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Convergent Synthesis of Near-Infrared Absorbing, "Push–Pull", Bisthiophene-Substituted, Zinc(II) Phthalocyanines and their Application in Dye-Sensitized Solar Cells

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Abstract: Zinc(II) phthalocyanine dyes that contain triarylamine-terminated bisthiophene and hexylbisthiophene groups have been synthesized by a convergent approach by using carboxytriiodo–ZnPc as a precursor. Further transformation of the iodo groups by a Pd-catalyzed reaction allowed easy preparation of further extended π-conjugated carboxy–ZnPcs. These dyes have been used as sensitizers in dye-sensitized solar cells, which exhibit a panchromatic response and moderate overall efficiencies.

Keywords: bisthiophene · dye-sensitized solar cells · near-infrared dyes · phthalocyanines

Introduction

Dye-sensitized solar cells (DSSCs) based on nanocrystalline semiconductors have been intensively studied due to low costs and easy processing compared with conventional inorganic photovoltaic devices.[1,2] Ru^{II}–polypyridyl sensitizers have established record efficiencies for solar-energy-to-electricity conversion ($\eta = 11.5\,\%$).[2] However, drawbacks of this system are the lack of light-harvesting capability in the red region of the visible spectrum and high costs due to the scarcity of ruthenium metal. Organic dyes have some advantages over conventional Ru^{II}-based chromophores as photosensitizers. They exhibit high molar extinction coefficients and the absorption wavelengths, as well as the band gaps, are easily tuned by chemical modifications of structural motifs.[3] Due to strong absorption in the red and near-infrared (NIR) regions of the solar spectrum (between 640–700 nm), suitable photophysical properties, and remarkable chemical and thermal stability, phthalocyanines (Pcs) are perhaps the most extensively studied molecules, among the organic dyes, in the areas of molecular electronics and solar-energy conversion.[4] Serious efforts have been made to exploit the application of Pcs in DSSCs.[5] However, until very recently the photovoltaic performance of Pc-sensitized solar cells has been poor (below $\eta = 1\,\%$), owing to strong aggregation and lack of directionality in the excited state. We have previously reported overall efficiencies above 3 % by employing unsymmetrically substituted, "push–pull", carboxyl–Zn^{II}Pc derivatives,[6] such as **TT1** (Figure 1). In 2010, Mori et al. reported the highest-conversion-efficiency DSSC yet ($\eta = 4.6\,\%$), by using a ZnPc with six 2,6-diphenylphenoxy peripheral groups, which help to virtually suppress Pc aggregation.[7]

The use of *tert*-butyl as peripheral groups have proven to be the best compromise to get Pc dyes with good solubility, low aggregation tendency, and a "push–pull" character to

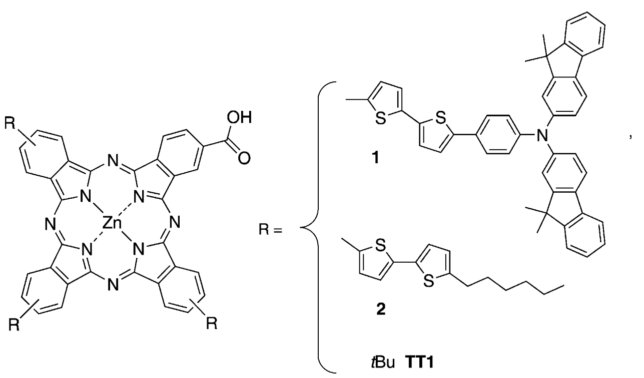

Figure 1. Molecular structures of ZnPcs dyes **1**, **2**, and **TT1.**

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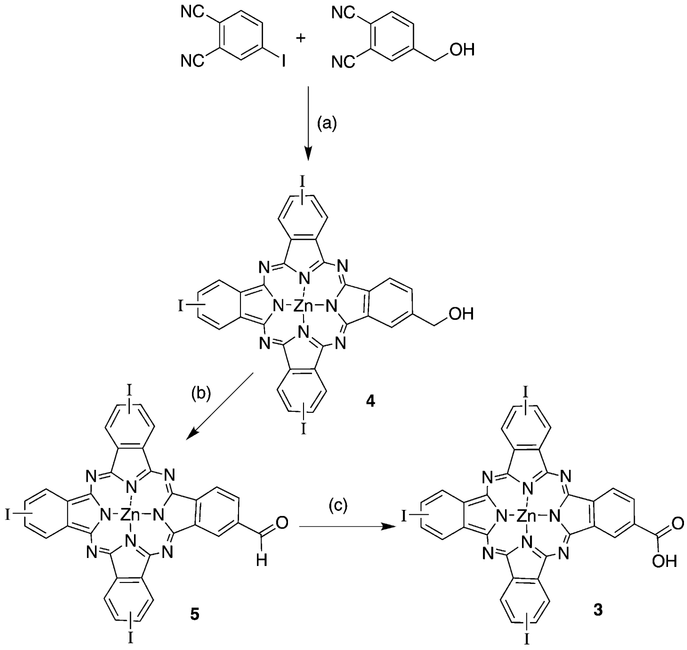
induce directionality in the excited state of Pcs. However, there are only a few reports on the influence of the peripheral substituents on the photovoltaic performance of Pc-sensitized solar cells and no rational trend has been found. For instance, substitution of the three *t*Bu substituents by six stronger electron-donating *n*-butoxy groups leads to remarkably lower overall efficiencies.[8] A decrease in the overall efficiency has also been observed in ZnPcs with hexakis (*tert*-butylphenyl) substituents.[9] On the contrary, as mentioned above, 2,6-diphenylphenoxy peripheral groups gives the most significant improvement in conversion efficiency of a ZnPc-sensitized solar cell.[7] None of these Pc sensitizers showed a strong tendency to aggregate. Therefore, 2,6-diphenylphenoxy substitution might both avoid macrocycle aggregation and block the interactions between the Pc aromatic surface and the I_3^- electrolyte and therefore reduces the dark current, as proposed by O'Regan et al.[10] Seeking to further optimize the photovoltaic properties of Pc-sensitized solar cells, we have carefully studied the structural modifications that have led to significant improvements in the overall efficiencies of porphyrin dyes, as a result of the common features of porphyrin and phthalocyanine dyes. Thus, the incorporation of electron-donating diarylamino groups, linked through a π-conjugated bisthiophene bridge to the *meso* position of the porphyrin, opposite the anchoring group, has led to enhancement of the charge-transfer directionality in the excited state, thus remarkably optimizing the device performance of this family of sensitizers.[11] This approach gives η values comparable to those of the Ru^{II} bipyridyl complexes.

Herein, we focus on the convergent synthesis of new, highly π-conjugated, "push–pull", ZnPc sensitizers (compounds **1** and **2**, Figure 1) with triarylamine-terminated bisthiophene and hexylbisthiophene units, respectively. These cells gave a panchromatic response and modest power-conversion efficiencies (close to 3 %) due to aggregation.

Results and Discussion

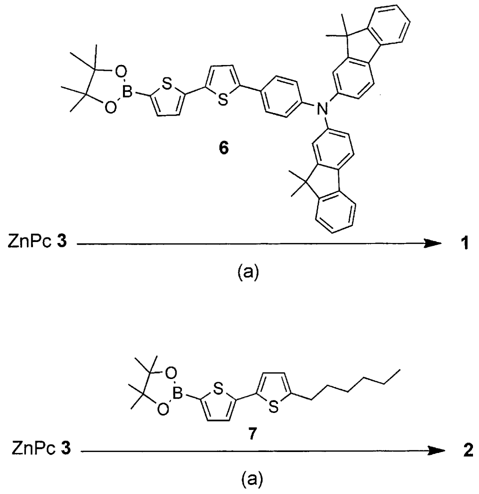
Synthesis: The most common method for the synthesis of unsymmetrically substituted phthalocyanines consists of statistical cyclotetramerization of a mixture of two phthalonitriles (A and B), for which one is used in excess (A) to increase the yield of the desired A_3B derivative.[12] This synthetic approach for the preparation of ZnPc **1**, following a complicated synthesis of phthalonitrile precursor **12** (Scheme S2 in the Supporting Information), failed to produce the desired, unsymmetrical, ZnPc **13**. The most probable reason may be the different reactivities of phthalocyanine precursors, because phthalonitriles with electron-donor substituents are significantly less reactive. Despite of the well-known advantages of mild Pd-mediated reactions that give easy preparation of many functionalized phthalonitrile precursors, this synthetic methodology have been scarcely used for Pc post-functionalization.[13] IodoPcs are ideal targets for these transformations. The low solubility of tetraiodoZnPc[14] in organic solvents has prevented the use in Pd-catalyzed coupling reactions. On the contrary, highly soluble tri(*tert*-butyl)iodoZnPc has been extensively employed by us and others as starting material in several transition-metal-mediated transformations that have led to highly π-conjugated Pcs for different applications.[12a, 13, 15]

Considering the advantages described above, we planned to apply a convergent synthetic strategy for the synthesis of compounds **1** and **2**, based on the key preparation of carboxytriiodo–ZnPc **3**, and subsequent introduction of the peripheral, π-conjugated substituents. Scheme 1 shows the synthetic route followed. The statistical cross condensation of 4-iodophthalonitrile[16] and 4-hydroxymethyl-phthalonitrile[17] yielded a mixture of two main Pc products, namely, the desired, unsymmetrically substituted, ZnPc **4** and the symmetrically substituted Zn^{II}tetraiodophthalocyanine.[14] After purification by column chromatography, ZnPc **4** was subjected to oxidation in the presence of the periodinane derivative IBX (1-hydroxy-1,2-benziodoxole-3(1 H)-one-1 oxide) in DMSO to yield the formyl-derivative ZnPc **5** in 64 % yield. By using sodium chlorite in the presence of sulfamic acid as hypochlorite scavenger, ZnPc **5** was converted to ZnPc **3** in 60 % yield. The triarylamine-terminated, bisthiophene boronic acid pinacol ester **6** was prepared by following a modification of the synthesis described by Kang and Ko[18] (Scheme S1 in the Supporting Information), whereas hexylbisthiophene boronic acid (**7**) was commercially available.



Scheme 1. a) Zn(AcO)$_2$/dimetylaminoethanol (DMAE), reflux, 20 h (23 %); b) IBX/DMSO, RT, 24 h (64 %); c) NaClO$_2$, H_3NO_3S, THF, RT, 1 h (60 %).

The final Suzuki cross-coupling reactions between ZnPc **3** and the corresponding boronates, **6** or **7**, were performed by using standard conditions (Scheme 2). ZnPcs **1** and **2** were obtained in 36% and 43% yield, respectively, after final purification by size-exclusion chromatography (Bio Beads).



Scheme 2. a) [Pd(PPh$_3$)$_4$], Na$_2$CO$_3$, 1,2-dimethoxyethane (DME), 95 °C, 24 h (**1** 36%, **2** 43%).

The structures of all new Pcs were confirmed by IR, UV/Vis, and MALDI-TOF spectroscopies. ^{1}H NMR spectra of triiodoPcs **3**–**5** in [D$_8$]THF gave well-resolved peaks between 8.5 and 9.7 ppm for the Pc aromatic macrocycle. However, the strong aggregation of ZnPcs **1** and **2** in common organic solvents, such as CHCl$_3$ and THF, caused very broad resonances, impossible to assign (Figure S7 and S9, respectively, in the Supporting Information). Elemental analyses were obtained for all new compounds with exception of **1** and **2**, which were identified by HRMS-MALDI-TOF.

The new ZnPcs **1** and **2** show an extended π-conjugation system, which produces an important redshift in the absorption maximum of about 30 nm, in comparison with that of **TT1**[6b] (Figure 2). The UV/Vis spectrum of **TT1** shows a Q-band at 679 nm, whereas compounds **1** and **2** show a maximum absorbance at 707 and 702 nm, respectively. Both Pcs, **1** and **2**, additionally present a broad absorption around 400–500 nm, which is assigned to the peripheral, π-conjugated, bisthiophene substituent. This absorption is more intense for derivative **1**. Aggregation of **1** is easily detected by optical absorption studies, which result in a broad absorption and a decrease of the extinction coefficient of the Q-band. The tail of the absorption extends to 850 nm, and **1** covers a broad range in the Vis/NIR region, in which conventional Pcs do not exhibit absorption. This behavior could infer important advantages to these new Pc dyes and could lead to increased photocurrent in photovoltaic devices.

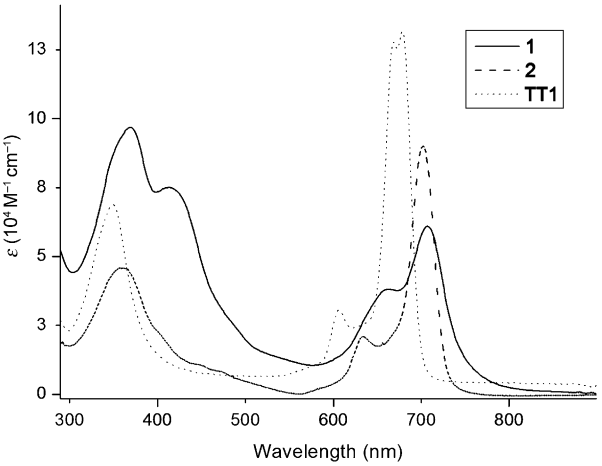


Figure 2. UV/Vis spectra in THF (1×10^{-5} M) of Pcs **1** and **2** compared to that of **TT1**.

Photovoltaic studies: Tables 1, 2, and 3 summarize the photocurrent–voltage relationship (*I*–*V*; short-circuit photocurrent density (J_{sc}), open-circuit voltages (V_{oc}), fill factors (*FF*), and conversion efficiencies (η)) of the DSSCs under various conditions. Coadsorbent molecules (i.e., chenodeoxycholic acid, CDCA) have been reported to improve the cell performance due to prevention of sensitizer aggregation.[5,6,19] Table 1 shows the photovoltaic performance of dyes **1** and **2** in DSSC devices with standard, mesoporous, double, TiO$_2$ films (6 μm thick transparent films) and a volatile acetonitrile-based electrolyte. Pcs dye solutions were prepared in THF at a concentration of 0.1 mM, without CDCA, or with 2 or 10 mM CDCA. The films were immersed into a dye solution for 5 h at room temperature. For both **1** and **2**, the J_{SC} (from 3.26 to 5.25 mA cm^{-2} for **1** and from 3.65 to 4.96 mA cm^{-2} for **2**) and the V_{OC} increased in the presence of 2 mM of CDCA compared with results from solutions without CDCA. The highest power conversion efficiencies, 2.07 and 1.98%, for **1** and **2**, respectively, were achieved with 2 mM CDCA. When the concentration of CDCA increased to 10 mM, the cells gave a lower J_{SC} value (4.17 mA cm^{-2} for **1** and 4.46 mA cm^{-2} for **2**), resulting in a decrease of the overall efficiency, even though the V_{OC} increased. The low photocurrent in high concentrations of CDCA could be a result of fewer adsorbed dye molecules, due to the competitive adsorption of CDCA. In other words, the presence of CDCA, not only prevents sensitizer

Table 1. Effect of a coadsorbent on Pc-sensitized solar cells.[a]

Dye	CDCA [mM]	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	*FF*	η [%]
1	0	3.26	503	0.68	1.11
	2	5.25	541	0.73	2.07
	10	4.17	554	0.75	1.72
2	0	3.65	525	0.71	1.36
	2	4.96	543	0.74	1.98
	10	4.46	549	0.74	1.82

[a] TiO$_2$ thickness 6 μm, dye concentration 0.1 mM, dipping time 5 h. Electrolyte: M1 = 0.6 M methyl-*N*-butylimidazolium iodide, 0.04 M iodine, 0.025 M LiI, 0.05 M guanidinium thiocyanate, and 0.28 M 4-*tert*-butylpyridine in a 15/85 (*v*/*v*) mixture of valeronitrile and acetonitrile.

aggregation, but also reduces the adsorption of sensitizers. Figure 3 shows the *I–V* curves of compound **1** and **2**.

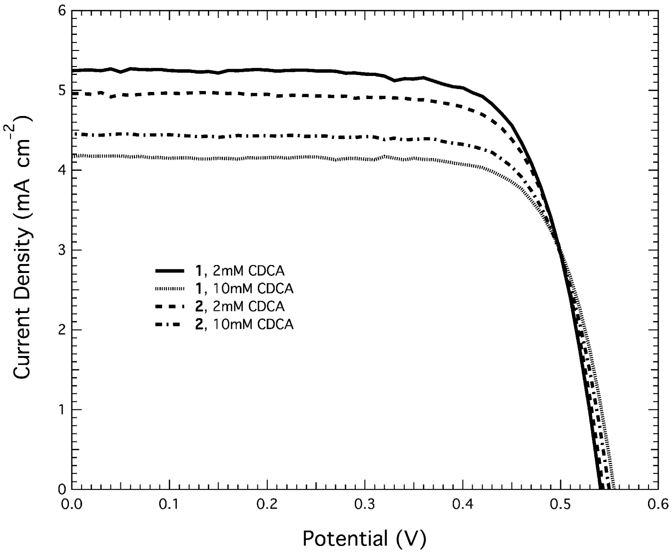


Figure 3. *I–V* characteristics of ZnPcs **1** and **2** sensitized DSSCs in the presence of CDCA.

To test the effect of the electrolyte, devices with 0.1 mM **1** or **2** and 2 mM CDCA in THF were prepared. Table 2 shows the photovoltaic performance of **1**- and **2**-sensitized solar cells in the presence of either M1 or A6986 electrolytes. The devices employing A6986 gave a higher J_{SC} (7.35 and 7.05 mA cm^{-2} for **1** and **2**, respectively), leading to a higher power-conversion efficiency (from 2.07 to 2.49 % for **1** and from 1.98 to 2.45 % for **2**), whereas the V_{OC} values were relatively low. The lower V_{OC} may be explained by the presence of more Li$^+$ cations in the case of A6986. The protonation of the titania surfaces has been reported to lower V_{OC}, because this value strongly depends on the position of the conduction-band edge of TiO_2.[20] The addition of more Li$^+$ cations in the electrolyte can provoke a positive shift of the TiO_2 conduction-band potential, because Li$^+$ cations are adsorbed on the TiO_2 surface. As a result, V_{OC} is expected to decrease. The increase in J_{SC} can also be related to the conduction-band-edge movement. The positive shift of the TiO_2 conduction band by Li$^+$ cations increases the injection efficiency from low-lying excited states of the adsorbed dye, resulting an enhanced photocurrent.[21]

Table 2. Effect of the electrolyte on Pc-sensitized solar cells.[a]

Dye	Electrolyte	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	*FF*	η [%]
1	M1	5.25	541	0.73	2.07
	A6986	7.35	483	0.70	2.49
2	M1	4.96	543	0.74	1.98
	A6986	7.05	498	0.70	2.45

[a] TiO_2 thickness 6 μm, dye concentration 0.1 mM + 2 mM CDCA, dipping time 5 h. Electrolyte M1: 0.6 M methyl-*N*-butylimidazolium iodide, 0.04 M iodine, 0.025 M LiI, 0.05 M guanidinium thiocyanate, and 0.28 M 4-*tert*-butylpyridine in a 15/85 (*v*/*v*) mixture of valeronitrile and acetonitrile. Electrolyte A6986: 0.6 M *N*-butyl *N*-butylimidazolium iodide, 0.05 M iodine, 0.1 M LiI, and 0.05 M 4-*tert*-butylpyridine in a 15:85 (*v*/*v*) mixture of valeronitrile and acetonitrile.

To push the power-conversion efficiency further, a scattering layer composed of bigger particles was incorporated on the TiO_2 nanolayer. In DSSCs, the energy-conversion efficiency depends on the morphology and structure of the dye-adsorbing TiO_2 film. The high surface area of nanocrystalline TiO_2 shows better light harvesting due to the high quantity of the adsorbed dye. However, increasing the TiO_2 film thickness would cause more recombination of photoinjected electrons. Instead of a pure nanocrystalline TiO_2 film, a bilayer structure, consisting of a light-scattering layer and a nanocrystalline semitransparent TiO_2 layer, can improve the photocurrent density due to the detention of incident light by light-scattering particles; this results in the enhancement of the overall power-conversion efficiency.[20,22] With a thickness of the bilayer of 6.8+5 (scattering) μm, the J_{SC} increased to 8.32 mA cm^{-2} for **1** and 8.34 mA cm^{-2} for **2**. The power-conversion efficiencies of the **1**- and **2**-sensitized cells are improved to 2.65 and 2.70 %, respectively. The *I–V* curves and the incident photon-to-current efficiency (IPCE) spectra of **1** and **2** are represented in Figure 4 and the data are collected in Table 3. The IPCEs show considerable, high-energy, photon-absorption contributions; this is in agreement with the absorption spectra in solution.

Table 3. Effect of a scattering layer on Pc-sensitized solar cells.[a]

Dye	CDCA [mM]	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	*FF*	η [%]
1	2	8.32	471	0.69	2.65
	10	8.18	490	0.71	2.85
2	2	8.34	466	0.69	2.70
	10	7.05	487	0.72	2.47

[a] TiO2 thickness 6.8+5 μm, dye concentration 0.1 mm, dipping time 15 h, electrolyte A6986.

Conclusion

A key compound, carboxytriiodo–ZnPc has been synthesized and used in a convergent strategy for preparing highly conjugated, panchromatic sensitizers **1** and **2**. This synthetic approach might represent a general method to prepare other carboxy–ZnPc dyes with elaborated, π-conjugated, peripheral substituents. When tested as dyes in DSSCs, **1** and **2** gave power-conversion efficiencies close to 3 %. The panchromatic response of these dyes is because of the complementary absorption in the visible region caused by the peripheral, π-conjugated, bisthiophene substituents and the ZnPc NIR absorption. However, aggregation phenomena may explain the moderate overall efficiencies achieved. We are currently investigating the preparation of other substi-

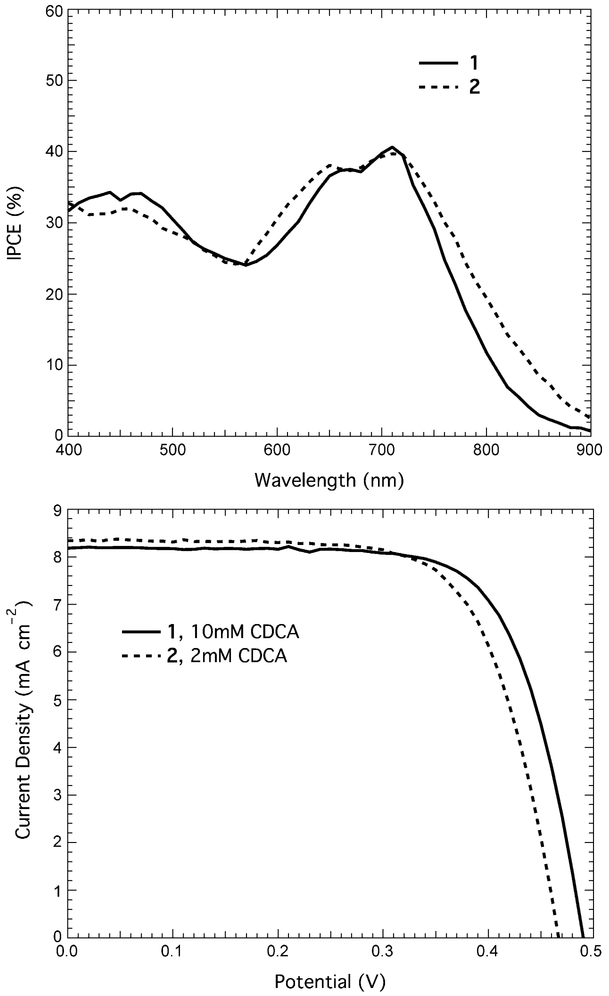


Figure 4. IPCE spectrum and *I–V* curves for devices of **1**- and **2**-sensitized solar cells. The cells were the same as those in Table 3.

tuted carboxy–ZnPc dyes by this method, in which aggregation phenomena are suppressed.

Experimental Section

2-Hydroxymethyl-9(10),16(17),23(24)-triiodophthalocyaninato zinc(II) (mixture of regioisomers) (4): A mixture of 4-iodophthalonitrile[16] (525 mg, 2.07 mmol), 4-(hydroxymethyl)phthalonitrile[17] (64 mg, 0.41 mmol), and $Zn(OAc)_2$ (121 mg, 0.66 mmol) in DMAE (6 mL) was heated at reflux and stirred for 20 h in an argon atmosphere. After cooling to room temperature, the solvent was removed and the residue was washed with a $MeOH/H_2O$ (5:1, *v*/*v*) mixture. The crude product was purified by column chromatography on silica gel. A toluene/THF (10:1, *v*/*v*) eluent removed most of the symmetric tetraiodo Pc,[14] and a second column in hexane/dioxane (3:2, *v*/*v*) was necessary to completely purify Pc **4**. Yield: 93 mg, 23 %. ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C, TMS): δ = 9.46–9.33 (m, 3H), 9.18–8.98 (m, 2H), 8.95–8.67 (m, 3H), 8.66–8.39 (m, 3H), 8.36–8.17 (m, 1H), 5.46 (s, 2H), 5.1–4.90 ppm (br, 1H); IR (KBr): $\tilde{\nu}$ = 3503, 2957, 2922, 2401, 1603, 1589, 1381, 1304, 1264, 1140, 1097, 1057, 901, 816, 741 cm^{-1}; UV/Vis (THF): λ_{max} (log ε) = 673 (5.08), 608 (sh) (4.37), 357 nm (4.69); MS (MALDI, dithranol): *m*/*z*: 983.8 [*M*]$^+$; HRMS (MALDI-TOF, dithranol): *m*/*z*: calcd for $C_{33}H_{15}I_3N_8OZn$ [*M*]$^+$: 983.7794; found: 983.7823; elemental analysis calcd (%) for $C_{33}H_{15}I_3N_8OZn$: C 40.21, H 1.53, N 11.37; found: C, 40.38, H 1.67, N 11.16.

2-Formyl-9(10),16(17),23(24)-triiodophthalocyaninato zinc(II) (mixture of regioisomers) (5): A solution of IBX (128 mg, 0.45 mmol) in DMSO (5 mL) was added to a stirred solution of Pc **4** (90 mg, 0.09 mmol) in THF (2 mL) in an argon atmosphere. The mixture was stirred at room temperature for 24 h. The reaction was monitored by TLC (toluene/THF, 10:1 *v*/*v*) until all the starting Pc had reacted. Brine was then added and the mixture was extracted with THF. The combined organic layers were dried over $MgSO_4$ and evaporated in vacuo. The solid residue was purified by column chromatography on silica gel (toluene/THF, 10:1 *v*/*v*) to give 57 mg (64 %) of **5**. ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C, TMS): δ = 10.85 (s, 1H, CHO), 9.67–9.31 (m, 4H), 9.30–9.05 (m, 1H), 8.94–8.68 (m, 4H), 8.67–8.44 ppm (m, 3H); IR (KBr): $\tilde{\nu}$ = 2954, 2923, 2854, 1691, 1594, 1484, 1456, 1431, 1378, 1304, 1139, 1091, 1053, 1033, 894, 755 cm^{-1}; UV/Vis (THF): λ_{max} (log ε) = 673 (5.19), 653 (sh) (4.48), 608 (sh) (4.46), 354 nm (4.76); MS (MALDI, dithranol): *m*/*z*: 981.8 [*M*]$^+$; HRMS (MALDI-TOF, dithranol): *m*/*z*: calcd for $C_{33}H_{13}I_3N_8OZn$ [*M*]$^+$: 981.7638; found: 981.7603; elemental analysis calcd (%) for $C_{33}H_{13}I_3N_8OZn$: C 40.30, H 1.33, N 11.39; found: C 40.52, H 1.62, N 11.08.

2-Carboxy-9(10),16(17),23(24)-triiodophthalocyaninato zinc(II) (mixture of regioisomers) (3): A solution of H_3NO_3S (9.7 mg, 0.1 mmol) in H_2O (1 mL) was added to a solution of phthalocyanine **5** (25 mg, 0.025 mmol) in THF (3 mL), at 0 °C. A solution of $NaClO_2$ (4.6 mg, 0.050 mmol) in H_2O (1 mL) was added dropwise while the temperature was kept at 0 °C. After the addition was complete, the mixture was further stirred for a 1 h at room temperature. Brine was then added and the mixture was extracted with THF. The combined organic layers were dried over $MgSO_4$ and evaporated in vacuo. The solid residue was purified by short column chromatography on silica gel (THF) to give 15 mg (60 %) of **3**. ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C, TMS): δ = 9.93–9.68 (m, 1H), 9.58–9.30 (m, 3H), 9.27–9.08 (m, 1H), 9.02–8.70 (m, 4H), 8.63–8.43 ppm (m, 3H); IR (KBr): $\tilde{\nu}$ = 3437, 2953, 2922, 2857, 1687, 1612, 1454, 1383, 1305, 1264, 1140, 1096, 1045, 923, 887, 812, 747 cm^{-1}; UV/Vis (THF): λ_{max} (log ε) = 675 (4.97), 641 (sh) (4.48), 611 (sh) (4.41), 349 nm (4.70); MS (MALDI, dithranol): *m*/*z*: 997.8 [*M*]$^+$; HRMS (MALDI-TOF, dithranol): *m*/*z*: calcd for $C_{33}H_{13}I_3N_8O_2Zn$ [*M*]$^+$: 997.7587; found: 997.7589; elemental analysis calcd (%) for $C_{33}H_{13}I_3N_8O_2Zn$: C 39.65, H 1.31, N 11.21; found: C 39.99, H 1.60, N 11.02.

2-Carboxy-9(10),16(17),23(24)-tris-[2-(*N*,*N*-bis-(9,9-dimethylfluoren-2-yl)-4-aminophenyl)-5,5′-bithiophene]phthalocyaninato zinc(II) (mixture of regioisomers) (1): A suspension of ZnPc **3** (33 mg, 0.033 mmol), bisthiopheneboronic acid pinacol ester **4** (102 mg, 0.13 mmol), $[Pd(PPh_3)_4]$ (3.5 mg, 0.003 mmol), and a solution of Na_2CO_3 (34 mg, 0.33 mmol) in H_2O (1 mL) in DME (5 mL) was stirred at 95 °C in an argon atmosphere for 24 h. The suspension was then cooled to room temperature and poured into a 1 M NH_4Cl solution (50 mL). The mixture was extracted with ethyl acetate (2 × 50 mL) and the combined organic extracts were washed with brine (10 mL), dried over $MgSO_4$ and evaporated in vacuo. The crude product was purified by preparative size-exclusion chromatography (Biobeads SX-1 in THF) to yield 30 mg (36 %) of a dark-green solid. ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C, TMS): δ = 10.41–6.32 (m, 78H, ArH), 1.82–0.92 ppm (m, 36H, alkylH); IR (KBr): $\tilde{\nu}$ = 3435, 2957, 2920, 2860, 1724, 1604, 1535, 1488, 1452, 1390, 1308, 1183, 1141, 1055, 822, 789 cm^{-1}; UV/Vis (THF): λ_{max} (log ε) = 707 (4.78), 662 (4.58), 413 (4.87), 369 nm (4.98); MS (MALDI, DCTB): *m*/*z*: 2537.7 [*M*]$^+$; HRMS (MALDI, DCTB): *m*/*z*: calcd for $C_{165}H_{115}N_{11}O_2S_6Zn$ [*M*]$^+$: 2537.685; found: 2537.695.

2-Carboxy-9(10),16(17),23(24)-tris[5′-hexyl-2,2′-bithiophene]phthalocyaninato zinc(II) (mixture of regioisomers) (2): ZnPc **2** was prepared as compound **1**, by using ZnPc **3** (20 mg, 0.02 mmol), 5′-hexyl-2,2′-bithiophene-5-boronic acid pinacol ester (**7**) (22.5 mg, 0.06 mmol), [Pd(PPh3)4] (2.3 mg, 0.002 mmol), and Na_2CO_3 (1 mL of a 1 M aqueous solution). The crude product was purified by preparative size-exclusion chromatography (Biobeads SX-1 in THF) to yield 12 mg (43 %) of a green solid. ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C, TMS): δ = 10.34–6.36 (several m, 24H, ArH), 1.82–0.92 ppm (m, 39H, alkyl); IR (KBr): $\tilde{\nu}$ = 3432, 2954, 2923, 2853, 1656, 1608, 1491, 1455, 1380, 1337, 1285, 1261, 1144, 1096, 1049, 1026, 885, 793 cm^{-1}; UV/Vis (THF): λ_{max} (log ε) = 702 (4.9), 634 (4.3), 361 (4.6); MS (MALDI, dithranol): *m/z*: 1364.3 $[M]^+$; HRMS (MALDI-TOF, dithranol): *m/z*: calcd for $C_{75}H_{64}N_8O_2S_6Zn$ $[M]^+$: 1364.277; found: 1364.271.

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