

Molecular Doping of Porous Organic Cages

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S Supporting Information

ABSTRACT: Porous organic cages can act as hosts for the three-dimensional alignment of guests such as halogens and organometallics. Porous single crystals are doped by vapor sublimation to produce diamondoid arrangements of guests such as I_5^- and OsO_4 , leading to marked conductivity enhancement in the case of I_5^- .

Microporous materials with pores smaller than 2 nm are of interest because of potential applications in storage, separation, and catalysis.¹ Most microporous solids are extended networks: well-known examples are metal–organic frameworks (MOFs),^{2–6} covalent organic frameworks (COFs),^{7,8} and organic polymer networks.^{9–11} There is also growing interest in porous molecular crystals and intrinsically porous molecules.^{12–16} For example, we recently described the synthesis of tetrahedral covalent organic cages formed via [4 + 6] cycloimination reactions, and these porous molecular solids can exhibit Brunauer–Emmett–Teller (BET) surface areas of up to 1333 m² g⁻¹.^{17–22} There has been a particular focus on gas sorption and storage in microporous solids. However, molecular-scale pores present a range of other opportunities in materials chemistry. For example, interconnected micropore structures can be used to direct the assembly of guests such as polymers,²³ metal nanoparticles,²⁴ drug molecules,²⁵ and halogens such as iodine,^{26–29} the latter species having been assembled in molecular crystals,^{26–28} in MOFs,^{29–34} and in single-walled carbon nanotubes (SWNTs).³⁵ In principle, porous molecular crystals composed of discrete, covalently prefabricated pores (Figure 1A) could serve as a platform for the modular, directed assembly of more complex functional materials.¹⁸ The host–guest chemistry of cage-like molecules has been explored widely in solution,^{36,37} and there are also examples of solid-state host–guest chemistry for gases^{17,18,20–22,38,39} and solvent molecules¹⁹ in conventionally porous molecular organic crystals. There are few studies that span both solution and solid-state behavior because porosity in molecular crystals is often extrinsic in nature and a result of inefficient packing.¹³

Polyiodides are extended structures with the general formula I_{2m+n}^{n-} (where m and n are integers >0 , $n = 1–4$) that form from the building blocks I^-/I_3^- and I_2 .²⁶ Polyiodides display a rich structural chemistry and can form extensive inorganic polymeric networks that can be interpreted in terms of both simple units (I_3^- , I_5^- , and I_7^-) and also complex, three-dimensional branched and linear chain forms.^{40–42} This rich diversity is governed by the counterion, which determines both the stoichiometry and geometry of the polyiodide.⁴³ There has been interest in iodine as an acceptor in mixed-valence donor–acceptor materials with unusual electrical behavior, where the polyiodide species occupy one-dimensional channels within stacks of partially oxidized donor

molecules.⁴¹ Conductivities range from insulating to metallic, and the availability of synthetic protocols for solid polyiodides is of importance; their properties impact many fields of application.²⁶ There is also recent interest in the use of MOFs for sequestering iodine in the context of controlling radioactive gases.³¹

In this communication, we describe a strategy for efficiently loading the pore structure of porous organic crystals via vapor sublimation. We show that the assembly of guests, such as iodine and osmium tetroxide, is directed by the inherent pore structure in the molecular organic crystal. A tetrahedral organic cage molecule, CC3 ($C_{72}H_{84}N_{12}$), was prepared as previously described (Scheme 1).¹⁷ This cage has tetrahedral symmetry: each cage is chiral and has four windows with a diameter of 5.8 Å. The cage molecules pack in a window-to-window arrangement to generate an interconnected diamondoid homochiral pore network (Figure 1A). Crystals of CC3 were thoroughly desolvated under dynamic vacuum before being placed in a sealed vessel in the presence of solid iodine. The iodine sublimed into the porous crystals over time at ambient temperature, and this was apparent from a color change in the crystal from white to almost black (Figure 1B). Gravimetric measurements taken at various time intervals during the iodine loading indicated that coloration was not merely a result of surface coating, since the mass of the crystal increased significantly (Figure 1C), corresponding to 36.4 wt % or 5.3 iodine atoms per cage molecule after 350 h. The rate of mass increase slowed as the pores became more occupied with the iodine guest. The fact that the mass increase does not plateau in the presence of excess iodine crystals suggests continued deposition onto the crystal surface, once the micropores have become filled. This is a significant guest uptake for a porous organic crystal, although lower than observed recently for ZIF-8.³¹

Crystal structures for the iodine-loaded species, $I@CC3$, were measured over a range of temperatures at the small molecule beamline 11.3.1 at the Advanced Light Source, Berkeley, USA. Structure refinement confirmed uptake of an average of 4.5 iodine atoms per cage molecule, incorporated in a continuous manner into the three-dimensional pore network. As illustrated in Figure 2A, the iodine atoms form a diamondoid chain arrangement, reminiscent of 1-D atomic chains in SWNTs³⁵ but extended here into three dimensions. The chemical nature of the doped iodine species was not immediately obvious due to guest disorder and the retained high symmetry of the host cage molecule (tetrahedral point group T , space group $F4_32$). Careful examination of the iodine atom arrangement and site occupancies, however, left only the V- (or L-) shaped pentaiodide I_5^- as a meaningful solution. The geometries of two such pentaiodides, incorporated into neighboring cage molecules, are illustrated in

Received: July 2, 2011

Published: August 24, 2011

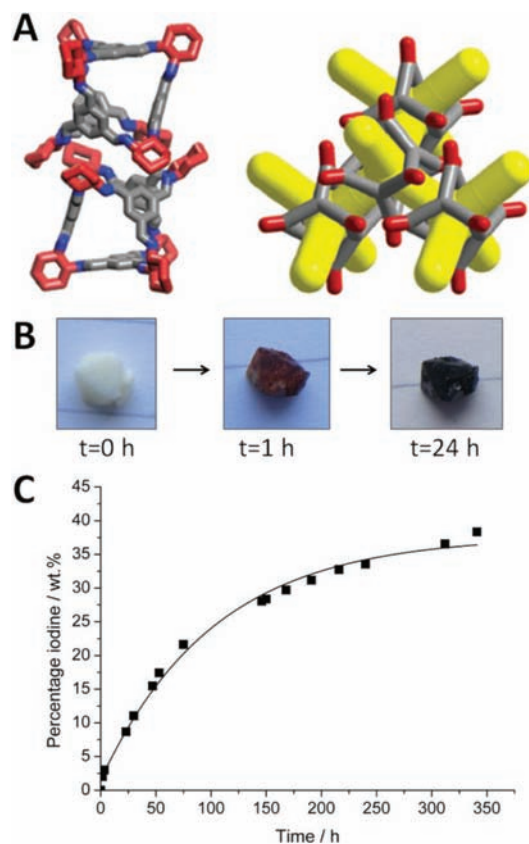


Figure 1. (A) Scheme showing packing in the crystal structure of CC3. Adjacent molecules are directed by the cyclohexyl groups (red) to pack window-to-window, thus generating an interconnected diamondoid-pore network, illustrated here in yellow. (B) Photographs showing the color change when a single crystal of CC3 (approximately 4 mm diameter) was exposed to iodine vapor. (C) Gravimetric uptake of iodine as a function of time at 20 °C.

Scheme 1. Chemical Structure of CC3, $C_{72}H_{84}N_{12}$

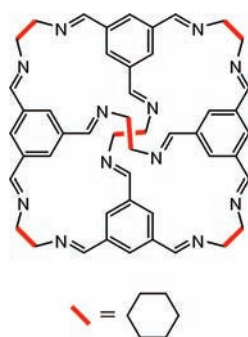


Figure 2B. The site occupancies of the crystallographically independent iodine atoms I3 (the center of the cage void) and I1 (in the interstitial void between cages) refine to near unit values of $\sim 90\%$, while I2 refines to $\sim 45\%$. Hence, every second I2 atom is grayed out in Figure 2B. Taking into account the crystallographic special positions gives an effective I1:I2:I3 ratio of 1:1:0.5 in I1–I2–I3–I2–I1, which from a stoichiometric point of view is in agreement with I_5^- at a 90% occupancy level. Also, the geometry refines most effectively to a V-shaped I_5^-

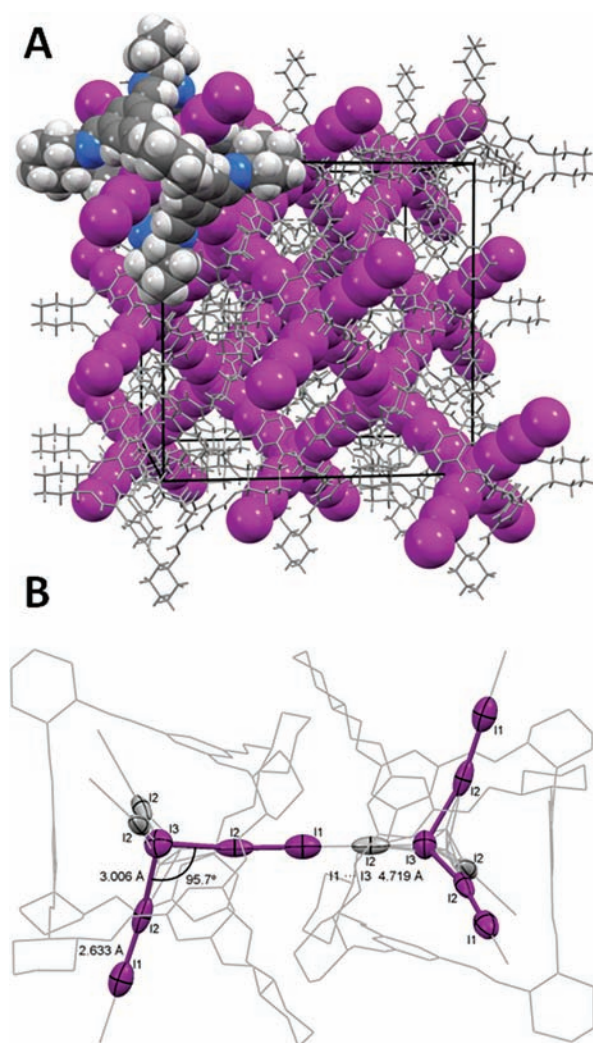


Figure 2. (A) Packing diagram for I@CC3 showing 3-D diamondoid pore network filled with iodine: one cage molecule is shown in space filling representation, and the others are in wireframe for clarity (C, gray; H, white; N, blue; I, purple). All I-containing sites are shown here with equal occupancy. (B) One possible conformation of two I_5^- species in neighboring cage molecules shown in purple, including I_5^- bond distances and angles (at 100 K); I2 sites ($\sim 50\%$ occupancy) which do not fit this configuration are grayed out.

species, as opposed to an L-shaped species, even though the I–I bond distances are ~ 0.1 – 0.2 Å shorter than comparable literature values.^{42,44} We rationalize this as a result of I_5^- disorder, reflected in elongated atomic displacement parameters. Allowing for the possibility of mixtures of polyiodides incorporated into CC3 leaves pyramidal I_7^- and linear I_3^- in a 1:1 ratio as an alternative structure model that fits the analytical data.

Each pentaiodide guest can occupy its tetrahedral cage host in 6 different orientations, but its arrangement affects and is affected by that of neighboring I_5^- species such that a high degree of extended correlation is required to achieve the high I_5^- loading of 90%. The uptake of iodine is fully reversible and was monitored by *in situ* single crystal X-ray diffraction. Variable temperature diffraction on the same crystal shows that iodine is slowly released at temperatures above 60 °C (Supporting Information, Figure S1). Upon heating, the occupancies of I1, I2, and I3 decrease at the same rates, giving no evidence that

preferred intermediate iodine species are formed inside the host crystal during the release process (for example, it could be envisaged that the release of molecular I_2 initially leads to enrichment of I_3^-). Iodine release also occurs if crystals of $I@CC3$ are placed in an organic solvent, such as ethanol, which dissolves I_2 but is a nonsolvent for $CC3$.

These crystallographic data were supported by Raman spectroscopy (Figures S2 and S3), which showed a peak at 165 cm^{-1} consistent with I_5^- in the V or L configuration.^{44–46} Each cage molecule is occupied, on average, with 4.5 iodine atoms, which is in fair agreement with the gravimetric uptake (Figure 1C) as well as thermogravimetric analysis for the loaded cages, which gives a value of 35.8 wt % iodine, or 4.9 iodine atoms per cage (Figure S4). Since the only molecules present in the system are I_5^- and $CC3$, it follows that the cage molecules must form the positive counterion in this system. However, no significant spectroscopic shifts were observed for $CC3$ either in solid state UV–visible or Fourier transform infrared (Figures S5 and S6), apart from a small shoulder peak on the imine stretch (1672 cm^{-1}) in the FTIR.⁴⁷ This may indicate that charge transfer occurs to the cage and is delocalized over this relatively large molecule (mol. wt. $CC3 = 1118\text{ g mol}^{-1}$). This might be expected given the conjugated nature of $CC3$, each molecule of which comprises four aryl groups and twelve imine bonds (Scheme S2).

The existence of this solid state $CC3$ –iodide system is further supported by experiments involving solution mixing of $CC3$ and iodine, which results in soluble iodide species that can be observed by UV–visible spectroscopy (peak at 362 nm; Figures S7, S8). It is also possible to load the iodine guest into $CC3$ from an organic solution (Figure S9), suggesting that this approach need not be restricted to highly volatile guests. The release of molecular iodine, I_2 , from the $CC3$ crystals was observed to happen spontaneously when exposed to ethanol, a poor solvent for $CC3$ (Figure S10). The rate of release was limited by the rate of diffusion from the undissolved crystals into solution. However, the release may be triggered rapidly by dissolving the $CC3$ crystals in an appropriate solvent such as chloroform (Figure S7), a release route not available in the case of iodine species loaded into insoluble porous frameworks. Electrical conductivity measurements were performed on single crystals of $I@CC3$ and undoped $CC3$ (details in Supporting Information). While the nonloaded $CC3$ was found to be essentially nonconductive ($2.8 \times 10^{-10}\text{ S/cm}$), conductivity for the $I@CC3$ sample falls within the semiconductor range with a σ value of $3.3 \times 10^{-5}\text{ S/cm}$. This supports the concept of charge-transfer complex formation and demonstrates that guest inclusion can strongly influence electric conductivity in these porous molecular crystals.

$CC3$ can also accommodate other guests in a similar fashion. It was found that dry, desolvated crystals of $CC3$ could adsorb OsO_4 by the same method.⁴⁸ Again, crystals of $CC3$ were placed in a sealed vessel containing crystals of OsO_4 , also in the solid state, and the guest was allowed to sublime into the porous host at room temperature. The crystals became black in color within 1 h, and a gravimetric uptake of 45 wt %, or 3.6 OsO_4 per cage, was recorded after 1 week. Single crystal analysis of the material (Figure 3) revealed the cage structure and extended packing to be unchanged. One crystallographically independent OsO_4 molecule occupies the center of each cage, and a second is located in the cage windows and bridges two cage molecules. The OsO_4 tetrahedra are rotationally disordered, and refinement of their occupancy factors yields ~ 2.5 OsO_4 per cage. There are four windows

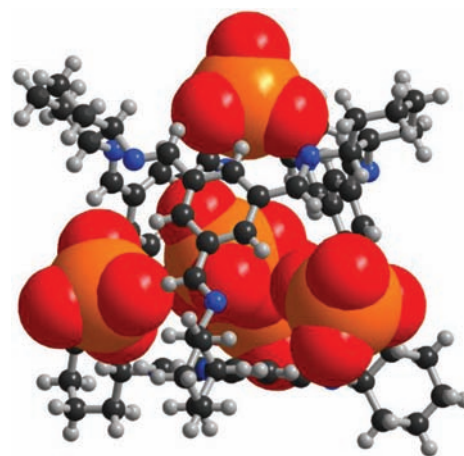


Figure 3. Single crystal X-ray structure of $OsO_4@CC3$, Os orange, O red, C gray, H white, N blue.

per cage, giving a maximum occupancy of 3 OsO_4 per cage (1 central + $(4 \times 0.5$ bridging)), which would correspond to 41 wt %, again, in fair agreement with the gravimetric mass increase and thermogravimetric analysis (39.7 wt % OsO_4 , Figure S11). Fourier transform infrared spectroscopy of $OsO_4@CC3$ also shows no significant change to the cage peaks, apart from a small shoulder peak on the imine stretch ($\sim 1690\text{ cm}^{-1}$) (Figure S12). The characteristic OsO_4 peak can be detected at 947 cm^{-1} , in line with literature values of $945\text{--}955\text{ cm}^{-1}$ for solid state OsO_4 .^{49,50} The quantitative release of the expected OsO_4 mass in TGA and the relatively unchanged OsO_4 and $CC3$ FTIR spectra both argue against any oxidation of the $CC3$ by OsO_4 , or other irreversible binding or reaction of the guest. It is conceivable that the slight shoulder appearing on the imine stretching band may indicate stabilization of the electropositive osmium by the lone pair of the nitrogen. Nitrogen ligands, especially good π donors, are well-known to stabilize octavalent osmium, giving a dark brown to black coloration as seen here.⁵⁰ However, the N–Os distance in the crystal structure for $OsO_4@CC3$ is $>5\text{ \AA}$, which seems too long to invoke any substantial coordination of this kind.⁵¹

Another volatile organometallic, $W(CO)_6$, was also evaluated, but this guest was size excluded by the cage window, despite the use of elevated temperatures ($70\text{ }^\circ\text{C}$) to increase its vapor pressure. No mass increase or other change in the crystals could be detected in this case, even after extended contact times.

In summary, we have shown that both halogen and organometallic guest molecules can be sublimed into the porous structure of a crystalline organic cage, $CC3$. Iodine appears to take the form of I_5^- within the $I@CC3$ structure, and this species is stabilized and oriented by the cage molecules. There are a growing number of reports of porous, cage-like molecular crystals,^{12–22,38} and doping strategies such as these are promising tools for the preparation of materials with new properties. For example, one can envisage the modular construction of multi-component organic crystals¹⁸ that adsorb more than one guest in specific, prearranged sites. Moreover, the molecular nature of these organic cages renders them soluble in common solvents, unlike extended porous networks. This might be utilized, for example, in the delivery of encapsulated guests upon dissolution of the cage framework.

■ ASSOCIATED CONTENT

S Supporting Information. Synthetic and crystallographic details, analysis equipment and conditions, and spectroscopic results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

We thank the Engineering and Research Council (EPSRC) for financial support under grant EP/H000925/1. A.I.C. is a Royal Society Wolfson Research Merit Award holder. We thank Paul R. Chalker and Peter J. King for access to and assistance with FT-Raman measurements and Michael Barrow for assistance with electrical conductivity measurement. We thank Simon J. Teat and Christine M. Beavers for their assistance at the Advanced Light Source, Berkeley Lab, 1 Cyclotron Rd, Berkeley, CA 94720 (USA). We thank the STFC for access to Diamond Light Source and the staff at beamline I19.

■ REFERENCES

- (1) Yaghi, O. M.; Li, H. L.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474.
- (2) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.
- (3) Bradshaw, D.; Claridge, J. B.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J. *Acc. Chem. Res.* **2005**, *38*, 273.
- (4) Li, J. R.; Kuppler, R. J.; Zhou, H. C. *Chem. Soc. Rev.* **2009**, *38*, 1477.
- (5) Farha, O. K.; Hupp, J. T. *Acc. Chem. Res.* **2010**, *43*, 1166.
- (6) Holst, J. R.; Cooper, A. I. *Adv. Mater.* **2010**, *22*, 5212.
- (7) Côté, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M. *Science* **2005**, *310*, 1166.
- (8) Furukawa, H.; Yaghi, O. M. *J. Am. Chem. Soc.* **2009**, *131*, 8875.
- (9) McKeown, N. B.; Budd, P. M. *Chem. Soc. Rev.* **2006**, *35*, 675.
- (10) Jiang, J. X.; Su, F.; Trewin, A.; Wood, C. D.; Campbell, N. L.; Niu, H.; Dickinson, C.; Ganin, A. Y.; Rosseinsky, M. J.; Khimyak, Y. Z.; Cooper, A. I. *Angew. Chem., Int. Ed.* **2007**, *46*, 8574.
- (11) Weber, J.; Thomas, A. *J. Am. Chem. Soc.* **2008**, *130*, 6334.
- (12) Atwood, J. L.; Barbour, L. J.; Jerga, A. *Science* **2002**, *296*, 2367.
- (13) Holst, J. R.; Trewin, A.; Cooper, A. I. *Nat. Chem.* **2010**, *2*, 915.
- (14) Barbour, L. J. *Chem. Commun.* **2006**, 1163.
- (15) McKeown, N. B. *J. Mater. Chem.* **2010**, *20*, 10588.
- (16) Cooper, A. I. *Angew. Chem., Int. Ed.* **2011**, *50*, 996.
- (17) Tozawa, T.; et al. *Nat. Mater.* **2009**, *8*, 973.
- (18) Jones, J. T. A.; Hasell, T.; Wu, X. F.; Bacsa, J.; Jelfs, K. E.; Schmidtman, M.; Chong, S. Y.; Adams, D. J.; Trewin, A.; Schiffmann, F.; Cora, F.; Slater, B.; Steiner, A.; Day, G. M.; Cooper, A. I. *Nature* **2011**, *474*, 367.
- (19) Jones, J. T. A.; Holden, D.; Mitra, T.; Hasell, T.; Adams, D. J.; Jelfs, K. E.; Trewin, A.; Willock, D. J.; Day, G. M.; Bacsa, J.; Steiner, A.; Cooper, A. I. *Angew. Chem., Int. Ed.* **2011**, *50*, 749.
- (20) Swamy, S. L.; Bacsa, J.; Jones, J. T. A.; Stylianou, K. C.; Steiner, A.; Ritchie, L. K.; Hasell, T.; Gould, J. A.; Laybourn, A.; Khimyak, Y. Z.; Adams, D. J.; Rosseinsky, M. J.; Cooper, A. I. *J. Am. Chem. Soc.* **2010**, *132*, 12773.
- (21) Hasell, T.; Wu, X. F.; Jones, J. T. A.; Bacsa, J.; Steiner, A.; Mitra, T.; Trewin, A.; Adams, D. J.; Cooper, A. I. *Nat. Chem.* **2010**, *2*, 750.
- (22) Jiang, S.; Jones, J. T. A.; Hasell, T.; Blythe, C. E.; Adams, D. J.; Trewin, A.; Cooper, A. I. *Nat. Commun.* **2011**, *2*, 207.
- (23) Uemura, T.; Uchida, N.; Higuchi, M.; Kitagawa, S. *Macromolecules* **2011**, *44*, 2693.
- (24) Hermes, S.; Schroter, M. K.; Schmid, R.; Khodeir, L.; Muhler, M.; Tissler, A.; Fischer, R. W.; Fischer, R. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 6237.
- (25) An, J. Y.; Geib, S. J.; Rosi, N. L. *J. Am. Chem. Soc.* **2009**, *131*, 8376.
- (26) Garcia, M. D.; Marti-Rujas, J.; Metrangolo, P.; Peinador, C.; Pilati, T.; Resnati, G.; Terraneo, G.; Ursini, M. *CrystEngComm* **2011**, *13*, 4411.
- (27) Gorbitz, C. H.; Nilsen, M.; Szeto, K.; Tangen, L. W. *Chem. Commun.* **2005**, 4288.
- (28) Hertzsch, T.; Budde, F.; Weber, E.; Hulliger, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2281.
- (29) Abrahams, B. F.; Moylan, M.; Orchard, S. D.; Robson, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1848.
- (30) Choi, H. J.; Suh, M. P. *J. Am. Chem. Soc.* **2004**, *126*, 15844.
- (31) Sava, D. F.; Rodriguez, M. A.; Chapman, K. W.; Chupas, P. J.; Greathouse, J. A.; Crozier, P. S.; Nenoff, T. M. *J. Am. Chem. Soc.* **2011**, DOI: 10.1021/ja204757x.
- (32) Wang, Z.; Zhang, Y.; Liu, T.; Kurmoo, M.; Gao, S. *Adv. Funct. Mater.* **2007**, *17*, 1523.
- (33) Zeng, M. H.; Wang, Q. X.; Tan, Y. X.; Hu, S.; Zhao, H. X.; Long, L. S.; Kurmoo, M. *J. Am. Chem. Soc.* **2010**, *132*, 2561.
- (34) Liu, Q.-K.; Ma, J.-P.; Dong, Y.-B. *Chem. Commun.* **2011**, 7185.
- (35) Guan, L. H.; Suenaga, K.; Shi, Z. J.; Gu, Z. N.; Iijima, S. *Nano Lett.* **2007**, *7*, 1532.
- (36) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1978**, *11*, 8.
- (37) Hof, F.; Craig, S. L.; Nuckolls, C.; Rebek, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1488.
- (38) Mastalerz, M.; Schneider, M. W.; Opper, I. M.; Presly, O. *Angew. Chem., Int. Ed.* **2010**, *50*, 1046.
- (39) Bezzu, C. G.; Helliwell, M.; Warren, J. E.; Allan, D. R.; McKeown, N. B. *Science* **2010**, *327*, 1627.
- (40) Svensson, P. H.; Gorlov, M.; Kloo, L. *Inorg. Chem.* **2008**, *47*, 11464.
- (41) Blake, A. J.; Devillanova, F. A.; Gould, R. O.; Li, W. S.; Lippolis, V.; Parsons, S.; Radek, C.; Schroder, M. *Chem. Soc. Rev.* **1998**, *27*, 195.
- (42) Svensson, P. H.; Kloo, L. *Chem. Rev.* **2003**, *103*, 1649.
- (43) Abate, A.; Brischetto, M.; Cavallo, G.; Lahtinen, M.; Metrangolo, P.; Pilati, T.; Radice, S.; Resnati, G.; Rissanen, K.; Terraneo, G. *Chem. Commun.* **2010**, 46, 2724.
- (44) Deplano, P.; Ferraro, J. R.; Mercuri, M. L.; Trogu, E. F. *Coord. Chem. Rev.* **1999**, *188*, 71.
- (45) Alvarez, L.; Bantignies, J. L.; Le Parc, R.; Aznar, R.; Sauvajol, J. L.; Merlen, A.; Machon, D.; San Miguel, A. *Phys. Rev. B* **2010**, *82*.
- (46) Cambedouzou, J.; Sauvajol, J. L.; Rahmani, A.; Flahaut, E.; Peigney, A.; Laurent, C. *Phys. Rev. B* **2004**, *69*.
- (47) Wang, Y. L.; Poirier, R. A. *J. Phys. Chem. A* **1997**, *101*, 907.
- (48) Safety note: OsO₄ is volatile, highly toxic, and has other associated hazards. This compound should be used only with appropriate containment and safety precautions, and in minimal quantities.
- (49) Woodward, L. A.; Roberts, H. L. *Trans. Faraday Soc.* **1956**, *52*, 615.
- (50) Hanker, J. S.; Romanovicz, D. K.; Padykula, H. A. *Histochemistry* **1976**, *49*, 263.
- (51) Collin, R.; Griffith, W. P.; Phillips, F. L.; Skapski, A. C. *Biochim. Biophys. Acta* **1973**, *320*, 745.