# **Electronic Supplementary Information (ESI)**

# Fluorescence quenching in $\beta$ -cyclodextrin vesicles: Membrane confinement and host-guest interaction

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**Chemicals:** All chemicals used were purchased from *Acros Organics* (Schwerte, Germany), *Sigma-Aldrich* (Taufkirchen, Germany), *Alfa Aesar* (Karlsruhe, Germany), *Merck* (Darmstadt, Germany) and *TCI* (Eschborn, Germany) and used without further purification.  $\beta$ - $\Omega$  was kindly donated by *Wacker ChemieAG* (München, Germany). The solvents used for synthesis were of analytical grade. *N*,*N*-dimethyl formamide was dried over molecular sieve under argon atmosphere.

**Synthesis:** Synthesis of **4** is depicted in Scheme **1**. First an ethylene glycol linker was a ttached to **1**-bromoadamantane. After tosylation of the product, nitrophenol was connected to the linker by a nucleophilic substitution.



**Scheme 1**: Synthesis of **4**: i) ethylene glycol, NEt<sub>3</sub>, 180 °C, 18 h, ii) TsCl, NEt<sub>3</sub>, 4-DMAP, DCM, RT, 18 h, iii) 4-Nitrophenol, K<sub>2</sub>CO<sub>3</sub>, MeCN, 85 °C, 18 h.

## 2-((adamant-1-yl)oxy)ethanol (7)



1-Bromoadamantane (1.00 g, 4.65 mmol, 1.0 eq.), triethylamine (1.9 mL, 13.95 mmol, 3.0 eq.) and ethylene glycol (20 mL) were added to a round bottom flask and stirred overnight at 180°C. After cooling to RT, DCM (50 mL) was added and the mixture was washed with 2 M  $HCl_{aq}$  (3×30 mL) and brine (3×30 mL). The organic layer was dried over MgSO<sub>4</sub>. After purification by column chromatography (DCM/MeOH 20:1), product **7** (419 mg, 2.14 mmol, 46%) was obtained as yellow brown solid.

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 3.71 – 3.64 (2H, m, CH<sub>2</sub>O), 3.56 – 3.48 (2H, m, CH<sub>2</sub>O), 2.15 (3H, s, CH-2), 2.07 (1H, s, OH), 1.74 (6H, d, J = 3.0 Hz, CH<sub>2</sub>-1), 1.69 – 1.54 (6H, m, CH<sub>2</sub>-3).

 $^{13}$ C-NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 72.46, 62.45, 60.97, 41.74 (CH<sub>2</sub>, C-1), 36.55 (CH<sub>2</sub>, C-3), 30.62 (CH, C-2).

HRMS (ESI): m/z calculated: 219.1361 [( $C_{12}H_{20}O_2$ )Na]<sup>+</sup>, measured: 219.1361.

The obtained results are in agreement with literature data.1

#### 2-((adamant-1-yl)oxy)ethyl 4-methylbenzenesulfonate (8)



2-((adamant-1-yl)oxy)ethanol (7) (400 mg, 2.04 mmol, 1.0 eq.) and 4-DMAP (catalytic) were dissolved in DCM (20 mL). First triethylamine (0.42 mL, 3.06 mmol, 1.5 eq.), then tosylchloride (427 mg, 2.24 mmol, 1.1 eq.) dissolved in DCM (5 mL) were added dropwise at 0°C. The mixture was stirred overnight, washed with  $H_2O$  (2×20 mL) and 2 M HCl<sub>aq</sub> (20 mL) and dried over MgSO<sub>4</sub>. After evaporating the solvent and purification by column chromatography (EtOAc), product **8** (540 mg, 1.54 mmol, 75%) was obtained as yellow oil.

<sup>1</sup>**H-NMR** (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.80 (2H, d, *J* = 8.3 Hz, Ar**H**), 7.33 (2H, d, *J* = 8.1 Hz, Ar**H**), 4.10 (2H, t, *J* = 5.5, 5.0 Hz, OCH<sub>2</sub>), 3.60 (2H, t, *J* = 5.4, 5.0 Hz, OCH<sub>2</sub>), 2.44 (3H, s, CH<sub>3</sub>), 2.11 (3H, s, CH-2), 1.65 – 1.50 (12H, m, CH<sub>2</sub>-1, CH<sub>2</sub>-3).

<sup>13</sup>**C-NMR** (75 MHz, CDCl<sub>3</sub>) δ (ppm): 144.75, 133.33, 129.87, 128.14, 72.88, 70.22, 57.98, 41.42 (CH<sub>2</sub>, C-1), 36.45 (CH<sub>2</sub>, C-3), 30.56 (CH, C-2), 21.77 (CH<sub>3</sub>, Ar-CH<sub>3</sub>).

HRMS (ESI): m/z calculated: 373.1449 [( $C_{19}H_{26}O_4S$ )Na]<sup>+</sup>, measured: 373.1436.

#### 4-(2-((adamant-1-yl)oxy)ethoxy)nitrobenzene (4)



2-((a damant-1-yl) oxy) ethyl 4-methylbenzenesulfonate (8) (492 mg, 1.40 mmol, 1.0 eq.) and 4-nitrophenol (214 mg, 1.54 mmol, 1.1 eq.) were dissolved in acetonitrile (15 mL). K<sub>2</sub>CO<sub>3</sub> (213 mg, 1.54 mmol, 1.1 eq.) was added and the solution was stirred overnight under reflux. After cooling to RT, H<sub>2</sub>O (50 mL) was added and the product was extracted with ethyl acetate (3×40 mL). The organic phase was washed with water (2×20 mL) and brine (2×20 mL) and dried over MgSO<sub>4</sub>. After purification by column chromatography (EtOAc), product 4 (368 mg, 1.16 mmol, 83%) was obtained as yellow solid.

**IR** (ART) v<sub>max</sub> (cm<sup>-1</sup>): 3121, 2921, 2890, 2853, 1591, 1513, 1497, 1450, 1336, 1300, 1255, 1189, 1170, 1105, 1096, 1071, 1064, 1018, 980, 963, 927, 875, 845, 811, 752, 721, 691, 660.

<sup>1</sup>**H-NMR** (300 MHz, CDCl<sub>3</sub>) δ (ppm): 8.22 – 8.14 (2H, m, ArH), 7.01 – 6.93 (2H, m, ArH), 4.20 – 4.13 (2H, m, CH<sub>2</sub>O), 3.84 – 3.77 (2H, m, CH<sub>2</sub>O), 2.16 (3H, s, CH-2), 1.77 (6H, d, *J* = 2.9 Hz, CH<sub>2</sub>-1), 1.70 – 1.53 (6H, m, CH<sub>2</sub>-3).

<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm): 164.26, 141.47, 125.95, 114.80, 73.00, 69.00, 58.50, 41.57 (CH<sub>2</sub>, C-1), 36.50 (CH<sub>2</sub>, C-3), 30.62 (CH, C-2). HRMS (ESI): m/z calculated: 340.1525 [(C<sub>18</sub>H<sub>23</sub>NO<sub>4</sub>)Na]<sup>+</sup>, measured: 340.1508.

Absorbance and fluorescence spectra:



Figure S1: Absorption (left), normalized fluorescence (middle) and corrected fluorescence (right) spectra ( $\lambda_{exc}$  = 375 nm) of 1 (6  $\mu$ M) incorporated in  $\beta$ -CDV in phosphate buffer (pH 7.2) in dependence of the concentration of quencher 3. The vertical lines indicate the excitation ( $\lambda_{exc}$ ) and emission ( $\lambda_{em}$ ) wavelength at which the correction factor was calculated.



Figure S2: Absorption (left), normalized fluorescence (middle) and corrected fluorescence (right) spectra ( $\lambda_{exc}$  = 375 nm) of 1 (6  $\mu$ M) incorporated in  $\beta$ -CDV in phosphate buffer (pH 7.2) in dependence of the concentration of quencher 4. The vertical lines indicate the excitation ( $\lambda_{exc}$ ) and emission ( $\lambda_{em}$ ) wavelength at which the correction factor was calculated.



**Figure S3:** a) Correction of intensity.  $F_{measured}$ : measured fluorescence intensity,  $A(exc)_{total}$ : total absorption at  $\lambda_{exc}$ , b: optical length (approximated to ½), A(em); total absorption at  $\lambda_{em}$ .<sup>2</sup> b) Correction of quantum yield. QY: measured quantum yield,  $A_{total}$ : absorption of fluorophore and quencher,  $A_{fluorophor}$ : absorption of fluorophore.



**Figure S4:** Comparison of the corrected and uncorrected emission ( $\lambda_{exc}$  = 375 nm) of 1 (6  $\mu$ M) incorporated in  $\beta$ -CDV in phosphate buffer (pH7.2) in dependence of the concentration of quencher (Q) **3** and **4**. F and F<sub>0</sub> are the emission maxima at 420 nm in presence and absence of quenchers, respectively.



Figure S5: Absorption spectra of 1 incorporated in  $\beta$ -CDV at different pH in dependence of the concentration of quencher 3.  $\lambda_{exc}$  = 375 nm and  $\lambda_{em}$  = 420 nm are indicated. The vertical lines indicate the excitation ( $\lambda_{exc}$ ) and emission ( $\lambda_{em}$ ) wavelength at which the correction factor was calculated.



Figure S6: Stern-Volmer plot of 1 incorporated in  $\beta$ -CDV in dependence of the concentration of quencher 3 at different pH. F and F<sub>0</sub> are the emission maxima at 420 nm in presence and absence of quenchers, respectively.

## References

1. R. Krishnan and K. R. Gopidas, J. Phys. Chem. Lett., 2011, 2, 2094-2098.

2. J. R. Lakowicz, Principles of fluorescence spectroscopy, Springer, New York, 3rd edn., 2006.