SUPPORTING INFORMATION

Reversible Magnetic Mercury Extraction from Water

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Materials and Methods

Commercially available chemicals were used without further purification. NovaPEG amino resin Novabiochem® (batch number: S6625326; loading: 0.59 mmol/g) was purchased from Merck KGaA. Column chromatography was performed with silica gel (Merck, Geduran 60, 0.063-0.200 mm particles size) and flash silica gel 60 (Merck, 0.04-0.063 mm particles size). ¹H NMR spectra were recorded on BRUKER Avance III 400 "Nanobay" (400 MHz) and BRUKER Avance 300 (300 MHz) spectrometer. ¹³C NMR spectra were recorded on BRUKER Avance III 400 "Nanobay" (101 MHz) and BRUKER Avance 300 (75 MHz) spectrometer. Attenuated total reflection infrared spectroscopy (ATR-IR) was carried out on a Biorad Excalibur FTS 3000, equipped with a Specac Golden Gate Diamond Single Reflection ATR-System or a Varian FTS 1000 spectrometer. Solid and liquid compounds were measured neatly and the wavenumbers are reported as cm⁻¹. Mass spectrometry was performed using a Finnigan ThermoQuest TSQ 7000 at the Central Analytical Laboratory (University of Regensburg). Elemental microanalysis was carried out by the micro analytical department of the University of Regensburg using a Vario EL III or Mikro-Rapid CHN apparatus (Heraeus). The inductively coupled plasma optical emission spectrometry (ICP-OES) was measured on a Spectroflame EOP (Spectro) at the University of Regensburg while the atomic fluorescence spectroscopy (AFS) was performed at Bachema AG Switzerland. Termogravimetric analysis (TGA) was done on a TGA 7 (Perkin Elmer). X-Ray Photoelectron Spectroscopy (XPS) analysis was performed at SuSoS (Switzerland). A PhI5000 VersaProbe spectrometer (ULVAC-PHI, INC.) equipped with a 180° spherical capacitor energy analyzer and a multi-channel detection system with 16 channels was used. Spectra were acquired at a base pressure of 5•10⁻⁸ Pa using a focused scanning monochromatic Al-Ka source (1486.6 eV) with a spot size of 200 um. The instrument was run in the FAT analyzer mode with electrons emitted at 45° to the surface normal. Pass energy used for survey scans was 187.85 eV and 46.95 eV for detail spectra. Charge neutralisation utilizing both a cool cathode electron flood source (1.2 eV) and very low energy Ar^+ –ions (10 eV) was applied throughout the analysis. Data were analyzed using the program CasaXPS [Version 2.3.12 www.casaxps.com]. The signals were integrated following Shirley background subtraction. Sensitivity factors were calculated using published ionization cross-sections (Scofield, J. H. J. Elec. Spec. Rel. Phen. 1976, 8, 129.) corrected for attenuation, transmission-function of the instrument and source to analyzer angle. As a result, the measured amounts are given as apparent normalized atomic concentration and the accuracy under the chosen condition is approximately $\pm 10\%$.

Synthesis of PAMAM Dendrimers

The synthesis of PAMAM dendrons was done according to a procedure described elsewhere.¹ Herein propargyl amine (1.0 equiv.) was reacted with methylacrylate (83 equiv.) under N_2 at room temperature giving rise to the dendron G0.5 (95%). Then ethylenediamine (60 equiv.) was added to the dendron (1.0 equiv.) to yield Dendron G1 with two amino functional groups (98%). After repetition of these two steps, consecutive generations of the dendrons could be obtained in good yields. For every half-generation dendron purification by silica column chromatography was required. NMR and EI-MS are in accordance with the literature values.¹

Synthesis and Characterization of Magnetic Co/C-PAMAM G2 (4) and Co/C-PS-PAMAM G2 (5)

In a typical experiment, 100 mg of azide functionalized nanoparticles **2** and **3** (1.0 equiv.) and 5 equivalents of the respective PAMAM dendrons were used. The PAMAM was previously dissolved in 5 mL of a THF/H₂O 3:1 mixture followed by the successive addition of Co/C- N₃ nanobeads **2** or **3**, Na-ascorbate (30 mol%) and CuSO₄ (10 mol%). Afterwards the reaction mixture was sonicated for 15 minutes and stirred for 48 hours at room temperature. The magnetic nanoparticles were separated applying an external magnet and washed with acetone (5 x 5 mL), H₂O (5 x 5 mL) and acetone (3 x 5 mL). In the end the nanobeads were dried under vacuum. The reactions were monitored by ATR-IR and the loadings estimated by TGA.

Co/C-PAMAM G2 (4): TGA (N₂): 0.02 mmol/g. Co/C-PS-PAMAM G2 (5): TGA (N₂): 0.6 mmol/g.



Figure S1. IR spectra of the azide tagged nanoparticles 2 (blue) and 3 (yellow) and the subsequent PAMAMclicked magnetic beads 4 (red) and 5 (green).



Figure S2. TGA spectra of the azide tagged nanoparticles **2** (blue) and **3** (yellow) and the subsequent PAMAMclicked magnetic beads **4** (red) and **5** (green). The loadings can be estimated from the weight loss % of the materials.



Figure S3. Magnetization of the pristine Co/C 1 (black) and functionalized nanoparticles 4 (red) and 5 (green) obtained from SQUID measurements at RT.

Synthesis of Magnetic Co/C-PEI 7²

Amino-functionalized carbon-coated Cobalt nanoparticles 6^3 (Co/C-NH₂) (946 mg, 0.1 mmol, 1.0 equiv.) were pre-dispersed in 95 mL DCM using an ultrasonic bath for 15 min. Under stirring, aziridine (5.4 mL, 103.6 mmol, 1000 equiv.) and conc. HCl (141.6 µL)) were added to the reaction mixture which then was heated to 80 °C for 48 h. Afterwards the NPs were collected using an external magnet, washed with DCM (2 x 50 mL), H₂O (5 x 50 mL) and again DCM (3 x 50 mL). Then the nanobeads were dried under vacuum at 50 °C. As the degree of polymerization was not satisfactory the whole procedure was repeated using 500 mg of the herein synthesized nanoparticles (1.0 equiv.) in 49 mL DCM, 2.85 mL aziridine (1000 equiv.) and 100 µL conc. HCl. After a reaction time of 69 h the extent of polymerization was estimated by TGA (66 wt%).

IR (v/cm⁻¹):3417, 2934, 2821, 2362, 1648, 1604, 1458, 1351, 1298, 1014.

Elemental microanalysis [%]: C, 30.46; H, 7.09; N, 14.97; Loading (N): 10.6 mmol N / g nanoparticles



Figure S4. Structure confirmation by IR spectra of C/Co nanoparticles functionalized with phenylethylamine 6 (top) and poly(ethyleneimine) 7 (bottom).²



Figure S5. TGA analysis of the phenylethylamine coated NPs 6 (red) PEI-coated NPs 7 (blue) to estimate % of polymerization.²



Figure S6. A) comparison of the magnetization values obtained for the PEI-functionalized 7 (blue) and Co/C 1 (red) nanoparticles, measured at RT (SQUID); B) TEM picture of the PEI functionalized nanoparticles 7^2 .





NovaPEG Amino Resin-PEI 9

The commercially available NovaPEG amino resin **8** (50 mg, 29.5 μ mol, 1.0 equiv.) was pre-swollen in 5 mL DCM. Then aziridine (775 μ L, 14.9 mmol, 506 equiv.) and conc. HCl (15.5 μ L) were added under stirring. The resulting reaction mixture was heated to 80 °C for 24 h. Afterwards the resin was filtered off, washed with DCM (2 x 20 mL), H₂O (5 x 20 mL) and DCM (3 x 20 mL) and dried under vacuum at 50 °C.

IR (v/cm⁻¹): 3413, 2936, 2823, 1653, 1614, 1457, 1357, 1292, 1098.

Elemental microanalysis [%]: C, 38.27; H, 8.18; N, 16.24. Loading (N):.10.9 mmol/g.

TGA (N₂): 65 wt% PEI.



Figure S8. IR spectra of NOVA PEG Amino Resin 8 (top) and NOVA PEG Amino Resin-PEI 9 (bottom).



Extraction Studies and Characterization of the NPs

Figure S9. Selectivity extraction of Hg^{2+} using the PEI-functionalized resin **9** in the presence of competitive metal ions. 100 mL aqueous solution was decontaminated within 10 minutes using 3 mg of NOVA PEG amino resin-PEI **9**.



Figure S10. Selectivity extraction of Hg^{2+} using the PEI-functionalized nanoparticles 7 in the presence of competitive metal ions. 100 mL aqueous solution at pH 8 was decontaminated within 10 minutes using 3 mg of NPs 7.



Figure S11. TEM pictures of the Co/C-PEI NPs 7 before (A) and after recycling process (B).

X-Ray Photoelectron Spectroscopy

XPS analysis was performed on 3 samples of Co/C nanoparticles after extraction of metals:

- SF-214.1: Co/C 1 after the extraction of HgCl₂
- SF-214.2: Co/C-PEI 7 after the extraction of HgCl₂
- SF-214.3: Co/C-PEI 7 after the extraction of HgCl₂⁻ from a mixture of different metal salts (HgCl₂⁻, BaCl₂.2H₂O⁻, CuCl₂⁻, CrCl₃•6H₂O, PbCl₂⁻, Ni(C₅H₇O₂)₂)

Results:

- SF-214.1 (Co/C NPs 1): The metallic Co core of the particle can still be detected, indicating, that the Ccoating is less than 10 nm thick. Mercury is oxidized with a binding energy for the Hg 4f7/2 peak of 101.1 eV.
- SF-214.2 (Co/C-PEI 7): The metallic Co core of the particle is not detected anymore on these particles. Hg is detected, also in its oxidized form (Hg 4f7/2 peak of 101.5 eV).
- SF-214.3 (Co/C-PEI 7): The metallic Co core of the particle is not detected anymore on these particles. Hg is detected (3.6 At.-%), also in its oxidized form (Hg 4f7/2 peak of 101.9 eV). Additionally some Cu (0.6 At.-%) was detected. Ni, Cr, Pb and Ba could not be detected.

Table 1. Normalized At.-% of all detected elements.

	At%	Со	Hg	Cu	Ba	Pb	Cr	Ni
Co/C 1	SF-214.1	8.0	1.5	N/A	N/A	N/A	N/A	N/A
Co/C-PEI 7	SF-214.2	0.0	0.4	N/A	N/A	N/A	N/A	N/A
Co/C-PEI 7	SF-214.3	0.0	3.6	0.6	0.0	0.0	0.0	0.0
N/A- not applicable								



Figure S11. Survey spectra of the powder samples (binding energy is calibrated to C-C at 284.5 eV): SF-214.1 (red; Co/C **1** after the extraction of HgCl₂), SF-214.2 (green; Co/C-PEI **7** after the extraction of HgCl₂), SF-214.3

(pink; Co/C-PEI 7 after the extraction of HgCl₂⁻ from a mixture of different metal salts (HgCl₂⁻, BaCl₂2H₂O⁻, CuCl₂⁻, CrCl₃•6H₂O, PbCl₂⁻, Ni(C₅H₇O₂)₂).

References

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