Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Construction of molecular rectangles with titanium–oxo clusters and rigid aromatic carboxylate ligands

Qing-Rong Ding,[a] Jin-Xiu Liu,[a] Nagaraju Narayanam,[a,b] Lei Zhang*[a] and Jian Zhang[a]

[a]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China.

[b]International College, University of Chinese Academy of Sciences, 100049 Beijing,China.

E-mail: LZhang@fjirsm.ac.cn

Experimental Section

Materials and Instrumentation. All reagents and solvents employed are commercially available and are used as received without further purification. Commercially available reagents were bought from Aladdin. $Ti(O^iPr)_4$ (96%) and isopropyl alcohol were bought from Admas-beta. The phase purity of products were confirmed by PXRD using a Rigaku Dmax2500 diffractometer with Cu Kα radiation (λ= 1.54056 Å) with a step size of 5 °/min. Thermogravimetric analyses (TGA) were performed using a NETSCHZ STA-449C thermoanalyzer with a heating rate of 10 °C/min under a nitrogen atmosphere. Fourier transform infrared (FT-IR) spectra were recorded with a Spectrum One FT-IR Spectrometer in the 500-4000 cm^{-1} range. UV-Vis absorption spectra were measured on a Perkin-Elmer Lambda 950 UV-Vis spectrophotometer. The elemental analyses were performed on an EA1110 CHNS-0 CE elemental analyzer.

Synthesis

Synthesis of PTC-121: Salicylic acid (0.0993 g, 0.72 mmol), terephthalic acid (0.0598 g, 0.36 mmol), and isopropyl alcohol (5.5 ml) were mixed at room temperature and then dropwise $Ti(O^iPr)_4$ (0.9 ml, 2.8 mmol) was added. The resultant solution was heated at 80 °C for three days in a scintillation vial. After cooling to room temperature, colorless crystals were obtained (yield: 65%). EA (%) calculated for $C_{104}H_{164}O_{44}Ti_{10}$: C, 48.10; H, 6.36. Found: C, 48.54; H, 6.12.

Synthesis of PTC-122: It was synthesized in the same way as that of **PTC-121** except that terephthalic acid was replaced by 2-aminoterephthalic acid (0.065 g, 0.36 mmol). The resultant solution was heated at 80 °C for four days in a scintillation vial. After cooling to room temperature, yellow colored crystals were obtained (yield: 50%). EA (%) calculated for $C_{104}H_{166}O_{44}N_2Ti_{10}$: C, 47.58; H, 6.37; N, 1.07. Found: C, 47.76; H, 6.03; N, 0.98.

Synthesis of PTC-123: 1-Hydroxy-2-naphthoic Acid (0.1128 g, 0.6 mmol), terephthalic acid (0.0416 g, 0.25 mmol), and isopropyl alcohol (5.5 ml) were mixed at room temperature and then dropwise $Ti(O^iPr)_4$ (0.9 ml, 2.8 mmol) was added. The resultant solution was heated at 80 °C for two days in a scintillation vial. After cooling to room temperature, yellow colored crystals were obtained (yield: 67%). EA (%) calculated for $C_{120}H_{172}O_{44}Ti_{10}$: C, 51.52; H, 6.2. Found: C, 51.67; H, 6.12.

Synthesis of PTC-124: It was synthesized in the same way as that of **PTC-123** except that terephthalic acid was replaced by 2-aminoterephthalic acid (0.0453 g, 0.25 mmol). The resultant solution was heated at 80 °C for two days in a scintillation vial. After cooling to room temperature, yellow colored crystals were obtained. EA (%) calculated for $C_{120}H_{174}O_{44}N_2Ti_{10}$: C, 50.98; H, 6.2; N, 0.99. Found: C, 51.13; H, 6.11; N, 1.08.

X-ray crystallography: Diffraction intensity data of the single crystal of **PTC-121** to **PTC-124** were collected on an 'Oxford SuperNova Dual Mo at zero, Atlas' CCD diffractometer equipped with a mirror-monochromated Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were applied using SADABS.[1] Structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL.[2]

Table S1. Crystallographic data and structure refinement summary for **PTC-121** to **PTC-124**.

	PTC-121	**PTC-122**	**PTC-123**	**PTC-124**
Empirical formula	$C_{104}H_{164}O_{44}Ti_{10}$	$C_{104}H_{166}O_{44}N_2Ti_{10}$	$C_{120}H_{172}O_{44}Ti_{10}$	$C_{120}H_{174}O_{44}N_2Ti_{10}$
M_r	2597.34	2635.44	2783.45	2813.49
T/K	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Trigonal	Trigonal
Space group	$P2_1/c$	$P2_1/c$	R-3	R-3
a/Å	17.2643(4)	18.6395(4)	36.3512(11)	36.5052(9)
b/Å	18.9646(4)	17.7825(3)	36.3512(11)	36.5052(9)
c/Å	19.8713(4)	19.4352(4)	26.7591(10)	26.8206(6)
α (°)	90	90	90	90
β (°)	99.975(2)	95.404(2)	90	90
γ (°)	90	90	120	120
V/Å^3	6407.7(2)	6413.3(2)	30622(2)	30953.4(17)
Z	2	2	9	9
Dc/mg m^{-3}	1.346	1.365	1.358	1.358
μ/mm^{-1}	5.675	5.681	5.386	5.339
indep reflns [I >2σ(I)]	12728	12744	13397	10435
F(000)	2720	2768	13050	13194
GOF	1.052	1.017	1.006	1.053
CCDC No.	1572540	1572541	1572542	1572543
R_1[a], wR_2[b] [I >2σ(I)]	0.0737, 0.2034	0.0495, 0.1266	0.1054, 0.3356	0.1127, 0.3094
R_1[a], wR_2[b] (all data)	0.0856, 0.2181	0.0682, 0.1459	0.1343, 0.3797	0.1963, 0.3559

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

Table S2 Selected bond lengths [Å] for **PTC-121**.

Ti(1)-O(15)	1.798(3)	Ti(3)-O(9)	1.992(3)
Ti(1)-O(20)	1.799(3)	Ti(3)-O(6)	2.066(3)
Ti(1)-O(8)	1.917(3)	Ti(3)-O(5)	2.208(3)
Ti(1)-O(17)	2.029(3)	Ti(4)-O(18)	1.774(3)
Ti(1)-O(3)	2.139(3)	Ti(4)-O(2)	1.784(3)
Ti(1)-O(4)	2.141(3)	Ti(4)-O(12)	2.048(3)
Ti(2)-O(27)	1.760(3)	Ti(4)-O(7)	2.054(3)
Ti(2)-O(1)	1.848(3)	Ti(4)-O(10)	2.077(3)
Ti(2)-O(10)	1.960(3)	Ti(4)-O(1)	2.115(3)
Ti(2)-O(17)	2.027(3)	Ti(5)-O(19)	1.776(3)
Ti(2)-O(11)	2.030(3)	Ti(5)-O(22)	1.791(3)
Ti(2)-O(3)	2.199(3)	Ti(5)-O(14)	1.921(3)
Ti(3)-O(16)	1.751(3)	Ti(5)-O(9)	2.045(3)
Ti(3)-O(2)	1.874(3)	Ti(5)-O(13)	2.127(3)
Ti(3)-O(1)	1.937(3)	Ti(5)-O(5)	2.137(3)

Table S3 Selected bond lengths [Å] for **PTC-122**.

Ti(01)-O(19)	1.757(2)	Ti(03)-O(4)	2.035(2)
Ti(01)-O(8)	1.880(2)	Ti(03)-O(2)	2.137(2)
Ti(01)-O(1)	1.940(2)	Ti(03)-O(11)	2.150(2)
Ti(01)-O(10)	1.984(2)	Ti(04)-O(22)	1.771(2)
Ti(01)-O(3)#1	2.069(2)	Ti(04)-O(8)	1.793(2)
Ti(01)-O(6)	2.187(2)	Ti(04)-O(12)	2.050(2)
Ti(02)-O(20)	1.762(2)	Ti(04)-O(16)	2.063(2)
Ti(02)-O(1)	1.852(2)	Ti(04)-O(5)	2.067(2)
Ti(02)-O(16)	1.957(2)	Ti(04)-O(1)	2.110(2)
Ti(02)-O(7)	2.026(2)	Ti(05)-O(21)	1.776(2)
Ti(02)-O(4)	2.028(2)	Ti(05)-O(17)	1.804(2)
Ti(02)-O(2)	2.198(2)	Ti(05)-O(15)	1.908(2)
Ti(03)-O(18)	1.807(2)	Ti(05)-O(10)	2.054(2)
Ti(03)-O(13)	1.808(2)	Ti(05)-O(14)#1	2.082(2)

Ti(03)-O(9)	1.920(2)	Ti(05)-O(6)	2.161(2)

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

Table S4 Selected bond lengths [Å] for **PTC-123**.

Ti(1)-O(8)	1.7550(10)	Ti(3)-O(10)	2.0436(15)
Ti(1)-O(12)	1.8573(12)	Ti(3)-O(9)	2.0488(9)
Ti(1)-O(10)	1.9287(12)	Ti(3)-O(12)	2.1181(9)
Ti(1)-O(7)	2.0215(13)	Ti(4)-O(23)	1.7666(13)
Ti(1)-O(6)	2.0260(10)	Ti(4)-O(21)	1.7732(18)
Ti(1)-O(4)	2.2270(9)	Ti(4)-O(20)	1.9316(19)
Ti(2)-O(13)	1.7409(12)	Ti(4)-O(16)	2.0496(14)
Ti(2)-O(15)	1.8875(9)	Ti(4)-O(22)	2.1078(12)
Ti(2)-O(12)	1.9260(12)	Ti(4)-O(19)	2.1143(15)
Ti(2)-O(16)	1.9715(13)	Ti(5)-O(2)	1.7680(17)
Ti(2)-O(14)	2.0860(10)	Ti(5)-O(1)	1.7944(18)
Ti(2)-O(19)	2.1950(12)	Ti(5)-O(3)	1.9229(14)
Ti(3)-O(11)	1.7638(12)	Ti(5)-O(7)	2.0318(11)
Ti(3)-O(15)	1.8094(14)	Ti(5)-O(4)	2.1166(11)
Ti(3)-O(17)	2.0206(10)	Ti(5)-O(5)	2.1682(11)

Table S5 Selected bond lengths [Å] for **PTC-124**.

Ti(1)-O(2)	1.7603(18)	Ti(3)-O(6)	2.0256(13)
Ti(1)-O(23)	1.796(2)	Ti(3)-O(14)	2.0294(16)
Ti(1)-O(4)	1.9255(12)	Ti(3)-O(1)	2.1217(12)
Ti(1)-O(3)	2.0247(15)	Ti(4)-O(16)	1.7267(13)
Ti(1)-O(5)	2.1095(15)	Ti(4)-O(13)	1.8847(13)
Ti(1)-O(7)	2.1448(16)	Ti(4)-O(1)	1.9188(15)
Ti(2)-O(9)	1.7567(14)	Ti(4)-O(19)	1.999(2)
Ti(2)-O(1)	1.8558(14)	Ti(4)-O(17)	2.0826(12)
Ti(2)-O(10)	1.9240(13)	Ti(4)-O(15)	2.1755(13)

Ti(2)-O(8)	2.0124(12)	Ti(5)-O(20)	1.7463(16)
Ti(2)-O(3)	2.0176(18)	Ti(5)-O(21)	1.816(3)
Ti(2)-O(5)	2.2256(12)	Ti(5)-O(22)	1.9468(15)
Ti(3)-O(11)	1.7459(14)	Ti(5)-O(19)	2.0200(16)
Ti(3)-O(13)	1.8547(17)	Ti(5)-O(18)	2.1206(14)
Ti(3)-O(10)	1.9822(16)	Ti(5)-O(15)	2.124(2)

Table S6. Trending relationships between band gaps and their reduction patterns**.**

No.	Compound	Bandgap	Stabilizing ligand	Bridging ligand	observation
1	PTC-121	2.84	H_2sac	H_2bdc	Highest bandgap among all isomorphs
2	PTC-122	2.71	H_2sac	2-NH_2-H_2bdc	Band gap reduced due to additional -NH2 group
3	PTC-123	2.55	H_2npc	H_2bdc	Bandgap reduced due to additional benzene ring
4	PTC-124	2.43	H_2npc	2-NH_2-H_2bdc	Lowest bandgap among all isomorphs due to both additional -NH_2 and benzene rings

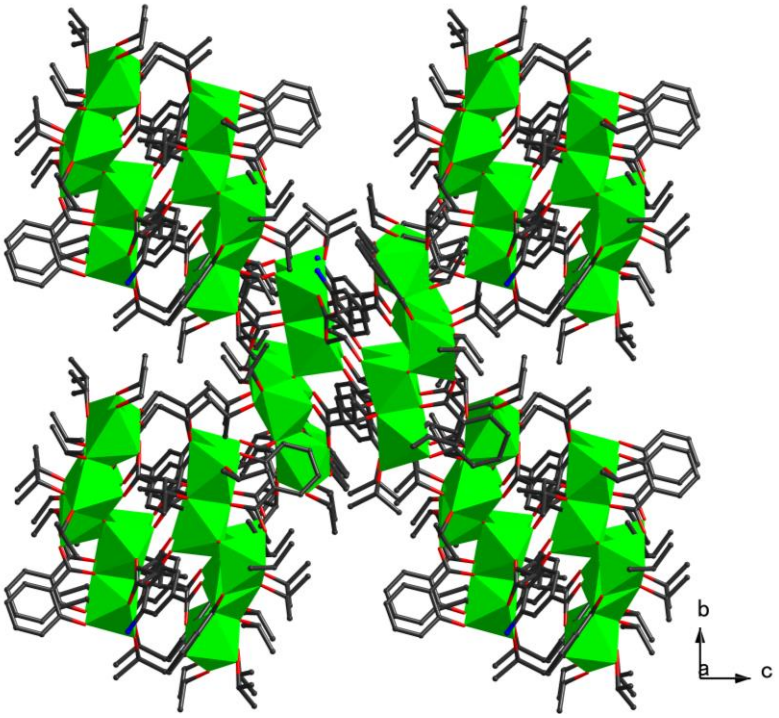

Fig. S1 The packing structures of **PTC-121**.

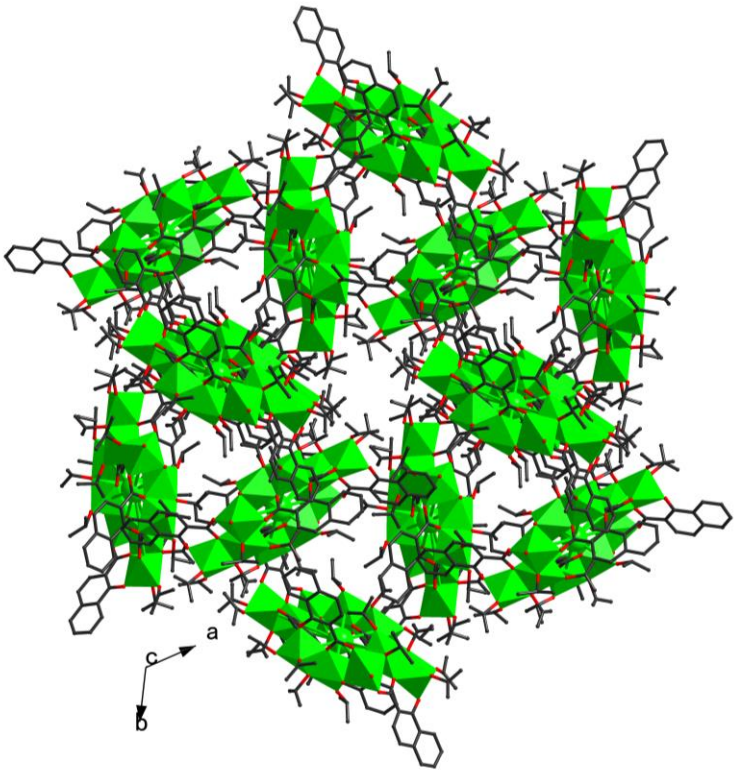

Fig. S2 The packing structures of **PTC-123**.

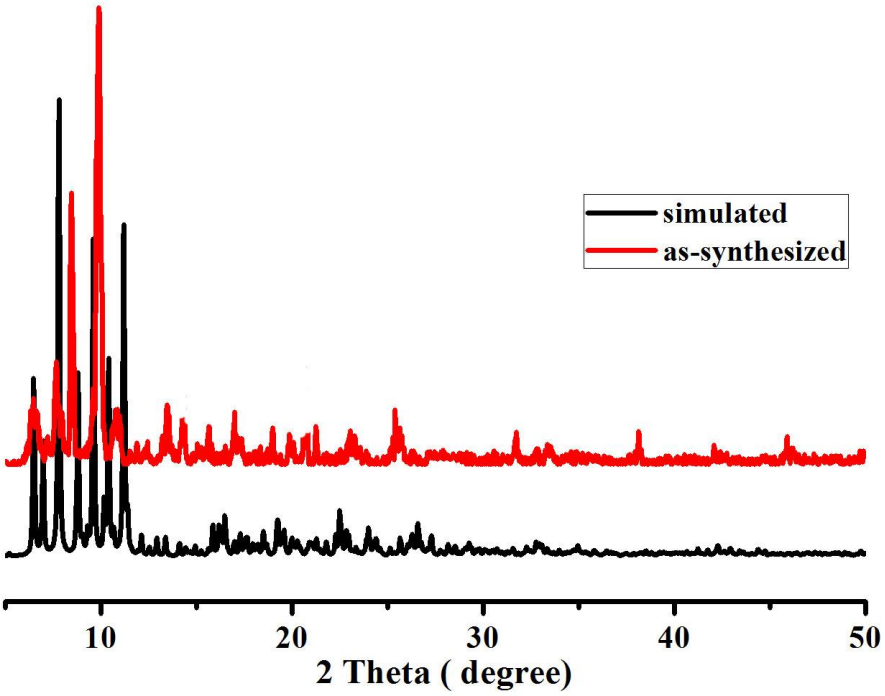

Fig. S3 The PXRD of **PTC-121**: simulated pattern (black), experimental (red).

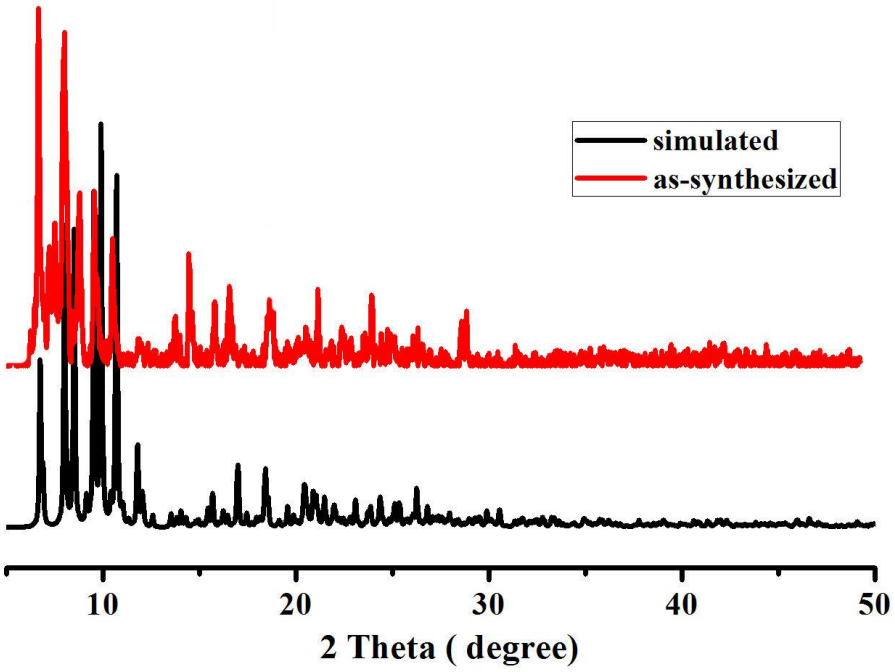

Fig. S4 The PXRD of **PTC-122**: simulated pattern (black), experimental (red).

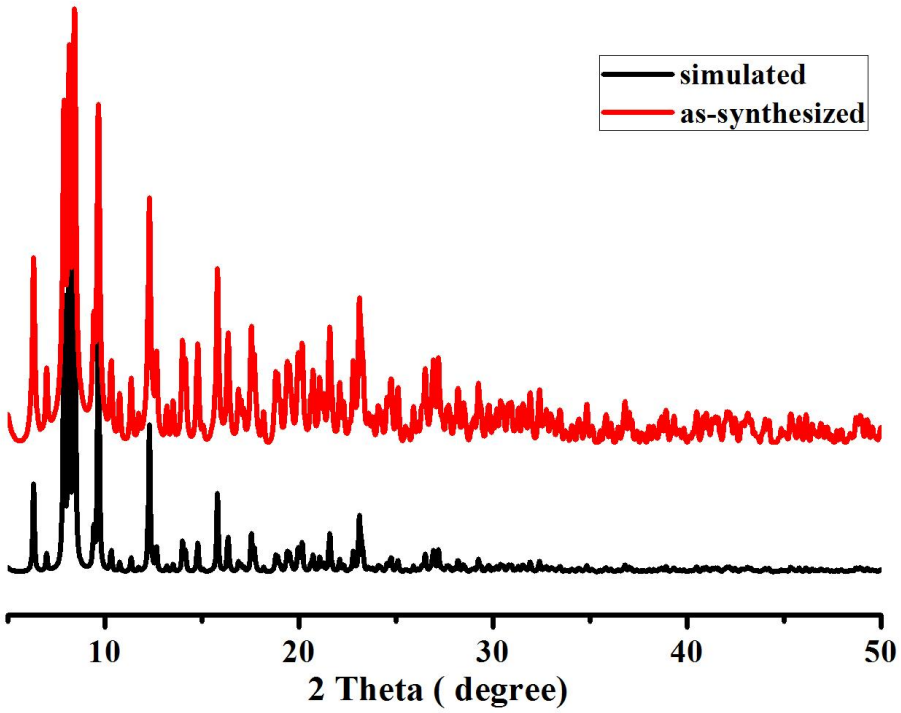

Fig. S5 The PXRD of **PTC-123**: simulated pattern (black), experimental (red).

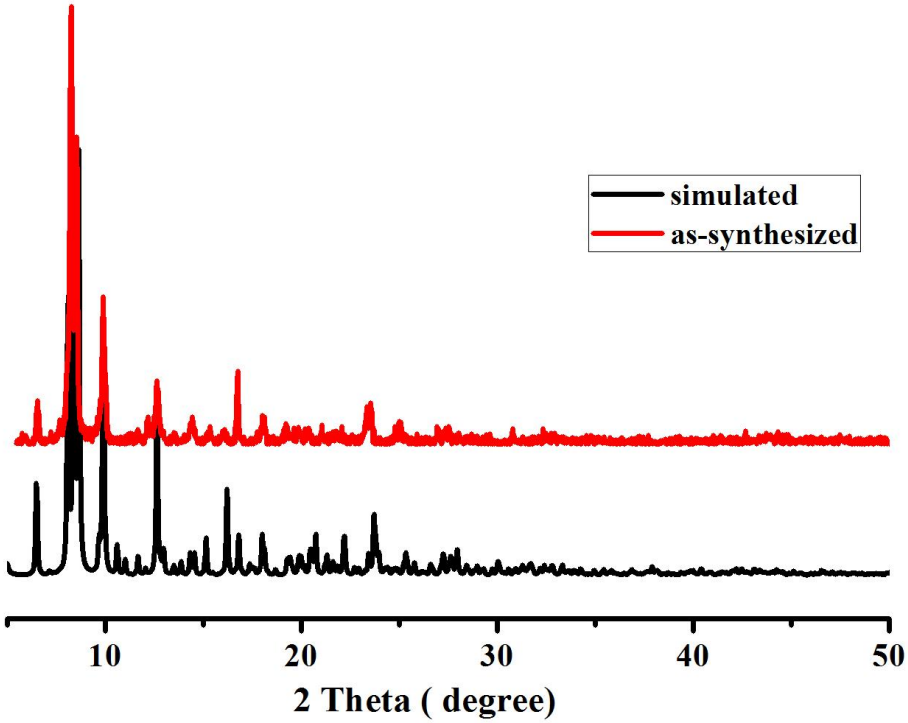

Fig. S6 The PXRD of **PTC-124**: simulated pattern (black), experimental (red).

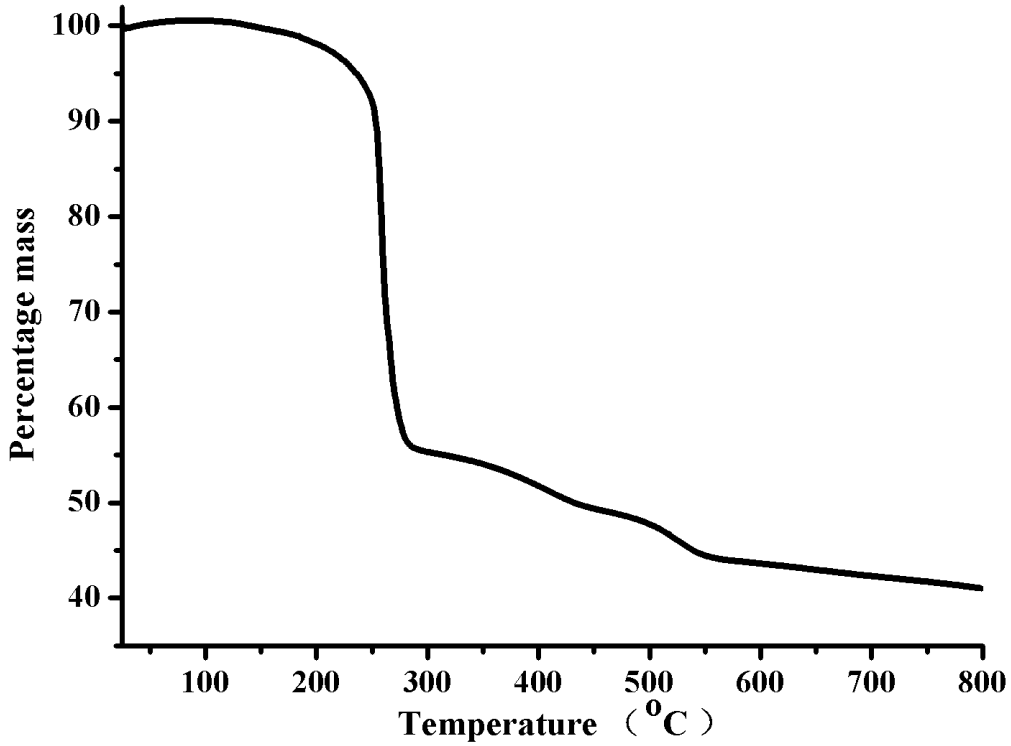

Fig. S7 TGA curve of **PTC-121**.

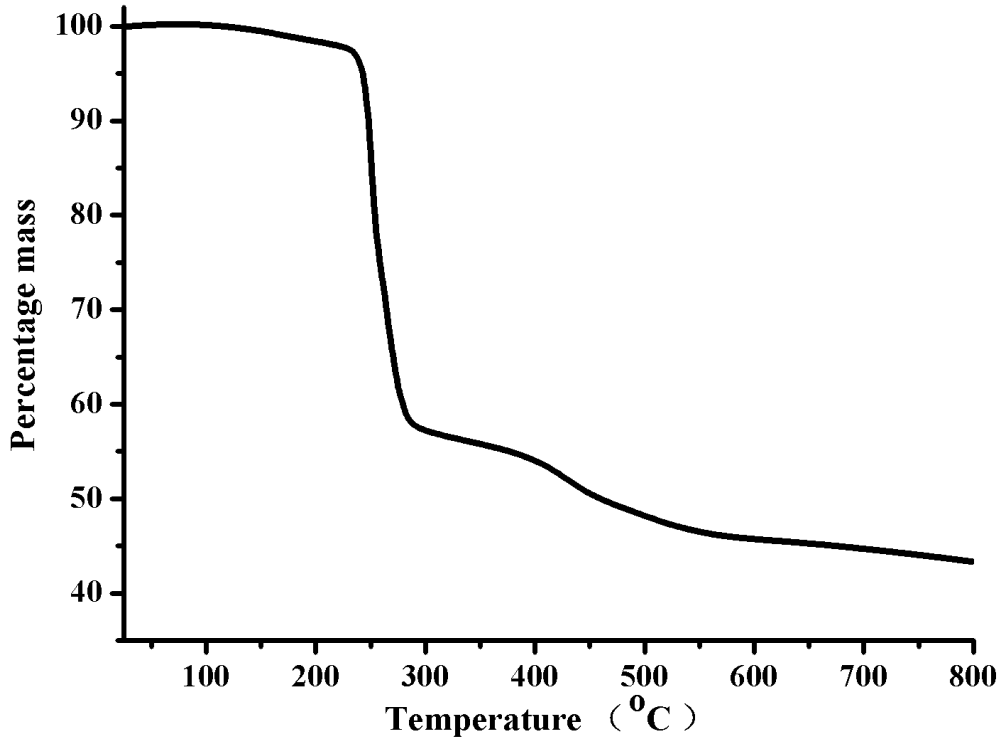

Fig. S8 TGA curve of **PTC-122**.

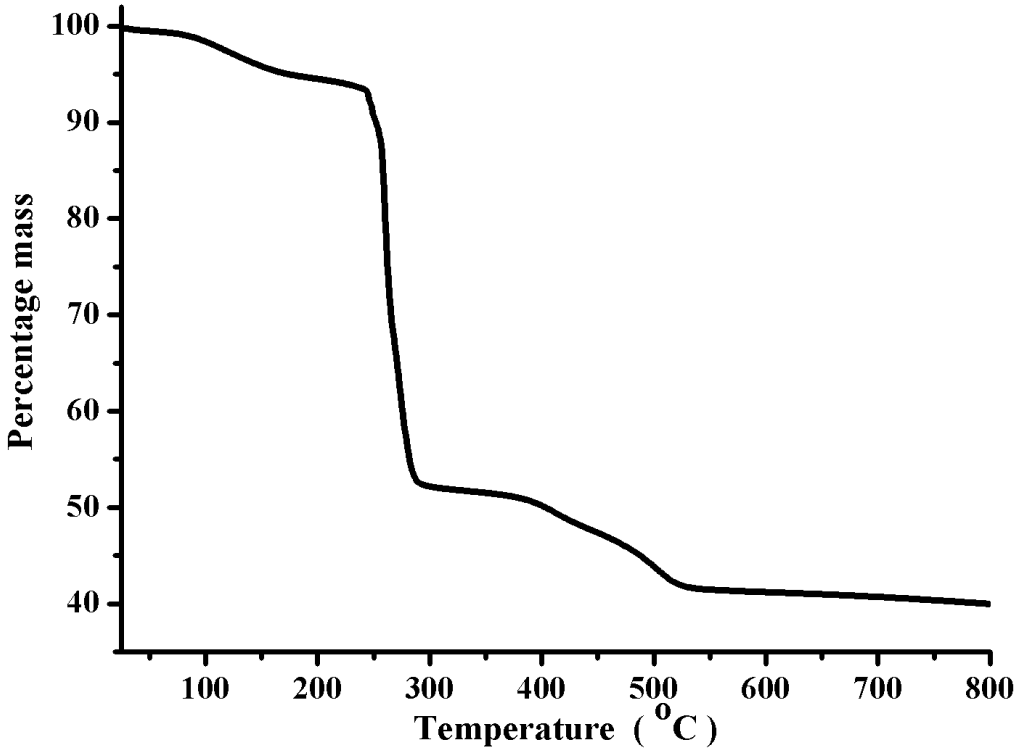

Fig. S9 TGA curve of **PTC-123**.

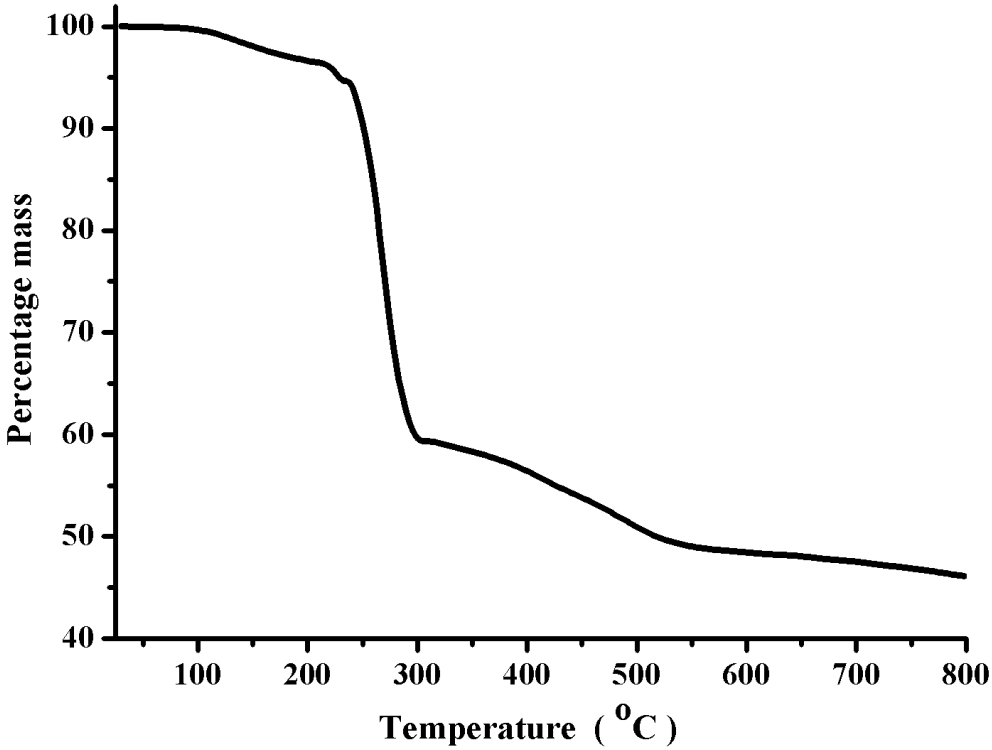

Fig. S10 TGA curve of **PTC-124**.

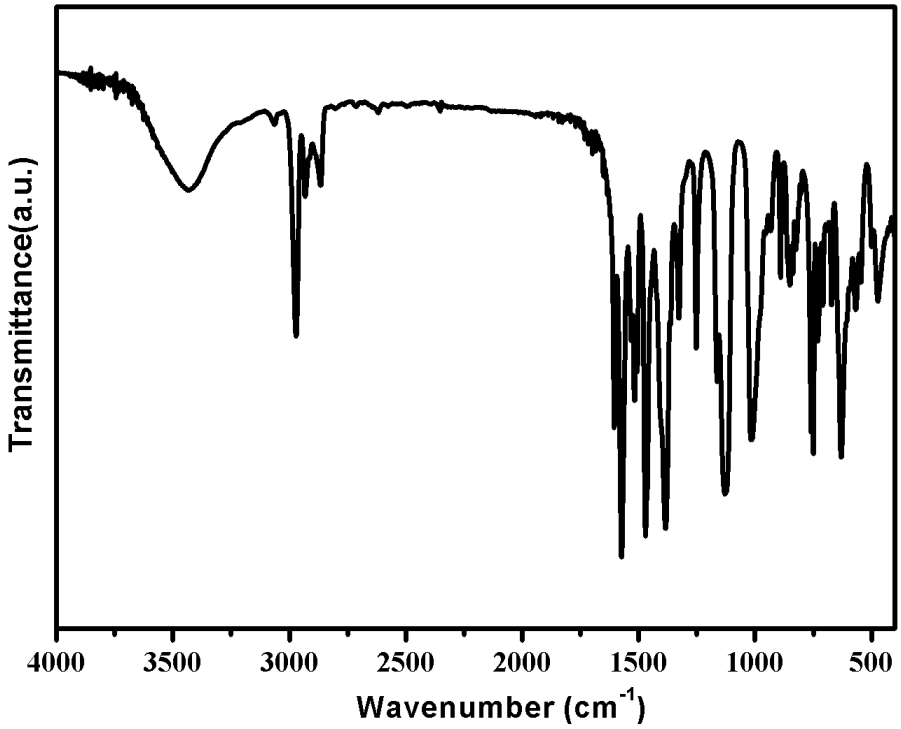

Fig. S11 IR spectrum of **PTC-121**.

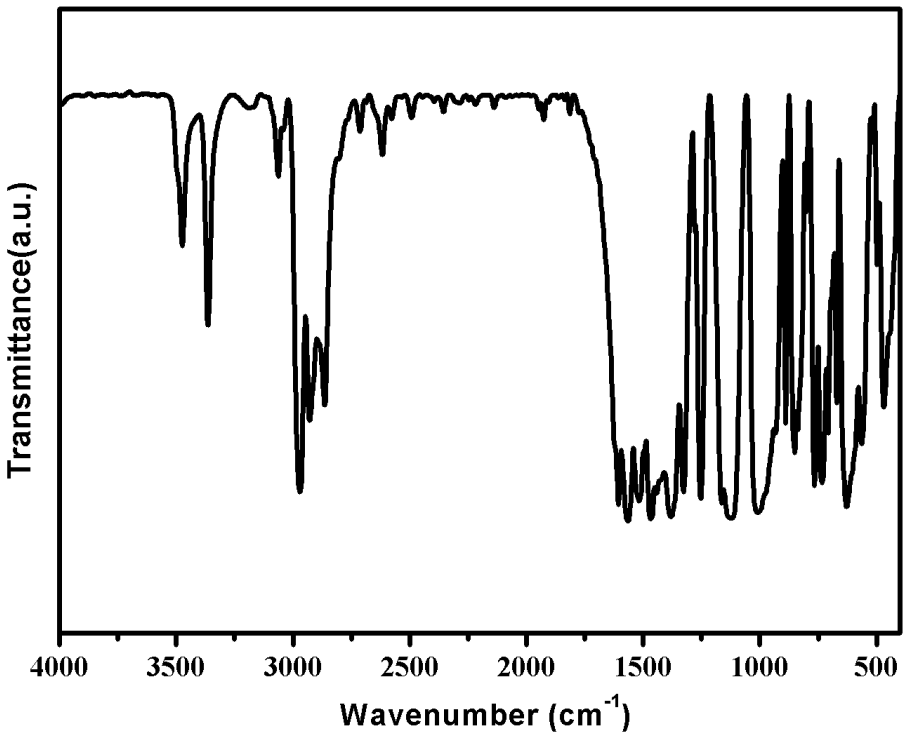

Fig. S12 IR spectrum of **PTC-122**.

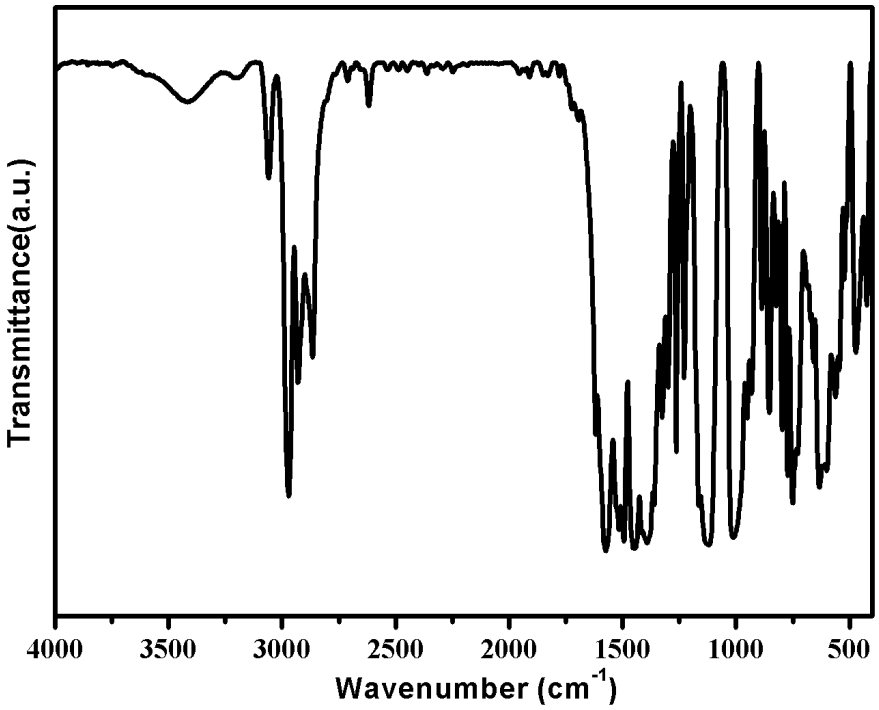

Fig. S13 IR spectrum of **PTC-123**.

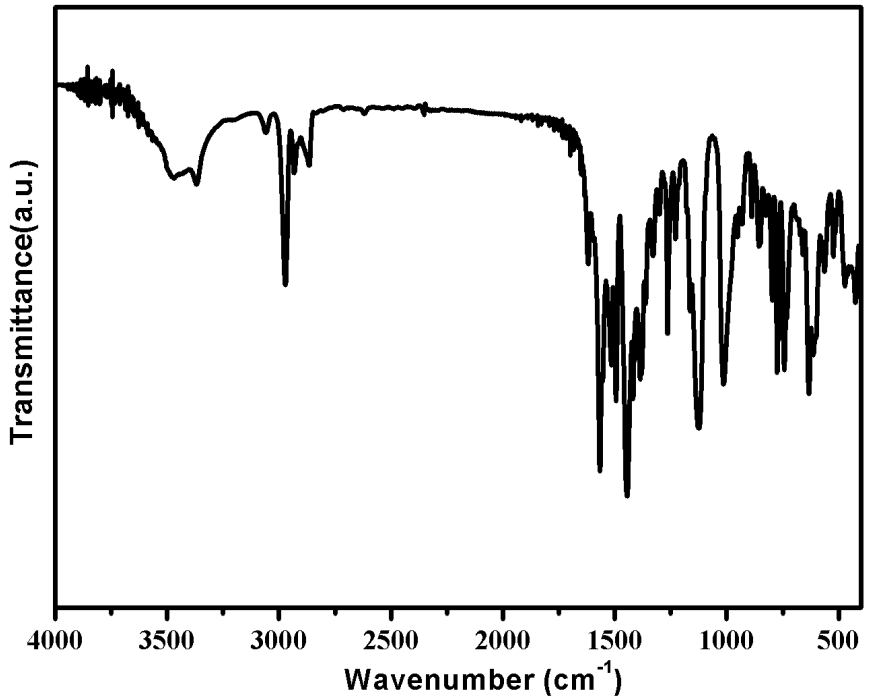

Fig. S14 IR spectrum of **PTC-124**.

(1) Sheldrick, G. M. SADABS, Program for area detector adsorption correction. Institute for Inorganic Chemistry, University of Göttingen, Göttingen (Germany), 1996.
(2) Sheldrick, G. M. SHELXL-97, Program for solution of crystal structures. University of Göttingen, Göttingen (Germany), 1997.