Electronic Supplementary Material (ESI) for Dalton Transactions.


# Supporting Information

# Ligands directed assembly engineering of trapezoidal {$Ti_5$} building blocks stabilized by dimethylglyoxime

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## Content

## 1. Materials and Methods

All reagents and solvents employed are commercially available and are used as received without further purification. Dimethylglyoxime were bought from Alfa Aesar. $Ti(O^iPr)_4$ (96%), Terephthalic acid, 2-aminoterephthalic acid, 2-Nitroterephthalic acid, 2,5-Dihydroxyterephthalic acid, 2,6-Naphthalenedicarboxylic acid, 4,4'-Biphenyldisulfonic acid, 1,2,4,5-Benzenetetracarboxylic acid and tetrakis(4-carboxyphenyl)porphyrin 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 400-4000 $cm^{-1}$ range. The UV-vis diffuse reflection data were recorded at room temperature using a powder sample with $BaSO_4$ as a standard on a Perkin-Elmer Lambda950 UV-vis spectrophotometer and scanned at 200-800 nm in the reflectance mode with application of the Kubelka-Munk equation, ($F$(R) = (1-R)$^2$/2R),[1] where R representing the reflectance. The elemental analyses were performed on an EA1110 CHNS-0 CE elemental analyzer.

## 2. Syntheses

**Synthesis of PTC-211**

Dimethylglyoxime (0.035 g, 0.3 mmol), terephthalic acid (0.033 g, 0.2 mmol), and isopropyl alcohol (6 ml) were mixed at room temperature and then dropwise $Ti(O^iPr)_4$ (0.5 ml, 1.6 mmol) was added. The resultant solution was heated at 100 °C for three days in a glass vial with a polyethylene screw cap. After cooling to and kept at room temperature for a week, yellow rod-like crystals of **PTC-211** were obtained (yield: 70% based on dimethylglyoxime). EA (%) calculated for $C_{82}H_{170}N_4O_{36}Ti_{10}$ (2266.90): C, 43.44; H, 7.56; N, 2.47. Found: C, 44.03; H, 7.34; N, 2.39. FT-IR (KBr pellet, $cm^{-1}$ ): 2975(m), 2926(w), 2867(w), 2357(w), 1688(m), 1554(s), 1370(s), 1220(s), 1006(s), 945(m), 858(s), 816(w), 738(s), 684(w), 615(w).

**Synthesis of PTC-212**

It was synthesized in the same way as that of **PTC-211** except that terephthalic acid was replaced by 2-aminoterephthalic acid (0.036 g, 0.2 mmol). Yellow rod-like crystals of **PTC-212** were obtained (yield: 72% based on dimethylglyoxime). EA (%) calculated for $C_{82}H_{171}N_5O_{36}Ti_{10}$ (2281.91): C, 43.16; H, 7.55; N, 3.07. Found: C, 43.28; H, 7.46; N, 2.98. FT-IR (KBr pellet, $cm^{-1}$ ): 3349(w), 2968(m), 2928(w), 2862(w), 2354(w), 2324(w), 1609(w), 1543(m), 1430(w), 1366(m), 1324(w), 1253(w), 1122(s), 995(s), 956(s), 858(s), 759(s), 627(s), 590(s), 558(s), 445(m).

**Synthesis of PTC-213**

It was synthesized in the same way as that of **PTC-211** except that terephthalic acid was replaced by 2-Nitroterephthalic acid (0.042 g, 0.2 mmol). Yellow rod-like crystals of **PTC-213** were obtained (yield: 40% based on dimethylglyoxime). EA (%) calculated for $C_{82}H_{169}N_5O_{38}Ti_{10}$ (2311.89): C, 42.60; H, 7.37; N, 3.03. Found: C, 42.76; H, 7.23; N, 2.96. FT-IR (KBr pellet, $cm^{-1}$ ): 2975(m), 2926(w), 2857(w), 2352(w), 1585(m), 1543(m), 1460(w), 1376(s), 1317(m), 1131(s), 1082(m), 995(s), 955(s), 857(m), 769(m), 604(s), 456(m).

**Synthesis of PTC-214**

It was synthesized in the same way as that of **PTC-211** except that terephthalic acid was replaced by 2,6-Naphthalenedicarboxylic acid (0.043 g, 0.2 mmol). Yellow rod-like crystals of **PTC-214** were obtained (yield: 47% based on dimethylglyoxime). EA (%) calculated for $C_{86}H_{172}N_4O_{36}Ti_{10}$ (2316.95): C, 44.58; H, 7.48; N, 2.42. Found: C, 44.65; H, 7.41; N, 2.36. FT-IR (KBr pellet, $cm^{-1}$ ): 2989(w), 2356(w), 2324(w), 1619(m), 1541(m), 1492(w), 1404(s), 1355(s), 1195(s), 1068(m), 960(w), 924(w), 764(m), 647(w), 569(w), 461(m).

**Synthesis of PTC-215**

It was synthesized in the same way as that of **PTC-211** except that terephthalic acid was replaced by 4,4'-Biphenyldisulfonic acid (0.064 g, 0.2 mmol). Yellow rod-like crystals of **PTC-215** were obtained (yield: 77% based on Dimethylglyoxime). EA (%) calculated for $C_{86}H_{174}N_4O_{38}S_2Ti_{10}$ (2415.10): C, 42.77; H, 7.26; N, 2.32. Found: C, 42.84; H, 7.23; N, 2.28. FT-IR (KBr pellet, $cm^{-1}$ ): 2968(m), 2928(w), 2870(w), 2360(m), 2332(m), 1608(m), 1460(w), 1373(m), 1324(w), 1266(w), 1138(s), 992(s), 953(s), 845(m), 757(m), 718(m), 591(s), 463(m).

**Synthesis of PTC-216**

Dimethylglyoxime (0.035 g, 0.3 mmol), 2,5-Dihydroxyterephthalic acid (0.040 g, 0.2 mmol), and isopropyl alcohol (6 ml) were mixed at room temperature and then dropwise $Ti(O^iPr)_4$ (0.5 ml, 1.6 mmol) was added. The resultant solution was heated at 100°C for three days. After cooled to room temperature, red block crystals of **PTC-216** were obtained (yield: 80% based on dimethylglyoxime). EA (%) calculated for $C_{111}H_{220}O_{57}N_4Ti_{16}$ (3288.79): C, 40.53; H, 6.74; N, 1.71. Found: C, 40.37; H, 6.78; N, 1.61. FT-IR (KBr pellet, $cm^{-1}$ ): 2971(m), 2932(w), 2873(w), 2364(w), 1611(m), 1552(m), 1445(s), 1366(m), 1327(m), 1249(m), 1220(w), 1141(s), 1005(s), 907(m), 828(m), 780(w), 672(w), 613(s), 466(m).

**Synthesis of PTC-217**

It was synthesized in the same way as that of **PTC-211** except that terephthalic acid was replaced by 1,2,4,5-Benzenetetracarboxylic acid (0.051 g, 0.2 mmol). Yellow rod-like crystals of **PTC-217** were obtained (yield: 61% based on dimethylglyoxime). EA (%) calculated for $C_{96}H_{198}N_4O_{46}Ti_{12}$ (2718.99) : C, 42.41; H, 7.34; N, 2.06. Found: C, 41.78; H, 6.93; N, 2.11. FT-IR (KBr pellet, $cm^{-1}$ ): 2968(m), 2925(w), 2857(w), 2362(w), 2331(w), 1719(m), 1581(m), 1420(m), 1360(m), 1247(m), 1121(s), 999(s), 956(s), 853(m), 820(w), 797(w), 763(m), 590(s), 503(w), 463(w).

**Synthesis of PTC-218**

It was synthesized in the same way as that of **PTC-211** except that terephthalic acid was replaced by meso-Tetra(4-carboxyphenyl)porphine (0.079 g, 0.1 mmol). Crimson block crystals of **PTC-218** were obtained (yield: 60% based on dimethylglyoxime). EA (%) calculated for $C_{196}H_{358}O_{72}N_{12}Ti_{20}$ (4992.30): C, 47.15; N, 3.37; H, 7.23. Found: C, 47.28; N, 3.21; H, 7.16. FT-IR (KBr pellet, $cm^{-1}$ ): 2975(m), 2916(w), 2857(w), 2358(w), 1605(m), 1543(m), 1468(w), 1390(s), 1331(m), 1135(s), 1077(m), 998(s), 959(s), 842(m), 803(w), 754(m), 725(w), 578(s), 451(m).

## 3. Structural information and physical characterization of PTC-211 to 218

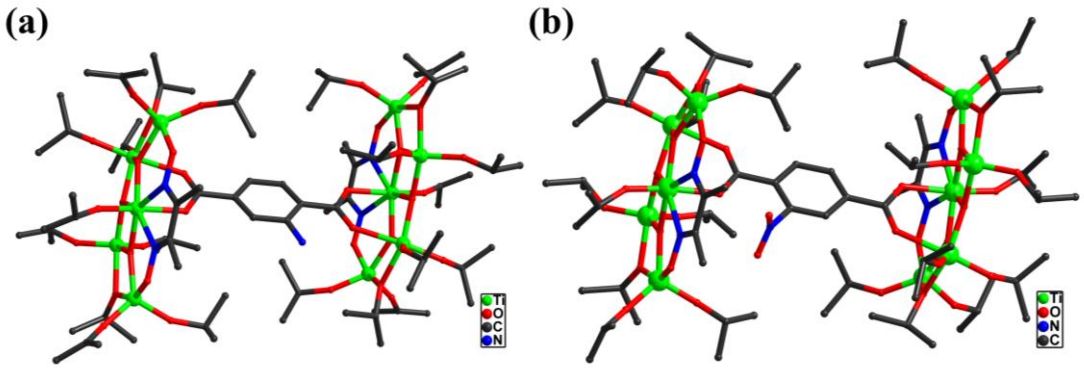


**Fig. S1** The sandwich-like {$Ti_{10}$} molecular cluster of **PTC-212** (a), **PTC-213** (b). All the H atoms are omitted for clarity. Color codes: green Ti; black C; red O; blue N.

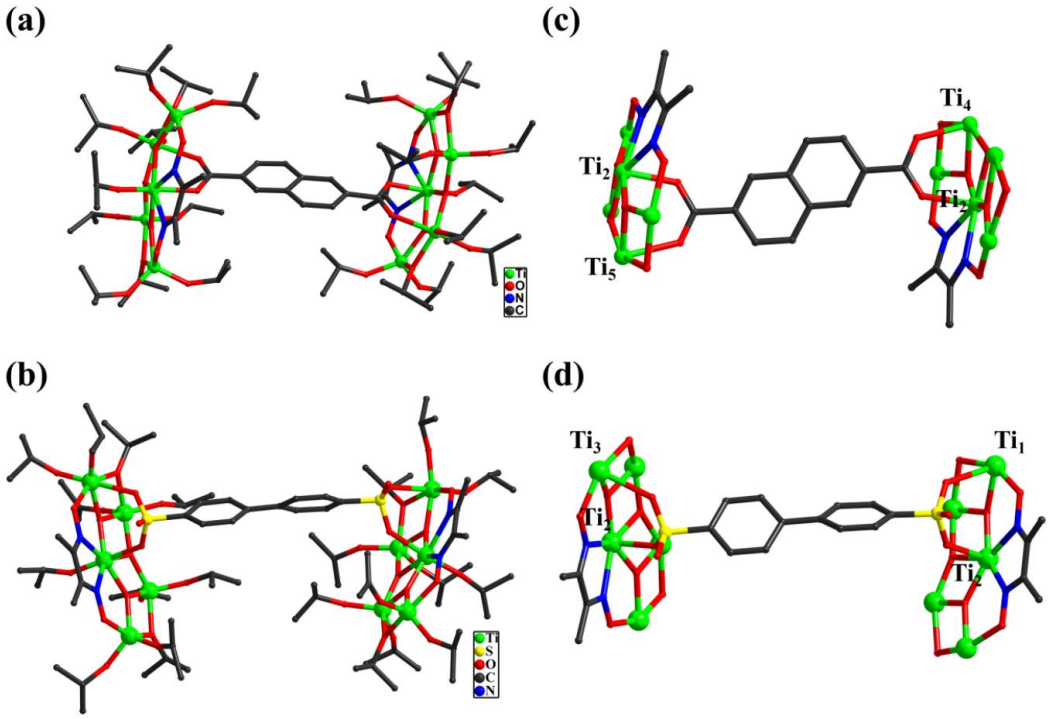


**Fig. S2** The sandwich-like {$Ti_{10}$} molecular cluster of **PTC-214** (a, c) and **PTC-215** (b, d) with different coordination environments. All the H atoms are omitted for clarity. Color codes: green Ti; black C; red O; yellow S; blue N.

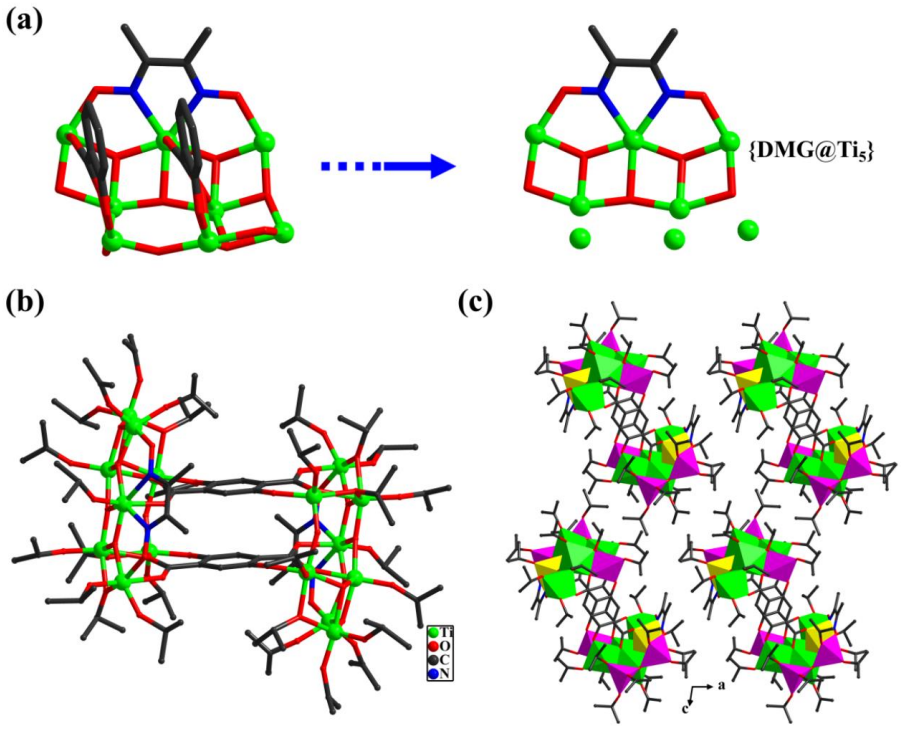


**Fig. S3** The Synthetic and structural evolution of $\{Ti_8\}$ unit in **PTC-216** containing one $\{DMG@Ti_5\}$ unit (a); the sandwich-like $\{Ti_{16}\}$ molecular cluster of **PTC-216** (b); and the packing view of **PTC-216** along the b-axis (c). All the H atoms are omitted for clarity. Color codes: green Ti; black C; red O; blue N. Polyhedral color code: pink $TiO_5$; green $TiO_6$; yellow $TiO_5N_2$.

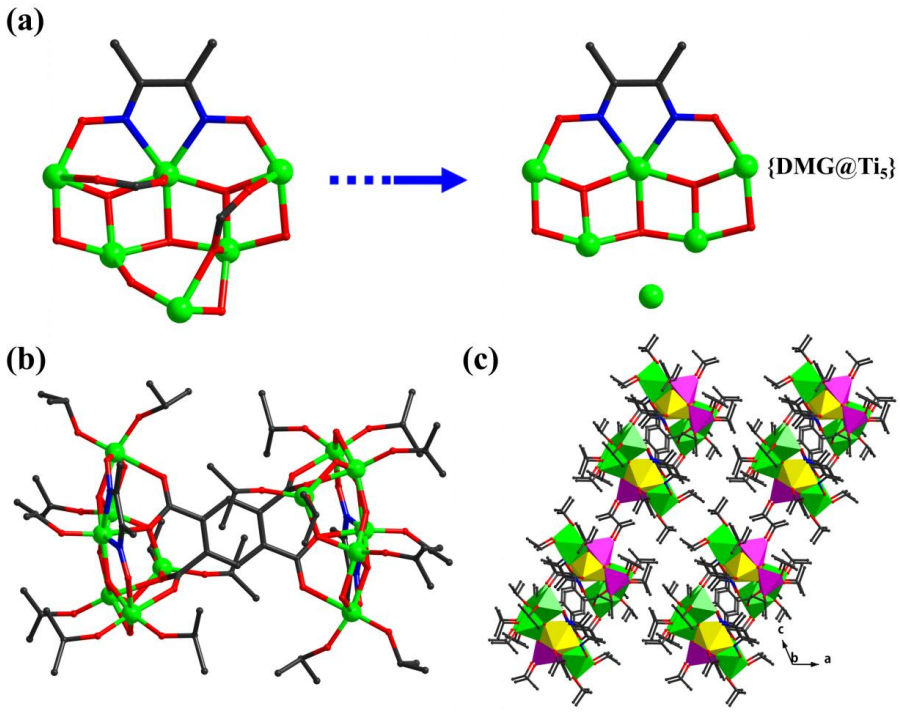


**Fig. S4** The Synthetic and structural evolution of $\{Ti_6\}$ unit in **PTC-217** containing one {DMG@Ti5} unit (a); the sandwich-like $\{Ti_{12}\}$ molecular cluster of **PTC-217** (b); and the packing view of **PTC-217** along the b-axis (c). All the H atoms are omitted for clarity. Color codes: green Ti; black C; red O; blue N. Polyhedral color code: pink $TiO_5$; green $TiO_6$; yellow $TiO_5N_2$.

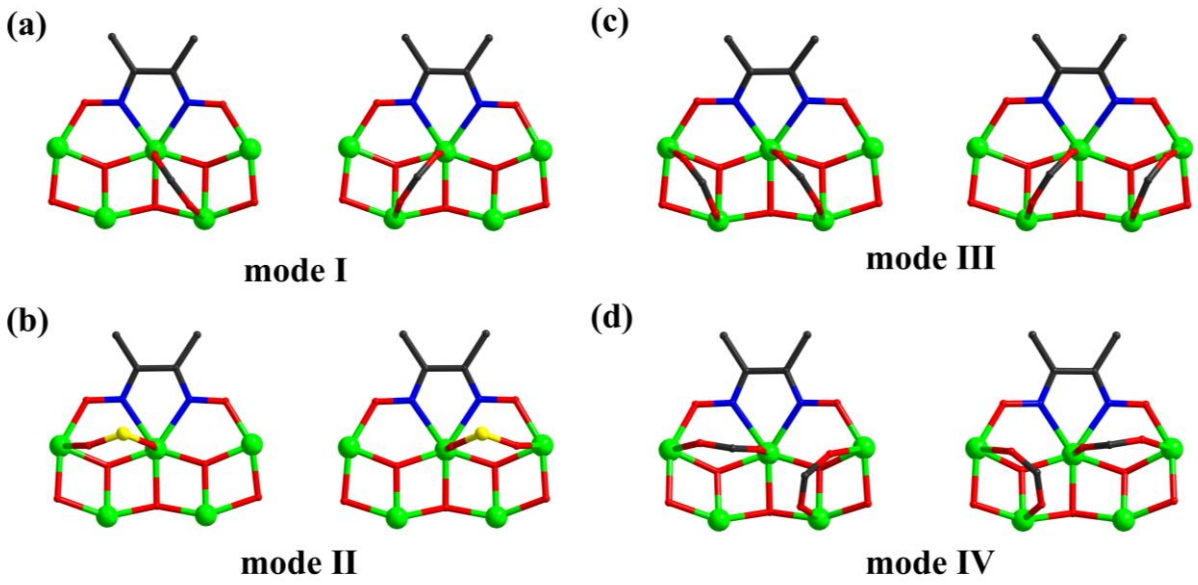


**Fig. S5** Bridging coordination modes of {DMG@$Ti_5$} unit. Color codes: green Ti; black C; red O; yellow S; blue N.

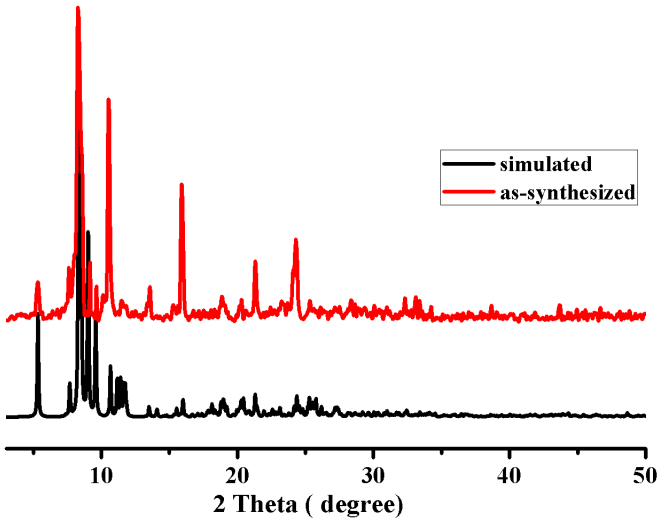


**Fig. S6** The PXRD of **PTC-211**: simulated pattern (black), experimental (red).

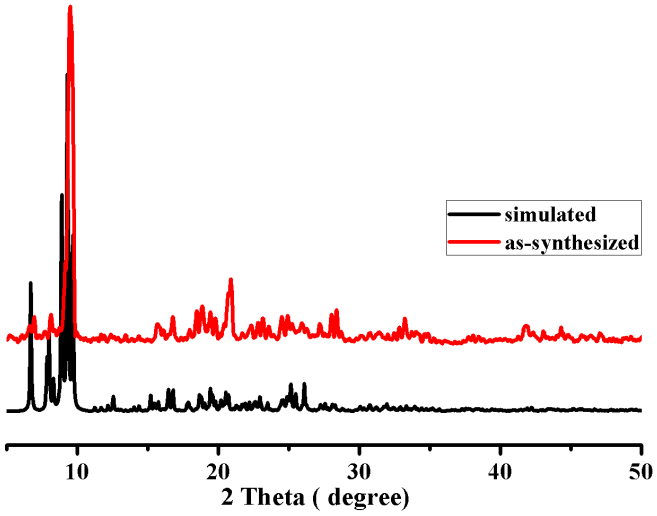


**Fig. S7** The PXRD of **PTC-212**: simulated pattern (black), experimental (red).

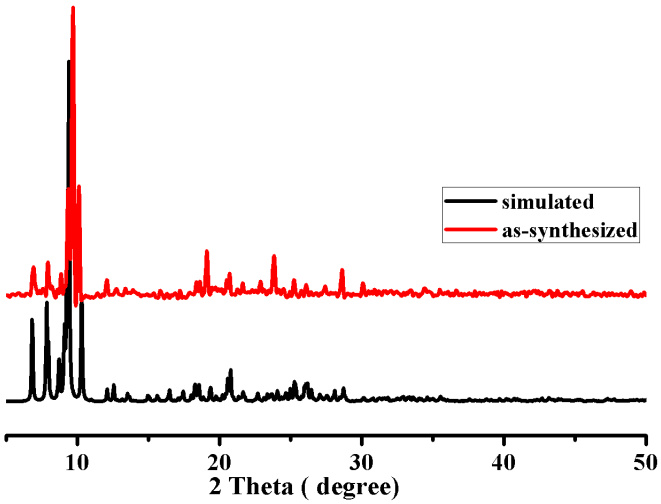


**Fig. S8** The PXRD of **PTC-213**: simulated pattern (black), experimental (red).

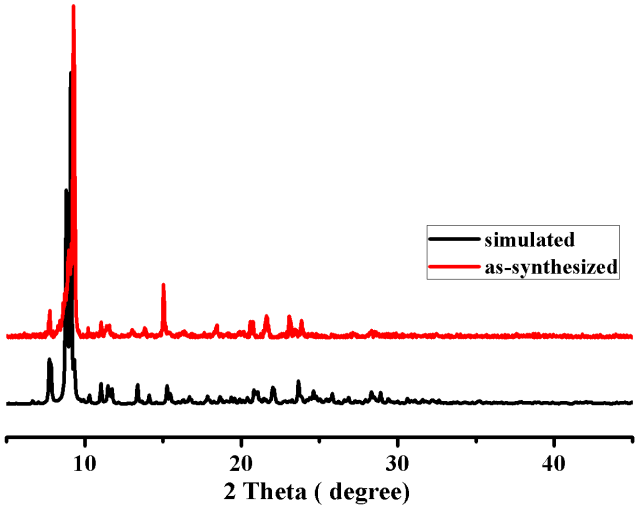


**Fig. S9** The PXRD of **PTC-214**: simulated pattern (black), experimental (red).

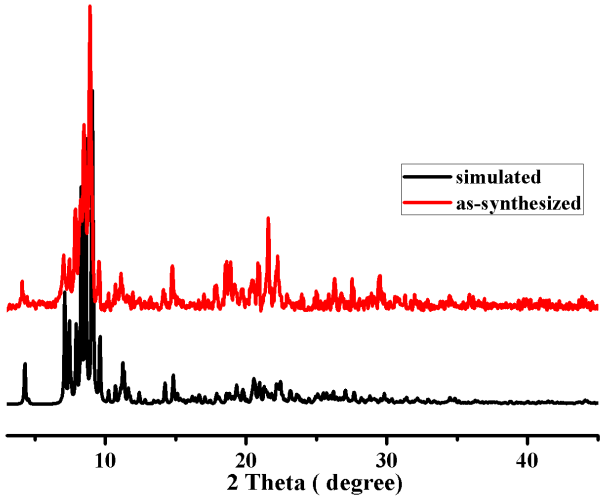


**Fig. S10** The PXRD of **PTC-215**: simulated pattern (black), experimental (red).

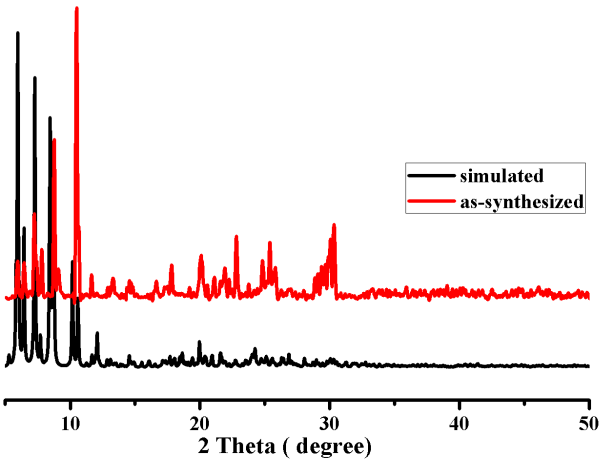


**Fig. S11** The PXRD of **PTC-216**: simulated pattern (black), experimental (red).

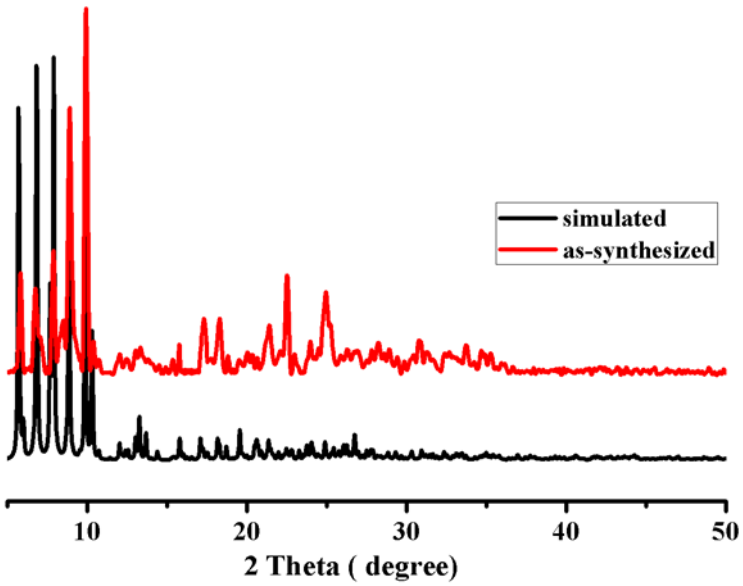


**Fig. S12** The PXRD of **PTC-217**: simulated pattern (black), experimental (red).

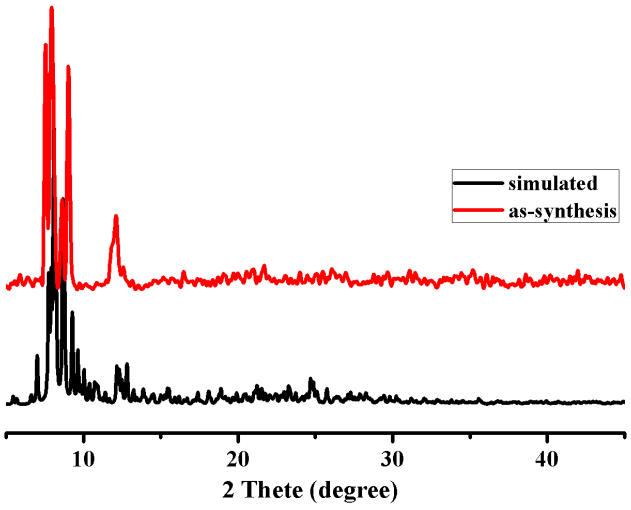


**Fig. S13** The PXRD of **PTC-218**: simulated pattern (black), experimental (red).

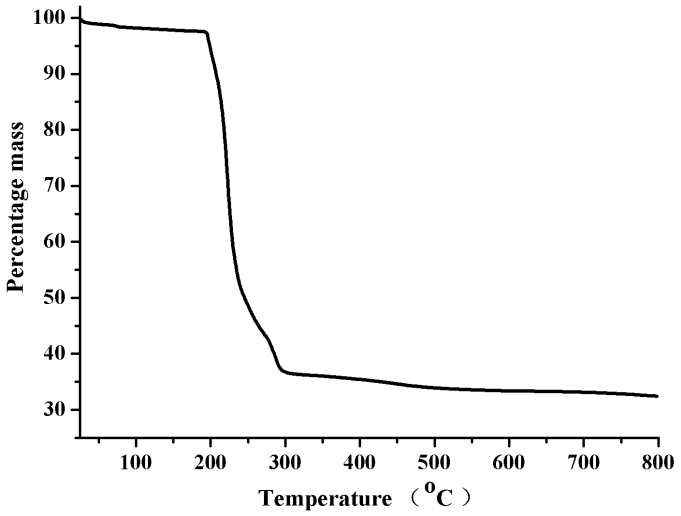


**Fig. S14** TGA curve of **PTC-211**.

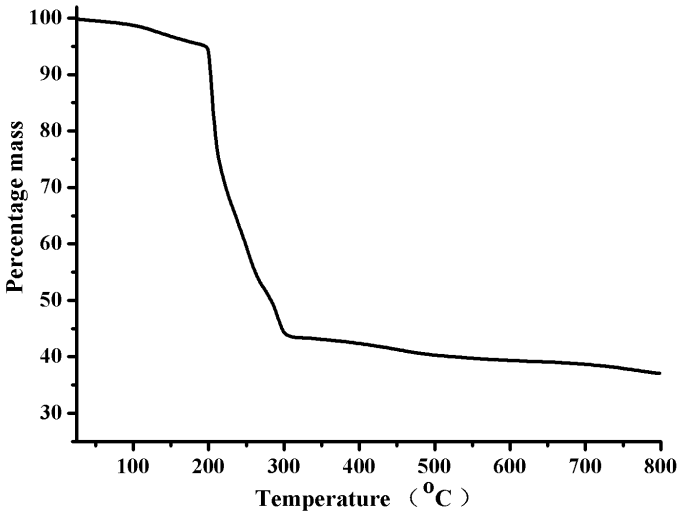


**Fig. S15** TGA curve of **PTC-212**.

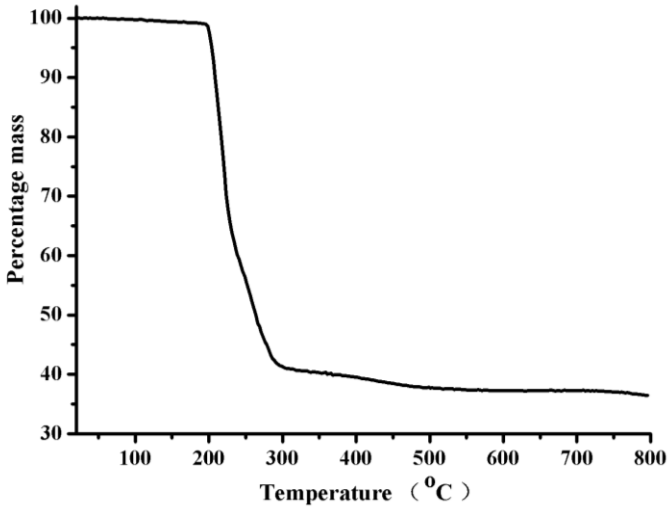


**Fig. S16** TGA curve of **PTC-213**.

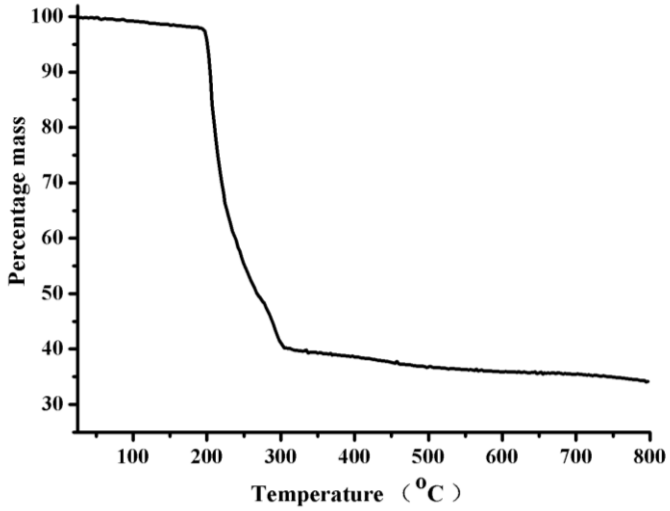


**Fig. S17** TGA curve of **PTC-214**.

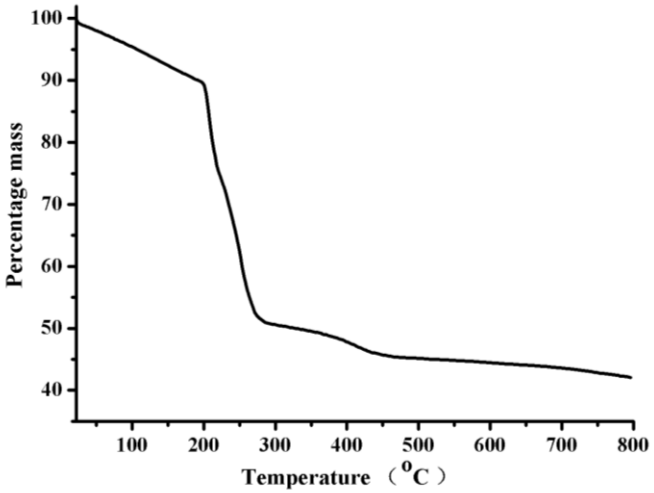


**Fig. S18** TGA curve of **PTC-215**.

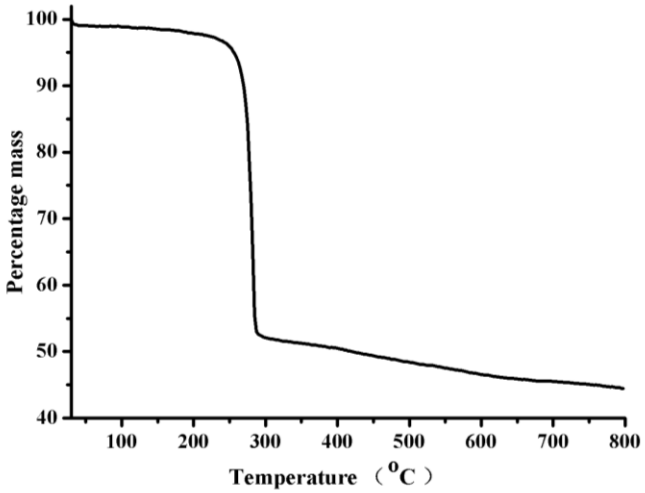


**Fig. S19** TGA curve of **PTC-216**.

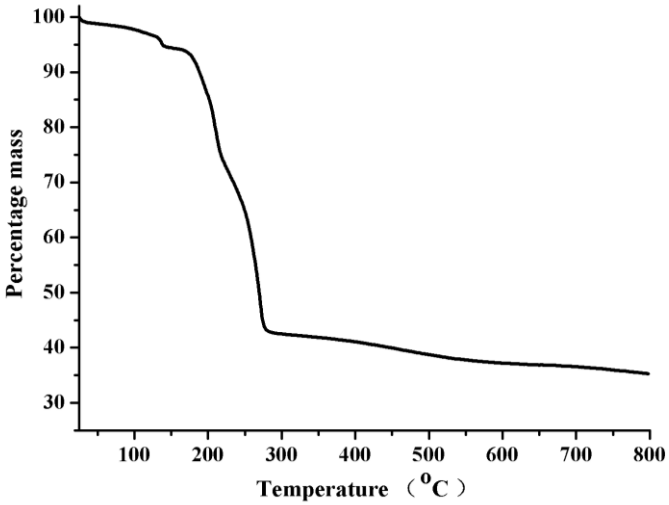


**Fig. S20** TGA curve of **PTC-217**.

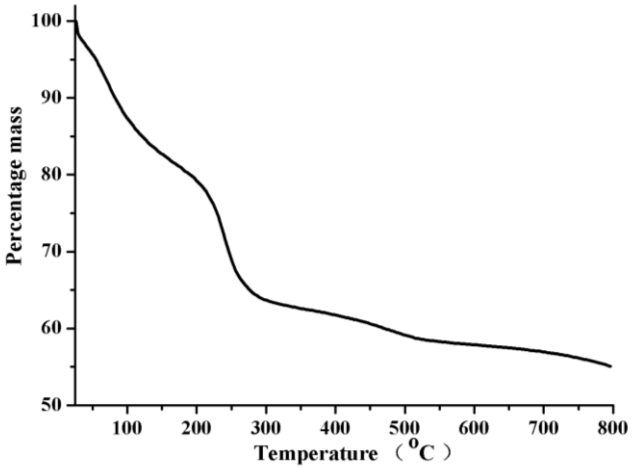


**Fig. S21** TGA curve of **PTC-218**.

**Table S1.** Summary of bandgaps of the reported complexes.

| No. | Complex | Bandgap | Stabilizing ligand | Bridging ligand |
|---|---|---|---|---|
| 1 | **PTC-211** | 2.31 | DMG | BDC |
| 2 | **PTC-212** | 2.26 | DMG | 2-$NH_2$-BDC |
| 3 | **PTC-213** | 2.21 | DMG | 2-$NO_2$-BDC |
| 4 | **PTC-214** | 2.45 | DMG | 2.6-NDC |
| 5 | **PTC-215** | 2.27 | DMG | BPDC |
| 6 | **PTC-216** | 1.78 | DMG | DHPC |
| 7 | **PTC-217** | 2.34 | DMG | BETC |
| 8 | **PTC-218** | 1.56 | DMG | TCPP |

## 4. General Methods for X-ray Crystallography

Crystallographic data of **PTC-214** was collected on a Mercury single crystal diffractometer equipped with graphite-monochromatic Mo K$\alpha$ radiation (λ = 0.71073 Å). Crystallographic data of **PTC-215, PTC-216** and **PTC-217** were collected on a oxford XCalibur E CCD diffractometer equipped with graphite-monochromatic Mo K$\alpha$ radiation (λ = 0.71073 Å). While crystallographic data of **PTC-211, PTC-212, PTC-213** and **PTC-218** were collected on Supernova single crystal diffractometer equipped with graphite-monochromatic Cu K$\alpha$ radiation (λ = 1.54178 Å) at room temperature. The structures were solved with direct methods using SHELXS-97[2] and refined with the full-matrix least-squares technique based on $F^2$ using the SHELXL-97[3]. Non-hydrogen atoms were refined anisotropically, and all hydrogen atoms bond C were generated geometrically. The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC 1914954-1914961 for **PTC-211** to **PTC-218**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

**5. Supplementary Table S2.** A summary of crystallography data for **PTC-211 to PTC-218.** Detailed data are given in **Tables S3** and **S4.**

| No. | Complex | Forumla | $M_w$ (g/mol) | Sp. Gr. | a(Å) | b(Å) | c(Å) | α (°) | β(°) | (°) | V(Å$^3$) | R/% |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. | **PTC-211** | $Ti_{10}O_6(DMG)_2(BDC)(O^iPr)_{22}$ | 2266.90 | $P2_1/n$ | 10.9245(2) | 23.0505(6) | 23.9209(6) | 90 | 92.241(2) | 90 | 6019.0(2) | 6.87 |
| 2. | **PTC-212** | $Ti_{10}O_6(DMG)_2(2\text{-}NH_2\text{-}BDC)(O^iPr)_{22}$ | 2281.91 | *P*-1 | 12.2992(10) | 14.3904(15) | 19.0996(17) | 85.923(8) | 85.061(7) | 66.484(9) | 3085.7(5) | 8.05 |
| 3. | **PTC-213** | $Ti_{10}O_6(DMG)_2(2\text{-}NO_2\text{-}BDC)(O^iPr)_{22}$ | 2311.89 | *P*-1 | 11.8011(4) | 13.8482(7) | 18.9934(7) | 82.343(4) | 85.367(3) | 70.160(4) | 2891.6(2) | 8.55 |
| 4. | **PTC-214** | $Ti_{10}O_6(DMG)_2(2,6\text{-}NDC)(O^iPr)_{22}$ | 2316.95 | $P2_1/c$ | 19.4857(4) | 26.4883(7) | 22.5872(5) | 90 | 94.059(2) | 90 | 11629.0(5) | 7.71 |
| 5. | **PTC-215** | $Ti_{10}O_6(DMG)_2(BPDC)(O^iPr)_{22}$ | 2415.10 | *P*-1 | 13.1334(4) | 23.0232(10) | 23.9960(11) | 63.989(4) | 78.288(3) | 82.373(3) | 6377.2(5) | 8.43 |
| 6. | **PTC-216** | $Ti_{16}O_{12}(DMG)_2(DHPC)_2(O^iPr)_{28}$ | 3288.79 | *P*-1 | 15.4097(7) | 15.8879(6) | 17.9294(7) | 109.617(3) | 96.107(3) | 95.889(3) | 4066.3(3) | 6.78 |
| 7. | **PTC-217** | $Ti_{12}O_8(DMG)_2(BETC)(O^iPr)_{24}$ | 2718.99 | *P*-1 | 14.7714(7) | 15.1120(7) | 16.8580(7) | 93.516(4) | 111.982(4) | 100.404(4) | 3397.7(3) | 7.19 |
| 8. | **PTC-218** | $Ti_{20}O_{12}(DMG)_4(TCPP)(O^iPr)_{44}$ | 4992.30 | $P2_1/c$ | 22.1405(13) | 26.7150(10) | 25.288(3) | 90 | 120.487(5) | 90 | 12889.5(19) | 12.53 |

**Table S3.** Crystallographic data and structure refinement summary for **PTC-211** to **PTC-214**.

| | **PTC-211** | **PTC-212** | **PTC-213** | **PTC-214** |
|---|---|---|---|---|
| Empirical formula | $C_{82}H_{170}N_4O_{36}Ti_{10}$ | $C_{82}H_{171}N_5O_{36}Ti_{10}$ | $C_{82}H_{169}N_5O_{38}Ti_{10}$ | $C_{86}H_{172}N_4O_{36}Ti_{10}$ |
| $M_r$ | 2266.90 | 2281.91 | 2311.89 | 2316.95 |
| T/K | 293(2) | 293(2) | 99.98(13) | 293(2) |
| Crystal system | Monoclinic | Triclinic | Triclinic | Monoclinic |
| Space group | $P2_1/n$ | *P-1* | *P-1* | $P2_1/c$ |
| a/Å | 10.9245(2) | 12.2992(10) | 11.8011(4) | 19.4857(4) |
| b/Å | 23.0505(6) | 14.3904(15) | 13.8482(7) | 26.4883(7) |
| c/Å | 23.9209(6) | 19.0996(17) | 18.9934(7) | 22.5872(5) |
| α (°) | 90 | 85.923(8) | 82.343(4) | 90 |
| β (°) | 92.241(2) | 85.061(7) | 85.367(3) | 94.059(2) |
| γ (°) | 90 | 66.484(9) | 70.160(4) | 90 |
| V/Å$^3$ | 6019.0(2) | 3085.7(5) | 2891.6(2) | 11629.0(5) |
| Z | 2 | 1 | 1 | 4 |
| Dc/mg m$^{-3}$ | 1.251 | 1.228 | 1.324 | 1.325 |
| μ/mm$^{-1}$ | 5.919 | 5.778 | 6.187 | 0.720 |
| indep reflns [$I > 2\sigma(I)$] | 11931 | 12141 | 11438 | 18245 |
| F(000) | 2396 | 1205 | 1213 | 4904 |
| GOF | 1.032 | 1.065 | 0.989 | 1.094 |
| $R_1$[a], $wR_2$[b] [$I > 2\sigma(I)$] | 0.0691, 0.2097 | 0.1334, 0.3760 | 0.0991, 0.2935 | 0.0771, 0.1818 |
| $R_1$[a], $wR_2$[b] (all data) | 0.0955, 0.2353 | 0.1869, 0.4470 | 0.1234, 0.3370 | 0.1024, 0.1911 |

[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 S4.** Crystallographic data and structure refinement summary for **PTC-215** to **PTC-218**.

| | **PTC-215** | **PTC-216** | **PTC-217** | **PTC-218** |
|---|---|---|---|---|
| Empirical formula | $C_{86}H_{174}N_4O_{38}S_2Ti_{10}$ | $C_{111}H_{220}O_{57}N_4Ti_{16}$ | $C_{96}H_{198}N_4O_{46}Ti_{12}$ | $C_{196}H_{358}N_{12}O_{72}Ti_{20}$ |
| $M_r$ | 2415.10 | 3288.79 | 2718.99 | 4992.30 |
| T/K | 293(2) | 293(2) | 293(2) | 293(2) |
| Crystal system | Triclinic | Triclinic | Triclinic | Monoclinic |
| Space group | *P*-1 | *P*-1 | *P*-1 | $P2_1/c$ |
| a/Å | 13.1334(4) | 15.4097(7) | 14.7714(7) | 22.1405(13) |
| b/Å | 23.0232(10) | 15.8879(6) | 15.1120(7) | 26.7150(10) |
| c/Å | 23.9960(11) | 17.9294(7) | 16.8580(7) | 25.288(3) |
| α (°) | 63.989(4) | 109.617(3) | 93.516(4) | 90 |
| β (°) | 78.288(3) | 96.107(3) | 111.982(4) | 120.487(5) |
| γ (°) | 82.373(3) | 95.889(3) | 100.404(4) | 90 |
| V/Å$^3$ | 6377.2(5) | 4066.3(3) | 3397.7(3) | 12889.5(19) |
| Z | 2 | 1 | 1 | 2 |
| Dc/mg m$^{-3}$ | 1.252 | 1.313 | 1.269 | 1.286 |
| μ/mm$^{-1}$ | 0.691 | 0.812 | 0.735 | 5.583 |
| indep reflns [$I$ >2σ($I$)] | 22977 | 14264 | 11911 | 24068 |
| F(000) | 2534 | 1674 | 1364 | 5268 |
| GOF | 1.174 | 1.074 | 1.090 | 1.087 |
| $R_1$[a], $wR_2$[b] [$I$ >2σ($I$)] | 0.1219, 0.3269 | 0.1228, 0.3639 | 0.1115, 0.3081 | 0.1490, 0.3694 |
| $R_1$[a], $wR_2$[b] (all data) | 0.2051, 0.4041 | 0.1695, 0.4190 | 0.1663, 0.3594 | 0.2870, 0.4859 |

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

**6. References**

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