Clickable Complexing Agents: Functional Crown Ethers for Immobilisation Onto Polymers and Magnetic Nanoparticles

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Crown ethers and monoazacrown ethers supported onto well defined cobalt and Fe_3O_4 magnetic nanoparticles have been prepared and used as magnetically recoverable extracting materials for Pb^{2+} from aqueous and organic solutions. The assembly of the functional nanoparticles involves the integration of the complexing units by means of a copper-catalysed alkyne–azide cycloaddition reaction leading to a 1,2,3-triazole linker. The same binding motifs have been also used to functionalise polystyrene (PS) and polystyrene-polyethyleneglycol (PS-PEG) resins, and the resulting materials were also employed in the removal of Pb^{2+} from solutions. The relative merits of these two approaches are compared.

Introduction

Crown ethers, for their extraordinary ability to bind cations, have revolutionised the field of coordination chemistry since its introduction in the late 60's of the last century.[1] The removal of metal ions from aqueous and organic solutions is a subject of great interest due to the high environmental impact associated with the presence of toxic heavy metal (e.g. As^{III}, As^V, Cd^{2+}, Hg^{2+} and Pb^{2+}) in clean and waste waters,[2] the recovery of highly valuable metals used in industry and jewellery (e.g. Pt, Pd or Au)[3] and even the removal of metals from the body after exposure and contamination.[4]

A potentially important, yet underdeveloped approach for the removal of metal cations from solutions is represented by the use of complexing agents that could be readily separated from the solution once loaded with the target contaminants. Metal oxides, for instance, have the ability to bind metal ions in solution, by adsorption and ion exchange mechanisms.[5] Therefore, a number of remediation techniques make use of the sorptive and extracting properties of metal and metal oxide nanomaterials to remove or stabilise inorganic, organic and radioactive contaminants.[6]

Functional magnetic nanoparticles (MNPs)[7] stabilized with ligands that have the ability to coordinate metal cations could be applied in metal recovery and in decontamination processes. In this approach, the ligands decorating the nanoparticle's surface would bind the cations, and the nanoparticles could then be removed from the solution by the application of an external magnetic field. Recently, some examples of this approach have appeared in the literature.[8] MNPs encapsulated by a thiol containing polymer have been used as adsorbent for Pb^{2+}, Ag^+ and Hg^{2+}.[9] Also, thiol functionalised superparamagnetic iron oxide (Fe_3O_4) nanoparticles (5.8 nm) have been reported for the removal of heavy metal ions from aqueous solutions,[10] and a fluorescent receptor for Pb^{2+} has been reported using a diaza-*s*-indacene ligand bound to magnetic nickel nanoparticles (30-40 nm).[11] In a recent report, an ethylenediamine tetraacetic acid-like ligand has been placed onto the surface of carbon coated nanomagnets and used in the removal of cadmium, lead and copper from contaminated water.[12]

Polymeric materials can also be used for the separation of metal ions from solutions. Setting apart the classical ion exchange resins, a more specific interaction with the metal ion can be achieved through the functionalisation of polymers with ligands containing donor atoms with affinity for the target metal. For example aminobenzo-18-crown-6 and aminomethyl-18-crown-6 ethers bonded to Merrifield resin have been used for the separation of alkaline and alkaline-earth isotopes (Li^+, Mg^{2+})[13] and aza-crown ethers immobilised onto a copolymer of ethylene glycol methacrylate and glycidyl methacrylate were used in the extraction of metal ions (Ag^+, Pb^{2+}, Cd^{2+}) from aqueous solutions.[14]

We reasoned that, for future applications, it would be interesting to develop immobilisation strategies suitable for the incorporation of the same complexing agents onto different platforms. In this way, *libraries* combining sets of receptors with sets of suitably functionalized supports (organic polymers and magnetic nanoparticles) could be easily constructed and this could allow the ready optimization of the resulting modular detoxification agents for specific situations.

Probably the most general synthetic strategy available today for the predictable and fully reliable combination of molecular fragments is the copper-catalyzed alkyne-azide cycloaddition (CuAAC) reaction,[15] the archetypal example of click chemistry.[16] Over the last years, we and other groups[17,18] have demonstrated the validity of this strategy for the immobilization of catalytic species without negative effects on either catalytic activity or stereoselectivity, and we considered that it would be particularly suitable for the purpose of this research.[19,20]

As part of the ongoing work in our group on the preparation of functional ε-cobalt[21] and Fe_3O_4[22] magnetic nanoparticles (MNPs) as easily recoverable and reusable catalysts,[23] we decided to use these nanomaterials, functionalized in their surfaces with azido groups, as platforms for the grafting of cation receptors. In the same manner, azido-functionalised polystyrene (PS, Merrifield type) and polystyrene-polyethyleneglycol (PS-PEG) resins would also be used as immobilization platforms. This set of materials could provide different alternatives with respect to the nature of the solution to be detoxified (aqueous or organic) and with respect to the separation technique to be used (simple filtration or magnetic decantation).
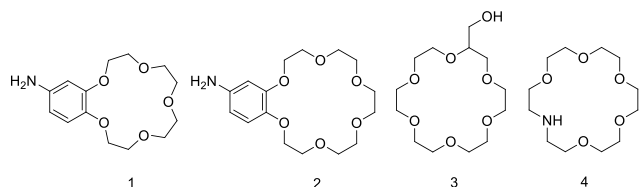
Figure 1 Crown ethers and azacrown ethers suitable for the preparation of metal extracting composites.

Crown ethers and aza-crown ethers **1-4** (Figure 1) are suitable binding motifs for their ready availability and for the high selectivity depicted in front of various types of metal ions and for their adaptability to the strategy envisaged for anchoring them to the different platforms. Thus, all of them can be easily functionalized by alkylation to species containing terminal alkyne moieties. These structures are well known for their ability to act as ligands for a wide range of metal ions and cationic organic species[24] for different purposes but, to our knowledge, MNPs functionalised with crown ether have not yet been used for the removal of cations from solutions.[25]

We report in the present paper the preparation of a family of immobilised functional crown ethers prepared according to the principles outlined above. Units **3** and **4**, involving binding through different atoms and positions (exo- and endocyclic) were selected for this study. As a model system to test their performance we have selected the extraction of Pb^{2+} from aqueous and organic solutions. The 18-crown-6 and 1-aza-crown-6 units have been shown to bind this metal cation with a significant association constant. According to literature data, association constants for the binding of the unsubstituted 18-crown-6 with Pb^{2+} are in the range of $\log K = 3.58\text{-}4.27$ in water,[26,27] $\log K = 6.99$ in methanol,[27] and $\log K = 6.5$ in a 70:30 v/v methano:water mixture,[28] while the 1-aza-18-crown-6 (**4**), binds to Pb^{2+} with an even larger association constant, $\log K = 8.4$ in a methanol/water (95:5 v/v) mixture, at 25ºC.[29]

Results and discussion

Synthesis of functionalised cobalt nanoparticles

Monodisperse cobalt nanoparticles can be synthesised through the thermal decomposition of organometallic compounds in high-boiling organic solvents containing stabilizing surfactants.[30] Puntes *et al.* reported the use of cobalt octacarbonyl $[Co_2(CO)_8]$ in the presence of a mixture of surfactants as a way to obtain ε-phase Co nanoparticles.[31,32] Surface functionalisation of these nanoparticles can be achieved by incorporating to the surfactant mixture used during their synthesis long chain carboxylic acids functionalised at the ω-position with the desired groups.[21c] For this purpose we prepared bifunctional molecules that contained a carboxy group at one end (for immobilisation purposes) and a crown ether (for cation binding purposes) at the other end.

For the assembly of functional cobalt nanoparticles **6a-b** it was more convenient to follow a slightly modified procedure where the functional units **5a-b** were prepared in a separate step, being then used as ligands for cobalt nanoparticles generated in their presence (Scheme 1).[31] The implementation of this procedure

required the prior preparation of both 11-azidoundecanoic acid[33] and propargyl derivatives of crown ethers **3-4**. These intermediates were then cycloadded through a well established protocol for CuAAC reactions, using $CuSO_4$/sodium ascorbate in a 1:1 mixture of water and *tert*-butyl alcohol under microwave irradiation (see ESI). With compounds **5a-b** in hand, functionalised nanoparticles **6a-b** were prepared (Scheme 1). In both cases, transmission electron microscopy (TEM; see Figure 2 for the case of **6a**) showed the formation of regular, spherical nanoparticles. Elemental analysis of the materials confirmed the presence of nitrogen containing species on the surface of the nanoparticles.
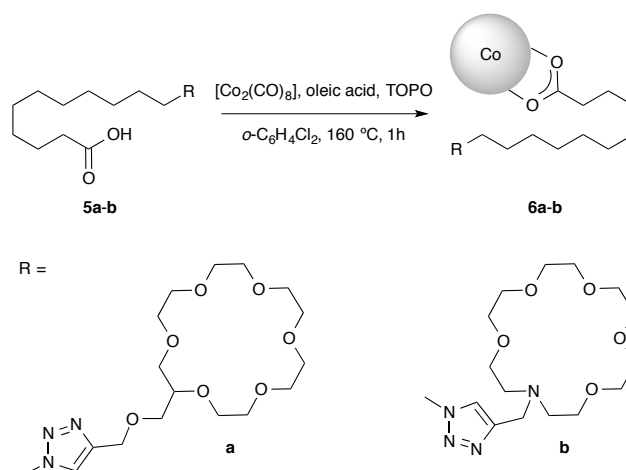
Scheme 1 Preparation of functionalised cobalt nanoparticles. TOPO= trioctylphosphine oxide.
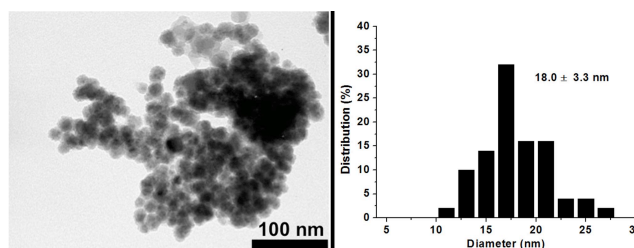

Figure 2 TEM image and size distribution of cobalt nanoparticles **6a**.

The nitrogen content (%N) allowed us to calculate the degree of ligand incorporation onto the nanoparticles. The functionalisation was 0.091 mmol/g for **6a** and 0.113 mmol/g in the case of **6b**.
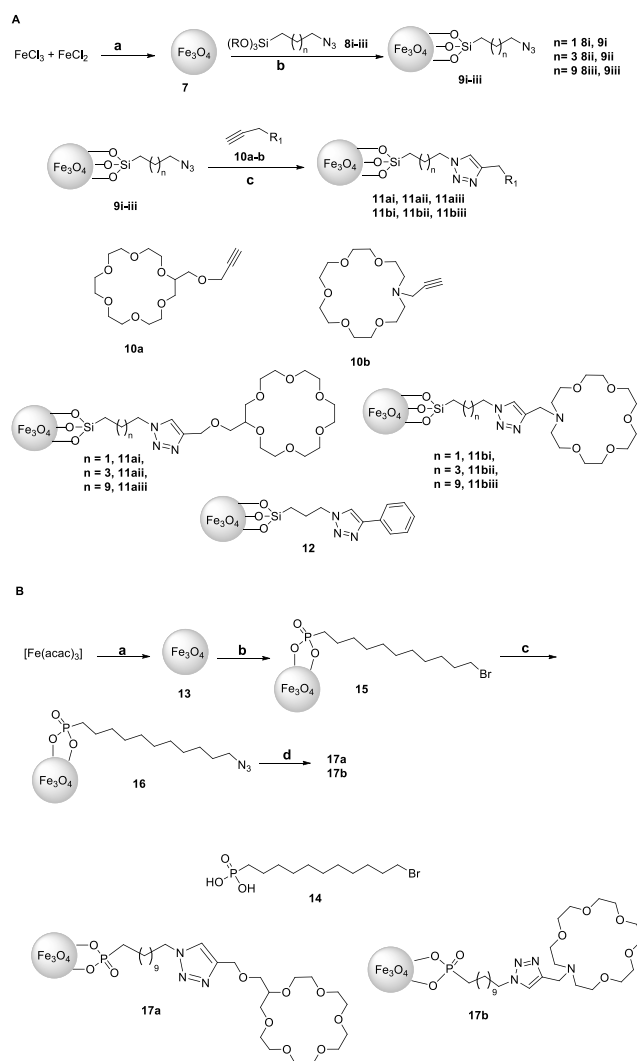
Synthesis of functionalised iron oxide nanoparticles

ε-Cobalt nanoparticles, although showing well-controlled shapes and allowing high levels of functionalisation, present the inconvenient of a rather cumbersome preparation: high temperatures are required to induce the decomposition of $[Co_2(CO)_8]$ and the isolated yield of nanoparticles is usually low. To avoid these difficulties the use of readily available Fe_3O_4 nanoparticles as an alternative support was pursued. To modify the surface of the iron oxide nanoparticles, a ligand exchange reaction can be used starting from the as-prepared oleic acid

stabilised MNPs. We investigated two different types of functional agents suitable for this purpose, namely alkoxysilanes with variable chain length and phosphonic acid derivatives. Fe_3O_4 nanoparticles coated with alkoxysilanes were prepared following the route shown in Scheme 2A. In the first step, oleic acid stabilised nanoparticles **7** were produced by coprecipitation of aqueous solutions of Fe^{II} and Fe^{III} chlorides with ammonium hydroxide, in the presence of oleic acid following a previously reported procedure.[34] In this manner, fairly disperse Fe_3O_4 nanoparticles of 8.4 ± 2.6 nm mean diameter (Figure 3, a) were obtained (see ESI for X-ray diffraction spectrum). The presence of oleic acid on the nanoparticle surface was confirmed by IR spectroscopy (Figure 4).[35,36] ω-Azidoalkyltrialkoxysilanes **8i-iii**, which would be placed in the surface of the magnetite nanoparticles for further functionalisation through CuAAC reactions were prepared by standard procedures (see ESI).[37] Then, the functionalisation of the oleic acid stabilised nanoparticles was achieved following a ligand exchange process previously reported,[36] (Scheme 2A, step b). In all cases spherically shaped 7–10 nm nanoparticles were obtained as shown by TEM images (Figure 3b). The incorporation of the ω-azidoalkyltrialkoxysilane in nanoparticles **9i-iii** was evidenced by IR spectroscopy, through the appearance of a band at around 2097 cm^{-1}, corresponding to the N_3 asymmetric stretching and the appearance of bands between 1020-1050 cm^{-1}, due to Si-O-Si vibrations (Figure 4).[36] What is more, the almost complete disappearance of the bands at 3005 cm^{-1} (=C-H) and 1684 cm^{-1} (C=C) evidenced the effective exchange of the oleic acid ligand by the different ω-azidoalkyltrialkoxysilanes.[38] Nitrogen elemental analysis allowed the calculation of the degree of ligand incorporation onto the nanoparticles (f = 0.238[%N]). The determined functionalisation were 0.480 mmol/g for **9i**, 0.297 mmol/g for **9ii**, and 0.233 mmol/g for **9iii**.[39] Finally, the incorporation of the cation binding units **10a** and **10b** onto the MNP was carried out using the CuAAC reaction in dimethylformamide (DMF), with CuI as catalyst in the presence of *N,N*-diisopropylethylamine (DIPEA). Following this procedure six new types of silane-coated iron oxide nanoparticles (**11ai-iii** and **11bi-iii**) were prepared, incorporating two different macrocycles on their surfaces and three different spacers (with 3, 5 or 11 carbon atoms) between the 1,2,3-triazole unit and the surface of the nanoparticle. The incorporation of the ion-binding units onto the nanoparticles could be easily monitored by IR spectroscopy. This showed the disappearance of the azide band at 2097 cm^{-1} while the presence of the macrocycles was shown by the appearance of a band at *ca.* 1105 cm^{-1}, as can be seen in Figure 4 for the case of **11biii**. The functional nanoparticles **11** were obtained as a mixture of small aggregates and discrete particles of 9 to 11 nm (TEM images Figure 3, c and d), no change in the appearance or size of the nanoparticles being observed over the CuAAC reactions. Additionally, functional nanoparticles **12** obtained by CuAAC reaction of phenylacetylene with azide nanoparticles **9i** were prepared (see ESI), to evaluate any possible effect of the triazole ring on the extraction of metal ions. In this case, the tris(triazolyl)methanol copper(I) chloride complex, [CuCl(TTM)],[40] was used as the catalyst to promote the CuAAC reaction. Elemental analysis (%N) indicated a functionalisation of 0.32 mmol/g for the resulting MNPs.

As a preliminary step for the preparation of nanoparticles **17**, where binding with the functional unit takes place through interaction with a phosphonic acid group (Scheme 2B), the preparation of 11-bromoundecylphosphonic acid (**14**) was first required. This was achieved through a five-step sequence starting from 11-bromoundecanol (see ESI for full details).[41]

Scheme 2 A) Preparation MNPs of Fe_3O_4 functionalised with cation binding groups. Conditions: a) Oleic acid, 30% NH_3, H_2O, 80 ºC, 30 min; b) Acetic acid, toluene, rt, 5 days or 100 ºC, 24 h; c) CuI, DIPEA, DMF, 40 ºC. B) Preparation of functional iron oxide nanoparticles coated with phosphonic acid derivatives. Conditions: a) Oleic acid, oleylamine, 1,2-hexadecanediol, benzyl ether, 200 ºC, 2 h, then 300 ºC, 1 h; b) **14**, $CHCl_3$, rt, 24 h; c) NaN_3, DMF, 65 ºC, 12 h; d) **10a** or **10b**, CuI, DIPEA, DMF, 40 ºC.

Compound **14** was then grafted onto the surface of 6.2±2.0 nm oleic acid/oleylamine stabilised iron oxide nanoparticles **13** prepared by the thermal decomposition method reported by Sun.[42] The functionalisation reaction was performed in chloroform and the incorporation of **14** was evidenced in the IR spectrum of MNPs **15** (Figure 5) by the appearance of very intense bands in the region between 1260 and 850 cm^{-1} that have been assigned to P-O and P-O-Fe stretchings.[20a] The obtained nanoparticles were spherically shaped (6.4±1.0 nm) and well dispersed (see ESI for TEM images). The degree of ligand

incorporation onto the nanoparticles was determined to be 2.36 mmol/g by quantitative phosphorus determination.
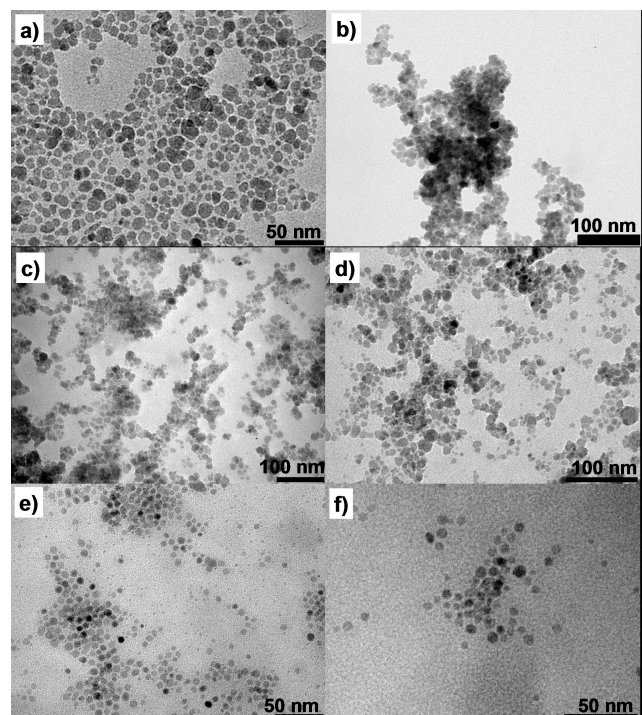

Figure 3 TEM images of a) MNPs **7**, b) azide functionalised MNPs **9i**, c) and d) MNPs after the functionalisation with crown ethers derivatives (**11ai** and **11bi**), e) and f) MNPs **17a** and **17 b**.
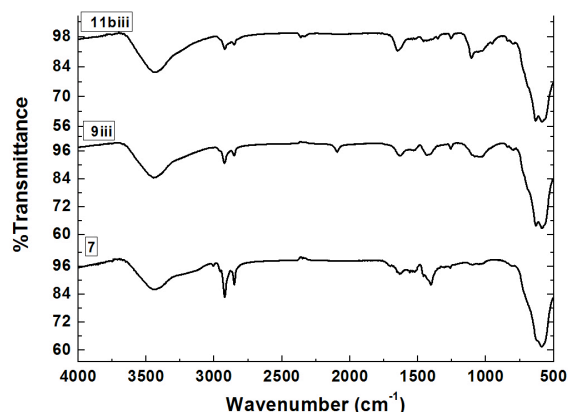

Figure 4 IR spectrum of MNPs **7**, azide functionalised MNPs **9iii** and MNPs after the incorporation of the azacrown ether residue (**11biii**).

Magnetic nanoparticles **15** were next transformed into the ω-azidoalkylphosphonyl functionalised nanoparticles **16** (5.6±1.0 nm) by reaction with an excess of sodium azide in DMF at 65 ℃ (Scheme 2B, step c), a transformation evidenced by the appearance of the strong N$_3$ band in the IR spectrum (Figure 5) at 2097 cm^{-1}. The presence of nitrogen in the surface of the nanoparticles was confirmed by elemental analysis and the degree of functionalisation of MNPs **16** was found to be 2.2 mmol/g. For the incorporation of the metal-binding units, ω-azidoalkylphosphonyl functionalised MNPs **16** were reacted with alkynes **10a** and **10b** with CuI catalysis. The presence of the macrocycles in the resulting MNPs **17a-b** was evidenced by the

appearance of bands at around 1100 cm^{-1} and 1353 cm^{-1} in the IR spectrum (Figure 5).
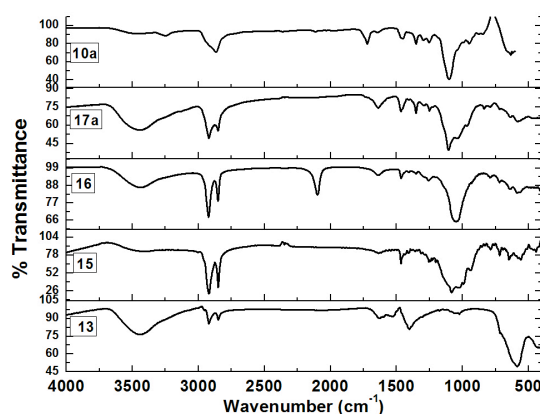

Figure 5 IR spectrum of MNPs **13**, bromo functionalised MNPs **15**, azide functionalised MNPs **16** and MNPs after the incorporation of the crown ether residue (**17a**). For comparison the spectrum of **10a** was included.
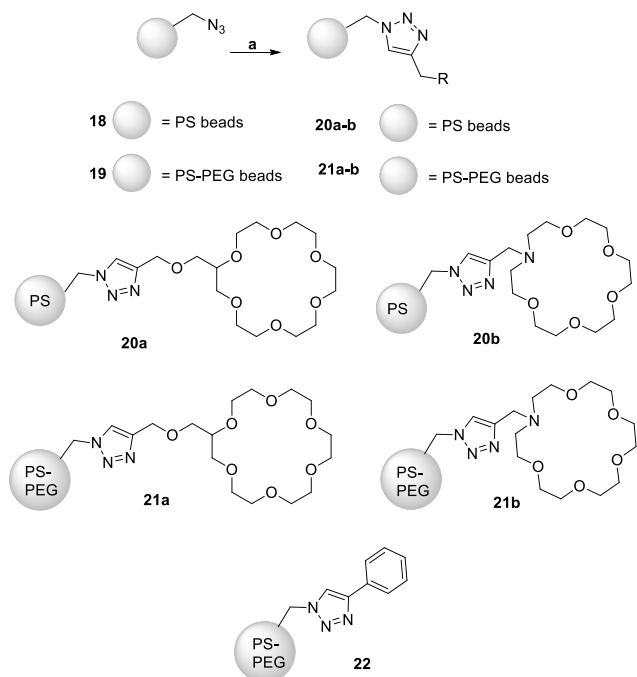
The loading of the binding units in the ready-to-act MNPs was determined by elemental analysis (%N), being 1.0 mmol/g for **17a** and 1.27 mmol/g for **17b**. TEM images (Figure 3e and 3f) indicated that the macrocycle-functionalised nanoparticles had a narrow size distribution, with average diameters of about 6.0 nm. Moreover there was no change neither in size nor in the spherical shape of the nanoparticles during the functionalisation reactions.

Preparation of functionalised polystyrene and polystyrene-polyethyleneglycol resins.

(Azidomethyl)polystyrene (**18**) and (2-azidoethoxy)polystyrene-polyethyleneglycol (**19**) were prepared by reaction of the corresponding halogenated commercial resins with sodium azide following previously reported procedures.[17b,17d] Alkynes **10a** and **10b** were reacted with the azide-functionalised polymers using CuI/DIPEA as catalyst and a 1:1 DMF/THF mixture as solvent (Scheme 3). The completeness of the reaction was established by IR spectroscopy, in a similar fashion as with the iron oxide nanoparticles (see above). The obtained resins **20a-b** and **21a-b** have extractant loadings of around 0.2 mmol/g for the PS-PEG polymers and around 0.6 mmol/g for the PS resins (determined by nitrogen elemental analysis). These functionalisations accurately reflect those of the starting commercial resins (see ESI). To evaluate any possible contribution of the triazole unit to the extraction of metal ions, functional PS-PEG resin **22** was also prepared by CuAAC reaction with phenylacetylene.

Scheme 3 Preparation of crown ether-functionalised polymers. Conditions: a) **10a** or **10b**, CuI, DIPEA, 1:1 DMF/THF, 40 ºC, 1-5 days.

Metal extraction experiments

Once the different types of extracting materials were prepared and fully characterised, their ability to extract metal ions from aqueous and organic solutions was evaluated. The main goal of these studies was the identification of optimal combinations of support and complexing agent for specific situations (solvent nature, pH of aqueous solutions), and also determining the influence of additional factors (immobilization strategy, complexing unit loading) on the performance of these combinations. To perform these studies, the extraction of Pb^{2+} from aqueous and organic solutions was selected as a representative and yet not fully solved case.[43]

Extraction with MNPs

The metal extracting capability of the nanoparticles was investigated by placing the extracting material in contact with either aqueous or acetonitrile solutions of $Pb(ClO_4)_2$ of known concentration ($[Pb]_{initial}$). The samples were shacken in a closed flask for the specified period of time, and then the nanoparticles were separated with the help of an external magnet. The resulting clear solution was analysed to determine the final concentration of Pb^{2+} ($[Pb]_{final}$). Both concentrations of Pb^{2+} were determined by flame atomic absorption spectroscopy (FAAS). The amount of lead that was extracted from the solution by the nanoparticles was calculated according to equation 1.

$$\% \text{ Pb extracted} = 100 \times ([Pb]_{initial} - [Pb]_{final})/ [Pb]_{initial} \qquad (1)$$

Table 1 shows the results for the removal of Pb^{2+} from acetonitrile solutions, using functionalised cobalt and iron oxide nanoparticles. Extractant **6a**, functionalised with a 18-crown-6 ether was first tested. Interestingly, up to 79% of the initially present cation was removed from solution (entry 1). In a similar manner, a significant amount of Pb^{2+} was also removed form the solution using extractant **6b** (entry 2).

Functionalised iron oxide nanoparticles were also employed in the removal of Pb^{2+} from acetonitrile solutions. Also in this case, the nanoparticles are able to bind and remove Pb^{2+} from the solution (entries 3 and 4, Table 1). However the extracted percentages are much smaller than in the case of cobalt nanoparticles. In particular, for the case of **11bi**, just 10% of the Pb^{2+} was removed because the nanoparticles were dissolved in the solution, and could not be separated by the external magnetic field.

Table 1 Extraction of Pb^{2+} from CH_3CN solutions using functionalised Co and Fe_3O_4 nanoparticles.

	Entry	Extractant	Extractant to Pb^{2+} ratio	Contact time /h	% Pb extracted[a]
Functionalised ε-Cobalt nanoparticles	1	**6a**	1:1	21	79(1)
	2	**6b**	1:1	21	68(1)
Functionalised Fe_3O_4 nanoparticles	3	**11ai**	1:1	21	47(1)
	4	**11bi**[b]	1.5:1	21	10(1)

[a]Mean values of two independent determinations. Observed result variability is given in parentheses. [b]Nanoparticles of 8.1 nm diameter and f = 0.604 mmol/g were used.

In view of the promising results obtained in the removal of lead cation from acetonitrile solutions, we decided to test the behaviour of our systems in aqueous media. Table 2 shows data of the extracting experiments using functional iron oxide MNPs, in the removal of Pb^{2+} from aqueous solutions.

Table 2 Extraction of Pb^{2+} form aqueous solutions using functionalised Fe_3O_4 nanoparticles.

Entry	Extractant	Contact time /h	Extractant to Pb^{2+} ratio	% Pb^{2+} extracted[a]
1	**11ai**	41	1:1	29(1)
2	**11bi**	41	1:1	21(1)
3	**11aii**	41	1:1	45(4)
4	**11bii**	41	1:1	30(6)
5	**11aii**	41	2:1	66(3)
6	**11aiii**	41	1:1	53(5)
7	**11biii**	41	1:1	62(1)
8	**9i**	41	1.5:1	2(1)
9	**12**	41	2:1	14(1)
10	**17a**	21	1:1	49(4)
11	**17b**	21	1.1	38(2)
12	**17a**	21	2.8:1	92(2)
13	**17a**	41	2.6:1	86(4)

[a]Mean values of two independent determinations. Observed result variability is given in parentheses.

Using an equimolar amount of extracting groups and metal cations in solution, between 21% to 62% of the Pb can be removed from the aqueous solution in a single operation. The nanoparticles containing the 18-crown-6 moiety in combination

with the shorter, more readily available spacers (n = 1 and 3) allow higher extraction percentages than those bearing monoaza-18-crown-6 units. In general, as the chain length increases a slightly positive effect on the extraction values is noted independently of the nature of the extracting unit. In order to secure that the extracting power of these materials arises from the binding units present in their structures, control experiment were performed with MNPs **9i** (<2%, entry 8) and **12** (14%, entry 9). This last result seems to indicate that the triazole group can contribute to some extent to the extraction of lead cations from the aqueous solution. As we will see later, this impression is not confirmed by the results obtained with the same complexing agents clicked on polymers. Functional nanoparticles **17a** and **17b**, where the functional unit is bonded to the magnetic core through a phosphonate unit, were also used in the extraction experiments from aqueous solution. The experiments were performed in a similar manner as with MNPs **11**, and the results are also shown in Table 2 (entries 10-13). Again, 18-crown-6 functionalised nanoparticles seem to be more effective than monoaza-18-crown-6 in removing lead from the solutions achieving nearly a 49% of removal with **17a**. Interestingly, when a 2.8:1 ratio of extractant was used, 92% of the initially present metal loading was removed from the solution in a single extraction (entry 12).

Table 3 Effect of the amount of extractant in the removal of Pb^{2+} form aqueous solutions using MNPs of Fe_3O_4

Entry	Extractant	Contact time /h	Extractant to Pb^{2+} ratio	% Pb^{2+} extracted[a]
1	**11ai**	41	1:1	29(1)
2	**11ai**	41	2:1	38(1)
3	**11ai**	41	4:1	61(2)
4	**11ai**	41	10:1	91(2)

[a]Mean values of two independent determinations. Observed result variability is given in parentheses.

With the goal of determining conditions for the extraction of >90% of the initially present Pb^{2+} in a single operation using the more readily available MNPs **11ai**, a set of experiments was performed using increasing amounts of this extractant (Table 3). As it can be seen, a 91% of the initially present lead was removed from the solution in a single treatment when a 10:1 extractant to metal ratio was used.

Extraction with functional polymers

Functional polymers **20a** and **20b** were also used for the selective removal of lead from organic solvents. THF was chosen as solvent, because it was adequate for the swelling of the polymers. Results of the extraction experiments are shown in Table 4.

Table 4 Extraction of Pb^{2+} from THF solutions, using functional polystyrene resins.

Entry	Extractant	Extractant to Pb^{2+} ratio	Contact time /h	% Pb extracted[a]
1	**20a**	1:1	24	91(2)
2	**20b**	1:1	24	86(3)
3	**18**	2:1	24	0

[a]Mean values of two independent determinations. Observed result variability is given in parentheses.

As it can be seen, high extraction percentages, of around 90% were achieved with polystyrene-immobilised complexing agents **20a-b**. To show that there was no unspecific binding to the resin, the extraction experiment was also carried out using polymer **18**, and, no decrease in the amount of Pb in the solution being observed (entry 3).

Resins **20b** and **21a-b** were also tested for extraction from water (Table 5). Polystyrene resin **20b** was inefficient under these conditions (entry 1), likely because of poor swelling. Amphiphilic resins **21a** and **21b** performed much better with respect to swelling in water, and its extracting potential was studied at different pH values. Using resin **21b** a 43% of extraction was achieved in water under neutral conditions, while in acidic media (pH 1 and pH 3) the extraction capacity was highly reduced due to the protonation of the tertiary amine in the monoaza-18-crown-6 moiety. Resin **21a** works poorly in water at pH = 7 (14%), but its extraction ability was improved at pH 1 (45%). Again, control experiments were performed using azido resin **19** (entry 13) and phenyltriazole functionalised resin **22** (entry 14). No decrease in the amount of Pb was observed in any of the cases. The result in entry 14 indicates that, at least in this case, the presence of the triazole group does not contribute to any extent to the binding of cations, in contrast with what we observed for the case of magnetite nanoparticles (see above). As observed for the extraction with functional MNPs, increasing the amount functional resin used as extractant allows increasing the removal of lead up to 72% in a single operation (entry 11).

Table 5 Extraction of Pb^{2+} using functionalised PS-PEG in water at different pH.

Entry	Extractant	Extractant to Pb^{2+} ratio	Solvent (pH)[a]	Contact time/h	% Pb extracted
1	**20b**	2:1	H_2O[b]	41	14(1)
2	**21b**	1:1	H_2O[b]	24	43(3)
3	**21b**	1:1	H_2O (1)	24	0
4	**21b**	1:1	H_2O (3)	24	0
5	**21b**	1:1	H_2O[b]	16	37(2)
6	**21b**	1:1	H_2O[b]	41	43(1)
7	**21b**	2:1	H_2O[b]	24	60(1)
8	**21a**	1:1	H_2O[b]	24	14(1)
9	**21a**	1:1	H_2O (1)	24	45(3)
10	**21a**	2.6:1	H_2O (1)	24	59(2)
11	**21a**	4.5:1	H_2O (1)	24	72(2)
12	**21a**	1:1	H_2O (3)	24	6(2)
13	**19**	1:1	H_2O[b]	24	0
14	**22**	1:1	H_2O[b]	24	0

[a]The corresponding pH values are given in parentheses. [b]Pure water, pH = 7. [c]Mean values of two independent determinations. Observed result variability is given in parentheses.

Experimental

General information

Unless otherwise stated, all commercial compounds were used as received without any further purification. Ultra pure water was obtained from an SG Water Ultra clear basic system, that provides water with a conductivity at 25 ºC of 0.055 µS. Dry solvents (CH_2Cl_2, THF, DMF, diethyl ether, hexane and toluene) were obtained from a Puresolv™ purification system. Dry o-dichlorobenzene and methanol were obtained by treatment with

pellets of 4 Å molecular sieves (previously activated by microwave irradiation) under argon atmosphere. When degassed solvents were required, an argon stream was passed through the solvent. IR spectra of nanoparticles were recorded on a Bruker Tensor 27 FTIR spectrophotometer or in a Thermo Nicolet 5700 FTIR spectrometer, using KBr pellets. [1]H and ^{13}C experiments of polymers were performed with a Bruker Avance spectrometer operating at a frequency of 500.13 MHz using a Bruker 4 mm ^{1}H/^{13}C/^{2}H gradient HR-MAS probe. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-1011 transmission electron microscope equipped with a lanthanum hexaboride filament operated at an acceleration voltage of 100 kV. Flame atomic absorption measurements were performed in a Hitachi Polarized Zeeman Atomic Absorption Spectrometer. All the glassware used in the metal extraction experiments was previously treated overnight with 20% v/v HNO_3 and rinsed with ultra pure water. The solutions for the metal extraction experiments were prepared using ultra pure water. Reactions heated under microwave irradiation were performed in a CEM Discover microwave synthesis apparatus using 10 mL vessels with septa for reactions performed at elevated temperatures and pressures. Phosphorus content determinations were performed by Inductively Coupled Plasma Atomic Emmision Spectroscopy (ICP-AES) at the Service Central d'Analyse of the Centre National de la Recherche Scientifique (France).

Preparation and functionalisation of cobalt nanoparticles for extraction of metals

Typical procedure for the preparation of cobalt nanoparticles functionalised with crown ether derivatives: Preparation of functional nanoparticles 6a

These nanoparticles were prepared by slight modifications of a previously reported procedure.[21c,31] Crown ether derivative **5a** (0.29 g, 0.529 mmol) and trioctylphosphine oxide (TOPO) >97% (0.042 g, 0.0363 mmol) were weighed in a 50 mL two-necked round-bottomed flask and dissolved under an argon atmosphere in 6 mL of anhydrous and degassed *o*-dichlorobenzene. To this suspension, 85.5 µL of oleic acid 98% (0.0762 g, 0.2644 mmol) were injected and the mixture was heated in a silicone oil bath at 160 ºC, with mechanical stirring using a shaker. When the bath had reached the desired temperature, a solution of 0.201 g (0.529 mmol) of $[Co_2(CO)_8]$ (≥ 90 %) in 5 mL of anhydrous, degassed, *o*-dichlorobenzene was rapidly transferred into the reaction media by injection. The reaction mixture was mechanically stirred at 160 ºC for 1 hour. After cooling to room temperature, 24 mL of anhydrous and degassed methanol were added. The resulting suspension was stored in the freezer under argon until the precipitation of the particles (3 hours). The particles were separated by magnetic decantation and washed once with anhydrous, degassed methanol (20 mL) and with anhydrous, degassed dichloromethane (40 mL) The solvents were removed *in vacuo* and the residual solid was dried under a nitrogen stream. In this manner, 35.3 mg of cobalt nanoparticles **6a** were obtained with particle size of 18 nm (s = 3.3) and f = 0.091 mmol/g. Elemental analysis: C, 5.81; H, 0.84; N, 0.38. FTIR v_{max}/cm^{-1} 3443, 2958, 2922, 2853, 1620, 1460, 1413, 1225, 1101, 801, 524,

457.

Preparation and functionalisation of magnetite nanoparticles

Typical procedure for the preparation of magnetite nanoparticles coated with oleic acid (7)

These nanoparticles were prepared by slight modifications of a previously reported procedure.[34] Iron(II) chloride tetrahydrate (99%) (3.01 g, 15 mmol) and iron(III) chloride hexahydrate (97%) (8.36 g, 30.0 mmol) were dissolved in degassed ultra pure water (140 mL) in a 500 mL round-bottomed flask and heated to 80 ºC, shaking vigorously with a shaker. Oleic acid (98%) (2.1 mmol, 0.60 g, 0.68 mL) dissolved in degassed acetone (15 mL) was added to the reaction mixture, followed by 30% aqueous NH_3 solution (18.2 mL). After addition, further amounts of oleic acid were added (5 × 1.0 mL) over a 5 to 10 minutes period. The black reaction mixture was hold for 30 minutes at 80 ºC and then slowly cooled to room temperature. A 1:1 v/v mixture of methanol and acetone (100 mL) was then added to support the precipitation. After allowing the nanoparticles to settle overnight with the help of a magnet, the supernatant was separated using a cannula and the particles were washed with a 1:1 v/v mixture of methanol and acetone (5 × 100 mL). The nanoparticles were dried, first with an argon stream and then under vacuum. In this manner, 3.8 g of nanoparticles were isolated as a dark brown solid with a particle size of 8.40 nm (s = 2.56). FTIR v_{max}/cm^{-1} 3453, 3005, 2956, 2923, 2852, 1632, 1426, 1409, 1261, 1229, 1100, 1056, 802, 580. TGA (30-1000 ºC, 10 ºC/min, N_2) %weight loss (onset [ºC]): 6.89 (306.64), 6.71 (663.09).

Typical procedure for the preparation of magnetite nanoparticles coated with oleic acid (13)

These nanoparticles were prepared by slight modifications of a previously reported procedure.[42] Iron(III) acetylacetonate 98% (0.706 g, 1.96 mmol), oleic acid (1.9 mL, 5.99 mmol) oleylamine (1.60 g, 1.93 mL, 5.99 mmol) and 1,2-hexadecanediol 90% (2.58 g, 8.98 mmol) were mixed in 20 mL of benzyl ether 99% under nitrogen. The mixture was heated at 200 ºC for 2 hours and then at 300 ºC for one more hour. The mixture was then allowed to cool down to room temperature and 40 mL of ethanol were added. Centrifugation allowed the separation of a dark-brown solid that was dissolved in hexane (5 mL) and reprecipitated by addition of 40 mL of ethanol. The nanoparticles were obtained as a black solid (80 mg) with a particle size of 6.18 nm (s = 1.98). FTIR v_{max}/cm^{-1} 3440, 2955, 2920, 2850, 1630, 1594, 1524, 1401, 585. TGA (30-900 ºC, 10 ºC/min, N_2) %weight loss (onset [ºC]): 17.23 (293.49), 8.57 (634.07).

Typical procedure for the preparation of azido-magnetite nanoparticles: Synthesis of functional nanoparticles 9i

These nanoparticles were prepared by slight modifications of a previously reported procedure.[36] Nanoparticles **7** (0.96 g) were dispersed by sonication (20 minutes) in about 480 mL of degassed toluene and then 3-azidopropyltrimethoxysilane **8i** (1.92 g, 9.33 mmol) was added, followed by glacial acetic acid 99.5%,

d = 1.05 g/mL (0.192 mL, 3.36 mmol) and ultrapure water (0.269 mL, 14.93 mmol). The reaction mixture was stirred at room temperature for 3.5 days. The black particles were allowed to settle overnight with the help of an external magnet. The supernatant was separated using a cannula, and the nanoparticles were washed with toluene (3 × 42 mL) and methanol (3 × 26 mL) and dried under vacuum. In this manner, 0.78 g of nanoparticles were recovered as a brown powder with a particle size of 8.83 nm (s = 3.01) and f = 0.35 mmol/g. Elemental analysis: C, 3.61; H, 0.80; N, 1.48. FTIR v_{max}/cm^{-1} 3442, 2955, 2924, 2852, 2098 (N$_3$), 1637, 1420, 1239, 1182, 1103, 1022, 585. TGA (30-1000 ºC, 10 ºC/min, N$_2$) %weight loss (onset [ºC]): 9.79 (244.01), 4.58 (633.10).

Typical preparation of MNPs functionalised with crown ether: Synthesis of functional nanoparticles 11ai

Magnetite nanoparticles **9i** (90 mg, f = 0.480 mmol of ligand/g) were dispersed in 5 mL of anhydrous DMF in a Schlenk flask under argon, using ultrasonication for 15 min to ensure dispersion. The alkyne **10a** (43 mg, 0.13 mmol), dissolved in 1 mL anhydrous DMF was then added to the reaction media, followed by DIPEA 99.5% (0.136 mL, 0.78 mmol), and finally CuI (3.3 mg, 0.017 mmol) as a solid. The reaction mixture was stirred at 40 ºC under argon and the reaction progress was followed by IR spectroscopy. Once the IR bands associated to N$_3$ had disappeared (2-10 days) the reaction was cooled to room temperature, methanol was added (c.a. 50 mL), and the mixture was left overnight in the freezer. The precipitating particles were separated by magnetic decantation. The supernatant was discarded and the particles were washed with methanol (3 × 10 mL) using centrifugation to separate the solvent. The solid material was dried with an argon stream and then *in vacuo*. In this manner 68.1 mg of functional magnetite nanoparticles were obtained as a brown solid, with a particle size of 10.88 nm (s = 3.97) and f = 0.343 mmol/g. Elemental analysis: C, 8.88; N, 1.47; H, 1.44. FTIR v_{max}/cm^{-1} 3405, 2919, 1726, 1629, 1454, 1350, 1248, 1103, 835, 584.

Magnetite nanoparticles stabilised by 11-bromoundecylphosphonic acid (15)

Compound **14** (0.235 g, 0.75 mmol) and 0.111 g of magnetite nanoparticles **13** were shacken in 15 mL of CHCl$_3$ at room temperature for 24 hours. Then the nanoparticles were collected using an external magnet and the organic solution was removed. The nanoparticles were washed 3 times with ethanol sonicating each time to ensure total abstraction of ligands in excess. The product was obtained as a brown solid (0.40 g), with a particle size of 6.37 nm (s = 0.97). According to the %P determined by ICP-AES, a functionalisation f = 2.36 mmol/g was calculated. Elemental analysis: C, 31.97; H, 5.66; N, 0.10; P, 7.32. FTIR v_{max}/cm^{-1}2917, 2850, 1466, 1082, 940, 559.

Magnetite nanoparticles stabilised by 11-azidoundecylphosphonic acid (16)

To a dispersion of **15** (0.13 g, 0.31 mmol, f = 2.36 mmol/g) in 4 mL of DMF, NaN$_3$ 95.5% (0.15 g, 2.3 mmol) was added and the mixture was heated at 65 ºC for 12 hours. The mixture was allowed to reach room temperature, the nanoparticles were separated and washed with water (3×5 mL) and methanol (3×5 mL). The product was obtained as a brown solid (0.122 g), with a particle size of 5.56 nm (s = 1.04). According to the %N determined by elemental analysis a functionalisation of the nanoparticles of f = 2.25 mmol/g was determined. According to the %P determined by ICP-AES a functionalisation f = 2.28 mmol/g was calculated. Elemental analysis: C, 33.15; H, 5.82; N, 9.11; P, 7.07. FTIR v_{max}/cm^{-1} 2917, 2851, 2097, 1079, 560.

Typical example of CuAAC reaction between functional magnetite nanoparticles 16 and alkynes: Synthesis of MNPs 17a

Magnetite nanoparticles **16** (70 mg, f = 2.25 mmol/g) were dispersed in 5 mL dry DMF in a Schlenk flask under an argon atmosphere. The alkyne **10a** (100 mg, 0.302 mmol), dissolved in 1 mL dry DMF was added to the suspension of the nanoparticles, followed by DIPEA 99.5% (0.474 mL, 352.0 mg, 2.72 mmol), and finally CuI (11.5 mg, 0.0605 mmol) as a solid. The reaction mixture was magnetically stirred at 40 ºC under argon. The progress of the reaction was monitored by IR spectroscopy, following the decrease of intensity of the azide band. If required, additional amounts of CuI and alkyne were added. Once the azide band had dissapeared (between 4 to 7 days), the reaction mixture was cooled to room temperature, and the DMF was evaporated in the vaccum line to about one half of its volumen. Then, 40 mL of methanol (HPLC grade) were added and the particles left to precipitate overnight in the freezer, with the aid of an external magnet. The supernatant was separated *via* cannula, the particles were washed twice with 5 mL methanol (HPLC grade) and two times with distilled water (5 mL each) using centrifugation to separate the particles. The particles were again washed with methanol (2 × 5 mL) and were dried with an argon stream. 66.6 mg of magnetite nanoparticles were isolated, with a particle size of 6.37 nm (s = 1.08) and f = 1.00 mmol/g. Elemental analysis: C, 36.65; H, 5.78; N, 4.24. FTIR v_{max}/cm^{-1}3445, 2920, 2851, 1638, 1467, 1352, 1291, 1249, 1106, 1038, 956, 836, 791, 719.

Preparation of functionalised polymers for metal extraction

Typical functionalisation of (azidomethyl)polystyrene with crown ethers: Preparation of polystyrene resin 20a

Alkyne **10a** (0.14 g, 0.421 mmol), DIPEA 99.5% (0.384 mL, 2.202 mmol) and copper(I) iodide (0.0043 g, 0.02 mmol) were added to a suspension of 0.22 g (azidomethyl)polystyrene **18** (f = 0.77 mmol/g) in 1:1 DMF/THF (2 mL) and the mixture was stirred at 40 ºC for 5 days. The reaction mixture was monitored and once the IR-signal of the azido group had completely disappeared, the resin was collected by filtration and sequentially washed with water (60 mL), THF (60 mL), MeOH (120 mL) and THF (60 mL). The solid was dried *in vacuo* for 24 hours at 40 ºC to afford 0.185 g of **10a** with a functionalisation f = 0.597 mmol/g. Elemental analysis: C, 79.96; H, 7.65; N, 2.51. FTIR v_{max}/cm^{-1} 3059, 3025, 2919, 2850, 1945, 1719, 1601, 1493, 1451, 1350, 1115, 1068, 903, 754, 693. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$)

δ_H 7.46 (H, triazole), 7.11 (s, br, polymer backbone), 6.64 (s, br, polymer backbone), 5.37, 4.63 (2 H, s br) 3.74 (2 H, m, CH_2-CH_2-N_3), 3.65 (s, -(O-CH_2-CH_2-O)-), 1.86 (s, polymer backbone), 1.52 (s, polymer backbone) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ_C 145.73, 128.58, 128.2, 126.26, 123.1 (*CH* triazole), 111.30, 78.67, 71.09, 70.97, 70.06, 68.31, 65.28, 40.92 ppm.

Typical functionalisation of azido-polystyrene-polyethyleneglycol with crown ethers: Preparation of polystyrene-polyethyleneglycol resin 21a

Alkyne **10a** (0.037 g, 0.113 mmol) dissolved in 1:1 DMF/THF (3 mL), DIPEA 99.5% (0.17 mL, 0.975 mmol) and copper(I) iodide (0.0015 g, 0.0075 mmol) were added to a suspension of 0.3 g of azido-terminated polystyrene–polyethyleneglycol **19** (*f* = 0.25 mmol/g) in 1:1 DMF/THF (3 mL) at 40 ºC and the mixture was shaken for 24 hours. The reaction mixture was monitored and once the IR signal of the azido group had completely disappeared, the resin was collected by filtration and sequentially washed with water (180 mL), MeOH (160 mL) and THF (160 mL). The solid was dried *in vacuo* for 24 hours at 40 ºC to afford 0.203 g of **21a** with *f* = 0.252 mmol/g. Elemental analysis: C, 62.61; H, 8.74; N, 1.06; FTIR ν_{max}/cm^{-1} 2865, 1638, 1602, 1492, 1453, 1348, 1296, 1249, 1093, 946, 845, 761, 701; ^{1}H NMR (500 MHz, CD_2Cl_2) δ_H 7.79 (1 H, s, triazole), 7.04 (s, br, polymer backbone), 6.57 (s, br, polymer backbone), 4.60 (2 H, s), 4.52 (2 H, s), 3.86, 3.72, 3.59, 3.45, 2.09, 1.73 (s, br, polymer backbone). ^{13}C NMR (126 MHz, CD_2Cl_2) δ_C 145.3 128.5, 110.2, 85.3, 71.9, 70.8, 70.5, 69.7, 50.5, 40.9.

Metal extraction experiments using functionalised MNPs and resins

General procedure for the Pb^{2+} extraction from acetonitrile solutions with nanoparticles

An exactly measured aliquot (5 mL) of a solution of Pb(ClO$_4$)$_2$ (of around 83 ppm) was added to a closed vial containing an equimolar amount of functional MNPs. The samples were sonicated for at least 15 min to achieve the dispersion of the nanoparticles and the vials were shaken on a horizontal shaker for specified periods of time. The nanoparticles were then magnetically decanted with the help of an external magnet. The supernatant was transferred *via* cannula to a Schlenk flask, the solvent was evaporated under vaccum and the residue was dissolved in an exactly measured volume of 1% v/v HNO$_3$. The concentration of lead in the supernatant was determined by FAAS.

General procedure for the Pb^{2+} extraction from aqueous solutions with nanoparticles

An aliquot (5 mL) of a solution of Pb(ClO$_4$)$_2$ (of around 83 ppm) was added to a closed vial containing the required amount of magnetite nanoparticles. The samples were sonicated for at least 15 min to achieve the dispersion of the nanoparticles and the vials were shaken on a horizontal shaker for specified periods of time. The nanoparticles were then magnetically decanted with the help of an external magnet. The supernatant was separated with a syringe, filtrated through a Nylon filter (0.45 μm) and acidified with concentrated HNO$_3$ (65%, puriss. p.a. grade) to achieve a final acid concentration of 1% v/v. The concentration of lead in the supernatant was determined by FAAS.

General procedure for the Pb^{2+} extraction from aqueous solutions with PS resins

An aliquot (5 mL) of a solution of Pb(ClO$_4$)$_2$ was added to a closed vial containing the required amount of polymer. The samples were orbitally shaken on a horizontal shaker for specified periods of time. The samples were allowed to decant and a 2 mL aliquot of the supernatant was transferred to another vial, evaporated to dryness in an argon stream and the residue was dissolved in 5 mL aqueous 1% v/v HNO$_3$. The concentration of lead in the supernatant was determined by FAAS.

General procedure for the Pb^{2+} extraction from aqueous solutions with PS and PS-PEG resins

An aliquot (5 mL) of a solution of Pb(ClO$_4$)$_2$ (of around 83 ppm) was added to a closed vial containing the required amount of polymer. The samples were shaken on a horizontal shaker for specified periods of time. The samples were allowed to decantate and the supernatant was separated with a syringe, filtered through a Nylon filter (0.45 μm) and acidified with concentrated HNO$_3$ (65%, purissim. p.a. grade) to achieve a final acid concentration of 1% v/v. The concentration of lead in the supernatant was determined by FAAS.

Conclusions

In summary, we have shown that CuAAC reactions (the popular and widely used *click* chemistry) can be used as a most practical ligation methods for the preparation of immobilized complexing agents involving a clickable crown ether or aza-crown ether complexing unit and a support allowing easy separation (a magnetic nanoparticle or a resin). The prepared library of clicked extractants covers different types of magnetic nanoparticles (ε-Co and Fe$_3$O$_4$) and resins (PS and PS-PEG), different approaches to the binding of the azido group to the nanoparticles (two-point carboxylic acid binding, three-point phosphonic acid binding and covalent silicate binding through ω-azidoalkyl(trialkoxy)silanes, and different spacer lengths separating the functional unit from the support. Some of these complex extracting materials, such as **11ai-bi**, **20a-b**, and **21a-b**, are remarkably easy to prepare being only a few steps away from commercial precursors.

To illustrate the potential of this approach, we have studied the application of the clicked complexing agents to the removal of Pb^{2+} from aqueous and organic solutions. Remarkably, conditions have been developed for removing >90% of the initial Pb^{2+} in a single operation from water and from organic solvents (acetonitrile and tetrahydrofuran).

When the performance of both types of materials (MNP-based and resin-based) in the planned complexation of Pb^{2+} from its solutions is considered, the merits of functional polymers and functional nanoparticles depends on the nature of the media from which Pb^{2+} needs to be extracted. To remove lead contamination from organic solvents, functional polymers such as **20a-b**

probably represent the best alternative. Thus, very high extraction levels (> 90%) can be achieved at stoichiometric extractant to Pb^{2+} ratios. On the other hand, small and readily dispersable, functional Fe_3O_4 nanoparticles offer the advantage of being equally suitable for organic (**11ai**) and aqueous (**17a**) solutions, while functional polymers provides only mediocre results in this last situation. Taking into account the experimental simplicity of the complexation of the Pb^{2+} cations in combination with the ready separation of the corresponding complexes by magnetic decantation, the use of complexing agents clicked onto MNPs offers substantial potential for future applications in the detoxification area.

Notes and references

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