SUPPORTING INFORMATION

Rational design of a phthalocyanine-perylenediimide dyad a with long-lived charge-separated state

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CONTENTS

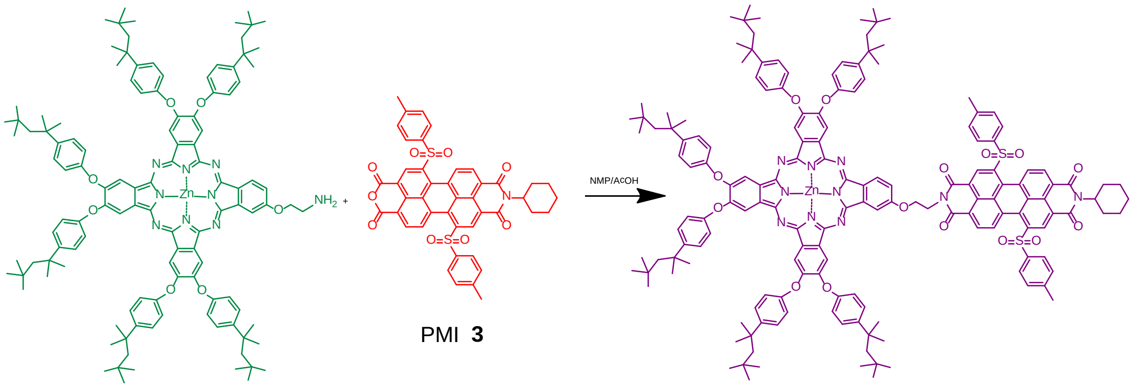
Materials and methods for the synthesis of new compounds.

General methods. Solvents and reagents were obtained from commercial source and used as received. Column chromatography: SiO_2 (40-63 μm) TLC plates coated with SiO_2 60F254 were visualized by UV light. NMR spectra were recorded at 25°C using a Bruker AC300 spectrometer. The solvents for spectroscopic studies were of spectroscopic grade and used as received. UV/Vis spectra were measured with a Helios Gamma spectrophotometer. IR spectra were recorded with Nicolet Impact 400D spectrophotometer. High resolution Mass spectra were obtained from a Bruker Reflex II matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) using dithranol as matrix. Melting points were measured with Melting Point Apparatus SMP3.

Transient absorption measurements. Femtosecond transient absorption spectroscopy experiments were conducted using an ultrafast source: Integra-C (Quantronix Corp.), an optical parametric amplifier: TOPAS (Light Conversion Ltd.) and a commercially available optical detection system: Helios provided by Ultrafast Systems LLC. The source for the pump and probe pulses were derived from the fundamental output of Integra-C (780 nm, 2 mJ/pulse and fwhm = 130 fs) at a repetition rate of 1 kHz. 75% of the fundamental output of the laser was introduced into TOPAS, while the rest of the output was used for white light generation. Prior to generating the probe continuum, a variable neutral density filter was inserted in the path in order to generate stable continuum, then the laser pulse was fed to a delay line that provides an experimental time window of 3.2 ns with a maximum step resolution of 7 fs. In our experiments, a wavelength at 410 nm of TOPAS output, which is fourth harmonic of signal or idler pulses, was chosen as the pump beam. As this TOPAS output consists of not only desirable wavelength but also unnecessary wavelengths, the latter was deviated using a wedge prism with wedge angle of 18°. The desirable beam was irradiated at the sample cell with a spot size of 1 mm diameter where it was merged with the white probe pulse in a close angle ($< 10^{\circ}$). The probe beam after passing through the 2 mm sample cell was focused on a fiber optic cable that was connected to a CCD spectrograph for recording the time-resolved spectra (410-800 nm). Typically, 2500 excitation pulses were averaged for 5 seconds to obtain the transient spectrum at a set delay time. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. All measurements were conducted at room temperature, 295 K.

Nanosecond laser flash photolysis experiments were performed using a Panther OPO pumped by Nd:YAG laser (Continuum, SLII-10, 4-6 ns fwhm) at λ = 355 and 530 nm with the power of 10 mJ per pulse. The transient absorption measurements were performed using a continuous wave xenon lamp (150 W) and a photomultiplier (Hamamatsu 2949) as a probe light and a detector, respectively. The output from a photomultiplier was recorded on a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz).

Synthesis of Dyad ZnPc-PDI 1



ZnPc **2**

PMI **3**

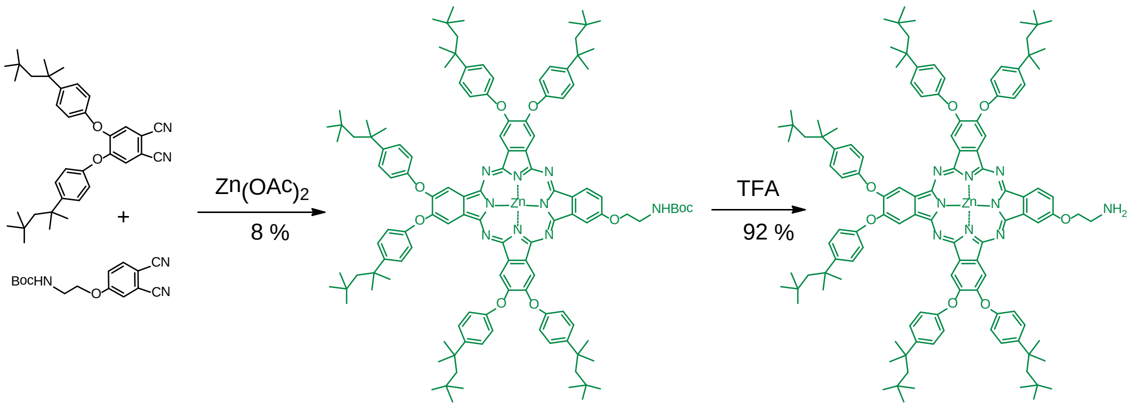
Dyad ZnPc-PDI **1**

2,3,9,10,16,17-Hexakis(*p-tert*-octylphenoxyl)-23-[2'-[*N*-Cyclohexyl-1'',7''-bis(*p*-tolylsulfonyl)perylene-3'',4'':9'',10''-tetracarboxydiimide-N'-yl]ethoxy]phthalocyaninate zinc (II) (1)

48 mg (0.025 mmol) of ZnPc **2** and 20 mg (0.025mmol) of PMI **3** were dissolved in 1 mL of a NMP:AcOH/25:1 solution. The mixture was heated up to 85°C under argon during 24 h. The crude was diluted in DCM, washed with $NaHCO_3$ (aq) and H_2O. The organic layer was dried with Na_2SO_4 and concentrated in vacuum. The compound was purified by column chromatography ($CHCl_3$:THF/99:1), affording 36.6 mg of dyad ZnPc-PDI **1** (54 %).

- ^{1}H RMN (THF-d_8) δ 0.83-0.94 (54H, H-Pc), 1.39-1.51 (44H, H-Pc and H-PDI), 1.80-1.93 (12H, H-Pc), 2.45 (8H, H-PDI), 4.81 (3H, H-Pc and H-PDI), 5.04 (2H, H-Pc), 6.70-7.60 (36H, H-Pc and H-PDI) and 8.14-9.12 ppm (11H, H-Pc and H-PDI).
- FT-IR (KBr): ν 2951, 1703, 1666, 1590, 1505, 1452, 1397, 1335, 1266, 1216, 1088, 1028 and 891 cm^{-1}.
- UV-Vis (THF), λ_{max}/nm (log ε): 358 (4.73), 535 (4.34), 615 (4.24) and 681 (5.06).
- HRMS (MALDI-TOF): *m/z* for $C_{162}H_{170}N_{10}O_{15}S_2Zn$ calcd. 2623.1575; found 2623.1527 (M$^+$).

Synthesis of ZnPc 2



ZnPc **4** ZnPc **2**

2,3,9,10,16,17-Hexakis-[*p*-(*tert*-octyl)phenoxyl]-23-(2’-*tert*-butoxycarbonylaminoethoxy) phthalocyaninate zinc (II) (ZnPc 4)

A mixture of 197 mg (0.67 mmol) of 4-(2-*tert*-butoxycarbonylaminoethoxy)phthalonitrile,[1] 1.1 g (2 mmol) of 4,5-bis(*p*-*tert*-octylphenoxyl)phthalonitrile,[2] 246 mg (1.34 mmol) of zinc acetate and two drops of DBN were dissolved in 3 mL of DMAE in argon atmosphere. The reaction mixture was refluxed for 14 hours, then was cooled to room temperature and precipitated with a mix MeOH:H_2O/9:1 two times. The crude was purified by column chromatography ($CHCl_3$:EtOAc/95:5), yielding 105 mg of **4** (8%).

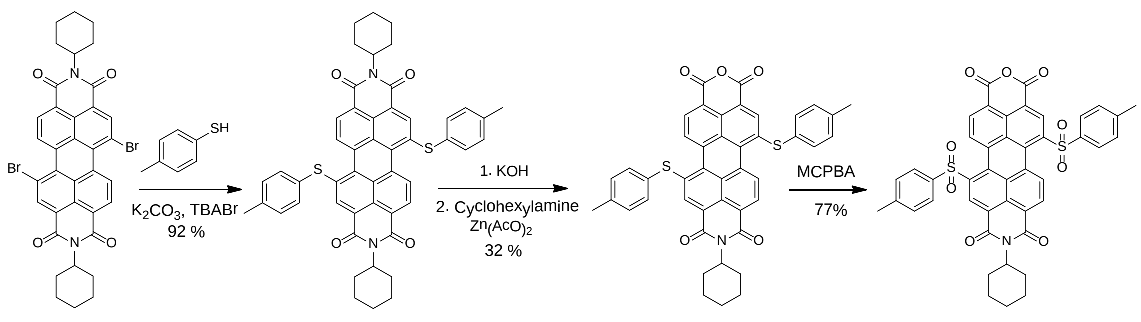
- ^{1}H RMN (THF-d_8) δ 0.83-0.94 (m, 54H), 1.42-1.49 (m, 45H), 1.83-1.93 (m, 12H), 3.69 (m, 2H), 4.50 (t, *J*= 5.4 Hz, 2H), 6.50 (br s, 1H), 7.16-7.73 (25H) and 8.87-9.20 ppm (8H).
- FT-IR (KBr): ν 2952, 2901, 1719, 1606, 1506, 1488, 1452, 1269, 1217, 1179, 1088, 1029 and 892 cm^{-1}.
- UV-Vis (DMF), λ_{max}/nm (log ε): 363 (4.96), 611 (4.59) and 679 (5.30).
- HRMS (MALDI-TOF): *m/z* for $C_{123}H_{149}N_9O_9Zn$ calcd. 1960.0764; found 1960.1026 (M^+).

2,3,9,10,16,17-Hexakis-[*p*-(*tert*-octyl)phenoxyl]-23-(2’-aminoethoxy)phthalocyaninate zinc (II) (ZnPc 2)

136 mg (0.07 mmol) of ZnPc **4** was dissolved in 2 mL of a mixture DCM:TFA/1:1. The solution was cooled at 0°C during 3 hours. EtOAc (20 mL) was added and the organic layer was washed with NaOH (2M) and H_2O two times. The organic layer was dried with Na_2SO_4 and concentrated in vacuum. Purification by column chromatography (DCM:EtOAc/9:1) afforded 119 mg of **2** (92%).

- FT-IR (KBr): ν 3449, 3061, 2953, 1736, 1607, 1506, 1453, 1269, 1218, 1180, 1089, 1029 and 891 cm^{-1}.
- UV-Vis (THF), λ_{max}/nm (log ε): 362 (4.72), 611 (4.33) and 679 (5.03).
- HRMS (MALDI-TOF): *m/z* for $C_{118}H_{141}N_9O_7Zn$ calcd. 1860.0240; found 1860.0367 (M^+).

Synthesis of PMI-3



PDI 5 PMI 6 PMI 3

N,*N'*-Dicyclohexyl-1,7-bis(*p*-tolylthio)perylene-3,4:9,10-tetracarboxylic acid diimide (PDI 5)

A solution of 1.04 g (1.46 mmol) of dibromo-*N*,*N'*-dicyclohexyl-3,4:9,10-perylenetetracarboxylic acid diimide[1] (mixture of 1,7 and 1,6 isomers), 105 mg (0.19 mmol) of tetrabutylammonium bromide, 2.01 g (14.6 mmol) of K_2CO_3 and 492.9 mg (3.97 mmol) of *p*-toluenethiol were diluted in a mixture xylene:water/5:1. The solution was heated to reflux under argon for 2 hours, then $CHCl_3$ (300 mL) was added and the organic layer was washed with NH_4Cl (2M) and H_2O two times. The organic layer was dried with $MgSO_4$ and concentrated in vacuum. The residue was purified by recrystallization (Hx:Tol/2:1), yielding 1.08 g of a purple solid **5** (92%).

- m.p. > 300°C.
- ^{1}H NMR ($CDCl_3$): δ 1.27-1.90 (m, 16H), 2.39-2.56 (m, 10H), 4.93-5.01 (tt, *J*= 12, 3.8 Hz, 2H), 7.23-7.39 (M, 8H), 8.40 (s, 2H) and 8.66-8.74 ppm (M, 4H).
- ^{13}C NMR ($CDCl_3$): δ 21.4, 25.3, 26.5, 29.1, 53.9, 122.1, 122.6, 125.6, 128.1, 128.8, 129, 129.2, 130.9, 131.6, 132.4, 132.8, 134.4, 139.2, 140.1, 163.5 and 163.7 ppm.
- FT-IR (KBr): v 2929, 2850, 1692, 1655, 1584, 1396, 1324, 1240, 1186 and 809 cm^{-1}.
- UV-vis (THF): λ_{max}/nm (log ε): 225 (4.87), 437 (4.15) and 555 (4.50).
- HRMS (MALDI-TOF): *m/z* for $C_{50}H_{42}N_2O_4S_2$ calcd. 798.2580; found 798.2616 (M^-).

N-Cyclohexyl-1,7-bis(*p*-tolylthio)perylene-3,4-dicarboxyanhydride-9,10-dicarboximide (PMI 6).

A suspension of 1.5 g (1.87 mmol) of **5** and 12.89 g (43.01 mmol) of KOH in 97 mL of 2-propanol and 7ml of water was vigorously stirred and refluxed under argon for 3h. During the course of the reaction the color changed from purple (diimide) to brown (tetracarboxylate anion). After cooled to room temperature, the saponification was quenched by adding 430 mL of acetic acid. The purple precipitate was filtered off and repeatedly washed with water and methanol. A mixture of 33 mg (0.052 mmol) of this crude product, 69 mg (0.19 mmol) of $Zn(AcO)_2 \cdot 2H_2O$, and 23 mg (0.23 mmol) of cyclohexylamine in 1.4 mL of pyridine was warmed to 80°C under argon and stirred for 3 days. After cooling to room temperature, the reaction mixture was poured into 15 ml of acetic acid for 1 hour. $CHCl_3$ (50 ml) was added and the organic layer was washed with 2M HCl and water 2 times. The residue was purified by column chromatography over silica gel with $CHCl_3$:Hx/8:2, to give 12 mg of purple solid **6** (32%).

- m.p. > 300 °C;

- ^{1}H NMR (CDCl$_3$): δ 1.36-1.86 (m, 8H), 2.41-2.52 (m, 8H), 4.97 (tt, *J*= 12, 3.8 Hz, 1H), 7.24-7.41 (m, 8H), 8.34 (s, 1H), 8.37 (s, 1H) and 8.66-8.73 ppm (m, 4H).
- ^{13}C NMR (CDCl$_3$): δ 21.4, 21.5, 25.3, 26.4, 29.1, 54.1, 122.7, 123.3, 125.5, 127.8, 128.3, 128.6, 128.6. 128.8, 128.9, 129.0, 129.7, 130.6, 130.9, 131.0, 131.1 (2C), 131.2 (2C), 131.7, 132.6 132.7, 133.2, 134.1, 134.5 (2C), 134.6 (2C), 134.6, 134.7, 134.8, 139.9, 140.5, 140.7, 140.8, 159.7, 159.8, 163.3 and 163.5 ppm.
- FT-IR (KBr): ν 2924, 2852, 1774, 1736, 1699, 1659, 1587, 1397, 1380, 1314, 1239, 1217, 1160 and 807 cm^{-1}.
- UV-vis (THF): λ_{max}/nm (log ε): 225 (4.82), 437 (4.09) and 553 (4.39).
- HRMS (MALDI-TOF): *m/z* for $C_{44}H_{31}NO_5S_2$ calcd. 717.1649; found 717.1549 (M$^-$).

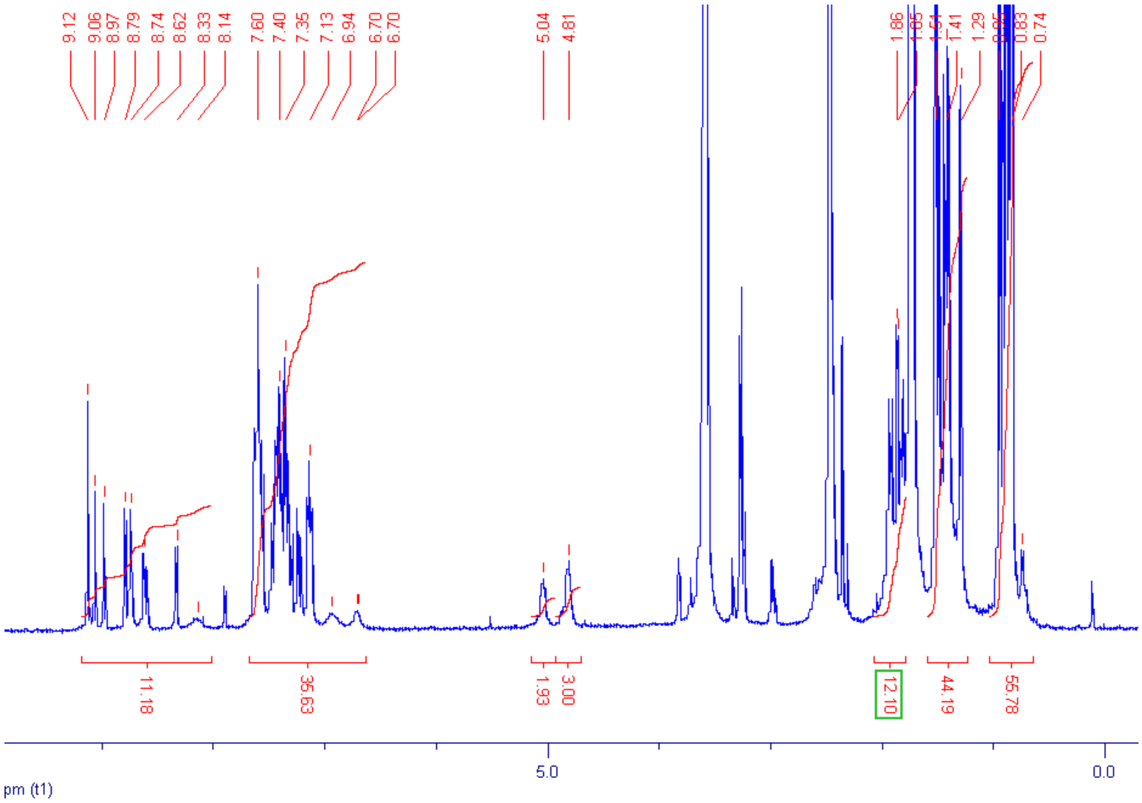
N-Cyclohexyl-1,7-bis(*p*-tolylsulfonyl)perylene-3,4-dicarboxyanhydride-9,10-dicarboximide (PMI 3)

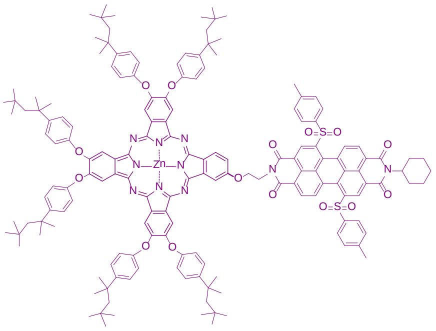
To a solution of 91 mg (0.12mmol) of **6** in 22 mL of CH_2Cl_2 were added 234 mg (0.95 mmol) of *m*-CPBA at 0ºC. The reaction mixture was stirred at room temperature overnight. The resulting solution was washed with $Na_2S_2O_3$ saturated solution, $NaHCO_3$ saturated solution and water. After drying over Na_2SO_4, the solvent was removed *in vacuo* and the resultant residue was purified by recrystallization (CHCl$_3$:Hx/1:1), affording 72 mg of PMI **3** as an orange solid (77%).

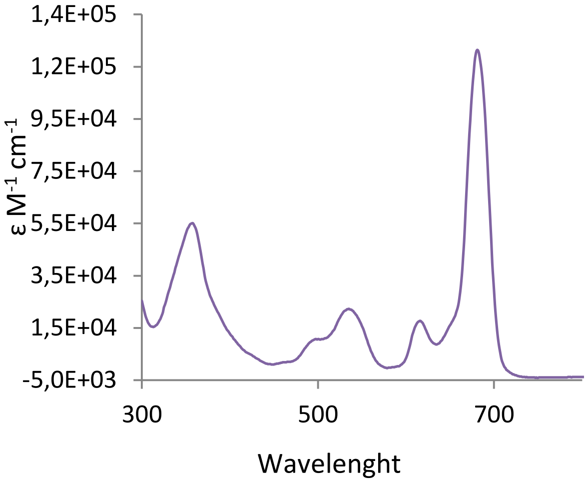
- m.p > 300 °C.
- ^{1}H NMR (CDCl$_3$): δ 1.36-1.87 (m, 8H), 2.37-2.50 (m, 8H), 4.95 (m, 1H), 7.45 (m, 4H), 7.87 (m, 4H), 8.57 (s, 1H), 8.58 (s, 1H), 8.79 (d, *J*= 8 Hz, 1H), 8.85 (d, *J*= 8 Hz, 1H), 9.21 (d, *J*= 8 Hz, 1H) and 9.27 ppm (d, *J*= 8 Hz, 1H).
- ^{13}C NMR (CDCl$_3$): δ 21.7, 21.8, 25.2, 26.3, 28.9, 54.4, 117.9, 119.4, 123.4, 124.9, 127.7, 127.8, 127.9, 128.8 (2C), 128.9 (2C), 129.9, 130.5 (2C), 130.6 (2C), 130.9, 131.2, 131.6, 132.9, 133.1, 133.5, 133.6, 135.1, 135.3, 135.4, 136.0, 136.3, 141.3, 141.9, 146.2 and 146.4 ppm.
- FT-IR (KBr): ν 2928, 2854, 1780, 1741, 1703, 1662, 1591, 1400, 1320, 1303, 1241, 1220, 1147 and 810 cm^{-1}.
- UV-vis (THF): λ_{max}/nm (log ε): 225 (4.75), 490 (4.36) and 523 (4.53).
- HRMS (MALDI-TOF): *m/z* for $C_{44}H_{31}NO_9S_2$ calcd. 781.1446; found 781.1368 (M$^-$).

^{1}H- ,^{13}C-NMR, UV-vis and MS spectra of characterized compounds.

^{1}H-NMR THF-d_8

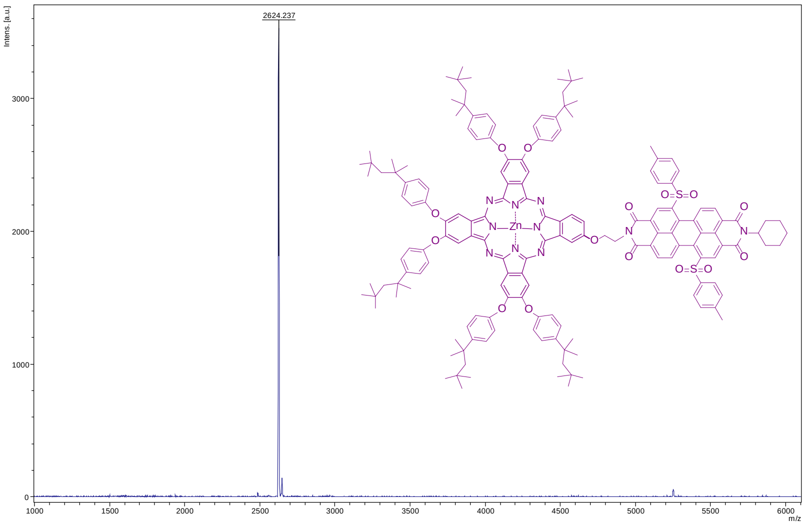






UV-Vis (THF)

MALDI-TOF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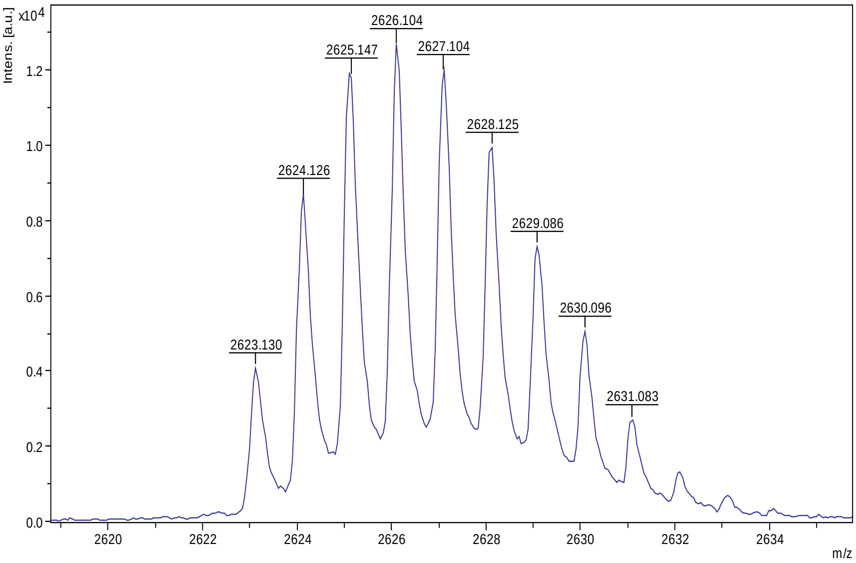
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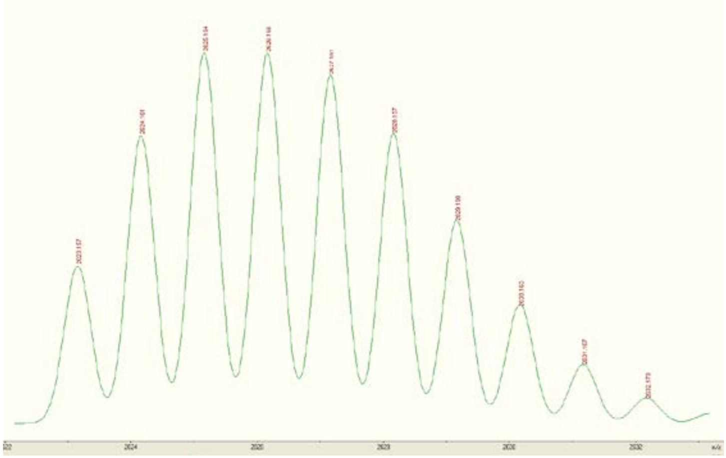
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2628
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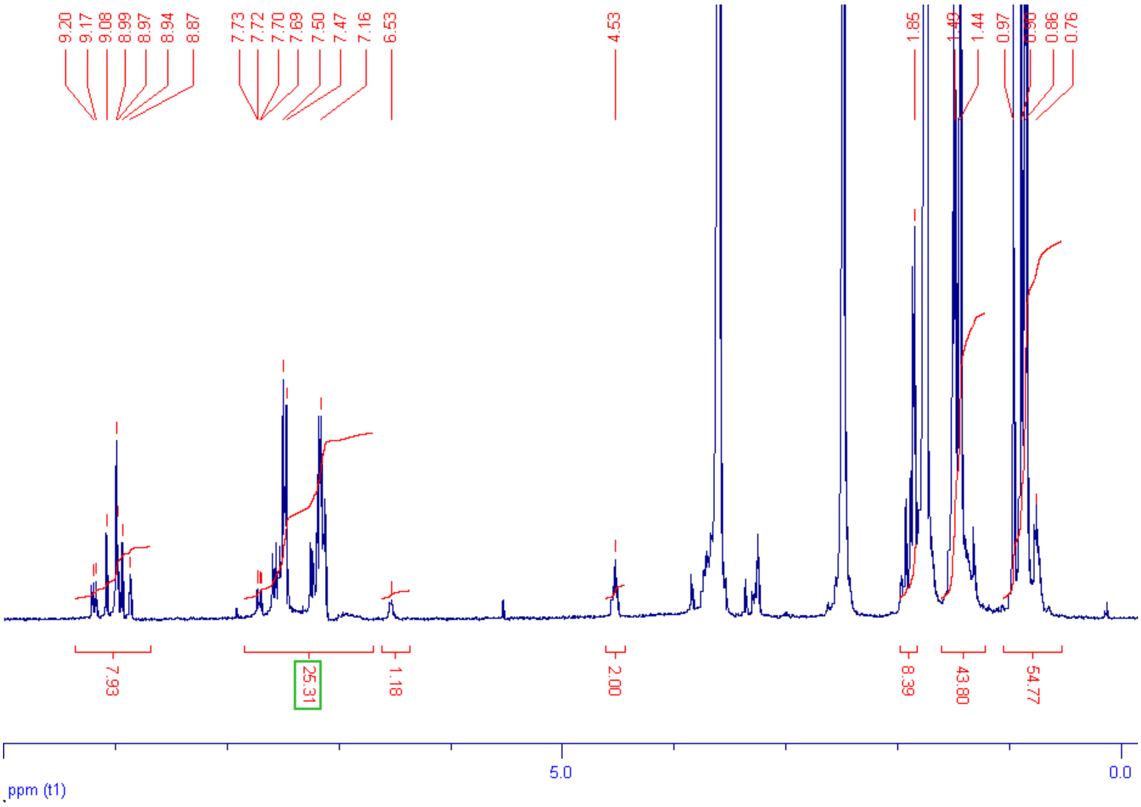
2632
m/z

^{1}H-NMR THF-d_8



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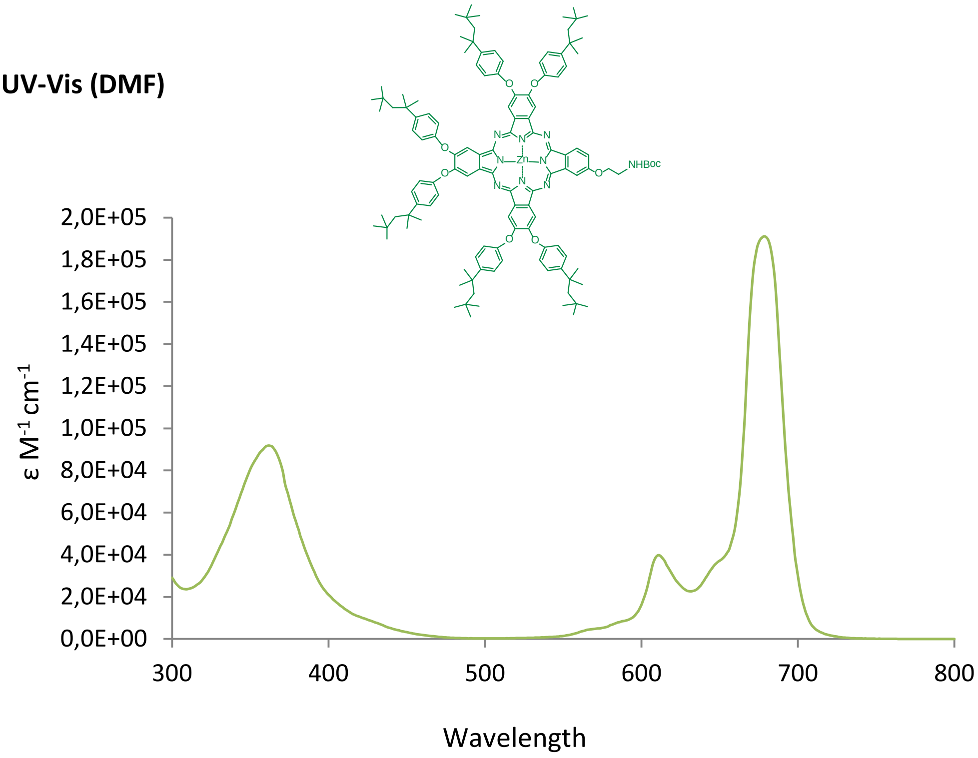

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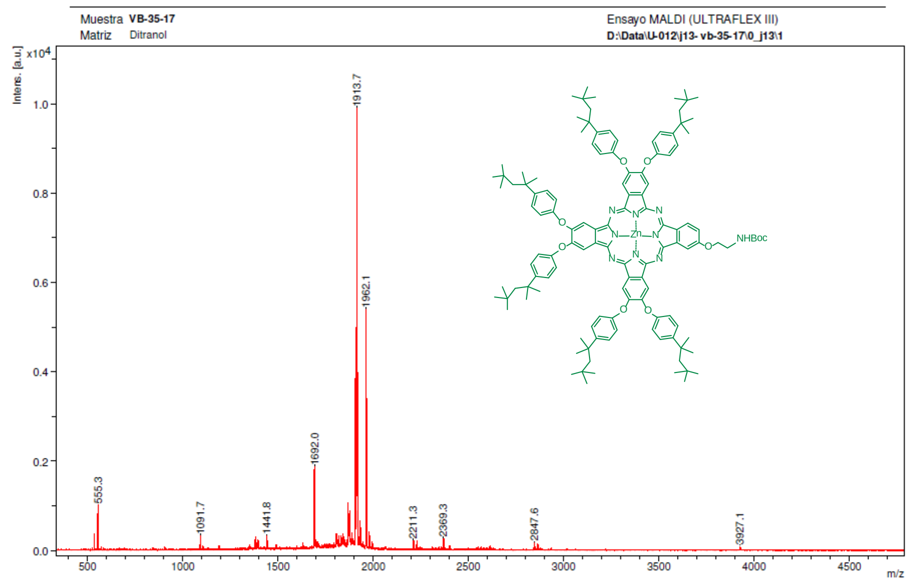

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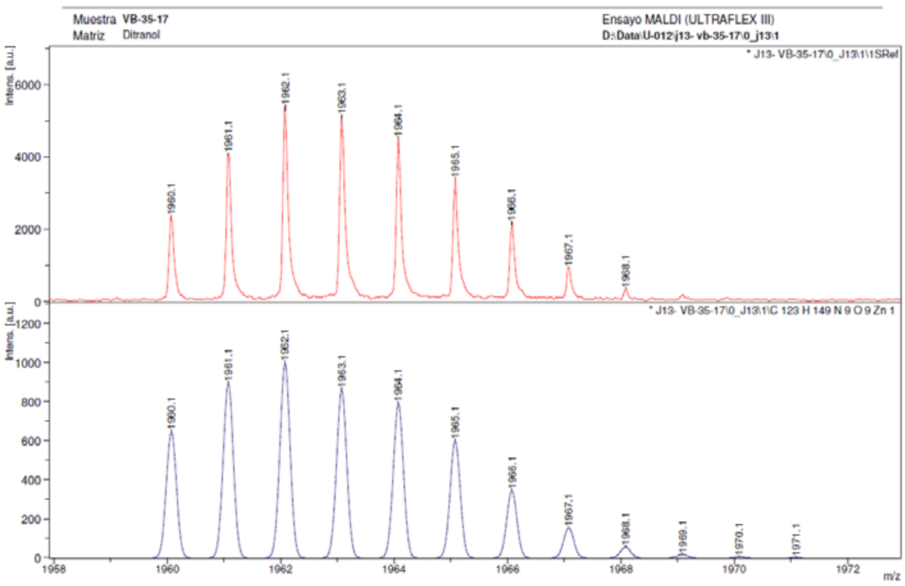

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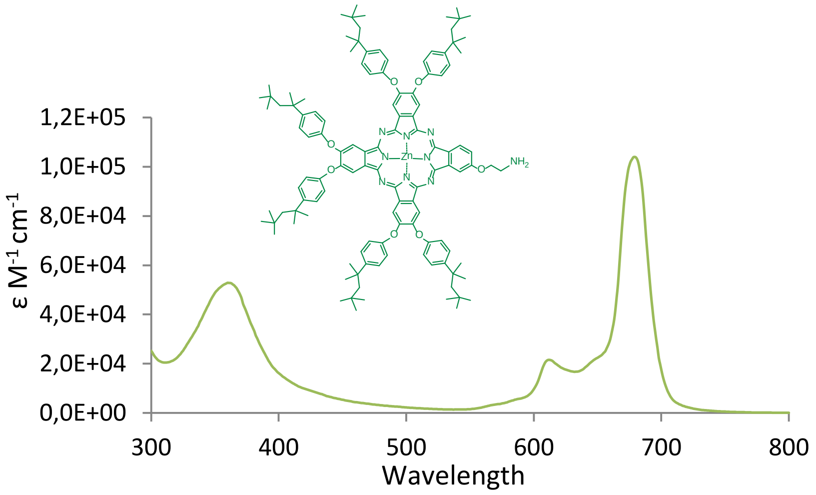
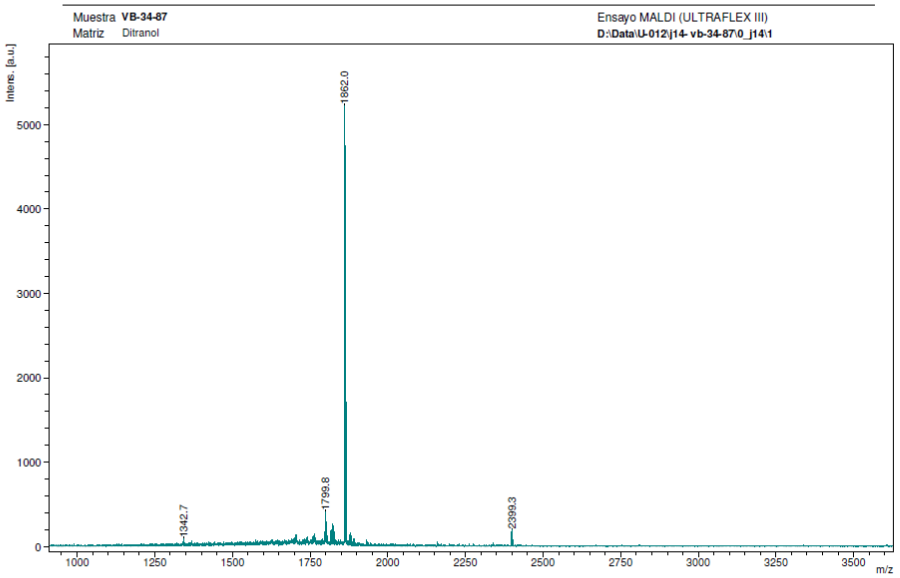
UV-Vis (DMF)





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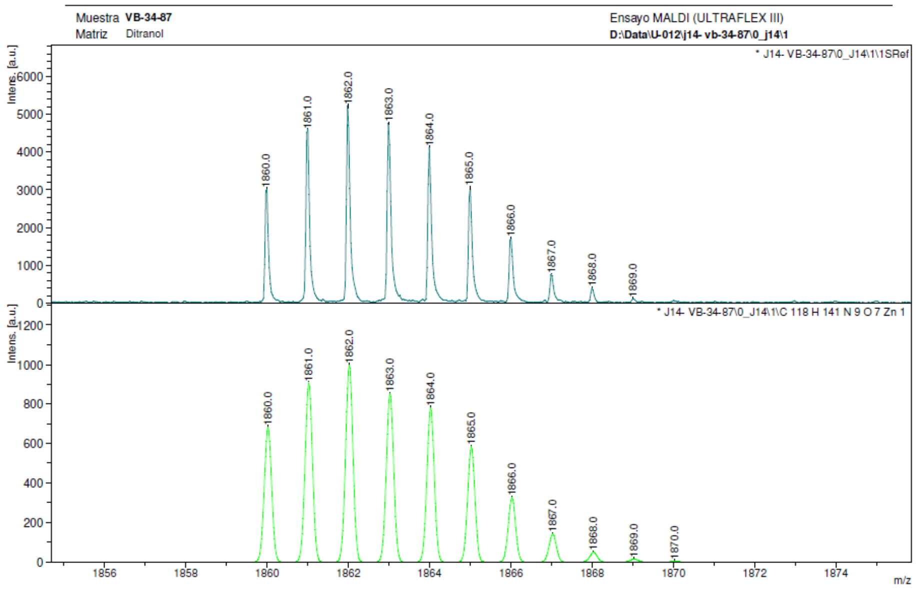

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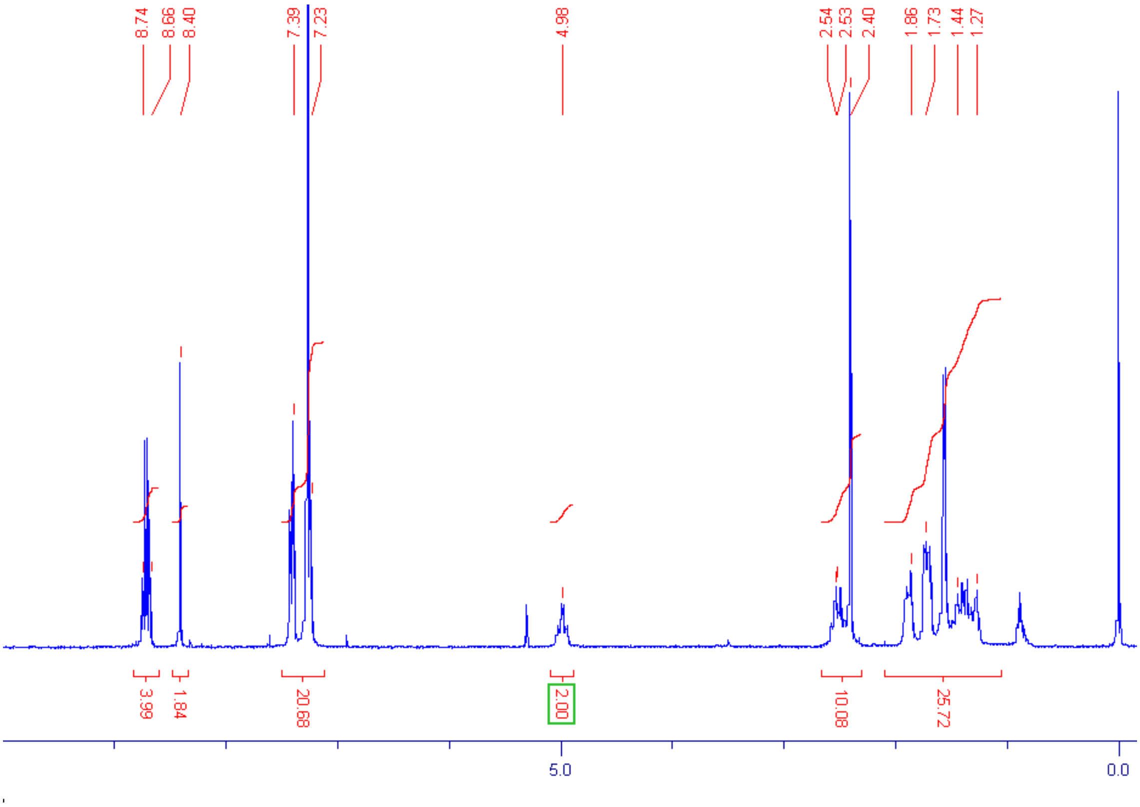

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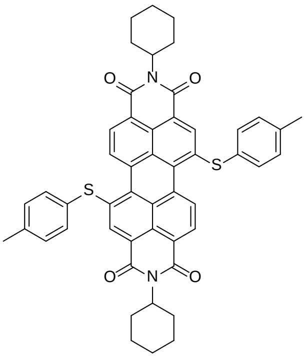
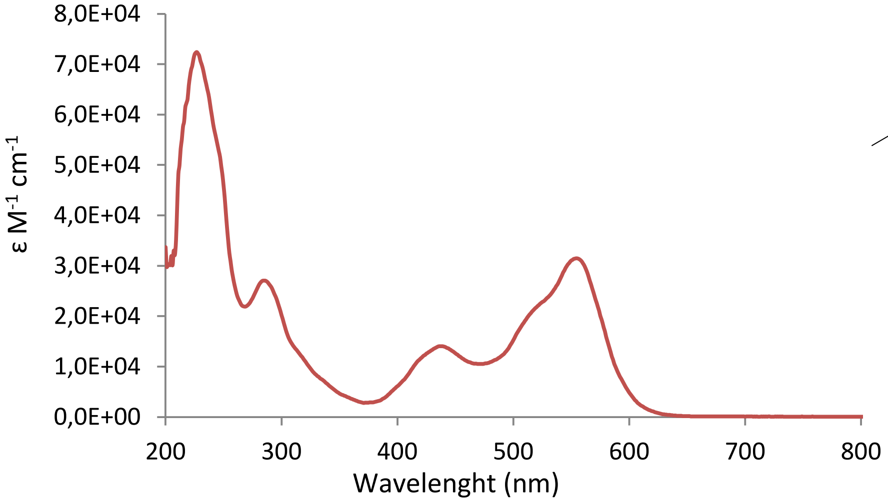
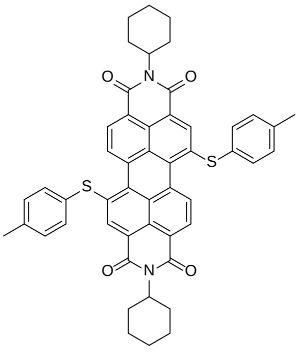


PDI 5

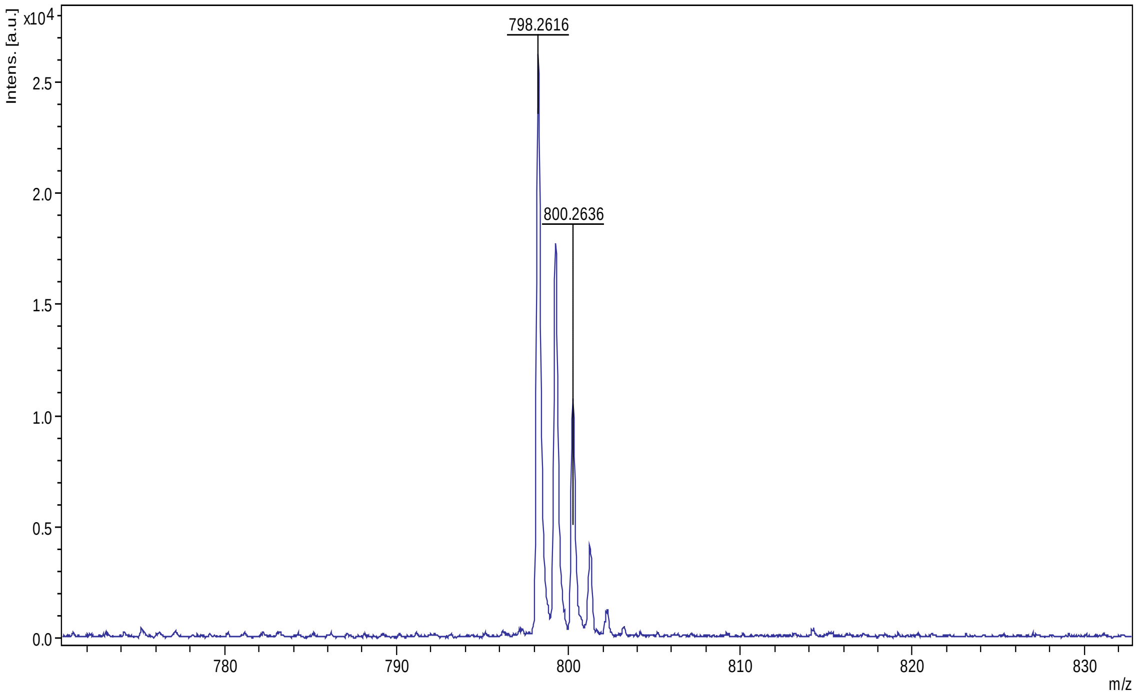
UV-Vis (THF)

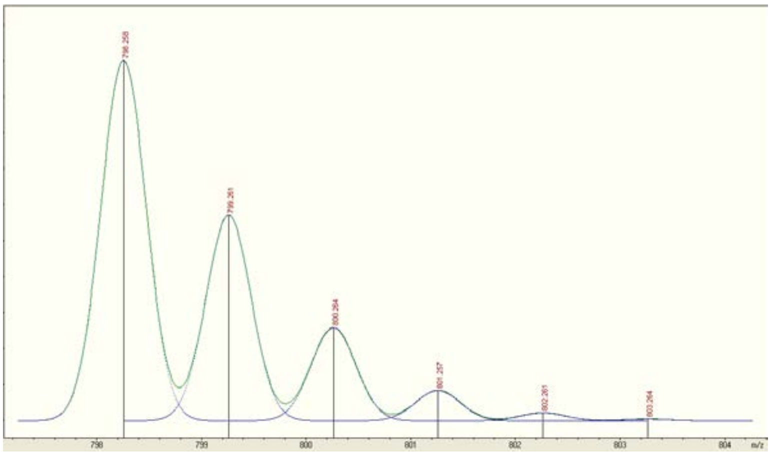




PDI 5

MALDI-TOF Negative Matrix Ditranol





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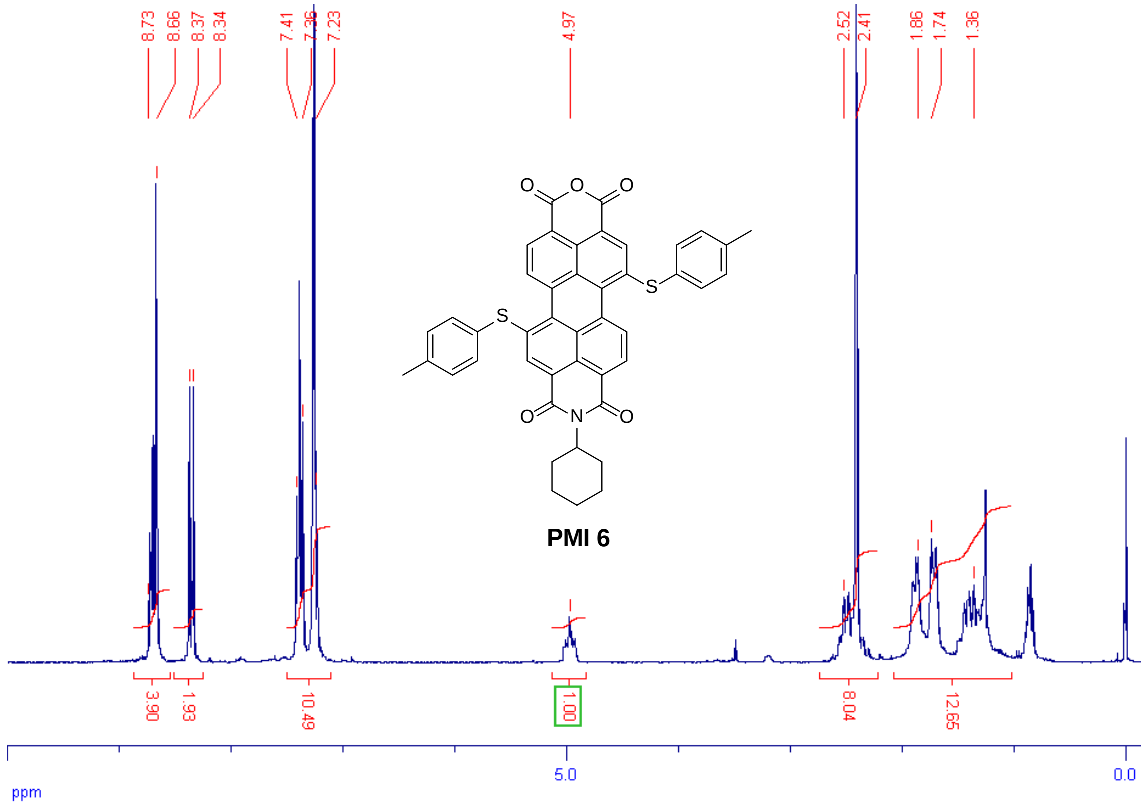

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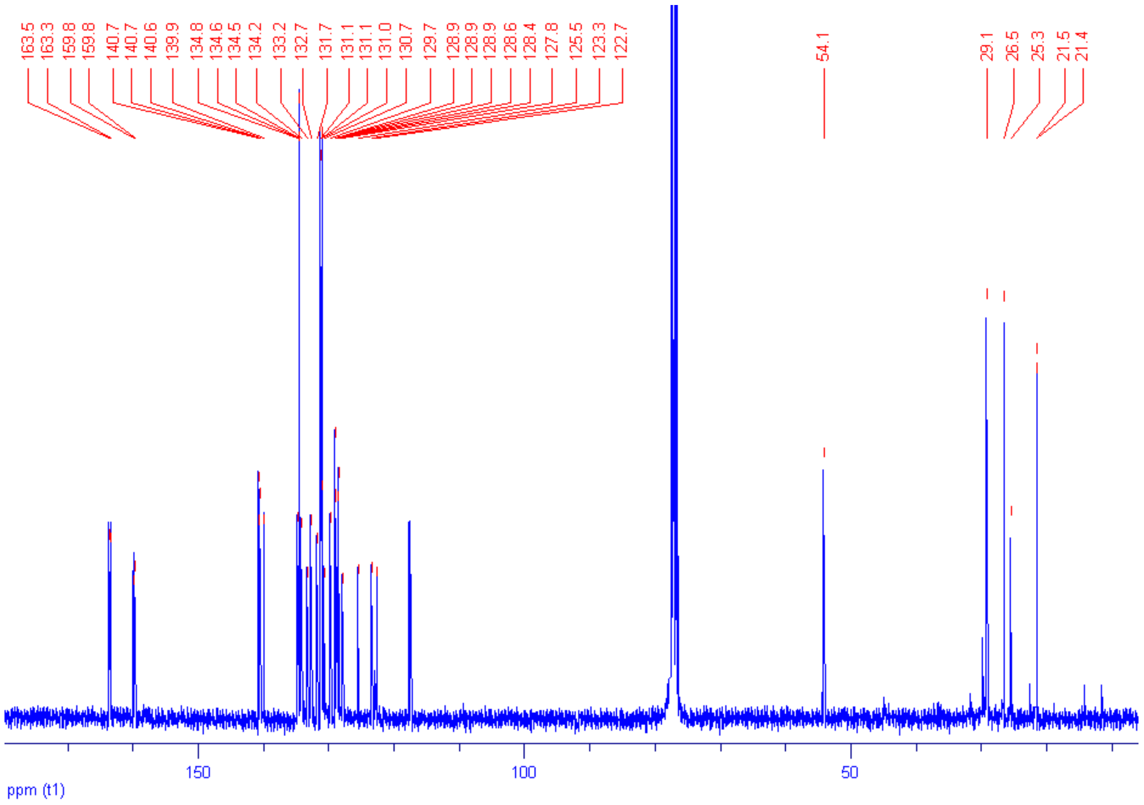
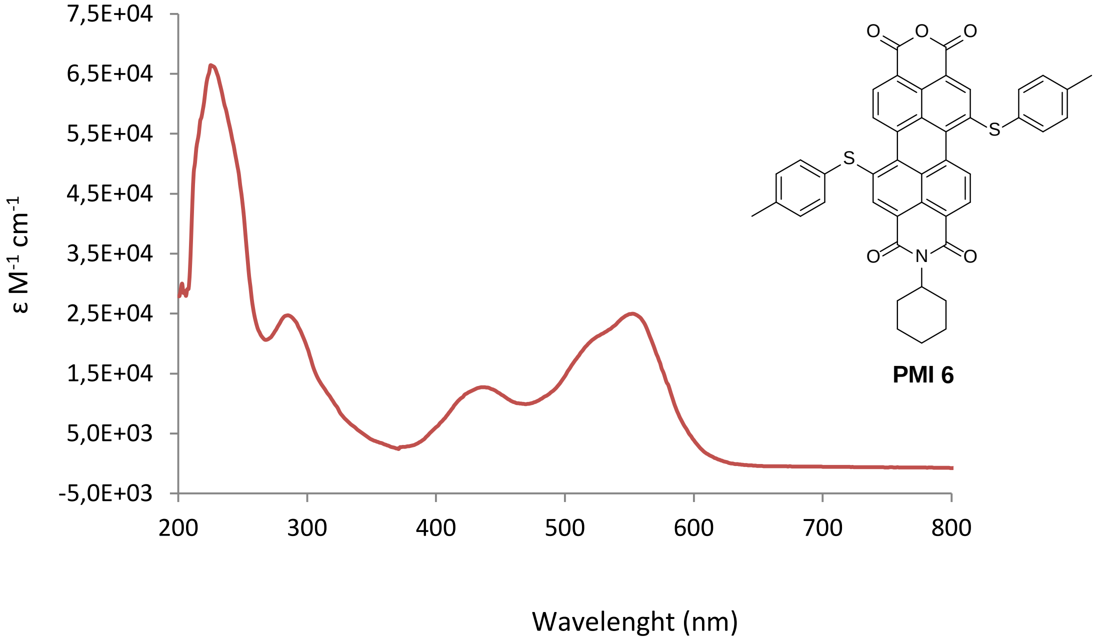
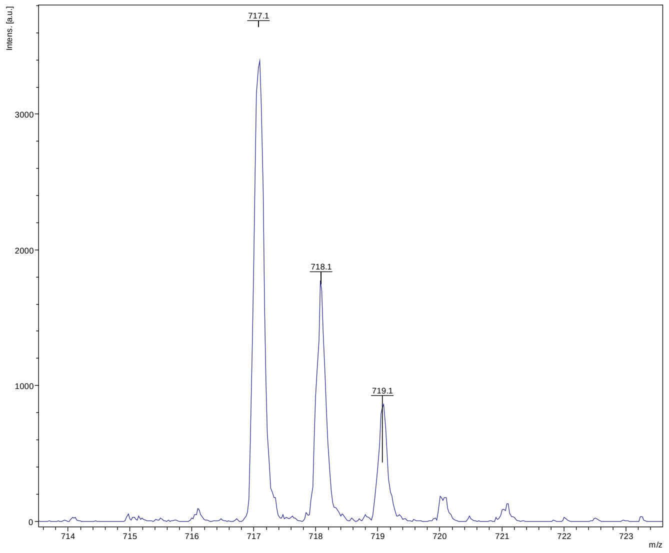


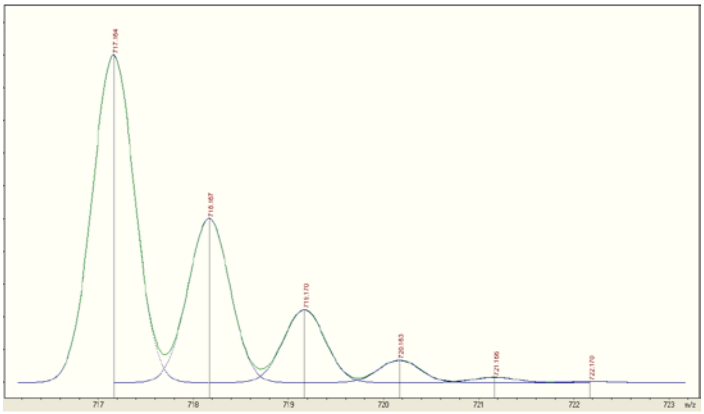
UV-Vis (THF)



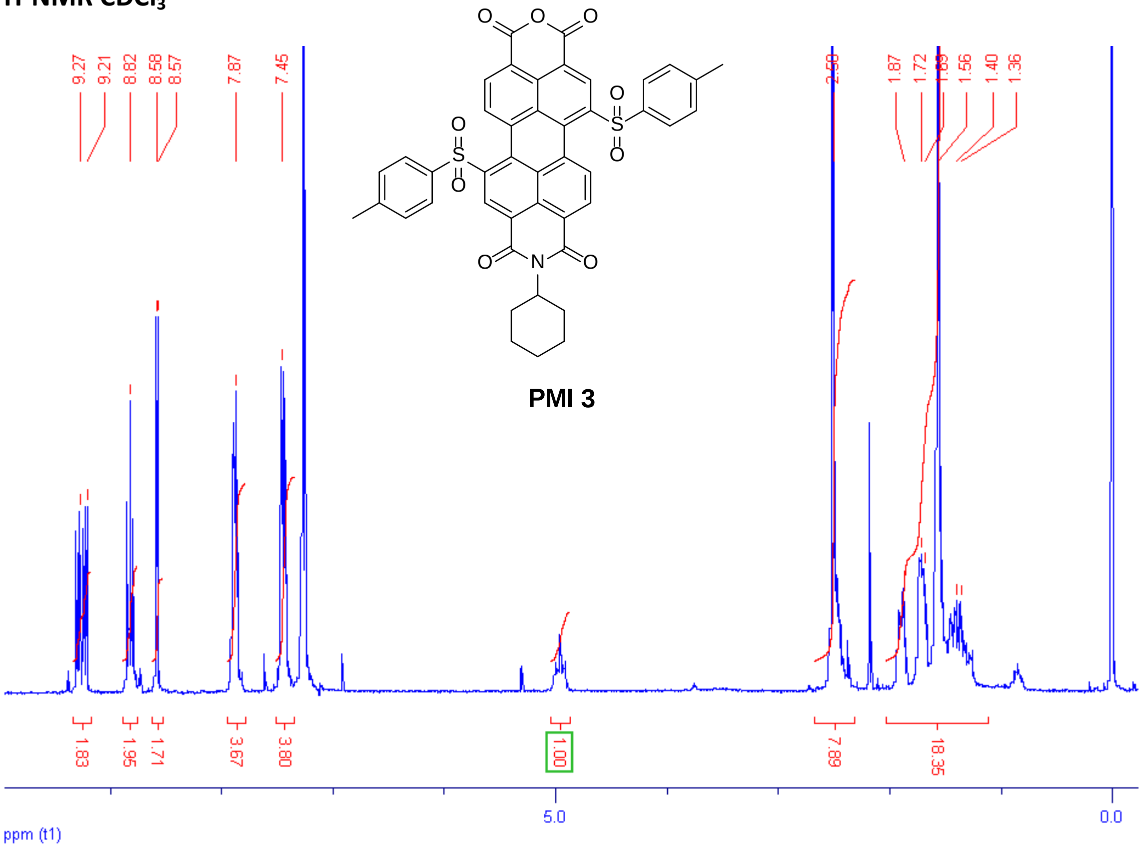
PMI 6

MALDI-TOF Negative Matrix Ditranol

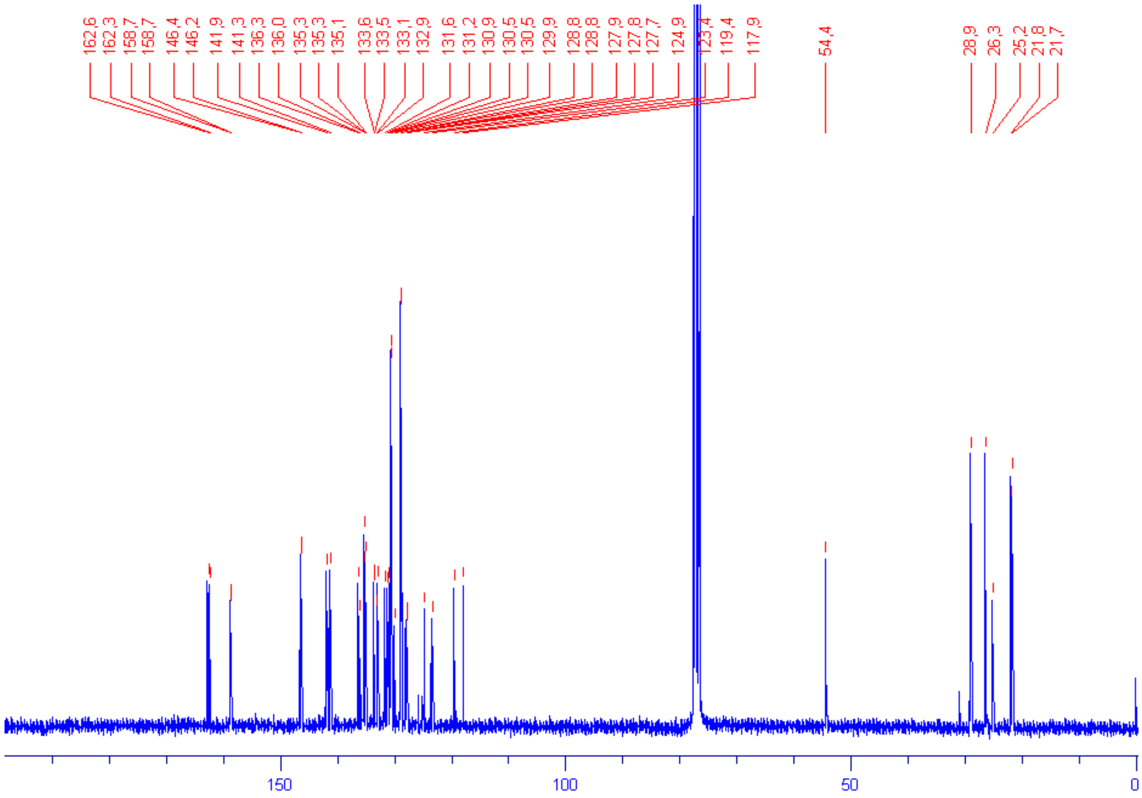




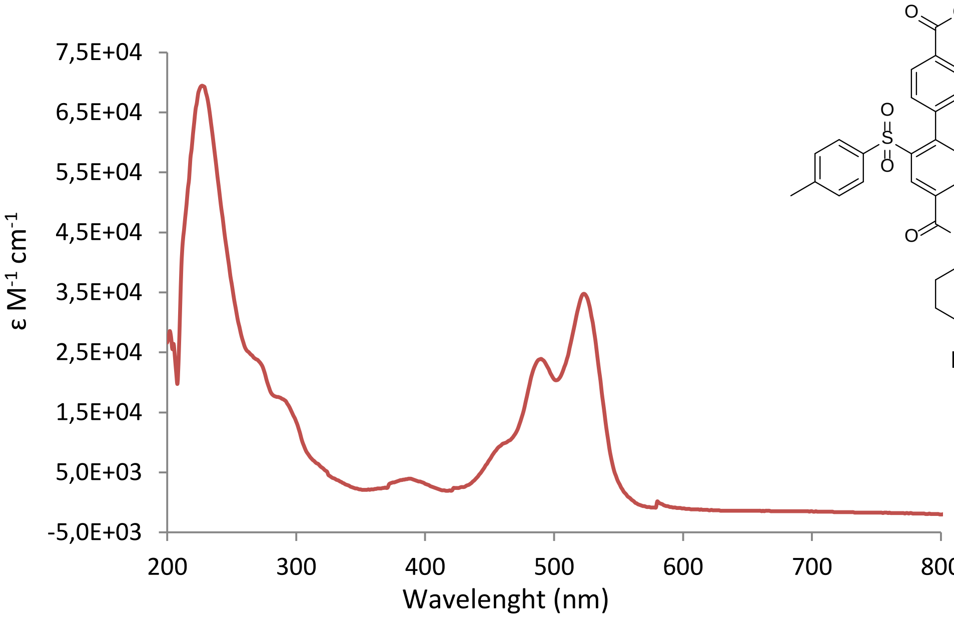
^{1}H-NMR CDCl$_3$

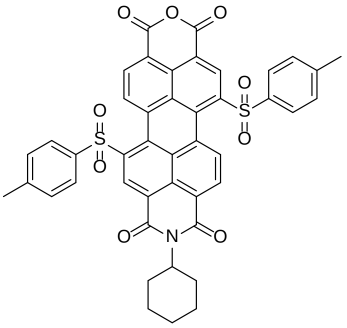


^{13}C-NMR CDCl$_3$



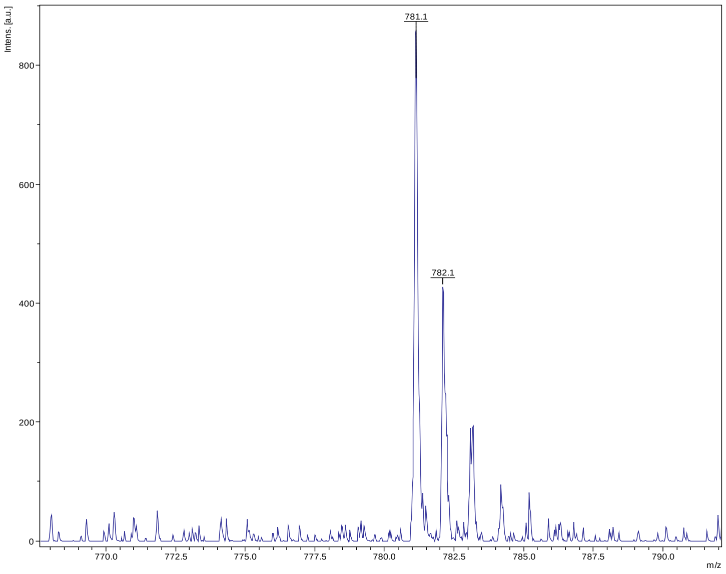
UV-Vis (THF)

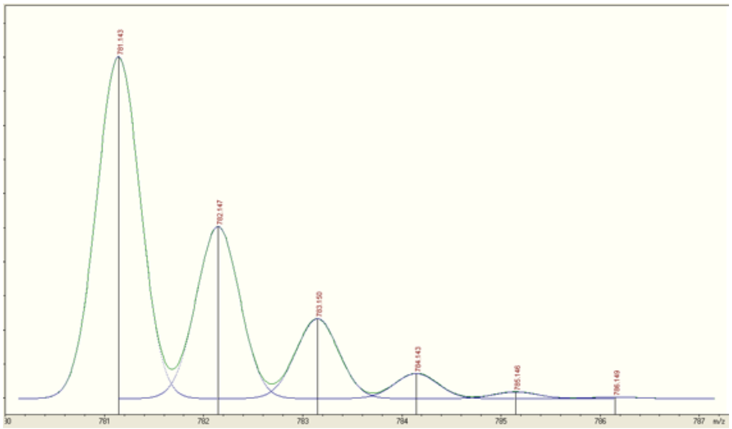




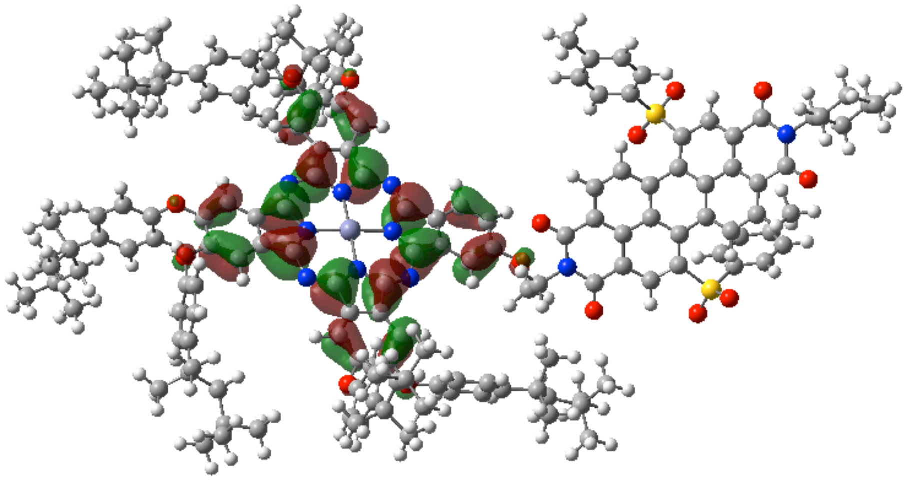
PMI 3

MALDI-TOF Negative Matrix Ditranol





(a) HOMO



(b) LUMO

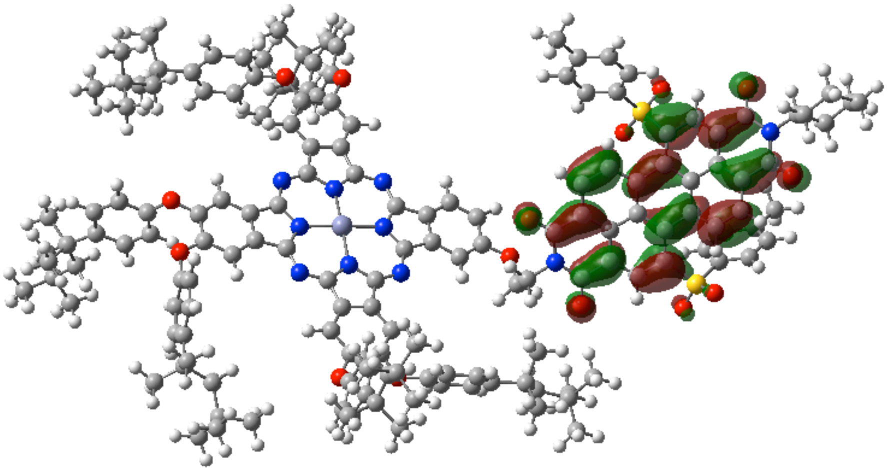


Fig. S18 (a) HOMO and LUMO orbitals of ZnPc–PDI calculated by DFT B3LYP/6-31G(d).

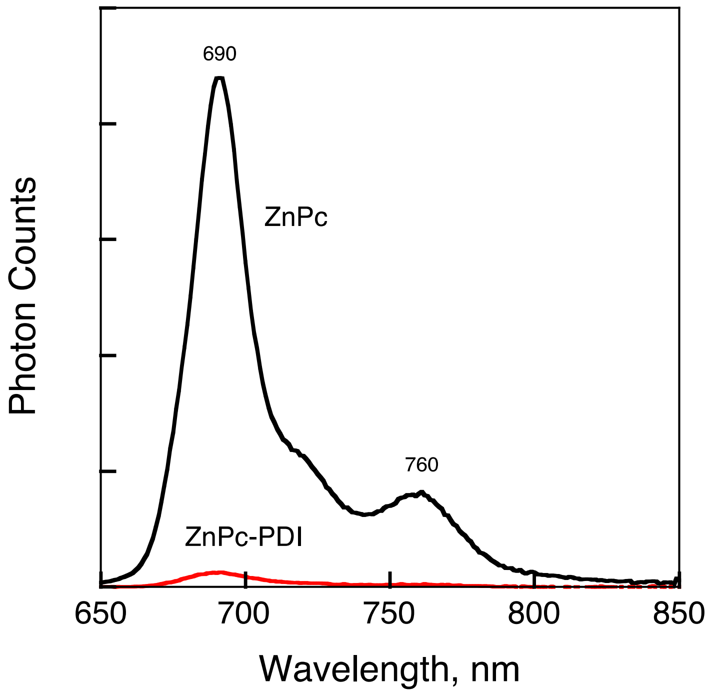


Fig. S19 Fluorescence spectra of ZnPc **2** (black) and ZnPc–PDI **1** (red) in deaerated PhCN at 298 K. λ_{ex} = 620 nm. OD at 620 nm = 0.2.

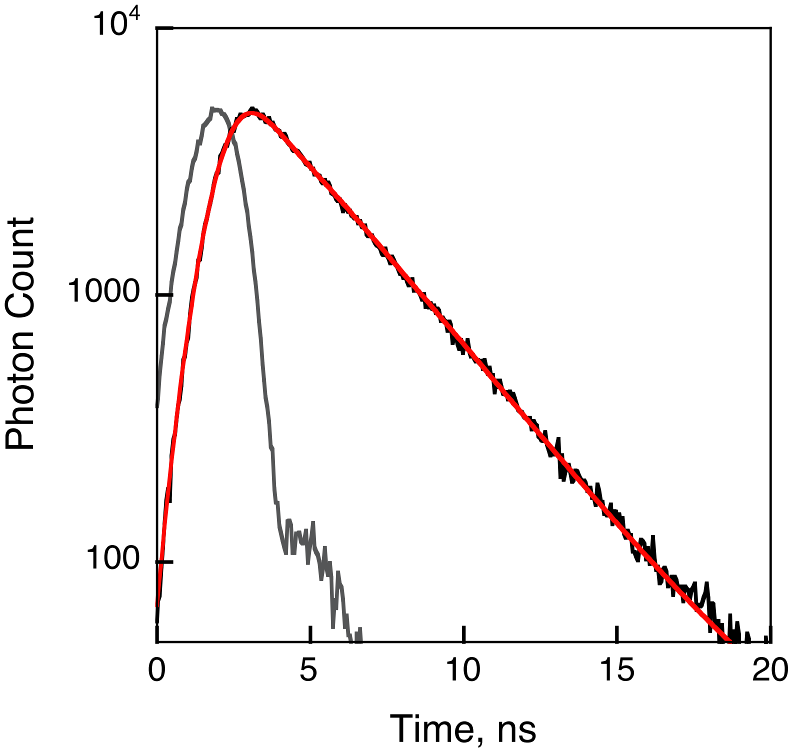


Fig. S20 Fluorescence decay of ZnPc **2** in deaerated PhCN at 298 K. λ_{ex} = 650 nm. The instrument response (gray line), decay data (solid line), and single-exponential fitted line (red).

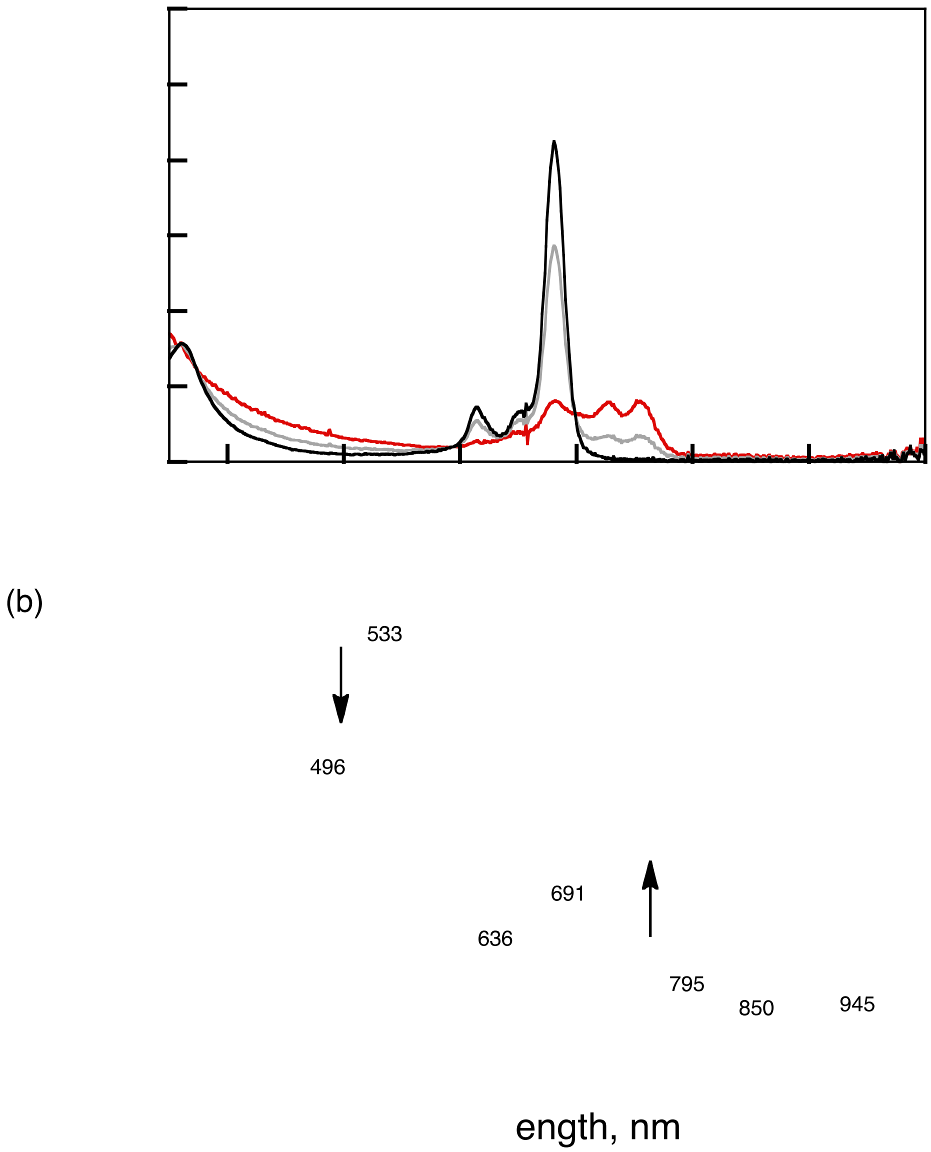


Fig. S21 Thin-layer UV-Vis-NIR spectral changes during (a) the electrochemical oxidation of ZnPc (**2**) in deaerated PhCN containig TBAPF$_6$ (0.1 M) at a controlled potential at +0.80 V *vs.* SCE; (b) the electrochemical resuction of PDI (**3**) in deaerated PhCN containig TBAPF$_6$ (0.1 M) at a controlled potential at –0.60 V *vs.* SCE.

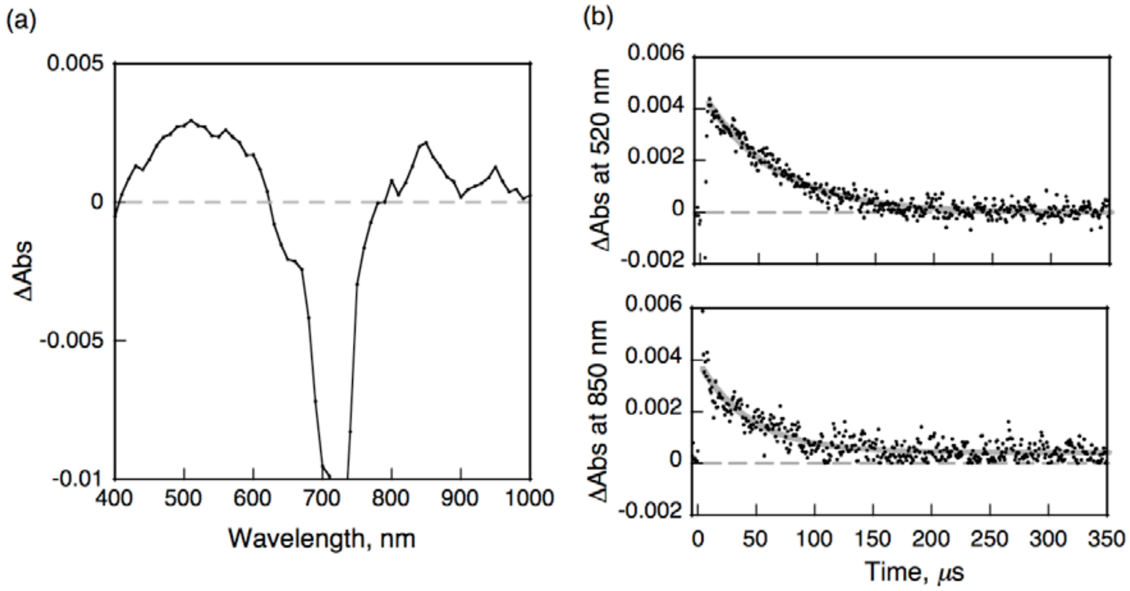


Fig. S22 (a) Nanosecond transient absorption spectra of ZnPc-PDI dyad **1** in deaerated PhCN at 298 K after 530 nm laser excitation; Time profiles at (b) 520 nm and (c) 850 nm. Gray lines: single-exponential fitting.

References.

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