Electronic Supplementary Information (ESI) for CrystEngComm
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Electronic Supplementary Information

Structural Design of Porous Coordination Networks from Tetrahedral Building Units

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Section 1. Single-Crystal X-ray Crystallography of PCN-511 – PCN-517

All colorless crystals were taken from the solution directly without further treatment, transferred to oil and mounted into a loop for single crystal X-ray data collection. Diffraction was measured on a Bruker Smart Apex diffractometer equipped with a Mo-Kα sealed-tube X-ray source (λ = 0.71073 Å, graphite monochromated) and a low temperature device (110 K). The data frames were recorded using the program APEX2 and processed using the program *SAINT* routine within APEX2. The data were corrected for absorption and beam corrections based on the multi-scan technique as implemented in *SADABS*. The structures were solved by direct method using *SHELXS* and refined by full-matrix least-squares on F^2 using *SHELXL* software.[*]

1.1 Refinement Details of PCN-511

Diffraction frames were integrated in Monoclinic (b-unique) C by APEX2. *XPREP* agreed that the R(sym) is 0.025 for this highest symmetric Bravais lattice and *c*-glide plane exists based on statistics of systematic absence. *C*2/*c* was the best choice with lowest CFOM factor (1.32), as is well-transformed to get Fourier peaks by direct method. The disordered benzene part was refined as 57% and 43% respectively. By using geometry restraints for disorder part, we obtained R value is 0.1198 before *SQUEEZ E* routine and 0.0536 after *SQUEEZE* routine of *PLATON*. The squeezed void volume was 3708.2 Å^3, equivalent to 45.6% of the unit cell.

<u>Validation Reply Form</u>

Alert B: D-H Without Acceptor O8 - H8A

Author Response: This warning could be deleted if H8A were excluded; however, this MOF would be in the simply deprotonated form. In order to get a neutral-charged structure, O5 and O8 are the possible positions to locate protons. O6, the counterpart of O5 in the same carboxylate group, is coordinated to two metal atoms, while O8's counterpart, only one metal atom. Hence, the electronegativity of O8 should be stronger than O5 to attract positive protons. Consequently, we assigned the protons on O8.

1.2 Refinement Details of PCN-513

Diffraction frames were integrated in Triclinic P by APEX2, and *XPREP* also agreed this Bravais lattice. $P\bar{1}$ was the best candidate with lowest CFOM factor (1.40). 1024 phase sets were refined and gave perfect RE values (0.23) for Fourier peak search by direct method. The Fourier peaks for main frameworks were clear and sharp; but those for solvent molecules were confusing because the Q-peaks looked like a pentagon which could be recognized as either two disordered DMF solvents or one single NMP solvent. We firstly dealt with the Q-peaks (O41S, N41S, C41S, C42S, C43S) connected to Zn clusters and made them a single DMF molecule, whose atomic displacement parameters ranged between 0.07 and 0.16. Based on the thermal ellipsoids of this coordinated solvent, understandably, it is expected to have larger atomic displacement parameters for free solvents. Consequently, we identified the free solvents as NMPs with atomic displacement parameters ranging from 0.16 to 0.19. After fixing geometry of solvents, R value is 0.1084 without *SQUEEZE* treatment and 0.0777 with *SQUEEZE* treatment.

Validation Reply Form

Alert C: Large Reported Max. (Positive) Residual Density 2.61 eA^{-3}

Author Response: The most significant residual electron density (2.61eÅ^{-3}) in the structure is located at (0.65, 1.39, 0.54), near Zn2 coordinate (0.53, 1.20, 0.44). It's more possible to be assigned as oxygen instead of carbon, nitrogen, or hydrogen on account of chemical sense. However, there are two reasons we left this high Q-peak there. One is due to its enormous thermal ellipsoids (0.99). It indicates too many electrons are assigned on the position, inferring the occupancy of this atom should be lower. The other reason is due to the distortion of five-membered coordinated form constructed with O1, O4, O7, Zn2 and this Q-peak. Based on the structure deposition in CCDC, five-membered coordinated form of Zn prefers square pyramid rather than trigonal bipyramid. Even compared with trigonal bipyramid form, the plane constructed with O1, O4, O7, Zn2 looks more distorted. Therefore, we decide to propose a structure without partially coordinated oxygen and leave this high Q-peak.

1.3 Refinement Details of PCN-514·DMA and PCN-514·DMF

For both compounds, diffraction frames were integrated in Triclinic P by APEX2, and *XPREP* also agreed with this Bravais lattice. $P\bar{1}$ was the best choice with lowest CFOM factor of 0.63 for PCN-514·DMA, and that of 0.95 for PCN-514·DMF. 1024 phase sets were refined and gave perfect RE values (0.232 for PCN-514·DMA, 0.271 for PCN-514·DMF) for Fourier peak search by direct method. All atoms, including solvents and hydrogen, were easily found after using *SHELXS*. *SQUEEZE* routine of *PLATON* was not applied to these two structures due to insignificant electron residue. R value is 0.0326 for PCN-514·DMA and 0.0491 for PCN-514·DMF, respectively.

1.4 Refinement Details of PCN-515

Diffraction frames could be integrated in either Monoclinic or Triclinic, but it was extremely hard to solve with monoclinic space groups ($P2_1/c$). Therefore we applied low-symmetry strategy to get initial solution with $P\bar{1}$. Addsym unit in *PLATON* suggested that correct space group should be *Pc* when most carbon atoms were found. Note that higher centrosymmetric space group, $P2_1/c$, was promoted from *Pc* in the final check. By using restraints of geometry and atomic displacement parameters, R value is 0.2061 before *SQUEEZE* treatment and 0.0803 after *SQUEEZE* treatment. The squeezed void volume was 20067 Å^3, equivalent to 70% of the unit cell.

Validation Reply Form

Alert A: Ratio Observed / Unique Reflections too Low .... 22 %

Author Response: Experiments were performed on Bruker SMART APEXII Diffractometer with Mo X-ray tube and low-temperature system (110K). Due to the ultraporous nature of this compound, the diffraction from the crystal was very weak and there were no reflections after 2Theta=30deg, even after we used data collection time 80s/frame. This crystal appears to be more than 0.3mm. However, it's a 50%-50% twinned crystal with twin law 0 0 1 0 1 0 -1 0 0. The presence of twinning might result in destructive interference, which further impairs the diffraction intensity.

1.5 Refinement Details of PCN-516

Diffraction frames were integrated in Tetragonal P by APEX2, and *XPREP* also agreed that the R(sym) is 0.071 for this highest symmetric Bravais lattice. 4_2 screw axis and c-glide plane should be observed based on statistics of systematic absence. $P4_2/mmc$ was the best centrosymmetric space group with lowest CFOM factor (28.60), well-transformed to get Fourier peaks by direct method. Without any geometry restraints, we obtained R value is 0.1348 before *SQUEEZE* routine and 0.0537 after *SQUEEZE* routine of *PLATON*. The squeezed void volume was 2812 Å^3, equivalent to 73% of the unit cell.

1.6 Refinement Details of PCN-517

Diffraction frames were integrated in Triclinic P by APEX2, and *XPREP* also agreed this Bravais lattice.

*P*T was the best candidate with lowest CFOM factor (1.11), generating Fourier peaks by direct method. Most non-hydrogen atoms were straightforwardly found. For those confusing Fourier peaks, they were assigned as split benzenes and Cd disorder, as refinement results of 50%-50%. On the other hand, there were 4 extremely heavy peaks existing around the main frameworks. We figured that they should be 4 Cd atoms with a valence of plus two. However, they needed to be modified as 25% occupancy, making charge balance for the frameworks with a valence of minus two. Similarly, the corresponding occupancies of the oxygen coordinated to free Cd atoms should be also set to 25%, like their attached atoms. By using geometry restraints for all ligands and dangling oxygen atoms, we obtained R value is 0.1644 before *SQUEEZ E* routine and 0.1254 after *SQUEEZE* routine of *PLATON*.

Response to minor defects in PCN-517

1. The most significant residual electron density (2.43eÅ^{-3}) in the structure is located at (0.68, -0.10, -0.28), near O5 coordinate (0.63, -0.12, -0.31). It is located in the range that the rotational carboxylate group is able to reach. We had tried to model it as a disordered carboxylate group, but another high Q-peak was generated nearby. Since this Q-peak is also close to heavy atoms, we suppose it might arise from Fourier truncation errors. Therefore, we decided to propose a structure without the disordered carboxylate group and leave this high Q-peak.
2. The ADPs for Si2 and the attached carboxylatophenyl group at C56 are elongated. By reviewing the structure, it was found that this elongated carboxylatophenyl group is coordinated to the disordered Cd atoms, Cd3 and Cd3’, which are arranged along the direction pointing toward Si2. That means it could be split into two disordered aromatic rings connected to disordered Cd atoms. But we prefer not to model it as disorder for structural clarity. Since it does not give rise

to Alert A and B in CIF, and there are no Q-peaks around this carboxylatophenyl group for potential disordered positions, we decided to keep it as elongated thermal ellipsoids in the structure.

PLATON addsym unit were performed twice for every compound: one is checking the heavy atom moiety, the other is checking the final structure. After reasonable geometry of all ligands and solvents were done, crazy atoms were refined with the help of EADP restrains on each ligand as well as solvent molecules to clear the warnings about non-positive definite matrices and unreasonable thermal ellipsoids. All non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles, whereas organic hydrogen atoms were located with isotropic displacement parameters set to 1.2 × U_{eq} of the attached atoms. Attempts to locate and refine the strong solvent peaks were successful, but contributions to scattering due to those highly disordered solvent molecules were removed using the *SQUEEZE* routine of *PLATON*; structures were then refined again using the data generated.

The CIF files can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (CCDC 942372 for PCN-511, CCDC 942373 for PCN-513, CCDC 942374 for PCN-514·DMA, CCDC 942375 for PCN-514·DMF, CCDC 942376 for PCN-515, CCDC 942377 for PCN-516, CCDC 942378 for PCN-517).

*APEX2 v2012.2.0 and SAINT v7.68A data collection and data processing programs, respectively. Bruker Analytical X-ray Instruments, Inc., Madison, WI; SADABS v2008/1 semi-empirical absorption and beam correction program. G.M. Sheldrick, University of Göttingen, Germany.

G. M. Sheldrick, *SHELXTL*, Version 6.14, Structure Determination Software Suite, Bruker AXS, Madison, WI, **2003.

Section 2. IR and TGA of PCN-511 and PCN-512

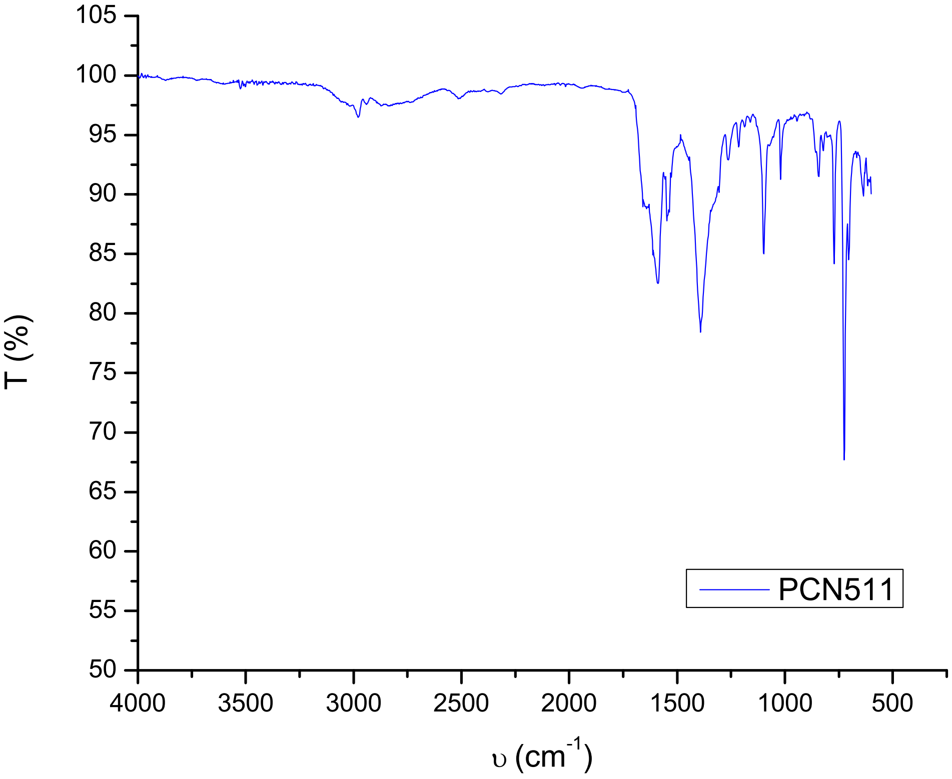

Figure S1. IR of PCN-511

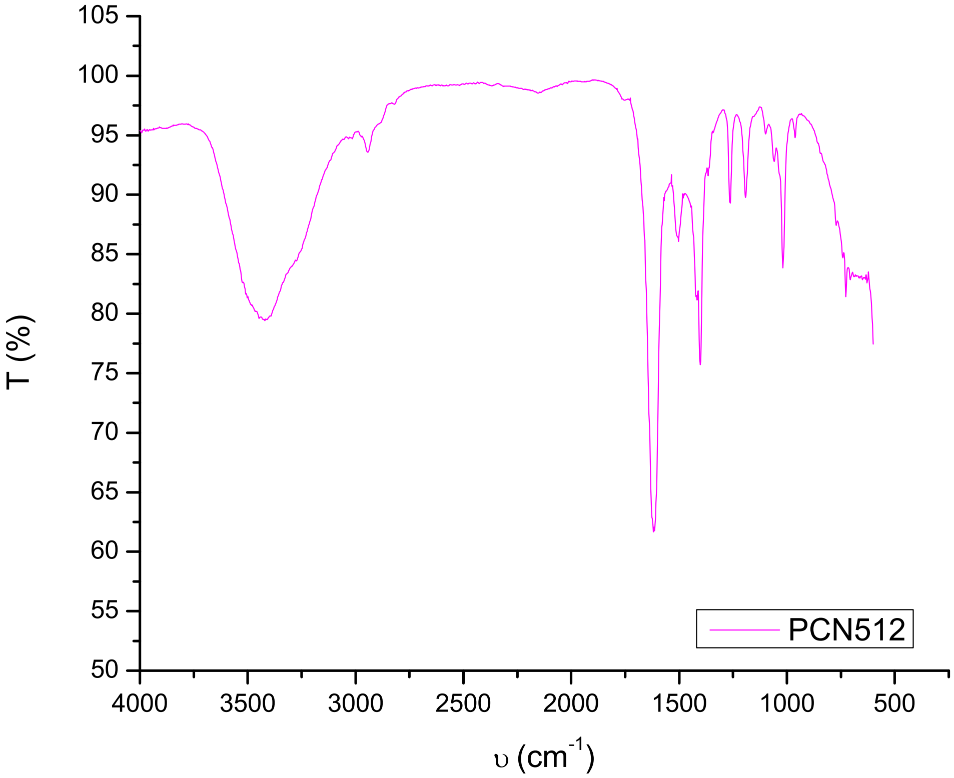

Figure S2. IR of PCN-512

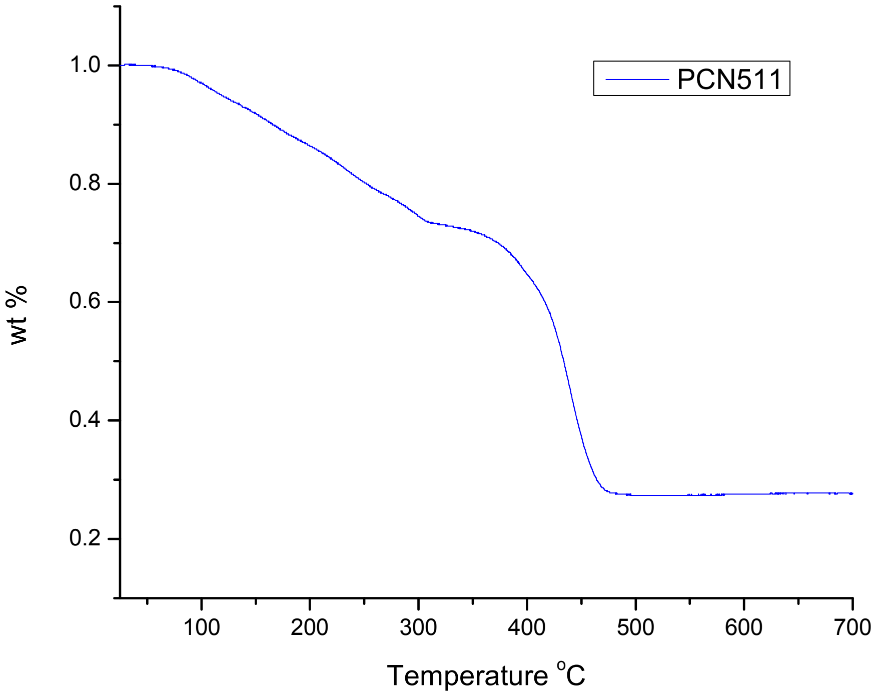

Figure S3. TGA of PCN-511

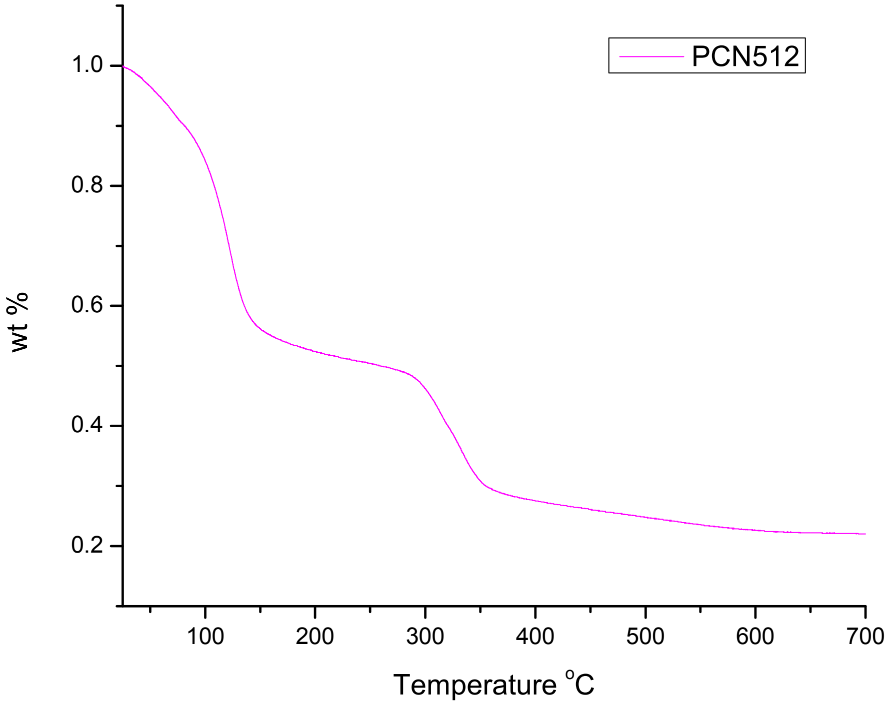

Figure S4. TGA of PCN-512

Section 3. High-Resolution Pictures of Crystal Structures

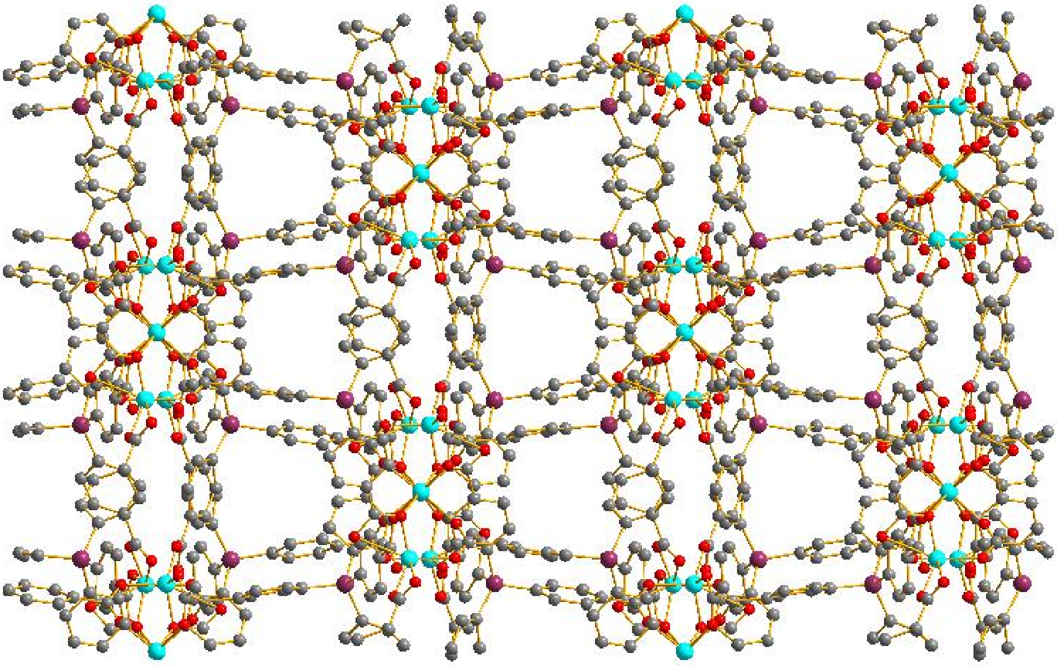

Figure S5. The representation of the crystal structure of PCN-511 along *c* axis.

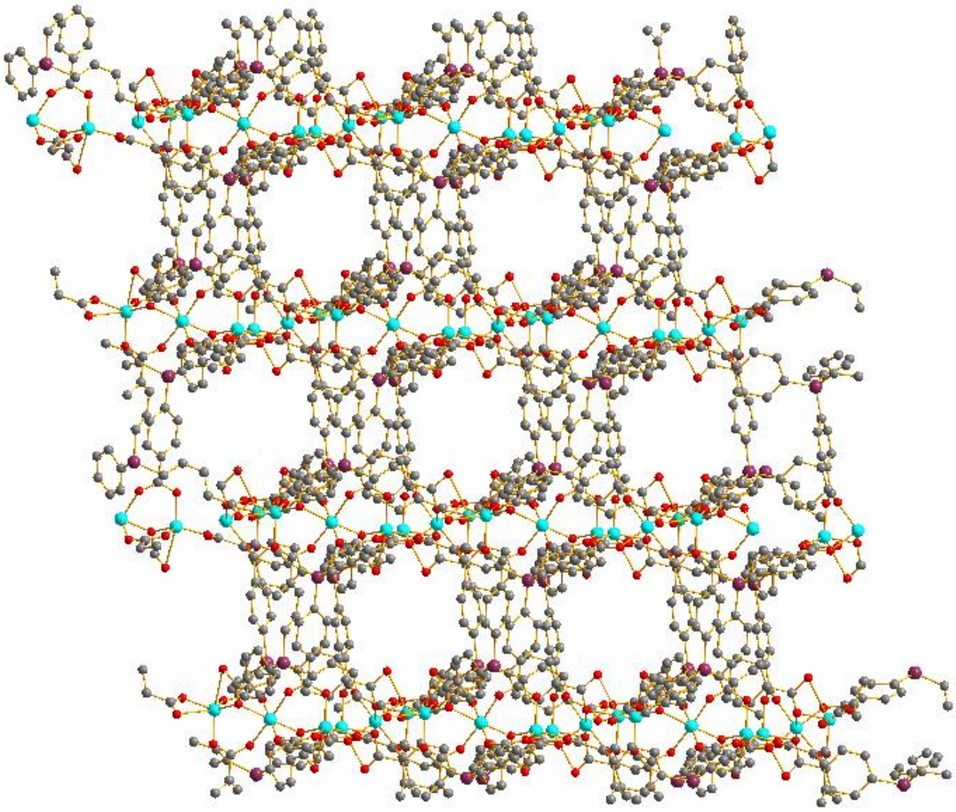

Figure S6. The representation of the crystal structure of PCN-511 along 011 axis.

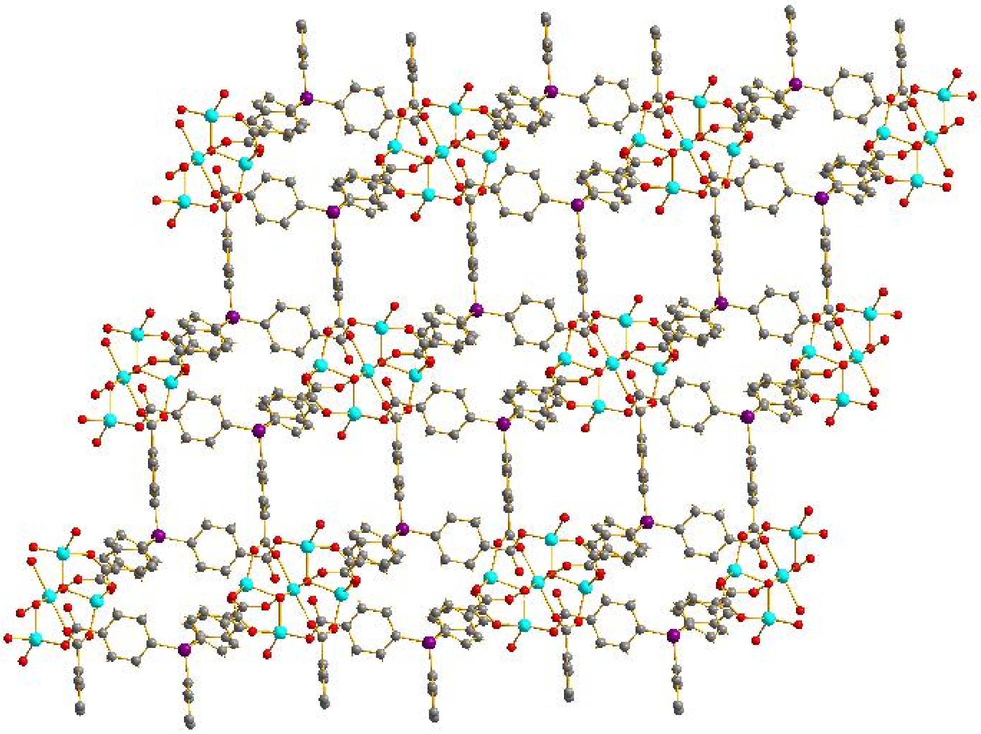

Figure S7. The representation of the crystal structure of PCN-513 along *c* axis after removal of solvents

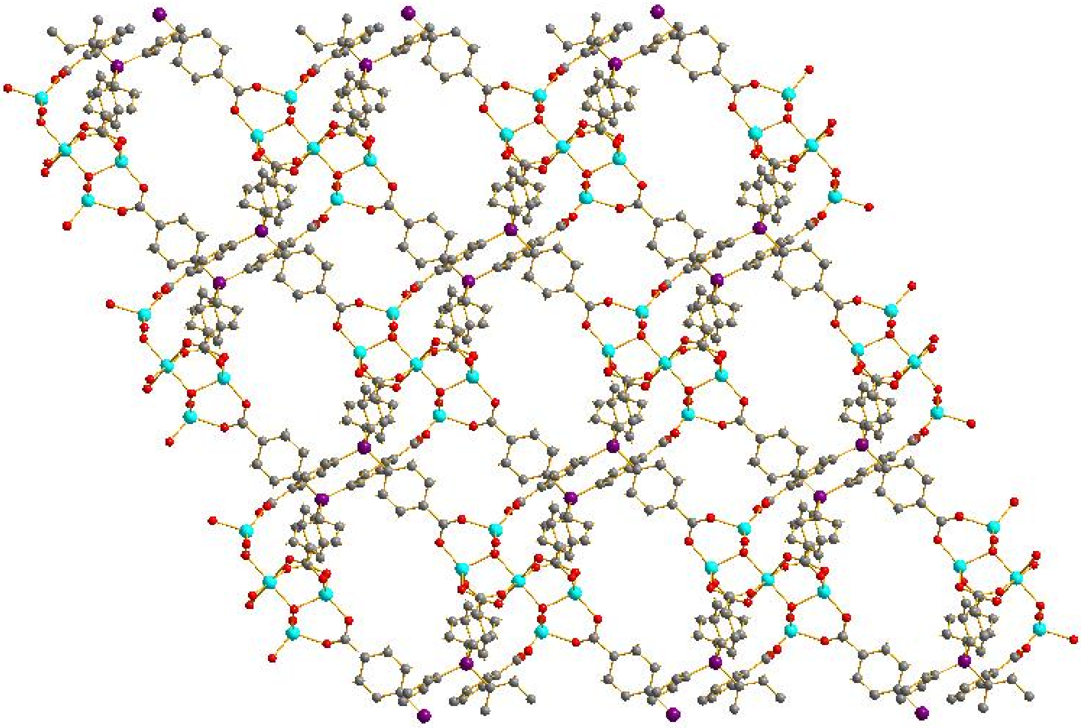

Figure S8. The representation of the crystal structure of PCN-513 along *a* axis after removal of solvents

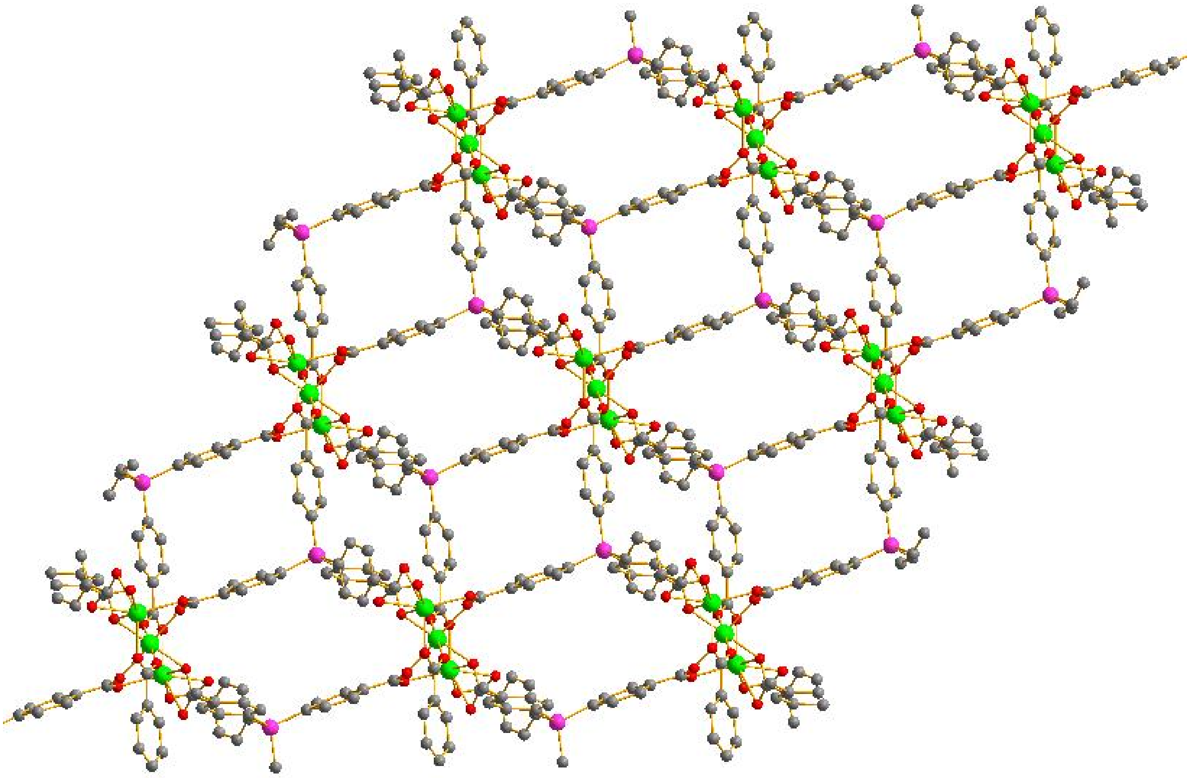

Figure S9. The representation of the crystal structure of PCN-514 along *a* axis after removal of solvents

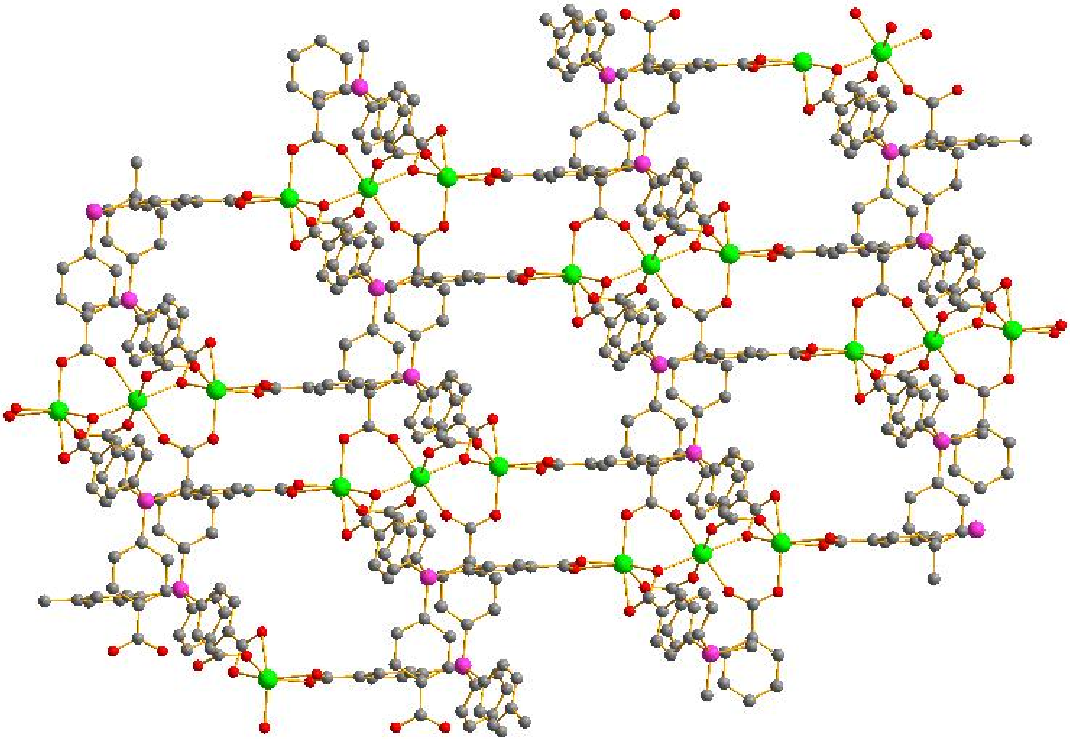

Figure S10. The representation of the crystal structure of PCN-514 along *b* axis after removal of solvents

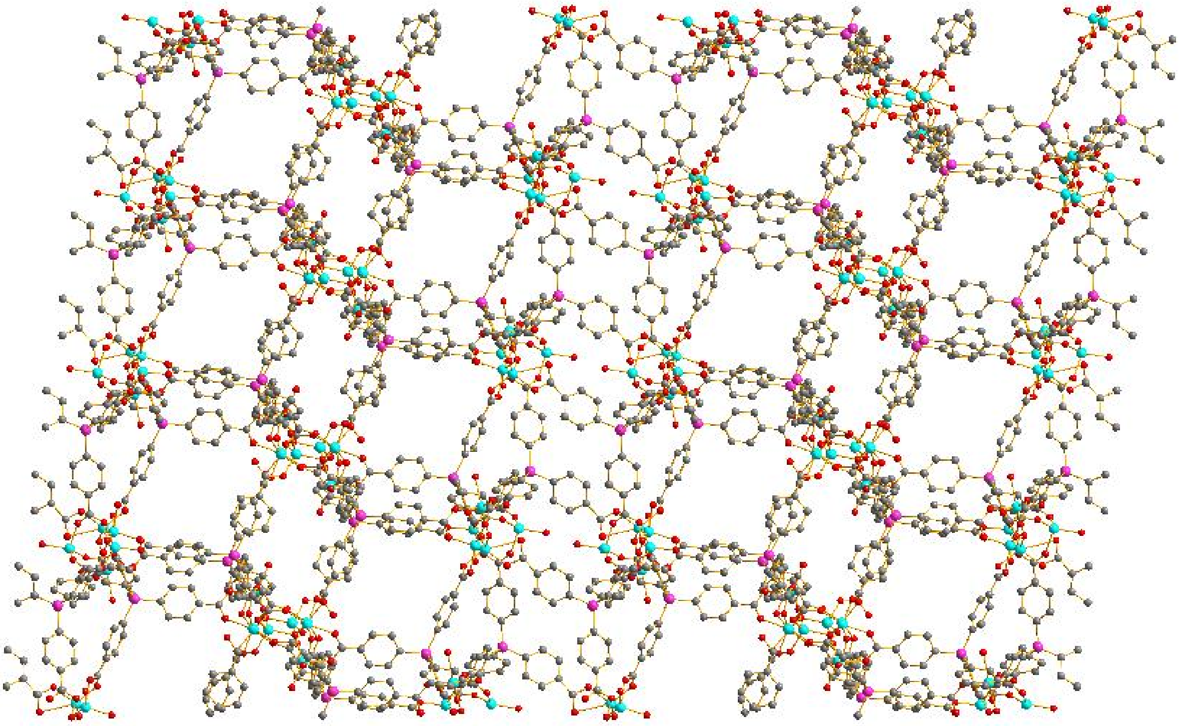

Figure S11. The representation of the crystal structure of PCN-515 along *b* axis

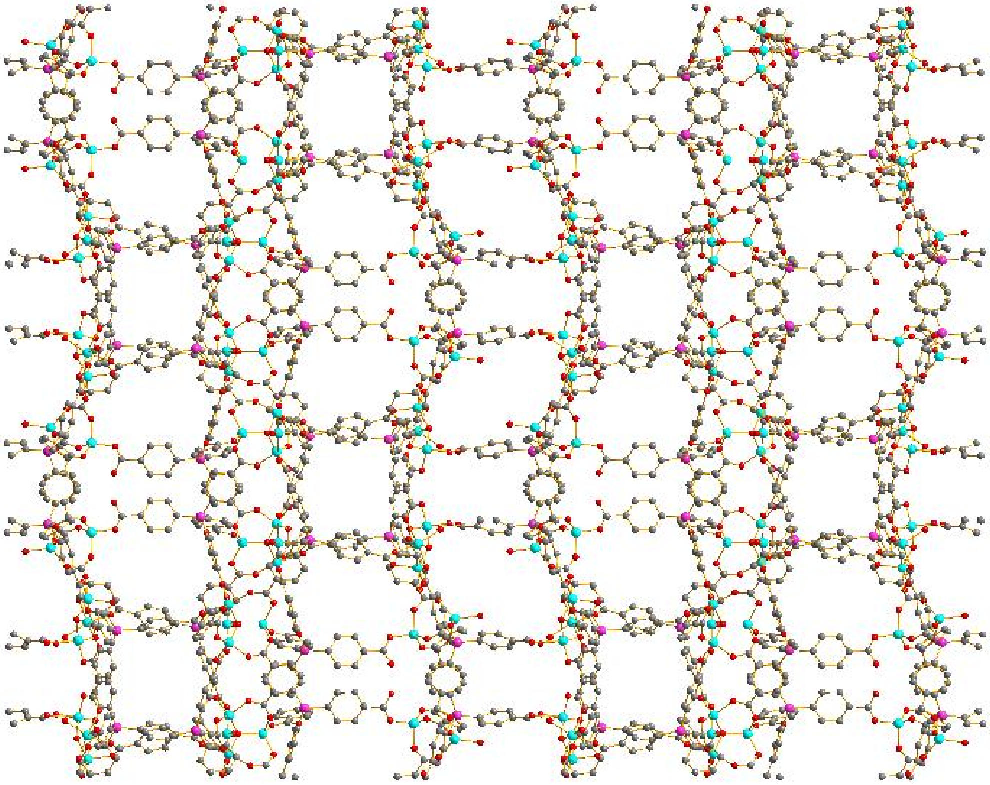

Figure S12. The representation of the crystal structure of PCN-515 along *c* axis

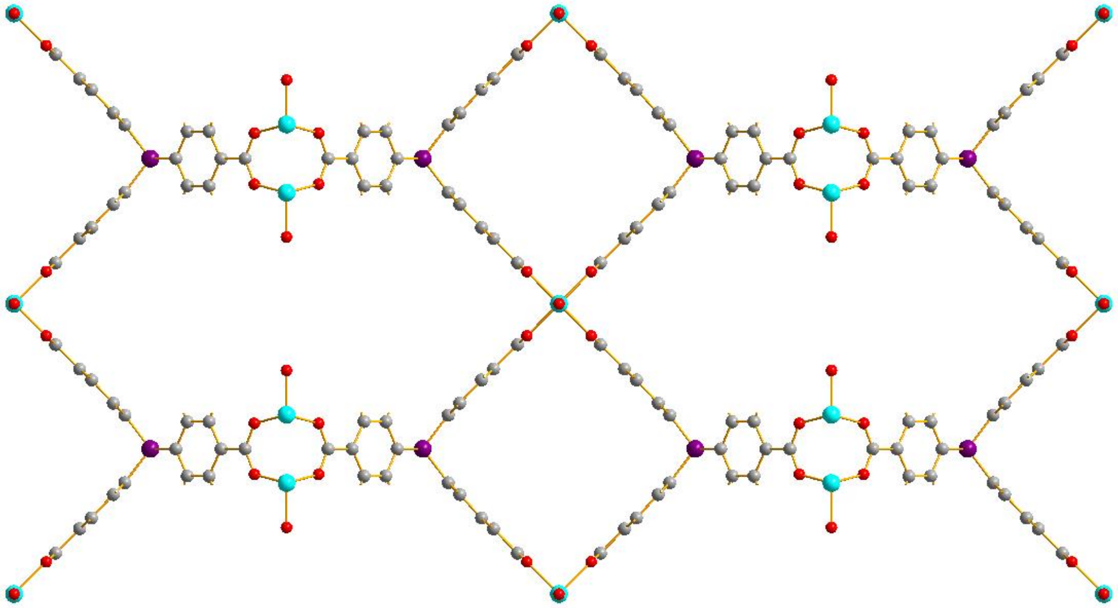

Figure S13. The representation of the crystal structure of PCN-516 along *a* axis

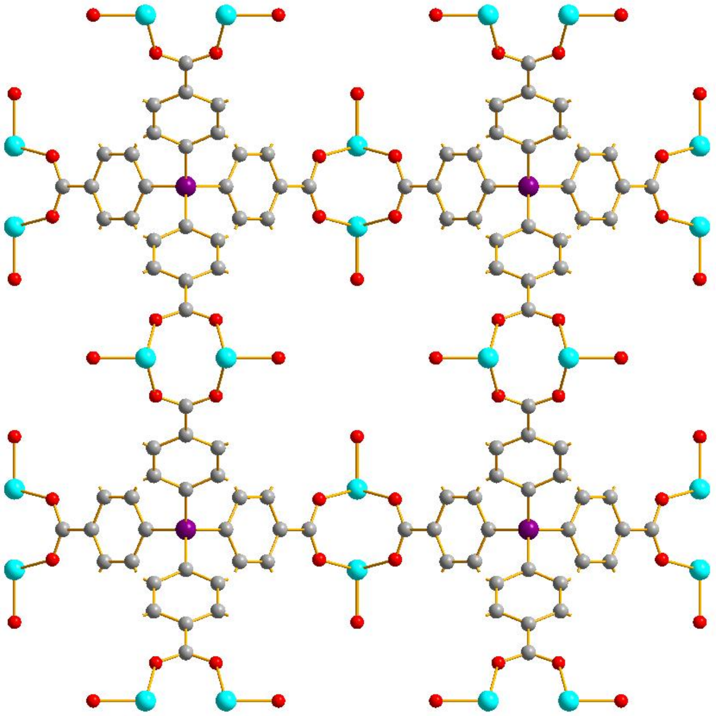

Figure S14. The representation of the crystal structure of PCN-516 along *c* axis

Section 4. Funding Resources of All Contributors

The authors sincerely acknowledge the following funding resources:

M. Z. was supported by ARPA-E Methane Opportunities for Vehicular Energy (MOVE) Program under the award number DE-AR0000249.

Y.-P. C. was supported by Welch foundation under the award number A-1725.