Dear Jon

Thank you for you message of 13 April 2015 concerning ID CC-COM-04-2015-002719. We have revised the manuscript as follows:

- Typographical errors have been corrected in the manuscript text and references
- CCDC numbers have been added to the manuscript as a footnote
- CHN analysis and FTIR data have been added to the ESI

We therefore believe that we have addressed the issues raised by the reviewers and look forward to your final decision.

Sincerely

Mike Zaworotko

ARTICLE TYPE

A New Family of Anionic Organic-Inorganic Hybrid Doughnut-Like Nanostructures†

Zhuxiu Zhang [a], **Wen-yang Gao** [b], **Lukasz Wojtas** [b], **Zhenjie Zhang** [b] and **Michael J. Zaworotko** [a]

A family of soluble organic-inorganic hybrid doughnut-like anions, hy-doughnuts, has been prepared by self-assembly of polyoxovanadate anions and 1,3-benzenedicarboxylate, bdc, linkers. Derivatives of the parent hy-doughnut,
10 **$[(V_4O_8Cl)_4(bdc)_8]^{4-}$, can be obtained by changing the counter-ion or by using a variant of bdc.**

Macrocyclic compounds[1] such as cyclams[2], crown-ethers[3], calixarenes[4] and their inorganic counterparts[5] are an extensively developed aspect of contemporary supramolecular chemistry.
15 Molecular compounds that can serve as "doughnut-shaped" hosts (cyclodextrins[6], cucurbiturils[7], calixarene assemblies[4(d)] and pillararenes[8]) are of particular interest in the area of supramolecular host-guest chemistry[9]. The nature of doughnut-shaped compounds is that they exhibit intrinsic porosity (Fig. 1)
20 and their versatile interior and exterior surfaces means that they can be fine-tuned for applications such as drug delivery,[6(c),7(e),8(c)] and recognition[6(a),7(d),8(b)]. Polyoxometalates (POMs)[10] are a class of compound typically comprised of early-transition metals in higher oxidation states (e.g. V^{5+}, $Mo^{5+,6+}$) bridged by oxygen
25 anions. They can exist as purely inorganic doughnuts or "nano-wheels"[11] which are typically prepared by reaction of the appropriate metal oxide (MO_x) under carefully controlled conditions that address pH, concentration and the presence of a reducing agent and/or template. In this contribution we introduce
30 a new class of hybrid organic-inorganic doughnut structure or metal-organic material (MOM)[12] that bridges these two classes of doughnut compound.
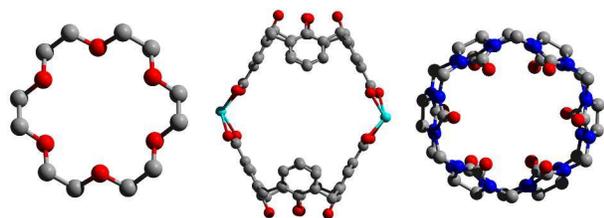
Fig. 1 Macrocyclic molecular structures are exemplified by 18-crown-6-
35 ether (left), a metal-organic calixarene dimer (middle) and cucurbituril, a doughnut-shaped molecule (right)

MOMs are usually constructed by linking metals or metal clusters by a poly-functional organic ligand. Their modular nature and the potential for extra-large porosity have captured the imagination of

40 materials scientists and their amenability to crystal-engineering[13] has enabled the rational design of new 3D structures using a "node-and-spacer" approach.[12] Importantly, the ability to pre-select nodes and spacers enables control over pore size and chemistry that in turn facilitates target specific properties for
45 important sorbates such as CO_2 and CH_4. The same approach has also enabled the design of 0D structures such as polyhedral[15] and doughnut-like[14] structures. For example, the synthesis of a "coordination macrocycle/doughnut" was recently reported by Barbour et al., who exploited Ag(I) cations linked by ditopic
50 angular ligands[14(a),14(b)]. Most recently, our group reported that polyoxovanadates (POVs) and 1,3,5-benzenetricaboxylate (btc) could be used as molecular building blocks (MBBs) to construct cage-like organic-inorganic hybrid nanoballs (hyballs)[15(f)]. It occurred to us that the use of bdc 2-connected linkers instead of
55 btc 3-connected nodes might facilitate the generation of a very different type of compound, a doughnut-like nanostructure that represents a new class of hybrid materials (Fig. 2). We herein introduce the prototypal **hydoughnut** which is based upon a well-known POV, $[V_4O_8Cl(COO)_4]^{1-}$, linked by bdc anions.
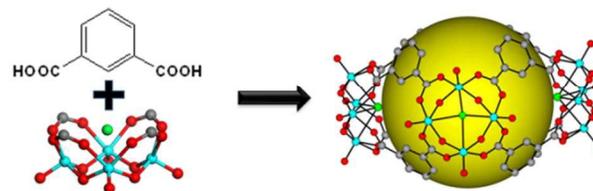
60
Fig. 2 The prototypal hydoughnut, **hydoughnut-1**, is constructed from 4-connected polyoxovanadate MBBs that are vertex-linked by bdc anions.

Single crystals of DMA_**hydoughnut-1**, $[(V_4O_8Cl)_4(1,3-bdc)_8](NH_2Me_2)_4)$•[solvent] (solvent = DMF, H_2O) were prepared
65 by reaction of 1,3-H_2bdc with VCl_3 in DMF and H_2O (10:1) at 85 ºC over 3 days. A single crystal x-ray diffraction (SCXRD) study revealed that DMA_**hydoughnut-1** adopts the monoclinic space group $P2_1$/a with a=21.2958(6) Å, b=21.3300(6) Å, c=21.9581(6) Å, β=105.8678(13)°. The bulk purity of DMA_**hydoughnut-1**
70 and other compounds reported herein was verified by comparing the calculated and experimental X-ray powder diffraction patterns (Figs S1-S4). **Hydoughnut-1** is comprised of four POVs linked by eight bdc ligands. The four vanadium cations of each POV are co-planar and they are each bridged by a μ_2-O^{2-} anion (d(V-
75 O)=1.797(4)~1.824(6)Å) and a carboxylate moiety (d(V-

O)=2.027(5)~2.047(5)Å). They are also bonded to a μ_4-Cl$^-$ anion that lies below the plane of the four V cations (d[V-Cl] = 2.819(2)-2.880(2) Å). Each V cation is also bonded to a terminal oxygen atom with V=O distances ranging from 1.598(6) to 5 1.613(6) Å. The distance between two Cl atoms across the resulting cavity is ~1.2nm in diameter with a volume of ca. 519 Å^3 after van der Waals distances are taken into account. Adjacent **hydoughnut-1** anions form sheets in the *ab* plane in which they lie perpendicular to another in such a manner that a POV moiety 10 of a given **hydoughnut-1** lies above and below the centre of windows of adjacent **hydoughnut-1** anions (Fig. 3a). This crystal packing motif is sustained by hydrogen bonding between phenyl CH atoms and bridging μ_2-O moieties. C⋯O distances lie in the range 3.145(10) to 3.186(11)Å (Fig S9), which is consistent with 15 what would be expected for CH⋯O hydrogen bonds.[16(a),16(b)] These sheets are in turn cross-linked by disordered DMA cations in a nearly eclipsed fashion along the c direction *via* charge-assisted HN–H⋯O hydrogen bonds(d[N-O]=3.075(11)Å) and CH⋯O bonds(d[C-O]=3.263(7)Å) (Figs 3b, S10). In addition, 20 free $[NH_2Me_2]^+$ cations lie close to POV clusters to balance the overall charge.
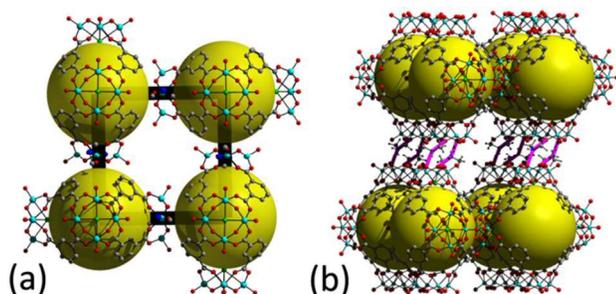
Fig. 3 (a) Sheets of **hydoughnut-1** anions lie in the *ab* plane; (b) Crystal packing of sheets is sustained by cross-linking of **hydoughnut-1** anions 25 by $NH_2Me_2^+$ cations *via* charge-assisted H-bonding.

Similar conditions to those utilized to prepare **hydoughnut-1** except a different solvent system (DEF/H$_2$O) afforded single crystals of DEA_**hydoughnut-1**, $[(V_4O_8Cl)_4(1,3$-bdc)$_8](NH_2Et_2)_4$•[solvent]. SCXRD analysis revealed that 30 DEA_**hydoughnut-1** crystallizes in I4/mmm with a = b = 14.9098(9)Å, c=38.069(2)Å. DEA_**hydoughnut-1** carboxylate groups are disordered over three places and the site occupancies of C_1, C_2 and C_3, are refined as 0.5, 0.5 and 1.0 respectively (Fig S11), which means that **hydoughnut-1** monomers lie 35 perpendicular to each other in the *ab* plane.(Fig. 4a). This is feasible because the distance between C_4 and the centroid of two adjacent vanadium atoms is ~3.8Å, rendering bdc with the freedom to use either hydrogen bonding similar to that observed in hydoughnut-1 or one of its carboxylate groups to bond to 40 adjacent POVs. The distance between the C_4 atom of bdc ligands (Fig S11) and adjacent μ_2-O moieties from POVs is 3.083(11)Å, which is in accordance with expected values.[16(a),16(b)] A sheet of **hydoughnut-1** anions thereby form in the *ab* plane sustained by hydrogen bonding between phenyl CH atoms and bridging μ_2-O 45 moieties (Fig S12). The sheets stack in an ABAB arrangement along the *c axis via* charged assisted h-bond between diethylammonium cations and POVs (Fig 4b, S13). There are no HN–H⋯O interactions between DEA and POVs, but there are

CH⋯O interactions of 3.126(2)Å. Additionally, free DEA 50 cations and solvent molecules occupy the void space to balance the charge of each **hydoughnut-1** anion.
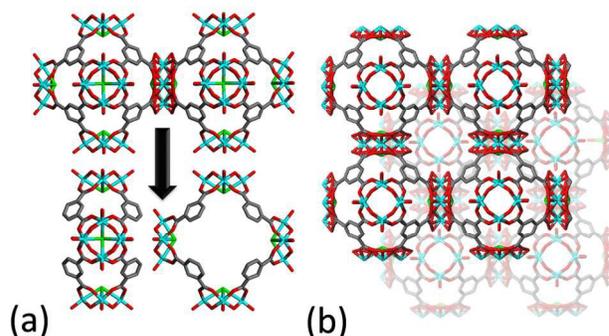
Fig. 4 (a) packing of **hydoughnut-1** anions in a perpendicular arrangement; (b) sheets of **hydoughnut-1** anions pack in ABAB fashion.

55 A variant of **hydoughnut-1**, DMA_**hydoughnut-2**, was prepared under similar conditions to those used to prepare DMA_**hydoughnut-1** but with 5-bromo-benzenedicarboxylate linkers, 5-Br-bdc, instead of bdc. Analysis of SCXRD revealed that DMA_**hydoughnut-2** crystallizes in the triclinic space group 60 *P*-1 with a=15.1975(5) Å, b=19.1532(6) Å, c=19.3115(6) Å, α= 103.8173(18)°, β=95.3294(16)°, γ=98.3478(17)°. The structure of the each **hydoughnut-2** anion is similar to **hydoughnut-1** except that the window of **hydoughnut-2** is smaller than **hydoughnut-1** because of the presence of Br atoms in position 5 of the bdc 65 linkers (Fig. 5a). The crystal packing in DMA_**hydoughnut-2** is different from that seen in the structures of **hydoughnut-1**. The *a* direction is sustained by Br⋯O interactions of 3.199(8)Å. The C-Br⋯O angle is 154.2(4)° and V-O⋯Br angle is 175.2(4)°, consistent with directional polarization of bromine atoms (Fig. 70 S14)[16(c),16(d)] There are two crystallographically independent DMA cations in the asymmetric unit, but no NH⋯O interactions were observed between DMA cations and POVs. Rather, each **hydoughnut-2** anion is surrounded by ten DMF molecules. In the *a* and *b* directions, **hydoughnut-2** anions pack in an eclipsed 75 manner. Two DMF molecules locate in the void between two adjacent hydoughnuts (Fig. S15). In addition, DMF molecules lie between adjacent POVs in the *bc* plane (C⋯O = 3.173(4)-3.196(9) Å, Fig. S16). The consequence of these interactions is a distorted **pcu** net (Fig. 5b). The internal cavity of **hydoughnut-2** anions is 80 ~486 Å^3.

A second variant of **hydoughnut-1**, DMA_**hydoughnut-3**, was prepared under similar conditions to those used to prepare DMA_**hydoughnut-1** but with 5-methoxy-benzenedicarboxylate linkers, 5-MeO-bdc, instead of bdc. $[(V_4O_8Cl)_4(5-MeO-$ 85 1bdc)$_8](NH_2Me_2)_8Cl_4$•[DMF$_1$H$_2$O$_{10}$]) crystallizes in the triclinic space group *P*-1 with a=14.9214(6)Å, b=16.0334(7)Å, c=16.7794(7)Å, α= 79.476(2)°, β=82.828(3)°, γ=81.284(2)°. Crystal packing similar to that seen in DMA_**hydoughnut-2** is supported by CH⋯O and NH⋯O interactions and also affords a 90 distorted **pcu** net (Fig. S17).
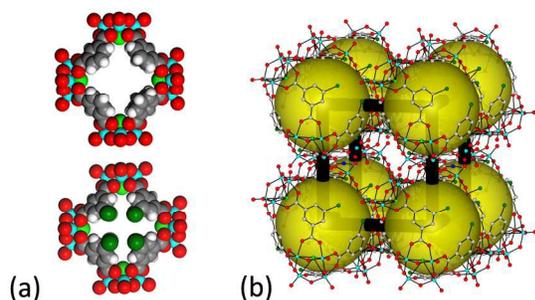
Fig. 5 (a) Comparison of the windows in **hydoughnut-1 (**above**)** and **hydoughnut-2 (**below**)** anions in space-filling mode; (c) Packing of **hydoughnut-2** anions as a **pcu** net.

Thermogravimetric analysis (Fig. S4, S5 and S6) revealed that DMA_**hydoughnut-1** and DMA_**hydoughnut-2** exhibit similar thermal stability with 23.6% and 18.2% weight loss, respectively, from 20°C to 280°C and 230°C, respectively. These weight losses correspond to loss of DMF or H_2O and are followed by a nearly steady plateau from 150°C to 280°C and 100°C to 230°C, respectively, before decomposition. DEA_**hydoughnut-1** exhibits a slightly different TGA pattern, in which there is a ~5% weight loss before 100°C followed by a steady plateau until 180°C before decomposition as temperature is increased further.

Conclusions

In conclusion, we introduce herein a new family of organic-inorganic hybrid compounds, **hydoughnuts**, which are formed by self-assembly of two simple building blocks: a well-known POV and bdc, a simple, inexpensive organic linker. The anionic nature of **hydoughnuts**, their intrinsic porosity and their multi-functional exterior surfaces should afford opportunities for host guest chemistry in both solution and in the solid state. Future studies in our laboratory will focus upon not only the synthesis and characterisation of new variants of **hydoughnuts**, but also their use as supermolecular building blocks[15(a)] in the solid state.

Notes and references

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A New Family of Anionic Organic-Inorganic Hybrid Doughnut-Like Nanostructures

TOC entry

A family of soluble organic-inorganic hybrid doughnut-like anions has been prepared by self-assembly of polyoxovanadate anions and 1,3-benzenedicarboxylate linkers.
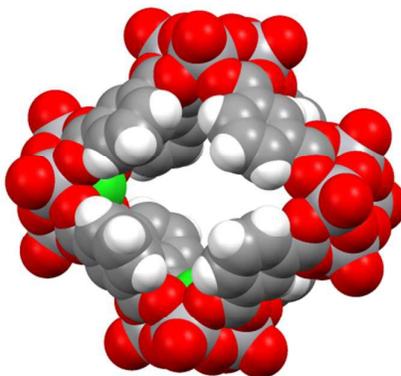
Electronic Supplementary Information

A New Family of Anionic Organic-Inorganic Hybrid Doughnut-Like Nanostructures

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General methods.

Commercially available reagents were purchased as high purity from Fisher Scientific or Sigma Aldrich and used without further purification. Solvents were purified according to standard methods and stored in the presence of molecular sieve. Thermogravimetric analysis (TGA) was performed under nitrogen on a TA Instrument Q50 from 30°C-600°C at the speed of 10°C/min. Elemental analysis were test on elementar vario EL cube. X-ray powder diffraction (XPRD) data were recorded on a Panalytical Empyrean diffractometer at 40 kV, 40 mA for Cu_{kR}(λ=1.5418 Å), with a scan speed of 0.5s/step (6°/min) and a step size of 0.05° in 2θ at room temperature. The calculated PXRD patterns were produced using Powder Cell for Windows Version 2.4 (programmed by W. Kraus and G. Nolze, BAM Berlin, 2000).

Synthetic Details

Synthesis of DMA_hydoughnut-1

A mixture of 1,3-bdc(10.0mg), VCl_3(20.0mg) and 5 mL mixture solvent(DMF:H_2O =10:1) were put in a 20mL scintillation vials and heated to 85 °C for 3 days until dry, The resulting dark green plate-like crystals were washed with DMF to give pure DMA_hydoughnut-1 of 12.2mg (yield of 40% based on 1,3-bdc). Elemental analysis Calculated: C 28.68%; H 2.83%; N 3.72%; Experimental: C 27.32%; H 2.95%; N 3.64%;

Synthesis of DEA_hydoughnut-1

A mixture of 1,3-bdc(10.0mg), VCl_3(20.0mg) and 5 mL mixture solvent(DEF:H_2O =10:5) were put in a 20mL scintillation vials and heated to 105 °C for 3 days until dry, The resulting dark green needle crystals were washed with MeOH to give pure DEA_hydoughnut-1 of 15.8mg (yield of 60% based on 1,3-bdc). Elemental analysis Calculated: C 28.61%; H 2.40%; N 1.67%; Experimental: C 28.77%; H 2.58%; N 1.74%;

Synthesis of DMA_hydoughnut-2

A mixture of 5-bromo-1,3-bdc (12.0mg), VCl_3(20.0mg) and 5 mL mixture solvent(DMF:H_2O =10:1) were put in a 20mL scintillation vials and heated to 105 °C for 3 days until dry, The resulting residue were dissolved in DMF and dark green block crystals were obtained by slow diffusion of diethyl ether. Crystals were washed with ether to give pure DMA_hydoughnut-2 of 18.1mg (yield of 51% based on the ligand). Elemental analysis Calculated: C 27.38%; H 2.87%; N 4.47%; Experimental: C 26.64%; H 3.06%; N 4.69%;

Synthesis of DMA_hydoughnut-3

A mixture of 5-Methoxy-1,3-bdc(12.0mg), VCl_3(20.0mg) and 5 mL mixture solvent(DMF:H_2O =10:1) were put in a 20mL scintillation vials and heated to 105 °C for 3 days until dry, The resulting dark green block crystals were washed with DMF/MeOH(1:1) to give pure DMA_hydoughnut-3 of 10.9mg (yield of 29.6% based on the ligand) Elemental analysis Calculated: C 29.27%; H 3.21%; N 3.38%; Experimental: C 29.59%; H 3.33%; N 3.31%;

X-ray Structure Determinations

X-ray diffraction data for DMA_hydoughnut-1 were measured on a Bruker D8 VENTURE PHOTON 100 CMOS system equipped with a Cu K_α INCOATEC Iμs micro-focus source (λ=1.54178Å). Indexing was performed using *APEX2*[1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01[2]. Absorption correction was performed by multi-scan method implemented in SADABS[3]. Space groups were determined using XPREP implemented in APEX2 [1]. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-2013[7] (full-matrix least-squares on F^2) contained in APEX2[1,7], WinGX v1.70.01[4,5,6,7] and OLEX2 [7,8]. All Non-H atoms in rigid part of structure were found in the difference Fourier map and refined anisotropically. Counter-ions in the structure were modeled as disordered dimethylammonium (DMA) cations with fractional occupancies. DMA cations were refined using restraints (DFIX, DANG, SIMU). The possible source of DMA could be a hydrolysis of DMF which is very common reaction with the presence of water at high temperature. Same case in which dimethylammonium obtained from hydrolysis of DMF serves as counter-ion could also be found in the literature [9]. DMF molecules were refined using 1,2, 1,3, FLAT and SIMU restraints with fractional occupancy. Disordered molecules other than DMA and DMF molecules were modeled as water molecules with fractional occupancies. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH). Crystal data and refinement conditions are shown in Table S1 below.

Table S1 Crystal data and structure refinement for DMA_hydoughnut-1.	
Identification code	DMA_hydoughnut-1
Empirical formula	$C_{90}H_{106}Cl_4N_{10}O_{92.75}V_{16}$
Formula weight	3768.68
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/a$
a/Å	21.2958(6)
b/Å	21.3300(6)
c/Å	21.9581(6)
α/°	90
β/°	105.8678(13)
γ/°	90
Volume/Å^3	9594.2(5)
Z	2
ρ_{calc}g/cm^3	1.305
μ/mm^{-1}	7.485
F(000)	3788.0
Crystal size/mm^3	0.1 × 0.1 × 0.02
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.888 to 133.336
Index ranges	-25 ≤ h ≤ 25, -25 ≤ k ≤ 25, -25 ≤ l ≤ 26
Reflections collected	83383
Independent reflections	16852 [R_{int} = 0.1167, R_{sigma} = 0.0769]
Data/restraints/parameters	16852/88/1054
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0885, wR_2 = 0.2376
Final R indexes [all data]	R_1 = 0.1453, wR_2 = 0.2886
Largest diff. peak/hole / e Å^{-3}	0.83/-0.78

X-ray diffraction data for DEA_hydoughnut-1 were collected using synchrotron radiation (λ = 0.51800 Å, T = 100(2) K) at Advanced Photon Source Beamline 15-ID-B of ChemMatCARS in Argonne National Lab, Argonne, IL. Indexing was performed using *APEX2*[1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01[2]. Absorption correction was performed by multi-scan method implemented in SADABS[3]. Space groups were determined using XPREP implemented in APEX2[1]. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-2013[7] (full-matrix least-squares on F^2) contained in APEX2[1,7], WinGX v1.70.01 [4,5,6,7] and OLEX2[7,8]. All Non-H atoms in rigid part of structure were found in the difference Fourier map and refined anisotropically. Site occupancies of carboxylate moieties (C11, O3, O4), bridging oxygen atom (O11) and terminal oxygen atoms (O40, O12) from the V-based cluster were determined through occupancy refinement and were equal to 0.5 - which confirms the presence of anticipated ligand (1,3-BDC) in the structure. Counter-ions in the structure were modeled as disordered diethylammonium (DEA) cations with fractional occupancies. DEA cations were refined using restraints (DFIX, DANG, SIMU). The possible source of DEA could be a hydrolysis of DEF which is very common reaction with the presence of water at high temperature. Similar case in which dimethylammonium obtained from hydrolysis of DMF serves as counter-ion could also be found in the literature [9]. Disordered molecules other than DEA molecules were modeled as water molecules with fractional occupancies. The crystal did not diffract past approximately 0.95Å resolution limit. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH). Crystal data and refinement conditions are shown in Table S2 below.

Table S2 Crystal data and structure refinement for DEA_hydoughnut-1	
Identification code	DEA_hydoughnut-1
Empirical formula	$C_{80}H_{80}Cl_4N_4O_{81.5}V_{16}$
Moiety formula	'C64 H32 Cl4 O64 V16, 4(C4 H12 N), 17.5(O)'
Formula weight	3358.32
Temperature/K	296.15
Crystal system	tetragonal
Space group	I4/mmm
a/Å	14.9098(9)
b/Å	14.9098(9)
c/Å	38.069(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	8462.8(12)
Z	2
ρ_{calc}g/cm^3	1.318
μ/mm^{-1}	0.407
F(000)	3352.0
Crystal size/mm^3	0.02 × 0.02 × 0.01
Radiation	synchrotron (λ = 0.518)
2Θ range for data collection/°	2.138 to 31.642
Index ranges	-14 $\leq$ h $\leq$ 15, -15 $\leq$ k $\leq$ 13, -40 $\leq$ l $\leq$ 40
Reflections collected	55527
Independent reflections	1527 [R_{int} = 0.1153, R_{sigma} = 0.0332]
Data/restraints/parameters	1527/15/203
Goodness-of-fit on F^2	1.149
Final R indexes [I>=2σ (I)]	R_1 = 0.0753, wR_2 = 0.2072

Final R indexes [all data]	$R_1 = 0.1013$, $wR_2 = 0.2364$
Largest diff. peak/hole / e Å^{-3}	0.39/-0.47

The X-ray diffraction data for DMA_hydoughnut-2 were measured on a Bruker D8 QUEST PHOTON 100 CMOS system equipped with a Cu K$_\alpha$ INCOATEC Iµs micro-focus source (λ=1.54178Å). Indexing was performed using *APEX2*[1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01[2]. Absorption correction was performed by multi-scan method implemented in SADABS[3]. Space groups were determined using XPREP implemented in APEX2 [1]. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-2013 [7] (full-matrix least-squares on F^2) contained in APEX2 [1,7], WinGX v1.70.01 [4,5,6,7] and OLEX2 [7,8]. All Non-H atoms in rigid part of structure were found in the difference Fourier map and refined anisotropically. Counter-ions in the structure were modeled as disordered dimethylammonium (DMA) cations with fractional occupancies. DMA cations were refined using restraints (DFIX, DANG, SIMU). The possible source of DMA could be a hydrolysis of DMF which is very common reaction with the presence of water at high temperature. Same case in which dimethylammonium obtained from hydrolysis of DMF serves as counter-ion could also be found in the literature [9]. DMF molecules were refined using 1,2, 1,3, FLAT and SIMU restraints with fractional occupancy. Disordered molecules other than DMA and DMF molecules were modeled as water molecules with fractional occupancies. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH). Crystal data and refinement conditions are shown in Table S3 below.

Table S3 Crystal data and structure refinement for DMA_hydoughnut-2	
Identification code	DMA_hydoughnut-2
Empirical formula	$C_{51.75}H_{64.75}Br_4Cl_2N_{7.25}O_{42.75}V_8$
Formula weight	2270.41
Temperature/K	100.23
Crystal system	triclinic
Space group	P-1
a/Å	15.1975(5)
b/Å	19.1532(6)
c/Å	19.3115(6)
α/°	103.8173(18)
β/°	95.3294(16)
γ/°	98.3478(17)
Volume/Å^3	5352.9(3)
Z	2
ρ_{calc}g/cm^3	1.409
µ/mm^{-1}	8.467
F(000)	2252.0
Crystal size/mm^3	0.1 × 0.1 × 0.08
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.842 to 118.21
Index ranges	-16 ≤ h ≤ 16, -21 ≤ k ≤ 21, -21 ≤ l ≤ 21
Reflections collected	106978
Independent reflections	15233 [$R_{int} = 0.0878$, $R_{sigma} = 0.0679$]
Data/restraints/parameters	15233/200/1073
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	$R_1 = 0.0982$, $wR_2 = 0.2603$
Final R indexes [all data]	$R_1 = 0.1491$, $wR_2 = 0.2992$
Largest diff. peak/hole / e Å^{-3}	2.51/-1.63

The X-ray diffraction data for DMA_hydoughnut-3 were measured on a Bruker D8 QUEST PHOTON 100 CMOS system equipped with a Cu K$_\alpha$ INCOATEC Iμs micro-focus source (λ=1.54178Å). Indexing was performed using *APEX2*[1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01[2]. Absorption correction was performed by multi-scan method implemented in SADABS[3]. Space groups were determined using XPREP implemented in APEX2 [1]. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-2013 [7] (full-matrix least-squares on F^2) contained in APEX2 [1,7], WinGX v1.70.01 [4,5,6,7] and OLEX2 [7,8]. All Non-H atoms in rigid part of structure were found in the difference Fourier map and refined anisotropically. Counter-ions in the structure were modeled as disordered dimethylammonium (DMA) cations with fractional occupancies. Two DMA cations in asymmetrical unit are disordered (N2, N6, N5, N7) and were refined using restraints (DFIX, DANG, SIMU). The possible source of DMA could be a hydrolysis of DMF which is very common reaction with the presence of water at high temperature. Same case in which dimethylammonium obtained from hydrolysis of DMF serves as counter-ion could also be found in the literature [9]. DMF molecule was refined using restraints (DFIX, DANG, SIMU) with fractional occupancy. One benzene ring (C39, C40, C41, C52, C53, C54) was disordered over two places and were refined by using 1,2, 1,3, FLAT and SIMU restraints with fractional occupancy. All of the methoxy group are disordered over two places and were refined using restraints (DFIX and SIMU) with fractional occupancies. Disordered molecules other than DMA and DMF molecules were modeled as water molecules with fractional occupancies. The concentration of Cl in the DMA_hydoughnut-3 was determined by using Cl-selective electrode and the concentration of V was determined by Atom Absorption Spectroscopy. The formula of DMA_hydoughnut-3 as presented in the text was only determined after the test after analysis of all data including Atom Absorption Spectroscopy (AAS), Cl-selective electrode and TGA. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH). Crystal data and refinement conditions are shown in Table S4 below.

Table S4. Crystal Data and structural refinement of DMA_hydoughnut-3	
Identification code	DMA_hydoughnut-3
Empirical formula	$C_{91}H_{119}Cl_7N_9O_{83.25}V_{16}$
Formula weight	3734.13
Temperature/K	100.0
Crystal system	triclinic
Space group	*P*-1
a/Å	14.a9214(6)
b/Å	16.0334(7)
c/Å	16.7794(7)
α/°	79.476(2)
β/°	82.828(3)
γ/°	81.284(2)
Volume/Å^3	3881.7(3)
Z	1
ρ$_{calc}$g/cm^3	1.597
μ/mm^{-1}	9.656
F(000)	1881.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.656 to 130.166
Index ranges	-17 ≤ h ≤ 17, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19
Reflections collected	47498

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Independent reflections	13009 [R_{int} = 0.0826, R_{sigma} = 0.0715]
Data/restraints/parameters	13009/160/1081
Goodness-of-fit on F^2	1.072
Final R indexes [$I>=2\sigma$ (I)]	R_1 = 0.0755, wR_2 = 0.1788
Final R indexes [all data]	R_1 = 0.1101, wR_2 = 0.1980
Largest diff. peak/hole / e $Å^{-3}$	0.75/-0.94
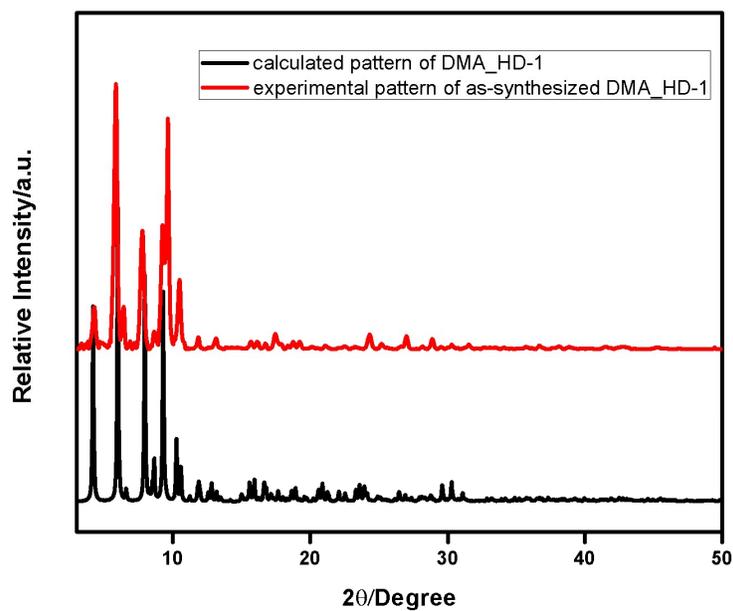
Figure S1 Comparison of experimental and calculated powder x-ray diffraction patterns of DMA_hydoughnut-1
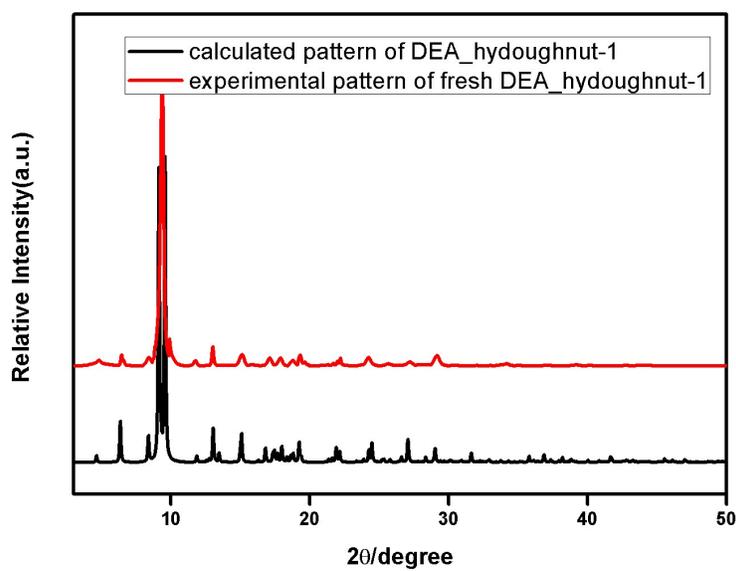
Figure S2 Comparison of experimental and calculated powder x-ray diffraction patterns of DEA_hydoughnut-1
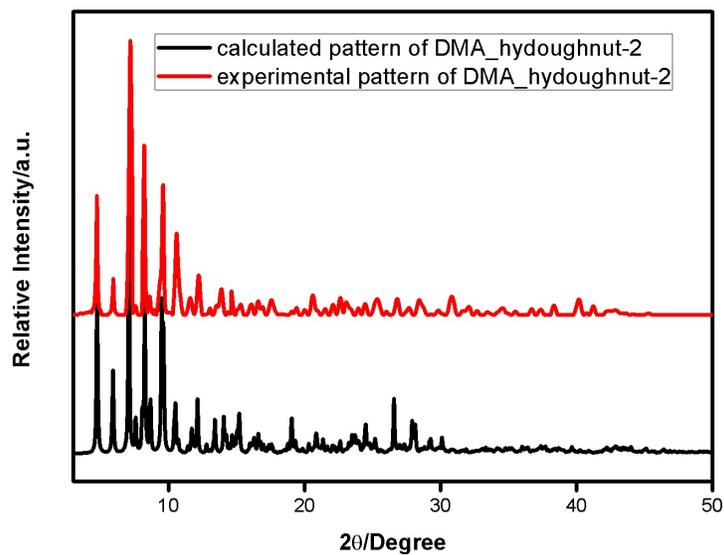
Figure S3 Comparison of experimental and calculated powder x-ray diffraction patterns of DMA_hydoughnut-2
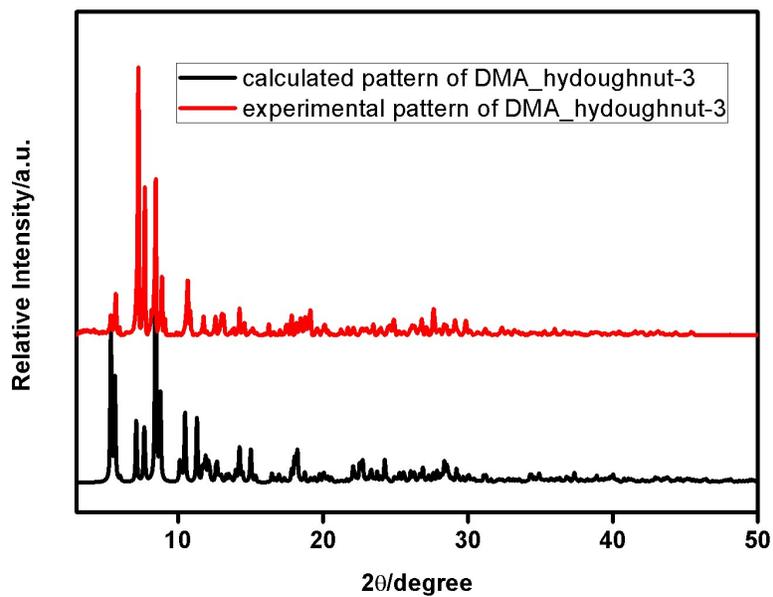
Figure S4 Comparison of experimental and calculated powder x-ray diffraction patterns of DMA_hydoughnut-3
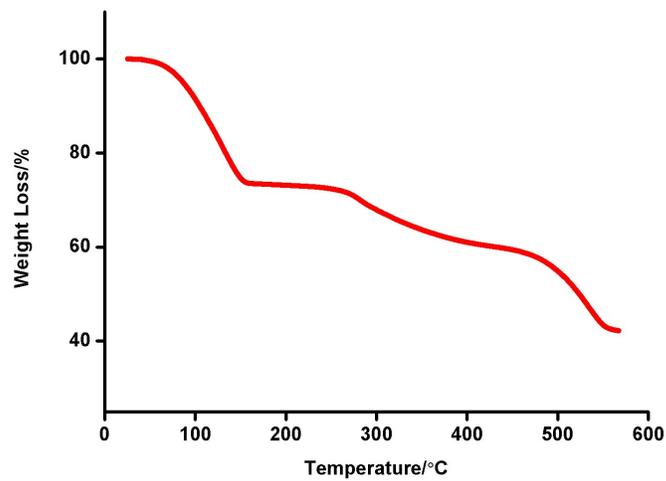
Figure S5 Thermogravimetric analysis of DMA_hydoughnut-1
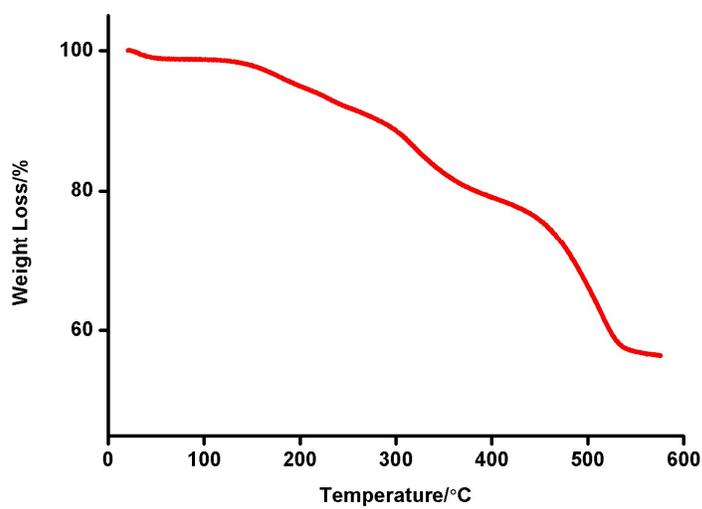
Figure S6 Thermogravimetric analysis of DEA_hydoughnut-1
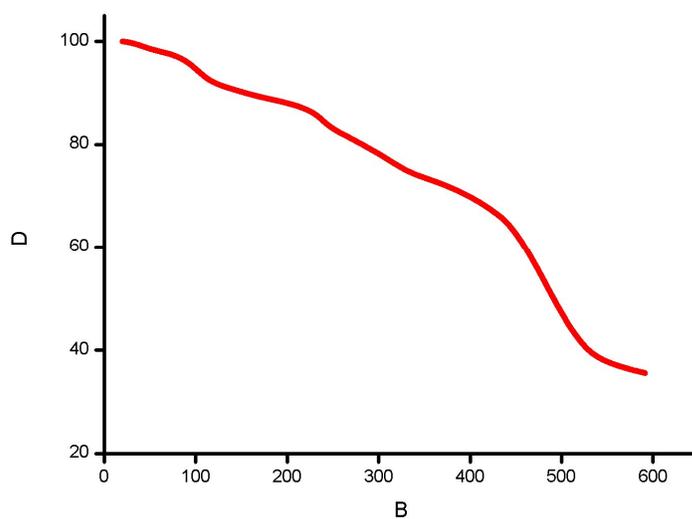
Figure S7 Thermogravimetric analysis of DMA_hydoughnut-2
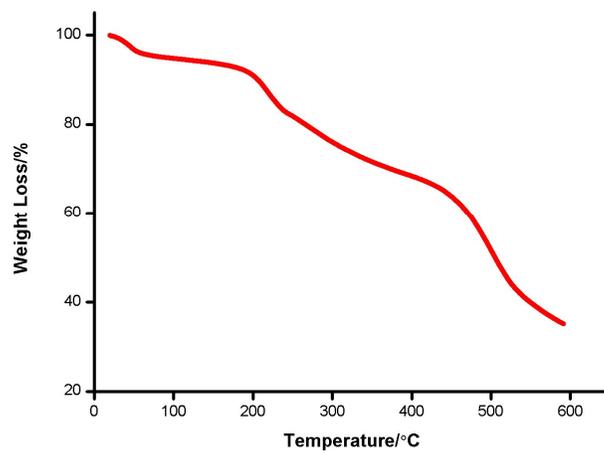
Figure S8. Thermogravimetric analysis of DMA_hydoughnut-3

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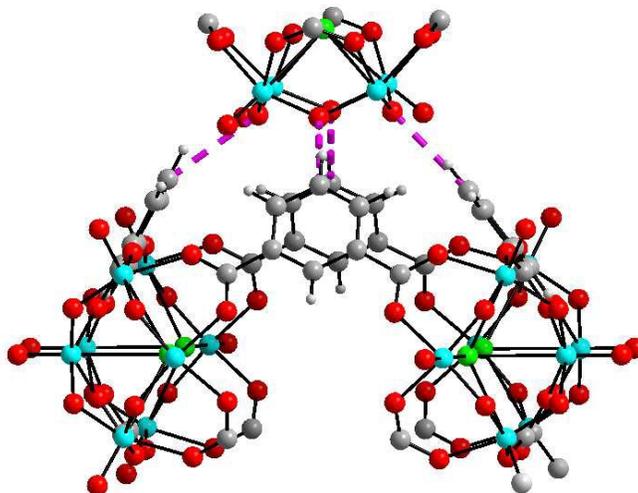
Figure S9   CH···O bond between two hydoughnut monomers(highlighted in pink)
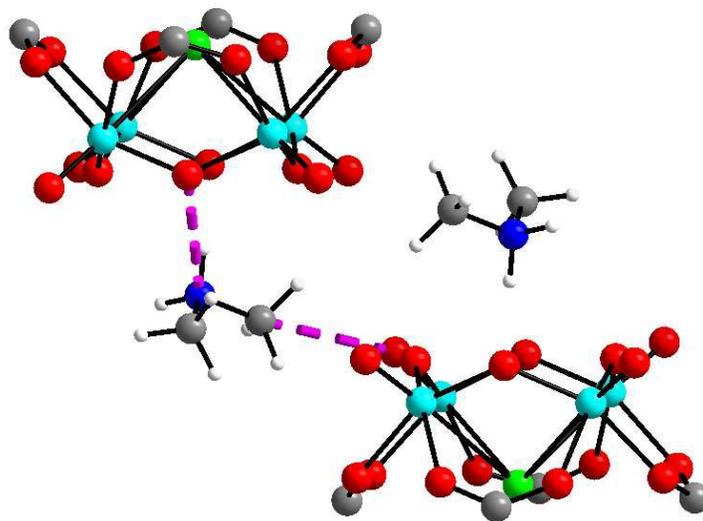
Figure S10   Charge-assisted H-bond between two sheets (highlighted in pink).

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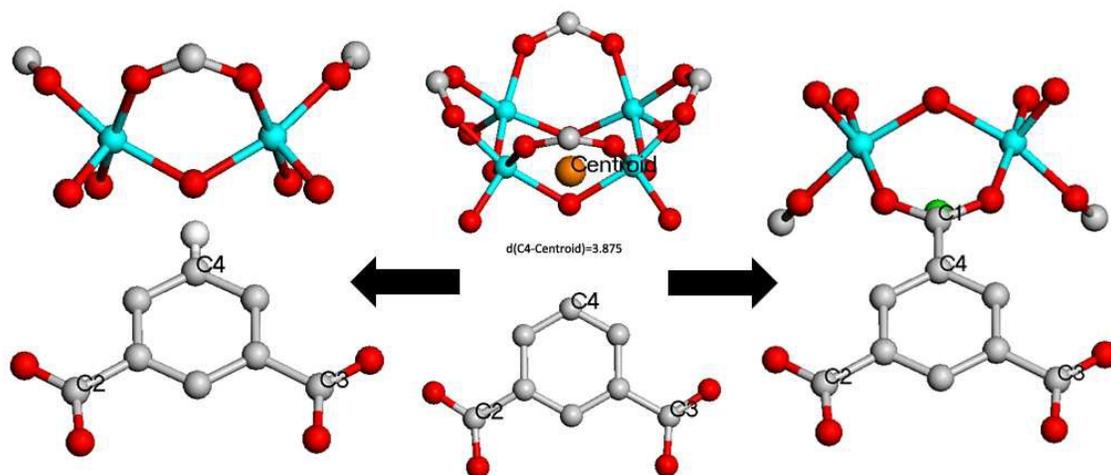
Figure S11 Two possible ways of connectivity between 1,3-BDC and POVs along *c-axis*: H-bond(left) and coordination bond(right)
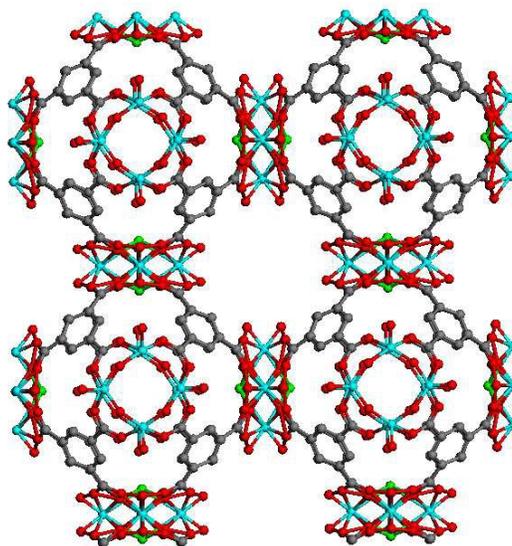
Figure S12 Disordered hydoughnut-1 anions packs with each other to form 2-D sheet in *ab* plane
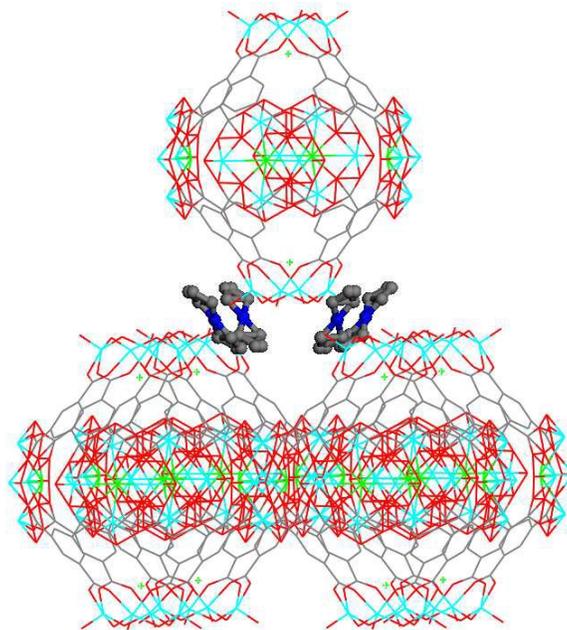
Figure S13 Interactions between DEA cations and POV moieties. Molecules in ball and stick mode: diethylammonium; Molecules in stick mode: hydoughnut-1 anions.
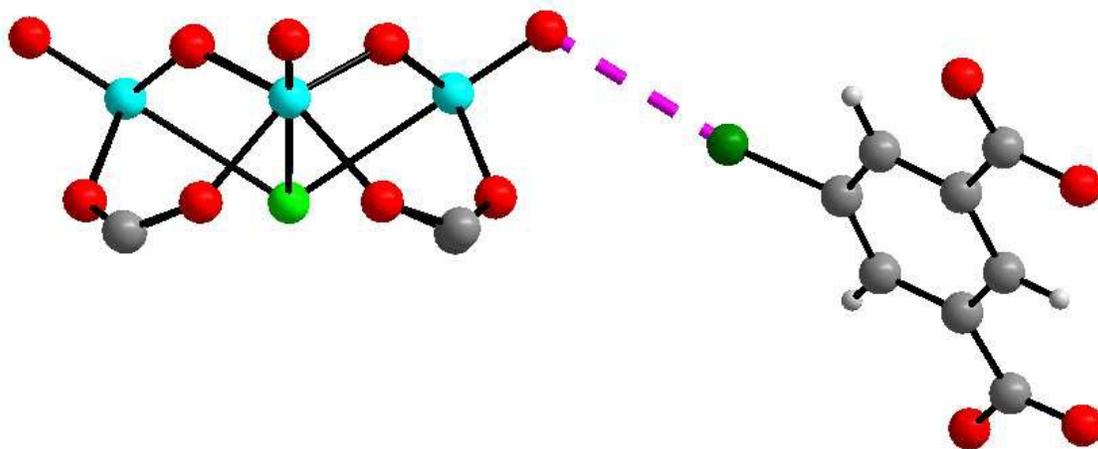
Figure S14　Br···O interaction along *a-axis* between POV clusters and Br atom

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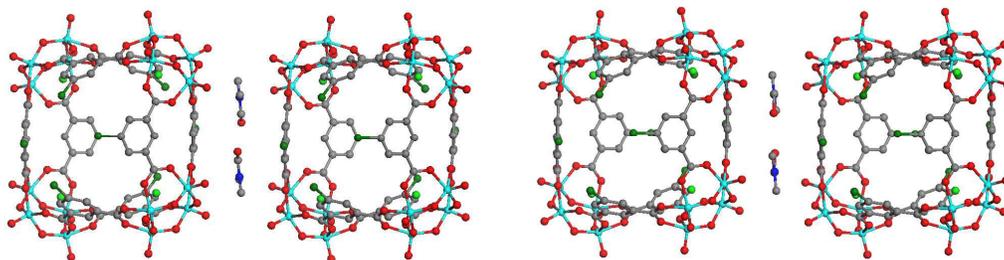
Figure S15 Packing of hydoughnut-2 anions along *b-axis*(left) and *c-axis*(right). Two DMF molecules are located between two ligands in a parallel fashion.
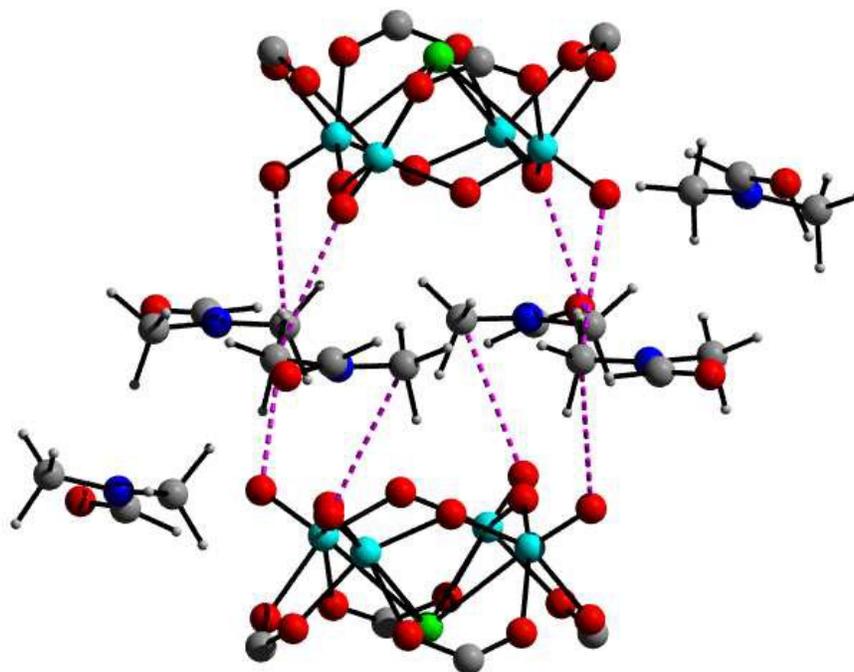
Figure S16 CH···O interactions between DMF molecules and POVs in the diagonal direction of *bc*-plane(highlighted in pink)
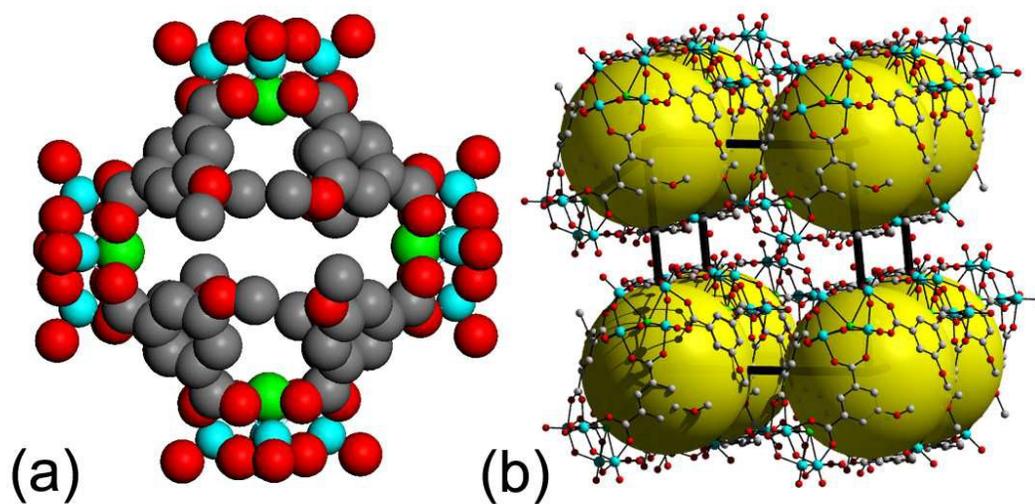
Figure S17 (a) the hydoughnut-3 anion; (b) crystal packing of hydoughnut-3 anions
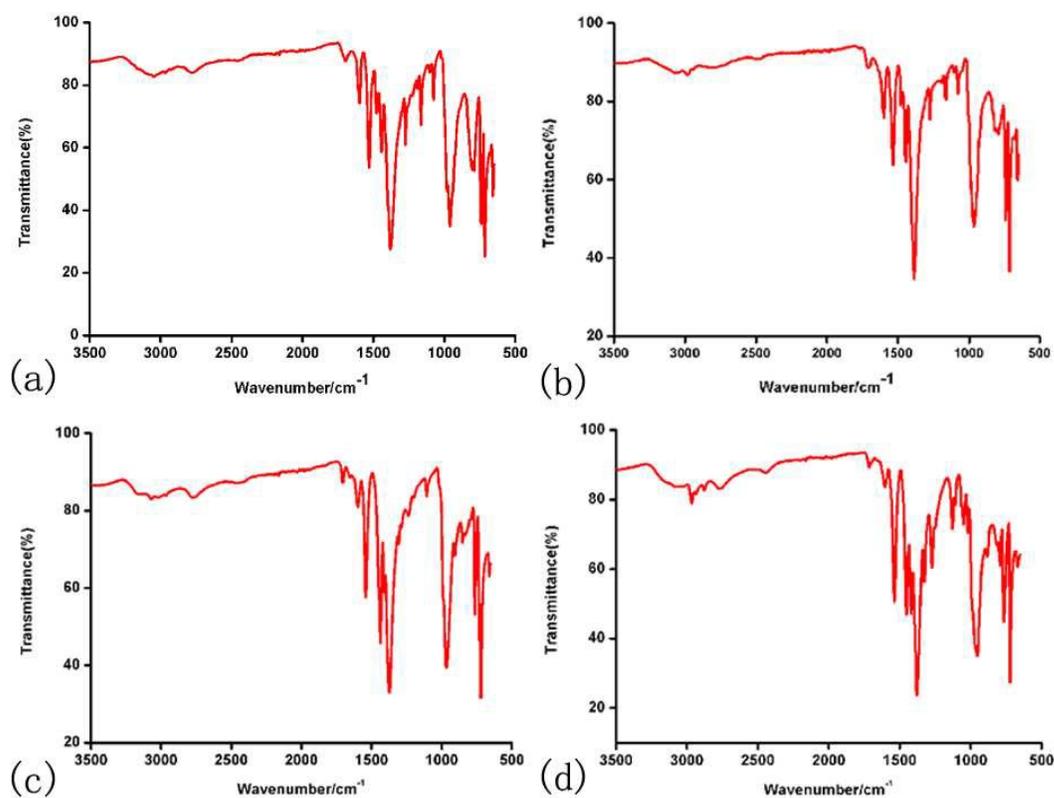
Figure S18 FT-IR of (a) DMA_hydoughnut-1; (b) DEA_hydoughnut-1; (c) DMA_hydoughnut-2; (d) DMA_hydoughnut-3

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