Electronic Supplementary Information

Graphene performs the role of an electron donor in covalently interfaced porphyrin-boron azadipyrromethene dyads and manages photoinduced charge-transfer processes

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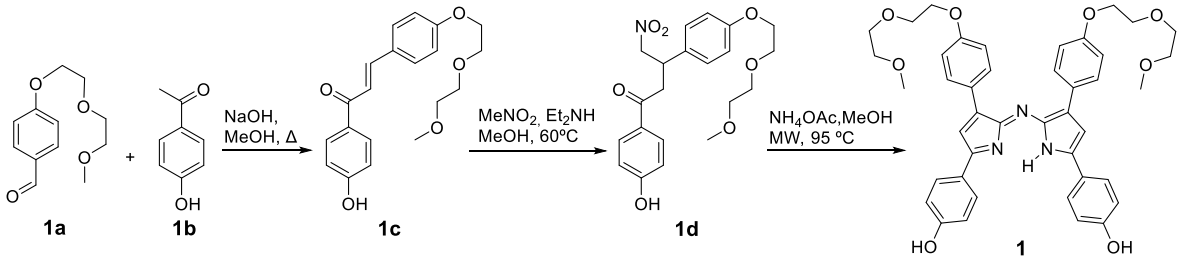
SUPPLEMENTARY EXPERIMENTAL SECTION

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded in a 300 MHz Varian instrument operated by Vjnmr software, with TMS used as internal standard and D_2O as solvent. Steady-state UV-Vis electronic absorption spectra were recorded on a Perkin-Elmer (Lambda 19) UV-Vis-NIR spectrophotometer. Steady-state emission spectra were recorded on a Fluorolog-3 JobinYvon-Spex spectrofluorometer (model GL3-21). Pico-second time-resolved fluorescence spectra were measured by the time-correlated-single-photon-counting (TCSPC) method on a Nano-Log spectrofluorometer (Horiba JobinYvon), by using a laser diode as an excitation source (NanoLED 375 nm) and a UV-Vis detector TBX-PMT series (250-850 nm) by Horiba JobinYvon. Lifetimes were evaluated with the DAS6 Fluorescence-Decay Analysis Software. Mid-infrared spectra in the region 500−4500 cm^{-1} were obtained on a Fourier transform IR spectrometer (Equinox 55 from Bruker Optics) equipped with a single reflection diamond ATR accessory (DuraSamp1IR II by SensIR Technologies). A drop of the solution was placed on the diamond surface, followed by evaporation of the solvent, in a stream of nitrogen, before recording the spectrum. Typically, 100 scans were acquired at 2 cm^{-1} resolution. Micro-Raman scattering measurements were performed at room temperature in the backscattering geometry using a RENISHAW inVia Raman microscope equipped with a CCD camera and a Leica microscope. A 2400 lines mm^{-1} grating was used for all measurements, providing a spectral resolution of ± 1 cm^{-1}. As an excitation source the Ar^{+} laser (633 nm with less than 2.65 mW laser power) was used. Measurements were taken with 60 seconds of exposure times at varying numbers of accumulations. The laser spot was focused on the sample surface using a long working distance 50x objective. Raman spectra were collected on numerous spots on the sample and recorded with Peltier cooled CCD camera. The intensity ratio I_D/I_G was obtained by taking the peak intensities following any baseline corrections. The data were collected and analyzed with Renishaw Wire and Origin software. Thermogravimetric analysis was performed using a TGA Q500 V20.2 Build 27 instrument by TA in a nitrogen (purity >99.999%) inert atmosphere. TEM images were taken at room temperature using a JEOL JEM-2100F, operated at an acceleration voltage of 80 keV under a pressure of 10^{-5} Pa. The samples were sonicated in hexane (3 mL) for 1 minute using an ultrasonic bath sonicator (Nanoruptor, NR-350, Cosmo Bio Co. Ltd), and 10 drops of the dispersion solution were deposited onto carbon-coated copper grids. TEM images were recorded on a Gatan MSC 794 1 k×1 k CCD camera with a typical exposure time of 0.3 s. Electrochemistry studies were performed using a standard three-electrode cell. Glassy carbon was used as a working electrode, and platinum wires were used as counter and pseudoreference electrodes (ferrocene as an internal reference). $TBAPF_6$ (98%) was recrystallized three times from acetone and dried in a vacuum at 100 °C before being used as an electrolyte. Before each experiment, the cell was purged with N_2 for 120 s. Measurements were recorded using an EG&G Princeton Applied Research potentiostat/ galvanostat Model 2273A instrument connected to a personal computer running PowerSuite software. The working electrode was cleaned before each experiment through polishing with a cloth and 6, 3, and 1 mm diamond pastes. Femtosecond transient absorption spectroscopy

experiments were performed using an ultrafast femtosecond laser source (Libra) by Coherent incorporating a diode-pumped, modelocked Ti:sapphire laser (Vitesse) and a diode-pumped intracavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.45 W. For optical detection, a Helios transient absorption spectrometer coupled with a femtosecond harmonics generator, both provided by Ultrafast Systems LLC, was used. The sources for the pump and probe pulses were derived from the fundamental output of Libra (Compressed output 1.45 W, pulse width 100 fs) at a repetition rate of 1 kHz; 95% of the fundamental output of the laser was introduced into a TOPAS-Prime-OPA system with a 290−2600 nm tuning range from Altos Photonics Inc., (Bozeman, MT), while the rest of the output was used for generation of a white light continuum. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K. The estimated error in the reported rate constants is ±10%.

Synthesis of compounds and materials.

Procedure for the synthesis of 1.



(E)-1-(4-hydroxyphenyl)-3-(4-(2-(2-methoxyethoxy)ethoxy)phenyl)prop-2-en-1-one (1c). In a stirred solution of 4-[2-(2-methoxyethoxy)ethoxy]benzaldehyde (**1a**) (11 g, 0.049 mol) and 4'-hydroxyacetophenone (**1b**) (6.67 g, 0.049 mol) in ethanol (80 mL), 10% aq. NaOH (20 mL) was added and the resulting mixture was heated to reflux for 18 h. After cooling down, the solvent evaporated and water (300 mL) was added. Washing with dichloromethane (pH = 12) removed mainly unreacted **1a**. The aqueous layer was acidified with 10N HCl to pH = 10 and washed with dichloromethane (minor impurities removed). Further acidification to pH 9–7 and subsequently dichloromethane washings extracted product **1c**. Further acidification extracted unreacted 4-hydroxyacetophenone. The pH 9–7 washings were combined, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was treated with cold methanol and filtered, affording **1c** (4.64 g, 28 %) as yellow dust. ^{1}H-NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.47 (bs, 1H), 7.92 (d, *J* = 8.7 Hz, 2H), 7.72 (d, *J* = 15.6 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 15.6 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 4.10-4.06 (m, 2H), 3.86-3.82 (m, 2H), 3.74-3.71 (m, 2H), 3.62-3.59 (m, 2H), 3.40 (s, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): *δ* (ppm) 189.55, 161.52, 160.77, 144.32, 131.21, 130.38, 130.22, 127.85, 119.43, 115.77, 114.97, 71.98, 70.68, 69.70, 67.43, 59.06. MALDI-MS calcd for $C_{20}H_{22}O_5$: 342.1457 $[M]^+$, found: m/z 342.1454.

1-(4-hydroxyphenyl)-3-(4-(2-(2-methoxyethoxy)ethoxy)phenyl)-4-nitrobutan-1-one (1d). A stirred solution of **1c** (6.0 g, 17.52 mmol), $MeNO_2$ (5.35 g, 87.62 mmol) and Et_2NH (6.41 g, 87.62 mmol) in MeOH (125 mL) was heated to reflux for 5 h. Another round of $MeNO_2$/Et_2NH was added and heating continued for 18 h. Another round of $MeNO_2$/Et_2NH was added and heating continued for 4 days. After cooling down, aq. sat. NH_4Cl (≈ 250 mL) was added, the mixture was extracted with dichloromethane (3x150 mL), the combined organics washed with H_2O and dried over Na_2SO_4. Evaporation of the solvent left 7.07 g of compound **1d** as orange/red viscous oil, which was considered of adequate purity and used in the next step without further purification. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.78 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.82 – 6.79 (m, 4H), 4.77 (dd, *J* = 12.4, 6.5 Hz, 1H), 4.65 – 4.58 (m, 2H), 4.16-4.05 (m, 3H), 3.83-3.80 (m, 2H), 3.71-3.69 (m, 2H), 3.60-3.57 (m, 2H), 3.38 (s, 3H), 3.37-3.23 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 195.94, 161.93, 158.27, 131.49, 130.83, 128.95, 128.61, 115.81, 115.17, 80.00, 72.03, 70.71, 69.80, 67.46, 59.12, 41.36, 39.09.

Azadipyrromethene compound (1). Compound **1d** (50 mg, 0.124 mmol), ammonium acetate (334 mg, 4.338 mmol), MeOH (1 mL) and a magnetic stirrer were placed in a 7 mL

microwave vial, and the suspension was microwave-irradiated for 1h at 95°C (set: 100W, 95°C, 60 min; during the course: 5 W, 10 psi). A blue / purple solid was formed, methanol (5 mL) was added, the mixture was centrifuged, and the residue was washed with methanol and petroleum ether leaving **1** (20 mg, 44%) as blue / iridescent violet solid. ^{1}H-NMR (300 MHz, DMSO-d_6): δ (ppm) 13-9.5 (br, 3H), 8.04 (d, *J* = 8.7 Hz, 4H), 7.89 (d, *J* = 8.6 Hz, 4H), 7.40 (s, 2H), 7.04 (d, *J* = 8.9 Hz, 4H), 7.00 (d, *J* = 8.7 Hz, 4H), 4.19-4.16 (m, 4H), 3.79-3.76 (m, 4H), 3.62-3.59 (m, 4H), 3.49-3.46 (m, 4H), 3.26 (s, 6H); ^{13}C-NMR (75 MHz, DMSO-d_6): δ (ppm) 159.87, 158.51, 154.05, 148.37, 140.57, 129.83, 128.36, 126.23, 122.64, 116.37, 114.36, 113.55, 71.31, 69.75, 68.94, 67.22, 58.08. MALDI-MS calcd for $C_{42}H_{44}N_3O_8$: 718.3128 $[M+H]^+$, found: m/z 718.3130.

Azadipyrromethene-laurate (2). In a round bottom flask, lauric acid (88 mg, 1.05 equiv), azadipyrromethane **1** (300 mg, 1 equiv.), EDCI (252 mg, 3 equiv.) and DMAP (205, 3 equiv.) were added in dry dichloromethane (50 mL). The reaction mixture was stirred under nitrogen at room temperature for 18 hours. Then, the organic phase was extracted with H_2O (5 x 100 mL), dried over $MgSO_4$ and purified by column chromatography (Hexane/DCM/acetone 50/90-80/10-20%) affording **2** (F3, 100 mg, 25%) as dark blue solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.99 (d, *J* = 8.8 Hz, 2H), 7.92-7.82 (m, 4H), 7.66-7.60 (m, 2H), 7.23 (s, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 7.04 (s, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 9.3 Hz, 2H), 6.85-6.77 (m, 2H), 6.76 (d, *J* = 3.9 Hz, 1H), 4.25-4.10 (m, 4H), 3.97-3.90 (m, 4H), 3.84-3.74 (m, 4H), 3.70-3.62 (m, 4H), 3.45-3.43 (m, 6H), 2.65-2.57 (m, 2H), 1.81-1.77 (m, 2H), 1.29 (m, 16H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 172.13, 160.44, 158.93, 158.68, 158.45, 158.01, 153.66, 151.74, 150.68, 149.40, 145.98, 144.93, 143.68, 141.85, 137.32, 130.18, 129.80, 129.61, 128.85, 127.44, 127.28, 126.66, 126.47, 124.26, 122.11, 121.80, 115.90, 115.29, 114.18, 113.97, 113.72, 113.23, 110.11, 71.94, 70.67, 70.55, 69.90, 69.84, 69.78, 67.32, 67.10, 59.01, 58.97, 34.40, 31.88, 29.62, 29.60, 29.49, 29.31, 29.27, 29.17, 24.92, 22.65, 14.09. ESI HRMS calcd for $C_{54}H_{66}N_3O_9$: 900.4799 $[M+H]^+$, found: m/z 900.4799.

Azadipyrromethene-laurate-N_3 (3). In a round bottom flask, **2** (100 mg, 1 equiv.), EDCI (252 mg, 3 equiv.) and DMAP (205, 3 equiv.) were added in dry dichloromethane (50 mL) and then was added 0.1 ml of azidoacetic acid. The reaction mixture was stirred under nitrogen at room temperature for 18 hours. Then, the solvent was evaporated *in vacuo* without heating. The solid residue was washed with water, dissolved in DCM, dried over $MgSO_4$ and purified by column chromatography (Hexane/DCM/acetone 50/40-30/10-20%), yielding **3** (F2, 20 mg, 17%) as dark blue solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.93-7.72 (m, 4H), 7.68-7.46 (m, 4H), 7.35 (bs, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.92-6.52 (m, 8H), 4.26-3.87 (m, 10H), 3.89-3.74 (m, 4H), 3.72-3.59 (m, 4H), 3.54-3.36 (m, 6H), 2.40-2.35 (m, 2H), 2.08-1.60 (m, 2H), 1.25 (m, 16H), 0.97-0.77 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.37, 160.25, 158.86, 158.55, 158.08, 158.04, 153.48, 150.70, 143.66, 137.63, 130.18, 129.90, 129.77, 128.88, 127.92, 127.34, 126.62, 124.39, 121.84, 115.95, 115.23, 114.05, 113.80, 113.70, 110.33, 109.97, 71.96, 70.57, 69.93, 67.30, 67.17, 58.99, 58.94, 31.91, 30.91, 29.64, 29.50, 29.44, 29.12, 24.95, 22.67, 21.21, 14.10.

azaBDP (4). In a stirred solution of **1** (200 mg, 0.279 mmol) in dry dichloromethane (30 mL) under N_2, was added diisopropylethylamine (361 mg, 2.79 mmol). The mixture was

stirred for 0.5 h, $BF_3{\cdot}Et_2O$ was added (593 mg, 4.179 mmol) add stirring continued for 18 h. Then, sat. aq. NH_4Cl (3 mL) was added, and the mixture stirred for 5 min. CH_2Cl_2 evaporated, water (20 mL) was added, the suspension filtered *in vacuo* and the filter cake washed successively with water, 1:1 MeOH/H_2O, MeOH (2x3 mL), Et_2O (3 mL) and petroleum ether affording **4** (213 mg, 100%) as violet dust. ^{1}H-NMR (300 MHz, DMSO-d_6): δ (ppm) 10.38 (bs, 2H), 8.14 (d, *J* = 8.6 Hz, 4H), 8.05 (d, *J* = 8.6 Hz, 4H), 7.41 (s, 2H), 7.12 (d, *J* = 8.6 Hz, 4H), 6.94 (d, *J* = 8.6 Hz, 4H), 4.22-4.17 (m, 4H), 3.80-3.75 (m, 4H), 3.64-3.58 (m, 4H), 3.50-3.45 (m, 4H), 3.26 (s, 6H); ^{13}C-NMR (75 MHz, DMSO-d_6): δ (ppm) 160.59, 159.77, 156.99, 144.08, 141.29, 131.84, 130.51, 124.69, 121.98, 117.75, 115.75, 114.84, 71.31, 69.75, 68.90, 67.37, 58.08. MALDI-MS calcd for $C_{42}H_{42}BF_2N_3O_8$: 765.3033 $[M]^+$, found: m/z 765.3021.

H_2P-azaBDP-N_3 (5). In a round bottom flask, H_2P-COOH (21 mg, 0.9 equiv.), **4** (28 mg, 1 equiv.), EDCI (19 mg, 3 equiv.) and DMAP (12 mg, 3 equiv.) were added in dry dichloromethane (50 mL) and the reaction was stirred under nitrogen at room temperature over 48 h. Once free porphyrin was not detected by thin layer chromatography, 0.1 mL of azidoacetic acid and EDCI was added to the reaction. The reaction mixture was stirred under nitrogen at room temperature for three days. Then, the solvent was evaporated *in vacuo* without heating. The residue was washed with water, dissolved in dichloromethane, dried over $MgSO_4$ and purified by column chromatography (Hexane/DCM/acetone 50/40-30/10-20%) (20 mg, 15%) as dark blue solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.98-8.78 (m, 8H), 8.62 (d, *J* = 7.9 Hz, 2H), 8.40 (d, *J* = 8.0 Hz, 2H), 8.30-8.15 (m, 7 H), 8.15-7.95 (m, 6H), 7.75 (m, 9 H), 7.54 (m, 3H), 7.12-6.85 (m, 8H), 4.22 (m, 4H), 4.22 (m, 2H), 3.94 (m, 4H), 3.82-3.69 (m, 4H), 3.63 (m, 4H), 3.46-3.35 (m, 6H), -2.75 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.00, 160.28, 152.96, 147.98, 145.57, 143.87, 142.02, 142.01, 141.98, 134.81, 134.53, 132.07, 131.59, 131.20, 131.18, 131.16, 131.10, 130.93, 130.88, 130.78,130.75, 130.62, 130.61, 129.62, 128.70, 128.66, 128.59, 127.79, 127.77,126.70, 126.58, 126.54, 125.42, 122.06, 121.80, 121.36, 120.66, 120.64, 120.44, 120.42, 118.22, 118.20, 114.89, 114.70, 71.98, 70.82, 69.69, 67.56, 59.11, 50.46. MALDI-MS calcd for $C_{89}H_{72}BF_2N_{10}O_{10}$: 1489.5494 $[M+H]^+$, found: m/z 1489.5518.

ZnP-azaBDP-N_3 (6). Zinc acetate (20 mg) in 2 mL of MeOH was added to a solution of **5** (20 mg) in dichloromethane (8 mL) at room temperature and stirred under N_2 atmosphere. The reaction was stirred overnight. After that the solvent was evaporated *in vacuo*, the residue was dissolved in DCM (20 mL) and the solution washed with H_2O (2 x 50 mL), dried over $MgSO_4$ and concentrated *in vacuo* affording **6** as dark blue/purple solid in 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.96 (s, 8H), 8.61 (d, *J* = 7.9 Hz, 2H), 8.40 (d, *J* = 6.8 Hz, 2H), 8.31-7.85 (m, 13H), 7.78 (m, 9H), 7.53 (m, 3H), 6.98 (m, 8H), 4.19 (s, 6H), 3.89 (s, 4H), 3.74 (s, 4H), 3.60 (s, 4H), 3.40 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.12, 165.05, 164.62, 160.20, 159.72, 158.06, 152.98, 150.38, 150.27, 150.20, 149.48, 148.74, 143.80, 142.71, 134.70, 134.41, 132.38, 132.28, 132.16, 132.08, 132.01, 131.46, 131.15, 130.90, 130.88, 130.74, 129.55, 128.44, 127.53, 126.76, 126.55, 125.42, 122.04, 121.80, 121.55, 121.35, 119.24, 115.94, 114.86, 114.68, 110.00, 77.00, 71.82, 70.65, 70.59, 69.68, 69.61, 67.48, 62.97, 59.52, 58.99, 53.41, 50.41.

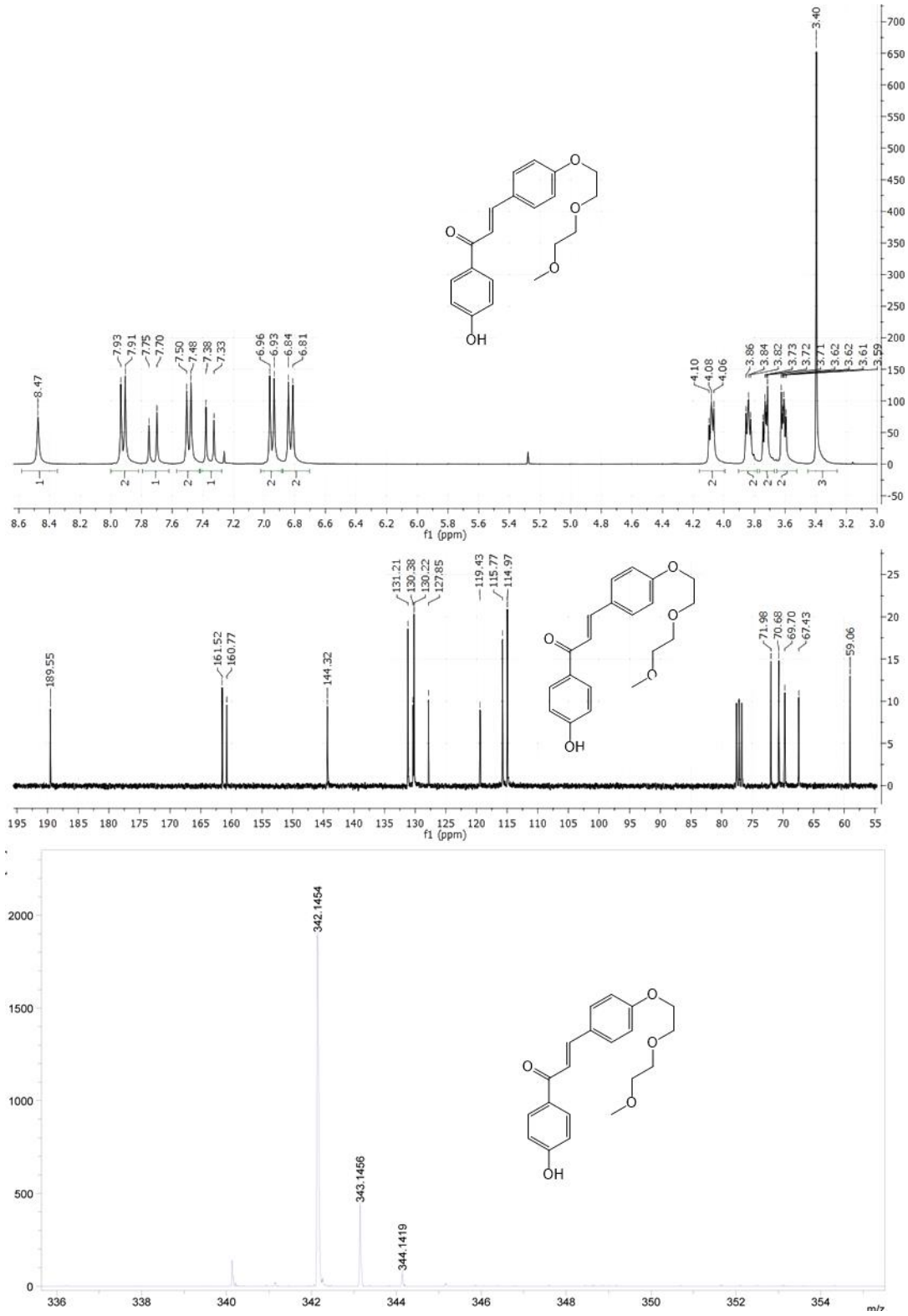


Figure S1. ^{1}H-NMR (top) and ^{13}C-NMR (middle) spectra and MALDI-MS (bottom) of **1c**.

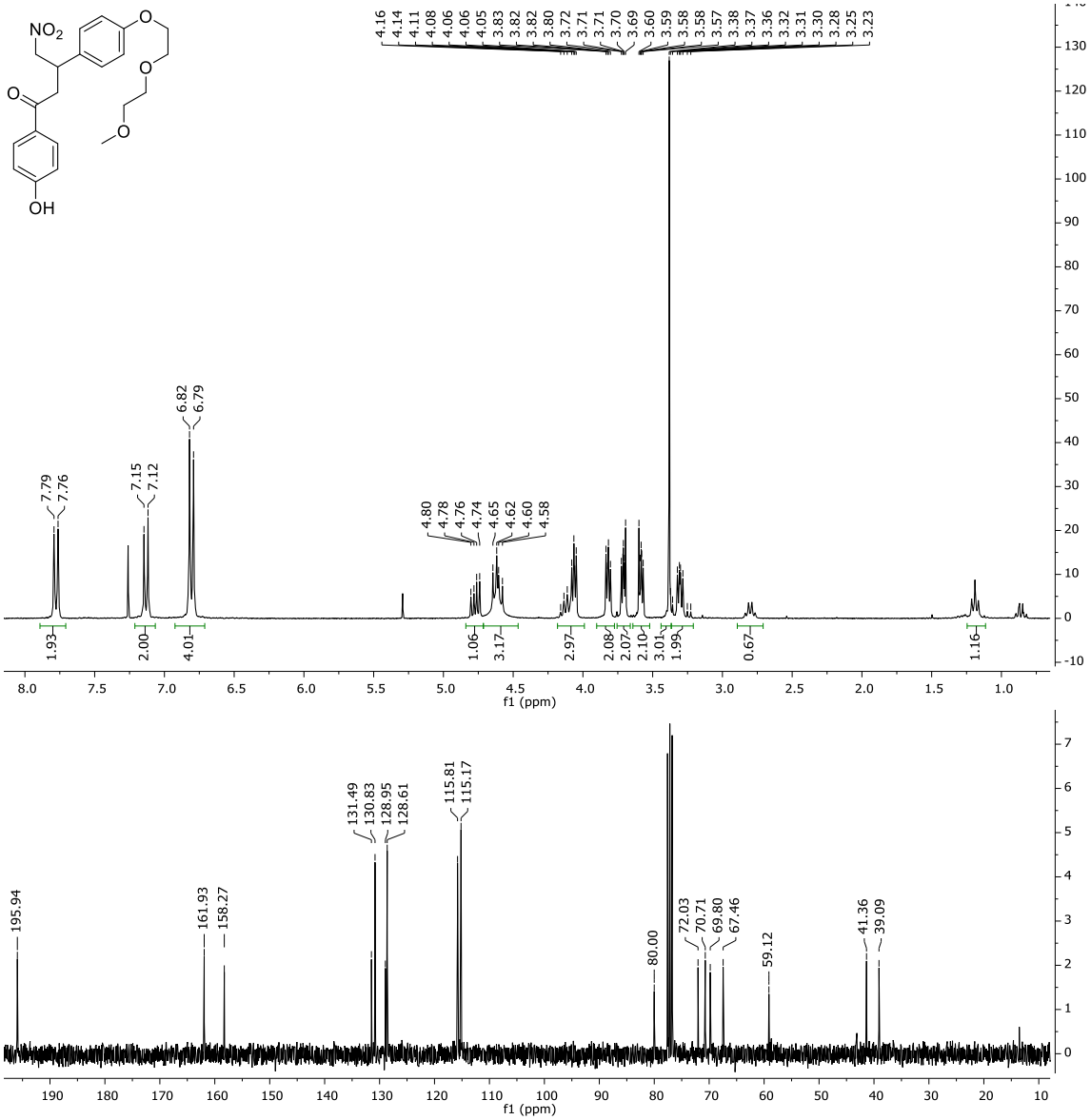


Figure S2. ^{1}H-NMR (top) and ^{13}C-NMR (bottom) spectra of **1d**.

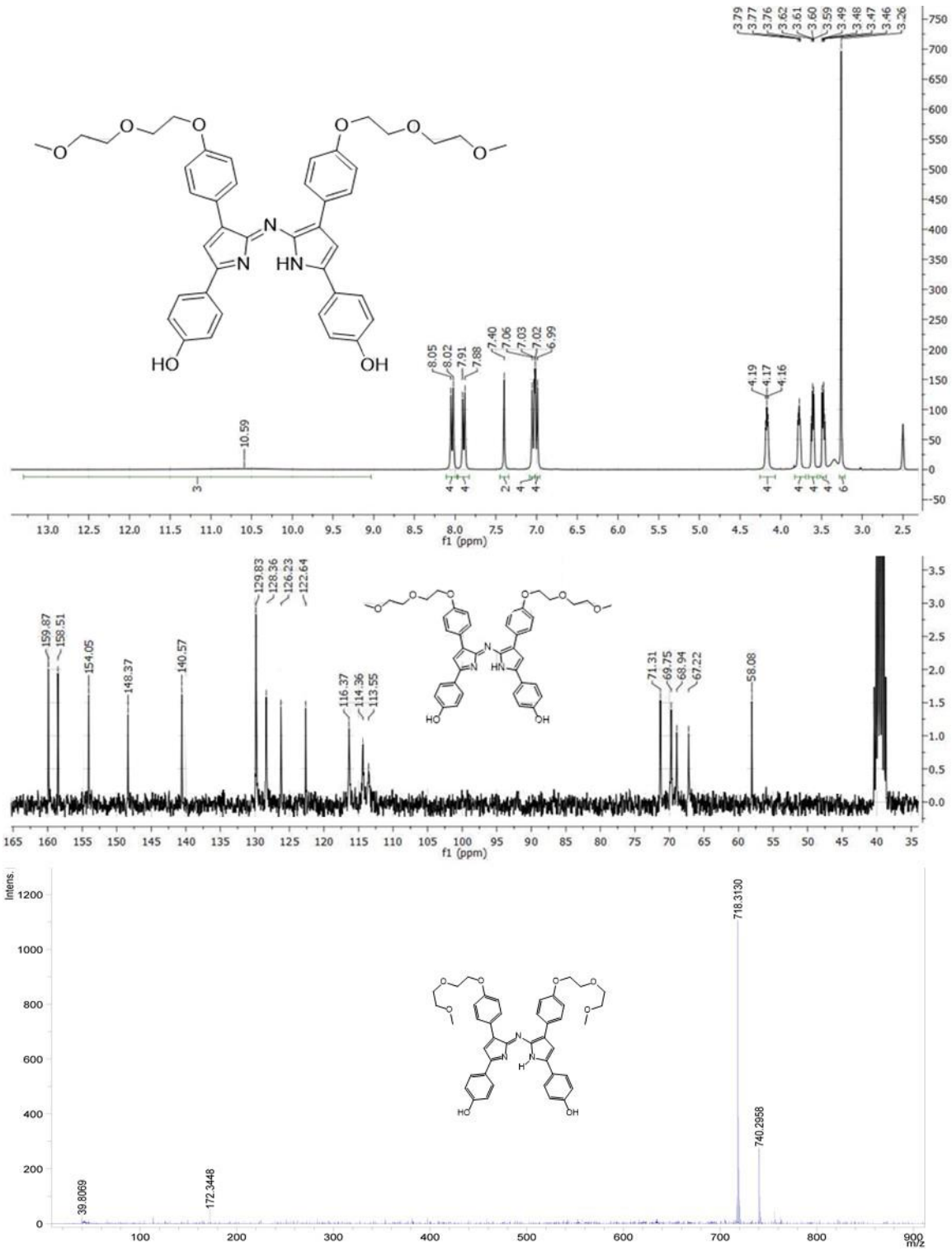


Figure S3. ^{1}H-NMR (top) and ^{13}C-NMR (middle) spectra and MALDI-MS (bottom) of **1**.

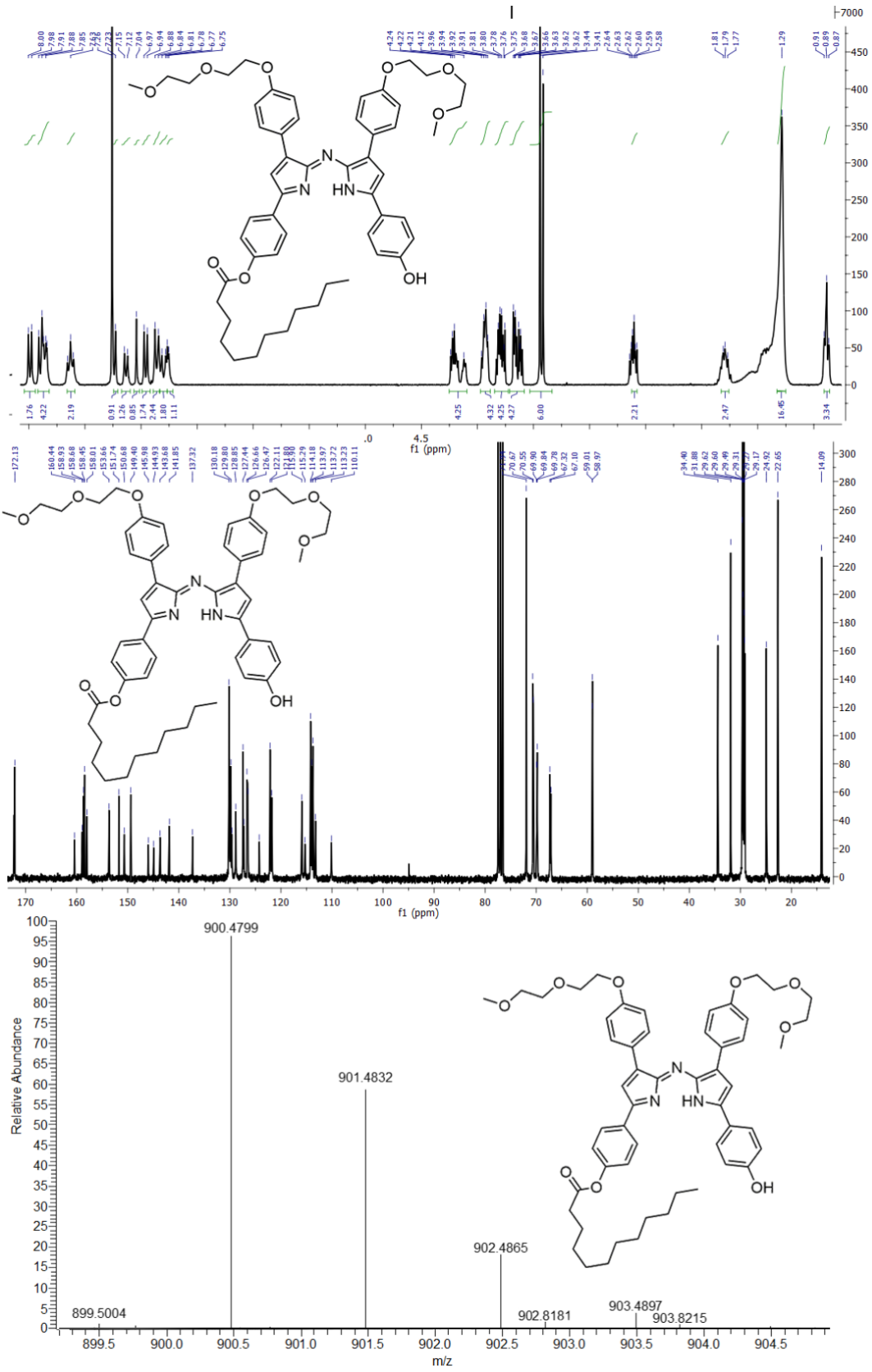


Figure S4. ^{1}H-NMR (top) and ^{13}C-NMR (middle) spectra and ESI-MS (bottom right) of **2**.

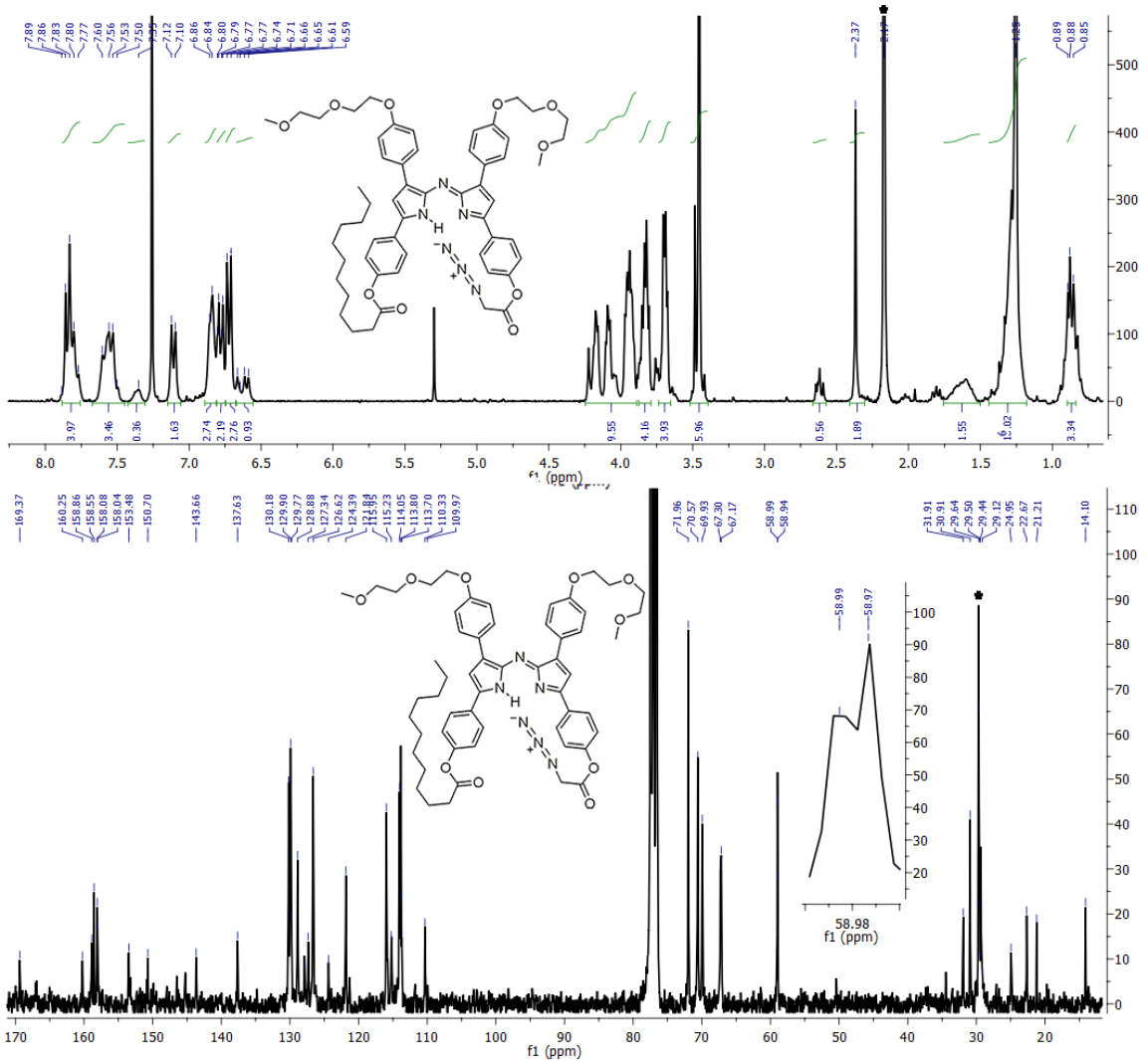


Figure S5. ^{1}H-NMR (top) and ^{13}C-NMR (bottom left) spectra of **3**. The symbol * shows impurity of acetone.

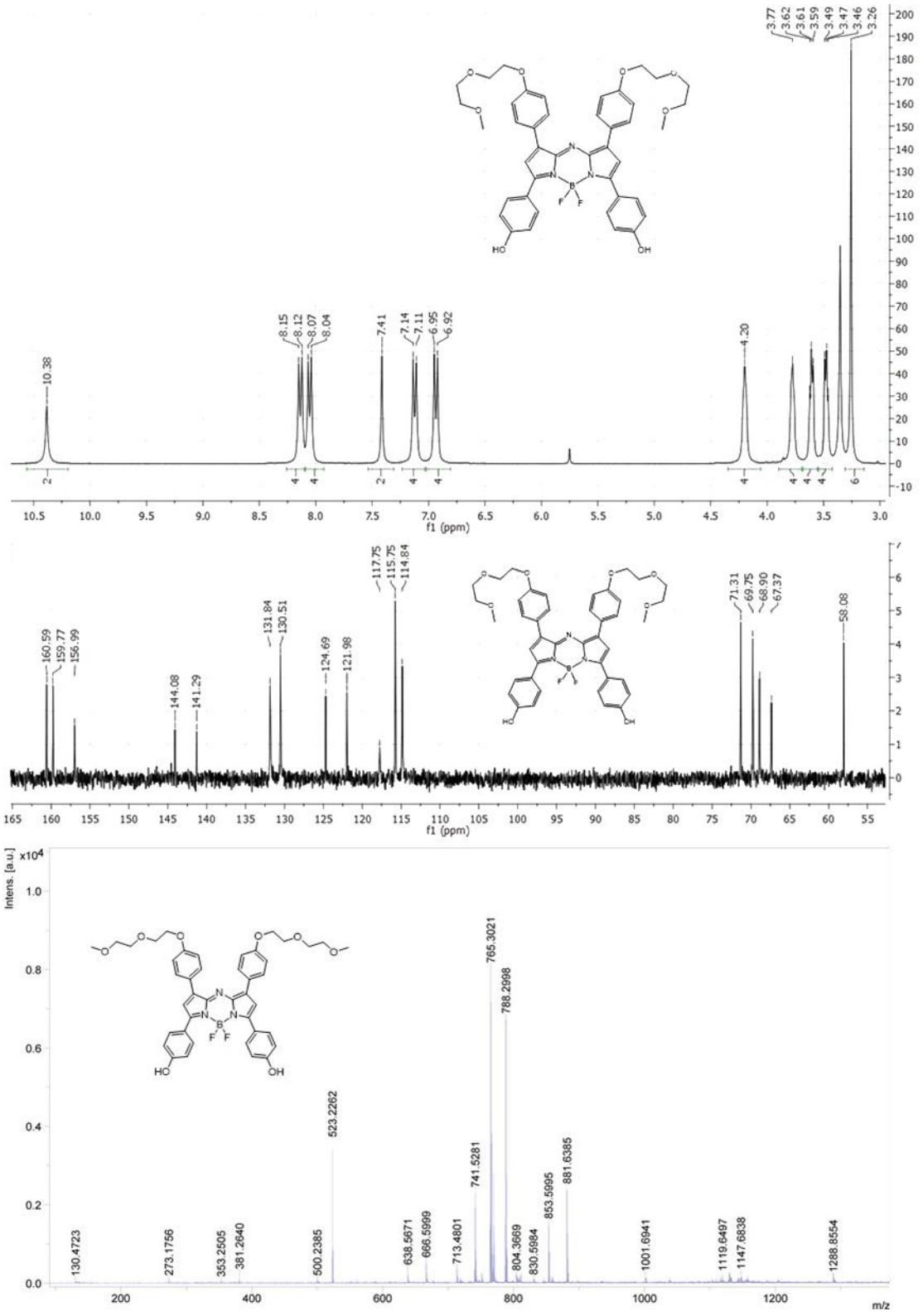


Figure S6. ^{1}H-NMR (top) and ^{13}C-NMR (middle) spectra and MALDI-MS (bottom) of **4**.

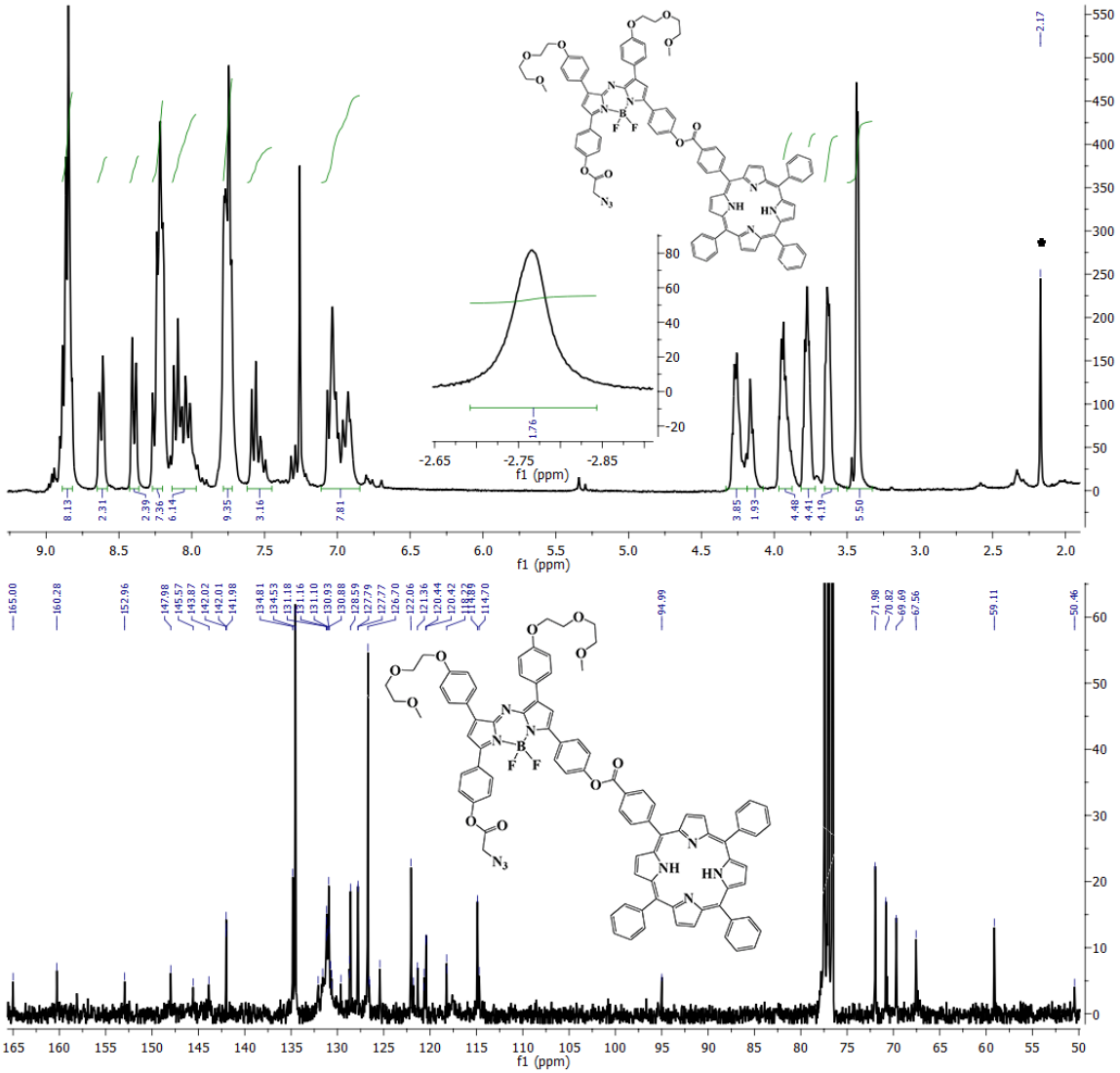


Figure S7. ^{1}H-NMR (top) and ^{13}C-NMR (bottom) spectra of **5**. The symbol * shows impurity of acetone.

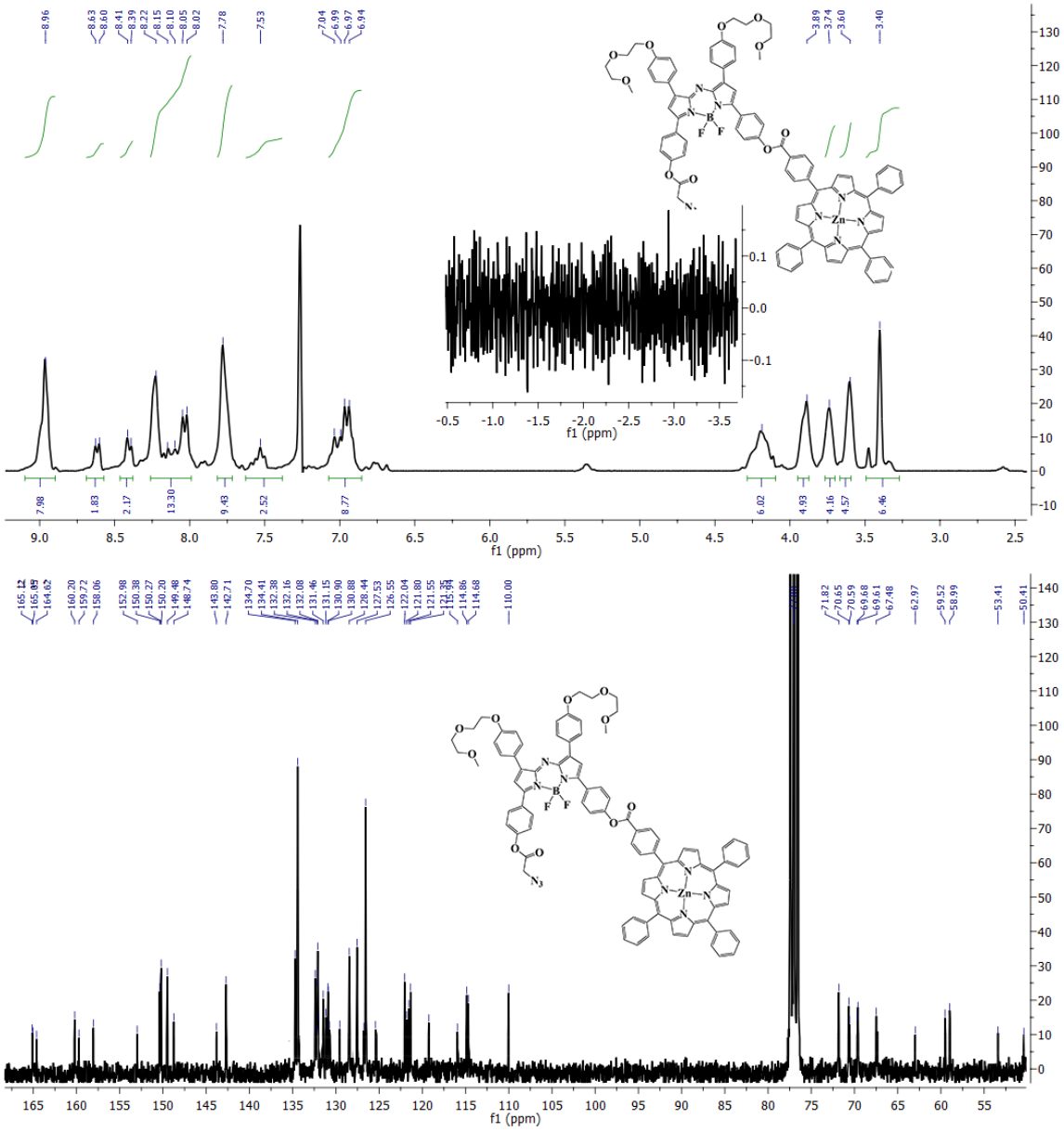


Figure S8. ^{1}H-NMR (top) and ^{13}C-NMR (bottom) spectra of **6**.

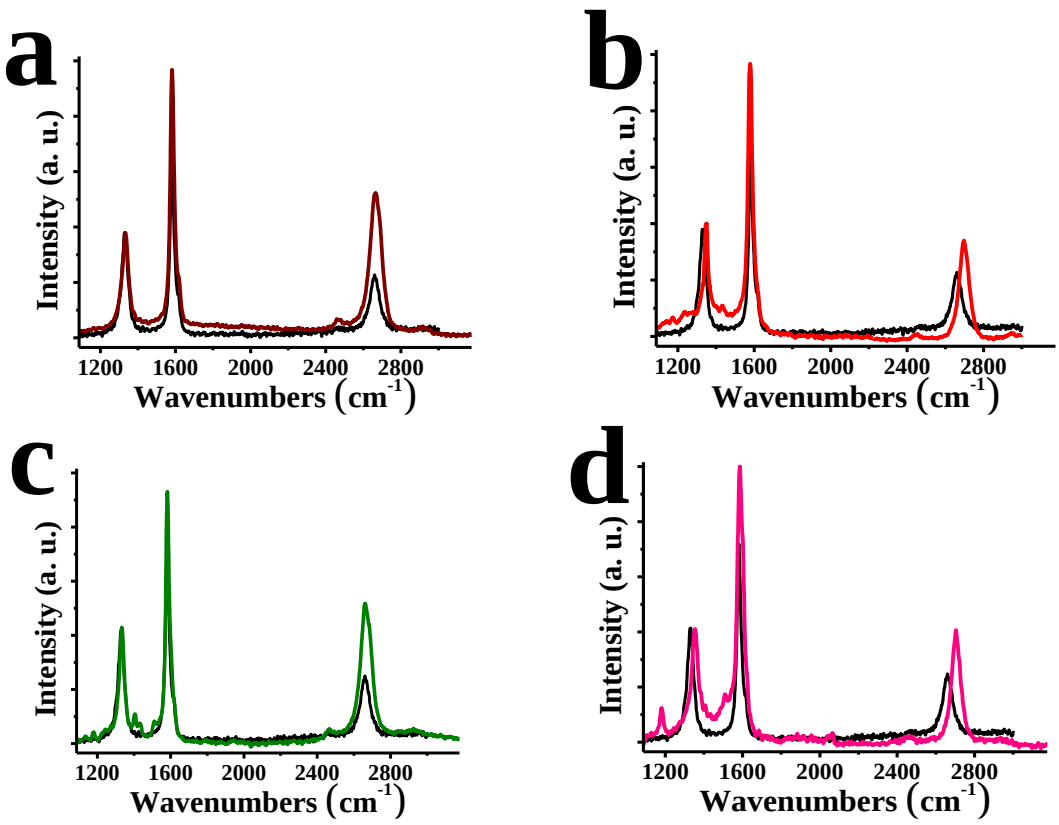


Figure S9. Raman spectra for graphene-based hybrid materials (a) **8**, (b) **9**, (c) **10**, and (d) **11**, compared to graphene-based material **7** (black) normalized at the D-band and obtained upon 633 nm excitation.

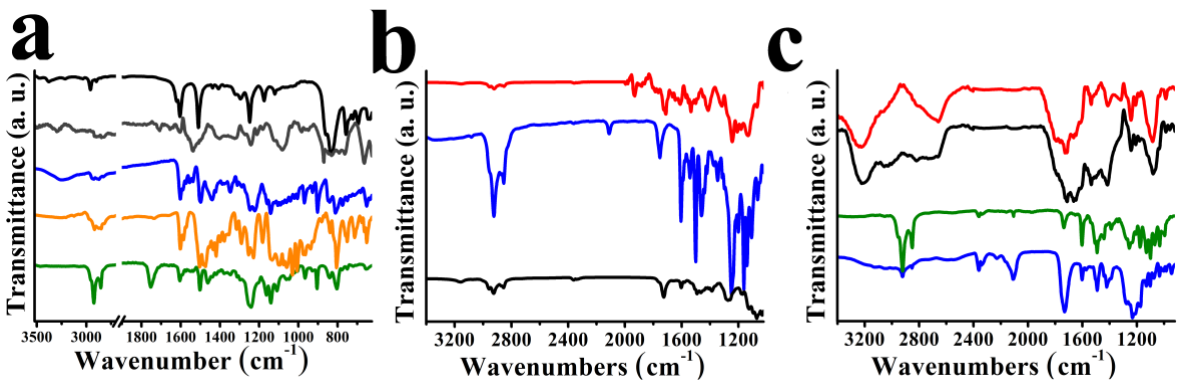


Figure S10. ATR-IR spectra for (a) 4-((trimethylsilyl)ethynyl)aniline (black), graphene-based material **7** (gray), **1** (blue), **2** (olive) and **4** (orange), (b) **3** (blue) and graphene-based hybrid materials **8** (black) and **9** (red), (c) **5** (blue), **6** (green) and graphene-based hybrid materials **10** (black) and **11** (red).

Figure S11. HR-TEM micrographs of graphene-based hybrid materials (a) **7**, (b) **8**, (c) **9** and (d) **10**. Representative HR-TEM micrographs of graphene-based hybrid materials (e) **9** and (f) **10**, at low magnification.

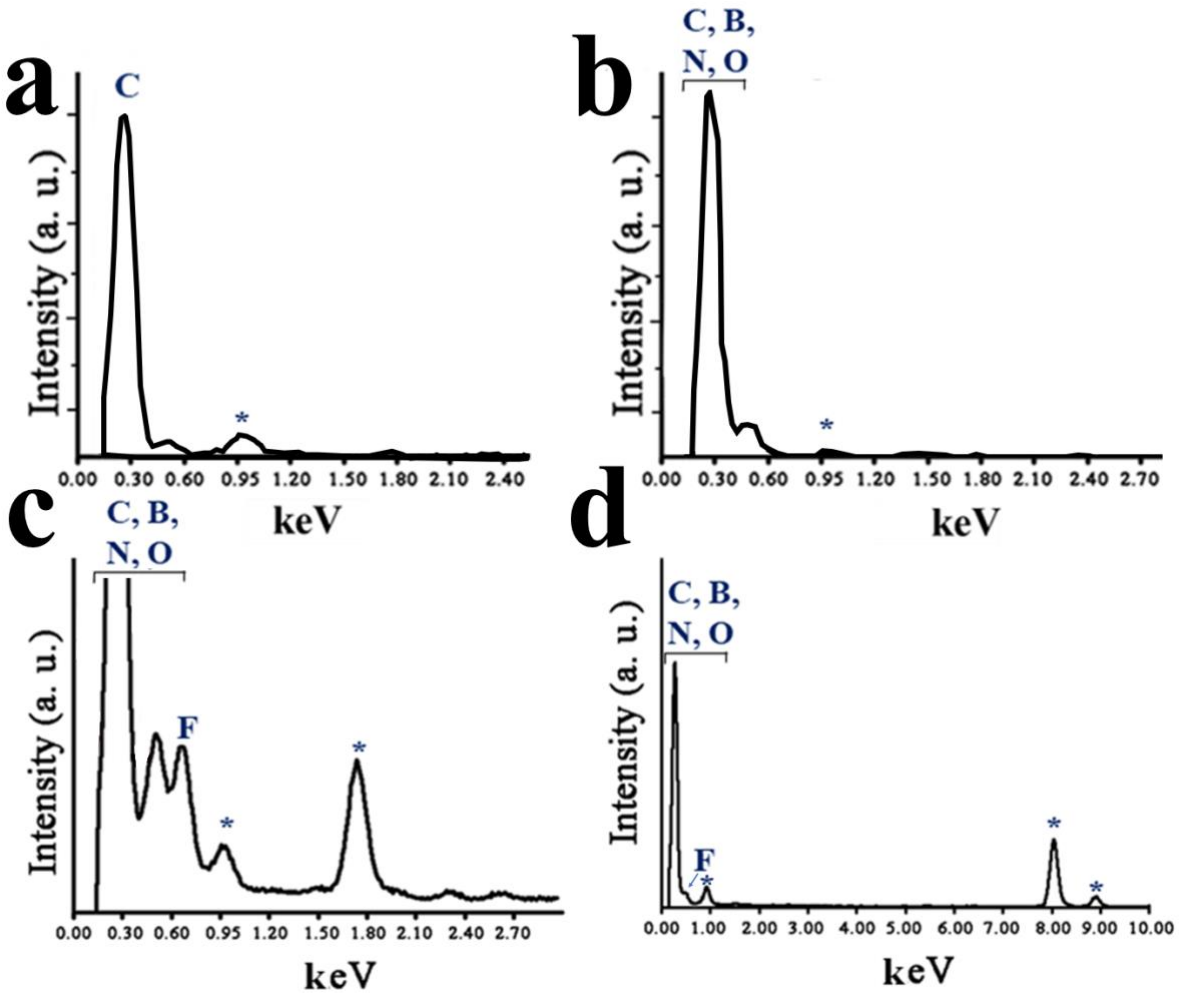


Figure S12. EDX of graphene-based hybrid materials (a) **7**, (b) **8**, (c) **9** and (d) **10**. The element of Cu, shown with *, is identified due to the TEM grid used.

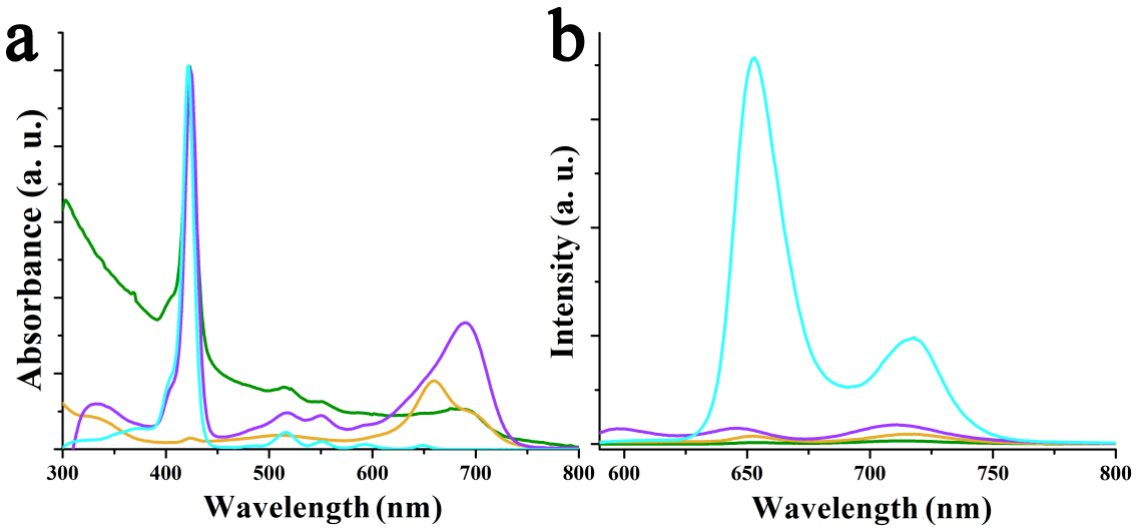


Figure S13. (a) UV-Vis and (b) fluorescence spectra of azaBDP compound **4** (orange), H_2P (cyan), H_2P-azaBDP dyad **5** (purple), (ZnP-azaBDP)-graphene hybrid **10** (green), upon excitation at 424 nm in *o*-DCB.

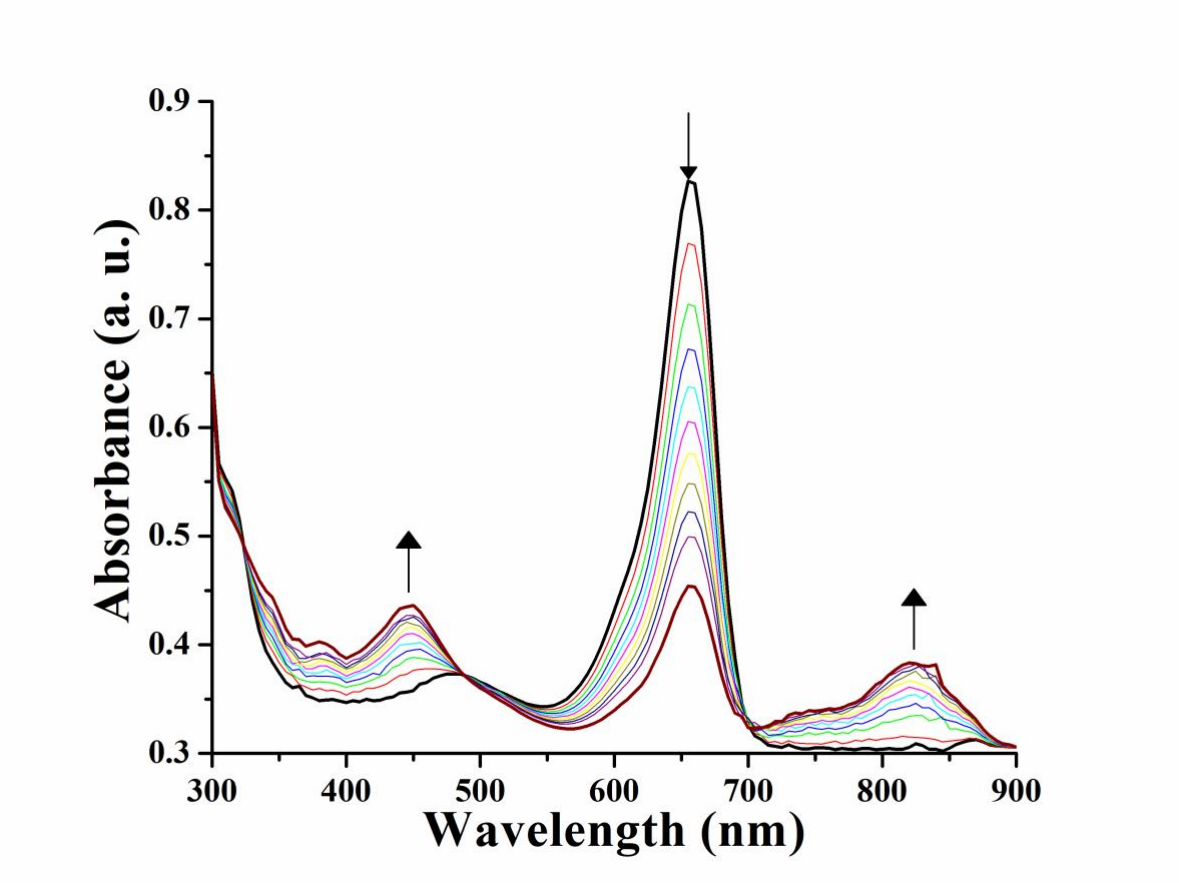


Figure S14. Spectral changes observed during first reduction of azaBDP compound **4** in *o*-DCB.

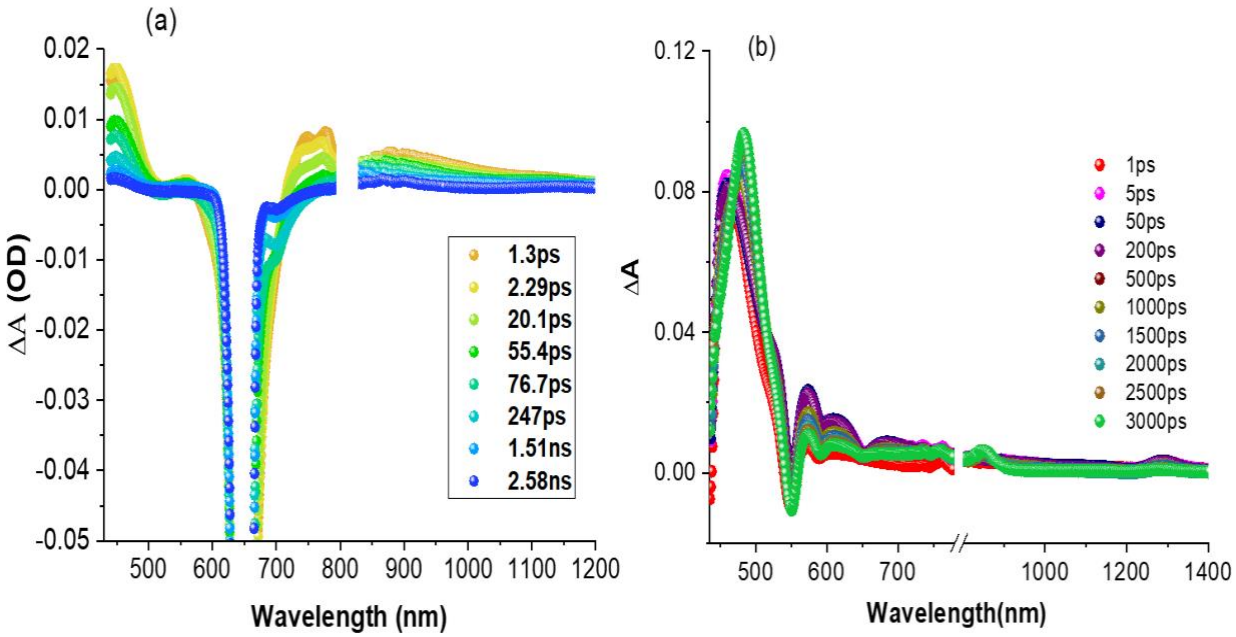


Figure S15. fs-TA at the indicated delay times of (a) azaBDP compound **4** (660 nm excitation) and (b) ZnP (424 nm excitation), in *o*-DCB.