Electronic Supplementary Information

Assembly of porphyrin-based uranium organic frameworks with (3,4)-connected *pto* and *tbo* topology

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Synthetic procedures

Caution! The uranyl nitrate hexahydrate $UO_2(NO_3)_2 \cdot 6H_2O$ is a radioactive and chemically toxic reactant, precautions with suitable care and protection for handling such substances should be followed although it was used in the experiment.

Synthesis of Compound TCPP-U1. A mixture of $UO_2(NO_3)_2 \cdot 6H_2O$ (30 mg), H_4TCPP (5 mg) and 0.14 ml trifluroacetic acid (TFA) in the mixed solvent of 4 ml DMF and 1ml H_2O was loaded into a 10 mL autoclave. The autoclave was sealed and heated to 120 ℃ in an oven for 12 h, then cooled to room temperature naturally. purple column crystals of TCPP-U1 formulated with $[(CH_3)_4N]_4[(UO_2)_4(TCPP)_3] \cdot (solvent)_x$ were produced (70% yield based on H_4TCPP).

Synthesis of Compound TCPP-U2. A mixture of $UO_2(NO_3)_2 \cdot 6H_2O$ (30 mg), H_4TCPP (5 mg) and 0.14 ml TFA in the mixed solvent of 4 ml DMF and 1ml ethanol was loaded into a 10 mL autoclave. The autoclave was sealed and heated to 120 ℃ in an oven for 12 h, then cooled to room temperature naturally. Purple polyhedral crystals of TCPP-U1 formulated with $[(CH_3)_4N]_4[(UO_2)_4(TCPP)_3] \cdot (solvent)_x$ were produced (80% yield based on H_4TCPP).

Synthesis of Compound ZnTCPP-U2. A mixture of $UO_{2(}NO_3)_2 \cdot 6H_2O$ (20 mg), $Zn(NO_3)_2 \cdot 6H_2O$ (10 mg), H_4TCPP (5 mg) and 0.10 ml TFA in the mixed solvent of 4 ml DMF and 1ml H_2O was loaded into a 10 mL autoclave. The autoclave was sealed and heated to 120 ℃ in an oven for 12 h, then cooled to room temperature naturally. Purple polyhedral crystals of TCPP-U1 formulated with $[(CH_3)_4N]_4[(UO_2)_4(ZnTCPP)_3] \cdot (solvent)_x$ were produced (75% yield based on H_4TCPP).

The synthesis conditions of the above three compounds were summarized in Table S1.

Single crystal X-ray Crystallography and Powder X-ray Diffraction

Single crystal X-ray data were collected on a Bruker D8-Venture diffractometer with a Turbo X-ray Source (Mo–Kα radiation, λ = 0.71073 Å) adopting the direct-drive rotating anode technique and a CMOS detector at 273 K. Data processing was accomplished using the SAINT processing program. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELXTL software package (SHELXL-2014). Anisotropic thermal parameters were used for the non-hydrogen atoms. The diffraction contributions from these disordered solvents were removed by The SQUEEZE routine of PLATON. The structure details are given in Table S2. Selected bond distances and angles are listed in Table S3 and S4. CCDC number 1866998 for TCPP-U1 and 1866930 for ZnTCPP-U2.

Powder X-ray diffraction data were collected from 3° to 30° with a step of 0.02 on a Bruker D8 Advance diffractometer using Cu Kα radiation (λ = 1.54056 Å). The experimental powder X-ray diffraction patterns and the simulated ones are in agreement with each other, confirming the phase purity of the as-synthesized products (Figure S1). After soaking in water for 12h, the diffraction intensities of these compounds are very weak, indicating that these are unstable in water (Figure S2).

Table S1. The synthesis conditions of the three compounds

Name	H_4TCPP	$UO_2(NO_3)_2$•$6H_2O$	$Zn(NO_3)_2$•$6H_2O$	TFA	DMF	H_2O	ethanol
TCPP-U1	5 mg	30 mg	\	0.14 mL	4 mL	1 mL	\
TCPP-U2	5 mg	30 mg	\	0.14 mL	4 mL	\	1 mL
ZnTCPP-U2	5 mg	20 mg	10 mg	0.10 mL	4 mL	1 mL	\

Table S2. Crystallographic data of TCPP-U1 and ZnTCPP-U2

Identification code	TCPP-U1	ZnTCPP-U2
Empirical formula	$C_{384}H_{156}N_{24}O_{64}U_8$	$C_{144}H_{72}N_{12}O_{32}U_4Zn_3$
Formula weight	6880.62	3630.07
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Trigonal	Cubic
Space group	$R\bar{3}c$	$Fm\bar{3}m$
Unit cell dimensions	a = 48.144(6) Å c = 58.101(14) Å	a = 58.595(4) Å
Volume	116624(41) $Å^3$	201179(41) $Å^3$
Z	6	8
Density (calculated)	0.588 mg/m^3	0.240 mg/m^3
Absorption coefficient	1.689 mm^{-1}	0.723 mm^{-1}
F(000)	19800	13872
Theta range for data collection	2.158 to 18.881°.	2.085 to 13.622°.
Index ranges	-43<=h<=43, -43<=k<=43, -52<=l<=52	-38<=h<=38, -38<=k<=38, -38<=l<=38
Reflections collected	197406	74792
Independent reflections	10207 [R(int) = 0.0870]	1565 [R(int) = 0.0775]
Completeness to theta	99.5 %	98.8 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.125	1.170
Final R indices [I>2sigma(I)][a]	R_1 = 0.0750, wR_2 = 0.1796	R_1 = 0.0655, wR_2 = 0.2058
R indices (all data)	R_1 = 0.1184, wR_2 = 0.2164	R_1 = 0.0875, wR_2 = 0.2485
Largest diff. peak and hole	1.093 and -1.084 e.$Å^{-3}$	0.293 and -0.305 e.$Å^{-3}$

[a] $R_1 = \Sigma(\Delta F/\Sigma F_o)$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)]\}/\Sigma[w(F_o^2)^2]^{1/2}$, where $w = 1/\sigma^2(F_o^2)$

Table S3. Selected bond distances (Å) and angles (°) for TCPP-U1

U(001)—O(12)	1.776(11)	U(2) — O(00D)	2.447(11)
U(001)—O(13)	1.770(14)	U(2) — O(00D) #1	2.447(11)
U(001)—O(004)	2.456(9)	U(2) — O(00D) #2	2.447(11)
U(001)—O(005)	2.466(9)	U(2) — O(001)	2.389(11)
U(001)—O(006)	2.430(9)	U(2) — O(001) #1	2.389(11)
U(001)—O(007)	2.420(9)	U(2) — O(001) #2	2.389(11)
U(001)—O(009)	2.472(9)	O(13)—U(001)—O(12)	179.2(4)
U(001)—O(00A)	2.393(10)	O(10)—U(2)—O(11)	180.0
U(2)—O(10)	1.77(2)		
U(2)—O(11)	1.78(2)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+y+1,-x+1,z #2 -y+1,x-y,z

Table S4. Selected bond distances (Å) and angles (°) for ZnTCPP-U2

U(1)—O(90)	1.74(3)	U(1)—O(1)#3	2.457(10)
U(1)—O(91)	1.75(3)	U(1)—O(1)#4	2.457(10)
U(1)—O(1)	2.457(10)	U(1)—O(1)#5	2.457(10)
U(1)—O(1)#1	2.457(10)	O(90)—U(1)—O(91)	180(2)
U(1)—O(1)#2	2.457(10)		

Symmetry transformations used to generate equivalent atoms:
#1 y, z, x #2 z, x, y #3 x, z, y #4 y, x, z #5 z, y, x

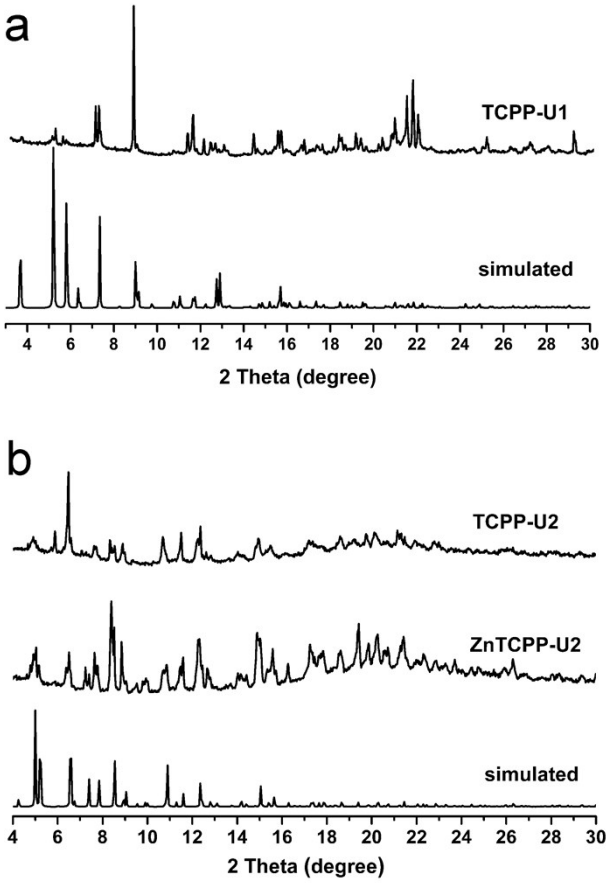

Figure S1. The XRD patterns of the as-synthesized samples and the simulated ones based on the single crystal structures

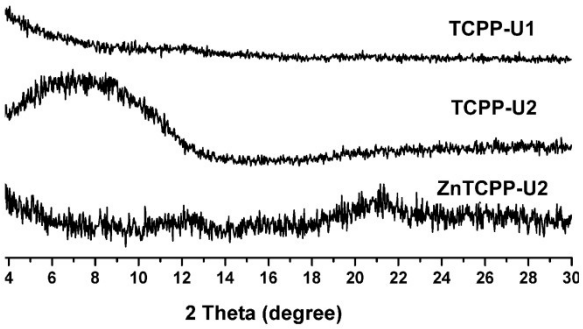

Figure S2. The XRD patterns of the compounds soaked in water for 12h.

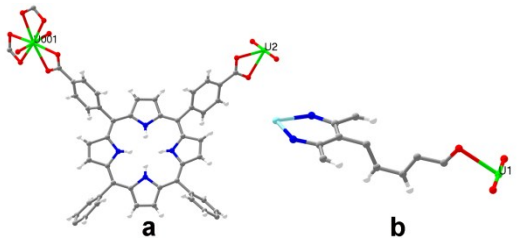

Figure S3. The asymmetric units of (a) TCPP-U1 and (b) ZnTCPP-U2. U, green; C, gray; N, blue; O, red; Zn, aqua.

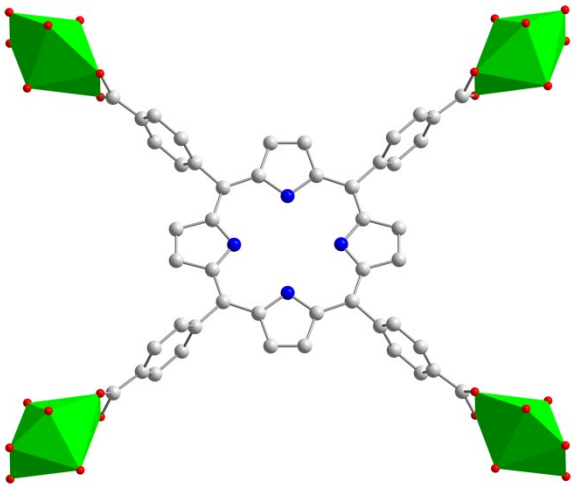

Figure S4. The coordination mode in compounds TCPP-U1 and ZnTCPP-U2.

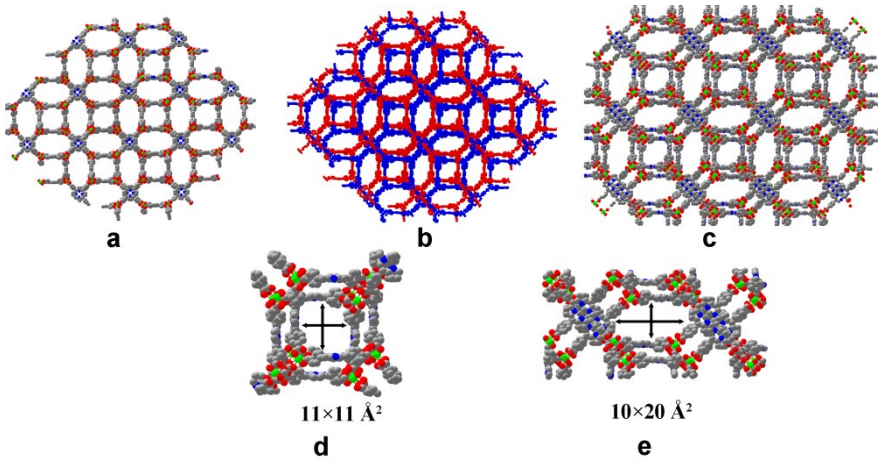

Figure S5. (a) Singlet network of TCPP-U1. (b) 2-fold interpenetrating network of TCPP-U1. (c) The structure of TCPP-U1 viewed along the [211] direction. (d) The small openings in TCPP-U1. (e) The large opening in TCPP-U1.

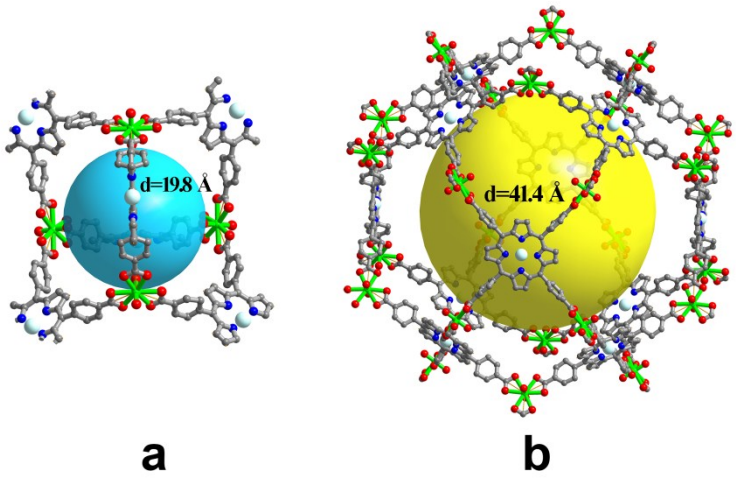

Figure S6. The small (a) and large cavities (b) of ZnTCPP-U2.

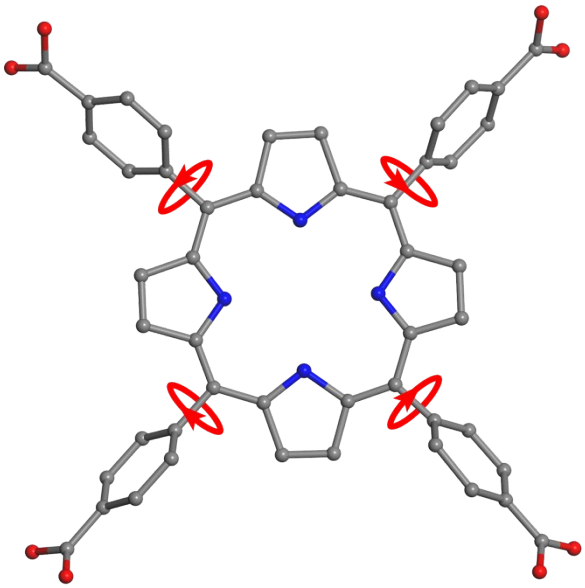

Figure S7. Schematic representation of the free rotation of four outer phenyl rings of H_4TCPP.

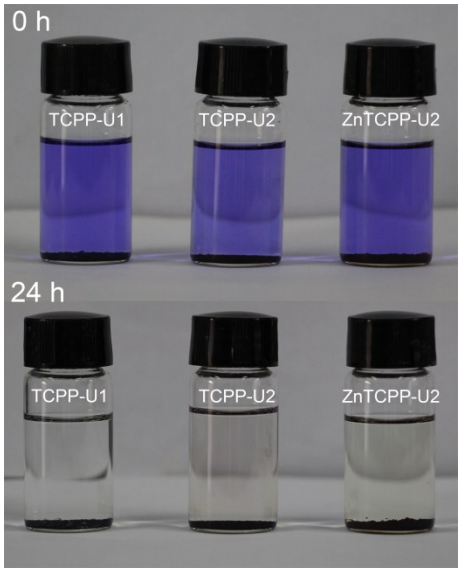

Figure S8. The photographs of UOFs before and after absorb crystal violet.

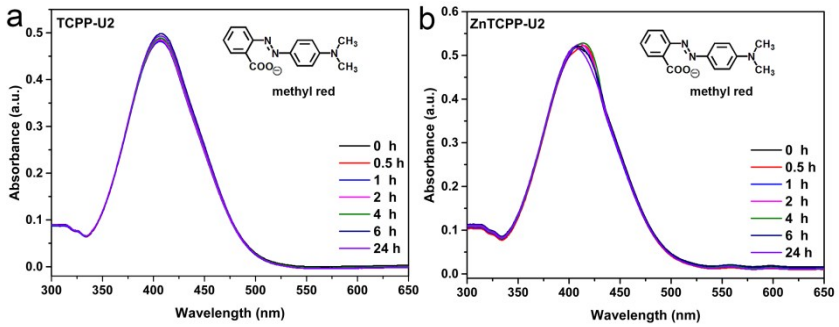

Figure S9. UV/Vis spectra of CH_3OH solutions of methyl red in the presence of (a) TCPP-U2 and (b) ZnTCPP-U2.