Carbazole-Based Conjugated Polymer Covalently Coated Fe₃O₄ Nanoparticle as Efficient and Reversible Hg²⁺ Optical Probe

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ABSTRACT: A type of fluorescent-magnetic dual-function nanocomposite, Fe₃O₄@SiO₂@P-2, was successfully obtained by Cu⁺-catalyzed click reaction between acetylene (C=C–H)-substituted carbazole-based conjugated polymer (**P-2**) and azideterminated silica-coated magnetic iron oxide nanoparticles (Fe₃O₄@SiO₂-N₃). Optical and magnetization analyses indicate that Fe₃O₄@SiO₂@P-2 exhibits stable fluorescence and rapid magnetic response. The fluorescence of Fe₃O₄@SiO₂@P-2 was quenched significantly in the presence of *I*⁻ and gave a detection limit (DL) of ~8.85 × 10⁻⁷ M. Given the high binding constant and matching ratio between Hg²⁺ and *I*⁻, the fluorescence of Fe₃O₄@SiO₂@P-2/*I*⁻ complex recovered efficiently with the addition of Hg²⁺. A DL of ~4.17 × 10⁻⁷ M was obtained by this probing system. Recycling of Fe₃O₄@SiO₂@P-2 probe was readily achieved by simple magnetic separation. Results indicate that Fe₃O₄@SiO₂@P-2 can be used as an "on-off-on" fluorescent switchable and recyclable Hg²⁺ probe. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *00*, 000–000

KEYWORDS: carbazole; conjugated polymers; fluorescent-magnetic nanoparticles; Hg²⁺ ion

INTRODUCTION Mercury (II) is one of the most harmful pollutants because of its severe effects on human health and the environment.^{1,2} Thus, rapid and efficient detection of trace Hg^{2+} in environmental and biological samples is very important. Considerable efforts have been devoted to detect Hg²⁺ by using different approaches such as neutron activation analysis,³ anodic stripping voltammetry,⁴ inductively coupled plasma mass spectrometery,⁵ and optical probes.⁶⁻⁸ Compared with other probing methods, fluorescent sensors exhibit advantages such as high selectivity and sensitivity, ease in sample preparation, and relatively low-cost operating equipment. Therefore, fluorescent sensors represent a new family of high-performance probing substrates.9 To date, many fluorescent sensors for Hg²⁺ detection have been reported for operating platforms, including small molecules,^{10,11} polymers,^{12,13} nanomaterials,¹⁴ and nanocomposites.^{15,16} These fluorescent sensors can be implemented in both organic^{10,12,15} and aqueous^{11,13,14,16} environments.

Given the unique "signal-amplification" effect (attributed to the transfer of excitation energy along the whole backbone), nontoxicity, and photostability, fluorescent-conjugated polymers (CPs) have been developed rapidly in recent years as chemical and biological sensors.¹⁷⁻²¹ A series of CP-based fluorescence turn-off probes have been successfully synthesized with different conjugated backbones and Hg²⁺ reporter substituents (such as thieno[3,4b]-pyrazine,²² benzo[2,1,3]thiadiazole,²³ thymine,²⁴ and cationic quaternary ammonium²⁵). These CP-based fluorescence turn-off probes have shown good sensitivity and selectivity. Fluorescence turn-on detection exhibits ease of detection and reduced interference and is thus preferable to turn-off mode probing. However, few CP-based turn-on sensors have been reported, and their probing cannot take effect without the use of certain compensating components such as expensive DNA derivative²⁶ or signal receptors with complex chemical structures that need to be synthesized artificially.²⁷ Most of these turn-on probes are disposable and cannot be recycled from the probing mixture. The design and preparation of a CP-based turn-on Hg²⁺ probing system with simple and inexpensive components, as well as recoverability, is practically favorable and remains an important challenge.

Fluorescent-magnetic composites have attracted increasing attention as a new type of nanomaterial in recent years. Such composite nanoparticles combine fluorescence,

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magnetism, and the physical properties of nanosize structures into one entity. Thus, fluorescent-magnetic composites are widely used in magnetic separation,²⁸ bioimaging,²⁹ medicine delivery,³⁰ tumor cell localization,³¹ and cancer treatment.³² The use of CPs as optical reporters combined with magnetic nanoparticles improves the comprehensive properties of such composites. Given this consideration, some CP-based fluorescent-magnetic nanocomposites have been successfully obtained by electrostatic coassembly,³³ surface-active agentassisted coencapsulation,³⁴ and covalent binding processes.³⁵ Compared with other protocols, covalently binding CPs onto magnetic particles exhibits strong associations between two key matrixes. The fluorescence quenching provided by the Febased magnetic substrates can be weakened significantly by the introduction of a blocking interlayer such as silica to separate the magnetic core from the fluorescent shell.³⁶⁻³⁸

Previous reports have shown that small carbazole-based molecules and CPs can be used as sensitive and selective optical probes for I^- . The heavy-atom effect of I^- on the *N*-atom in a carbazole ring is the presumable reason for their fluorescence quenching.³⁹⁻⁴¹ Such interaction between the I^- and the *N*-atom is transient and weak,³⁹ suggesting that the quenched fluorescence can be recovered if I^- is distracted from the I^- -*N* complex. High association constants and composition ratios exist between Hg²⁺ and I^- (i.e., 8.3 × 10²³ for HgI₂ and 6.31 × 10²⁹ for [HgI₄]²⁻).^{25,42} By taking advantage of such strong associations, trials have been conducted to realize the reciprocal detection of these two ions.^{25,42-44} These finding indicate that Hg²⁺ has the potential to act as a suitable I^- abstractor.

On the basis of these findings, a type of acetylene bared carbazole-based CP (**P-2**) was synthesized and **P-2** was covered onto azide-terminated silica-coated magnetic iron oxide nanoparticles (Fe₃O₄@SiO₂–N₃) by high-reactive Cu⁺-catalyzed click reaction to obtain a novel fluorescent-magnetic nanocomposite (Fe₃O₄@SiO₂@P-2). The influence of the optical properties of Fe₃O₄@SiO₂@P-2 by I^- , as well as further turn-on detection of Hg²⁺ by using this complex as a probing substrate, was investigated systematically in this study. Intrinsic magnetic properties of Fe₃O₄@SiO₂@P-2 facilitate probe recovery by simple magnetic separation. Results show that such nanocomposites can act as sensitive, selective, and reversible optical probes for Hg²⁺.

EXPERIMENTAL

All reagents, unless otherwise specified, were purchased from Aldrich, Acros, and TCI Chemical and used without further purification. Diisopropylamine, toluene, and tetrahydrofuran (THF) were distilled from sodium in the presence of benzophenone and degassed before use. Solutions of Al^{3+} , Pb^{2+} , Cu^{2+} , Mg^{2+} , Ni^{2+} , Cd^{2+} , Fe^{3+} , Ag^+ , Ba^{2+} , and Zn^{2+} were prepared from their nitrate salts; Hg^{2+} was prepared from its acetate salts; Fe^{2+} , Co^{2+} , and Sr^{2+} were prepared from their chloride salts. Concentrations of metal solutions were controlled at 10^{-1} M in deionized water and were diluted subsequently to different concentration stocks for next use.

Instrumentations

IR spectra were recorded on an EQUINOX 55 FTIR spectrometer with KBr pellets. ¹H NMR and ¹³C NMR spectra were collected on a VARIAN INOVA-400 spectrometer operating respectively at 400 MHz (for ¹H) and 100 MHz (for ¹³C) in deuterated chloroform solution with tetramethylsilane as reference. Number-average (M_n) and weight-average (M_w) molecular weights were determined by UltiMate3000 in THF using a calibration curve of polystyrene standards. UV-visible absorption spectra were recorded on a SHIMADZU UV-2450 UV-vis spectrophotometer. Photoluminescence (PL) spectra were recorded on HITACHIF-4500 spectrophotometer. Transmission electron microscopy (TEM) was conducted on JEM-2100 (JEOL). Energy-dispersive X-ray spectroscopy and scanning electron microscopy (SEM) were conducted on a Leo1430VP microscopy. Magnetic characterization was performed on a Lakeshore 7404 vibrating sample magnetometer at 300 K.

Synthesis

Synthetic route of monomers and polymers is shown in Scheme 1. 9-(4-Iodophenyl) carbazole,⁴⁵ 3,6-dibromo-9-(4-iodophenyl) carbazole,⁴⁶ 9-(4-(4-methoxyphenylethynyl)-phenyl) carbazole,⁴⁷ 1-(4-(3,6-dibromo carbazol-9-yl)phenyl)-2-(4-methoxyphenylethane)-1,2-dione,⁴⁸ 2,7-*bis*(4,4,5,5-tetra-methyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene,⁴⁹ and 3,6-dibromo-9-(4-triisopropylsilyl-phenylacetylene) carbazole⁵⁰ were prepared and purified via similar procedures in the reported literatures.

The synthetic route of magnetic nanoparticles is shown in Scheme 2. Fe₃O₄ nanoparticles, 3-azidopropyltriethoxysilane⁵¹ and Fe₃O₄@SiO₂-N₃ nanoparticles,³⁶ were fabricated by following the literatures.

Synthesis of 9-(4-(3-(4-Methoxyphenyl) quinoxaline)phenyl)-3,6-dibromo carbazole (5)

Monomer **5** was synthesized according to the method reported previously.⁴⁸ Diketone-containing intermediate (**4**) (0.563 g, 1 mmol) was refluxed with 1,2-phenylenediamine (0.321 g, 2.92 mmol) in 50 mL of acetic acid under nitrogen atmosphere overnight. The reaction mixture was cooled to room temperature and poured into a large amount of cold water. The yellow precipitate was filtered and washed several times with hot water. The crude product was purified by column chromatography to afford the target compound as bright yellow solid (0.510 g, 80%).

Fourier transform infrared spectroscopy (FTIR) (KBr, cm⁻¹): 3059, 2837, 1602 (C=N), 1512 (C=N), 1466, 1435, 1340, 1256, 1170, 1053, 1024, 975, 835, 801, 764, 633, 596, 544. ¹H NMR (CDCl₃, ppm) δ : 8.20–8.17 (m, 4 H), 7.81–7.79 (m, 4 H), 7.58–7.50 (m, 6 H), 7.31–7.26 (m, 2 H), 6.95–6.93 (m, 2 H), 3.86 (s, 3 H). ¹³C NMR (CDCl₃, ppm) δ : 160.48, 152.93, 152.12, 141.50, 140.99, 139.54, 139.04, 137.20, 131.57, 131.44, 131.10, 130.30, 129.96, 129.50, 129.2316, 126.53, 124.12, 123.29, 113.91, 113.31, 111.48, 55.39.



SCHEME 1 Synthetic route of monomers and polymers.

Synthesis of Poly[(9,9-dioctyl)-2,7-fluorene-(9-(4-(3-(4-methoxyphenyl)quinoxaline)phenyl)-3,6-carbazole)]-*co*-[(9,9-dioctyl)-2,7-fluorene-(*N*-4triisopropylsilylphenylacetylene)-3,6-carbazole] (P-1) Under nitrogen, 2,7-*bis*(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (0.321 g, 0.5 mmol), **5** (0.1905 g, 0.3 mmol), and 3,6-dibromo-9-(4-triisopropylsilyl-phenylacetylene)carbazole (0.116 g, 0.2 mmol) were added in degassed toluene (8 mL) and 0.2 M of potassium carbonate aqueous solution (1.5 mL). Pd(OAc)₂ (0.003 g, 0.013 mmol) and three drops of aliquat336 were placed later. This mixture was degassed for several times, tricyclohexyl phosphine (0.006 g, 0.021 mmol) was added afterward. The reaction was refluxed at 90 °C for 72 h before it was cooled to room temperature. The crude product was purified by flash column chromatography by using toluene as eluent, then



SCHEME 2 Synthesis of $Fe_3O_4@SiO_2-N_3$ (6) and copper(I)-catalyzed azide-alkyne cycloaddition reaction of $Fe_3O_4@SiO_2@P-2$ nanoparticles (7).

concentrated, and reprecipitated into a large amount of methanol. The formed precipitate was recovered by filtration. The obtained polymer was dried after vacuum drying at 50 °C overnight (0.200 g, 50%).

FTIR (KBr, cm⁻¹): 3042, 2920, 2850, 2153 (C=C), 1882, 1602 (C=N), 1510 (C=N), 1451, 1340, 1286, 1248, 1223, 1172, 975, 877, 830, 803, 757, 650, 536. ¹H NMR (CDCl₃, ppm) δ : 8.61–8.49 (m, 2.81 H), 8.28–8.18 (m, 2.16 H), 7.92–7.52 (m, 26.58 H), 7.04–6.94 (m, 2.06 H), 3.90 (s, 3.0 H), 2.15 (s, 6.17 H), 1.37–1.01 (m, 49.51 H), 0.94–0.66 (m, 18.08 H). Gel permeation chromatography (GPC): $M_{\rm w} = 15,900, M_{\rm n} = 7790$, and $M_{\rm w}$ - $M_{\rm n} = 2.04$.

Synthesis of Poly[(9,9-dioctyl)-2,7-fluorene-(9-(4-(3-(4methoxyphenyl)quinoxaline)phenyl)-3,6-carbazole)]-*co*-[(9,9-dioctyl)-2,7-fluorene-(*N*-4-phenylacetylene)-3,6carbazole] (P-2)

A solution of **P-1** (0.090 g, 0.2 mmol) in anhydrous THF (8 mL) was vigorously stirred under nitrogen atmosphere in a round-bottom flask and tetrabutylammonium fluoride (1 M in THF, 0.5 mL, 0.5 mmol) was added to this solution. The mixture was stirred at room temperature overnight. The crude product was purified by flash column chromatography, using toluene as eluent, then concentrated, and reprecipitated into methanol. The final product was obtained after vacuum drying at 50 °C overnight (0.086 g, 96%).

FTIR (KBr, cm⁻¹): 3296 (=C-H), 3042, 2922, 2850, 2107 (C=C), 1882, 1603 (C=N), 1511 (C=N), 1454, 1341, 1287, 1249, 1226, 1172, 975, 877, 832, 805, 758, 649, 538. ¹H NMR (CDCl₃, ppm) δ : 8.59–8.49 (m, 2.82 H), 8.27–8.19 (m, 2.17 H), 7.92–7.52 (m, 26.46 H), 7.03–6.95 (m, 2.08 H), 3.90 (s, 3.0 H), 3.21 (s, 0.62 H, =C-H), 2.15 (s, 6.39 H), 1.37–1.01 (m, 37.96 H), 0.92–0.67 (m, 18.14 H). GPC: M_w = 14,680, M_n = 7210, and M_w - M_n = 2.04.

Synthesis of Fe₃O₄@SiO₂@P-2 Nanoparticles

P-2 (0.010 g) was dissolved in dry THF (15 mL) and diisopropylamine (0.5 mL) under nitrogen atmosphere, then $Cu(PPh_3)_3Br$ (0.005 g, 0.0054 mmol) and $Fe_3O_4@SiO_2-N_3$ nanoparticles (0.005 g) were added sequentially. The above mixture was stirred at 40 °C overnight, and then the product was washed with THF several times. The final product was separated with the aid of magnet and was dried under vacuum at 50 °C overnight.

RESULTS AND DISCUSSION

Synthesis of Monomers and Polymers

The synthetic procedure used to prepare the monomers and polymers is shown in Scheme 1. Electron-withdrawing quinoxaline moiety was introduced into monomer **5** by intermolecular condensation between phenylenediamine and diketone-containing intermediate (**4**) with a relatively high yield. Previous reports indicate that simultaneous introduction of electron-rich and electron-deficient moieties into fluorescent compounds is a potential protocol for improving quantum efficiency.^{47,52} **P-1** was prepared by Pd-catalyzed



FIGURE 1 FTIR spectra of $Fe_3O_4@SiO_2-N_3$, P-2, and $Fe_3O_4@SiO_2@P-2$.

Suzuki coupling reaction. The high stability of triisopropylsilyl group ensures that the acetylene is well protected throughout the reaction. The acetylene-group pendant-substituted polymer P-2 was readily obtained by introducing the strong desilylation agent tetra-n-butylammonium fluoride under ambient reaction conditions. Both P-1 and P-2 exhibit good solubility in common organic solvents such as CHCl₃, CH₂Cl₂, toluene, and THF. The chemical structures of all intermediates and polymers were verified by nuclear magnetic resonance (NMR) and FTIR analyses. The ¹H NMR spectra of P-1 and P-2 are shown in Supporting Information Figure S1. The signals at \sim 3.9 ppm in both curves can be ascribed to the -OCH₃ groups attached directly on the carbazole-quinoxaline moieties. Comparison of these two spectra reveals a small peak at \sim 3.20 ppm appearing only in the spectrum of P-2; this peak can be ascribed to the signal of substituted acetylene (≡C−H) groups.⁵⁰ Supporting Information Figure S2 compares the FTIR spectra of monomer 5 and polymers. Vibration bands at ${\sim}1600$ and ${\sim}1510$ cm $^{-1}$ appear in all three spectra because of the stretching vibrations of the C=N group in the quinoxaline ring.⁴⁷ Weak absorption signals appear at $\sim 2100 \text{ cm}^{-1}$ in the FTIR spectra of P-1 and P-2. These signals correspond to the $C \equiv C$ stretching vibration-weakened significantly in the P-2 spectrum and moved to $\sim 2107 \text{ cm}^{-1}$ after desilylation reaction. A new band at \sim 3300 cm⁻¹ is observed exclusively in the P-2 spectrum. The appearance of this band can be ascribed to the typical stretching absorption signal of \equiv C-H. The aforementioned discussion suggests that the desilylation reaction is successfully realized.

Preparation of P-2-Coated Fluorescent-Magnetic Composites

The synthetic procedure of **P-2** covalently modified fluorescent–magnetic nanoparticles (Fe₃O₄@SiO₂@P-2) is shown in Scheme 2. Fe₃O₄ nanoparticles were synthesized by



FIGURE 2 TEM image (a) and SEM image (b) of Fe₃O₄@SiO₂@P-2 (inset is the enlarged selected region of TEM image).

coprecipitation and decorated further with azide-functionalized silica shell to provide the intermediate, that is, $Fe_{3}O_{4}@SiO_{2}\text{--}N_{3}\text{.}^{36}$ P-2 was then covalently coated onto Fe₃O₄@SiO₂ by the high-chemoselective Cu⁺-catalyzed click reaction between the $-C \equiv H$ and the $-N_3$ groups. The successful functionalization of magnetic nanoparticles was evaluated by FTIR analysis. Figure 1 compares the FTIR spectra of Fe₃O₄@SiO₂@P-2, Fe₃O₄@SiO₂-N₃, and P-2. The spectrum of Fe₃O₄@SiO₂-N₃ displays signals at \sim 566, \sim 1081, \sim 1647, ${\sim}3270\text{, and }{\sim}2103\text{ cm}^{-1}\text{, which can be attributed to the}$ characteristic absorption bands of Fe-O stretching, Si-O-Si stretching, O-H stretching, O-H deformation, and -N₃ stretching, respectivly.^{36,53} In addition to the appearance of the characteristic signals of $Fe_3O_4@SiO_2$ in the spectrum of $Fe_3O_4@SiO_2@P-2$, the absorption intensity at ~2960 and 2850 cm⁻¹ assigned to the $-CH_3$ and $-CH_2$ groups on the alkyl side chains in P-2 is found to be stronger than that in the spectrum of Fe₃O₄@SiO₂-N₃. This result suggests successful coating of P-2 onto Fe₃O₄@SiO₂ (optical properties discussed in the following section further support the successful coating). Energy-dispersive X-ray spectroscopy analysis shows that Fe₃O₄@SiO₂@P-2 contains the elements Fe, Si, O, and C (Supporting Information Fig. S3). Fe₃O₄@SiO₂@P-2 nanoparticle displays good dispersity in THF, whereas apparent aggregates exist in the dispersion of water (Supporting Information Fig. S4). Although Fe₃O₄@SiO₂@P-2 can also be dispersed in ethanol, the fluorescence of corresponding dispersion is much weaker than that in THF (Supporting Information Fig. S4), this might be stem from the organic intrinsic and the solubility of the CP's coating.

Morphology of Fe₃O₄@SiO₂@P-2

The morphology of $Fe_3O_4@SiO_2@P-2$ was characterized by transmission electron microscopy (TEM) and SEM analyses.

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The corresponding results are shown in Figure 2. The TEM [Fig. 2(a)] and SEM [Fig. 2(b)] images indicate that the Fe₃O₄@SiO₂@P-2 profiles are approximately spherical, with an average diameter of ~52 nm (obtained using the average of more than 100 particles). Apparent aggregation exists between Fe₃O₄@SiO₂@P-2 particles. To elucidate the reason for such morphology, TEM analysis of the click-coating precursor nanoparticle, that is, Fe₃O₄@SiO₂=N₃, was conducted (Supporting Information Fig. S5). Fe₃O₄@SiO₂=N₃ aggregate formation was observed (which could be attributed to the



FIGURE 3 Magnetic hysteresis curve of Fe₃O₄ and Fe₃O₄@SiO₂@P-2 at 300 K (the inset shows the curve of Fe₃O₄@SiO₂@P-2 with the external magnetic field is near zero, wherein the two markers present the values of saturation remanence $[M_{\rm rs} = 0.54 \text{ emu g}^{-1}]$ and coercivity $[h_{\rm c} = 33.06 \text{ Oe}]$, respectively).



FIGURE 4 UV-vis absorption (a) and PL spectra (b) of Fe₃O₄@SiO₂-N₃ and Fe₃O₄@SiO₂@P-2 in ethanol and THF, respectively. ([Fe₃O₄@SiO₂-N₃] = 200 μ g mL⁻¹, [Fe₃O₄@SiO₂@P-2] = 200 μ g mL⁻¹; λ_{ex} = 365 nm).

magnetic dipolar interaction among the magnetic nanoparticles, as observed in the previous reports⁵⁴), suggesting that the coating of **P-2** occurred only on the surface of the aggregate (Supporting Information Fig. S5).

Magnetic Properties of Fe₃O₄@SiO₂@P-2

The superparamagnetism of as-prepared Fe₃O₄ and Fe₃O₄@SiO₂@P-2 was compared by using a vibrating sample magnetometer at 300 K in an external magnetic field. Figure 3 shows the magnetization curves of the nanoparticles. The magnetization of Fe₃O₄ and Fe₃O₄@SiO₂@P-2 reaches a saturation magnetization (M_s) of 63.2 and 17.2 emu g⁻¹, respectively, with an increase in magnetic field strength. The inset of Figure 3 shows an enlarged section of the magnetization plot near the zero magnetic fields. Saturation remanence (M_{rs}) and coercivity (h_c) can be determined from the intersection of the hysteresis loop with the two axes at 0.52 emu g⁻¹ and 20.8



FIGURE 5 Photographs of dispersions of Fe₃O₄@SiO₂-N₃ (in ethanol) (1) and Fe₃O₄@SiO₂@P-2 (in THF) (2) taken under normal room lighting and UV illumination (360 nm, provided by potable UV lamp), in the absence (a, c) and presence (b, d) of external magnet (concentration of both nanoparticles is ~400 μ g mL⁻¹).



FIGURE 6 Fluorescence changes of Fe₃O₄@SiO₂@P-2 in THF ([Fe₃O₄@SiO₂@P-2] = 50 μ g mL⁻¹) in the presence of common anions ([anions] = 3.33 × 10⁻⁴ M; λ_{ex} = 365 nm).

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FIGURE 7 Fluorescence changes of Fe₃O₄@SiO₂@P-2-*I*⁻ in THF ([Fe₃O₄@SiO₂@P-2] = 50 μ g mL⁻¹, [I⁻] = 3.33 × 10⁻⁴ M) in the presence of various metal ions ([metal ions] = 1.33 × 10⁻⁴ M; λ_{ex} = 365 nm).

Oe, respectively. These two values indicate that a rather low residual magnetization is present when the external magnetic field is required to reduce the magnetization to zero. These data reflect that the $Fe_3O_4@SiO_2@P-2$ nanoparticles are in the superparamagnetic state.^{35,55} A lower $Fe_3O_4@SiO_2@P-2$ magnetization can likely to occur because the nanoparticles are covered by thick shells of silica and polymer, significantly diminishing the inductive effect of the magnetic field.^{36,56}

Optical Properties

Figure 4 compares the UV-vis absorption and PL spectra of the suspensions of $Fe_3O_4@SiO_2-N_3$ (in ethanol) and $Fe_3O_4@SiO_2@P-2$ (in THF), respectively. For $Fe_3O_4@SiO_2-N_3$, almost no distinguishable absorption and fluorescence signals can be recorded. In contrast, under the same measurement conditions, obvious absorption and PL signals can be observed for $Fe_3O_4@SiO_2@P-2$ at ~380 and ~420 nm, respectively. Figure 5 shows the images of $Fe_3O_4@SiO_2-N_3$ and $Fe_3O_4@SiO_2@P-2$ dispersions under natural and UV light, with and without the external magnet. The results show that the dispersion of $Fe_3O_4@SiO_2@P-2$ emits a bright blue light and that the nanocomposites can be separated by a magnet.

Spectral Response of Fe₃O₄@SiO₂@P-2 Toward I⁻

Carbazole-containing CPs and oligomers can be applied as sensitive and selective Γ optical probes.^{39,40} Carbazole moieties are also involved in Fe₃O₄@SiO₂@P-2, and the optical investigation of Fe₃O₄@SiO₂@P-2 verifies the intrinsic fluorescence properties of Fe₃O₄@SiO₂@P-2. Thus, Fe₃O₄@SiO₂@P-2 might be used as a probing substrate for Γ . The optical response of Fe₃O₄@SiO₂@P-2 to Γ was investigated to validate the aforementioned hypothesis. Various anionic ions were added into the dispersion of Fe₃O₄@SiO₂@P-2 (with a concentration of ~50 μ g mL⁻¹ in THF), and the corresponding fluorescence responses are shown in Figure 6. The addition of I^{-} led to significant fluorescence quenching, whereas the presence of other

anions only slightly influenced the PL intensity of Fe₃O₄@SiO₂@P-2. The mechanism of fluorescence quenching presumably involves the presence of a "heavy-atom" interaction between the excited state of the carbazole-containing polymer and I^{-} , thereby enhancing spin-orbit coupling, as mentioned in the previous reports.^{39–41} The detailed fluorescence response of $Fe_3O_4@SiO_2@P-2$ to I^- is shown in Supporting Information Figure S6(a). The fluorescence intensity of Fe₃O₄@SiO₂@P-2 decreases gradually with the increase in I^- . A detection limit of ${\sim}8.85\,\times\,10^{-7}$ M for \it{I}^- (calculation was based on the threesigma criteria⁵⁷) can be obtained by $Fe_3O_4@SiO_2@P-2$ from the corresponding Stern-Volmer curve [Supporting Information Fig. S6(b)]. The apparent color of Fe₃O₄@SiO₂@P-2 undergoes visible deepening by fluorescence quenching, suggesting that Fe₃O₄@SiO₂@P-2 can act as a colorimetric probe for naked eye detection of I^- (Supporting Information Fig. S7).

The interference of other common background anions was investigated to evaluate the applicability of $Fe_3O_4@SiO_2@P-2$ as an I^- selective probe (Supporting Information Fig. S8). The presence of background anions causes no obvious quenching. However, significant quenching was observed with the subsequent addition of I^- , suggesting that $Fe_3O_4@SiO_2@P-2$ exhibits excellent selectivity toward I^- .

Optical Response of $Fe_3O_4@SiO_2@P-2-I^-$ Complex Toward Hg^{2+}

The aforementioned results substantially support the interaction between $Fe_3O_4@SiO_2@P-2$ and I^- . This finding raises another issue, that is, whether the fluorescence of $\rm Fe_3O_4@SiO_2@P-2$ can be recovered when $\it I^-$ is distracted from the $Fe_3O_4@SiO_2@P\mbox{-}2\mbox{-}l^-$ complex by the introduction of stronger I^- -binding agents. Various cationic metal ions were thus added into $Fe_3O_4@SiO_2@P-2-I^-$ to explore this issue. The addition of Hg2+ nearly induces the PL characteristic of Fe₃O₄@SiO₂@P-2 to revert to its pristine state, whereas the curves of other metal ions are altered slightly compared with that of Hg^{2+} (Fig. 7). Figure 8 shows in detail the PL response of $Fe_3O_4@SiO_2@P-2-I^-$ to the incremental addition of Hg²⁺. The fluorescence intensity of $Fe_3O_4@SiO_2@P-2-I^-$ increases gradually with the incremental addition of Hg²⁺. This effect indicates the successful distraction of I^- from the Fe₃O₄@SiO₂@P-2- I^- complex because of the strong association and high matching ratio between I^- and Hg²⁺ (Fig. 8). The detection limit of Hg²⁺ was evaluated as ${\sim}4.17\,\times\,10^{-7}$ M according to the threesigma criteria.⁵⁷ The slightly yellow color of Fe₃O₄@SiO₂@P-2-I⁻ dispersion becomes colorless with PL intensity recovery (Fig. 9).

To evaluate the selectivity of $Fe_3O_4@SiO_2@P-2-I^-$ toward Hg^{2+} , the responses of common background metal ions $(Cu^{2+}, Co^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Sn^{2+}, Sr^{2+}, Cd^{2+}, Ag^+, Ba^{2+}, Al^{3+}, Zn^{2+}, and Fe^{3+})$ were investigated in comparison experiments. Supporting Information Figure S9 shows that the presence of background metal ions causes no significant interference to Hg^{2+} . In contrast, significant fluorescence





FIGURE 8 Fluorescence changes of Fe₃O₄@SiO₂@P-2-*I*⁻ complexes (a) and relationship between *I*-*I*₀ and Hg²⁺ (b) in THF ([Fe₃O₄@SiO₂@P-2] = 50 μ g mL⁻¹, [I⁻] = 3.33 × 10⁻⁴ M) with addition of different concentrations of Hg²⁺ (from 3.33 × 10⁻⁸ to 1.54 × 10⁻⁴ M; λ_{ex} = 365 nm).

recovery was found in the comparison experiment for every metal ion with the subsequent addition of Hg^{2+} .

The magnetic identity of Fe₃O₄@SiO₂@P-2 indicates that it can be recycled by simple magnetic separation and the photostability of CPs ensures that their emission will not be sacrificed during recycling. The reusability of Fe₃O₄@SiO₂@P-2 was evaluated here. I^- (3.33 × 10⁻⁴ M) and Hg²⁺ (1.67 × 10⁻⁴ M) were added alternately into the THF dispersion of Fe₃O₄@SiO₂@P-2; this procedure was repeated 10 times. The

degrees of fluorescence quenching and recovery exhibit slight losses (Supporting Information Fig. S10), suggesting good recyclability of $Fe_3O_4@SiO_2@P-2$.

CONCLUSIONS

A type of fluorescent–magnetic dual-function nanocomposite obtained by covalently coating a carbazole-based CP onto magnetic iron oxide was reported in this study. The fluorescence of $Fe_3O_4@SiO_2@P-2$ was efficiently quenched by I^- ,



FIGURE 9 Photographs of Fe₃O₄@SiO₂@P-2- Γ dispersions with various metal ions in the normal room lighting (upper) and ultraviolet light (360 nm) (bottom), respectively, ([Fe₃O₄@SiO₂@P-2] = 50 μ g mL⁻¹, [I⁻] = 1 × 10⁻³ M, [metal ions] = 5 × 10⁻⁴ M).

and the corresponding emission was recovered significantly with the introduction of ${\rm Hg}^{2+}$. The magnetic property of ${\rm Fe}_3{\rm O}_4@{\rm SiO}_2@{\rm P-2}$ endows it with good recoverability. This novel nanocomposite can act as a sensitive, selective, and reusable turn-on type optical probe for ${\rm Hg}^{2+}$.

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