Supporting Information

Diastereoselective Formation of Homochiral Flexible Perylene Bisimide Cyclophanes and their Hybrids with Fullerenes

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1. Materials and Methods

**General:** All chemicals and HPLC solvents were purchased from chemical suppliers and were used as received without further purification. C$_{60}$ (99.0%) was purchased from IoLiTec nanomaterials. All analytical-reagent grade solvents were purified by distillation with a rotary evaporator. Reactions were monitored by thin layer chromatography on silica gel 60 F254 0.2 mm on aluminium foil (Merck). Detection of the compounds was accomplished by means of a UV-lamp (254 nm or 366 nm). For column chromatography silica gel 60 M (230 - 400 mesh ASTM, 0.04 - 0.063 mm) from Marchery-Nagel & Co. KG was used. Size exclusion chromatography was performed with polystyrene gel of the type S-X1 with a dry mesh size of 28-74 μ, marketed by Bio-Rad Laboratories.

**UV/Vis-NIR Spectroscopy:**
UV-vis absorption spectroscopy was performed using UV WinLab software on PerkinElmer Lambda 2 dual beam absorption spectrophotometer, with a scan rate of 480 nm/min. The samples were measured in a 10 mm×10 mm quartz cuvette.

**Fluorescence Spectroscopy:**
Steady-state emission spectra were obtained using Horiba Jobin Yvon FluoroMax-3 emission spectrometer, with a slit width of 3 nm and an integration time of 0.1 s in the wavelength range of 525 – 850 nm. The data were processed in FluorEssence software. The samples were measured in a 10 mm×10 mm quartz cuvette. Quantum yields of the samples were calculated following the relative method using Rhodamine B in ethanol (φ = 0.70) as reference. O$_2$ quantum yield measurements were performed on FluoroLog3 spectrometer (Horiba) with Symphony II detector in the NIR detection range. The samples were purged with oxygen for 20 -30 mins. Quantum yields were calculated using C$_{60}$ in air-equilibrated toluene (Φ$_{\text{ref}}$ = 0.98 ± 0.05) as reference.

**Spectroelectrochemistry:**
Spectroelectrochemistry was performed using a PGSTAT101 Autolab potentiostat and AvaSpec spectrometer. A three-electrode setup comprising a Pt-gauze as working electrode, a Pt-wire as counter electrode and a silver wire as a reference electrode was used. 0.1 M tetrabutylammonium hexafluorophosphate was used as supporting electrolyte. The data were recorded with NOVA 1.10 software.

**Transient absorption spectroscopy:**
Femtosecond and nanosecond transient absorption spectroscopy measurements were performed using the pump/probe systems HELIOS (0 to 5500 ps) and EOS (1 ns to 350 μs) from Ultrafast Systems.
The laser source was CPA2101 and 2110 Ti:Sapphire amplifier (775 nm output, 1 kHz repetition rate, 150 fs pulse width; 500 nJ excitation laser energy) from Clark-MXR Inc. The desired excitation pulse of 550 nm was generated with NOPA. The white light for the femtosecond experiments was generated using a Sapphire crystal. The white light for the nanosecond transient measurements came from a supercontinuum laser source (2 kHz repetition rate, 1 ns pulsewidth). Samples were taken in 2 x 10 mm optical glass cuvettes and purged with argon for 20 min. Optical densities (OD) of the samples were around 0.4 at the excitation wavelength. Global analyses of the resulting data were performed with the GloTarAn software.[2]

**FTIR-ATR Spectroscopy:** The FTIR-ATR spectra were obtained on a Bruker Tensor 27, Pike MIRacleTM ATR, Pike Technologies as well as on a ThermoFisher Scientific Nicolet iS5. The spectra were measured as pure solids or liquids and absorptions are given in wavenumbers $\tilde{\nu}$ (cm$^{-1}$).

**Analytical HPLC:** Analytical HPLC was carried out in a LC20-AT prominence liquid chromatograph, SHIMADZU CORPORATION, Analytical Instruments Division, Kyoto, Japan using a Nucleosil Column (EC250/4 Nucleosil 100-5) from Macherey-Nagel and 150 ul injection volume. Before the injection, small aliquots of the reaction mixture (0.2 mL) were filtered through silica to avoid the possible blocking of the employed column due to the polymers formed in the reaction mixture. All chromatograms were processed with SHIMADZU LabSolution software and exported as ASCII files. The chromatograms are depicted at a wavelength of $\lambda = 280$ nm or $\lambda = 530$ nm and the following solvent gradient was used: CH$_2$Cl$_2$:ethyl acetate:MeOH 1:0:0 $\rightarrow$ 75:20:5.

**NMR Spectroscopy:** NMR spectra were recorded on a BRUKER Avance 600 (1H: 600 MHz, 13C: 151 MHz), BRUKER Avance 500 (1H: 500 MHz, 13C: 125 MHz), BRUKER Avance 400 (1H: 400 MHz, 13C: 101 MHz) spectrometers. Chemical shifts are given in ppm, referenced to residual solvent signals and reported relative to external SiMe$_4$. Chloroform-d1 (99.8%) and 1,1,2,2-tetrachloroethane-d2 (99.5%) were purchased from Sigma Aldrich and were used as received without further purification. The resonance multiplicities are indicated as s (singlet), d (doublet), t (triplet) and m (multiplet).

**Mass spectrometry:** Spectra were recorded on BRUKER microTOF II focus (BRUKER Daltonik GmbH) and SHIMADZU Axima Confidence maXis 4G instruments (Nitrogen UV laser, 50 Hz, 337 nm). MALDI-TOF HRMS were recorded on a Bruker UltrafleXtreme TOF/TOF and trans-2-[3-(4-tert-butylphenyl)-2-methyl-propenylidene]malonitrile (DCTB) and 2,5-dihydroxy-benzoic acid (DHB) were used as matrices. The APPI mass spectra were obtained on Bruker maXis 4G TOF-mass spectrometer. ESI mass spectra were recorded on BRUKER microTOF II focus ESI-TOF spectrometer.
2. Synthesis

Synthesis of cyclophane P2

Experiment F: Pyridine anhydrous (18.7 mg, 19.2 μL, 237 μmol, 4 eq.) was added to a solution of compound 1 (130 mg, 118 μmol, 2 eq.) and tetrathiafulvalene (12.5 mg, 61.1 μmol, 97% purity, 1 eq.) in CH₂Cl₂ anhydrous (225 mL). To the stirred reaction mixture, malonyl dichloride (17.2 mg, 11.9 μL, 122 μmol, 97% purity, 2 eq.) in CH₂Cl₂ anhydrous (5 mL) was added with an automatic syringe pump within 3 h. After 29 h, 47 h and 51 h the previously described addition of malonyl dichloride was repeated three times. In total the solution was stirred at rt for 3 d. Afterwards, the solvent was removed under vacuum without drying completely and the crude product solution was separated by size exclusion chromatography (Biobeads S-X1, dry mesh size: 28-74 μ, CH₂Cl₂). The fractions containing compound P2 (as indicated by TLC) were purified by column chromatography (SiO₂, CH₂Cl₂:ethyl acetate, 1:0 -> 99:1). The mixed fractions containing compound P2 were further purified by column chromatography (SiO₂, CH₂Cl₂:ethyl acetate, 1:0 -> 90:10) to obtain P2 (11.2 mg, 4.80 μmol, 8.1%) as dark purple solid.

TLC (Hexane:ethyl acetate, 3:1): R_f = 0.22.

^1H NMR (500 MHz, C₂D₂Cl₄, 90 °C): δ = 7.84 (s, 8H, C(H₃PBI)), 7.16 – 7.10 (m, 16H, CH₃phenoxy), 6.75 – 6.66 (m, 16H, CH₃phenoxy), 4.19 – 4.08 (m, 8H, CH₂), 4.07 – 3.90 (m, 8H, CH₂), 3.21 (bs, 4H, OCCH₂CO), 2.01 – 1.82 (m, 8H, CH₂), 1.26 ppm (s, 72H, C(H₃).)

^13C NMR (126 MHz, C₂D₂Cl₄, 90 °C): δ = 166.30 (4C, O-C=O), 163.08 (8C, N-C=O), 155.91 (8C, C-O), 153.33 (8C, Cphenoxy-O), 147.56 (8C, Cphenoxy), 132.77 (4C, CPh₂), 126.60 (16C, HPhenoxy), 122.24 (8C, CPh₂), 120.69 (8C, CPh₂), 120.19 (8C, HPhen), 119.55 (16C, HPhenoxy), 119.44 (4C, CPh₂), 63.65 (4C, CH₂), 42.12 (2C, O=CCH₂C=O), 38.04 (4C, CH₂), 34.48 (8C, C(CH₃)₃), 31.70 (24C, CH₃), 27.46 ppm (4C, CH₂).

HRMS (APPI): m/z calcd for [C₁₄₆H₁₄₆N₄O₂₄]⁺ 2332.9852, found: 2332.9897.

IR (ATR, rt): v = 2958, 2924, 2853, 1732, 1694, 1659, 1584, 1505, 1459, 1292, 1260, 1217, 1152, 1091, 1016, 799, 745, 700 cm⁻¹.

UV-vis (CH₂Cl₂): ε (λ_max) = 18143 (536), 15833 (576) M⁻¹·cm⁻¹ (nm).
Synthesis of cyclophane P3

Pyridine anhydrous (28.8 mg, 29.5 μL, 364 μmol, 2 eq.) was added to a solution of compound 1 (200 mg, 182 μmol, 1 eq.) in CH₂Cl₂ anhydrous (250 mL). Malonyl dichloride (25.6 mg, 17.7 μL, 182 μmol, 1 eq.) in CH₂Cl₂ anhydrous (24 mL) was added dropwise with a dropping funnel. The solution was stirred at rt for 5 d. Afterwards, the solvent was removed under vacuum without drying completely and the crude product solution was separated by size exclusion chromatography (Biobeads S-X1, dry mesh size: 28–74 μ, CH₂Cl₂). The fractions containing P3 (as indicated by TLC) were purified by column chromatography (SiO₂, CH₂Cl₂:ethyl acetate:methanol, 1:0:0 -> 6:0:1) to yield compound P3 (7.29 mg, 2.08 μmol, 3.4%) as purple solid.

TLC (Hexane:ethyl acetate, 3:1): Rf = 0.17.

¹H NMR (500 MHz, C₂D₂Cl₄, 60 °C): δ = 8.11 (s, 12H, CH₃PBI), 7.14 – 7.10 (m, 24H, CH₃phenoxy), 6.77 – 6.72 (m, 24H, CH₃phenoxy), 4.11 – 4.05 (m, 24H, CH₂), 3.20 (s, 6H, OCC₂H₂CO), 1.98 – 1.91 (m, 12H, CH₂), 1.18 ppm (s, 108H, CH₃).

¹³C NMR (126 MHz, C₂D₂Cl₄, 60 °C): δ = 166.55 (6C, O-C=O), 163.55 (12C, N-C=O), 156.20 (12C, C-O), 153.07 (12C, Cphenoxy-O), 147.62 (12C, Cphenoxy), 133.14 (6C, PBI), 126.81 (24C, Hphenoxy), 122.45 (12C, PBI), 120.97 (12C, PBI), 120.24 (12C, PBI), 119.66 (6C, PBI), 119.50 (24C, Hphenoxy), 63.83 (6C, CH₂), 41.55 (3C, O=CCH₂CO), 37.86 (6C, CH₂), 34.47 (12C, C(CH₃)₃), 31.68 (36C, CH₃), 27.60 ppm (6C, CH₂).

HRMS (MALDI-TOF, dctb): m/z calcld for [C₂₁₉H₂₁₀N₆O₁₆]⁺ 3499.4781, found: 3499.4762.

IR (ATR, rt): ν = 2965, 2364, 2343, 1753, 1699, 1662, 1589, 1505, 1440, 1412, 1288, 1217, 1174, 697, 668, 643, 633 cm⁻¹.

UV-vis (CH₂Cl₂): ε (λmax) = 75823 (539), 104860 (579) M⁻¹·cm⁻¹ (nm).
The reaction conditions and the purification by size exclusion and column chromatography are as described for compound P3. The fraction containing most of compound P4 (as indicated by TLC) was further purified by preparative TLC (CH₂Cl₂:ethyl acetate 98:2) and subsequently purified by column chromatography (SiO₂, hexane:ethyl acetate:CH₂Cl₂, 4:1:0 -> 0:1:9) to yield P4 (2.70 mg, 578 nmol, 1.3%) as purple solid.

**TLC (Hexane:ethyl acetate, 3:1):** R<sub>f</sub> = 0.10.

**¹H NMR (400 MHz, CDCl₃, rt):** δ = 8.08 (s, 16H, CH₂PBI), 7.19 – 7.15 (m, 32H, CH₃phenox), 6.78 – 6.72 (m, 32H, CH₃phenox), 4.19 – 4.09 (m, 32H, CH₂), 3.31 (bs, 8H, OCCH₂CO), 1.99 – 1.94 (m, 16H, CH₂), 1.26 ppm (s, 144H, CH₃).

**DEPTQ NMR (151 MHz, CDCl₃, rt):** δ = 166.55 (8C, C=O), 163.33 (16C, N-C=O), 155.95 (16C, C-O), 153.03 (16C, Cphenox-O), 147.30 (16C, Cphenox), 132.88 (8C, CPBI), 126.71 (32C, HCphenox), 122.24 (16C, Cphenox), 120.68 (16C, CPBI), 120.10 (16C, HCPBI), 119.48 (8C, CPBI), 119.37 (32C, HCphenox), 63.49 (8C, CH₂), 41.54 (4C, O=CCCH₂=O), 37.66 (8C, CH₂), 34.48 (16C, C(CH₃)₃), 31.59 (48C, CH₃), 27.33 ppm (8C, CH₂).

**HRMS (MALDI-TOF, dactb):** m/z calcd for [C<sub>292</sub>H<sub>280</sub>N₈O₄₈]⁺ 4665.9710, found: 4665.9701.

**IR (ATR, rt):** ν = 2957, 2920, 2851, 1738, 1697, 1657, 1587, 1503, 1409, 1338, 1288, 1217, 1171, 1015, 887, 837, 802 cm<sup>-1</sup>.

**UV-vis (CH₂Cl₂):** ε (λ<sub>max</sub>) = 58960 (540), 71264 (580) M<sup>-1</sup>.cm<sup>-1</sup> (nm).
Synthesis of model compound P1

To a solution of 1 (200 mg, 0.1819 mmol, 1 eq.) in anhydrous CH₂Cl₂ (100 mL) pyridine (122.3 mg, 1.546 mmol, 8.5 eq.) was added under inert atmosphere. The mixture was cooled in an ice bath for 10 min. Methyl malonyl chloride (99.3 mg, 72 μmol, 97% purity, 4 eq.) was added dropwise over 5 min. The reaction was warmed to rt and stirred overnight. The crude was washed with aq. HCl (40 mL), water (40 mL) and two times with brine (2x 40 mL). The combined organic layers were dried over MgSO₄ and the solvent was removed under vacuum. The solid was rotated onto SiO₂ and purified by column chromatography three times (SiO₂, 1. CH₂Cl₂:EA 100:0 - > 98:2, 2. CH₂Cl₂:EA 100:0 - > 97:3, 3. CH₂Cl₂:Hex:THF 80:40:0 - > 80:20:5) to yield PBI P1 (140.2 mg, 108 μmol, 59%) as a purple solid.

TLC (CH₂Cl₂:ethyl acetate 98:2): Rₛ = 0.71.

¹H NMR (400 MHz, CDCl₃, rt): δ = 8.22 (s, 4H, CH₃PBI), 7.25 – 7.21 (m, 8H, CH₃phenoxy), 6.84 – 6.80 (m, 8H, CH₃phenoxy), 4.23 (t, J= 6.4 Hz, 8H, N(CH₃)₂), 3.70 (s, 6H, OCH₃), 3.36 (s, 4H, COCH₂CO), 2.10 – 2.02 (m, 4H, CH₂), 1.29 ppm (s, 36H, CH₃).

¹³C NMR (101 MHz, CDCl₃, rt): δ = 167.03 (2C, O-C=O), 166.59 (2C, O-C=O), 163.54 (4C, N-C=O), 156.15 (4C, C-O), 153.00 (4C, Cphenoxy-O), 147.52 (4C, Cphenoxy), 133.06 (2C, C₁₈₋₁₆), 126.84 (2, 8C, HCPbenzy), 122.41 (4C, C₁₈₋₁₆), 120.78 (4C, C₁₈₋₁₆), 120.14 (4C, HCPbenzy), 119.59 (2C, C₁₈₋₁₆), 119.46 (8C, HCPbenzy), 63.55 (2C, O-CH₂), 52.65 (2C, O-CH₃), 41.41 (2C, COCO), 37.69 (2C, NCH₂), 34.53 (4C, C(CH₃)₃), 31.60 (12C, CH₃), 27.41 ppm (2C, CH₂).

HRMS (MALDI-TOF, dctb): m/z calcd for [C₇₈H₇₈N₂O₁₆]⁺ 1298.5346, found: 1298.5364.

IR (ATR, rt): ν = 2958, 2928, 2866, 1757, 1737, 1693, 1655, 1585, 1504, 1437, 1412, 1358, 1337, 1311, 1287, 1217, 1170 cm⁻¹.

UV-vis (DCM): ε (λ_max) = 24 823 (541), 40 558 (580) M⁻¹·cm⁻¹ (nm).
Synthesis of model compound P1F2Et

Pentakisadduct FEt (34.9 mg, 23.1 μmol, 3 eq.) was dissolved in CH2Cl2 anhydrous (15 mL) together with PBI derivative P1 (10.0 mg, 7.70 μmol, 1 eq.) and CBr4 (5.62 mg, 16.9 μmol, 2.2 eq.). After stirring at rt for 15 min under inert atmosphere, P1·tBu (4.09 mg, 4.35 μL, 17.5 μmol, 97% purity, 2.2 eq.) was added and the mixture was stirred for additional 30 min. Then the solvent was removed under vacuum without drying completely and the crude was plug-filtered (SiO2, CH2Cl2:ethyl acetate:methanol, 1:0:0-> 95:0:5). After purification by column chromatography (SiO2, CH2Cl2:ethyl acetate, 1:0-> 95:5) model compound P1F2Et (20.7 mg, 4.79 μmol, 62%) was obtained as purple solid.

TLC (CH2Cl2:ethyl acetate, 99:1): Rf = 0.18.

1H NMR (400 MHz, CDCl3, rt): δ = 8.21 (s, 4H, CHPBI), 7.25 – 7.21 (m, 8H, CHphenoxy), 6.86 – 6.78 (m, 8H, CHphenoxy), 4.32 (m, 40H, CH2 / 4H, CH2), 4.26 – 4.19 (m, 4H, CH2), 3.87 (s, 6H, OCH3), 2.16 – 2.04 (m, 4H, CH2), 1.36 – 1.27 ppm (m, 60H, CH3 / 36H, CH3).

13C NMR (151 MHz, CDCl3, rt): δ = 164.37 (2C, O=C=O), 163.99, 163.98, 163.96, 163.93, 163.91, 163.85 (22C, CO), 163.46 (4C, N-C=O), 156.10 (4C, C-O), 153.01 (4C, Cphenoxy-O), 147.44 (4C, Cphenoxy), 146.05, 145.99, 145.97, 145.93, 145.84, 145.82, 145.77, 141.34, 141.32, 141.30, 141.27, 141.21, 141.00 (96C, C60-sp2), 133.07 (2C, CPBI), 126.82 (8C, HCphenoxy), 122.43 (4C, CPBI), 120.79 (4C, CPBI), 120.14 (4C, HCphenoxy), 119.63 (2C, CPBI), 119.45 (8C, HCphenoxy), 69.22, 69.21, 69.20, 69.18, 69.17 (24C, C60-sp3), 64.96 (2C, O-CH2), 62.99, 62.96 (20C, CH2), 53.95 (2C, CH3), 53.57, 45.53, 45.49, 45.29 (12C, CCOCO), 37.54 (2C, NCH3), 34.53 (4C, C(CH3)3), 31.61 (12C, CH3), 27.49 (2C, CH2), 14.28, 14.20 ppm (20C, CH3).

HRMS (MALDI-TOF, dcb): m/z calcd for [C268H174N2NaO56]⁺ 4338.0721, found: 4338.0825.

IR (ATR, rt): ν [cm⁻¹] = 2957, 2922, 2851, 1744, 1697, 1260, 1209, 1173, 1076, 1040, 1015, 802, 729, 714 cm⁻¹.

UV-vis (CH2Cl2): ε (λmax) = 23374 (541), 38138 (580) M⁻¹·cm⁻¹ (nm).
Synthesis of functional hybrid \( \text{P}2\text{F}_2\text{Et} \)

Cyclopane \( \text{P}2 \) (5.00 mg, 2.14 \( \mu \)mol, 1 eq.), pentakisadduct \( \text{F}_\text{Et} \) (9.71 mg, 6.42 \( \mu \)mol, 3 eq.) and \( \text{CBr}_4 \) (1.56 mg, 4.71 \( \mu \)mol, 2.2 eq.) were dissolved in \( \text{CH}_2\text{Cl}_2 \) anhydrous (4.20 mL) under inert atmosphere. The solution was stirred for 10 min at rt. \( \text{P}_1\text{-tBu} \) (1.14 mg, 1.21 \( \mu \)L, 4.86 \( \mu \)mol, 97% purity, 2.2 eq.) was added and the mixture was stirred at rt. After 40 min more pentakisadduct \( \text{F}_\text{Et} \) (4.86 mg, 3.21 \( \mu \)mol, 1.5 eq.) was added. After stirring overnight \( \text{CBr}_4 \) (780 \( \mu \)g, 2.36 \( \mu \)mol, 1.1 eq.) and \( \text{P}_1\text{-tBu} \) (570 \( \mu \)g, 1.21 \( \mu \)L, 2.43 \( \mu \)mol, 97% purity, 1.1 eq.) dissolved in \( \text{CH}_2\text{Cl}_2 \) anhydrous (1.00 mL) were added to complete the reaction. The solution was directly purified by column chromatography (SiO\(_2\), \( \text{CH}_2\text{Cl}_2\):ethyl acetate, 1:0 \( \rightarrow \) 90:10) to obtain cyclophane fullerene adduct \( \text{P}2\text{F}_2\text{Et} \) (8.00 mg, 1.49 \( \mu \)mol, 70%) as purple solid.

\[ \text{TLC (CH}_2\text{Cl}_2\text{-ethyl acetate, 99.8:0.2): R}_f = 0.12. \]

\[ \text{^1H NMR (400 MHz, C}_2\text{D}_2\text{Cl}_4, 90 °C): } \delta = 7.82 (s, 8H, CH}_\text{PBI}), 7.15 – 7.10 (m, 16H, CH}_\text{phenoxy}), 6.77 – 6.64 (m, 16H, CH}_\text{phenoxy}), 4.43 – 4.25 (m, 8H, CH\_2 / 40H, CH\_2), 4.15 – 4.03 (m, 8H, CH\_2), 2.13 – 1.95 (m, 8H, CH\_2), 1.31 – 1.25 ppm (m, 72H, CH\_3 / 60H, CH\_2). \]

\[ \text{^13C NMR (101 MHz, C}_2\text{D}_2\text{Cl}_4, 90 °C): } \delta = 163.95, 163.92, 163.87, 163.83 (24C, CO), 162.98 (8C, N-C=O), 153.45 (8C, C\_\text{phenox}-O), 147.54 (8C, C\_\text{phenox}), 146.03, 145.98, 145.94, 145.92, 145.89, 145.84, 141.49, 141.45, 141.41, 141.40, 141.39, 141.35 (96C, C\_60-sp\textsuperscript{3}), 132.65 (4C, C\_\text{PBI}), 126.57 (16C, C\_\text{phenox}), 122.22 (8C, C\_\text{PBI}), 120.57 (8C, C\_\text{PBI}), 120.40 (8C, C\_\text{PBI}), 119.61 (16C, C\_\text{phenox}), 119.37 (4C, C\_\text{PBI}), 69.78, 69.56 (24C, C\_60-sp\textsuperscript{3}), 64.88 (4C, O-CH\_2), 63.22, 63.21 (20C, CH\_2), 46.12, 46.07 (12C, COCCO), 34.48 (8C, C(CH\_3\_3)), 31.70 (24C, CH\_3), 27.48 (4C, CH\_2), 14.21 ppm (20C, CH\_3). \]

\[ \text{HRMS (MALDI-TOF, dctb): } m/z \text{ calcd for [C}_{236}\text{H}_{236}\text{N}_{4}\text{O}_{64}^+ = 5349.5330, found: 5349.5487.} \]

\[ \text{IR (ATR, rt): } \tilde{\nu} = 2959, 2926, 2867, 2854, 1743, 1698, 1660, 1589, 1505, 1263, 1206, 1171, 1076, 1012, 713, 528 \text{ cm}^{-1}. \]

\[ \text{UV-vis (CH}_2\text{Cl}_2): } \varepsilon (\lambda\_\text{max}) = 82483 (537), 62564 (575) \text{ M}^{-1}\text{cm}^{-1} (\text{nm}). \]
Synthesis of functional hybrid P2F2\textsubscript{TEG}

Cyclophane P2 (5.00 mg, 2.14 μmol, 1 eq.), pentakisadduct F\textsubscript{TEG} (20.1 mg, 6.42 μmol, 3 eq.) and CBr\textsubscript{4} (1.56 mg, 4.71 μmol, 2.2 eq.) were dissolved in CH\textsubscript{2}Cl\textsubscript{2} anhydrous (4.20 mL). P\textsubscript{1}-tBu (1.14 mg, 1.21 μL, 4.86 μmol, 97% purity, 2.2 eq.) was added and the mixture was stirred at rt under inert atmosphere. After 21 h, CBr\textsubscript{4} (780 μg, 2.36 μmol, 1.1 eq.) and P\textsubscript{1}-tBu (570 μg, 605 nL, 2.43 μmol, 97% purity, 1.1 eq.) were added to the mixture and stirred for additional 4 d. The process was repeated together with pentakisadduct F\textsubscript{TEG} (10.1 mg, 3.21 μmol, 1.5 eq.) and the reaction mixture was stirred for another 6 d. The crude mixture was directly purified by column chromatography (SiO\textsubscript{2}, CH\textsubscript{2}Cl\textsubscript{2}:toluene:methanol, 100:60:15). The mixed fractions containing P2F2\textsubscript{TEG} were further purified by four fold column chromatography (SiO\textsubscript{2}, 1. CH\textsubscript{2}Cl\textsubscript{2}:toluene:methanol, 100:60:12 -> 100:60:15, 2. CH\textsubscript{2}Cl\textsubscript{2}:toluene:methanol, 100:60:8 -> 90:70:25, 3. CH\textsubscript{2}Cl\textsubscript{2}:toluene:methanol, 90:70:15 -> 100:60:20, 4. CH\textsubscript{2}Cl\textsubscript{2}:toluene:methanol, 100:60:8 -> 100:60:12). The combined pure fractions yielded cyclophane fullerene adduct P2F2\textsubscript{TEG} (5.00 mg, 582 nmol, 27%) as purple viscous oil.

**TLC (CH\textsubscript{2}Cl\textsubscript{2}:toluene:methanol, 100:60:12):** \(R_f = 0.12\)

\(^1\text{H} \text{NMR (500 MHz, C}_2\text{D}_2\text{Cl}_4, 110 \text{°C)}: \delta = 7.82 \text{ (s, 8H, CH}_\text{PBI}), 7.21 – 7.06 \text{ (m, 16H, CH}_\text{phenoxyl}), 6.83 – 6.60 \text{ (m, 16H, CH}_\text{phenoxyl}), 4.51 – 4.23 \text{ (m, 8H, CH}_2 / 40H, COOCH}_2), 4.16 – 4.06 \text{ (m, 8H, CH}_2), 3.84 – 3.37 \text{ (m, 280H, OCH}_2), 3.36 – 3.23 \text{ (m, 60H, OCH}_3), 2.14 – 2.04 \text{ (m, 8H, CH}_2), 1.28 \text{ ppm (s, 72H, CH}_3).\]

**DEPTQ NMR (126 MHz, C}_2\text{D}_2\text{Cl}_4, 110 \text{°C)}:** \(\delta = 163.72, 163.68, 163.65, 163.58 (24C, CO), 162.93 (8C, N-C=O), 155.81 (8C, C-O), 153.50 (8C, C\text{phenoxyl-O}), 147.59 (8C, C\text{phenoxyl}), 146.03, 145.99, 145.97, 145.92, 141.33 (96C, C\text{60-sp}^3), 132.67 (4C, C\text{PBI}), 126.54 (16C, H\text{Cphenoxyl}), 122.31 (8C, C\text{PBI}), 120.59 (8C, C\text{PBI}), 120.40
HRMS (ESI): m/z calcd for [C₄₇H₅₁₆N₄Na₄O₁₄4⁺] 2170.8187, found: 2170.8206.

IR (ATR, rt): $\tilde{\nu} = 2953, 2920, 2868, 2853, 1742, 1698, 1505, 1350, 1282, 1258, 1214, 1171, 1093, 1025, 1016, 942, 872, 841, 803, 714, 551, 528 \text{ cm}^{-1}$.

UV-vis (CH₂Cl₂): $\varepsilon(\lambda_{\text{max}}) = 76456 (537), 57932 (575) \text{ M}^{-1}\text{cm}^{-1} (\text{nm})$.

**Synthesis of side product P2F1₅EG**

Cyclophane P2 (5.00 mg, 2.14 µmol, 1 eq.), pentakisadduct F₅EG (20.1 mg, 6.42 µmol, 3 eq.) and CBr₄ (1.56 mg, 4.71 µmol, 2.2 eq.) were dissolved in CH₂Cl₂ anhydrous (4.20 mL). P₁-tBu (1.14 mg, 1.21 µL, 4.86 µmol, 97% purity, 2.2 eq.) was added and the mixture was stirred at rt under inert atmosphere. After 80 min, another portion of CBr₄ (2.2 eq.) and P₁-tBu (2.2 eq.) were added and the mixture was stirred for additional 100 min. The crude solution was directly purified by column chromatography (SiO₂, CH₂Cl₂:toluene:methanol, 100:60:12 -> 100:60:20) to obtain compound P2F1₅EG (4.50 mg, 800 nmol, 37%) as purple viscous oil.

**TLC (CH₂Cl₂:toluene:methanol, 100:60:12):** $R_f = 0.19$

$^1$H NMR (500 MHz, C₂D₂Cl₂, 110 °C): δ = 7.84 (s, 4H, C₈PB), 7.80 (s, 4H, C₈PB), 7.18 – 7.10 (m, 16H, C₈p), 6.76 – 6.65 (m, 16H, C₈p), 4.50 – 4.28 (m, 8H, CH₂ / 20H, COOCH₃), 4.16 – 4.05 (m, 8H,
$\text{CH}_2)$, 3.75 – 3.43 (m, 140H, OCH$_2)$, 3.34 – 3.25 (m, 30H, OCH$_3$), 2.12 – 1.98 (m, 8H, CH$_2$), 1.28 ppm (s, 72H, CH$_3$).

**DEPTQ NMR (126 MHz, C$_2$D$_2$Cl$_4$, 100 °C):** δ = 163.70, 163.67, 163.32, 163.30, 162.99, 162.94 (14C, CO), 155.84, 155.82 (8C, C-O), 153.45, 153.41 (8C, Cphenoxy-O), 147.62, 147.60, 147.58 (8C, Cphenxy), 146.10, 146.04, 146.00, 145.97, 145.94, 141.33, 141.31 (48C, C$_{60}$-sp$^2$), 132.74, 132.65 (4C, C$_{PBI}$), 126.58 (16C, H$_2$phenxy), 122.17 (8C, C$_{PBI}$), 120.66 (8C, C$_{PBI}$), 120.37 (8C, H$_2$phenxy), 119.60 (16C, H$_2$phenxy), 119.36 (4C, C$_{PBI}$), 72.26, 72.24, 70.91, 70.89, 70.87, 70.85, 70.81, 70.80, 70.77, 70.63, 70.61, 68.75 (70C, OCH$_2$), 69.53 (12C, C$_{60}$-sp$^2$), 66.22 (10C, OCH$_3$), 65.09, 65.07, 65.05 (4C, CH$_2$), 58.91 (10C, OCH$_3$), 46.17, 45.92 (12C, COCCO), 37.49, 37.47, 37.44 (4C, CH$_2$), 34.48 (8C, C(CH$_3$)$_3$), 31.67 (24C, CH$_3$), 27.34, 27.32, 27.30 ppm (4C, CH$_2$).

**HRMS (ESI):** m/z calcd for [C$_{311}$H$_{326}$Br$_2$Na$_4$NaO$_{84}$]$_2^+$ 2831.9756, found: 2831.9770.

**IR (ATR, rt):** $\tilde{\nu}$ = 2953, 2919, 2868, 2853, 1742, 1698, 1659, 1591, 1343, 1284, 1266, 1212, 1172, 1104, 1038, 1025, 1013, 945, 902, 873, 839, 822, 803, 715, 554, 528 cm$^{-1}$.

**UV-vis (CH$_2$Cl$_2$):** $\epsilon$ ($\lambda_{max}$) = 78287 (537), 60178 (575) M$^{-1}$-cm$^{-1}$ (nm).
3. HPLC chromatograms

Figure S1. a) HPLC chromatograms of the crude mixtures of experiment A and C as well as the macrocycles P2, P3 and P4 analysed at a wavelength of 530 nm. b) Corresponding MALDI MS spectrum of P2_{open}. c) Chemical structure of P2_{open} with a retention time of approximately 20 min.
Figure S2. Comparison of the HPLC chromatograms of P2 (top), P3 (bottom) and a mixture of both cyclophanes (middle). The retention time of pure P2 is less than the retention times of the two-membered ring in the different crude mixtures or in a mixture of only P2 and P3 (middle). It can be concluded that P2 interacts with other molecules, which leads to a delay in the retention time.

Figure S3. Comparison of the HPLC chromatograms of the crude mixture of experiment D evaluated both in the absorption region of P2 (530 nm) and TTF (280 nm).
Figure S4. HPLC chromatograms of the crude mixture of experiment E at different times analysed at a wavelength of 530 nm.
4. Temperature-dependent $^1$H NMR spectra

Figure S5. $^1$H NMR (600 MHz) spectrum of P2 in C$_2$D$_2$Cl$_4$ at -5 °C, enlarged at 2.87 ppm with labelled peaks in Hz.

Figure S6. $^1$H and EXSY (600 MHz) NMR spectra of P2 in C$_2$D$_2$Cl$_4$ at 5 °C showing the selective excitation at 2.92 ppm.
**Figure S7.** $^1$H (600 MHz) NMR spectrum of P2 in C$_2$D$_2$Cl$_4$ at -15 °C showing the ratio of \((P,P)/(M,M) : (P,M)/(M,P)\) of 10:1.
Figure S8. Temperature-dependent $^1$H (500 MHz) NMR spectra of P2 and P2F$_2$Et dissolved in C$_2$D$_2$Cl$_4$. 
**Figure S9.** Temperature-dependent $^1$H (400 MHz) NMR spectra of P2 dissolved in CD$_2$Cl$_2$.

**Figure S10.** Temperature-dependent $^1$H (500 MHz) NMR spectra of P2 and P3 in C$_2$D$_2$Cl$_4$. 
Figure S11. $^{13}$C (600 MHz) NMR spectrum of P3 dissolved in CD$_2$Cl$_2$ recorded at -20 °C.

Figure S12. $^{13}$C (600 MHz) NMR spectrum of P3 dissolved in CD$_2$Cl$_2$ recorded at -38 °C.
Figure S13. $^1$H and EXSY (600 MHz) NMR spectra of P3 in CD$_2$Cl$_2$ at -20 °C showing the selective excitation at 3.24 ppm.
5. Calculation of the activation energy $\Delta G^I$

To calculate the activation energy $\Delta G^I$ the following equation was used\(^2\):

$$\Delta G^I = RT_c \cdot \ln \left( \frac{RT_c \sqrt{2}}{\pi N_A h |\nu_A - \nu_B|} \right)$$

$\Delta G^I$: activation energy for conformational interconversion; $R$: universal gas constant; $N_A$: Avogadro constant, $h$: Planck’s constant, $\nu$: chemical shift

**Table S1.** Summary of the coalescence temperature and the difference in frequencies for the calculation of the activation energy.

| Compound  | Solvent | $T_c$ [K] | $|\nu_A - \nu_B|$ [Hz] at $T$ [K] | $\Delta G^I$ [kJ/mol] |
|-----------|---------|-----------|---------------------------------|------------------------|
| P2        | CD$_2$Cl$_2$ | 273       | 205.45 at 233                   | 52.77                  |
| P2        | C$_2$D$_2$Cl$_4$ | 298       | 291.21 at 248                   | 56.95                  |
| P2F$_2$et | CD$_2$Cl$_2$ | 292       | 29.27 at 253                    | 61.33                  |
| P2F$_2$et | C$_2$D$_2$Cl$_4$ | 333       | 283.83 at 268                   | 64.02                  |
6. NMR spectra

Figure S14. $^1$H NMR (500 MHz, C$_2$D$_2$Cl$_4$, 90 °C) spectrum of macrocycle P2.

Figure S15. $^{13}$C NMR (126 MHz, C$_2$D$_2$Cl$_4$, 90 °C) spectrum of macrocycle P2.
Figure S16. $^1$H NMR (500 MHz, C$_2$D$_2$Cl$_4$, 60 °C) spectrum of macrocycle P3.

Figure S17. $^{13}$C NMR (126 MHz, C$_2$D$_2$Cl$_4$, 60 °C) spectrum of macrocycle P3.
Figure S18. $^1$H NMR (400 MHz, CDCl$_3$, rt) spectrum of macrocycle P4.

Figure S19. DEPTQ NMR (151 MHz, CDCl$_3$, rt) spectrum of macrocycle P4.
**Figure S20.** $^1$H NMR (400 MHz, CDCl$_3$, rt) spectrum of precursor P1.

**Figure S21.** $^{13}$C NMR (101 MHz, CDCl$_3$, rt) spectrum of model precursor P1.
Figure S22. $^1$H NMR (400 MHz, CDCl$_3$, rt) spectrum of model compound P1F$_2$Et.

Figure S23. $^{13}$C NMR (151 MHz, CDCl$_3$, rt) spectrum of model compound P1F$_2$Et.
Figure S24. $^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$, 90 °C) spectrum of the functional hybrid P2F2$_{Et}$.

Figure S25. $^{13}$C NMR (101 MHz, C$_2$D$_2$Cl$_4$, 90 °C) spectrum of the functional hybrid P2F2$_{Et}$.
Figure S26. $^1$H NMR (500 MHz, C$_2$D$_2$Cl$_4$, 110 °C) spectrum of the functional hybrid P2F$_2$TEG.

Figure S27. $^{13}$C NMR (126 MHz, C$_2$D$_2$Cl$_4$, 110 °C) spectrum of the functional hybrid P2F$_2$TEG.
Figure S28. $^1$H NMR (500 MHz, C$_2$D$_2$Cl$_4$, 110 °C) spectrum of the functional hybrid P2F1$_{TEG}$.

Figure S29. DEPTQ NMR (126 MHz, C$_2$D$_2$Cl$_4$, 110 °C) spectrum of the functional hybrid P2F1$_{TEG}$.
7. MS spectra

Figure S30. APPI HRMS spectrum of macrocycle P2.

Figure S31. MALDI HRMS spectrum of macrocycle P3.
Figure S32. MALDI HRMS spectrum of macrocycle P4.

Figure S33. MALDI HRMS spectrum of precursor P1.
Figure S34. MALDI HRMS spectrum of model compound P1F2Et.

Figure S35. MALDI HRMS spectrum of functional hybrid P2F2Et.
Figure S36. ESI HRMS spectrum of functional hybrid P2F2<sub>TEG</sub>.

Figure S37. APPI HRMS spectrum of side product P2F1<sub>TEG</sub>. 
8. UV-Vis absorption spectroscopy

Figure S38. Normalized absorption spectra of P1, P2, P3, and P4 in tetrahydrofuran, toluene, benzonitrile, and 1,1,2,2-tetrachloroethane measured at room temperature.
Figure S39. Absorption spectra of cyclophane P2 at different concentrations in toluene, tetrahydrofuran and benzonitrile measured at room temperature.
Figure S40. Normalized absorption spectra of $P1F2_{El}$, $P2F2_{El}$, and $P2F2_{TEG}$ in tetrahydrofuran, toluene, benzonitrile, and 1,1,2,2-tetrachloroethane measured at room temperature.
Table S2. The peak wavelengths (in nm) for 0–*0 and 0–*1 vibrational transitions, molar extinction coefficient at the peak positions (in M$^{-1}$ cm$^{-1}$) and the 0–*1 : 0–*0 transition intensity ratios for all the samples in different solvents, measured at room temperature.

| Sample | Toluene | THF | Benzonitrile | 5% THF/water |
|--------|---------|-----|--------------|--------------|
|        | 0–*1   | 0–*0 | 0–*1   | 0–*0 | 0–*1   | 0–*0 | 0–*1   | 0–*0 |
| P1     | Peak position (nm) | 534 | 575 | 531 | 570 | 541 | 580 |
|        | $\epsilon$ (M$^{-1}$ cm$^{-1}$) | $2.6 \times 10^4$ | $4.4 \times 10^4$ | $2.4 \times 10^4$ | $3.8 \times 10^4$ | $2.4 \times 10^4$ | $3.8 \times 10^4$ |
|        | 0–*1 : 0–*0 | 0.60 : 1 | 0.63 : 1 | 0.62 : 1 |  |
| P2     | Peak position (nm) | 532 | 572 | 530.5 | 571.5 | 539 | 578 |
|        | $\epsilon$ (M$^{-1}$ cm$^{-1}$) | $5.6 \times 10^4$ | $5.6 \times 10^4$ | $4.8 \times 10^4$ | $4.7 \times 10^4$ | $4.4 \times 10^4$ | $4.8 \times 10^4$ |
|        | 0–*1 : 0–*0 | 0.99 : 1 | 1.03 : 1 | 0.92 : 1 |  |
| P3     | Peak position (nm) | 535.5 | 574.5 | 534 | 572 | 541.5 | 579.5 |
|        | $\epsilon$ (M$^{-1}$ cm$^{-1}$) | $3.4 \times 10^4$ | $4.8 \times 10^4$ | $1.1 \times 10^5$ | $1.5 \times 10^5$ | $8.2 \times 10^4$ | $1.2 \times 10^5$ |
|        | 0–*1 : 0–*0 | 0.71 : 1 | 0.72 : 1 | 0.69 : 1 |  |
| P4     | Peak position (nm) | 538 | 579.5 | 538 | 577.5 | 543 | 582 |
|        | $\epsilon$ (M$^{-1}$ cm$^{-1}$) | $2.6 \times 10^4$ | $3.3 \times 10^4$ | $3.4 \times 10^4$ | $4.4 \times 10^4$ | $4.7 \times 10^4$ | $6.6 \times 10^4$ |
|        | 0–*1 : 0–*0 | 0.77 : 1 | 0.79 : 1 | 0.71 : 1 |  |
| P1F2Et | Peak position (nm) | 534 | 575 | 531.5 | 571.5 | 543 | 582.5 |
|        | $\epsilon$ (M$^{-1}$ cm$^{-1}$) | $2.1 \times 10^4$ | $3.5 \times 10^4$ | $2.5 \times 10^4$ | $4.0 \times 10^4$ | $2.2 \times 10^4$ | $3.5 \times 10^4$ |
|        | 0–*1 : 0–*0 | 0.61 : 1 | 0.54 : 1 | 0.62 : 1 |  |
| P2F2Et | Peak position (nm) | 530.5 | 568.5 | 529 | 567 | 537.5 | 576 |
|        | $\epsilon$ (M$^{-1}$ cm$^{-1}$) | $6.8 \times 10^4$ | $5.9 \times 10^4$ | $8.0 \times 10^4$ | $6.0 \times 10^4$ | $6.3 \times 10^4$ | $5.7 \times 10^4$ |
|        | 0–*1 : 0–*0 | 1.16 : 1 | 1.33 : 1 | 1.11 : 1 |  |
| P2F2TEG | Peak position (nm) | 531 | 569 | 530 | 568 | 538 | 576 | 537 | 577 |
|        | $\epsilon$ (M$^{-1}$ cm$^{-1}$) | $4.6 \times 10^4$ | $4.2 \times 10^4$ | $5.5 \times 10^4$ | $4.2 \times 10^4$ | $4.2 \times 10^4$ | $3.8 \times 10^4$ | $4.6 \times 10^4$ | $3.6 \times 10^4$ |
|        | 0–*1 : 0–*0 | 1.12 : 1 | 1.30 : 1 | 1.10 : 1 | 1.30 : 1 |  |
9. Fluorescence spectroscopy

Figure S41. Normalized fluorescence spectra of \( P1 \), \( P2 \), \( P3 \), and \( P4 \) in tetrahydrofuran, toluene, benzonitrile, and 1,1,2,2-tetrachloroethane obtained upon photo-excitation at 510 nm at room temperature.
Figure S42. Normalized fluorescence spectra of $P_1F_2_{Et}$, $P_2F_2_{Et}$, and $P_2F_2_{TEG}$ in tetrahydrofuran, toluene, benzonitrile, and 1,1,2,2-tetrachloroethane obtained upon photo-excitation at 510 nm at room temperature.
Table S3. Fluorescence quantum yields measured in different solvents at room temperature (Rhodamine B in ethanol used as reference).

| Emission quantum yield | Toluene | THF  | Benzonitrile | 5% THF/water |
|------------------------|---------|------|--------------|--------------|
| P1                     | 0.904   | 0.792| 0.722        | -            |
| P2                     | 0.176   | 0.015| 0.016        | -            |
| P3                     | 0.254   | 0.085| 0.118        | -            |
| P4                     | 0.183   | 0.058| 0.104        | -            |
| P1F2_Et                | 0.391   | 0.536| 0.531        | -            |
| P2F2_Et                | 0.152   | 0.007| 0.012        | -            |
| P2F2_TEG               | 0.234   | 0.025| 0.027        | 0.007        |
10. Temperature-dependent absorption and fluorescence spectra

Figure S43. Temperature-dependent absorptions of P2 (a) and P3 (b) as well as fluorescence of P2 (c) and P3 (d) in 1,1,2,2-tetrachloroethane.
11. Spectroelectrochemistry

Figure S44. Differential absorption spectra of P1, P2, P3, and P4 in argon-saturated benzonitrile containing 0.1 M TBAPF₆ supporting electrolyte, obtained upon electrochemical oxidation and reduction using Ag wire as reference electrode.
12. Transient absorption measurements

Figure S45. Femtosecond differential absorption spectra of P1 in argon-purged toluene (a), THF (b), and PhCN (c), at time delays between 0 and 5500 ps after 550 nm photo-excitation at rt. Nanosecond differential absorption spectra of P1 in argon-purged toluene (d), THF (e), and PhCN (f), at time delays between 1 ns and >100 μs after 550 nm photo-excitation at rt.
Figure S46. Femtosecond differential absorption spectra of P2 in argon-purged toluene (a), THF (b), and PhCN (c), at time delays between 0 and 5500 ps after 550 nm photo-excitation at rt. Nanosecond differential absorption spectra of P2 in argon-purged toluene (d), THF (e), and PhCN (f), at time delays between 1 ns and >100 μs after 550 nm photo-excitation at rt.
Figure S47. Femtosecond differential absorption spectra of P3 in argon-purged toluene (a), THF (b), and PhCN (c), at time delays between 0 and 5500 ps after 550 nm photo-excitation at rt. Nanosecond differential absorption spectra of P3 in argon-purged toluene (d), THF (e), and PhCN (f), at time delays between 1 ns and >100 μs after 550 nm photo-excitation at rt.
Figure S48. Femtosecond differential absorption spectra of P4 in argon-purged toluene (a), THF (b), and PhCN (c), at time delays between 0 and 5500 ps after 550 nm photo-excitation at rt. Nanosecond differential absorption spectra of P4 in argon-purged toluene (d), THF (e), and PhCN (f), at time delays between 1 ns and >100 μs after 550 nm photo-excitation at rt.
Figure S49. Femtosecond differential absorption spectra of P1F2_{Et} in argon-purged toluene (a), THF (b), and PhCN (c), at time delays between 0 and 5500 ps after 550 nm photo-excitation at rt. Nanosecond differential absorption spectra of P1F2_{Et} in argon-purged toluene (d), THF (e), and PhCN (f), at time delays between 1 ns and >100 μs after 550 nm photo-excitation at rt.
Figure S50. Femtosecond differential absorption spectra of $\text{P}_2\text{F}_2\text{Et}$ in argon-purged toluene (a), THF (b), and PhCN (c), at time delays between 0 and 5500 ps after 550 nm photo-excitation at rt. Nanosecond differential absorption spectra of $\text{P}_2\text{F}_2\text{Et}$ in argon-purged toluene (d), THF (e), and PhCN (f), at time delays between 1 ns and >100 μs after 550 nm photo-excitation at rt.
Figure S51. Femtosecond differential absorption spectra of $\text{P}_2\text{F}_2\text{TEG}$ in argon-purged toluene (a), THF (b), and PhCN (c), at time delays between 0 and 5500 ps after 550 nm photo-excitation at rt. Nanosecond differential absorption spectra of $\text{P}_2\text{F}_2\text{TEG}$ in argon-purged toluene (d), THF (e), and PhCN (f), at time delays between 1 ns and $>100$ μs after 550 nm photo-excitation at rt.
13. Global analysis of transient absorption spectra

Figure S52. Evolution associated spectra reconstructed from the sequential global analysis of fs-TA spectra of P1 in toluene (a), THF (b), PhCN (c) and the corresponding population kinetics in toluene (d), THF (e), and PhCN (f).
Figure S53. Evolution associated spectra reconstructed from the sequential global analysis of ns-TA spectra of P1 in toluene (a), THF (b), PhCN (c) and the corresponding population kinetics in toluene (d), THF (e), and PhCN (f).
Figure S54. Evolution associated spectra reconstructed from the sequential global analysis of fs-TA spectra of P2 in toluene (a), THF (b), PhCN (c) and the corresponding population kinetics in toluene (d), THF (e), and PhCN (f).
Figure S55. Evolution associated spectra reconstructed from the sequential global analysis of ns-TA spectra of P2 in toluene (a), THF (b), PhCN (c) and the corresponding population kinetics in toluene (d), THF (e), and PhCN (f).
Figure S56. Evolution associated spectra reconstructed from the sequential global analysis of fs-TA spectra of P3 in toluene (a), THF (b), PhCN (c) and the corresponding population kinetics in toluene (d), THF (e), and PhCN (f).
Figure S57. Evolution associated spectra reconstructed from the sequential global analysis of ns-TA spectra of P3 in toluene (a), THF (b), PhCN (c) and the corresponding population kinetics in toluene (d), THF (e), and PhCN (f).
Figure S58. Evolution associated spectra reconstructed from the sequential global analysis of fs-TA spectra of P4 in toluene (a), THF (b), PhCN (c) and the corresponding population kinetics in toluene (d), THF (e), and PhCN (f).
Figure S59. Evolution associated spectra reconstructed from the sequential global analysis of ns-TA spectra of P4 in toluene (a), THF (b), PhCN (c) and the corresponding population kinetics in toluene (d), THF (e), and PhCN (f).
Figure S60. Evolution associated spectra reconstructed from the sequential global analysis of fs-TA spectra of \( \text{P1F2a} \) in toluene (a), THF (b), PhCN (c) and the corresponding population kinetics in toluene (d), THF (e), and PhCN (f).
Figure S61. Evolution associated spectra reconstructed from the sequential global analysis of ns-TA spectra of P1F2Et in toluene (a), THF (b), PhCN (c) and the corresponding population kinetics in toluene (d), THF (e), and PhCN (f).
Figure S62. Evolution associated spectra reconstructed from the sequential global analysis of fs-TA spectra of P2F2 Eli in toluene (a), THF (b), PhCN (c) and the corresponding population kinetics in toluene (d), THF (e), and PhCN (f).
Figure S63. Evolution associated spectra reconstructed from the sequential global analysis of ns-TA spectra of $\text{P}_2\text{F}_2\text{Et}$ in toluene (a), THF (b), PhCN (c) and the corresponding population kinetics in toluene (d), THF (e) and PhCN (f).
Figure S64. Evolution associated spectra reconstructed from the sequential global analysis of fs-TA spectra of P2F2TEG in toluene (a), THF (b), PhCN (c) and the corresponding population kinetics in toluene (d), THF (e), and PhCN (f).
Figure S65. Evolution associated spectra reconstructed from the sequential global analysis of ns-TA spectra of P2F2TEG in toluene (a), THF (b), PhCN (c) and the corresponding population kinetics in toluene (d), THF (e), and PhCN (f).
Table S4. Lifetimes of different species involved in the excited state decay dynamics of P1 and P1F2Et, determined from the global sequential analysis of fs-TA and ns-TA measurements.

|           | $^1S_{hot}$ (ps) | $^1S_{rel}$ (ps) | $^1S_{fluor}$ (ns) | $^1T$ (μs) |
|-----------|------------------|------------------|--------------------|------------|
| P1        |                  |                  |                    |            |
| Tol       | 8.5              | 350.6            | 6.0                | > 350      |
| THF       | 6.2              | 340.1            | 6.4                | > 350      |
| PhCN      | 15.1             | 570.2            | 6.1                | > 350      |
| P1F2Et    |                  |                  |                    |            |
| Tol       | 11.5             | 1397.9           | 5.5                | 232        |
| THF       | 7.9              | 621.0            | 5.4                | 137        |
| PhCN      | 4.4              | 637.3            | 5.4                | 222        |
Table S5. Lifetimes of different species involved in the excited state decay dynamics determined from the global sequential analysis of fs-TA and ns-TA measurements for P2, P3, P4 as well as P2F2_{Et} and P2F2_{TEG}.

|       | $^{1}S_{\text{hot}}$ (ps) | $^{1}S_{\text{rel}}$ (ps) | SBCT$_{\text{hot}}$ (ns) | SBCT$_{\text{rel}}$ (ns) | SBCS (ns) | $^1T$ (μs) |
|-------|---------------------------|---------------------------|--------------------------|--------------------------|-----------|-----------|
| **P2** |                           |                           |                          |                          |           |           |
| Tol   | 16.3                      | 324.6                     | 5.9                      | 14.7                     | -         | 35        |
| THF   | 4.6                       | -                         | 0.6                      | -                        | 3.3       | 139       |
| PhCN  | 23.7                      | -                         | 0.8                      | -                        | 4.1       | 118       |
| Tol   | 2.2                       | 104.3                     | 6.1                      | 12.3                     | -         | 47        |
| THF   | 2.0                       | 27.8                      | 1.3                      | -                        | 6.2       | 183       |
| PhCN  | 17.7                      | 256.1                     | 2.0                      | -                        | 12.8      | 167       |
| Tol   | 2.2                       | 48.5                      | 4.5                      | 9.9                      | -         | 83        |
| THF   | 2.7                       | 39.4                      | 1.3                      | -                        | 4.6       | 148       |
| PhCN  | 10.0                      | 725.5                     | 4.0                      | -                        | 19.9      | 180       |
| Tol   | 17.7                      | 987.0                     | 3.0                      | 12.8                     | -         | 97        |
| **P2F2_{Et}** |                           |                           |                          |                          |           |           |
| THF   | 3.8                       | -                         | 2.2                      | -                        | 6.4       | 155       |
| PhCN  | 26.4                      | -                         | 1.2                      | -                        | 4.4       | 165       |
| Tol   | 6.6                       | 102.8                     | 2.8                      | 11.2                     | -         | 112       |
| **P2F2_{TEG}** |                           |                           |                          |                          |           |           |
| THF   | 4.4                       | -                         | 0.8                      | -                        | 2.9       | 143       |
| PhCN  | 23.6                      | -                         | 0.9                      | -                        | 2.2       | 148       |
14. Singlet oxygen quantum yield measurements

Figure S66. Singlet oxygen phosphorescence of P2, P3 and P4 measured in oxygen saturated toluene and benzonitrile after 532 nm photo-excitation (OD = 0.08).
**Table S6.** Singlet oxygen quantum yields of \( \text{P2, P3, and P4} \) in toluene and benzonitrile, measured using \( \text{C}_{60} \) in air-equilibrated toluene as reference (\( \Phi_{\Delta \text{ref}} = 0.98 \pm 0.05 \)).

| Compound | Solvent | \( \Phi_\Delta \) |
|----------|---------|------------------|
| **P2**   | Tol     | 0.67 ± 0.08      |
|          | PhCN    | 0.53 ± 0.07      |
| **P3**   | Tol     | 0.37 ± 0.08      |
|          | PhCN    | 0.43 ± 0.07      |
| **P4**   | Tol     | 0.76 ± 0.07      |
|          | PhCN    | 0.44 ± 0.06      |
15. 3D Fluorescence heat map

**Figure S6.** 3D fluorescence heat map of (a) P1, (b) P1F2Et, (c) P2, and (d) P2F2Et in toluene at room temperature.
**Figure S6.** 3D fluorescence heat map along with the absorption and emission spectra of fullerene hexakisadduct in toluene at room temperature.

**16. Literature**

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[2] M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der organischen Chemie*, Georg Thieme Verlag, 2005.