Supplementary Information

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

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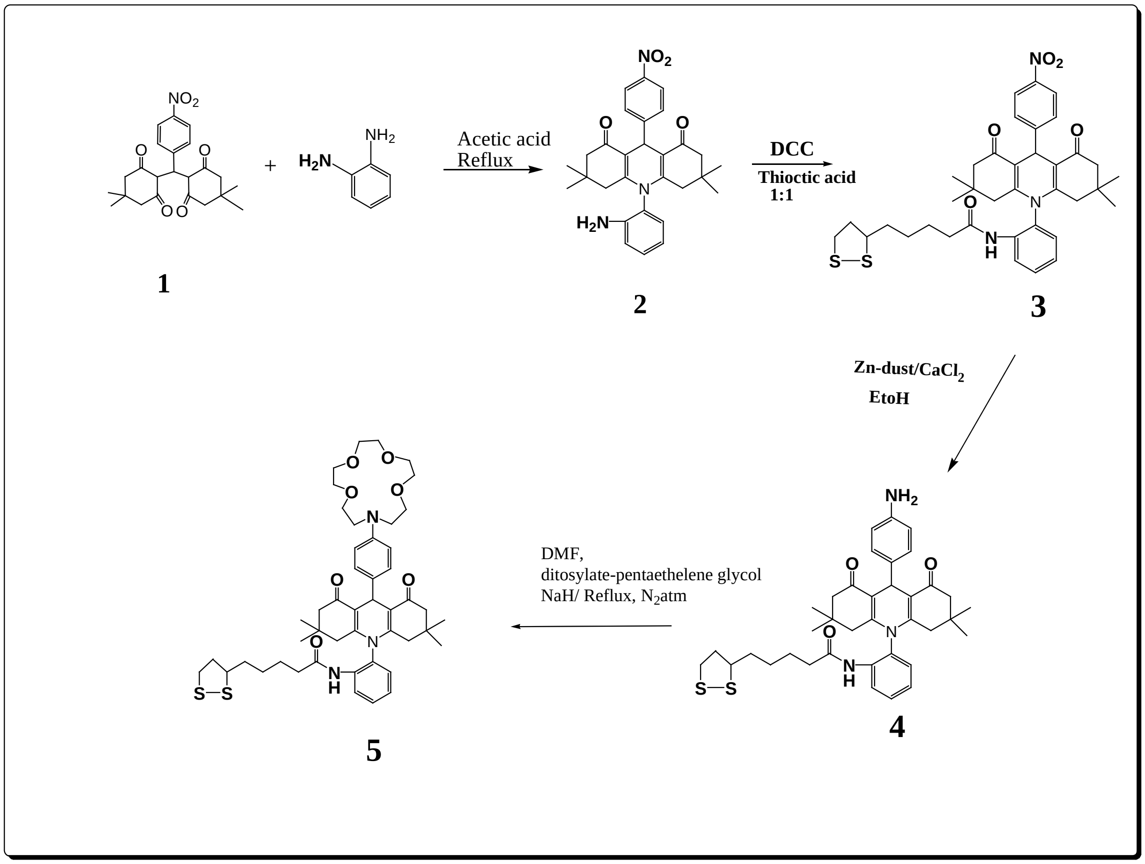
Experimental Details

Materials

Solvents used were HPLC grade obtained from Qualigens (India) Ltd. (±)-α-Lipoic acid, N,N′-dicyclohexylcarbodiimide (DCC), Zn (dust, ≥98%), pentaethyene glycol ditosylate (95%) were purchased from Sigma-Aldrich.

ACEADD synthesis scheme



Preparation of 2,2’-(4-nitrobenzylidene) bis (5,5- dimethylcyclohexane-1,3-dione) (1): To a mixture of dimedone (5.0 g, 36 mmol) in aq.methanol was added 4-nitrobenzaldehyde (2.7 g, 18 mmol) and the mixture was warmed until the solution became cloudy. The (4-nitrobenzylidene) bis dimedone started to separate out. The reaction mixture was diluted with water (250 mL) and allowed to stand overnight. The tetraketone **1** was collected by filtration, dried and recrystallised from methanol. (Yield : 6.9 g (94%), M.P.: 182-184°C (Lit M.P.: 188-190°C))

9-(4-Nitrophenyl)-3,3,6,6-tetramethyl-10-(2-amino phenyl)-3,4,6,7,9,10-hexahydro-1,8(2H,5H) acridinedione (2): A mixture of the tetraketone **1** (2.0 g, 4.85 mmol) and 1, 2-phenylenediamine (1.0 g, 9.2 mmol, excess) in acetic acid (20 mL) was refluxed for 12 hours. The reaction mixture was cooled and poured into crushed ice. The solid obtained was filtered and dried. The acridinedione **2** was purified by recrystallisation from a mixture of methanol and chloroform (1:4). (Yield: 1.2 g (52%), M.P.: 258-260°C.)

9-(4-Nitrophenyl)-3,3,6,6-tetramethyl-10-(2-thioctinoylaminophenyl)-3,4,6,7,9,10-hexahydro-1,8(2H,5H)acridinedione (3): A mixture of nitroacridinedione **2** (1.0 g, 2.12 mmol) and lipoic acid (0.5 g, 2.4 mmol) in dry dichloromethane (20 mL) with DCC on reflux, afforded the acridinedione derivative **3**. The product was purified by column chromatography over silica gel and eluting with 4% methanol in chloroform. (Yield: 1.2 g (83%), M.P.: 220°C.)

9-(4-Aminophenyl)-3,3,6,6-tetramethyl-10-(2-thioctinoylaminophenyl)-3,4,6,7,9,10-hexahydro-1,8-(2H,5H)acridinedione(4): A mixture of nitroacridinedione **3** (1.0 g, 1.477 mmol) was dissolved in 95% ethanol (25 mL) and added a solution of a catalytic amount of $CaCl_2$ in water (2 mL) followed by Zn-dust(10.0 g). The mixture was thoroughly mixed and refluxed for 2 hours. After completion of the reaction, as indicated by TLC, the hot solution was filtered; the filtrate was then diluted with ice-cold water and the separated solid was filtered and dried. The product was purified by column chromatography over silica gel and eluting with 4% methanol in chloroform. (Yield: 0.72 g (75%), M.P.: 212°C.)

9-(4-Azo-15-crown-5)-3,3,6,6-tetramethyl 10-(2-thioctinoylamino phenyl)-3,4,6,7,9,10-hexahydro- 1,8 (2H,5H)acridinedione 5: A mixture of aminoacridinedione **4 (**1.0 g, 1.55 mmol**),** pentaethyene glycol ditosylate (0.5 g, 91 mmol) and NaH in DMF (30 mL) was throughly mixed and refluxed for 24 hours under nitrogen atmosphere. After completion of the reaction as indicated by TLC, the mixture was concentrated, the solid obtained was filtered and dried under vacuum. The respective acridinedione derivative **5** was purified by column chromatography over silica gel. A mixture of 2% methanol in chloroform was used to elute the product **5**. (Yield: 0.69g (52%), M.P.: 172-174°C)

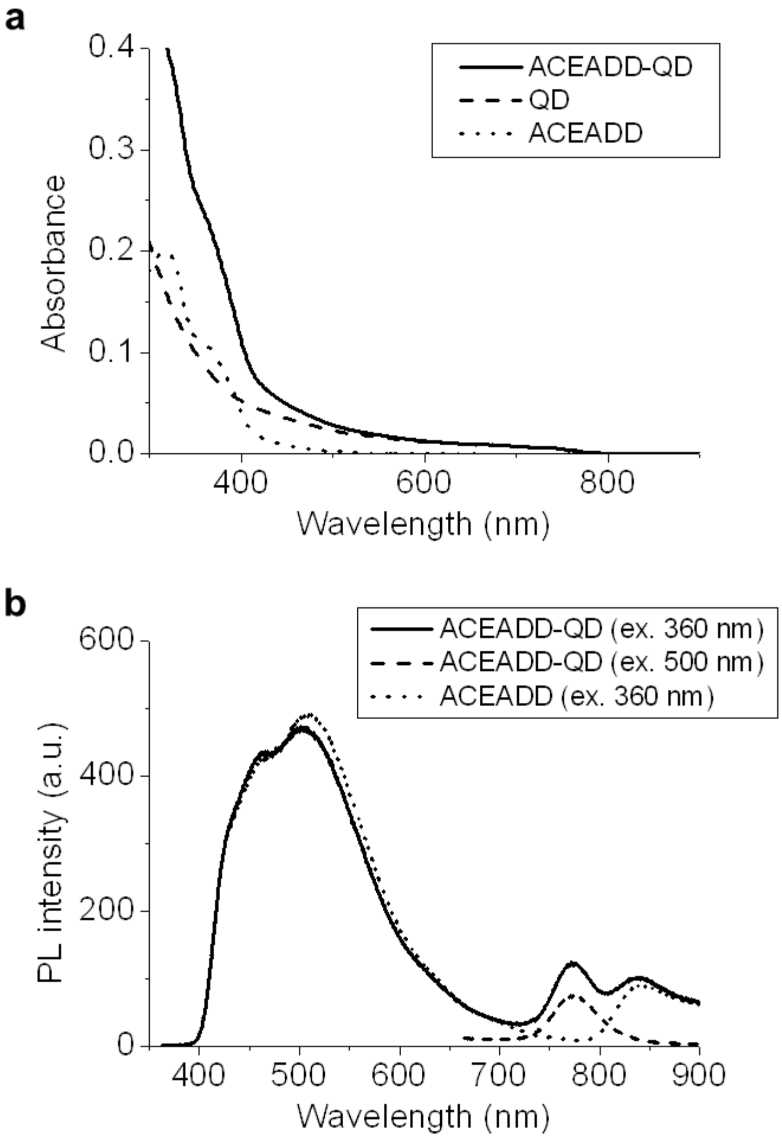


Fig. S1 (a) Absorption spectra of aza-crown ether acridinedione-functionalized quantum dots (ACEADD-QD), QD, and ACEADD in acetonitrile. (b) photoluminescence (PL) spectra of ACEADD-QD and ACEADD in acetonitrile.

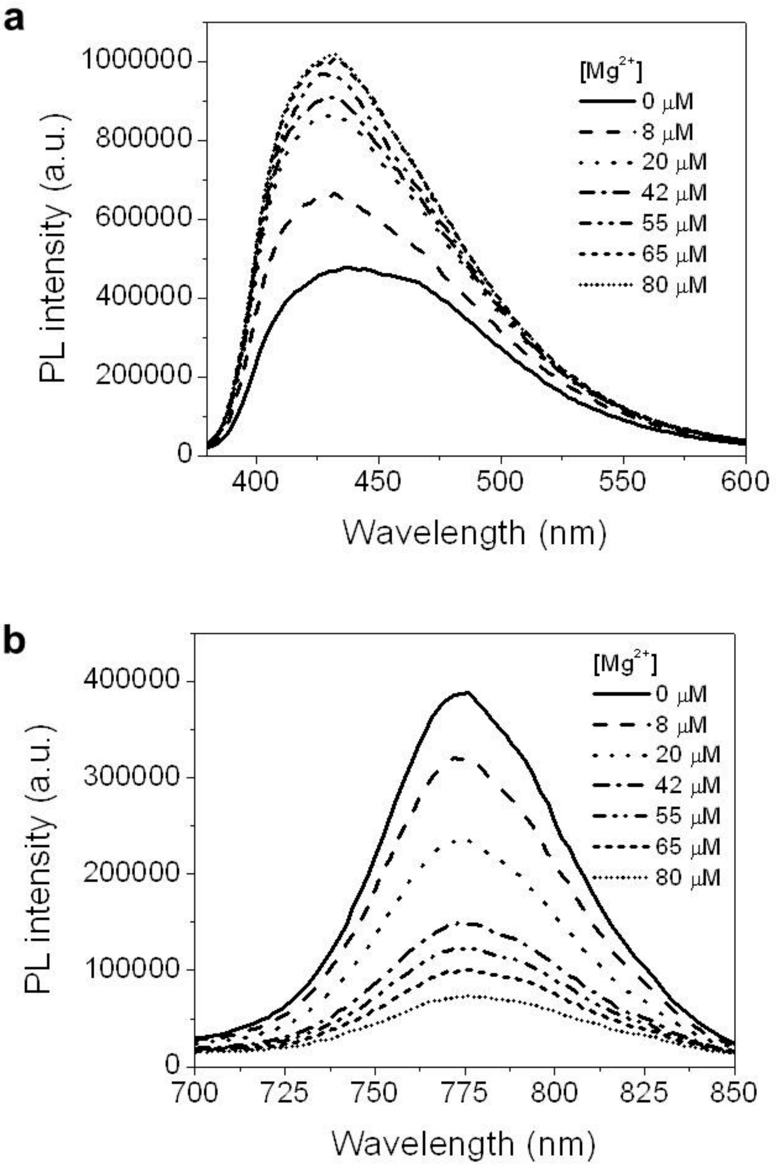


Fig. S2 Photoluminescence (PL) spectra of the mixture of aza-crown ether acridinedione-functionalized gold nanorods and aza-crown ether acridinedione-functionalized quantum dots upon addition of Mg^{2+} in acetonitrile. (a) λ_{ex}= 360 nm, (b) λ_{ex} = 500 nm.

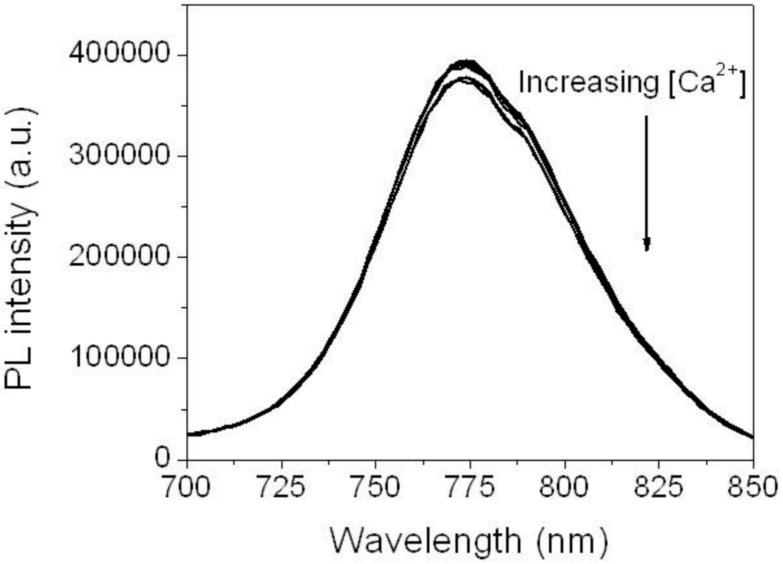


Fig. S3 Photoluminescence (PL) spectra of aza-crown ether acridinedione-functionalized CdTeSe quantum dots upon the addition of Ca^{2+} in acetonitrile (λ_{ex}= 500 nm).

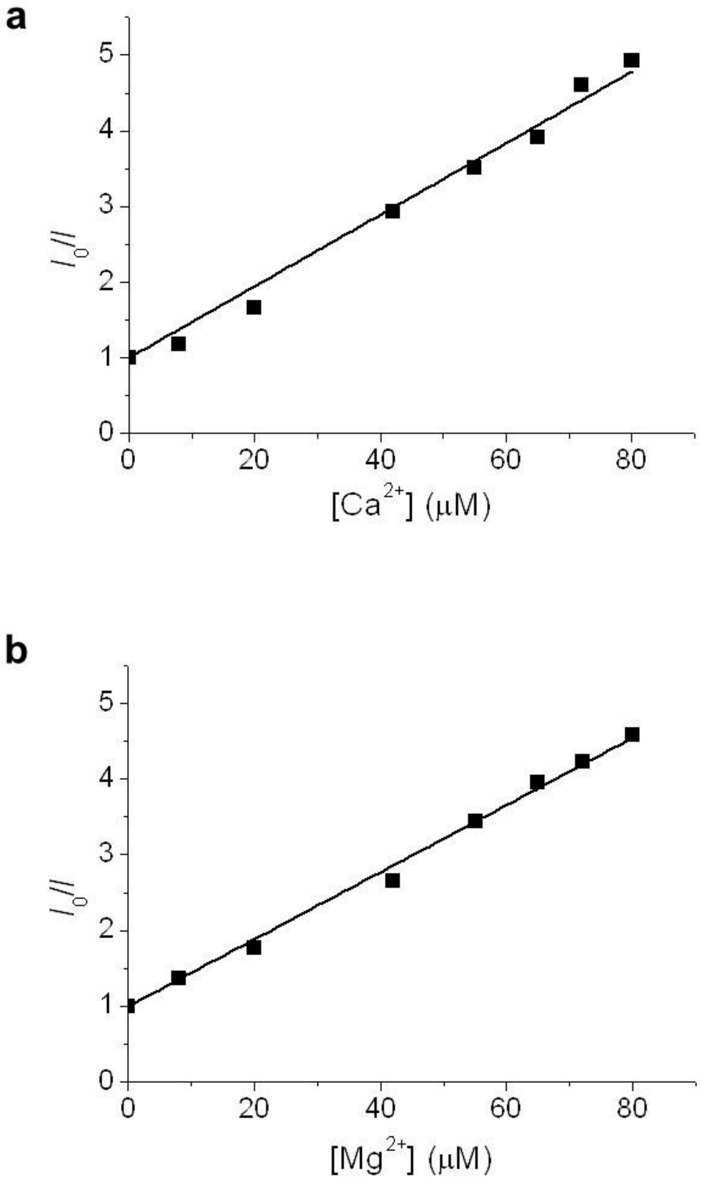


Fig. S4 Stern-Volmer plots showing the efficiencies of quenching for the mixture of aza-crown ether acridinedione-functionalized gold nanorods and aza-crown ether acridinedione-functionalized quantum dots upon the addition of Ca^{2+} (a) and Mg^{2+} (b).

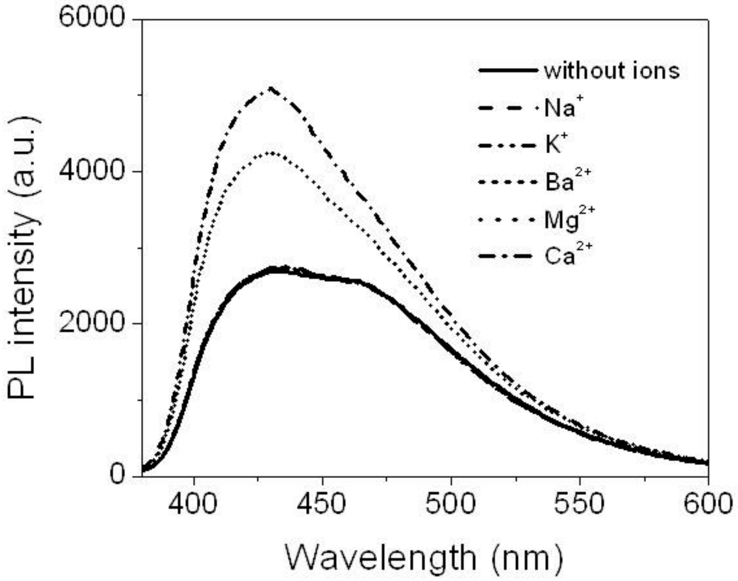


Fig. S5 Photoluminescence (PL) spectra of the mixture of aza-crown ether acridinedione-functionalized gold nanorods and aza-crown ether acridinedione-functionalized quantum dots upon the addition of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} or Ba^{2+} in acetonitrile (λ_{ex} = 360 nm).