Supporting Information for:

Fluorescent sensing of transition metal ions based on the encapsulation of dithranol in a polymeric core shell architecture.

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Experimantal Details

Materials. Solvents were purchased from Biosolve Ltd. (Valkenswaard, The Netherlands). All other chemicals and inorganic salts were purchased from Aldrich (Oakville, On, Canada). All chemicals and solvents were used as recived.

Instrumentation. UV/Vis as well as fluorescence spectra were recorded on a FlashScan 530 (AnalytikJena, Germany) in 96-well microtiter plates (polypropylene, flat bottom) from Greiner (Greiner Bio-One, Germany). All spectra were referenced to an empty microtiter plate.

NMR spectra were measured on a Bruker Mercury 400 NMR spectrometer in deuterated chloroform. The chemical shifts were calibrated to TMS.

MALDI-TOFMS measurements were carried out on a Voyager-DE™ PRO Biospectrometry™ Workstation time-of-flight mass spectrometer using linear mode for operation. All spectra were obtained in the positive ion mode. Ionisation was performed with a 337 nm pulsed nitrogen laser. Samples were prepared with dithranol as matrix and NaI as cationizing agent in a multiple-layer approach as described previously.[1]

Gel permeation chromatograms were measured on a Waters GPC system consisting of an isocratic pump, solvent degasser, column oven, 2996 photo diode array (PDA) detector, 2414 refractive index detector, 717plus autosampler and a Styragel HT 4 GPC column with precolumn installed. Linear PMMA standards were used for calibration. The solvent was DMF containing 5 mmol/L NH_4PF_6. The flow speed was 0.5 mL/min.

Synthesis of polymer P1. To a stirred suspension of KOH (224.4 mg, 4.0 mmol) in dry DMSO (30 mL) at 65 °C, the starting 5-arm poly(ethylene glycol) polymer (131.2 mg, 1.0 mmol) was added. After 30 min, 4'-chloro-2,2':6',2''-terpyridine was added (267.7 mg, 1.0 mmol) and the mixture was stirred for 16 h at 65 °C, added to dichloromethane and subsequently washed with water (3 x). The organic layer was dried over $MgSO_4$. The pure product was obtained after column chromatography (CH_2Cl_2, Al_2O_3). ^{1}H NMR ($CDCl_3$): δ = 2.55-2.80 [m, 18 H, $CH_2OCH_2C\mathbf{H_2}NC\mathbf{H_2}C\mathbf{H_2}N$], 3.50 [t, 10 H, J = 5.86 Hz, $CH_2OC\mathbf{H_2}CH_2NCH_2$], 3.55-3.80 [m, 180 H, $CH_2OC\mathbf{H_2}C\mathbf{H_2}OCH_2$], 4.39 [t, 10 H, J = 4.39 Hz, tpy-$OC\mathbf{H_2}CH_2O$], 3.93 [t, 10 H, J = 4.39 Hz, tpy-$OCH_2C\mathbf{H_2}O$], 7.32 [m, 10 H, H5,5''], 7.84 [m, 10 H, H4,4''], 8.04 [s, 10 H, H3',5'], 8.61 [d, 10 H, J = 8.06 Hz, H3,3''], 8.67 [d, 10 H, J = 4.93 Hz, H6,6'']. M_n (GPC) = 3100 Da, PDI (GPC) = 1.15; M_n (MALDI) = 3350 Da, PDI (MALDI) = 1.01.

Encapsulation and titration experiments. All stock-solutions were prepared fresh prior to the experiments. This is especially necessary for dithranol solutions, since dithranol is known to decompose rapidly.[2,3]

Characterization of Polymer P1

P1 was characterized by ^{1}H NMR in $CDCl_3$ as described above revealing the full functionalization of the 5-arm poly(ethylene glycol) polymer. Moreover, Figure 1 displays a MALDI-TOFMS spectrum of **P1** with corresponding peak assignment and the expected 44 Da peak spacing for poly(ethylene glycol) undeniably proofing the structure of polymer **P1**.

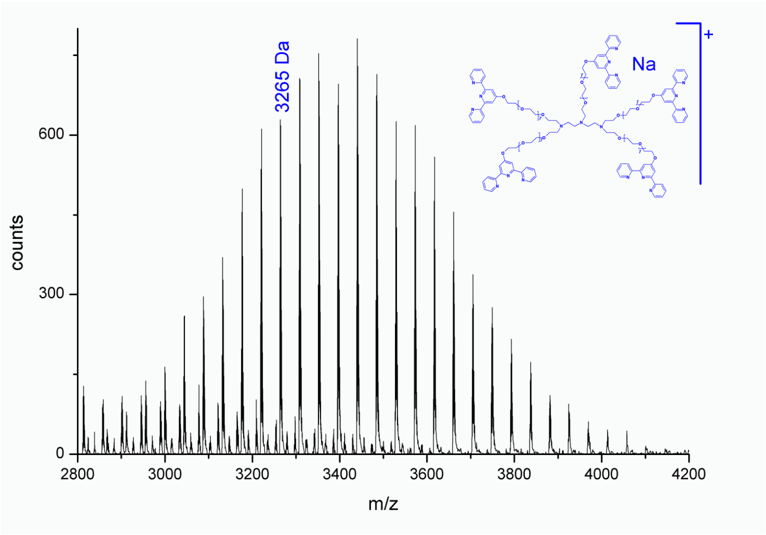

Figure 1. *MALDI-TOFMS spectrum of polymer **P1** with corresponding peak assignment.*

Layout of the parallel titration experiments

Figure 2 depicts a microtiter plate layout applied to the parallel investigation of polymer **P1** with different transition metal ions.

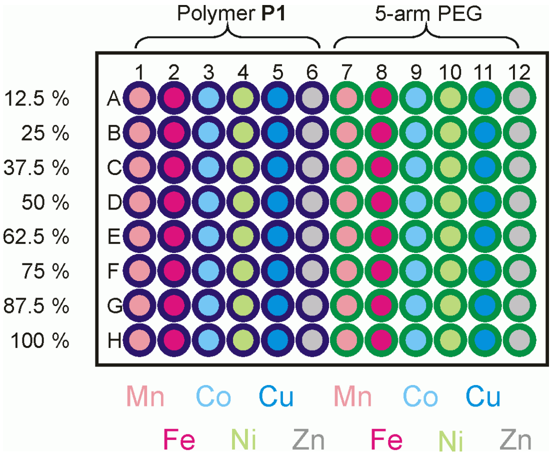

Figure 2. *Microtiter plate layout applied to the parallel property investigation of polymer **P1**.*

Chemical structures of the investigated guest molecules

Figure 3 depicts the chemical structures of the investigated guest molecules.

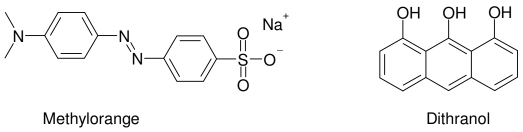
Methylorange
Dithranol

Figure 3. *Chemical structures of the investigated guest molecules.*

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1 M. A. R. Meier and U. S. Schubert, *Rapid Commun. Mass Spectrom.*, 2003, **17**, 713-716.

2 J. Taskinen, J. Haarlara, E. Wartiovaara and J. Halmekoski, *Arch. Pharm.*, 1988, **321**, 103-106.

3 H. M. Elsabbagh, C. W. Whitworth and L. C. Schramm, *J. Pharm. Sci.*, 1979, **68**, 388-390.