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(54) Title: METAL-FREE PHOTOSENSITIZERS

(57) Abstract: The present invention relates to metal-free organic photosensitizers and to the process for their preparation; the use of such compounds for manufacturing solar cells is contemplated as well.

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DESCRIPTION

"Metal-free photosensitizers"

[0001] The present invention describes photosensitizers free from metal ions, which are used for manufacturing photovoltaic cells.

[0002] The energy demand of modern society has promoted the development of new technologies based on renewable resources, as an alternative to the traditionally employed fossil fuels.

[0003] One of the most promising technologies is photovoltaics, exploiting the inexhaustible energy of the sun. Today, within the third generation of photovoltaic cells, dye sensitized solar cells (DSSC) exhibit the best performances in terms of efficiency in converting the solar energy into electric energy; furthermore, they can advantageously be manufactured at low costs.

[0004] From a technical point of view, a solar cell, as shown in Figure 1, comprises a light-absorbing component (photosensitizer) (a), a semiconductor material (b), typically titanium dioxide, on which the light- absorbing compound is adsorbed, a charge carrier component (electrolyte) (c), a working electrode (d), and a typically opaque counter electrode (e).

[0005] The current DSSC cells, however, are not able to guarantee high efficiencies that make their use convenient from an economical point of view.

[0006] Currently, the best conversion efficiency were reported for ruthenium (II) complexes, based on 2,2′- bipyridylium (bpy) binders which act as a photosensitizing dye. The most efficient photosensibilizer of this series is *cis*-di(thiocyanate) bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium (II), also known as N3 or N719 depending on the presence of 4 or 2 non-dissociated carboxylic groups (Nazeeruddin, *J. Am. Chem. Soc.* **2005**, *127*, 16835). Such complex, however, has shown a light-electricity conversion efficiency of only 11%. Furthermore, the ruthenium cost and its poor availability represent further limitations hindering a wide application of such complexes.

[0007] On the other hand, the massive use of compounds containing ruthenium is undesirable even from an environmental point of view, as it is a toxic and polluting metal.

[0008] Therefore, the developing of new photosensitizing compounds, which may be used for manufacturing DSSC solar cells, able to guarantee a high conversion efficiency, time stability and which may be produced at low costs at industrial level is a top priority in this field.

OBJECT OF THE INVENTION

[0009] According to a first object, the present invention describes metal-free photosensitizers of the push-pull type.

The synthesis of the compounds and their intermediate preparation represents another embodiment of the invention.

The use of the photosensitizers of the invention for manufacturing photoelectrochemical devices and the devices themselves are all further objects of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Figure 1 represents a simplified draft of a photoelectrochemical solar cell;

Figures 2A and 2B show the synthesis reaction of intermediates according to the present invention;

Figures 3 and 4 show the synthesis of compounds according to the present invention;

Figure 5 shows the JV curve related to cell B1;

Figures 6 and 7 illustrate the JV curves of the measurements carried out 4 days after the cell sealing.

DETAILED DESCRIPTION OF THE INVENTION

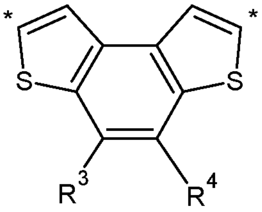
[0011] According to a first object, the present invention describes organic photosensitizing/light-absorbing compounds free of metal ions.

[0012] In particular, such photosensitizers are characterized by the following general structure (I):

$$\mathrm{GD}{-}\mathrm{R}^2{-}\mathrm{L}{-}\mathrm{A} \quad \text{(I)}$$

wherein A is an electron-withdrawing group, L is a spacer, R^2 is an unsaturated $-(\mathrm{C{=}C})_n-$ or $-(\mathrm{C{\equiv}C})_n-$ group where n=0-2 and GD is an electron-donating group, wherein

the spacer group L is selected among



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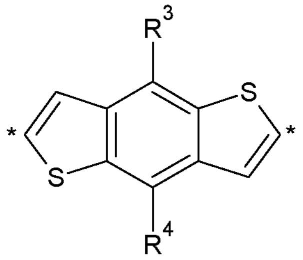
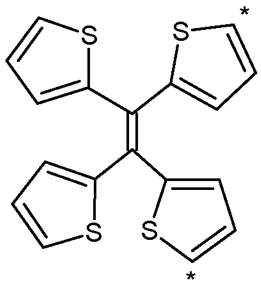
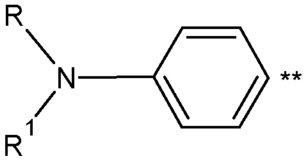
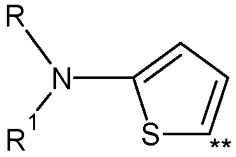




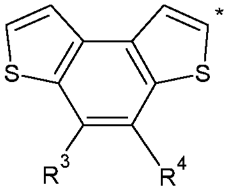
(wherein the asterisk * represents the bonding point with R^2 and A) wherein R^3 and R^4, equal or different from each other, are selected from among the group comprising hydrogen, $-R^5$ or $-OR^5$, where R^5 is a C_1-C_{10} linear or branched alkyl chain.

In an embodiment, the GD group is a group of formula





(wherein double asterisk ** represents the bonding point with R^2) where R and R^1, equal or different from each other, are selected from among the group comprising



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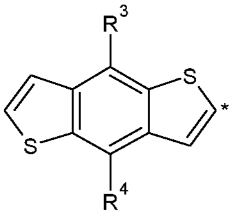

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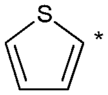

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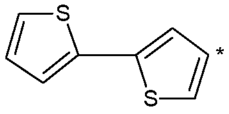

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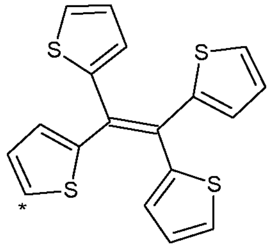
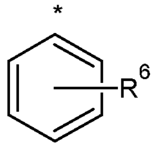


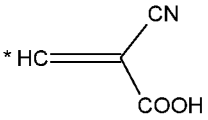
,

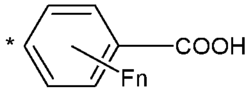
(wherein the asterisk * represents the bonding point with the N of the GD group), wherein R^3 and R^4, equal or different from each other, may be H, $-R^5$ or $-OR^5$, where R^5 is a C_1-C_{10} linear or branched alkyl chain;

and comprising  wherein R^6 is H or a $-R^5$ or $-OR^5$ group, wherein R^5 is a C_1-C_{10} linear or branched alkyl chain.

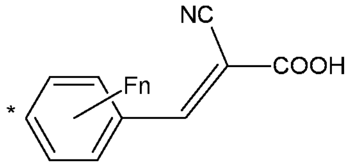
In an embodiment, in compounds of formula (I) group A is an electron-withdrawing group binding the substrate selected from among:

*COOH



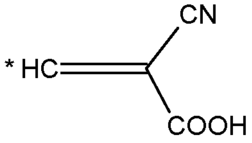


or



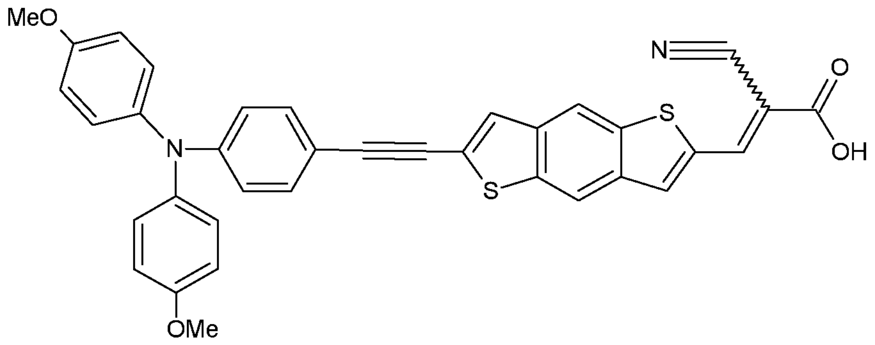
wherein n=1-4 (the asterisk * represents the attachment point of the residue or the substituent to the rest of the molecule).

[0013] According to a preferred aspect of the invention, in compounds of formula (I) A is COOH or

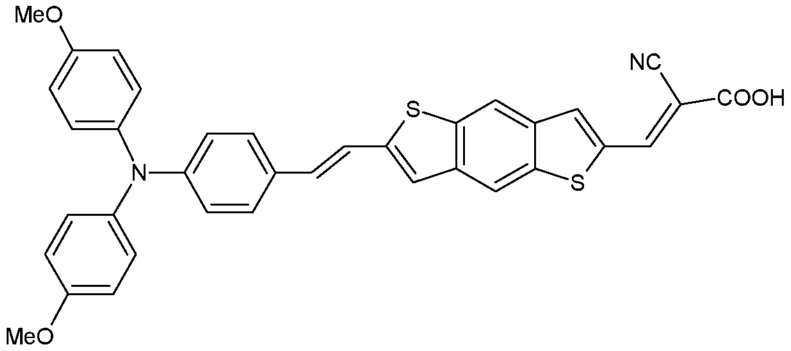


[0014] Preferably, in GD and L groups, R^3 and R^4 are both H or, if R and R^1 are both substituted phenyl groups, R^6 is a $-OR^5$ group where R^5=$-CH_3$, preferably in para position.

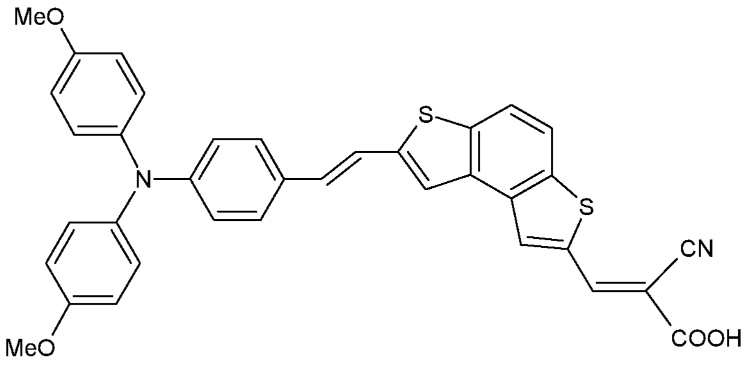
[0015] According to an even more preferred embodiment, the compounds of the invention have the following formulas:


MeO
N
OMe
S
S
N
O
OH

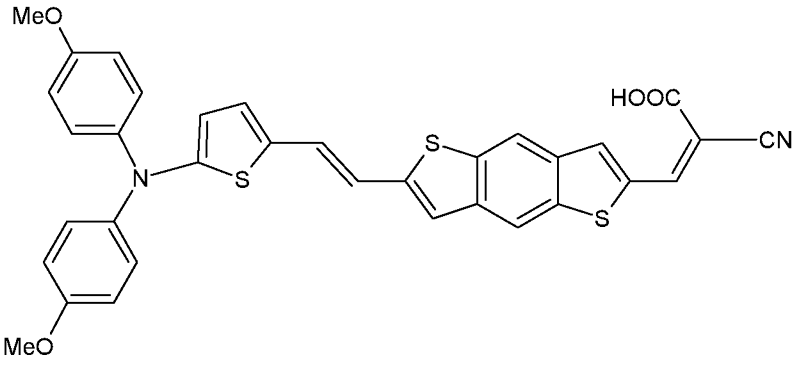
(1)


MeO
N
MeO
S
S
NC
COOH

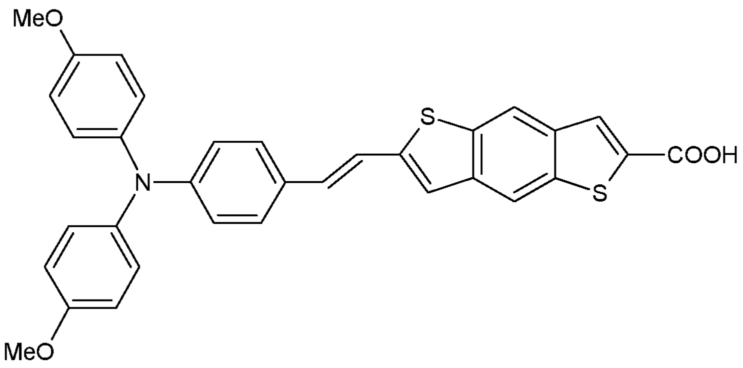
(2)


MeO
N
MeO
S
S
CN
COOH

(52)


MeO
N
MeO
S
S
S
HOOC
CN

(46)



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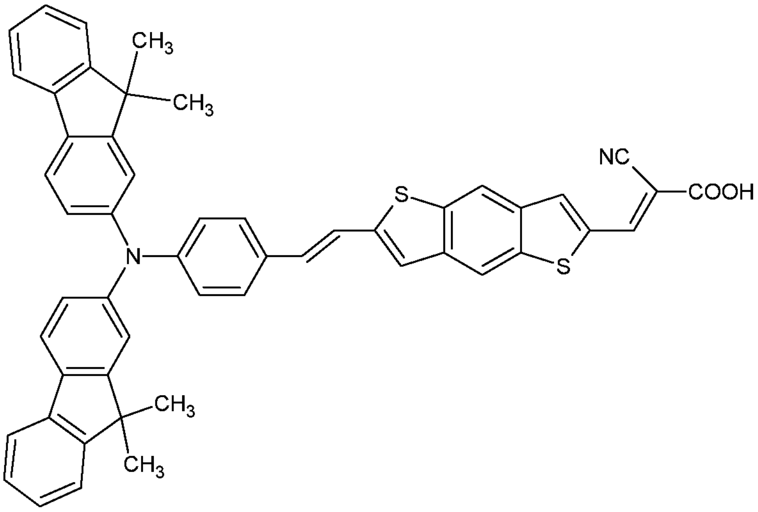


(71)

[0016] According to a further object of the invention, a process for preparing the above-mentioned intermediates and compounds is described.

This process is detailed in the experimental section below with particular reference to some compounds within the scope of the present invention.

In general, the compound preparation comprises the steps of:

a) reacting a GD-X′(II) group, where GD is the above-described electron-donating group carrying a reactive group X′ able to condense or to couple with a X-L-Y (III) group, precursor of a dibenzothiophene spacer group L carrying a reactive group X able to condense or to couple with a molecule (II), precursor of GD, generating R_2, and Y is a reactive group precursor of an electron-withdrawing substrate-linking group, as reported in the following reaction:

$$GD\text{-}X' \text{ (II)} + X\text{-}L\text{-}Y \text{ (III)} \rightarrow GD\text{-}R_2\text{-}L\text{-}Y \text{ (IV)}$$

wherein R_2 is an unsaturated $-(C{=}C)_n-$ or $-(C{\equiv}C)_n-$ group where n=0-2

b) converting the previously obtained intermediate (IV) into a compound comprising an electron-withdrawing substrate-linking group A, according to the following reaction:

$$GD\text{-}R_2\text{-}L\text{-}Y \text{ (IV)} \rightarrow GD\text{-}R_2\text{-}L\text{-}A \text{ (I)}.$$

According to a preferred embodiment of the invention, in step a) reactive groups X able to condense or couple with a GD precursor molecule are represented by a $-C{\equiv}CH$ triple bond or by a $-CHO$ aldehyde residue.

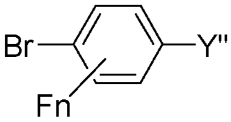
On the other hand, regarding X′ groups, these are preferably represented by a halogen group, selected from among chlorine, fluorine, bromine and iodine, where iodine is the preferred halogen group, or by other suitable condensing groups.

A preferred example of condensing group is represented by triphenylphosphonium.

In particular, in step a) a GD-X′ group, where X′ is a halogen, shall react with a X-L-Y group where X is a triple bond.

Alternatively, a GD-X′ group where X′ is triphenylphosphonium shall react with a X-L-Y group where X is an aldehyde group.

Regarding step b), according to an aspect of the invention, the conversion may occur (i) by oxidizing group Y to A, or (ii) by condensing group Y with a molecule A-Y′ comprising acid hydrogen atoms such as, for example, cyanoacetic acid, or iii) by coupling GD-R_2-L-Y with groups



wherein Y″ is -CHO, which is precursor, according to the above-mentioned items i) and ii) of -COOH and =CN(COOH) groups. For example, from an oxidation step i), where Y is an aldehyde group, the corresponding carboxylic derivative will be obtained.

As far as the preparation of the X-L-Y group is concerned, this generally comprises the step of

c) reacting the precursor L-H_2 of the spacer group with a precursor Y′′′ of a reactive group Y according to the following reaction

H-L-H (V)+ Y''' (VI) → H-L-Y (VII)

d) reacting the intermediate H-L-Y (VII) with a precursor X-X'' of the reactive group able to condense or to couple with a molecule precursor of GD, according to the following reaction:

H-L-Y (VII) + X-X'' (VIII) → X-L-Y (III)

According to a preferred embodiment of the present invention, the reactive group Y in the intermediate (VII) of step c) is an aldehyde group and a suitable precursor thereof Y''' is represented by N-formylpiperidine or dimethylformamide (DMF).

Regarding step d), on the other hand, a suitable reactant X-X'' is represented, for example, by trimethylsilylacetylene or N- formylpiperidine or DMF and, therefore, X will be a -C≡CH triple bond or a -CHO aldehyde residue, as described above.

According to a particular embodiment of the present invention, the reactive group Y and the reactive group X are equal to each other.

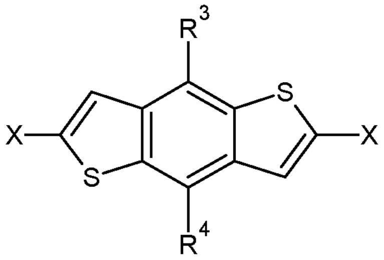
For example, if X and Y are both a -CHO aldehyde group, the preparation of the OHC-L-CHO (IX) group will comprise a single step c') of reacting H-L-H with a molecule precursor of the aldehyde group in suitable reaction conditions according to the following reaction :

c') H-L-H + Y''' → OHC-L-CHO (IX)

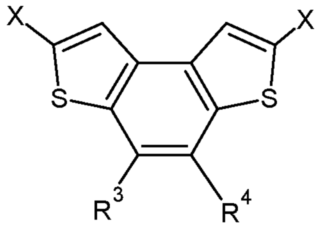
where Y''' is represented, for example, by N-formylpiperidine or DMF.

[0017] The person skilled in the art will appreciate that the above-mentioned processes with reference to a spacer group L can also be applied even if L has a benzo[1,2-b:4,5-b']dithiophene or benzo[1,2-b:4,3-b'] dithiophene structure.

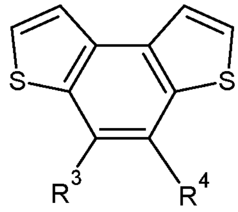
[0018] As for the preparation of the space groups L within the frame of the present invention, a group of formula



can be prepared according to the process disclosed in the following Example 1 and a group of formula



can be prepared according to the method of Example 3. In addition, the present invention discloses the preparation of the starting compound


(74e).

In particular, compound 74e can also be obtained by performing a McMurry coupling as illustrated in Figure 2B.

More in particular, said process comprises the steps of:

a) reacting 2 moles of a suitable 1-(thiophen-2-yl)alkyl-1-one, which are coupled in the presence of $TiCl_4$ and Zn;
b) protecting the α-carbons (those for coupling with the GD group) of the resulting 2-((Z)-5-thiophen-2-yl)alkyl-4-en-4yl)thiophene;
c) performing an oxidation phase under suitable condition so as to yield the corresponding 2,7-disubstituted 4,5-dialkyl-benzo[1,2-b:4,3-b’] dithiophene; and
d) deprotecting the α-carbons.

According to a preferred embodiment, a suitable starting 1-(thiophen-2-yl)alkyl-1-one is 1-(thiophen-2-yl)butan-1-one as disclosed in the following Example 13.

[0019] According to a further object, the photosensitizing/light-absorbing compounds of the invention may be used for manufacturing reference photoelectrochemical devices (described, for example, by Graetzel, M. Nature **2001**, *414*,338), photoelectric conversion devices, photovoltaic devices and/or solar cells.

[0020] Preparing photoelectrochemical solar cells, for example, will comprise the step of making a semiconductor material, typically represented by monolayer or multilayer titanium dioxide, adsorb a solution comprising one or more compounds of the present invention.

[0021] Preferably, said solution has a concentration ranging from about 10^{-4} to about 10^{-3} M.

[0022] In order to prevent molecules from possibly aggregating on the semiconductor surface, it is possible to coadsorb chenodeoxycholic acid or other molecules having a similar function.

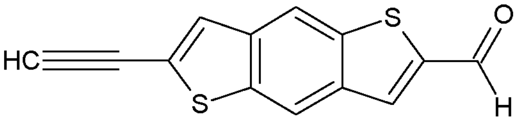
[0023] For such purpose, a solution of chenodeoxycholic acid in a concentration ranging from about 10^{-4} to about 10^{-3} M is added to the solution of one or more light-absorbing compounds.

[0024] Photoelectrochemical solar cells thus obtained revealed the properties of the above-described compounds to convert solar energy into electric energy, with significant performances at this step of technological development.

[0025] The invention will now be described more in detail with the aid of some non-limiting examples.

EXAMPLE 1

Preparation of 6-ethynylbenzo[1,2-b:4,5-b′]dithiophene-2-carboxaldehyde (3)



(3)

The synthesis of compound **3** is represented in Figure 2.

1)benzo[1,2-b:4,5-b′]dithiophene-2-carboxaldehyde (4)

1.44 ml of n-BuLi 1.6 M in hexane (2.31 mmol) are added to a suspension of benzo[1,2-b:4,5-b′]dithiophene (**5**) (prepared according to what has been described by Beimling, P.; Koβmehl *Chem. Ber.* **1986**, 119, , 3198-3203) 400 mg (2.10 mmol) in 7 ml of THF at -75°C under nitrogen atmosphere. The suspension is left under stirring for one hour; the color changes from white to yellow. 0.5 ml of formylpiperidine (4.20 mmol) are then added dropwise thus obtaining a lemon yellow solution which is left reacting for 2 hours at -75°C. The reaction is monitored by TLC (eluent: hexane/AcOEt 9/1, Rf:

0.44). After this time, a saturated solution of NH_4Cl (15 ml) is added and an extraction with AcOEt (3x15 ml) is carried out. The combined organic phases are washed firstly with HCl 1 M (2x10ml) and then with H_2O (3x10ml) until reaching neutral pH, they are anhydrified on Na_2SO_4, filtered and the solvent is removed at reduced pressure. 546 mg of a yellow solid are recovered, which is purified by silica gel column chromatography (eluent: hexane/AcOEt, 9:1). The product **4** is obtained as a yellow solid: 380 mg (83%).

Melting point: 185-187°C.

^1H NMR (300 MHz, $CDCl_3$): δ, ppm = 7.43 (d; CH_{tiof}, J = 5.5 Hz; 1H), 7.65 (d ; CH_{tiof}, J = 5.5 Hz; 1H), 8.12 (s; CH_{tiof}, 1H); 8.37 (s, CH_{ar}, 1H); 8.50 (s, CH_{ar}, 1H); 10.17 (s; CH_{ald}, 1H).

^{13}C NMR (300 MHz, $CDCl_3$): δ, ppm = 117.61 (CH); 120.01 (CH); 123.04 (CH); 129.88 (CH); 133.95 (CH); 184,52 (C=O 1); Cq N.O.

HRMS-EI (m/z): $[M]^+$ calcd for $C_{11}H_6O_1S_2$: 217.986008, found: 217.986420.

MS-EI (m/z): $[M]^+$: 218, 189 (– CHO), 145 (– CHS^+).

IR (nujol, cm^{-1}): 1682 cm^{-1} (CO)

UV-vis (10^{-5} in CH_2Cl_2): λ_{max} = 240; 277; 330; 387

2) 6-Bromobenzo[1,2-b:4,5-b']dithiophene-2-carboxaldehyde (6)

770 mg of NBS (4.33 mmol) are added to a suspension of the compound **4**, 430 mg (1.97 mmol), in 28 ml of DMF, the mixture is heated at 70°C for one hour (the color turns from yellow into orange) monitoring the reaction by TLC (eluent: hexane/AcOEt, 8:2, R_f: 0.32). The solvent is distilled off at low pressure, the orange oil obtained is taken up with 20 ml of H_2O and an extraction with CH_2Cl_2 (3x15 ml) is carried out. The combined organic phases are dried on Na_2SO_4, filtered and the solvent is removed at reduced pressure. 580 mg of a yellow solid are recovered, which is purified by silica gel column flash chromatography (eluent: hexane/AcOEt, 8:2). The product **6** is obtained as a yellow solid: 470 mg (80%).

Melting point.: 184-185°C

^1H NMR (200 MHz, $CDCl_3$): δ, ppm = 7.60 (s; 1H; CH_{tiof}); 8.10 (s; 1H; CH_{tiof}); 8.37 (s; 1H; CH_{ar}); 8.44 (s; 1H; CH_{ar}); 10.15 (s; 1H; CH_{ald})

HRMS-EI (m/z): [M]+ calcd for $C_{11}H_5OS_2Br$: 295.896520, found: 295.896120.

MS-EI (m/z): [M]+: 298, 269 (- CHO).

IR (nujol, cm-1): 1662 (CO).

UV (10^{-6} in CH_2Cl_2): λ_{max} = 243; 280; 329; 390.

3)6-Trimethylsilylethinylbenzo[1,2-b:4,5-b′]dithiophene-2-carboxaldehyde (7)

In a glass tube for microwave oven, under nitrogen atmosphere, 25 mg of $Pd_2(dba)_3$ ($2.83 \bullet 10^{-2}$ mmol), 5.4 mg of CuI ($2.83 \bullet 10^{-2}$ mmol), 26 mg of $P(Cy)_3$ ($9.42 \bullet 10^{-2}$ mmol), 833 mg of trimethylsilylacetylene (8.50 mmol) and 1 ml of Et_3N (714 mg, 7,06 mmol) are subsequently added to a solution of **6**, 140 mg (0.47 mmol) in 4 ml of DMF. The mixture is then irradiated in a microwave oven at 100 W and 120°C for 25 minutes. The suspension, formerly orange, turns into a black solution. The reaction is monitored by TLC (eluent: hexane/CH_2Cl_2, 4:6, Rf: 0.34). The solvent is distilled off at reduced pressure, 10 ml of H_2O are added and extraction with CH_2Cl_2 (3x10 ml) is carried out. The organic phases are combined, dried on Na_2SO_4, filtered and the solvent is removed at reduced pressure. A black oil (365 mg) is recovered, which is purified by silica gel column chromatography (hexane/CH_2Cl_2, 4:6) The product **7**, 95 mg (64%), is obtained as of a yellow-orange solid.

Melting point.: 141-142°C (dec.)

^{1}H NMR (75 MHz, C_6D_6): δ, ppm = 0.23 (s, 9H, CH_3), 6.91 (s, 1H, CH_{tiof}), 7.21 (s, 1H, CH_{tiof}), 7.51(s, 1H, CH_{ar}),8.43 (s, 1H, CH_{ar}), 9.55 (s, 1H, CH_{ald}).

^{13}C NMR (300 MHz, $CDCl_3$): δ, ppm = 0.07, 14.34, 61.70, 97.81, 116.86, 117.69, 119.19, 129.48, 133.00, 134.96, 136.49, 136.95, 138.90, 139.47, 163.00.

HRMS-EI (m/z): $[M]^+$ calcd for $C_{16}H_{14}OSiS_2$: 314.025537, found: 314.025420.

MS-EI (m/z): $[M]^+$: 314, 299(– CH_3).

IR (nujol, cm^{-1}): 1668 (CO), 2149 (C≡C),

UV-vis (10^{-4} in CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$)= 230 (7855); 239 (8742); 280 (9830); 293 (6459); 330 (7201); 392 (2780).

4)6-ethynylbenzo[1,2-b:4,5-b′]dithiophen-2-carboxaldehyde (3)

1,8 ml of KOH 2 M (3.60 mmol) are added to a suspension of **7**, 315 mg (0.42 mmol), in 6 ml of MeOH, the suspension is left stirring for 14 hours, the orange suspension turns into an orange solution. The reaction is monitored by TLC (eluent: hexane/AcOEt, 9:1, Rf: 0.33). At the end, the solvent is evaporated at reduced pressure, the residue taken up with 8 ml of H_2O and extracted with CH_2Cl_2 (3x10 ml) are carried out. The combined organic phases are washed with H_2O

until reaching neutral pH, dried on Na_2SO_4 and the solvent is evaporated at reduced pressure. The product **3** is obtained as 103 mg (90%) of an orange solid, which is pure enough to be used as such for the subsequent step.

Melting point: 125-126°C

^1H NMR (300 MHz, $CDCl_3$): δ, ppm = 3.38 (s, 1H, $CH_{C≡C}$), 7.84 (s, 1H, CH_{tiof}), 8.09 (s, 1H, CH_{tiof}), 8.43 (s, 1H, CH_{ar}), 8.48 (s, 1H, CH_{ar}), 10.14 (s, 1H, CH_{ald}).

^{13}C NMR (300 MHz, $CDCl_3$): δ, ppm = 80.67, 117.34, 120.17, 133.59, 134.42, 139.89, 144.40, 184.56.

HRMS-EI (m/z): $[M]^+$ calcd for $C_{13}H_6OS_2$: 241.986008, found: 241.986530.

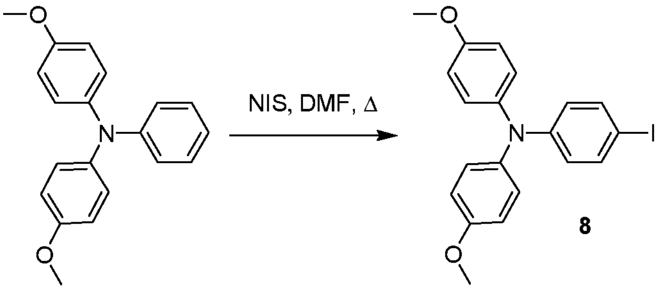
MS-EI (m/z): $[M]^+$: 242, 213 (- CHO).

IR (nujol, cm^{-1}): 1659 (CO), 3259 (C≡H).

UV-vis (10^{-4} in CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 230 (6601); 237 (6551); 278 (7993); 329 (6166); 376 (1927); 390 (2130).

EXAMPLE 2

Preparation of (4-Iodophenyl)bis(4-metoxyphenyl)amine (8)

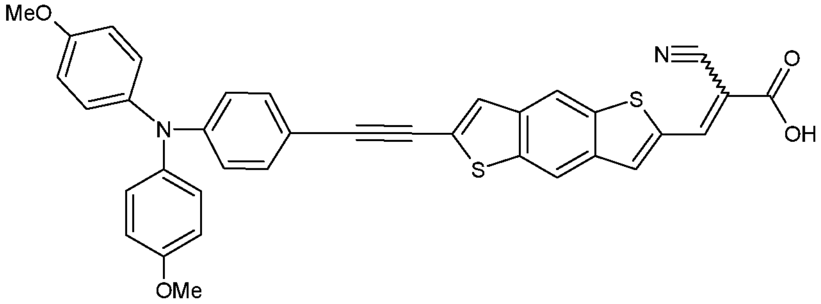


324 mg of N-iodosuccinimmide (NIS) (1.44 mmol) are added to a solution of bis(4-metoxyphenyl)amine (prepared according to what has been reported in *J. Am. Chem.Soc.,* **2008**, *130,* 6259-6266) 400 mg (1.31 mmol) in 10.5 ml of DMF, the solution is then left under stirring at 30°C for one hour, the orange solution turns brown. The reaction is monitored by TLC (eluent: CH_2Cl_2 Rf: 0.73). At the end, the solvent is distilled off at reduced pressure, taken up with 10 ml of H_2O and an extraction with CH_2Cl_2 (3x10 ml) is carried out. The combined organic phases are dried on Na_2SO_4, filtered and the solvent is evaporated at reduced pressure. A black oil (620 mg) is recovered, which is purified by silica gel column chromatography (CH_2Cl_2). The product **8** is obtained as 500 mg (90% yield) of a transparent rose-colored oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm = 3.80 (s, 6H, CH_3), 6.71 (d, J = 8.8 Hz, 2H, CH_{ar}), 6.85 (d, J = 6.7, 4H, CH_{ar}), 7.06 (d, J = 6.7, 4H, CH_{ar}), 7.43 (d, J = 8.8, 2H, CH_{ar}).

EXAMPLE 3

Preparation of 2-cyano-3-{6-[4-(bis(4-metoxyphenylamino) phenylethynyl] benzo[1,2-b:4,5-b′]dithiophene-2-yl} acrylic acid (1)



(1)

The synthesis of compound 1 is represented in Figure 3.

1)6-[(4-(bis-4-metoxyphenylamino) phenylethynyl]-ethynylbenzo[1,2-b:4,5-b′]dithiophene-2-carboxaldehyde (9)

In a glass tube for microwave oven, under nitrogen atmosphere, **8** (320 mg, 0.73 mmol), 19 mg of $PdCl_2(PPh_3)_2$ (2,71•10^{-2} mmol), 2 mg of CuI (1.11•10^{-2} mmol) and 0.6 ml of Et_3N (407 mg, 5.56 mmol) are added in sequence to a solution of **3**, 90 mg (0.37 mmol), in 10.5 ml of DMF. The mixture is then irradiated in a microwave oven at 100 W and 80°C performing two cycles of 25 minutes. The initially orange solution becomes a black suspension. The reaction is monitored by TLC (eluent: hexane/AcOEt, 8:2, Rf: 0.17). After that, the solvent is distilled off at reduced pressure, 10 ml of H_2O are added and the solvent is extracted with CH_2Cl_2 (3x10 ml). The combined organic phases are dried on Na_2SO_4, filtered and the solvent is evaporated at reduced pressure. A 500 mg black oil is recovered, which is purified by silica gel column flash chromatography (hexane/AcOEt, 8:2). The product **9** is obtained as 112 mg (yield 56%)of a yellow-orange solid.

^{1}H NMR (300 MHz, CDCl3): δ, ppm = 3.81 (s, 6H, CH_3 OMe), 6.87 (m, 4H, CH_{ar}), 7.10 (d, J = 8.64, 2H, CH_{ar}), 7.41 (d, J = 8.6, 2H, CH_{ar}), 7.74 (s, 1H, $CH_{tiofBDT1}$), 8.09 (s, 1H, $CH_{tiofBDT1}$), 8.42 (s, 1H, CH_{arBDT1}), 8.50 (s, 1H, CH_{arBDT1}), 10.13 (s, 1H, CH_{ald}).

^{13}C NMR (75 MHz, $CDCl_3$): δ, ppm = 55.47, 80.83, 93.39, 113.00, 114.83, 117.41, 118.19, 119.03, 120.14, 127.17, 131.72, 132.56, 133.84, 136.54, 136.91, 139.47, 140.02, 144.14, 149.17, 156.41, 184.56.

HRMS-EI (m/z): [M]+ calcd for $C_{33}H_{23}NO_3S_2$: 545.111937, found: 545.111760.

MS-EI (m/z): [M]+: 545, 530 (- CH3).

IR (nujol, cm^{-1}): 1670(CO).

UV-vis (10^{-5} in CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 288 (9722), 330 (12278), 332 (12222).

2) 2-cyano-3-{6-[4-(bis(4-metoxyphenylamino) phenylethynyl]benzo[1,2-b:4,5-b′]dithiophene-2-yl} acrylic acid (1)

31 mg of cyanoacetic acid (0.37 mmol) and 0.7 µl of pyperidine (6 mg, 7,32•10^{-2} mmol) are added in sequence and under nitrogen atmosphere to a suspension of **9** obtained as described above, 100 mg (0.18 mmol) in 7 ml of CH$_3$CN, the suspension is then left under stirring at 80°C for 8 hours, the suspension turns into an orange-red solution. The reaction is monitored by TLC (eluent: hexane/AcOEt/AcOH, 6:2:2). At the end the solvent is evaporated at reduced pressure, the residue taken up with 6 ml of H$_2$O and hexane (4 ml), a red solid is formed, which is filtered, thus obtaining 100 mg of **1** (95% yield).

^{1}H NMR (300 MHz, DMSO): δ, ppm = 3.73 (s, 6H, CH$_3$, OMe), 6.70 (d, J = 7.66, 2H, CH$_{ar}$), 6.93 (d, J = 7.80, 4H, CH$_{ar}$), 7.08 (d, J = 7.840, 4H, CH$_{ar}$), 7.47 (d, J = 7.66, 2H, CH$_{ar}$), 8.18 (s, 1H, CH$_{tiofBDT1}$), 8.34 (s, 1H, CH$_{tiofBDT1}$), 8.59 (s, 1H, CH$_{c=c}$), 8.69 (s, 2H, CH$_{arBDT1}$).

^{13}C NMR (75 MHz, DMSO): δ, ppm = 55.20, 81.02, 93.16, 111.82, 115.06, 115.97, 116.55, 116.84, 117.45, 120.13, 132.54, 133.28, 135.86, 136.31, 136.45, 136.59, 139.06, 139.15, 146.79, 148.91, 156.37, 162.99.

HRMS-ESI (m/z): [M]- calcd for $C_{36}H_{23}N_2O_4S_2$ (-1): 611.11047, found: 611.10944

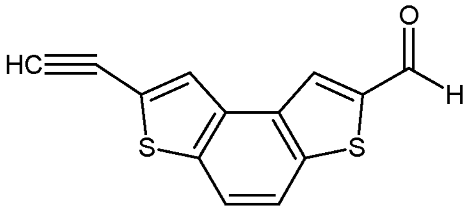
MS-ESI (m/z): [M]-: 567.11876 (- CO_2).

IR (nujol, cm^{-1}): 3447 (OH), 2213 (CN),1716 (CO).

UV-vis (10^{-4} in CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 299 (6076), 368 (9495).

EXAMPLE 3

Preparation of 6-Ethynylbenzo[1,2-b:4,3-b′]dithiophene-2-carboxaldehyde (10)



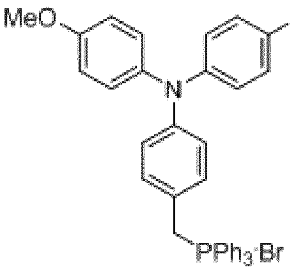
(10)

6-ethynylbenzo[1,2-b:4,3-b′]dithiophene-2-carboxyaldehyde **10** is synthesized from benzo[1,2-b:4,3-b′]dithiophene-2-carboxyaldehyde following the same procedures as indicated for the synthesis of compound **3**.

IR (nujol) 1674 cm^{-1}. ^1H NMR(300 MHz, CDCl3), δ:ppm(s, 1H), 7.70(s, 1H), 7.75(d, J=8.7 Hz, 1H), 7.91(d, J=8.7 Hz, 1H), 8.31 (s, 1H), 10.16(s, 1H).

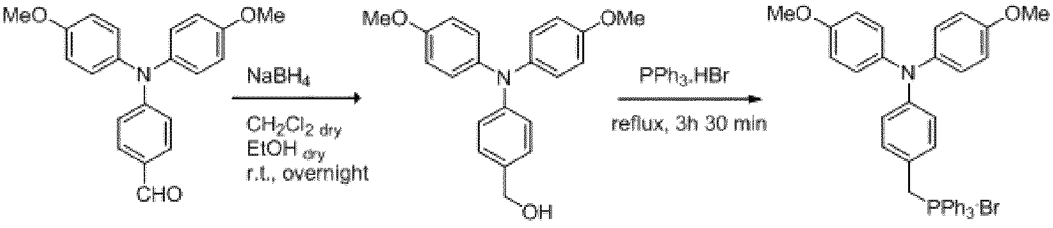
EXAMPLE 4

Preparation of the intermediate (11)



(11)

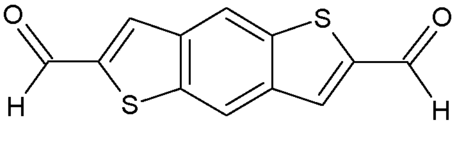
The electron-donating intermediate (11) may be prepared according to what has been described by Haining,T et al (Haining,T.; Xichuan, Y.; Ruikui, C.; Rong, Z.; Anders, H.; Licheng, S.; *J. Phys. Chem.*, **2008**, 11023) according to the reaction scheme below.



12 **13** **11**

EXAMPLE 5

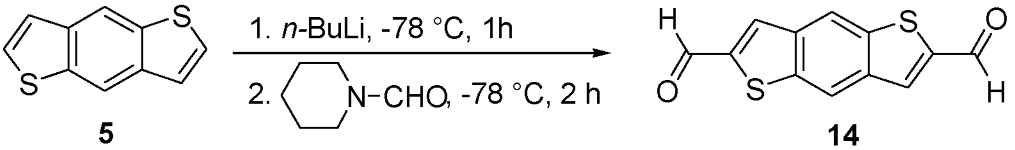
Preparation of the intermediate (14)



(14)

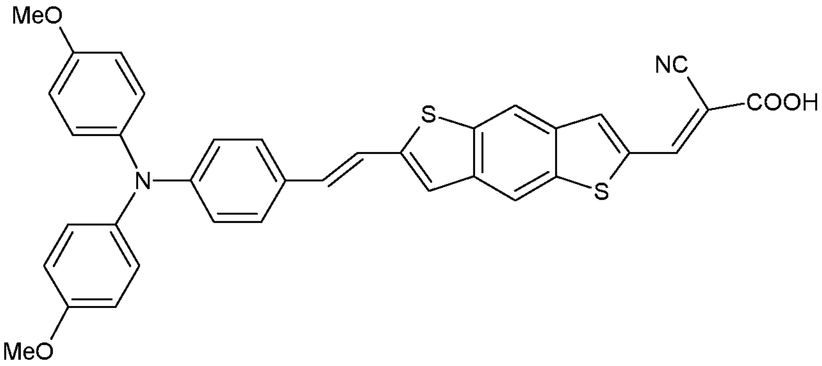
The intermediate of formula (14) may be prepared according to what has been described by *Makromolek.*

Chem. **1983**, *184*, 627-650 or as reported in the following reaction scheme.



EXAMPLE 6

Preparation of 2-cyano-3-{6-[2-(4-[bis(4-metoxyphenyl)amino]phenyl] ethenyl]benzo[1,2-b:4,5-b′]dithiophene-2-yl} acrylic acid (2)



(2)

The reaction for the synthesis of compound **2** of the invention is represented in Figure 4.

1)6-[2-(4-[bis-4metoxyphenyl)amino] phenyl] ethenyl]benzo[1,2-b:4,5-b′]dithiophene-2-carboxaldehyde (15)

A solution of **11** (100.0 mg, 0.15 mmol) in 4 ml of DMF is slowly added under vigorous stirring, at room temperature, to a solution of **14** (44.6 mg, 0.18

mmol), 18-crown-6 ether (2.4 mg, 0.009 mmol) and anhydrous potassium carbonate (31.7 mg, 0.30 mmol) in 4 ml of DMF. An orange solution is obtained. The reaction is monitored by TLC (eluent: hexane/AcOEt 1:1, Rf:0.72). The solution is left under stirring overnight at room temperature. Finally, water (10 ml) is added and extraction with CH_2Cl_2 (3x10ml) is carried out. The combined organic phases are dried on Na_2SO_4, filtered and the solvent is evaporated at reduced pressure. The crude reaction product is purified by silica gel column chromatography (CH_2Cl_2/hexane, 9:1). The desired product **15** is obtained as 50.2 mg (63%)of a red solid.

^{1}H NMR (300 MHz, DMSO): δ, ppm = 3.73 (s, 6H), 6.72 (d, 2H, J=8.6 Hz), 6.92 (d, 4H, J=8.9 Hz), 6.97 (d, 1H, J=16.4 Hz), 7.05 (d, 4H, J=8.9 Hz), 7.39 (d, 1H, J=16.4 Hz), 7.44 (d, 2H, J=8.6), 7.45 (s, 1H), 8.41 (s, 2H), 8.6 (s, 1H), 10.11 (s, 1H).

UV-vis (CH_3CN): λ_{max} = 260 nm, 435 nm

2)2-cyano-3-{6-[2-(4-[bis(4-metoxyphenyl) amino]phenyl]ethenyl]benzo[1,2-b:4,5-b']dithiophene-2-yl}acrylic acid (2)

A solution of **15** (30.27 mg, 0.055 mmol) and cyanoacetic acid (9.4 mg, 0.11 mmol) is heated to reflux in the presence of piperidine (1.9 mg, 0.022

mmol) for 4 hours. A red solution is obtained. The reaction is monitored by TLC (eluent: AcOH/hexane/AcOEt 2:6:2, Rf:0.46). The solvent is evaporated at reduced pressure. The residue is precipitated from hexane and HCl and filtered to yield **2** (dark purple solid, 34 mg, 0.055 mmol, quantitative yield).

^{1}H NMR (300 MHz, DMSO): δ, ppm = 3.76 (s, 6H), 6.74 (d, 2H, J=8.5 Hz), 6.95 (d, 4H, J=9 Hz), 6.97 (d, 1H, J=16.4 Hz), 7.08 (d, 4H, J=9 Hz), 7.42 (d, 1H, J=16.4 Hz), 7.47 (d, 2H, J=8.5), 7.45 (s, 1H), 8.35 (s, 2H), 8.47 (s, 1H), 8.58 (s, 1H), 8.64 (s,1H)

^{13}C NMR (75 MHz, $CDCl_3$): δ, ppm = 55.13, 101.17, 114.88, 115.84, 116.44, 118.26, 118.50, 119.02, 119.08, 121.51, 126.83, 126.95, 127.27, 127.55, 127.68, 127.81, 132.05, 135.06, 135.28, 135.35, 136.97, 139.06, 139.33, 140.89, 146.50, 147.12, 148.63, 155.98, 163.09.

IR (nujol, cm^{-1}): 2360.44, 1376.93

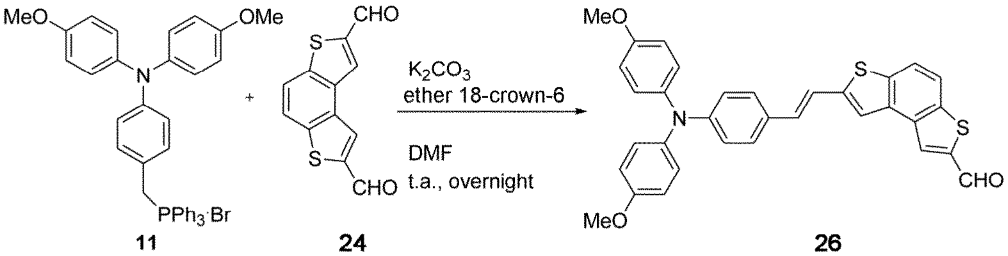
UV-vis (CH_2Cl_2, 6EXP-5 M): λ_{max} = 388 nm, 502 nm; (EtOH, 5EXP-5 M) λ_{max} = 298 nm, 472 nm; (THF, 5.7EXP-5 M) λ_{max} = 378 nm, 476 nm; (toluene, 5.9EXP-5 M) λ_{max} = 401 nm, 451 nm, 484 nm; (CH_3CN, 5.7EXP-5 M) λ_{max} = 397 nm, 473 nm

HRMS-ESI (m/z): $[M]^-$ calcd for $C_{36}H_{25}N_2O_4S_2$ (-1): 613.12612 ; found: 613.12579

MS-ESI (m/z): $[M]^-$ 569.13647 ($-CO_2$).

Example 7

Preparation of 2-cyano-3-{7-[2-[4-[bis(4-methoxyphenyl)amino]phenyl]ethenyl]benzo[1,2-b:4,3-b′]dithiophen-2-yl} acrylic acid 52



1) 7-[2-[4-[bis-(4-methoxyphenyl) amino]phenyl] ethenyl] benzo[1,2-b:4,3-b′]dithiophen-2-carboxy aldehyde (**26**)

Following the same procedure used for the synthesis of **15**, the phosphonium salt **11** (0.30 mmol) was reacted with benzo[1,2-b:4,3-b′]-2,7-dithiophenedicarboxyaldehyde (prepared as described in Larsen, J.; Bechgaard, K. *Acta Chem. Scand.* **1996**, 50, 71-76) **24** (0.36 mmol) in DMF. A crude dark orange product was obtained which was purified by silica gel column chromatography (eluent:

CH_2Cl_2/hexane 9:1) to give 76 mg (46%) of **26** a as a red solid.

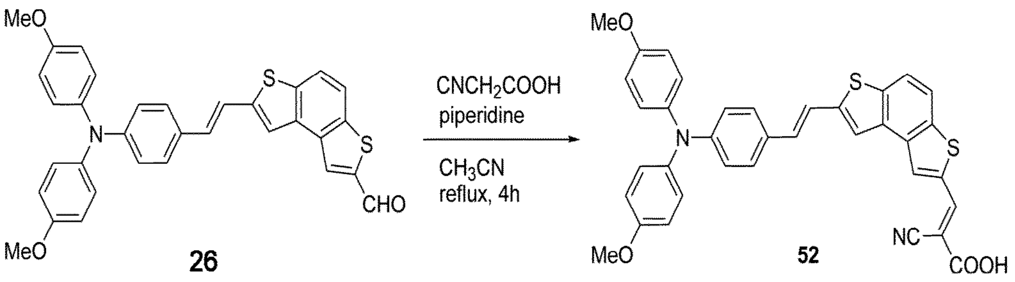
M.p.: 160-162°C. ^1H NMR (300 MHz,$CDCl_3$): δ, ppm = 3.81 (s, 6H), 6.83-6.91 (m, 6H), 7.01 (d, 1H, *J*=15.9 Hz), 7.03-7.09 (m, 4H), 7.13 (d, 1H, *J*=15.9 Hz), 7.32 (d, 2H, *J*=8.7 Hz), 7.5 (s, 1H,), 7.70 (d, 1H, *J*=8.7 Hz), 7.80 (d, 1H, *J*=8.7 Hz), 8.26 (s, 1H), 10.12 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ, ppm = 55.51; 114.83; 117.15; 118.81; 119.40; 119.9; 122.54; 126.97; 127.37; 127.52; 128.17; 131.64; 133.28; 135.74; 136.97; 140.57; 143.03; 146.10; 148.95; 156.34; 184.09. IR (nujol, cm^{-1}): 1646 (ν_{CO}).

HRMS-EI *m/z*: calcd. for $C_{33}H_{25}NO_3S_2$: 547.12758, found: 547.127588.

UV-vis: CH_3CN ($6.3\cdot10^{-5}$ M), λ_{max}= 299 nm ($1.84\cdot10^4$ $M^{-1}cm^{-1}$), 354 nm ($2.72\cdot10^4$ $M^{-1}cm^{-1}$), 439 nm ($3.42\cdot10^4$ $M^{-1}cm^{-1}$).

2) 2-Cyano-3-{7-[2-[4-[bis(4-methoxyphenyl)amino] phenyl]ethenyl] benzo[1,2-b:4,3-b′]dithiophen-2-yl} acrylic acid **(52)**



Compound **52** was synthesized following the same procedure of 2, starting from 70 mg (0.13 mmol) of **26** to give 46 mg (55%) of **52** as a red solid.

M.p.: 198-200°C.

^{1}H NMR (300 MHz, DMF-*d*$_7$): δ, ppm = 3.80 (s, 6H), 6.74 (d, 2H, *J*=8.5 Hz), 6.95 (d, 4H, *J*=9 Hz), 6.97 (d, 1H, *J*=16.4 Hz), 7.08 (d, 4H, *J*=9 Hz), 7.42 (d, 1H, *J*=16.4 Hz), 7.47 (d, 2H, *J*=8.5 Hz), 7.45 (s, 1H), 8.35 (s, 2H), 8.47 (s, 1H), 8.58 (s, 1H), 8.64 (s,1H).

^{13}C NMR (75 MHz, DMF-*d*$_7$): δ, ppm = 55.78, 115.67, 116.84, 119.57, 119.73, 121.23, 123.60, 127.97, 128.56, 128.76, 132.17, 133.59, 135.92, 136.50, 140.76, 146.84, 147.93, 149.85, 157.32, 164.13.

IR (nujol, cm^{-1}): 3393 (ν_{OH}), 2342(ν_{CN}), 1560 (ν_{CO})

HRMS-ESI-(m/z) [M-H]$^-$, calcd. for $C_{36}H_{25}N_2O_4S_2$, 613.12612, found 613.12504; MS-ESI (m/z): [M]- 614.3, 570.4 (-CO_2), 555.4 (-CH_3).

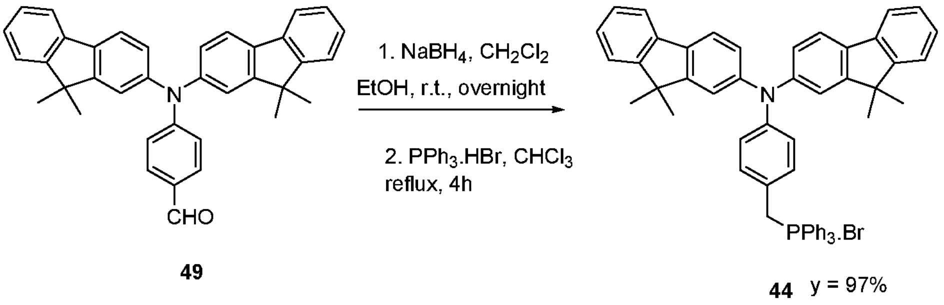
UV-vis: EtOH ($3.18\cdot10^{-5}$ M), λ_{max} = 391 nm ($3.8\cdot10^{4}$ M^{-1}cm^{-1}); 441 nm ($2.7\cdot10^{4}$ M^{-1}cm^{-1}); THF ($3.21\cdot10^{-5}$ M), λ_{max}

= 394 nm ($4.2\cdot10^4$ $M^{-1}cm^{-1}$), 460 nm ($2.6\cdot10^4$ $M^{-1}cm^{-1}$); toluene ($3.03\cdot10^{-5}$ M), λ_{max} = 399 nm ($3.8\cdot10^4$ $M^{-1}cm^{-1}$), 478 nm ($2.1\cdot10^4$ $M^{-1}cm^{-1}$); CH_3CN ($2.97\cdot10^{-5}$ M), λ_{max} = 393 nm ($4.2\cdot10^4$ $M^{-1}cm^{-1}$), 451 nm ($2.6\cdot10^4$ $M^{-1}cm^{-1}$); CH_2Cl_2 ($3.21\cdot10^{-5}$ M), λ_{max} = 399 nm ($5.6\cdot10^4$ $M^{-1}cm^{-1}$); 486 ($2.74\cdot10^4$ $M^{-1}cm^{-1}$).

Example 8

Preparation of 2-cyano-3-{6-[2-[4-[bis(dimethylfluorenyl)amino]phenyl]ethenyl]benzo[1,2-b:4,5-b′]dithiophen-2-yl} propenoic acid

(71)



1)

Compound **44** was synthesized following the same procedure of **11**, starting from 115 mg (0.23 mmol) of **49** (as described in Kim, Chulwoo; Choi, Hyunbong; Kim, Sanghoon; Baik, Chul; Sang, Ook Kang; Ko, Jaejung; Song, Kihyung; Kang, Moon-Sung *J. Org. Chem.*, **2008**, 73 (18) 7072 - 7079) to give 190 mg of **44**, which was used, without further purification, for the subsequent step.

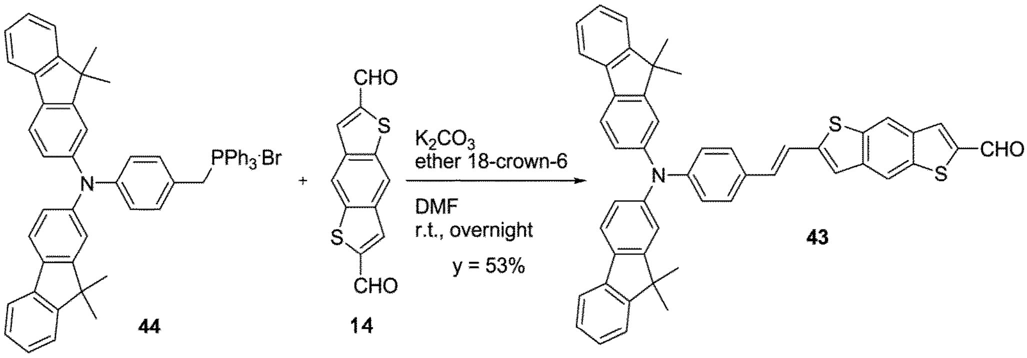
^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm = 1.35 (s, 12H), 2.02 (s, 2H), 7.11-7.73 (m, 18H).

^{31}P-NMR (121 MHz, $CDCl_3$): δ, ppm = 23.43.

^{13}C-NMR (75 MHz, $CDCl_3$): δ, ppm = 27.05, 29.66, 46.80, 117.34, 118.48, 118.84, 119.50, 120.66, 122.49, 123.26, 127.04, 128.68, 129.57, 130.17, 132.27, 134.09, 134.34, 135.11, 138.73, 146.72, 148.27, 153.44, 155.13.

IR (film, cm^{-1}): 2090. MS-EI (m/z): $[M]^+$: 491 (-PPh_3·Br), 477(-CH_3)

2)6-[2-[4-[Bis-(9,9-dimethylfluorenyl)amino]phenyl]ethenyl] benzo[1,2-b:4,5-b′]dithiophen-2-carboxy aldehyde **43**



Compound **43** was synthesized following the same procedure of **15**, starting from 64 mg (0.26 mmol) of **14** and 180 mg of **44** to give 82.4 mg (53%) of **43** as an orange solid, after purification over column chromatography (CH_2Cl_2/hexane, 4:6).

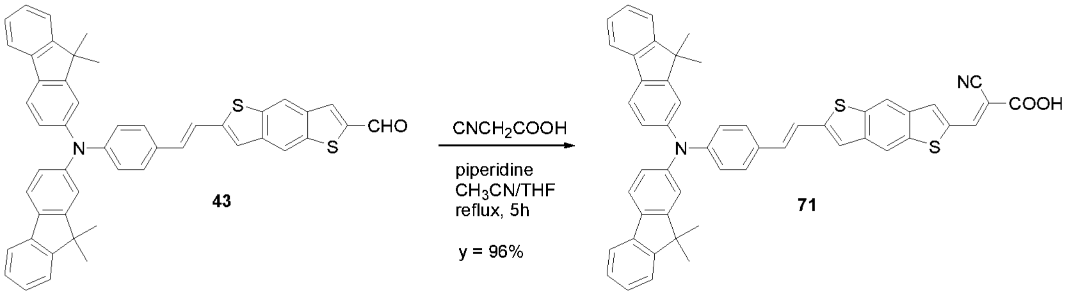
^{1}H-NMR (300 MHz, $CDCl_3$): δ, ppm = 1.43 (s, 12H), 6.99-7.44 (m, 17H), 7.61-7.67 (m, 4H), 8.02 (s, 1H), 8.14 (s, 1H), 8.30 (s, 1H), 10.10 (s, 1H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ, ppm = 27.05, 29.71, 46.88, 116.89, 119.10, 119.52, 120.05, 120.70, 121.43, 122.53, 123.16, 123.62, 126.68, 127.05, 127.80, 130.00, 134.00, 134.74, 136.14, 137.04, 138.87, 141.50, 146.85, 148.43, 153.59, 155.21, 184.42.

IR (nujol, cm-1): 1674 (ν_{CO}). MS-EI (m/z): [M]+: 719, 691(-CHO).

UV-vis: CH_2Cl_2 (4.3 •10-5M), λmax = 361 nm (4.3 •104 M-1cm-1), 454 nm (4.3•104 $M^{-1}cm^{-1}$)

2) 2-cyano-3-{6-[2-[4-[bis(dimethylfluorenyl)amino]phenyl]ethenyl] benzo[1,2-b:4,5-b']dithiophen-2-yl} propenoic acid **71**



Compound **71** is synthesized following the same procedure of **2**, using a mixture CH_3CN/THF (2:1) as solvent and starting from 34.00 mg (0.047 mmol) of **43**, 35 mg of product **71** (96% yield) was obtained as a dark orange solid.

^{1}H-NMR (300 MHz, DMSO-d6): δ, ppm = 1.31 (s, 12H), 7.01-7.7 (m, 21H), 8.29 (s, 1H), 8.41 (s, 1H), 8.50 (s, 1H), 8.60 (s, 1H).

^{13}C-NMR (75 MHz, DMSO-d6): δ, ppm = 27.18, 29.48, 46.94, 101.79, 109.60, 116.48, 117.28, 119.22, 119.82, 119.95, 120.10, 121.03, 121.65, 122.79, 123.14, 123.82, 127.25, 127.56, 128.40, 128.63, 130.45, 132.28, 134.69, 135.80, 136.04, 137.00, 137.72, 138.66, 139.69, 141.44, 146.78, 147.84, 148.12, 153.66, 155.32, 163.72.

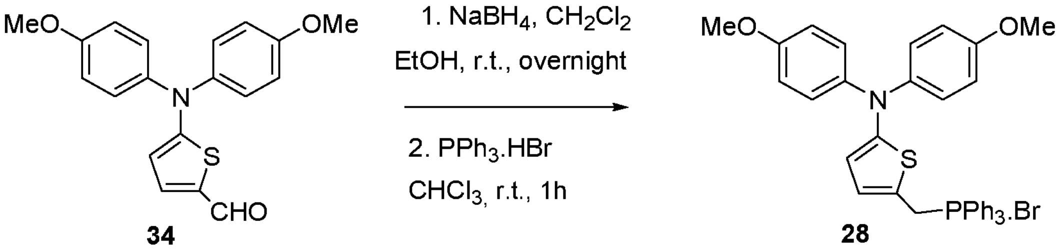
IR (nujol, cm^{-1}): 3403 (ν_{OH}), 1713 (ν_{CO}).

MS-EI (m/z): $[M]^+$ 742 ($-CO_2$), 705 ($-C_3H^+$). UV-vis, EtOH($2.9 \cdot 10^{-5}$ M), λ_{max} = 368($1.4 \cdot 10^4$); 442 nm ($1.4 \cdot 10^4$ $M^{-1}cm^{-1}$) - THF($3.3 \cdot 10^{-5}$ M): 371 nm (2.4 10^4 $M^{-1}cm^{-1}$); 473($1.8 \cdot 10^4$ $M^{-1}cm^{-1}$) - Toluene ($3.3 \cdot 10^{-5}$ M): 374 nm ($2.2 \cdot 10^4$ $M^{-1}cm^{-1}$); 451 nm ($1.6 \cdot 10^4$ $M^{-1}cm^{-1}$); 457 nm ($1.6 \cdot 10^4$ $M^{-1}cm^{-1}$) - CH_3CN ($3.2 \cdot 10^{-5}$ M): 368 nm ($2.1 \cdot 10^4$ $M^{-1}cm^{-1}$); 438 nm ($1.9 \cdot 10^4$ $M^{-1}cm^{-1}$) - CH_2Cl_2 ($4.0 \cdot 10^{-5}$ M): 373 nm ($2.2 \cdot 10^4$ $M^{-1}cm^{-1}$); 493 nm ($1.5 \cdot 10^4$ $M^{-1}cm^{-1}$).

EXAMPLE 9

Preparation of 2-cyano-3-{7-[2-[5-[bis(4-methoxyphenyl)amino]thiophenyl] ethenyl] benzo[1,2-b:4,3-b′]dithiophen-2-yl} acrylic acid (46)

1)[[4-[Bis(4-methoxyphenyl)amino]thiophenyl]methyl]triphenyl phosphonium bromide **28**

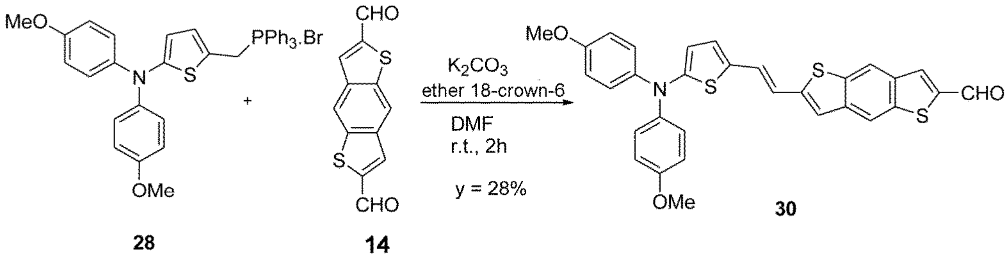


Compound **28** was synthesized following the same procedure of 11, starting from 270 mg (0.80 mmol) of 34 (as described in Davies, Joshua A.; Elangovan, Arumugasamy; Sullivan, Philip A.; Olbricht, Benjamin C.; Bale, Denise H.; Ewy, Todd R.; Isborn, Christine M.; Eichinger, Bruce E.; Robinson, Bruce H.; Reid, Philip J.; Li, Xiaosong; Dalton, Larry R. *J. Am. Chem. Soc.* **2008**, vol. 130(32), 10565 - 10575) to give in 400 mg of **28** as a green solid (97% yield). P.f.: 78-83 °C.

^{1}H-NMR (300 MHz, $CDCl_3$): δ, ppm = 3.73 (s, 2H) 3.75 (s, 6H), 5.50 (d, 1H), 6.73 (d, 5H), 6.90 (d, 4H), 7.78-7.63(m, 15H).

^{31}C-NMR (75 MHz, $CDCl_3$): δ, ppm = 27.40, 28.06, 55.57, 114.74, 117.30, 118.44, 124.34, 125.39, 130.34, 130.94, 134.24, 135.09, 141.05, 154.70, 155.95.

2) 7-[2-[5-[bis-(4-methoxyphenyl)amino]thiophenyl] ethenyl]benzo[1,2-b:4,3-b']dithiophen-2-carboxy aldehyde **30**



Compound **30** was prepared following the same procedure used for the synthesis of **15**, the phosphonium salt **28** (337 mg, 0.52 mmol) was reacted with **14** (129 mg, 0.52 mmol) in DMF for 2 h. The crude product was purified by silica gel column chromatography (eluent: CH_2Cl_2/hexane 8:2) to give 80 mg (28%) of **30** as a dark red solid.

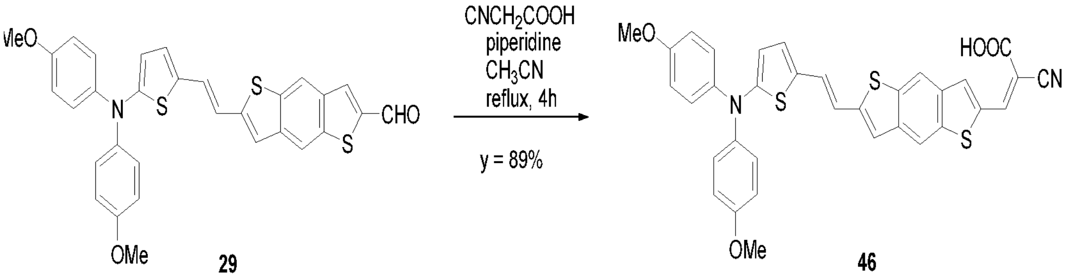
^{1}H-NMR (300 MHz, $CDCl_3$): δ, ppm = 3.81 (s, 6H, $CH_{3,MeO}$), 6.25 (d, 1H, *J*=3.9 Hz), 6.79-6.73 (d, 1H, *J*=15.5 Hz), 6.81 (m, 1H), 6.87-6.84 (d, 4H, *J*=8.9 Hz), 7.04-6.99 (d, 1H, *J*=15.5 Hz), 7.08 (s, 1H), 7.18-7.15 (d, 4H, *J*=8.9 Hz), 8.01 (s, 1H), 8.6 (s, 1H), 8.09 (s, 1H), 8.26 (s, 1H), 10.09 (s, 1H, CHO).

^{13}C-NMR (75 MHz, $CDCl_3$): δ, ppm = 29.72; 55.54; 113.42; 114.72; 116.56; 117.64; 119.30; 120.45; 125.25; 126.63; 128.35; 130.54; 133.62; 135.90; 136.90; 139.65; 140.59; 141.65; 143.09; 146.61; 155.31; 156.65; 184.45.

IR (nujol, cm^{-1}): 1663 (ν_{CO}). MS-EI (m/z): $[M]^+$ 553 (100%), 540 (10%, $-CH_3$), 517 (6%), 316(9%). HRMS-EI (m/z): $[M]^+$ calcd. for $C_{31}H_{23}NO_3S_3$: 553.084009, found: 553.090270.

UV-vis CH_2Cl_2 ($1.08 \cdot 10^{-5}$ M) λ_{max} = 321 nm ($1.84 \cdot 10^4$ $M^{-1}cm^{-1}$), 345 nm ($1.78 \cdot 10^4$ $M^{-1}cm^{-1}$), 477 nm ($3.92 \cdot 10^4$ $M^{-1}cm^{-1}$).

3) 2-cyano-3-{7-[2-[5-[bis(4-methoxyphenyl)amino] thiophenyl] ethenyl] benzo[1,2-b:4,3-b′]dithiophen-2-yl} acrylic acid 46



Compound **46** was synthesized following the same procedure of 2, starting from 60 mg (0.11 mmol) of **29** to give 62 mg (89%) of **46** as a red solid.

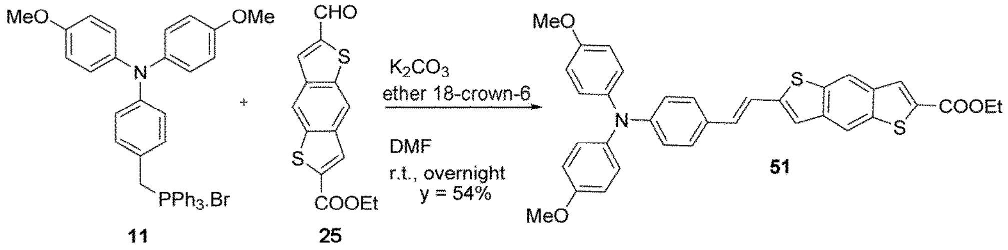
^{1}H-NMR (300 MHz, DMSO-d6): δ, ppm = 3.75 (s, 6H), 6.15 (d, 1H, *J*=3.9 Hz), 6.92-6.86 (d, 1H, *J*=17.2 Hz), 6.96 (d, 4H, *J*=8.9 Hz), 6.98 (d, 1H, *J*=3.9 Hz), 7.04 (s, 1H), 7.09 (m, 1H), 7.14 (d, 4H, **J**=8.9 Hz), 7.34 (s, 1H), 7.97 (s, 1H), 8.23 (s, 1H), 8.33 (s,1H), 8.35 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ, ppm = 55.48, 113.34, 114.40, 114.68, 116.47, 117.56, 119.22, 120.39, 123.26, 123.77, 125.64, 126.56, 130.46, 134.05, 135.82, 136.82, 139.60, 140.57, 141.56, 143.00, 146.53, 155.27, 156.62, 184.26.

IR (nujol, cm^{-1}): 3393 (ν_{OH}), 1606 (ν_{CO}), 1504 (ν_{CN}). UV-vis: THF($1.3 \cdot 10^{-5}$ M), λ_{max} = 381 nm ($1.81 \cdot 10^4$ $M^{-1}cm^{-1}$); 499 nm ($3.41 \cdot 10^4$ $M^{-1}cm^{-1}$) ;Toluene ($2.3 \cdot 10^{-5}$ M): 393 ($4.43 \cdot 10^3$ $M^{-1}cm^{-1}$); 519 ($7.43 \cdot 10^3$ $M^{-1}cm^{-1}$) - CH_2Cl_2 ($1.2 \cdot 10^{-5}$ M) λ_{max} = 396 nm ($2.11 \cdot 10^3$ $M^{-1}cm^{-1}$); 502 nm ($2.70 \cdot 10^4$ $M^{-1}cm^{-1}$) - EtOH($1.4 \cdot 10^{-5}$ M) λ_{max} = 303 nm ($9.21 \cdot 10^3$ $M^{-1}cm^{-1}$); 370 nm ($1.11 \cdot 10^3$ $M^{-1}cm^{-1}$); 480 nm ($2.30 \cdot 10^3$ $M^{-1}cm^{-1}$) - CH_3CN ($1.5 \cdot 10^{-5}$ M) λ_{max} = 301 nm ($5.40 \cdot 10^3$ $M^{-1}cm^{-1}$); 392 nm ($6.73 \cdot 10^4$ $M^{-1}cm^{-1}$); 507 nm ($1.22 \cdot 10^4$ $M^{-1}cm^{-1}$).

EXAMPLE 10

Preparation of Synthesis of 6-[2-[4-[Bis-(4-methoxyphenyl)amino]phenyl]ethenyl]benzo[1,2-b:4,5-b′]dithiophen-2-carboxylic acid 69

1) 6-[2-[4-[Bis-(4-methoxyphenyl)amino]phenyl]ethenyl]benzo[1,2-b:4,5-b′]dithiophen-2-ethoxycarbonyl **51**



Compound **51** was synthesized following the same procedure used for the synthesis of **15**, the phosphonium salt **11** (55.0 mg, 0.083 mmol) was reacted with 2-formyl-(benzo[1,2-b:4,5-b′]dithiophen-6-carboxyethyl **52** (prepared as described in Colombo Rossana, Laurea thesis, 2011. University of Milan) (20.0 mg, 0.07 mmol) in DMF (2 mL). The crude product was purified by silica gel column chromatography (eluent: CH_2Cl_2/hexane 1:1) to afford 23 mg (54%) of **51** a as a yellow solid.

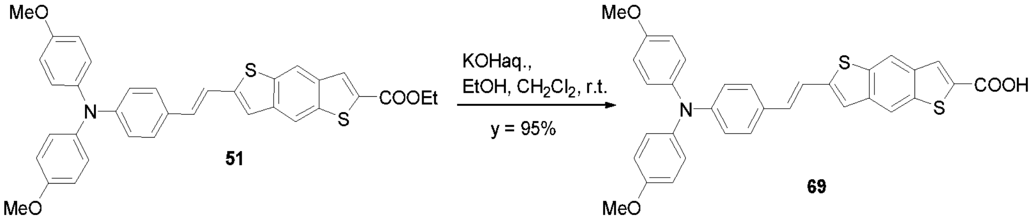
^{1}H-NMR (300 MHz, C_6D_6): δ, ppm = 1.03 (t, 3H, J=6.9Hz), 3.31 (s, 6H), 4.13 (q, 2H, J=6.9Hz), 6.70 (d, 1H, J=17.3Hz), 6.75 (d, 4H, J=8.9Hz), 7.08 (d, 2H, J=9.0Hz), 7.09 (d, 4H, J=8.9Hz), 7.10 (d, 1H, J=17.3Hz), 7.24 (d, 2H, J=9.0Hz), 7.25 (s, 1H), 7.55 (s, 1H), 7.61 (s, 1H), 7.97 (s, 1H).

^{13}C-NMR (75 MHz, C_6D_6): δ, ppm = 14.65, 30.5, 55.40, 61.81, 115.62, 117.10, 119.31, 120.31, 120.83, 122.15, 127.60, 127.69, 128.56, 129.29, 130.51, 132.76, 141.29, 146.44, 149.94, 157.26.

IR (nujol, cm-1): 1714 (ν_{CO}). MS-EI (m/z): [M]+: 591, 576(-CH3)

UV-vis: CH_2Cl_2 ($7.2\bullet10^{-5}$M), λmax = 301 nm ($1.1\bullet10^{4}$ $M^{-1}cm^{-1}$), 336 nm (9.99•103 $M^{-1}cm^{-1}$), 431 nm (2.5•104 $M^{-1}cm^{-1}$).

2) 6-[2-[4-[Bis-(4-methoxyphenyl)amino]phenyl] ethenyl]benzo[1,2-b:4,5-b′]dithiophen-2-carboxylic acid 69



An aqueous solution of KOH (2M, 0.15mL) was added to a solution of **51** (20.0mg, 0.034mmol) in CH_2Cl_2 (3mL) and EtOH (4mL). The mixture was stirred at room temperature overnight. The solvent was then removed under vacuum. The residue was dissolved in CH_2Cl_2 (5 mL) and HCl 0.1N (3 mL) was added; water phase was extracted with CH_2Cl_2 (5x5mL). The organic phase was dried (Na_2SO_4), filtered and the solvent evaporated, affording 19 mg of **69** (yellow solid, 95%).

^{1}H-NMR (300 MHz, DMSO): δ, ppm = 3.75 (s, 6H), 6.71 (d, 2H, J=7.9Hz), 6.90 (d, 4H, J=8.8Hz), 6.92 (d, 1H, J=18.5Hz), 7.03 (d, 4H, J=8.8Hz), 7.90 (d, 1H, J=18.5Hz), 7.42 (d, 2H, J=7.9Hz), 8.07 (s, 1H), 8.34 (s, 1H), 8.46 (s, 1H), 13.06 (broad, 1H).

^{13}C-NMR (300 MHz, DMSO): δ, ppm = 55.74, 115.51, 117.23, 118.98, 119.43, 119.74, 122.13, 127.58, 128.01, 128.35, 130.11, 132.16, 135.12, 136.26, 136.82, 139.02, 140.02, 140.49, 145.83, 149.16, 156.59, 163.93. IR (nujol, cm-1): 3407 (ν_{OH}), 1679.69 (ν_{CO}). MS-EI (m/z): [M]+: 563, 519(-CO_2), 504 (-CH_3). HRMS-EI (m/z): [M]+ calcd. for C33H25NO4S2: calcd. :563.122502 found: 563.123050. UV-vis,: EtOH(3.8•10-5M), λmax = 416 nm (3.8 •104 $M^{-1}cm^{-1}$) - THF(4.1•10-5M), λmax = 426 ($3.9 \bullet 10^4$ $M^{-1}cm^{-1}$) - Toluene ($4.3 \bullet 10^{-5}$M), λmax = 432 nm ($3.3 \bullet 10^4$ M-1cm-1)- CH_3CN ($2.8 \bullet 10^{-5}$M) λmax = 418 nm ($4.8 \bullet 10^4$ $M^{-1}cm^{-1}$) - CH_2Cl_2 ($2.9 \bullet 10^{-5}$M), λmax = 433 nm ($3.2 \bullet 10^4$ $M^{-1}cm^{-1}$).

EXAMPLE 11

Photovoltaic performances of solar cells manufactured using 2-cyane-3-{6-[4-(bis(4-metoxyphenylamino)phenylethynyl] benzo[1,2-b:4,5-

b′]dithiophene-2-yl} acrylic acid (1) as photosensibilizer

Four cells (A1, A2, B1, B2) and two solutions of compound **1** of the invention, in ethanol (A1, A2) and dichloromethane (B1, B2), respectively, at a concentration of $2\cdot10^{-4}$ M were prepared.

Chenodeoxycholic acid was added to both solutions as disaggregating at a concentration of $4\cdot10^{-3}$ M.

The four photoanodes (0.20 cm^2, a single coat of Dyesol 18NR-AO treated with $TiCl_4$ 0.04 M) were immersed for a time period of 18 hours in the above-mentioned solutions (two anodes for solution).

The commercial electrolyte Iolitech ES-0004-HP with LiI at a concentration of 0.06 M added was used.

The IV curves reporting the conversion data were recorded at an incident radiation power of 0.94 sun (94 mW/cm^2).

Data reported in the following Table were collected in the cells 24 hours after sealing and without the aid of a mask; where

J_{sc} = maximum density of obtainable photocurrent, measured under short circuit (mA/cm^2) conditions;

V_{oc} = maximum obtainable potential, measured under open circuit (V) conditions ;

FF = fill factor, which is obtained from the ratio between $J_{mp} x V_{mp}$ and $J_{sc} x V_{oc}$, where J_{mp} is the photocurrent density at the maximum power value and V_{mp} is the cell potential at the maximum power value;

η = light energy conversion efficiency - electric energy (%), measured under standard lighting conditions AM 1.5 corresponding to 100 mW/cm^2 or 1000 W/m^2, obtained applying the following relation:

$\eta = J_{sc}$ [mA/cm^2] x V_{oc} [V] x FF / I_0 [mWcm^{-2}]

where I_0 = 100 mW/cm^2 or 1000 W/m^2 under AM 1.5 conditions.

Cell (1 day)	Jsc (mA/cm^2)	Voc (volt)	FF	η %
A1	4.63	0.677	0.676	2.25%
A2	5.47	0.656	0.644	2.46%
B1	4.88	0.721	0.705	2.64%
B2	4.17	0.730	0.672	2.18%

Figure 5 shows the JV curve obtained for cell B1, exhibiting the best efficiency for compound 1.

EXAMPLE 12

Photovoltaic performances of cells manufactured using 2-cyane-3-{6-[2-(4-[bis(4-metoxyphenyl)amino]phenyl] ethenyl]benzo[1,2-b:4,5-

b′]dithiophene-2-yl} acrylic acid (2) as photosensibilizer

Two cells (A and B) were made using the following procedure.

A solution $2\cdot10^{-4}$ M of photosensibilizer 2 in CH_3CN was prepared with the addition of chenodeoxycholic acid at a concentration of $3\cdot10^{-3}$ M. The photoanode (0.20 cm^2, a single coat of Dyesol 18NR-AO treated with $TiCl_4$ 0.04 M) was immersed in the photosensibilizer solution for 6 hours. The commercial electrolyte Iolitech ES-0004-HP was used with the addition of LiI at a 0,06 M concentration. In order to optimize the electrical contacts, an Ag conductive alloy was laid on the electrodes.

IV curves were recorded at 1 sun (100 mW/cm^2).

Two measurements were carried out:

i) without using an opaque mask and with a white resting surface, able to maximize the light reflection phenomena inside the cell (results are reported in Table 2);

ii) using an opaque black mask of cardboard, with an aperture slightly greater than the active area (0.5 cm^2) and a resting surface made of the same material (results are reported in Table 3).

Reported parameters are those which were measured immediately after sealing (0 days) and 3 and 4 days after assembling regarding two cells (A, B) made under the same conditions.

Data measured after three days also comprise Ag contacts .

Table 2: measurements without mask and with white background

Cell	**Jsc (mA/cm^2)**	**Voc (volt)**	**FF**	**η %**
A (0 days)	10.35	0.680	0.477	3.36%
A (3 days)	13.51	0.715	0.592	5.71%
A+Ag (3 days)	13.20	0.717	0.655	6.20%
A+Ag (4 days)	13.37	0.725	0.658	6.38%
B (0 days)	10.23	0.687	0.601	4.23%
B (3 days)	14.33	0.715	0.555	5.73%
B+Ag (3 days)	13.47	0.724	0.622	6.07%
B+Ag (4 days)	13.19	0.745	0.636	6.25%

Table 3: measurements with opaque mask and black background

Cell	**Jsc (mA/cm^2)**	**Voc (volt)**	**FF**	**η %**
A (0 days)	unavailable datum			
A (3 days)	10.23	0.706	0.618	4.46%
A+Ag (3 days)	10.59	0.705	0.670	5.00%
A+Ag (4 days)	10.65	0.710	0.675	5.11%

B (0 days)	7.67	0.676	0.640	3.32%
B (3 days)	10.43	0.703	0.595	4.36%
B+Ag (3 days)	10.48	0.711	0.650	4.84%
B+Ag (4 days)	10.09	0.727	0.664	4.88%

Figures 5 and 6 show JV curves, respectively obtained for cells A and B, measured 4 days after sealing.

[0026] The tests carried out with the compounds of the present invention have therefore confirmed the particularly advantageous light-absorbing properties of the compounds of the present invention, when used for producing photoelectrical conversion devices such as, for example, solar cells or photovoltaic devices.

In fact, they ensure a good conversion efficiency, comparable to the one offered by devices comprising the already known molecules, such as, for example, ruthenium complexes.

Furthermore, being completely organic and therefore free from metal ions, the compounds of the invention are particularly advantageous from an economical point of view, since they can be prepared at a lower cost. In addition, their disposal is simpler, cheaper and less harmful for the environment.

Furthermore, since they are chemically stable over time, the compounds of the invention are particularly useful and advantageous.

EXAMPLE 13

Photovoltaic performances of compound 2 and 46

Experimental fabrication conditions

Dye: 2 x 10^{-4} M EtOH (with traces of DMF) for 4 h + chenodeoxycholic acid (1:15 mol/mol).

Electrolyte: 1.0 M dimethyl imidazolium iodide, 0.03 M I2, 0.05 M LiI, 0.1 M guanidinium thiocyanate, 0.5 M 4-*t*-butylpyridine in acetonitrile/valeronitrile 85:15.

CONDITIONS A:

Monolayer of active-opaque 350-450 nm nanoparticles TiO_2 (9 µm).

Table A1. Main photovoltaic parameters of DSCs based on **2** and **46**, in comparison with reference dye N719

dye	***Jsc*** **[mA cm^{-2}]**	***Voc*** **[mV]**	**FF**	**η [%]**
2	11.2	663	0.70	5.2
46	9.5	609	0.69	4.0
N719 [a]	13.1	734	0.69	6.6

[a] Commercial electrolyte (Dyesol EL-HPE).

CONDITIONS B:

Double layer of transparent 20 nm nanoparticles TiO_2 with a scattering layer of 150-250 nm nanoparticles TiO_2 (total thickness 15 μm).

Table B1. Main photovoltaic parameters of DSCs based on **2** and **46**, in comparison with reference dye N719.

dye	***Jsc*** **[mA cm-2]**	***Voc*** **[mV]**	**FF**	**η [%]**
2	15.5	658	0.68	6.9[a]
	11.4	632	0.70	5.0[a]
46	14.8	609	0.68	6.2
	10.8	601	0.70	4.6[a]
N719[b]	20.1	728	0.66	9.6

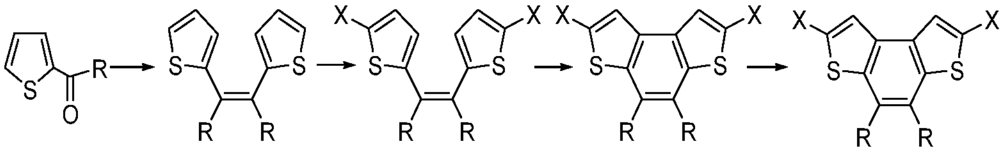
[a] With mask

[b] Commercial electrolyte (Dyesol EL-HPE).

EXAMPLE 14

Preparation of 4,5-Dipropyl-benzo[1,2-b:4,3-b′]dithiophene (74e)

The preparation of compound 74e is performed as depicted in the below scheme following the procedure here below described and also shown in Figure 2B.



71
R : *n*Pr

72

73a : X=Br
73b : X=I
73c : X=COOEt
73d : X=CHO

74a : X=Br
74b : X=I
74c : X=COOEt
74d : X=CHO

74e : X=H

The starting compound 1-(thiophen-2-yl)butan-1-one (**71**) was prepared according to the literature (Sundby, E.; Andersen, M. M.; Hoff, B. H.; Anthonsen, T. *Arkivoc* **2001**, 76-84.)

1) 2-((*Z*)-5-(thiophen-2-yl)oct-4-en-4-yl)thiophene (**72**)

Under a nitrogen atmosphere, $TiCl_4$ (3.0 mL, 27.2 mmol, 1.2 equiv) was added dropwise to a solution of ketone **71** (3.5 g, 22.6 mmol) in dry THF (55 mL) at -20°C. After 30 min at -20°C, Zn powder (3.7 g, 56.6 mmol, 2.5 equiv) was added in 6 portions in 10 min, and then the mixture was refluxed for 3.5 h. Ice-water (40 mL) and an aqueous solution of HCl (1N, 40 mL) were added at room temperature. THF was removed under reduced pressure, the crude material was taken up with CH_2Cl_2 (50 mL) and the aqueous phase was extracted into CH_2Cl_2 (4 × 20 mL). The organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel (hexane) to give **72** as a pale yellow oil (2.31 g; 74 %). ^{1}H NMR (300 MHz, $CDCl_3$): 0.97 (t, J = 7.31 Hz, 6H), 1.47 (m, 4H), 2.53 (m, 4H), 6.71 (m, 2H), 6.84 (m, 2H), 7.13 ppm (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.1 (CH_3, 2C), 21.8 (CH_2, 2C), 37.6 (CH_2, 2C), 111.8 (Cq, 2C), 124.9 (CH, 2C), 126.3 (CH, 2C), 126.5 (CH, 2C), 133.0 (Cq, 2C), 145.1 ppm (Cq, 2C). MS (EI): *m/z* (%) = 276 (65, $[M]^+$), 247 (60), 97 (100). HRMS (EI): calcd. for $C_{16}H_{20}S_2$ 276.0939; found 276.0948.

2) 2-Bromo-5-((*Z*)-5-(5-bromothiophen-2-yl)oct-4-en-4-yl)thiophene (**73a**)

Under a nitrogen atmosphere, N-bromosuccinimide (0.270 g, 1.52 mmol, 2.1 equiv) was added to a solution of **72** (0.200 g, 0.723 mmol) in dry DMF (2 mL) under ice-water bath. The mixture was stirred in the dark at room temperature and the progress of the reaction was monitored by TLC (hexane). After 3 h, the mixture was quenched with water (10 mL) and the aqueous phase was extracted into CH_2Cl_2 (3 × 10 mL). The organic phase was washed with water and dried with Na_2SO_4. After the removal of solvent under reduce pressure, the residue was purified by chromatography on silica gel (hexane) to give **73a** as a pale yellow oil (0.201 g; 64 %). ^{1}H NMR (300 MHz, $CDCl_3$): 0.93 (t, J = 7.2 Hz, 6H), 1.44 (m, 4H), 2.44 (m, 4H), 6.50 (d, J = 3.8 Hz, 2H), 6.81 ppm (d, J = 3.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 13.9 (CH_3, 2C), 21.7 (CH_2, 2C), 37.2 (CH_2, 2C), 111.8 (Cq, 2C), 127.1 (CH, 2C), 129.4 (CH, 2C), 133.0 (Cq, 2C), 145.9 ppm (Cq, 2C). MS (EI): *m/z* (%) = 434 (100, $[M]^+$), 326 (52), 297 (18), 216 (20). HRMS (EI): calcd. for $C_{16}H_{18}Br_2S_2$ 431.9217; found 431.9224.

3) 2-Iodo-5-((*Z*)-5-(5-iodothiophen-2-yl)oct-4-en-4-yl)thiophene (**73b**).

A solution of *n*BuLi (1.5 M in hexane, 1.93 mL, 2.89 mmol, 4 equiv) was added dropwise to a stirring solution of **72** (0.200 g, 0.723 mmol) in dry THF (5 mL) at -78°C under a nitrogen atmosphere. The solution was stirred 10 min at –78°C and 30 min at -10°C. The resulting orange mixture was cooled to -78°C and a solution of I_2 (0.734 g, 2.89 mmol, 4 equiv) in dry THF (3 mL) was added dropwise. The mixture was stirred at -78°C for 10 min then warmed to room temperature. The progress of the reaction was monitored by TLC (hexane). After 30 min at room temperature, the mixture was added to a saturated aqueous solution of Na_2SO_3 (20 mL) and the aqueous phase was extracted into CH_2Cl_2 (3 × 15 mL). The organic phase was washed with water, dried with Na_2SO_4 and concentrated under reduce pressure. The crude product was purified by chromatography on silica gel (hexane) to give **73b** as a yellow oil (0.332 g; 87 %). ^1H NMR (300 MHz, $CDCl_3$): 0.92 (t, J = 7.3 Hz, 6H), 1.43 (m, 4H), 2.44 (m, 4H), 6.40 (d, J = 3.7 Hz, 2H), 6.99 ppm (d, J = 3.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 13.9 (CH_3, 2C), 21.7 (CH_2, 2C), 37.3 (CH_2, 2C), 73.0 (Cq, 2C), 128.4 (CH, 2C), 133.0 (Cq, 2C), 136.5 (CH, 2C), 150.6 ppm (Cq, 2C). MS (EI): *m/z* (%) = 528 (100, $[M]^+$), 402 (68), 372 (75), 246 (48), 203 (45), 171 (58). HRMS (EI): calcd. for $C_{16}H_{18}I_2S_2$ 527.8939; found 527.8927.

4) Ethyl 5-((*Z*)-5-(5-(ethoxycarbonyl)thiophen-2-yl)oct-4-en-4-yl)thiophene-2-carboxylate (**73c**).

A solution of *n*BuLi (1.3 M in hexane, 2.22 mL, 2.89 mmol, 4 equiv) was added dropwise to a stirring solution of **72** (0.200 g, 0.723 mmol) in dry THF (5 mL) at -78° C under a nitrogen atmosphere. The solution was stirred 10 min at –78°C and 30 min at -10°C. The resulting orange solution was cooled to -78°C and treated with ClCOOEt (0,275 mL, 2.89 mmol, 4 equiv). The mixture was stirred at -78°C for 30 min then warmed to room temperature. The progress of the reaction was monitored by TLC (hexane/AcOEt, 9:1). After 5h at room temperature, the mixture was added to water (20 mL) and the aqueous phase was extracted into CH_2Cl_2 (3 × 15 mL). The organic phase was washed with water, dried with Na_2SO_4 and concentrated under reduce pressure. The crude product was purified by chromatography on silica gel (hexane/AcOEt, 9:1) to give **73c** as a pale orange oil (0.230 g; 76 %). ^1H NMR (300 MHz, $CDCl_3$): 0.93 (t, J = 7.3 Hz, 6H), 1.33 (t, J = 7.1 Hz, 6H), 1.43 (m, 4H), 2.50 (m, 4H), 4.29 (q, J = 7.1 Hz, 4H), 6.62 (d, J = 3.9 Hz, 2H), 7.50 ppm (d, J = 3.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 13.9 (CH_3, 2C), 14.3 (CH_3, 2C), 21.6 (CH_2, 2C), 37.6 (CH_2, 2C), 61.0 (CH_2, 2C), 127.7 (CH, 2C), 133.0 (CH, 2C), 134.3 (Cq, 4C), 151.8 (Cq, 2C), 162.2 ppm (Cq, 2C). MS (EI): *m/z* (%) = 420 (100, $[M]^+$), 391 (21), 375 (10), 318 (18). HRMS (EI): calcd. for $C_{22}H_{28}O_4S_2$ $[M]^+$ 420.1429; found 420.1427. IR (neat): ν = 1707 (C=O) cm^{-1}.

5) 5-((*Z*)-5-(5-formylthiophen-2-yl)oct-4-en-4-yl)thiophene-2-carbaldehyde (**73d**).

A solution of *n*BuLi (1.5 M in hexane, 1.93 mL, 2.89 mmol, 4 equiv) was added dropwise to a stirring solution of **72** (0.200 g, 0.723 mmol) in dry THF (5 mL) at -78°C under a nitrogen atmosphere. The solution was stirred 10 min at -78°C and 30 min at -10°C. The resulting orange solution was cooled to -78°C and treated with DMF (0.560 mL, 7.23 mmol, 10 equiv). The mixture was stirred at -78°C for 30 min then warmed to room temperature. The progress of the reaction was monitored by TLC (hexane/AcOEt, 8:2). After 1h at room temperature, the mixture was added to water (20 mL) and the aqueous phase was extracted into CH_2Cl_2 (3 × 15 mL). The organic phase was washed with water, dried with Na_2SO_4 and concentrated under reduce pressure. The crude product was purified by chromatography on silica gel (hexane/AcOEt, 8:2) to give **73d** as an orange oil (0.202 g; 84%).

^{1}H NMR (300 MHz, $CDCl_3$): 0.95 (t, J = 7.3 Hz, 6H), 1.44 (m, 4H), 2.56 (m, 4H), 6.76 (d, J = 3.9 Hz, 2H), 7.49 (d, J = 3.9 Hz, 2H), 9.79 ppm (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 13.8 (CH_3, 2C), 21.6 (CH_2, 2C), 37.6 (CH_2, 2C), 61.0 (CH_2, 2C), 128.4 (CH, 2C), 135.0 (Cq, 2C), 136.2 (CH, 2C), 143.0 (Cq, 2C), 154.6 (Cq, 2C), 182.7 ppm (CHO, 2C). MS (EI): *m/z* (%) = 332 (85, $[M]^+$), 303 (20), 275 (33), 134 (100), 84 (40). HRMS

(EI): calcd. for $C_{18}H_{20}O_2S_2$ $[M]^+$ 332.0905; found 332.0921. IR (neat): ν= 1665 (C=O) cm^{-1}.

6) 2,7-Dibromo-4,5-dipropyl-benzo[1,2-b:4,3-b′]dithiophene (**7<u>4a</u>**).

The alkene **73a** (0.185 g, 0.427 mmol) was dissolved in dry CH_2Cl_2 (60 mL), and the solution was constantly sparged with nitrogen. After 10 min, $FeCl_3$ (0.277 g, 1.70 mmol, 4 equiv) was added to the solution at room temperature, and the resulting mixture was stirred under a nitrogen purge. The progress of the reaction was monitored by HPLC (MeCN/H_2O, 9:1). After 2 h, methanol (approx. 50 mL) was added and the reaction mixture was stirred for 30 min. The mixture was concentrated under reduce pressure, and the crude product was purified by chromatography on silica gel (hexane) to give **74a** as a white solid (0.139 g; 76 %).

m.p. 94-95°C (hexane).

^1H NMR (200 MHz, $CDCl_3$): 1.06 (t, J = 7.3 Hz, 6H), 1.73 (m, 4H), 2.85 (m, 4H), 7.55 ppm (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.5 (CH_3, 2C), 22.9 (CH_2, 2C), 34.2 (CH_2, 2C), 114.1 (Cq, 2C), 125.0 (CH, 2C), 129.8 (Cq, 2C), 131.6 (Cq, 2C), 140.0 ppm (Cq, 2C). MS (EI): *m/z* (%) = 432 (100, $[M]^+$), 403 (65), 375 (25), 322 (42).

HRMS (EI): calcd. for $C_{16}H_{16}Br_2S_2$ $[M]^+$ 429.9060; found 429.9072.

7) 2,7-Diiodo-4,5-dipropyl-benzo[1,2-b:4,3-b′]dithiophene (**74b**).

The alkene **73b** (0.141 g, 0.267 mmol) was dissolved in dry CH_2Cl_2 (50 mL), and the solution was constantly sparged with nitrogen. After 10 min, $FeCl_3$ (0.173 g, 1.07 mmol, 4 equiv) was added to the solution at room temperature, and the resulting mixture was stirred under a nitrogen purge. The progress of the reaction was monitored by HPLC ($MeCN/H_2O$, 9:1). After 1.5 h, methanol (approx. 50 mL) was added and the reaction mixture was stirred for 30 min. The mixture was concentrated under reduce pressure, and the crude product was purified by chromatography on silica gel (hexane) to give **74b** as a white solid (46 mg; 33 %): m.p. 117-118°C (hexane).

^1H NMR (200 MHz, $CDCl_3$): 1.06 (t, J = 7.3 Hz, 6H), 1.71 (m, 4H), 2.86 (m, 4H), 7.76 ppm (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.6 (CH_3, 2C), 23.0 (CH_2, 2C), 34.2 (CH_2, 2C), 65.2 (Cq, 2C), 129.6 (Cq, 2C), 132.2 (CH, 2C), 132.5 (Cq, 2C), 143.7 ppm (Cq, 2C). MS (EI): *m/z* (%) = 526 (100, $[M]^+$), 497 (60), 469 (21), 370 (50), 227 (37). HRMS (EI): calcd. for $C_{16}H_{16}I_2S_2$ $[M]^+$ 525.8783; found 525.8773.

8) 2,7-Diethyl ester 4,5-dipropyl-benzo[1,2-b:4,3-b′]dithiophene-2,7-dicarboxylic acid (**74c**).

Under a nitrogen atmosphere, $FeCl_3$ (0.232 g, 1.43 mmol, 6 equiv) was added to a solution of alkene **73c** (0.100 g, 0.238 mmol) in dry CH_2Cl_2 (20 mL) at room temperature, and the resulting mixture was stirred under a nitrogen purge. The progress of the reaction was monitored by HPLC ($MeCN/H_2O$, 9:1). After 2 h, methanol (approx. 20 mL) was added and the reaction mixture was stirred for 30 min. The mixture was concentrated under reduce pressure, and the crude product was purified by chromatography on silica gel (hexane/AcOEt, 9:1) to give **74c** as a pale yellow solid (65 mg; 66 %).

m.p. 179-180 °C (hexane/CH_2Cl_2).

^1H NMR (300 MHz, $CDCl_3$): 1.10 (t, J = 7.3 Hz, 6H), 1.44 (t, J = 7.1 Hz, 6H), 1.78 (m, 4H), 2.97 (m, 4H), 4.44 (q, J = 7.1 Hz, 4H), 8.38 ppm (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 14.4 (CH_3, 2C), 14.6 (CH_3, 2C), 23.0 (CH_2, 2C), 34.3 (CH_2, 2C), 61.6 (CH_2, 2C), 128.3 (CH, 2C), 132.0 (Cq, 2C), 133.1 (Cq, 2C), 133.2 (Cq, 2C), 142.4 (Cq, 2C), 162.8 ppm (Cq, 2C). MS (EI): *m/z* (%)

= 418 (100, $[M]^+$), 389 (22), 361 (15). HRMS (EI): calcd. for $C_{22}H_{26}O_4S_2$ $[M]^+$ 418.1272; found 418.1280. IR (neat): ν= 1719 (C=O) cm^{-1}.

9) 4,5-Dipropyl-benzo[1,2-b:4,3-b′]dithiophene-2,7-dicarboxaldehyde (**74d**).

Under a nitrogen atmosphere, the alkene **73d** (0.050 g, 0.150 mmol) was dissolved in anhydrous dichloroethane (30 mL), and the resulting solution was heated to 80 °C. After 10 min, $FeCl_3$ (0.100 g, 0.601 mmol, 4 equiv) was added to the solution at 80°C, and the resulting mixture was stirred under a nitrogen purge. The progress of the reaction was monitored by HPLC ($MeCN/H_2O$, 9:1). After 5 h, the mixture was cooled to room temperature and quenched with methanol (approx. 30 mL). The reaction mixture was stirred for 30 min, concentrated under reduce pressure, and the crude product was purified by chromatography on silica gel (hexane/AcOEt, 8:2) to give **74d** as an orange solid (22 mg; ^1H NMR purity: 90%, 40 %): m.p. 108-113 °C (hexane/CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): 1.11 (t, J = 7.3 Hz, 6H), 1.77 (m, 4H), 3.00 (m, 4H), 8.37 (s, 2H), 10.1 ppm (s, CHO). ^{13}C NMR (75 MHz, $CDCl_3$): 14.5 (CH_3, 2C), 22.9 (CH_2, 2C), 34.3 (CH_2, 2C), 131.3 (CH, 2C), 133.2 (Cq, 2C), 134.9 (Cq, 2C), 142.8 (Cq, 2C), 143.7 (Cq, 2C), 184.0 ppm (CHO, 2C). MS (EI): *m/z* (%) = 330 (100, $[M]^+$), 301 (83), 273 (36). IR (neat): ν= 1672 (C=O) cm^{-1}.

10) 4,5-Dipropyl-benzo[1,2-b:4,3-b′]dithiophene (**74e**)

A solution of *n*BuLi (1.3 M in hexane, 0.142 mL, 0.185 mmol, 2 equiv) was added dropwise to a stirring solution of **74a** (40 mg, 0.0925 mmol) in dry Et_2O (3 mL) at 0°C under a nitrogen atmosphere. The solution was stirred 10 min at 0°C and 5h at room temperature. The mixture was cooled to 0°C and treated with MeOH (1 mL). After 5 min, the mixture was warmed to room temperature and added to a saturated aqueous solution of NH_4Cl (10 mL). The aqueous phase was extracted into CH_2Cl_2 (2 × 10 mL) and the organic phase was dried with Na_2SO_4, and concentrated under reduce pressure. The crude product was purified by chromatography on silica gel (hexane) to give **74e** as a white solid (19.5 mg; 89 %): m.p. 65-66°C. ^1H NMR (300 MHz, $CDCl_3$): 1.11 (t, J = 7.3 Hz, 6H), 1.80 (m, 4H), 3.01 (m, 4H), 7.48 (d, J = 5.4 Hz, 2H), 7.68 ppm (d, J = 5.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 17.8 (CH_3, 2C), 23.2 (CH_2, 2C), 34.4 (CH_2, 2C), 122.5 (CH, 2C), 125.0 (CH, 2C), 130.2 (Cq, 2C), 132.8 (Cq, 2C), 138.8 ppm (Cq, 2C). MS (EI): *m/z* (%) = 274 (90, $[M]^+$), 245 (100), 229 (17). HRMS (EI): calcd. for $C_{16}H_{18}S_2$ $[M]^+$ 274.0850; found 274.0832.

[0027] From the above description of the present invention, the man skilled in the art, for the purpose of satisfying specific current needs, can make a number of modifications, additions or replacements of elements with functionally equivalent ones, without however departing from the scope of the attached claims. Each of the characteristics described as belonging to a possible embodiment can be performed independently from other embodiments described.

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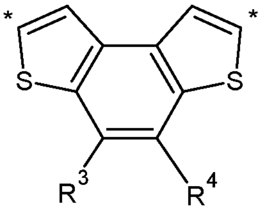
CLAIMS

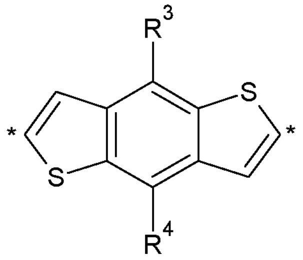
1. Photosensitizers having the general structure (I):

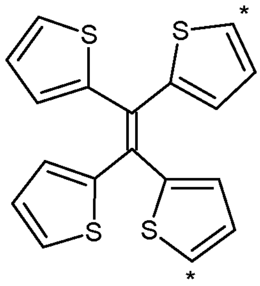
$$GD—R^2——L——A \quad (I)$$

wherein A is an electron-withdrawing group, L is a spacer of formula:



and

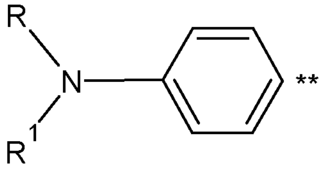


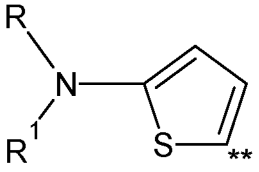


wherein R_3 and R_4, equal or different from each other, are selected from the group comprising H, $-R^5$ or $-OR^5$, where R^5 is a C_1-C_{10} linear or branched alkyl chain;

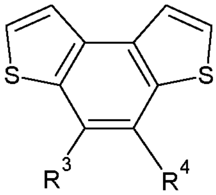
R^2 is an unsaturated $-(C{=}C)_n-$ or $-(C{\equiv}C)_n-$ wherein n=0-2 and GD is an electron-donor group.

2. Compounds, according to claim 1, wherein the GD electron-donor group is a group of formula





wherein R and R^1, equal or different from each other, are selected from among the group comprising



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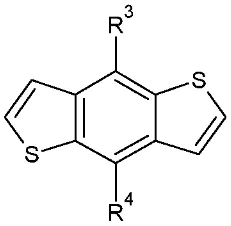

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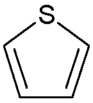

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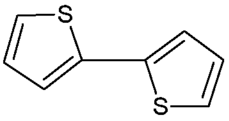

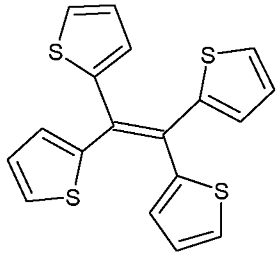

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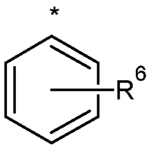
wherein R^3 and R^4, equal or different from each other, may be H, $-R^5$ or $-OR^5$, where R^5 is a C_1-C_{10} linear or branched alkyl chain;

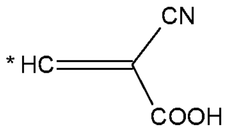
and comprising

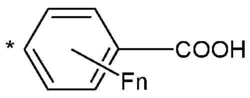


wherein R^6 is H or a $-R^5$ or $-OR^5$ group, wherein R^5 is a C_1-C_{10} linear or branched alkyl chain.

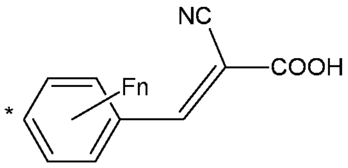
3. The compound according to claim 1 or 2, wherein the group A is an electron-withdrawing group selected among:

*COOH





or



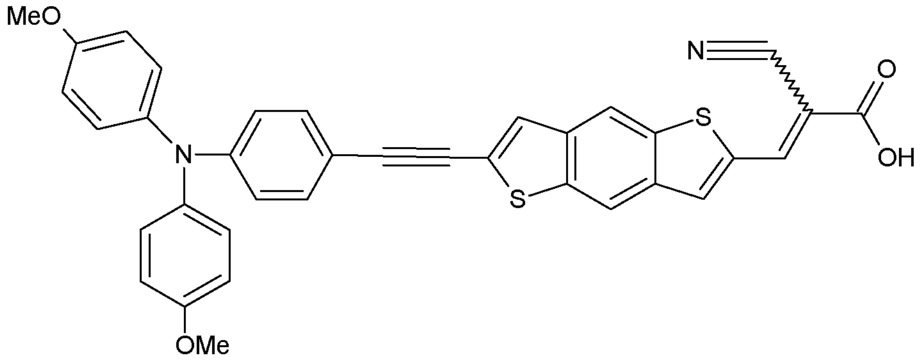
wherein n=1-4.

4. The compound according to any one of claims 1 to 3, wherein in the spacer L, R^3 and R^4, equal or different from each other, are selected from the group comprising H, $-R^5$ or $-OR^5$, where R^5 is a C_1-C_{10} linear or branched alkyl chain.

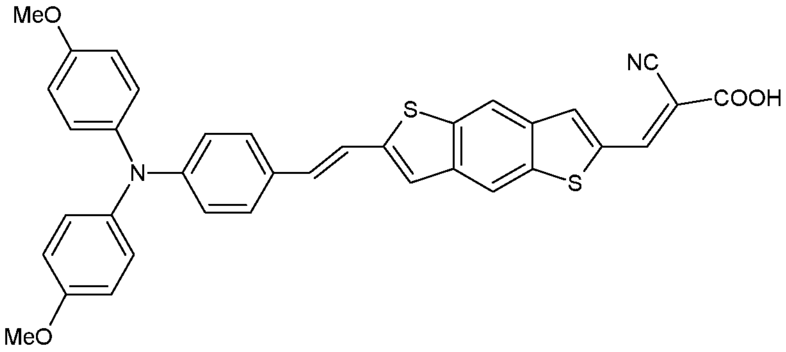
5. The compound according to claim 4, wherein in the GD group R^3 and R^4 are H and in the L group R^3 and R^4 are H.

6. The compound according to any one of claims 1 to 5, wherein R and R^1 are both a paramethoxy substituted phenyl group.

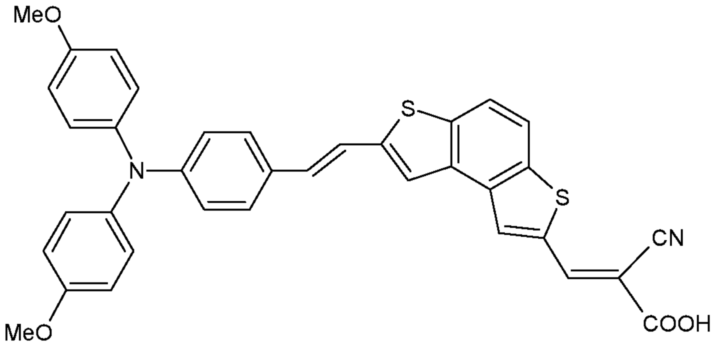
7. The compound according to any one of claims 1 to 6, having the following formula:



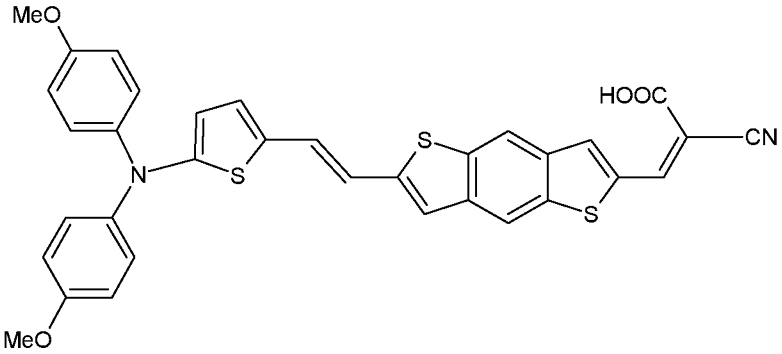
(1)


MeO
NC
COOH
S
N
S
MeO

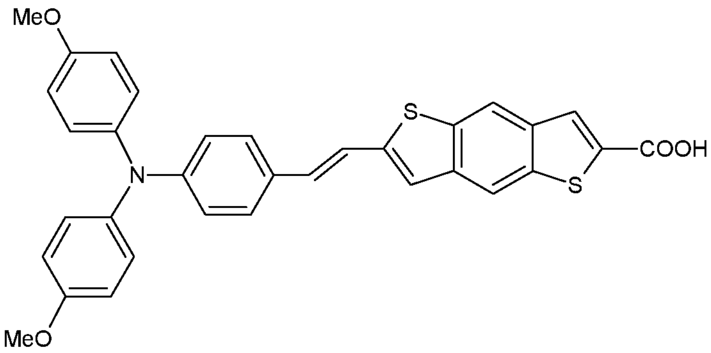
(2)


MeO
S
N
S
CN
MeO
COOH

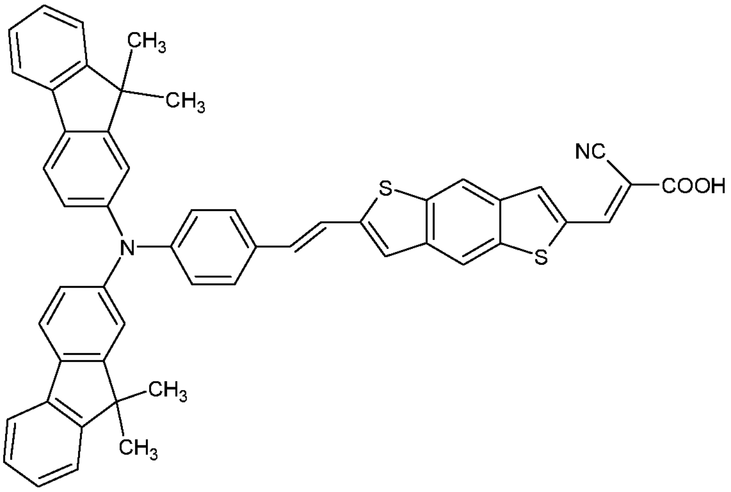
(52)


MeO
HOOC
CN
S
N
S
S
MeO

(46)

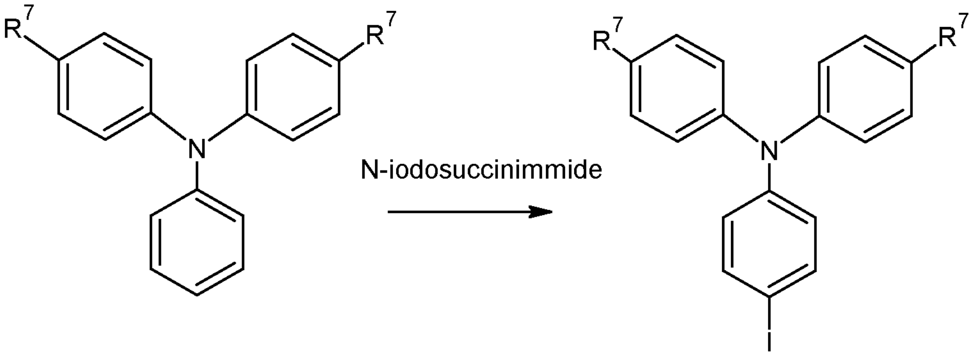

MeO
S
COOH
N
S
MeO

(69)



(71)

8. A process for preparing a (4-iodo-phenyl)bis(4-alkoxyphenyl)amine comprising the step of reacting bis(4-alcoxyphenyl)phenylamine with N-iodosuccinimide



wherein R^7 is a $-R^8$ or $-OR^8$ group, where R^8 is a C_1-C_{10} alkyl chain.

9. A process for preparing the compounds of claims 1 to 7, comprising the steps of:

a) reacting a GD-X′(II) group, where GD is an electron-donating group and X′ is a reactive group able to condense or couple with a X-L-Y group (III), precursor of a dibenzothiophene spacer group L carrying a reactive group X able to condense or couple with a molecule (II), precursor of GD, generating R_2, and Y is a reactive group precursor of an electron-withdrawing substrate-linking group, according to the reaction:

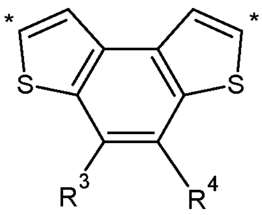
GD-X′ (II) + X-L-Y (III) → GD-R2-L-Y (IV)

wherein R^2 is an unsaturated $-(\mathrm{C{=}C})_n-$ or $-(\mathrm{C{\equiv}C})_n-$ wherein n=0-2;

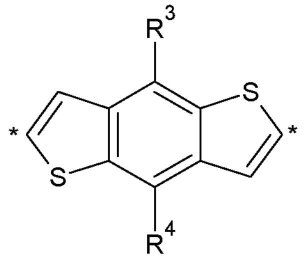
b) converting the intermediate (IV) from the step a) into a compound comprising an electron-withdrawing substrate-linking group A, according to the following reaction:

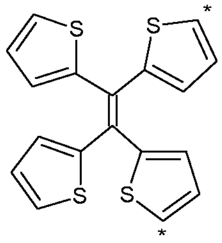
$$\text{GD-}R_2\text{-L-Y (IV)} \rightarrow \text{GD-}R_2\text{-L-A(I)}.$$

10. A compound of formula X-L-Y, wherein L is a spacer group of formula



,





or

wherein R_3 and R_4, equal or different from each other, are selected from the group comprising H, $-R^5$

or $-OR^5$, where R^5 is a C_1-C_{10} linear or branched alkyl chain; Y is a reactive group precursor of an electron-withdrawing substrate-linking group A and X is a reactive group able to condense or couple with a molecule precursor of a GD donor group.

11. A process for preparing a photoelectric conversion device comprising the step of making a semiconductor material layer adsorb a solution comprising one or more of the photosensitizers according to any one of claims 1 to 7.

12. The process according to claim 11, wherein said solution has a concentration ranging from 10^{-4} and 10^{-3} M.

13. The process according to claim 11 or 12, wherein said semiconductor material is titanium dioxide.

14. The process according to any one of claims 11 to 13, wherein said solution further comprises chenodeoxycholic acid.

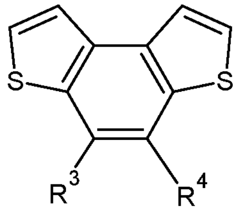
15. The process according to claim 14, wherein said chenodeoxycholic acid solution has a concentration ranging from 10^{-4} and 10^{-3} M.

16. A photoelectric conversion device comprising a semiconductor material layer comprising one or more of the compounds according to any one of claims 1 to 7.

17. A photoelectric conversion device obtained according to the process of any one of claims 11 to 15.

18. Use of the compounds according to any one of claims 1 to 7 as photosensitizers in photoelectric conversion devices.

19. A process for the preparation of a compound of formula



(74e).

wherein R^3 and R^4 equal or different from each other, are selected from the group comprising H, $-R^5$ or $-OR^5$, wherein R^5 is a C_1-C_{10} linear or branched alkyl chain, said process comprising the steps of:

a) performing a Mc Murry coupling on 1-(thiophen-2-yl)alkyl-1-one;

b) protecting the α-carbons of the resulting 2-((Z)-5-thiophen-2-yl)alkyl-4-en-4yl)thiophen;

c) performing an oxidation phase so as to yield the corresponding 2,7-disubstituted 4,5-dialkyl-benzo[1,2-b:4,3-b′] dithiophene.

20. The process according to claim 19, wherein in step a) the coupling is performed on 1-(thiophen-2-yl)butan-1-one.

21. The process according to claim 19 or 20, further comprises the step:

d) of deprotecting the α-carbons.

FIG. 1

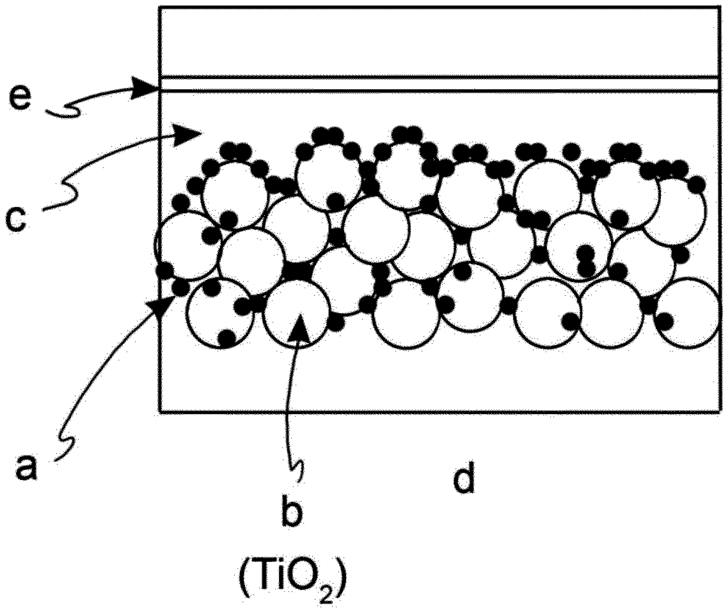


FIG. 2A

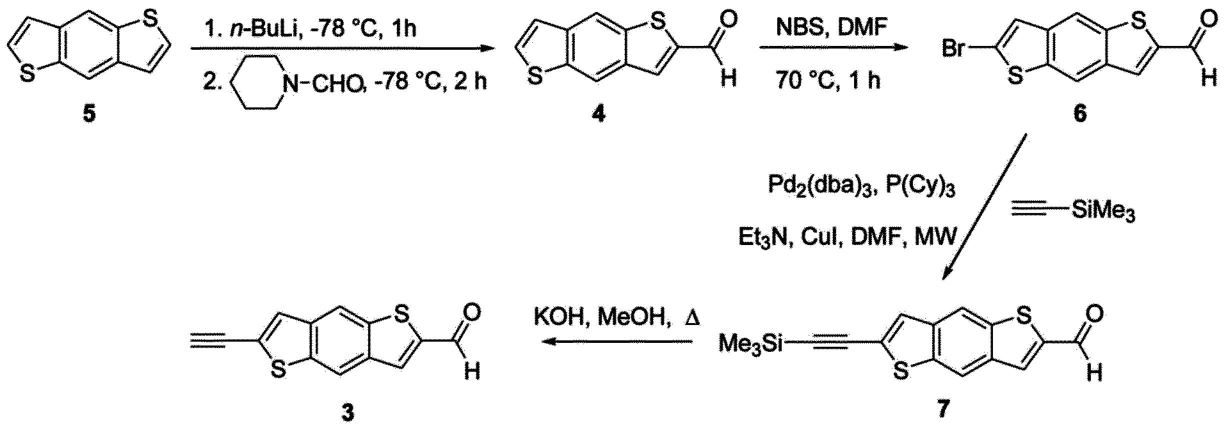

5
1. n-BuLi, -78 °C, 1h
2. N-CHO, -78 °C, 2 h
4
NBS, DMF
70 °C, 1 h
Br
6
Pd2(dba)3, P(Cy)3
Et3N, CuI, DMF, MW
SiMe3
Me3Si
7
KOH, MeOH, Δ
3
S
O
H

FIG. 2B

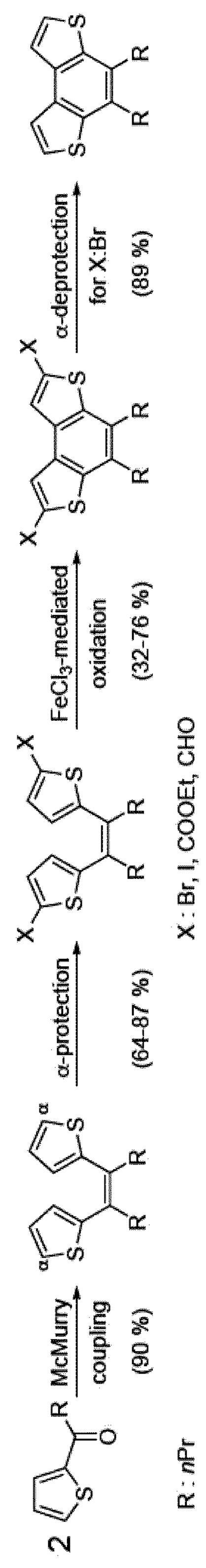

2
R
O
S
McMurry
coupling
(90 %)
α
α
S
S
R
R
α-protection
(64-87 %)
X
X
S
S
R
R
FeCl3-mediated
oxidation
(32-76 %)
X
X
S
S
R
R
α-deprotection
for X:Br
(89 %)
S
S
R
R
R : nPr
X : Br, I, COOEt, CHO

FIG.3

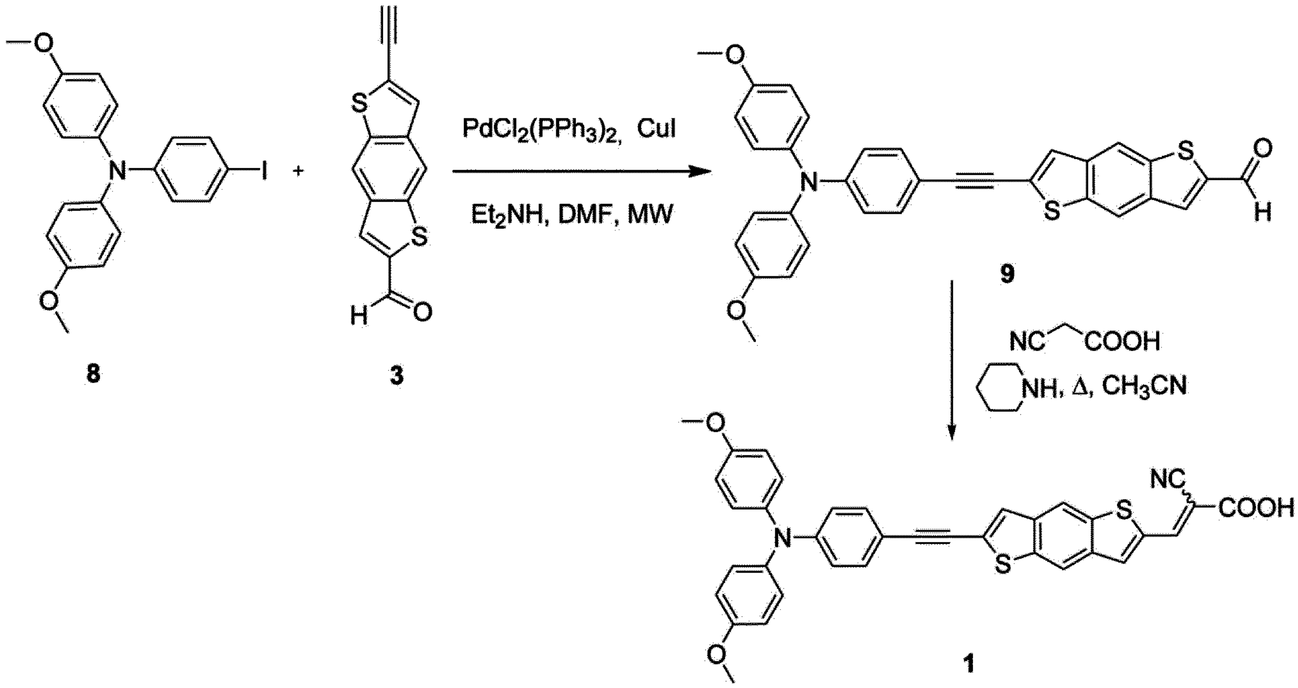


FIG.4

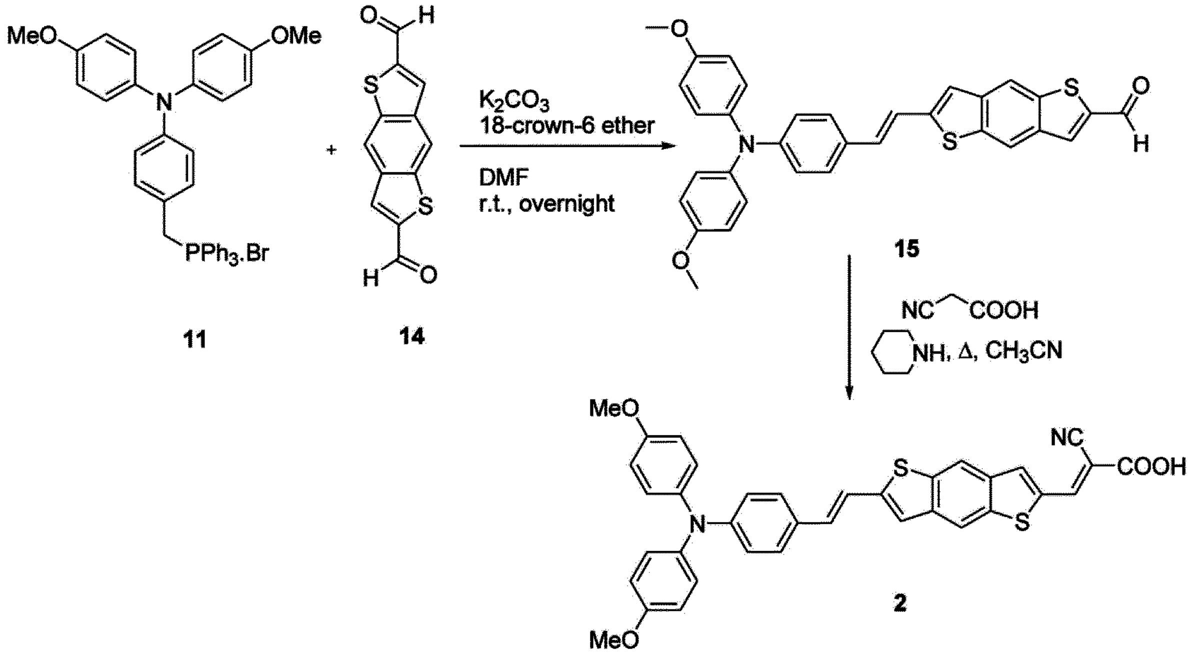

MeO
OMe
N
PPh3.Br
11
+
S
S
H
O
14
K2CO3
18-crown-6 ether
DMF
r.t., overnight
O
N
S
S
O
H
15
NC COOH
NH, Δ, CH3CN
MeO
N
MeO
S
S
NC
COOH
2

FIG. 5

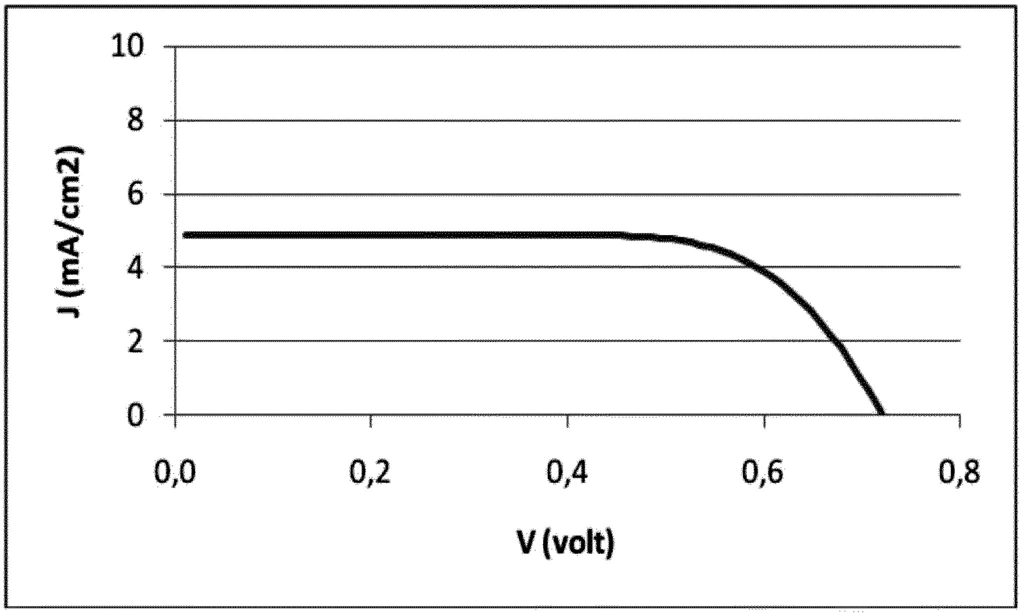


FIG. 6

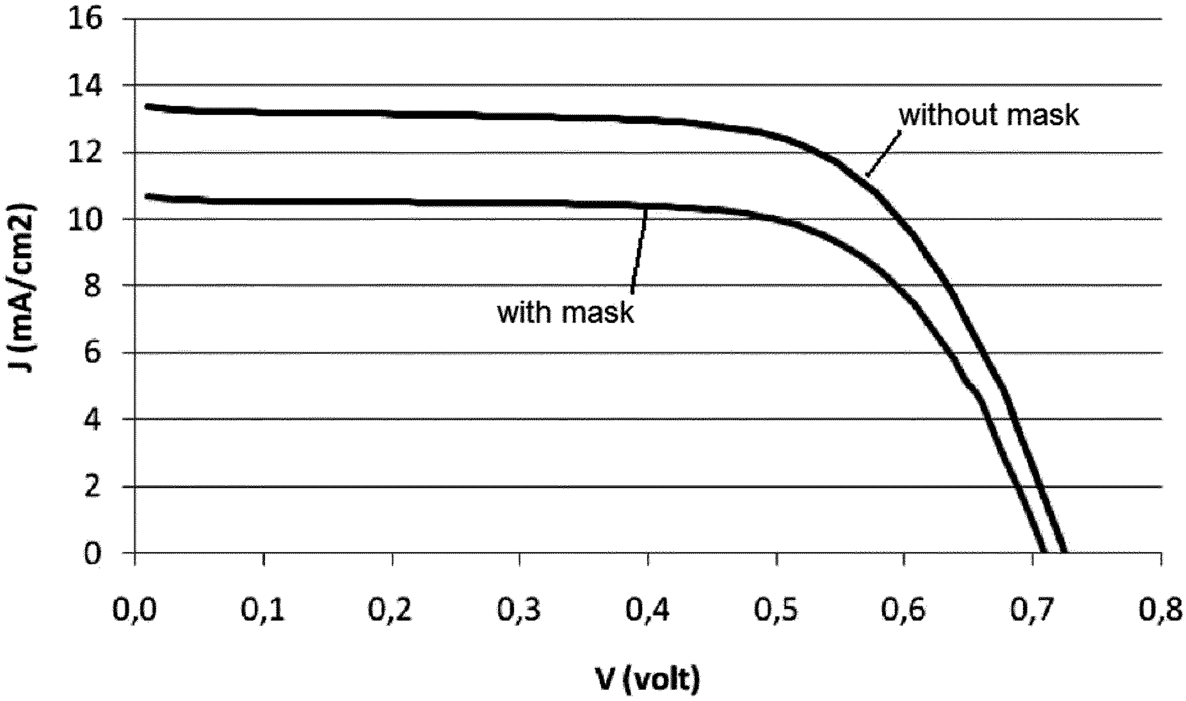
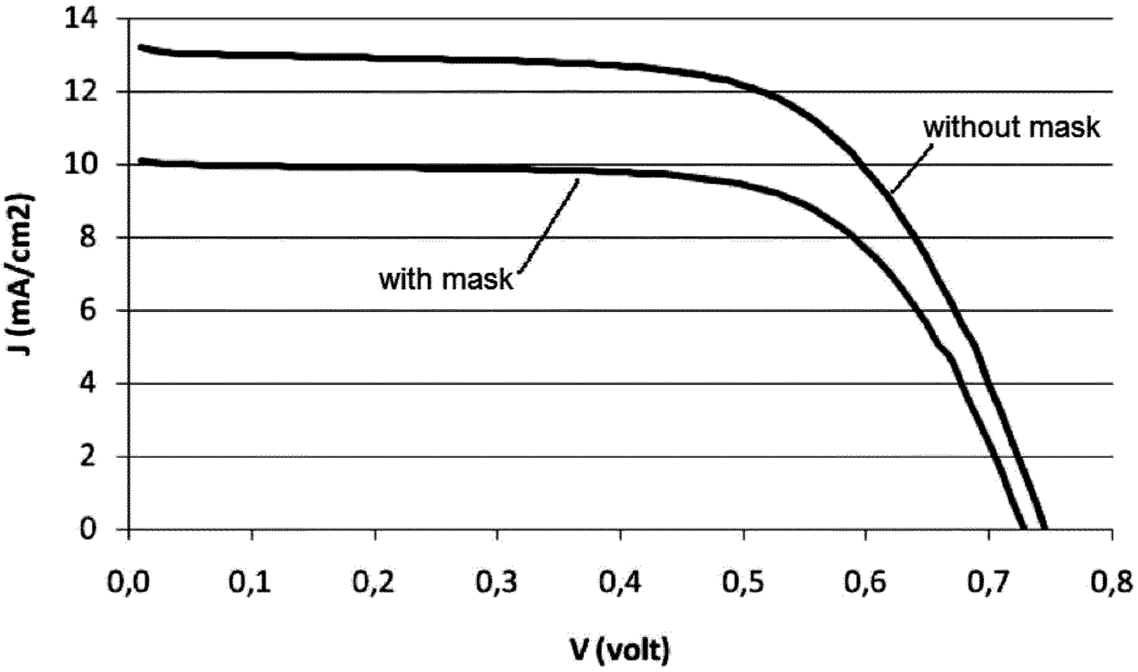

16
14
12
10
8
6
4
2
0
J (mA/cm2)
without mask
with mask
0,0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
V (volt)

FIG. 7


14
12
10
8
6
4
2
0
0,0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
J (mA/cm2)
V (volt)
without mask
with mask