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SUPPORTING INFORMATION

Rational molecular design enhancing the photonic performance of red-emitting perylene bisimide dyes

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General

Synthesis. All starting materials and reagents were obtained commercially, unless otherwise indicated, and used without further purifications. Common solvents were dried and distilled by standard procedures. Flash chromatography was performed using silica gel (230-400 mesh). NMR spectra were recorded at 20 ºC, and the residual solvent peaks used as internal standards. FTIR spectra were obtained from neat samples using the ATR technique. High resolution mass spectrometry (HRMS) was performed using the EI and MALDI-TOF techniques.

Photophysical signatures. Diluted dye solutions (around 2×10^{-6} M) in ethyl acetate (spectroscopic grade) were prepared by diluting a concentrated stock solution in the same solvent. UV-Vis absorption and steady-state fluorescence were recorded on a Varian model CARY 4E spectrophotometer and an Edinburgh Instruments spectrofluorimeter (model FLSP920), respectively, using 1 cm path length quartz cuvettes. The emission spectra were corrected from the monochromator wavelength dependence, the lamp profile and the photomultiplier sensitivity. Fluorescence quantum yields (ϕ) were calculated upon excitation at 530 nm using commercial cresyl violet (ϕ^r = 0.54 in methanol) as reference. The values were corrected by the refractive index of the solvent. Besides, absolute fluorescence quantum yields at different excitation wavelengths have been recorded by an integrating sphere coupled to the above spectrofluorimeter. Such data were used to evaluate the EET efficiency by means of the ratio between the acceptor ϕ upon excitation at the donor and the free acceptor ϕ upon its direct excitation. Radiative decay curves were registered with the time correlated single-photon counting technique as implemented also in the above spectrofluorimeter. To this aim a tunable supercontinuum Fianium pulsed laser (5 MHz and 150 ps full width at half maximum) was used instead of the above Xe flash lamp as excitation source, whereas the emission was monitored at the maximum emission wavelength (around 600 nm). The fluorescence lifetime (τ) was obtained after the deconvolution of the instrumental response signal from the recorded decay curves by means of an iterative method. The goodness of the exponential fit was controlled by statistical parameters (chi-square, Durbin-Watson) and the analysis of the residuals. Radiative (k_{fl}) and non-radiative (k_{nr}) rate constants were calculated as follows; $k_{fl} = \phi/\tau$ and $k_{nr} = (1-\phi)/\tau$. The energy transfer efficiency was calculated by means of the fluorescence quenching of the energy donor (7-hydroxi-coumarine or 8-aminoBODIPY) when linked to the corresponding energy acceptors; $\phi_{EET} = 1-(\phi_D/\phi_D^0)$, where ^{0} superscript accounts for the free coumarin or 8-aminoBODIPY. The required fluorescence quantum yields were calculated using quinine sulphate as reference (ϕ^r = 0.93 in water 0.1 M NaOH).

Computational methods. Ground state geometries were optimized at the Density Functional Theory (DFT) level using the B3LYP hybrid method and the double valence basis set (6-31g). More extended basis set were unavailable owing to the large size of the molecules. The energy minimization was conducted without any geometrical restriction and the geometries were considered as energy minimum when the corresponding frequency analysis did not give any negative value. The simulation of the absorption spectra (from the ground state geometry) was performed by the Time Dependent method (TD-DFT). The solvent effect (ethyl acetate) was also simulated during the calculations by the Self Consistent Reaction Field (SCRF) using the Polarizable Continuum Model (PCM). All the theoretical calculations were carried out using the Gaussian 09 implemented in the computational cluster provided by the SGIker resources of the UPV/EHU.

Laser experiments. Liquid solutions of dyes were contained in 1 cm optical-path length cells, which were carefully sealed to avoid solvent evaporation during the experiments. The dye solutions were transversely pumped with nanosecond pulses either at 532 nm (6 ns FWHM and 5.5 mJ/pulse) or at 355 nm (8 ns FWHM and 3.5 mJ/pulse). The source of the 532 nm pulses was a frequency-doubled Q-switched Nd:YAG laser (Monocrom OPL-10). The 355 nm pulses were the third harmonic of a Q-switched Nd:YAG laser (Spectron SL282G). In both cases the excitation pulses were line-focused onto the cell, providing pump fluences on the active medium of 180 mJ/cm^{-2} and 110 mJ/cm^{-2} for 532 nm and 355 nm pumping, respectively. The oscillation cavity (2 cm length) consisted of a 90% reflectivity back aluminum mirror and the lateral face of the cell as output coupler. The energy of dye and pump laser pulses was measured with GenTec ED-100A and ED-200 pyroelectric energy meters. The spectral characteristics of the laser emission were determined by collecting a fraction of the emission by an optical fiber attached to the input slit of a spectrograph/monochromator (SpectraPro-300i, Acton Research Corporation) equipped with a charge-coupled device (CCD) /SpectruMM:GS 128B). The photostability of the dyes in liquid solution was evaluated by irradiating under lasing conditions 10 µL of a solution in ethyl acetate. The solutions were contained in a cylindrical Pyrex tube (1 cm height, 1 mm internal diameter) carefully sealed to avoid solvent evaporation during the experiments. Although the low optical quality of the capillary tube prevents laser emission from the dyes, information about photostabilities can be obtained by monitoring the decrease in laser-induced fluorescence intensity, excited transversally to the capillary tube, as a function of the number of pump pulses at a given repetition rate. The fluorescence emission was monitored perpendicular to the exciting beam, collected by an optical fiber, and imaged onto the input slit of the monochromator and detected with the CCD. The fluorescence emission was recorded by feeding the signal to the boxcar (Stanford Research, model 250) to be integrated before being digitized and processed by a computer. Each experience was repeated at least three times. The estimated error in the energy and photostability measurements was 10%.

Synthetic procedures and characterization data

Perylene red (**Per-Red**) and 7-hydroxy-4-methylcoumarin (**C456**) were purchased from Exciton and used without further purification. Compounds **1**,[1] **2**,[2] **12**,[3] **14**,[4] **15**,[5] **16**,[6] **18**[7] and **19**[7] were synthesized as described in the literature.

General Procedures

1. Nucleophilic substitution of 1,6,7,12-tetrachloroperylene bisimide. A solution of 1,6,7,12-tetrachloroperylene bisimide (1 equiv), 4-*tert*butylphenol (10 equiv), and K_2CO_3 (5 equiv) in DMF was stirred at 90 ºC for 16-24 h. After the mixture was cooled to r. t., a half-concentrated HCl solution was added and the precipitate was filtered and washed with water and dried under vacuum. The product was purified by flash chromatography on silica gel.

2. Miyaura borylation. A solution of the corresponding halogenated, or triflate, derivative (1 equiv.), bis(pinacolato)diboron (2-8 equiv), Pd(dppf)Cl_2 (10% mol) and dry potassium acetate (2-8 equiv) in ethylene glycol dimethyl ether (DME) was refluxed for 16-24 h under argon. After cooling to r. t., the solvent was removed in vacuum. The product was purified by flash chromatography on silica gel.

3. Suzuki reaction. The corresponding halogenated derivative (1 equiv) and pinacol boronate derivative (8 equiv) were dissolved in toluene/ethanol/water (2:2:1, v/v/v). K_2CO_3 (8 equiv) was added and argon was bubbled through the solution for 30 min. Then, $Pd(PPh_3)_4$ (10% mol) was added and the mixture was heated at reflux under argon for 1-8 h. After removal of the solvent under reduced pressure, the crude product was purified by flash chromatography on silica gel.

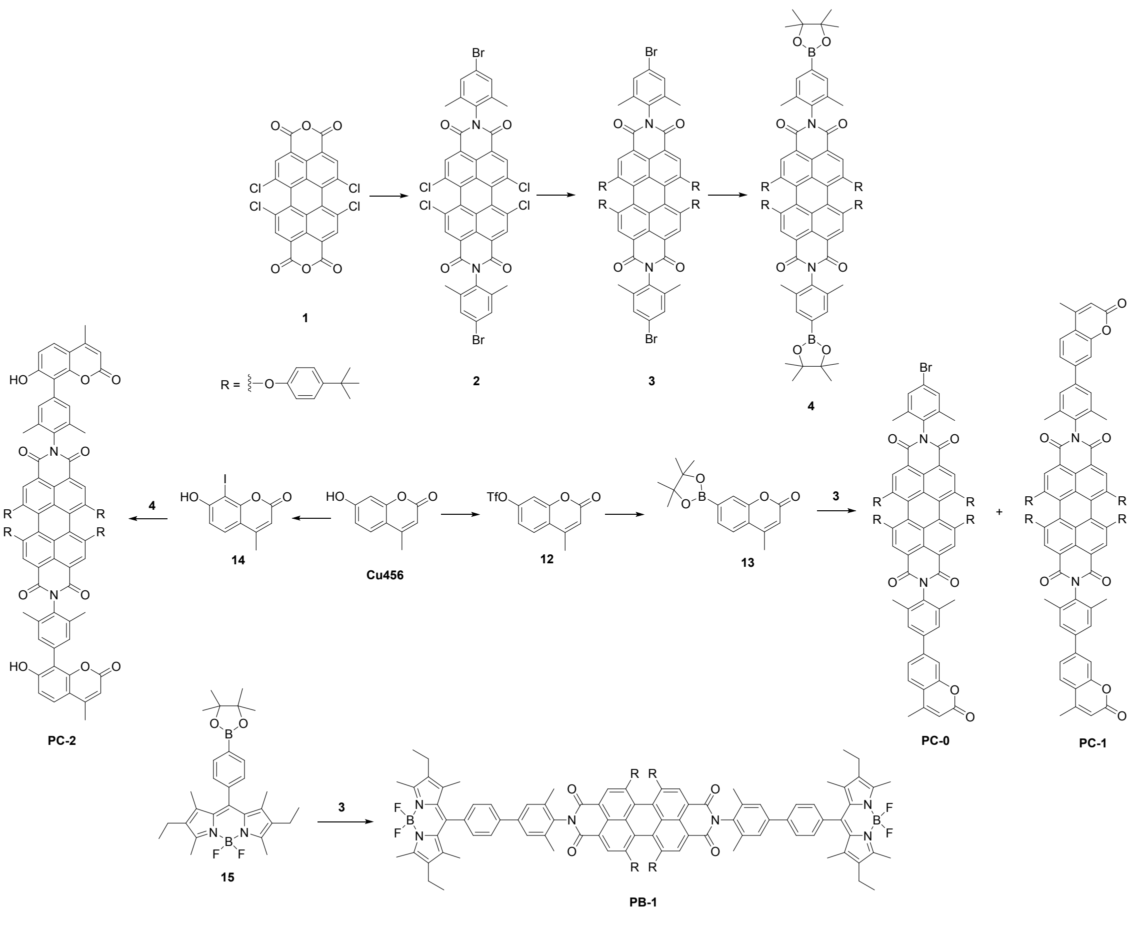
4. Synthesis of perylene bisimide from anhydride.

Method A: Perylene mono- or dianhydride (1 equiv), the corresponding amine (5-10 equiv.) and propionic acid were refluxed for 16 h. After the mixture was cooled to r. t., water was added and the precipitate was filtered and washed with water and dried under vacuum. The product was purified by flash chromatography on silica gel.

Method B: Perylene mono- or dianhydride (1 equiv), the corresponding amine (2.5-5 equiv) and toluene were stirred at 60 ºC for 3 h. After the mixture was cooled to r. t., the solvent was removed in vacuum. The product was purified by flash chromatography on silica gel.

5. Synthesis of perylene bisimide-BODIPY. To a solution of perylene bisimide (1 equiv) in CH_3CN (10 mL), under argon atmosphere at r.t., was added 8-thiomethylBODIPY (2 equiv), and the reaction mixture was stirred at r.t. for 3 h. Solvent was evaporated in vacuum, and the crude product was purified by flash chromatography on silica gel.

Synthesis of dyads PC-1, PC-2 and PB-1



Scheme S1. Synthetic route of dyads **PC-1**, **PC-2** and **PB-1**.

3: According to the general procedure 1., perylene bisimide **2**[2] (500 mg, 0.56 mmol), 4-*tert*butylphenol (840 mg, 5.6 mmol) and K_2CO_3 (386 mg, 2.8 mmol) in DMF (20 mL) were refluxed for 24 h. Flash chromatography (hexane/CH_2Cl_2, 7:3) afforded **3** (315 mg, 42%) as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 4H, 4CH), 7.38 (s, 4H, 4CH), 7.30 (d, *J* = 8.7 Hz, 8H, 8CH), 6.93 (d, *J* = 8.7 Hz, 8H, 8CH), 2.14 (s, 12H, $4CH_3$), 1.33 (s, 36H, $12CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6 (CO), 156.2, 152.6, 147.6, 137.8, 133.2, 133.0, 131.3 (CH), 126.8 (CH), 122.5, 122.4, 120.8, 120.1 (CH), 119.4 (CH), 34.4, 31.5 (CH_3), 17.8 (CH_3) ppm. FTIR ν 2960, 1711, 1675, 1590, 1504, 1402, 1340, 1315, 1281, 1209, 1171 cm^{-1}. HRMS (MALDI TOF) *m/z* 1346.3645 (calcd for $C_{80}H_{72}Br_2N_2O_8$: 1346.3655).

4: According to the general procedure 2., dibromoperylene bisimide **3** (50 mg, 0.037 mmol), bis(pinacolato)diboron (76 mg, 0.3 mmol), Pd(dppf)Cl_2 (3 mg, 0.004 mmol) and KOAc (30 mg, 0.3 mmol) in DME (10 mL) were refluxed for 16 h. Flash chromatography (hexane/EtOAc, 6:4) afforded **4** (48 mg, 90%) as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (s, 4H, 4CH), 7.62 (s, 4H, 4CH), 7.23 (d, *J* = 8.7 Hz, 8H, 8CH), 6.86 (d, *J* = 8.7 Hz, 8H, 8CH), 2.11 (s, 12H, $4CH_3$), 1.26 (s, 60H, $20CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6 (CO), 156.1, 152.7, 147.4, 136.6, 134.9 (CH), 134.8, 133.2, 126.7 (CH), 122.5, 120.7, 120.0 (CH), 119.4 (CH), 83.9 (C-O), 34.4, 31.4 (CH_3), 24.9 (CH_3), 17.7 (CH_3) ppm. FTIR ν 2962, 2928, 1707, 1672, 1587, 1505, 1369, 1283, 1125 cm^{-1}. HRMS (MALDI TOF) *m/z* 1442.7141 (calcd for $C_{92}H_{96}B_2N_2O_{12}$: 1442.7149).

13: According to the general procedure 2., chromenone triflate **12**[3] (144 mg, 0.47 mmol), bis(pinacolato)diboron (237 mg, 0.93 mmol), Pd(dppf)Cl_2 (34 mg, 0.047 mmol) and KOAc (92 mg, 0.93 mmol) in DME (10 mL) were refluxed for 24 h. Flash chromatography (hexane/EtOAc, 8:2) afforded **6** (108 mg, 81%) as a yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (s, 1H, CH), 7.59 (d, *J* = 7.8 Hz, 1H, CH), 7.48 (d, *J* = 7.8 Hz, 1H, CH), 6.21 (d, *J* = 1.2 Hz, 1H, CH), 2.34 (d, *J* = 1.2 Hz, 3H, CH_3), 1.27 (s, 12H, $4CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7 (CO), 152.9, 152.1, 131.5, 130.0 (CH), 123.7 (CH), 123.1 (CH), 120.8, 116.1 (CH), 83.5 (C-O), 25.0 (CH_3), 18.7 (CH_3) ppm. FTIR ν 2979, 1727, 1620, 1508, 1353, 1278, 1123, 850 cm^{-1}. HRMS (EI) *m/z* 286.1384 (calcd for $C_{16}H_{19}BO_4$: 286.1376).

PC-0 and **PC-1:** According to the general procedure 3., dibromoperylene bisimide **3** (200 mg, 0.15 mmol), pinacol boronate **13** (340 mg, 1.19 mmol), K_2CO_3 (164 mg, 1.19 mmol) and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) in toluene/ethanol/water (10 mL) were refluxed for 8 h. Flash chromatography (hexane/DCM, 9:1) afforded **PC-0** (56 mg, 26%) and **PC-1** (105 mg, 47%) as red solids.

PC-0: ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.28 (s, 2H, 2CH), 8.27 (s, 2H, 2CH), 7.65 (d, *J* = 8.4 Hz, 1H, CH), 7.57 (d, *J* = 1.4 Hz, 1H, CH), 7.55 (d, *J* = 8.4 Hz, 1H, CH), 7.42 (s, 2H, 2CH), 7.33 (s, 2H, 2CH), 7.25 (d, J = 8.4 Hz, 8H, 8CH), 6.86 (d, J = 8.4 Hz, 8H, 8CH), 6.30 (s, 1H, CH), 2.47 (s, 3H, CH_3), 2.20 (s, 6H, $2CH_3$), 2.09 (s, 6H, $2CH_3$), 1.27 (s, 18H, $6CH_3$), 1.26 (s, 18H, $6CH_3$) ppm. ^{13}C NMR (176 MHz, $CDCl_3$) δ 162.7 (CO), 162.6 (CO), 160.9 (CO), 156.2, 156.1, 153.9, 152.6, 152.2, 147.6, 144.5, 139.6, 137.7, 136.4, 134.2, 133.2, 132.9, 131.4 (CH), 127.4 (CH), 126.8 (CH), 124.8 (CH), 123.3 (CH), 122.5, 122.4, 122.3, 120.9, 120.8, 120.11 (CH), 120.08 (CH), 119.43 (CH), 119.38 (CH), 119.0, 115.4 (CH), 114.9 (CH), 34.4, 31.4 (CH_3), 18.7 (CH_3), 18.2 (CH_3), 17.8 (CH_3) ppm. FTIR ν 2963, 1725, 1705, 1670, 1587, 1505, 1403, 1353, 1339, 1285, 1172, 1058 cm^{-1}. HRMS (MALDI TOF) m/z 1426.4906 (calcd for $C_{90}H_{79}BrN_2O_{10}$: 1426.4918).

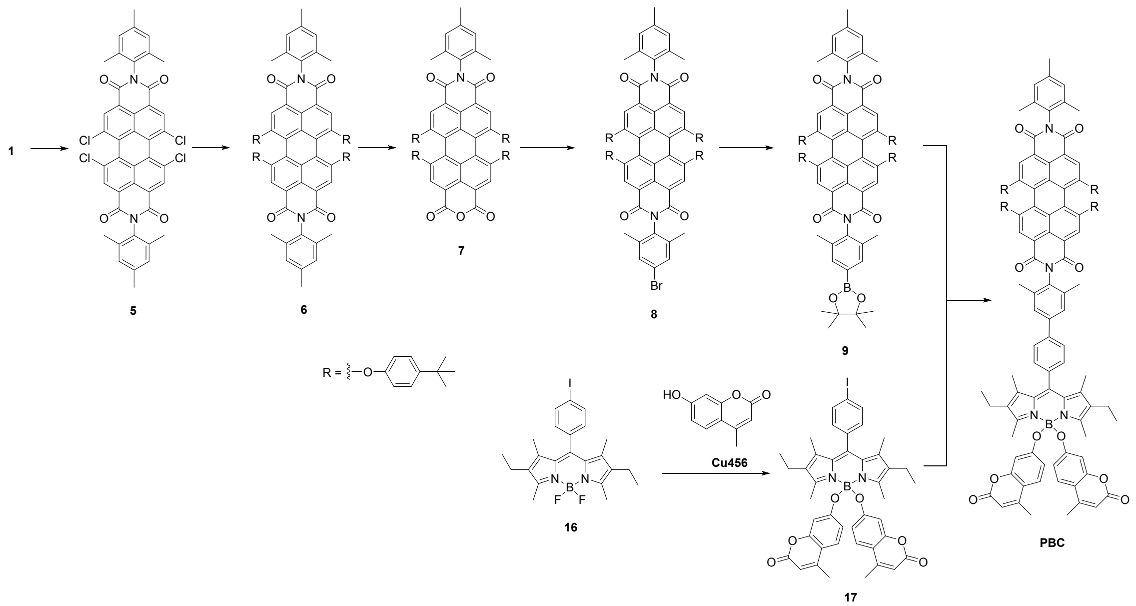
PC-1: ^1H NMR (300 MHz, $CDCl_3$) δ 8.30 (s, 4H, 4CH), 7.65 (d, J = 8.1 Hz, 2H, 2CH), 7.56-7.54 (m, 4H, 4CH), 7.43 (s, 4H, 4CH), 7.27 (d, J = 8.7 Hz, 8H, 8CH), 6.90 (d, J = 8.7 Hz, 8H, 8CH), 6.30 (d, J = 1.2 Hz, 2H, 2CH), 2.47 (d, J = 1.2 Hz, 6H, $2CH_3$), 2.21 (s, 12H, $4CH_3$), 1.27 (s, 36H, $12CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8 (CO), 160.9 (CO), 156.2, 153.9, 152.7, 152.2, 147.6, 144.5, 139.6, 136.4, 134.2, 133.2, 127.4 (CH), 126.8 (CH), 124.9 (CH), 123.3 (CH), 122.4, 120.8, 120.1 (CH), 119.4 (CH), 119.0, 115.4 (CH), 114.9 (CH), 34.4, 31.4 (CH_3), 18.7 (CH_3), 18.2 (CH_3) ppm. FTIR ν 2961, 1710, 1672, 1590, 1504, 1403, 1342, 1283, 1210, 1174 cm^{-1}. HRMS (MALDI TOF) m/z 1506.6177 (calcd for $C_{100}H_{86}N_2O_{12}$: 1506.6181).

PC-2: According to the general procedure 3., bis(pinacol boronate) **4** (65 mg, 0.045 mmol), 8-iodocoumarin **14**[4] (109 mg, 0.36 mmol), K_2CO_3 (50 mg, 0.36 mmol) and $Pd(PPh_3)_4$ (3.3 mg, 0.0045 mmol) in toluene/ethanol/water (10 mL) were refluxed for 8 h. Flash chromatography (hexane/EtOAc, 7:3) afforded **PC-2** (22 mg, 32%) as a red solid. ^1H NMR (700 MHz, $CDCl_3$) δ 8.31 (s, 4H, 4CH), 7.52 (d, J = 8.4 Hz, 2H, 2CH), 7.26 (d, J = 8.4 Hz, 8H, 8CH), 7.24 (s, 4H, 4CH), 6.98 (d, J = 8.4 Hz, 2H, 2CH), 6.89 (d, J = 8.4 Hz, 8H, 8CH), 6.13 (s, 2H, 2CH), 2.42 (s, 6H, $2CH_3$), 2.19 (s, 12H, $4CH_3$), 1.28 (s, 36H, $12CH_3$) ppm. ^{13}C NMR (176 MHz, $CDCl_3$) δ 162.7 (CO), 161.0 (CO), 156.5, 156.2, 152.7, 152.5, 151.8, 147.6, 137.3, 134.6, 133.2, 132.0, 130.6 (CH), 126.8 (CH), 125.0 (CH), 122.4, 120.9, 120.2 (CH), 120.1, 119.4 (CH), 115.8, 113.6, 112.5 (CH), 111.9 (CH), 34.4, 31.4 (CH_3), 18.9 (CH_3), 18.1 (CH_3) ppm. FTIR ν 3060, 2959, 2924, 1706, 1670, 1590, 1504, 1339, 1287, 1209, 1175 cm^{-1}. HRMS (MALDI TOF) m/z 1538.6067 (calcd for $C_{100}H_{86}N_2O_{14}$: 1538.6079).

PB-1: According to the general procedure 3., dibromoperylene bisimide **3** (100 mg, 0.074 mmol), pinacol boronate-BODIPY **15**[5] (113 mg, 0.22 mmol), K_2CO_3 (61 mg, 0.44 mmol) and $Pd(PPh_3)_4$ (8 mg, 0.007 mmol) in toluene/ethanol/water (10 mL) were refluxed for 1 h. Flash chromatography (hexane/DCM, 5:5) afforded **PB-1** (96 mg, 83%) as a red solid. ^1H NMR (300 MHz, $CDCl_3$) δ 8.34 (s, 4H, 4CH), 7.79 (d, J = 8.1 Hz, 4H, 4CH), 7.52 (s, 4H, 4CH), 7.37 (d, J = 8.1

Hz, 4H, 4CH), 7.29 (d, *J* = 8.7 Hz, 8H, 8CH), 6.93 (d, *J* = 8.7 Hz, 8H, 8CH), 2.56 (s, 12H, $4CH_3$), 2.33 (q, *J* = 7.2 Hz, 8H, $4CH_2$), 2.24 (s, 12H, $4CH_3$), 1.37 (s, 12H, $4CH_3$), 1.30 (s, 36H, $12CH_3$), 1.01 (t, *J* = 7.2 Hz, 12H, $4CH_3$), ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8 (CO), 156.2, 153.7, 152.7, 147.6, 141.1, 140.6, 140.0, 138.5, 136.1, 134.9, 133.6, 133.3, 132.8, 130.8, 128.7 (CH), 127.7 (CH), 127.3 (CH), 126.8 (CH), 122.5, 120.9, 120.21, 120.19 (CH), 119.4 (CH), 34.4, 31.5 (CH_3), 18.2 (CH_3), 17.1 (CH_2), 14.7 (CH_3), 12.6 (CH_3), 11.9 (CH_3) ppm. FTIR ν 2939, 1711, 1669, 1585, 1502, 1264, 1213, 1170 cm^{-1}. HRMS (MALDI TOF) *m/z* 1946.9596 (calcd for $C_{126}H_{124}B_2F_4N_6O_8$: 1946.9603).

Synthesis of triad PBC



Scheme S2. Synthetic route of triad **PBC**

5: According to the general procedure 4., method A, perylene dianhydride **1**[1] (750 mg, 1.41 mmol), 2,4,6-trimethylaniline (2 mL, 14.1 mmol) and propionic acid (50 mL) were refluxed for 16 h. Flash chromatography (hexane/DCM, 5:5) afforded **5** (1 g, 92%) as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (s, 4H, 4CH), 7.09 (s, 4H, 4CH), 2.39 (s, 6H, $2CH_3$), 2.14 (s, 12H, $4CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7 (CO), 139.2, 135.6, 135.0, 133.4 (CH), 131.7, 130.4, 129.6 (CH), 128.9, 123.9, 123.3, 21.2 (CH_3), 17.9 (CH_3) ppm. FTIR ν 2917, 1704, 1667, 1584, 1382, 1239, 1194, 1017 cm^{-1}. HRMS (EI) *m/z* 764.0639 (calcd for $C_{42}H_{26}Cl_4N_2O_4$: 764.0647).

6: According to the general procedure 1., 1,6,7,12-tetrachloroperylene bisimide **5** (1.2 g, 1.6 mmol), 4-*tert*butylphenol (2.4 g, 16 mmol) and K_2CO_3 (1.08 g, 8 mmol) in DMF (50 mL) were refluxed for 16 h. Flash chromatography (hexane/DCM, 7:3) afforded **6** (1.5 g, 78%) as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (s, 4H, 4CH), 7.24 (d, *J* = 8.7 Hz, 8H, 8CH), 6.97 (s, 4H, 4CH), 6.86 (d, *J* = 8.7 Hz, 8H, 8CH), 2.32 (s, 6H, 2CH_3), 2.06 (s, 12H, 4CH_3), 1.26 (s, 36H, 12CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3 (CO), 156.5, 153.2, 147.8, 138.8, 135.4, 133.6, 131.4, 129.7 (CH), 127.1 (CH), 123.0, 121.1, 120.6, 120.5 (CH), 119.8 (CH), 34.8, 31.9 (CH_3), 21.6 (CH_3), 18.3 (CH_3) ppm. FTIR ν 2960, 1710, 1673, 1590, 1502, 1404, 1337, 1283, 1209, 1173 cm^{-1}. HRMS (MALDI TOF) *m/z* 1218.5750 (calcd for $C_{82}H_{78}N_2O_8$: 1218.5758).

7: Perylene bisimide **6** (200 mg, 0.16 mmol) and KOH (27 mg, 0.48 mmol) dissolved in *tert*-butanol (30 mL) were refluxed under argon for 90 min. Then, acetic acid (15 mL) was added under stirring, and refluxed for 15 min. After cooling to r.t., the solution was poured into water and the precipitate was filtrated and purified by flash chromatography on silica gel (hexane/DCM, 7:3) to obtain **7** (139 mg, 77%) as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (s, 4H, 4CH), 7.28 (d, *J* = 8.7 Hz, 4H, 4CH), 7.26 (d, *J* = 8.7 Hz, 4H, 4CH), 6.99 (s, 2H, 2CH), 6.88 (d, *J* = 8.7 Hz, 4H, 4CH), 6.87 (d, *J* = 8.7 Hz, 4H, 4CH), 2.33 (s, 3H, CH_3), 2.07 (s, 6H, 2CH_3), 1.32 (s, 18H, 6CH_3), 1.29 (s, 18H, 6CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1 (CO), 160.4 (CO), 157.1, 156.3, 153.0, 152.8, 148.2, 148.1, 138.9, 135.3, 133.9, 133.6, 131.3, 129.7 (CH), 127.3 (CH), 127.2 (CH), 123.5, 122.6, 122.1, 122.0 (CH), 120.3, 120.2 (CH), 119.9 (CH), 119.7 (CH), 118.5, 34.84, 34.81, 31.85 (CH_3), 31.83 (CH_3), 21.5 (CH_3), 18.2 (CH_3) ppm. FTIR ν 2923, 1770, 1740, 1710, 1588, 1504, 1339, 1290, 1213, 991 cm^{-1}. HRMS (MALDI TOF) *m/z* 1101.4812 (calcd for $C_{73}H_{67}NO_9$: 1101.4816).

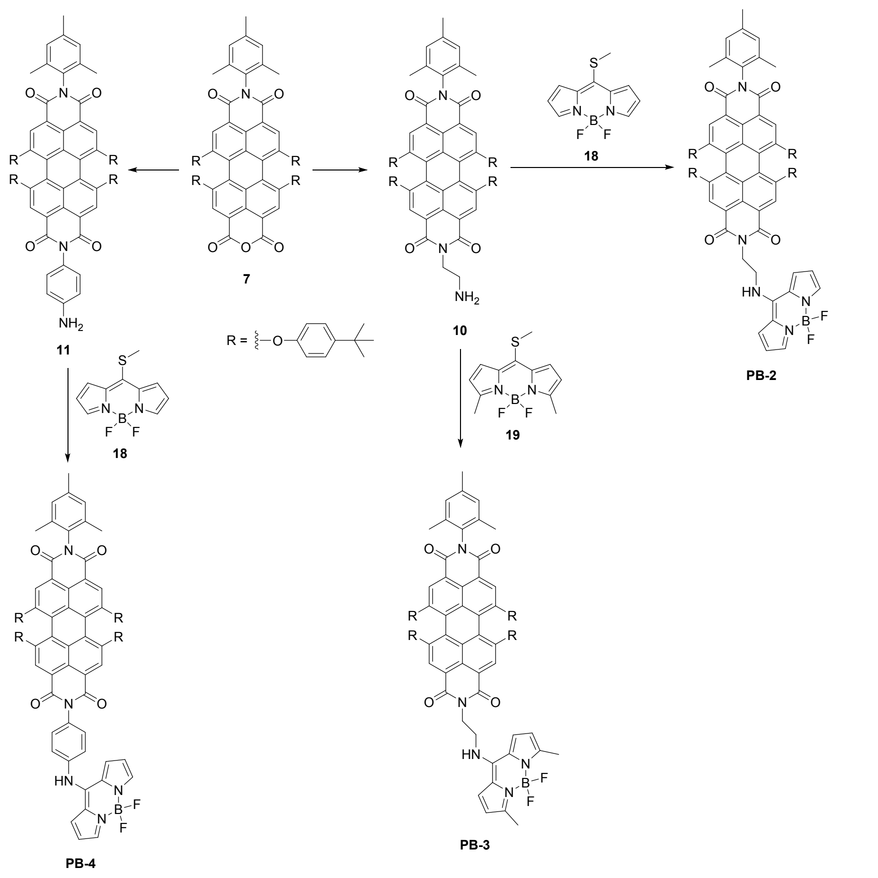
8: According to the general procedure 4., method A, perylene monoimide **7** (100 mg, 0.1 mmol), 4-bromo-2,6-dimethylaniline (0.06 mL, 0.5 mmol) and propionic acid (10 mL) were refluxed for 16 h. Flash chromatography (hexane/EtOAc, 9:1) afforded **8** (90 mg, 77%) as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (s, 4H, 4CH), 7.34 (s, 2H, 2CH), 7.27 (d, *J* = 8.7 Hz, 4H, 4CH), 7.26 (d, *J* = 8.7 Hz, 4H, 4CH), 6.99 (s, 2H, 2CH), 6.89 (d, *J* = 8.7 Hz, 4H, 4CH), 6.88 (d, *J* = 8.7 Hz, 4H, 4CH), 2.33 (s, 3H, CH_3), 2.10 (s, 6H, 2CH_3), 2.08 (s, 6H, 2CH_3), 1.29 (s, 18H, 6CH_3), 1.28 (s, 18H, 6CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8 (CO), 162.6 (CO), 156.2, 156.0, 152.7, 147.5, 138.5, 137.8, 135.0, 133.3, 133.2, 133.0, 131.4 (CH), 131.0, 129.3 (CH), 128.2, 127.8, 127.5, 126.8 (CH), 122.8, 122.5, 122.2, 121.0, 120.5, 120.1 (CH), 120.0 (CH), 119.4 (CH), 34.4, 31.5 (CH_3), 21.2 (CH_3), 17.84 (CH_3), 17.80 (CH_3) ppm. FTIR ν 2958, 1710, 1675, 1592, 1504, 1420, 1340, 1315, 1280, 1210, 1170 cm^{-1}. HRMS (MALDI TOF) *m/z* 1282.4695 (calcd for $C_{81}H_{75}BrN_2O_8$: 1282.4707).

9: According to the general procedure 2., perylene bisimide **8** (80 mg, 0.06 mmol), bis(pinacolato)diboron (47 mg, 0.18 mmol), Pd(dppf)Cl_2 (5 mg, 0.006 mmol) and KOAc (18 mg, 0.18 mmol) in DME (10 mL) were refluxed for 16 h. Flash chromatography (hexane/EtOAc, 9:1) afforded **9** (72 mg, 87%) as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (s, 2H, 2CH), 8.26 (s, 2H, 2CH), 7.62 (s, 2H, 2CH), 7.24 (d, *J* = 8.7 Hz, 8H, 8CH), 6.97 (s, 2H, 2CH), 6.87 (d, *J* = 8.7 Hz, 8H, 8CH), 2.31 (s, 3H, CH_3), 2.11 (s, 6H, 2CH_3), 2.06 (s, 6H, 2CH_3), 1.26 (s, 36H, 12CH_3), 1.25 (s, 12H, 4CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9 (CO), 162.6 (CO), 156.1, 156.0, 152.7, 147.4, 138.4, 136.6, 135.0, 134.9 (CH), 134.8, 133.2, 131.0, 129.2 (CH), 126.7 (CH), 122.6, 122.5, 120.8, 120.7, 120.2, 120.1 (CH), 120.0 (CH), 119.40 (CH), 119.38 (CH), 83.9 (C-O), 34.4, 31.4 (CH_3), 24.6 (CH_3), 24.1 (CH_3), 21.1 (CH_3), 17.8 (CH_3), 17.7 (CH_3) ppm. FTIR ν 2960, 1710, 1670, 1578, 1505, 1370, 1280, 1125 cm^{-1}. HRMS (MALDI TOF) *m/z* 1330.6440 (calcd for $C_{87}H_{87}BN_2O_{10}$: 1330.6454).

17: BODIPY **16**[6] (100 mg, 0.2 mmol) and $AlCl_3$ (53 mg, 0.4 mmol) in 1,2-dichloroethane (10 mL), under argon, were refluxed for 30 min. Then, coumarin **Cu456** (174 mg, 0.99 mmol) was added and the resulting mixture was refluxed for an additional 30 min. After cooling to r. t., the reaction was hydrolyzed with H_2O and extracted with DCM. The organic phase was dried over $MgSO_4$, filtered and concentrated to dryness. The crude was purified by flash chromatography on silica gel (DCM/MeOH, 9:1) to afford **17** (65 mg, 40%) as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H, 2CH), 7.38 (d, *J* = 8.7 Hz, 2H, 2CH), 7.19 (d, *J* = 8.4 Hz, 2H, 2CH), 6.78 (dd, *J* = 8.7 and 2.4 Hz, 2H, 2CH), 6.42 (d, *J* = 2.4 Hz, 2H, 2CH), 6.05 (d, *J* = 1.2 Hz, 2H, 2CH), 2.44 (s, 6H, 2CH_3), 2.34 (d, *J* = 1.2 Hz, 6H, 2CH_3), 2.17 (q, *J* = 7.5 Hz, 4H, 2CH_2), 1.38 (s, 6H, 2CH_3), 0.84 (t, *J* = 7.5 Hz, 6H, 2CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0 (CO), 160.1, 155.2, 154.9, 152.9, 139.7, 139.4, 138.6 (CH), 134.6, 134.2, 131.2, 130.2 (CH), 125.3 (CH), 116.5 (CH), 113.0, 111.3 (CH), 105.2 (CH), 94.9 (C-I), 18.6 (CH_3), 17.1 (CH_2), 14.4 (CH_3), 12.8 (CH_3), 12.3 (CH_3) ppm. FTIR ν 2925, 1719, 1606, 1548, 1476, 1388, 1190, 1138, 1068, 1002, 987 cm^{-1}. HRMS (EI) *m/z* 818.2018 (calcd for $C_{43}H_{40}BIN_2O_6$: 818.2024).

PBC: According to the general procedure 3., perylene bisimide **9** (342 mg, 0.26 mmol), BODIPY-coumarin **17** (70 mg, 0.085 mmol), K_2CO_3 (47 mg, 0.34 mmol) and $Pd(PPh_3)_4$ (10 mg, 0.009 mmol) in toluene/ethanol/water (10 mL) were refluxed for 8 h. Flash chromatography (hexane/EtOAc, 7:3) afforded **PBC** (32 mg, 20%) as a red solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.30 (s, 2H, 2CH), 8.27 (s, 2H, 2CH), 7.86 (d, *J* = 8.4 Hz, 2H, 2CH), 7.53 (s, 2H, 2CH), 7.48 (d, *J* = 8.4 Hz, 2H, 2CH), 7.38 (d, *J* = 9.1 Hz, 2H, 2CH), 7.25 (d, *J* = 8.4 Hz, 4H, 4CH), 7.24 (d, *J* = 8.4 Hz, 4H, 4CH), 6.98 (s, 2H, 2CH), 6.89 (d, *J* = 8.4 Hz, 4H, 4CH), 6.88 (d, *J* = 8.4 Hz, 4H, 4CH), 6.77 (dd, *J* = 9.1 and 2.1 Hz, 2H, 2CH), 6.51 (d, *J* = 2.1 Hz, 2H, 2CH), 6.06 (d, *J* = 1.4 Hz, 2H, 2CH), 2.46 (s, 6H, $2CH_3$), 2.35 (d, *J* = 1.4 Hz, 6H, $2CH_3$), 2.32 (s, 3H, CH_3), 2.22 (s, 6H, $2CH_3$), 2.18 (q, *J* = 7.7 Hz, 4H, $2CH_2$), 2.07 (s, 6H, $2CH_3$), 1.41 (s, 6H, $2CH_3$), 1.27 (s, 36H, $12CH_3$), 0.85 (t, *J* = 7.7 Hz, 6H, $2CH_3$) ppm. ^{13}C NMR (176 MHz, $CDCl_3$) δ 162.9 (CO), 162.8 (CO), 161.9 (CO), 160.2, 156.2, 156.0, 155.2, 154.5, 152.8, 152.74, 152.71, 147.5, 141.4, 140.0, 138.4, 136.2, 135.0, 133.9, 133.2, 131.4, 131.0, 129.3 (CH), 128.7 (CH), 128.0 (CH), 127.3 (CH), 126.7 (CH), 125.2 (CH), 122.7, 122.4, 120.9, 120.6, 120.2 (CH), 120.1 (CH), 119.41 (CH), 119.39 (CH), 116.3 (CH), 113.0, 111.3 (CH), 105.4 (CH), 34.4, 31.4 (CH_3), 21.1 (CH_3), 18.6 (CH_3), 18.2 (CH_3), 17.8 (CH_3), 17.1 (CH_2), 14.5 (CH_3), 12.7 (CH_3), 12.3 (CH_3) ppm. FTIR ν 2939, 1725, 1711, 1670, 1587, 1504, 1350, 1274, 1210, 1170, 1014 cm^{-1}. HRMS (MALDI TOF) *m/z* 1894.8499 (calcd for $C_{124}H_{115}BN_4O_{14}$: 1894.8503).

Synthesis of dyads PB-2, PB-3 and PB-4



Scheme S3. Synthetic route of dyads **PB-2**, **PB-3** and **PB-4.**

10: According to the general procedure 4., method B, perylene monoimide **7** (50 mg, 0.05 mmol), ethylenediamine (0.02 mL, 0.25 mmol) and toluene (10 mL) were stirred at 60 ºC for 3 h. Flash chromatography (DCM/MeOH, 95:5) afforded **10** (43 mg, 83%) as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (s, 2H, 2CH), 8.23 (s, 2H, 2CH), 7.25 (d, *J* = 8.7 Hz, 4H, 4CH), 7.23 (d, *J* = 8.7 Hz, 4H, 4CH), 6.97 (s, 2H, 2CH), 6.86 (d, *J* = 8.7 Hz, 4H, 4CH), 6.83 (d, *J* = 8.7 Hz, 4H, 4CH), 4.23 (t, *J* = 6.3 Hz, 2H, CH_2), 3.03 (t, *J* = 6.3 Hz, 2H, CH_2), 2.31 (s, 3H, CH_3), 2.05 (s, 6H, $2CH_3$), 1.29 (s, 18H, $6CH_3$), 1.26 (s, 18H, $6CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7 (CO), 162.8 (CO), 156.1, 155.9, 152.9, 152.7, 147.4, 147.3, 138.4, 135.0, 133.1, 133.0, 131.0, 129.2 (CH), 126.7 (CH), 122.6, 122.4, 120.8, 120.6, 120.1 (CH), 120.0 (CH), 119.4 (CH), 119.3 (CH), 43.2 (CH_2), 40.4 (CH_2), 34.40, 34.39, 31.48 (CH_3), 31.45 (CH_3), 21.1 (CH_3), 17.8 (CH_3) ppm. FTIR ν 3354, 3277, 2959, 1702, 1668, 1588, 1502, 1442, 1288, 1209, 1212, 1174, 1017 cm^{-1}. HRMS (MALDI TOF) *m/z* 1143.5390 (calcd for $C_{75}H_{73}N_3O_8$: 1143.5398).

PB-2: According to the general procedure 5., perylene bisimide **10** (43 mg, 0.037 mmol), 8-thiomethylBODIPY **18**[7] (18 mg, 0.075 mmol) in CH_3CN (10 mL) were stirred at r.t. for 3 h. Flash chromatography (hexane/EtOAc, 5:5) afforded **PB-2** (26 mg, 52%) as a purple solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (t, *J* = 3.9 Hz, 1H, NH), 8.35 (s, 2H, 2CH), 8.21 (s, 2H, 2CH), 7.68 (broad s, 1H, CH), 7.46 (broad s, 1H, CH), 7.27 (d, *J* = 8.7 Hz, 4H, 4CH), 7.23 (d, *J* = 8.7 Hz, 4H, 4CH), 7.11 (broad s, 1H, CH), 7.09 (broad s, 1H, CH), 6.97 (s, 2H, 2CH), 6.88 (d, *J* = 8.7 Hz, 4H, 4CH), 6.79 (d, *J* = 8.7 Hz, 4H, 4CH), 6.50 (broad s, 1H, CH), 6.33 (broad s, 1H, CH), 4.73 (broad s, 2H, CH_2), 4.06 (broad s, 2H, CH_2), 2.31 (s, 3H, CH_3), 2.04 (s, 6H, $2CH_3$), 1.32 (s, 18H, $6CH_3$), 1.27 (s, 18H, $6CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0 (CO), 162.8 (CO), 156.7, 155.6, 153.1, 152.4, 148.4, 147.6, 147.4, 138.5, 135.8 (CH), 134.9, 133.1, 132.9, 132.4 (CH), 130.9, 129.3 (CH), 126.8 (CH), 125.1, 123.7 (CH), 123.0, 122.2, 121.1 (CH), 119.9, 119.84, 119.79, 119.72 (CH), 119.5 (CH), 119.0 (CH), 115.8 (CH), 114.9 (CH), 113.7, 48.6 (CH_2), 39.2 (CH_2), 34.5, 31.4 (CH_3), 21.2 (CH_3), 17.8 (CH_3) ppm. FTIR ν 3306, 2960, 1698, 1672, 1583, 1503, 1407, 1341, 1284, 1210, 1173, 1088, 834 cm^{-1}. HRMS (MALDI TOF) *m/z* 1333.5901 (calcd for $C_{84}H_{78}BF_2N_5O_8$: 1333.5912).

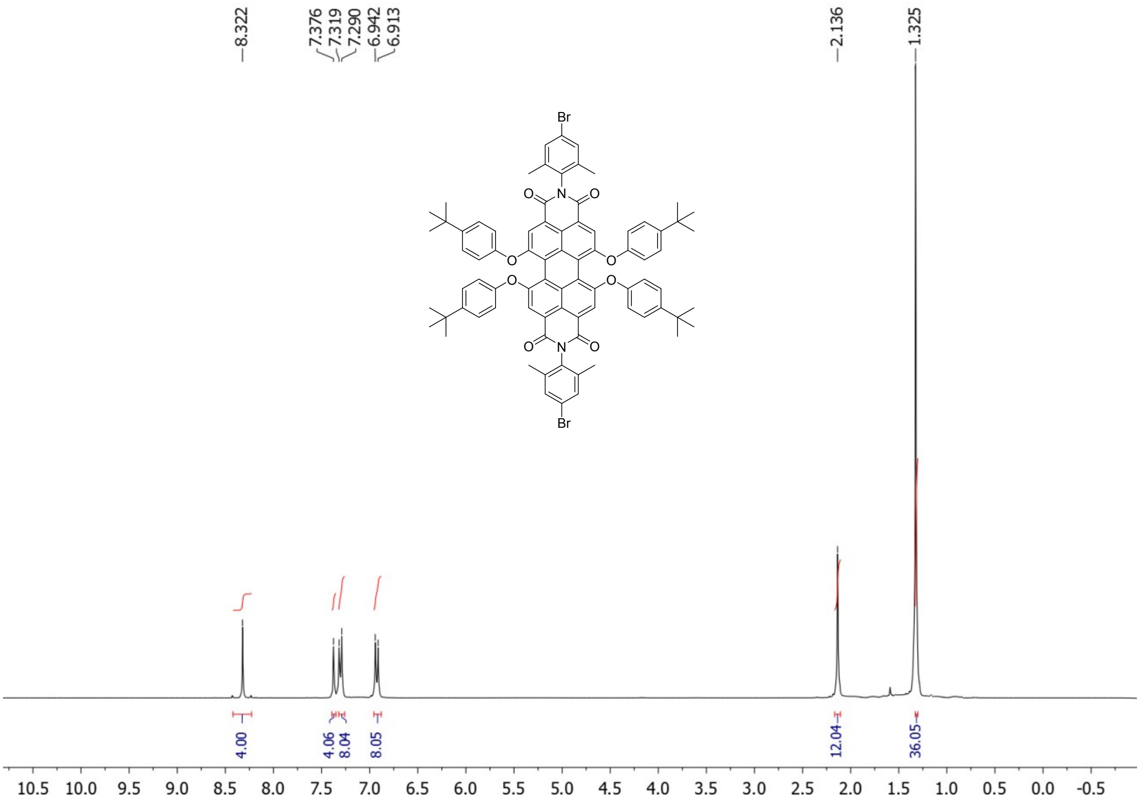
PB-3: According to the general procedure 5., perylene bisimide **10** (52 mg, 0.045 mmol), 3,5-dimethyl-8-thiomethylBODIPY **19**[7] (24 mg, 0.09 mmol) in CH_3CN (10 mL) were stirred at r.t. for 3 h. Flash chromatography (hexane/EtOAc, 5:5) afforded **PB-3** (26 mg, 42%) as a purple solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (s, 2H, 2CH), 8.21 (s, 2H, 2CH), 7.82 (broad s, 1H, NH), 7.27 (d, *J* = 8.7 Hz, 4H, 4CH), 7.23 (d, *J* = 8.7 Hz, 4H, 4CH), 6.97 (s, 2H, 2CH), 6.95 (broad s, 2H, 2CH), 6.88 (d, *J* = 8.7 Hz, 4H, 4CH), 6.79 (d, *J* = 8.7 Hz, 4H, 4CH), 6.13 (broad s, 2H, 2CH), 4.68 (broad s, 2H, CH_2), 3.99 (broad s, 2H, CH_2), 2.53 (s, 6H, $2CH_3$), 2.31 (s, 3H, CH_3), 2.05 (s, 6H, $2CH_3$), 1.32 (s, 18H, $6CH_3$), 1.27 (s, 18H, $6CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9 (CO), 162.8 (CO), 156.6, 155.6, 153.1, 152.5, 147.6, 147.4, 138.5, 134.9, 133.1, 132.9, 130.9, 129.3 (CH), 126.7 (CH), 123.0, 122.1, 121.3, 121.1 (CH), 120.0, 119.9, 119.8, 119.7 (CH), 119.5 (CH), 119.0 (CH), 48.3 (CH_2), 39.5 (CH_2), 34.4, 31.5 (CH_3), 31.4 (CH_3), 21.1 (CH_3), 17.8 (CH_3), 14.1 (CH_3) ppm. FTIR ν 3336, 2960, 2924, 2854, 1698, 1584, 1504, 1409, 1341, 1288, 1211, 1172 cm^{-1}. HRMS (MALDI TOF) *m/z* 1361.6197 (calcd for $C_{86}H_{82}BF_2N_5O_8$: 1361.6225).

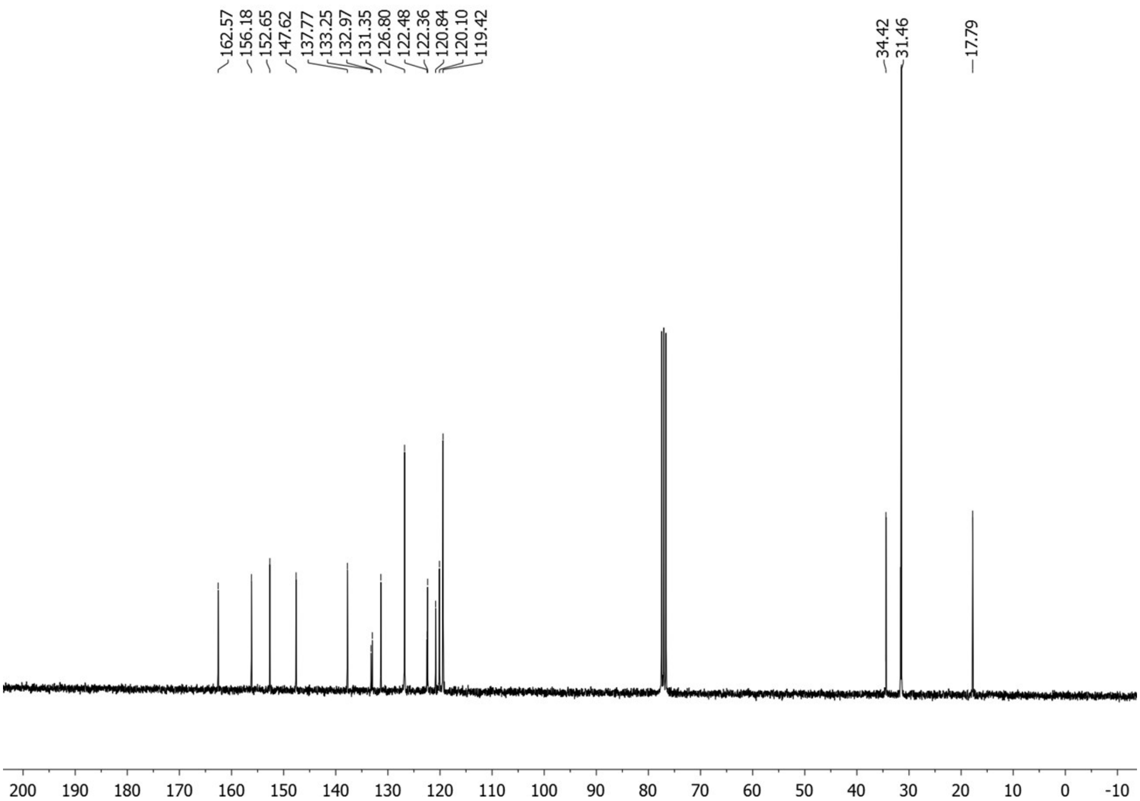
11: According to the general procedure 4., method B, perylene monoimide **7** (70 mg, 0.064 mmol), 1,4-diaminobenzene (17 mg, 0.16 mmol) and toluene (10 mL) were stirred at 60 ºC for 3 h. Flash chromatography (hexane/DCM, 3:7) afforded 21 (27 mg, 36%) as a red solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.25 (s, 2H, 2CH), 8.24 (s, 2H, 2CH), 7.24 (d, J = 8.7 Hz, 4H, 4CH), 7.23 (d, J = 8.4 Hz, 4H, 4CH), 7.00 (d, J = 8.4 Hz, 2H, 2CH), 6.97 (s, 2H, 2CH), 6.85 (d, J = 8.4 Hz, 8H, 8CH), 6.76 (d, J = 8.4 Hz, 2H, 2CH), 3.84 (broad s, 2H, NH_2), 2.32 (s, 3H, CH_3), 2.06 (s, 6H, $2CH_3$), 1.26 (s, 36H, $12CH_3$) ppm. ^{13}C NMR (176 MHz, $CDCl_3$) δ 163.9 (CO), 162.8 (CO), 160.0, 152.8, 152.6, 147.3, 146.6, 138.4, 134.9, 133.1, 133.0, 130.9, 129.2 (CH), 129.1 (CH), 126.65 (CH), 126.62 (CH), 125.5, 122.7, 122.5, 120.6, 120.2 (CH), 120.04, 119.97 (CH), 119.7, 119.34 (CH), 119.27 (CH), 115.5 (CH), 34.3, 31.4 (CH_3), 21.1 (CH_3), 17.7 (CH_3) ppm. FTIR ν 3376, 2925, 1706, 1670, 1588, 1507, 1290, 1210, 1176 cm^{-1}. HRMS (MALDI TOF) *m/z* 1191.5388 (calcd for $C_{79}H_{73}N_3O_8$: 1191.5398).

PB-4: Perylene bisimide **11** (27 mg, 0.023 mmol), 8-thiomethylBODIPY **18**[7] (6 mg, 0.025 mmol), copper(I) thiophene-2-carboxylate (4.8 mg, 0.025 mmol) in CH_3CN (10 mL) were stirred at 70 ºC for 24 h. Solvent was evaporated in vacuum, and the crude product was purified by flash chromatography (hexane/DCM, 5:5) affording **PB-4** (14 mg, 45%) as a purple solid. ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.30 (s, 2H, 2CH), 8.25 (s, 2H, 2CH), 7.95 (s, 1H, NH), 7.61 (s, 2H, 2CH), 7.53 (d, J = 8.4 Hz, 2H, 2CH), 7.41 (d, J = 8.4 Hz, 2H, 2CH), 7.24 (d, J = 8.4 Hz, 8H, 8CH), 6.97 (s, 2H, 2CH), 6.87 (d, J = 8.4 Hz, 4H, 4CH), 6.86 (d, J = 8.4 Hz, 4H, 4CH), 6.66 (d, J = 2.8 Hz, 2H, 2CH), 6.36 (d, J = 2.8 Hz, 2H, 2CH), 2.31 (s, 3H, CH_3), 2.06 (s, 6H, $2CH_3$), 1.271 (s, 18H, $6CH_3$), 1.266 (s, 18H, $6CH_3$) ppm. ^{13}C NMR (176 MHz, $CDCl_3$) δ 163.5 (CO), 162.8 (CO), 156.4, 156.0, 152.8, 152.6, 147.6, 147.5, 147.3, 138.5, 137.8, 136.0 (CH), 134.9, 133.3, 133.1, 131.0 (CH), 130.9, 129.3 (CH), 127.6 (CH), 126.8 (CH), 124.0, 122.8, 122.0, 121.4, 120.8 (CH), 120.4 (CH), 120.3, 120.0, 119.9 (CH), 119.5 (CH), 119.3 (CH), 115.0 (CH), 34.4, 31.4 (CH_3), 21.1 (CH_3), 17.8 (CH_3) ppm. FTIR ν 3366, 2925, 1710, 1668, 1585, 1504, 1274, 1210, 1173 cm^{-1}. HRMS (MALDI TOF) *m/z* 1381.5908 (calcd for $C_{88}H_{78}BF_2N_5O_8$: 1381.5912).

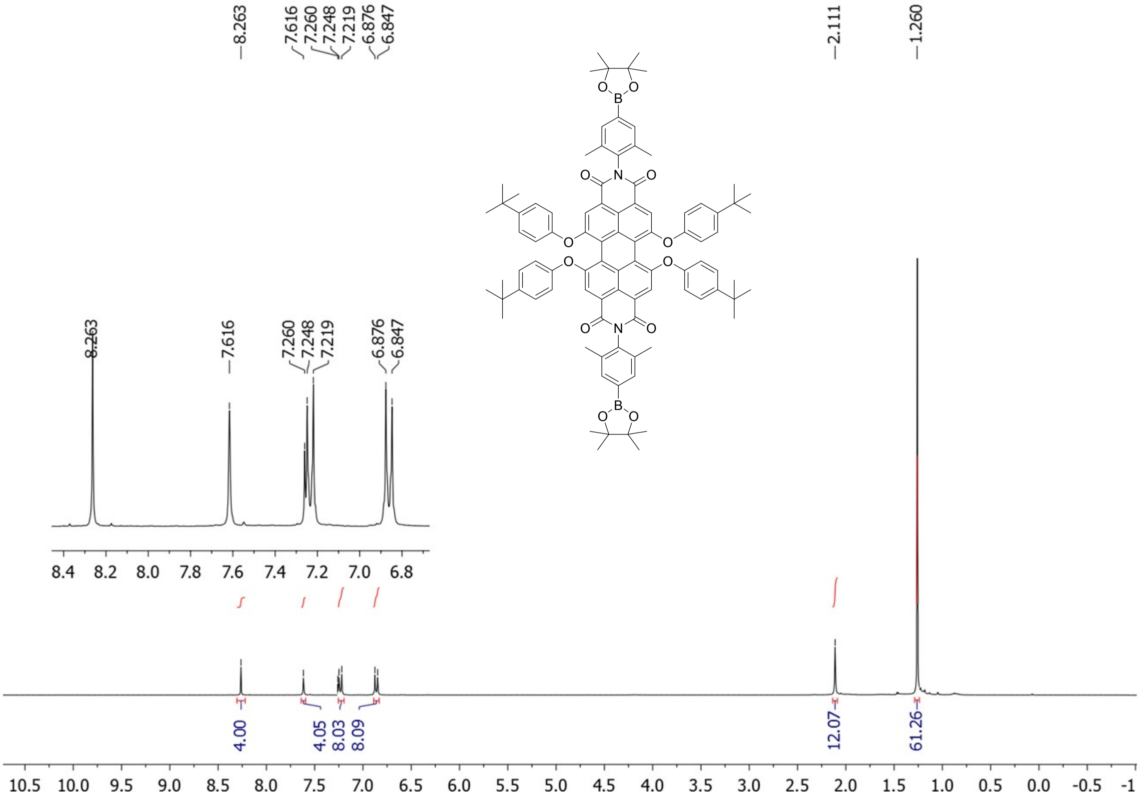
^{1}H and ^{13}C NMR spectra

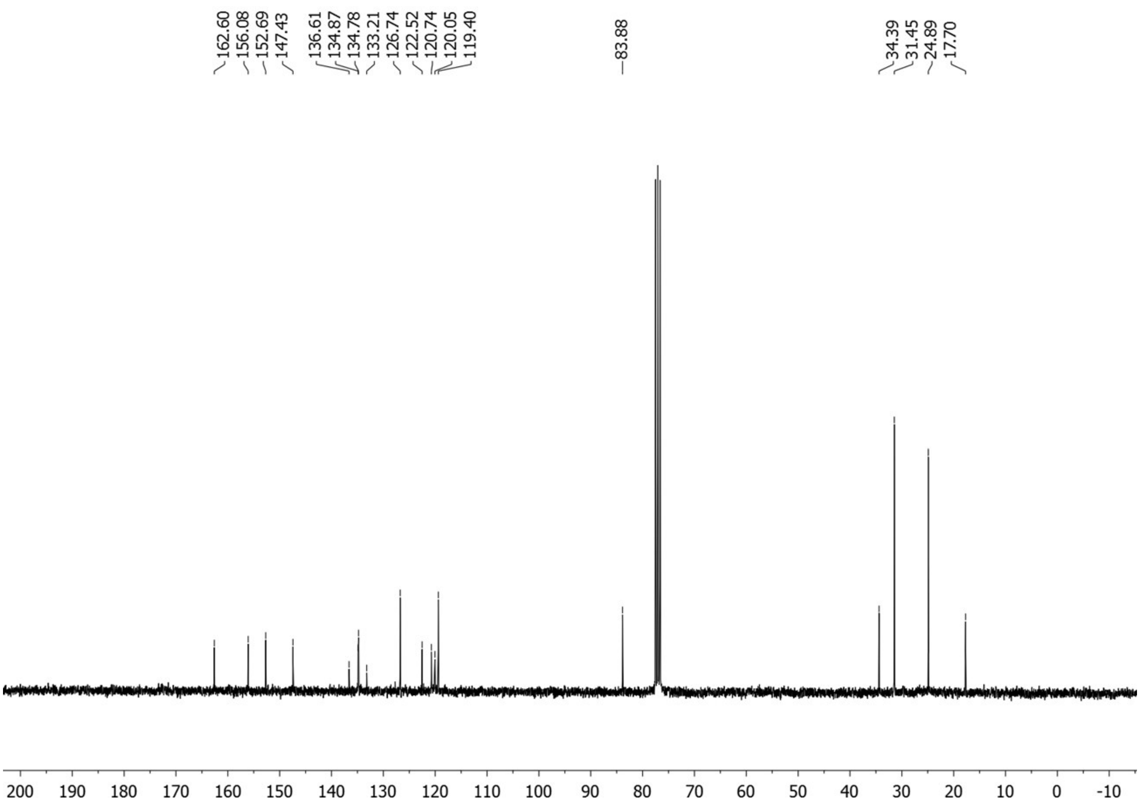
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of **3**



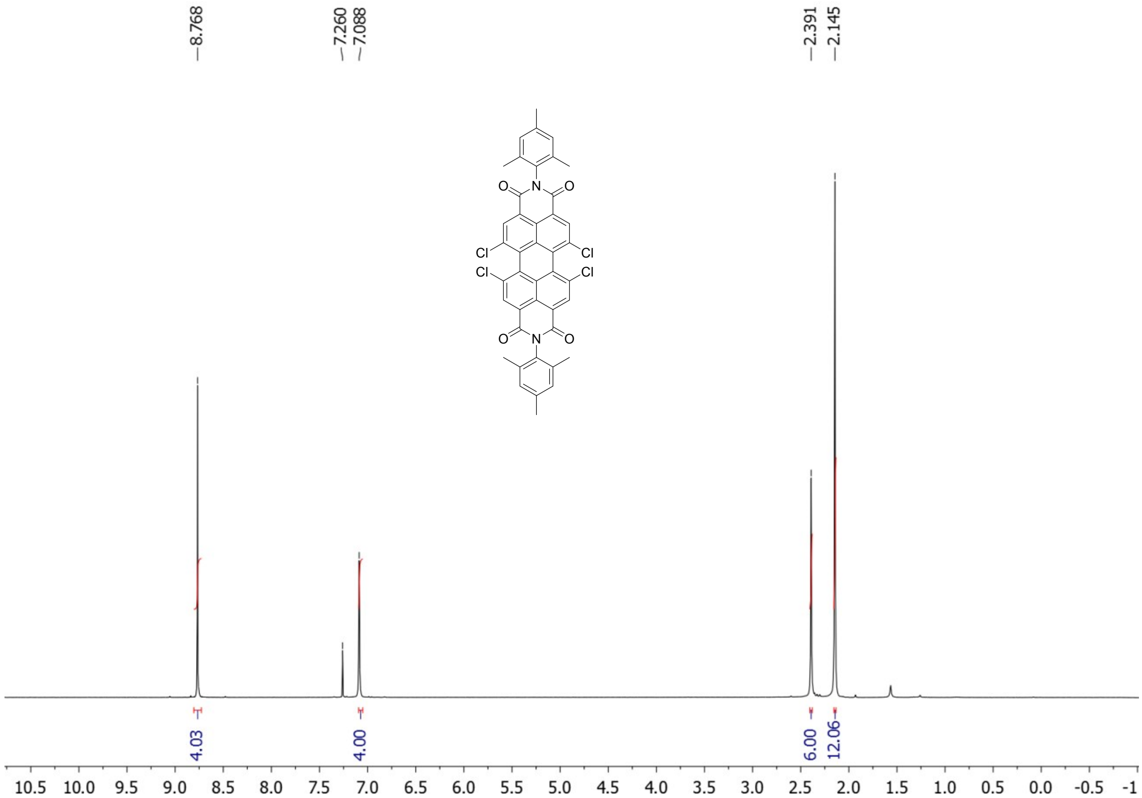


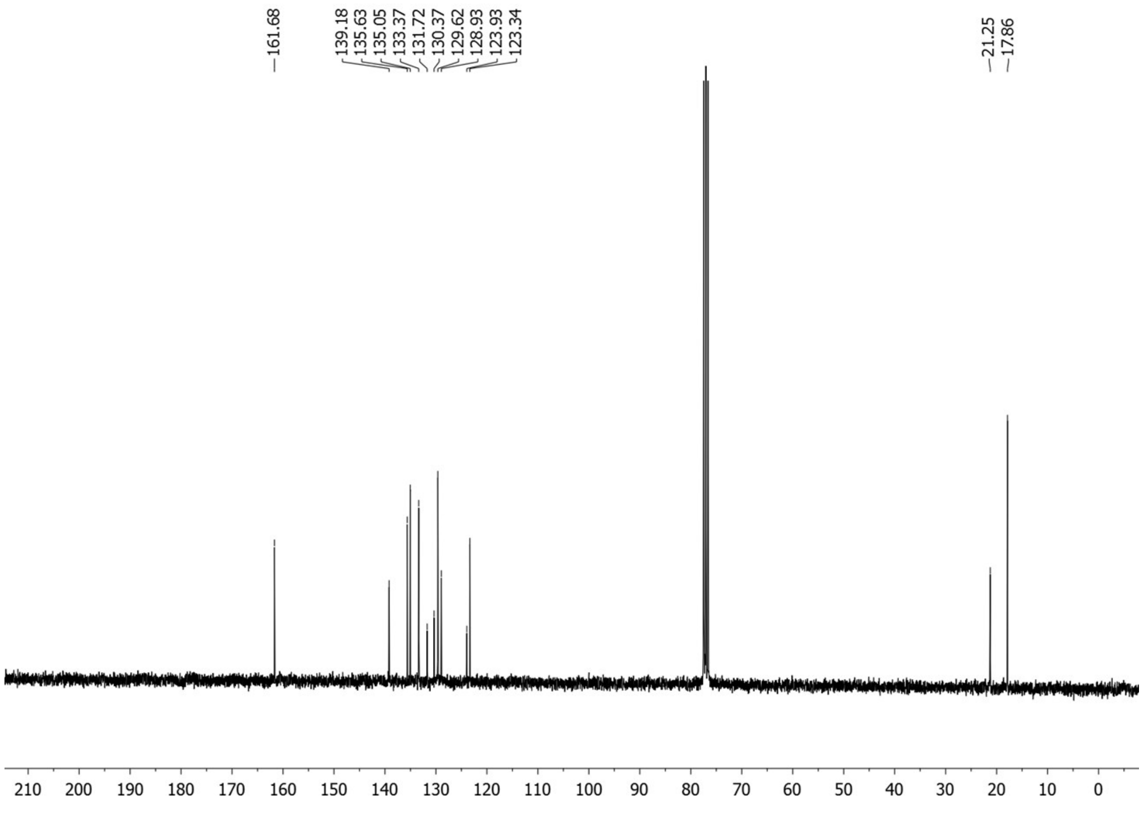
[1]H (300 MHz, $CDCl_3$) and [13]C (75 MHz, $CDCl_3$) spectra of **4**



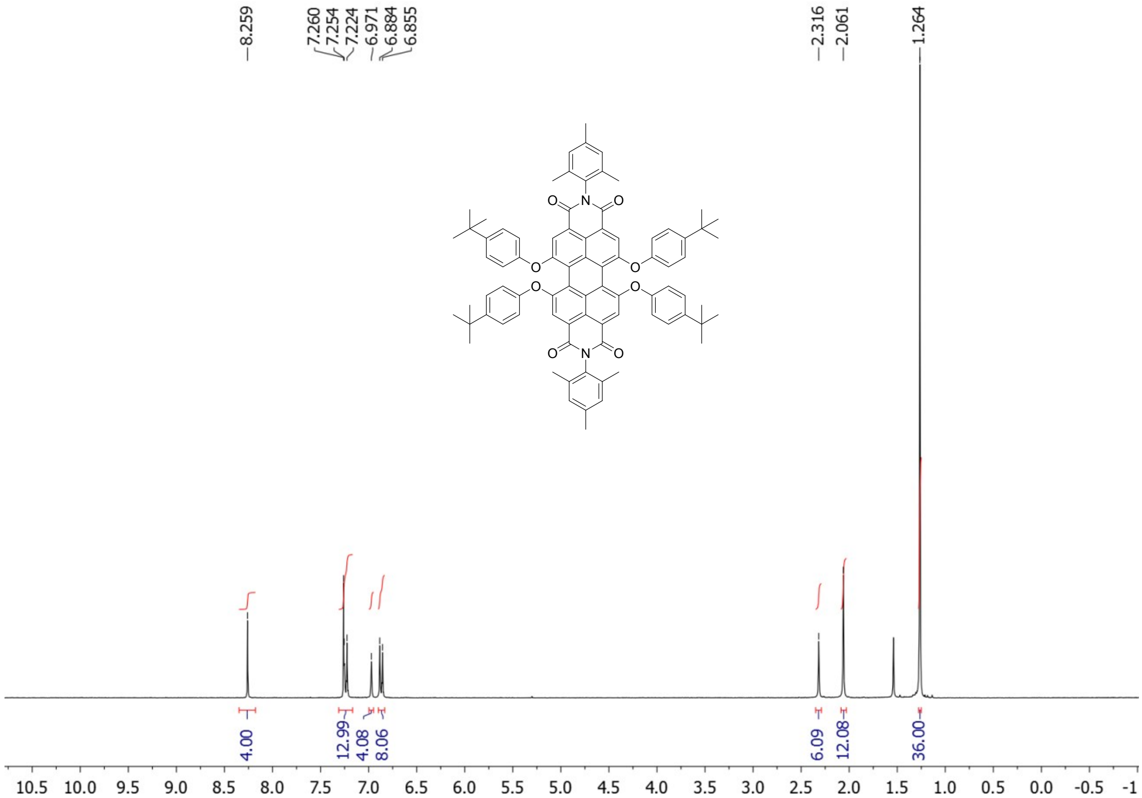


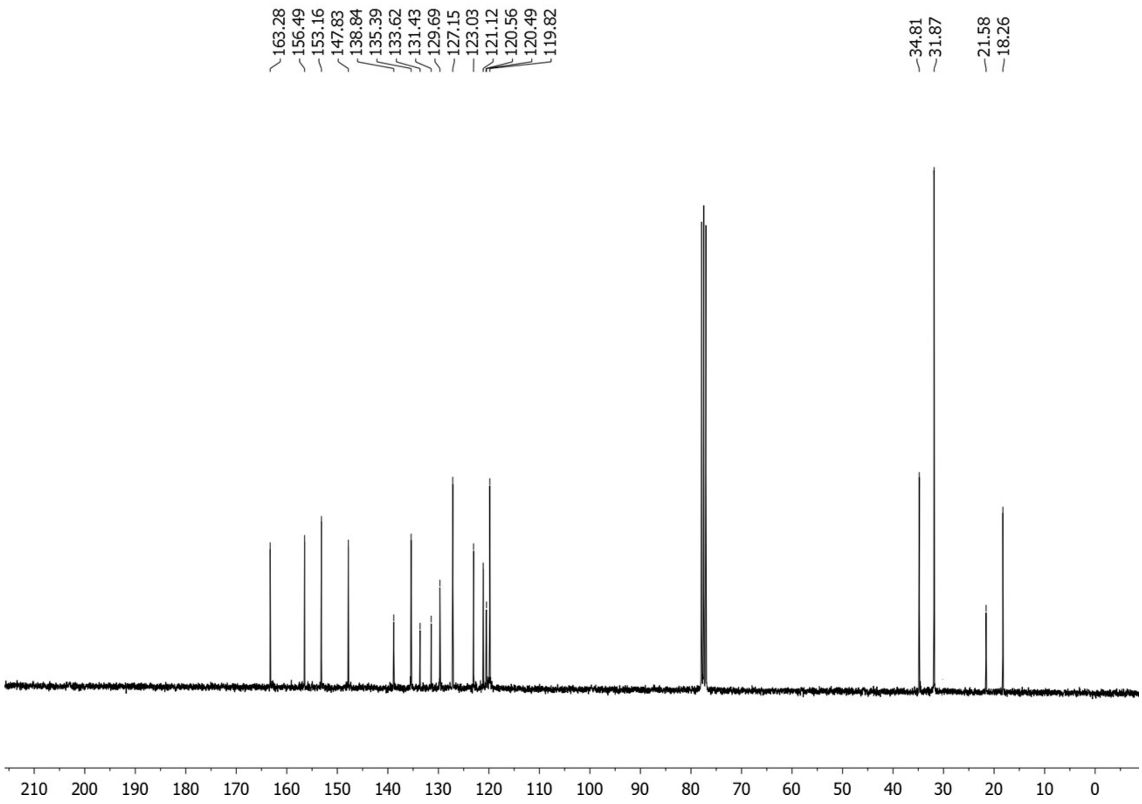
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of **5**



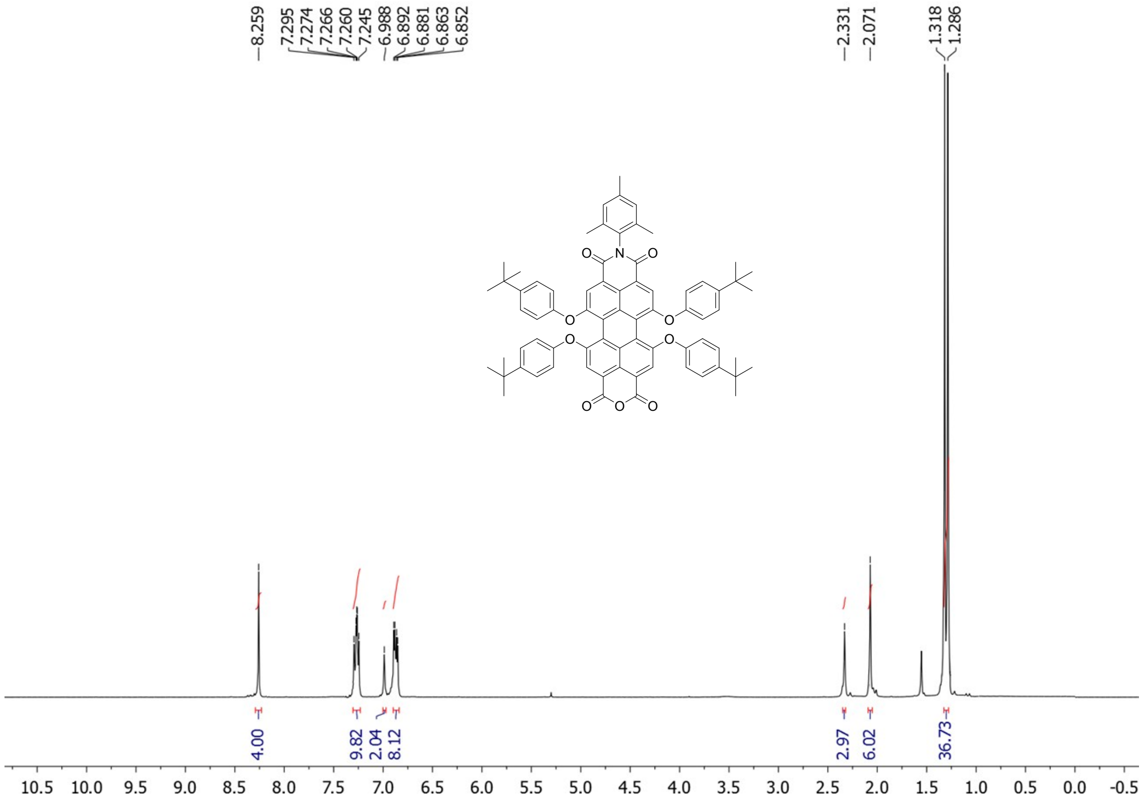


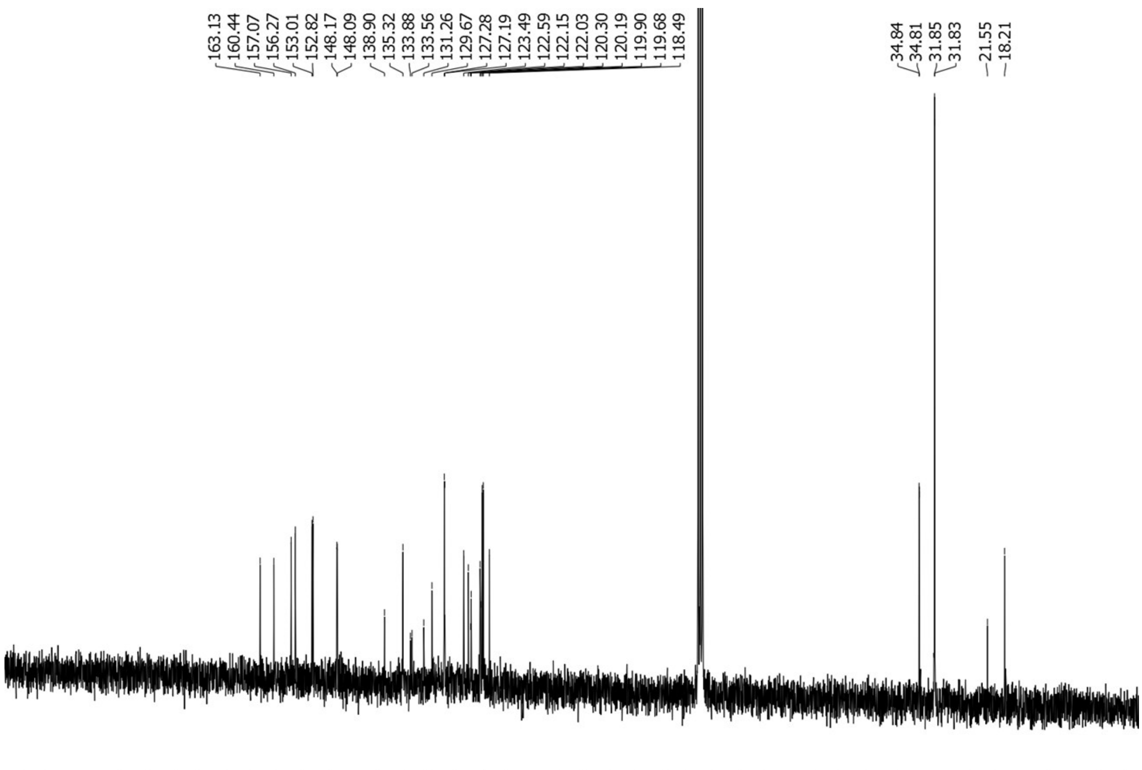
^1H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of **6**



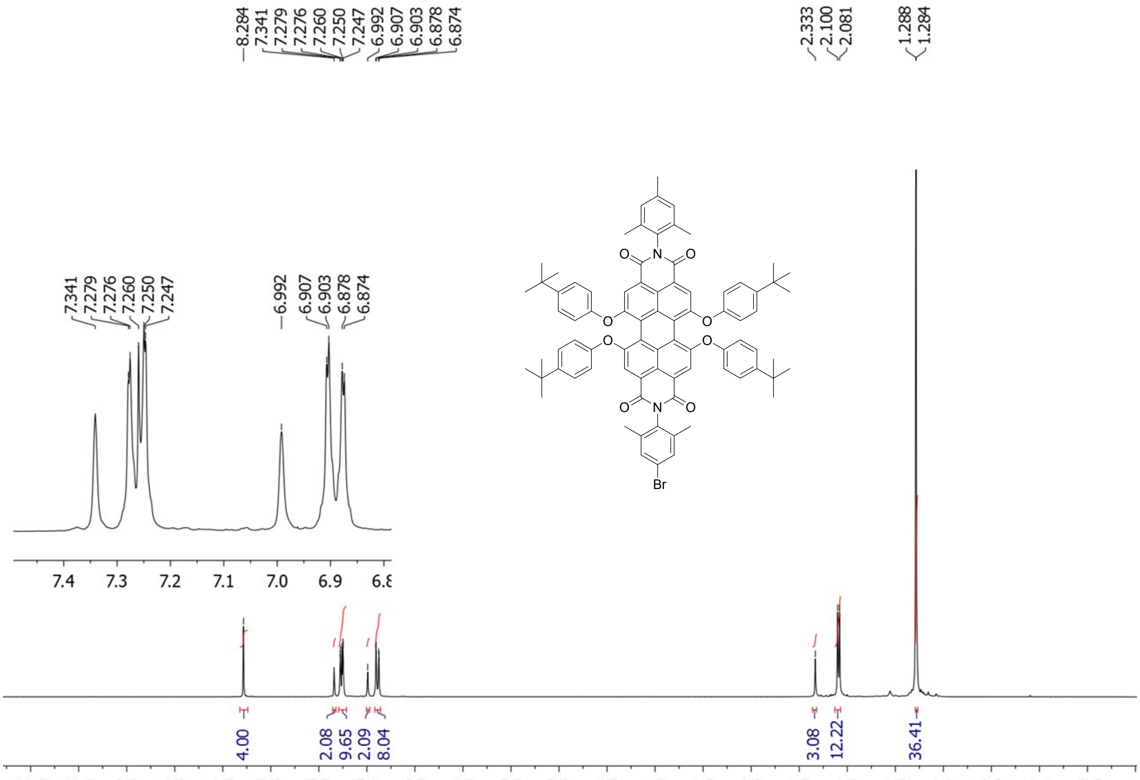


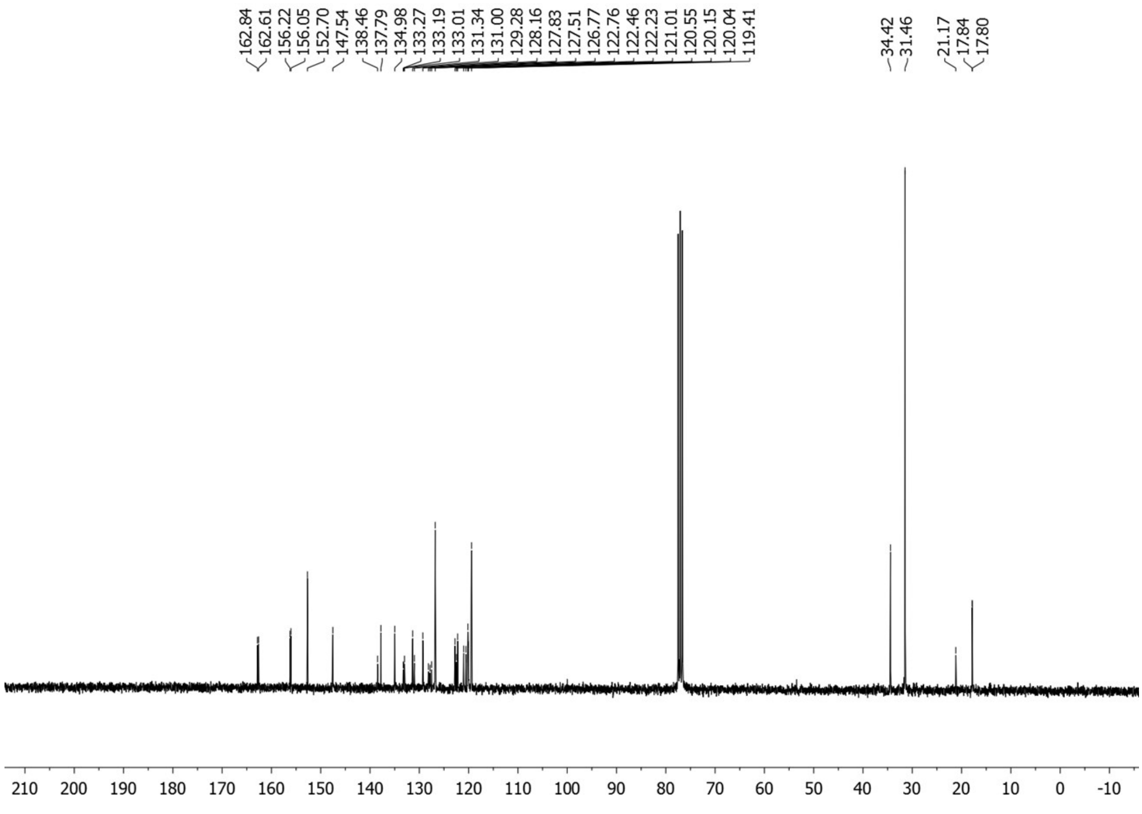
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of **7**



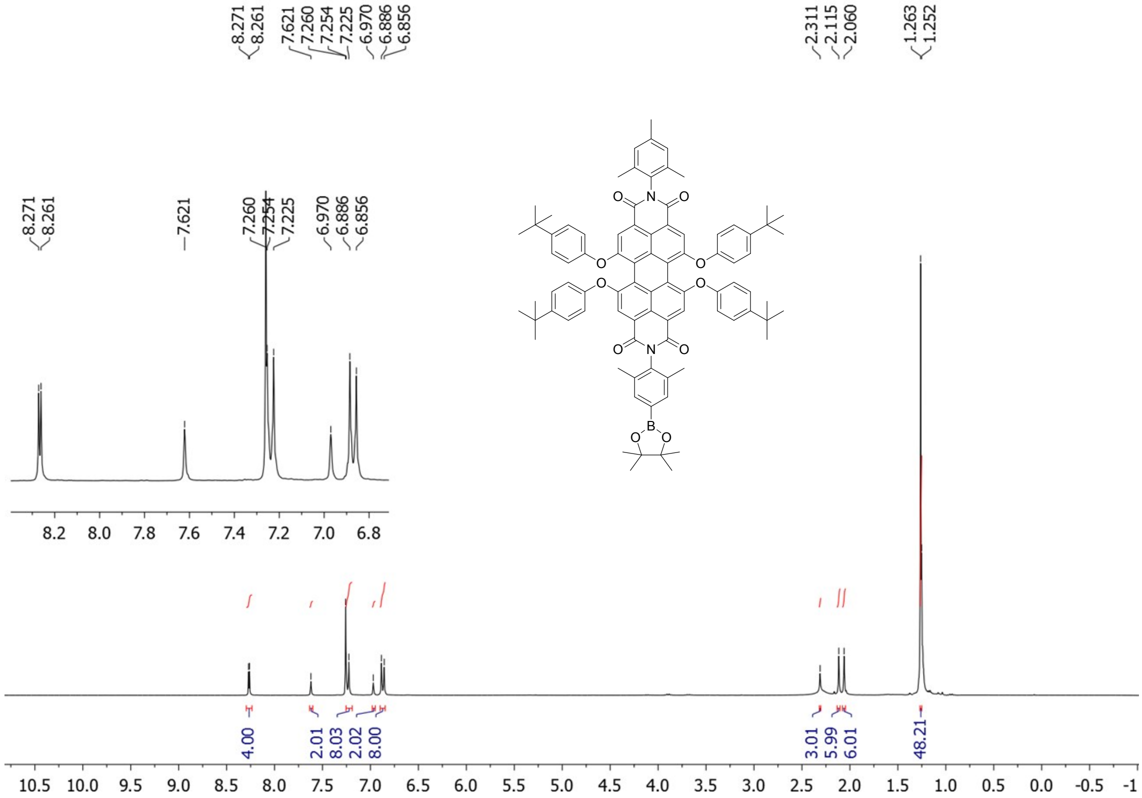


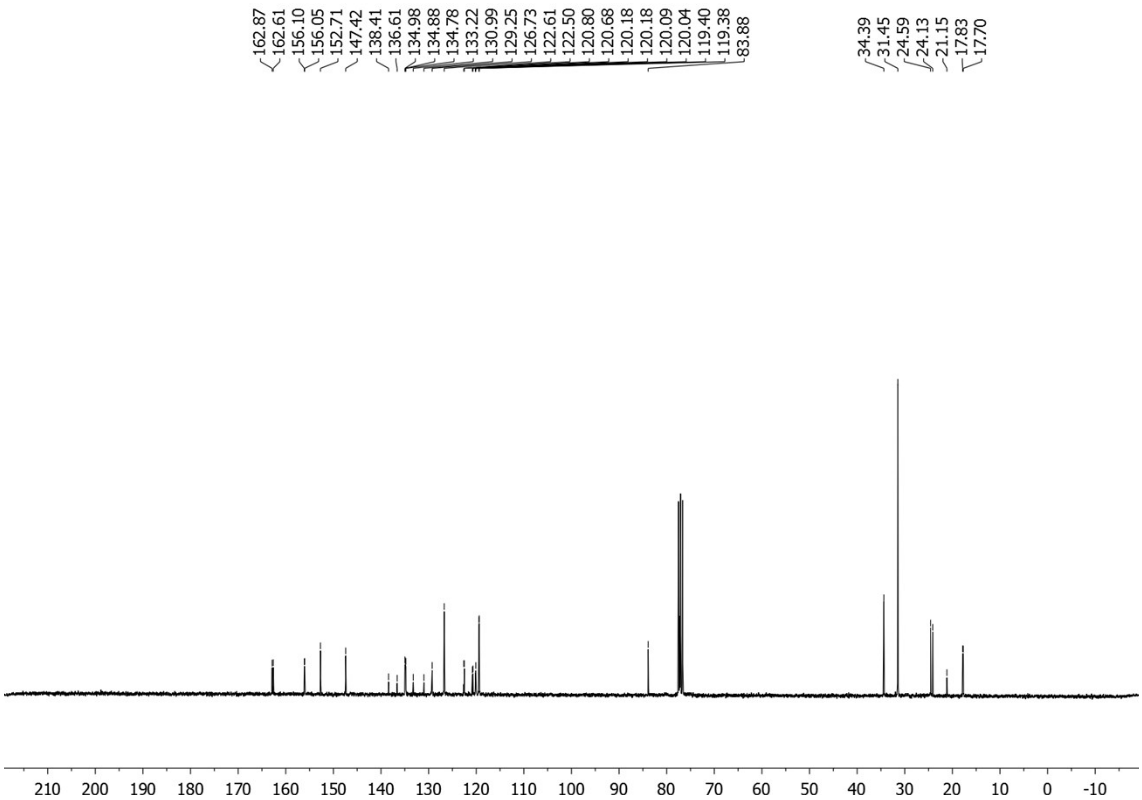
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of **8**



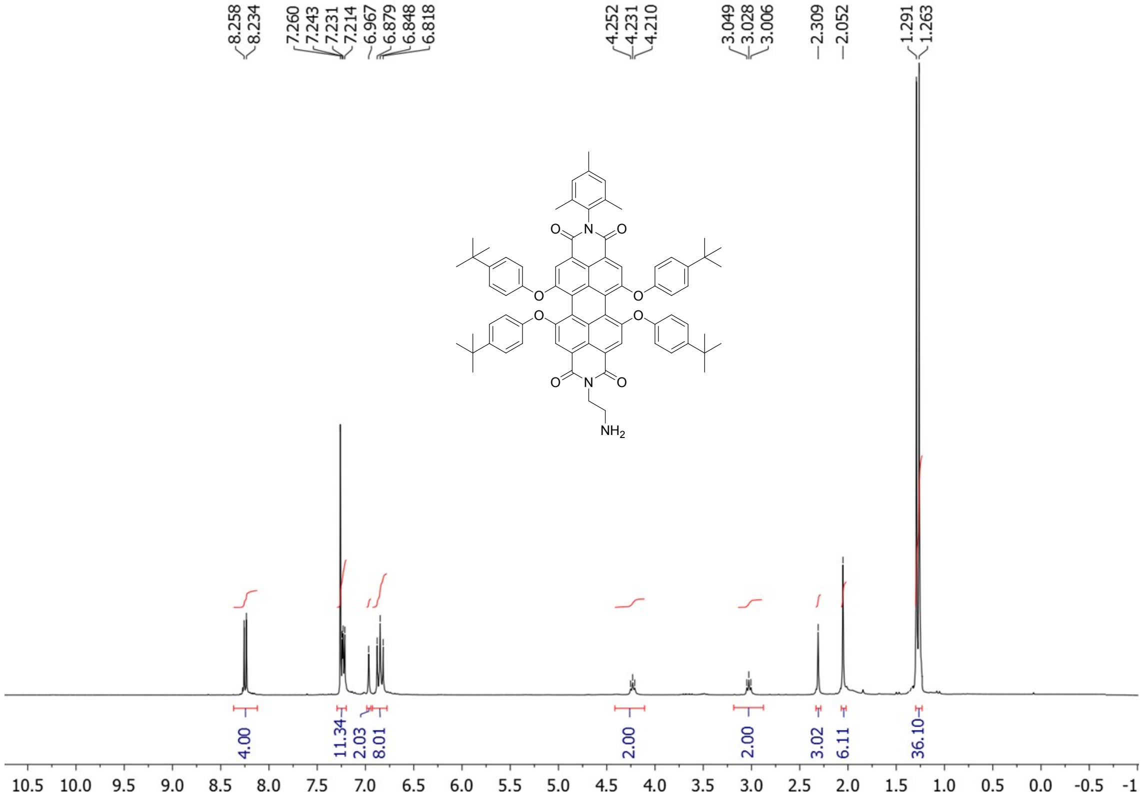


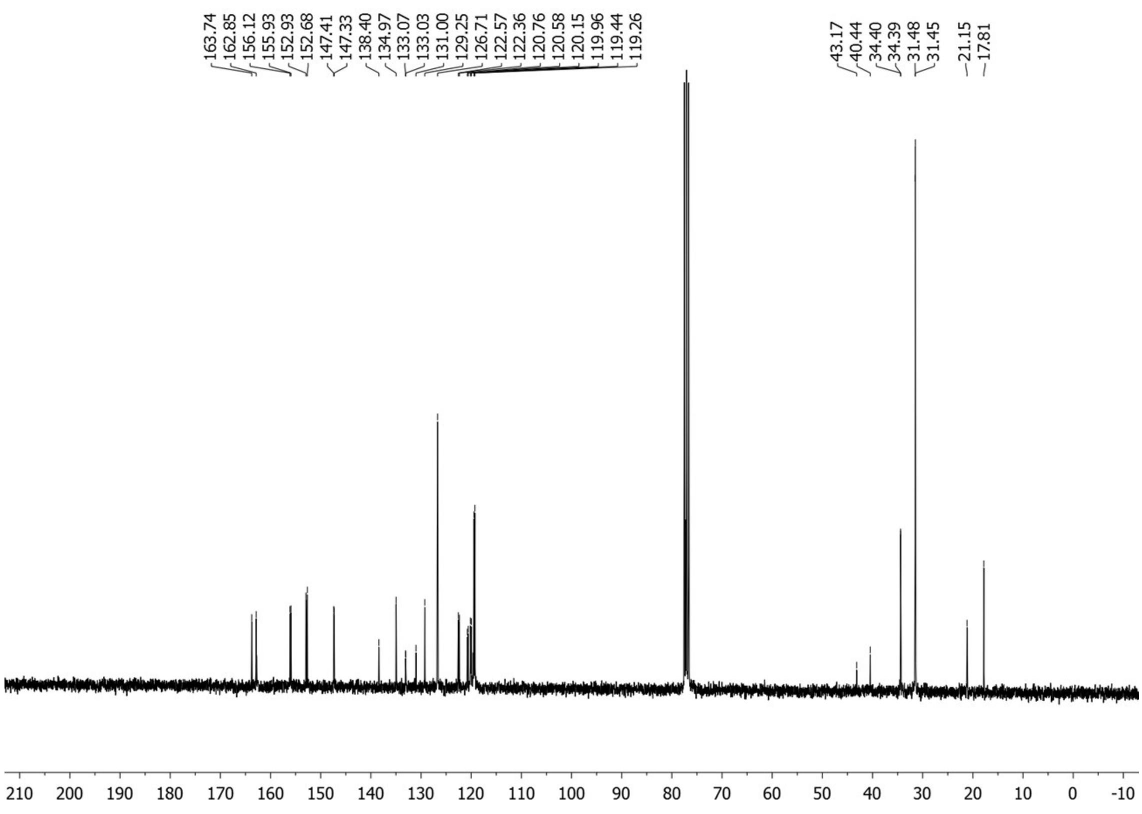
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of **9**



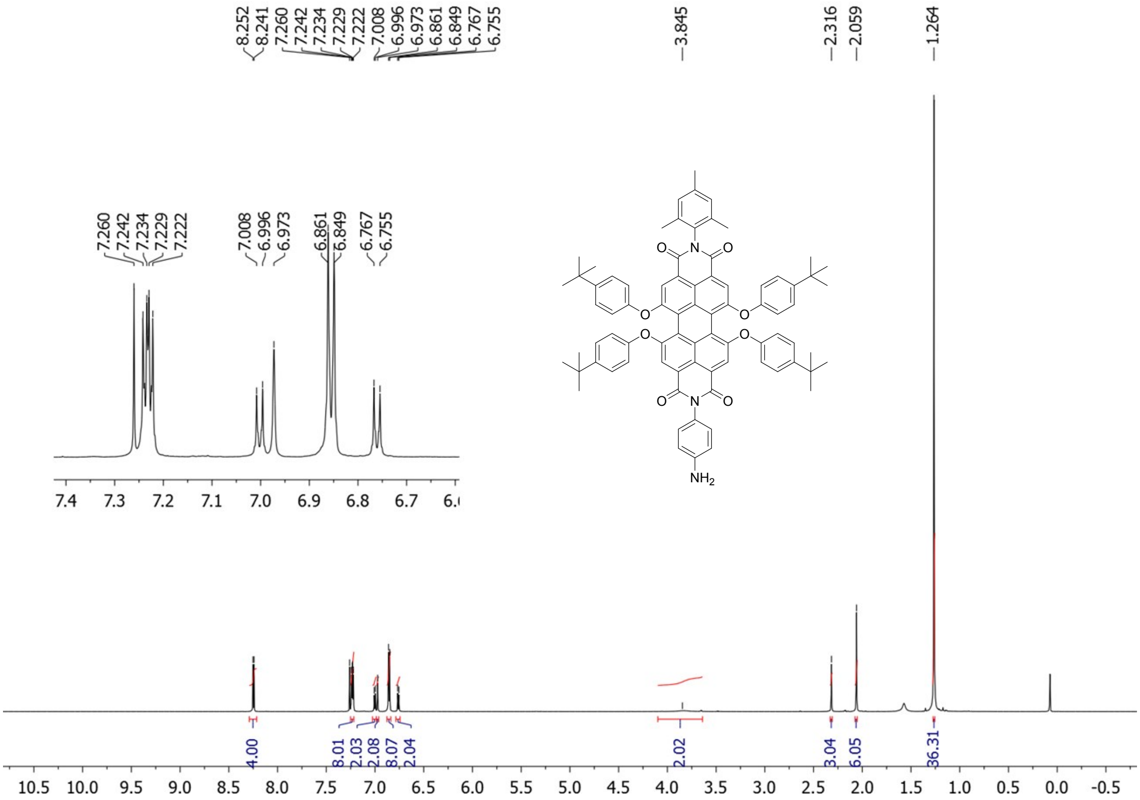


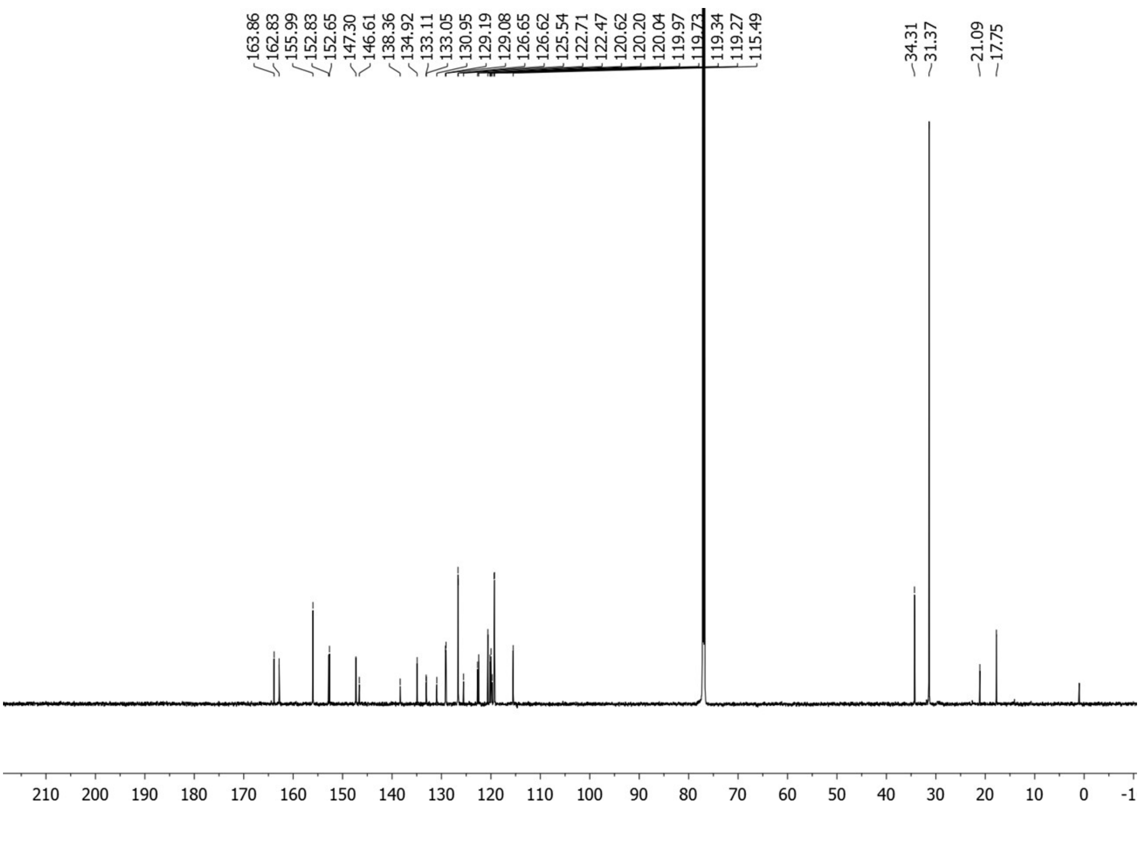
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of **10**



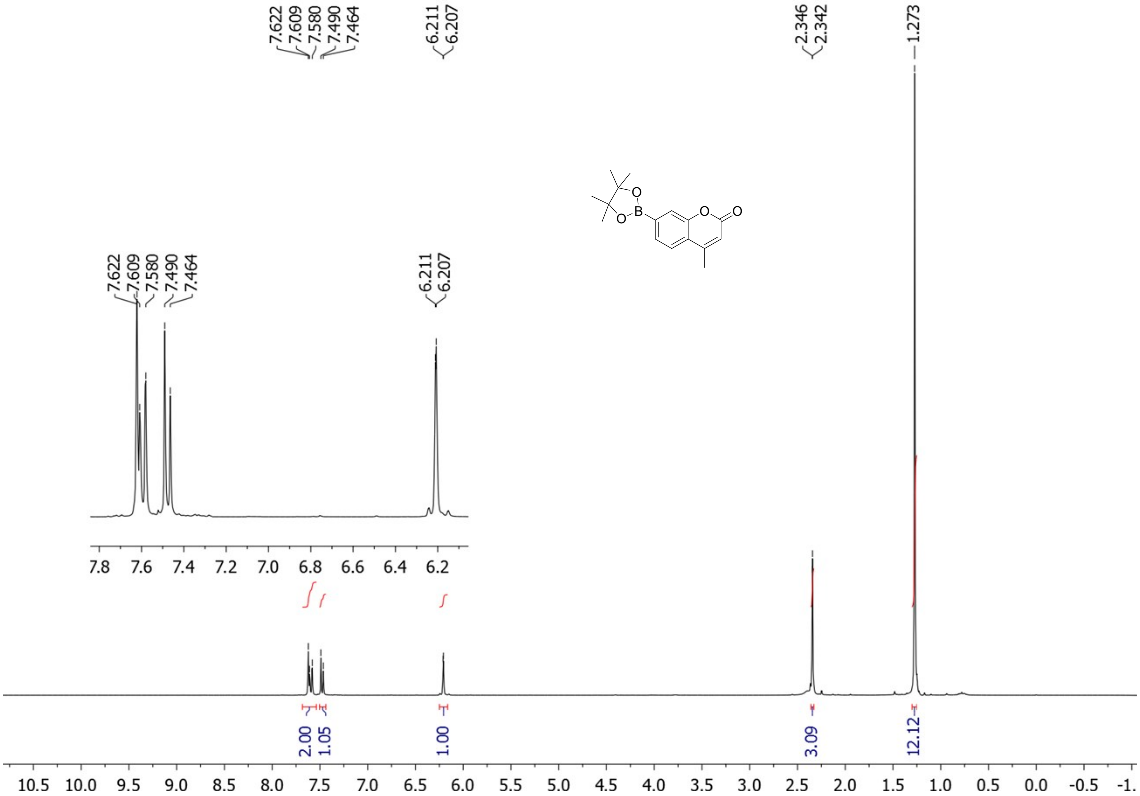


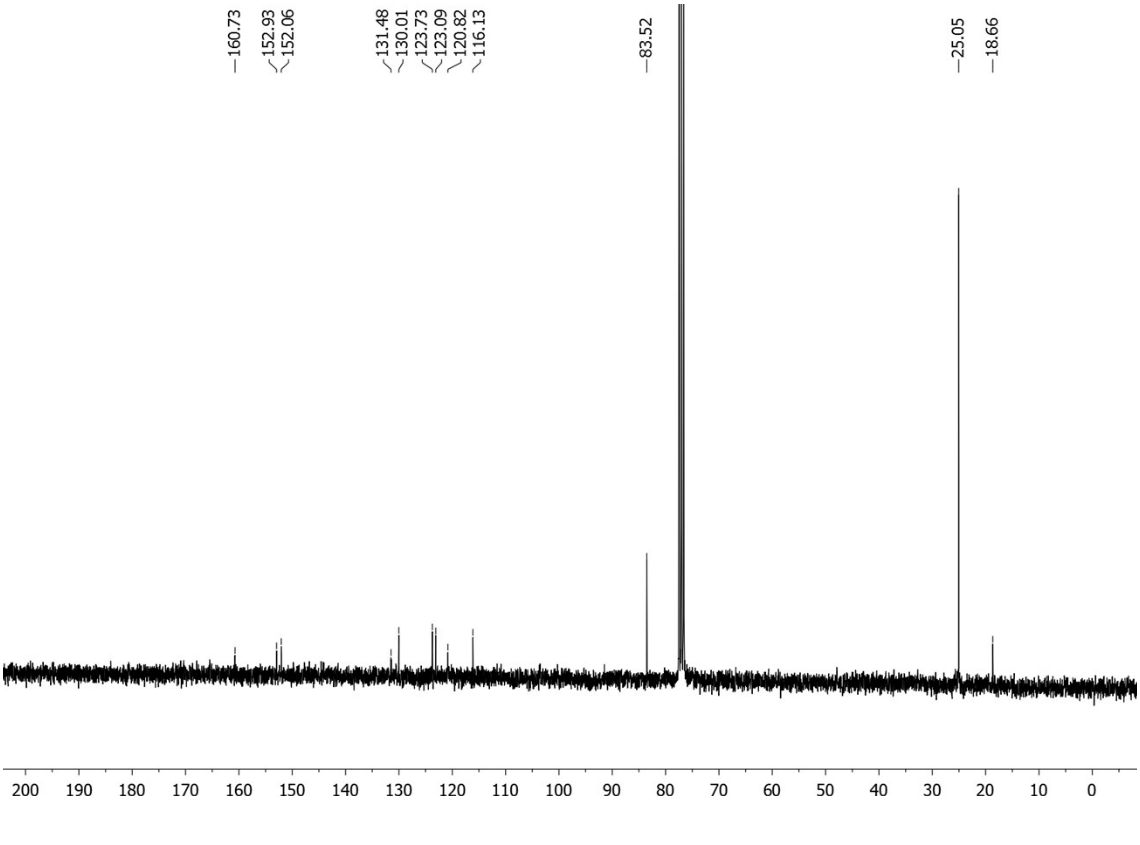
[1]H (700 MHz, $CDCl_3$) and [13]C (176 MHz, $CDCl_3$) spectra of **11**



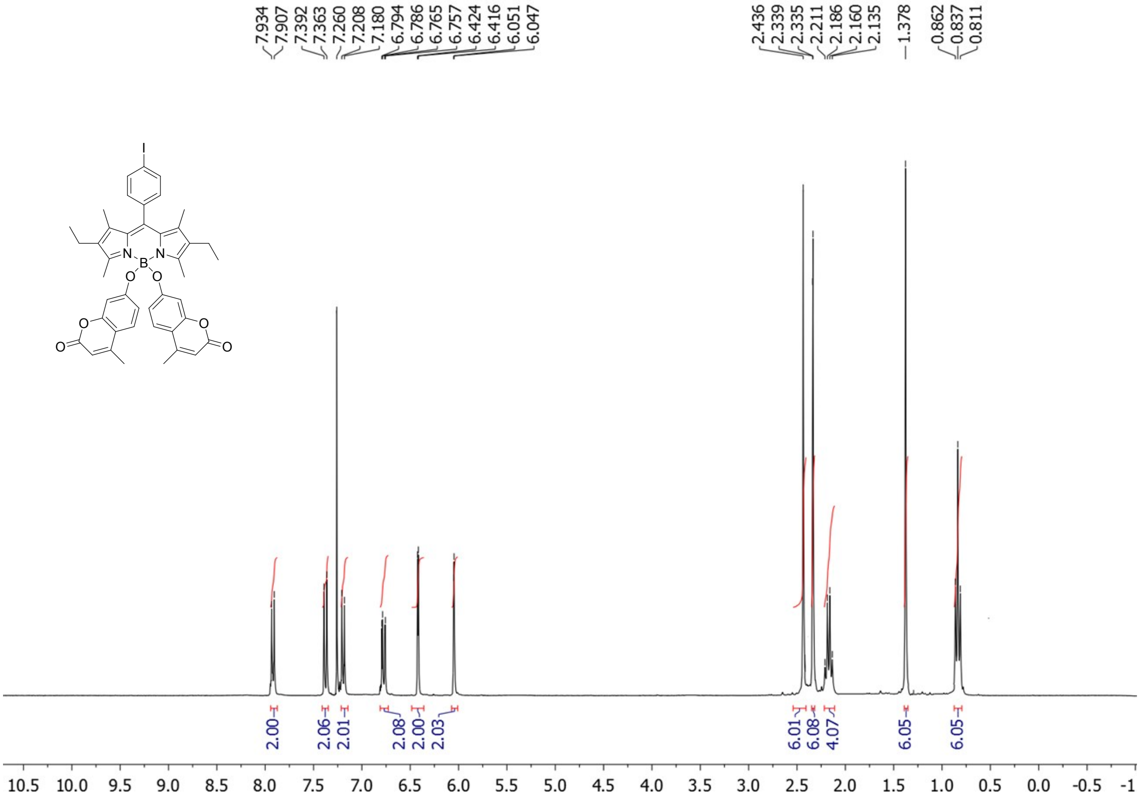


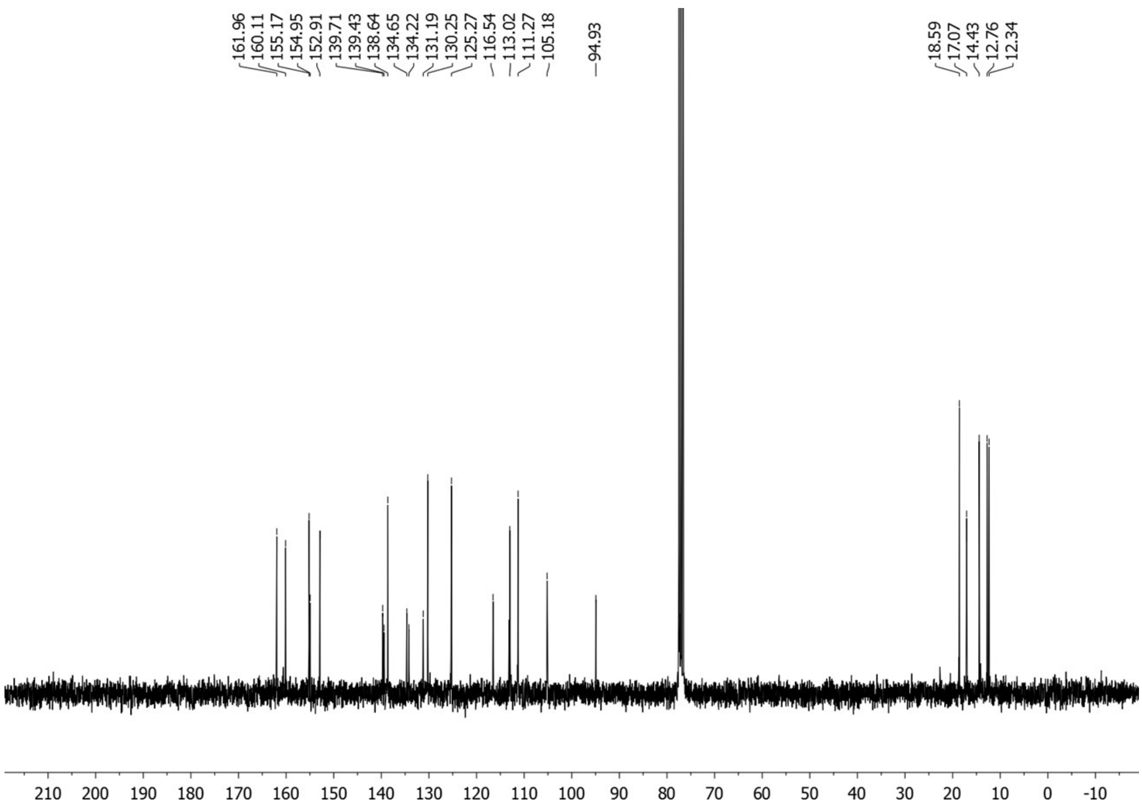
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of **13**



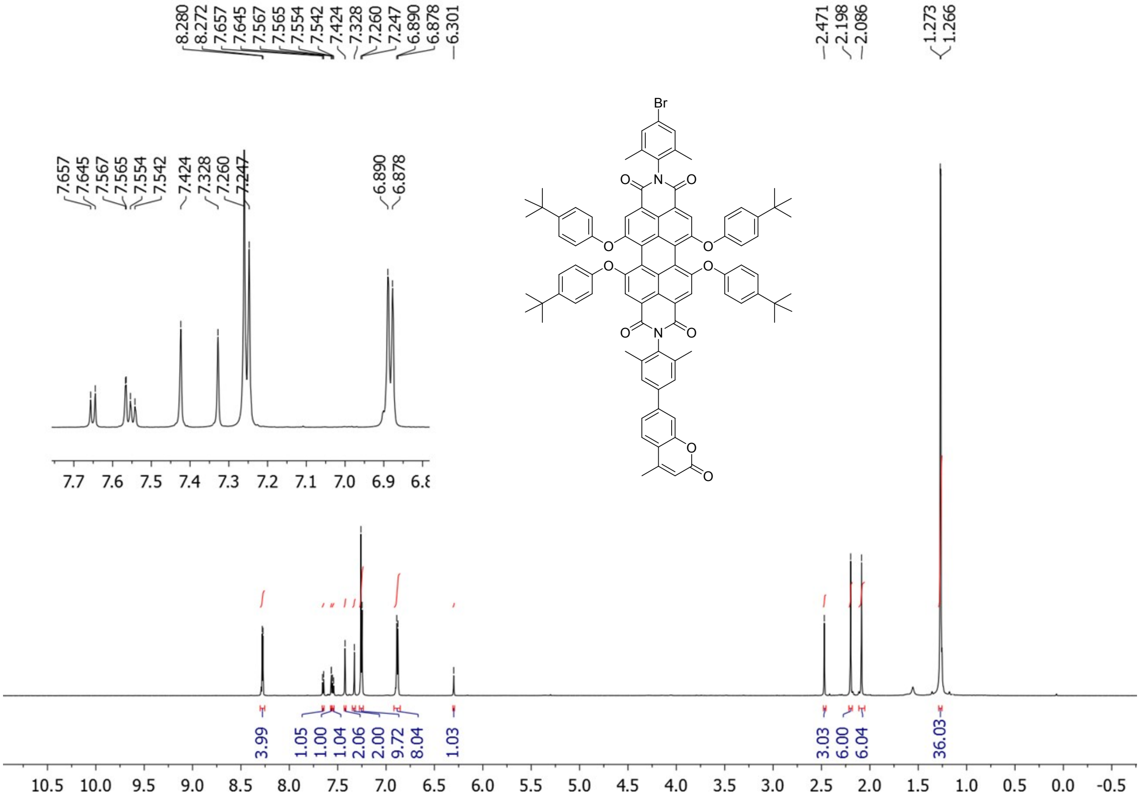


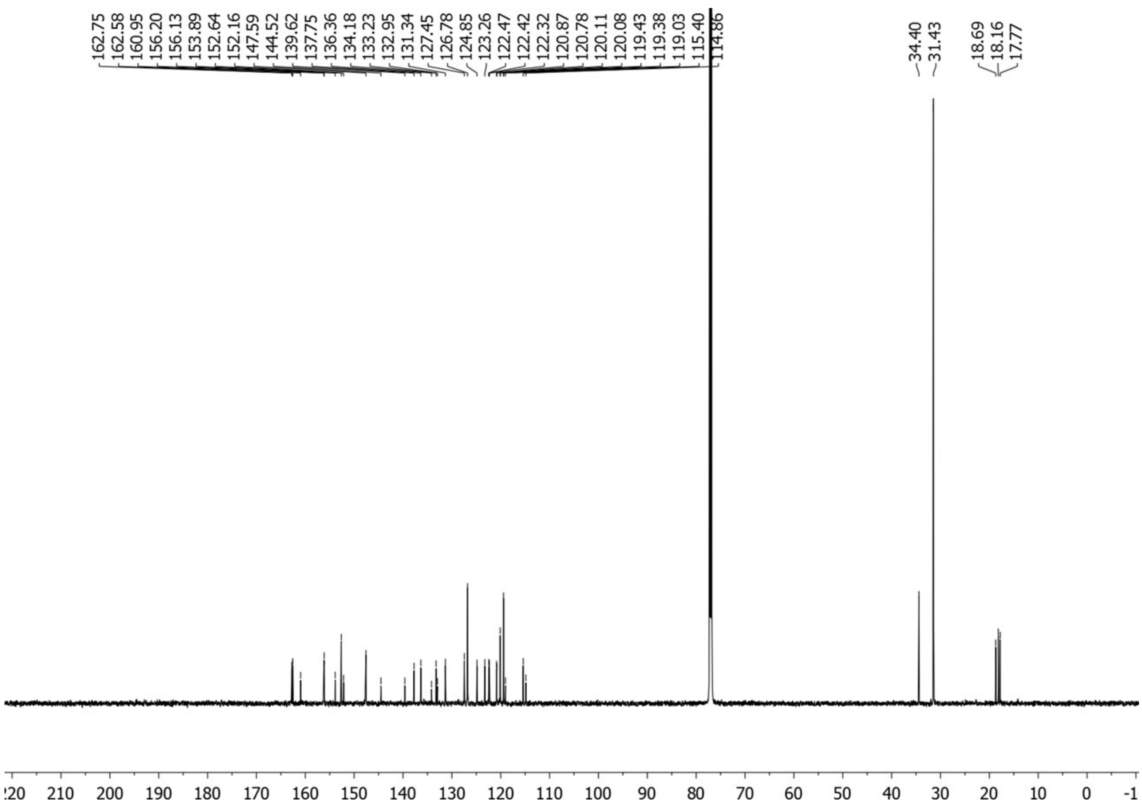
^1H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of **17**





^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) spectra of **PC-0**





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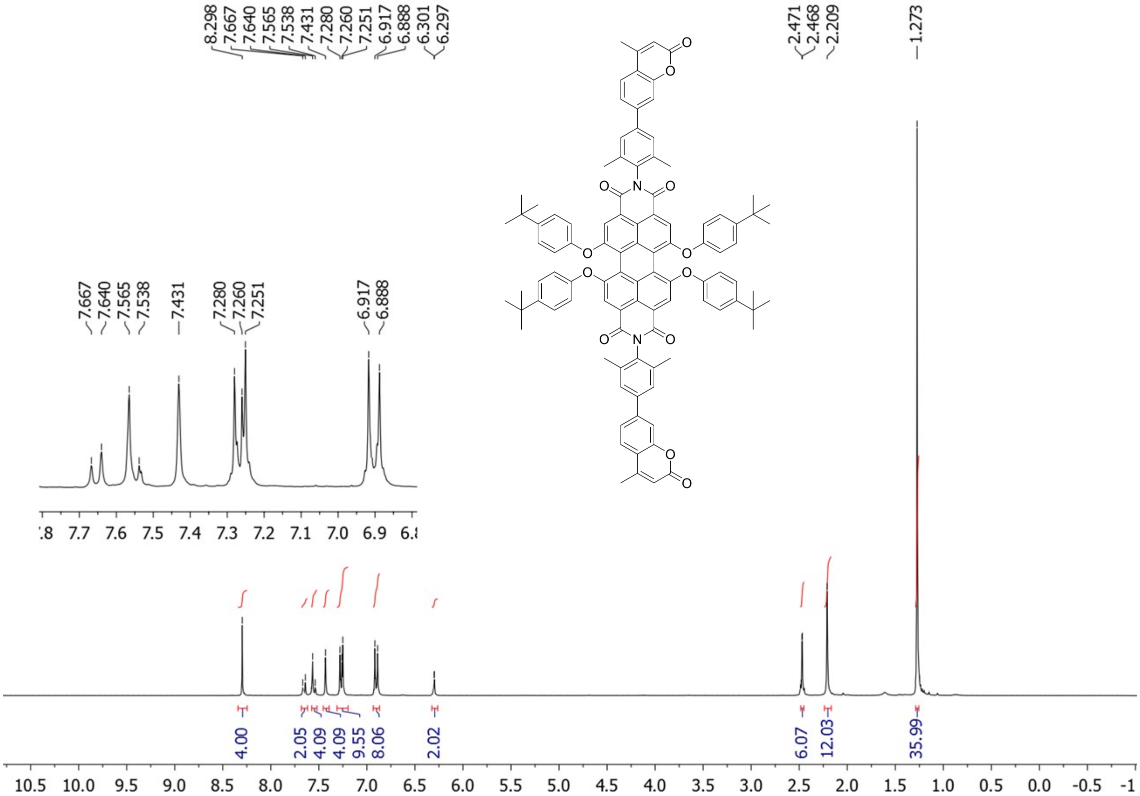
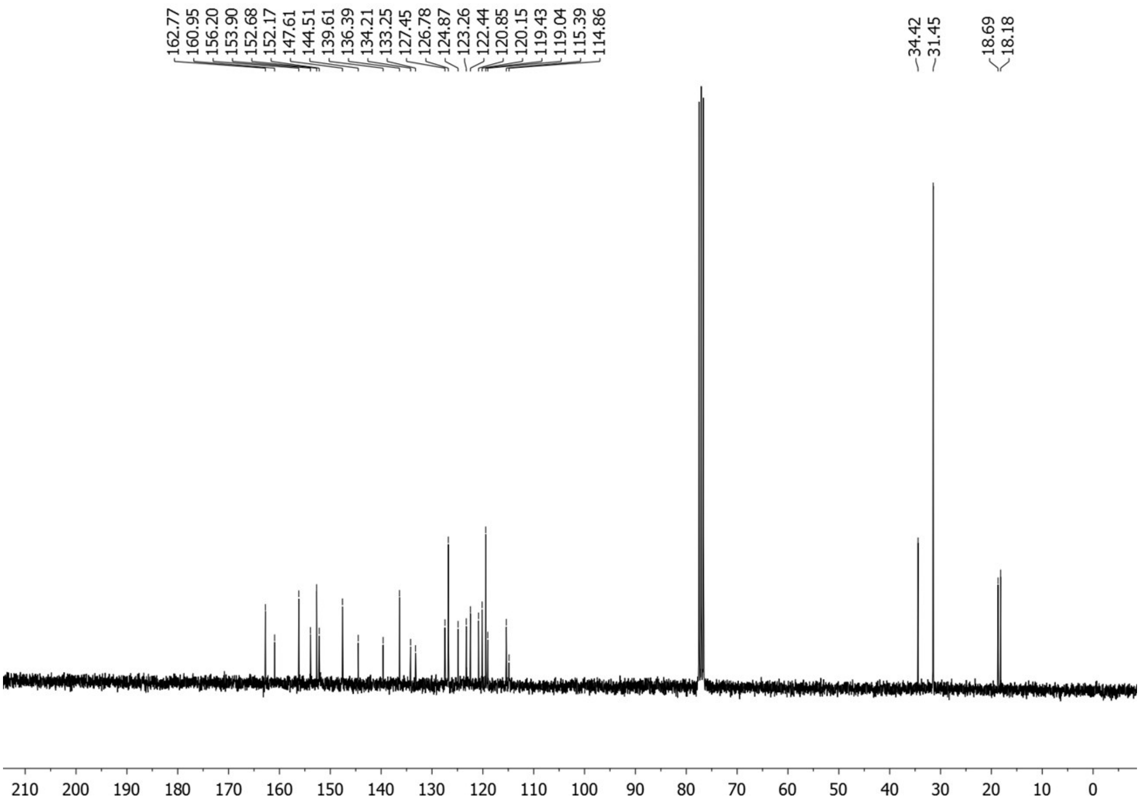
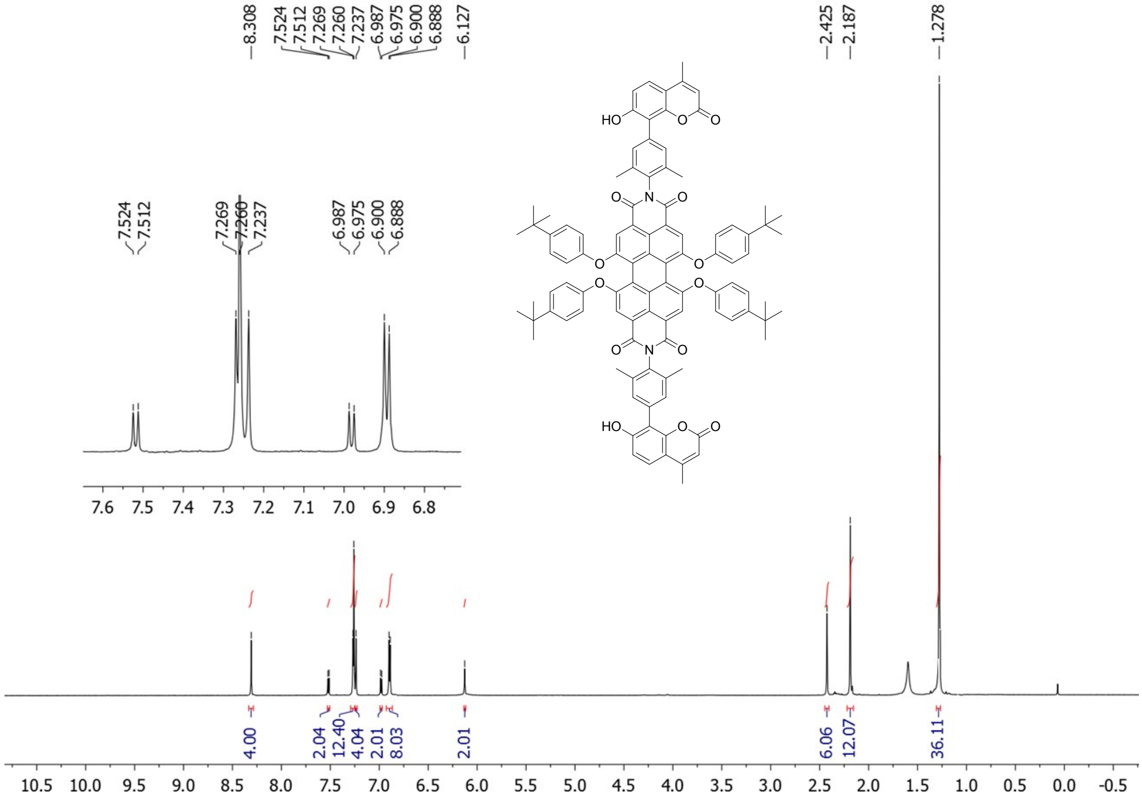
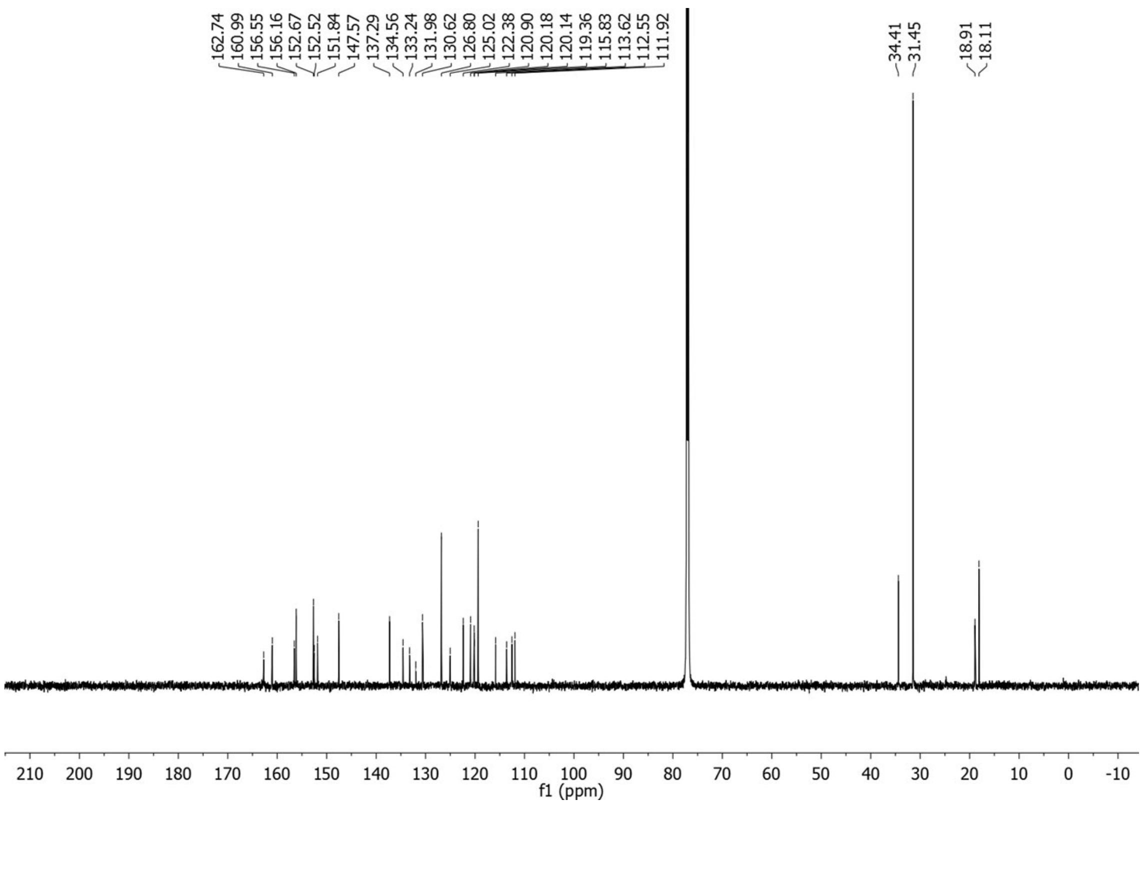


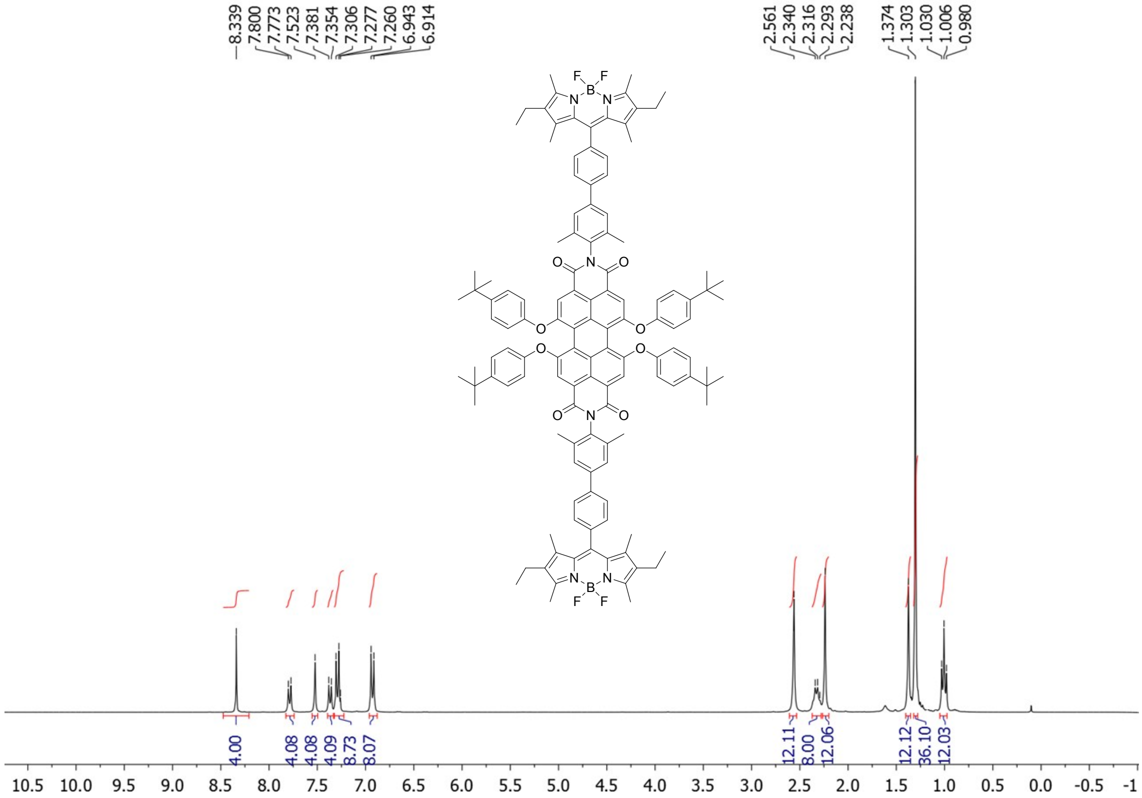


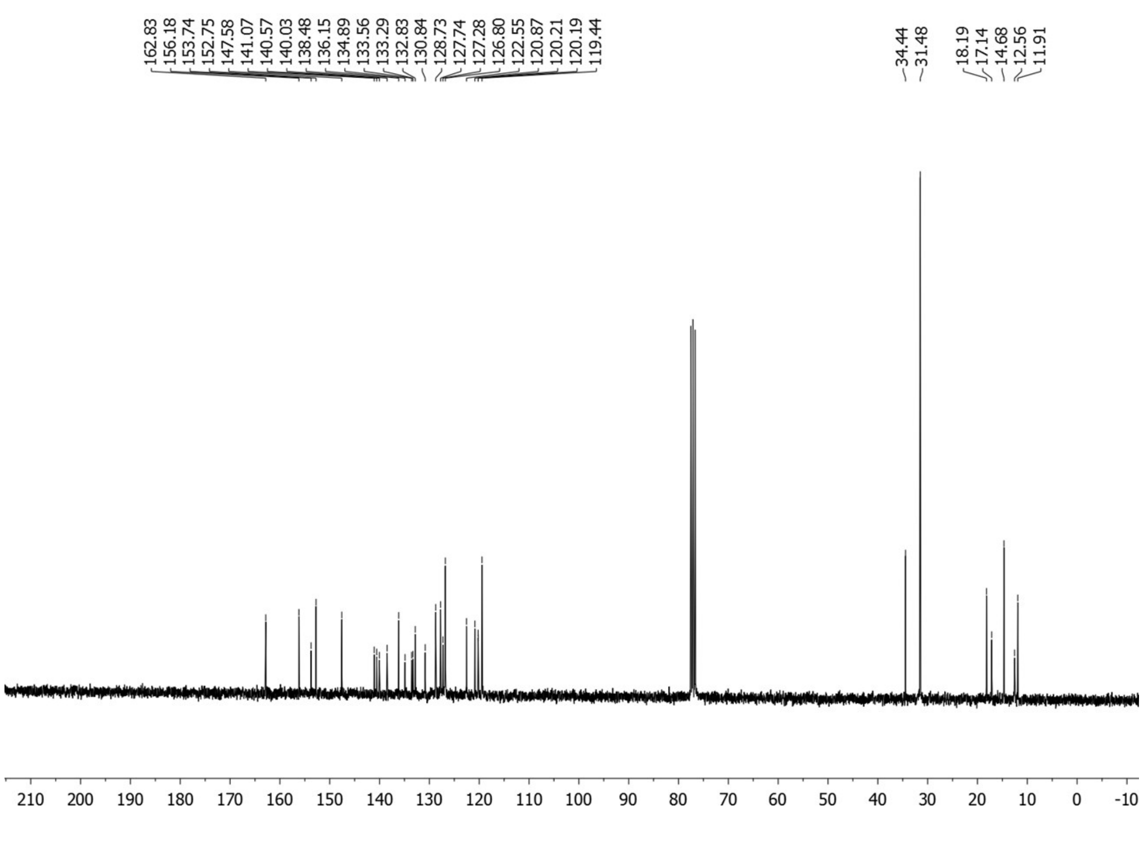
^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) spectra of **PC-2**



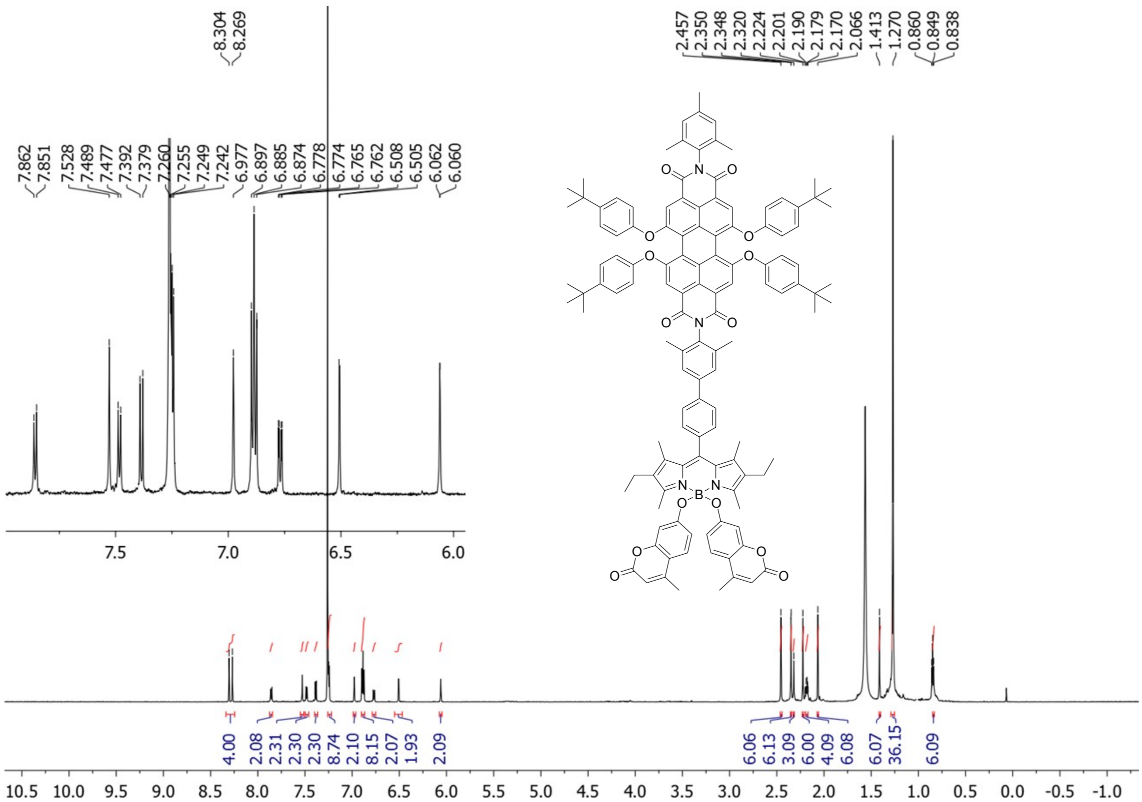


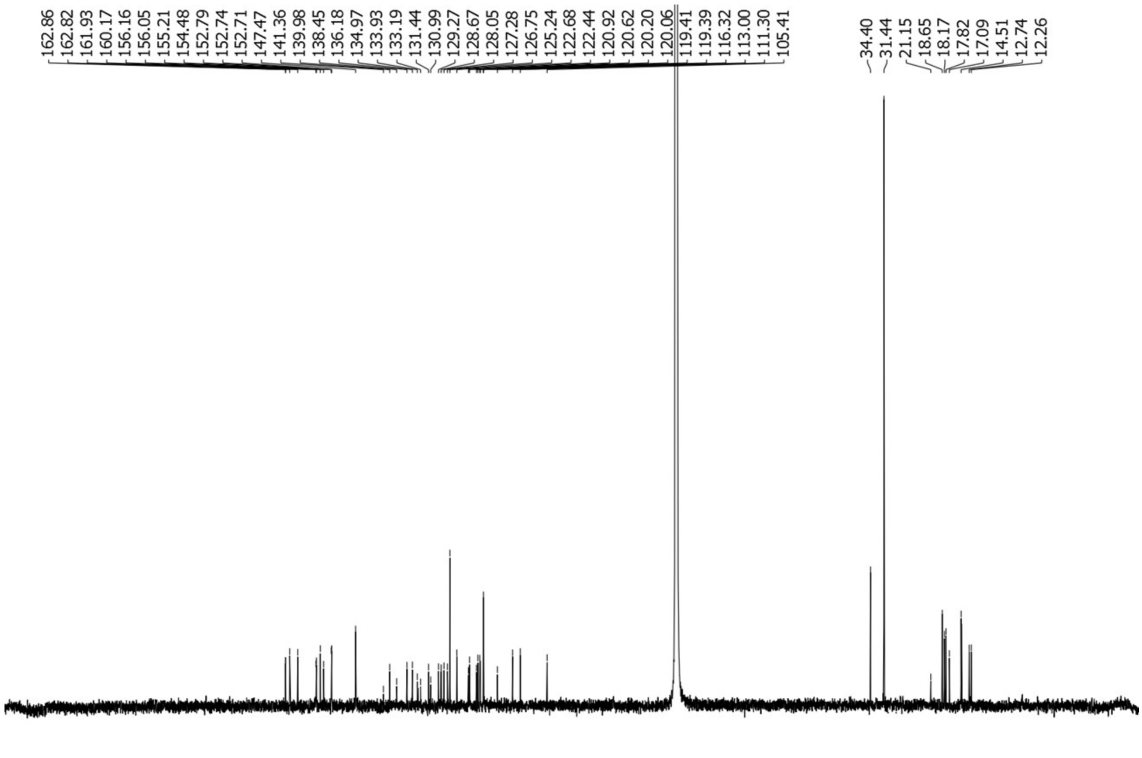
^1H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of **PB-1**





^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) spectra of **PBC**





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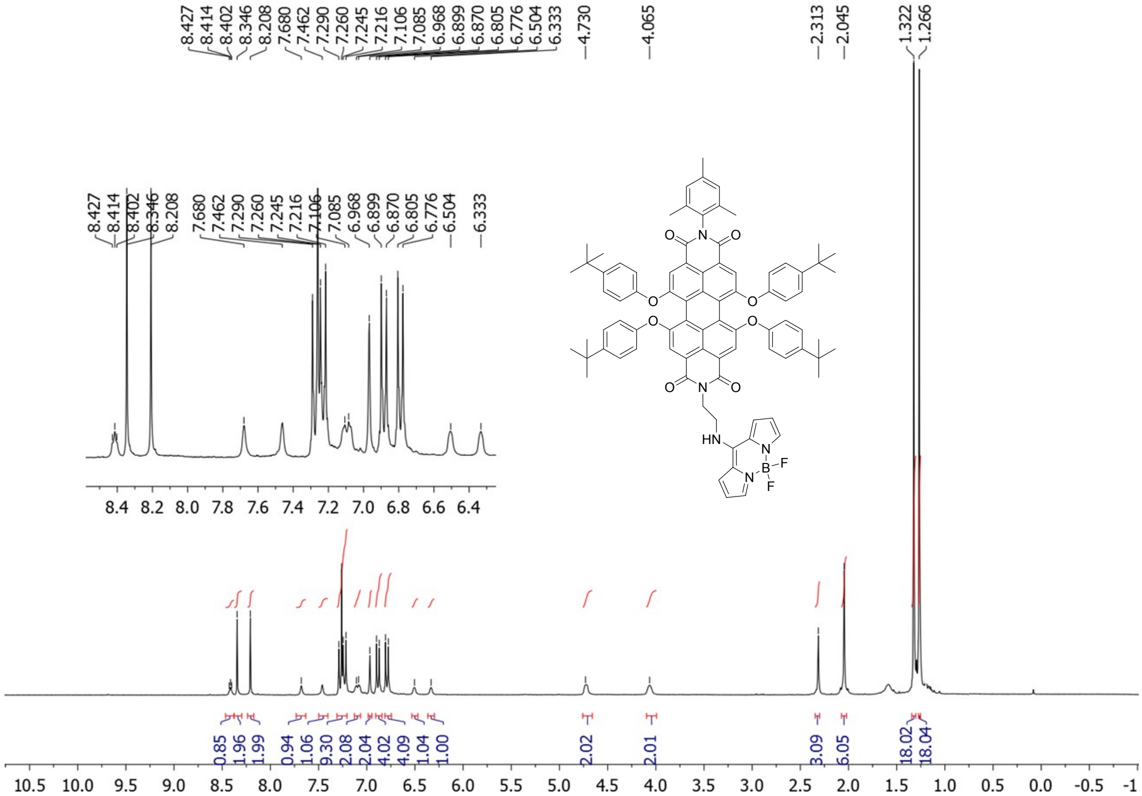
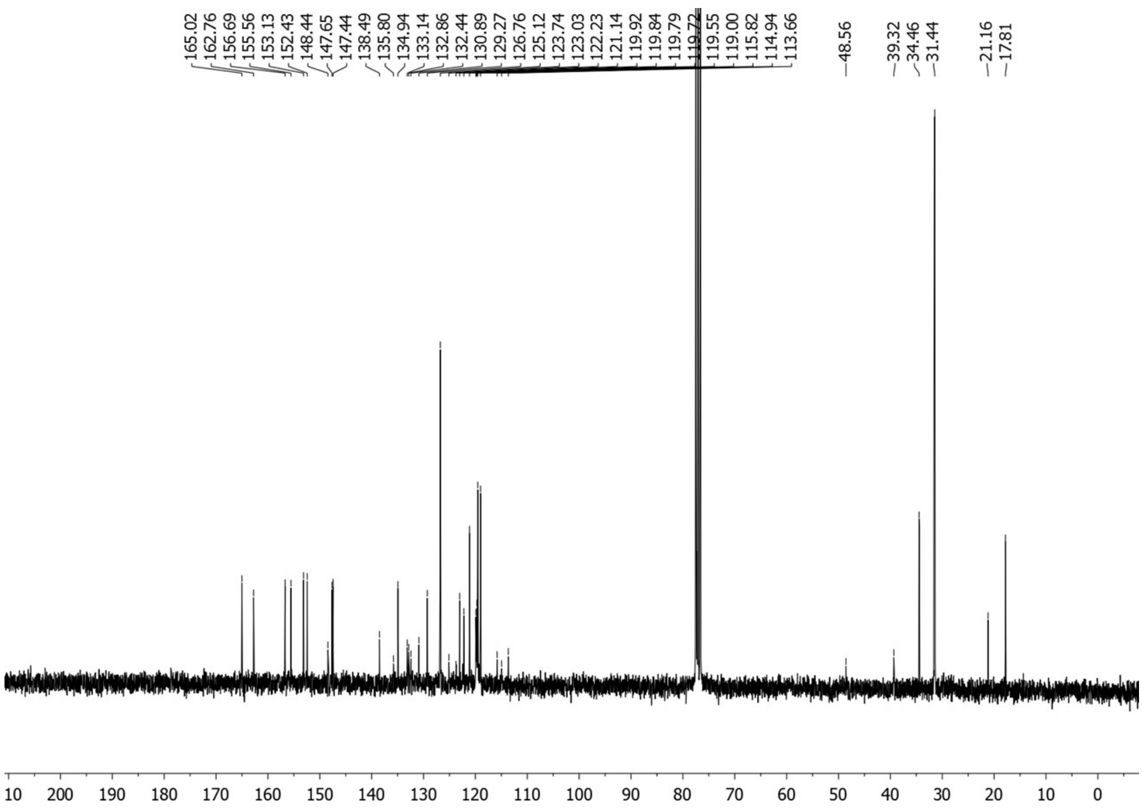
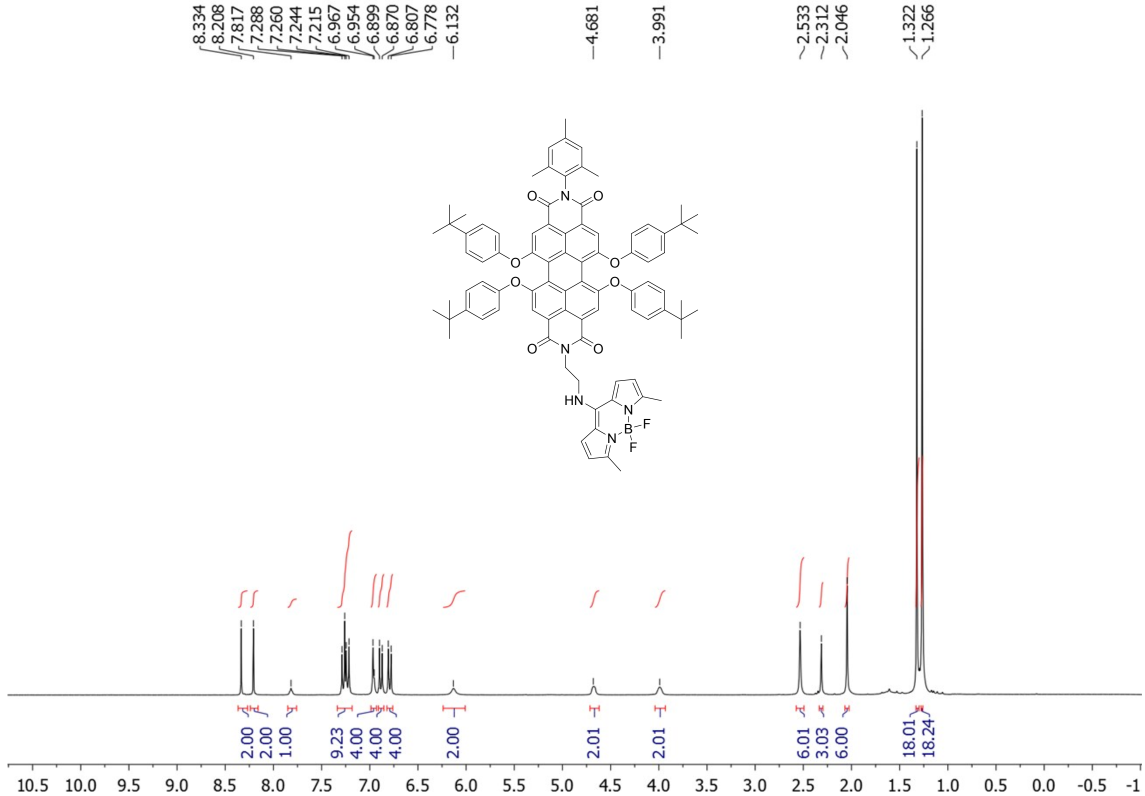
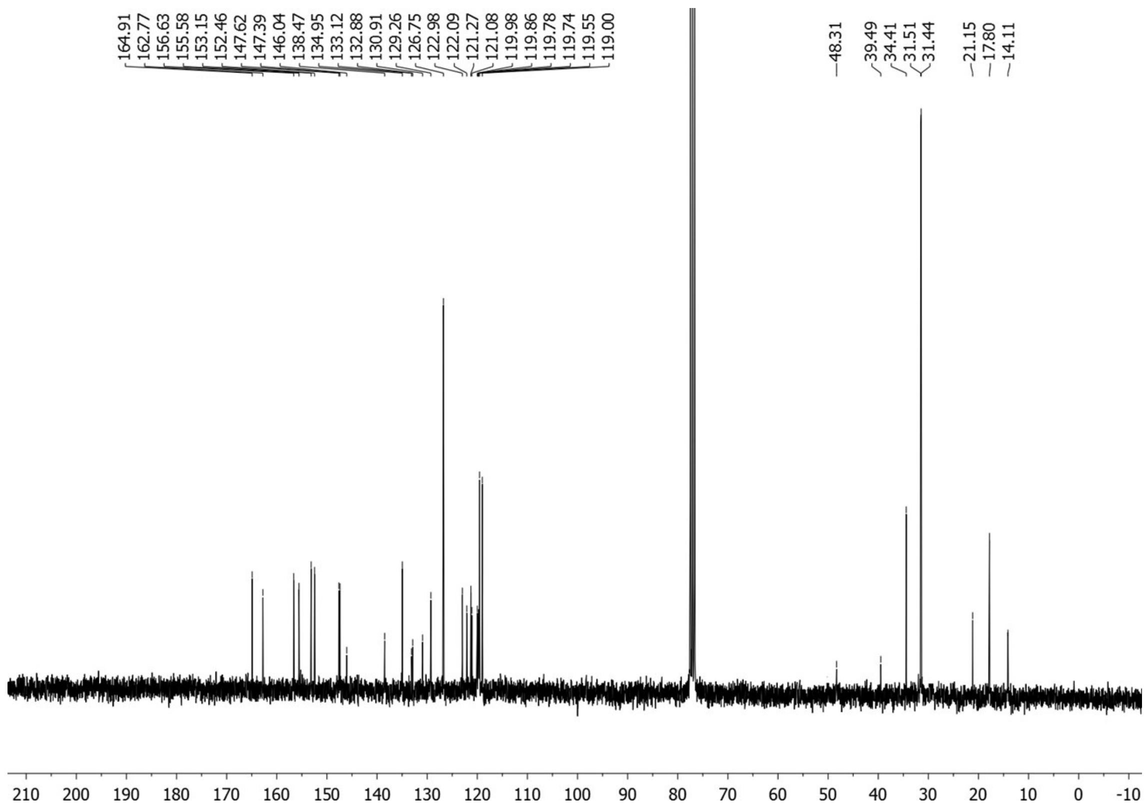


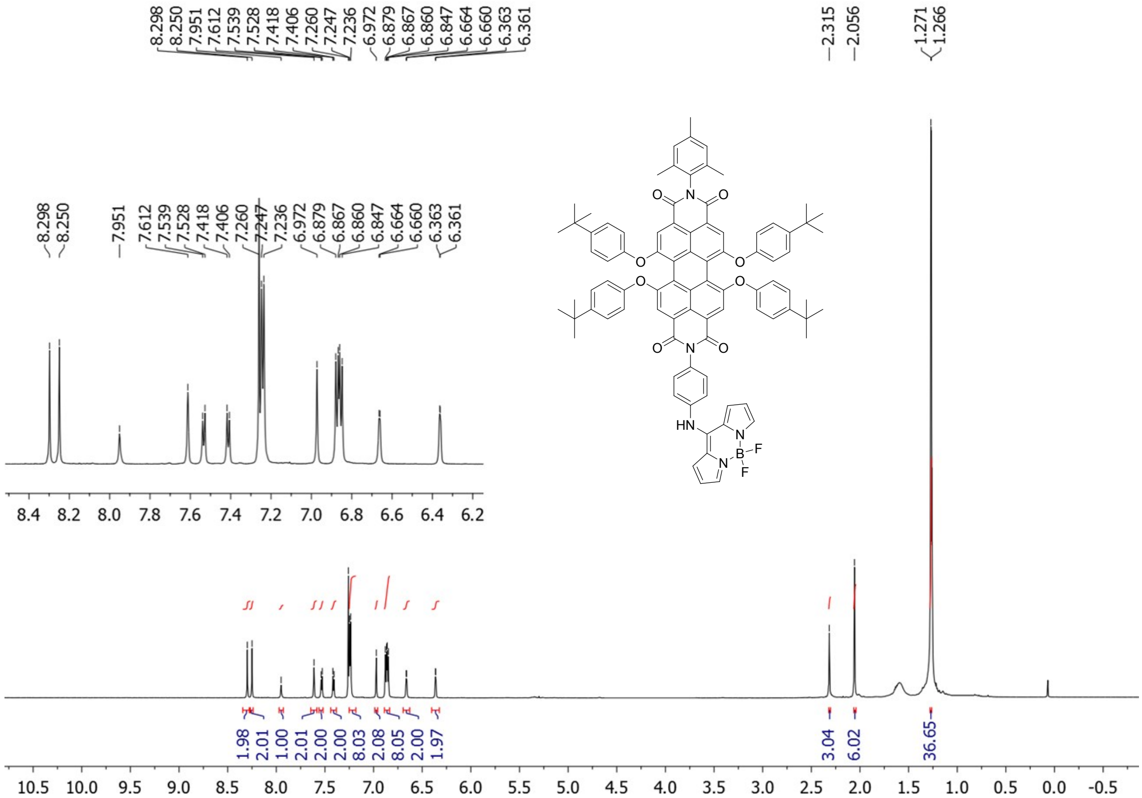


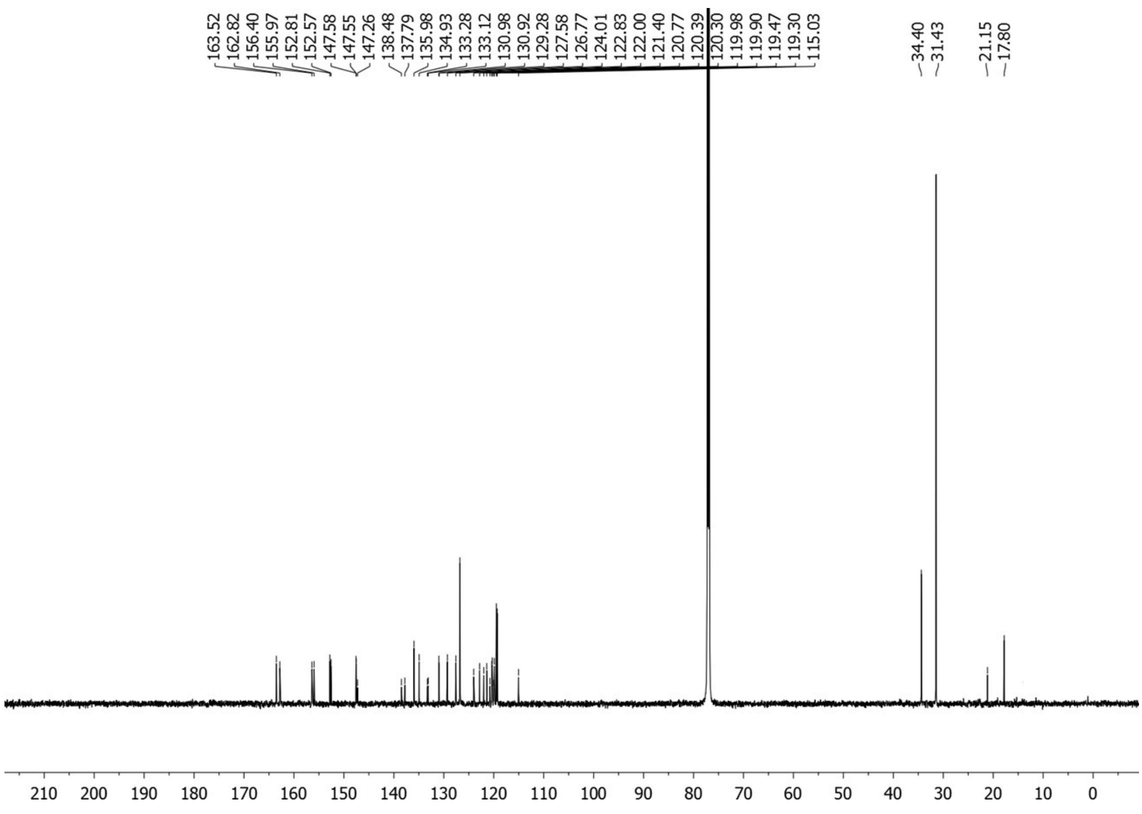
^{1}H (300 MHz, $CDCl_3$) and ^{13}C (75 MHz, $CDCl_3$) spectra of **PB-3**





^{1}H (700 MHz, $CDCl_3$) and ^{13}C (176 MHz, $CDCl_3$) spectra of **PB-4**





Photophysical properties

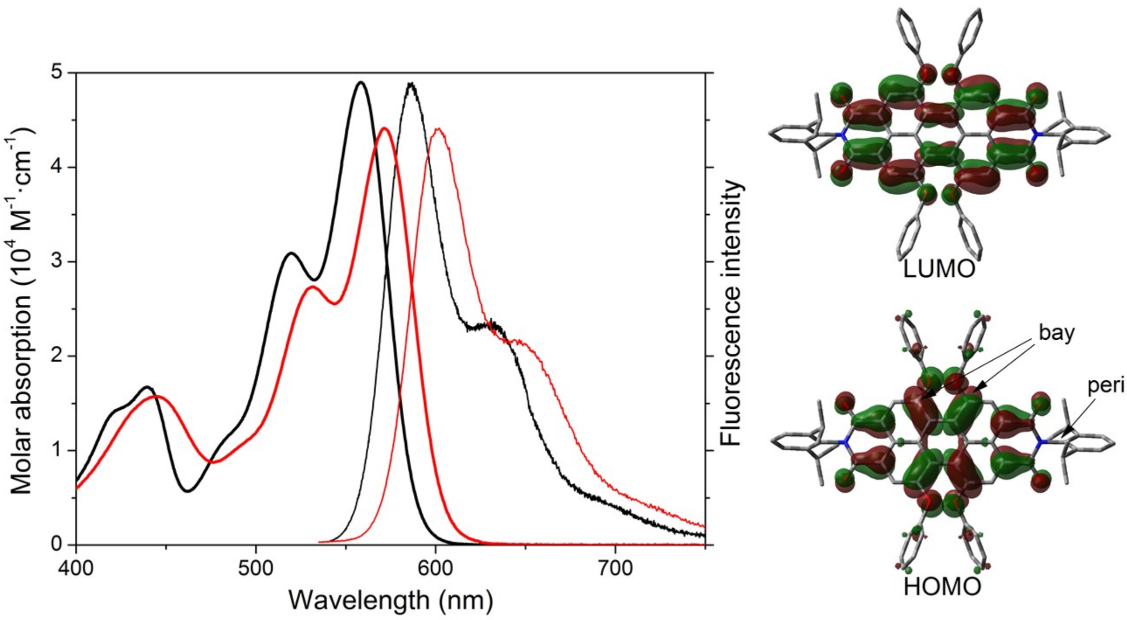


Fig. S1. Absorption (bold line) and fluorescence (thin line) spectra of the commercial Per-Red (black) and its *peri*-functionalized derivative (red) in ethyl acetate (**8** has been taken as representative compound of these set of compounds). The corresponding frontier molecular orbitals of the former dye are also included.

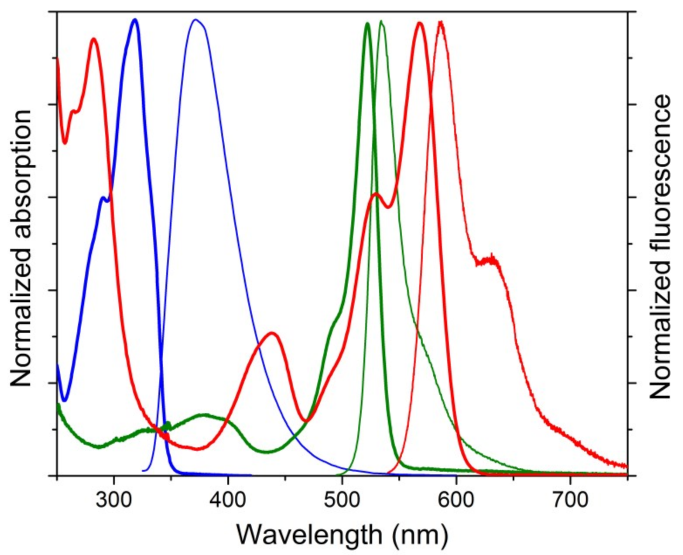


Fig. S2. Spectral overlap between hydroxycoumarin (**Cu456**, in blue), BODIPY (**15**, in green) and Per-Red (in red) to enable FRET.

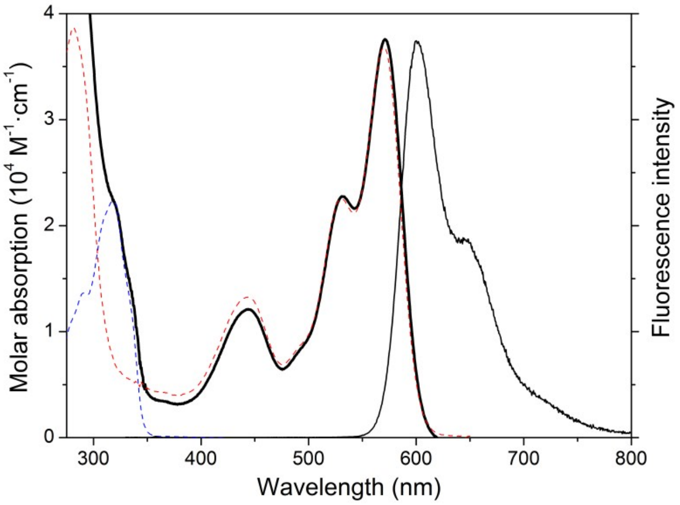


Fig. S3. Absorption (bold line) and fluorescence spectra (thin line), upon selective excitation of the coumarin (λ_{exc} = 325 nm), of the coumarin-perylene cassette **PC-2** in ethyl acetate. The corresponding absorption bands of its chromophoric fragments (dashed lines, hydroxycoumarin in blue and Per-Red in red) are also depicted.

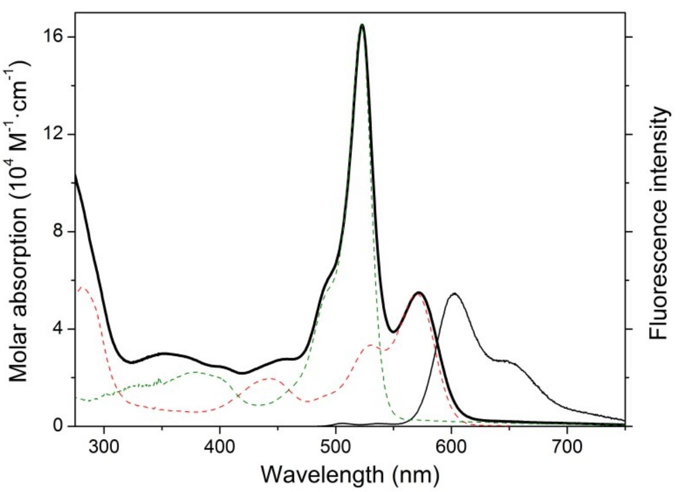


Fig. S4. Absorption (bold line) and fluorescence spectra (thin line), upon main excitation of the BODIPY (λ_{exc} = 490 nm), of the BODIPY-perylene cassette **PB-1** in ethyl acetate. The corresponding absorption bands of its chromophoric fragments (dashed lines, BODIPY in green and Per-Red in red) are also depicted.

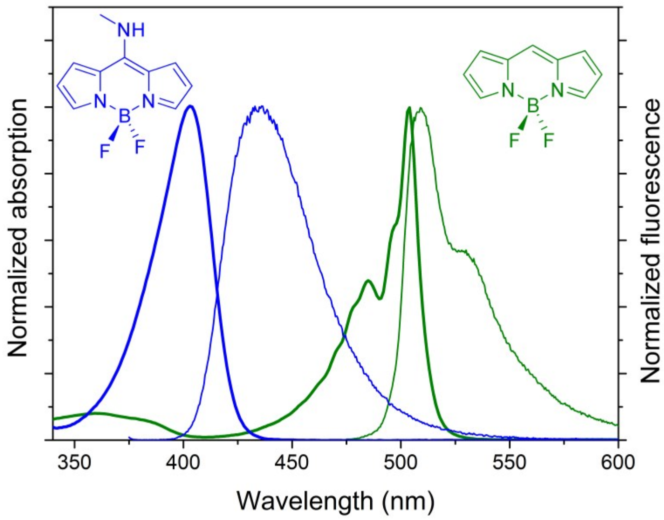


Fig. S5. Normalized absorption (bold line) and fluorescence spectra (thin line) of the simplest BODIPY (trademark BDP) and its derivative bearing 8-methylamino in ethyl acetate.

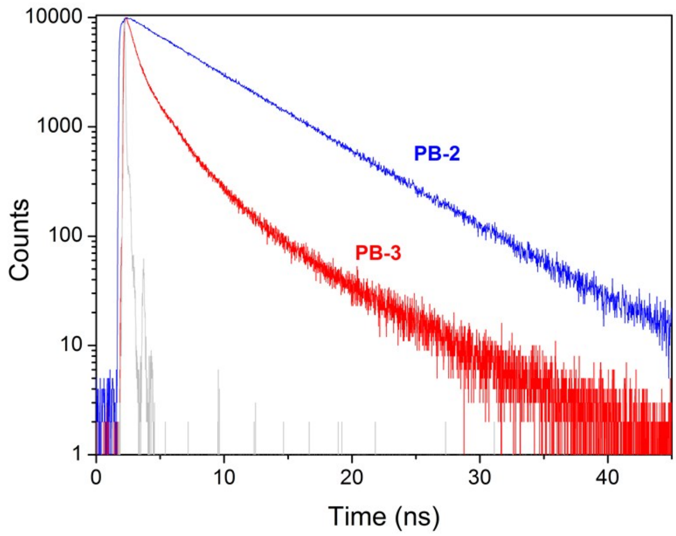


Fig. S6. Fluorescence decay curves of the cassettes bearing 8-aminoBODIPY linked to perylene red via an aliphatic chain as spacer (**PB-2** and **PB-3**) in ethyl acetate.

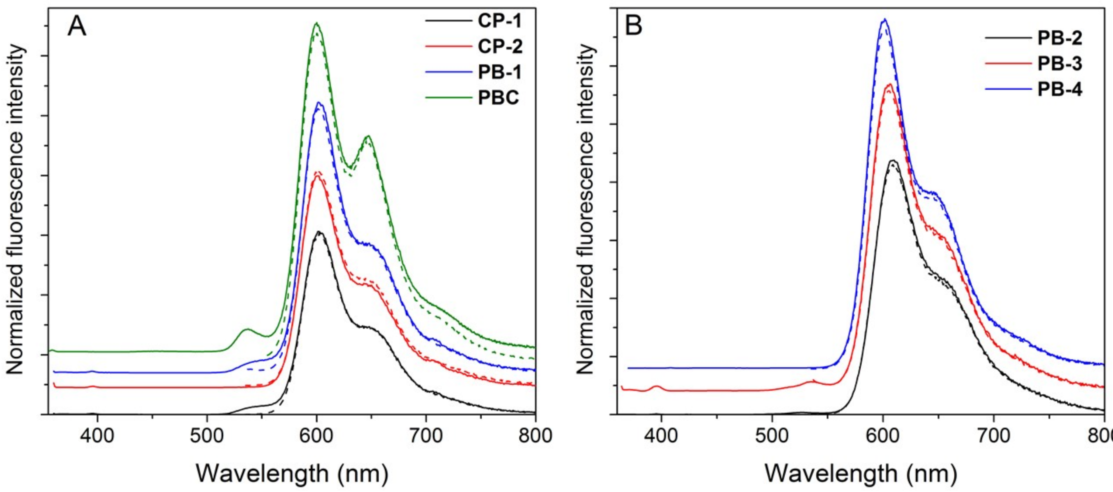


Fig. S7. Normalized fluorescence spectra of the cassettes bearing coumarin or BODIPY (A) and 8-aminoBODIPY (B) linked to perylene red under excitation at the laser pumping wavelengths 355 nm (solid line) and 532 nm (dashed line). Some spectra are lifted up to highlight the absence of emission from the energy donors.

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