Supramolecular Chemistry

Deutsche Ausgabe: DOI: 10.1002/ange.201411985
Internationale Ausgabe: DOI: 10.1002/anie.201411985

Guest-Induced Transformation of a Porphyrin-Edged $Fe^{II}_4L_6$ Capsule into a $Cu^{I}Fe^{II}_2L_4$ Fullerene Receptor**

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Abstract: *The combination of a bent diamino(nickel(II) porphyrin) with 2-formylpyridine and Fe^{II} yielded an $Fe^{II}_4L_6$ cage. Upon treatment with the fullerenes C_{60} or C_{70}, this cage was found to transform into a new host–guest complex incorporating three Fe^{II} centers and four porphyrin ligands, in an arrangement that is hypothesized to maximize π interactions between the porphyrin units of the host and the fullerene guest bound within its central cavity. The new complex shows coordinative unsaturation at one of the Fe^{II} centers as the result of the incommensurate metal-to-ligand ratio, which enabled the preparation of a heterometallic cone-shaped $Cu^{I}Fe^{II}_2L_4$ adduct of C_{60} or C_{70}.*

Coordination-driven self-assembly has proven to be a useful tool in the preparation of intricate and functional chemical species, the structural complexity of which would be difficult to achieve by using conventional covalent chemistry.[1] Of particular recent interest are the three-dimensional coordination cages, which possess internal cavities suitable for guest binding.[2] Metal–organic cages may be designed to incorporate ligands that are not merely inert scaffolds, but which contain functionality that can interact with guest molecules selectively.[3] This approach has been used to design cage assemblies that bind specific guests, in some cases altering their reactivity.[4] Metalloporphyrin-based subunits for cages are particularly attractive owing to interactions between prospective guests and the large aromatic faces of the porphyrins.[5]

In certain cases, the same system of molecular building blocks can form different metal–organic structures under different conditions.[6] For example, systems containing soft metal ions with flexible coordination spheres, such as Ag^{I} and Hg^{II}, undergo structural rearrangement when prompted by a change in stoichiometry,[7] and anionic guests can induce the reconfiguration of a dynamic library of components into different polyhedral architectures.[8]

Herein, we show how maximization of π interactions between the bent porphyrinato nickel(II) groups of a $Fe^{II}_4L_6$ host and its fullerene guest causes the host to reconstitute into a new kind of $Fe^{II}_3L_4$ receptor for the fullerenes C_{60} and C_{70}. Furthermore, we demonstrate that the delicate balance of orthogonal supramolecular interactions in this system can lead to the expression of a heterometallic host–guest ensemble. These complexes are built from a saddled Ni^{II} metalloporphyrin subcomponent **1** that forms tetrahedral $Fe^{II}_4L_6$ assembly **2** when combined with Fe^{II} and 2-formylpyridine (Scheme 1). On addition of C_{60} or C_{70}, this structure reconfigures into a $Fe^{II}_3L_4$ cone-shaped host–guest complex $C_{60/70}$⊂**3**. This species can be modified through the incorporation of additional ancillary ligands to form heteroleptic species $C_{60/70}$⊂**3**(phen). Through these observations, we were also able to predict and observe the formation of heterometallic host–guest species $C_{60/70}$⊂**4** that incorporates both Cu^{I} and Fe^{II} metal centers into the same assembly.

The reaction of the nickel-porphyrin-containing dianiline **1** (6 equiv), 2-formylpyridine (12 equiv), and iron(II) triflate (4 equiv) in acetonitrile yielded $Fe^{II}_4L_6$ assembly **2**, as confirmed by NMR spectroscopy (Figure S5–S8 in the Supporting Information) and ESI-MS (Figures S9, S10). The ^{1}H NMR spectrum of **2** was consistent with the presence of a mixture of all three possible diastereomers, each with a distinct symmetry: the homochiral *T* (ΔΔΔΔ/ΛΛΛΛ), heterochiral C_3 (ΔΔΔΛ/ΛΛΛΔ), and achiral S_4 (ΛΛΔΔ) diastereomers, as has been observed in analogous M_4L_6 assemblies.[9]

The crystal structure of **2** confirmed a tetrahedral geometry, with one bis-bidentate bridging ligand lying along each of the six edges of the Fe_4 tetrahedron (Figure 1).[10] Only the *T*-symmetric diastereomer of **2** was observed in the crystal lattice, and both enantiomers (ΔΔΔΔ/ΛΛΛΛ) are present in the unit cell. The metal–metal separation between neighboring Fe^{II} centers is 20.040(3) Å.

The crystal structure of **2** also highlights the saddled nature of the porphyrin ligands, with each possessing a 151° bend (measured as the N_{imine}-Ni-N_{imine} angle). Whereas other crystal structures of $Fe^{II}_4L_6$ tetrahedra have ligands that lie flat along the tetrahedron's edges,[11] the edges of **2** clearly

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[**] This work was supported by the UK Engineering and Physical Sciences Research Council (EPSRC). We thank Diamond Light Source (UK) for synchrotron beam time on I19 (MT8464) and Chris Sporikou for preparing precursor molecules.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201411985.

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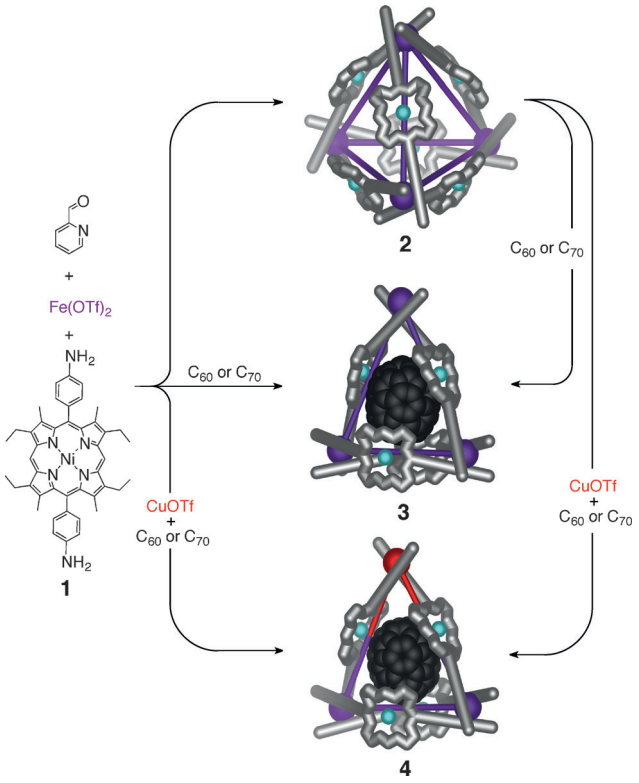

Scheme 1. Subcomponent self-assembly of 2-formylpyridine, iron(II) triflate, and the Ni-porphyrin-containing dianiline **1** to yield $Fe^{II}_4L_6$ tetrahedral assembly **2** in the absence of a templating guest. On the addition of different fullerenes, $Fe^{II}_3L_4$ cone-like host–guest complex $C_{60/70}\subset$**3** is obtained. Simultaneous addition of fullerenes and Cu^{I} yielded heterometallic host–guest complex $C_{60/70}\subset$**4**. L, gray; Fe, purple; Cu, red; Ni, light blue.

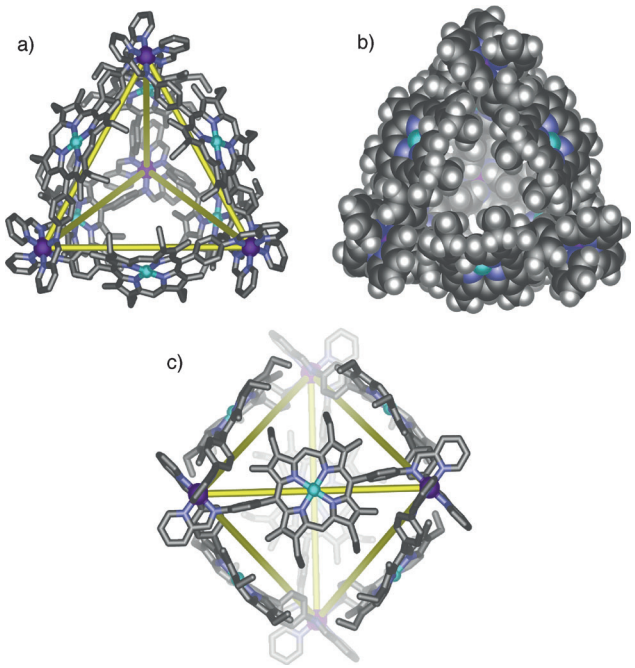

Figure 1. Crystal structure of **2**. a) View through one face of the tetrahedral assembly, b) space-filling representation, and c) view down one of the edges. Hydrogen atoms, counterions, and solvent molecules of crystallization are omitted for clarity. Connections between the Fe^{II} centers (yellow lines) are included in (a) and (c) to highlight the tetrahedral framework and saddled nature of the Ni porphyrin ligands. C, grey; N, blue; Fe, purple; H, white; Ni light blue.

bow outwards (Figure 1). In other cases involving bent ditopic ligands, helicates are observed.[12] We infer that in the present case, the steric demands imposed by the porphyrins preclude helicate formation. The bending of the ligands increases the effective size of the central cavity (estimated to be 2230 Å^3 by using VOIDOO,[13] Figure S35). The saddled conformation of the porphyrin unit is also observed in the crystal structure of **1** (Figures S33, S34).

Upon treatment with excess C_{70} (5 equiv), **2** was observed to undergo a remarkable transformation into the C_{70} adduct of the new host $C_{70}\subset$**3** (Scheme 1). ESI-MS analysis of $C_{70}\subset$**3** indicated an incommensurate metal-to-ligand ratio of $Fe^{II}_3L_4$. The unsaturated Fe^{II} center within $C_{70}\subset$**3**, bound by only two bis-bidendate pyridylimine ligands, was observed to bind further ligands by ESI-MS. Signals corresponding to $[C_{70}\subset\mathbf{3}]\cdot X_2$ were detected, where X = MeCN, OTf^-, or Cl^- (Figures S13, S14). Chloride is inferred to be present as an impurity in $Fe(OTf)_2$ or present in the mass spectrometer.[2c,8a]

The addition of 1,10-phenanthroline (phen) to a solution of $C_{70}\subset$**3** gave a product with an ESI-MS (Figures S16, S17) spectrum consistent with complete conversion into $C_{70}\subset$**3**-(phen). The ^{1}H NMR spectrum also showed changes consistent with binding of the chelating phen ligand to the unsaturated Fe^{II} center in $C_{70}\subset$**3**, to yield a new product of lower symmetry (Figure S15). When C_{60} was added to a solution of **2**, $C_{60}\subset$**3** was obtained in an analogous fashion, however, the reaction did not proceed as cleanly as in the case of C_{70}. Complex NMR and ESI spectra were observed, which are attributed to a mixture of products. We infer that the oblong geometry of C_{70} may fit the cavity of **3** better than spherical C_{60}.[14] Subsequent addition of 1,10-phenanthroline to this mixture, however, gave a product with an ESI-MS spectrum consistent with $C_{60}\subset$**3**(phen) (Figures S19, S20). The complex ^{1}H NMR spectrum of this product (Figure S18) did not contain resonances from **2** or its subcomponents.

The bent geometry of the nickel(II) porphyrins within the framework of **2** thus appears to destabilize this framework with respect to that of **3**. Models of $C_{70}\subset$**3** (Figure S36) reveal no features that would be indicative of strain, with the porphyrins bowed outwards in a similar fashion to that observed in the crystal structure of **2** (Figure 1) to create the internal cavity necessary to house C_{70}. Fullerene encapsulation thus appears to provide enough of an energetic driving force, in the form of more favorable π interactions between the porphyrin units of the host and the guest,[5c,f,15] to drive the transformation of **2** into **3**. Geometric factors and the strength of guest binding thus tip the balance against the tendency for iron(II) to maintain coordinative saturation.[16] We anticipate that **3**, which comprises fewer components, would also be entropically favored with respect to **2**.

The ^{1}H NMR spectrum of $C_{70}\subset$**3** prepared from **2** showed multiple new signals and none of the resonances corresponding to **2**. The ^{13}C NMR spectrum showed resonances in the range of 140–150 ppm, thus confirming the presence of C_{70}

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(Figure S11).[17] The change in stoichiometry from **2** to C_{70}⊂**3** also led to the release of excess ligand, which was observed to hydrolyze to the free subcomponents: free 2-formylpyridine was observed by ^{1}H NMR upon the formation of C_{70}⊂**3** from **2** and the excess **1**, being insoluble in MeCN, precipitated from solution. The complex stereochemistry of C_{70}⊂**3** and its derivatives (discussed below in the context of $C_{60/70}$⊂**4**) precluded an unambiguous assignment of its NMR spectra, and our attempts to grow crystals of $C_{60/70}$⊂**3** and its derivatives were unsuccessful. We thus hypothesize a cone-shaped structure for **3** analogous to that of **4** (see below). Such a structure would be consistent with all of the observed data, although the range of data available precludes structural certainty.

The proposed structure for **3** requires the formation of a single metal center that only binds two bidentate pyridylimine ligands. We thus hypothesized that it would be possible to form an analogous structure in which the coordinatively unsaturated Fe^{II} in $C_{60/70}$⊂**3** is replaced with a tetrahedral Cu^{I} center. In the absence of fullerenes, no reaction was observed between **2** and copper(I) triflate (2 equiv) by NMR and ESI-MS. Following the addition of excess C_{60} (5 equiv), however, ESI-MS analysis showed only signals corresponding to the C_{60} adduct of a new receptor with the formula $Cu^{I}Fe^{II}{}_2L_4$ (complex C_{60}⊂**4**). An analogous complex C_{70}⊂**4** was also prepared through the addition of C_{70}. $C_{60/70}$⊂**4** could also be obtained directly through subcomponent self-assembly from the ligand precursors, metal ions, and fullerene template in the correct ratio.

The ^{1}H NMR spectrum of C_{60}⊂**4** showed new resonances, distinct from those of **2** or **3** (Figure S21). Two sets of ^{1}H signals were observed in a 2:1 ratio. DOSY analysis showed both sets of signals to diffuse at the same rate (Figure S23), which is consistent with the signals corresponding to different diastereomers of C_{60}⊂**4**, rather than to constitutionally distinct species.

The presence of three metal stereocenters in $C_{60/70}$⊂**4** gives rise to $2^3 = 8$ stereochemically distinct species, comprising four diastereomeric pairs of enantiomers (Figure 2b). Two of the diastereomers possess C_2 point symmetry, whereas the other two are asymmetric (C_1). Two-dimensional NMR analyses of C_{60}⊂**4** (Figures S24–S26) gave results consistent with the presence of the two C_2-symmetric diastereomers of C_{60}⊂**4** but not the asymmetric diastereomers, which would have given rise to many more NMR signals. Models of the different diastereomers of C_{60}⊂**4** (Figure S37) suggested that the asymmetric diastereomers suffer more strain than their symmetric congeners, thus supporting our inference that they were not formed.

The preparation of $C_{60/70}$⊂**4** thus represents a singular example of guest-binding-driven metal exchange within a complex metal–organic assembly, and illustrates a novel means to generate a heterometallic architecture. This work builds upon prior demonstrations of metal–organic assemblies that incorporate different metal centers.[18] Previous examples of heterometallic ensembles have been obtained by: providing a mixture of hard and soft ligands that bind different metals preferentially,[2d,19] preforming kinetically inert metal–organic building blocks,[20] or using ligands of different denticity.[21] In the case of $C_{60/70}$⊂**4**, Cu^{I} and Fe^{II} are both incorporated into a host–guest complex that possesses a single type of ligand environment. The stability of $C_{60/70}$⊂**4** is highlighted by the observation that it is uniquely expressed from a system capable of producing a library of different complexes, including the homometallic tetrahedron **2**.

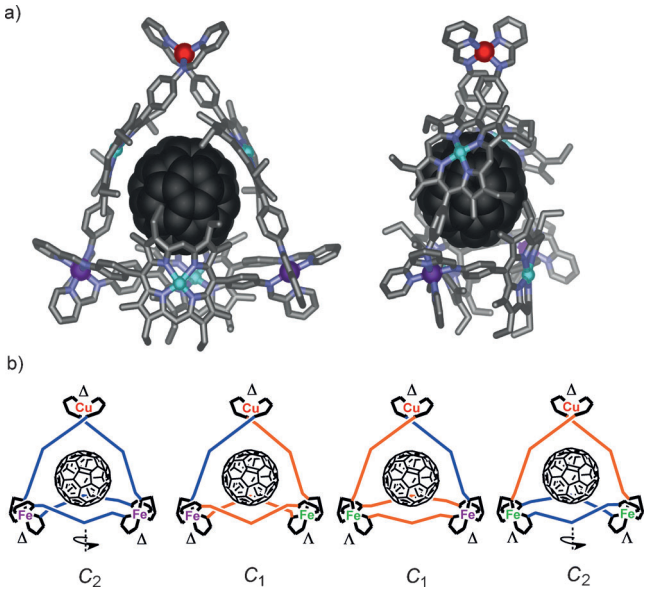

Figure 2. a) Two views of the MM2 model of C_{60}⊂**4**, showing the C_2-symmetric $\Delta_{Cu}\Delta\Delta/\Lambda_{Cu}\Lambda\Lambda$ diastereomer and b) a schematic representation of the different diastereomers of **4**. Purple and green Fe^{II} centers are of opposite chirality. Blue lines represent ligands arranged in an *anti* conformation between metal centers, while orange lines represent ligands arranged in a *syn* conformation between metal centers.

Complexes $C_{60/70}$⊂**3** and $C_{60/70}$⊂**4** thus represent rare examples of heterometallic host–guest species that employ different metal centers arranged in similar ligand environments.[22] They are only accessible through a delicate balance of orthogonal supramolecular interactions and their formation points toward a new approach for achieving structural complexity in supramolecular systems, which would complement existing strategies.[5e,23] Future investigations will focus on utilizing the rich coordination chemistry of different metalloporphyrins in these ensembles to see whether selective guest functionalization might be achieved through the use of metalloporphyrin-based catalysts,[24] or whether the rich axial coordination chemistry of zinc–porphyrin assemblies[25] might be employed to develop receptors that are structurally similar to the ones described herein.

Keywords: coordination chemistry · host–guest chemistry · metal–organic assemblies · self-assembly · supramolecular chemistry

Zitierweise: *Angew. Chem. Int. Ed.* **2015**, *54*, 3988–3992
Angew. Chem. **2015**, *127*, 4060–4064

[1] a) M. Albrecht, *Chem. Rev.* **2001**, *101*, 3457–3497; b) D. Caulder, K. Raymond, *Acc. Chem. Res.* **1999**, *32*, 975–982; c) R. Chakrabarty, P. S. Mukherjee, P. J. Stang, *Chem. Rev.* **2011**,

© 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

111, 6810 – 6918; d) R. S. Forgan, J.-P. Sauvage, J. F. Stoddart, *Chem. Rev.* **2011**, *111*, 5434 – 5464; e) J. E. Beves, B. A. Blight, C. J. Campbell, D. A. Leigh, R. T. McBurney, *Angew. Chem. Int. Ed.* **2011**, *50*, 9260 – 9327; *Angew. Chem.* **2011**, *123*, 9428 – 9499; f) J. E. Beves, C. J. Campbell, D. A. Leigh, R. G. Pritchard, *Angew. Chem. Int. Ed.* **2013**, *52*, 6464 – 6467; *Angew. Chem.* **2013**, *125*, 6592 – 6595; g) D. M. Engelhard, S. Freye, K. Grohe, M. John, G. H. Clever, *Angew. Chem. Int. Ed.* **2012**, *51*, 4747 – 4750; *Angew. Chem.* **2012**, *124*, 4828 – 4832; h) Q.-Q. Wang, V. W. Day, K. Bowman-James, *Chem. Commun.* **2013**, *49*, 8042 – 8044; i) S. Pasquale, S. Sattin, E. C. Escudero-Adán, M. Martínez-Belmonte, J. de Mendoza, *Nat. Commun.* **2012**, *3*, 785; j) G. Zhang, O. Presly, F. White, I. M. Oppel, M. Mastalerz, *Angew. Chem. Int. Ed.* **2014**, *53*, 5126 – 5130; *Angew. Chem.* **2014**, *126*, 5226 – 5230; k) A. D. Faulkner, R. A. Kaner, Q. M. A. Abdallah, G. Clarkson, D. J. Fox, P. Gurnani, S. E. Howson, R. M. Phillips, D. I. Roper, D. H. Simpson, P. Scott, *Nat. Chem.* **2014**, *6*, 1 – 7; l) J. B. Beck, S. J. Rowan, *J. Am. Chem. Soc.* **2003**, *125*, 13922 – 13923.

[2] a) Q.-F. Sun, J. Iwasa, D. Ogawa, Y. Ishido, S. Sato, T. Ozeki, Y. Sei, K. Yamaguchi, M. Fujita, *Science* **2010**, *328*, 1144 – 1147; b) K. Harris, Q.-F. Sun, S. Sato, M. Fujita, *J. Am. Chem. Soc.* **2013**, *135*, 12497 – 12499; c) S. Freye, J. Hey, A. Torras-Galán, D. Stalke, R. Herbst-Irmer, M. John, G. H. Clever, *Angew. Chem. Int. Ed.* **2012**, *51*, 2191 – 2194; *Angew. Chem.* **2012**, *124*, 2233 – 2237; d) M. M. J. Smulders, I. A. Riddell, C. Browne, J. R. Nitschke, *Chem. Soc. Rev.* **2013**, *42*, 1728 – 1754; e) S. Mirtschin, A. Slabon-Turski, R. Scopelliti, A. H. Velders, K. Severin, *J. Am. Chem. Soc.* **2010**, *132*, 14004 – 14005; f) C. Y. Su, Y. P. Cai, C. L. Chen, M. D. Smith, W. Kaim, H. C. zur Loye, *J. Am. Chem. Soc.* **2003**, *125*, 8595 – 8613.

[3] a) 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; b) M. Yoshizawa, J. K. Klosterman, M. Fujita, *Angew. Chem. Int. Ed.* **2009**, *48*, 3418 – 3438; *Angew. Chem.* **2009**, *121*, 3470 – 3490; c) 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; d) C. Gütz, R. Hovorka, C. Klein, Q.-Q. Jiang, C. Bannwarth, M. Engeser, C. Schmuck, W. Assenmacher, W. Mader, F. Topić, K. Rissanen, S. Grimme, A. Lützen, *Angew. Chem. Int. Ed.* **2014**, *53*, 1693 – 1698; *Angew. Chem.* **2014**, *126*, 1719 – 1724; e) C. Gütz, R. Hovorka, G. Schnakenburg, A. Lützen, *Chem. Eur. J.* **2013**, *19*, 10890 – 10894; f) W. J. Ramsay, T. K. Ronson, J. K. Clegg, J. R. Nitschke, *Angew. Chem. Int. Ed.* **2013**, *52*, 13439 – 13443; *Angew. Chem.* **2013**, *125*, 13681 – 13685; g) S. P. Black, A. R. Stefankiewicz, M. M. J. Smulders, D. Sattler, C. A. Schalley, J. R. Nitschke, J. K. M. Sanders, *Angew. Chem. Int. Ed.* **2013**, *52*, 5749 – 5752; *Angew. Chem.* **2013**, *125*, 5861 – 5864.

[4] a) C. J. Hastings, M. D. Pluth, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **2010**, *132*, 6938 – 6940; b) T. Furusawa, M. Kawano, M. Fujita, *Angew. Chem. Int. Ed.* **2007**, *46*, 5717 – 5719; *Angew. Chem.* **2007**, *119*, 5819 – 5821; c) M. D. Pluth, R. G. Bergman, K. N. Raymond, *Acc. Chem. Res.* **2009**, *42*, 1650 – 1659.

[5] a) N. Fujita, K. Biradha, M. Fujita, *Angew. Chem. Int. Ed.* **2001**, *40*, 1718 – 1721; *Angew. Chem.* **2001**, *113*, 1768 – 1771; b) A. K. Bar, S. Mohapatra, E. Zangrando, P. S. Mukherjee, *Chem. Eur. J.* **2012**, *18*, 9571 – 9579; c) T. Nakamura, H. Ube, R. Miyake, M. Shionoya, *J. Am. Chem. Soc.* **2013**, *135*, 18790 – 18793; d) T. Nakamura, H. Ube, M. Shionoya, *Angew. Chem. Int. Ed.* **2013**, *52*, 12096 – 12100; *Angew. Chem.* **2013**, *125*, 12318 – 12322; e) T. Nakamura, H. Ube, M. Shiro, M. Shionoya, *Angew. Chem. Int. Ed.* **2013**, *52*, 720 – 723; *Angew. Chem.* **2013**, *125*, 748 – 751; f) W. Meng, B. Breiner, K. Rissanen, J. D. Thoburn, J. K. Clegg, J. R. Nitschke, *Angew. Chem. Int. Ed.* **2011**, *50*, 3479 – 3483; *Angew. Chem.* **2011**, *123*, 3541 – 3545; g) S. Durot, J. Taesch, V. Heitz, *Chem. Rev.* **2014**, *114*, 8542; h) S. K. Samanta, M. Schmittel, *J. Am. Chem. Soc.* **2013**, *135*, 18794 – 18797; i) S. Pramanik, S. De, M. Schmittel, *Angew. Chem. Int. Ed.* **2014**, *53*, 4709 – 4713; *Angew. Chem.* **2014**, *126*, 4798 – 4803.

[6] a) H. T. Chifotides, I. D. Giles, K. R. Dunbar, *J. Am. Chem. Soc.* **2013**, *135*, 3039 – 3055; b) X.-P. Zhou, J. Liu, S.-Z. Zhan, J.-R. Yang, D. Li, K.-M. Ng, R. W.-Y. Sun, C.-M. Che, *J. Am. Chem. Soc.* **2012**, *134*, 8042 – 8045.

[7] a) N. Kishi, M. Akita, M. Kamiya, S. Hayashi, H.-F. Hsu, M. Yoshizawa, *J. Am. Chem. Soc.* **2013**, *135*, 12976 – 12979; b) S. Hiraoka, K. Harano, M. Shiro, M. Shionoya, *Angew. Chem. Int. Ed.* **2005**, *44*, 2727 – 2731; *Angew. Chem.* **2005**, *117*, 2787 – 2791; c) S. Hiraoka, T. Yi, M. Shiro, M. Shionoya, *J. Am. Chem. Soc.* **2002**, *124*, 14510 – 14511.

[8] a) I. A. Riddell, M. M. J. Smulders, J. K. Clegg, Y. R. Hristova, B. Breiner, J. D. Thoburn, J. R. Nitschke, *Nat. Chem.* **2012**, *4*, 751 – 756; b) I. A. Riddell, Y. R. Hristova, J. K. Clegg, C. S. Wood, B. Breiner, J. R. Nitschke, *J. Am. Chem. Soc.* **2013**, *135*, 2723 – 2733; c) I. A. Riddell, T. K. Ronson, J. K. Clegg, C. S. Wood, R. A. Bilbeisi, J. R. Nitschke, *J. Am. Chem. Soc.* **2014**, *136*, 9491 – 9498.

[9] a) T. Beissel, R. E. Powers, T. N. Parac, K. N. Raymond, *J. Am. Chem. Soc.* **1999**, *121*, 4200 – 4206; b) M. C. Young, L. R. Holloway, A. M. Johnson, R. J. Hooley, *Angew. Chem. Int. Ed.* **2014**, *53*, 9832 – 9836; *Angew. Chem.* **2014**, *126*, 9990 – 9994; c) W. Meng, J. K. Clegg, J. D. Thoburn, J. R. Nitschke, *J. Am. Chem. Soc.* **2011**, *133*, 13652 – 13660.

[10] CCDC 1038794 and 1038795 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] T. K. Ronson, S. Zarra, S. P. Black, J. R. Nitschke, *Chem. Commun.* **2013**, *49*, 2476 – 2490.

[12] a) M. C. Young, A. M. Johnson, R. J. Hooley, *Chem. Commun.* **2014**, *50*, 1378 – 1380; b) M. Han, D. M. Engelhard, G. H. Clever, *Chem. Soc. Rev.* **2014**, *43*, 1848 – 1860; c) D. L. Caulder, K. N. Raymond, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1440 – 1442; *Angew. Chem.* **1997**, *109*, 1508 – 1510.

[13] G. J. Kleywegt, T. A. Jones, *Acta Crystallogr. Sect. D* **1994**, *50*, 178 – 185.

[14] T. K. Ronson, A. B. League, L. Gagliardi, C. J. Cramer, J. R. Nitschke, *J. Am. Chem. Soc.* **2014**, *136*, 15615 – 15624.

[15] a) K. Tashiro, T. Aida, *Chem. Soc. Rev.* **2007**, *36*, 189 – 197; b) K. Mahata, P. D. Frischmann, F. Würthner, *J. Am. Chem. Soc.* **2013**, *135*, 15656 – 15661; c) L. H. Tong, J.-L. Wietor, W. Clegg, P. R. Raithby, S. I. Pascu, J. K. M. Sanders, *Chem. Eur. J.* **2008**, *14*, 3035 – 3044.

[16] V. E. Campbell, X. de Hatten, N. Delsuc, B. Kauffmann, I. Huc, J. R. Nitschke, *Chem. Eur. J.* **2009**, *15*, 6138 – 6142.

[17] A. R. Stefankiewicz, E. Tamanini, G. D. Pantoş, J. K. M. Sanders, *Angew. Chem. Int. Ed.* **2011**, *50*, 5725 – 5728; *Angew. Chem.* **2011**, *123*, 5843 – 5846.

[18] a) C. Dietrich-Buchecker, B. Colasson, D. Jouvenot, J. P. Sauvage, *Chem. Eur. J.* **2005**, *11*, 4374 – 4386; b) R. Maity, C. Schulte to Brinke, F. E. Hahn, *Dalton Trans.* **2013**, *42*, 12857 – 12860.

[19] a) M. B. Duriska, S. M. Neville, J. Lu, S. S. Iremonger, J. F. Boas, C. J. Kepert, S. R. Batten, *Angew. Chem. Int. Ed.* **2009**, *48*, 8919 – 8922; *Angew. Chem.* **2009**, *121*, 9081 – 9084; b) K. Li, L.-Y. Zhang, C. Yan, S.-C. Wei, M. Pan, L. Zhang, C.-Y. Su, *J. Am. Chem. Soc.* **2014**, *136*, 4456 – 4459.

[20] A. J. Metherell, W. Cullen, A. Stephenson, C. A. Hunter, M. D. Ward, *Dalton Trans.* **2014**, *43*, 71 – 84.

[21] M. M. J. Smulders, A. Jiménez, J. R. Nitschke, *Angew. Chem. Int. Ed.* **2012**, *51*, 6681 – 6685; *Angew. Chem.* **2012**, *124*, 6785 – 6789.

[22] H. Fenton, I. S. Tidmarsh, M. D. Ward, *Dalton Trans.* **2009**, 4199 – 4207.

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[23] a) Z. Liu, M. Frasconi, J. Lei, Z. J. Brown, Z. Zhu, D. Cao, J. Iehl, G. Liu, A. C. Fahrenbach, Y. Y. Botros, O. K. Farha, J. T. Hupp, C. A. Mirkin, J. F. Stoddart, *Nat. Commun.* **2013**, *4*, 1855; b) C. G. Oliveri, S. T. Nguyen, C. A. Mirkin, *Inorg. Chem.* **2008**, *47*, 2755 – 2763; c) W. Jiang, J. Rebek, *J. Am. Chem. Soc.* **2012**, *134*, 17498 – 17501.

[24] a) M. Kuil, T. Soltner, P. W. N. M. van Leeuwen, J. N. H. Reek, *J. Am. Chem. Soc.* **2006**, *128*, 11344 – 11345; b) T. S. Koblenz, J. Wassenaar, J. N. H. Reek, *Chem. Soc. Rev.* **2008**, *37*, 247 – 262; c) M. Otte, P. F. Kuijpers, O. Troeppner, I. Ivanovic-Burmazovic, J. N. Reek, B. de Bruin, *Chem. Eur. J.* **2013**, *19*, 10170 – 10178.

[25] I. Beletskaya, V. S. Tyurin, A. Y. Tsivadze, R. Guilard, C. Stern, *Chem. Rev.* **2009**, *109*, 1659 – 1713.

Received: December 12, 2014
Published online: February 5, 2015

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