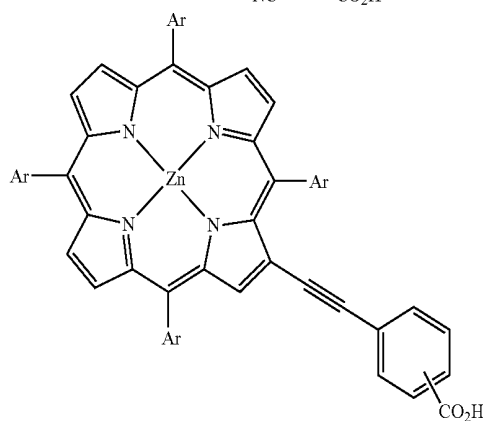
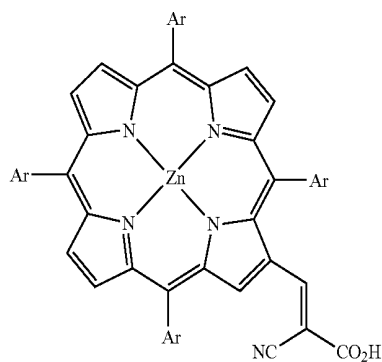
The Synthesis of Photosensitizer Dye 5



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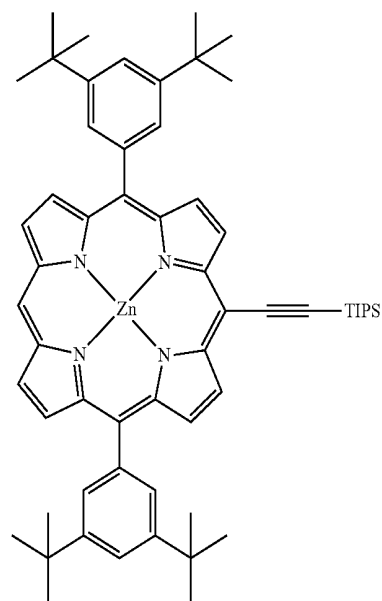
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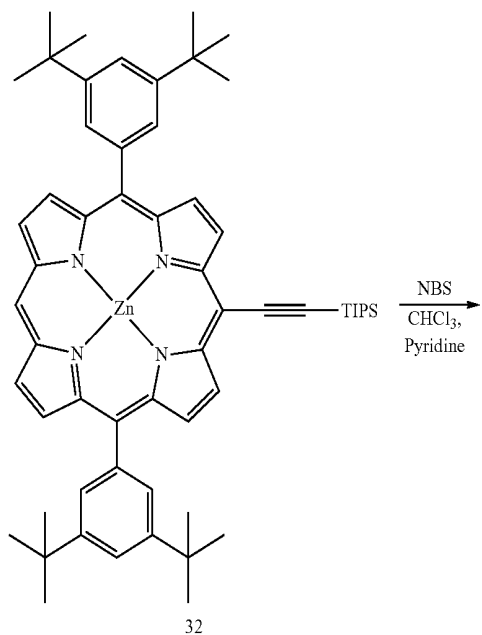
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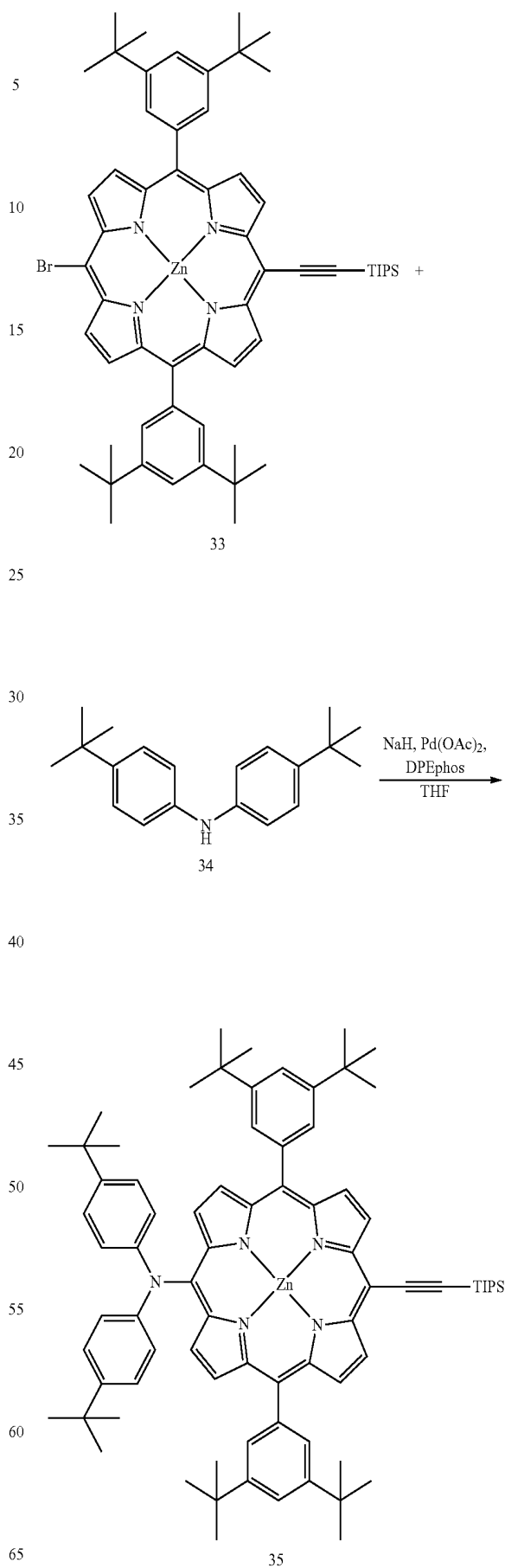
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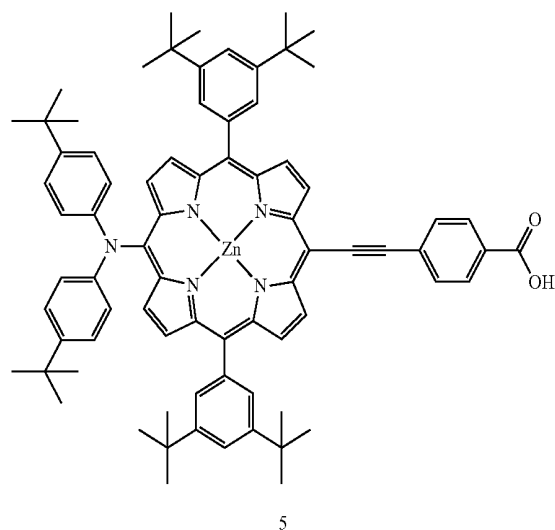
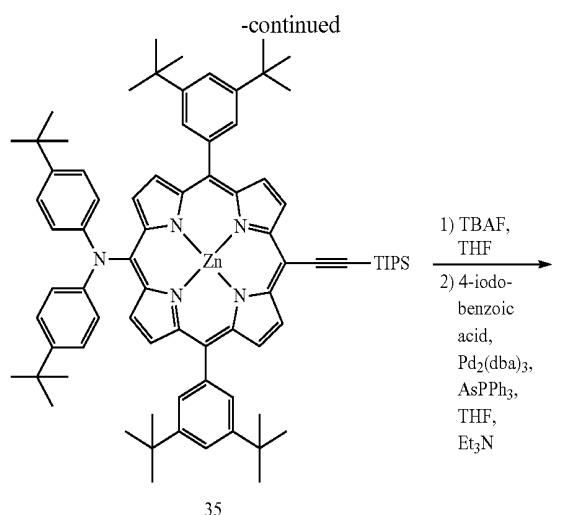


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The chemical reactions listed above are those occur during the synthesis of porphyrin-based photosensitizer dye 5 (referred to as ZnP-5, hereinafter). 373 mg of porphyrin compound 31 (Ka, J. W. et al., *Tetrahedron Lett.* 2000, 41, 4609; Plater, M. J. et al., *Tetrahedron*, 2002, 58, 2405; and Susumu, K. et al., *J. Am. Chem. Soc.* 2002, 124, 8550) was placed in a dry two-necked flask equipped with a stirring bar at the presence of nitrogen gas, followed by adding 80 mL of dry tetrahydrofuran (THF) and 26.8 mL of dry triethylamine (Et₃N) thereinto and mix them well. Then the mixture was deoxygenated with nitrogen for 10 minutes. After that, 32.1 mg of bis(triphenylphosphine)palladium(II) chloride (Pd(PPh₃)₂Cl₂, Strem Chemicals, Inc.), 8.7 mg of cuprous iodide (CuI, Strem Chemicals, Inc.), and 0.67 mL of (triisopropylsilyl) acetylene (Acros Organics, Inc.) were added into the flask. The mixture was heated to be refluxed for 2 hours and then cooled to ambient temperature. The solvents were removed

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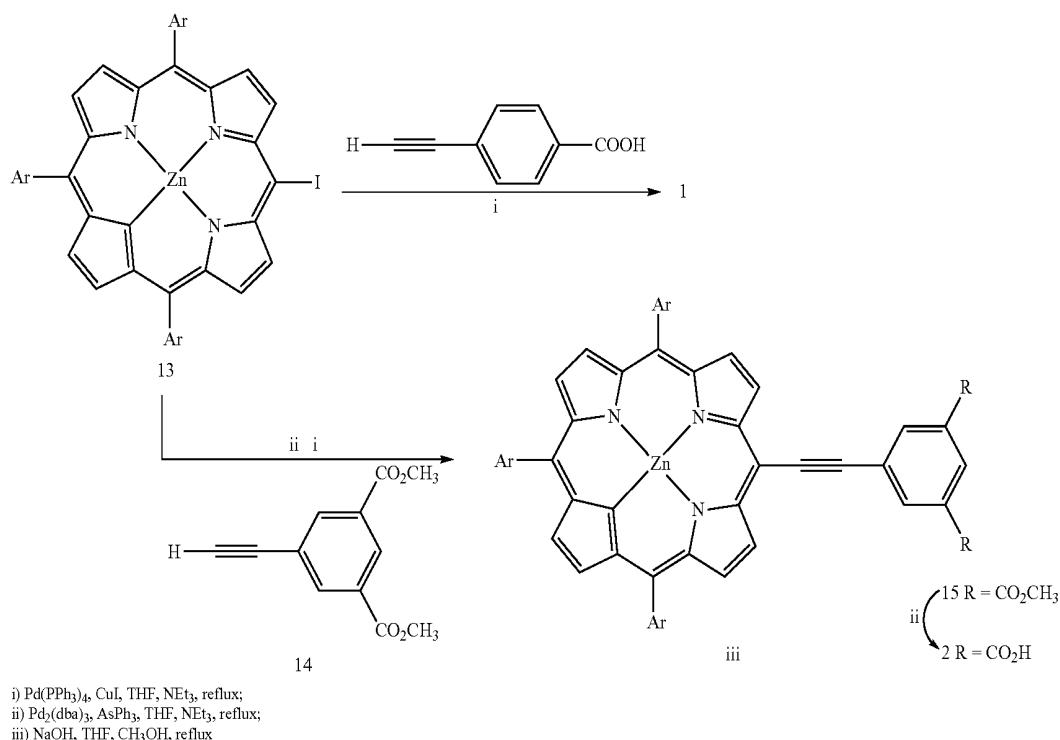
under reduced pressure, and the residue was purified by column chromatograph (packed with silica gel) using a CH₂Cl₂/n-hexane solution (1:4, v/v) as eluent. Recrystallization was then performed using CH₂Cl₂/CH₃OH, thus resulting in 341.4 mg of porphyrin 32 with the yield of 80%.

100 mg of porphyrin 32 was placed in a two-necked flask equipped with a stirring bar at the presence of nitrogen gas, then 65 mL of dry chloroform (CHCl₃) and 6.5 mg of dry pyridine were added thereto. With the stirring bar activated, the mixture was deoxygenated with nitrogen for 10 minutes. 37 mg of N-bromosuccinimide (NBS, Acros Organics, Inc.) was added to undergo bromination for 10 minutes, and then the reaction was terminated by adding 1.0 mL of acetone. The solvents were removed under reduced pressure, and the residue was purified by column chromatograph (packed with silica gel) using a CH₂Cl₂/n-hexane solution (1:4, v/v) as eluent. Recrystallization was then performed using CH₂Cl₂/CH₃OH, thus leading to 95 mg of porphyrin 33 with the yield of 88%.

50 mg of compound 34 (Zhao, H. et al., *Tetrahedron Lett.* 2001, 42, 4421) and 16.8 mg of sodium hydride (NaH) were placed in a two-necked flask equipped with a stirring bar at the presence of nitrogen, followed by adding 10 mL of dry THF and stirring the mixture for 3 minutes. Next, 50 mg of porphyrin 33, 2.2 mg of palladium(II) acetate (Pd(OAc)₂, Strem Chemicals, Inc.), and 8 mg of bis[(2-diphenylphosphino)phenyl]ether (DPEphos, Acros Organics, Inc.) were added thereto. The mixture were deoxygenated with nitrogen for 10 minutes, refluxed for 5 hours, and then cooled to ambient temperature. The solvent was removed under reduced pressure, and the residue was purified by column chromatograph (packed with silica gel) using a CH₂Cl₂/n-hexane solution (1:4, v/v) as eluent. Recrystallization was then performed using CH₂Cl₂/CH₃OH, thus resulting in 30 mg of porphyrin 35 with the yield of 50%.

23.2 mg of porphyrin 35 was placed in a two-necked flask equipped with a stirring bar at the presence of nitrogen, and 4 mL of THF and 0.08 mL of tetrabutylammonium fluoride (TBAF, 1 M in THF, Acros Organics, Inc.) were added thereinto afterwards. The mixture was stirred for reaction for 30 minutes at ambient temperature. The solvent was removed under reduced pressure, and the residue was extracted using H₂O and CH₂Cl₂. The organic layer was collected, dehydrated using anhydrous sodium sulfate, and filtered by suction. The filtrate was collected into a two-necked flask, and concentrated under reduced pressure to remove the solvent. After that, 5 mg of 4-iodobenzoic acid (Acros Organics, Inc.) was added at the presence of nitrogen, followed by adding 5 mL of dry THF and 1 mL of dry Et₃N. The mixture was deoxygenated with nitrogen for 10 minutes. 2.2 mg of tris(dibenzylideneacetone)dipalladium(0) (Pd₂(dba)₃, Strem Chemicals, Inc.) and 7 mg of triphenyl arsine (AsPh₃, Acros Organics, Inc.) were added. The mixture was refluxed for 2 hours and then cooled to ambient temperature. The solvent was removed under reduced pressure, and the residue was purified by column chromatograph (packed with silica gel) using a CH₂Cl₂/CH₃OH solution (9:1, v/v) as eluent. Recrystallization was then performed using CH₂Cl₂/CH₃OH, thus leading to 14 mg of ZnP-5 with the yield of 62%.

The Synthesis of Photosensitizer Dyes 1 and 2



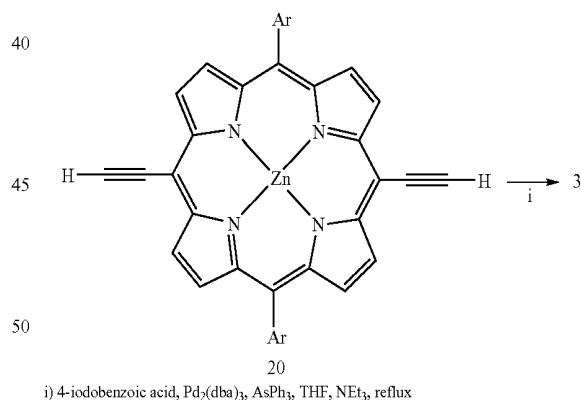
Referring to the above chemical equations. A mixture of porphyrinyl iodide 13 (21 mg) and 4-ethynylbenzoic acid (4.4 mg) in dry THF (2 mL) and Et_3N (1 mL) was prepared and deoxygenated with nitrogen for 10 minutes, followed by adding palladium(0) tetra(triphenylphosphine) ($\text{Pd}(\text{PPh}_3)_4$, 4.6 mg) and CuI (0.4 mg) thereto. The mixture was refluxed under nitrogen for 2 hours. The solvent was removed by vacuum, and the residue was purified by column chromatograph (packed with silica gel) using a CH_2Cl_2 /n-hexane solution (9:1, v/v) as eluent. Recrystallization was then performed using CH_2Cl_2 / CH_3OH , thus resulting in 19.4 mg of photosensitizer dye 1 (ZnP-1) with the yield of 90%.

Besides, a mixture of porphyrinyl iodide 13 (10 mg) and dimethyl 5-ethynyl-isophthalate 14 (6.5 mg) in dry THF (5 mL) and Et_3N (1 mL) was prepared and deoxygenated with nitrogen for 10 minutes, followed by adding $\text{Pd}_2(\text{dba})_3$ (2.2 mg) and AsPh_3 (6 mg) thereto. The mixture was refluxed under nitrogen for 1 hour. The solvent was removed by vacuum, and the residue was purified by column chromatograph (packed with silica gel) using a CH_2Cl_2 /n-hexane solution (4:6, v/v) as eluent. Recrystallization was then performed using CH_2Cl_2 / CH_3OH , thus leading to 10.4 mg of porphyrin 15 with the yield of 90%.

A mixture of porphyrin 15 (23 mg) and NaOH (0.5 M, 1 mL) in THF (5 mL) and CH_3OH (2 mL) was heated and refluxed for 4 hours. After being cooled to 25°C ., the solution was extracted using H_2O and CH_2Cl_2 . The organic layer was collected and then washed sequentially using HCl (1%, 10 mL) and H_2O (10 mL*3). The solvent was removed by vacuum. Recrystallization was then performed using CH_2Cl_2 / CH_3OH , thus resulting in 22.2 mg of photosensitizer dye 2 (ZnP-2) with the yield of 99%.

Third Embodiment

The Synthesis of Photosensitizer Dyes 3 and 4



A mixture of N,N-bis(4-methoxyphenyl)-4'-iodophenylamine 19 (10.4 mg), 4-iodobenzoic acid (4 mg), and porphyrin 20 (16 mg) in dry THF (10 mL) and Et_3N (2 mL) was prepared and deoxygenated with nitrogen for 10 minutes, followed by adding $\text{Pd}_2(\text{dba})_3$ (4.4 mg) and AsPh_3 (12 mg) thereto. The mixture was heated and refluxed under nitrogen for 2.5 hours. The solvent was removed by vacuum, and the residue was purified by column chromatograph (packed with silica gel) using a CH_2Cl_2 / CH_3OH solution (9:1, v/v) as eluent. Recrystallization was then performed using CH_2Cl_2 / CH_3OH , leading to 9.8 mg of photosensitizer dye 3 (ZnP-3) with the yield of 40%.

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Similarly, a mixture of 5-iodo-2-methoxy-1,3-di-tert-butylbenzene (8.3 mg), 4-iodobenzoic acid (4 mg), and porphyrin 20 (16 mg) in dry THF (10 mL) and Et₃N (2 mL) was prepared and deoxygenated with nitrogen for 10 minutes, followed by adding Pd₂(dba)₃ (4.4 mg) and AsPh₃ (12 mg) thereinto. The mixture was heated and refluxed under nitrogen for 4 hours, and then purified according to a method similar to that for ZnP-3 to obtain 8.2 mg of photosensitizer dye 4 (ZnP-4) with the yield of 36%.

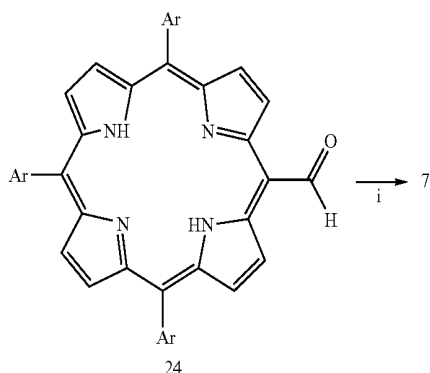
Fourth Embodiment

The Synthesis of Photosensitizer Dye 6

Photosensitizer dye 6 can be prepared according to a method similar to that disclosed in the literature (C. Luo et al., *J. Am. Chem. Soc.* 2000, 122, 6535).

Fifth Embodiment

The Synthesis of Photosensitizer Dye 7

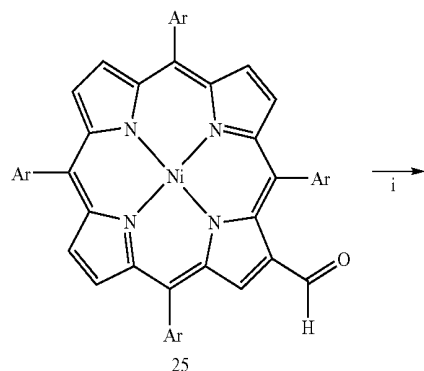


i) Piperidine, acetonitrile, cyanoacetic acid, reflux; then Zn(OAc)₂·2H₂O, CH₃OH, CH₂Cl₂, room temperature

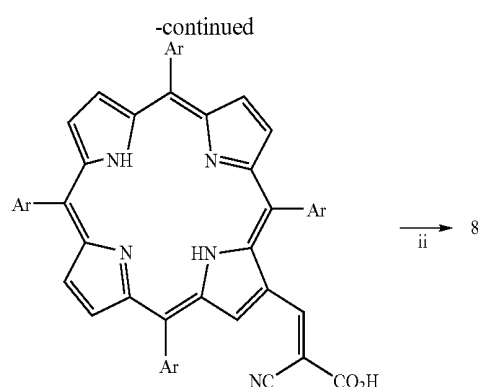
Referring to the above chemical equation, a mixture of compound 24 (36 mg), cyanoacetic acid (18 mg), piperidine (0.13 mL), and acetonitrile (10 mL) was heated and refluxed for 6 hours. The solvent was removed by vacuum, and the residue was purified by column chromatograph (packed with silica gel) using a CH₂Cl₂/CH₃OH solution (9:1, v/v) as eluent. Subsequently, zinc insertion was performed using zinc acetate dihydrate (Zn(OAc)₂·2H₂O), thus resulting in 41 mg of photosensitizer dye 7 (ZnP-7) with the yield of 99%.

Sixth Embodiment

The Synthesis of Photosensitizer Dye 8



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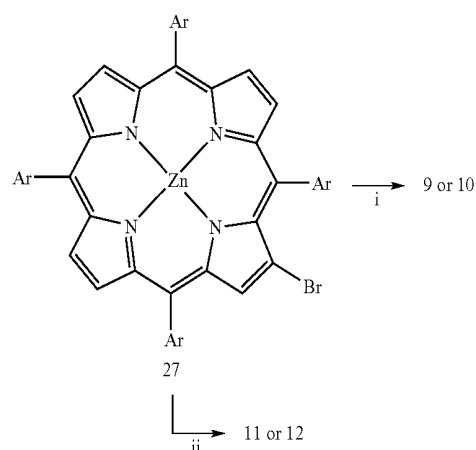


i) Piperidine, acetonitrile, cyanoacetic acid, reflux; then H₂SO₄
ii) Zn(OAc)₂·2H₂O, CH₃OH, CH₂Cl₂, room temperature

Referring to the above chemical equation, a mixture of porphyrin 25 (45.8 mg), cyanoacetic acid (18 mg), piperidine (0.13 mL), acetonitrile (5 mL), and dichloroethane (5 mL) was heated and refluxed for 6 hours. The solvent was removed by vacuum, and the residue was purified by column chromatograph (silica gel) using CH₂Cl₂/CH₃OH (9/1) as eluent. Demetallation was performed using a mixture of H₂SO₄ (2 mL) and CH₂Cl₂ (10 mL), followed by adding H₂O (10 mL) and CH₂Cl₂ (10 mL) and collecting the organic layer. The solvent was removed in vacuo to give compound 26, which was then subjected to zinc insertion using Zn(OAc)₂·2H₂O. Recrystallization of the crude product from CH₂Cl₂/CH₃OH gave photosensitizer dye 8 (ZnP-8, 33 mg, 70%).

Seventh Embodiment

The Synthesis of Photosensitizer Dyes 9, 10, 11, and 12



i) methylbenzoate boronic acid, K₂CO_{3(aq)}, Pd(PPh₃)₄, ethandiol methyl ester, reflux; then NaOH, THF, CH₃OH, reflux.
ii) ethynylbenzoic acid, Pd₂(dba)₃, AsPh₃, THF, NEt₃, reflux.

In light of the disclosure of J. P. C. Tomé et al., *Eur. J. Org. Chem.* 2006, 257, bromination of 5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)porphyrin with NBS followed by a zinc insertion reaction gives porphyrin 27.

Referring to the above chemical equation, a mixture of porphyrin 27 (21.3 mg), 4-methylbenzoate boronic acid (20 mg), and aqueous K₂CO₃ (1 M, 0.1 mL) in ethandiol methyl ether (10 mL) was deoxygenated with nitrogen for 10 minutes, followed by adding Pd(PPh₃)₄ (8 mg) thereinto. The mixture was heated and refluxed under nitrogen for 18 hours.

The solvent was removed by vacuum, and the residue was purified by column chromatograph (packed with silica gel) using a CH₂Cl₂/n-hexane solution (4:6, v/v) as eluent. Next, recrystallization was performed using CH₂Cl₂/CH₃OH, thus 11 mg of an intermediate was obtained with the yield of 45%. According to a method similar to that for ZnP-2, the intermediate was hydrolyzed under an alkaline condition (NaOH/THF/CH₃OH) and then purified to obtain photosensitizer dye 9 (ZnP-9) with the yield of 99%.

Besides, a mixture of porphyrin 27 (28 mg), 3-methylbenzoate boronic acid (20 mg), and aqueous K₂CO₃ (1 M, 0.1 mL) in ethanediol methyl ether (10 mL) was deoxygenated with nitrogen for 10 minutes, followed by adding Pd(PPh₃)₄ (8 mg) thereinto. The mixture was heated and refluxed under nitrogen for 18 hours. The solvent was removed by vacuum, and the residue was purified by column chromatograph (packed with silica gel) using a CH₂Cl₂/n-hexane solution (4:6, v/v) as eluent. Recrystallization was performed using CH₂Cl₂/CH₃OH, thus 12.4 mg of an intermediate was obtained with the yield of 50%. According to a method similar to that for ZnP-2, the intermediate was hydrolyzed under an alkaline condition (NaOH/THF/CH₃OH) and then purified to obtain photosensitizer dye 10 (ZnP-10, 99%).

A mixture of porphyrin 27 (24 mg), 4-ethynylbenzoic acid (29.2 mg) in dry THF (10 mL) and Et₃N (2 mL) was deoxygenated with nitrogen for 10 minutes, followed by adding Pd₂(dba)₃ (9.2 mg) and AsPh₃ (24.5 mg). The mixture was refluxed under nitrogen for 24 hours. The solvent was removed in vacuo, and the residue was purified by column chromatograph (silica gel) using CH₂Cl₂/CH₃OH (9/1) as eluent. Recrystallization from CH₂Cl₂/CH₃OH gave photosensitizer dye 11 (ZnP-11, 7.6 mg, 30%).

A mixture of porphyrin 27 (24 mg), 3-ethynylbenzoic acid (29.2 mg) in dry THF (10 mL) and Et₃N (2 mL) was deoxygenated with nitrogen for 10 minutes, followed by adding Pd₂(dba)₃ (9.2 mg) and AsPh₃ (24.5 mg). The mixture was refluxed under nitrogen for 24 hours, and then purified according to a method similar to that for ZnP-11 to obtain photosensitizer dye 12 (ZnP-12, 8.3 mg, 33%).

Photosensitizer dyes ZnP-1~ZnP-12 were dissolved in a CH₂Cl₂/pyridine solution (100:1, v/v), and the absorption spectra thereof were determined by a UV/Vis spectrophotometer. The absorption coefficients of ZnP-1~ZnP-12 of the present invention are summarized in Table 1. Furthermore, one of the representative photosensitizer dyes in the literature is N3, which is a poly-pyridyl Ru complex disclosed by Grätzel (M. Grätzel, *J. Photochem. A*, 2004, 164, 3, and M. K. Nazeeruddin et al., *J. Am. Chem. Soc.* 1993, 115, 6382). The spectral absorption coefficient of N3 was also measured for comparison.

TABLE 1

Photosensitizer Dye	Absorption Peak λ_{max} /nm (Absorption Coefficient $\epsilon/10^3 \text{ M}^{-1}\text{cm}^{-1}$)
ZnP-1	445 (282), 579 (9.5), 636 (24.8)
ZnP-2	445 (231), 582 (8.2), 632 (19.4)
ZnP-3	451 (117), 680 (30.6)
ZnP-4	454 (283), 668 (51.0)
ZnP-5	448 (194), 601 (8.3), 654 (29.7)
ZnP-6	430 (616), 565 (20.7), 605 (14.7)
ZnP-7	455 (106), 571 (7.1), 636 (8.4)
ZnP-8	451 (129), 564 (11.7), 613 (11.1)
ZnP-9	434 (326), 567 (12.9), 607 (7.7)
ZnP-10	433 (409), 566 (16.3), 609 (10.7)
ZnP-11	442 (348), 574 (21.0), 618 (13.0)
ZnP-12	444 (375), 575 (25.1), 618 (16.3)
N3	314 (482), 389 (140), 534(142)

Then, DSSC devices using the photosensitizer dyes of the present invention were fabricated and measured for the photovoltaic properties thereof. ZnP-5 is exemplified herein as a photosensitizer dye. The TiO₂ nanoparticles having a diameter around 20 nm prepared with a sol-gel method were screen-printed onto the F-doped SnO₂ (FTO) glass substrate. Crystallization of TiO₂ film (thickness ~9 μm and active area 0.16 cm²) was performed by two-stage annealing: heating the TiO₂ film at 450° C. for 5 minutes, followed by another heating at 500° C. for 30 minutes. The TiO₂ film was then immersed in an aqueous solution of TiCl₄ (50 mM, 70° C.) for 30 minutes, followed by the same two-stage thermal treatment for final annealing of the electrode. In one embodiment, the electrode was then immersed in the ZnP-5/ethanol solution (20 mM, 25° C.) containing CDCA (20 mM) for 2 hours for dye loading onto the TiO₂ film. The Pt counter electrodes were prepared by spin-coating H₂PtCl₆ solution onto the FTO glass and heating at 400° C. for 15 minutes. To prevent a short circuit, the two electrodes were assembled into a cell of sandwich type and sealed with a hot-melt film (SX1170, Solaronix, 25 μm). In light of the disclosure of Q. Wang et al., *J. Phys. Chem. B* 2005, 109, 15397, the electrolyte solution containing LiI (0.1 M), I₂ (0.05 M), BMII (0.6 M), 4-tert-butylpyridine (0.5 M) in a mixture of acetonitrile and valeronitrile (1:1, v/v) was introduced into the space between the two electrodes, and the fabrication of the DSSC device was complete. In this embodiment, the concentration ratio of ZnP-5 to CDCA is 1:1; however, in another embodiment, the concentration ratio of ZnP-5 to CDCA may be varied.

Besides, according to the method similar to that mentioned above, the DSSC device using N3 dye was prepared for comparison.

Then, DSSC devices using ZnP-5 and N3 were analyzed for the photovoltaic properties and visible absorption spectra thereof. Through analyzing an I-V curve with respect to ZnP-5 and N3 by a solar simulator (Newport-Oriel 91160) having an air mass (AM) of 1.5, the performance of DSSC devices were assessed. The solar simulator uses filters and other optical components to simulate solar radiation having an AM of 1.5, and the output intensity is evenly distributed on a large area. When the DSSC device is irradiated with the solar simulator, the source meter (Keithley 2400) controlled by a computer transmits a voltage to the device, and the corresponding photocurrent is read at each step. The photoelectric conversion efficiency (η) is obtained by the relations below,

$$\eta = \frac{P_{mp}}{P_{in}} = \frac{J_{mp} * V_{mp}}{P_{in}} = \frac{J_{SC} * V_{OC} * FF}{P_{in}}$$

wherein P_{in} is the input radiation power, and P_{mp} is the maximum output power ($=J_{mp} * V_{mp}$), and FF indicates the fill factor defined as

$$FF = \frac{J_{mp} * V_{mp}}{J_{SC} * V_{OC}}$$

wherein J_{SC} is the short circuit current density, and V_{OC} is the open circuit voltage.

In this embodiment, CDCA was used as a co-adsorbate to prevent aggregation of the dyes on the TiO₂ surface. Besides, the concentration ratio of ZnP-5 to CDCA was varied as 1:0, 1:1, 1:2, 1:4, and 1:10 for seeking an optimal condition that can impede aggregation of ZnP-5 and increase the power conversion efficiency more effectively.

The measured visible absorption spectra of the ZnP-5 and the conventional N3 on the TiO₂ film are shown in FIG. 1(a), and the I-V curves of the corresponding DSSC devices are shown in FIG. 1(b). The photovoltaic parameters thereof are summarized in Table 2 respectively.

TABLE 2

[ZnP-5]:[CDCA]	I_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF	η (%)
1:0	12.22	686	0.645	5.4
1:1	14.33	710	0.594	6.0
1:2	13.22	708	0.640	6.0
1:4	12.05	710	0.662	5.7
1:10	11.23	701	0.668	5.3
N3	12.08	756	0.666	6.1

According to Table 2, it is concluded that when a solar simulator of AM 1.5 is employed, the DSSC devices using ZnP-5 with a ratio of 1:1 or 1:2 (ZnP-5:CDCA) have a overall conversion efficiency comparable to that using N3 dye.

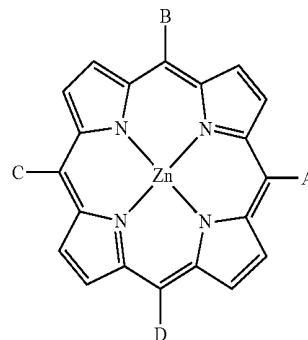
As shown in FIG. 1(a), when comparing the visible absorption spectra of DSSC devices using ZnP-5 and N3, it is found that the maximum wavelength of absorption peaks for N3 is at about 530 nm, whereas the Q-band of ZnP-5 is red-shifted to 650 nm because ZnP-5 comprises one of the special groups represented by the general formulae (131)~(140) in the above. Besides, the absorption coefficient of ZnP-5 is larger than that of N3. Therefore, in the visible region, ZnP-5 has longer absorption wavelength and larger absorption coefficient than N3.

Referring back to Table 1, it is found that since the porphyrin photosensitizer dyes of the present invention comprise one of the special groups represented by the general formulae (131)~(140), they have longer absorption wavelength and larger absorption coefficient in the visible region and are particularly applicable to indoor (artificial) light sources. Furthermore, the porphyrin photosensitizer dyes of the present invention are not Ru-containing complexes, so they provide the advantages of lower cost and better safety.

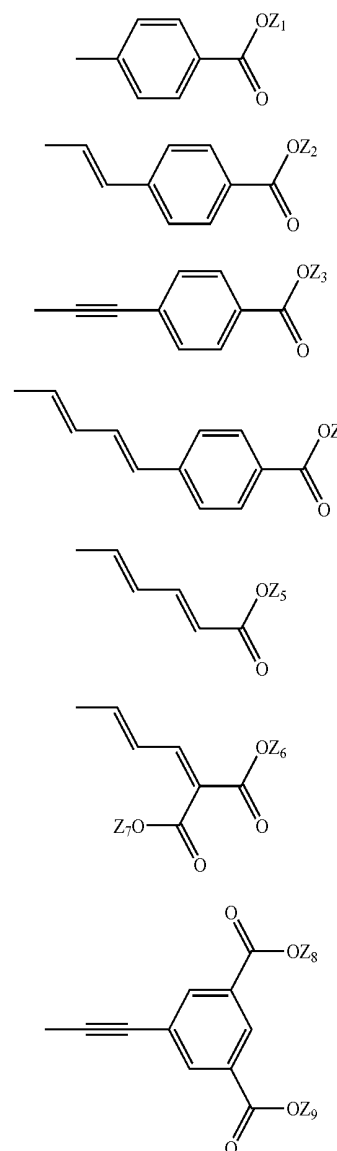
While some embodiments of the present invention are described above, it is intended that the scope of the invention be limited not by this detailed description, but rather by the claims appended hereto. Besides, it is intended that the following appended claims be interpreted as including all such alterations, permutations, and equivalents as fall within the true spirit and scope of the present invention.

What is claimed is:

1. A dye for a dye-sensitized solar cell, the dye being represented by the following general formula (100):

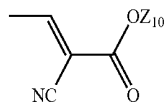


wherein A is represented by one of the following general formulae (111) to (118),



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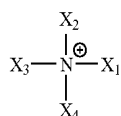


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wherein Z_1 to Z_{10} independently represent a hydrogen atom (H), lithium (Li), sodium (Na), or tetra-alkyl ammonium group represented by the following general formula (120),

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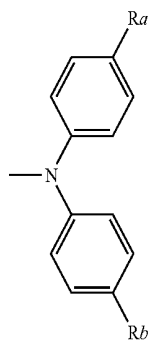
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wherein X_1 to X_4 independently represent C_mH_{2m+1} ($m=1$ to 6), and B, C, and D are the same or different, and independently represented by one of the following general formulae (131) to (140):

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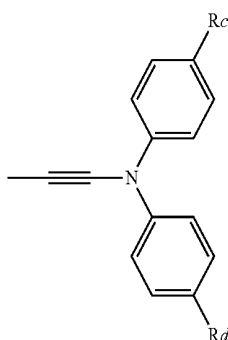
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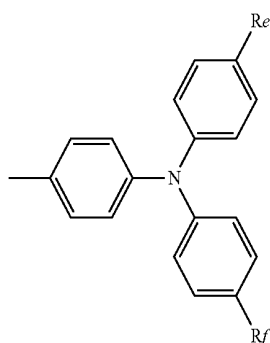
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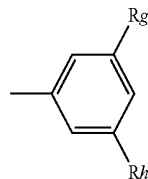
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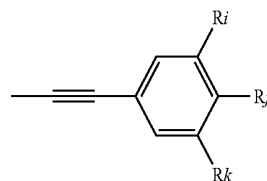
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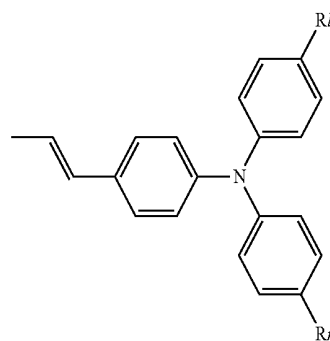
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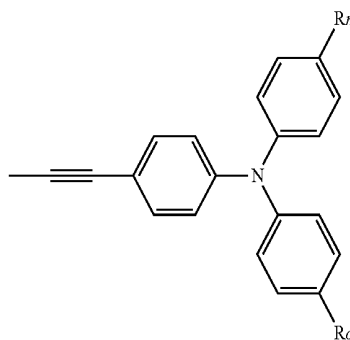
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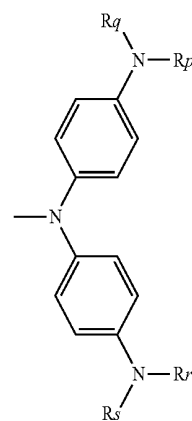
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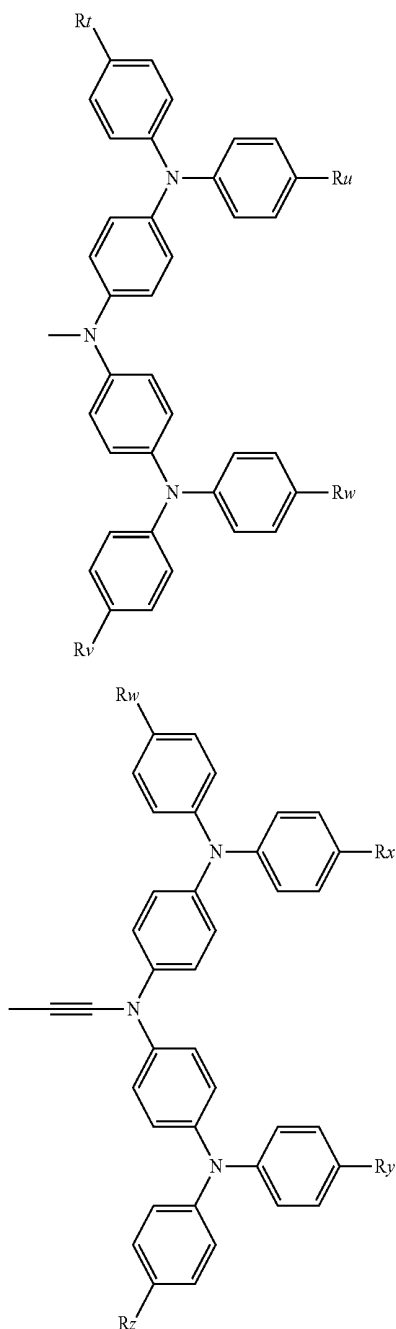
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wherein R_a to R_f and R_i to R_z , are independently selected from the group consisting of H, C_mH_{2m+1} ($m=1$ to 15), OC_pH_{2p+1} ($p=1$ to 15), $CH_2[OC_2H_4]_nOCH_3$ ($n=1$ to 30), and $[OC_2H_4]_qOCH_3$ ($q=1$ to 30), and R_g and R_h are independently selected from the group consisting of C_mH_{2m+1} ($m=1$ to 15), OC_pH_{2p+1} ($p=1$ to 15), $CH_2[OC_2H_4]_nOCH_3$ ($n=1$ to 30), and $[OC_2H_4]_qOCH_3$ ($q=1$ to 30).

2. The dye of claim 1, wherein A is represented by the general formula (113).

3. The dye of claim 2, wherein Z_3 represents a hydrogen atom (H).

4. The dye of claim 1, wherein B and D each are represented by the general formula (134) and C is represented by the general formula (131).

5. The dye of claim 4, wherein R_a , R_b , R_g , and R_h each represent C_mH_{2m+1} ($m=1$ to 15) or OC_pH_{2p+1} ($p=1$ to 15).

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6. The dye of claim 5, wherein R_a , R_b , R_g , and R_h each represent tert-butyl or $-C_6H_{13}$.

7. The dye of claim 1, wherein B, C, and D each are represented by the general formula (134).

8. The dye of claim 7, wherein R_g and R_h each represent C_mH_{2m+1} ($m=1$ to 15) or OC_pH_{2p+1} ($p=1$ to 15).

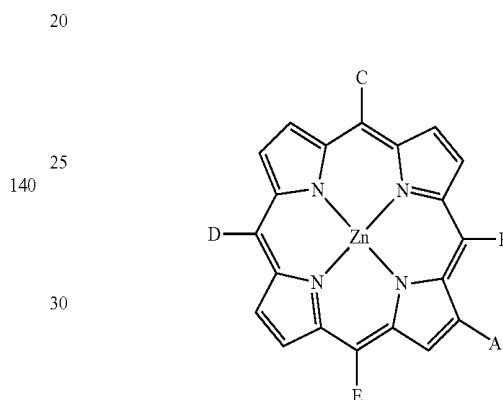
9. The dye of claim 8, wherein R_g and R_h each represent tert-butyl or $-C_6H_{13}$.

10. The dye of claim 1, wherein B, C, and D each are represented by the general formula (131).

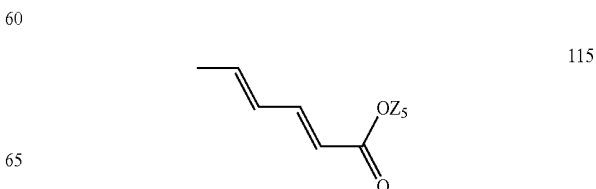
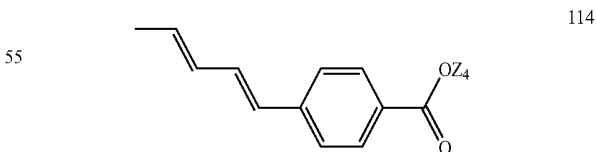
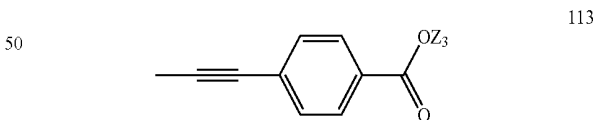
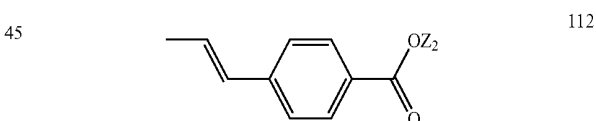
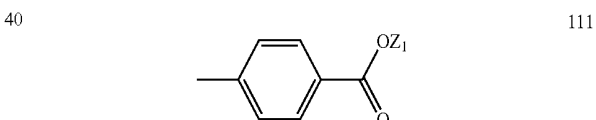
11. The dye of claim 10, wherein R_a and R_b each represent C_mH_{2m+1} ($m=1$ to 15) or OC_pH_{2p+1} ($p=1$ to 15).

12. The dye of claim 11, wherein R_a and R_b each represent tert-butyl or $-C_6H_{13}$.

13. A dye for a dye-sensitized solar cell, wherein the dye is represented by the following general formula (200):

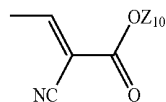
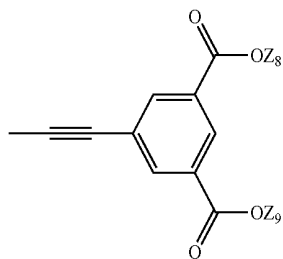
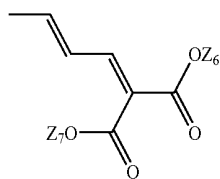


wherein A is represented by one of the following general formulae (111) to (118),



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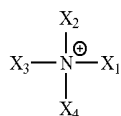
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wherein Z_1 to Z_{10} independently represent a hydrogen atom (H), lithium (Li), sodium (Na), or tetra-alkyl ammonium group represented by the following general formula (120),



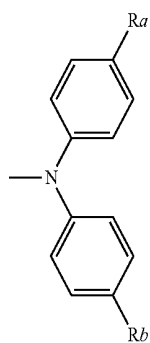
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wherein X_1 to X_4 independently represent C_mH_{2m+1} ($m=1$ to 6), and B, C, D, and E are the same or different, and independently represented by one of the following general formulae (131) to (140):

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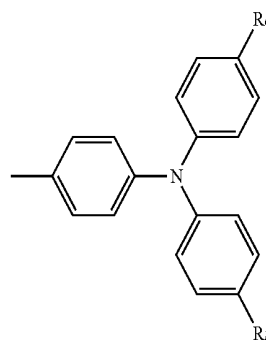
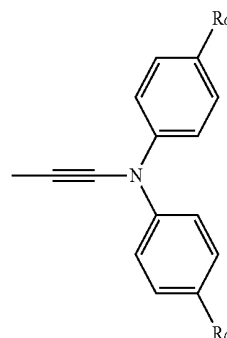


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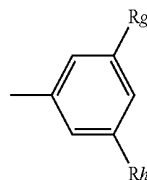
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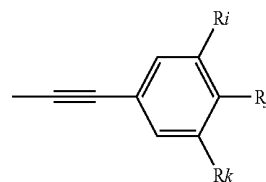
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134



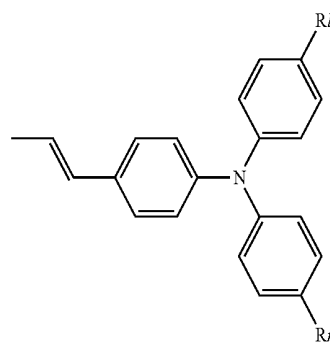
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135



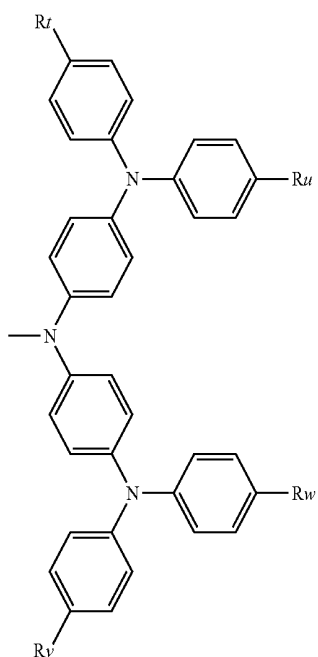
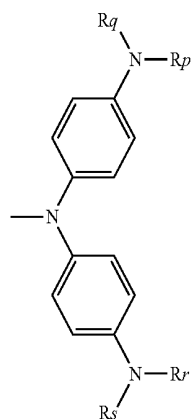
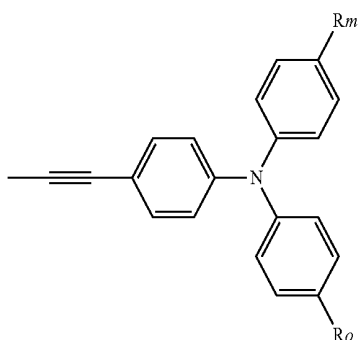
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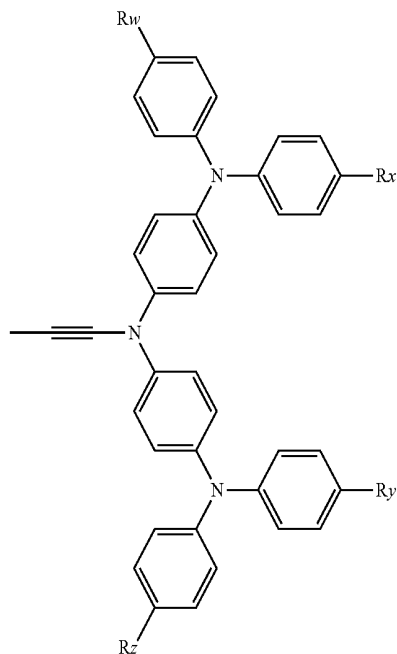
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wherein R_a to R_z are independently selected from the group consisting of H, C_mH_{2m+1} ($m=1$ to 15), OC_pH_{2p+1} ($p=1$ to 15), $CH_2[OC_2H_4]_nOCH_3$ ($n=1$ to 30), and $[OC_2H_4]_qOCH_3$ ($q=1$ to 30).

14. The dye of claim 13, wherein A is represented by the general formula (113).

15. The dye of claim 14, wherein Z_3 represents a hydrogen atom (H).

16. The dye of claim 13, wherein B, C, and E each are represented by the general formula (134) and D is represented by the general formula (131).

17. The dye of claim 16, wherein R_a , R_b , R_g , and R_h each represent C_mH_{2m+1} ($m=1$ to 15) or OC_pH_{2p+1} ($p=1$ to 15).

18. The dye of claim 17, wherein R_a , R_b , R_g , and R_h each represent tert-butyl or $-C_6H_{13}$.

19. The dye of claim 13, wherein B, C, D and E each are represented by the general formula (134).

20. The dye of claim 19, wherein R_g and R_h represent C_mH_{2m+1} ($m=1$ to 15) or OC_pH_{2p+1} ($p=1$ to 15).

21. The dye of claim 20, wherein R_g and R_h each represent tert-butyl or $-C_6H_{13}$.

22. The dye of claim 13, wherein B, C, D, and E each are represented by the general formula (131).

23. The dye of claim 22, wherein R_a and R_b each represent C_mH_{2m+1} ($m=1$ to 15) or OC_pH_{2p+1} ($p=1$ to 15).

24. The dye of claim 23, wherein R_a and R_b each represent tert-butyl or $-C_6H_{13}$.

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