Electronic Supplementary Information

Inorganic acid influenced formation of Ti_{26} and Ti_{44} oxysulfates clusters with toroidal and capsule structures

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1 Materials and methods

All the reagents and solvents employed are commercially available and are used as received without further purification. $Ti(^{i}OPr)_4$ was purchased from adamas-beta.Co. Ltd. 1-Ethyl-3-Methyl Imidazolium ethyl ester sulfate ($EMImEtOSO_3$) ionic liquid was purchased from Green Chem. ILs Co. (China) Ltd.

1.1 Analytical

Elemental analyses are performed using a Perkin-Elmer 240C elemental analyzer. X-ray powder diffraction (PXRD) analysis is performed on a Mini Flex-II diffractometer with Mo K_α radiation (λ = 1.54056 Å) in the 2θ range of 3-50° with a scanning rate of 1°min^{-1}. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on an ABB Bomem MB102 spectrometer over a range of 400-4000 cm^{-1}. Thermal stability studies are carried out using a NETSCHZ STA-449C thermo analyzer with a heating rate of 10°C min^{-1} under a N_2 gas flow. Optical absorbance of solid state materials is measured by a solid state UV−Vis diffuse reflectance measurement method at room temperature with a Perkin-Elmer Lambda 950 UV/Vis spectrophotometer. The absorption data are calculated from the Kubelka-Munk function, ($F(R) = (1-R)^2/2R$),[1] where R representing the reflectance, K the absorption, and S the scattering. ESI-MS analysis is carried out for the dissolved samples (~200 mM) in methanol of **PTC-119** and **PTC-120** in the negative ion mode using Thermo Scientific Exactive Plus.

1.2 Single crystal x-ray diffraction data collection, structure solution and refinement procedures

Suitable single crystals are carefully selected under an optical microscope and glued to thin glass fibres. Crystals are found to be air stable at room temperature. Thereafter, single crystal X-ray diffraction analyses are performed on Super Nova diffractometer operated at 1200 W power (40 kV, 30 mA) to generate Cu K_α radiation (λ = 1.5418 Å) at 100K for **PTC-119** and **PTC-120**. The structures are solved by direct methods and refined on F^2 by full matrix least-squares using new SHELXL and OLEX2 program.[2,3] All of the non-hydrogen atoms are located from Fourier maps and are re-fined anisotropically. Even though, basic structural units were refined until full convergence was achieved, the EMIM cationic guests essentially show solvent disorders. Modeling of electron density within the voids and surrounding the cluster

units shows higher solvent disorders. Owing to large disorder of the solvent present in the cavities of these structures, the SQUEEZE command has been applied to remove disordered solvents. Solvent masking was applied during structure refinement.[4] **PTC-119:** A solvent mask was calculated and 944 electrons were found in a volume of 2990 V**(Å**^{3}) in 3 voids per unit cell. This possibly indicates the presence of 4[$C_6N_2H_{11}$], 0.125[H_2O], 0.125[H_2O] per Asymmetric Unit which account for 986 electrons per unit cell. **PTC-120:** A solvent mask was calculated and 539 electrons were found in a volume of 1703 V**(Å**^{3}) in 3 voids per unit cell. This possibly indicates the presence of 3[$C_6N_2H_{11}$], 1[$C_6N_2H_{11}$], 0.5[$C_6N_2H_{11}$] per Asymmetric Unit which account for 549 electrons per unit cell. The crystallographic data is listed in *Table S1*. CCDC numbers 1964507 **(PTC-119)** and 1964508 **(PTC-120)** contains the supplementary crystallographic data for this paper. Supplementary single crystal XRD data, including structure factors, is available free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

1.3 Synthesis of $(EMIm)_{16}[Ti_{26}(\mu_2\text{-}O)_{26}(SO_4)_{34}(H_2O)_8]$ (PTC-119)

$Ti(O^iPr)_4$ (1.8 ml, 6.0 mmol) and 0.15 mL (2.82 mmol) of 36.8 N sulfuric acid and 0.125 mL (2.08 mmol) of 10M H_3PO_3 solution were added to $EMImEtOSO_3$ (2 ml) ionic liquid and mixed thoroughly at room temperature. The resultant colorless transparent solution was transferred to Teflon lined autoclave and heated at 160°C for five days. Colorless rectangular shaped crystals of **PTC-119** were obtained after cooling to room temperature. The crystals are washed with excess amount of ethanol until excess ionic liquid washed off. Yield: 375 mg (about 75% based on Ti).

1.4 Synthesis of $(EMIm)_{27}[Ti_{44}(\mu_3\text{-}O)_{22}(\mu_2\text{-}OH)_{21}(\mu_2\text{-}O)_{17}(SO_4)_{40}(PO_3)_8]$ PTC-120

$Ti(O^iPr)_4$ (1.8 ml, 6.0 mmol) and 0.1 mL (1.8 mmol) of 36.8 N sulfuric acid and 0.25 mL (4.16 mmol) of 10M H_3PO_3 solution were added to $EMImEtOSO_3$ (2 ml) ionic liquid and mixed thoroughly at room temperature. The resultant colorless transparent solution was transferred to Teflon lined autoclave and heated at 160°C for five days. Colorless plate like crystals of **PTC-120** were obtained after cooling to room temperature. The crystals were washed with excess amount of ethanol until excess ionic liquid washed off. Yield: 425 mg (about 85% based on Ti).

2 Supporting data

Table S1. Crystal data and structure refinements summary for **PTC-119** and **PTC-120**.

	PTC-119	PTC-120
CCDC Number	1964507	1964508
Chemical formula	$C_{96}H_{177}N_{32}O_{169.3}S_{34}Ti_{26}$	$C_{162}H_{297}N_{54}O_{244}P_8S_{40}Ti_{44}$
Formula weight	6823.93	10543.28
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	P -1
Crystal size (μm)	0.306 × 0.269 × 0.138	0.223 × 0.134 × 0.039
a (Å)	22.7296(6)	19.0655(6)
b (Å)	22.0828(5)	20.2491(7)
c (Å)	27.8147(8)	27.7950(9)
α (deg)	90	92.296(3)
β (deg)	96.068(2)	98.803(3)
γ (deg)	90	117.541(3)
V (Å^3)	13882.9(6)	9327.0(6)
F(000)	6895.0	5327.0
Z	2	1
T(K)	100.0(3)	100.0(3)
ρcalc (g/cm^3)	1.632	1.877
μ (mm^{-1})	9.337	11.019
reflns coll.	54248	65751
unique reflns	244722	32915
GOF on F^2	1.040	1.106
R_1, wR_2 [I> 2σ(I)]	0.0869, 0.2429	0.1114, 0.2967
R_1, wR_2 (all data)	0.1183, 0.2803	0.1527, 0.3467

$^a R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$. $^b wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$

2.1 Photographs of crystals

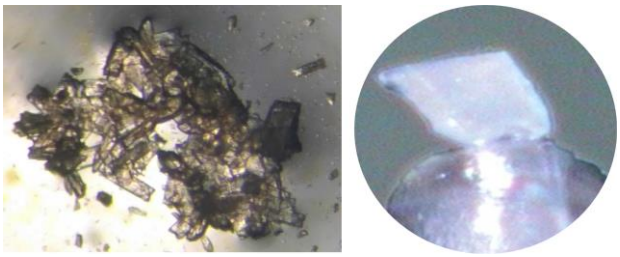

Figure S1. Crystals of **PTC-119** washed with ethanol.

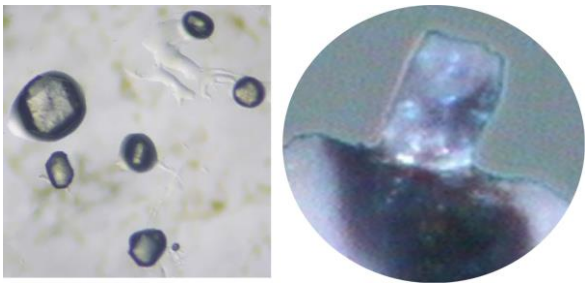

Figure S2. Crystals of **PTC-120** washed with ethanol.

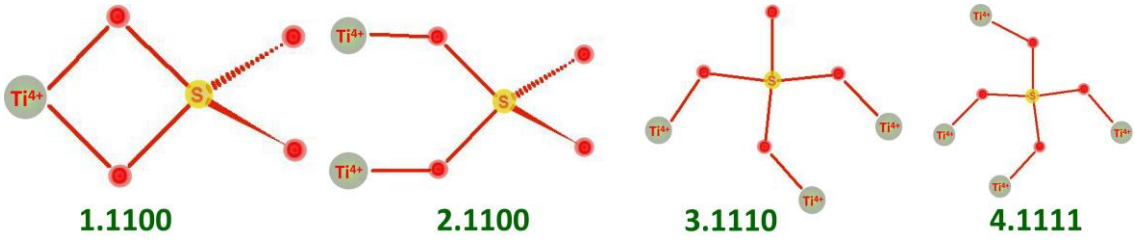

Figure S3. Representation of coordination modes (Harris notation) of sulfates observed in **PTC-119** and **PTC-120**.

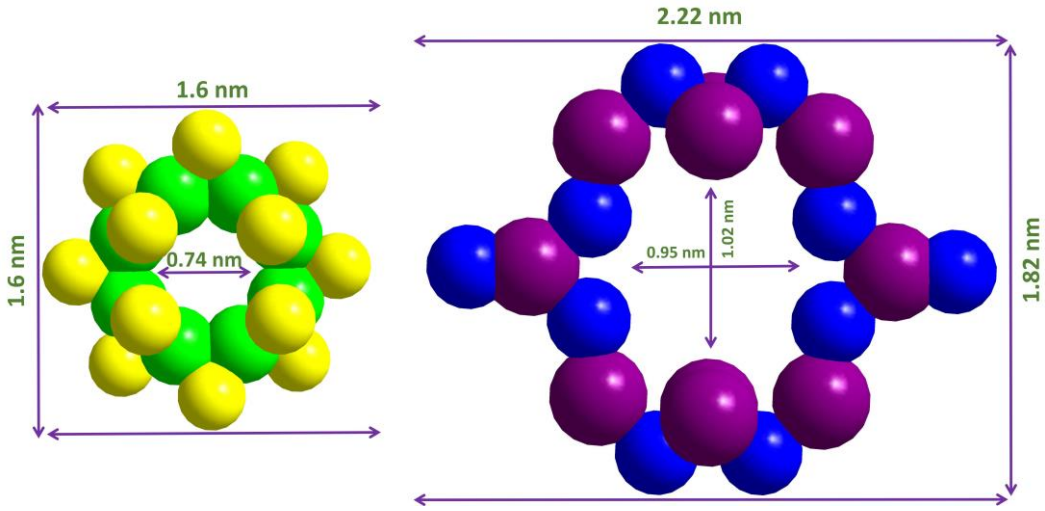

Figure S4. Representation of size dimensions for upper, lower and middle molecular rings in **PTC-119**. Color codes: green and violet: Ti; yellow and blue: S. Atoms represented in space-filling mode.

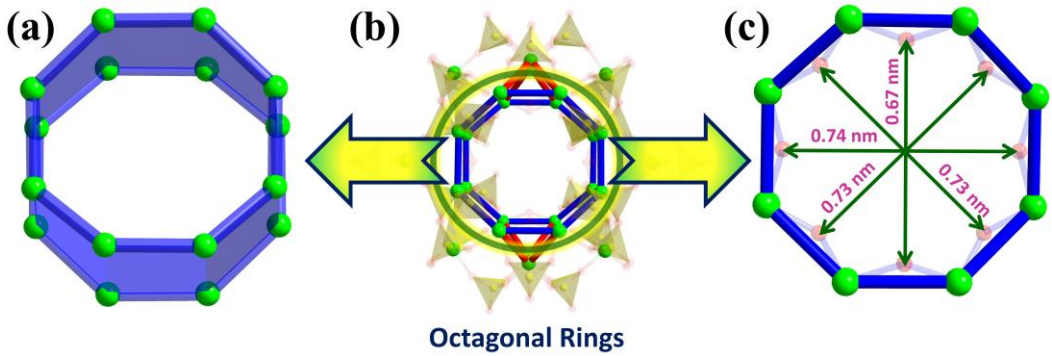

Figure S5. Octagonal ring (a); cluster core unit (b); dimensionalities of octagonal ring (c) in **PTC-119** molecular ring.

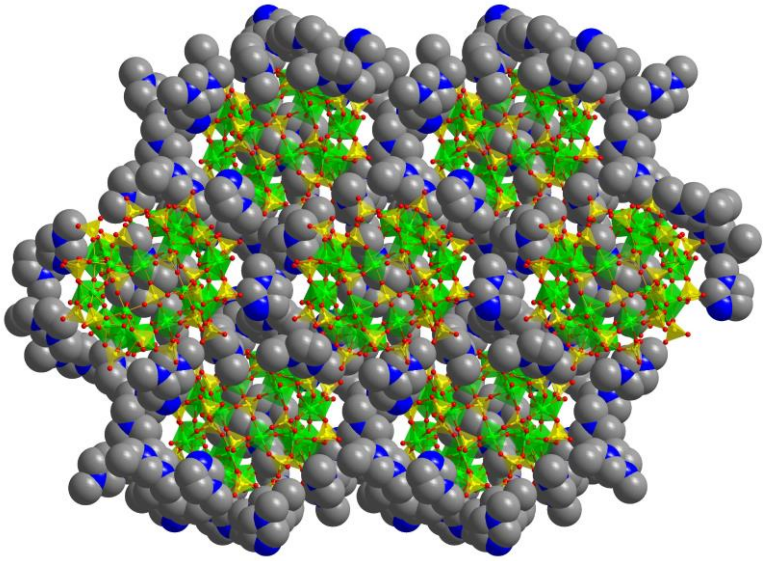

Figure S6. Infinite Ti_{26} molecular ring-supramolecular (EMIm) spacers packing structure in three dimensions in **PTC-119.** Green polyhedra: TiO_6; Yellow polyhedra: SO_4.

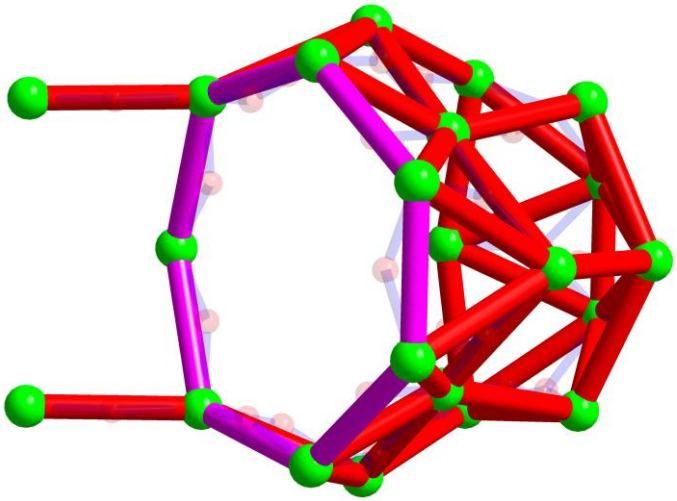

Figure S7. **{**$Ti_{22}O_{28}$**}** cavity like building unit with Ti-O-Ti bridging bonds in **PTC-120**. SO_4, PO_3 and EMIM cationic groups are omitted for clarity.

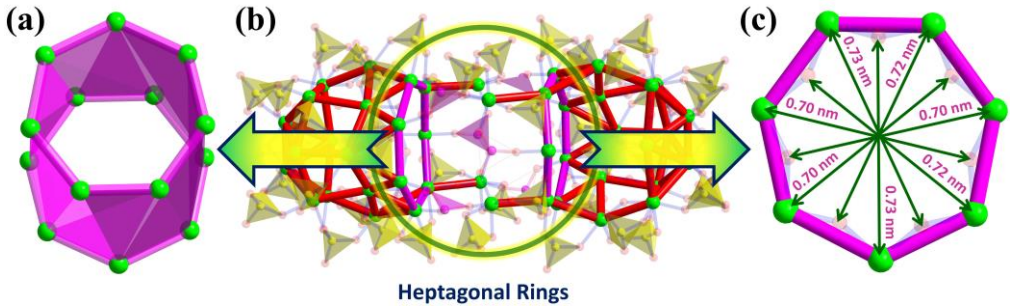

Figure S8. Heptagonal ring (a); cluster core unit (b); dimensionalities of heptagonal ring (c) in **PTC-120** molecular capsule.

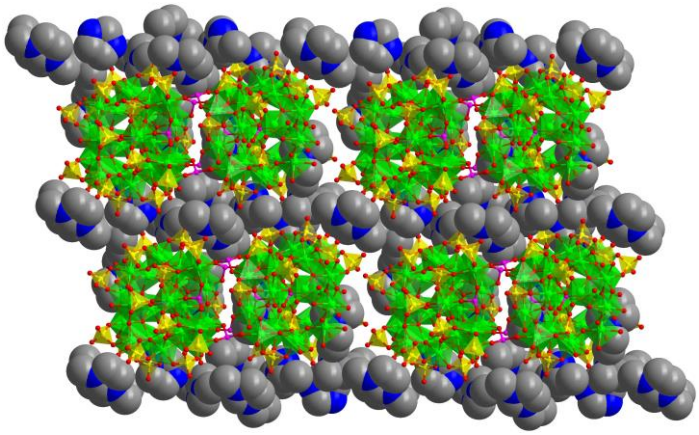

Figure S9. Infinite Ti_{44} molecular capsule-supramolecular (EMIm) spacers packing structure in three dimensions in **PTC-120.** Green polyhedra: TiO_6; Yellow polyhedra: SO_4; Pink polyhedra: PO_3.

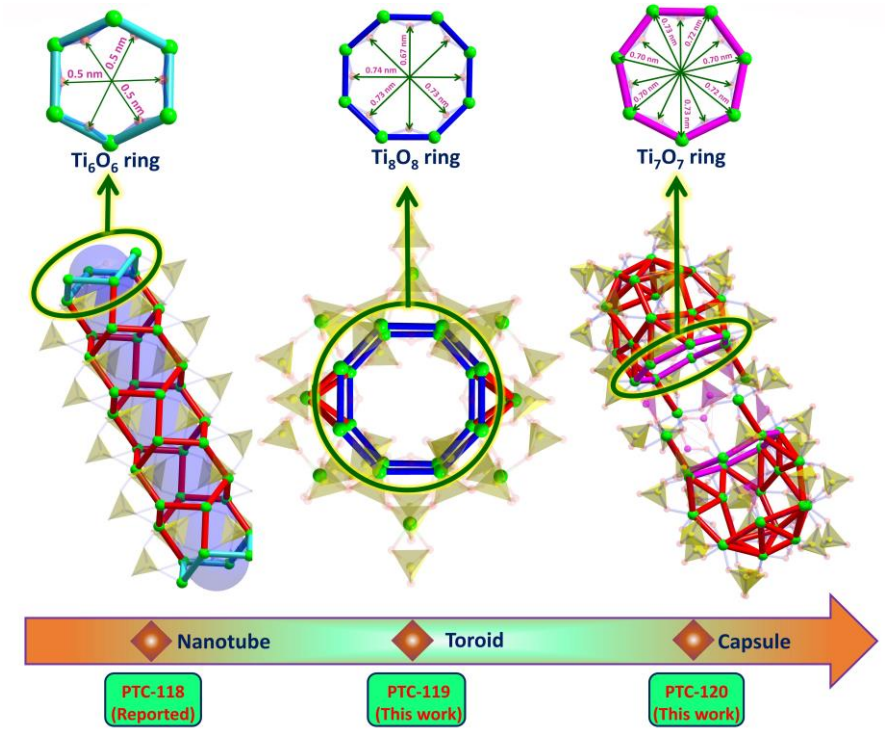

Figure S10. Representation of different symmetrical rings formed in the crystal structures of **PTC-118**, **PTC-119** and **PTC-120**.

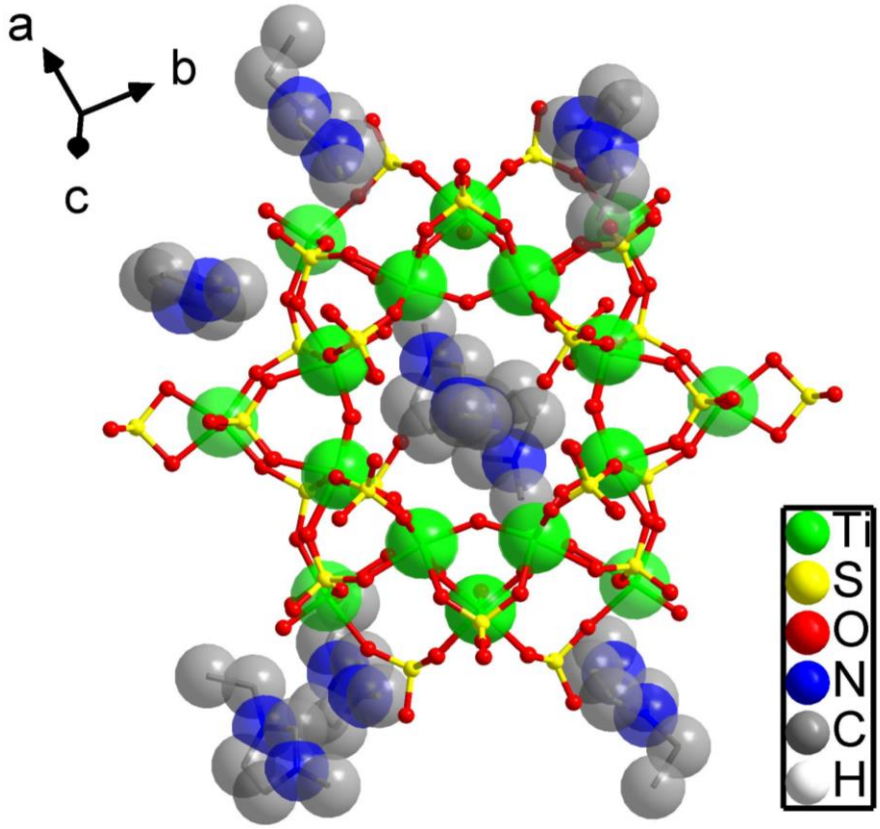

Figure S11. Representation of crystal structure of **PTC-119** with EMIm counter cations. Hydrogens are omitted for clarity.

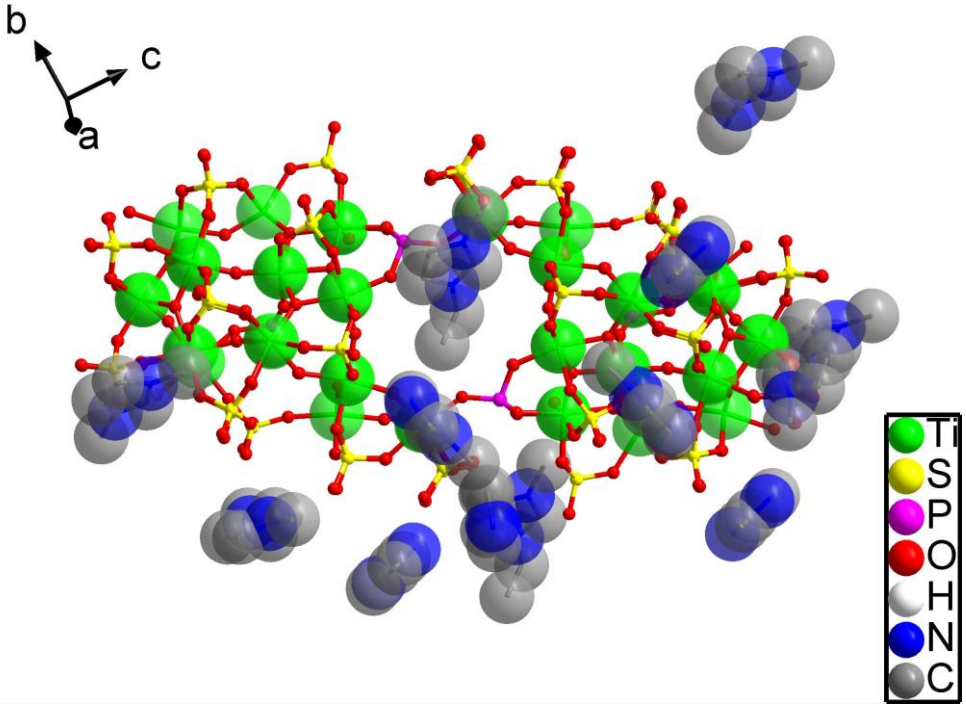

Figure S12. Representation of crystal structure of **PTC-120** with EMIm counter cations. Hydrogens are omitted for clarity.

2.2 Powder X-ray Diffraction (PXRD) Studies

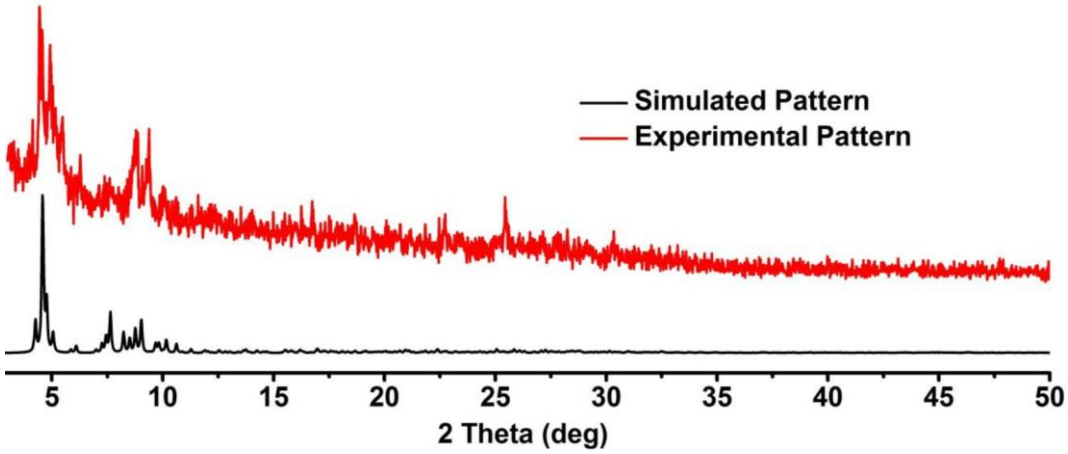

Figure S13. Comparative powder X-ray diffraction (PXRD) pattern for **PTC-119**.

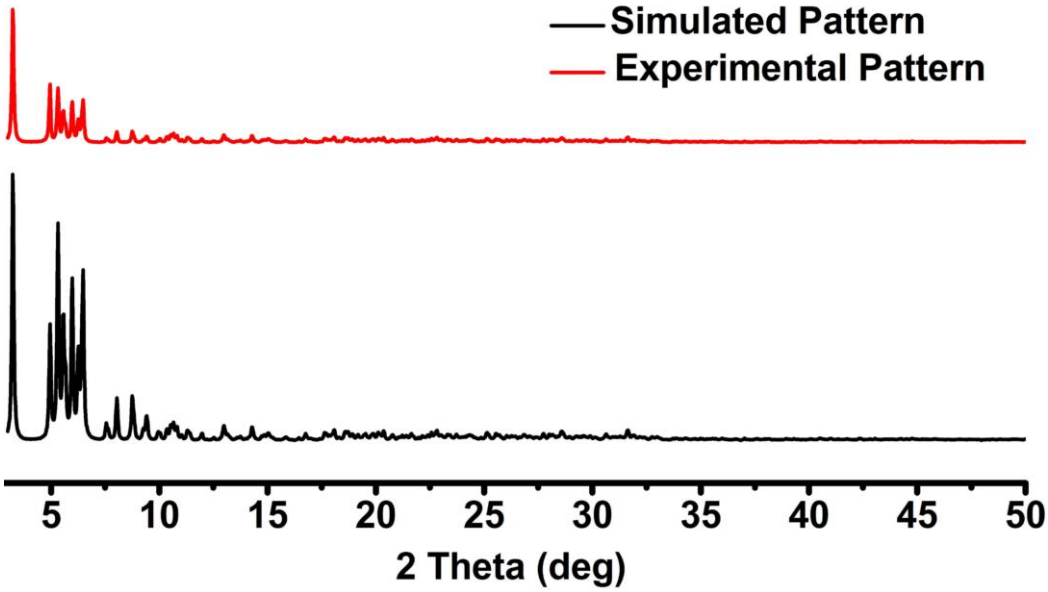

Figure S14. Comparative powder X-ray diffraction (PXRD) pattern for **PTC-120**.

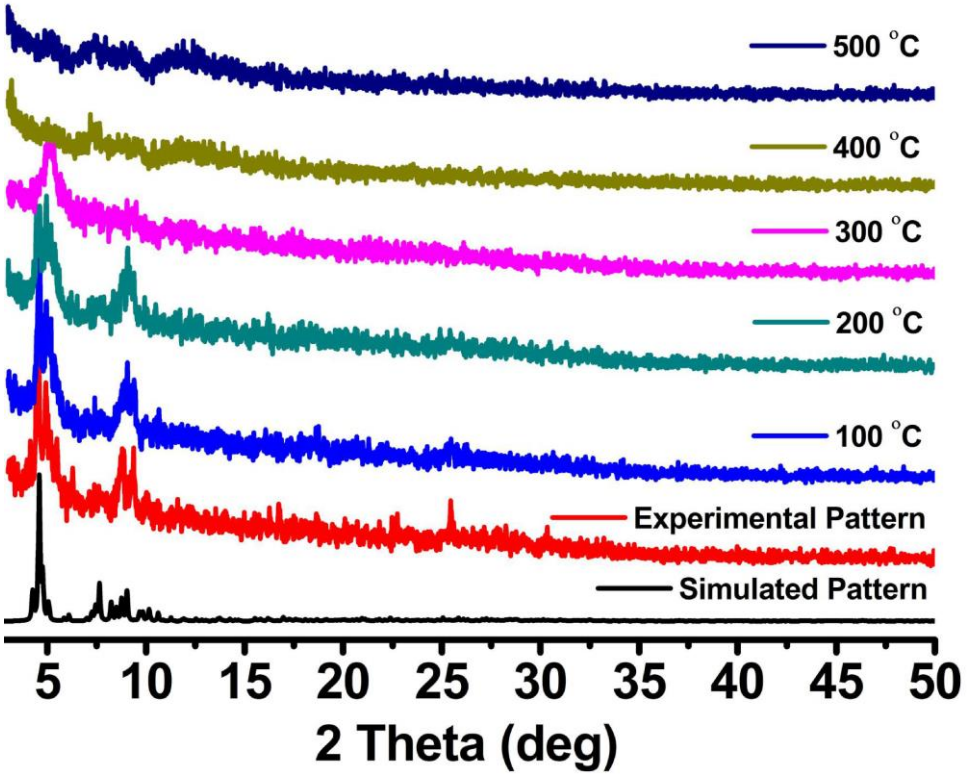

Figure S15. Differential temperature dependent powder X-ray diffraction (PXRD) pattern for **PTC-119**.

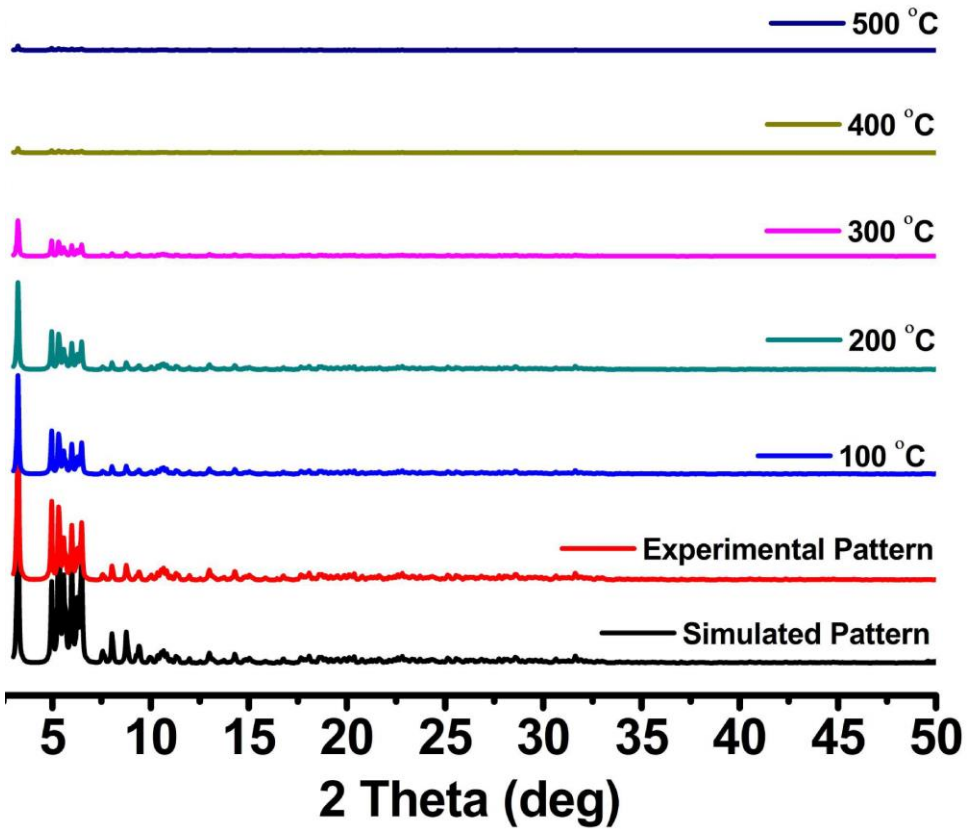

Figure S16. Differential temperature dependent powder X-ray diffraction (PXRD) pattern for **PTC-120**.

2.3 Fourier-Transform Infrared (FT-IR) spectra

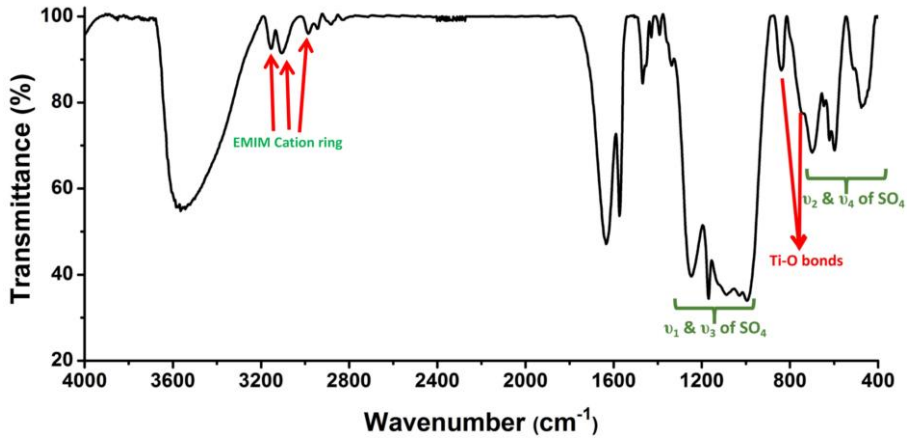

Figure S17. FT-IR spectra for **PTC-119**.

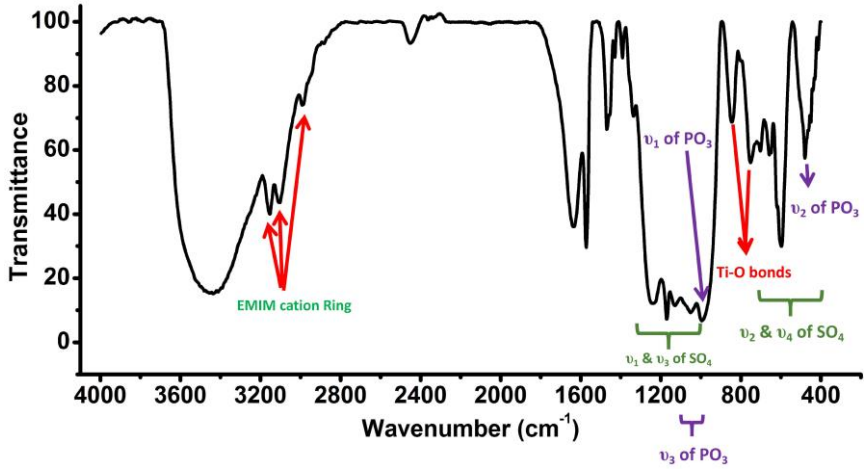

Figure S18. FT-IR spectra for **PTC-120**.

2.4 Solid state Ultraviolet-visible diffuse reflectance spectra (DRS)

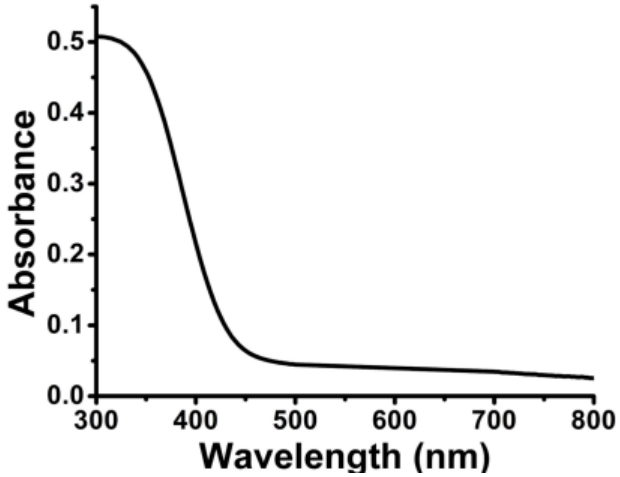

Figure S19. Solid state UV-visible diffuse reflectance spectrum for **PTC-119**.

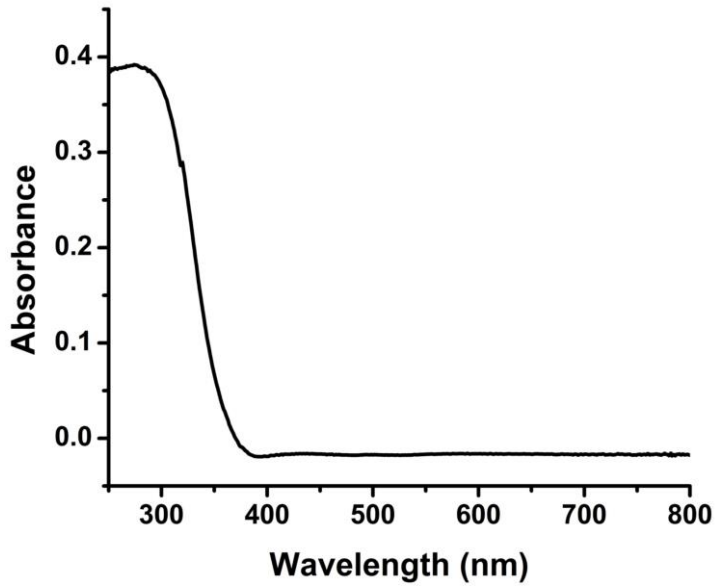

Figure S20. Solid state UV-visible diffuse reflectance spectrum for **PTC-120**.

2.5 Thermogravimetric Analysis (TGA)

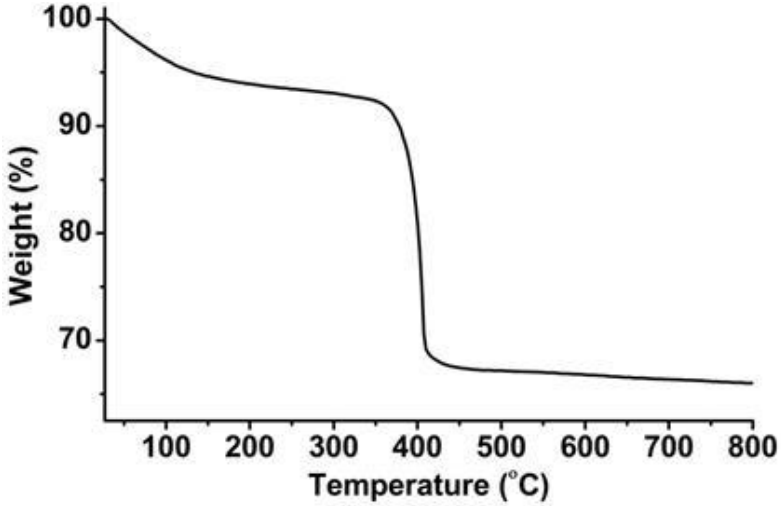

Figure S21. Thermo Gravimetric Analysis (TGA) for **PTC-119**.

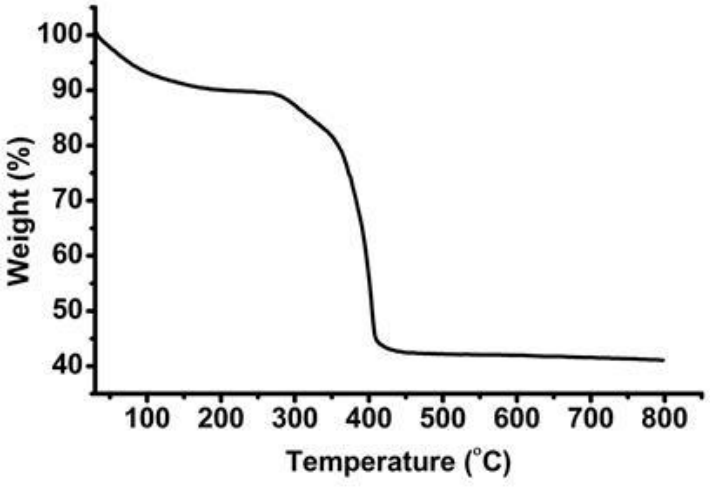

Figure S22. Thermo Gravimetric Analysis (TGA) for **PTC-120**.

References

1. W. W. Wendlandt; H. G. Hecht *Reflectance Spectroscopy; Interscience: New York*, **1966**.
2. Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.***2008**, 64, 112.
3. Sheldrick, G. M. *SHELXL-2014 Program for Crystal Structure Solution and refinement; University of Göttingen: Germany*, **2014**.
4. A. L. Spek, PLATON SQUEEZE: A tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Crystallogr. C Struct. Chem.* **2015**, 71, 9.