

# Electronic Supplementary Information

## Magnetic-Luminescent Bifunctional Nanosensors

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### Experimentals in detail:

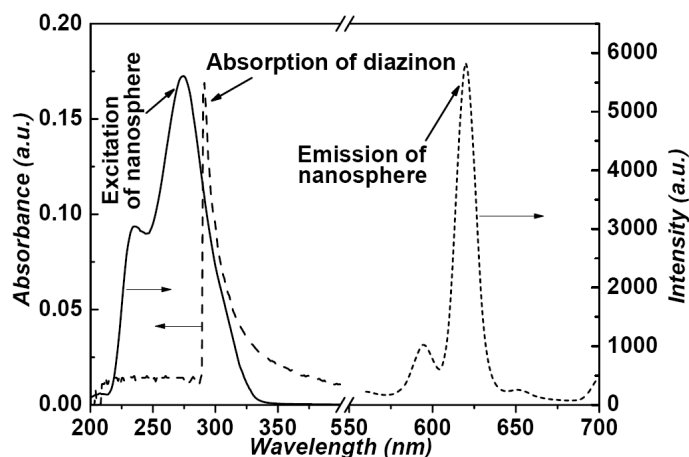
**Reagents and Chemicals.** Oleic acid was obtained from Alfa.  $\text{Fe}(\text{NH}_4)_2 \cdot (\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NH}_4\text{VO}_3$  were from Tianjin Fuchen Chemicals Co. (Tianjin, China).  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  were purchased from Beijing  
10 Ouhe Chemical Reagent Company. NaOH, ethanol, cyclohexane, chloroform and methanol were purchased from Beijing Chemical Factory. The monomers, methacrylic acid (MAA) as well as styrene (St), and azoinitiator 2,2'-azobisisobutyronitrile (AIBN) were obtained from Tianjin Chemical Factory (China) and used as such. The pesticides and polyethylene alcohol (PVA) used in this work were obtained from Sigma-Aldrich. All reagents are analytical grade and used as received without further purification.

15 **Characterization.** A Shimadzu XRD-7000 X-ray diffractometer which employed Cu  $K\alpha$  radiation of wavelength  $\lambda = 1.5418 \text{ \AA}$  was used to record the X-ray diffraction (XRD) pattern. The shape and size of the as-prepared NCs and MIP nanocomposites were examined with an H-800 transmission electron microscope with a tungsten filament at an accelerating voltage of 100 kV. High resolution transmission electron microscopy (TEM) images were obtained on a JEOL JEM-2100F transmission electron  
20 microscope operated at 200 kV. The photoluminescence measurements were performed on an F-4600 spectrophotometer (Hitachi, Japan) equipped with a plotter unit and a quartz cell (1cm×1cm).

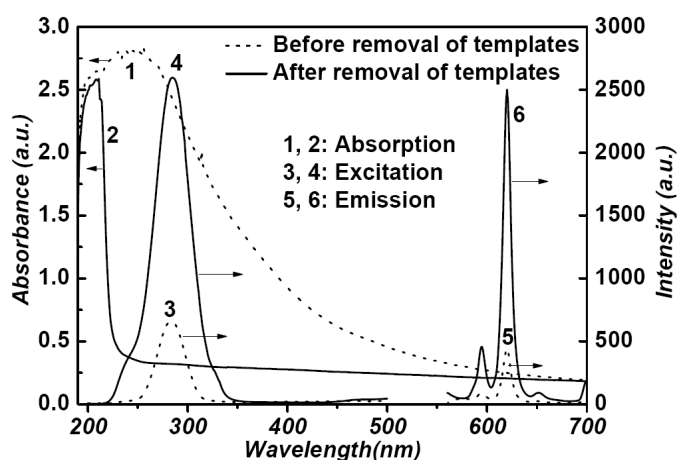
**Synthesis of Luminescent  $\text{LaVO}_4:\text{Eu}^{3+}$  nanocrystals.**  $\text{LaVO}_4:\text{Eu}^{3+}$  luminescent nanoparticles (LNPs) were prepared according to the reported method with some alteration.<sup>1</sup> In brief,  $\text{NH}_4\text{VO}_3$  (0.06 g) and NaOH (0.6 g) were first dissolved in deionized water (5 mL) followed by addition of ethanol (20 mL) and oleic acid (10 mL). Finally, 1 mL of the mixed solution (Total  $[\text{Re}^{3+}] = 1.0 \text{ M}$ ) of  $\text{La}(\text{NO}_3)_3$  and  $\text{Eu}(\text{NO}_3)_3$  ( $\text{La}^{3+}/\text{Eu}^{3+} = 98/2$ ) was added. The mixture was stirred thoroughly and then transferred into a Teflon-lined autoclave. Thereafter the autoclave was heated at 140 °C for 5 h and then allowed to cool to room temperature. The product deposited onto the bottom of the autoclave was collected and washed with cyclohexane. The obtained white product was then dispersed in chloroform (1 mL) and stored for later use.

30 **Preparation of  $\text{Fe}_3\text{O}_4$  nanoparticles.** To make the luminescent-magnetic multifunctional MIP nanocomposites, the  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles (MNPs) as the magnetic core building blocks were also prepared.<sup>2</sup> Briefly, into an autoclave, NaOH (1.0 g) and deionized water (5.0 mL) were added. After the mixture was stirred at room temperature for 10 min, ethanol (15 mL) and oleic acid (10 mL) were added, respectively. Thereafter, 10 mL of aqueous solution containing  $\text{Fe}(\text{NH}_4)_2 \cdot (\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.784 g) was added,  
35 and the stirring was kept for another 10 min. The autoclave was treated at 180 °C for 10 h. After the autoclave was allowed to cool to room temperature, the black products were collected and washed with cyclohexane and ethanol. This purification cycle was repeated for twice. The final products were dispersed in chloroform (1 mL) and stored for use.

**Synthesis of Poly(St-Co-MAA).** The synthesis of the copolymer polystyrene-co-methacrylic acid  
40 poly(St-co-MAA) reported here is a modified version of the one used before.<sup>3</sup> In brief, MAA (0.2 g), Styrene (4.6 g) and AIBN (0.096 g) were added to chloroform (35 mL) under stirring. Thereafter, the mixture was transferred into an autoclave and heated at 100 °C for 10 h, and allowed to cool to room temperature. The poly(St-Co-MAA) copolymer was precipitated by adding 100 mL of methanol and collected via centrifugation. And the final products were obtained after two cycles of purification.

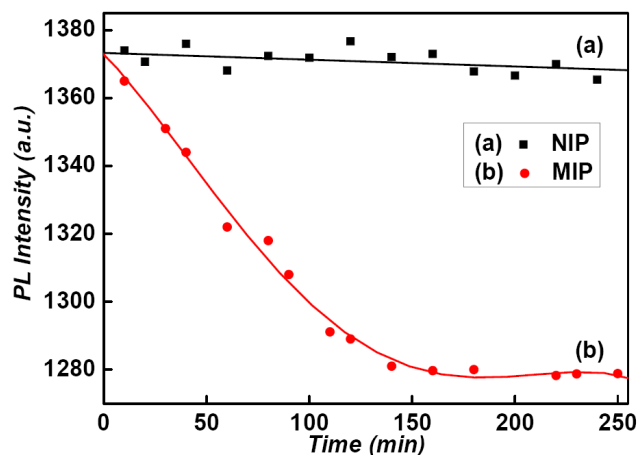


**Figure S1.** Absorption spectrum of diazinon, excitation and emission spectra of the MIP nanocomposites.  $\lambda_{ex}/\lambda_{em} = 254/620$  nm.



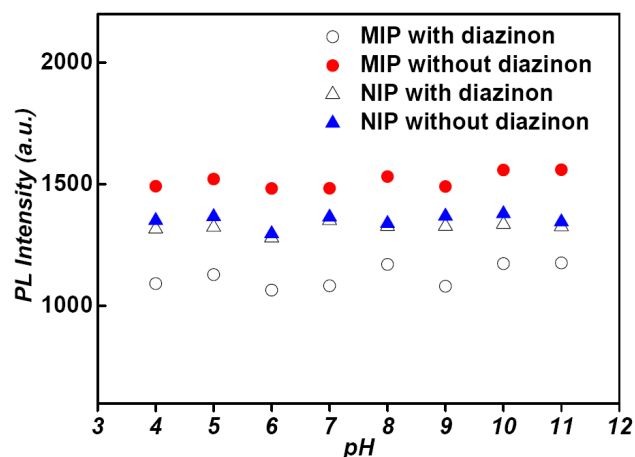
**Figure S2.** Absorption (spectrum 1 and 2), excitation (spectrum 3, 4) and emission (spectrum 5, 6) spectra of the nanocomposite colloidal solution before (spectrum 1, 3, 5) and after (spectrum 2, 4, 6) the removal of the templates from the recognition cavities in the MIP nanocomposites. The concentration of the MIP nanocomposites is 70  $\mu\text{g}/\text{mL}$ .  $\lambda_{ex}/\lambda_{em} = 254/620$  nm.

In order to investigate the luminescence quenching mechanism, the excitation and emission spectrum of 10 nanocomposites before and after the removal of diazinon and the absorption spectrum of diazinon were carried out. As depicted in Figure S1, the absorption peak of diazinon is located in the range of the excitation of nanocomposites. Meanwhile, the absorption and excitation spectra of the MIP nanocomposites were carried out before and after the removal of the templates from the MIP matrixes. As shown in Figure S2, the absorption spectra of the MIP nanocomposites before (spectrum 1) and after (spectrum 2) removing the templates are centered at 251 and 208 nm, respectively. In addition, the absorption spectrum widened and enhanced dramatically when the templates rebinding to the recognition cavities. The widened absorption spectrum then overlapped the excitation spectrum (spectrum 3 and 4) of the MIP nanocomposites, which results in the dramatic decrease of the excitation intensity. This should be attributed to the energy transfer from the excited  $\text{Eu}^{3+}$  to pesticides' organic groups whose high frequency vibration 15 will dissipate the energy. After removing the templates from the recognition cavities in the MIP nanocomposites, the excitation increased greatly from spectrum 3 to spectrum 4, which causes the obvious enhancement of the photoluminescence (from spectrum 5 to spectrum 6). These observations of spectra clearly demonstrate that a strong luminescence quenching occurs when the pesticide templates rebinding to the recognition cavities retained in the MIP nanocomposites.



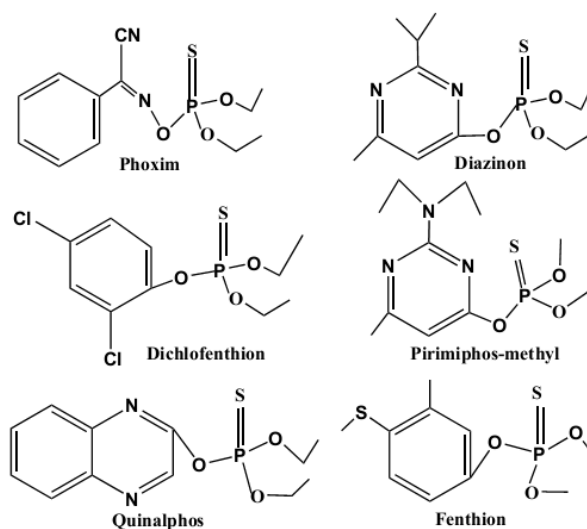
**Figure S3.** Effect of incubation time on the photoluminescence intensity after adding pesticides into the MIP (curve b, represented by solid circles) and NIP (curve a, represented by solid squares) nanosphere colloidal solution. (Diazinon: 5.0  $\mu\text{g/mL}$ . MIP: 210  $\mu\text{g/mL}$ ; NIP: 270  $\mu\text{g/mL}$ . Temperature 25  $^{\circ}\text{C}$ ).

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**Figure S4.** pH effects on the photoluminescence intensity of MIP (represented by circles) and NIP (represented by triangles) nanosphere colloidal solution (70  $\mu\text{g/mL}$ ) before (represented by solid) and after (represented by open) adding diazinon (3  $\mu\text{g/mL}$ ). Buffer solution and concentration: at pH = 4, 5, 10  $\text{CH}_3\text{COOH}-\text{CH}_3\text{COONa}$  (0.02 mol/L); at pH 6–8,  $\text{NaH}_2\text{PO}_4-\text{Na}_2\text{HPO}_4$  (0.02 mol/L); at pH 9–11,  $\text{Na}_2\text{CO}_3-\text{NaHCO}_3$  (0.02 mol/L).

The pH effect on the detection was also checked and the results suggested the pH has no influence on the detection. As shown in Figure S4, the pH change almost has no effects on the photoluminescence intensity of the MIP nanocomposites before and after the addition of diazinon. Meanwhile the difference of 15 photoluminescence intensity ( $\Delta I$ ,  $\Delta I = I_0 - I$ ) also keeps stable under different pH value. Herein, the  $I_0$  and  $I$  are the photoluminescence intensity of the nanocomposites before ( $I_0$ ) and after ( $I$ ) the addition of diazinon, respectively. On the other hand, in the case of NIP, the luminescence intensity of NIP nanocomposites has no change under different pH value before and after the addition of diazinon, suggesting the diazinon can not get into the polymer matrixes. These results indicate that the pH has no influence on the pesticide 20 analysis, which can be attributed to the good chemical and optical stability of the  $\text{LaVO}_4:\text{Eu}^{3+}$  nanocrystals.



**Figure S5.** Chemical structures of the templates and other analogues used in this work.

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**Table S1.** Detection of Trace Diazinon in Real Water Samples <sup>a</sup>

sample	Concentration ( $\mu\text{g/mL}$ )		recovery (%)
	taken	found (mean, n = 6)	
lake water	0.2	$0.21 \pm 0.015$	$105 \pm 7.5$
	5.0	$5.17 \pm 0.07$	$103.4 \pm 1.4$
	8.5	$8.40 \pm 0.1$	$98.8 \pm 1.2$

<sup>a</sup> n is the repetitive measurement number.

## References

- 1 J. F. Liu, Y. D. Li, *Adv. Mater.* **2007**, *19*, 1118-1122.
- 10 2 a) X. Liang, X. Wang, J. Zhuang, Y. T. Chen, D. S. Wang, Y. D. Li, *Adv. Funct. Mater.* **2006**, *16*, 1805-1813; b) X. Wang, J. Zhuang, Q. Peng, Y. D. Li, *Nature* **2005**, *437*, 121-124.
- 3 F. Bai, X. L. Yang, R. Li, B. Huang, W. Q. Huang, *Polymer* **2006**, *47*, 5775-5784.

15