

Introducing rigid π -conjugated peripheral substituents in phthalocyanines for DSSCs

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Dedicated to Professor Tomás Torres on the occasion of his 65th birthday

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> **ABSTRACT:** A new carboxy-Zn(II)phthalocyanine bearing rigid 2,6-diarylphenyl peripheral substituents linked to the macrocycle through alkynyl spacers has been prepared by a convergent approach, which implies a triple Sonogashira coupling between the formyltriiodoZnPc and the corresponding terminal alkyne. Indeed, the introduction of this type of π -conjugated peripheral substituents accounts for a remarkable red shift of the phthalocyanine Q-band until *ca*. 700 nm. However, aggregation phenomena could not be supressed and may explain the moderate overall efficiencies achieved with these devices.

KEYWORDS: phthalocyanines, solar cells, π -conjugated systems, near IR dyes

INTRODUCTION

During the last years, a number of unsymmetrically substituted phthalocyanines (A₃B type) have emerged as efficient red absorbing molecules for Dye Sensitized Solar Cells (DSSCs), reaching power conversion efficiencies (PCE) of up to 6% [1] when used as a single sensitizer. Commun structural requirements, such as incorporation of peripheral bulky donor substituents (typically *tert*-butyl and 2,6-diphenylphenoxy substituents), have resulted crucial in order to both minimize aggregation of the dye on the TiO₂ surface and achieve a directional excited state to facilitate efficient injection of electrons onto the

and the macrocycle. Moreover, **TT40** leads to a slightly higher efficiency than that for **TT58** [2b] with the COOH group directly linked to the macrocycle. Our work consists of exploring new bulky peripheral substituents to further improve the possibilities of phthalocyanines as sensitizers for DSSCs. Taking all the above requirements into consideration, we have designed a new unsymmetrical A₃B-type carboxy-ZnPc for

a new unsymmetrical A₃B-type carboxy-ZnPc for DSSCs, **TT65**, in which the bulky and rigid peripheral substituents are linked to the macrocycle through a π -conjugated bridge (Chart 1). As mentioned earlier,

semiconductor. Not only the presence of bulky groups is

paramount for obtaining good efficiencies in ZnPc-based

DSSCs, but also the anchoring group that should be close

and π -conjugated to the macrocycle ZnPc core. The results

shown in Table 1 point to the effectiveness of the alkynyl

bridge as a connecting group. Thus, TT40 [2] largely

outperforms the efficiency of PcS6 [3] which presents a

phenylene bridge betweeen the anchoring carboxy group

⁶ SPP full and ⁶⁰ student member in good standing

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Table 1. Efficiency values of **TT40**, **TT58** and **PcS6** under 1 sun irradiation (100 mW.cm⁻²)



Chart 1. ZnPc TT65

alkynyl bridges are considered the most efficient groups to electronically connect the Pc core and the anchoring COOH group, but they have never been used as units to link the bulky peripheral groups and the ZnPc core. Using this new approach we sought both being able to avoid dye aggregation by the introduction of bulky and rigid donor substituents at the periphery of the macrocycle, and to take advantage of the red-shift induced in the absorption properties of the new Pc dye because of the extended π -conjugated system.

RESULTS AND DISCUSSION

Synthesis

In view of our previous experience on the functionalization of iodoZnPcs by Pd-mediated reactions [4,6], we planned the preparation of target TT65 by a convergent synthetic strategy which implies the macrocyclization of two phthalonitriles, one bearing a precursor of the anchoring group, and the other bearing the iodo-substitution which will suffer the subsequent functionalization. Thus, a 4:1 molar ratio mixture of 4-iodophthalonitrile (1) and 4-hydroxymethylphthalonitrile (2) was reacted at reflux in DMAE in the presence of $Zn(OAc)_2$. The desired A₃B ZnPc 3 was obtained in 24% yield after isolation by column chromatography (Scheme 1). ZnPc 3 was then oxidized under mild conditions with periodinane derivative IBX in DMSO to yield the formyl derivative ZnPc 4 in 90% yield (Scheme 1). Given the good solubility of 4 in organic solvents, the subsequent triple Sonogashira coupling was performed on this compound, employing the arylethynyl 8 and standard conditions, giving rise to a regioisomeric mixture of β -triarylalkynyl-substituted ZnPc **9** in 70% yield (Scheme 1) which has three pretty bulky aromatic groups linked to the macrocycle via sp carbon-aromatic sp² carbon bonds. By using sodium hypochlorite in the presence of sulfamic acid, ZnPc 9 was converted to ZnPc **TT65** in 90% yield (Scheme 1) after a final purification by gel permeation chromatography (GPC).

The synthesis of the bulky substituents was addressed by reacting the comercially available 2,6-dibromo-4methylaniline in a Sandmeyer reaction to obtain product 5 in 61% yield. Thus, the aromatic amino group was displaced with iodide anion via preparation of its diazonium salt catalized by copper(I) salts. Derivative 5 was subjected to a Sonogashira coupling reaction with a propargyl alcohol giving rise to compound 6 in 64% yield. This reaction resulted highly selective and none competitive reaction of the bromine atoms was detected. Afterthat, the double Suzuki-Miyaura cross-coupling reaction was performed on derivative 6, employing 4-biphenylboronic acid and standard conditions, giving rise to the bulky derivative 7 in 65% yield, which was subjected to a elimination reaction in the presence of NaOH to obtain the ethynylarene 8 in 71% yield (Scheme 2).

The structures of all new compounds were confirmed by mass spectrometry and IR, UV-vis, and NMR spectroscopies (see the Supporting information). The ¹H NMR spectrum in d₈-THF of final carboxyZnPc **TT65** showed



Scheme 1. Convergent synthesis of β -triarylalkynyl-substituted ZnPc 9 by triple Sonogashira coupling reaction on triiodo ZnPc 4 and final oxidation to obtain the target TT65



Scheme 2. Synthesis of the bulky peripheral substituents

bad resolution due to both mixture of regioisomers and strong aggregation due to π - π stacking induced by the peripheral large aromatic substituents.

Optical and electrochemical properties

The normalized UV-vis absorption spectra for **3**, **4**, **9** and **TT65** in THF are shown in Fig. 1. Molecules **9** and **TT65** show nearly superimposable spectra with a maximum absorbance in the near-infrared region at 696 nm. Moreover, an overall 23 nm red-shift was achieved in the Q-band of the Pcs due to the peripheral incorporation of π -conjugated groups. The electrochemical measurements were performed at room temperature in CH₂Cl₂ containing [TBA]PF₆ (0.1 M) as supporting electrolyte and using Ag/AgCl electrode as internal reference. The results of Table 2 allowed us to determine the HOMO–LUMO levels energy of **TT65**. Thus, the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are related to the ground-state redox



Fig. 1. UV-visible spectra of 3, 4, 9 and TT65 in THF (5 \times 10 M⁻¹)

potentials ($E_{HOMO} = E_{ox1} vs.$ NHE; $E_{LUMO} = E_{red1} vs.$ NHE). Potentials measured vs. Fc/Fc+ (Table 2) were converted to normal hydrogen electrode (NHE) by addition of +0.64 V [7]. Therefore, $E_{HOMO} = 0.901$ V and $E_{LUMO} =$



Fig. 2. J–V curves for DSSC based on TT65/CDCA at several light intensities

Table 2. Electrochemical data of **TT65** determined bySquare-Wave Voltammetry (SWV)

E _{red1} ^a , V	E_{ox1}^{a} , V	E ₀₋₀ ^b , nm (eV)	E_{0-0}^{*c} , V
-1.511	0.261	701 (1.769)	-1.508

^aPotentials are reported *vs.* the ferrocene/ferrocenium (Fc/ Fc⁺) couple as external reference. ^bThe zero-zero excitation energy (E_{0-0}) is obtained from the intersection between the normalized absorption and emission spectra. Converted to eV according to the relation E_{0-0} (eV) = 1240/ E_{0-0} (nm). ^cThe excited-state oxidation potential (E_{0-0}^{*}) reported *vs.* Fc/Fc⁺ is calculated from $E_{0-0}^{*} = E_{ox1}^{-} E_{0-0}$.

-0.871 V, being the latter more negative than the TiO_2 conduction band (*ca.* -0.5 V vs. NHE), consequently making the electron injection from the excited state of **TT65** into the TiO_2 termodinamically feasible.

Dye-sensitized solar cells

Table 3 shows the short-circuit photocurrent density (J_{sc}) , open-circuit photovoltage (V_{oc}) , fill factor (FF) and PCE obtained under 1 sun irradiation for TT65 devices, either prepared with the coadsorption of chenodeoxycholic acid (CDCA) or without any co-adsorbent. The latter exhibits a J_{sc} of 4.2 mA.cm⁻², a V_{oc} of 508 mV, a FF of 0.72, yielding a PCE of 1.5%. The coadsorption of CDCA can hinder the formation of dye aggregates and improve electron injection yield, and thus J_{sc}. Therefore, the photovoltaic performance of TT65 in the presence of CDCA increases in comparison with the absence of it. In such a way, in the presence of 0.05 mM of CDCA, the cell exhibits a J_{sc} of 4.4 mA.cm⁻², a V_{oc} of 500 mV, a FF of 0.73, yielding a PCE of 1.6%. Moreover, the maximum PCE value of 1.7% was achieved in the presence of 0.10 mM of CDCA into the dye solution, besides exhibiting a J_{sc} of 4.8 mA.cm⁻², a V_{oc} of 491 mV and a FF of 0.72. Figure 2 shows the photocurrent density-voltage (J-V) curves at several light intensities of DSSCs based on TT65 and 10 mM CDCA .The IPCE for this cell, plotted in Fig. 3 as a function of excitation wavelength, reaches 30% at the maximum absorption of the Q-band (700 nm), and shows a remarkable broadening due to the aggregates formation on TiO₂ surface. When adding more co-adsorbent into the dye solution, i.e. 0.15 mM of CDCA, the efficiency value of the device does not increase anymore owing to the loss of dye loaded. Thus, the cell exhibits a J_{sc} of 4.2 mA.cm⁻², a V_{oc} of 514 mV and a FF of 0.74, yielding a PCE of 1.6%.

EXPERIMENTAL

General

Chemicals employed were purchased from Aldrich Chemical Co. and used without further purification. Dry solvents were obtained from a Solvent Drying System (SPS). The monitoring of the reactions was carried out by TLC employing aluminum sheets coated with silica gel $60 F_{254}$ purchased from Merck. Purification of compounds

Table 3. Photovoltaic performance of DSSCs^a based on TT65, with and without co-adsorbent, under 1 sun irradiation (100 mW.cm⁻²)

CDCA, mM	V _{oc} , mV	J _{sc} , mA.cm ⁻²	FF	РСЕ ^ь , %	PCE ^c , %
	508	4.2	0.72	1.5	1.3 ± 0.2
0.05	500	4.4	0.73	1.6	1.6 ± 0.0
0.10	491	4.8	0.72	1.7	1.6 ± 0.1
0.15	514	4.2	0.74	1.6	1.5 ± 0.1

^aTwo devices were made for each configuration. ^bEfficiency values of the best cells are presented. ^cAverage efficiency values of the devices presented with the standard deviation.



Fig. 3. IPCE spectrum for DSSC based on TT65/CDCA

was performed by column chromatography using silica gel Merck-60 (40–63 μ m) and Bio-Beads S-X1 Support from Bio-Rad (200–400 mesh) for gel permeation chromatography (GPC). Solvents were purchased from Carlo Erba Reagents and Scharlab in a synthesis grade.

NMR spectra were recorded by using Bruker AV-300 or Bruker DRX-500 spectrometers. Deuterated solvent employed is indicated in brackets for each case. UV-vis spectra were recorded in solution using solvents in spectroscopic grade on a Jasco V-660 spectrophotometer. The logarithm of the absorption coefficient (ε) is indicated in brackets for each maximum. Mass Spectrometry (Electron Impact and Matrix-Assisted Laser Desorption Ionization Time-Of-Flight) as well as HR-MS were performed in a VG-AutoSpec and Bruker-ULTRAFLEX-III apparatus respectively, the latter with a Nd:YAG laser operating at 355 nm. DCTB, and PEGNa 2000 poly(ethylenglycol)-2000 were used as matrix and internal reference, respectively.

Synthesis

Phthalocyanines **3** and **4** were prepared according to procedures reported by us [4]. 2,6-Dibromo-4-methylio-dobenzene **5** was used after its preparation following the literature [5].

Preparation of 4-(2,6-Dibromo-4-methylphenyl)-2methylbut-3-yn-2-ol (6). Compound **5** (0.61 g, 1.6 mmol), PdCl₂(PPh₃)₂ (0.0112 g, 1 mol%) and CuI (0.0015 g, 0.5 mol%) were dissolved in a mixture of dry THF and distilled NEt₃ (2:1, 6 mL). The mixture was degassed and fluxed with argon for 10 min. Then the 2-methylbut-3-yn-2-ol (0.19 mL, 1.9 mmol) was added dropwise. The reaction mixture was heated at 50 °C for 20 h. The solvent was eliminated under reduced pressure and the solid dissolved in CH₂Cl₂. The organic phase was washed with brine and dried over anhydrous MgSO₄. After filtration, the solvent was removed under vacuum. The solid was purified by column chromatography on silica gel (eluent: hexane/THF 10:1). A light yellow solid was obtained. Yield 0.34 g (64%), mp 123 °C. ¹H NMR (300 MHz, CDCl₃): δ , ppm 7.35 (s, 2H), 2.30 (s, 3H), 2.20 (s, 1H), 1.66 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): δ , ppm 141.0, 132.3, 126.3, 123.9, 102.5, 80.7, 66.2, 31.5, 21.1. IR (KBr): v, cm⁻¹ 3242, 2981, 2923, 1733, 1594, 1530, 1455, 1381, 1360, 1275, 1192, 1166, 1143, 1062, 1035, 1007, 965, 916, 883, 849, 788, 742, 712, 623, 586, 570. HR-MS (EI): *m/z* 329.9262 [M]⁺, calcd. for C₁₂H₁₂Br₂O: 329.9255.

5

Preparation of 4-(2,6-bis-(4-biphenyl)-4-methylphenyl)-2-methylbut-3-yn-2-ol (7). A Na₂CO₃ 1 M solution (1 mL) was added to a mixture of compound 6 (0.34 g, 1.0 mmol), Pd(PPh₃)₄ (0.12 g, 0.1 mmol) and 4-biphenylboronic acid (0.55 g, 2.8 mmol) in DME (5 mL). The mixture was degassed and fluxed with argon for 10 min. The reaction mixture was heated at 80°C for 20 h. The crude was poured onto an NH₄Cl 1 M solution (100 mL), and extracted with ethyl acetate (3 \times 30 mL). The organic phases were collected and washed with brine and dried over anhydrous MgSO₄. After filtration, the solvent was removed under vacuum. The solid was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate 5:1) and recrystallized from methanol. A white solid was obtained. Yield 0.32 g (65%). ¹H NMR (300 MHz, CDCl₃): δ, ppm 7.69 (m, 12H), 7.43 (m, 8H), 2.47 (s, 3H), 1.31 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): δ, ppm 144.9, 141.2, 140.5, 140.4, 138.6, 130.2, 129.6, 129.1, 127.6, 127.4, 126.7, 117.1, 100.0, 81.7, 65.8, 31.2, 21.8. IR (KBr): v, cm⁻¹ 3575, 3442, 3060, 3031, 2972, 2924, 2864, 2854, 2366, 2340, 1954, 1929, 1636, 1598, 1561, 1521, 1487, 1452, 1398, 1383, 1359, 1314, 1264, 1158, 1107, 1076, 1036, 1006, 952, 918, 876, 846, 759, 729, 692, 633, 608, 581. HR-MS (EI): *m/z* 478.2280 [M]⁺, calcd. for C₃₆H₃₀O: 478.2297.

Preparation of 1,3-bis-(4-biphenyl)-2-ethynyl-5methylbenzene (8). Compound 7 (0.32 g, 0.67 mmol) and powdered NaOH (0.029 g, 0.74 mmol) were dissolved in dry toluene (19 mL) under argon atmosphere. The reaction mixture was heated to reflux for 20 h. The solvent was eliminated under reduced pressure and the solid dissolved in CH_2Cl_2 . The organic phase was washed with brine and dried over anhydrous MgSO₄. After filtration, the solvent was removed under vacuum and the solid recrystallized from isopropanol. A white solid was obtained. Yield 0.20 g (71%). mp 184 °C. ¹H NMR (300 MHz, CDCl₃): δ, ppm 7.71 (m, 12H), 7.43 (m, 8H), 2.99 (s, 1H), 2.47 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ, ppm 145.6, 141.0, 140.3, 140.0, 138.8, 130.1, 129.7, 128.9, 127.4, 127.3, 126.7, 116.2, 83.8, 82.3, 21.6. IR (KBr): v, cm⁻¹ 3313, 3290, 3278, 3051, 3031, 2914, 2852, 2098, 1922, 1598, 1581, 1561, 1519, 1487, 1451, 1395, 1159, 1114, 1077, 1039, 1006, 914, 873, 841, 775, 759, 732, 695, 651, 624, 608. HR-MS (EI): m/z 420.1894 [M]+, calcd. for C₃₃H₂₄: 420.1878.

Preparation of β -triarylalkynyl-substituted formylphthalocyanine (9) (mixture of regioisomers). Phthalocyanine 4 (0.074 g, 0.075 mmol), terminal alkyne 8 (0.12 g, 0.28 mmol), PdCl₂(PPh₃)₂ (0.0053 g, 10 mol%) and CuI (0.0014 g, 10 mol%) were dissolved in a mixture of dry THF and distilled NEt₃ (8:1, 15 mL). The mixture was degassed and fluxed with argon for 10 min. The reaction mixture was heated at 35 °C for 20 h. The solvent was eliminated under reduced pressure and the solid dissolved in CHCl₃. The organic phase was washed with brine and dried over anhydrous MgSO₄. After filtration, the solvent was removed under vacuum. The solid was purified by gel permeation chromatography (eluent: THF). A dark green solid was obtained. Yield 0.098 g (70%), mp > $250 \,^{\circ}$ C. ¹H NMR (500 MHz, THF- d_8): δ , ppm 10.39–10.04 (m, 1H), 9.10-8.61 (br m, 8H), 8.06-7.32 (br m, 64H), 2.58-2.45 (br m, 9H). UV-vis (THF): λ_{max} , nm (log ϵ) 696 (4.25), 626 (3.56), 359 (3.83), 284 (4.15). IR (KBr): v, cm⁻¹ 3055, 3029, 2958, 2922, 2852, 2597, 2554, 2201, 1912, 1695, 1608, 1486, 1447, 1391, 1363, 1339, 1311, 1276, 1250, 1200, 1159, 1141, 1088, 1047, 1006, 934, 897, 870, 837, 757, 745, 730, 697, 671. HR-MS (MALDI-TOF, DCTB+PEGNa 2000): m/z 1858.5937 [M]⁺, calcd. for C₁₃₂H₈₂N₈OZn: 1858.5898.

Preparation of β -triarylalkynyl-substituted carboxyphthalocyanine (TT65) (mixture of regioisomers). Phthalocyanine 9 (0.071 g, 0.038 mmol) was dissolved in dry THF (7 mL). An aqueous solution of sulfamic acid (0.15 mmol in 1 mL of miliQ water) was added. The reaction was cooled down to 0°C and an aqueous solution of NaClO₂ (0.095 mmol in 0.5 mL of miliQ water) was added dropwise. The reaction was stirred at 0°C for half an hour, and then at room temperature for two and a half hours. Then, it was poured over HCl 1 M (50 mL). The solution was extracted with ethyl acetate $(3 \times 25 \text{ mL})$, the organic phases washed with brine and dried over anhydrous MgSO₄. After filtration, the solvent was removed under reduced pressure. The solid was purified by gel permeation chromatography (eluent: THF). A dark green solid was obtained. Yield 0.064 g (90%), mp > 250 °C. ¹H NMR (500 MHz, THF-d₈): δ , ppm 10.18-9.83 (m, 1H), 9.16-8.59 (br m, 8H), 8.04-7.28 (br m, 64H), 2.58–2.48 (br m, 9H). UV-vis (THF): λ_{max} , nm (log ε) 696 (4.35), 625 (3.55), 346 (3.85), 284 (4.20). IR (KBr): v, cm⁻¹ 3634, 3423, 3058, 3028, 2957, 2919, 2851, 2205, 1721, 1690, 1669, 1644, 1600, 1485, 1460, 1434, 1391, 1363, 1338, 1308, 1246, 1234, 1142, 1092, 1047, 1008, 935, 881, 838, 771, 757, 744, 698, 577. HR-MS (MALDI-TOF, DCTB+PEGNa 2000): m/z 1874.5849 $[M]^+$, calcd. for $C_{132}H_{82}N_8O_2Zn$: 1874.5847.

Dye-sensitized solar cells

The TiO₂ film composed of *ca.* 8 μ m (transparent layer) and *ca.* 4 μ m (scattering layer) was prepared by screen-printing and treated with a 0.04 M titanium tetrachloride solution for 30 min at 70 °C. The film was heated to 500 °C in air for 30 min before use. Dye solutions were prepared in a concentration of 0.05 mM in a 4/1 (v/v) mixture of ethanol and THF containing

chenodeoxycholic acid (CDCA) as co-adsorbent when indicating. The electrodes were dipped into the dye solutions for 5 h at room temperature. The dye-coated electrodes were rinsed quickly with ethanol to remove the loosely bounded dye molecules and used as such for photovoltaic measurements. The electrolyte was composed of 0.86 M 1,3-dimethylimidazolium iodide, 0.4 M LiI, 0.04 M I₂, 0.29 M 4-*tert*-butylpyridine and 0.05 M guanidine thiocyanate in acetonitrile. The dyeadsorbed TiO₂ electrode and thermally platinized counter electrode were assembled into a sealed sandwich-type cell with a gap of a hot-melt ionomer film (25 μ m) (SurlynTM, DuPont, USA).

For photovoltaic measurements of the DSSCs, the irradiation source was a 450 W xenon light source (Oriel, USA) equipped with a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) to match the emission spectra to the AM1.5G standard in the region of 350–750 nm. The current–voltage characteristics of the devices were obtained by applying external potential bias to the cell while recording the generated photocurrent using a Keithley (Model 2400) digital source meter (Keithley, USA). The J-V curves of all devices were measured by fixing the active area with a metal mask of 0.16 cm². The measurement of incident photon-to-current conversion efficiency (IPCE) was plotted as a function of excitation wavelength by using the incident light from a 300 W xenon lamp (ILC Technology, USA), which was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd., U.K.).

CONCLUSION

We have prepared a new family of carboxy-phthalocyanines for DSSCs showing a strong absorption at *ca*. 700 nm by linking rigid and π -conjugated peripheral aryl substituents to the macrocycle through alkynyl spacers. Aggregation phenomena may explain the moderate overall efficiencies achieved with these devices, as in previously reported Pc-sensitized solars cells incorporating three peripheral bisthiophene substituents [4]. We are currently exploring new molecular designs wherein aggregation through the peripheral substituents is suppressed.

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Supporting information

Figures S1–S8 are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

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7

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