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Polyether-tethered imidazole-2-thiones, imidazole-2-selenones and imidazolium salts as collectors for the flotation of lithium aluminate and spodumene†

 Sophie Acker,^a Jan C. Namyslo,^a Martin Rudolph,^b Franziska Strube,^b Ursula E. A. Fittschen,^c Hao Qiu,^d Daniel Goldmann^d and Andreas Schmidt^{ID}*^a

Imidazolium salts were prepared which possess 2-ethoxyethyl pivalate or 2-(2-ethoxyethoxy)ethyl pivalate groups as amphiphilic side chains with oxygen donors as well as *n*-butyl substituents as hydrophobic groups. The N-heterocyclic carbenes of the salts, characterized by ⁷Li and ¹³C NMR spectroscopy as well as by Rh and Ir complex formation, were used as starting materials for the preparation of the corresponding imidazole-2-thiones and imidazole-2-selenones. Flotation experiments in Hallimond tubes under variation of the air flow, pH, concentration and flotation time were performed. The title compounds proved to be suitable collectors for the flotation of lithium aluminate and spodumene for lithium recovery. Recovery rates up to 88.9% were obtained when the imidazole-2-thione was used as collector.

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1. Introduction

As a consequence of a steadily increasing demand for critical raw materials (CRMs)¹ including elements such as lithium,² the development of new recycling technologies is constantly being sought and developed. Lithium is considered to be a strategic metal in the world,³ as a considerably increasing demand for this element can be expected in the next years. This is mainly due to its application in lithium-ion batteries for e-mobility, as the share of lithium consumption for batteries was already 71% in 2020. Recycling's contribution to the current lithium demand, however, is close to 0%.¹ This is in sharp contrast to the projection of the global lithium demand, which is expected to surpass two million metric tons of lithium carbonate equivalent in 2030. This is more than doubling the forecast for 2025.⁴ Apart from batteries, lithium is also currently used in ceramics,⁵ glass,⁶ lubricants,⁷ refrigeration⁸ and the nuclear⁹ and optoelectronic industries.¹⁰ Unfortunately, numerous critical raw

materials and other industrially important elements such as lithium are often dissipated in the waste streams. Lithiumaluminate (LiAlO₂) formation in slags can be initiated by the addition of Al to the pyrometallurgical process. Minerals which are purposely engineered in a slag to facilitate their recovery have recently been termed engineered artificial minerals (EnAM).¹¹ This strategy has been overlooked as effective method for the recovery of numerous elements in the past. For the recycling of batteries, intense efforts are currently directed toward lithiumaluminate formation during the slag solidification after the thermal decomposition of the batteries. Apart from the removal of heavy metal ions and the simple and rapid dewatering of suspensions by removal of the concentrated sludge fraction along with the froth,¹² flotation is an effective method to separate minerals from gangue materials and is the most important and versatile mineral processing technique.¹³ Flotation is based on the difference in surface hydrophobicity of dispersed particles, obtained by crushing and grinding of raw minerals to liberate valuable components from interlocking particles. After suspending in water and conditioning with a selection of appropriate reagents, air is conducted into the dispersion to separate hydrophobic particles which collide with and attach to the rising air bubbles, whereas hydrophilic particles remain suspended in the pulp. Collectors, frothers, depressants, activators, and regulators take influence on interfacial properties of particles and bubbles affecting their interactions and, besides hydrodynamic parameters, take influence on the success of the flotation.¹⁴ Optimization is often directed towards the maximization of the adsorption of the particles on

^aClausthal University of Technology, Institute of Organic Chemistry, Leibnizstrasse 6, D-38678 Clausthal-Zellerfeld, Germany. E-mail: schmidt@ioc.tu-clausthal.de

^bFreiberg, Helmholtz Institute Freiberg for Resource Technology, Chemnitz Str. 40, D-09599 Freiberg, Germany

^cClausthal University of Technology, Institute of Inorganic and Analytical Chemistry, Arnold-Sommerfeld-Str. 4, D-38678 Clausthal-Zellerfeld, Germany

^dClausthal University of Technology, Institute of Mineral and Waste Processing, Recycling and Circular Economy Systems, Walther-Nernst-Str. 9, D-38678 Clausthal-Zellerfeld, Germany

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the surfaces to selectively enhance particle's hydrophobicity and thus improving particle-bubble attractive interactions.¹⁵ Another key lithium mineral is spodumene ($\text{LiAlSi}_2\text{O}_6$) which is considered to be one of the most critical minerals due to its high lithium contents and high rate extraction.¹⁶ Concerning the flotation of lithium bearing minerals such as lithium aluminate and spodumene, sodium oleate is often employed as surfactant-type collector,¹⁷ and other collector formulations and methods have also been developed.¹⁸

In continuation of a current project dealing with the detection and recycling of metals,¹⁹ collector design, and our interest in the chemistry of nitrogen heterocycles including their N-heterocyclic carbenes (NHCs),²⁰ we prepared polyether-tethered imidazolium salts and studied them in metal complex formations with lithium, silver, rhodium and iridium as well as in flotation of lithium minerals. We intended to combine *n*-butyl-groups as hydrophobic moieties with polyether chains of two different lengths as amphiphilic and relatively electron-rich side chains of an imidazole core (Scheme 1).

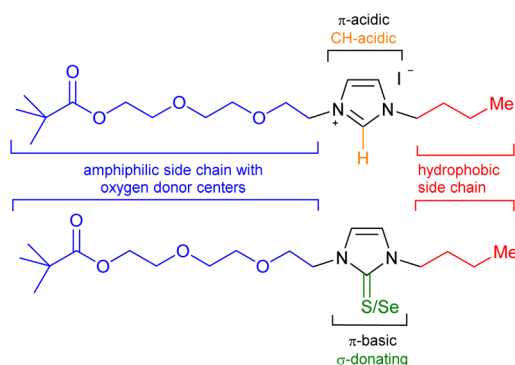
The central heteroaromatic imidazolium ring of the salts is strongly electron-deficient and π -acidic, and is known to initiate anion- π and π - π -interactions *e.g.* to copper species,²¹ σ -hole and π -hole interactions to silicon compounds,²² anion- π and lone-pair- π interactions to halogens,²³ and π - π -interactions to adsorb organic substrates on surfaces²⁴ such as anthracite coal.²⁵ The electronic compatibility of the surface of galena (PbS) and π -conjugated systems to gain insight into the flotation's mechanism has been calculated.²⁶ Furthermore, the 2-position of imidazolium salts is CH-acidic so that a structural variation can easily be achieved *via* their N-heterocyclic carbenes. We therefore planned reactions with sulfur and selenium to get imidazole-2-thiones and imidazole-2-selenones as potential new collectors for the flotation of lithium minerals. Imidazole-based ionic liquids such as dodecyl-trimethylimidazolium chloride have *i.a.* been used for the separation of quartz from phosphorite,²⁷ for the flotation of quartz²⁸ and lithium aluminate.²⁹ Nanoparticles of imidazole functionalized polystyrene are known to bind nickel ions.³⁰ Imidazole-2-thiones combine structure elements of imidazole and thioureas and have been applied in the flotation of copper sulfides and pyrite.³¹ Thioureas have been used for the flotation of silver,³² gold,³³

chalcopyrite,³⁴ copper,³⁵ and many others. In contrast to imidazolium salts, the thiones and selenones are π -bases which are known to undergo cation- π -interactions, as examined in the flotation of molybdenite.³⁶ We applied the imidazolium salts as well as their thiones and selenones in microflotation experiments of lithium aluminate, spodumene and gehlenite in Hallimond tubes under variation of the conditions. Gehlenite is a representative slag gangue material. To the best of our knowledge, the application of selenoureas in flotation have never been described before.

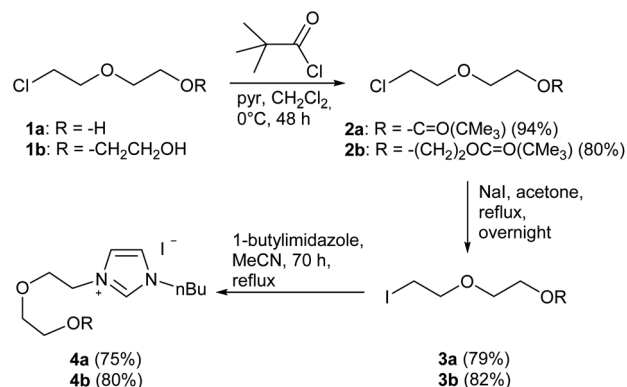
2. Results and discussion

In the first step, the desired imidazolium salts were synthesized *via* a synthetic route which is shown in Scheme 2. The syntheses were accomplished in several steps. First, EINHORN esterification of the alcohol group of 2-(2-chloroethoxy)ethan-1-ol **1a** and of its derivative **1b** with pivaloyl chloride in the presence of pyridine protected the side chain toward deprotonation during the carbene generation with bases. Finkelstein reaction induced the halogen exchange of chloride toward iodide (**3a,b**) which proved to be the better leaving group for the subsequent nucleophilic substitution to *n*-butylimidazole, which resulted in the formation of the imidazolium salts **4a,b** as orange-colored oils in high yields (75% and 80%).

We then proceeded with reactions under water-free conditions in an inert atmosphere. *Via* DFT calculations on the B3LYP/6-311++G** level we determined the CREF (carbene relative energy of formation)³⁷ value of **4a** in advance. The calculated value (0.416) indicates, as expected, a relative ease of carbene formation from its precursor **4a**. Indeed, we generated the N-heterocyclic carbenes **4aA** and **4bA** by addition of bases to a solution of the imidazolium salts **4a,b**. The N-heterocyclic carbenes **4aA** and **4bA** are suitable precursors for the synthesis of thiones **5a,b** and selenones **6a,b** which we wanted to test as collectors for the flotation of lithium minerals. Thus treatment of the salts **4a,b** with elemental sulfur and elemental selenium in the presence of cesium carbonate yielded the target thiones **5a,b** and the selenones **6a,b** in acceptable yields (77% and 41%), respectively (Scheme 3). In order to characterize the N-heterocyclic carbene we performed the deprotonation of **4b** in

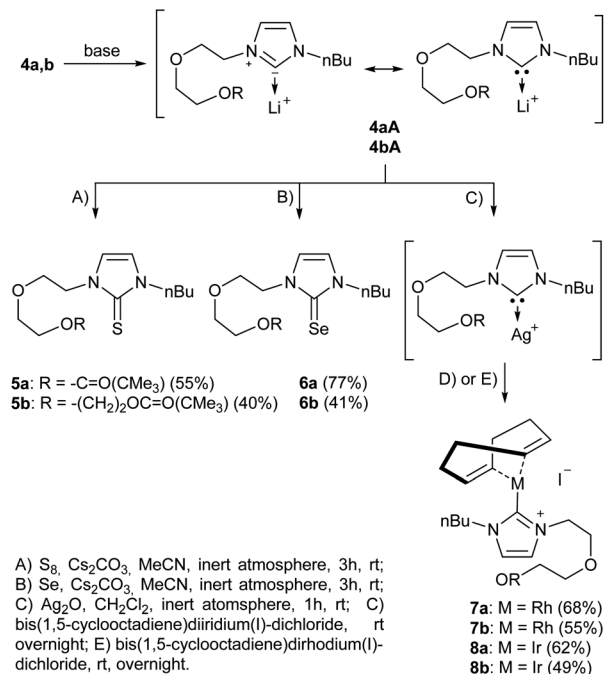


Scheme 1 Target imidazolium salts and thiones/selenones.



Scheme 2 Synthesis of imidazolium salts.





Scheme 3 Synthesis of thiones and selenones as potential collectors for lithium mineral flotation. Trapping of the reactive N-heterocyclic carbenes with rhodium and iridium *via* silver complexes.

THF-*d*₈ with lithium bis(trimethylsilyl)amide [LHMDS] as the base and measured the ¹³C NMR as well as ⁷Li NMR spectra. The 2-position of the imidazolium salt **4b** shifted from 137.9 ppm to 201.7 ppm in the ¹³C NMR spectra during the carbene formation. The ⁷Li spectrum of **4bA** shows a signal at +0.64 ppm (Fig. 1). The selenones **6a,b** display ⁷⁷Se NMR resonance frequencies at -12.4 ppm, respectively. Reaction of the *in situ* generated N-heterocyclic carbenes **4aA** and **4bA** with silver oxide (Ag₂O) gave non-isolable silver adducts which were subjected to a silver → iridium and silver → rhodium exchange reaction with bis-(1,5-cyclo-octadiene)dirhodium(i)-dichloride and its iridium analog to give the stable and fully characterizable complexes **7a,b** and **8a,b**.

Further DFT calculations (B3LYP/6-311++G**) have been carried out to gain knowledge about the molecular orbitals which contribute to, or even govern the formation of π-complexes and σ-bonds to organic or inorganic substrates including metals. As expected, the lowest unoccupied molecular orbital (LUMO: -5.10 eV) of the salt **4a** is located in the imidazolium moiety, whereas the highest occupied molecular orbital (HOMO: -9.34 eV) consists of atomic orbital coefficients

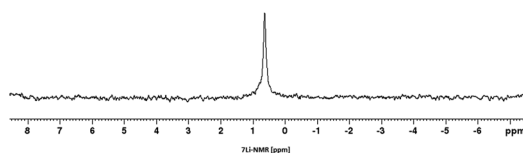


Fig. 1 ⁷Li NMR spectrum of the lithium adduct of imidazol-2-ylidene **4bA**.

of the σ-framework of the pivaloyl group including the non-bonding electron pairs of its carbonyl oxygen (Fig. 2). HOMO-1 (-10.37 eV), HOMO-2 (-10.59 eV), HOMO-3 (-10.80 eV), HOMO-4 (-10.80 eV) as well as HOMO-5 (-11.44 eV) are all located in the polyether chain (see ESI†).

The LUMO of the N-heterocyclic carbene **4aA** (-0.35 eV) has very small atomic orbital coefficients, whereas the HOMO (-5.98 eV) displays the characteristic geometry with a large coefficient of the σ-lone pair plus coefficients in the σ-framework of the imidazole ring (Fig. 3). The σ-lone pair is capable of metal complexations as proved by the formation of Ag, Rh and Ir complexes as mentioned before. All other molecular orbitals are shown in the ESI.†

The calculated frontier orbitals of the thione **5a** and the selenone **6a** are very similar. Thus, the LUMOs of the thione (-0.46 eV) and of the selenone (-0.50 eV) have small atomic orbital coefficients in the imidazole ring (Fig. 4). The HOMO (-5.18 eV) of the thione and the HOMO (-5.37 eV) of the selenone are located in the imidazole moiety; they are π-orbitals. The molecular orbitals of the thione are shown in Fig. 4 and those of the selenone can be found in the ESI.†

Flotation experiments

We applied the imidazolium salts **4a,b**, the thiones **5a,b** and the selenones **6a,b** in microflotation experiments of fine particle fractions, the particle distributions of which are provided in Fig. 5. The chosen three different minerals are, lithium aluminate (LiAlO₂), spodumene (LiAlSi₂O₆) and gehlenite (Ca₂Al[AlSiO₇]). The latter is a potential gangue material especially of the former mentioned slag formation processes.

In addition, we performed a phase analysis of spodumene by quantitative XRD, showing a composition by weight of 5.1% quartz, 93.5% spodumene and 1.4% topaz. The mineral gehlenite was measured *via* ICP-OES. Theoretically it consists of 19.7% aluminium, 29.2% calcium and 10.2% silicon. The chemical analysis also revealed a small content (<5%) of iron and magnesium (Fig. 6).

Different concentrations of the six imidazole derivatives and the frother (pine oil) were used for the flotation. The stock solutions of the individual collectors have a concentration of 1% by mass in distilled water. To achieve better solubility of the collectors, 0.05 ml of tetrahydrofuran (THF) were added. Exclusion of any effects of THF was accomplished by floating 1 wt% solution of THF in distilled water as a blind sample for

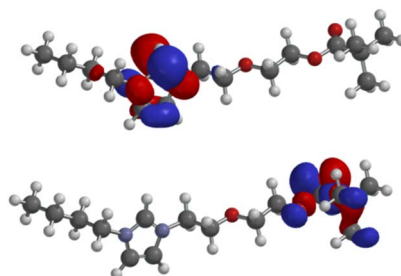


Fig. 2 LUMO (above) and HOMO (below) of **4a**.



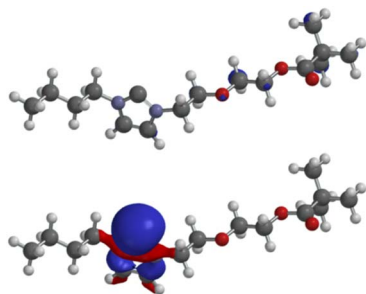


Fig. 3 LUMO (above) and HOMO (below) of the non-complexed N-heterocyclic carbene **4aA**.

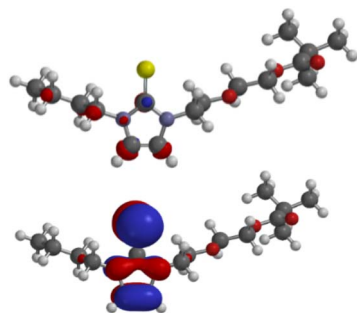


Fig. 4 LUMO (above) and HOMO (below) of thione **5a**.

both spodumene and lithium aluminate. The conversion of the amount of collectors into the molar concentration are shown in Table 1.

Flotation under variation of the air flow

First, we performed flotation experiments of lithium aluminate and gehlenite under an air flow of $170 \text{ cm}^3 \text{ min}^{-1}$, respectively. For the experiments, samples of 2 g of each mineral were floated and the recovery yields were calculated from the ratios of the flotation recovery and the residue. As can be seen from the results presented in Table 2, each of the four imidazoles which we examined proved to be a suitable collector for the flotation of lithium aluminate. Best results of the flotation of LiAlO_2 (88.9% recovery) were obtained, when $18.28 \mu\text{mol l}^{-1}$ of imidazole-2-thione **5a** were employed after a flotation time of 10 min and $1.2 \times 10^{-3} \text{ g l}^{-1}$ of frother (pine oil) at the natural pH values of the mineral in water, *i.e.* between 10 and 11. Lower pH values resulted in lower recovery rates. The yields of the flotation of the gangue material gehlenite are very low (>15%) under the conditions applied and with the material used.

Table 3 summarizes the results of flotation experiments under an air flow of $32 \text{ cm}^3 \text{ min}^{-1}$ under variation of the pH value, the concentrations of the imidazoles as collector as well as of the frother α -pinene, and the flotation time. The blind value for 1 wt% solution of THF in distilled water gave a recovery of 16.7%, indicating no effect of THF on the flotation. The recovery yields under these conditions are slightly lower than those obtained applying a higher air flow. As can be seen, the

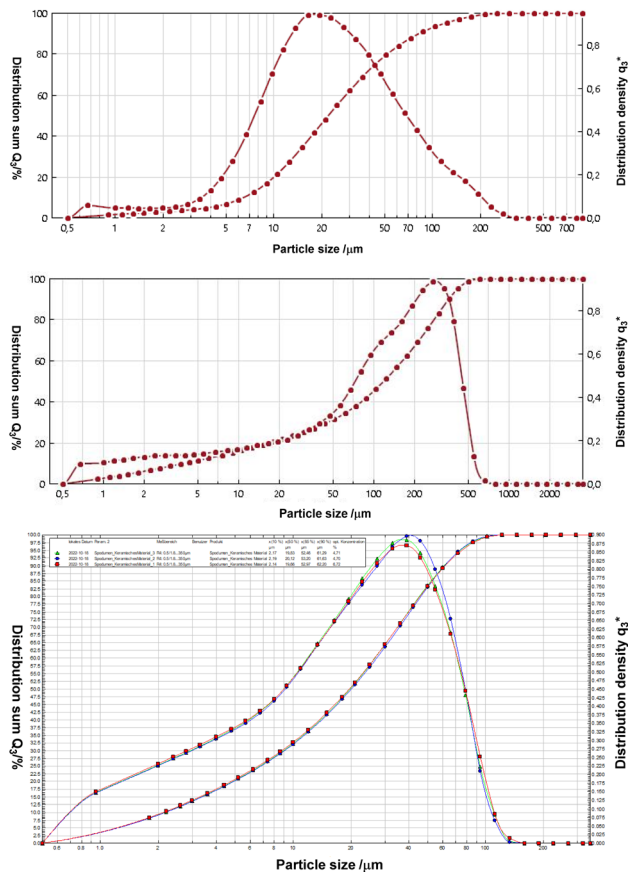


Fig. 5 Particle size distributions by means of laser diffraction of lithium aluminate (top), gehlenite (middle) and spodumene (bottom).

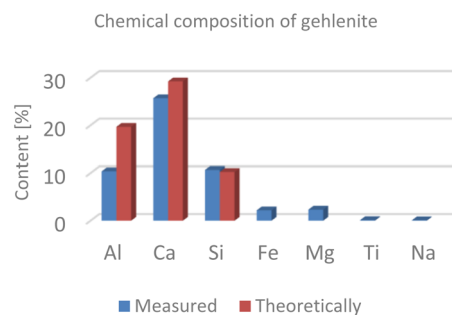


Fig. 6 Chemical analysis of gehlenite.

collectors gave good results at strongly acidic as well as at strongly basic pH values. Again, imidazole-thione **5a** gave the highest yields of lithium aluminate recovery. Imidazolium salt **4b**, which has a longer side chain, gave slightly better recovery rates than imidazolium salt **4a**. Apart from the minerals lithium aluminate and gehlenite, we also examined the flotation of spodumene. A suspension of spodumene in distilled water has a pH value of 8. The results with an air flow of $32 \text{ cm}^3 \text{ min}^{-1}$ are shown in Table 4.

As a test experiment, we performed flotations without the addition of any collector and frother. The flotation of pure



Table 1 Molar concentrations of collectors 4a, 4b, 5a, 5b, 6a and 6b

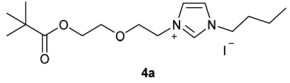
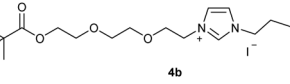
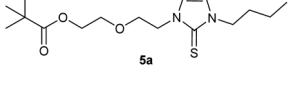
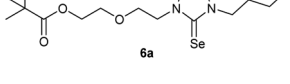
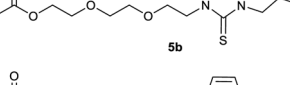

Collector	Vol. added [μl]	Conc. [μmol l ⁻¹]
	60	5.66
	120	11.32
	300	28.29
	600	56.59
	60	5.13
	120	10.25
	300	25.63
	600	51.27
	60	7.31
	120	14.63
	300	36.57
	600	73.13
	60	6.38
	120	12.76
	300	31.90
	600	63.81
	60	6.45
	120	12.90
	60	5.71
	120	11.42

Table 2 Microflotation recoveries with an air flow of 170 cm³ min^{-1a}

Collector	Mineral	Conditions	Recovery ± confidence interval [%]
4a	LiAlO ₂	pH 2	A 61.5 ± 4.31
	LiAlO ₂	pH 10–11	A 68.0 ± 4.29
	LiAlO ₂		B 85.1 ± 1.06
	Gehlenite		A 11.1 ± 1.70
4b	LiAlO ₂	pH 2	A 63.0 ± 1.29
	LiAlO ₂	pH 10–11	A 67.5 ± 7.71
	LiAlO ₂		B 84.4 ± 12.67
	Gehlenite		A 10.8 ± 2.40
5a	LiAlO ₂	pH 2	A 65.2 ± 8.09
	LiAlO ₂	pH 10–11	A 67.7 ± 2.58
	LiAlO ₂		B 88.9 ± 2.47
	Gehlenite		A 12.2 ± 7.37
6a	LiAlO ₂	pH 2	A 61.4 ± 3.56
	LiAlO ₂	pH 10–11	A 64.6 ± 5.60
	LiAlO ₂		B 82.7 ± 3.29
	Gehlenite		A 14.0 ± 3.97

^a Flotation conditions: A: conditioning time $C_T = 3$ min, flotation time $F_T = 5$ min, **4a**: 28.29, **4b**: 25.63, **5a**: 36.57 and **6a**: 31.90 μmol l⁻¹ of collector, 6.0×10^{-3} g l⁻¹ (750 g per ton) frother. B: $F_T = 10$ min, collector 56.59, 51.27, 73.13 and 63.81 μmol l⁻¹, 1.2×10^{-2} g l⁻¹ (1500 g per ton) frother (pine oil). Each measurement consists of three repetitions. 95% confidence interval.

spodumene gives a recovery yield of 22.2% after a flotation time of 3 min, and adding 1 wt% solution THF in distilled water gave a recovery of 23.4%, so that the influence of THF can be neglected. All six imidazoles achieve yields between 40 and 50% in combination with the frother with a flotation time of 3 minutes at a pH of 2 and also at a pH of 8 with molar

Table 3 Microflotation recoveries with an air flow of 32 cm³ min^{-1a}

Collector	Mineral	Conditions	Recovery ± confidence interval [%]
4a	LiAlO ₂	pH 2	A 45.3 ± 7.75
			C 73.5 ± 1.64
		pH 10–11	A 33.6 ± 6.23
			B 60.7 ± 14.35
			C 70.1 ± 8.10
4b	LiAlO ₂	pH 2	A 46.0 ± 3.05
			C 76.3 ± 6.32
		pH 10–11	A 33.1 ± 6.28
			B 64.7 ± 3.77
			C 76.4 ± 4.13
5a	LiAlO ₂	pH 2	A 47.2 ± 3.75
			C 79.3 ± 4.10
		pH 10–11	A 43.4 ± 8.01
			B 75.1 ± 10.78
			C 78.9 ± 5.90
5b	LiAlO ₂	pH 2	A 45.1 ± 5.41
		pH 10–11	A 35.5 ± 0.84
			B 59.9 ± 13.50
			C 76.7 ± 4.66
6a	LiAlO ₂	pH 2	A 43.8 ± 2.62
			C 77.9 ± 4.85
		pH 10–11	A 36.5 ± 21.12
			B 63.4 ± 13.01
			C 74.2 ± 2.00
6b	LiAlO ₂	pH 2	A 47.3 ± 7.67
		pH 10–11	A 31.9 ± 2.64
			B 62.6 ± 1.72
			C 75.5 ± 8.48

^a Flotation conditions: A: conditioning time $C_T = 3$ min, flotation time $F_T = 3$ min, 5.66 (**4a**), 5.13 (**4b**), 7.31 (**5a**), 6.45 (**5b**) 6.38 (**6a**), 5.71 (**6b**) μmol l⁻¹ of collector, 1.2×10^{-3} g l⁻¹ (150 g per ton) frother (pine oil). B: $F_T = 10$ min, 5.66 (**4a**), 5.13 (**4b**), 7.31 (**5a**), 6.45 (**5b**) 6.38 (**6a**), 5.71 (**6b**) μmol l⁻¹ of collector, 1.2×10^{-3} g l⁻¹ (150 g per ton) frother. C: $F_T = 10$ min, collector 11.32 (**4a**), 10.25 (**4b**), 14.63 (**5a**), 12.90 (**5b**), 12.76 (**6a**), 11.42 (**6b**) μmol l⁻¹, 1.2×10^{-3} g l⁻¹ (150 g per ton) frother. Each measurement consists of three repetitions. 95% confidence interval.

concentrations of 5.66 (**4a**), 5.13 (**4b**), 7.31 (**5a**), 6.45 (**5b**) 6.38 (**6a**), 5.71 (**6b**) μmol l⁻¹. Best results were achieved employing the imidazole-thione **5a** and **5b** with 71.8% with a flotation time of ten minutes at the same concentration. The values for the long-chained salt **4b** are better than those of the shorter-chained salt **4a**.

Next, we determined the zeta potentials of lithium aluminate in neat form and of samples of this mineral conditioned with the four imidazoles described here.

Zeta potential

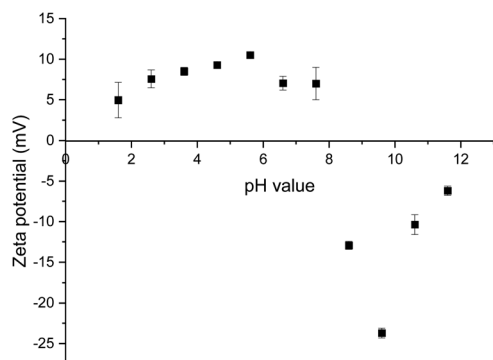
For the neat mineral lithium aluminate, a zeta potential measurement was carried out over a pH range of 2 to 12. It turned out that the mineral does not provide stable values at certain pH values. The fitted trend line shows a large deviation between the individually measured values. Because of this, the zeta potential for the following measurements was determined at a pH value around 8. Fig. 7 shows the diagram for pure lithium aluminate.



Table 4 Microflotation recoveries with spodumene with an air flow of $32 \text{ cm}^3 \text{ min}^{-1a}$

Collector	Mineral	Conditions	Recovery confidence interval [%]
4a	Spodumene	pH 2	A 45.6 ± 5.82
		pH 8	A 41.3 ± 11.12
			B 60.3 ± 25.04
4b	Spodumene	pH 2	A 49.4 ± 4.68
		pH 8	A 43.7 ± 2.71
			B 60.7 ± 7.66
5a	Spodumene	pH 2	A 47.3 ± 5.70
		pH 8	A 46.3 ± 5.81
			B 71.8 ± 2.71
5b	Spodumene	pH 2	A 48.7 ± 11.01
		pH 8	A 44.0 ± 4.03
			B 71.8 ± 4.15
6a	Spodumene	pH 2	A 47.7 ± 1.46
		pH 8	A 41.9 ± 19.19
			B 65.7 ± 28.52
6b	Spodumene	pH 2	A 42.2 ± 11.97
		pH 8	A 39.7 ± 19.69
			B 54.2 ± 14.97

^a Flotation conditions: A: conditioning time $C_T = 3$ min, flotation time $F_T = 3$ min, 5.66 (**4a**), 5.13 (**4b**), 7.31 (**5a**), 6.45 (**5b**) 6.38 (**6a**), 5.71 (**6b**) $\mu\text{mol l}^{-1}$ of collector, resp., $1.2 \times 10^{-3} \text{ g l}^{-1}$ (150 g per ton) frother. B: conditioning time $C_T = 3$ min, flotation time $F_T = 10$ min, 5.66 (**4a**), 5.13 (**4b**), 7.31 (**5a**), 6.45 (**5b**) 6.38 (**6a**), 5.71 (**6b**) $\mu\text{mol l}^{-1}$ of collector, resp., $1.2 \times 10^{-3} \text{ g l}^{-1}$ (150 g per ton) frother (pine oil). Each measurement consists of three repetitions. 95% confidence interval.

**Fig. 7** Zeta potential of pure lithium aluminate in distilled water.

The results of the different zeta potential measurements for lithium aluminate conditioned with the collectors are listed in Table 5. The zeta potential of the pure lithium aluminate in 10^{-3} M KCl solution at a pH value of 8.44 was determined to be -0.75 mV .

A comparison of the values shows that an increase in the concentration of the respective collector leads to an increase in the measured zeta potential with the exception of collector **4a**. Here the opposite occurs, as the zeta potential becomes even more negative with increased concentration. The measured values for collector **5a** and **6a** are close to 0 mV in the potential, which indicates that the particles are destabilizing, which is beneficial for flotation.

Table 5 Measured values for the zeta potentials of the conditioned lithium aluminate

Collector	Amount of collector	pH value	Zeta potential [mV]
4a	60 μl	8.2	-3.80
4a	600 μl	8.2	-6.70
4b	60 μl	8.2	-9.70
4b	600 μl	8.4	-4.40
5a	60 μl	8.5	-0.38
5a	600 μl	8.4	-0.09
6a	60 μl	8.3	-0.38
6a	600 μl	8.4	-0.33

In conclusion, the prepared imidazolium salts, imidazole-2-thiones and imidazole-2-selenones proved to be suitable collectors for the flotation of lithium aluminate and spodumene for lithium recovery. Best results were achieved employing the imidazole-2-thione, possessing a polyether and an *n*-butyl side chain. The thione and the selenone were prepared starting from the corresponding imidazolium salts *via* the N-heterocyclic carbenes, the imidazol-2-ylidenes **4a,bA**, which were characterized by means of ^7Li and ^{13}C NMR spectroscopy and trapping reactions with rhodium and iridium.

3. Experimental section

General

All used chemicals were purchased from commercial suppliers and used as received unless noted otherwise. The measurements for the ^1H and ^{13}C spectra have been performed on Bruker Avance (400 MHz) and Avance III (600 MHz) NMR spectrometer. The multiplicities are given with the following abbreviations: s = singlet, bs = broad singlet, d = doublet, dd = doublet of a doublet, t = triplet, tt = triplet of a triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet. In ^{13}C NMR the following abbreviations are used: * = quaternary carbon atom, + = primary and tertiary carbon atom, - = secondary carbon atom. IR-spectroscopy has been performed by the FT-IR-spectrometer Alpha-T from Bruker with a platinum-ATR-module. The spectra consider a range of 400 to 4000 cm^{-1} . The high-resolution mass spectra were measured with an Impact II from Bruker.

The chemical analysis of gehlenite was performed with a Varian model Vista MPX and with an evaluation program from Varian. The sample was digested in two steps. In the first step, *aqua regia* was used, followed by diluted HF (0.8%) in the second. The value shown is the average of three measurements.

Spodumene was analyzed by quantitative XRD from PANalytical Empyrean by a X-ray diffractometer with a Co X-ray source. A voltage of 35 kV and a current of 35 mA was applied. Prior to the measurement the samples were split into 2.5 ml sample ($<400 \mu\text{m}$) then were ground in ethanol with zirconium-oxide grinding media in a McCrone mill, ideally producing particles with a narrow size distribution below $1 \mu\text{m}$ and an intact crystallographic structure. Afterwards the sample was dried overnight and the dried sample homogenized with



small steel balls (4 mm diameter) by using the mixer mill MM 400 from Retsch. The diffractogram and quantitative phase determination were performed *via* Rietveld refinement using Profex 4.1.0 software.

Lithium aluminate (LiAlO_2) was bought from Alfa Aesar. Spodumene was provided by the Helmholtz Institute Freiberg for Resource Technology, and gehlenite was provided by the Institute of Mineral and Waste Processing, Recycling and Circular Economy Systems, Clausthal-Zellerfeld.

Flotation experiments

The flotation experiments have been performed in a Hallimond tube (Fig. 8) with a volume of 250 ml. Lithium aluminate and gehlenite were tested as the single minerals (2 g for each measurement). The collector concentrations are in a range of $5.13 \mu\text{mol l}^{-1}$ to $73.13 \mu\text{mol l}^{-1}$ and for the frother (pine oil) between $1.2 \times 10^{-3} \text{g l}^{-1}$ and $1.2 \times 10^{-2} \text{g l}^{-1}$. In addition to the concentrations and the flotation time, the pH-value was varied. The air flows were $32 \text{cm}^3 \text{min}^{-1}$ and $170 \text{cm}^3 \text{min}^{-1}$. The continuous stirring speed is 500 rpm. The conditioning time was three times one minute for each addition step. The flotation time varied between three and ten minutes as indicated in the tables.

The Hallimond tubes used (250 ml) possess a medium-pore fritted glass through which the air can flow into the apparatus. A magnetic stirrer, adjusted to 500 rpm, ensures continuous mixing. The flotation tailings are collected separated in the upper area during flotation. In the first step, the mineral is conditioned in distilled water or buffer (one minute). The buffer consisted of 0.04 M boric acid, 0.04 M phosphoric acid, and 0.04 M acetic acid, and the required pH was achieved by the addition of 0.1 M NaOH. The buffer was used for measurements at a pH of 2. Then the collector is added and, after another minute, the frother. The remaining volume is filled up to 250 ml and floated for 3 or 10 minutes. The natural pH value of lithium aluminate is between 10–11 and for spodumene at pH 8.

Zeta potential measurements

The measurements were conducted with a Zetasizer Nano from Malvern. The mineral sample (lithium aluminate, 0.5 g) was prepared in 1000 ml of 10^{-3}M KCl solution. The respective collector was added to the solution with a molar concentration of 5.66 (4a), 5.13 (4b), 7.31 (5a), 6.38 (6a) $\mu\text{mol l}^{-1}$ for

the first measurement and with 56.59 (4a), 51.27 (4b), 73.13 (5a), 63.81 (6a) $\mu\text{mol l}^{-1}$ for the second measurement. The solution was mixed and sedimented for two hours. The measurements have been performed with the supernatant. Lithium aluminate samples were exclusively measured at the natural pH value.

Particle size

The particle sizes for lithium aluminate and gehlenite were measured at the Institute of Mineral and Waste Processing, Recycling and Circular Economy Systems with a HELOS (H2387) & QUIXEL apparatus from Sympatec. Spodumene was measured at the Helmholtz Institute Freiberg for Resource Technology with a HELOS (H2634) & RODOS from Sympatec. For future microflotation testwork it should be considered to have comparable settling velocities of the particles in microflotation, which was not the case in this study. Gehlenite's median size was about six times the median of lithium aluminate. Nonetheless, this does not affect the trend of enhanced flotation ability upon collector adsorption.

DFT calculations (molecular geometries, HOMO–LUMO values and orbital pictures, CREF-values) were performed using the Spartan Software (Spartan'20, Wavefunction, Inc., Irvine, CA, available from: <http://www.wavefun.com>) running on a MS Windows 10 Pro PC system with an AMD Ryzen Threadripper 3970X 32-Core and 128 GB RAM. MMFF optimized structures were used as starting geometries for the geometry optimizations with the B3LYP density functional and the 6-311++G** basis set carried out as vacuum calculations. Subsequent frequency calculations of all final structures evidenced the absence of imaginary frequencies and thus the presence of true minima on the potential energy surface.

Preparation of 2-(2-chloroethoxy)ethyl-2,2-dimethylpropanoate (2a)

Under a nitrogen atmosphere, 1.48 ml (14.00 mmol) of 2-[2-chloroethoxy]ethanol **1a** was dissolved in 50 ml of anhyd. diethyl ether and then 10 ml anhyd. pyridine were added. 2.34 ml (19.00 mmol) of pivalic acid chloride was then added at 0 °C. The reaction mixture was stirred at room temperature for 48 hours. The reaction was then quenched with 1 M HCl (*ca.* 20 ml). The aqueous phase was extracted with three portions of 50 ml of diethyl ether, respectively. The combined organic phases were then washed with $3 \times 20 \text{ml}$ of 1 M HCl and $3 \times 50 \text{ml}$ water and dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the oil obtained was dried *in vacuo*. The reaction yielded 2.743 g (94%) of a colorless liquid. ^1H NMR (600 MHz, CDCl_3): $\delta = 4.23\text{--}4.21$ (m, 2H, H-5), 3.72 (t, $J_{\text{H-H}} = 5.8 \text{ Hz}$, 2H, H-8), 3.72–3.70 (m, 2H, H-6), 3.61 (t, $J_{\text{H-H}} = 5.8 \text{ Hz}$, 2H, H-9), 1.20 (s, 9H, H-1/1') ppm. ^{13}C NMR (150 MHz, CDCl_3): $\delta = 178.6$ (*, 1C, C-3), 71.3 (–, 1C, C-8), 69.3 (–, 1C, C-6), 63.5 (–, 1C, C-5), 42.8 (–, 1C, C-9), 38.8 (*, 1C, C-2), 27.3 (+, 3C, C-1/1') ppm. IR (ATR): $\nu = 2972, 2874, 1809, 1728, 1702, 1481, 1460, 1397, 1366, 1284, 1158, 1130, 1042, 1006, 940, 861, 770, 747, 669, 579, 546 \text{ cm}^{-1}$. HR-ESI-MS: calculated for $[\text{C}_9\text{H}_{17}\text{ClO}_3 + \text{Na}]^+$: 231.0758. Found: 231.0762.

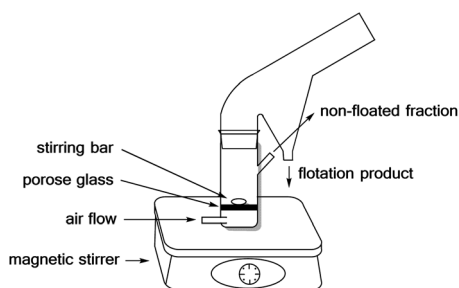


Fig. 8 Pictorial representation of a Hallimond tube.



Preparation of 2-[2-(2-chloroethoxy)ethoxy]ethyl-2,2-dimethylpropanoate (2b)

Under a nitrogen atmosphere, 2.04 ml (14.00 mmol) of 2-[2-(2-chloroethoxy)ethoxy]ethanol **1b** was dissolved in 50 ml of anhyd. diethyl ether and then 10 ml of anhyd. pyridine were added. 2.34 ml (19.00 mmol) of pivalic acid chloride were added at 0 °C. The reaction mixture was then stirred at room temperature for 48 hours. The reaction was then quenched with 1 M HCl (*ca.* 20 ml). The aqueous phase was extracted with 3 × 50 ml of diethyl ether, and the combined organic phases were washed with 3 × 20 ml of 1 M HCl and 3 × 50 ml of water, and finally dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the oil obtained was dried *in vacuo*. The reaction yielded 2.810 g (80%) of a slightly yellow liquid. ¹H NMR (600 MHz, CDCl₃): δ = 4.22–4.20 (m, 2H, H-5), 3.75 (t, *J*_{H-H} = 5.9 Hz, 2H, H-11), 3.70–3.69 (m, 2H, H-6), 3.67–3.65 (m, 4H, H-8, H-9), 3.62 (t, *J*_{H-H} = 5.9 Hz, 2H, H-12), 1.20 (s, 9H, H-1/1'/1'') ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 178.6 (*, 1C, C-3), 71.5 (–, 1C, C-11), 70.8 (–, 1C, C-8), 70.7 (–, 1C, C-9), 69.4 (–, 1C, C-6), 63.6 (–, 1C, C-5), 42.8 (–, 1C, C-12), 38.8 (*, 1C, C-2), 27.3 (+, 3C, C-1/1'/1'') ppm. IR (ATR): ν = 2972, 2873, 1810, 1729, 1701, 1481, 1460, 1398, 1366, 1284, 1200, 1123, 1043, 1006, 940, 863, 769, 745, 668, 589, 547, 524 cm^{–1}. HR-ESI-MS: calculated for [C₁₁H₂₁ClO₄ + Na]⁺: 275.1021. Found: 275.1025.

Preparation of 2-(2-iodoethoxy)ethyl-2,2-dimethylpropanoate (3a)

A reaction mixture of 13.506 g (90.11 mmol) of sodium iodide and 1.500 g (7.21 mmol) of 2-(2-chloroethoxy)ethyl-2,2-dimethylpropanoate **2a** was dissolved in 20 ml of acetone and refluxed overnight. After cooling, 10 ml of water were added. The aqueous phase was then extracted with 3 × 50 ml of diethyl ether. The combined organic phases were washed with 3 × 50 ml of water and dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the oil obtained was dried *in vacuo*. The reaction yielded 1.714 g of a red liquid which according to the spectra consist of a 0.35:1 mixture of compound **2b** and **3a**. This results in a yield of 51% for **3a**. However, further purification was not necessary since only the iodo-compound **3a** is reactive in the subsequent steps. ¹H NMR (600 MHz, CDCl₃): δ = 4.22–4.20 (m, 2H, H-5), 3.75–3.73 (m, 2H, H-8), 3.70–3.68 (m, 2H, H-6), 3.23 (t, *J*_{H-H} = 6.8 Hz, 2H, H-9), 1.20 (s, 9H, H-1/1'/1'') ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 178.6 (*, 1C, C-3), 71.9 (–, 1C, C-8), 68.9 (–, 1C, C-6), 63.5 (–, 1C, C-5), 39.2 (*, 1C, C-2), 27.3 (+, 3C, C-1/1'/1''), 2.7 (–, 1C, C-9) ppm. IR (ATR): ν = 2972, 2873, 1809, 1727, 1702, 1480, 1460, 1397, 1366, 1283, 1156, 1128, 1041, 1003, 940, 864, 770, 746, 669, 618, 579, 523 cm^{–1}. HR-ESI-MS: calculated for [C₉H₁₇IO₃ + Na]⁺: 323.0115. Found: 323.0123.

Preparation of 2-[2-(2-iodoethoxy)ethoxy]ethyl-2,2-dimethylpropanoate (3b)

A reaction mixture of 11.148 g (74.37 mmol) of sodium iodide and 1.500 g (5.95 mmol) of 2-[2-(2-chloroethoxy)ethoxy]ethyl-2,2-di-methylpropanoate **2b** was dissolved in 20 ml of acetone

and refluxed overnight. After cooling, 10 ml of water were added. The aqueous phase was then extracted with 3 × 50 ml of diethyl ether. The combined organic phases were then washed with 3 × 50 ml of water and dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the oil obtained was dried *in vacuo*. The reaction yielded 1.688 g (82%) of a red liquid. ¹H NMR (600 MHz, CDCl₃): δ = 4.21–4.20 (m, 2H, H-5), 3.74 (t, *J*_{H-H} = 6.8 Hz, 2H, H-11), 3.70–3.68 (m, 2H, H-6), 3.64 (s, 4H, H-8, H-9), 3.24 (t, *J*_{H-H} = 6.8 Hz, 2H, H-12), 1.19 (s, 9H, H-1/1'/1'') ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 178.6 (*, 1C, C-3), 72.1 (–, 1C, C-11), 70.7 (–, 1C, C-8), 70.4 (–, 1C, C-9), 69.4 (–, 1C, C-6), 63.6 (–, 1C, C-5), 38.8 (*, 1C, C-2), 27.3 (+, 3C, C-1/1'/1''), 2.9 (–, 1C, C-12) ppm. IR (ATR): ν = 2971, 2872, 1809, 1728, 1701, 1481, 1460, 1398, 1365, 1284, 1133, 1042, 1003, 939, 863, 769, 619, 589, 578, 546, 523 cm^{–1}. HR-ESI-MS: calculated for [C₁₁H₂₁IO₄ + Na]⁺: 367.0377. Found: 367.0391.

Preparation of 1-butyl-3-(2-[2-(2,2-dimethylpropanoyl)oxy]ethoxy)ethyl-1H-imidazolium iodide (4a)

0.500 g of crude **3a**, which corresponds to 1.11 mmol of 2-(2-iodoethoxy)ethyl-2,2-dimethylpropanoate **3a** and 0.13 ml (1.00 mmol) of 1-butylimidazole were dissolved in 10 ml of acetonitrile and refluxed for 70 hours. After the reaction had cooled, the solvent was removed on a rotary evaporator. The oil obtained was washed with 3 × 10 ml of diethyl ether and dried *in vacuo*. The reaction yielded 0.318 g (75%) of an orange oil. ¹H NMR (600 MHz, CDCl₃): δ = 9.91–9.88 (m, 1H, H-2), 7.59 (dd, *J*_{H-H} = 3.6, 1.8 Hz, 1H, H-5), 7.37 (dd, *J*_{H-H} = 3.6, 1.8 Hz, 1H, H-4), 4.59 (t, *J*_{H-H} = 4.7 Hz, 2H, H-10), 4.29 (t, *J*_{H-H} = 7.5 Hz, 2H, H-6), 4.17 (t, *J*_{H-H} = 4.7 Hz, 2H, H-14), 3.87 (t, *J*_{H-H} = 4.7 Hz, 2H, H-11), 3.66 (t, *J*_{H-H} = 4.7 Hz, 2H, H-13), 1.89 (quint, *J*_{H-H} = 7.5 Hz, 2H, H-7), 1.36 (sext, *J*_{H-H} = 7.5 Hz, 2H, H-8), 1.15 (s, 9H, H-18/18'/18''), 0.93 (t, *J*_{H-H} = 7.5 Hz, 3H, H-9) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 178.4 (*, 1C, C-16), 136.5 (+, 1C, C-2), 123.5 (+, 1C, C-5), 121.6 (+, 1C, C-4), 69.5 (–, 1C, C-13), 68.8 (–, 1C, C-11), 63.0 (–, 1C, C-14), 50.0 (–, 1C, C-6), 50.0 (–, 1C, C-10), 38.7 (*, 1C, C-17), 32.0 (–, 1C, C-7), 27.2 (+, 3C, C-18/18'/18''), 19.5 (–, 1C, C-8), 13.5 (+, 1C, C-9) ppm. IR (ATR): ν = 3135, 3074, 2962, 2872, 1722, 1623, 1563, 1457, 1395, 1361, 1284, 1161, 1124, 1042, 938, 856, 822, 732, 698, 640, 521, 480 cm^{–1}. HR-ESI-MS: calculated for [C₁₆H₂₉N₂O₃]⁺: 297.2173. Found: 297.2178.

Preparation of 1-butyl-3-[2-(2-[2-(2,2-dimethylpropanoyl)oxy]ethoxy)ethoxy]ethyl-1H-imidazolium iodide (4b)

0.500 g (1.45 mmol) of 2-[2-(2-iodoethoxy)ethoxy]ethyl-2,2-dimethylpropanoate **3b** and 0.17 ml (1.31 mmol) of 1-butylimidazole were dissolved in 10 ml of acetonitrile and refluxed for 70 hours. After the reaction had cooled, the solvent was removed on a rotary evaporator. The oil obtained was washed with 3 × 10 ml of diethyl ether and dried *in vacuo*. The reaction yielded 0.542 g (80%) of an orange-brown oil. ¹H NMR (600 MHz, CDCl₃): δ = 9.91–9.88 (m, 1H, H-2), 7.66 (dd, *J*_{H-H} = 3.6, 1.8 Hz, 1H, H-5), 7.37 (dd, *J*_{H-H} = 3.6, 1.8 Hz, 1H, H-4), 4.58 (t, *J*_{H-H} = 4.7 Hz, 2H, H-10), 4.29 (t, *J*_{H-H} = 7.5 Hz, 2H, H-6), 4.17 (t, *J*_{H-H} = 5.0 Hz, 2H, H-17), 3.88 (t, *J*_{H-H} = 4.7 Hz, 2H, H-11), 3.65–3.60 (m,



4H, H-16), 3.60–3.57 (m, 2H, H-13), 3.60–3.58 (m, 2H, H-14), 1.88 (quint, $J_{\text{H-H}} = 7.5$ Hz, 2H, H-7), 1.36 (sext, $J_{\text{H-H}} = 7.5$ Hz, 2H, H-8), 1.15 (s, 9H, H-21/21'/21''), 0.93 (t, $J_{\text{H-H}} = 7.5$ Hz, 3H, H-9) ppm. ^{13}C NMR (150 MHz, CDCl_3): $\delta = 178.5$ (*, 1C, C-19), 136.4 (+, 1C, C-2), 123.6 (+, 1C, C-5), 121.7 (+, 1C, C-4), 70.4 (–, 1C, C-13), 70.3 (–, 1C, C-14), 69.2 (–, 1C, C-16), 68.9 (–, 1C, C-11), 63.2 (–, 1C, C-17), 50.0 (–, 1C, C-6), 49.9 (–, 1C, C-10), 38.7 (*, 1C, C-20), 32.1 (–, 1C, C-7), 27.2 (+, 3C, C-21/21'/21''), 19.5 (–, 1C, C-8), 13.5 (+, 1C, C-9) ppm. IR (ATR): $\nu = 3136, 3075, 2961, 2871, 1722, 1625, 1563, 1457, 1396, 1359, 1284, 1162, 1120, 1040, 939, 858, 827, 732, 698, 641, 482$ cm^{-1} . HR-ESI-MS: calculated for $[\text{C}_{18}\text{H}_{33}\text{N}_2\text{O}_4]^+$: 341.2435. Found: 341.2444.

Preparation of 2-[2-(3-butyl-2-sulfanylidene-2,3-dihydro-1H-imidazol-1-yl)ethoxy]ethyl-2,2-dimethylpropanoate (5a)

0.205 g (0.48 mmol) of 1-butyl-3-(2-{2-[(2,2-dimethylpropanoyl)oxy]ethoxy}ethyl)-1H-imidazolium iodide was dissolved in 15 ml of anhyd. acetonitrile and 0.313 g (0.96 mmol) of cesium carbonate were added. After that, 0.019 g (0.58 mmol) of sulfur were added at room temperature. The reaction mixture was stirred at room temperature for three hours. The solvent was removed on a rotary evaporator and the residue was taken up in dichloromethane. The reaction mixture was filtered through a glass frit filled with Celite and then concentrated. The product obtained was dried *in vacuo*. The reaction yielded 0.087 g (55%) of a yellow-green oil. ^1H NMR (600 MHz, CDCl_3): $\delta = 6.85$ (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, H-5), 6.62 (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, H-4), 4.25 (t, $J_{\text{H-H}} = 4.9$ Hz, 2H, H-10), 4.17 (t, $J_{\text{H-H}} = 4.8$ Hz, 2H, H-14), 4.02 (t, $J_{\text{H-H}} = 7.5$ Hz, 2H, H-6), 3.76 (t, $J_{\text{H-H}} = 4.9$ Hz, 2H, H-11), 3.62 (t, $J_{\text{H-H}} = 4.8$ Hz, 2H, H-13), 1.74 (quint, $J_{\text{H-H}} = 7.5$ Hz, 2H, H-7), 1.38 (sext, $J_{\text{H-H}} = 7.5$ Hz, 2H, H-8), 1.17 (s, 9H, H-18/18'/18''), 0.94 (t, $J_{\text{H-H}} = 7.5$ Hz, 3H, H-9) ppm. ^{13}C NMR (150 MHz, CDCl_3): $\delta = 178.5$ (*, 1C, C-16), 161.6 (*, 1C, C-2), 118.5 (+, 1C, C-5), 116.2 (+, 1C, C-4), 69.2 (–, 1C, C-11), 69.2 (–, 1C, C-13), 63.5 (–, 1C, C-14), 47.9 (–, 1C, C-10), 47.8 (–, 1C, C-6), 38.8 (*, 1C, C-17), 31.1 (–, 1C, C-7) 27.3 (+, 3C, C-18/18'/18''), 19.9 (–, 1C, C-8), 13.8 (+, 1C, C-9) ppm. IR (ATR): $\nu = 2959, 2934, 2869, 1725, 1450, 1414, 1364, 1283, 1229, 1157, 1122, 1044, 936, 857, 764, 714, 674, 527$ cm^{-1} . HR-ESI-MS: calculated for $[\text{C}_{16}\text{H}_{28}\text{N}_2\text{O}_3\text{S} + \text{Na}]^+$: 351.1713. Found: 351.1716.

Preparation of 2-[2-(3-butyl-2-selanylidene-2,3-dihydro-1H-imidazol-1-yl)ethoxy]ethyl-2,2-dimethylpropanoate (5b)

0.210 g (0.50 mmol) of 1-butyl-3-(2-{2-[(2,2-dimethylpropanoyl)oxy]ethoxy}ethyl)-1H-imidazolium iodide was dissolved in 15 ml of dry acetonitrile and 0.326 g (1.00 mmol) of cesium carbonate were added. After that, 0.047 g (0.59 mmol) of selenium were added at room temperature. The reaction mixture was stirred at reflux for three hours. The solvent was removed on a rotary evaporator and the residue was taken up in dichloromethane. The reaction mixture was filtered through a glass frit filled with Celite and then concentrated. The product obtained was dried *in vacuo*. The reaction yielded 0.144 g (77%) of a yellow oil. ^1H NMR (600 MHz, CDCl_3): $\delta = 7.02$ (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, H-5), 6.78 (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, H-4), 4.34 (t, $J_{\text{H-H}} = 4.9$ Hz, 2H, H-10), 4.16 (t, $J_{\text{H-H}} = 4.8$ Hz, 2H,

H-14), 4.10 (t, $J_{\text{H-H}} = 7.5$ Hz, 2H, H-6), 3.78 (t, $J_{\text{H-H}} = 4.9$ Hz, 2H, H-11), 3.61 (t, $J_{\text{H-H}} = 4.8$ Hz, 2H, H-13), 1.76 (quint, $J_{\text{H-H}} = 7.5$ Hz, 2H, H-7), 1.37 (sext, $J_{\text{H-H}} = 7.5$ Hz, 2H, H-8), 1.16 (s, 9H, H-18/18'/18''), 0.94 (t, $J_{\text{H-H}} = 7.5$ Hz, 3H, H-9) ppm. ^{13}C NMR (150 MHz, CDCl_3): $\delta = 178.5$ (*, 1C, C-16), 154.9 (*, 1C, C-2), 120.7 (+, 1C, C-5), 118.2 (+, 1C, C-4), 69.2 (–, 1C, C-11), 69.2 (–, 1C, C-13), 63.4 (–, 1C, C-14), 49.8 (–, 1C, C-10), 49.7 (–, 1C, C-6), 38.8 (*, 1C, C-17), 31.1 (–, 1C, C-7) 27.3 (+, 3C, C-18/18'/18''), 19.9 (–, 1C, C-8), 13.8 (+, 1C, C-9) ppm. ^{77}Se NMR (114 MHz, CDCl_3): $\delta = -12.4$ (s) ppm. IR (ATR): $\nu = 2960, 2869, 1724, 1565, 1455, 1407, 1363, 1283, 1228, 1161, 1123, 1044, 936, 858, 762, 716, 669, 522, 481$ cm^{-1} . HR-ESI-MS: calculated for $[\text{C}_{16}\text{H}_{28}\text{N}_2\text{O}_3\text{Se} + \text{Na}]^+$: 399.1157. Found: 399.1159.

Preparation of 2-{2-[2-(3-butyl-2-sulfanylidene-2,3-dihydro-1H-imidazol-1-yl)ethoxy]ethoxy}ethyl 2,2-dimethylpropanoate (6a)

0.100 g (0.21 mmol) of 1-butyl-3-[2-(2-{2-[(2,2-dimethylpropanoyl)oxy]ethoxy}ethoxy)ethyl]-1H-imidazolium iodide was dissolved in 15 ml of dry acetonitrile and 0.137 g (0.42 mmol) of cesium carbonate were added. After that, 0.008 g (0.26 mmol) of sulfur were added at room temperature. The reaction mixture was stirred at room temperature for three hours. The solvent was removed on a rotary evaporator and the residue was taken up in dichloromethane. The reaction mixture was filtered through a glass frit filled with Celite and then concentrated. The product obtained was dried *in vacuo*. The reaction yielded 0.031 g (40%) of a yellow oil. ^1H NMR (600 MHz, CDCl_3): $\delta = 6.89$ (d, $J_{\text{H-H}} = 2.1$ Hz, 1H, H-5), 6.63 (d, $J_{\text{H-H}} = 2.1$ Hz, 1H, H-4), 4.25 (t, $J_{\text{H-H}} = 5.0$ Hz, 2H, H-10), 4.19 (t, $J_{\text{H-H}} = 4.9$ Hz, 2H, H-17), 4.02 (t, $J_{\text{H-H}} = 7.3$ Hz, 2H, H-6), 3.77 (t, $J_{\text{H-H}} = 5.0$ Hz, 2H, H-11), 3.65 (t, $J_{\text{H-H}} = 4.9$ Hz, 2H, H-16), 3.61–3.57 (m, 4H, H-13, H-14), 1.74 (quint, $J_{\text{H-H}} = 7.3$ Hz, 2H, H-7), 1.37 (sext, $J_{\text{H-H}} = 7.3$ Hz, 2H, H-8), 1.19 (s, 9H, H-21/21'/21''), 0.95 (t, $J_{\text{H-H}} = 7.3$ Hz, 3H, H-9) ppm. ^{13}C NMR (150 MHz, CDCl_3): $\delta = 178.6$ (*, 1C, C-19), 161.6 (*, 1C, C-2), 118.5 (+, 1C, C-2), 116.3 (+, 1C, C-4), 70.5 (–, 2C, C-14, C-13), 69.3 (–, 1C, C-16), 69.1 (–, 1C, C-11), 63.5 (–, 1C, C-17), 47.8 (–, 1C, C-6), 47.7 (–, 1C, C-10), 38.8 (*, 1C, C-20), 31.1 (–, 1C, C-7), 27.3 (–, 3C, C-21/21'/21''), 19.9 (–, 1C, C-8), 13.8 (+, 1C, C-9) ppm. IR (ATR): $\nu = 2959, 2934, 2869, 1725, 1450, 1414, 1362, 1284, 1230, 1117, 1044, 938, 861, 764, 715, 675, 528$ cm^{-1} . HR-ESI-MS: calculated for $[\text{C}_{18}\text{H}_{32}\text{N}_2\text{O}_4\text{S} + \text{Na}]^+$: 395.1975. Found: 395.1969.

Preparation of 2-{2-[2-(3-butyl-2-selanylidene-2,3-dihydro-1H-imidazol-1-yl)ethoxy]ethoxy}ethyl 2,2-dimethylpropanoate (6b)

0.100 g (0.21 mmol) of 1-butyl-3-[2-(2-{2-[(2,2-dimethylpropanoyl)oxy]ethoxy}ethoxy)ethyl]-1H-imidazolium iodide was dissolved in 15 ml of anhyd. acetonitrile and 0.137 g (0.42 mmol) of cesium carbonate were added. After that, 0.021 g (0.26 mmol) of selenium were added at room temperature. The reaction mixture was stirred at reflux for three hours. The solvent was then removed on a rotary evaporator and the residue was dissolved in dichloromethane. The reaction mixture was filtered through a glass frit filled with Celite and



then concentrated. The product obtained was dried *in vacuo*. The reaction yielded 0.036 g (41%) of a yellow oil. ^1H NMR (600 MHz, CDCl_3): δ = 7.08 (d, $J_{\text{H-H}}$ = 1.9 Hz, 1H, H-5), 6.81 (d, $J_{\text{H-H}}$ = 1.9 Hz, 1H, H-4), 4.35 (t, $J_{\text{H-H}}$ = 5.0 Hz, 2H, H-10), 4.19 (t, $J_{\text{H-H}}$ = 4.9 Hz, 2H, H-17), 4.10 (t, $J_{\text{H-H}}$ = 7.5 Hz, 2H, H-6), 3.79 (t, $J_{\text{H-H}}$ = 5.0 Hz, 2H, H-11), 3.65 (t, $J_{\text{H-H}}$ = 4.9 Hz, 2H, H-16), 3.59–3.57 (m, 4H, H-13, H-14), 1.76 (quint, $J_{\text{H-H}}$ = 7.5 Hz, 2H, H-7), 1.37 (sext, $J_{\text{H-H}}$ = 7.5 Hz, 2H, H-8), 1.18 (s, 9H, H-21/21'/21''), 0.94 (t, $J_{\text{H-H}}$ = 7.5 Hz, 3H, H-9) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 178.5 (*, 1C, C-19), 154.5 (*, 1C, C-2), 120.7 (+, 1C, C-5), 118.4 (+, 1C, C-4), 70.5 (–, 1C, C-14), 70.5 (–, 1C, C-13), 69.3 (–, 1C, C-16), 69.2 (–, 1C, C-11), 63.5 (–, 1C, C-17), 49.7 (–, 1C, C-6), 49.6 (–, 1C, C-10), 38.8 (*, 1C, C-20), 31.3 (–, 1C, C-7), 27.3 (–, 3C, C-21/21'/21''), 19.9 (–, 1C, C-8), 13.8 (+, 1C, C-9) ppm. ^{77}Se NMR (114 MHz, CDCl_3): δ = –12.4 (s) ppm. IR (ATR): ν = 2960, 2934, 2870, 1724, 1456, 1408, 1362, 1284, 1229, 1162, 1120, 1044, 912, 726, 670, 645 cm^{-1} . HR-ESI-MS: calculated for $[\text{C}_{18}\text{H}_{32}\text{N}_2\text{O}_4\text{Se} + \text{Na}]^+$: 443.1420. Found: 443.1417.

Preparation of [1-butyl-3-(2-{2-[(2,2-dimethylpropanoyl)oxy]ethoxy}ethyl)-1H-imidazolium-2-yl](cycloocta-1,5-diene-1,5-diyl- $\kappa^2\text{C}^1, \text{C}^5$)rhodium(i)-iodide (7a)

Under a nitrogen atmosphere, 0.175 g (0.41 mmol) of 1-butyl-3-(2-{2-[(2,2-dimethylpropanoyl)oxy]ethoxy}ethyl)-1H-imidazolium iodide was dissolved in 8 ml of dry dichloromethane and 0.049 g (0.21 mmol) of silver oxide were added. The reaction mixture was stirred at room temperature for one hour until the solution decolorized. 0.104 g (0.21 mmol) of bis-(1,5-cyclooctadiene)dirhodium(i)-dichloride was then added. The reaction was stirred at room temperature overnight. It was then filtered through Celite and purified by column chromatography using a solvent mixture of petroleum ether (PE) and ethyl acetate (EE) = 1 : 1. The obtained product was dried *in vacuo*. The reaction yielded 0.177 g (68%) of an orange oil. ^1H NMR (600 MHz, CDCl_3): δ = 7.04 (d, $J_{\text{H-H}}$ = 1.8 Hz, 1H, H-4), 6.76 (d, $J_{\text{H-H}}$ = 1.8 Hz, 1H, H-5), 5.03–4.99 (m, 1H, CH-COD), 4.95–4.89 (m, 2H, H-6), 4.54–4.43 (m, 3H, CH-COD, H-10), 4.20–4.17 (m, 2H, H-14), 3.92–3.88 (m, 2H, H-11), 3.65–3.63 (m, 2H, H-13), 3.29–3.21 (m, 2H, CH-COD), 2.40–2.29 (m, 4H, CH_2 -COD), 1.97–1.73 (m, 6H, H-7, CH_2 -COD), 1.46 (sext, $J_{\text{H-H}}$ = 7.6 Hz, 2H, H-8), 1.17 (s, 9H, H-18/18'/18''), 1.02 (t, $J_{\text{H-H}}$ = 7.6 Hz, 3H, H-9) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 181.8 (*, d, $J_{\text{Rh-C}}$ = 51.2 Hz, 1C, C-2), 178.5 (*, 1C, C-16), 122.1 (+, 1C, C-4), 119.8 (+, 1C, C-5), 98.5 (+, d, $J_{\text{Rh-C}}$ = 6.7 Hz, 1C, CH-COD), 98.3 (+, d, $J_{\text{Rh-C}}$ = 6.7 Hz, 1C, CH-COD), 71.0 (–, 1C, C-11), 69.2 (–, 1C, C-13), 68.4 (+, d, $J_{\text{Rh-C}}$ = 14.5 Hz, 1C, CH-COD), 67.7 (+, d, $J_{\text{Rh-C}}$ = 14.5 Hz, 1C, CH-COD), 63.4 (–, 1C, C-16), 50.8 (–, 1C, C-6 or C-10), 50.6 (–, 1C, C-10 or C-6), 38.8 (*, 1C, C-17), 33.4 (–, 1C, CH_2 -COD), 33.1 (–, 1C, CH_2 -COD), 32.7 (–, 1C, CH_2 -COD or C-7), 29.3 (–, 1C, CH_2 -COD or C-7), 28.6 (–, 1C, CH_2 -COD or C-7), 27.3 (+, 3C, C-18/18'/18''), 20.2 (–, 1C, C-8), 13.9 (+, 1C, C-9) ppm. IR (ATR): ν = 2958, 2934, 2872, 2831, 1725, 1561, 1459, 1415, 1398, 1366, 1283, 1227, 1160, 1124, 1080, 1044, 917, 861, 728, 699, 644, 520, 485, 446 cm^{-1} . HR-ESI-MS: calculated for $[\text{C}_{24}\text{H}_{40}\text{RhN}_2\text{O}_3]^+$: 507.2088. Found: 507.2087.

Preparation of {1-butyl-3-[2-(2-{2-[(2,2-dimethylpropanoyl)oxy]ethoxy}ethyl)-1H-imidazolium-2-yl](cycloocta-1,5-diene-1,5-diyl- $\kappa^2\text{C}^1, \text{C}^5$)rhodium(i)iodide (7b)

Under a nitrogen atmosphere, 0.200 g (0.43 mmol) of 1-butyl-3-[2-(2-{2-[(2,2-dimethylpropanoyl)oxy]ethoxy}ethyl)-1H-imidazolium iodide was dissolved in 8 ml of dry dichloromethane and 0.050 g (0.21 mmol) of silver oxide were added. The reaction mixture was stirred at room temperature for one hour until the solution decolorized. 0.104 g (0.21 mmol) of bis-(1,5-cyclooctadiene)dirhodium(i)-dichloride was then added. The reaction was stirred at room temperature overnight. The reaction mixture was then filtered through Celite and finally purified by column chromatography in a solvent mixture of petroleum ether (PE) and ethyl acetate (EE) = 1 : 1. The obtained product was dried *in vacuo*. The reaction yielded 0.160 g (55%) of a red oil. ^1H -NMR (600 MHz, CDCl_3): δ = 7.06 (d, $J_{\text{H-H}}$ = 2.0 Hz, 1H, H-4), 6.78 (d, $J_{\text{H-H}}$ = 2.0 Hz, 1H, H-5), 5.02–4.99 (m, 1H, CH-COD), 4.96–4.89 (m, 3H, CH-COD, H-6), 4.51–4.44 (m, 2H, H-10), 4.20–4.19 (m, 2H, H-17), 3.94–3.89 (m, 2H, H-11), 3.67–3.65 (m, 2H, H-16), 3.64–3.58 (m, 4H, H-13, H-14), 3.28–3.22 (m, 2H, CH-COD), 2.41–2.29 (m, 4H, CH_2 -COD), 1.99–1.77 (m, 6H, H-7, CH_2 -COD), 1.47 (sext, $J_{\text{H-H}}$ = 7.5 Hz, 2H, H-8), 1.19 (s, 9H, H-21/21'/21''), 1.02 (t, $J_{\text{H-H}}$ = 7.5 Hz, 3H, H-9) ppm. ^{13}C -NMR (150 MHz, CDCl_3): δ = 181.8 (*, d, $J_{\text{Rh-C}}$ = 50.7 Hz, 1C, C-2), 178.5 (*, 1C, C-19), 122.2 (+, 1C, C-4), 119.8 (+, 1C, C-5), 98.5 (+, d, $J_{\text{Rh-C}}$ = 6.6 Hz, 1C, CH-COD), 98.3 (+, d, $J_{\text{Rh-C}}$ = 6.6 Hz, 1C, CH-COD), 71.0 (–, 1C, C-11), 70.5 (–, 1C, C-13), 70.5 (–, 1C, C-14), 69.2 (–, 1C, C-16), 68.4 (+, d, $J_{\text{Rh-C}}$ = 14.6 Hz, 1C, CH-COD), 67.8 (+, d, $J_{\text{Rh-C}}$ = 14.6 Hz, 1C, CH-COD), 63.6 (–, 1C, C-17), 50.7 (–, 1C, C-6), 50.6 (–, 1C, C-10), 38.8 (*, 1C, C-20), 33.3 (–, 1C, CH_2 -COD), 33.1 (–, 1C, CH_2 -COD), 32.7 (–, 1C, CH_2 -COD or C-7), 29.2 (–, 1C, CH_2 -COD or C-7), 28.7 (–, 1C, CH_2 -COD or C-7), 27.3 (+, 3C, C-21/21'/21''), 20.2 (–, 1C, C-8), 13.9 (+, 1C, C-9) ppm. IR (ATR): ν = 2957, 2929, 2870, 1725, 1560, 1459, 1398, 1366, 1283, 1228, 1161, 1114, 1041, 938, 861, 732, 689, 517 cm^{-1} . HR-ESI-MS: calculated for $[\text{C}_{26}\text{H}_{44}\text{RhN}_2\text{O}_4]^+$: 551.2351. Found: 551.2355.

Preparation of [1-butyl-3-(2-{2-[(2,2-dimethylpropanoyl)oxy]ethoxy}ethyl)-1H-imidazolium-2-yl](cycloocta-4,8-diene-1,4-diyl- $\kappa^2\text{C}^1, \text{C}^5$)iridium(i)iodide (8a)

Under a nitrogen atmosphere, 0.178 g (0.42 mmol) of 1-butyl-3-(2-{2-[(2,2-dimethylpropanoyl)oxy]ethoxy}ethyl)-1H-imidazolium iodide was dissolved in 8 ml of dry dichloromethane and 0.049 g (0.21 mmol) of silver oxide were added. The reaction mixture was stirred at room temperature for one hour until the solution decolorized. 0.141 g (0.21 mmol) of bis-(1,5-cyclooctadiene)diiridium(i)-dichloride was then added. The reaction was stirred at room temperature overnight. It was then filtered through Celite and finally purified by column chromatography in a solvent mixture of petroleum ether (PE) and ethyl acetate (EE) = 1 : 1. The obtained product was dried *in vacuo*. The reaction yielded 0.187 g (62%) of a red oil. ^1H NMR (600 MHz, CDCl_3): δ = 7.06 (d, $J_{\text{H-H}}$ = 2.0 Hz, 1H, H-5), 6.78 (d, $J_{\text{H-H}}$ = 2.0 Hz, 1H, H-4), 4.77–4.73 (m, 1H, H-10), 4.62–4.58 (m, 1H, CH-COD), 4.53–4.49 (m, 1H, CH-COD), 4.42–4.39 (m, 1H,



H-10), 4.38–4.33 (m, 2H, H-6), 4.20–4.18 (m, 2H, H-14), 3.85 (t, $J_{\text{H-H}} = 4.5$ Hz, 2H, H-11), 3.64 (t, $J_{\text{H-H}} = 5.0$ Hz, 2H, H-13), 2.91–2.85 (m, 2H, CH-COD), 2.25–2.09 (m, 4H, CH₂-COD), 1.79–1.72 (m, 2H, H-7), 1.70–1.54 (m, 4H, CH₂-COD), 1.49–1.39 (m, 2H, H-8), 1.19 (s, 9H, H-18/18'/18''), 1.00 (t, $J_{\text{H-H}} = 7.4$ Hz, 3H, H-9) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 179.9$ (*, 1C, C-2), 178.5 (*, 1C, C-16), 121.9 (+, 1C, C-5), 119.5 (+, 1C, C-4), 84.6 (+, 1C, CH-COD), 84.1 (+, 1C, CH-COD), 71.0 (–, 1C, C-11), 69.2 (–, 1C, C-13), 63.4 (–, 1C, C-14), 52.0 (+, 1C, CH-COD), 51.4 (+, 1C, CH-COD), 50.5 (–, 1C, C-6 or C-10), 50.3 (–, 1C, C-6 or C-10), 38.8 (*, 1C, C-17), 34.0 (–, 1C, CH₂-COD), 33.4 (–, 1C, CH₂-COD), 33.1 (–, 1C, C-7), 30.0 (–, 1C, CH₂-COD), 29.4 (–, 1C, CH₂-COD), 27.3 (+, 3C, C-18/18'/18''), 20.1 (–, 1C, C-8), 13.9 (+, 1C, C-9) ppm. IR (ATR): $\nu = 2957, 2931, 2872, 2831, 1725, 1556, 1457, 1414, 1366, 1327, 1283, 1227, 1159, 1125, 1078, 1044, 969, 917, 862, 818, 770, 730, 706, 645, 591, 521, 474$ cm^{–1}. HR-ESI-MS: calculated for [C₂₄H₄₀IrN₂O₃]⁺: 597.2663. Found: 597.2664.

Preparation of {1-butyl-3-[2-(2-{2-[(2,2-dimethylpropanoyl)oxy]ethoxy}ethoxy)ethyl]-1H-imidazolium-2-yl}(cycloocta-1,5-diene-1,5-diyl-κ²C¹,C⁵)-iridium(i)iodide (8b)

Under a nitrogen atmosphere, 0.166 g (0.35 mmol) of 1-butyl-3-[2-(2-{2-[(2,2-dimethylpropanoyl)oxy]ethoxy}ethoxy)ethyl]-1H-imidazolium iodide was dissolved in 8 ml of dry dichloromethane and 0.041 g (0.18 mmol) of silver oxide were added. The reaction mixture was stirred at room temperature for one hour until the solution decolorized. 0.121 g (0.18 mmol) of bis-(1,5-cyclo-octadiene)diiridium(i)-dichloride was then added. The reaction was stirred at room temperature overnight. It was then filtered through Celite and finally purified by column chromatography in a solvent mixture of petroleum ether (PE) and ethyl acetate (EE) = 1 : 1. The obtained product was dried *in vacuo*. The reaction yielded 0.131 g (49%) of an orange oil. ¹H NMR (600 MHz, CDCl₃): $\delta = 7.07$ (d, $J_{\text{H-H}} = 1.8$ Hz, 1H, H-4), 6.78 (d, $J_{\text{H-H}} = 1.8$ Hz, 1H, H-5), 4.77–4.72 (m, 1H, H-6), 4.61–4.57 (m, 1H, CH-COD), 4.52–4.48 (m, 1H, CH-COD), 4.41–4.32 (m, 3H, H-10, H-6), 4.21–4.18 (t, $J_{\text{H-H}} = 4.8$ Hz, 2H, H-17), 3.89–3.83 (m, 2H, H-16), 3.63–3.59 (m, 4H, H-13, H-14), 2.91–2.85 (m, 2H, CH-COD), 2.22–2.12 (m, 4H, CH₂-COD), 1.94–1.88 (m, 1H, H-7), 1.76–1.65 (m, 3H, CH₂-COD, H-7), 1.63–1.40 (m, 2H, H-8), 1.19 (s, 9H, H-21/21'/21''), 0.99 (t, $J_{\text{H-H}} = 7.5$ Hz, 3H, H-9) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 179.8$ (*, 1C, C-2), 178.6 (*, 1C, C-16), 121.9 (+, 1C, C-4), 119.5 (+, 1C, C-5), 84.4 (+, 1C, CH-COD), 84.0 (+, 1C, CH-COD), 70.9 (–, 1C, C-11), 70.5 (–, 2C, C-13, C-14), 69.3 (–, 1C, C-16), 63.6 (–, 1C, C-17), 51.9 (+, 1C, CH-COD), 51.4 (+, 1C, CH-COD), 50.3 (–, 1C, C-6 or C-10), 50.3 (–, 1C, C-6 or C-10), 38.8 (*, 1C, C-20), 33.9 (–, 1C, CH₂-COD), 33.4 (–, 1C, CH₂-COD), 33.1 (–, 1C, CH₂-COD or C-7), 29.9 (–, 1C, CH₂-COD or C-7), 29.4 (–, 1C, CH₂-COD or C-7), 27.3 (+, 3C, C-21/21'/21''), 20.1 (–, 1C, C-8), 13.9 (+, 1C, C-9) ppm. IR (ATR): $\nu = 2957, 2931, 2872, 2832, 1725, 1567, 1457, 1414, 1366, 1327, 1284, 1228, 1161, 1119, 1042, 969, 916, 863, 838, 819, 770, 729, 707, 591, 510, 474$ cm^{–1}. HR-ESI-MS: calculated for [C₂₆H₄₄IrN₂O₄]⁺: 641.2925. Found: 641.2923.

Conflicts of interest

No conflicts of interest to declare.

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