

Supporting Information for:

Cavity-promotion by pillar[5]arenes expedites organic  
photoredox-catalysed reductive dehalogenations

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# 1 Materials and Methods

**Chemicals** and reagents were purchased from ACROS-ORGANICS, ALFA-AESAR, CHEMPUR or SIGMA ALDRICH and used directly without further purification unless specified otherwise. Moisture- or oxygen-sensitive reactions were carried out in dried glassware—heated under vacuum—using standard Schlenk techniques in a dry argon atmosphere (Argon 5.0 from SAUERSTOFFWERKE FRIEDRICHSHAFEN). Anhydrous toluene was obtained from an M. BRAUN solvent purification system (MB-SPS-800) and stored over activated molecular sieves (3 Å) for several days. Anhydrous 1,4-dioxane and DMF were purchased from ACROS-ORGANICS (extra dry, < 50 ppm H<sub>2</sub>O, AcroSeal™) and further stored over activated molecular sieves (3 Å). Other anhydrous solvents were obtained by drying over activated molecular sieves (3 Å) for several days.<sup>[1]</sup> Cyclohexane for column chromatography was purchased in technical grade and purified by distillation under reduced pressure. Other solvents were purchased and used in analytical grade.

**Thin layer chromatography** was carried out using silica gel-coated aluminum plates with a fluorescence indicator (MERCK 60 F<sub>254</sub>). The visualization of spots was achieved using UV-light ( $\lambda_{\text{max}} = 254$  and 366 nm) or Seebach staining reagent (5.0 g molybdato-phosphoric acid, 2.0 g CeSO<sub>4</sub> · 4 H<sub>2</sub>O, 20 mL H<sub>2</sub>SO<sub>4</sub> conc., 150 mL H<sub>2</sub>O). In some cases, the thin layer chromatography plates were deactivated with triethylamine (NEt<sub>3</sub>) before they were used.

**Flash column chromatography** was carried out using silica gel 60 (grain size 40–63 μm) from MACHERY-NAGEL or aluminum oxide basic 90 from MACHERY-NAGEL. Desactivated silica gel. In specially denoted cases the silica gel was deactivated with triethylamine (NEt<sub>3</sub>). Therefore, silica gel was suspended in NEt<sub>3</sub> and cyclohexane (v/v: 1/1) for 1 solvent was removed under reduced pressure.

**Nuclear magnetic resonance (NMR) spectra** were recorded at 300 K using BRUKER Avance II [400.1 MHz (<sup>1</sup>H), 101.6 MHz (<sup>13</sup>C)] and BRUKER Avance III HD [500.3 MHz (<sup>1</sup>H), 125.8 MHz (<sup>13</sup>C)] spectrometers. Chemical shifts are reported in parts per million (ppm, δ scale) relative to the signal of tetramethylsilane (δ = 0.00 ppm). <sup>1</sup>H NMR spectra are referenced to tetramethylsilane as an internal standard or the residual solvent signal of CDCl<sub>3</sub> (δ = 7.26 ppm). <sup>13</sup>C NMR spectra are referenced to tetramethylsilane as an internal standard or the solvent signal of CDCl<sub>3</sub> (δ = 77.16 ppm).<sup>[2]</sup> <sup>19</sup>F spectra are referenced to

tetramethylsilane following the IUPAC recommendations.<sup>[3]</sup> Coupling constants  $J$  are given in Hertz [Hz].

The analysis followed first order, and the multiplets were abbreviated using the following codes: singlet (s), broad singlet (br), doublet (d), triplet (t), quartet (q), multiplet (m) and combinations thereof, such as doublet of doublets (dd).

**High Resolution Mass Spectrometry (HRMS)** were measured on a THERMO FISCHER SCIENTIFIC INC. Exactive via electro spray ionization (ESI) or atmospheric pressure chemical ionization (APCI) with an orbitrap analyzer.

**Cyclic voltammograms (CVs)** were measured in solution and inside a glovebox using a METROHM Autolab PGSTAT 128N. As working electrode, a glassy carbon or platinum disc electrode (2 mm diameters) was used. A platinum rod served as counter electrode, and as reference electrode a Ag/AgNO<sub>3</sub> electrode containing a silver wire immersed in an inner chamber filled with 0.1 M AgNO<sub>3</sub> containing 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> in the outer chamber were used. For the internal reference, the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple was used.

**UV/Vis absorption spectra** were measured on a SHIMADZU UV-1800 using *Quartz (Suprasil)* cuvettes (10 mm path length) from HELMA ANALYTICS.

**Fluorescence spectra** were recorded on a JASCO FP-8300 and were measured in *Quartz (Suprasil)* cuvettes (10 mm path length) from HELMA ANALYTICS at 25 °C. Unless otherwise noted, the respective absorption maxima with the longest wavelength of the compound was used for excitation.

The **Light source** for the reductive dehalogenations was a commercially available nail dryer lamp, which contains four UV-A bulbs (9 W, 365 nm), purchased from MYLEE BEAUTY (<https://www.justbeauty.co.uk>) and used as shown below (Figure S1). Reaction vessels were placed in front of the UV-A bulbs under vigorous stirring while cooling with compressed air (see Figure S1).

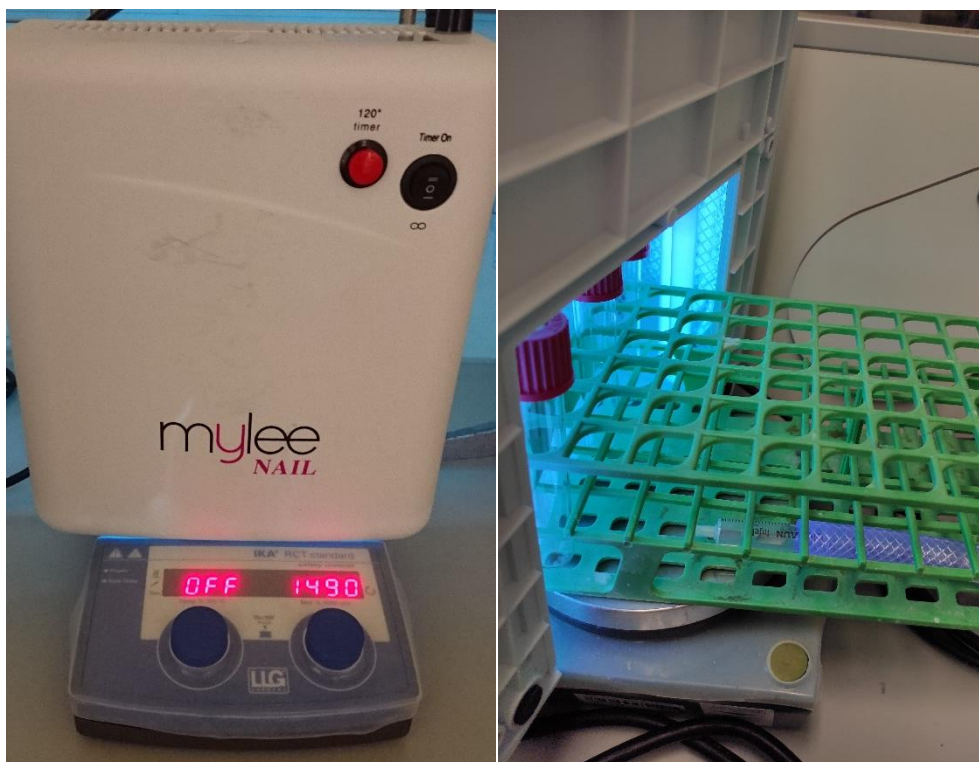
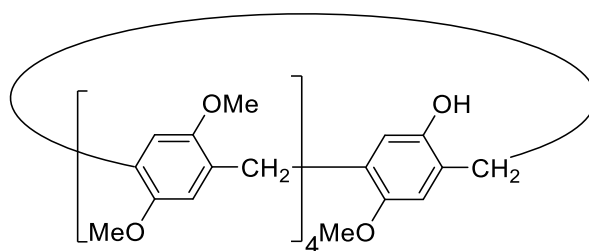


Figure S1: Representative reaction set-up in front (left) and side view (right) with the reaction vessels placed in front of the nail dryer lamp.



## 2.2 Hydroxynonamethoxypillar[5]arene (**2**)



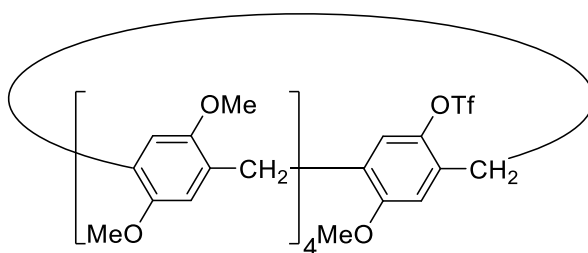
**2**

The synthesis was carried out following a modified procedure by HAN *et al.*<sup>[7]</sup> Dimethoxypillar[5]arene (**1**, 1.00 g, 1.33 mmol) was dissolved in anh. CHCl<sub>3</sub> (40 mL) at -15 °C. BBr<sub>3</sub> (0.51 mL, 1.33 g, 5.33 mmol, 4 eq.) in CHCl<sub>3</sub> (2 mL) was slowly added via syringe. The mixture was kept below -8 °C for 2.5 h. Then H<sub>2</sub>O (40 mL) was added. The organic layer was separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 70 mL). The combined organic layers were washed with brine (50 mL). The solvent was removed under reduced pressure, and the brown residue was purified by column chromatography (silica gel, cyclohexane/EtOAc: 10/1 to 3/1) to afford **2** (399 mg, 0.541 mmol, 41%) as a slightly red solid.

**R<sub>f</sub>** 0.24 (cyclohexane/EtOAc: 3/1); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>, spectrum contains residues of CH<sub>2</sub>Cl<sub>2</sub> bound by the pillararene at 4.79 ppm): δ 6.87 (s, OH, 1H), 6.73 (s, 1H), 6.70 (s, 2H), 6.69 (s, 1H), 6.65 (s, 1H), 6.65 (s, 1H), 6.61 (s, 1H), 6.60 (s, 2H), 6.59 (s, 1H), 3.79 (s, OCH<sub>3</sub>, 3H), 3.78 (3 × s, CH<sub>2</sub>, 6H), 3.75 (s, CH<sub>2</sub>, 2H), 3.73 (s, CH<sub>2</sub>, 2H), 3.73 (s, OCH<sub>3</sub>, 3H), 3.69 (s, OCH<sub>3</sub>, 3H), 3.62 (s, OCH<sub>3</sub>, 3H), 3.60 (s, OCH<sub>3</sub>, 6H), 3.59 (s, OCH<sub>3</sub>, 3H), 3.56 (s, OCH<sub>3</sub>, 3H), 3.50 (s, OCH<sub>3</sub>, 3H); **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>, spectrum contains residues of CH<sub>2</sub>Cl<sub>2</sub> complexed in the pillararene at 53.18 ppm)<sup>a</sup> δ 151.95, 151.19, 151.07, 151.05, 151.03, 151.01, 150.90, 148.70, 147.64, 130.10, 129.43, 128.79, 128.48, 128.42, 128.37, 128.22, 127.81, 126.91, 125.08, 118.98, 114.67, 114.59, 114.41, 114.18, 113.95, 113.07, 113.00, 56.44, 56.20, 56.14, 56.07, 55.97, 55.92, 31.03, 30.18, 30.02, 29.70, 28.95; **HRMS** (ESI<sup>+</sup>): *m/z* calcd. for C<sub>44</sub>H<sub>49</sub>O<sub>10</sub>N 737.3314 [M+H]<sup>+</sup>, found 737.3320.

<sup>a</sup> Signals of six C-atoms are missing due to overlap with the peaks at 151.01, 114.67, 114.18, 56.44, 55.9 (overlap of 3 C-atoms) ppm.

### 2.3 Nonamethoxypillar[5]arene triflate (**S1**)



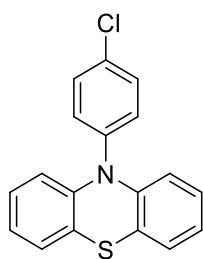
**S1**

The synthesis was carried out following a modified procedure by HAN *et al.*<sup>[7]</sup> Monohydroxypillar[5]arene (250 mg, 339  $\mu\text{mol}$ ) and anh. pyridine (50  $\mu\text{L}$ , 54 mg, 535  $\mu\text{mol}$ , 1.8 eq.) were dissolved in anh.  $\text{CH}_2\text{Cl}_2$  at 0  $^\circ\text{C}$ , and the mixture was stirred for 30 min at 0  $^\circ\text{C}$ .  $\text{Tf}_2\text{O}$  (90  $\mu\text{mL}$ , 143 mg, 619  $\mu\text{mol}$ , 1.6 eq.) was slowly added. The resulting purple-brown mixture was stirred at 0  $^\circ\text{C}$  for 30 min and at rt for 2.5 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel, cyclohexane/EtOAc: 3/1) to afford **S1** (271 mg, 312  $\mu\text{mol}$ , 92%) as a brown solid.

**R<sub>f</sub>** 0.30 (cyclohexane/EtOAc: 3/1); **<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.11 (s, 1H), 6.82 (s, 1H), 6.78 (s, 1H), 6.763 (s, 1H), 6.759 (s, 2H), 6.755 (s, 1H), 6.73 (s, 1H), 6.71 (s, 2H), 3.84 (s, 2H), 3.79 (s, 2H), 3.78 (s, 4H), 3.76 (s, 2H), 3.69 (s, 3H), 3.68 (s, 3H), 3.68 (s, 3H), 3.66 (s, 3H), 3.65 (s, 3H), 3.64 (s, 3H), 3.64 (s, 3H), 3.63 (s, 3H), 3.60 (s, 3H); **<sup>13</sup>C NMR** (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.1, 151.10, 151.06, 151.04, 150.96, 150.9, 150.75, 150.72, 141.2, 132.4, 129.8, 129.3, 128.9, 128.4, 128.3, 127.2, 126.9, 123.2, 118.9 (q,  $^1J_{\text{C-F}} = 322.4$  Hz), 114.39, 114.37, 114.34, 114.26, 114.18, 114.16, 113.9, 113.8, 113.7, 56.1, 55.99, 55.96, 55.89, 55.87, 55.7, 55.6, 55.5, 30.8, 29.8, 29.73, 29.65, 29.6; **<sup>19</sup>F NMR** (471 MHz,  $\text{CDCl}_3$ ):  $\delta$  -74.0; **HRMS** (ESI<sup>+</sup>): *m/z* calcd. for  $\text{C}_{45}\text{H}_{51}\text{O}_{12}\text{NF}_3\text{S}$  886.3079[M+NH<sub>4</sub>]<sup>+</sup>, found 886.3065.



## 2.4 10-(4-Chlorophenyl)-10*H*-phenothiazine (**S2**)

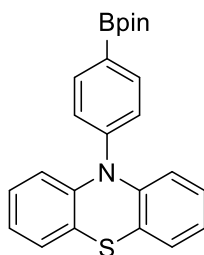


**S2**

Phenothiazine (500 mg, 2.51 mmol), 1-bromo-4-chlorobenzene (481 mg, 2.51 mmol, 1.0 eq.), KO<sup>t</sup>Bu (338 mg, 3.01 mmol, 1.2 eq.), Pd(OAc)<sub>2</sub> (15.5 mg, 75.0 μmol, 3 mol%) and SPhos (30.9 mg, 75.0 μmol, 3 mol%) were dissolved in anh. and degassed toluene (10 mL) and stirred at 100 °C for 16 h. After cooling to rt the mixture was filtered through a pad of Celite<sup>®</sup> and rinsed with EtOAc. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel, cyclohexane) to afford **S2** (565 mg, 1.83 mmol, 73%) as a white solid.

**R<sub>f</sub>** 0.08 (cyclohexane); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.57–7.54 (m, 2H), 7.34–7.31 (m, 2H), 7.05–7.02 (m, 2H), 6.90–6.81 (m, 4H), 6.23 (dd, *J* = 8.1, 1.4 Hz, 2H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 144.05, 139.97, 133.88, 131.93, 131.12, 127.08, 127.05, 123.00, 121.16, 116.55; **HRMS** (ESI<sup>+</sup>): *m/z* calcd. for C<sub>18</sub>H<sub>12</sub>NCIS<sup>+</sup> 309.0373 [M]<sup>+</sup>, found 309.0378.

## 2.5 10-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-10H-phenothiazine (**3**)



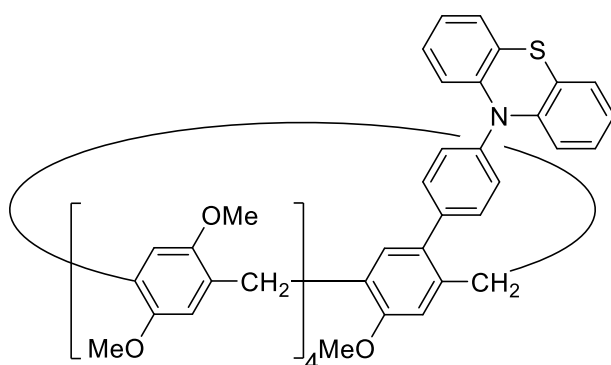
**3**

The synthesis was carried out following a modified procedure by Hou *et al.*<sup>[8]</sup> Phenothiazine **S2** (500 mg, 1.61 mmol), Pd<sub>2</sub>dba<sub>3</sub> (7.40 mg, 8.00 μmol, 0.5 mol%), XPhos (15.6 mg, 32.0 μmol, 2.0 mol%), bis(pinacolato)diboron (492 mg, 1.94 mmol, 1.2 eq.) and KOAc (475 mg, 4.84 mmol, 3.0 eq.) were dissolved in anh. and degassed 1,4-dioxane (16 mL) and stirred at 100 °C for 16 h. After cooling to rt the reaction mixture was filtered through a pad of Celite® and rinsed with EtOAc. The solvent was removed under reduced pressure and the residue was purified by recrystallisation from *i*PrOH to obtain **3** (580 mg, 1.45 mmol, 90%) as colorless crystals.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.01–7.99 (m, 2H), 7.37–7.34 (m, 2H), 7.04 (dd, *J* = 7.3, 1.8 Hz, 2H), 6.88–6.80 (m, 4H), 6.29 (dd, *J* = 7.9, 1.5 Hz, 2H), 1.38 (s, 12H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 144.28, 144.04, 137.26, 128.95, 127.01, 126.98, 122.90, 121.57, 117.20, 84.22, 67.26, 25.08<sup>a</sup>; HRMS (ESI<sup>+</sup>): *m/z* calcd. for C<sub>24</sub>H<sub>24</sub>O<sub>2</sub>NBS 401.1615 [M]<sup>+</sup>, found 401.1618.

<sup>a</sup> One Signal is missing due to coupling to <sup>10</sup>B/<sup>11</sup>B.

## 2.6 Pillar[5]arene **PA-PhPT**



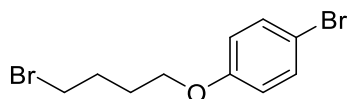
**PA-PhPT**

Pillarene triflate **S1** (209.5 mg, 241.0  $\mu\text{mol}$ ), boronic ester **3** (120.0 mg, 299.0  $\mu\text{mol}$ , 1.2 eq.),  $\text{Pd}_2(\text{dba})_3$  (22.2 mg, 24.2  $\mu\text{mol}$ , 10 mol%), XPhos (19.8 mg, 48.2  $\mu\text{mol}$ , 20 mol%) and  $\text{K}_3\text{PO}_4$  (520 mg, 2.45 mmol, 10.2 eq.) were dissolved in a mixture of degassed toluene (15 mL) and degassed  $\text{H}_2\text{O}$  (1.5 mL). The resulting mixture was stirred at 100 °C for 16 h. After cooling to rt,  $\text{H}_2\text{O}$  (20 mL) was added and the aq. layer was extracted with  $\text{CH}_2\text{Cl}_2$  (3  $\times$  30 mL). The combined organic layers were washed with brine (20 mL), dried over  $\text{Na}_2\text{SO}_4$  and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel deactivated with  $\text{NEt}_3$ , cyclohexane/EtOAc: 10/1 to 3/1) to afford **PA-PhPT** (232 mg, 234  $\mu\text{mol}$ , 97%) as a light-yellow solid.

**R<sub>f</sub>** 0.16 (cyclohexane/EtOAc: 3/1); **<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43–7.42 (m, 2H), 7.38–7.37 (m, 2H), 7.18 (s, 1H), 7.04 (dd,  $J = 7.5, 1.7$  Hz, 2H), 6.89 (ddd,  $J = 8.2, 7.8, 1.6$  Hz, 2H), 6.86 (s, 1H), 6.83 (ddd,  $J = 7.6, 7.5, 1.3$  Hz, 2H), 6.81 (s, 1H), 6.79 (s, 1H), 6.77 (s, 2H), 6.75 (s, 1H), 6.69 (s, 1H), 6.68 (s, 1H), 6.33 (dd,  $J = 8.2, 1.3$  Hz, 2H), 6.00 (s, 1H), 3.94 (s, 2H), 3.82 (s, 2H), 3.80 (s, 2H), 3.79 (s, 2H), 3.73 (s, 2H), 3.67 (s, 3H), 3.66 (s, 3H), 3.65 (s, 6H), 3.64 (s, 3H), 3.62 (s, 3H), 3.60 (s, 3H), 3.57 (s, 3H), 3.35 (s, 3H); **<sup>13</sup>C NMR** (126 MHz,  $\text{CDCl}_3$ )<sup>a</sup>  $\delta$  156.94, 151.43, 151.18, 151.11, 151.02, 150.87, 150.54, 144.49, 142.65, 139.30, 138.21, 132.85, 132.46, 132.34, 130.26, 128.71, 128.62, 128.60, 128.54, 128.04, 127.88, 127.55, 127.01, 126.95, 122.70, 120.62, 116.35, 114.74, 114.72, 114.46, 114.41, 114.23, 114.04, 113.50, 112.76, 56.10, 56.07, 56.03, 55.97, 55.96, 55.95, 55.89, 55.84, 55.10, 32.51, 30.51, 30.17, 29.92, 29.77; **HRMS** (ESI<sup>+</sup>):  $m/z$  calcd. for  $\text{C}_{62}\text{H}_{60}\text{O}_9\text{NS}$  994.3983  $[\text{M}+\text{H}]^+$ , found 994.3970.

<sup>a</sup> Signals of five C-atoms are missing due to the overlap with the peaks 151.02, 128.71, 128.54, 114.23 (overlap of 3 C-atoms).

## 2.7 1-(4-Bromobutoxy)-4-bromobenzene (**S3**)

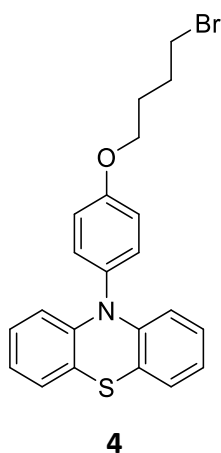


**S3**

The synthesis was carried out following a modified procedure by Li *et al.*<sup>[9]</sup> 4-Bromophenol (400 mg, 2.32 mmol) and 1,4-dibromobutane (1.7 mL, 3.1 g, mmol, 6.2 eq.) were dissolved in acetone (240 mL). K<sub>2</sub>CO<sub>3</sub> (2.00 g, 14.5 mmol, 6.3 eq.) was added and the mixture was stirred at 70 °C for 16 h. Remaining K<sub>2</sub>CO<sub>3</sub> and KBr were separated by filtration and the solvent was removed under reduced pressure. The remaining oil was purified by distillation at 10 mbar to recover the excess of 1,4-dibromobutane (bp: 65 °C) and at 5.5 · 10<sup>-2</sup> mbar (bp: 120 °C) to obtain **S3** (2.00 g, 7.72 mmol, 96%) as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.39–7.34 (m, 2H), 6.78–6.74 (m, 2H), 3.96 (t, *J* = 6.0 Hz, 2H), 3.48 (t, *J* = 6.6 Hz, 2H), 2.09–2.02 (m, 2H), 1.95–1.87 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 158.2, 132.4, 116.5, 113.1, 67.3, 33.4, 29.6, 28.0; HRMS (APCI<sup>+</sup>): *m/z* calcd. for C<sub>8</sub>H<sub>16</sub><sup>79</sup>Br<sub>2</sub>O 303.9006 [M+NH<sub>4</sub>]<sup>+</sup>, found 303.9004.

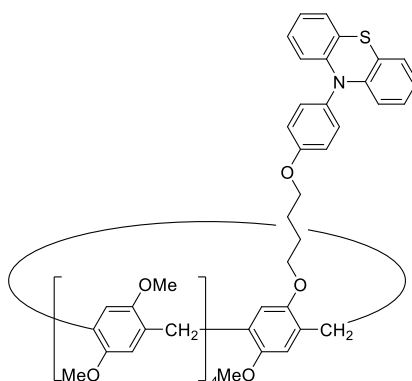
## 2.8 10-(4-(4-Bromobutoxy)phenyl)-10*H*-phenothiazine (**4**)



Phenothiazine (1.58 g, 7.94 mmol), aryl bromide **S3** (2.50 g, 8.11 mmol, 1.02 eq.), Pd(OAc)<sub>2</sub> (18.9 mg, 84 μmol, 10 mol%), SPhos (33.4 mg, 81.0 μmol, 10 mol%) and Cs<sub>2</sub>CO<sub>3</sub> (5.28 g, 16.2 mmol, 2.0 eq.) were dissolved in a mixture of anh. and degassed 1,4-dioxane (20 mL) and anh. and degassed toluene (20 mL) and stirred at 100 °C for 16 h. The reaction mixture was filtered through a pad of Celite® and rinsed with CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel deactivated with NEt<sub>3</sub>, cyclohexane/EtOAc: 50/1) to afford **4** (1.20 g, 3.45 mmol, 43%) as a light beige solid.

**R<sub>f</sub>** 0.34 (cyclohexane/EtOAc: 50/1); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.31–7.28 (m, 2H), 7.10–7.07 (m, 2H), 6.98 (dd, *J* = 7.4, 1.7 Hz, 2H), 6.82 (ddd, *J* = 8.2, 7.9, 1.7 Hz, 2H), 6.78 (ddd, *J* = 7.4, 7.3, 1.7 Hz, 2H), 6.18 (dd, *J* = 8.1, 1.3 Hz, 2H), 4.07 (t, *J* = 6.0 Hz, 2H), 3.53 (t, *J* = 6.6 Hz, 2H), 2.12 (tt, *J* = 7.2, 6.5 Hz, 2H), 2.00 (tt, *J* = 7.2, 5.9 Hz, 2H); **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>): δ 158.7, 144.8, 133.5, 132.4, 126.9, 126.8, 122.4, 119.8, 116.5, 115.8, 67.3, 33.5, 29.6, 28.1; **HRMS** (ESI<sup>+</sup>): *m/z* calcd. for C<sub>22</sub>H<sub>20</sub>ONBrS<sup>+</sup> 425.0443 [M]<sup>+</sup>, found 425.0446.

## 2.9 Pillar[5]arene **PA-C4-PhPT**



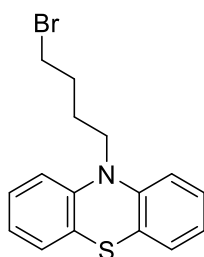
**PA-C4-PhPT**

Phenothiazine **4** (70 mg, 136  $\mu\text{mol}$  mmol, 1.2 eq.) and NaH (60% in mineral oil, 11 mg, 280  $\mu\text{mol}$ , 2.0 eq.) were dissolved in anh. DMF (2 mL) at 0 °C. After the solution was stirred at 0°C for 1 h, hydroxypillarene **2** (100.0 mg, 136  $\mu\text{mol}$ ) was added, and the mixture was stirred at 0°C for 1 h and at rt for 16 h. H<sub>2</sub>O (10 mL) was added and the aq. layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3× 30 mL). The combined organic layers were washed with H<sub>2</sub>O (3 × 30 mL) and brine (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO<sub>2</sub>/NEt<sub>3</sub>, cyclohexane/EtOAc: 5/1). **PA-C4-PhPT** (135 mg, 133  $\mu\text{mol}$ , 97%) was obtained as a colorless solid.

**R<sub>f</sub>** 0.28 (cyclohexane/EtOAc: 5/1); **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.31–7.28 (m, 2H), 7.11–7.08 (m, 2H), 6.99 (dd,  $J$  = 7.4, 1.7 Hz, 2H), 6.83 (ddd,  $J$  = 7.5, 7.2, 1.7 Hz, 2H), 6.78–6.76 (m, 8H), 6.75 (s, 1H), 6.74 (s, 1H), 6.734 (s, 1H), 6.732 (s, 1H), 6.19 (dd,  $J$  = 8.1, 1.3 Hz, 2H), 4.09 (t,  $J$  = 6.2 Hz, 2H), 3.93 (t,  $J$  = 6.0 Hz, 2H), 3.81 (s, 2H), 3.78 (s, 2H), 3.77 (s, 6H), 3.641 (s, 3H), 3.636 (s, 12H), 3.634 (s, 3H), 3.628 (s, 3H), 3.623 (s, 6H), 2.08–2.03 (m, 2H), 2.01–1.96 (m, 2H); **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>)<sup>a</sup>  $\delta$  158.84, 151.06, 151.02, 151.00, 150.98, 150.95, 150.13, 144.80, 133.39, 132.42, 128.52, 128.45, 128.41, 128.35, 128.31, 126.94, 126.76, 122.38, 119.82, 116.46, 115.76, 115.19, 114.39, 114.37, 114.34, 114.27, 114.25, 68.17, 67.98, 56.05, 56.00, 55.97, 55.93, 55.89, 30.00, 29.96, 29.86, 29.83, 29.72, 26.60, 26.50; **HRMS** (ESI<sup>+</sup>):  $m/z$  calcd. for C<sub>66</sub>H<sub>71</sub>O<sub>11</sub>N<sub>2</sub>S 1099.4773 [M+NH<sub>4</sub>]<sup>+</sup>, found 1099.4773.

<sup>a</sup> Signals of 17 C-atoms are missing due to overlap with the peaks at 151.06 (overlap of 3 C-atoms), 150.98 (overlap of 3 C-atoms), 128.45, 128.41 (overlap of 5 C-atoms), 114.39, 114.37, 114.34, 114.25, 56.00, 55.97 (overlap of 3 C-atoms), and 55.93 ppm.

10-(4-Bromobutyl)-10*H*-phenothiazine (**5**)

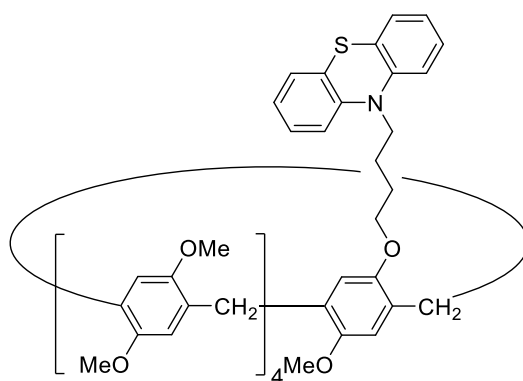


**5**

1,4-Dibromobutane (0.88 mL, 1.62 g, 7.46 mmol, 2.9 eq.) and NaH (60% in mineral oil, 150 mg, 3.75 mmol, 1.5 eq.) were suspended in anh. DMF (10 mL). A solution of phenothiazine (500 mg, 2.51 mmol) in DMF (2.5 mL) was added over 2.5 h with a syringe pump. After addition the mixture was stirred at rt for 16 h. H<sub>2</sub>O (10 mL) was added, and the resulting precipitate was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The aq. layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 30 mL). The combined organic layers were washed with H<sub>2</sub>O (4 × 30 mL), brine (30 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO<sub>2</sub>/NEt<sub>3</sub>, cyclohexane/EtOAc: 1/0 to 100/1). **5** (531 mg, 1.60 mmol, 63%) was obtained as a colorless oil.

**R<sub>f</sub>** 0.27 (cyclohexane); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, spectra contains EtOAc): δ 7.17–7.13 (m, 4H), 6.94–6.86 (m, 4H), 3.90 (br, 2H), 3.39 (t, *J* = 6.3 Hz, 2H), 2.00–1.94 (m, 4H); **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>): δ 127.7, 127.4, 125.7, 122.8, 115.8, 46.5, 33.5, 30.1, 25.5; **HRMS** (ESI<sup>+</sup>): *m/z* calcd. for C<sub>16</sub>H<sub>16</sub><sup>79</sup>BrNS 330.0181 [M]<sup>+</sup>, found 330.0182.

## 2.10 Pillar[5]arene **PA-C4-PT**



**PA-C4-PT**

10-(4-Bromobutyl)-10*H*-phenothiazine (**5**, 136 mg, 407  $\mu\text{mol}$ , 1.5 eq.) and NaH (60% in mineral oil, 22 mg, 550  $\mu\text{mol}$ , 2.0 eq.) were dissolved in anh. DMF (3.5 mL) at 0 °C. After the solution had been stirred at 0 °C for 1 h, hydroxypillararene **2** (200.0 mg, 271  $\mu\text{mol}$ ) was added and the mixture was stirred at 0 °C for 1 h and at rt for 16 h. H<sub>2</sub>O (10 mL) was added and the aq. layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3  $\times$  30 mL). The combined organic layers were washed with H<sub>2</sub>O (3  $\times$  30 mL) and brine (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO<sub>2</sub>/NEt<sub>3</sub>, cyclohexane/EtOAc: 5/1). **PA-C4-PT** (230 mg, 232  $\mu\text{mol}$ , 84%) was obtained as a colorless solid.

*R*<sub>f</sub> 0.27 (cyclohexane/EtOAc: 5/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.15–7.10 (m, 4H), 6.91–6.87 (m, 4H), 6.77 (s, 1H), 6.76 (s, 1H), 6.75 (s, 1H), 6.74 (s, 1H), 6.734 (s, 1H), 6.732 (s, 1H), 6.71 (s, 2H), 6.70 (s, 1H), 6.66 (s, 1H), 3.95 (t, *J* = 6.9 Hz, 2H), 3.84 (t, *J* = 6.1 Hz, 2H), 3.77 (s, 2H), 3.76 (s, 4H), 3.74 (s, 2H), 3.73 (s, 2H), 3.63 (3  $\times$  s, 9H), 3.62 (s, 3H), 3.613 (s, 3H), 3.605 (s, 3H), 3.595 (s, 3H), 3.57 (s, 3H), 3.52 (s, 3H), 2.08–2.02 (m, 2H), 1.93–1.88 (m, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)<sup>a</sup>  $\delta$  151.04, 151.01, 150.98, 150.95, 150.94, 150.91, 150.08, 145.37, 128.50, 128.46, 128.43, 128.40, 128.36, 128.33, 128.28, 127.67, 127.38, 125.38, 122.65, 115.59, 115.11, 114.39, 114.37, 114.33, 114.31, 114.25, 114.20, 114.14, 67.98, 55.96, 55.93, 55.86, 47.04, 30.03, 29.96, 29.82, 29.58, 27.28, 27.07, 23.82; HRMS (ESI<sup>+</sup>): *m/z* calcd. for C<sub>60</sub>H<sub>64</sub>O<sub>10</sub>N<sub>2</sub>S 990.4245 [M+H]<sup>+</sup>, found 990.4244, C<sub>60</sub>H<sub>67</sub>O<sub>10</sub>N<sub>2</sub>S 1007.4511 [M+NH<sub>4</sub>]<sup>+</sup>, found 1007.4509.

<sup>a</sup> Signals of 14 C-atoms are missing due to the overlap with the peaks at 151.01, 150.98, 150.95, 128.36, 128.33, 128.28, 114.33, 114.25, 55.96 (overlap of four C-atoms), 55.93 (overlap of three C-atoms), 55.86 and 29.82 ppm.



## 2.11 General Procedure for Reductive Dehalogenation

The respective bromide **6** or **7** (200  $\mu\text{mol}$ ) was dissolved in anh. acetonitrile (2.5 mL) in a 10 mL reaction tube equipped with a septum cap and a magnetic stir bar. The respective photoredox catalyst (10.0  $\mu\text{mol}$ , 5 mol%), *N,N*-diisopropylethylamine (5.0 eq.) and formic acid (5.0 eq.) were added. The reaction mixture was degassed with three freeze-pump-thaw cycles. The tube was backfilled with argon and vigorously stirred in front of a nail dryer lamp (365 nm) for 48 hours (see Figure S1). The reaction was cooled with compressed air. After the irradiation 0.3 mL of the reaction mixture were diluted with 0.3 mL of  $\text{MeCN-}d_3$  and the conversion was determined by the ratio of starting material to product in the  $^1\text{H}$  NMR spectra. In some cases,  $\text{Na}_2\text{SO}_3$  was added to reduce phenothiazine radical cations. Each reaction was performed three times, and the conversions were averaged.

### 3 NMR Spectra

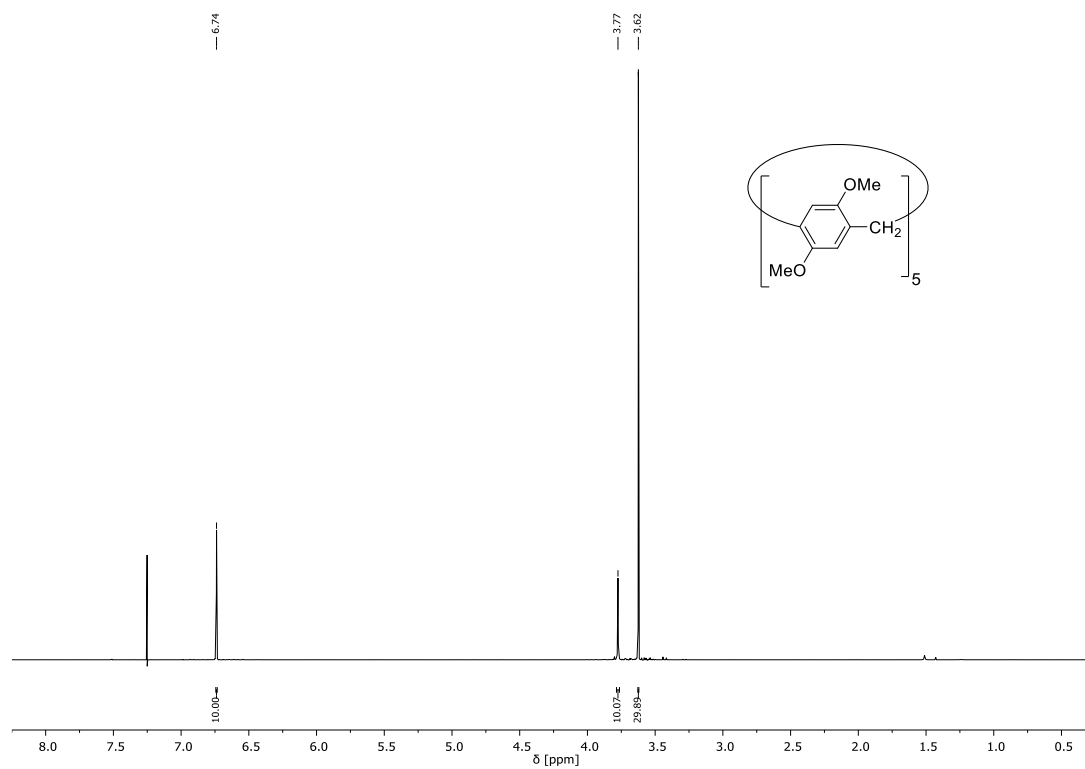


Figure S2: <sup>1</sup>H NMR spectrum of **1** in CDCl<sub>3</sub> (400 MHz).

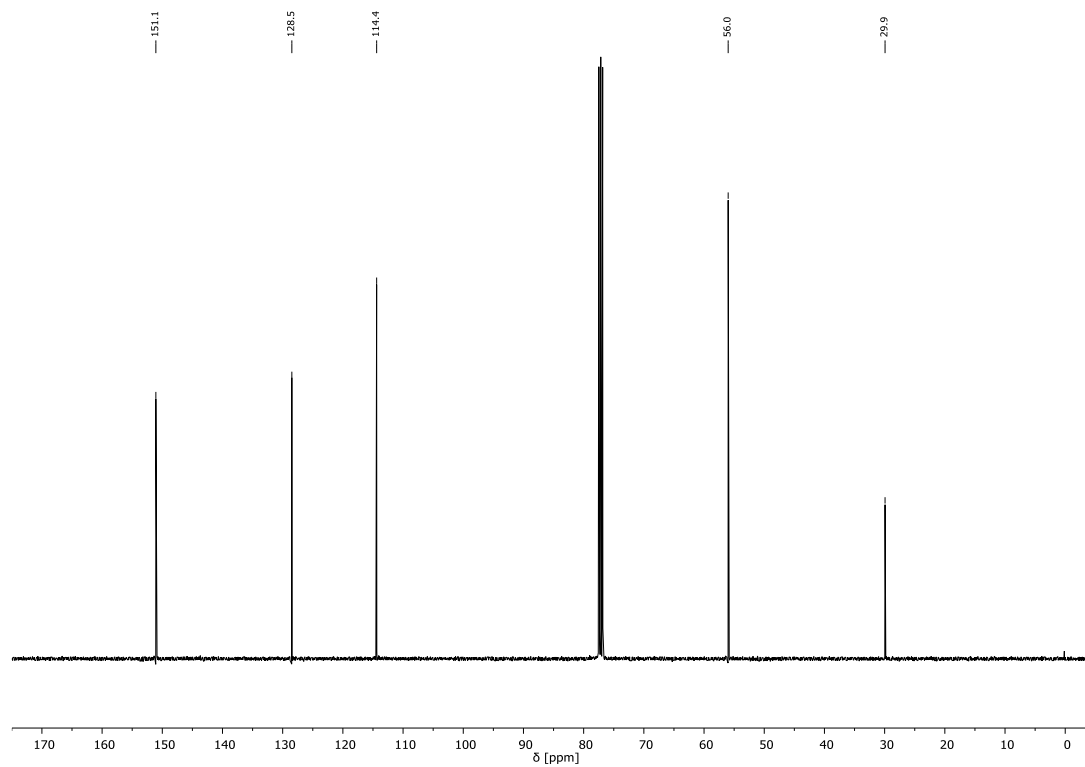


Figure S3: <sup>13</sup>C NMR spectrum of **1** in CDCl<sub>3</sub> (101 MHz).

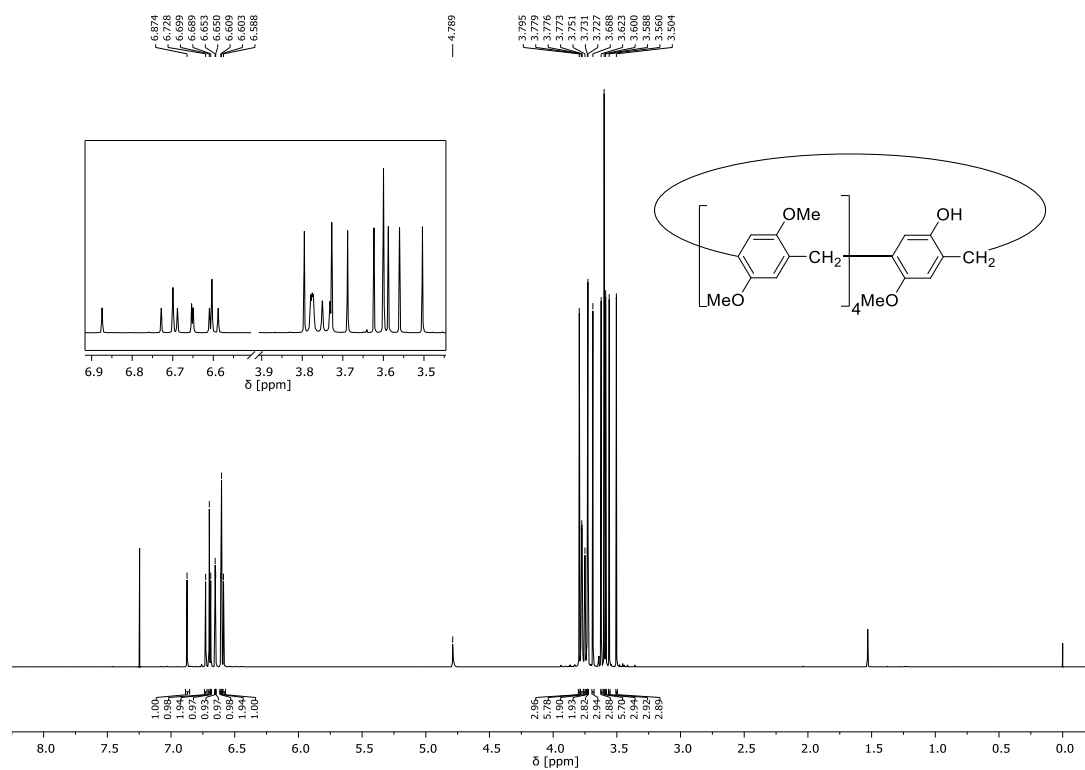


Figure S4:  $^1\text{H}$  NMR spectrum of **2** in  $\text{CDCl}_3$  (500 MHz, spectrum contains residues of  $\text{CH}_2\text{Cl}_2$  bound by the pillarene at 4.789 ppm).

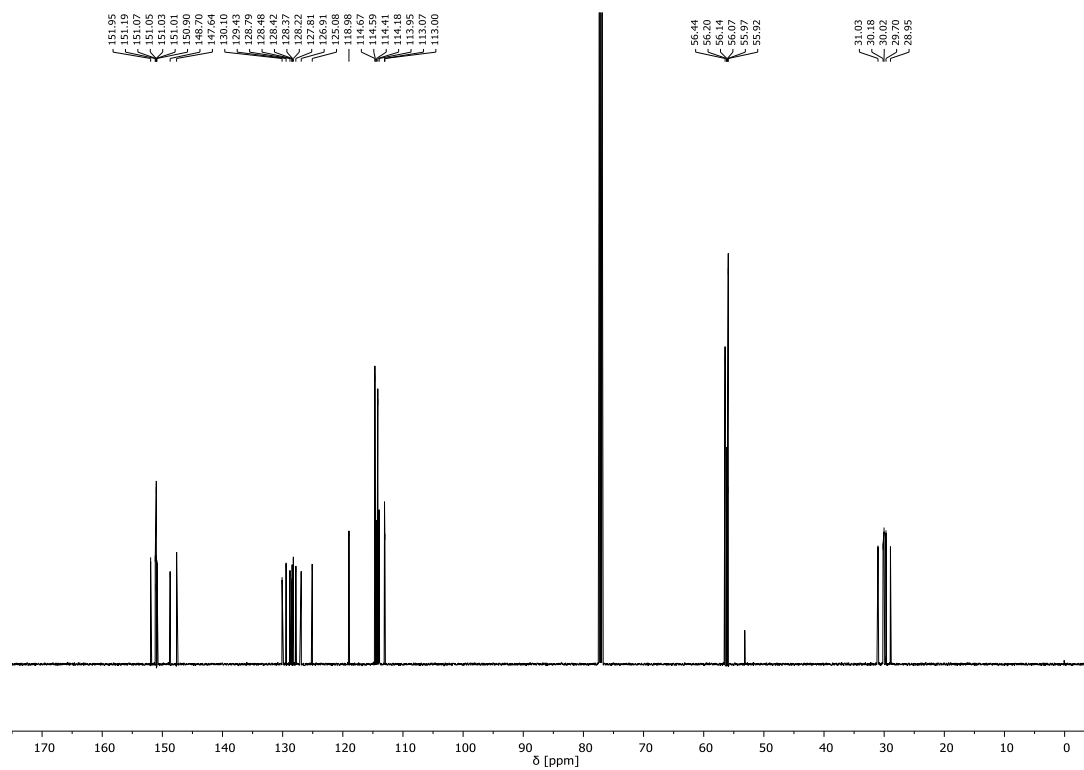


Figure S5:  $^{13}\text{C}$  NMR spectrum of **2** in  $\text{CDCl}_3$  (126 MHz, spectrum contains residues of  $\text{CH}_2\text{Cl}_2$  bound by the pillarene at 53.18 ppm).

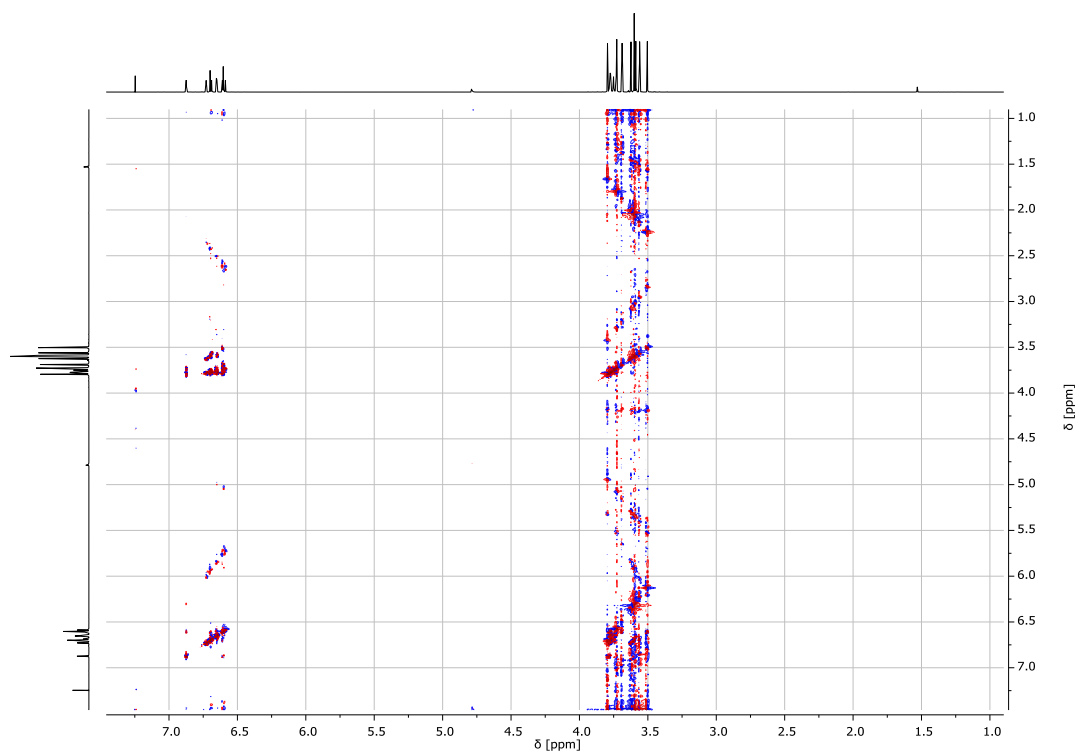


Figure S6: H,H-COSY spectrum of **2** in CDCl<sub>3</sub> (500 MHz).

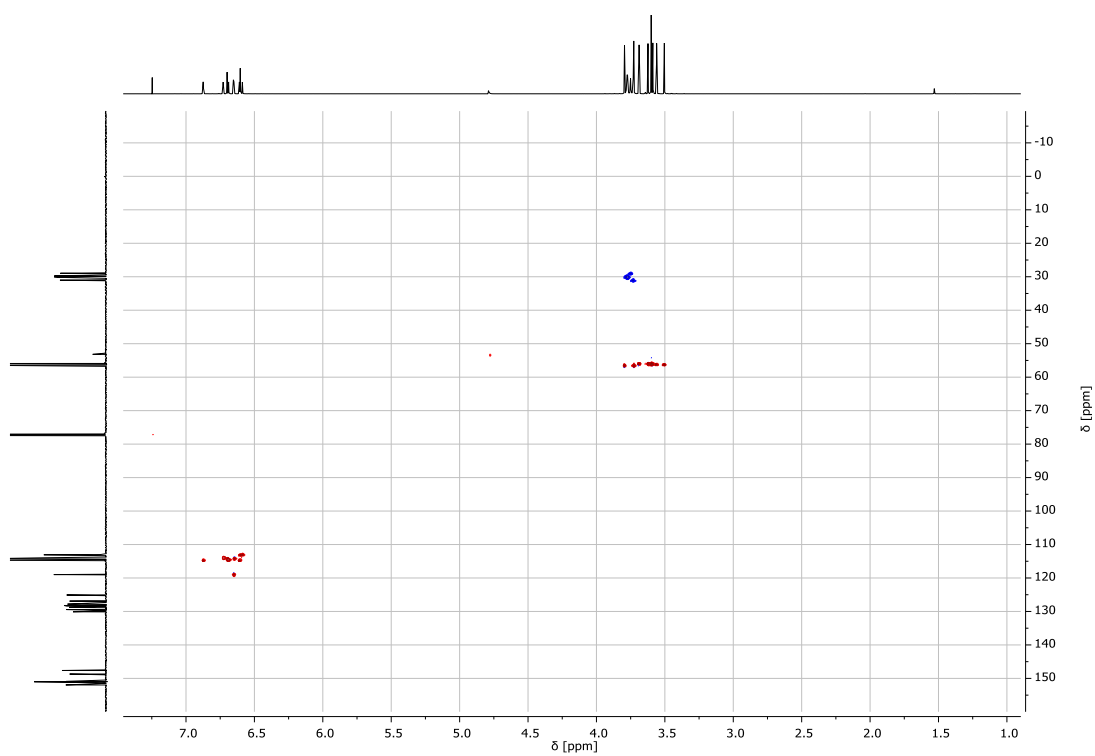


Figure S7: HSQC spectrum of **2** in CDCl<sub>3</sub> (500/126 MHz). Blue: CH<sub>2</sub> groups, red: CH or CH<sub>3</sub> groups.

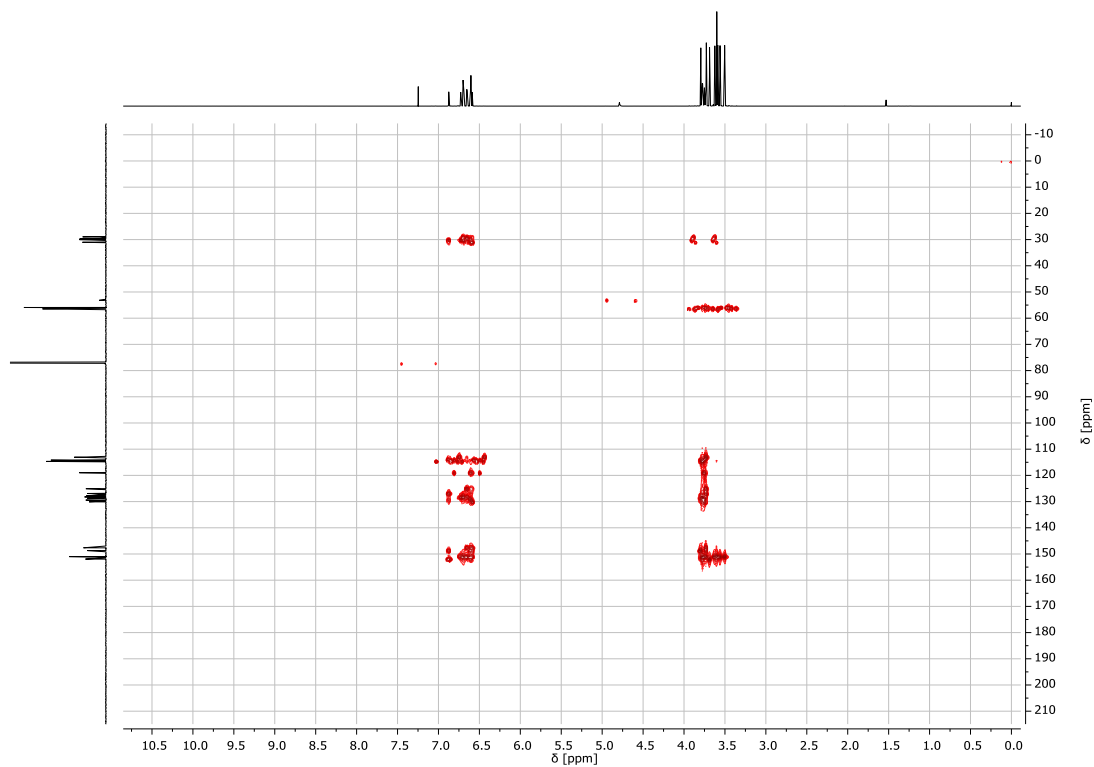


Figure S8: HMBC spectrum of **2** in  $\text{CDCl}_3$  (500/126 MHz).

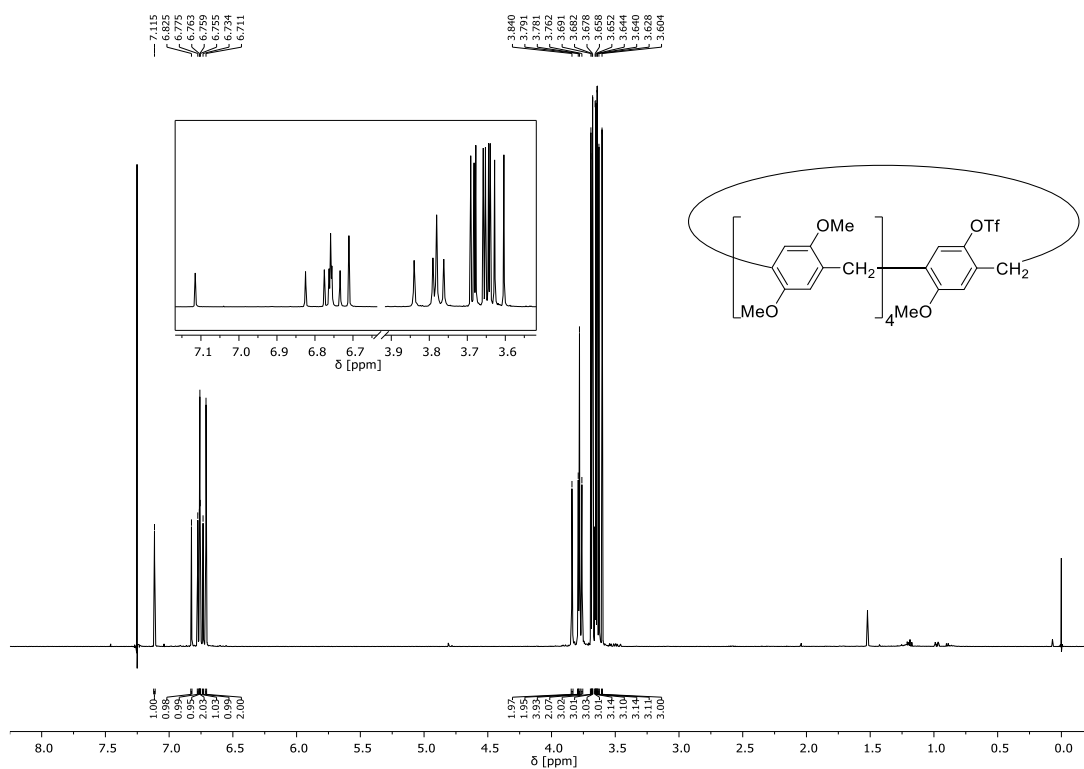


Figure S9:  $^1\text{H}$  NMR spectrum of **1** in  $\text{CDCl}_3$  (500 MHz).

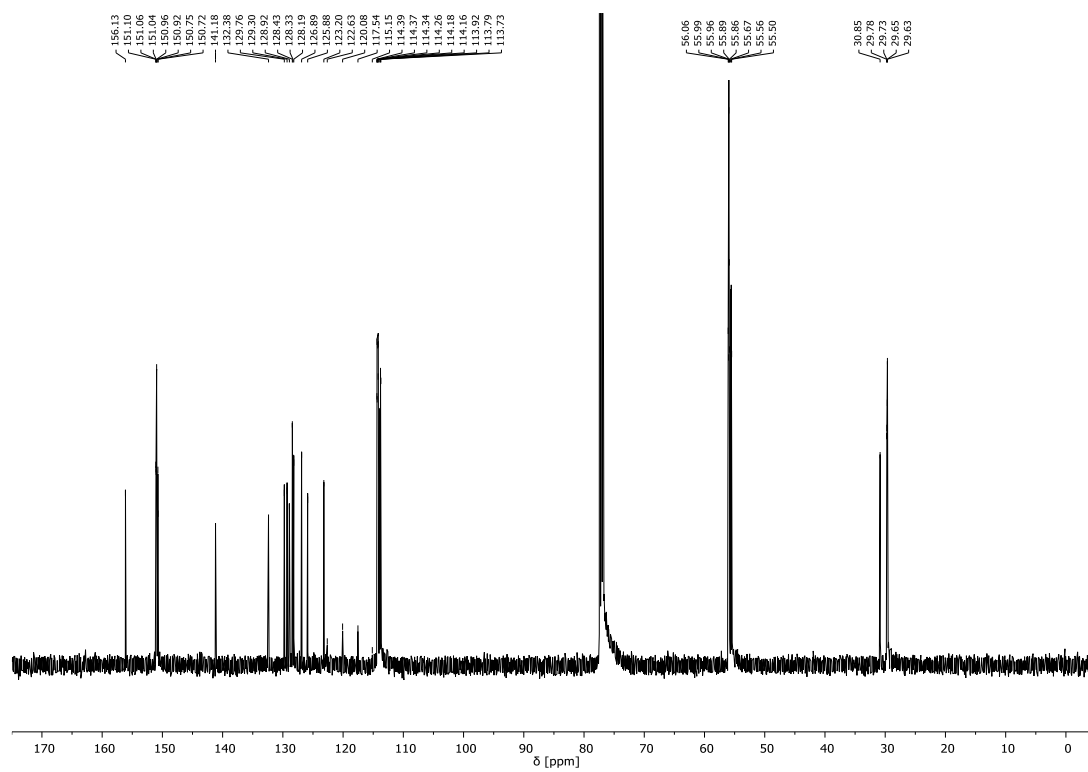


Figure S10:  $^{13}\text{C}$  NMR spectrum of **S1** in  $\text{CDCl}_3$  (126 MHz).

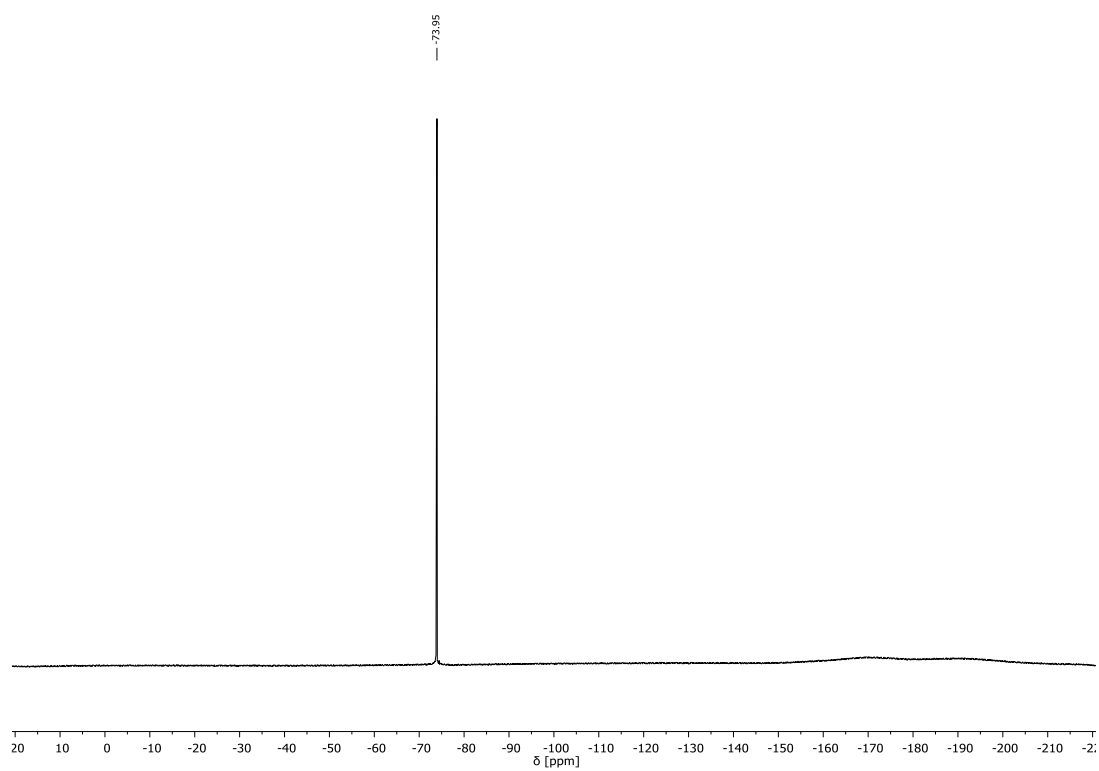


Figure S11:  $^{19}\text{F}$  NMR spectrum of **S1** in  $\text{CDCl}_3$  (471 MHz).

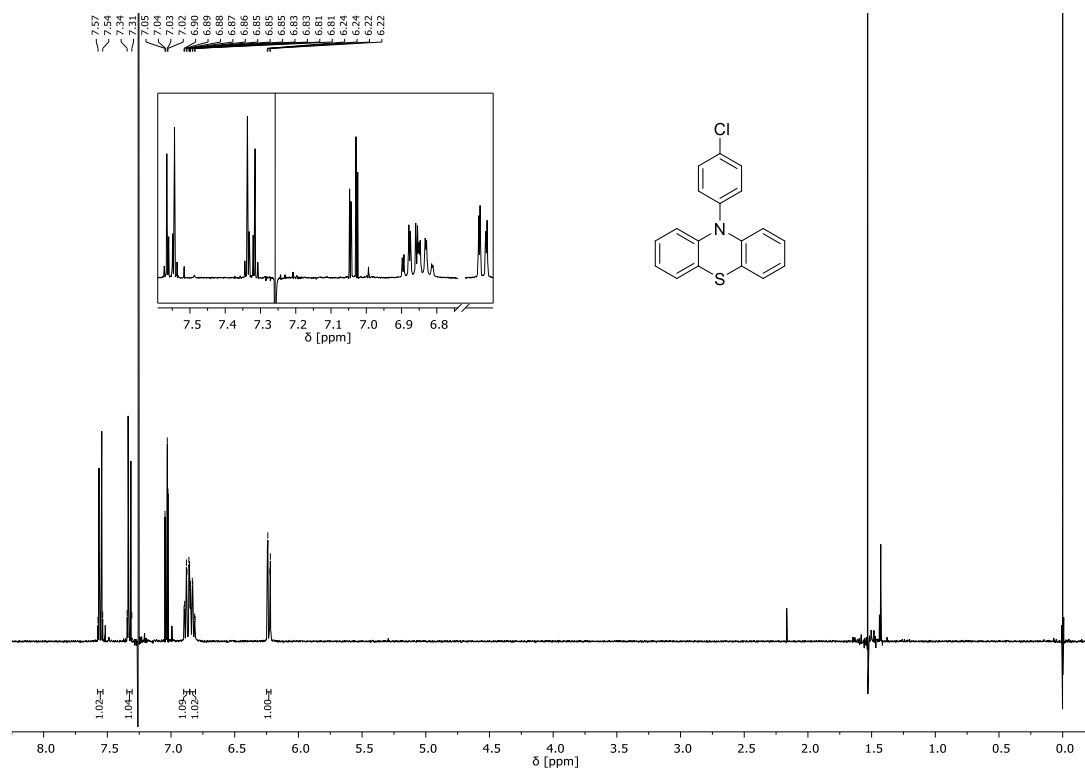


Figure S12: <sup>1</sup>H NMR spectrum of 10-(4-chlorophenyl)-10H-phenothiazine (S2) in CDCl<sub>3</sub> (400 MHz).

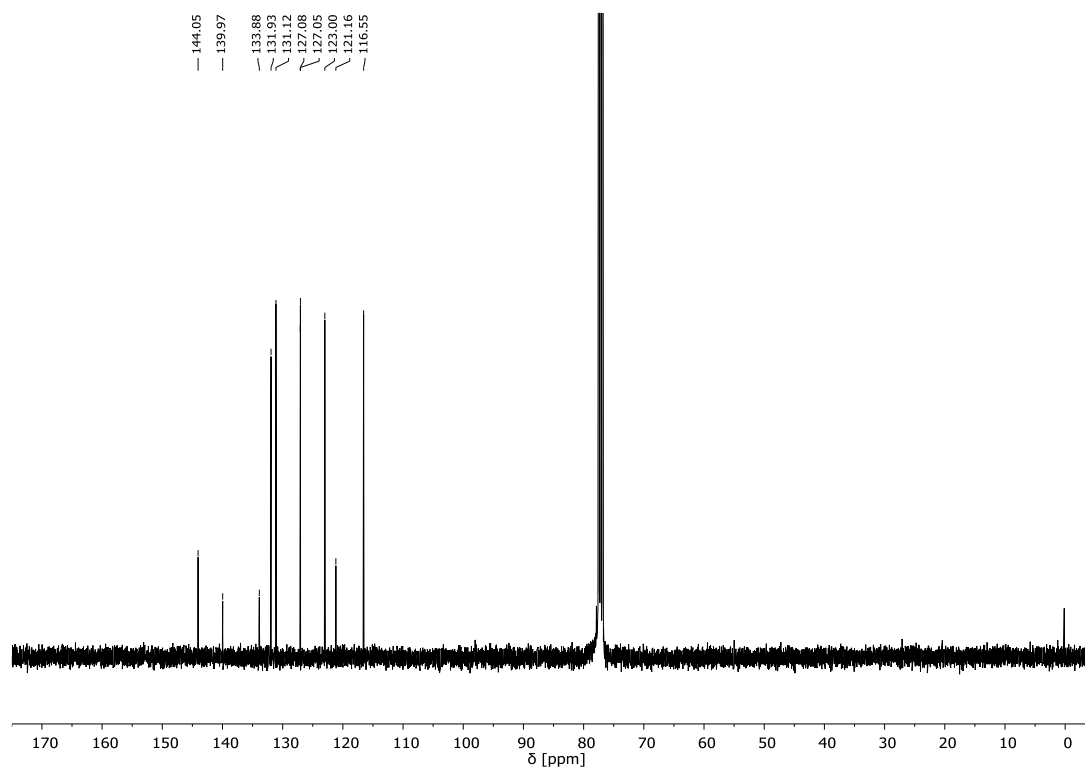


Figure S13: <sup>13</sup>C NMR spectrum of 10-(4-chlorophenyl)-10H-phenothiazine (S2) in CDCl<sub>3</sub> (101 MHz).

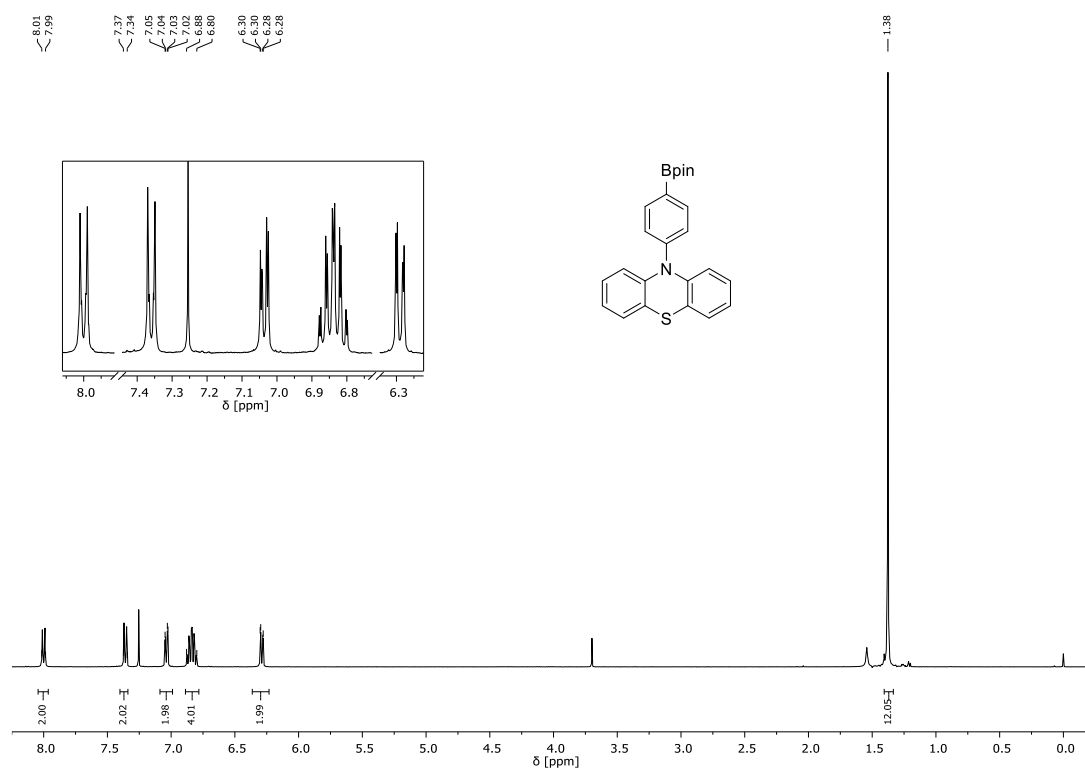


Figure S14: <sup>1</sup>H NMR spectrum of 10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-10H-phenothiazine (**3**) in CDCl<sub>3</sub>(400 MHz).

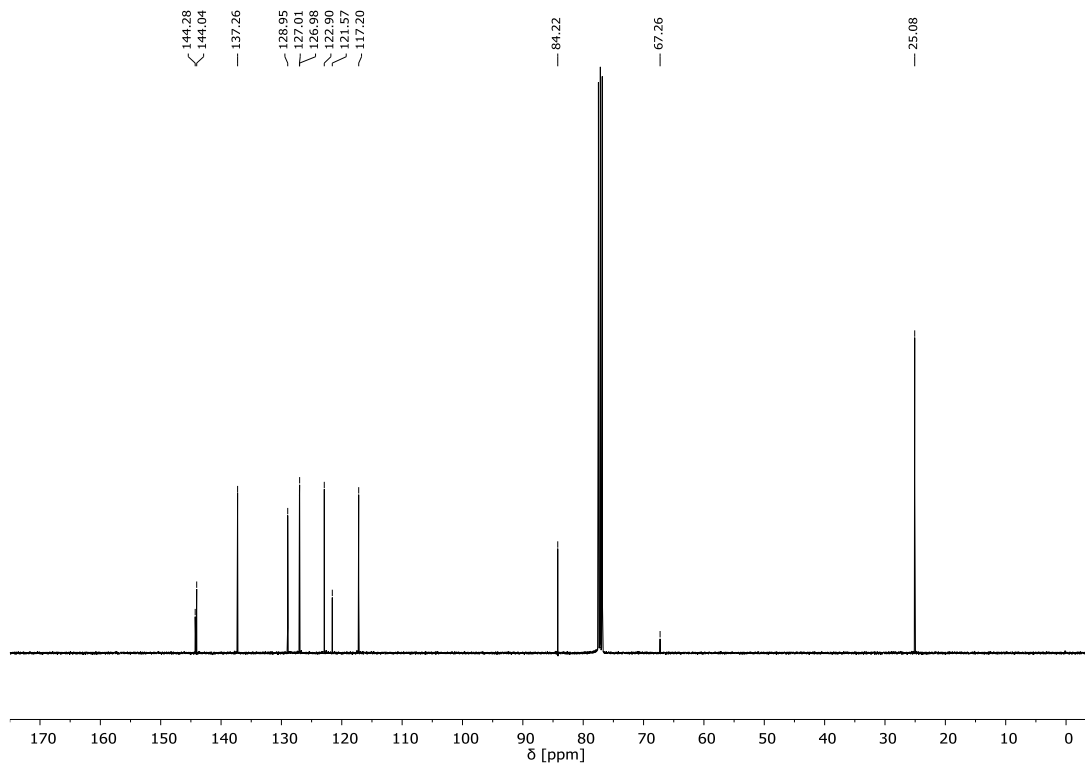


Figure S15: <sup>13</sup>C NMR spectrum of 10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-10H-phenothiazine (**3**) in CDCl<sub>3</sub>(101 MHz).



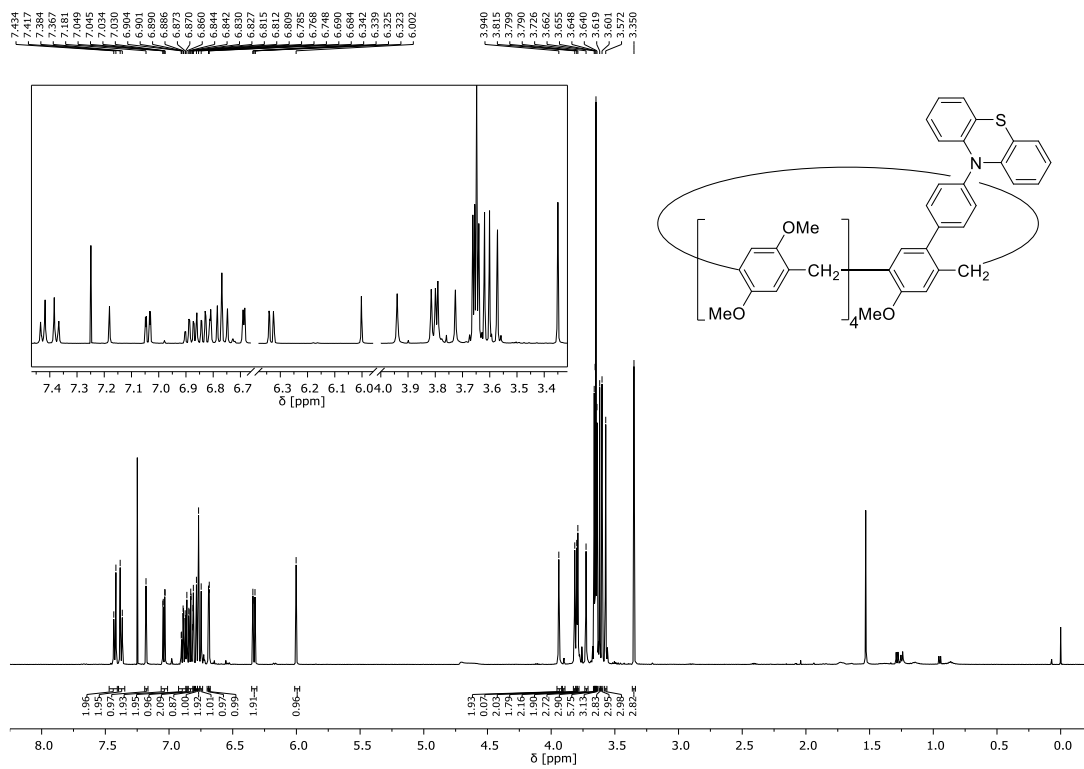


Figure S16: <sup>1</sup>H NMR spectrum of PA-PhPT in CDCl<sub>3</sub> (500 MHz).

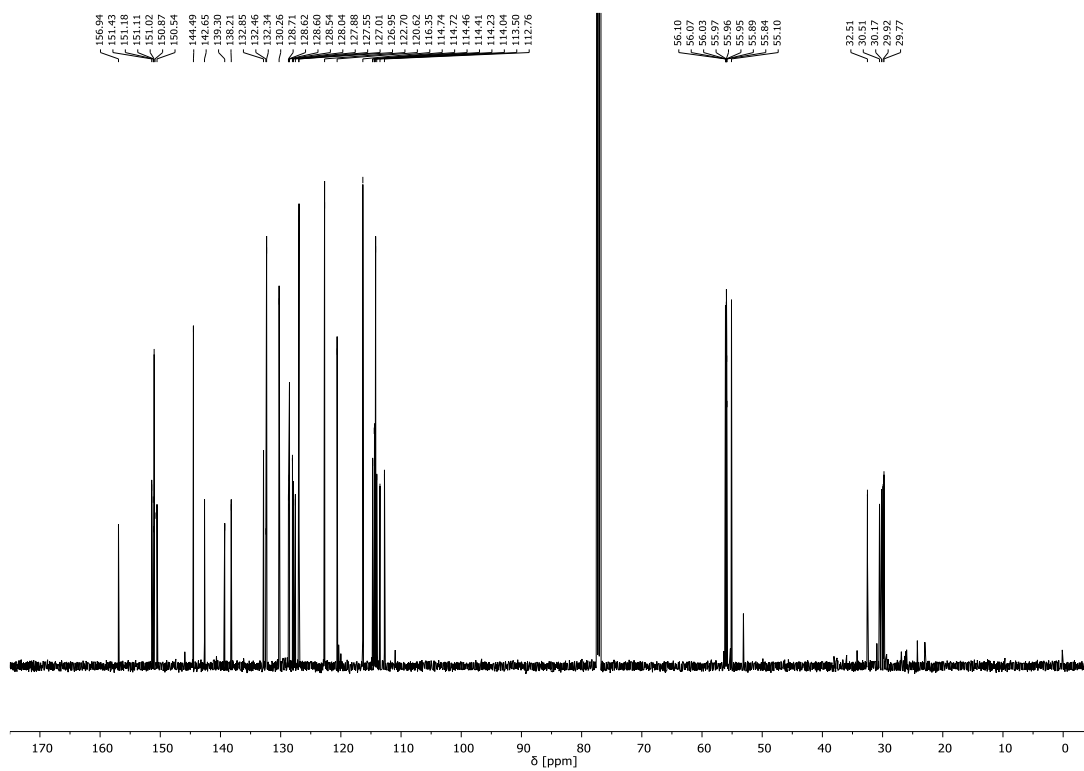


Figure S17: <sup>13</sup>C NMR spectrum of PA-PhPT in CDCl<sub>3</sub> (126 MHz).

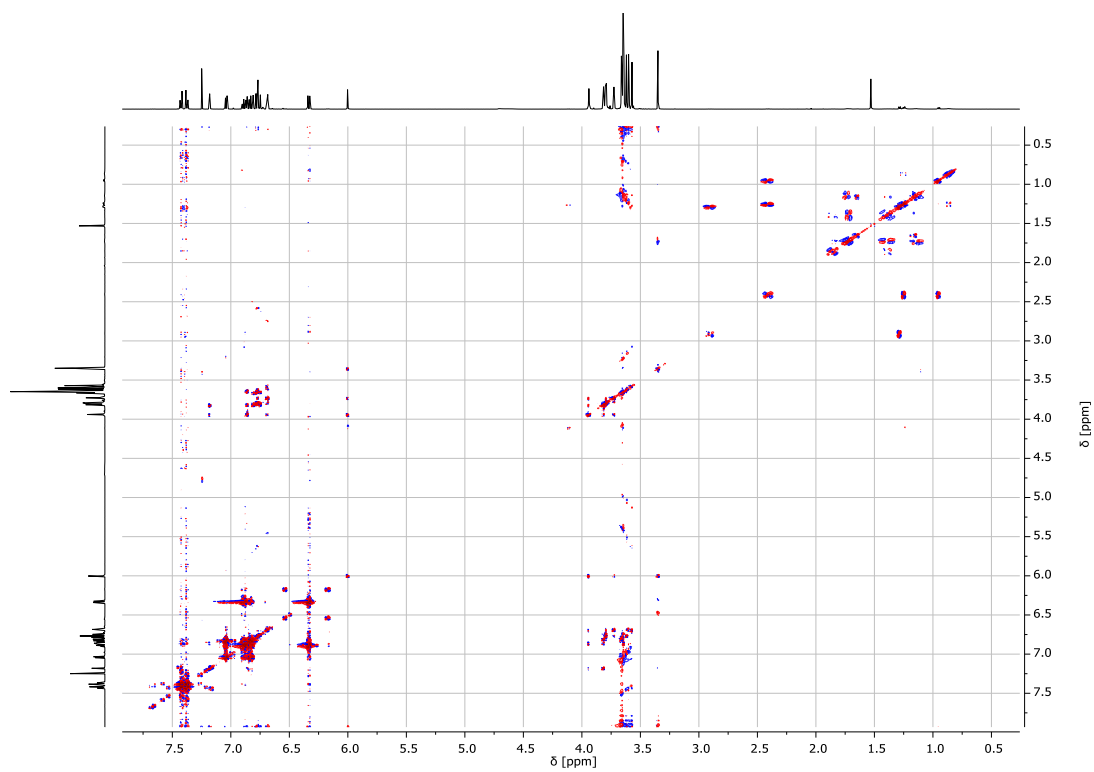


Figure S18: H,H-COSY spectrum of **PA-PhPT** in  $\text{CDCl}_3$  (500 MHz).

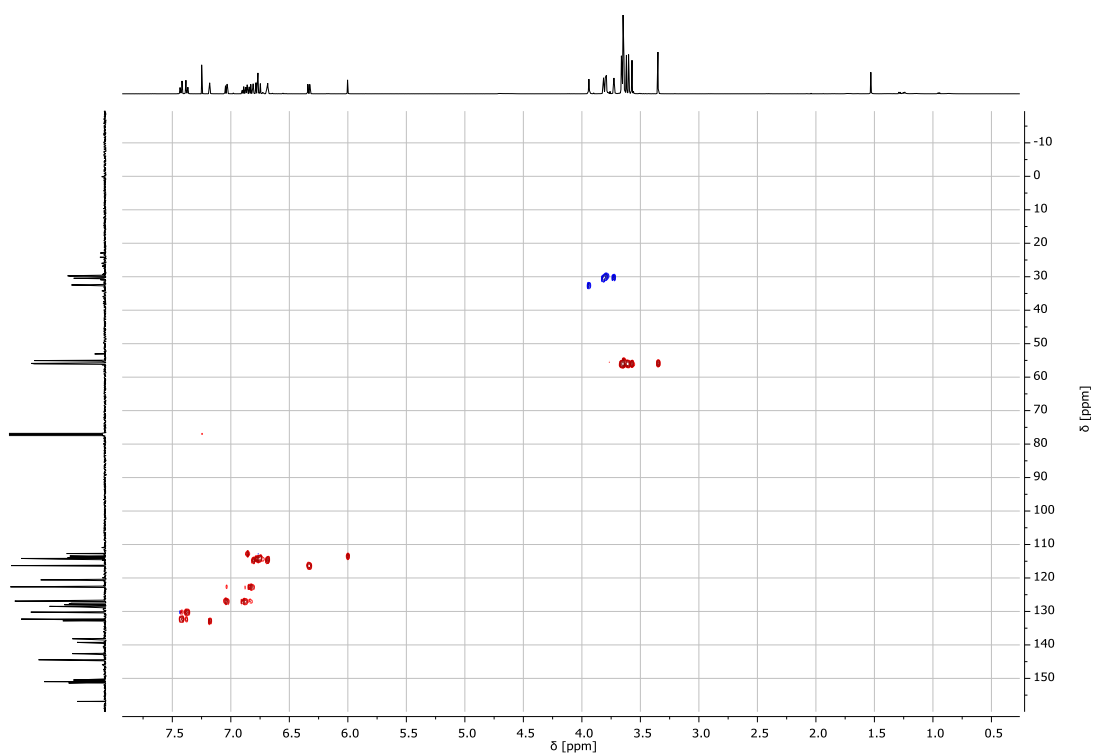


Figure S19: HSQC spectrum of **PA-PhPT** in  $\text{CDCl}_3$  (500, 126 MHz). Blue:  $\text{CH}_2$  groups, red:  $\text{CH}$  or  $\text{CH}_3$  groups.

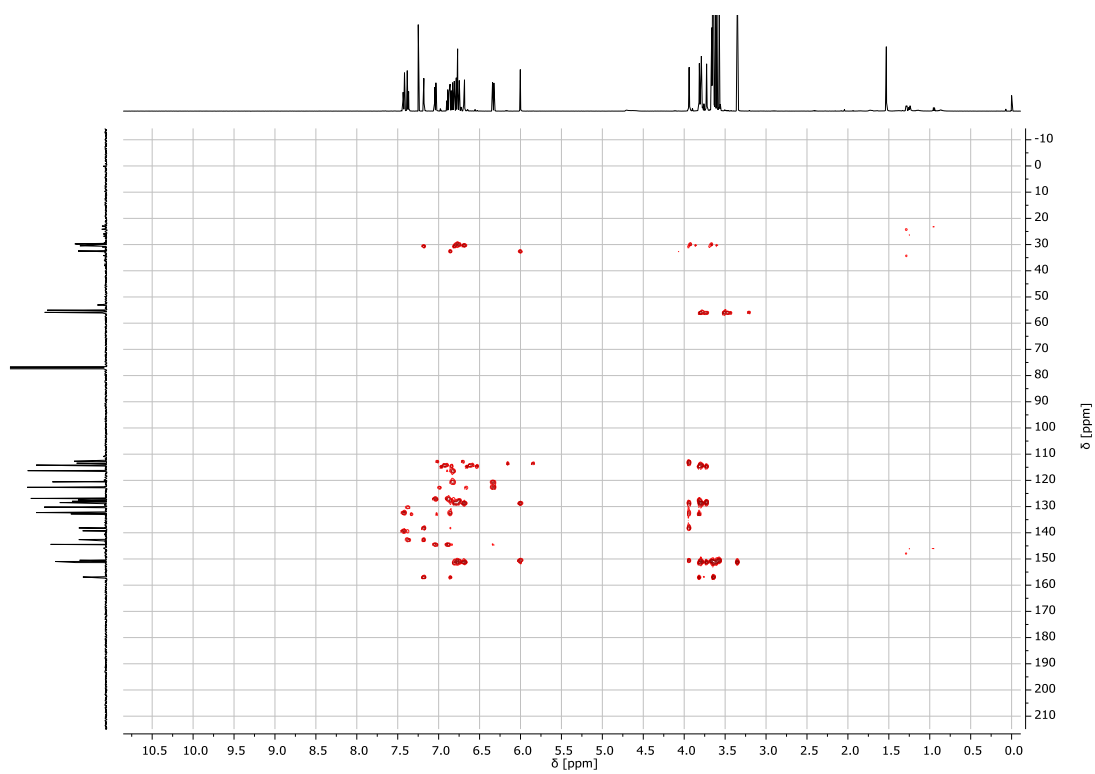


Figure S20: HMBC spectrum of **PA-PhPT** in  $\text{CDCl}_3$  (500, 126 MHz).

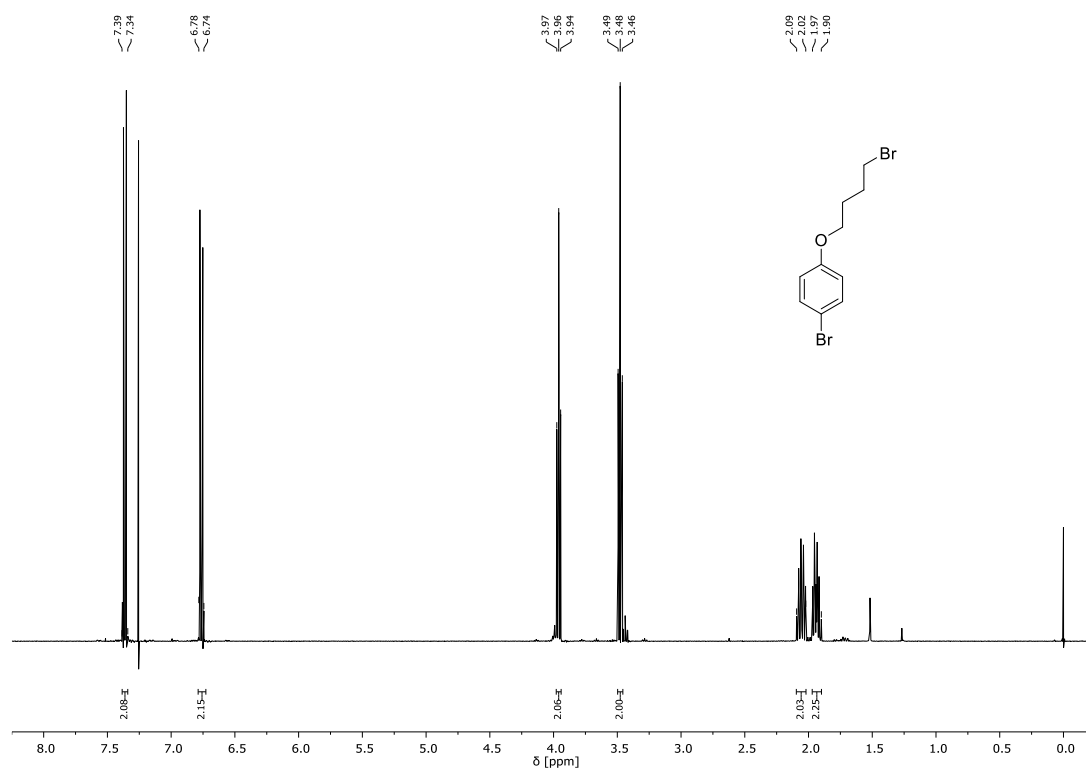


Figure S21:  $^1\text{H}$  NMR spectrum of 1-(4-bromobutoxy)-4-bromobenzene (**S3**) in  $\text{CDCl}_3$  (400 MHz).

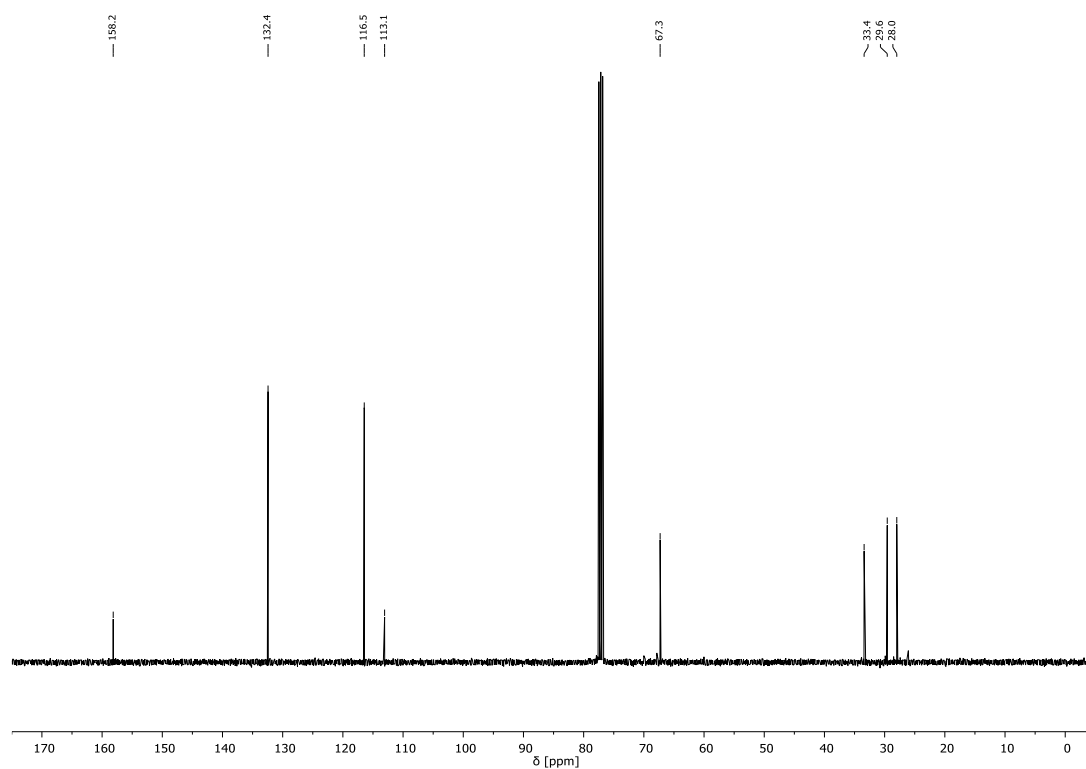


Figure S22:  $^{13}\text{C}$  NMR-spectrum of 1-(4-bromobutoxy)-4-bromobenzene (**S3**) in  $\text{CDCl}_3$  (101 MHz).

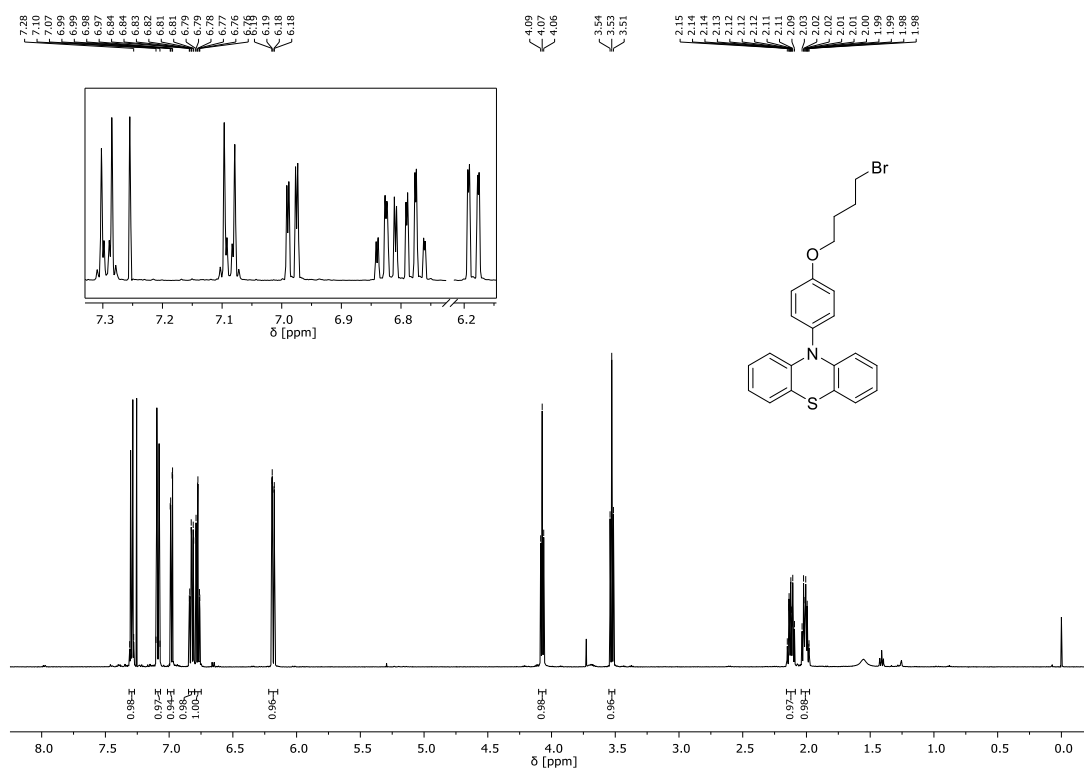


Figure S23: <sup>1</sup>H NMR-spectrum of 10-(4-(4-bromobutoxy)phenyl)-10H-phenothiazine (**4**) in CDCl<sub>3</sub> (500 MHz).

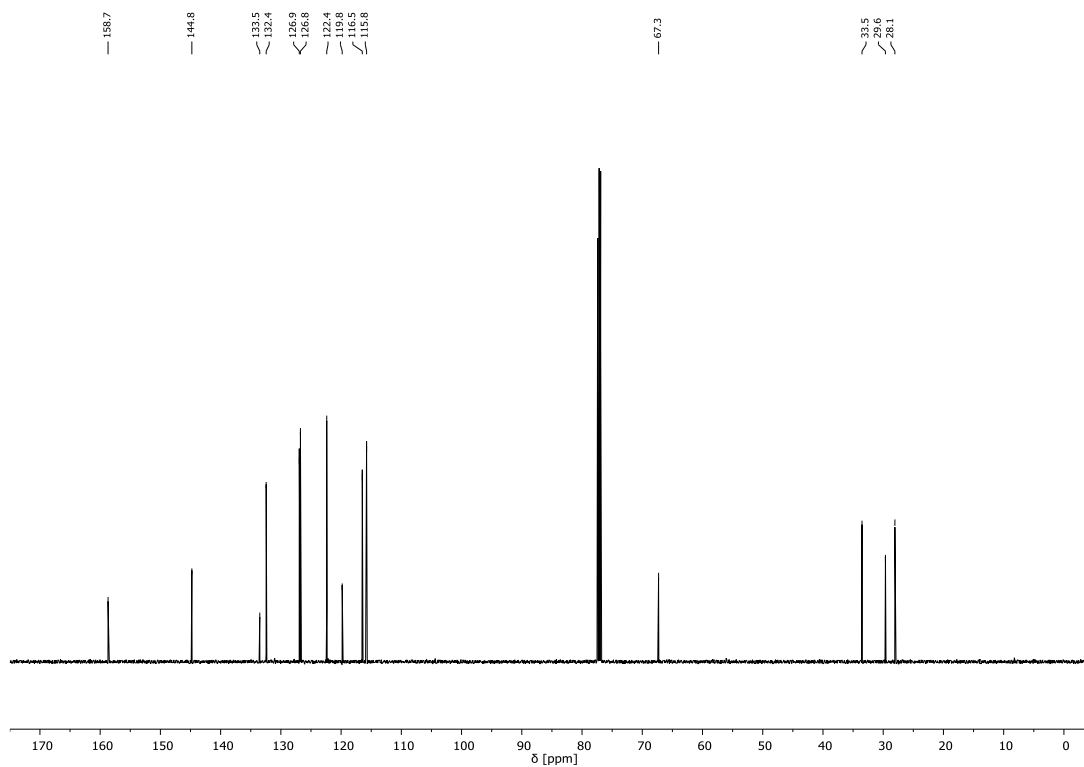


Figure S24: <sup>13</sup>C NMR-spectrum of 10-(4-(4-bromobutoxy)phenyl)-10H-phenothiazine (**4**) in CDCl<sub>3</sub> (126 MHz).

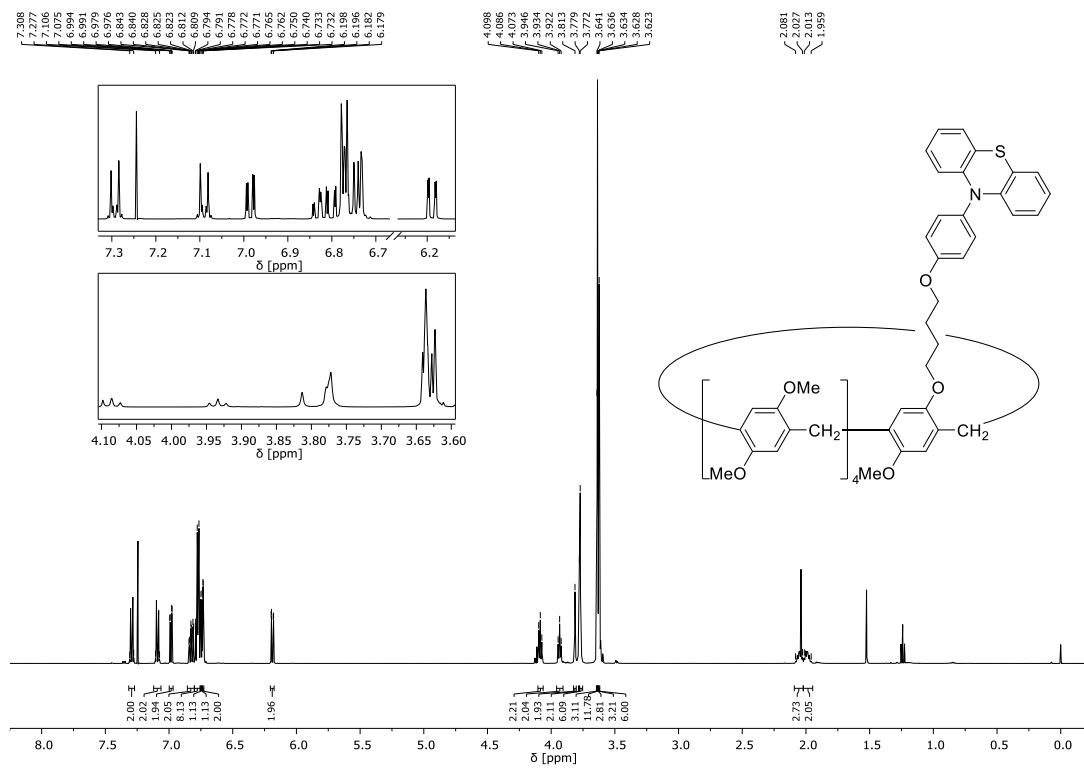


Figure S25: <sup>1</sup>H NMR-spectrum of PA-C4-PhPT in CDCl<sub>3</sub> (500 MHz).

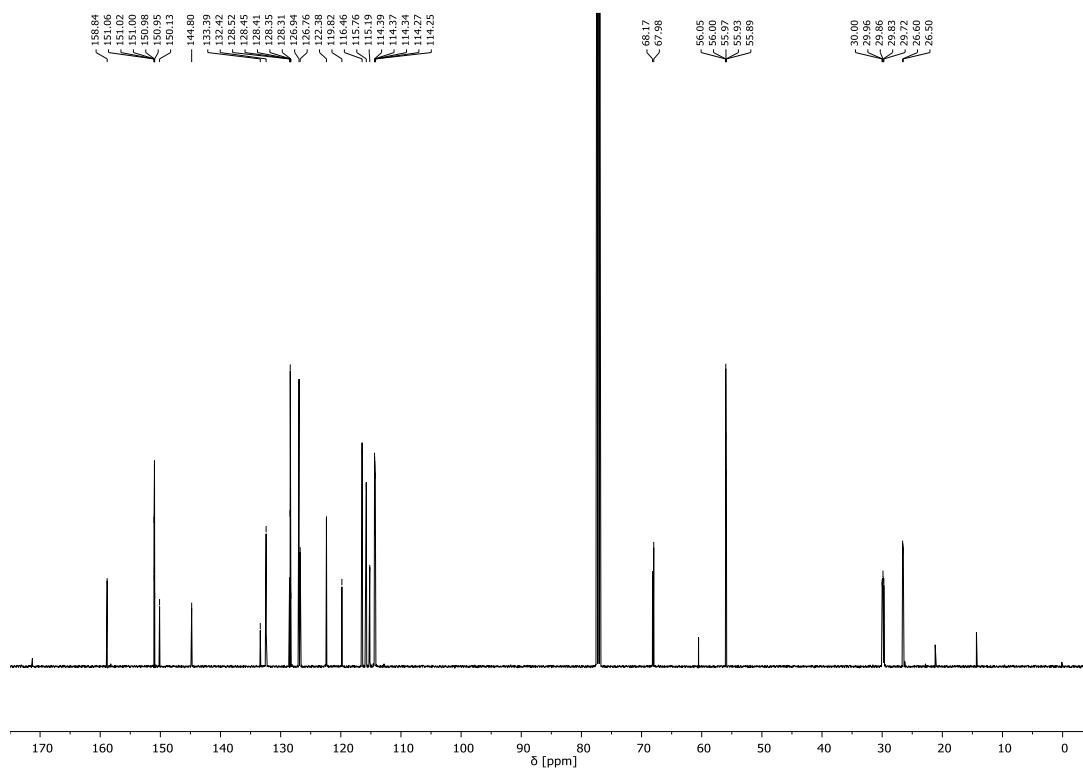


Figure S26: <sup>13</sup>C NMR-spectrum of PA-C4-PhPT in CDCl<sub>3</sub> (500 MHz).

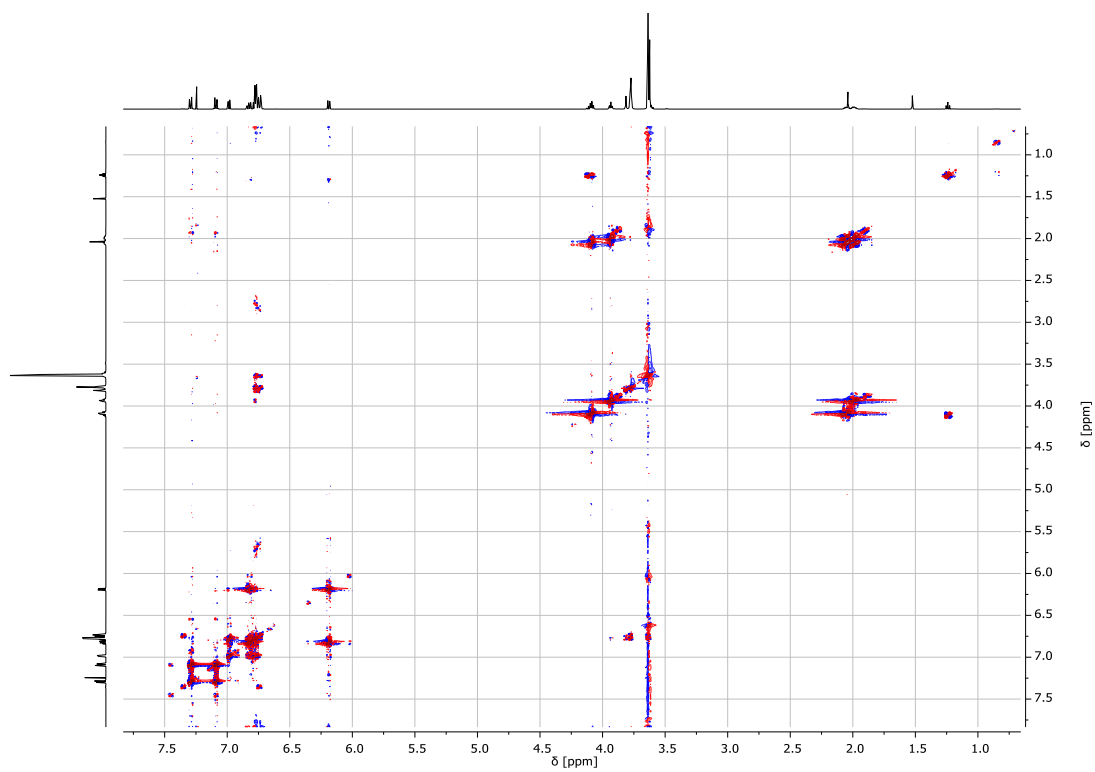


Figure S27: H,H-COSY spectrum of **PA-C4-PhPT** in  $\text{CDCl}_3$  (500, 126 MHz).

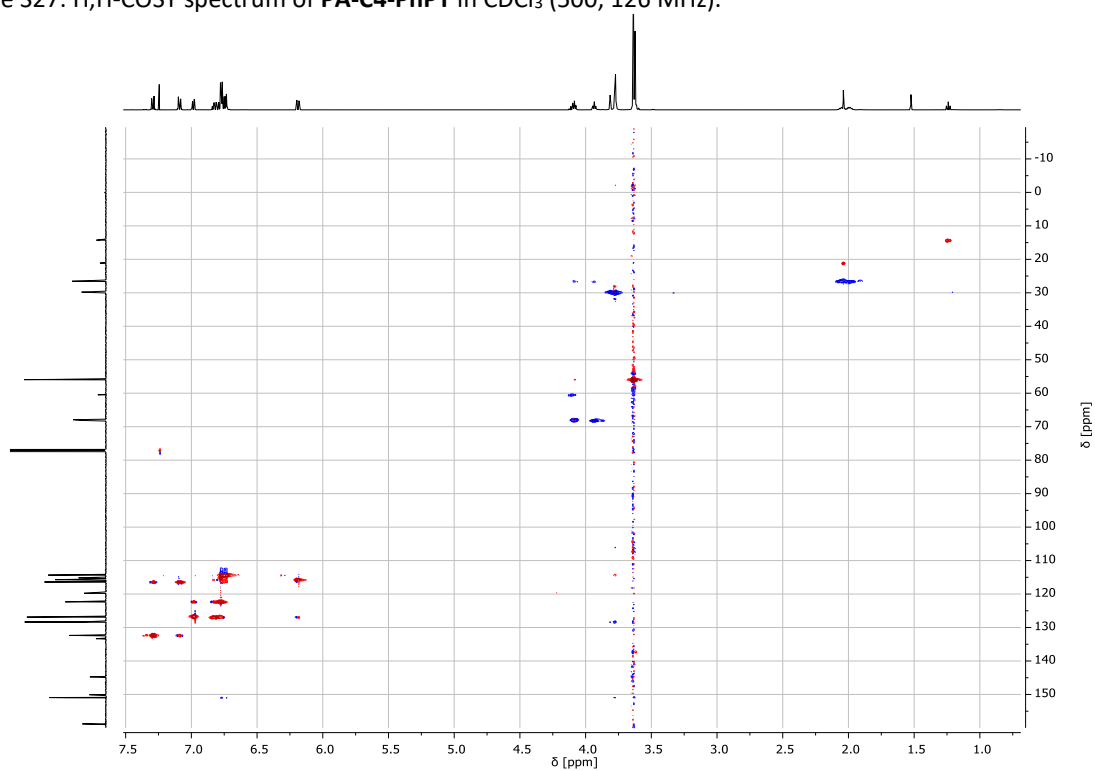


Figure S28: HSQC spectrum of **PA-C4-PhPT** in  $\text{CDCl}_3$  (500, 126 MHz). Blue:  $\text{CH}_2$  groups, red: CH or  $\text{CH}_3$  groups.

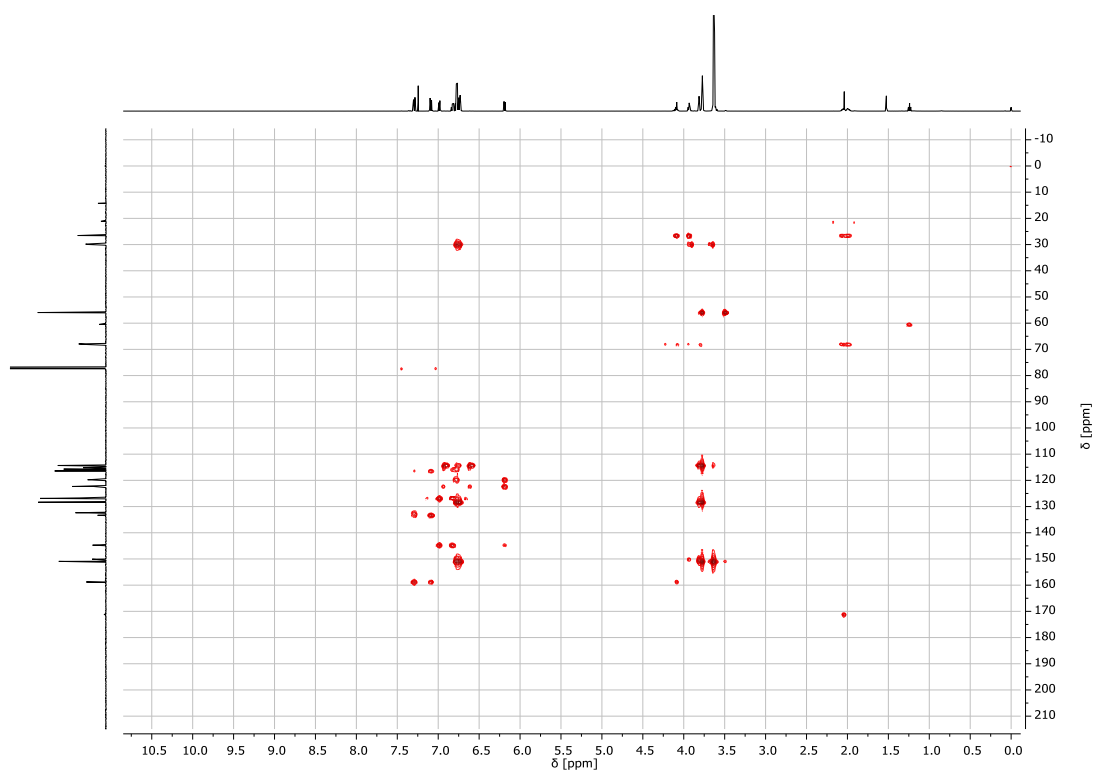


Figure S29: HMBC spectrum of **PA-C4-PhPT** in CDCl<sub>3</sub> (500, 126 MHz).



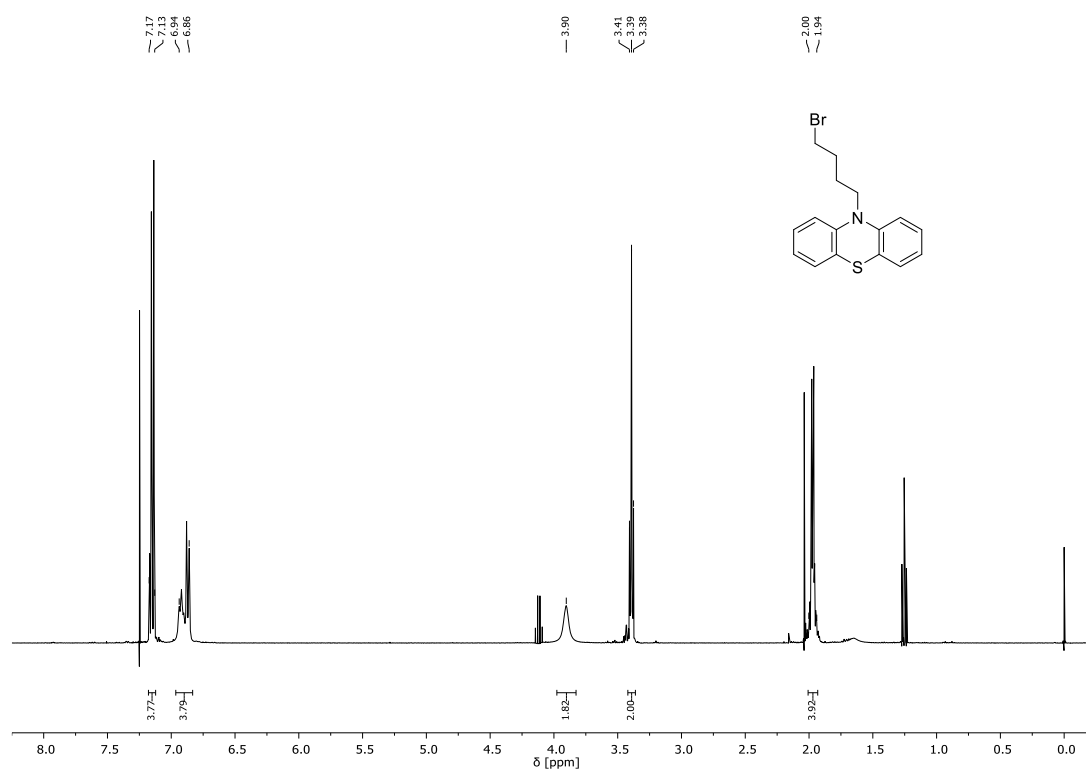


Figure S30: <sup>1</sup>H NMR-spectrum of 10-(4-bromobutyl)-10H-phenothiazine (5) in CDCl<sub>3</sub> (400 MHz).

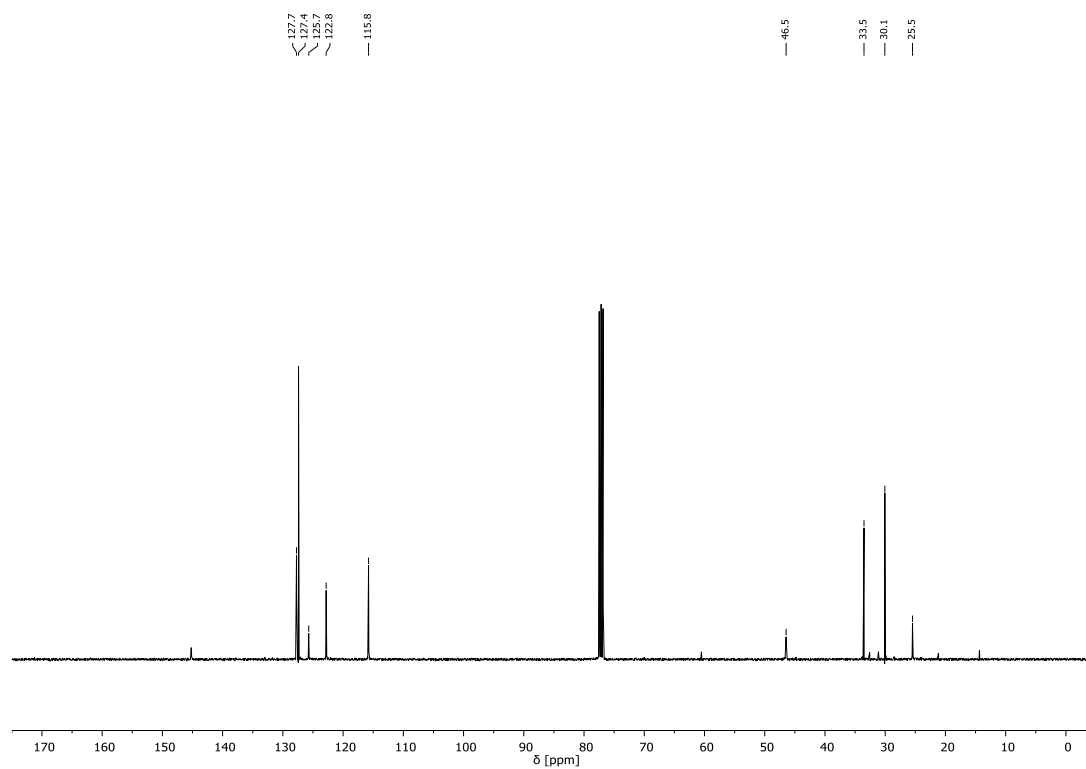


Figure S31: <sup>13</sup>C NMR-spectrum of 10-(4-bromobutyl)-10H-phenothiazine (5) in CDCl<sub>3</sub> (101 MHz).

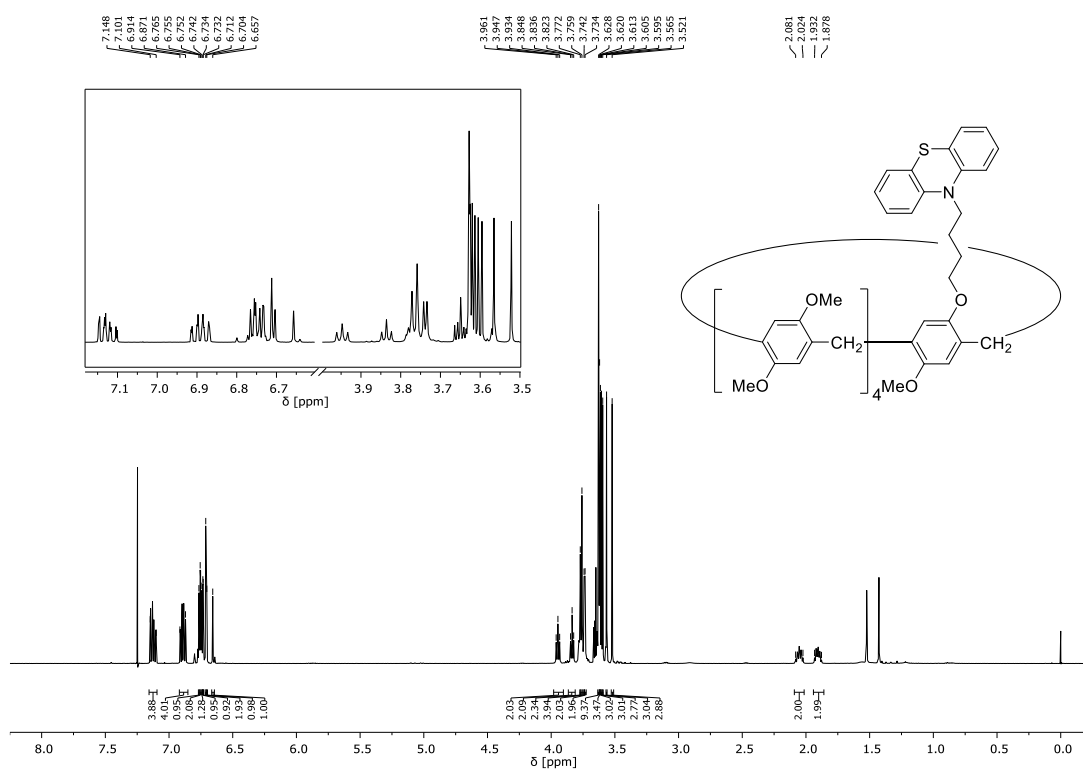


Figure S32: <sup>1</sup>H NMR-spectrum of PA-C4-PT in CDCl<sub>3</sub> (500 MHz).

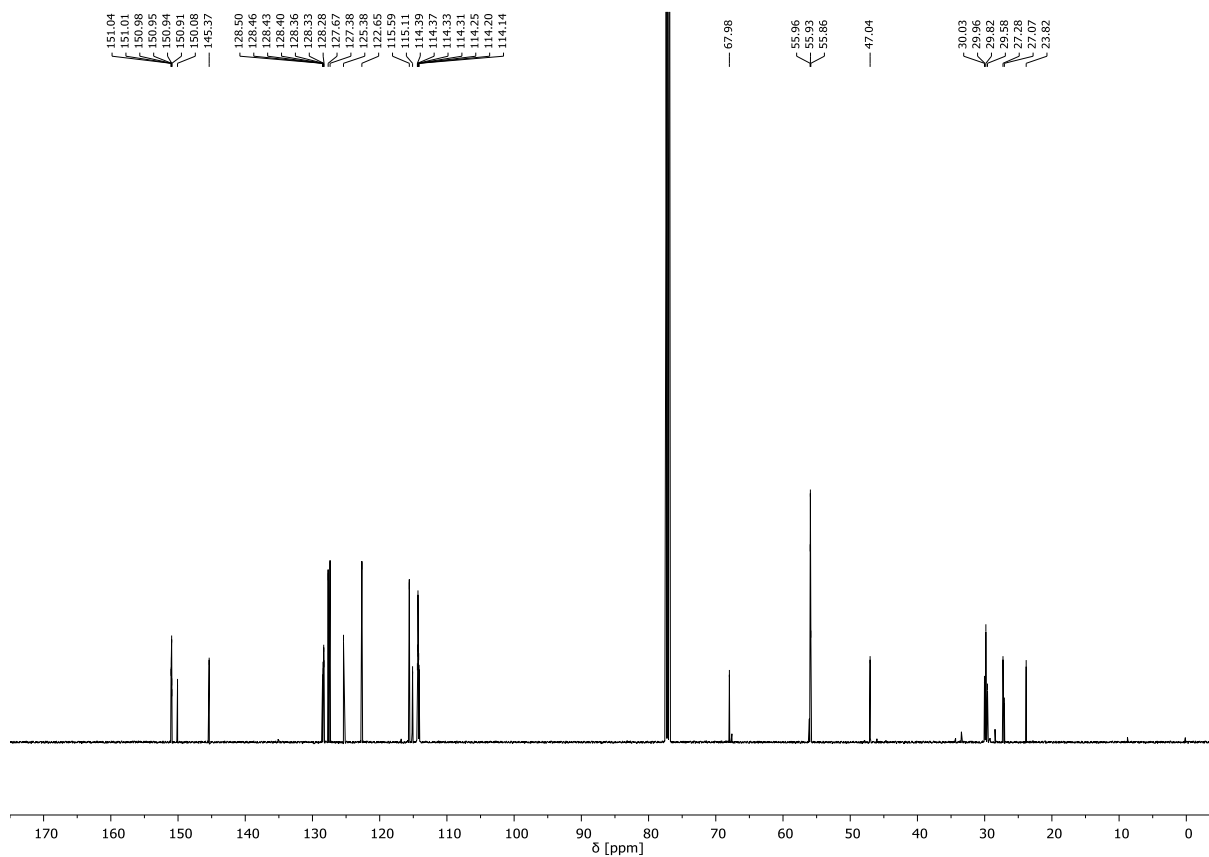


Figure S33:  $^{13}\text{C}$  NMR-spectrum of **-C4-PT** in  $\text{CDCl}_3$  (126 MHz).

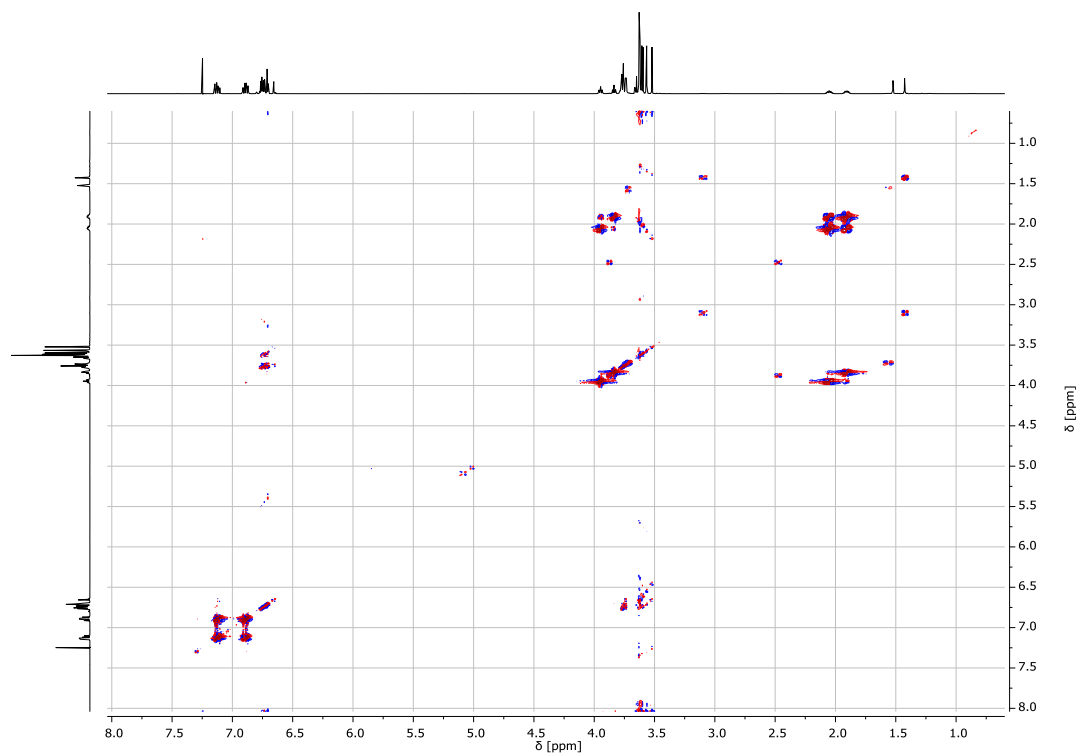


Figure S34: H,H-COSY spectrum of **PA-C4-PT** in  $\text{CDCl}_3$  (500, 126 MHz).

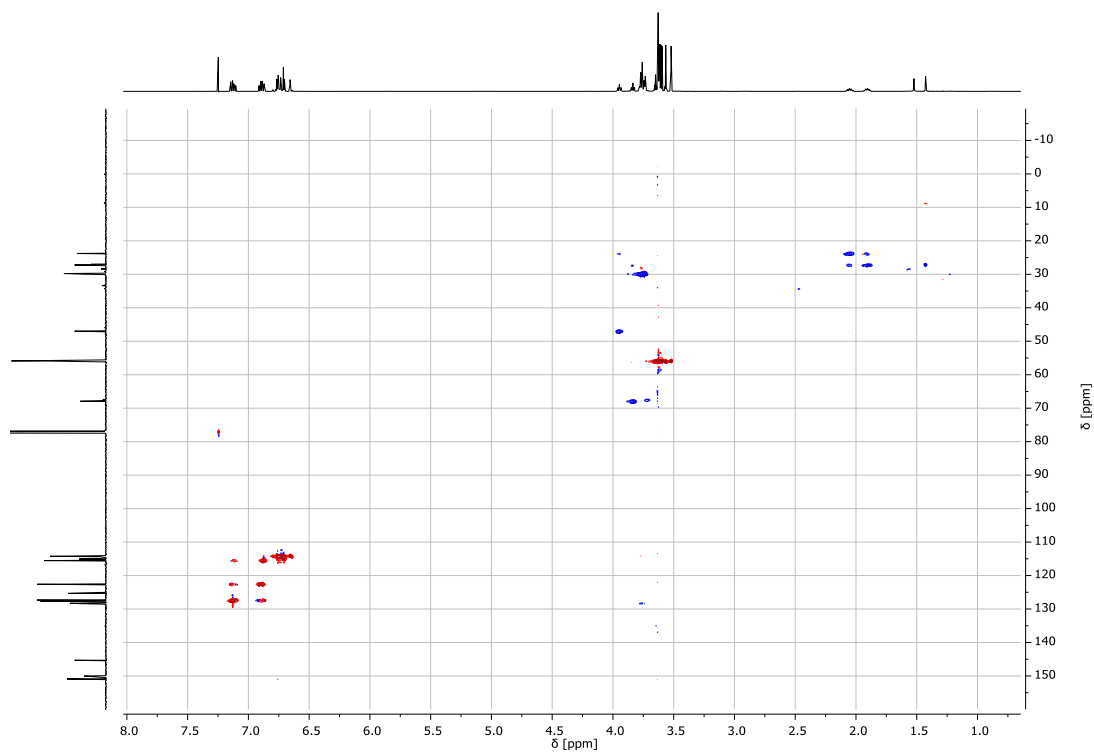


Figure S35: HSQC spectrum of **PA-C4-PT** in  $\text{CDCl}_3$  (500, 126 MHz). Blue:  $\text{CH}_2$  groups, red:  $\text{CH}$  or  $\text{CH}_3$  groups.

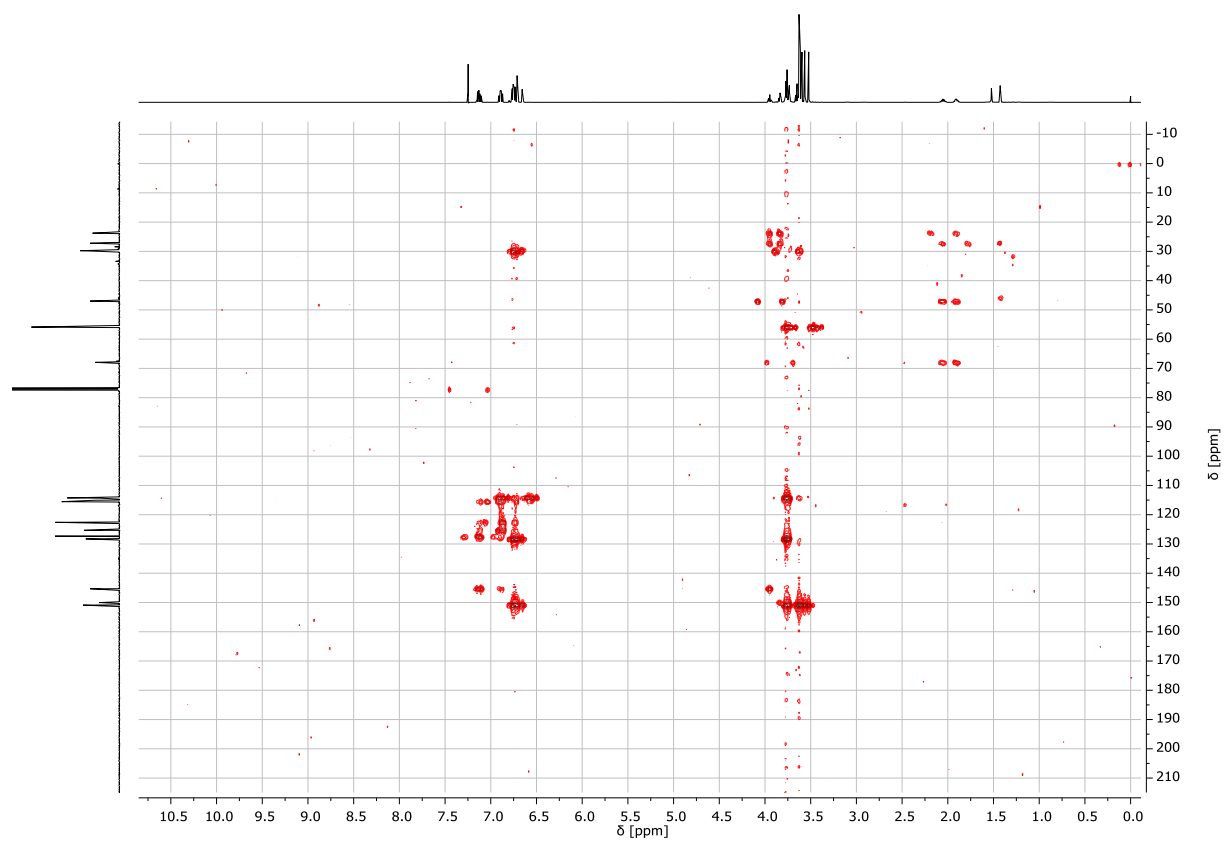


Figure S36: HMBC spectrum of **PA-C4-PT** in  $\text{CDCl}_3$  (500, 126 MHz).

## 4 Cyclic Voltammograms

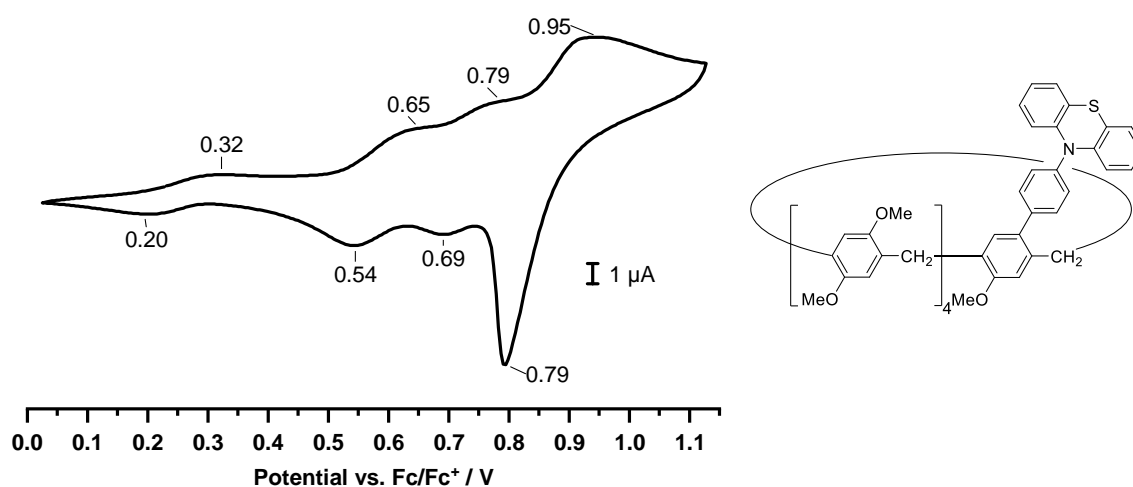


Figure S37: Cyclic voltammogram of PA-PhPT (1 mM in CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>, scan rate 0.1 V/s, WE = Pt).

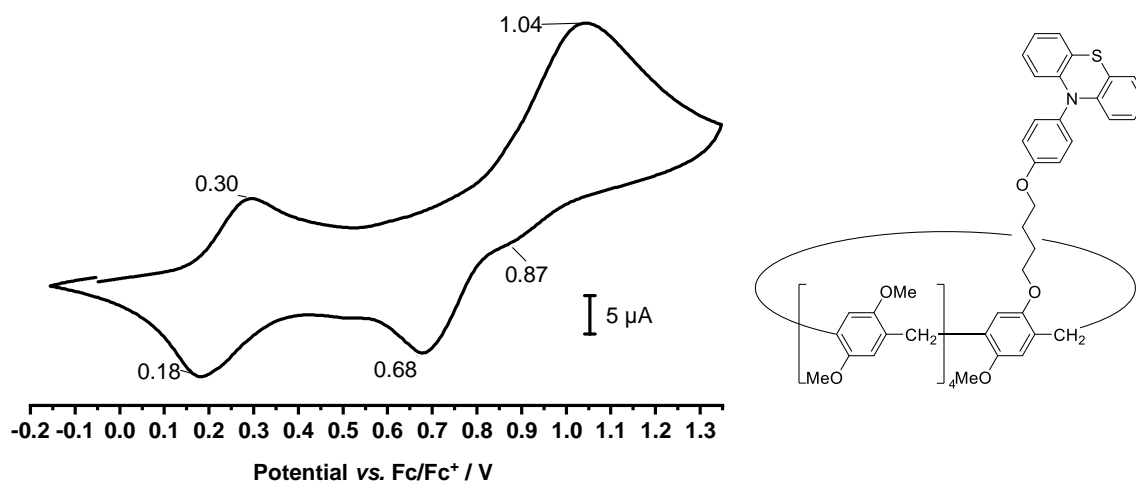


Figure S38: Cyclic voltammogram of PA-C4-PhPT (1 mM in CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>, scan rate 0.1 V/s, WE = Pt).

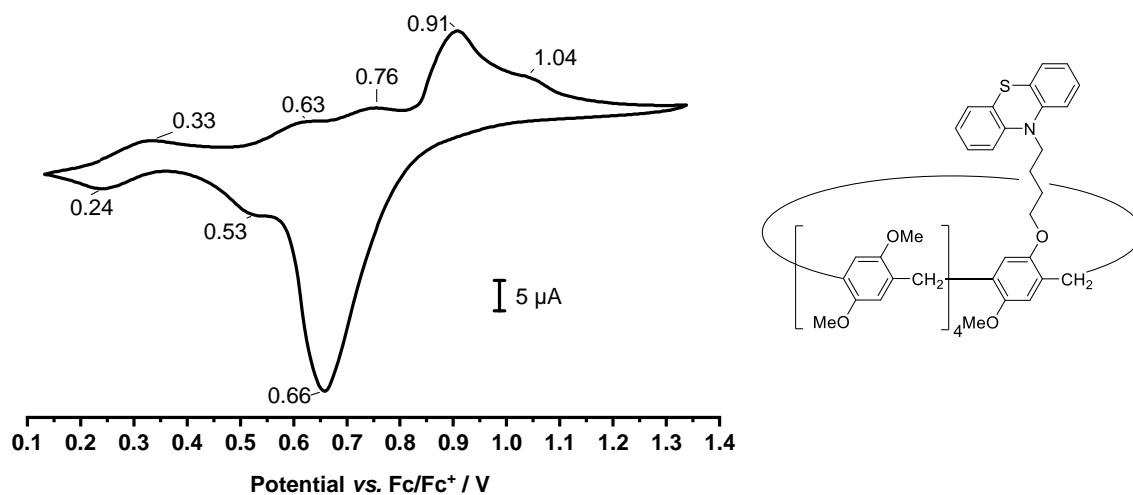


Figure S39: Cyclic voltammogram of PA-C4-PT (1 mM in CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>, scan rate 0.1 V/s, WE = Pt).

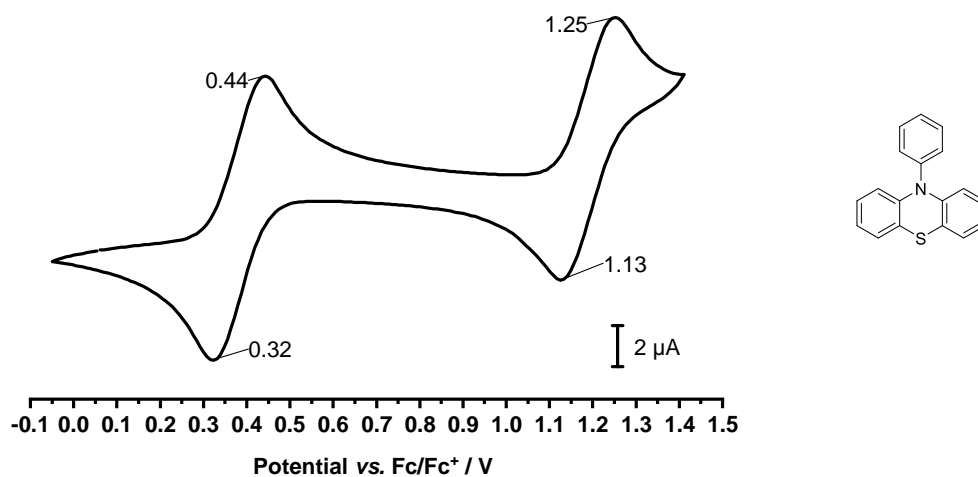


Figure S40: Cyclic voltammogram of PhPT (1 mM in CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>, scan rate 0.1 V/s, WE = GC).

## 5 Absorption and Emission Spectra

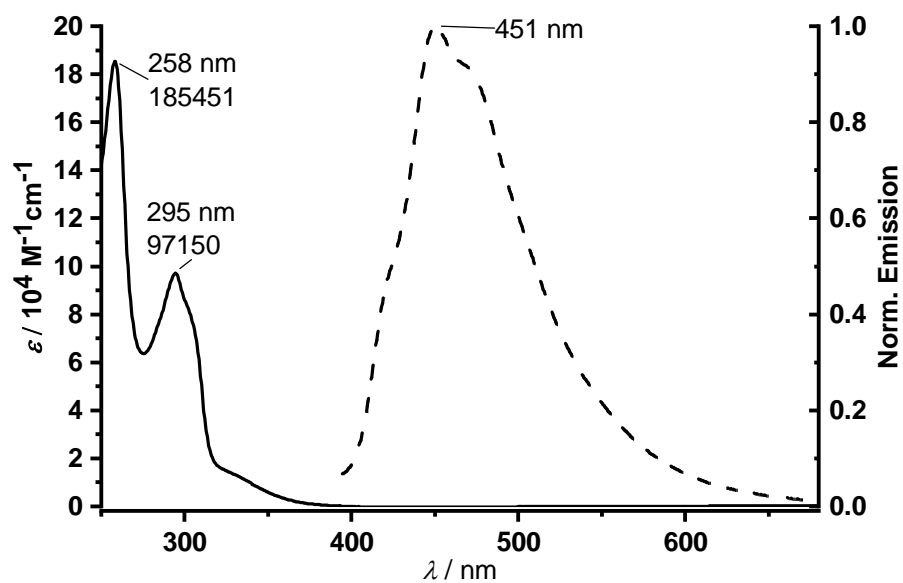


Figure S41: UV/Vis absorption (solid line) and emission spectrum (dashed line) of **PA-PhPT** in CH<sub>2</sub>Cl<sub>2</sub> solution with epsilon values.

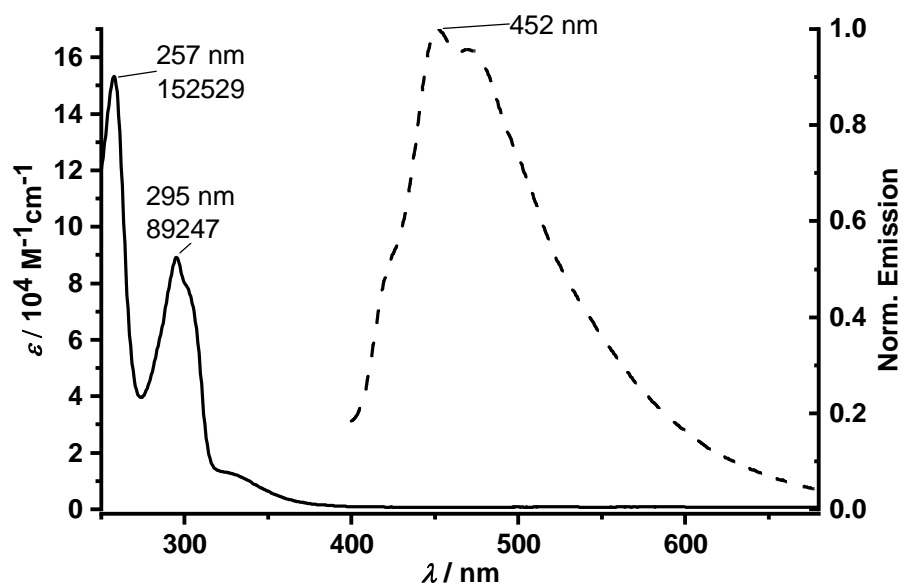


Figure S42: UV/Vis absorption (solid line) and emission spectrum (dashed line) of **PA-C<sub>4</sub>-PhPT** in CH<sub>2</sub>Cl<sub>2</sub> solution with epsilon values.

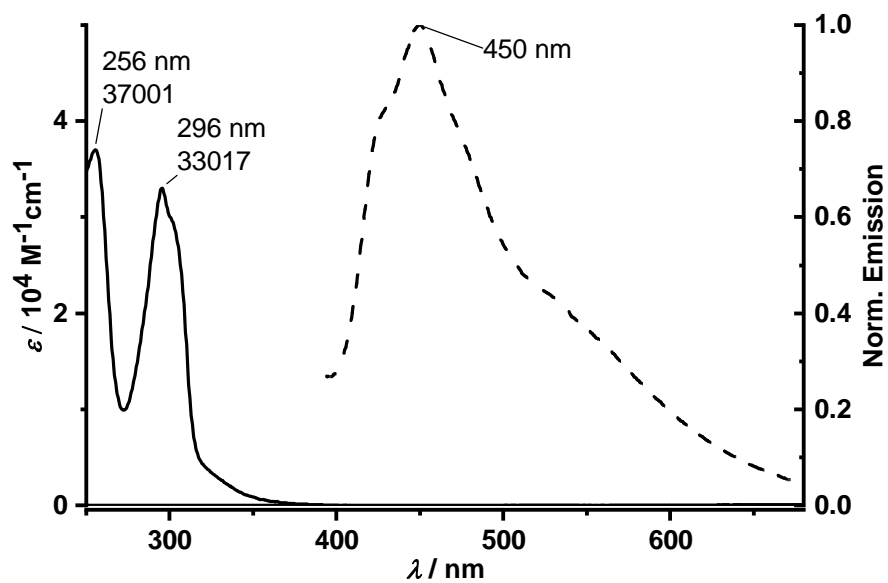


Figure S43: UV/Vis absorption (solid line) and emission spectrum (dashed line) of PA-C4-PT in CH<sub>2</sub>Cl<sub>2</sub> solution with epsilon values.

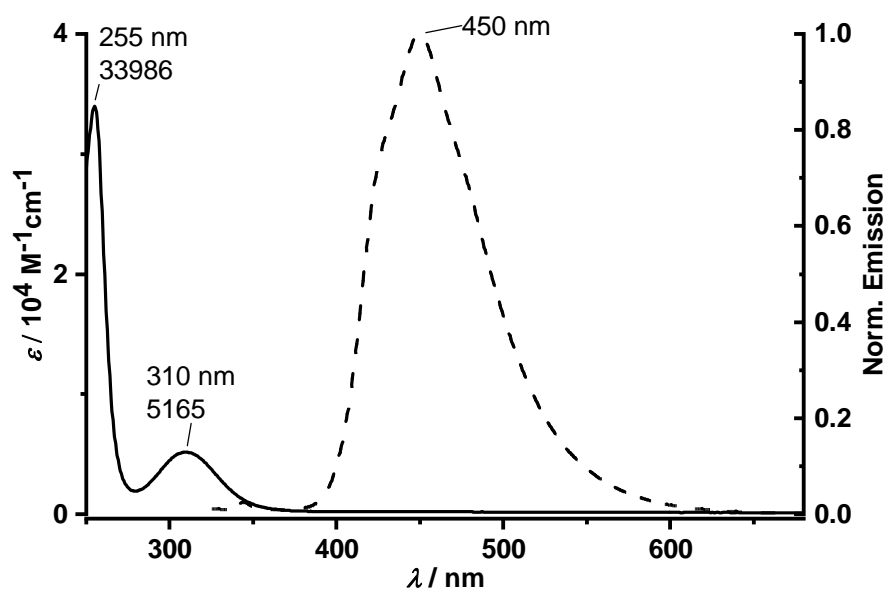


Figure S44: UV/Vis absorption (solid line) and emission spectrum (dashed line) of MePT in CH<sub>2</sub>Cl<sub>2</sub> solution with epsilon values.



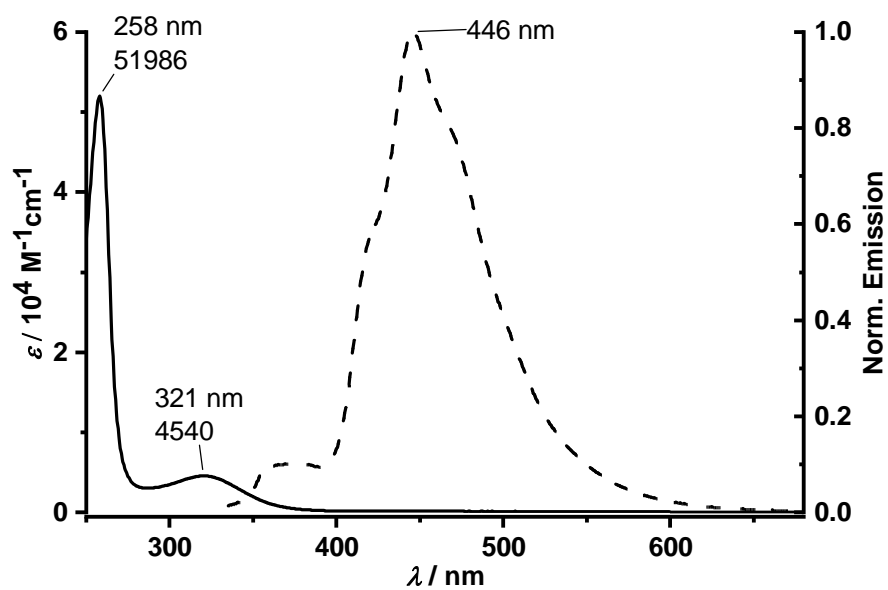


Figure S45: UV/Vis absorption (solid line) and emission spectrum (dashed line) of PhPT in  $\text{CH}_2\text{Cl}_2$  solution with epsilon values.

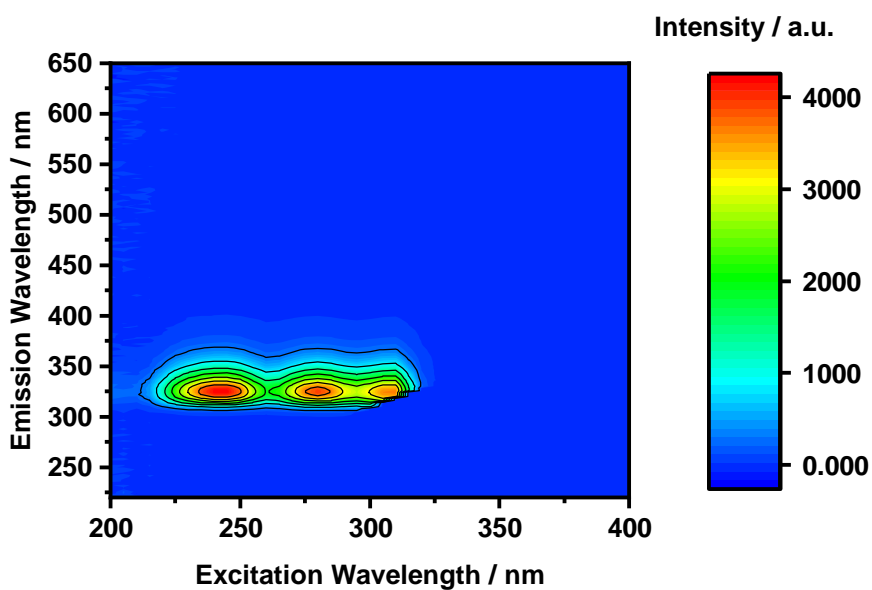


Figure S46: 2D-Plot of emission spectra for different excitation wavelengths of **1** in MeCN.

## 6 Excited State Reduction Potentials

The reduction potentials of the excited states were calculated from the oxidation potential in the ground state  $E_{1/2}^{\text{Ox}}$  and the energy of the first excited singlet state  $E_{0,0}^{S_1}$ , meaning the energy of the transition from  $S_0(v=0)$  to  $S_1(v=0)$ .

$$E_{1/2}^* = E_{1/2}^{\text{Ox}} - E_{0,0}^{S_1} \quad (1)$$

The energy of the excited state can be estimated by the intersection of the absorption maximum and the emission maximum after converting from wavelength axis to energy scale.<sup>[10]</sup>

$$E_{0,0}^{S_1} = \frac{E_{\text{Abs}}[\text{eV}] + E_{\text{Em}}[\text{eV}]}{2} \quad (2)$$

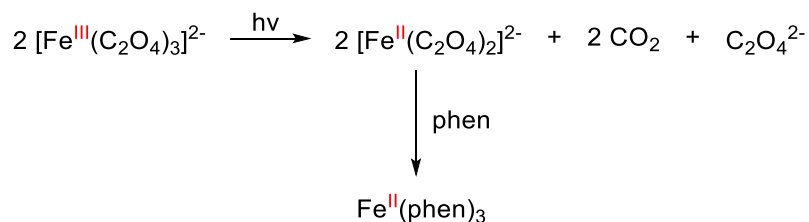
Table S1: Calculation of the excited state reduction potentials of the different phenothiazine derivatives.

Compound	$E_{1/2}^{\text{Ox}} /$ V	$\lambda_{\text{Abs}} /$ nm	$E_{\text{Abs}} / \text{eV}^{[a]}$	$\lambda_{\text{Em}} /$ nm	$E_{\text{Em}} /$ eV <sup>[a]</sup>	$E_{0,0} /$ eV	$E_{1/2}^* /$ V vs. Fc/Fc <sup>+</sup>	$E_{1/2}^* /$ V vs. SCE <sup>[b]</sup>
<b>PA-PhPT</b>	0.26	295	4.20	451	2.75	3.48	-3.22	-2.84
<b>PA-C4-PhPT</b>	0.24	295	4.20	452	2.74	3.47	-3.23	-2.85
<b>PA-C4-PT</b>	0.29	296	4.19	450	2.76	3.47	-3.18	-2.80
MePT <sup>[c]</sup>	0.31	310	4.00	450	2.76	3.38	-3.07	-2.69
PhPT	0.38	321	3.86	446	2.78	3.32	-2.94	-2.56

[a] Calculated by  $E = \frac{hc}{\lambda}$  ( $h = 6.626 \cdot 10^{-34}$  Js;  $c = 299792458$  m s<sup>-1</sup>). [b] Using  $E_{1/2}^{\text{Ox}}(\text{Fc}/\text{Fc}^+) = 0.38$  V vs. SCE.<sup>[11]</sup> [c] Oxidation potential taken from literature.<sup>[5]</sup>

## 7 Determination of Photon Flux/Irradiance of the Nail Dryer Lamp

The photon flux of the nail dryer lamp was determined by ferrioxalate actinometry. The ferrioxalate complex is a versatile actimeter with an active range from 250 to 500 nm.<sup>[12]</sup> In solution the  $[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]^{2-}$  complex absorbs a photon and decomposes to  $[\text{Fe}^{\text{II}}\text{C}_2\text{O}_4]^{2-}$  and  $\text{CO}_2$ . The amount of formed  $\text{Fe}^{\text{II}}$  can be determined by the characteristic absorption at 510 nm of its 1,10-phenanthroline complex (ferriin).



A 0.15 M ferrioxalate solution was prepared by dissolving  $\text{K}_3[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3] \cdot 3 \text{H}_2\text{O}$  (1.47 g, 3.00 mmol) in aq.  $\text{H}_2\text{SO}_4$  (0.2 M, 20 mL).<sup>a</sup> A buffered 0.15 M phenanthroline solution was prepared by dissolving 1,10-phenanthroline (1.35 g, 7.5 mmol) and sodium acetate (3.08 g, 37.5 mmol) in aq.  $\text{H}_2\text{SO}_4$  (0.2 M, 20 mL). To a vial with a septum-cap equipped with a magnetic stir bar was added 1 mL of the ferrioxalate solution. The vial was placed in front of the nail dryer lamp. After irradiation for 5 s, 3 mL of the aq.  $\text{H}_2\text{SO}_4$  (0.2 M) and 4.0 mL of the buffered phenanthroline solution were added to the vial. The solution was allowed to rest for 1 h. Then 100  $\mu\text{L}$  of the solution were diluted with 2.0 mL of the aq.  $\text{H}_2\text{SO}_4$  (0.2 M) and an absorption spectrum was measured. A non-irradiated sample and other samples with different irradiation times (up to 25 s) were also measured.



<sup>a</sup> Due to the light sensitivity of ferrioxalate in solution the experiment should be performed under exclusion of light, once the solution is prepared.

Figure S47: Different samples of the ferrioxalate actinometry after resting time. Irradiation time from left to right: 0.00, 5.43, 10.51, 15.43, 20.45, 25.45 s.

The molar equivalents of the  $\text{Fe}^{2+}$  formed can be calculated using Lambert-Beer's law:

$$n_{\text{Fe}^{2+}} = \frac{V_{\text{cuv}} \cdot V_{\text{vial,tot}} \cdot \Delta A}{10^3 \cdot V_{\text{vial,sample}} \cdot l \cdot \varepsilon_{510 \text{ nm}}} \quad (3)$$

$V_{\text{cuv}}$  (2.1 mL) is the volume in the cuvette,  $V_{\text{vial,tot}}$  (8 mL), is the final volume in the vial after complexation with phenanthroline,  $V_{\text{vial,sample}}$  (0.1 mL) is the aliquot taken from the solution after complexation for the determination via absorption spectroscopy,  $l$  (1 cm) is the path length of the cuvette,  $\Delta A$  is the difference in absorbance between the irradiated and non-irradiated solutions, and  $\varepsilon_{510 \text{ nm}}$  ( $11100 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) is the molar absorptivity of  $\text{Fe}^{\text{II}}(\text{phen})^{2+}$  at 510 nm.

Table S2: Calculation of the amount of  $\text{Fe}^{2+}$  formed for the different irradiation times.

#	1	2	3	4	5	6
$t_{\text{irr}} / \text{s}$	0.00	5.43	10.51	15.43	20.45	25.45
$A_{510 \text{ nm}} / \text{a.u.}$	0.0176	0.0507	0.0846	0.1352	0.1748	0.2218
$\Delta A_{510 \text{ nm}} / \text{a.u.}$	0	0.0331	0.0670	0.1176	0.1572	0.2042
$n_{\text{Fe}^{2+}} / 10^{-6} \text{ mol}$	0	1.25	2.53	4.45	5.95	7.73

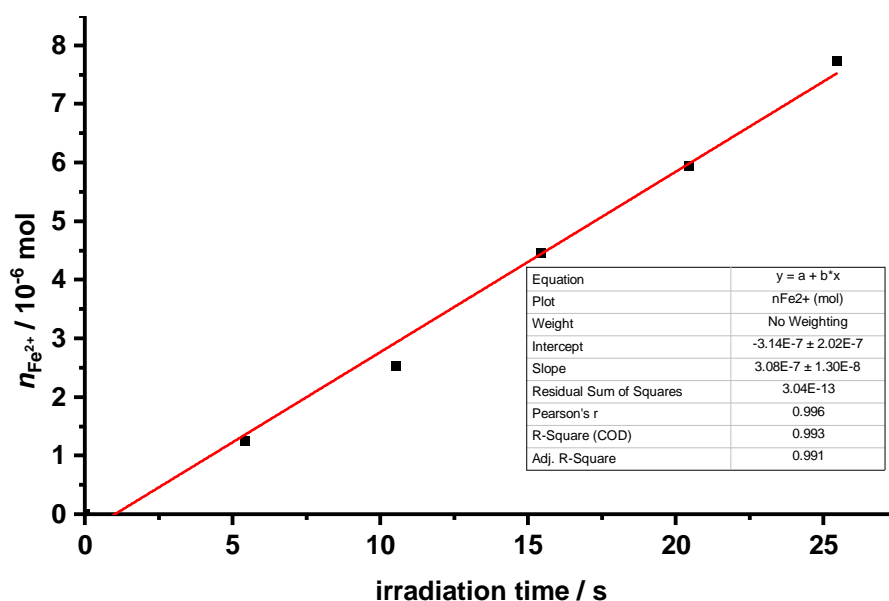


Figure S48: Moles of  $\text{Fe}^{2+}$  of the different samples vs. irradiation time. Red line shows the linear fit for determination of the photon flux.

With the determined slope the photon radiant flux  $\Phi_{\text{Ph}}$  per irradiated volume can be calculated as:

$$\Phi_{\text{Ph}} = \frac{n_{\text{Fe}^{2+}}}{\Phi \cdot t \cdot f} = \frac{\frac{dn_{\text{Fe}^{2+}}}{dt}}{\Phi \cdot f} = \frac{3.08 \cdot 10^{-7}}{1.146 \cdot 0.999} = 2.74 \cdot 10^{-7} \text{ einstein} \cdot \text{s}^{-1} \quad (4)$$

$\frac{dn_{\text{Fe}^{2+}}}{dt}$  ( $3.08 \cdot 10^{-6}$  mols $\cdot$ s $^{-1}$ ) is the slope of the linear fit,  $\Phi$  (1.146 for a 0.15 M solution at 363.8 nm) is the quantum yield for the ferrioxalate actinometer,  $t$  is the irradiated time, and  $f$  is the fraction of light absorbed at  $\lambda = 365$  nm ( $f = 1 - 10^{-A}$ ). The absorbance of the ferrioxalate solution at 365 nm is 3.845, indicating  $f = 0.999$ .

Assuming monochromatic light, the irradiance  $E$  can be calculated with Planck's relation:

$$E = \frac{\Phi_{\text{E}}}{A} = \frac{h \cdot \Phi_{\text{Ph}} \cdot \nu}{A} = \frac{h \cdot c \cdot \Phi_{\text{Ph}}}{A \cdot \lambda} = 14.3 \text{ mW cm}^{-2} \quad (5)$$

$h$  ( $6.626 \cdot 10^{-34}$  Js) is the Planck constant;  $c$  ( $299792458$  m s $^{-1}$ ) is the speed of light;  $A$  ( $6.28$  cm $^2$ ) is the irradiated area;  $\lambda$  (365 nm) is the wavelength of the light source.

Table S3: Irradiance/light intensity of different in photoredox catalysis used light sources.

Type	$E / \text{mW cm}^{-2}$	$E / \text{mW ml}^{-1}$	Light Intensity / $\mu\text{W cm}^{-2}$	photon flux / $\text{E m}^{-2} \text{s}^{-1}$	Determined by
Nail dryer lamp	14.3	35.9		0.0027	
Commercially available Photoreactors					
Penn PhD					
Photoreactor M2	100 <sup>[13]</sup>				Calorimetry
PhotoRedOx Box		80–180 <sup>[14][b]</sup>			Ferrioxalate actinometry
Used in Phenothiazine catalysis					
		37.4 <sup>[15]</sup>			-
dehalogenation reaction			1.8–2.2 <sup>[16,17]</sup>		-
2 8W bulbs		2.86 <sup>[18]</sup>			-
LED-setup				1.22 <sup>[19]</sup>	LED specification sheet
LED-setup		5.65 <sup>[20]</sup>			-
LED-setup		2.2 <sup>[21]</sup>			-

[a] Depending on the lamp used in the setup.

## 8 Kinetic Profiles

To determine the kinetic profiles for the dehalogenation of **7** with cavity-free PhPT and cavity-linked **PA-PhPT**, reactions were performed as described in chapter 2.11, but on a 400  $\mu\text{M}$ -scale. After 0, 0.5, 1, 2, 5, 8.5, 24, 48 h of irradiation time small samples were taken and the conversion was analyzed by  $^1\text{H}$  NMR-spectroscopy using 1,2,4,5-tetramethylbenzene as internal standard.

Table S4: Conversion of **7** in the photoredox-catalyzed dehalogenation with PhPT and **PA-PhPT** as PRC after different irradiation times.

#	<i>t</i> / h	Conversion <sup>[a]</sup> for / %	
		PhPT	PA-PhPT
0	0.0	0	0
1	0.5	1	1
2	1.0	1	3
3	2.0	2	4
5	5.0	7	6
6	8.5	12	17
7	24.0	15	19
8	48.0	20	31

[a] Determined by  $^1\text{H}$  NMR spectroscopy using 1,2,4,5-tetramethylbenzene as internal standard.

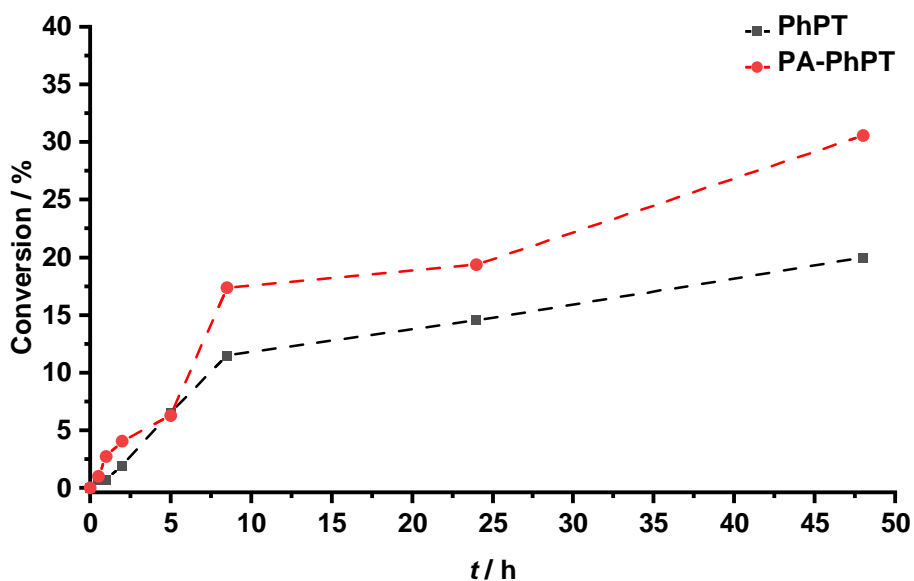


Figure S49: Temporal course of the conversion of **7** with PhPT and **PA-PhPT** as PRC.

## 9 Fluorescence Quenching and Stern-Volmer Plots

In a typical experiment a stock solution of the respective PRC in degassed acetonitrile (20-70  $\mu\text{M}$ ) was prepared in an argon-filled glovebox, filled into a screw-capped 10 mm quartz cuvette and was used to measure the initial fluorescence spectra after excitation at 365 nm. The remaining stock solution was used to dissolve the respective quencher. Aliquots of this solution were added to the cuvette, and fluorescence spectra were measured. To ensure the exclusion of oxygen, an argon line was placed into the photometer.

The quenching was analyzed by plotting the fluorescence intensity  $F/F_0$  at 446 nm vs. the quencher concentration according to the STERN-VOLMER-relation, and the STERN-VOLMER quenching constant was determined by a linear fit:<sup>[22]</sup>

$$\frac{F}{F_0} = K_{\text{SV}} \cdot [\text{Q}] + 1 \quad (6)$$

$F$  is the fluorescence intensity of the sample with the respective quencher concentration,  $F_0$  is the fluorescence intensity with no quencher,  $K_{\text{SV}}$  is the Stern-Volmer-constant and  $[\text{Q}]$  is the concentration of the quencher.

Table S5: Stern-Volmer quenching constants for the PRCs PhPT, **PA-PhPT** and **PA-C4-PhPT** and different substrates.

Catalyst (PRC)	Quencher (Substrate)	$K_{\text{SV}} / \text{M}^{-1}$
PhPT	<b>1</b>	$0.07 \pm 0.17$
	<b>6</b>	$1.40 \pm 0.22$
	<b>7</b>	$1.98 \pm 0.09$
<b>PA-PhPT</b>	<b>6</b>	$2.42 \pm 2.28$
	<b>7</b>	$2.29 \pm 0.19$
<b>PA-C4-PhPT</b>	<b>6</b>	$2.49 \pm 0.97$
	<b>7</b>	$2.21 \pm 0.22$

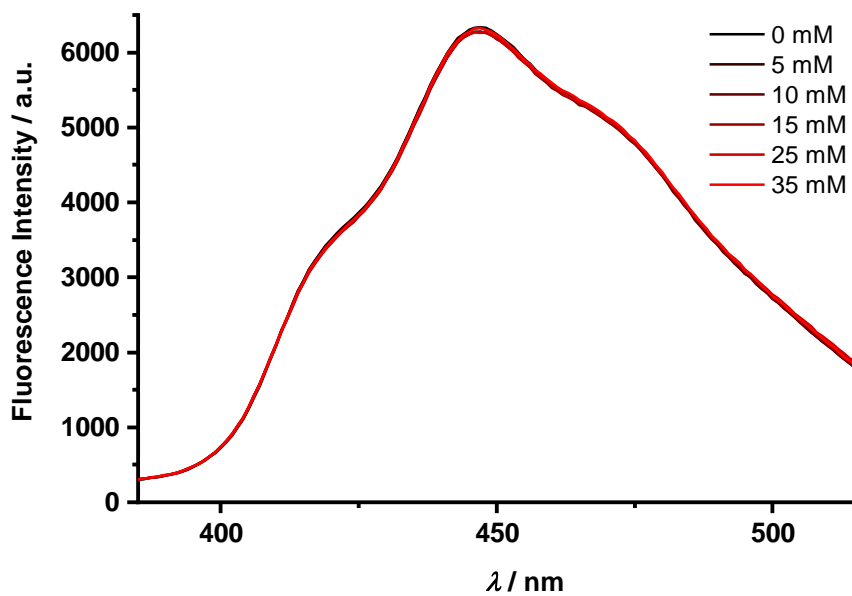


Figure S50: Emission spectra of PhPT in acetonitrile with different concentrations of **1**.

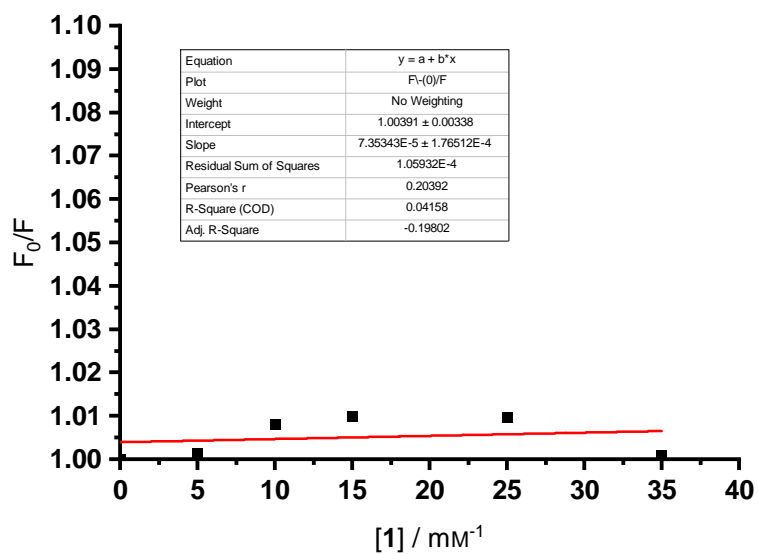


Figure S51: Stern-Volmer plot and linear fit for the fluorescence quenching of PhPT by **1**.



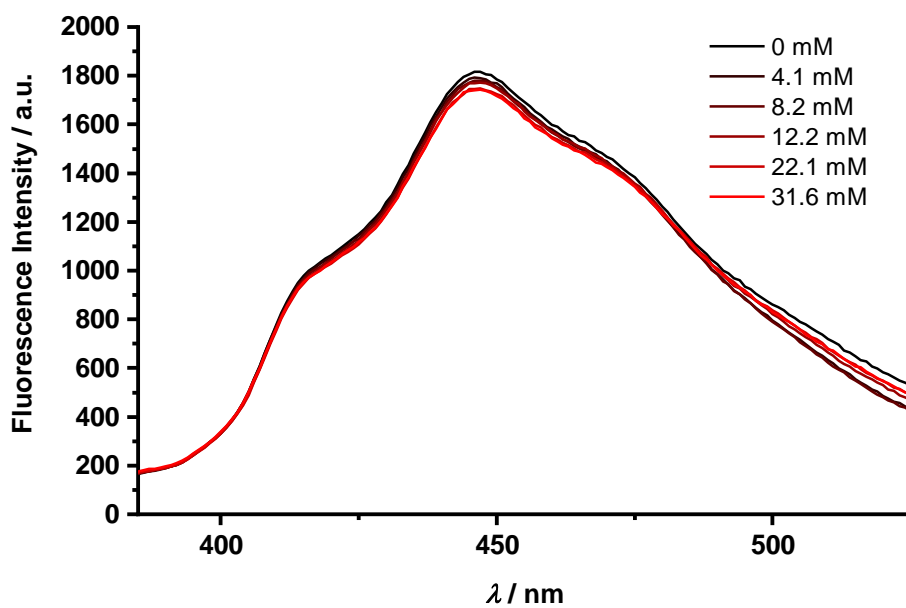


Figure S52: Emission spectra of PhPT in acetonitrile with different concentrations of **6**.

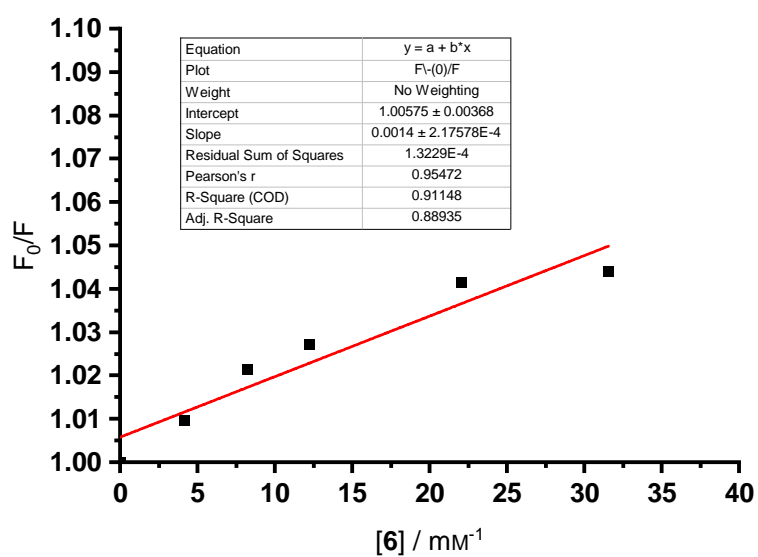


Figure S53: Stern-Volmer plot and linear fit for the fluorescence quenching of PhPT by **6**.

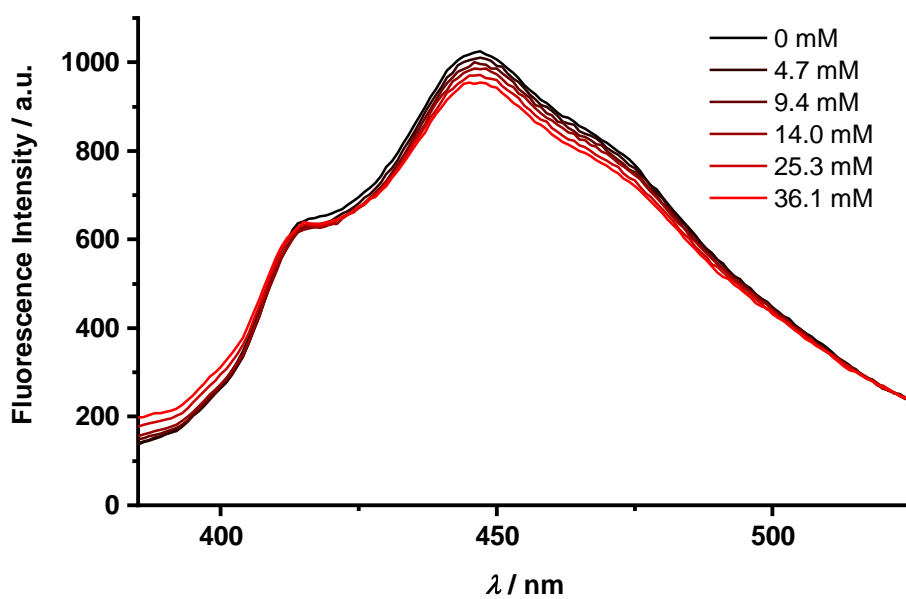


Figure S54: Emission spectra of PhPT in acetonitrile with different concentrations of **7**.

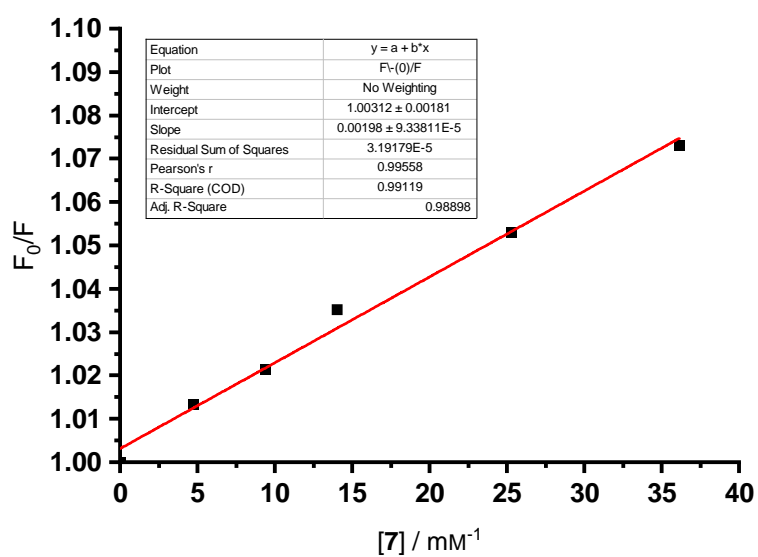


Figure S55: Stern-Volmer plot and linear fit for the fluorescence quenching of PhPT by **7**.

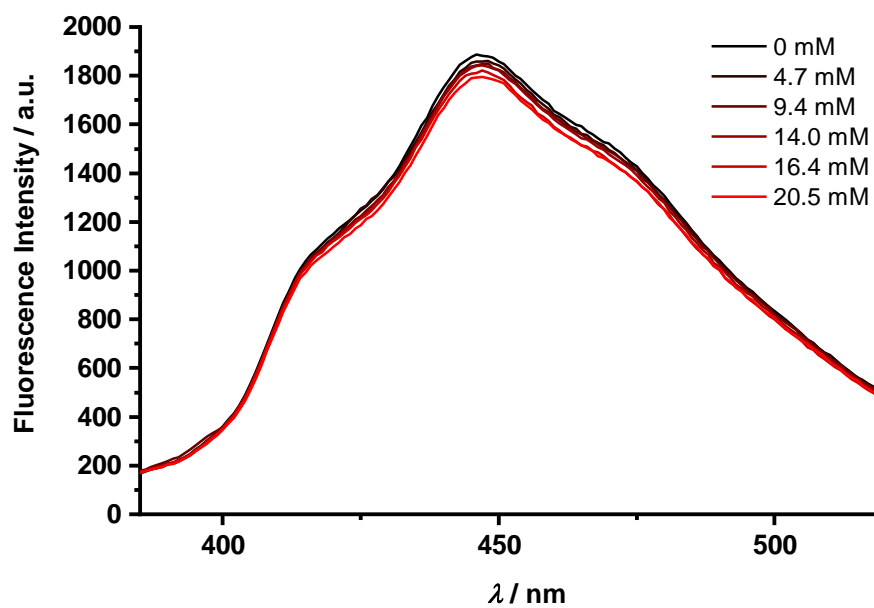


Figure S56: Emission spectra of **PA-PhPT** in acetonitrile with different concentrations of **6**.

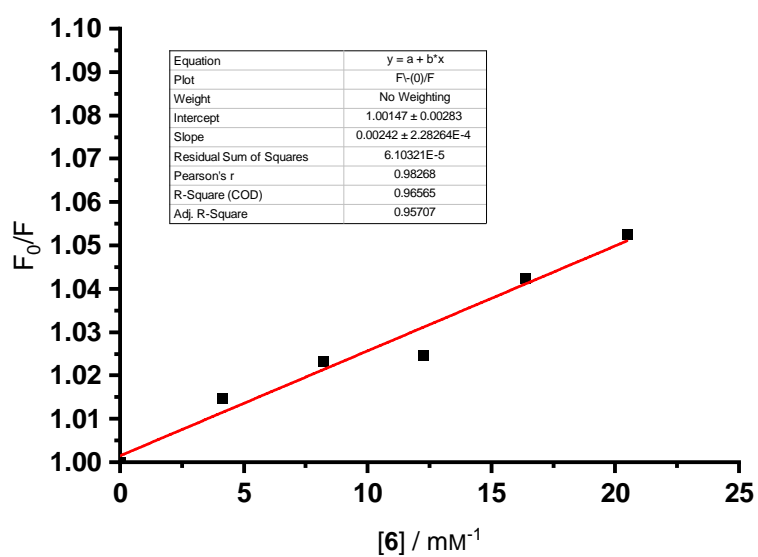


Figure S57: Stern-Volmer plot and linear fit for the fluorescence quenching of **PA-PhPT** by **6**.

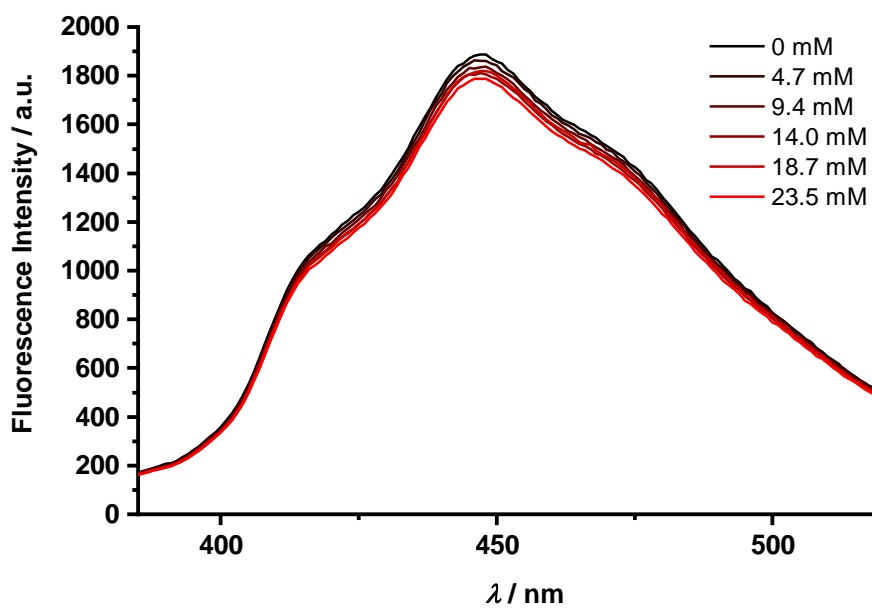


Figure S58: Emission spectra of **PA-PhPT** in acetonitrile with different concentrations of **7**.

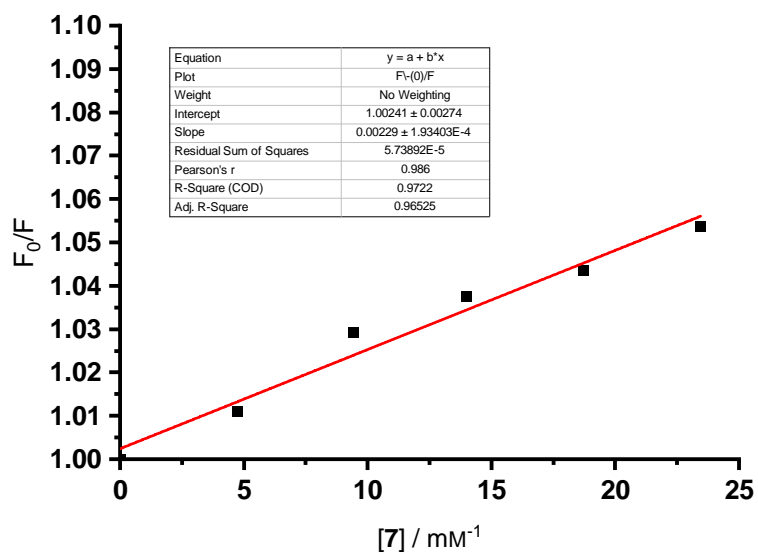


Figure S59: Stern-Volmer plot and linear fit for the fluorescence quenching of **PA-PhPT** by **7**.

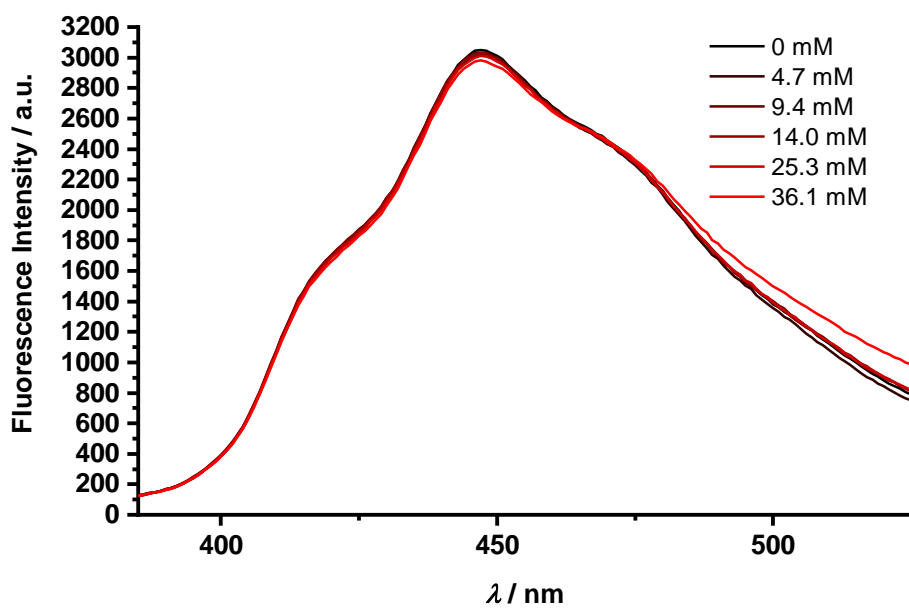


Figure S60: Emission spectra of **PA-C4-PhPT** in acetonitrile with different concentrations of **6**.

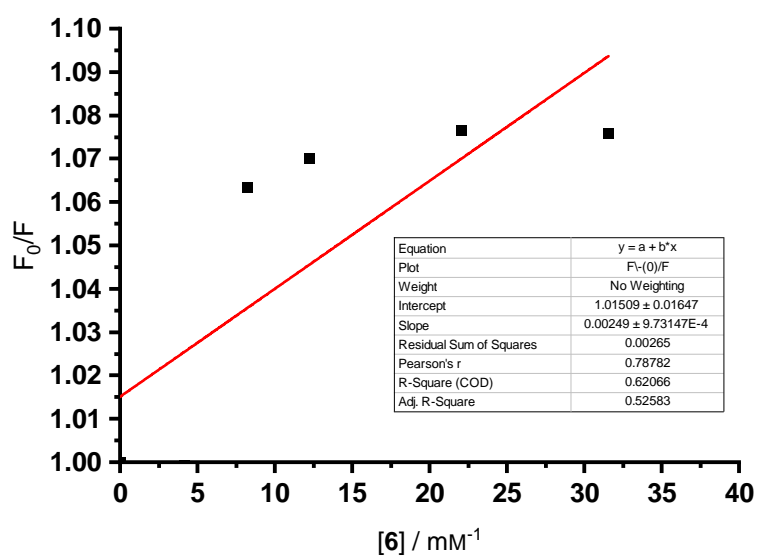


Figure S61: Stern-Volmer plot for the fluorescence quenching of **PA-C4-PhPT** by **6**.

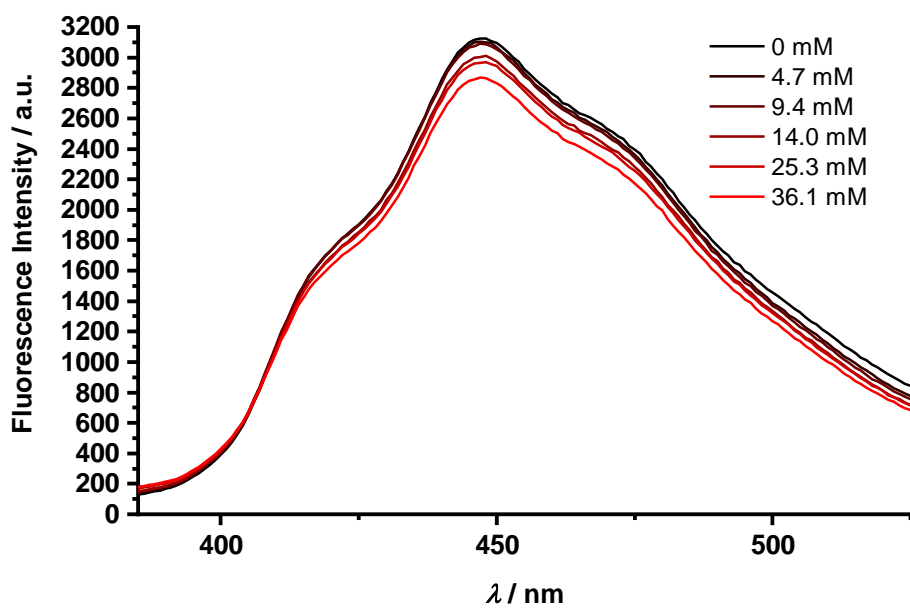


Figure S62: Emission spectra of **PA-C4PhPT** in acetonitrile with different concentrations of **7**.

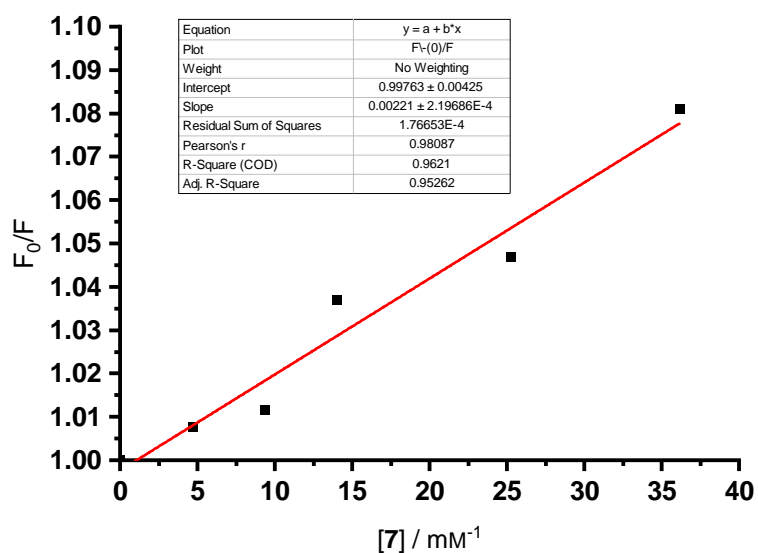


Figure S63: Stern-Volmer plot for the fluorescence quenching of **PA-C4PhPT** by **7**.

## 10 DFT calculations

DFT calculations were performed with the TURBOMOLE v7.5.0 program package.<sup>[23]</sup> The resolution-of-identity<sup>[24]</sup> (RI) approximation for the Coulomb integrals was used in all DFT calculations. Further, the D3 dispersion correction scheme<sup>[25,26]</sup> with the Becke-Johnson damping function was applied.<sup>[27,28]</sup> Using TURBOMOLE, the geometries of all molecules were optimized without symmetry restrictions with the PBEh-3c<sup>[29]</sup> composite scheme followed by harmonic vibrational frequency analyses to confirm minima as stationary points.

### 10.1 Direction of Complexation of Bromopentannitrile in **PA-PhPT**

Table S6: Electronic Energies ( $E_0$ ), zero-point vibrational energies (ZPE) of the two different complexes of bromopentannitrile in **PA-PhPT** calculated using PBEh-3c.

	Nitrile and PT on the same side	Bromide and PT on the same side
$E_0$ / Hartree	-6343.4005	-6343.3923
$E_{ZPE}$ / Hartree	1.2433	1.2435
$E_{total}$ / Hartree	-6342.1572	-6342.1488
$E_{total}$ / kcal	-3979764.8	-3979759.5
$\Delta E$ (vs. Nitrile and PT on the same side) / kcal	0	-5.3

### 10.2 Calculated structures

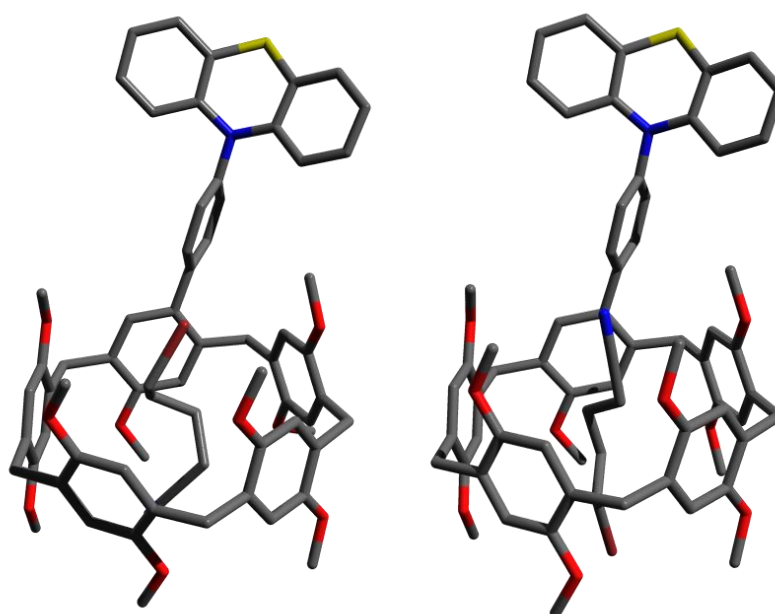


Figure S64: Calculated structures of bromopentanitrile in **PA-PhPT** with bromine and PT on the same side (left) and nitrile and PT on the same side (right) using PBEh-3c.

### 10.3 Cartesian Coordinates of the Calculated Structures

The Cartesian coordinates are listed in angstrom.

Table S7: Coordinates of the calculated structure of bromopentanitrile in **PA-PhPT** (bromide and PT on the same side) (PBEh-3c/def2-mSVP).

	x	y	z		x	y	z
				O	2.0402311	-1.3214825	-4.3303627
C	3.5283806	-0.1222057	-0.6555823	C	2.0210608	-2.6822462	-4.6715658
C	2.8711743	0.7636726	-1.5032692	O	4.0080137	0.2256195	0.56422
C	2.3574634	0.3642753	-2.7304256	C	3.8334719	1.5469662	0.9996748
C	2.5403008	-0.9627111	-3.121728	O	1.5057522	-2.7879823	3.8404979
C	3.219291	-1.8422675	-2.2855136	C	2.2105844	-1.7267717	4.434479
C	3.7129957	-1.4486068	-1.0471725	O	3.2922903	-4.9301851	-0.8964976
C	2.9399284	-2.6691219	1.8974674	C	2.7176469	-6.1129669	-1.3835918
C	3.3859197	-3.2127183	0.6984114	O	-3.479883	-2.1873114	4.0638507
C	2.8433391	-4.4295127	0.2836638	C	-2.8225098	-1.7813875	5.2350829
C	1.8740047	-5.0558358	1.0591746	O	-1.1654626	-5.962898	0.8057829
C	1.410549	-4.5011293	2.2454777	C	-1.8737393	-6.4641904	-0.2999285
C	1.966812	-3.2928625	2.670226	O	-4.2231529	1.7403927	0.3864564
C	-1.0542451	-4.624427	2.7241301	C	-4.2190924	2.1354812	1.7317695
C	-1.7591006	-5.0306902	1.5890203	O	-5.0586228	-3.5237497	-0.9606216
C	-3.0074205	-4.4867078	1.3186959	C	-4.9525281	-3.921093	-2.3047225
C	-3.5918935	-3.5320813	2.1438918	O	-2.8595325	-0.5863055	-4.1872409
C	-2.8936333	-3.1337736	3.2835138	C	-2.3067823	-1.537153	-5.0634239
C	-1.6455371	-3.6857349	3.560281	C	0.2709195	3.3683851	-1.7195087
C	-4.6312188	-1.2376555	-1.6065499	C	0.3633504	3.4105261	-0.3291622
C	-4.4120545	0.0888926	-1.2624488	C	0.9806987	4.4719866	0.3124363
C	-4.4419872	0.4343113	0.0893284	C	1.5206074	5.5167776	-0.4291789
C	-4.6523876	-0.5513834	1.0492361	C	1.4442401	5.4817884	-1.8131856
C	-4.8227143	-1.8880786	0.7042815	C	0.8221816	4.4189993	-2.4497964
C	-4.835448	-2.2234719	-0.6500185	N	2.1325508	6.636934	0.2005003
C	-0.6898673	0.4087399	-3.8785416	C	3.4562174	6.5065393	0.6467458
C	0.1180717	1.3746058	-3.2804528	C	4.1901054	7.6402827	1.0081899
C	-0.4671935	2.2696408	-2.3841627	S	3.5191564	9.2361133	0.70623
C	-1.8300347	2.1444436	-2.1000115	C	1.8330339	8.8871188	1.0607718
C	-2.6418572	1.1863526	-2.6785361	C	1.2941536	7.6495983	0.696888
C	-2.0460701	0.3113915	-3.5978743	C	4.0830384	5.2655357	0.7385869
C	4.3879465	-2.4582324	-0.1459756	C	5.3916179	5.160059	1.1850116
C	0.3162054	-5.1806622	3.0346509	C	6.095496	6.2840643	1.5796862
C	-4.9389365	-2.9448788	1.7784255	C	5.4818739	7.5244182	1.4966106
C	-4.1136044	1.1058037	-2.3403856	C	1.0314701	9.8820288	1.5974637
C	1.6028762	1.3594737	-3.5838212	C	-0.3348537	9.6897034	1.7292478



C	-0.8835983	8.4823347	1.3345533	H	3.1946095	-6.3198887	-2.3396505
C	-0.0805713	7.4664185	0.83812	H	1.638596	-6.0136344	-1.5444937
Br	-0.1586235	0.8955843	2.7790831	H	2.8928352	-6.9659705	-0.7201793
C	-1.1964984	-0.5864284	1.9680701	H	-3.4661944	-1.0462245	5.7138999
C	-1.3014946	-0.4588552	0.4681655	H	-1.8543627	-1.3116335	5.0296276
C	-0.0339358	-0.8186864	-0.2859279	H	-2.6659777	-2.611067	5.9320509
C	0.1700149	-2.3270784	-0.4244552	H	-1.2354266	-7.2173572	-0.7586764
C	-0.7169926	-2.9344556	-1.4035947	H	-2.0869136	-5.6903544	-1.0419926
N	-1.3892403	-3.4226538	-2.2010456	H	-2.812975	-6.9424222	-0.0033559
H	2.7190142	1.7952877	-1.2118395	H	-4.0463455	3.2096852	1.7399237
H	3.3708806	-2.8731582	-2.5762644	H	-3.4186529	1.6564982	2.3057963
H	3.3665793	-1.7248281	2.2070426	H	-5.174043	1.9338477	2.2277323
H	1.4392991	-5.9941558	0.7459711	H	-5.1161651	-4.9972112	-2.3208611
H	-3.5577772	-4.7911303	0.4408478	H	-3.9623818	-3.7084941	-2.7165168
H	-1.089598	-3.3791106	4.4357653	H	-5.7142633	-3.4506709	-2.9352926
H	-4.6178326	-1.4894152	-2.6564935	H	-3.1322259	-2.162373	-5.3974517
H	-4.6624906	-0.3046631	2.1035886	H	-1.5708874	-2.1718908	-4.5642425
H	-0.224902	-0.2794841	-4.5694573	H	-1.849396	-1.0701566	-5.9412971
H	-2.2796331	2.8427104	-1.4036598	H	-0.0536499	2.6019681	0.2576246
H	5.1022994	-1.9586886	0.5079619	H	1.0365456	4.4940894	1.3943514
H	4.9643444	-3.1524962	-0.7568413	H	1.8583728	6.3016737	-2.3852597
H	0.5086945	-5.0750548	4.1029224	H	0.738292	4.4176213	-3.5294017
H	0.3375328	-6.2505696	2.8222796	H	3.5534696	4.3725513	0.4415756
H	-5.595943	-3.7483344	1.4436428	H	5.8559862	4.1834037	1.2290825
H	-5.4102141	-2.5110986	2.6592365	H	7.1114424	6.2031707	1.940607
H	-4.6849721	0.851623	-3.234286	H	6.0144927	8.4193614	1.7918583
H	-4.455656	2.0927343	-2.0301061	H	1.4837899	10.8201388	1.8926775
H	2.0343934	2.3456082	-3.4162856	H	-0.9585118	10.4772424	2.1291146
H	1.7516646	1.138074	-4.641192	H	-1.9489394	8.3142641	1.4190735
H	1.5161789	-2.7545218	-5.6329451	H	-0.5393119	6.5334551	0.5450652
H	3.0269671	-3.0998095	-4.7815233	H	-0.6996521	-1.5014003	2.2877616
H	1.468476	-3.2827428	-3.9410615	H	-2.1748291	-0.5384956	2.4392464
H	4.2767827	1.6123135	1.9912984	H	-2.1152197	-1.1224857	0.1570176
H	2.777152	1.8263609	1.0719777	H	-1.6307709	0.5451063	0.2000218
H	4.3419184	2.2625926	0.3448074	H	-0.0530886	-0.367219	-1.2758975
H	1.735332	-1.5373883	5.3948421	H	0.8444761	-0.410207	0.215989
H	2.1608142	-0.8090833	3.843284	H	1.1901171	-2.5344897	-0.7437356
H	3.2613329	-1.9813612	4.6063408	H	0.0338034	-2.8472707	0.5265826

Table S8: Coordinates of the calculated structure of bromopentannitrile in **PA-PhPT** (nitrile and PT on the same side) (PBEh-3c/def2-mSVP).

	x	y	z	C	3.449389	-1.839038	-1.7495181
C	3.4890757	-0.1362554	-0.0697696	C	3.7441466	-1.4557167	-0.4473707
C	2.9666556	0.7570488	-0.998747	C	2.7121761	-2.6076028	2.4814608
C	2.6793408	0.3755372	-2.3038466	C	3.1807263	-3.150983	1.2925207
C	2.9218865	-0.9470056	-2.6760902	C	2.5715645	-4.3078466	0.8038578

C	1.5103124	-4.8736393	1.5013528	C	1.4792929	5.4790361	-0.0722519
C	1.0308171	-4.3192891	2.682914	C	1.6398687	5.5077383	-1.4490731
C	1.6505894	-3.1719153	3.1791225	C	1.1505016	4.470841	-2.2285847
C	-1.4555504	-4.3661285	2.8066081	N	1.9540477	6.5764085	0.7000431
C	-2.1616834	-5.0110251	1.7920372	C	3.1868713	6.4437455	1.3564914
C	-3.3277905	-4.4386338	1.2933011	C	3.8268217	7.5696712	1.8829229
C	-3.8083693	-3.2232774	1.7624431	S	3.182694	9.168366	1.5403883
C	-3.0994649	-2.5768799	2.7775551	C	1.4686879	8.7811637	1.5921909
C	-1.9422382	-3.1542057	3.2840765	C	1.023807	7.5543923	1.090686
C	-4.3203251	-1.1420627	-2.2708055	C	3.8144354	5.2082397	1.4998597
C	-4.0899953	0.1969494	-1.9802178	C	5.0319289	5.0998159	2.1545376
C	-4.177046	0.6097554	-0.6506556	C	5.6372396	6.2141766	2.7081267
C	-4.5121316	-0.3074324	0.336815	C	5.0212232	7.4490011	2.5753468
C	-4.7330803	-1.6483298	0.0496002	C	0.5684199	9.7398164	2.0290714
C	-4.622237	-2.0669904	-1.2768199	C	-0.7964983	9.5238191	1.9215754
C	-0.07803	0.4987131	-4.0371364	C	-1.2466565	8.32855	1.3893399
C	0.6137424	1.432182	-3.2673636	C	-0.3512118	7.3471057	0.9914811
C	-0.1161465	2.3228706	-2.4808204	Br	-0.8029017	-4.8886409	-2.8574123
C	-1.5074525	2.2231791	-2.4677587	C	-0.9996636	-3.6334009	-1.3452624
C	-2.2055852	1.2785579	-3.1977939	C	-0.7166632	-2.2166364	-1.7885059
C	-1.4625191	0.4145559	-4.0103999	C	-0.9156828	-1.2040823	-0.6662266
C	4.2906019	-2.4646344	0.5344111	C	0.0540328	-1.4199593	0.4980849
C	-0.1697893	-4.92844	3.3649949	C	0.008456	-0.3180555	1.4429912
C	-5.0539767	-2.6163076	1.1633911	N	-0.0408699	0.5725539	2.1724711
C	-3.7051598	1.1621725	-3.0766403	H	2.7708814	1.7857411	-0.7243291
C	2.1253206	1.3938686	-3.2734041	H	3.644402	-2.8669716	-2.021747
O	2.6319439	-1.2890975	-3.9570268	H	3.1951957	-1.7118835	2.8452139
C	2.7920994	-2.6277232	-4.347909	H	1.0196365	-5.7659205	1.1348791
O	3.7802051	0.1968598	1.2100926	H	-3.890488	-4.9267722	0.508758
C	3.5524991	1.5165606	1.6292595	H	-1.3824282	-2.6668376	4.0701205
O	1.164055	-2.6633814	4.3372705	H	-4.2397433	-1.4490893	-3.3046297
C	1.722135	-1.4757039	4.8396577	H	-4.5975556	0.0035546	1.3681227
O	3.0666315	-4.8192302	-0.3503621	H	0.5013455	-0.1824219	-4.6434176
C	2.5693671	-6.0494256	-0.8083056	H	-2.0690754	2.9198699	-1.8595377
O	-3.608164	-1.405655	3.227378	H	4.9605438	-1.9753398	1.2414692
C	-2.9173562	-0.7106216	4.2347096	H	4.8911519	-3.1983598	-0.0030777
O	-1.6489668	-6.1823355	1.3348702	H	-0.1315169	-4.7399701	4.4376832
C	-2.3899333	-6.9227666	0.4009645	H	-0.1451149	-6.0104833	3.2403874
O	-3.9278597	1.9168028	-0.3954418	H	-5.6232415	-2.0951151	1.933673
C	-3.6967359	2.3067234	0.9343361	H	-5.6976104	-3.4142557	0.7930094
O	-4.8199213	-3.3886834	-1.5193279	H	-4.1253245	2.1477154	-2.8749525
C	-4.7679656	-3.8421513	-2.8463988	H	-4.1398432	0.82864	-4.0190242
O	-2.1649717	-0.4890354	-4.7312673	H	2.5298093	2.3706402	-3.0094241
C	-1.4703922	-1.3696258	-5.5781064	H	2.4782459	1.1807701	-4.283121
C	0.4954104	3.3867103	-1.6497228	H	2.4818238	-2.6858479	-5.3894011
C	0.3539026	3.3608731	-0.2624363	H	2.1684603	-3.3100514	-3.7605112
C	0.8412718	4.3950917	0.5207507	H	3.8333045	-2.9588448	-4.2805803

H	3.8520191	1.5694651	2.6740489	H	-0.7936343	-2.0293664	-5.0258088
H	2.4983429	1.7998326	1.5574331	H	-0.8973943	-0.8385158	-6.3442476
H	4.1547767	2.2321405	1.0593804	H	-0.1384535	2.5209221	0.2114236
H	2.7825649	-1.5895719	5.0865467	H	0.7190408	4.363167	1.5968741
H	1.1810228	-1.2440252	5.7548342	H	2.1325998	6.3562605	-1.9053315
H	1.6061321	-0.638687	4.1450803	H	1.2524193	4.5168211	-3.3057122
H	1.5103644	-5.9997502	-1.0793417	H	3.3596214	4.3227524	1.0816563
H	2.7058657	-6.8484995	-0.072563	H	5.5014431	4.1280146	2.235564
H	3.1375821	-6.3009613	-1.7015932	H	6.5798568	6.1303185	3.2309997
H	-3.4951932	0.1883289	4.4404764	H	5.4790244	8.336723	2.9926444
H	-1.9132809	-0.4132963	3.9195969	H	0.9457341	10.6693017	2.4358665
H	-2.843317	-1.2911358	5.1599658	H	-1.4942047	10.2841316	2.2443202
H	-1.8320213	-7.838859	0.218051	H	-2.307493	8.1428723	1.2867935
H	-2.5074326	-6.3980726	-0.5525937	H	-0.73512	6.4224611	0.5860688
H	-3.382288	-7.1891136	0.7787127	H	-2.0214778	-3.7447644	-0.9848104
H	-2.9124038	1.7080487	1.4090855	H	-0.3183125	-3.9885499	-0.5721623
H	-3.370235	3.3445163	0.9016565	H	-1.3975322	-1.9514717	-2.5969856
H	-4.6011104	2.2515013	1.5487914	H	0.3009589	-2.1328538	-2.1777583
H	-5.5259668	-3.3653344	-3.4762621	H	-0.7644678	-0.2088466	-1.0875542
H	-4.965211	-4.9118461	-2.8178453	H	-1.9437262	-1.2396474	-0.3012213
H	-3.7848055	-3.6870013	-3.3024743	H	1.0814725	-1.507565	0.1369027
H	-2.2224556	-1.9823175	-6.0706619	H	-0.1693719	-2.3358948	1.0500109

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