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Terpyridine-based silica supports prepared by ring-opening metathesis polymerization for the selective extraction of noble metals

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Abstract

The synthesis of a terpyridine-based sorbent for solid-phase extraction (SPE) of noble metal ions is described. For this purpose, 4'-(norborn-2-en-5-ylmethylenoxy)terpyridine was copolymerized with norborn-2-ene via Mo(N-2,6-*i*-Pr₂-C₆H₃)(=CHCMe₂Ph)(OC(CH₃)(CF₃)₂)₂-catalyzed ring-opening metathesis polymerization (ROMP) to give a poly(norbornene₉₀₀-*b*-4'-(norborn-2-en-5-ylmethylenoxy)terpyridine₆₀) block-copolymer. This block-copolymer was used for the preparation of polymer-coated silica 60 (4.8 wt.% coating), which was investigated for its extraction capabilities for Cr(III), Mn(II), Re(II), Fe(III), Ru(III), Co(II), Rh(III), Ir(III), Ni(II), Pd(II), Pt(II), Cu(II), Ag(I), Au(III), Zn(II), Cd(II) and Hg(II), at different pH. Under competitive conditions and at pH < 0.6, the selectivity order was Pd ≈ Ag ≈ Au ≈ Pt > Re > Ir > Rh > Ru > Fe > Cr ≈ Mn ≈ Cd ≈ Zn. Enhanced selectivity was observed at pH = 3.5, the order was Au > Hg > Pd ≈ Ag > Rh > Pt > Ir ≈ Re > Cu > Co ≈ Zn ≈ Cd ≈ Ni > Cr > Mn. The maximum metal loading that was achieved under non-competitive conditions was >6 mg/g for Au(III), Hg(II), Pd(II) and Ag(I). Even under competitive conditions, loadings of >6 mg/g were realized for Au(III) and Hg(II). Quantitative recoveries >97% were observed for all metals in case loading was stopped before reaching the point of breakthrough.

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1. Introduction

The selective extraction of metal ions, either toxic or precious ones, is still an intensively investigated area of research. While silver and gold are found in high purities and sometimes large quantities, the

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occurrence of other noble metals is usually limited to a few gram of pure metal per tonnes of ore. For example, one of the richest occurrences of palladium (South Africa) contains only 5 g of Pd/t of ore. In addition, the elements of interest are often accompanied by other metals with similar chemistry, i.e. Pd by Pt, Rh by Ir, etc. For use in chemical reactions, these metals must be obtained in a pure form. Since all of them (i.e. Au, Ag, Pd, Pt, Rh, Ir, Re, Ru) are catalytically active [1], their extraction from ore as well as from catalyst sludges is of high interest. Noble metal purification is still accomplished by traditional precipitation–complexation procedures that require the use of large amounts of mineral acids and highly toxic complexing agents such as sodium or potassium cyanide. The negative impact of such procedures on the environment is obvious and known. To circumvent the use of such chemicals, leaching of ores with thiourea [2], liquid–liquid extraction [3–14] as well as solid-phase extraction (SPE) techniques, applying numerous sorbents, have already been developed. Though ion-exchange resins and solid-supported extractants, usually based on PS-DVB or certain (meth)acrylates are cheap “working horses” [15–25], they sometimes suffer from insufficient selectivity or require special conditions such as pH or ionic strength of the solution, which are hard to realize starting from standard metal ion containing aqua regia solutions. Alternatively, highly selective ligands such as crown ethers [26–29], which can be prepared in a way that they possess high selectivity for the metal ions of interest [30], have been developed and successfully bound to suitable supports, e.g. silica [31]. Standard silica chemistry was used for these purposes [32]. Additional reports describe the use of PS-DVB sorbents impregnated with guanidines [33], poly(amide-ester)-based pyridine-2,6-dicarboxylic acids [34], activated carbon [35,36], poly(glycidyl methacrylate)-bound oligoamines [37], extractant-impregnated membranes [38–40], and supercritical fluid extraction [41].

A variety of different sorbents for the selective extraction of other metal ions such as lanthanides [42–44], Pd, or Hg [45] prepared by various metathesis polymerization-based techniques has already been described by our group. In this contribution we report on the synthesis and extraction capabilities of

a silica-supported poly(terpyridine-*b*-norborn-2-ene) prepared via a ROMP-based technology.

2. Experimental

2.1. General details

All synthetic experiments were performed under a nitrogen atmosphere in a MBraun glove box (Labmaster 130) or by using standard Schlenk techniques. Size exclusion chromatography (SEC) versus poly(styrene) (PS) was carried out in tetrahydrofuran on PLGel 10 μm mixed Bed LS columns (Polymer Laboratories) using a 2414 differential refractometer and a 484 UV-detector (all Waters Corp.). The flow was set to 0.7 ml/min. Prior to SEC, samples were filtered through a 0.22 μm Teflon filter (Millipore) in order to remove particles. SEC columns were calibrated versus polystyrene standards (Polymer Standards Service (PSS), molecular weights 347– 2.7×10^6 g/mol). UV-Vis spectra were recorded on a Hitachi U 2000 spectrophotometer in the range 300–800 nm using quartz cuvettes. NMR data were obtained at 300.13 MHz (^1H) and are listed in parts per million downfield from tetramethylsilane. SPE experiments were carried out using 1.5 ml PP Iso-lute SPE cartridges equipped with PP frits. ICP-OES measurements were carried out on a Jobin Yvon JY 38 plus. Dichloromethane was distilled from calcium hydride under nitrogen and passed through a column of activated alumina prior to use. Mo(N-2,6-*i*-Pr₂-C₆H₃)(=CHCMe₂Ph)(OC(CH₃)(CF₃)₂)₂ was prepared according to a known literature procedure [46]. The synthesis of 4'-(norborn-2-en-5-ylmethyleneoxy)terpyridine (**1**) is described elsewhere [47]. Deionized water was used throughout. Aqueous standard solutions of RuCl₃ (in 1 M HCl, Fluka), Re(NO₃)₂, H₂[PtCl₄], IrCl₃ (all Johnson Matthey GmbH, Alfa Products), H[AuCl₄], (NH₄)₃[RhCl₆] (all Sigma–Aldrich), H₂[PdCl₄] (in 1 M HCl), AgNO₃ (in 0.5 M HNO₃), Zn(NO₃)₂ (in 0.5 M HNO₃), Mn(NO₃)₂ (in 0.5 M HNO₃), Cu(NO₃)₂ (in 0.5 M HNO₃), Co(NO₃)₂ (in 0.5 M HNO₃), Cr(NO₃)₃ (in 0.5 M HNO₃), Hg(NO₃)₂ (in 0.5 M HNO₃), Cd(NO₃)₂ (in 0.5 M HNO₃), FeCl₃ (in 1 M HCl), Ni(NO₃)₂ (in 0.5 M HNO₃) (all Merck, Germany) were used.

2.2. Poly-(norborn-2-ene-*b*-1)

1 (0.316 g, 0.889 mmol) was dissolved in methylene chloride and treated with a solution of Mo(N-2,6-*i*-Pr₂-C₆H₃)(CHC(CH₃)₂Ph)(OC(CH₃)(CF₃)₂)₂ (6.8 mg, 8.9 μmol). The yellow solution was stirred for 5 min. Then a solution of norborn-2-ene (0.251 g, 2.67 mmol) in 5 ml of methylene chloride was added and the reaction mixture was stirred for 9 h. The reaction was terminated by the addition of ferrocene aldehyde (20 mg, 90 μmol). After 12 h, the polymer was precipitated by the addition of pentane, filtered off, washed with pentane and dried *in vacuo*. Yield: 0.43 g (76%, brown solid). $M_n = 105000$ g/mol; PDI = 1.50; NBE-block size = 900; terpyridine-block size = 60. ¹H NMR (CDCl₃) δ 8.5 (bs), 7.7 (bs), 7.22 (bs), 5.32 (s, C=C), 5.15 (s, C=C), 4.0 (bs), 3.7 (s), 2.77 (bs), 2.41 (bs), 1.80 (bs), 1.34 (bs), 1.0 (m).

2.3. Coating of silica

Poly-(norborn-2-ene-*b*-1) (0.43 g, corresponding to 4.8% coating) was dissolved in methylene chloride. Vinyltrimethoxysilane-derivatized silica (8.6 g) was added. The solvent was slowly removed *in vacuo* (800–900 mbar) and the residue was dried under high vacuum.

2.4. SPE experiments

For all experiments, the SPE material was first stirred in methanol:water (20:80) for 30 min. Columns were slurry-packed and further conditioned by passing 100 ml of methanol:water (20:80) through the column, followed by 100 ml water (flow rate 3 ml/min). For SPE, solutions containing 100 ppm single element standards and multi-element standards, respectively, were passed through a slurry-packed filtration column (Isolute™ Accessories, 200 mg sorbent). Recoveries were determined under competitive and non-competitive conditions by ICP-OES. Ion lines and background lines for all elements are summarized in Table 2.

2.5. Recovery experiments

Fifty milliliters of the mixed standards A–E and single metal ions standards, respectively, were passed

over a SPE cartridge (one mix and element, respectively, per cartridge). Elution was performed using 3 ml of 5 M nitric acid. The eluent was diluted with water up to total volume of 10 ml and measured by ICP-OES. Quantitative recoveries in the range of 97–102% (R.S.D. = 5%) were observed throughout.

3. Results and discussion

3.1. Synthesis of SPE sorbent

The synthesis of 4'-(norborn-2-en-5-ylmethylenoxy)terpyridine (**1**) from norborn-2-ene methanol and 4'-bromoterpyridine is described elsewhere [47]. Since the structure of the ligand is not changed during polymerization, **1** was directly used for preliminary investigations concerning the complex formation capabilities with various transition metals. For this purpose, solutions of the metals summarized in Table 1 were mixed with the ligand at different pH and the resulting complex was extracted into methylene chloride. By subtracting the spectrum of the free ligand,

Table 1
Summary of UV experiments performed with **1** and various metal ions in water at different pH followed by extraction into CH₂Cl₂

| Metal ion | pH | λ_{\max} (nm) ^a |
|-----------|----|------------------------------------|
| Zn(II) | 5 | 307, 319 |
| Cd(II) | 8 | 307, 319 |
| Cd(II) | 6 | 307, 319 |
| Hg(II) | 6 | 311 |
| Co(II) | 6 | 307 |
| Co(II) | 1 | 306 |
| Rh(III) | 1 | 313, 327 |
| Rh(III) | 6 | 295, 300 |
| Ir(III) | 1 | 307, 328 |
| Ir(III) | 6 | 315, 327 |
| Mn(II) | 6 | 307, 320 |
| Re(II) | 6 | 300 |
| Cu(II) | 6 | 314, 329 |
| Ni(II) | 2 | 295, 300 |
| Ni(II) | 6 | 295, 300 |
| Pd(II) | 1 | 313, 327 |
| Pd(II) | 6 | 313, 327 |
| Pt(II) | 3 | 315, 327 |
| Pt(II) | 6 | 315, 327 |
| Fe(III) | 6 | 290, 300 |
| Ru(III) | 6 | 295 |

^a Ligand (pH = 6): 283, 289, 300 (sh); (pH = 1): 289, 300 (sh).

complexation was clearly observed for all metals. A summary of the absorption maxima of the corresponding complexes in methylene chloride is given in Table 1.

The polymerization of **1** by metathesis-based techniques has already been investigated in a previous work [47]. Ring-opening metathesis polymerization (ROMP) allows the polymerization of functional monomers such as **1**. In addition, block-copolymers are accessible if the polymerization itself can be conducted in a “living” way. The polymerization system **1**/Mo(N-2,6-*i*-Pr₂-C₆H₃)(=CHCMe₂Ph)(C(CH₃)(CF₃)₂)₂ fulfills the criteria of a “class IV” living system [47,48]. Therefore, the synthesis of the block-copolymer was accomplished by reaction of the catalyst with **1** followed by addition of norborn-2-ene (Scheme 1).

Polymerizations were terminated with ferrocene aldehyde. The resulting block-copolymer revealed a molecular weight of 120,000 g/mol with a norborn-2-ene block size of roughly 900 and a 4'-(norborn-2-en-5-ylmethylenoxy)terpyridine block size of roughly 60. Such a large poly(norborn-2-ene) block size on one hand ensures sufficient solubility in organic solvents, on the other hand prevents any solubility in aqueous media under strongly acidic conditions. Due to its good solubility in methylene chloride, solutions thereof were coated onto silica 60. Such an approach fulfills the criteria of simplicity and provides entirely pH stable extractants [49], necessary for the extraction of metal ions originating from ore break down with aqua regia.

3.2. SPE experiments

The coated silica was used in standard SPE experiments. Competitive conditions were chosen in order

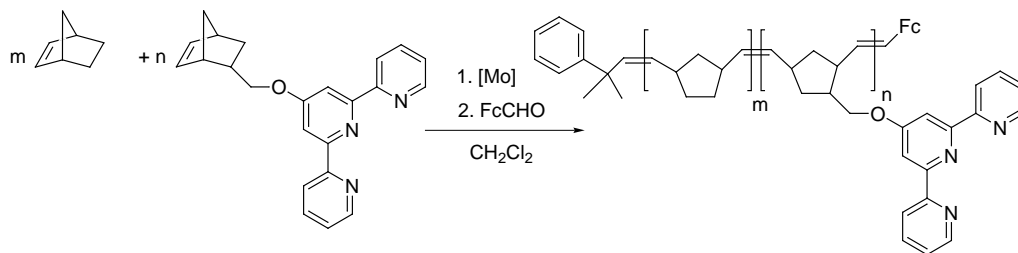
Table 2

Ion lines and background lines for all elements

| Element | Ion line (nm) | Background (nm) |
|---------|---------------|-----------------|
| Cr | 284.325 | ±0.0295 |
| Mn | 293.930 | ±0.0286 |
| Re | 197.313 | ±0.0312 |
| Fe | 310.050 | ±0.0245 |
| Ru | 266.161 | ±0.0272 |
| Co | 238.892 | ±0.0290 |
| Rh | 233.477 | ±0.0335 |
| Ir | 224.268 | ±0.0299 |
| Ni | 232.003 | ±0.0294 |
| Pd | 340.458 | ±0.0278 |
| Pt | 214.423 | ±0.0304 |
| Cu | 213.598 | ±0.0304 |
| Ag | 328.068 | ±0.0280 |
| Au | 242.795 | ±0.0329 |
| Zn | 213.856 | ±0.0304 |
| Cd | 214.438 | ±0.0308 |
| Hg | 253.652 | ±0.0421 |

to setup an extraction order for all metals of interest in the presence of other, potentially interfering ions. Since the noble metals of interest are easily reduced by other, less noble metal ions, we could not use one single mixture containing all metal ions for our investigations. Instead, the following sets of metals were chosen. Mix A (Re, Pt, Ir, Rh, Au, Pd); Mix B (Cd, Cr, Mn); Mix C (Zn, Ni, Co, Hg, Cu, Cd, Ag); Mix D (Fe, Mn, Ru, Re, Cr); Mix E (Au, Hg, Pd); Mix F (Ag, Hg, Pd, Co, Au). Mixes A–F were subject to SPE and measured at pH 0.6 and pH = 3.5. In addition, Au, Ag, Pd, and Co were measured as single ion standards at both pH values. All measurements were carried out by ICP-OES at the indicated wavelengths (Table 2).

Measurements at pH > 3.5 could not be carried out due to insufficient solubility of some metal hydroxides (Fe, Ag, etc.), respectively, due to change in redox



Scheme 1. Synthesis and structure of ferrocene (Fc)-aldehyde terminated poly(norborn-2-ene-*b*-1).

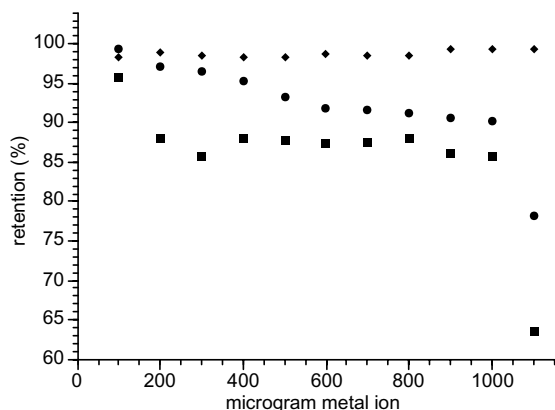


Fig. 1. Breakthrough curves for (□) Pt; (○) Pd; (△) Au; (◆) Ag; (■) Rh; (●) Ir. pH = 0.6, 200 mg silica, 100 ppm each.

potentials. Two representative breakthrough curves are shown in Figs. 1 and 2.

Fig. 1 shows the breakthrough curves for Pt, Pd, Au, Ag, Rh, Ir and Au, Pd, Rh, Pt, Re, Ir, respectively, measured under competitive conditions at pH = 0.6 and 3.5, respectively. From the entire set of data, the following extraction order for pH = 0.6 was deduced: Pd ≈ Ag ≈ Au ≈ Pt > Re > Ir > Rh > Ru > Fe > Cr ≈ Mn ≈ Cd ≈ Zn (see also Fig. 1). This clearly illustrates that the new sorbent allows the selective co-extraction of Pd, Ag, Au, Pt, Pd from ore or other highly acid solutions such as extracts from catalyst sludges at low pH. An even enhanced selectivity was observed at pH = 3.5 with an extraction order Au >

Hg > Pd ≈ Ag > Rh > Pt > Ir ≈ Re > Cu > Co ≈ Zn ≈ Cd ≈ Ni > Cr > Mn (Fig. 2). The maximum amounts of metal ions that can be sorbed onto the material under competitive and non-competitive conditions at pH = 3.5 are summarized in Table 3.

The loadings, which reach the theoretical amount in the case of Pd and Ag are indicative for a 1:1 complex formed by the ligand with the corresponding metal ion. The formation of such 1:1 complexes also serves as an explanation for the selectivity of the sorbent for certain metal ions, since stable bis(terpyridyl)-complexes are known for most transition metal ions and these are usually characterized by high complex-forming constants (K_c). Both under competitive and non-competitive conditions, metals sorbed onto the material were quantitatively (i.e. >97%) desorbed by using nitric acid (5 M) in case loading was stopped before reaching the corresponding point of breakthrough. Sorption capacities are lower than that of other sorbents containing less selective ligands such as phosphonates or amines (Table 4). Nevertheless, this material allows the extraction of Au, Hg, Pd, Ag, Rh, Pt, Re and Ir in a simple, fast and selective SPE setup, leaving less precious metal ions such as Fe, Cr, Mn, Cd, and Zn behind.

The data presented illustrate the potential of this new sorbent for the selective extraction of noble metals, which may be used to substitute traditional purification techniques and may certainly be considered competitive to other selective extraction techniques such as liquid–liquid extraction [4,17,35,50,51].

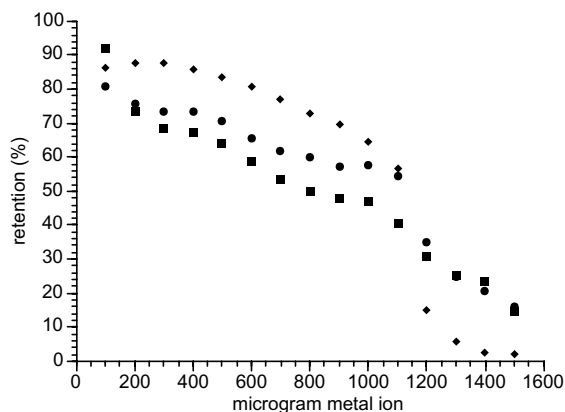


Fig. 2. Breakthrough curves for (□) Au; (○) Pd; (◆) Rh; (●) Pt; (■) Re; (△) Ir. pH = 3.5, 200 mg silica, 100 ppm each.

Table 3
Extraction capabilities of the sorbent for selected metal ions at pH = 3.5

| Metal ion | Mode | Loading (mg metal/g support) | Recovery (%) ^a |
|-----------|------------------------|------------------------------|---------------------------|
| Hg(II) | Single element | >6 | 97 |
| Co(II) | Single element | <0.5 | 98 |
| Au(III) | Single element | >6 | 97 |
| Pd(II) | Single element | >6 | 99 |
| Ag(I) | Single element | >6 | 100 |
| Hg(II) | Competitive conditions | >6 | 102 |
| Au(III) | Competitive conditions | >6 | 102 |

^a Relative standard deviation ±5%.

Table 4
Comparison of extraction capabilities of various sorbents for Au(III)

| Sorbent (brand name) | Functional group | Loading (mg Au/g resin) | Reference |
|----------------------|--------------------------------------|-------------------------|-----------|
| – | Phosphonates | 70 ^a | [21] |
| – | Amines | ≤5 | [37] |
| Cyanex 921 | Tri(<i>n</i> -octylphosphine oxide) | <4 | [18] |
| PS-PIP | Tertiary amine | 150 ^b | [15,17] |
| – | Pyridine-2,6-dicarboxylic acid | ≤40 ^c | [34] |
| Terpyridine | Terpyridine | ≥6 | This work |

^a Low selectivity.

^b No data on selectivity.

^c Reaction time = 24 h.

4. Summary

A new silica-derived sorbent based on a poly(4'-(norborn-2-en-5-ylmethylenoxy)terpyridine-*b*-norborn-2-ene) copolymer was developed and successfully used for the selective extraction of noble metals such as Au, Pd, Ag, Pt, Re, Ir, and Rh. The material provides sufficient extraction capabilities of >6 mg metal ion/g sorbent over a broad range of pH, allows quantitative recoveries and shows no leaching. It may therefore be reused. Elution is simply achieved by treatment with diluted nitric acid. Therefore, the use of toxic reagents such as KCN or of reagents requiring special waste treatment (e.g. thiourea) can be avoided. At different pH, different selectivities can be achieved.

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