Selective Anion Extraction and Recovery Using a $Fe^{II}_4L_4$ Cage

*Dawei Zhang, Tanya K. Ronson, Jesús Mosquera, Alexandre Martinez, and
Jonathan R. Nitschke**

*Abstract: Selective anion extraction is useful for the recovery
and purification of valuable chemicals, and in the removal of
pollutants from the environment. Here we report that $Fe^{II}_4L_4$
cage **1** is able to extract an equimolar amount of ReO_4^-, a high-
value anion and a nonradioactive surrogate of TcO_4^-, from
water into nitromethane. Importantly, the extraction was
efficiently performed even in the presence of 10 other
common anions in water, highlighting the high selectivity of
1 for ReO_4^-. The extracted guest could be released into water
as the cage disassembled in ethyl acetate, and then **1** could be
recycled by switching the solvent to acetonitrile. The versatile
solubility of the cage also enabled complete extraction of
ReO_4^- (as the tetrabutylammonium salt) from an organic
phase into water by using the sulfate salt of **1** as the extractant.*

Rhenium is among the rarest elements in the Earth's crust,[1]
but it is a key ingredient for modern industry. It is used as
catalyst for petroleum refining,[2] in the high-melting super-
alloys of jet engines,[3] and in new superhard materials,[4] to
cite only three examples. The limited supply and great
demand lead to a high cost, generating an economic incentive
for new means to extract, separate, and recycle rhenium as
perrhenate (ReO_4^-).[5]

Because of its similar structure and almost identical
charge density, perrhenate is also used as a nonradioactive
surrogate for pertechnetate $(^{99}TcO_4^-)$,[6] which is an important
radiopharmaceutical and one of the most problematic radio-
active ions in nuclear waste.[7] Significant advances have been
made in designing sorbent materials for removing $ReO_4^-/
TcO_4^-$ from aqueous solution by liquid–solid extraction.[7,8]
These solid materials take up anionic targets from water via
anion exchange. An attractive alternative to such sorbents is
the use of supramolecular receptors as liquid-phase extrac-
tants,[9] although only a few such ReO_4^-/TcO_4^- receptors have
been reported.[10] Compared to solid-state anion exchange
materials, supramolecular extractants functioning through

molecular recognition offer the potential for better selectivity
toward target anions. Their flexibility in solution may provide
a better size and shape match in order to optimize specific
interactions between receptors and substrates.[7] Such recep-
tors can thus help address the major challenge in supra-
molecular chemistry of anion recognition in water.[11]

Most supramolecular anion extractants have been robust
covalent receptors[12] as opposed to coordination cages.[13]
Such extractants must be stable in the presence of both
water and organic solvents,[14] properties that are easier to
engineer for covalent systems. Nevertheless, compared to the
synthesis of covalent cages, the preparation of self-assembled
coordination capsules usually involves less synthetic complex-
ity. The dynamic nature of coordination bonds[15] may also
enable guest release and subsequent recycling of the extrac-
tant.[16]

We recently reported the water-soluble sulfate salt of
azaphosphatrane-based $Fe^{II}_4L_4$ tetrahedron **1** (Figure 1),
which can adaptively encapsulate different anions via hydro-
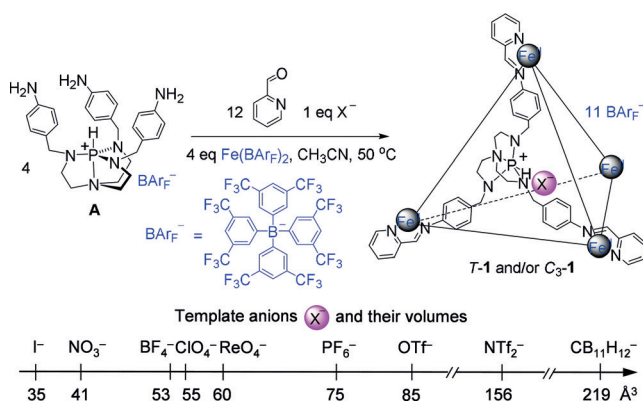

Figure 1. Subcomponent self-assembly of **1** around 1 equiv of template
anion.

gen bonding and electrostatic interactions in water.[17] Herein,
we develop **1** as an efficient and selective extractant, capable
of extracting ReO_4^- in either direction between organic and
aqueous phases. We also establish a simple solvent-switching
procedure that allows **1** to be disassembled, releasing its
anionic cargo and allowing it to be recycled.

Non-coordinating tetrakis(3,5-bis(trifluoromethyl)phe-
nyl)borate (BAr_F^-) was selected as the counter-anion for
1 in this work based on its lipophilicity and bulk (Figure 1).
The lipophilic nature of BAr_F^- renders **1** soluble in water-
immiscible organic solvents such as nitromethane. BAr_F^- is
larger (968 Å^3)[18] than the cavity volume of **1** at its most
expansive (253 Å^3; see below), precluding competition with
any of the anions discussed below.

[*] Dr. D. Zhang, Dr. T. K. Ronson, Dr. J. Mosquera, Prof. J. R. Nitschke
Department of Chemistry, University of Cambridge
Lensfield Road, Cambridge CB2 1EW (UK)
E-mail: jrn34@cam.ac.uk

Prof. A. Martinez
Aix Marseille Univ, CNRS, Centrale Marseille
iSm2, Marseille (France)

The BAr$_F^-$ salt of subcomponent **A** (Figure 1) was obtained by anion metathesis (Supporting Information section 2.1). As was observed in water,[17] the reaction of **A** (4 equiv) with Fe(BAr$_F$)$_2$ (4 equiv) and 2-formylpyridine (12 equiv) in acetonitrile failed to give the expected cage complex **1**·[BAr$_F$]$_{12}$, which required an internal template anion (listed in Figure 1) for its formation.

In acetonitrile, template anions with volumes below 53 Å^3 gave rise to both a C_3-symmetric isomer (C_3-**1**, with one azaphosphatrane $^+$P-H group oriented away from the inner cavity and the other three pointed inward) and a T-symmetric isomer (T-**1**, containing four inwardly-directed $^+$P-H groups) (Figure S1), whereas larger anionic templates, having volumes $\geq$ 55 Å^3, resulted in the formation of T-**1** exclusively (Figure S2), as was observed in water.[17] The initially obtained mixture of isomers in the former case is kinetically metastable and gradual interconversion between cage isomers was observed. Energy barriers of conversion in CD$_3$CN at 323 K were determined to be similar to the values previously obtained in water at 298 K[17] (Figures S3–S6).

We then tested the stability of the cage, as Tf$_2$N$^-$⊂ **1**·[BAr$_F$]$_{11}$ (Tf = CF$_3$SO$_2$), in ethyl acetate and nitromethane, both of which are water-immiscible organic solvents suitable for liquid–liquid extraction experiments. Circa 65% of **1** was observed to disassemble at a concentration of 1.5 mm in EtOAc after 4 h (Figure S7), with complete disassembly occurring at more dilute concentrations. In contrast, the cage was stable without any decomposition in CD$_3$NO$_2$ for at least two weeks at room temperature (Figure S9). We infer that the more polar solvent nitromethane offers a greater degree of stabilization to highly cationic **1** than does less polar ethyl acetate.[19] Nitromethane was thus chosen as the organic solvent for liquid–liquid extractions.

Interestingly, cage reassembly was observed after evaporation of EtOAc and redissolution of **1** in CD$_3$CN, indicating a reversible process (Figure S8). This phenomenon provides an original means of guest release and extractant recovery, as explored further below.

Through competitive guest exchange, we were able to gauge the relative binding affinities of different anions in CD$_3$NO$_2$. The following hierarchy was observed: CB$_{11}$H$_{12}^-$ > ReO$_4^-$ > TfO$^-$ > PF$_6^-$ > ClO$_4^-$ > Tf$_2$N$^-$ > BF$_4^-$ > I$^-$ > NO$_3^-$ (Figures S10–S17, Table S1). This ordering differs from the one observed in water: PF$_6^-$ > ReO$_4^-$ > TfO$^-$ > ClO$_4^-$ > CB$_{11}$H$_{12}^-$ > Tf$_2$N$^-$ > BF$_4^-$ > I$^-$ > NO$_3^-$,[17] especially as regards the binding affinity of CB$_{11}$H$_{12}^-$. To accommodate this largest anion, the cage framework must expand; we infer that this larger conformation in water is unfavorable because it involves greater exposure of hydrophobic surface to water. In both solvents, ReO$_4^-$ binds more strongly than other common anions, indicating potential for its selective extraction.

We obtained single crystals of **1** encapsulating the two most strongly bound anions in nitromethane, CB$_{11}$H$_{12}^-$ and ReO$_4^-$. X-ray diffraction analyses[20] (Figure 2) showed a T-symmetric framework for both structures. The structures demonstrate the flexibility of the cage skeleton, allowing adaptation to guests of different sizes. Calculated cavity volumes of 157 Å^3 and 253 Å^3 were obtained for the ReO$_4^-$
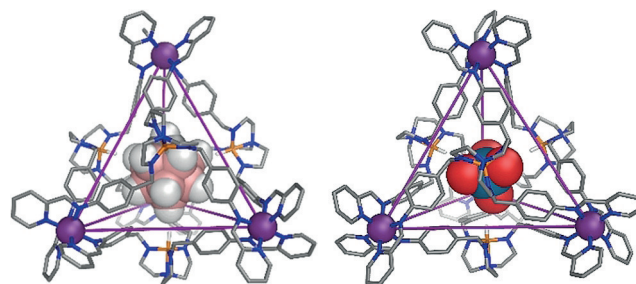

Figure 2. X-ray crystal structures of CB$_{11}$H$_{12}^-$⊂**1** (left) and ReO$_4^-$⊂**1** (right). Disorder, unbound counterions, non-P-bound hydrogen atoms, and solvents are omitted for clarity.

(volume 60 Å^3) and CB$_{11}$H$_{12}^-$ (volume 219 Å^3) complexes, respectively (Figure S18). Cavity expansion occurs through outward motion of the azaphosphatrane faces, resulting in a more open surface having pores of ca. 2.5 Å in CB$_{11}$H$_{12}^-$⊂**1**, compared to ca. 1.2 Å in ReO$_4^-$⊂**1**.

Since Tf$_2$N$^-$ is the most weakly bound among anions capable of templating T-**1** exclusively, extraction of ReO$_4^-$ was initially investigated using Tf$_2$N$^-$⊂**1**·[BAr$_F$]$_{11}$ as the extractant. After mixing 0.8 mm Tf$_2$N$^-$⊂**1**·[BAr$_F$]$_{11}$ in CD$_3$NO$_2$ with 0.8 mm NaReO$_4$ in D$_2$O for 7 h, no further uptake of ReO$_4^-$ by **1** was observed. ^{1}H NMR spectroscopy of the CD$_3$NO$_2$ phase revealed that 60% of the ReO$_4^-$ from the aqueous phase had been extracted as ReO$_4^-$⊂**1**·[BAr$_F$]$_{11}$, with the remainder of **1** binding Tf$_2$N$^-$ (Figure S19). After displacement by the extracted ReO$_4^-$, free Tf$_2$N$^-$ thus transferred from CD$_3$NO$_2$ to D$_2$O as the sodium salt.

We investigated the effect of the counterions of the Tf$_2$N$^-$ template by adding TBANTf$_2$ (TBA = tetra-n-butylammonium), KNTf$_2$, or LiNTf$_2$ during the self-assembly, but no cation effect on the efficiency of ReO$_4^-$ extraction was observed (Figure S20). Similarly, increasing the concentrations of Tf$_2$N$^-$⊂**1**·[BAr$_F$]$_{11}$ in CD$_3$NO$_2$ and NaReO$_4$ in D$_2$O to 1.3 mm (Figure S20f) did not impact extraction efficiency.

The extraction of TfO$^-$ (using NaOTf) from water under identical liquid–liquid conditions was also successful but with a lower efficiency (43%, Figure S21). Control experiments confirmed that without the cage, NaOTf did not transfer to the CD$_3$NO$_2$ phase (Figure S22).

In order to improve the extraction efficiency, we sought a more weakly bound template anion that avoided the complexity of generating a mixture of cage diastereomers. Such an anion was found to be n-butyltrifluoroborate (^{n}BuBF$_3^-$). We found ^{n}BuBF$_3^-$ to be able to template T-**1** exclusively (Figures S23–S28), and the resultant ^{n}BuBF$_3^-$⊂**1**·[BAr$_F$]$_{11}$ to be stable in CD$_3$NO$_2$ for weeks. Moreover, 1 equiv of Tf$_2$N$^-$ in CD$_3$NO$_2$ almost completely displaced the encapsulated ^{n}BuBF$_3^-$ (Figure S29), marking ^{n}BuBF$_3^-$ as the weaker binder.

When the extractant ^{n}BuBF$_3^-$⊂**1**·[BAr$_F$]$_{11}$ in CD$_3$NO$_2$ was mixed with an equimolar amount of NaReO$_4$ in D$_2$O, only ReO$_4^-$⊂**1**·[BAr$_F$]$_{11}$ was observed after extraction, indicating complete removal of ReO$_4^-$ from water (Figures 3c and S30). Complete extraction of TfO$^-$ from aqueous NaOTf was also achieved by using ^{n}BuBF$_3^-$⊂**1**·[BAr$_F$]$_{11}$ (Figure S31).
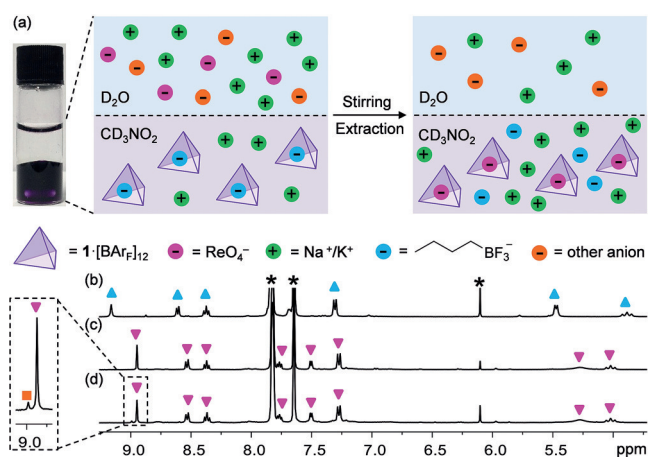
Figure 3. a) Selective liquid–liquid extraction of ReO_4^- in the presence of other anions. Conditions: 0.8 mM $^nBuBF_3^- \subset 1 \cdot [BAr_F]_{11}$ in CD_3NO_2; 0.8 mM in D_2O of each of $NaReO_4$, NaF, $NaCl$, $NaBr$, NaI, Na_2SO_4, $KClO_4$, KNO_3, $NaBF_4$, NaH_2PO_4, and $NaOAc$; 7 hours stirring at RT; b–d) Partial ^1H NMR spectra of (b) the CD_3NO_2 phase before extraction, showing only the presence of $^nBuBF_3^- \subset 1 \cdot [BAr_F]_{11}$ (blue ▲); c) the CD_3NO_2 phase after extraction in the absence of competing anions, showing only the presence of $ReO_4^- \subset 1 \cdot [BAr_F]_{11}$ (pink ▼); d) the CD_3NO_2 phase after extraction in the presence of competing anions, showing the presence of 97% $ReO_4^- \subset 1 \cdot [BAr_F]_{11}$ (pink ▼) and 3% $ClO_4^- \subset 1 \cdot [BAr_F]_{11}$ (orange ■). The peaks of BAr_F^- and the trimethoxybenzene standard are denoted by asterisks.

Encouraged by these results, we evaluated the selectivity of **1** toward ReO_4^- in the presence of 10 other different anions simultaneously in water: F^-, Cl^-, Br^-, I^-, SO_4^{2-}, ClO_4^-, NO_3^-, BF_4^-, $H_2PO_4^-$, and AcO^- (1 equiv to ReO_4^- in each case). The extraction efficiency for ReO_4^- by $^nBuBF_3^- \subset 1 \cdot [BAr_F]_{11}$ in the presence of this anion library was 97%, with ClO_4^- comprising the other 3% extracted (Figure 3).

We also developed a strategy to release and separate the extracted guest and recover the cage extractant by exploiting the instability of **1** in less polar solvents. As shown in Figure 4, after extraction, the nitromethane layer was separated and the solvent evaporated. The isolated cage was then redissolved in degassed EtOAc. As described above, the cage disassembled in this solvent. The extracted guest transferred to the water phase as $KReO_4$, pairing with K^+ from $^nBuBF_3K$, allowing its removal as the phases were separated. Regener-
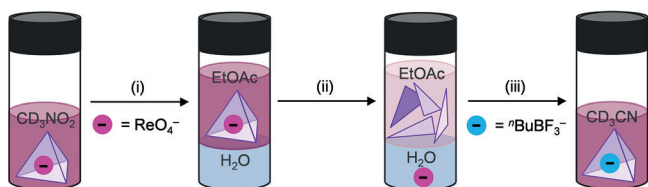
ation of $^nBuBF_3^- \subset 1 \cdot [BAr_F]_{11}$, which could be reused for further extraction experiments, was realized by evaporating the ethyl acetate and adding acetonitrile, along with $^nBuBF_3K$ (Figure S32).

Interestingly, due to the versatile solubility of **1**, either ReO_4^- or TfO^- could also be extracted from an organic phase into water, in the opposite direction to what was described above. In this case, $Tf_2N^- \subset 1 \cdot [SO_4]_{5.5}$ as extractant completely removed either ReO_4^- or TfO^- from CD_3NO_2 into D_2O (Figures 5 and S33). Control experiments showed that with-
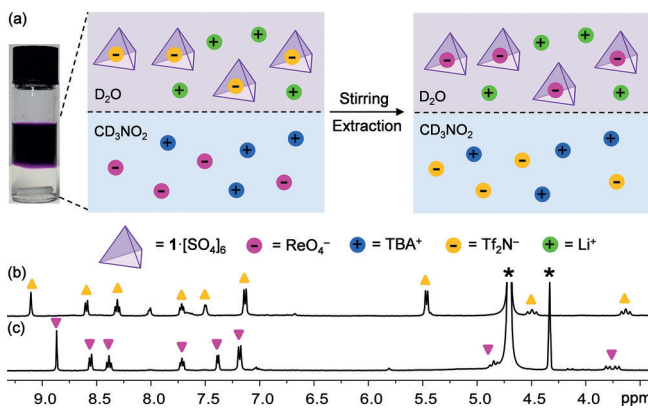

Figure 5. a) Illustration of the liquid–liquid extraction of ReO_4^- from an organic phase into water. Conditions: 0.8 mM $Tf_2N^- \subset 1 \cdot [SO_4]_{5.5}$ in D_2O; 0.8 mM $TBAReO_4$ in CD_3NO_2; 3 hours stirring. b,c) Partial ^1H NMR spectra of (b) the D_2O phase before extraction, showing only $Tf_2N^- \subset 1 \cdot [SO_4]_{5.5}$ (yellow ▲), and (c) the D_2O phase after extraction, showing only $ReO_4^- \subset 1 \cdot [SO_4]_{5.5}$ (pink ▼). HDO and CHD_2NO_2 peaks are represented by asterisks.

out the cage, $TBAReO_4$ and TBAOTf did not transfer to D_2O (Figures S34).

In summary, we have demonstrated for the first time the feasibility of using a coordination cage for biphasic extraction. By employing BAr_F^- as counter-anion and $^nBuBF_3^-$ as template, $^nBuBF_3^- \subset 1 \cdot [BAr_F]_{11}$ was capable of completely extracting ReO_4^- from water into nitromethane. An efficiency of 97% was achieved even in the presence of 10 competing anions. A novel strategy for extractant regeneration was developed by taking advantage of the differential stability of **1** across solvents. Moreover, due to the versatile solubility of **1** when paired with different counter-anions, complete extraction of ReO_4^- ($TBAReO_4$) from an organic phase into water could also be accomplished by using $Tf_2N^- \subset 1 \cdot [SO_4]_{5.5}$. The selective extraction properties of the cage toward perrhenate suggest great potential for recycling rhenium compounds, purification of chemicals, and for pertechnetate removal from water. Concepts developed in this study may also be generalized to enable the purification of other species using different coordination cages.

Figure 4. Illustration of cage extractant recycling: (i) After evaporation of CD_3NO_2, $ReO_4^- \subset 1 \cdot [BAr_F]_{11}$ was redissolved in degassed EtOAc; degassed H_2O was then added. (ii) After stirring for 4 h, the cage disassembled and ReO_4^- was released, transferring to the H_2O phase. (iii) After separation and evaporation of the EtOAc layer, addition of CD_3CN and $^nBuBF_3^-$ resulted in regeneration of the extractant $^nBuBF_3^- \subset 1 \cdot [BAr_F]_{11}$.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

Keywords: anion receptor · coordination cage · liquid–liquid extraction · self-assembly · supramolecular chemistry

How to cite: *Angew. Chem. Int. Ed.* **2018**, *57*, 3717–3721
Angew. Chem. **2018**, *130*, 3779–3783

[1] E. Scerri, *Nat. Chem.* **2010**, *2*, 598.

[2] S. A. D'Ippolito, C. R. Vera, F. Epron, P. Samoila, C. Especel, P. Marécot, L. B. Gutierrez, C. L. Pieck, *Ind. Eng. Chem. Res.* **2009**, *48*, 3771–3778.

[3] S. Tian, Y. Su, B. Qian, X. Yu, F. Liang, A. Li, *Mater. Des.* **2012**, *37*, 236–242.

[4] R. B. Kaner, J. J. Gilman, S. H. Tolbert, *Science* **2005**, *308*, 1268–1269.

[5] a) X. Lan, S. Liang, Y. Song, *Hydrometallurgy* **2006**, *82*, 133–136; b) S. Ghorbanzadeh Mashkani, P. Tajer Mohammad Ghazvini, D. Agha Aligol, *Bioresour. Technol.* **2009**, *100*, 603–608.

[6] a) J. Shen, W. Chai, K. Wang, F. Zhang, *ACS Appl. Mater. Interfaces* **2017**, *9*, 22440–22448; b) D. Banerjee, S. K. Elsaidi, B. Aguila, B. Li, D. Kim, M. J. Schweiger, A. A. Kruger, C. J. Doonan, S. Ma, P. K. Thallapally, *Chem. Eur. J.* **2016**, *22*, 17581–17584; c) D. Banerjee, W. Xu, Z. Nie, L. E. Johnson, C. Coghlan, M. L. Sushko, D. Kim, M. J. Schweiger, A. A. Kruger, C. J. Doonan, P. K. Thallapally, *Inorg. Chem.* **2016**, *55*, 8241–8243.

[7] D. Banerjee, D. Kim, M. J. Schweiger, A. A. Kruger, P. K. Thallapally, *Chem. Soc. Rev.* **2016**, *45*, 2724–2739.

[8] a) P. V. Bonnesen, G. M. Brown, S. D. Alexandratos, L. B. Bavoux, D. J. Presley, V. Patel, R. Ober, B. A. Moyer, *Environ. Sci. Technol.* **2000**, *34*, 3761–3766; b) S. Wang, E. V. Alekseev, J. Diwu, W. H. Casey, B. L. Phillips, W. Depmeier, T. E. Albrecht-Schmitt, *Angew. Chem. Int. Ed.* **2010**, *49*, 1057–1060; *Angew. Chem.* **2010**, *122*, 1075–1078; c) L. Zhu, D. Sheng, C. Xu, X. Dai, M. A. Silver, J. Li, P. Li, Y. Wang, Y. Wang, L. Chen, C. Xiao, J. Chen, R. Zhou, C. Zhang, O. K. Farha, Z. Chai, T. E. Albrecht-Schmitt, S. Wang, *J. Am. Chem. Soc.* **2017**, *139*, 14873–14876; d) L. Zhu, C. Xiao, X. Dai, J. Li, D. Gui, D. Sheng, L. Chen, R. Zhou, Z. Chai, T. E. Albrecht-Schmitt, S. Wang, *Environ. Sci. Technol. Lett.* **2017**, *4*, 316–322; e) H. Fei, M. R. Bresler, S. R. Oliver, *J. Am. Chem. Soc.* **2011**, *133*, 11110–11113.

[9] a) K. T. Holman, M. M. Halihan, J. W. Steed, S. S. Jurisson, J. L. Atwood, *J. Am. Chem. Soc.* **1995**, *117*, 7848–7849; b) J. A. Gawenis, K. T. Holman, J. L. Atwood, S. S. Jurisson, *Inorg. Chem.* **2002**, *41*, 6028–6031; c) P. D. Beer, P. K. Hopkins, J. D. McKinney, *Chem. Commun.* **1999**, 1253–1254; d) D. Farrell, K. Gloe, K. Gloe, G. Goretzki, V. McKee, J. Nelson, M. Nieuwenhuyzen, I. Pal, H. Stephan, R. M. Town, K. Wichmann, *Dalton Trans.* **2003**, 1961–1968; e) A. M. Wilson, P. J. Bailey, P. A. Tasker, J. R. Turkington, R. A. Grant, J. B. Love, *Chem. Soc. Rev.* **2014**, *43*, 123–134; f) R. M. Izatt, G. A. Clark, J. J. Christensen, *Sep. Sci. Technol.* **1986**, *21*, 865–872.

[10] a) E. A. Katayev, G. V. Kolesnikov, J. L. Sessler, *Chem. Soc. Rev.* **2009**, *38*, 1572–1586; b) R. Alberto, G. Bergamaschi, H. Braband, T. Fox, V. Amendola, *Angew. Chem. Int. Ed.* **2012**, *51*, 9772–9776; *Angew. Chem.* **2012**, *124*, 9910–9914; c) V. Amendola, G. Bergamaschi, M. Boiocchi, R. Alberto, H. Braband, *Z. Naturforsch. B* **2014**, *5*, 1820–1826; d) R. Custelcean, *Chem. Commun.* **2013**, *49*, 2173–2182.

[11] a) N. Busschaert, C. Caltagirone, W. Van Rossom, P. A. Gale, *Chem. Rev.* **2015**, *115*, 8038–8155; b) P. Ballester, *Chem. Soc. Rev.* **2010**, *39*, 3810–3830; c) Y. Zhou, J. F. Zhang, J. Yoon, *Chem. Rev.* **2014**, *114*, 5511–5571; d) P. Sokkalingam, J. Shraberg, S. W. Rick, B. C. Gibb, *J. Am. Chem. Soc.* **2016**, *138*, 48–51; e) M. J. Langton, C. J. Serpell, P. D. Beer, *Angew. Chem. Int. Ed.* **2016**, *55*, 4629–4629; *Angew. Chem.* **2016**, *128*, 4705–4705; f) S. O. Kang, J. M. Llinares, V. W. Day, K. Bowman-James, *Chem. Soc. Rev.* **2010**, *39*, 3980–4003; g) J. Jo, A. Olasz, C. H. Chen, D. Lee, *J. Am. Chem. Soc.* **2013**, *135*, 3620–3632; h) S. Kubik, *Chem. Soc. Rev.* **2010**, *39*, 3648–3663; i) Q. Q. Wang, V. W. Day, K. Bowman-James, *Angew. Chem. Int. Ed.* **2012**, *51*, 2119–2123; *Angew. Chem.* **2012**, *124*, 2161–2165; j) L. Fabbrizzi, A. Poggi, *Chem. Soc. Rev.* **2013**, *42*, 1681–1699; k) M. Lisbjerg, H. Valkenier, B. M. Jessen, H. Al-Kerdi, A. P. Davis, M. Pittelkow, *J. Am. Chem. Soc.* **2015**, *137*, 4948–4951.

[12] a) Q. He, G. M. Peters, V. M. Lynch, J. L. Sessler, *Angew. Chem. Int. Ed.* **2017**, *56*, 13396–13400; *Angew. Chem.* **2017**, *129*, 13581–13585; b) A. L. Sisson, J. P. Clare, A. P. Davis, *Chem. Commun.* **2005**, 5263–5265; c) S. K. Kim, G. I. Vargas-Zuniga, B. P. Hay, N. J. Young, L. H. Delmau, C. Masselin, C. H. Lee, J. S. Kim, V. M. Lynch, B. A. Moyer, J. L. Sessler, *J. Am. Chem. Soc.* **2012**, *134*, 1782–1792; d) C. Jia, B. Wu, S. Li, X. Huang, Q. Zhao, Q. S. Li, X. J. Yang, *Angew. Chem. Int. Ed.* **2011**, *50*, 486–490; *Angew. Chem.* **2011**, *123*, 506–510; e) S. Kharel, H. Joshi, S. Bierschenk, M. Stollenz, D. Taher, N. Bhuvanesh, J. A. Gladysz, *J. Am. Chem. Soc.* **2017**, *139*, 2172–2175; f) X. Chi, G. M. Peters, F. Hammel, C. Brockman, J. L. Sessler, *J. Am. Chem. Soc.* **2017**, *139*, 9124–9127.

[13] M. Wenzel, Q. W. Knapp, P. G. Plieger, *Chem. Commun.* **2011**, *47*, 499–501.

[14] E. G. Percástegui, J. Mosquera, J. R. Nitschke, *Angew. Chem. Int. Ed.* **2017**, *56*, 9136–9140; *Angew. Chem.* **2017**, *129*, 9264–9268.

[15] a) X.-P. Zhou, Y. Wu, D. Li, *J. Am. Chem. Soc.* **2013**, *135*, 16062–16065; b) L. Yang, X. Tan, Z. Wang, X. Zhang, *Chem. Rev.* **2015**, *115*, 7196–7239; c) W. Wang, Y. X. Wang, H. B. Yang, *Chem. Soc. Rev.* **2016**, *45*, 2656–2693; d) E. Krieg, M. M. C. Bastings, P. Besenius, B. Rybtchinski, *Chem. Rev.* **2016**, *116*, 2414–2477; e) D. Ray, J. T. Foy, R. P. Hughes, I. Aprahamian, *Nat. Chem.* **2012**, *4*, 757–762; f) S. Erbas-Cakmak, S. D. P. Fielden, U. Karaca, D. A. Leigh, C. T. McTernan, D. J. Tetlow, M. R. Wilson, *Science* **2017**, *358*, 340–343; g) Z. He, W. Jiang, C. A. Schalley, *Chem. Soc. Rev.* **2015**, *44*, 779–789; h) D. E. Barry, D. F. Caffrey, T. Gunnlaugsson, *Chem. Soc. Rev.* **2016**, *45*, 3244–3274; i) M. Mauro, A. Aliprandi, D. Septiadi, N. S. Kehr, L. De Cola, *Chem. Soc. Rev.* **2014**, *43*, 4144–4166; j) S. Wang, T. Sawada, K. Ohara, K. Yamaguchi, M. Fujita, *Angew. Chem. Int. Ed.* **2016**, *55*, 2063–2066; *Angew. Chem.* **2016**, *128*, 2103–2106; k) P. Wei, X. Yan, F. Huang, *Chem. Soc. Rev.* **2015**, *44*, 815–832; l) R. Custelcean, P. V. Bonnesen, N. C. Duncan, X. Zhang, L. A. Watson, G. Van Berkel, W. B. Parson, B. P. Hay, *J. Am. Chem. Soc.* **2012**, *134*, 8525–8534.

[16] a) S. K. Samanta, D. Moncelet, V. Briken, L. Isaacs, *J. Am. Chem. Soc.* **2016**, *138*, 14488–14496; b) M. Han, R. Michel, B. He, Y. S. Chen, D. Stalke, M. John, G. H. Clever, *Angew. Chem. Int. Ed.* **2013**, *52*, 1319–1323; *Angew. Chem.* **2013**, *125*, 1358–1362; c) A. K. Chan, W. H. Lam, Y. Tanaka, K. M. Wong, V. W. Yam, *Proc. Natl. Acad. Sci. USA* **2015**, *112*, 690–695; d) K. Kurihara, K. Yazaki, M. Akita, M. Yoshizawa, *Angew. Chem.*

Int. Ed. **2017**, *56*, 11360–11364; *Angew. Chem.* **2017**, *129*, 11518–11522; e) T. R. Cook, P. J. Stang, *Chem. Rev.* **2015**, *115*, 7001–7045.

[17] D. Zhang, T. K. Ronson, J. Mosquera, A. Martinez, L. Guy, J. R. Nitschke, *J. Am. Chem. Soc.* **2017**, *139*, 6574–6577.

[18] J. Cullinane, A. Jolleys, F. S. Mair, *Dalton Trans.* **2013**, *42*, 11971–11975.

[19] a) W. L. Smith, *J. Chem. Educ.* **1977**, *54*, 228–229; b) M. Roseman, W. P. Jencks, *J. Am. Chem. Soc.* **1975**, *97*, 631–640.

[20] CCDC 1812469 and 1812470 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.