

# Supplementary Material (ESI) for Chemical Communications

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## Potassium Ion Recognition by 15-Crown-5 Functionalized CdSe/ZnS Quantum Dots in H<sub>2</sub>O

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### Supporting Information:

#### Synthetic Procedures:

All reactions were performed under nitrogen atmosphere. Solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with Macherey-Nagel pre-coated glassic sheets (0.20 mm with fluorescent indicator UV<sub>254</sub>). Tri-*n*-octylphosphine oxide (TOPO, 99 %), tri-*n*-butylphosphine (TBP, tech. grade 98 %) and hexadecylamine (HDA, 90 %) were purchased from Aldrich, SHOWA and TCI, respectively. CdO (99.99 %), selenium (Se) powder 200 mesh (> 99.5 %) and sulfur (S) powder (99.5 %) were obtained from Strem, ACROS respectively. Zinc stearate was purchased from Riedel-deHaën.

Compounds were visualized with UV light at 254 nm and 365 nm. Flash column chromatography was carried out using silica gel from Merck (230-400 mesh). <sup>1</sup>H NMR and <sup>13</sup>C NMR in CDCl<sub>3</sub> were recorded using a Varian (Unity Plus 400) spectrometer at 400 MHz and 100 MHz, respectively.

#### Synthesis of compound 3 (see Scheme 1 in text)

2-(hydroxymethyl)-15-crown-5-ether and thioctic acid were added to CH<sub>2</sub>Cl<sub>2</sub>.

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The mixture was stirred for 15 min at 0 °C under N<sub>2</sub>. Then, dicyclohexyl carbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) in cold CH<sub>2</sub>Cl<sub>2</sub> were added to the above solution, and the mixture was stirred for another 15 min at 0 °C. The cooling bath was then removed, and the solution allowed to warm to room temperature. After stirring for ~6 h under N<sub>2</sub>, the reaction mixture was filtered through a fine glass frit to yield a clear, pale yellow filtrate and insoluble urea byproduct as a fine, white gray powder. The clear filtrate was washed with water, acetic acid aqueous solution, and finally again with water. The organic layer was subjected to column chromatography on silica gel to obtain compound **3**. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 1.40-1.52 (m, 2H), 1.61-1.73 (m, 4H), 1.84-1.93 (m, 1H), 2.33 (t, *J*=7.2 Hz, 2H), 2.40-2.48 (m, 1H), 3.06-3.19 (m, 2H), 3.51-3.57 (m, 2H), 3.58-3.76 (m, 16H), 3.78-3.84 (m, 2H), 4.04-4.09 (m, 1H), 4.19-4.23 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 24.8, 28.9, 34.1, 34.7, 38.6, 40.3, 56.4, 64.2, 70.3, 70.4, 70.5, 70.6, 70.8, 70.9, 71.0, 71.1, 173; HRMS Calcd. for C<sub>19</sub>H<sub>34</sub>O<sub>7</sub>S<sub>2</sub>: 438.1746 found:438.1744.

#### **Synthesis of Mecaptoalkanoic crown ether (15-crown-5, compound 4, see text)**

Compound **3** (6.00 g) in 117 ml of 0.25 *N* sodium bi-carbonate, a total of 1.2 g of sodium borohydride was added portionwise. The mixture was well stirred and kept below 5 °C. After 30 minutes 100 ml of benzene was added and the colorless reaction mixture was acidified to pH = 1 with ice-cold 5 *N* HCl. The content of the benzene layer was distilled under reduced pressure, bp 169-172 °C (1 mm), yielding 15-crown-5 (4.50 g, 80%).

#### **Synthesis of 15-crown-5 capped CdSe/ZnS QDs**

The water-soluble CdSe/ZnS QDs were prepared using a stepwise procedure reported by Mattoussi et al.<sup>1</sup> with a slight modification. Briefly, TBP/TOPO-capped CdSe-ZnS core-shell particles were prepared from the growth and annealing of CdO. TBP/TOPO

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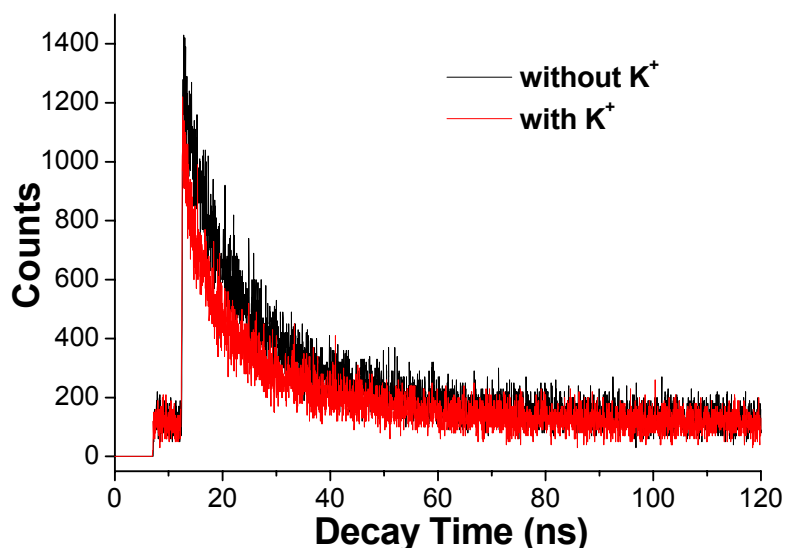
capping groups were subsequently exchanged with 40 mg 15-crown-5 placed in a reaction vessel 15 mL of methanol was added and the pH was adjusted to  $> 10$  with tetramethylammonium hydroxide pentahydrate. Under dark conditions, 10 mg of CdSe/ZnS nanocrystals were dissolved in the mixture, and the vessel was placed under regular airflow. The mixture was heated under reflux at 65 °C overnight, and then the reaction was terminated and the mixture allowed to cooling to room temperature overnight. The 15-crown-5-capped CdSe/ZnS nanocrystals were then precipitated with ethyl acetate. For further purification, methanol was added to dissolve the precipitate, followed by the addition of ethyl acetate to reprecipitate the nanocrystals.

#### **Preparation of 15-crown-5-QDs aqueous solution**

The vacuum dried CdSe/ZnS QDs were diluted in a 100-mL 0.05 M Tris-HCl buffer solution at pH 7.1. The concentration of QDs was calculated on the basis of an estimated molar absorption coefficient (see text). The final concentration of 15-crown-5-CdSe/ZnS QDs was  $\sim 0.5$  mM. This solution was used as a stock solution for the subsequent experiments.

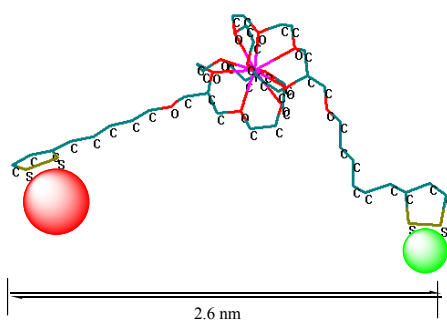
**Spectroscopic Measurements** Steady-state absorption and emission spectra were recorded with a Hitachi (U-3310) spectrophotometer and an Edinburgh (FS920) fluorimeter, respectively. Quinine sulfate with an emission yield of  $\Phi \sim 0.57$  ( $\lambda_{\max} \sim 460$  nm) in 0.1 M H<sub>2</sub>SO<sub>4</sub> served as a standard to calculate the emission quantum yield. Nanosecond lifetime studies were performed with an Edinburgh FL 900 photon-counting system with a hydrogen-filled/or a nitrogen lamp as the excitation source. Data were analyzed using the nonlinear least squares procedure in combination with an iterative convolution method. The emission decays were analyzed by the sum of exponential functions, which allows partial removal of the instrument time broadening and consequently renders a temporal resolution of  $\sim 200$  ps.

Fig. S-1 shows the relaxation dynamics of green QDs (in H<sub>2</sub>O, pH~ 7.1) emission (monitored at 545 nm) in a mixture containing green and red QDs (see text). The decay profile in black color was acquired before adding from K<sup>+</sup>. The decay can be fitted with a single exponential component with a lifetime  $\tau \sim 28$  ns. In comparison, after adding  $2 \times 10^{-4}$  M KClO<sub>4</sub> the decay could only be well fitted by two components with  $\tau$  of 30 and 7.2 ns. Within experimental error, the 30 ns component can be ascribed to the decay of green QDs free from K<sup>+</sup>, while the 7.2 ns component accordingly originates from networked green-K<sup>+</sup>-red structure, in which emission of green QDs is quenched via the energy transfer to red QDs.



**Fig. 1-S** (black) The emission trace of green QDs monitored at 545 nm in a mixture of green and red QDs in H<sub>2</sub>O. (red) Similar condition, except for the addition of  $2.0 \times 10^{-4}$  M KClO<sub>4</sub>.  $\lambda_{\text{ex}}$ : 430 nm.

Fig. 2-S depicts the geometry optimized 15-crown-5-K<sup>+</sup>-15-crown-5 based on AM1 method. The emission is assumed to be from the surface of QDs linked to 15-crown-5, so that both green and red QDs are treated to be a point source.



F-2S

Fig. 3-S depicts the proposed  $K^+$  recognition scheme through an intermolecular 15-crown5-CdSe/ZnS| $K^+$ |15-crown-5-CdSe/ZnS sandwich type of association.

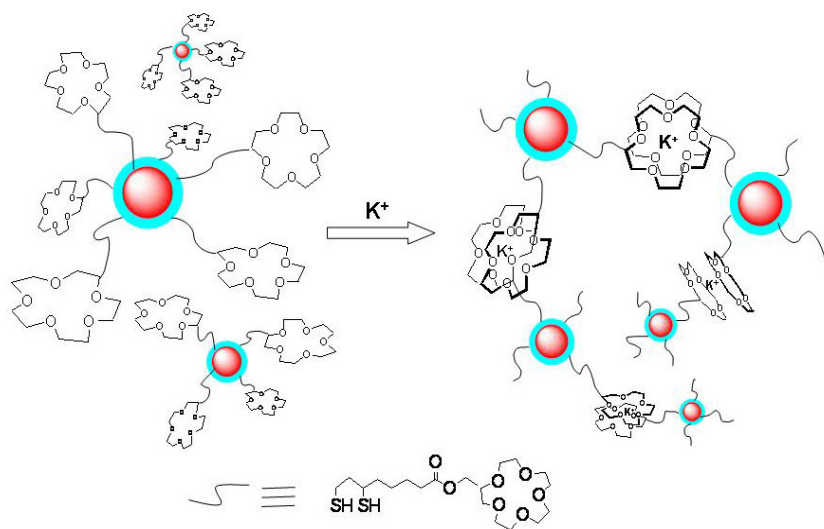
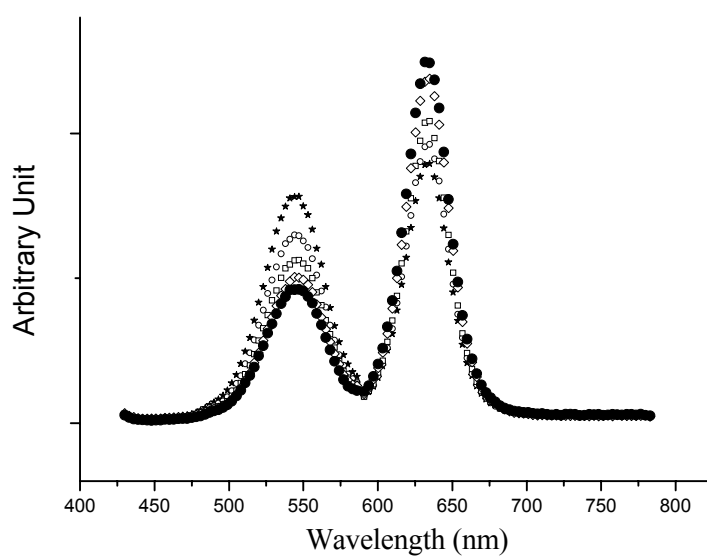


Fig. 3-S.



**Fig. 4-S** The fluorescence titration spectra of green and red QDs in water (pH ~ 7.1) by adding Ba(ClO<sub>4</sub>)<sub>2</sub> concentrations of (\*) 0, (o) 4, (□) 16, (◇) 64, (●) 256 equiv (1 equiv = 3.4 x 10<sup>-6</sup> M).  $\lambda_{\text{ex}} = 430$  nm.

1. H. Mattoussi, J. M. Mauro, E. R. Goldman, G. P. Anderson, V. C. Sundar, F. V. Mikulec and M. G. Bawendi, *J. Am. Chem. Soc.*, 2000, **122**, 12142.