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Supporting Information

Anti-Stokes Stress Sensing: Mechanochemical Activation of Triplet–Triplet Annihilation Photon Upconversion

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Experimental Procedure

Materials and Methods

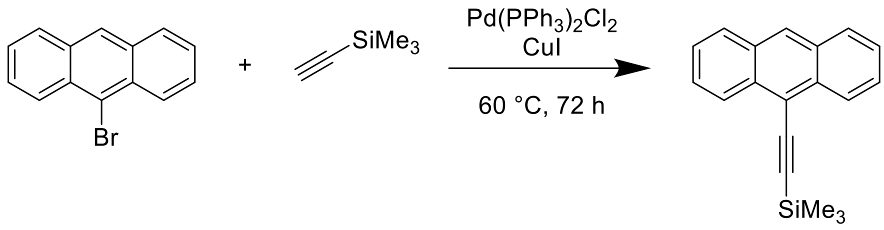
NMR spectra were recorded at room temperature in DMSO-d$_6$ or CHCl$_3$-d on a 400 MHz Bruker Avance 400 spectrometer (^{13}C: 101 MHz) or a 300 MHz Bruker DPX 300 spectrometer (^{13}C: 75 MHz). Chemical shifts are reported in δ units using residual protonated solvent signals as internal standard[1] (^{1}H: DMSO-d$_6$ (δ_H = 2.50 ppm) or CHCl$_3$-d (δ_H = 7.26 ppm); ^{13}C: DMSO-d$_6$ (δ_C = 39.52 ppm) or CHCl$_3$-d (δ_C = 77.16 ppm)). The following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, sept. = septet, dd = doublet of doublet etc., m = multiplet. Coupling constants (*J*) are given in Hz and refer to the given H,H-couplings. TLC was performed on Merck TLC Silica gel 60 F$_{254}$ TLC plates with a fluorescent indicator employing a 254 nm or 365 nm UV-lamp for visualization. Solvents and commercial starting materials were used as supplied and used without purification. Silica gel for chromatography (40-63 µm) was used for flash column chromatography. Precursor *N*-(2-hydroxyethyl)maleimide was synthesized according to the literature.[2–4] Prior to the polymerization, methyl acrylate was filtered over basic Al$_2$O$_3$. Cu^0-wire was activated with hydrazine and stored in the glovebox.[5] High-resolution ESI-TOF mass spectrometry was performed on a micrOTOF-QII instrument from Bruker Daltonik.

GPC (SEC) with THF (HPLC grade, VWR) as eluent was performed using a HPLC pump (PU-2080plus, Jasco) equipped with a refractive index detector (RI-2031plus, Jasco). The sample solvent contained 250 mg·mL^{-1} 3,5-di-*t*-4-butylhydroxytoluene (BHT, ≥99%, Fluka) as internal standard. One pre-column (8×50 mm) and four SDplus gel columns (8×300 mm, SDplus, MZ Analysentechnik) were applied at a flow rate of 1.0 mL·min^{-1} at 20 °C. The diameter of the gel particles was 5 µm, the nominal pore widths were 50, 10^2, 10^3, and 10^4 Å. Calibration was achieved using narrowly distributed poly(methyl methacrylate) standards (Polymer Standards Service). Molecular weights ($M_{n,\mathrm{SEC}}$ and $M_{w,\mathrm{SEC}}$) and molar mass distributions (M_w/M_n) were calculated by using the PSS WinGPC UniChrom software (Version 8.1.1).

Sonochemical irradiation experiments were carried out with a VibraCell$^{\mathrm{TM}}$ ultrasonic processor VCX500 purchased from Sonics & Materials in a Suslick vessel purchased from Sonics & Materials under inert atmosphere while cooling with an ice bath.

Syntheses

(Anthracen-9-ylethynyl)trimethylsilane (4)



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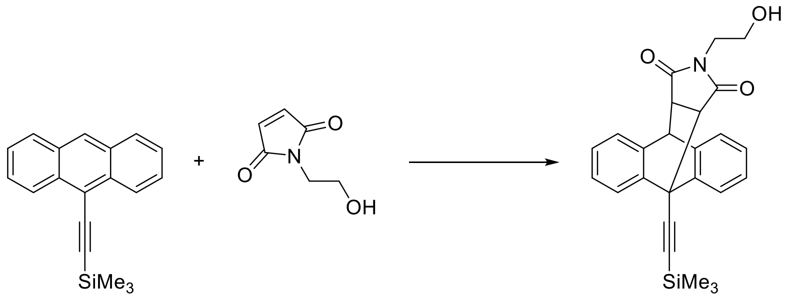
9-Bromoanthracene (10.0 g, 39.1 mmol, 1 eq.), $Pd(PPh_3)_2Cl_2$ (274 mg, 0.391 mmol, 0.01 eq.) , and CuI (74.5 mg, 0.391 mmol, 0.01 eq.) were degassed with three vacuum/N_2 cycles, dissolved in dry THF (70 mL) and DIPA (70 mL), followed by three Freeze-Pump-Thaw cycles. To this solution was added TMS-acetylene (6.67 mL, 46.9 mmol, 1.2 eq.) and the solution turned black. The mixture was stirred at 60 °C under N_2 for 72 h. After 24 h and 48 h, additional TMS-acetylene (3.34 mL, 23.5 mmol, 0.6 eq.) was added. Afterwards, the solution was cooled down and the solvent was removed *in vacuo*. Column chromatography (silica, cyclohexane with 1% toluene) yielded a red solid that was recrystallized from MeCN at -20 °C to give (anthracen-9-ylethynyl)trimethylsilane **4** (38% yield) as orange needles. **^{1}H NMR (400 MHz, Chloroform-d):** δ = 8.56 (dq, J = 8.7, 0.9 Hz, 2H), 8.42 (s, 1H), 8.00 (ddt, J = 8.5, 1.4, 0.7 Hz, 2H), 7.54 (m, 4H), 0.43 (s, 9H). See Figure S13. **^{13}C NMR (101 MHz, Chloroform-d):** δ = 133.05, 131.21, 128.78, 128.03, 126.93, 126.83, 125.79, 117.27, 106.35, 101.69, 0.43. See Figure S14.

13-(2-Hydroxyethyl)-9-((trimethylsilyl)ethynyl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione (5)

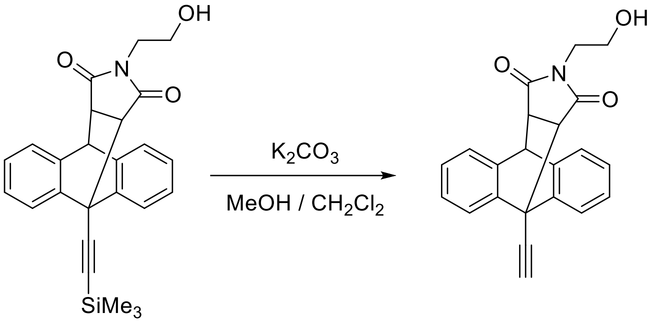


4

5

(Anthracen-9-ylethynyl)trimethylsilane **4** (1.95 g, 7.10 mmol, 1 eq.) and *N*-(2-hydroxyethyl)maleimide (1.50 g, 10.7 mmol, 1.5 eq.) were dissolved in Toluene (80 mL) and stirred o.n. at 120 °C. Evaporation of the solvent *in vacuo* and column chromatography (silica, cyclohexane : EtOAc = 1 : 1) yielded 13-(2-hydroxyethyl)-9-((trimethylsilyl)ethynyl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione **5** (89% yield) as white solid. **^{1}H NMR (400 MHz, Chloroform-d):** δ = 7.83 – 7.75 (m, 1H), 7.68 (dd, J = 7.3, 1.4 Hz, 1H), 7.42 – 7.35 (dd, J = 7.3, 1.4 Hz, 1H), 7.34 – 7.18 (m, 5H), 4.79 (d, J = 3.1 Hz, 1H), 3.33 (m, 2H), 3.29 – 3.22 (m, 2H), 3.09 (m, 2H), 1.17 (s, 1H), 0.41 (s, 9H). See Figure S15. **^{13}C NMR (101 MHz, Chloroform-d):** δ = 176.74, 174.46, 140.63, 140.12, 138.41, 137.63, 127.95, 127.50, 127.36, 127.07, 125.07, 124.28, 124.04, 124.03, 100.11, 96.83, 60.47, 50.74, 47.69, 47.46, 45.20. 41.52, 0.33. See Figure S16.

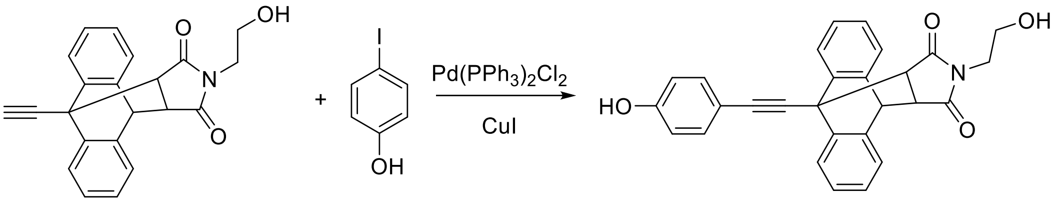
9-Ethynyl-13-(2-hydroxyethyl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione (6)



5 **6**

Potassium carbonate (332 mg, 2.40 mmol, 1 eq.) and 13-(2-hydroxyethyl)-9-((trimethylsilyl)ethynyl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione **5** (997 mg, 2.40 mmol, 1 eq.) were dissolved in a mixture of CH_2Cl_2 (25 mL) and MeOH (50 mL) and stirred at r.t. for 2 h. The conversion was monitored via TLC (EtOAc : PE = 1 : 1). Subsequently, to the solution was added brine and it was extracted with Et_2O (3×30 mL). The combined organic phases were dried over $MgSO_4$. The solvent was removed *in vacuo* and the resulting solid again dissolved in a small amount of CH_2Cl_2. Removal of the volatiles *in vacuo* yielded pure 9-ethynyl-13-(2-hydroxyethyl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione **6** (96% yield) as white foam. **^{1}H NMR (400 MHz, Chloroform-d):** δ = 7.87 – 7.79 (m, 1H), 7.77 – 7.68 (m, 1H), 7.43 – 7.38 (m, 1H), 7.36 – 7.19 (m, 5H), 4.82 (d, *J* = 3.0 Hz, 1H), 3.36 – 3.27 (m, 4H), 3.17 (s, 1H), 3.09 (q, *J* = 4.9 Hz, 2H). See Figure S17. **^{13}C NMR (101 MHz, Chloroform-d):** δ = 176.53, 174.85, 140.24, 140.00, 137.98, 137.59, 127.75, 127.65, 127.41, 127.15, 125.19, 124.14, 123.88, 79.67, 78.73, 60.36, 50.68, 47.61, 46.71, 45.16, 41.61. See Figure S18.

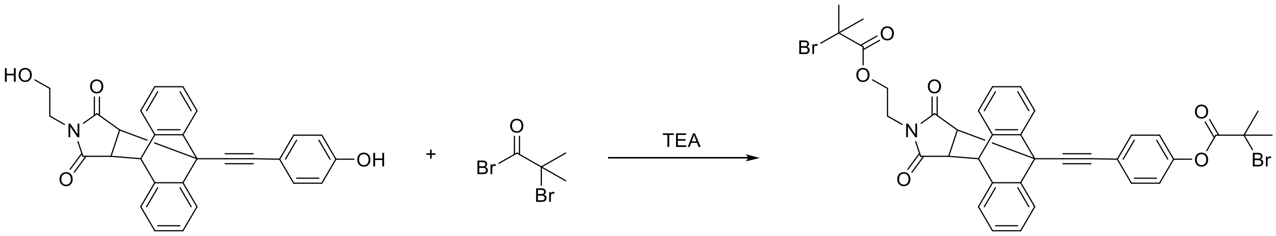
13-(2-Hydroxyethyl)-9-((4-hydroxyphenyl)ethynyl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione (7)



6 **7**

9-Ethynyl-13-(2-hydroxyethyl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione **6** (1.76 g, 5.13 mmol, 0.9 eq.), 4-iodophenol (1.25 g, 5.7 mmol, 1 eq.), $Pd(PPh_3)_2Cl_2$ (200 mg, 0.285 mmol, 0.05 eq.), and $Cu^{I}I$ (54.3 mg, 0.285 mmol, 0.05 eq.) were degassed with three vacuum/N_2 cycles. The mixture was dissolved in dry THF (15 mL). Dry DIPA (15 mL) was added whereupon the solution turned yellow. The whole was stirred at r.t. under N_2 for 24 h. Afterwards, the solution was cooled down, diluted with THF, and filtered over celite to remove the hydroiodide salt. Subsequent removal of the solvent *in vacuo* and column chromatography (silica, cyclohexane : EtOAc = 1 : 1, gradient to pure EtOAc) yielded 13-(2-hydroxyethyl)-9-((4-hydroxyphenyl)ethynyl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione **7** (40% yield) as off-white solid. **^{1}H NMR (400 MHz, DMSO-d$_6$):** δ = 9.94 (s, 1H), 7.76 (dd, *J* = 7.1, 1.6 Hz, 1H), 7.60 – 7.52 (m, 4H), 7.32 – 7.18 (m, 5H), 6.89 – 6.86 (m, 2H), 4.84 (d, *J* = 3.2 Hz, 1H), 4.62 (t, *J* = 5.9 Hz, 1H), 3.31 (s, 2H), 3.01 (t, *J* = 7.5 Hz, 2H), 2.60 – 2.52 (m, 2H). See Figure S19.

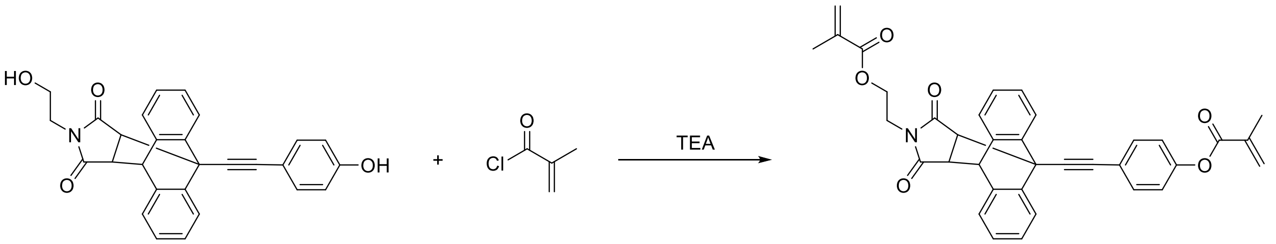
4-((13-(2-((2-Bromo-2-methylpropanoyl)oxy)ethyl)-12,14-dioxo-9,10-[3,4]epipyrroloanthracen-9(10H)-yl)ethynyl)phenyl 2-bromo-2-methylpropanoate (8)



7 **8**

Mechanophore **7** (96.3 mg, 0.220 mmol, 1 eq.) and Et_3N (57.1 µL, 0.462 mmol, 2.1 eq.) were placed in a Schlenk flask under N_2. To this mixture was added dry THF (2 mL) and the solution was cooled to 0 °C with an ice bath. Subsequently, α-bromoisobutyryl bromide (64.4 µL, 0.462 mmol, 2.1 eq) was added dropwise and the final solution was left to stir o.n. at r.t. All volatiles were removed *in vacuo* and subsequent column chromatography (silica, cyclohexane : EtOAc = 1 : 1 with 1% toluene) yielded 4-((13-(2-((2-bromo-2-methylpropanoyl)oxy)ethyl)-12,14-dioxo-9,10-[3,4]epipyrroloanthracen-9(10H)-yl)ethynyl)phenyl 2-bromo-2-methylpropanoate **8** (74% yield) as off-white solid. **^{1}H NMR (400 MHz, Chloroform-d):** δ = 7.86 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.83 – 7.78 (m, 2H), 7.72 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.41 (dd, *J* = 6.9, 1.5 Hz, 1H), 7.34 – 7.17 (m, 6H), 4.82 (d, *J* = 1.8 Hz, 1H), 3.69 (dt, *J* = 11.5, 6.0 Hz, 1H), 3.58 (dt, *J* = 11.5, 6.0 Hz, 1H), 3.40 (ddt, *J* = 19.7, 14.0, 6.8 Hz, 2H), 3.32 (d, *J* = 1.7 Hz, 2H), 2.10 (s, 6H), 1.89 (s, 6H). See Figure S20. **^{13}C NMR (101 MHz, Chloroform-d):** δ = 175.83, 173.93, 171.39, 170.18, 151.08, 140.91, 140.20, 138.08, 137.33, 133.51, 127.80, 127.56, 127.48, 127.10, 125.14, 124.21, 124.18, 123.90, 121.52, 121.02, 90.60, 84.57, 62.29, 55.73, 55.38, 51.06, 47.82, 47.34, 45.13, 36.87, 30.85, 30.78. See Figure S21.

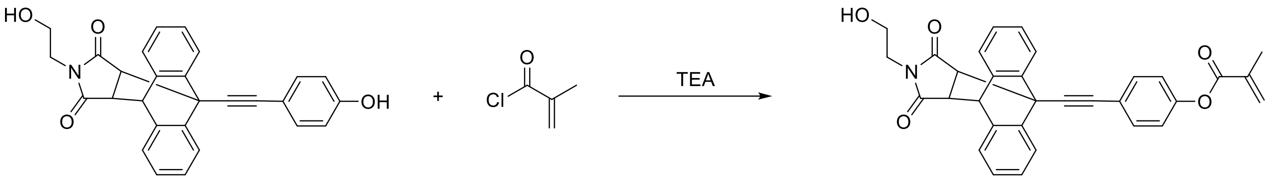
4-((13-(2-(methacryloyloxy)ethyl)-12,14-dioxo-9,10-[3,4]epipyrroloanthracen-9(10H)-yl)ethynyl)phenyl methacrylate) (9)



7 **9**

Mechanophore **7** (525 mg, 1.20 mmol, 1 eq.) and Et_3N (0.327 mL, 2.52 mmol, 2.1 eq.) were dissolved in dry THF (5 mL) in a Schlenk tube under N_2. To this solution methacryloyl chloride (0.246 mL, 2.52 mmol, 2.1 eq.) was added at 0 °C whereupon the HCl salt precipitated. The whole was stirred at r.t. o.n. The volatiles were removed *in vacuo* and the residue filtered through neutral Al_2O_3 to yield 4-((13-(2-(methacryloyloxy)ethyl)-12,14-dioxo-9,10-[3,4]epipyrroloanthracen-9(10H)-yl)ethynyl)phenyl methacrylate **9** (40% yield) as colorless powder. The Material was stored at -20 °C in a Schlenk flask under Ar. **^{1}H NMR (300 MHz, Chloroform-d):** δ = 7.89 – 7.84 (m, 1H), 7.81 (dd, *J* = 8.9, 2.3 Hz, 2H), 7.71 – 7.65 (m, 1H), 7.41 (dd, *J* = 6.8, 1.8 Hz, 1H), 7.33 – 7.11 (m, 6H), 6.44 – 6.06 (m, 2H), 5.70 (dq, *J* = 64.7, 1.7 Hz, 2H), 4.83 (d, *J* = 2.0 Hz, 1H), 3.67 – 3.39 (m, 4H), 3.31 (d, *J* = 1.7 Hz, 2H), 2.10 (q, *J* = 1.7 Hz, 3H), 1.97 – 1.89 (m, 3H). See Figure S22.

4-((13-(2-hydroxyethyl)-12,14-dioxo-9,10-[3,4]epipyrroloanthracen-9(10H)-yl)ethynyl)phenyl methacrylate (10)



7 **10**

Mechanophore **7** (114 mg, 0.26 mmol, 1 eq.) and Et_3N (0.034 mL, 0.25 mmol, 0.95 eq.) were dissolved in dry THF (1.1 mL) in a Schlenk tube under N_2. To this solution methacryloyl chloride (0.024 mL, 0.25 mmol, 0.95 eq.) was added at 0 °C whereupon the HCl salt precipitated. The whole was stirred at r.t. o.n. The volatiles were removed *in vacuo* and subsequent column chromatography (silica, petrolether : EtOAc 3:7) yielded 4-((13-(2-hydroxyethyl)-12,14-dioxo-9,10-[3,4]epipyrroloanthracen-9(10H)-yl)ethynyl)phenyl methacrylate **10** (76% yield) as colorless powder. The Material was stored at -20 °C in a Schlenk flask under Ar. **^{1}H NMR (300 MHz, Chloroform-d):** δ = 7.92 – 7.70 (m, 4H), 7.49 – 7.06 (m, 8H), 6.39 (t, J = 1.2 Hz, 1H), 5.80 (p, J = 1.6 Hz, 1H), 4.84 (d, J = 1.8 Hz, 1H), 3.38 – 3.28 (m, 4H), 3.11 (dt, J = 7.3, 4.3 Hz, 2H), 2.09 (d, J = 1.2 Hz, 3H). See Figure S23. **^{13}C NMR (101 MHz, Chloroform-*d*):** δ = 176.71, 174.71, 165.70, 151.32, 140.83, 140.11, 138.59, 137.71, 135.85, 133.52, 133.46, 127.75, 127.68, 127.59, 127.38, 127.13, 125.18, 124.31, 124.18, 123.99, 122.04, 121.71, 120.45, 90.86, 84.15, 60.39, 51.00, 47.73, 47.39, 45.22, 41.55, 18.54. See Figure S24. **ESI$^+$ HRMS:** *m*/*z* = 504.1831 (calcd. 504.1805 for MH^+). See Figure S25.

Polymerizations

Controlled Radical Polymerization (PMA 2)

Stock solutions of $CuBr_2$ (ρ = 11.6 mg·mL^{-1}) and Me_6-TREN (ρ = 36.8 mg·mL^{-1}) in DMSO were prepared. Cu^0-wire (4.5 cm) was wrapped around a stir bar and attached to the top of the Schlenk flask with the help of a magnet. Filtered monomer methyl acrylate (3.16 mL, 34.9 mmol, 697 eq.), mechanophore initiator **8** (36.6 mg, 0.05 mmol,1 eq.), an aliquot of the $CuBr_2$ stock solution (2.50 µmol, 0.05 eq.), an aliquot of the Me_6-TREN stock solution (8.0 µmol, 0.16 eq.), and dry DMSO (3 mL) were degassed by Freeze-Pump-Thaw cycling. The polymerization commenced after dropping the copper-wire into the degassed mixture. The reaction mixture was stirred at 30 °C for 6 h. The mixture was diluted with THF and filtered over basic Al_2O_3. Subsequent removal of the solvent *in vacuo* and precipitation in cold MeOH (3×) yielded the desired polymer. M_n = 63.9 kDa and $Đ_M$ = 1.17 (Figure S26).

Bulk Rubber Network with 0.02 mol% Mechanophore Crosslinker (PHMA 1)

Hexyl methacrylate (3.85 mL, 19.5 mmol, 1 eq.) was mixed with dibenzoylperoxide (31.2 mg, 0.129 mmol, 0.0066 eq.), tetraethylene glycol dimethacrylate (0.191 mL, 98.0 µmol, 0.0098 eq), and methacrylate **9** (2.22 mg, 3.90 µmol, 0.0002 eq.) in a vial and flushed with Ar for 30 s. The mixture was pipetted into a Teflon mold and put in an oven at 60 °C for 6 h under N_2. The total crosslink percentage of the final material was 1 mol% of which 0.02 mol% consisted of mechanophore and 0.98% of TEGDMA.

Bulk Rubber Network with 1.00 mol% Mechanophore Crosslinker (PHMA 2)

Hexyl methacrylate (1.42 mL, 7.18 mmol, 1 eq.) was mixed with dibenzoylperoxide (11.5 mg, 47.5 µmol, 0.0066 eq.) and methacrylate **9** (41.0 mg, 71.8 µmol, 0.01 eq.) in a vial and flushed with Ar for 30 s. The mixture was pipetted into a Teflon mold and put in an oven at 60 °C for 6 h under N_2. The total crosslink percentage of the final material was 1 mol% of which 1 mol% consisted of mechanophore.

Bulk Rubber Network with 0.02 mol% Terminal Mechanophore (PHMA 3)

A stock solution of methacrylate **10** in toluene (6.38 mg·mL^{-1}) was prepared. Hexyl methacrylate (1.25 mL, 6.33 mmol, 1 eq.) was mixed with dibenzoylperoxide (20.5 mg, 0.042 mmol, 0.0066 eq.), tetraethylene glycol dimethacrylate (20.5 mg, 0.042 mmol, 0.0066 eq.), and an aliquot of methacrylate stock solution (100 µL, 1.27 µmol, 0.0002 eq.) in a vial and flushed with Ar for 30 s. The mixture was pipetted into a Teflon mold and put in an oven at 60 °C for 6 h under N_2. The total crosslink percentage of the final material was 0.098 mol% (TEGDMA). Additionally, 0.02 mol% terminal mechanophore was incorporated into the polymer network.

Bulk Rubber Network with 0.02 mol% ATRP Mechanophore (PHMA 4)

A stock solution of mechanophore **8** in toluene (9.29 mg·mL^{-1}) was prepared. Hexyl methacrylate (1.25 mL, 6.33 mmol, 1 eq.) was mixed with dibenzoylperoxide (20.5 mg, 0.042 mmol, 0.0066 eq.), tetraethylene glycol dimethacrylate (18.9 µL, 62.0 µmol, 0.0098 eq.), and an aliquot of mechanophore stock solution (100 µL, 12.7 µmol, 0.0002 eq.) in a vial and flushed with Ar for 30 s. The mixture was pipetted into a Teflon mold and put in an oven at 60 °C for 6 h under N_2. The total crosslink percentage of the final material was 0.098 mol% (TEGDMA). Additionally, 0.02 mol% mechanophore was blended into the polymer matrix.

Bulk Rubber Network without Mechanophore (PHMA 5)

Hexyl methacrylate (3.85 mL, 19.5 mmol, 1 eq.) was mixed with dibenzoylperoxide (31.2 mg, 0.129 mmol, 0.0066 eq.), tetraethylene glycol dimethacrylate (0.191 mL, 98.0 µmol, 0.01 eq) in a vial and flushed with Ar for 30 s. The mixture was pipetted into a Teflon mold and put in an oven at 60 °C for 6 h under N_2. The total crosslink percentage of the final material was 1 mol% (TEGDMA).

Sonication Experiments

Polymer **2** (520 mg, 8.14 µmol) was dissolved in degassed toluene (10 mL) under nitrogen and placed in an ice bath. The solution ($8.14{\cdot}10^{-4}$ M) was sonicated with a 13 mm probe. The frequency of ultrasonication was 20 kHz, at 30% of the maximum amplitude of 125 µm. Samples were collected before sonication and every 90 min for 6 h. The samples were filtrated with a 0.45 µm syringe filter and diluted with degassed toluene by a factor of 3 to prepare stock solutions to reduce the perturbation in spectra resulting from the inner filter effect as well as to accommodate the Lambert-Beer law. The stock solutions were used for GPC (Figures S26 and S27) and further analysis.

UV-vis and Fluorescence Spectroscopy

UV-vis absorption spectroscopy was performed on a Thermo Evolution 300 spectrometer and fluorescence spectroscopy on a Horiba Fluoromax-4P spectrometer at room temperature. The absorption spectra were acquired with a background correction function. For fluorescence measurements, spectral bandwidths were set to 1 and 0.5 nm, respectively for excitation and emission. The data interval was set to 1 nm and the integration time was 0.1 sec. All spectroscopic measurements were carried out with quartz cuvettes purchased from Hellma Analytics. Table S1 summarizes the photophysical properties of *p*-methoxyphenylethynylanthracene (PMPEA) and PtOEP **3**.

Upconversion Experiments

Experiments with PMPEA

The upconversion data of PMPEA in toluene was recorded on an AIQTEC microscopic imaging spectrometer (MIS1000). The samples were irradiated at 540 nm (0.955 $\mathrm{mW{\cdot}cm^{-2}}$) tuned by a frequency tripled Nd:YAG laser source with an optical parametric oscillator. The pulse duration was 10 ns at a repetition rate of 10 or 20 Hz. The system is equipped with a monochromator using diffraction grating of 300 lines and a cooled intensified charge-coupled device detector. Background correction and spectra were acquired by accumulating 100 pulses. The excitation intensity was adjusted by neutral density filters purchased by Thorlabs and the power of the laser is measured with a thermoelectric detector. The solutions were prepared in toluene degassed with N_2 for 30 min prior to use. Quartz cuvettes containing the solutions were placed horizontally on the inverted microscope, collinearly to the detector, and the focal point of the laser beam was focused within the solution. The emission was recorded by focusing onto the entrance slit of the spectrometer (Figures S1 – S4).

Experiments with PMA-2

The upconversion data of PMA before and after sonication were recorded on Horiba Fluoromax-4P spectrometer (150 W ozone-free Xenon arc-lamp) through a shortpass filter (500 nm) purchased from Thorlabs placed on the detection window. The spectral bandwidths were set to 10 and 5 nm, respectively for excitation and emission and the excitation wavelength was set to 540 nm. The samples were prepared by adding PtOEP under Ar to the stock solutions from sonication experiments to have the final concentration of 8.8 µM PtOEP. The quartz cuvettes containing solutions were placed in a square sample holder and the UC signal was recorded by the detector at right angle to the incident beam (Figures S5 – S7).

Experiments with PHMA in the Solid State

The upconversion experiments in solid state were performed with 532 nm Green DPSS Laser Pointer (50 mW) purchased by Roithner Lasertechnik. Shortpass filter (500 nm) purchased from Thorlabs was used to isolate the laser beam from the spectra and the pictures. The crosslinked polymers (1.00 and 0.02 mol%) were fractured by uniaxial compression with a pellet press (10 t for 30 s). The polymers containing 0.02 mol% mechanophore crosslinker (10-15 mg) were submerged in 1 mL of PtOEP solutions (15 and 72 $\mathrm{\mu g{\cdot}mL^{-1}}$) in $CHCl_3$ either before or after compression, as stated. The ones containing 1.00 mol% mechanophore crosslinker (15 mg) were submerged in

1 mL of PtOEP solutions (15, 30, 55 and 72 µg·mL^{-1}), respectively. The volume of remaining solution was measured to determine the volume of swollen PtOEP solution and the wt% of PtOEP in the sample was calculated accordingly. The mixtures were stirred for overnight in the dark, followed by evaporation of the solvent at 60 °C. The samples were deoxygenated by evacuating *in vacuo* and purging with Ar three times prior to the upconversion experiments (Figures S8 – S12).

Quantum Yield Measurements

The upconversion quantum yields of PMPEA/PtOEP **3** and PMA **1**/PtOEP **3** in toluene were calculated using the equation below, as described in the literature:[6]

$$\phi_{UC} = 2 \times \phi_{std} \times \frac{A_{std}}{A_{UC}} \times \frac{I_{UC}}{I_{std}} \times \left(\frac{\eta_{UC}}{\eta_{std}}\right)^2$$

where ϕ represents quantum yield, A represents absorbance, I represents the integrated area under the upconversion emission spectra, and η represents the refractive index of the solvent. The equation is multiplied by 2, because the upconversion process requires absorption of two photons to yield one upconverted photon emission. Rhodamine B in ethanol was used as reference fluorophore for the calculations. The fluorescence quantum yield of Rhodamine B is 0.5 in ethanol under 540 nm excitation. The integrated area under the emission spectrum of Rhodamine B was measured in the region from 560-590 nm, whereas it was measured in the region of 390-500 nm for the upconversion. The refractive indices of ethanol[7] and toluene[8] are 1.361 and 1.497, respectively.

All quantum yield measurements were carried out on the Horiba Fluoromax-4P spectrometer (150 W ozone-free Xenon arc-lamp). The spectral bandwidths were set to 2 and 1 nm, respectively for excitation and emission. The data interval was set to 0.1 nm and the integration time was 0.1 s. The stock solution collected from sonication experiments after 270 min was used for PLQY measurements. The free anthracene concentration was calculated to 128 µM *via* UV-vis absorption spectroscopy and PtOEP was added to the solution to yield a PMA anthracene **1**:PtOEP **3** ratio of 1:15. The solution containing PMPEA and PtOEP **3** are prepared with the same concentrations as the references.

DFT Calculations

The density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations presented in this paper were performed using GAMESS.[9,10] Geometry optimizations were carried out by hybrid functional B3LYP with PCSEG-1 basis set. The geometries obtained were verified as global minima. Molecular visualizations (Figure S28) were done with MacMolPlt.

Results and Discussion

Table S1. Photophysical Properties of PMPEA and PtOEP **3**[a]

	Absorbtion (λ_{exc})	Emission (λ_{em})	ε_{max}[b] [L·mol^{-1}·cm^{-1}]
PMPEA	407* 428	435 458	17900 15700
PtOEP	385 540*	643	62800

[a] Measured in deoxygenated toluene. [b] Molar absorptivity was calculated for maximum absorption indicated with *.

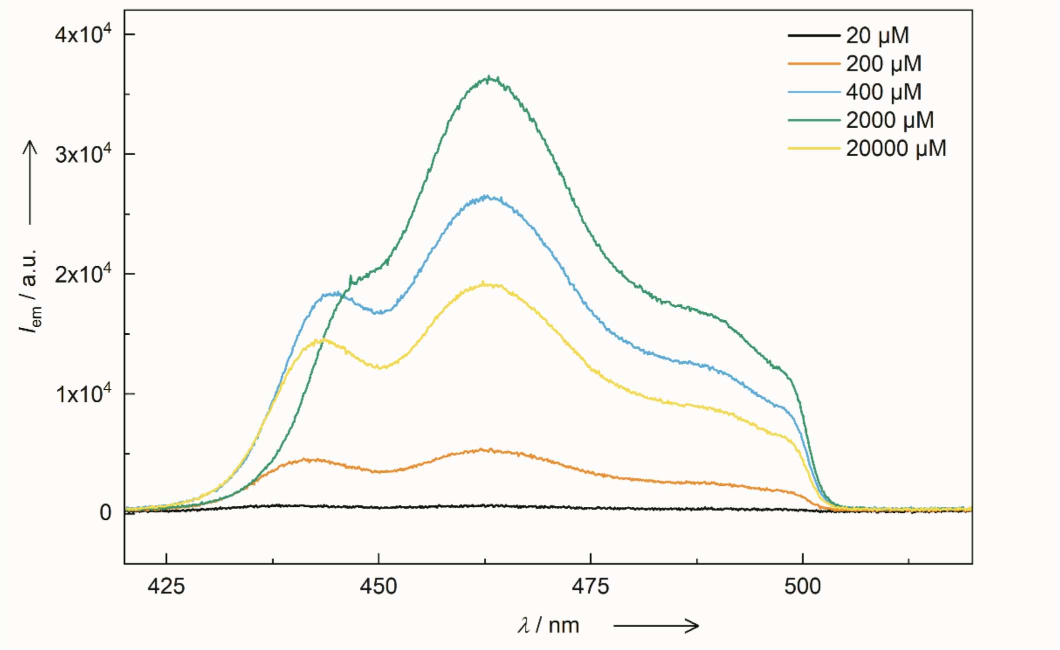


Figure S1. TTA-UC spectra of solutions containing PtOEP **3** (20 µM) with different concentrations of *p*-methoxyphenylethynylanthracene (1, 10, 20, 100, and 1000 eq.) in deoxygenated toluene (λ_{exc} = 540 nm). We attribute the altered vibronic substructure with increasing concentrations to self-quenching and inner-filter effects of the emitter **1**. The spectra were recorded on an AIQTEC microscopic imaging spectrometer in collinear detection mode.

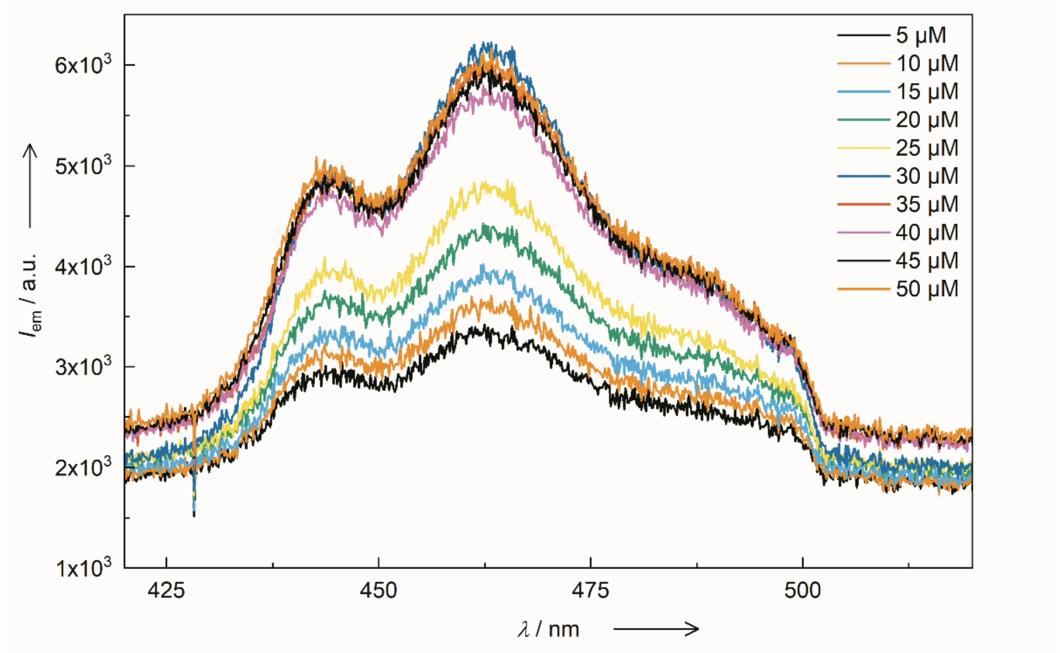


Figure S2. TTA-UC spectra of solutions containing *p*-methoxyphenylethynylanthracene (400 µM) with different PtOEP **3** concentrations in deoxygenated toluene (λ_{exc} = 540 nm). The spectra were recorded on an AIQTEC microscopic imaging spectrometer in collinear detection mode.

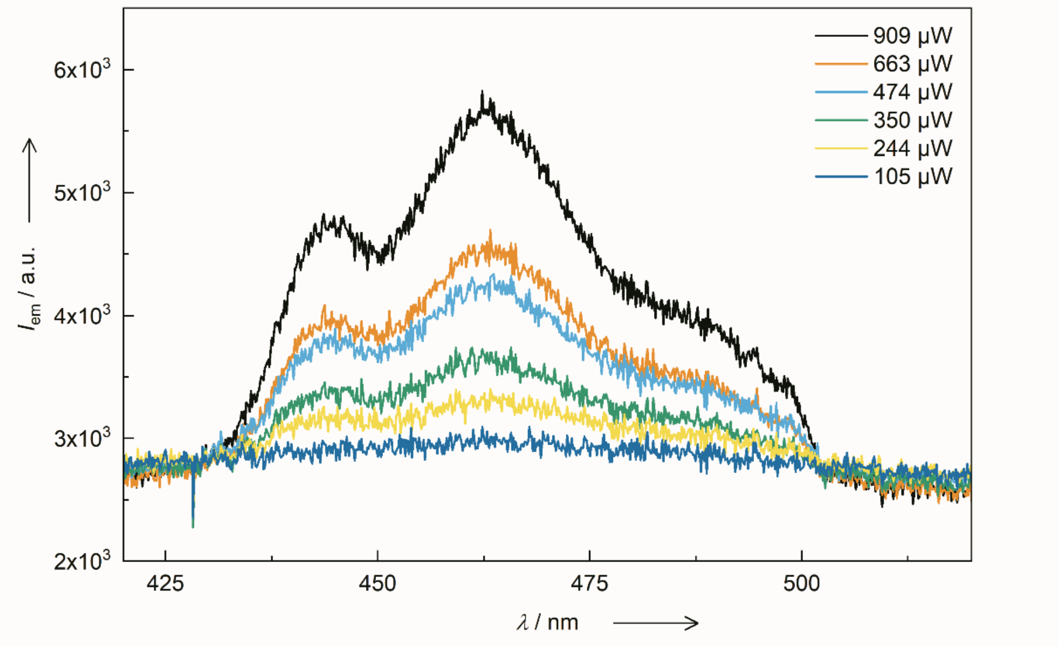


Figure S3. TTA-UC spectra of solution containing PtOEP **3** (30 µM) and *p*-methoxyphenylethynylanthracene (400 µM) in deoxygenated toluene under varying excitation energies (λ_{exc} = 540 nm). The spectra were recorded on an AIQTEC microscopic imaging spectrometer in collinear detection mode.

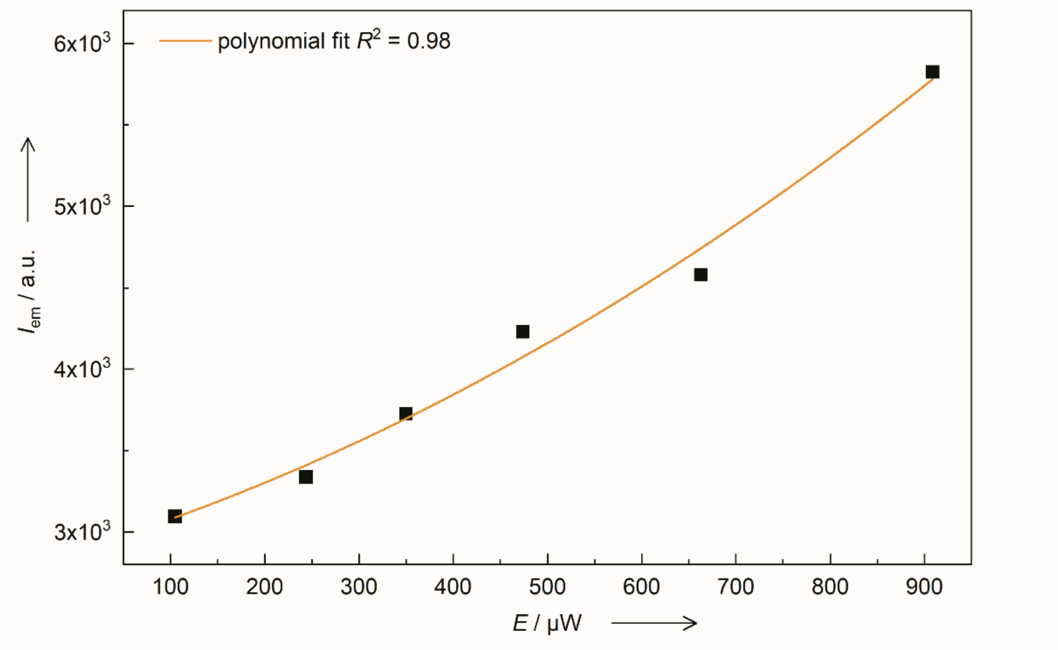


Figure S4. TTA-UC intensity at λ_{em} = 462 nm of solution containing PtOEP **3** (30 µM) and *p*-methoxyphenylethynylanthracene (400 µM) in deoxygenated toluene under varying excitation energies (λ_{exc} = 540 nm). Polynomial fit is shown demonstrating the characteristic non-linear dependency of the emission intensity from the excitation energy. Linear fit of the data set yielded a worse R^2 of 0.96.

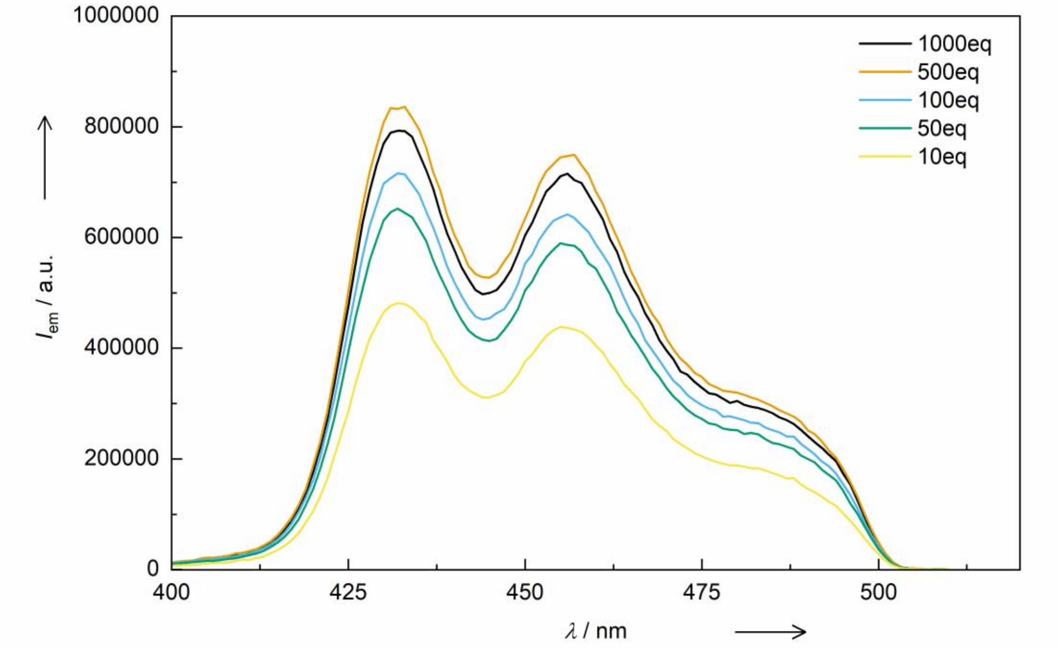


Figure S5. TTA-UC spectra of solution containing PtOEP **3** (0.184 µM, 0.368 µM, 1.84 µM, 3.68 µM, and 18.4 µM) and PMA-anthracene **1** (6 h sonicated sample, 184 µM free anthracene) in different molar ratios in deoxygenated toluene (λ_{exc} = 540 nm). The spectra were recorded on a Horiba Fluoromax-4P spectrometer in rectangular detection mode.

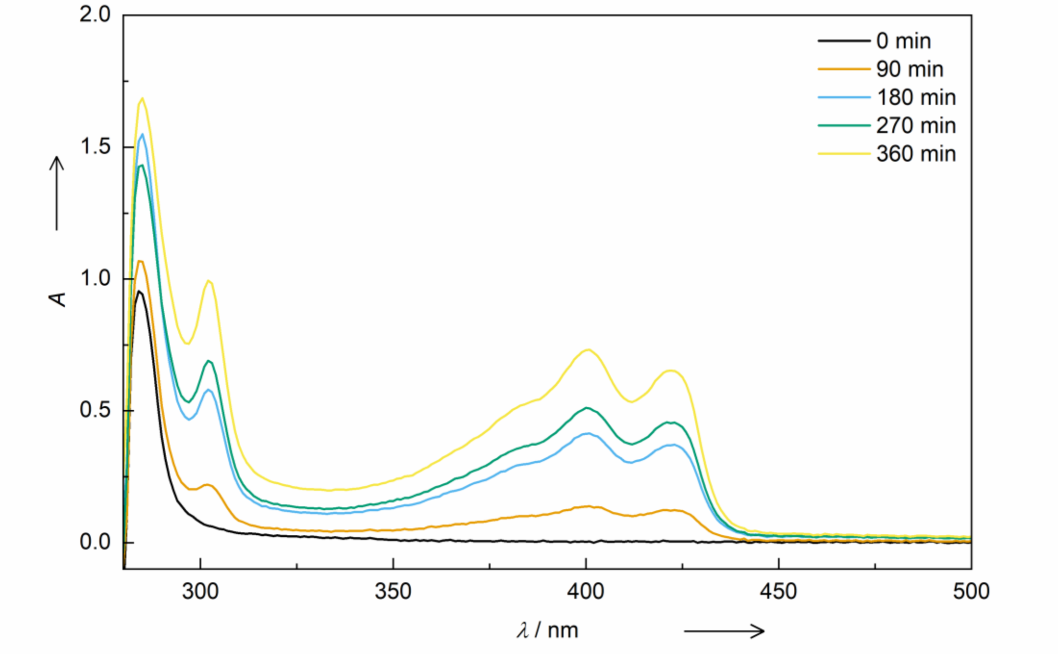


Figure S6. Snapshots of UV-vis absorption spectra of toluene solution containing polymer **2** (ρ = 52 mg·mL^{-1}, 8.14·10^{-4} M) at different times during the irradiation with ultrasound generating PMA-anthracene **1** as basis for the calculation of concentrations of PMA-anthracene **1** in Figure 2b. The spectra were recorded on a Thermo Evolution 300 spectrometer. Note that the samples were diluted by a factor of 3 before measurement accommodating the Lambert-Beer law.

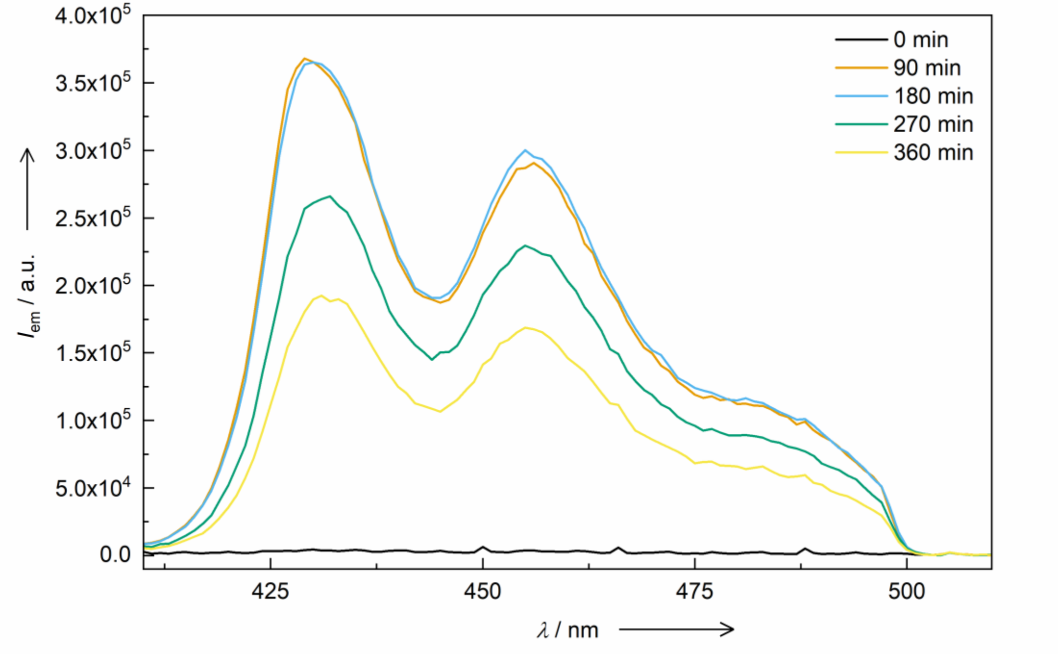


Figure S7. Snapshots of fluorescence spectra of toluene solution containing polymer **2** (ρ = 52 mg·mL^{-1}, 8.14·10^{-4} M) and PtOEP **3** (8.8 µM) at different times during the irradiation with ultrasound generating PMA-anthracene **1** as basis for Figure 2d (λ_{exc} = 407 nm). The spectra were recorded on a Horiba Fluoromax-4P spectrometer in rectangular detection mode. Note that the samples were diluted by a factor of 3 before measurement.

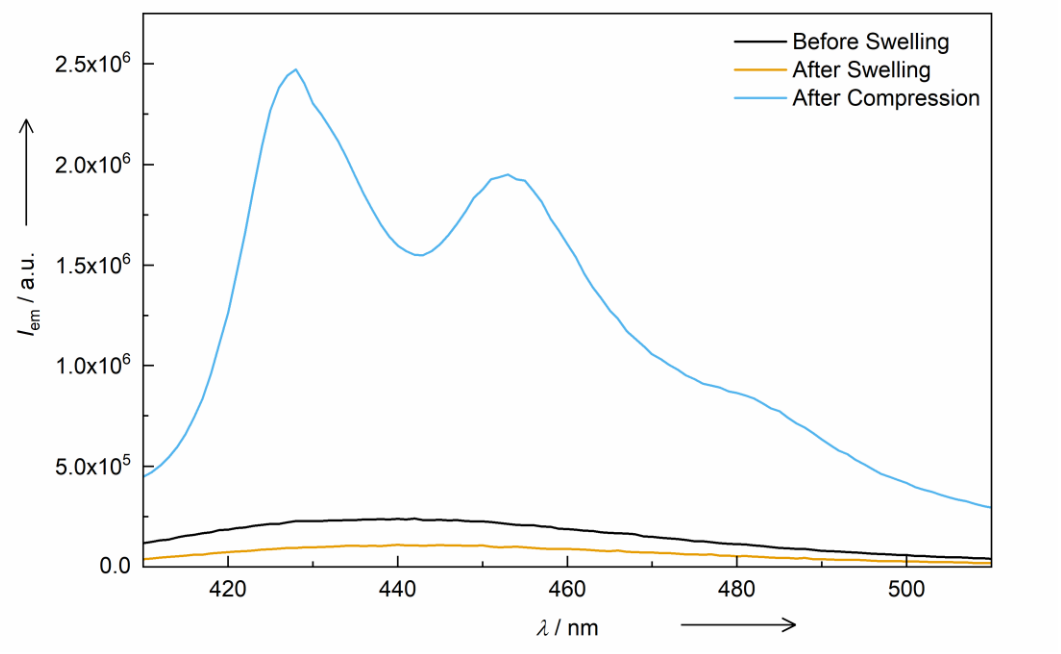


Figure S8. Fluorescence Spectra of PHMA networks containing 0.02 mol% mechanophore crosslinker **9** before and after swelling in a PtOEP **3** solution (15 mg·mL^{-1}) and after compression (λ_{exc} = 390 nm). The samples were dried and deoxygenated prior to measurements. The spectra were recorded on a Horiba Fluoromax-4P spectrometer in rectangular detection mode on a solid-state sample holder.

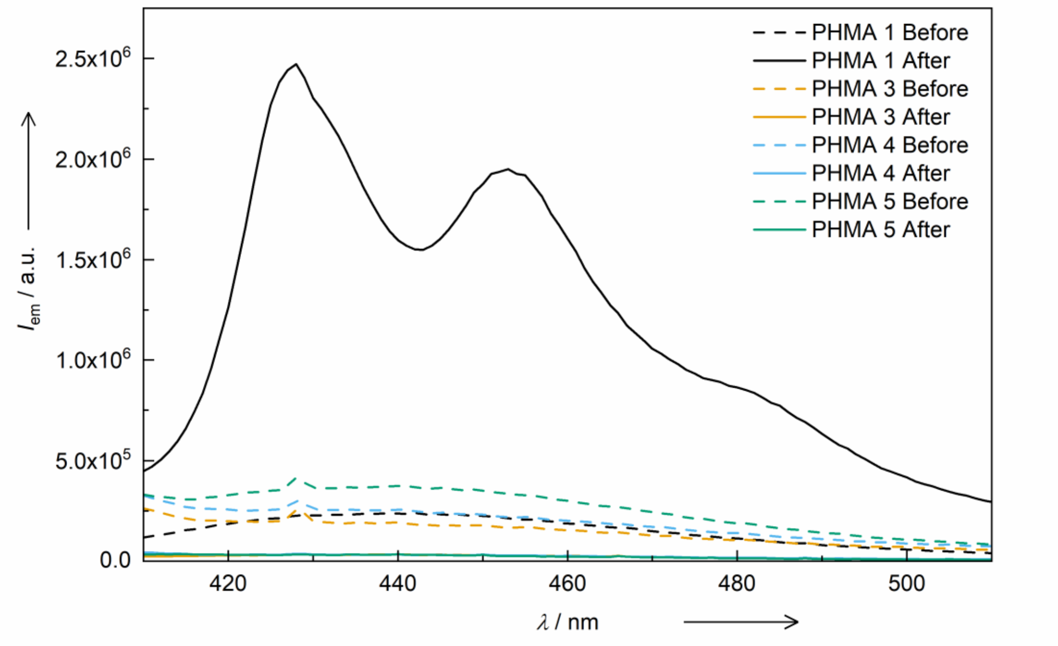


Figure S9. Fluorescence Spectra of PHMA networks containing 0.02 mol% mechanophore and without any mechanophore crosslinker before and after compression (λ_{exc} = 390 nm). The samples were dried and deoxygenated prior to measurements. The spectra were recorded on a Horiba Fluoromax-4P spectrometer in rectangular detection mode on a solid-state sample holder.

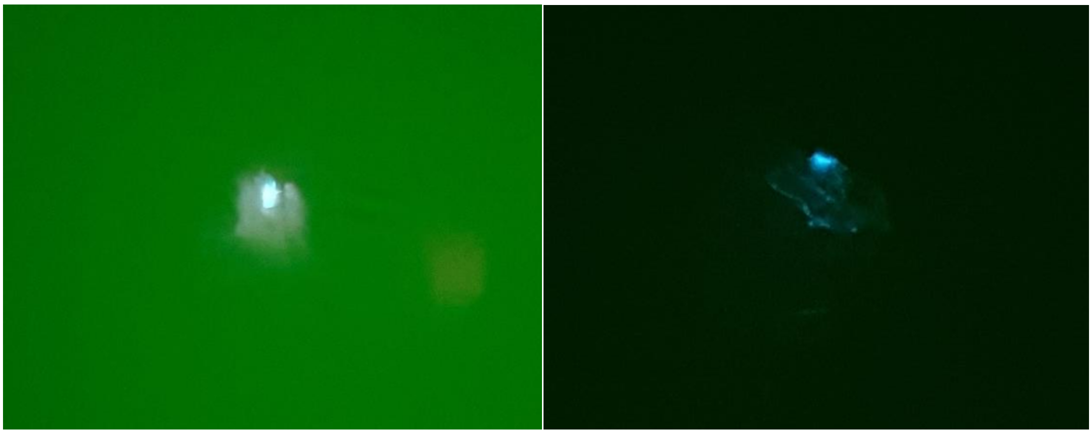


Figure S10. Photographs of fractured PHMA networks containing 0.02 mol% (left) and 1.00 mol% (right) mechanophore crosslinker blended by submerging in a PtOEP solution (15 mg·mL^{-1}) after compression under irradiation with green DPSS laser (50 mW, λ_{exc} = 532 nm). The blue UC emission was recorded through a 500 nm shortpass filter. The samples blended with higher PtOEP content did not exhibit upconverting emission.

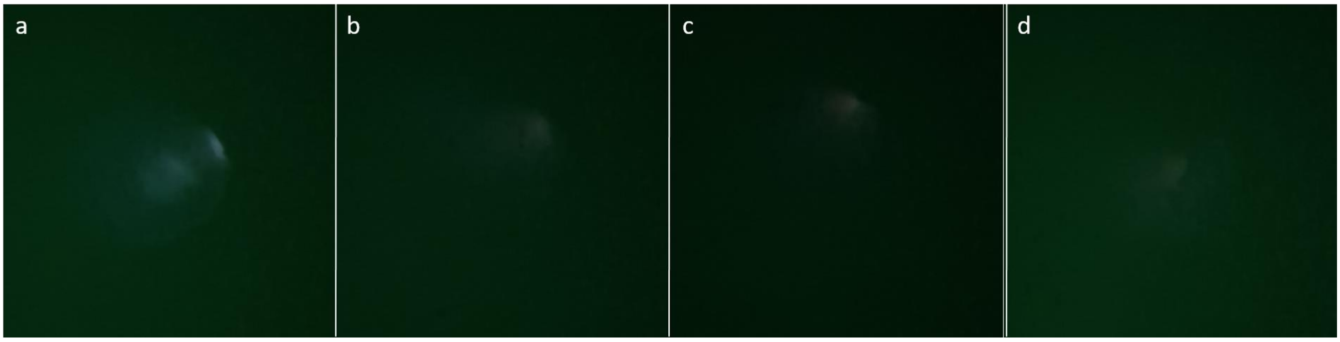


Figure S11. Photographs of fractured PHMA networks containing 0.02 mol% mechanophore blended by submerging in a PtOEP solution (15 mg·mL^{-1}) before compression under irradiation with green DPSS laser (50 mW, λ_{exc} = 532 nm): a) PHMA 1 (containing mechanophore), b) PHMA 3 (containing terminal mechanophore), c) PHMA 4 (containing blended but not bound mechanophore), d) PHMA 5 (containing no mechanophore). The emission was recorded through a 500 nm shortpass filter. In photos b, c, and d, the reflection of the laser beam is visible from the side the sample was irradiated.

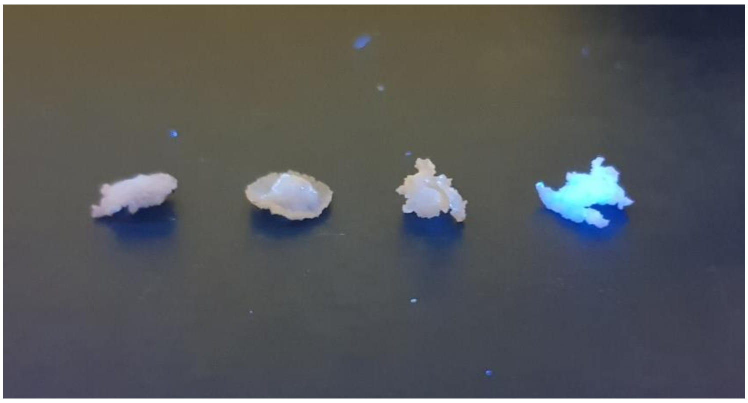


Figure S12. Photographs of fractured PHMA networks containing 0.02 mol% mechanophore under a UV hand lamp (λ_{exc} = 365 nm). From left to right: PHMA 3 (containing terminal mechanophore), PHMA 4 (containing blended but not bound mechanophore), PHMA 5 (containing no mechanophore), PHMA 1 (containing mechanophore).

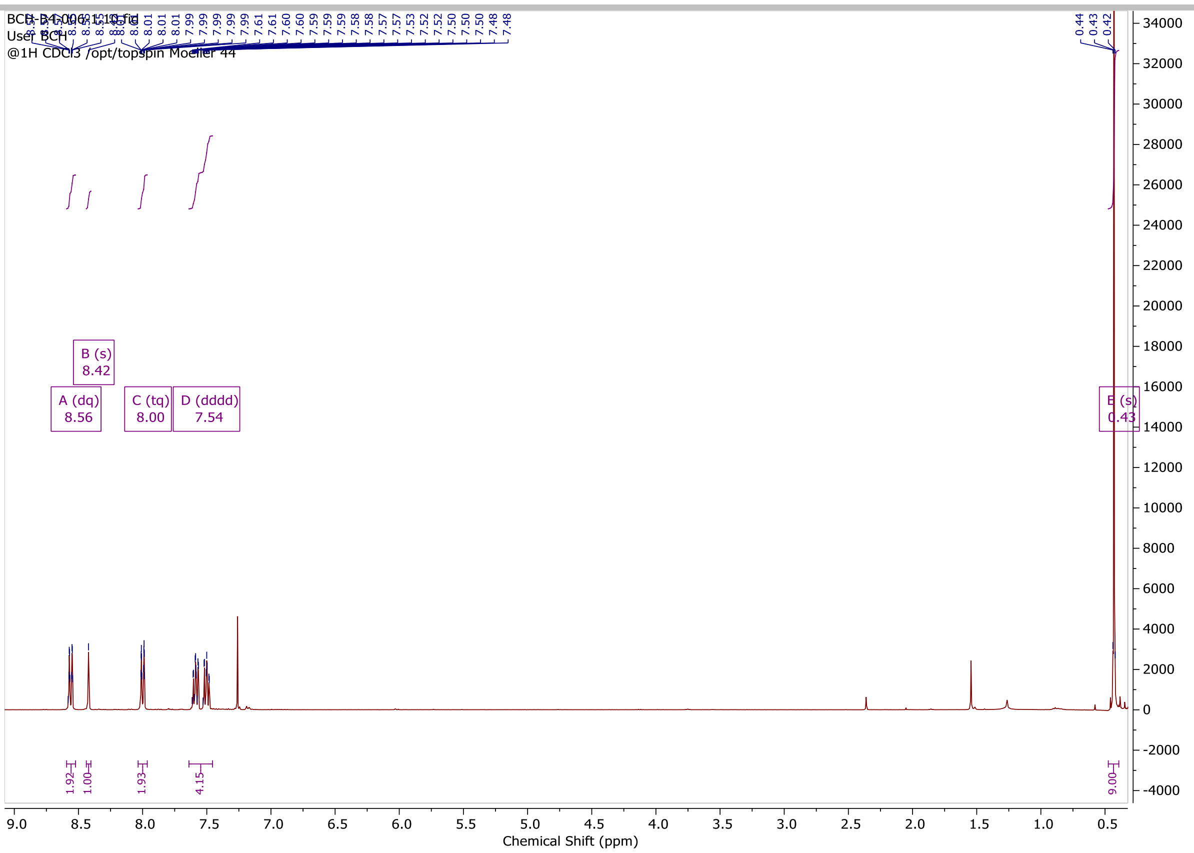


Figure S13. ^{1}H NMR spectra of (anthracen-9-ylethynyl)trimethylsilane.(**4**)

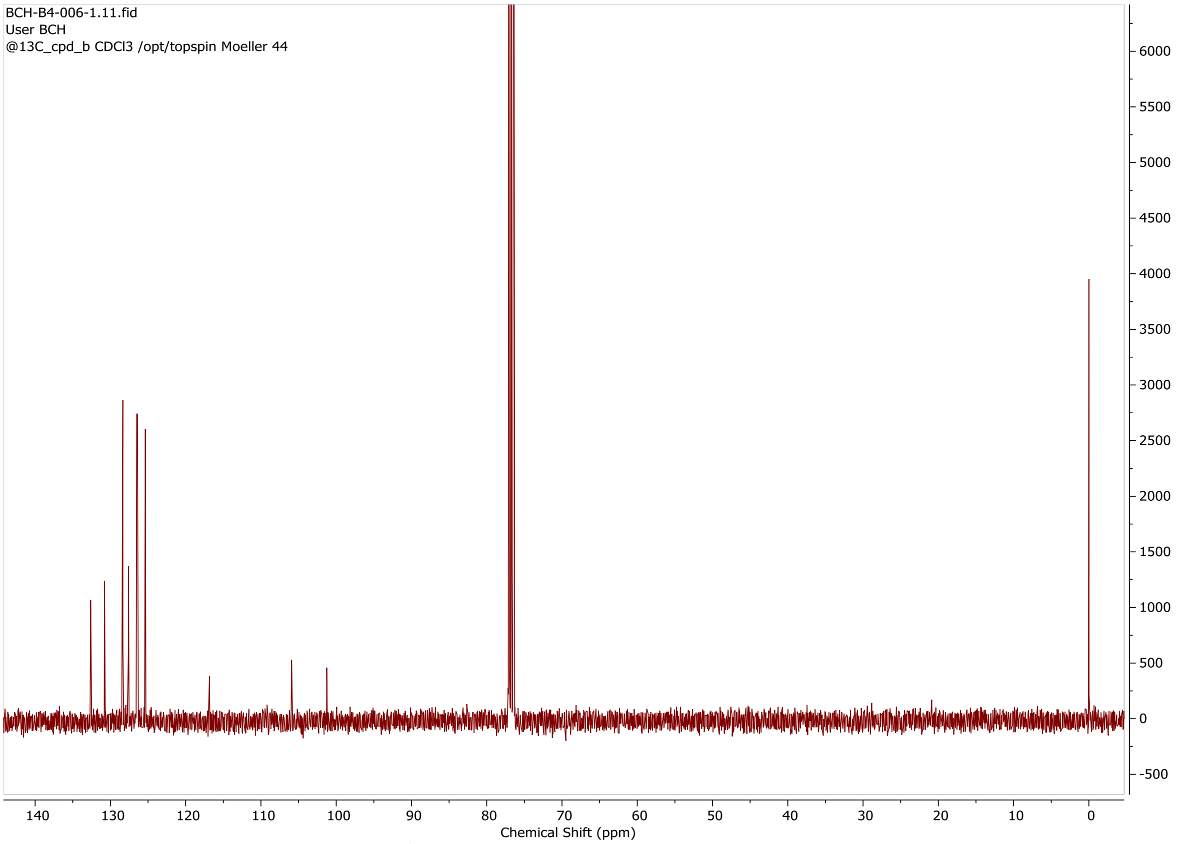


Figure S14. ^{13}C NMR Spectra of (anthracen-9-ylethynyl)trimethylsilane (**4**).

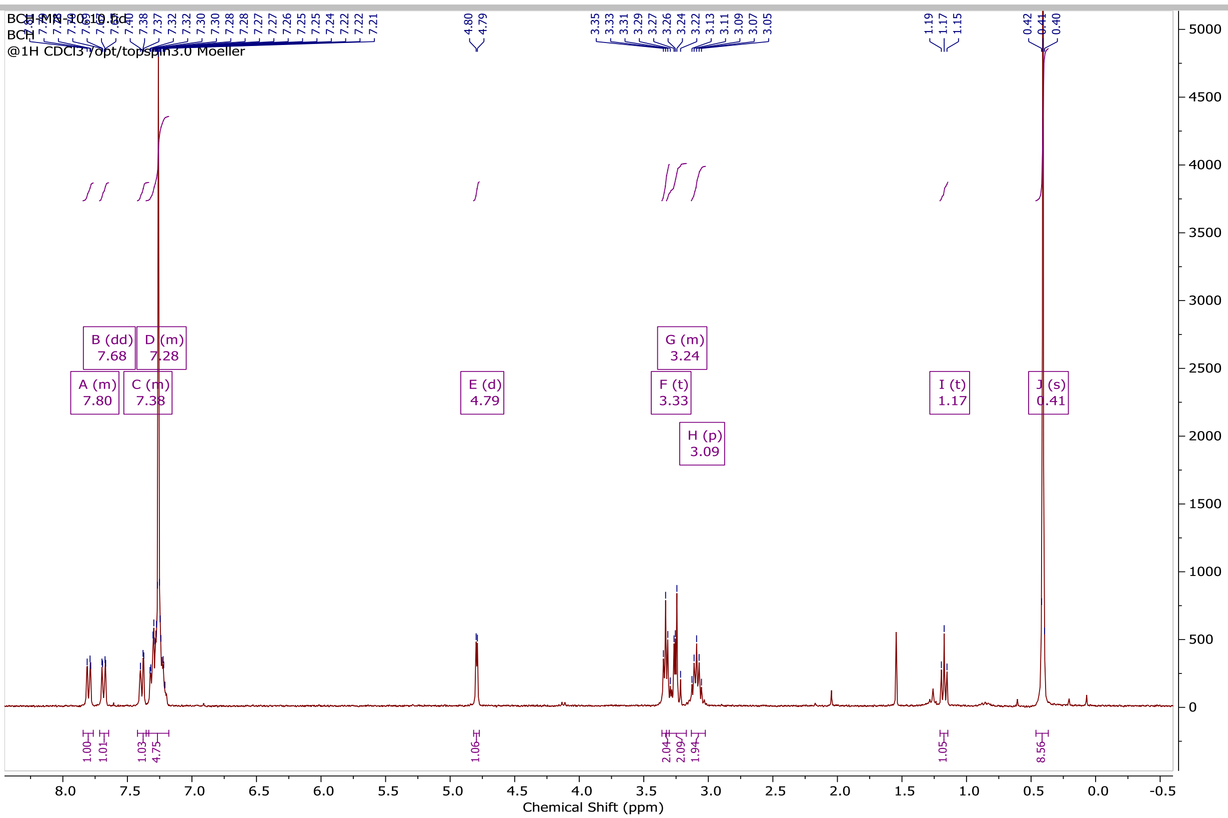


Figure S15. ^{1}H NMR Spectra of 13-(2-hydroxyethyl)-9-((trimethylsilyl)ethynyl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione (**5**).

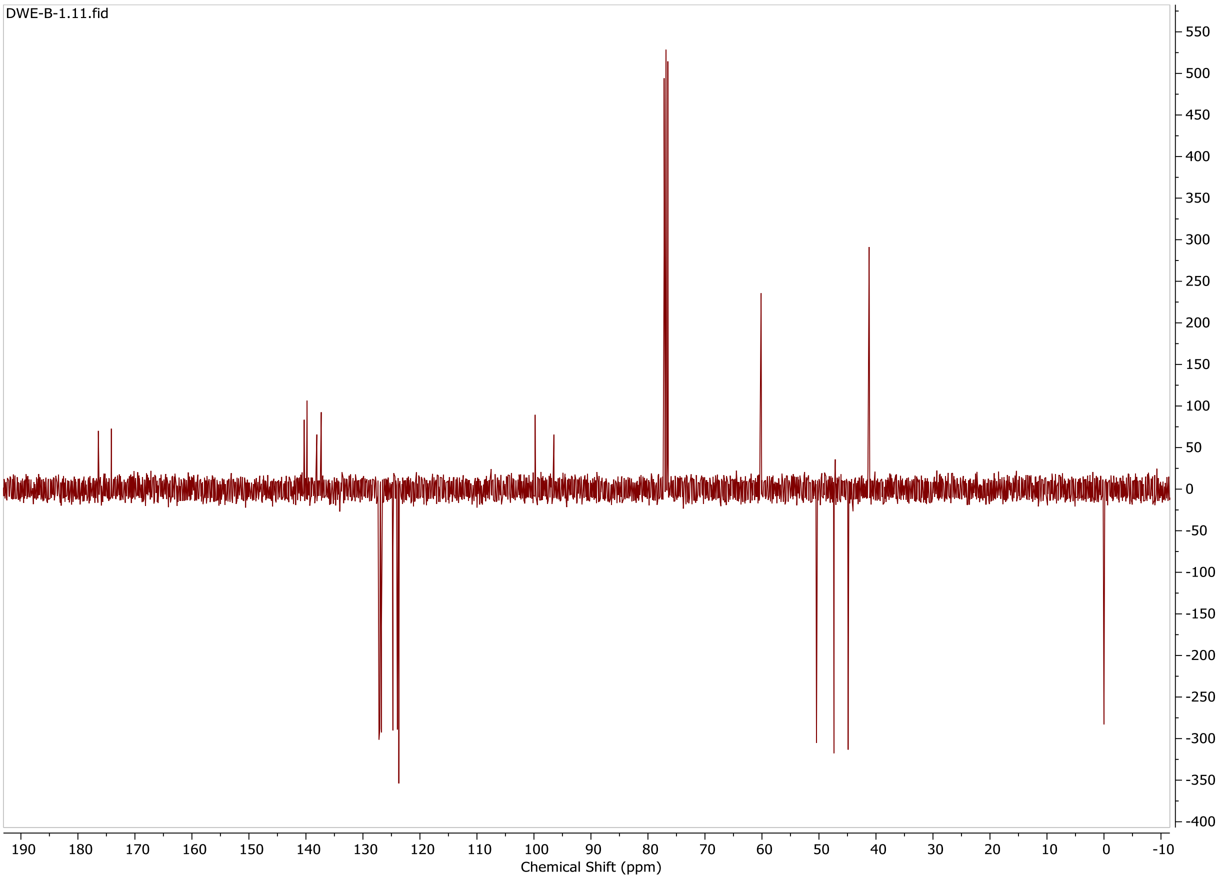


Figure S16: ^{13}C NMR APT spectra of 13-(2-hydroxyethyl)-9-((trimethylsilyl)ethynyl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione (**5**).

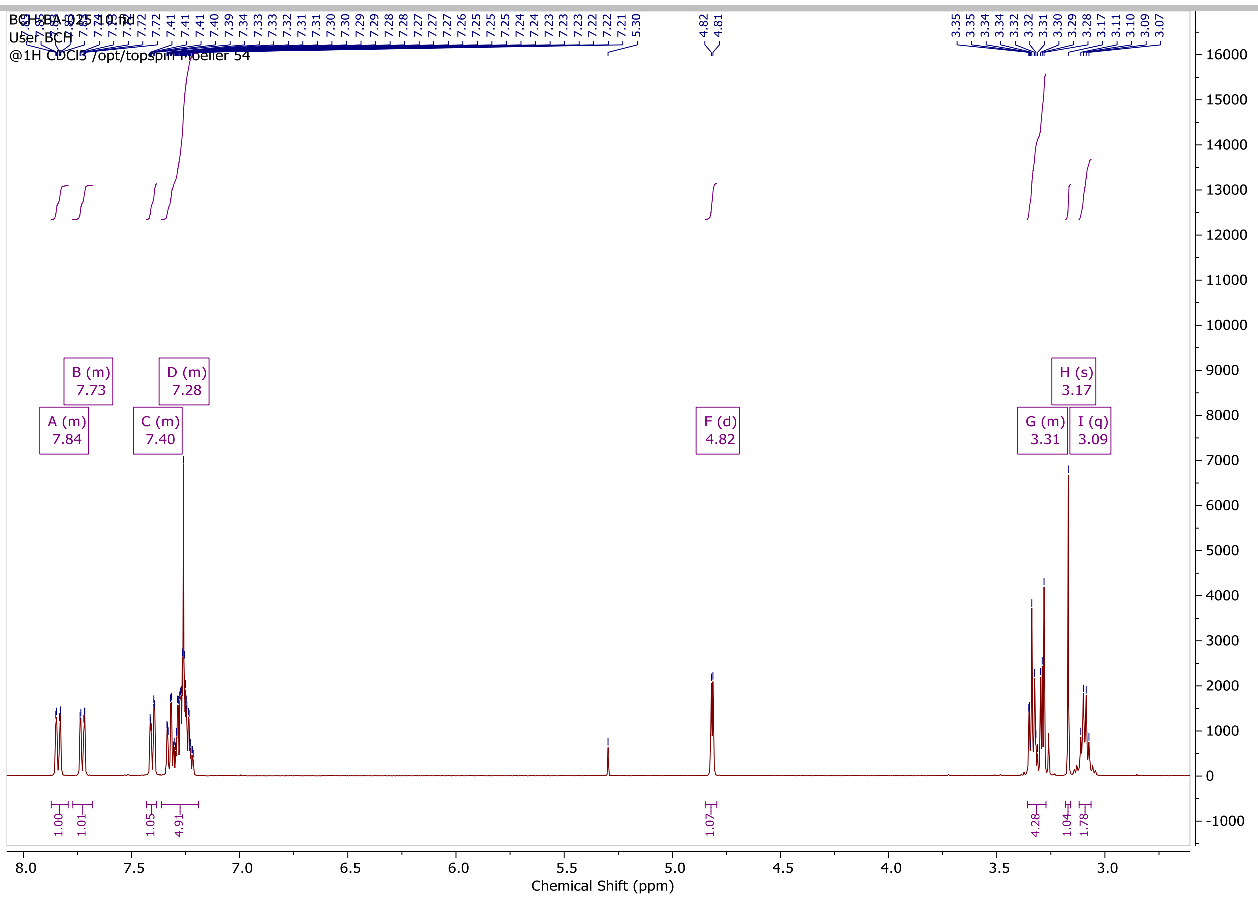


Figure S17. ^{1}H NMR spectra of 9-ethynyl-13-(2-hydroxyethyl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione (**6**).

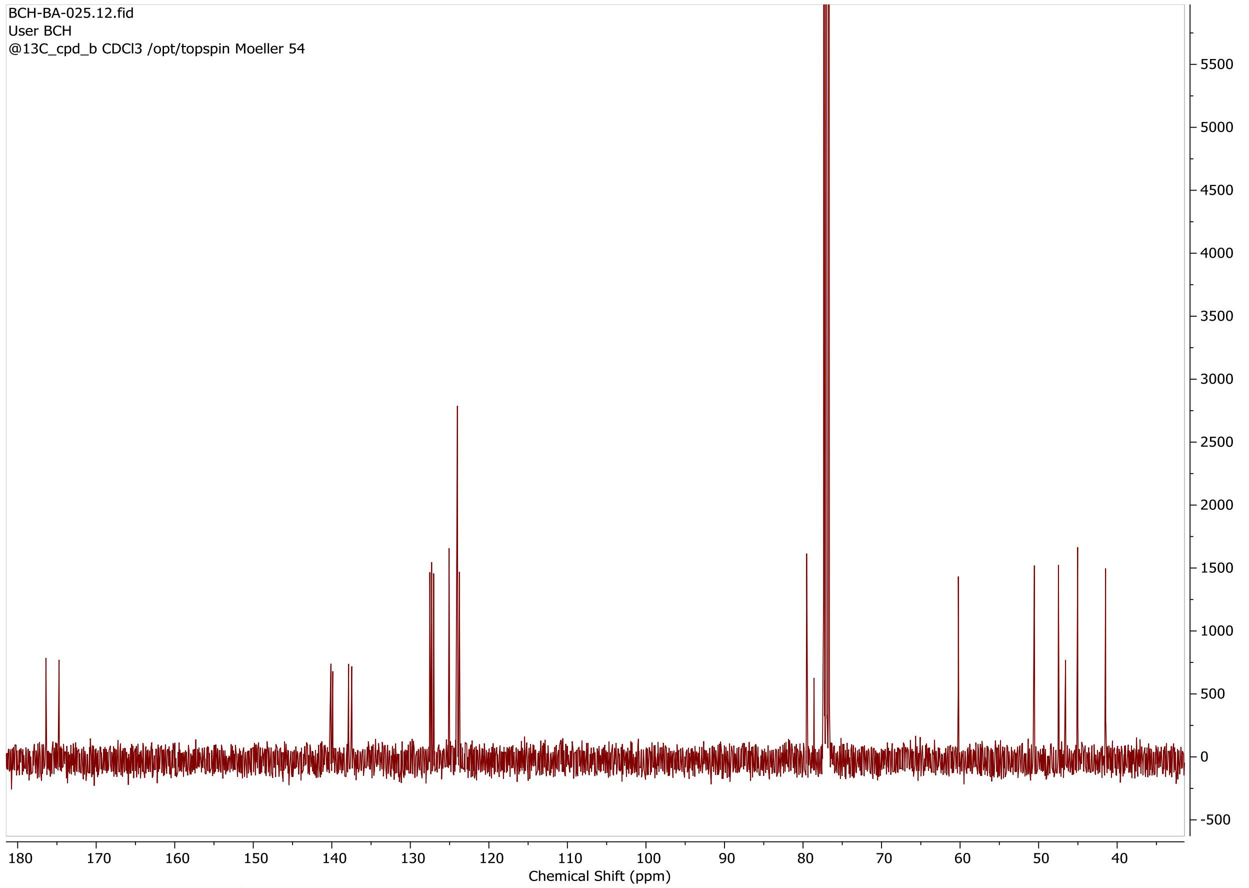


Figure S18. ^{13}C NMR spectra of 9-ethynyl-13-(2-hydroxyethyl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione (**6**).

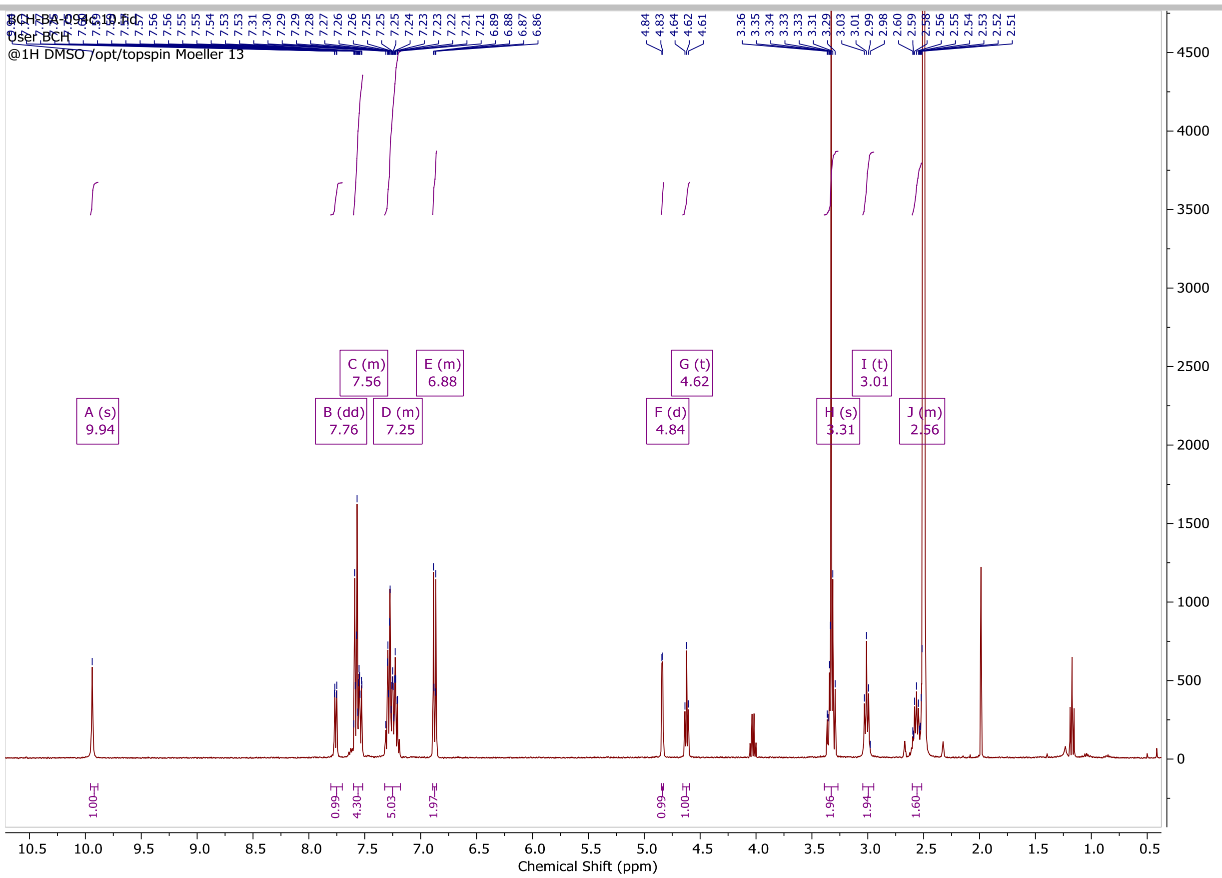


Figure S19. ^{1}H-NMR spectra of 13-(2-hydroxyethyl)-9-((4-hydroxyphenyl)ethynyl)-9,10-dihydro-9,10-[3,4]epipyrroloanthracene-12,14-dione (**7**).

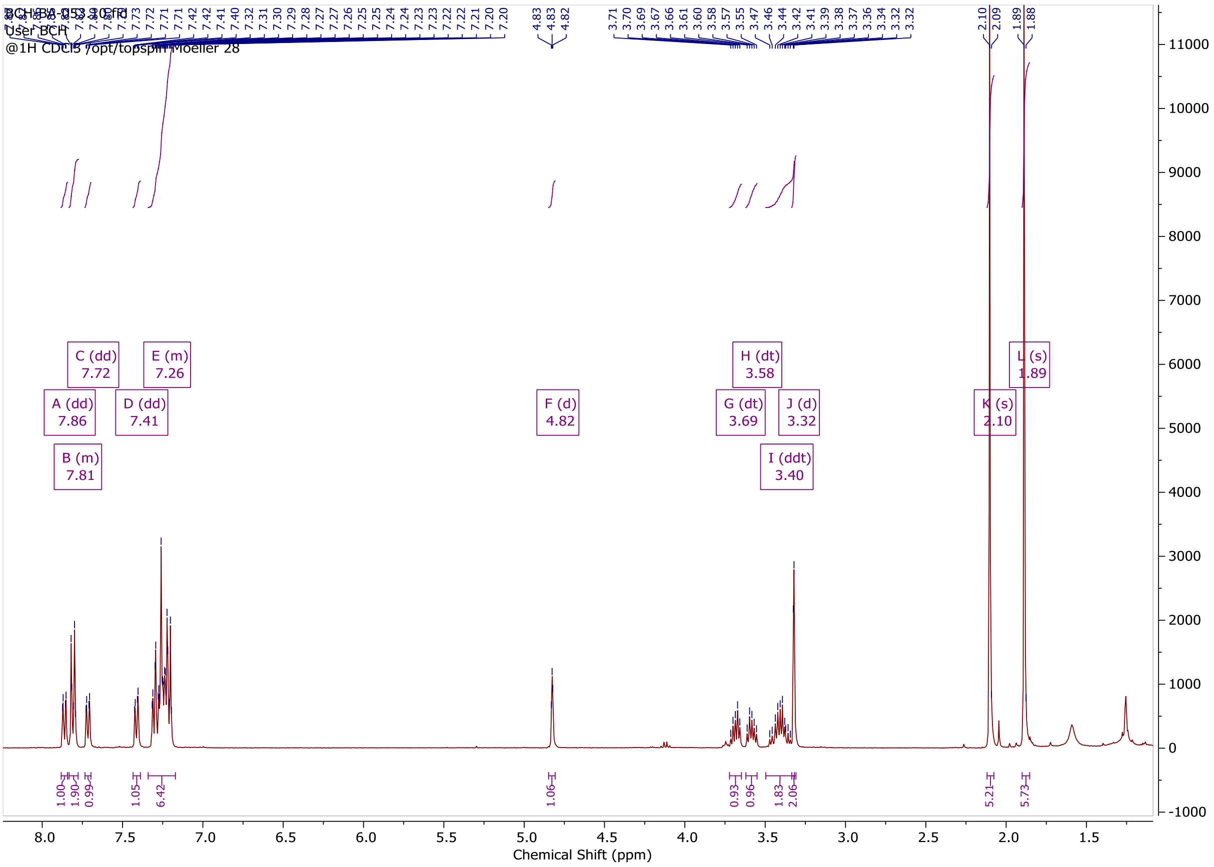


Figure S20. ^{1}H NMR spectra of 4-((13-(2-((2-bromo-2-methylpropanoyl)oxy)ethyl)-12,14-dioxo-9,10-[3,4]epipyrroloanthracen-9(10H)-yl)ethynyl)phenyl 2-bromo-2-methylpropanoate (**8**).

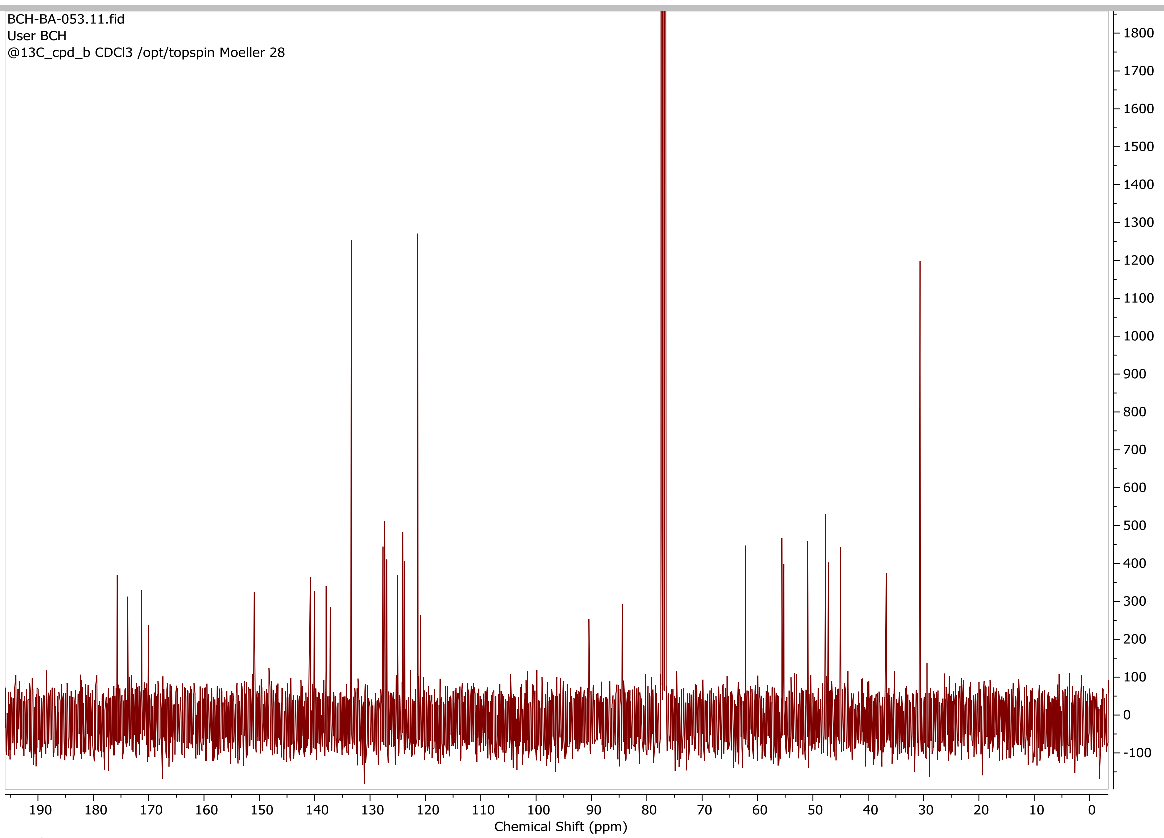


Figure S21. ^{13}C NMR spectra of 4-((13-(2-((2-bromo-2-methylpropanoyl)oxy)ethyl)-12,14-dioxo-9,10-[3,4]epipyrroloanthracen-9(10H)-yl)ethynyl)phenyl 2-bromo-2-methylpropanoate (**8**).

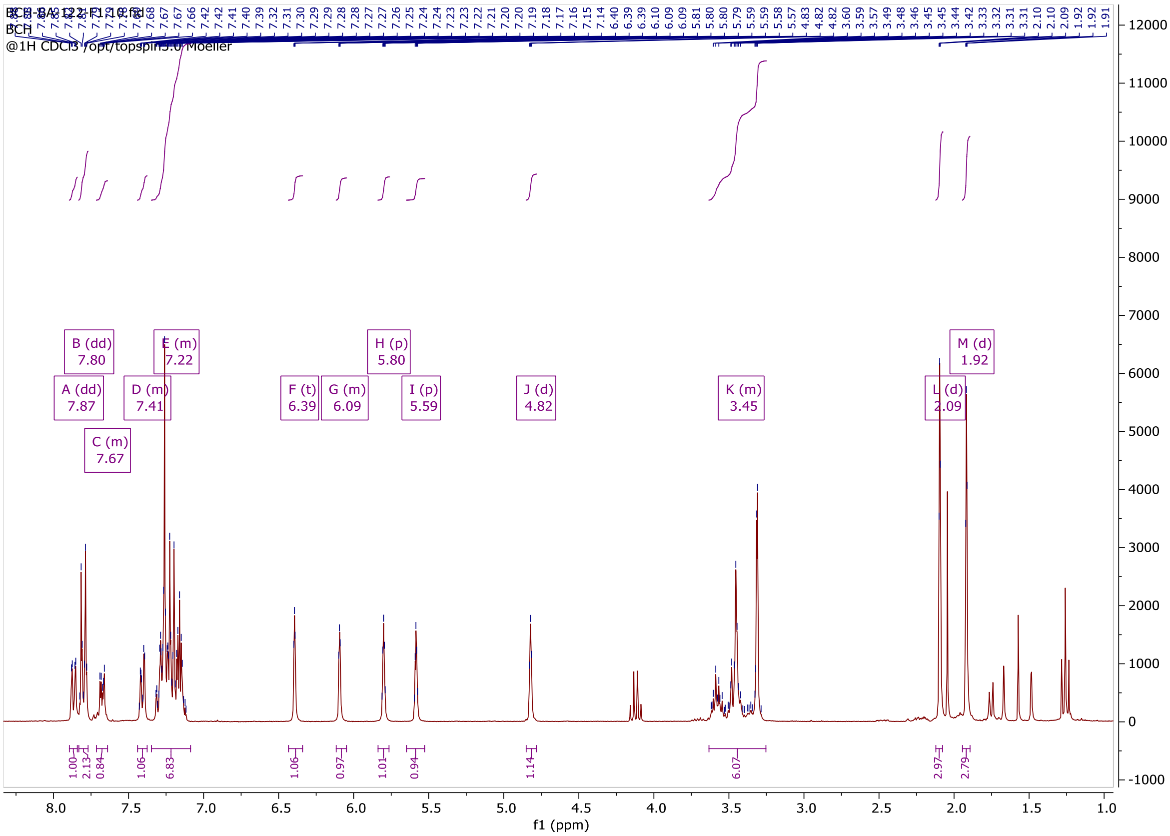


Figure S22. ^{1}H NMR spectra of 4-((13-(2-(methacryloyloxy)ethyl)-12,14-dioxo-9,10-[3,4]epipyrroloanthracen-9(10H)-yl)ethynyl)phenyl methacrylate (**9**).

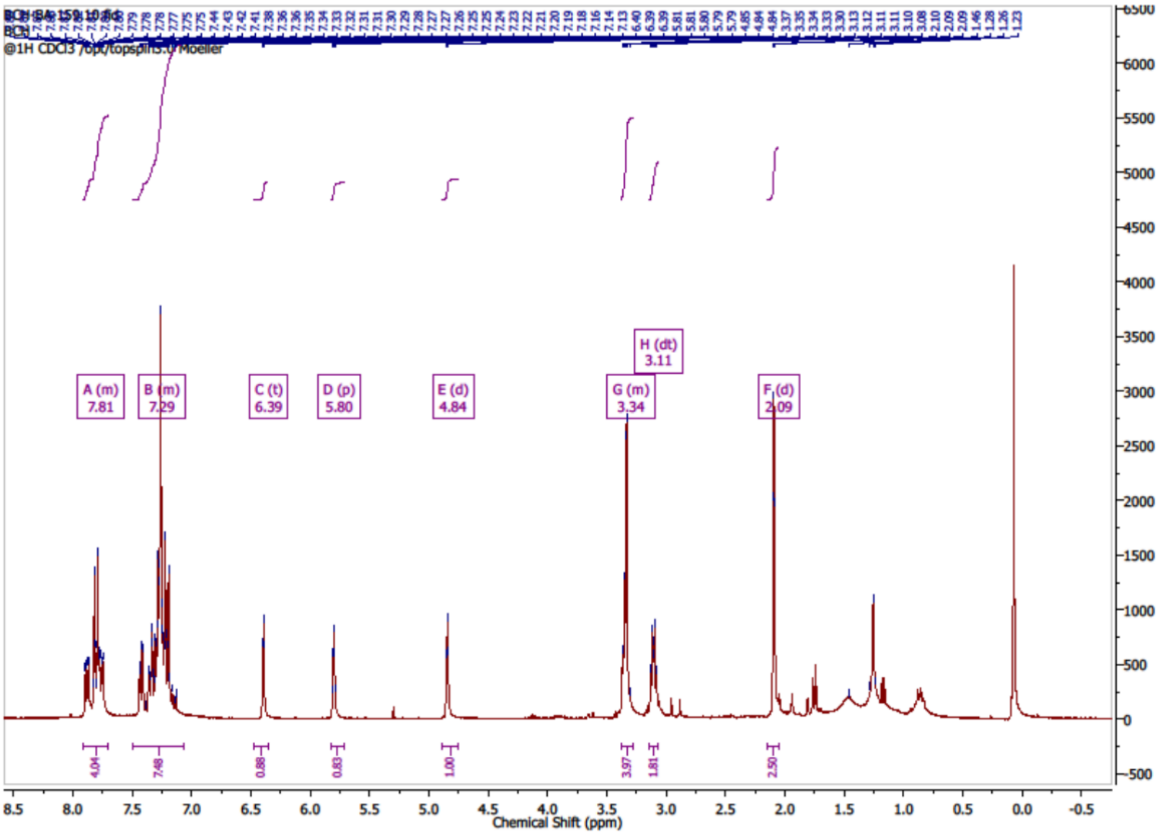


Figure S23. ^{1}H NMR spectra of 4-((13-(2-hydroxyethyl)-12,14-dioxo-9,10-[3,4]epipyrroloanthracen-9(10H)-yl)ethynyl)phenyl methacrylate (**10**).

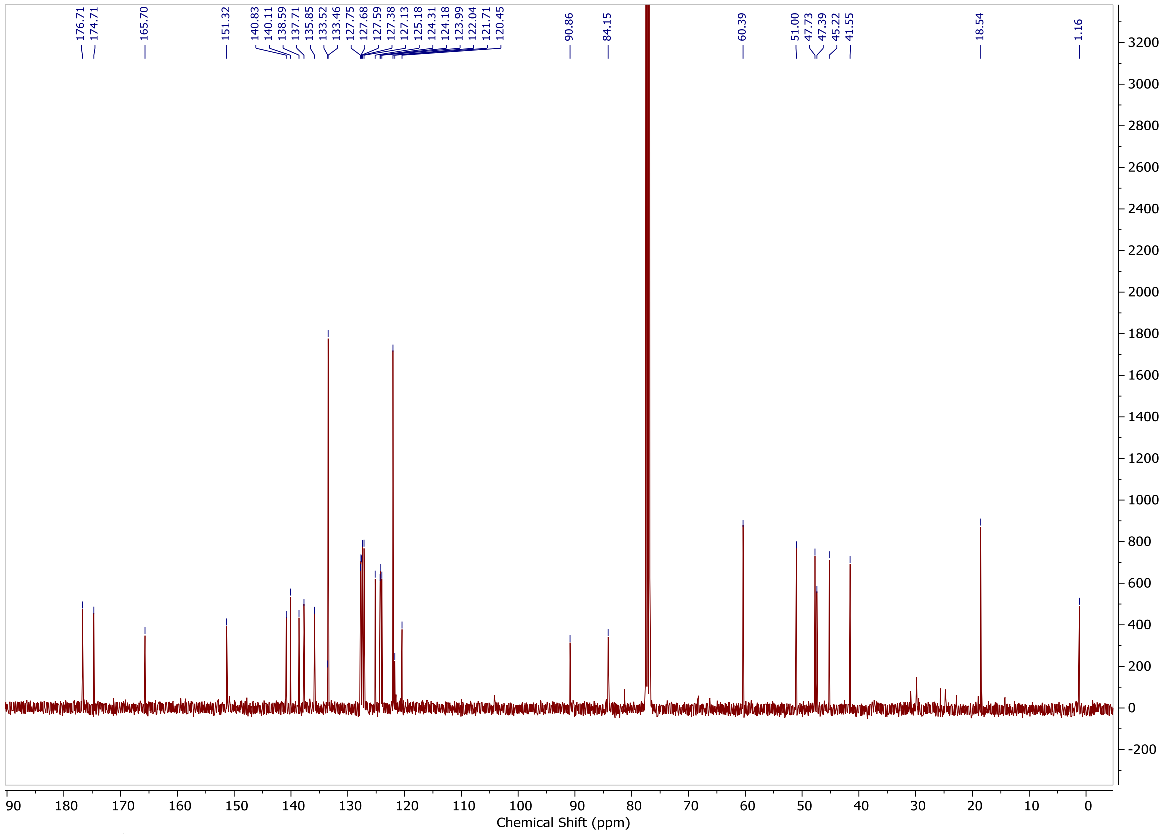


Figure S24. ^{13}C NMR spectra of 4-((13-(2-hydroxyethyl)-12,14-dioxo-9,10-[3,4]epipyrroloanthracen-9(10H)-yl)ethynyl)phenyl methacrylate (**10**).

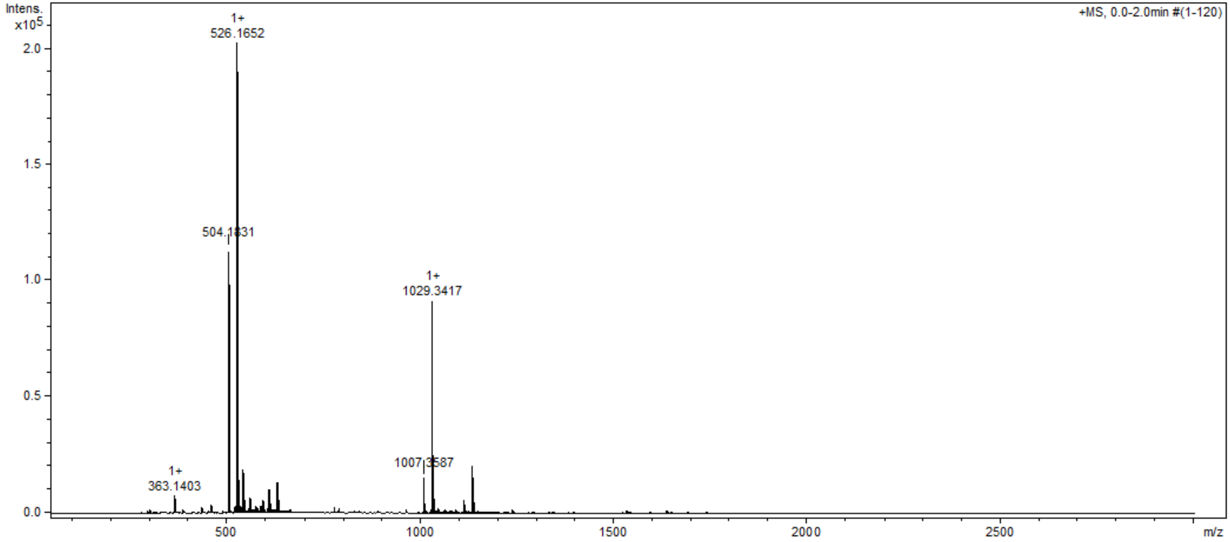


Figure S25. Deconvoluted ESI$^+$ HRMS spectrum of 4-((13-(2-hydroxyethyl)-12,14-dioxo-9,10-[3,4]epipyrroloanthracen-9(10H)-yl)ethynyl)phenyl methacrylate (**10**).

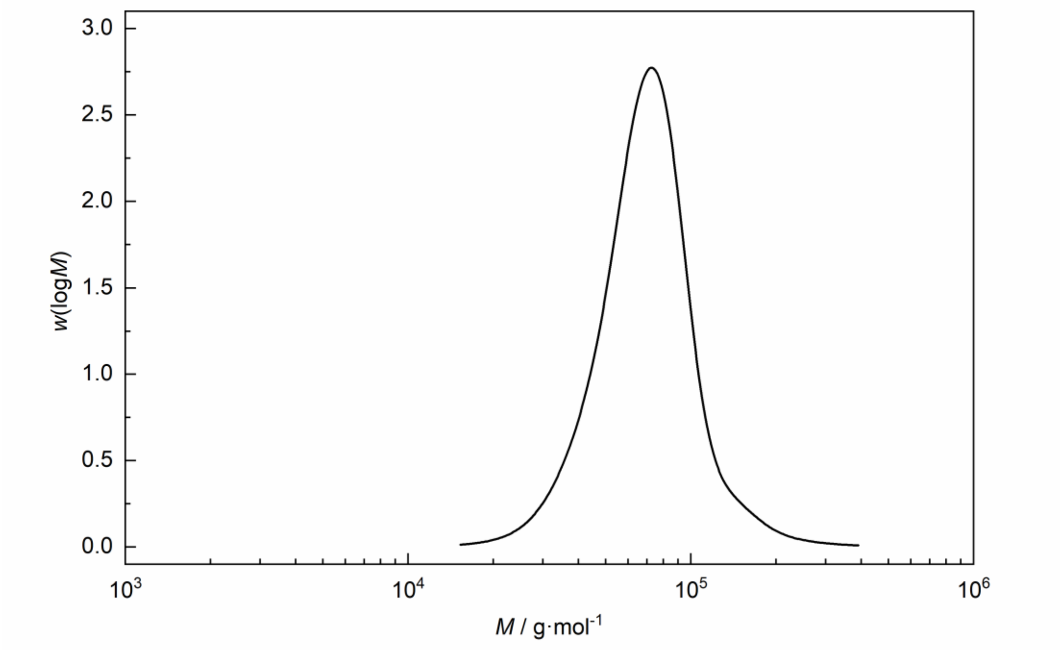


Figure S26. Differential molar mass distribution of GPC RI chromatogram of PMA **2**.

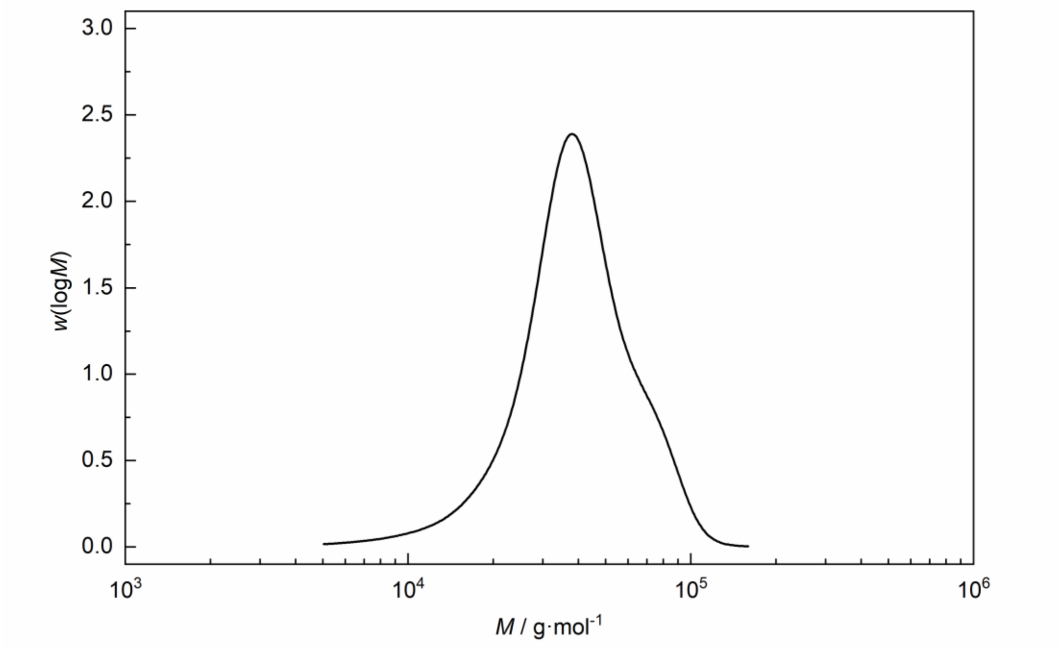


Figure S27. Differential molar mass distribution of GPC RI chromatogram of PMA **2** after sonication for 360 min.

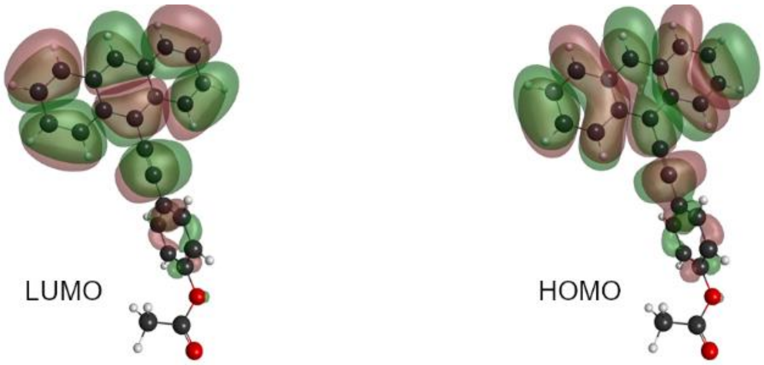


Figure S28. DFT-calculated HOMO and LUMO levels of 9-π-extended anthracene moiety.

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