SUPPORTING INFORMATION

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Coordination Assembly of Tetrahedral Ti_4(embonate)$_6$ Cages with Alkaline-Earth Metal Ions

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Table S1. Crystallographic Data and Structure Refinement Details for **PTC-306** to **PTC-309**.

Compounds	**PTC-306**	**PTC-307**
CCDC	2108023	2108024
Formula	$C_{148}H_{94}Mg_4N_2O_{58}Ti_4$	$C_{162}H_{142.05}Ba_4O_{56}S_{12}Ti_4$
Formula weight	3116.98	4110.48
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c*	$P\bar{1}$
a (Å)	21.6563(2)	18.0321(2)
b (Å)	29.1042(3)	18.4434(2)
c (Å)	31.9709(3)	30.0998(4)
α (º)	90	89.7710(10)
β (º)	99.1780(10)	84.3900(10)
γ (º)	90	85.3170(10)
V (Å^3)	19892.9(3)	9929.1(2)
Z	4	2
D_{calcd} (g·cm^{-3})	1.049	1.101
μ (Mo/Ga K*a*) (mm^{-1})	1.305	6.252
F (000)	6384	4132.0
Temperature (K)	100	100
Theta min, max (º)	2.229, 60.523	2.090, 51.922
Tot., uniq. data	84097, 22110	113852, 33100
Observed data [($I > 2\sigma(I)$]	20375	28625
R_{int}	0.0316	0.0377
Data/restraints/parameters	22110/975/0	33100/4662/2160
R_1, wR_2 [$I > 2\sigma(I)$]	0.1169, 0.3258	0.1202, 0.3091
R_1, wR_2 (all data)	0.1214, 0.3289	0.1304, 0.3175
Goodness-of-fit on F^2	1.028	1.020
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e·Å^{-3})	–0.728, 0.482	–4.016, 4.382

Compounds	PTC-308	PTC-309
CCDC	2108025	2108025
Formula	$C_{95}H_{54}Ca_2NO_{31}Ti_{2.67}$	$C_{144}H_{87}Mg_3N_3O_{48}Ti_4$
Formula weight	1986.31	2891.58
Crystal system	Trigonal	Cubic
Space group	$R\bar{3}c$	$Pa\bar{3}$
a (Å)	25.8287(4)	32.2887(2)
b (Å)	25.8287(7)	32.2887(2)
c (Å)	208.621(3)	32.2887(2)
α (º)	90	90
β (º)	90	90
γ (º)	120	90
V (Å^3)	120530(4)	33662.9(6)
Z	36	8
D_{calcd} (g·cm^{-3})	0.985	1.155
μ (Mo/Cu K*a*) (mm^{-1})	0.292	1.539
F (000)	36636.0	12064.0
Temperature (K)	100	100
Theta min, max (º)	1.577, 26.372	2.060, 60.731
Tot., uniq. data	263098, 27167	47617, 12654
Observed data [($I > 2\sigma(I)$)]	14620	10624
R_{int}	0.1566	0.0321
Data/restraints/parameters	27167/193/1164	12654/6/617
R_1, wR_2 [$I > 2\sigma(I)$)]	0.1394, 0.3798	0.1184, 0.3354
R_1, wR_2 (all data)	0.1925, 0.4086	0.1284, 0.3424
Goodness-of-fit on F^2	1.285	1.077
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e·Å^{-3})	–0.562, 1.359	–0.89, 1.09

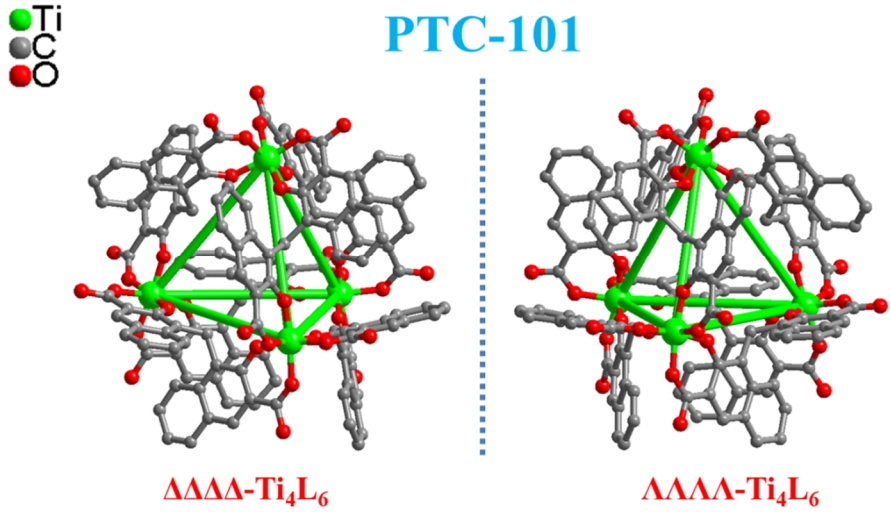

Figure S1. Structures of the ΔΔΔΔ-[Ti_4L_6] and ΛΛΛΛ-[Ti_4L_6] isomers in PTC-101.

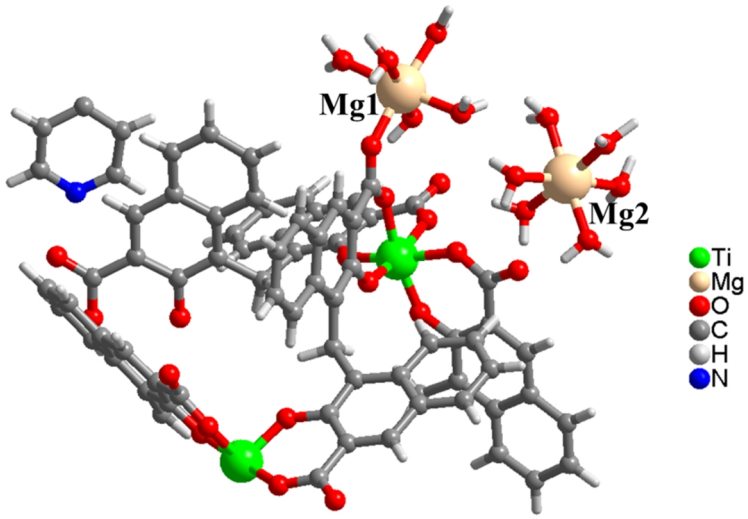

Figure S2. The asymmetric unit of **PTC-306**, showing a half of Ti_4L_6 cage, one Mg^{2+} ion, five coordinated waters, one free $[Mg(H_2O)_6]^{2+}$ cation, a half of bpy (4,4'-bipyridine) ligand and some free $(Me_2NH_2)^+$ cations which could not be located because of high disorder.

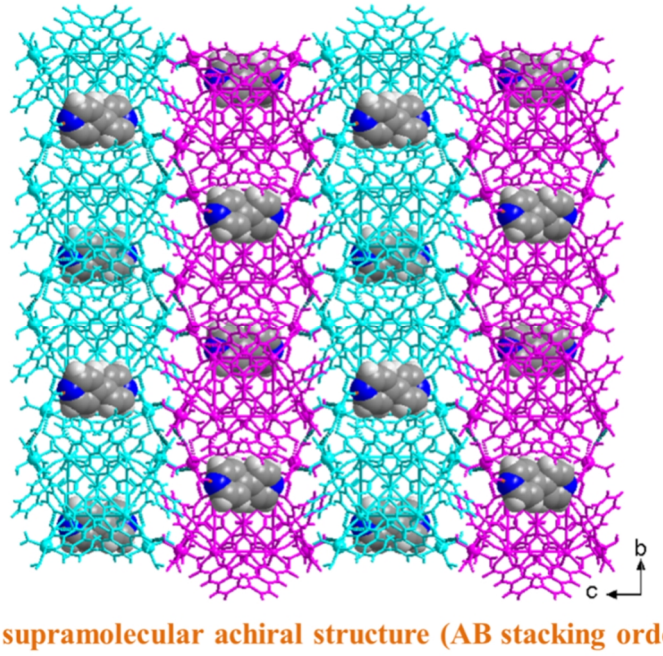

Figure S3. Packed H-bonding chiral layers of **PTC-306** in an AB fashion, in which the bpy ligands are filled in the 3D supramolecular structure.

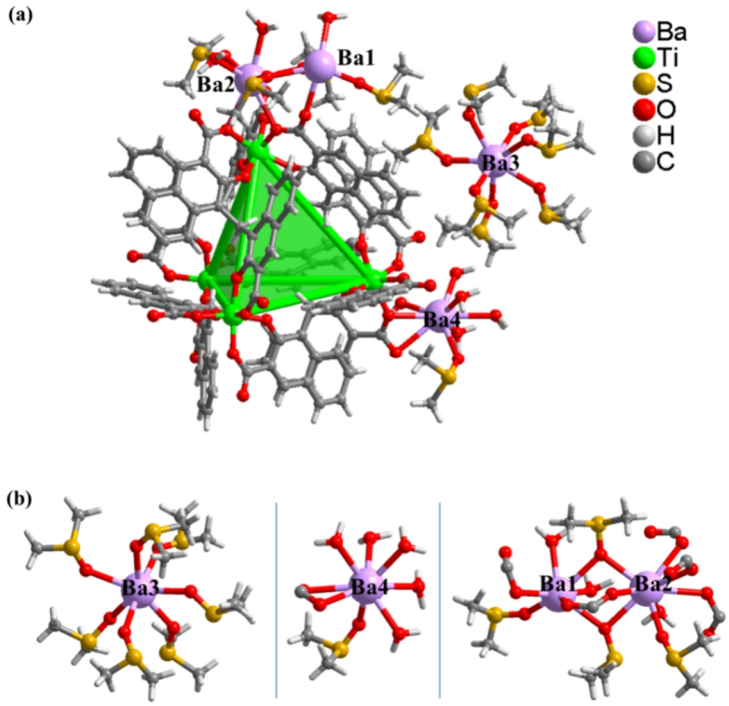

Figure S4. (a) The asymmetric unit of **PTC-307**, showing one Ti_4L_6 cage, four Ba^{2+} ions, five coordinated H_2O, five coordinated DMSO molecules, one free $[Ba(DMSO)_6]^{2+}$ cation and two Cl^- anions which could not be located because of high disorder; (b) the coordination environment of Ba atoms in **PTC-307**.

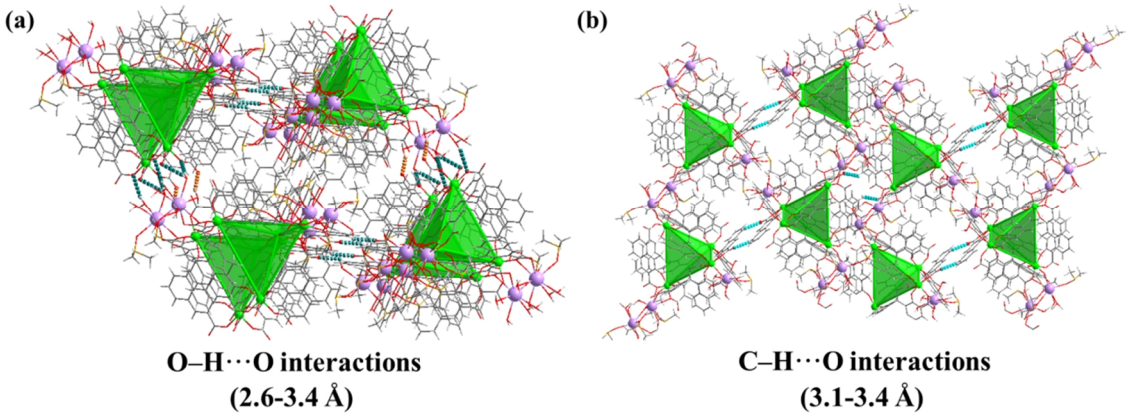

Figure S5. Highlighting of the O−H···O and C−H···O interactions between adjacent chains in **PTC-307**.

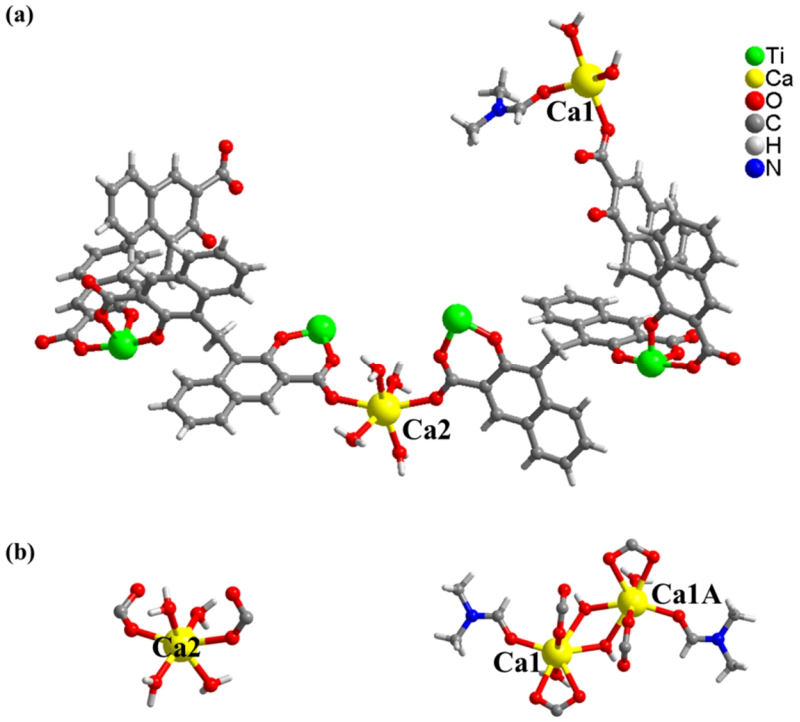

Figure S6. The asymmetric unit of **PTC-308**, showing two Ti_4L_6 cages with one third of occupancy, two Ca^{2+} ions, one μ_2-OH^- group, five coordinated H_2O and some free $(Me_4N)^+$ cations which could not be located because of high disorder; (b) the coordination environment of Ca atoms in **PTC-308**.

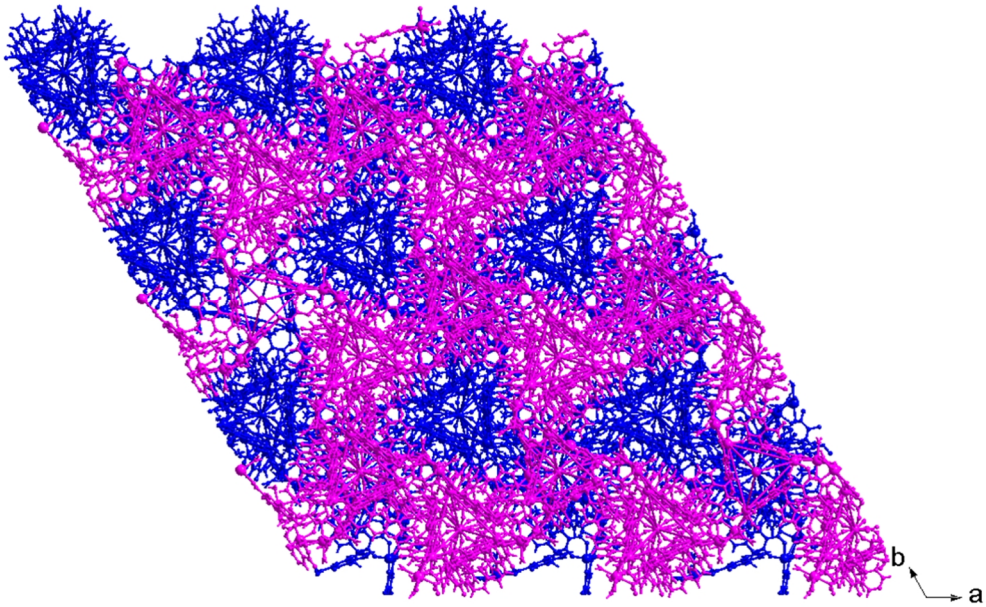

Figure S7. Packed layers of **PTC-308** along the c-axis.

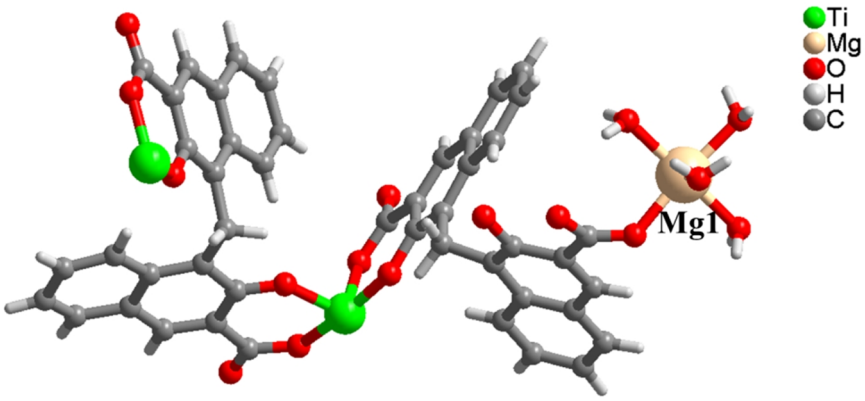

Figure S8. The asymmetric unit of **PTC-309**, showing one third of the Ti_4L_6 cage, one Mg^{2+} ion, four coordinated H_2O molecules and some free $(Me_2NH_2)^+$ cations which could not be located because of high disorder.

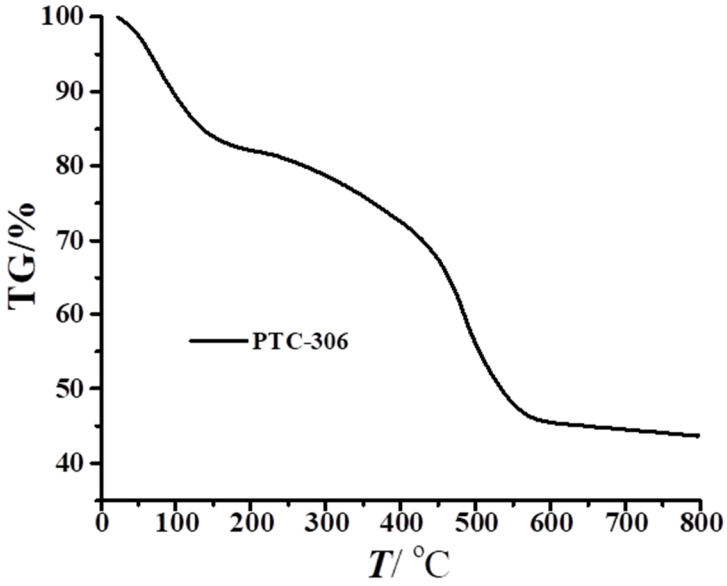

Figure S9. TGA curve of **PTC-306**.

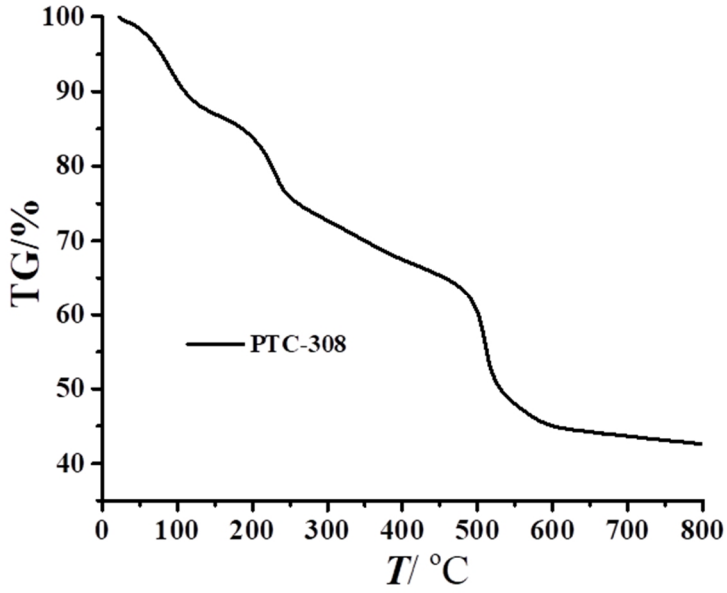

Figure S10. TGA curve of **PTC-308**.

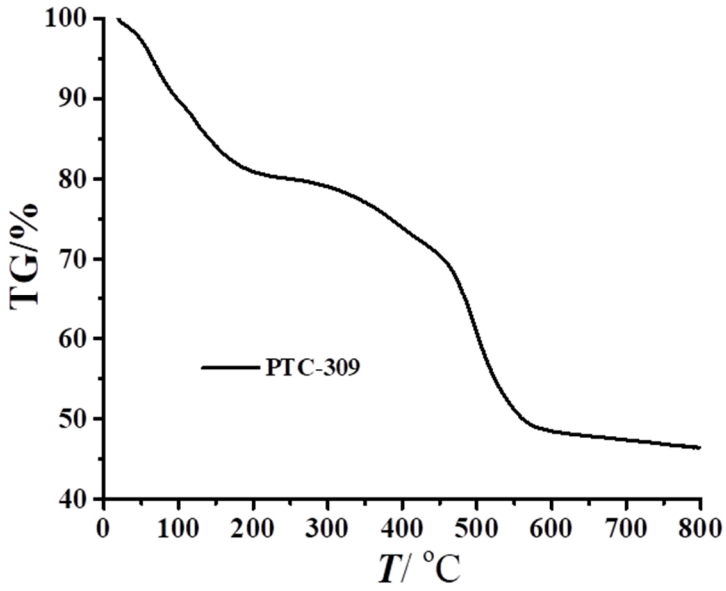

Figure S11. TGA curve of **PTC-309**.

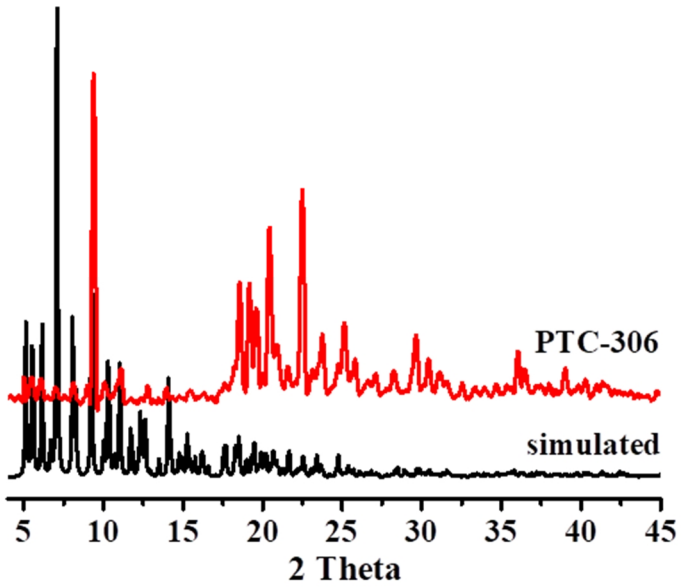

Figure S12. PXRD patterns of simulated from the single-crystal data of **PTC-306** (black), as-synthesized **PTC-306** (red).

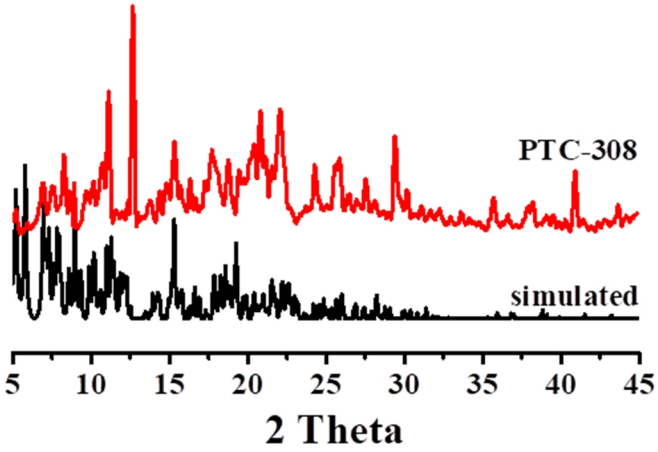

Figure S13. PXRD patterns of simulated from the single-crystal data of **PTC-308** (black), as-synthesized **PTC-308** (red).

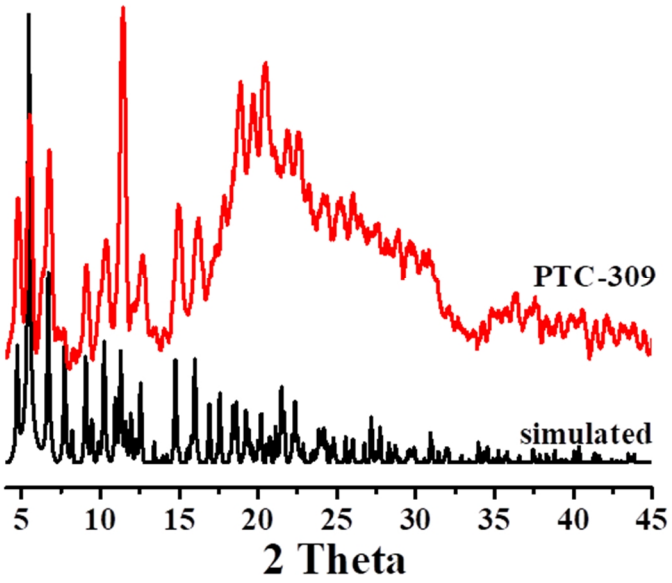

Figure S14. PXRD patterns of simulated from the single-crystal data of **PTC-309** (black), as-synthesized **PTC-309** (red).

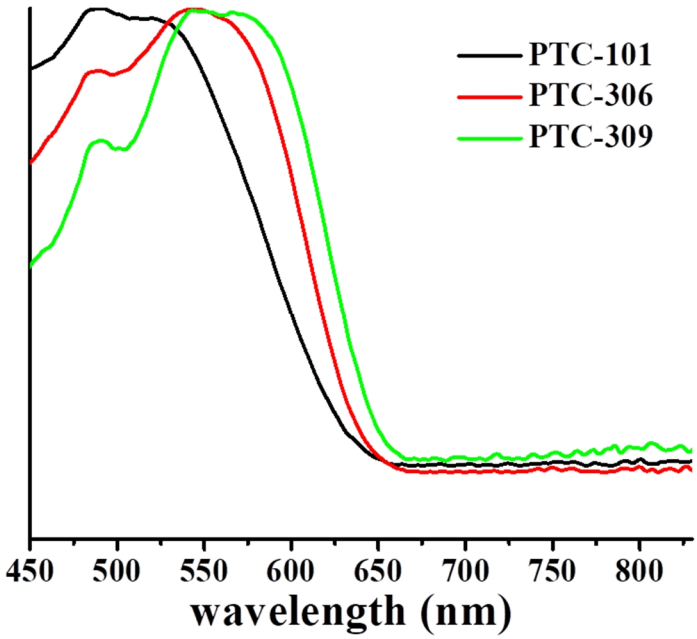

Figure S15. Solid-state UV/vis absorption spectra of PTC-101, **PTC-306** and **PTC-309**.

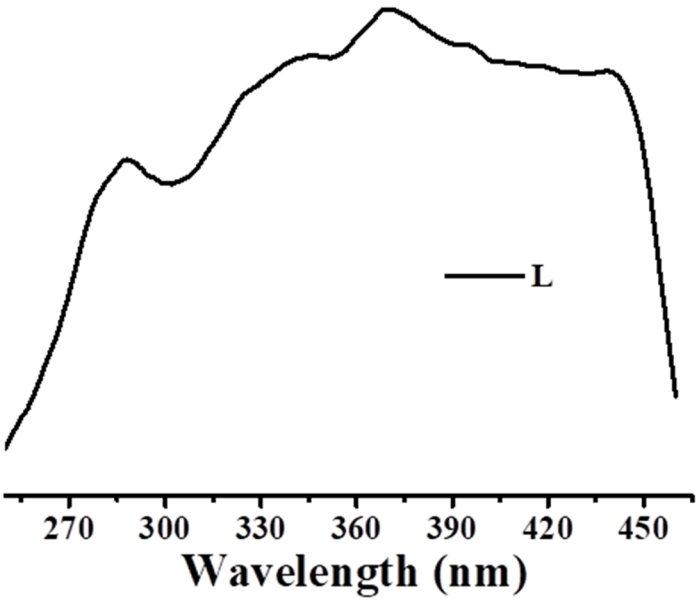

Figure S16. The excitation spectrum of L (embonate) ligand.

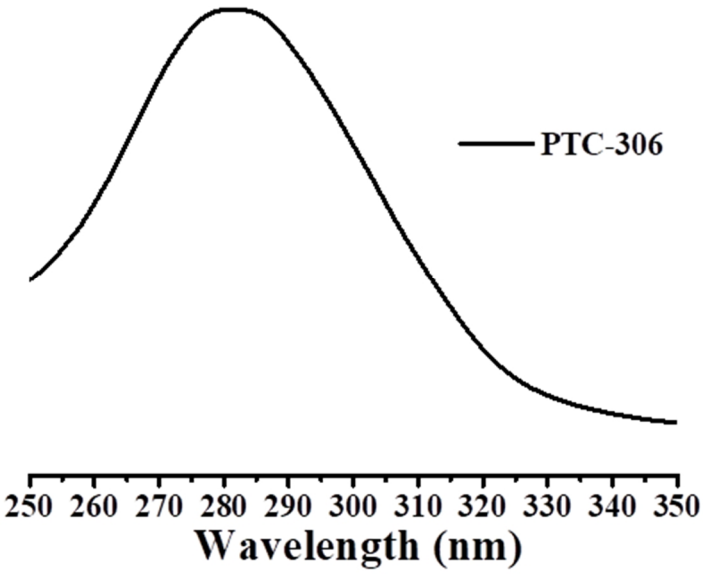

Figure S17. The excitation spectrum of compound **PTC-306**.

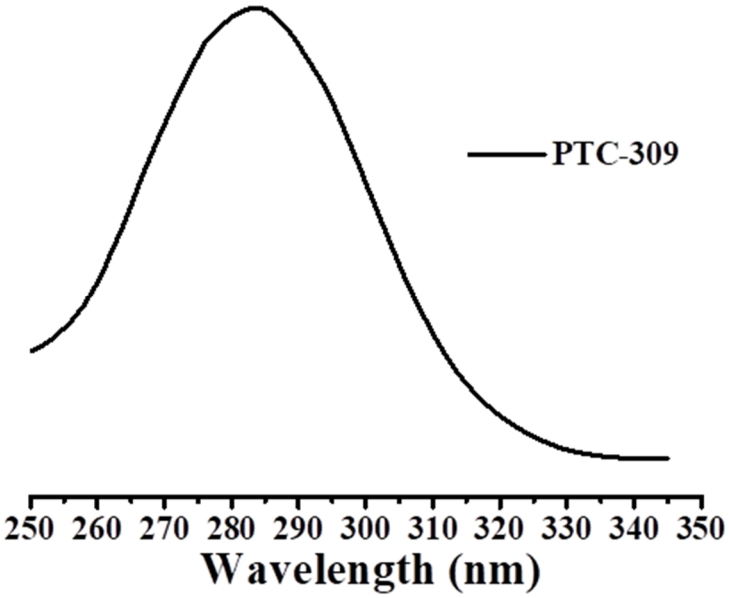

Figure S18. The excitation spectrum of compound **PTC-309**.