Supporting Information

Title: Magnetic nanocrystals coated by molecularly imprinted polymers for the recognition of Bisphenol A

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1. Experimental Section

- **Materials and chemicals:**

Terbutylnitrite, thionyl chloride ($SOCl_2$), tetrafluorobric acid (HBF_4), 2-(4-aminophenyl) ethanol, sodium hydroxyde (NaOH), iron chloride ($FeCl_3$), iron sulphate ($FeSO_4$), diethyldithiocarbamate (DEDTC), methacrylic acid (MAA) and ethylene glycol dimethylacrylate (EGDMA) were purchased from Aldrich and were used without further purification. All the solvents were obtained from Acros and used as received.

- **Synthesis of $BF_{4,2}N$-C_6H_4-CH_2-DEDTC**

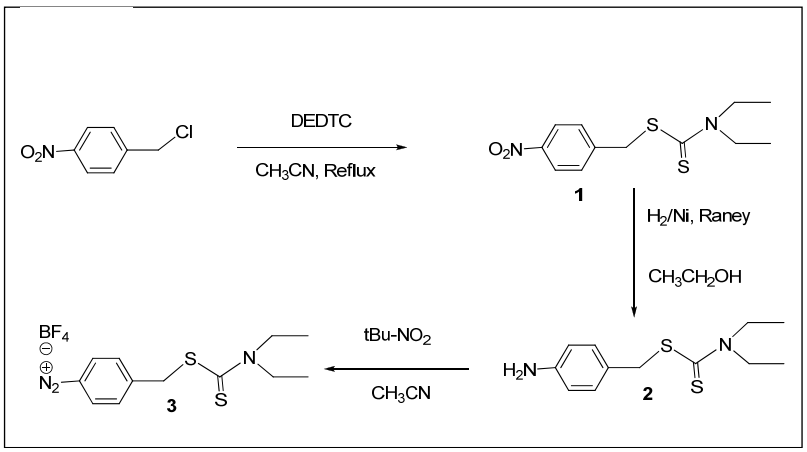

Figure S-1: Schematic Illustration for the synthesis of $BF_{4,2}N$-C_6H_4-CH_2-DEDTC

This diazonium salt was prepared in three steps. 1) The 4-nitrobenzyl chloride reacts with the DEDTC to give the thiocarbamate **1** in a good yield. 2) This last intermediate was hydrogenated using Raney Nickel and leads to the corresponding primary amine **2** in quantitative yield. 3)A cold solution of terbutylnitrite in anhydrous acetonitrile was added

dropwise to a cold solution (in an ice bath) composed of the compound **2**, tetrafluoroboric acid and anhydrous acetonitrile. The reaction was conducted at -20°C during 24 hours. The viscous diazonium salt was washed 3 times with ether then finally dissolved in acetone and evaporated at room temperature.

- **Ferric oxide NPs synthesis and funtionnalization**

The functionalization of Fe_2O_3 nanoparticles by the diazonium salt was done in-situ during the nanoparticle synthesis: in a typical reaction, 2.9 mmol of $FeCl_3$ and 1.2 mmol of $FeSO_4$ were dissolved in 5 mL of deionised water. The solution was purged with nitrogen, and the inert atmosphere was maintained for the duration of the synthesis. Then 3 mL of NaOH (c = 1 M) were rapidly added under vigorous stirring. The color of the solution changed immediately from yellow to dark, indicating the formation of ferric oxidenanoparticles. Then, the diazonium salt (0.5 mmol, c = 0.3 M) synthesized above was added directly into the reaction vessel. The mixture was stirred for 1 h.

Concerning the polymerisation, typically Fe_2O_3 NPs containing DEDTC on the surface (0.015 g) were mixed with MAA (0.04 g), BPA (0,02 g) and EGDMA (0.04 g) in ethanol (1 mL). The mixture was deoxygenated under argon during 15 minutes and put under UV light during 4 hours. The polymerisation was performed 4 times on the same sample.

The purified particles were characterised by IR, ATG and TEM.

- **Characterization Methods:**

Powder X-ray diffraction data were collected on a Siemens D5000 Kevex diffractometer (30 min) using Cu- Ka radiation (l ~ 1.5405 A°). Electron microscopy and diffraction studies were conducted on a JEOL-100 CX II microscope. Differential thermal and thermogravimetric analyses were carried out on a Setaram TG 92-12 thermal analyser in the temperature range 20–800 °C with a heating rate of 10 °C min^{-1} under a flow of air at 80 ml/min in an alumina crucible. FT-IR spectra were obtained by transmission on an Equinox 55 spectrometer on pressed KBr pellets in the range 400–4000 cm^{-1}. The magnetic measurements on powdered samples were carried out at low temperature (5K) using a commercial SQUID magnetometer ‘‘MPMS–5S’’ from Quantum Design Corp. Field constant and isothermal dc magnetisation were performed with a field. Raman spectra were obtained with a LABRAM Jobin-Yvon micro-spectrometer using a He-Ne excitation laser (632.8 nm, 1

mW power). All spectra were taken with 1s integration time in the 250-2500 cm^{-1} spectral range.

2. XRD

Typical XRD patterns of the bare iron oxide NPs and the aryl-coated NPs are shown in Fig. SI-2.

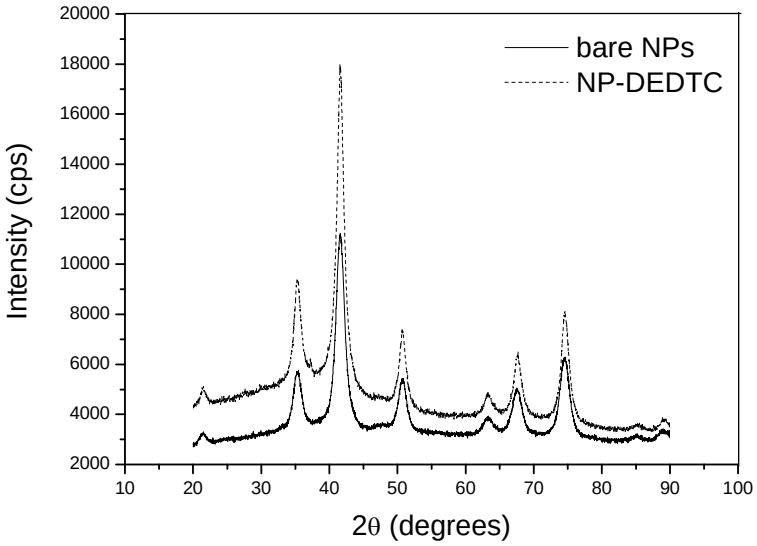

Figure S-2. XRD patterns of (a) bare NPs and (b) functionalized NP-DEDTC

3. IR analysis

The IR spectra of the free diazonium salt BF_4,$_2$N-C_6H_4-CH_2-DEDTC and the coated NP-DEDTC are displayed in Figure SI-3.

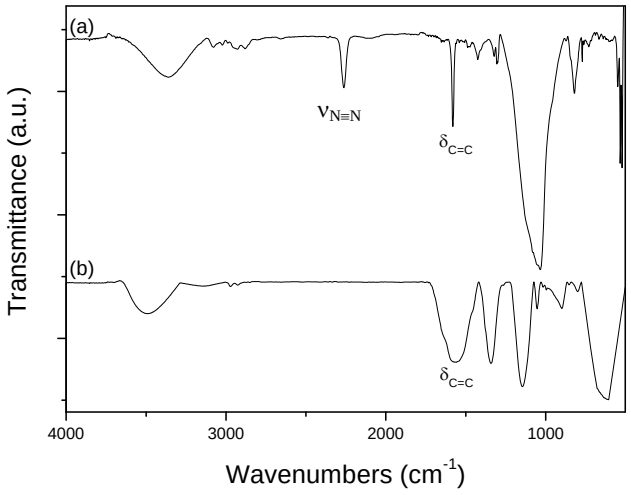

Figure S-3. FT-IR spectra of the free diazonium salt (a) BF_4,$_2$N-C_6H_4-CH_2-DEDTC and (b) the coated NP-DEDTC.

4.TGA analysis

The TGA weight loss profiles of NP@NIP and NP@MIP are shown in Figure SI-4.

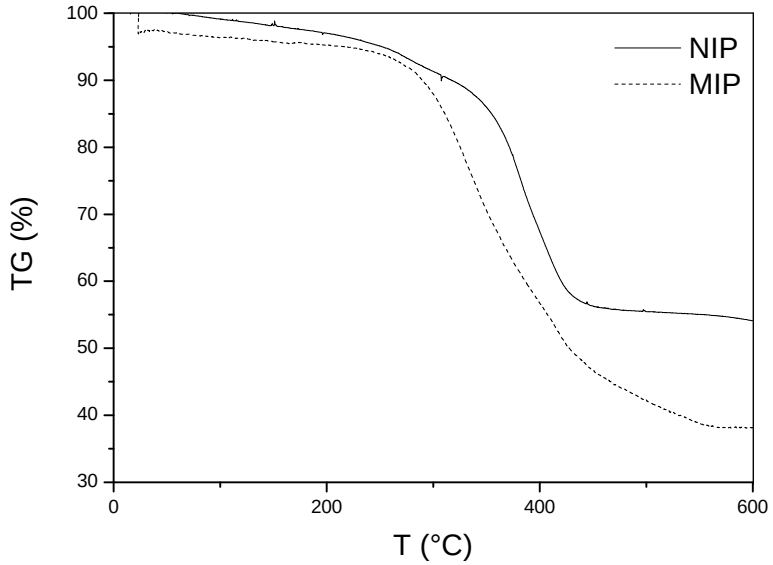

Figure S-4. Thermogravimetric analysis for the iron oxide nanoparticles coated by NIPs (full line) and MIPs (dotted line).

5. HRTEM

Figure SI-5 displays a HRTEM image of NP@MIP. It evidences the presence of an iron oxide core showing a crystalline phase covered by an amorphous phase corresponding to the polymer overlayer.

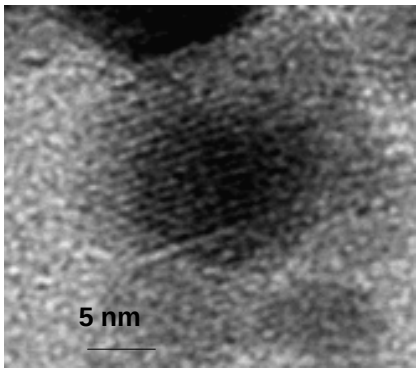

Figure S-5. High resolution transmission electron micrograph of NP@MIP samples after 4h polymerization from NP-DEDTC.

6. Selectivity evaluation of NP@MIP

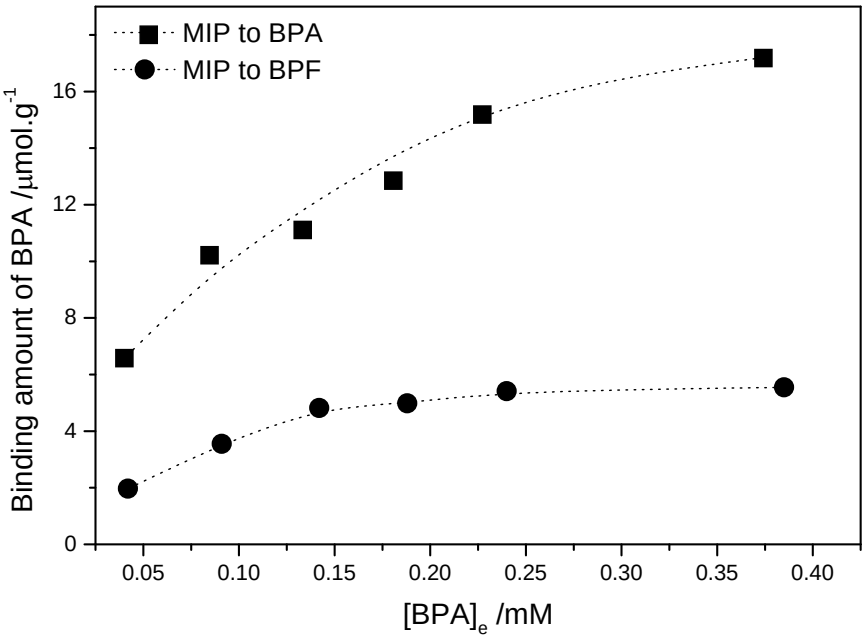

Figure S-6. Binding isotherms of NP@MIP for BPA (squares) and NP@MIP for BPF (circles).