Electronic Supplementary Information

“Superparamagnetic Iron Oxide Nanoparticles with Photoswitchable Fluorescence”

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General consideration.

Any reagent including FeCl₃, Sodium Oleate (TCI), Oleic acid (Aldrich), Octafluorocyclopentene (TCI), and F127 (BASF) were used as purchased without any purification. Melting points were determined with Laboratory Devices Mel-Temp 3.0 melting point apparatus. The ¹H and ¹³C NMR spectra were obtained using JEOL JNMAL300 spectrometer at 300 and 75 MHz in CDCl₃, respectively, with tetramethylsilane as the internal reference. HRMS spectra were obtained with JEOL JMS-700 spectrometer. FTIR measurements were performed using a JASCO FTIR-430 instrument. Analyses of transmission electron microscopy (TEM) were conducted with JEOL JEM 2100F. Magnetic properties of nanoparticles were measured using superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS5XL), which is equipped with a 5 T superconducting magnet. The cell cytotoxicity of the nanoparticles was evaluated by measuring the effect of the nanoparticles on the cell viability after their incubation with Raw 264.7 cells (murine macrophage cells) using MTT colorimetric assay.

Preparation of materials

1,2-bis(2-methyl-1-benzothiophene-1,1-dioxide-2-yl)perfluorocyclopentene (2), were synthesized following the procedure described in Ref. 1. Iron oxide nanoparticles having 7 nm of average core size were prepared through the previously reported procedure in Ref. 2.

Preparation of 1,2-bis(2-propyl-1-benzothiophene-1,1-dioxide-2-yl)perfluorocyclopentene (1). To a stirred THF solution (30 mL) containing 3-bromo-2-propyl-1-benzothiophene (5.45 g, 21.5 mmol) was slowly added 9.4 mL of n-
butyllithium solution in hexane (2.5 M, 23.6 mmol) at -78°C, and the solution was stirred for 1 hr at -78°C. Then the octafluorocyclopentene (1.15 mL, 8.58 mmol) was added dropwise to the reaction mixture at -78°C, and the solution was slowly warmed to room temperature. The reaction mixture was poured into concentrated sodium chloride solution and extracted with diethyl ether. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated in vacuum. The crude product was purified by column chromatography on silica gel (hexane) to give 1.10 g (2.10 mmol, 24% yield) of 1,2-bis(2-propyl-1-benzothiophene-2-yl)perfluorocyclopentene (PBTF6). Mp. 198-199°C. 1H NMR (CDCl3, 300MHz) δ 7.17-7.01 (m, 4H), 6.85-6.68 (m, 3H), 6.62-6.59 (m, 1H), 2.34-2.24 (m, 0.4H), 2.13-1.99 (m, 1.9H), 1.79-1.69 (m, 1.5), 1.22-1.15 (m, 0.9H), 0.96-0.84 (m, 1.5H), 0.51-0.46 (m, 3H), 0.085 (t, J=7.5Hz, 4.8H). 13C NMR (CDCl3, 75MHz) δ 149.11, 148.45, 138.33, 138.10, 138.01, 137.97, 124.59, 124.30, 124.26, 122.38, 122.17, 121.91, 118.27, 31.93, 31.42, 24.91, 24.36, 13.92, 13.30. HRMS (EI+) m/z calcd. for C27H22F6S2: 524.1067 found: 524.1069

The PBTF6 (1.0 g, 1.90 mmol) was dissolved in CH2Cl2 (20 mL) and m-CPBA (70%, 3.43 g, 15.3 mmol) was added to the solution. The reaction mixture was stirred for 24 hr at room temperature and aqueous NaHSO3 was added. Product was extracted with CH2Cl2 (2 × 50 mL), and the organic layer was dried over MgSO4, filtered, and the solvent was removed. The residue was purified by chromatography on silica gel to obtain 1 (800 mg, 1.36 mmol, 71%). Mp. 217-218°C. 1H NMR (CDCl3, 300MHz) δ 7.76 (d, J=7.32Hz, 1.27H), 7.67-7.55 (m, 3.33H), 7.47-7.42 (m, 1.46H), 7.21 (d, J=7.14Hz, 1.26H), 7.12 (d, J=7.32Hz, 0.68H), 2.64-2.56 (m, 0.67H), 2.42-2.21 (m, 3.10H), 1.87-1.61 (m, 3.38H), 1.35-1.33 (m, 1.30H), 1.05 (t, J=7.32Hz, 1.95H), 0.78 (t,
$J=7.32\text{Hz, }3.60\text{H}$. $^{13}$C NMR (CDCl$_3$, 75MHz) $\delta$ 147.66, 147.30, 135.52, 135.44, 133.75, 133.30, 130.81, 130.67, 129.54, 129.35, 123.70, 122.93, 122.87, 122.66, 122.60, 122.39, 122.26, 27.75, 27.56, 20.75, 20.36, 14.23, 13.92. HRMS (EI$^+$) $m/z$ calcd. for C$_{27}$H$_{22}$F$_6$O$_4$S$_2$: 588.0864 found: 588.0862.

**Preparation of 1 (or 2) encapsulated Magnetic NanoParticles (MNP-1 or MNP-2).** 40 mg of iron oxide nanoparticle, 20 mg of 1 (or 2), and 160 mg of F127 were mixed into 10 ml CHCl$_3$ solution. After shaking the reaction solution for several minutes, solvent was evaporated with rotary evaporator generating black film on a bottom of flask. Reaction flask was connected to vacuum line and evacuated for 1 hr. 20 ml of water was poured and sonicated for 10 min, affording dark-brown suspension with slight amount of white floating matters. Filtration with syringe filter (Cellulose acetate, 0.20 μm of pore size, MFS) gave transparent suspension. Twice repetition of purification process by addition of 15 ml of water, centrifugation (13,000 rpm, 20 °C, 30 min), and removal of supernatant gave highly concentrated suspension of MNP-1 (or MNP-2).

**Determination of number of encapsulated 1 molecules.**

**(Method 1)** The iron concentration in a MNP-1 were determined by using ICP AES. The number of nanoparticles was calculated based on the approximation as sphere of 7 nm diameter. MNP-1 were collected by the centrifugation of 100 μl aliquot of their suspensions (0.45 mg/ml of iron concentration) and dried *in vacuo*. The number of 1 molecules in a solid was determined by measuring the sulfur contents using elemental analysis.

**(Method 2)** The number of nanoparticles was derived though the same procedure in Method 1 using ICP AES. The solid of nanoparticles collected by the centrifugation
were re-dispersed in an ethyl acetate and sonicated for extracting 1 molecules. The nanoparticles were removed from the solution by the centrifugation and the concentration of 1 in the supernatant was irradiated by the UV light at 312 nm for 40 min. The concentration of 1 were determined by using a fluorescence spectrophotometer at $\lambda_{\text{ex}} = 505$ nm with excitation at 410 nm. A standard plot was prepared under identical conditions to calculate the amount of 1 encapsulated in the nanoparticles.

**Spectroscopic investigations** The spectroscopic investigations was carried out with an aqueous suspension of MNP-1 (0.017 mg/ml of iron conc., 0.04 mM of PBTFO4 conc.) and an ethyl acetate solution of 1 (0.01 mM). UV absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. UV and visible irradiations for inducing the photoisomerization were performed with standard lamps used for visualizing TLC plates (VL6L; 312 nm, 8 mWcm$^{-2}$) and a 100 W tungsten lamp and the samples were placed in a glass chamber maintained at room temperature. Fluorescence spectra were measured with 410 nm excitation light by using 410Fluoro Max-2 spectrophotometer equipped with a 150 W ozone-free xenon lamp. Fluorescent quantum yield were determined using 3-aminofluoranthene in cyclohexane as a standard.
Figure S1. (a) Absorption spectra of an aqueous suspension of MNP-1 with UV irradiation at 315 nm (b) Absorption change profile, derived by subtracting the absorption of the MNP-1 measured before the UV irradiation from the spectra after the UV irradiation.

Figure S2. Absorption spectra of 1 in ethyl acetate solution with UV irradiation at 315 nm.
**Figure S3.** Fluorescence spectra change of 1 in ethyl acetate solution with UV irradiation at 315 nm.

**Figure S4.** Modulation of the fluorescence signal of 1 in ethyl acetate solution, monitored at 505 nm with excitation at 420 nm, upon alternative illumination with UV at 312 nm (solid line) and visible light at 420 nm (dotted line).
Figure S5. Temperature dependence of magnetization for (a) the iron oxide nanoparticle stabilized by oleic acid and (b) MNP-1 measured after zero-field cooling (black lines) and field cooling (red lines) with an applied field of 100 Oe. Field dependence of the magnetization for (c) the iron oxide nanoparticle stabilized by oleic acid and (d) MNP-1 measured at 300 K.

Figure S6. The cytotoxicity of MNP-1 to Raw 264.7 cells after the incubation for (a) 24 hr and (b) for 48 hr.
References
