

## SUPPORTING INFORMATION

### Fluorescence Enhancement of di-*p*-Tolyl Viologen by Complexation in Cucurbit[7]uril Marina Freitag, Lars Gundlach,<sup>‡</sup> Piotr Piotrowiak, and Elena Galoppini\*

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## Synthesis.

*General.*  $^1\text{H}$  (499.90 MHz) and  $^{13}\text{C}$  NMR (124.98 MHz) spectra were recorded on a Varian INOVA 500 spectrometer in  $\text{D}_2\text{O}$  at room temperature. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts ( $\delta$ ) are reported in ppm and are referenced to the central line of the solvent (4.82 ppm for  $\text{D}_2\text{O}$ ). Coupling constants ( $J$ ) are reported in Hz. High resolution mass spectra (ESI) were recorded using a Bruker Daltonics FT MS. UV-VIS absorbance spectra were collected using an Ocean Optics USB4000+ Spectrometer in combination with a PX-2 Pulsed Xenon Light Source (150 ms for integration time and 20 scans to average). FT-IR-ATR spectra were acquired on a Thermo Electron Nicolet 6700 FT-IR spectrometer equipped with a Smart iTR ATR accessory with ZnSe HATR.

*Materials:* CB7 was synthesized<sup>i</sup> and purified following the procedure described by Nau et al.**Error! Bookmark not defined.** The spectral data, including  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , 25 °C):  $\delta$  = 4.25 (d,  $J$  = 15.5, 14 H,  $\text{CH}_2$ ), 5.56 (s, 14 H, CH), 5.81 ppm (d,  $J$  = 15.5, 14 H,  $\text{CH}_2$ ), FT-IR-ATR; 3434 (N-H), 2930 (C-H), 1717 (C=O), 1643 (C=C), 1477 (C-N), 1373, 1319, 1214, 1192, 968, 799  $\text{cm}^{-1}$ , were consistent with those reported in literature,**Error! Bookmark not defined.****Error! Bookmark not defined.** and were compared with data obtained from a commercial CB7 sample (See Supporting Information, Figures S1 and S2). HPLC-grade acetone, 4,4'-bipyridine, 1-chloro-2,4-dinitrobenzene, and *p*-toluidine are commercially available and were used without further purification. Nanopure water (Millipore Gradient A10) was used to prepare the aqueous solutions.

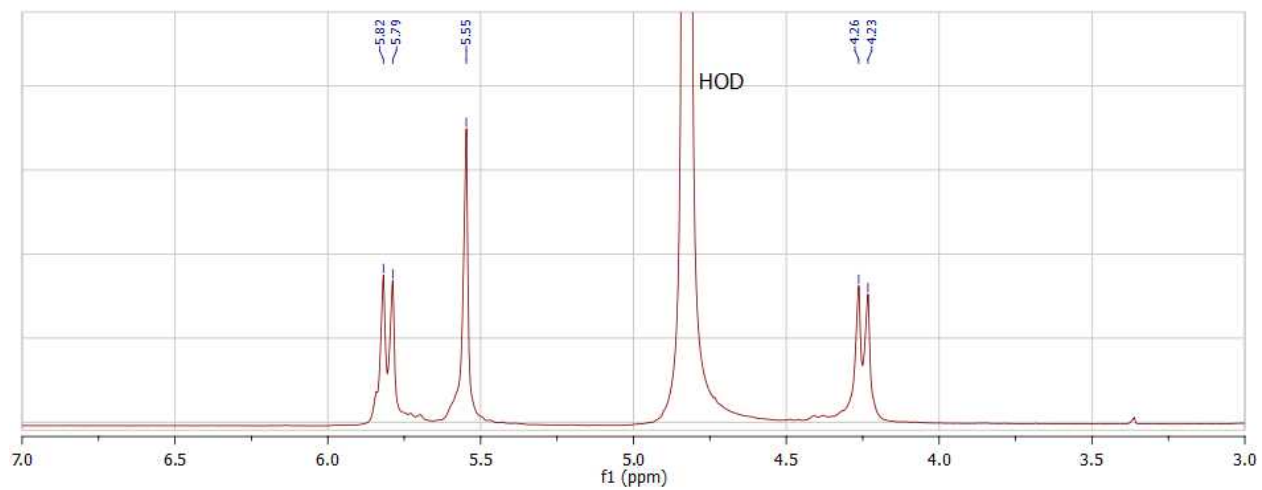
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<sup>i</sup> We observed that commercial samples of CB7 occasionally contained variable amounts of salts including sodium chloride (MS-ESI) and small amounts of CB[5] ( $^1\text{H}$  NMR). To minimize the presence of impurities we synthesized CB7.

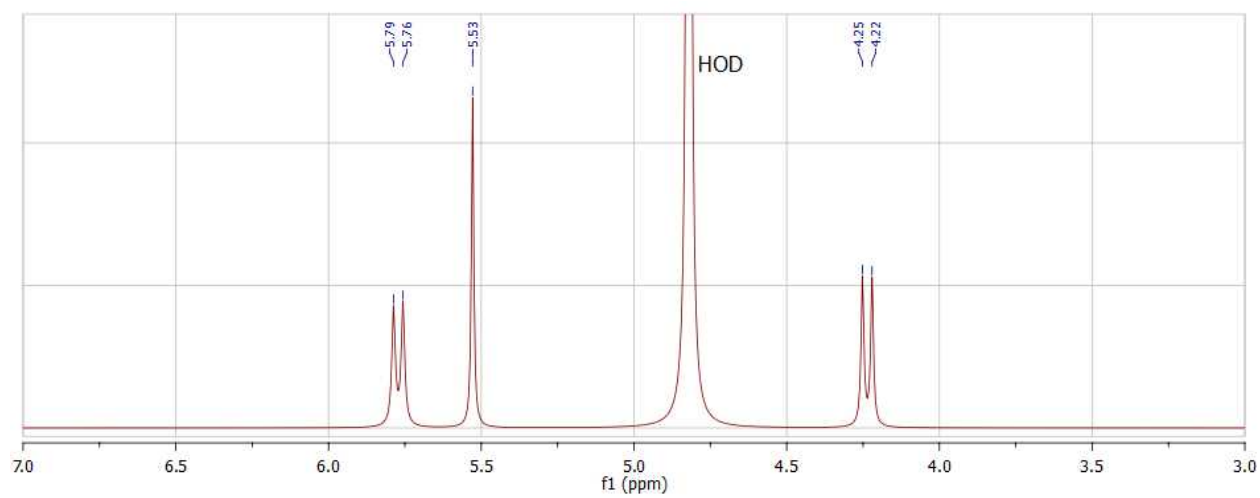
**1,1'-Bis(2,4-dinitrophenyl)-(4,4'-bipyridine)-1,1'-diium dichloride (4).**<sup>ii</sup> 4,4'-Bipyridine (**2**, 0.25 g, 1.6 mmol) and 2,4-dinitrochlorobenzene (**3**, 1.30 g, 6.4 mmol) were dissolved in acetone (20 mL). The solution was refluxed for 24 h, during which time a pale grey precipitate formed. The precipitate was collected by filtration and triturated twice with *n*-pentane and acetone. The product was dried *in vacuo* to yield the Zincke salt **4** as a yellow-grey powder (0.4 g, 44% yield). <sup>1</sup>H NMR (D<sub>2</sub>O, 25°C): δ = 9.55 (d, *J* = 6.46, 4H, ArH), 9.49 (d, *J* = 2.0, 2 H, ArH), 9.03 (d, *J* = 2.0, 2 H, ArH), 9.00 (d, *J* = 6.47, 4 H, ArH), 8.38 ppm (d, *J* = 2.0 Hz, 2 H, ArH); <sup>13</sup>C NMR (D<sub>2</sub>O): δ = 152.60, 149.82, 146.82, 142.77, 138.21, 131.12, 130.72, 127.33, 122.82 ppm.

**1,1'-Di-*p*-tolyl-(4,4'-bipyridine)-1,1'-diium dichloride (DTV<sup>2+</sup>) (1).** Compound **4** (0.50 g, 9.0 mmol) was dissolved with *p*-toluidine (**5**, 0.24 g, 22.5 mmol) in ethanol (20 mL) under nitrogen atmosphere. The resulting solution was refluxed for 24 h and the formed precipitate was filtered and discarded. The filtrate was evaporated *in vacuo* and the pale yellow crude product was triturated with acetone (250 mL), filtered, triturated again with acetone (2 x 500 mL), and dried *in vacuo* to yield **1** as a very pale yellow powder (0.33 g, 90% yield). <sup>1</sup>H NMR (D<sub>2</sub>O, 25°C): δ = 9.44 (d, *J* = 6.0, 2 H, ArH), 8.83 (d, *J* = 6.0, 2 H, ArH), 7.77 (d, *J* = 8.0, 2 H, ArH), 7.66 (d, *J* = 8.0, 2 H, ArH), 2.57 (s, 3 H, CH<sub>3</sub>); <sup>13</sup>C NMR (D<sub>2</sub>O): δ = 150.20, 145.25, 143.15, 139.15, 131.01, 126.93, 123.69, 20.31 ppm. FT-IR-ATR: 3387 (N-H), 3005 (C-H), 1635 (aromatic C=C), 1472 (C-N), 808 cm<sup>-1</sup>; MALDI-MS: *m/z* (%): 338.1787 (90) (M<sup>+</sup>), calcd. for C<sub>24</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>2</sub>: 338.1783. Elem. Anal. Calcd. for DTV<sup>2+</sup> (C<sub>24</sub>H<sub>22</sub>Cl<sub>2</sub>N<sub>2</sub>·3H<sub>2</sub>O): C 62.21 %, H 6.08 %, N 6.05 %. Found: C 62.41 %, H 5.94 %, N 6.09 %.

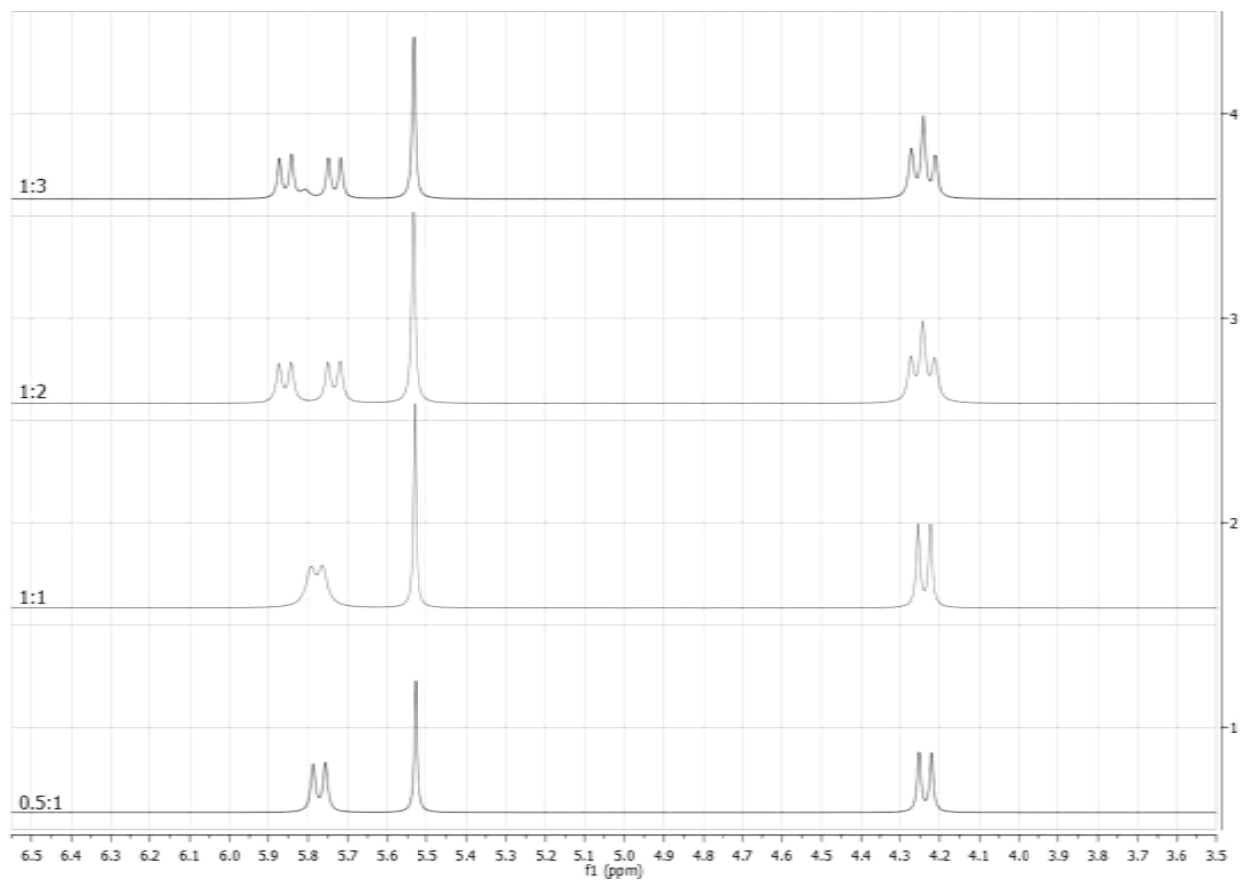
<sup>ii</sup> Yamaguchi, I.; Higashi, H.; Shigesue, S.; Shingai, S. *Tetrahedron Lett.* **2007**, *48*, 7778–7781.



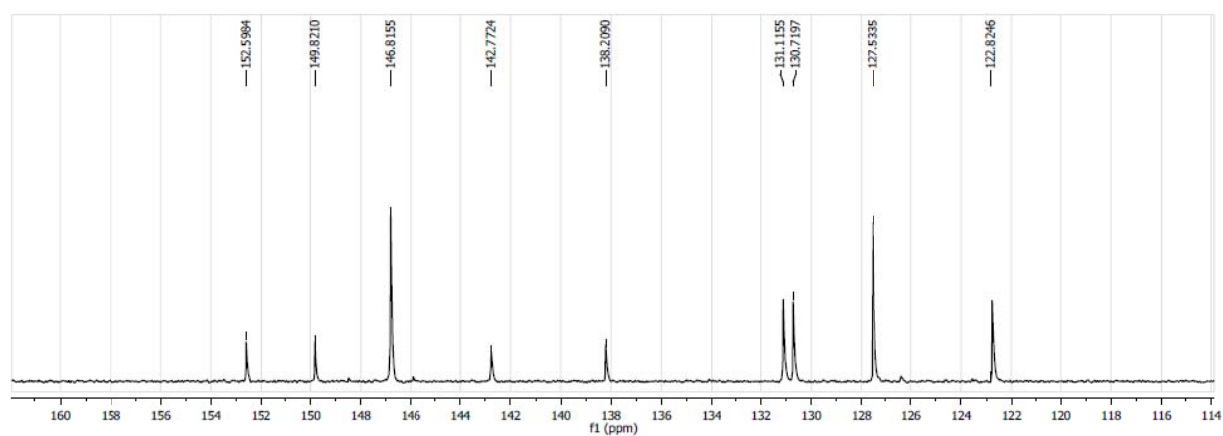
**Figure S1.**  $^1\text{H}$  NMR of commercially available CB7 in  $\text{D}_2\text{O}$  (Sigma-Aldrich, cat.# 545201).



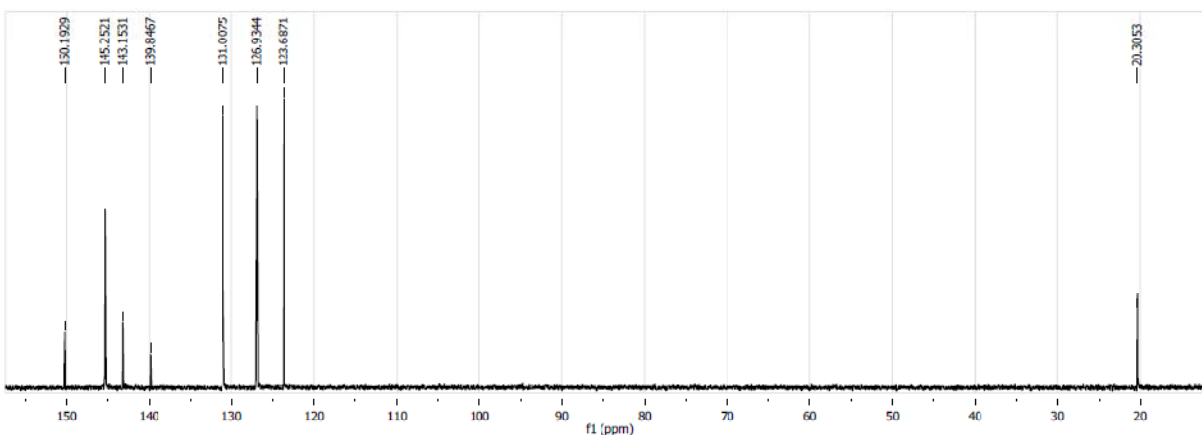
**Figure S2.**  $^1\text{H}$  NMR of synthesized CB7 in  $\text{D}_2\text{O}$ .



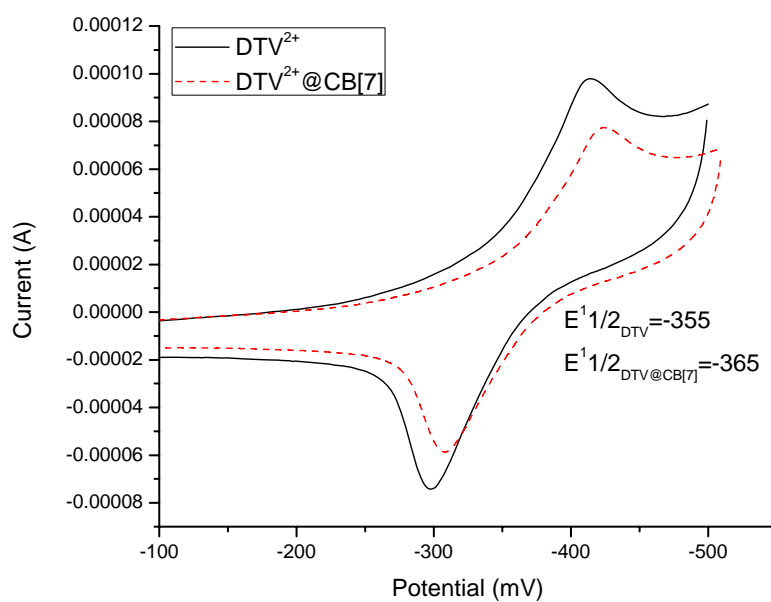
**Figure S3.**  $^1\text{H}$  NMR of the CB7 region (6.5 ppm - 3.5 ppm) in  $\text{D}_2\text{O}$ , at  $\text{DTV}^{2+}$  host : CB7 guest ratios 0.5:1, 1:1, 1:2, and 1:3.



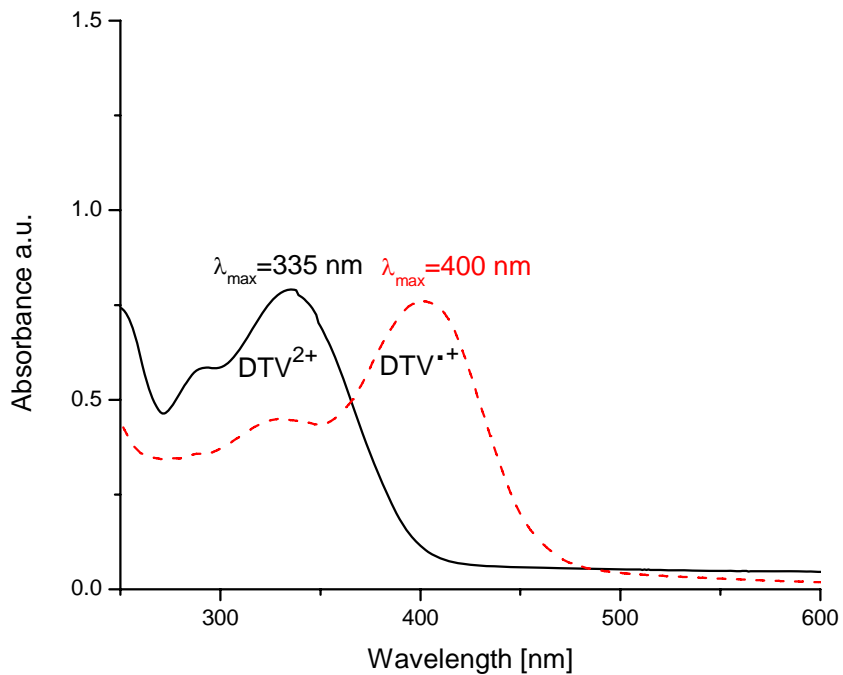
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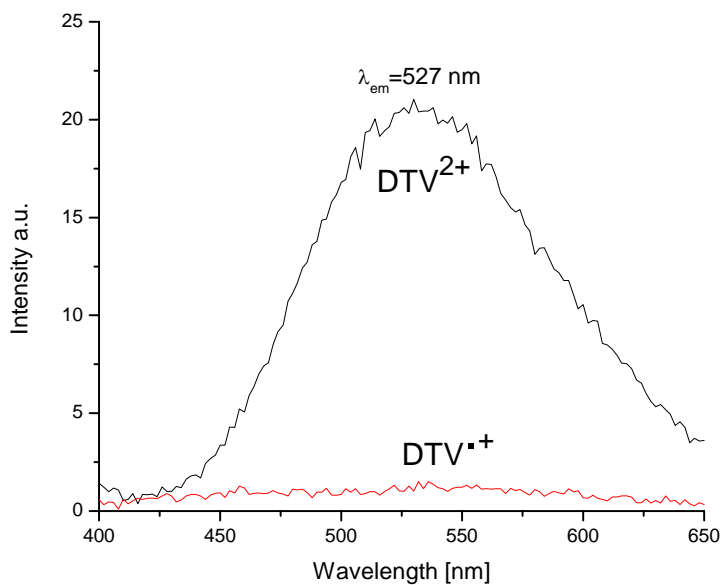
**Figure S5.**  $^{13}\text{C}$  NMR of  $\text{DTV}^{2+}$  (1).



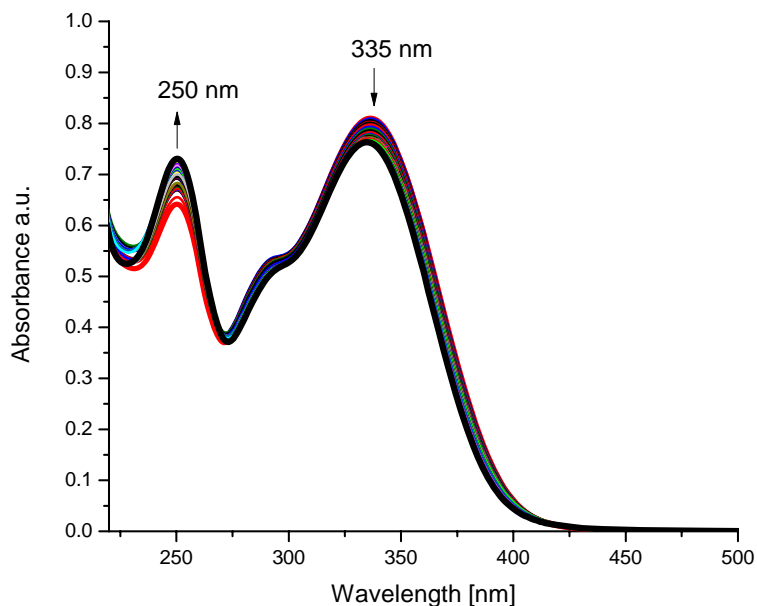
**Figure S6.** Cyclic voltammograms in 0.1 M phosphate buffer (pH 7.0) of 0.05 mM solutions of  $\text{DTV}^{2+}$  in the absence (black solid line) and in the presence (red dashed line) of CB7.



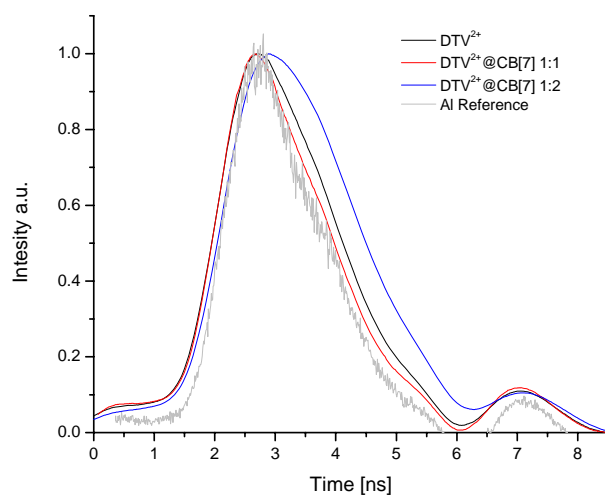
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**Figure S8.** Emission spectra of DTV<sup>2+</sup> in water before (black solid line) and after (red dashed line) one-electron reduction to DTV<sup>•+</sup> by application of a -1.0 V.  $\lambda_{\text{ex}} = 350 \text{ nm}$



**Figure S9.** Changes in the UV-vis spectrum during the complexation of  $\text{DTV}^{2+}$  ( $5 \mu\text{M}$ ) with CB7 (determination of complexation constant).



**Figure S10.** Fluorescence decay of  $\text{DTV}^{2+}$  and  $\text{DTV}^{2+}@CB7$  (1:1 and 1:2) in water at  $\lambda_{\text{ex}} = 335 \text{ nm}$

**Experimental Procedure for Job's Plot.** Solution A:  $1 \text{ mM DTV}^{2+}$ ; Solution B:  $1 \text{ mM CB7}$ .

Initial content of cuvette:  $2 \text{ ml H}_2\text{O}$  or  $2 \text{ ml } 0.05 \text{ mM NaCl}$ . The absorption and emission were measured for each step. A  $130 \mu\text{l}$  of Solution A or B in  $2 \text{ ml}$  water is  $0.6 \text{ mM}$ .