Ligand Replacement-Induced Fluorescence Switch of Quantum Dots for Ultrasensitive Detection of Organophosphorothioate Pesticides

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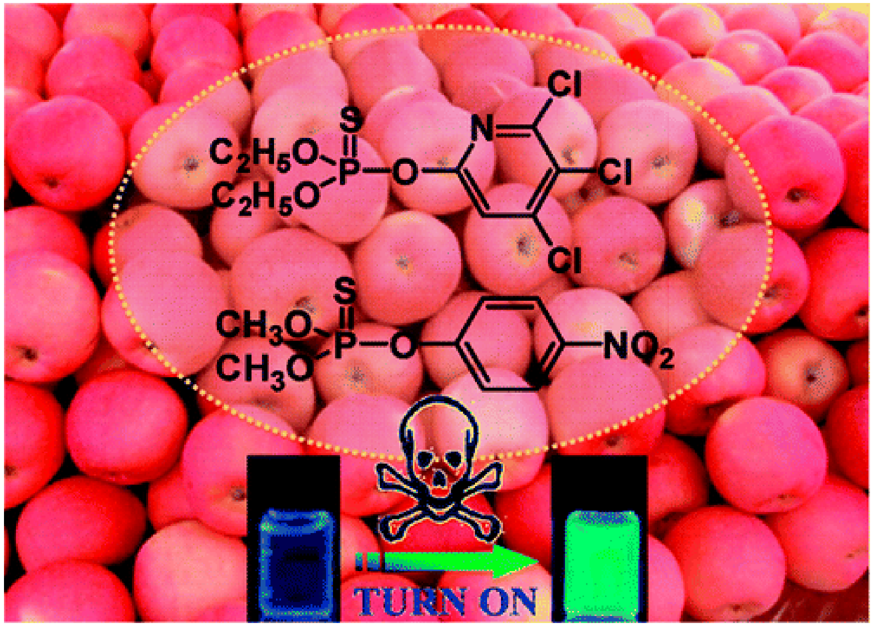

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Introduction

- About two million tons of organophosphorus (OP) pesticides are used annually all over world (~33000 tons of CP in U.S alone for agriculture use)
- OP pesticides irreversibly bind with acetylcholinesterase result in human nervous system, respiratory tract, and cardiovascular system problems
- More than 200000 people are estimated to die yearly from acute and chronic OP poisoning mainly in food and drinking water
- Chromatography-mass spectrometry, enzyme-linked immunosorbent assay (ELISA) tests are sophisticated, expensive and difficult sampling methods
- Carbon nanotubes, fluorescence quenching through enzyme-functionalized quantum dots, nanomaterials for the optical/electronic sensing of OP pesticides are there in the literature.

Preparation of CdTe QDs

$$\mathrm{Te} + \mathrm{NaBH_4} \xrightarrow[0\ ^{0}\mathrm{C}]{8\ \mathrm{h}} \mathrm{Na_2B_4O_7}\downarrow + \mathrm{NaHTe}$$

63.8 mg (Te); 100 mg, 10 mL water ($NaBH_4$)

$$\mathrm{CdCl_2\ 2.5H_2O} + \mathrm{MPA} \xrightarrow[\mathrm{Cd^{2+}/Te^{2-}/MPA} = 1:0.5:2.5]{\mathrm{pH}=9\quad \mathrm{N_2}\ 30\ \mathrm{min.}} \text{Reflux for 1 h}$$

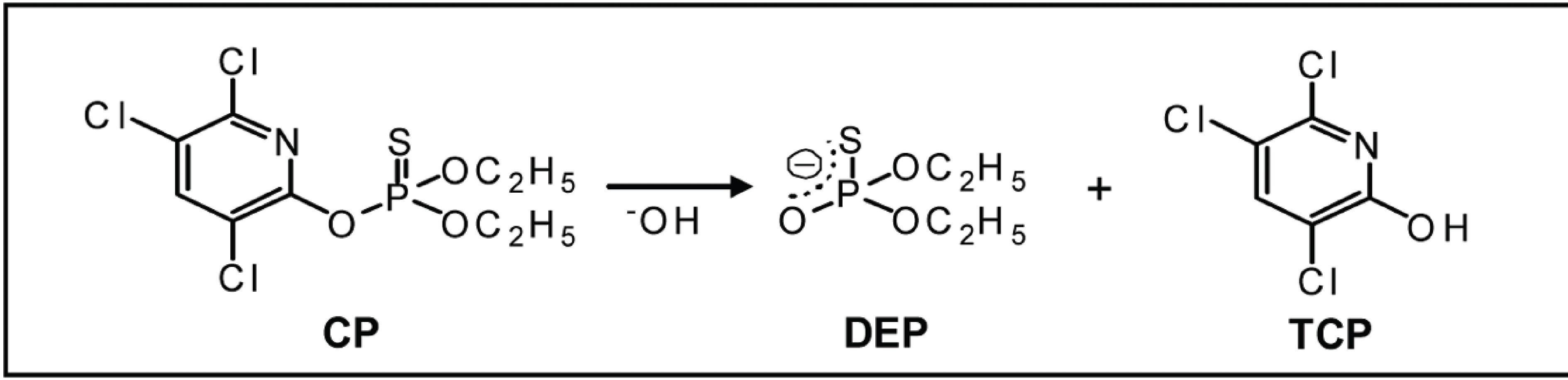
228 mg ($CdCl_2\ 2.5H_2O$); 210 μL (MPA)

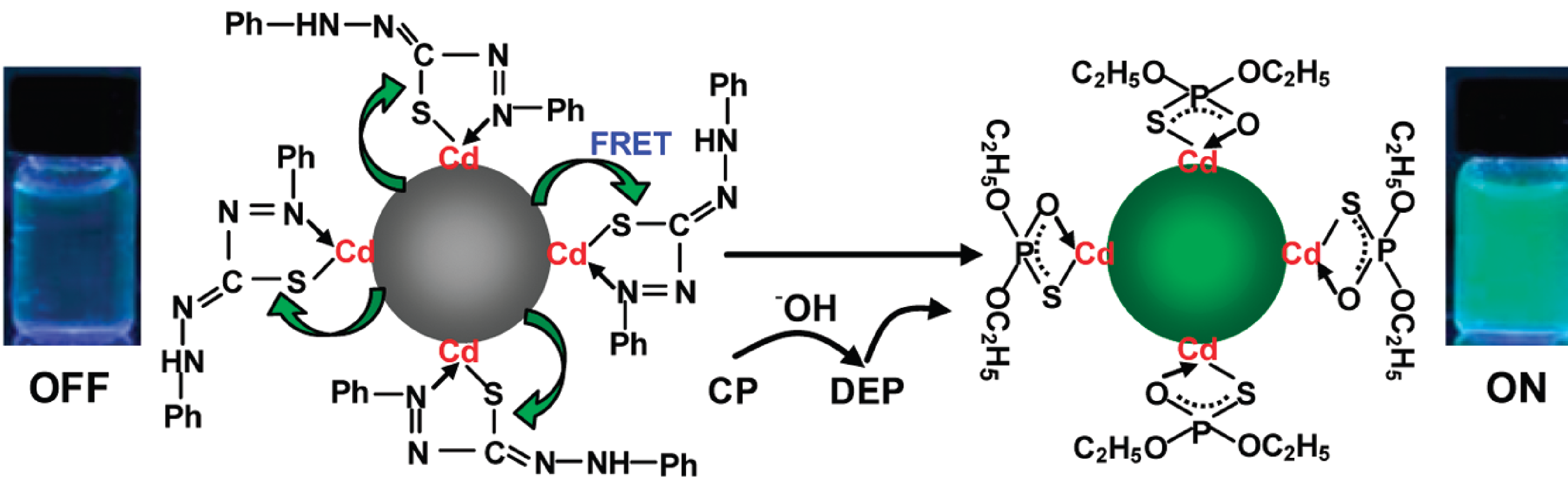
Preparation of CdTe QD Fluorescence Probe and Detection of Pesticides

$$\text{CdTe QDs} + 10\ \text{mM NaOH} + \text{DZ} \longrightarrow \text{QD-DZ}$$

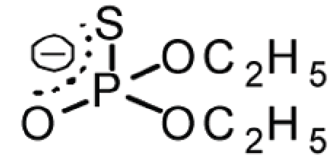
2 μL (CdTe QDs); 3 mL (10 mM NaOH); 30 μL (DZ)

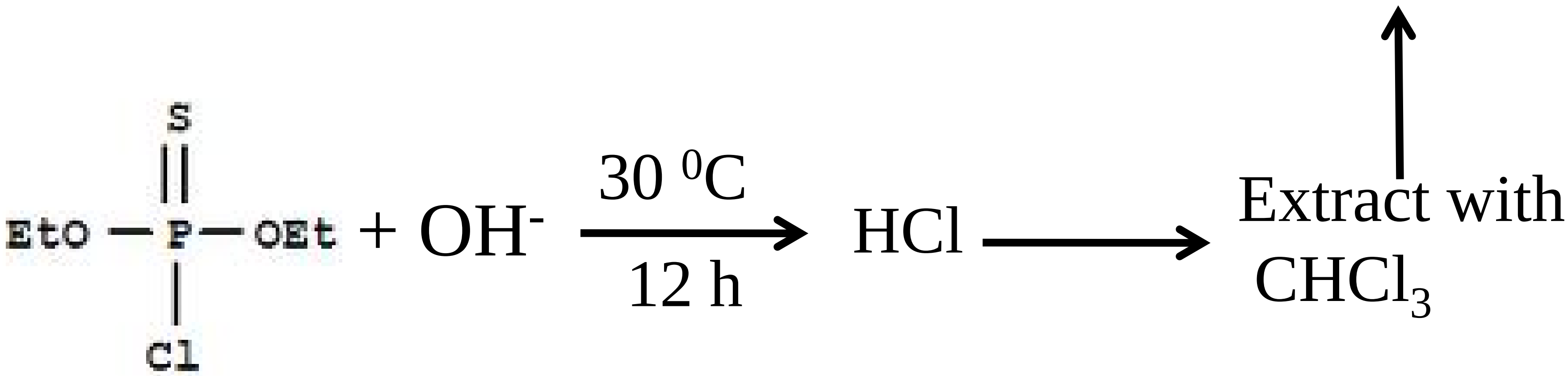
Results and Discussion



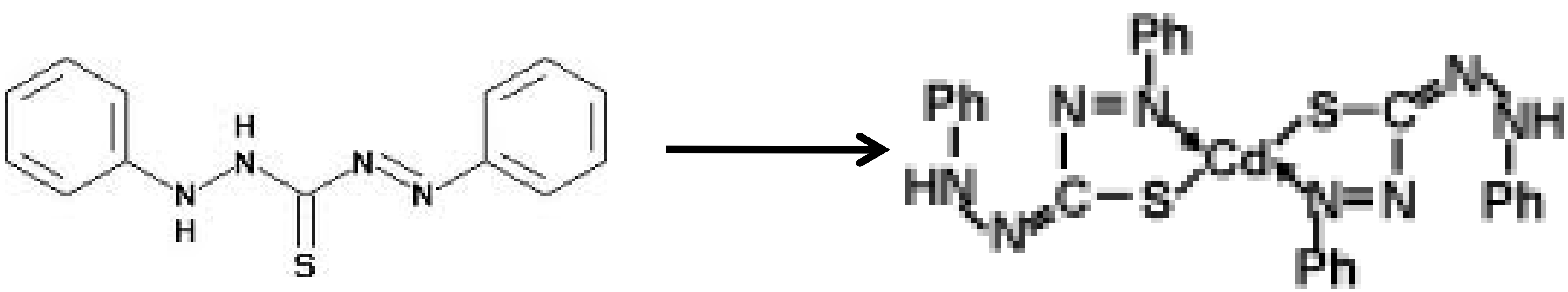


Synthesis of Diethyl Phosphorothioate (DEP)





Preparation of Cd Complexes and Characterization by Mass Spectrometry



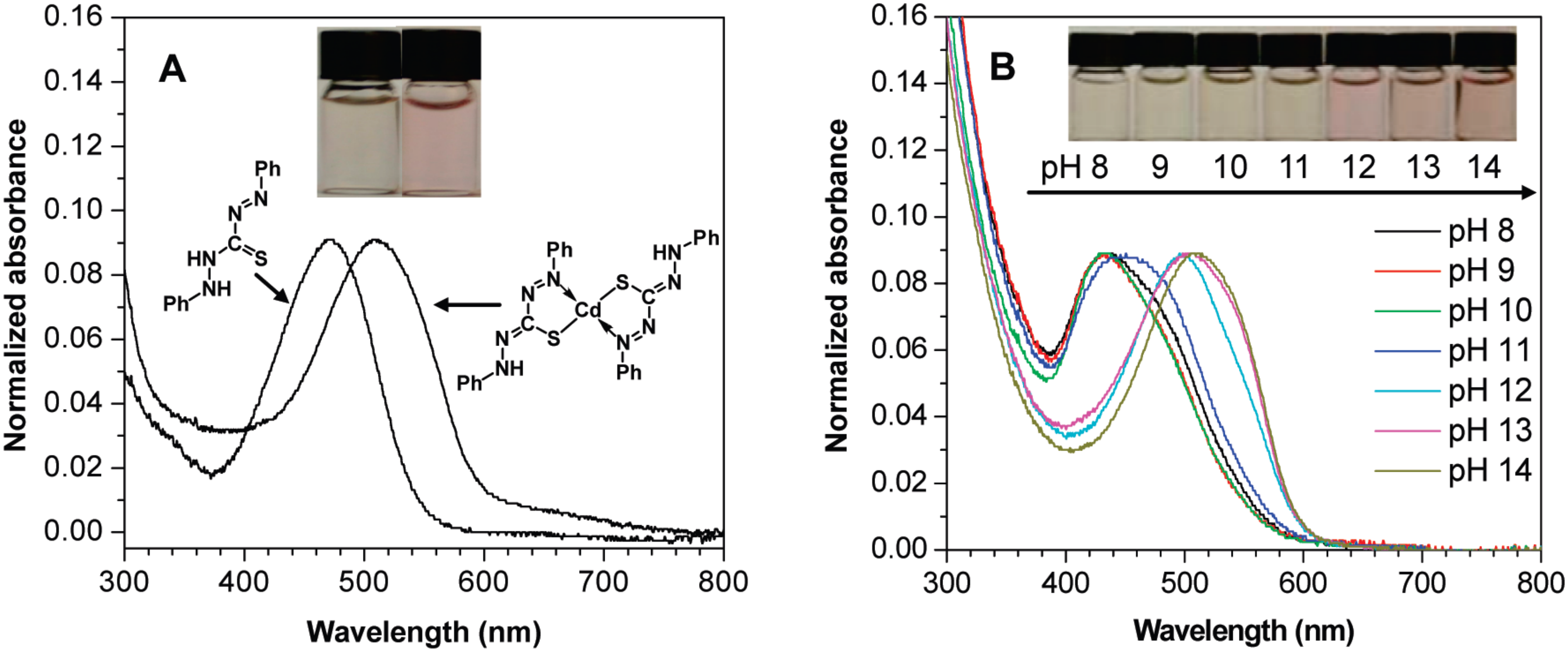


Figure. (A) Absorption spectra of dithizone and dithizone-Cd in 0.01 M NaOH solution (inset image shows the corresponding colors in natural light). (B) Evolution of absorbance spectra of the dithizone/CdTe QD mixture with pH value (2 μL of CdTe QDs is mixed with 10 μM dithizone. Inset image shows the corresponding color change with pH value).

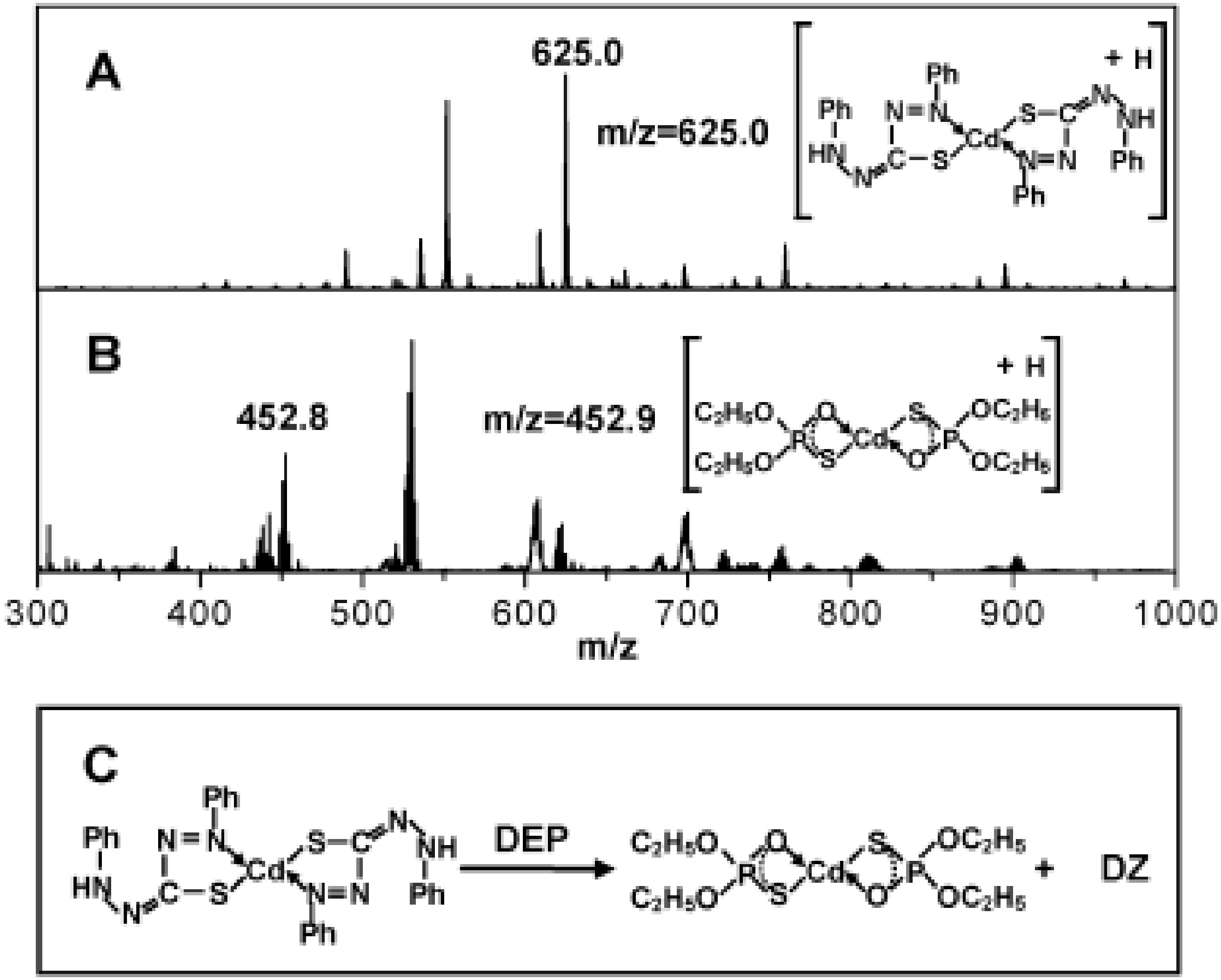


Figure. ESI-MS spectra of the mixtures of Cd ions with (A) dithizone (DZ) and (B) diethylphosphorothioate (DEP) in aqueous solution, respectively. (C) The replacement reaction from $Cd(DZ)_2$ to $Cd(DEP)_2$ complex

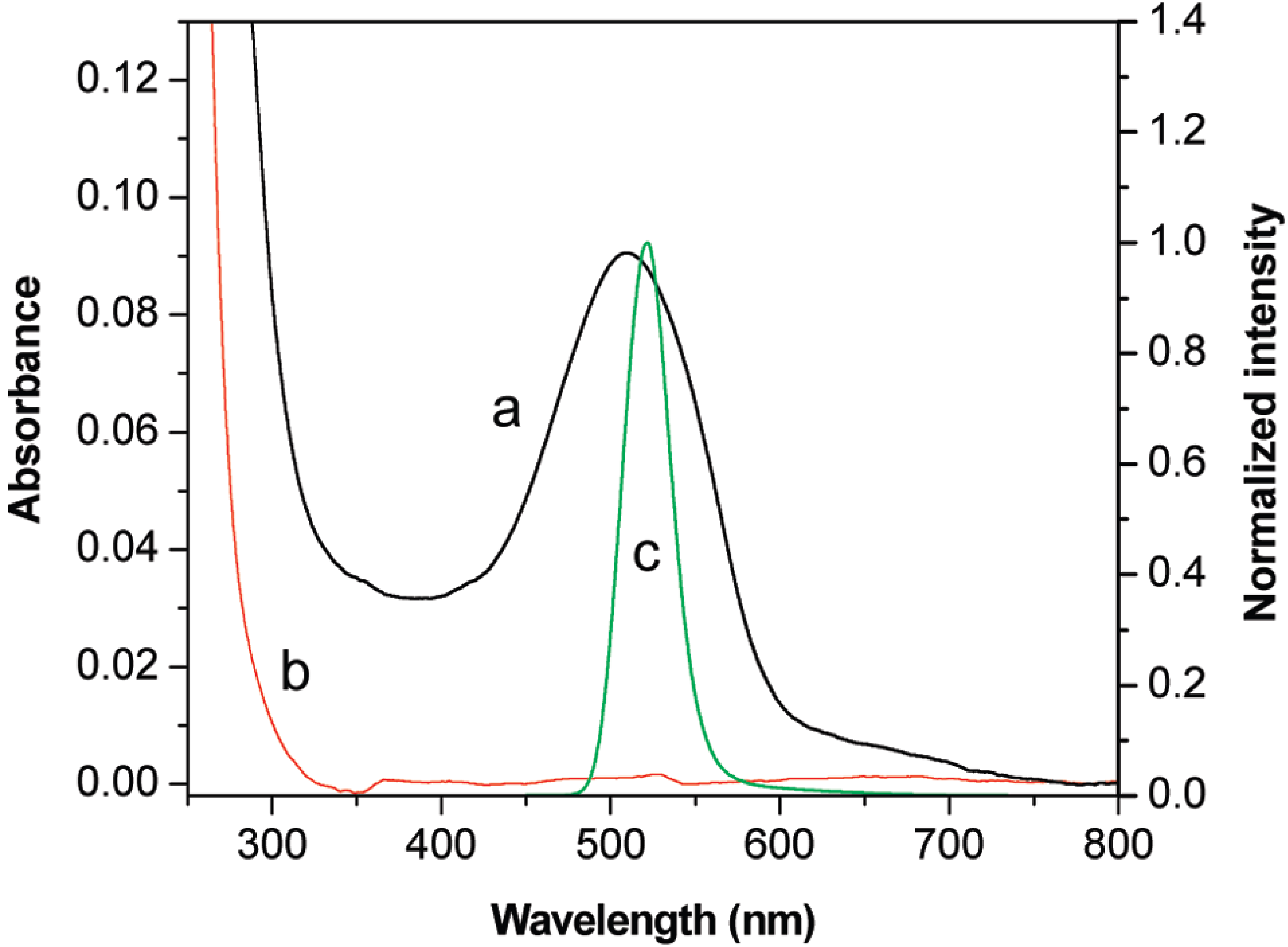


Figure. The absorption spectra of (a) dithizone-Cd and (b) DEP-Cd complexes and (c) the normalized emission spectrum of the CdTe QDs

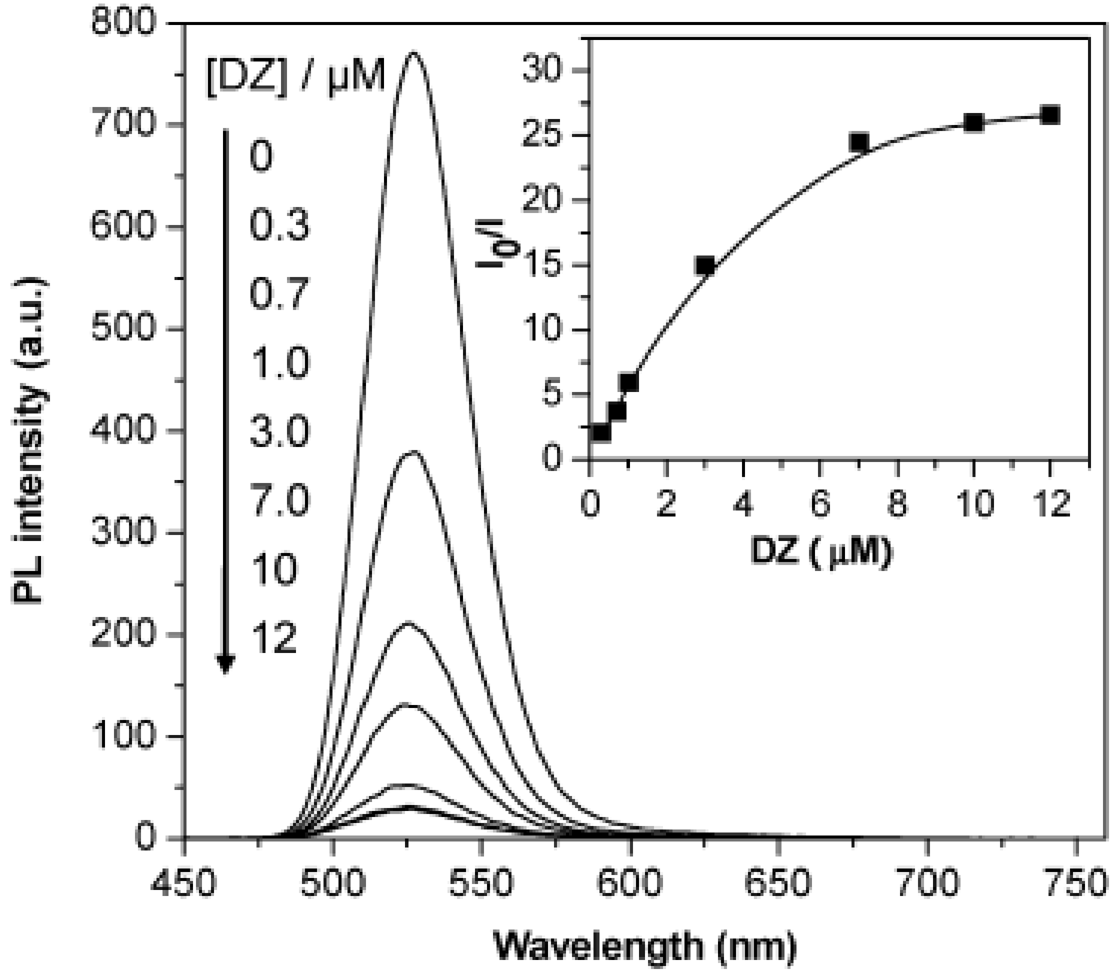


Figure. Fluorescence quenching of CdTe QDs (20 nM) upon the addition of dithizone. The inset shows the relationship between I_0/I and dithizone concentration (where I_0 and I are the fluorescence intensity of QDs in the absence and presence of dithizone, respectively).

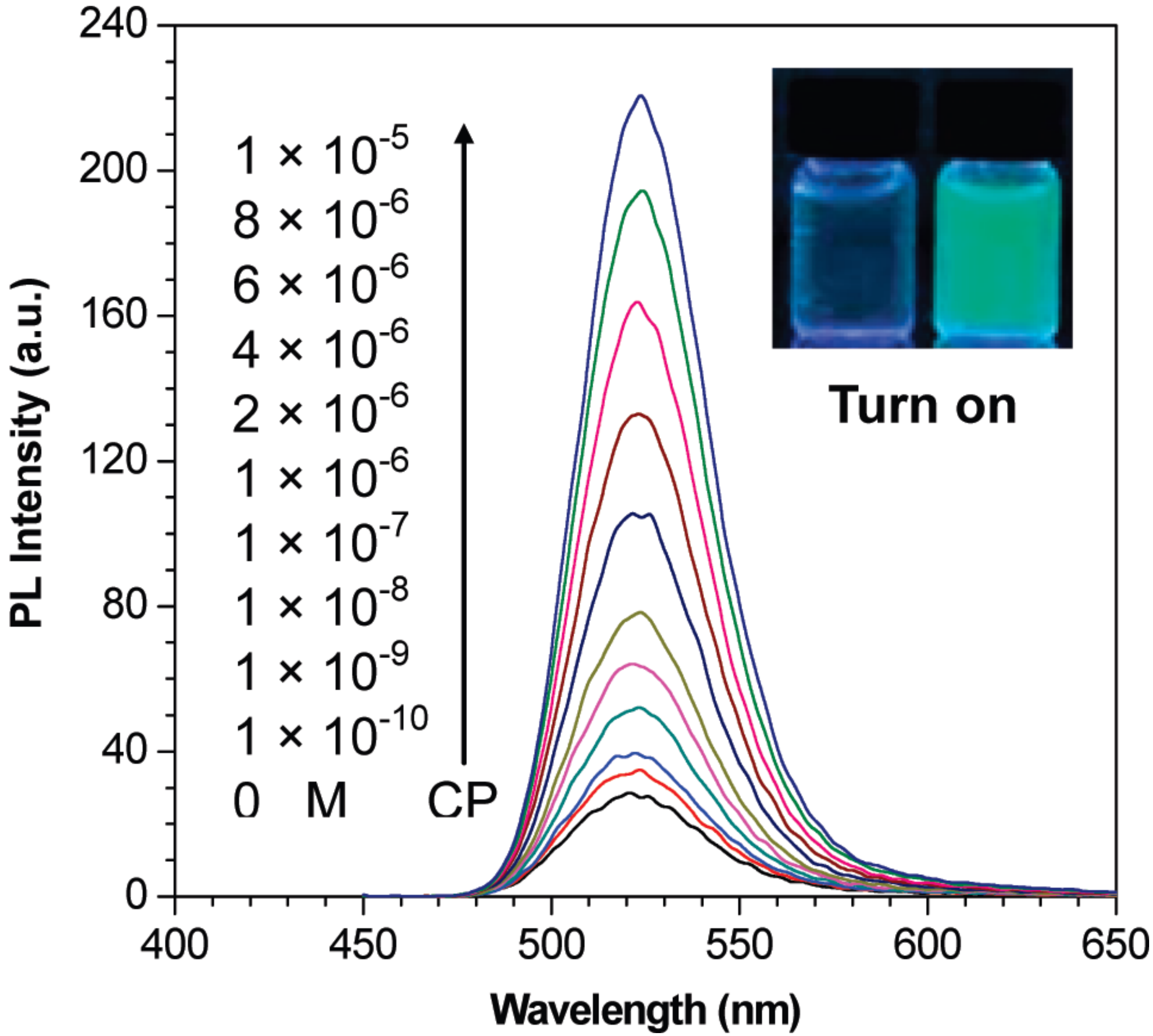


Figure. Fluorescence enhancement of the CdTe QD-DZ probe with the addition of CP (inset shows colorful images under a UV lamp before and after the addition of 10 μM CP).

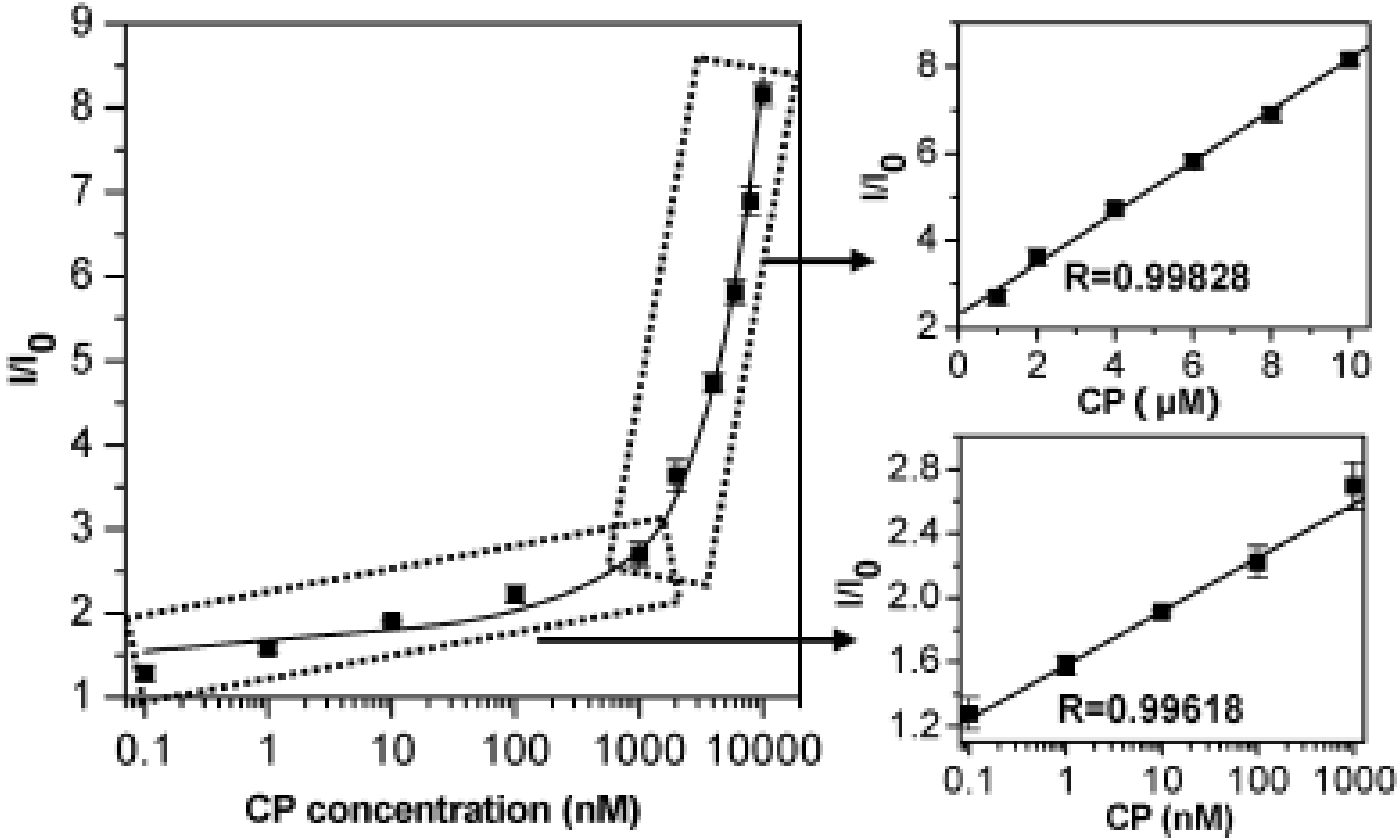


Figure. The plot of fluorescence enhancement vs CP concentration. The inserts on the right are linear correlations of the data included in the boxes

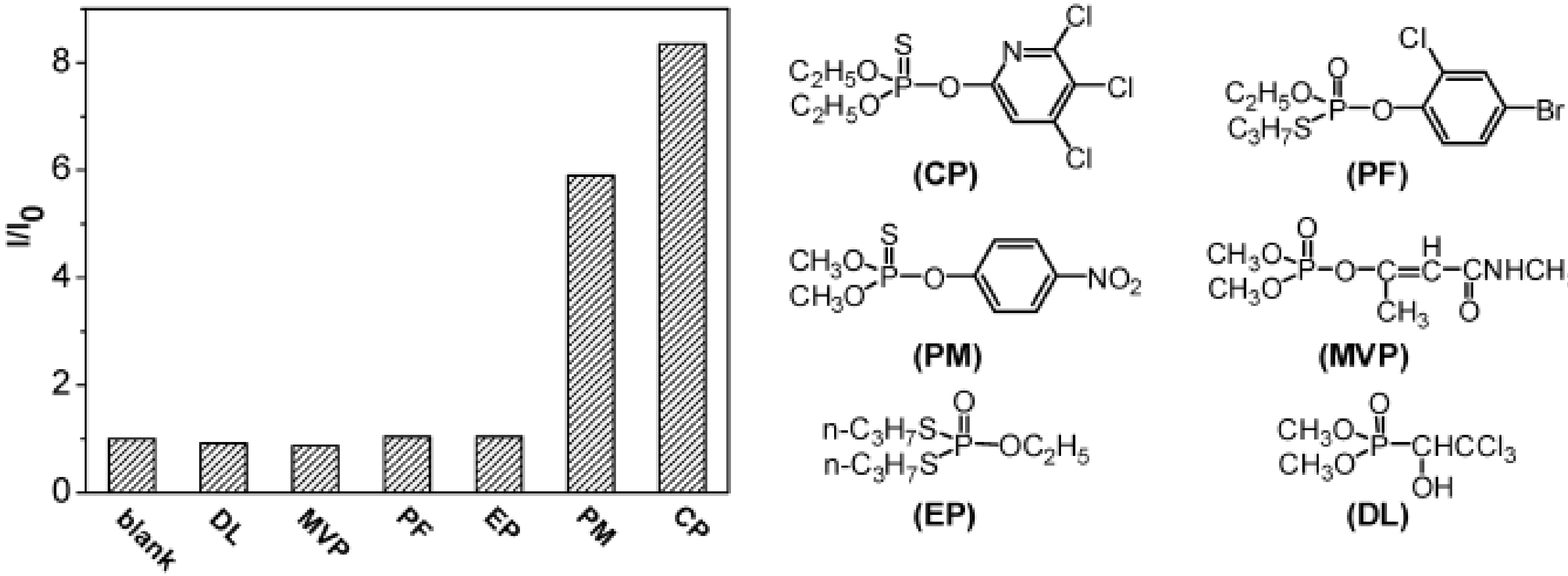


Figure. The fluorescence turn-on selectivity to various OP pesticides (10 μM) with $[(RO)_3PdS]$ and $[(RO/S)_3PdO]$ structures: chlorpyrifos (CP), parathion-methyl (PM), ethoprophos (EP), profenofos (PF), mevinphos (MVP), and dylox (DL)

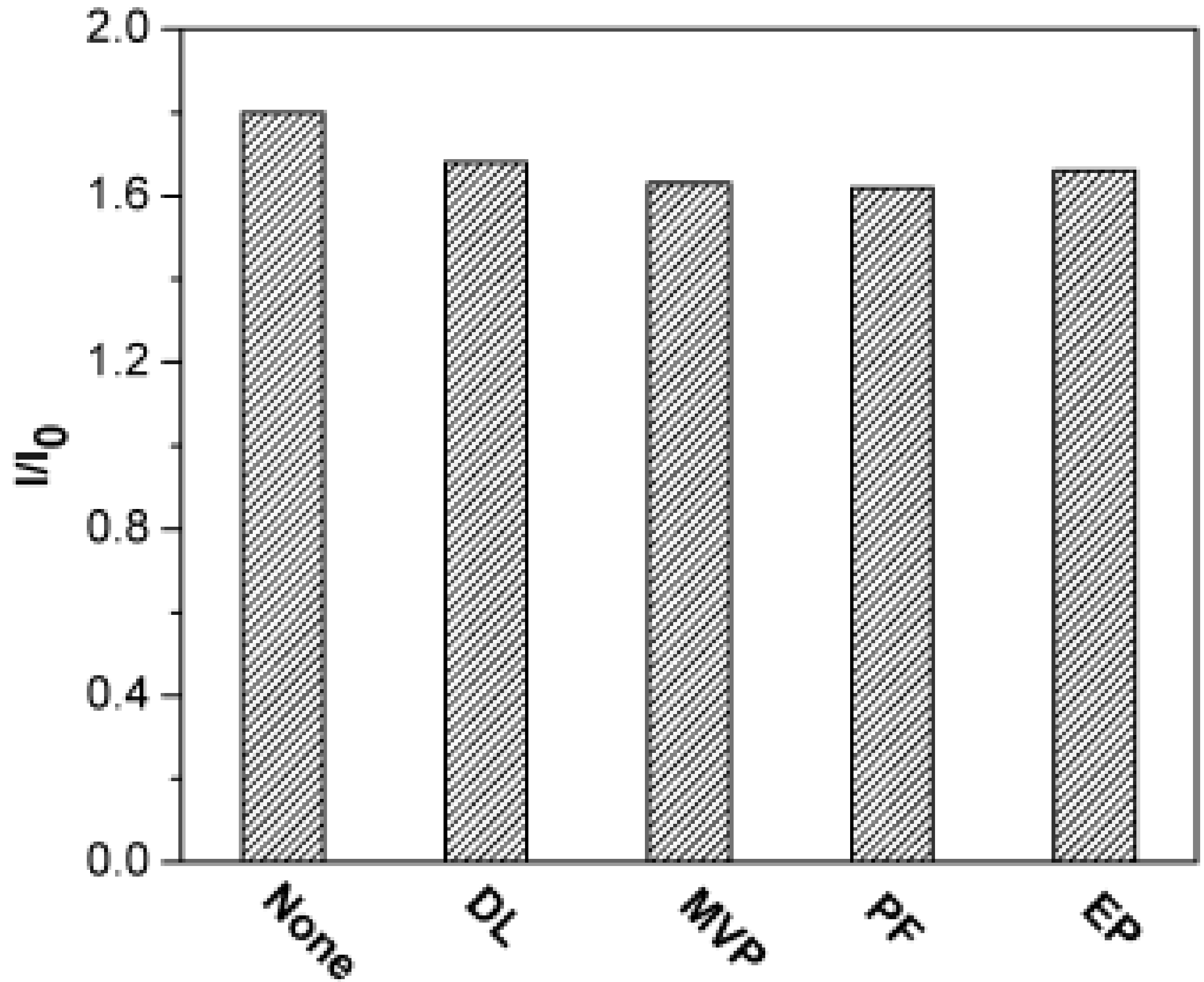


Figure. Fluorescence enhancement (I/I_0) of CdTe QD-DZ probe upon the addition of 0.1 μM of CP in the presence of other OP pesticides (10 μM).

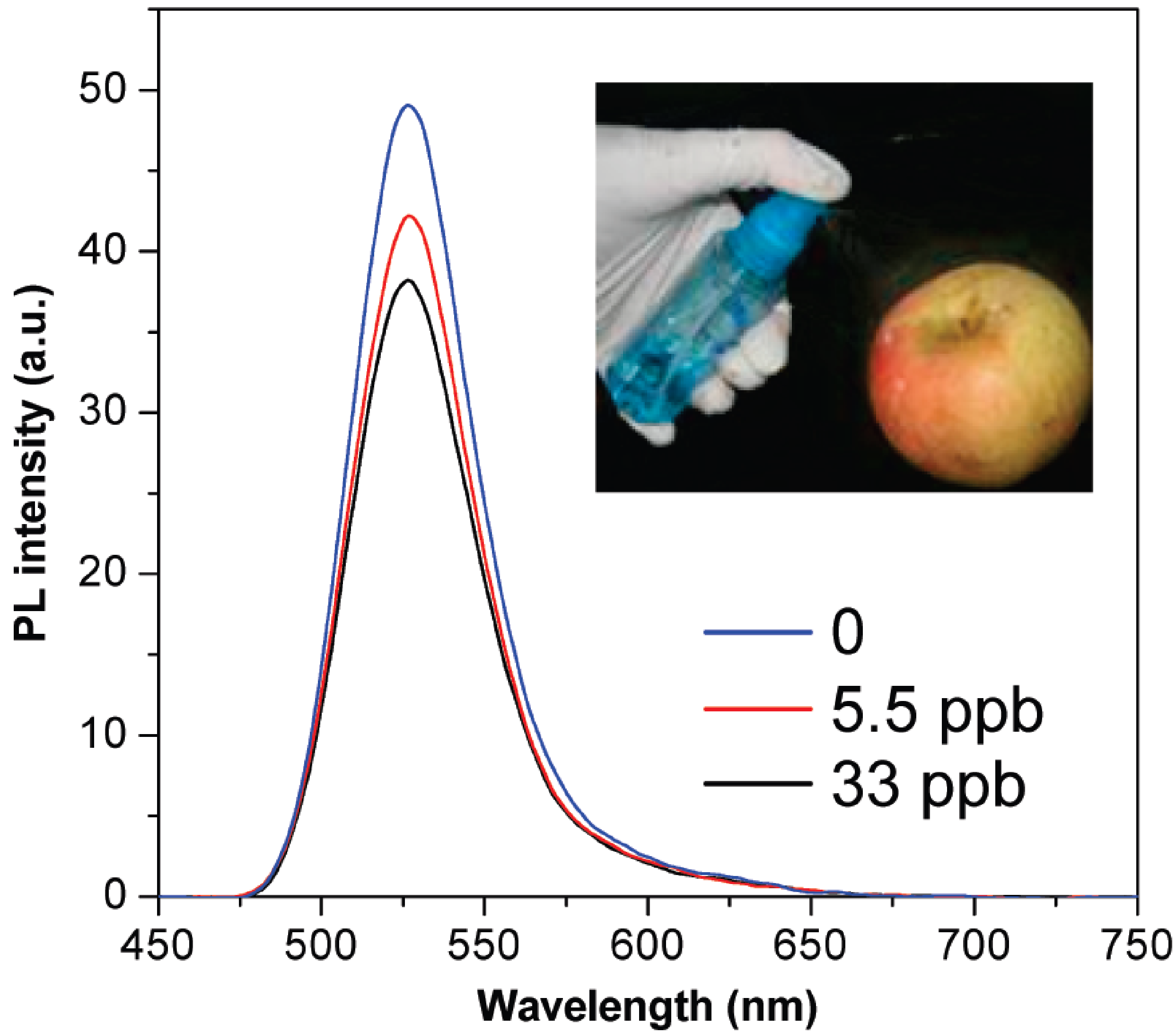


Figure. Fluorescence spectra before and after the addition of 30 μL of the juice from CP-spiked apples. The CP residues in two batches of apple samples are 6 and 25 ppb by HPLC calibration, respectively.

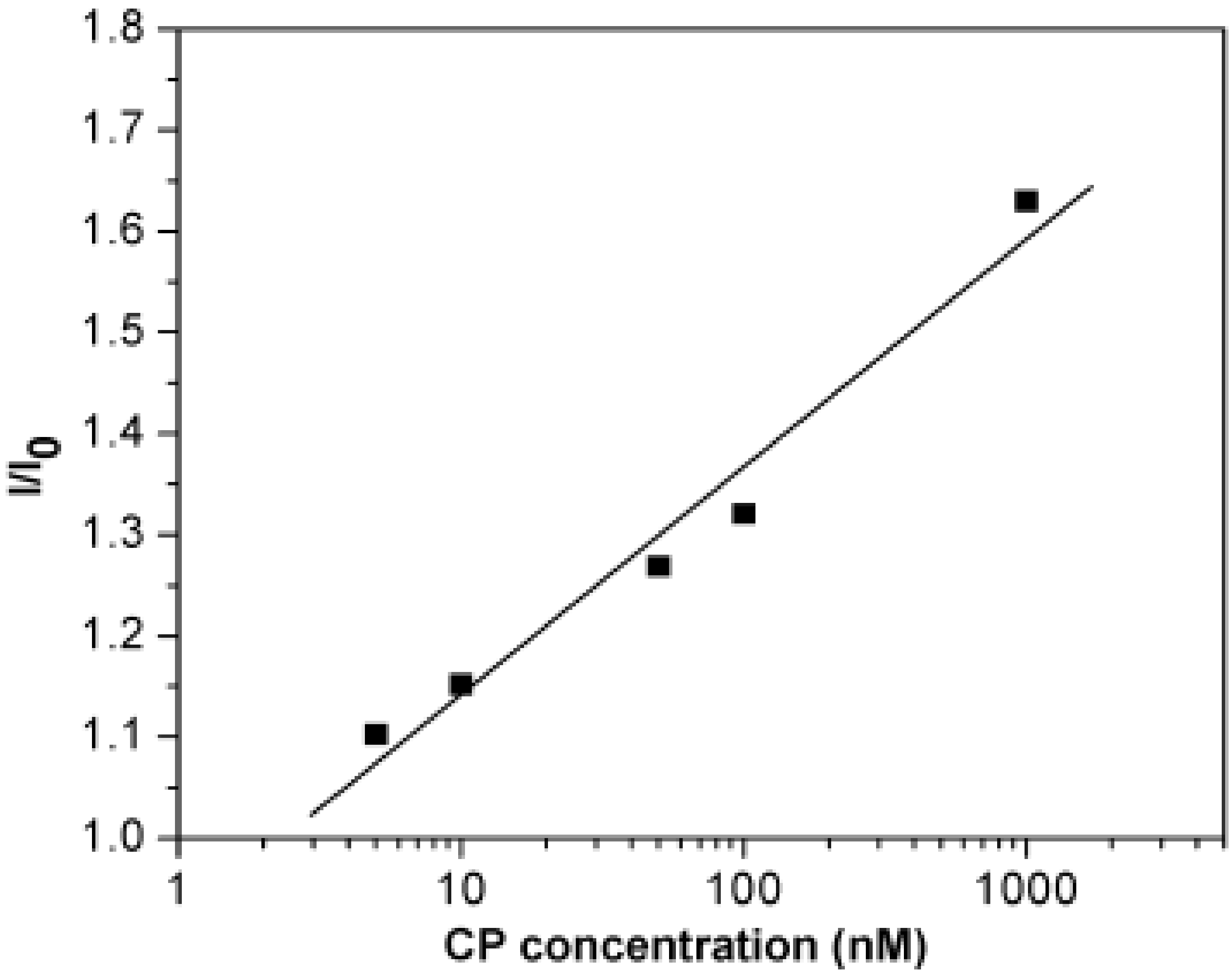


Figure. The standard curve of CP concentration in apple juice determined by the QD-DZ probe.

Conclusions

- The surface coordination-originated fluorescence resonance energy transfer (FRET) of CdTe quantum dots (QDs) is demonstrated
- A simple ligand-replacement turn-on mechanism for the highly sensitive and selective detection of organophosphorothioate pesticides
- QD chemosensor can directly detect chlorpyrifos residues at levels under the maximal residual limit in apples set by the EPA

Thank you