Supplementary Material (ESI) for Journal of Materials Chemistry

Electronic Supporting Information

for

Fluorescent Magnetic Nanoparticles Based on Ruthenium Complex and Fe_3O_4

Pinxian Xi,[a,b] Kai Cheng,[a] Xiaolian Sun,[a] Zhengzhi Zeng*[b] and Shouheng Sun*,[a]

[a]*Department of Chemistry, Brown University, Providence, Rhode Island 02912, U.S.A*. Fax: (+1)401 863 9046; Tel: (+1)401 863 3329; E-mail: ssun@brown.edu

[b]*Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry and College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China* Fax: (+86) 931 8912582; Tel: (+86) 931 8610877; E-mail: zengzhzh@yahoo.com.cn

Chemicals:

The synthesis was carried out using commercially available reagents. $Ru(dcbpy)_2(NCS)_2$ complex was purchased from Solaronix in Switzerland. Water was purified by a Millipore Milli-DI Water Purification system. All other reagents were purchased from Sigma Aldrich. The dialysis bags were purchased from Spectrum Laboratories, Inc. Nanosep 100kOMEGA filter was from Fisher.

Characterization:

UV/Vis absorption spectra were obtained with a PerkinElmer Lambda 35 UV/Vis spectrometer. TEM images were taken on Philips CM 20 (120kV). Hydrodynamic sizes of the nanoparticles (NPs) were measured by Malvern Zeta Sizer S90 dynamic light scattering instrument. The fluorescent spectra were acquired on Fluoromax 4 (HORIBA JOBIN YVON Inc.) spectrofluoremeter. Magnetic studies were carried out using a Lakeshore 7404 high sensitivity vibrating sample magnetometer (VSM) with fields up to 1.5 tesla at room temperature. The compositions of the samples were characterized by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). Optical images of SKBr-3 cells were obtained by a Leica inverted epifluorescence/reflectance laser scanning confocal microscope.

Cell experiments:

SK-BR-3 cells were purchased from American Type Culture Collection (ATCC, Manassas, VA) and cultured in a glass-bottom Petri dish (Mat Tek Corp.) with Dulbecco's modified Eagle Bs medium (DMEM) with 10% FBS and 1% antibiotics. Before incubation with NPs, the cells were washed with PBS (1× PBS buffer) three times. The NP dispersion in DMEM was incubated with cells for 4 h. Then, the incubated cells were washed with PBS (1× PBS buffer) three times and fixed by 4% paraformaldehyde solution. After 10 min fixation, the cells were again washed three times with the same PBS and subjected to optical imaging.

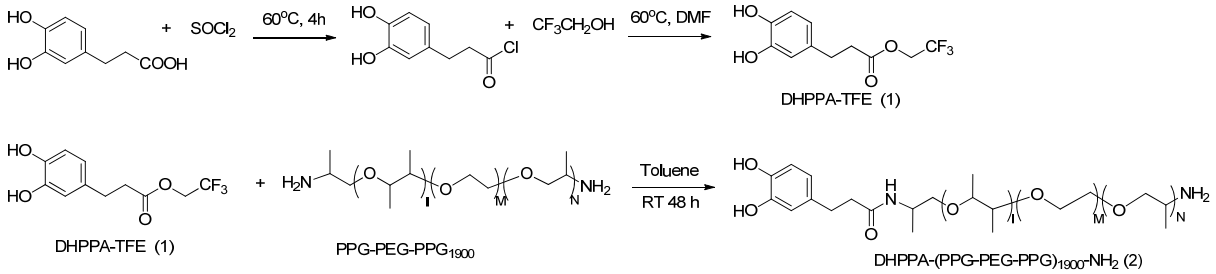
Cell viability test:

Viability of cells with particles was examined through MTT assay.[1] This cell viability test was based on the reduction of the tetrazolium salt MTT (3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) by mitochondrial reductase in metabolically active cells. The cells were seeded onto 96-well culture plates at a density of 4000 cells per well in DMEM (200 μL) containing 10% FBS. After 24 h incubation at 37 °C, NPs in DMEM buffer at different concentrations were added. The NPs were removed after 24 h incubation. Then MTT solution (5 mg/ml in PBS) was added to each well to evaluate cell viability. After 3 h at 37°C, the solution was removed. 100 μl DMSO was added to dissolve cells. After 30 min incubation at 37 °C, the viability was measured by microreader.

Synthesis of Fe_3O_4 NPs

Fe_3O_4 NPs and NH_2-terminaled water soluable Fe_3O_4 NPs were made by following the published method.[2] DHPPA-(PPG-PEG-PPG)-NH_2 was synthesized according the published paper.[3]

Synthesis of DHPPA-$(PPG\text{-}PEG\text{-}PPG)_{1900}$-$NH_2$



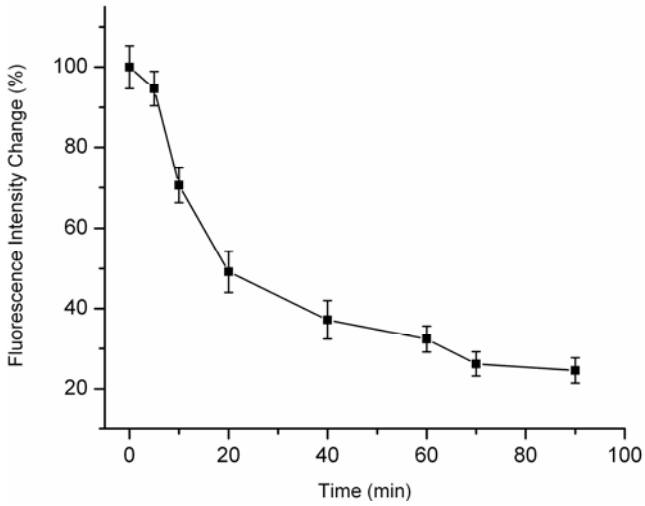


Fig. S1 The fluorescence intensity change of $Ru(dcbpy)_2(NCS)_2$ by directly mixing $Ru(dcbpy)_2(NCS)_2$ and the as-synthesized Fe_3O_4 NPs.

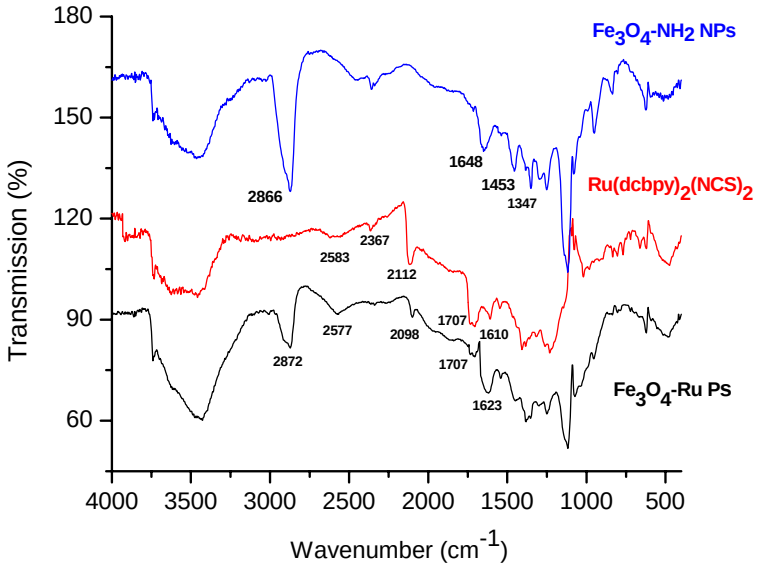


Fig. S2 IR spectra of the Fe_3O_4-DHPPA-$(PPG\text{-}PEG\text{-}PPG)_{1900}$-$NH_2$ (abbreviated as Fe_3O_4-NH_2) NPs, $(Ru(dcbpy)_2(NCS)_2)$ complex and Fe_3O_4-DHPPA-$(PPG\text{-}PEG\text{-}PPG)_{1900}$-$(NH\text{-}C(S)NH)_2Ru(dcbpy)_2$ (abbreaviated as Fe_3O_4-Ru) NPs.

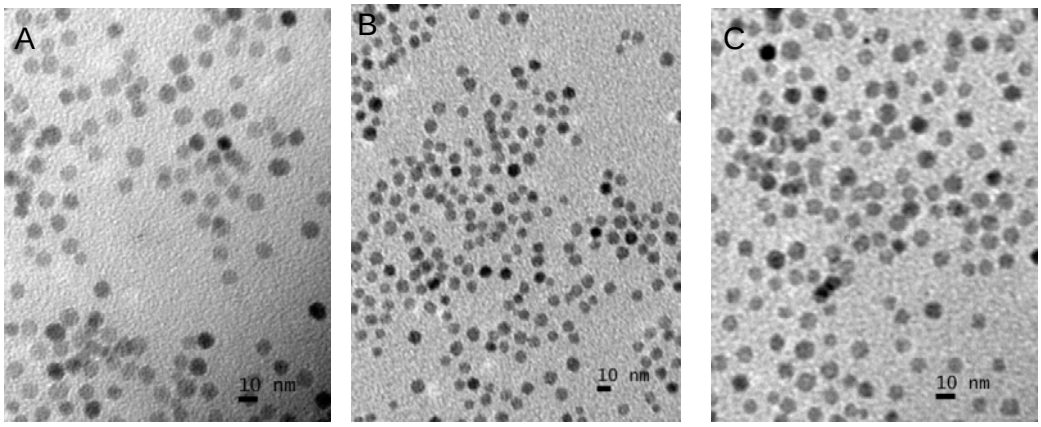


Fig. S3 TEM images of (A) $(PPG\text{-}PEG\text{-}PPG)_{3000}$, (B) $(PPG\text{-}PEG\text{-}PPG)_{1900}$ and (C) $(PPG\text{-}PEG\text{-}PPG)_{500}$ coated Fe_3O_4 NPs.

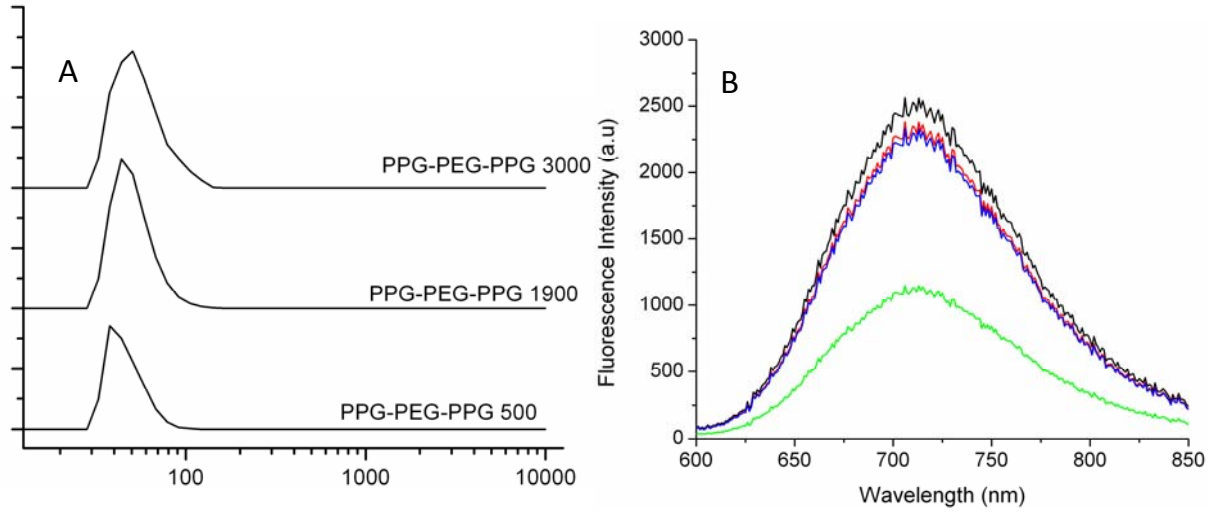


Fig. S4 (A) DLS results of the Fe_3O_4 NPs coated with different PPG-PEG-PPG. (B) Fluorescent spectra of the Fe_3O_4 NPs coated with different PPG-PEG-PPG (Green line: PPG-PEG-PPG(500) polymer, Blue line: PPG-PEG-PPG(1900), Red line: PPG-PEG-PPG(3000), Black line: $Ru(dcbpy)_2(NCS)_2$).

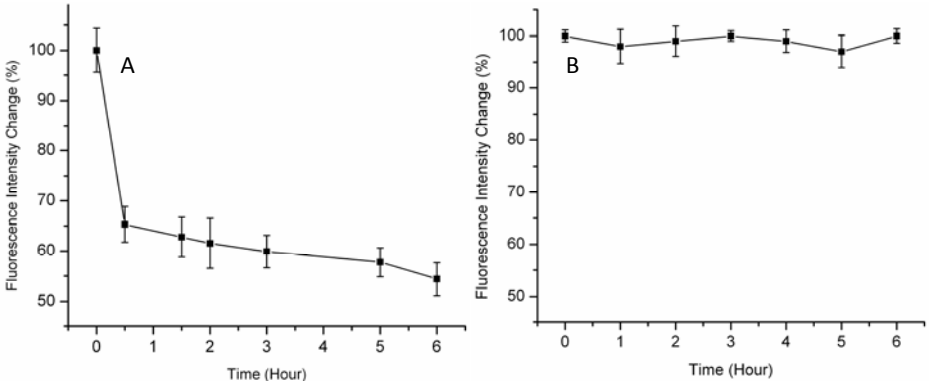


Fig. S5 Fluorescence intensity change of (A) the Fe_3O_4-DHPPA-$(PPG\text{-}PEG\text{-}PPG)_{1900}$-(NH-C(S)NH)-RhB and (B) the Fe_3O_4-DHPPA-$(PPG\text{-}PEG\text{-}PPG)_{1900}$-$(NH\text{-}C(S)NH)_2Ru(dcbpy)_2$ NPs in water (150 μg Fe/ml) under UV lamp (365 nm) with time.

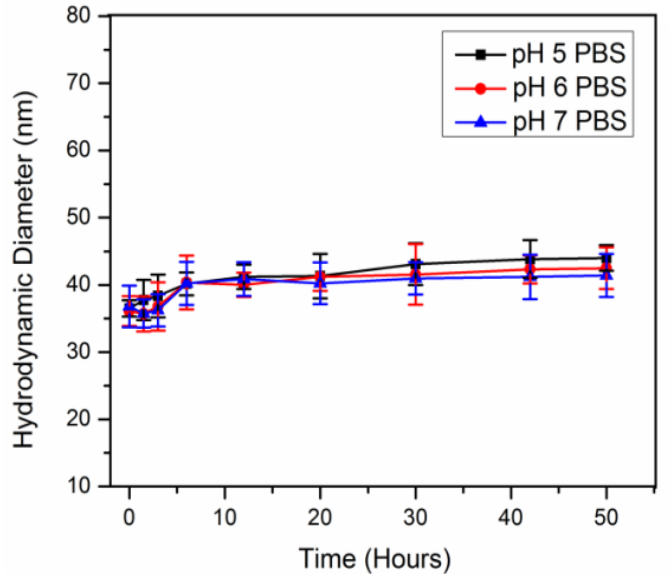


Fig. S6 Hydrodynamic diameter of the Fe_3O_4-DHPPA-$(PPG\text{-}PEG\text{-}PPG)_{1900}$-$(NH\text{-}C(S)NH)_2$ $Ru(dcbpy)_2$ NPs in PBS + 10% FBS measured at 37°C over 50 h.

References:

1. K. Cheng, S. Peng, C. Xu and S. Sun, *J. Am. Chem. Soc.* **2009**, *131*, 10637-10644.
2. S. Sun and H. Zeng, *J. Am. Chem. Soc.* **2002**, *124*, 8204-8205.