

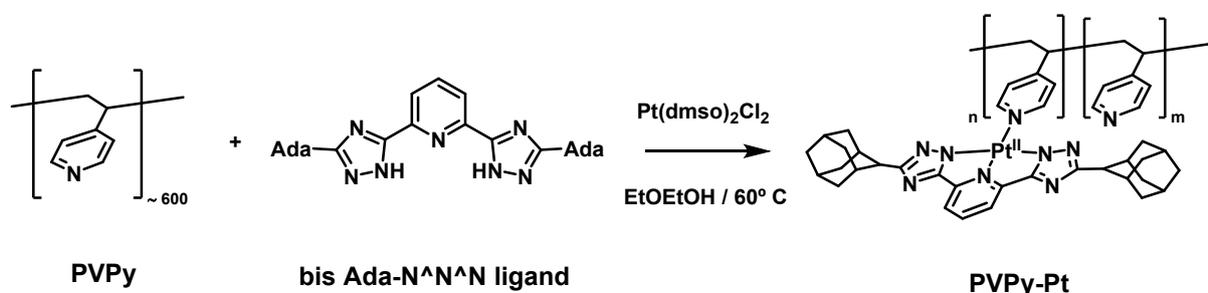
## Oxygen-insensitive phosphorescence in water from a Pt-doped supramolecular array

Laura Straub, Darío González-Abradelo and Cristian A. Strassert

### S1. Detailed synthetic procedures

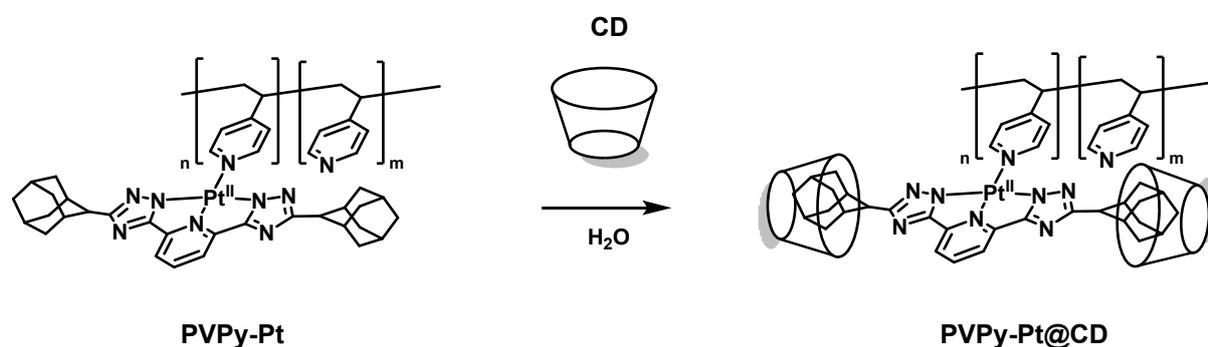
All reagents were analytical grad and used as received. Dialysis was performed with ZelluTrans T2 (MWCO 6000-8000, Carl Roth). NMR spectra were recorded on an DPX/Advance 300 or an Avance 400 from Bruker Analytische Messtechnik (Karlsruhe, Germany). The  $^1\text{H}$  NMR chemical shifts ( $\delta$ ) of the signals are given in parts per million and referenced to residual protons in the deuterated solvents: DMSO- $d_6$  (2.50 ppm) and MeOH- $d_4$  (3.31 ppm). Time-resolved online ATR FT-IR spectra were recorded on an Alpha instrument (Bruker) with a platinum ATR module using a single reflection diamond ATR accessory. Educts and **PVP-Pt** were measured as a solid, **PVPy-Pt@CD** and **PVP-Pt@ipCD** in solution. Standard abbreviations were used to describe the signal intensity: b = broad, w = weak, m = medium, s = strong.

#### S1.1 Synthesis of PVPy-Pt



2,6-bis(3-adamantyl-1,2,4-triazol-5-yl)pyridine (113 mg, 0.234 mmol) and Pt(dmsO)<sub>2</sub>Cl<sub>2</sub> (80.0 mg, 0.234 mmol) were dissolved in ethoxyethanol (50 mL) and deaerated under a stream of dried argon. The solution was heated up to 60 °C and poly(4-vinylpyridine) (65.0 mg, 0.001 mmol) dissolved in ethoxyethanol (2 mL) was added. The reaction mixture was stirred over night at 60° C to yield a yellow precipitate. The solid was separated from the solution by centrifugation and washed several times with acetone. A lower load of the Pt(II) tridentate was achieved by increasing the initial amount of PVPy to 2.43·mmol (10 times) and 1.17 mmol (5 times) at the beginning of the synthesis. C,H,N Analysis: C 76.59 %, H 7.35 %, N 12.10 %. FTIR (solid, cm<sup>-1</sup>): 2923m (ν<sub>as</sub> CH<sub>2</sub>), 2855m (ν<sub>s</sub> CH<sub>2</sub>), 1619m (ν C=C), 1602m (ν C=C), 1437w ,1361w , 1150w , 1087m , 1027s , 1002m , 820w , 567w .

## S1.2 Synthesis of Pt-PVPy@CD



**Pt-PVPy** was dispersed in a water-isopropanol mixture (9:1) and CD was added.<sup>1</sup> The dispersion was sonicated for 1 h and stirred overnight. After removing the solid residue by centrifugation, the supernatant was cleaned up via dialysis against water to receive the product in aqueous solution. <sup>1</sup>H-NMR (300 MHz, dms<sub>o</sub>-d<sub>6</sub>) δ 7.68 (PVPy), 6.61 (PyPy), 5.72, 4.83 (CD), 4.46, 3.61 (CD), 3.33, 2.10, 1.23 (CD), 1.14 (PVPy). FTIR (solid, cm<sup>-1</sup>): 3687-2999*b* (ν OH, CD), 2923*m* (ν<sub>as</sub> CH<sub>2</sub>, PVPy), 2841*m* (ν<sub>s</sub> CH<sub>2</sub>, PVPy), 1617*m* (ν C=C, PVPy), 1603*m* (ν C=C aromatic, PVPy), 1430*w* (δ<sub>in-plane</sub> OH, CD), 1153*w* (ν<sub>as</sub> C-O-C, CD), 1077*m* (ν<sub>as</sub> C-O-C, CD), 1027*m* (ν<sub>as</sub> CCO secondary face, CD), 1005*m* (ν<sub>as</sub> CCO primary face, CD), 833*w* (ν<sub>s</sub> C-O-C, CD).

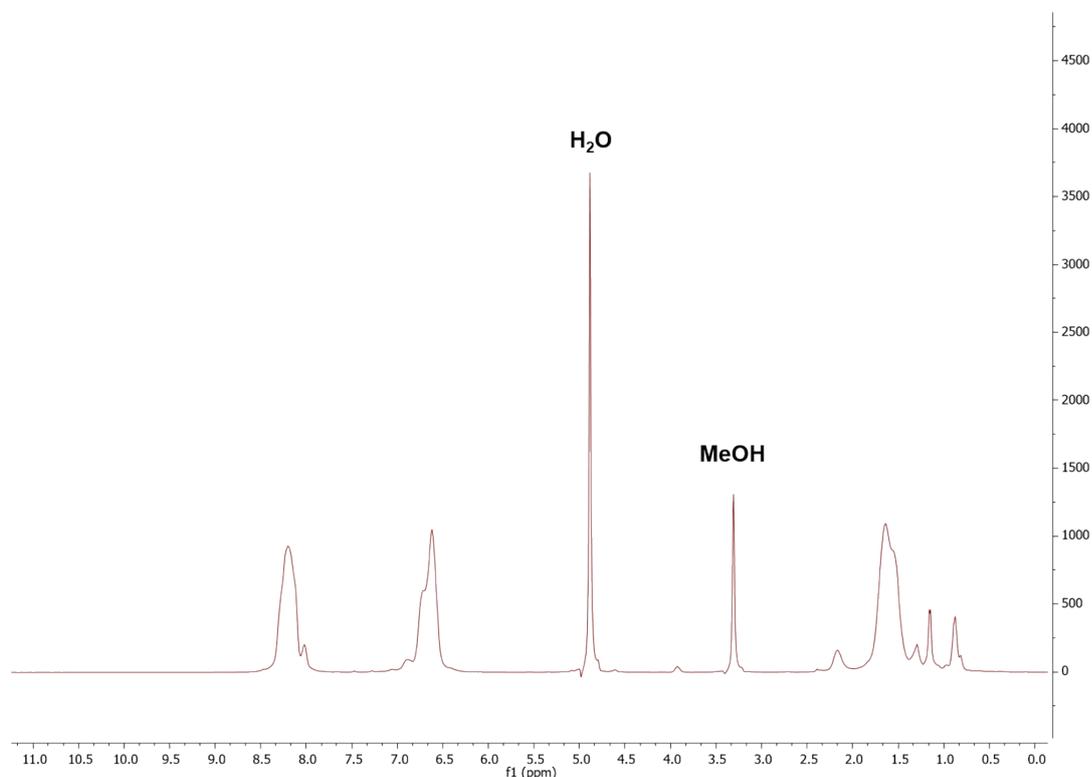


Figure S1.1. NMR spectrum of **PVPy** without functionalization in MeOH-d<sub>4</sub> at 295 K.

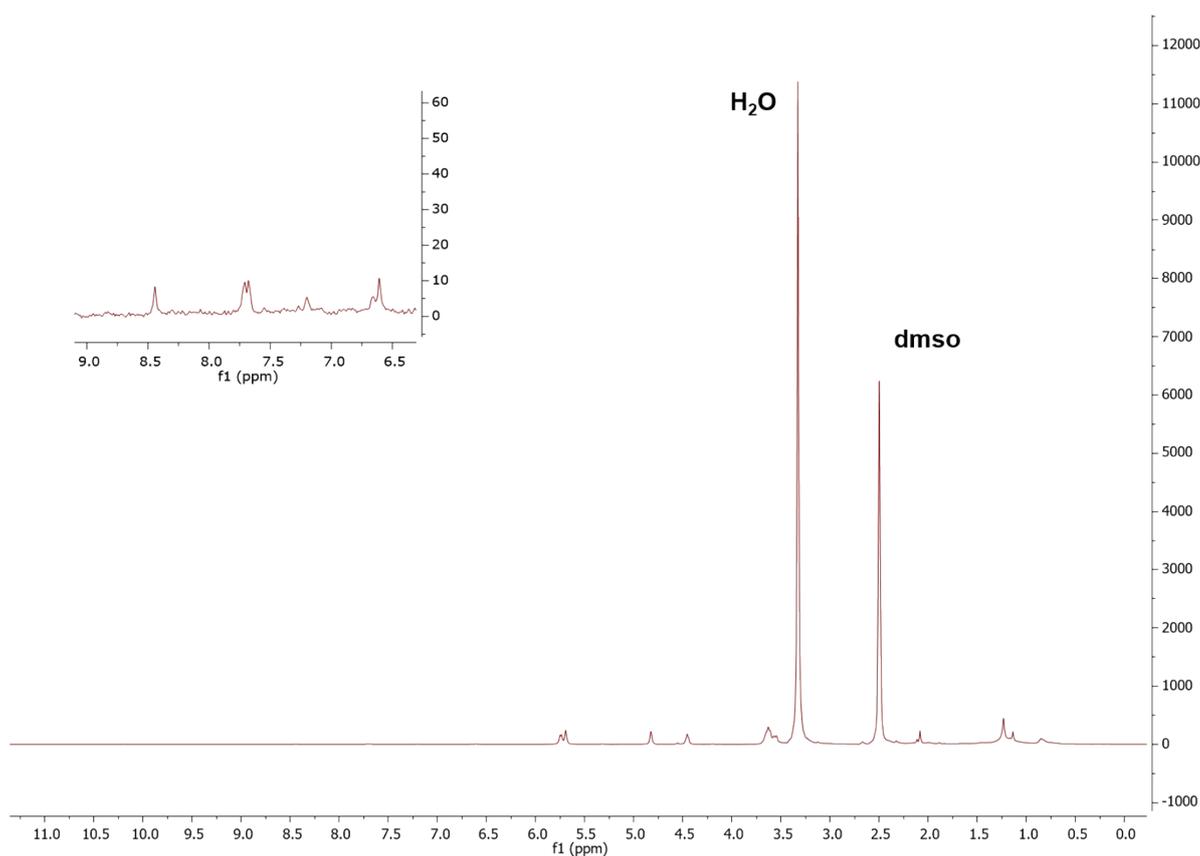
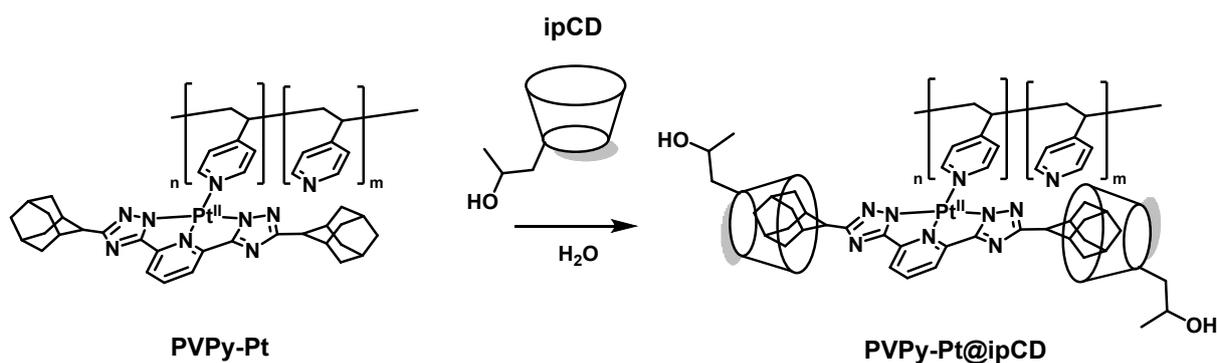


Figure S1.2. NMR spectrum of **Pt-PVPy@CD** in  $\text{dms0-d}_6$  at 295 K.

### S1.3 Synthesis of **Pt-PVPy@ipCD**



**Pt-PVPy** was dispersed in methanol and ipCD was added. The dispersion was sonicated for 1 h and stirred overnight. After removing the solid residue by centrifugation, the supernatant was cleaned up via dialysis against methanol to yield the product in solution.  $^1\text{H-NMR}$  (300 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  8.91 (PVPy), 8.04 (PVPy), 4.90 (CD), 3.72 (CD), 1.29 (CD), 1.13 (PVPy), 0.90. FT-IR (solid,  $\text{cm}^{-1}$ ): 3694-3020 $b$  ( $\nu$  OH, CD), 2965 $w$  ( $\nu_{\text{as}}$   $\text{CH}_3$ ), 2931 $w$  ( $\nu_{\text{as}}$   $\text{CH}_2$ ), 1446 $w$ , 1412 $w$ , 1370 $w$ , 1327 $w$ , 1147 $m$  ( $\nu_{\text{as}}$  C-O-C, CD), 1081 $m$  ( $\nu_{\text{as}}$  C-O-C, CD), 1005 $s$  ( $\nu_{\text{as}}$  CCO primary face, CD), 849 $w$  ( $\nu_{\text{s}}$  C-O-C, CD).

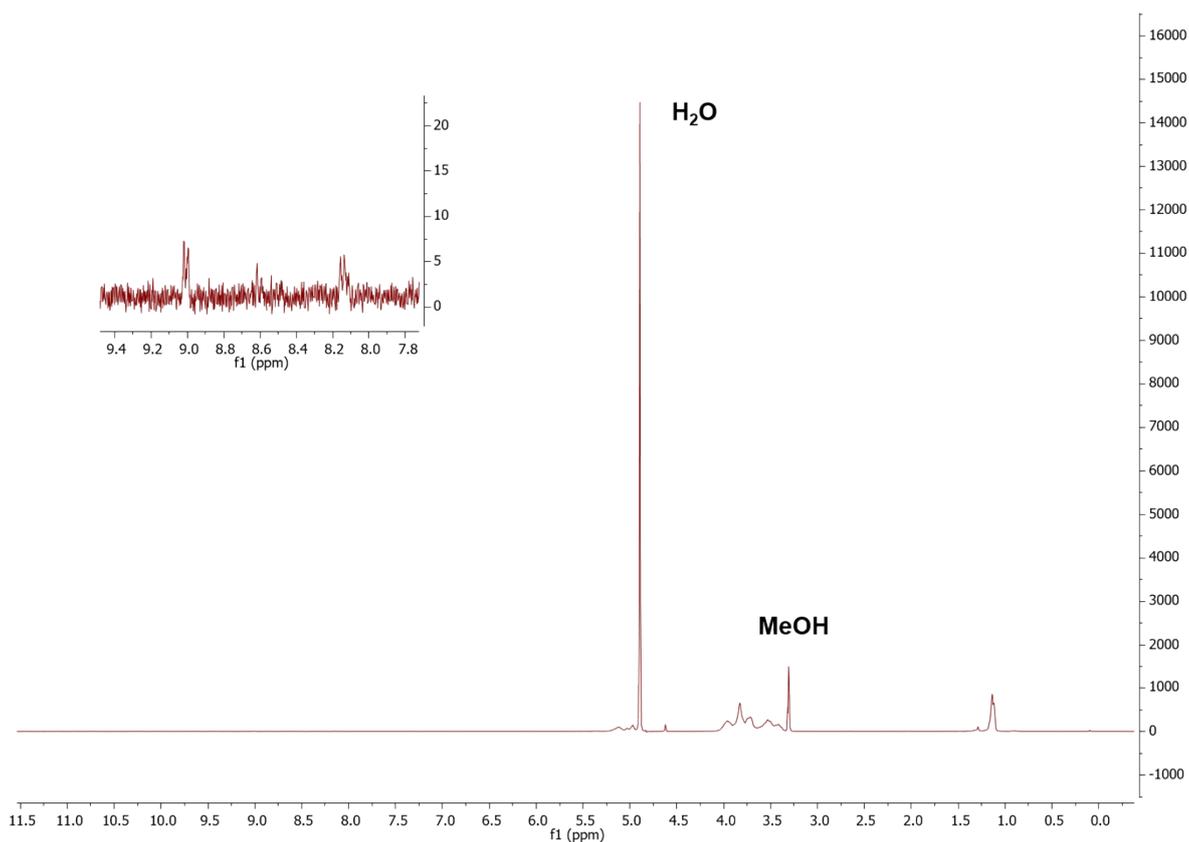


Figure S1.3. NMR spectrum of **Pt-PVPy@ipCD** in MeOH-d<sub>4</sub> at 295 K.

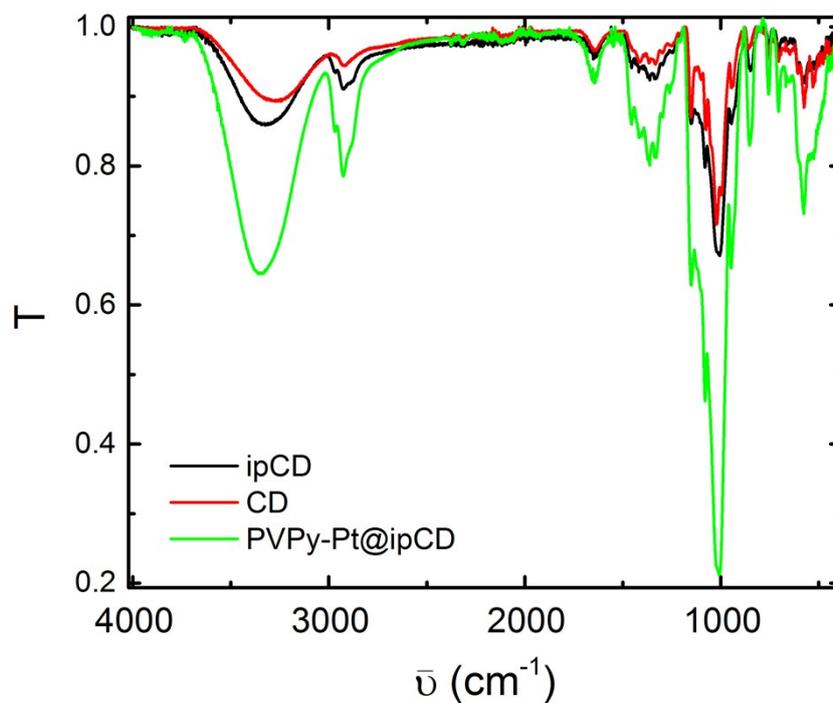


Figure S1.4. Comparative FTIR spectrum: **Pt-PVPy@ipCD** and cyclodextrins.

## **S2. Spectroscopic measurements**

Absorption spectra were measured on an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. DLS measurements were performed on a Malvern Zetasizer Nano ZS. All solvents used were of spectroscopic grade. Steady-state emission spectra were recorded on a FluoTime300 spectrometer from PicoQuant equipped with a 300 W ozone-free Xe lamp (250-900nm), an excitation monochromator (Czerny-Turner 2.7 nm/mm dispersion, 1200 grooves/mm, blazed at 300 nm), diode lasers (pulse width < 80 ps) operated by a computer-controlled laser driver PDL-820 (repetition rate up to 80 MHz, burst mode for slow and weak decays where the burst spikes were removed by tail-fitting), two emission monochromators (Czerny-Turner, selectable gratings blazed at 500 nm with 2.7 nm/mm dispersion and 1200 grooves/mm, or blazed at 1250 nm with 5.4 nm/mm dispersion and 600 grooves/mm), and two detectors, namely a PMA Hybrid 40 (transit time spread FWHM < 120 ps, 300 – 720 nm) and a R5509-42 NIR-photomultiplier tube (transit time spread FWHM 1.5 ns, 300-1400 nm) with external cooling (-80 °C) from Hamamatsu. Steady-state spectra and fluorescence lifetimes were recorded in TCSPC mode by a PicoHarp 300 (minimum base resolution 4 ps). Emission and excitation spectra were corrected for source intensity (lamp and grating) and detection response (detector and grating) by standard correction curves. Lifetime analysis was performed using the commercial FluoFit software. The quality of the fit was assessed by minimizing the reduced chi squared function ( $\chi^2$ ) and visual inspection of the weighted residuals and their autocorrelation. Luminescence quantum yields were measured with a Hamamatsu Photonics absolute PL quantum yield measurement system (C9920-02) equipped with a L9799-01 CW Xenon light source (150 W), monochromator, C7473 photonic multi-channel analyzer, integrating sphere, a calibrated quartz Dewar with matching tubes for 77K measurements, and employing U6039-05 PLQY measurement software (Hamamatsu Photonics, Ltd., Shizuoka, Japan). All solvents used were of spectroscopic grade. All measurements were performed in quartz cuvettes.

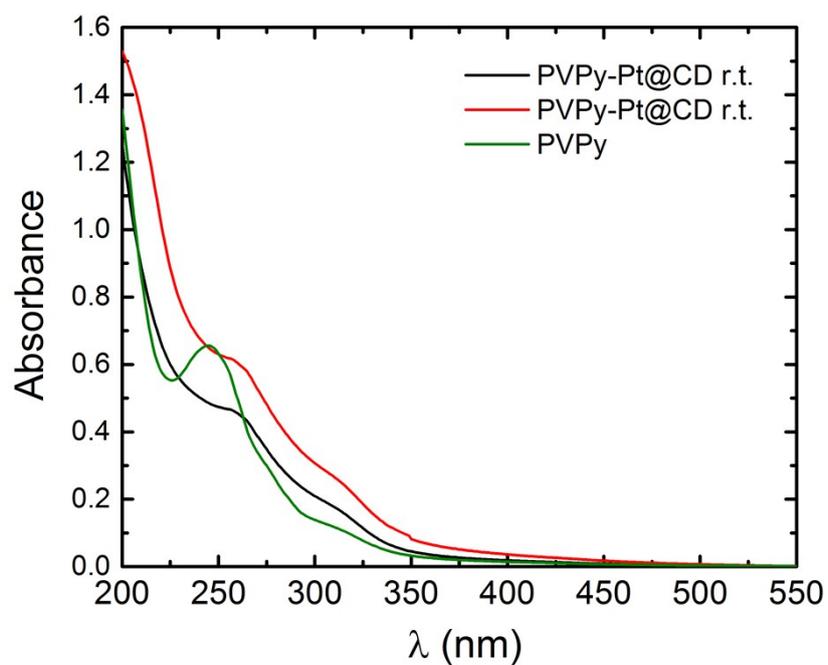
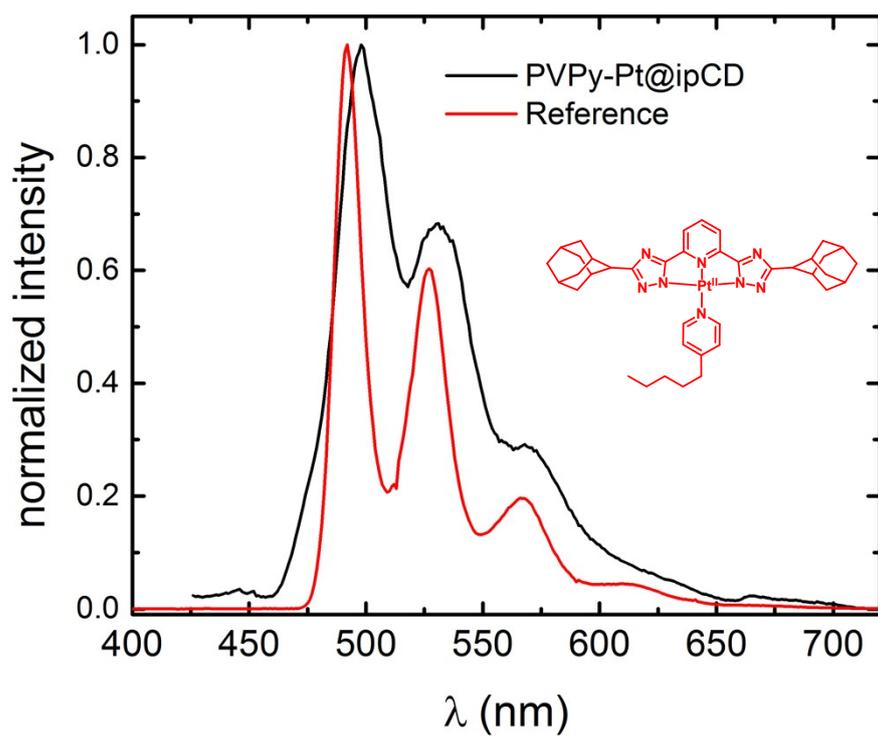


Figure S2.1. Absorption spectra in water at 295 K.

Figure S2.2. Emission spectra of **PVP-Pt@ipCD** and an analogous monomeric complex in DCM/MeOH 1:1 at 77 K. The picture shows the increased peak width of the polymer in comparison with the monomer.<sup>2</sup>

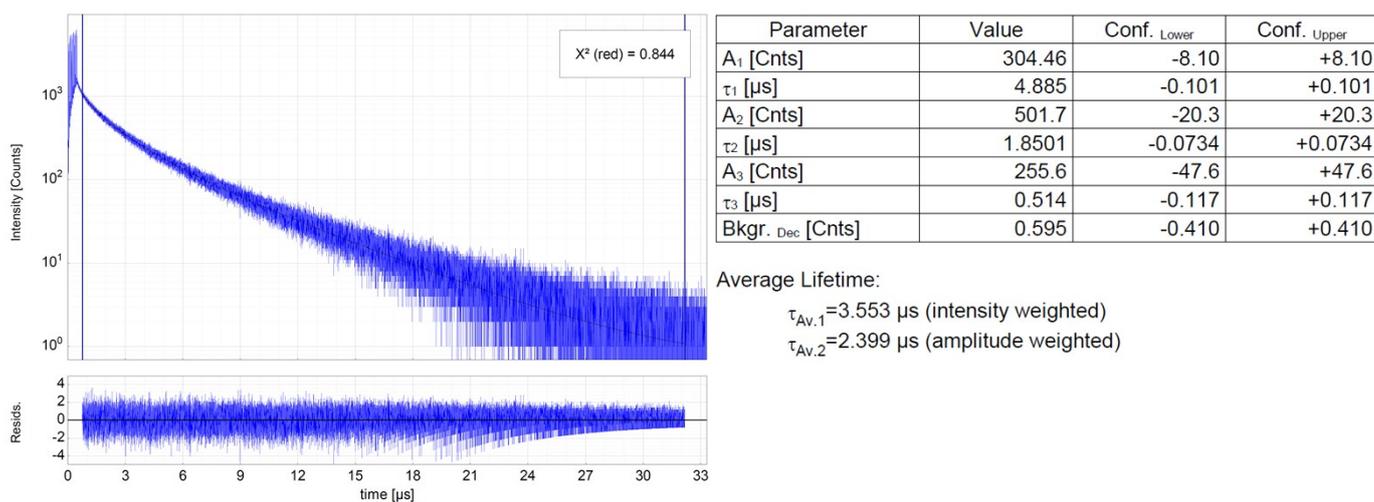


Figure S2.3. Left: Time-resolved luminescence decay of **PVPy-Pt@CD** in aerated H<sub>2</sub>O at room temperature including the residuals ( $\lambda_{exc} = 376.7$  nm). Right: Fitting parameters including pre-exponential factors and confidence limits.

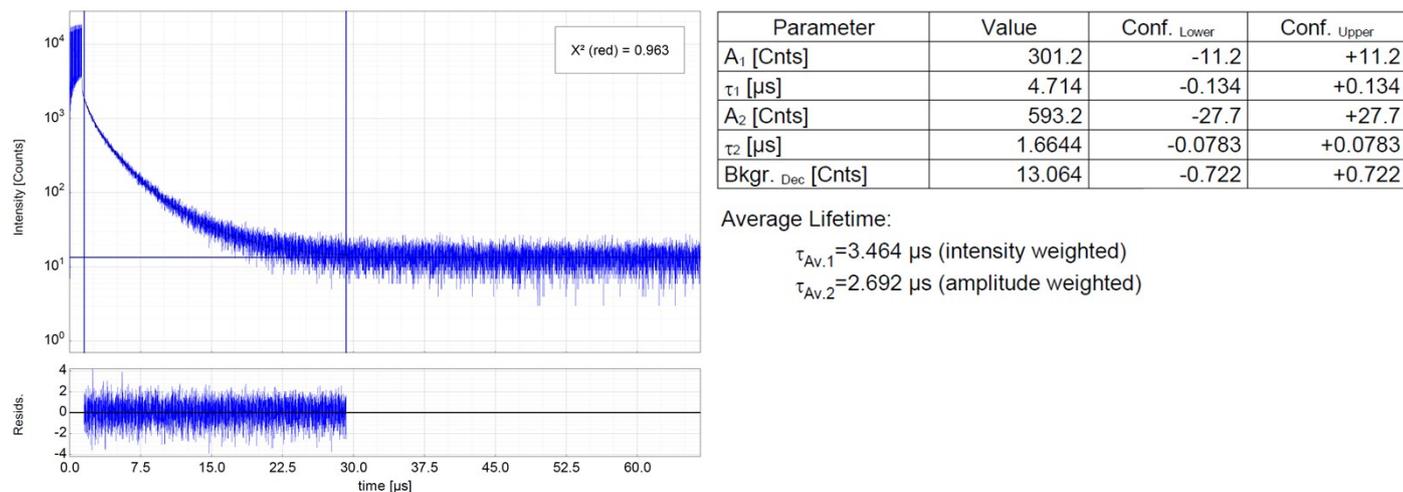


Figure S2.4. Left: Time-resolved luminescence decay of **PVPy-Pt@CD** in deaerated H<sub>2</sub>O at room temperature including the residuals ( $\lambda_{exc} = 376.7$  nm). Right: Fitting parameters including pre-exponential factors and confidence limits.

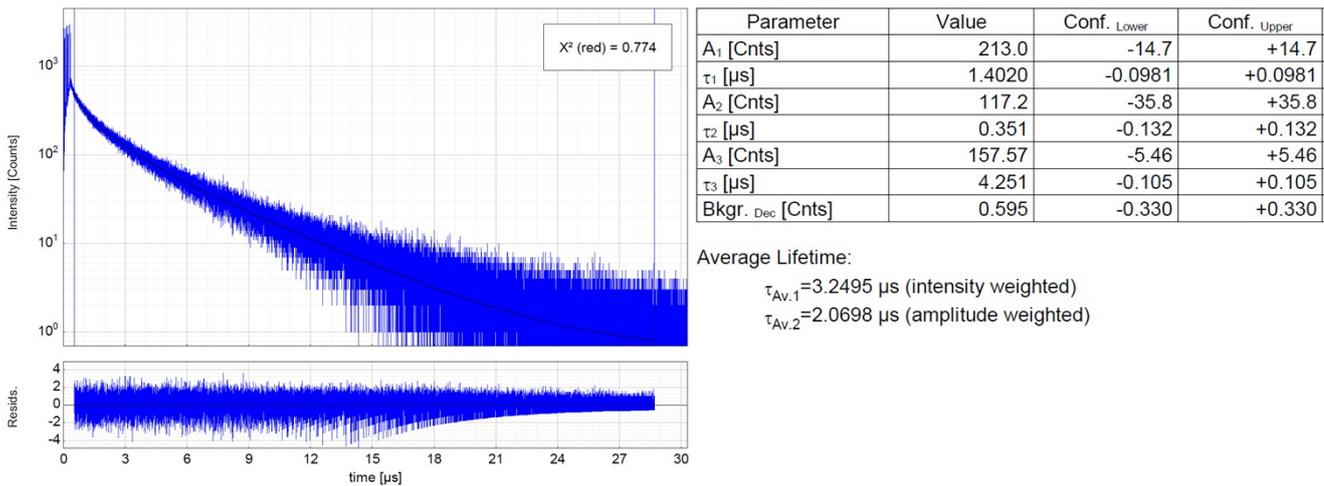


Figure S2.5. Left: Time-resolved luminescence decay of **PVPy-Pt@ipCD** in aerated H<sub>2</sub>O at room temperature including the residuals ( $\lambda_{exc} = 376.7$  nm). Right: Fitting parameters including pre-exponential factors and confidence limits.

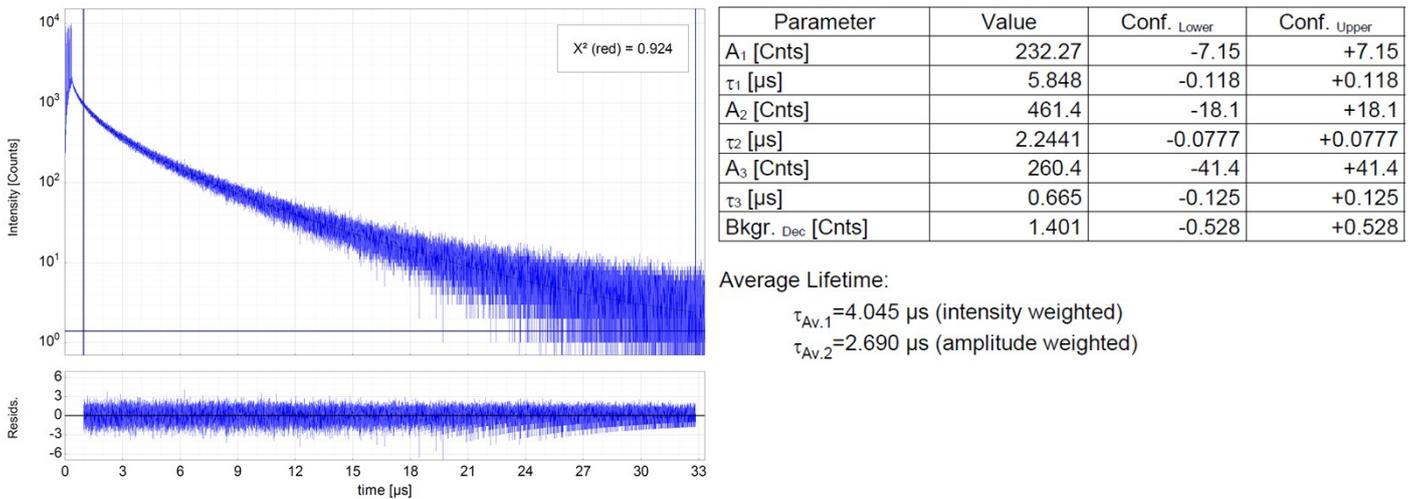


Figure S2.6. Left: Time-resolved luminescence decay of **PVPy-Pt@ipCD** in deaerated H<sub>2</sub>O at room temperature including the residuals ( $\lambda_{exc} = 376.7$  nm). Right: Fitting parameters including pre-exponential factors and confidence limits.

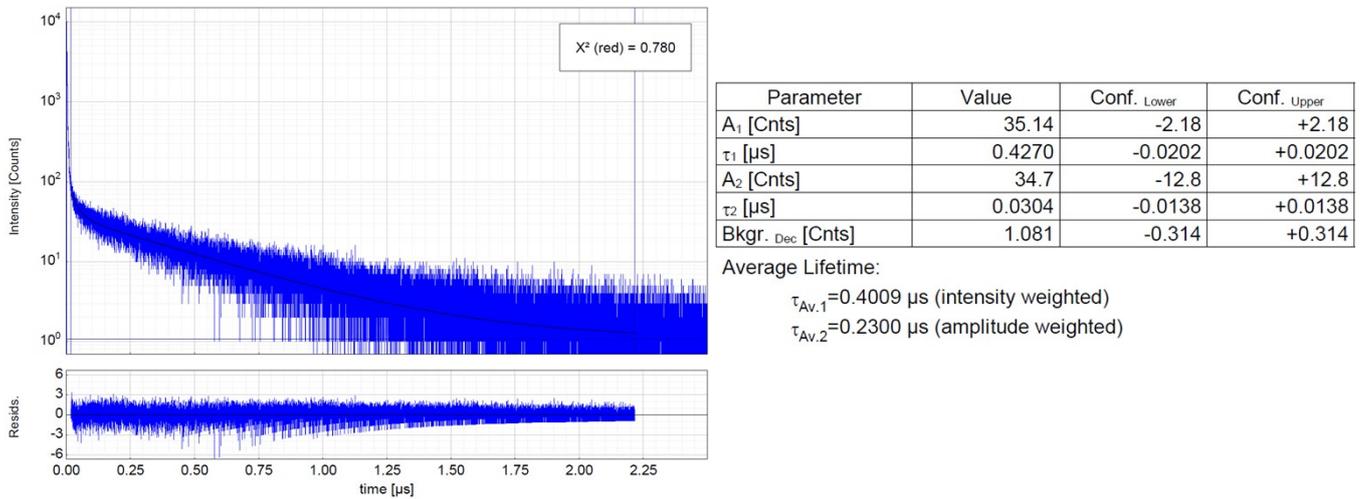


Figure S2.7. Left: Time-resolved luminescence decay of **PVPy-Pt@ipCD** in aerated DCM/MeOH 1:1 at room temperature including the residuals ( $\lambda_{exc} = 376.7$  nm). Right: Fitting parameters including pre-exponential factors and confidence limits.

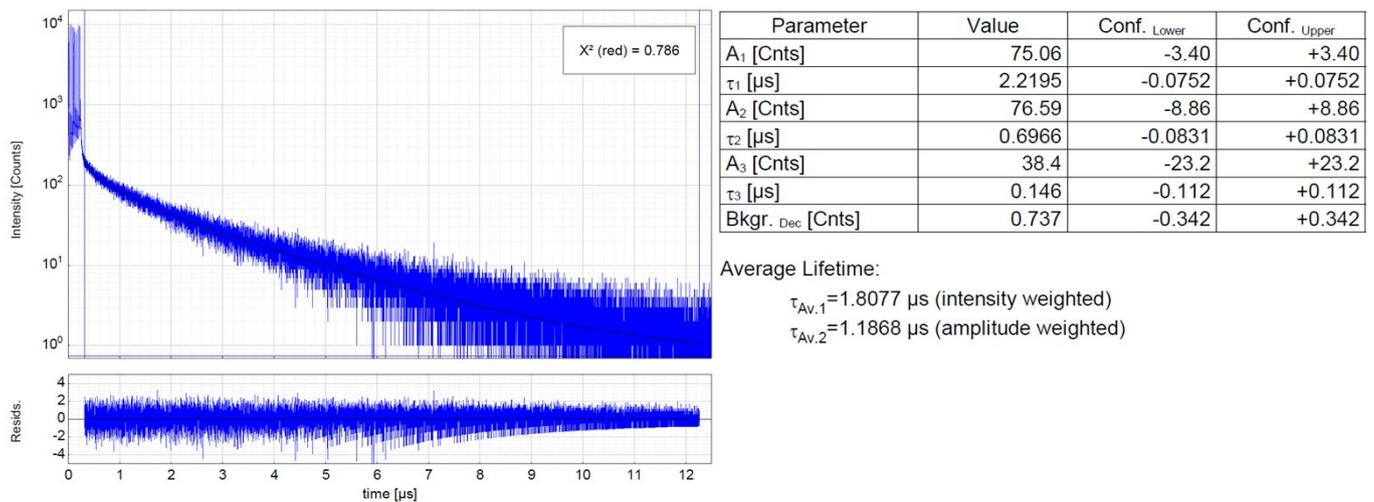


Figure S2.8. Left: Time-resolved luminescence decay of **PVPy-Pt@ipCD** in deaerated DCM/MeOH 1:1 at room temperature including the residuals ( $\lambda_{exc} = 376.7$  nm). Right: Fitting parameters including pre-exponential factors and confidence limits.

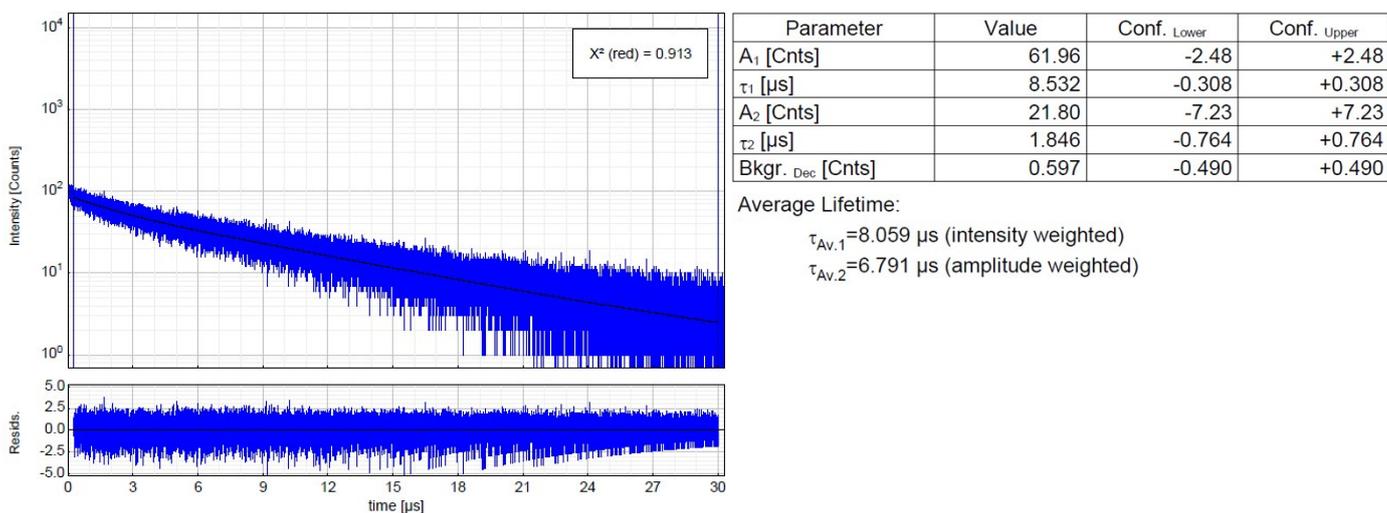


Figure S2.9. Left: Time-resolved luminescence decay of **PVPy-Pt@ipCD** in frozen glassy matrices DCM/MeOH 1:1 at 77 K including the residuals ( $\lambda_{exc} = 376.7$  nm). Right: Fitting parameters including pre-exponential factors and confidence limits.

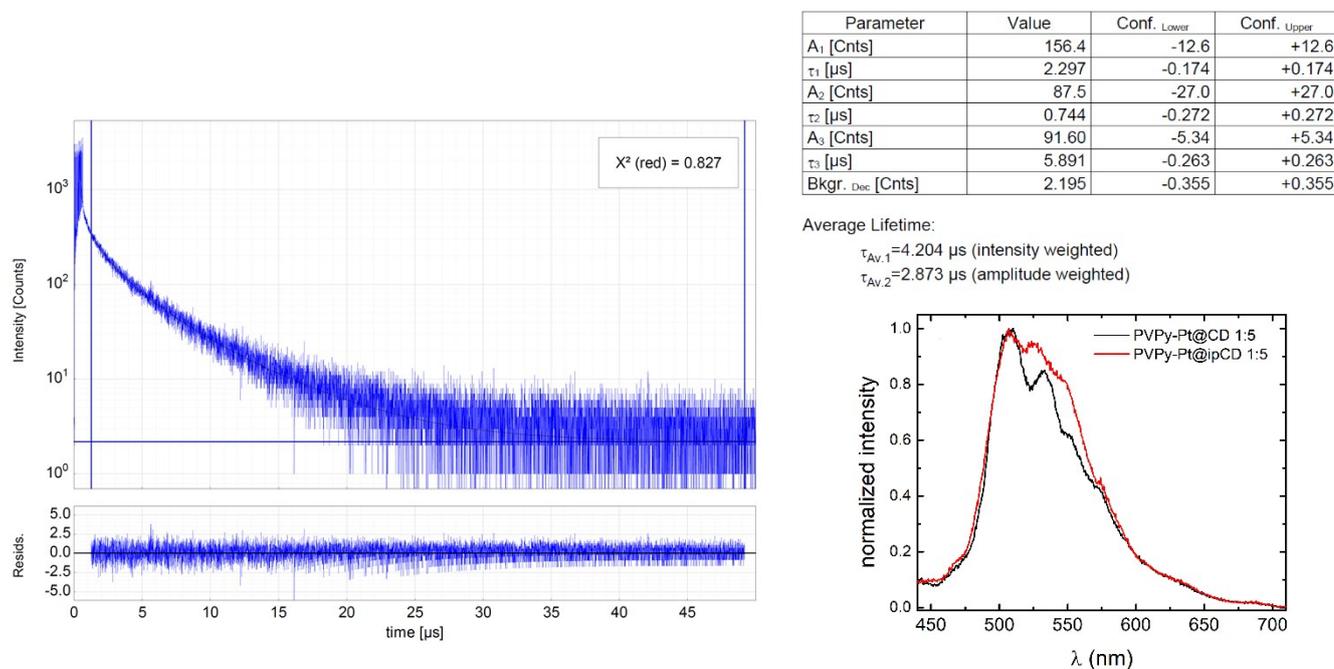


Figure S2.10. Left: Time-resolved luminescence decay of **PVP-Pt@CD** after a synthesis with 20 % of the initial amount of Pt(II) precursor used in deaerated H<sub>2</sub>O at room temperature including the residuals ( $\lambda_{exc} = 376.7$  nm). Upper right: Fitting parameters including pre-exponential factors and confidence limits. Lower right: Emission spectra in water at room temperature of **PVP-Pt@CD** and **PVP-Pt@ipCD** after a synthesis with 20 % of the initial amount of Pt(II) precursor used ( $\lambda_{exc} = 330$  nm).

- 1 A. K. Chatjigakis, C. Donze, A. W. Coleman and P. Cardot, *Anal. Chem.*, 1992, **64**, 1632–1634.
- 2 M. Mydlak, M. Mauro, F. Polo, M. Felicetti, J. Leonhardt, G. Diener, L. De Cola and C. A. Strassert, *Chem. Mater.*, 2011, **23**, 3659–3667.