***Supporting Information for:***

# Ligands dependent assembly of trinuclear titanium-oxo units into coordination tetrahedron and capsule

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## Experimental Section

**Materials and Instrumentation.** We collected the Fourier transform infrared spectroscopy (FTIR) data on a PerkinElmer Spectrum 100 FT-IR Spectrometer. Thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/SDTA 851e analyzer in $N_2$ with a heating rate of 10℃min-1 from 20℃ to 800℃. Powder X-ray diffraction (PXRD) data analysis were collected on a Rigaku Mini Flex II diffractometer using CuKα radiation (λ =1.54056 Å) in the 2θ range of 5–50° with a scanning rate of 5° $min^{-1}$. The UV diffuse reflection data were recorded at room temperature using a powder sample with $BaSO_4$ as a standard (100% reflectance) on a PerkinElmer Lamda-950 UV spectrophotometer and scanned at 200-800 nm. The absorption data are calculated from the Kubelka-Munk function, ($F$(R) = $(1-R)^2/2R$), where R representing the reflectance.

**Chemicals and Materials**

All the reagents and solvents were purchased commercially and were not further purified when used. $Ti(O^iPr)_4$ were purchased from Adamas, while as isopropanol and formic acid were bought from Sino pharm Chemical Reagent Beijing.

**Synthesis of PTC-75:** Phosphorous acid (0.053 g, 0.65 mmol), nicotinic acid (0.080 g, 0.65 mmol), and isopropyl alcohol (5.5 ml) were mixed at room temperature; then $Ti(O^iPr)4$ (0.92 ml, 3.0 mmol) was added dropwise. The resultant solution was heated at 80°C for four 2 days. After cooled to room temperature, colourless crystals of **PTC-75** were obtained.

**Synthesis of PTC-76:** Phosphorous acid (0.051 g, 0.65 mmol), nicotinic acid (0.082 g, 0.65 mmol), CuCl (0.022 g, 0.22mmol) and isopropyl alcohol (5.5 ml) were mixed at room temperature; then $Ti(O^iPr)_4$ (0.92 ml, 3.0 mmol) was added dropwise. The resultant solution was heated at 80°C for four 2 days. After cooled to room temperature, yellow hexagonal crystals of **PTC-76** were obtained.

**Synthesis of PTC-77:** It was synthesized by a procedure similar to that of **PTC-76** except that the CuCl was replaced by CuBr (0.032 g, 0.22 mmol).

**Synthesis of PTC-78**: Phosphorous acid (0.053 g, 0.65 mmol), 4,4'-Biphenyldisulfonic acid (0.05 g, 0.159 mmol), and isopropyl alcohol (5.5 ml) were mixed at room temperature; then $Ti(O^iPr)4$ (0.92 ml, 3.0 mmol) was added dropwise. The resultant solution was heated at 60°C for four 2 days. After cooled to room temperature, colourless crystals of **PTC-78** were obtained.

**General Methods for X-ray Crystallography.** The structure determination of **PTC-75**, **PTC-76** and **PTC-77** was performed at 293(K) on the Xcalibur diffractometer using graphite-monochromated Mo-K radiation. Crystallographic data of complexes **PTC-78** were collected on a Supernova single crystal diffractometer equipped with graphite-monochromatic CuK radiation (λ = 1.54178 Å) at 100 K. The structure was solved with direct

methods using SHELXS-2014 and refined with the full-matrix least-squares technique based on $F^2$ using the SHELXL-2014. Non-hydrogen atoms were refined anisotropically, and all hydrogen atoms bond C were generated geometrically.

**Table S1. Crystal data and structure refinement for PTC-75.**

| *Identification code* | *PTC-75* |
|---|---|
| Empirical formula | $C_{42}H_{80}N_2O_{24}P_2Ti_6$ |
| Formula weight | 1346.42 |
| Temperature/K | 100 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| *a*/Å | 13.2246(5) |
| *b*/Å | 14.5545(4) |
| *c*/Å | 16.8862(5) |
| *α*/° | 90 |
| *β*/° | 99.369(3) |
| *γ*/° | 90 |
| *Volume*/Å$^3$ | 3206.86(18) |
| *Z* | 2 |
| $\rho_{calc}$ g/cm$^3$ | 1.394 |
| $\mu$/mm$^{-1}$ | 0.831 |
| *F*(000) | 1400.0 |
| Crystal size/mm$^3$ | 0.3× 0.2 × 0.2 |
| Radiation | MoK*α* (*λ* = 0.71073) |
| 2*Θ* range for data collection/° | 6.818 to 49.998 |
| Index ranges | -15 ≤ *h* ≤ 10, -17 ≤ *k* ≤ 17, -20 ≤ *l* ≤ 19 |
| Reflections collected | 14008 |
| Independent reflections | 5633 [$R_{int}$ = 0.0281, $R_{sigma}$ = 0.0424] |
| Data/restraints/parameters | 5633/0/352 |
| Goodness-of-fit on $F^2$ | 1.197 |
| Final *R* indexes **I>=2σ (I)+* | $R_1$ = 0.0545, $wR_2$ = 0.1694 |
| Final *R* indexes [all data] | $R_1$ = 0.0796, $wR_2$ = 0.1869 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.13/-0.74 |

**Table S2. Crystal data and structure refinement for PTC-76.**

| *Identification code* | *PTC-76* |
|---|---|
| Empirical formula | $C_{81}H_{162}ClCuN_3O_{39}P_3Ti_9$ |
| Formula weight | 2425.13 |
| Temperature/K | 100 |
| Crystal system | trigonal |
| Space group | *P-3* |
| *a*/Å | 19.3473(7) |
| *b*/Å | 19.3473(7) |
| *c*/Å | 20.4709(10) |
| *α*/° | 90 |
| *β*/° | 90 |
| *γ*/° | 120 |
| Volume/Å$^3$ | 6636.0(6) |
| *Z* | 2 |
| $\rho_{calc}$ g/cm$^3$ | 1.214 |

| | |
|---|---|
| $\mu/mm^{-1}$ | 0.789 |
| *F(000)* | 2540.0 |
| Crystal size/$mm_3$ | 0.5 × 0.44 × 0.28 |
| Radiation | MoK$\alpha$ ($\lambda$ = 0.71073) |
| 2$\Theta$ range for data collection/° | 6.734 to 47.998 |
| Index ranges | -22 ≤ *h* ≤ 16, -21 ≤ *k* ≤ 22, -16 ≤ *l* ≤ 22 |
| Reflections collected | 20546 |
| Independent reflections | 6816 [$R_{int}$ = 0.0648, $R_{sigma}$ = 0.1034] |
| Data/restraints/parameters | 6816/5/425 |
| Goodness-of-fit on $F^2$ | 0.994 |
| Final *R* indexes [*I>=2σ (I)*] | $R_1$ = 0.0801, $wR_2$ = 0.2250 |
| Final *R* indexes [all data] | $R_1$ = 0.1461, $wR_2$ = 0.2588 |
| Largest diff. peak/hole / *e* $Å^{-3}$ | 1.35/-0.36 |

**Table S3. Crystal data and structure refinement for PTC-77.**

| *Identification code* | *PTC-77* |
|---|---|
| Empirical formula | $C_{81}H_{162}BrCuN_3O_{39}P_3Ti_9$ |
| Formula weight | 2469.59 |
| Temperature/K | 100 |
| Crystal system | trigonal |
| Space group | *P-3* |
| *a*/Å | 19.3398(8) |
| *b*/Å | 19.3398(8) |
| *c*/Å | 20.4045(12) |
| *α*/° | 90 |
| *ß*/° | 90 |
| *γ*/° | 120 |
| Volume/$Å^3$ | 6609.4(7) |
| *Z* | 2 |
| $\rho_{calc}$ g/$cm^3$ | 1.241 |
| $\mu$/$mm^{-1}$ | 1.075 |
| *F(000)* | 2576.0 |
| Crystal size/$mm^3$ | 0.52 × 0.33 × 0.25 |
| Radiation | MoK$_\alpha$ ($\lambda$ = 0.71073) |
| 2$\Theta$ range for data collection/° | 7.298 to 49.984 |
| Index ranges | -17 ≤ *h* ≤ 22, -22 ≤ *k* ≤ 14, -24 ≤ *l* ≤ 17 |
| Reflections collected | 14635 |
| Independent reflections | 7716 [$R_{int}$ = 0.0390, $R_{sigma}$ = 0.1042] |
| Data/restraints/parameters | 7716/7/425 |
| Goodness-of-fit on $F^2$ | 0.950 |
| Final *R* indexes **I>=2σ (I)+* | $R_1$ = 0.0640, $wR_2$ = 0.1680 |
| Final *R* indexes [all data] | $R_1$ = 0.1215, $wR_2$ = 0.1954 |
| Largest diff. peak/hole / *e* $Å^{-3}$ | 0.71/-0.55 |

**Table S4. Crystal data and structure refinement for PTC-78.**

| *Identification code* | *PTC-78* |
|---|---|
| Empirical formula | $C_{162}H_{318}O_{84}P_6S_6Ti_{18}$ |
| Formula weight | 808.42 |
| Temperature/K | 100 |
| Crystal system | trigonal |
| Space group | *P-3$_1$c* |
| *a*/Å | 18.9359(5) |
| *b*/Å | 18.9359(5) |
| *c*/Å | 49.4964(14) |
| *α*/° | 90.00 |
| *β*/° | 90.00 |
| *γ*/° | 120.00 |
| Volume/Å$^3$ | 15370.1(7) |
| *Z* | 1 |
| $\rho_{calc}$ g/cm$^3$ | 1.048 |
| $\mu$/mm$^{-1}$ | 4.940 |
| *F(000)* | 5088.0 |
| Crystal size/mm$^3$ | 0.3 × 0.2 × 0.2 |
| Radiation | CuK*α* (*λ* = 1.54178) |
| 2*Θ* range for data collection/° | 7.14 to 106.78 |
| Index ranges | -12 ≤ *h* ≤ 19, -14 ≤ *k* ≤ 19, -27 ≤ *l* ≤ 50 |
| Reflections collected | 22333 |
| Independent reflections | 6029 [$R_{int}$ = 0.0422, $R_{sigma}$ = 0.0353] |
| Data/restraints/parameters | 6029/83/429 |
| Goodness-of-fit on $F^2$ | 1.407 |
| Final *R* indexes **I>=2σ (I)+* | $R_1$ = 0.1146, $wR_2$ = 0.3429 |
| Final *R* indexes [all data] | $R_1$ = 0.1397, $wR_2$ = 0.3645 |
| Largest diff. peak/hole / *e* Å$^{-3}$ | 0.98/-0.85 |

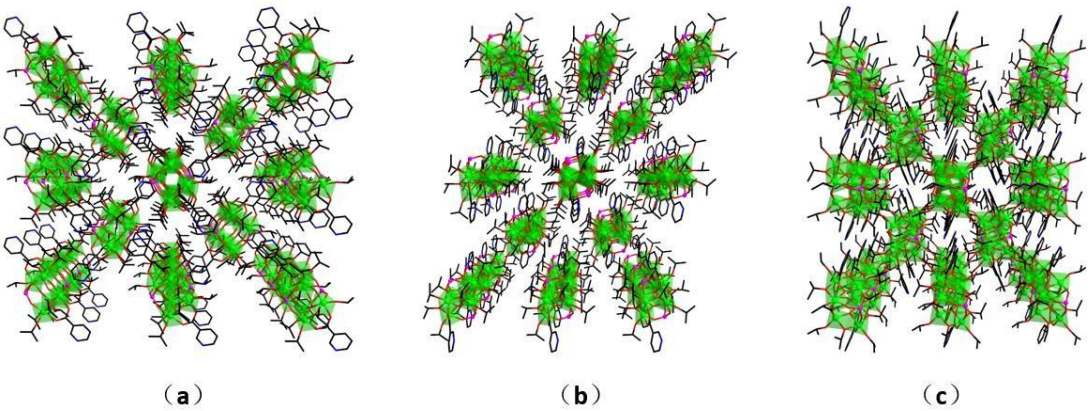



**Figure S1.** Packing diagram of **PTC-75** in the view of (a) *a*-axis**,** (b) *b*-axis and (c) *c*-axis.

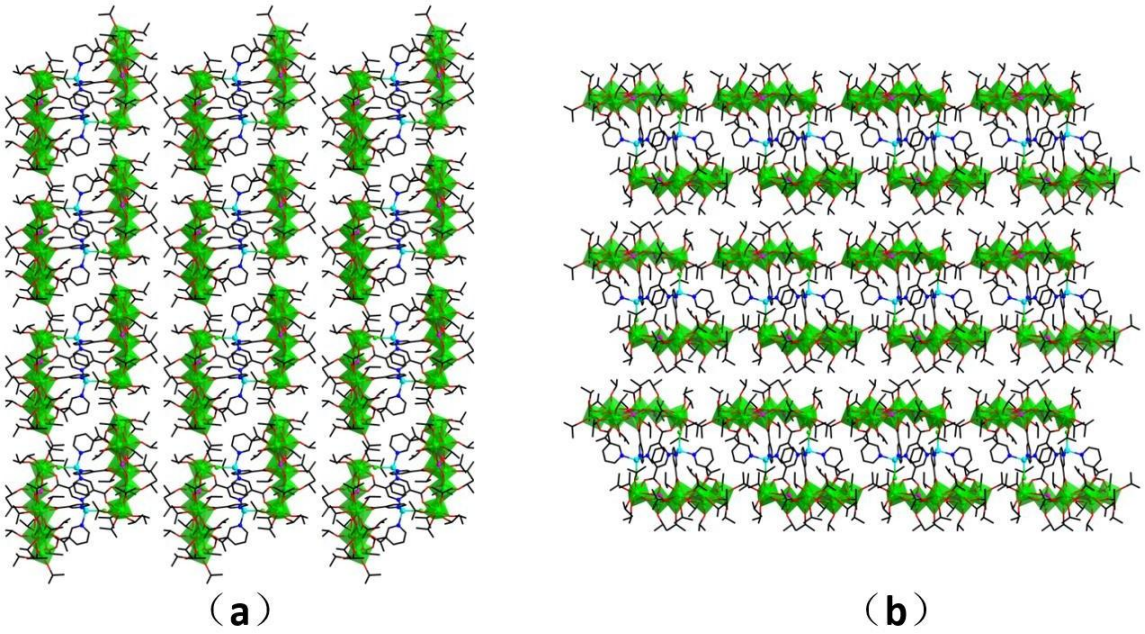



**Figure S2.** Packing diagram of **PTC-76** in the view of (a) *a*-axis and (b) *b*-axis.

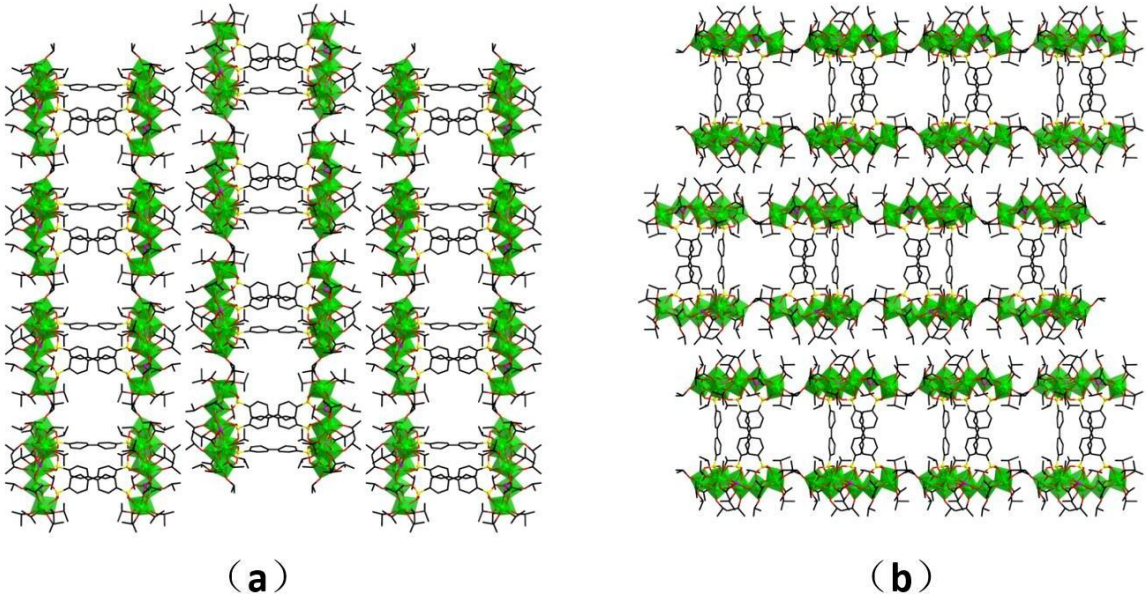



**Figure S3.** Packing diagram of **PTC-78** in the view of (a) *a*-axis and (b) *b*-axis.

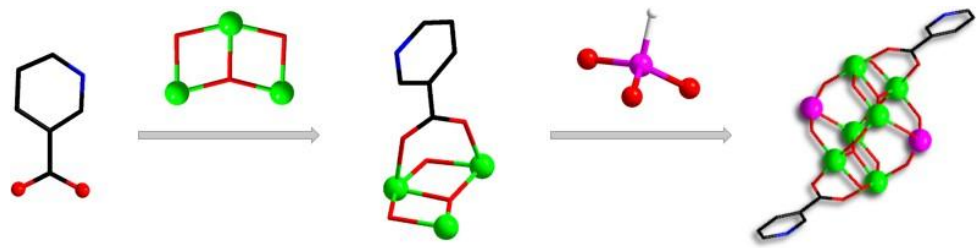


**Figure S4.** Illustration the formation of **PTC-75** from $Ti_3(\mu_3\text{-}O)$ units.

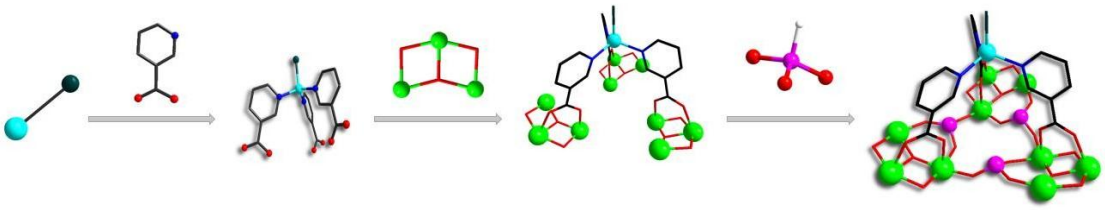


**Figure S5.** Illustration the formation of **PTC-76** and **PTC-77** from $Ti_3(\mu_3\text{-O})$ units.

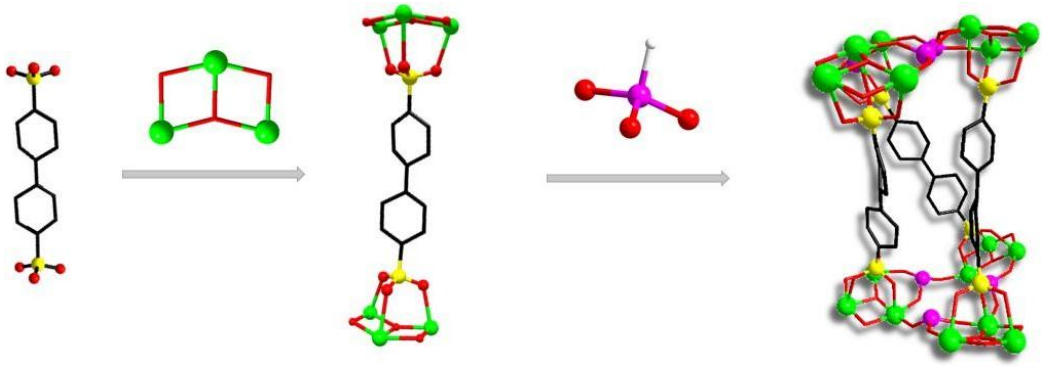


**Figure S6.** Illustration the formation of **PTC-78** from $Ti_3(\mu_3\text{-O})$ units.

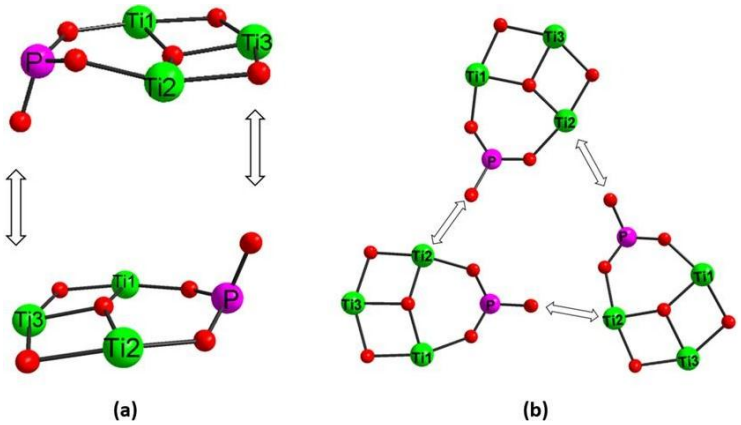



**Figure S7.** Comparison of the assembly of $Ti_3(\mu_3\text{-O})$ units into $\{Ti_6P_2\}$ cluster core of **PTC-75** (a), and triangular $\{Ti_9P_3\}$ layer in **PTC-76** or **PTC-77** (b).

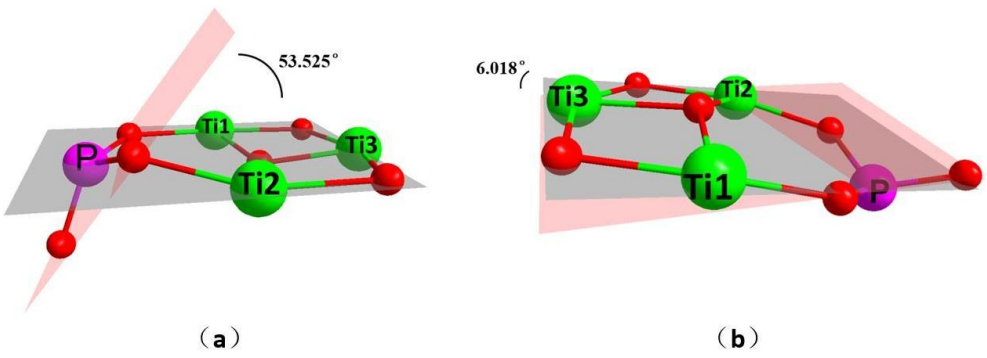
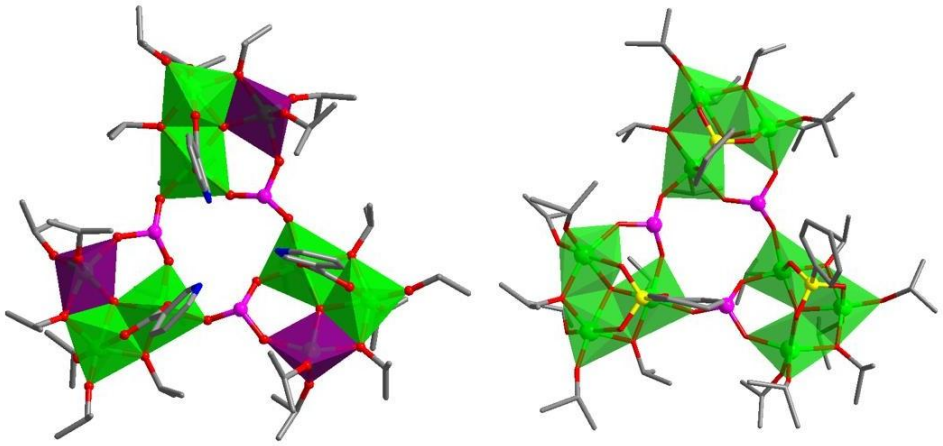



**Figure S8.** Illustration of the dihedral angle between the oxygen plane of the phosphite ligands and the titanium plane of $\{Ti_3(\mu_3\text{-O})\}$ unit in **PTC-75** (a) and **PTC-76** (b).



（a） （b）

**Figure S9.** Comparable illustration of titanium coordination environments in **PTC-76** (a) and **PTC-78** (b). Green polyhedrons represent six-coordinated titanium, purple polyhedron represent five-coordinated titanium.

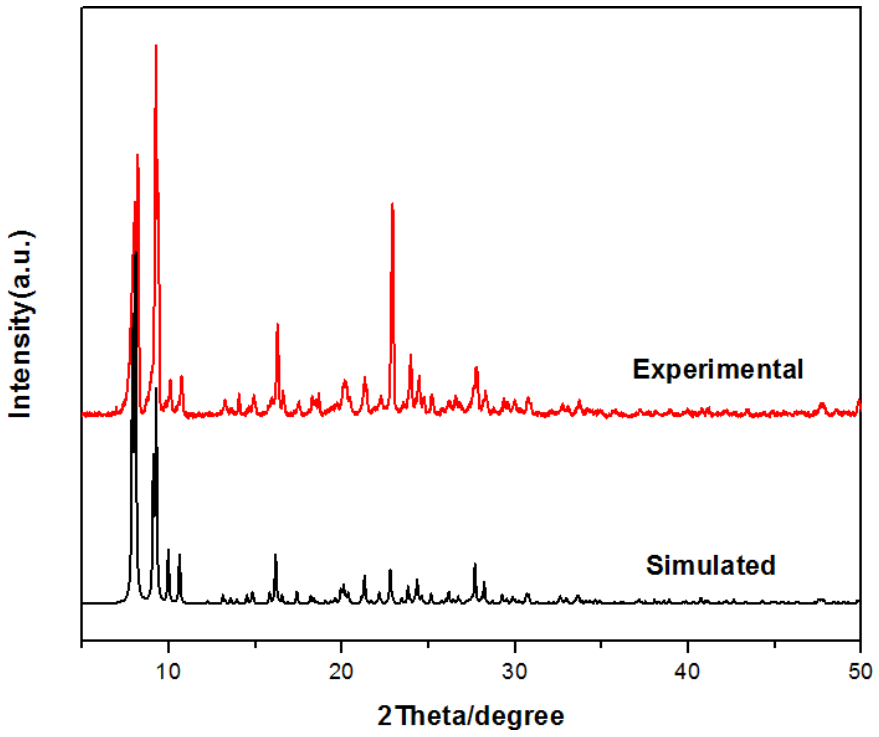



**Figure S10**. Experimental and simulated powder X-Ray diffraction patterns for **PTC-75**.

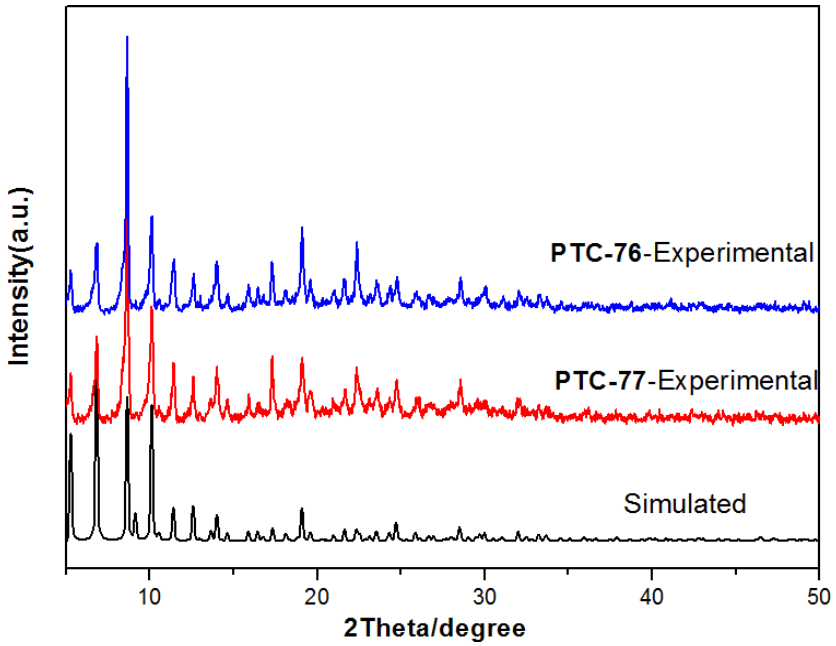



**Figure S11**. Experimental and simulated powder X-Ray diffraction patterns for **PTC-76** and **PTC-77**.

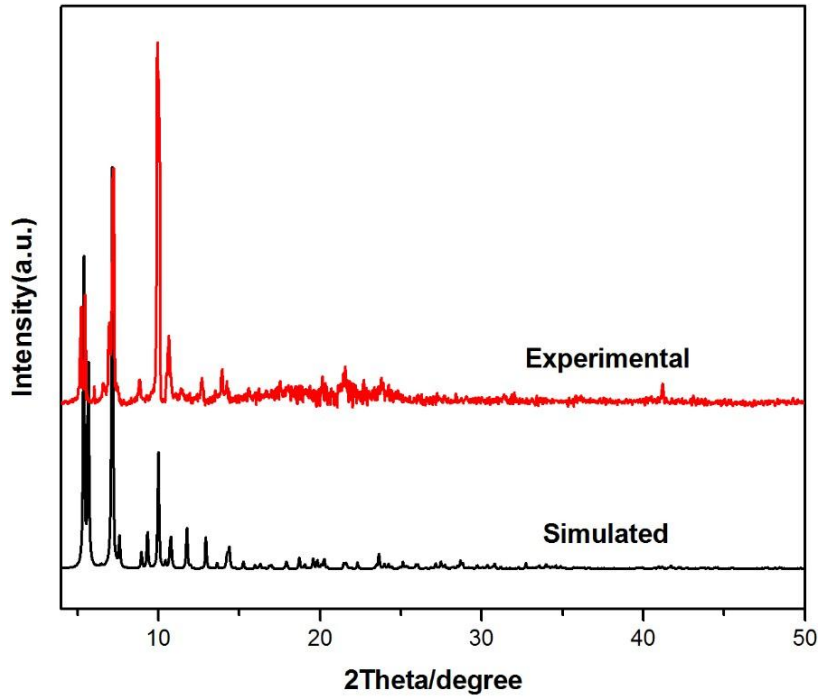



**Figure S12**. Experimental and simulated powder X-Ray diffraction patterns for **PTC-78**.

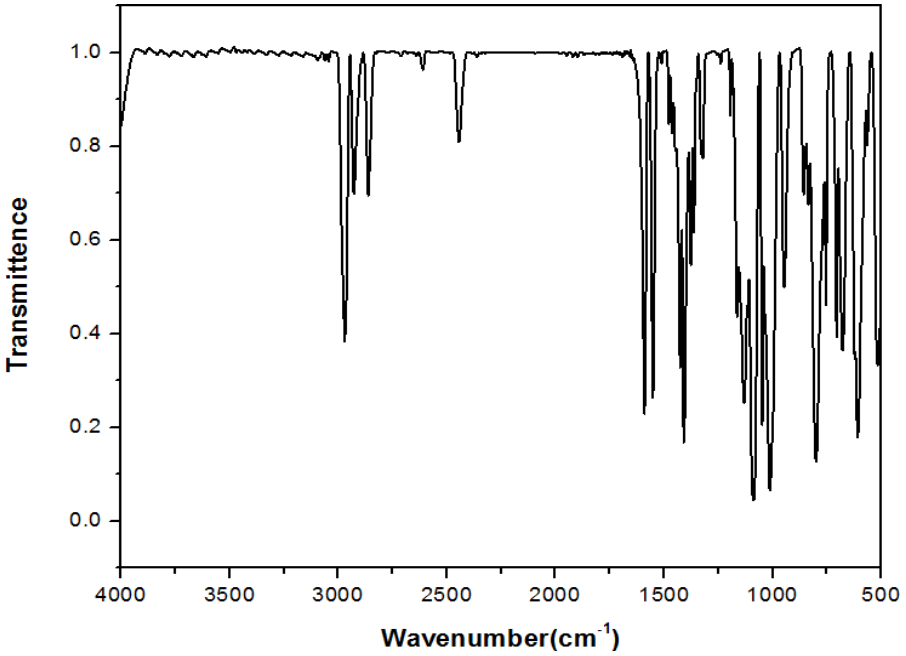



**Figure S13.** The IR spectrum of **PTC-75**.

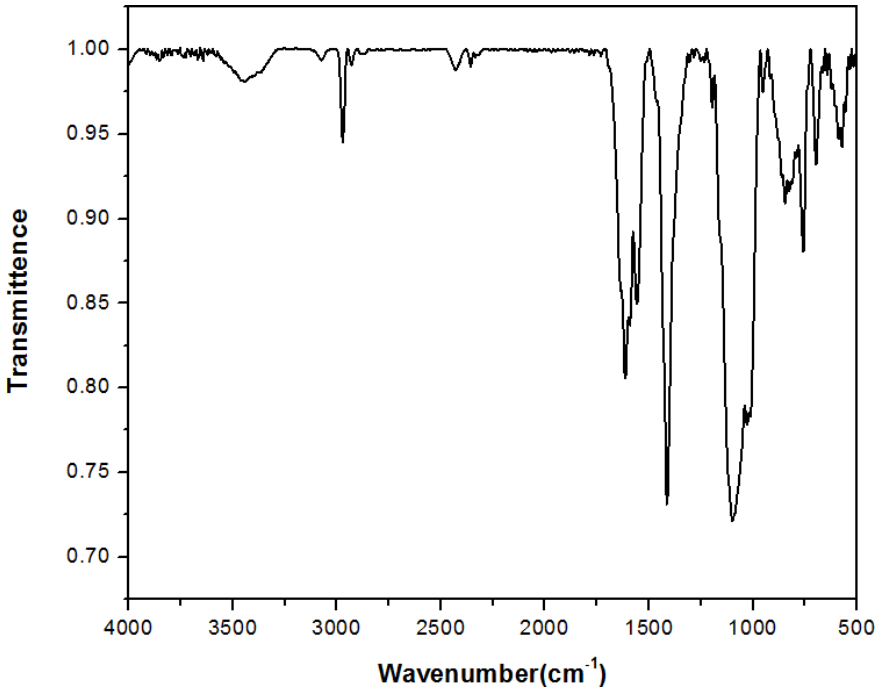



**Figure S14.** The IR spectrum of **PTC-76**.

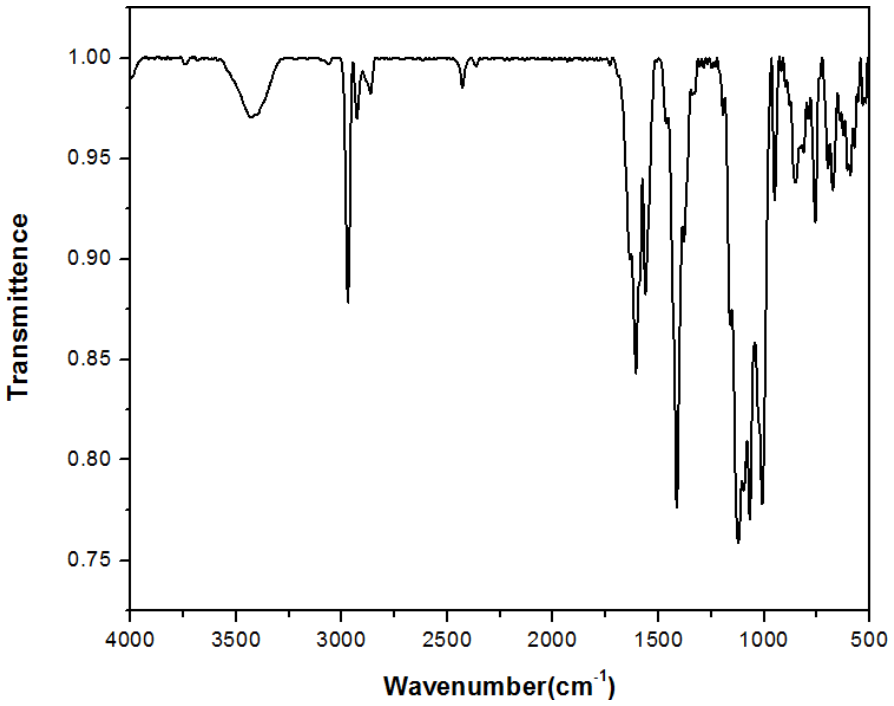



**Figure S15.** The IR spectrum of **PTC-77**.

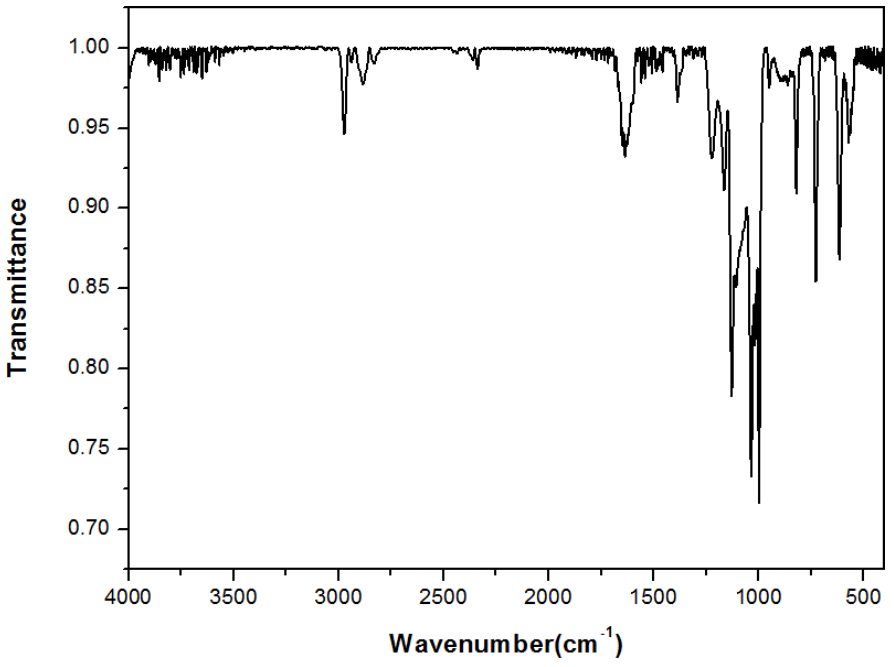



**Figure S16.** The IR spectrum of **PTC-78**.

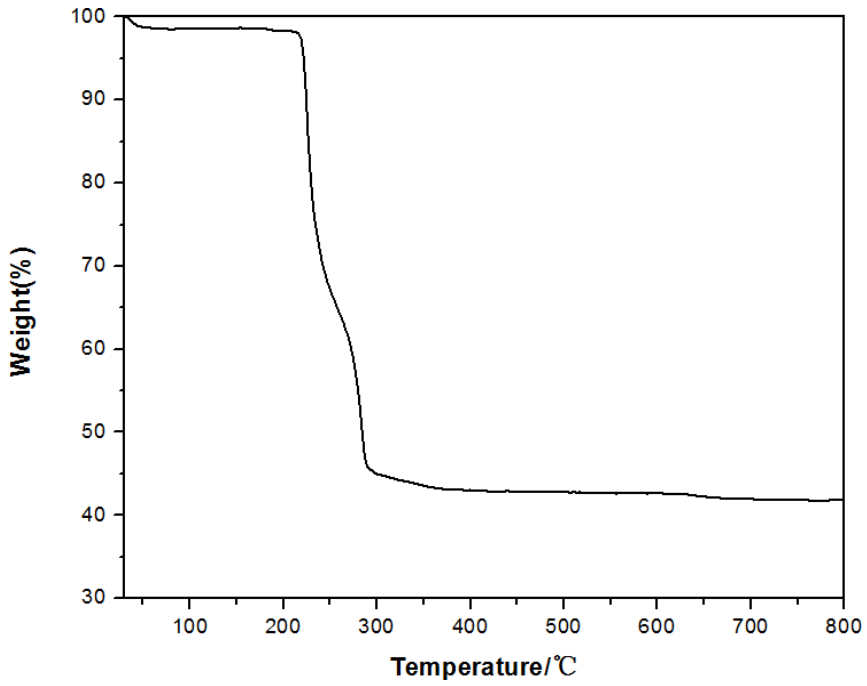



**Figure S17.** The TGA curve of **PTC-75**.

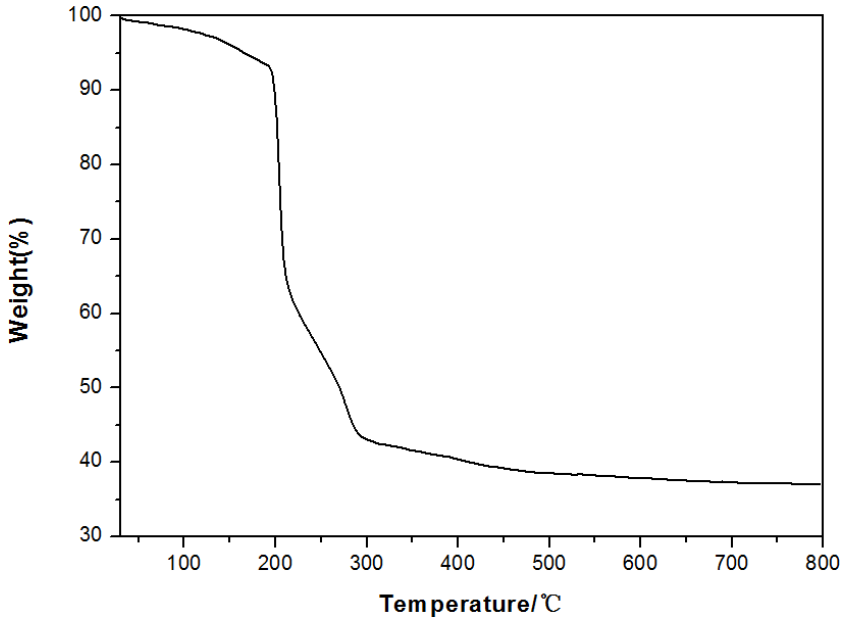



**Figure S18.** The TGA curve of **PTC-76**.

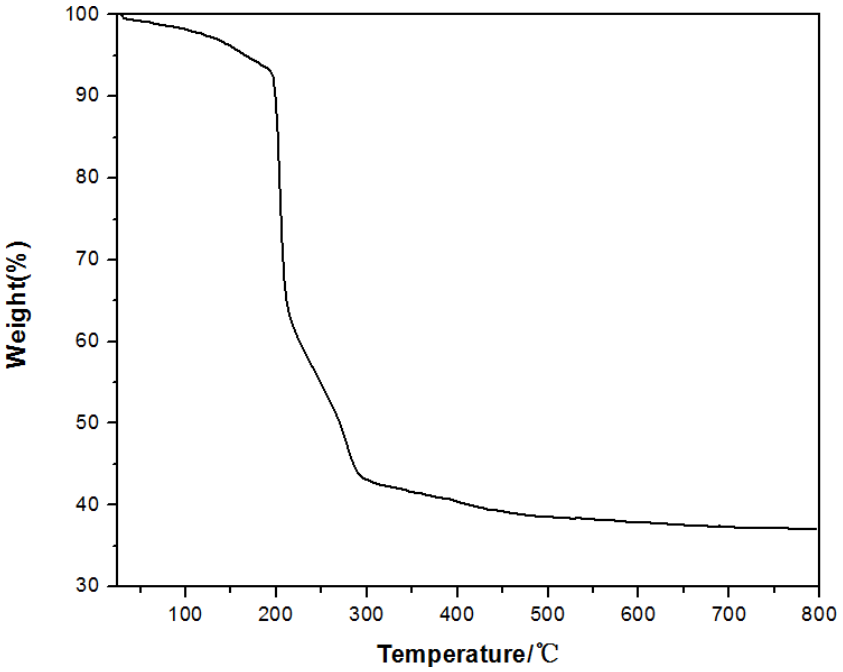



**Figure S19.** The TGA curve of **PTC-77**.

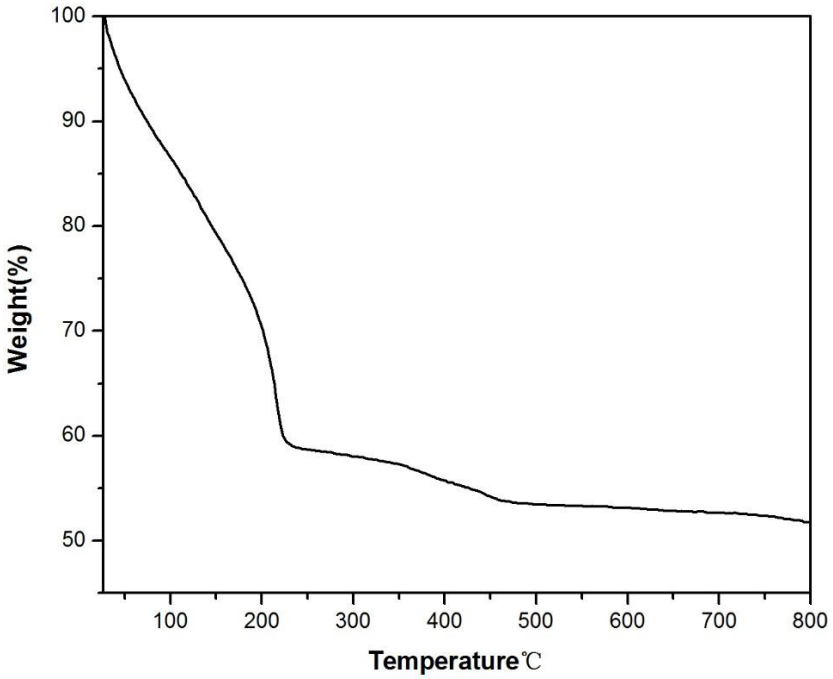



**Figure S20.** The TGA curve of **PTC-78**.

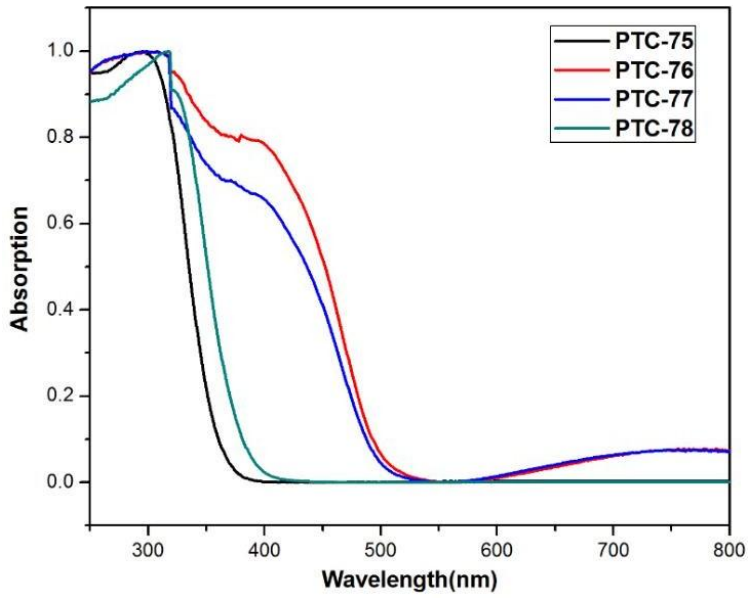



**Figure S21.** The solid-state absorption spectra of **PTC-75** to **PTC-78**.