

ELECTRONIC SUPPLEMENTARY INFORMATION

Synthesis of a new fluorescent conjugated polymer microsphere for chemical sensing in water media

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Intrumentation. NMR spectra were recorded on a Bruker AVANCE 500 spectrometer, with tetramethylsilane as an internal reference. FTIR spectra were obtained using a Nicolet model 520P spectrometer with samples prepared as KBr pellets. Coupled size exclusion chromatography (SEC) and light scattering measurements were carried out using a HP-1090 liquid chromatograph with autosampler, autoinjector and light scattering detector; ELSD 2000 Alltec. The size exclusion chromatogram was carried out in THF as eluent and data were calibrated using Polymer Laboratories EasiCal PS standards using two column PLGel 5 μm MIXED-C at room constant temperature. Excitation and emission spectra were recorded in a PTI Quantum Master-4 spectrofluorimeter at 90° detection angles. Excitation and emission wavelengths are selected by means of auto-calibrated, computer-controlled by FeliX32™ Software package. Scanning electron microscopy was obtained using a JEOL JEM-2010 Scanning Electron Microscope at an operating voltage of 3kV. Fluorescence microscopy measurements were performed with a Zeiss (Oberkochen, Germany) Axiovert 200 inverted microscope fitted with an ORCA-ER CCD camera (Hamamatsu Photonics, Bridgewater, NJ).

Synthesis P0: Poly[(9,9'-bis(6'-bromohexyl)fluoren-2,7-diyl)-alt-co-(benzen-1,4-diyl)] (P0). The synthesis of the precursor polymer was performed according to previous procedure, via Suzuki coupling. For batch used here, **P0** has Mw = 15.31 kg/mol and Mn = 8.83 kg/mol (based on PS calibration).^{1,2}

Synthesis P1: Poly{[(9,9-bis(6'-(vinylhexyl)-fluoren-2,7-diyl)-alt-(benzen-1,4-diyl)-co-(9,9-bis(6'-(1-imidazolene)hexyl)-fluoren-2,7-diyl)-alt-(benzen-1,4-diyl)]-co-[9,9'-bis(6'-bromohexyl)fluoren-2,7-diyl]-alt-(benzen-1,4-diyl)} (P1)

Step 1. To a solution of polymer, **P0** (300mg, 0.53 mmol) in 5mL of dry THF was added 5ml of freshly of potassium tert-butoxide solution 1.0M in THF (Sigma-Aldrich Corp.). The mixture was stirred at room temperature during 24 h. After, 10 mL methanol was added to precipitate out the polymer. The crude product was filtered and washed with abundant water, methanol and acetone, finally dried under vacuum at room temperature.

Step 2. This crude polymer was directly dissolved in dry THF (4mL) and DMF (2mL) with imidazole (50mg, 0.71 mmol) in the presence of potassium hydroxide (40 mg, 0.71 mmol) as an acid acceptor, with potassium iodide as catalyst. The mixture was stirred at 80°C during 12 h. The solution was allowed warm up to room temperature and methanol was added to precipitate out the polymer, which was filtered, washed with water, methanol and acetone. The residue was dissolved in the minimum amount of chloroform, filtered over celite and re-precipitated out twice more with methanol. After removal the solvent under reduced pressure, the dried polymer was obtained as a yellowish solid. (202 mg, 86%). ¹H NMR (CDCl₃, 500MHz): δ = 7.81–7.25 (m, 21H, Ar), 6.99 and 6.77 (bs, 1H, Hb-Im and Ha-Im, respectively), 5.65 (bs, 1H, -CH=CH₂), 4.84 (bs, 2H, as reference -CH=CH₂), 3.76 (bs, 1H integration over reference, corresponding to 25% composition, -CH₂-Im), 3.28 (bs, 1H integration over reference, corresponding to 25% composition, -CH₂-Br) and 2.15- 0.60 ppm (m, n-alkyl chain). IR (pellet KBr): 3121, 2928, 2850, 1643, 1480, 1265, 892, 812, 639 cm⁻¹.

Microsphere preparation

The fluorescent conjugated polymer (P1, 10 mg) and functional monomer (MAA, 150 μL) were dissolved in 5 mL of chloroform as a porogen. This is because a solvent non-miscible with water is needed to form the suspension. The cross-linker (EGDMA, 500 μL) and the initiator (AIBN, 50 mg) were added to this mixture and sonicated until dissolution. Polyvinyl alcohol (PVA, 6 g) was dissolved in 150 mL of hot water in a 250-mL flanged reactor flask fitted with magnetic stirring and nitrogen inlet. After cooling to room temperature, the organic mixture was ultrasonic during 30 min., was added drop by drop across the septum with a syringe and maintained at 65 °C in an oil bath with continuous and regular stirring at 2000 rpm overnight. The formed microspheres were washed with hot water to completely remove PVA from their surface, with THF and chloroform for removed conjugated polymer that not polymerized and other reactive, and finally the product was dried under vacuum.

Bibliography:

1. Mallavia, R.; Martinez-Perez, D.; Chmelka, B. F.; Bazan, G. C. *Bol. Soc. Esp. Ceram. V.* **2004**, *43*, 327-330.
2. Mallavia, R.; Montilla, F.; Pastor, I.; Velasquez, P.; Arredondo, B.; Alvarez, A. L.; Mateo, C. R. *Macromolecules* **2005**, *38*, 3185-3192.

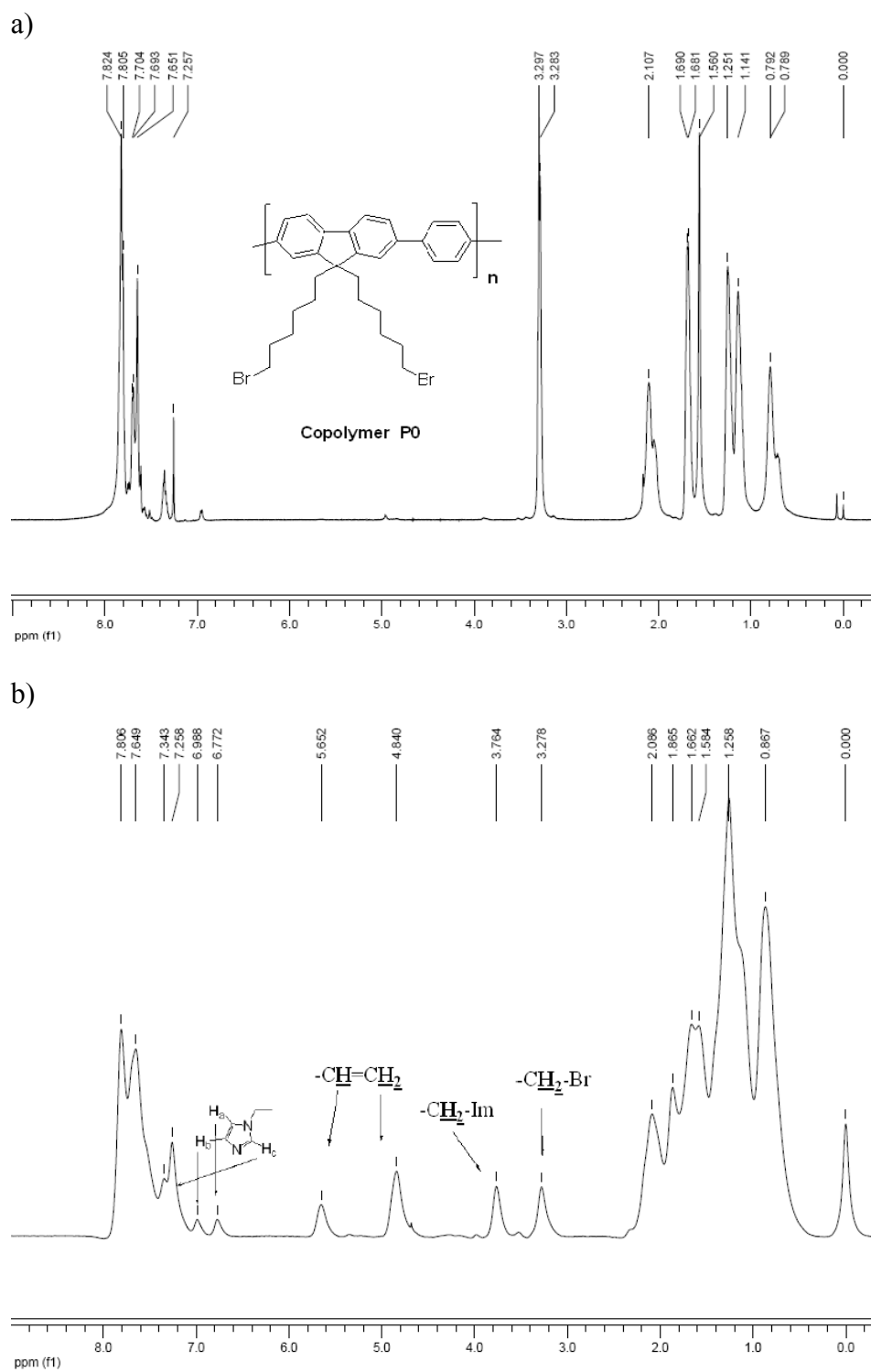


Figure S1. ^1H -NMR spectra of copolymer **P0** (a) and **P1** (b)

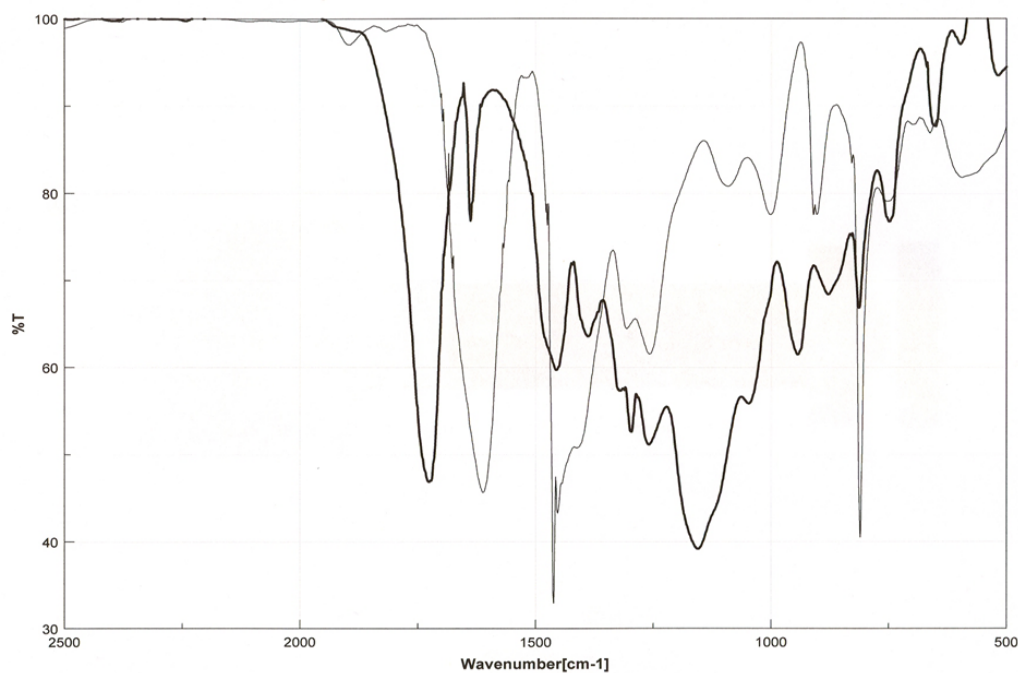


Figure S2. FTIR spectra of copolymer **P1** (---) and microsphere (—)

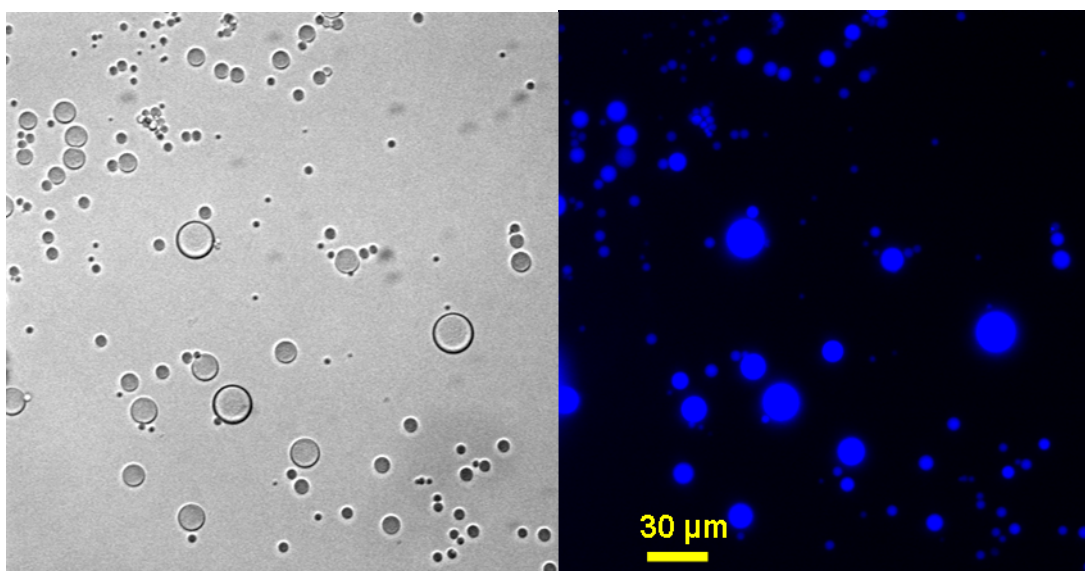


Figure S3. Transmission image in microscopy (left picture; magnification x40) and fluorescence microscopy image under $\lambda_{\text{ex}} = 375 \text{ nm}$ (right picture, magnification x40).

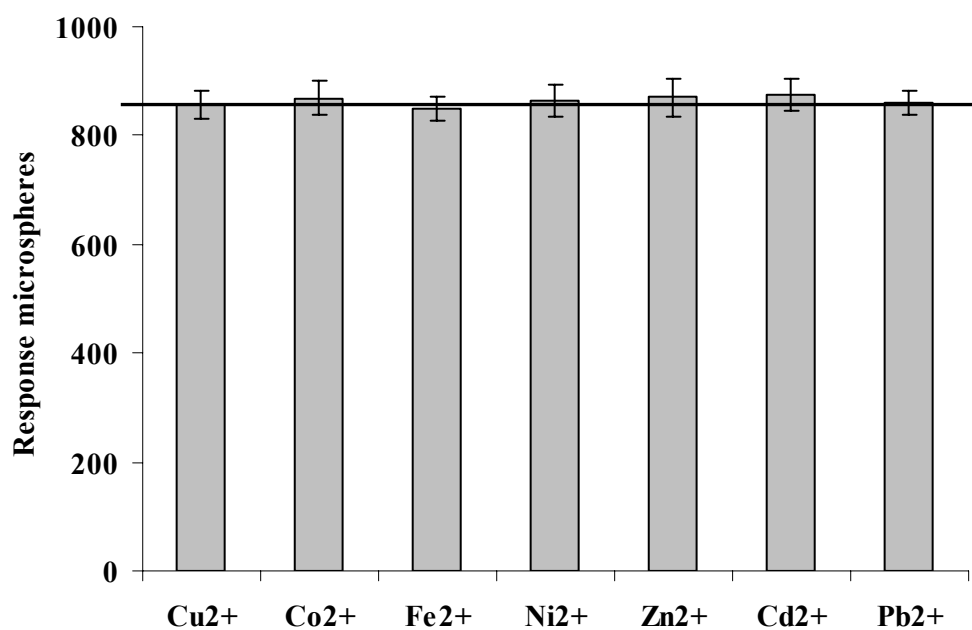


Figure S4. Fluorescence emission response profiles of microsphere by Cu²⁺ (1 μM) in presence of different metal ions (1 μM).

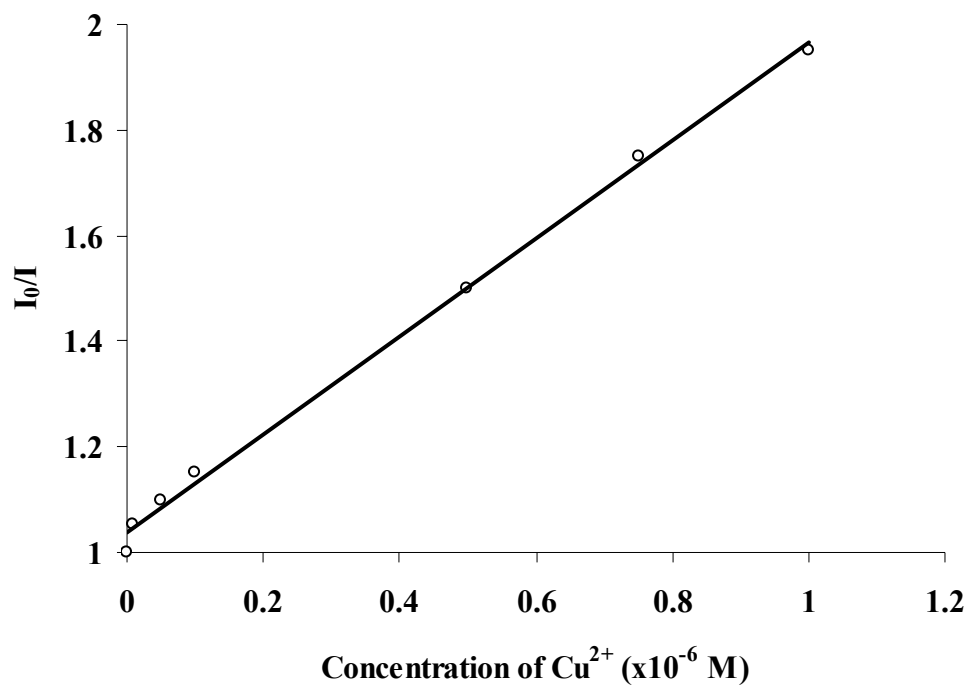


Figure S5. Stern-Volmer quenching of microspheres in flow-injection analysis fluorescence microscopy by Cu²⁺ in water.