Supplementary Information

A magnetic fluorescence molecularly imprinted polymer sensor with selectivity via Mn doped ZnS quantum dots for dibutyl phthalate

Wanzhen Xu^a, Tao Li^b, Weihong Huang^a, Yu Luan^c, Yanfei Yang^c, Songjun Li^{b,*},

Wenning Yang^{b,*}

^a School of the Environment and Safety Engineering, Jiangsu University, Zhenjiang 212013, China

^b Institute of Polymer Materials, School of Materials Science and Engineering, Jiangsu University,

Zhenjiang 212013, China

^c Zhenjiang Institute for Drug Control of Jiangsu Province, Zhenjiang 212003, China

2. Experimental

2.1 Reagents and materials

All reagents used were least analytical grade. Dibutyl phthalate (DBP), ammonia solution (25.0–28.0%), diethyl phthalate (DEP), ethylene glycol, polyethylene glycol, diallyl phthalate (DAP, 99%), MnCl₂·4H₂O, NaAc, dimethyl phthalate (DMP, 99%), ferric chloride (FeCl₃·6H₂O) and ethanol were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Tetraethoxysilane (TEOS), Na₂S·9H₂O, ethylene glycol dimethacrylate (EGDMA), 3-mercaptopropyltriethoxysilane (MPTS) and 2,2'-azobis (2-methylpropionitrile) (AIBN) were received from Aladdin reagent Co., Ltd. (Shanghai, China). ZnSO₄·7H₂O were purchased from Shanghai Chemical Reagents Co., Ltd. 3-(methacryloyloxy) propyltrimethoxysilane (KH-570) were purchased from Nanjing Chemical Reagents Co., Ltd. The ultrapure water was prepared throughout the experiment procedures.

2.2 Instruments

The microcosmic characteristic of the products were from transmission electron microscopy (TEM, JEOL, JEM-2100) and scanning electron microscopy (SEM, JEOL, JSM-7001F). Fourier transform infrared spectra (FT-IR) (4000–400 cm⁻¹) were recorded using KBr a Nicolet NEXUS-470 FTIR spectrophotometer (USA). The X-ray diffraction (XRD) data were collected on D8-ADVANCE X-ray Diffractometer (Bruker, Germany) with Cu Ka radiation over the range of $10 - 80^{\circ}$. Magnetic properties measurements were carried out using a VSM (7300, Lakeshore) at 300 K. The fluorescence spectra were recorded on lumina fluorospectro photometer (ThermoFisher, USA) equipped with a plotter unit and a quartz cell (1.0 cm*1.0 cm).



Fig. S1 FT-IR spectra of Fe_3O_4 (a), MQDs (b) and MQDs–MIPs (c).



Fig. S2 Recoverability of fluorescence intensity of MQDs-NIPs. Under experimental condition, MQDs-MIPs was 70 mg L⁻¹ and CBPA was 35 μmol L⁻¹.



Fig. S3 X-ray diffraction patterns of Fe₃O₄ (a), MQDs-MIPs (b), ZnS:Mn QDs (c) and ZnS

Coexisting substance	Coexistiong concentration (µmol L ⁻¹)	Change of fluorescent intensity (%) for MQDs-MIPs		
Na ⁺	40	0.78		
\mathbf{K}^+	40	0.85		
Mg^{2+}	20	1.53		
Ca ²⁺	20	1.29		
CO ₃ ²⁻	10	1.89		
NO ₃ -	10	2.02		

Table S1. The interference of different substance on the FL intensity of MQDs-MIPs (Under experiment condition, MQDs-MIPs was 70 mg L-1 and DBP was 35 μmol L-1).

Table S2. Performance Comparison with Other Reported MIP Based QDs Methods.

System	Template	Response time (min)	Linear range	Detection limit	Real sample	Ref.
CdSe/ZnS QDs@MIP	caffeine					28
MIPs-ZnS:Mn QDs	2,6-dichlorophenol	50	1.0-56µmol L ⁻¹	0.23 μmol L ⁻¹	Real water	29
MIP-coated CdTe QDs	cytochrome c		0.97-24µmol L ⁻¹	0.41 μmol L ⁻¹		30
MIP-capped CdTe QDs	2,4,6-trinitrotoluene	10	0.8-30 μmol L ⁻¹	0.28 μmol L ⁻¹	Soil	31
ZnS/Mn QDs@MIP	diazinon	120	50-600 ng mL ⁻¹	8.6 ng mL ⁻¹	Tap water	32
MIP-coated CdSe QDs	ractopamine	40	0.00121-3.03 μmol L ⁻¹	0.76 μmol L ⁻¹	pork	33
MQDs-MIPs	dibutyl phthalate	21	5-50 µmol L ⁻¹	0.08 μmol L ⁻¹	Tap water	This work