Cite this: New J. Chem., 2012, 36, 1725–1728



Metal ion-induced dual fluorescent change for aza-crown ether acridinedione-functionalized gold nanorods and quantum dots[†]

Ranganathan Velu,[‡]^a Nayoun Won,[‡]^a Jungheon Kwag,^b Sungwook Jung,^b Jaehyun Hur,^c Sungjee Kim^{*ab} and Nokyoung Park^{*c}

Received (in Montpellier, France) 29th May 2012, Accepted 8th July 2012 DOI: 10.1039/c2nj40444c

Aza-crown ether acridinedione-functionalized quantum dots (ACEADD-QDs) and aza-crown ether acridinedione-functionalized gold nanorods (ACEADD-GNRs) have been developed as a pair for a fluorescent chemosensor detecting metal ions. The ACEADD-QDs have dual emissions at a visible wavelength of \sim 430 nm from the acridinedione dye moiety and at a near-infrared (NIR) wavelength of \sim 775 nm from the CdTeSe QDs. In the presence of Ca²⁺ or Mg²⁺ ions, the ACEADD-OD and ACEADD-GNR pair can form a sandwich complex mediated by the metal ion. The ACEADD-QD and ACEADD-GNR complex pair shows visible fluorescence enhancement from the acridinedione dye and concurrent fluorescence quenching from the NIR QD. The aza-crown ether complex results in the suppression of photoinduced electron transfer from the aza-crown ether to the acridinedione dye moiety. At the same time, the OD fluorescence can be effectively quenched by the nanometal surface energy transfer from the QD to the GNR. This ACEADD-QD and ACEADD-GNR pair can effectively transduce the selective binding event of crown ethers with metal ions into the simultaneous modulation of the enhancement in dve fluorescence and the quenching of QD emission, which can open a new strategy for ratiometric sensors that are selective and robust against the environment conditions.

Energy transfer in nanoscale donor-acceptor systems has extensive applications in sensors, bioimaging, photovoltaic devices, light

emitters, and other optoelectronics.^{1–5} For example, many biosensors have been developed using photoluminescence modulations through fluorescence resonance energy transfer (FRET) between a donor and acceptor pair.⁶⁻⁹ Metallic surfaces or metal nanoparticles have been actively studied for the dipole-surface energy transfer and the induction of fluorescent probe quenching.^{10–13} Such donor–acceptor type fluorescent sensors are advantageous due to their high sensitivity, but may be influenced by many factors including photobleaching, analyte concentration, environmental changes (pH, polarity, temperature, and etc.), and instability under illumination. In comparison to simple luminescence-based detection, ratiometric sensors can afford simultaneous recording of two emission intensities at different wavelengths in the presence or absence of the analytes and thus can permit signal rationing and thus increase the dynamic range and provide built-in correction for the environmental effects.^{14,15}

Based on the well-known binding ability of crown ethers to host s-block metals, many fluorescent chemosensors have been designed in the recent years for alkali and alkaline earth ions containing at least one crown ether moiety (or a related derivative) which behaves as a 'recognition subunit' connected to one or more fluorophores.^{16–18} The efficiencies of energy transfer processes are related to the spectral overlap of the acceptor's absorption with the donor's emission, and sensitively depend on the distance between the two molecules.¹⁹ In the present work, we have developed aza-crown ether acridinedione-functionalized gold nanorods (ACEADD-GNRs, 1) and aza-crown ether acridinedionefunctionalized quantum dots (ACEADD-QDs, 2) towards specific sensors for Ca²⁺ and Mg²⁺ (Scheme 1).

The ACEADD-QDs have dual emissions at a visible wavelength of ~430 nm from the acridinedione (ADD) dye moiety and at a near-infrared (NIR) wavelength of ~775 nm from the CdTeSe QDs. QDs emitting at the NIR range are judiciously chosen for the efficient energy transfer to GNRs which has high extinction at the NIR range. The CdTeSe QD emission has been judiciously chosen for the maximal overlap with the longitudinal plasmon extinction of the GNR to achieve the efficient energy transfer from the QD to GNR.²⁰ The pair of **1** and **2** can effectively transduce the selective binding event of crown ether with metal ions into the simultaneous modulation of enhancement in ADD

^a Department of Chemistry, Pohang University of Science & Technology, Pohang, 790-784, Republic of Korea. E-mail: sungjee@postech.ac.kr; Fax: +82-54-279-1498;

Tel: +82-54-279-2108 ^b School of Interdisciplinary Bioscience and Bioengineering, Pohang University of Science & Technology, Pohang, 790-784, Republic of Korea

^c Samsung Advanced Institute of Technology, Mt. 14-1,

Nongseo-Dong, Giheung-Gu, Yongin-Si, Gyeonggi-Do, 446-712, Republic of Korea. E-mail: n2010.park@samsung.com

[†] Electronic supplementary information (ESI) available: Experimental details for the aza-crown ether acridinedione synthesis, PL spectra of the mixture of aza-crown ether acridinedione-functionalized gold nanorods and aza-crown ether acridinedione-functionalized quantum dots upon the addition of Ca^{2+} , Mg^{2+} , Na^+ , K^+ or Ba^{2+} ions, PL spectra of aza-crown ether acridinedione-functionalized quantum dots upon the addition of Ca^{2+} ions, and Stern–Volmer plots. See DOI: 10.1039/c2nj40444c

[‡] These authors contributed equally to this work.



Scheme 1 Schematic structures of aza-crown ether acridinedionefunctionalized gold nanorods (ACEADD-GNRs, 1) and aza-crown ether acridinedione-functionalized quantum dots (ACEADD-QDs, 2) and illustration of fluorescence change of the complex (3) upon the addition of metal ions.

dye fluorescence and quenching of the QD emission. When aza-crown ether (ACE) is conjugated to ADD dye, photoinduced electron transfer (PET) occurs from the nitrogen lone pair of the ACE to the relatively electron deficient ADD moiety inducing the fluorescence quenching of the ADD. As a 'recognition subunit', the ACE can bind metal ions and PET is suppressed resulting in the recovery of the ADD fluorescence. At the same time, ACE can form the sandwich complex in the presence of cations and can result in the formation of ACEADD-QDs and ACEADD-GNRs complex pair 3. The efficiency of energy transfer is critically related to the distance between the donor and the acceptor. The decreased distance between the OD and GNR in 3 leads to the efficient energy transfer from QDs to GNRs and results in the QD fluorescence quenching. Studies for Ca^{2+} sensors have been recently reported by various groups.²¹ Ca^{2+} specific sensors using the principle of PET was suggested by de Silva and Gunaratne.²² However, the chemosensors reported so far have been mostly achieved by charge or energy transfer processes in chromophores.^{23,24} In addition, to the best of our knowledge, s-block metal ion sensing based on dual fluorescence modulations in visible and NIR wavelengths has not been reported.

The ADD in acetonitrile has the absorption peak at 360 nm and emission peak at 430 nm.^{25,26} The peak at 360 nm is attributed to the intramolecular charge transfer from the nitrogen to the carbonyl oxygen in the ADD moiety and the emission at 430 nm to that of the local excited (LE) state. Fig. 1a shows absorption spectra of 1 in acetonitrile. The peaks around 515 and 770 nm are originated from the transverse and longitudinal surface plasmon resonances of GNRs. Upon the addition of Ca²⁺ ions, red-shift of the longitudinal peak was observed from 770 nm continuously up to 920 nm as the ion concentration increased, which is due to the inter-GNR plasmon mode coupling from the linearly linked GNRs (Fig. 1a). The QDs were prepared using previously reported methods.^{27,28} Absorption and emission spectra of CdTeSe QDs are shown in Fig. 1b. The QDs have the excitonic peak at 740 nm and emission peak at 775 nm. As can be seen from Fig. 1a and b, the CdTeSe QDs have been chosen so that the emission of the CdTeSe QDs overlaps well with the strong longitudinal plasmon resonance of GNRs. Absorption and photoluminescence spectra of ACEADD and ACEADD-QDs are shown in Fig. S1 (ESI[†]). The ACEADD-QDs show dual emissions from the ADD dye at a visible wavelength



Fig. 1 (a) Absorption spectra of aza-crown ether acridinedionefunctionalized gold nanorods upon the addition of $0-85 \ \mu\text{M}$ of Ca^{2+} ions in acetonitrile. (b) Absorption and photoluminescence spectra of CdTeSe quantum dots in hexanes.

of \sim 430 nm and from the CdTeSe QD at a NIR wavelength of \sim 775 nm under the excitation at 360 nm. The ACEADD showed marginal difference in the photoluminescence property after the conjugation with QD, which manifest the negligible FRET from the dye to the QD. Using the excitation wavelength at 500 nm, the ACEADD-QD sample showed the emission from QD only.

A mixture of 1 and 2 retained the optical properties of each, with the emission maxima at 430 nm from the ADD moiety and at 775 nm from 2. Upon the addition of Ca^{2+} ions, fluorescence from the ADD was enhanced as previously reported (Fig. 2a).²⁹ Upon increasing the Ca²⁺ ion concentration from 8 to 80 µM, the emission at 430 nm from the ADD moiety was gradually increased by up to 2.2 fold from the initial intensity. In the absence of cations, PET occurs from the N-atom of the cation receptor (1-aza-15-crown-5) to ADD, inducing the fluorescence quenching. In the presence of cations which can complex to the aza-crown ether, fluorescence of ADD can recover by the PET suppression. On the other hand, fluorescence from the QDs was quenched by the addition of Ca²⁺ ions (Fig. 2b). Upon increasing Ca²⁺ ion concentrations from 8 to 80 µM, the quenching efficiency for the QD emission was linearly increased by up to 80%, which suggests the high FRET efficiency over 80%. The dual emission changes at visible wavelength and NIR wavelength can be represented by the emission intensity ratios. Fig. 2c shows the emission intensity ratios between ADD emission at 430 nm and QD emission at 775 nm. The ratio was increased linearly with increasing Ca^{2+} concentration. This suggests that our ACEADD-QD and ACEADD-GNR pair based sensor functions well for the ratiometric detection of Ca²⁺ ions, which can potentially alleviate interferences from external environments. The QD fluorescence quenching is attributed to



Fig. 2 Photoluminescence (PL) spectra of the mixture of aza-crown ether acridinedione-functionalized gold nanorods (460 pM) and aza-crown ether acridinedione-functionalized quantum dots (920 pM) upon the addition of 0–80 μ M of Ca²⁺ ion in acetonitrile. (a) Emission from the acridinedione moieties ($\lambda^{ex} = 360$ nm). (b) Emission from the CdTeSe quantum dots ($\lambda^{ex} = 500$ nm). (c) Ratio of PL intensity at 430 nm to PL intensity at 775 nm.

the increased energy transfer from the QDs to GNRs in closer proximity. The proximity between the QD and GNR resulted from the sandwich formation of 3 mediated by the sandwiched cation-crown ether complex. The formation of 3 was further confirmed by HR-TEM images (Fig. 3). The TEM sample of 3 was prepared by drop-casting a dilute suspension on a carboncoated copper grid. QDs were found to have an average diameter of 7.0 nm. In the absence of cation, the free ACEADD-QDs and ACEADD-GNRs were well-dispersed and aggregates were not observed (Fig. 3a). When 80 µM of Ca^{2+} ions were added to the mixture of 1 and 2, the distance between nanoparticles became closer through the sandwich complex between ACEADDs. As a result, QDs gathered densely around the edges of GNRs (Fig. 3b). The decreased distances between QDs and GNRs enhanced the efficient energy transfer from QDs to GNRs and subsequent quenching of the QD emission. Our ACEADD-QD and ACEADD-GNR pair based cation sensor also showed the fluorescence modulation in the presence of Mg^{2+} ions (Fig. S2, ESI⁺). Similar to the case of Ca^{2+} ion, the fluorescence from the ADD moiety was gradually enhanced and the QD emission was simultaneously quenched as the concentration of Mg^{2+} ions increased from 8 to 80 μ M.

A control experiment was performed by adding Ca^{2+} ions to **2** in the absence of **1**. No noticeable change was found in the QD fluorescence, excluding possibilities of QD fluorescence change by direct interactions between the QDs (or QD surfaces) and Ca^{2+} ions (Fig. S3, ESI[†]). The quenching efficiencies on Ca^{2+} or Mg²⁺ ions were studied using the Stern–Volmer plot. Stern–Volmer constants (K_{SV}) were obtained for Ca^{2+} and



Fig. 3 (a) HR-TEM image of the mixture of aza-crown ether acridinedione-functionalized gold nanorods (aspect ratio of 3.7) and azacrown ether acridinedione-functionalized quantum dots. (b) HR-TEM image of the mixture after the addition of 80 μ M of Ca²⁺ ions.

 Mg^{2+} ions as 47 300 M⁻¹ and 44 400 M⁻¹, respectively (Fig. S4, ESI[†]). Other metal ions such as Na⁺, K⁺ and Ba²⁺ were also added to the mixture of **1** and **2**. No noticeable change in the absorption or emission was found, indicating the absence of complex **3** formation (Fig. S5, ESI[†]).

The reversible nature of our system was confirmed by the addition of ethylenediaminetetraacetic acid (EDTA) to complex **3** which was formed by the addition of 85 μ M of Ca²⁺ ions to the mixture of **1** and **2**. The fluorescence from ADD was enhanced about 2 fold by the addition of Ca²⁺ ions and gradually decreased by increasing the EDTA concentration up to 95 μ M (Fig. 4a). The fluorescence decrease is attributed to the detachment of Ca²⁺ ions from crown ether and subsequent recurrence of PET. At the same time, the QD fluorescence was quenched with the addition of Ca²⁺ ions and gradually recovered by increasing the EDTA concentration up to 95 μ M (Fig. 4b). The QD fluorescence recovery results from the increased distance between **1** and **2**.

In summary, we have demonstrated a fluorescent chemosensor for metal ions based on a pair of ACEADD-GNR and ACEADD-QD. The sensor shows excellent selectivity towards Ca²⁺ and Mg²⁺ ions resulting in the enhanced fluorescence from ADD in the visible range which is attributed to the PET suppression and concurrent QD fluorescence quenching at the NIR range which is due to the energy transfer from QD to GNR. In the successive work, the surface-coating of GNRs can be modified with multilayer polyelectrolytes for the improved biocompatibility for various biological applications.³⁰ As for the potential QD toxicity issue, the CdTeSe QDs are desired to be replaced by QDs that consist of less toxic elements such as InP or CuInS₂ based QDs.³¹⁻³³ Our ACEADD-QD and ACEADD-GNR pair system can be a prototype for a general dual fluorescence modulation (turn-on at the visible range and turn-off at NIR) sensor for robust and sensitive sensing applications.

Experimental

Materials

All the metal ions used in this assay were in the form of their perchlorates. Gold(III) chloride hydrate (HAuCl₄·3H₂O, \geq 99.9%), silver nitrate (AgNO₃, \geq 99.9%), L-ascorbic acid, sodium borohydride (NaBH₄, 99%), cetyl trimethylammonium bromide (CTAB, 98%), and polyvinylpyrrolidone (PVP) were purchased from Sigma-Aldrich.



Fig. 4 Photoluminescence (PL) spectra of the mixture of aza-crown ether acridinedione-functionalized gold nanorods (460 pM) and aza-crown ether acridinedione-functionalized quantum dots (920 pM) which was previously treated with 85 μ M of Ca²⁺ ions in acetonitrile. 0–95 μ M of ethylenediaminetetraacetic acid (EDTA) were added to the solution. (a) Emission from the acridinedione moieties. (b) Emission from the CdTeSe quantum dots.

Synthesis of ACEADD-GNRs

The ACEADD was synthesized by our previously reported method (synthetic details and characterization data are available in the ESI[†]).²⁹ The GNRs used in this study were synthesized by a surfactant-stabilized, seedless one-step technique following a procedure reported in the literature.^{34,35} HAuCl₄ (20 mM), AgNO₃ (0.1 mM), and ascorbic acid (0.1 M) were mixed in 5 mL of 0.1 M aqueous CTAB solution. 20 μ L of 1.6 mM NaBH₄ was used as the reducing agent to generate GNRs. The GNRs were further stabilized by adding PVP. They were centrifuged and re-dispersed in ethanol by adapting a procedure utilized by Liz-Marzan and coworkers.^{36,37} 25 μ M of ACEADD was added to the PVP-stabilized GNR solutions under stirring and the solution was kept undisturbed for 24 h to allow adequate time for the self-assembly of the ACEADD monolayer onto the ends of the GNR.

Acknowledgements

This work was supported by a Korea Science and Engineering Foundation grant funded by Ministry of Science and Technology (20110018601), the Korea Health 21 R&D Project Ministry of Health & Welfare (A101626), the Priority Research Center Program through National Research Foundation of Korea (NRF) (2011-0031405 and 20110027727), the Ministry of Education, Science and Technology through NRF (20110019635), the Basic Science Research Programs (20110027236), and Defense Acquisition Program Administration and Agency for Defense Development under the contract (ADD-10-70-06-02).

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