

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
4 December 2008 (04.12.2008)

PCT

(10) International Publication Number
WO 2008/145172 A1

(51) International Patent Classification:

C07D 487/22 (2006.01) **H01L 31/042** (2006.01)
C07F 3/06 (2006.01) **H01M 14/00** (2006.01)
C09B 47/04 (2006.01)

(21) International Application Number:

PCT/EP2007/055110

(22) International Filing Date: 25 May 2007 (25.05.2007)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicants (for all designated States except US): **UNIVERSIDAD AUTÓNOMA DE MADRID** [ES/ES]; Einstein, 3, E-28049 Cantoblanco - Madrid (ES). **INSTITUT CATALÀ DE INVESTIGACIÓ QUÍMICA** [ES/ES]; Avinguda Països Catalans, 16, E-43007 Tarragona (ES). **ECOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE** [CH/CH]; SRI Station, 10, CH-1015 Lausanne (CH).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **TORRES CEBADA, Tomás** [ES/ES]; Universidad Autónoma De Madrid, Einstein, 3, E-28049 Cantoblanco - Madrid (ES). **CID MARTÍN, Juan José** [ES/ES]; Universidad Autónoma de Madrid, Einstein, 3, E-28049 Cantoblanco - Madrid (ES). **KHAJA NAZEERUDIN, Mohammad** [IN/CH]; Ecole Polytechnique Fédérale de Lausanne, SRI Station, 10, CH-1015 Lausanne (CH). **HO YUM, Jun**

[KR/CH]; Ecole Polytechnique Fédérale de Lausanne, SRI Station, 10, CH-1015 Lausanne (CH). **GRAETZEL, Michael** [CH/CH]; Ecole Polytechnique Fédérale de Lausanne, SRI Station, 10, CH-1015 Lausanne (CH). **PALOMARES, Emilio** [ES/ES]; Institut Català de Investigació Química, Avinguda Països Catalans, 16, E-43007 Tarragona (ES).

(74) Agent: **BERNARDO NORIEGA, Francisco**; ABG Patentes, S.L., Orense, 68 7th floor, E-28020 Madrid (ES).

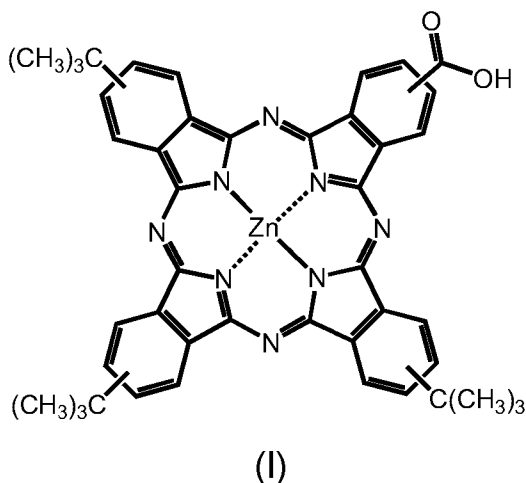
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

(54) Title: TRI-*TERT*-BUTYLCARBOXYPHTHALOCYANINES, USES THEREOF AND A PROCESS FOR THEIR PREPARATION



(57) Abstract: Substituted carboxyphthalocyanines (I), wherein both the *tert*-butyl and carboxyl groups located in the four isoindole rings are located independently in any of the four positions of the corresponding benzene ring of each isoindole ring, its regioisomers and mixtures thereof, can be used in the manufacture of organic and hybrid solar cells or as a photoactive dyes for molecular photovoltaic devices.

**TRI-*TERT*-BUTYLCARBOXYPHthalOCYANINES, USES THEREOF AND A
PROCESS FOR THEIR PREPARATION**

FIELD OF THE INVENTION

5 The present invention relates to substituted carboxyphthalocyanines, to their uses, e.g., in the manufacture of organic and hybrid solar cells or as a photoactive dyes for molecular photovoltaic devices, and to a process for obtaining said compounds.

BACKGROUND OF THE INVENTION

10 The molecular materials and polymers with “non-conventional properties” have attracted the attention of a wide scientific community. Thus, the spectacular electrical and optical properties of the organic conducting polymers have generated an intense work by chemists, physicists and technologists during the last few years in order to synthesize this type of materials, study their properties and apply them in the industry.

15 The applications are many: solar cells, light emitting diodes (LED), intelligent windows capable of filtering the solar light, screens for mobile phones and small television sets, among others. Molecular electronics are the basis of all these applications. The possibility of producing electronic components constituted by individual organic molecules will allow the reduction in size of computers and other electronic systems, as

20 well as increase the speed of information transmission to a level difficult to imagine. These materials can be easily obtained by conventional organic synthesis.

 Solar or photovoltaic cells are devices that allow the conversion of light energy into electric power. Until now, the conversion of solar radiation into electricity has been made almost exclusively by means of devices based on an inorganic material: silicon. The

25 average efficiency of these cells is ca. 25%. However, producing electricity through this system is still expensive.

 There is another type of solar cells, the organic ones that can efficiently complement the former ones and even surpass them in several aspects. They are based either on organic conduction polymers or on semiconducting nanostructures sensitized

30 by dyes (hybrid cells). These cells have conversion efficiencies close to 5%, the first ones, and above 10% the latter, but both have a large potential of improvement. The organic solar cells will be fabricated in a much cheaper way and give rise to much more

versatile products. They are constituted by carbon compounds, so that the produced materials, unlike the silicon-based cells, can be ultrathin, light and flexible. They can be put on almost all surfaces like walls or windows of buildings, canvas tents for providing energy to people inside, as well as on clothes for fuelling personal electronic devices.

- 5 This fact has given rise to the development of new photovoltaic technologies that have a great commercial potential.

Among the organic molecules that can be employed as active elements in the preparation of organic solar cells, phthalocyanines are starting to play a relevant role. The phthalocyanines are synthetic analogues of porphyrins, compounds that are

10 components of several systems like haemoglobine and chlorophyll. They are chemically and thermically robust and stable against electromagnetic radiations. Phthalocyanines are very colourful compounds (green and blue) largely used in the industry ranging from dyes and pigments in paintings to active components in CDs. Incorporated in an organic or inorganic structure, they can act as “antenna” elements, harvesting light, since they

15 absorb strongly in the same region of the emission spectrum of solar light. These materials have a strong absorption in the 650-700 nm region (Q band), whose position can be altered by introducing adequate substituents. On the other hand, phthalocyanines fulfill all the necessary conditions for being incorporated as essential components of photovoltaic devices. Thus, for example, mixed with an organic polymer or in pure state

20 they can be processed as thin films by the spin-coating technique. Moreover, these compounds are soluble in organic solvents and can be processed by the Langmuir-Blodgett technique and some of them show liquid crystal characteristics that enhance their possible technological applications in the mentioned field.

These and other properties and features of organic materials in general, and of

25 phthalocyanines in particular, are collected in many monographies and scientific articles such as (a) Leznoff, C.C.; Lever, A.B.P.; *Phthalocyanines. Properties and Applications*, Vols. 1, 2, 3 y 4, VCH publishers, Inc. 1989, 1993, 1996. (b) N. B. McKeown; *Phthalocyanine Materials*, Cambridge University Press 1998. (c) Kadish, K.M.; Smith, K.M.; Guillard, R.; *The Porphyrin Handbook*; Vols. 15-20, Academic Press: San Diego,

30 2003.

From this and related literature, and especially from the current drawbacks in the application of phthalocyanines in the preparation of photovoltaic cells, can be deduced

the importance and interest of preparing new related compounds with improved properties.

The present invention not only intends to offer synthetic process for the medium-scale preparation of carboxyphthalocyanines, but also to improve the optical properties and stability of these compounds, as well as their processability in order to be applied as active elements to solar cells with organic basis. Inventors have found that certain phthalocyanines gather many of the desired features at the same time: optical and chemical stability, solar light absorption efficiency, low aggregation and capability to anchor to polymeric or inorganic substrates like silicon oxide, zinc oxide and titanium oxide, among others, that allow their application to the fabrication of photovoltaic devices with a higher efficiency than that described so far in the literature.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing the Incident Photon to Current Conversion Efficiency (IPCE) at different wavelengths for a mixture comprising several regioisomers of 9(10), 16(17), 23(24)-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazaacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II), identified as **TT1** (Example 1) in this description.

Figure 2 is a graph showing the light-to-electricity conversion efficiency of a molecular photovoltaic device comprising a mesoporous semiconducting film of titanium oxide nanoparticles, sensitised with the same mixture of 9(10), 16(17), 23(24)-tri-*tert*-butyl-2-carboxy derivatives (**TT1**) mentioned above and a red/ox electrolyte (iodine/iodide) when irradiated with simulated sun light 1.5 AM G at 100 mW/cm². The compound W900 [2,9,16,23-tetracarboxyphthalocyanine zinc (II)] was used as a reference for comparison.

Figure 3 is a graph showing the visible spectrum of **TT1** in the presence of the different amounts of chenodeoxycholic acid (CHENO) mentioned in the figure. The spectra were measured using a Shimadzu spectrophotometer.

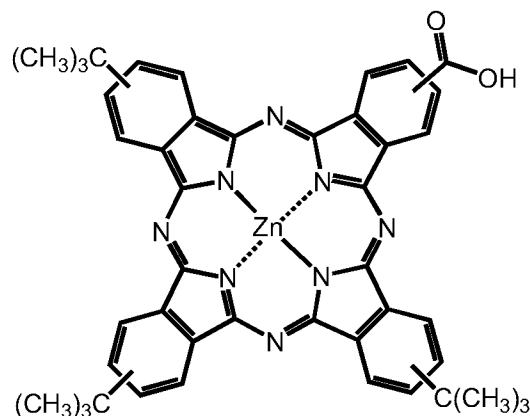
Figure 4 is a graph showing the Incident Photon to Current Conversion Efficiency (IPCE) at different wavelengths covering practically all the Visible-IR solar spectra for different compounds, namely, the mixture of 9(10), 16(17), 23(24)-tri-*tert*-

butyl-2-carboxy derivatives (**TT1**) mentioned above, JK2 (3-{5'-[N,N-bis(9,9-dimethylfluorene-2-yl)phenyl]-2,2'-bithiophene-5-yl}-2-cyanoacrylic acid) and a mixture of JK2 and **TT1**.

5

DESCRIPTION OF THE INVENTION

In an aspect, the present invention relates to a substituted carboxyphthalocyanine of structural formula **I**,



I

10 wherein both the *tert*-butyl and carboxyl groups located in the four isoindole rings can be located indiscriminately in any of the four positions of the corresponding benzene ring, its regioisomers and mixtures thereof.

As it is well-known, “regioisomers” are position isomers having the same functional group or substituent in different positions; regioisomers have the same
15 molecular formula but different chemical and physical properties.

In a particular embodiment, the carboxyl group located in the isoindole ring is located in any of positions 1 or 2 (equivalents to positions 4 and 3, respectively) of the benzene ring of the corresponding isoindole ring. In a preferred embodiment, the carboxyl group is located in position 2 of said benzene ring.

20 In another particular embodiment, the *tert*-butyl groups located in the three isoindole rings are located indiscriminately in any of the two central positions of each one

of the corresponding benzene rings, i.e., in positions 9 or 10 [9(10)], 16 or 17 [16(17)], and 23 or 24 [23(24)] of the isoindole rings of compound **I**.

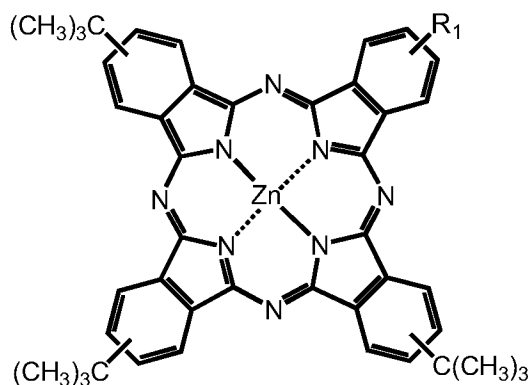
In a particular embodiment, the compound **I** is selected from the group of regioisomers consisting of:

- 5 9, 16, 23-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II);
- 9, 16, 24-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II);
- 9, 17, 23-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II);
- 10 9, 17, 24-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II);
- 10, 16, 23-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II);
- 15 10, 16, 24-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II);
- 10, 17, 23-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II); and
- 10, 17, 24-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II).
- 20

In another particular embodiment, the compound **I** comprises a mixture of two or more of said regioisomers in any ratio among them, e.g., in a statistical ratio (i.e., in the ratio of regioisomers resulting from the production process taking into account, among other things, the starting materials and the steric hinderance and electronic influence due to their substituents). In a preferred embodiment, the compound **I** is a mixture of regioisomers of 9(10), 16(17), 23(24)-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-

7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II) (mixture of regioisomers) identified in this description as **TT1**.

In other aspect, the present invention relates to a process for obtaining a compound of formula **I** which comprises reacting an adequately substituted tri-*tert*-butylphthalocyanine of structural formula **II**



II

10 wherein

the *tert*-butyl groups located in the three isoindole rings can be located indiscriminately in any of the four positions of the corresponding benzene ring, and

15 R^1 represents a functional group or a carbon-containing substituent that can be converted into a carboxylic group, said R^1 group being located indiscriminately in any of the four positions of the corresponding benzene ring,

with an adequate oxidizing reagent, to yield the compound **I**.

As mentioned above, R^1 represents a functional group or a substituent that can be converted into a carboxylic group, in one or more steps, with an appropriate reagent, to yield the compound **I**. The preferred R^1 groups or substituents are carbon-containing groups such as hydroxyalkyl, alkylcarbonyl, aldehyde, alkenyl or alkynyl, among others, wherein the terms “alkyl”, “alkenyl” and “alkynyl” represent, linear or branched, saturated or unsaturated carbon-containing chains having one (two in the cases of alkenyl and alkynyl) to sixteen carbon atoms, such as methyl, n-octyl, n-hexadecyl, ethenyl

(vinyl), ethynyl, etc., optionally substituted with aromatic groups, e.g., phenyl groups, etc. In a particular embodiment, R¹ is formyl or vinyl.

In a particular embodiment, R¹ is located in position 1 or 2 of the corresponding benzene ring. In a preferred embodiment, R¹ is located in position 2 of the benzene ring
5 of the isoindole ring (compound **II**).

In another particular embodiment, the *tert*-butyl groups located in the three isoindole rings are located indiscriminately in any of the two central positions of each one of the corresponding benzene rings, i.e., in positions 9 or 10 [9(10)], 16 or 17 [16(17)], and 23 or 24 [23(24)] of the isoindole rings of compound **II**.

10 The compounds **II** can exist in the form of pure compounds (regioisomers) or in the form of mixtures of two or more regioisomers. Thus, the starting compounds of formula **II**, that can be prepared following methods described in the state of the art (see for example, Gouloumis, A; Liu, S.-G.; Sastre, A.; Echegoyen, L.; Vázquez, P.; Torres, T. *Chem. Eur. J.* **2000**, 6, 3600-3607. Guldi, D. M; Gouloumis, A.; Vázquez, P.;
15 Torres, T.; Georgakilas, V.; Prato, M. *J. Am. Chem. Soc.* **2005**, 127, 5811-5813. Maya, E.M; Vázquez, P.; Torres, T. *Chem. Comm.* **1997**, 1175), can be either pure compounds (regioisomers) or mixtures of two or more regioisomers. In the manufacture of the compound **I**, the starting compounds **II** can be used as pure compounds (regioisomers) or as mixtures of two or more regioisomers.

20 The reagents for the conversion of compounds **II** into the title compounds **I** are suitable oxidizing reagents. Illustrative, non-limitative examples of said oxidizing reagents include potassium permanganate, ozone, sodium chlorite/sulfamic acid, and any other reagent adequate to each one of the functional group or carbon-containing substituents above mentioned.

25 In a particular embodiment, the oxidation of a compound **II**, wherein R¹ represents an aldehyde group, is performed with an adequate oxidizing agent, such as sodium chlorite/sulfamic acid, etc. In other particular embodiment, the oxidation of a compound **II**, wherein R¹ represents a hydroxymethyl or methylcarbonyl group is performed with an adequate oxidizing agent, such as potassium permanganate, etc.
30 Further, in another particular embodiment, the oxidation of a compound **II**, wherein R¹

represents a vinyl or ethynyl group, is performed with an adequate oxidizing agent, such as ozone in non-reductive conditions, etc.

The oxidation reaction can take place in both polar and non-polar solvents according to the reagent employed, as it is well known in the technique for this kind of
5 oxidations. Illustrative, non-limitative examples of said solvents include acetone, dichloromethane, etc. Temperatures for carrying out the oxidation reaction (conversion) can vary within a broad range, however, conversions taking place between -78°C and 100°C are preferred.

As mentioned above, compounds **I** can be used in the fabrication (manufacture)
10 of organic and hybrid solar cells, where they can be used as pure compounds (regioisomers) or as mixtures of two or more of them, i.e. two or more regioisomers, preferably, as a mixture of two or more regioisomers.

Alternatively, in the manufacture of organic and hybrid solar cells, compounds **I** can also be mixed in any ratio with other dye(s) or with organic material(s), electronically
15 active or non-active ones, such as an organic conducting polymer, oligomer or copolymer, e.g., polyphenylenevinylene (PPV) or a polythiophene, or they can be covalently incorporated to the backbone of a polymer, oligomer or copolymer.

Moreover, in the manufacture of hybrid solar cells, the compounds **I** can be adsorbed into a nanocrystalline semiconductor, such as a nanocrystalline semiconducting
20 film, e.g., titanium oxide or zinc oxide films, having the advantage that the compounds are not aggregated on the inorganic surface.

The compounds **I**, due to their versatility, can be processed in thin films using evaporation techniques, spin-coating or drop cast procedures, and in Langmuir-Blodgett films (i.e., they can be processed by the Langmuir-Blodgett technique).

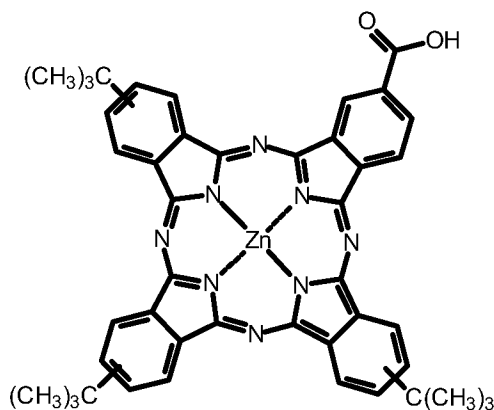
25 Thus, in other aspect, the invention relates to an organic or hybrid solar cell comprising a compound **I**, optionally mixed with a dye or with an organic material, electronically active or not, or covalently incorporated to the backbone of a polymer, oligomer or copolymer.

In a further aspect, the invention relates to a hybrid solar cell comprising a compound **I** adsorbed in a nanocrystalline semiconductor, such as a nanocrystalline semiconducting film, e.g., titanium oxide or zinc oxide films.

The compounds **I** have a strong absorption (Q Band) around 700 nm and are soluble in organic solvents like tetrahydrofurane, acetone, acetonitrile, methanol, dioxane and diethyl ether, which have great advantages in the practical application of the products of this invention (compounds **I**), that have not been described in the previous scientific literature, neither as chemical products nor as molecular organic materials with adequate properties to be used in photovoltaic devices.

Thus, compounds **I** can also be used as photoactive dyes in molecular photovoltaic devices comprising a mesoporous semiconductor, a photoactive dye and an electrolyte (e.g., a liquid or solid electrolyte) as well as photoactive dyes in molecular photovoltaic devices in the manufacture of tandem devices (combination of several, equal or different, molecular photovoltaic devices) or mesoporous co-sensitized films (combination of several dyes in the same device, "all-in-one") [i.e., the compound **I** can also be used as photoactive dyes to form, together with one or more additional dye(s), a mesoporous co-sensitized film]. The photoactive dye is able to absorb light in the near infrared region of the solar spectra and efficiently convert the sunlight into electrical power.

For example, a mixture of the compounds **I** named **TT1**, which is depicted below, and whose production is disclosed in Example 1,



TT1

constituted by several regioisomers, namely by the 9(10), 16(17), 23(24)-tri-*tert*-butyl-2-carboxy derivatives, wherein the *tert*-butyl groups may be placed on any of the two
5 central positions of each one of the four benzene rings, shows an incident photon to current conversion efficiency (IPCE) higher than 80% at 700 nm (Figure 1) which is in agreement with the absorbance maximum on the UV-Vis spectra of the molecule.

On the other hand, molecular photovoltaic devices made using a mesoporous
10 semiconducting film of titanium oxide nanoparticles, sensitised with the same mixture of the regioisomers (**TT1**) depicted above, and a red/ox electrolyte (iodine/iodide), have efficiencies for the conversion of light-to-electricity higher than 3% when irradiated with simulated sun light 1.5 AM G at 100mW/cm² (Figure 2).

The high efficiency in the solar light conversion of the molecular photovoltaic
15 devices made of substituted carboxyphthalocyanines (**TT1**) is due to the lack of molecular aggregates of these compounds on the surface of the nanoparticles of TiO₂, which form the photoelectrode (Figure 3). The lack of molecular aggregates is directly related to the new design of the molecules that prevents the aggregation.

Moreover, **TT1** can be combined with other dyes to widen the absorption of light
20 into the visible region. This combination can allow the conversion of light-to-electrons in almost all the Visible-IR solar spectra (Figure 4). Such property is extremely valuable for the preparation of tandem devices (combination of two or more devices that absorb light at different wavelengths) or "all-in-one" mesoporous sensitised film (co-sensitisation).

Thus, in other aspect, the invention relates to a molecular photovoltaic device
25 comprising a photoactive dye, wherein said photoactive dye comprises a substituted carboxyphthalocyanine **I**; said molecular photovoltaic device further comprises a mesoporous semiconductor and an electrolyte (e.g., a liquid or solid electrolyte).

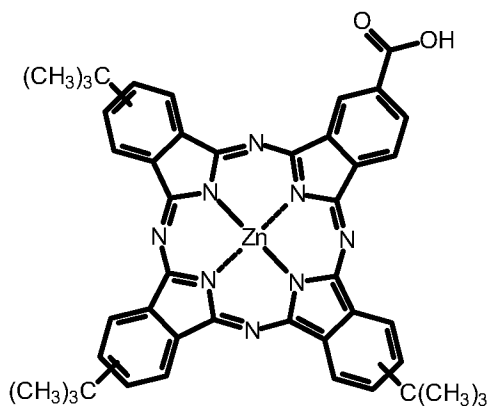
In another aspect, the invention relates to a tandem device comprising a
combination of two or more, equal or different, molecular photovoltaic devices wherein
30 at least one of said molecular photovoltaic devices comprises a substituted carboxyphthalocyanine **I** as photoactive dye.

In a further aspect, the invention relates to a co-sensitized mesoporous film comprising a substituted carboxyphthalocyanine **I** together with one or more additional dye(s).

The following examples illustrate the present invention and as such are not to be considered as limiting the invention set forth in the claims appended hereto.

EXAMPLE 1

9(10), 16(17), 23(24)-Tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo- tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)- N²⁹, N³⁰, N³¹, N³² zinc (II) (mixture of regioisomers) (TT1)



Method A: To a vigorously stirred solution of 9(10), 16(17), 23(24)-tri-*tert*-butyl-2-formyl-5,28:14,19-diimino-7,12:21,26-dinitrilotetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II) (statistical mixture of regioisomers) (130 mg, 0.17 mmol) in acetone (96 mL), cooled at 0°C, NaClO₂ (47 mg, 0.50 mmol) was added in a few portions. Then, a solution of sulfamic acid (51 mg, 0.50 mmol) in deionised water (12 mL) was added at once. The ice bath was removed and the reaction was allowed to proceed at room temperature for 4 h. After the starting compound disappeared, the solution was poured into aqueous HCl 0.1 M (400 mL) and a blue-greenish solid precipitated. The solid was filtered over Celite® and washed with water and mixtures water/MeOH (3:1) and (2:1) (100 mL each). The solid was dried in vacuum and extracted with THF. The solvent was evaporated and the crude product was triturated in hexane, filtered and washed with a cold solution of water/MeOH (1:1) (50

mL) and finally with MeOH (25 mL). In this way, 103 mg (0.13 mmol) of carboxyphthalocyanines were obtained as a dark blue solid. Yield 78%.

Method B: A stirred solution of 9(10), 16(17), 23(24)-tri-*tert*-butyl-2-vinyl-5,28:14,19-diimino-7,12:21,26-dinitrilotetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacyclo-
 5 eicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc(II) (statistical mixture of regioisomers) (320 mg, 0.416 mmol) in CH₂Cl₂ (200 mL) was brought to -78°C and an ozone current (excess) was passed through the solution for 2 min. Then, under a nitrogen gas flow, the reaction was allowed to reach the room temperature. An aqueous solution (80 mL) containing AcOH and H₂O₂ (30%) (15 mL each) was then added, and the mixture stirred vigorously
 10 for 15 min. The organic layer was separated and the solvent removed. The crude product was purified as described above in Method A to give 31 mg (0.04 mmol) of carboxyphthalocyanines. Yield 9%.

Mp: > 250°C

15 **¹H-NMR (500 MHz, DMSO-*d*₆), δ (ppm):** 13.4 (bs, 1H; COOH), 9.9-8.0 (m, 12H; Pc-H), 1.8 (m, 27H; C(CH₃)₃)

FT-IR (KBr) ν (cm⁻¹): 3442 ν_{st}(COO-H) (free monomer), 2955-2865 ν_{st}(COO-H) (associated dimer), 1695 ν_{st}(C=O), 1612, 1484, 1394, 1364, 1323, 1281, 1256, 1192, 1139, 1081, 1046, 922, 833, 745, 728, 689

20 **UV-Vis (THF), λ_{max} (nm) (log ε) :** 680 (5.2), 668 (5.2), 606 (4.5), 350 (4.9)

MS (MALDI, dithranol), *m/z*: 788-796 [(M+H)⁺]

Elemental Analysis: C₄₅H₄₀N₈O₂Zn (790.24)

Calculated: C 68.40, H 5.10, N 14.18%

Found: C 68.31, H 5.19, N 14.40 %

25

TT1 was used for preparing molecular photovoltaic devices (Example 2) which comprise a mesoporous semiconductor film sensitized with the photoactive dye **TT1**. Such devices are efficient converting sun light into electrical power in the near IR-region of the sun light spectrum, as indicated in the description.

30

EXAMPLE 2

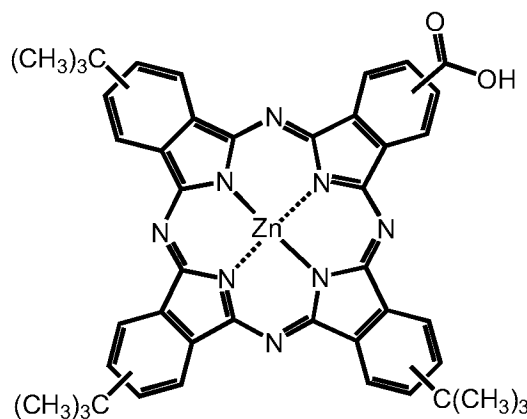
Preparation of molecular photovoltaic devices

The molecular photovoltaic devices were made using as working electrode a transparent glass coated with a conducting metal oxide such as indium tin oxide (ITO) or fluorine doped tin oxide (FTO). On top of this conductive glass a TiO_2 mesoporous semiconductor film was deposited. The thickness can vary between 2 to 20 micrometers.

- 5 The film was sensitised with the photoactive dye (**TT1**). The working electrode was assembled into a device using a polymer that seals the working electrode together with a counter electrode made of the same conducting glass with a thin layer of a platinum catalyst. The electrolyte was made using as red/ox couple a solution of iodine/iodide, and it was introduced through holes that previously had been made on the counter electrode.

CLAIMS

1. A substituted carboxyphthalocyanine of structural formula **I**,

**I**

wherein both the *tert*-butyl and carboxyl groups located in the four isoindole rings are located indiscriminately in any of the four positions of the corresponding benzene ring, its regioisomers and mixtures thereof.

10

2. Compound according to claim 1, wherein the carboxyl group located in the isoindole ring is located in any of positions 1 or 2 of the benzene ring.

3. Compound according to claim 1, wherein the *tert*-butyl groups located in the three isoindole rings are located indiscriminately in any of the two central positions of each one of the corresponding benzene rings of the isoindole rings of compound **I**.

4. Compound according to claim 1, selected from the group of regioisomers consisting of:

- 9, 16, 23-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II);

- 9, 16, 24-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II);
- 9, 17, 23-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II);
- 5 9, 17, 24-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II);
- 10, 16, 23-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II);
- 10, 16, 24-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II);
- 10 10, 17, 23-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II);
- 10, 17, 24-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II); and
- 15 mixtures thereof.

5. Compound according to claim 1, comprising a mixture of regioisomers 9(10), 16(17), 23(24)-tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilo-tetrabenzo[c, h, m, r][1, 6, 11, 16]tetraazacycloeicosinato-(2⁻)-N²⁹, N³⁰, N³¹, N³² zinc (II).

20

6. A process for obtaining a substituted carboxyphthalocyanine of structural formula **I** according to anyone of claims 1 to 5, which comprises reacting a substituted tri-*tert*-butylphthalocyanine of structural formula **II**

**II**

wherein

- 5 the *tert*-butyl groups located in the three isoindole rings are located indiscriminately in any of the four positions of the corresponding benzene ring, and

- R^1 represents a functional group or a carbon-containing substituent which is converted into a carboxylic group, said R^1 group being located indiscriminately in
 10 any of the four positions of the corresponding benzene ring,
 with an adequate oxidizing reagent, to yield the compound **I**.

7. The process of claim 6, wherein R^1 is hydroxyalkyl, alkylcarbonyl, aldehyde, alkenyl or alkynyl.

15

8. The process of claim 7, wherein

- the oxidation of a compound **II**, wherein R^1 represents an aldehyde group, is performed with sodium chlorite/sulfamic acid; or wherein
- the oxidation of a compound **II**, wherein R^1 represents a hydroxymethyl or methylcarbonyl group, is performed with potassium permanganate; or
 20 wherein
- the oxidation of a compound **II**, wherein R^1 represents a vinyl or ethynyl group, is performed with ozone in non-reductive conditions.

9. Use of a substituted carboxyphthalocyanine according to anyone of claims 1 to 5 in the manufacture of an organic or hybrid solar cell, both as a pure regioisomer or as a mixture of two or more of them.

5 10. The use according to claim 9, wherein said substituted carboxyphthalocyanine is mixed with a dye or with an organic material, electronically active or not, or covalently incorporated to the backbone of a polymer, oligomer or copolymer.

11. The use according to claim 10, wherein said dye or organic material,
10 electronically active or not, is an organic conducting polymer, oligomer or copolymer.

12. Use according to claim 11, wherein said organic conducting polymer, oligomer or copolymer, is a polyphenylenevinylene (PPV) or a polythiophene.

15 13. Use of a substituted carboxyphthalocyanine according to anyone of claims 1 to 5, in the manufacture of a hybrid solar cell, wherein said substituted carboxyphthalocyanine is adsorbed in a nanocrystalline semiconductor.

14. Use of a substituted carboxyphthalocyanine according to anyone of claims 1
20 to 5, as photoactive dye in a molecular photovoltaic device, said device comprising a mesoporous semiconductor, a photoactive dye and an electrolyte, wherein said photoactive dye comprises a substituted carboxyphthalocyanine according to anyone of claims 1 to 5.

25 15. The use according to claim 14, wherein said molecular photovoltaic device is combined to one or more, equal or different, molecular photovoltaic device(s) to form a tandem molecular photovoltaic device.

16. Use of a substituted carboxyphthalocyanine according to anyone of claims 1
30 to 5, as photoactive dye for co-sensitizing, together with one or more additional dye(s), a mesoporous film.

17. An organic or hybrid solar cell comprising a substituted carboxyphthalocyanine according to anyone of claims 1 to 5, optionally mixed with a dye or with an organic material, electronically active or not, or covalently incorporated to the backbone of a polymer, oligomer or copolymer.

5

18. A hybrid solar cell comprising a substituted carboxyphthalocyanine according to anyone of claims 1 to 5, adsorbed in a nanocrystalline semiconductor.

19. A molecular photovoltaic device comprising a photoactive dye, wherein said
10 photoactive dye comprises a substituted carboxyphthalocyanine according to anyone of claims 1 to 5.

20. A tandem device comprising a combination of two or more molecular photovoltaic devices according to claim 19.

15

21. A co-sensitized mesoporous film comprising a substituted carboxyphthalocyanine according to anyone of claims 1 to 5 together with one or more additional dye(s).

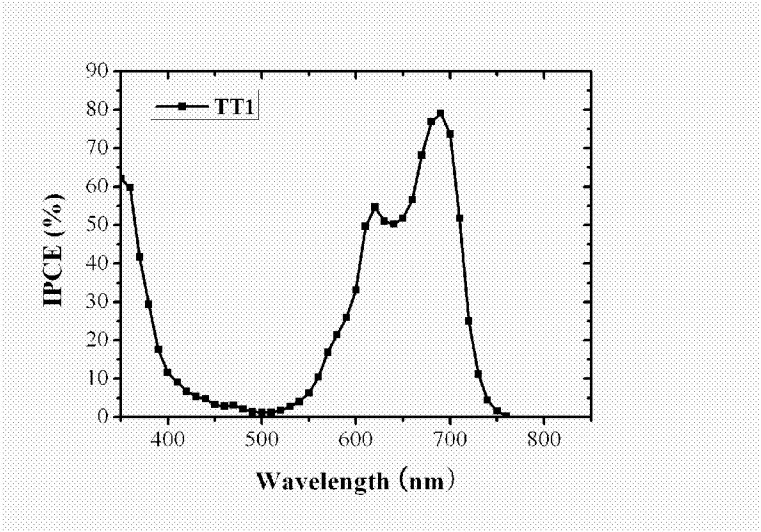


Figure 1

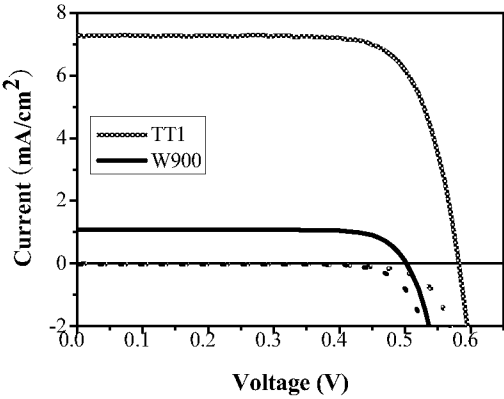
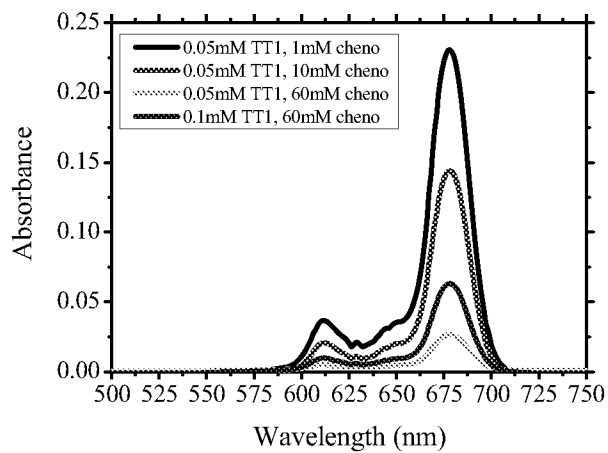
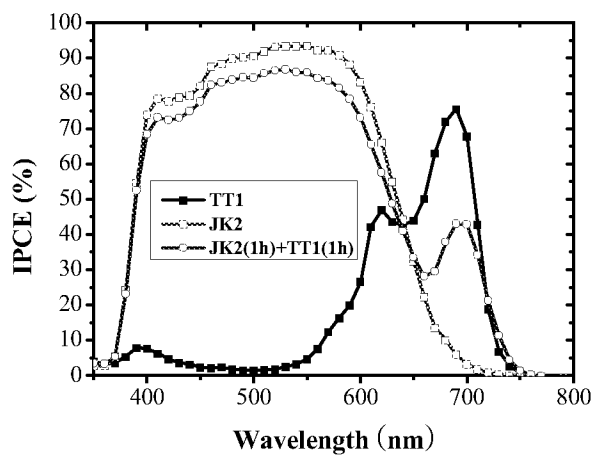


Figure 2

**Figure 3****Figure 4**

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/055110

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07D487/22 C07F3/06 C09B47/04 H01L31/042 H01M14/00

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)

C07D C09B H01L H01M C07F

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

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

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	P.Y. REDDY ET AL: "Efficient sensitization of nanocrystalline TiO ₂ films by a near-IR-absorbing unsymmetrical tinc phthalocyanine" ANGEWANDTE CHEMIE. INTERNATIONAL EDITION., vol. 46, 5 December 2006 (2006-12-05), pages 373-376, XP002469442 DEVCH VERLAG, WEINHEIM. example PCH001	1-21
A	US 2003/134824 A1 (BRESLOW RONALD [US] ET AL) 17 July 2003 (2003-07-17) claims 1,11,14,16 ----- -/--	1-21



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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

E earlier document but published on or after the international filing date

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

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

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

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

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

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

& document member of the same patent family

Date of the actual completion of the international search

18 February 2008

Date of mailing of the international search report

06/03/2008

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

VOYIAZOGLOU, D

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/055110

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BAUGH S D P ET AL: "Cyclodextrin dimers as cleavable carriers of photodynamic sensitizers" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC, US, vol. 123, 2001, pages 12488-12494, XP002458589 ISSN: 0002-7863 page 12489, right-hand column; example 6 -----	1-21
E	JP 2007 231040 A (AISIN SEIKI; COUNCIL SCIENT IND RES) 13 September 2007 (2007-09-13) abstract -----	1-21

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2007/055110

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2003134824 A1	17-07-2003	AU 2002364950 A1 WO 03052060 A2	30-06-2003 26-06-2003
JP 2007231040 A	13-09-2007	NONE	