Electronic Supplementary Information

Fluorescent Methylammonium Lead Halide Perovskite Quantum Dots as Sensing Material for Detection of Polar Organochlorine Pesticide Residues

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Experimental Section

Chemicals

Hydrobromic acid (48 wt% in water), $PbBr_2$, oleylamine, oleic acid, *N,N*-dimethylformamide (DMF), tert-butanol, n-hexane, acetonitrile and anhydrous magnesium sulfate were purchased from Aladdin Co. (Shanghai, China). Hexachlorocyclohexane (HCH), tetradifon cypermethrin, 2,2-bis(4-Chlorophenyl)-1,1,1-trichloroethane (p,p'-DDT), dicofol, toxaphene, chlorothalonil, terpene polychlorinates, tetradifon were obtained from Dr. Ehrenstorfer GmbH (Germany). Methylamine solution (33 wt% in absolute ethanol), ethyl paraoxon, ethyl parathion, carbaryl, pirimicarb and methomyl were brought from Sigma-Aldrich (Milwaukee, USA). Diethyl ether and toluene were purchased from Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd (China). PDMS elastomer and crosslinker (Sylgard 184) were brought from Dow Corning (USA).

Characterization

UV-Vis absorption spectra were obtained by a Puxi universal TU-1900 double beam UV-Vis spectrophotometer (Puxi Co., Beijing). Fluorescence spectra was recorded on a Thermo Lumina fluorescence spectrophotometer. Transmission electron microscope (TEM) and high resolution TEM (HRTEM) measurements were conducted using a JEOL JEM-2100F electron microscope. The X-ray photoelectron spectroscopy (XPS) were conducted with an VG ESCALAB MKII spectrometer. The binding energy scale of the spectra was aligned through the C (1s) peak at 284.6 eV. Fourier-transform infrared spectroscopy (FTIR) was collected with Thermo Scientific Nicolet iS50. ^{1}H NMR spectra were acquired with BRUKER AV III 400M. X-ray diffraction (XRD) measurement were conducted on a D8 ADVANCE diffractometer (Bruker Co., Germany) using Cu Kα (0.15406 nm) radiation.

The pesticide residues analysis of standard solutions (10, 20, 60, 80, 150 μM tetradifon dissolved in acetone) and the extracted solution was complished using GC-MS (Scion TQ GC-MS, Bruker Inc.). The carrier gas was helium whose flow rate was 1 mL/min. The temperature of column was firstly kept at 150 °C for 2 min, then increased to 280 °C at the rate of 8 °C/min. The end time of column oven was 30 min. The sample solution (1 μL) was manually injected in splitless mode. The standard sample was detected by selective scanning and the retention time of tetradifon was centered at 26.18 min.

Real sample detection

Apple, grape which were purchased from a supermarket in Tianjin, China were chosen as the model samples to test OCPs residues to identify the practicability of fluorescent probe. The detailed pretreatment procedures of fruits were according to NY/T1379-2007 (China). 15 g of the fruits sprayed with tetradifon were placed in a centrifugal tube, in which 30 mL of acetonitrile was added. The mixture was homogenized using a high-speed disperser for 2 min. Then 7.5 g of anhydrous magnesium sulfate was added in that mixture and it was homogenized repeatedly for 1 min. Afterwards the mixture was centrifugated for 5 min at 3000 rpm and the supernatant was collected into 50 mL round-bottomed flask for the purpose of rotary evaporation under vacuum at 50 ℃ to about 1mL. Then 10 ml acetonitrile was added into the mixture that continued to be evaporated to 1 mL concentrated solution so as to remove the small amount of water. In order to extract the OCPs residues, the concentrated solution and 10 mL mixture solution of acetonitrile and toluene (3:1, v/v) which was used to wash the round-bottomed flask before were added to the graphite carbon black solid-phase extraction column that was connected with an alanine solid-phase extraction column in series from up to down. The OCPs were eluted with 25 mL of acetonitrile and toluene (3:1, v/v) drop by drop into another 50 mL round-bottomed flask. The eluent was rotary evaporated to near dryness and toluene was added to dissolve the OCPs residues, whose volume was adjusted to 2.5 mL and stored in a refrigerator at −18 °C for further use.

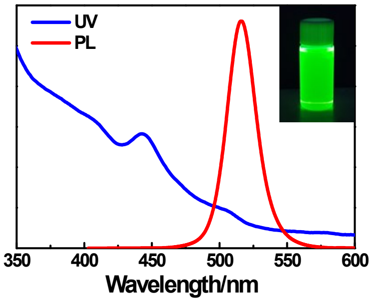

Fig. S1. UV-vis absorption spectra and fluorescence emission spectra of the MAPB-QDs in toluene. (λ_{ex} = 298 nm). Inset: photograph of MAPB-QDs (dissolved in toluene) under 302 nm UV light.

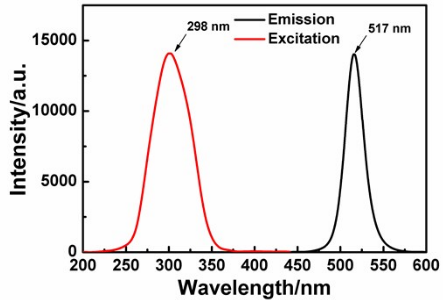

Fig. S2. Excitation and emission (excited at 298 nm) wavelength of MAPB-QDs (dissolved in toluene).

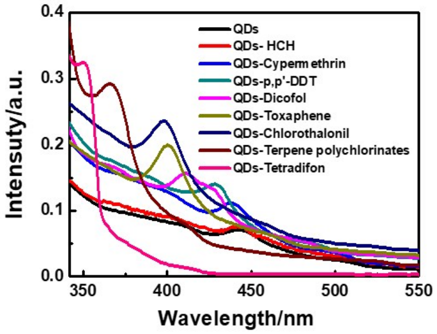

Fig. S3. UV-vis absorption spectra of MAPB-QDs and MAPB-QDs reacted with OCPs (dissolved in toluene).

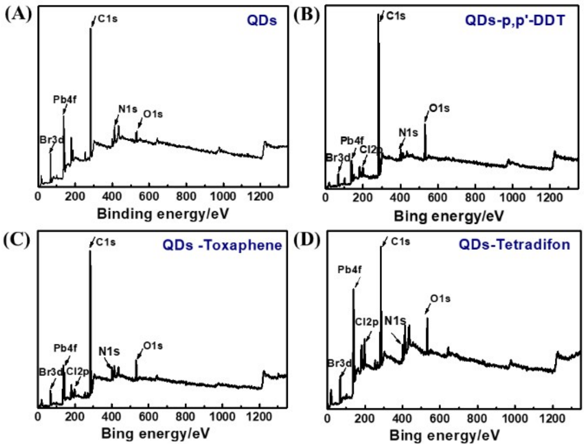

Fig. S4. The X-ray photoelectron spectroscopy represented the survey spectrum of MAPB-QDs (A) and MAPB-QDs reacted with p,p'-DDT (B), toxaphene (C) and tetradifon (D).

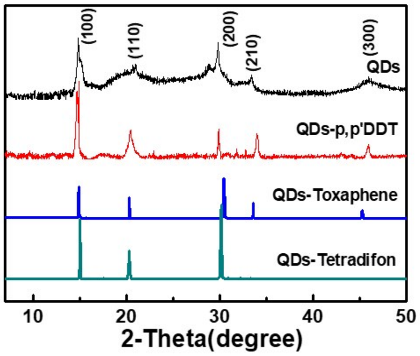

Fig. S5. XRD spectra of MAPB-QDs and MAPB-QDs reacted with p, p'-DDT, toxaphene and tetradifon.

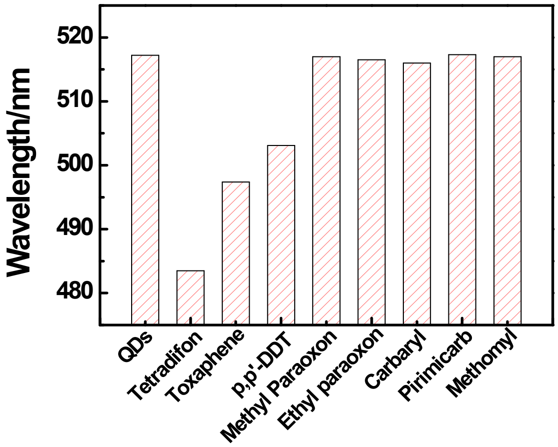

Fig. S6. Effect of various pesticides (including tetradifon, toxaphene, p,p'-DDT, ethyl paraoxon, methyl parathion, carbaryl, pirimicarb, methomyl) on the fluorescence characteristics of MAPB-QDs (dissolved in toluene).

Fig. S7. Photographs of PDMS film and PDMS film placed in sealable bag for 1 month.(under 302nm UV light)

Table S1 Analysis of tetradifon in real samples.

Real sample	additive amount(μM)	initial value	Results (mean±RSD, n=3) GC-MS		FL		colorimetric measurement
			Detective density	Recovery (%)	Detective density	Recovery (%)	
apple	15	0	13.39±0.43	89.26±2.87	13.36±0.56	89.06±3.73	5~20
	55	0	50.89±1.92	92.52±3.49	50.23±1.78	91.32±3.23	50~60
	120	0	110.75±4.45	92.29±3.71	111.43±4.05	92.86±3.38	110~140
grape	15	0	13.48±0.32	89.86±2.13	13.57±0.21	90.46±1.40	5~20
	55	0	51.04±1.93	92.80±3.51	50.75±1.23	92.27±2.24	50~60
	120	0	111.23±3.88	92.69±3.23	110.89±3.05	92.40±2.54	110~140