Cucurbituril Polymers

Iodine-Assisted Assembly of Helical Coordination Polymers of Cucurbituril and Asymmetric Copper(II) Complexes**

Feng Zhang, Tatsuo Yajima, Yi-Zhi Li, Guo-Zheng Xu, Hui-Lan Chen, Qi-Tao Liu,* and Osamu Yamauchi**

Iodine has long been paid considerable attention for its fascinating chemical behavior[1,2] and biological essentiality.[3] The use of iodine as electrical conductor in the synthesis of donor–acceptor charge-transfer materials is well known.[4] In recent years, iodine in various forms has found applications in catalysis[5] as well as the creation of novel structures[6] and materials.[7] When covalently bound to an aromatic ring, iodine and other halogen atoms are versatile, assembly-organizing factors that direct extended networks[8,9] and induce helical aggregation of copper(II) complexes.[9,10] Furthermore, iodine is an essential element and plays an important role in the life processes of mammals and most vertebrates by forming the iodophenol moieties of thyroid hormones, growth hormones that function by binding to nuclear receptors.[11–13] The effect of the iodo substituent on these biological events has yet to be understood.

Cucurbituril (CB6) is a pumpkin-shaped macrocyclic compound synthesized by acid-catalyzed condensation of glycoluril and formaldehyde.[14] It is composed of six symmetrically arranged glycoluril units covalently linked by twelve methylene bridges to form a rigid, annular, hollow cavitand with two highly polar carbonyl openings.[15] CB6 has

[*] Dr. F. Zhang, Dr. Y.-Z. Li, Prof. H.-L. Chen
State Key Laboratory of Coordination Chemistry
Nanjing University
22 Hankou Road, Nanjing 210093 (P.R. China)
Fax: (+86) 25-8331-4502
E-mail: hlchen@netra.nju.edu.cn

Dr. F. Zhang, G.-Z. Xu, Prof. Q.-T. Liu
Institute of Chemistry and Engineering
Liaoning University
Huanggu, Shenyang 110036 (P.R. China)
Fax: (+86) 24-8685-4241
E-mail: qtliu@lnu.edu.cn

Dr. T. Yajima, Prof. O. Yamauchi
Faculty of Engineering
Kansai University
Suita, Osaka 564-8680 (Japan)
Fax: (+81) 6-6330-3770
E-mail: osamuy@ipcku.kansai-u.ac.jp

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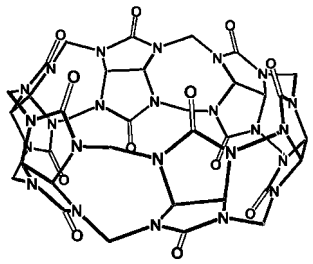
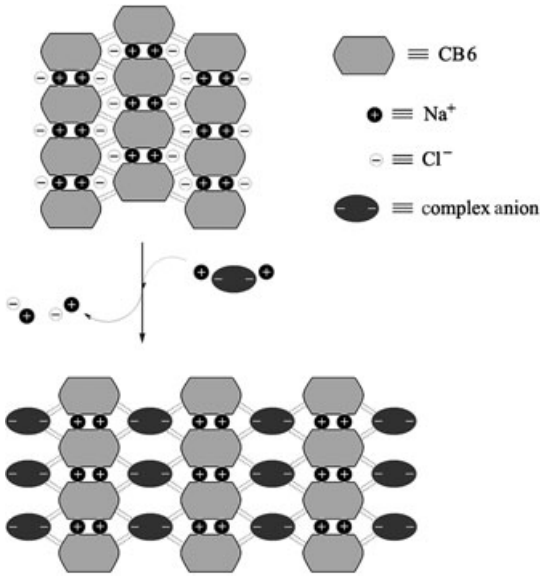


Cucurbituril (CB6)

received much interest in the last two decades as synthetic receptor[16–22] and has found discrete uses in inclusion catalysis,[20] interlocked architectures,[21] and functional molecular devices.[22] The guest-binding properties and inclusion mechanisms of CB6 have been investigated in detail.[16,18] Recently, various CB6 homologues, CB7 and CB8 in particular,[23] have been used for the development of functional molecular devices.[17c,24]

To date, investigations of the weak interactions leading to CB6-mediated molecular assembly are still lacking. The chemical behavior of the convex-shaped outer walls of CB6 and its homologues remains unknown and needs to be explored for the development of novel structures and functional materials incorporating cucurbiturils with transition metal complexes. CB6 can form more stable complexes with alkali metal ions[18] than with transition metal ions,[19g] and thus drives the assembly of alkali metal one-dimensional coordination polymers through wall-to-wall, shape-matching interactions of CB6.[19c,d] A negatively charged transition metal complex with aromatic moieties can bind to a positively charged CB6–alkali metal complex in aqueous solution and compete with CB6 self-recognition. This leads to a hybrid assembly of the CB6–alkali metal coordination polymer incorporating the transition metal complex.



Scheme 1. Schematic representation of the anion-exchange strategy involving CB6 self-recognition (top) and CB6–ligand recognition (bottom).

Herein we report two novel helical structures that are synthesized by an anion-exchange strategy based on asymmetric, shape-matching recognition (Scheme 1). The anionic copper(II) complexes $[Cu(I_2sal)(Hqs)]^{2-}$ and $[Cu(Ibz)(Hqs)Cl]^{2-}$ (I_2sal = 3,5-diiodosalicylate, Ibz = 3-iodobenzoate, Hqs = 8-hydroxyquinoline-5-sulfonate) display a four-coordinate N_1O_3 and a five-coordinate N_1O_3Cl asymmetric structure, respectively, and are recognized by the cationic CB6–sodium(I) 1D coordination polymer. According to the structures of the two molecular assemblies, the convex-shaped glycoluril backbones of CB6 exhibit a much higher affinity to the iodoaromatic moieties of the copper(II) complexes than to the other CB6 units. This results in formation of the helical 1D polymer arrays with the assistance of the iodo substituents.

Compound **1** was isolated as rod-shaped colorless crystals from an aqueous NaCl solution of CB6. A dilute 1:1:1:1 mixture of **1** with Cu^{II}, Hqs, and I_2sal or Ibz in aqueous NaCl solution afforded complexes **2** or **3** as prismatic or needle-shaped green crystals (see the Experimental Section). The structures of **1**–**3** were determined by X-ray crystallography.[25]

$[Na_4(CB6)_2(H_2O)_{16}]Cl_4 \cdot 6H_2O$ **1**

$[Na_2(CB6)(H_2O)_2][Cu(I_2sal)(Hqs)] \cdot 6.5H_2O$ **2**

$[Na_2(CB6)(H_2O)_2][Cu(Ibz)(Hqs)Cl] \cdot 5.5H_2O$ **3**

In the crystal structure of **1**, the CB6 molecules display C_{2h} symmetry and are connected by twofold O(1)-Na^I-O(1) coordination linkages to form a linear 1D polymer (Figure 1a). The CB6 molecules in **2** and **3** are asymmetric in the presence of the complex anions. They are connected by asymmetric $O_{\mu2}$(water)–Na^I dinuclear clusters with formation of O–Na chelates for one of the carbonyl openings and one Na(1)-$O(12)_{\mu2}$-Na(2) bridging and two O–Na coordination bonds for the other. The resulting 1D polymers in **2** and **3** exhibit a zig-zag, folded helical conformation; neighboring CB6 molecules in the same polymer are in close contact with each other (Figure 1b,c). The closest distances between the carbonyl O(3) atom of the glycoluril unit G3 and the carbonyl C(12) atom of unit G6 are 3.07 and 3.13 Å, with corresponding CB6–CB6 tilting angles of 31.1° and 32.6° for **2** and **3**, respectively.

The 1D polymer in **2** exists as a pair of helical enantiomers, and the enantiomeric CB6 molecules of the *P* and *M* helices bind with the corresponding enantiomeric $[Cu(I_2sal)(Hqs)]^{2-}$ anions along the same $P2_1$ axis through asymmetric shape-matching interactions between the aromatic moieties of $Cu(I_2sal)(Hqs)$ and the outer walls of the CB6 molecules. The 1D polymer in **3**, on the other hand, exists only as an *M*-type helix, whose CB6 molecules are closely contacted by the $[Cu(Ibz)(Hqs)Cl]^{2-}$ anions through *P*-type helical shape-matching accommodation. The complex anions of **2** and **3** assume a rigid skew-bent conformation connected by asymmetric Cu^{II} ion centers with a distorted square-planar coordination geometry for $[Cu(I_2sal)(Hqs)]^{2-}$ and a distorted square-pyramidal coordination geometry for $[Cu(Ibz)(Hqs)Cl]^{2-}$ (Figure 2); the dihedral angles between the

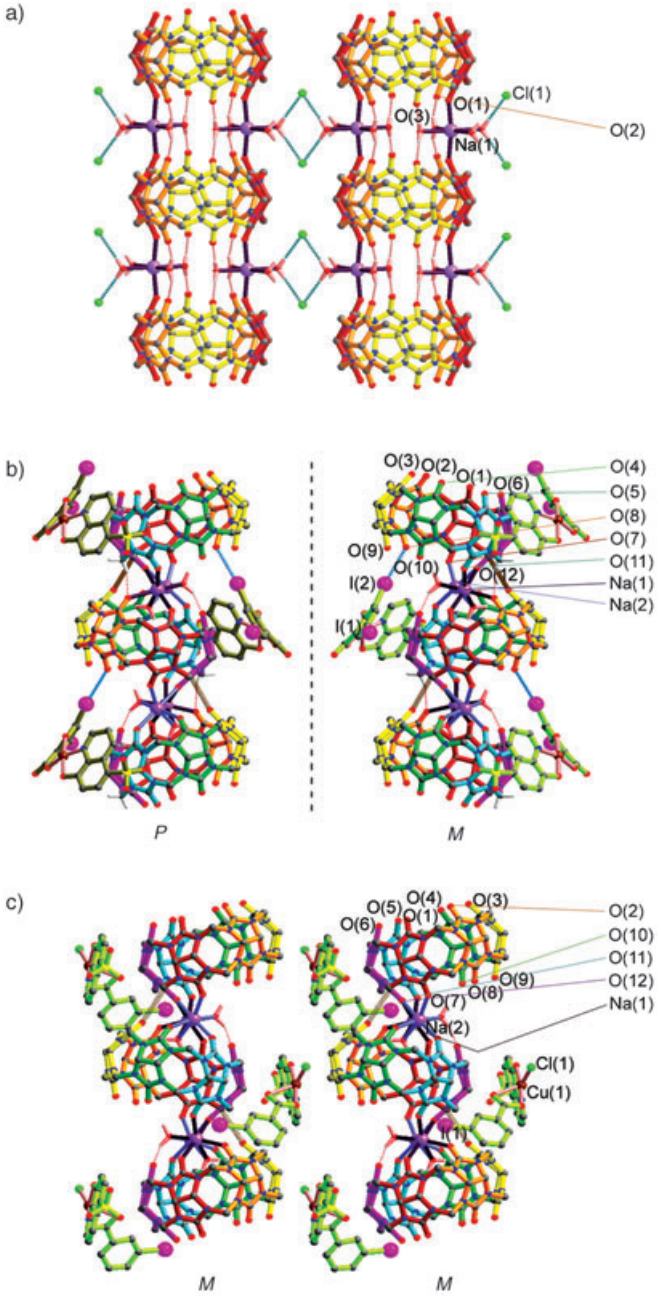


Figure 1. Ball-and-stick representations for the linear 1D-polymer in **1** (a) and the helical 1D polymers in **2** (b) and **3** (c) with the asymmetric glycoluril units G1–G6 (G1 red, G2 orange, G3 yellow, G4 green, G5 cyan, G6 purple).[26]

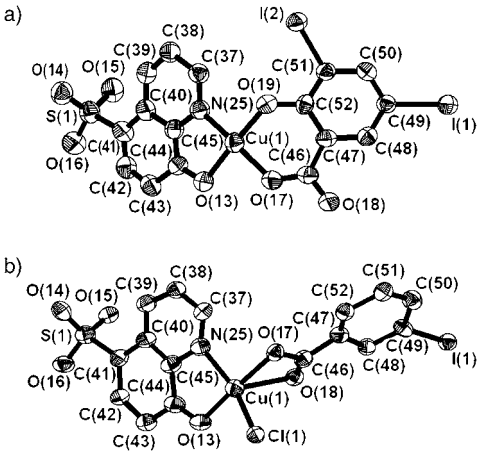


Figure 2. ORTEP views of a) $[Cu(I_2sal)(Hqs)]^{2-}$ in **2** and b) $[Cu(Ibz)(Hqs)Cl]^{2-}$ in **3** with the thermal ellipsoids at the 50% probability level.[26]

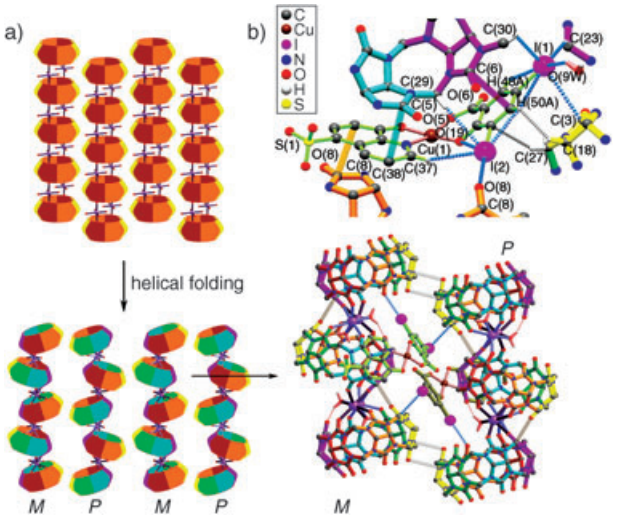


Figure 3. a) Schematic representation of the polymer 2D layer in **1**, the 2D open-cavity framework in **2** (left), and the structure for the accommodation of $Cu(I_2sal)(Hqs)$ into the homocenter-symmetric open cavity (lower right). b) The host–guest shape-matching mode in **2** involving I–O, I–C, and I–H weak interactions.[26]

coordinated aromatic rings are 130.3 and 106.1°, respectively. It is these discrete and properly skew-bent conformations that allow the asymmetric shape-matching and thus result in the discrete helical structures (Figures 3 and 4). The skew-bent conformations are reminiscent of that of thyroid hormones, whose inner and outer phenol rings are asymmetrically bridged by an ether oxygen atom instead of the Cu^{II} ion of the complexes presented here.[3b]

In complex **2**, the positively charged *P* and *M* polymer helices are alternately packed with opposite orientations (Figure 3a) and assembled as a two-dimensional layer structure with open cavities. Each cavity is composed of the half walls of three CB6 enantiomer pairs through shape-matching interactions between the G3 semi-glycoluril rings of two CB6 enantiomer pairs with a ring–ring distance of 3.29 Å. Most importantly, each open cavity holds homocenter symmetry, tightly accommodating a pair of $[Cu(I_2sal)(Hqs)]^{2-}$ enantiomers in the same symmetry. To our knowledge, this is the first example of a helical enantiomeric host–guest assembly constructed from an asymmetric transition metal complex anion (guest) and the outer walls of CB6 molecules within the cavity-forming cation aggregates (host) through asymmetric shape-matching interactions.

The skew-bent form of $[Cu(I_2sal)(Hqs)]^{2-}$ in **2** is arranged in such a way that the inward I_2sal and Hqs ring faces fit to the semi-glycoluril rings of units G6 and G5, respectively, of the same CB6 molecule. The outward I_2sal and Hqs ring faces

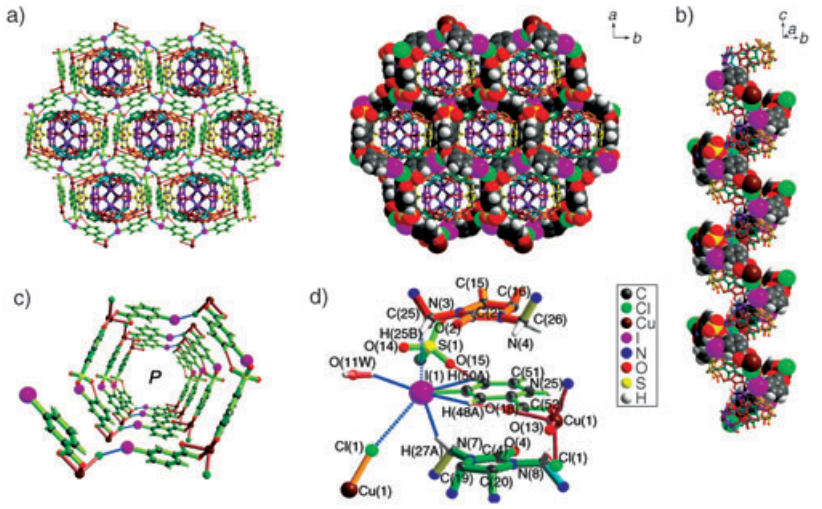


Figure 4. a) Top views for the helical inclusion structure of **3**. b) Side view for the complex anion-wrapped polymer helix in **3**. c) Top view for the *P*-type anionic helical net channel. d) Representation of the asymmetric shape-matching mode of Ibz to G2 (orange) and G4 (green) involving I–H and I–Cl weak interactions.[26]

contact with the semi-glycoluril rings of units G3 and G2, respectively, of the CB6 molecules in the neighboring polymers (Figure 3b). The inward G6–I_2sal and G5–Hqs and outward Hqs–G2 matching pairs form face-to-face π–π stacking interactions, with closest ring–ring distances of 3.38, 3.47, and 3.43 Å and ring–ring tilting angles of 19.6, 5.9, and 5.8°, respectively. In contrast, the outward I_2sal–G3 matching pair is achieved by complementary iodine–G3 ring charge transfer and C–H···π interactions between a G3 hydrogen atom and the I_2sal ring. This places the I_2sal and G3 rings in edge-to-edge contact with a closest ring–ring distance and angle of 3.50 Å and 15.7°.

In **3**, unique helical polymer-inclusion assembly by the $[Cu(Ibz)(Hqs)Cl]^{2-}$ anion is achieved with formation of helical networks (Figure 4). The complex anion is arranged leaning toward the corresponding hinge site of the polymer helix, with the inward Ibz and Hqs ring faces contacting the semi-glycoluril rings of units G2 and G6, respectively, of the neighboring CB6 molecules. The outward Ibz and Hqs ring faces close to G4 and G3, respectively, of the CB6 molecules in the neighboring polymer (Figure 1c and 4d). The closest ring–ring distances are 3.67, 3.46, 3.60, and 3.44 Å, respectively, for the G2–Ibz, G6–Hqs, Ibz–G4, and Hqs–G3 matching pairs with corresponding ring–ring angles of 3.3, 4.6, 1.5, and 4.2°, indicating face-to-face π–π stacking interactions.

The same striking point for compounds **2** and **3** is the assembly-assisting role of the iodo substituents, whose multiple weak interactions with CB6 amplify the asymmetry and enhance the stability of the asymmetric shape-matching interactions. In **2**, the iodo substituents are involved in multiple hydrogen-bonding interactions with the G6 methine and the hydrogen atoms of the C(29) and C(30) methylene groups as well as charge-transfer interactions with the ureido G2 oxygen and G3 carbon atoms (Figure 3b). The interatomic distances for I(1)–C(3), I(2)–O(8), and I–H(23A, 30A, 9WA, 29B, 37A) are 3.78, 3.34, and 3.25–3.30 Å, respectively, and thus all lie within the corresponding van der Waals distances[27] of 3.85, 3.55, and 3.35 Å, respectively. The interatomic distances involving the iodo substituent in **3** (Figure 4d), that is, I(1)–H(25B) (2.98 Å) and I(1)–H(27A) (3.07 Å), are distinctly shorter than the van der Waals distance for I–H. All these distances are comparable with those previously observed for other systems (I–C 3.63–3.82, I–O 3.08–3.37, I–H 2.85–3.20 Å)[9] and some thyroactive species (I–O 2.99–3.45 Å).[3c] In addition, the iodo substituent in **3** also contacts the coordinated Cl^- anion within the van der Waals distance and favors the hydrogen-bonding interaction of its *ortho*-hydrogen atom with the sulfonate oxygen atom of Hqs (O···C 3.37, O···H 2.39 Å; ∢O···H–C 176.2°). These results suggest that the iodine atoms of coordinated I_2sal and Ibz may play an important role in the formation of **2** and **3** by serving as an efficient asymmetric weak-binding knot and template.

In conclusion we present two novel helical structures established by iodine-assisted asymmetric shape-matching interactions between the convex outer walls of CB6 and the aromatic moieties of asymmetric copper(II) complexes. The synthetic strategy may also be suitable for other hybrid structures and the construction of cucurbiturils incorporating various transition metal complexes. Our results suggest that the iodo substituent may exert a profound effect on its covalently bound aromatic moiety in specific asymmetric recognition to a given structural environment through selective shape-matching interactions. The observed structural change due to the interactions between CB6 and the iodophenol moiety may suggest the possible function of thyroid hormones as an iodine-assisted asymmetric template in the hormone–receptor binding switches inducing the biologically active conformation of the receptor.

Experimental Section

CB6 was synthesized following a literature procedure[15] and obtained as a white powder in 40–45% yield after drying at 110°C. Elemental analysis calcd for $(C_{36}H_{36}N_{24}O_{12})\cdot 9H_2O$ [%]: C 37.31, H 4.70, N 29.01; found: C 37.68, H 4.84, N 28.70; ^{1}H NMR (Bruker, 500 MHz, in D_2O): $\delta = 5.65$ (s, CH), 5.74 (d, C*H*H), 4.38 ppm (d, CH*H*).

1: A solution of CB6 (0.5 mmol) in 0.2 M aqueous NaCl was concentrated to near saturation followed by slow vapor diffusion of ethanol into the solution at room temperature for one week. The colorless rod-shaped crystals were dried in air at room temperature (60–70% yield). Elemental analysis calcd for $(C_{72}H_{104}N_{48}Na_4O_{40})Cl_4\cdot 6H_2O$ [%]: C 32.96, H 4.46, N 25.62; found: C 33.12, H 4.32, N 25.76.

2: Compound **1** (0.05 mmol) was dissolved in 0.2 M aqueous NaCl and the solution was added dropwise to an aqueous 1:1:1 mixture of $CuCl_2$, I_2sal, and Hqs (0.05 mmol) at pH 6 under stirring. Slow evaporation of the filtrate over two weeks provided prismatic green crystals of **2** (40–50% yield based on CB6). Elemental analysis calcd for $(C_{52}H_{47}N_{25}I_2SNa_2O_{21}Cu)\cdot 6.5H_2O$ [%]: C 33.39, H 3.23, N 18.72; found: C 33.67, H 3.02, N 18.90.

3: Compound **3** was prepared in a similar manner to **2** with Ibz in place of I_2sal. Slow evaporation of the filtrate for two weeks provided needle-shaped green crystals of **3** (40–50% yield based on CB6). Elemental analysis calcd for $(C_{52}H_{49}N_{25}O_{20}SICuClNa_2)\cdot 5.5H_2O$ [%]: C 35.75, H 3.46, N 20.04; found: C 36.07, H 3.09, N 20.25.

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[25] The crystal structures of **1**–**3** were determined with a Bruker P4 four-circle diffractometer with graphite-monochromatic $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data were collected at room temperature (293 K) in the range $1.53 \le \theta \le 25.00°$ for **1**, $1.33 \le \theta \le 24.99°$ for **2**, and $1.36 \le \theta \le 26.00°$ for **3**. The structures were solved by direct methods and refined using full-matrix least squares on F^2 (SHELXTL, Bruker, 2000). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were generated geometrically or determined from the difference Fourier map and refined isotropically. Crystal data for **1**: monoclinic, space group $C2/m$, $a = 23.363(8)$, $b = 10.680(2)$, $c = 14.530(3)$ Å, $\beta = 113.36(4)°$, $V = 3328(2)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.309$ g cm^{-3}, $\mu = 0.196$ mm^{-1}, $R_1 = 0.0465$ for 2611 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.1445$ for 3114 unique reflections. Crystal data for **2**: monoclinic, space group $P2_1/n$, $a = 17.180(3)$, $b = 18.550(4)$, $c = 25.950(3)$ Å, $\beta = 99.34(3)°$, $V = 8160(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.523$ g cm^{-3}, $\mu = 1.148$ mm^{-1}, $R_1 = 0.0481$ for 8816 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.1243$ for 14307 unique reflections. Crystal data for **3**: orthorhombic, space group $P2_12_12_1$, $a = 25.270(5)$, $b = 16.410(3)$, $c = 18.570(4)$ Å, $V = 7701(3)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.507$ g cm^{-3}, $\mu = 0.847$ mm^{-1}, $R_1 = 0.0424$ for 15130 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.1210$ for 15130 unique reflections. CCDC 257203, 257204, and 227936 (for **1**, **2**, and **3**, respectively) 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.

[26] For ORTEP views of the structure and details concerning the weak interactions, see the Supporting Information.

[27] Based on Pauling radii; see L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, **1960**, p. 260.

