

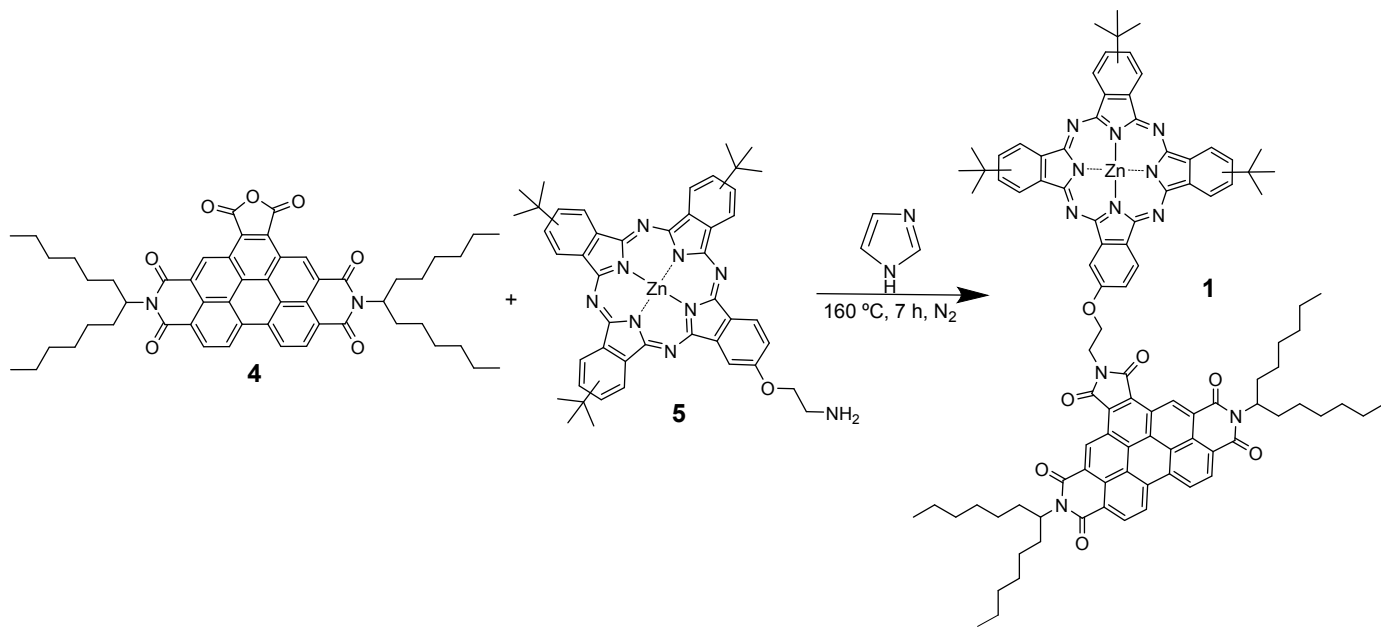
ELECTRONIC SUPPLEMENTARY INFORMATION

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

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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*]perylene diimide monoanhydride **4** and 470 mg (6.9 mmol) of imidazole was heated under argon at 160 °C 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*, 8xAr*H*), 8.87 (br, 3H, 3xAr*H*), 8.50 (br, 1H, Ar*H*), 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).

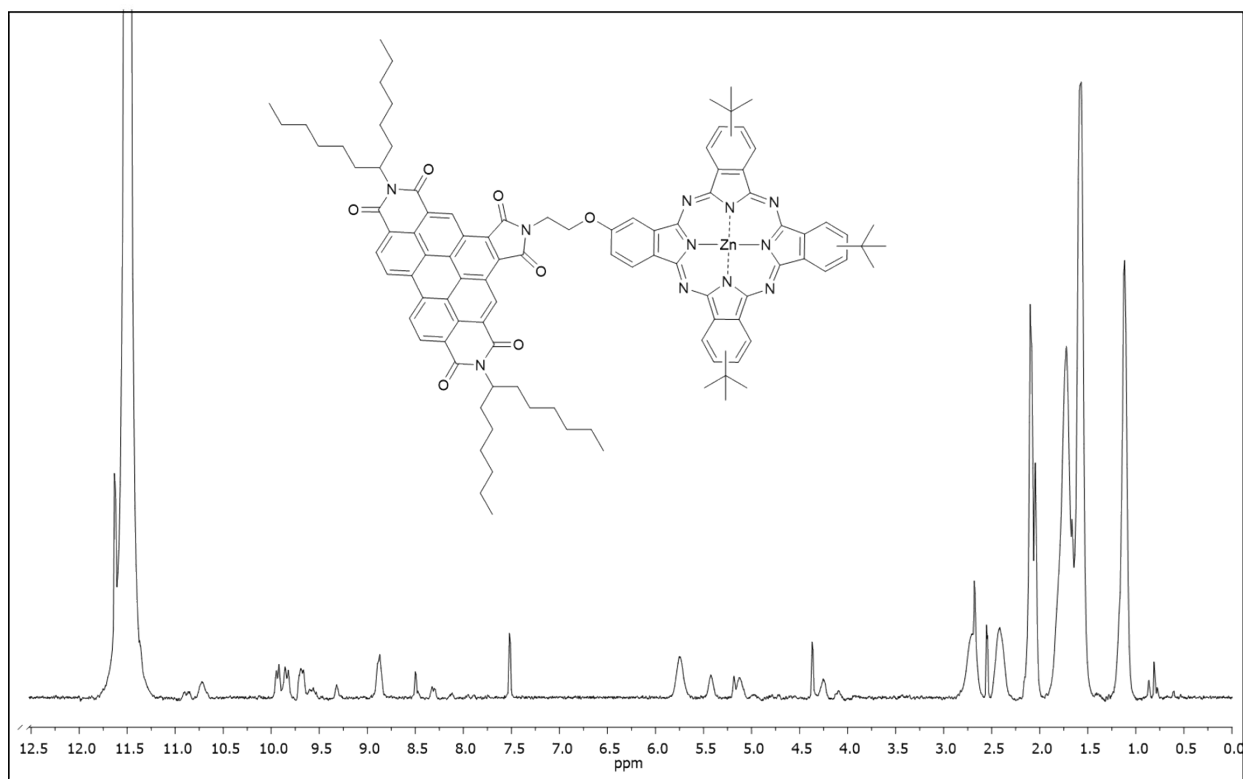


Figure S1: $^1\text{H-NMR}$ spectrum of **1** in TFA

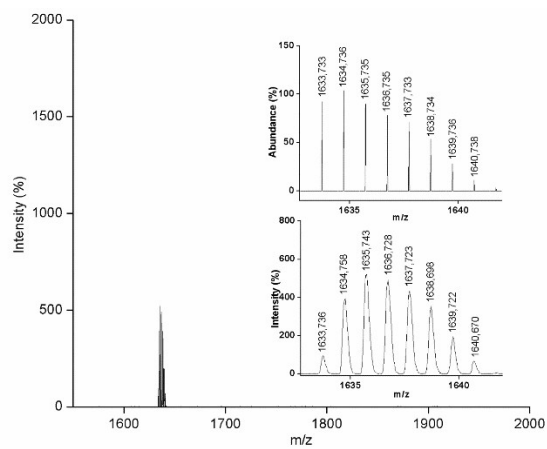


Figure S2: HRMS MALDI-TOF spectrum of **1**

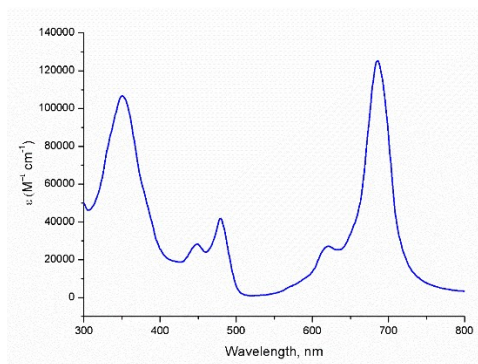


Figure S3: UV-vis spectrum of **1** in CHCl_3

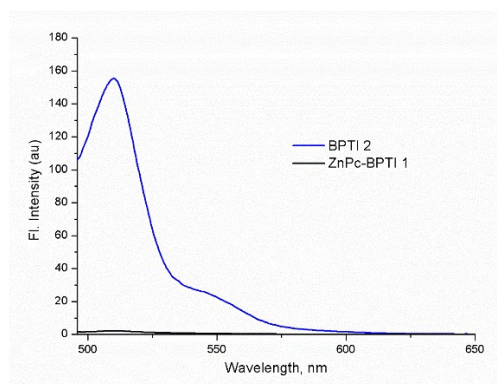
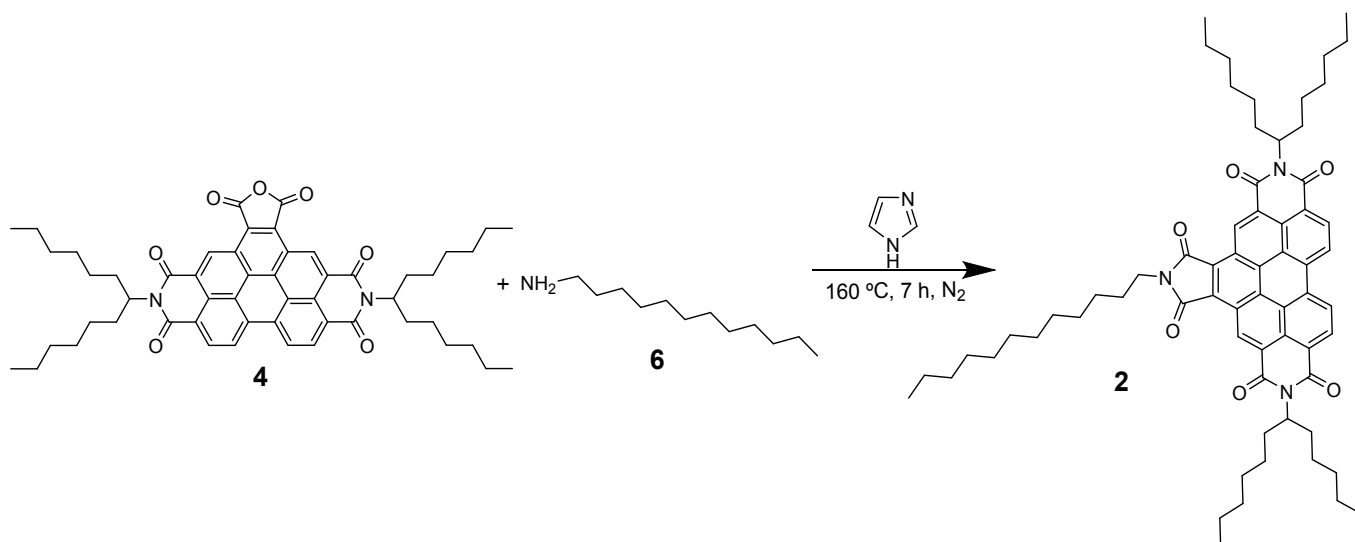


Figure S4: Fluorescence spectrum of **1** in CHCl₃



Scheme S2: Synthesis of 2

Synthesis of *N*-dodecyl-*N'*,*N''*-di(hexylheptyl)benzo[*ghi*]perylene-1,2:4,5:10,11-tris(dodecyl)diimide (2). A mixture of 100 mg (0.12 mmol) of benzoperylene diimide monoanhydride **4**, 1 g (0.01 mmol) of imidazole and 26.7 mg (0.14 mmol) of dodecylamine was heated under argon at 160 °C 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 K₂CO₃ (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 CH₂Cl₂) obtaining 41 mg of the desired product (34%) as an orange wax.

- **¹H-NMR** (300 MHz, CDCl₃, 25 °C) 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 C₆₆H₈₅N₃O₆ *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** (CHCl₃), λ_{max}/nm (log ε):= 374 (4.55), 410 (4.16), 436 (4.57), 466 (4.75).

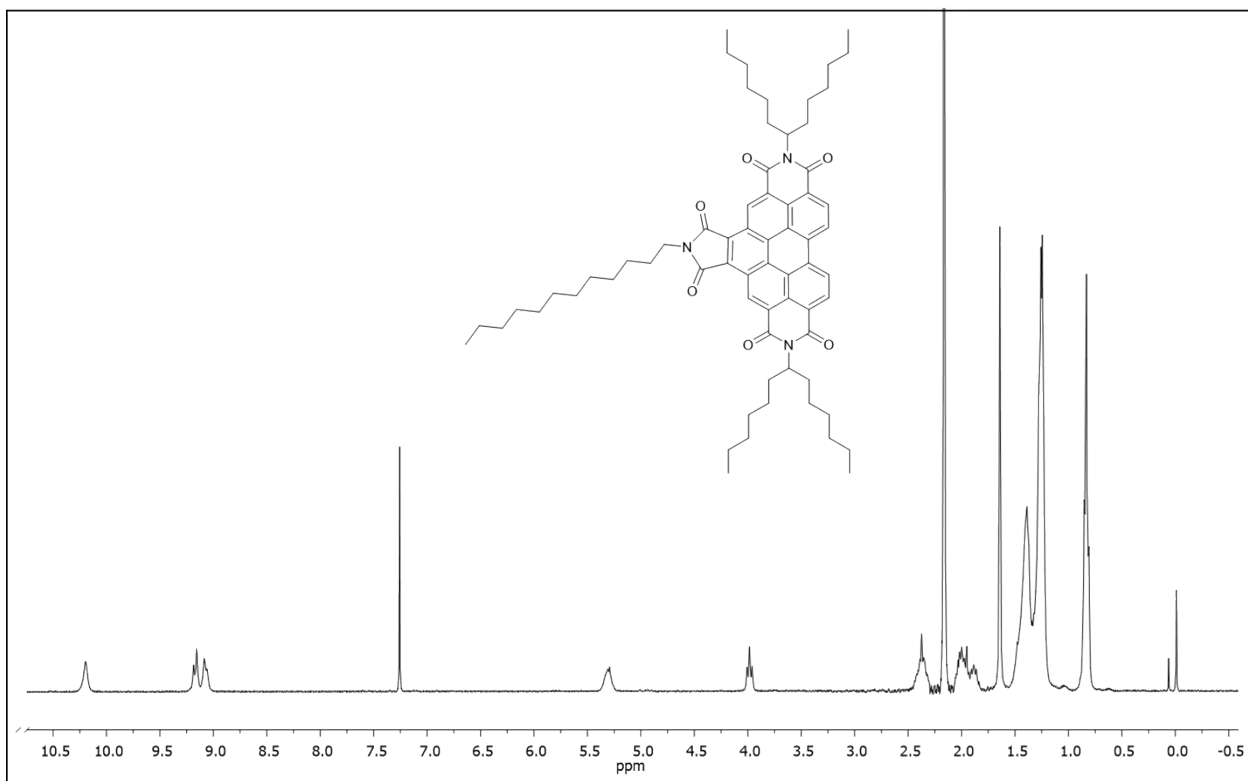


Figure S5: $^1\text{H-NMR}$ spectrum of **2** in CDCl_3

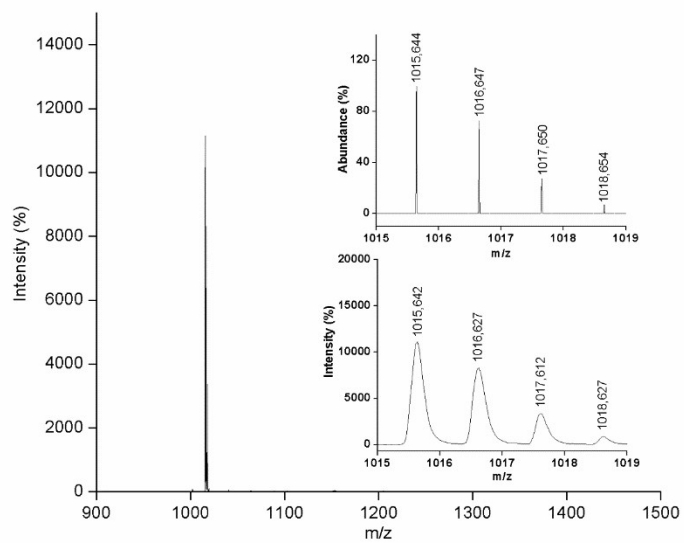


Figure S6: HRMS MALDI-TOF spectrum of **2**

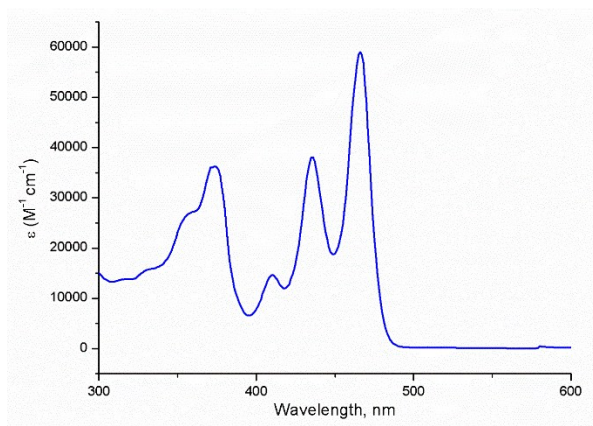


Figure S7: UV-vis spectrum of **2** in CHCl_3

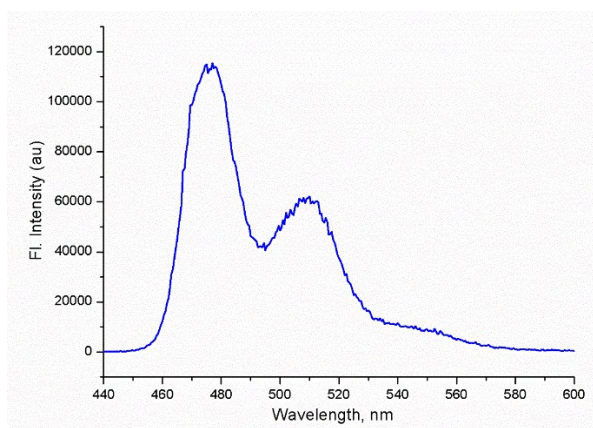


Figure S8: Fluorescence spectrum of **2** in CHCl_3

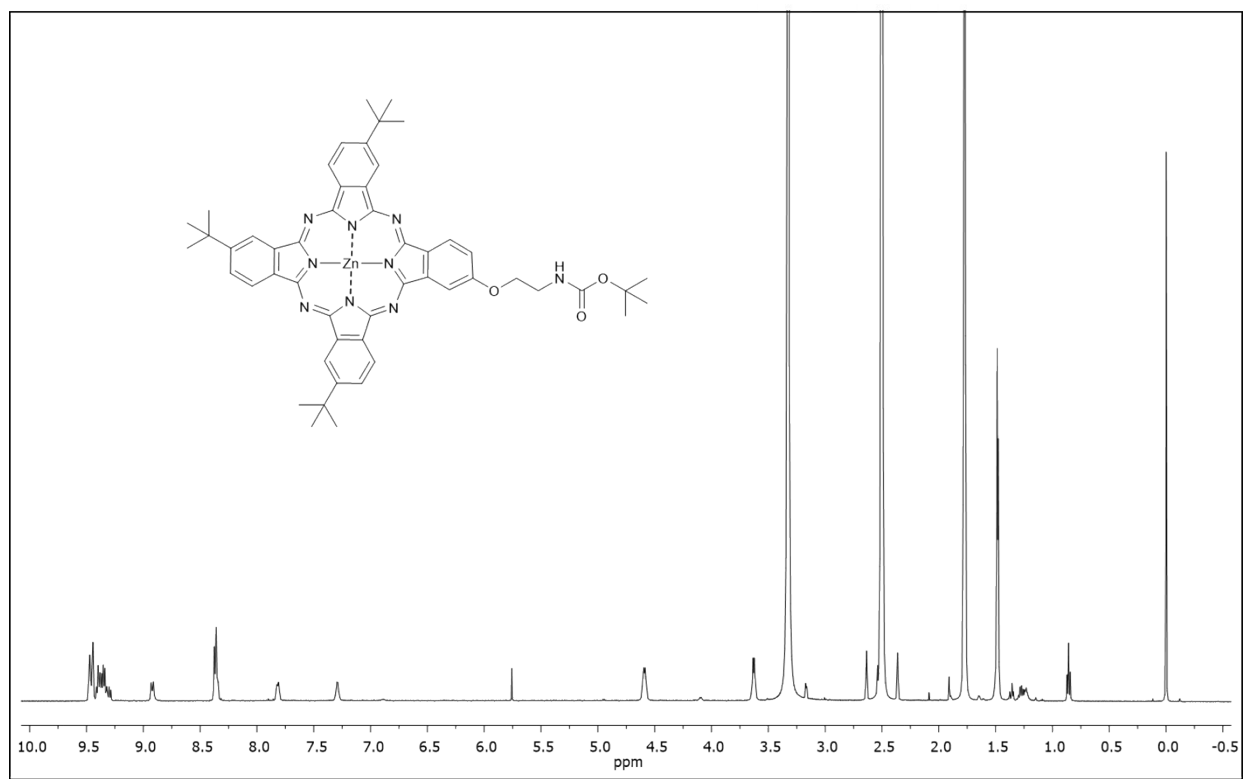


Figure S9: ¹H-NMR spectrum of **3** in DMSO

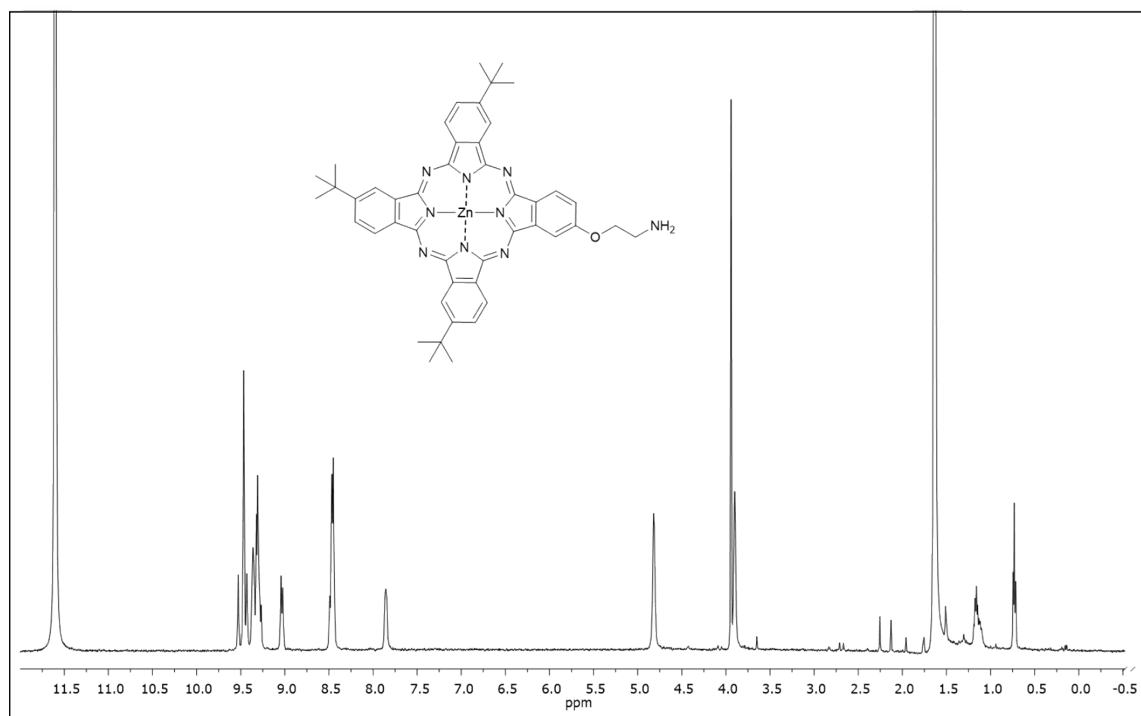


Figure S10: ¹H-NMR spectrum of **5** in TFA-*d*₁

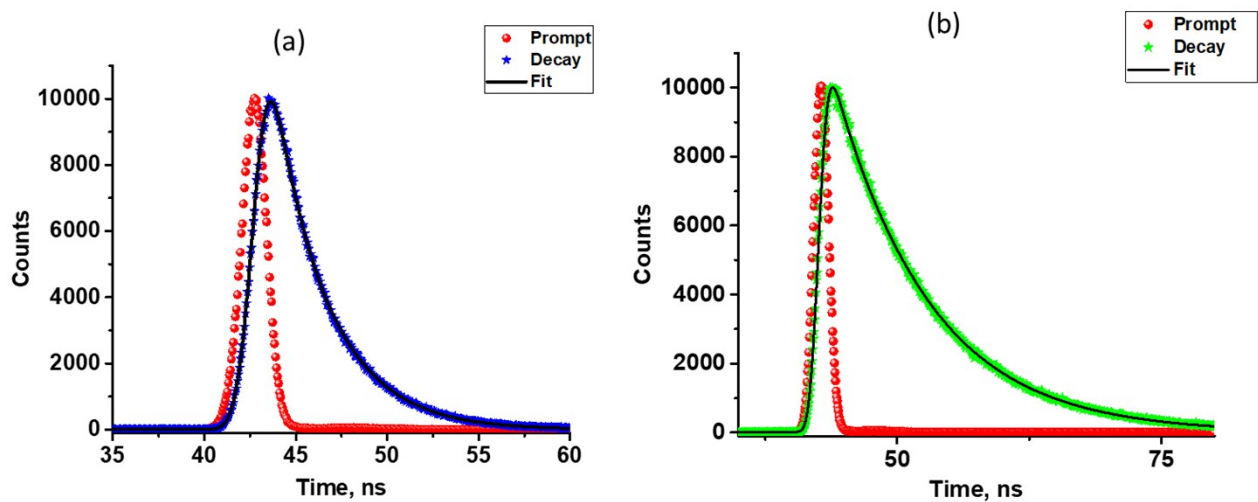


Figure S11. Decay profiles of (a) ZnPc ($\lambda_{\text{ex}} = 690$ nm) and (b) BPTI ($\lambda_{\text{ex}} = 494$ nm) in benzoni trile.

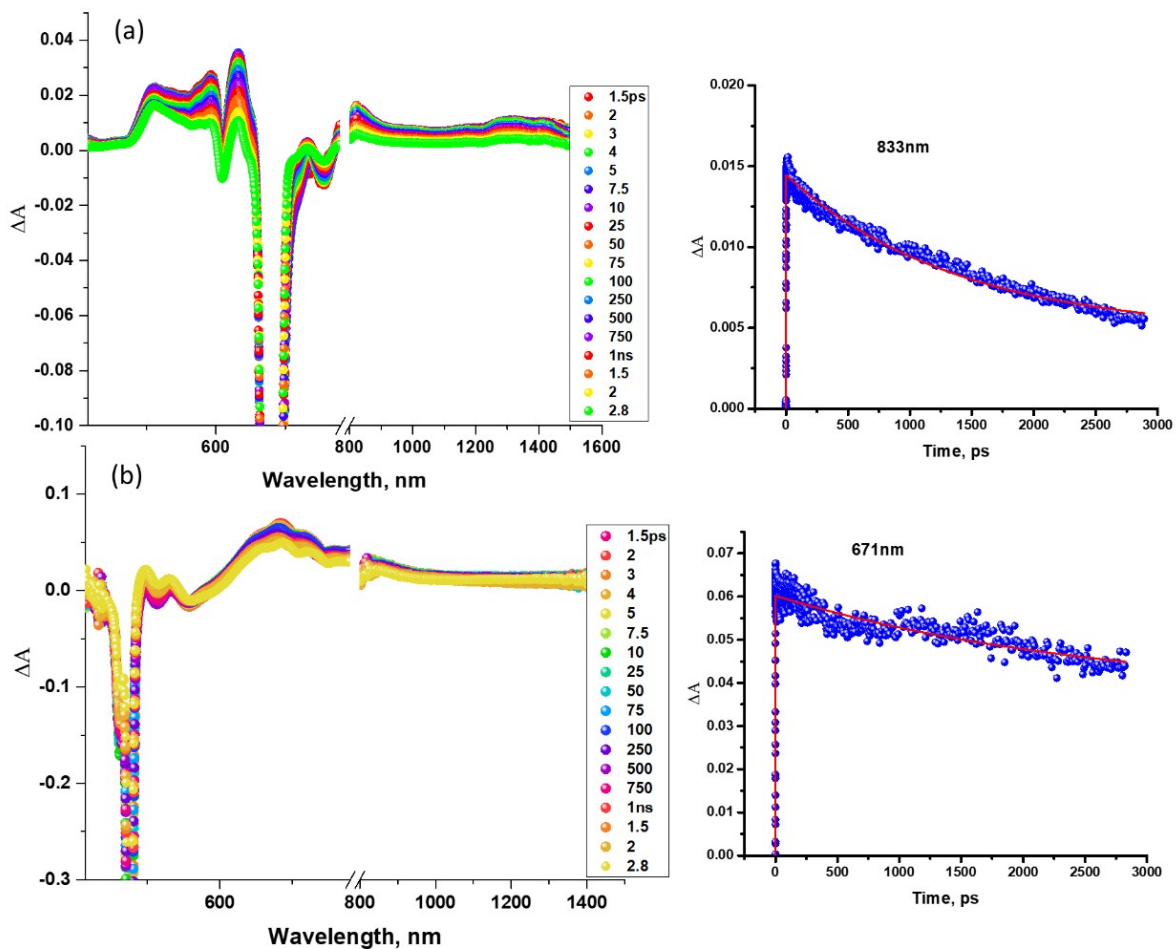


Figure S12. Fs-TA spectra at the indicated delay times of ZnPc and BPTI in toluene. ZnPc was excited at 686 nm while BPTI was excited at 480 nm. The time profiles of the 833 nm peak of $^1\text{ZnPc}^*$ and 671 nm peak of $^1\text{BPGI}^*$ are shown in the right hand panel.