Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Synergistic ligands effect for the construction of titanium-oxo clusters with planar chirality and high solution stability

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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 was bought from Alfa Aesar. $Ti(O^iPr)_4$ (96%) and diphenic acid were bought from Admas-beta. Cis-4-cyclohexene-1,2-dicarboxylic acid and phthalic acid were bought from Aladdin. 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-67
Dimethylglyoxime (0.035 g, 0.3 mmol), Diphenic acid (0.048 g, 0.2 mmol), and isopropyl alcohol (6 ml) were mixed at room temperature and then dropwise $Ti(O^iPr)_4$ (0.5 ml, 1.56 mmol) was added. The resultant solution was heated at 80 °C for three days in a glass vial with a polyethylene screw cap. After cooling to and kept at room temperature for a week, pale yellow rodlike crystals of **PTC-67** were obtained (yield: 80% based on Dimethylglyoxime). EA (%) calculated for $C_{67}H_{126}N_4O_{29}Ti_8$ (1834.70): C, 43.86; H, 6.92; N, 3.05. Found: C, 43.45; H, 6.73; N, 3.14. FT-IR (KBr pellet, cm-1): 2975(m), 2916(w), 2857(w), 2358(w), 1605(m), 1533(m), 1445(w), 1376(s), 1327(m), 1132(s), 1073(m), 1014(m), 985(s), 958(s), 858(s), 760(s), 701(m), 672(m), 592(s), 564(s), 457(m).

Synthesis of PTC-68
Dimethylglyoxime (0.035 g, 0.3 mmol), Diphenic acid (0.048 g, 0.2 mmol), and isopropyl alcohol (6 ml) were mixed at room temperature and then dropwise $Ti(O^iPr)_4$ (0.5 ml, 1.56 mmol) was added. The resultant solution was heated at 100 °C for one day in a glass vial with a polyethylene screw cap. After cooling to and kept at room temperature for a week, yellow block crystals of **PTC-68A** and **PTC-68B** were obtained (yield: 70% based on Dimethylglyoxime). EA (%) calculated for $C_{62}H_{110}N_6O_{30}Ti_9$ (1850.65): C, 40.24; H, 5.99; N, 4.54. Found: C, 40.39; H, 6.08; N, 4.47. FT-IR (KBr pellet, cm-1): 2975(m), 2916(w), 2857(w), 2358(w), 1605(m), 1546(m), 1448(w), 1390(s), 1331(m), 1135(s), 1087(m), 969(s), 842(m), 773(s), 679(m), 619(s), 538(s), 460(m).

Synthesis of PTC-69
Dimethylglyoxime (0.035 g, 0.3 mmol), Cis-4-cyclohexene-1,2-dicarboxylic acid (0.034 g, 0.2 mmol), and isopropyl alcohol (6 ml) were mixed at room temperature and then dropwise $Ti(O^iPr)_4$ (0.5 ml, 1.56 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 rodlike crystals of **PTC-69** were obtained (yield: 82% based on Dimethylglyoxime). EA (%) calculated for $C_{56}H_{110}N_6O_{30}Ti_9$ (1778.30): C, 37.82; H, 6.23; N, 4.73. Found: C, 37.94; H, 6.43; N, 4.67. FT-IR (KBr pellet, cm^{-1}): 2968(m), 2919(w), 2857(w), 2352(w), 1608(m), 1549(m), 1432(m), 1360(m), 1324(m), 1129(s), 1080(s), 1010(s), 962(s), 855(m), 800(s), 770(s), 692(w), 643(m), 594(s), 555(s), 438(w).

Synthesis of PTC-70

Dimethylglyoxime (0.035 g, 0.3 mmol), Phthalic 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, 1.56 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 rodlike crystals of **PTC-70** were obtained (yield: 60% based on Dimethylglyoxime). EA (%) calculated for $C_{56}H_{106}N_6O_{30}Ti_9$ (1774.26): C, 37.91; H, 6.02; N, 4.74. Found: C, 37.84; H, 6.31; N, 4.60. FT-IR (KBr pellet, cm^{-1}): 2968(m), 2929(w), 2860(w), 2360(w), 1597(m), 1559(s), 1382(s), 1363(s), 1324(m), 1135(s), 1078(s), 998(s), 959(s), 846(m), 778(s), 650(m), 591(s), 542(s), 462(w).

3. Structural information and physical characterization of PTC-67 to PTC-70

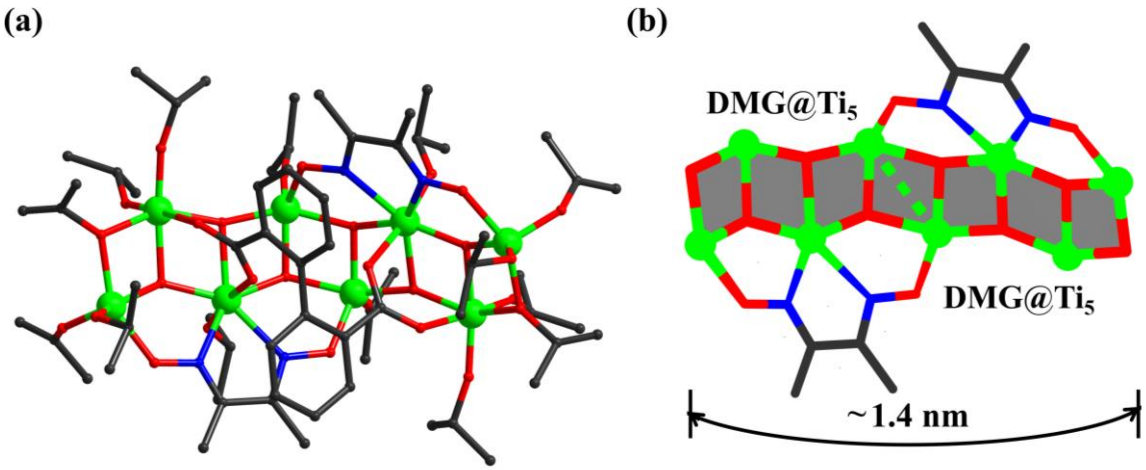

Figure S1. (a) The ladder-like Ti_8 molecular cluster structure of **PTC-67**; (b) the Ti_8 cluster core structure of **PTC-67** containing two {DMG@Ti_5} units. All the H atoms are omitted for clarity. Color codes: green Ti; black C; red O; blue N.

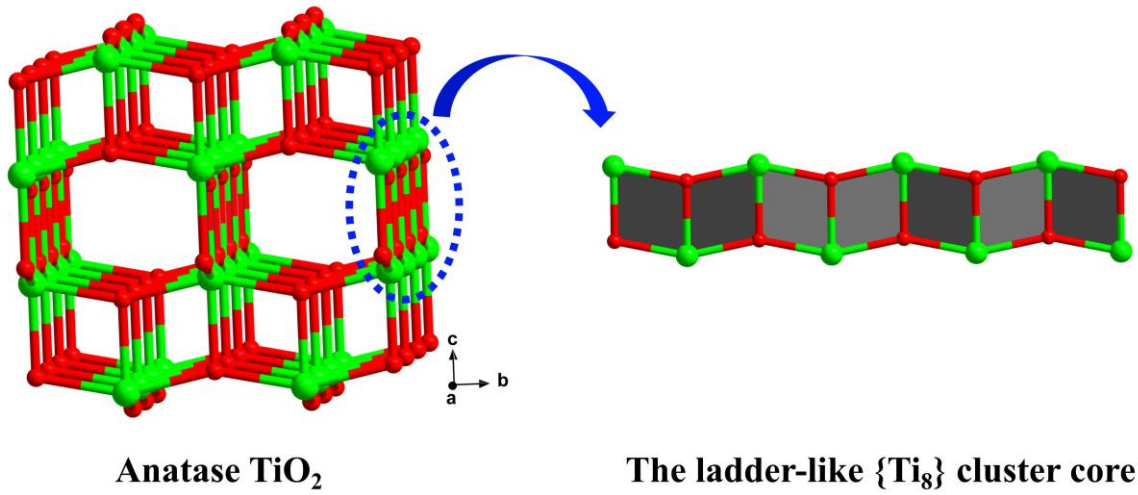

Figure S2. The ladder-like Ti_8 core in anatase TiO_2. Color codes: green Ti; red O.

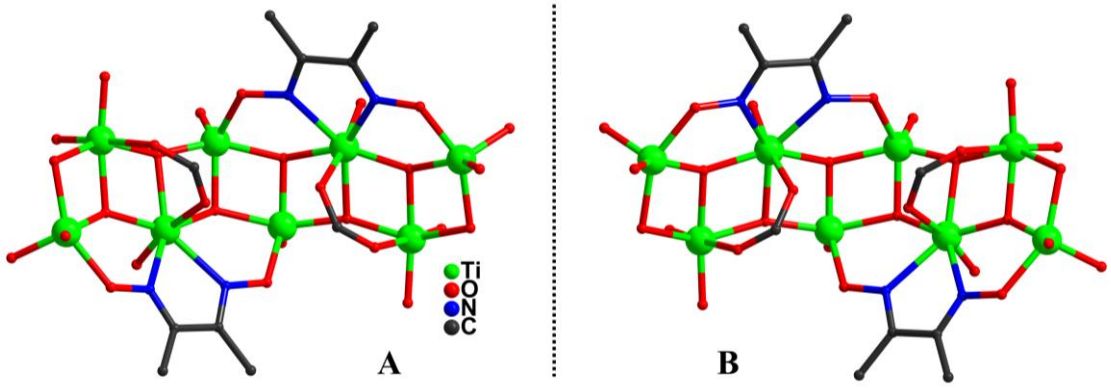

Figure S3. Crystal structure of **PTC-67** containing a pair of Ti_8 enantiomers (A and B). Color codes: green Ti; black C; red O; blue N.

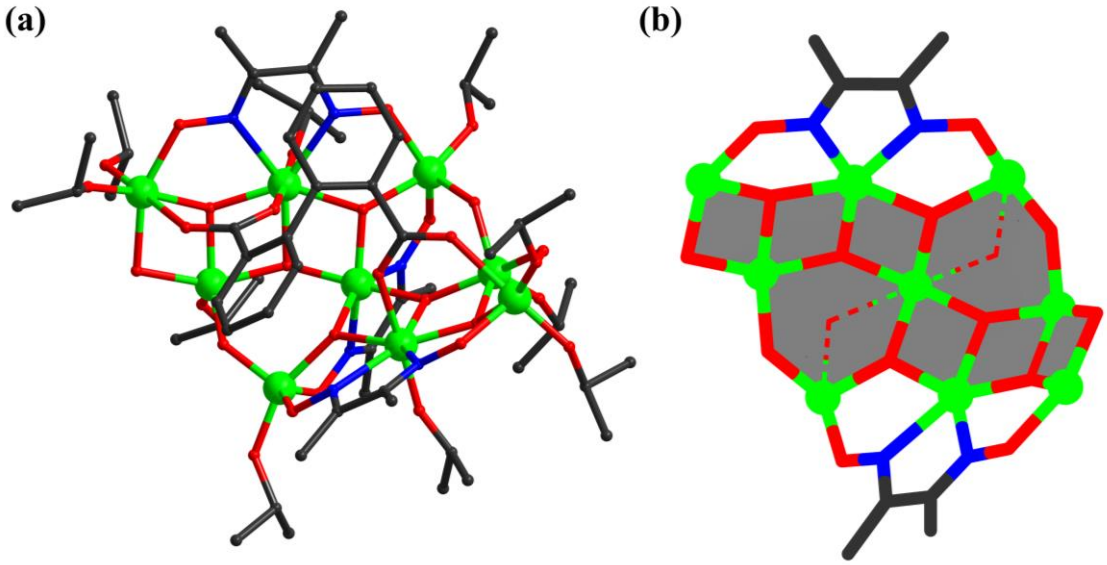

Figure S4. (a) The Ti_9 molecular cluster structure of **PTC-68**; (b) the Ti_9 cluster core structure of **PTC-68** containing two {DMG@Ti_5} units. All the H atoms are omitted for clarity. Color codes: green Ti; black C; red O; blue N.

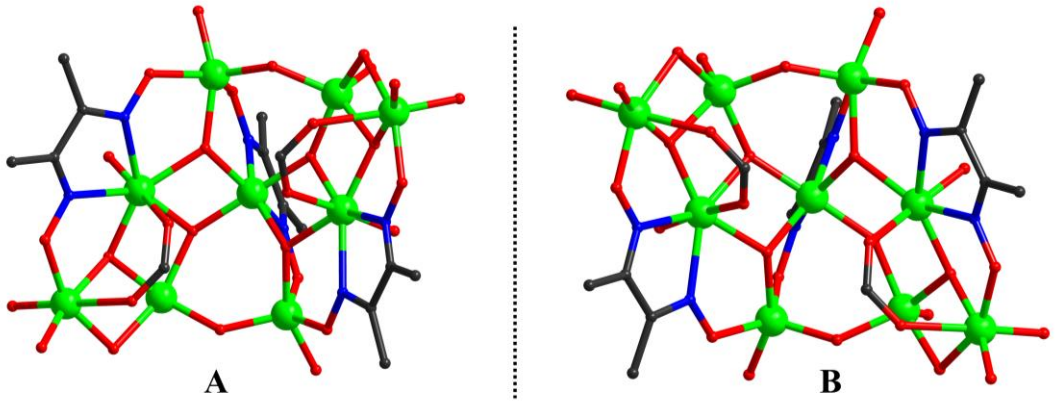

Figure S5. Crystal structures of **PTC-68A** and **PTC-68B** containing one of the pair of Ti_9 enantiomers (A and B) respectively. Color codes: green Ti; black C; red O; blue N.

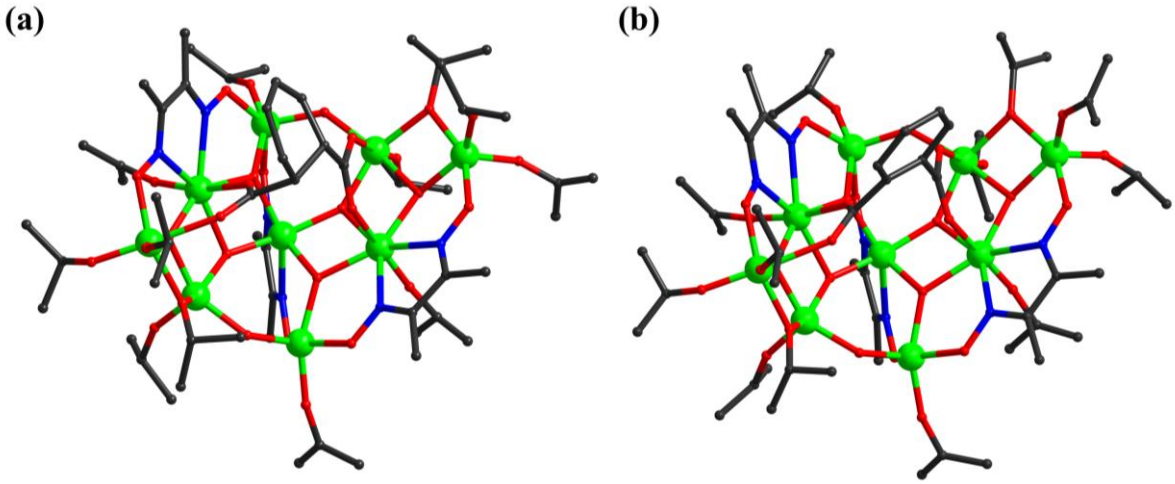

Figure S6. The Ti_9 molecular cluster structures of **PTC-69** (a) and **PTC-70** (b). All the H atoms are omitted for clarity. Color codes: green Ti; black C; red O; blue N.

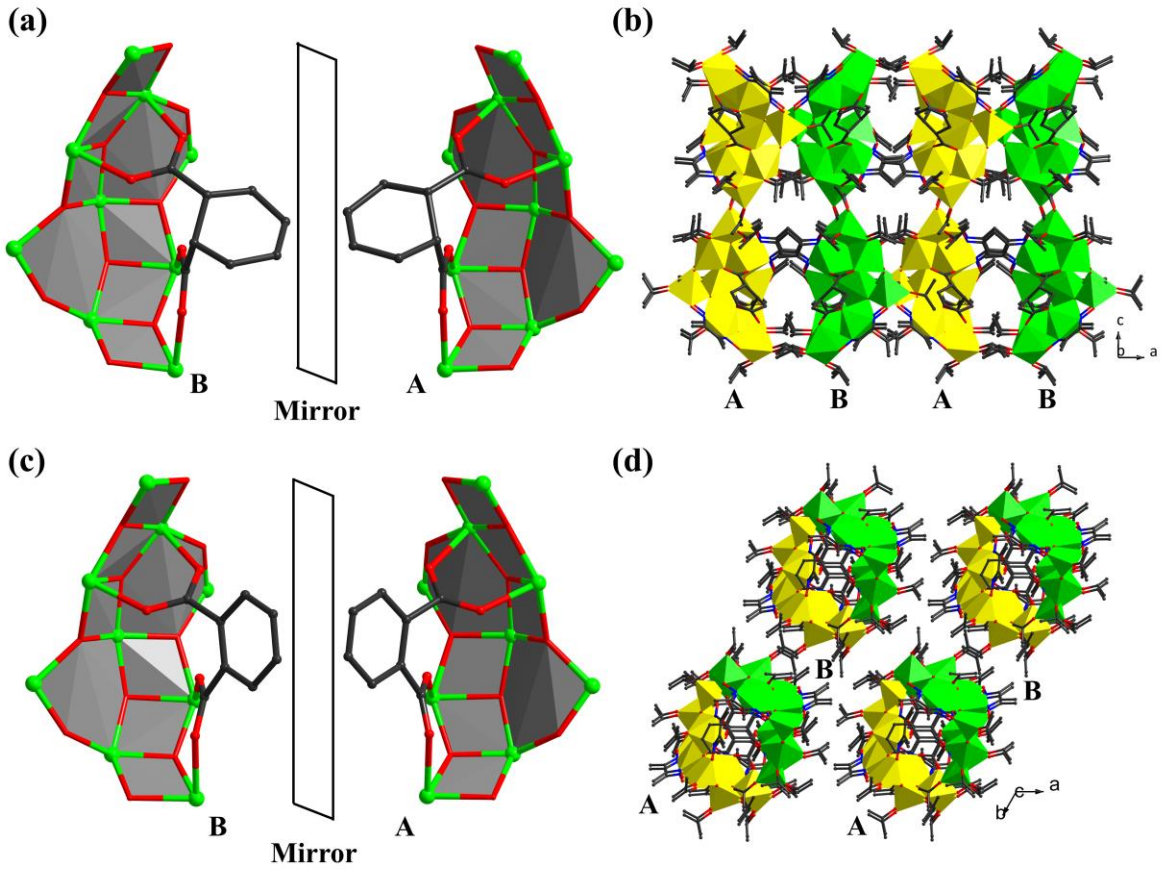

Figure S7. (a) A pair of Ti_9 enantiomers in **PTC-69** coordinated by CHDC ligand; (b) the packing structure of **PTC-69**; (c) a pair of Ti_9 enantiomers in **PTC-70** coordinated by PAC ligand; (d) the packing structure of **PTC-70**. All the H atoms are omitted for clarity. Color codes: green Ti; black C; red O; blue N.

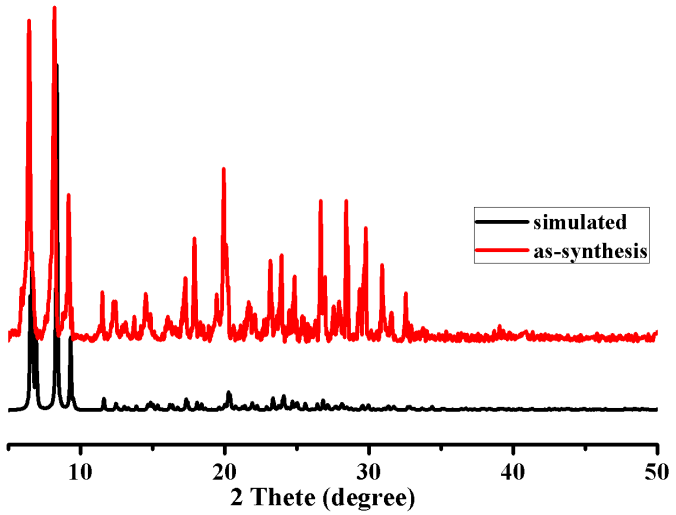

Figure S8. The simulated (black) and experimental (red) PXRD patterns of **PTC-67**.

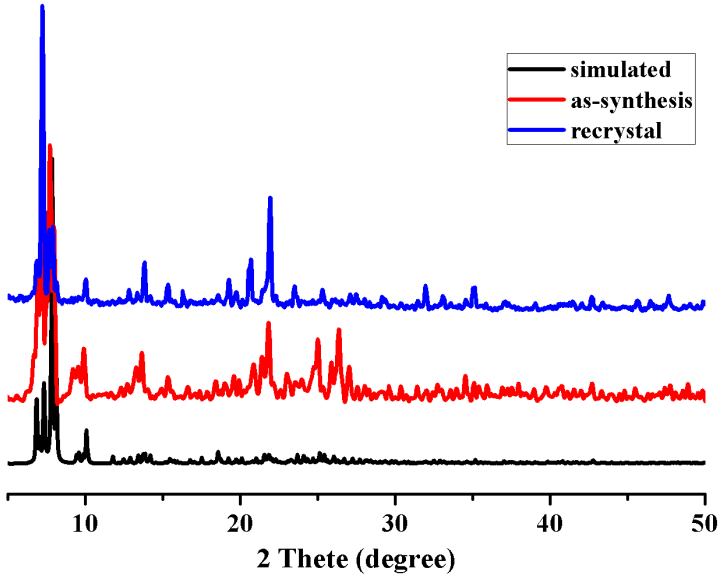

Figure S9. The simulated (black), experimental (red) and recrystallized (blue) PXRD patterns of **PTC-68**.

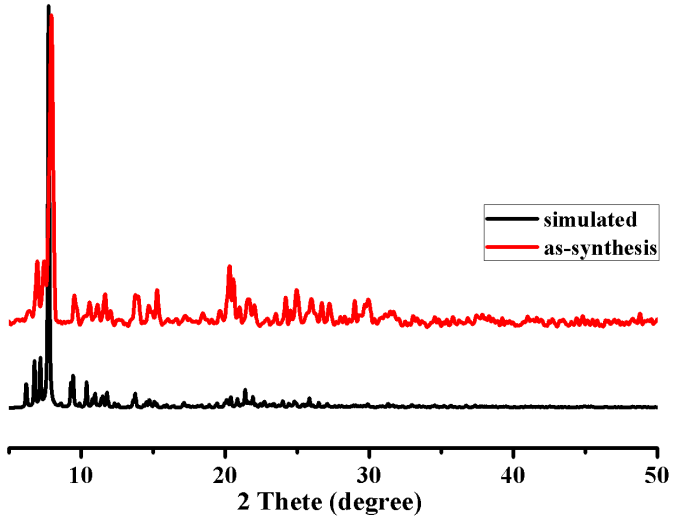

Figure S10. The simulated (black) and experimental (red) PXRD patterns of **PTC-69**.

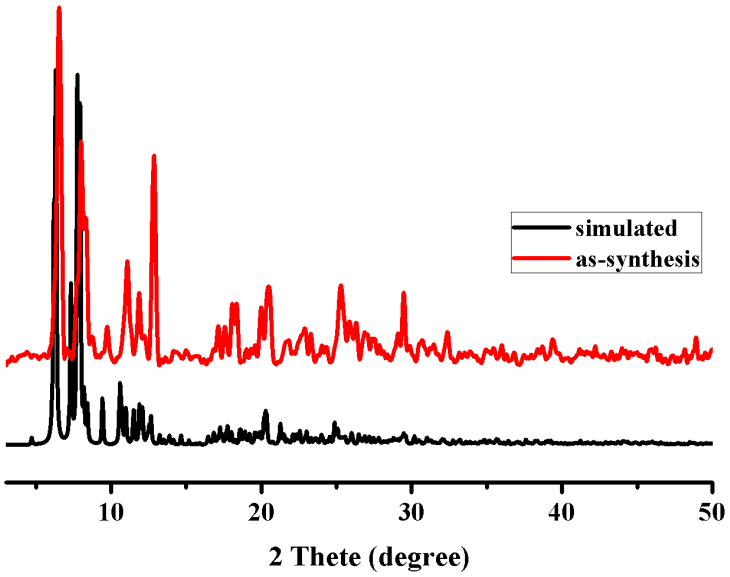

Figure S11. The simulated (black) and experimental (red) PXRD patterns of **PTC-70**.

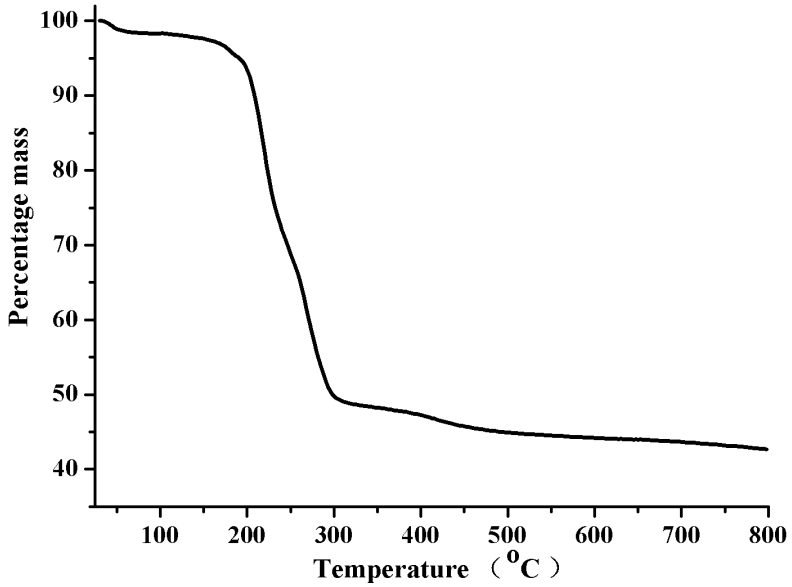

Figure S12. TGA curve of **PTC-67**.

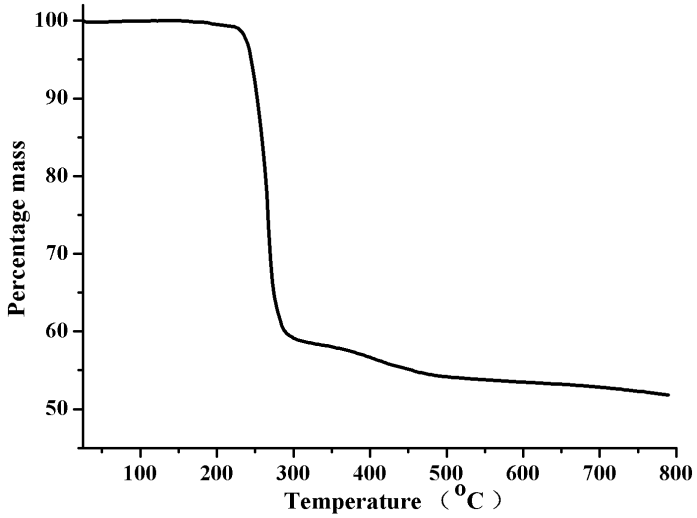

Figure S13. TGA curve of **PTC-68**.

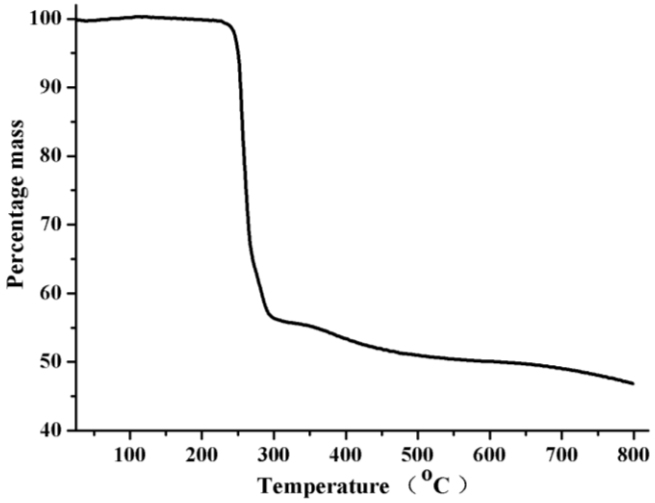

Figure S14. TGA curve of **PTC-69**.

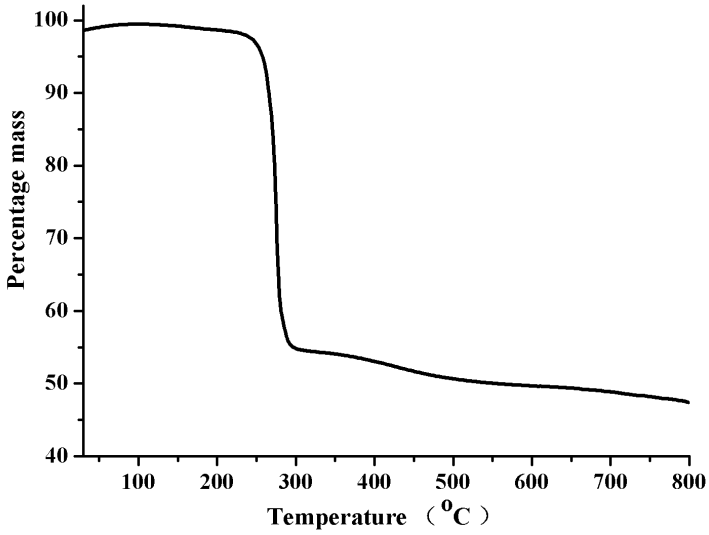

Figure S15. TGA curve of **PTC-70**.

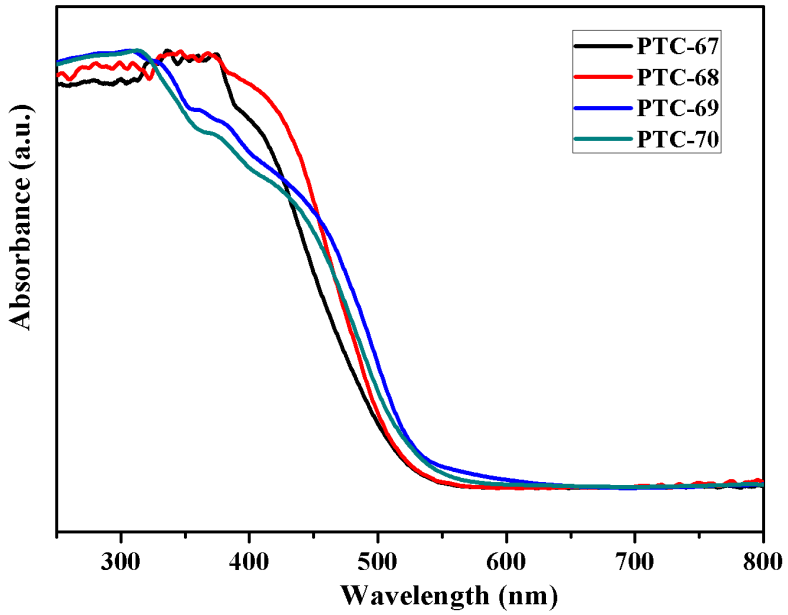

Figure S16. Solid state UV-vis absorption spectra of the obtained materials.

Table S1. Summary of bandgaps of the reported complexes.

No.	Complex	Bandgap	Stabilizing ligand	Bridging ligand
1	**PTC-67**	2.41	Dimethylglyoxime	Diphenic acid
2	**PTC-68**	2.36	Dimethylglyoxime	Diphenic acid
3	**PTC-69**	2.29	Dimethylglyoxime	Cis-4-cyclohexene-1,2-dicarboxylic acid
4	**PTC-70**	2.26	Dimethylglyoxime	Phthalic acid

4. General Methods for X-ray Crystallography

Crystallographic data of **PTC-68A** and **PTC-70** were collected on a Mercury single crystal diffractometer equipped with graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å) at room temperature. Crystallographic data of **PTC-67** and **PTC-69** were collected on a oxford XCalibur E CCD diffractometer equipped with graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å) at room temperature. While crystallographic data of **PTC-68B** and **PTC-68R** were collected on Supernova single crystal diffractometer equipped with graphite-monochromatic Cu Kα radiation (λ = 1.54178 Å) at 100 K and room temperature. The structures were solved with the dual-direct methods using *ShelxT* and refifined with the full-matrix least-squares technique based on F^2 using the *SHELXL*-2014[2]. 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 1973835-1973840 for **PTC-67** to **PTC-70**. 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-67** to **PTC-70**. More details are given in **Tables S3** and **S4**.

No.	Complex	Forumla	Sp. Gr.	a(Å)	b(Å)	c(Å)	α (°)	β(°)	(°)	V(Å^3)	Flack
1.	**PTC-67**	$[Ti_8O_6(DMG)_2(DPC)(O^iPr)_{14}] \cdot (IPA)$	*P2/n*	18.9555(7)	12.7596(6)	19.0307(6)	90	91.243(4)	90	4601.8(3)	None
2.	**PTC-68A**	$Ti_9O_8(DMG)_3(DPC)(O^iPr)_{12}$	$P2_12_12_1$	13.686(2)	25.029(4)	25.781(5)	90	90	90	8831(3)	0.207(4)
3.	**PTC-68B**	$Ti_9O_8(DMG)_3(DPC)(O^iPr)_{12}$	$P2_12_12_1$	13.4809(5)	24.6175(6)	25.6441(7)	90	90	90	8510.4(4)	-0.031(4)
4.	**PTC-68R**	$Ti_9O_8(DMG)_3(DPC)(O^iPr)_{12}$	$P2_12_12_1$	13.6676(2)	25.0164(4)	25.7877(3)	90	90	90	8817.2(2)	0.093(9)
5.	**PTC-69**	$Ti_9O_8(DMG)_3(CHDC)(O^iPr)_{12}$	*Pbca*	17.0355(4)	19.0161(7)	52.224(2)	90	90	90	16917.8(10)	None
6.	**PTC-70**	$Ti_9O_8(DMG)_3(PAC)(O^iPr)_{12}$	*P*-1	16.191(12)	16.550(12)	18.984(12)	93.273(10)	95.531(6)	119.230(9)	4387(5))	None

Table S3. Crystallographic data and structure refinement summary for **PTC-67** and **PTC-68**.

	PTC-67	**PTC-68A**	**PTC-68B**	**PTC-68R**
Empirical formula	$C_{67}H_{126}N_4O_{29}Ti_8$	$C_{62}H_{110}N_6O_{30}Ti_9$	$C_{62}H_{110}N_6O_{30}Ti_9$	$C_{62}H_{110}N_6O_{30}Ti_9$
M_r	1834.70	1850.65	1850.65	1850.65
T/K	293(2)	293(2)	100.0(3)	293(2)
Crystal system	Monoclinic	Orthorhombic,	Orthorhombic,	Orthorhombic,
Space group	*P*2/*n*	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	18.9555(7)	13.686(2)	13.4809(5)	13.6676(2)
b/Å	12.7596(6)	25.029(4)	24.6175(6)	25.0164(4)
c/Å	19.0307(6)	25.781(5)	25.6441(7)	25.7877(3)
α (°)	90	90	90	90
β (°)	91.243(4)	90	90	90
γ (°)	90	90	90	90
V/Å^3	4601.8(3)	8831(3)	8510.4(4)	8817.2(2)
Z	2	4	4	4
Dc/mg m^{-3}	1.281	1.392	1.444	1.394
μ/mm $^{-1}$	0.725	0.843	7.469	0.844
indep reflns [I >2σ(I)]	8088	17301	16847	15338
F(000)	1860	3848	3848	3848
GOF	1.095	1.045	1.072	1.035
CCDC No.	1973835	1973836	1973837	1973838
R_1[a], wR_2[b] [I >2σ(I)]	0.0946, 0.2823	0.0618, 0.1646	0.0523, 0.1251	0.0486, 0.1283
R_1[a], wR_2[b] (all data)	0.1116, 0.3003	0.0637, 0.1669	0.0651, 0.1370	0.0561, 0.1333

[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-69** and **PTC-70**.

	PTC-69	**PTC-70**
Empirical formula	$C_{56}H_{110}N_6O_{30}Ti_9$	$C_{56}H_{106}N_6O_{30}Ti_9$
M_r	1778.30	1774.26
T/K	293(2)	293(2)
Crystal system	Orthorhombic	Triclinic
Space group	*Pbca*	*P*-1
a/Å	17.0355(4)	16.191(12)
b/Å	19.0161(7)	16.550(12)
c/Å	52.224(2)	18.984(12)
α (°)	90	93.273(10)
β (°)	90	95.531(6)
γ (°)	90	119.230(9)
V/Å^3	16917.8(10)	4387(5)
Z	8	2
Dc/mg m^{-3}	1.398	1.344
μ/mm^{-1}	0.877	0.845
indep reflns [I >2σ(I)]	40891	15391
F(000)	7424	1844
GOF	1.042	1.083
CCDC No.	1973839	1973840
$R_1{}^a$, $wR_2{}^b$ [I >2σ(I)]	0.1088, 0.2903	0.1035, 0.2927
$R_1{}^a$, $wR_2{}^b$ (all data)	0.1392, 0.3093	0.1258, 0.3141

$^aR_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. $^bwR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(F_o^2)]^{1/2}$.

6. References

(1) W. W. Wendlandt, H. G. Hecht, *Reflectance Spectroscopy*. Interscience: New York, 1966; p593.

(2) G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.,* 2015, **71**, 3.