Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

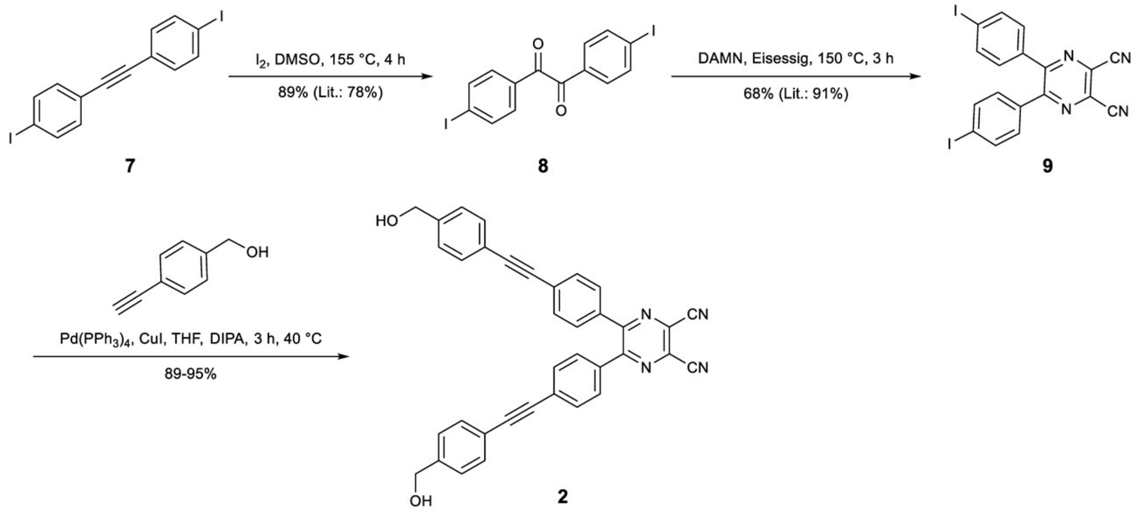
Schemes, Figures, Tables, and Experimental Details

N- versus p-doping of graphite: What drives its wet-chemical exfoliation?

Bingzhe Wang,[a] Verena Engelhardt,[b] Alexandra Roth,[a] Rüdiger Faust*[b] and Dirk M. Guldi*[a]

[a]*Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials, Friedrich-Alexander University Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany. E-mail: dirk.guldi@fau.de; Fax: +49 9131-8528307; Tel: +49 9131-8527340*

[b]*Institute for Chemistry and CINSaT – Center for Interdisciplinary Nanostructure Science and Technology, University of Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany. E-mail: r.faust@uni-kassel; Fax: +49 561 8044752; Tel: +49 561 8044750*



Scheme S1: Synthetic route to the precursor dinitrile **2**.

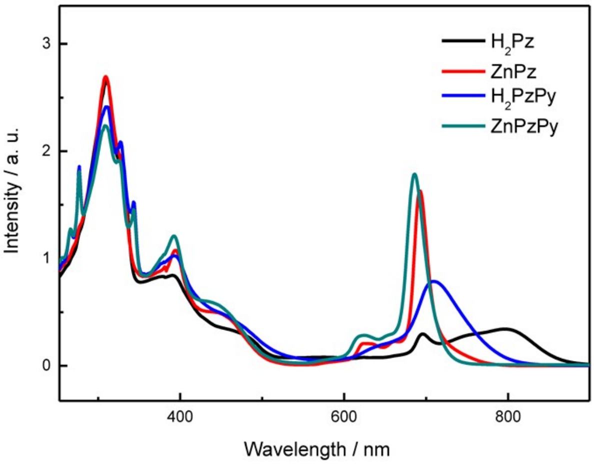


Figure S1: Room temperature absorption spectra of **H_2Pz** (black), **ZnPz** (red), **H_2PzPy** (blue), and **ZnPzPy** (green) measured in THF with a concentration of 1.1 x 10^{-5} M.

Table S1: Fluorescence quantum yields of **H$_2$Pz**, **ZnPz**, **H$_2$PzPy**, and **ZnPzPy** measured in THF upon 410 and 680 nm excitation using zinc phthalocyanine as reference[31] at room temperature.

Excitation wavelength	Emission Max	ZnPz	H$_2$Pz	ZnPzPy	H$_2$PzPy
410 nm	475 nm	0.049	0.10		
410 nm	700 nm	0.071	0.026	0.086	0.016
680 nm	700 nm	0.27	0.072	0.33	0.093

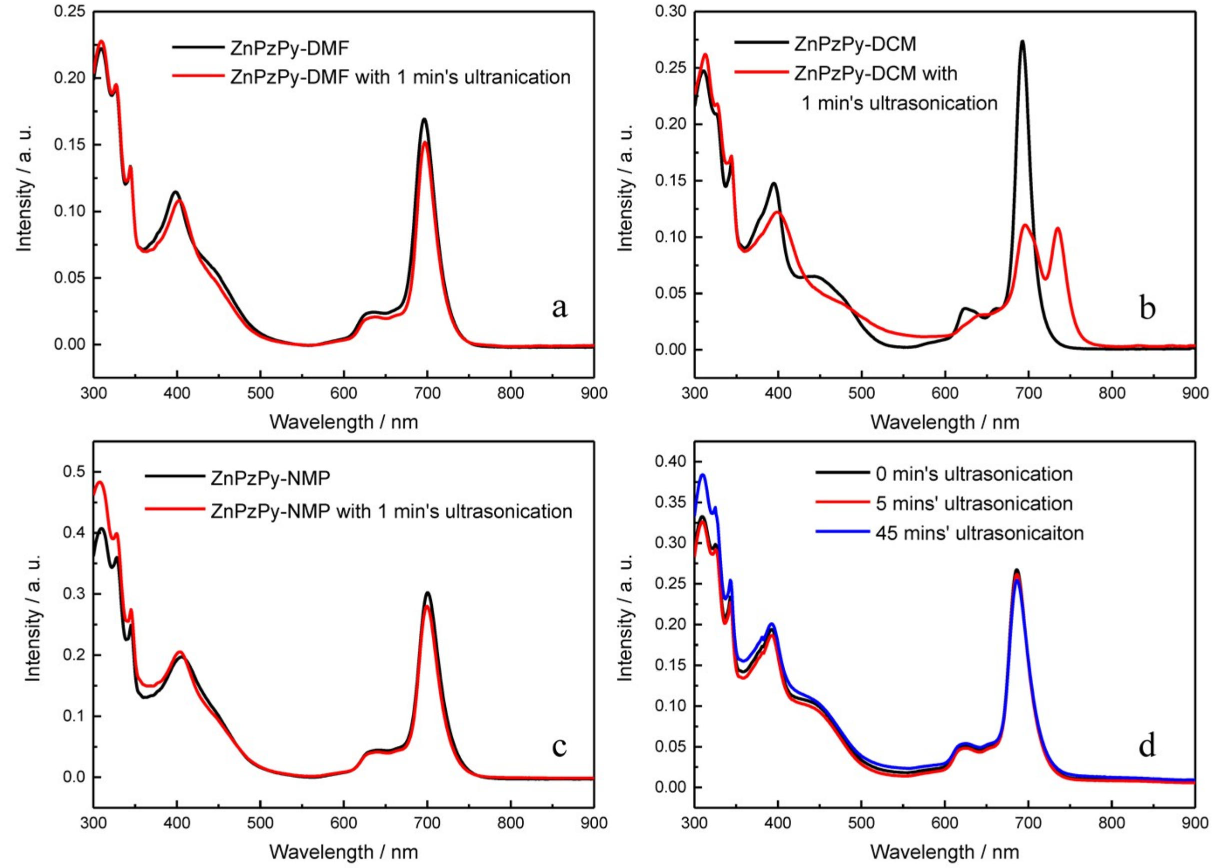


Figure S2: The comparison of absorption spectra of **ZnPzPy** in (a) DMF, (b) DCM, (c) NMP with and without 1 minute of ultrasonication, and (d) THF with 0, 5, and 45 minutes of ultrasonication – 37 KHz, 25℃.

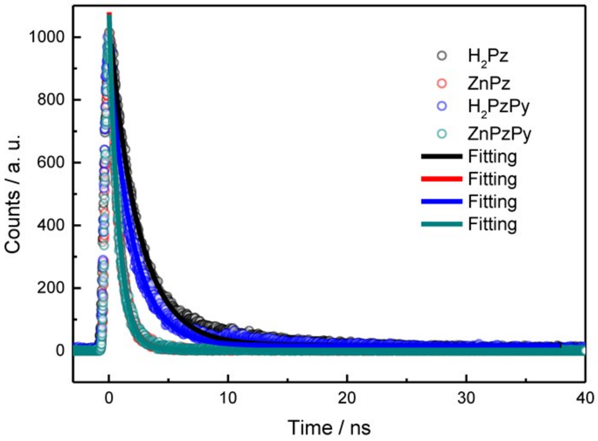


Figure S3: Fluorescence time profiles of $\mathbf{H_2Pz}$ (black), **ZnPz** (red), $\mathbf{H_2PzPy}$ (blue), and **ZnPzPy** (green) upon 410 nm excitation at their corresponding fluorescence maxima.

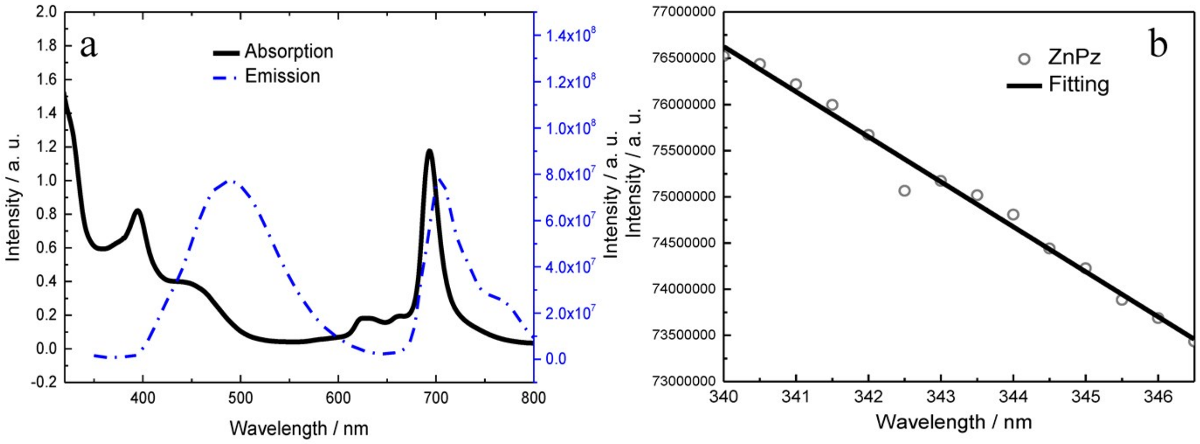


Figure S4: Room temperature absorption (black) and fluorescence (blue) spectra (a) of **ZnPz** with a concentration of 0.6 x 10^{-5} M in THF upon 344 nm excitation. Excitation spectrum (b) recorded at the 700 nm fluorescence.

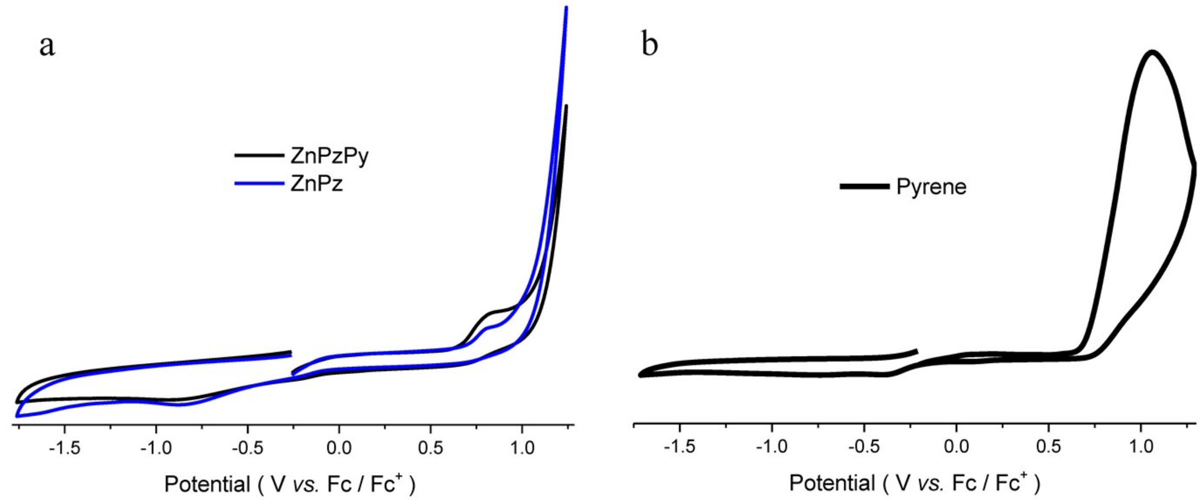


Figure S5: Cyclic voltammograms (a) of **ZnPzPy** (black), **ZnPz** (blue) and (b) of pyrene measured at room temperature in THF with 0.1 M TBAPF$_6$ as supporting electrolyte.

Table S3: Redox and oxidation potentials of pyrene, **ZnPz**, and **ZnPzPy** *vs*. Fc/Fc$^+$ in THF with 0.1 M TBAPF$_6$ as supporting electrolyte.

Compound	$E_{p,red}$	$E_{p,oxi}$
Pyrene	-0.37	1.06
ZnPz	-0.87	0.81
ZnPzPy	-0.91	0.83

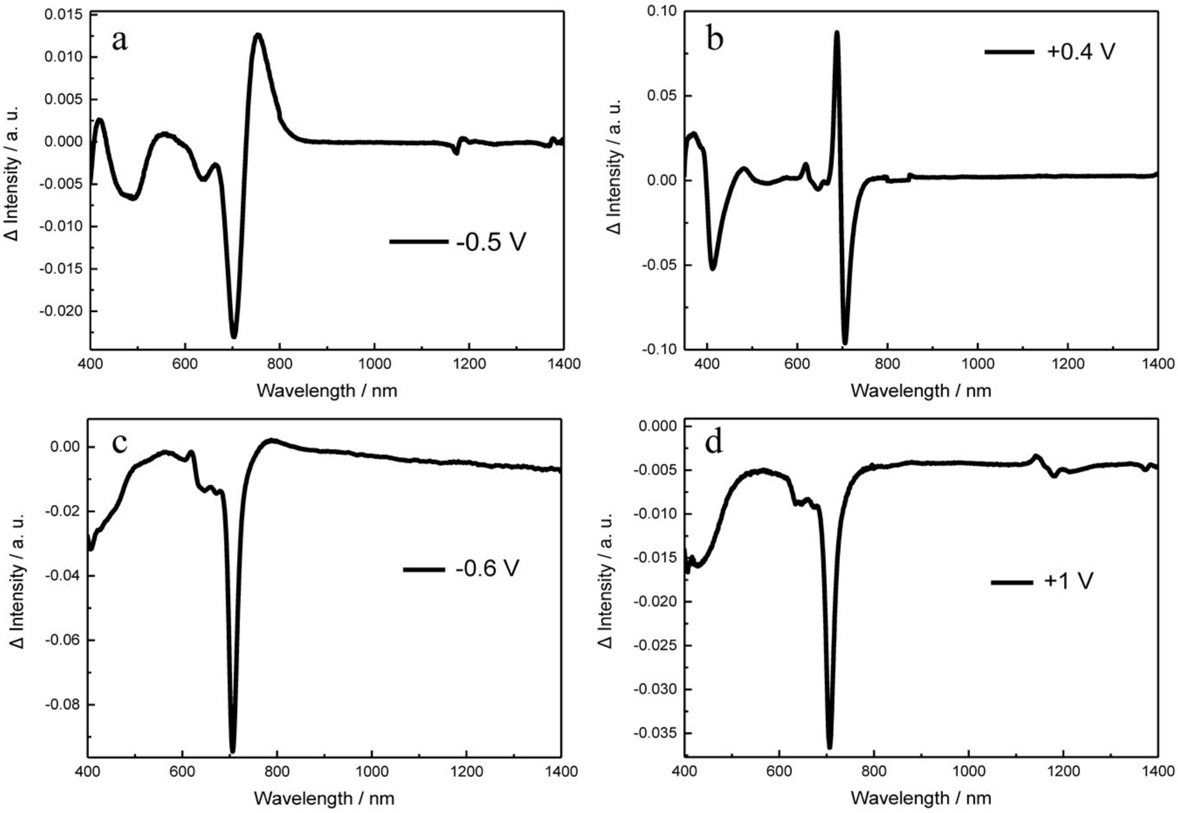


Figure S6: Differential absorption spectra (visible and near-infrared) obtained upon electrochemical reduction and oxidation of **ZnPzPy** and **ZnPz** in toluene-acetonitrile (4 : 1 v/v) with 0.1 M TBAPF$_6$ and applied potentials of -0.5 V (a), -0.6 V (c), +0.4 V (b), and +1.0 V (d) *vs.* Ag-wire.

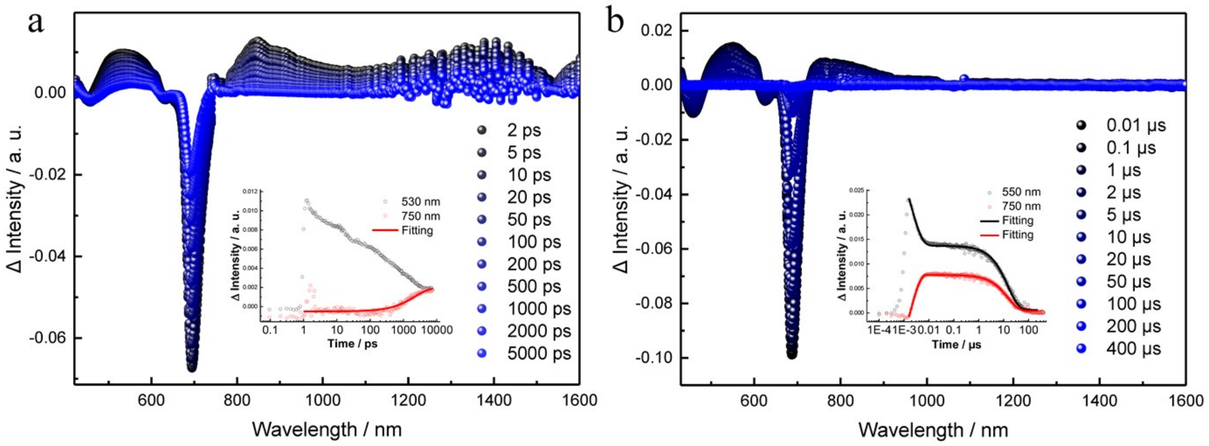


Figure S7: Differential absorption spectra obtained upon femtosecond pump probe experiments (258 nm and 500 nJ) of (a) **ZnPz** and (b) **ZnPzPy** in THF with time delays between 3 and 5000 ps at room temperature - for time delays see Figure legend. Inserts show the time-absorption profiles of the spectra shown at 550 and 750 nm to demonstrate the singlet and triplet excited state decays.

Table S4: Singlet and triplet excited state lifetimes as well as fluorescence lifetimes in THF at room temperature obtained from exponential fittings of the time profiles upon femtosecond / nanosecond pump probe experiments (258, 387 nm and 500 nJ) and time resolved fluroescence spectra under 410 nm excitation.

	Excitation wavelength	$S_1 \longrightarrow T_1$	$T_1 \longrightarrow S_0$	Fluorescence (410 nm)
H_2Pz	387 nm	4.12±0.18 ns	7.83±0.33 µs	3.1 ns
H_2PzPy	387 nm	1.01±0.12 ns	3.79±0.05 µs	2.3 ns
ZnPz	387 nm	2.22±0.03 ns	2.59±0.03 µs	1.7 ns
	258 nm	0.81±0.07 ns		
ZnPzPy	387 nm	2.04±0.07 ns	15.02±0.19 µs	1.5 ns
	258 nm	1.66±0.04 ns		

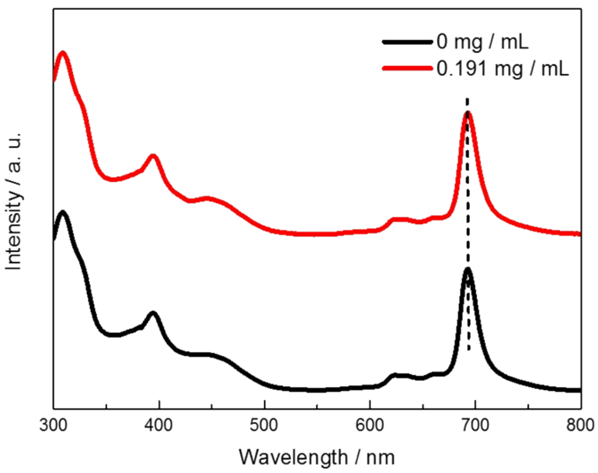


Figure S8: Room temperature absorption spectra of the **ZnPz-G** hybrids prepared after 2 minutes of ultrasonication with graphene concentrations of 0 (black) and 0.191 (red) mg / mL.

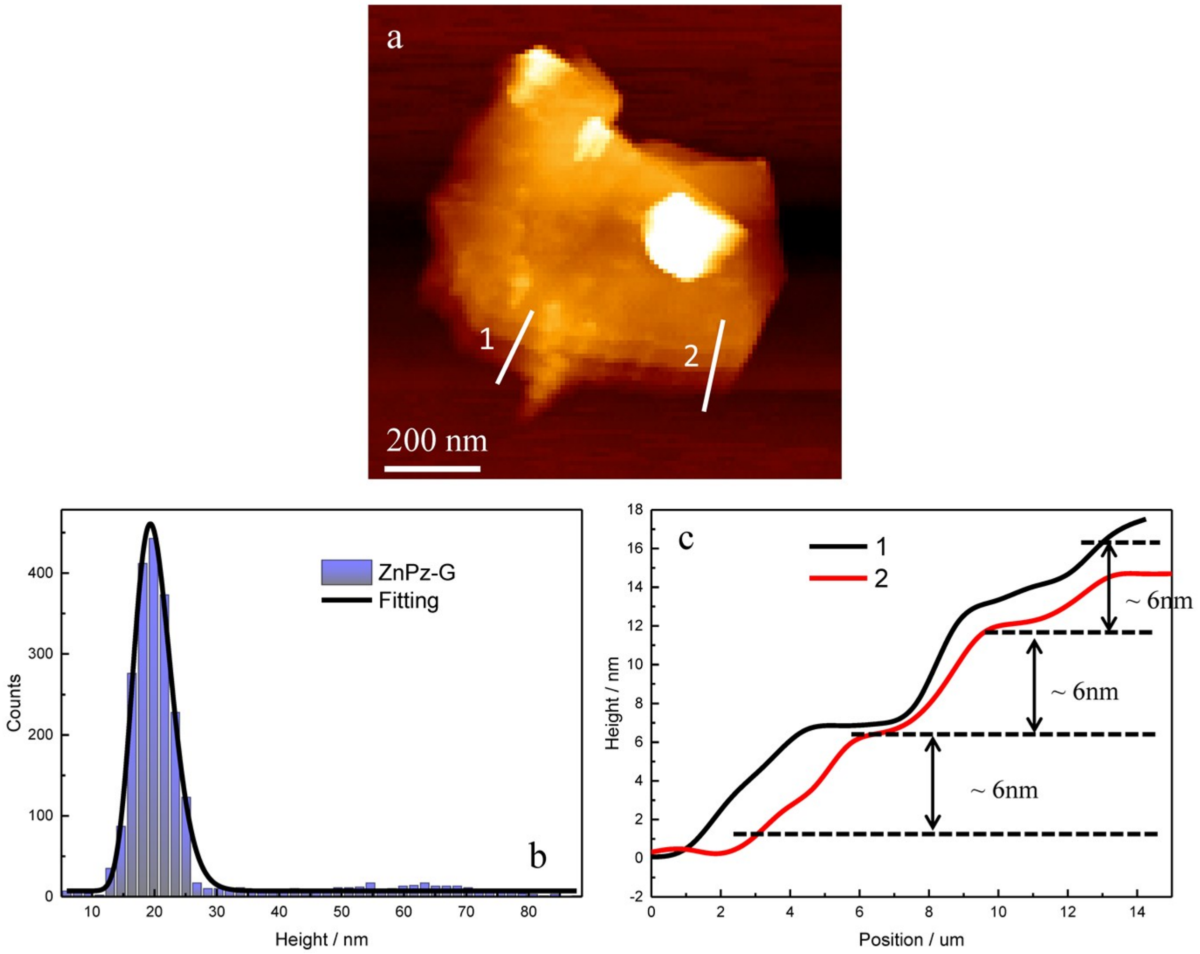


Figure S9: AFM image (a) of **ZnPz-G** after 1 hour of ultrasonication. Height distribution (b) of graphite flakes. (c) Height profiles (c) at position 1 and 2 shown in a.

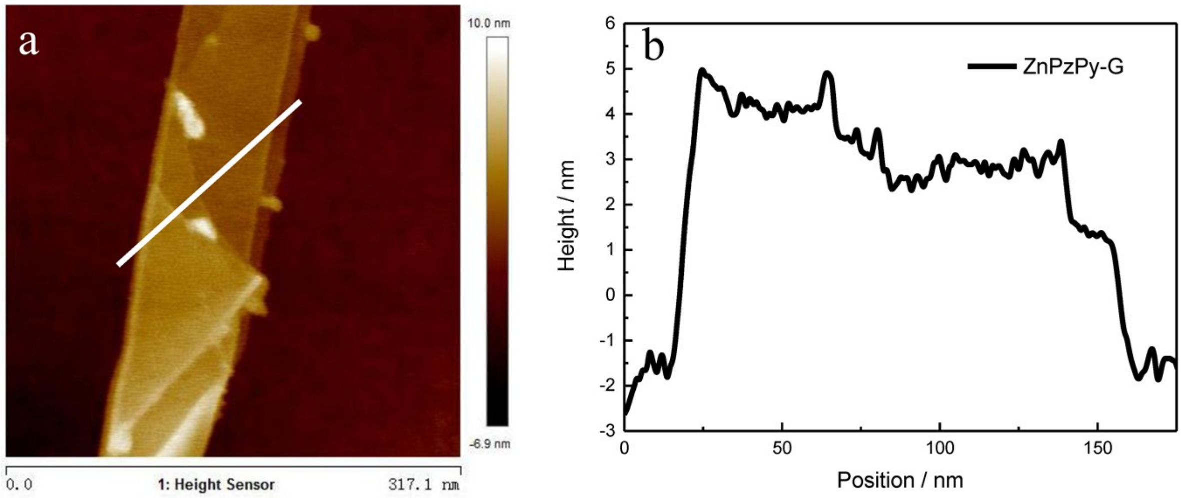


Figure S10: AFM image (a) of **ZnPzPy-G** which shows the folded structure and height profile (b) of the cross section shown in a.

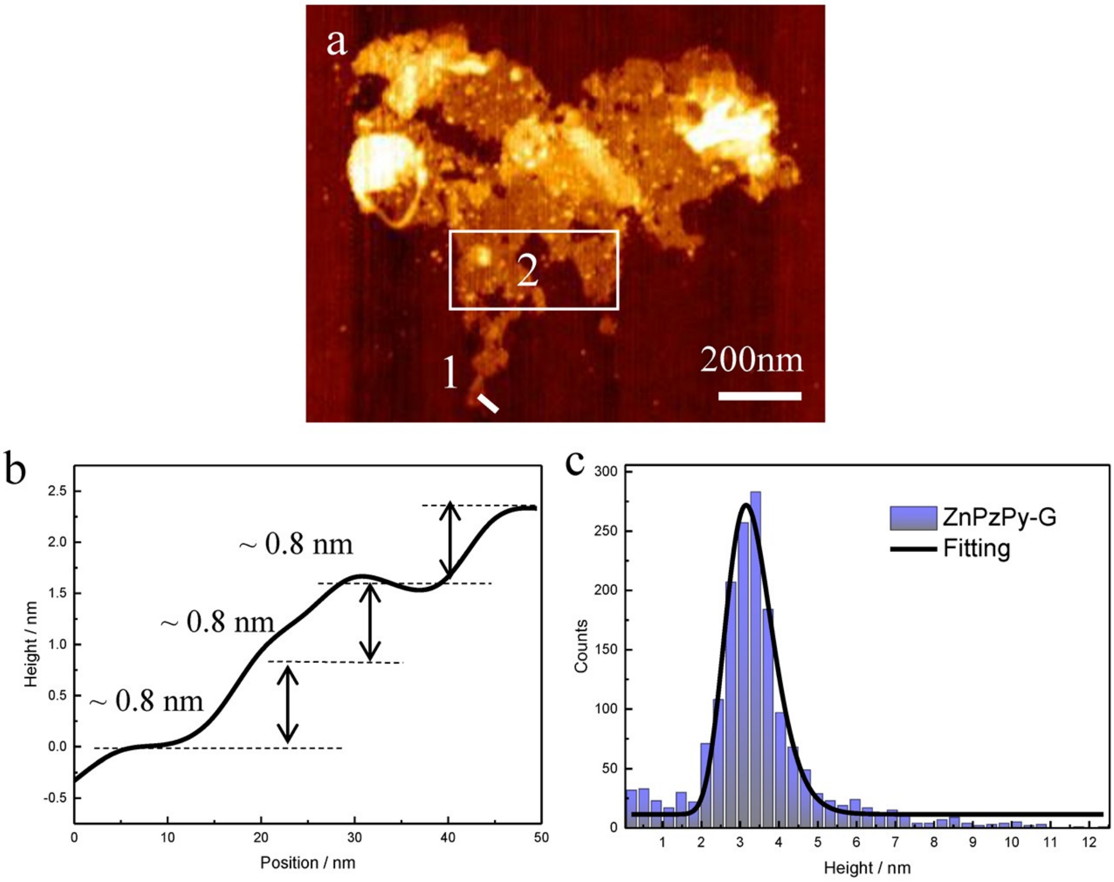


Figure S11: AFM image (a) of **ZnPzPy-G**, which shows the aggregation, height profile (b) of the cross section across line 1 shown in (a), which shows the layer by layer structure, and height distribution (c) of **ZnPzPy-G** of area 2 shown in (a).

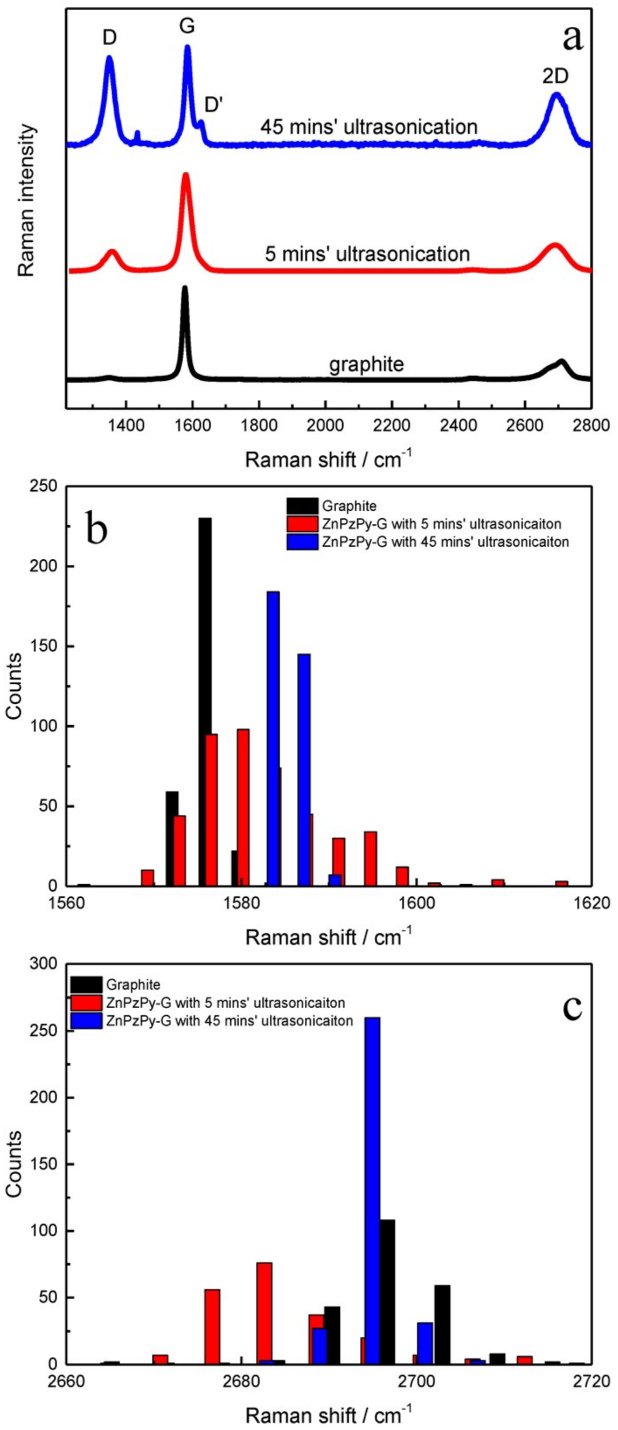


Figure S12: Raman spectra (a) of graphite (black) and **ZnPzPy-G** with either 5 (red) or 45 (blue) minutes of ultrasonication. Histograms with counts *vs.* G- (b) and 2D-mode (c) position of graphite (black), **ZnPzPy-G** with 5 minutes of ultrasonication (red), and **ZnPzPy-G** with 45 minutes of ultrasonication (blue). The sample was drop casted from **ZnPzPy-G** THF dispersion onto Si/SiO$_2$ wafers and photoexcited at 532 nm.

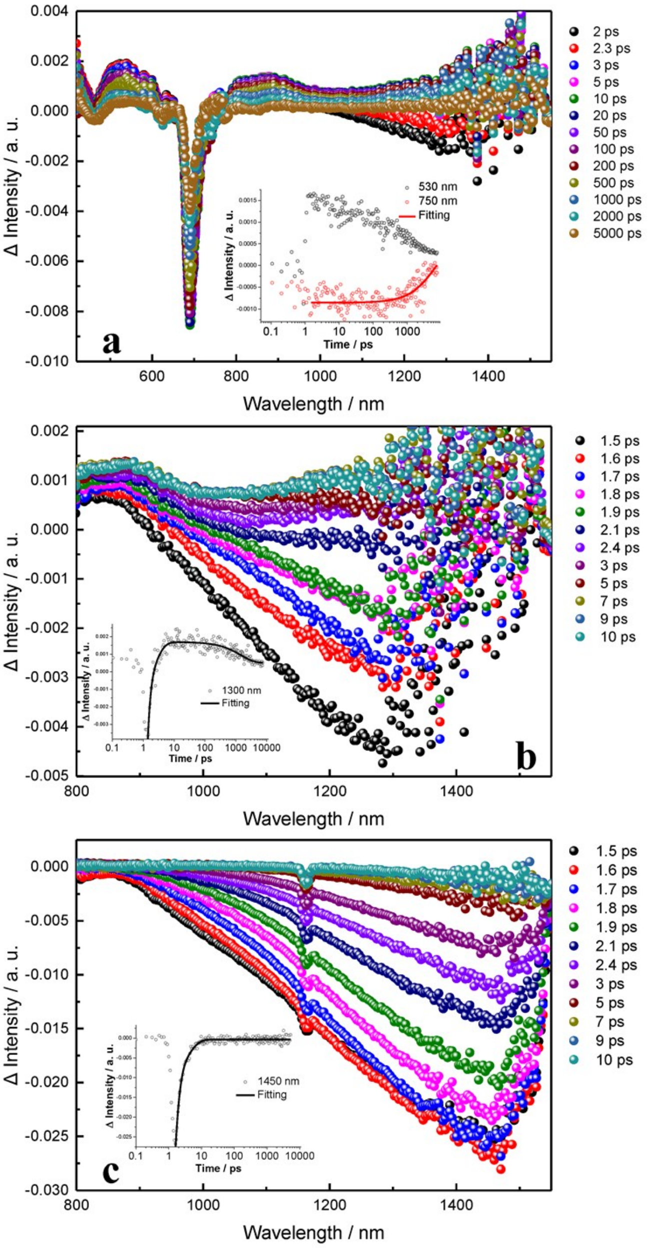


Figure S13: Differential absorption spectra (a) obtained upon femtosecond pump probe experiments (387 nm and 500 nJ) of **ZnPzPy-G** in THF with time delays between 2 and 5000 ps at room temperature - for time delays see Figure legend. Insert shows the time-absorption profiles of the spectra shown at 550 and 750 nm to demonstrate the singlet excited state decay. Differential absorption spectra (b) obtained upon femtosecond pump probe experiments (387 nm and 500 nJ) of **ZnPzPy-G** in THF with time delays between 1.5 and 10 ps at room temperature - for time delays see Figure legend. Insert shows the time-absorption profile of the spectra shown at 1300 nm to demonstrate the ground state bleaching of graphene with a lifetime of 1.6 ± 0.5 ps. Differential absorption spectra (c) obtained upon femtosecond pump probe experiments (387 nm and 500 nJ) of 45 minutes of ultrasonicated graphite in THF with time delays between 1.5 and 10 ps at room temperature - for time delays see Figure legend. Insert shows the time-absorption profile of the spectra shown at 1450 nm to demonstrate the ground state bleaching of graphene with a lifetime of 2.8 ± 0.5 ps.

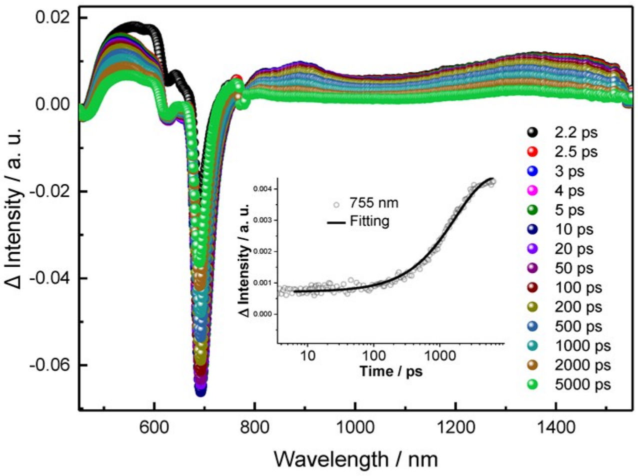


Figure S14: Differential absorption spectra obtained upon femtosecond pump probe experiments (258 nm and 500 nJ) of **ZnPzPy** in THF with time delays between 2 and 5000 ps at room temperature - for time delays see Figure legend. Inserts show the time-absorption profile of the spectra shown at 755 nm to demonstrate the singlet excited state decay with a lifetime of 1.66 ± 0.04 ns.

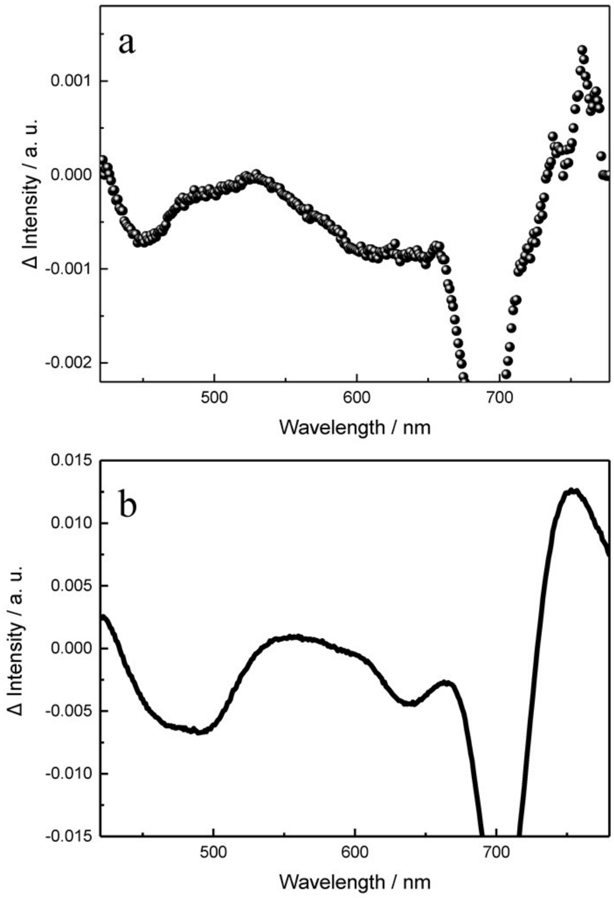


Figure S15: Differential spectrum (a) derived from transient absorption spectra of Figure 8 at 2.3 and 5.4 ps. The positive feature shows the absorption of the **ZnPzPy** radical anion. Differential absorption spectrum (b) obtained upon electrochemical reduction of **ZnPzPy** in toluene-acetonitrile (4 : 1 v/v) with 0.1 M TBAPF$_6$ and an applied potential of -0.5 V.

Experimental Details

Steady state UV/vis absorption spectroscopy

Steady state absorption spectra were obtained using either a Perkin Elmer Lambda2 or a Perkin-Elmer Lambda 40 UV/vis two-beam spectrophotometer using a slit width of 2 nm and a scan rate of 480 nm/ min. All spectra were recorded using a quartz glass cuvette of 10 x 10 mm.

Steady state emission spectroscopy

Steady state emission spectra were recorded using a Horiba Jobin Yvon FluoroMax-3 spectrometer using a slit width of 2 nm for excitation and emission and an integration time of 0.5 s. The studied were performed in a 10 x 10 mm quartz glass cuvette. Quantum yields were determined from corrected emission spectra following the standard methods using zinc phthalocyanine as standards.

Time resolved emission studies

Emission lifetimes were determined via time correlated single photon counting (TCSPC) on a Horiba Jobin Yvon Flourolog3 emission spectrometer with a Hamamatsu MCP photomultiplier (R3809U-58). All measurements were performed in a 10 x 10 mm quartz glass cuvette.

Electrochemistry

Electrochemical data were obtained by cyclic voltammetry using a convential single-compartment three-electrode cell arrangement in combination with a potentiostat “AUTOLABR, eco chemie”. As auxiliary and reference electrode Pt and silver wires were used; working electrode: glassy carbon. The measurements were carried out in argon saturated toluene/acetonitrile (4:1). Tetrabutylammonium hexafluorophosphate ($TBAPF_6$ = 0.1 M) was used as supporting electrolyte at room temperature. All potentials are referenced to ferrocene/ferrocenium with a scan rate of 0.05 V/s.

Spectroelectrochemistry

A Pt net was used as working electrode, a Pt sheet as counter electrode, and an Ag wire as quasi reference electrode. The potentials were applied with a METROHM PGSTAT 101 and the absorption spectra taken with a UV/nIR Cary5000 spectrometer.

Femtosecond transient absorption spectroscopy

Femtosecond transient absorption spectra were obtained with a Ti:sapphire laser system CPA-2101 (Clark-MXR, Inc.) in combination with a Helios TAPPS detection unit from Ultrafast Inc. The initial laser excitation wavelength is 775 nm with a pulse width of 150 fs. The used excitation wavelength was 387 nm, which was generated with a SHG crystal. For the generation of the white light a sapphire crystal of adequate thickness was used. The chirp-effect between 420 and 770 nm is approximately 350 fs. The detection was carried out with two CCD cameras, each for a specific measuring range. The spectral window is therefore 415 to 770 nm and 770 to 1600 nm. The delay line allows spectral acquisition up to time delays of 8000 ps. All samples were measured in a fused quartz glass cuvette with a thickness of 2 mm. Data was acquired with the software HELIOS Visible/nIR (Newport / Ultrafast Systems).

Raman spectroscopy

Raman measurements were carried out with a 35 mW helium-neon laser, REO with 532 nm excitation. The sample was prepared by drop casting a dispersion of the materials on a Si/SiO_2 wafer.

Atomic force microscopy

AFM images of Figure S9 and S11 were obtained with a NanoWizard® 4 NanoScience AFM, JPK in tapping mode. Figure 6 and S10 were obtained with a "Bruker Dimension FastScan" system. The samples were prepared by drop coating a dispersion of the materials on a Si/SiO_2 wafer.

Transmission electron microscopy

Sample preparation was performed by drop casting and drying the hybrids on lacey carbon coated copper grids. Bright-field TEM images were recorded with an 80 kV EM 900 from Carl Zeiss AG.

NMR spectroscopy

NMR spectra were recorded on Varian MR-400 or Varian 500 VNMRS instruments. ^{1}H NMR spectra were referenced to the residual solvent peaks at $\delta = 7.26$ ($CDCl_3$) and 3.58 (THF-d_8). ^{13}C NMR spectra were referenced to the solvent peaks at $\delta = 77.16$ ($CDCl_3$) and 25.31 ppm (THF-d_8).

Mass spectrometry

Mass spectra were recorded with a Finnigan LCQ Deca (ESI and APCI ionisation). MALDI-TOF mass spectrometry was either carried out on a Bruker Biflex IV or UltraFlex MALDI-TOF mass spectrometer with a N2-Laser (337 nm and 3 ns pulse length). High-resolution mass spectrometry was carried out on a Bruker microTOF equipped with an ApolloTM ion funnel. Elemental analyses were carried out with a HEKAtech Euro EA-CHNS analyzer.

Melting Point

Melting points were determined with a BÜCHI melting point M-565 hot stage and are uncorrected.

Chromatography

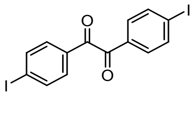
Flash column chromatography was executed on Machery-Nagel silica gel (230–400 mesh).

Materials

Natural graphite was purchased from Graphit Kropfmühl AG. All other reagents were purchased from commercial suppliers and used, unless otherwise noted, without further purification. 4,4’-Diiodotolane (**7**) and (4-ethynylphenyl)methanol were prepared according to literature procedures, cited in the text. Water and/or oxide sensitive reactions were carried out under an atmosphere of dry argon with oven-dried glassware. Anhydrous THF was freshly distilled from sodium benzophenone ketyl; anhydrous diisopropylamine (DIPA) and dichloromethane (DCM) were distilled from CaH_2.

Syntheses

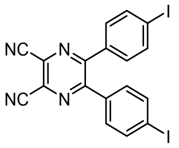
4,4’-Diiodobenzil (8)



A suspension of 1,2-bis(4-iodophenyl)ethyne (**7**)[1] (0.81 g, 1.89 mmol) and iodine (0.24 g, 0.95 mmol) in DMSO (8 mL) was heated at 155 °C for 4 h. The reaction mixture was cooled to room temperature and treated with half saturated aqueous solution of $Na_2S_2O_3$ (10 mL). The pale yellow precipitate was filtered off and washed with water to give **8** (0.78 g, 1.69 mmol) in 89% yield (Lit.:[1] 78%).

m.p. 256 °C (Lit.:[1] 255–260 °C); **^{1}H-NMR** (400 MHz; $CDCl_3$, 25°C, TMS): $\delta = 7.90$ (d, $^3J_{HH} = 8.6$ Hz, 4H, $H_{arom.}$), 7.66 ppm (d, $^3J_{HH} = 8.6$ Hz, 4H, $H_{arom.}$); **^{13}C-NMR** (101 MHz; $CDCl_3$, 25°C, TMS): $\delta = 193.1$ ($C_{carbonyl.}$), 138.6, 132.2, 131.2, 104.1 ppm.

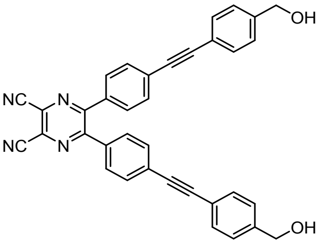
5,6-Bis(4-iodophenyl)pyrazine-2,3-dicarbonitrile (9)



A suspension of 4,4'-diiodobenzil (**8**) (0.46 g, 0.98 mmol) and diaminomaleonitrile (DAMN) (0.32 g, 2.95 mmol) in acetic acid (10 mL) was heated in a sealed pressure tube at 150 °C for 3 h. The resulting solution was cooled to room temperature and diluted with DCM (20 mL) and water (30 mL). The water layer was extracted with DCM (3 x 30 mL). The combined organic layers were washed with water (3 x 30 mL) and brine (30 mL), dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. The crude product was further purified by flash column chromatography (hexane/DCM - 1:1) to give **9** (0.36 g, 0.67 mmol) as yellow solid (yield 68%, Lit.:[2] 91%).

m.p. 193 °C (Lit.:[2] 183–187 °C); **^{1}H-NMR** (400 MHz; $CDCl_3$, 25°C, TMS): $\delta = 7.76$ (d, $^3J_{HH} = 8.5$ Hz, 4H, $H_{arom.}$), 7.27 ppm (d, $^3J_{HH} = 8.5$ Hz, 4H, $H_{arom.}$); **^{13}C-NMR** (101 MHz; $CDCl_3$, 25°C, TMS): $\delta = 154.3$, 138.5, 134.4, 131.3, 130.1, 113.0, 99.0 ($C_{C\text{-}I}$) ppm.

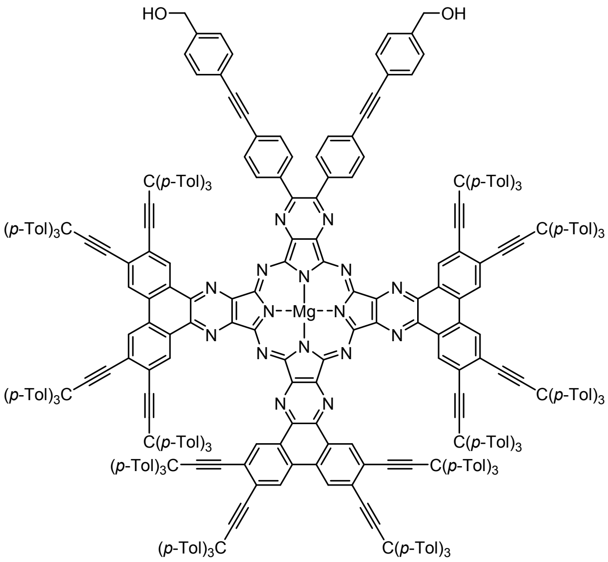
5,6-Bis{4-([4-(hydroxymethyl)phenyl]ethynyl)phenyl}pyrazine-2,3-dicarbonitrile (2)



5,6-Bis(4-iodophenyl)pyrazine-2,3-dicarbonitrile (**9**) (100.0 mg, 187 µmol), (4-ethynylphenyl)methanol[3] (54.0 mg, 412 µmol), CuI (4.3 mg, 22 µmol, 12 mol%) and $Pd(PPh_3)_4$ (13.0 mg, 11 µmol, 6 mol%) were dissolved in anhydrous THF (5 mL) and anhydrous diisopropylamine (2.5 mL). The solution was stirred for 3 h at 40 °C. Ethyl acetate (30 mL) was added and the organic phase was washed with saturated aqueous NH_4Cl-solution, water and brine (each 30 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. After purification by flash column chromatography (DCM/MeOH - 20:1) dinitrile **2** (96.0 mg, 177 µmol) was obtained as yellow solid (yield 95%).

Decomp. 221–223 °C; **^{1}H-NMR** (400 MHz; THF-d$_8$, 25°C, TMS): δ = 7.60 (d, $^3J_{HH}$ = 8.2 Hz, 4H, H$_{arom.}$), 7.53 (d, $^3J_{HH}$ = 8.3 Hz, 4H, H$_{arom.}$), 7.46 (d, $^3J_{HH}$ = 8.0 Hz, 4H, H$_{arom.}$), 7.35 (d, $^3J_{HH}$ = 8.0 Hz, 4H, H$_{arom.}$), 4.58 (d, $^3J_{HH}$ = 5.8 Hz, 4H, H$_{methylene}$), 4.27 ppm (t, $^3J_{HH}$ = 5.8 Hz, 2H, H$_{hydroxyl}$); **^{13}C-NMR** (101 MHz; THF-d$_8$, 25°C, TMS): δ = 155.1, 145.1, 136.3, 132.5, 132.2, 131.1, 130.9, 127.1, 127.1, 121.8, 114.4, 93.2 (C$_{ethynyl}$), 88.8 (C$_{ethynyl}$), 64.3 (C$_{methylene}$) ppm; **HRMS** (ESI): *m/z* [M+Na]$^+$ calcd for $[C_{36}H_{22}N_4NaO_2]^+$ = 565.1635; found 565.1630; **IR** (neat, diamond ATR): $\tilde{\nu}$ =, 3053, 2922 und 2866, 1915, 1600, 1508, 1371, 1017, 832 cm^{-1}; **UV/Vis** (DCM): λ_{max} (ε [10^4 M^{-1}cm^{-1}]) = 278 (3.93), 353 (3.55), 377 (3.56) nm; **Elemental Anal.**: Found: C 78.74, H 4.56, N 9.79. calcd for $C_{36}H_{22}N_4O_2$ + ⅓ MeOH[1]: C 78.88, H 4.25, N 10.13%.

Porphyrazine 4



Magnesium turnings (93 mg, 3.82 mmol) and a small bead of iodine were stirred in anhydrous *n*-butanol (35 mL) at 160 °C for 2.5 h under an argon atmosphere. To increase the concentration of the magnesium butanolate solution 10 mL of the solvent were removed via distillation. Dinitrile **3**[4] (650 mg, 0.429 mmol) and dinitrile **2** (26 mg, 0.048 mmol) were dissolved together in 2–3 mL of hot o-DCB and added to the refluxing solution of magnesium butanolate. The reaction mixture was stirred for another 2 h at 160 °C. After cooling to room temperature the green reaction mixture was poured into methanol saturated with NH_4Cl. The precipitate was filtered, washed several times with water (3x25 mL) and methanol

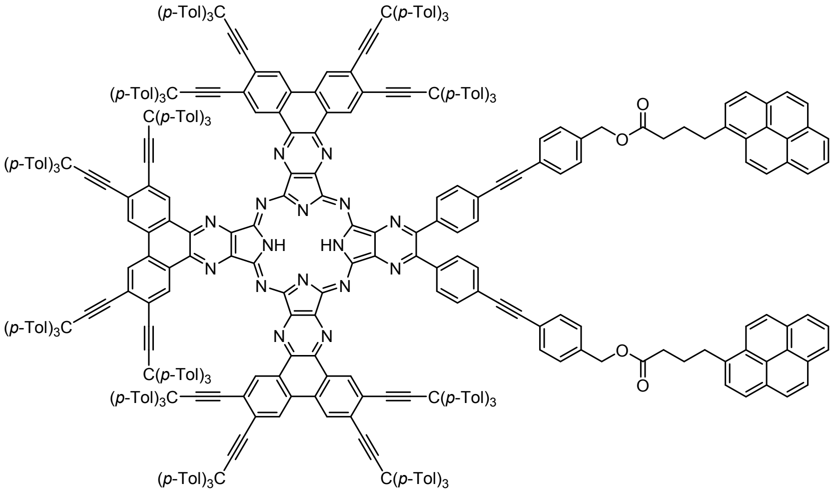
---

[1] The sample was contaminated with MeOH. This impurity was quantified in the ^{1}H-NMR-spectrum to a ratio of 3:1 (compound **2** : MeOH).

(3x25 mL) and dried *in vacuo*. The A_3B-derivative **4** (136 mg, 0.027 mmol) was separated by column chromatography (toluene/THF - 5:1) from the crude and obtained as dark green solid (yield 56%).

^{1}H-NMR (400 MHz; THF-d_8, 25°C, TMS): δ = 10.35 (m), 10.25 (s), 10.17 (s) (overall 6H, $H_{phenanthrene}$); 9.14–9.07 (m, 6H, $H_{phenanthrene}$), 8.08 (d, $^3J_{HH}$ = 7.9 Hz, 4H, $H_{arom.-phenyl}$), 7.54 (d, $^3J_{HH}$ = 8.0 Hz, 4H, $H_{arom.-phenyl}$), 7.50 (d, $^3J_{HH}$ = 8.2 Hz, 8H, $H_{arom.-tolyl}$), 7.42 (d, $^3J_{HH}$ = 7.7 Hz 8H, $H_{arom.-phenyl}$), 7.30 und 7.26 (2 d, $^3J_{HH}$ = 8.1, 8.2 Hz, 36H, $H_{arom.-tolyl}$), 7.20–7.12 (m, 28H, $H_{arom.-tolyl}$), 7.07 (d, $^3J_{HH}$ = 7.8 Hz, 12H, $H_{arom.-tolyl}$), 7.01 (d, $^3J_{HH}$ = 8.1 Hz, 12H, $H_{arom.-tolyl}$), 6.96–6.91 (m, 24H, $H_{arom.-tolyl}$), 6.87–6.84 (m, 24H, $H_{arom.-tolyl}$), 4.64 (d, $^3J_{HH}$ = 5.8 Hz, 4H, $H_{methylene}$), 4.30 (t, $^3J_{HH}$ = 5.8 Hz, 2H, $H_{hydroxyl}$), 2.29–2.21 (m, 72H, H_{methyl}), 2.07–1.93 ppm (m, 36H, H_{methyl}); **^{13}C-NMR** (101 MHz; THF-d_8, 25°C, TMS): δ = 151.1, 150.9, 144.6, 143.7, 143.5, 143.5, 143.4, 142.5, 140.4, 136.9, 136.9, 136.8, 136.6, 132.6, 132.2, 131.7, 131.6, 131.4, 131.2, 131.2, 130.2, 130.0, 130.0, 130.0, 129.5, 129.4, 127.2, 127.1, 126.8, 126.6, 124.9, 122.5, 109.1, 103.6, 103.1, 102.9, 91.7, 89.7, 85.2, 84.6, 64.5, 57.0, 56.8, 56.8, 56.7, 21.2, 21.1, 21.1, 21.0, 20.9 ppm; **MALDI-TOF MS** (DCTB, +): *m/z* $[M]^+$ calcd for $[C_{378}H_{286}MgN_{16}O_2]^+$ = 5108.9 average mass, found 5108.7; **IR** (neat, diamond ATR): $\tilde{\nu}$ = 3319 (br), 3021, 2917 und 2859, 2209, 1502, 1448, 1350, 1254, 1181, 1101, 1019, 808, 778 cm^{-1}; **UV/Vis** (DCM): λ_{max} (ε [10^5 M^{-1}cm^{-1}]) = 309 (2.70), 395 (1.69), 633 (0.40), 662 (S; 0.43), 697 (2.99) nm.

Porphyrazine 6 (H_2PzPy)

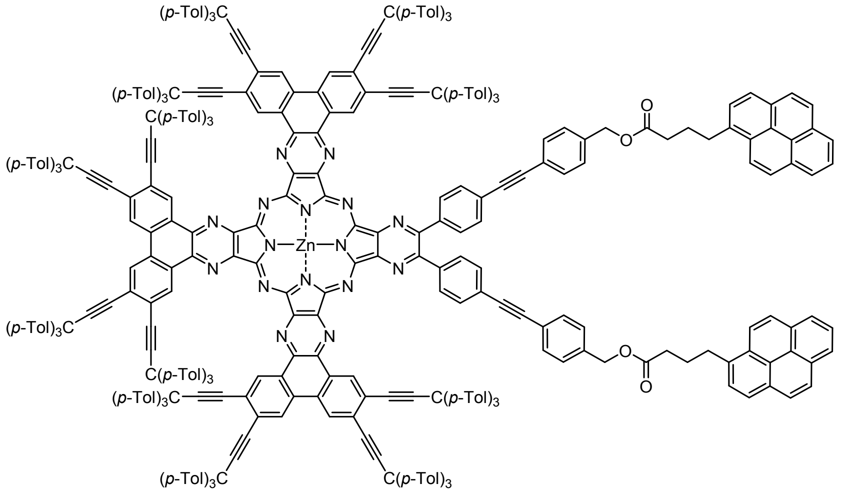


Pz **4** (100.0 mg, 0.020 mmol), 1-pyrenebutyric acid (12.0 mg, 0.042 mmol), DMAP (5.0 mg, 0.041 mmol) and DCC (8.5 mg, 0.041 mmol) were suspended in anhydrous DCM (8 mL) and stirred for 24 h at room temperature (TLC: toluene/THF 5:1). Another 5.0 mg DMAP und 8.5 mg DCC were added and the reaction mixture stirred for 24 h. To finally achieve complete conversion, the same amounts of DMAP and DCC as well as 1-pyrenebutyric acid (8.0 mg, 0.027 mmol) were added. After 3.5 h the reaction was complete. The solvent was removed *in vacuo* and the resulting reaction crude was purified by flash column chromatography (toluene/THF - 5:1).

The product was dissolved in THF (40 mL) and treated with 6*N* HCl_{aq} (0.03 mL, 0.180 mmol) to remove the central coordinated magnesium cation. The resulting solution was stirred for 2 h at room temperature. The volume of the solvent was reduced to 20 mL, the residue diluted with ethyl acetate (30 mL) and washed with water (2 x 30 mL). The organic layer was separated and the solvent removed *in vacuo*. The residue was purified by flash column chromatography (toluene/THF - 20:1). After trituration with methanol and water **6** (74.3 mg, 0.013 mmol) was obtained as olive-green solid (yield 65%).

^{1}H-NMR (500 MHz; THF-d_8, 25°C, TMS): δ = 10.27 (s, 3H, $H_{phenanthrene}$), 10.20 (s, 3H, $H_{phenanthrene}$), 9.09 (m, 6H, $H_{phenanthrene}$), 8.22 (d, $^3J_{HH} = 8.5$ Hz, 2H, H_{pyrene}), 8.11 (d, $^3J_{HH} = 7.0$ Hz, 4H, H_{pyrene}), 7.98–7.93 (m, 6H, H_{pyrene}), 7.83–7.72 (m, $^3J_{HH} = 7.8$ Hz, 10H, $H_{pyrene+arom.\text{-}phenyl}$), 7.56 (d, $^3J_{HH} = 6.8$ Hz, 4H, $H_{arom.\text{-}phenyl}$), 7.48 (d, $^3J_{HH} = 7.5$ Hz, 12H, $H_{arom.\text{-}tolyl}$), 7.43 (m, 8H, $H_{arom.\text{-}phenyl}$), 7.30–7.23 (m, 36H, $H_{arom.\text{-}tolyl}$), 7.18–7.12 (m, 24H, $H_{arom.\text{-}tolyl}$), 7.06 (d, $^3J_{HH} = 8.2$ Hz, 12H, $H_{arom.\text{-}tolyl}$), 7.00 (d, $^3J_{HH} = 8.0$ Hz, 12H, $H_{arom.\text{-}tolyl}$), 6.94–6.90 (m, 24H, $H_{arom.\text{-}tolyl}$), 6.85 (m, 24H, $H_{arom.\text{-}tolyl}$), 5.15 (s, 4H, $H_{methylene}$), 3.33 (br. m, 4H, $H_{methylene}$), 2.46 (br. s, 4H, $H_{methylene}$), 2.30–2.18 (m, 72H, H_{methyl}), 2.08–1.96 ppm (m, 40H, $H_{methylene.+methyl}$); **MALDI-TOF MS** (DCTB, +): *m/z* $[M]^+$ calcd for $[C_{418}H_{316}N_{16}O_4]^+ = 5627.2$ average mass, found 5626.7; **UV/Vis** (DCM): λ_{max} (ε [10^5 $M^{-1}cm^{-1}$]) 267 (1.51), 277 (2.20), 312 (2.74), 327 (2.24), 344 (1.88), 395 (1.22), 464 (br, 0.57), 497 (S, 0.52), 635 (0.35), 691 (S, 1.30), 704 (1.87) nm.

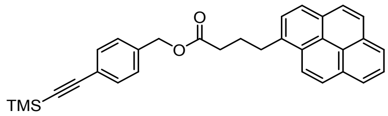
Porphyrazine 1 (ZnPzPy)



$Zn(OAc)_2$ (5 mg, 22.8 µmol) was added to a solution of Pz **6** (25 mg, 4.4 µmol) in THF (10 mL). The solution was stirred for 3 h at room temperature. After reducing the solvent to the half, the residue was diluted with ethyl acetate (30 mL). The organic phase was washed with water (2 x 30 mL) and brine (30 mL). The organic layer was dried over $NaSO_4$, filtered and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography (toluene/THF - 5:1) to give Pz **1** (23 mg, 4.0 µmol) as green solid (yield 91%).

^{1}H-NMR (400 MHz; THF-d_8, 25°C, TMS): δ =10.35 (m), 10.24 (s), 10.16 (s) (overall 6H, $\text{H}_{\text{phenanthrene}}$); 9.11 (m, 6H, $\text{H}_{\text{phenanthrene}}$), 8.37 (d, $^{3}J_{\text{HH}}$ = 9.4 Hz, 2H, H_{pyrene}), 8.16–8.07 (m, 12H, $\text{H}_{\text{pyrene+arom.-phenyl}}$), 8.00 (s, 4H, H_{pyrene}), 7.94 (m, 2H, H_{pyrene}), 7.88 (d, $^{3}J_{\text{HH}}$ = 7.6 Hz, 2H, H_{pyrene}), 7.57 (d, $^{3}J_{\text{HH}}$ = 7.8 Hz, 4H, $\text{H}_{\text{arom.-phenyl}}$), 7.49 (d, $^{3}J_{\text{HH}}$ = 8.0 Hz, 12H, $\text{H}_{\text{arom.-tolyl}}$), 7.45 (d, $^{3}J_{\text{HH}}$ = 8.2 Hz, 4H, $\text{H}_{\text{arom.-phenyl}}$), 7.42 (d, $^{3}J_{\text{HH}}$ = 8.2 Hz, 4H, $\text{H}_{\text{arom.-phenyl}}$), 7.30–7.22 (m, 36H, $\text{H}_{\text{arom.-tolyl}}$), 7.20–7.12 (m, 24H, $\text{H}_{\text{arom.-tolyl}}$), 7.05 (d, $^{3}J_{\text{HH}}$ = 7.7 Hz, 12H, $\text{H}_{\text{arom.-tolyl}}$), 7.00 (d, $^{3}J_{\text{HH}}$ = 8.0 Hz, 12H, $\text{H}_{\text{arom.-tolyl}}$), 6.96–6.89 (m, 24H, $\text{H}_{\text{arom.-tolyl}}$), 6.85 (m, 24H, $\text{H}_{\text{arom.-tolyl}}$), 5.20 (s, 4H, $\text{H}_{\text{methylene}}$), 3.43 (t, $^{3}J_{\text{HH}}$ = 7.7 Hz, 4H, $\text{H}_{\text{methylene}}$), 2.55 (t, $^{3}J_{\text{HH}}$ = 7.3 Hz, 4H, $\text{H}_{\text{methylene}}$), 2.29–2.18 (m, 72H, H_{methyl}), 2.08–1.89 ppm (m, 40H, $\text{H}_{\text{methylene+methyl}}$); **MALDI-TOF MS** (dithranol, +): *m/z* $[\text{M+H}]^+$ calcd for $[\text{C}_{418}\text{H}_{315}\text{N}_{16}\text{O}_4\text{Zn}]^+$ = 5691.6 average mass, found 5691.7; **UV/Vis** (DCM): $\lambda_{\max}$ (ε [10^5 M^{-1}cm^{-1}]) 267 (1.57), 277 (2.28), 312 (2.85), 326 (2.38), 344 (1.88), 395 (1.47), 449 (S, 0.64), 624 (0.37), 661 (S, 0.37), 692 (2.70) nm.

4-(1-Pyrenyl)butyric acid-{4-[(trimethylsilyl)ethynyl]phenyl}methylester (Pyrene-Ref.)



1-Pyrenebutyric acid (100 mg, 0.347 mmol), (4-ethynylphenyl)methanol[3] (72 mg, 0.352 mmol) and DMAP (11 mg, 0.090 mmol) were suspended in anhydrous DCM (30 mL). DCC (72 mg, 0.349 mmol) was added at room temperature and the reaction mixture was stirred over night (18 h). The solvent was removed *in vacuo* and the resulting reaction crude was purified by flash column chromatography (PE/EA - 10:1) to give the product (115 mg, 0.242 mmol) as colorless oil (yield 70%).

^{1}H-NMR (400 MHz; CDCl$_3$, 25°C, TMS): δ = 8.25 (d, $^{3}J_{\text{HH}}$ = 9.3 Hz, 1H, H_{pyrene}), 8.17 (d, $^{3}J_{\text{HH}}$ = 7.5 Hz, 1H, H_{pyrene}), 8.16 (d, $^{3}J_{\text{HH}}$ = 7.8 Hz, 1H, H_{pyrene}), 8.10 (d, $^{3}J_{\text{HH}}$ = 7.8 Hz, 1H, H_{pyrene}), 8.07 (d, $^{3}J_{\text{HH}}$ = 9.3 Hz, 1H, H_{pyrene}), 8.03 (m, 2H, H_{pyrene}), 7.99 (dd, $^{3}J_{\text{HH}}$ = 7.6 Hz, 7.6 Hz, 1H, H_{pyrene}), 7.83 (d, $^{3}J_{\text{HH}}$ = 7.8 Hz, 1H, H_{pyrene}), 7.45 (d, $^{3}J_{\text{HH}}$ = 8.3 Hz, 2H, H_{phenyl}), 7.28 (d, $^{3}J_{\text{HH}}$ = 8.1 Hz, 2H, H_{phenyl}), 5.11 (s, 2H, $\text{H}_{\text{methylene}}$), 3.39 (t, $^{3}J_{\text{HH}}$ = 7.7 Hz, 2H, $\text{H}_{\text{methylene}}$), 2.51 (t, $^{3}J_{\text{HH}}$ = 7.2 Hz, 2H, $\text{H}_{\text{methylene}}$), 2.21 (quin, $^{3}J_{\text{HH}}$ = 7.5 Hz, 2H, $\text{H}_{\text{methylene}}$), 0.26 ppm (s, 9H, H_{TMS}); **^{1}H-NMR** (400 MHz; THF-d_8, 25°C, TMS): δ 8.32 (d, $^{3}J_{\text{HH}}$ = 9.3 Hz, 1H, H_{pyrene}), 8.15 (d, $^{3}J_{\text{HH}}$ = 7.6 Hz, 1H, H_{pyrene}), 8.14 (d, $^{3}J_{\text{HH}}$ = 7.0 Hz, 1H, H_{pyrene}), 8.08 (d, $^{3}J_{\text{HH}}$ = 7.6 Hz, 1H, H_{pyrene}), 8.06 (d, $^{3}J_{\text{HH}}$ = 9.1 Hz, 1H, H_{pyrene}), 8.00 (m, 2H, H_{pyrene}), 7.95 (dd, $^{3}J_{\text{HH}}$ = 7.6 Hz, 7.6 Hz, 1H, H_{pyrene}), 7.83 (d, $^{3}J_{\text{HH}}$ = 7.8 Hz, 1H, H_{pyrene}), 7.42 (d, $^{3}J_{\text{HH}}$ = 8.1 Hz, 2H, H_{phenyl}), 7.33 (d, $^{3}J_{\text{HH}}$ = 8.1 Hz, 2H, H_{phenyl}), 5.12 (s, 2H, $\text{H}_{\text{methylene}}$), 3.37 (t, $^{3}J_{\text{HH}}$ = 7.8 Hz, 2H, $\text{H}_{\text{methylene}}$), 2.48 (t, $^{3}J_{\text{HH}}$ = 7.1 Hz, 2H, $\text{H}_{\text{methylene}}$), 2.15 (quin, $^{3}J_{\text{HH}}$ = 7.6 Hz, 2H, $\text{H}_{\text{methylene}}$), 0.24 ppm (s, 9H, H_{TMS}); **^{13}C-NMR** (101 MHz; CDCl$_3$, 25°C, TMS): δ = 173.3 (C_{ester}), 136.4, 135.7, 132.3, 131.5, 131.0, 130.1, 128.9, 128.1, 128.1, 127.6, 127.6, 127.5, 126.9, 126.0, 125.2, 125.1, 125.1, 124.9, 123.4, 123.2, 104.8 ($\text{C}_{\text{ethynyl.}}$), 94.9 ($\text{C}_{\text{ethynyl.}}$), 65.9 ($\text{C}_{\text{methylene}}$), 34.0 ($\text{C}_{\text{methylene}}$), 32.8 ($\text{C}_{\text{methylene}}$), 26.9 ($\text{C}_{\text{methylene}}$), 0.1 ($\text{C}_{\text{TMS}}$) ppm; **^{13}C-NMR** (101 MHz; THF- d_8, 25°C, TMS):

δ = 173.1 (C_{ester}), 138.3, 136.9, 132.6, 132.4, 131.9, 131.0, 129.7, 128.8, 128.8, 128.2, 128.2, 128.1, 127.4, 126.6, 126.0, 125.9, 125.6, 125.5, 124.2, 123.8, 105.8 ($C_{ethynyl}$), 94.6 ($C_{ethynyl.}$), 66.0 ($C_{methylene}$), 34.1 ($C_{methylene}$), 33.4 ($C_{methylene}$), 27.8 ($C_{methylene}$), 0.0 (C_{TMS}) ppm. **HRMS** (ESI): *m/z* $[M+Na]^+$ calcd for $[C_{32}H_{30}NaO_2Si]^+$ = 497.1907, found 497.1903; **IR** (neat, diamond ATR): $\tilde{\nu}$ 3039, 2955 und 2875, 2157, 1732, 1625, 1508, 1247, 1157, 837 cm^{-1}; **UV/Vis** (DCM): λ_{max} (ε [10^4 $M^{-1}cm^{-1}$]) 253 (4.49), 266 (5.63), 277 (6.26), 314 (1.59), 328 (3.85), 344 (5.17) nm; **Elemental Anal.**: Found: C 81.74, H 6.70. calcd for $C_{32}H_{30}O_2Si$ C 80.97, H 6.37.

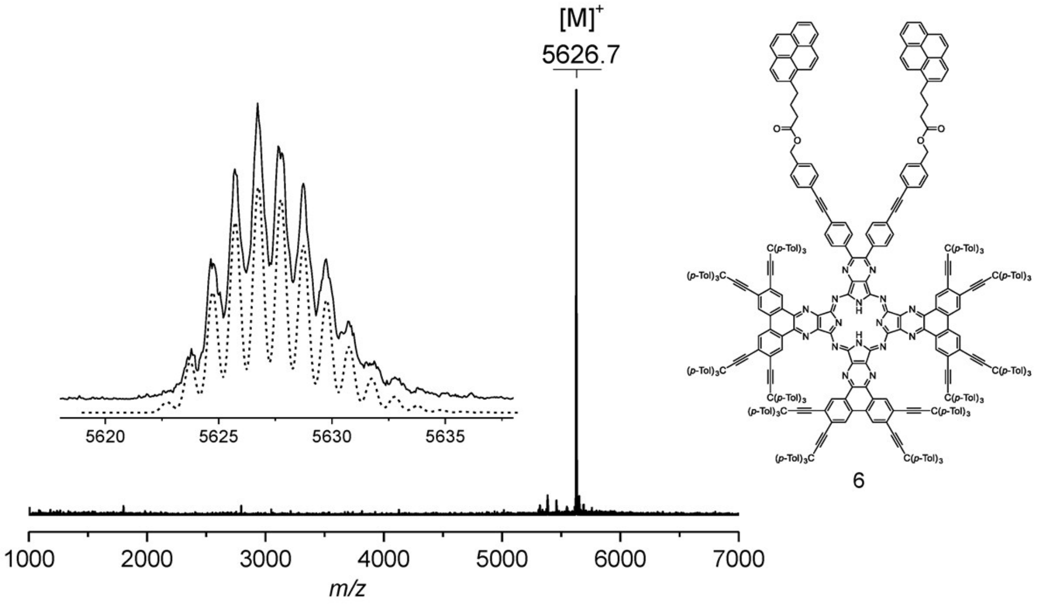


Figure S16: MALDI-TOF mass spectrum (DCTB/+) of H_2-Pyrene-Pz **6** ($C_{418}H_{316}N_{16}O_4$; M = 5627.2). Inset: Isotopic pattern of the molecular ion peak (solid: measured; dashed: calculated).

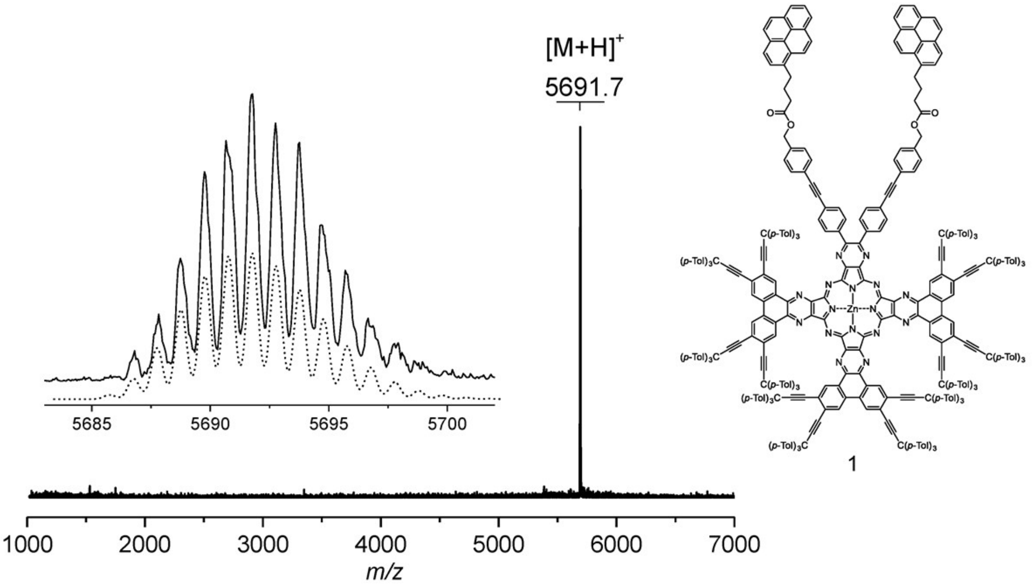


Figure S17: MALDI-TOF mass spectrum (dithranol/+) of Zn-Pyrene-Pz **1** ($C_{418}H_{315}N_{16}O_4Zn$; M=5691.6). Inset: Isotopic pattern of the molecular ion peak (solid: measured; dashed: calculated).

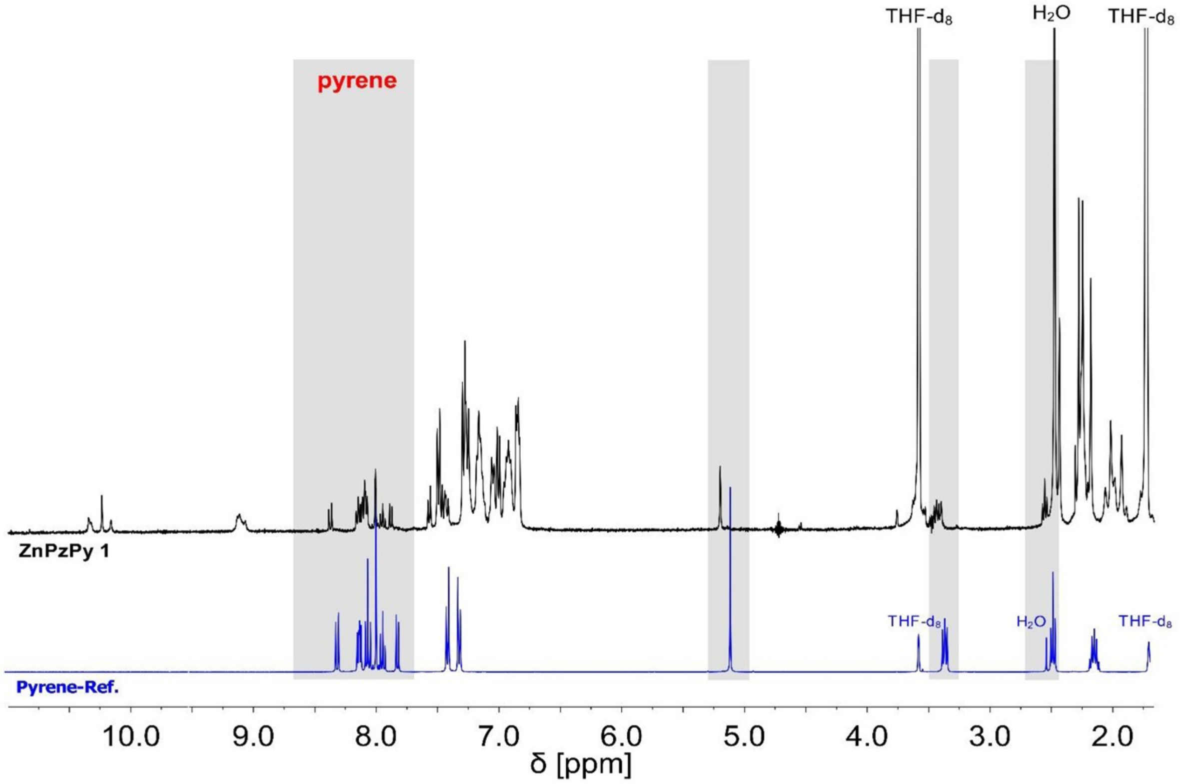


Figure S18: ^{1}H-NMR spectrum of **1** and a pyrene reference compound in THF-d_8.

1 A. L. Rusanov, M. L. Keshtov, M. M. Begretov, I. A. Khotina, A. K. Mikitaev, *Russ. Chem. Bull. Int. Ed.*, 1996, **45**, 1169-1175.

2 F. Bureš, H. Čermáková, J. Kulhánek, M. Ludwig, W. Kuznik, I. V. Kityk, T. Mikysek, A. Růžička,

Eur. J. Org. Chem., 2012, 529-538.

3 A. C. Warden, F. H. M. Graichen, M. S. O'Shea, (Eds.: S. Commonwealth, O. Industrial Research), 2008.

4 V. Engelhardt, S. Kuhri, J. Fleischhauer, M. García-Iglesias, D. González-Rodríguez, G. Bottari, T. Torres, D. M. Guldi, R. Faust, *Chem. Sci*., 2013, **4**, 3888-3893.