

# Photoinduced double charge accumulation in a molecular compound

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## 1. Materials and Methods

All chemicals for synthesis were obtained from commercial suppliers (Thermo Scientific, Fluorochem, Alfar Aesar, Acros Organics or Sigma-Aldrich/Merck) in “reagent grade” purity or better and used as received. Dry solvents were either purchased “extra dry” in 99.8% purity from Thermo Scientific in sealed bottles or were dried in a “PureSolv” solvent purification system by Innovative Technologies. To remove fine particles in solvents dried over molecular sieves, they were filtered through 0.22  $\mu\text{m}$  nylon membrane syringe filters (VWR) prior to their use in analytical measurements. Deuterated solvents used for NMR experiments were purchased from Cambridge Isotope Laboratories.

For purification of reaction products by flash column chromatography, silica gel from SiliCycle (SilicaFlash P60, particle size: 40–64  $\mu\text{m}$ , 230–400 mesh) was used. Automated flash column chromatography was performed with an Isolera One system from Biotage. Thin layer chromatography was performed using aluminium sheets pre-coated with silica gel 60 and the fluorescence indicator F254, purchased from Merck. Visualization of the compounds occurred under UV light of either 254 or 365 nm wavelength.

NMR spectra were recorded on a Bruker Avance III instrument operating at either 400 or 500 MHz proton frequency. All samples were recorded at 295 K in 5 mm diameter tubes. Routine, gradient selected 2D NMR experiments were used (COSY, NOESY, ROESY, HSQC, HMBC). NMR spectra of the ligand and the final pentad were recorded on a Bruker Avance III instrument operating at 600 MHz proton frequency using a BBI probe head. Chemical shifts were referenced internally to residual solvent peaks relative to TMS ( $\delta = 0$  ppm) using  $\delta$  values as reported previously.<sup>1</sup> Coupling patterns are abbreviated with s (singlet), d (doublet), dd (doublet of doublets), ddd (doublet of doublet of doublets), t (triplet), hept (heptet) and m (multiplet) with indicated coupling constants  $J$  in Hertz (Hz).

High-resolution electrospray ionization mass spectra (HR ESI-MS) were recorded by Dr. Michael Pfeffer (University of Basel, Department of Chemistry) on a Bruker maxis 4G ESI-Q-TOF instrument by direct injection of samples in  $\text{CH}_3\text{CN}$ . The data was analyzed with the DataAnalysis 4.0 software.

Steady-state UV-vis absorption spectra were recorded using a Cary5000 spectrophotometer from Varian. Samples were prepared in dry solvents under ambient conditions and measured in quartz cuvettes (10  $\times$  10 mm), unless stated otherwise.

Cyclic voltammetry was performed under  $\text{N}_2$  or Ar atmosphere in a three-necked electrochemical cell. A glassy carbon disc electrode, a silver wire, and a saturated calomel electrode were used as working, counter, and reference electrodes, respectively. Sample solutions (1.0 mM) were prepared in dry  $\text{CH}_2\text{Cl}_2$  or  $\text{CH}_3\text{CN}$  with supporting electrolyte (0.1 M, tetra-*n*-butylammonium hexafluorophosphate, TBAPF<sub>6</sub>) and solutions were bubbled with  $\text{N}_2$  or Ar for 5 min prior to each measurement. The scan rate was 100 mV s<sup>-1</sup> unless stated otherwise and the response current signals were recorded on a Versastat4-200 potentiostat from Princeton Applied Research.

Spectro-electrochemical measurements (SEC) by recording the UV-vis absorbance spectral changes upon electrochemical reduction or oxidation were measured using  $\text{N}_2$  bubbled samples in dry solvents

(CH<sub>2</sub>Cl<sub>2</sub> or CH<sub>3</sub>CN) in a cuvette with an optical path length of 1 mm. To a sample solution (typically 250 μM) containing a supporting electrolyte (0.1 M, TBAPF<sub>6</sub>), continuous voltage was applied using Pt mesh, Pt wire, and saturated calomel electrodes as working, counter, and reference electrodes, respectively. The applied voltage was controlled by a Versastat4-200 potentiostat from Princeton Applied Research. The resulting UV-vis absorbance differences were recorded on a OceanHDX miniature spectrometer from Ocean Optics.

Sample preparation for spectrophotometric measurements were performed using quartz cuvettes with screw septum caps. Solutions were purged with argon for 10 min to remove oxygen.

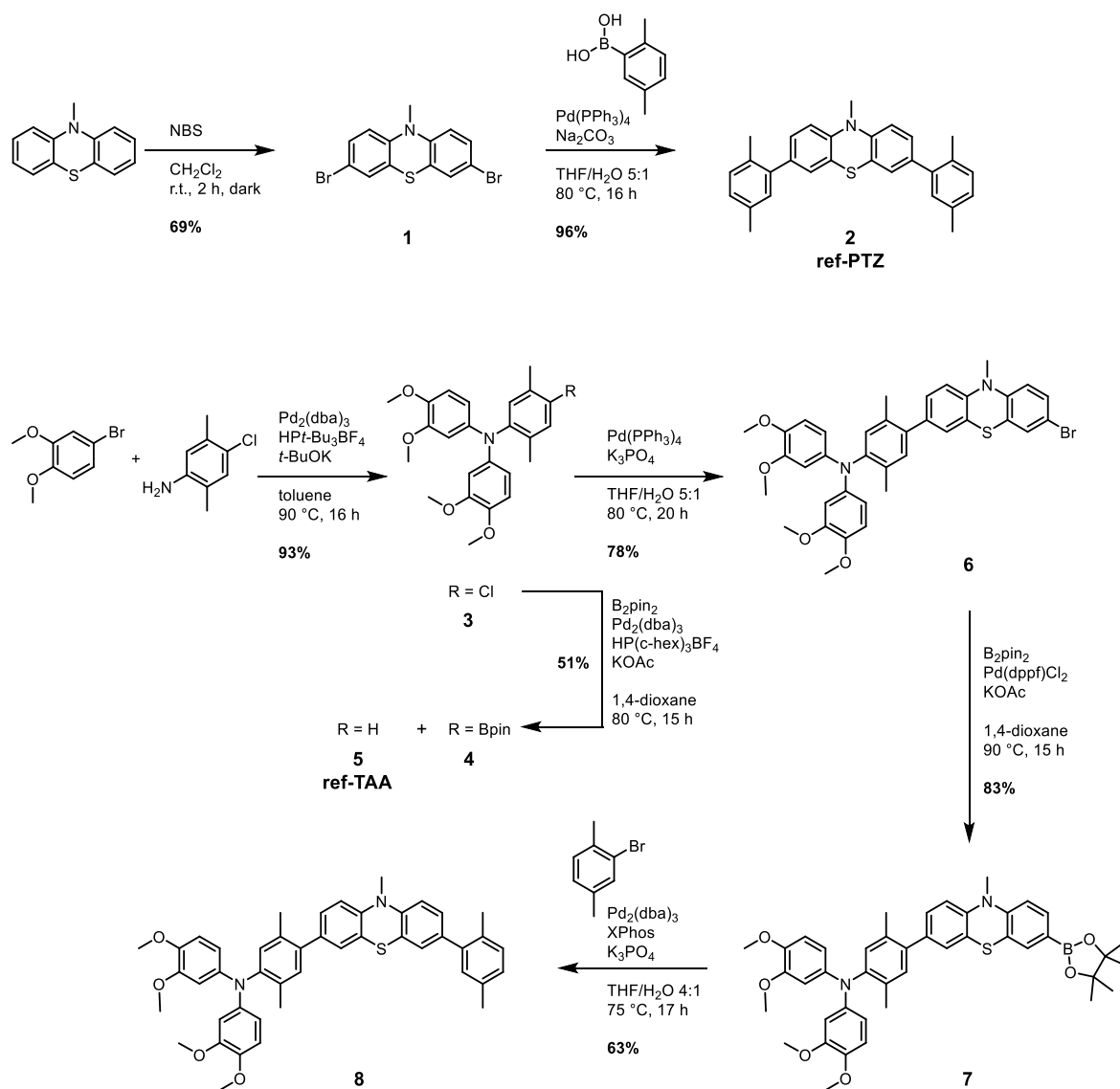
Transient UV-Vis absorption spectroscopy with nanosecond time resolution was performed on an LP920-KS apparatus from Edinburgh Instruments. A frequency-tripled Nd:YAG laser (Quintel Brilliant, ca. 10 ns pulse width and a pulse frequency of 10 Hz) equipped with an OPO from Opotek was used for excitation at 460-470 nm with a pulse energy of ca. 15 mJ. An iCCD camera from Andor was used to detect transient absorption spectra and single-wavelength kinetics were recorded with a photomultiplier tube.

Transient UV-Vis absorption spectroscopy with picosecond time resolution was measured using a commercial pump-probe instrument from Light Conversion using a HARPIA spectrometer and a Kymera 193i-B2 iCCD camera from ANDOR. In this experimental setup, the excitation light is generated by a PHAROS laser (Light Conversion, Yb:KGW laser, source wavelength = 1030 nm, pulse duration = ca. 190 fs, repetition rate = 50 kHz, output power = 10 W, pulse energy = 0.2 mJ), and the actual pump light was generated by an optical parametric amplifier called ORPHEUS (Light Conversion, using ca. 90% of the fundamental pulse). Probe pulses for the spectral range of 500–900 nm were generated using the second optical harmonic of PHAROS (515 nm) and a 5 mm thick sapphire white light supercontinuum generator (WLSc, ca. 10% of the fundamental pulse were used to generate a white light supercontinuum). Sample solutions (typically 0.3 mM) were measured in a 1 mm quartz cuvette at room temperature under air. The obtained femtosecond transient absorption datasets were chirp- and background-corrected, and analyzed using the CarpetView software provided by Light Conversion.

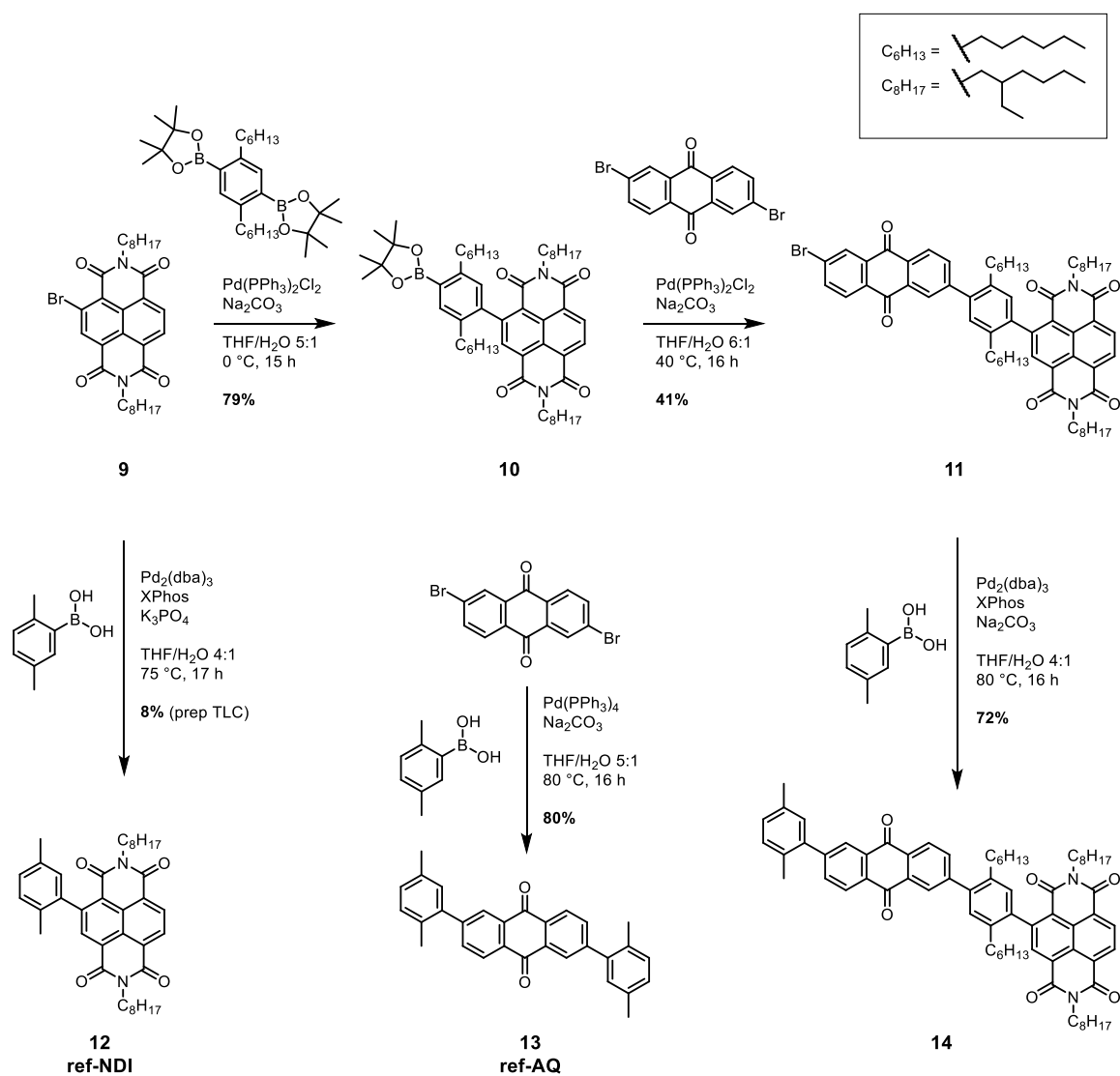
The external laser used for the pump-pump-probe experiment was a 447 nm continuous wave laser from Roithner Lasertechnik with an output power set to 460 mW.

Abbreviations used are: xy = *p*-xylene, hxy = 1,4-di(*n*-hexyl)benzene, TAA = *N,N*-bis(3,4-dimethoxyphenyl)-2,5-dimethylaniline, PTZ = 10-methyl-10*H*-phenothiazine, bpy = 2,2'-bipyridine, AQ = 9,10-anthraquinone, NDI = naphthalene diimide, 2,7-bis(2-ethylhexyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone, TMS = trimethylsilyl, XPhos = 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl, c-hex = cyclohexane, NBS = *N*-bromosuccinimide, THF = tetrahydrofuran, DMF = *N,N*-dimethylformamide, dba = dibenzylideneacetone, B<sub>2</sub>pin<sub>2</sub> = bis(pinacolato)diboron, dppf = 1,1'-bis(diphenylphosphino)ferrocene.

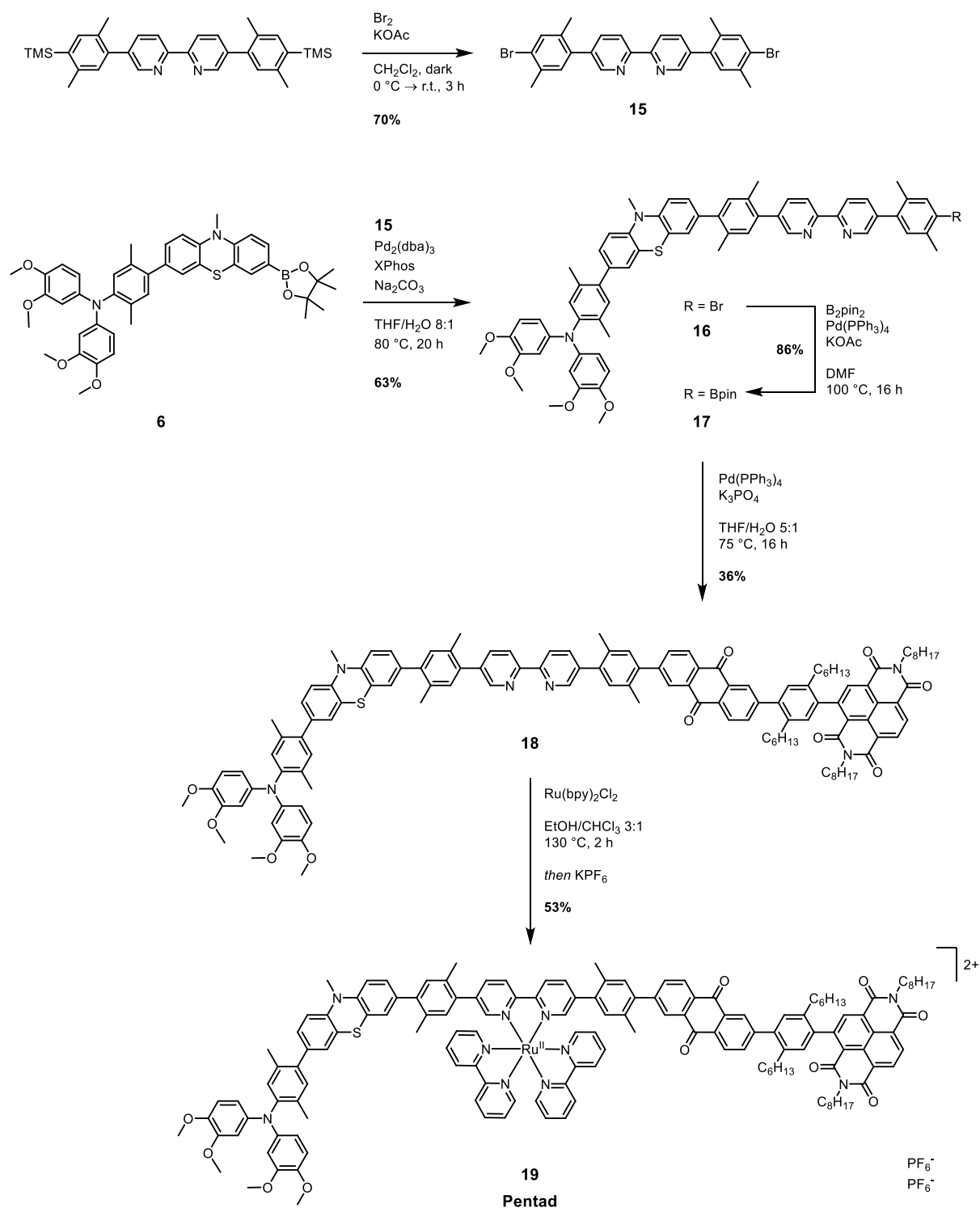
## 2. Synthetic Schemes



**Supplementary Figure 1.** Synthetic route to the donor branch of the pentad and related reference molecules.



**Supplementary Figure 2.** Synthetic route to the acceptor branch of the pentad and related reference molecules.



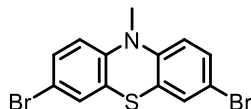
**Supplementary Figure 3.** Synthetic route to the central 2,2'-bipyridine building block and the final assembly of the pentad.



### 3. Synthetic Procedures

Bpin-hxy-Bpin,<sup>2</sup> Br-NDI<sup>3</sup> and TMS-xy-bpy-xy-TMS<sup>4</sup> were prepared according to published procedures.

#### Br-PTZ-Br (**1**)

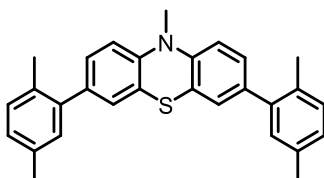


This synthesis is based on a published procedure.<sup>5</sup> 10-methyl-10*H*-phenothiazine (599 mg, 2.81 mmol, 1.0 eq) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and cooled to 0 °C. NBS (1.25 mg, 7.02 mmol, 2.5 eq.) was added in portions and the solution was stirred for 2 h at room temperature. H<sub>2</sub>O (10 mL) was added and the phases were separated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (4× 20 mL) and the combined organic layers were washed with brine (2× 100 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The crude mixture was purified by flash column chromatography (SiO<sub>2</sub>, EtOAc/c-hex: 0% → 10%) to yield Br-PTZ-Br (724 mg, 1.95 mmol, 69%) as a colorless solid.

<sup>1</sup>H-NMR (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>), δ [ppm]: 7.29 (dd, *J* = 8.6, 2.3 Hz, 2H), 7.24 (d, *J* = 2.3 Hz, 2H), 6.69 (d, *J* = 8.6 Hz, 2H), 3.30 (s, 3H).

<sup>13</sup>C{<sup>1</sup>H}-NMR (126 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>), δ [ppm]: 145.2 130.7, 129.7, 125.2, 115.9, 115.1, 35.8.

#### ref-PTZ (**2**)

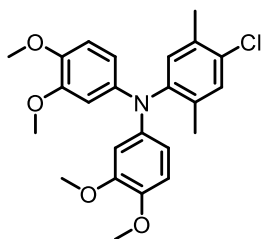


3,7-Dibromo-10-methyl-10*H*-phenothiazine (80.0 mg, 216 μmol, 1.0 eq.), 2,5-(dimethylphenyl)boronic acid (97.0 mg, 647 μmol, 3.0 eq.) and Na<sub>2</sub>CO<sub>3</sub> (114 mg, 1.08 mmol, 5.0 eq.) were suspended in THF/H<sub>2</sub>O (3.0 mL/0.6 mL) in a microwave vial. The suspension was sparged with N<sub>2</sub> for 5 min before Pd(PPh<sub>3</sub>)<sub>4</sub> (24.9 mg, 21.6 μmol, 10 mol%) was added. Sparging was continued for 5 min and the vial was sealed. The reaction mixture was heated to 80 °C for 16 h and then let cool to room temperature. H<sub>2</sub>O (5.0 mL) and EtOAc (5.0 mL) were added, the phases separated and the aqueous layer was extracted with EtOAc (2 × 5.0 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The crude mixture was purified by flash column chromatography (SiO<sub>2</sub>, EtOAc/c-hex: 0% → 20%) to yield ref-PTZ- (87.0 mg, 206 μmol, 96%) as a colorless solid.

**<sup>1</sup>H-NMR** (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>), δ [ppm]: 7.15 (dd, *J* = 8.2, 2.1 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 2.0 Hz, 2H), 7.04 (dd, *J* = 7.8, 1.3 Hz, 2H), 7.01 (d, *J* = 1.2 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 2H), 3.45 (s, 3H), 2.32 (s, 6H), 2.22 (s, 6H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (126 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>), δ [ppm]: 144.9, 141.0, 136.9, 135.7, 132.5, 130.7, 130.6, 128.8, 128.2, 128.0, 123.2, 114.1, 35.7, 21.0, 20.2.

### TAA-xy-Cl (**3**)

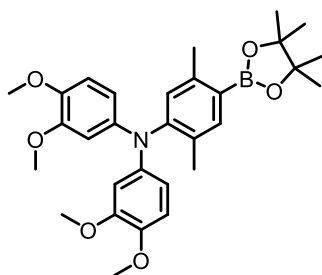


This synthesis is based on a published procedure and slightly modified.<sup>6</sup> 4-Chloro-2,5-dimethylaniline (860 mg, 5.53 mmol, 1.0 eq.), KO<sup>t</sup>Bu (1.86 g, 16.6 mmol, 3.0 eq.), tris(dibenzylideneacetone)-dipalladium (127 mg, 138 μmol, 3.0 mol%), and tri-*tert*-butylphosphonium tetrafluoroborate (96 mg, 332 μmol, 6.0 mol%) were combined and three vacuum/N<sub>2</sub> cycles were performed. Dry toluene (20 mL) and 4-bromoveratrole (2.00 mL, 3.00 g, 13.8 mmol, 2.5 eq.) were added and the suspension was sparged with N<sub>2</sub> for 10 min. The reaction mixture was heated to 90 °C for 16 h and then let cool to room temperature. H<sub>2</sub>O (50 mL) and EtOAc (30 mL) were added, the phases separated and the aqueous layer was extracted with EtOAc (2× 30 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The crude mixture was purified by flash column chromatography (SiO<sub>2</sub>, EtOAc/c-hex: 0% → 25%) to yield TAA-xy-Cl (2.19 g, 5.12 mmol, 93%) as a red foam.

**<sup>1</sup>H-NMR** (500 MHz, 298 K, acetone-*d*<sub>6</sub>), δ [ppm]: 7.24 (s, 1H), 6.99 (s, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.61 (d, *J* = 2.6 Hz, 2H), 6.35 (dd, *J* = 8.6, 2.6 Hz, 2H), 3.75 (s, 6H), 3.65 (s, 6H), 2.24 (s, 3H), 1.98 (s, 3H).

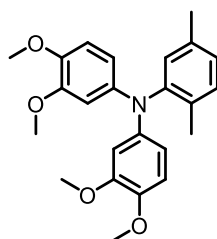
**<sup>13</sup>C{<sup>1</sup>H}-NMR** (126 MHz, 298 K, acetone-*d*<sub>6</sub>), δ [ppm]: 151.0, 146.1, 145.8, 142.7, 135.8, 135.2, 132.3, 131.5, 130.6, 114.9, 113.7, 108.2, 56.5, 56.1, 19.6, 18.3.

#### TAA-xy-Bpin (**4**)



This synthesis is based on a published procedure and slightly modified.<sup>6</sup> TAA-xy-Cl (967 mg, 2.26 mmol, 1.0 eq.), bis(pinacolato)diboron (860 mg, 3.39 mmol, 1.5 eq.) KOAc (886 mg, 9.03 mmol, 4.0 eq.), tris(dibenzylideneacetone)dipalladium (103 mg, 113  $\mu$ mol, 5.0 mol%), and tricyclohexylphosphonium tetrafluoroborate (83 mg, 226  $\mu$ mol, 10 mol%) were combined and three vacuum/ $N_2$  cycles were performed. Dry 1,4-dioxane (15 mL) was added and the suspension was sparged with  $N_2$  for 10 min. The reaction mixture was heated to 80 °C for 15 h and then let cool to room temperature. The solvent was removed under reduced pressure and the crude mixture was purified by flash column chromatography ( $SiO_2$ , EtOAc/c-hex: 0%  $\rightarrow$  10%) to yield a mixture<sup>6</sup> of TAA-xy-Bpin (595 mg, 1.15 mmol, 51%) and ref-TAA (361 mg, 917  $\mu$ mol, 41%) as a brown foam. The mixture was used without further characterization for the next step since ref-TAA is not interfering with the subsequent reaction and can be separated afterwards.

#### ref-TAA (**5**)

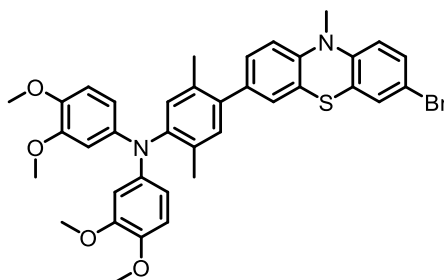


Obtained as side product from the synthesis of TAA-xy-Bpin (**4**).

**$^1H$ -NMR** (500 MHz, 298 K, acetone- $d_6$ ),  $\delta$  [ppm]: 7.12 (d,  $J$  = 7.7 Hz, 1H), 6.94 (dd,  $J$  = 7.7, 1.3 Hz, 1H), 6.88 (d,  $J$  = 1.3 Hz, 1H), 6.80 (d,  $J$  = 8.6 Hz, 2H), 6.61 (d,  $J$  = 2.6 Hz, 2H), 6.34 (dd,  $J$  = 8.6, 2.6 Hz, 2H), 3.75 (s, 6H), 3.64 (s, 6H), 2.23 (s, 3H), 1.99 (s, 3H).

**$^{13}C\{^1H\}$ -NMR** (126 MHz, 298 K, acetone- $d_6$ ),  $\delta$  [ppm]: 150.9, 146.9, 145.5, 143.0, 137.5, 133.3, 132.2, 129.9, 127.0, 114.6, 113.8, 108.0, 56.5, 56.1, 20.9, 18.4.

## TAA-xy-PTZ-Br (6)

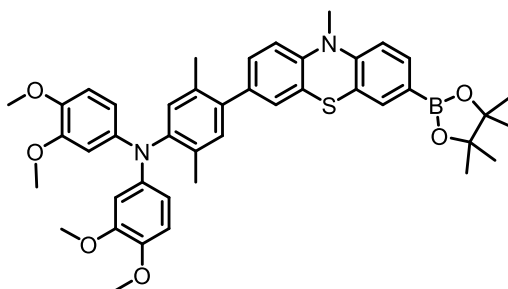


TAA-xy-Bpin (62%, 940 mg, 1.12 mmol, 1.0 eq.), 3,7-dibromo-10-methyl-10*H*-phenothiazine (1.67 g, 4.50 mmol, 4.0 eq.), and  $K_3PO_4$  (714 mg, 3.37 mmol, 3.0 eq.) were combined and three vacuum/ $N_2$  cycles were performed. THF (15 mL) and  $H_2O$  (3.0 mL) were added and the suspension was sparged with  $N_2$  for 10 min.  $Pd(PPh_3)_4$  (135 mg, 117  $\mu$ mol, 10 mol%) was added and sparging was continued for 5 min. The vial was sealed and the reaction mixture was heated to 80  $^{\circ}C$  for 20 h. The crude was purified by flash column chromatography ( $SiO_2$ , EtOAc/c-hex: 0%  $\rightarrow$  30%) to yield TAA-xy-PTZ-Br (601 mg, 879  $\mu$ mol, 78%) as an off-white foam.

**$^1H$ -NMR** (500 MHz, 298 K,  $CDCl_3$ ),  $\delta$  [ppm]: 7.29 – 7.26 (m, 2H), 7.16 (dd,  $J$  = 8.3, 2.0 Hz, 1H), 7.13 (d,  $J$  = 2.0 Hz, 1H), 7.01 (s, 1H), 6.92 (s, 1H), 6.84 (d,  $J$  = 8.3 Hz, 1H), 6.73 (d,  $J$  = 8.7 Hz, 2H), 6.68 (d,  $J$  = 9.2 Hz, 1H), 6.63 (d,  $J$  = 2.5 Hz, 2H), 6.43 (dd,  $J$  = 8.6, 2.6 Hz, 2H), 3.85 (s, 6H), 3.75 (s, 6H), 3.38 (s, 3H), 2.16 (s, 3H), 1.99 (s, 3H).

**$^{13}C\{^1H\}$ -NMR** (126 MHz, 298 K,  $CDCl_3$ ),  $\delta$  [ppm]: 149.5, 145.2, 145.1, 144.2, 144.1, 142.2, 137.4, 136.5, 134.1, 132.9, 132.8, 130.2, 130.1, 129.5, 128.7, 128.0, 125.6, 122.4, 115.3, 114.8, 114.2, 113.9, 112.0, 106.9, 56.3, 56.1, 35.5, 20.2, 18.4.

## TAA-xy-PTZ-Bpin (7)



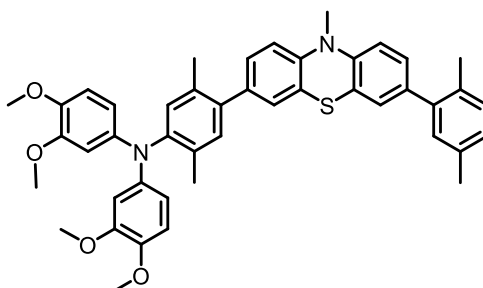
TAA-xy-PTZ-Br (538 mg, 787  $\mu$ mol, 1.0 eq.), bis(pinacolato)diboron (300 mg, 1.18 mmol, 1.5 eq.), KOAc (232 mg, 2.36 mmol, 3.0 eq.) and  $Pd(dppf)Cl_2$  (64.3 mg, 79  $\mu$ mol, 10 mol%) were combined. Dry 1,4-dioxane (10 mL) was added and the suspension was sparged with  $N_2$  for 10 min. The vial was sealed and the reaction mixture was heated to 90  $^{\circ}C$  for 15 h. After cooling to room temperature, the reaction mixture was filtered through a plug of celite with  $CH_2Cl_2$  and the solvents were removed under reduced

pressure. The crude was purified by flash column chromatography (SiO<sub>2</sub>, EtOAc/c-hex: 0% → 15% → 25%) to yield TAA-xy-PTZ-Bpin (475 mg, 650 μmol, 83%) as a yellow foam.

**<sup>1</sup>H-NMR** (500 MHz, 298 K, acetone-d<sub>6</sub>), δ [ppm]: 7.59 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.46 (d, *J* = 1.4 Hz, 1H), 7.22 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.14 (d, *J* = 2.1 Hz, 1H), 7.09 (s, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.97 (s, 1H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.66 (d, *J* = 2.6 Hz, 2H), 6.38 (dd, *J* = 8.6, 2.6 Hz, 2H), 3.77 (s, 6H), 3.67 (s, 6H), 3.47 (s, 3H), 2.18 (s, 3H), 2.03 (s, 3H), 1.32 (s, 12H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (126 MHz, 298 K, acetone-d<sub>6</sub>), δ [ppm]: 150.9, 149.2, 146.1, 145.6, 144.9, 143.0, 138.4, 137.1, 135.5, 134.7, 133.8, 133.7, 133.5, 131.0, 129.3, 128.3, 123.6, 122.9, 115.1, 114.9, 114.7, 113.8, 108.2, 84.5, 56.5, 56.2, 35.8, 25.2, 20.3, 18.5. *C-(Bpin)* not observed in the <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum but found in the HMBC spectrum.

### TAA-xy-PTZ-xy (**8**)

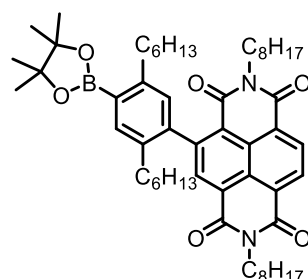


TAA-xy-PTZ-Bpin (30 mg, 41 μmol, 1.0 eq.), K<sub>3</sub>PO<sub>4</sub> (33 mg, 155 μmol, 3.8 eq.), tris(dibenzylideneacetone)dipalladium (2 mg, 2 μmol, 5 mol%), and XPhos (3 mg, 6 μmol, 15 μmol) were combined and three vacuum/N<sub>2</sub> cycles were performed. THF (0.8 mL), H<sub>2</sub>O (0.2 mL) and 2-bromo-1,4-dimethylbenzene (10 μL, 13 μg, 72 μmol, 1.8 eq.) were added and the suspension was sparged with N<sub>2</sub> for 10 min. The vial was sealed and the reaction mixture was heated to 75 °C for 17 h. The solvent was removed under reduced pressure and the crude was purified by flash column chromatography (SiO<sub>2</sub>, EtOAc/c-hex: 0% → 35%) to yield TAA-xy-PTZ-xy (18 mg, 26 μmol, 63%) as a yellow solid.

**<sup>1</sup>H-NMR** (500 MHz, 298 K, acetone-d<sub>6</sub>), δ [ppm]: 7.24 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.19 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.16 – 7.14 (m, 2H), 7.11 (d, *J* = 2.1 Hz, 1H), 7.11 (s, 1H), 7.07 – 7.01 (m, 4H), 6.97 (s, 1H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.67 (d, *J* = 2.6 Hz, 2H), 6.39 (dd, *J* = 8.6, 2.6 Hz, 2H), 3.77 (s, 6H), 3.67 (s, 6H), 3.49 (s, 3H), 2.31 (s, 3H), 2.22 (s, 3H), 2.19 (s, 3H), 2.03 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR** (126 MHz, 298 K, acetone-d<sub>6</sub>), δ [ppm]: 150.9, 146.1, 145.6, 145.4, 145.4, 143.0, 141.4, 138.5, 137.4, 136.8, 136.0, 134.7, 133.7, 133.6, 132.7, 131.2, 131.1, 131.0, 129.4, 129.3, 128.7, 128.3, 128.2, 123.6, 123.5, 114.9, 114.9, 114.9, 113.8, 108.2, 56.5, 56.2, 35.7, 20.9, 20.3, 20.2, 18.5.

## Bpin-hxy-NDI (**10**)



Br-NDI (250 mg, 439  $\mu$ mol, 1.0 eq.), Bpin-hxy-Bpin (1.55 g, 3.11 mmol, 7.1 eq.),  $\text{Na}_2\text{CO}_3$  (162 mg, 1.53 mmol, 3.5 eq.), and  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (20 mg, 28  $\mu$ mol, 6 mol%) were combined and five vacuum/ $\text{N}_2$  cycles were performed. The vial was cooled in an ice-bath, THF (10 mL) and  $\text{H}_2\text{O}$  (1.6 mL) were added and the suspension was sparged with  $\text{N}_2$  for 10 min. The vial was sealed and the reaction mixture was stirred for 20 h while the ice bath was allowed to warm to room temperature.  $\text{CH}_2\text{Cl}_2$  (5.0 mL) and  $\text{H}_2\text{O}$  (5 mL) were added and the phases were separated. The organic layer was washed with  $\text{H}_2\text{O}$  (2 $\times$  5.0 mL) and brine (5.0 mL) and the solvent was removed under reduced pressure. The crude was purified by repeated flash column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ /c-hex: 0%  $\rightarrow$  100%) to yield Bpin-hxy-NDI (300 mg, 349  $\mu$ mol, 79%) as a red sticky solid and to recover excess starting material.

**$^1\text{H}$ -NMR** (500 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ),  $\delta$  [ppm]: 8.80 (d,  $J$  = 7.6 Hz, 1H), 8.75 (d,  $J$  = 7.6 Hz, 1H), 8.46 (s, 1H)\*, 7.73 (s, 1H), 6.90 (s, 1H), 4.17 – 4.08 (m, 2H), 4.04 – 3.96 (m, 2H), 2.93 – 2.79 (m, 2H), 2.40 – 2.25 (m, 2H), 1.96 – 1.81 (m, 2H), 1.62 – 1.51 (m, 2H), 1.39 (s, 12H), 1.36 – 1.22 (m, 24H), 1.09 – 0.98 (m, 6H), 0.93 (t,  $J$  = 7.4 Hz, 3H), 0.89 – 0.83 (m, 12H), 0.67 (t,  $J$  = 7.0 Hz, 3H).

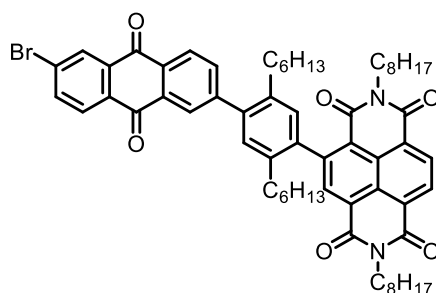
**$^{13}\text{C}\{^1\text{H}\}$ -NMR** (126 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ),  $\delta$  [ppm]: 163.7, 163.5, 162.7, 148.1, 148.1, 143.3, 137.0, 137.0, 135.8, 135.6, 131.4, 130.7, 128.7, 128.7, 128.0, 127.3, 127.1, 126.6, 125.7, 124.0, 123.9, 83.9, 44.8, 44.7, 38.4, 38.1, 35.9, 33.9, 33.4, 32.2, 31.8, 31.1, 31.1, 31.0, 31.0, 30.1, 29.9, 29.9, 29.5, 29.5, 29.1, 29.1, 25.2, 25.1, 24.4, 24.3, 24.3, 23.5, 23.5, 23.5, 23.1, 22.8, 14.3, 14.3, 14.2, 14.1, 10.8, 10.8.\*

*\*Both sidechains of the imides possess a stereogenic center ( $\text{CHR}^1\text{R}^2\text{R}^3$ ). This provides a set of four stereoisomers ( $R,R$ ;  $S,S$ ;  $R,S$ ;  $S,R$ ) of the target compound containing two diastereomers (and their enantiomers). In NMR spectroscopy, this results in two sets of signals whereby those of similar energies overlap. Therefore, more carbon signals than expected are observed and cannot be disentangled. In the  $^1\text{H}$ -NMR spectrum there are two signals observed at 8.46 ppm separated by 0.0038 ppm (1.9 Hz at 500 MHz proton frequency).*

**Reaction optimization to prevent dicoupling:** The very electron-poor Br-NDI undergoes oxidative addition to  $\text{Pd}(0)$  unusually fast for a Suzuki cross-coupling reaction. Initial reaction conditions differed from the optimized procedure in using  $\text{Pd}(\text{XPhos})$  as a catalyst at a typical reaction temperature of 60  $^\circ\text{C}$ . This procedure provided the product **10** in only 22% yield and the main by-product was doubly coupled NDI-hxy-NDI despite using the boronic ester in a large excess (8.0 eq.). Using a less electron-rich Pd

catalyst ( $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ ) at room temperature while keeping the other parameters constant provided a better yield with 57%. The temperature was further decreased by cooling the reaction mixture in an water/ice bath before  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  was added. The reaction was subsequently stirred in the ice bath which was let warm to room temperature overnight. This optimized procedure provided a yield of 79% and almost none of the dicoupled by-product. Other effects like differences in solubility at lower temperatures resulting in a higher effective excess or precipitation of the desired product could also contribute to the improved yield.

### Br-AQ-hxy-NDI (**11**)



2,6-Dibromoanthraquinone (Br-AQ-Br) (755 mg, 2.06 mmol, 8.0 eq.) and  $\text{Na}_2\text{CO}_3$  (109 mg, 1.03 mmol, 4.0 eq.) were combined and THF (12 mL) and  $\text{H}_2\text{O}$  (2.5 mL) were added. The suspension was sparged with  $\text{N}_2$  for 10 min and then heated to 40 °C in order to dissolve Br-AQ-Br. Bpin-hxy-NDI (222 mg, 258  $\mu\text{mol}$ , 1.0 eq.) was dissolved in THF (6.0 mL) and quickly sparged with  $\text{N}_2$ . A third of that solution (2.0 mL) and  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (18 mg, 26  $\mu\text{mol}$ , 10 mol%) were added to the reaction mixture. The vial was sealed and the reaction mixture was heated to 40 °C. Consumption of the boronic species was monitored by TLC and more of the Bpin-hxy-NDI solution ( $2 \times 2.0$  mL) was added after 2 h and 4 h. The reaction mixture was heated to 40 °C overnight. After cooling to room temperature, the excess Br-AQ-Br was filtered-off and washed with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 15.0$  mL). The filtrate was washed with  $\text{H}_2\text{O}$  (50 mL) and the layers were separated. The organic phase was dried over  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under reduced pressure. The crude was purified by flash column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{c-hex}$ : 0%  $\rightarrow$  50%) to yield Br-AQ-hxy-NDI (109 mg, 107  $\mu\text{mol}$ , 41%) as a yellow sticky solid.

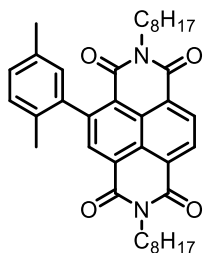
**$^1\text{H}$ -NMR** (500 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ),  $\delta$  [ppm]: 8.82 (d,  $J = 7.6$  Hz, 1H), 8.77 (d,  $J = 7.6$  Hz, 1H), 8.53 (s, 1H)\*, 8.47 (d,  $J = 2.1$  Hz, 1H), 8.40 – 8.37 (m, 2H), 8.21 (d,  $J = 8.3$  Hz, 1H), 7.97 (dd,  $J = 8.3, 2.0$  Hz, 1H), 7.95 (dd,  $J = 7.9, 1.8$  Hz, 1H), 7.29 (s, 1H), 7.10 (s, 1H), 4.19 – 4.09 (m, 2H), 4.09 – 3.97 (m, 2H), 2.67 – 2.61 (m, 2H), 2.48 – 2.40 (m, 1H), 2.40 – 2.31 (m, 1H), 1.99 – 1.92 (m, 1H), 1.90 – 1.84 (m, 1H), 1.53 – 1.46 (m, 2H), 1.45 – 1.27 (m, 18H), 1.22 – 1.02 (m, 12H), 0.94 (t,  $J = 7.4$  Hz, 3H), 0.91 – 0.88 (m, 6H), 0.86 (t,  $J = 7.2$  Hz, 3H), 0.76 (t,  $J = 7.0$  Hz, 3H), 0.68 (t,  $J = 6.8$  Hz, 3H).

**$^{13}\text{C}\{^1\text{H}\}$ -NMR** (126 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ),  $\delta$  [ppm]: 182.3, 181.8, 163.3, 163.0, 163.0, 162.4, 162.4, 148.5, 147.1, 147.1, 140.9, 140.9, 139.2, 139.2, 137.7, 137.1, 137.0, 135.3, 134.8, 133.2, 132.4, 131.7, 131.1, 130.4, 130.1, 130.1, 130.0, 129.6, 129.0, 128.9, 128.1, 127.6, 127.3, 126.9, 126.7, 126.2, 125.4,

123.7, 123.7, 44.4, 44.3, 38.0, 37.7, 33.0, 32.6, 31.4, 31.4, 31.3, 30.7, 30.6, 30.6, 30.4, 30.4, 29.0, 29.0, 29.0, 28.6, 28.6, 24.0, 23.9, 23.9, 23.1, 23.1, 23.0, 22.4, 22.4, 13.8, 13.7, 13.7, 10.4, 10.4, 10.4.\*

*\*Both sidechains of the imides possess a stereogenic center ( $CHR^1R^2R^3$ ). This provides a set of four stereoisomers ( $R,R$ ;  $S,S$ ;  $R,S$ ;  $S,R$ ) of the target compound containing two diastereomers (and their enantiomers). In NMR spectroscopy, this results in two sets of signals whereby those of similar frequencies overlap. Therefore, more carbon signals than expected are observed and cannot be disentangled. In the  $^1H$ -NMR spectrum there are two signals observed at 8.53 ppm separated by 0.0029 ppm (1.46 Hz at 500 MHz proton frequency).*

## ref-NDI (12)



Br-NDI (31 mg, 55  $\mu$ mol, 1.0 eq.), 2,5-dimethylphenylboronic acid (20 mg, 129  $\mu$ mol, 2.3 eq.),  $K_3PO_4$  (27 mg, 129  $\mu$ mol, 2.3 eq.), tris(dibenzylideneacetone)dipalladium (2 mg, 2  $\mu$ mol, 5 mol%), and XPhos (4 mg, 7  $\mu$ mol, 13  $\mu$ mol) were combined and three vacuum/ $N_2$  cycles were performed. THF (0.8 mL) and  $H_2O$  (0.2 mL) were added and the suspension was sparged with  $N_2$  for 15 min. The vial was sealed and the reaction mixture was heated to 75  $^{\circ}C$  for 17 h. The solvent was removed under reduced pressure and the crude was resuspended in  $CH_2Cl_2$  and filtered. The filtrate was loaded on  $SiO_2$  and pre-purified by repeated flash column chromatography ( $SiO_2$ ,  $CH_2Cl_2$ /c-hex: 0%  $\rightarrow$  10%). Final purification of a part of the impure fractions by preparative TLC ( $SiO_2$ , EtOAc/c-hex: 10%) afforded pure ref-NDI (3 mg, 4  $\mu$ mol, 8%) as a yellow solid.

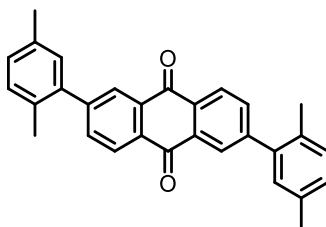
**$^1H$ -NMR** (500 MHz, 298 K,  $CD_2Cl_2$ ),  $\delta$  [ppm]: 8.80 (d,  $J$  = 7.6 Hz, 1H), 8.74 (d,  $J$  = 7.6 Hz, 1H), 8.45 (s, 1H)\*, 7.22 (d,  $J$  = 7.9 Hz, 1H), 7.19 (dd,  $J$  = 7.8, 1.8 Hz, 1H), 6.95 (m, 1H), 4.16 – 4.07 (m, 2H), 4.04 – 3.97 (m, 2H), 2.37 (s, 3H), 1.99 (s, 3H), 1.95 – 1.90 (m, 1H), 1.86 – 1.81 (m, 1H), 1.43 – 1.22 (m, 12H), 0.93 (t,  $J$  = 7.4 Hz, 3H), 0.91 – 0.83 (m, 9H).

**$^{13}C\{^1H\}$ -NMR** (126 MHz, 298 K,  $CD_2Cl_2$ ),  $\delta$  [ppm]: 135.3, 131.3, 131.2, 130.5, 129.5, 128.8, 128.0, 44.5, 44.4, 44.4, 38.1, 38.1, 37.9, 30.3, 29.9, 29.3, 24.0, 23.3, 20.8, 19.3, 14.0, 10.5, 10.5.  $^{13}C$  shifts were obtained indirectly with 2D NMR spectroscopy (HMBC, HSQC) due to the low availability of pure material. One of the naphthalene's quaternary carbons does not have a  $^3J$   $^1H$ - $^{13}C$  correlation and was therefore not observed.

*\*Both sidechains of the imides possess a stereogenic center ( $CHR^1R^2R^3$ ). This provides a set of four stereoisomers ( $R,R$ ;  $S,S$ ;  $R,S$ ;  $S,R$ ) of the target compound containing two diastereomers (and their*

enantiomers). In NMR spectroscopy, this results in two sets of signals whereby those of similar frequencies overlap. In the  $^1\text{H}$ -NMR spectrum there are two signals observed at 8.45 ppm separated by 0.0029 ppm (1.5 Hz at 500 MHz proton frequency).

### ref-AQ (13)

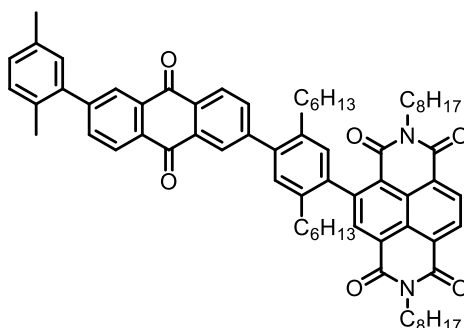


2,6-Dibromoanthraquinone (103 mg, 280  $\mu\text{mol}$ , 1.0 eq.), 2,5-dimethylphenylboronic acid (127 mg, 849  $\mu\text{mol}$ , 3.0 eq.) and  $\text{Na}_2\text{CO}_3$  (86 mg, 814  $\mu\text{mol}$ , 2.9 eq.) were combined and three vacuum/ $\text{N}_2$  cycles were performed. THF (2.0 mL) and  $\text{H}_2\text{O}$  (0.4 mL) were added and the suspension was sparged with  $\text{N}_2$  for 5 min.  $\text{Pd}(\text{PPh}_3)_4$  (9 mg, 8  $\mu\text{mol}$ , 3 mol%) was added and sparging was continued for 5 min. The vial was sealed and the reaction mixture was heated to 80  $^\circ\text{C}$  for 16 h. After cooling to room temperature,  $\text{H}_2\text{O}$  (2.0 mL) was added to the reaction mixture and the precipitate was filtered off. The precipitate was washed with  $\text{H}_2\text{O}$  (4 $\times$  4.0 mL) and  $\text{Et}_2\text{O}$  (3 $\times$  4.0 mL) and dried under vacuum to yield ref-AQ (93 mg, 223  $\mu\text{mol}$ , 80%) as a brown solid.

$^1\text{H}$ -NMR (500 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ),  $\delta$  [ppm]: 8.35 (d,  $J$  = 7.9 Hz, 2H), 8.28 (d,  $J$  = 1.8 Hz, 2H), 7.79 (dd,  $J$  = 7.9, 1.8 Hz, 2H), 7.23 (d,  $J$  = 7.7 Hz, 2H), 7.18 – 7.13 (m, 4H), 2.38 (s, 6H), 2.28 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ),  $\delta$  [ppm]: 183.4, 148.8, 140.2, 136.1, 135.3, 133.9, 132.5, 132.5, 131.0, 130.6, 129.4, 128.1, 127.5, 21.0, 20.1.

### xy-AQ-hxy-NDI (14)



Br-AQ-hxy-NDI (15 mg, 15  $\mu\text{mol}$ , 1.0 eq.), 2,5-dimethylphenylboronic acid (9 mg, 59  $\mu\text{mol}$ , 4.0 eq.),  $\text{Na}_2\text{CO}_3$  (8 mg, 74  $\mu\text{mol}$ , 5.0 eq.), tris(dibenzylideneacetone)dipalladium (1 mg, 1  $\mu\text{mol}$ , 10 mol%), and XPhos (1 mg, 3  $\mu\text{mol}$ , 20  $\mu\text{mol}$ ) were combined and three vacuum/ $\text{N}_2$  cycles were performed. THF

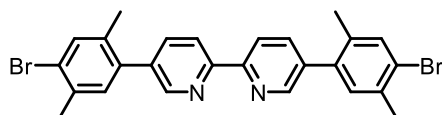
(1.0 mL) and H<sub>2</sub>O (0.2 mL) were added and the suspension was sparged with N<sub>2</sub> for 5 min. The vial was sealed and the reaction mixture was heated to 80 °C for 16 h. The reaction mixture was cooled to room temperature and H<sub>2</sub>O (5.0 mL) was added. The mixture was extracted with EtOAc (3× 5.0 mL) and the solvent of the combined organic phases was removed under reduced pressure. The crude was purified by flash column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/c-hex: 0% → 60%) to yield xy-AQ-hxy-NDI (11 mg, 11 μmol, 72%) as a yellow solid.

**<sup>1</sup>H-NMR** (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>), δ [ppm]: 8.83 (d, *J* = 7.7 Hz, 1H), 8.78 (d, *J* = 7.6 Hz, 1H), 8.53 (s, 1H)\*, 8.42 (d, *J* = 1.8 Hz, 1H), 8.41 (d, *J* = 7.9 Hz, 1H), 8.38 (d, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 1.8 Hz, 1H), 7.93 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.81 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.31 (s, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.19 – 7.14 (m, 2H), 7.09 (s, 1H), 4.19 – 4.09 (m, 2H), 4.08 – 3.98 (m, 2H), 2.71 – 2.63 (m, 2H), 2.39 (s, 3H), 2.30 (s, 3H), 2.05 – 1.99 (m, 2H), 1.99 – 1.92 (m, 1H), 1.92 – 1.82 (m, 1H), 1.44 – 1.30 (m, 16H), 1.27 – 0.97 (m, 16H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.91 – 0.84 (m, 12H), 0.77 (t, *J* = 6.9 Hz, 3H), 0.68 (t, *J* = 7.0 Hz, 3H).

**<sup>13</sup>C-NMR**: not enough material for <sup>13</sup>C-NMR spectroscopy.

*\*Both sidechains of the imides possess a stereogenic center (CHR<sup>1</sup>R<sup>2</sup>R<sup>3</sup>). This provides a set of four stereoisomers (R,R; S,S; R,S; S,R) of the target compound containing two diastereomers (and their enantiomers). In NMR spectroscopy, this results in two sets of signals whereby those of similar frequencies overlap. In the <sup>1</sup>H-NMR spectrum there are two signals observed at 8.53 ppm separated by 0.0032 ppm (1.59 Hz at 500 MHz proton frequency).*

### Br-xy-bpy-xy-Br (**15**)

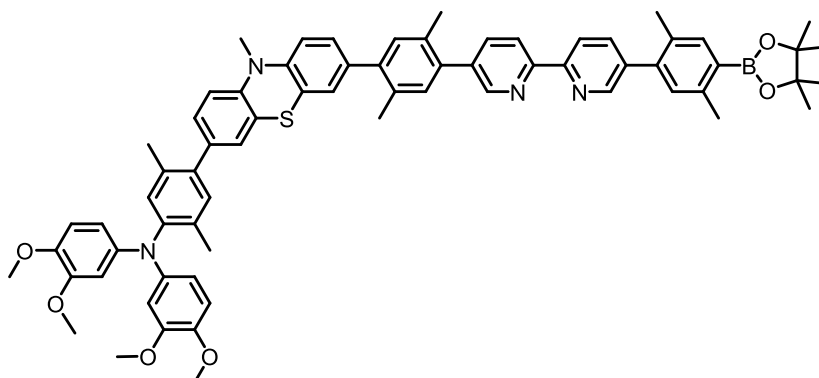


This synthesis is based on a published procedure.<sup>7</sup> TMS-xy-bpy-xy-TMS (630 mg, 1.24 mmol, 1.0 eq.) and KOAc (243 mg, 2.48 mmol, 2.0 eq.) were combined in a dried flask under N<sub>2</sub> and three vacuum/N<sub>2</sub> cycles were performed. Dry THF (15 mL) was added and the flask was covered with aluminum foil. Br<sub>2</sub> (250 μL, 791 mg, 4.95 mmol, 4.0 eq.) was added and the reaction mixture was stirred at room temperature for 2.5 h. Et<sub>3</sub>N (1.7 mL, 1.25 g, 12.4 mmol, 10.0 eq.) was added, followed by a 10% aq. solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (50 mL). The suspension was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3× 50 mL). The combined organic phases were washed with brine (100 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed under reduced pressure. The crude was carefully triturated with cold MeOH in a dry-ice/acetone bath until the MeOH was not colored anymore. The solid was dried under vacuum to yield Br-xy-bpy-xy-Br (450 mg, 862 μmol, 70%) as an off-white powder.

**<sup>1</sup>H-NMR** (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>), δ [ppm]: 8.63 (d, *J* = 2.3 Hz, 2H), 8.52 (d, *J* = 8.1 Hz, 2H), 7.80 (dd, *J* = 8.1, 2.3 Hz, 2H), 7.52 (s, 2H), 7.18 (s, 2H), 2.42 (s, 6H), 2.28 (s, 6H).

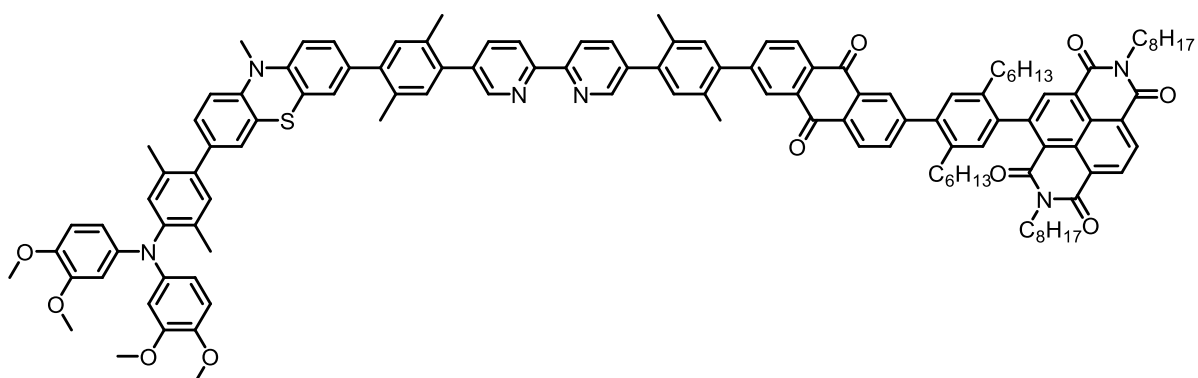


### TAA-xy-PTZ-xy-bpy-xy-Bpin (**17**)



TAA-xy-PTZ-xy-bpy-xy-Br (60 mg, 49  $\mu\text{mol}$ , 1.0 eq.), bis(pinacolato)diboron (29 mg, 114  $\mu\text{mol}$ , 2.3 eq.), KOAc (17 mg, 173  $\mu\text{mol}$ , 3.6 eq.) were combined and three vacuum/ $\text{N}_2$  cycles were performed. Dry DMF (2.0 mL) was added and the suspension was sparged with  $\text{N}_2$  for 10 min.  $\text{Pd}(\text{PPh}_3)_4$  (7 mg, 6  $\mu\text{mol}$ , 12 mol%) was added and sparging was continued for 5 min. The vial was sealed and the reaction mixture was heated to 100  $^\circ\text{C}$  for 16 h. After cooling to room temperature,  $\text{CH}_2\text{Cl}_2$  (20 mL) was added and the mixture was washed with  $\text{H}_2\text{O}$  (4  $\times$  70 mL). The organic phase was dried over  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under reduced pressure. The crude was purified by flash column chromatography ( $\text{SiO}_2$ , EtOAc/c-hex: 0%  $\rightarrow$  30%) to yield TAA-xy-PTZ-xy-bpy-xy-Bpin (46 mg, 42  $\mu\text{mol}$ , 86%) as a yellow solid. The product was isolated in 82% purity (yield is corrected for purity) according to NMR. The impurity is probably a protodeborylated species from this step or the step before and was not separable by column chromatography. Since it will not interfere in the next step, the product was used as obtained for the next reaction without full characterization.

### TAA-xy-PTZ-xy-bpy-xy-AQ-hxy-NDI (**18**)



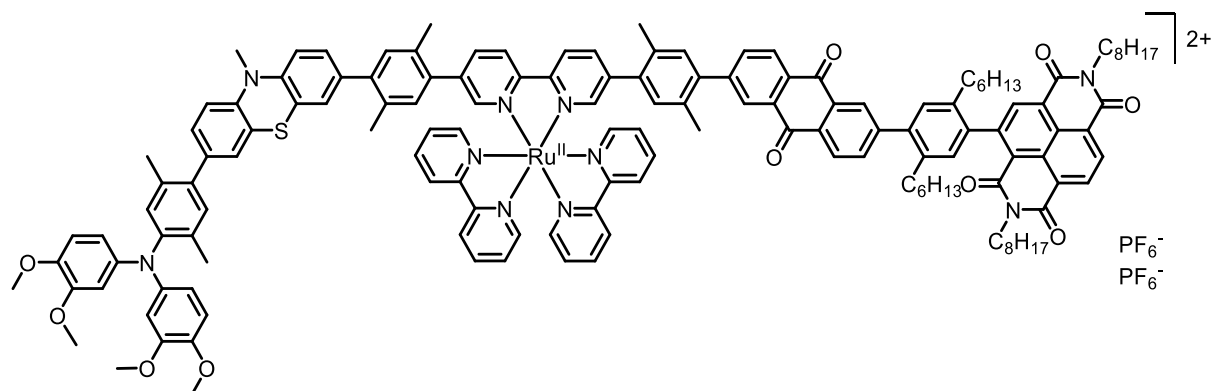
TAA-xy-PTZ-xy-bpy-xy-Bpin (43 mg, 32  $\mu\text{mol}$ , 1.0 eq.), Br-AQ-hxy-NDI (36 mg, 36  $\mu\text{mol}$ , 1.1 eq.) and  $\text{K}_3\text{PO}_4$  (34 mg, 161  $\mu\text{mol}$ , 5 eq.) were combined and three vacuum/ $\text{N}_2$  cycles were performed. THF (2.5 mL) and  $\text{H}_2\text{O}$  (0.5 mL) were added and the suspension was sparged with  $\text{N}_2$  for 10 min.  $\text{Pd}(\text{PPh}_3)_4$

(5 mg, 4  $\mu$ mol, 13 mol%) was added and sparging was continued for 5 min. The vial was sealed and the reaction mixture was heated to 75 °C for 16 h. After cooling to room temperature, H<sub>2</sub>O (20 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL) were added to the reaction mixture and the layers separated. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and the solvent of the combined organic layers was removed under reduced pressure. The crude was purified by flash column chromatography (SiO<sub>2</sub>, EtOAc/c-hex: 0% → 50%). The obtained yellow solid was dissolved in an acetone/CH<sub>2</sub>Cl<sub>2</sub> mixture by dropwise addition of CH<sub>2</sub>Cl<sub>2</sub>. The product was precipitated with MeCN, filtered-off and eluted with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed to yield TAA-xy-PTZ-xy-bpy-xy-AQ-hxy-NDI (22 mg, 12  $\mu$ mol, 36%) as a yellow solid.

**<sup>1</sup>H-NMR** (600 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>),  $\delta$  [ppm]: 8.83 (d,  $J$  = 7.6 Hz, 1H), 8.78 (d,  $J$  = 7.6 Hz, 1H), 8.75 (dd,  $J$  = 2.3, 0.9 Hz, 1H), 8.72 (dd,  $J$  = 2.3, 0.9 Hz, 1H), 8.60 – 8.56 (m, 2H), 8.54 (d,  $J$  = 1.9 Hz, 1H), 8.45 – 8.42 (m, 3H), 8.39 (d,  $J$  = 1.9 Hz, 1H), 7.95 (dd,  $J$  = 7.8, 1.9 Hz, 1H), 7.91 (dd,  $J$  = 8.0, 2.3 Hz, 1H), 7.89 (dd,  $J$  = 7.8, 1.9 Hz, 1H), 7.88 (dd,  $J$  = 8.0, 2.3 Hz, 1H), 7.34 (s, 1H), 7.32 (s, 1H), 7.32 (s, 1H), 7.23 (s, 1H), 7.23 (dd,  $J$  = 8.1, 2.1 Hz, 1H), 7.21 (dd,  $J$  = 8.3, 2.1 Hz, 1H), 7.20 – 7.19 (m, 2H), 7.17 (d,  $J$  = 2.0 Hz, 1H), 7.10 (s, 1H), 7.06 (s, 1H), 6.96 – 6.92 (m, 3H), 6.74 (d,  $J$  = 8.7 Hz, 2H), 6.62 (d,  $J$  = 2.6 Hz, 2H), 6.41 (dd,  $J$  = 8.6, 2.6 Hz, 2H), 4.19 – 4.10 (m, 2H), 4.09 – 4.01 (m, 2H), 3.79 (s, 6H), 3.69 (s, 6H), 3.48 (s, 3H), 2.69 – 2.64 (m, 2H), 2.41 (s, 3H), 2.39 (s, 3H), 2.44 – 2.27 (m, 2H), 2.35 (s, 3H), 2.33 (s, 3H), 2.19 (s, 3H), 2.01 (s, 3H), 1.98 – 1.92 (m, 1H), 1.90 – 1.85 (m, 1H), 1.51 – 1.29 (m, 24H), 1.23 – 1.02 (m, 18H), 0.95 (t,  $J$  = 7.4 Hz, 3H), 0.92 – 0.88 (m, 6H), 0.87 (t,  $J$  = 7.1 Hz, 3H), 0.78 (t,  $J$  = 6.9 Hz, 3H), 0.69 (t,  $J$  = 7.1 Hz, 3H).

**<sup>13</sup>C** chemical shifts of carbon atoms connected to hydrogen. Obtained via an aliased high resolution <sup>1</sup>H-<sup>13</sup>C HSQC NMR spectrum (See Supplementary Figure 58) (151 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>),  $\delta$  [ppm]: 149.7, 149.6, 137.7, 137.7, 135.7, 135.4, 135.2, 133, 132.5, 132.2, 132.2, 132.2, 131.4, 130.7, 130.5, 130.4, 129.3, 128.8, 128.7, 128.3, 128, 128, 127.9, 127.5, 127.5, 120.5, 120.5, 114.3, 114.1, 114, 112.6, 107.3, 56.5, 56.2, 44.8, 44.7, 38.4, 38.1, 35.7, 33.4, 33.1, 31.8, 31.8, 31.7, 31.7, 31, 31, 30.8, 29.7, 29.4, 29, 24.4, 24.3, 23.5, 23.5, 22.9, 22.8, 20.2, 20.1, 20.1, 20.1, 20.1, 18.4, 14.2, 14.2, 14.1, 14.1, 10.8, 10.7.

[TAA-xy-PTZ-xy-Ru(bpy)<sub>3</sub>-xy-AQ-hxy-NDI][PF<sub>6</sub>]<sub>2</sub> (**19**)



TAA-xy-PTZ-xy-bpy-xy-AQ-hxy-NDI (21 mg, 11  $\mu$ mol, 1.0 eq.) and Ru(bpy)<sub>2</sub>Cl<sub>2</sub> (8 mg, 17  $\mu$ mol, 1.4 eq.) were suspended in CHCl<sub>3</sub> (1.0 mL) and EtOH (3.0 mL) and the reaction mixture was sparged with N<sub>2</sub> for 15 min. The vial was sealed and heated in a microwave reactor to 130 °C for 2 h under the exclusion of light. The reaction mixture was cooled to room temperature and was diluted with acetone (10 mL). This solution was directly loaded on the column for purification by flash column chromatography (SiO<sub>2</sub>, acetone  $\rightarrow$  acetone/H<sub>2</sub>O: 10:1  $\rightarrow$  acetone/H<sub>2</sub>O/sat. aq. KNO<sub>3</sub>: 40:4:1). Excess Ru(bpy)<sub>2</sub>Cl<sub>2</sub> (purple) was eluted with acetone and acetone/H<sub>2</sub>O, the target complex only with addition of KNO<sub>3</sub> and can be followed by its dark red color. The acetone was removed under reduced pressure and exclusion of light and the formed precipitate was redissolved by dropwise addition of acetone. A sat. aq. solution of KPF<sub>6</sub> was added and the resulting red precipitate was filtered off and washed with water (20 mL). The solid was dried under vacuum to yield [TAA-xy-PTZ-xy-Ru(bpy)<sub>3</sub>-xy-AQ-hxy-NDI][PF<sub>6</sub>]<sub>2</sub> (16 mg, 6  $\mu$ mol, 53%) as a red powder.

<sup>1</sup>H-NMR (600 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>),  $\delta$  [ppm]: 8.95 (d, *J* = 8.4 Hz, 1H), 8.93 (d, *J* = 8.4 Hz, 1H), 8.83 (d, *J* = 7.6 Hz, 1H), 8.78 (d, *J* = 7.6 Hz, 1H), 8.72 – 8.65 (m, 4H), 8.53 (d, *J* = 1.9 Hz, 1H), 8.43 (d, *J* = 1.8 Hz, 1H), 8.41 (d, *J* = 7.8 Hz, 1H), 8.40 (d, *J* = 7.9 Hz, 1H), 8.28 (d, *J* = 1.9 Hz, 1H), 8.20 (dd, *J* = 8.2, 2.0 Hz, 1H), 8.19 – 8.14 (m, 3H), 8.10 (ddd, *J* = 8.0, 8.0, 1.5 Hz, 1H), 8.08 (ddd, *J* = 8.0, 7.9, 1.5 Hz, 1H), 7.99 (d, *J* = 5.4 Hz, 1H), 7.97 (d, *J* = 5.8 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.84 (d, *J* = 5.1 Hz, 1H), 7.82 (d, *J* = 5.6 Hz, 1H), 7.80 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.72 (d, *J* = 2.0 Hz, 1H), 7.71 (d, *J* = 2.0 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.49 – 7.45 (m, 2H), 7.30 (s, 1H), 7.22 (s, 1H), 7.20 (s, 1H), 7.20 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.15 (d, *J* = 2.0 Hz, 1H), 7.14 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.11 – 7.08 (m, 4H), 7.04 (s, 1H), 6.93 (s, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 2.6 Hz, 2H), 6.41 (dd, *J* = 8.6, 2.6 Hz, 2H), 4.20 – 4.10 (m, 2H), 4.09 – 3.99 (m, 2H), 3.79 (s, 6H), 3.69 (s, 6H), 3.45 (s, 3H), 2.68 – 2.63 (m, 2H), 2.47 – 2.39 (m, 1H), 2.40 – 2.32 (m, 1H), 2.31 (s, 3H), 2.26 (s, 3H), 2.17 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.97 – 1.93 (m, 1H), 1.90 – 1.85 (m, 1H), 1.54 – 1.47 (m, 2H), 1.44 – 1.38 (m, 6H), 1.37 – 1.28 (m, 12H), 1.19 – 1.12 (m, 6H), 1.12 – 1.06 (m, 4H), 1.08 – 0.99 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.91 – 0.88 (m, 6H), 0.86 (t, *J* = 7.1 Hz, 3H), 0.77 (t, *J* = 6.9 Hz, 3H), 0.68 (t, *J* = 7.0 Hz, 3H).

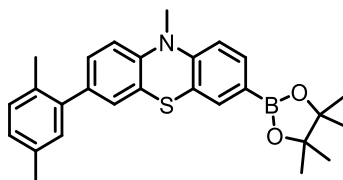
**<sup>13</sup>C** chemical shifts of carbon atoms connected to hydrogen. Obtained via an aliased high resolution <sup>1</sup>H-<sup>13</sup>C HSQC NMR spectrum (See Supplementary Figure 67) (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>), δ [ppm]: 151.7, 151.6, 151.6, 151.6, 150.7, 139, 139, 138.6, 138.4, 135.5, 135.4, 134.8, 132.9, 132.6, 132.6, 132.3, 132, 131.3, 130.6, 130.3, 130.3, 129.1, 128.7, 128.4, 128.4, 128.2, 128.2, 127.9, 127.7, 127.5, 127.4, 127.3, 125, 124.9, 124.8, 114.1, 114, 113.9, 112.5, 107.2, 56.3, 56, 44.6, 44.6, 38.2, 37.9, 35.5, 33.2, 32.9, 31.7, 31.6, 31.5, 30.9, 30.9, 30.6, 29.2, 28.9, 28.8, 24.2, 24.1, 23.3, 23.3, 22.6, 22.6, 20.1, 19.9, 19.8, 19.8, 19.8, 18.2, 14, 14, 14, 13.9, 10.6, 10.6.

**<sup>19</sup>F-NMR** (471 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>), δ [ppm]: -72.9 (d, *J* = 711 Hz).

**<sup>31</sup>P-NMR** (202 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>), δ [ppm]: -144.5 (hept, *J* = 711 Hz).

**HR-MS** (ESI): *m/z* = calculated for [M-2 PF<sub>6</sub>]<sup>2+</sup>: 1159.9937; measured: [M-2 PF<sub>6</sub>]<sup>2+</sup>: 1159.9917.

### xy-PTZ-Bpin (**21**)



3,7-Dibromo-10-methyl-10*H*-phenothiazine (338 mg, 911 μmol, 1.0 eq.), 2,5-dimethylphenylboronic acid (205 mg, 1.37 mmol, 1.5 eq.) and Na<sub>2</sub>CO<sub>3</sub> (290 mg, 2.73 μmol, 3.0 eq.) were combined and three vacuum/N<sub>2</sub> cycles were performed. THF (4.0 mL) and H<sub>2</sub>O (0.4 mL) were added and the suspension was sparged with N<sub>2</sub> for 5 min. Pd(PPh<sub>3</sub>)<sub>4</sub> (53 mg, 46 μmol, 5 mol%) was added and sparging was continued for 5 min. The vial was sealed and the reaction mixture was heated to 75 °C for 16 h. After cooling to room temperature, the reaction mixture was filtered through a short plug of SiO<sub>2</sub>.

Separation of Br-PTZ-Br, xy-PTZ-Br and xy-PTZ-xy (ratio of 0.15/0.60/0.25) was only successful by preparative TLC (SiO<sub>2</sub>, EtOAc/*c*-hex 5%) but not by column chromatography. The crude was used as obtained for the subsequent borylation after which separation was possible.

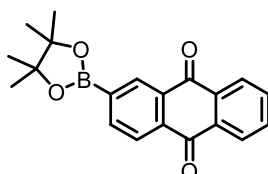
Bis(pinacolato)diboron (384 mg, 1.51 mmol, 1.7 eq.), KOAc (223 mg, 2.27 μmol, 2.5 eq.) were added to the crude mixture and three vacuum/N<sub>2</sub> cycles were performed. Dry 1,4-dioxane (5.0 mL) was added and the suspension was sparged with N<sub>2</sub> for 5 min. Pd(dppf)Cl<sub>2</sub> (31 mg, 38 μmol, 5 mol%) was added and sparging was continued for 5 min. The vial was sealed and the reaction mixture was heated to 80 °C for 16 h. After cooling to room temperature, the reaction mixture was filtered through a short plug of SiO<sub>2</sub> and the solvent was removed under reduced pressure. The crude was purified by flash column chromatography (SiO<sub>2</sub>, EtOAc/*c*-hex: 10%) to yield xy-PTZ-Bpin (120 mg, 271 μmol, 30% over two steps) as a yellow sticky oil.

**<sup>1</sup>H-NMR** (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>), δ [ppm]: 7.57 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.50 (d, *J* = 1.5 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.12 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.08 (d, *J* = 2.0 Hz, 1H), 7.04 (dd, *J* = 7.7, 1.9

Hz, 1H), 7.00 (d,  $J = 1.9$  Hz, 1H), 6.87 (d,  $J = 8.3$  Hz, 1H), 6.84 (d,  $J = 8.1$  Hz, 1H), 3.41 (s, 3H), 2.31 (s, 3H), 2.21 (s, 3H), 1.31 (s, 12H).

**$^{13}\text{C}\{^1\text{H}\}$ -NMR** (126 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ),  $\delta$  [ppm]: 148.7, 144.4, 140.9, 137.1, 135.7, 134.8, 133.7, 132.5, 130.7, 130.6, 128.6, 128.3, 128.0, 123.3, 122.6, 114.2, 113.9, 84.1, 35.7, 25.1, 21.0, 20.1.

### AQ-Bpin (**22**)

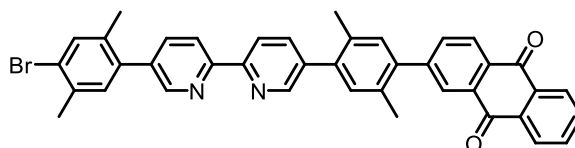


This synthesis is based on a published procedure.<sup>8</sup> 2-Bromoanthraquinone (1.02 g, 3.55 mmol, 1.0 eq.), bis(pinacolato)diboron (1.17 g, 4.62 mmol, 1.3 eq.), KOAc (1.05 g, 10.7 mmol, 3.0 eq.) were combined and three vacuum/ $\text{N}_2$  cycles were performed. Dry 1,4-dioxane (25 mL) was added and the suspension was sparged with  $\text{N}_2$  for 20 min.  $\text{Pd}(\text{dppf})\text{Cl}_2$  (130 mg, 178  $\mu\text{mol}$ , 5 mol%) was added and sparging was continued for 10 min. The reaction mixture was heated to 80  $^\circ\text{C}$  for 6 h. After cooling to room temperature, the reaction mixture was filtered through a short plug of  $\text{SiO}_2$ , eluted with EtOAc and the solvent was removed under reduced pressure. The crude material was redissolved in EtOAc (50 mL) and washed with  $\text{H}_2\text{O}$  (50 mL). The organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under reduced pressure. The obtained solid was triturated with little cold Et $_2\text{O}$  and dried under vacuum to yield Bpin-AQ (1.00 g, 2.99 mmol, 84%) as an off-white powder.

**$^1\text{H}$ -NMR** (500 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ),  $\delta$  [ppm]: 8.66 (s, 1H), 8.32 – 8.28 (m, 2H), 8.27 (d,  $J = 7.6$  Hz, 1H), 8.18 (dd,  $J = 7.6, 1.3$  Hz, 1H), 7.85 – 7.81 (m, 2H), 1.38 (s, 12H).

**$^{13}\text{C}\{^1\text{H}\}$ -NMR** (126 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ),  $\delta$  [ppm]: 183.2, 183.0, 139.9, 135.1, 134.2, 134.1, 133.6, 133.6, 133.4, 132.5, 127.0, 127.0, 126.0, 84.6, 24.7.

### Br-xy-bpy-xy-AQ (**23**)



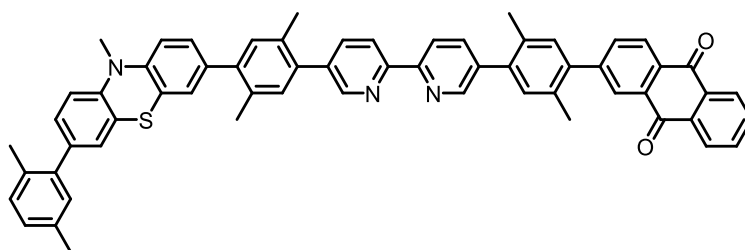
Br-xy-bpy-xy-Br (200 mg, 383  $\mu\text{mol}$ , 1.0 eq.), Bpin-AQ (166 mg, 497  $\mu\text{mol}$ , 1.3 eq) and  $\text{Na}_2\text{CO}_3$  (121 mg, 1.15 mmol, 3.0 eq.) were combined and three vacuum/ $\text{N}_2$  cycles were performed. THF (6.0 mL) and  $\text{H}_2\text{O}$  (0.6 mL) were added and the suspension was sparged with  $\text{N}_2$  for 5 min.  $\text{Pd}(\text{PPh}_3)_4$

(44 mg, 38  $\mu$ mol, 10 mol%) was added and sparging was continued for 5 min. The vial was sealed and the reaction mixture was heated to 80 °C for 22 h. After cooling to room temperature, H<sub>2</sub>O (30 mL) and CH<sub>2</sub>Cl<sub>2</sub> (30 mL) were added and the layers were separated. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 $\times$  30 mL) and the combined organic layers were washed with brine (100 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure. The crude was purified by flash column chromatography (SiO<sub>2</sub>, EtOAc/c-hex: 30%) to yield Br-xy-bpy-xy-AQ (117 mg, 180  $\mu$ mol, 47%) as a yellow solid.

**<sup>1</sup>H-NMR** (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  [ppm]: 8.73 (dd, *J* = 2.3, 0.9 Hz, 1H), 8.65 (dd, *J* = 2.3, 0.9 Hz, 1H), 8.56 (dd, *J* = 8.1, 0.9 Hz, 1H), 8.55 (dd, *J* = 8.1, 0.9 Hz, 1H), 8.38 (d, *J* = 8.0 Hz, 1H), 8.35 – 8.31 (m, 2H), 7.89 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.87 – 7.84 (m, 2H), 7.81 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.53 (s, 1H), 7.30 (s, 1H), 7.30 (s, 1H), 7.20 (s, 1H), 2.43 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 2.29 (s, 3H).

**<sup>13</sup>C{<sup>1</sup>H}-NMR**: not soluble enough in all tested solvents.

#### xy-PTZ-xy-bpy-xy-AQ (24)

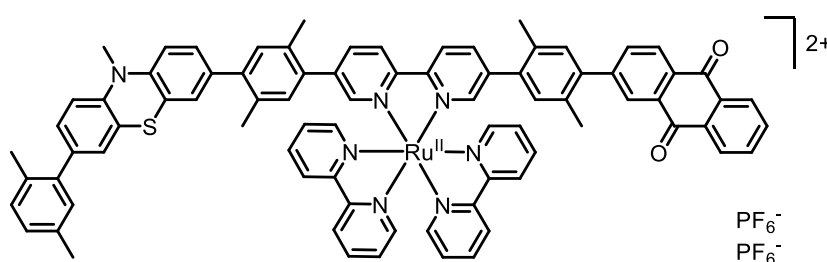


xy-PTZ-Bpin (157 mg, 354  $\mu$ mol, 2.0 eq) was dissolved in THF (6.0 mL) and combined with Br-xy-bpy-xy-AQ (116 mg, 179  $\mu$ mol, 1.0 eq.) and Na<sub>2</sub>CO<sub>3</sub> (57 mg, 537  $\mu$ mol, 3.0 eq.). H<sub>2</sub>O (0.6 mL) was added and the suspension was sparged with N<sub>2</sub> for 5 min. Pd(PPh<sub>3</sub>)<sub>4</sub> (31 mg, 27  $\mu$ mol, 15 mol%) was added and sparging was continued for 5 min. The vial was sealed and the reaction mixture was heated to 80 °C for 24 h. After cooling to room temperature, H<sub>2</sub>O (20 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL) were added and the layers were separated. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 $\times$  30 mL) and the combined organic layers were washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure. The crude was suspended in MeOH, the solid filtered off on a plug of celite and washed with ample MeOH. The product was eluted with CH<sub>2</sub>Cl<sub>2</sub> and the solvent removed under reduced pressure to yield xy-PTZ-xy-bpy-xy-AQ (122 mg, 138  $\mu$ mol, 77%) as a yellow powder.

**<sup>1</sup>H-NMR** (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>),  $\delta$  [ppm]: 8.74 (dd, *J* = 2.3, 0.9 Hz, 1H), 8.72 (dd, *J* = 2.3, 0.9 Hz, 1H), 8.59 – 8.55 (m, 2H), 8.38 (d, *J* = 8.0 Hz, 1H), 8.37 – 8.31 (m, 3H), 7.90 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.89 – 7.84 (m, 4H), 7.30 (s, 2H), 7.23 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.23 (s, 1H), 7.20 – 7.18 (m, 2H), 7.16 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 7.13 (d, *J* = 2.0 Hz, 1H), 7.05 (dd, *J* = 7.7, 2.0 Hz, 1H), 7.02 (s, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 3.47 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H), 2.35 (s, 3H), 2.33 (s, 3H), 2.32 (s, 3H), 2.23 (s, 3H).

**$^{13}\text{C}\{^1\text{H}\}$ -NMR** (126 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ),  $\delta$  [ppm]: 183.5, 183.2, 155.0, 154.7, 149.8, 149.7, 148.1, 145.1, 144.9, 141.0, 141.0, 140.1, 138.6, 137.9, 137.8, 137.7, 137.3, 137.3, 137.0, 136.2, 135.7, 135.3, 134.6, 134.5, 134.1, 134.1, 133.9, 133.9, 133.5, 133.5, 133.4, 132.6, 132.6, 132.5, 132.4, 132.3, 132.2, 130.7, 130.6, 128.8, 128.8, 128.3, 128.1, 128.1, 128.0, 127.6, 127.5, 127.5, 123.4, 123.1, 120.6, 120.6, 114.2, 114.1, 35.7, 21.0, 20.2, 20.2, 20.1, 20.1, 20.1.

**[xy-PTZ-xy-Ru(bpy)<sub>3</sub>-xy-AQ][PF<sub>6</sub>]<sub>2</sub> (**25**)**



xy-PTZ-xy-bpy-xy-AQ (33 mg, 37  $\mu\text{mol}$ , 1.0 eq.) and  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  (20 mg, 41  $\mu\text{mol}$ , 1.1 eq.) were suspended in  $\text{CHCl}_3$  (1.0 mL) and EtOH (3.0 mL) and the reaction mixture was sparged with  $\text{N}_2$  for 15 min. The vial was sealed and heated in a microwave reactor to 130  $^\circ\text{C}$  for 2 h under the exclusion of light. The reaction mixture was cooled to room temperature and the solvents were removed under exclusion of light. The crude was purified by flash column chromatography ( $\text{SiO}_2$ , acetone/ $\text{H}_2\text{O}$ : 10:1  $\rightarrow$  acetone/ $\text{H}_2\text{O}$ /sat. aq.  $\text{KNO}_3$ : 40:4:1). Excess  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  (purple) was eluted with acetone/ $\text{H}_2\text{O}$ , the target complex only with addition of  $\text{KNO}_3$  and was followed by its dark red color. Most of the acetone was removed under reduced pressure and exclusion of light. A sat. aq. solution of  $\text{NH}_4\text{PF}_6$  was added and the resulting red precipitate was filtered off and washed with water (50 mL). The solid was dried under vacuum to yield [xy-PTZ-xy-Ru(bpy)<sub>3</sub>-xy-AQ][PF<sub>6</sub>]<sub>2</sub> (57 mg, 36  $\mu\text{mol}$ , 97%) as a red powder.

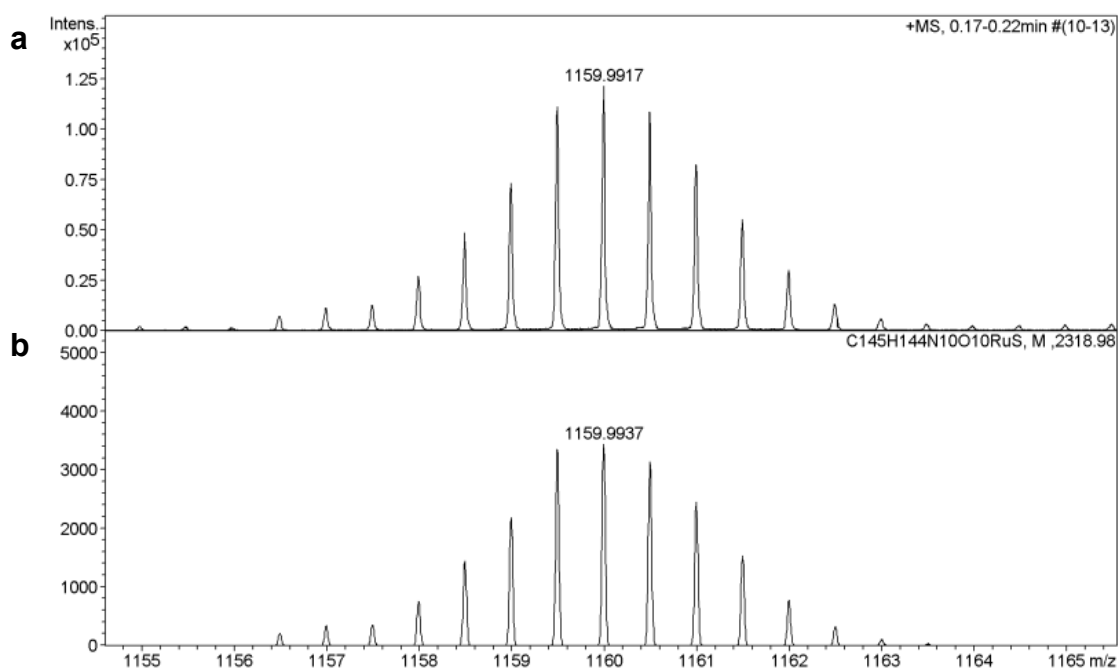
**$^1\text{H}$ -NMR** (400 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ,  $\text{K}_2\text{CO}_3$ ),  $\delta$  [ppm]: 8.64 – 8.58 (m, 2H), 8.51 – 8.42 (m, 4H), 8.35 (d,  $J$  = 8.0 Hz, 1H), 8.34 – 8.29 (m, 2H), 8.22 (d,  $J$  = 1.8 Hz, 1H), 8.15 (qd,  $J$  = 5.0, 2.1 Hz, 4H), 8.09 – 8.03 (m, 2H), 7.94 – 7.89 (m, 2H), 7.86 – 7.84 (m, 2H), 7.80 – 7.74 (m, 3H), 7.71 – 7.68 (m, 2H), 7.62 – 7.56 (m, 2H), 7.49 – 7.44 (m, 2H), 7.19 (s, 1H), 7.17 – 7.07 (m, 8H), 7.05 (dd,  $J$  = 7.8, 1.9 Hz, 1H), 7.00 (d,  $J$  = 2.0 Hz, 1H), 6.94 – 6.89 (m, 2H), 3.45 (s, 3H), 2.32 (s, 3H), 2.28 (s, 3H), 2.25 (s, 3H), 2.22 (s, 3H), 1.99 (s, 3H), 1.96 (s, 3H).

**$^{19}\text{F}$ -NMR** (376 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ),  $\delta$  [ppm]: -72.8 (d,  $J$  = 711 Hz).

**HR-MS** (ESI):  $m/z$  = calculated for  $[\text{M}-2\text{PF}_6]^{2+}$ : 649.6909; measured:  $[\text{M}-2\text{PF}_6]^{2+}$ : 649.6898.

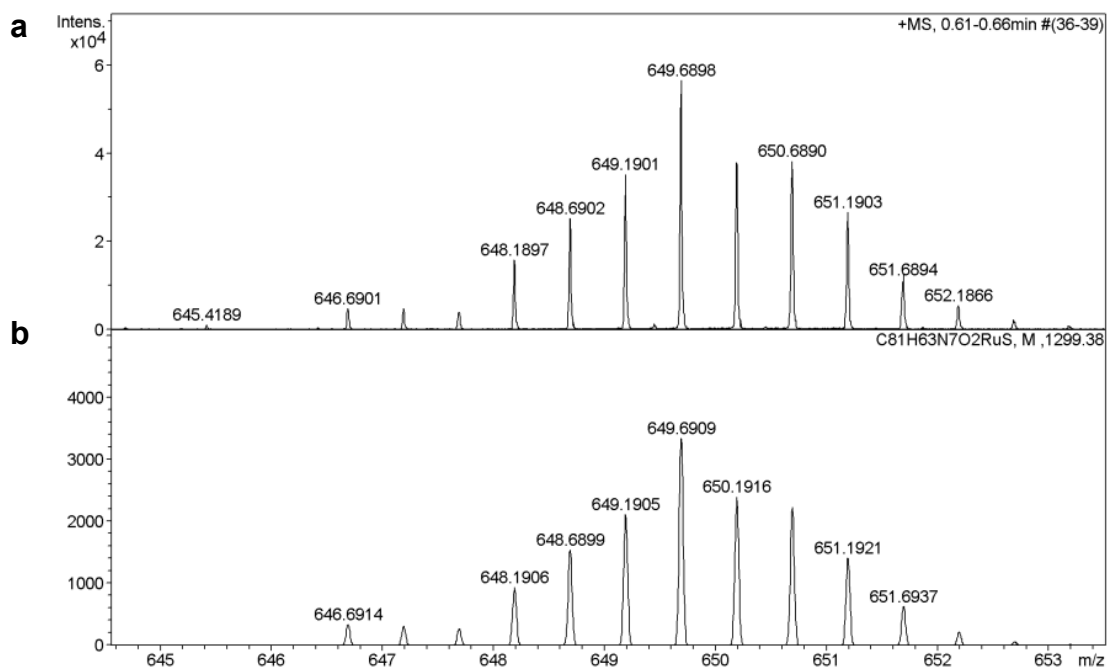
## 4. HR-ESI Mass Spectra

### Pentad (19)



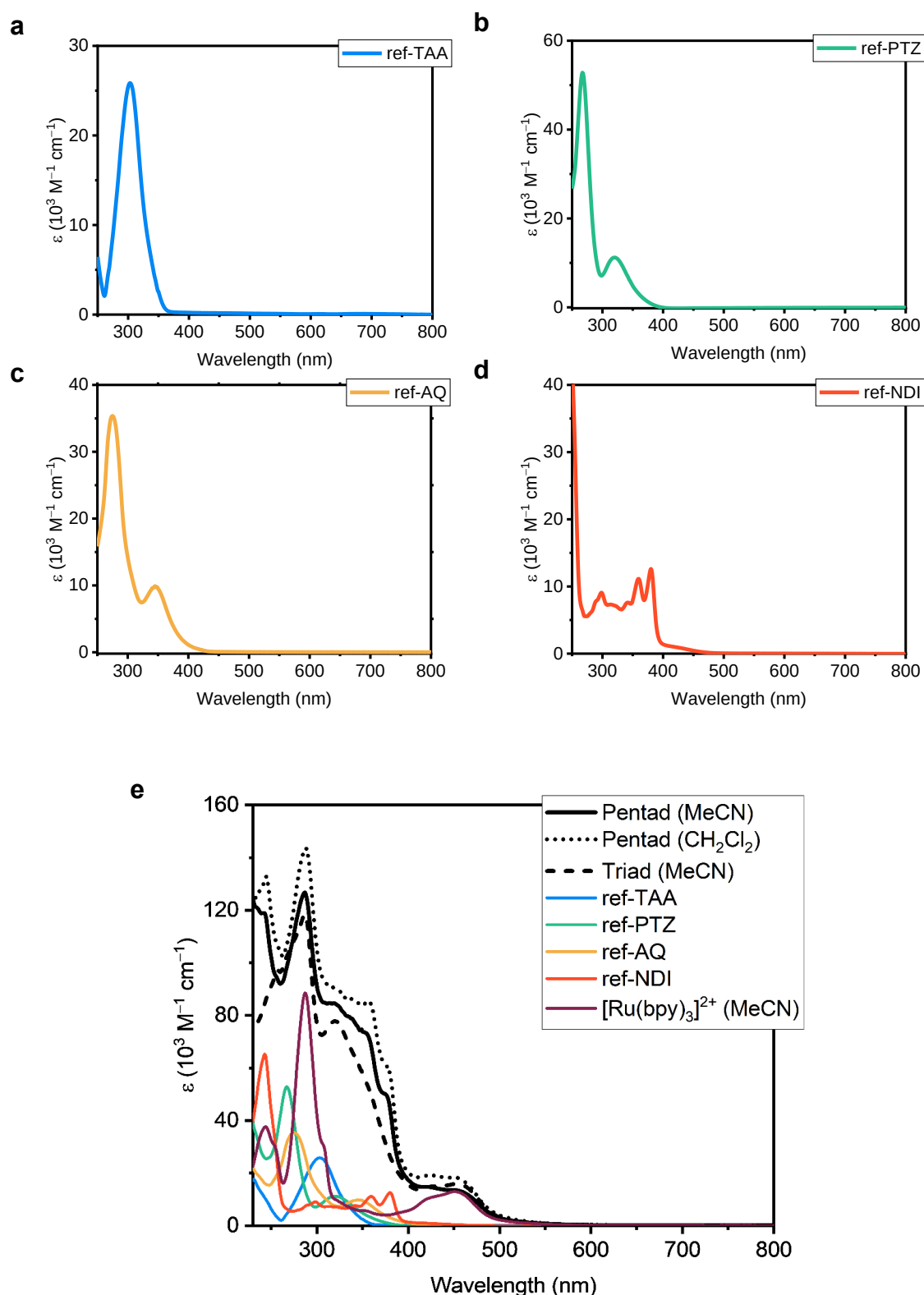
**Supplementary Figure 5. a**, HRMS-ESI (positive ions) mass spectrum of the pentad (19). **b**, Simulated mass spectrum of the pentad (19).

### Triad (25)



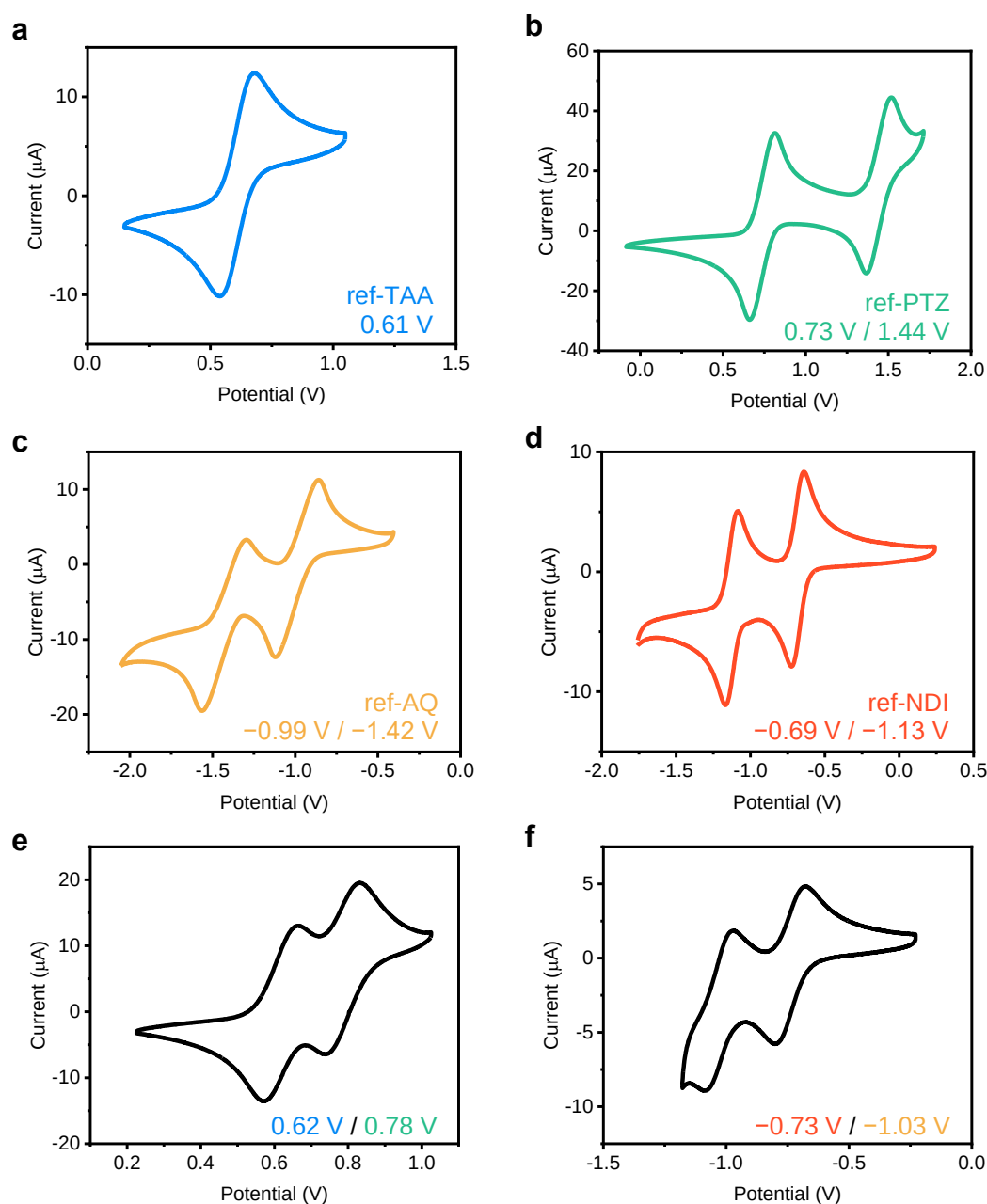
**Supplementary Figure 6. a**, HRMS-ESI (positive ions) mass spectrum of the triad (25). **b**, Simulated mass spectrum of the triad (25).

## 5. UV-vis Absorption Spectroscopy



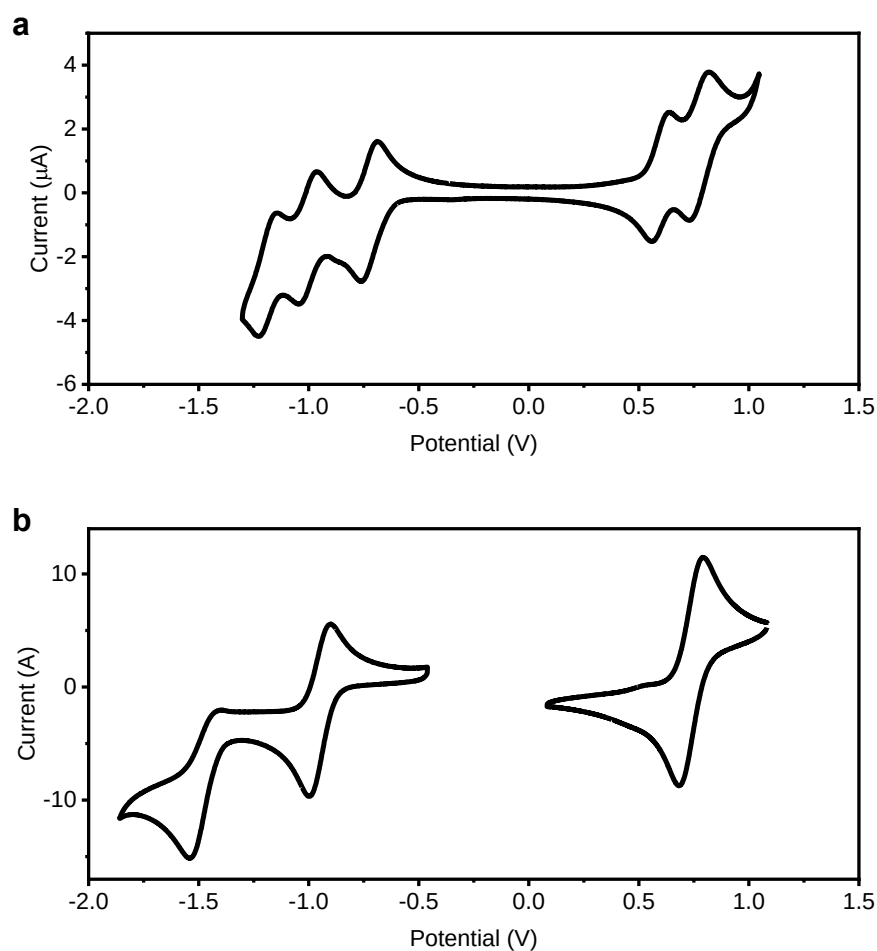
**Supplementary Figure 7.** UV-vis absorption spectra of **a**, ref-TAA (**5**), **b**, ref-PTZ (**2**), **c**, ref-AQ (**13**), **d**, ref-NDI (**12**) in  $\text{CH}_2\text{Cl}_2$  at 20 °C. **e**, UV-vis absorption spectra of the pentad (**19**) in  $\text{CH}_2\text{Cl}_2$  (solid black line) and MeCN (dotted black line) and the triad (**25**) in MeCN (dashed black line) at 20 °C. The spectra from a-d and [Ru(bpy)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> in MeCN (purple) are included for direct comparison.

## 6. Electrochemistry



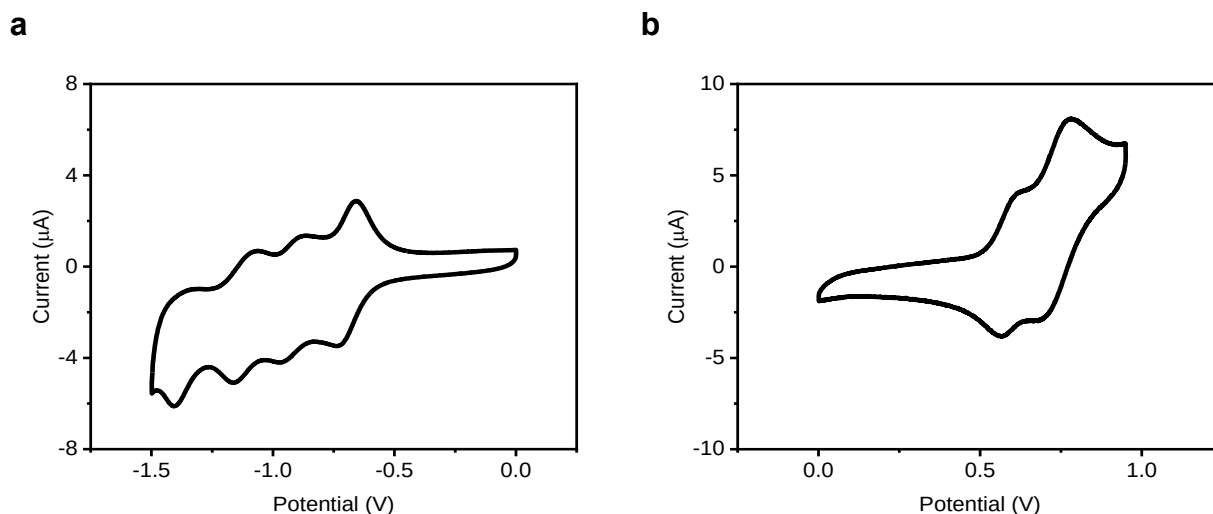
**Supplementary Figure 8.** Cyclic voltammograms of **a**, 1.0 mM ref-TAA (5), **b**, 1.0 mM ref-PTZ (2), **c**, 1.0 mM ref-AQ (13), **d**, 1.0 mM ref-NDI (12), **e**, 1.0 mM TAA-xy-PTZ-xy (8), and **f**, 1.0 mM xy-AQ-hxy-NDI (14) in Ar-saturated  $\text{CH}_2\text{Cl}_2$  solutions at room temperature, referenced against a saturated calomel electrode (SCE). A glassy carbon disk was used as working electrode and a silver wire served as the counter electrode. The scan rates were  $100 \text{ mV s}^{-1}$  and tetrabutylammonium hexafluorophosphate (100 mM) was used as the supporting electrolyte.

## Ligands



**Supplementary Figure 9.** Cyclic voltammograms of **a**, 1.0 mM pentad main ligand (**18**) and **b**, 1.0 mM ligand of the triad (**24**) in Ar-saturated  $\text{CH}_2\text{Cl}_2$  solutions at room temperature, referenced against a saturated calomel electrode (SCE). A glassy carbon disk was used as working electrode and a silver wire served as the counter electrode. The scan rate was  $10 \text{ mV s}^{-1}$  (a) and  $100 \text{ mV s}^{-1}$  (b) and tetrabutylammonium hexafluorophosphate (100 mM) was used as the supporting electrolyte.

## Pentad



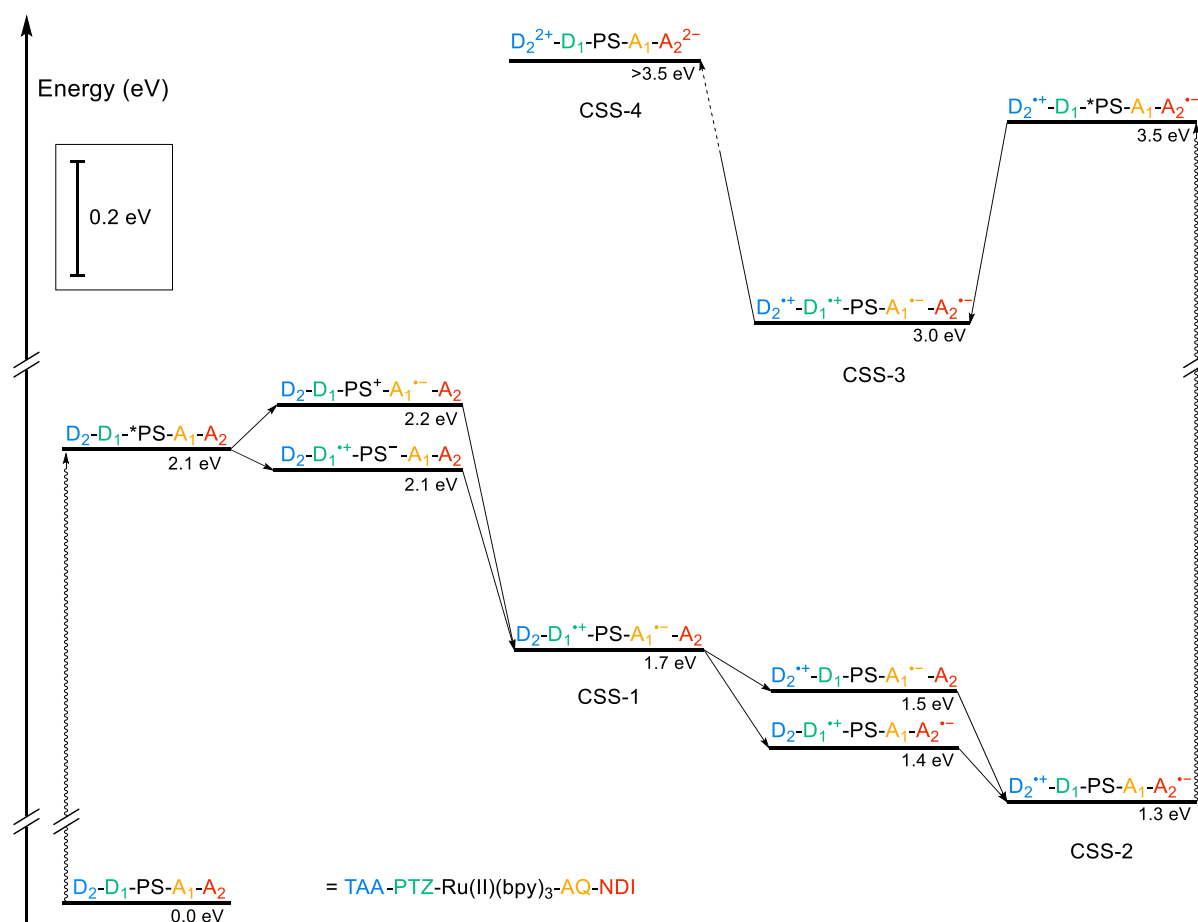
**Supplementary Figure 10.** Cyclic voltammograms of a 0.5 mM solution of the pentad (**19**) in Ar-saturated  $\text{CH}_2\text{Cl}_2$  (**a**) and a 1.0 mM solution of the pentad (**19**) in Ar-saturated MeCN (**b**) at room temperature, referenced against a saturated calomel electrode (SCE). A glassy carbon disk was used as working electrode and a silver wire served as the counter electrode. The scan rate was  $100 \text{ mV s}^{-1}$  and tetrabutylammonium hexafluorophosphate (100 mM) was used as the supporting electrolyte.

All cyclic voltammetry measurements were carried out in dichloromethane for reasons of comparison as some of the organic reference molecules are not sufficiently soluble in acetonitrile. In contrast to the CV measurement of the pentad main ligand (Supplementary Figure 9a), we did not succeed in measuring a well-resolved current signal for the oxidation of  $\text{D}_1$  and  $\text{D}_2$  in the pentad in dichloromethane in several attempts. We therefore changed the solvent to acetonitrile for the oxidation of  $\text{D}_1$  and  $\text{D}_2$  in the pentad (Supplementary Figure 10b and Supplementary Table 1).

**Supplementary Table 1.** Summary of the redox potentials of the individual units measured at 1.0 mM in dry, Ar-saturated  $\text{CH}_2\text{Cl}_2$  containing 100 mM  $\text{NBu}_4\text{PF}_6$ . Potentials are given against SCE.

|                                    | References<br>(S. Fig. 8 a-d) | Dyads<br>(S. Fig. 8 e-f) | Ligand (18)<br>(S. Fig. 9 a) | Pentad (19)<br>(S. Fig. 10) |
|------------------------------------|-------------------------------|--------------------------|------------------------------|-----------------------------|
| $\text{TAA}^{+/0}$                 | 0.61 V                        | 0.62 V                   | 0.60 V                       | 0.60 V <sup>a</sup>         |
| $\text{PTZ}^{+/0}$                 | 0.73 V                        | 0.79 V                   | 0.78 V                       | 0.73 V <sup>a</sup>         |
| $\text{AQ}^{0/-}$                  | -0.99 V                       | -1.03 V                  | -1.00 V                      | -0.92 V                     |
| $\text{NDI}^{0/-}$                 | -0.69 V                       | -0.71 V                  | -0.72 V                      | -0.69 V                     |
| $[\text{Ru}(\text{bpy})_3]^{2+/+}$ | -1.30 V <sup>9</sup>          |                          |                              | -1.35 V                     |

<sup>a</sup> measured in MeCN



**Supplementary Figure 11.** Energy-level diagram based on the redox potentials from Supplementary Table 1 and literature values for  $[\text{Ru}(\text{bpy})_3]^{2+}$ .<sup>9</sup> The energies of the individual states are presented proportionally on a two-fold segmented energy axis. Energies are rounded to one decimal place.

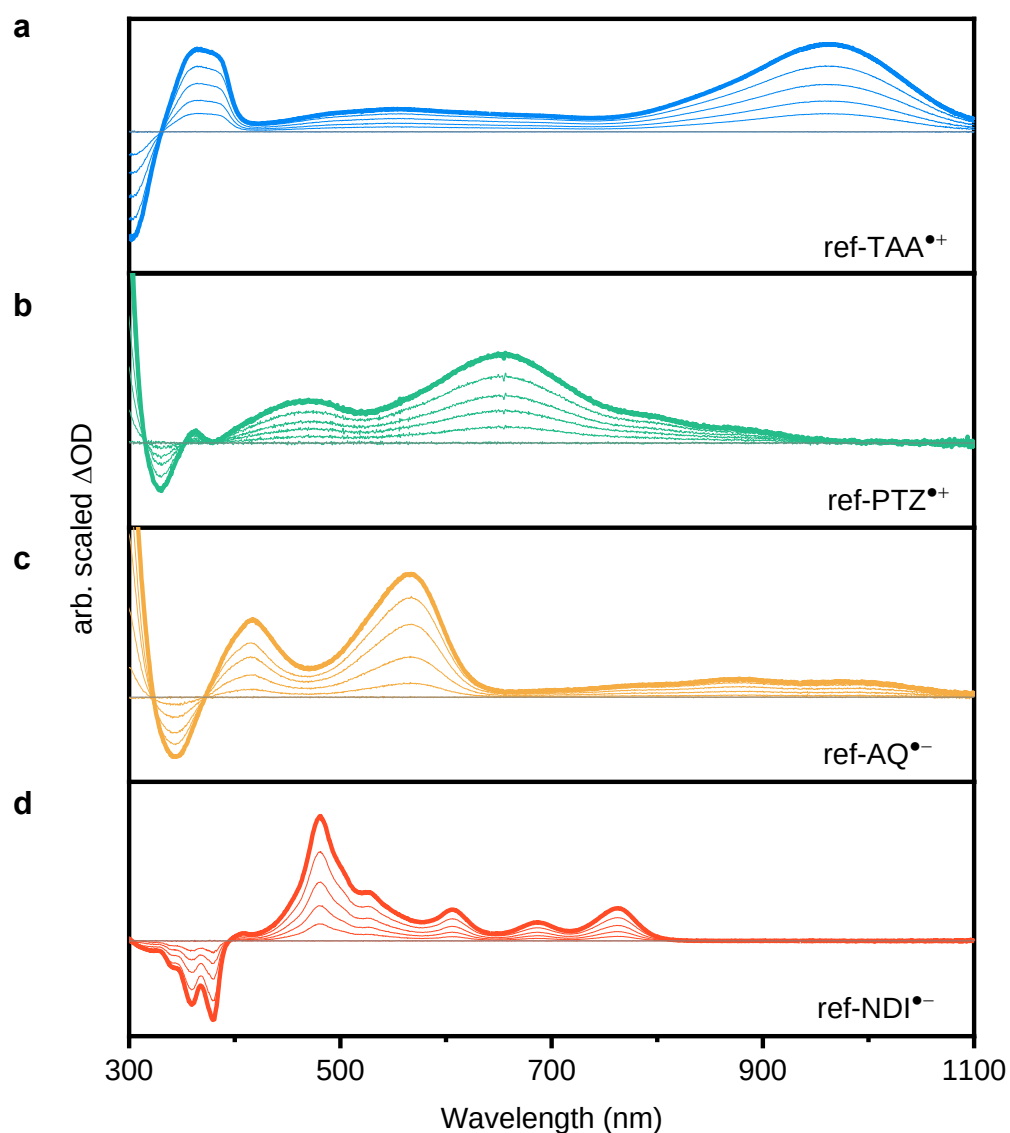
$[\text{Ru}(\text{bpy})_3]^{2+}$  is oxidized at 1.29 V vs SCE and reduced at  $-1.33$  V vs SCE in MeCN. The photoactive  $^3\text{MLCT}$  excited state lies 2.12 eV above the electronic ground state, making the  $^3\text{MLCT}$ -excited  $[\text{Ru}(\text{bpy})_3]^{2+}$  both a strong reductant ( $E([\text{Ru}(\text{bpy})_3]^{3+}/[\text{Ru}(\text{bpy})_3]^{2+}) = -0.81$  V vs SCE) and a strong oxidant ( $E^*([\text{Ru}(\text{bpy})_3]^{2+}/[\text{Ru}(\text{bpy})_3]^{+}) = 0.77$  V vs SCE).<sup>9</sup> These properties of  $[\text{Ru}(\text{bpy})_3]^{2+}$  along with the redox potentials from Supplementary Table 1 allow to sketch the expected photoinduced electron transfer (ET) processes in the pentad (Supplementary Figure 11).  $^3\text{MLCT}$ -excited  $[\text{Ru}(\text{bpy})_3]^{2+}$  is able to oxidize PTZ ( $\Delta G_{\text{ET}}^0 = -0.04$  eV) forming  $\text{PTZ}^{•+}$  and  $[\text{Ru}(\text{bpy})_3]^+$ . This one-electron reduced species is able to reduce AQ, generating the charge-separated state CSS-1 with a hole on  $\text{PTZ}^{•+}$  and an electron on  $\text{AQ}^{•-}$ , and  $[\text{Ru}(\text{bpy})_3]^{2+}$  in its electronic ground state. Oxidative quenching of  $^3\text{MLCT}$ -excited  $[\text{Ru}(\text{bpy})_3]^{2+}$  forming  $\text{AQ}^{•-}$  and  $[\text{Ru}(\text{bpy})_3]^{3+}$  is less likely as it is slightly endergonic ( $\Delta G_{\text{ET}}^0 = +0.1$  eV). If this electron transfer step occurs nonetheless, the subsequent oxidation of PTZ by  $[\text{Ru}(\text{bpy})_3]^{3+}$  is exergonic ( $\Delta G_{\text{ET}}^0 = -0.5$  eV) and yields  $\text{PTZ}^{•+}$  and  $[\text{Ru}(\text{bpy})_3]^{2+}$ . Both pathways (reductive and oxidative quenching of  $^3\text{MLCT}$ -excited  $[\text{Ru}(\text{bpy})_3]^{2+}$ ) provide the same intermediate CSS-1 that stores ca. 1.7 eV.

TAA is easier to oxidize than PTZ ( $\Delta G_{\text{ET}}^0 = -0.2$  eV) and the electron transfer from TAA to  $\text{PTZ}^{•+}$  will therefore occur spontaneously. Similarly, on the acceptor arm,  $\text{AQ}^{•-}$  can reduce NDI ( $\Delta G_{\text{ET}}^0 = -0.3$  eV).

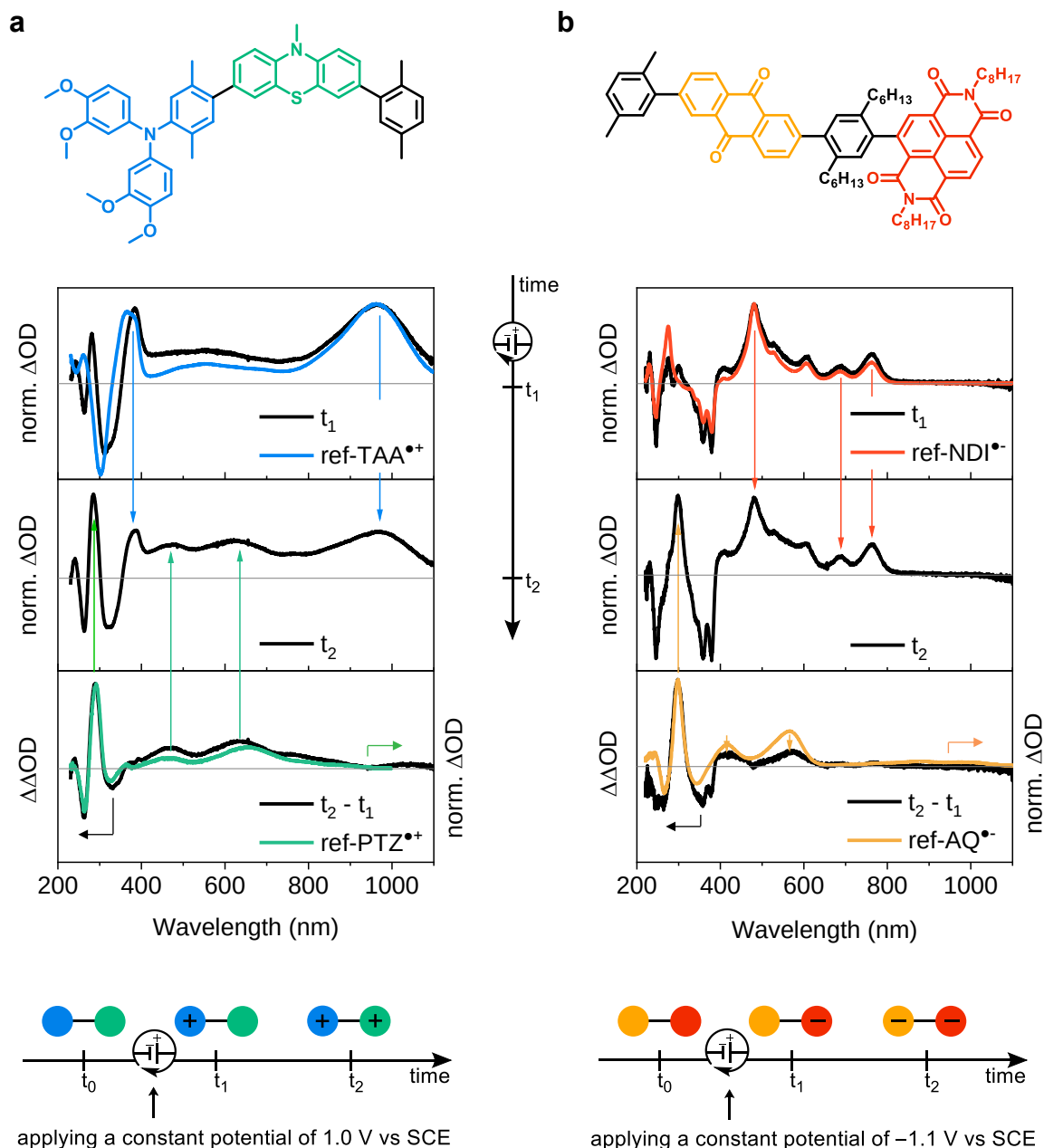
Those two secondary electron transfers are independent of each other and result in the charge-separated state (CSS-2) with a hole stored on the terminal electron donor ( $\text{TAA}^{\bullet+}$ ) and an electron stored on the terminal electron acceptor ( $\text{NDI}^{\bullet-}$ ). This CSS-2 stores an energy of 1.3 eV. Importantly, PTZ and AQ are back in their charge-neutral forms and  $[\text{Ru}(\text{bpy})_3]^{2+}$  is in the electronic ground-state offering the possibility of a re-excitation. Upon excitation of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  photosensitizer unit while the pentad is in its CSS-2, the first two electron transfers are repeated and result again in  $\text{PTZ}^{\bullet+}$ ,  $\text{AQ}^{\bullet-}$ , and  $[\text{Ru}(\text{bpy})_3]^{2+}$  in its ground state. The resulting photoproduct is the CSS-3 and stores ca. 3.0 eV. In this case, however, the electron transfers from  $\text{TAA}^{\bullet+}$  to  $\text{PTZ}^{\bullet+}$  or from  $\text{AQ}^{\bullet-}$  to  $\text{NDI}^{\bullet-}$  are endergonic ( $\Delta G_{\text{ET}}^0 > 0.2$  eV) and the equilibrium will strongly favor  $\text{PTZ}^{\bullet+}$  and  $\text{AQ}^{\bullet-}$  over the formation of  $\text{TAA}^{2+}$  and  $\text{NDI}^{2-}$ . This (hypothetical) CSS-4 thus will not be populated.

In the CSS-2, the positive charge on  $\text{D}_2$  slightly influences the redox properties of  $\text{D}_1$  and makes it more difficult to oxidize by ca. 50 mV (see Supplementary Table 1 for comparison of the PTZ oxidation potentials in ref-PTZ and in the ligand, where  $\text{TAA}^{\bullet+}$  is present). This additional energy penalty corresponds roughly to the driving force for the first photoinduced electron transfer step (the reductive quenching of the  $^3\text{MLCT}$  excited state by PTZ), making this essentially a thermoneutral reaction ( $\Delta G_{\text{ET}}^0 = 0$  eV) when the PS is excited while the pentad is in CSS-2.

## 7. Spectroelectrochemistry



**Supplementary Figure 12.** Normalized difference spectra during electrochemical oxidation of **a**, 250  $\mu\text{M}$  ref-TAA (**5**) by applying 0.8 V vs. SCE and **b**, 250  $\mu\text{M}$  ref-PTZ (**2**) by applying 1.0 V vs. SCE in  $\text{N}_2$ -saturated  $\text{CH}_2\text{Cl}_2$ . Normalized difference spectra during electrochemical reduction of **c**, 250  $\mu\text{M}$  ref-AQ (**13**) by applying -1.0 V vs. SCE and **d**, 250  $\mu\text{M}$  ref-NDI (**12**) by applying -0.7 V vs. SCE in  $\text{N}_2$ -saturated  $\text{CH}_2\text{Cl}_2$ . For all solutions,  $\text{TBAPF}_6$  (100 mM) was used as supporting electrolyte. In a cuvette with an optical pathlength of 1.0 mm, a platinum mesh electrode was used as working electrode and a platinum wire as the counter electrode.

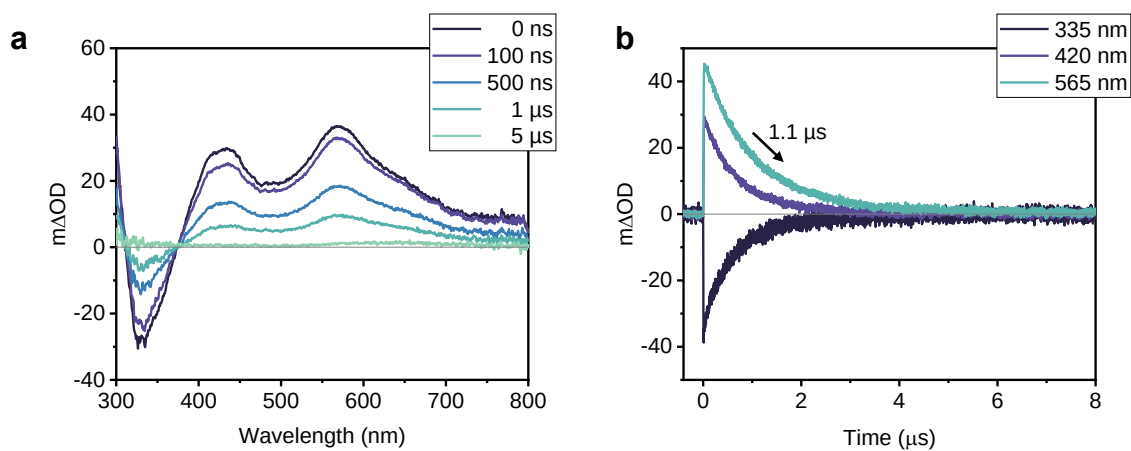


**Supplementary Figure 13.** **a**, Normalized difference spectra during electrochemical oxidation by applying 1.0 V vs. SCE to a solution of 250  $\mu$ M TAA-xy-PTZ-xy (**8**) in  $N_2$ -saturated  $CH_2Cl_2$ . This potential is sufficient to oxidize both electron donors. At time  $t_1$ , the spectral signatures (black) can be assigned to TAA $^{\bullet+}$  by comparison to the difference spectrum of ref-TAA $^{\bullet+}$  (blue). After prolonged electrochemical oxidation, the additional signals at time  $t_2$  can be assigned to the formation of PTZ $^{\bullet+}$  when comparing the double difference spectrum of  $t_2 - t_1$  (black) to ref-PTZ $^{\bullet+}$  (green). **b**, Normalized difference spectra during electrochemical reduction by applying -1.1 V vs. SCE to a solution of 250  $\mu$ M xy-AQ-hxy-NDI (**14**) in  $N_2$ -saturated  $CH_2Cl_2$ . This potential is sufficient to reduce both electron acceptors. At time  $t_1$ , the spectral signatures (black) can be assigned to NDI $^{\bullet-}$  by comparison to the difference spectrum of ref-NDI $^{\bullet-}$  (red). After prolonged electrochemical reduction, the additional signals at time  $t_2$  can be assigned to the formation of AQ $^{\bullet-}$  when comparing the double difference spectrum of  $t_2 - t_1$  (black) to ref-AQ $^{\bullet-}$  (orange). For both solutions, TBAPF $_6$  (100 mM) was used as supporting electrolyte. In a cuvette with an

optical pathlength of 1.0 mm, a platinum mesh electrode was used as working electrode and a platinum wire as the counter electrode.

This experiment underpins the successful establishment of the redox chain. The first hole is stored on TAA while the first electron is stored on NDI. Only when TAA is already oxidized, the formation of  $\text{PTZ}^{\bullet+}$  does not result in hole transfer to TAA but  $\text{PTZ}^{\bullet+}$  begins to be observable. Similar for the acceptor dyad, the formation of  $\text{NDI}^{\bullet-}$  is necessary to make  $\text{AQ}^{\bullet-}$  observable.

## 8. Transient Absorption Spectroscopy of the Triad (25)



**Supplementary Figure 14.** **a**, Transient absorption spectra of a 16  $\mu\text{M}$  solution of the triad (**25**) in dry Ar-saturated MeCN following excitation with 460 nm pulses of ca. 10 ns. The spectra are time-integrated over 200 ns after the indicated delays. The spectroscopic features of  $\text{PTZ}^{2+}$  (shoulder at around 650 nm) and  $\text{AQ}^{\bullet-}$  (420 nm and 565 nm) are observable. **b**, Decay traces of the transient absorption features (at 420 and 565 nm) and recovery of the ground state bleach (at 335 nm). An exponential fit provided a lifetime of the CSS of 1.1  $\mu\text{s}$ .

## 9. Relative Actinometry

The efficiency of the charge separation processes was investigated in a relative actinometry experiment.

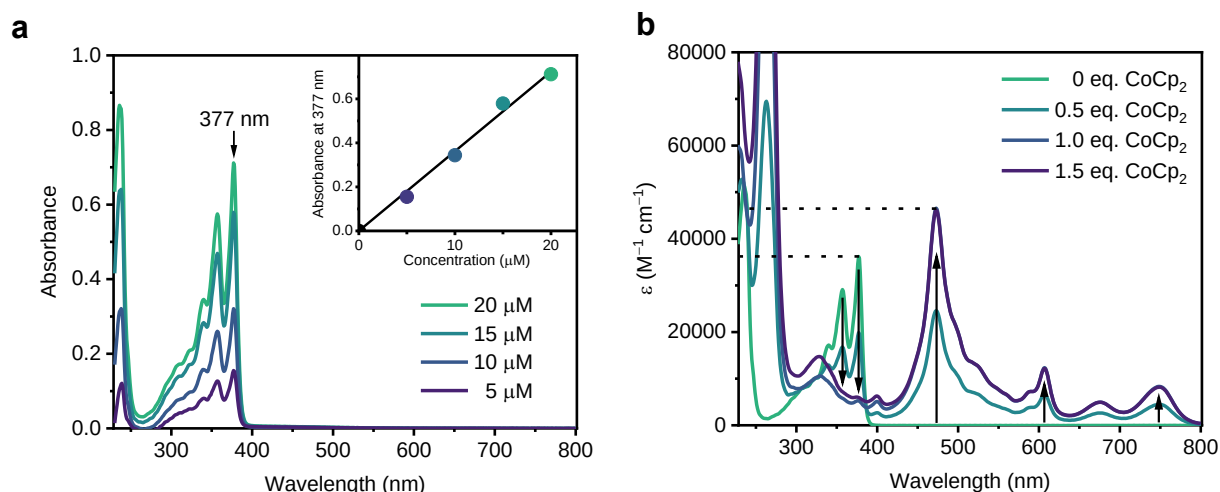
The quantum yield for charge separation is defined as the number of charge separated states formed per absorbed photons:

$$\Phi_{\text{CSS-2}} = \frac{n_{\text{CSS-2}}}{n_{\text{photons}}} \quad (1)$$

While the number of molecules in a charge-separated state ( $n_{\text{CSS-2}}$ ) can be quantified via the difference in optical density of the solution upon excitation ( $\Delta\text{OD}_{\text{CSS-2}}$ ) and the change in molar extinction coefficient of the charge separated state ( $\Delta\epsilon_{\text{CSS-2}}$ ), the number of absorbed photons ( $n_{\text{photons}}$ ) is less straight forward to quantify. This number, however, can be obtained indirectly from a suitable reference with a known change in molar extinction coefficient. The ground state MLCT absorption bleach of  $[\text{Ru}(\text{bpy})_3]^{2+}$  is regularly used as a reference in this context and has a well known change in molecular extinction coefficient at 450 nm ( $\Delta\epsilon = -11'000 \text{ M}^{-1} \text{ cm}^{-1}$ ) in water.<sup>10</sup> At 455 nm, the  $^3\text{MLCT}$  bleach is 95% of the bleach at 450 nm, corresponding to  $\Delta\epsilon_{\text{ref}} = -10'450 \text{ M}^{-1} \text{ cm}^{-1}$  at 455 nm (Supplementary Figure 17a). Since the intersystem crossing quantum yield of  $[\text{Ru}(\text{bpy})_3]^{2+}$  is unity, every absorbed photon will result in an  $^3\text{MLCT}$  excited  $^*[\text{Ru}(\text{bpy})_3]^{2+}$  species. The concentration of this species and thereby the number of absorbed photons can be quantified with the change in optical density at 455 nm upon excitation ( $\Delta\text{OD}_{\text{ref}}$ ) and  $\Delta\epsilon_{\text{ref}}$ .

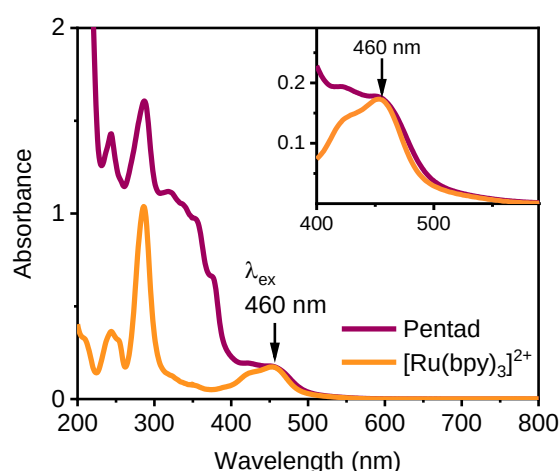
At 460 nm both  $[\text{Ru}(\text{bpy})_3]^{2+}$  and the pentad are mainly excited into their MLCT state. A solution of the pentad with an identical absorbance at the excitation wavelength ( $\lambda_{\text{ex}} = 460 \text{ nm}$ ) as the  $[\text{Ru}(\text{bpy})_3]^{2+}$  reference solution will therefore absorb the same number of photons under identical excitation conditions. This will allow the quantification of  $n_{\text{photons}}$  from Eq. 1.

We first aimed at determining the change in molar extinction coefficient of CSS-2 ( $\Delta\epsilon_{\text{CSS-2}}$ ). At 476 nm,  $\Delta\epsilon_{\text{CSS-2}}$  can be approximated with the molar extinction coefficient of  $\text{NDI}^{\bullet-}$  ( $\epsilon_{\text{NDI}^{\bullet-}}$ ) which is the dominant species absorbing at this wavelength in CSS-2. From the stoichiometric reduction with cobaltocene, the molar extinction coefficient of  $\text{NDI}^{\bullet-}$  was determined to be  $46'600 \text{ M}^{-1} \text{ cm}^{-1}$  at 476 nm (Supplementary Figure 15b).



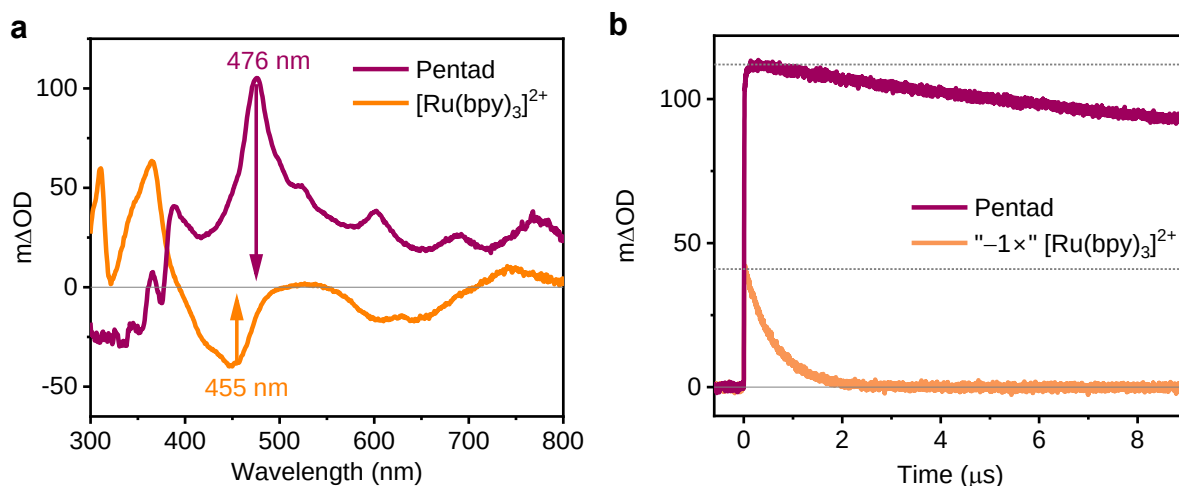
**Supplementary Figure 15.** **a**, UV-vis absorption spectra of solutions of *N,N*-bis(2-ethylhexyl)naphthalenediimide (NDI) in MeCN with concentrations ranging from 5  $\mu\text{M}$  to 20  $\mu\text{M}$ . A molar extinction coefficient at 377 nm of  $36'200 \text{ M}^{-1} \text{ cm}^{-1}$  was obtained from linear regression of the absorbance at 377 nm. **b**, UV-vis absorption spectra of Ar-saturated MeCN solutions of NDI that was chemically reduced with increasing amounts of cobaltocene ( $\text{CoCp}_2$ , 325 nm) to form  $\text{NDI}^{\bullet-}$  (476 nm) and  $[\text{CoCp}_2]^+$  (265 nm). The addition of  $\text{CoCp}_2$  occurred in small aliquots of a 5.0 mM solution in Ar-saturated MeCN (most spectra omitted for clarity) and the point of stoichiometric reduction was determined when the absorption of  $\text{NDI}^{\bullet-}$  (at 476 nm) stopped to increase and instead an increase of unoxidized  $\text{CoCp}_2$  (at 325 nm) was observed.

With  $\Delta\epsilon_{\text{ref}}$  and  $\Delta\epsilon_{\text{CSS-2}}$  in hand, the actual relative actinometry experiment was the next step. A solution of the pentad in MeCN was adjusted to have an identical absorbance at 460 nm as a solution of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  in water (Supplementary Figure 16). Both solutions were sparged with Ar for 11 min and the absorbance at 460 nm was checked to be identical again. A correction for the different refractive indexes of water and MeCN is not necessary as they differ by less than 1%.<sup>11</sup>



**Supplementary Figure 16.** UV-vis absorption spectra of a 15  $\mu\text{M}$  solution of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  in Ar-saturated water (orange) and a 12  $\mu\text{M}$  solution of the pentad in Ar-saturated MeCN (purple). The inset shows a zoom into the spectral region of the MLCT absorption bands. The two solutions were adjusted to have an identical absorbance at the excitation wavelength of 460 nm.

Both solutions were excited with 460 nm pulses without switching off the laser in between measurements to guarantee identical laser pulse powers. Transient absorption spectra and kinetic traces at 455 nm ( $[\text{Ru}(\text{bpy})_3]^{2+}$ ) and at 476 nm (pentad) were recorded (Supplementary Figure 17).



**Supplementary Figure 17.** **a**, Transient absorption spectra of the pentad (purple) and  $[\text{Ru}(\text{bpy})_3]^{2+}$  (orange) solutions from Supplementary Figure 16 after excitation with 460 nm pulses of ca. 10 ns. The spectra are time-integrated over 200 ns after the laser pulses. The kinetic traces were recorded at 476 nm for the pentad (purple arrow) and at 455 nm for  $[\text{Ru}(\text{bpy})_3]^{2+}$  (orange arrow). **b**, Kinetic traces at 476 nm for the pentad (purple) and at 455 nm for  $[\text{Ru}(\text{bpy})_3]^{2+}$  (orange, multiplied by  $-1$  to turn the bleach recovery into a positive signal that is directly comparable in intensity to the purple trace). The laser was not stopped between the measurements and is assumed to be of identical power for both measurements (ca. 11 mJ per pulse).

The concentration of CSS-2 ( $c_{\text{CSS-2}}$ ) that is formed upon excitation is obtained with

$$c_{\text{CSS-2}} = \frac{\Delta\text{OD}_{\text{CSS-2}}}{\Delta\epsilon_{\text{CSS-2}} \times d} \quad (2)$$

where  $\Delta\text{OD}_{\text{CSS-2}}$  is the difference in optical density at 476 nm after excitation of the pentad solution,  $\Delta\epsilon_{\text{CSS-2}}$  is the change in molar extinction coefficient of the pentad in MeCN at 476 nm and  $d$  is the optical pathlength.

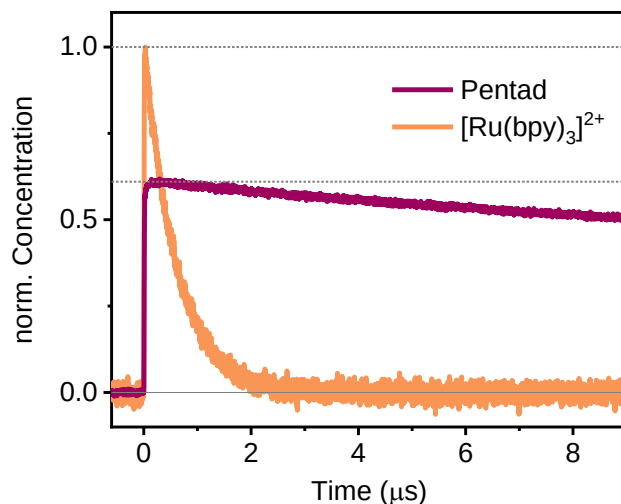
Given an intersystem crossing quantum yield of unity for  $[\text{Ru}(\text{bpy})_3]^{2+}$ ,<sup>12</sup> the concentration of  $^3\text{MLCT}$  excited  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $c_{\text{ref}}$ ) can be determined analogously with

$$c_{\text{ref}} = \frac{\Delta\text{OD}_{\text{ref}}}{\Delta\epsilon_{\text{ref}} \times d} \quad (3)$$

where  $\Delta\text{OD}_{\text{ref}}$  is the difference in optical density at 455 nm after excitation of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  solution,  $\Delta\epsilon_{\text{ref}}$  is the change in molar extinction coefficient of  $[\text{Ru}(\text{bpy})_3]^{2+}$  in water at 455 nm and  $d$  is the optical pathlength.

Dividing the kinetic traces from Supplementary Figure 17b by their respective changes in molar extinction coefficients ( $\Delta\epsilon_{\text{CSS-2}}$  and  $\Delta\epsilon_{\text{ref}}$ ) (Eqs. 2 and 3) gives the concentration profiles of the CSS-2

and  $^3\text{MLCT}$ -excited  $[\text{Ru}(\text{bpy})_3]^{2+}$ . Normalization to the maximum  $^3\text{MLCT}$  excited  $[\text{Ru}(\text{bpy})_3]^{2+}$  concentration gives a visual representation of the relative concentrations and the charge separation quantum yield for the pentad (Supplementary Figure 18).



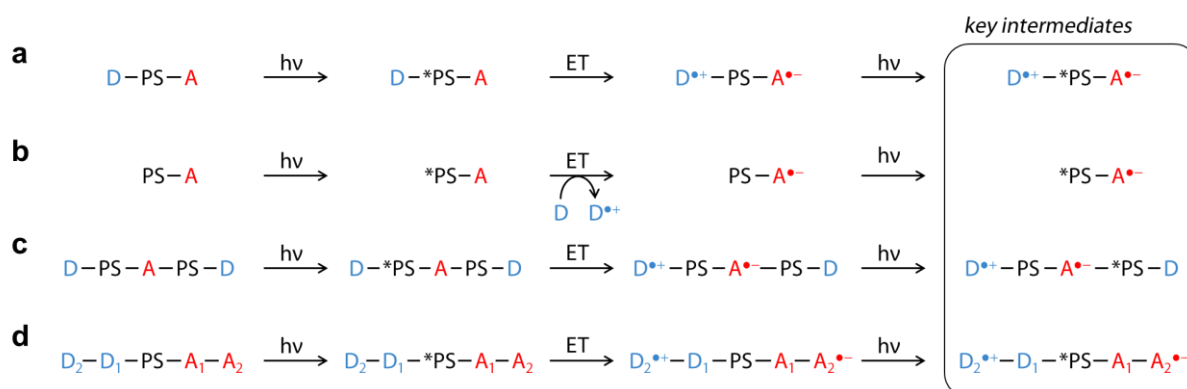
**Supplementary Figure 18.** Concentration profiles of the CSS-2 (purple) and  $^3\text{MLCT}$ -excited  $[\text{Ru}(\text{bpy})_3]^{2+}$  (orange) normalized to the maximum of concentration reached for  $^3\text{MLCT}$ -excited  $[\text{Ru}(\text{bpy})_3]^{2+}$ . The maximal value of CSS-2 is representing the charge separation quantum yield ( $\Phi_{\text{CSS-2}}$ ).

Eq. 1 can now be rewritten with the ratio of the maximal concentrations of CSS-2 ( $c_{\text{CSS-2, max}}$ ) and of  $^3\text{MLCT}$  excited  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $c_{\text{ref, max}}$ ). The quantum yield for the formation of CSS-2 ( $\Phi_{\text{CSS-2}}$ ) is therefore given by

$$\Phi_{\text{CSS-2}} = \frac{n_{\text{CSS-2}}}{n_{\text{photons}}} = \frac{c_{\text{CSS-2, max}}}{c_{\text{ref, max}}} = \frac{\frac{\Delta\text{OD}_{\text{CSS-2, max}}}{\Delta\epsilon_{\text{CSS-2}} \times d}}{\frac{\Delta\text{OD}_{\text{ref, max}}}{\Delta\epsilon_{\text{ref}} \times d}} = 61\% \quad (4)$$

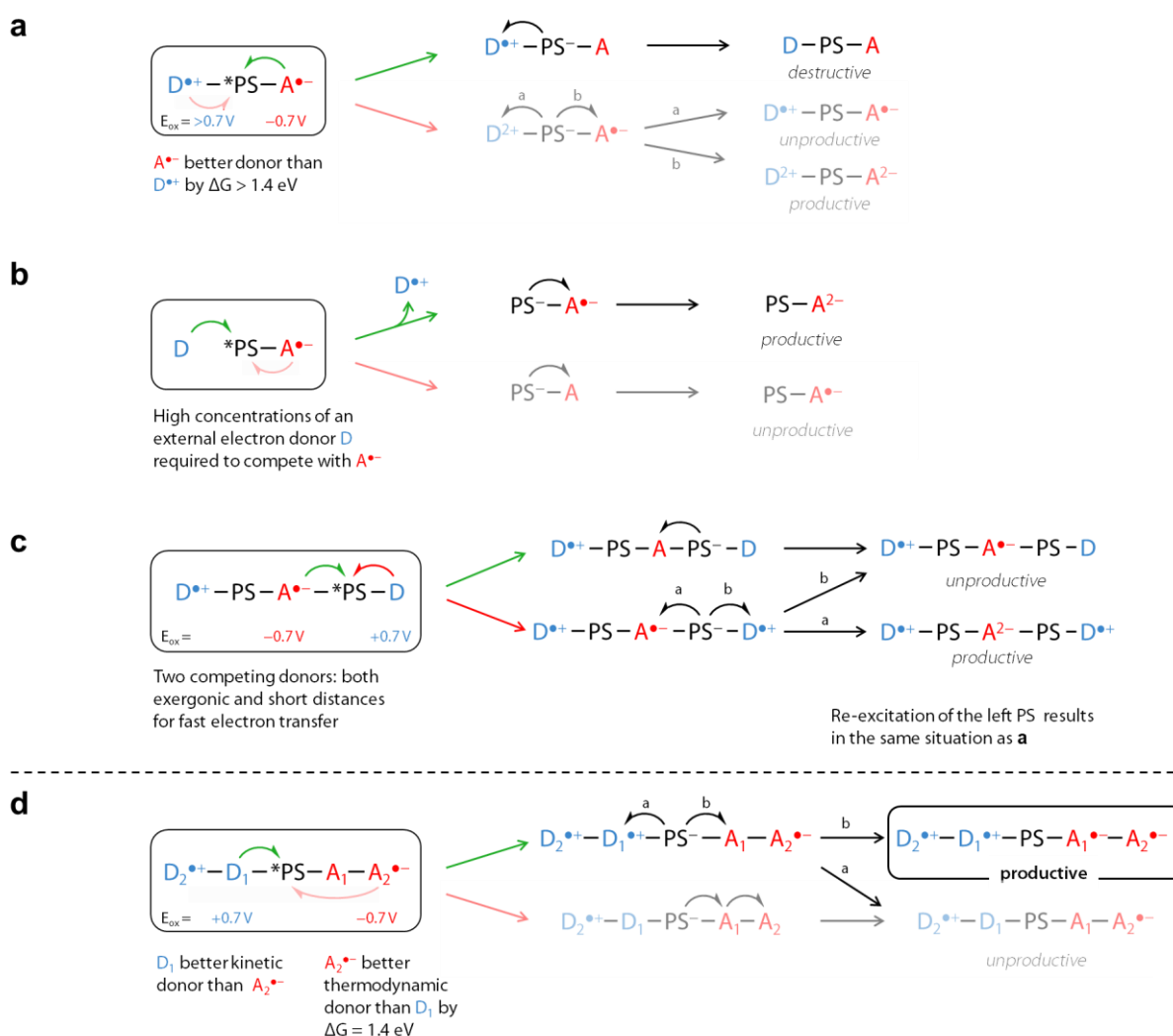
where  $n_{\text{CSS-2}}$  is the total number of CSS-2 formed,  $n_{\text{photons}}$  is the total number of photons absorbed, and  $c_{\text{CSS-2, max}}$  and  $c_{\text{ref, max}}$  are the maximal concentrations of the respective species and obtained via the respective experimentally determined maximal  $\Delta\text{OD}$  values ( $\Delta\text{OD}_{\text{CSS-2, max}}$  and  $\Delta\text{OD}_{\text{ref, max}}$ ).

## 10. Re-excitation of the Photosensitizer in a CSS



**Supplementary Figure 19.** Photoinduced formation of charge separated states in the case of a D-PS-A triad (**a**), a PS-A dyad in the presence of an external electron donor (**b**), a D-PS-A-PS-D pentad (**c**) as explored for example in refs.<sup>13-16</sup> and the D<sub>2</sub>-D<sub>1</sub>-PS-A<sub>1</sub>-A<sub>2</sub> pentad (**d**) from the main paper.

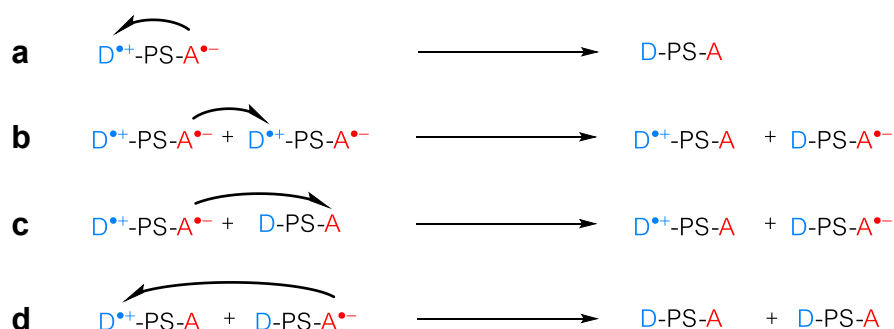
Possible onward reactions of the intermediates from above upon further excitation of the photosensitizer:



**Supplementary Figure 20.** Qualitative analysis of the electron transfers that are expected to occur in the key intermediates from Supplementary Figure 19 based on their driving forces and relative

distances. Typical redox potentials for electron donors and acceptors used in such molecules are given for instructive purposes. These redox potentials of +0.7 V for the oxidation of a donor and -0.7 V for the reduction of an acceptor match the redox potentials of TAA and NDI. In a given small-molecule redox unit, the second oxidation and reduction is typically 0.5–1.0 V more difficult than the first one.<sup>17</sup> **a**, Competition of  $D^{\bullet+}$  and  $A^{\bullet-}$  for the reductive quenching of  $^*PS$ . Both electron transfers have to occur over similar distances but  $A^{\bullet-}$  is the stronger electron donor than  $D^{\bullet+}$  by more than 1.4 eV. Moreover,  $D^{\bullet+}$  is also a good electron acceptor resulting in photo-induced charge recombination being the prevalent pathway. Reductive quenching by  $D^{\bullet+}$  is less likely and if it occurs,  $PS^-$  is thermodynamically more likely to reduce  $D^{2+}$  than  $A^{\bullet-}$  resulting in a nonproductive process. Hence, the path for charge accumulation has to go twice over the thermodynamically less favored electron transfer. **b**, In a PS-A dyad, large quantities of an external donor can be used to quench  $^*PS$  reductively while decreasing the likelihood of charge recombination as the radical cations can diffuse away. The reduced  $PS^-$  can then reduce the acceptor a second time in an exergonic process. Reductive quenching by  $A^{\bullet-}$  results in  $PS^-A$  for which  $PS^-$  is expected to reduce the uncharged acceptor A again, in an overall unproductive pathway. **c**, In a D-PS-A-PS-D pentad<sup>13–16</sup> where the PS that is not involved in the first charge separation process is excited, D will be competing with  $A^{\bullet-}$  for the reductive quenching. Both processes are exergonic and occur over similar and comparatively short distances. Hence, reductive quenching by  $A^{\bullet-}$  is thermodynamically more likely and will result in an unproductive path. However, reductive quenching by D is possible and a second thermodynamically less favored process (a) can result in charge accumulation. For such D-PS-A-PS-D pentads, charge accumulation is more likely to occur if both PS are excited at the same time. **d**, In the pentad from the main paper, re-excitation of PS in  $D_2^{\bullet+}$ - $D_1$ -PS- $A_1$ - $A_2^{\bullet-}$  (CSS-2) results in a constellation where  $D_1$  is competing with  $A_2^{\bullet-}$  for the reductive quenching of  $^*PS$ .  $A_2^{\bullet-}$  is thereby thermodynamically the stronger electron donor but the longer distance decreases the likelihood of this electron transfer to occur. The transfer from  $D_1$  is also exergonic and is due to the proximity kinetically favored to occur. Subsequent electron transfer from  $PS^-$  to  $A_1$  results in the charge accumulation of CSS-3.

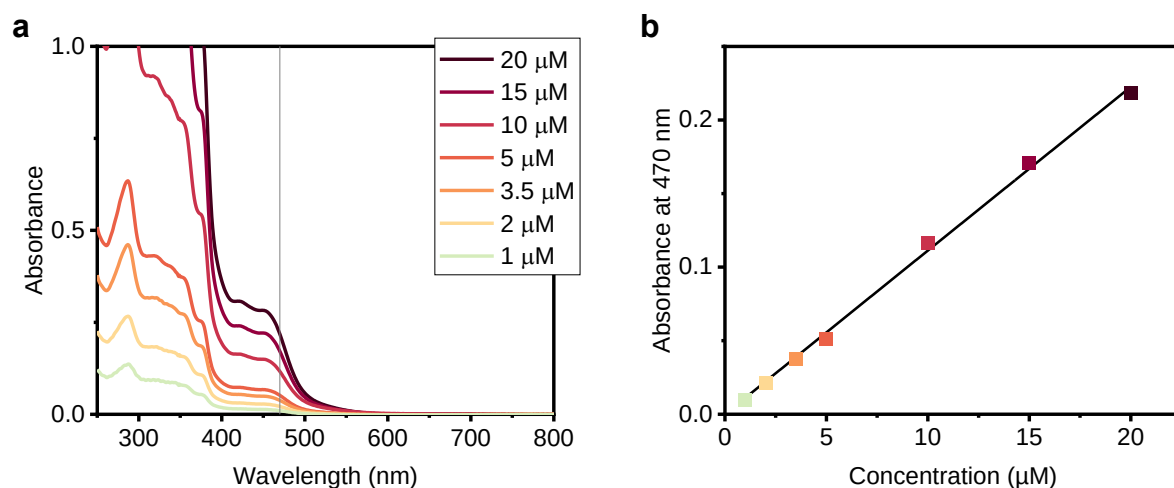
## 11. Charge Recombination Processes on Millisecond Timescales



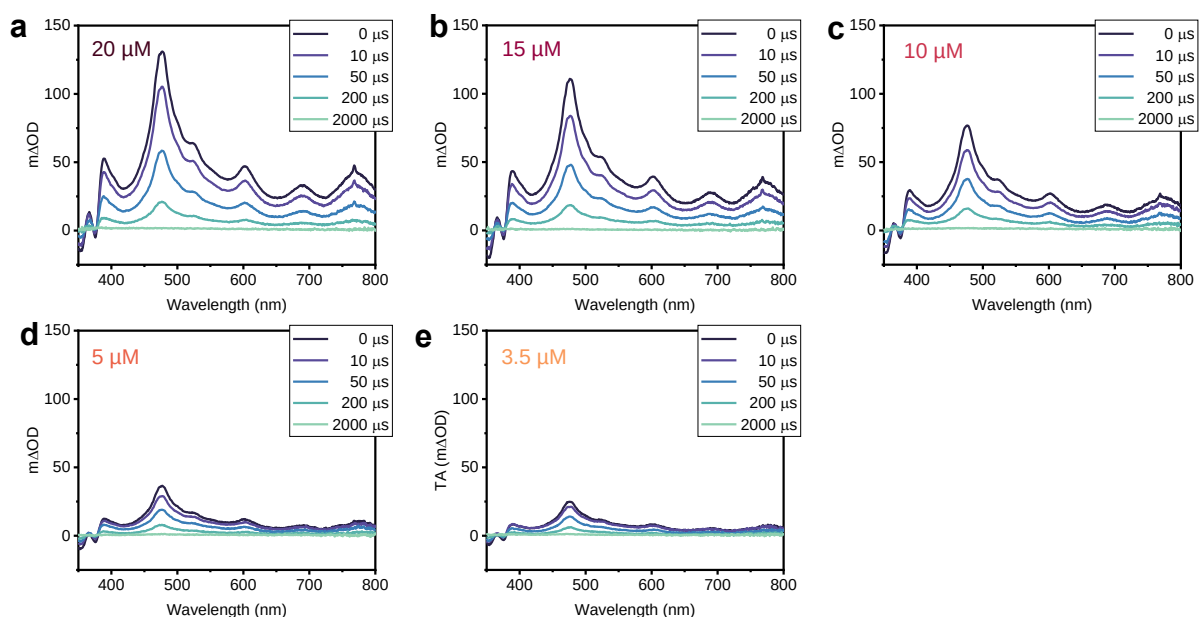
**Supplementary Figure 21.** The charge separated state CSS-2 of the pentad can be simplified to a  $D^{\bullet+}\text{-PS-A}^{\bullet-}$  picture where  $D^{\bullet+}$  and  $A^{\bullet-}$  are the terminal donor  $D_2^{\bullet+}$  and acceptor  $A_2^{\bullet-}$ . On the long timescales observed for the charge recombination in this CSS-2, multiple recombination pathways can be expected and the most likely processes are illustrated in this scheme. **a**, Depicts the intramolecular process where the electron and the hole of the same molecule recombine. This is the process that is dominant in short-lived charge separated states and results in the simultaneous decrease of the transient spectroscopic features of both  $D^{\bullet+}$  and  $A^{\bullet-}$ . **b**, When the CSS-2 decays on a 100  $\mu\text{s}$  timescale, it is possible that two molecules in CSS-2 encounter by diffusion even under the dilute conditions used for these experiments. In that case, electron and hole recombination can occur in an intermolecular process. This results in the formation of two singly charged molecules and the simultaneous decrease of the transient spectroscopic features of both  $D^{\bullet+}$  and  $A^{\bullet-}$ . **c**, It is also possible that a pentad molecule in CSS-2 encounters a pentad molecule in the redox-neutral (ground) state. In such an encounter, electron transfer from  $A^{\bullet-}$  to A or hole transfer from  $D^{\bullet+}$  to D is an equilibrium process that can occur despite having no driving force ( $\Delta G = 0$ ). Such an electron transfer results in the formation of two singly charged species and no change in the transient spectroscopic features. **d**, The electrons and holes stored in those singly charged species formed in a and b cannot recombine intramolecularly. The simplest recombination pathway depends on the encounter with another singly charged molecule of opposite sign and results in the simultaneous decrease of the transient spectroscopic features of both  $D^{\bullet+}$  and  $A^{\bullet-}$ . This bimolecular process depends on the concentration of the singly charged species which is decreasing with time.

The recombination processes in a, b and d all result in the same simultaneous decrease of spectroscopic features of both  $D^{\bullet+}$  and  $A^{\bullet-}$ , resulting in a multiexponential decay that cannot be disentangled. However, they are expected to occur on different timescales and in addition, b and d depend on the concentrations of both CSS-2 and/or the redox neutral state. Of main interest for our study is the determination of the time constant associated with the intramolecular process illustrated in a. For this purpose, we performed a study with varying concentration of the pentad as described in the following.

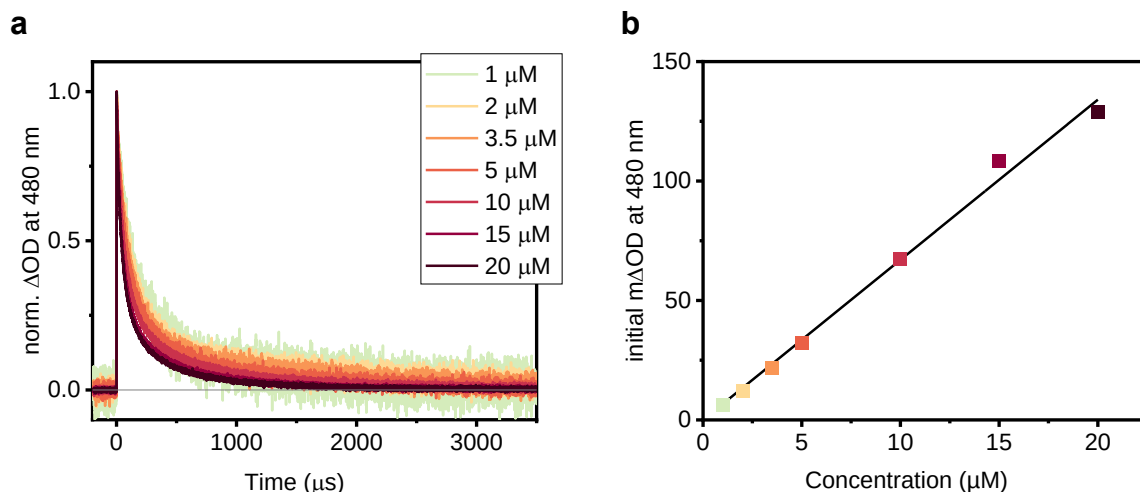
## 12. Concentration Dependence of Charge Recombination



**Supplementary Figure 22.** **a**, UV-vis absorption spectra of solutions of the pentad in Ar-saturated MeCN with concentrations ranging from 1  $\mu\text{M}$  to 20  $\mu\text{M}$ . The excitation wavelength (470 nm) is indicated with a vertical black line. **b**, Absorbance of the solutions from **a** at the excitation wavelength of 470 nm. A linear regression fit (black line) of the experimental points is given as a guide for the eye.



**Supplementary Figure 23.** **a-e**, Transient absorption spectra of the solutions from Supplementary Figure 22 of the pentad at 20  $^{\circ}\text{C}$  following excitation at 470 nm with laser pulses of ca. 10 ns. The signals were time-integrated over 200 ns after the indicated delay times.



**Supplementary Figure 24.** **a**, Normalized kinetic decays of the transient absorption signal at 480 nm of Ar-saturated MeCN solutions of the pentad following excitation at 470 nm at 20 °C. The concentration of the pentad was varied as described in Supplementary Figure 22, the relevant spectral data is in Supplementary Figure 23. **b**, The difference in optical density at 480 nm recorded directly after the pulse at the different concentrations (prior to normalization). Increasing the concentration of the pentad resulted in a linear increase in the formation of CSS-2.

**Supplementary Table 2.** Fitting the decay kinetics at 480 nm with a triexponential decay function as a simplistic model in an attempt to capture the processes a, b and d from Supplementary Figure 21 in a semi-quantitative fashion.

|           | 3.5 μM                     | 5.0 μM                     | 10 μM                      | 15 μM                      | 20 μM                      |
|-----------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| $\tau_1$  | $31.5 \pm 2.6 \mu\text{s}$ | $31.8 \pm 1.7 \mu\text{s}$ | $29.4 \pm 0.6 \mu\text{s}$ | $25.9 \pm 0.3 \mu\text{s}$ | $24.7 \pm 0.2 \mu\text{s}$ |
| $A_1$     | 20%                        | 25%                        | 37%                        | 43%                        | 48%                        |
| $A_1/A_2$ | 34%                        | 50%                        | 88%                        | 116%                       | 137%                       |
| $\tau_2$  | $139 \pm 3 \mu\text{s}$    | $132 \pm 3 \mu\text{s}$    | $119 \pm 2 \mu\text{s}$    | $106 \pm 1 \mu\text{s}$    | $106 \pm 1 \mu\text{s}$    |
| $A_2$     | 58%                        | 50%                        | 42%                        | 37%                        | 35%                        |
| $\tau_3$  | $1182 \pm 33 \mu\text{s}$  | $824 \pm 14 \mu\text{s}$   | $700 \pm 6 \mu\text{s}$    | $576 \pm 4 \mu\text{s}$    | $535 \pm 3 \mu\text{s}$    |
| $A_3$     | 17%                        | 20%                        | 20%                        | 19%                        | 17%                        |
| $A_3/A_2$ | 29%                        | 40%                        | 48%                        | 51%                        | 49%                        |
| $R^2$     | 98.0%                      | 98.9%                      | 99.6%                      | 99.8%                      | 99.8%                      |

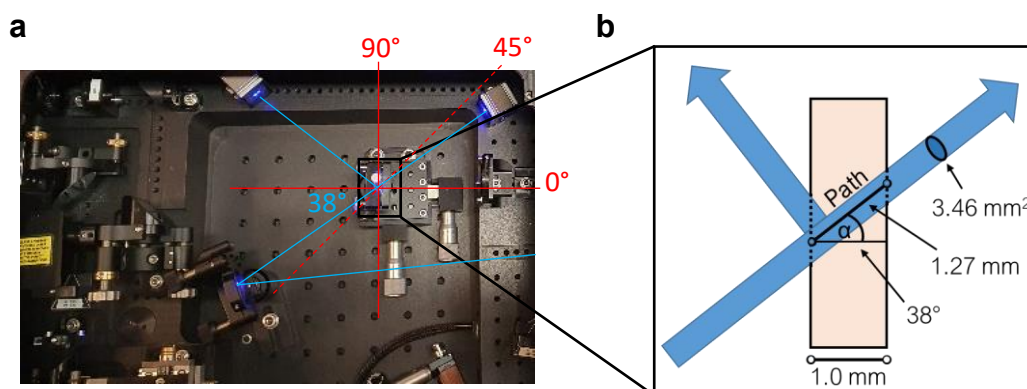
The increasing contribution (amplitude  $A_1$  in the fitting function) of the fastest component ( $\tau_1$ ) with increasing concentration is more compatible with an inter- rather than an intramolecular process. The component decaying with  $\tau_1$  is therefore attributed to the bimolecular charge recombination between

two molecules in CSS-2 (process b in Supplementary Figure 21). Process b is particularly probable to occur at short delay times after the excitation pulses, when the concentration of CSS-2 is greatest.

The time constant of the slowest process ( $\tau_3$ ) experiences the strongest dependence on the increasing concentration (decreases from 1182 ns to 535 ns) and is assigned to the bimolecular recombination of the singly charged species (process d in Supplementary Figure 21). This process is more probable to occur when more of the singly charged species has been formed (coming along with increasing CSS-2 formation from increasing the concentration of the pentad) and will decrease the observed time constant ( $\tau_3$ ) of this process. Since this process depends on the diffusional encounter of two singly charged species, it is expected to be slowed down with prolonged delay time and thus delay the complete decay to the baseline.

The time constant of the remaining component ( $\tau_2$ ) does not change much as a function of concentration and contributes less with increasing concentration ( $A_2$  decreases). This component is therefore assigned to the intramolecular charge recombination (process a in Supplementary Figure 21). In principle, the rate of this process should be fully independent of the concentration of CSS-2. The decrease of  $A_2$  with increasing concentration is likely an artefact of the simplistic tri-exponential fitting approach used here. There exist several concentration dependent processes as outlined in Supplementary Figure 21 and the CSS-2 concentration changes over time. The numerical solution of a series of coupled differential equations describing the individual processes in Supplementary Figure 21 should provide more accurate time constants and weighting factors for the individual elementary steps. The simplified analysis performed here is sufficient for the purpose of determining the approximate lifetime of CSS-2 in the pentad.

### 13. Number of Photons from the cw Laser



**Supplementary Figure 25. a**, Photograph of the setup, including guiding lines to illustrate the laser path (blue) and the angle of incidence on the cuvette. **b**, Schematic representation of the situation at the cuvette indicating the numbers used for the calculations below.

The continuous wave laser used for the cw-pump-pump-probe experiment has a beam area of  $3.46 \text{ mm}^2$  and an incident angle ( $\alpha$ ) of  $38^\circ$ , when  $0^\circ$  is perpendicular to the cuvette's surface. The actual pathlength of the beam through the 1 mm cuvette is therefore

$$\text{path} = \frac{d}{\cos(\alpha)} = \frac{1 \text{ mm}}{\cos(38^\circ)} = 1.27 \text{ mm} \quad (5)$$

and the sample volume irradiated by the cw beam is

$$1.27 \text{ mm} \times 3.46 \text{ mm}^2 = 4.39 \text{ mm}^3 \quad (6)$$

Such a volume at a sample concentration of  $300 \mu\text{M}$  contains

$$n = V \times c = 4.39 \text{ mm}^3 \times 300 \times 10^{-6} \text{ M} = 1.32 \times 10^{-9} \text{ mol} \quad (7)$$

$$n \times N_A = 1.32 \times 10^{-9} \text{ mol} \times 6.022 \times 10^{23} \text{ mol}^{-1} = 7.95 \times 10^{14} \quad (8)$$

molecules, where  $N_A$  is Avogadro's constant.

Photons with a wavelength of 447 nm have an energy of 2.77 eV or  $4.44 \times 10^{-19} \text{ J}$ .

$$E_{\text{photon}} = \frac{h \times c}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1}}{447 \text{ nm}} = 4.44 \times 10^{-19} \text{ J} \quad (9)$$

The power output  $P$  of the CW laser was measured to be  $460 \pm 10 \text{ mW}$  at the laser source as well as at the sample position ( $460 \pm 10 \text{ mW}$ ). The reflection at the cuvette surface that is visible in the image was measured to be very small ( $25 \pm 10 \text{ mW}$ ) and almost within the fluctuation of the power measurement.

The incident photon rate therefore is

$$\text{rate}_{\text{photons}} = \frac{P}{E_{\text{photon}}} = \frac{460 \text{ mW}}{4.44 \times 10^{-19} \text{ J}} = 1.04 \times 10^{18} \text{ s}^{-1} \quad (10)$$

This provides a photon flux or irradiance  $I$  per area of

$$I = \frac{\text{rate}_{\text{photons}}}{A} = \frac{1.04 \times 10^{18} \text{ s}^{-1}}{3.46 \times 10^{-6} \text{ m}^2} = 3.01 \times 10^{23} \text{ photons m}^{-2} \text{ s}^{-1} \quad (11)$$

When comparing the number of molecules present and the number of incident photons per time, the cw laser provides on average a photon per molecule every 760  $\mu\text{s}$ . This is on the order of the lifetime of the long-lived charge separated state CSS-2.

$$\frac{7.95 \times 10^{14} \text{ J}}{1.04 \times 10^{18} \text{ s}^{-1}} = 7.6 \times 10^{-4} \text{ s} \quad (12)$$

Additionally, the processes relevant for the cw-pump-pump-probe experiment occur in the overlapping volume of the two pump beams. The cross-sectional area of the 460 nm pump of the fs-setup is ca. 0.48  $\text{mm}^2$  and therefore smaller than the cw laser by a factor of 7.3. (The cross-sectional area of the probe pulse is ca. 0.023  $\text{mm}^2$ .)

$$\frac{4.39 \text{ mm}^3}{7.3} = 0.60 \text{ mm}^3 \quad (13)$$

The relevant volume therefore is 0.60  $\text{mm}^3$  which contains  $1.1 \times 10^{14}$  molecules. This volume is in the center of the cw laser where its flux is roughly 3 times higher than the average flux as described in the following:

Assuming a 2D normal distribution of the beam intensity in its cross section (in x and y direction, when z is the axis of propagation), ca. 39% of the provided photons are within one standard deviation ( $\pm 1 \sigma_x$ ,  $\pm 1 \sigma_y$ ) around the center. This area corresponds approximately to 1/7 of the overall area. By coincidence, this is also the area of overlap between the cw laser and the pulsed pump laser. Hence, 39% of the photon flux is in the central 1/7 of the cw laser where both pump laser overlap, resulting in a ca. 3 times higher flux at the center compared to the average flux.

$$\frac{\text{part of total flux}}{\text{part of total area}} = \frac{39\%}{\frac{1}{7}} = \frac{0.39}{0.14} = 2.8 \quad (14)$$

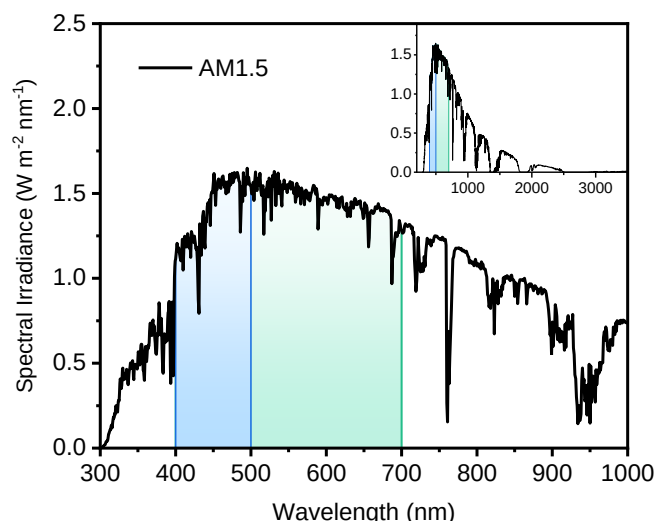
$$\frac{760 \mu\text{s}}{2.8} = 270 \mu\text{s} \quad (15)$$

At the center of the cw pulse, a photon is provided every 270  $\mu\text{s}$  per pentad molecule.

The success of the cw-pump-pump-probe experiment depended strongly on the alignment of the two pump laser paths. This is very likely indicating that the cw-pump-pump-probe experiment is indeed probing the very center of the cw laser beam where its maximum photon density is reached.

## Comparison to AM1.5 conditions

The sun (under AM1.5 conditions)<sup>18,19</sup> provides ca.  $140 \text{ W m}^{-2}$  in the spectral region from 400 nm to 500 nm (integral of the blue area in Supplementary Figure 26). When the entire photosynthetically active radiation (PAR) from 400 nm to 700 nm is considered, it is ca.  $430 \text{ W m}^{-2}$  (blue and green areas in Supplementary Figure 26).



**Supplementary Figure 26.** Spectral irradiance under AM1.5 conditions emphasizing the spectral regions relevant for the  $\text{Ru}(\text{bpy})_3^{2+}$  (blue) and natural photosynthesis (blue and green). The inset shows the entire spectrum.<sup>19,20</sup>

In the range from 400 nm to 500 nm, the median photon ( $\lambda = 450 \text{ nm}$ ) has an energy of  $4.4 \times 10^{-19} \text{ J}$ :

$$E_{\text{photon}} = \frac{h \times c}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 3.00 \times 10^8 \text{ m s}^{-1}}{450 \times 10^{-9} \text{ m}} = 4.4 \times 10^{-19} \text{ J} \quad (16)$$

Hence, the photon flux or irradiance  $I$  per area is

$$I = \frac{P}{E_{\text{photon}}} = \frac{140 \text{ W m}^{-2}}{4.4 \times 10^{-19} \text{ J photon}^{-1}} = 3.1 \times 10^{20} \text{ photons m}^{-2} \text{ s}^{-1} \quad (17)$$

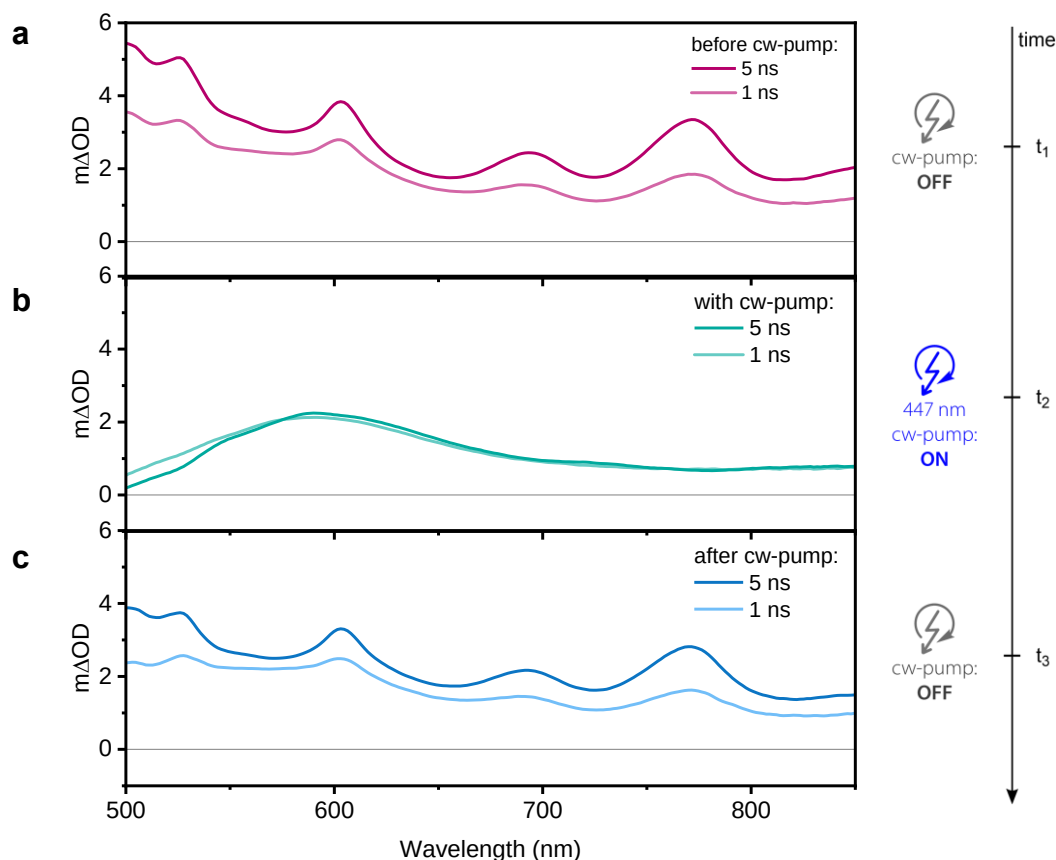
The cw laser that was used has an average intensity of  $3.0 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1}$  (Eq. 11), which provided on average one photon every 760  $\mu\text{s}$  (Eq. 12) per molecule. When comparing Eq. 17 to Eq. 11, we have a photon flux that is ca. 3 orders of magnitude lower under sunlight compared to the cw laser. We conclude that our system does not work efficiently under AM1.5 conditions and further modifications are required to achieve efficient charge accumulation without external redox reagents under ambient sunlight.

These irradiances can be compared with the harsh excitation conditions that prevail in the 10 ns pulses that are typically used for nanosecond transient absorption experiments described herein (a 10 ns pulse of 450 nm with a pulse energy of 20 mJ irradiating an area of 1 cm<sup>2</sup>):

$$I = \frac{E_{\text{pulse}}}{t_{\text{pulse}} \times A \times E_{\text{photon}}} = \frac{20 \times 10^{-3} \text{ J}}{10 \times 10^{-9} \text{ s} \times 1 \times 10^{-4} \text{ m}^2 \times 4.4 \times 10^{-19} \text{ J}} = 4.52 \times 10^{28} \text{ photons m}^{-2} \text{ s}^{-1} \text{ (18)}$$

The photon flux during these short pulses is 5 orders of magnitude higher than the one of the cw laser and 7 orders of magnitude higher compared to what the sun provides over the entire visible spectrum. It becomes evident that under such conditions simultaneous excitations of both PS in D-PS-A-PS-D compounds can be achieved as described in Fig. 1b.

## 14. Reversibility of the cw-Pump-Pump-Probe Experiment

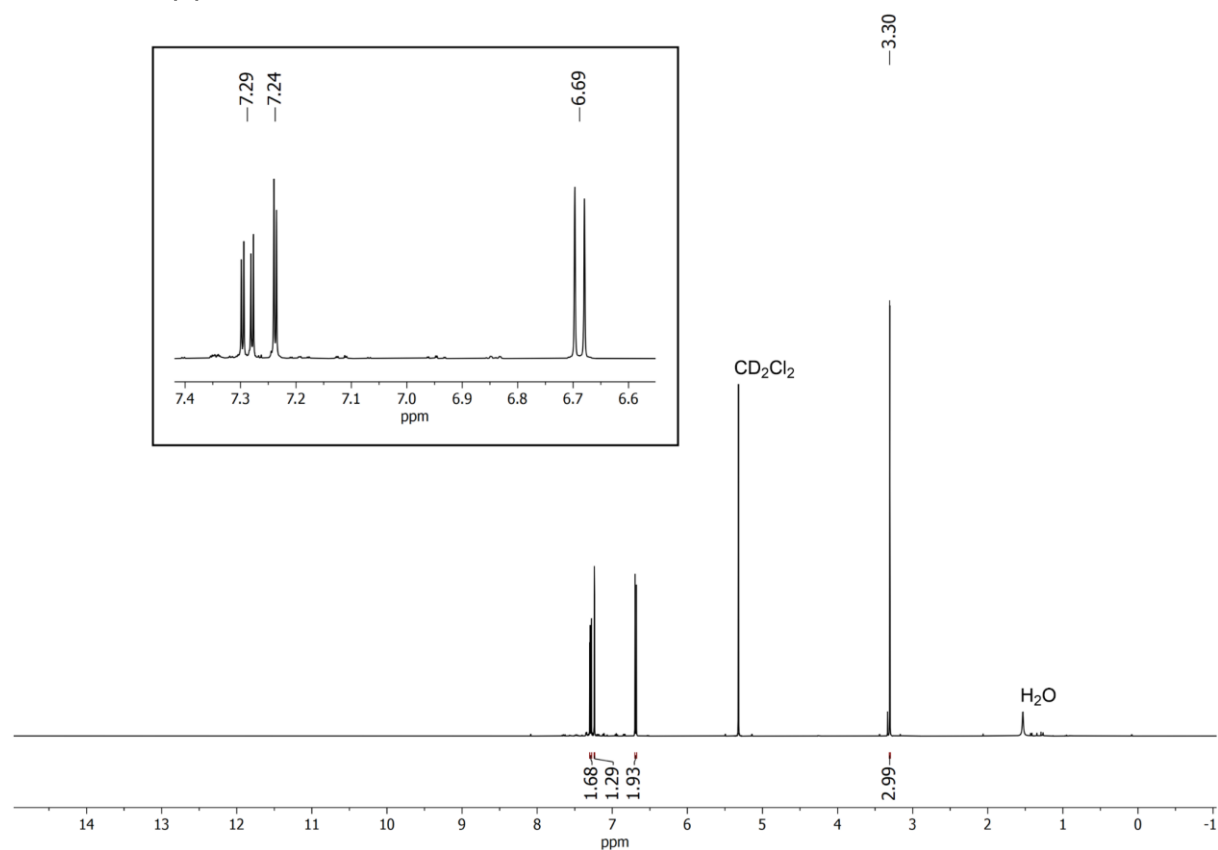


**Supplementary Figure 27.** **a**, Transient absorption spectra of a 300  $\mu\text{M}$  solution of the pentad in dry DMF at 20  $^{\circ}\text{C}$  with delays of 1 ns and 5 ns after the excitation with 460 nm pulses of ca. 250 fs duration. This classical pump-probe experiment is shown in Fig. 5b of the main paper and the spectroscopic features of the CSS-2 can be observed. **b**, Transient absorption spectra of the same solution with delays of 1 ns and 5 ns after the excitation with 460 nm pulses of ca. 250 fs duration while a blue continuous wave laser (447 nm) was used as a continuous pump. This cw-pump-pump-probe experiment is explained in detail in Figs. 4 and 5c of the main paper. The spectroscopic features arising from  $\text{PTZ}^{\bullet+}$  and  $\text{AQ}^{\bullet-}$ , the spectroscopic differences between CSS-3 and CSS-2, are observed. **c**, After the experiment from b, the classical pump-probe experiment from a (without the cw pump) was repeated again with the same solution. The transient absorption spectra were again recorded with delays of 1 ns and 5 ns after the excitation with a 460 nm pulse. These spectra are very similar to those in a and show again the formation of CSS-2.

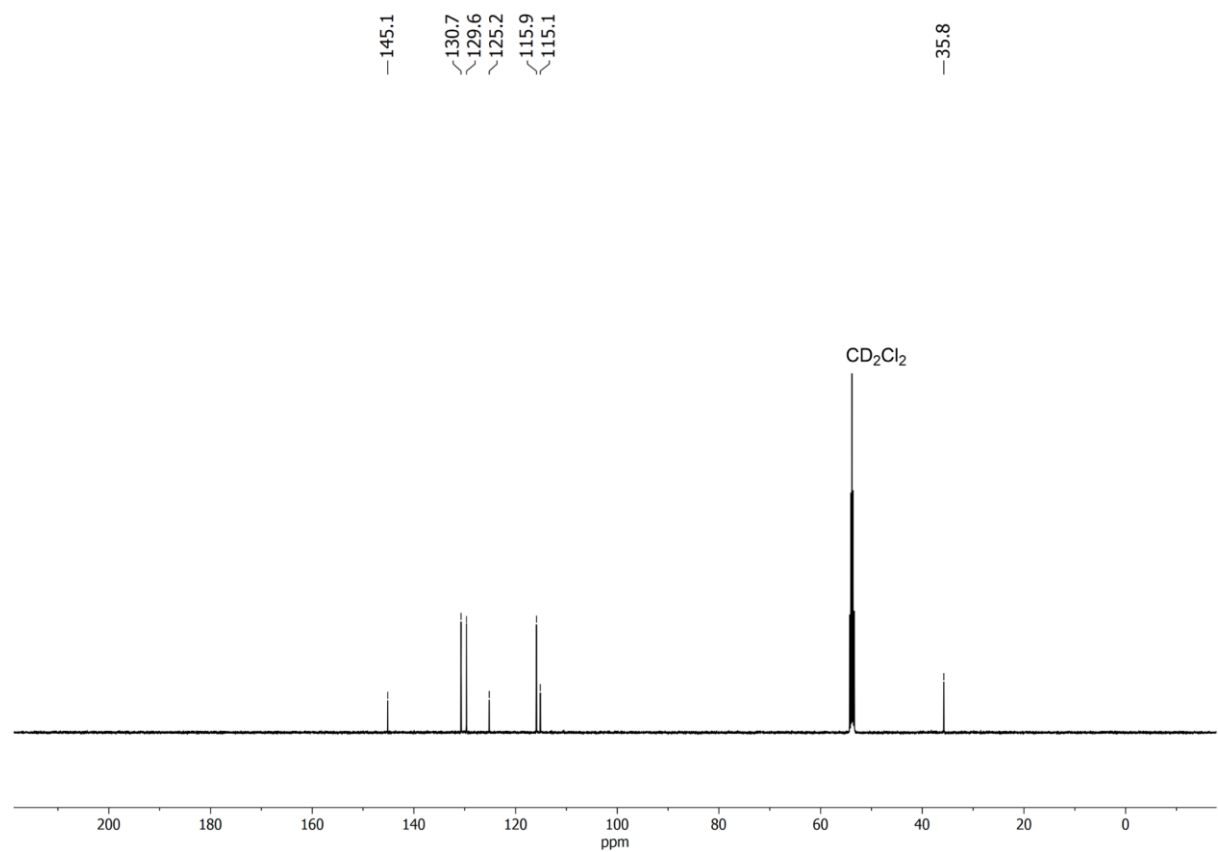
From these experiments, we conclude that the system is stable under the experimental conditions. A small decrease in absorption is observable at 500 nm indicating small amounts of decomposition.

## 15. NMR-Spectra

Br-PTZ-Br (**1**)

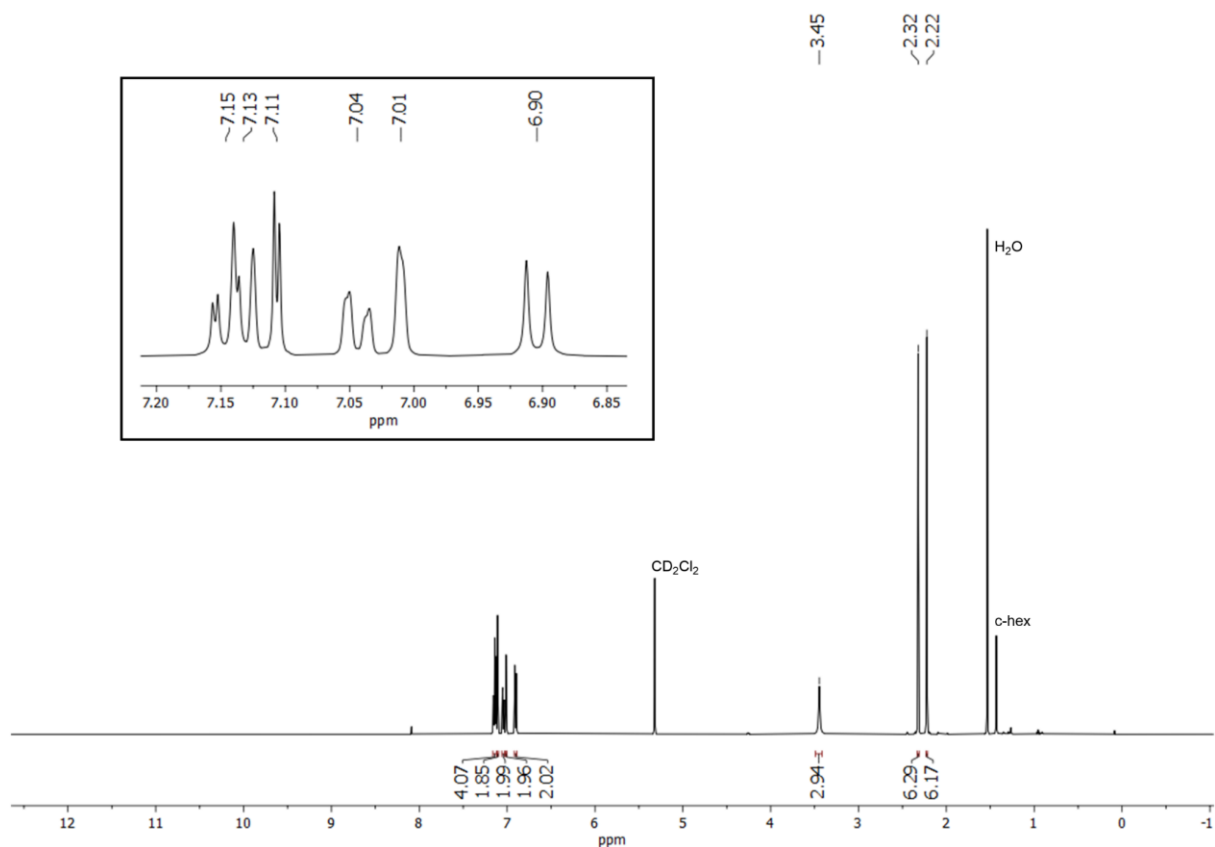


Supplementary Figure 28. <sup>1</sup>H-NMR spectrum (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of Br-PTZ-Br (**1**).

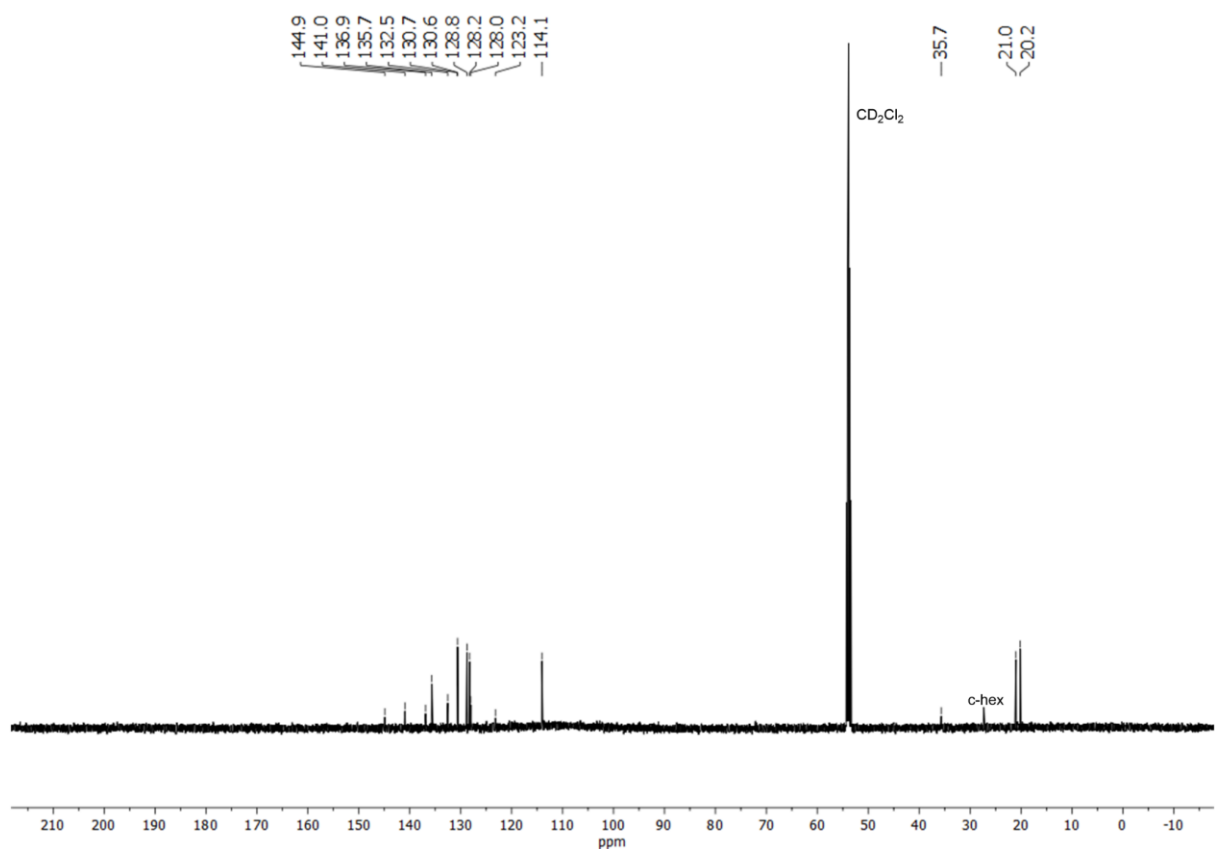


Supplementary Figure 29. <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum (126 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of Br-PTZ-Br (**1**).

ref-PTZ (2)

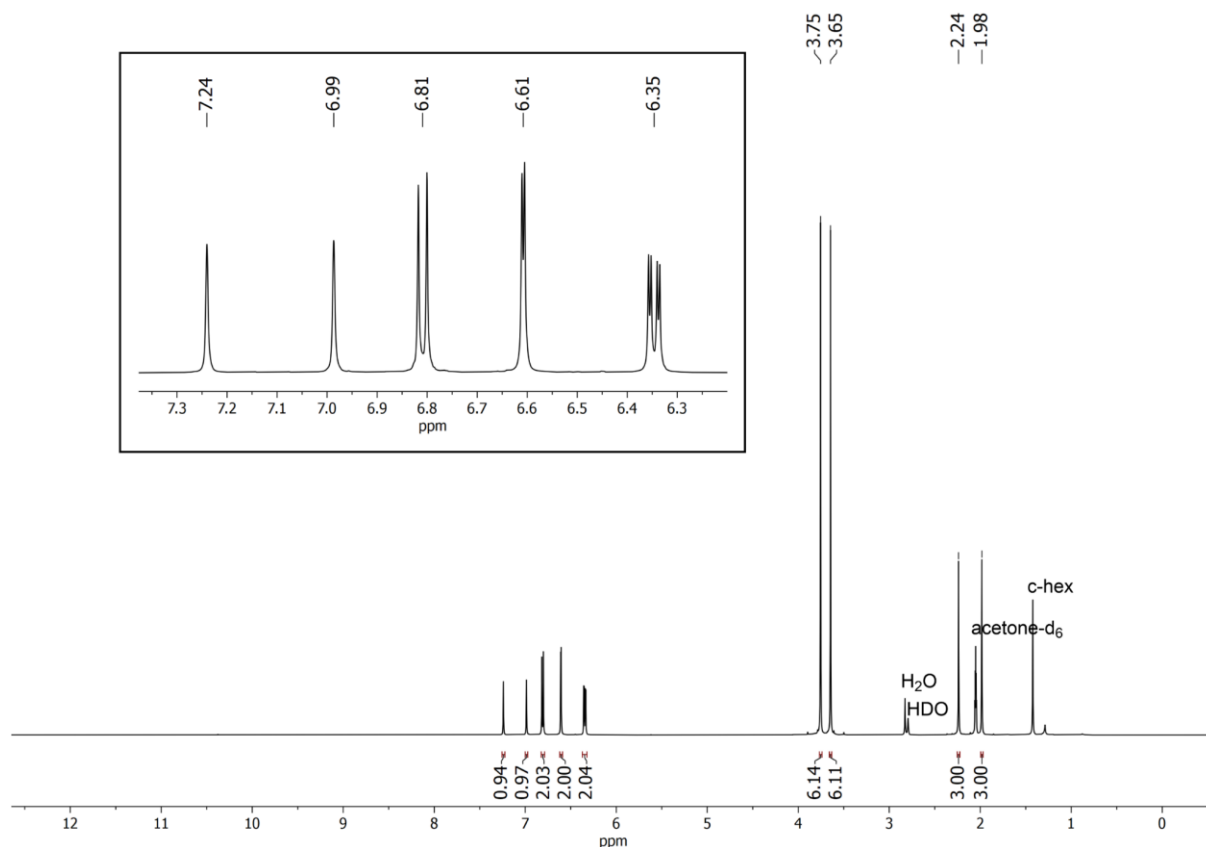


Supplementary Figure 30. <sup>1</sup>H-NMR spectrum (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of ref-PTZ (2).

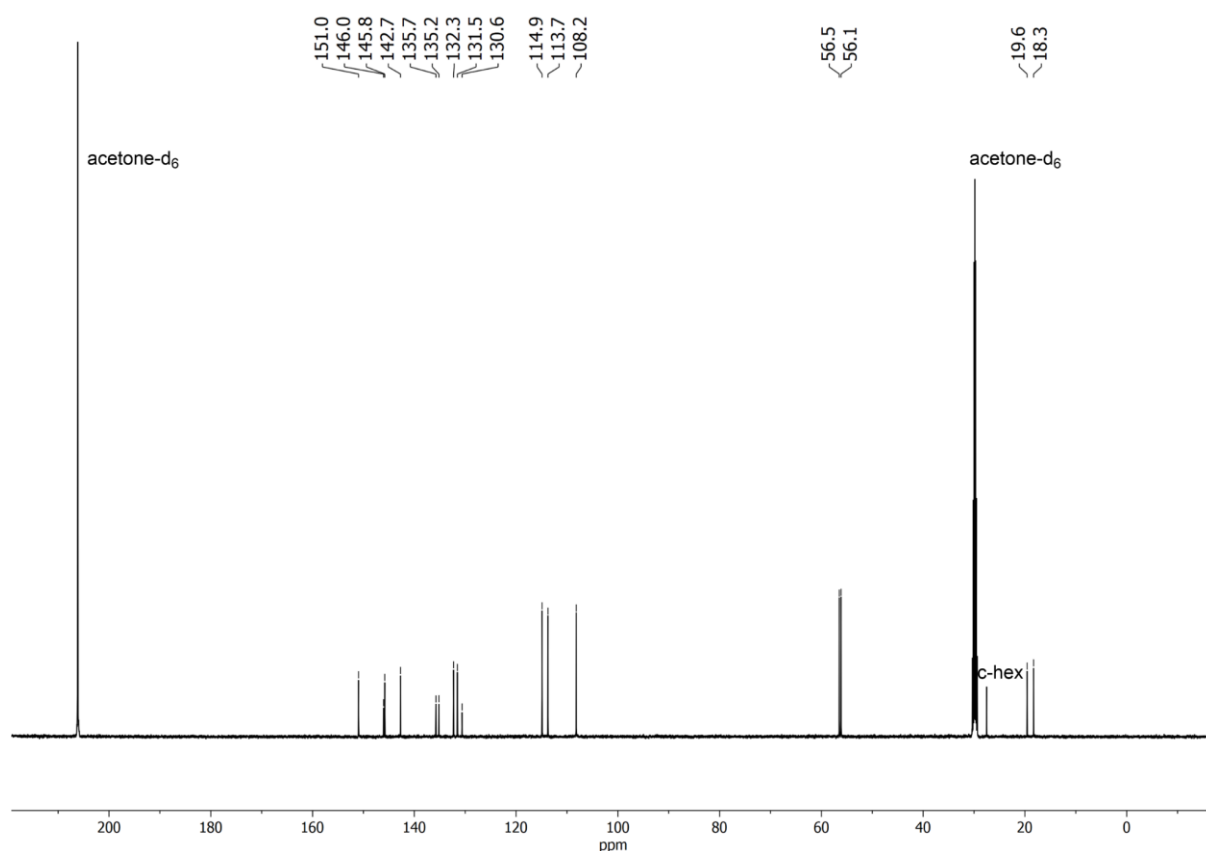


Supplementary Figure 31. <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum (126 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of ref-PTZ (2).

TAA-xy-Cl (**3**)

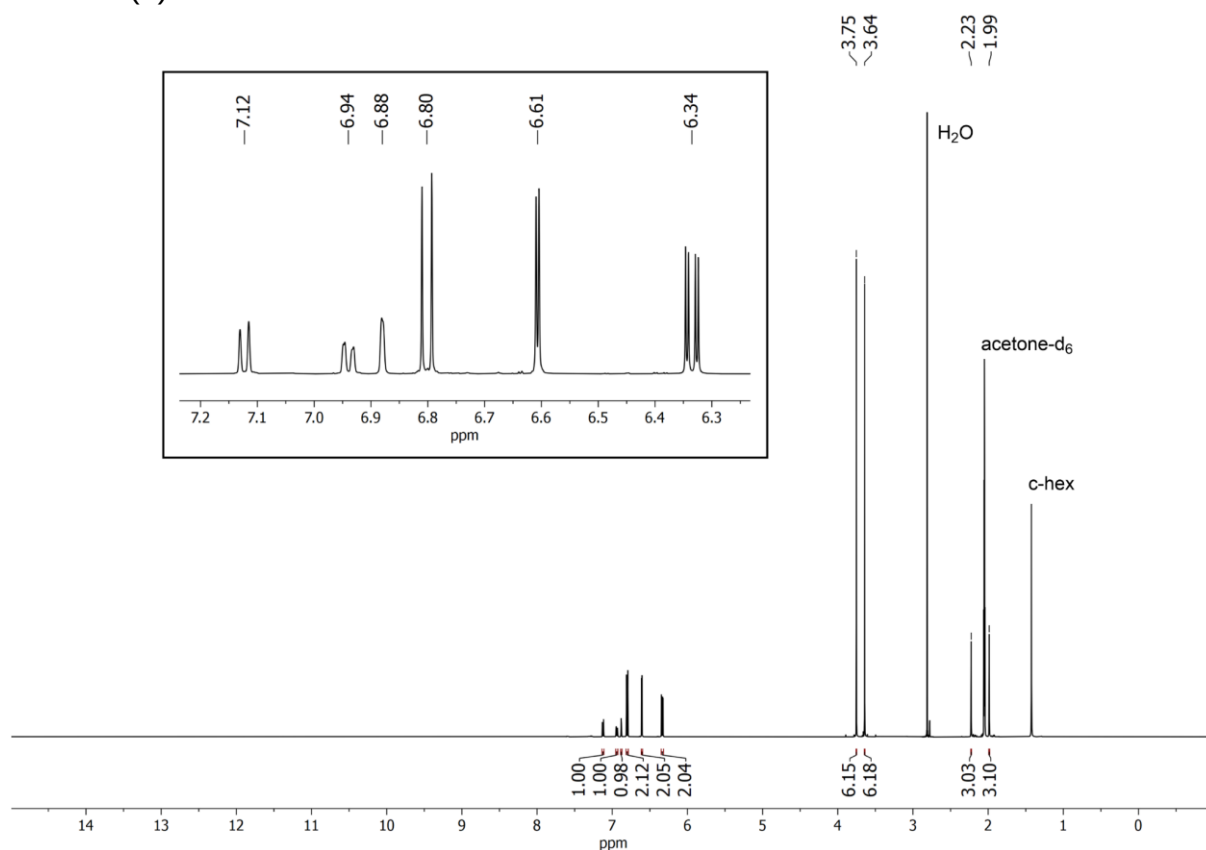


**Supplementary Figure 32.** <sup>1</sup>H-NMR spectrum (500 MHz, 298 K, acetone-d<sub>6</sub>) of TAA-xy-Cl (**3**).

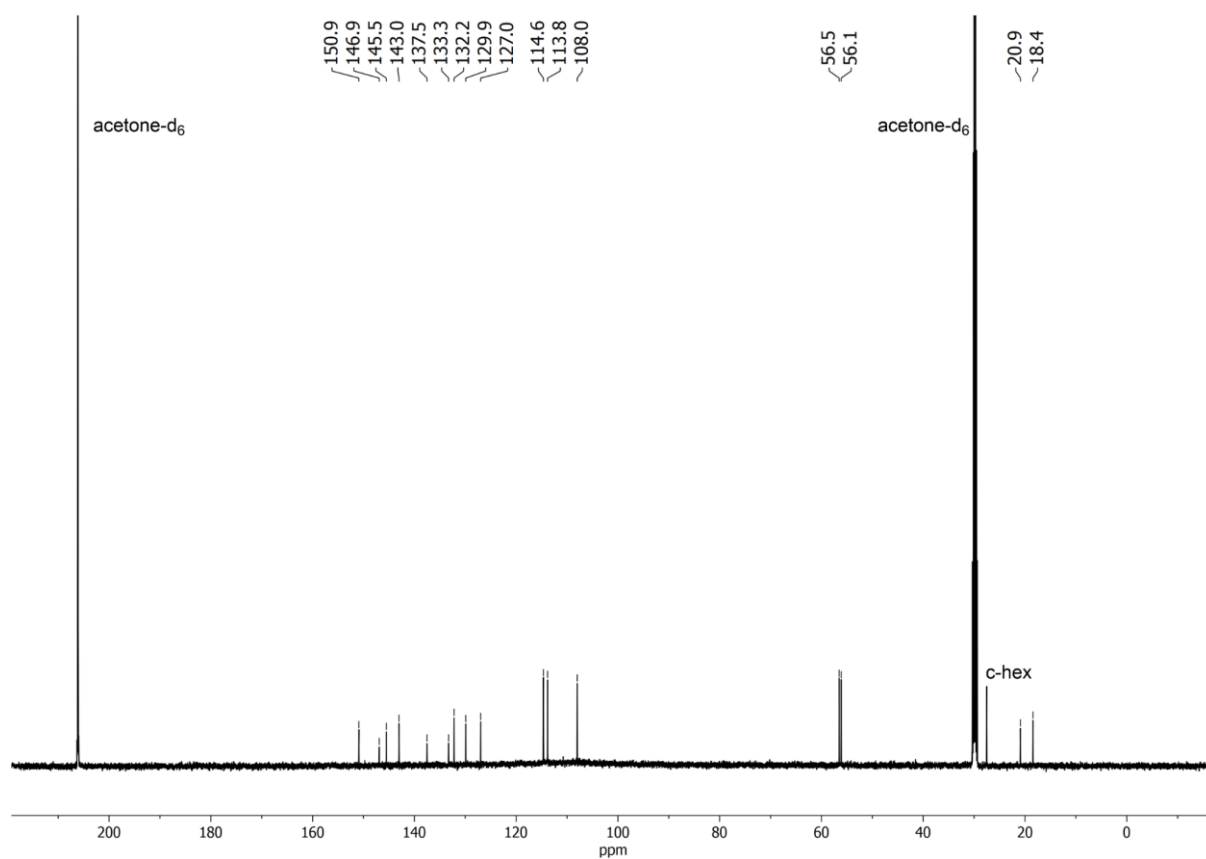


**Supplementary Figure 33.** <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum (126 MHz, 298 K, acetone-d<sub>6</sub>) of TAA-xy-Cl (**3**).

ref-TAA (5)

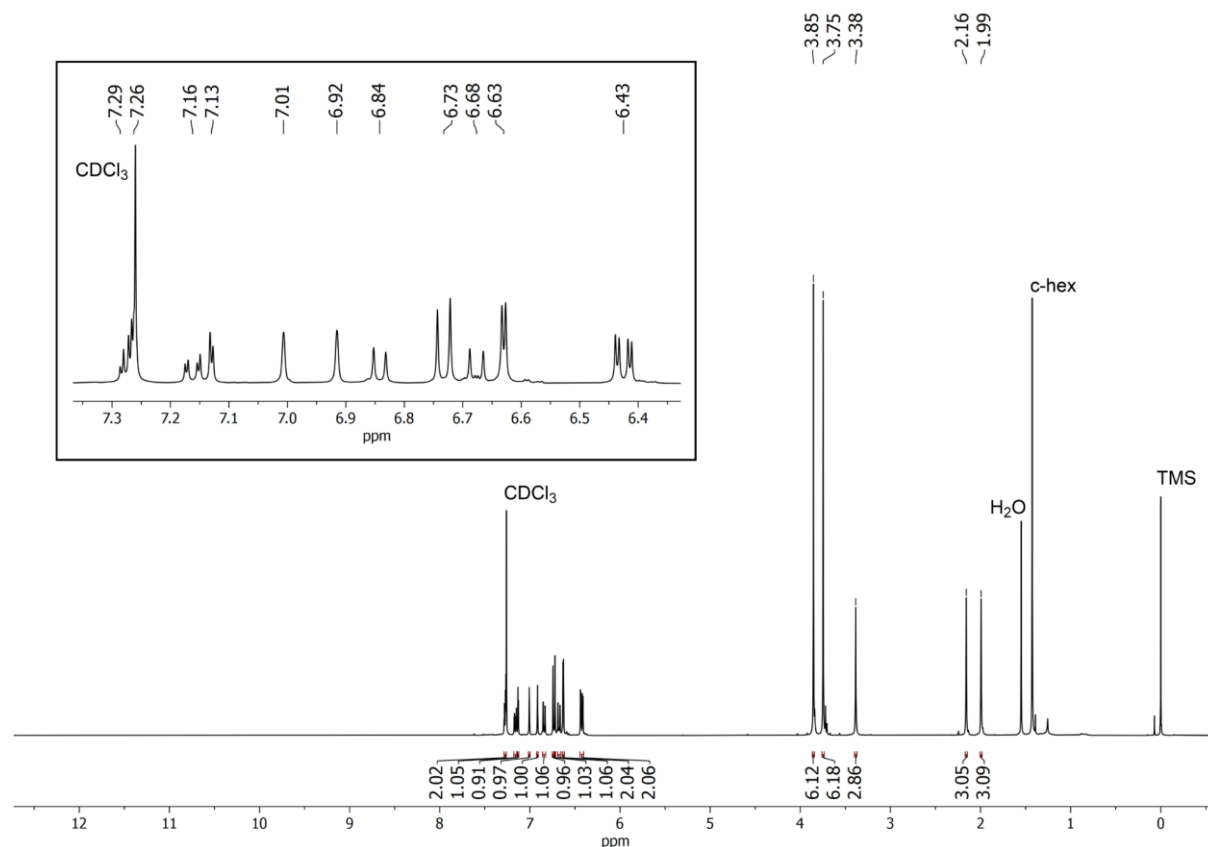


**Supplementary Figure 34.** <sup>1</sup>H-NMR spectrum (500 MHz, 298 K, acetone-d<sub>6</sub>) of ref-TAA (5).

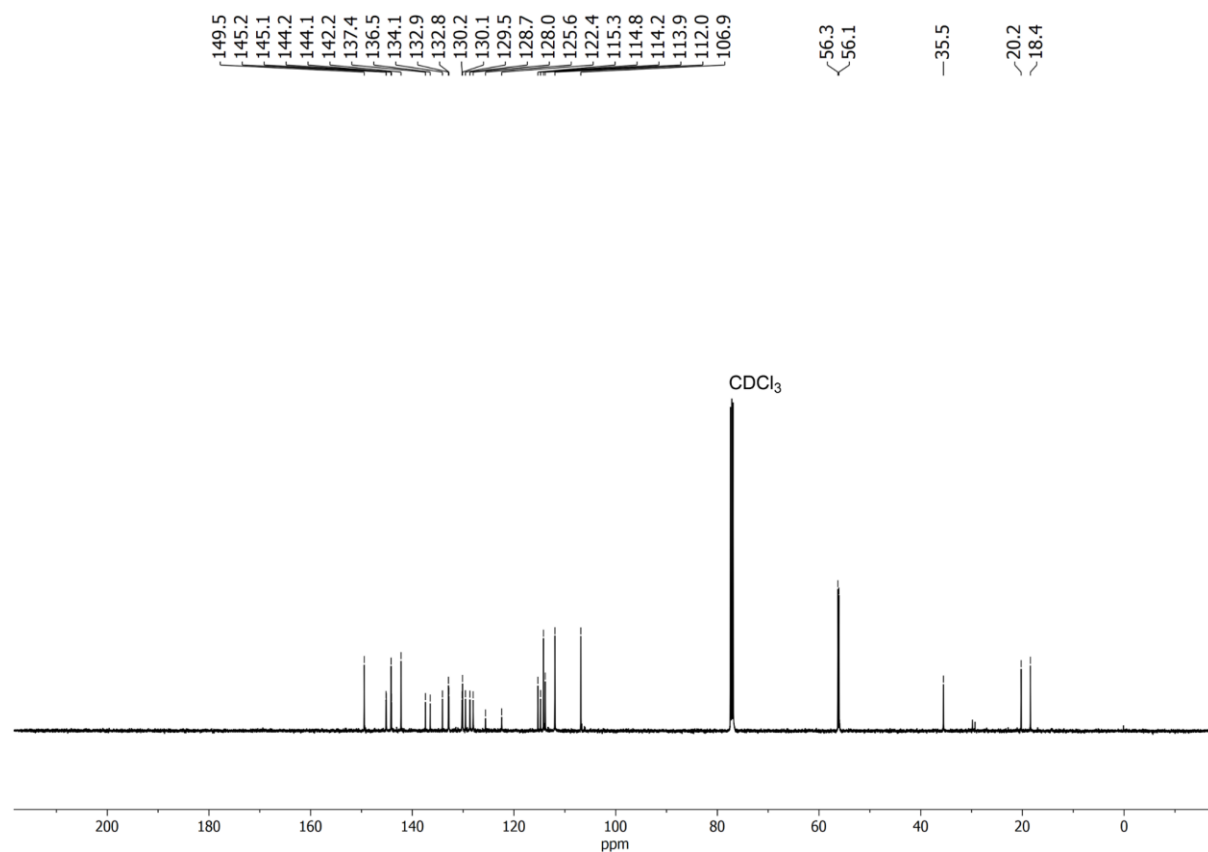


**Supplementary Figure 35.** <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum (126 MHz, 298 K, acetone-d<sub>6</sub>) of ref-TAA (5).

TAA-xy-PTZ-Br (6)

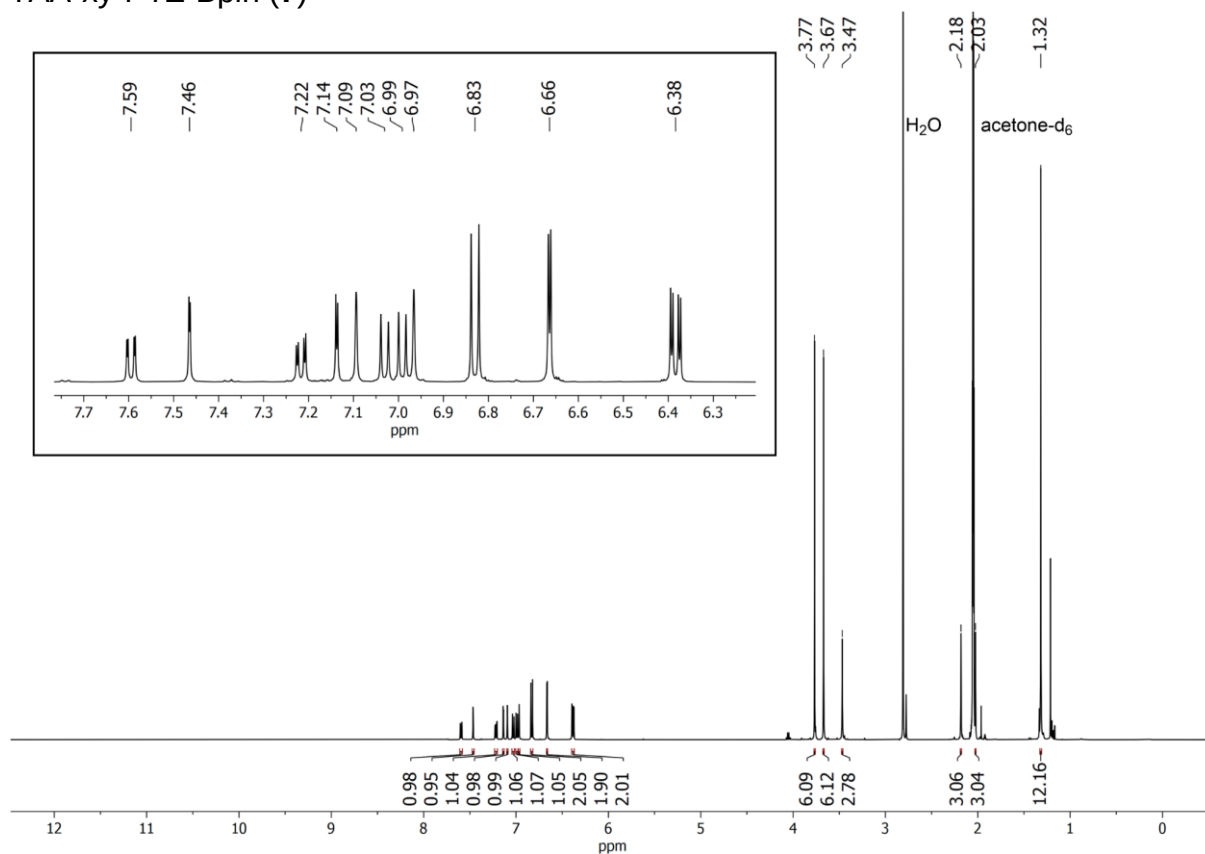


**Supplementary Figure 36.** <sup>1</sup>H-NMR spectrum (500 MHz, 298 K, CDCl<sub>3</sub>) of TAA-xy-PTZ-Br (6).

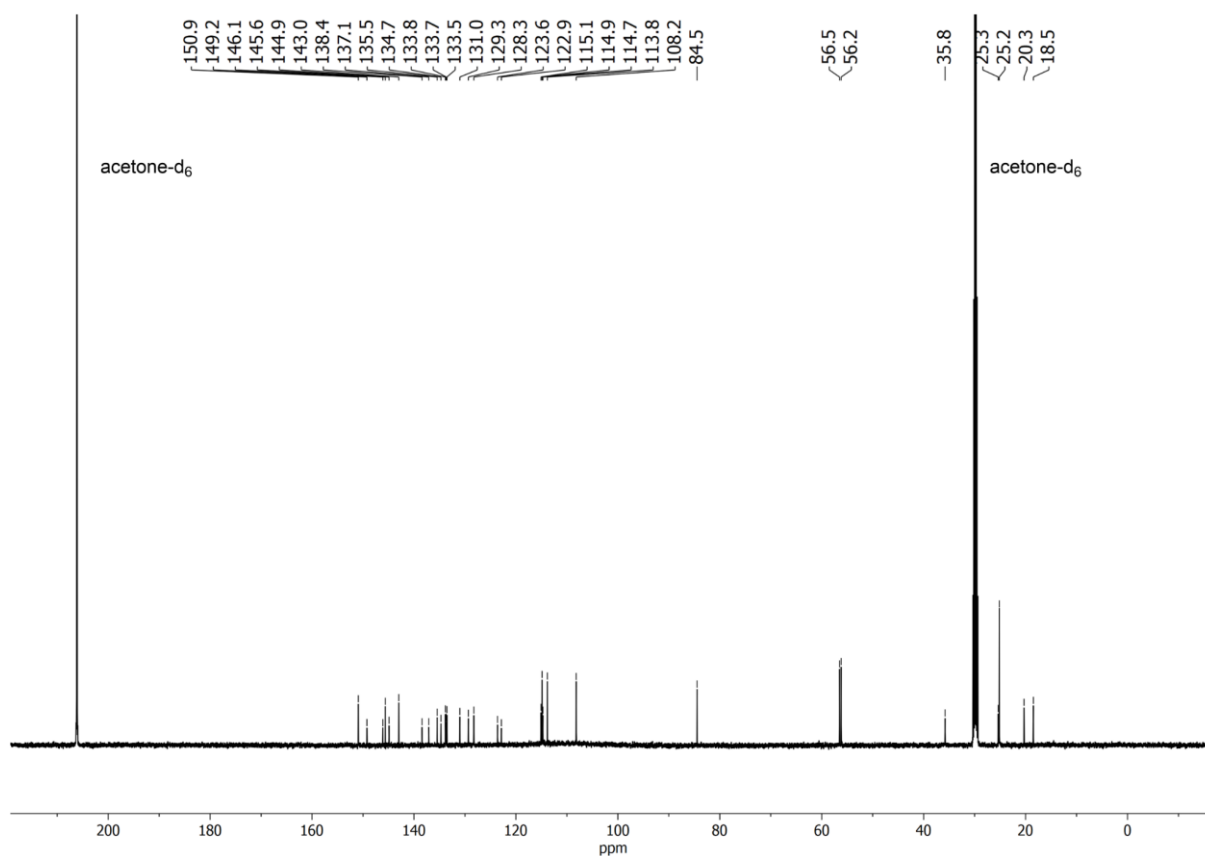


**Supplementary Figure 37.** <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum (126 MHz, 298 K, CDCl<sub>3</sub>) of TAA-xy-PTZ-Br (6).

TAA-xy-PTZ-Bpin (7)

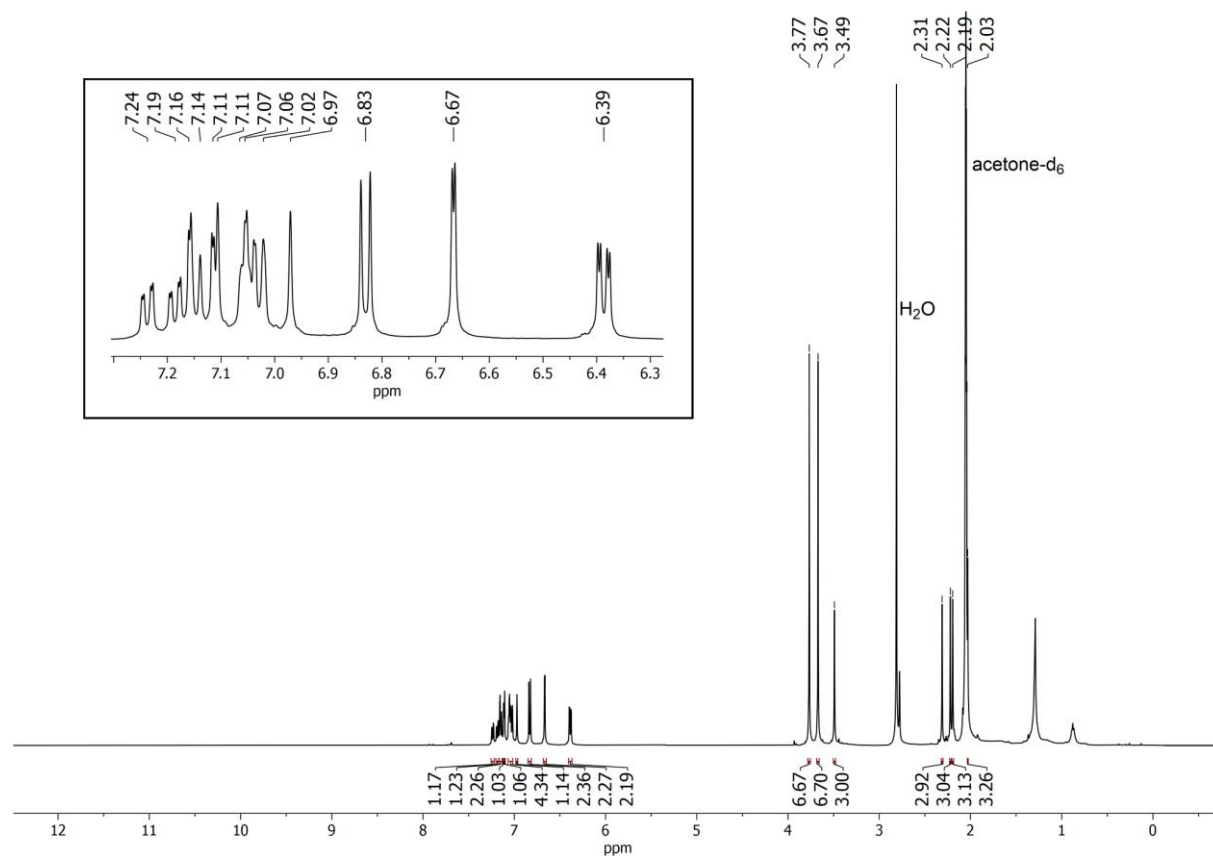


**Supplementary Figure 38.** <sup>1</sup>H-NMR spectrum (500 MHz, 298 K, acetone-d<sub>6</sub>) of TAA-xy-PTZ-Bpin (7).

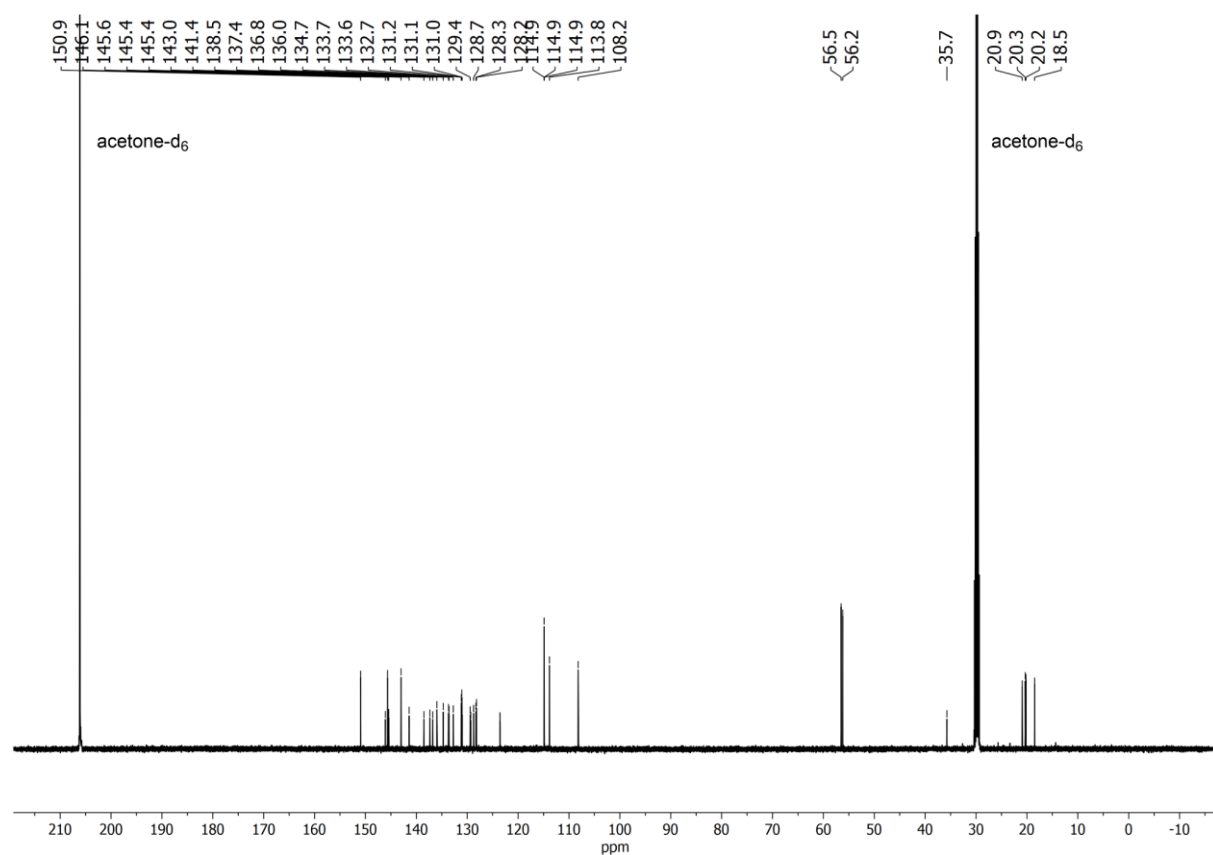


**Supplementary Figure 39.** <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum (126 MHz, 298 K, acetone-d<sub>6</sub>) of TAA-xy-PTZ-Bpin (7).

TAA-xy-PTZ-xy (8)

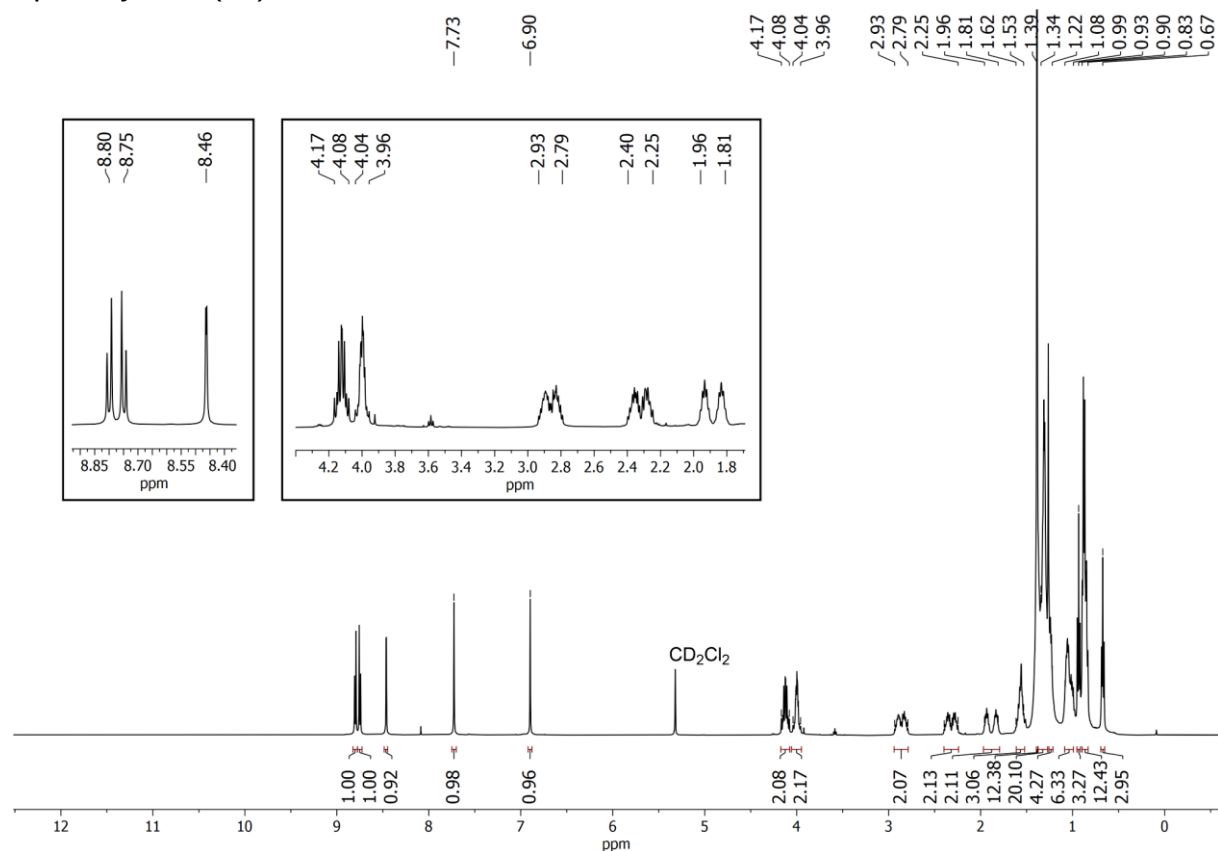


**Supplementary Figure 40.** <sup>1</sup>H-NMR spectrum (500 MHz, 298 K, acetone-d<sub>6</sub>) of TAA-xy-PTZ-xy (8).

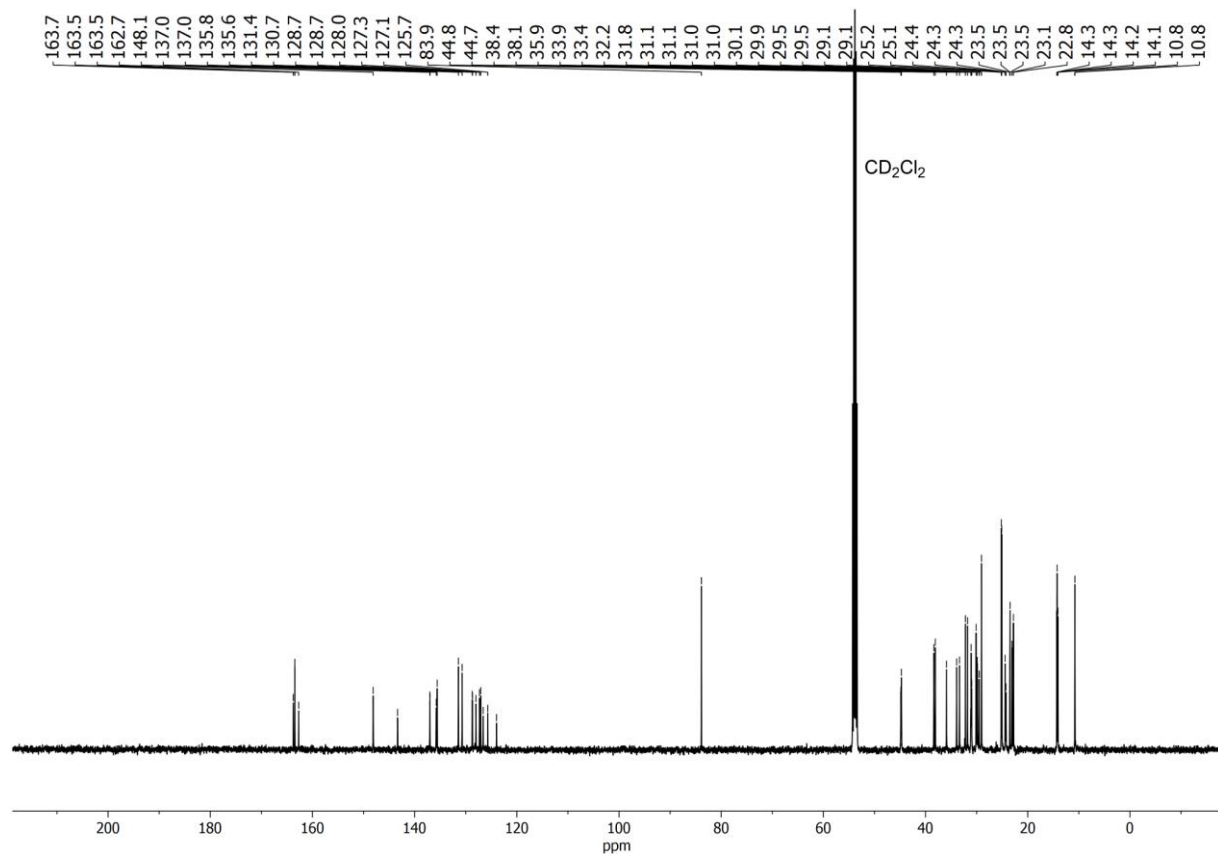


**Supplementary Figure 41.** <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum (126 MHz, 298 K, acetone-d<sub>6</sub>) of TAA-xy-PTZ-xy (8).

Bpin-hxy-NDI (**10**)

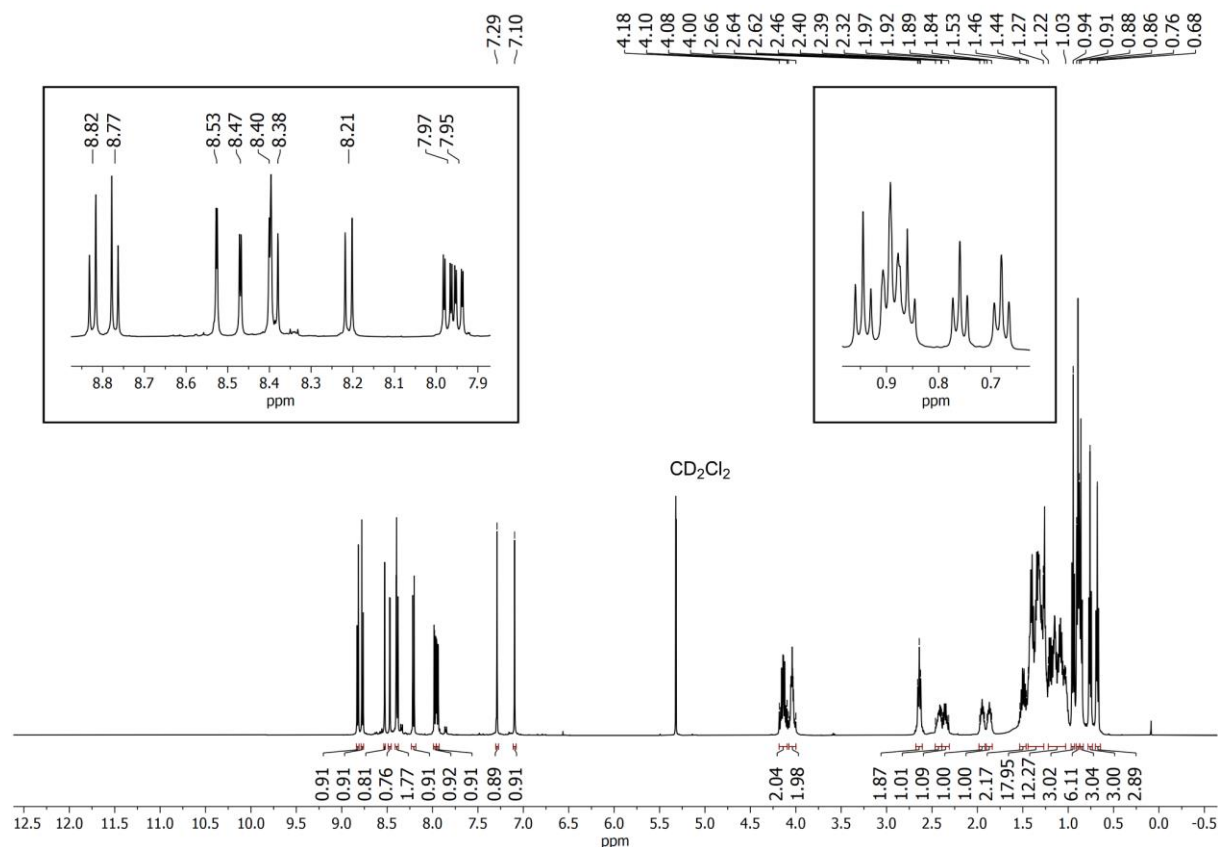


**Supplementary Figure 42.** <sup>1</sup>H-NMR spectrum (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of Bpin-hxy-NDI (**10**).

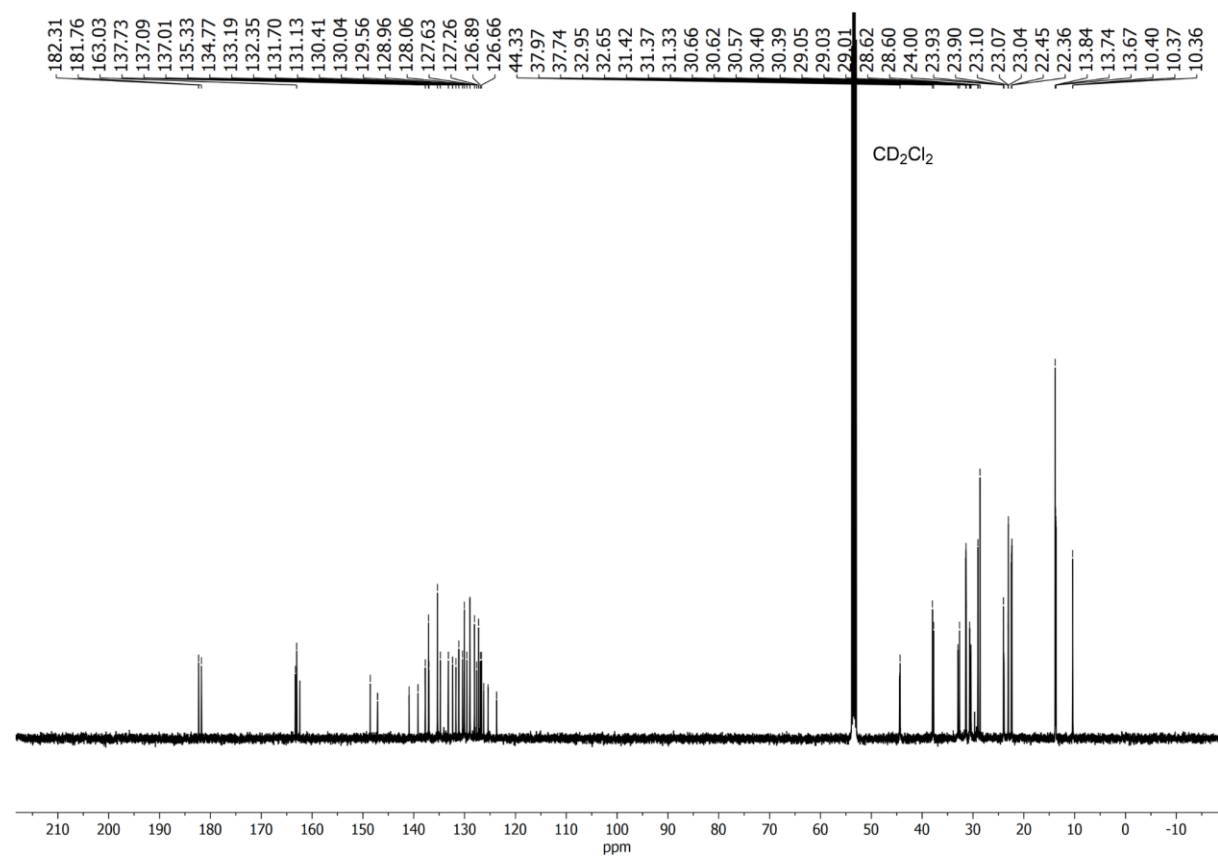


**Supplementary Figure 43.** <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum (126 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of Bpin-hxy-NDI (**10**).

Br-AQ-hxy-NDI (**11**)

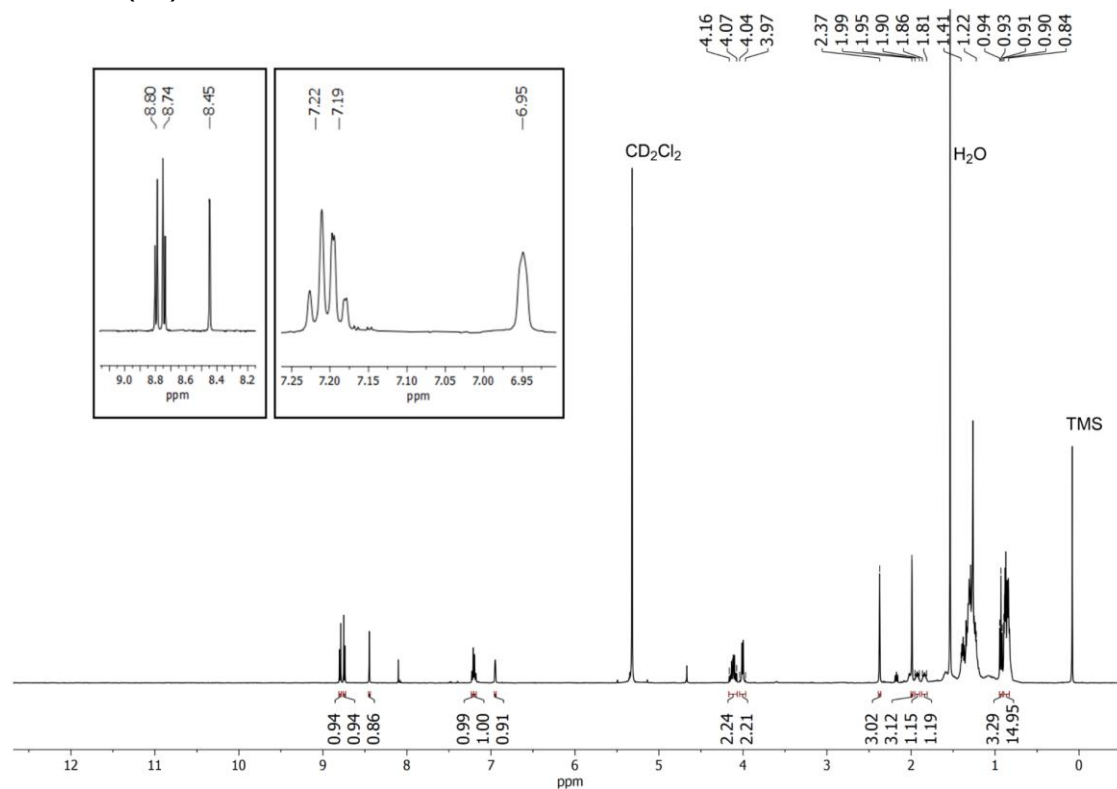


**Supplementary Figure 44.** <sup>1</sup>H-NMR spectrum (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of Br-AQ-hxy-NDI (**11**).

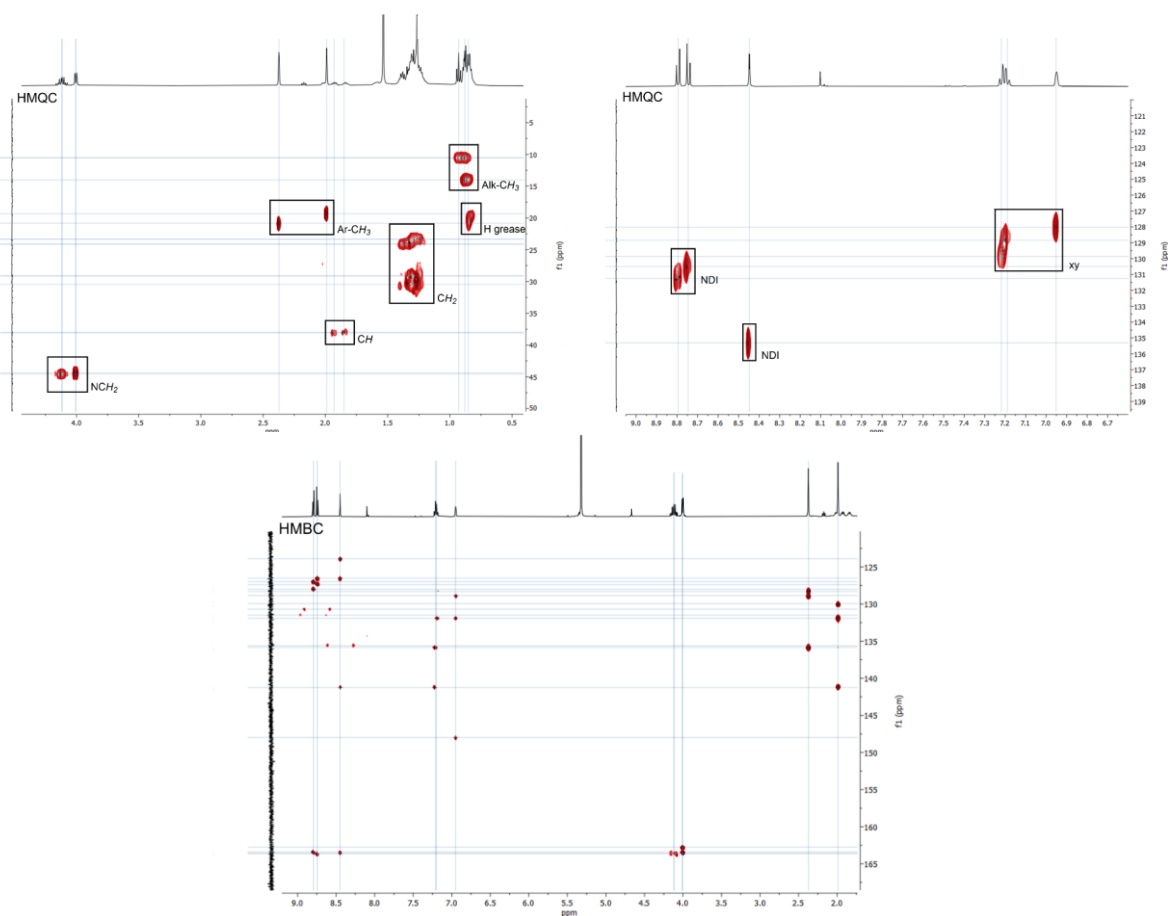


**Supplementary Figure 45.** <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum (126 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of Br-AQ-hxy-NDI (**11**).

ref-NDI (12)

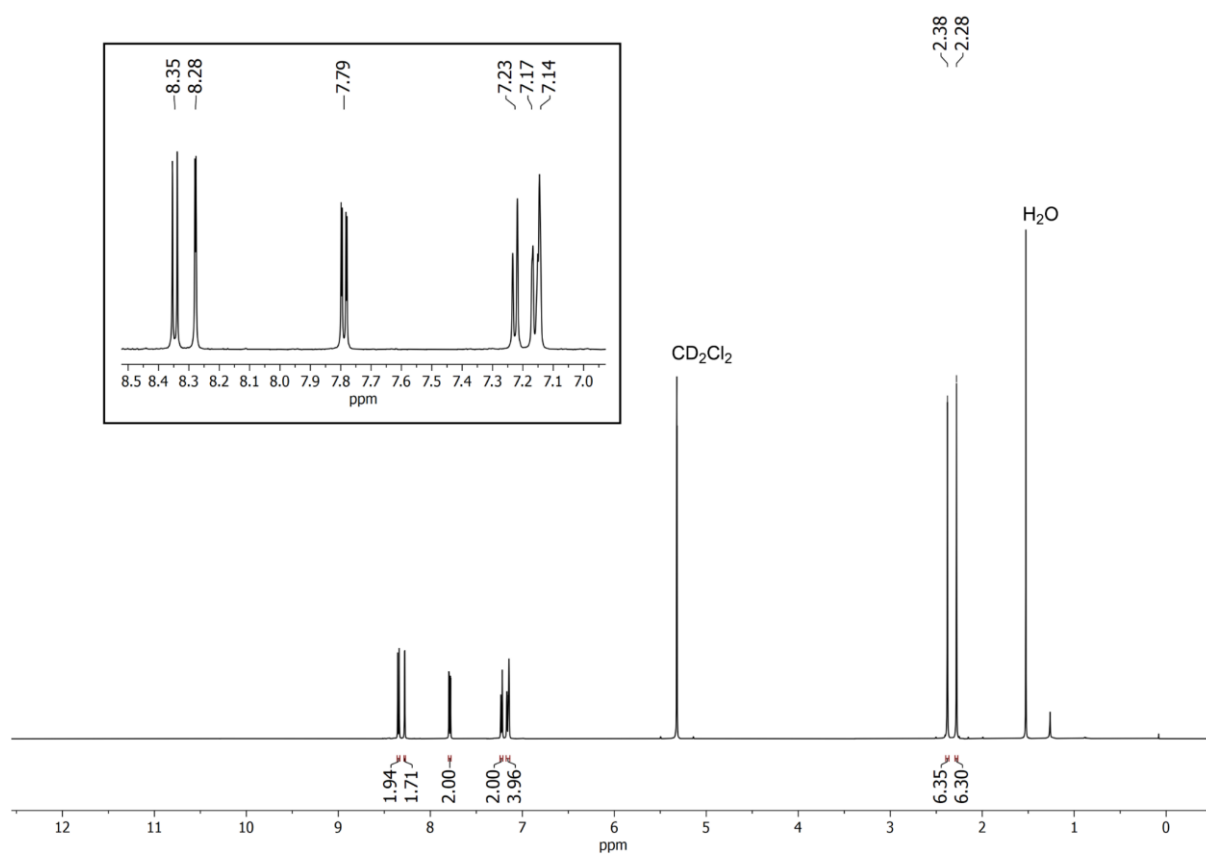


Supplementary Figure 46. <sup>1</sup>H-NMR spectrum (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of ref-NDI (12).

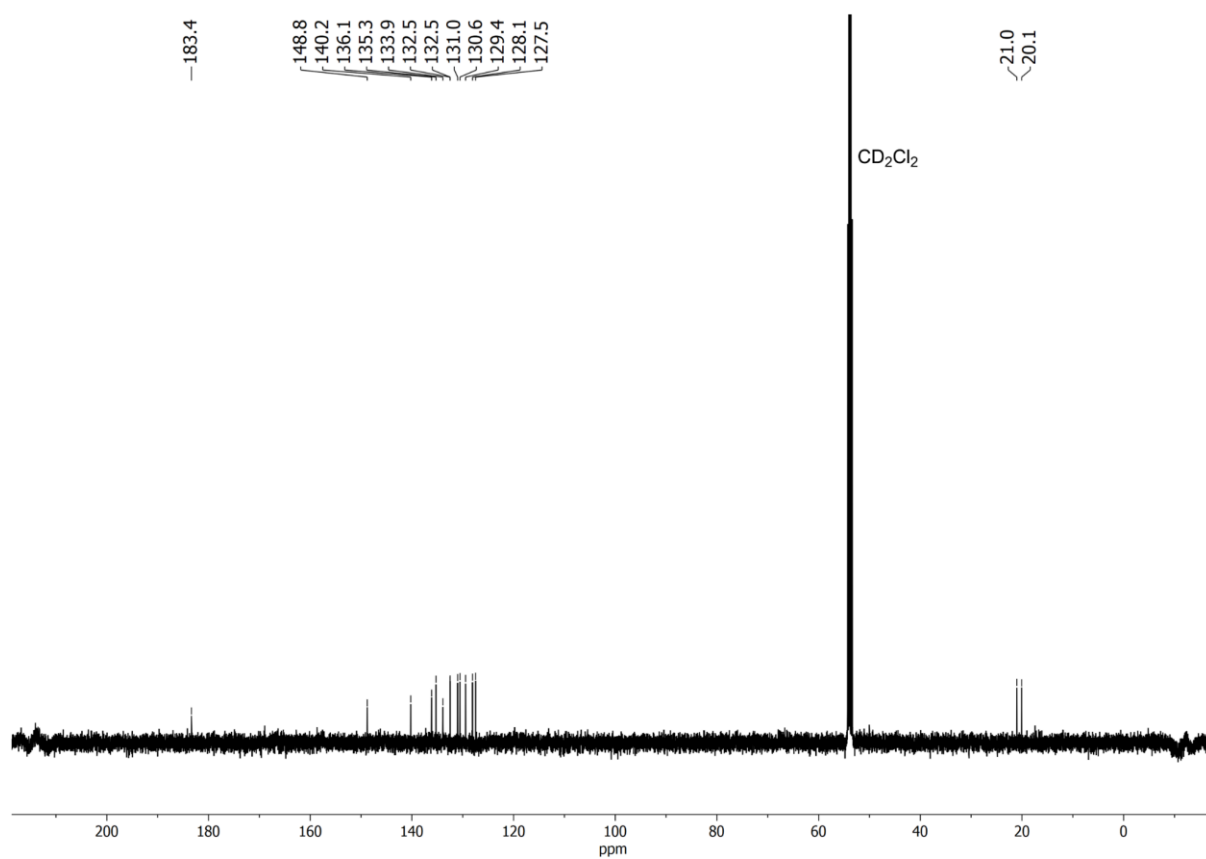


Supplementary Figure 47. HMQC and HMBC NMR spectra (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of ref-NDI (12).

ref-AQ (**13**)

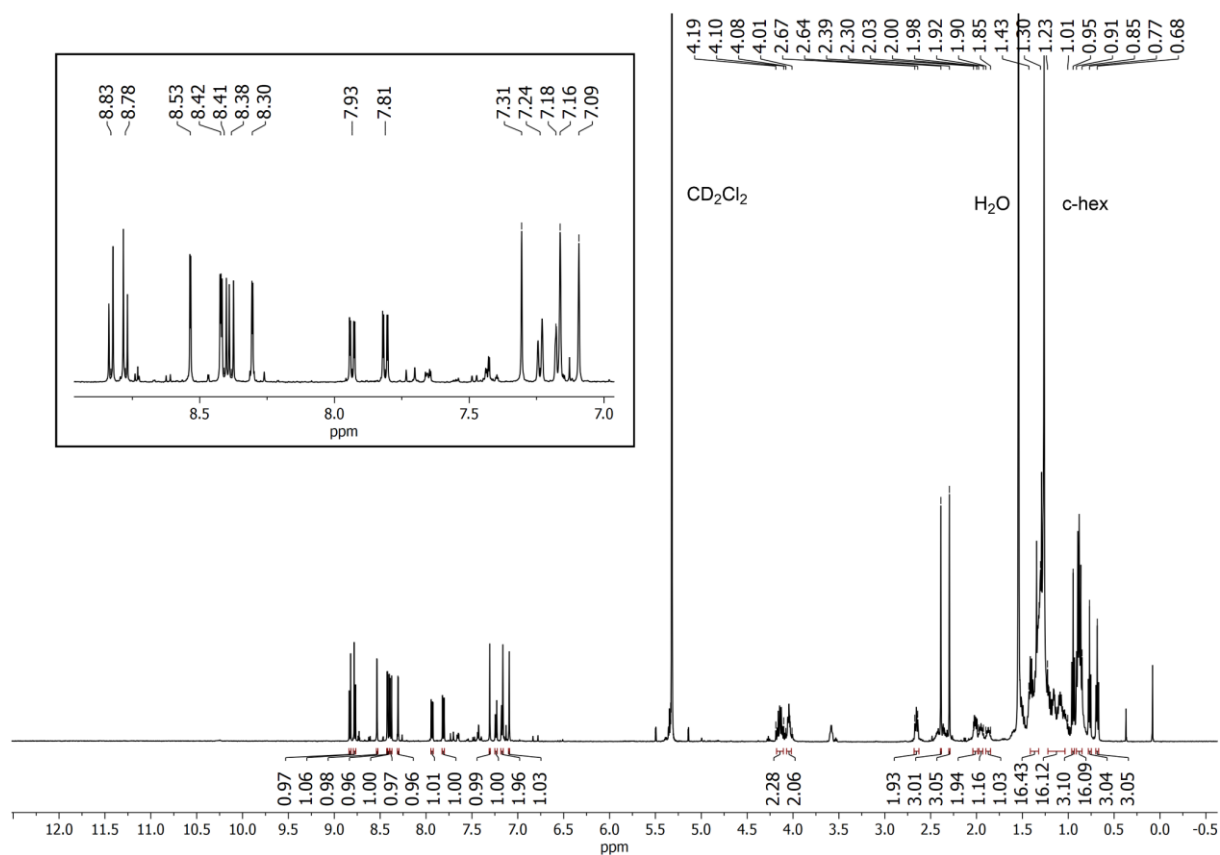


**Supplementary Figure 48.** <sup>1</sup>H-NMR spectrum (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of ref-AQ (**13**).



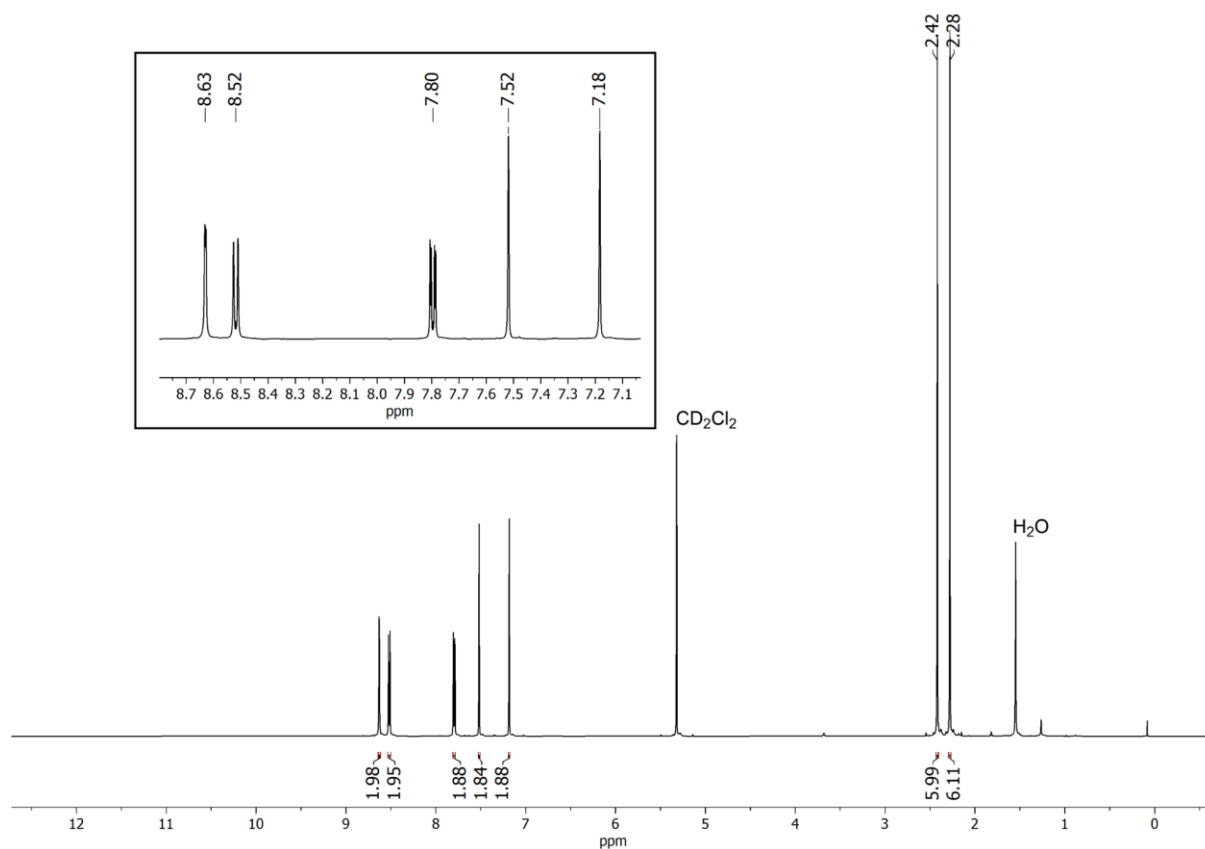
**Supplementary Figure 49.** <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum (126 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of ref-AQ (**13**).

xy-AQ-hxy-NDI (**14**)

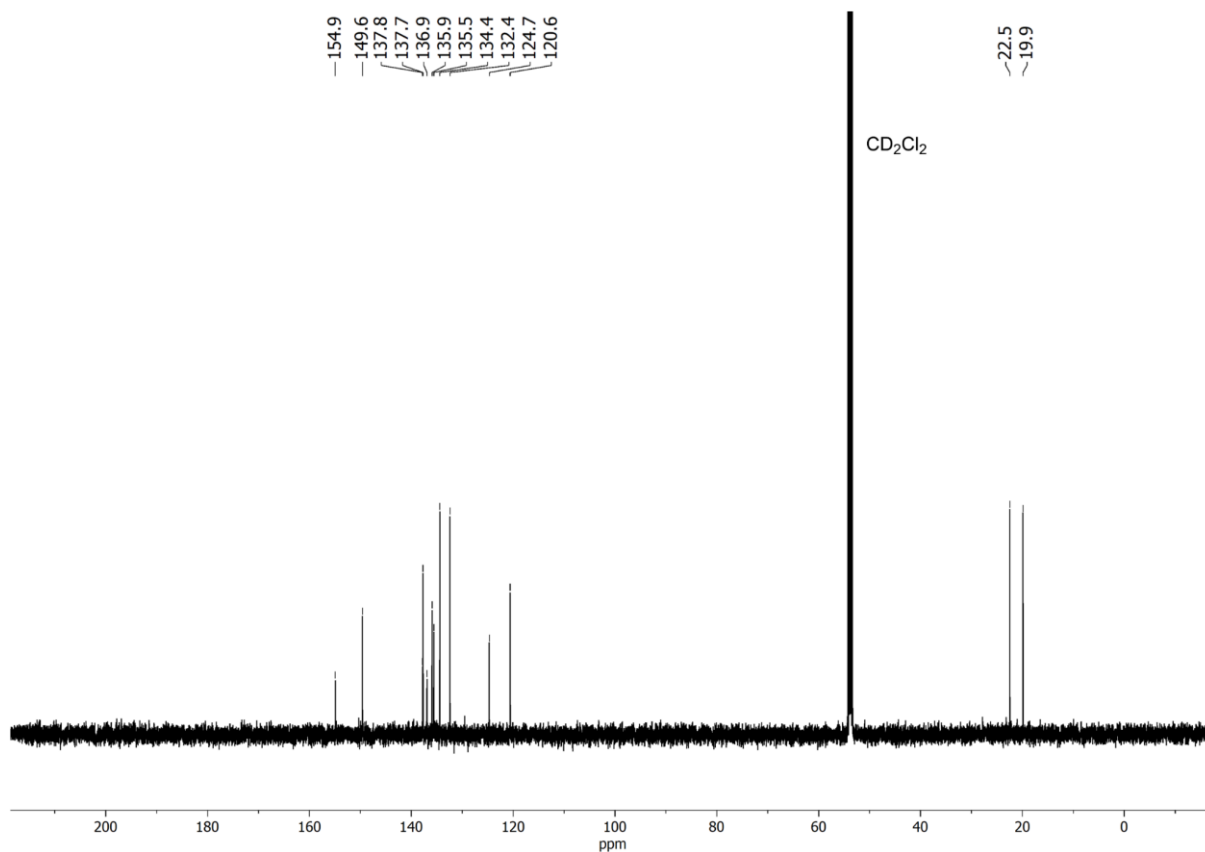


**Supplementary Figure 50.** <sup>1</sup>H-NMR spectrum (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of xy-AQ-hxy-NDI (**14**).

Br-xy-bpy-xy-Br (**15**)

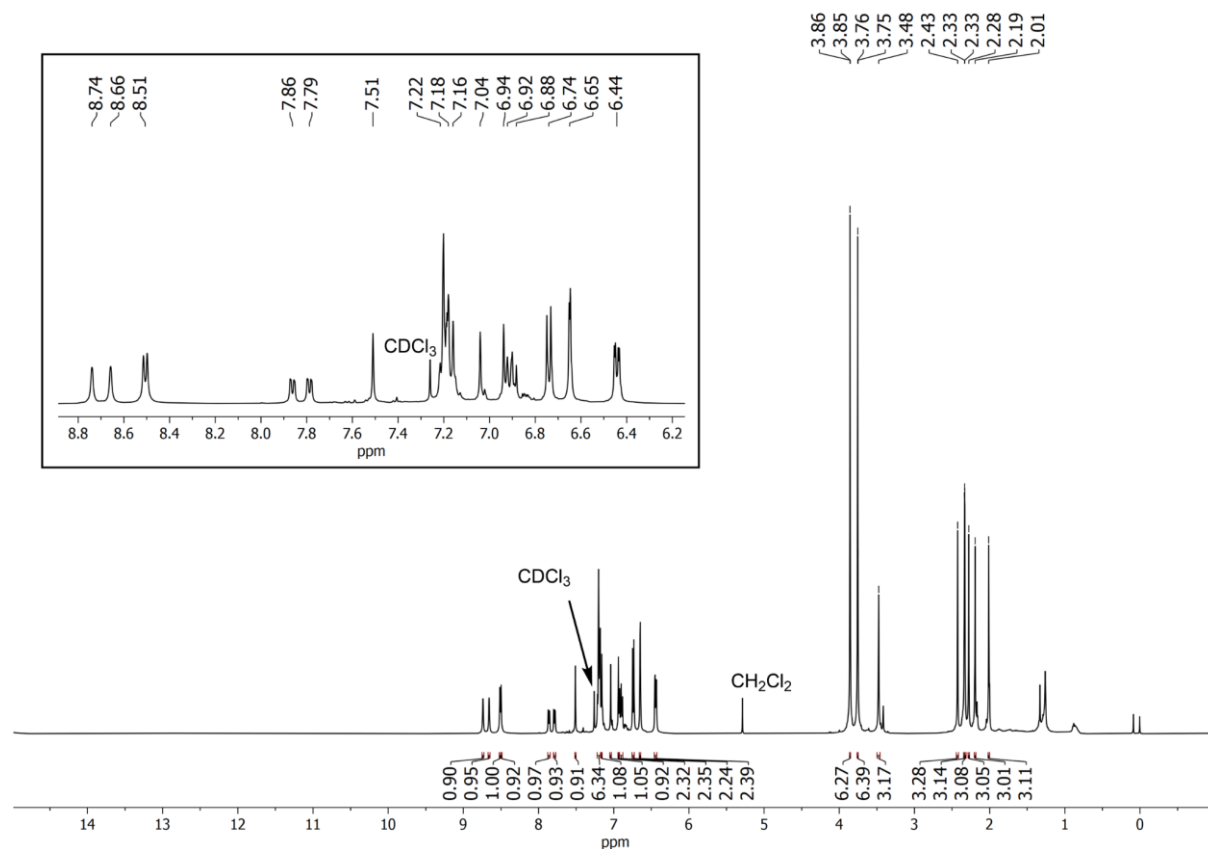


**Supplementary Figure 51.** <sup>1</sup>H-NMR spectrum (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of Br-xy-bpy-xy-Br (**15**).

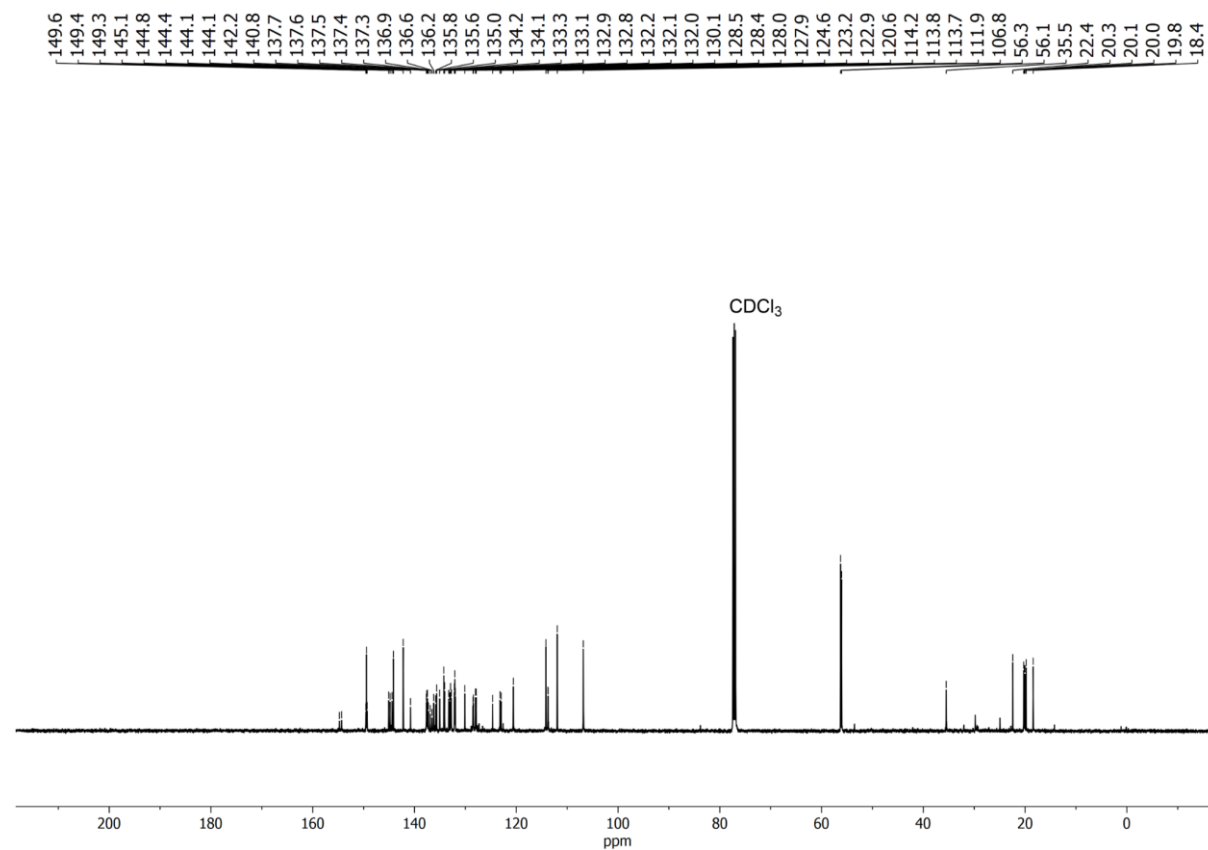


**Supplementary Figure 52.** <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum (126 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of Br-xy-bpy-xy-Br (**15**).

TAA-xy-PTZ-xy-bpy-xy-Br (**16**)

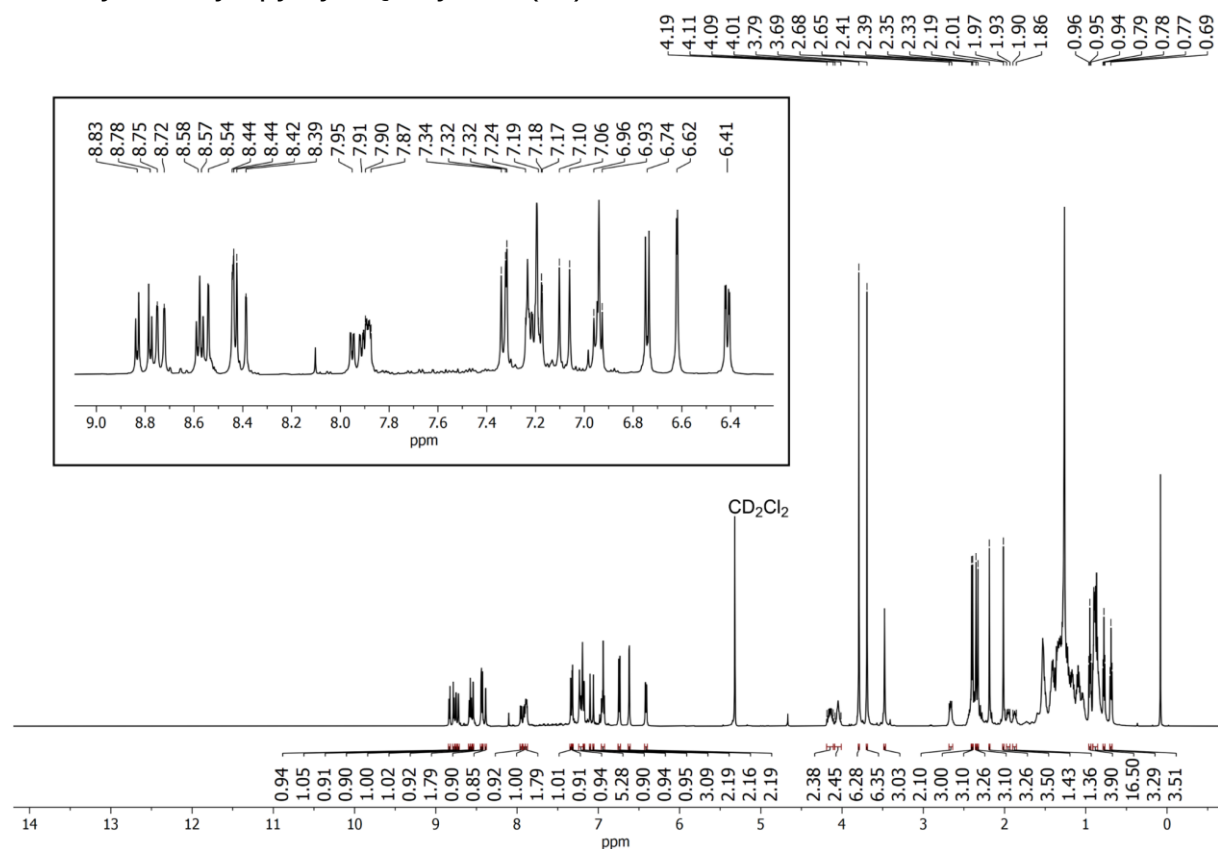


**Supplementary Figure 53.** <sup>1</sup>H-NMR spectrum (500 MHz, 298 K, CDCl<sub>3</sub>) of TAA-xy-PTZ-xy-bpy-xy-Br (**16**).

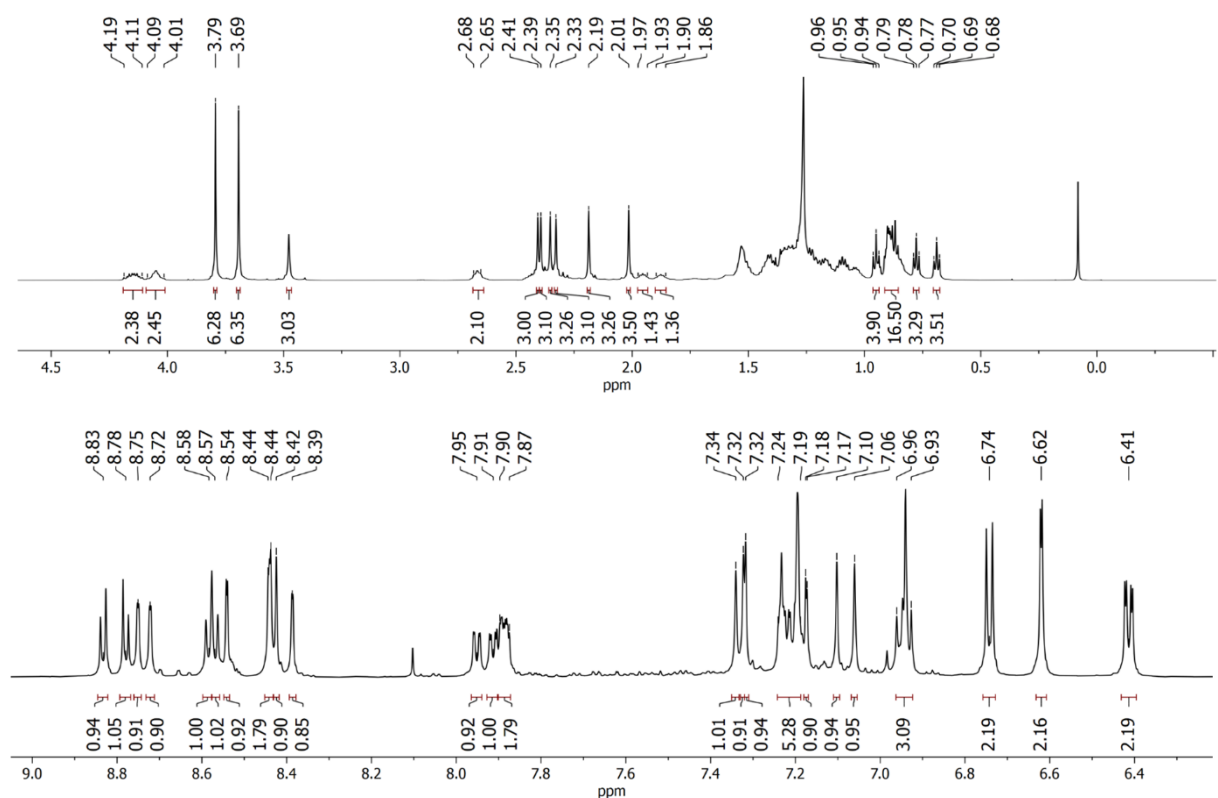


**Supplementary Figure 54.** <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum (126 MHz, 298 K, CDCl<sub>3</sub>) of TAA-xy-PTZ-xy-bpy-xy-Br (**16**).

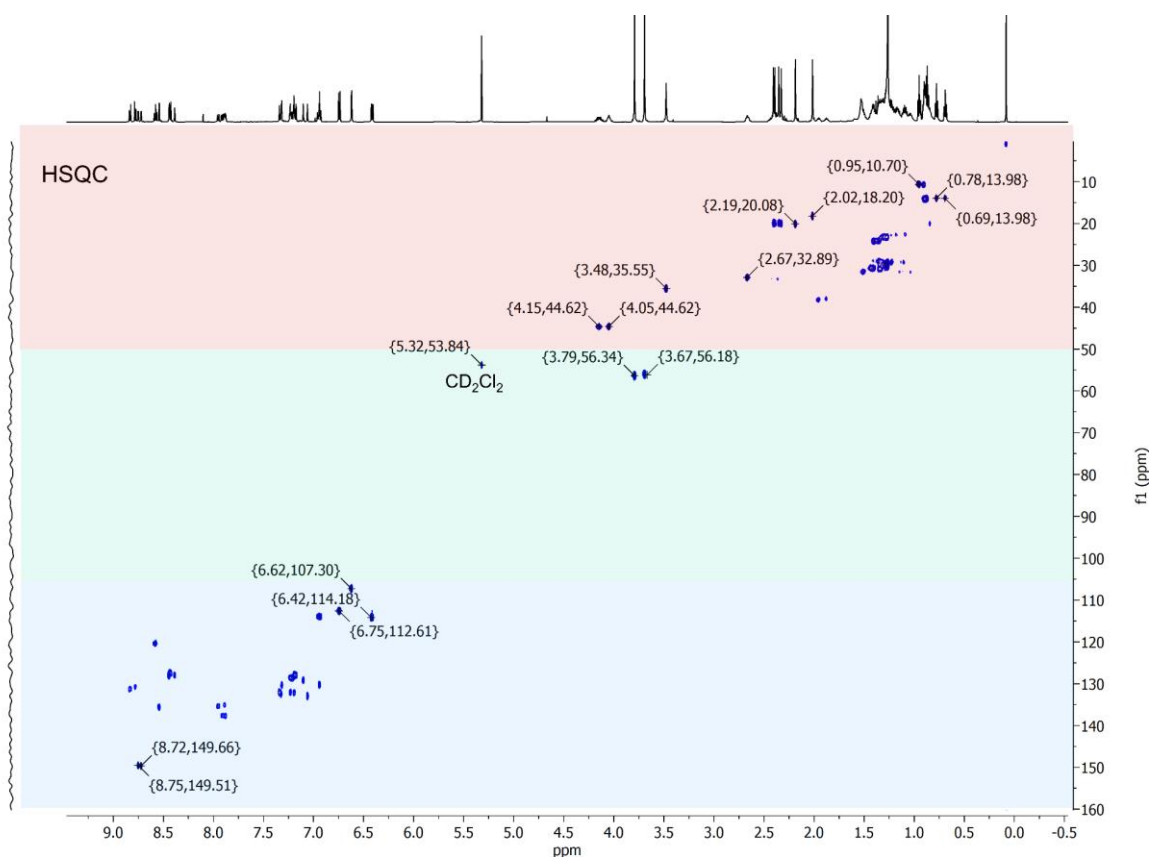
TAA-xy-PTZ-xy-bpy-xy-AQ-hxy-NDI (**18**)



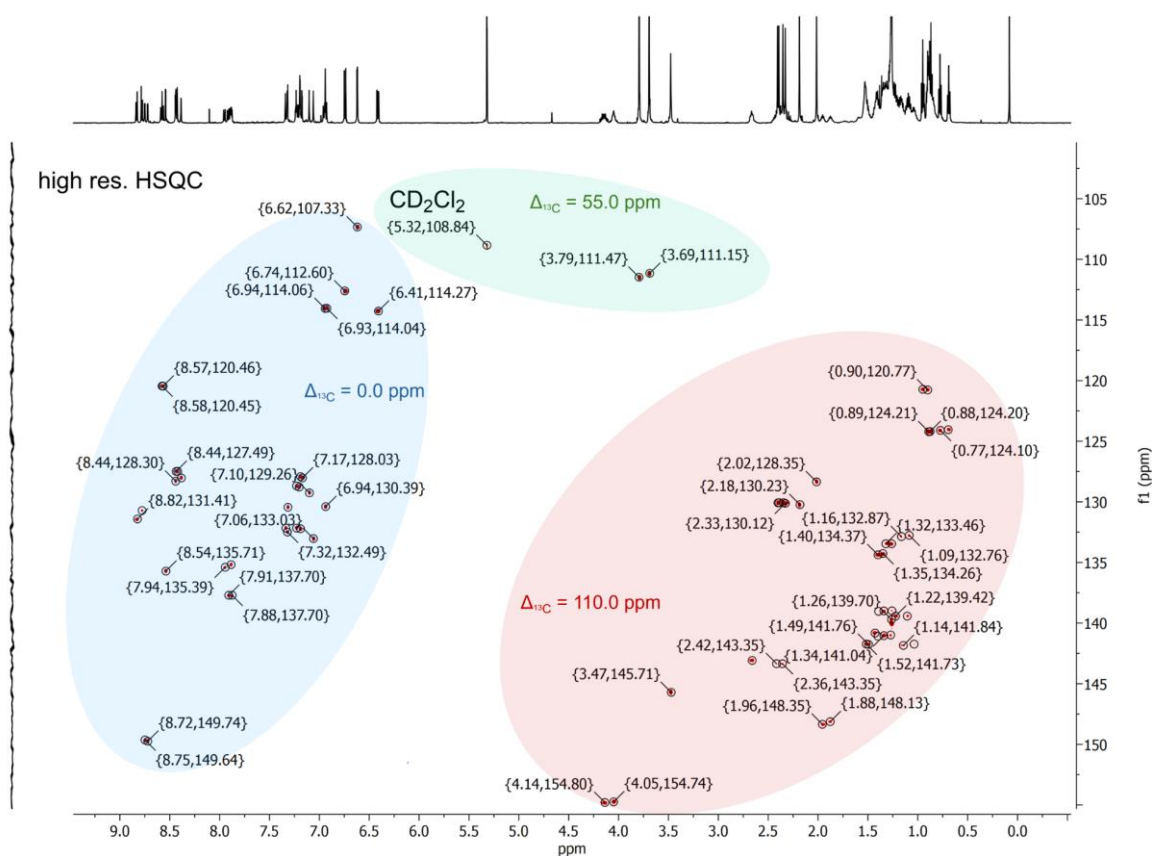
**Supplementary Figure 55.** <sup>1</sup>H-NMR spectrum (600 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of the main ligand TAA-xy-PTZ-xy-bpy-xy-AQ-hxy-NDI (**18**).



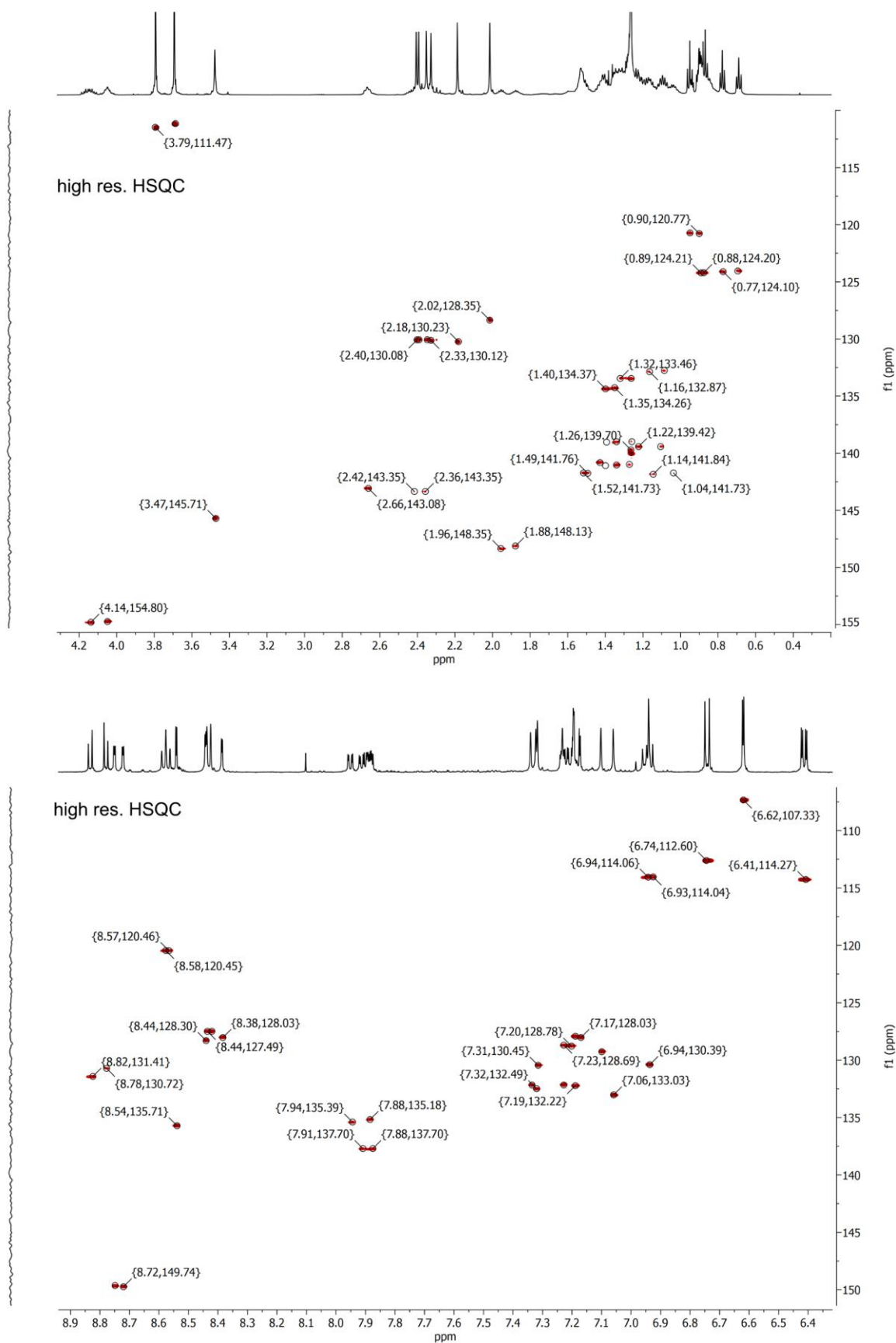
**Supplementary Figure 56.** Zoom into the aliphatic (*top*) and the aromatic (*bottom*) region of Supplementary Figure 55.



**Supplementary Figure 57.** HSQC NMR spectrum (600 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of the main ligand **18**.

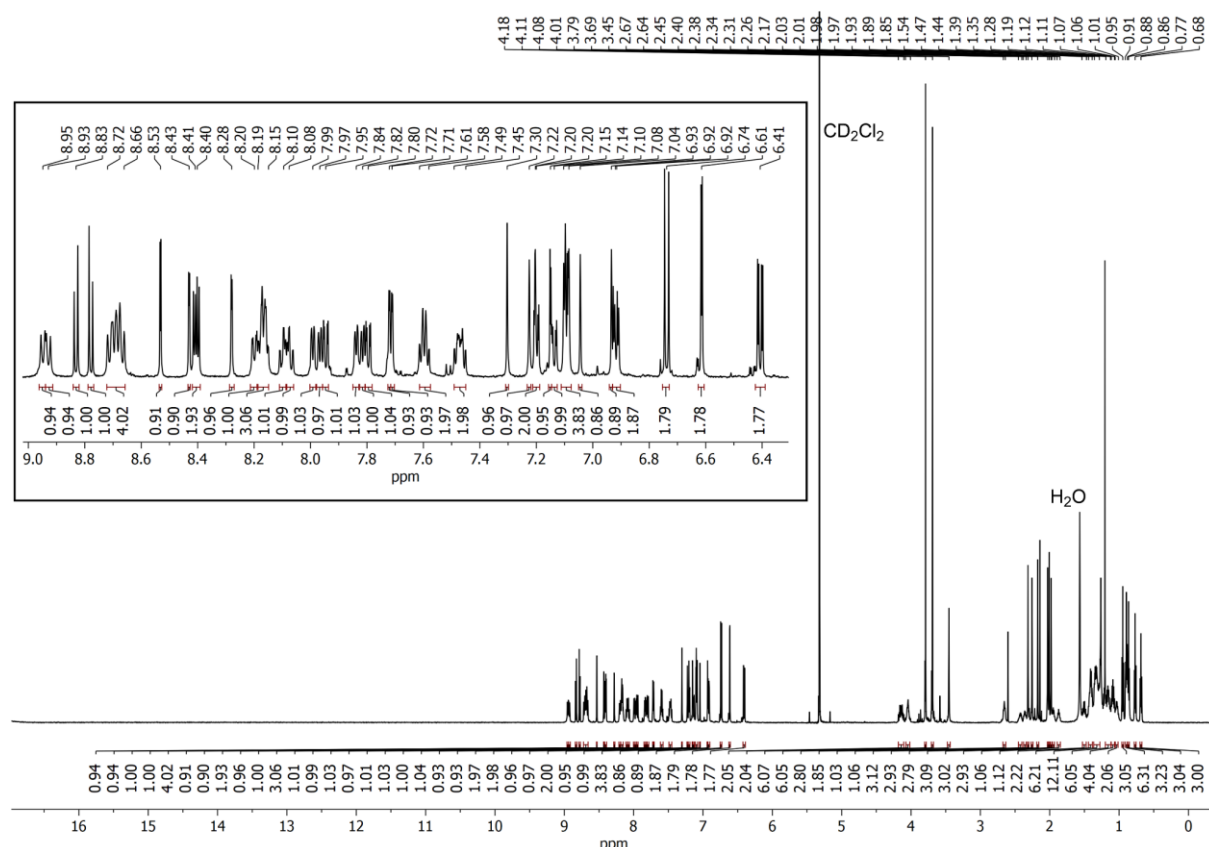


**Supplementary Figure 58.** Aliased high-resolution HSQC NMR spectrum (600 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of the main ligand **18** with a spectral width of 55 ppm.

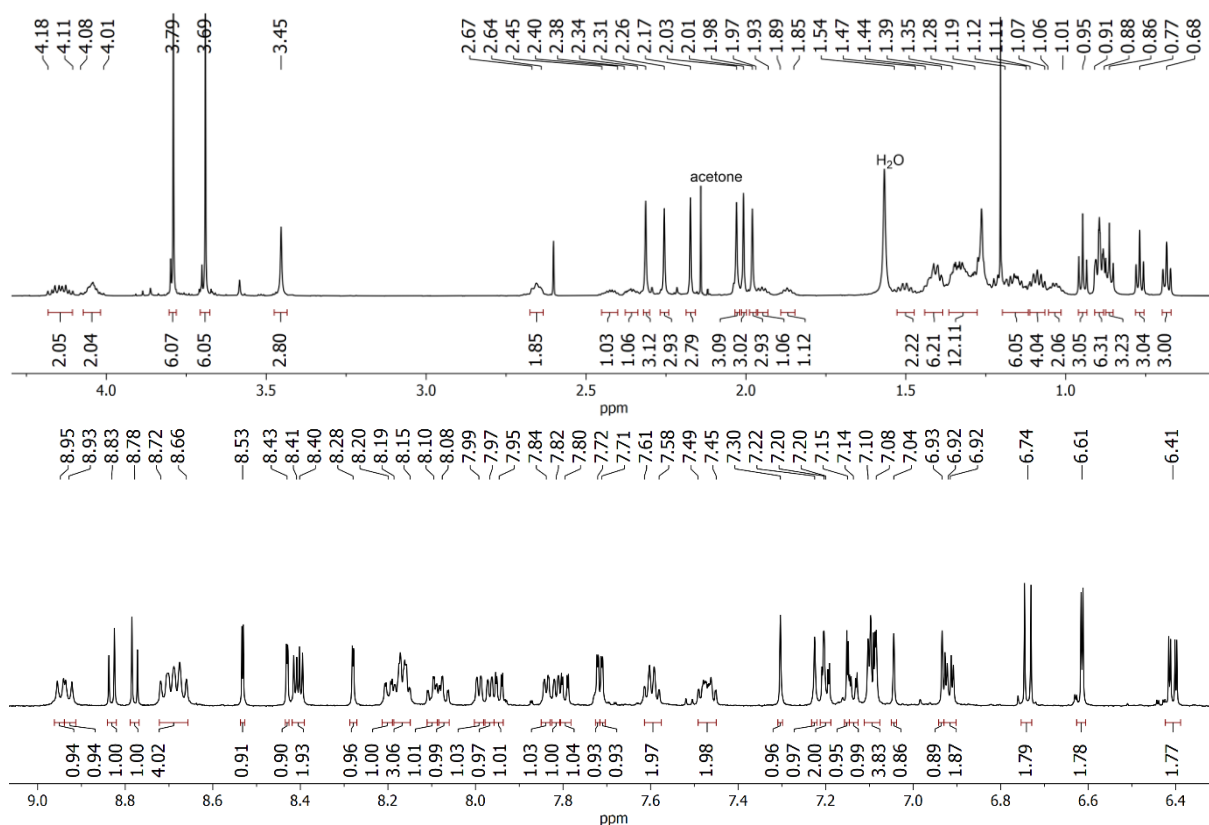


**Supplementary Figure 59.** Zoom into the aliphatic (*top*) and the aromatic (*bottom*) region of the high-resolution HSQC NMR spectrum from Supplementary Figure 58.

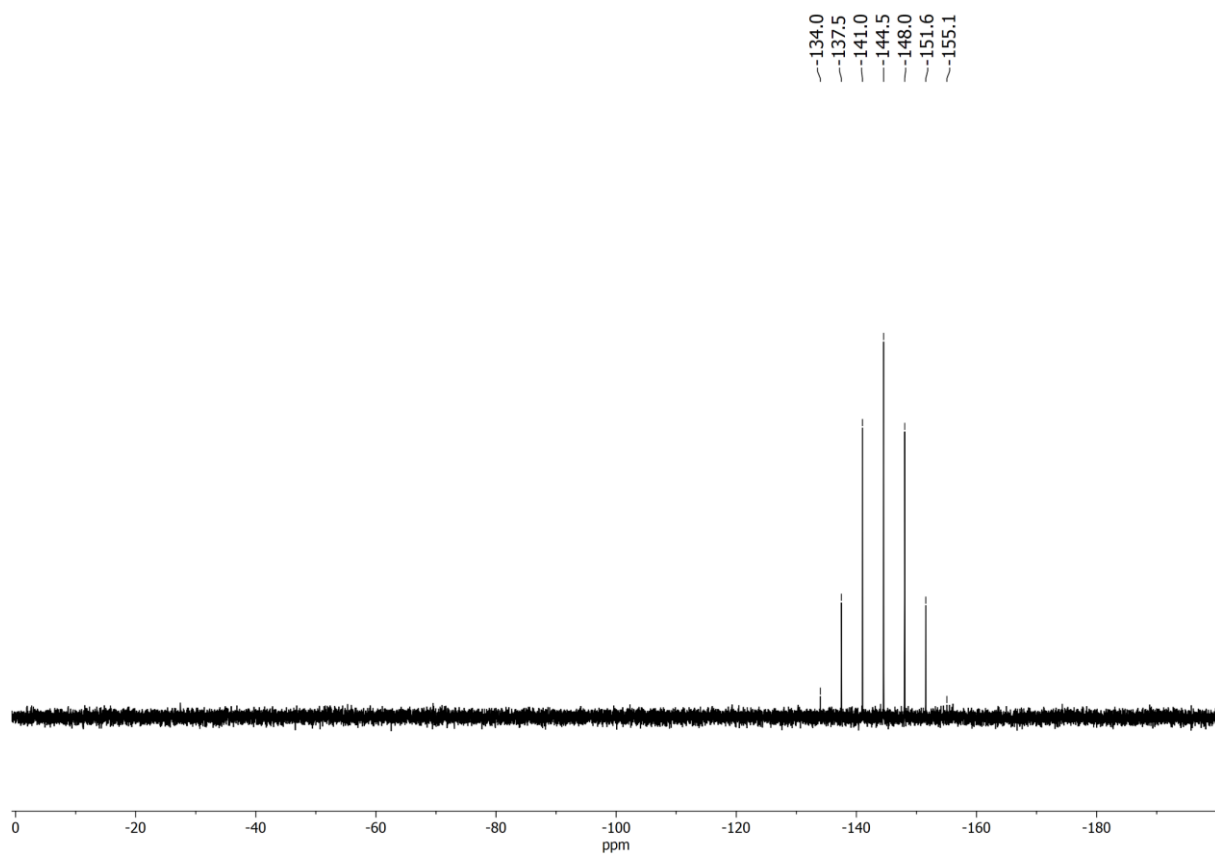
[TAA-xy-PTZ-xy-Ru(bpy)<sub>3</sub>-xy-AQ-hxy-NDI][PF<sub>6</sub>]<sub>2</sub> (**19**)



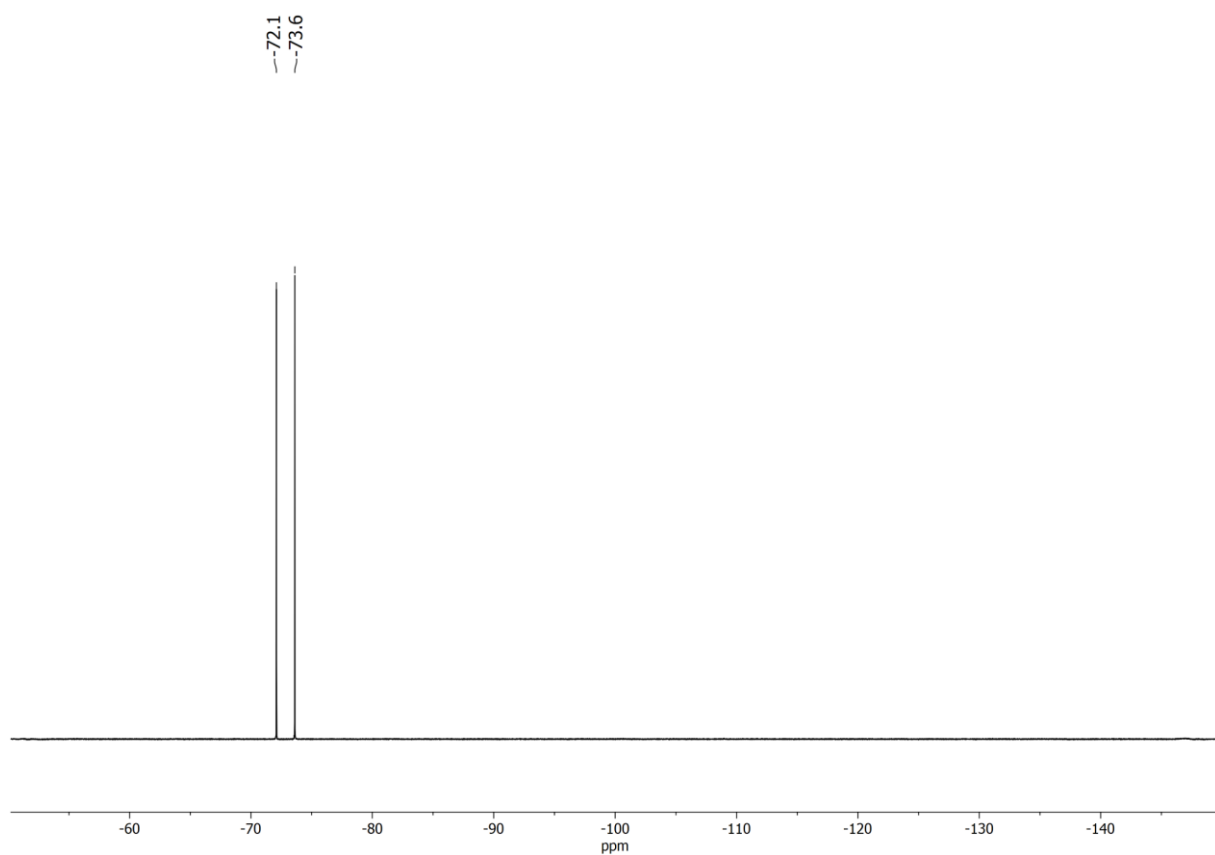
**Supplementary Figure 60.** <sup>1</sup>H-NMR spectrum (600 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of the pentad [TAA-xy-PTZ-xy-Ru(bpy)<sub>3</sub>-xy-AQ-hxy-NDI][PF<sub>6</sub>]<sub>2</sub> (**19**).



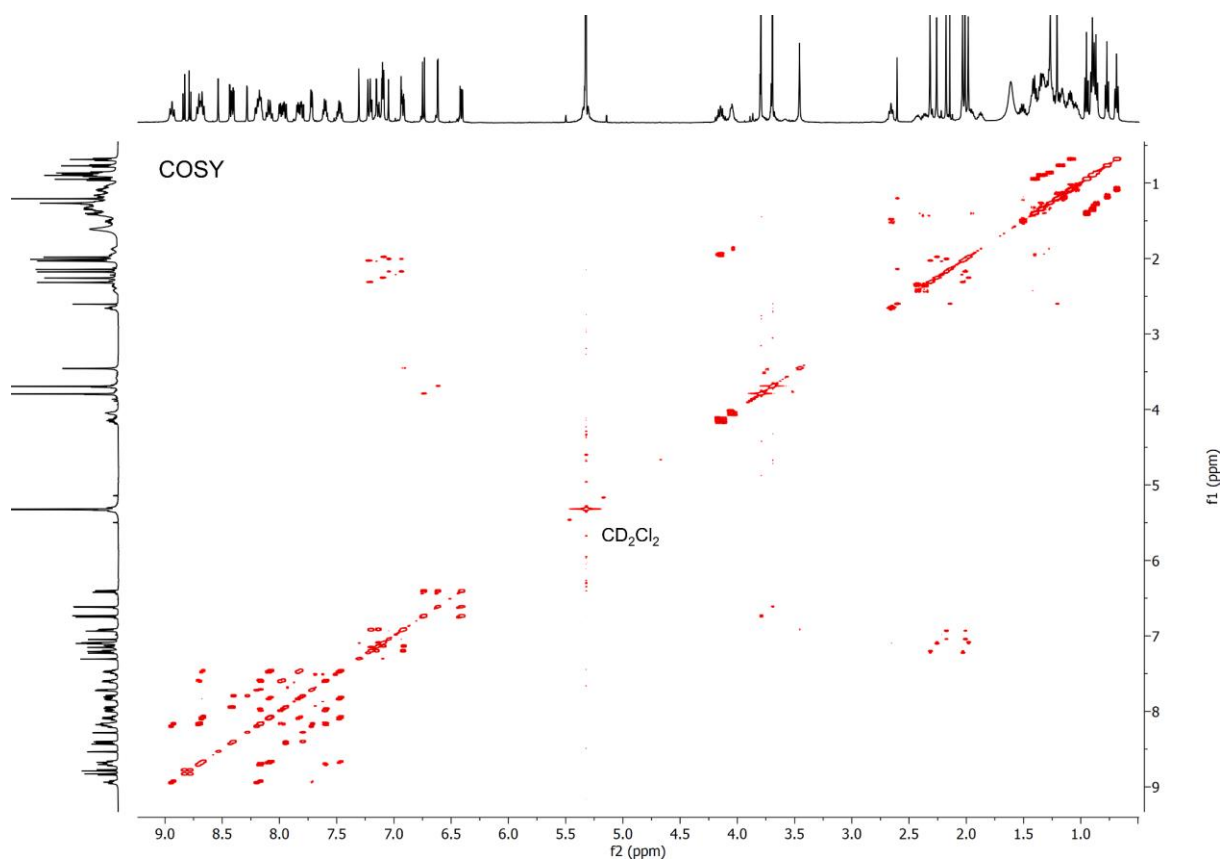
**Supplementary Figure 61.** Zoom into the aliphatic (*top*) and the aromatic (*bottom*) region of Supplementary Figure 60.



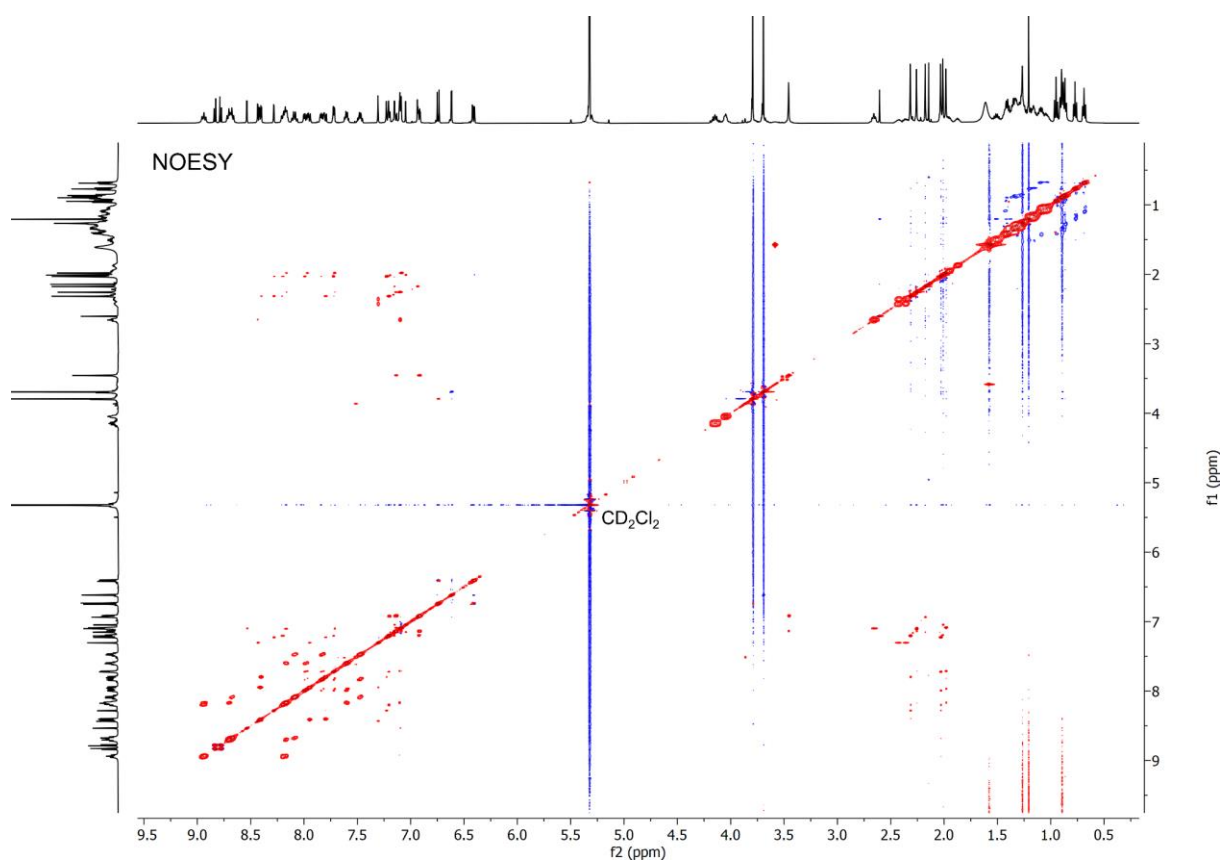
**Supplementary Figure 62.** <sup>31</sup>P-NMR spectrum (202 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of the pentad (**19**).



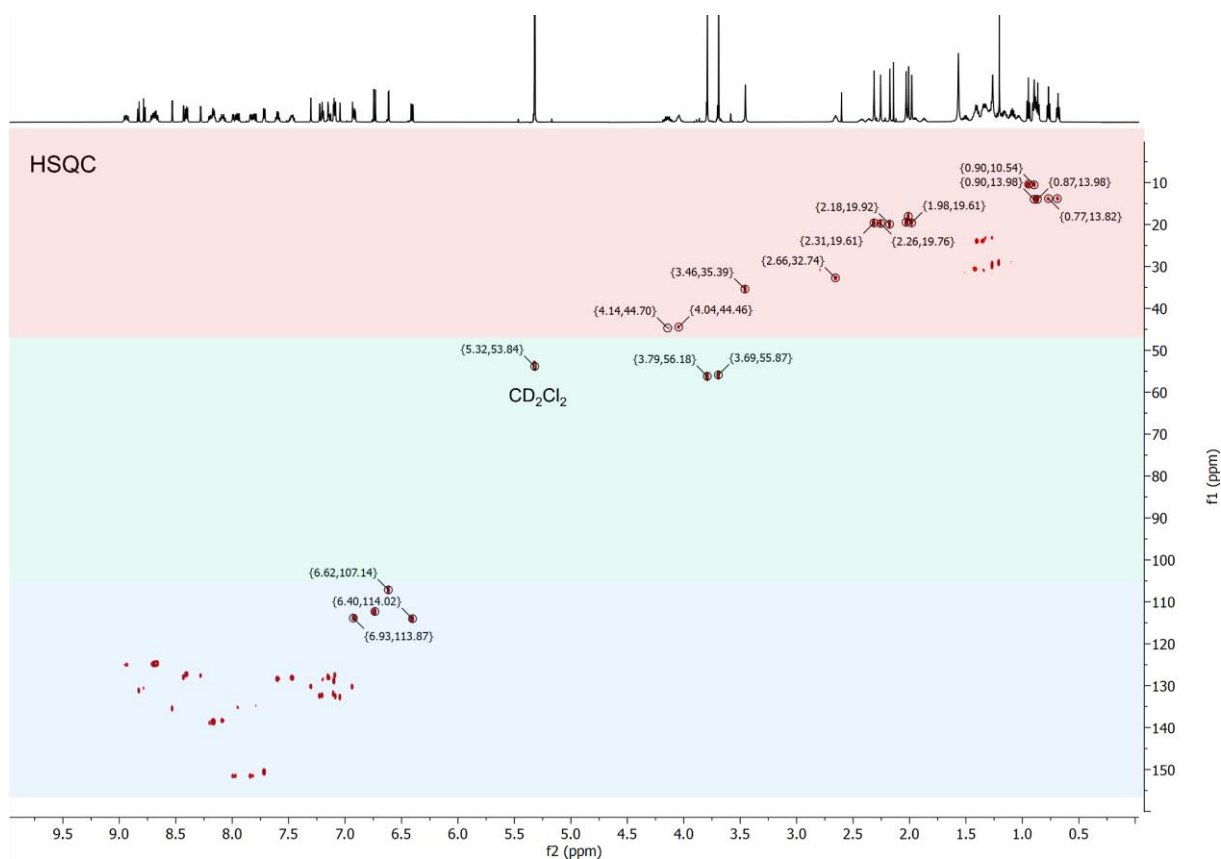
**Supplementary Figure 63.** <sup>19</sup>F{<sup>1</sup>H}-NMR spectrum (471 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of the pentad (**19**).



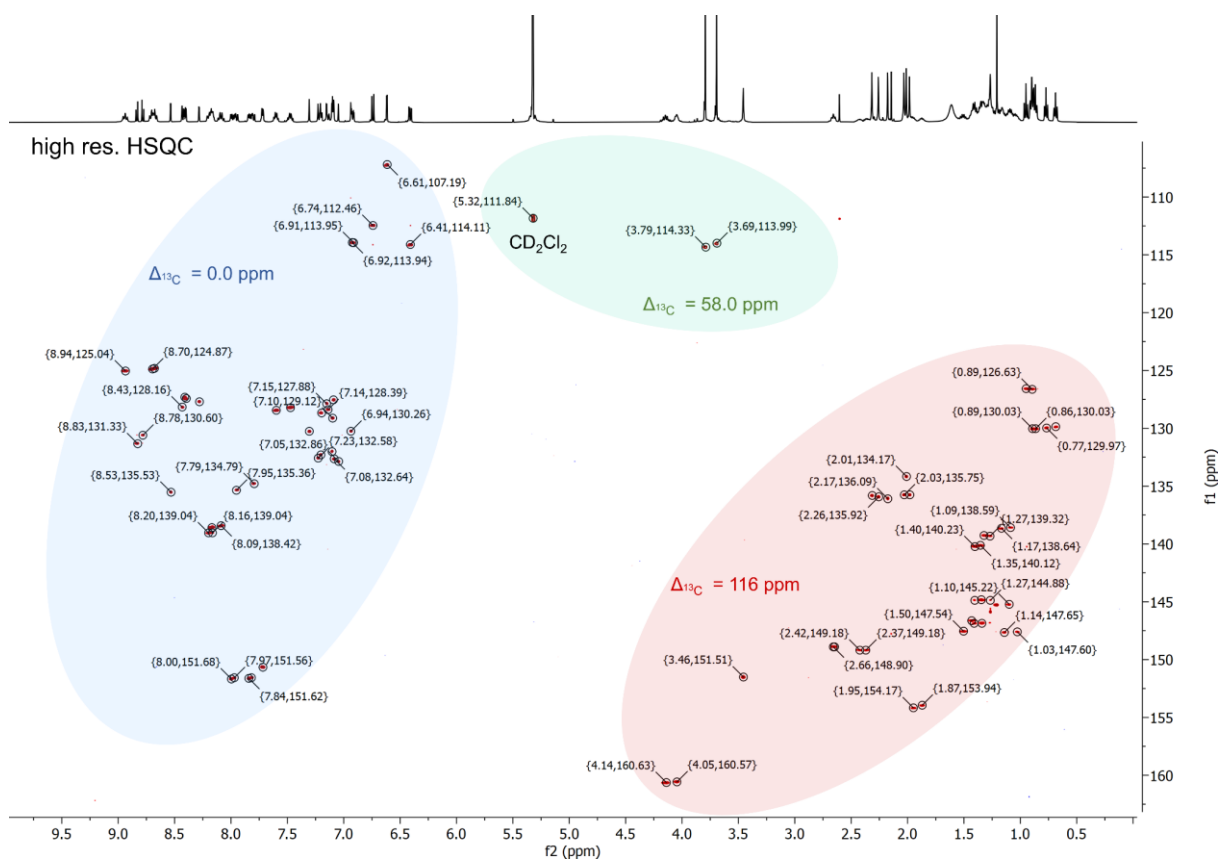
**Supplementary Figure 64.** COSY NMR spectrum (600 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of the pentad (19).



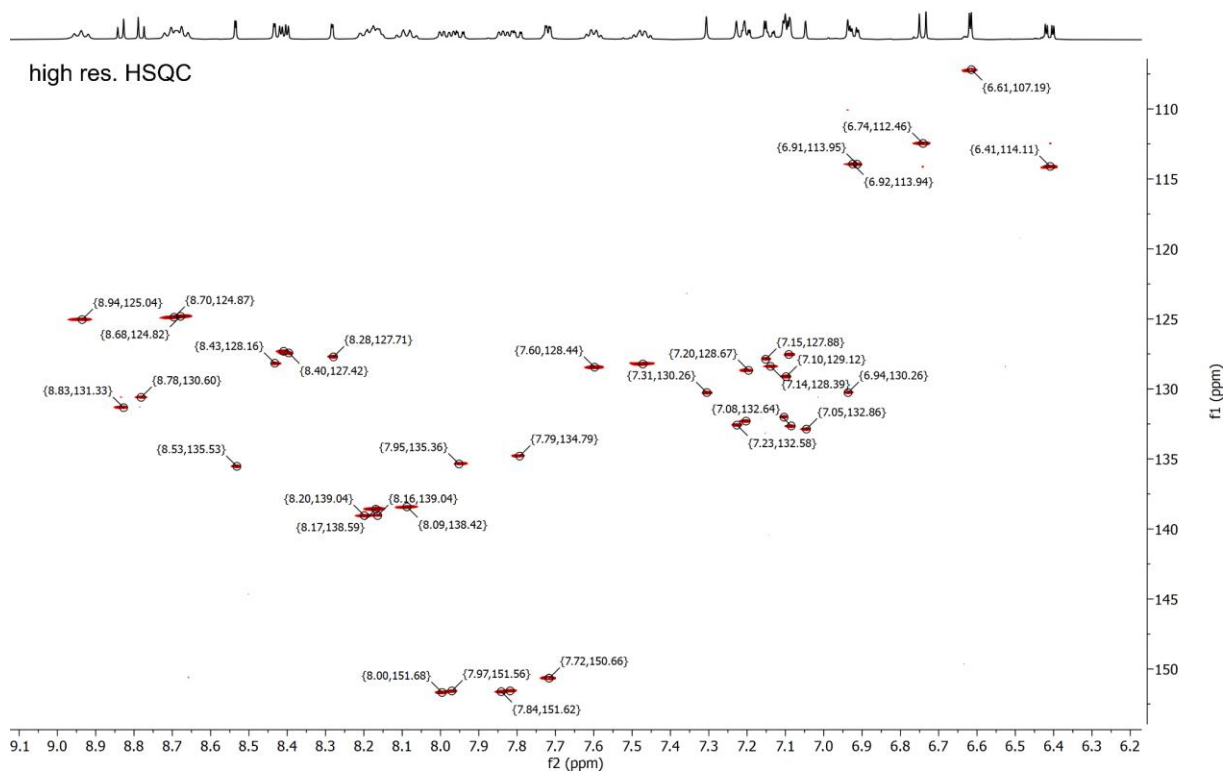
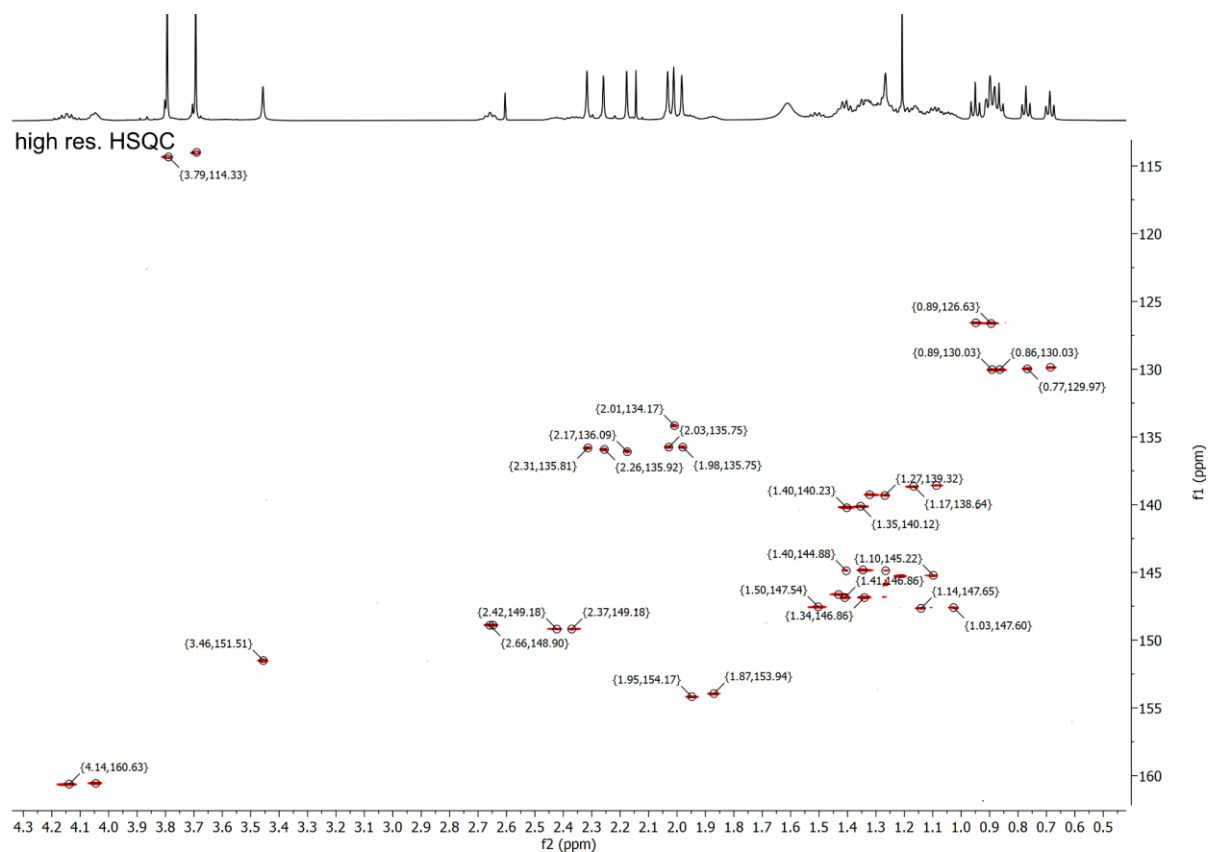
**Supplementary Figure 65.** NOESY NMR spectrum (600 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of the pentad (19).



**Supplementary Figure 66.** HSQC NMR spectrum (600 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of the pentad (**19**).

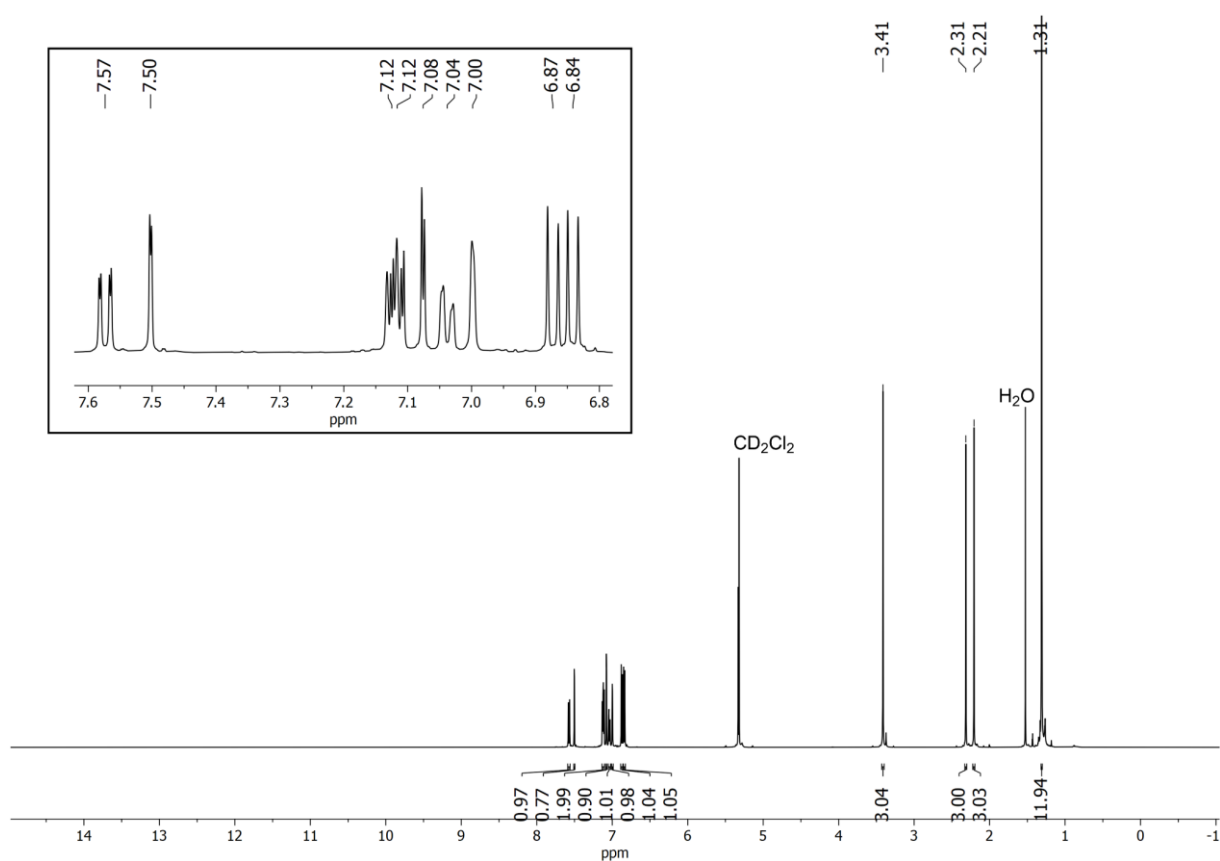


**Supplementary Figure 67.** Aliased high-resolution HSQC NMR spectrum (600 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of the pentad (**19**) with a spectral width of 58 ppm.

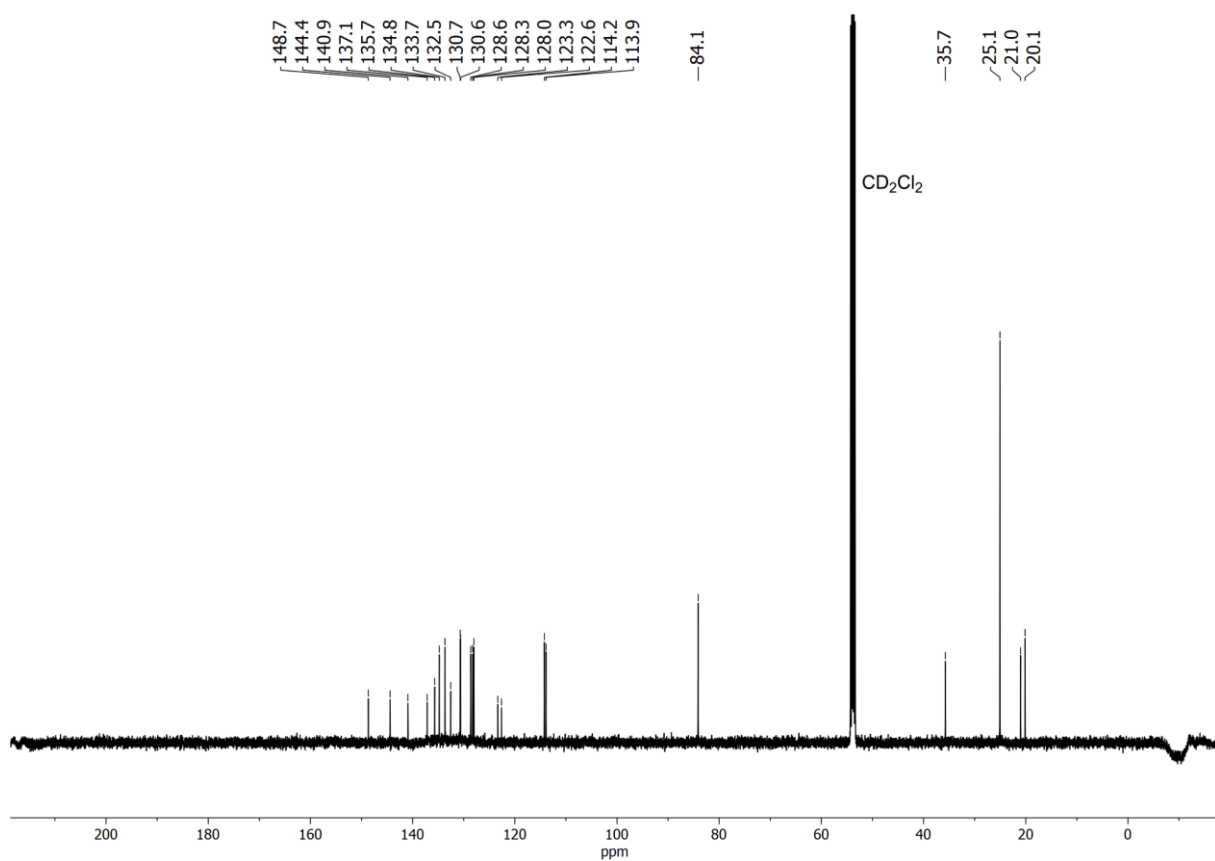


**Supplementary Figure 68.** Zoom into the aliphatic (*top*) and the aromatic (*bottom*) region of the high-resolution HSQC spectrum from Supplementary Figure 67.

xy-PTZ-Bpin (**21**)

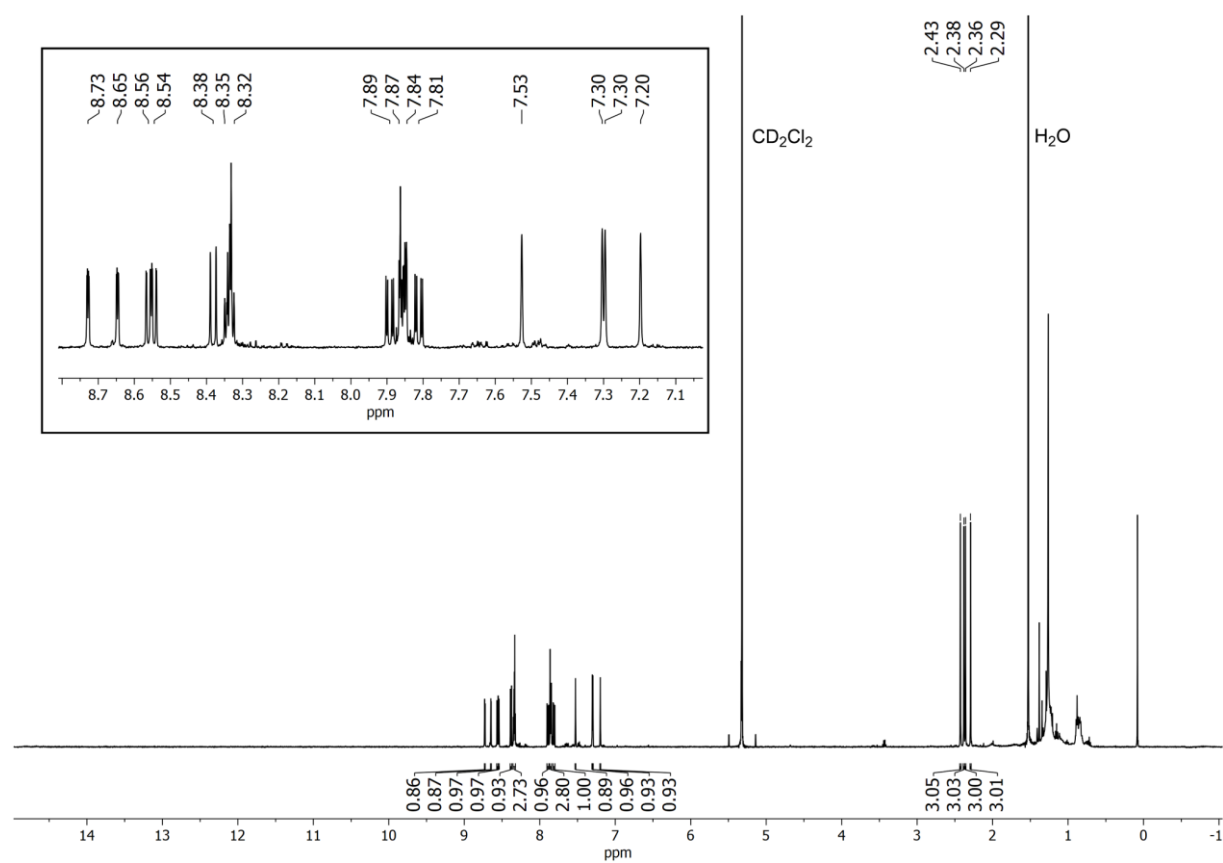


**Supplementary Figure 69.** <sup>1</sup>H-NMR spectrum (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of xy-PTZ-Bpin (**21**).



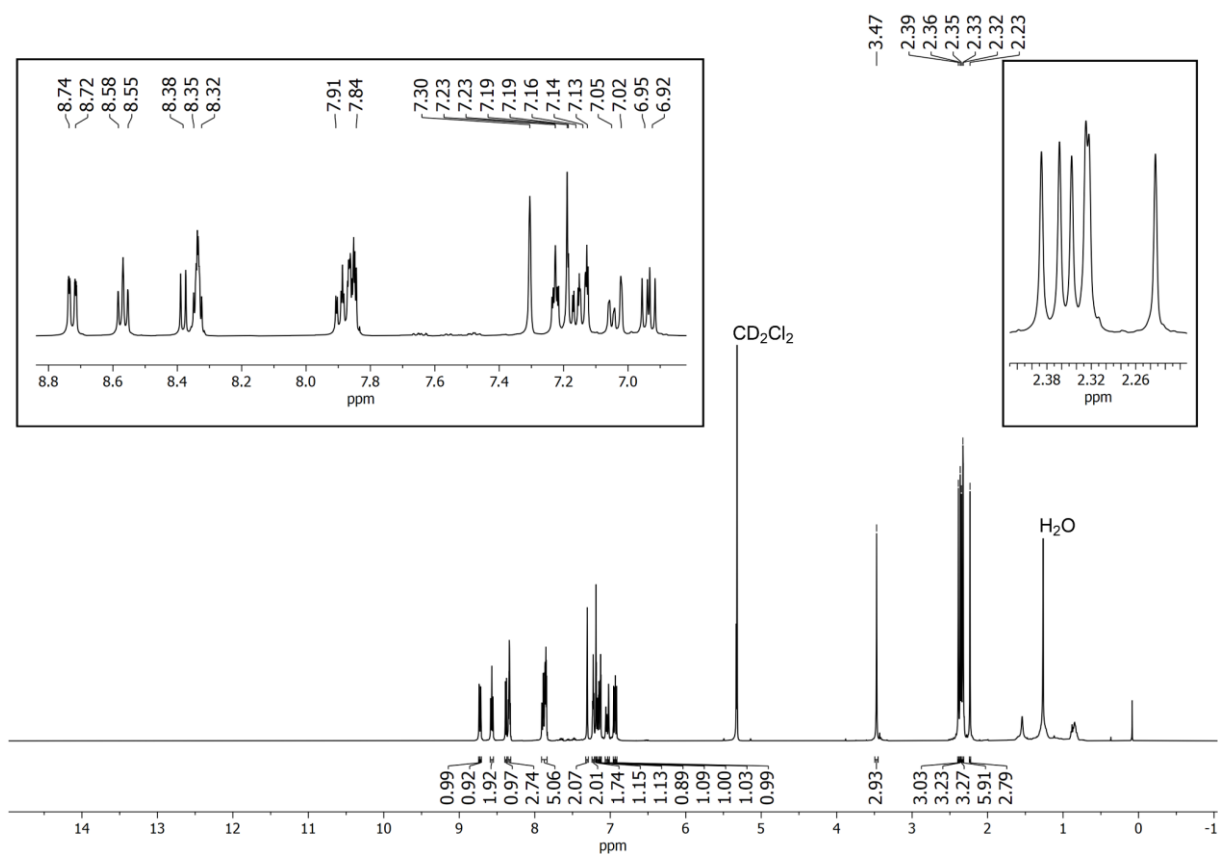
**Supplementary Figure 70.** <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum (126 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of xy-PTZ-Bpin (**21**).

Br-xy-bpy-xy-AQ (23)

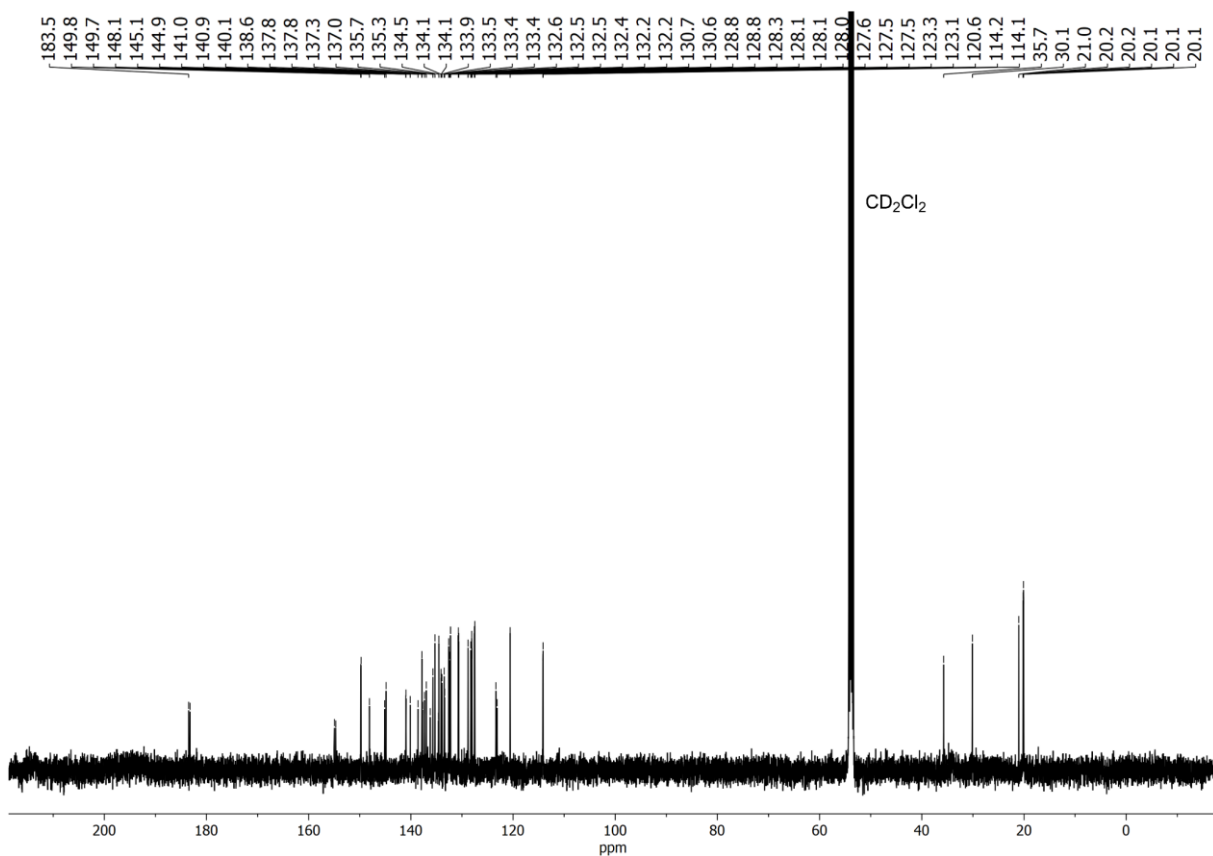


**Supplementary Figure 71.**  $^1\text{H}$ -NMR spectrum (500 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) of Br-xy-bpy-xy-AQ (23).

xy-PTZ-xy-bpy-xy-AQ (**24**)

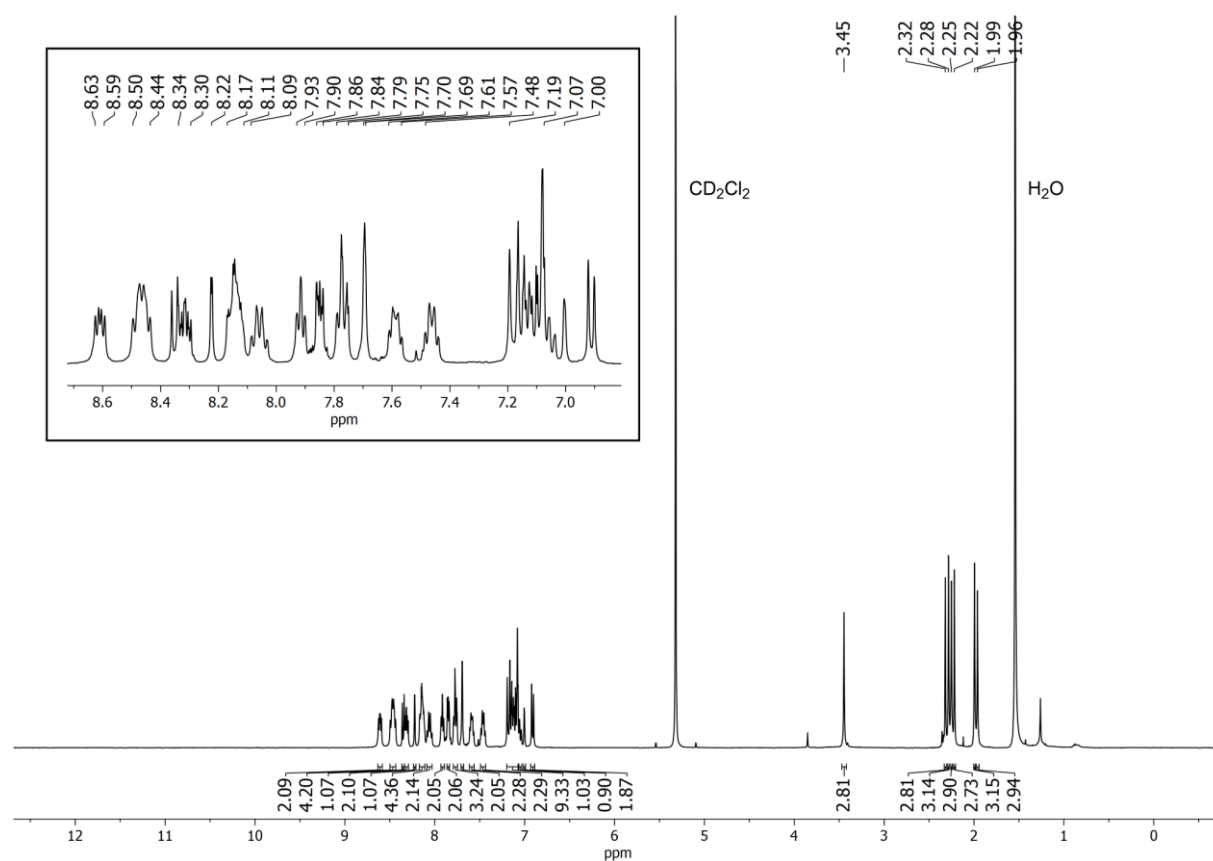


**Supplementary Figure 72.** <sup>1</sup>H-NMR spectrum (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of xy-PTZ-xy-bpy-xy-AQ (**24**).

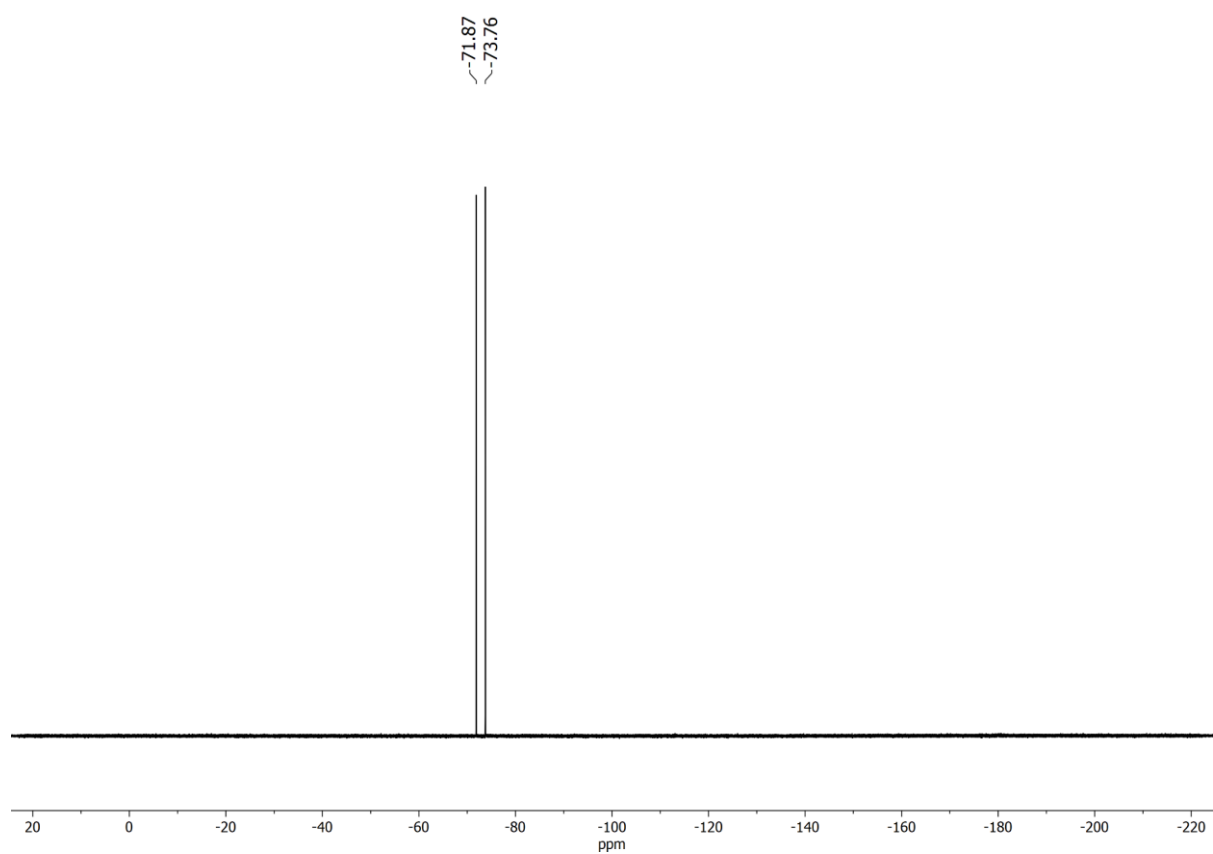


**Supplementary Figure 73.** <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum (126 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of xy-PTZ-xy-bpy-xy-AQ (**24**).

[xy-PTZ-xy-Ru(bpy)<sub>3</sub>-xy-AQ][PF<sub>6</sub>]<sub>2</sub> (**25**)



**Supplementary Figure 74.** <sup>1</sup>H-NMR spectrum (400 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of the triad [xy-PTZ-xy-Ru(bpy)<sub>3</sub>-xy-AQ][PF<sub>6</sub>]<sub>2</sub> (**25**).



**Supplementary Figure 75.** <sup>19</sup>F{<sup>1</sup>H}-NMR spectrum (376 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>) of the triad (**25**).

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