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Multinuclear Zinc Pentafluorobenzene Carboxylates: Synthesis, Characterization, and Hydrogen Storage Capability

Carl Redshaw,*,† Surajit Jana,† Congxiao Shang,† Mark R. J. Elsegood,‡ Xuesong Lu,§ and Zheng Xiao Guo§

†*Energy Materials Laboratory, School of Chemistry and School of Environmental Sciences, The University of East Anglia, NR4 7TJ, U.K.,* ‡*Chemistry Department, Loughborough University, Loughborough, Leicestershire, LE11 3TU, U.K., and* §*Department of Chemistry, University College London, WC1H 0AJ, U.K.*

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Summary: Three zinc carboxylate complexes, $[(C_6F_5Zn)_4Zn(Ar^1)_6]\cdot 1.5$*toluene,* $[(C_6F_5Zn)_4Zn(Ar^2)_6]\cdot 2$*toluene, and* $[(Ar^3)_6Zn_4(\mu_4\text{-}O)]\cdot MeCN$ *(where* Ar^1 *= 2-chlorobenzoic acid (**1**),* Ar^2 *= 2,4,6-trimethylbenzoic acid (**2**), and* Ar^3 *= 3-dimethylaminobenzoic acid (**3**)), have been prepared from the reaction of* $(C_6F_5)_2Zn\cdot$*toluene and the corresponding functionalized benzoic acid. Complexes **1**−**3** were structurally characterized and screened for hydrogen absorption (uptake < 0.3 wt %).*

Zinc carboxylates are of great interest owing to their role in biochemical systems, catalysis, and materials chemistry. For instance, alkoxyzinc carboxylates are attracting attention owing to their importance as highly active catalysts for the polymerization or copolymerization of a wide range of organic monomers.[1] Recently, they have been utilized as structural units/nodes in metal−organic polymers (MOPs) and frameworks (MOFs); such systems have shown promising adsorption behavior with a variety of small molecules including methane, nitrogen, and hydrogen.[2−4] A variety of related alkylzinc complexes containing carboxylate-based ligands have also been prepared, most notably alkyl(R)zinc carbamato complexes, $[RZn(O_2CNR'_2)]$, and alkylzinc carboxylates for which the carboxylate group contains a second coordinating functionality, $[RZn(O_2CR'X)]$ (X = OH, NH_2, SH).[5−8] The alkylzinc carbamato species, prepared by CO_2 insertion into Zn−N bonds, form discrete tetramers of the type $[MeZn(\mu_3\text{-}O_2CNR'_2)]_4$, which become dimers of the form $[MeZn(\mu_2\text{-}O_2CNR'_2)(py)]_2$ on the addition of pyridine (py) (NR'_2 = $N(iPr)_2$, $N(iBu)_2$, and piperidinyl). Dickie et al. reported the reaction of diethylzinc with 2,6-bis(2,4,6-trimethylphenyl)benzoic acid, in which the bulky carboxylate groups enforce a low coordination number at the metal centers, leading to dimeric $[EtZn(\mu_2\text{-}O_2CR)]_2$.[9] Mitzel et al. reported the pentanuclear zinc hydroxylamide cluster $[(iPrZn)_4Zn(ONMe_2)_6]$,[10] comprising an octahedral-based structure with all six O,N ligands O-bound to the central Zn^{2+}; similar findings were observed in the cadmium hydroxylamide cluster $[(MeCd)_4Cd(ONEt_2)_6]$.[11] Lewinski et al. reported the alkylzinc carboxylate $[EtZn(O_2CPh)]_6$, a precursor to zinc oxocarboxylates $[Zn_4O(O_2CPh)_6]$ and the sulfidocarboxylates $[Zn_3(\mu_3\text{-}S)(OOCPh)(thf)]_2$.[12] The double tetrahedral core complex $[Zn_7O_2(O_2CMe)_{10}(1\text{-}Meim)_2]$ (1-Meim = 1-methylimidazole) has been isolated from the reaction of $Zn(OAc)_2\cdot H_2O$ and 1-methylimidazole in refluxing acetonitrile.[13] More recently, Shaffer and Williams et al. reported the pentanuclear alkylzinc carboxylate $[Zn_5(O_2CCH_3)_6(Et)_4]$, formed by the reaction of diethylzinc with zinc acetate.[14]

In zinc-based MOFs such as MOF-5 (derived from terephthalic acid and zinc(II) ions), there has been much discussion as to where the hydrogen is adsorbed. For example, neutron powder diffraction and first-principles calculations, backed up by other studies, revealed that the zinc oxide node was primarily responsible for H_2 uptake, with the organic linker playing only a secondary role.[15] Given the aforementioned utility of zinc carboxylate clusters as nodes in MOF construction and the reports that the node was pivotal to H_2 adsorption, we have embarked upon a program of synthesizing and screening potential new nodes. Here, we report three new zinc carboxylate complexes, prepared via the reaction of $(C_6F_5)_2Zn\cdot$toluene with functionalized benzoic acids, namely, 2-chlorobenzoic acid, 2,4,6-trimethylbenzoic acid, and 3-dimethylaminobenzoic acid. Crystal structure determinations reveal, in the first two cases, rare pentanuclear structural motifs (see Scheme 1), while in the latter case, the structure is

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*Corresponding author. E-mail: carl.redshaw@uea.ac.uk.

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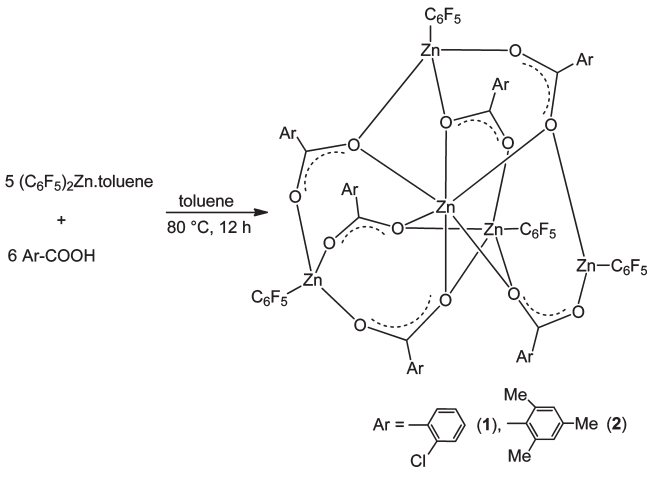
Scheme 1



akin to the $Zn_4(\mu_4\text{-}O)$ building block that has been employed to great effect by Yaghi and others.[2−4]

A diagram of the core (for **1**) is shown in Figure 1 and reveals how the peripheral zinc atoms form a tetrahedron. Each of these zinc centers is four-coordinate and possesses a C_6F_5 group. The six carboxylate groups link the four zinc ions approximately along the edges of the tetrahedron. For each of the carboxylate groups, one oxygen bonds to only one of Zn(2)−Zn(5), while the other oxygen bridges one of Zn(2)−Zn(5) plus the central, pseudo-octahedral, zinc (Zn(1)) center. The Zn−O bonds in **1** [1.975(3)−2.135(2) Å] are similar to those reported in $[Zn_5(OAc)_6(Et)_4]$ [1.997(2)−2.1695(17) Å][14] and $[(i\text{PrZn})_4Zn(ONMe_2)_6]$ (1.974(2)−2.205(2) Å),[10] with those to the central Zn(1) [2.061(2)−2.135(2) Å] being generally longer than those to the four-coordinate zinc ions [1.975(3)−2.099(2) Å]. There are four significant pairwise intramolecular $\pi-\pi$ interactions involving a C_6F_5 ring with a chlorobenzene ring with significant C···C separations in the range 3.25 to 3.60 Å. There are also a number of intermolecular $\pi-\pi$ interactions, parallel to the *b* axis, whereby the aforementioned intramolecular $\pi-\pi$ stacked rings form extended stacks, effectively linking the structure into a 3D supramolecular network. There are also two significant F···F interactions between molecules, namely, F(11)···F(17) [2.825 Å] and F(3)···F(12) [2.756 Å]. Two types of solvent-filled voids are present between the clusters. In the first void, there are two well-defined toluene molecules, which were modeled as point atoms. Half a toluene molecule per cluster was disordered across a center of symmetry and was poorly resolved, so it was modeled with the Platon Squeeze procedure.[16] Overall, therefore, there are 1.5 molecules of toluene per zinc cluster.

For **2**, there is one zinc complex and two molecules of toluene in the asymmetric unit. The pentanuclear core is closely related to that in **1**, although in this case, the Zn−O bonds to the central zinc ion (Zn(1)) [2.092(2)−2.191(2) Å] are significantly longer than those to the four-coordinate zinc centers [1.971(3)−2.086(2) Å]. There are four significant groups of intramolecular interactions involving the aromatic rings, which either pair up or in threes and align in almost parallel fashion via $\pi-\pi$ interactions with closest C···C separations in the range 3.22 to 3.60 Å (see Figure 2).

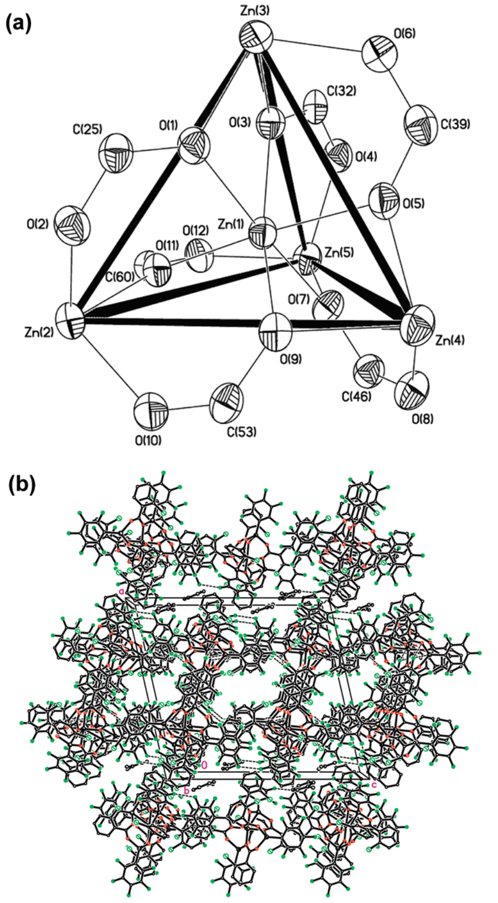


Figure 1. (a) Core structure of **1** highlighting the approximately tetrahedral arrangement of the peripheral zinc atoms {note: thick black lines are not bonds}. Ellipsoids are drawn at the 50% probability level. (b) Packing of **1**.

In the case of 3-dimethylaminobenzoic acid, repeated reactions under similar conditions failed to yield clean products, and so the reaction stoichiometry was changed in favor of excess zinc. Following a similar workup, a complex possessing only four zinc centers was isolated in good yield as small colorless crystals suitable for an X-ray crystallographic study using synchrotron radiation. Interestingly, the core resembled that found in **1** and **2**, except that the central pseudo-octahedral zinc was now missing (Figure 3), and instead the position is occupied by a $\mu_4\text{-}O^{2-}$. This central oxo group is thought to result from trace water in the reaction solvent. The Zn−O bonds to the central oxygen atom (O(1)) [1.925(2)−1.940(2) Å] are similar in length to the Zn−O bonds involving the carboxylate groups. We note that Pálinko et al. have recently prepared a range of $Zn_4O(\text{acid})_6$ complexes using ZnO, acid, and water.[17]

The zinc complexes were screened for hydrogen uptake at the isothermal temperature of 90 K. MOF-5 was employed as the reference material and was prepared according to the method of Deng et al.[18] The isothermal adsorptions of hydrogen on materials **1**−**3** and MOF-5 were tested as a function of pressure (*P*); see Figure 4. For all three complexes (Figure 4b), there was a near linear increase in uptake with increasing pressure. At 90 K and 9 bar, the hydrogen uptake of freshly prepared MOF-5 was found to be 2.82 wt %, which

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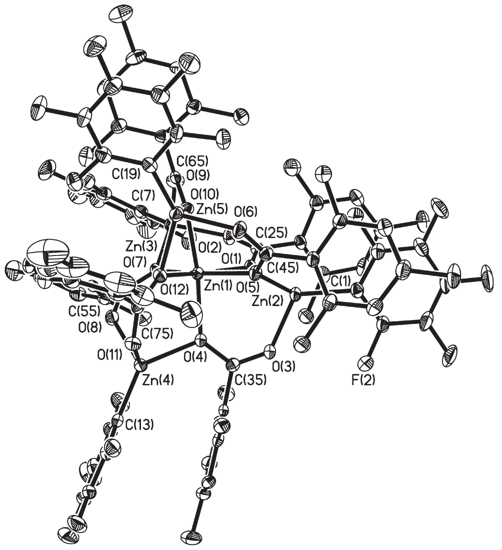

Figure 2. Molecular structure of **2** with ellipsoids drawn at the 40% probability level.

is comparable with the literature,[19] while the absorption for **1** was 0.27 wt %, **2** was 0.07 wt %, and **3** was 0.02 wt %; see Table 1. Although the hydrogen uptake of the prepared zinc complexes is somewhat lower than that of MOF-5, it is promising for this group of structures that hydrogen uptake can be improved substantially through modification of peripheral functional groups. For example, the performance of the zinc complex **1**, bearing the electronegative Cl on the substituents, versus **2** and **3** is an order of magnitude higher (0.27 wt % for **1** versus 0.07 wt % uptake for **2**) under the conditions employed (90 K/9 bar). We note that fluorinated MOFs have been shown to exhibit favorable electrostatic interactions with gases.[20]

In summary, complexes **1** and **2** are rare examples of pentanuclear zinc complexes and the first to be derived from arylcarboxylate ligands to adopt such a core. Complex **3** is a member of the Zn_4O family, which are attracting great attention as building blocks for MOF construction. Screening for hydrogen storage using the zinc clusters **1**−**3** as hosts indicated that uptake is not very promising (<0.3 wt % uptake), compared with a complete MOF structure (MOF-5 uptake 2.82 wt %), but can be controlled by ligand modification. The results suggest that the hydrogen is more likely to be adsorbed along the MOF cavities, rather than on specific binding sites.

Experimental Section

General Procedures. All manipulations involving zinc were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glovebox. Solvents were refluxed over an appropriate drying agent and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the School of Chemistry at The University of East Anglia. NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400 or a Gemini at 300 MHz (^1H) and 282.4 MHz (^{19}F) at 298 K; chemical shifts are referenced to the residual protio impurity of the deuterated solvent. IR spectra (Nujol mulls, KBr/CsI windows) were obtained on Perkin-Elmer 577 and 457 grating spectrophotometers. $(C_6F_5)_2Zn\cdot$toluene was prepared by the method of Bochmann.[21] All other chemicals were obtained commercially and used as received unless stated otherwise.

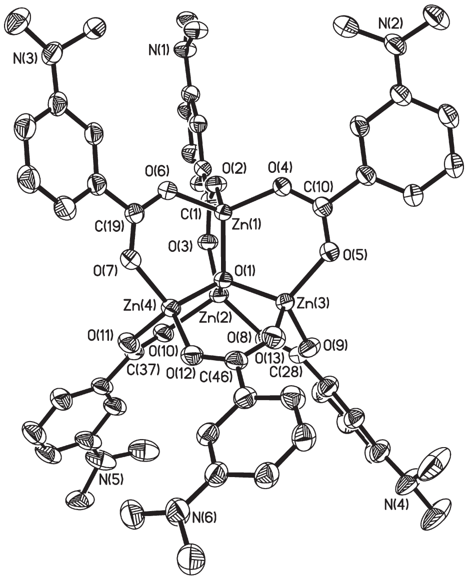

Figure 3. Molecular structure of **3** with ellipsoids drawn at the 40% probability level.

Synthesis of 1. 2-Chlorobenzoic acid (0.38 g, 2.43 mmol) and $(C_6F_5)_2Zn\cdot$toluene (1.00 g, 2.03 mmol) were heated at 80 °C for 12 h in toluene (30 mL). Following removal of volatiles *in vacuo*, the residue was extracted into hot toluene (20 mL). The colorless solution was stored at −20 °C to afford colorless block-shaped crystals of **1**. Yield: 0.65 g (80%). ^1H NMR ($CDCl_3$, 298 K): δ 7.98−7.04 (m, aryl H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz, 298 K): δ 133.2, 131.6, 131.4, 131.2, 130.9, 130.0, 129.5, 125.3, 125.1 (s, aryl C). ^{19}F NMR ($CDCl_3$, 298 K): δ −139.9 (m, 8 F, *o*-F), −154.8 (triplet of triplet, $^3J_{FF}$ = 17.7 Hz, $^4J_{FF}$ = 2.5 Hz, 4 F, *p*-F,), −163.2 (m, 8 F, *m*-F). IR (Nujol mull): ν 629 (vs), 1563 (s), 1506 (vs), 1265 (s), 1158 (s), 1072 (s), 1055 (s), 954 (vs), 863 (w), 795 (w), 754 (s) cm^{-1}. Anal. Calcd for $C_{66}H_{24}Cl_6F_{20}O_{12}Zn_5$ (sample dried *in vacuo* for 12 h, − 1.5 toluene): C 41.10, H 1.25. Found: C 40.74, H 1.08. MS: 1438 ($M^+ - 2C_6F_5 - ClC_6H_4CO_2H$), 1373 ($M^+ - 2C_6F_5 - ClC_6H_4CO_2H - Zn$).

Synthesis of 2. 2,4,6-Trimethylbenzoic acid (0.44 g, 2.68 mmol) and $(C_6F_5)_2Zn\cdot$toluene (1.10 g, 2.23 mmol) were heated at 80 °C for 12 h in toluene (30 mL). Following removal of volatiles *in vacuo*, the residue was extracted into hot toluene (20 mL). The colorless solution was stored at −20 °C to afford crystals of **2**. Yield: 0.72 g (75%). ^1H NMR ($CDCl_3$, 298 K): δ 7.20−6.49 (m, 17 H, aryl H + aryl $H_{toluene}$), 2.31 (brs, 30 H, aryl $H_{o\text{-}Me}$), 2.26 (brs, 6 H, aryl $H_{o\text{-}Me}$), 1.93 (s, 6 H, aryl H_{Me} + aryl $H_{toluene}$), 1.19 (brs, 15 H, aryl H_{Me}). ^{19}F NMR ($CDCl_3$, 298 K): δ −116.1 (d, $^3J_{FF}$ = 21.3 Hz, 8 F, *o*-F), −159.6 (t, $^3J_{FF}$ = 19.4 Hz, 4 F, *p*-F,), −164.7 (m, 8 F, *m*-F). IR (Nujol mull): ν 1617 (br), 1566 (s), 1505 (vs), 1263 (s), 1182 (s), 1110 (s), 1057 (s), 954 (vs), 848 (w), 791 (w), 735 (s) cm^{-1}. Anal. Calcd for $C_{98}H_{82}F_{20}O_{12}Zn_5$: C 54.53, H 3.83. Found: C 54.40, H 3.84. MS: 1413 ($M^+ - C_6F_5 - 2Me_3C_6H_2CO_2 - Zn$), 1282 ($M^+ - C_6F_5 - 2Me_3C_6H_2CO_2 - 3Zn$).

Synthesis of 3. 3-Dimethylaminobenzoic acid (0.23 g, 1.38 mmol) and $(C_6F_5)_2Zn\cdot$toluene (1.10 g, 2.23 mmol) were heated under reflux in toluene (30 mL) for 4 h. Following removal of volatiles *in vacuo*, the residue was extracted into acetonitrile

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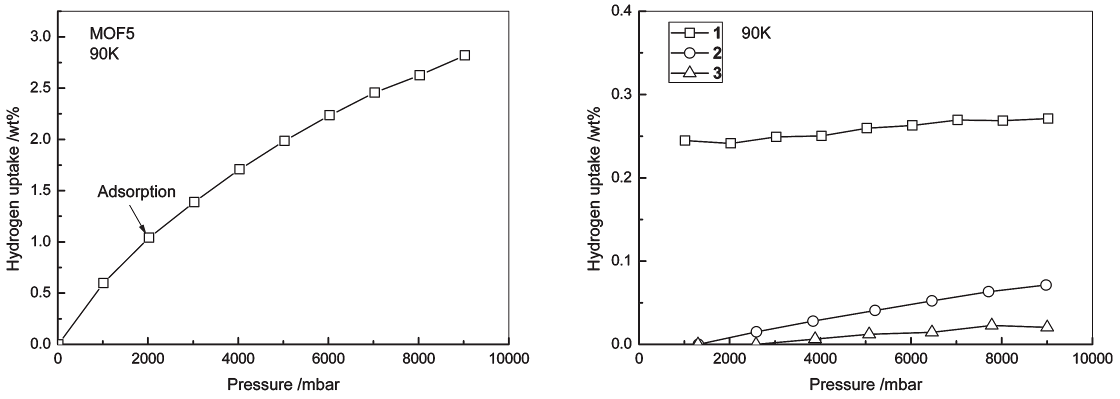

(a) MOF-5

(b) Zinc nodes **1**, **2** and **3**.

Figure 4. H_2 uptake of samples at 90 K: (a) MOF-5; (b) zinc nodes **1**, **2**, and **3**.

Table 1. Maximum Hydrogen Uptakes of MOFs in wt % at 9 bar

material	H_2 uptake/ wt%	temperature/ K	pressure/ bar	calcd density/ g/cm^3	equipment
MOF-5	2.82	90	9	1.92	IGA-003, static
zinc node **1**	0.27	90	9	1.80	IGA-003, static
zinc node **2**	0.07	90	9	1.56	IGA-003, static
zinc node **3**	0.02	90	9	1.75	IGA-003, static

(20 mL). The yellowish solution was allowed to stand at −20 °C, affording crystals of **3**. Yield: 0.23 g (77%, based on acid). ^{1}H NMR (CDCl$_3$, 298 K): δ 7.54 (m, 12H, aryl*H*), 7.24 (m, 6H, aryl*H*), 6.86 (m, 6H, aryl*H*), 2.96 (s, 36H, N*Me*$_2$), 1.98 (s, 3H, *Me*CN). IR (Nujol mull): ν 1626 (m), 1603 (w), 1588 (m), 1574 (m), 1505 (m), 1403 (s), 1261 (s), 1234 (w), 1182 (w), 1094 (bs), 1072 (s), 1051 (s), 1020 (s), 953 (m), 867 (w), 801 (s), 760 (m), 722 (w), 684 (w), 670 (w) cm^{-1}. Anal. Calcd for $C_{56}H_{63}N_7O_{13}Zn_4$: C 51.59, H 4.87, N 7.52. Found: C 51.41, H 4.83, N 7.38. MS ((EI): 1262 (M$^+$), 1096 (M$^+$ − $NMe_2C_6H_4CO_2$), 932 (M$^+$ − $2NMe_2C_6H_4CO_2$).

X-ray Structure Analysis. All crystals were transferred from Schlenk tubes under an inert atmosphere into an inert oil and mounted onto a glass fiber using the oil drop technique. All were solvent dependent.

Crystal data for 1: $C_{76.5}H_{36}Cl_6F_{20}O_{12}Zn_5$, M = 2066.60, monoclinic, $P2_1/c$, a = 23.311(2) Å, b = 13.5883(12) Å, c = 25.442(2) Å, β = 102.7617(13)°, V = 7859.9(11) Å^3, Z = 4, D_c = 1.746 g cm^{-3}, μ(Mo Kα) = 1.816 mm^{-1}, T = 150(2) K, colorless block; 72 086 reflections measured on a Bruker APEX 2 CCD diffractometer, of which 17 393 were independent (R_{int} = 0.0482), data corrected for absorption on the basis of symmetry equivalent and repeated data (min. and max. transmission factors: 0.603, 0.839) and *Lp* effects, structure solved by direct methods, F^2 refinement, R_1 = 0.0473 for 12 397 data with $F^2 > 2\sigma(F^2)$, wR_2 = 0.1370 for all data, 1046 parameters. One toluene molecule per Zn_5 cluster well defined and modeled with point atoms, half a toluene molecule per cluster badly disordered, so modeled as a diffuse region of electron density by the Platon Squeeze procedure.[16] Squeeze recovered ca. 47 electrons in a void of ca. 225 Å^3, which is consistent with 50 electrons in one toluene molecule.

Crystal data for 2: $C_{98}H_{82}F_{20}O_{12}Zn_5$, M = 2158.48, triclinic, $P\bar{1}$, a = 14.3253(9) Å, b = 16.3138(10) Å, c = 25.7460(14) Å, α = 106.5017(10)°, β = 98.0313(10)°, γ = 110.5396(10)°, V = 4600.0(5) Å^3, Z = 2, D_c = 1.558 g cm^{-3}, μ(Mo Kα) = 1.387 mm^{-1}, T = 150(2) K, colorless block; 43 221 reflections measured as above; 20 247 independent (R_{int} = 0.0548), data corrected as above (min. and max. transmission factors: 0.779, 0.809), structure solved by direct methods, F^2 refinement, R_1 = 0.0467 for 12 167 data with $F^2 > 2\sigma(F^2)$, wR_2 = 0.1092 for all data, 1237 parameters.

Crystal data for 3: $C_{56}H_{63}N_7O_{13}Zn_4$, M = 1303.61, triclinic, $P\bar{1}$, a = 10.635(3) Å, b = 12.927(4) Å, c = 21.656(6) Å, α = 81.727(3)°, β = 84.749(3)°, γ = 77.053(3)°, V = 2865.9(14) Å^3, Z = 2, D_c = 1.511 g cm^{-3}, λ = 0.6889 Å, μ = 1.589 mm^{-1}, T = 120(2) K, colorless plate; 37 270 reflections measured on Station I19 at the Diamond Light Source using a Rigaku Saturn 724+ detector on a Crystal Logics diffractometer; 9917 independent (R_{int} = 0.0342), data corrected as above (min. and max. transmission factors: 0.832, 0.992), structure solved by direct methods, F^2 refinement, R_1 = 0.0333 for 8350 data with $F^2 > 2\sigma(F^2)$, wR_2 = 0.0976 for all data, 787 parameters. Atoms C(30), C(31), C(32), C(35), C(36), and N(4) were modeled as disordered over two sets of positions with major occupancy = 58.6(5)%. Geometric and displacement parameter restraints were applied to help model this group.

Hydrogen Absorption Analysis. The hydrogen uptake method was referred to in ref 22. The hydrogen sorption was measured from 0 to 10 bar at the isothermal temperature of 90 K for all the materials, using a gas sorption analyzer, IGA-003 (Hiden Isochema, Warrington, UK). Static mode was applied for all the measurements. The buoyancy effect was corrected according to the hydrogen and sample densities. The Peng−Robinson gas-state equation was used.[23] MOF-5 has been studied in the past for hydrogen uptake by other research groups.[24] Here it was prepared and tested in our laborotory as reference sample to compare with other materials for hydrogen storage.

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Supporting Information Available: 40% ellipsoid plot for **1**, selected bond lengths and angles for **1**−**3**, and CIF files are available free of charge via the Internet at http://pubs.acs.org.

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