Potassium ion recognition by 15-crown-5 functionalized CdSe/ZnS quantum dots in H_2O†

Chun-Yen Chen,[a] Chiu-Ting Cheng,[a] Chih-Wei Lai,[a] Pei-Wen Wu,[a] Kun-Chan Wu,[a] Pi-Tai Chou,*[a]
Yi-Hsuan Chou[b] and Hsin-Tien Chiu[b]

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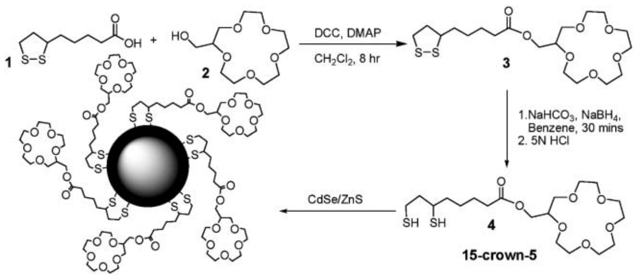
Based on 15-crown-5 functionalized CdSe/ZnS quantum dots (QDs), we report a novel fluorogenic sensor to probe K^+ ions in H_2O; recognition of K^+ can be achieved *via* the Förster type of energy transfer between two different color QDs, so that $[K^+]$ of the order of 10^{-6} M can be promptly detected.

The development of molecule-based ion sensors has been a pivotal issue currently receiving considerable attention. Among numerous methodologies, the exploitation of ionophores incorporated with optical transduction as a reporter seems to be a very promising one.[1] Recently, metal nanoparticles have emerged as important colorimetric reporters due to their high absorptivity which is also very sensitive to the transition from mono-dispersion to aggregation, resulting in a distinct color change.[2–8] For gold nanoparticles, the color change upon aggregation is due to the coupling of the surface plasmon resonance as a result of the proximity among Au nanoparticles.[9,10] Recently, based on a sandwich complex of 2 : 1 between 15-crown-5 and K^+, Chen and coworkers[11] reported on capping the Au nanoparticles with 2-(12-bromododecyloxy)methyl-15-crown-5 ether and the resulting 15-crown-5 functionalized Au nanoparticles were successfully exploited to probe K^+. On this fundamental basis, we propose that other crown ether-modified nanoparticles, especially those of II–VI semiconductor composites with highly luminescent properties, may serve as an alternative. If subtle changes in luminescence can be monitored upon metal ion binding, a highly sensitive probe can be developed, taking advantage of superior fluorescence properties such as high quantum efficiency and narrow bandwidth, *etc.* in II–VI quantum dots.

Herein, we report the synthesis of 15-crown-5 functionalized, water soluble II–VI quantum dots (QDs) as well as their exploitation as a sensing unit toward K^+ in aqueous solution. To avoid other metal ion (*e.g.* Zn^{2+}) interference using core only QDs (*e.g.* CdS),[12] we alternatively designed 15-crown-5–capped CdSe/ZnS (core/shell) QDs. In addition, this type I core/shell formation enhances the CdSe emission intensity and, to a certain degree, avoids the electron transfer from CdSe to the metal ions.

The water-soluble CdSe/ZnS QDs were prepared using a stepwise procedure reported by Mattoussi *et al.*[13] with a modification suited for capping mercaptoalkanoic crown ether (15-crown-5). Scheme 1 depicts the synthetic route. Briefly, tri-*n*-butylphosphine (TBP)/tri-*n*-octylphosphine oxide(TOPO)/hexadecylamine (HDA)-capped CdSe–ZnS core-shell particles were prepared from CdO.[14] TBP/TOPO/HDA capping groups were subsequently exchanged with 15-crown-5 (40 mg in 15 mL ethanol) placed in a reaction vessel, and the pH was adjusted to > 10 with tetramethylammonium hydroxide pentahydrate. Approx. 10 mg of CdSe/ZnS nanocrystals were dissolved in the mixture, and the vessel was placed under a regular airflow. The mixture was heated under reflux at 65 °C overnight, and then the reaction was terminated and allowed to cool 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.

Fig. 1A and B depict typical transmission IR spectra of neat 15-crown-5 and 15-crown-5-capped CdSe/ZnS QDs, respectively. Fig. 1C depicts the TOPO/HDA capped CdSe/ZnS QDs prior to the modification with 15-crown-5. Comparing Fig. 1A and 1B, the gross resemblance in both spectral features and peak positions for several vibrational modes such as C–H stretching (2800–3000 cm^{-1}) and bending ($\sim$1340 cm^{-1}), especially the C=O stretching motion of the ester functional group at 1732 cm^{-1} seems to guarantee a successful attachment of 15-crown-5 onto CdSe/ZnS QDs. Furthermore, the absence of a S–H stretch band in the range 2400–2600 cm^{-1} in Fig. 1B unambiguously supports the formation of the CdSe/ZnS-sulfur bond. However, the IR spectrum of 15-crown-5 capped CdSe/ZnS QDs, also seems to have subtle differences from the neat 15-crown-5which can be qualitatively ascribed to those belonging to HDA and TOPO spectra (see Fig. 1C), indicating that certain HDA and TOPO still exist in the 15-crown-5 capped CdSe/ZnS QDs. Nevertheless, the characteristic band associated with $>$P=O at $\sim$1100 cm^{-1} for



Scheme 1 The synthetic route of preparing 15-crown-5 and 15-crown-5-capped CdSe/ZnS QDs.

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[a] *Department of Chemistry, National Taiwan University, Taipei 106, Taiwan. E-mail: chop@ntu.edu.tw; Fax: +886 (2) 2369 5208; Tel: +886 (2) 2364 3876 ext. 3988*
[b] *Department of Applied Chemistry, National Chiao Tung University, Hsinchu, 300, Taiwan*

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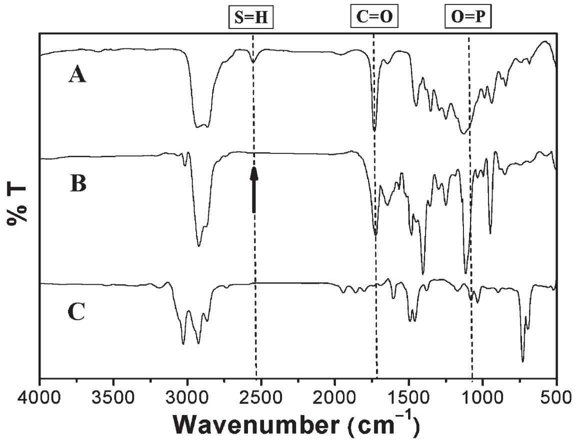

Fig. 1 Transmission IR spectra of (A) neat MCE, (B) MCE-modified CdSe/ZnS QDs (5.6/0.8 nm, KBr pellet), (C) TOPO capped CdSe/ZnS QDs. Note, the arrow pointing to the disappearance of S–H stretching in the 15-crown-5-modified CdSe/ZnS QDs.

TOPO nearly disappears upon encapsulating 15-crown-5 (see Fig. 1B), suggesting that 15-crown-5-capped particles have very few of the adsorbed TOPO remaining.

Fig. 2 depicts the fluorescence titration spectra of CdSe/ZnS (3.2/0.9 nm) and CdSe/ZnS (5.6/0.8 nm) QDs in water by adding $KClO_4$. In this approach, pH was fixed at 7.1 by using Tris-HCl buffer solution, and the terms "green" (545 nm) and "red" QDs (635 nm) were used to represent CdSe/ZnS (3.2/0.9 nm) and CdSe/ZnS (5.6/0.8 nm), respectively. For clarity, the absorption spectrum of the corresponding QDs prior to the K^+ titration is also depicted. However, negligible changes on the absorption features were observed during the K^+ titration. Furthermore, it is difficult to determine actual concentrations of green and red QDs due to the lack of precise molar absorptivity for CdSe/ZnS QDs. Qualitatively, we took the value at 430 nm for green and red QDs to be the same as those for the core only, *i.e.* CdSe (3.2 nm) $\sim 1.0 \times 10^5\ M^{-1}\ cm^{-1}$ and CdSe (5.6 nm) $\sim 5.0 \times 10^5\ M^{-1}\ cm^{-1}$, reported by Peng and coworkers.[15]

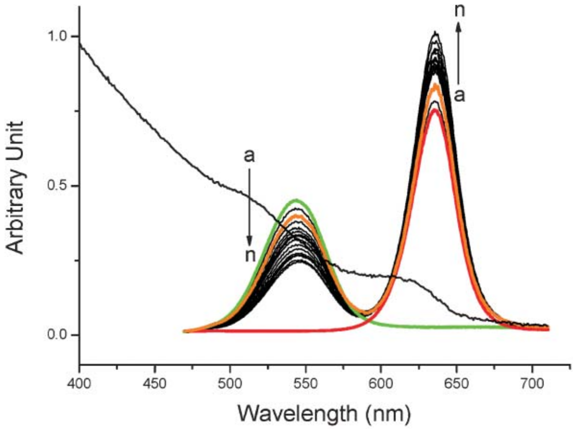

Fig. 2 The fluorescence titration spectra of green (absorbance ~0.10 at 430 nm) and red QDs (absorbance ~0.25 at 430 nm) in water (pH ~ 7.1) by adding $KClO_4$ concentrations of (black) (a) 0, (b) 1, (c) 2, (d) 4, (e) 8, (f) 12, (g) 16, (h) 20, (i) 24, (j) 32, (k) 64, (l) 128, (m) 256, (n) 512 equiv. (1 equiv. = 3.4×10^{-6} M). $\lambda_{ex} \sim 430$ nm. (Grey line) the absorption spectrum of the corresponding QDs prior to the K^+ titration. (Green) single green QD, (red) single red QD in the presence of 10^{-4} M K^+ to show negligible K^+ effect on spectra. (Orange) Adding 10^{-1} M [Na^+] in dual QDs containing 32 equiv. K^+ to show the reversibility.

Prior to titration, dual emission was observed with peak wavelengths at 545 and 635 nm (λ_{ex} = 430 nm). Since the excitation spectra monitored at 545 and 635 nm resembled each individual, *i.e.* solely green or red QDs absorption spectra, there is no interaction between the prepared green and red QDs, and quantum yields for the green and red QDs were measured to be 0.15 and 0.21, respectively. One can thus safely conclude that negligible energy or electron transfer takes place between green and red QDs in this dilute solution. Upon adding $KClO_4$, the 545 nm emission intensity gradually decreased, accompanied by an increase of the 635 nm band (Fig. 2). We also performed a controlled experiment in which only green (or red) 15-crown-5-QDs was titrated by K^+ under identical experimental conditions. In each controlled experiment, the 15-crown-5-QDs emission showed negligible changes in intensity upon adding $KClO_4$ up to 10^{-4} M (see Fig. 2). Thus, the decrease (increase) of green (red) emission in the mixed 15-crown-5–capped QDs (green and red) during the K^+ titration should be associated with a type of energy transfer mechanism. For either dual or single QDs system, when the added [K^+] was higher than 5.0 mM, appreciable precipitation was formed and visualized by the naked eye (see graphical abstract). Moreover, significant differences in the TEM images can be promptly perceived. For K^+ free CdSe/ZnS (5.0/0.8 nm) the TEM images (see Fig. 3) show semi-separately, dispersed particles, although the contrast for each individual QD is vague due to the interaction of MCE chains among QDs when concentrated. In contrast, an apparent aggregation of QDs was observed upon adding 5.0 mM K^+. In another approach, energy transfer and aggregation effect was not observed upon adding [Na^+] up to 0.1 M, although the 1 : 1 Na^+/15-crown-5 complex formation has been reported.[11,16]

It is well documented that the recognition of K^+ based on 15-crown-5 derivatives incorporates a 15-crown-5/K^+/15-crown-5 sandwich type of association.[11,16] In view of 15-crown-5 capped QDs, two possible binding schemes for the sandwich complexation are proposed, one of which incorporates two 15-crown-5 molecules from neighboring arms of the same QDs[16,17] clipping a K^+ ion (*i.e.* the intraparticle association). Alternatively, two 15-crown-5 molecules may originate from different QDs, forming an intermolecular type of association.

On the one hand, the mechanism of intraparticle K^+ formation has the advantage of possibly explaining the high association constant. Flink *et al.*[16] reported a high association constant for the intramonolayer complex of K^+ with 15-crown-5-SAM attached on

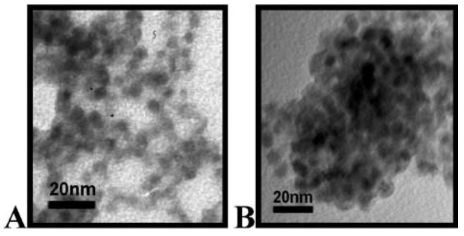

Fig. 3 TEM micrographs of 15-crown-5 functionalized CdSe/ZnS (5.0/0.8 nm) QDs (A) before and (B) after addition of 5.0 mM K^+ into 55 nM colloidal CdSe/CdTe solutions.

the Au electrode. In our case, the high K^+ selectivity would be attributable to the suitable configuration of two 15-crown-5 rings anchored on the QDs, so that the two adjacent crown ether rings act as a bis(15-crown-5) ether. The experimental results of aggregation (no aggregation) of QDs by excess addition of K^+ (Na^+) may possibly be explained by the difference of the nature of the metal ions. According to the Hofmeister series,[18] the hydrophobicity of K^+ is greater in water than Na^+. If almost all the 15-crown-5 rings on the QDs bind the metal cations under excess addition of them, K^+ ion may cause the aggregates of QDs more easily than Na^+ ion due to van der Waals interaction in aqueous media, resulting in precipitation. At low concentration, energy transfer may take place *via* dimer-like formation of the two different color K^+ encapsulated QDs.

On the other hand, the interparticle 15-crown-5/K^+/15-crown-5 formation can explain the K^+ experiments well with regard to the Förster type energy transfer as well as aggregation phenomena that were not observed in the Na^+ titration (1 : 1 15-crown-5/K^+ formation). Upon adding excess [K^+], QDs and K^+ may be networked *via* the sandwich complexes, followed by precipitation as soon as the entire network becomes water insoluble. It should be noted that this mechanism is also consistent with the proposed interparticle K^+ sandwich mechanism recently reported by Lin, *et al.* by using 15-crown-5 capped Au nanoparticles for K^+ recognition.[11] However, under the conditions of $< 10^{-4}$ M [K^+], this proposed mechanism requires an extraordinarily high association constant (M^{-2}) for the crown–K^+–crown sandwich complex. Unfortunately, due to the aggregation effect further quantitative studies on the thermodynamic properties of complexation are not possible. This leads to the difficulty in differentiating these two proposed mechanisms at this stage.

Nevertheless, the Förster type of energy transfer is apparently operative during the K^+ titration. *Via* semi-empirical (AM1) calculation, the distance between K^+ bridged two QDs (interparticle model) was estimated to be ~26 Å (only surface to surface between two QDs, see ESI†). Thus, the occurrence of a Coulombic, *i.e.* Förster, type of energy transfer is plausible. It is apparent that the 545 nm green emission overlaps well with the continuous absorption of red QDs. These, in combination with a value of $\sim 1.5 \times 10^5\ M^{-1}\ cm^{-1}$ around 545 nm for the red QDs and large transition dipole for the green QDs, unambiguously supports the occurrence of the Förster type of energy transfer upon K^+ association. Statistically, there will be three possible combinations regarding QDs/K^+/QDs association, namely the green/K^+/green, red/K^+/red and green/K^+/red structures, in which the probability of forming green/K^+/red configuration is predicted to be 50% under the condition of equal molarity for green and red quantum dots. We further estimated the Förster radius R_0 based on eqn (1) and (2) expressed as follows.

$$R_0^6 = \frac{9000 \times (\ln 10)\kappa_p^2 \times Q_D \times I}{N_A \times 128 \times \pi^5 \times n_d^4} \quad (1)$$

$$I = \int PL_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda \quad (2)$$

where $\kappa_p^2 = 2/3$ for randomly oriented dipoles, Q_D is the quantum efficiency of the donor, N_A denotes the Avogadro's number, n_d is the refractive index of the solution. I is the spectral overlap between the donor (green QDs) emission and acceptor (red QDs) absorption, and can be further expressed in (2), in which $PL_D(\lambda)$ is the normalized emission intensity of the donor (green QDs), $\varepsilon_A(\lambda)$ is the absorption extinction coefficient of the acceptor (red QDs). Taking $Q_D = 0.15$ and $n_d = 1.333$ (H_2O at 580 nm), R_0 was calculated to be 53.5 Å.

From a selectivity viewpoint, one remarkable feature of this QDs system is in that the ratiometric changes for the dual emission intensities are insensitive to the addition of numerous physiologically important cations, such as Li^+, Cs^+, Mg^{2+}, and Ca^{2+}. We have also performed the Ba^{2+} titration and did observe similar energy transfer and aggregation phenomenon as that for the K^+ titration (see ESI†). Since K^+ (1.52 Å) and Ba^{2+} (1.49 Å) have similar ionic radii, the 15-crown-5/Ba^{2+}/15-crown-5 sandwich type of association is also operative.

In conclusion, we have demonstrated that CdSe/ZnS QDs modified with 15-crown-5 in water exhibit excellent selectivity towards K^+. The recognition is achieved by the 15-crown-5/K^+/15-crown-5 sandwich type of complexation. Signal transduction can be achieved through the energy transfer which takes place between dual color QDs, resulting in a ratiometric change of dual emission intensity and hence the emission color. Taking the intensity ratio of 1.8 for 635 nm *versus* 545 nm emission in the K^+ free solution and that of 2.2 in 3.4×10^{-6} M K^+ solution, the ratiometric fluorescence is easily differentiated, the result of which concludes the K^+ detection limit to be of the order of 10^{-6} M. In view of sensitivity and selectivity, we thus present a conceptual design of 15-crown-5 functionalized CdSe/ZnS QDs and apply dual color energy transfer as a general detection scheme to probe K^+ in H_2O. This recognition scheme should spark a broad spectrum of interest due to its great versatility and flexibility for future applications.

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