



Synthesis of polyimide from 5,5''-bis(bromomethyl)-2,2':6',2''-terpyridine and investigation of the polymer sorption behavior towards some metal ions

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ABSTRACT

The synthesis of a terpyridine-based polyimide sorbent for solid-phase extraction (SPE) of some metal ions is described. For this purpose, 5,5''-bis(bromomethyl)-2,2':6',2''-terpyridine was polymerized with the corresponding diimide derivatives of dianhydrides to give polyimides utilizing terpyridine unit in the main chain. This polymer was used for its extraction capabilities for Pb(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II), at different pH. Under competitive conditions and at pH < 0.6, the selectivity order was Pb ≈ Cd ≈ Zn. Enhanced selectivity was observed at pH 3.5, the order was Cu > Ni > Zn ≈ Cd ≈ Pb. Quantitative recoveries > 97% were observed for all metals in case loading was stopped before reaching the point of breakthrough. As the synthesized polyimides are insoluble in water, solid–liquid extractions have been carried out and the resins sorption for mixture of basic and/or precious metals have been studied under various experimental conditions (reaction time and hydrochloric acid concentration).

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1. Introduction

The selective extraction of noble metals such as Zn, Cd, Mn, Hg, Au, Pd, Ag, Pt, Ir and Co is still an intensively investigated area of research [1–5]. Noble metal purification is still accomplished by traditional precipitation and complexation procedures that require the large amount of highly toxic mineral acids and complexation agents such sodium or potassium cyanide which have negative impact on environment. In order to circumvent the use of such chemicals liquid–liquid extraction, as well as solid-phase extraction (SPE) techniques applying numerous sorbents, have already been developed. Polymer-supported extractants, usually based on PS-DVB or some methacrylates suffer from insufficient selectivity and reduced chemical stability in the extraction media [6,7].

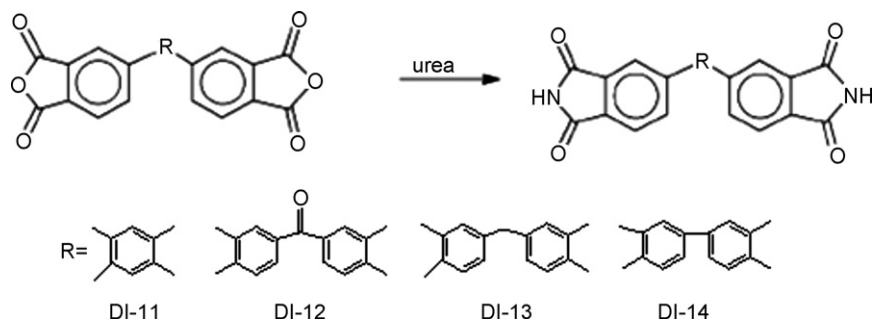
Alternatively, crown ethers on silica [8–11] possessed high selectivity for the metal ions of interest, the use of PS-DVB sorbents impregnated with guanidines [12], poly(amide-ester)-based pyridine-2,6-dicarboxylic acids [13], poly(glycidyl methacrylate)-supported oligoamines [14], etc., have been described. Though ion-exchange resins and solid-supported extractants, usually based on PS-DVB or certain methacrylates 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. A variety of different sorbents for the selective extraction of other metal ions such as lanthanides prepared by various metathesis polymerization-based techniques has already been described [26–36]. Since there is a great interest in pyridine-based ligand which is primarily due to their stability under a variety of oxidative and reductive conditions and the fact that pyridine ligands are mild Lewis bases and capable of bonding abilities toward metals.

Several complexes containing pyridine ligands have appeared in the literature. To the best of our knowledge, however, no paper has dealt with the preparation of polyimide from 5,5''-bis(bromomethyl)-2,2':6',2''-terpyridine by one-stage polycondensation for solid-phase extraction. This paper reports on the synthesis of 5,5''-bis(bromomethyl)-2,2':6',2''-terpyridine acting as tridentate ligand that could be used to build supramolecular architectures by the self assembling of terpyridine component with metal ions. The synthesis of the new terpyridine-containing polyimides is reported. The ligand contains a chain linking the 6,6'' positions of a terpyridine unit. A UV–vis spectrophotometric study used to determine basicity of in aqueous solutions in which the terpyridine nitrogens are involved in proton binding. The last protonation step at strongly acidic pH values. Cu(II), Zn(II), Ni(II), Hg(II), Cd(II) and Pb(II) complexation was studied in aqueous solution by means of spectrophotometric measurements. Cu(II) and Zn(II) can form both mono- and di-nuclear complexes in solution, while the larger Cd(II) and Pb(II) give only mononuclear complexes. In the

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Scheme 1. Dimide synthesis.

$[ML]^{(2+)}$ complexes ($M = Zn(II)$ or $Cd(II)$) the metal is unequivocally bound to the terpyridine unit.

2. Experimental

All synthetic experiments were performed under a nitrogen atmosphere in an 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 UV-diode array 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 to 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. Differential scanning calorimeter (DSC), differential thermal analysis (DTA) and thermogravimetry (TG) were performed with Shimadzu DSC-60, DTA-50 and TGA-50 thermal analyzers, respectively. Inherent viscosities ($\eta_{\text{inh}} = \ln \eta_r/c$ at polymer concentration of 0.5 g/dL) were measured with an Ubbelohde suspended-level viscometer at 30 °C using NMP as the solvent. SPE experiments were carried out using 1.5 mL PP Iso-lute SPE cartridges equipped with PP frits. A Philips (Eindhoven, The Netherlands) PU 9100 X flame atomic absorption spectrophotometer (FAAS) was used for elemental analysis. Cu, Ni hollow cathode lamps operating at 5 mA were used with an air/acetylene flame. Wavelengths were adjusted to 324, 8 for Cu and 232 nm for Ni. Bandpass was used chosen at

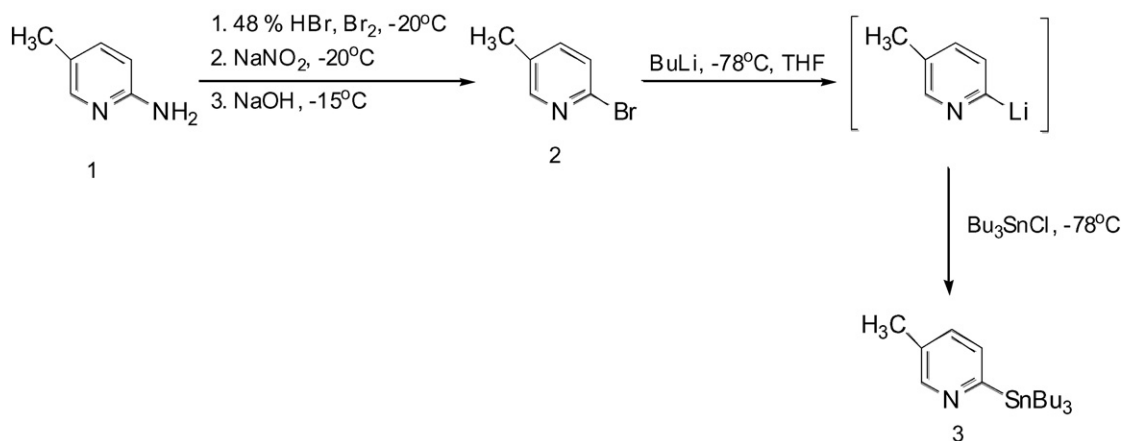
0, 5 nm. A sequential deuterium lamp was used for background correction.

Deionized water was used throughout. Aqueous standard solutions of $Zn(NO_3)_2$ (in 0.5 M HNO_3), $Cu(NO_3)_2$ (in 0.5 M HNO_3), $Hg(NO_3)_2$ (in 0.5 M HNO_3), $Cd(NO_3)_2$ (in 0.5 M HNO_3), $Ni(NO_3)_2$ (in 0.5 M HNO_3) (all Merck, Germany) were used. Other chemicals were purchased from Aldrich and used after purification. 1-Methyl-2-pyrrolidinone (NMP) was distilled over CaH_2 under reduced pressure and stored over 4 Å molecular sieves.

Reagent grade aromatic dianhydrides such as pyromellitic dianhydrides (PMDAs), 3,3',4,4'-benzophenonetetracarboxylic dianhydrides (BPDAs), 4,4'-oxydiphthalic anhydride (ODPAs) that was sublimed at 250 °C under reduced pressure and 3,3',4,4'-biphenyltetracarboxylic dianhydrides (BTDA) were used after crystallization from the proper solvents. All the dianhydrides were dried under vacuum at 120 °C prior to use.

2.1. 2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane diimide (Scheme 1)

The neat mixture of the dianhydrides **2** (2.18 g, 4.19 mmol) and urea (0.25 g, 41.6 mmol) was reacted at 200 °C for 2 h and then cooled to room temperature. The solid was ground into a one powder and further reacted at 200 °C for 1 h and cooled to room temperature. The powder produced was washed with distilled water several times and dried thoroughly. 1.95 g of product was obtained (yield ~89.8%); mp 252 ± 254 °C. Calc. for $C_{31}H_{22}N_2O_6$: C, 71.8; H, 4.3; N, 5.4%. Found: C, 71.7; H, 4.1; N, 5.3%. ^1H NMR (DMSO- d_6) δ 11.27 (br s, 2H), 7.78 (d, 2H), 7.33 (m, 6H), 7.18 (s, 2H), 7.07 (d, 4H), 1.68 (br s, 6H) (FT-IR and NMR spectra of dimides are given in Figs. 1 and 2a and b).



Scheme 2. Synthesis of 5-methyl-2-tributylstannyl pyridine (**3**).

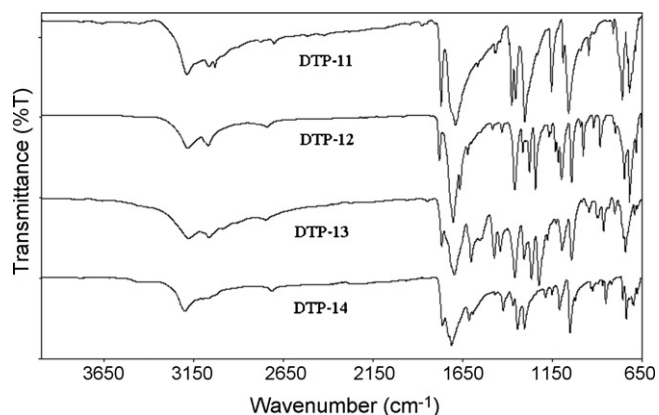


Fig. 1. FT-IR spectra of imidized dianhydrides DTP-11 to DTP-14.

2.2. 2-Bromo-5-methylpyridine (2) (Scheme 2)

To a stirred HBr (48%, 500 mL) solution was added 2-amino-5-methylpyridine (**1**; 100 g, 0.926 mol) at 20–30 °C. As soon as **1** had dissolved completely, the mixture was cooled to –20 °C. The suspension was stirred and Br₂ cooled to –5 °C (133 mL, 2.59 mol) was added drop wise. After stirring for 90 min at –20 °C solution of NaNO₂ [170 g (2.46 mol) in H₂O (250 mL)] was added drop wise. The mixture was allowed to warm to r.t. and stirred for 1 h. The mixture was cooled to –20 °C and NaOH [667 g (16.68 mol) in H₂O (1000 mL)] was added drop wise. The mixture was warmed to r.t. and extracted six times with Et₂O. The combined organic layers were dried (Na₂SO₄) and the solvent was evaporated in vacuum. The solid was purified by sublimation resulting in 135 g (85%) of **2**; mp 39–40 °C.

¹H NMR (CDCl₃): *d* = 2.28 (3 H, s, H-7), 7.35 (2 H, m, H-3, 4), 8.19 (1 H, s, H-6). ¹³C NMR (CDCl₃): *d* = 17.64 (C-7), 127.39 (C-3), 132.38 (C-5), 138.88 (C-2), 139.20 (C-4), 150.32 (C-6). MS (EI, 70 eV): *m/z* (%) = 171 (44) [M⁺], 92 (100) [M±79]. Anal. C₆H₆BrN (172.0). Calc. C, 41.86; H, 3.49, Br, 46.45, N, 8.14. Found: C, 41.76; H, 3.50; Br, 46.55; N, 8.19.

2.3. 5-Methyl-2-tributylstannyl pyridine (3) (Scheme 2)

A solution of **2** (32.14 g, 0.187 mol) in THF (300 mL) was cooled to –78 °C and BuLi (122 mL, 1.6 M in hexane, 0.195 mol) was added drop wise during 30 min. After stirring for further 90 min, Bu₃SnCl (60.5 mL, 0.224 mol) was added. The mixture was stirred for another 8 h at –78 °C and was then allowed to warm to r.t. After adding H₂O (100 mL) the aqueous layer was extracted four times with Et₂O. The combined organic fractions were dried (Na₂SO₄) and the solvent was evaporated in vacuum. The resulting liquid product was purified by Kugelrohr distillation to yield 70.59 g (98%) of **3**; bp 130 °C/0.0038 Torr.

¹H NMR (CDCl₃): *d* = 0.88 (9 H, t, *J* = 7.3 Hz, H-4'), 1.11 (6 H, t, *J* = 8.0 Hz, H-1'), 1.32 (6 H, q, *J* = 7.25 Hz, H-3'), 1.56 (6 H, m, H-2'), 2.28 (3 H, s, H-7), 7.30 (2 H, m, H-3,4), 8.59 (1 H, s, H-6). ¹³C NMR (CDCl₃): *d* = 9.71 (C-1'), 13.63 (C-4'), 18.46 (C-7), 27.30 (C-3'), 29.06 (C-2'), 131.19 (C-5), 131.78 (C-3), 133.92 (C-4), 151.27 (C-6), 169.57 (C-2). MS (EI, 70 eV): *m/z* (%) = 326 (50) [M±56], 268 (45) [M±114], 212 (100) [M±170]. Anal. C₁₈H₃₃NsSn (382.2). Calc. C, 56.56; H, 8.64; N, 3.67; Sn, 31.08. Found: C, 56.29; H, 8.84; N, 3.78; Sn, 31.09.

2.4. 5,5'-Dimethyl-2,2':6',6''-terpyridine (4) (Scheme 3)

A mixture of **3** (70.59 g, 0.185 mol), **2**, 6-dibromopyridine (17.54 g, 0.074 mol) and (Ph₃P)₄Pd (5.18 g, 4.48 mmol) in toluene

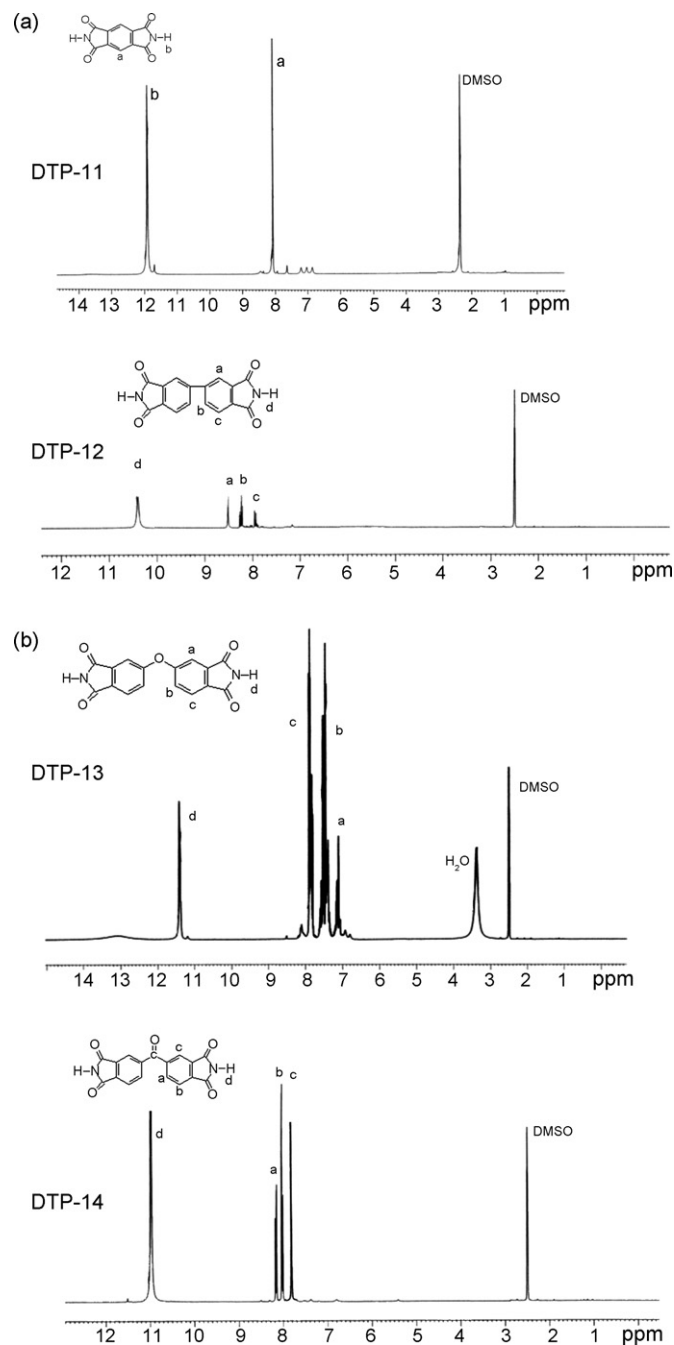
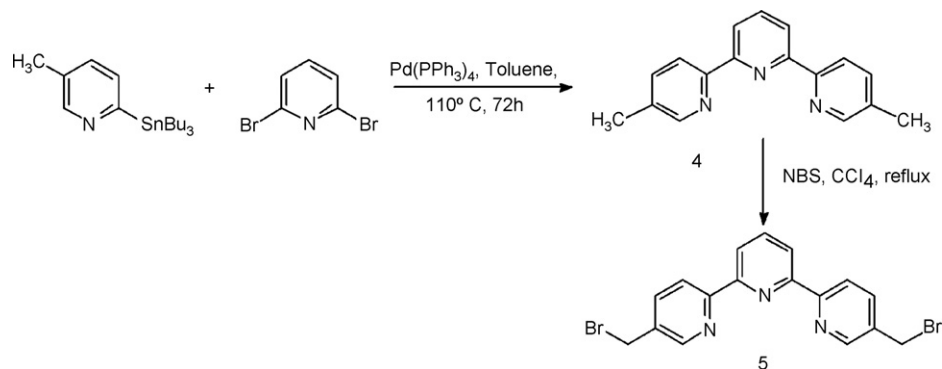


Fig. 2. (a) ¹H NMR spectra of imidized dianhydrides and (b) ¹H NMR spectra of imidized dianhydrides.

(500 mL) were heated under reflux for 120 h. The solvent was removed in vacuum and the brown residue was treated with 6 M HCl (300 mL). The suspension was extracted with CH₂Cl₂ and the organic layers were washed with 6 M HCl (3 × 150 mL). The combined HCl solutions were treated with aq. NH₃ (25%) and the pH adjusted to 9. The precipitate was separated, dissolved in CH₂Cl₂ and dried (Na₂SO₄). After removal of the solvent in vacuum the light yellow solid was recrystallized from EtOAc to afford **4** as a white solid; yield: 17.38 g (90%); mp 174–175 °C.

IR (KBr): *n* = 2916 w, 1591 w, 1557 s, 1484 m, 1443 m, 1375 w, 1257 w, 1132 m, 1024 m, 812 s, 754 m cm⁻¹.

UV–vis (MeCN): λ_{max} (ε) = 245 (1.89), 286 (2.17).



Scheme 3. Synthesis of 5,5'-dimethyl-2,2':6',2''-terpyridine (**4**).

^1H NMR (CDCl_3): $d = 2.39$ (6 H, s, H-7,7''), 7.63 (2 H, d, $J = 8.01$ Hz, H-4,4''), 7.91 (1 H, t, $J = 7.82$ Hz, H-4'), 8.38 (2 H, d, $J = 7.62$ Hz, H-3',5'), 8.49 (2 H, d, $J = 8.40$ Hz, H-3,3''), 8.50 (2 H, s, H-6,6''). ^{13}C NMR (CDCl_3): $d = 18.34$ (C-7,7''), 120.32 (C-3,3''), 120.64 (C-3',5'), 133.32 (C-5,5''), 137.32 (C-4,4''), 137.70 (C-4'), 149.46 (C-6,6''), 153.75 (C-2,2''), 155.33 (C-2',6'). MS (EI, 70 eV): m/z (%) = 261 (100) [M^+], 233 (12) [$\text{M} \pm \text{CHN}$], 219 (16) [$\text{M} \pm \text{C}_3\text{H}_6$], 169 (14) [$\text{M} \pm \text{C}_6\text{H}_6\text{N}$], 130 (10) [$\text{M} \pm 131$]. Anal. $\text{C}_{17}\text{H}_{15}\text{N}_3$ (261.3). Calc. C, 78.16; H, 5.75; N, 16.09. Found C, 77.92; H, 5.73; N 16.07.

2.5. 5,5'-Bis(bromomethyl)-2,2':6',2''-terpyridine (**5**)

A mixture of **4** (2.27 g, 8.69 mmol), NBS (7.75 g, 43.5 mmol) and AIBN (221 mg, 1.35 mmol) in CCl_4 (120 mL) was refluxed under N_2 for 32 min and the precipitated succinimide was removed immediately from the hot mixture by filtration. The precipitate was washed with CCl_4 , the combined CCl_4 phases were reduced to 50 mL in vacuum and the precipitate was removed by filtration. The solid was dissolved in CH_2Cl_2 (100 mL) and extracted with 0.5 M $\text{Na}_2\text{S}_2\text{O}_3$ solution (2×150 mL). The combined $\text{Na}_2\text{S}_2\text{O}_3$ fractions were extracted with CH_2Cl_2 (50 mL) and the combined CH_2Cl_2 layers were dried (Na_2SO_4) yielding 870 mg (24%) of **5** after recrystallization from CHCl_3 ; mp 195–196 °C.

^1H NMR (CDCl_3): $d = 4.56$ (4 H, s, H-7,7''), 7.92 (2 H, dd, $J = 8.39$, 2.29 Hz, H-4,4''), 7.97 (1 H, t, $J = 8.01$ Hz, H-4'), 8.47 (2 H, d, $J = 8.02$ Hz, H-3',5'), 8.61 (2 H, d, $J = 8.01$ Hz, H-3,3''), 8.72 (2 H, d, $J = 2.29$ Hz, H-6,6'').

^{13}C NMR (CDCl_3): $d = 29.54$ (C-7,7''), 121.24 (C-3,3''), 121.55 (C-3',5'), 133.87 (C-5,5''), 137.79 (C-4,4''), 138.08 (C-4'), 149.06 (C-6,6''), 154.61 (C-2,2''), 155.78 (C-2',6').

MS (EI, 70 eV), m/z (%) = 419 (20) [M^+]. Anal. $\text{C}_{17}\text{H}_{13}\text{Br}_2\text{N}_3$ (419.1). Calc. C, 48.72; H, 3.13; N, 10.03. Found: C, 48.63; H, 2.68; N, 10.05.

2.6. Synthesis of polyimides

A typical polyimide (DTP-PI-11 to DTP-PI-14) synthesis was performed as follows: monomer 5,5'-bis(bromomethyl)-2,2':6',2''-terpyridine (1.75 g, 4.15 mmol) was dissolved in NMP (15 mL) in a 50-mL Schlenk tube equipped with a nitrogen line, overhead stirrer, a xylene-filled Dean–Stark trap, and a condenser. PDI-11 (pyromellitic diimide) (0.86 g, 4.15 mmol) was added to this solution and stirred overnight to give a viscous solution. The mixture was heated to 70 °C, xylene (5 mL) was added, and the mixture was refluxed for 3 h. Following the removal of xylene by distillation, the reaction mixture was cooled at room temperature and the product was precipitated by addition of a large excess of methanol. The dark yellow product was isolated and dried at 100 °C under vacuum and then at 200–250 °C under nitrogen for 2 h; yield, 89%. ^1H and ^{13}C NMR

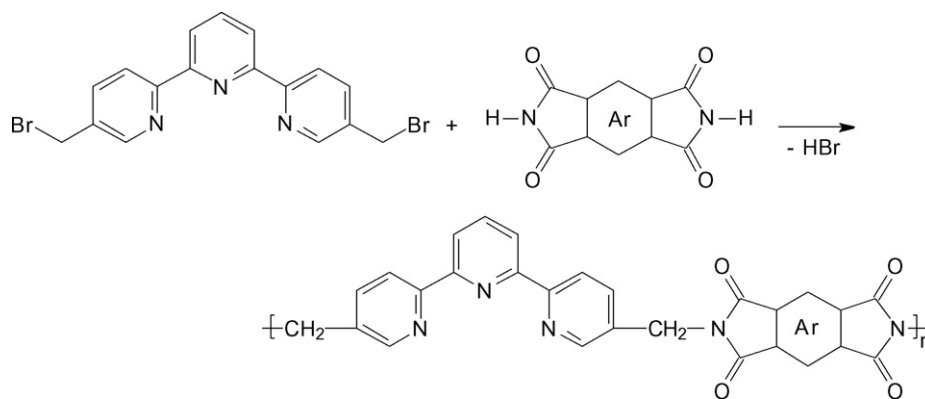
spectra. δ_{H} (300 MHz, $\text{DMSO}-d_6$) 2.38 (s, H-d), 6.82 (d, J 9.0, H-3), 6.78 (d, J 8.9, H-2), 7.85 (t, J 8.0, H-a), 8.32 (d, J 7.7, H-b), 9.01 (s, pyromellitic).

2.7. SPE experiments

For all experiments the SPE material was first stirred in methanol–water (20:80) for 1 h. Columns were slurry packed and conditioned by passing 100 mL of methanol–water solution through the column, followed by 100 mL water flow rate of 3 mL/min. For SPE, solutions containing 100 ppm single element standards, respectively, were passed through a slurry-packed filtration column (Isolute™ accessories, 200 mg sorbent). Fifty milliliters of the mixed standards 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 Recoveries were determined under non-competitive conditions by AAS.

3. Results and discussion

The polyimides used throughout the SPE experiments were prepared from 5,5'-bis(bromomethyl)-2,2':6',2''-terpyridine (**5**) and the desired diimide as shown in Scheme 4. Incorporating terpyridine groups in the main chain facilitated not only polyimide synthesis but also a potent to prepare metal coordinated polymers. FT-IR, ^1H and ^{13}C NMR spectra and elemental analysis were used to confirm the structures of the monomer, 5,5'-bis(bromomethyl)-2,2':6',2''-terpyridine. The NMR spectra of the monomer were diagnostic. Only a single set of signals were observed for two pendant groups of terpyridine complexes in both ^1H and ^{13}C NMR spectra that indicate the two arms of the ligand are magnetically equivalent in solution and the ligand is tridentate. All the polymerizations proceeded in homogeneous solution and the precipitation was prevented in all cases by adjusting the solvent to the monomer ratio. The FT-IR spectra (Fig. 3) showed that aliphatic C–H stretching frequencies were appeared between 2850 and 2890 cm^{-1} , 1720–1730 cm^{-1} sym. imide $\nu(\text{C}=\text{O})$, 1765–1790 cm^{-1} asym. imide $\nu(\text{C}=\text{O})$ stretching, C–N imide ring stretching 1360 cm^{-1} , whereas imide ring deformation was appeared at near 1070 cm^{-1} and C–N bending at 730–760 cm^{-1} and the C=N peak in the monomers gave two peaks at 1440–1660 cm^{-1} , respectively. Polyimides were synthesized in NMP solvent in a one-stage solution polycondensation in which the dibromo groups were reacted with a stoichiometric amount of the diimide (Scheme 4). The polymers were isolated in almost quantitative yield by precipitation from methanol. The formation of the imide ring was confirmed by FT-IR that was



Scheme 4. Synthesis of polyimides.

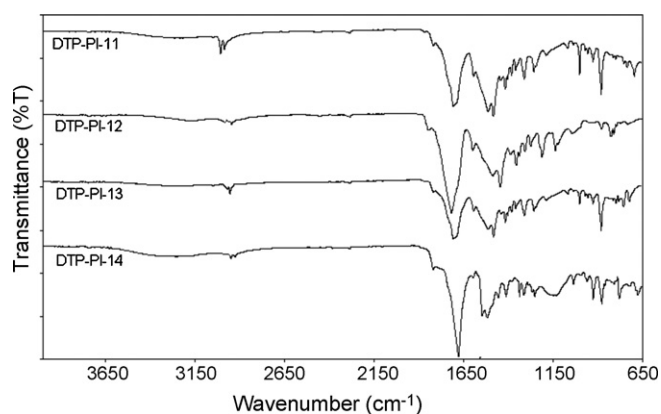


Fig. 3. FT-IR spectra of polyimides DTP-PI-11 to DTP-PI-14.

discussed in our previous papers [37–40]. The thermal properties of the polyimides were evaluated by DSC, DTA (Fig. 4) and TG (Fig. 5). The thermal behavior data of all the polymers are presented in Table 1. DSC experiments were conducted at a heating rate of 10 °C/min in nitrogen. Rapid cooling from 400 °C to room temperature produced predominantly amorphous samples, so T_g 's of all the polyimides could easily be read in the subsequent heating DSC traces. The T_g values of polyimides DI-PI-11 to DI-PI-14 were in the 172–206 °C range depending on the structure of the dianhydrides component and decreasing with increasing flexibility of the poly-

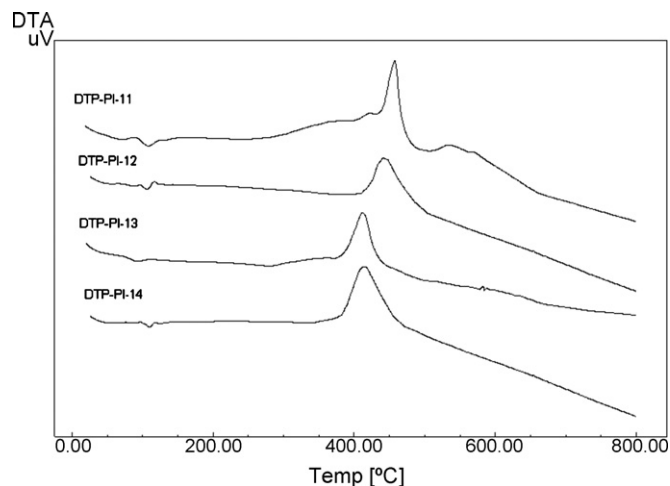


Fig. 4. DTA thermograms of polyimide DTP-PI-11 to DTP-PI-14.

mer backbones. As expected, the polyimide DTP-PI-11 derived from PMDA exhibited the highest T_g because of the rigid pyromellitimide unit. The thermal stability of the polymers was evaluated by TGA conducted at a heating rate of 10 °C/min in nitrogen atmosphere. The temperatures of 10% weight loss in nitrogen stayed within 440–490 °C range. DTP-PI-14 having oxygen group in dianhydrides exhibited the lowest T_{10} values than the other polyimides. The solubility of the polyimides was tested in various organic solvents, and the results are summarized in Table 2. Polymers had excellent solubilities in aprotic polar solvents such as NMP, DMAc, DMF and DMSO. This high solubility might be attributed to the formation of some intermolecular spacing due to the tridentate ligand.

For each of the polymers, high molecular weights have been achieved as was confirmed by GPC (Table 2). The results show a unimodal molecular weight distribution with a polydispersity index of about two, which is expected for step-growth polymerizations.

3.1. SPE experiments

The polymer-supported organic reactions in which the structure of the ligand was not changed during polymerization was directly used for preliminary investigations concerning the complex formation capabilities with various metals. The loadings that reach the theoretical amount were indicative for the complex formations which explain for the selectivity of the sorbent for certain metal ions. Metals sorbed onto the material (>90%) desorbed by nitric acid (5 M). In case loading was stopped before reaching the

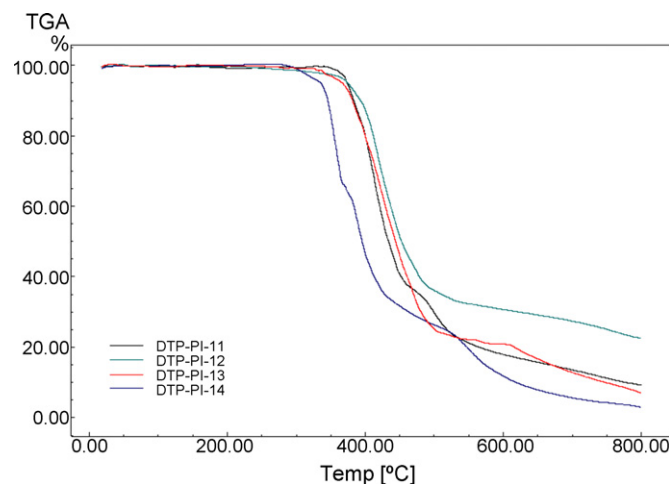


Fig. 5. TGA thermograms of polyimides DTP-PI-11 to DTP-PI-14.

Table 1
Basic properties of the polyimides

Polyimide	Basic properties			Solubility ^a				
	Yield (%)	d^b (g/cm ³)	η^c (dL/g)	NMP	DMF	DMAC	THF	DMSO
DTP-PI-11	62	1.31	1.52	+	±	±	–	+
DI-PI-12	71	1.25	1.38	+	+	+	–	+
DI-PI-13	75	1.22	1.27	+	+	+	±	±
DI-PI-14	64	1.30	1.49	+	±	+	–	+

^a Solubility tested at 2% solid concentration; +, soluble at room temperature (25 °C); ±, soluble upon heating; –, insoluble at room temperature.

^b Determined by suspension method at 30 °C.

^c Measured at a concentration of 0.5 dL/g in NMP at 30 °C using an Ubbelohde viscometer.

Table 2
Thermal properties of the polyimides

Polyimide	TGA			DTA ^a		DSC ^b	
	10 ^c (%)	Char ^d	IDT ^e	TDP ^f	Heat (kJ/g)	T_g (°C)	M_w/M_n
DI-PI-11	384	10	408	457	0.58	176	1.81
DI-PI-12	394	23	406	440	0.48	–	1.69
DI-PI-13	379	7	370	411	0.40	126	1.70
DI-PI-14	349	3	371	412	0.68	142	1.73

^a DTA thermograms of polyimides with a heating rate of 10 °C/min in a air atmosphere.

^b DSC thermograms of polyimides with a heating rate of 10 °C/min in a nitrogen atmosphere.

^c 10% weight loss, as assessed by TGA at a heating rate of 10 °C/min in nitrogen.

^d Char yields, calculated as the percentage of the solid residue after heating from room temperature to 900 °C in nitrogen.

^e IDT (initial decomposition temperature) is the temperature at which an initial loss of mass was observed.

^f TDP (thermal decomposition peak).

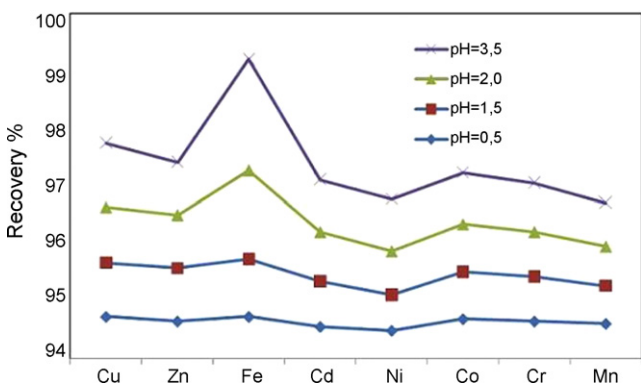


Fig. 6. Simultaneous sorption of metals (1.5×10^{-1} mol/L of each metal, 24 h) for the resin DTP-PI-11.

corresponding point of breakthrough. From the entire set of data, the following extraction order for pH 0.6 was deduced: $Pb \approx Cd \approx Zn$. An even enhanced selectivity was observed at pH 3.5 with an extraction order $Cu > Ni > Zn \approx Cd \approx Pb > Hg$ (Figs. 6–8).

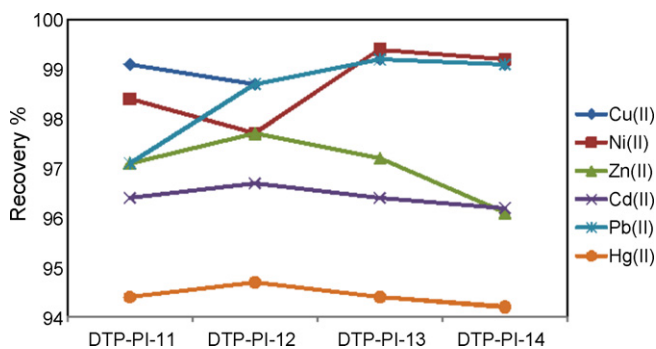


Fig. 7. Non-competitive sorption of metals (1.5×10^{-1} M of each metal, 24 h at pH 3.5).

The hydrochloric acid contraction of the aqueous feed has a more pronounced influence on the extraction yields of each resin. The sorption of metals is higher in 3.5 M HCl. The other polyimides DTP-PI-11, DTP-PI-13 and DTP-PI-14 showed somewhat different sorption characteristics that could be attributed to the structure of the polymer chain (statistics or regular chain). The formation of such 1:1 complexes also serves as an explanation for the selectivity of the sorbent for certain metal ions, since stable 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. 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. UV–vis spectrophotometric study on the basicity properties of in aqueous solutions shows that the terpyridine nitrogens are involved in proton binding only in the last protonation step at strongly acidic pH values. Cu(II), Zn(II), Cd(II) and Pb(II) complexation was studied in aqueous solution by means of spectrophotometric measurements. Cu(II) and Zn(II) can form both mono-

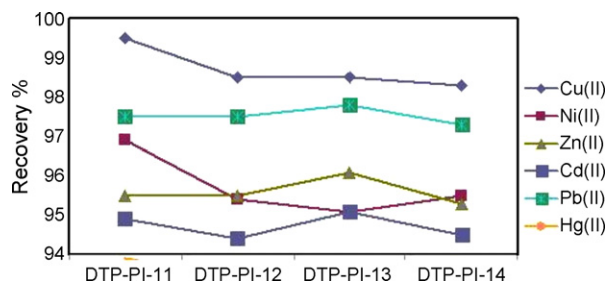


Fig. 8. Competitive sorption of metals (1.5×10^{-1} M of each metal, 24 h at pH 3.5).

and di-nuclear complexes in solution, while the larger Cd(II) and Pb(II) give only mononuclear complexes. In the $[ML]^{2+}$ complexes ($M = Zn(II)$ or $Cd(II)$) the metal is unequivocally bound to the terpyridine unit. The strongly ionic nature of the bonding in complexes results in coordination geometries that reveal a balance between electrostatic and steric demands. This balance is the determining factor for complexation insolubility with solvation as an important aspect to be considered. In their complexes the cations act as typical “hard” acids and interact preferentially with bases such. The hard acid character of the metal is evidence that their complexation in aqueous solution can be interpreted in terms of electrostatic demand. Metal interaction with the softer donors can nevertheless be achieved in organic solvents of low solvating power (in aqueous solutions the soft base sites can rarely compete with water) or, more importantly, by the construction of molecules with specific topologies where the appropriate placement of soft donor atoms fulfill the coordination sphere of the metal. In that way the interaction between metal and nitrogen donor sites can be attained in aqueous solutions thus avoiding the otherwise favorable water coordination in the hydration sphere of the metals. This is the case of macrocyclic structures of well-defined geometry. In these complexes the orientation of the nitrogen donor sites and their interaction with the cations produces sufficient metal dehydration while allowing for the softer atoms to effectively interact with the metals to produce the pursued ligand-to-metal energy-transfer process.

4. Conclusion

A new polyimide-derived sorbent based on a poly(5,5'-bis(bromomethyl)-2,2':6',2''-terpyridine) was developed and successfully used for the selective extraction of noble metals such as Cu, Zn, Cd, Ni, Hg, and Pb. The material provides sufficient extraction capabilities of >8 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 selectivity can be achieved.

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