

Supplementary Information

***Cu₄Ti₄-oxo clusters functionalized by in situ generated
2,2'-biphenolate ligands from oxidative coupling of phenols***

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Experimental Section

Materials and Instrumentation.

All the reagents and solvents employed were purchased commercially and used as received without further purification. $\text{Ti}(\text{OiPr})_4$ was purchased from Adamas, while 2,2'-biphenol, phenol, p-cresol and propanoic acid were acquired from Sinopharm Chemical Reagent Beijing. Powder X-ray diffraction (PXRD) analyses data were mounted on a Rigaku Mini Flex II diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) collected with the angular range (2θ) from 3° to 50° at 298 K. Fourier transform infrared spectroscopy (FT-IR) data were collected on a PerkinElmer Spectrum 100 FT-IR Spectrometer using KBr pellets ranging from 400 cm^{-1} to 4000 cm^{-1} . Proton nuclear magnetic resonance ($^1\text{H NMR}$) spectra were recorded on a Bruker AVANCE III HD400 (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane ($\delta = 0.00$ ppm). $^1\text{H NMR}$ splitting patterns are designated as singlet (s), doublet (d), m (multiplet), etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m). UV-vis diffuse reflectance data were recorded under ambient conditions using a powder sample with BaSO_4 as a standard (100% reflectance) on a PerkinElmer Lambda-950 UV spectrophotometer and scanned in the range 200–850 nm. The absorption data are calculated from the Kubelka-Munk function, $(F(R) = (1-R)^2/2R)$,^[1] where R representing the reflectance. Elemental analysis (C and H) was carried out on a Vario Micro E III analyzer. ICP analysis was conducted by using Inductively Coupled Plasma MS spectrometer (Agilent 7700). X-ray photoelectron spectroscopy (XPS) analysis was carried out on ESCALAB Xi+ XPS system (Thermo Fisher Scientific) with $\text{Al K}\alpha$ X-ray radiation (1486.6 eV). Electron Paramagnetic Resonance (EPR) spectra were recorded on a Bruker ER-420 spectrometer with a 100 kHz magnetic field at room temperature. Gas chromatography and mass spectrometry (GC-MS) was carried out on MSD 5977B (Agilent Technologies, 7820A GC System).

Synthesis of PTC-331: copper acetate monohydrate (0.20 g, 1.0 mmol) was dissolved in a solution of 5 mL phenol, and then propanoic acid (100 μL) and $\text{Ti}(\text{OiPr})_4$ (0.50 mL, 1.5 mmol) were added to the mixed solution. The resulted solution was heated at 80°C for about one week. After cooled to the room temperature, red crystals of **PTC-331** were obtained (yield: $\sim 39\%$ based on Ti). Elemental analysis calcd (%) for $\text{C}_{105}\text{H}_{81}\text{Cu}_4\text{O}_{21.5}\text{Ti}_4$ (MW 2132.41): C 59.14, H 3.82; found: C 58.92, H 3.90.

Synthesis of PTC-332: copper acetate monohydrate (0.20 g, 1.0 mmol) was dissolved in a mixed solution of 4 mL p-cresol and 2 mL phenol, then propanoic acid (100 μL) and $\text{Ti}(\text{OiPr})_4$ (0.50 mL, 1.5 mmol) were added to the mixed solution. The resulted solution was heated at 80°C for about one week. After cooled to the room temperature, red crystals of **PTC-332** were obtained (yield: $\sim 33\%$ based on Ti). Elemental analysis calcd (%) for $\text{C}_{84}\text{H}_{72}\text{Cu}_4\text{O}_{16}\text{Ti}_4$ (MW 1783.17): C 56.58, H 4.07; found: C 56.52, H 4.40.

Synthesis of PTC-333: A mixture of 2,2'-biphenol (0.93 g, 5.0 mmol) and copper acetate monohydrate (0.20 g, 1.0 mmol) was dissolved in a mixed solution of 4 mL acetonitrile and 2 mL n-propanol, and then 0.5 mL (1.5 mmol) $\text{Ti}(\text{OiPr})_4$ was added to the mixed solution. The resulted solution was heated at 80°C for about one day. After cooled to the room temperature, red block crystals of **PTC-333** were obtained (yield: $\sim 49\%$ based on Ti). Elemental analysis calcd (%) for $\text{C}_{82}\text{H}_{66}\text{CuO}_{16}\text{Ti}_4\text{N}_5$ (MW 1632.4395): C 60.33, H 4.08, N 4.29; found: C 60.07, H 4.11, N 3.68.

X-ray Crystallographic Analyses: Crystallographic data of **PTC-331** was collected on a Supernova single crystal diffractometer equipped with graphite-monochromatic Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) at about 100 K. The structure determination of **PTC-332** was performed on a Synergy-R-Mo equipped with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at about 100 K. The structure determination of **PTC-333** was performed on a Hybrid Pixel Array detector equipped with Ga K α radiation ($\lambda = 1.3405 \text{ \AA}$) at about 100 K. Their structures were solved with direct methods using SHELXS-2014 and refined with the full-matrix least-squares technique based on F^2 using SHELXL-2014.^[2] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically, riding on the concerned atoms, and refined with fixed thermal factors. All absorption corrections were performed using the multi-scan program. The diffused electron densities resulting from these residual cations and solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated.^[3] CCDC 2211330-2211332 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Supporting Figures:

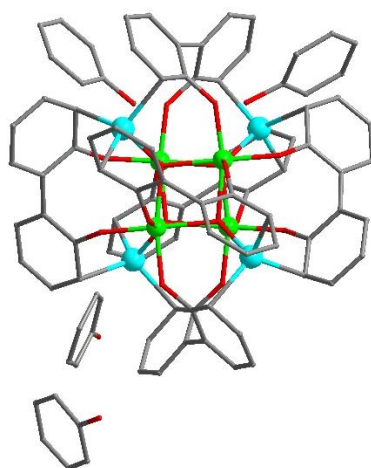


Fig. S1 The crystal structure of **PTC-331**. Atom color codes: green Ti; red O; wathet Cu; gray C. H atoms have been omitted for clarity.

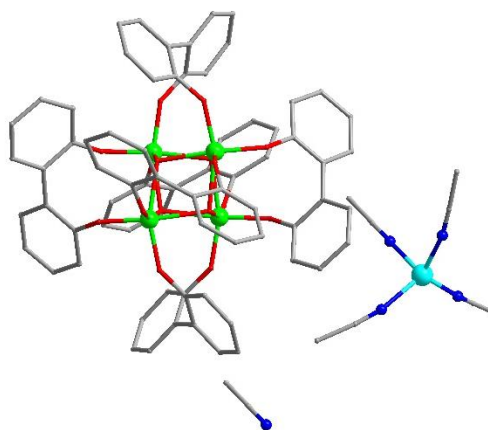


Fig. S2 The crystal structure of **PTC-333**. Atom color codes: green Ti; red O; wathet Cu; dark blue N; gray C. H atoms have been omitted for clarity.

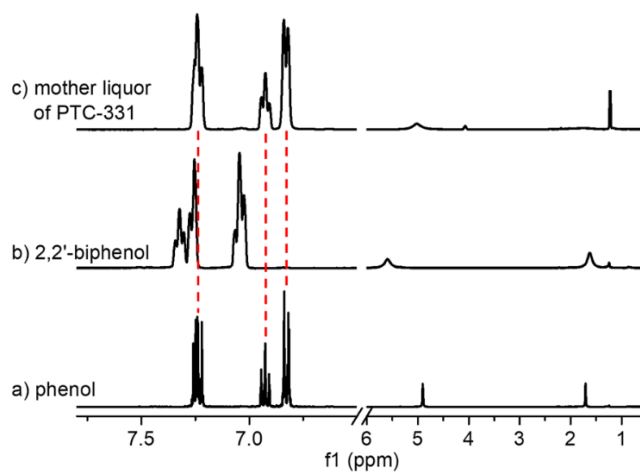


Fig. S3 ¹H NMR spectrum of phenol (a), 2,2'-biphenol (b) and mother liquor of **PTC-331**(c) in CDCl₃.

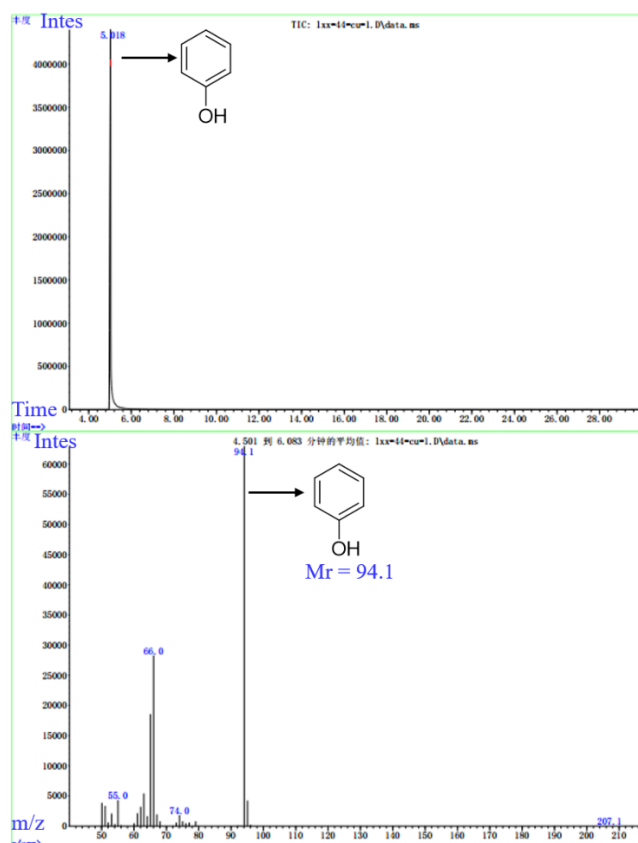


Fig. S4 The GC-MS spectra of reaction mixtures for PTC-331 before $\text{Ti}(\text{OiPr})_4$ and propionic acid were added. The reaction mixture tested was purified by column chromatography. The retention time for phenol is 5.018 min. Calculated m/z value for phenol is 94.1.

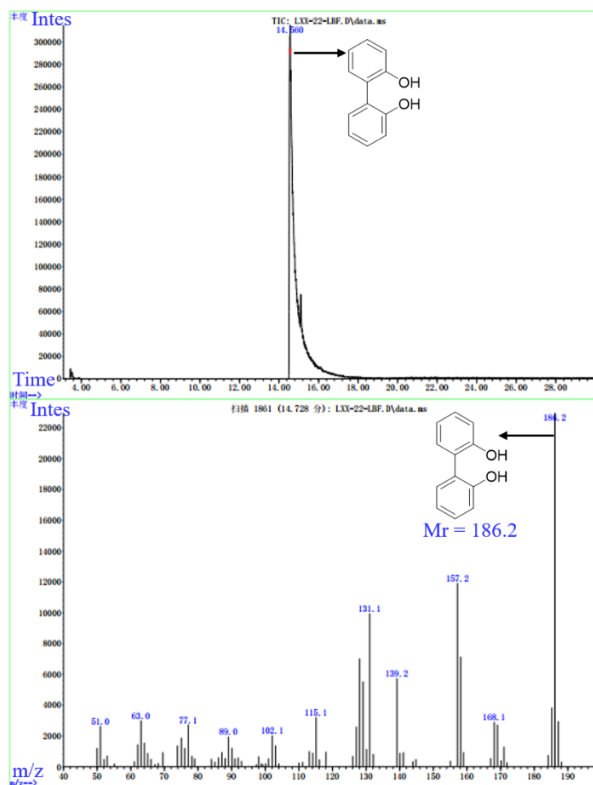


Fig. S5 The GC-MS spectra of $\text{H}_2\text{L1}$ ($\text{H}_2\text{L1}$ is 2,2'-biphenol). The retention time for $\text{H}_2\text{L1}$ is 14.560 min. Calculated m/z value for $\text{H}_2\text{L1}$ is 186.2.

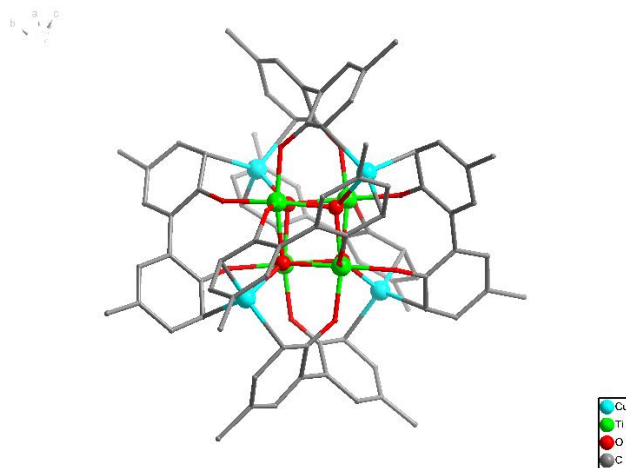


Fig. S6 The crystal structure of **PTC-332**. Atom color codes: green Ti; red O; wathet Cu; gray C. H atoms have been omitted for clarity.

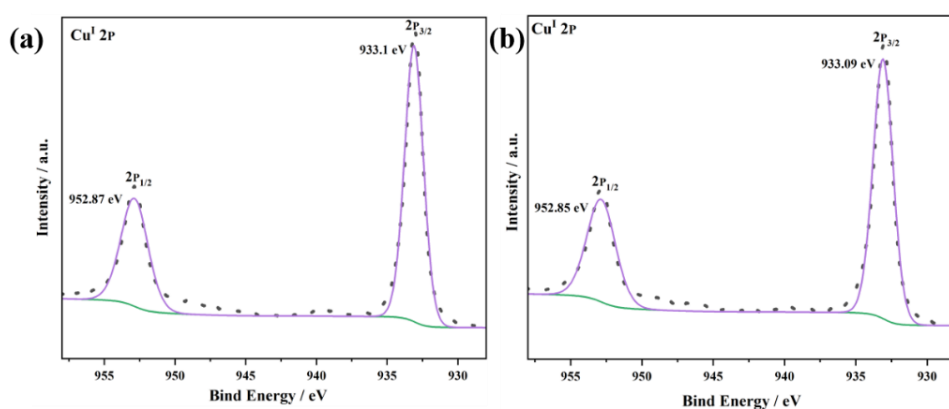
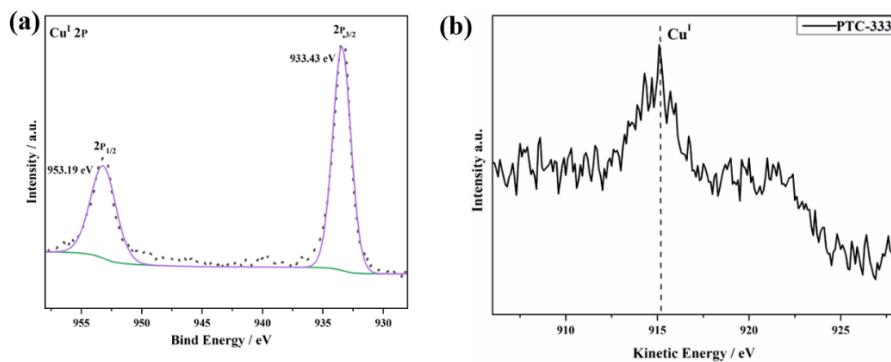


Fig. S7 Cu^+ 2P XPS spectra of **PTC-331** (a) and **PTC-332** (b).



Values of $\text{Cu}2p_{3/2}$, CuLMM and Auger parameter of **PTC-333**

Sample	$\text{Cu}2p_{3/2}$ Peak BE	CuLMM Peak KE	Auger parameter
PTC-333	933.43 eV	915.10 eV	1848.53 eV

Fig. S8 Cu 2P XPS spectra of **PTC-333** (a), Cu *LMM* XPS spectra of **PTC-333** (b) and values of $\text{Cu}2p_{3/2}$, Cu *LMM* and Auger parameter of **PTC-333** (Table).

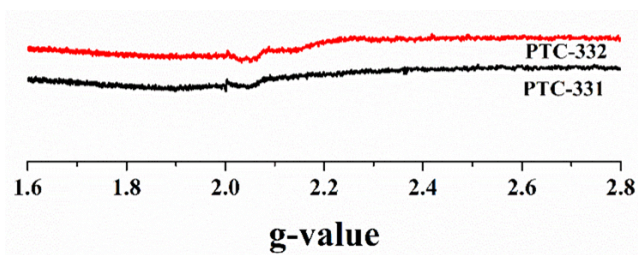


Fig. S9 EPR Spectra of Cu(I) in **PTC-331** and **PTC-332**.

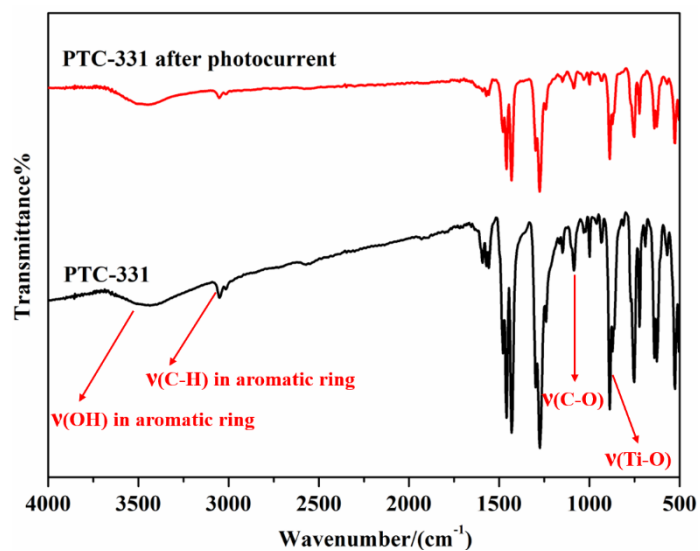


Fig. S10 FT-IR spectra of **PTC-331**.

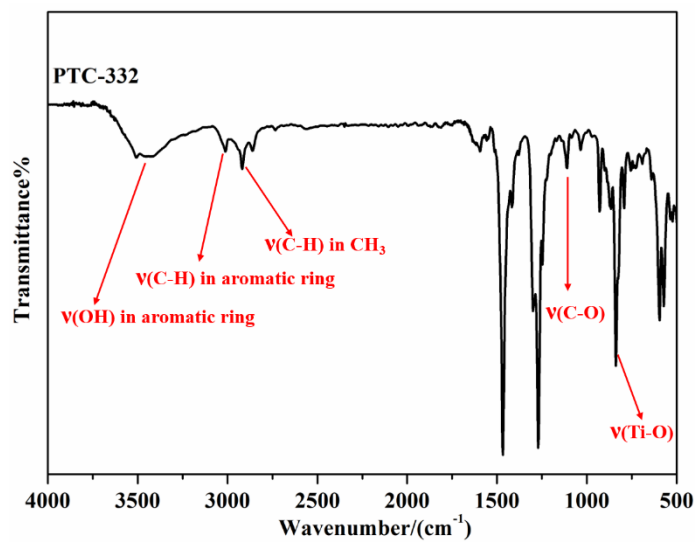


Fig. S11 FT-IR spectra of **PTC-332**.

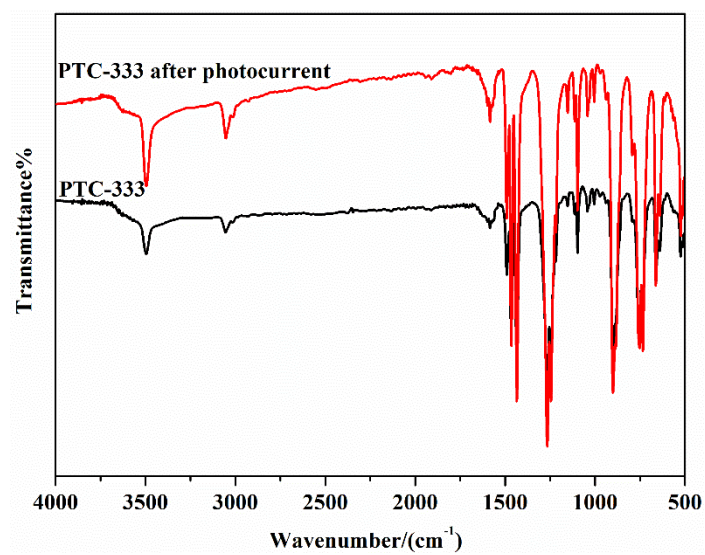


Fig. S12 FT-IR spectra of PTC-333.

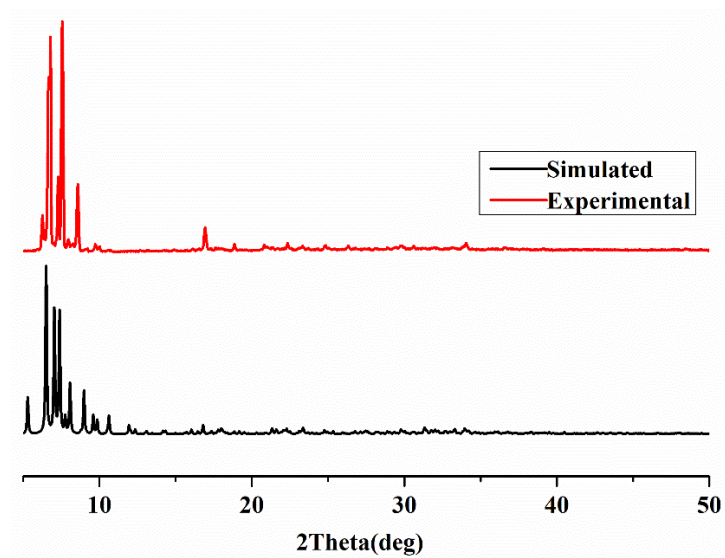


Fig. S13 PXRD spectra for PTC-331.

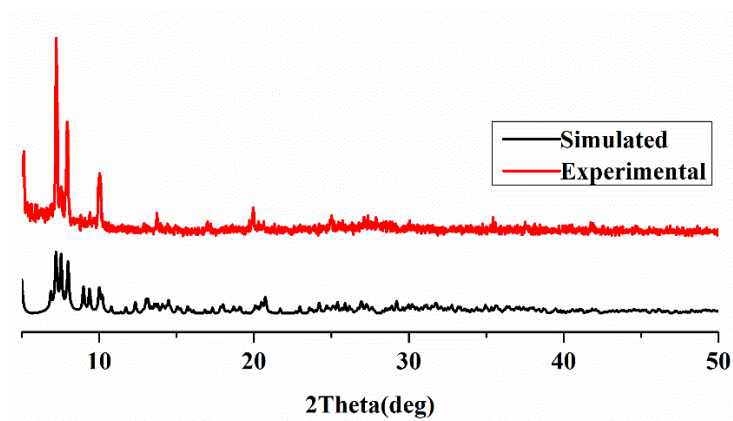


Fig. S14 PXRD spectra for PTC-332.

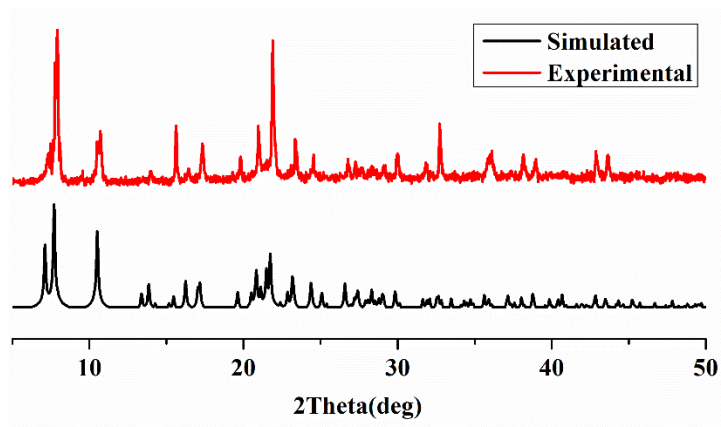


Fig. S15 PXRD spectra for **PTC-333**.

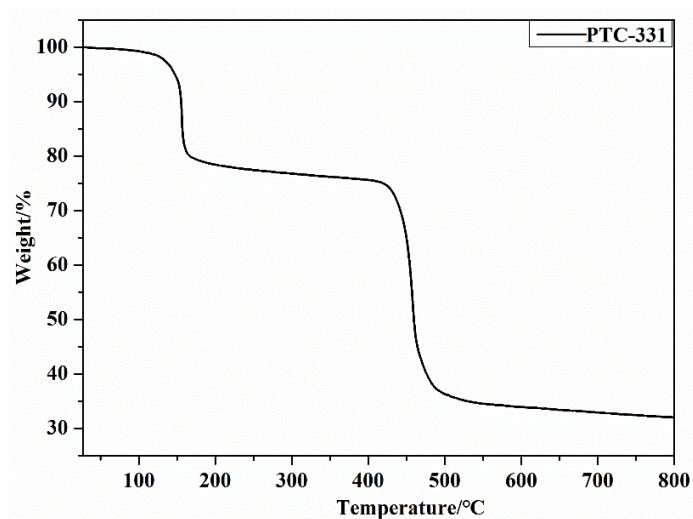


Fig. S16 The TGA spectra of **PTC-331**.

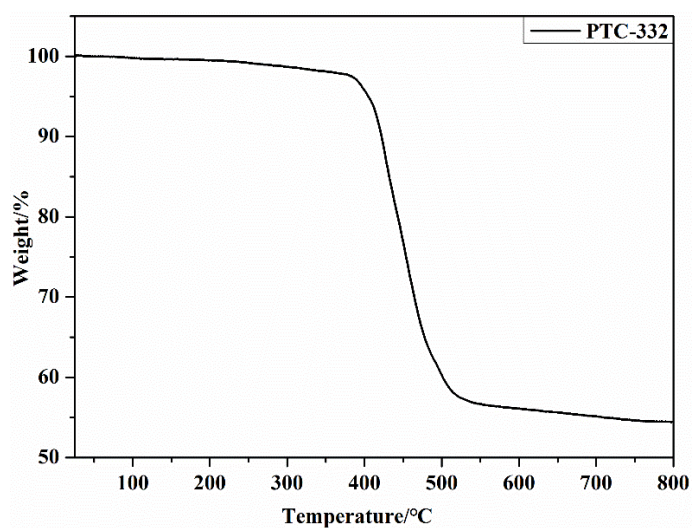


Fig. S17 The TGA spectra of **PTC-332**.

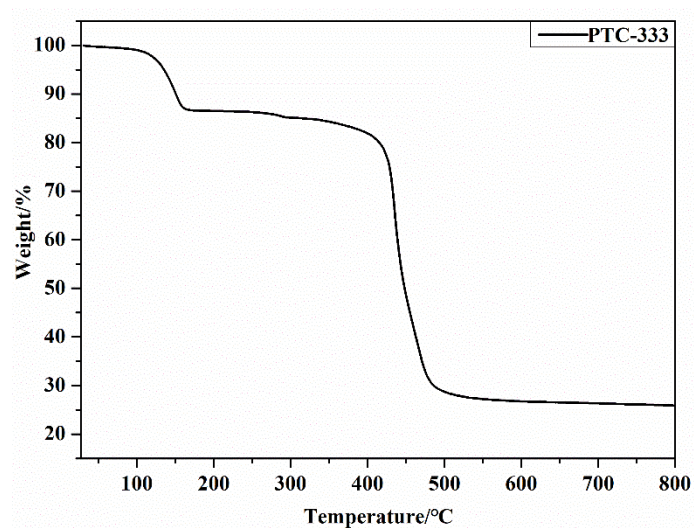


Fig. S18 The TGA spectra of **PTC-333**.

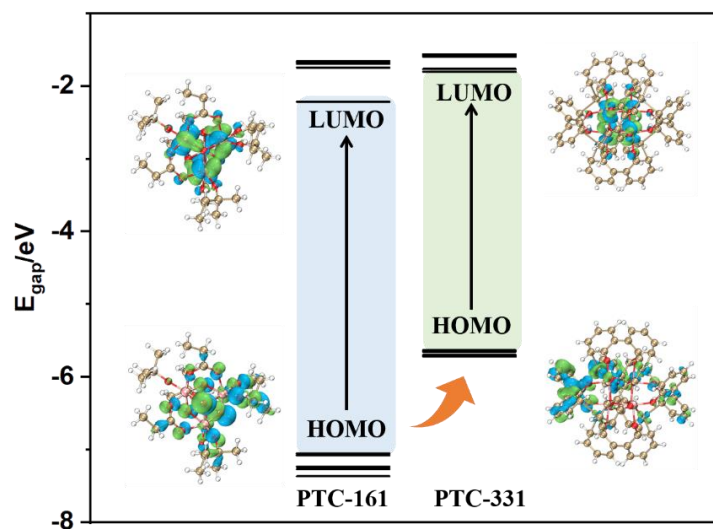


Fig. S19 The HOMO-LUMO gaps of **PTC-331** and **PTC-161**.

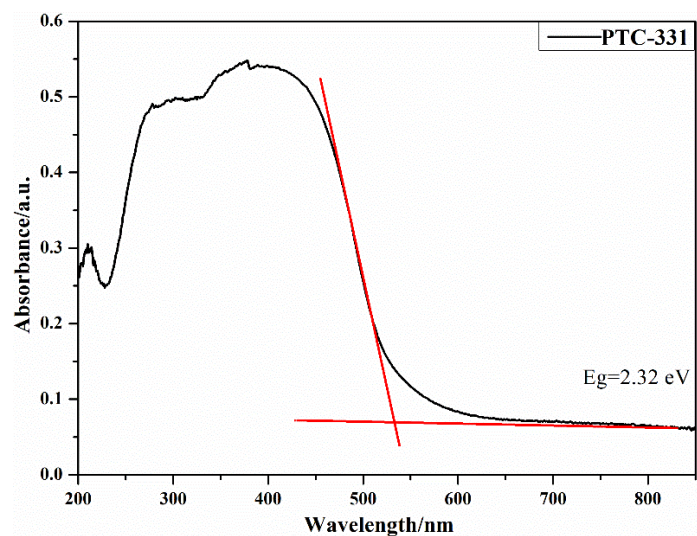


Fig. S20 The solid-state absorption spectra of **PTC-331**.

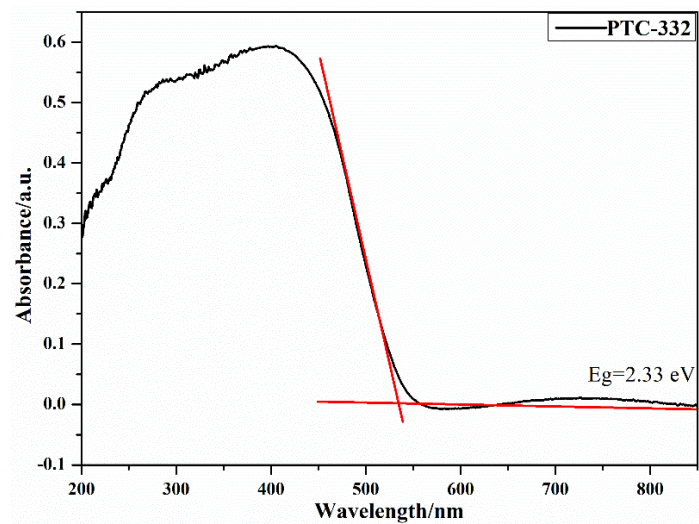


Fig. S21 The solid-state absorption spectra of **PTC-332**.

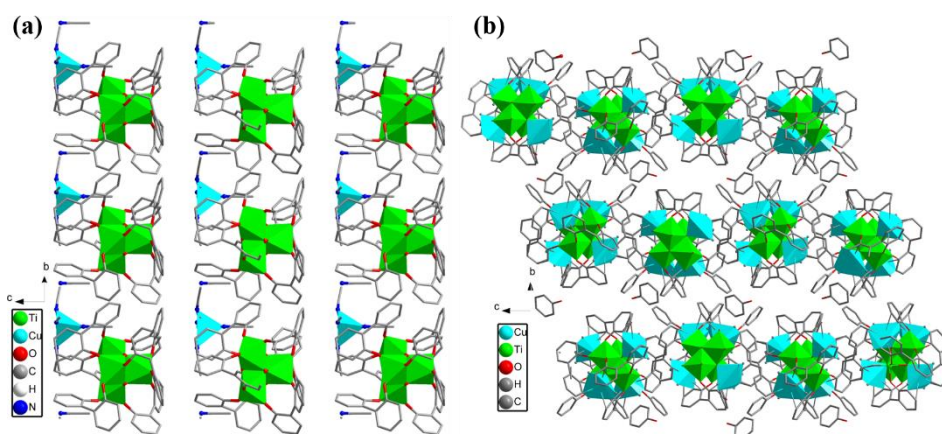


Fig. S22 Packing structure of (a) **PTC-333**, (b) **PTC-331**.

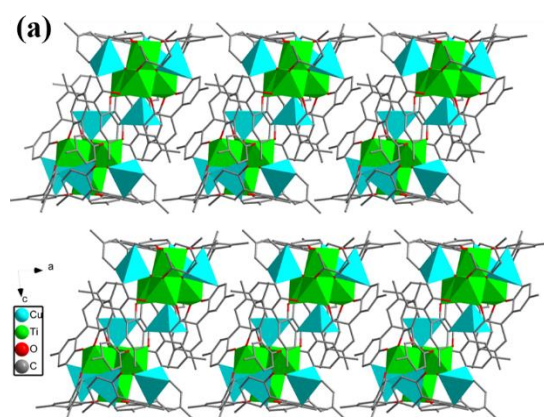


Fig. S23 Packing structure of (a) **PTC-332**.

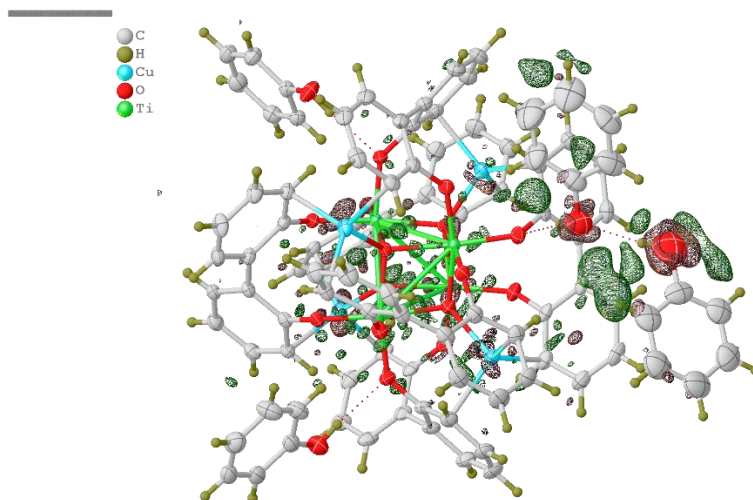


Fig. S24 Ellipsoid model and electron residual density map of compound PTC-331.

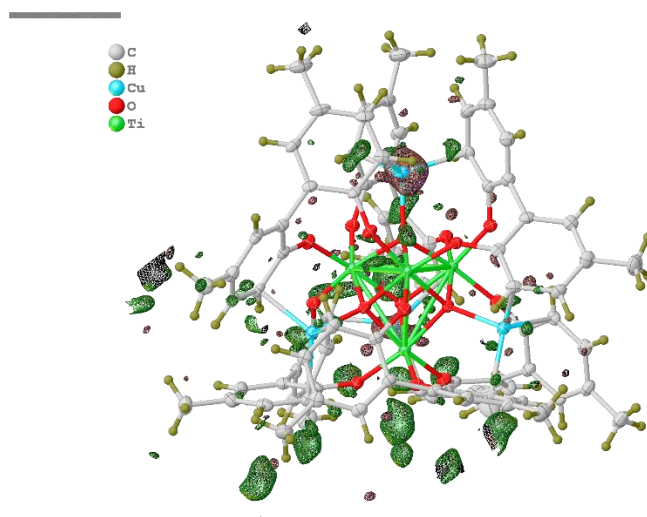


Fig. S25 Ellipsoid model and electron residual density map of compound PTC-332.

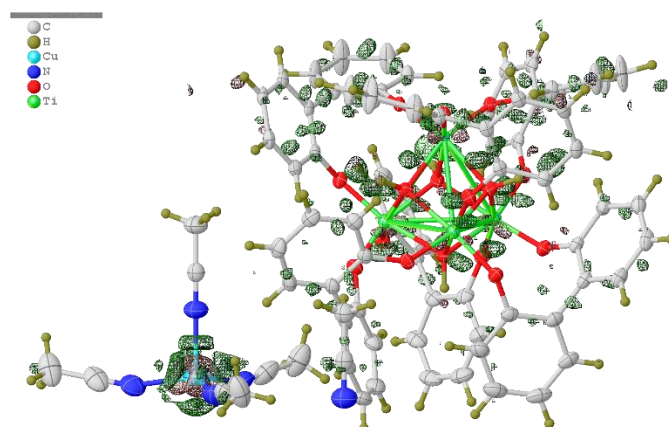


Fig. S26 Ellipsoid model and electron residual density map of compound PTC-333.

Supporting Table:

Tab. S1 The summary of ICP-AES results

	Ti	Cu	Ti: Cu	Calcu(Ti:Cu)
PTC-331	11.40 wt%	15.25 wt%	1	1
PTC-332	12.07 wt%	15.22 wt%	1.05	1
PTC-333	12.41 wt%	4.40 wt%	3.75	4

References:

[1] W. W. Wendlandt and H. G. Hecht, *Anal. Chim. Acta*, 1967, **39**, 408-408.

[2] G. M. Sheldrick, *Acta Cryst. C* 2015, **71**, 3-8.

[3] Spek, A. L. PLATON, a multipurpose crystallographic tool; Utrecht University: 2001.