Supporting Information

Synthesis, Characterization, and Photophysical properties of a melamine-mediated hydrogen-bonded phthalocyanine-perylenediimide assembly

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Experimental Section

General

Synthesis: UV/Vis spectra were recorded with a Hewlett-Packard 8453 instrument. IR spectra were recorded with a Bruker Vector 22 spectrophotometer. FAB-MS spectra were determined on a VG AutoSpec instrument. MALDI-TOF spectra were recorded with Bruker Reflex III. NMR spectra were recorded with Bruker AC-300 and Bruker DRX-500 instruments. Column chromatography was carried out on silica gel Merck-60 (230-400 mesh, 60 Å) and Biobeads SX-3. TLC was performed on aluminum sheets precoated with silica gel 60 F254 (E. Merck). Compounds **4** and **6** were prepared following reported procedures (references 24b and 23, respectively). All the other chemicals were purchased from Aldrich Chemical Co. and used as received without further purification.

Photophysics:

All solvents used were of spectroscopic grade (99.5%) and were purchased from Sigma-Aldrich. TBu4NPF6 was purchased from Sigma-Aldrich. All solvents and chemicals were used without further purification. Steady-state absorption spectroscopy was performed using a Lambda 2 UV/Vis spectrophotometer (Perkin Elmer). Steady state fluorescence studies were carried out with a FluoroMax3 Fluorometer (HORIBA). Femtosecond transient absorption studies were performed using 530 and 680 nm laser pulses (1 kHz, 150 fs pulse width) from an amplified Ti:Sapphire laser system (Model CPA 2101, Clark-MXR Inc.). Square wave voltammetry (SWV) measurements were performed under argon atmosphere in toluene/acetonitrile (4:1) containing 0.2 M TBu4NPF6 as supporting electrolyte and ferrocene as internal standard. A glassy carbon electrode (3mm diameter) was used as working electrode, a platinum wire as counter electrode, and an Ag wire as reference electrode. All electrochemical measurements were performed with an METROHM FRA 2 µAutolab Type III potentiostat.

Spectroelectrochemistry was performed with an Analytc Jena AG SPECORD S600 spectrophotometer, potentiostat/galvanostat from HEKA elektronics, and WinASPECT software from Analytic Jena AG. Working electrode: Pt-grid from ChemPur, counter electrode: Pt-wire, reference electrode: Ag-wire. All measurements were carried out under argon-atmosphere in toluene/acetonitrile (4:1) and with 0.1 M TBu4NPF6 as supporting electrolyte.

6-chloro-*N*^{2},*N*^{4}-dioctyl-1,3,5-triazine-2,4-diamine (6). A mixture of trichlotriazine (1 g, 5.5 mmol) and DIPEA (1.98 mL, 11.5 mmol) was stirred in THF (25 mL) while 1-octylamine (1.88 mL, 11.5 mmol) was added dropwise. The solution was stirred overnight at room temperature. The solvent was then rotary evaporated and the solid was chromatographed on silica gel using a 4:1 mixture of hexane/ethyl acetate as eluent, to yield 0.9 g (45%) of **6** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ= 6.18 (s, 2H, NH), 3.52, 3.50 (2t, J= 6 Hz, 4H, $NHCH_2$), 1.6-1.7 (m, 4H, $NHCH_2CH_2$), 1.2-1.4 (m, 20H), 0.92 (t, J= 9 Hz, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ= 171.1 (C^6) 165.7 (C^2, C^4), 41.6, 40.5, 31.7, 29.4, 26.9, 22.9, 14.2; FT-IR (KBr) υ(cm^{-1}): 3253, 3119, (NH), 2963, 2922, 2855 (C-H), 1644, 1562, 1411, 1364, 1109, 988, 800, 739; MS (FAB): m/z = 370 $[M+H]^+$.

4-(4,6-bis(octylamino)-1,3,5-triazin-2-amino)phthalonitrile (5). A solution of **6** (0.5 g, 1.4 mmol), 4-aminophthalonitrile (0.38 g, 2.6 mmol), $Pd(PPh_3)_4$ (156 mg, 0.1 mmol), K_2CO_3 (0.26 g, 2.8 mmol) and BINAP (0.23 g, 0.4 mmol) were stirred under

Ar, at reflux temperature in toluene (10 mL) overnight. After cooling to room temperature, the solvent was rotary evaporated and the crude was chromatographed on silica gel using toluene as eluent, to yield 0.23 g (46%) of **5** as a white solid. ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 120 ºC): δ= 8.38 (s, 1H, H^3), 7.71, 7.69 (2d, *J*= 9 Hz, 2H, H^5, H^6), 6.83 (bs, 1H, NH$_{arom}$), 4.98 (bs, 2H, NH$_{aliph}$), 3.36 (t, *J*= 9 Hz, 4H, NHC*H*$_2$), 1.60 (t, *J*= 9 Hz, 4H, NHC*H*$_2$), 1.2-1.4 (m, 20H, CH$_2$), 0.89 (t, *J*= 9 Hz, 6H, CH$_3$); ^{1}H NMR (300 MHz, CDCl$_3$, 25 ºC): δ= 8.49 (bs, 1H, H^3), 7.61 (bs, 2H, H^5, H^6), 7.15 (bs, 1H, NH$_{arom}$), 5.12 (bs, 1H, NH$_{aliph}$), 4.98 (bs, 1H, NH$_{aliph}$), 3.36 (bs, 4H, NHC*H*$_2$), 1.5-1.6 (m, 4H, CH$_2$), 1.2-1.4 (m, 20H, CH$_2$), 0.89 (t, *J*= 9 Hz, 6H, CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, 25 ºC): δ = 166.2, 155.4, 144.5, 133.8, 123.1, 122.0, 117.0, 115.4, 40.8, 31.7, 29.0, 26.8, 22.2, 14.1; FT-IR (KBr) υ(cm^{-1}): 2953, 2928, 2856 (C-H), 2224 (C≡N), 1606, 1566, 1512, 1417, 1366, 1243, 809; UV/Vis (CHCl$_3$) λ_{max}(nm) (log ε) 294; MS (MALDI-TOF, dithranol): *m/z* = 476.3 [M]$^+$.

Synthesis of 9,10,16,17,23,24-hexakis(hexathio)-2-(4,6-bis(octylamino)-1,3,5-triazin-2-amino)-phthalocyanine (3). A solution of 14 mg of Li was stirred in pentanol (10 mL) until complete consume. Then, phthalonitriles **4** (0.6 g, 1.66 mmol) and **5** (0.2 g, 0.42 mmol) were added and the mixture was refluxed for 15 h. The reaction was cooled to room temperature and a 1:1 mixture of water and methanol was added. The solid was collected after centrifugation and chromatographed on silica gel using a 16:1 mixture of DCM and THF as eluent, affording 94 mg (15%) of **3** as a green solid. ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 120 ºC): δ= 9.27 (s, 1H, H^1), 9.08 (d, *J*= 5 Hz, 1H, H^4), 8.99 (s, 1H, NH$_{arom}$), 8.97, 8.96, 8.95 (3s, 6H, H^8, H^{11}, H^{15}, H^{18}, H^{22}, H^{25}), 8.53 (d, *J*= 5 Hz, 1H, H^3), 5.14 (bs, 1H, NH$_{aliph}$), 3.60-3.63 (m, 4H, NHC*H*$_2$), 3.40-3.44 (m, 12H, SC*H*$_2$), 1.2-2.0 (5 m, 72H, CH$_2$), 0.96-0.99 (t, 18H, CH$_3$), 0.81 (t, *J*= 9 Hz, 6H, CH$_3$), −1.20 (bs, 2H, NH$_{Pc}$); ^{1}H NMR (300 MHz, CDCl$_3$, 25 ºC): δ = 7.6-8.8 (bm, 10H, H_{arom}, NH_{arom}), 5.98, 5,62, 5.20 (3bs, 3H, N*H*), 3.6-3.8 (broad s, 4H, $NHCH_2$), 3.2-3.5 (m, 12H, SCH_2), 1.0-2.2 (5 m, 72H, CH_2) 0.5-1.0 (3m, 24H, CH_3), −3.0-(−4.0) (bs, 2H, NH_{Pc}); FT-IR (KBr) υ(cm^{-1}): 2953, 2926, 2853 (C-H), 1712, 1591, 1517, 1408, 1375, 1079, 943, 804, 739; UV/Vis ($CHCl_3$) λ_{max}(nm) (log ε)= 332 (4.96), 429 (4.65), 643 (4.65), 663 (4.84), 697 (5.15), 726 (5.14); MS (MALDI-TOF, dithranol): *m/z* = 1559 $[M+H]^+$.

4,5-bis(hexylthio)phthalonitrile (4).

Figure S1: ^{1}H NMR ($CDCl_3$) of **4**

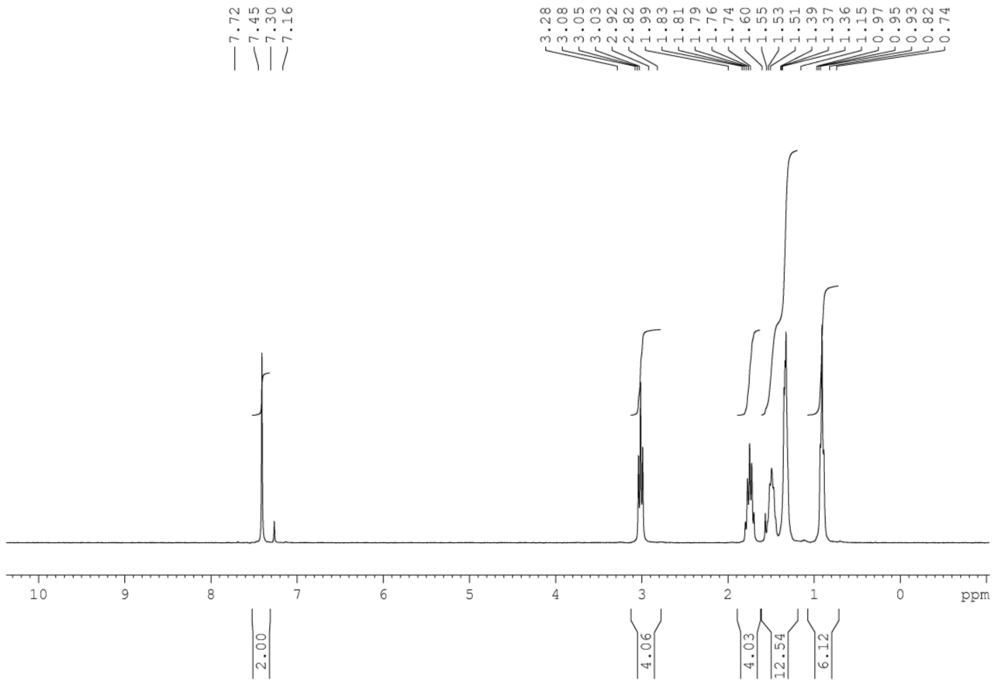
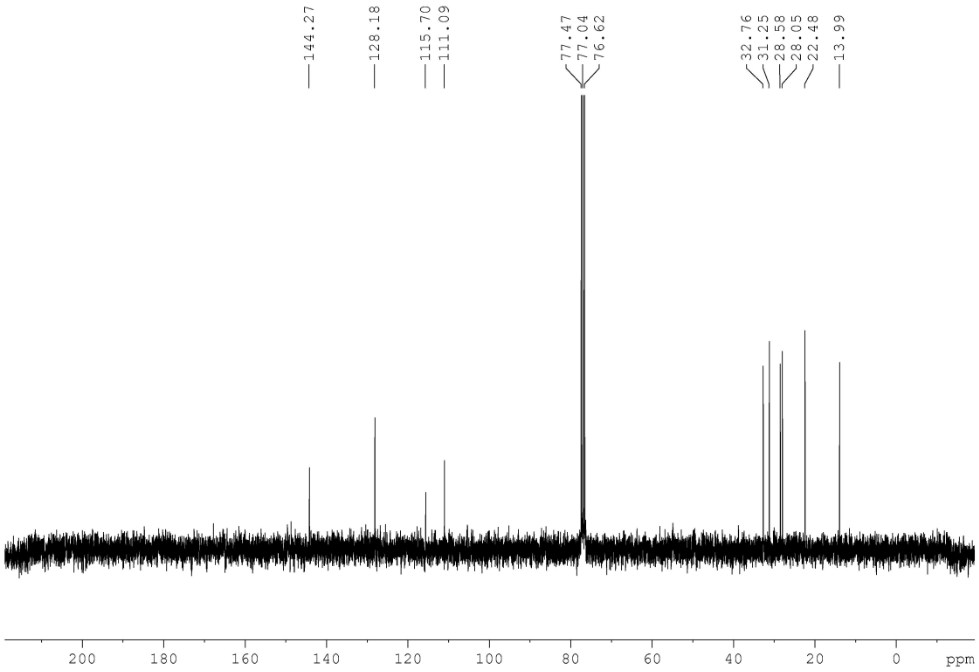


Figure S2: ^{13}C NMR ($CDCl_3$) of **4**



6-chloro-*N*^{2},*N*^{4}-dioctyl-1,3,5-triazine-2,4-diamine (6).

Figure S3: ^{1}H NMR ($CDCl_3$) of **6**

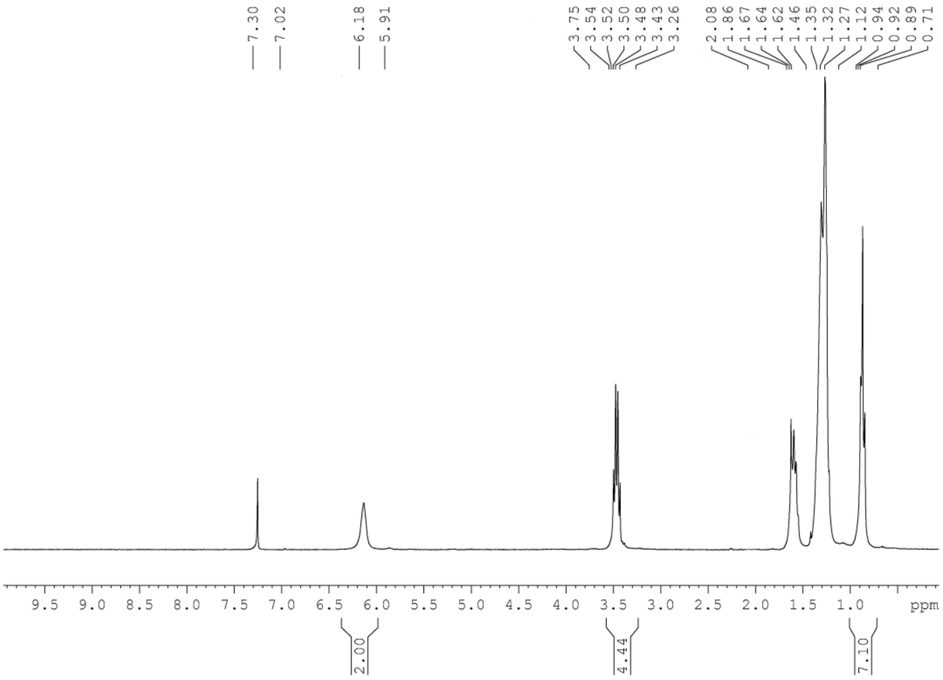


Figure S4: ^{13}C NMR ($CDCl_3$) of **6**

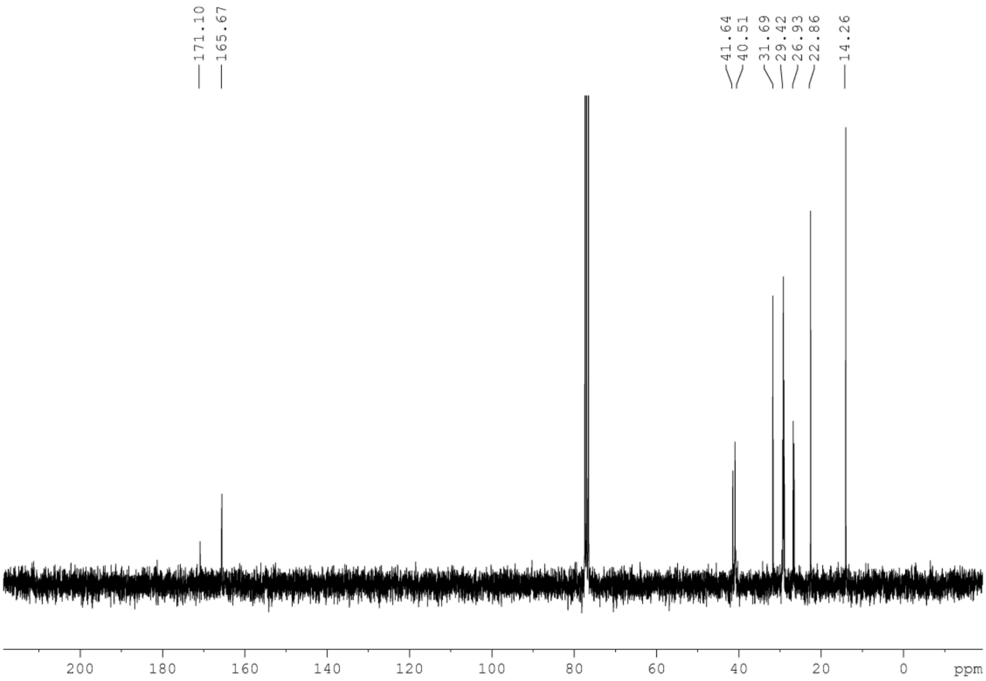
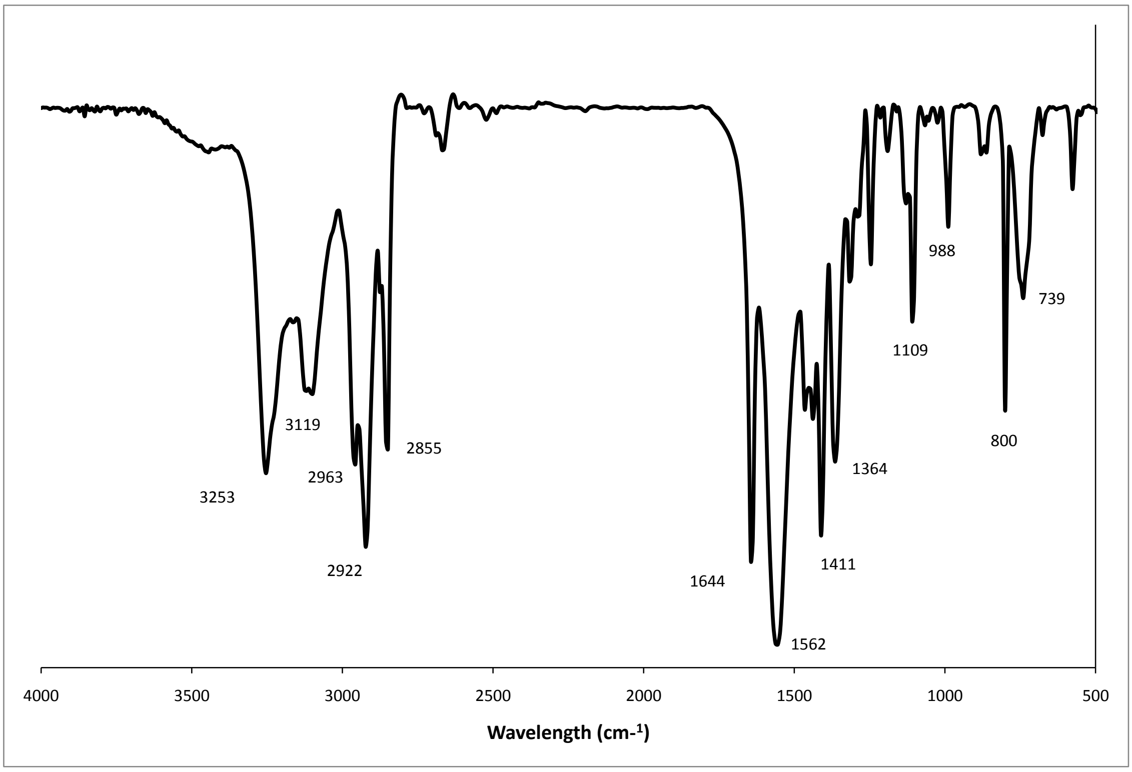


Figure S5: IR spectrum (KBr) of **6**



4-(4,6-bis(octylamino)-1,3,5-triazin-2-amino)phthalonitrile (5)

Figure S6: ^{13}C NMR ($CDCl_3$) of **5**

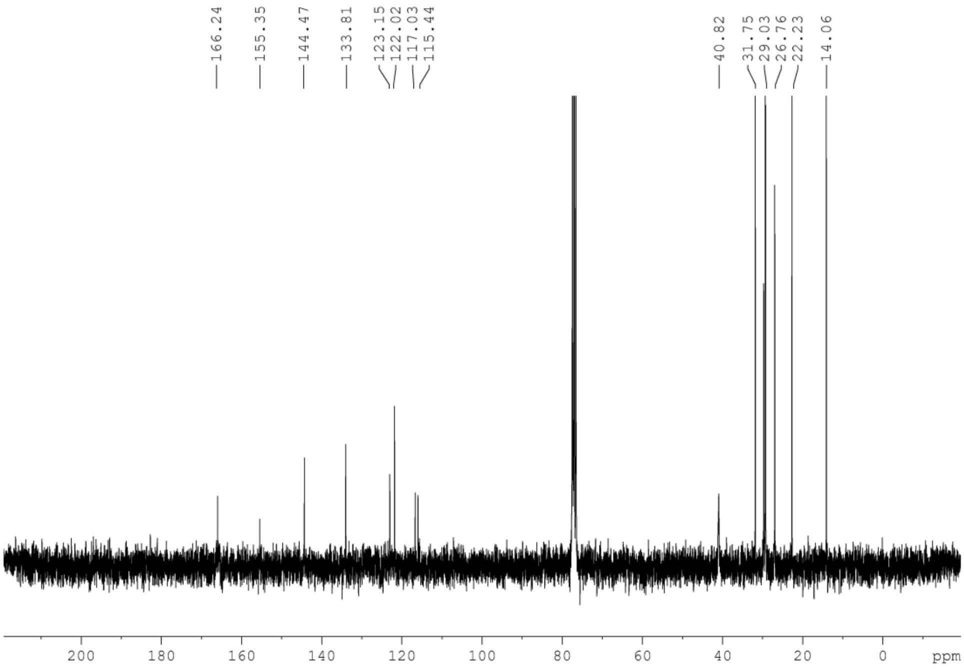


Figure S7: IR (KBr) of **5**

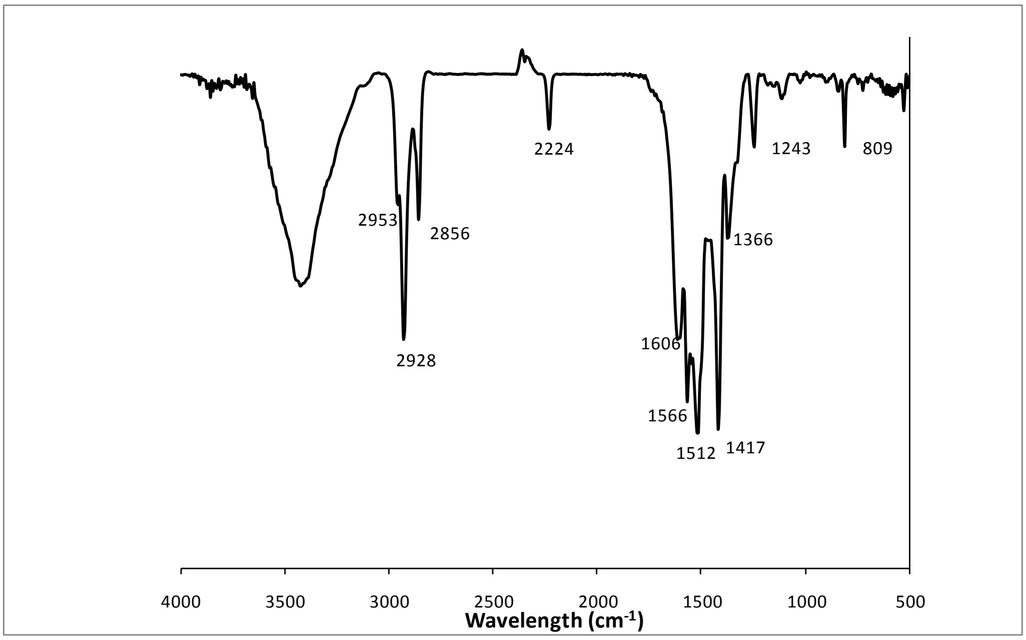
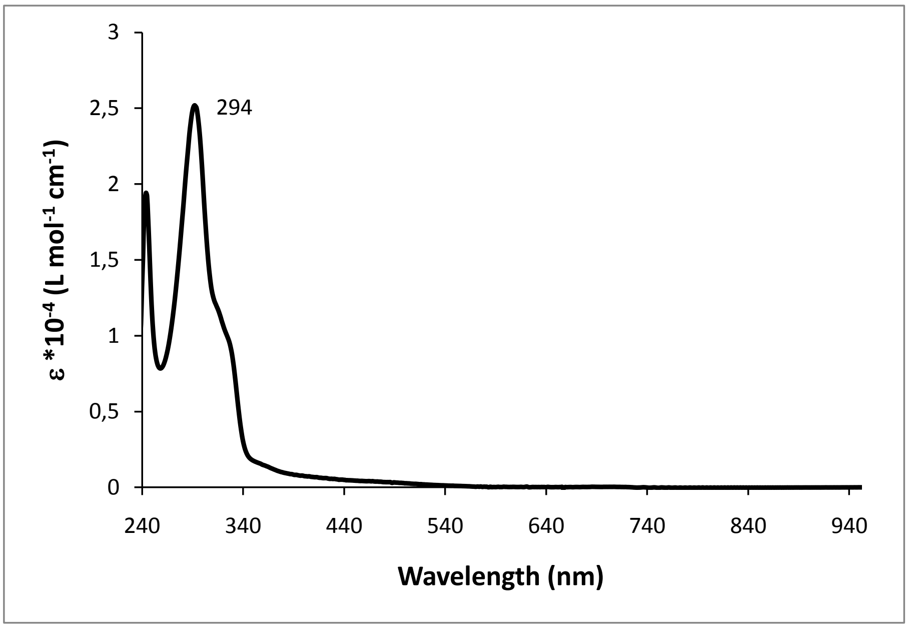


Figure S8: UV/Vis spectrum ($CHCl_3$) of **5**



1,3,9,10,16,17-hexakis(hexathio)-23-4-(4,6-bis(octylamino)-1,3,5-triazin-2-amin-)-phthalocyanine (3)

Figure S9: ^{1}H NMR ($C_2D_2Cl_4$, 393K) of **3**

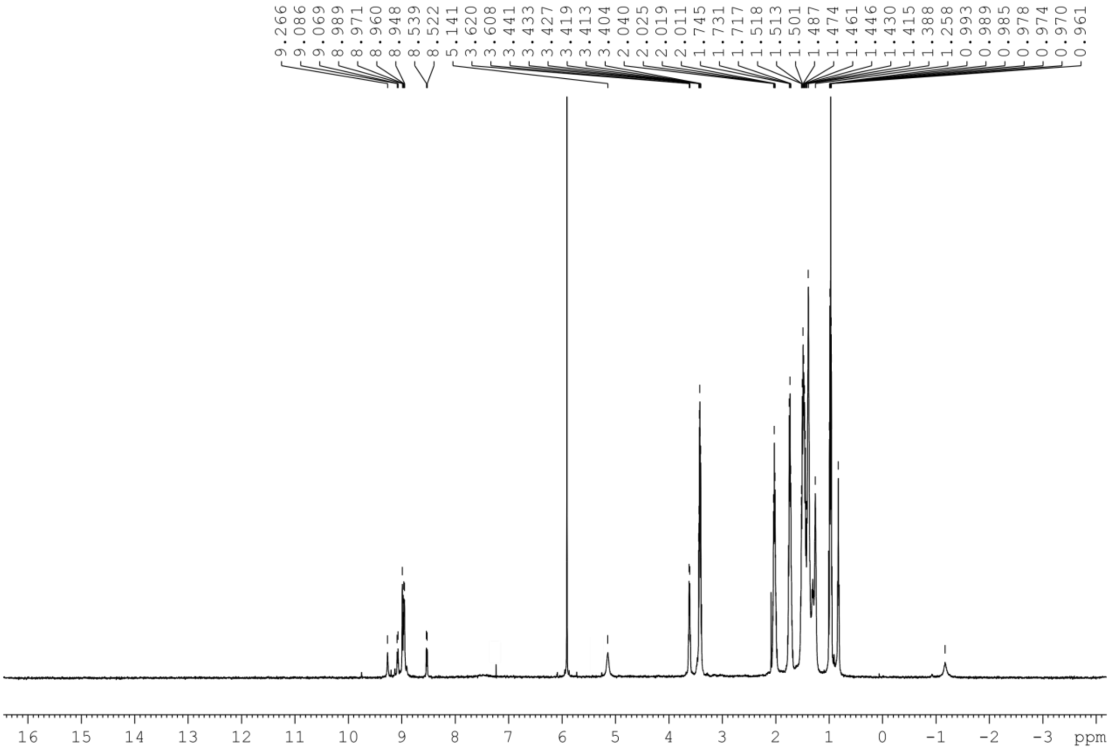


Figure S10: IR spectrum (KBr) of **3**

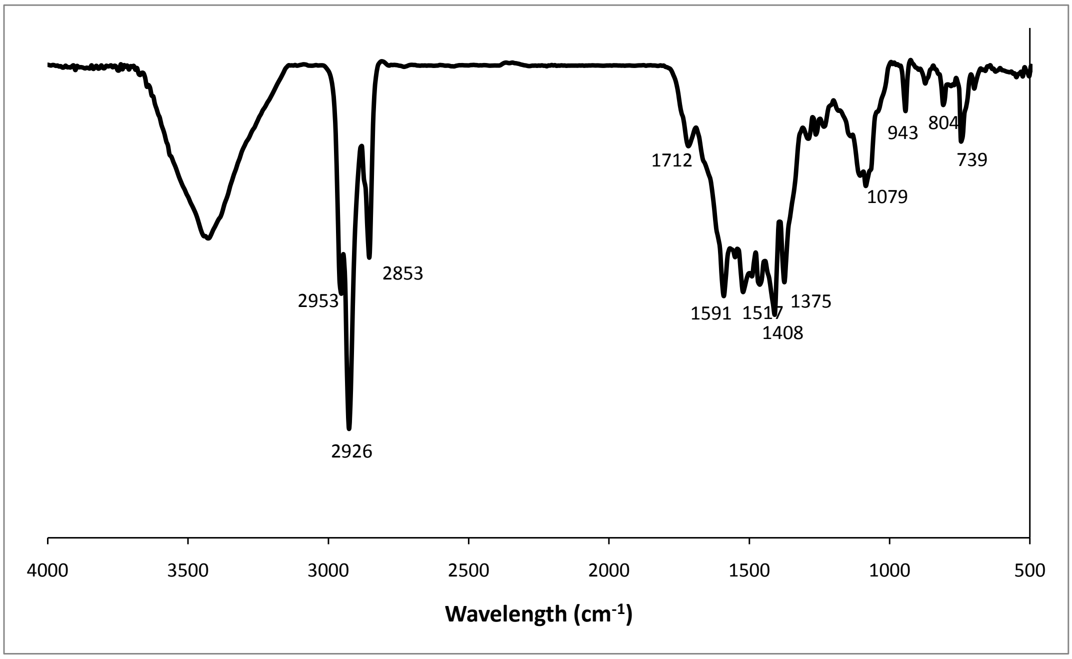
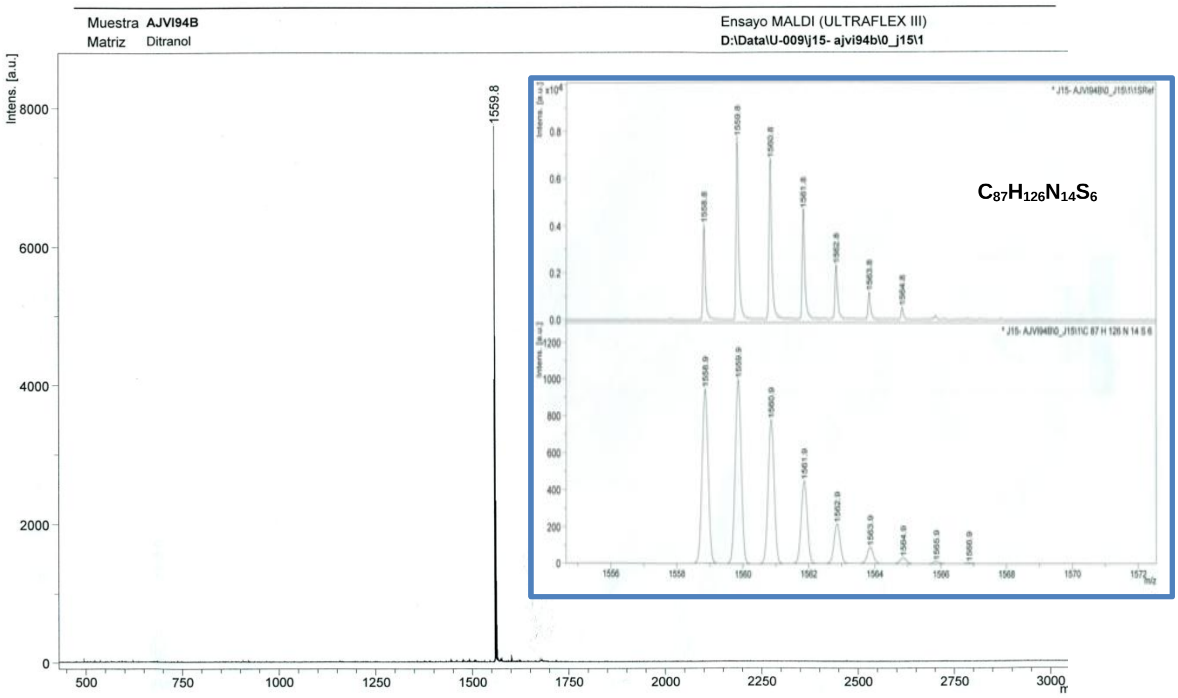


Figure S11: MS of **3**



1,6,7,12-tetrakis(4-*tert*-butylphenyl)perylene)-3,4:9,10-perylene-diimide (2)

Figure S12. ^{1}H NMR of **2**

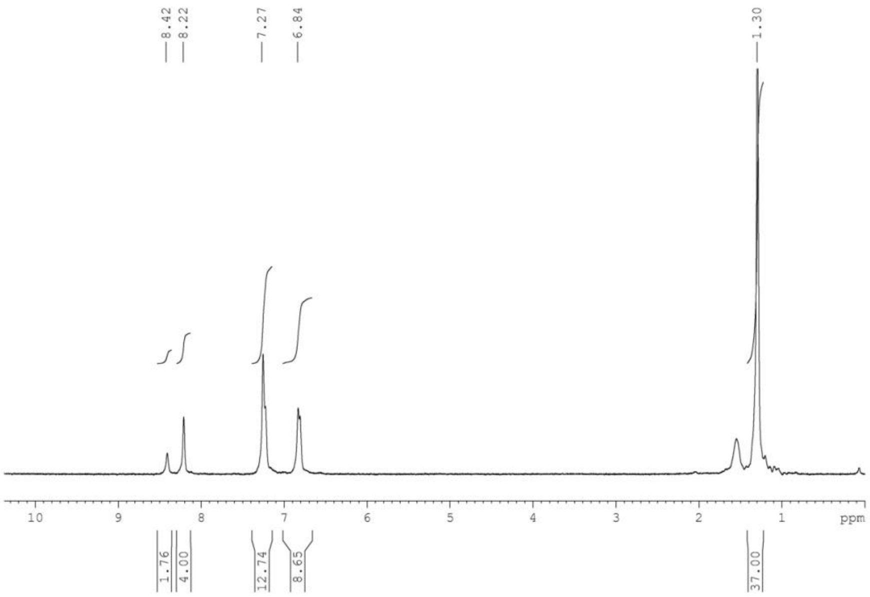


Figure S13. ^{13}C NMR of **2**

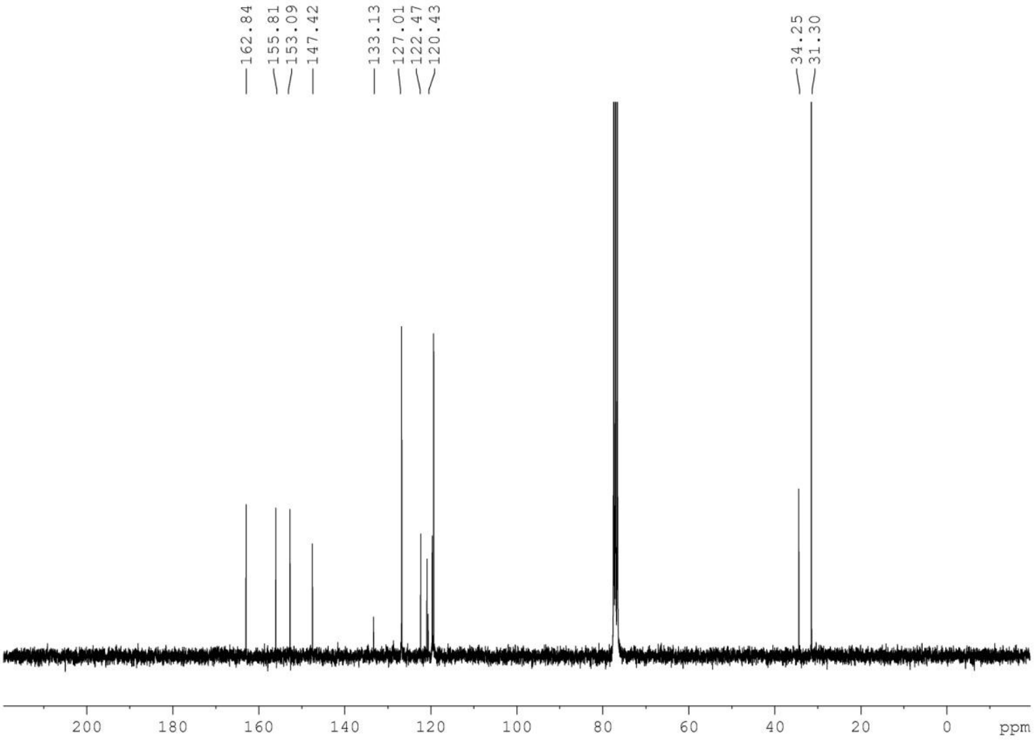


Figure S14. IR spectrum of **2**

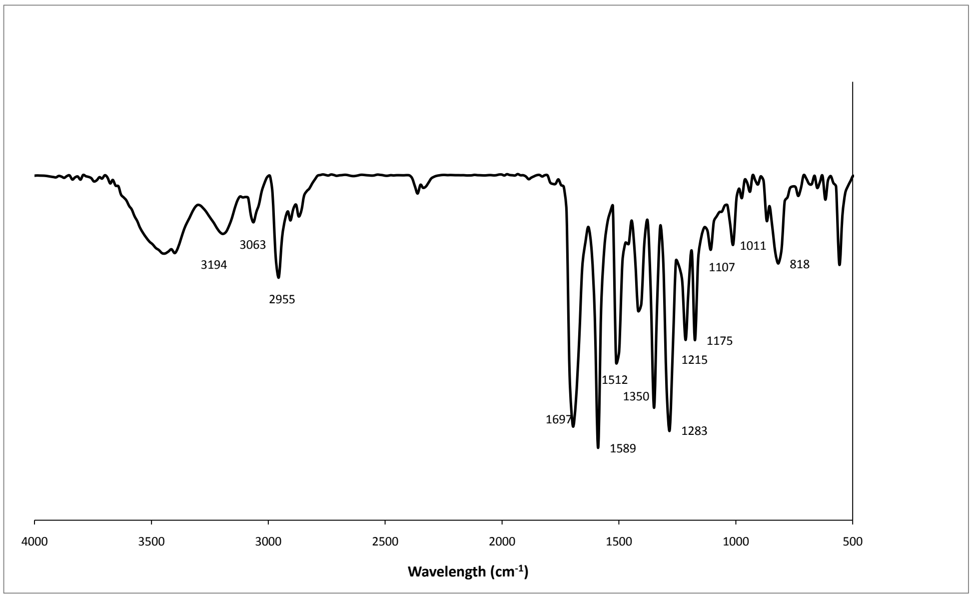


Figure S15. Absorption spectra of a dilute chlorobenzene solution of H_2Pc **3** (5 x 10^{-6}M) with variable concentrations of PDI **2** (0, 0.5 x 10^{-7}; 2.0 x 10^{-7}; 2.0 x 10^{-7}; 4.9 x 10^{-7}; 9.5 x 10^{-7}; 1.4 x 10^{-6}; 2.2 x 10^{-6}; 4.0 x 10^{-6}; 5.5 x 10^{-6}; 6.7 x 10^{-6} M). Arrows indicate the progression of the titration.

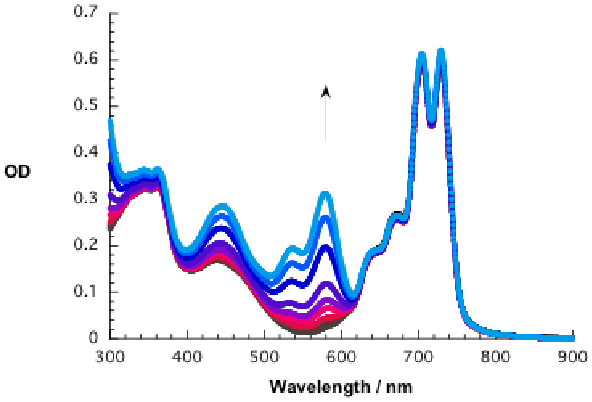


Figure S16. Fluorescence spectra upon 680 nm excitation of a dilute chlorobenzene solution of H_2Pc **3** (5 x 10^{-6} M) with variable concentrations of PDI **2** (0, 0.5 x 10^{-7}; 2.0 x 10^{-7}; 2.0 x 10^{-7}; 4.9 x 10^{-7}; 9.5 x 10^{-7}; 1.4 x 10^{-6}; 2.2 x 10^{-6}; 4.0 x 10^{-6}; 5.5 x 10^{-6}; 6.7 x 10^{-6}) – corrected for absorption.

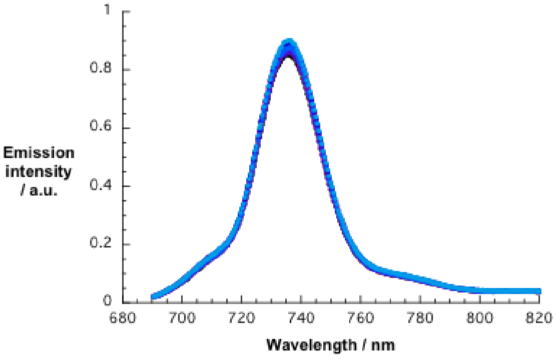


Figure S17. Differential absorption spectra obtained upon electrochemical reduction of PDI 2 in toluene/acetonitrile (4:1) at an applied potential of -1.0 V versus Ag wire.

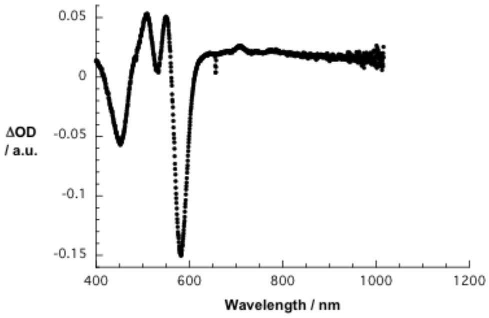


Figure S18. Differential absorption spectra obtained upon electrochemical oxidation of H2Pc 3 in toluene/acetonitrile (4:1) at an applied potential of +1.0 V versus Ag wire.

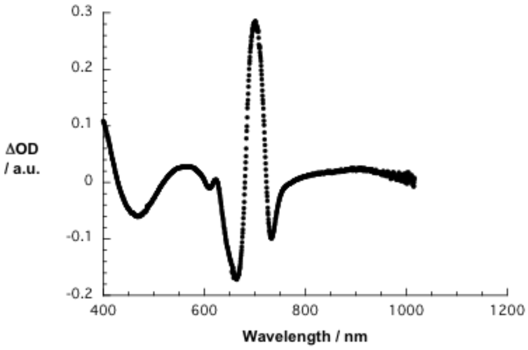


Figure S19. Upper part – differential absorption spectra (visible) obtained upon femtosecond flash photolysis (680 nm) of a 1:10 mixture of 2 / 3 (OD680 = 0.4) in deoxygenated chlorobenzene with several time delays between 1 and 7500 ps at room temperature. Lower part – time-absorption profiles of the femtosecond spectra at 550 and 700 nm.