

Supporting Information

Selective separation of cadmium (II) from Zinc (II) by a novel hydrophobic ionic liquid including *N,N,N',N'*-tetrakis(2-methylpyridyl)-1,2-phenylenediamine-4-amido structure: A hard-soft donor combined method

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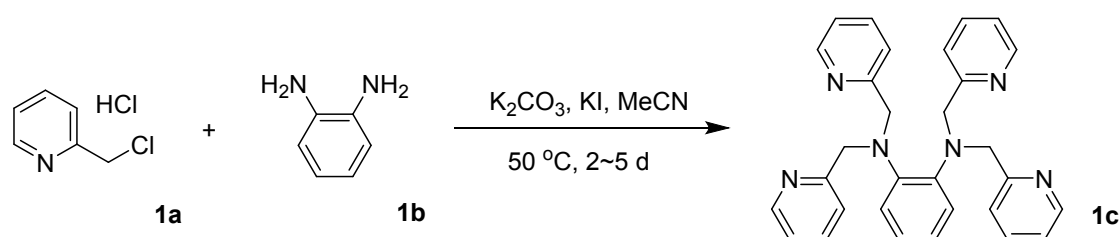
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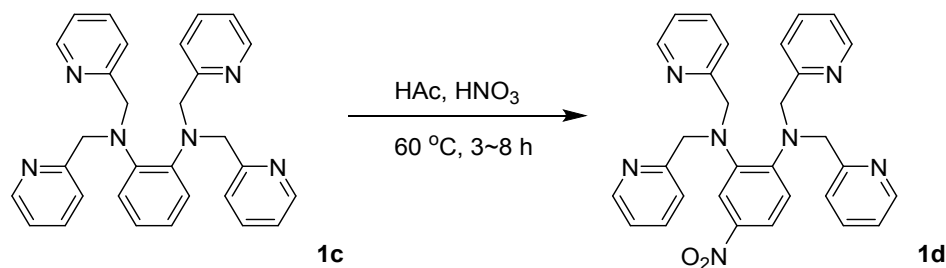
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Synthesis procedures:

Thin layer chromatography analyses (TLC) were performed using analytical TLC plates coated with aluminum oxide 60 F₂₄₅ basic and silica gel 60 F₂₄₅ (Merck Darmstadt, Germany). Activated alumina (about 75µm) and silica gel 60 (0.063-0.200 mm) purchased from Wako chemical was utilized for column chromatography purification. Nuclear magnetic resonance spectroscopy (NMR: 400MHz for ¹H, 100MHz for ¹³C and 376 MHz for ¹⁹F) was utilized for characterization of each product by using deuterated solvent (Chloroform-d, DMSO-d₆). Fourier transform infrared spectroscopy (FTIR) was recorded in JIR-SPX200. All reagents were obtained from commercial suppliers in the highest grade which could be commercially obtained and used without any further purification. All aqueous solutions were made with deionized water.

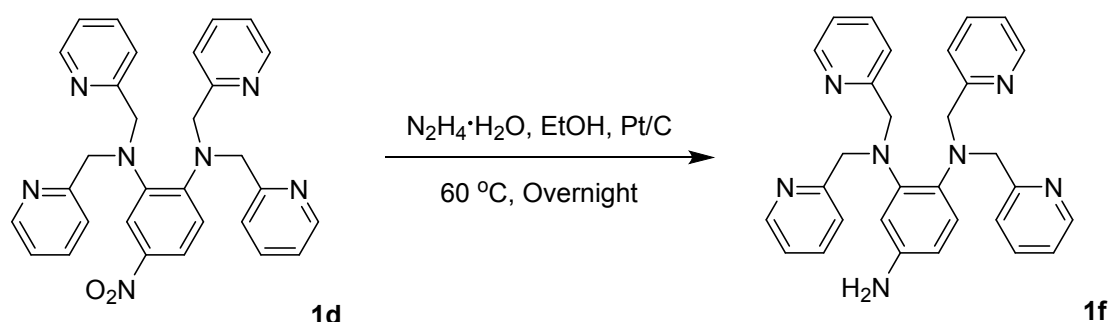


To a dehydrated acetonitrile solution (30 mL) of **1b** (0.54 g, 5.0 mM), 2-(chloromethyl) pyridine hydrochloride (3.61 g, 22.0 mM), potassium iodide (3.65 g, 22.0 mM), and potassium carbonate (10.0 g, 75.0 mM) were added. The mixture was refluxed for 2-5 days at 50 °C under the protection of N₂. The reaction mixture was cooled to room temperature and the solvent of MeCN was removed under rotary evaporator. Then the paste was diluted in deionized water. The solution was thoroughly extracted with chloroform (3 × 20 mL) and the combined organic phase was washed with water, saturated NaHCO₃ solution, and dried by adding anhydrous Na₂SO₄. The dried chloroform was concentrated to a gummy residue which was purified by alumina column chromatography (R_f= 0.25, dichloromethane: ethyl acetate= 4:1) to give **1c** (0.89 g, 1.9 mM, yield= 38%) as an orange oil. ¹H NMR (CDCl₃-d, 400 MHz, 25°C), δ/ppm: 4.74 (s, 8H), 6.77-6.90 (m, 4H, CH), 7.09 (m, 8H, C3, C5-pyr-H), 7.44 (td, 4H, C4-pyr-H), 8.51 (dt, 4H, C6-pyr-H). ¹³C NMR (CDCl₃-d, 400 MHz, 25°C), δ/ppm: 57.3, 121.7, 122.1, 122.3, 123.0, 135.9, 142.1, 148.9, 158.7.

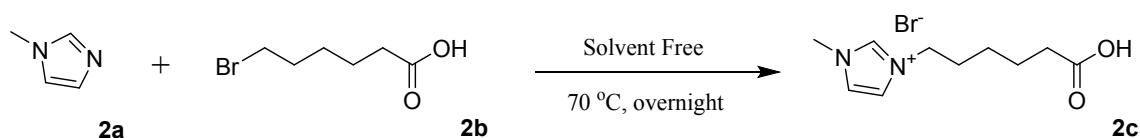


To a dehydrated chloroform solution (10 mL) of **1c** (0.89 g, 1.9 mM), acetic acid (10 mL) was added slowly while stirring. Nitration agent was prepared by mixing 5 mL HNO₃ (65%) with 15 mL acetic acid, and then added dropwise over 30 min. After

stirring for 1 h at room temperature, the solution was heated to 60 °C and refluxed for another 3-8 h. After cooling to room temperature, pH value of the mixture was adjusted to around 8-9 by slowly adding saturated Na₂CO₃ solution. Aqueous phase was extracted with chloroform for three times (3×20 mL). The combined chloroform phase was dried over dehydrated Na₂SO₄. After filtration, the solvent was removed by evaporation under reduced pressure at 50 °C. The residue was purified by alumina column chromatography (dichloromethane: ethyl acetate= 8:1, R_f= 0.2) to give **1d** as light-yellow oil (0.65 g, 1.25 mM, yield= 66%). ¹H NMR (CDCl₃-d, 400 MHz, 25°C), δ/ppm: 4.75 (s, 4H), 4.99 (s, 4H), 6.89 (d, 1H, CH), 7.12 (m, 8H, C3, C5-pyr-H), 7.52 (tt, 4H, C4-pyr-H), 7.65 (d, 1H, CH), 7.73 (d, 1H, CH), 8.51 (tt, 4H, C6-pyr-H). ¹³C NMR (CDCl₃-d, 400 MHz, 25°C), δ/ppm: 56.4, 117.7, 118.2, 120.5, 122.0, 122.8, 123.3, 136.2, 140.8, 141.4, 148.4, 149.2, 157.4, 157.8.

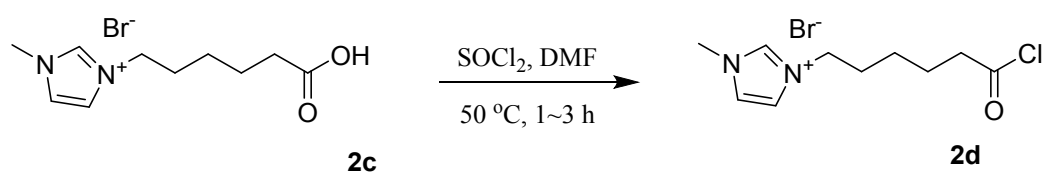


Dehydrated ethanol solution (15 mL) of **1d** (0.65 g, 1.25 mM) was degassed with nitrogen flow, followed by the addition of 0.2 g Pd/C catalyst and 15 mL hydrazine hydrate. The reduction reaction was carried out under reflux at 60 °C with the protection of N₂ for the whole night. After reaction, catalyst was separated by filtration and the obtained filtrate was cooled in the refrigerator for crystallization to give **1f** as yellow crystal (0.55 g, 1.13 mM, yield > 90%). ¹H NMR (DMSO-d₆, 400 MHz, 25°C), δ/ppm: 4.39 (s, 4H, CH₂), 4.46 (s, 2H, C-NH₂), 4.57 (s, 4H, CH₂), 5.89 (dd, 1H, CH), 6.13 (d, 1H, CH), 6.53 (d, 1H, CH), 7.11 (m, 8H, C3, C5-pyr-H), 7.52 (m, 4H, C4-pyr-H), 8.37 (m, 4H, C6-pyr-H). ¹³C NMR (DMSO-d₆, 400 MHz, 25°C), δ/ppm: 57.7, 108.7, 109.5, 111.9, 121.6, 123.3, 129.5, 133.7, 135.5, 135.9, 141.9, 143.6, 148.9, 159.1.

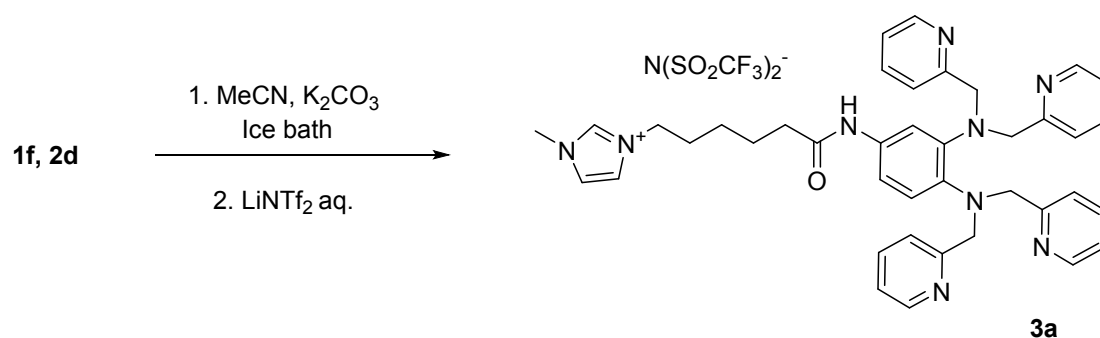


2c was prepared by a simple solvent free method as described in previously published papers. **2b** (2.64 g, 12.6 mM) was added dropwise into **2a** (1.03 g, 12.6 mM). The mixture was stirred vigorously for 12 h at 70 °C under the protection of N₂. The resulting viscous liquid was allowed to cool to RT, then treated with ethyl acetate (3 × 20 mL) and stirred vigorously for 30 min. The solvent was decanted and the process repeated several times. The product **2c** (2.09 g, 60%) was dried under vacuum at 70 °C. ¹H NMR (DMSO-d₆, 400 MHz, 25°C), δ/ppm: δ 1.23 (quint, 2H, CH₂), 1.49 (quint, 2H, CH₂), 1.79 (quint, 2H, CH₂), 2.19 (t, 2H, CH₂), 3.88 (s, 3H, N-CH₃), 4.19 (t, 2H, CH₂-N_{ring}), 7.79 (t, 1H, CH), 7.87 (t, 1H, CH), 9.38 (s, 1H, CH). ¹³C NMR

(DMSO-d₆, 400 MHz, 25°C), δ /ppm: 24.7, 25.5, 29.6, 36.1, 49.1, 118.4, 122.7, 136.9, 148.6, 158.2.



Excess thionyl chloride (1.64 g, 13.8 mmol) was used as reagent and solvent, stoichiometry amount of **2c** (0.18 g, 0.67 mM) was weighed and added. The mixture was stirred vigorously to dissolve, and later 3 drops of dry DMF was added as catalyst. The mixture was heated at 50 °C for 2 h. After reaction, the excess thionyl chloride was distilled off under reduced pressure and the residue was dissolved in 5mL dehydrated MeCN and used in the next procedure as soon as possible.



To a dehydrated MeCN solution (10 mL) of **1f** (0.55 g, 1.13 mM) was added Na₂CO₃ followed by dropwise adding **2d** dissolved in dehydrated MeCN solution (2 mL). The mixture was stirred for 12 h under the protection of N₂. The color of the solution was changed gradually from yellow to brown while adding **2d**. The resulting solution was filtered, and the solvent was evaporated under reduced pressure to give precursor as dark brown oil. The residue was dissolved in deionized water (20 mL), excess LiNTf₂ (1.0 g, 3.5 mM) dissolved in deionized water (10 mL) was added and stirred at room temperature for 24 h. **3a** was formed in the bottom of the aqueous layer. **3a** was separated by centrifugation, and washed several times with aliquots of water until bromide residue were no longer detected by the AgNO₃ test. The pure product **3a** (0.58 g, 0.63 mM, Total yeild= 9.87%) was obtained as an orange viscous liquid. ¹H NMR (DMSO-d₆, 400 MHz, 25°C), δ /ppm: 1.25(m, 2H, CH₂), 1.57(m, 2H, CH₂), 1.82(m, 2H, CH₂), 2.22(m, 2H, CH₂), 3.85(s, 3H, CH₃), 4.17(dt, 2H, CH₂), 4.58(s, 4H, CH₂), 4.63(s, 4H, CH₂), 6.93(dd, 1H, CH), 7.12(dd, 1H, CH), 7.20(d, 1H, CH), 7.31(m, 8H, C3, C5-pyr-H), 7.76(m, 4H, C4-pyr-H), 8.52(m, 4H, C6-pyr-H), 9.07(s, 1H, CH), 9.10(s, 1H, CH), 9.57(s, 1H, CH). ¹³C NMR (DMSO-d₆, 400 MHz, 25°C), δ /ppm: 24.2, 24.7, 25.6, 29.6, 36.2, 49.1, 56.8, 64.1, 113.1, 113.7, 115.2, 118.4, 121.6, 122.7, 124.2, 135.3, 136.9, 138.3, 143.3, 148.1, 157.7. ¹⁹F NMR (DMSO-d₆, 400 MHz, 25°C), δ /ppm: -78.7.

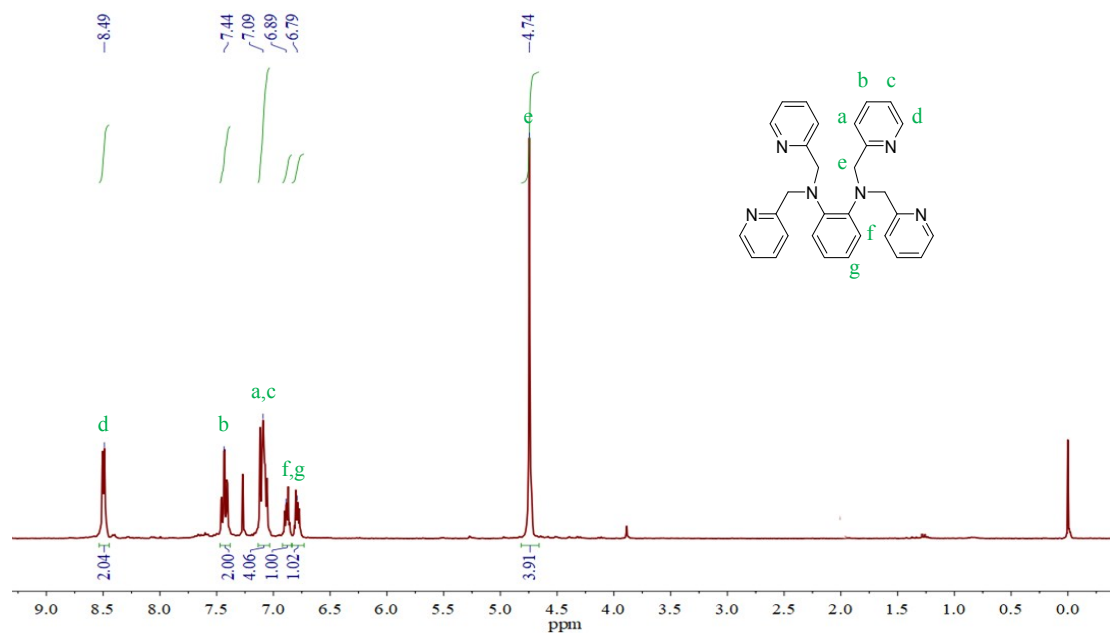


Figure S1. ^1H NMR of **1c** in CDCl_3

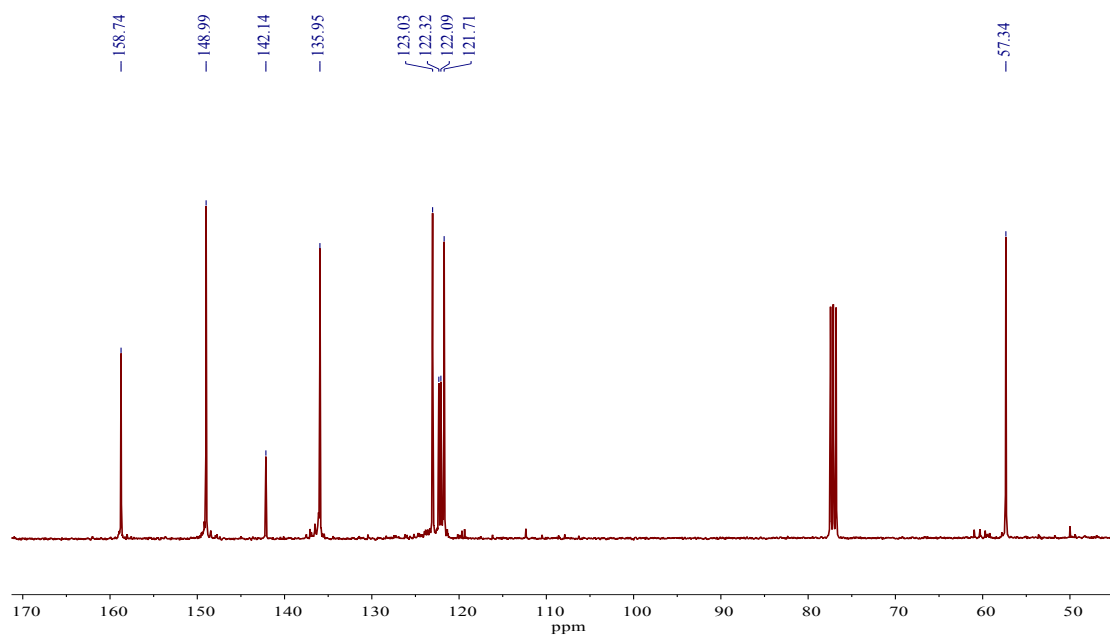


Figure S2. ^{13}C NMR of **1c** in CDCl_3

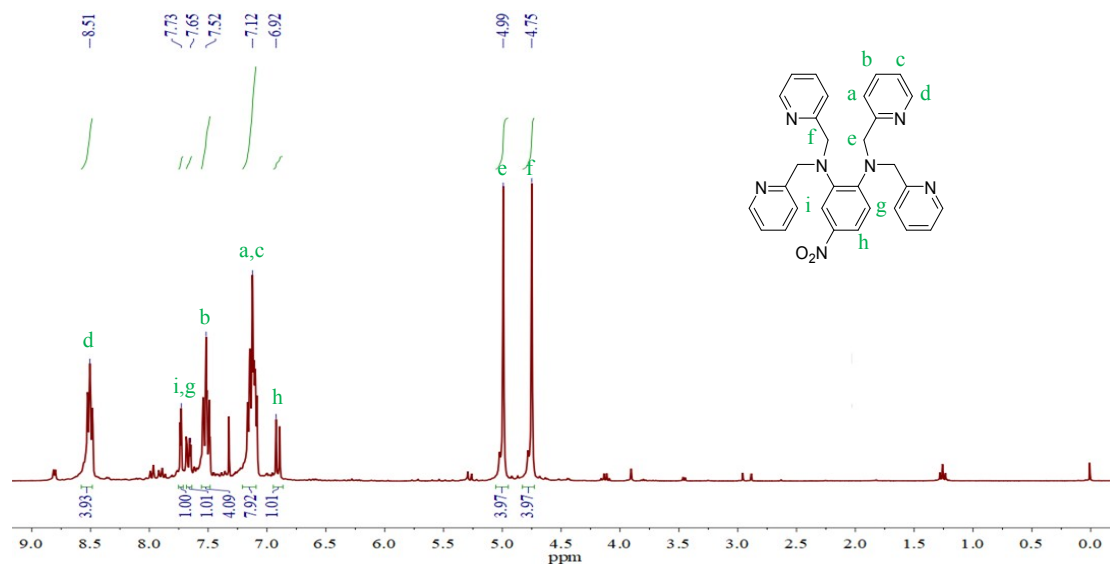


Figure S3. ^1H NMR of **1d** in CDCl_3

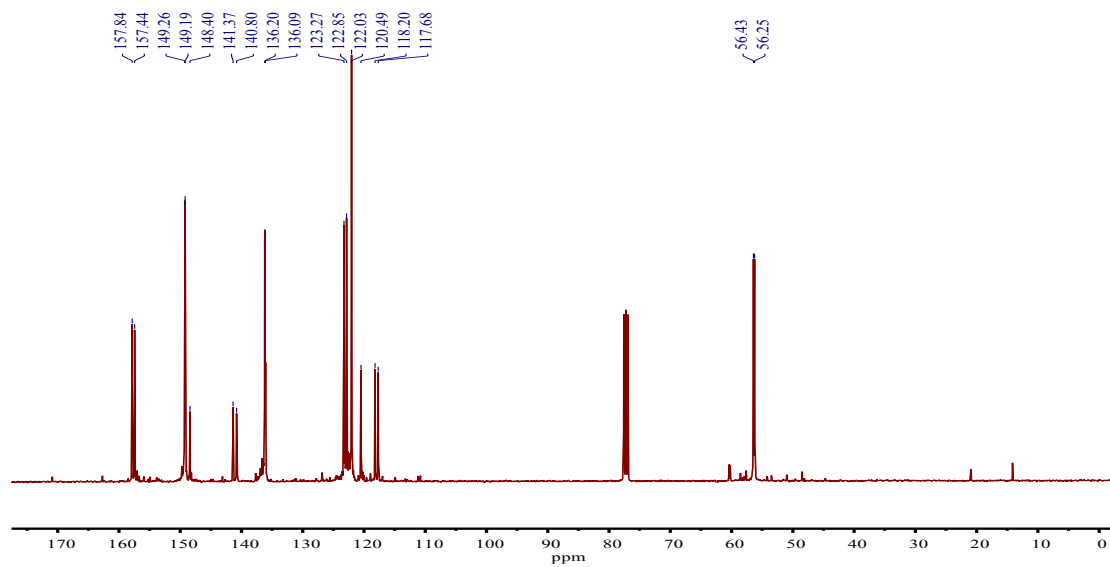


Figure S4. ^{13}C NMR of **1d** in CDCl_3

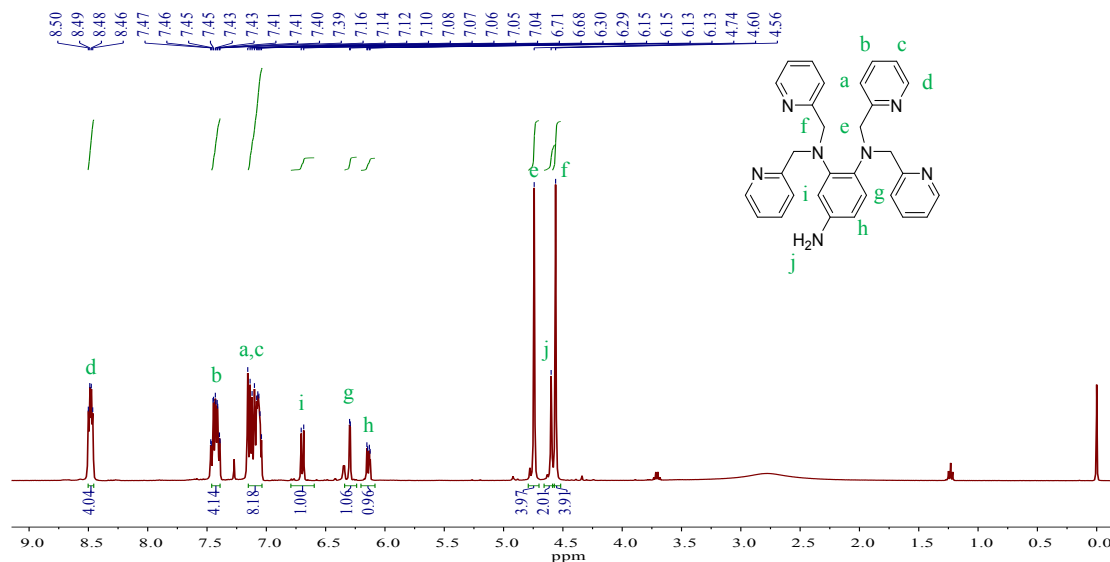


Figure S5. ^1H NMR of **1f** in CDCl_3

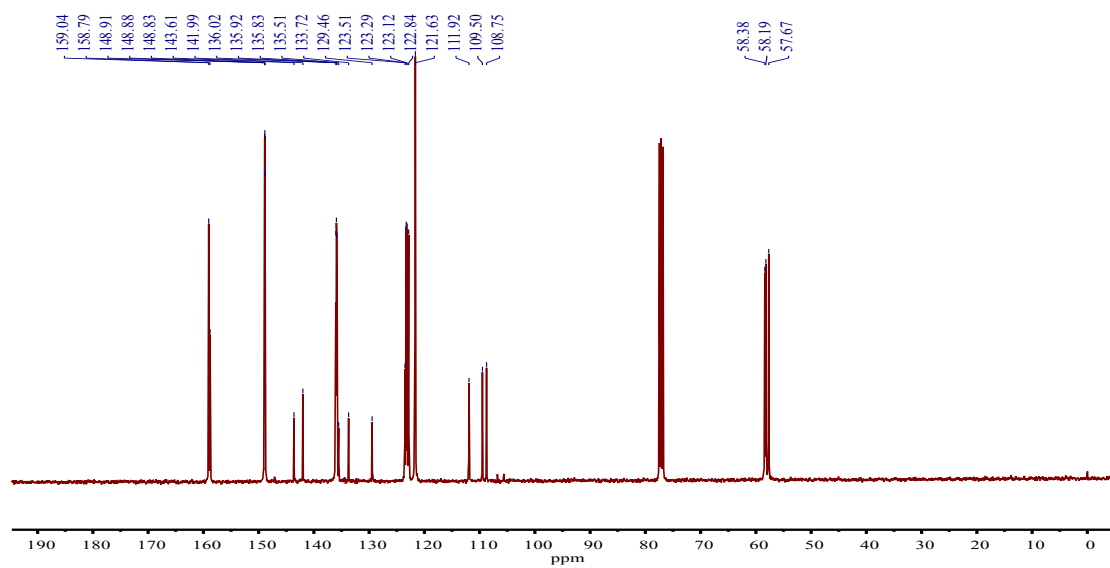


Figure S6. ^{13}C NMR of **1f** in CDCl_3

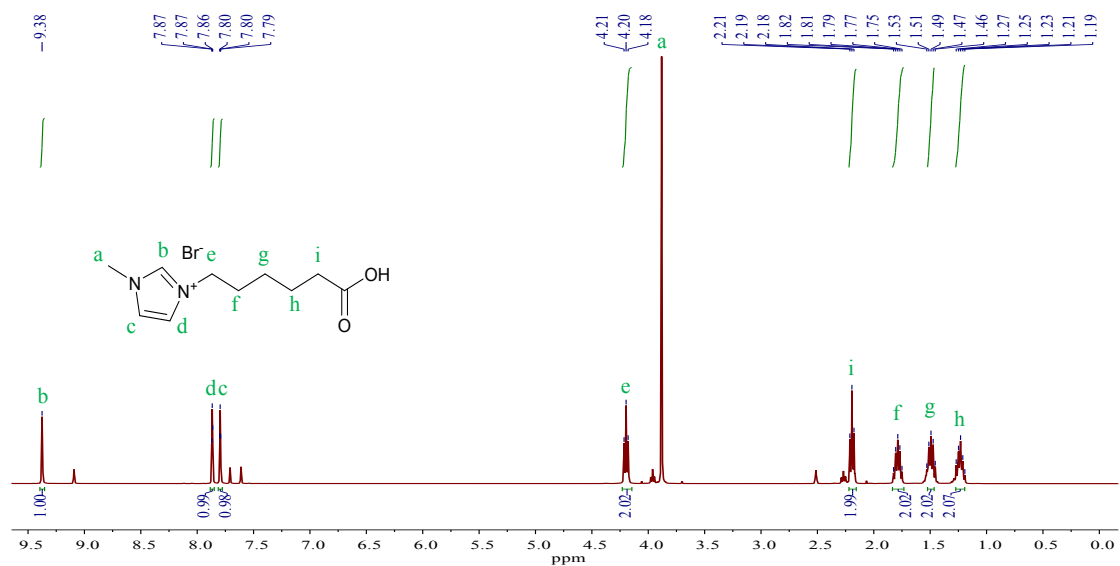


Figure S7. ¹H NMR of **2c** in DMSO-d₆

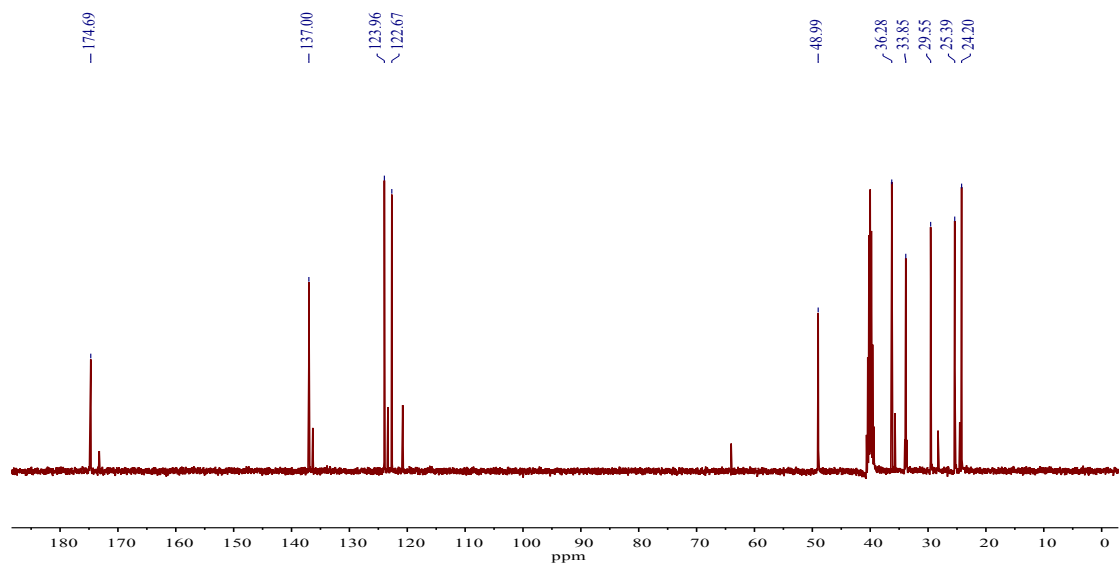


Figure S8. ¹³C NMR of **2c** in DMSO-d₆

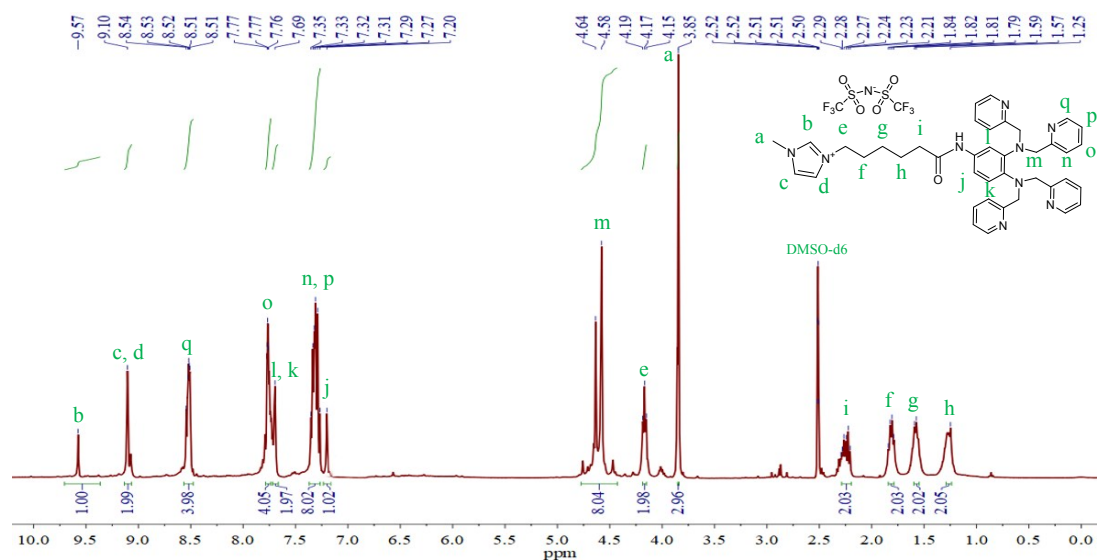


Figure S9. ^1H NMR of 3a in DMSO- d_6

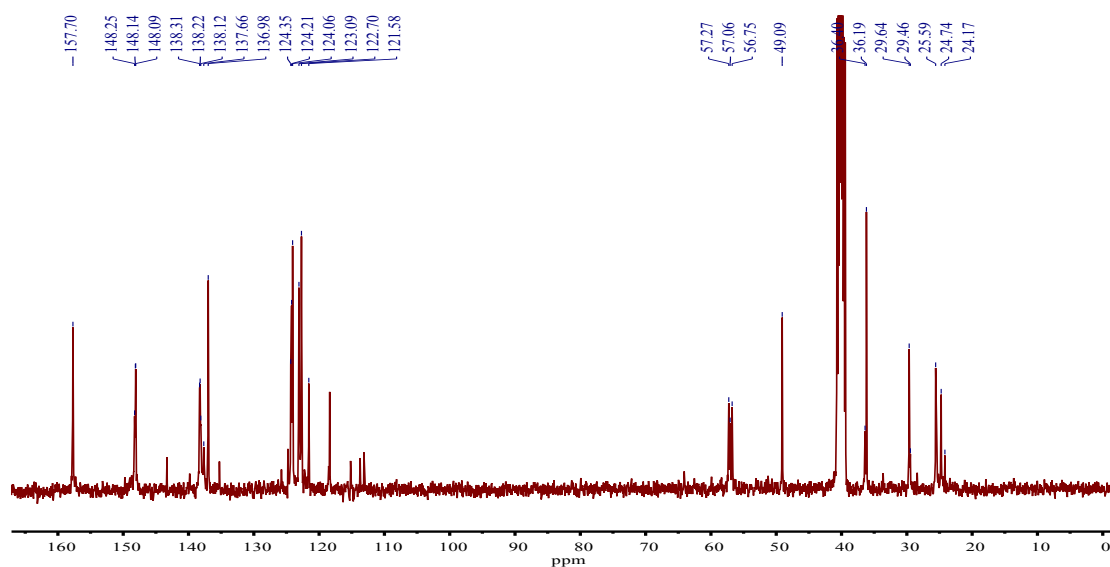


Figure S10. ^{13}C NMR of 3a in DMSO- d_6

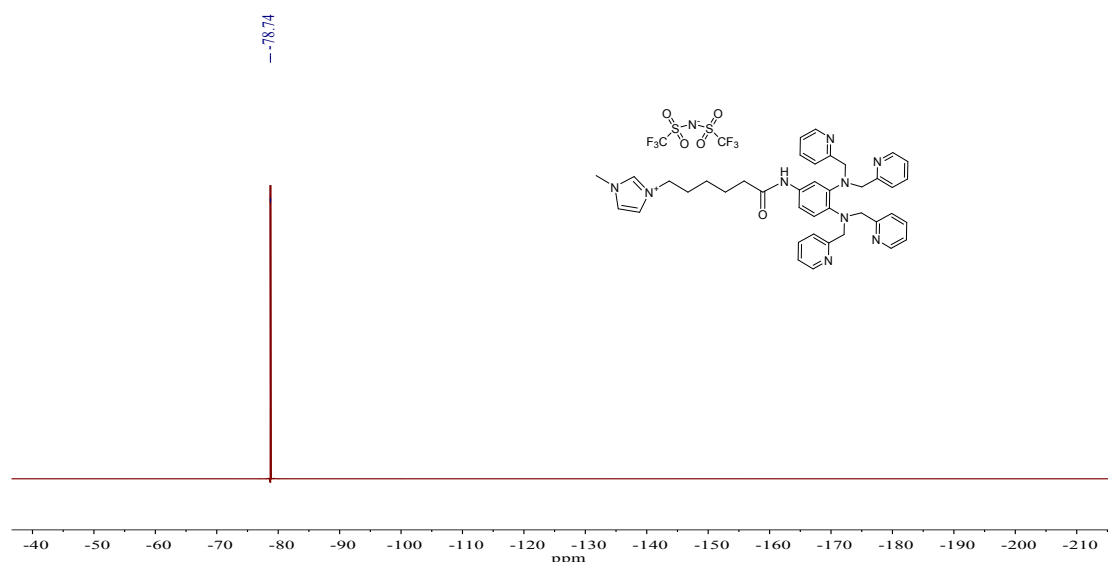


Figure S11. ^{19}F NMR of **3a** in DMSO- d_6

Table S1 Summary numerical data in **Fig. 2**

Time (h)	E_{Cd} (%)	E_{Zn} (%)
0.2	12.88 ± 0.3	3.01 ± 0.3
0.5	30.41 ± 0.1	12.08 ± 0.1
1	42.95 ± 0.3	27.17 ± 0.2
2	75.01 ± 0.2	39.75 ± 0.2
3	83.63 ± 0.2	43.22 ± 0.1
4	90.53 ± 0.2	42.98 ± 0.2
5	90.29 ± 0.1	43.41 ± 0.2

Table S2 Summary numerical data in **Fig. 3**

pH_{eq}	E_{Cd} (%)	E_{Zn} (%)
5.2	90.19 ± 0.1	50.01 ± 0.1
4.3	90.16 ± 0.08	48.98 ± 0.06
3.1	90.85 ± 0.08	43.73 ± 0.05
1.8	89.83 ± 0.06	43.81 ± 0.07
0.9	26.58 ± 0.07	12.52 ± 0.1
0.5	12.6 ± 0.1	5.61 ± 0.08

Table S3 Summary numerical data in **Fig. 4** [HNO_3] = 1.0 M (upper), 2.0 M (lower)

pH_{eq}	BE_{Cd} (%)	BE_{Zn} (%)
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5.2	66.85 ± 0.1	60.95 ± 0.1
4.3	69.23 ± 0.1	61.14 ± 0.06
3.1	69.016 ± 0.08	50.34 ± 0.1
1.8	71.94 ± 0.05	46.26 ± 0.08
0.9	59.27 ± 0.1	35.67 ± 0.08
0.5	66.85 ± 0.2	60.95 ± 0.1

pH _{eq}	BE _{Cd} (%)	BE _{Zn} (%)
5.2	96.85 ± 0.06	94.95 ± 0.07
4.3	99.23 ± 0.08	90.13 ± 0.08
3.1	99.02 ± 0.06	92.34 ± 0.08
1.8	95.94 ± 0.06	92.26 ± 0.05
0.9	99.27 ± 0.1	88.67 ± 0.1
0.5	96.85 ± 0.1	94.95 ± 0.06

Table S4 Summary numerical data in **Fig. 5**

[(C ₆ mim) ⁺] (M)	E _{Cd} (%)	E _{Zn} (%)
0.0	90.08 ± 0.04	43.19 ± 0.07
0.1	89.01 ± 0.06	42.39 ± 0.06
0.2	88.18 ± 0.06	40.18 ± 0.04
0.3	84.71 ± 0.05	37.09 ± 0.07
0.4	82.96 ± 0.05	33.11 ± 0.08
0.5	80.58 ± 0.08	25.19 ± 0.06
0.6	79.61 ± 0.1	20.21 ± 0.06
0.8	76.54 ± 0.06	18.29 ± 0.06
1.0	68.13 ± 0.05	16.2 ± 0.03

Table S5 Summary numerical data in **Fig. 6**

[NO ₃ ⁻] (M)	E _{Cd} (%)	E _{Zn} (%)
0.00	89.52 ± 0.05	42.1 ± 0.04
0.02	93.23 ± 0.05	42.015 ± 0.05
0.04	85.61 ± 0.06	44.74 ± 0.04
0.06	88.72 ± 0.05	41.93 ± 0.05
0.08	89.08 ± 0.07	43.53 ± 0.05

Table S6 Summary numerical data in **Fig. 7**

log [(IL-1,2-tpbd) ⁺]	log D _{Cd}	log D _{Zn}
-1	-2.698 ± 0.06	-3 ± 0.07
-0.301	-1.301 ± 0.06	-1.698 ± 0.08

0	0.191 ± 0.05	-0.715 ± 0.06
0.301	0.379 ± 0.04	-0.566 ± 0.04
0.477	0.98 ± 0.06	-0.109 ± 0.06

Table S7 Summary numerical data in **Fig. 10**

Metal ions	E (%)
Cd	100 ± 0.07
Pb	76.348 ± 0.09
Zn	45.179 ± 0.05
Ni	13.769 ± 0.06
Co	6.2098 ± 0.06
Fe	0.892 ± 0.08
Mg	0 ± 0.1
Ca	0 ± 0.06

Table S8 A brief comparison of various IL extraction systems for Cd^{2+}

Extractant	Diluent	Target metal ions	Aqueous phase	Equilibration time (min)	Ref.
$[\text{N}_{1888}][\text{C}_4\text{SAC}]$ etc.	-	Cd, Cu	HNO_3 aq.	30	1
Cyphos IL 104	toluene	Cd, Zn	$1.0 \times 10^{-3} \square 2.0 \text{ M}$ $\text{HCl}/\text{HNO}_3/\text{H}_2\text{SO}_4$	< 6	2
[Nano-Si-OH-Bmim ⁺ Tf ₂ N ⁻] sorbent	-	Cd	$\text{pH}_{\text{eq}} > 1.0$ HCl aq.	≥ 15	3
thio- and urea-based IL	$[\text{C}_4\text{mim}][\text{PF}_6]$	Cd, Hg	$\text{pH}_{\text{eq}} = 1.0$ and 7.0 HCl aq.	4	4
Dithizone	$[\text{C}_4\text{mim}][\text{PF}_6]$	Cd, Pb, Zn	$\text{pH}_{\text{eq}} > 1.9$	2	5
[A336][TS]-modified Fe_3O_4	-	Cd	$\text{pH}_{\text{eq}} > 2.0$ HNO_3 aq.	30	6
Cyphos IL 101	kerosene	Cd	$\text{pH}_{\text{eq}} > 2.46$ H_2SO_4 aq.	5	7
$[\text{P}_{66614}][\text{PTB}]$ etc.	-	Cd, Zn, Cu	$\text{pH}_{\text{eq}} = 7$ HNO_3 aq.	> 24 h	8
$(\text{IL-1,2-tpbd})^+\text{NTf}_2^-$	$(\text{C}_6\text{mim})^+\text{NTf}_2^-$	Cd	$\text{pH}_{\text{eq}} = 0.5 \square 5.2$ HNO_3 aq.	≈ 5 h	Present study

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