Photoinduced Electron Transfer in a New Bis(C₆₀)-Phthalocyanine Triad

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Experimental procedures and spectral characterization:

General and Materials. Melting points were determined on a Büchi 504392(S) apparatus and are uncorrected. Infrared spectra were recorded on a Bruker Vector 22 spectrophotometer. The ^1H NMR spectra were obtained on a Bruker AC-300 (300 MHz) and Bruker DRX-500 (500 MHz), and the ^{13}C NMR spectra were obtained on a Bruker AC-300 (75 MHz) spectrometers. UV-Vis spectra were recorded on a Hewlett-Packard 8453 spectrophotometer. The mass spectra (LSIMS) were determined on a VG AutoSpec spectrometer. The MALDI-TOF-MS spectra were determined on a Bruker Reflex III spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400 CHN equipment.

Picosecond laser flash photolysis experiments were carried out with 532-nm laser pulses from a mode-mode-locked, Q-switched Quantel YG-501 DP Nd:YAG laser system (18 ps pulse width, 2-3 mJ / pulse). Nanosecond Laser Flash Photolysis experiments were performed with laser pulses from a Quanta-Ray CDR Nd:YAG system (532 nm, 6 ns pulse width) in a front face excitation geometry.

Fluorescence lifetimes were measured with a Laser Strobe Fluorescence Lifetime Spectrometer (Photon Technology International) with 337 nm laser pulses from a nitrogen laser fiber-coupled to a lens-based T-formal sample compartment equipped with a stroboscopic detector. Details of the Laser Strobe systems are described on the manufactures web site, <http://www.pti-nj.com>.

Emission spectra were recorded with a SLM 8100 Spectrofluorometer. The experiments were performed at room temperature. Each spectrum was an average of at least 5 individual scans and the appropriate corrections were applied whenever necessary.

Tri-tert-butyl-[4-(2''-ethylhexyloxy)-2,5-bis{3'-hexyl-3',4'-fulleropyrrolidine}]phenoxyphthalocyaninatoZn(II) (I). A well stirred mixture of **2** (102 mg, 0.1 mmol), C_{60} (144 mg, 0.2 mmol) and hexylglycine (159 mg, 1.0 mmol) in 100 mL of dry toluene under argon atmosphere was

heated to reflux during 24 h. After cooling, the mixture was purified by flash column chromatography (SiO₂, eluent polarity was gradually increased from toluene to toluene/ethyl acetate 3:1). The resulting green solid was triturated with methanol, filtered, and washed with methanol and hexane, yielding 125 mg (47%) of **1**. M.p.: >300 °C. ¹H NMR (500 MHz, CDCl₃), δ = 9.8-7.0 (br. m, 14H; ArH), 5.4-4.6 (m, 4H; pyrrolidine), 4.1-3.8 (m, 2H; OCH₂), 2.0-0.8 (br. m, 68H; CH, CH₂, CH₃ (CH₃)₃). UV/Vis (CHCl₃): λ_{max} (log ϵ) = 682 (5.13), 336 (5.01), 255 nm (5.27). FT-IR (KBr) ν = 3413, 2955, 2871, 1613, 1512, 1463, 1380, 1192, 1085, 927, 744 cm⁻¹. HR MALDI-TOF MS: m/z = 2654.6328 [M⁺]; calcd for C₁₉₄H₈₆N₁₀O₂Zn: 2654.2626.

Tri-tert-butyl-[4-(2-ethylhexyloxy)-2,5-diformylphenoxy]phthalocyaninatoZn(II) (**2**) (Mixture of regioisomers). To a suspension of OsO₄ (200 mg, 1% w/w in polyvinylpyridine) and phthalocyanine **6** (61 mg, 0.06 mmol) in THF (100 mL) was added dropwise a saturated aqueous solution of NaIO₄ (30 mL), and the mixture was allowed at room temperature for 24h. The suspension was filtered through a bed of Celite[®] and the solvents were eliminated under reduced pressure. The crude product was finally purified by column chromatography (SiO₂, dioxane/hexane 1:4) to yield **2** (43 mg, 70%) as a blue solid, M.p. >300 °C. ¹H NMR (300 MHz, CDCl₃), δ = 10.8 and 10.5 (br. m, 2H; CHO), 9.3-7.1 (m, 14H; ArH), 4.2-3.8 (m, 2H; OCH₂), 1.9-0.9 (m, 42H; CH, CH₂, CH₃ (CH₃)₃). UV/Vis (CHCl₃): λ_{max} (log ϵ) = 680 (5.13), 610 (4.40), 351 nm (4.76). FT-IR (KBr) ν = 2953, 2868, 1693, 1612, 1460, 1389, 1333, 1196, 1086, 924, 829, 748 cm⁻¹. MALDI-TOF MS: m/z = 1020 [M⁺]. Elemental analysis (%) calculated for C₆₀H₆₀N₈O₄Zn (1022.56): C 70.48, H 5.91, N 10.96. Found: C 69.97, H 5.99, N 10.57.

4-(2,5-Dibromo-4-hydroxy)phenoxy-1,2-dicyanobenzene (**3**). A mixture of 4-nitrophthalonitrile (0.866 g, 5 mmol), 2,5-dibromohydroquinone (1.18 g, 10 mmol) and potassium carbonate (0.69 g, 5 mmol) in DMF (25 mL) was allowed to react under argon atmosphere with stirring during 9h. After this time another equivalent (0.69 g, 5 mmol) of potassium carbonate was added and the stirring was continued for further 9h. The mixture was poured in to a 0.1 N HCl solution (100 mL), extracted with CH₂Cl₂ (2 x 50 mL) and washed with water. After elimination of the solvent under reduced pressure,

the residue was purified by flash chromatography (SiO₂, CH₂Cl₂/MeOH 100:1) to yield **3** (1.5 g, 76%) as a white solid. M.p.: 163-165 °C. ¹H NMR (300 MHz, CDCl₃/CD₃COCD₃ 2:1), δ = 7.60 (d, *J* = 8.6 Hz, 1H; 6-H), 7.13 (s, 1H, 12-H), 7.08 (s, 1H; 9-H), 7.06 (d, *J* = 2.7 Hz, 1H; 3-H), 7.00 (dd, *J* = 8.6 Hz, *J'* = 2.7 Hz, 1H; 5-H). ¹³C NMR (75 MHz, CDCl₃/CD₃COCD₃ 2:1), δ = 160.7 (C-4), 152.7 (C-7), 142.6 (C-10), 135.3 (C-6), 126.5 (C-3), 120.3 (C-5), 117.2, 114.9, 114.7, 114.5, 109.3, 108.8 (C-11). MS-LSIMS (3-NOBA): *m/z*: 393 [M+H⁺].

4-[(2,5Dibromo-4-(2-ethylhexyloxy)]phenoxy-1,2-dicyanobenzene (4). To a well-stirred mixture of **3** (1.5 g, 3.8 mmol) and potassium carbonate (2.62 g, 19 mmol) in DMF (30 mL) under argon atmosphere, 2-ethyl-1-hexylbromide (0.81 g, 4.2 mmol) was added and the mixture was heated at 100 °C overnight. After cooling, the reaction mixture was poured in water and extracted with CH₂Cl₂ (2 x 50 mL). The solvent was evaporated under reduced pressure and the crude was finally purified by column chromatography (SiO₂, CH₂Cl₂/hexane 2:1) yielding **4** as a viscous oil (1.58 g, 82%). ¹H NMR (300 MHz, CDCl₃), δ = 7.40 (d, *J* = 8.6 Hz, 1H; 6-H), 7.36 (s, 1H; 12-H), 7.22-7.16 (m, 2H; 3-H, 5-H), 7.15 (s, 1H; 9-H), 3.93 (d, *J* = 5.4 Hz, 2H; OCH₂), 1.8 (m, 1H; CH), 1.6-1.2 (m, 8H; CH₂), 1.1-0.9 (m, 6H; CH₃). ¹³C NMR (75 MHz, CDCl₃), δ = 160.9 (C-4), 154.8 (C-7), 143.3 (C-10), 135.5 (C-6), 127.1 (C-3), 120.5 (C-5), 117.8, 117.2, 115.2, 115.0, 114.8, 112.1, 109.3, 72.3 (OCH₂), 39.3 (CH), 30.4 (CH₂), 29.0 (CH₂), 23.8 (CH₂), 22.9 (CH₂), 14.0 (CH₃), 11.2 (CH₃). MS-LSIMS (3-NOBA): *m/z*: 505 [M+H⁺].

Tri-tert-butyl-[4-(2-ethylhexyloxy)-2,5-dibromophenyloxy]phthalocyaninatoZn(II) (5) (Mixture of regioisomers). Phthalonitrile **4** (157 mg, 0.31 mmol), 4-*tert*-butylphthalonitrile (177 mg, 0.96 mmol) and ZnCl₂ (45 mg, 0.33 mmol) in 2 mL of DMAE was heated at reflux under argon atmosphere during 16h. After cooling, the reaction mixture was triturated with 20 mL of water/methanol (2:1), filtered through a bed of Celite[®], washed with methanol and dried. The residue was extracted with dichloromethane and the solvent was evaporated under reduced pressure. Further purification by flash chromatography (Al₂O₃, dioxane/hexane 1:5) yielded **5** as a blue solid (80 mg, 23%). M.p. >300 °C. ¹H NMR (300 MHz, CDCl₃), δ = 9.0-7.2 (m, 14H; ArH), 4.2-4.0 (m, 2H; OCH₂), 1.8-0.9 (m, 42H; CH,

CH₂, CH₃ (CH₃)₃). UV/Vis (CHCl₃): $\lambda_{\max}$ (log ϵ) = 680 (5.14), 610 (4.39), 350 nm (4.80). FT-IR (KBr) ν = 2964, 1618, 1456, 1362, 1254, 1213, 1092, 835, 754 cm⁻¹. MALDI-TOF MS: m/z = 1120-1129 [M⁺]. Elemental analysis (%) calculated for C₅₈H₅₈Br₂N₈O₂Zn (1124.33): C 61.96, H 5.20, N 9.97. Found: C 61.55, H 5.41, N 9.51.

Tri-tert-butyl-[4-(2-ethylhexyloxy)-2,5-divinylphenoxy]phthalocyaninatoZn(II) (**6**) (Mixture of regioisomers). To a stirred solution of phthalocyanine **5** (78 mg, 0.07 mmol) and Pd(PPh₃)₄ (8 mg, 7 μ mol) in dry toluene (50 mL) under argon atmosphere, tributyl(vinyl)tin (0.12 mL, 0.42 mmol) was added and the mixture was heated at 100 °C during 24h. After elimination of the solvent under reduced pressure, the residual was triturated with methanol, filtered and washed with the same solvent. The solid was purified by flash chromatography (SiO₂, dioxane/hexane 1:5), yielding **6** (62 mg, 87%) as a blue solid. M.p. > 300 °C. ¹H NMR (300 MHz, CDCl₃), δ = 8.9-7.0 (m, 20H; ArH and vinyl H), 6.1-5.9 (m, 2H), 5.6-5.4 (m, 2H), 4.1-3.9 (m, 2H; OCH₂), 1.9-0.9 (m, 42H; CH, CH₂, CH₃ (CH₃)₃). UV/Vis (CHCl₃): $\lambda_{\max}$ (log ϵ) = 680 (5.13), 612 (4.36), 350 nm (4.79). FT-IR (KBr) ν = 2953, 1614, 1466, 1385, 1182, 1088, 1047, 744 cm⁻¹. MALDI-TOF MS: m/z = 1016 [M⁺]. Elemental analysis (%) calculated for C₆₂H₆₄N₈O₂Zn (1018.62): C 73.11, H 6.33, N 11.00. Found: C 73.59, H 6.56, N 10.64.

MALDI-TOF spectrum of triad 1:

Applied Biosystems 4700 Proteomics Analyzer 347000029

4700 Reflector Spec #1 MC=>MC[BP = 1936.7, 1604]

Applied Biosystems 4700 Proteomics Analyzer 347000029

4700 Reflector Spec #1 MC[BP = 1214.7, 5626]

UV/Vis spectra of compounds **1**, **2**, **5** and **6**:

UV/Vis spectra of compounds **2**, **5** and **6** in chloroform

UV/Vis spectra of compound **1** in chloroform

^1H NMR spectrum of compound **1**:

^1H NMR spectrum of compound **2**:

S10

^1H NMR spectrum of compound **5**:

S11

^1H NMR spectrum of compound **6**:

S12

Time dependence of the PIA signal for triad **1**:

Modulation frequency dependence of the 850 nm features of triad **1**. The continuous lines are obtained following a fitting procedure [Ephstein, O.; Nakhmanovich, G.; Eichen, Y.; Ehrenfreund, E. *Phys. Rev. B* **2001**, 63, 125206-125211]. The resulting lifetime of the charge separated state is 1 ms.

Electrochemistry of triad **1**

The CV shows that compound triad **1** is electrochemically active in both anodic and cathodic sweep directions between +1.0 and -2.2 V. In the cathodic scan there are three groups of waves that is the sum of the corresponding redox processes to each electroactive moiety ([60]fullerene and Pc). However the first ($\Delta E_p^1 = 95$ mV) at around -0.82 V and the third ($\Delta E_p^3 = 140$ mV) at -1.83 V can be easily assigned as the two electron C_{60} -based processes, the second wave are poorly resolved and is the sum of the second C_{60} -based process and to the two Pc-based reduction processes at around -1.30 V. In the anodic scan there is only one significant two electron redox process at around 0.41 V and can be easily assigned as Pc-based.

CVs (sweep rate 0.1 V s^{-1}) for triad **1** in $\text{BzCN-Bu}_4\text{N}^+\text{ClO}_4^-$ system at room temperature

OSWVs for triad **1** in BzCN-Bu₄N⁺ClO₄⁻ system at room temperature.

Table 1. Electrochemical data (V vs Ag/AgNO₃) of the redox processes of compound **1**, detected by OSWV in BzCN solution (0.05 mol dm⁻³ Bu₄N⁺ClO₄⁻) at room temperature under identical experimental conditions. Errors are estimated at less than 2 mV in all OSWV measurements

	$E_{\text{red}}^{1[\text{a}]}$	$E_{\text{red}}^{2[\text{a}+\text{b}]}$	$E_{\text{red}}^{3[\text{a}]}$	$E_{\text{ox}}^{1[\text{b}]}$
1	-0.82	-1.27	-1.84	0.42

[a] C₆₀-based reduction.

[b] Pc-based redox process.

Current-voltage features of a solar cell built with triad **1**:

Current-voltage characteristics of a photovoltaic diode with **1** in the dark (dashed line) and under illumination by a solar simulator at 100 mW cm^{-2} (full line).