Self-Assembly

Narcissistic Self-Sorting in Self-Assembled Cages of Rare Earth Metals and Rigid Ligands[**]

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Abstract: Highly selective, narcissistic self-sorting can be achieved in the formation of self-assembled cages of rare earth metals with multianionic salicylhydrazone ligands. The assembly process is highly sensitive to the length of the ligand and the coordination geometry. Most surprisingly, high-fidelity sorting is possible between ligands of identical coordination angle and geometry, differing only in a single functional group on the ligand core, which is not involved in the coordination. Supramolecular effects allow discrimination between pendant functions as similar as carbonyl or methylene groups in a complex assembly process.

Self-sorting and the controlled organization of self-assembled systems are vital for the controlled formation of macromolecular constructs. The selective assembly of DNA is the classical example, but the selective folding of proteins could also be thought of as "self-sorting", in that some individual, highly similar hydrogen-bond interactions are favored over others as part of a greater self-assembly process. On the whole, the discrimination between individual hydrogen-bonding interactions is strong, but each interaction by itself is weak. Self-sorting can be achieved in the formation of synthetic supramolecular assemblies.[1] There are two possible types of self-sorting upon multicomponent self-assembly: narcissistic self-sorting, whereby the individual component forms an assembly solely with itself,[2] or social self-sorting, in which mixed assemblies (heterocomplexes) are favored.[3] Social self-sorting is relatively common, and multiple different components can be engineered to form impressively complex structures. Social self-sorting in metal–ligand assemblies can exploit different coordination motifs in the formation of polygons, polyhedra, catenanes, and knots.[4] Obviously, each of these sorting outcomes can be favored by maximizing the difference between the coordinating ligands. The greater the difference in geometry, size, coordination angle, and coordination denticity, the easier the self-sorting becomes. When using ligands with highly similar, or even identical coordination motifs, discrimination becomes far

more difficult, and geometrical differences are often exploited for good selectivity.[4]

Narcissistic self-sorting is less common, and generally observed in hydrogen-bonded systems. Isaacs and Wu showed that a mixture of ten components can narcissistically self-sort, despite the fact that each component contains complementary hydrogen-bonding motifs.[2a] There are also capsular aggregates that display this effect, and these examples take advantage of geometrical differences in the components.[5] Narcissistic sorting in metal–ligand assemblies is rarer still. Discrimination between identical coordinating motifs is challenging, unless geometric constraints are added. The pioneering example showed narcissistic self-sorting of bipyridyl ligands of varied lengths in the formation of self-assembled M_2L_3 helices; other groups have applied this concept to bis(catecholate) coordinators.[6] Other tactics that confer some type of selectivity in sorting (not necessarily narcissistic) between identical coordinating groups are to vary the coordination angle or distance,[7] employ stereoinduction,[8] or provide steric hindrance in the internal cavity.[9]

This leads to a question: how similar can individual components be, while still allowing narcissistic self-sorting? In complexes with very similar geometry and the same coordinating motif, mixing is most commonly observed, and highly controlled narcissistic selectivity is rare.[10] We recently showed that multianionic salicylhydrazone ligands display subtle selectivity for differently sized rare earth metals, an effect that is maximized by supramolecular cooperativity.[11] Other groups have investigated self-assembly exploiting lanthanide coordinators,[12] and this also focuses on the selectivity between different metal ions.[13] The delicate discrimination we observed between metals of very similar charge, size, and coordination sphere suggested that ligand-based self-sorting behavior might be possible. Here we show that highly selective narcissistic self-sorting can be achieved in the lanthanide-mediated self-assembly of highly similar bis(salicylhydrazone) ligands. Most remarkably, changing a single function (from CH_2 to $C=O$) that is not involved in the coordination process can allow ligand discrimination.

A number of bis(salicylhydrazone)-based ligands were synthesized to investigate the effect of variable coordination geometry/angle, length, and pendant substitution on the narcissistic self-sorting behavior (Figure 1). Each ligand displayed two identical salicylhydrazone coordination motifs, a tridentate coordinator known to form polyhedral self-assemblies upon exposure to lanthanide salts.[14] Fluorene-based ligand cores are good candidates for controlling self-assembly properties.[15] Ligands **1–4** display identical coordination lengths and angles, and differ only in the

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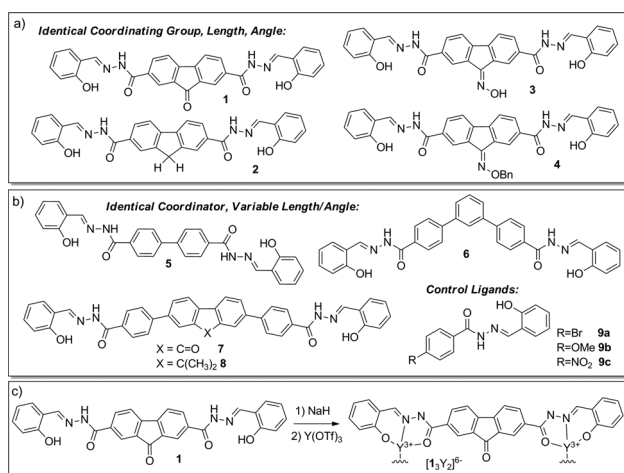
Figure 1. a) Ligands with identical shape and variable functions; b) ligands with variable lengths and coordination angles; c) representative self-assembly process forming $[1_3Y_2]^{6-}$.

group on the central carbon atom. These ligands were synthesized from commercially available 9-fluorenone-2,7-dicarboxylic acid (see the Supporting Information for synthetic procedures and characterization). Four different internal groups were employed, with slightly different sizes and polarities: fluorenone ligand **1**, fluorene ligand **2**, which displays a smaller CH_2 group, and the larger ligands oxime **3**, or benzyl oxime **4**. Other ligands were synthesized to study larger changes. Known ligands **5**[14] and **6**[11] vary in both coordination length and angle. The length of the ligand can be varied without changing the coordination angle by extending the core fluorenone motif with a rigid linear spacer. These longer ligands required an alternate synthetic route, and were accessed by Suzuki coupling between 2,7-dibromofluorene and 4-ethoxycarbonylphenylboronic acid followed by derivatization. The extended ligand with an unsubstituted fluorene core proved susceptible to oxidation, so we focused on the extended fluorenone ligand **7** and α,α-dimethylfluorene ligand **8**. Finally, control ligands **9a–c**, which contain only a single salicylhydrazone motif, were synthesized to evaluate the selectivity of the coordinating motif itself, without any supramolecular considerations.

Ligands **1–8** are all capable of multicomponent assembly with Ln^{3+} ions. The assembly properties of ligands **5**,[14] **6**,[11] and **9a**[11] are known and the complexes were previously characterized. Upon treatment with a strong base (e.g., NaH) and variable Ln^{3+} salts, three salicylhydrazone motifs form a complex with a single metal ion. The V-shaped ligand **6** forms an M_2L_3 helicate complex (e.g. $[6_3La_2]^{6-}$), while the rigid, linear ligand **5** is incapable of this and an M_4L_6 assembly is formed in this case.[14] Obviously, ligand **9a** can only complex one metal ion and forms an $[ML_3]^{3-}$ complex. Ligands **1–4**, **7**, and **8** show a slightly V-shaped ligand geometry and M_2L_3 assembly would be expected, consistent with the vast majority of self-assembled rare-earth-metal complexes.[12]

The initial tests of the sorting properties were the simplest, and involved geometrically distinct ligands **1**, **5**,

and **6**. After treatment with sodium hydride and isolation as the tetrasodium salts, pairs of these ligands were combined with Ln^{3+} salts in [D$_6$]DMSO at a total M:L ratio of 2:3 (i.e. 1 molar equivalent Ln^{3+}, 0.75 equivalents of each ligand), and the resulting assemblies were analyzed by ^{1}H NMR spectroscopy (Figure 2). While complexes could be assembled from
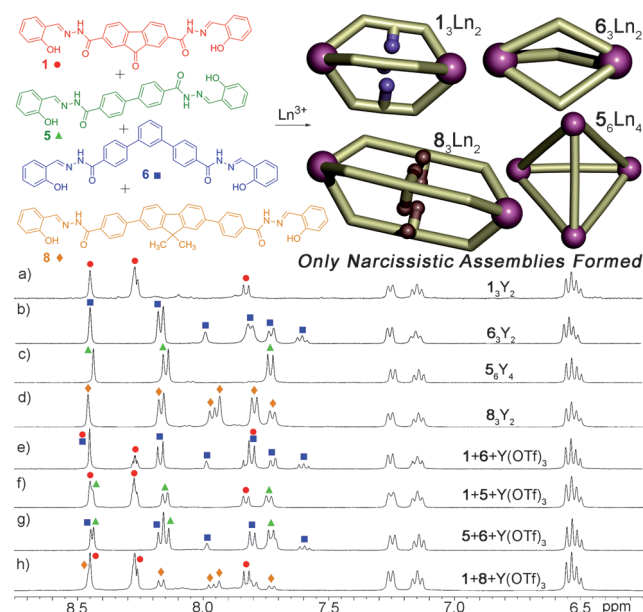
Figure 2. Narcissistic self-sorting in ligands of different geometry: a) $[1_3Y_2]^{6-}$; b) $[6_3Y_2]^{6-}$; c) $[5_6Y_4]^{12-}$; d) $[8_3Y_2]^{6-}$; e) **1**+**6**+Y(OTf)$_3$; f) **1**+**5**+Y(OTf)$_3$; g) **5**+**6**+Y(OTf)$_3$; h) **1**+**8**+Y(OTf)$_3$ (400 MHz, [D$_6$]DMSO, 298 K).

a range of lanthanide salts, assembly was primarily studied with diamagnetic La^{3+} and lanthanide surrogate Y^{3+} for ease of NMR analysis. These metals represent variation in the lanthanide series (Y is similar in size to Ho) and should provide representative data for both larger and smaller metals.[11] The initial ligand combinations test the self-sorting behavior of species with relatively large changes in coordination angle. Even though the coordinators are identical, one might expect narcissistic sorting to be easily achieved. The lengths of the ligands are obviously different, but not vastly so. Modeling indicates that the M–M distances in $[1_3Y_2]^{6-}$, $[6_3Y_2]^{6-}$, and $[5_6Y_4]^{12-}$ are 14.41 Å, 16.44 Å, and 16.61 Å, respectively.

As expected, only single species were observed in the ^{1}H NMR spectra of the various combinations of **1**, **5**, **6**, and Y(OTf)$_3$. For example, ^{1}H NMR analysis of the $[(1+6)_3Y_2]^{6-}$ mixture only showed resonances corresponding to those of $[1_3Y_2]^{6-}$ and $[6_3Y_2]^{6-}$, and this selectivity was also observed for the other combinations (Figure 2). Each mixture contained signals for the homocomplexes alone. While some resonances overlap (most notably from the protons in *ortho* position of the salicyl groups), the NMR spectra were quite distinguishable, and no resonance broadening or extra resonances for heterocomplexes were observed. The selectivity appeared to be both kinetically and thermodynamically favorable. The

homocomplexes were formed immediately and no equilibration to other species occurred. When the samples were heated for up to 5 days at 60 °C, no other products were observed. It has been previously shown that stirring for 6–12 h at ambient temperature gave complete exchange between different lanthanide ions in M_2L_3 complexes of **6**.[11] Additionally, ESI-MS analysis in positive mode confirmed the stoichiometry of the process. Only M^+ ions of the M_2L_3 complexes were observed for ligands **1–4** and **7** (see the Supporting Information for spectra). The observed M^+ ions were assigned as the $[M_2L_3\text{-}4H]^{2+}$ ion in each case. Other fragments were observed, corresponding to the free ligand and $[M_2L_2\text{-}4H]^{2+}$ species. MS/MS analysis of the $[M_2L_3\text{-}4H]^{2+}$ ion showed these ions originated from fragmentations of the M_2L_3 complex.

Ligands **1**, **5**, and **6** are quite different in both length and geometry, so this selectivity is encouraging, but not surprising. A more challenging test is the combination of ligands **1** and **7**/**8**. The fluorene cores are rigid, and so the introduction of additional phenyl groups between the core and the salicylhydrazone coordinator confers a change in the length, but not in the angle (the M–M distance in $[\mathbf{8}_3Y_2]^{6-}$ is 23.08 Å, by modeling). As can be seen in Figure 2h (and in the Supporting Information), combination of the short and long fluorenone ligands **1** and **8** with $Y(OTf)_3$ led to the observation of two sets of signals in the ^1H NMR spectrum, corresponding to self-sorted homocomplexes $[\mathbf{1}_3Y_2]^{6-}$ and $[\mathbf{8}_3Y_2]^{6-}$. Even though the ligands vary only in length, no mixing is observed.

These results are also encouraging, but hardly unprecedented, as they corroborate results seen with more flexible bis(catecholate) and bipyridyl ligands.[6] The most exciting possibility would be to achieve sorting between ligands of identical coordination angle, length, and coordinating motif. The fluorenone cores provided this. By simple alteration of the central carbonyl group, very subtle changes can be made to the ligands without appreciably altering the coordination geometry or the length. Fluorenone-derived ligands **1–4** are of the same size and shape and contain the same coordination motif, and they differ only in their endohedral functionality. The sorting experiments were performed as before. Ligands **1–4** were treated with sodium hydride, isolated and combined with $Y(OTf)_3$, and the results are shown in Figure 3. Remarkably, complete narcissistic self-sorting was observed in all cases when mixing these highly similar ligands.

Complete discrimination was observed immediately after the addition of the metal ions to the mixture of the ligands. Spectra were acquired periodically, and no evidence of mixed complexes was observed, even after several days. Figure 3 shows the ^1H NMR spectra of various combinations of endohedrally derivatized fluorenone ligands **1–4**. As with the other mixing experiments, only single species were observed in the ^1H NMR spectra, and can be identified by comparison with the spectra of the individual complexes (Figure 3b–e). While ligands **1–4** have the same length, shape, and coordination motif, there are size differences in the endohedral functionality. Ligands **1** and **2** are symmetrical, and display simple spectra upon complexation. The oxime ligands **3** and **4** are desymmetrized and display more complex spectral patterns, but the species are obviously assignable and present in the assembled complexes (Figure 4g–i). The size of
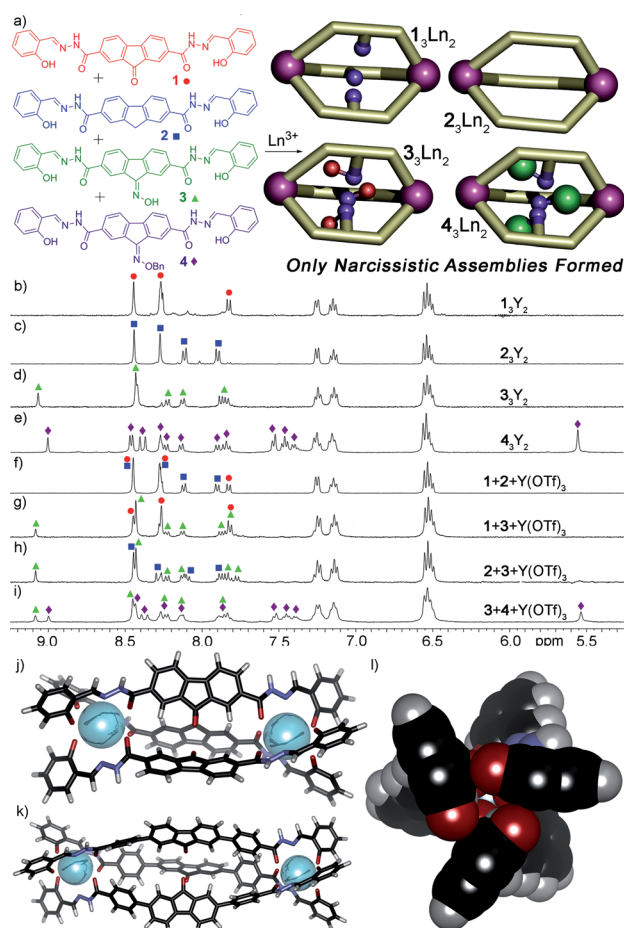
Figure 3. Narcissistic self-sorting between ligands of identical angle and length, differing only in endohedral functionality: a) cartoon of narcissistic self-sorting; b) $[\mathbf{1}_3Y_2]^{6-}$; c) $[\mathbf{2}_3Y_2]^{6-}$; d) $[\mathbf{3}_3Y_2]^{6-}$; e) $[\mathbf{4}_3Y_2]^{6-}$; f) $\mathbf{1}+\mathbf{2}+Y(OTf)_3$; g) $\mathbf{1}+\mathbf{3}+Y(OTf)_3$; h) $\mathbf{2}+\mathbf{3}+Y(OTf)_3$; i) $\mathbf{3}+\mathbf{4}+Y(OTf)_3$ (400 MHz, $[D_6]DMSO$, 298 K). Minimized structures of j) $[\mathbf{1}_3Y_2]^{6-}$; k) $[\mathbf{7}_3Y_2]^{6-}$; l) space-filling representation of the central core of $[\mathbf{1}_3Y_2]^{6-}$. (SPARTAN, AM1 force field).

the internal groups has no effect on the self-assembly. Even though benzyl oxime **4** is significantly larger than the other internal groups, the bulk of the benzyl group can be oriented away from the central cavity, thus allowing self-assembly.[9b] Of particular note in the ^1H NMR spectra are the singlets near 9.0 and 5.5 ppm (Figure 3d,e,i). If mixed complexes were forming, multiplicity would be observed in these resonances.[9]
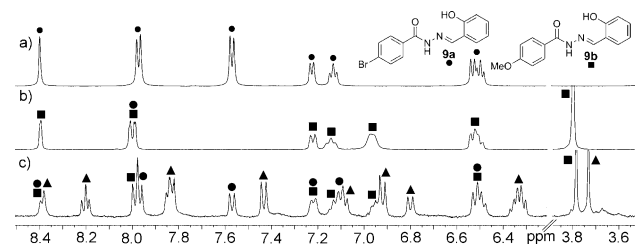
Figure 4. Heteroleptic complex formation with singly coordinating control ligands: a) $[\mathbf{9a}_3Y]^{3-}$; b) $[\mathbf{9b}_3Y]^{3-}$; c) $[(\mathbf{9a})_x(\mathbf{9b})_yY]^{3-}$ (400 MHz, $[D_6]DMSO$, 298 K).

While there is a large difference between **2/4** and **3/4** with regard to the size of the internal functional groups, the sorting selectivity is remarkable. Similar variation in internal steric hindrance in self-assembled Pd–pyridine and Fe–iminopyridine complexes shows little control of sorting behavior, and no narcissistic sorting whatsoever.[9] Most interestingly, sorting was also observed with combinations of ligands that are much more similar in size, such as fluorenone **1** and oxime **3** (Figure 3g). The most striking result is the combination of fluorenone **1** and fluorene **2** (Figure 3f), with which narcissistic self-sorting is observed in ligands that differ in the addition of only one atom. As with the previously described experiments, the samples from Figure 3 were exposed to equilibrating conditions[11] in an attempt to induce exchange, but no change in the composition was observed by ^{1}H NMR spectroscopy. MS analysis was consistent with these results. No ions for heterocomplexes were observed when the solutions from mixing experiments were subjected to ESI analysis. Unfortunately, the low ionization efficiency of the complexes led to preferential ionization of single species in the mixture, and accurate MS analysis of the mixtures was not possible, even under a variety of ionization conditions.

The extended fluorene-based ligands **7** and **8** were also tested for their sorting behavior, and the results were identical to the shorter fluorene-based ligands **1**–**4** (see the Supporting Information for spectra). Combination of deprotonated **7**$^{4-}$ and **8**$^{4-}$ with Y(OTf) gave rise to only self-sorted homocomplexes $[\mathbf{7}_3Y_2]^{6-}$ and $[\mathbf{8}_3Y_2]^{6-}$, with no new signals representing the formation of mixed complexes. These larger assemblies were substantially less soluble than those from **1**–**4**, and far more challenging to characterize by MS methods, so we limited our study to the **7**/**8** combination alone.

One obvious question is whether this is a supramolecular effect, or a quirk of the coordinating ligand itself. To test this, we applied control ligands **9a**–**c**, which contain single salicylhydrazone coordinating motifs. Ligands **9a**–**c** have very slight electronic differences because of the substituent in *para* position of the aryl ring (Br, OMe, and NO$_2$ for **9a**, **b**, and **c** respectively) and can be easily distinguished in the ^{1}H NMR spectra. Figure 4 shows the results for $(\mathbf{9a})_x(\mathbf{9b})_y$Y. Upon immediate addition of **9a**$^{2-}$ and **9b**$^{2-}$ to a solution of Y(OTf)$_3$ in [D$_6$]DMSO, a single species was initially observed, but it was quickly replaced by a mixture of different species. Complete formation of heteroleptic complexes was ensured by heating at 60°C overnight. As can be seen in Figure 4, while resonances that correspond to homoleptic complexes $[(\mathbf{9b})_3Y]^{3-}$ and $[(\mathbf{9a})_3Y]^{3-}$ are observed, a statistical mixture of species is present. The new resonances in the ^{1}H NMR spectrum (labeled with triangles) do not correspond to either of the component complexes, and can be assigned as the $[(\mathbf{9a})_2(\mathbf{9b})_1Y]^{3-}$ or $[(\mathbf{9a})_1(\mathbf{9b})_2Y]^{3-}$ heterocomplexes. ESI-MS analysis confirmed the ML$_3$ stoichiometry of this process, and the presence of heteroleptic complexes. The same results were obtained when the other control ligands were mixed (see the Supporting Information for other spectra). Small variations in donor ability of singly coordinating ligands are not sufficient to allow self-sorting, and it can be deduced that the supramolecular nature of the M$_2$L$_3$ assembly is essential for successful sorting.

This level of self-sorting is extremely surprising, and the explanation is unclear. An analysis of the minimized molecular structures of the complexes does shed some light on the process. The almost linear nature of the fluorene-based cores forms an M$_2$L$_3$ assembly with virtually no internal cavity at all. Figure 3l shows a space-filling model of the central core of $[\mathbf{1}_3Y_2]^{6-}$, which shows the close-packed nature of the C=O groups. The slight kink in the ligand ensures that the pendant functions cannot orient "outward", and so the central groups are forced into close proximity upon assembly. The assembly is therefore sensitive to the steric environment inside the cavity, and close packing of functional groups appears to disfavor mismatches. The interaction is such that even small changes in the size of internal groups are "felt" by the other ligands in the assembly, promoting the narcissistic sorting that is seen. The control ligands **9a**–**c** cannot exploit this effect, and so heteroleptic complexes are formed that show minimal narcissistic self-sorting.

In conclusion, we have shown that highly selective narcissistic self-sorting is possible in the formation of rigid M$_2$L$_3$ rare-earth helicates with identical salicylhydrazone coordinating motifs. Variations in ligand length and coordination geometry are easily discriminated, as might be expected. However, when ligands derived from fluorenone cores are applied, complete narcissistic self-sorting between species that vary only by one atom, which is not involved in the coordination process, is possible. The sorting process is a supramolecular effect, that is, the application of singly coordinating control ligands leads to heteroleptic complexes with little discrimination. The ability of self-assembled complexes to show self-sorting between ligands that are so similar in structure is reminiscent of the selectivity observed in nature. Further investigations of this phenomenon in the formation of selective photoactive lanthanide assemblies are underway in our laboratory.

[1] a) S. Ghosh, A. Wu, J. C. Fettinger, P. Y. Zavalij, L. Isaacs, *J. Org. Chem.* **2008**, *73*, 5915; b) Q. Shi, K.-E. Bergquist, R. Huo, J. Li, M. Lund, R. Vácha, A. Sundin, E. Butkus, E. Orentas, K. Wärnmark, *J. Am. Chem. Soc.* **2013**, *135*, 15263.

[2] a) A. Wu, L. Isaacs, *J. Am. Chem. Soc.* **2003**, *125*, 4831; b) K. Acharyya, S. Mukherjee, P. S. Mukherjee, *J. Am. Chem. Soc.* **2013**, *135*, 554; c) A. S. Singh, S.-S. Sun, *Chem. Commun.* **2012**, *48*, 7392; d) A. Jiménez, R. A. Bilbeisi, T. A. Ronson, S. Zarra, C. Woodhead, J. R. Nitschke, *Angew. Chem. Int. Ed.* **2014**, *53*, 4556; *Angew. Chem.* **2014**, *126*, 4644; e) W. Wang, Y. Zhang, B. Sun, L.-J. Chen, X.-D. Xu, M. Wang, X. Li, Y. Yu, W. Jiang, H.-B. Yang, *Chem. Sci.* **2014**, *5*, 4554; f) J.-F. Ayme, J. E. Beves, C. J. Campbell, D. A. Leigh, *Angew. Chem. Int. Ed.* **2014**, *53*, 7823; *Angew. Chem.* **2014**, *126*, 7957.

[3] a) M. Yamanaka, Y. Yamada, Y. Sei, K. Yamaguchi, K. Kobayashi, *J. Am. Chem. Soc.* **2006**, *128*, 1531; b) P. Mukhopadhyay, A. Wu, L. Isaacs, *J. Org. Chem.* **2004**, *69*, 6157; c) Q.-F. Sun, S. Sato, M. Fujita, *Angew. Chem. Int. Ed.* **2014**, *53*, 13510; *Angew. Chem.* **2014**, *126*, 13728; d) M. Lal Saha, M. Schmittel, *J. Am.*

Chem. Soc. **2013**, *135*, 17743; e) M. M. J. Smulders, A. Jiménez, J. R. Nitschke, *Angew. Chem. Int. Ed.* **2012**, *51*, 6681; *Angew. Chem.* **2012**, *124*, 6785; f) M. L. Saha, S. Pramanik, M. Schmittel, *Chem. Commun.* **2012**, *48*, 9459; g) L.-P. Cao, J.-G. Wang, J.-Y. Ding, A.-X. Wu, L. Isaacs, *Chem. Commun.* **2011**, *47*, 8548; h) M. L. Pellizzaro, K. A. Houton, A. J. Wilson, *Chem. Sci.* **2013**, *4*, 1825.

[4] a) M. M. Safont-Sempere, G. Fernández, F. Würther, *Chem. Rev.* **2011**, *111*, 5784; b) M. D. Ward, P. R. Raithby, *Chem. Soc. Rev.* **2013**, *42*, 1619; c) M. L. Saha, M. Schmittel, *Org. Biomol. Chem.* **2012**, *10*, 4651; d) M. L. Saha, S. De, S. Pramanik, M. Schmittel, *Chem. Soc. Rev.* **2013**, *42*, 6860; e) D. Schultz, J. R. Nitschke, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 11191; f) V. E. Campbell, X. de Hatten, N. Delsuc, B. Kauffmann, I. Huc, J. R. Nitschke, *Nat. Chem.* **2010**, *2*, 684; g) J. R. Nitschke, J.-M. Lehn, *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 11970.

[5] a) D. Ajami, J.-L. Hou, T. J. Dale, E.; Barrett, J. Rebek, Jr., *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 10430; Barrett, J. Rebek, Jr., *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 10430; b) A. Lledó, S. Kamioka, A. C. Sather, J. Rebek, Jr., *Angew. Chem. Int. Ed.* **2011**, *50*, 1299; *Angew. Chem.* **2011**, *123*, 1335.

[6] a) R. Krämer, J.-M. Lehn, A. Marquis-Rigault, *Proc. Natl. Acad. Sci. USA* **1993**, *90*, 5394; b) D. L. Caulder, K. N. Raymond, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1440; *Angew. Chem.* **1997**, *109*, 1508; c) M. Albrecht, M. Schneider, H. Röttele, *Angew. Chem. Int. Ed.* **1999**, *38*, 557; *Angew. Chem.* **1999**, *111*, 512.

[7] a) Q.-F. Sun, J. Iwasa, D. Ogawa, Y. Ishido, S. Sato, T. Ozeki, Y. Sei, K. Yamaguchi, M. Fujita, *Science* **2010**, *328*, 1144; b) R. Pinalli, V. Cristini, V. Sottili, S. Geremia, M. Campagnolo, A. Caneschi, E. Dalcanale, *J. Am. Chem. Soc.* **2004**, *126*, 6516; c) D. Samanta, P. S. Mukherjee, *Chem. Eur. J.* **2014**, *20*, 12483; d) J. J. Henkelis, J. Fisher, S. L. Warriner, M. J. Hardie, *Chem. Eur. J.* **2014**, *20*, 4117.

[8] a) C. Gütz, R. Hovorka, G. Schnakenburg, A. Lützen, *Chem. Eur. J.* **2013**, *19*, 10890; b) S. W. Sisco, J. S. Moore, *Chem. Sci.* **2014**, *5*, 81; c) T. Kamada, N. Aratani, T. Ikeda, N. Shibata, Y. Higuchi, A. Wakamiya, S. Yamaguchi, K. S. Kim, Z. S. Yoon, K. Dongho, A. Osuka, *J. Am. Chem. Soc.* **2006**, *128*, 7670; d) O. Gidron, M.-O. Ebert, N. Trapp, F. Diederich, *Angew. Chem. Int. Ed.* **2014**, *53*, 13614; *Angew. Chem.* **2014**, *126*, 13833.

[9] a) A. M. Johnson, R. J. Hooley, *Inorg. Chem.* **2011**, *50*, 4671; b) M. C. Young, A. M. Johnson, A. S. Gamboa, R. J. Hooley, *Chem. Commun.* **2013**, *49*, 1627.

[10] a) A. M. Johnson, O. Moshe, A. S. Gamboa, B. W. Langloss, J. F. K. Limtiaco, C. K. Larive, R. J. Hooley, *Inorg. Chem.* **2011**, *50*, 9430; b) M. Frank, L. Krause, R. Herbst-Irmer, D. Stalke, G. H. Clever, *Dalton Trans.* **2014**, *43*, 4587; c) R. A. Bilbeisi, J. K. Clegg, R. Elgrishi, X. de Hatten, M. Devillard, B. Breiner, P. Mal, J. R. Nitschke, *J. Am. Chem. Soc.* **2012**, *134*, 5110.

[11] A. M. Johnson, M. C. Young, X. Zhang, R. R. Julian, R. J. Hooley, *J. Am. Chem. Soc.* **2013**, *135*, 17723.

[12] a) C. Piguet, G. Bernardinelli, G. Hopfgartners, *Chem. Rev.* **1997**, *97*, 2005; b) J. Shi, Y. Hou, W. Chu, X. Shi, H. Gu, B. Wang, Z. Sun, *Inorg. Chem.* **2013**, *52*, 5013; c) P. E. Ryan, L. Guénée, C. Piguet, *Dalton Trans.* **2013**, *42*, 11047.

[13] a) T. B. Jensen, R. Scopelliti, J.-C. G. Bünzli, *Dalton Trans.* **2008**, 1027; b) T. B. Jensen, R. Scopelliti, J.-C. G. Bünzli, *Chem. Eur. J.* **2007**, *13*, 8404; c) L. Aboshyan-Sorgho, H. Nozary, A. Aebischer, J.-C. G. Bünzli, P.-Y. Morgantini, K. R. Kittilstved, *J. Am. Chem. Soc.* **2012**, *134*, 12675; d) M. Albrecht, O. Osetska, J.-C. G. Bünzli, F. Gumy, R. Fröhlich, *Chem. Eur. J.* **2009**, *15*, 8791; e) T. Riis-Johannessen, G. Bernardinelli, Y. Filinchuk, S. Clifford, N. D. Favera, C. Piguet, *Inorg. Chem.* **2009**, *48*, 5512.

[14] a) Y. Liu, Z. Lin, C. He, L. Zhao, C. Duan, *Dalton Trans.* **2010**, *39*, 11122; b) X. Zhu, C. He, D. Dong, Y. Liu, C. Duan, *Dalton Trans.* **2010**, *39*, 10051.

[15] T. Schulte, M. Krick, C. I. Asche, S. Freye, G. H. Clever, *RSC Adv.* **2014**, *4*, 29724.