

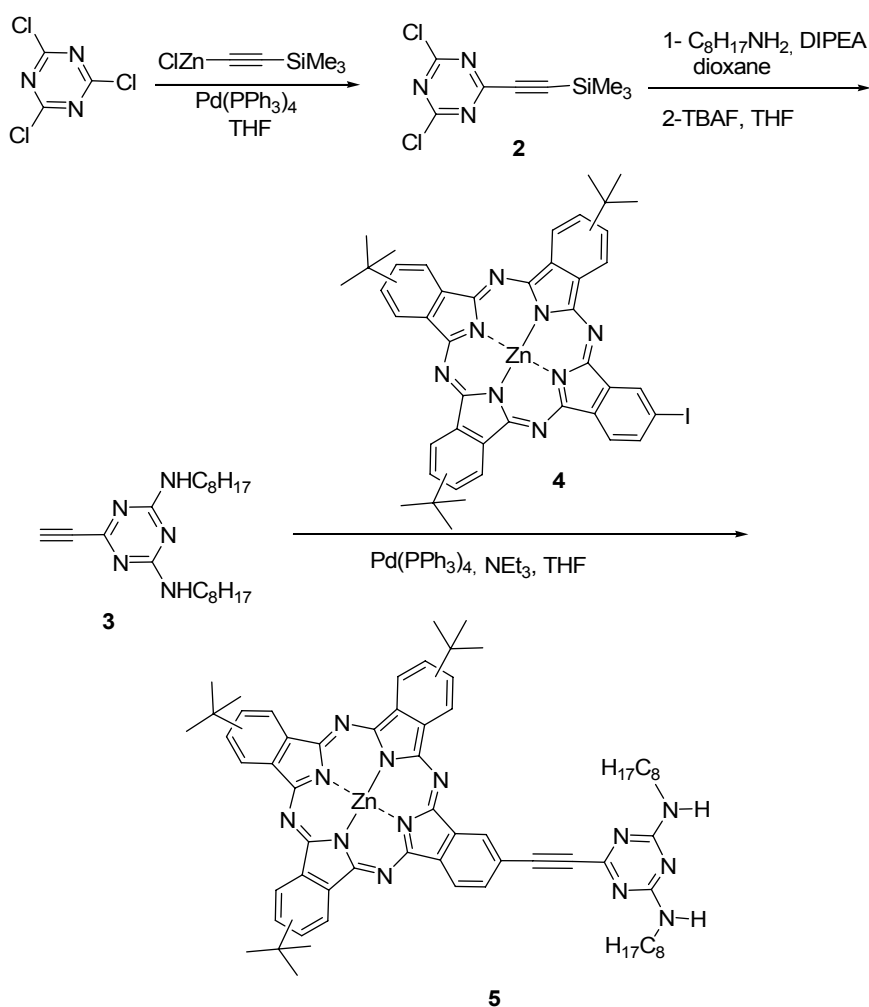
Synthesis and Photophysical Properties of a Hydrogen-Bonded Phthalocyanine-Perylenediimide Assembly

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Scheme 1. Synthesis of the melamine-functionalized phthalocyanine **5**.



The characterization of compound **5** was accomplished by spectroscopic methods including ^1H NMR, IR and UV/Vis spectroscopies, as well as MS spectrometry.

General Procedures:

Synthesis: UV/Vis spectra were recorded with a Hewlett-Packard 8453 instrument. IR spectra were recorded with Bruker Vector 22 spectrophotometer. FAB-MS spectra were determined on a VG AutoSpec instrument. MALDI-TOF MS and HRMS spectra were recorded with a Bruker Reflex III spectrometer. NMR spectra were recorded with a Bruker AC-300 instrument. Column chromatographies were carried out on silica gel Merck-60 (230-400 mesh, 60 Å) and TLC was performed on aluminum sheets precoated with silica gel 60 F254 (E. Merck). Chemicals were purchased from Aldrich Chemical Co. and used as received without further purification. Solvents were dried using microwave to activate molecular sieves. Phthalocyanine **4** was prepared used a reported procedure (reference 18 in the text).

2,4-dichloro-6-(2-(trimethylsilyl)ethynyl)-1,3,5-triazine (**2**)

To a solution of trimethylsilylacetylene (0.14 mL, 0.9 mmol) in 20 mL of THF, *n*-BuLi (0.1 mL, 1 mmol) was added at -78 °C under Ar and the reaction was stirred for 30 minutes. A solution of ZnCl₂ (136 mg, 1mmol) in THF (5mL) was added dropwise and the reaction was stirred at room temperature for 30 minutes. Then, Pd(PPh₃)₄ (25 mg, 22.5 μmol) and 2,4,6-trichloro-1,3,5-triazine (486 mg, 3.6 mmol) were added. The mixture was stirred at room temperature for 2 hours. The reaction was quenched with HCl 1M (20 mL) and the solution was extracted with DCM, washed with water and dried over MgSO₄. The mixture was filtered and the solvent was rotary evaporated affording 44 mg (20%) of **2** as an oil. ¹³C-NMR (75.5 MHz, CDCl₃): δ = 172.1, 160.6, 105.7 (C≡C), 99.7 (C≡C), -0.96 ppm.

6-ethynyl-N²,N⁴-dioctyl-1,3,5-triazine-2,4-diamine (**3**)

A solution of octylamine (0.04 mL, 0.24 mmol) and DIPEA (0.042 mL, 0.24 mmol) in 1,4-dioxane (10 mL), **2** (20 mg, 82 μmol) was added in 1,4-dioxane (2 mL) at room temperature. The reaction was stirred under Ar for 4 hours. The crude was then quenched with HCl 1M and the reaction mixture was extracted with CHCl₃, washed with water and dried over MgSO₄. After filtration and evaporation of the solvent, the crude was redissolved in 20mL THF, and TBAF (64 mg, 0.24 mmol) was added. The mixture was stirred for 30 minutes, water (20mL) was added and the reaction mixture was extracted with dichloromethane, dried (MgSO₄), filtered and rotary evaporated. The residue was chromatographed on silica gel using hexanes:ethyl acetate (1:1) as eluent, yielding 17 mg (58%) of **3** as a solid. ¹³C-NMR (75.5 MHz, CDCl₃): δ= 165.0, 157.5, 81.2 (C≡C), 74.1 (C≡C), 58.7, 40.5, 31.7, 29.1, 26.8, 24.0, 22.5, 19.6, 14.0 ppm. MS (MALDI-TOF, Dithranol): *m/z* = 360.32 [M]⁺.

Phthalocyanine **5**

To a deaerated solution of **3** (10 mg, 27.8 μmol) and **4** (48 mg, 55.7 μmol) in a 1:1 mixture of THF and Et₃N (20 mL), CuI (1 mg, 2.78 μmol) and Pd₂Cl₂(PPh₃)₂ (1 mg, 1.39 μmol) were added under Argon and the mixture was refluxed for 24 h. After cooling to room temperature, the solvent was rotary evaporated, and the residue was suspended in methanol, filtered and washed with methanol. Gel permeation chromatography (Bio-Beads S-X1) was carried out using THF as the eluent. The first fraction was suspended in hexanes, filtered, washed with hexanes and then with dichloromethane. Finally it was dried at 90 °C and 10⁻¹ mmHg, affording 14 mg (43%) of **5** as a blue solid. ¹H-NMR (300 MHz, d₈-THF): δ = 9.5-9.1 (2 broad m, 8H arom), 8.4-8.2 (m, 4H arom), 6.9-6.6 (bs, 2H, NH), 3.5-3.3 (m, NCH₂), 2.45 (broad s, CH₂), 1.90. 1.88 (4s, 36H, C(CH₃)₃)1.5-1.2 (m, CH₂), 0.8-1.0 (m, 6H, CH₃); IR (KBr): ν = 3441 (NH), 3265, 2961, 2920, 2853 (C-H), 2222 (C≡C), 1553, 1485, 1418, 1256, 1094, 920, 831, 752 cm⁻¹; UV/Vis (THF): λ_{max} (log ε) = 282 (4.65), 347(5.01), 605 (4.55), 628 (4.55), 668 (5.23), 684 nm (5.28); (MALDI-TOF, Dithranol): *m/z* = 1102-1106 [M]⁺. HRMS (MALDI-TOF): calcd for C₆₅H₇₅N₁₃Zn, 1101.556. Found, 1101.555.

Figure S-1. ^{13}C NMR of 2

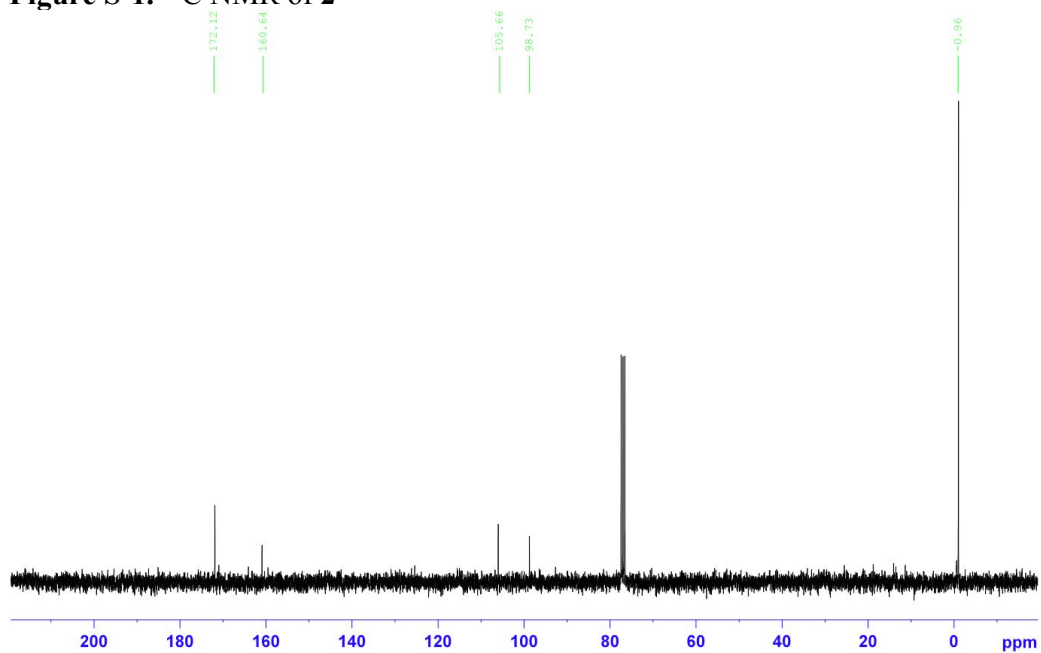


Figure S-2. ^{13}C NMR of 3

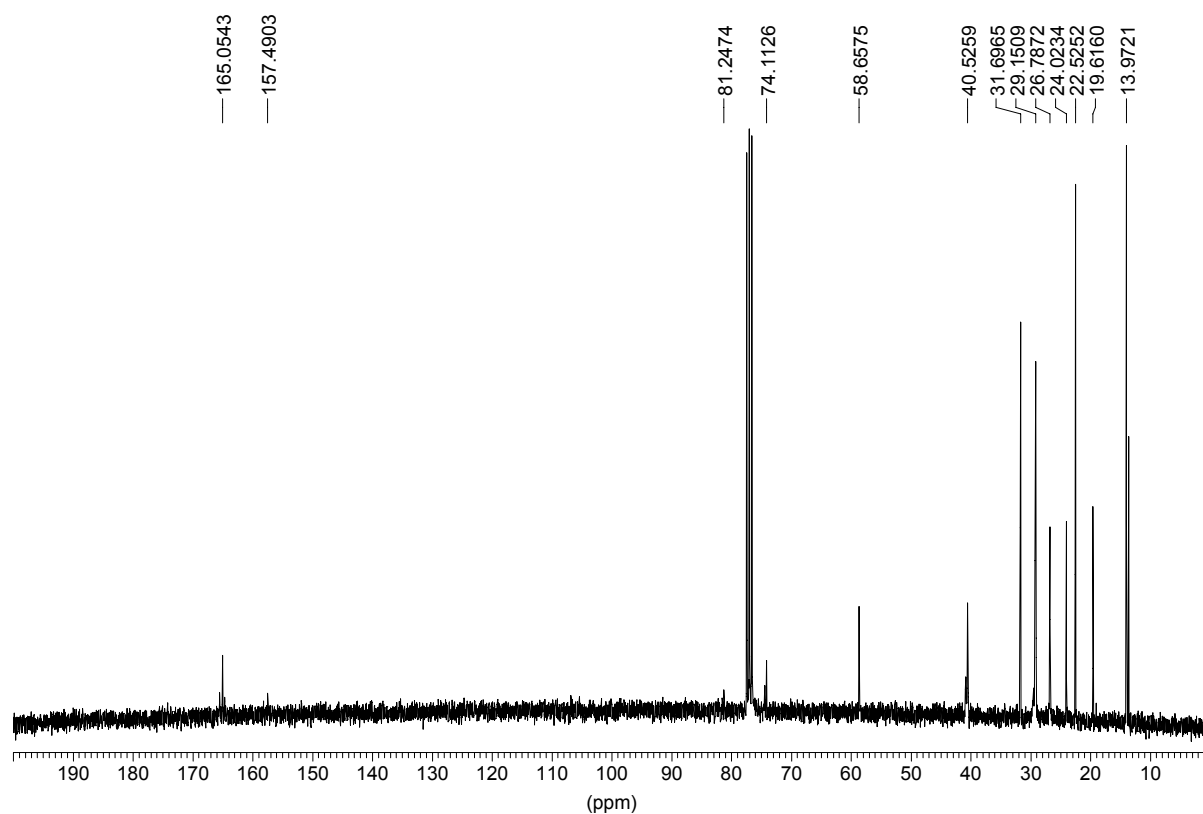


Figure S-3. MS (MALDI-TOF) of 3

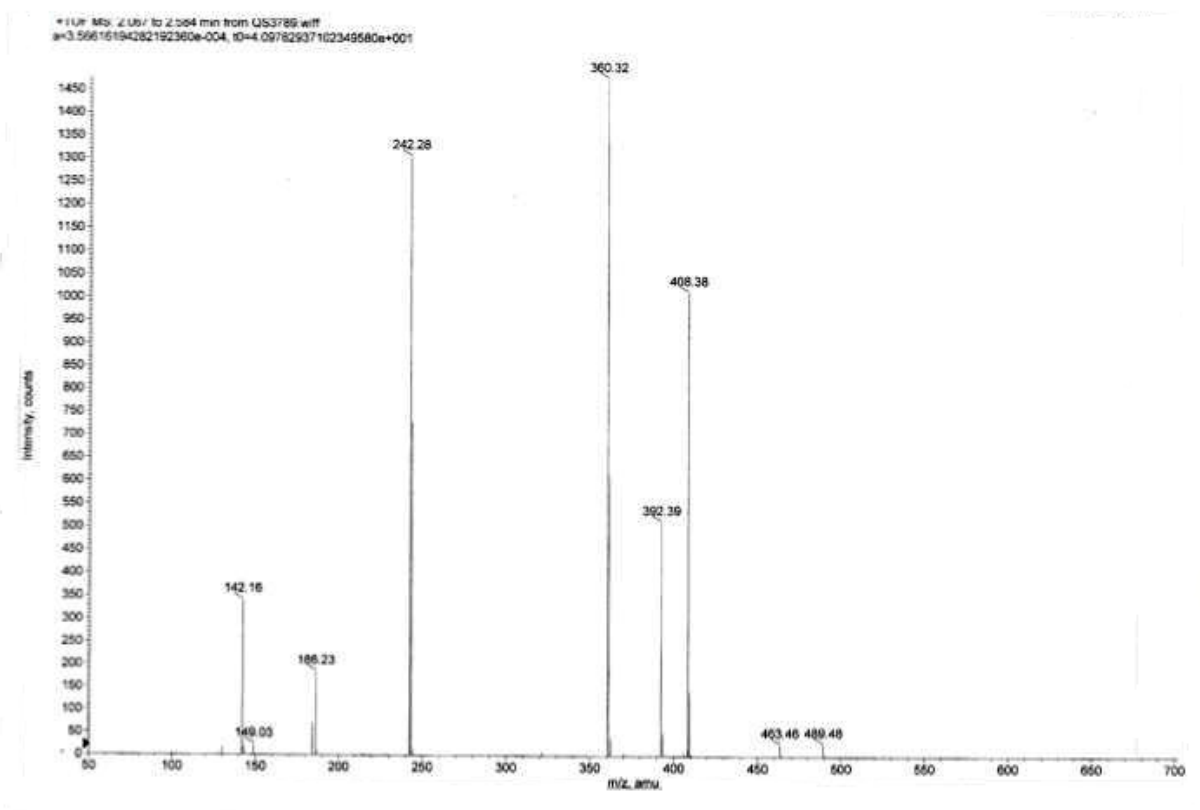


Figure S-4. ^1H NMR of 5 in $\text{d}^8\text{-THF}$

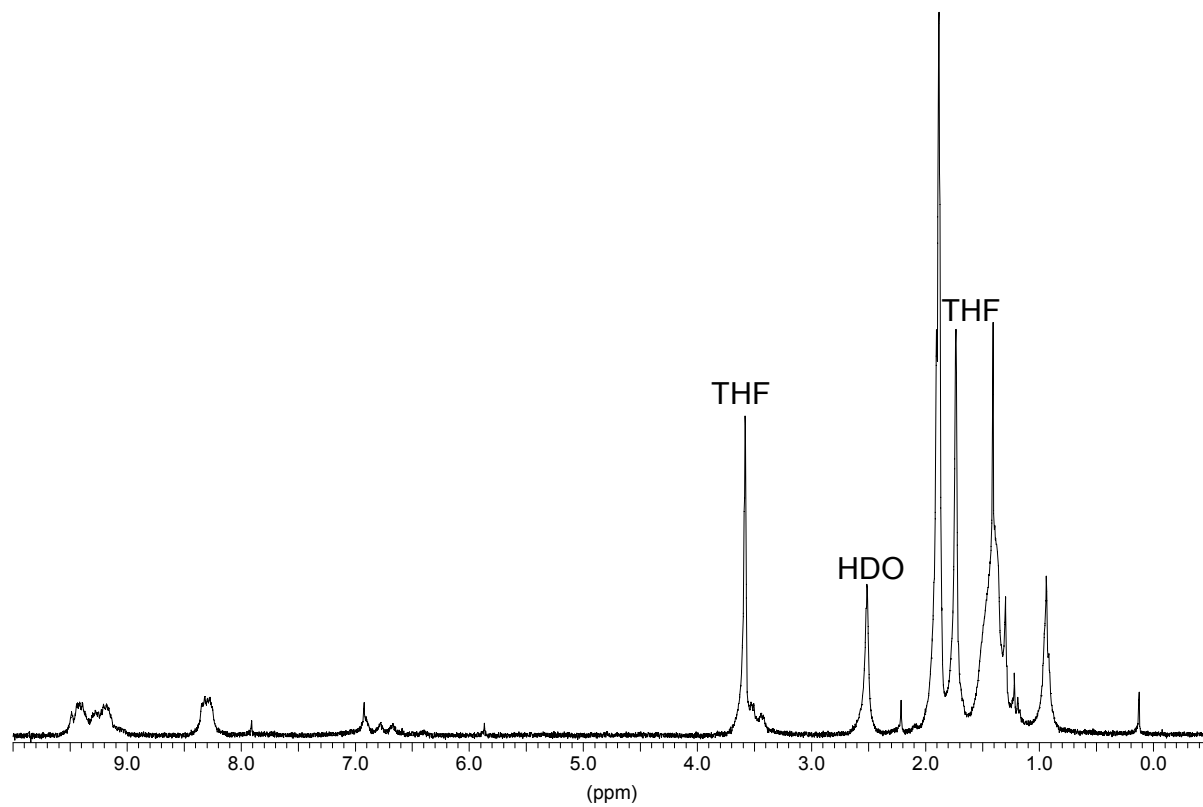


Figure S-5. UV/Vis of **5** in THF

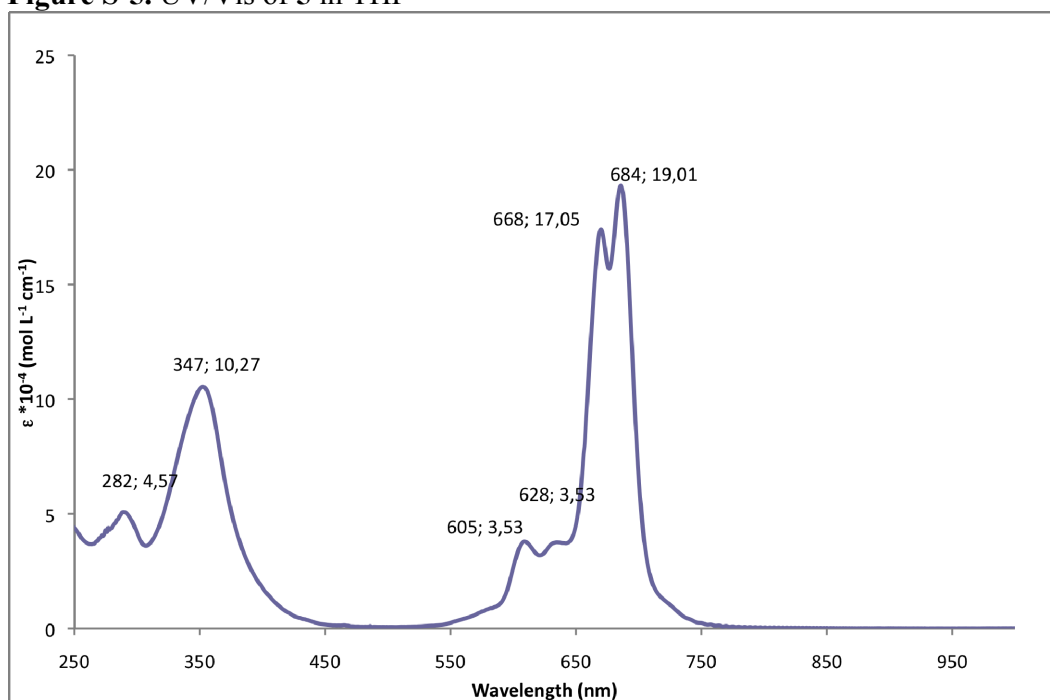


Figure S-6. IR spectrum of **5** in KBr

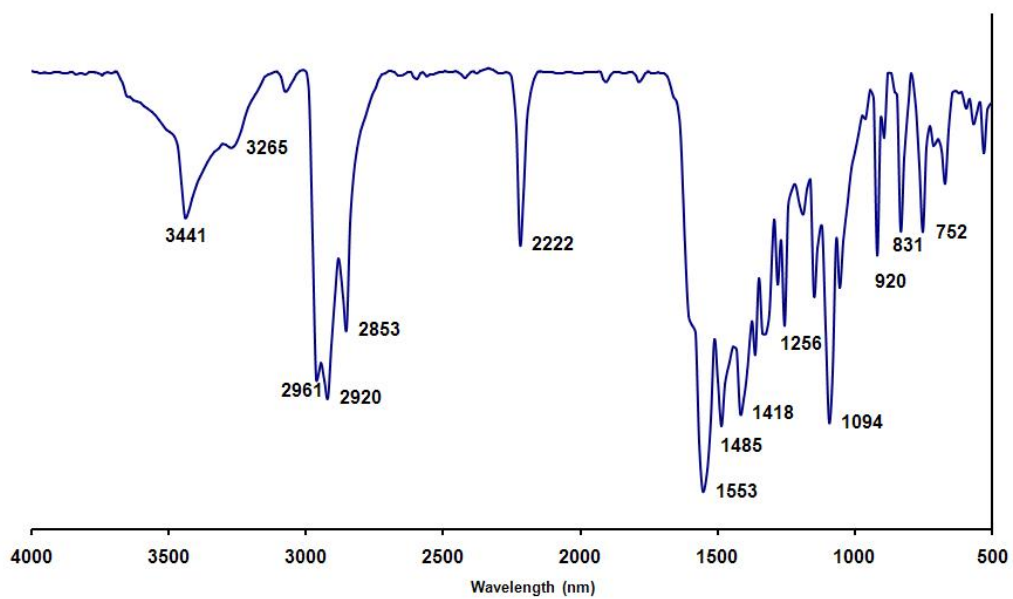


Figure S-7. MS (MALDI-TOF) of **5**

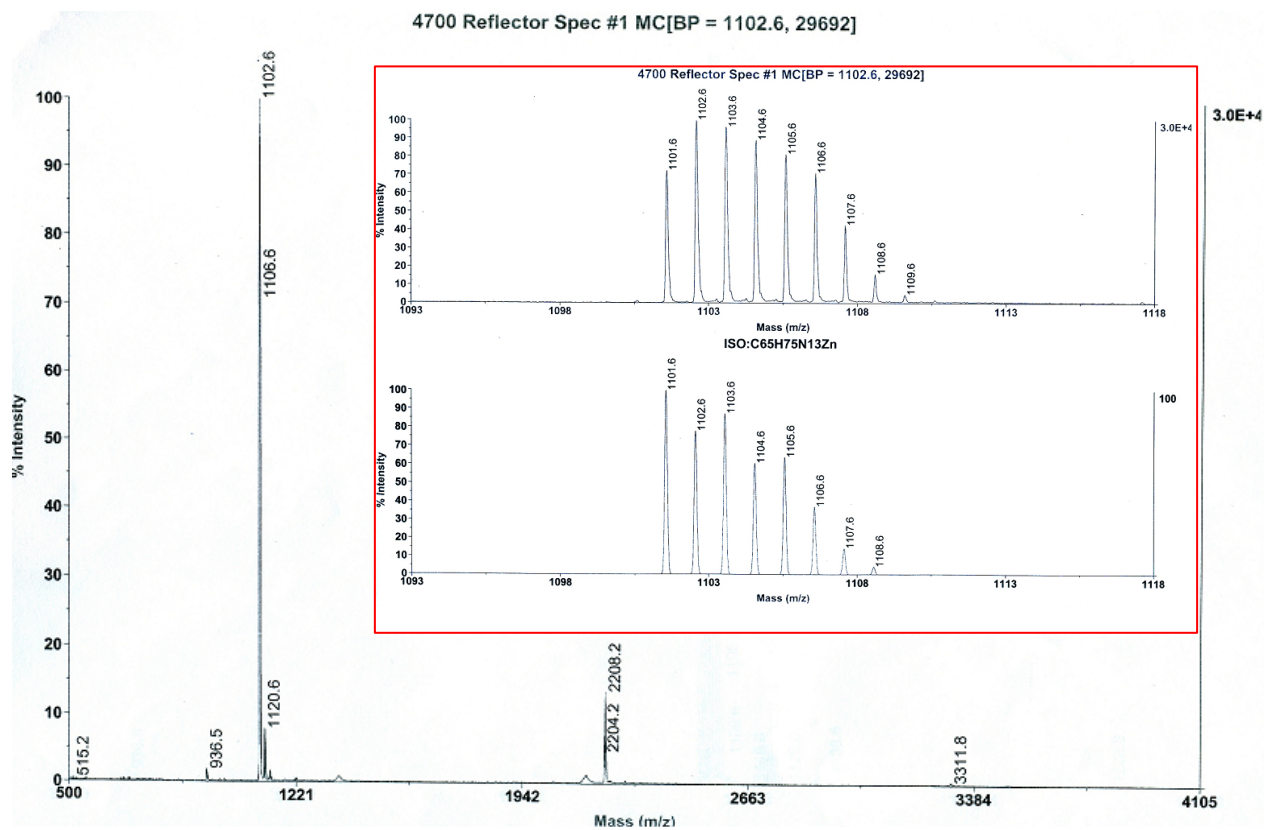


Figure S-8. UV/Vis spectra of Pc **5** in chloroform (blue line, $c = 2.2 \times 10^{-6}$), Pc **5**/PDI **1** (2:1) (red line) and Pc **5**/PDI **1** (1:1) (green line), illustrating the disaggregating effect of Pc upon addition of PDI.

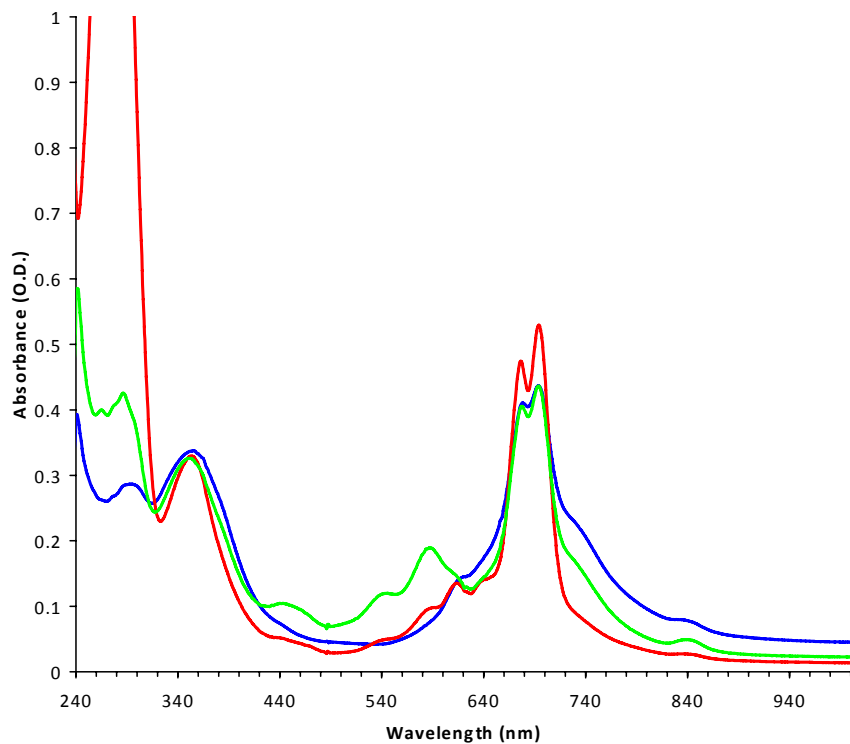


Figure S-9. Upper part – differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (530 nm) of PDI **1** (10^{-5} M) in deoxygenated THF with several time delays between 0 and 3000 ps at room temperature. Lower part – time-absorption profiles of the femtosecond spectra at 440 and 704 nm, monitoring the intersystem crossing in THF.

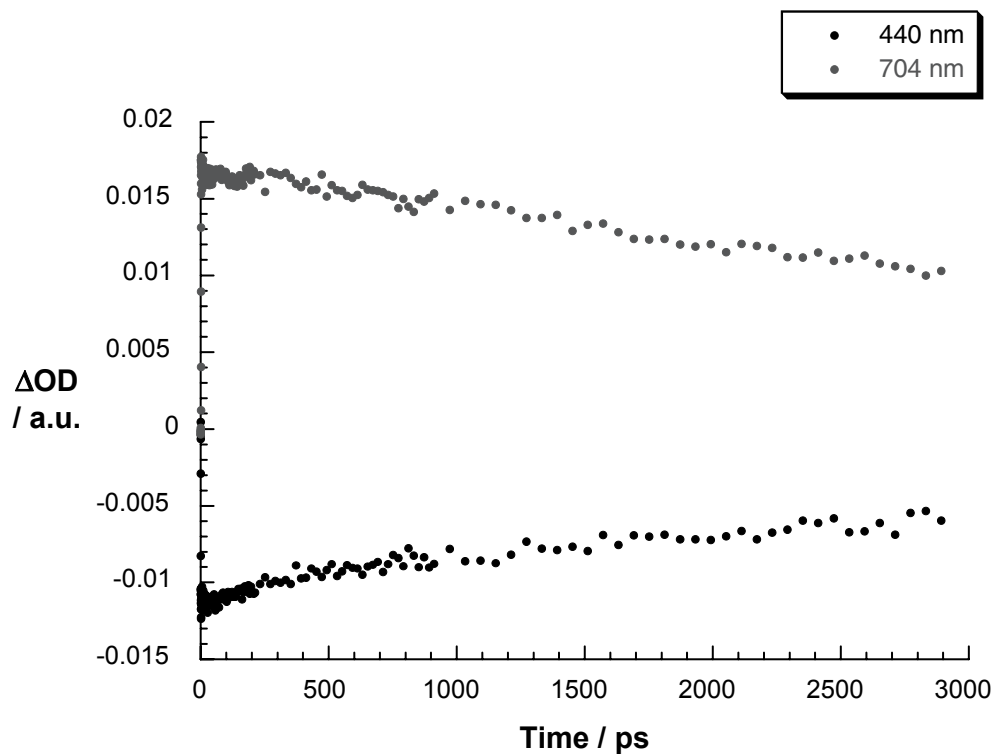
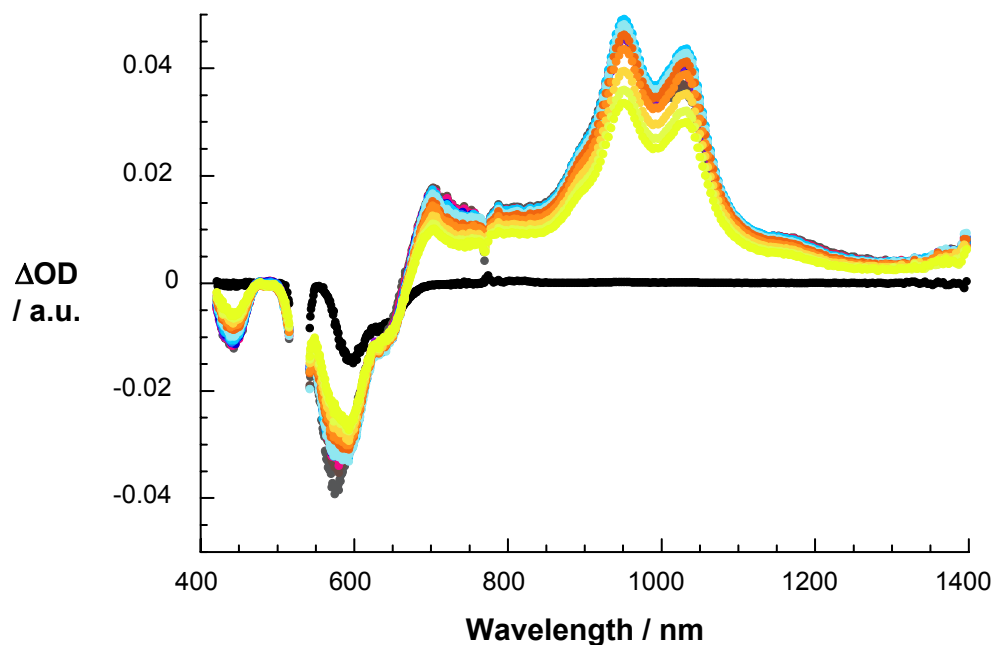


Figure S-10. Upper part – differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (680 nm) of ZnPc **5** (10^{-5} M) in deoxygenated THF with several time delays between 0 and 3000 ps at room temperature. Lower part – time-absorption profile of the femtosecond spectra at 866 nm, monitoring the intersystem crossing in THF.

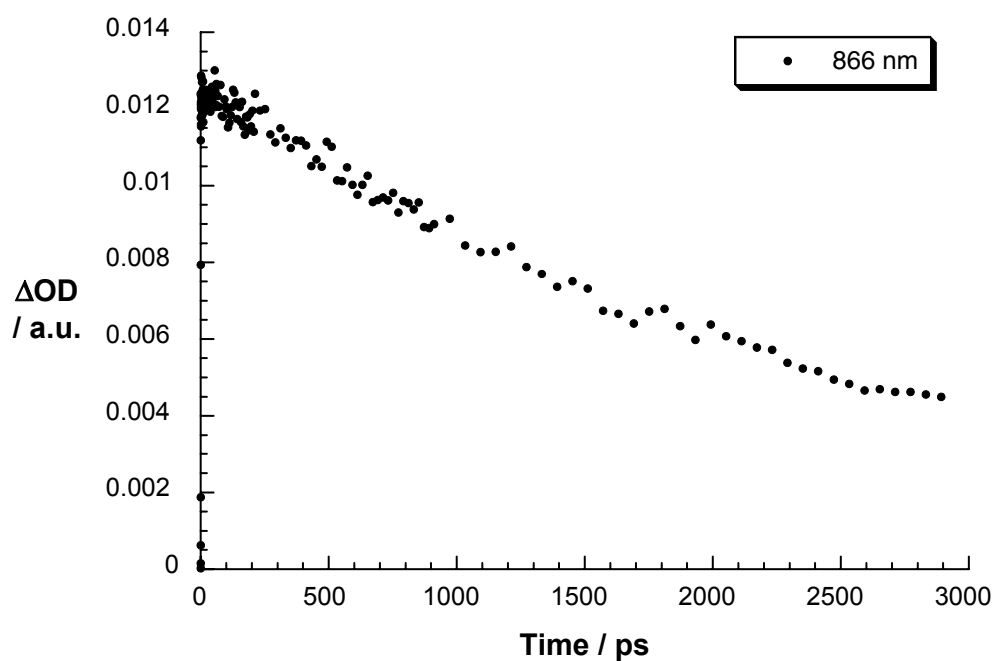
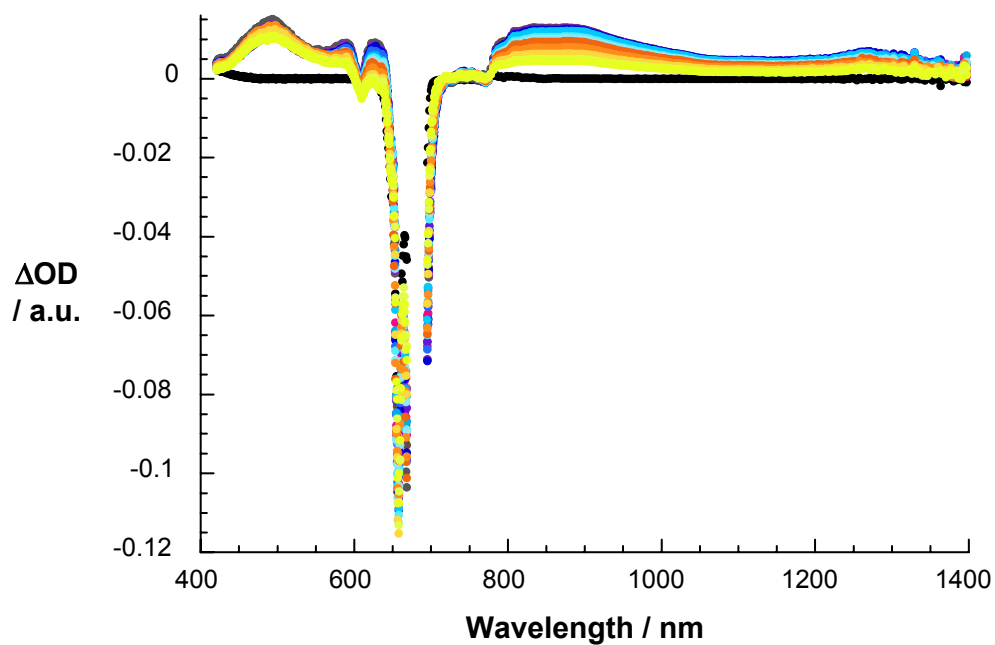


Fig. S-11. Upper part – differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (530 nm) of PDI / ZnPc (1:1) in deoxygenated THF with several time delays between 0 and 3000 ps at room temperature. Lower part – time-absorption profiles of the femtosecond spectra at 480, 580, 680, and 711 nm, monitoring the energy transfer in THF.

