Supplementary information

'Clicked' magnetic nanohybrids with a soft polymer interlayer

Hongkun He,[a,b] Yu Zhang,[b] Chao Gao,*[a] and Jiayan Wu[a,b]

[a] *Department of Polymer Science and Engineering, and Key Laboratory of Macromolecular Synthesis and Functionalization, Ministry of Education, Zhejiang University, 38 Zheda Road, 310027 Hangzhou, P. R. China.*

[b] *College of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, 200240 Shanghai, P. R. China.*

** Corresponding author. E-mail: chaogao@zju.edu.cn.*

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Figure S4. Raman spectra of (a) pristine MWNTs, (b) MWNT-pAz, (c) MWNT-pAz@Fe_3O_4, (d) MWNT-pAlk, and (e) MWNT-pAlk@Fe_3O_4. The I_D/ I_G ratios of each sample are (a) 1.62, (b) 2.04, (c) 1.86, (d) 2.34, and (e) 1.96, respectively.

Figure S5. TGA curves of (a) pristine MWNTs, (b) MWNT-COOH, (c) MWNT-C≡CH, (d) MWNT-pAz@Fe_3O_4, (e) MWNT-pAz, (f) MWNT-pAlk@Fe_3O_4, and (g) MWNT-pAlk.

Figure S6. TGA curves of (a) pristine silica spheres, (b) azide-functionalized silica spheres (SiO_2-N_3), (c) alkyne polymer-functionalized silica spheres (SiO_2-pAlk), and (d) SiO_2@Fe_3O_4 nanohybrids.

Figure S7. The photographs of Fe_3O_4@RhB under 365 nm ultraviolet (UV) light without (a) and with (b) magnetic field; the photographs of Fe_3O_4-N_3 under 365 nm ultraviolet (UV) light without (c) and with (d) magnetic field; the photographs of Fe_3O_4@RhB under room light without (e) and with (f) magnetic field; the photographs of Fe_3O_4-N_3 under room light without (g) and with (h) magnetic field. All of these samples were dispersed in THF.

Materials

Anhydrous iron (III) chloride ($FeCl_3$, 98%), diethylene glycol (DEG, 99%), succinic anhydride (98%), *N,N,N',N",N"*-pentamethyldiethylenetriamine (PMDETA, 99%), *N,N*-(dimethylamino)pyridine (DMAP, 98%), propargyl alcohol (99%), methacrylic acid (99%), 1,3-dicyclohexylcarbodiimide (DCC, 98%), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC·HCl, 99%), *N*-hydroxysuccinimide (NHS, 98%), poly(ethylene glycol) monomethyl ether (PEG-OH, M_n=350), and silicon(IV) oxide (spherical, 250 nm) were obtained from Alfa Aesar and used as received. Poly(acrylic acid) (M_w=1800) and (+)-sodium L-ascorbate (98%) were purchased from Aldrich and used as received. The multiwalled carbon nanotubes (MWNTs) were purchased from Tsinghua-Nafine Nano-Powder Commercialization Engineering Center in Beijing (purity > 95%, diameter 10-30 nm). Cu(I)Br (Aldrich, 99.999%) was purified before use by extraction with glacial acetic acid overnight and then washed with ethanol and diethyl ether. Triethylamine (Et_3N), dichloromethane (CH_2Cl_2) and toluene were dried with CaH_2 and distilled under reduced pressure before use. Tetrahydrofuran (THF), *N,N*-dimethylacetamide (DMF), rhodamine B,

$CuSO_4 \cdot 5H_2O$, 2-chloroethanol, 3-chloropropylamine hydrochloride, palmitic acid and other organic reagents or solvents were obtained from Shanghai Reagents Company and used as received.

Instrumentation

Thermal gravimetric analysis (TGA) was carried out on a TA Instruments TGA-2050 Thermogravimetric Analyzer with a heating rate of 20 °C/min under a nitrogen flow rate of 60 mL/min. Fourier-transform infrared (FTIR) spectra were recorded on a PE Paragon 1000 spectrometer (KBr disk). Hydrogen nuclear magnetic resonance (^1H NMR) spectra were measured with a Varian Mercury Plus 400 MHz spectrometer with $CDCl_3$ as the solvent. Transmission electron microscopy (TEM) analysis was performed on a JEOL JEM2010 electron microscope at 200 kV. The X-ray diffractions (XRD) were recorded on a Rigaku X-ray diffractometer D/max-2200/PC equipped with Cu Kα radiation (40 kV, 20 mA) at the rate of 3.0 deg/min over the range of 10–70° (2θ). Fluorescence spectra were recorded at room temperature on a Varian Cary Fluorescence spectrometer. The magnetic properties were measured using a sample-vibrating magnetometer (VSM, Lake Shore 7410). Raman spectra were collected on a LabRam-1B Raman spectroscope equipped with a 632.8 nm laser source.

Synthesis of Fe_3O_4-COOH, Fe_3O_4-N_3, and Fe_3O_4-C≡CH

The water-soluble magnetite colloidal nanocrystals with an average diameter of *ca.* 6 nm were prepared following the procedure of Ge et al.[1] Typically, a NaOH/DEG stock solution was prepared by dissolving NaOH (5 g, 125 mmol) in DEG (50 mL); this solution was heated at 120 °C for 1 h under nitrogen, and cooled down and kept at 70 °C. A mixture of poly(acrylic acid) (M_w=1800, 2.88 g, 40 mmol -COOH), $FeCl_3$ (3.25 g, 20 mmol) and DEG (80 mL) were heated to ≈220 °C in a nitrogen atmosphere for 45 min under vigorous stirring, forming a transparent light-yellow solution. A NaOH/DEG stock solution (40 mL) was injected rapidly into the above hot mixture, which induced the reaction solution turned black immediately. The resulting mixture was further heated at 220 °C for 2 h and 175 °C for 24 h. The final products (Fe_3O_4-COOH) were washed by repeated actions of precipitation with ethanol and subsequent redispersion in deionized water several times, and finally redispersed in water (60 mL, 50 mg/mL).

3-Azidopropan-1-amine was synthesized in our lab previously by the reaction of 3-chloropropylamine hydrochloride and sodium azide in water at 75-78 °C for 96 h.[2] ^{1}H NMR ($CDCl_3$, δ, ppm): 3.35 (t, 2H, CH_2N_3), 2.78 (t, 2H, NH_2CH_2), 1.71 (p, 2H, $CH_2CH_2CH_2$) and 1.27 (s, 2H, NH_2).

The as-synthesized Fe_3O_4-COOH (500 mg) and H_2O (40 mL) were placed into a 100 mL round-bottom flask. 3-Azidopropan-1-amine (2.00 g, 20.0 mmol), EDC·HCl (3.83 g, 20.0 mmol) and NHS (2.30 g, 20.0 mmol) were added into the flask before the mixture was stirred at room temperature for 18 h. The product was separated using an external magnetic field and washed repeatedly with distilled water (eight times) and stored in 80 mL of water (Fe_3O_4-N_3, *ca.* 5 mg/mL).

The as-synthesized Fe_3O_4-COOH (100 mg) and H_2O (25 mL) were placed into a 100 mL round-bottom flask. Propargyl alcohol (0.11 g, 2.0 mmol), EDC·HCl (0.38 g, 2.0 mmol), NHS (0.12 g, 1.0 mmol) and DMAP (49 mg, 0.4 mmol) were added into the flask before the mixture was stirred at room temperature for 24 h. The product was separated using an external magnetic field and washed repeatedly with distilled water (eight times) and stored in 20 mL of water (Fe_3O_4-C≡CH, *ca.* 2.5 mg/mL).

Synthesis of PEG-Alk and Fe_3O_4@PEG

4-Oxo-4-(prop-2-ynyloxy)butanoic acid (HOOC-Alk) was synthesized in our lab previously.[3] ^{1}H NMR ($CDCl_3$, δ, ppm): 4.70 (d, 2H, CH_2O), 2.68 (m, 4H, $OCCH_2CH_2CO$), and 2.48 (t, 1H, C≡CH).

Monoalkyne-terminated poly(ethylene glycol) (PEG-Alk) was synthesized as follows. To a 500 mL round-bottom flask DCC (21.2 g, 102.8 mmol), freshly distilled CH_2Cl_2 (100 mL), PEG (M_n=350, 30.0 g, 85.7 mmol) and DMAP (1.26 g, 10.3 mmol) were added. The flask was immersed in an ice-water bath before a solution of HOOC-Alk (16.0 g, 102.5 mmol) in distilled CH_2Cl_2 (20 mL) was added dropwise into the previous solution. The reaction mixture was kept stirring for 21 h, filtered, washed successively with 1 M HCl solution (15×100 mL), de-ionized water (3×100 mL), 1 M NaOH solution (10×100 mL) and de-ionized water (2×100 mL). The organic fraction was dried over anhydrous $MgSO_4$ overnight, filtered and concentrated on a rotary evaporator to produce PEG-Alk. Yield: 37.4 g, 89.5%. ^{1}H NMR ($CDCl_3$, δ, ppm): 4.7 (d, HC≡CCH_2O), 4.2 (m, $OCH_2CH_2OOCCH_2CH_2COO$), 3.6 (b, $(OCH_2CH_2)_n$), 3.4 (s, CH_3O), 2.7 (s, $OOCCH_2CH_2COO$), and 2.5 (t, C≡C*H*).

In a round bottomed flask Fe_3O_4-N_3 in aqueous solution (2.0 mL, 5 mg/mL) was dissolved in 10 mL deionized water followed by ultrasonication for 3 min. PEG-Alk (102 mg, 0.208 mmol), $CuSO_4{\cdot}5H_2O$ (52 mg, 0.208 mmol) and (+)-sodium L-ascorbate (41 mg, 0.208 mmol) were sequentially added to the solution, which was stirred in the dark at room temperature for 24 h. Finally, Fe_3O_4@PEG was washed repeatedly with distilled water and separated using an external magnetic field. One part of the product was further dried in vacuum overnight and used for analytical measurement.

Synthesis of C_{16}–Alk and Fe_3O_4@C_{16}

To a 500 mL round-bottom flask DCC (45.5 g, 0.22 mol), freshly distilled CH_2Cl_2 (150 mL), propargyl alcohol (22.4 g, 0.4 mol), DMAP (2.69 g, 22 mmol) and palmitic acid (51.2 g, 0.2 mol) were added. The flask was immersed in an ice-water bath and kept stirring for 30 h. The reaction mixture was filtered, washed successively with 1 M HCl solution (10 ×100 mL), de-ionized water (2×100 mL), 1 M NaOH solution (4 ×100 mL) and de-ionized water (3×100 mL). After concentrated on a rotary evaporator under reduced pressure, the organic phase was precipitated in methanol. The white precipitate was collected by filtration, washed several times with methanol and dried under vacuum, giving alkyne-functionalized palmitic acid (C_{16}-Alk). Yield: 43.1 g, 73.3%. ^{1}H NMR ($CDCl_3$, δ, ppm): 4.7 (d, OCH_2C≡CH), 2.5 (t, C≡C*H*), 2.3 (m, CH_2CO), 1.2-1.7 (m, alkyl chain) and 0.9 (t, CH_3).

In a round bottomed flask Fe_3O_4-N_3 (10 mg) were dissolved in 10 mL CH_2Cl_2 followed by ultrasonication for 3 min. C_{16}-Alk (62 mg, 0.208 mmol), CuBr (10 mg, 0.070 mmol) and PMDETA (15 μL, 0.070 mmol) were sequentially added to the solution, which was stirred in the dark at room temperature for 24 h. Finally, Fe_3O_4@C_{16} was washed repeatedly with CH_2Cl_2 and THF, and separated using an external magnetic field. One part of the product was further dried in vacuum overnight and used for analytical measurement.

Synthesis of RhB-Alk and Fe_3O_4@RhB

Alkyne-modified rhodamine dye (RhB-Alk) was prepared by the esterification reaction of rhodamine B and propargyl alcohol.[4] A 50 mL round-bottom flask was charged with rhodamine B (2.395 g, 5 mmol), EDC (1.535 g, 8 mmol) and NHS (635 mg, 5.5 mmol), and anhydrous CH_2Cl_2 (15 mL). The reaction mixture was cooled in an ice-water bath. A solution of propargyl alcohol (295 μL, 5 mmol), 4-dimethylaminopyridine (DMAP) (65 mg, 0.5 mmol) and CH_2Cl_2 (5 mL) was added dropwise over a period of 1 h under magnetic stirring. The mixture was stirred in an ice-water bath for 1 h and then at room temperature for 24 h. The product was first purified by precipitation in ether, then by flash column chromatography (methanol/ethyl acetate = 2:10, v/v). Yield: 49%. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.32 (d, 1H), 7.80 (m, 2H), 7.34 (m, 1H), 7.21 (d, 2H), 7.05 (d, 2H), 6.81 (d, 2H), 4.62 (s, 2H), 3.59 (q, 8H), 2.42 (s, 1H) and 1.32 (t, 12H).

In a round bottomed flask Fe_3O_4-N_3 in aqueous solution (2.0 mL, 5 mg/mL) were dissolved in 20 mL deionized water followed by ultrasonication for 3 min. RhB-Alk (21 mg, 0.0416 mmol), $CuSO_4·5H_2O$ (52 mg, 0.208 mmol) and (+)-sodium L-ascorbate (206 mg, 1.040 mmol) were sequentially added to the solution, which was agitated in the dark at room temperature for 24 h. Finally, Fe_3O_4@RhB was washed repeatedly with distilled water, ethanol and THF (at least twenty times), and separated using an external magnetic field.

Synthesis of MWNT-pAz@Fe_3O_4 and MWNT-pAlk@Fe_3O_4

MWNT-C≡CH, pAz, pAlk, MWNT-pAz and MWNT-pAlk were prepared in our lab previously.[3, 5] In order to facilitate the readers, some details are also given below.

a) Synthesis of MWNT-C≡CH [3]

MWNT-C≡CH was prepared following the procedure of Ref. 3. The density of alkyne group is calculated to be *ca.* 1.8 mmol (-C≡CH)/g from the TGA data.

b) Synthesis of pAlk [5]

Synthesis of propargyl methacrylate (PgMA). Propargyl methacrylate was synthesized by the esterification reaction of propargyl alcohol and methacrylic acid. Typically, a 500 mL round-bottom flask was charged with propargyl alcohol (14 g, 0.25 mol), methacrylic acid (21.5 g, 0.25 mol), DMAP (1.68 g) and anhydrous CH_2Cl_2 (100 mL). The reaction mixture was cooled in an ice-water bath. A solution of DCC (54.18 g, 0.263 mol) in CH_2Cl_2 (200 mL) was added dropwise over a period of 1 h under magnetic stirring. The mixture was stirred at 0 °C for 1 h and then at room temperature for 24 h. After removing the insoluble dicyclohexylurea by filtration, the filtrate was washed with an aqueous solution of hydrochloric acid (1 M, 3×200 mL), water (3×200 mL), aqueous NaOH (1 M, 3×200 mL), and again with water (2×200 mL) and was dried over magnesium sulfate overnight. After removing the solvents on a rotary evaporator, the obtained residues were distilled under reduced pressure to give a colorless oil with a yield of 51%. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.13 (m, 1H, $=CH_2$), 5.58 (m, 1H, $=CH_2$), 4.70 (t, 2H, CH_2O), 2.47 (t, 1H, $C{\equiv}CH$), and 1.91 (m, 3H, $-CH_3$).

Synthesis of pAlk by reversible addition-fragmentation chain transfer (RAFT) polymerization. A mixture of propargyl methacrylate (3.72 g, 30 mmol), S-1-dodecyl-S'-(α,α'-dimethyl-α''-acetic acid)trithiocarbonate (DDAT) (36.4 mg, 0.1 mmol), AIBN (3.6 mg, 0.022 mmol), and toluene (18.75 mL) was placed in a Schlenk flask and freeze-pump-thaw degassed three times. The polymerization was started by immersing the flask into an oil bath at 80 °C. After 3 h, the Schlenk flask was quenched in liquid nitrogen and exposed to the air. The reaction mixture was concentrated and precipitated into an excess of methanol. The products were collected and redissoved in methylene chloride, and the solution was reprecipitated into an excess of methanol. This purification cycle was repeated twice. The obtained product was dried overnight in a vacuum oven for 24 h to give polyPgMA (pAlk, 2.19 g, M_n = 25 000; M_w/M_n = 1.64). ^{1}H NMR ($CDCl_3$, δ, ppm): 4.62 (s, 2H, CH_2O), 2.52 (s, 1H, $C{\equiv}CH$), 2.17~1.20 (m, 22H, $C-CH_2-C$ of polyPgMA, $-CH_2-(CH_2)_{10}-CH_3$) and 1.14~0.85 (m, 12H, $-CH_3$ of polyPgMA, $-C(CH_3)_2$-polyPgMA, $-CH_2-(CH_2)_{10}-CH_3$). IR spectrum (cm^{-1}): 3300 and 2132 ($C{\equiv}CH$) and 1734 (C=O).

c) Synthesis of pAz [5]

Synthesis of 2-azidoethyl methacrylate (AzEMA). 2-Azidoethyl methacrylate was synthesized by the esterification reaction of 2-azidoethanol and methacryloyl chloride. Typically, a 500 mL round-bottom flask was charged with 2-azidoethanol (21.75 g, 0.25 mol), anhydrous triethylamine (32.30 g, 0.32 mol) and anhydrous CH_2Cl_2 (150 mL). The reaction mixture was cooled in an ice-water bath. A solution of methacryloyl chloride (27.1 mL, 0.28 mol) in CH_2Cl_2 (30 mL) was added dropwise over a period of 1 h under magnetic stirring. The mixture was stirred at 0 °C for 1 h and then at room temperature for 24 h. After removing the insoluble triethylamine hydrochloride by filtration, the filtrate was washed with an aqueous solution of hydrochloric acid (1 M, 3×150 mL), water (3×150 mL), aqueous NaOH (1 M, 3×150 mL), and again with water (2×150 mL) and was dried over magnesium sulfate overnight. After removing the solvents on a rotary evaporator, the obtained residues were distilled under reduced pressure to give a colorless oil with a yield of 73%. ^1H NMR ($CDCl_3$, δ, ppm): 6.16 (m, 1H, $=C\mathit{H_2}$), 5.63 (m, 1H, $=C\mathit{H_2}$), 4.29 (t, 2H, $C\mathit{H}_2O$), 3.50 (t, 2H, $C\mathit{H}_2N_3$) and 1.98 (m, 3H, $-C\mathit{H}_3$).

Synthesis of pAz by atom transfer radical polymerization (ATRP). Typically, a mixture containing AzEMA (3.10 g, 20 mmol), CuBr (14.4 mg, 0.1 mmol), and acetone (3.1 g) was deoxygenated by bubbling with nitrogen for at least 30 min. 2,2'-Bipyridine (bpy, 31.3 mg, 0.2 mmol) was introduced under the protection of nitrogen flow. The reaction mixture was stirred for 15 min to allow the formation of CuBr/bpy complex. The reaction mixture was heated to 50 °C, and ethyl 2-bromoisobutyrate (14.7 μL, 0.1 mmol) was added to the mixture under a nitrogen flow. The mixture was stirred at 50 °C for 3 h and then the Schlenk flask was removed from heat and opened to expose the catalyst to air. The mixture was diluted with THF and passed through a neutral alumina column to remove copper catalyst. The collected eluents were concentrated and precipitated into an excess of methanol. This purification cycle was repeated twice. The obtained product was dried overnight in a vacuum oven for 24 h to give polyAzEMA (pAz, 0.95 g, M_n = 12 500; M_w/M_n = 1.37). ^1H NMR ($CDCl_3$, δ, ppm): 4.32~4.26 (m, 2H, $CH_3C\mathit{H}_2O-$), 4.22~4.00 (s, 2H, $-CH_2C\mathit{H}_2O-$), 3.60~3.44 (s, 2H, $-C\mathit{H}_2N_3$), 2.17~1.83 (m, 2H, $C-C\mathit{H}_2-C$) and 1.17~0.90 (m, 9H, $-C\mathit{H}_3$, $-C(C\mathit{H}_3)_2-$). IR spectrum (cm^{-1}): 2106 (N_3) and 1732 (C=O).

d) Synthesis of MWNT-pAz and MWNT-pAlk [5]

Typically, 30 mg of alkyne-functionalized MWNTs (MWNT-C≡CH) was suspended in 10 mL of DMF in a 25 mL round-bottom flask. The suspension was deoxygenated by bubbling with nitrogen for at least 30 min. pAz (300 mg), CuBr (28.7 mg, 0.2 mmol) and PMDETA (42.2 μL, 0.2 mmol) were added under the protection of nitrogen flow. The mixture was stirred at room temperature for 24 h. The solid was separated from the mixture by centrifugation. The collected solid was redispersed in DMF (50 mL) and separated by centrifugation. This purification cycle was repeated thrice. After purification, the resulting solid was dried overnight in vacuum, obtaining clickable polymer-functionalized MWNTs (MWNT-pAz). The density of azide group is calculated to be *ca.* 1.6 mmol ($-N_3$)/g from the TGA data.

MWNT-pAlk was prepared using the same protocol as described above, except that MWNT-C≡CH was replaced by the as-prepared MWNT-pAz and pAz was replaced by pAlk, respectively. The density of alkyne group of MWNT-pAlk is calculated to be *ca.* 4.3 mmol (-C≡CH)/g from the TGA data.

e) Synthesis of MWNT-pAz@Fe_3O_4 and MWNT-pAlk@Fe_3O_4

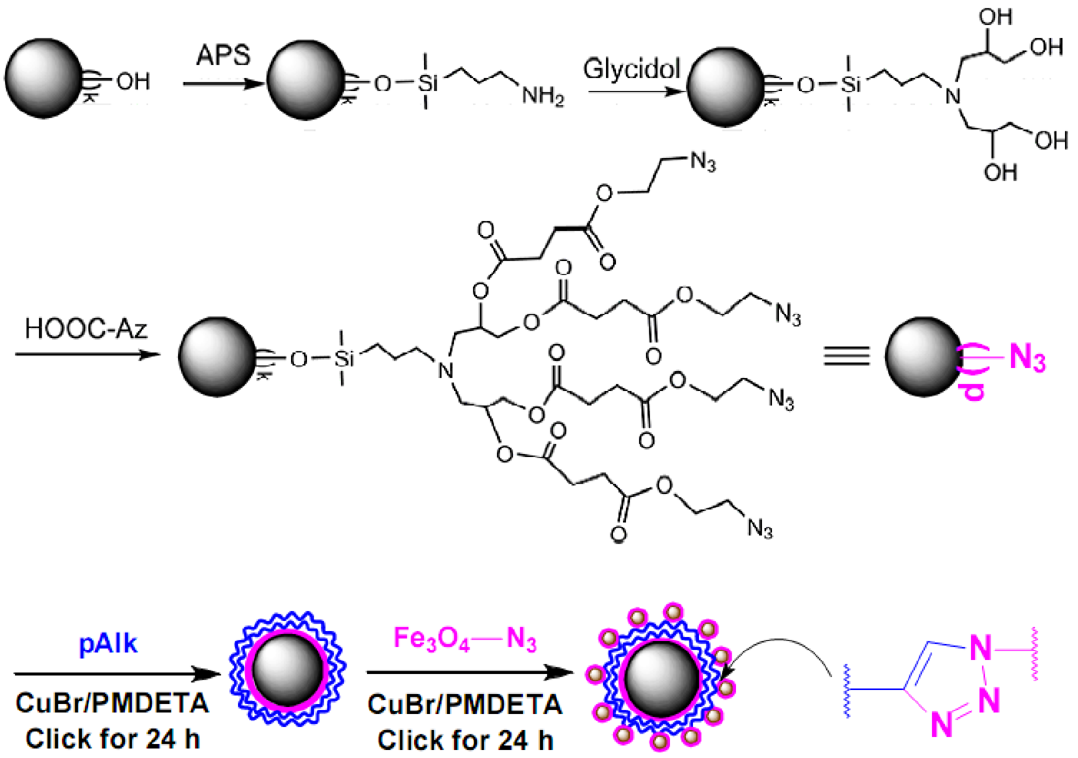
In a 25 mL Schlenk flask, MWNT-pAz (3 mg) and Fe_3O_4-C≡CH in aqueous solution (1.2 mL, 2.5 mg/mL) were dispersed via ultrasonication for 1 min in 5 mL of DMF. After CuBr (5 mg, 0.035 mmol) and PMDETA (8 μL, 0.035 mmol) were added under a nitrogen atmosphere, the reaction was allowed to proceed at room temperature in the dark for 24 h. The product was isolated by centrifugation and washed repeatedly with THF. The black solid (MWNT-pAz@Fe_3O_4) was collected and dried at 60 °C overnight under vacuum.

In a 25 mL Schlenk flask, MWNT-pAlk (5 mg) and Fe_3O_4-N_3 in aqueous solution (0.5 mL, 5 mg/mL) were dispersed via ultrasonication for 1 min in 5 mL of DMF. After CuBr (5 mg, 0.035 mmol) and PMDETA (8 μL, 0.035 mmol) were added under a nitrogen atmosphere, the reaction was allowed to proceed at room temperature in the dark for 24 h. The product was isolated by centrifugation and washed repeatedly with THF. The black solid (MWNT-pAlk@Fe_3O_4) was collected and dried at 60 °C overnight under vacuum.

Synthesis of SiO_2-N_3, SiO_2-pAlk, and SiO_2@Fe_3O_4

Scheme S1 depicts the procedures for synthesis of SiO_2@Fe_3O_4 by click chemistry.

4-(2-Azidoethoxy)-4-oxobutanoic acid (HOOC-Az) was synthesized as follows. Succinic anhydride (23.0 g, 0.230 mol) was added into a three-neck round-bottom flask equipped with a condenser and a dropping funnel. Under nitrogen atmosphere and magnetic stirring, freshly distilled methylene chloride (150 mL), DMAP (2.3 g, 19 mmol) and freshly distilled Et_3N (46.46 g, 0.460 mol) was sequentially added. After the flask was immersed into ice-water bath, 2-azidoethanol (20.0 g, 0.230 mol) was added dropwise into the previous solution. The solution was later heated at 40 °C for 48 h, and the reaction mixture was washed successively with 1 M HCl solution (5×100 mL) and de-ionized water (2×100 mL). The organic phase was dried over anhydrous $MgSO_4$ overnight. After filtering and removal of methylene chloride under reduced pressure, HOOC-Az was obtained. Yield: 39.1 g, 91%. ^{1}H NMR ($CDCl_3$, δ, ppm): 4.27 (t, 2H, $N_3CH_2\mathit{CH}_2O$), 3.48 (t, 2H, $N_3\mathit{CH}_2$) and 2.68 (m, 4H, $\mathit{CH}_2\mathit{CH}_2COOH$).



Scheme S1. Synthesis procedures of $SiO_2@Fe_3O_4$.

The silica spheres were modified successively with 3-aminopropyl-triethoxysilane (APS) and glycidol.[6] Then the modified silica spheres (500 mg) and H_2O (50 mL) were placed into a round-bottom flask. HOOC-Az (1.87 g, 10.0 mmol), EDC (1.9 g, 10.0 mmol), NHS (0.6 g, 5.0 mmol) and DMAP (245 mg, 2.0 mmol) were added into the flask before the mixture was stirred at room temperature for 24 h. The product was separated by centrifugation and washed repeatedly with distilled water. After purification, the resulting solid was dried overnight in vacuum, obtaining azido-functionalized silica spheres (SiO_2-N_3). IR spectrum (cm^{-1}): 2110 (N_3).

30 mg of SiO_2-N_3 was suspended in 10 mL of DMF in a 25 mL round-bottom flask. The suspension was deoxygenated by bubbling with nitrogen for at least 30 min. The materials of pAlk (300 mg), CuBr (28.7 mg, 0.2 mmol) and PMDETA (42.2 μL, 0.2 mmol) were added under the protection of nitrogen flow. The mixture was stirred at room temperature for 24 h. The solid was separated from the mixture by centrifugation. The collected solid was redispersed in DMF (50 mL) and separated by centrifugation. This purification cycle was repeated thrice. After purification, the resulting solid was dried overnight in vacuum, obtaining alkyne polymer-functionalized silica spheres (SiO_2-pAlk).

In a 25 mL Schlenk flask, 4 mg of SiO_2-pAlk and Fe_3O_4-N_3 in aqueous solution (1.0 mL, 5 mg/mL) were dispersed via ultrasonication for 3 min in 5 mL of DMF. After CuBr (5 mg, 0.035 mmol) and PMDETA (8 μL, 0.035 mmol) were added under a nitrogen atmosphere, the reaction was allowed to proceed at room temperature in the dark for 24 h. The product was isolated by centrifugation and washed repeatedly with THF. The brown solid ($SiO_2@Fe_3O_4$) was collected and dried at 60 °C overnight under vacuum.

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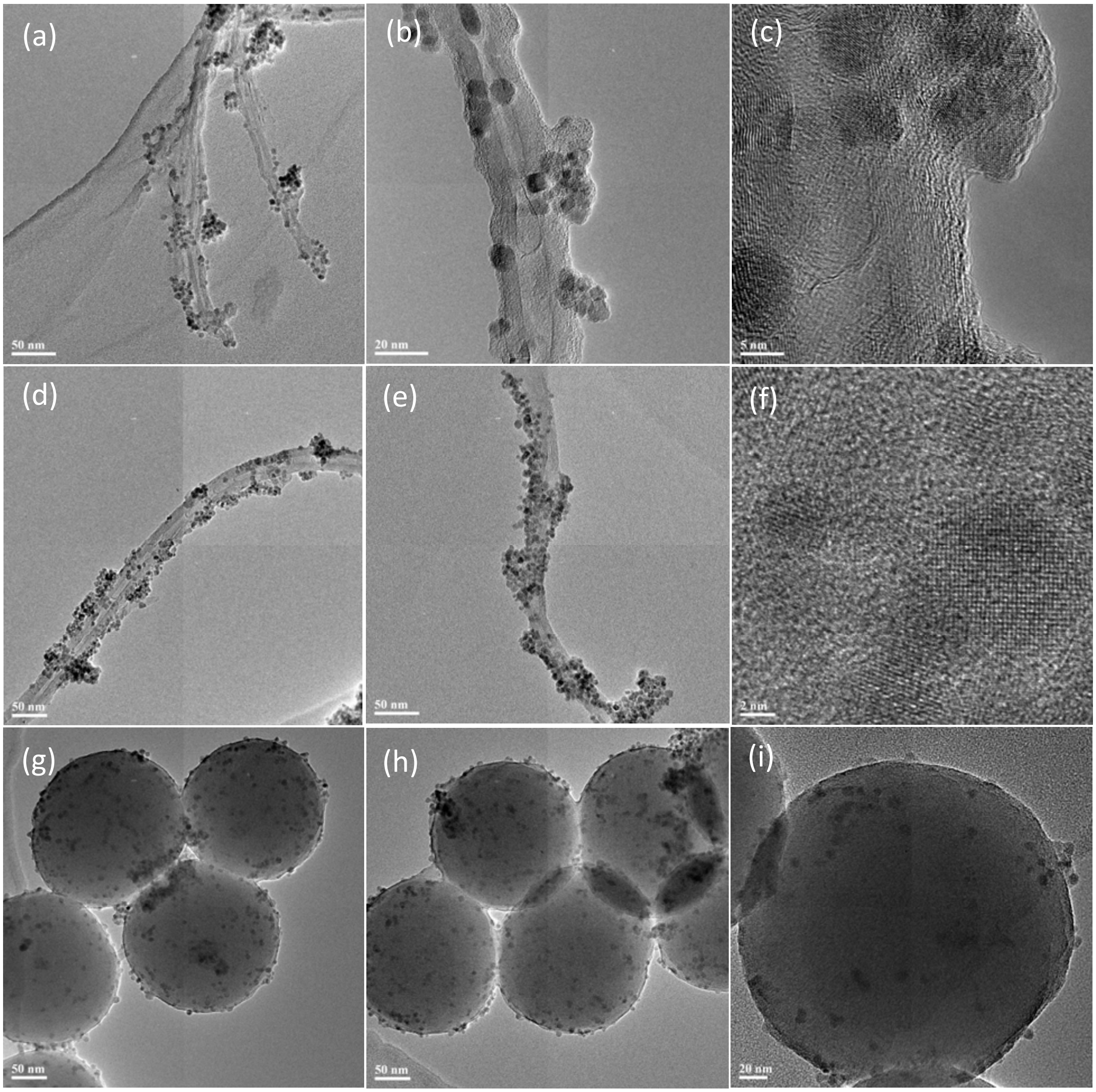
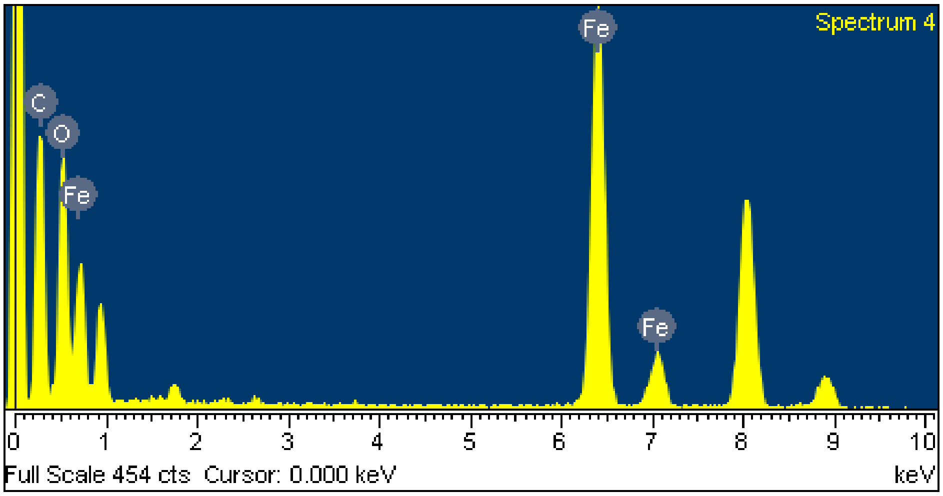


Fig. S1. Additional TEM images of (a, b, c) MWNT-pAlk@Fe_3O_4, (d, e, f) MWNT-pAz@Fe_3O_4, and (g, h, i) SiO_2@Fe_3O_4.



Element	Weight/%	Atomic/%
C K	28.98	51.32
O K	22.79	30.30
Fe K	48.23	18.37
Totals	100.00	100.00

Fig. S2. Energy dispersive X-ray spectroscopy (EDS) results of MWNT-pAz@Fe_3O_4.

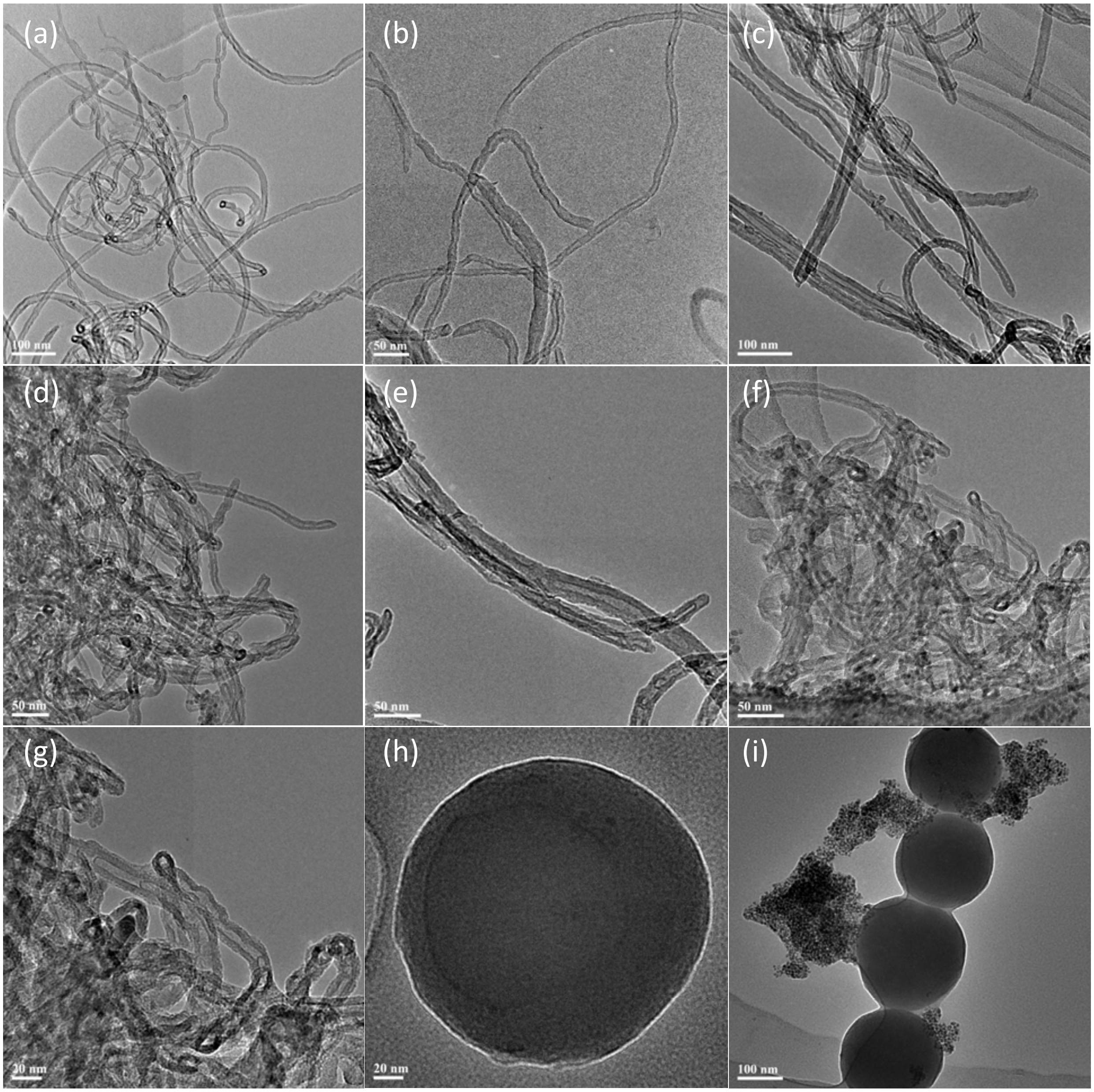


Fig. S3. TEM images of selected samples in control experiments (a, b) control ‘click’ reaction of MWNT-C≡CH and Fe_3O_4-N_3; (c, d, e) control ‘click’ reaction of MWNT-pAz and Fe_3O_4-C≡CH with no CuBr added; (f, g) control ‘click’ reaction of MWNT-pAlk and Fe_3O_4-N_3 with no CuBr added; (h, i) control ‘click’ reaction of azide modified SiO_2 spheres and Fe_3O_4-C≡CH.

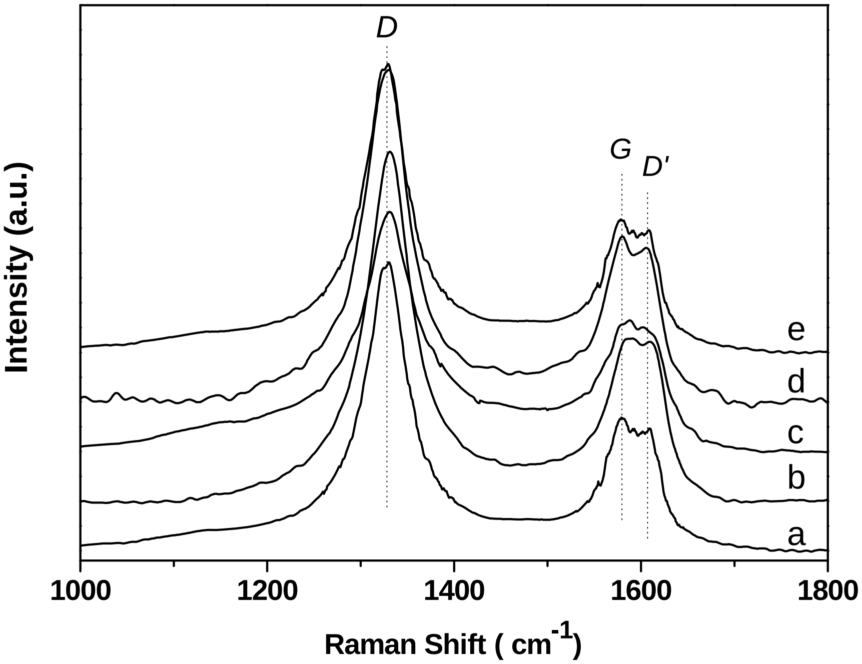


Fig. S4. Raman spectra of (a) pristine MWNTs, (b) MWNT-pAz, (c) MWNT-pAz@Fe_3O_4, (d) MWNT-pAlk, and (e) MWNT-pAlk@Fe_3O_4. The I_D/I_G ratios of each sample are (a) 1.62, (b) 2.04, (c) 1.86, (d) 2.34, and (e) 1.96, respectively.

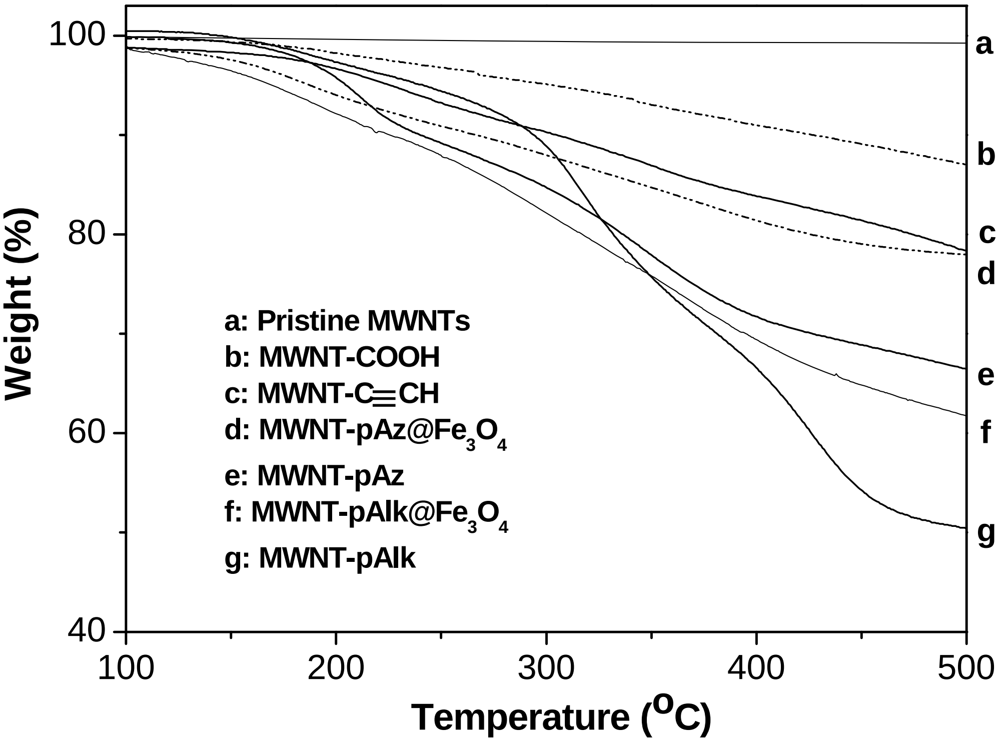


Fig. S5. TGA curves of (a) pristine MWNTs, (b) MWNT-COOH, (c) MWNT-C≡CH, (d) MWNT-pAz@Fe$_3$O$_4$, (e) MWNT-pAz, (f) MWNT-pAlk@Fe$_3$O$_4$, and (g) MWNT-pAlk.

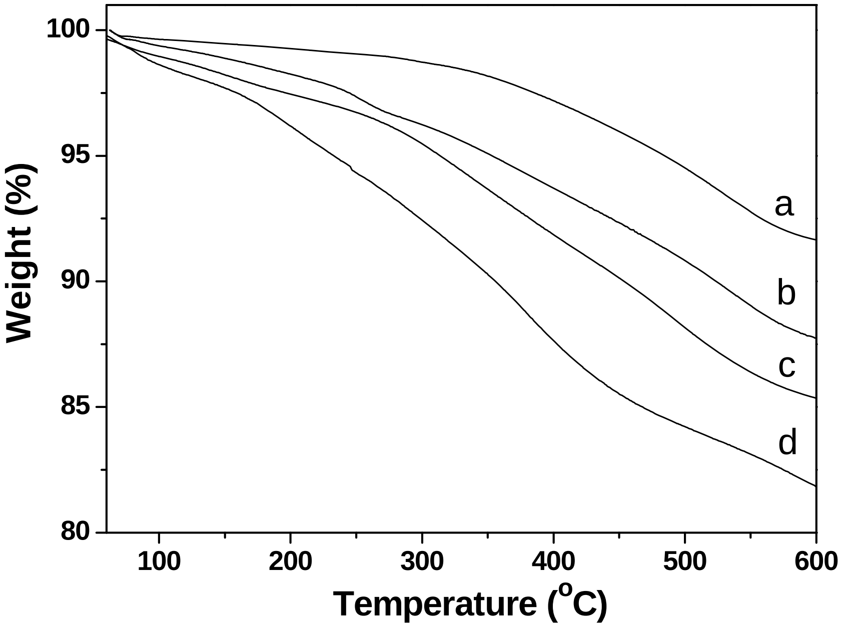


Fig. S6. TGA curves of (a) pristine silica spheres, (b) azide-functionalized silica spheres (SiO_2-N_3), (c) alkyne polymer-functionalized silica spheres (SiO_2-pAlk), and (d) SiO_2@Fe_3O_4 nanohybrids.

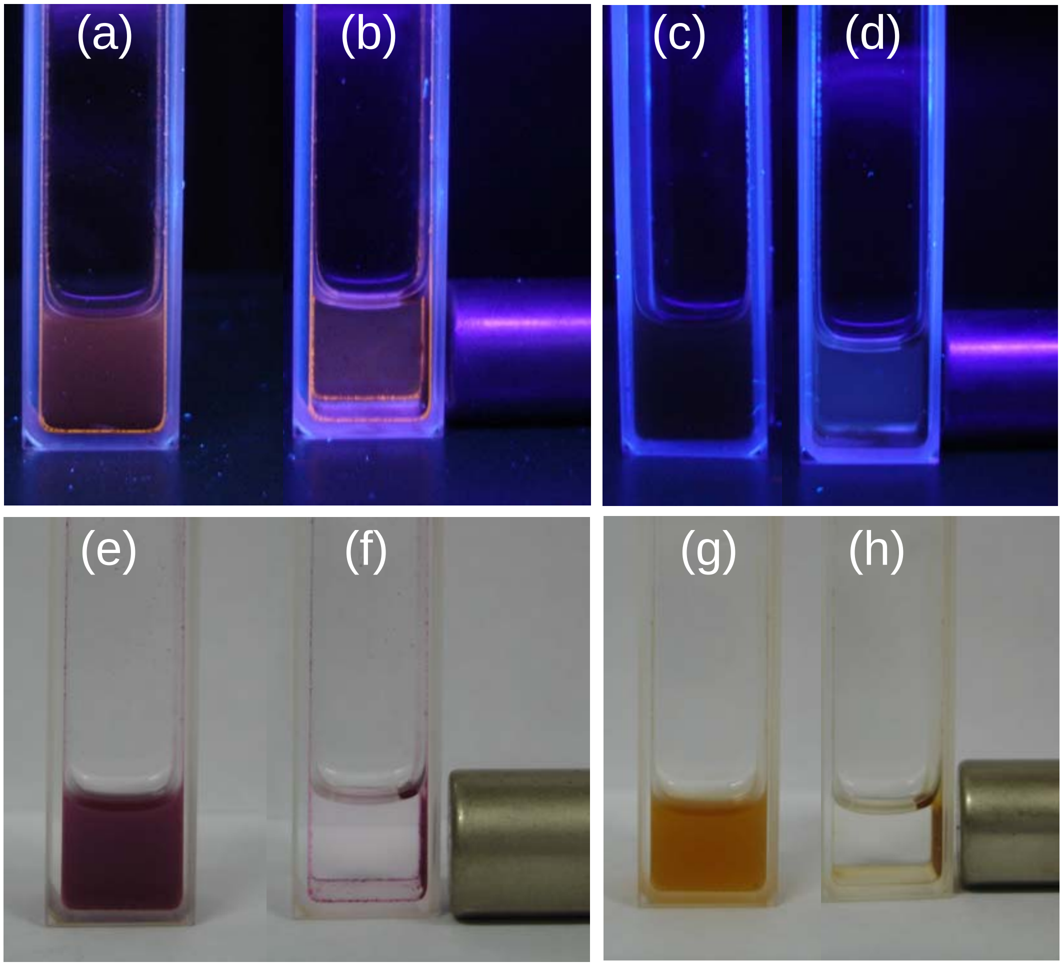


Fig. S7. The photographs of Fe_3O_4@RhB under 365 nm ultraviolet (UV) light without (a) and with (b) magnetic field; the photographs of Fe_3O_4-N_3 under 365 nm ultraviolet (UV) light without (c) and with (d) magnetic field; the photographs of Fe_3O_4@RhB under room light without (e) and with (f) magnetic field; the photographs of Fe_3O_4-N_3 under room light without (g) and with (h) magnetic field. All of these samples were dispersed in THF.