Electronic Supplementary Information

Green Separation Process of Ag via $Ti_4(embonate)_6$ Cage

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Table S1. Crystallographic Data and Structure Refinement Details for **PTC-201** to **PTC-204** and **PTC-206**.

Compounds	**PTC-201**	**PTC-202**	**PTC-203**	**PTC-204**	**PTC-206**
Formula	$C_{138}H_{126}Ag_6N_{12}O_{36}Ti_4$	$C_{138}H_{90}Ag_3N_6O_{36}Ti_4$	$C_{142}H_{105}Ag_3N_7O_{37.5}Ti_4$	$C_{142}H_{175}Ag_6N_{13}O_{64}Ti_4$	$C_{138}H_{72}O_{36}Ti_4$
Formula weight	3349.21	2923.39	3024.53	3926.80	2497.58
Crystal system	Trigonal	Trigonal	Trigonal	Trigonal	Trigonal
Space group	*R*3*c*	*R*-3*c*	*R*-3*c*	*R*3*c*	*R*-3*c*
a (Å)	24.1853(3)	25.8813(8)	26.338(2)	24.1540(2)	25.5719(8)
b (Å)	24.1853(3)	25.8813(8)	26.338(2)	24.1540(2)	25.5719(8)
c (Å)	48.9513(5)	71.8067(14)	71.462(4)	48.8604(5)	73.128(4)
α (°)	90	90	90	90	90
β (°)	90	90	90	90	90
γ (°)	120	120	120	120	120
V (Å)	24796.9(7)	41655(3)	42931(7)	24686.8(5)	41413(3)
Z	6	12	12	6	12
*D*calcd (g•cm^{-3})	1.346	1.398	1.404	1.585	1.202
μ (Mo K*a*) (mm^{-1})	7.702	5.838	5.692	0.974	2.521
F (000)	10608.0	17724.0	18420.0	12000.0	15312.0
Temperature (K)	100	100.00(18)	100.00(14)	100	100.01(16)
Theta min, max (deg)	4.551, 63.260	3.693, 58.930	3.142, 50.436	1.991, 33.328	2.332, 61.674
Tot., uniq. Data	44256, 6606	22070, 6665	21261, 5013	88557, 20101	27603, 7105
Observed data [($I > 2\sigma(I)$]	6431	5042	3015	18507	4224
Rint	0.0425	0.0347	0.0611	0.0270	0.0342
Data/restraints/parameters	6606/1/589	6665/14/560	5013/9/544	20101/55/684	7105/24/487
R_1, wR_2 *[I > 2σ(I)]*	0.0317, 0.0827	0.0820, 0.2143	0.1483, 0.4077	0.0535, 0.1490	0.0764, 0.2151
R_1, wR_2 *(all data)*	0.0328, 0.0838	0.1024, 0.2352	0.1917, 0.4588	0.0584, 0.1528	0.1136, 0.2498
Goodness-of-fit on F^2	1.068	1.040	1.561	1.085	1.032
$\Delta\rho$min, $\Delta\rho$max (e·Å^{-3})	-0.55, 0.58	-1.06, 1.00	-1.22, 1.49	-1.53, 1.75	-0.43, 0.33

[a] $R_1 = \Sigma||F_o| - |F_c|/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$

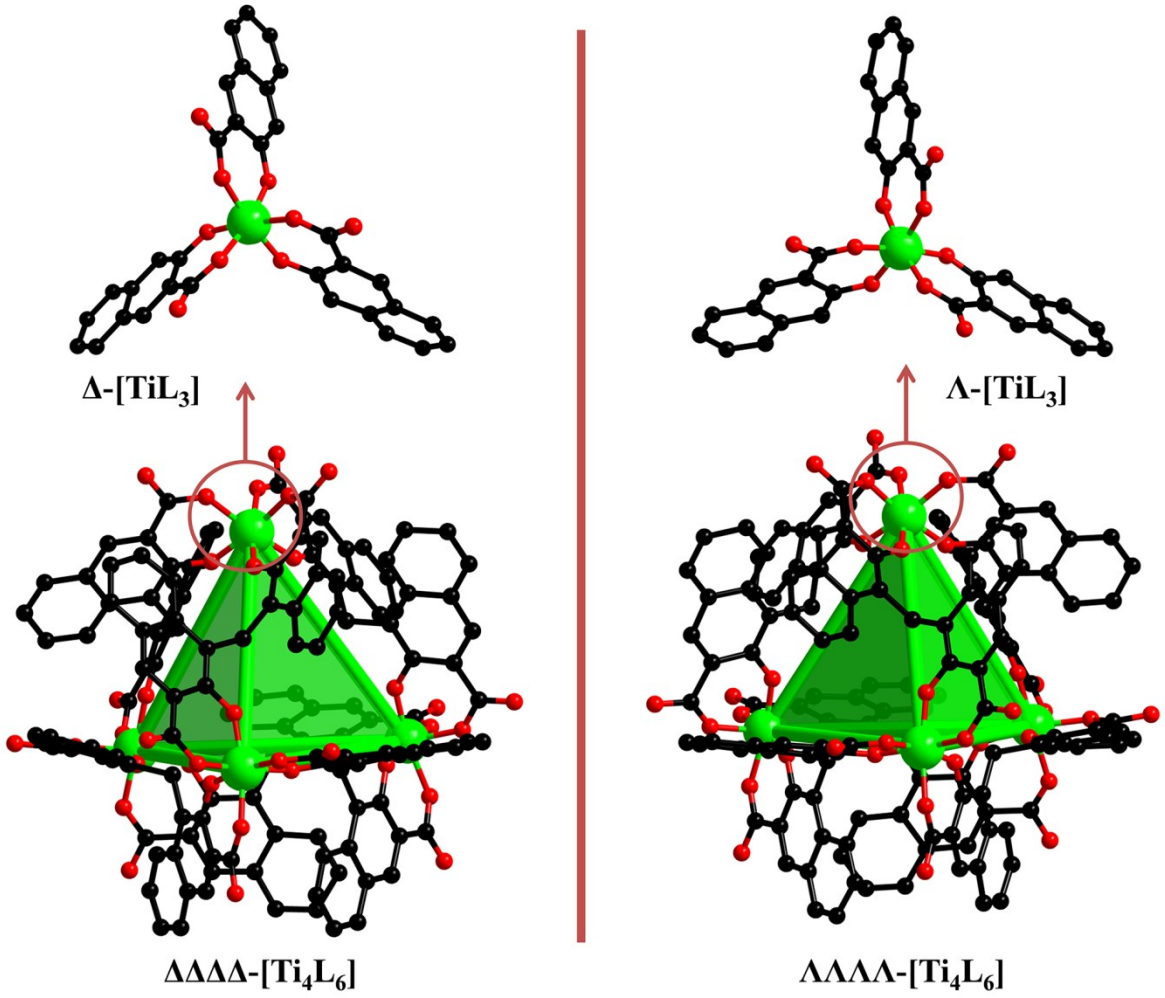

Figure S1 Illustration of the structures of the ΔΔΔΔ-[Ti_4L_6] and ΛΛΛΛ-[Ti_4L_6] isomers in PTC-101, highlighting the configuration of Δ-[TiL_3] and Λ-[TiL_3] corners. Atom color code: green Ti; red O; black C.

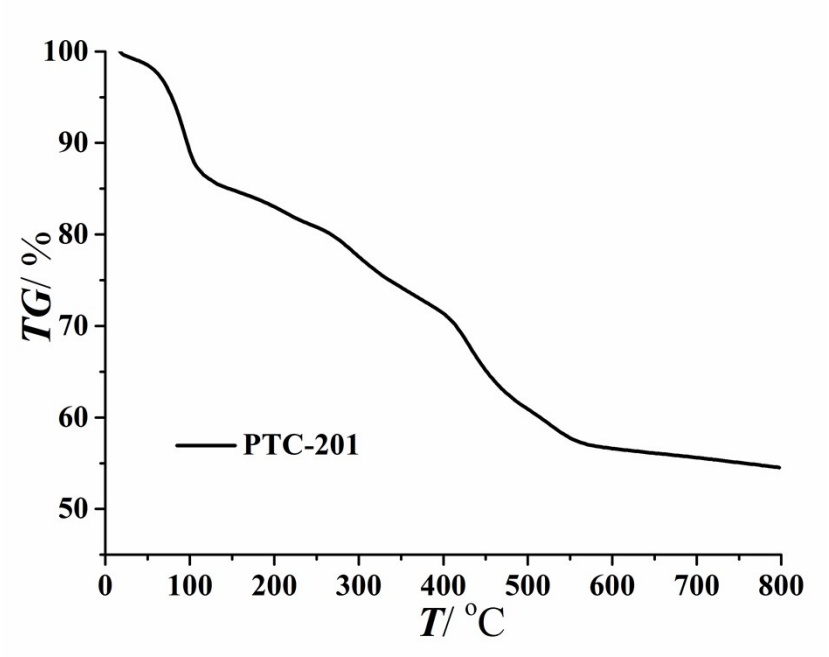

Figure S2 TGA curve of **PTC-201**.

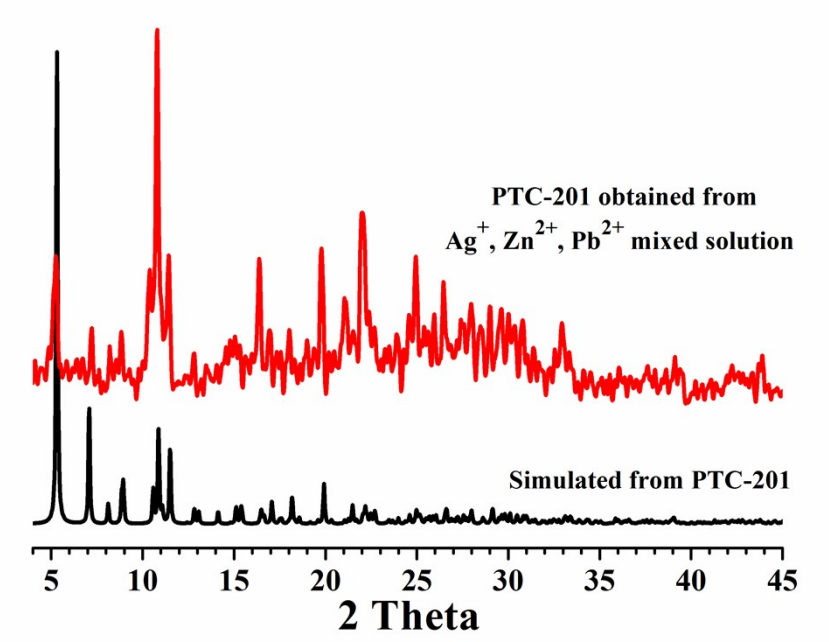

Figure S3 PXRD patterns of simulated from the single-crystal data of **PTC-201** (black) and the crystals of **PTC-201** obtained from Ag^{+}, Zn^{2+} and Pb^{2+} mixed solution.

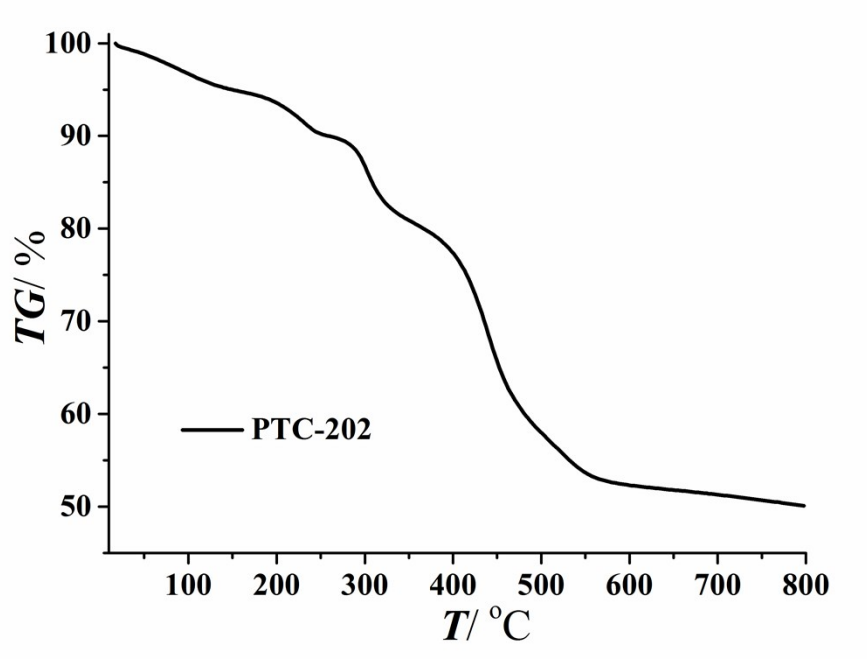

Figure S4 TGA curve of **PTC-202**.

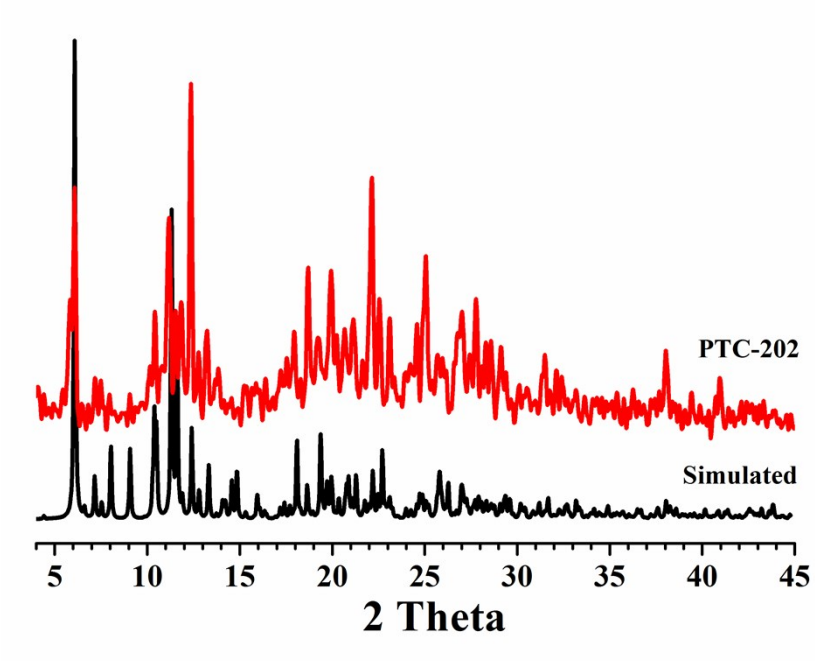

Figure S5 PXRD patterns of simulated from the single-crystal data of **PTC-202** (black) and as-synthesized **PTC-202** (red).

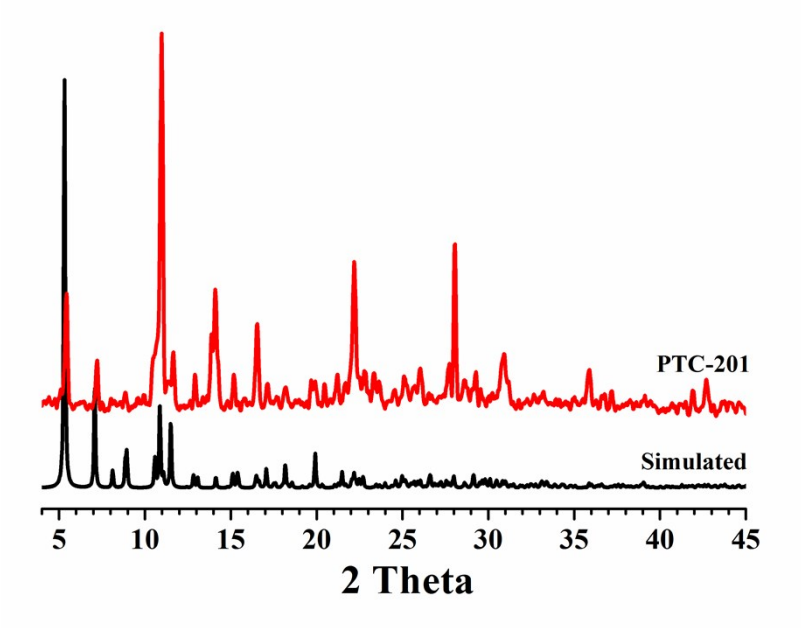

Figure S6 PXRD patterns of simulated from the single-crystal data of **PTC-201** (black) and **PTC-201** samples obtained by the transition from **PTC-202** (red).

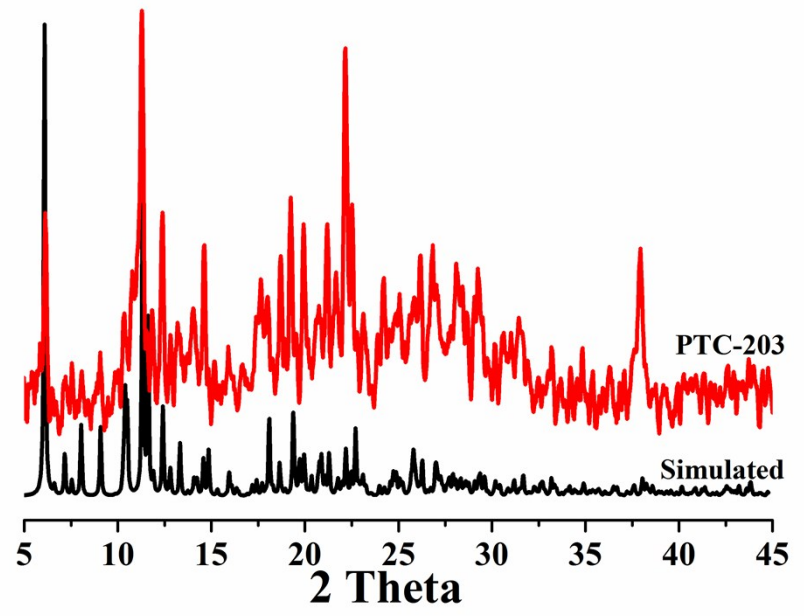

Figure S7 PXRD patterns of simulated from the single-crystal data of **PTC-203** (black) and as-synthesized **PTC-203** (red).

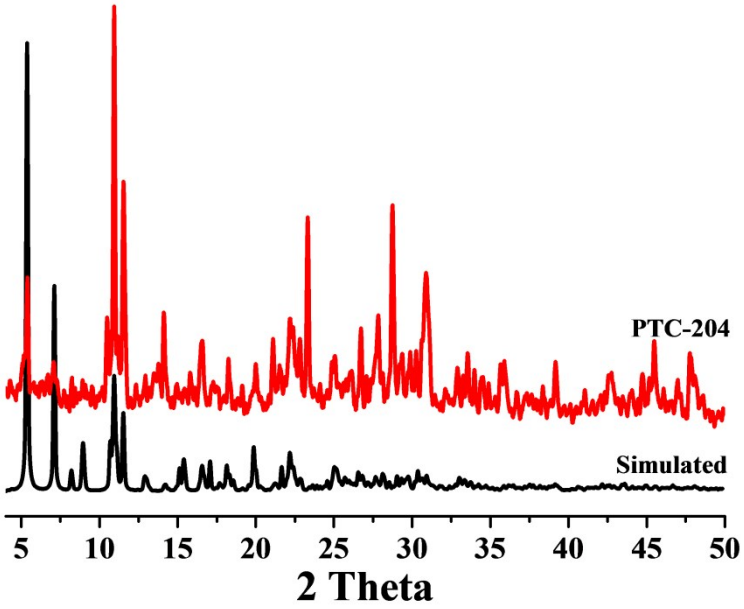

Figure S8 PXRD patterns of simulated from the single-crystal data of **PTC-204** (black) and as-synthesized **PTC-204** (red).

$$2[Ag(NH_3)_2]^+ + N_2H_4 + 2H_2O = 2Ag\downarrow + 4NH_3\uparrow + 2NH_3OH^+$$

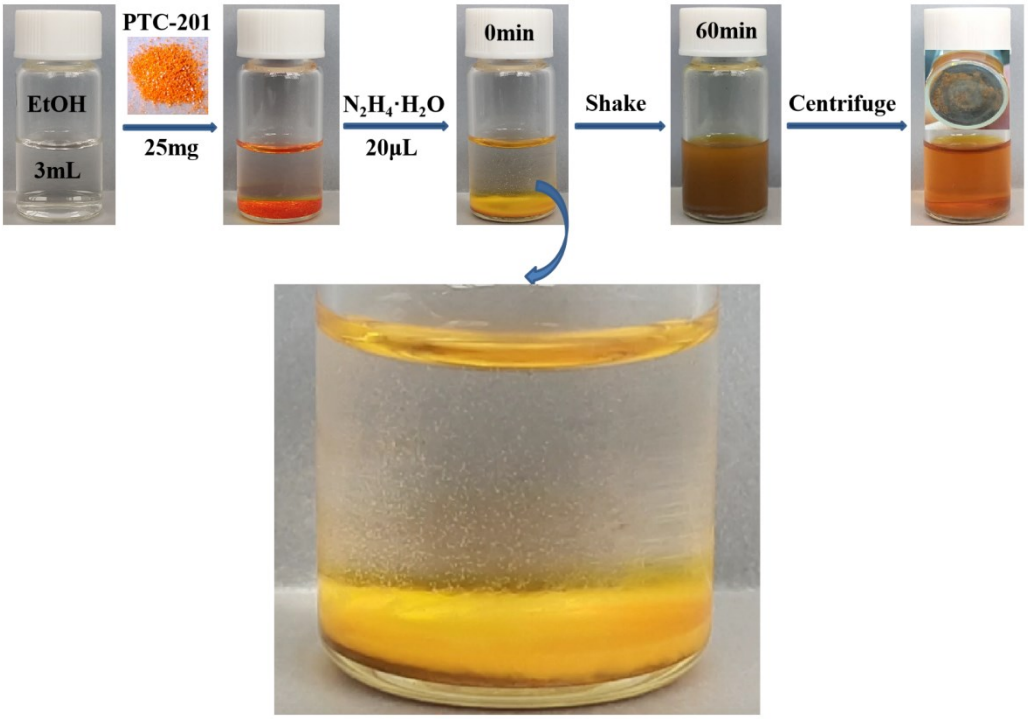

Figure S9 Equation and Photos of the reduction process of $[Ag(NH_3)_2]^+$ ions in **PTC-201** by $N_2H_4 \cdot H_2O$.

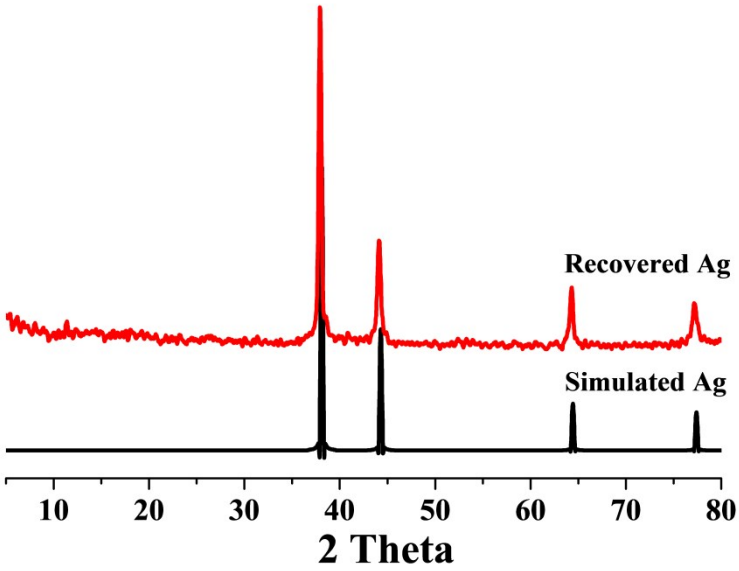

Figure S10 PXRD patterns of simulated Ag (black) and recovered Ag (red).

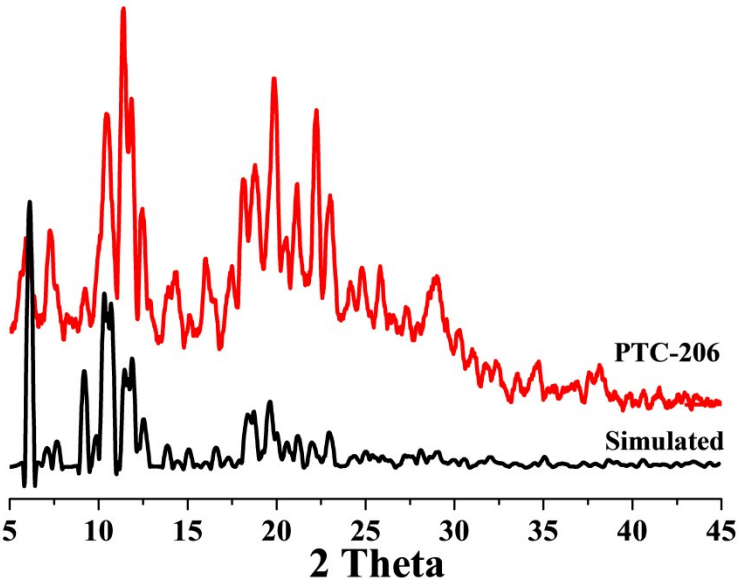

Figure S11 PXRD patterns of simulated from the single-crystal data of **PTC-206** (black) and as-synthesized **PTC-206** (red).