Supplementary Material (ESI) for Chemical Communications

**ELECTRONIC SUPPORTING INFORMATION (ESI) FOR:**

# Selective turn-on fluorescence detection of cyanide in water using hydrophobic CdSe quantum dots

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**QD synthesis.** CdSe QDs were synthesised and purified according to previously reported procedures.[1] Tri-*n*-butylphosphine selenide (TBP-Se, 1M) was prepared in a $N_2$-filled glove box by shaking 0.08 g of selenium powder (Alfa Aesar, 99.999%) in 1 mL of TBP. In a typical synthesis, CdO (0.013 g, 0.1mmol) and stearic acid (0.254 g, 0.89 mmol) were loaded into a three-neck flask and heated to 225 °C under $N_2$ flow and stirring. Once the mixture was completely dissolved, it was allowed to cool to room temperature. Then, 3 g of tri-*n*-octylphosphine oxide (TOPO) and 1 g of hexadecylamine were added and the mixture was heated to 225 °C under $N_2$ flow and vigorous stirring. At this temperature, 0.1 mL of the freshly prepared TPB-Se solution (0.1 M) was quickly injected into the flask. Following injection the temperature was adjusted to ~200 °C to promote nanocrystal growth. At various time intervals, portions of the mixture were removed and quickly cooled to obtain nanocrystals with different sizes (i.e. emission colours). The nanocrystals were dispersed in chloroform and precipitated by addition of methanol. After centrifugation the supernatant liquid phase was removed. This procedure was repeated at least three times. The results reported in this study are for nanocrystals grown for 3 hours, which had the first absorption band at 574 nm, and a maximum emission peak at 603 nm with excitation at 350 nm. The size and concentration of the QD solution was estimated from the position of the first absorption band.[2]

**Fluorescence studies.** Equimolar amounts of bipy and $MCl_2$ were mixed in acetonitrile and allowed to react for 1 h, after which the solvent was removed under vacuum. The resulting material was dissolved in chloroform for addition to the QD. The fluorescence studies were carried out using freshly prepared chloroform solutions of nanocrystals (1.1 μM). In a typical titration, 0.2 mL of this solution was mixed with 0.3 mL of the appropriate 1:1 mixture of $MCl_2$ and bipy in chloroform, and the fluorescence spectrum was recorded 1-2 hours later. For the titrations of ions in water, the chloroform and water layers were shaken for a few seconds and allowed to stand for 2 hours. Measurements were made with an Edinburgh Instruments FS900 fluorimeter. Excitation was at 350 nm with bandwidths of 2 nm for excitation (unpolarised) and emission (unpolarised). Temperature was maintained at 25 °C.

**Electrochemistry.** Electrochemical studies were carried out using an Autolab PGSTAT 20 potentiostat. The cyclic voltammograms were obtained by using a three-electrode configuration consisting of a 0.5 mm diameter Pt disk working electrode, a Pt rod counter electrode, and an Ag/AgCl (saturated KCl) reference electrode. All measurements were made under $N_2$ atmosphere in dry DMF (for bipy) or $CH_2Cl_2$ for the metal complexes with 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte at room temperature.

**Electron Microscopy.** High-resolution electron microscopy (HRTEM) studies were conducted on a JEOL JEM-2011 electron microscope operating at 200 kV. The samples were prepared by depositing a drop of a solution of nanocrystals in pyridine on a copper specimen grid coated with a holey carbon film and allowing it to dry.

## References:

1. L. Qu and X. Peng, *J. Am. Chem. Soc.*, 2002, **124**, 2049.
2. W. W. Yu, L. Qu, W. Guo and X. Peng, *Chem. Mater.*, 2003, **15**, 2854.

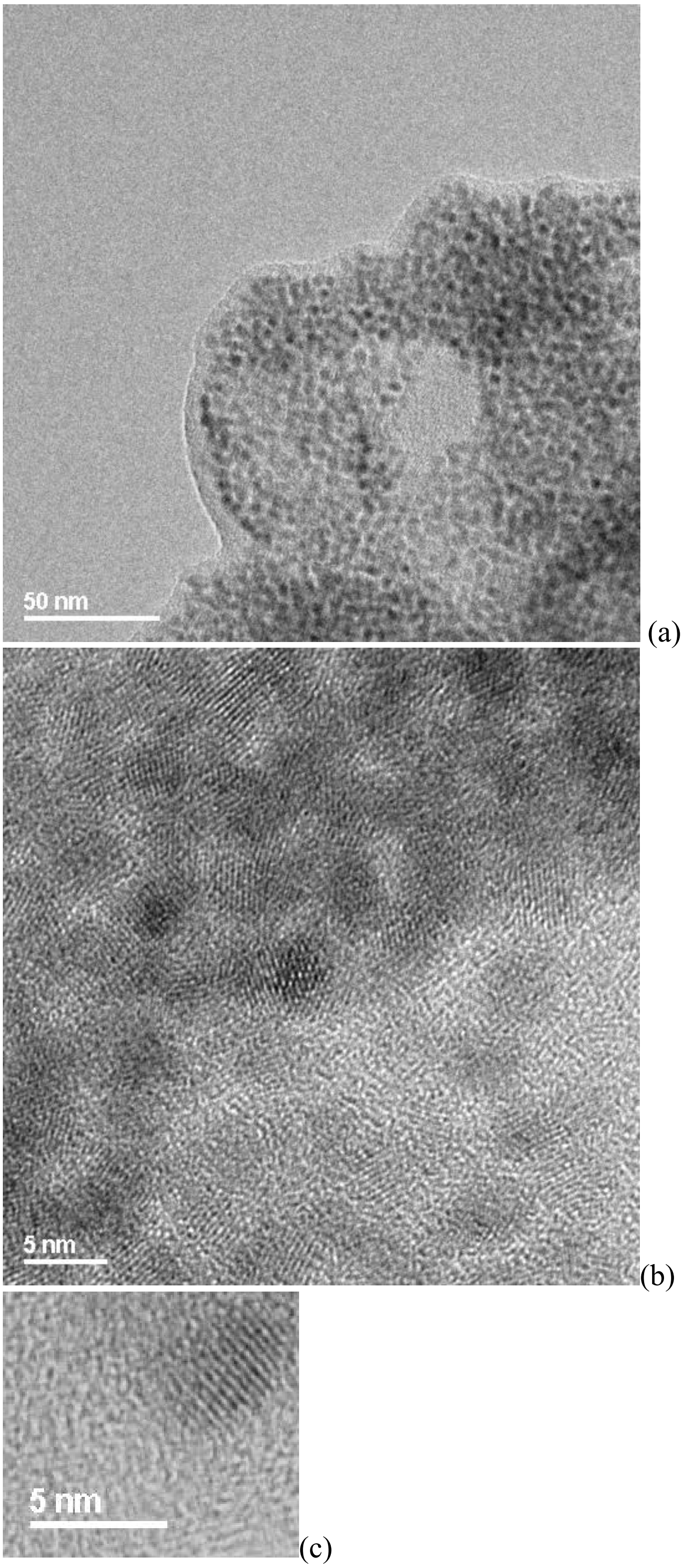

**Fig. S1** TEM (a) and HRTEM (b) and (c) images of the TOPO-coated CdSe nanocrystals.

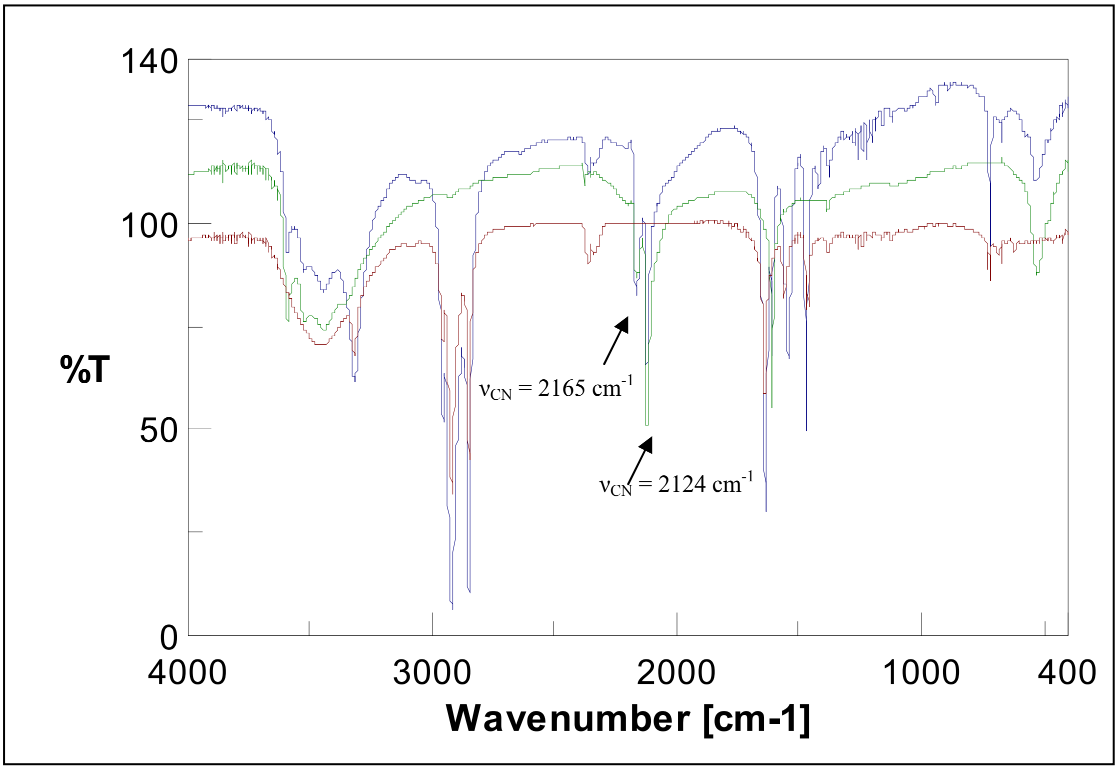

**Fig. S2** FTIR spectra (KBr pellet) of: TOPO-coated CdSe QD (red), CuCN (green) and TOPO-coated CdSe QD:[(bipy)CuCl$_2$] mixture after addition of 100 µ $CN^-$ (blue).

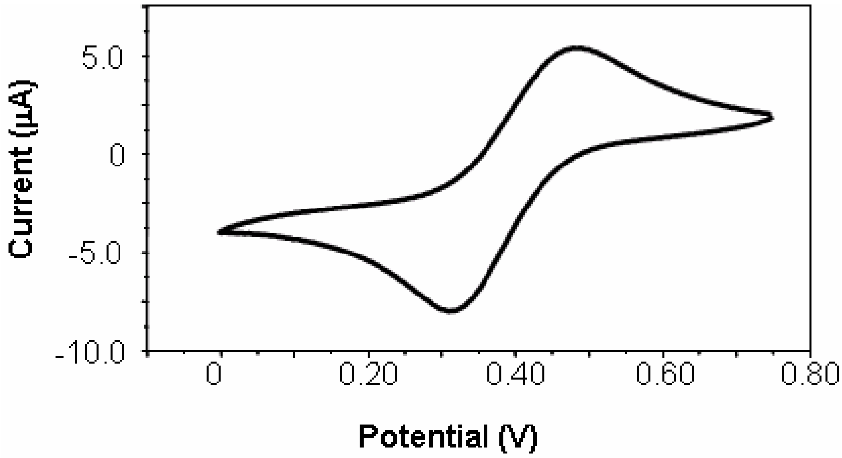

**Fig. S3** Cyclic voltammogram of the 1:1 mixture of $CuCl_2$ and bipy recorded in $CH_2Cl_2$ with 0.1 M [$^n$BuN][$BF_4$] as supporting electrolyte and a scan rate of 100 mV/s (*E* vs Ag/AgCl).

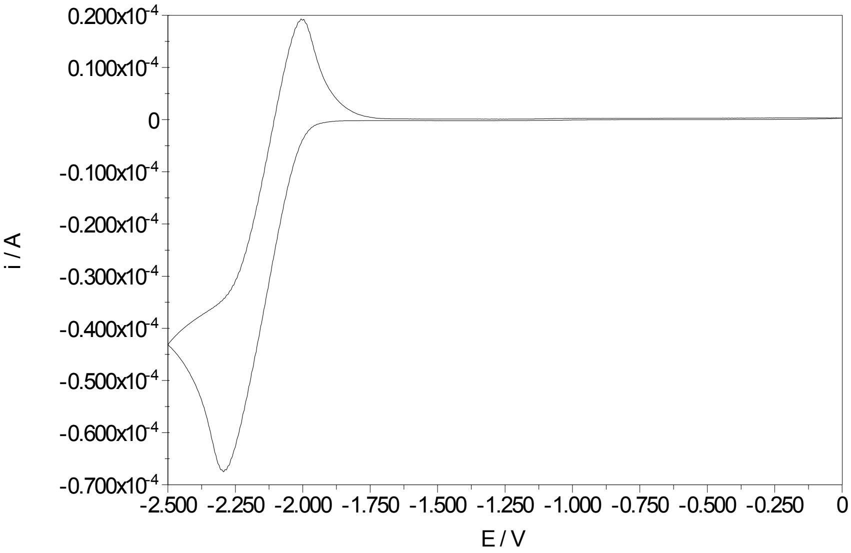

**Fig. S4** Cyclic voltammogram of bipy recorded in DMF with 0.1 M [$^n$BuN][$BF_4$] as supporting electrolyte and a scan rate of 100 mV/s (*E* vs Ag/AgCl).

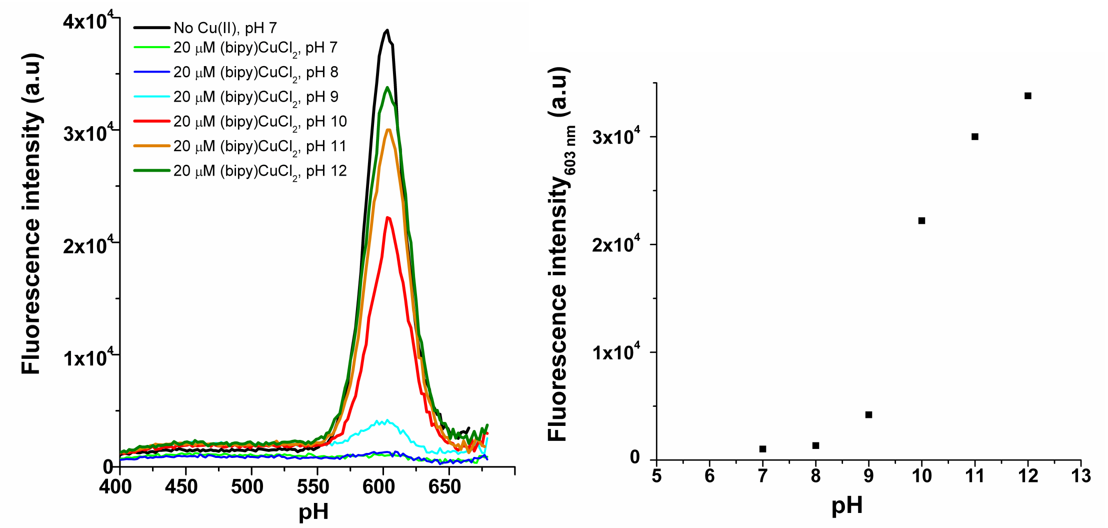

**Fig. S5.** Photoluminescence of TOPO-coated QDs (440 nM) without and with [(bipy)CuCl$_2$] (20 μM) in chloroform after mixing with water at different pH.

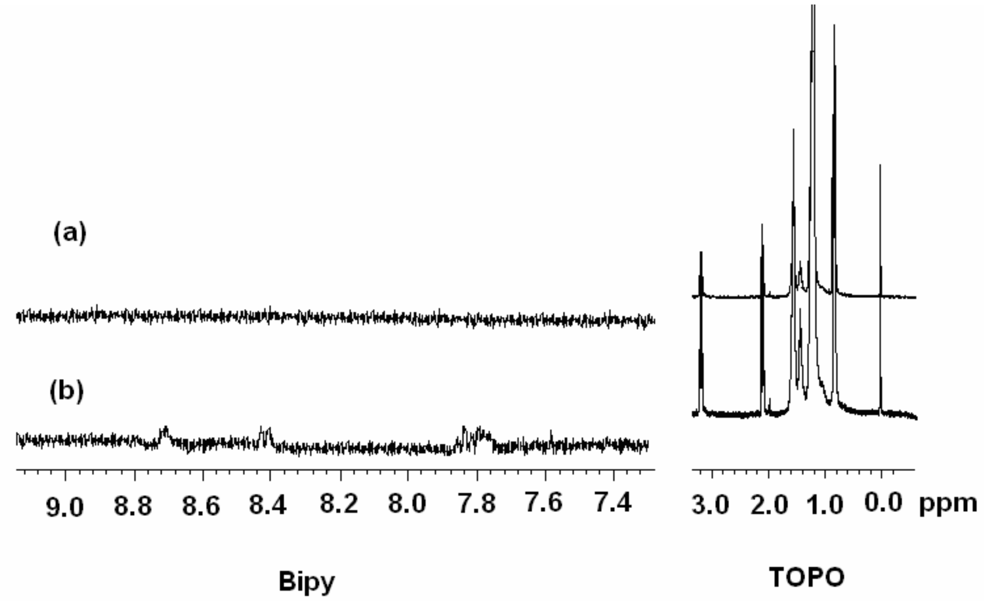

**Fig. S6.** $^1$H NMR spectra showing bipy and TOPO resonances for a mixture of TOPO-coated CdSe nanocrystals (440 nM) and [(bipy)CuCl$_2$] (1 mM) in CDCl$_3$ before (a) and after irradiation at 350 nm for 2 h (b).