Zinc phthalocyanine - benzoperylenetriimide conjugate for solvent dependent ultrafast energy vs electron transfer

Valeria Navarro-Pérez, Ana M. Gutiérrez-Vilchez, Javier Ortiz, Ángela Sastre-Santos, Fernando Fernández-Lázaro, Sairaman Seetharaman, M. J. Duffy, Paul A. Karr, and Francis D’Souza

CONTENTS

Scheme S1: Synthesis of 1 .........................................................................................................................................S2
Figure S1: 1H-NMR spectrum of 1 in TFA .............................................................................................................S3
Figure S2: HRMS MALDI-TOF spectrum of 1 ........................................................................................................S3
Figure S3: UV-vis spectrum of 1 in CHCl3 .............................................................................................................S3
Figure S4: Fluorescence spectrum of 1 in CHCl3 ....................................................................................................S4
Scheme S2: Synthesis of 2 .........................................................................................................................................S5
Figure S5: 1H-NMR spectrum of 2 in CDCl3 ............................................................................................................S6
Figure S6: HRMS MALDI-TOF spectrum of 2 ........................................................................................................S6
Figure S7: UV-vis spectrum of 2 in CHCl3 .............................................................................................................S7
Figure S8: Fluorescence spectrum of 2 in CHCl3 ....................................................................................................S7
Figure S9: 1H-NMR spectrum of 3 in DMSO ..........................................................................................................S8
Figure S10: 1H-NMR spectrum of 5 in TFA-d1 .......................................................................................................S8
Figure S11: Decay profiles of ZnPc and BPTI in benzonitrile .....................................................................................S9
Figure S12: Fs-TA spectra of ZnPc and BPTI in toluene ..........................................................................................S9

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Scheme S1: Synthesis of 1

Synthesis of zinc(II) 2,9,16-tri-tert-butyl-23-{2''-[N',N''-di(hexylheptyl)benzo[ghi]perylene-1''',2''':4''',5''':10''',11'''-trisdicarboximide-N-yl]ethoxy}phthalocyaninate (1). A mixture of 11 mg (0.01 mmol) of zinc (II) phthalocyaninate 5, 18 mg (0.02 mmol) of benzo[ghi]perylenediimidemonoanhydride 4 and 470 mg (6.9 mmol) of imidazole was heated under argon at 160 ºC for 7 hours. After cooling at room temperature, methanol was added and this mixture was sonicated. After centrifugation the solid obtained was dried in the vacuum oven for 24 h. The crude product was purified by column chromatography (SiO₂, CHCl₃/AcOEt 94:6 → CHCl₃/AcOEt/MeOH 93.5:6:0.5) to obtain 12 mg (75%) of a pale green powder.

- **¹H-NMR** (300 MHz, TFA, 25 °C) δ: 10.72 (br, 2H, 2xPDI-H), 9.49-10.01 (m, 12H, 4xPDI-H, 8xArH), 8.87 (br, 3H, 3xArH), 8.50 (br, 1H, ArH), 5.75 (br, 2H, -CH₂-N-), 5.43 (br, 1H, 1xN-CH), 5.16 (br, 1H, 1xN-CH), 4.25 (br, 2H, -O-CH₂-), 2.72 (br, 4H, 2x-CHH-CH-CHH-), 2.42 (br, 4H, 2x-CHH-CH-CHH-), 1.36-1.91 (m, 59H, 16x-CH₂-, 9xCH₃), 1.12 (br, 12H, 4x-CH₃).

- **HRMS MALDI-TOF** (dithranol): calculated for C₁₀₀H₁₀₃N₁₁O₇Zn m/z = 1633.733, found m/z = 1634.732 [M+H]+.

- **FT-IR** (KBr): 3424, 2955, 2924, 2855, 1704, 1663, 1613, 1490, 1464, 1396, 1318, 1235, 1089, 811, 765, 748 cm⁻¹.

- **UV-vis** (CHCl₃), λ_max/nm (log ε): 353 (4.89), 436 (4.60), 467 (4.76), 622 (4.17), 686 (4.81).
Figure S1: $^1$H-NMR spectrum of $1$ in TFA

Figure S2: HRMS MALDI-TOF spectrum of $1$

Figure S3: UV-vis spectrum of $1$ in CHCl$_3$
**Figure S4:** Fluorescence spectrum of 1 in CHCl₃
Scheme S2: Synthesis of 2

Synthesis of N-dodecyl-N',N''-di(hexylheptyl)benzo[ghi]perylene-1,2:4,5:10,11-tris(dicarboximide) (2). A mixture of 100 mg (0.12 mmol) of benzoperylenediimidemonaanhydride 4, 1 g (0.01 mmol) of imidazole and 26.7 mg (0.14 mmol) of docecylamine was heated under argon at 160 ºC for 7 hours. After cooling at room temperature ethanol was added and the mixture was sonicated. 5 mL of 2N HCl were added and the mixture was stirred for 24 h. The solid was filtered and washed with K$_2$CO$_3$ (10%) and with water until neutral pH. Then, it was dried overnight in the vacuum oven. The crude product was purified by CombiFlash chromatography (0-90% of AcOEt in CH$_2$Cl$_2$) obtaining 41 mg of the desired product (34%) as an orange wax.

- **^1H-NMR** (300 MHz, CDCl$_3$, 25 ºC) δ: 10.20 (br, 2H, 2xPDI-H), 9.17 (d, $J = 8.8$ Hz, 2H, 2xPDI-H), 9.07 (d, $J = 8.6$ Hz, 2H, 2xPDI-H), 5.31 (br, 2H, 2xN-CH), 3.99 (t, $J = 6.9$ Hz, 2H, -CH$_2$N-), 2.30-2.44 (m, 4H, 2x-CHH-CH-CHH-), 1.93-2.07 (m, 4H, 2x-CHH-CH-CHH-), 1.82-1.92 (m, 2H, -CH$_2$-), 1.18-1.52 (m, 50H, 25x-CH$_2$-), 0.83 (t, $J = 6.7$ Hz, 15H, 5x-CH$_3$).
- **HRMS MALDI-TOF** (dithranol): calculated for C$_{66}$H$_{85}$N$_3$O$_6$ m/z = 1015.644, found m/z= 1015.698 [M+].
- **FT-IR** (KBr): 3073, 2955, 2925, 2854, 1766, 1710, 1666, 1595, 1523, 1464, 1413, 1365, 1317, 1239, 1174, 945, 810, 765, 659 cm$^{-1}$.
- **UV-vis** (CHCl$_3$), $\lambda_{max}$/nm (log $\varepsilon$):= 374 (4.55), 410 (4.16), 436 (4.57), 466 (4.75).
Figure S5: $^1$H-NMR spectrum of 2 in CDCl$_3$

Figure S6: HRMS MALDI-TOF spectrum of 2
Figure S7: UV-vis spectrum of 2 in CHCl₃

Figure S8: Fluorescence spectrum of 2 in CHCl₃
Figure S9: $^1$H-NMR spectrum of 3 in DMSO

Figure S10: $^1$H-NMR spectrum of 5 in TFA-$d_1$
Figure S11. Decay profiles of (a) ZnPc ($\lambda_{ex} = 690$ nm) and (b) BPTI ($\lambda_{ex} = 494$ nm) in benzonitrile.
Figure S12. Fs-TA spectra at the indicated delay times of ZnPc and BPTI in toluene. ZnPc was excited at 686 nm while BPTI was excited at 480 nm. The time profiles of the 833 nm peak of \(^1\)ZnPc\(^*\) and 671 nm peak of \(^1\)BPGI\(^*\) are shown in the right hand panel.