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Electronic Supplementary Information

Pore-Controlled Formation of 0D Metal Complexes in Anionic 3D Metal-Organic Frameworks

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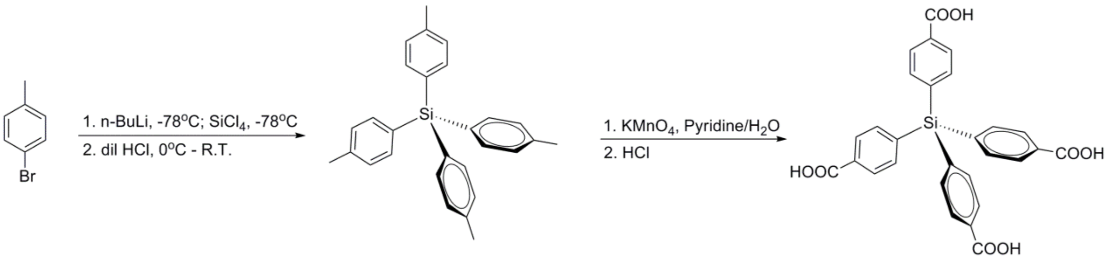
Section 1. Materials and Instrumentation

The H_4TCPS (4,4′,4″,4‴-tetrakiscarboxyphenylsilane) was synthesized by a reported procedure. [1] The *n*-butyl lithium (*n*-BuLi) and silicon tetrachloride ($SiCl_4$) were purchased from Sigma-Aldrich. All other commercial chemicals were purchased from VWR and used without further purification unless otherwise mentioned. The dry THF was produced by a THF still. ^{1}H nuclear magnetic resonance (NMR) data were recorded on a Mercury 300 MHz NMR spectrometer at the Center for Chemical Characterization and Analysis (CCCA), Department of Chemistry, Texas A&M University.

Section 2. Ligand Synthesis

The ligand H_4TCPS was synthesized from the following route (Scheme S1), according to a reported procedure. [1]



Scheme S1. The synthesis of H_4TCPS ligand

Section 3. Syntheses of PCN-514 series and PCN-518

1) PCN-514·DMF, $[Cd_3(TCPS)_2][Cd(DMF)_6](DMF)_2$

H_4TCPS (6.4 mg, 0.0125 mmol) and $Cd(NO_3)_2 \cdot 4H_2O$ (23 mg, 0.075 mmol) were ultrasonically dissolved in 1.7 mL DMF (*N*, *N*-dimethylformamide). The reaction mixture was then heated in an 85 ℃ oven for 48 h. Large, colorless, blocky crystals were harvested.

2) PCN-514·DMA, $[Cd_3(TCPS)_2][Cd(DMA)_4(H_2O)_2](DMA)_2$

H_4TCPS (6.4 mg, 0.0125 mmol) and $Cd(NO_3)_2 \cdot 4H_2O$ (23 mg, 0.075 mmol) were ultrasonically dissolved in 1.7 mL DMA (*N*, *N*-dimethylacetamide). The reaction mixture was then heated in an 85 ℃ oven for 48 h. Large, colorless, blocky crystals were harvested.

3) PCN-514·DMA·NMP, $[Cd_3(TCPS)_2][Cd(DMA)_2(NMP)_2(H_2O)_2](DMA)_2$

H_4TCPS (6.4 mg, 0.0125 mmol) and $Cd(NO_3)_2 \cdot 4H_2O$ (23 mg, 0.075 mmol) were ultrasonically dissolved in 1.4 mL DMA (*N*, *N*-dimethylacetamide) and 0.3 mL NMP (*N*-methyl-2-pyrrolidone). The reaction mixture was then heated in an 85 ℃ oven for 48 h. Large, colorless, blocky crystals were obtained.

4) PCN-518, $Cd_3(TCPS)_2$

H_4TCPS (6.4 mg, 0.0125 mmol) and $Cd(NO_3)_2 \cdot 4H_2O$ (23 mg, 0.075 mmol) were ultrasonically dissolved in 1.7 mL DEF (*N*, *N*-diethylformamide). The reaction mixture was then heated in an 85 ℃ oven for 48 h. Large, colorless, blocky crystals were harvested.

Note that the structures of PCN-514·DMF and PCN-514·DMA·NMP were already reported in a previous manuscript, without discussing their host-guest interactions. In the previous manuscript, PCN-514·DMA·NMP (with a formula of $[Cd_3(TCPS)_2][Cd(DMA)_2(NMP)_2(H_2O)_2](DMA)_2$) was named as “PCN-514·DMA”. Nevertheless, this compound is named as “PCN-514·DMA·NMP” in this manuscript for clarity.

Section 4. Single-Crystal X-ray Crystallography of PCN-514·DMA and PCN-518

The crystals of both PCN-514·DMA and PCN-518 were taken from the mother solution directly, transferred into oil, and mounted onto a loop for single crystal X-ray data collection. Diffractions were measured on a Bruker Smart Apex diffractometer equipped with a Mo-Kα sealed-tube X-ray source (λ = 0.71073 Å, graphite monochromator) and a cooling device (110 K). The data frames were recorded using APEX2 and processed using *SAINT* within APEX2. The data were corrected for absorption and beam corrections based on the semi-empirical technique as implemented in *SADABS*. The structures were solved by direct methods using *SHELXS* and refined by full-matrix least-squares on F^2 using *SHELXL* in OLEX2.

PCN-514·DMA was integrated and refined in the triclinic crystal system. *XPREP* showed an R(sym) of 0.000 as standard for the Bravais lattice, Triclinic *P*. There was no more probable reasonable symmetry shown. We obtained an R value of 0.0239 and wR_2 of 0.0602 for the solution in $P\bar{1}$.

PCN-518 was integrated and refined in the monoclinic crystal system. Initial refinement provided a solution with an R_1 of 0.0656, however, high electron density in the pores that could not be crystallographically identified even after considerable restraints, most likely due to disordered counterions or solvent, prompted us to use the solvent mask routine of OLEX2. After using the solvent mask routine, we obtained an R_1 of 0.0271 for and a wR_2 of 0.0754 for the solution in $C2/c$.

For both solutions, all non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were located in calculated positions with isotropic displacement parameters set to 1.2 × U_{eq} of the attached atoms. In PCN-518, attempts to crystallographically locate and refine the counterion and solvent peaks were unsuccessful. Contributions to scattering due to these solvent molecules were removed using the solvent mask routine of OLEX2, and structures were then refined again using the data generated. The contents of the solvent region are not represented in the unit cell contents in the crystal data. 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 1032924 for PCN-514·DMA and CCDC 1032925 for PCN-518. Note that the cif files of PCN-514·DMF (CCDC 942375) and PCN-514·DMA·NMP (CCDC 942374) were already submitted to CCDC with a previous manuscript. [1]

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**.

Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program (**2009**). J. Appl. Cryst., 42, 339-341.

The graphic representation of crystal structures in this manuscript were made by:

Diamond - Crystal and Molecular Structure Visualization

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http://www.crystalimpact.com/diamond

Table S1. Crystal data and structure refinements for PCN-514·DMA and PCN-518.

Compound	PCN-514·DMA	Compound	PCN-518
Formula	$C_{40}H_{45}Cd_2N_3O_{12}Si$	Formula	$C_{224}H_{128}Cd_{12}O_{64}Si_8$
CCDC #	1032924	*CCDC #*	1032925
Fw	1012.68	*Fw*	5416.78
Shape	Block	Shape	Block
Crystal system	Triclinic	Crystal system	Monoclinic
Space group	$P\bar{1}$	Space group	$C2/c$
a (Å)	14.0970(19)	a (Å)	26.567(5)
b (Å)	14.2015(19)	b (Å)	14.332(3)
c (Å)	14.2649(19)	c (Å)	25.354(7)
α (°)	115.663(1)	α (°)	90.00
β (°)	113.627(1)	β (°)	119.200(2)
γ (°)	97.603(2)	γ (°)	90.00
V (Å^3)	2190.6(5)	V (Å^3)	8427(3)
Z	1	Z	1
$d_{\mathrm{calcd.}}$ (g/cm^3)	1.535	$d_{\mathrm{calcd.}}$ (g/cm^3)	1.067
μ(mm^{-1})	1.060	μ(mm^{-1})	0.823
F(000)	1024.0	F(000)	2672.0
$\theta_{\max}$ [deg]	54.000	$\theta_{\max}$ [deg]	54.000
Completeness	0.993	Completeness	0.998
Collected reflections	24914	Collected reflections	11193
Unique reflections	9495	Unique reflections	9196
Parameters	543	Parameters	349
Restraints	0	Restraints	0
R_{int}	0.0282	R_{int}	0.0377
$R1$ [$I > 2\sigma(I)$]	0.0239	$R1$ [$I > 2\sigma(I)$]	0.0271
$wR2$ [$I > 2\sigma(I)$]	0.0602	$wR2$ [$I > 2\sigma(I)$]	0.0754
$R1$ (all data)	0.0269	$R1$ (all data)	0.0304
$wR2$ (all data)	0.0620	$wR2$ (all data)	0.0767
GOF on F^2	1.0450	GOF on F^2	1.0590
$\Delta\rho_{\max}/\Delta\rho_{\min}$ [e·Å^{-3}]	1.153/ -0.788	$\Delta\rho_{\max}/\Delta\rho_{\min}$ [e·Å^{-3}]	0.542/ -0.381

Section 5. Funding Resources of All Contributors

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1. Zhang, M.; Chen, Y.-P.; Zhou, H.-C., *CrystEngComm* **2013,** *15*, 9544-9552.