Supplementary Material for

Hydrophobic coordination polymer nanoparticles and application for oil/water separation

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S1. Methods

Solvents and starting materials were purchased from Sigma-Aldrich and used as received, without further purification, unless otherwise stated. 1,4-Bis(imidazol-1-ylmethyl)benzene (Bix)¹, 4-Heptadecylcatechol² and **CPP2** (Co/Fe) nanoparticles³ were synthesized according to a previously reported methods.

Synthesis of CPP1 nanoparticles. 1,4-Bis(imidazol-1-ylmethyl)benzene (59 mg, 0.25 mmol) and 4-heptadecyl cathecol (173.27 mg, 0.5 mmol) were firstly dissolved in 15 mL of ethanol. Under vigorous stirring (800 rpm), the solution was treated with an aqueous solution of $Co(CH_3COO)_2 \cdot 4H_2O$ (62.3 mg, 0.25 mmol in 2 mL H₂O), which turned it light brown and led to rapid formation of a precipitate. After the solution was stirred at room temperature for 30 minutes, the precipitate was collected by centrifugation, and then washed with ethanol several times. The solvent was removed and the solid was dried under vacuum. SEM and TEM images of the resulting spherical nanoparticles showed a size distribution of 143 ± 42 nm in basis of DLS measurements. C,H,N analysis (%) calcd for $C_{60}H_{90}O_4CoN_4$: C 72.77, H 9.16, N 5.66; found: C 71.80, H 9.52, N 5.70; FT-IR (ATR): v =2920.3 (s), 2851.3 (s), 1585.2 (s), 1502.7 (m), 1462.1(m), 1264.8 (m), 1111.1 (m), 1093.5 (m), 948.4 (m), 807.2 (m), 724.8 (m), 640.8 (m) cm⁻¹.

Functionalization of CPP2 (Co/Fe) CPPs with octadecylamine (ODA): To a stirring dispersion of 30 mg of nanoparticles in 15 mL of H₂O/EtOH (4:1) were added 8 mg (0.030 mmol) of ODA. After 10 minutes, EDC (10 mg, 0.05 mmol) and NHS (5.75 mg, 0.06 mmol) were added, and the mixture was stirred at room temperature for 6 hours. The resulting particles were purified by centrifugation, and then washed with ethanol several times to remove any excess starting material. The precipitate was dried under vacuum overnight. SEM and TEM images of the resulting spherical nanoparticles showed a size distribution of 112 ± 12 nm for **CPP3** (Co) and 98 ± 8 nm for **CPP4** (Fe) in basis of DLS measurements.

Scanning electron microscopy (SEM): SEM measurements were performed with a DITACHI S-570 operating at 15 kV. The samples were prepared by drop casting of the corresponding dispersion on aluminum tape followed by evaporation of the solvent under room conditions. Before analysis the samples were metalized with a thin layer of gold, using a sputter coater (Emitech K550).

SEM images for immobilization of CPPs onto solid supports were taken with FEI Magellan 400L XHR operating at 3.0 kV and 10⁻⁵ Pa of vacuum in the chamber

Dynamic light scattering (DLS) and zeta-potential measurements: Size distribution was measured by DLS, using the Zetasizer Nano 3600 instrument (Malvern Instruments, UK), whose size range limit is 0.6 nm to 6 μ m (5 nm to 10 μ m for zeta-potential). Note: the diameter measured by DLS is the *hydrodynamic diameter*. The samples comprised aqueous dispersions of the nanoparticles in water or ethanol. All samples were diluted to obtain an adequate nanoparticle concentration. The data reported are mean values for each sample, which were measured in quadruplicate.

Infrared (IR) spectrophotometry: The IR spectra have been recorded using a Tensor 27 (Bruker) spectrophotometer equipped with a single-reflection diamond window ATR accessory (MKII Golden Gate, Specac).

Powder X-ray diffractometry (XRD): Powder XRD spectra were recorded at room temperature on a high-resolution texture diffractometer (PANalytical X'Pert PRO MRD) equipped with a Co-K α radiation source ($\lambda = 1.7903$ Å) and operating in reflection mode. The solid samples were placed in an amorphous silicon oxide flat plate and measured directly.

X-Ray Photoelectron Spectroscopy: Measurements were carried out in a Phoibos 150 analyzer (SPECS GmbH, Berlin,Germany) in ultra-high vacuum conditions (base pressure $1 \cdot 10 - 10$ mbar). A monochromatic Al K α X-ray source (1486.7 eV) operating at 400W was used. Wide scans were acquired at analyzer pass energy of 50 eV, while high resolution narrow scans were performed at constant pass energy of 20 eV and steps of 0.1 eV. The photoelectrons were detected at a takeoff angle $\Phi = 0^{\circ}$ with respect to the surface normal. The spectra were obtained at room temperature. The binding energy (BE) scale was internally referenced to the C 1s peak (BE for C–C = 284.8 eV).

Electronic absorption measurements: Absorption spectra were recorded on a Hewlett Packard 8453 spectrophotometer in the range 300-1000 nm.

BET (Brunauer -Emmett -Teller) surface area measurement: BET analysis was made using a conventional BET multi-point N2 physisorption apparatus (ASAP 2000 Physisorption Analyzer, Micromeritics Instruments Corp). The N₂ adsorption was measured from a six-point isotherm in a relative pressure rang of 0.05 to 0.3. The assumption for the cross-sectional area of N₂ was taken to be 16.2 Å²/mol and the density used was 3.65 g/cm³. The sample was prepared by heating at 100 °C for 24h

while simultaneously a flow of N_2 gas across the sample tube seeps away the liberated contaminants.



S2. FT-IR characterization

Figure S2a| FT-IR spectra of **CPP1** nanoparticles and comparison with hexadecylcatechol (*hdcat*) and 1,4-bis(imidazol-1-ylmethyl)benzene (*bix*) free ligands. The disappearance of the typical OH bands from cathecol ligand at 3115.0 and 3229.1 cm⁻¹, and the presence of the aliphatic chains at 2917.1 and 2849.8 cm⁻¹. The infrared spectra show that the catechol and bridging bix ligands are coordinated to the cobalt ions, as evidenced by the presence of characteristic C-O bands at 1480.5 and 1446.2 cm⁻¹ and the bands at 1649.4, 1520.2, and 1100.1 cm⁻¹ typical of the bix ligand.



Figure S2b. FT-IR spectra of non-functionalized CPP2 nanoparticles, octadecylamine free ligand (ODA) and functionalized CPP3 nanoparticles. The infrared spectra show that the catechol and bridging bix ligands are coordinated to the cobalt ions, as evidenced by the presence of characteristic C-O bands

around 1450 cm⁻¹ and typical bands of the bix ligand (1650, 1520, and 1100 cm⁻¹). The overlapping signals do not allow to distinguish in **CPP3** the disappearance of primary amine stretching signals (3350-3150 cm⁻¹) and the corresponding amide C=O ((1700 cm^{-1})) and NH bending ((1600 cm^{-1})) bands. However the typical sharp signals corresponding to the aliphatic chains of ODA can be clearly observed at 2923.4 and 2852.6 cm⁻¹.



S3. UV-Vis characterization

Figure S3: UV-Vis spectra of **CPP1** (brown line), **CPP2** (pink line) and **CPP3** (blue line). The absorption bands at $\lambda = 410$, 600, and 760 nm are ascribed to intra-ligand and metal-to-ligand/ligand-to-metal charge-transfer electronic transitions of the cobalt polymeric system.

S4. XPS Characterization of CPP1, CPP2 and CPP3 nanoparticles



Figure S4a: The XPS survey spectra of CPP1, CPP2 and CPP3



Figure S4b: Comparative XPS spectra of cobalt 2p (a), carbon 1s (b), nitrogen 1s (c), and oxygen 1s (d) for the different CPPs.

XPS results & discussion:

Cobalt 2p: The three samples showed closely the same cobalt pattern attributed to Cobalt (II) as main oxidation state for the metal ion. The binding energy for the main peak $Co2p_{3/2}$ signal appears at 780.5 eV and the satellite signal at 783.3 eV. The main peak for $Co2p_{1/2}$ is showed at 796.5 eV and the corresponding satellite at 802.3 eV. These data are in agreement with magnetic measurements that reveals a main population of Co(II) oxidation state at room temperature.

Carbon 1s: The XPS data for C 1s core level present slightly differences between the three samples. For **CPP1** a sharper C1s signal centred at 285.0 eV is observed and integrates the signals from the aromatic and aliphatic carbons, and O-bound aromatic carbons. Additionally, the **CPP2** nanoparticles showed a wider C1s signal that include the C=C group (284.6 eV) and a small shoulder at 288.7 eV corresponding to COOH groups presented in the caffeic acid ligand; and the **CPP3** nanoparticles present a shoulder at 286.9 eV that can correspond to the amide group (-CO-NH-) obtained from the condensation of the carboxylic group with the amine.

Nitrogen 1s: Nitrogen-related bands arising from the imidazole ring of bix ligand (401.3 eV and 398.9 eV) can be observed as main peaks in **CPP1** and **CPP2**. In the case of **CPP3** nanoparticles the presence of the additional amide chemical groups (400.1 eV)

generates a more complex signal (W. Liu et al J. Mater. Chem., 2012, 22, 18395-18402).

Oxigen 1s: Oxygen-related bands arising in **CPP1** only from the cathecol oxigen atoms bound to aromatic carbons (532.1 eV). In **CPP2** nanoparticles additionally the presence of C=O and C-O-H from carboxylic groups results in three main peaks between 531.2 - 532.9 eV. The wider signal for **CPP3** in comparison with **CPP1** reveals a contribution of oxygen signal from the amide group (-CO-NH-).

S5. Colloidal stability



re S5. SEM images of colloidal solutions of **CPP3** (two left images) and **CPP1** (two right images) nanoparticles after dispersion on EtOH and Hexane (insets: images of each dispersion after 2 days).

S6. BET measurements

Gas physisorption experiments showed similarities between **CPP2** and **CPP3**. However **CPP1** exhibit a notable difference concerning gas absorption. The BET measurement indicated that the **CPP1** nanoparticles have a specific surface area of 35.8429 ± 1.2541 m²·g⁻¹ (21.3686 m²·g⁻¹ of external area and 9.3063 nm of average pore diameter). **CPP2** nanoparticles present a surface area of 62.7665 ± 0.2770 m²·g⁻¹ (56.9692 m²·g⁻¹ of external area and 10.5042 nm of average pore diameter). Finally, **CPP3** nanoparticles present a surface area of 62.8507 ± 0.2547 m²·g⁻¹ (56.2517 m²·g⁻¹ of external area and 13.9287 nm of average pore diameter).

S7. Thermal characterization



Figure S7. TGA/DSC studies of (top) CPP3 nanoparticles and (bottom) CPP1 nanoparticles.



S8. CPP4 characterization

Figure S8a. FT-IR spectra of octadecylamine free ligand (**ODA**), **CPP4** nanoparticles, and nonfunctionalized Fe nanoparticles. The infrared spectra show that the catechol and bridging bix ligands are coordinated to the cobalt ions, as evidenced by the presence of characteristic C-O bands around 1450 cm⁻¹ and typical bands of the bix ligand (around 1650, 1520, and 1100 cm⁻¹). The overlapping signals do not allow to distinguish in **CPP4** the disappearance of primary amine stretching signals (3350-3150 cm⁻¹) and the corresponding amide C=O (-1700 cm⁻¹) and NH bending (-1600 cm⁻¹) bands. However the typical

sharp signals corresponding to the aliphatic chains of ODA can be clearly observed at 2923.9 and 2853.1 cm^{-1} .



Figure S8b. SEM images of CPP4 nanoparticles at different magnifications.

References

¹ P. K. Dhal, F. H. Arnold *Macromolecules* **1992**, *25*, 7051.

² J. Saiz-Poseu, J. Faraudo, A. Figueras, R. Alibes, F. Busqué, D. Ruiz-Molina *Chem. Eur. J.* **2012**, *18*, 2056.

³ F. Novio, J. Lorenzo, F. Nador, K. Wnuk, D. Ruiz-Molina Adv. Healthcare Mat. Submitted.