Electronic Supporting Information for

Rational Assembly of Metal-oxo Clusters into Molecular Materials via a Wheel Mounting Mode

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Materials and Instrumentation

This Commercially available reagents were bought from Sigma-Aldrich and used as received without further purification, except that $Ti(O^iPr)_4$ (96%) and isopropyl alcohol were bought from Energy Chemical. Fourier transform infrared spectroscopy (FTIR) data were collected on a PerkinElmer Spectrum 100 FT-IR Spectrometer. UV-Vis absorption spectra were measured on a Perkin-Elmer Lambda 950 UV-Vis spectrophotometer. The elemental analyses were performed on a vario MICRO elemental analyzer. Powder X-ray diffraction (XRD) data were collected on a Rigaku Mini Flex II diffractometer using Cu K radiation (λ = 1.54056Å) under ambient conditions. The solid state nuclear magnetic resonance (S-NMR) data were collected on a AVANCE Ⅲ HD. The X-ray photoelectron spectroscopy (XPS) data were collected on a ESCALAB 250Xi. The thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/SDTA 851e analyzer in air atmosphere with a heating rate of 10 ºC/min from 30 ºC to 800 ºC

Crystallographic studies

the X-ray single crystal diffraction data of **PTC-137, PTC-140, PTC-144, PTC-145, PTC-148** to **150** and **PTC-150A** were collected on a SuperNova with graphite-monochromatic Mo Kα radiation (λ = 0.7103 Å). The X-ray single crystal diffraction data of **PTC-135, PTC-136, PTC-138, PTC-141, PTC-142, PTC-146, PTC-147** and **PTC-151** were collected on a SuperNova with graphite-monochromatic Cu Kα radiation (λ = 1.5418Å). The X-ray single crystal diffraction data of **PTC-131, PTC-132** and **PTC-134** were collected on a Xcalibur with graphite-monochromatic Mo Kα radiation (λ = 0.7103Å). The X-ray single crystal diffraction data of **PTC-133, PTC-132** and **PTC-139** were collected on a Saturn724+ with graphite-monochromatic Mo Kα radiation (λ = 0.7103 Å). The X-ray single crystal diffraction data of **PTC-143-Cu** and **PTC-143-Zn** were collected on a MM007 with graphite-monochromatic Mo Kα radiation (λ = 0.7103Å). The X-ray single crystal diffraction data of **PTC-143-Fe** and **PTC-143-Co** were collected on a Synergy Custom(Liquid MetalJet D2+) with graphite-monochromatic Ga Kα radiation (λ = 1.34050Å). The Structure solutions and

refinements were done with the OLEX2.[1] Contributions to scattering due to disordered solvent molecules were removed using the SQUEEZE routine of PLATON.[2]

Synthesis of TPyP-Fe:

The 5,10,15,20-tetrapyridylporphyrin (TPyP-H_2) (0.62 g, 1.0 mmol) and $FeCl_2 \cdot 4H_2O$ (1.60 g, 8 mmol) was added in 200 mL mixture of $CHCl_3$ and CH_3OH with ratio of 1:1. and the resultant mixture was heated to reflux for 12 h at 70°C under nitrogen protection. After cooling down to room temperature, the $CHCl_3/CH_3OH$ was removed under reduced pressure. The obtained solid was washed three times with H_2O, dried to give quantitative dark red crystals.[3]

Synthesis of TPyP-Co:

The 5,10,15,20-tetrapyridylporphyrin (TPyP-H_2) (0.62 g, 1.0 mmol) and $Co(OAc)_2 \cdot 4H_2O$ (2.49 g, 10 mmol) was added in 200 mL mixture of $CHCl_3$ and CH_3OH with ratio of 1:1. and the resultant mixture was heated to reflux for 12 h at 70°C. After cooling down to room temperature, the $CHCl_3/CH_3OH$ was removed under reduced pressure. The obtained solid was washed three times with H_2O, dried to give quantitative dark red crystals.[3]

Synthesis of TPyP-Cu:

The 5,10,15,20-tetrapyridylporphyrin (TPyP-H_2) (0.62 g, 1.0 mmol) and $Cu(OAc)_2 \cdot H_2O$ (2.00 g, 10 mmol) was added in 200 mL mixture of $CHCl_3$ and CH_3OH with ratio of 1:1. and the resultant mixture was heated to reflux for 12 h at 70°C. After cooling down to room temperature, the $CHCl_3/CH_3OH$ was removed under reduced pressure. The obtained solid was washed three times with H_2O, dried to give quantitative dark red crystals.[3]

Synthesis of TPyP-Zn:

The 5,10,15,20-tetrapyridylporphyrin (TPyP-H_2) (0.62 g, 1.0 mmol) and $Cu(OAc)_2 \cdot H_2O$ (2.20 g, 10 mmol) was added in 200 mL mixture of $CHCl_3$ and CH_3OH with ratio of 1:1. And the resultant mixture was heated to reflux for 12 h at 70°C. After cooling down to room temperature, the $CHCl_3/CH_3OH$ was removed under reduced pressure. The obtained solid was washed three times with H_2O, dried to give quantitative dark red crystals.[3]

Synthesis of PTC-131

Phenylphosphonic acid (0.10 g, 0.63 mmol), cobalt(II) acetate tetrahydrate (0.10 g, 0.40 mmol), 2-aminopyridine (0.06 g，0.64 mmol)，and isopropyl alcohol (5.0ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 80°C for four days. After cooled to room temperature, blue crystals of **PTC-131** were obtained. Yield: 120mg (50.17% based on phenylphosphonic acid). Anal. Calcd for $C_{41}H_{62}CoN_2O_{16}P_3Ti_3$: C, 43.41; H, 5.51; N, 2.47. Found: C, 41.65; H, 5.54; N, 2.45. FTIR (KBr, cm-1): ν= 3361 (w), 2972 (w), 2926 (w), 2867(w), 1625 (w),1580 (w),1490 (w),1448 (w), 1438 (w), 1377 (w),1363 (w), 1267 (w),1125 (m),1085 (m).

Synthesis of PTC-132

Phenylphosphonic acid (0.10 g, 0.63 mmol), cobalt(II) acetate tetrahydrate (0.10 g, 0.40 mmol), 3-aminopyridine (0.06 g，0.64 mmol)，and isopropyl alcohol (5.0ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 80°C for four days. After cooled to room temperature, dark blue crystals of **PTC-132** were obtained. Yield: 120mg (54.35% based on phenylphosphonic acid). Anal. Calcd for $C_{41}H_{62}CoN_2O_{16}P_3Ti_3$: C, 43.41; H, 5.51; N, 2.47. Found: C, 42.05; H, 5.47; N, 2.36. FTIR (KBr, cm-1): ν= 3361 (w), 2972 (w), 2926 (w), 2867(w), 1625 (w),1582 (w),1488 (w),1449 (w), 1437 (w), 1376 (w),1362 (w), 1360 (w),1121 (m),1088 (m).

Synthesis of PTC-133

Phenylphosphonic Phenylphosphonic acid (0.10 g, 0.63 mmol), cobalt(II) acetate tetrahydrate (0.10 g, 0.40 mmol), Urotropine (0.15 g，1.06 mmol)，and isopropyl alcohol (5.0 ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (1 ml, 3.3 mmol) was

added. The resultant solution was heated at 80°C for four days. After cooled to room temperature, blue crystals of **PTC-133** were obtained. Yield: 150mg (60.22% based on phenyl- phosphonic acid). Calcd for $C_{42}H_{69}CoN_4O_{16}P_3Ti_3$: C, 42.67; H, 5.89; N, 4.74. Found: C, 40.81; H, 4.57; N, 6.21. FTIR (KBr, cm-1): ν= 3358 (w), 2971 (w), 2917 (w), 2869 (w), 1459 (w),1438 (w),1378 (w),1363 (w), 1248 (w),1228 (w),1124 (m),1088 (m).

Synthesis of PTC-134

Phenylphosphonic acid (0.10 g, 0.63 mmol), cobalt(II) acetate tetrahydrate (0.10 g, 0.40 mmol), triphenylphosphine (0.10 g，0.36 mmol)，and isopropyl alcohol (5.0ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 80°C for four days. After cooled to room temperature, blusih green crystals of **PTC-134** were obtained. Yield: 180mg (64.70% based on phenylphosphonic acid).Anal. Calcd for $C_{54}H_{72}CoO_{16}P_4Ti_3$: C, 49.75; H, 5.56.Found: C, 47.16; H, 5.43. FTIR (KBr, cm-1): ν= 3472 (w), 2971 (w), 2917 (w), 2863 (w), 1437 (w),1375 (w),1363 (w), 1113 (m),1071 (m),1058 (m).

Synthesis of PTC-135

Phenylphosphonic acid (0.10 g, 0.63 mmol), cobalt(II) acetate tetrahydrate (0.10 g, 0.40 mmol), triphenylphosphine (0.10 g，0.34 mmol)，and isopropyl alcohol (5.0ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 80°C for four days. After cooled to room temperature, blue crystals of **PTC-135** were obtained. Yield: 180mg (64.70% based on phenylphosphonic acid). Calcd for $C_{54}H_{72}CoO_{17}P_4Ti_3$: C, 49.15; H, 5.49.Found: C, 49.68; H, 5.35. FTIR (KBr, cm-1): ν= 3395 (w), 2975 (m), 2929 (w), 2865 (w), 1571 (w), 1439 (m), 1375 (m), 1362 (m), 1327 (w), 1117 (s), 1091 (s), 985 (s), 946 (s).

Synthesis of PTC-136

Phenylphosphonic acid (0.10 g, 0.63 mmol), cobalt(II) acetate tetrahydrate (0.10 g, 0.40 mmol), 2,2'-Dithiodipyridine (0.10 g, 0.45mmol)，and isopropyl alcohol (5.0 ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 80°C for four days. After cooled to room temperature, blue crystals of

PTC-136 were obtained. Yield: 100mg (33.67% based on phenylphosphonic acid). $C_{46}H_{65}CoN_2O_{16}P_3S_2Ti_3$: C, 43.79; H, 5.19 ; N, 2.22. Found: C, 41.31; H, 5.16; N, 2.37. FTIR (KBr, cm-1): ν= 2972 (w), 2930 (w), 2863(w), 1593 (w), 1561 (w), 1461 (w), 1439 (w), 1418 (w), 1377 (w), 1363 (w), 1117 (m), 1088 (m).

Synthesis of PTC-137

Phenylphosphonic Phenylphosphonic acid (0.10 g, 0.63 mmol), cobalt(II) acetate tetrahydrate (0.10 g, 0.40 mmol), dimethylaminopyridine (DMAP) (0.06 g，0.49 mmol)，and isopropyl alcohol (5.0 ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 80°C for four days. After cooled to room temperature, blue crystals of **PTC-137** were obtained. Yield: 100mg (40.80% based on phenylphosphonic acid).Anal. Calcd for $C_{43}H_{67}CoO_{16}N_2P_3Ti_3$: C, 44.39; H, 5.80 ; N, 2.41. Found: C, 43.13; H, 5.49; N, 2.53. FTIR (KBr, cm-1): ν= 2972 (w), 2932 (w), 2863 (w), 1616 (w), 1538 (m), 1437 (m), 1378 (w), 1361 (w), 1231 (w), 1119 (m), 1084 (m).

Synthesis of PTC-138

Phenylphosphonic acid (0.10 g, 0.63 mmol), cobalt(II) acetate tetrahydrate (0.10 g, 0.40 mmol), Melamine (0.79g，0.38mmol)，and isopropyl alcohol (5.0 ml) were mixed at room temperature; then dropwise Ti(OiPr)4 (1 ml, 3.3 mmol) was added. The resultant solution was heated at 80°C for four days. After cooled to room temperature, blue crystals of **PTC-138** were obtained. Yield: 20mg (7.56% based on phenylphosphonic acid). Anal. Calcd for $C_{78}H_{129}Co_2N_6O_{33}P_6Ti_6$: C, 41.27; H, 5.73 ; N,3.70. Found: C, 39.53; H, 5.32; N, 3.72. FTIR (KBr, cm-1): ν= 2972 (w), 2930 (w), 2867 (w), 1627 (w), 1566 (w), 1535 (w), 1437 (m), 1376 (w), 1114 (m), 1078 (m), 1065 (m).

Synthesis of PTC-139

Phenylphosphonic acid (0.10 g, 0.63 mmol), cobalt(II) acetate tetrahydrate (0.10 g, 0.40 mmol), 4,4'bipyridinyl (0.06 g，0.38 mmol)，and isopropyl alcohol (5.0 ml) were mixed at room temperature; then dropwise Ti(OiPr)4 (1 ml, 3.3 mmol) was added. The resultant solution was heated at 80°C for four days. After cooled to room temperature, blue crystals of **PTC-139** were obtained. Yield: 60mg (24.61% based on phenylphosphonic acid). Anal.

Calcd for $C_{82}H_{120}Co_2N_2O_{32}P_6Ti_6$: C, 44.03; H, 5.41 ; N, 1.25. Found: C, 42.05; H, 5.37; N, 1.33. FTIR (KBr, cm-1): ν= 2972 (w), 2928 (w), 2864 (w), 1613 (w), 1437 (w), 1380 (w), 1361 (w), 1120 (m), 1082 (m).

Synthesis of PTC-140

Phenylphosphonic acid (0.10 g, 0.63 mmol), cobalt(II) acetate tetrahydrate (0.10 g, 0.40 mmol), 1,3,5-Triazine,2,4,6-tri-4-pyridinyl (0.06 g，0.19 mmol)，and isopropyl alcohol (5.0 ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 80°C for four days. After cooled to room temperature, ash black crystals of **PTC-140** were obtained. Yield: 80mg (31.69% based on phenylphosphonic acid). Anal. Calcd for $C_{90}H_{126}Co_2N_6O_{32}P_6Ti_6$: C, 45.14; H, 5.30; N, 3.51. Found: C, 40.70; H, 6.53. FTIR (KBr, cm-1): ν= 2972 (w), 2928 (w), 2863 (w), 1517 (m), 1438 (w), 1375 (w), 1375 (w),1361 (w), 1118 (m), 1080 (m).

2.11 Synthesis of PTC-141

Phenylphosphonic acid (0.10 g, 0.63 mmol), cobalt(II) acetate tetrahydrate (0.10 g, 0.40 mmol), 1,3,5-Triazine,2,4,6-tri-4-pyridinyl (0.06 g，0.19 mmol)，and isopropyl alcohol (5.0 ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 80°C for four days. After cooled to room temperature, blue crystals of **PTC-141** were obtained. Yield: 80mg (31.69% based on phenylphosphonic acid). Anal. Calcd for $C_{90}H_{126}Co_2N_6O_{32}P_6Ti_6$: C, 45.14; H, 5.30; N, 3.51. Found: C, 45.64; H, 5.35; N, 3.90. FTIR (KBr, cm-1): ν=2972 (w), 2932 (w), 2863 (w), 1518 (m), 1439 (w), 1376 (w), 1363 (w), 1326 (w), 1306 (w), 1262 (w), 1118 (m), 1085 (m), 1061 (w).

Synthesis of PTC-142

Phenylphosphonic acid (0.20 g, 0.126 mmol), cobalt(II) acetate tetrahydrate (0.10 g, 0.40 mmol), 1,3,5-Triazine,2,4,6-tri-4-pyridinyl (0.06 g，0.19 mmol)，and isopropyl alcohol (5.0 ml) were mixed at room temperature; then dropwise $Ti(O_iPr)_4$ (2 ml, 6.6 mmol) was added. The resultant solution was heated at 100°C for four days. After cooled to room temperature, blue crystals of **PTC-142** were obtained. Yield: ~80mg (31.69% based on phenylphosphonic acid). Anal. Calcd for $C_{135}H_{192}Co_3N_7O_{48}P_9Ti_9$: C, 45.45; H, 5.42; N, 2.75. Found: C, 44.16; H,

5.43; N, 2.65. FTIR (KBr, cm^{-1}): ν= 2972 (w), 2934 (w), 2864 (w), 1522 (m), 1438 (w), 1380 (w), 1360 (w), 1122 (w), 1084 (w) 1001 (w).

Synthesis of PTC-143

Phenylphosphonic acid (0.10 g, 0.63 mmol), cobalt(II) acetate tetrahydrate (0.10 g, 0.40 mmol), TPyP-Fe (0.04 g，0.06 mmol)，and isopropyl alcohol (3.0 ml) were mixed at room temperature; then dropwise $Ti(O_iPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 100°C for four days. After cooled to room temperature, purple crystals of **PTC-143-Fe** were obtained. Yield: ~60mg (23.59% based on phenylphosphonic acid). Anal. Calcd for $C_{184}H_{252}Co_4FeN_8O_{64}P_{12}Ti_{12}$: C, 45.68; H, 5.25; N, 2.32. Found: C, 42.13; H, 4.95; N, 2.52. FTIR (KBr, cm^{-1}): ν= 2970 (w), 2929 (w), 2866 (w), 1610(m), 1437(m), 1376(w), 1364 (w),1120 (s), 1084 (m), 998 (s).

Phenylphosphonic acid (0.10 g, 0.63 mmol), cobalt(II) acetate tetrahydrate (0.10g, 0.40 mmol), TPyP-Co (0.04 g，0.06 mmol)，and isopropyl alcohol (3.0 ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 100°C for four days. After cooled to room temperature, dark red crystals of **PTC-143-Co** were obtained. Yield: 60mg (23.59% based on phenylphosphonic acid). Anal. Calcd for $C_{184}H_{252}Co_5N_8O_{64}P_{12}Ti_{12}$: C, 45.65; H, 5.24; N, 2.31. Found: C, 43.54; H, 4.93; N, 2.60. FTIR (KBr, cm-1): ν= 2970 (w), 2929 (w), 2866 (w), 1610(m), 1437(m), 1376(w), 1364 (w), 1120 (s), 1084(m), 998(s).

Phenylphosphonic acid (0.10 g, 0.63 mmol), cobalt(II) acetate tetrahydrate (0.10g, 0.40 mmol), TPyP-Cu (0.04 g，0.06 mmol)，and isopropyl alcohol (3.0 ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 100°C for four days. After cooled to room temperature, dark red crystals of **PTC-143-Cu** were obtained. Yield: 80mg (31.45% based on phenylphosphonic acid). Anal. Calcd for $C_{184}H_{252}Co_4CuN_8O_{64}P_{12}Ti_{12}$: C, 45.61; H, 5.24; N, 2.31. Found: C, 43.95; H, 5.01; N, 2.43. FTIR (KBr, cm-1):ν= 2970 (w), 2929 (w), 2866 (w), 1610 (m), 1437 (m), 1376 (w), 1364 (w),1120 (s), 1084 (m), 998 (s).

Phenylphosphonic acid (0.10 g, 0.63 mmol), cobalt(II) acetate tetrahydrate (0.10 g, 0.40 mmol), TPyP-Zn (0.04 g，0.06 mmol)，and isopropyl alcohol (3.0 ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 100°C for four days. After cooled to room temperature, purple crystals of **PTC-143-Zn** were obtained. Yield: 80mg (31.45% based on phenylphosphonic acid).Anal. Calcd for $C_{184}H_{252}Co_4N_8O_{64}P_{12}Ti_{12}Zn$: C, 45.59; H,5.24; N,2.31. Found: C, 43.83; H,5.19; N,2.40. FTIR (KBr, cm-1): ν= 2970 (w), 2929 (w), 2866 (w), 1610 (m), 1437 (m), 1376(w), 1364 (w),1120 (s), 1084 (m), 998 (s).

Synthesis of PTC-144

Diethyl phosphite (0.2 ml, 1.35 mmol), cobalt(II) acetate tetrahydrate (0.12 g, 0.48 mmol), 2-aminopyridine (0.06 g，0.64 mmol)，and isopropyl alcohol (5.0 ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 80°C for four days. After cooled to room temperature, blue crystals of **PTC-144** were obtained. Yield: 170mg (42.45% based on diethyl phosphite). Anal. Calcd for $C_{22}H46CoN_2O_{16}P_3Ti_3$: C, 29.69; H, 5.21; N, 3.15. Found: C, 28.00; H, 5.19; N,3 .06. FTIR (KBr, cm-1): ν= 3420 (m), 2972 (w), 2934 (w), 2868 (w), 1557 (m), 1441 (m), 1371 (w), 1324 (w).

Synthesis of PTC-145

Diethyl phosphite (0.2 ml, 1.35 mmol), cobalt(II) acetate tetrahydrate (0.12 g, 0.48 mmol), 1,4-diazabicyclooctane (0.10 g，0.89 mmol)，and isopropyl alcohol (5.0 ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 80°C for four days. After cooled to room temperature, blue crystals of **PTC-145** were obtained. Yield: 150mg (39.13% based on diethyl phosphite). Anal. Calcd for $C_{40}H_{92}Co_2N_2O_{32}P_6Ti_6$: C, 28.19; H, 5.44; N, 1.64. Found: C, 27.04; H, 5.24; N, 1.72. FTIR (KBr, cm-1): ν= 2972 (w), 2923 (w), 2867 (w), 1380 (w), 1365(w), 1121 (m), 1094 (m), 1043 (w), 983 (w).

Synthesis of PTC-146

Diethyl phosphite (0.2 ml, 1.35 mmol), cobalt(II) acetate tetrahydrate (0.12 g, 0.48 mmol), 4,4'bipyridinyl (0.06 g，0.38 mmol)，and isopropyl alcohol (5.0 ml) were mixed at room temperature; then dropwise $Ti(O_iPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 80°C for four days. After cooled to room temperature, blue crystals of **PTC-146** were obtained. Yield: ~350mg (87.59% based on diethyl phosphite). Anal. Calcd for $C_{44}H_{88}Co_2N_2O_{32}P_6Ti_6$: C, 30.23; H, 5.07; N, 1.60. Found: C, 30.17; H, 5.41; N, 1.47. FTIR (KBr, cm^{-1}): ν= 2973 (w), 2924 (w), 2862 (w), 2417 (w), 1607 (w), 1375 (w), 1364(w), 1122 (m), 1091 (m), 1042 (m), 981 (m).

Synthesis of PTC-147

Diethyl phosphite (0.2 ml, 1.35 mmol), cobalt(II) acetate tetrahydrate (0.12 g, 0.48 mmol), TPyP-Zn (0.8 g，0.12 mmol)，an d isopropyl alcohol (3 ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 80°C for four days. After cooled to room temperature, blue crystals of **PTC-147** were obtained. Yield: 120mg (25.5% based on diethyl phosphite). Anal. Calcd for $C_{128}H_{240}Co_4N_{10}O_{62}P_{12}Ti_{12}Zn$: C, 36.97; H, 5.81; N, 3.37. Found: C, 36.57; H, 5.93; N, 3.17. FTIR (KBr, cm-1): ν= 2974 (w), 2925 (w), 2866 (w), 2416 (w), 1610 (m), 1420 (w), 1375 (w), 1363 (w), 1123 (m), 1093 (m), 983 (m).

Synthesis of PTC-148

Phenylphosphonic acid (0.10 g, 0.63 mmol), zinc Acetate Dihydrate (0.12 g, 0.55 mmol), dimethylaminopyridine (DMAP) (0.06 g, 0.49 mmol)，and isopropyl alcohol (5.0 ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 80°C for four days. After cooled to room temperature, colorless crystals of **PTC-148** were obtained. Yield: 150mg (60.82% based on phenylphosphonic acid).Anal. Calcd for $C_{43}H_{67}O_{16}N_2P_3Ti_3Zn$: C, 44.14; H, 5.77 ; N, 2.41. Found: C, 42.03; H, 5.62; N, 2.20. FTIR (KBr, cm-1):ν= 2970 (w), 2928 (w), 2864 (w), 1620 (w), 1539 (w), 1439 (m), 1375 (w), 1358 (w), 1123 (m), 1091 (m), 999 (m).

Synthesis of PTC-149

Phenylphosphonic acid (0.10 g, 0.63 mmol), zinc Acetate Dihydrate (0.10 g, 0.46 mmol), triphenylphosphine (0.10g，0.38mmol)，and isopropyl alcohol (5.0 ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 80°C for four days. After cooled to room temperature, colorless crystals of **PTC-149** were obtained. Yield: 170mg (67.88% based on phenyl- phosphonic acid). Anal. Calcd for $C_{54}H_{72}ZnO_{17}P_4Ti_3$: C, 48.91; H, 5.47. Found: C, 48.44; H, 5.22. FTIR (KBr, cm-1): ν= 2970 (w), 2929 (w), 2863 (w), 1522 (m), 1437 (m), 1376 (w), 1362 (w), 1127 (m), 1001 (m), 963 (m).

Synthesis of PTC-150

Diethyl phosphite (0.2 ml, 1.35 mmol), zinc Acetate Dihydrate (0.12 g, 0.55 mmol), 4,4'bipyridinyl (0.06 g, 0.38 mmol)，and isopropyl alcohol (5.0 ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (1 ml, 3.3 mmol) was added. The resultant solution was heated at 80 °C for four days. After cooled to room temperature, blue crystals of **PTC-150** were obtained. Yield: 200mg (50.48% based on diethyl phosphite). Anal. Calcd for $C_{40}H_{92}N_4O_{32}P_6Ti_6Zn_2$: C, 30.01; H, 5.03; N, 1.59. Found: C, 30.45; H, 5.37; N, 1.44. FTIR (KBr, cm-1): ν= 2974 (w), 2926 (w), 2867 (w), 2418 (w), 1610 (w), 1419 (m), 1378 (w), 1360 (w), 1160 (m), 1130 (m), 1107 (m), 981(m).

Synthesis of PTC-150A

The **PTC-150A** was obtained by irradiation of compound **PTC-150** with ultraviolet light or X-ray (Cu target).

Synthesis of PTC-151

Phosphonic acid (0.20g, 0.126mmol), zinc Acetate Dihydrate (0.20g, 0.92 mmol), triphenylphosphine (0.06 g，0.38 mmol)，and isopropyl alcohol (5.0 ml) were mixed at room temperature; then dropwise $Ti(OiPr)_4$ (2 ml, 6.6 mmol) was added. The resultant solution was heated at 80°C for four days. After cooled to room temperature, colorless crystals of **PTC-151** were obtained. Yield: 170mg (67.88% based on phenyl- phosphonic acid). Anal. Calcd for $C_{42}H_{69}N_4O_{16}P_3Ti_3Zn$: C, 42.46; H, 5.85; N, 4.71. Found: C, 44.21; H,

5.64; N, 4.28. FTIR (KBr, cm-1): ν= 2971 (w), 2930 (w), 2864 (w), 1521 (w), 1439 (m), 1375 (w), 1358 (w), 1123 (m), 1091 (m), 999 (m).

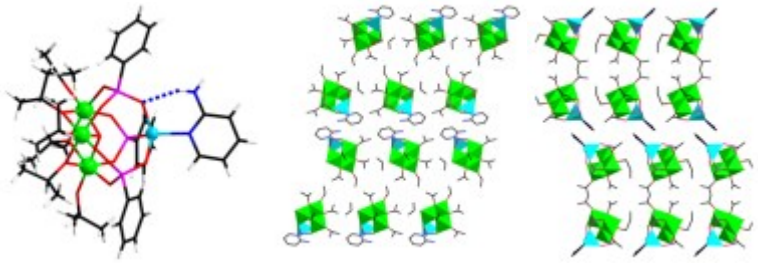

Figure S1. Crystal structure, packing-mode of **PTC-131**.

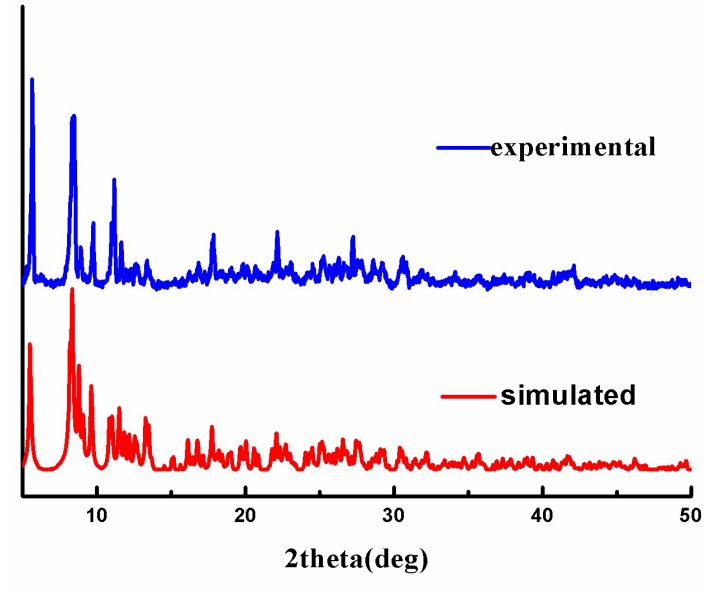

Figure S2. PXRD analysis of **PTC-131**.

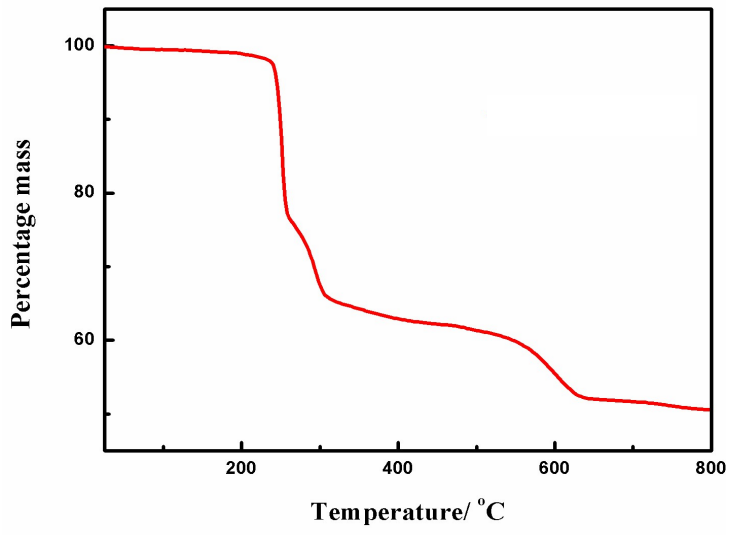

Figure S3. Thermal analysis of **PTC-131**

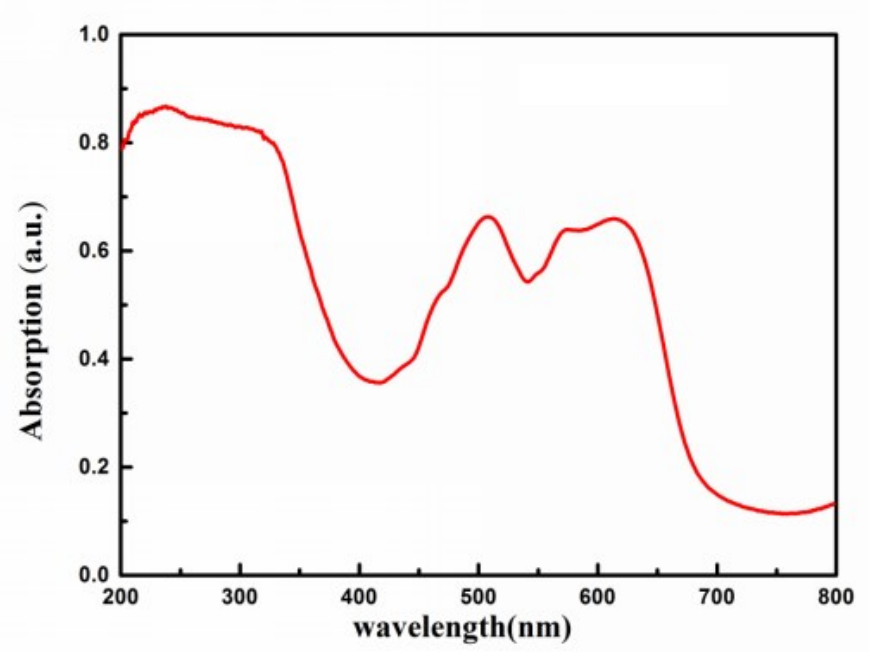

Figure S4. UV-vis spectra for **PTC-131**.

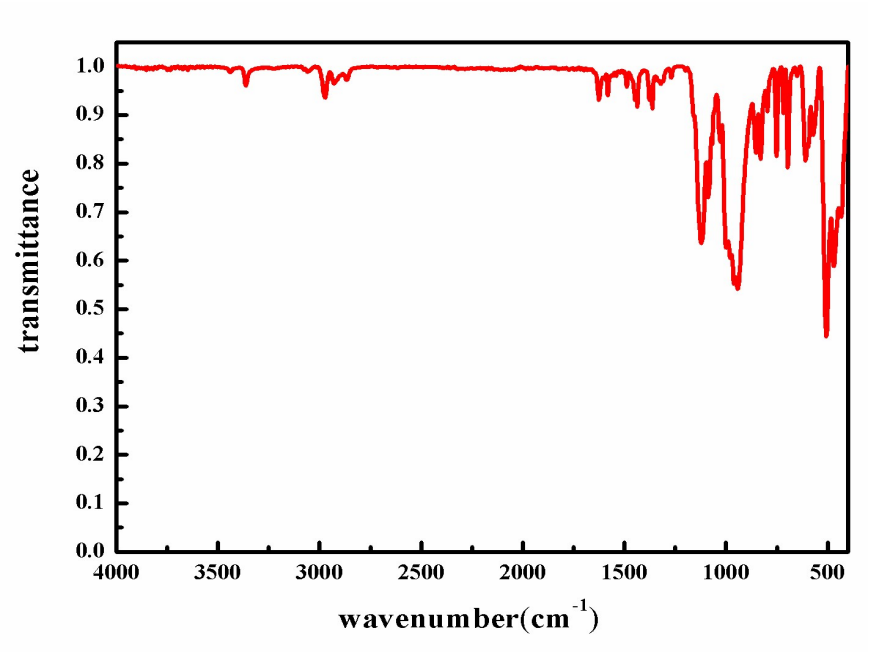

Figure S5. FTR-IR spectra for **PTC-131**.

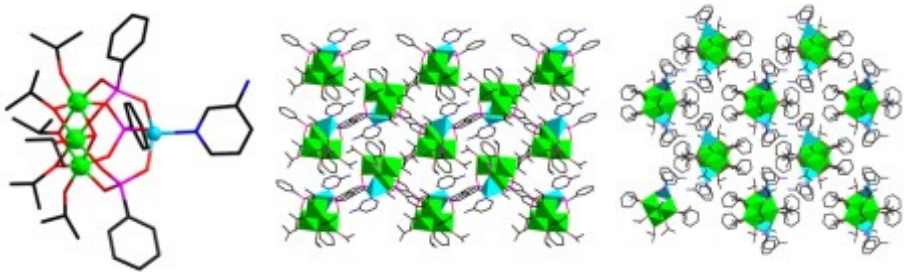

Figure S6. Crystal structure, packing-mode of **PTC-132**.

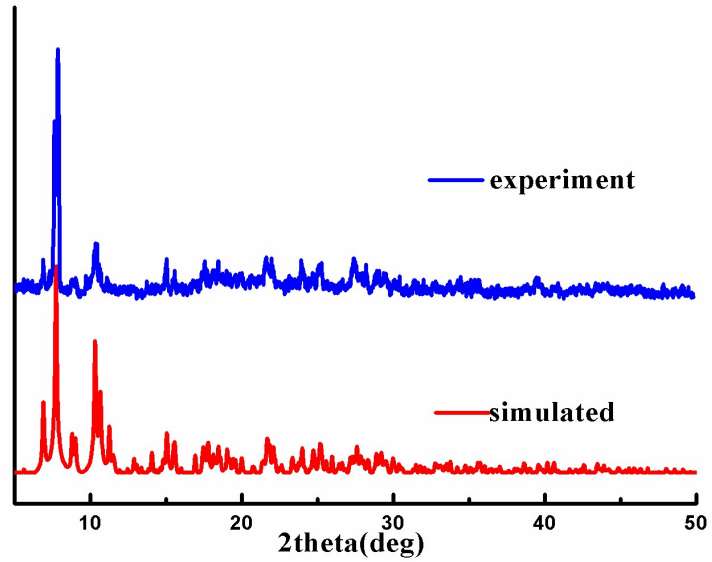

Figure S7.PXRD analysis of **PTC-132**.

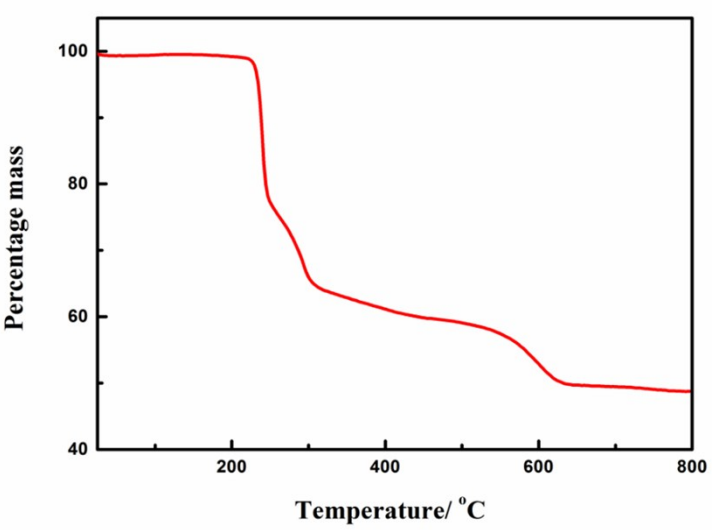

Figure S8. Thermal analysis of **PTC-132**

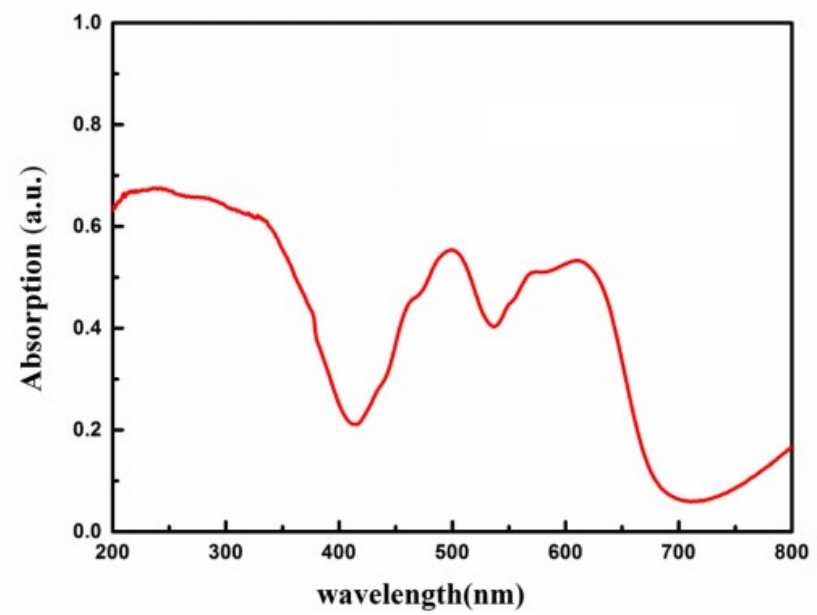

Figure S9. UV-vis spectra for **PTC-132**.

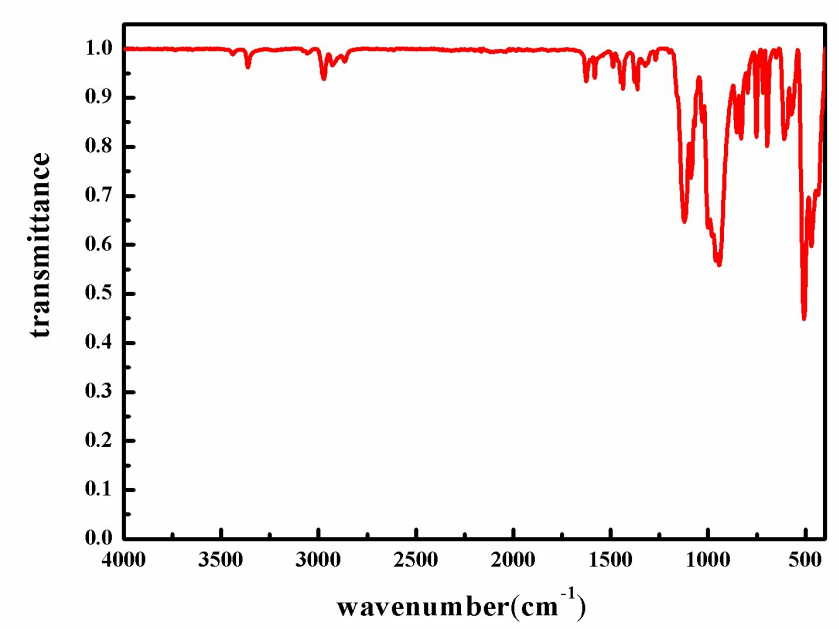

Figure S10. FTR-IR spectra for **PTC-132**.

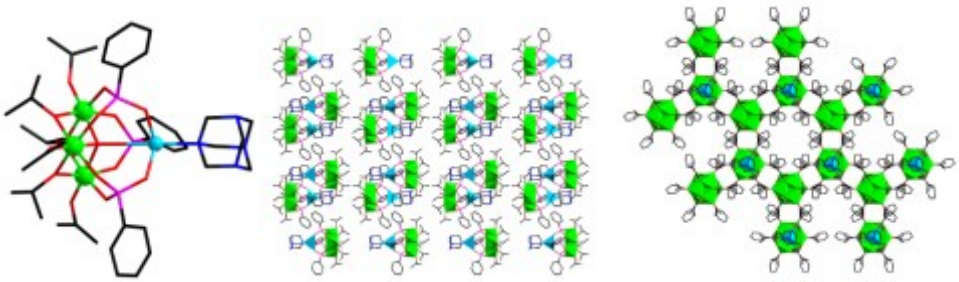

Figure S11. Crystal structure, packing-mode of **PTC-133**.

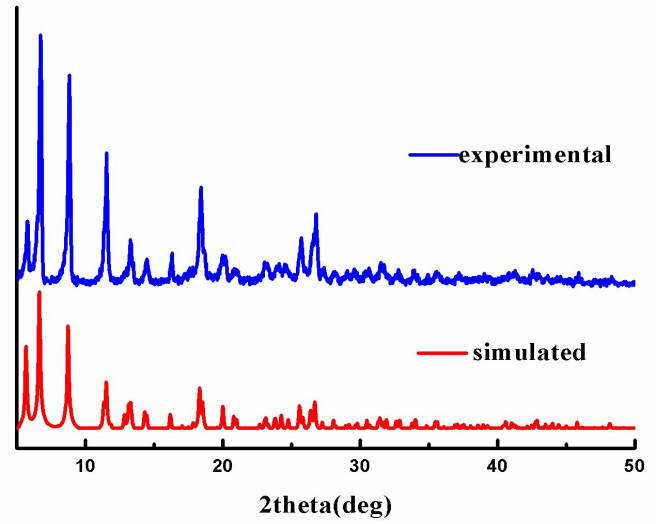

Figure S12. PXRD analysis of **PTC-133**.

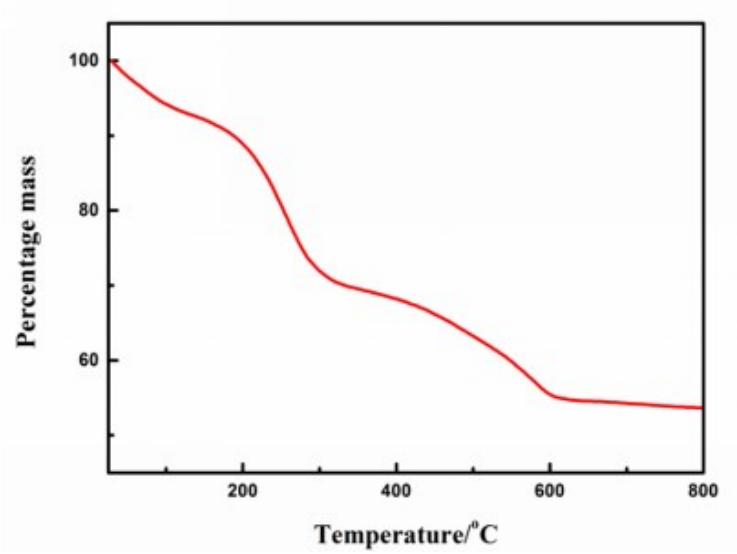

Figure S13. Thermal analysis of **PTC-133**

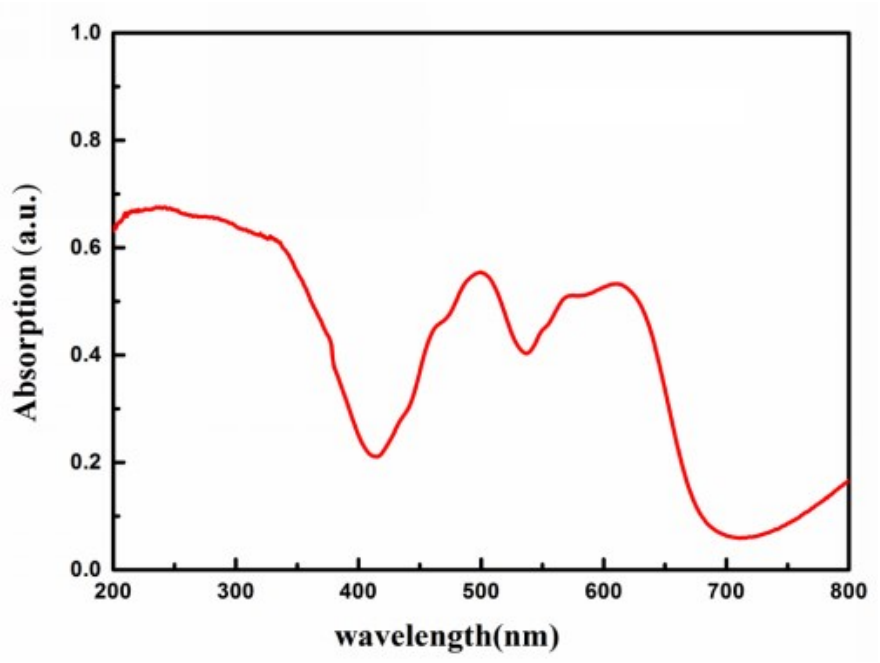

Figure S14. UV-vis spectra for **PTC-133**.

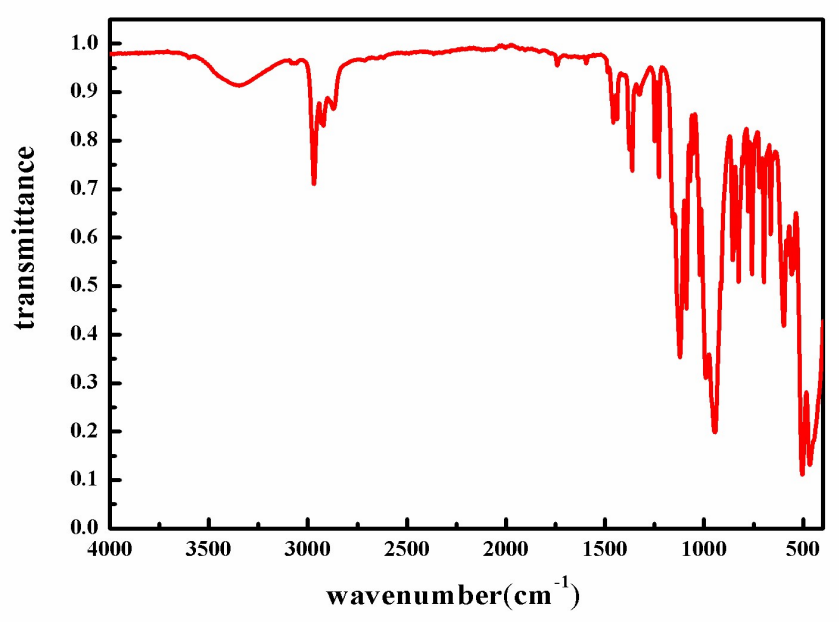

Figure S15. FTR-IR spectra for **PTC-133**.

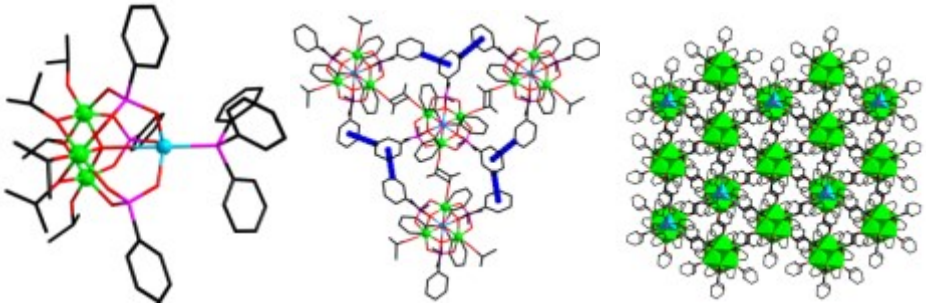

Figure S16. Crystal structure, packing-mode of **PTC-134**.

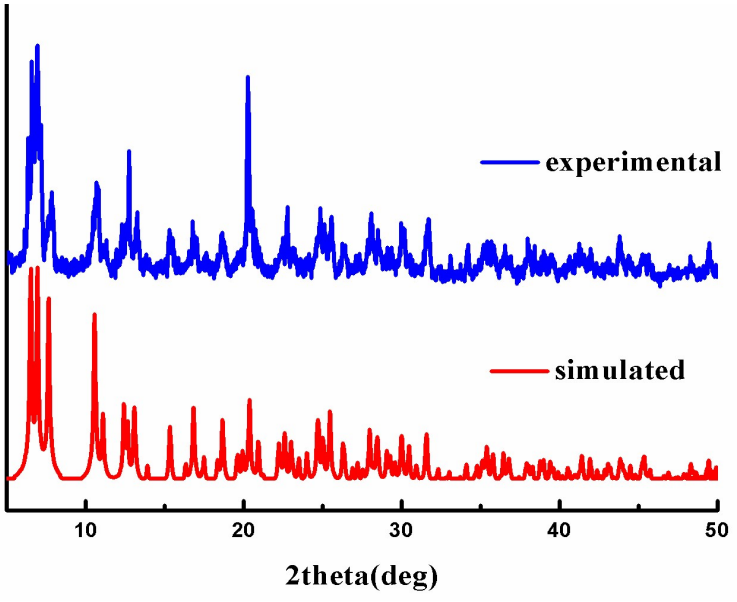

Figure S17. PXRD analysis of **PTC-134**.

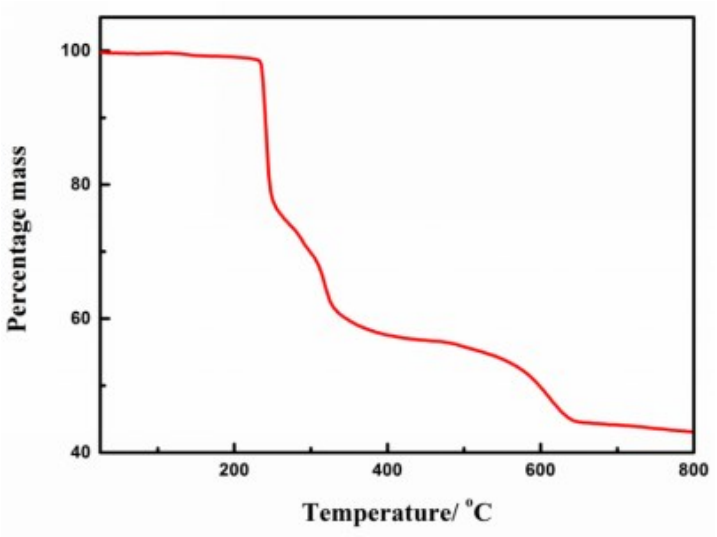

Figure S18. Thermal analysis of **PTC-134**

Figure S19. UV-vis spectra for **PTC-134**.

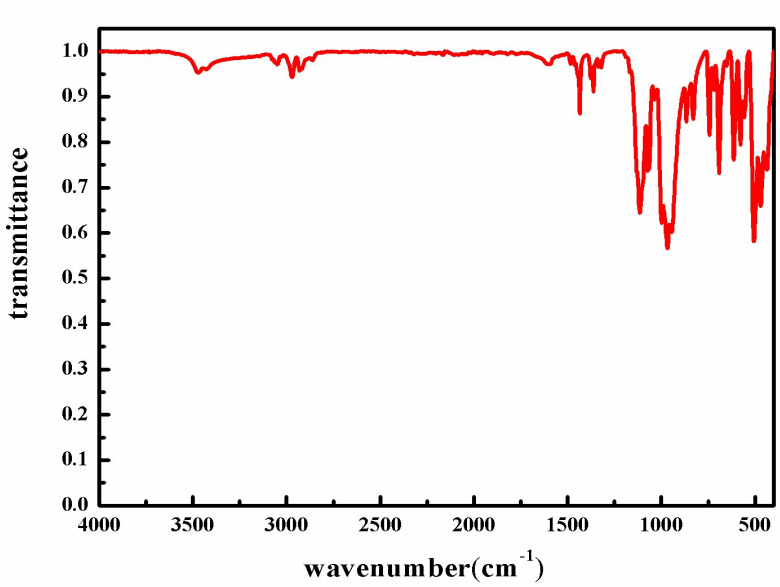

Figure S20. FTR-IR spectra for **PTC-134**.

Figure S21. Crystal structure, packing-mode of **PTC-135**.

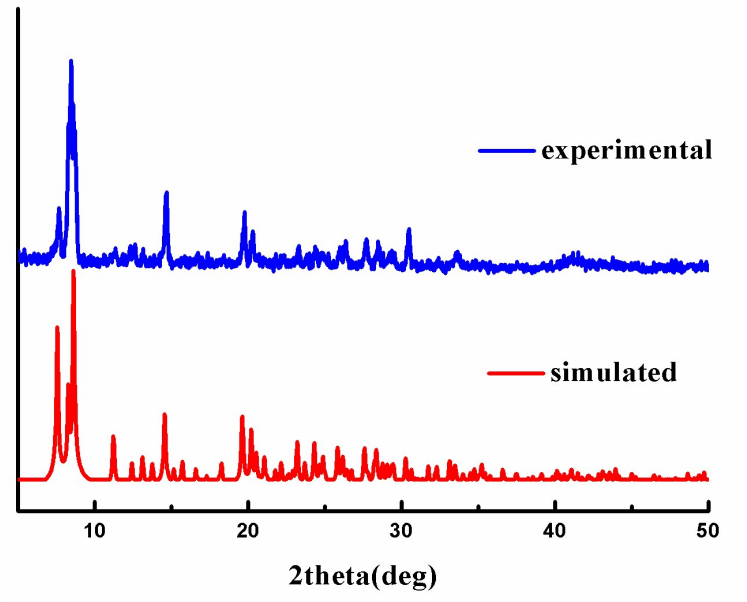

Figure S22. PXRD analysis of **PTC-135**.

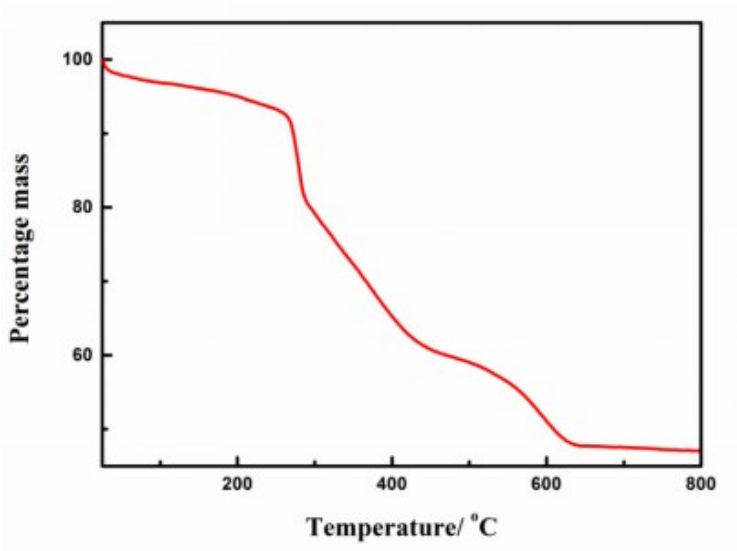

Figure S23. Thermal analysis of **PTC-135**

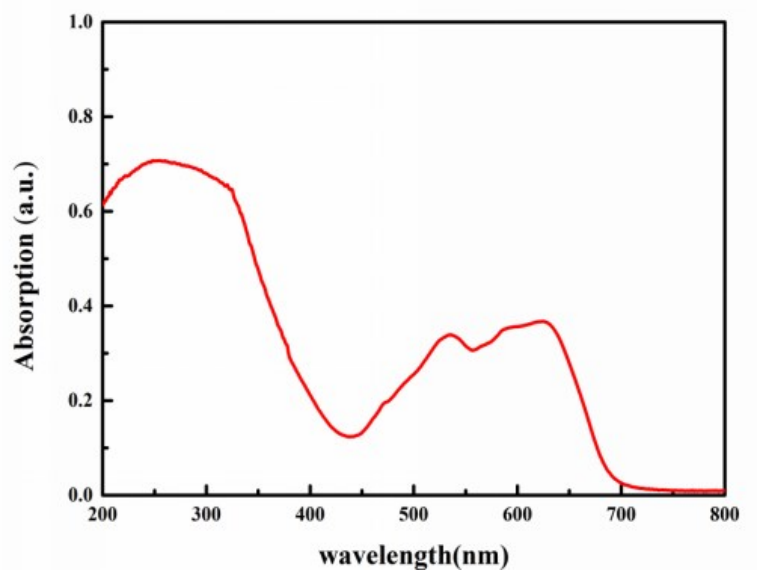

Figure S24. UV-vis spectra for **PTC-135**.

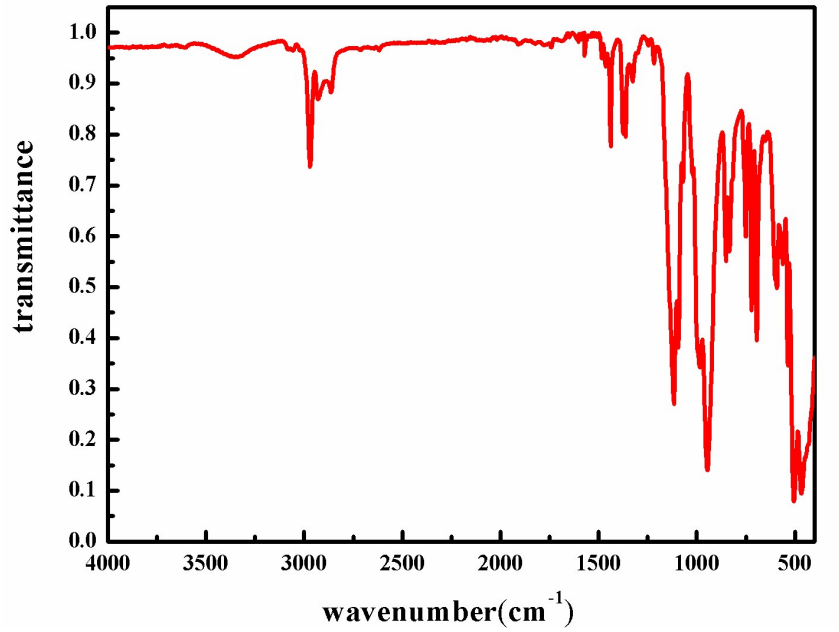

Figure S25. FTR-IR spectra for **PTC-135**.

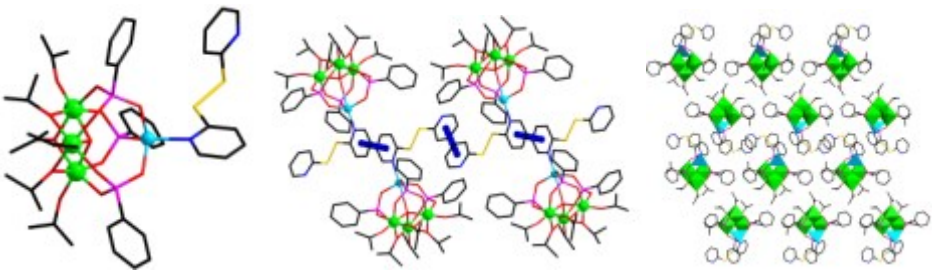

Figure S26. Crystal structure, packing-mode of **PTC-136**.

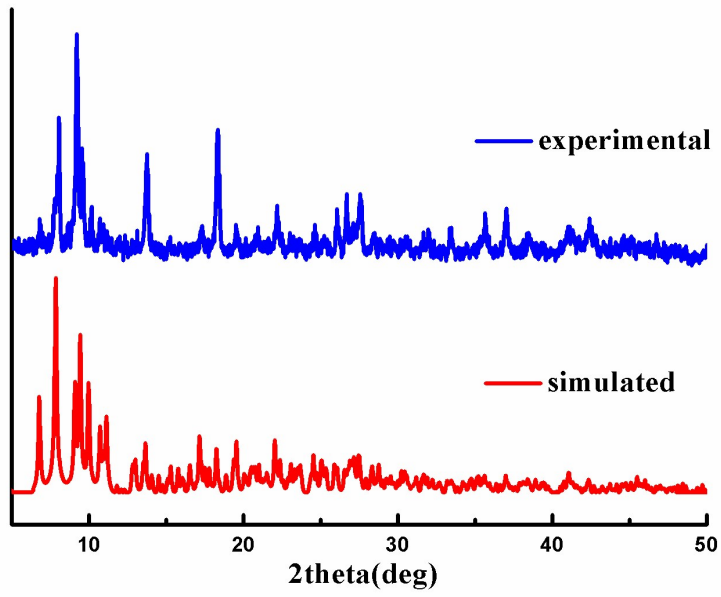

Figure S27. PXRD analysis of **PTC-136**.

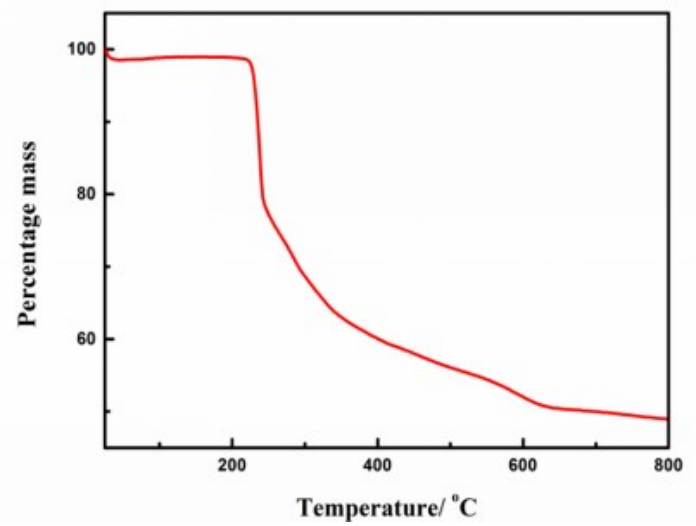

Figure S28. Thermal analysis of **PTC-136**

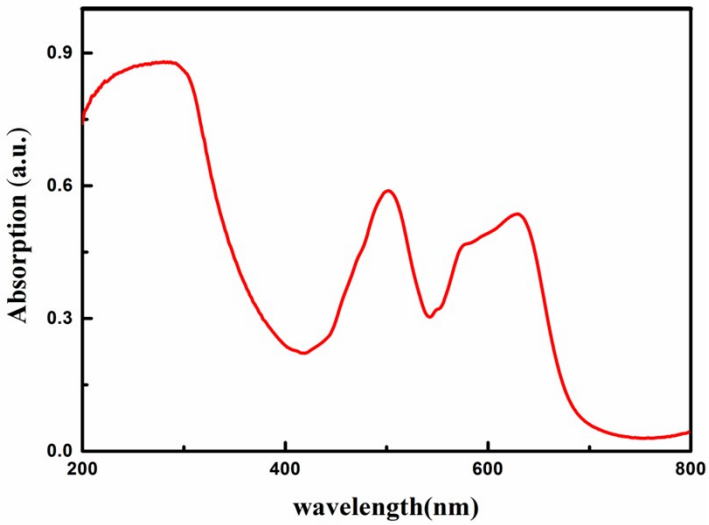

Figure S29. UV-vis spectra for **PTC-136**.

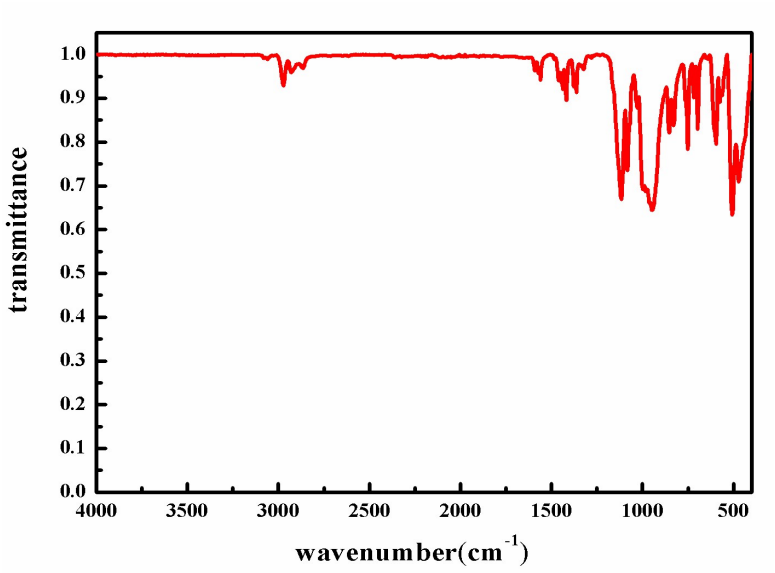

Figure S30. FTR-IR spectra for **PTC-136**.

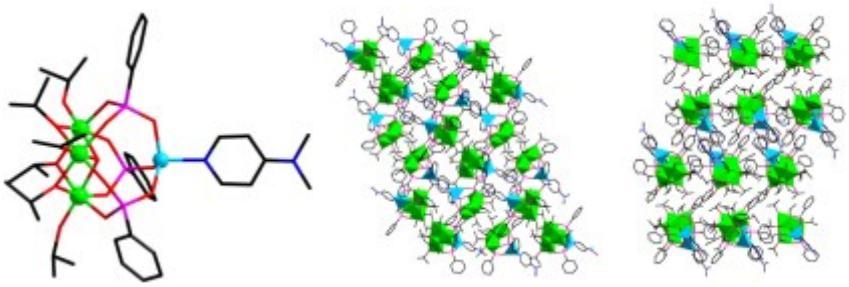

Figure S31. Crystal structure, packing-mode of **PTC-137**.

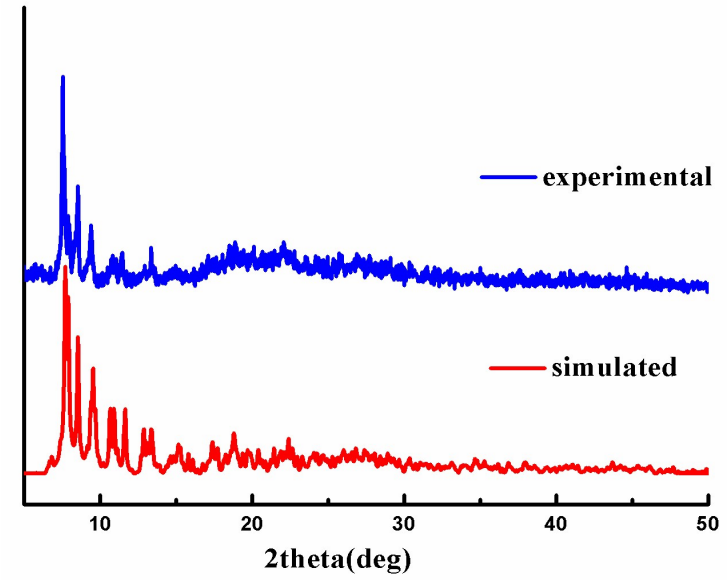

Figure S32. PXRD analysis of **PTC-137**.

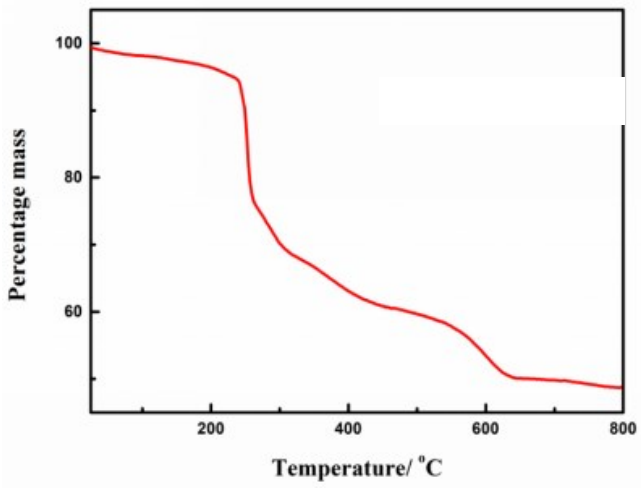

Figure S33. Thermal analysis of **PTC-137**

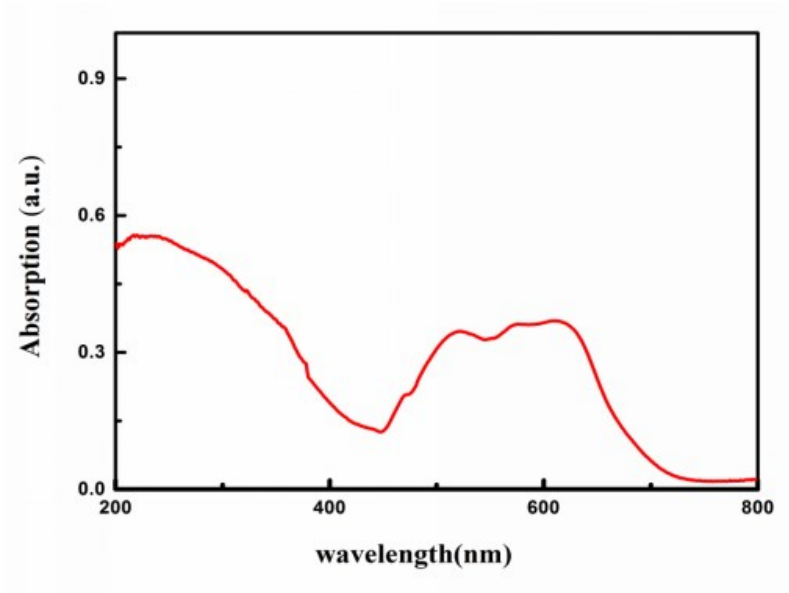

Figure S34. UV-vis spectra for **PTC-137**.

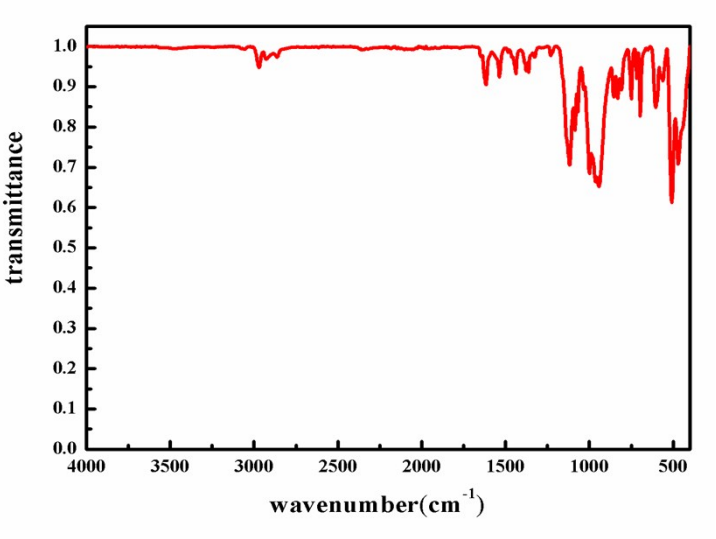

Figure S35. FTR-IR spectra for **PTC-137**.

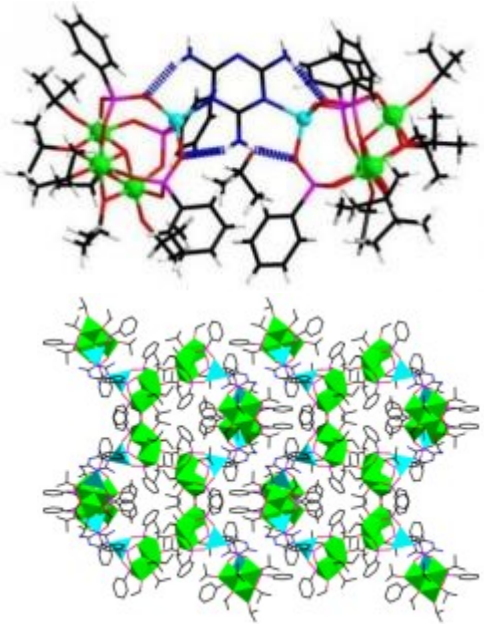

Figure S36. Crystal structure, packing-mode of **PTC-138**.

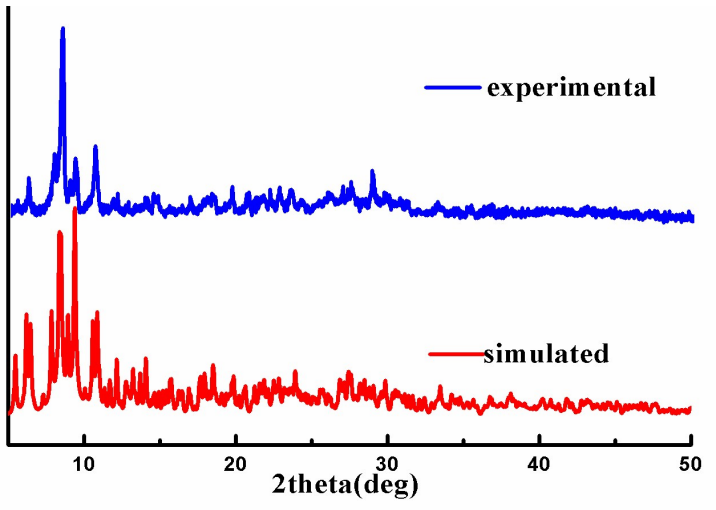

Figure S37.PXRD analysis of **PTC-138**.

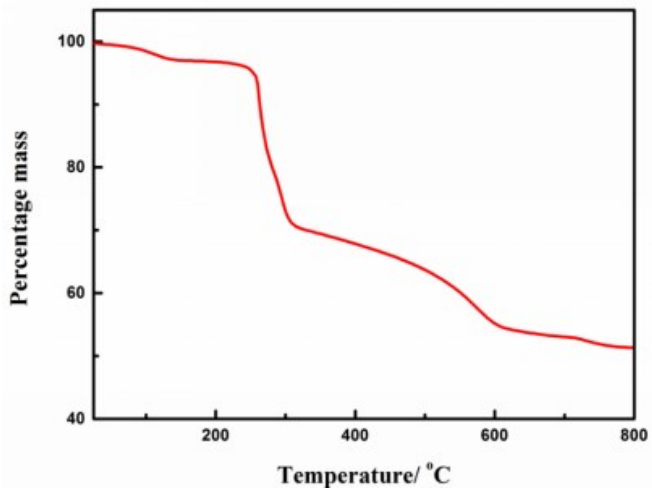

Figure S38. Thermal analysis of **PTC-138**

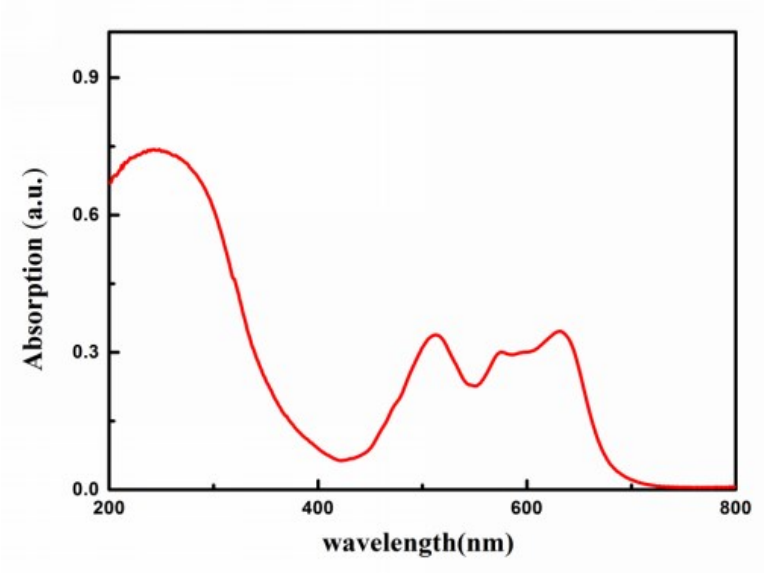

Figure S39. UV-vis spectra for **PTC-138**.

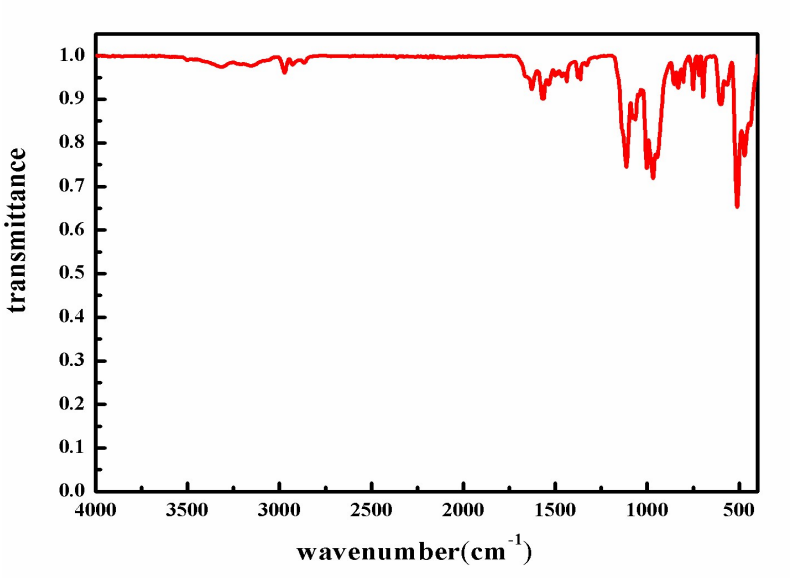

Figure S40. FTR-IR spectra for **PTC-138**.

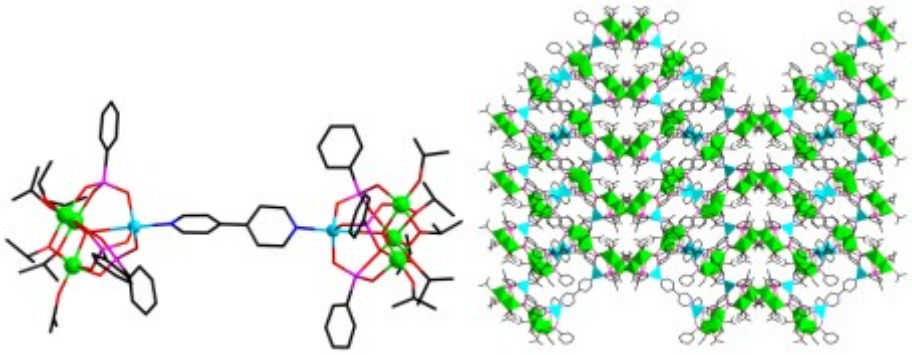

Figure S41. Crystal structure, packing-mode of **PTC-139**.

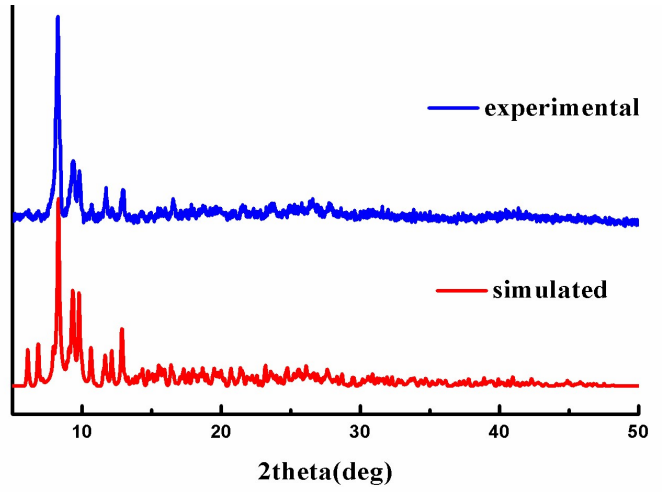

Figure S42. PXRD analysis of **PTC-139**.

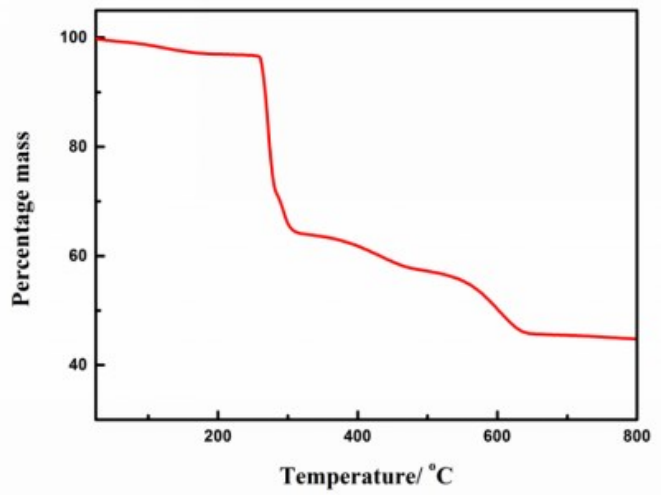

Figure S43. Thermal analysis of **PTC-139**

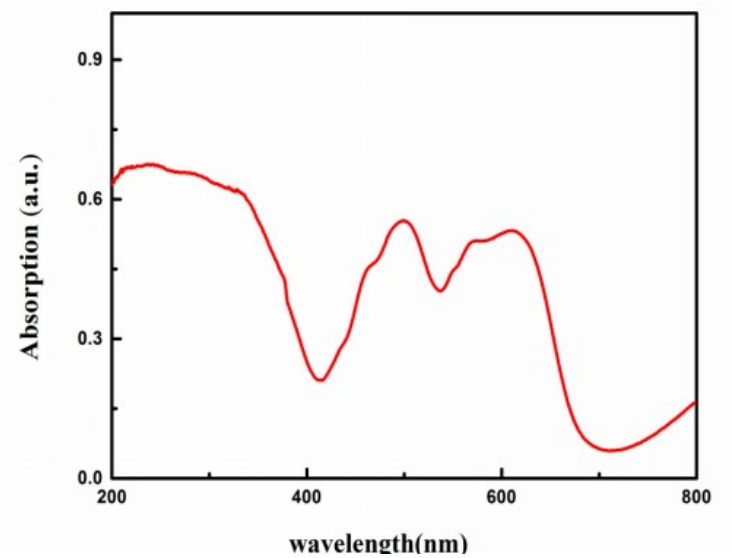

Figure S44. UV-vis spectra for **PTC-139**.

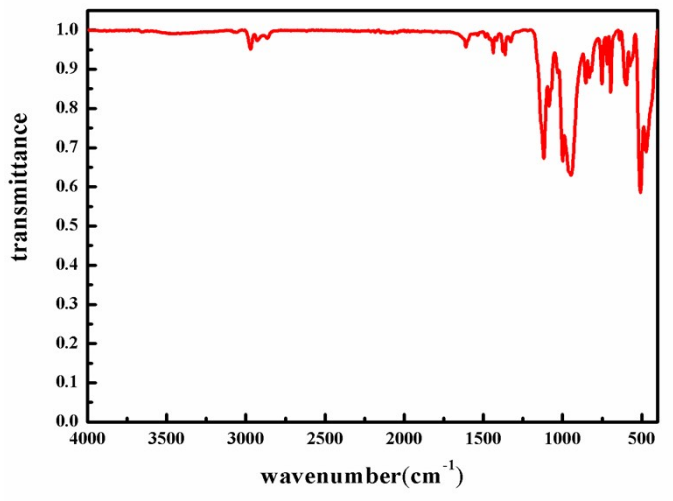

Figure S45. FTR-IR spectra for **PTC-139**.

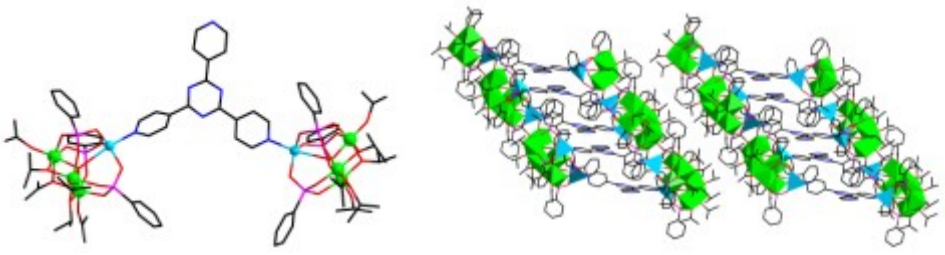

Figure S46. Crystal structure, packing-mode of **PTC-140**.

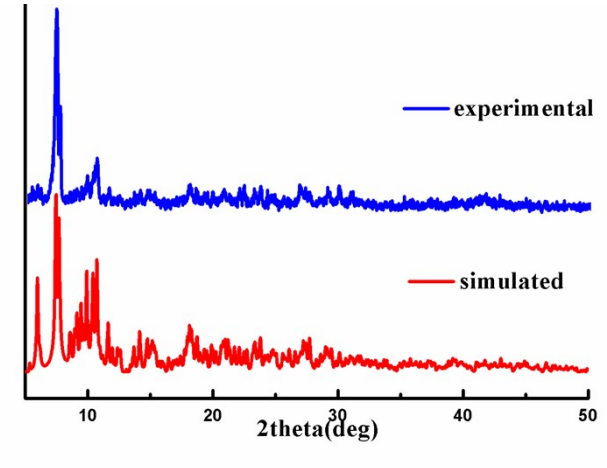

Figure S47. PXRD analysis of **PTC-140**.

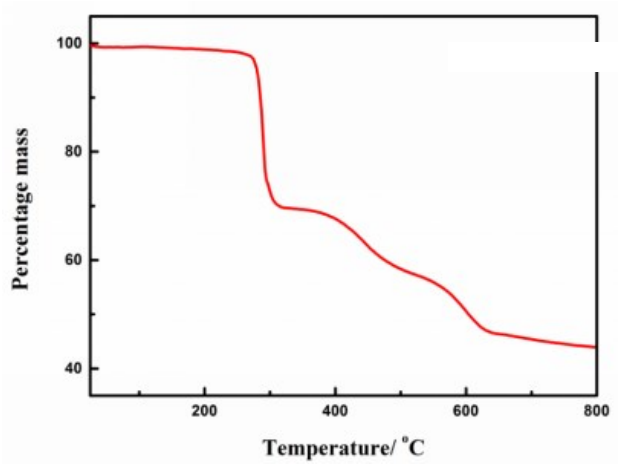

Figure S48. Thermal analysis of **PTC-140**

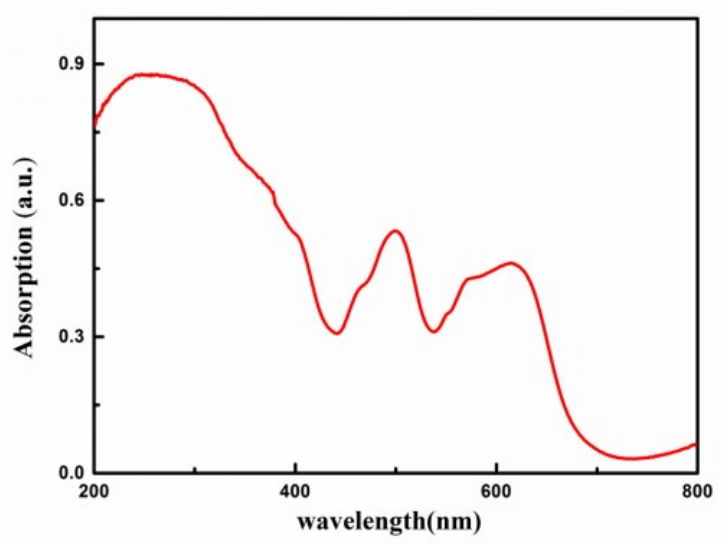

Figure S49. UV-vis spectra for **PTC-140**.

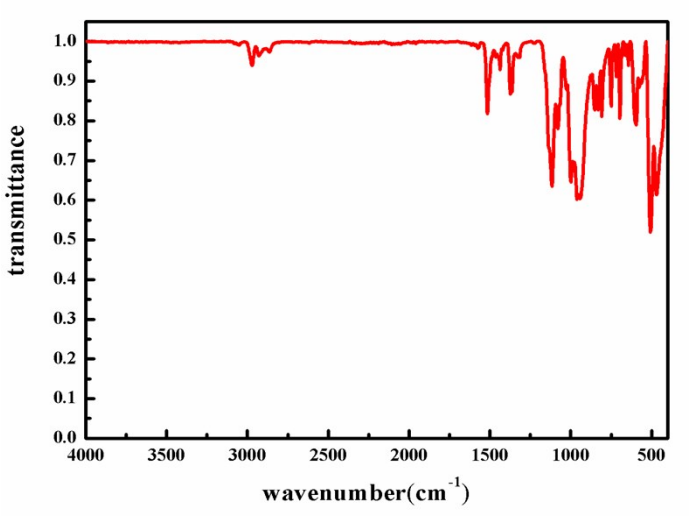

Figure S50. FTR-IR spectra for **PTC-140**.

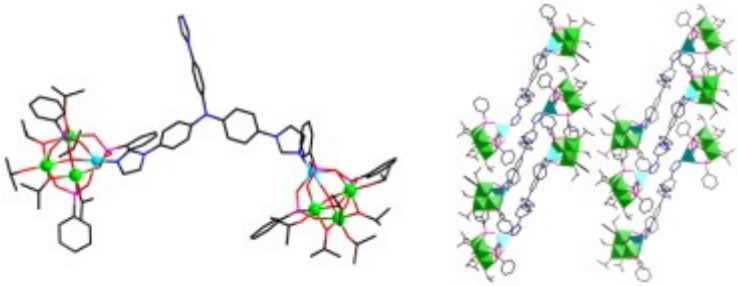

Figure S51. Crystal structure, packing-mode of **PTC-141**.

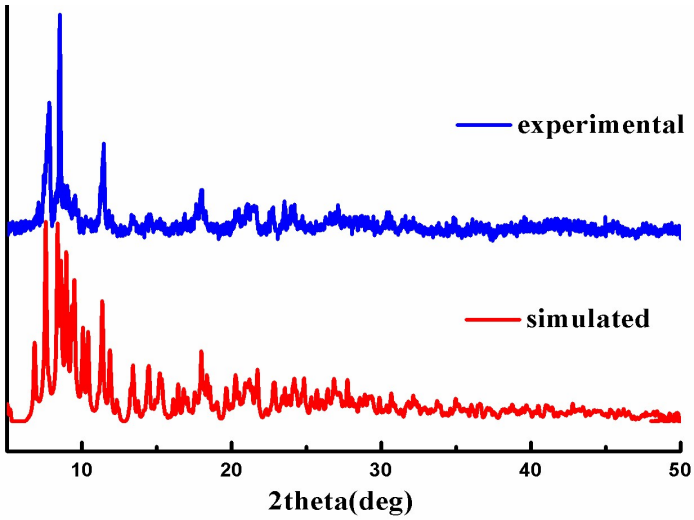

Figure S52. PXRD analysis of **PTC-141**.

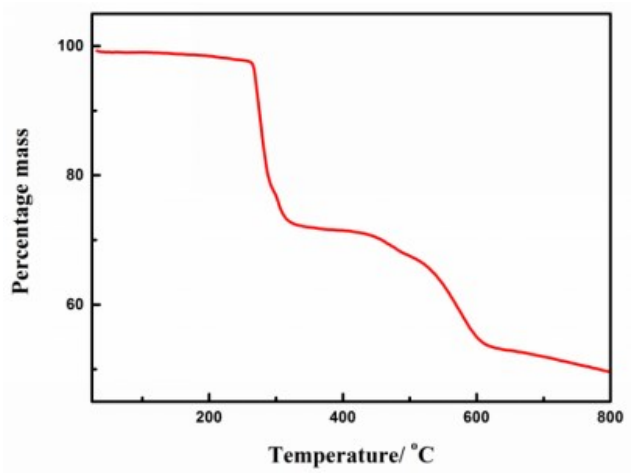

Figure S53. Thermal analysis of **PTC-141**

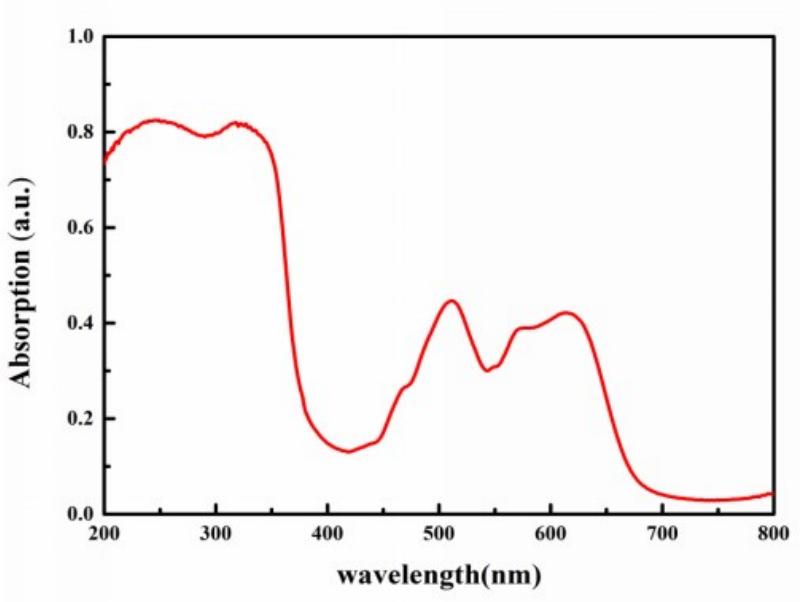

Figure S54. UV-vis spectra for **PTC-141**.

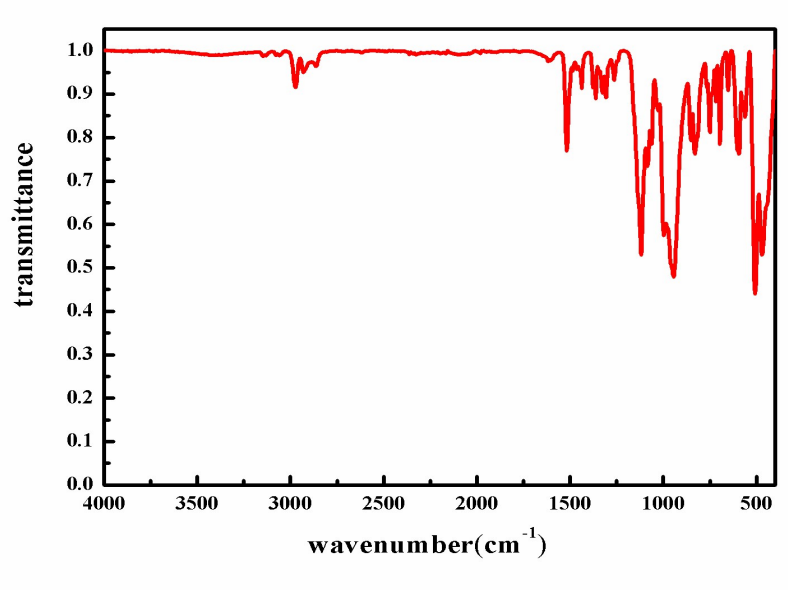

Figure S55. FTR-IR spectra for **PTC-141**.

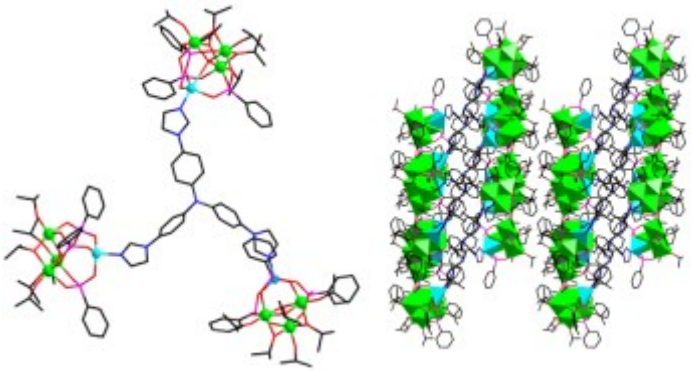

Figure S56. Crystal structure, packing-mode of **PTC-142**.

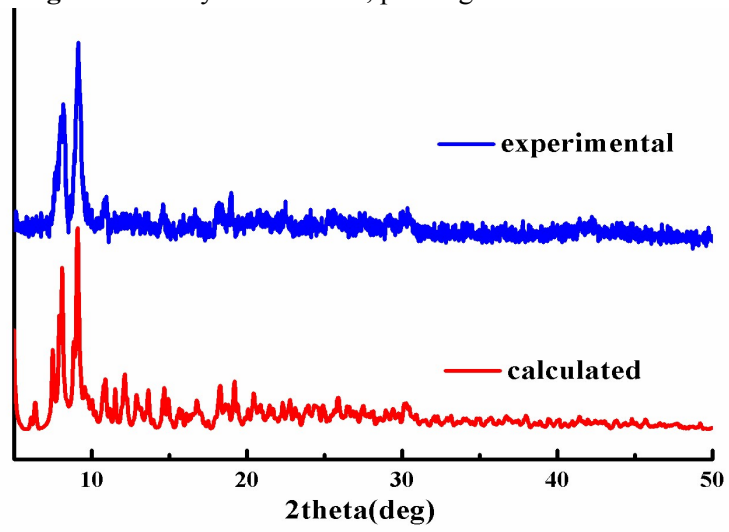

Figure S57. PXRD analysis of **PTC-142**.

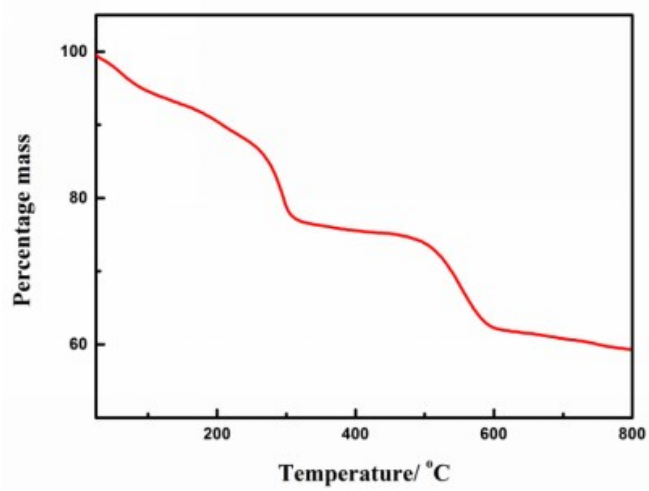

Figure S58. Thermal analysis of **PTC-142**

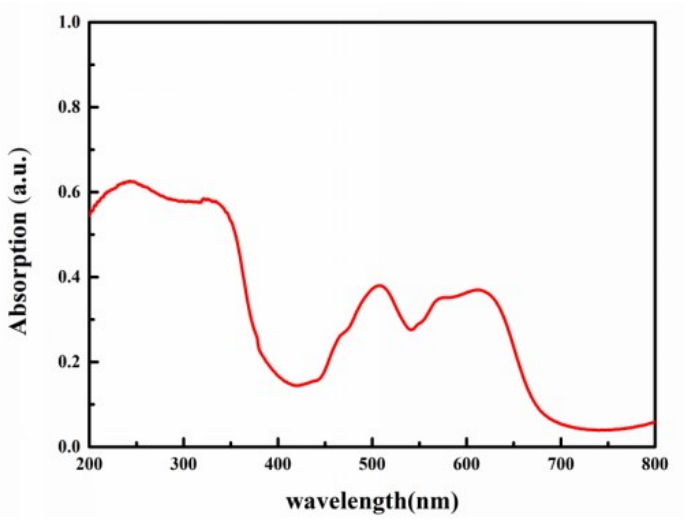

Figure S59. UV-vis spectra for **PTC-142**.

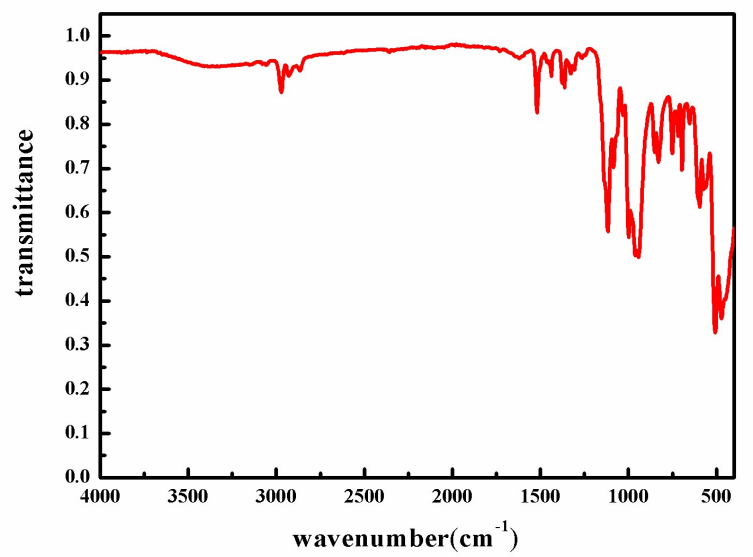

Figure S60. FTR-IR spectra for **PTC-142**.

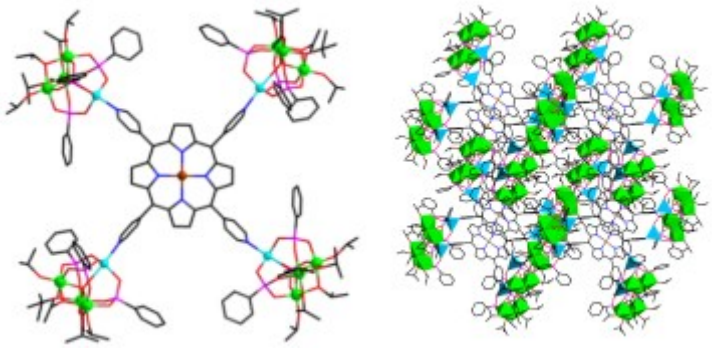

Figure S61. Crystal structure, packing-mode of **PTC-143**.

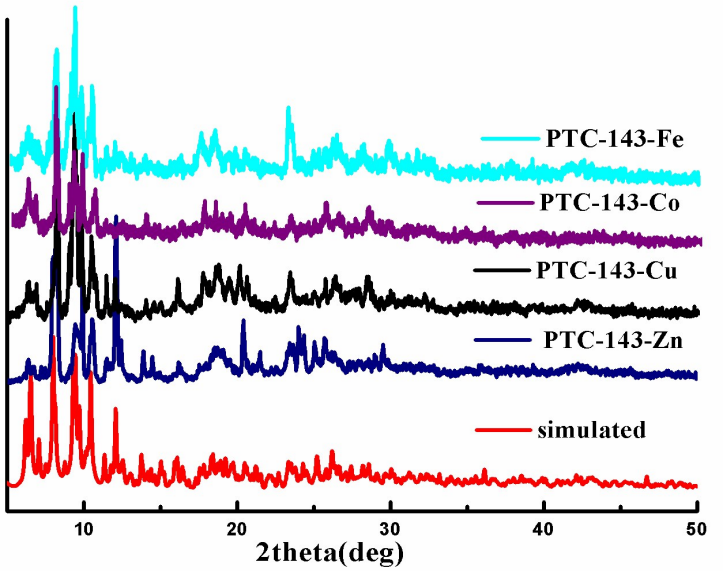

Figure S62.PXRD analysis of **PTC-143**.

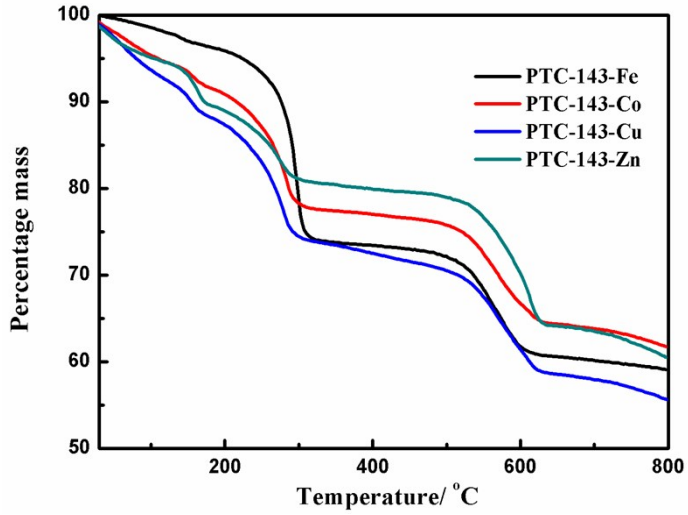

Figure S63. Thermal analysis of **PTC-143**

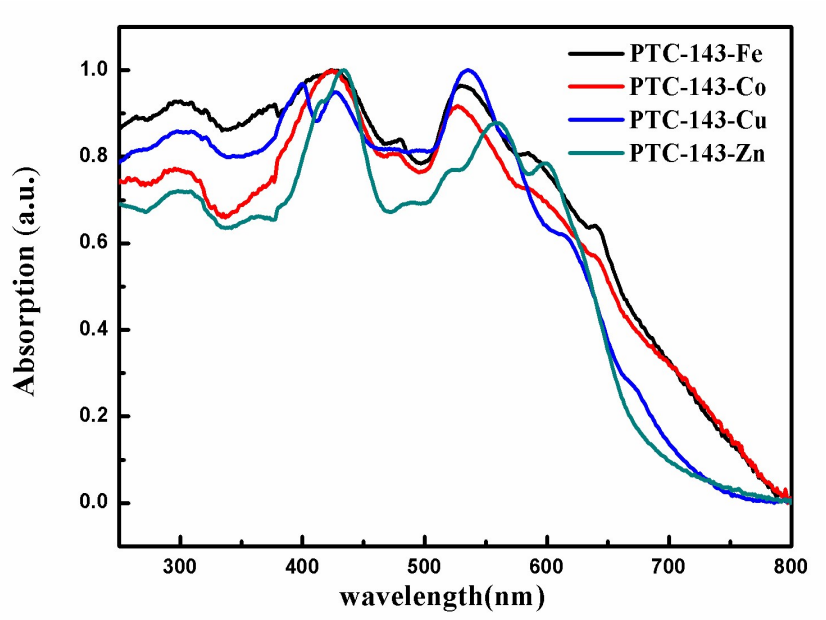

Figure S64 UV-vis spectra for **PTC-143**.

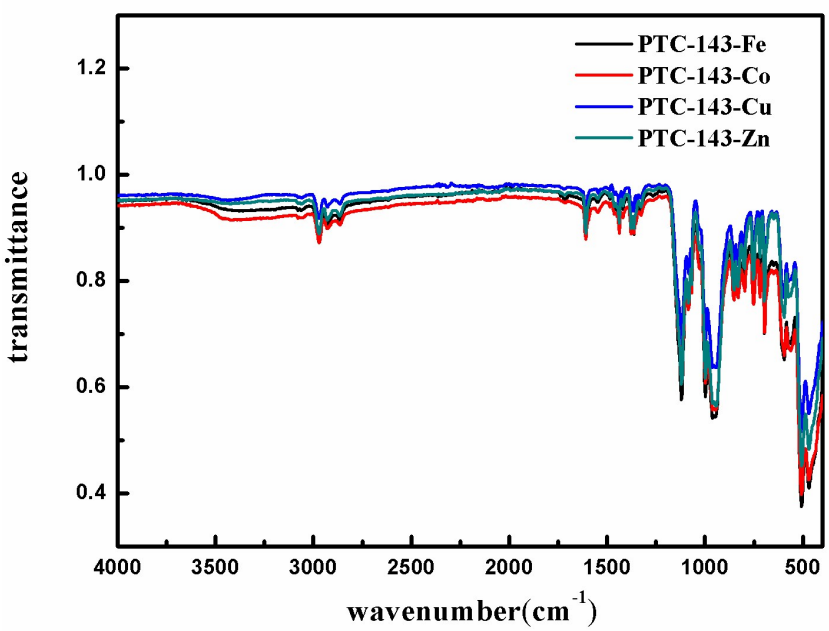

Figure S65.FTR-IR spectra for **PTC-143**.

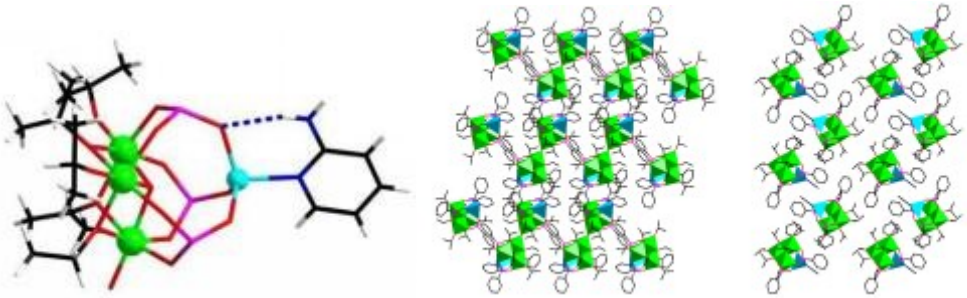

Figure S66. Crystal structure, packing-mode of **PTC-144**.

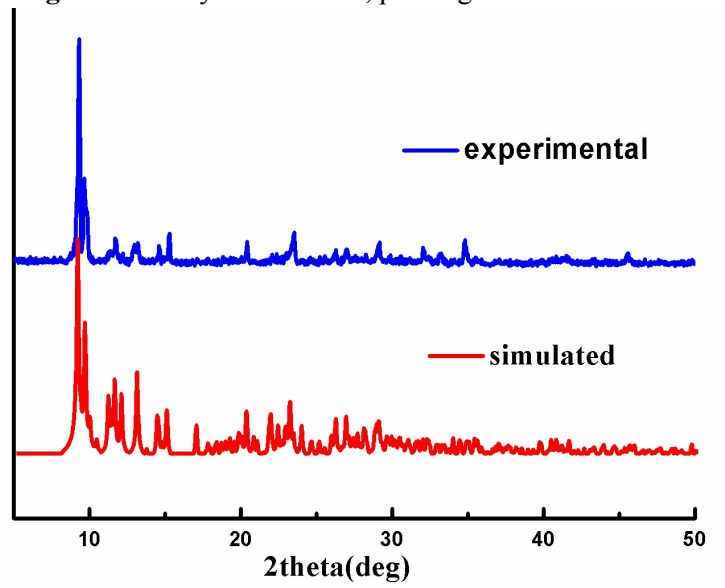

Figure S67. PXRD analysis of **PTC-144**.

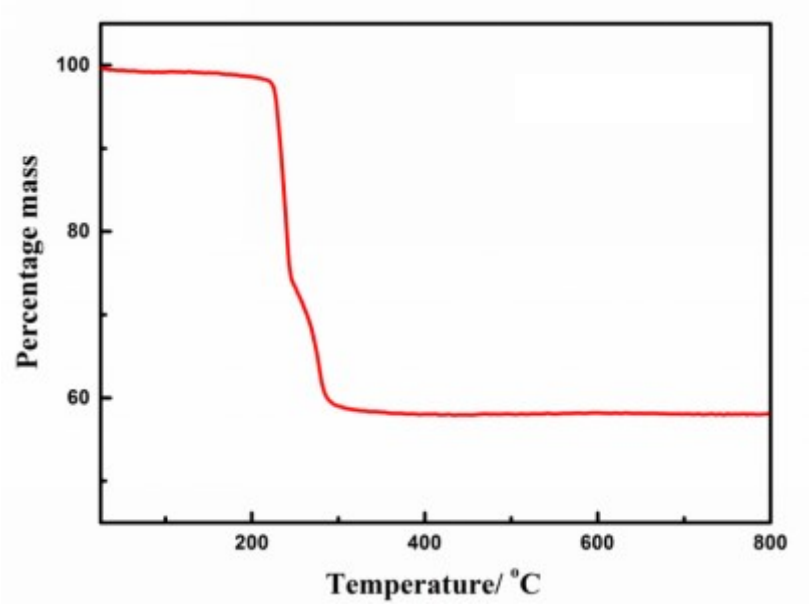

Figure S68. Thermal analysis of **PTC-144**

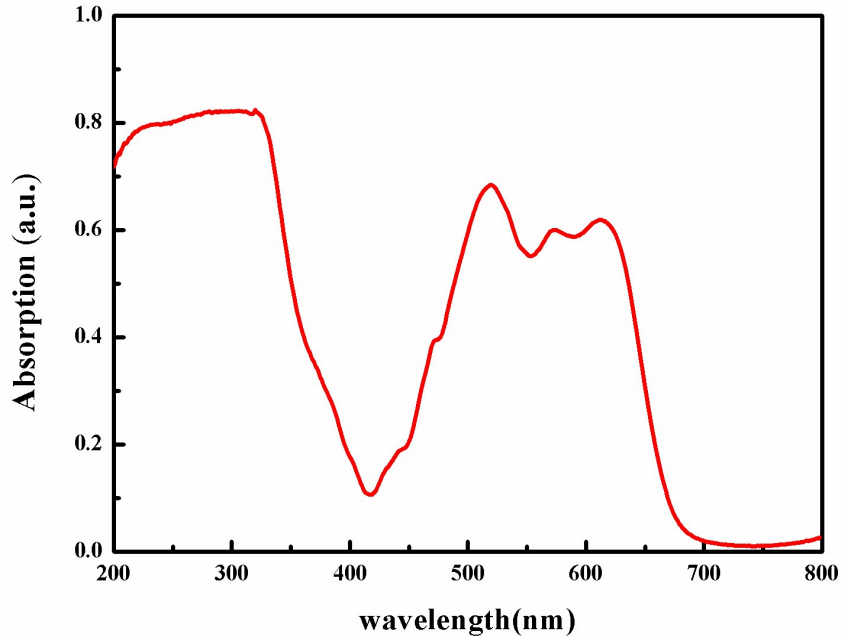

Figure S69. UV-vis spectra for **PTC-144**.

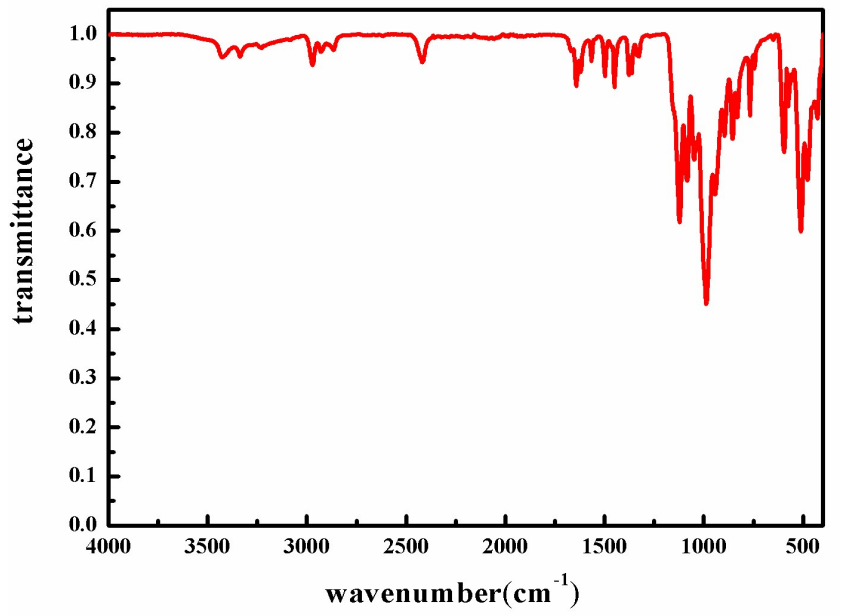

Figure S70. FTR-IR spectra for **PTC-144**.

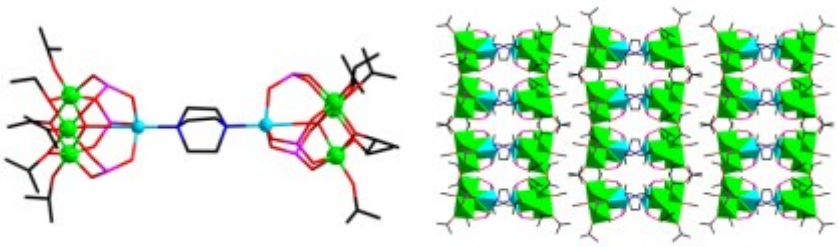

Figure S71. Crystal structure, packing-mode of **PTC-145**.

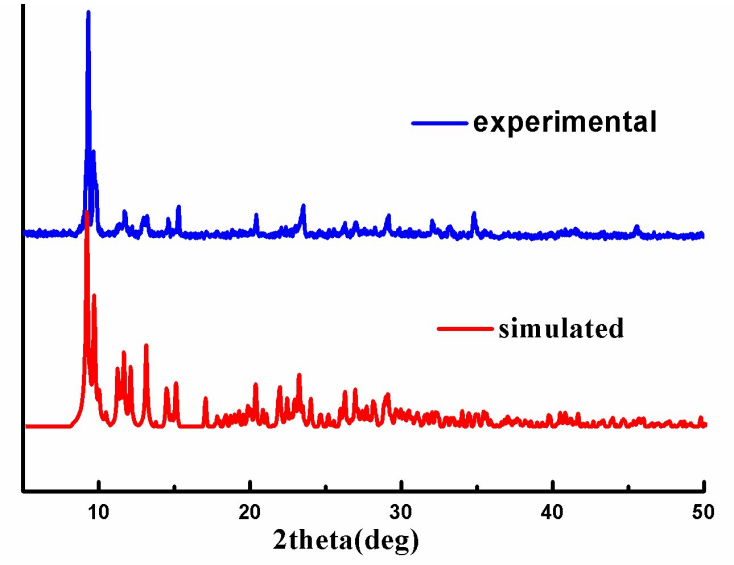

Figure S72.PXRD analysis of **PTC-145**.

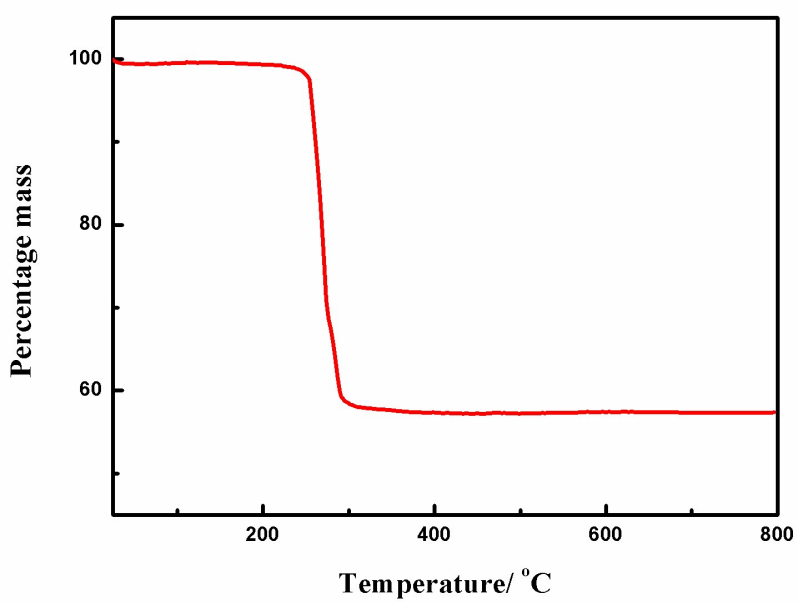

Figure S73. Thermal analysis of **PTC-145**

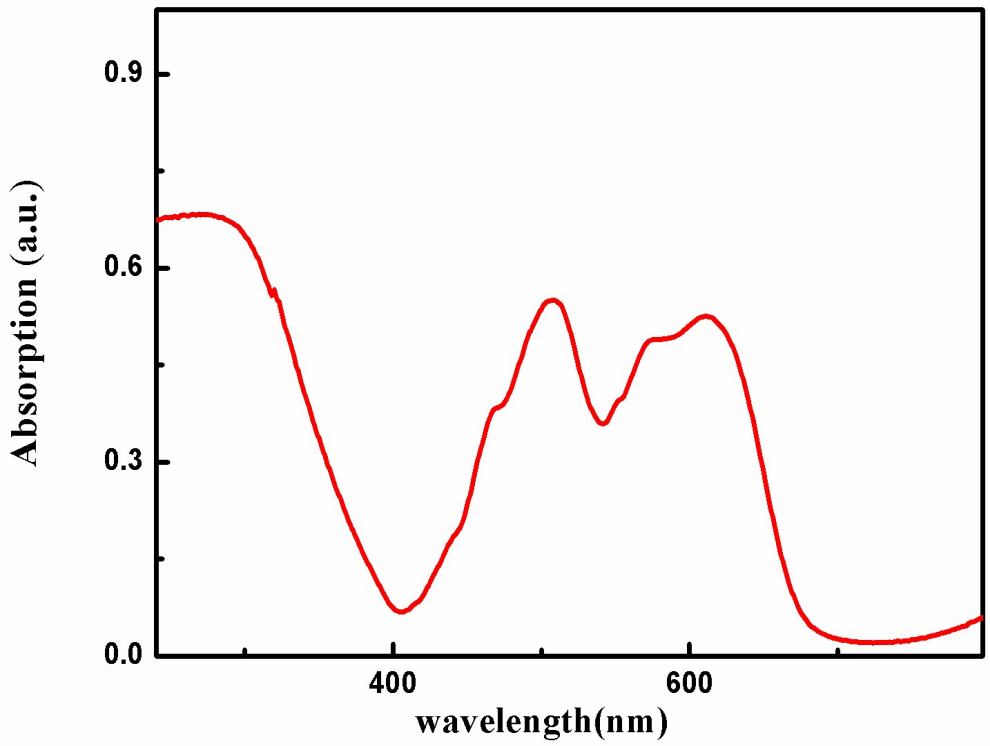

Figure S74. UV-vis spectra for **PTC-145**.

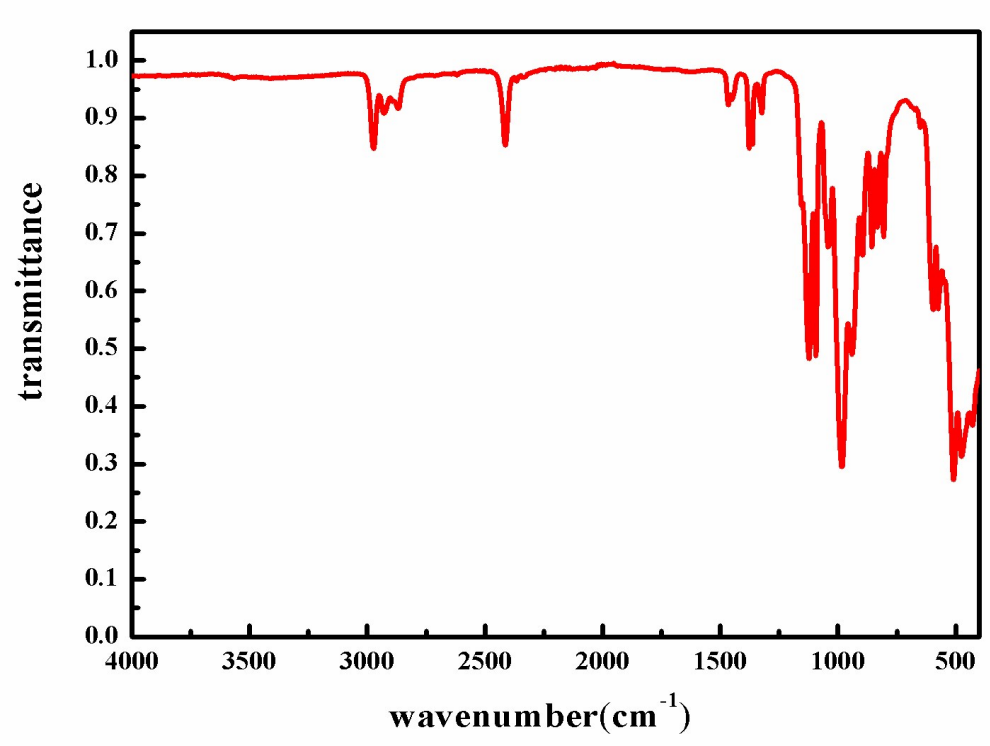

Figure S75.FTR-IR spectra for **PTC-145**.

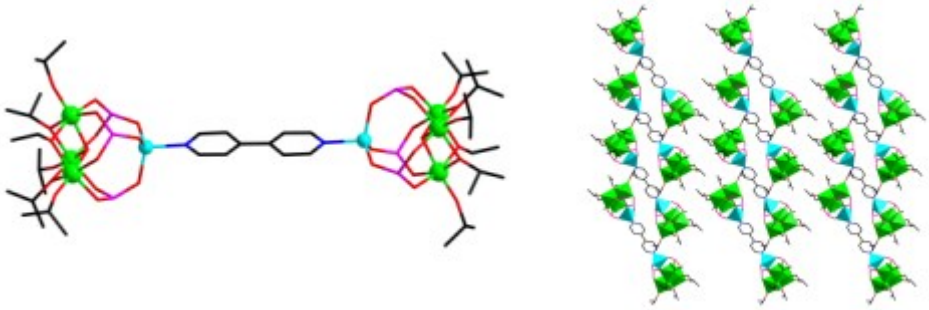

Figure S76. Crystal structure, packing-mode of **PTC-146**.

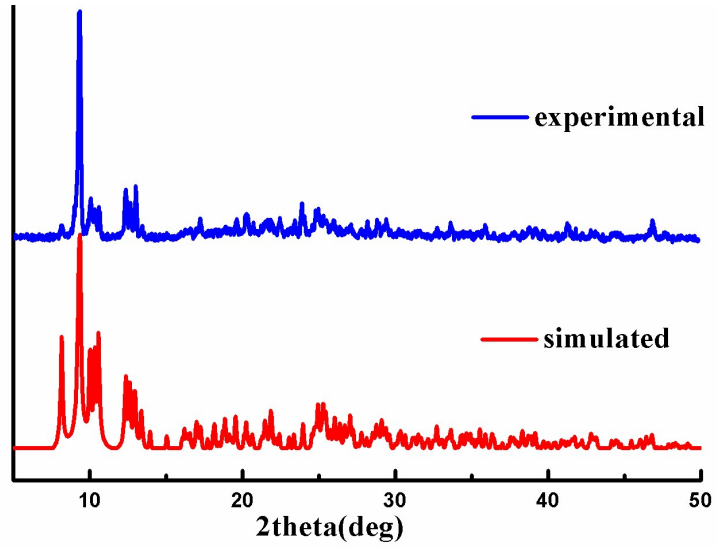

Figure S76. PXRD analysis of **PTC-146**

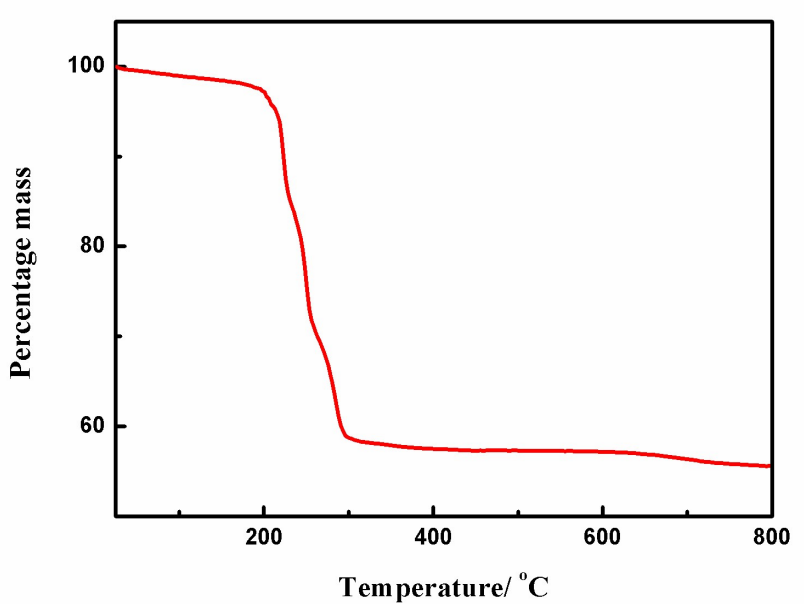

Figure S77. Thermal analysis of **PTC-146**

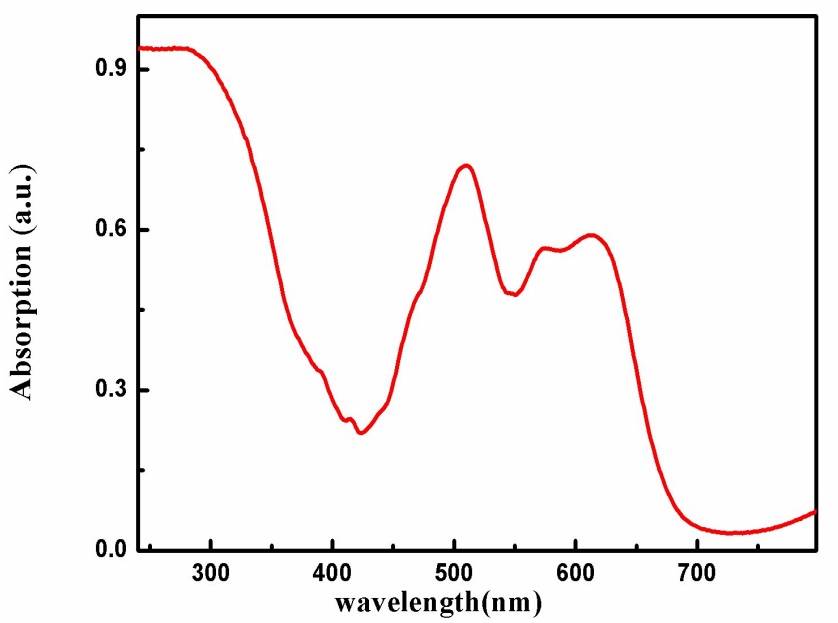

Figure S78. UV-vis spectra for **PTC-146**.

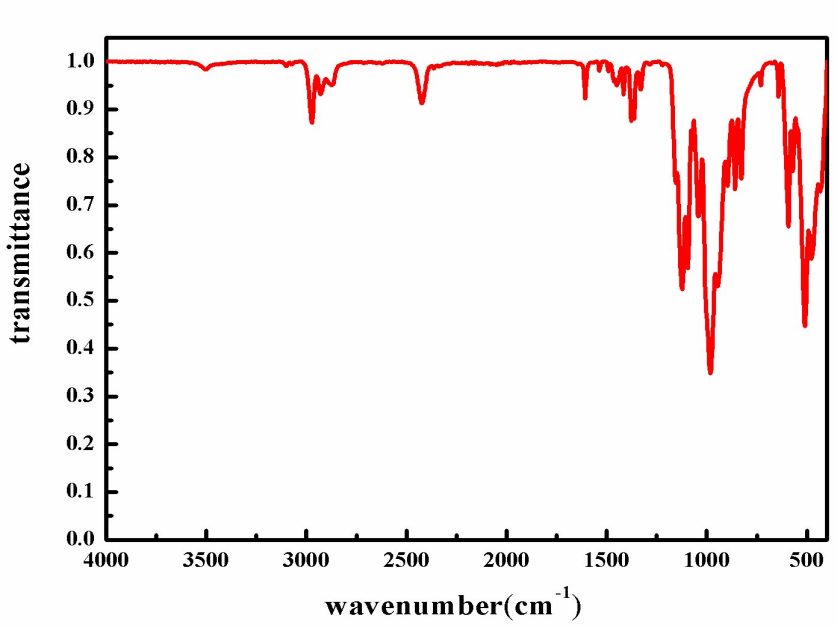

Figure S79. FTR-IR spectra for **PTC-146**.

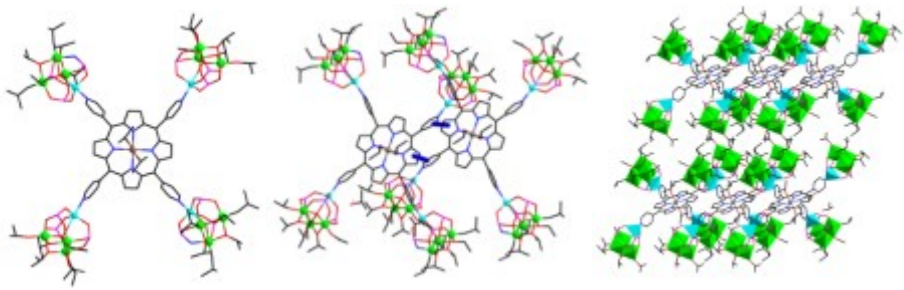

Figure S76. Crystal structure, packing-mode of **PTC-147**.

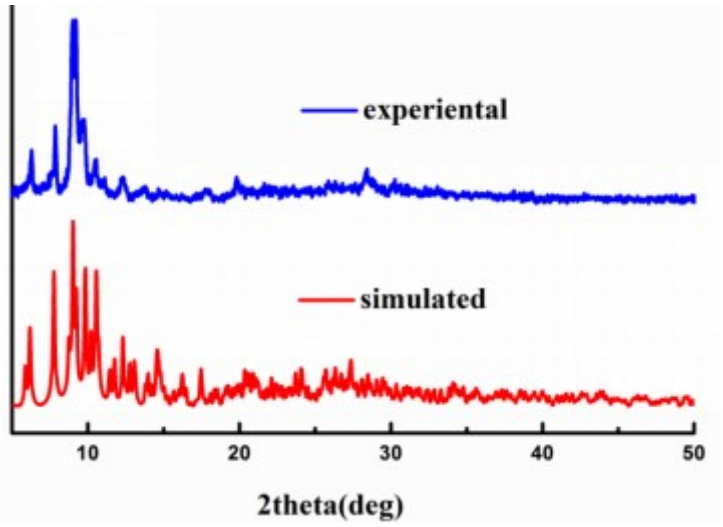

Figure S76. PXRD analysis of **PTC-147**

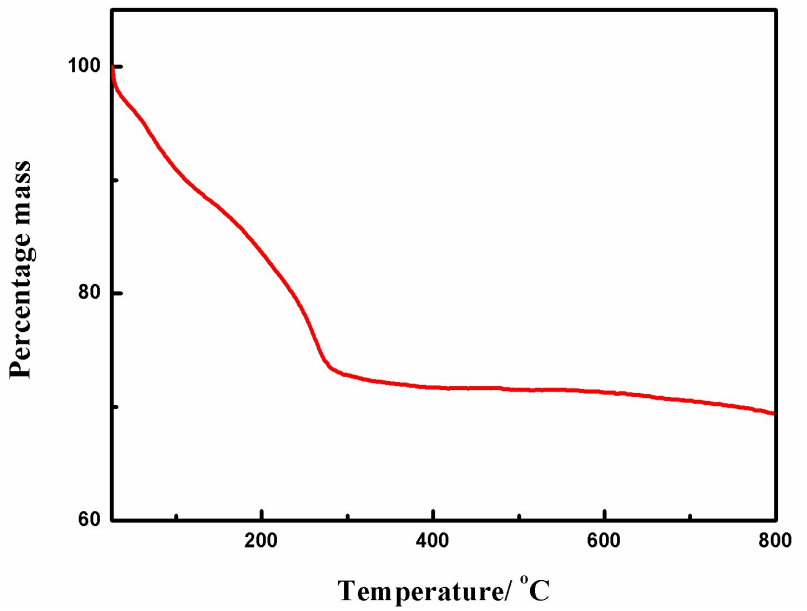

Figure S77. Thermal analysis of **PTC-147**

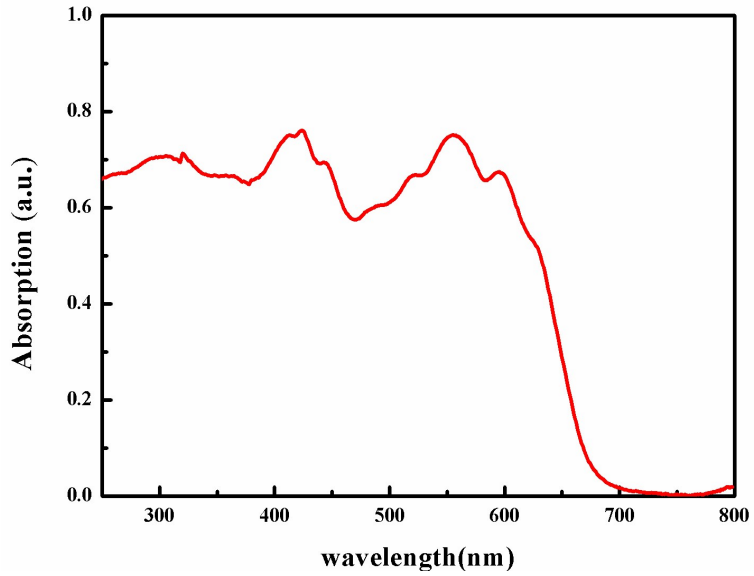

Figure S78. UV-vis spectra for **PTC-147**.

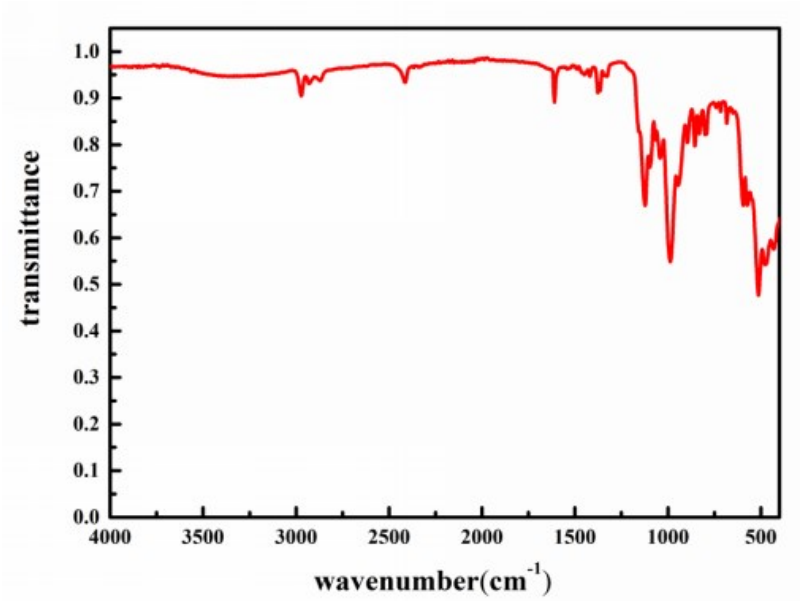

Figure S79. FTR-IR spectra for **PTC-147**.

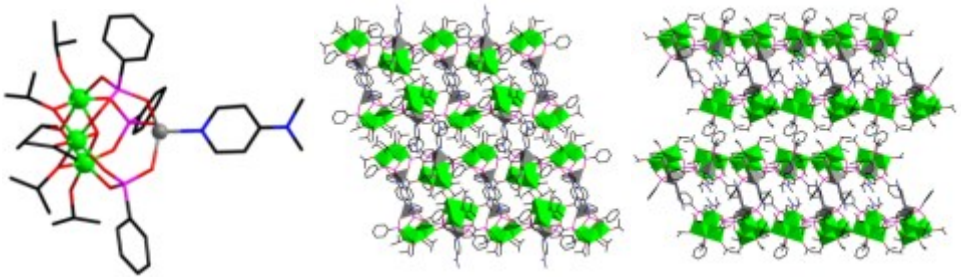

Figure S86. Crystal structure, packing-mode of **PTC-148**.

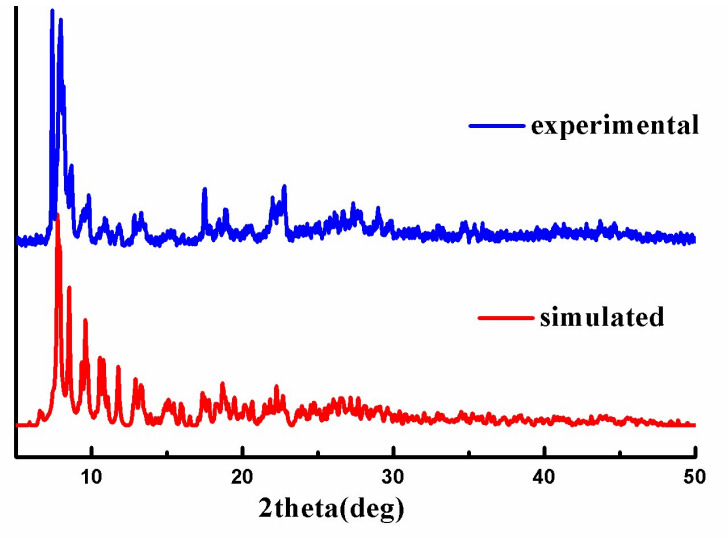

Figure S87. PXRD analysis of **PTC-148**.

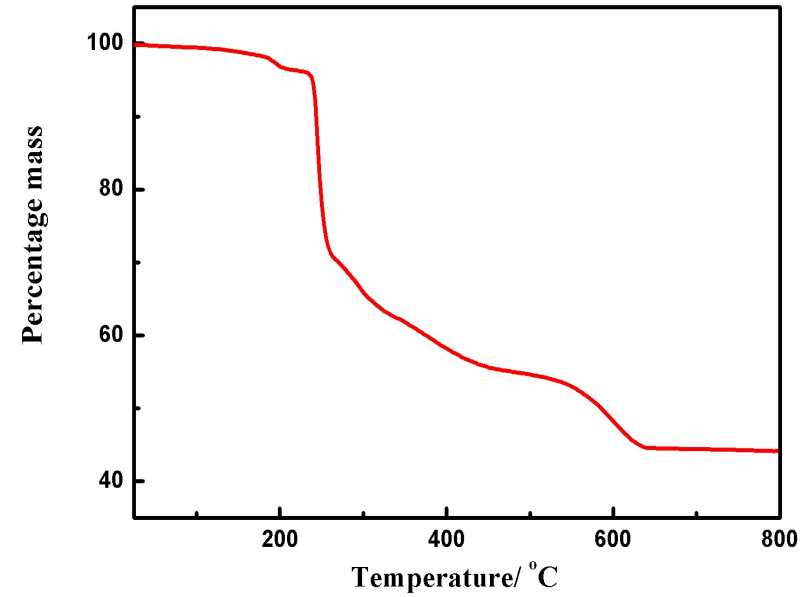

Figure S88. Thermal analysis of **PTC-148**

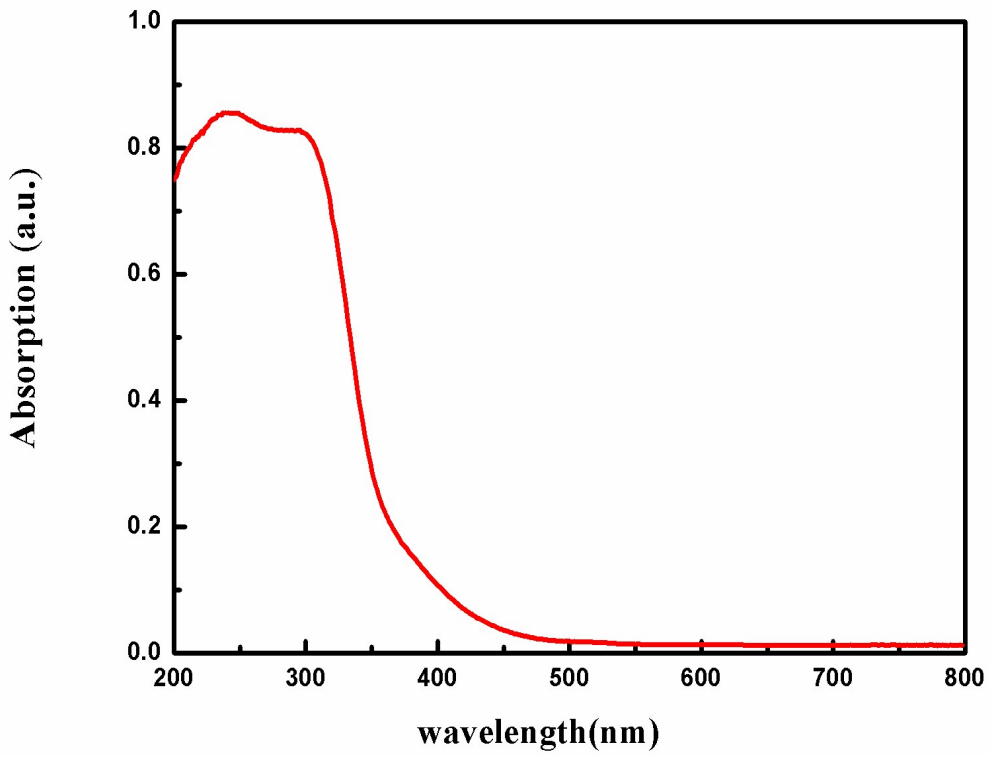

Figure S89. UV-vis spectra for **PTC-148**.

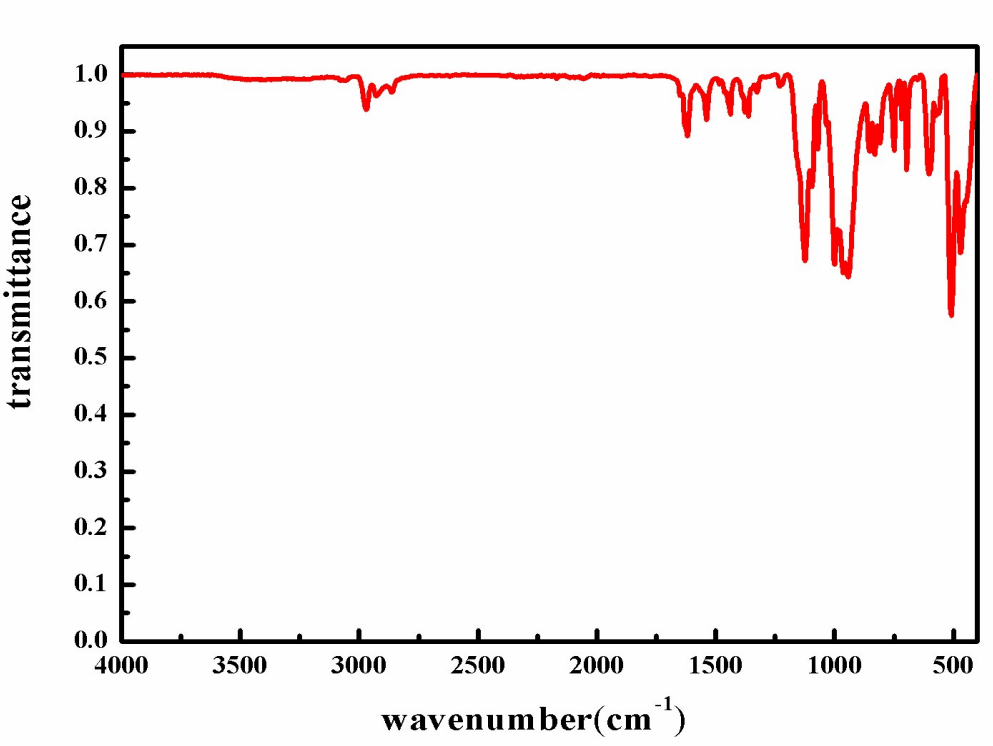

Figure S90. FTR-IR spectra for **PTC-148**.

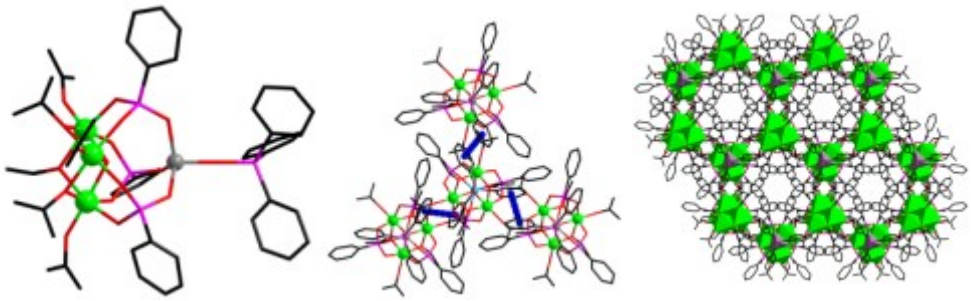

Figure S81. Crystal structure, packing-mode of **PTC-149**.

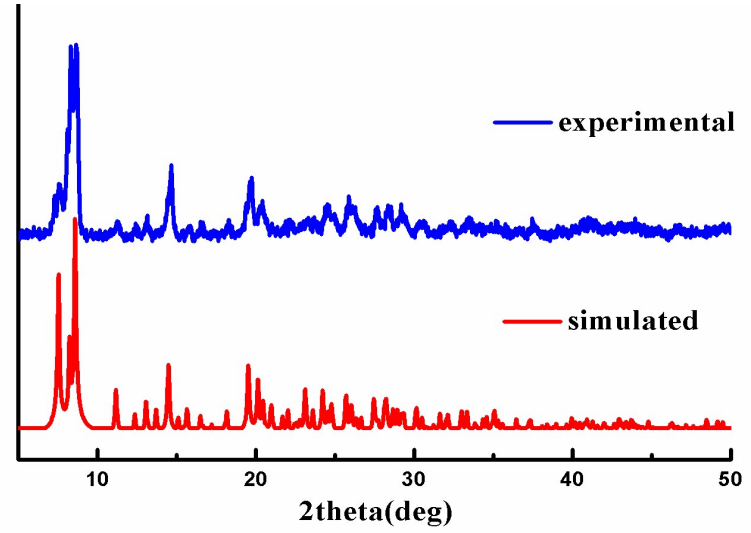

Figure S92. PXRD analysis of **PTC-149**.

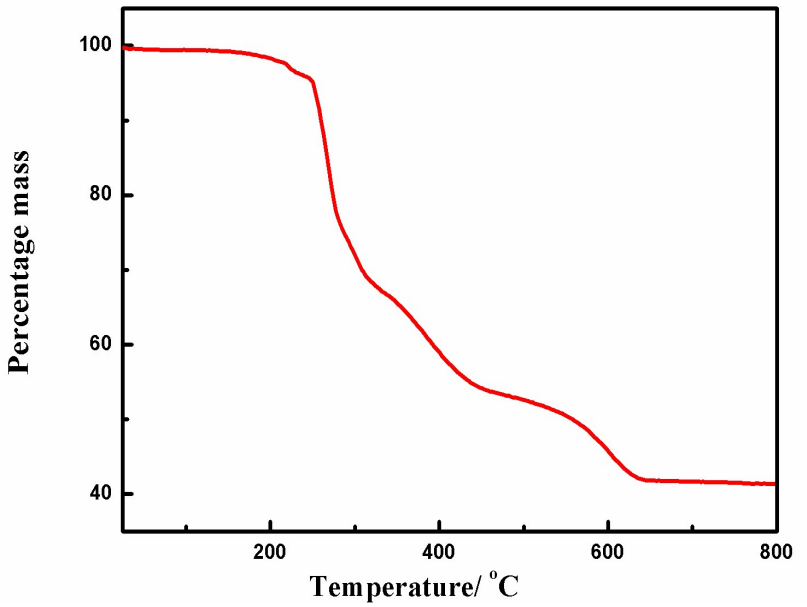

Figure S93. Thermal analysis of **PTC-149**

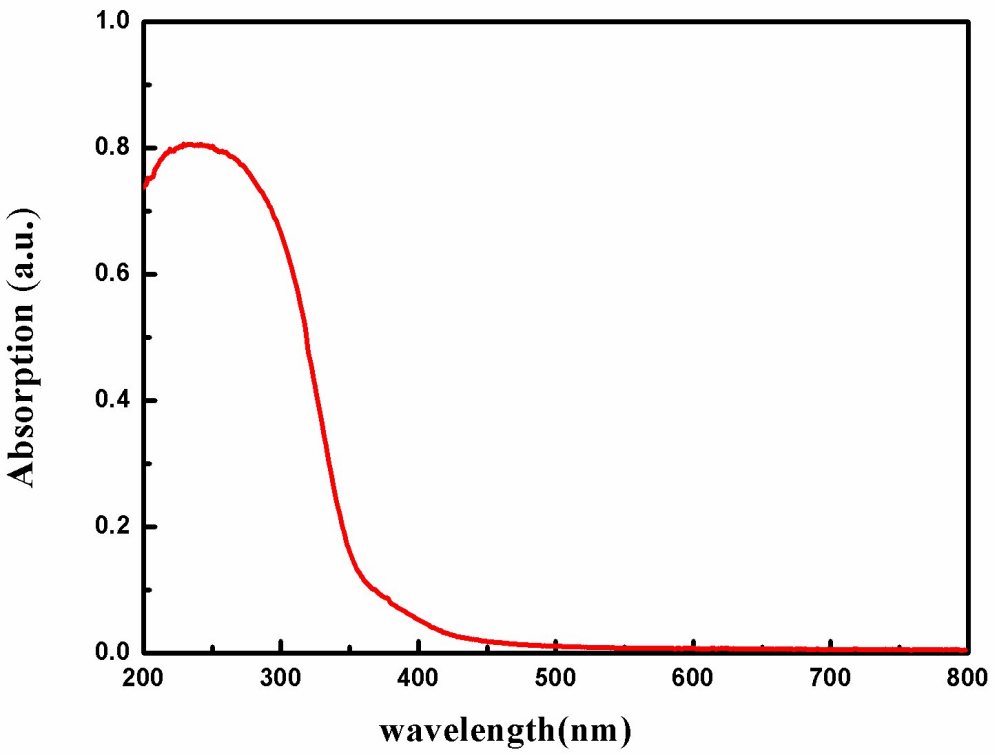

Figure S94. UV-vis spectra for **PTC-149**.

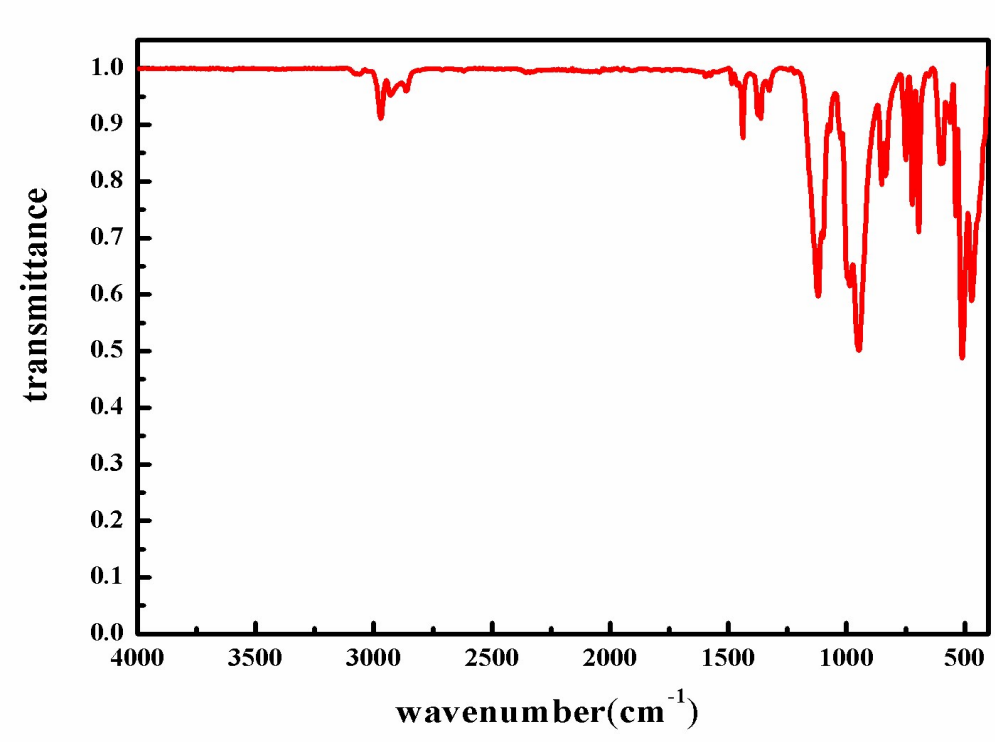

Figure S95. FTR-IR spectra for **PTC-149**.

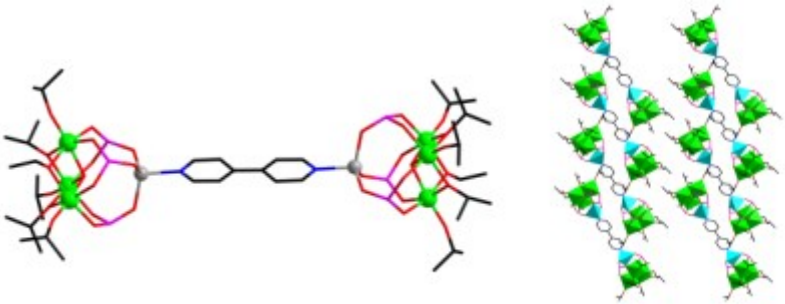

Figure S96. Crystal structure, packing-mode of **PTC-150**.

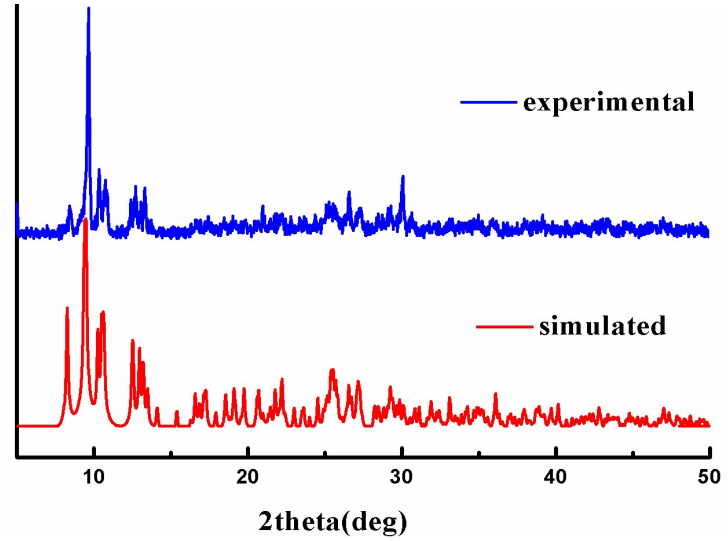

Figure S97. PXRD analysis of **PTC-150**.

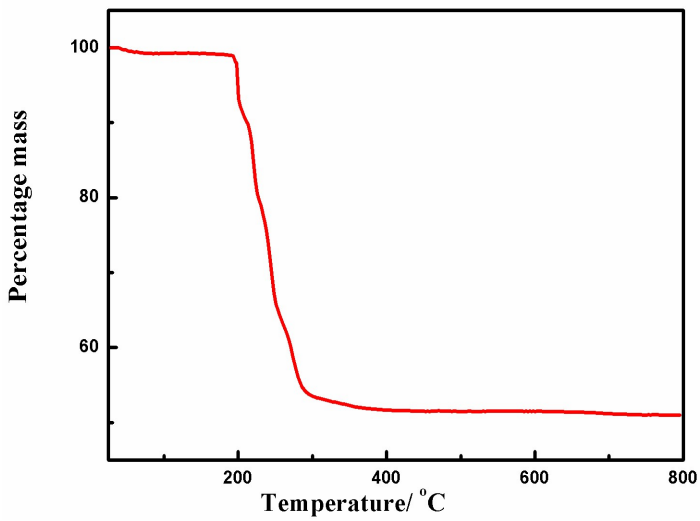

Figure S98. Thermal analysis of **PTC-150**

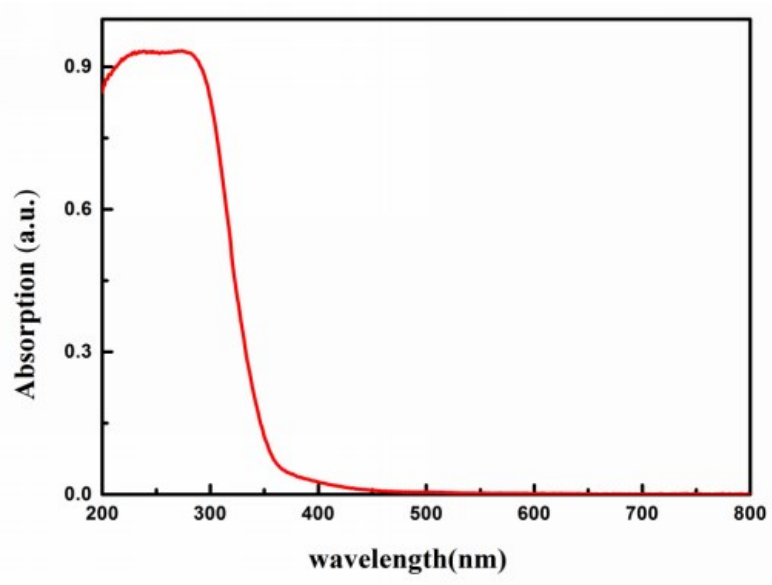

Figure S99. UV-vis spectra for **PTC-150**.

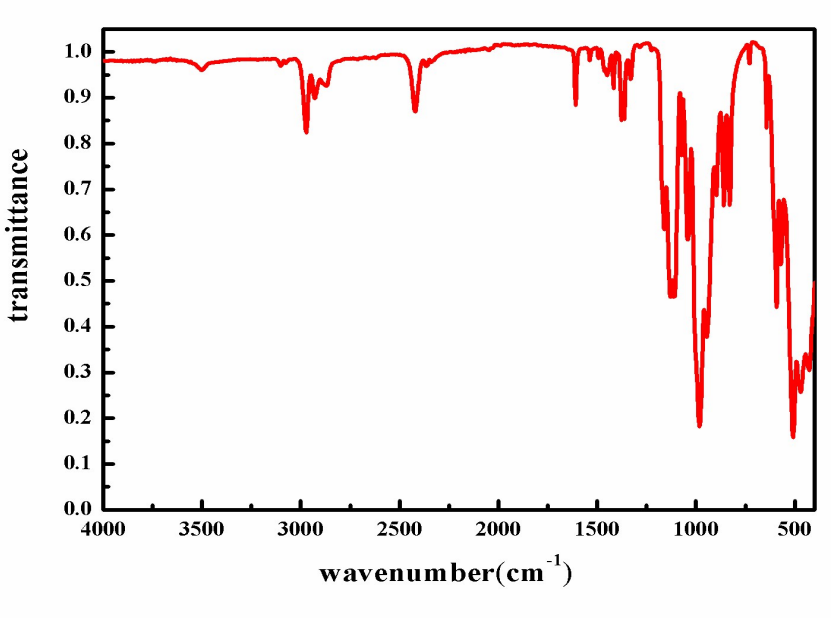

Figure S100. FTR-IR spectra for **PTC-150**.

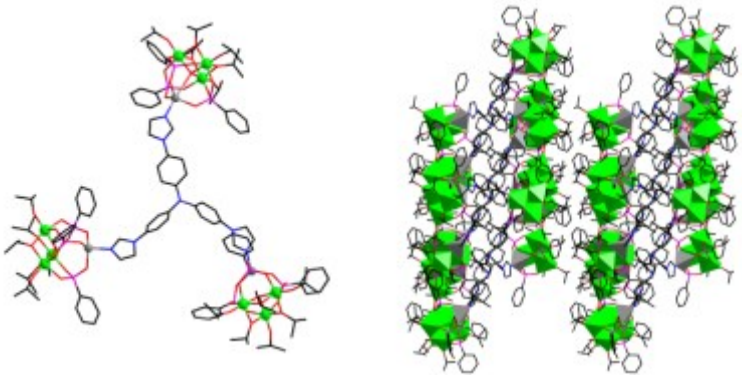

Figure S101. Crystal structure, packing-mode of **PTC-151**.

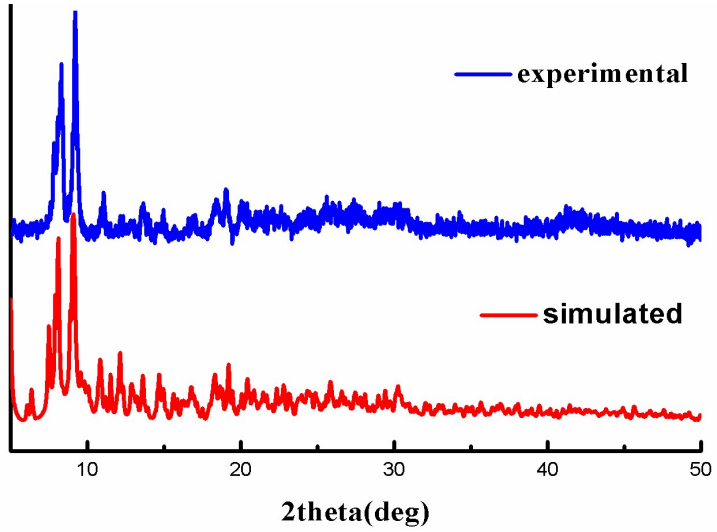

Figure S102. PXRD analysis of **PTC-151**.

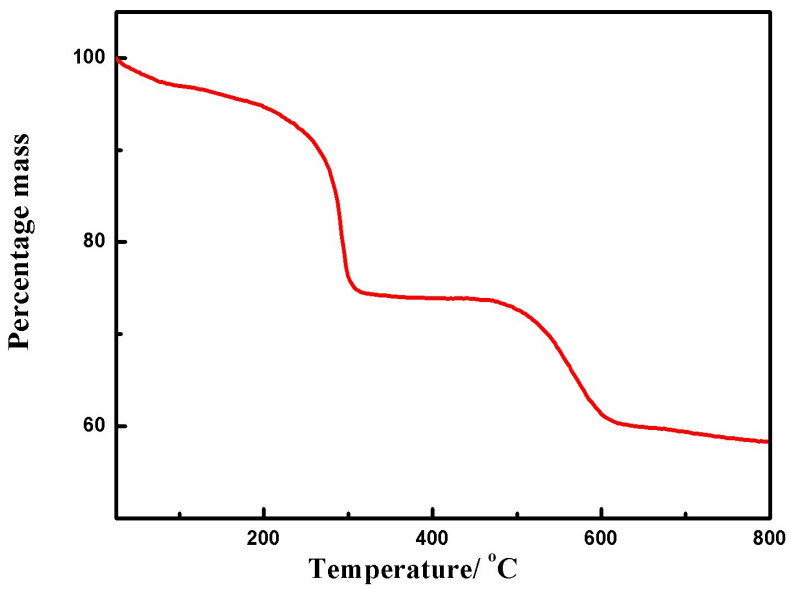

Figure S103. Thermal analysis of **PTC-151**

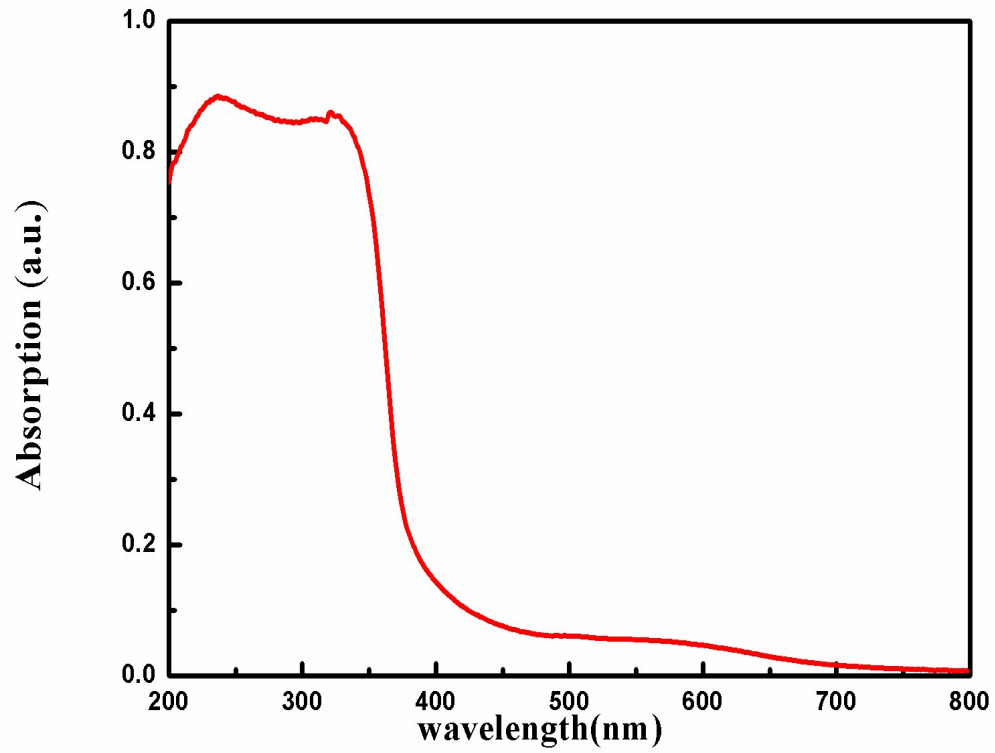

Figure S104. UV-vis spectra for **PTC-151**.

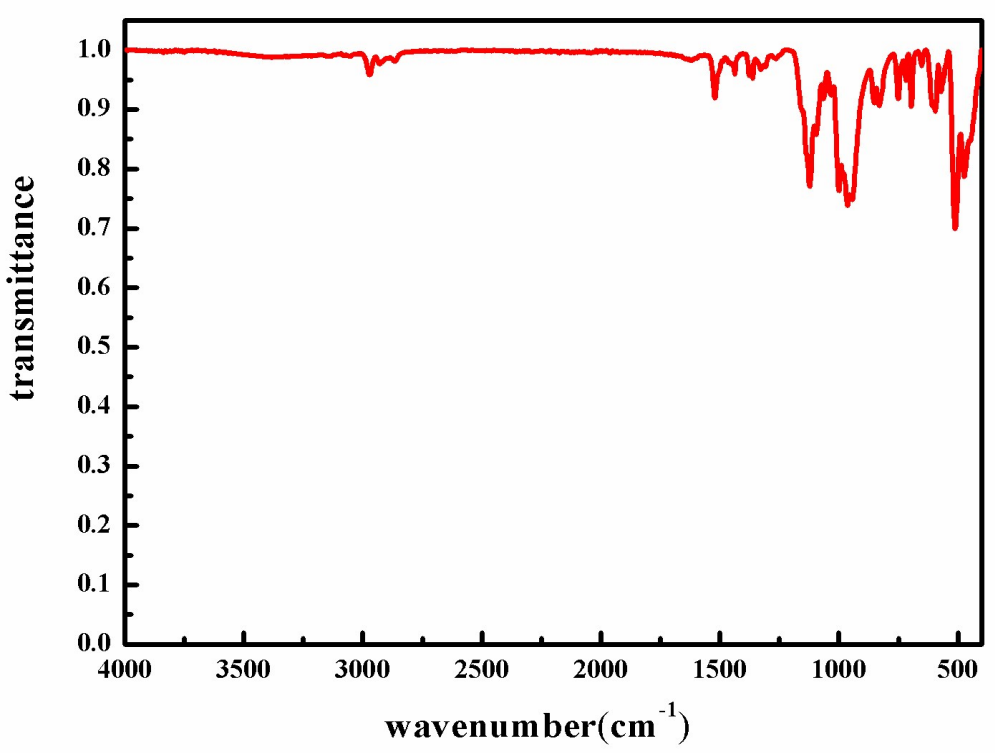

Figure S105. FTR-IR spectra for **PTC-151**.

Table S.1 Crystal data and structure refinement for PTC-131 -PTC-151.

Compound Reference	**PTC-131**	**PTC-132**	**PTC-133**
Crystal.determ. formula	$C_{41}H_{63}CoN_2O_{16}P_3Ti_3$	$C_{41}H_{63}CoN_2O_{16}P_3Ti_3$	$C_{42}H_{69}CoN_4O_{16}P_3Ti_3$
Mr	1135.47	1135.47	1181.56
crystal system	triclinic	monoclinic	trigonal
space group	*P-1*	*P21/c*	*P-3c1*
a [Å]	11.4128	15.7090	15.3726
b [Å]	14.5276	16.6419	15.3726
c [Å]	16.4809	19.9691	31.2089
α [o]	87.099	90.00	90.00
β [o]	76.719	92.228	90.00
γ [o]	76.096	90.00	120.00
V [$Å^3$]	2581.5	5216.5	6387.1
Z	2	4	4
T [K]	293	293	293
ρc[gcm^{-3}]	1.461	1.446	1.229
μ [mm^{-1}]	0.921	0.912	0.748
No. of Reflections Measured	16735	16571	38889
No. of Independent Reflections	9084	8426	3763
Goodness of Fit on F2	1.066	1.138	1.086
Final R1 Values (I > 2σ(I))	0.0700	0.0828	0.0965
Final wR(F2) Values (I > 2σ(I))	0.1066	0.1351	0.2695
CCDC No	2064328	2064329	2064330

Table S.1 (Continued) Crystal data and structure refinement for PTC-131 -PTC-151.

Compound Reference	**PTC-134**	**PTC-135**	**PTC-136**
Crystal.determ. formula	$C_{54}H_{72}CoO_{16}P_4Ti_3$	$C_{54}H_{72}CoO_{17}P_4Ti_3$	$C_{46}H_{65}CoN_2O_{16}P_3S_2Ti_3$
Mr	1303.63	1319.75	1266.70
crystal system	trigonal	trigonal	monoclinic
space group	*R-3*	*P-3c1*	*P 2$_1$/n*
a [Å]	16.7321	13.4886	10.7482
b [Å]	16.7321	13.4886	38.8651
c [Å]	38.173	42.690	13.8807
α [o]	90.00	90.00	90.00
β [o]	90.00	90.00	95.203
γ [o]	120.00	120.00	90.00
V [Å3]	9255.2	6726.5	5774.5
Z	4	4	4
T [K]	293	294.85	294.72
ρc[gcm-3]	1.403	1.303	1.457
μ [mm-1]	0.805	6.225	7.625
No. of Reflections Measured	6313	8244	21510
No. of Independent Reflections	3604	2913	10077
Goodness of Fit on F2	1.040	1.286	0.968
Final R1 Values (I > 2σ(I))	0.0384	0.1428	0.0534
Final wR(F2) Values (I > 2σ(I))	0.1001	0.3672	0.1404
CCDC No	2064331	2064332	2064333

Table S.1 (Continued) Crystal data and structure refinement for PTC-131 -PTC-151.

Compound Reference	**PTC-137**	**PTC-138**	**PTC-139**

Crystal.determ. formula	$C_{43}H_{67}CoN_2O_{16}P_3Ti_3$	$C_{78}H_{129}Co_2N_6O_{33}P_6Ti_6$	$C_{82}H_{122}Co_2N_2O_{32}P_6Ti_6$
Mr	1163.52	2269.94	2236.87
crystal system	triclinic	monoclinic	orthorhombic
space group	*P-1*	$P2_1/c$	*P -1*
a [Å]	20.6404	25.2586	21.201
b [Å]	20.9868	21.6811	21.613
c [Å]	28.6378	19.7154	49.326
α [o]	85.519	90.00	90.00
β [o]	70.770	106.915	90.00
γ [o]	80.672	90.00	90.00
V [Å3]	11554.1	10329.7	22603
Z	8	4	8
T [K]	291.91	100	293
ρc[gcm-3]	1.338	1.460	1.315
μ [mm-1]	0.825	7.731	0.840
No. of Reflections Measured	90677	36189	114504
No. of Independent Reflections	40576	16197	18272
Goodness of Fit on F2	0.996	1.057	1.126
Final R1 Values ($I > 2\sigma(I)$)	0.0743	0.0692	0.0929
Final wR(F2) Values ($I > 2\sigma(I)$)	0.1766	0.1763	0.2629
CCDC No	2064334	2064335	2064336

Table S.1 (Continued) Crystal data and structure refinement for PTC-131 -PTC-151.

Compound Reference	**PTC-140**	**PTC-141**	**PTC-142**
Crystal.determ. formula	$C_{90}H_{126}Co_2N_6O_{32}P_6Ti_6$	$C_{99}H_{135}Co_2N_7O_{32}P_6Ti_6$	$C_{135}H_{192}Co_3N_7O_{48}P_9Ti_9$

Mr	2395.04	2526.70	3567.56
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\ -1$	$P\ 2_1/c$
a [Å]	25.1666	13.2866	21.8183
b [Å]	22.9351	18.7055	38.8985
c [Å]	20.5381	25.4087	19.9793
α [o]	90.00	69.908	90.00
β [o]	109.582	76.318	90.730
γ [o]	90.00	83.913	90.00
V [Å3]	11168.9	5760.2	7374.1
Z	4	2	4
T [K]	295	100	100
ρc[gcm-3]	1.424	1.457	1.398
μ [mm-1]	0.856	6.993	7.084
No. of Reflections Measured	54922	35105	38892
No. of Independent Reflections	19630	18362	23246
Goodness of Fit on F2	1.044	1.080	0.973
Final R1 Values (I > 2σ(I))	0.0619	0.0852	0.0708
Final wR(F2) Values (I > 2σ(I))	0.1284	0.2239	0.1592
CCDC No	2064337	2064338	2064339

Table S.1 (Continued) Crystal data and structure refinement for PTC-131 -PTC-151.

Compound Reference	**PTC-143-Fe**	**PTC-143-Co**	**PTC-143-Cu**	**PTC-143-Zn**
Crystal.determ. formula	$C_{184}H_{252}Co_4FeN_8O_{64}P_{12}Ti_{12}$	$C_{184}H_{252}Co_5N_8O_{64}P_{12}Ti_{12}$	$C_{184}H_{252}Co_4CuN_8O_{64}P_{12}Ti_{12}$	$C_{184}H_{252}Co_4N_8O_{64}P_{12}Ti_{12}Zn$
Mr	4837.93	4841.01	4845.62	4849.47

crystal system	triclinic	triclinic	triclinic	triclinic
space group	*P-1*	*P-1*	*P-1*	*P-1*
a [Å]	15.2282	15.2098	15.1743	15.4495
b [Å]	20.0509	20.0403	20.0009	20.3294
c [Å]	20.4507	20.4559	20.3517	20.6180
α [o]	91.0400	91.0310	90.700	90.879
β [o]	96.5020	96.493	96.872	97.202
γ [o]	107.4070	107.496	107.437	107.740
V [Å3]	5911.18	5900.5	5843.0	6109.1
Z	1	1	1	1
T [K]	100.0	100.2	293	293
ρc[gcm-3]	1.359	1.362	1.377	1.318
μ [mm-1]	4.782	4.825	0.907	0.878
No. of Reflections Measured	95583	90347	47430	87256
No. of Independent Reflections	26630	26474	20069	42949
Goodness of Fit on F2	1.033	1.030	1.001	1.126
Final R1 Values (I > 2σ(I))	0.0718	0.0861	0.0967	0.1037
Final wR(F2) Values (I > 2σ(I))	0.1890	0.2118	0.2381	0.3122
CCDC No	2064340	2064341	2064342	2064343

Table S.1 (Continued) Crystal data and structure refinement for PTC-131 -PTC-151.

Compound Reference	**PTC-144**	**PTC-145**	**PTC-146**
Crystal.determ. formula	$C_{22}H_{46}CoN_2O_{16}P_3Ti_3$	$C_{40}H_{92}Co_2N_2O_{32}P_6Ti_6$	$C_{46}H_{92}Co_2N_2O_{32}P6Ti_6$
Mr	890.15	1704.23	1776.29
crystal system	monoclinic	monoclinic	monoclinic

space group	*P 2$_1$/c*	*C2/c*	*P 2/c*
a [Å]	9.8788	35.545	19.066
b [Å]	39.052	13.3157	10.826
c [Å]	10.4582	15.7163	19.278
α [o]	90.00	90.00	90.00
β [o]	104.359	95.365	93.896
γ [o]	90.00	90.00	90.00
V [Å3]	7304	7406.1	3970.1
Z	4	4	2
T [K]	292.7	291.80	293
ρc[gcm-3]	1.513	1.528	1.486
μ [mm-1]	1.193	1.255	1.174
No. of Reflections Measured	16596	16732	30277
No. of Independent Reflections	6866	6735	8972
Goodness of Fit on F2	1.117	1.026	1.076
Final R1 Values (I > 2σ(I))	0.1075	0.0592	0.0759
Final wR(F2) Values (I > 2σ(I))	0.2267	0.1431	0.2213
CCDC No	2064344	2064345	2064346

Table S.1 (Continued) Crystal data and structure refinement for PTC-131 -PTC-151.

Compound Reference	**PTC-147**	**PTC-148**	**PTC-149**
Crystal.determ. formula	$C_{128}H_{240}Co_4N_{10}O_{62}P_{12}Ti_{12}Zn$	$C_{43}H_{67}N_2O_{16}P_3Ti_3Zn$	$C_{54}H_{72}O_{17}P_4Ti_3Zn$
Mr	4158.82	1169.96	1326.06
crystal system	triclinic	triclinic	trigonal
space group	*P-1*	*P-1*	*P-3c1*

a [Å]	10.6262	14.5520	13.537
b [Å]	19.5486	20.1787	13.537
c [Å]	23.3267	20.9546	42.946
α [o]	84.685	96.619	90.00
β [o]	77.637	91.962	90.00
γ [o]	78.455	109.175	120.00
V [Å3]	4631.2	5755.9	7225.93
Z	1	4	4
T [K]	100.00	290.76	290.69
ρc[gcm-3]	1.419	1.350	1.292
μ [mm-1]	8.669	0.957	0.839
No. of Reflections Measured	31674	44889	13833
No. of Independent Reflections	16715	20141	4008
Goodness of Fit on F2	1.028	1.097	1.046
Final R1 Values (I > 2σ(I))	0.0833	0.0659	0.1375
Final wR(F2) Values (I > 2σ(I))	0.2156	0.1744	0.2667
CCDC No	2064347	2064348	2064349

Table S.1 (Continued) Crystal data and structure refinement for PTC-131 -PTC-151

Compound Reference	**PTC-150**	**PTC-150A**	**PTC-151**
Crystal.determ. formula	$C_{44}H_{88}N_2O_{32}P_6Ti_6Zn_2$	$C_{44}H_{88}N_2O_{32}P_6Ti_6Zn_2$	$C_{135}H_{192}N_7O_{48}P_9Ti_9Zn_3$
Mr	1761.12	1761.12	3586.88
crystal system	monoclinic	monoclinic	monoclinic
space group	*P 2/c*	*P 2/c*	*P 2_1/C*
a [Å]	18.9228	18.9713	21.8289

b [Å]	10.7876	10.7940	39.0049
c [Å]	19.2132	19.2344	19.9138
α [o]	90.00	90.00	90.00
β [o]	93.178	93.380	90.890
γ [o]	90.00	90.00	90.00
V [Å3]	3916.0	3931.9	16953.2
Z	2	2	4
T [K]	295.9	296.6	100
ρc[gcm-3]	1.494	1.482	1.405
μ [mm-1]	1.378	1.372	5.308
No. of Reflections Measured	17950	17013	118511
No. of Independent Reflections	8253	8337	34202
Goodness of Fit on F2	1.023	0.981	1.017
Final R1 Values (I > 2σ(I))	0.0698	0.0761	0.0721
Final wR(F2) Values (I > 2σ(I))	0.2206	0.2281	0.1905
CCDC No	2064350	/	2064351

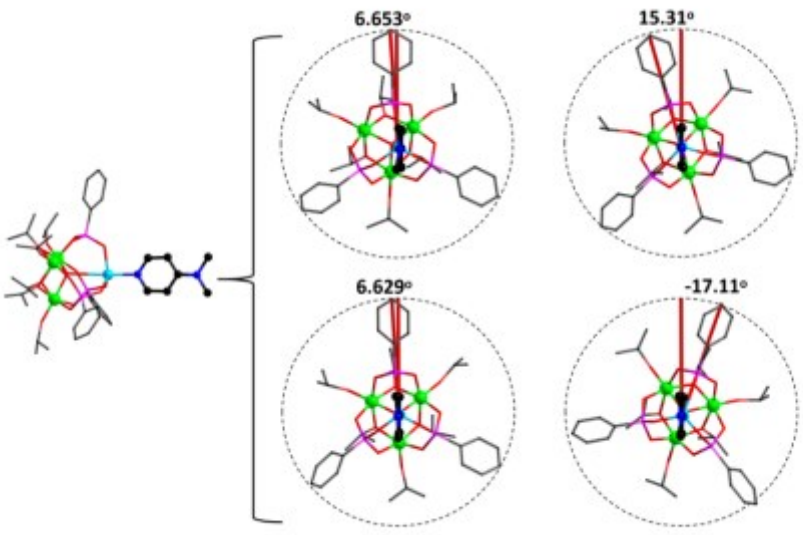

Figure S106. 4 kinds of molecular structure of **PTC-137** .

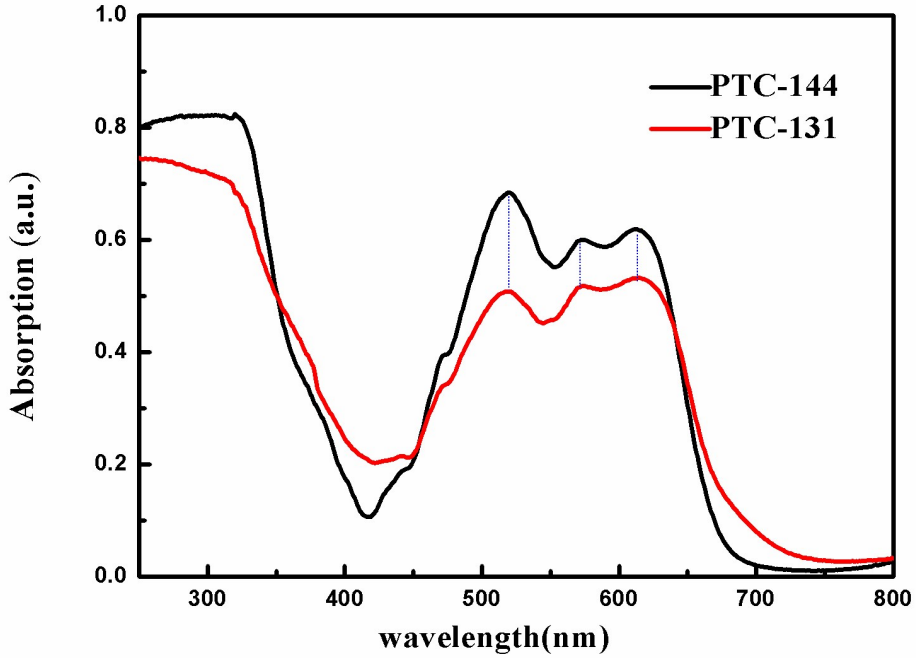

Figure S107. UV-vis spectra for **PTC-131** and **PTC-144**.

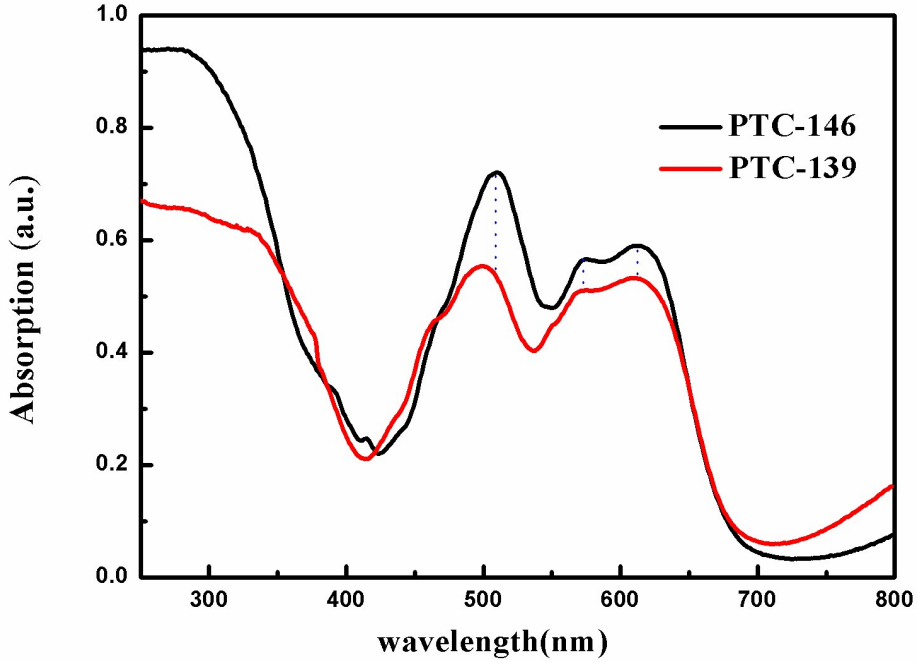

Figure S108. UV-vis spectra for **PTC-139** and **PTC-146**.

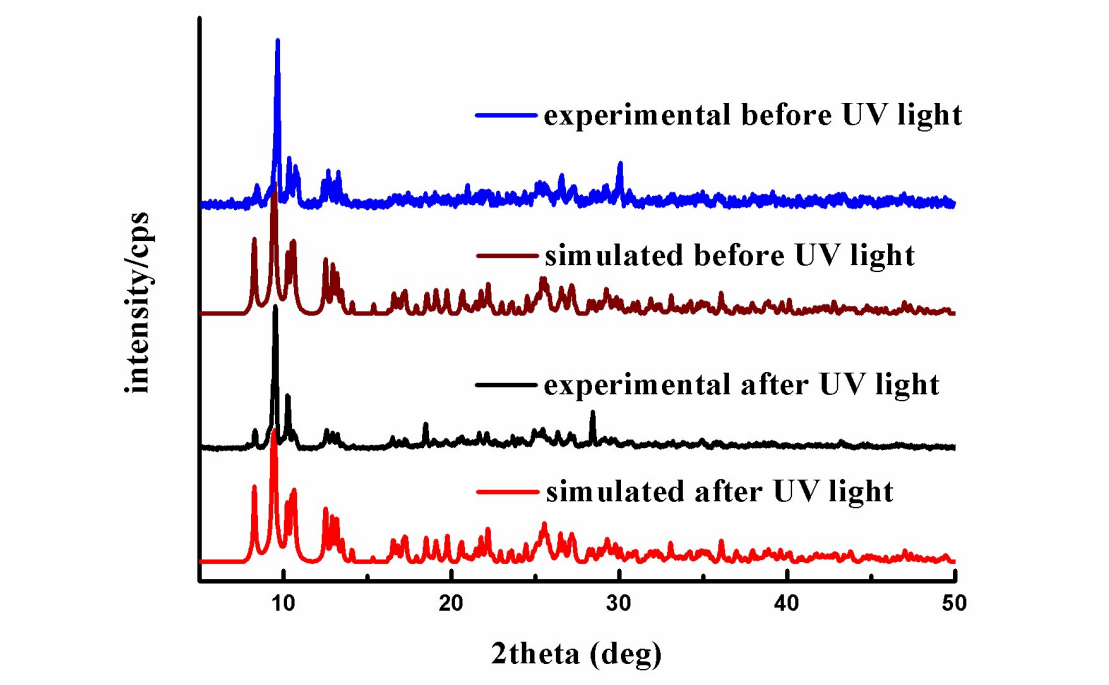

Figure S109. PXRD analysis of **PTC-150 and PTC-150A**

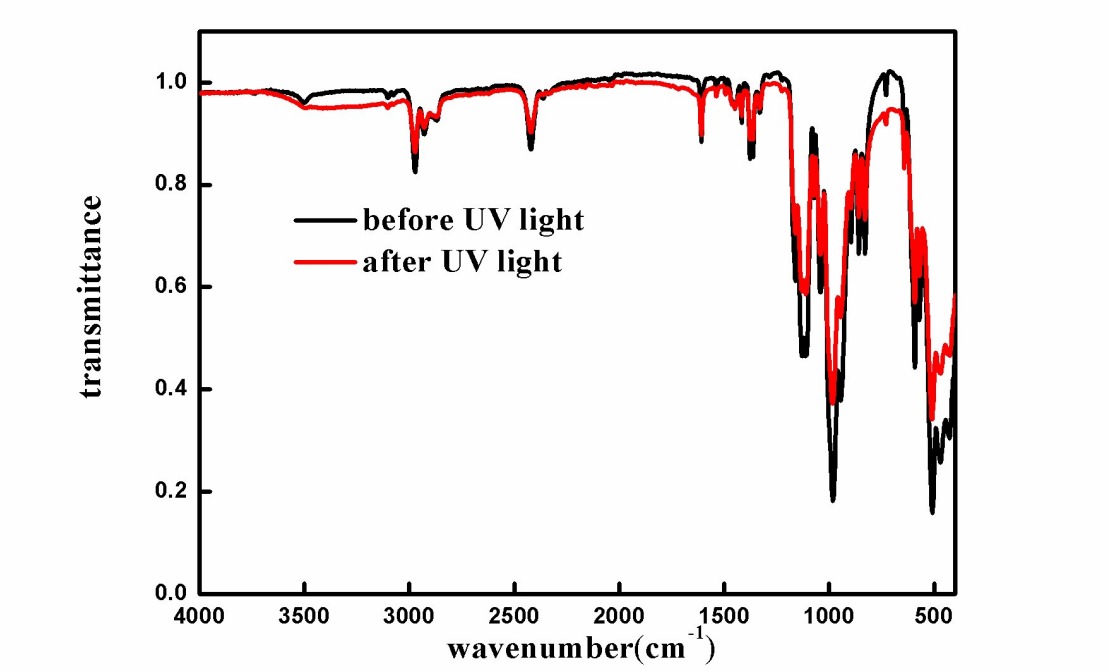

Figure S110 .FTR-IR spectra for **PTC-150** and **PTC-150A.**

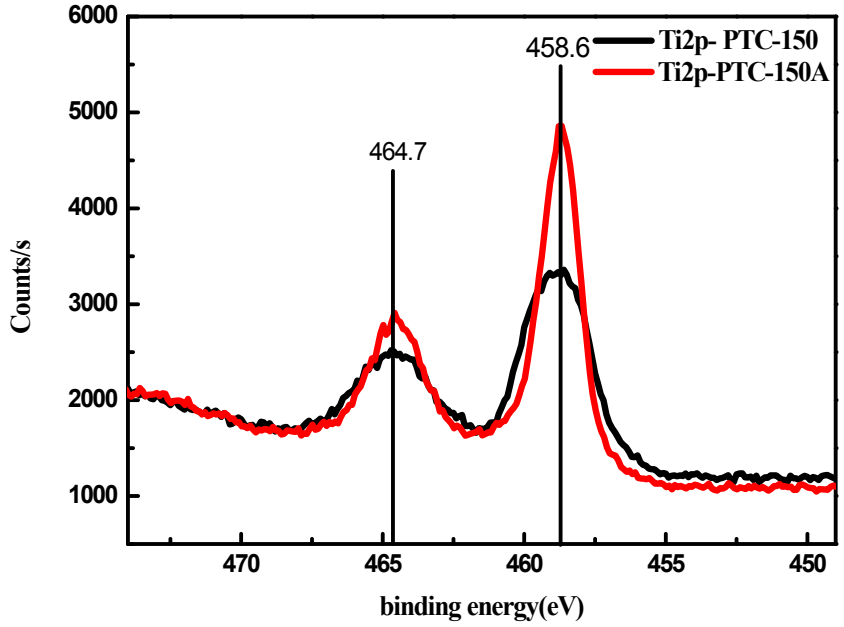

Figure S112. XPS for Ti2p of **PTC-150** and **PTC-150A**

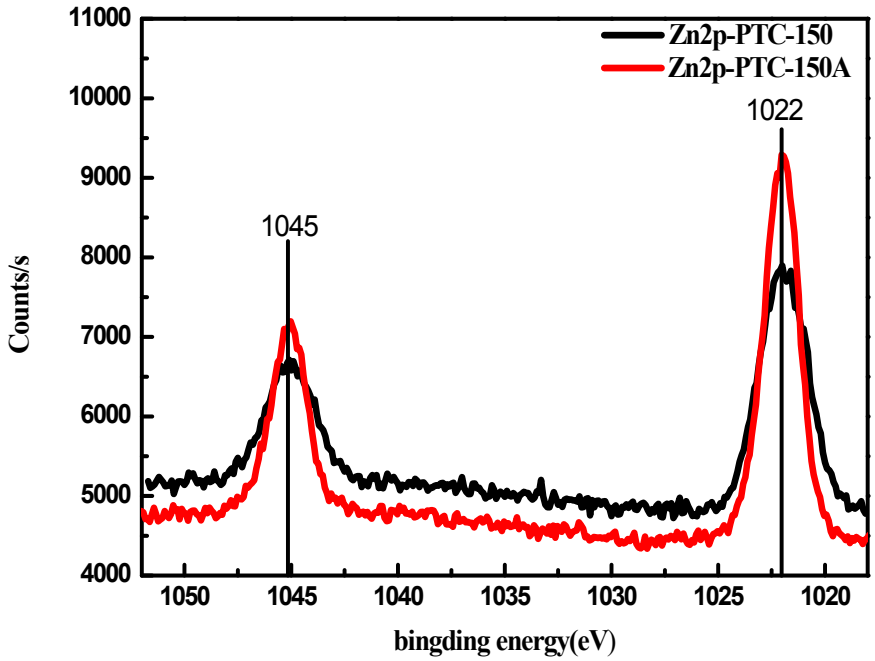

Figure S113.XPS for Zn2p for **PTC-150** and **PTC-150A**

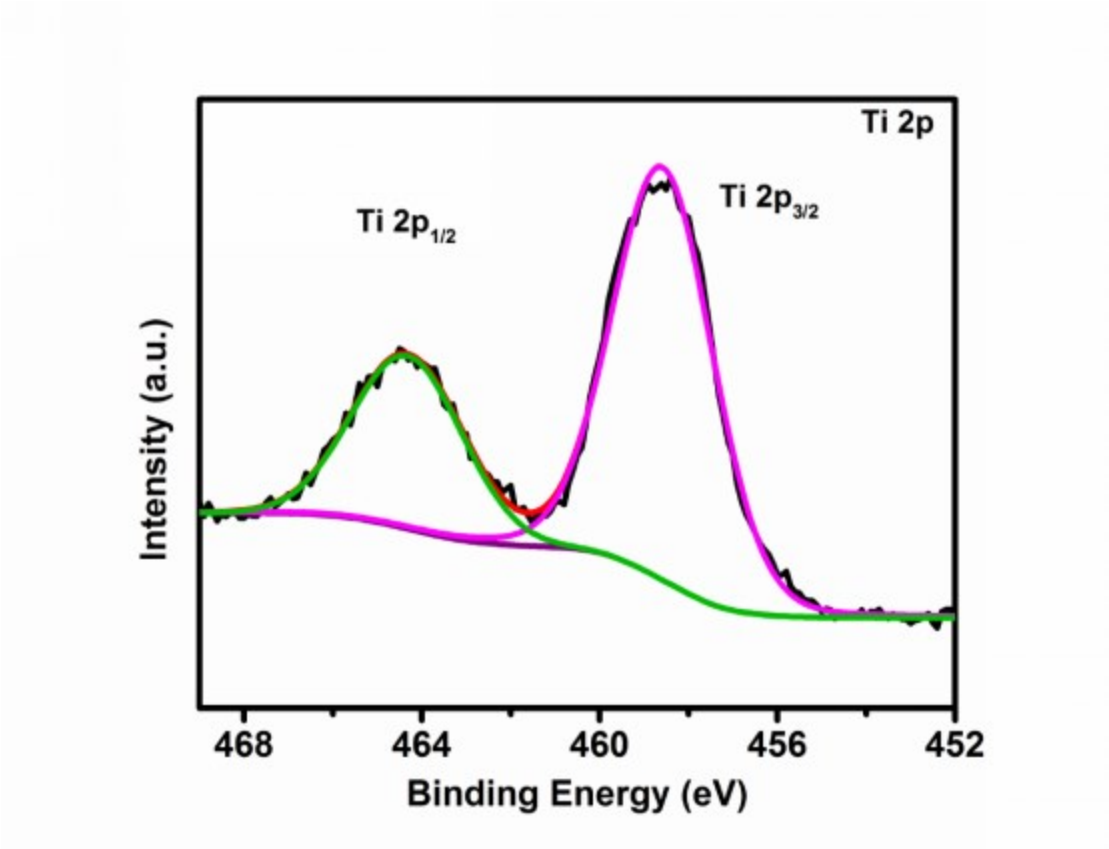

Figure S114.XPS for Ti2p for **PTC-150**

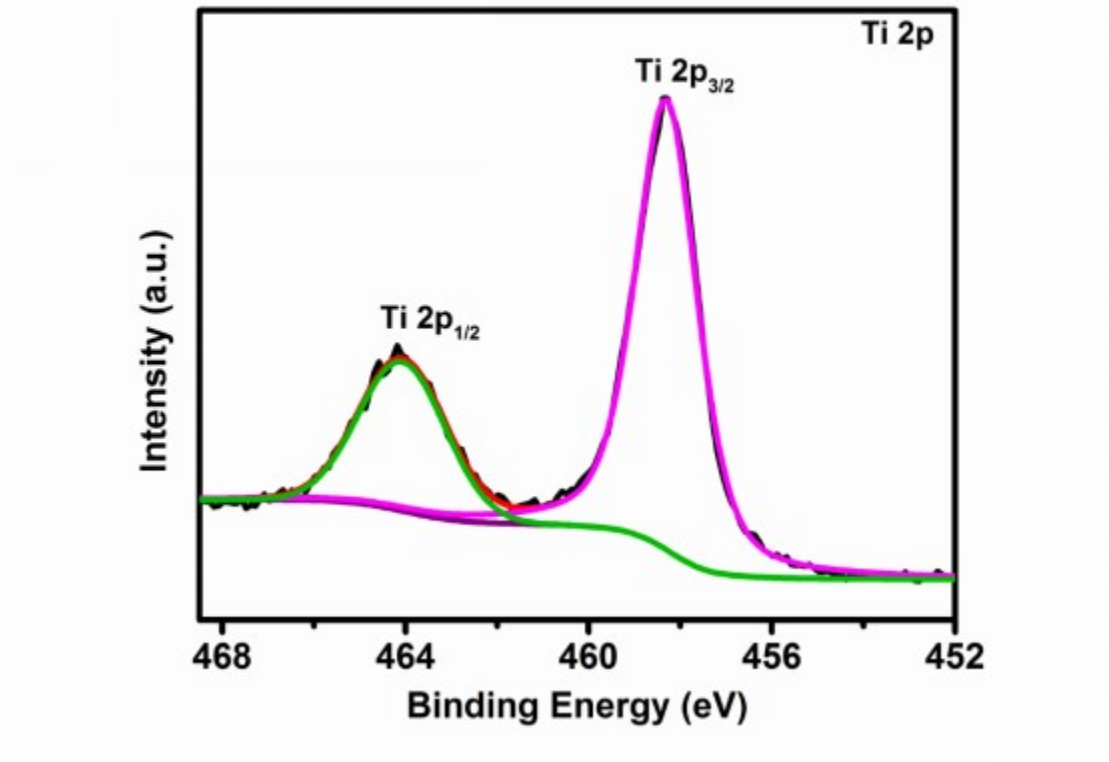

Figure S115.XPS for Ti2p for **PTC-150A**

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