ELECTRONIC SUPPORTING INFORMATION (ESI) FOR:

Turn-on fluorescence sensor for cyanide from mechanochemical reactions between quantum dots and copper complexes

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Materials. All reagents and chemicals were obtained from commercial sources and used without further purification. Copper (II) chloride, 2,2´-bipyridine, cadmium oxide (CdO, 99.5%), stearic acid (99%), tri-*n*-octylphosphine oxide (TOPO, 99%), hexadecylamine (HDA, 98%) and tri-*n*-butylphosphine (TBP, 97%) were purchased from Sigma Aldrich. Selenium powder (Se, 99.999%) was obtained from Alfa Aesar.

QD synthesis.[1] CdO (0.013 g, 0.1 mmol) and stearic acid (0.254 g, 0.89 mmol) were loaded into a three-neck flask and heated to 250 °C under N_2 flow and stirring. Once the mixture was completely dissolved, it was allowed to cool to room temperature. Then, TOPO (3 g) and HDA (1 g) were added and the mixture was heated to 260 °C under N_2 flow and vigorous stirring. At this temperature, 1 mL of freshly prepared TPB-Se solution (1 M) was quickly injected into the flask. Following injection the temperature was adjusted to ~250 °C to promote nanocrystal growth for 1 h. After cooling to room temperature, 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 twice. The precipitates were combined and dried under a stream of N_2 at room temperature.

Characterisation. High-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray spectroscopy (EDS) 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 onto a copper specimen grid coated with a holey carbon film and allowing it to dry. UV/Vis absorption spectra were measured by using a Varian UV/Vis spectrophotometer (Cary 50 Scan). Fluorescence Measurements in solution 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.

The handheld fluorescence detector was built in-house and was designed specifically for the detection of fluorescence from solid samples. The excitation source is a blue (475 nm) LED (Thorlabs) and fluorescence is detected by a photomultiplier tube (PMT) (Hamamatsu H5784-01). An epifluorescence optical geometry (excitation and detection via the same objective lens) is employed to insure co-registration of excitation and detection areas. The excitation spot on the sample surface is ~ 5 mm in diameter. Spectral discrimination between fluorescence and excitation light, scattered from the sample surface, is achieved by a dichroic mirror and a high extinction ratio band-pass filter, positioned between the objective lens and the PMT

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1 (a) A. Touceda-Varela, E. I. Stevenson, J. A. Galve-Gasión, D. T. F. Dryden and J. C. Mareque-Rivas, *Chem. Commun*. 2008, 1998; (b) L. Qu, X. Peng, *J. Am. Chem. Soc*. 2002, **124**, 2049.

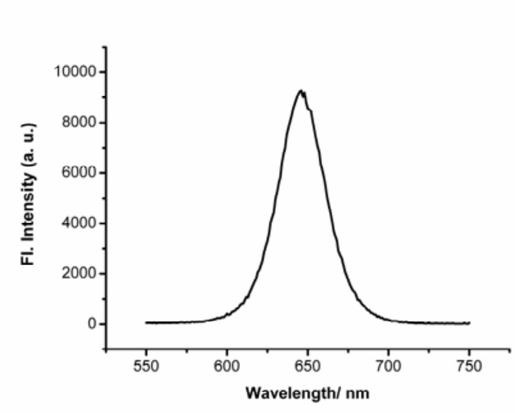

Fig S1 Photoluminescence spectrum of the CdSe QDs in chloroform.

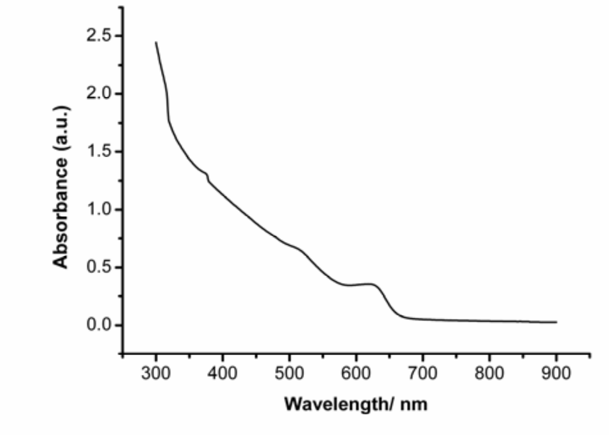

Fig S2 UV-vis spectrum of the CdSe QDs in chloroform.

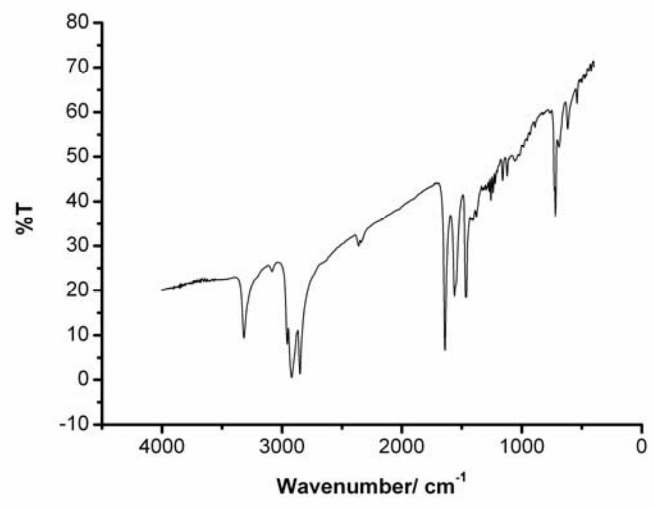

Fig S3 FT-IR spectrum of the CdSe QD (solid state in KBr pellets).

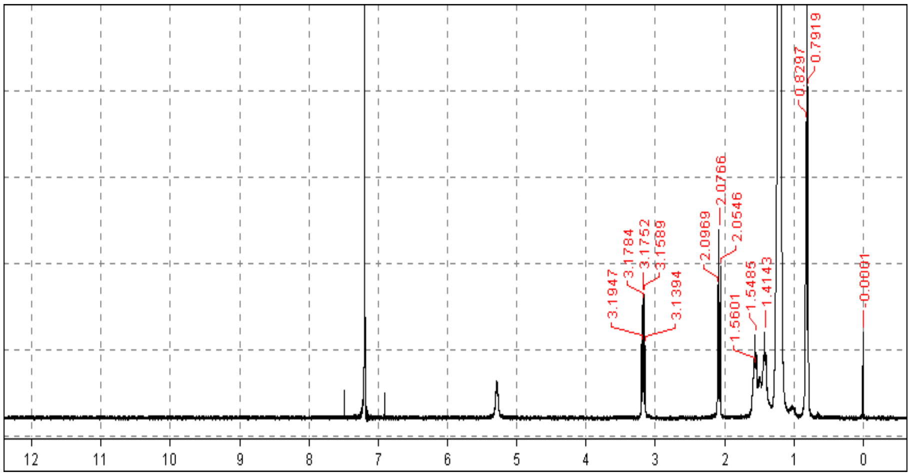

Fig S4 ^{1}H NMR spectra of the CdSe QD recorded in $CDCl_3$ at room temperature.

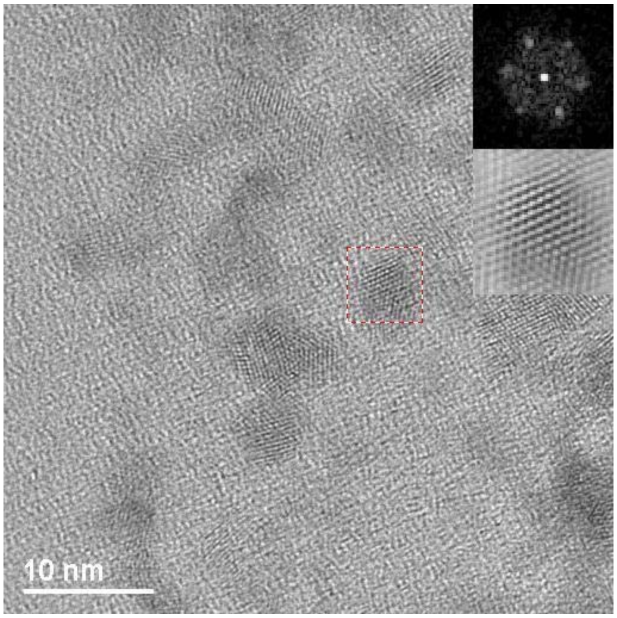

Fig S5 High-resolution transmission electron microscopy (HRTEM) image of CdSe QDs (a), fast Fourier transform (FFT) of the QD inside the box (5.72 × 5.72 nm) (b) and corresponding inverse FFT (IFFT) image (c).

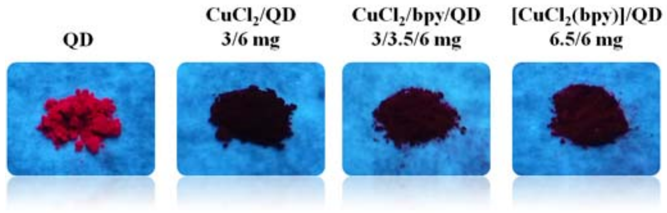

Fig S6. Effect of $CuCl_2$, $CuCl_2$:2,2'-bpy (1:1) and [$CuCl_2$(2,2'-bpy)] on the photoluminescence of CdSe QDs irradiated under a 365 nm lamp after manual grinding with a pestle and mortar.

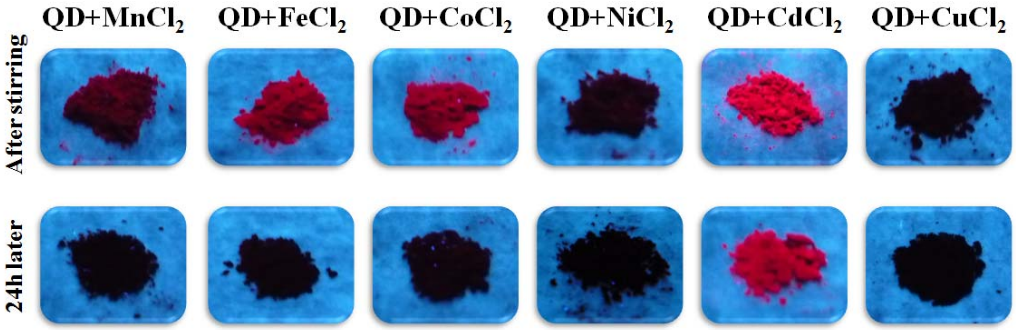

Fig S7. Effect of MCl_2 on the naked eye photoluminescence of CdSe QDs irradiated under a 365 nm lamp after manual grinding using a pestle and mortar.

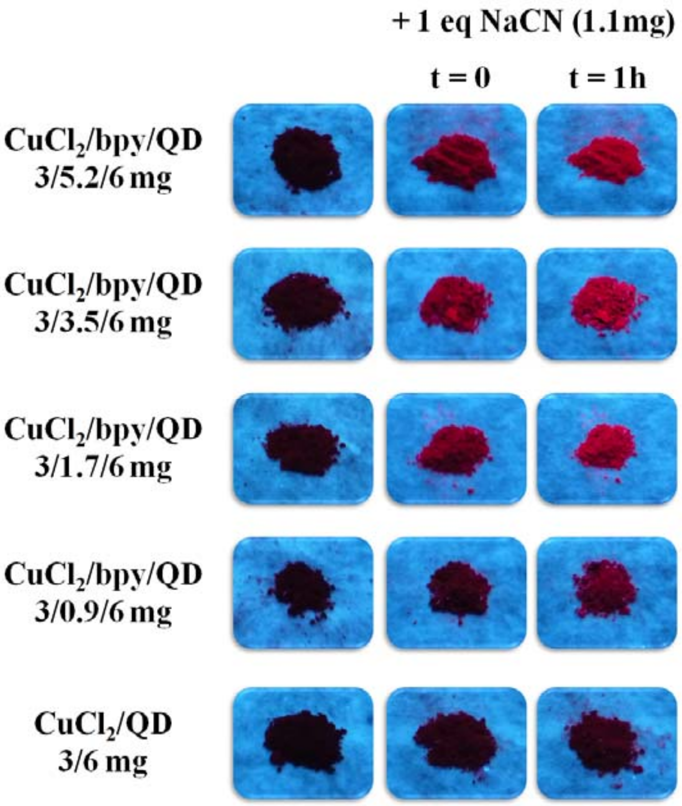

Fig S8. Effect of co-adding 2,2'-bpy and $CuCl_2$ (0:1, 0.25:1, 0.5:1, 1:1, 1.5:1) on the nayed eye photoluminescence of CdSe QDs before and after grinding with NaCN.

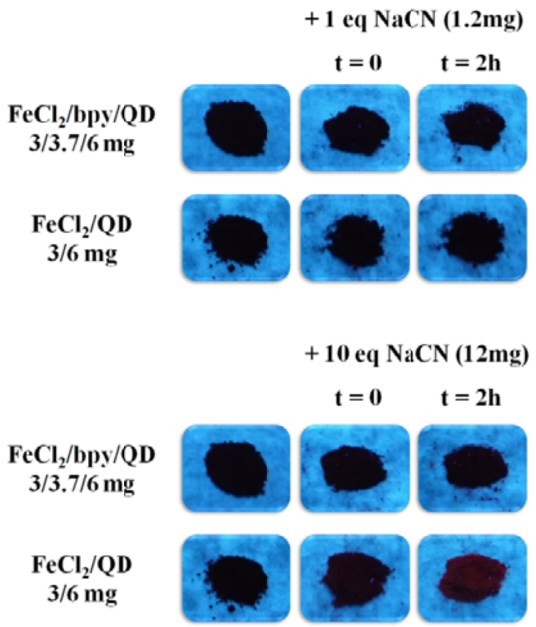

Fig. S9 Naked eye photoluminescence under a hand-held lamp (λ = 365 nm) of solids obtained by grinding $FeCl_2$ and $FeCl_2$:2,2'-bpy (1:1) with QDs before and after grinding with NaCN.

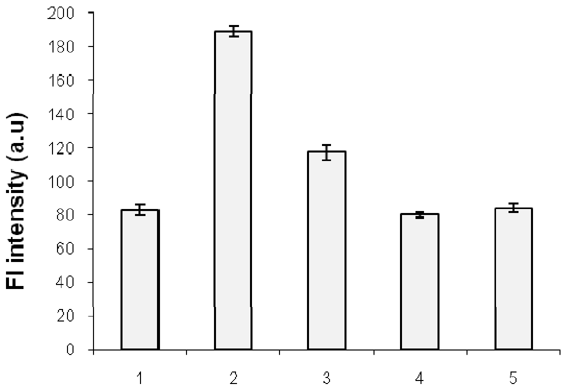

Fig S10. Fluorescence emission (580.5-653.5 nm) of sand (1 g) after manual grinding with $CuCl_2$: 2,2'-bpy (1:1)–quenched CdSe QDs (2 mg). 1 without NaCN, 2 with 1:1000 NaCN:sand, 3 with 1:10000 NaCN:sand, 4 with 1:50000 NaCN:sand and 5 1:100000 NaCN:sand.

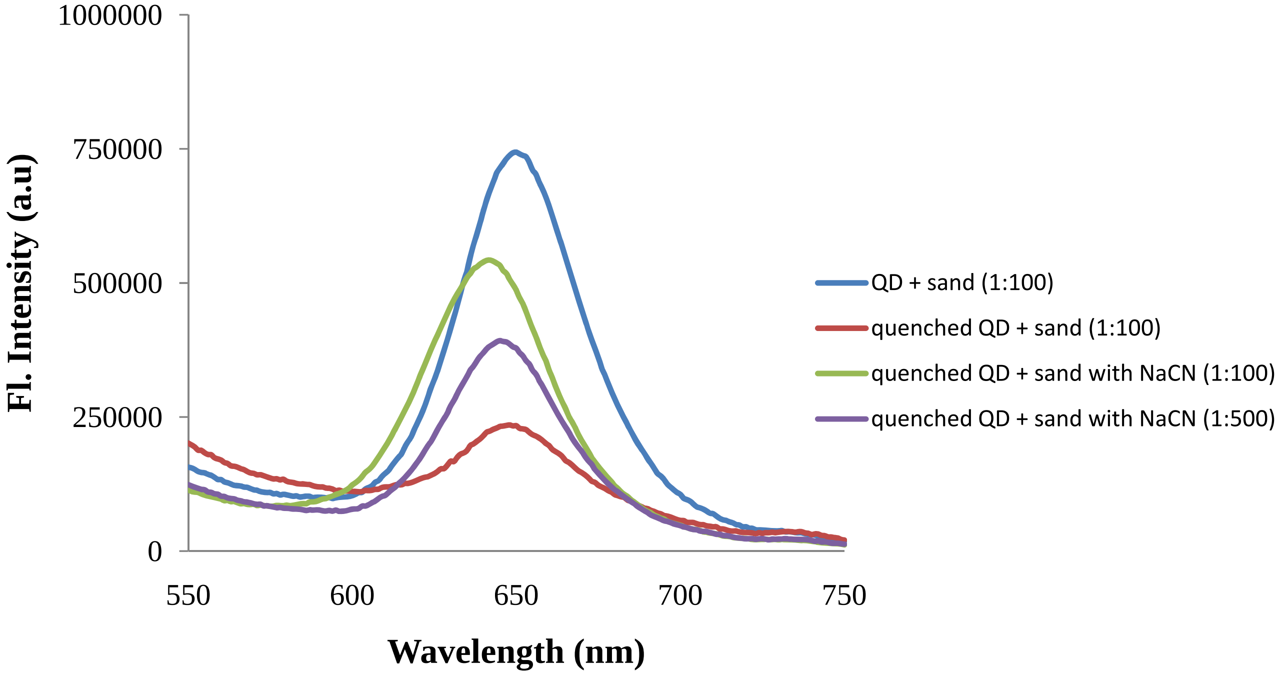

Fig S11. Fluorescence emission spectra of sand after manual grinding with CdSe QDs, and with $CuCl_2$: 2,2’-bpy (1:1)–quenched CdSe QDs without NaCN and with NaCN.