

Metal–Organic Frameworks from Edible Natural Products**

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Metal–organic frameworks (MOFs) represent^[1] an extensive class of porous crystals in which organic struts link metal-containing clusters. The success in controlling the functionality and structure of MOFs has led to numerous applications,^[2] most notably gas adsorption,^[3] storage of clean gas fuels,^[4] catalysis,^[5] separations,^[6] and drug delivery.^[7] However, the vast majority of MOFs described to date are composed of organic struts derived from non-renewable petrochemical feedstocks and transition metals. The challenge in preparing MOFs from natural products lies in the inherent asymmetry of the building units, which are not amenable to crystallization in the form of highly porous frameworks. Herein, we report a strategy to overcome this problem using γ -cyclodextrin (γ -CD), a symmetrical cyclic oligosaccharide that is mass-produced enzymatically from starch^[8] and comprised of eight asymmetric α -1,4-linked D-glucopyranosyl residues. These γ -CD building units are then linked by potassium ions, in aqueous media at ambient temperature and pressure, to form a body-centered cubic structure, termed CD-MOF-1, which has the empirical formula $[(C_{48}H_{80}O_{40})(KOH)_2]_n$. CD-MOFs can be prepared entirely from edible ingredients: combining food-grade γ -CD with salt substitute (KCl) or potassium benzoate (food additive E212) in bottled water and Everclear grain spirit (EtOH) yields porous frameworks which constitute *edible MOFs*.

While there have been a few reports of MOFs assembled from amino acids,^[9] nucleobases,^[7a,10] peptides,^[11] magnesium formates,^[12] and metal glutarates,^[13] examples of these materials are not common despite the rapidly growing desire to fabricate MOFs from naturally available building blocks. We suspect that the key to our success in assembling CD-MOFs lies in the symmetric arrangement (C_8) within the γ -CD torus of eight asymmetric (C_1) α -1,4-linked D-glucopyranosyl residues and the ready availability of γ -CD as a chiral molecular building block (Figure 1). CD-MOF-1 was prepared by combining 1.0 equiv of γ -CD with 8.0 equiv of KOH in aqueous solution, followed by vapor diffusion of MeOH into the solution during 2–7 days, resulting in colorless, cubic, single crystals, suitable for X-ray crystallography, in approximately 70% yield. Other CD-MOFs were readily obtained using salts of Na^+ , Rb^+ , and Cs^+ , giving rise to an extensive new family of porous materials. A complete list of metal salts employed to form CD-MOFs and the full synthesis of CD-MOFs are provided in Section S2 of the Supporting Information.

The X-ray crystal structure of CD-MOF-1^[14] reveals that eight-coordinate K^+ ions not only assist in the assembly of $(\gamma\text{-CD})_6$ cubes (Figure 2a,b), wherein six γ -CD units occupy the faces of a cube, but they also serve to link these cubes together in a three-dimensional array which extends throughout the crystal (Figure 2c). The $(\gamma\text{-CD})_6$ repeating motifs adopt a body-centered cubic packing arrangement wherein each symmetrically equivalent K^+ ion links two contiguous γ -CD

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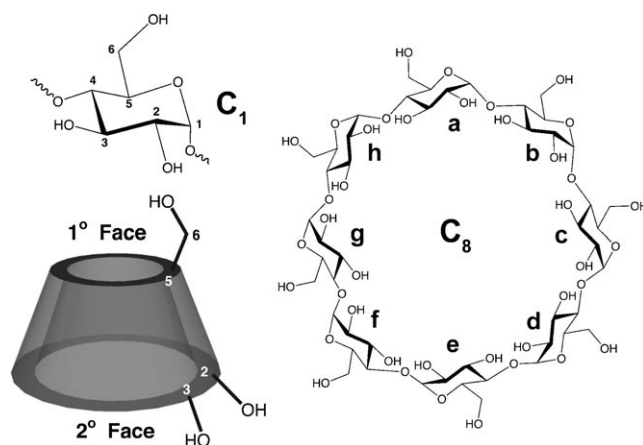


Figure 1. Structural formulas of the asymmetric (C_1) α -1,4-linked D-glucopyranosyl residues and γ -cyclodextrin (γ -CD), with its C_8 symmetry, incorporating eight of the monosaccharide residues in the form of a torus with an inner diameter of 0.9 nm. While the eight C6 hydroxy (OH) groups and the eight glycosidic ring oxygen atoms constitute the primary (1°) face of γ -CD, the 16 C2 and C3 OH groups constitute the secondary (2°) face.

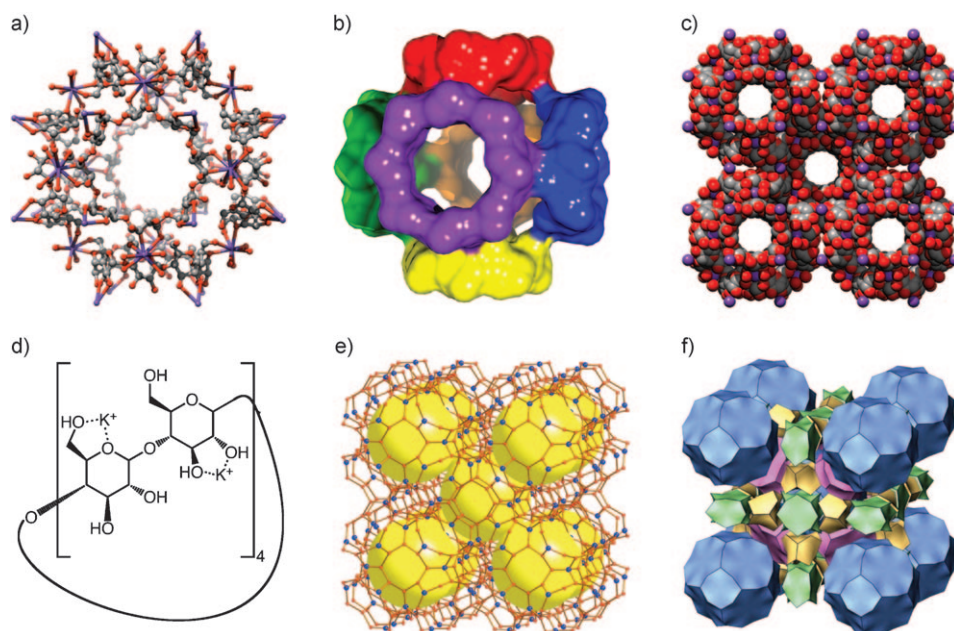


Figure 2. a) A ball-and-stick representation of the solid-state structure of the cubic $(\gamma\text{-CD})_6$ repeating motif which represents the unit cell (3.1 nm edge) of CD-MOF-1, illustrating the six $\gamma\text{-CD}$ units which constitute the sides of the cube wherein i) the primary faces of the $\gamma\text{-CD}$ units point inwards and ii) the secondary faces of the $\gamma\text{-CD}$ units point outwards (C gray, O red, K purple). b) The cuboidal orientation of the six $\gamma\text{-CD}$ tori, illustrating the 1.7 nm sized pore at the center of each $(\gamma\text{-CD})_6$ repeating motif. The surfaces of the $\gamma\text{-CD}$ units are portrayed in red, blue, yellow, purple, green, and orange. The K^+ ions have been removed for clarity. c) A space-filling representation of the extended solid-state structure, showing the $(\gamma\text{-CD})_6$ repeating motifs adopting a body-centered cubic packing arrangement (C gray, O red, K purple). d) A configurational representation of the structure of the maltosyl repeating unit in $\gamma\text{-CD}$, showing the alternating coordination of K^+ ions to i) the primary face, involving the C6 OH groups and glycosidic ring oxygen atoms on one of its α -1,4-linked D-glucopyranosyl residues, and ii) the secondary face, involving the C2 and C3 OH groups on the other. e) The previously unknown net (**rra**), defined by the body-centered cubic solid-state structure of CD-MOF-1, with the nine yellow spheres indicating the nanometer-sized pores found at the center of each $(\gamma\text{-CD})_6$ cube (the red balls represent single α -1,4-linked D-glucopyranosyl residues, while the blue balls represent K^+ ions). f) A representation of the different voids within the **rra** net. The approximately spherical blue pores are located at the center of each $(\gamma\text{-CD})_6$ cube, while the green segments represent the 0.78 nm windows defined by the inner diameter of each $\gamma\text{-CD}$ unit, forming infinite channels which propagate along the a , b , and c crystallographic axes and link the pores. The purple areas are defined by the corners of the cube which are “cut” on account of the spherical shape of the $\gamma\text{-CD}$ faces, while the yellow segments represent the voids between the same outer faces of two adjacent $(\gamma\text{-CD})_6$ cubes.

sides of the $(\gamma\text{-CD})_6$ cube by coordination to their primary faces, through the C6 OH groups ($\text{K}-\text{O}$ 2.843(13) Å) and glycosidic oxygen atoms ($\text{K}-\text{O}$ 2.824(6) Å). Each K^+ ion is also involved in the assembly of pairs of $(\gamma\text{-CD})_6$ repeating motifs by coordination to the secondary faces of adjacent $\gamma\text{-CD}$ tori, through their C2 ($\text{K}-\text{O}$ 2.787(15) Å) and C3 ($\text{K}-\text{O}$ 2.954(10) Å) OH groups, resulting in an overall coordination number of eight around each K^+ ion. Overall, the six $\gamma\text{-CD}$ units of the $(\gamma\text{-CD})_6$ cube are held together by four K^+ ions associated with the C6 OH groups and the glycosidic ring oxygen atoms of four alternating (**a**, **c**, **e**, **g**) α -1,4-linked D-glucopyranosyl residues (Figure 1 and Figure 2d) on the primary faces of the $\gamma\text{-CD}$ tori, whereas the $(\gamma\text{-CD})_6$ cubes are attached to one another by the coordination of four K^+ ions to the C2 and C3 OH groups of the other set of alternating (**b**, **d**, **f**, **h**) residues on the secondary faces of the $\gamma\text{-CD}$ tori. Thus, each K^+ ion is eight-coordinate, embracing two primary OH groups and two glycosidic ring oxygen atoms, as well as four

secondary OH groups. Isostructural CD-MOFs, prepared from RbOH (CD-MOF-2) and CsOH (CD-MOF-3), have also been characterized (see Supporting Information). We suspect that the local four-fold symmetry of the $\gamma\text{-CD}$ units in CD-MOF-1, 2, and 3 is not unimportant in the formation of cubic, crystalline CD-MOFs.^[15]

The extended solid-state structure of the isostructural CD-MOF series is reminiscent of a crystal structure reported by MacGillivray and Atwood^[16] in which six C_4 -symmetric calix[4]resorcinarenes and eight H_2O molecules form a hydrogen-bonded cuboctahedron with the same $I432$ space group. However, their topologies are very different; the CD-MOFs have open porous frameworks held together by metal ions in an extended fashion rather than being a closed framework consisting of large voids inaccessible one to the other and to incoming guests. The extended structures of the CD-MOFs constitute (Figure 2e) a new topological net^[17] (**rra**) that has not been previously observed or predicted. A large spherical pore of 1.7 nm diameter resides at the center of each $(\gamma\text{-CD})_6$ cube and is connected by a series of smaller voids (Figure 2f) to

form the porous framework. Six pore windows of 0.78 nm diameter are defined by the $\gamma\text{-CD}$ tori which adopt the faces of the cube, and are aligned along the a , b , and c crystallographic axes. Further, infinite pores propagate along the (111) direction with an aperture of 0.42 nm, and the framework has an estimated^[18] total pore volume of 54%.

In order to evaluate the thermal and architectural stabilities of CD-MOF-1 and CD-MOF-2 after solvent evacuation, or activation (see Supporting Information), we first examined their thermal stability using thermogravimetric analysis (TGA) of guest-free samples. TGA traces for CD-MOF-1 and CD-MOF-2 crystals did not show significant weight loss up to 175 °C and 200 °C respectively, indicating that the pores are fully evacuated while the frameworks are thermally stable. The permanent porosities of the activated CD-MOFs were demonstrated by measuring the N_2 gas adsorption of the guest-free samples. The isotherms (Figure 3) show steep N_2 uptake in the low-pressure regions

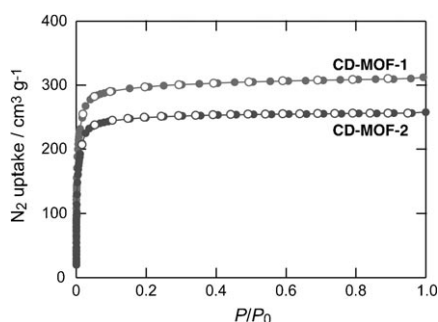


Figure 3. N_2 adsorption isotherms, for activated samples of CD-MOF-1 and CD-MOF-2 measured at 77 K. Filled and open symbols represent adsorption and desorption branches, respectively. Connecting traces are for guidance only.

($P/P_0 < 0.05$), an observation that indicates the microporosities of these materials, and the BET (Langmuir) surface areas for CD-MOF-1 and CD-MOF-2 are estimated to be 1220 (1320) and 1030 (1110) $m^2 g^{-1}$, respectively. This coverage corresponds to a measured pore density of $0.47 g cm^{-3}$, which is slightly lower than the theoretical pore density of $0.56 g cm^{-3}$ estimated from the crystal structure and is comparable to that reported in the recently published^[19] ZIF-95. X-Ray powder diffraction experiments on as-synthesized and solvent-free samples of CD-MOF-1 and CD-MOF-2 also confirm (Figure 4) that their structures remain intact upon activation.

Since it was not possible to locate H atoms associated with the OH groups on the γ -CD torus from the X-ray diffraction data, the precise nature of the ligands—either OH or O^- —coordinated to the alkali metal cations is difficult to determine directly. Charge balancing arguments are complicated by the commonly observed disorder of counterions and solvent molecules, on account of the vast openness of the CD-MOF structure.^[20] When potassium salts of 1H NMR-visible counterions, such as the benzoate monoanion and azoben-

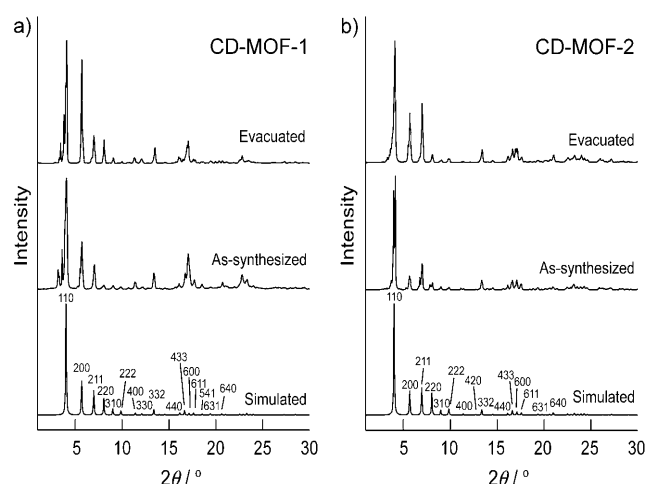


Figure 4. Powder X-ray diffraction patterns for evacuated (activated) and as-synthesized samples of a) CD-MOF-1, and b) CD-MOF-2, compared with calculated patterns derived from their crystal structures.

zene-4,4'-dicarboxylate dianion, are employed in the preparation of CD-MOF-1 (Figure 5a), the presence of these counterions can be detected by 1H NMR spectroscopy, following dissolution of the crystals in D_2O . The observation of a 2:1 ratio of benzoate anions to γ -CD units, and a 1:1 proportion in the case of the azobenzene-4,4'-dicarboxylate dianions, is in perfect agreement with the ratio of K^+ ions to γ -CD units in the crystal structure of CD-MOF-1. These experimental findings (see Supporting Information) support the conclusion that non-deprotonated γ -CD rings are coordinated to the K^+ ions in CD-MOF-1. This controlled inclusion of organic counterions into the CD-MOF-1 framework represents a simple, practical strategy for the derivatization of CD-MOFs. Also, the dissolution of CD-MOFs in H_2O is of particular interest since the framework simply dissociates into its precursor alkali metal salt and γ -CD and, upon vapor diffusion of MeOH, can be recrystallized, reforming the original CD-MOF. This property is atypical amongst porous materials, and has implications for the renewability and recyclability of CD-MOFs, with a potentially simple repair mechanism in place to renew the porosity of degraded samples.

Having established that organic anions can be incorporated inside CD-MOFs, the neutral small molecule storage capability of CD-MOF-2 was demonstrated using two different experimental approaches. Pre-crystallization addition of Rhodamine B to an aqueous methanolic solution of γ -CD and RbOH yielded single crystals, having an intense red color (Figure 5b). The presence of the dye within the framework was confirmed by 1H NMR spectroscopy (see Supporting Information). It transpires that four molecules of Rhodamine B frequent each $(\gamma\text{-CD})_6$ cube. As in the case of the

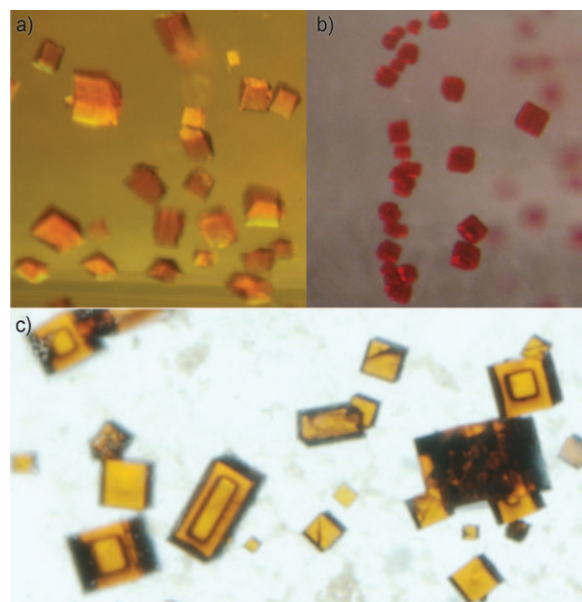


Figure 5. a) Orange crystals of CD-MOF-1 prepared with potassium azobenzene-4,4'-dicarboxylate. b) Red crystals of CD-MOF-2 co-crystallized with Rhodamine B. c) Orange crystals of CD-MOF-2 after activation and soaking in a solution of CH_2Cl_2 solution of 4-phenylazophenol for 24 h.

organic anions, X-ray crystallography established the existence of the underlying CD-MOF structure, but did not allow the pinpointing of the dye molecules within the extended framework—a situation which suggests neutral molecules are also highly disordered within the crystalline lattice. Likewise, when activated crystals of CD-MOF-2 were soaked for 24 h in a saturated solution of 4-phenylazophenol in CH_2Cl_2 (Figure 5c), ^1H NMR spectroscopy confirmed the post-crystallization uptake of the dye already suggested by visual inspection. Approximately four molecules of dye are absorbed into each $(\gamma\text{-CD})_6$ cube, a loading value commensurate with that observed in the Rhodamine B co-crystallization experiment.

The use of $\gamma\text{-CD}$ as a building unit results, in principle at least, in the placement of potential small molecule binding sites, or sorting domains,^[21] throughout the extended structure. However, in all the crystalline CD-MOFs obtained to date, we have been unable to locate all counterions or guest molecules definitively by X-ray crystallography, even when their presence was confirmed beyond any doubt by ^1H NMR spectroscopy.^[22] It follows that guest molecules and counterions tend to be disordered within the diverse collection of voids characteristic of the CD-MOF framework, and are not bound within the $\gamma\text{-CD}$ tori, which, in solution, are capable of hosting a prodigious variety of neutral and charged substrates by virtue of relatively strong interactions as a consequence of solvophobic/hydrophobic forces.^[8] The lack of bulk solvent, i.e., H_2O , within the CD-MOF frameworks may be detrimental to this mode of binding of organic molecules in the $(\gamma\text{-CD})_6$ cubes.

While CD-MOFs can be synthesized using chemicals and conditions that would be considered mild in the research laboratory setting, it can also be prepared from ingredients that can be obtained inexpensively in quality and purity suitable for food-grade applications. CD-MOF-1 can be assembled using $\gamma\text{-CD}$ and either salt substitute (KCl) or potassium benzoate (a common preservative, E212), certified as food-grade and readily available commercially, in molar ratios that are identical to the laboratory preparation of CD-MOF-1. Following dissolution in bottled distilled water, 190 proof grain alcohol (Everclear) replaces methanol in the crystallization process, and vapor diffusion yields colorless, cubic crystals, which are composed entirely from edible salts (KCl or potassium benzoate) and natural substances and products (water, ethanol, $\gamma\text{-CD}$). We believe that CD-MOFs constitute the forerunners of a large class of porous crystals which can be synthesized under benign conditions using building units derived from renewable natural products.

Experimental Section

CD-MOF-1: $\gamma\text{-CD}$ (1.30 g, 1 mmol) and KOH (0.45 g, 8 mmol) were dissolved in H_2O (20 mL). The aqueous solution was filtered and MeOH (ca. 50 mL) was allowed to vapor diffuse into the solution during the period of a week. Colorless cubic crystals (1.20 g, 66%), suitable for X-ray crystallographic analysis, were isolated, filtered and washed with MeOH (2×30 mL), before being left to dry in air. Elemental analysis (%) calcd for $[(\text{C}_{48}\text{H}_{80}\text{O}_{40})(\text{KOH})_2(\text{H}_2\text{O})_8(\text{CH}_3\text{OH})_8]_n$: C 37.2, H 7.33; found: C 37.2, H 7.24%. This elemental analysis data corresponds to 22% solvent composition by weight, a

percentage which is commensurate with thermogravimetric analytical data (see Supporting Information, Figure S1a) that show a weight loss of about 22% at 100°C. A sample was dried (see Supporting Information, Section S4). Elemental analysis (%) calcd for $[(\text{C}_{48}\text{H}_{80}\text{O}_{40})(\text{KOH})_2(\text{H}_2\text{O})_2]_n$: C 39.9, H 5.80; found: C 39.9, H 6.00.

CD-MOF-2: $\gamma\text{-CD}$ (1.30 g, 1 mmol) and RbOH (0.82 g, 8 mmol) were dissolved in H_2O (20 mL). The aqueous solution was filtered and MeOH (ca. 50 mL) was allowed to vapor diffuse into the solution during the period of a week. Colorless cubic crystals (1.25 g, 71%), suitable for X-ray crystallographic analysis, were isolated, filtered and washed with MeOH (2×30 mL) before being left to dry in air. Elemental analysis (%) calcd for $[(\text{C}_{48}\text{H}_{80}\text{O}_{40})(\text{RbOH})_2(\text{H}_2\text{O})_{11}(\text{CH}_3\text{OH})_2]_n$: C 34.0, H 6.40; found: C 34.1, H 6.32%. This elemental analysis data corresponds to 15% solvent composition by weight, a percentage which is commensurate with thermogravimetric analytical data (see Supporting Information, Figure S1b) that show a weight loss of about 15% at 100°C. A sample was dried (see Supporting Information, Section S4). Elemental analysis (%) calcd for $[(\text{C}_{48}\text{H}_{80}\text{O}_{40})(\text{RbOH})_2(\text{CH}_2\text{Cl}_2)_{0.5}]_n$: C 37.7, H, 5.42; found: C 37.8, H 5.24.

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- [14] Crystal data for CD-MOF-1: $K_2(C_{48}H_{80}O_{40})(OH)_2$, transparent cubes, $M_r = 1409.34$, crystal size $0.20 \times 0.20 \times 0.20$ mm, cubic, space group $I432$, $a = 31.006(8)$ Å, $V = 29807(14)$ Å³, $Z = 12$, $\rho_{\text{calcd}} = 0.942$, $S = 3.047$, $T = 93(2)$ K, $R_1(F^2 > 2\sigma F^2) = 23.91$, $wR2 = 0.5723$. The crystal data for CD-MOF-2: $Rb_2(C_{48}H_{80}O_{40})(OH)_2$, transparent cubes, $M_r = 1502.08$, crystal size $0.20 \times 0.20 \times 0.15$ mm, cubic, space group $I432$, $a = 31.0790(12)$ Å, $V = 30019(2)$ Å³, $Z = 12$, $\rho_{\text{calcd}} = 1.082$, $S = 2.678$ for 4515 reflections, $T = 93(2)$ K, $R_1(F^2 > 2\sigma F^2) = 11.47$, $wR2 = 0.3261$. Crystal data for CD-MOF-3: $Cs_2(C_{48}H_{80}O_{40})(OH)_2$, transparent cubes, $M_r = 1596.96$, crystal size $0.41 \times 0.31 \times 0.05$ mm, cubic, space group $I432$, $a = 30.868(10)$ Å, $V = 29411(16)$ Å³, $Z = 12$, $\rho_{\text{calcd}} = 0.813$, $S = 2.678$, $T = 93(2)$ K, $R_1(F^2 > 2\sigma F^2) = 21.28$, $wR2 = 0.5285$. The crystal data for “edible” CD-MOF-1 from potassium benzoate: $K_4(C_{96}H_{160}O_{80})(C_7H_5O_2)_2(OH)_2$, transparent cubes, $M_r = 3005.17$, crystal size $0.40 \times 0.35 \times 0.35$ mm, trigonal, space group $R32$, $a = 31.006(8)$, $c = 28.4636(5)$ Å, $\gamma = 120^\circ$, $V = 44842.8(9)$ Å³, $Z = 9$, $\rho_{\text{calcd}} = 1.002$, $S = 1.727$ for 7530 reflections, $T = 100(2)$ K, $R_1(F^2 > 2\sigma F^2) = 12.79$, $wR2 = 0.3814$. CCDC 773709 (CD-MOF-1), CCDC 773710 (CD-MOF-2), CCDC 773708 (CD-MOF-3), and CCDC 773711 (“edible” MOF) 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.
- [15] To the best of our knowledge, only one other set of X-ray diffraction data with a cubic cell has been reported for γ -CD in the literature and archived in the CCDC in 2004; see: D. Bonacchi, A. Caneschi, D. Dorignac, A. Falqui, D. Gatteschi, D. Rovai, C. Sangregorio, R. Sessoli, *Chem. Mater.* **2004**, 16, 2016–2020. Cubic-shaped orange-reddish single crystals of γ -Fe₂O₃/ γ -CD were isolated after an ethanolic solution of NaOH was added to a DMF solution of FeCl₃ and γ -CD: similar colorless cubic crystals were obtained when FeCl₃ was replaced by NaCl. In both cases, the researchers identified a cubic cell (space group $I432$) with a 30.217 Å edge, but were not able to determine the crystal structure of either compound. We are well-nigh certain that these γ -Fe₂O₃-doped (and undoped) crystals are isostructural with the CD-MOFs reported herein.
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- [20] Although CD-MOFs form more rapidly in the mildly basic aqueous solutions of alkali metal hydroxides at low concentrations when compared with neutral salts, the former conditions are not sufficiently basic ($pK_a \approx 13$) to deprotonate the OH groups of γ -CD.
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- [22] In one case, when potassium benzoate was employed as the K⁺ ion source, we were able to locate 50% of the benzoate counterions by X-ray diffraction. The remaining 50%, however, were disordered. See the Supporting Information.