– Electronic Supplementary Information –

p-Doping of graphene in hybrid materials with 3,10-diazapicenium dications

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Experimental Section

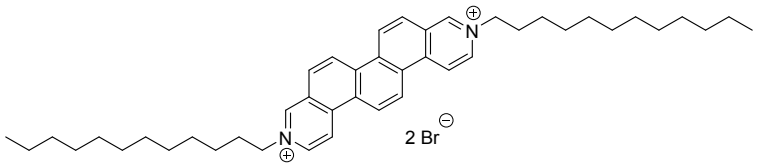
General procedures and methods

Reagents were purchased reagent grade from commercial suppliers and used without further purification. The graphite used for the preparation of graphene was purchased from Asbury (Nano99). $MgSO_4$ was used as the drying reagent after aqueous work-up. TLC analyses were carried out on TLC plates from Macherey-Nagel (ALUGRAM® SIL G/UV254) and visualized via UV-light (264/364 nm). Column chromatography was performed using Merck Silica Gel 60M. An Elmasonic p120 52 (330 W) ultrasonication bath from Elma was used to prepare the graphene dispersions. All microwave reactions were performed in septum-capped Biotage® microwave vials (10–20 mL) using Biotage® Initiator+ with stirring. Power required maintaining target temperature was controlled by Biotage® Initiator+ software. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300.1 MHz for ^{1}H NMR, 75.5 MHz for ^{13}C NMR, and 121.5 MHz for ^{31}P NMR or a Bruker Avance 400 spectrometer at 400.1 MHz for ^{1}H NMR, 100.5 MHz for ^{13}C NMR. NMR spectra were referenced to the residual solvent signal (^{1}H: $CDCl_3$ 7.24 ppm, CD_3CN 1.94 ppm, methanol-d_4 3.32 ppm, acetone-d_6 2.05 ppm; ^{13}C: $CDCl_3$ 77.0 ppm, CD_3CN 1.4 ppm, methanol-d_4 49.0 ppm, acetone-d_6 29.8 ppm) or to external 85% H_3PO_4 (^{31}P) and recorded at ambient probe temperature. $CDCl_3$ (Deutero GmbH, 99.8%), CD_3CN (Deutero GmbH, 99.0%), methanol-d_4 (Deutero GmbH, 99.8%), and acetone-d_6 (Deutero GmbH, 99.8%) were stored over molecular sieves (4 Å). Infrared (IR) spectra were recorded on a 660-IR (Varian, ATR mode) spectrometer. Characteristic IR absorptions are reported in cm^{-1} and denoted as strong (s), medium (m), and weak (w). Raman spectroscopy was performed with an InVia Raman Microscope from Renishaw that was equipped with a confocal microscope and an automated XYZ-table, using a laser excitation of 532 nm. The samples were prepared by drop casting it on a Si substrate with a 300 nm oxide layer. UV/vis absorption spectra were measured under ambient conditions on a Cary 5000 UV/vis/NIR (Varian) spectrophotometer. All measurements were carried out in QS Quartz Suprasil cells (10 mm light path). The absorption maxima (λ_{max}) are reported in nanometers (nm) and the extinction coefficient (ε) in $M^{-1}cm^{-1}$. Steady state absorption spectra were recorded with a Perkin Elmer Lambda 35 double beam spectrometer. Fluorescence measurements were done with a fluoromax-3 or a fluoromax-4 spectrophotometer (HORIBA Yobin Yvon). Femtosecond transient absorption measurements were performed with the transient absorption pump probe system HELIOS from Ultrafast Systems. To generate laser pulses with a pulse width of 150 fs and a

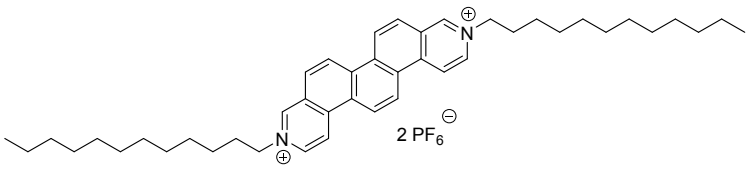
wavelength of 775 nm a CPA-2110 titanium:sapphire laser system from Clark-MXR Inc was utilized. Global analysis was performed with the open-source software package Glotaran, a free graphical user interface to the R package TIMP.[1] TEM images were recorded using an 80 kV EM 900 TEM from Carl Zeiss AG. Lacey carbon grids were used as sample holders.

Cyclic voltammetry measurements were carried out in a conventional three-electrode cell using Pt button working electrodes, a platinum wire counter electrode, and a Ag/AgCl reference electrode on a computer-controlled BAS CV-50W instruments at rt. The reported half-wave potentials are referenced to the ferrocene/ferrocenium (Fc/Fc^+) redox couple by adding ferrocene to the sample solution. Spectroelectrochemical measurements were done in a home-made three neck glass cell with a three-electrode setup comprised of a platinum mesh as working electrode, a Ag-wire as pseudo reference electrode, and a platinum wire as counter electrode. To control the applied potentials a Metrohm PGStat 101 was used. Mass spectra were obtained from a Bruker 9.4T Apex-Qe FTICR (MALDI) and Bruker micro TOF II (ESI) instruments. Melting points were measured with a Büchi Melting Point M-560 in open capillaries. “Decomp.” refers to decomposition.

Synthesis



***N*,*N*'-Didodecyl-3,10-diazapicenediium dibromide (2).**[2] 3,10-Diazapicene **1** (30.8 mg, 0.11 mmol) was dissolved in DMF (20 mL) and 1-bromododecane (0.53 g, 0.51 mL, 2.12 mmol) was added. The reaction was carried out under microwave assisted heating at 130 °C for 12 h. Et_2O (100 mL) was added and the formed precipitate was filtered off and washed with additional Et_2O providing product **2** as a yellow solid (76.2 mg, 89%). Mp 273 °C (decomp.). R_f 0.29 (SiO_2, $CHCl_3$/CH_3OH/acetone/H_2O 15:5:5:1). UV/vis (EtOH) λ_{max} (ε) 426, 402, 379, 291 nm. IR (ATR) $\tilde{\nu}$ 3023 (w), 2919 (s), 2849 (s), 2760, 1639 (s), 1579 (m), 1447 (m), 1412 (m), 1373 (m), 1280 (m), 1173 (m), 819 (s), 757 (m), 721 (m), 654 (m) cm^{-1}. ^1H NMR (300.1 MHz, methanol-d_4) δ 10.12 (s, 2H), 9.63 (d, J = 7.2 Hz, 2H), 9.57 (d, J = 9.4 Hz, 2H), 9.53 (s, 2H), 9.11 (d, J = 8.1 Hz, 2H), 8.65 (d, J = 9.4 Hz, 2H), 4.90 (t, J = 7.8 Hz, 4H), 2.27–2.19 (m, 4H), 1.54–1.25 (m, 36H), 0.86 (t, J = 6.6 Hz, 6H) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 137.9, 136.7, 131.1, 127.3, 127.1, 127.0, 126.6, 124.3, 123.1, 62.5, 34.8, 31.8, 31.6, 29.5, 29.43, 29.36, 29.2, 29.1, 26.4, 22.6, 14.0 (one signal coincident or not observed) ppm. HR ESI-MS (CH_3OH/CH_3CN) calcd for $C_{44}H_{62}N_2$ ($[M]^{2+}$) 309.2451, found 309.2463.



***N*,*N*'-Didodecyl-3,10-diazapicenediium dihexafluorophosphate (3).**[2] Dibromide **2** (20.2 mg, 26.0 μmol) was dissolved in EtOH/H_2O (2:2, 4.0 mL) at reflux. Ammonium hexafluorophosphate (62.8 mg, 0.39 mmol) was dissolved in hot H_2O (1.0 mL) and added to the solution of **2**. The resulting mixture was heated under reflux for 5 minutes and, after cooling to RT, the formed precipitate was collected by filtration. Product **2** was obtained as a pale yellow solid (22.2 mg, 94%). Mp 222 °C (decomp.). R_f 0.89 (SiO_2, $CHCl_3$/CH_3OH/acetone/H_2O 15:5:5:1). UV/vis (C_2H_5OH) λ_{max} (ε) 425, 402, 379, 291 nm. IR (ATR) $\tilde{\nu}$ 3120(w), 2922 (m), 2852 (m), 1642 (m), 1583 (w), 1450 (w), 1413 (w), 1375 (w), 1281 (w), 1172 (w), 824 (s), 555 (s) cm^{-1}. ^1H NMR (300.1 MHz, acetone-d_6) δ 10.20 (s, 2H), 9.68 (d, J = 6.9 Hz, 2H), 9.48 (d, J = 9.6 Hz, 2H), 9.44 (s, 2H), 9.24 (d, J = 6.9 Hz, 2H), 8.66 (d, J = 9.3 Hz, 2H), 5.09 (t, J = 7.5 Hz, 4H), 2.37–2.27 (m, 4H), 1.57–1.37 (m, 8H), 1.36–1.19 (m, 28H), 0.86–0.82 (m, 6H) ppm. ^{13}C NMR (75.5 MHz, acetone-d_6) δ 149.1, 138.6, 138.3, 133.7, 129.6, 129.1, 128.5, 127.9, 125.9, 124.0, 63.0, 32.6, 32.2, 30.2, 26.9, 23.3, 14.3 (five signals coincident or not observed) ppm. ^{31}P NMR (121.5 MHz, acetone-d_6) δ –143.0 (hept, J = 707.8 Hz) ppm. HR ESI-MS (CH_3CN) calcd for $C_{44}H_{62}N_2$ ($[M]^{2+}$) 309.2451, found 309.2450.

Hybrid preparation

Liquid phase exfoliated graphene in EtOH was prepared via ultrasonication of graphite in an ultrasonic bath. An established protocol is as follows: 2 mg of graphite are weighed and dispersed in 3ml EtOH and ultrasonicated for 1.5-2 h. The 37 kHz-ultrasonication bath is usually operated in a temperature range of 15-20°C. Slight changes in temperature or position of the vial in the ultrasonication bath can led to different exfoliation degrees which is seen already by eye. Adjustments regarding, for example, ultrasonication times were required. In general, after the exfoliation process, a centrifugation step to separate non-exfoliated graphite flakes, is conducted. Thereby the dispersion is centrifuged for 15 min at 1500 rpm. The freshly prepared dispersion is then added dropwise to a solution of the 3,10-diazapicenium dications in EtOH ($3x10^{-6}$ M). The procedure was monitored by steady state spectroscopic measurements.

Cyclic voltammetry

Cyclic voltammetry (scan rate ν = 200 mV s^{-1}) of compounds **2** and **3** measured in CH_2Cl_2 at room temperature (with 0.1 M $n$$Bu_4NPF_6$, *vs.* Fc^+/Fc as internal standard):

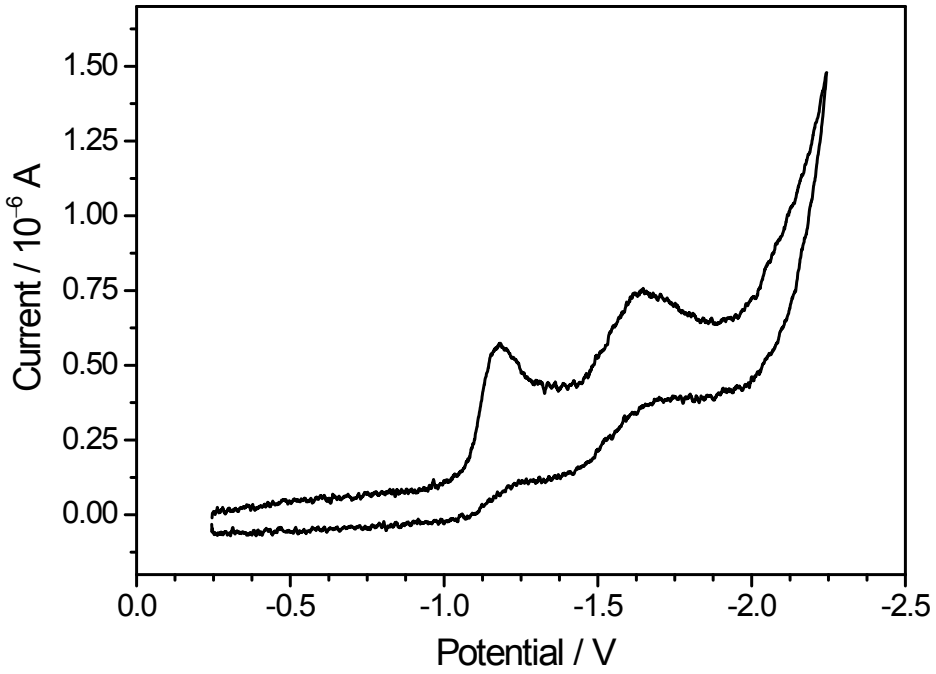


Figure S1. Cyclic voltammogram of **2** in CH_2Cl_2.

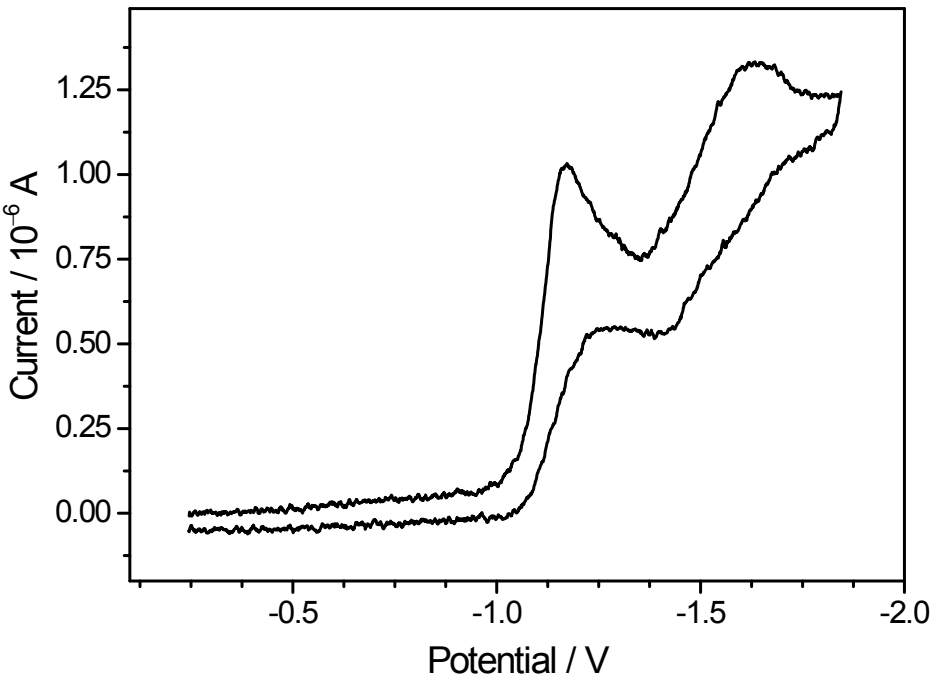


Figure S2. Cyclic voltammogram of **3** in CH_2Cl_2.

NMR Spectra

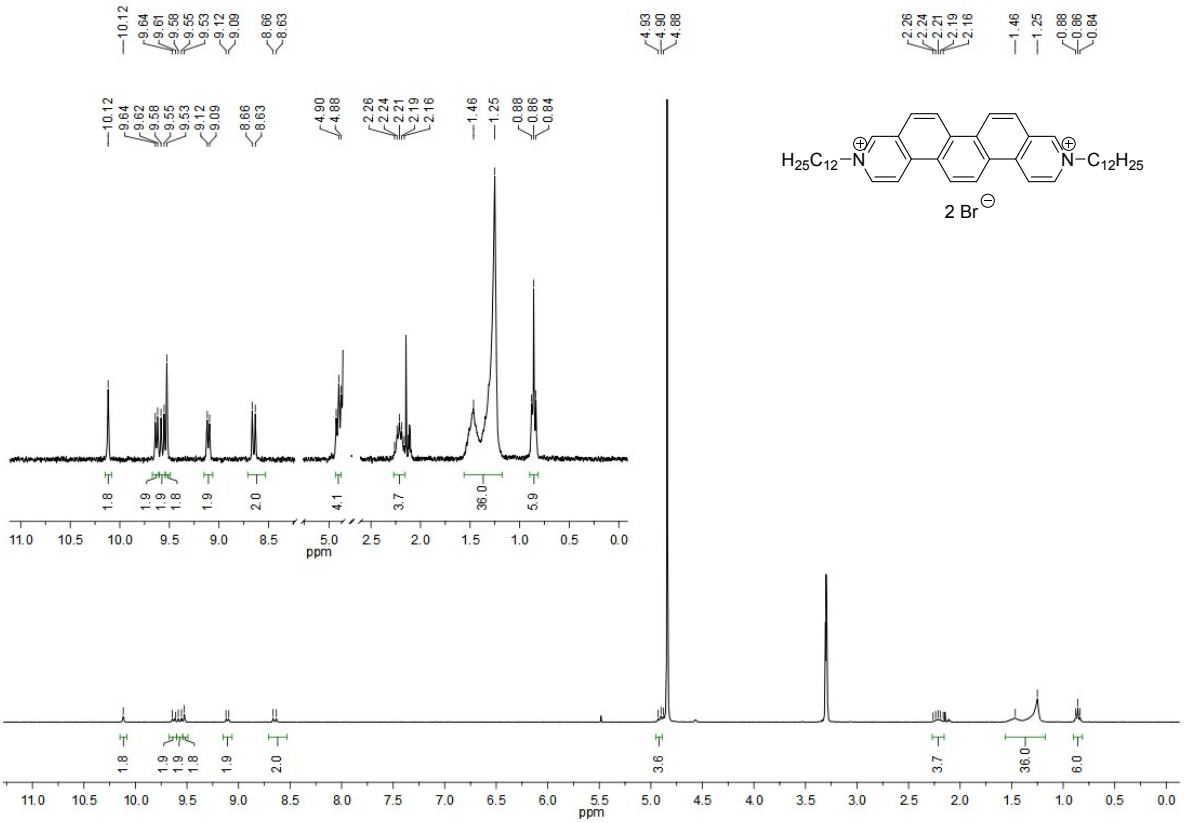


Figure S3. ^{1}H NMR (300.1 MHz, methanol-d_4) of **2** at RT.

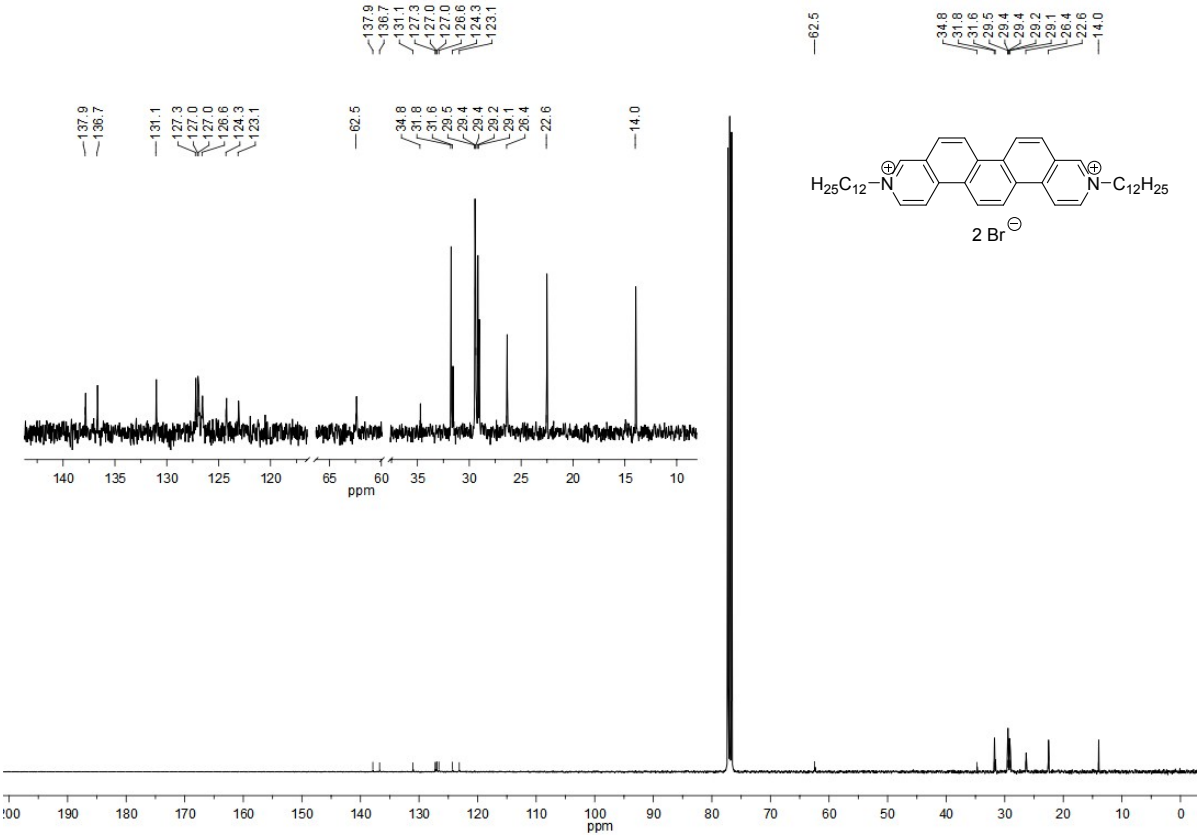


Figure S4. ^{13}C NMR (100.5 MHz, $CDCl_3$) of **2** at RT.

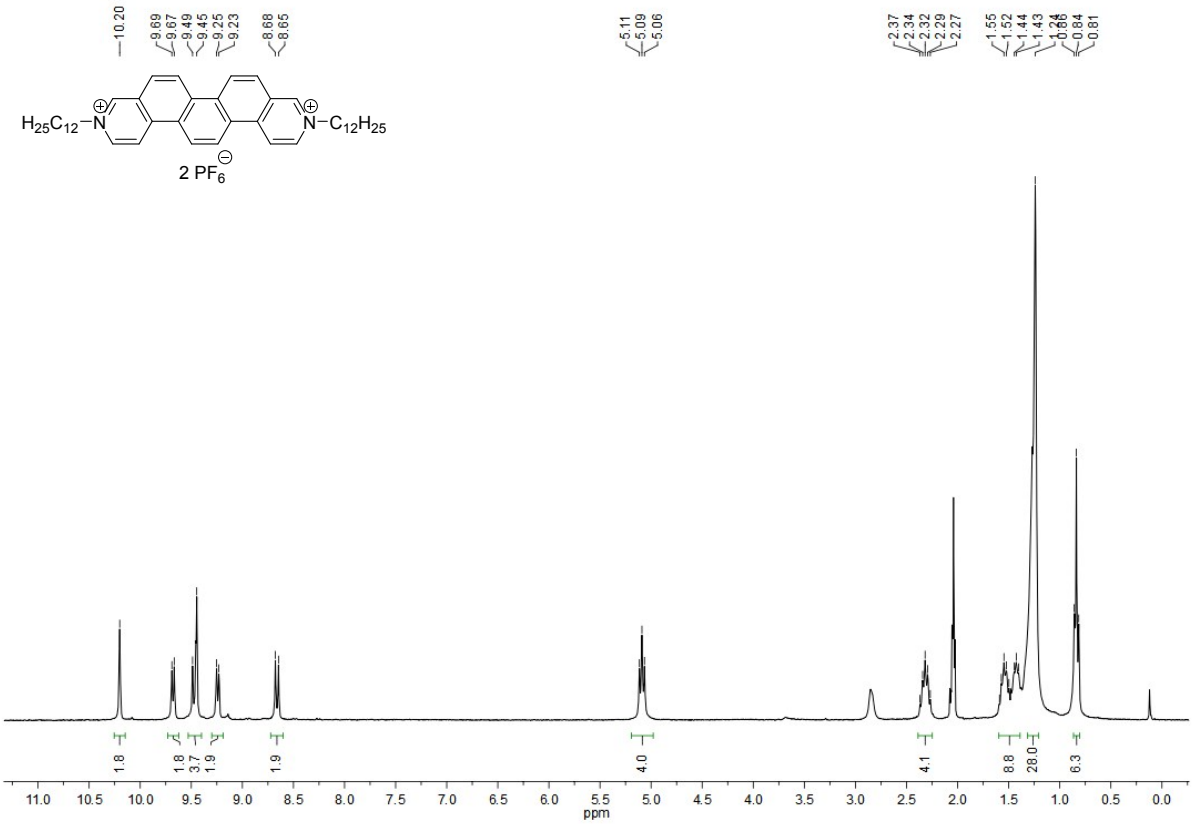


Figure S5. ^{1}H NMR (300.1 MHz, acetone-d_6) of **3** at RT.

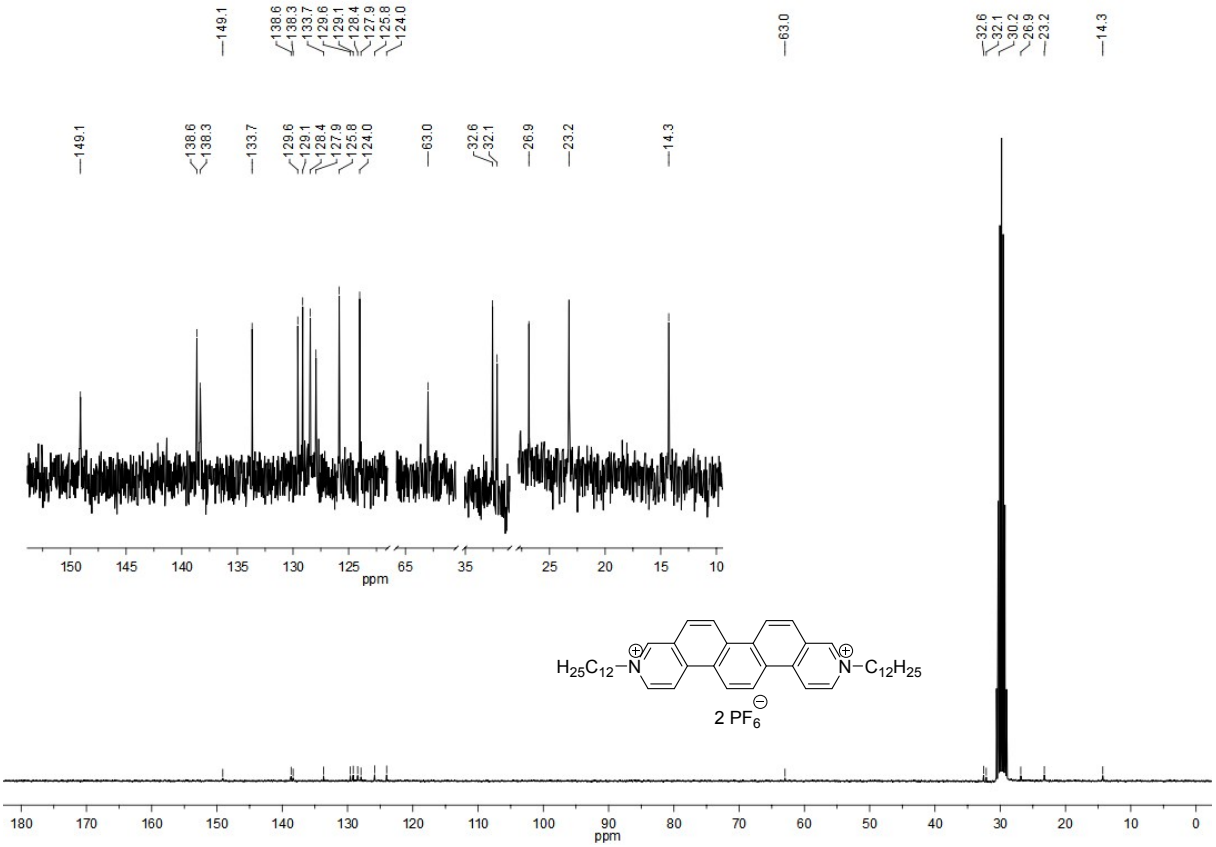


Figure S6. ^{13}C NMR (75.5 MHz, acetone-d_6) of **3** at RT.

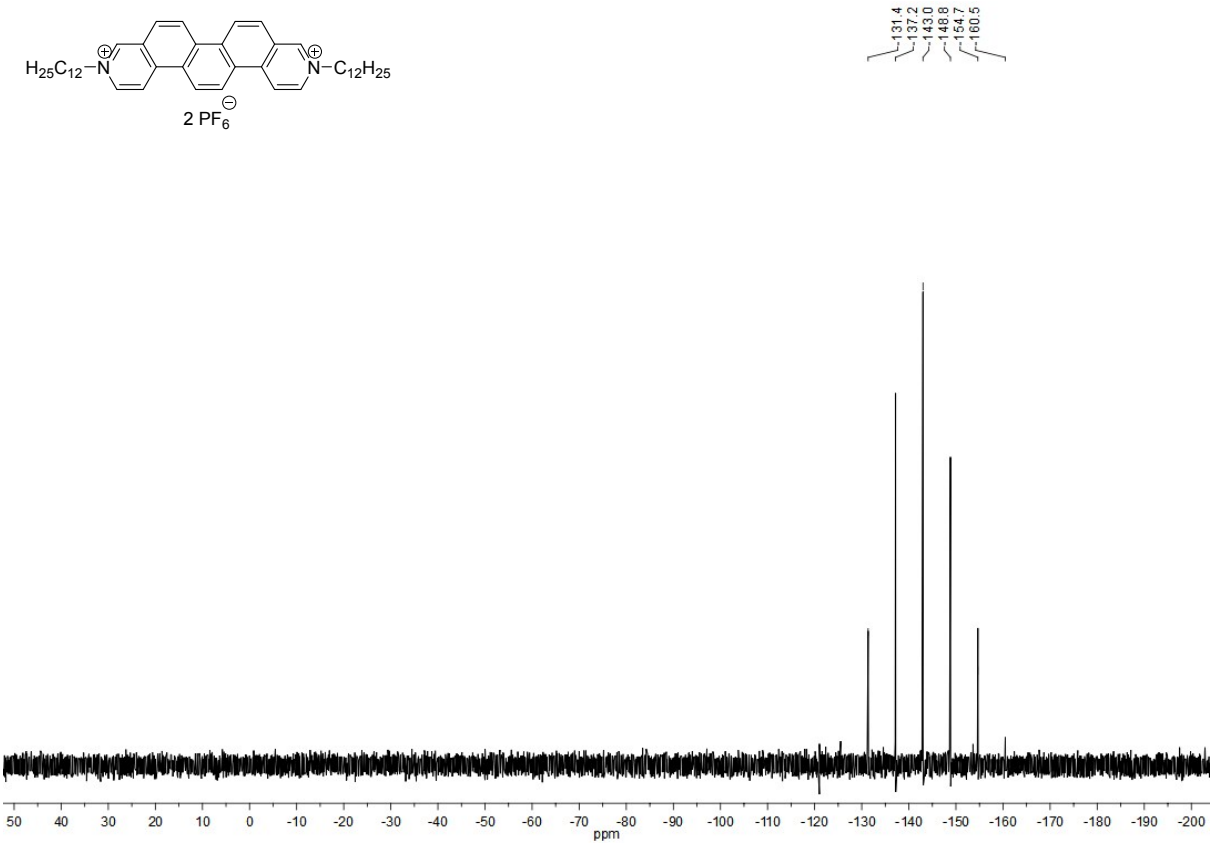


Figure S7. ^{31}P NMR (121.5 MHz, acetone-d_6) of **3** at RT.

Transient absorption spectroscopy

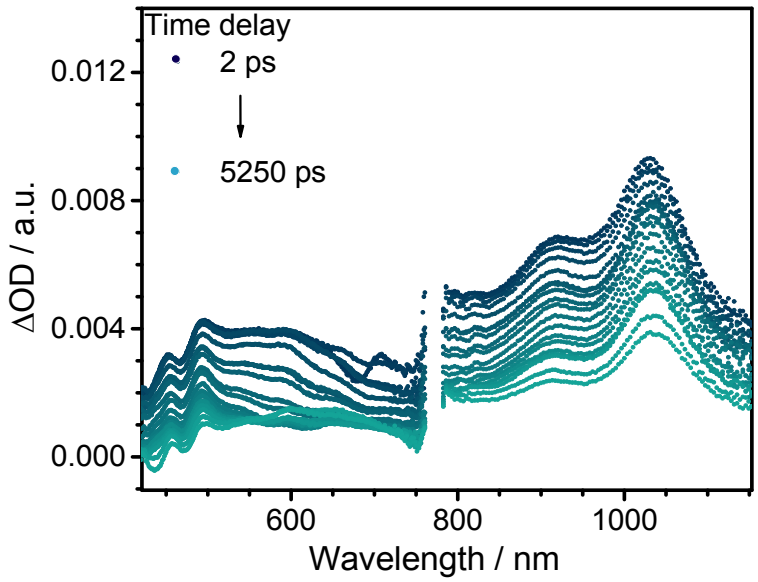


Figure S8. Differential absorption spectra obtained upon femtosecond pump probe experiments of **2** in EtOH ($\lambda_{exc.}$ 387 nm) with time delays between 2 and 5250 ps.

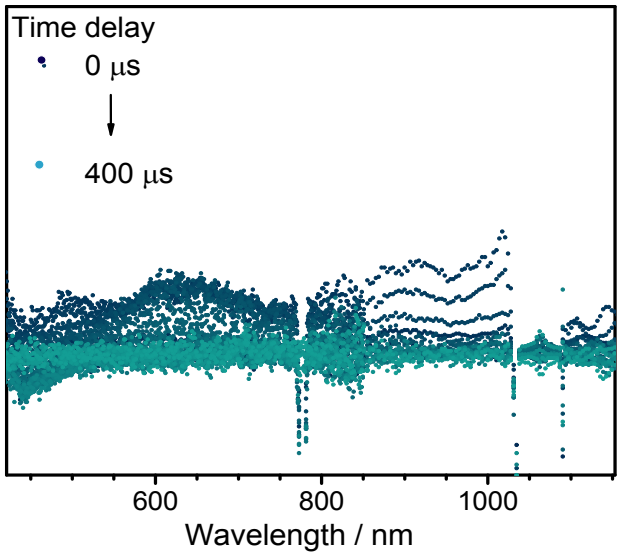


Figure S9. Differential absorption spectra obtained upon femtosecond pump probe experiments of **2** in EtOH ($\lambda_{exc.}$ 387 nm) with time delays between 0 μs and 400 μs.

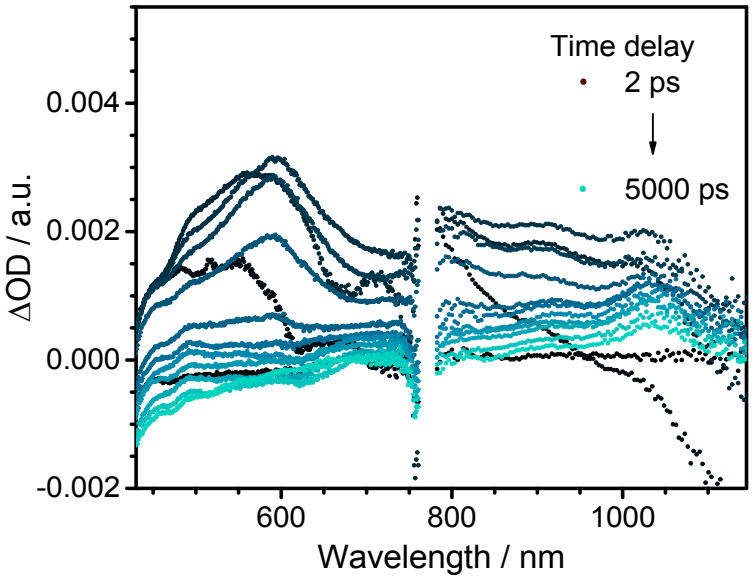


Figure S10. Differential absorption spectra obtained upon femtosecond pump probe experiments of **EG/2** in EtOH ($\lambda_{exc.}$ 387 nm) with time delays between 2 and 5000 ps.

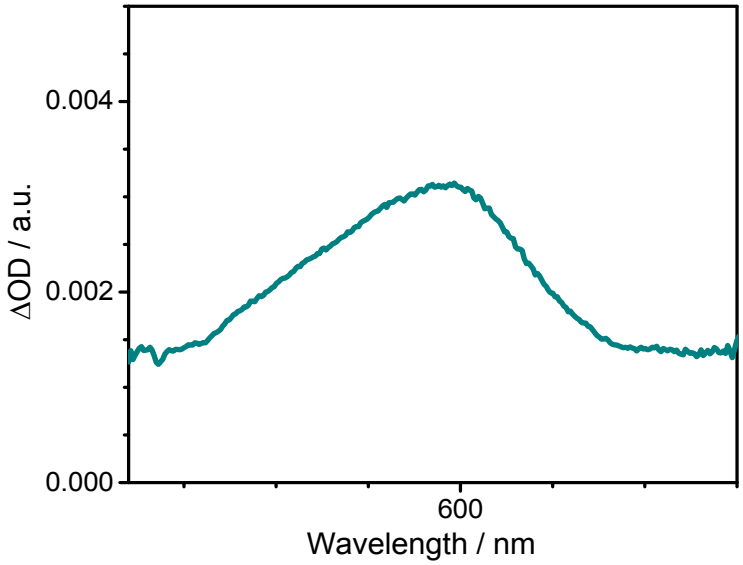


Figure S11. Deconvoluted transient absorption spectra of the charge separated state within **EG/2** in EtOH obtained by global analysis.

Time-correlated single photon counting

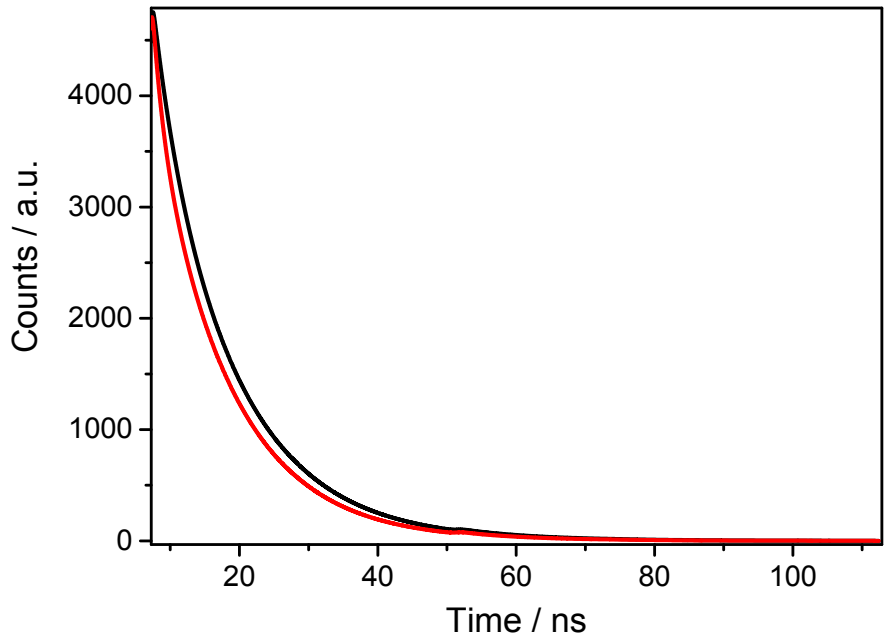


Figure S12. Fluorescence time profiles of **2** (black) and **3** (red) in EtOH.

Steady state absorption spectroscopy

In our procedure, the 3,10-diazapicenium salts were added after ultrasonication and, thus, did not have an effect on the exfoliation process. No precipitation was observed for the prepared EG/**2** and EG/**3** within days pointing at a comparable stabilizing effect. The electrochemical and photophysical characteristics of both 3,10-diazapicene derivatives **2** and **3** were similar, due to the formation of solvent separated ion pairs in solution. Hence, we expected also comparable results for the electronic interactions between the 3,10-diazapicenium dications and graphene regardless of the counterion used. To test this hypothesis, in analogy to the hybrids prepared with compound **2** steady state absorption measurements were also performed for compound **3** showing similar results (Figure S13).

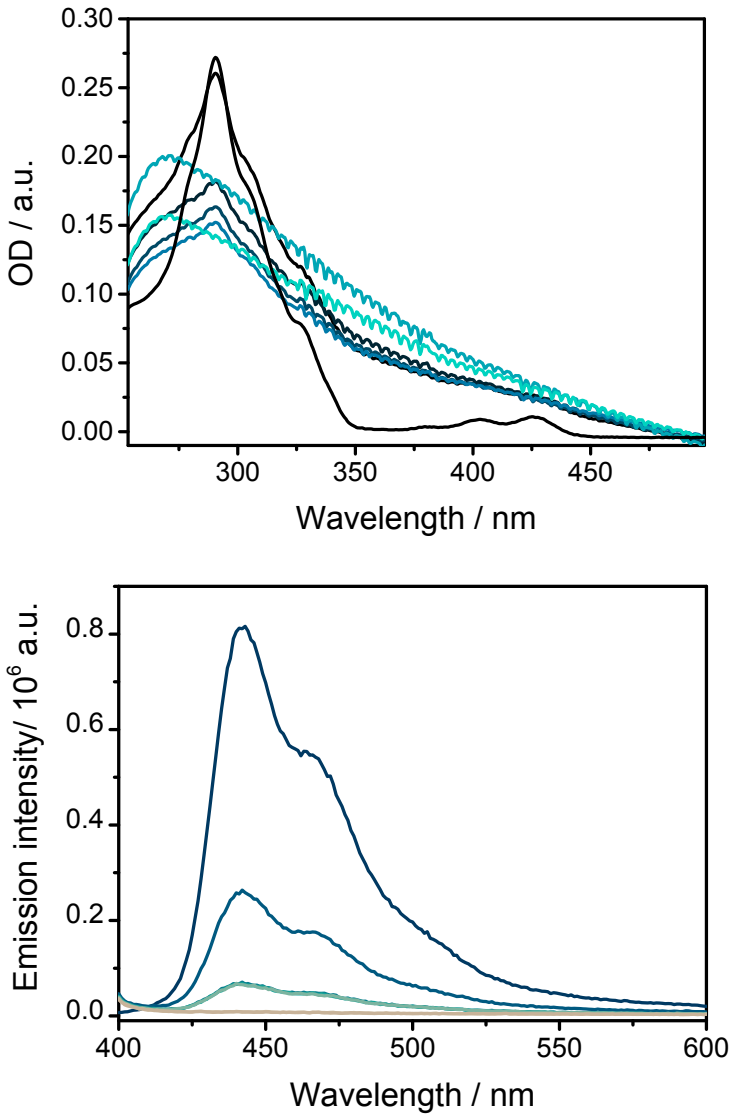


Figure S13. Top: Absorption (for clarity EG/**3** spectra shifted in y-direction to offset light scattering caused by the graphene/graphite flakes); Bottom: Fluorescence spectra of **3** (black) and EG/**3** (blue) upon stepwise addition of EG in EtOH.

Raman spectroscopy

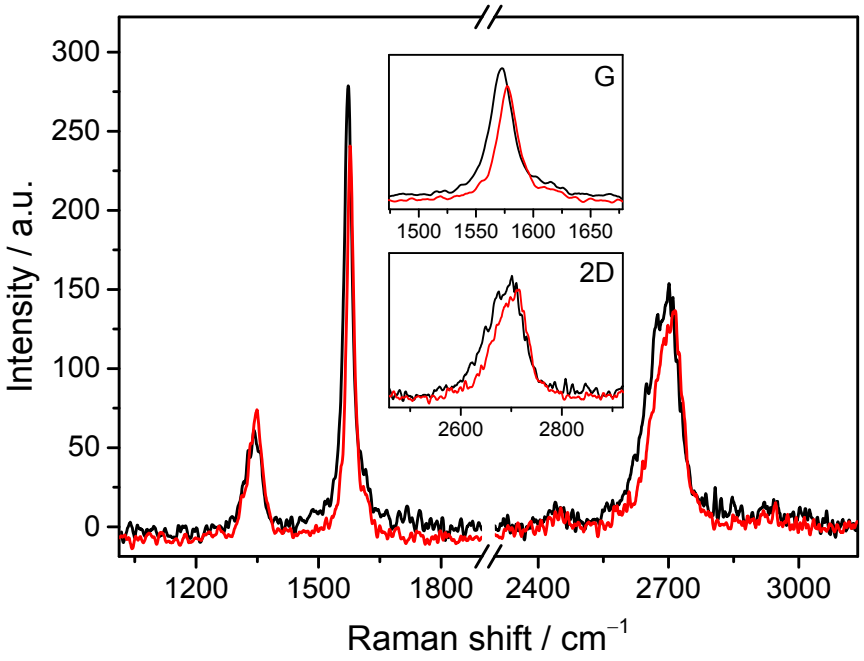


Figure S14. Exemplary Raman spectra of exfoliated graphene **EG** (black) and **EG/2** nanohybrid (red) ($\lambda_{exc.}$ 532 m) which were recorded after drop casting onto a Si/SiO_2 wafer. Zoom-in into the G- and 2D-modes.

References

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