Electronic Supplementary Material (ESI) for New Journal of Chemistry.

# *Supplementary Information(SI)*

# 1. Materials and Instrumentation

Materials: CuCl was purchased from Sinopharm Chemical Reagent, isopropanol, N,N-Dimethylformamide (DMF), isonicotinic acid (HINA), Phosphorous acid and titanium tetraisopropanolate ($Ti(O^iPr)_4$) were purchased from General Reagent. All the chemicals were commercially available and were used without further purification.

**Powder X-ray Diffraction (PXRD):** PXRD was recorded on a Haoyuan DX-2700B diffractometer equipped with monochromatized Cu-Kα ($\lambda$ = 1.5418 Å) radiation in the range of $3° \leq 2\theta \leq 45°$, with a scanning rate of 0.03° $s^{-1}$.

**Element Analyses:** Element analyses for P, Ti and Cu were performed on a Leeman Prodigy Plus inductivity-coupled plasma Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and C, N and H content were determined by VARIDEL III elemental Analyzer.

**Thermogravimetric Analysis (TGA):** Thermogravimetric analysis was performed on a PerkinElmer TGA 8000 Thermogravimetric Analyzer under $N_2$ atmosphere from 50 to 800 °C with a heating rate of 10 °C/min.

**Fourier-transform infrared (FT-IR) spectroscopy:** Fourier-transform infrared (FT-IR) spectra was performed on Nicolet iS50 FT-IR Spectrometer in the range of 500-4000 $cm^{-1}$.

**Solid-state UV−vis−NIR absorption spectroscopy:** All compounds were recorded at room temperature using a powder sample with $BaSO_4$ as a standard on UV3600 UV-vis-NIR spectrometer.

**Density functional theory (DFT) calculations:** Density functional theory (DFT) calculations were performed with the Gaussian 16 package. The geometries of the clusters were optimized using the B3LYP-D3(BJ) exchange-correlation functional with the 6-311G* basis set for H, C, O, N, P and SDD pseudo potential basis set for Ti. Except H, the positions of all other atoms were frozen. The initial geometries of clusters were taken from the corresponding crystal structure data. No symmetry constraints were used in the optimization. The DOS (density of states) analysis was performed by Multiwfn code[S1].

**Photoelectrochemistry (PEC) measurements:** All photoelectrochemistry measurements were carried out using a CHI660 electrochemical workstation using a three-electrode system, with the sample coated indium tin oxide (ITO) glass as the working electrode, a Pt wire as the counter electrode, and a saturated Ag/AgCl electrode as the reference electrode. The working electrode was ITO glass plates coated with a cluster-slurry and the electrolyte was $Na_2SO_4$ (0.5 M) aqueous solution. For the preparation of working photo-electrodes, the crystal sample (about 5 mg) was dissolved in 0.9 mL ethanol and 0.1 mL 5 Wt% Nafion mixed solution, which was then dropped onto a precleared ITO glass (1×2 $cm^2$, 50 $\Omega\cdot cm^{-2}$). The working photoelectrode was obtained after evaporation. The Mott-Schottky plots were also measured over an alternating current frequency of 1000 Hz and 1500 Hz. Electrochemical impedance spectra (EIS) measurements were recorded over a frequency range of 100 kHz-0.1 Hz. The photocurrent tests were carried out with a 300 W xenon lamp.

# 2. Synthesis of ligands and compound 1-4.

**Preparation of 3-[(4-Pyridinylmethylene) amino] benzoic acid (3-Hpyca):** The ligand 3-Hpyca was synthesized according to the literature [S2]. First, 40 mL of methanol solution of 4-pyridinecarboxaldehyde (1.88 mL, 20.0 mmol) was drop-wise added to a 25 mL methanol solution of 3-aminobenzoic acid (2.74 g, 20.0 mmol). Then, the mixture was refluxed for about 3 h. The acquired solid product was filtrated and washed with methanol before drying in air. Yield: ~80% (1.54 g). $^1$H NMR (400 MHz, DMSO): δ= 8.77-8.74 (m, 3H), 7.88-7.83 (m, 4H), 7.57 (d, 2H) ppm.

**Preparation of 4-[(4-Pyridinylmethylene) amino] benzoic acid (4-Hpyca):** The ligand 4-Hpyca was synthesized according to the literature[S3]. 4-pyridinecarboxaldehyde (1.18 g, 11.02 mmol) was dissolved in methanol (50 mL) and the mixture stirred at 75 °C. 4-aminobenzoic acid (1.51 g, 11.02 mmol) and 4-toluene sulfonic acid (15 mg) were added. After continuous stirring for 12 h, yellow precipitate formed and was filtered and washed with methanol (yield ~90%).$^1$H NMR (400 MHz, DMSO): δ=7.33 (m, 2H), 7.58 (m, 1H), 7.98 (m, 2H), 8.32 (m, 1H), 8.72 (m, 2H), 9.08 (m, 1H).

**Synthesis of 1**: Phosphorous acid (10.7 mg, 0.13 mmol), isonicotinic acid (16 mg, 0.13 mmol) and isopropanol (1.5 mL) were added to the glass vial and soniced at room temperature, then $Ti(O^iPr)_4$ (0.18 mL, 0.6 mmol) was added. The resultant solution was heated at 80 °C for one day. After cooled to room temperature, colourless crystals of **1** were obtained. Colourless crystals were obtained by washed with fresh isopropanol three times. Yield 80% based on Ti. EA and ICP (%): calculated for formula $C_{42}H_{80}N_2O_{24}P_2Ti_6$, C 37.47, H 5.99, N 2.08, Ti 21.34, P 4.60; found: C 36.60, H 5.79, N 2.00, Ti 20.75, P 4.41.

**Synthesis of 2**: Phosphorous acid (10.7 mg, 0.13 mmol), 3-[(4-Pyridinylmethylene)amino]-benzoic acid (29 mg, 0.13 mmol) and isopropyl alcohol (1.5 mL) were added to the glass vial and soniced at room temperature, then $Ti(O^iPr)_4$ (0.18 mL, 0.6 mmol) was added. The resultant solution was heated at 80 °C for three days. After cooled to room temperature, colourless crystals of **2** were obtained. Colourless crystals were obtained by washed with fresh isopropanol three times. Yield 35% based on Ti. EA and ICP (%): calculated for formula $C_{56}H_{88}N_4O_{24}P_2Ti_6$, C 43.37, H 5.72, N 3.61, Ti 18.52, P 3.99; found: C 43.26, H 5.78, N 3.47, Ti 17.85, P 3.63.

**Synthesis of 3**: Phosphorous acid (10.7 mg, 0.13 mmol), 4-[(4-Pyridinylmethylene)amino]-benzoic acid (29 mg, 0.13 mmol), isopropyl alcohol (1.5 mL) were added to the glass vial and soniced at room temperature, then $Ti(O^iPr)_4$ (0.18 mL, 0.6 mmol) was added. The resultant solution was heated at 80 °C for one day. After cooled to room temperature, faint yellow crystals of **3** were obtained. Faint yellow crystals were obtained by washed with fresh isopropanol three times. Yield 86% based on Ti. EA and ICP (%): calculated for formula $C_{56}H_{88}N_4O_{24}P_2Ti_6$, C 43.37, H 5.72, N 3.61, Ti 18.52, P 3.99; found: C 42.99, H 5.82, N 3.52, Ti 17.98, P 3.83.

**Synthesis of 4**: Phosphorous acid (53 mg, 0.65 mmol), isonicotinic acid (80 mg, 0.65 mmol), CuCl (22 mg, 0.22 mmol), N,N-Dimethylformamide (3.0 mL) and isopropyl alcohol (2.0 mL) were added to the glass vial and soniced at room temperature, then $Ti(O^iPr)_4$ (0.92 mL, 3 mmol) was added. The resultant solution was heated at 80 °C for two days. After cooled to room temperature, orange crystals of **4** were obtained. Orange crystals were obtained by washed with fresh isopropanol three times. Yield 40% based on Ti. EA and ICP (%): calculated for formula $C_{168}H_{350}Cl_3Cu_3N_6O_{85}P_6Ti_{18}$, C 39.07, H 6.83, N 1.70, Ti 17.43, P 3.76, Cu 3.85; found: C 38.82, H 6.56, N 1.63, Ti 17.08, P 3.67, Cu 3.54.

## 3. Single Crystal X-ray Crystallography

The crystallographic data of compounds **1-3** were collected using a Bruker D8 venture single crystal diffractometer equipped with graphite-monochromatic Mo-Kα radiation (λ = 0.71073 Å) at 150 K, and compound **4** was collected using the same device equipped with graphite-monochromatic Cu-Kα radiation (λ = 1.54184 Å) at 150 K. Their structures were solved and refined with OLEX2, All non-hydrogen atoms are anisotropically refined by the least square method, all hydrogen atoms are placed at calculated positions and refined using a riding model. The disordered pendant isopropoxy groups in **1-4** are in general treated by splitting into two moieties using PART instruction. SIMU and RIGU are then applied to set universal restraints on the disordered isopropoxy groups to obtain reasonable thermal displacement parameters. ISOR is further employed to some isopropyl groups that are severely disordered and N atoms on pyridine rings to achieve reasonable Uij values. Meanwhile, DFIX and SADI are specifically applied to fix the bond lengths of disordered isopropoxy groups. For compound **4**, the disordered pyridine group on isonicotinate is constrained by using AFIX 66 to make a coplanar six-membered ring, and the occupancy of the split part is set as 10.50. Meanwhile, solvent mask, a part of Olex2 package of crystallographic software, is used to calculate the solvent disorder volume in **4** and remove its contribution to the overall intensity data. The masked moieties, namely 2[$C_3H_8O$] and 5.25[$H_2O$] per formula, has been added to the sum formula. The calculated $e^-$ of 121 is almost equal to the $e^-$ of 118 for 2[$C_3H_8O$] and 5.25[$H_2O$]. Moreover, the solvent content of 2[$C_3H_8O$] and 5.25[$H_2O$] per formula is also consistent with the element analysis and TGA analysis. The X-ray crystallographic data for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre, under deposition number CCDC 2247993-2247996. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Table S1** Crystal data and structure refinements summary for compounds **1-4**

| Compound | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{42}H_{80}N_2O_{24}P_2Ti_6$ | $C_{56}H_{90}N_4O_{24}P_2Ti_6$ |
| Formula weight | 1346.42 | 1552.65 |
| T/K | 150.00 | 150.00 |
| Crystal system | Triclinic | Monoclinic |
| Space group | P-1 | $P2_1/n$ |
| a /Å | 11.3702(3) | 9.8651(5) |
| b /Å | 11.9984(4) | 20.88697(9) |
| c /Å | 12.4292(4) | 17.8564(8) |
| α/° | 70.8620(10) | 90 |
| β/° | 73.9500(10) | 105.759(2) |
| γ/° | 84.3280(10) | 90 |
| V/ $Å^3$ | 1539.42(8) | 3538.1(3) |
| Z | 1 | 2 |
| Dcalc /$Mg\cdot m^{-3}$ | 1.452 | 1.457 |
| μ /$mm^{-1}$ | 0.866 | 0.765 |
| Radiation | MoKα | MoKα |
| F (000) | 700 | 1616.0 |
| θ range /° | 2.577 to 25.360 | 2.357 to 25.376 |
| Reflections collected | 32051 | 108420 |
| Data completeness | 98.9% | 99.9% |
| Data/restraints/ parameters | 5571/292/387 | 6490/781/466 |
| Final R indices [$I>2\sigma(I)$] $^a$ | R1 = 0.0221, wR2 = 0.0631 | R1 = 0.0362, wR2 = 0.0938 |
| R indices (all data) | R1 = 0.0236, wR2 = 0.0637 | R1 = 0.0442, wR2 = 0.1012 |
| Goodness-of-fit on $F^{2b}$ | 1.062 | 1.039 |
| Largest diff. peak and hole/e$Å^{-3}$ | 0.299 and -0.298 | 0.686 and -0.354 |

| Compound | **3** | **4** |
|---|---|---|
| Empirical formula | $C_{56}H_{90}N_4O_{24}P_2Ti_6$ | $C_{168}H_{350.50}Cl_3Cu_3N_6O_{85.25}P_6Ti_{18}$ |
| Formula weight | 1552.66 | 5164.01 |
| T/K | 150.00 | 150.00 |
| Crystal system | Triclinic | Monoclinic |
| Space group | P-1 | C 2/c |
| a /Å | 12.0582(6) | 27.5953(7) |
| b /Å | 12.1208(7) | 19.5028(5) |
| c /Å | 14.3450(9) | 47.0477(12) |
| α/° | 112.778(2) | 90 |
| β/° | 94.618(2) | 92.5160(10) |
| γ/° | 110.303(2) | 90 |
| V/ $Å^3$ | 1756.13(18) | 25296(11) |
| Z | 1 | 4 |
| Dcalc /$Mg·m^{-3}$ | 1.468 | 1.300 |
| μ /$mm^{-1}$ | 0.771 | 6.074 |
| Radiation | MoKα | CuKα |
| F (000) | 808 | 10344 |
| θ range /° | 2.909 to 25.385 | 2.908 to 68.543 |
| Reflections collected | 29775 | 175523 |
| Data completeness | 99.6 % | 99.3 % |
| Data/restraints/ parameters | 6433 / 218/ 486 | 23087 / 2056 / 1735 |
| Final R indices [I>2σ(*I*)] [a] | R1 = 0.0328, wR2 = 0.0893 | R1 = 0.0987, wR2 = 0.2824 |
| R indices (all data) | R1 = 0.0376, wR2 = 0.0932 | R1 = 0.1103, wR2 = 0.2943 |
| Goodness-of-fit on $F^{2b}$ | 1.048 | 1.075 |
| Largest diff. peak and hole/$eÅ^{-3}$ | 0.624 and -0.373 | 1.897 and -1.016 |

[a] $R_1 = \sum||Fo|-|Fc||/\sum|Fo|$; $wR_2 = \{\sum w[(Fo)^2-(Fc)^2]^2/\sum w[(Fo)^2]^2\}^{1/2}$ ;

[b] $GooF = \{\sum w[(Fo)^2-(Fc)^2]^2/(n-p)\}^{1/2}$

# 4□Additional Figures

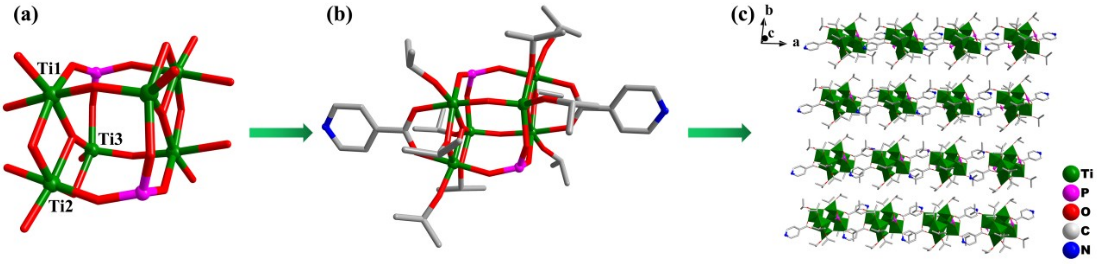

**Fig. S1** (a) The coordination environments of $\{Ti_6P_2\}$ core in **1**, (b) the molecular structure and (c) the packing structure of **1**.

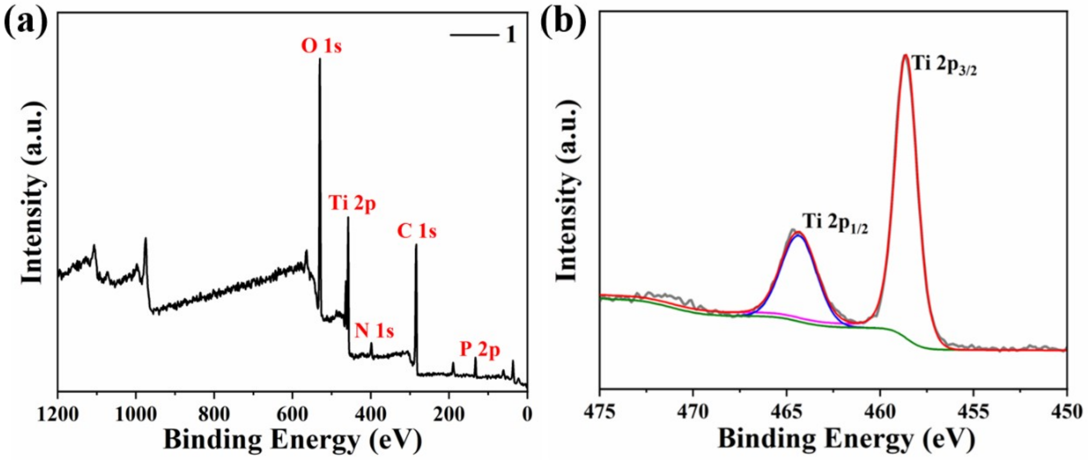

**Fig. S2** XPS spectrum of **1** (a) and the high resolution XPS spectra of Ti 2p (b).

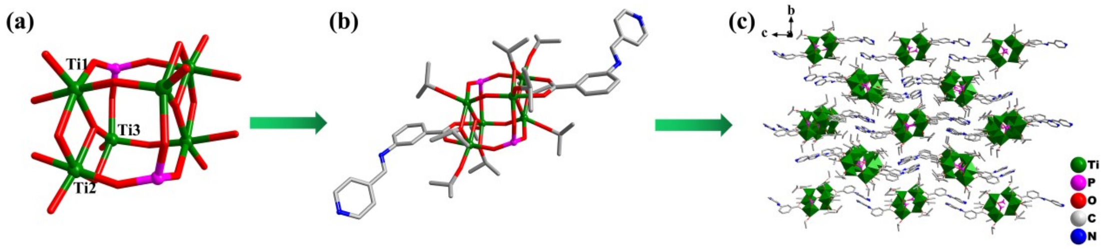

**Fig. S3** (a) The coordination environments of $\{Ti_6P_2\}$ core in **2**, (b) the molecular structure and (c) the packing structure of **2**.

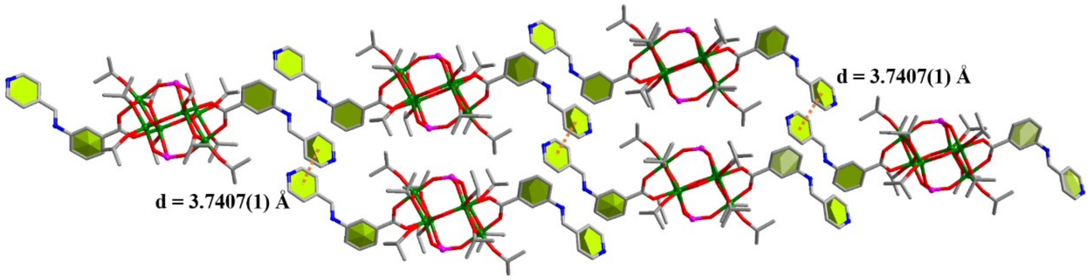

**Fig. S4** The π-π interactions (3.7407(1) Å) form between the peripheral pyridyl groups of 3-pyca ligands of **2**.

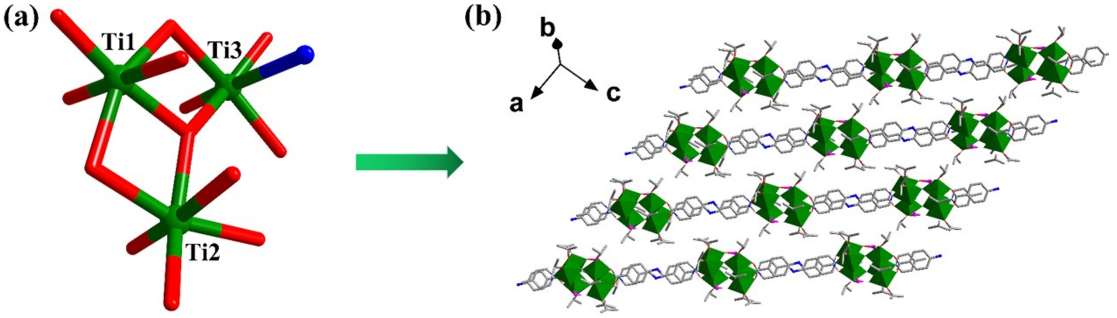

**Fig. S5** (a) The coordination environments of $Ti_3(\mu_3\text{-}O)$ unit of **3**, (b) the packing structure of **3**.

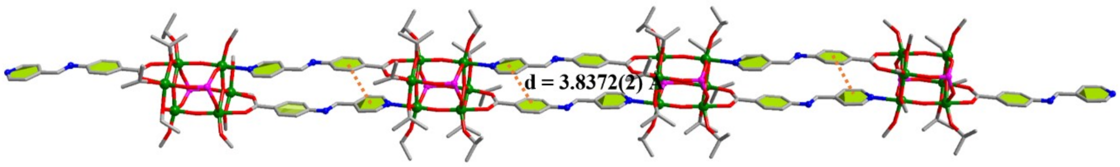

**Fig. S6** The π-π interactions (3.8372(2) Å) form between the two adjacent 4-pyca ligands of **3**.

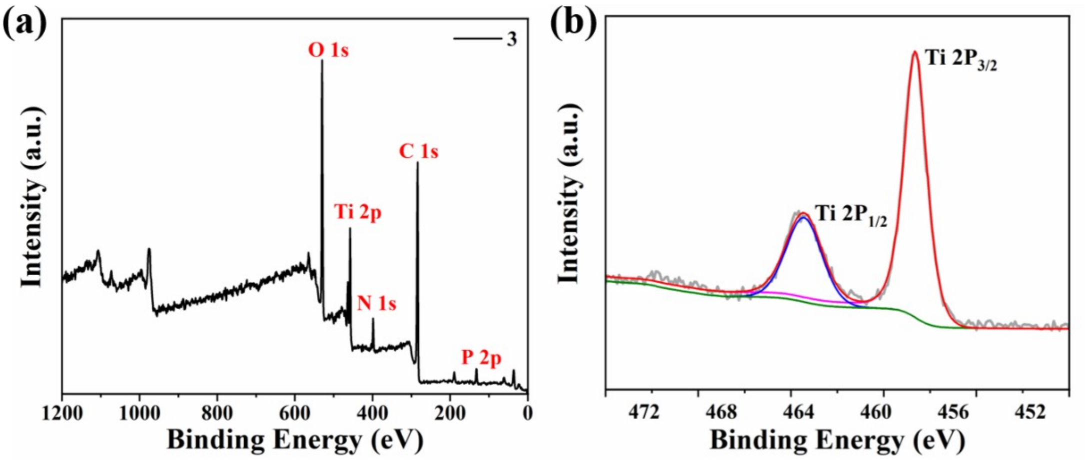

**Fig.S7** XPS spectrum of **3** (a) and the high resolution XPS spectra of Ti 2p (b).

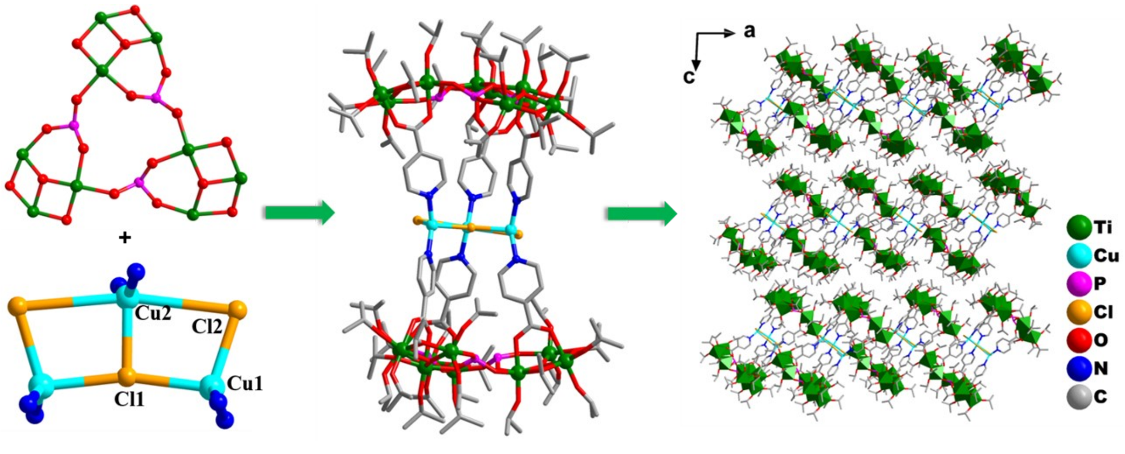

**Fig. S8** (a) The coordination environments of $\{Ti_9P_3\}$ core and copper atoms in **4**, (b) the molecular structure and (c) the packing structure of **4**.

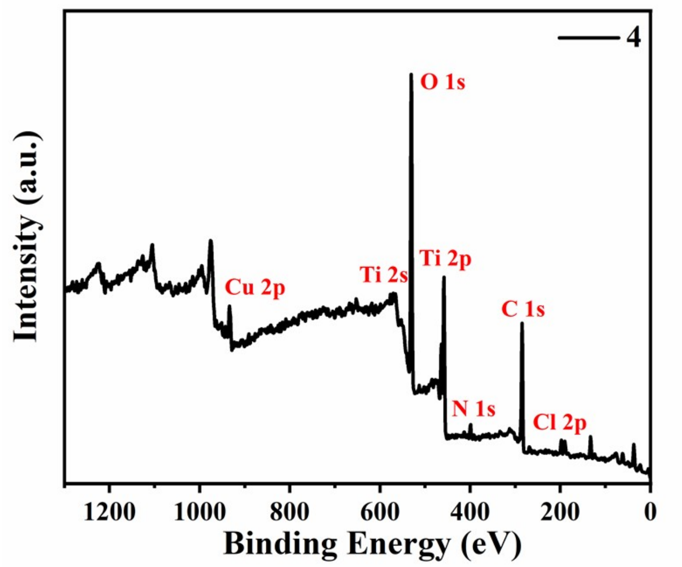

**Fig. S9** XPS spectrum of **4**.

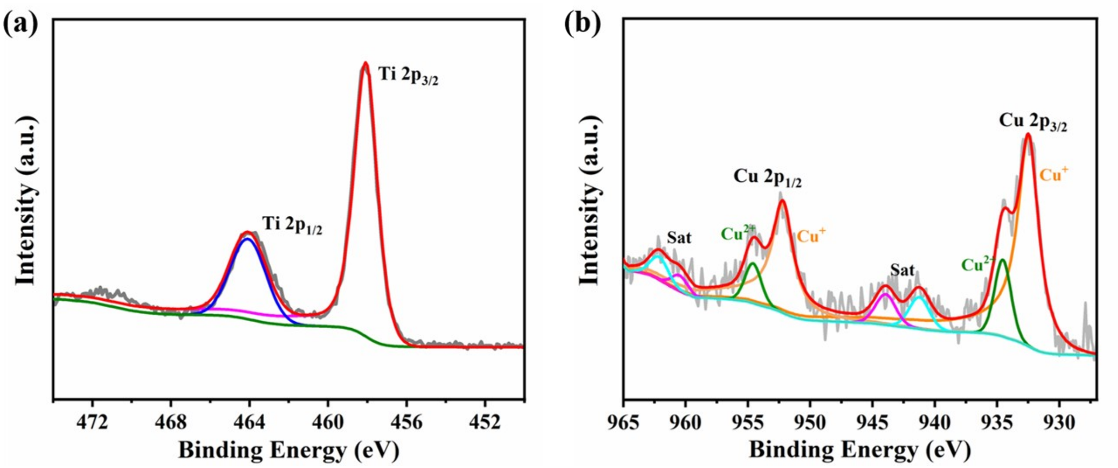

**Fig. S10** High resolution XPS spectra of (a) Ti 2p, (b) Cu 2p of **4**.

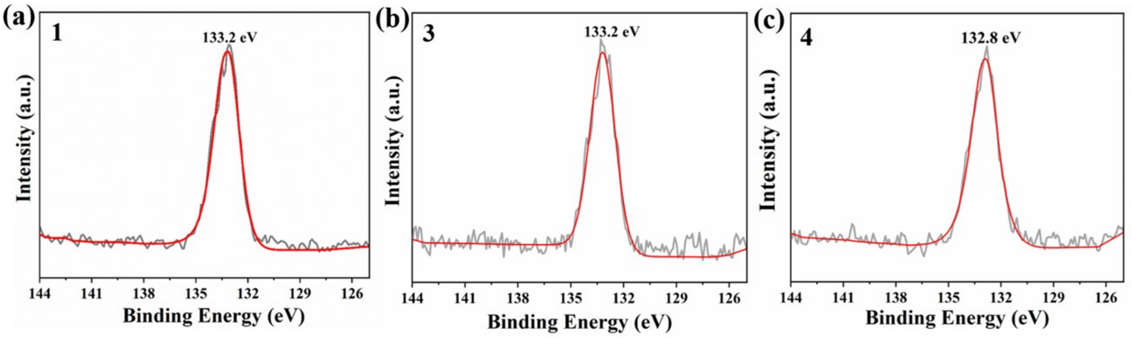

**Fig. S11** High resolution XPS spectra of **1, 3** and **4** for $P_{2p}$.

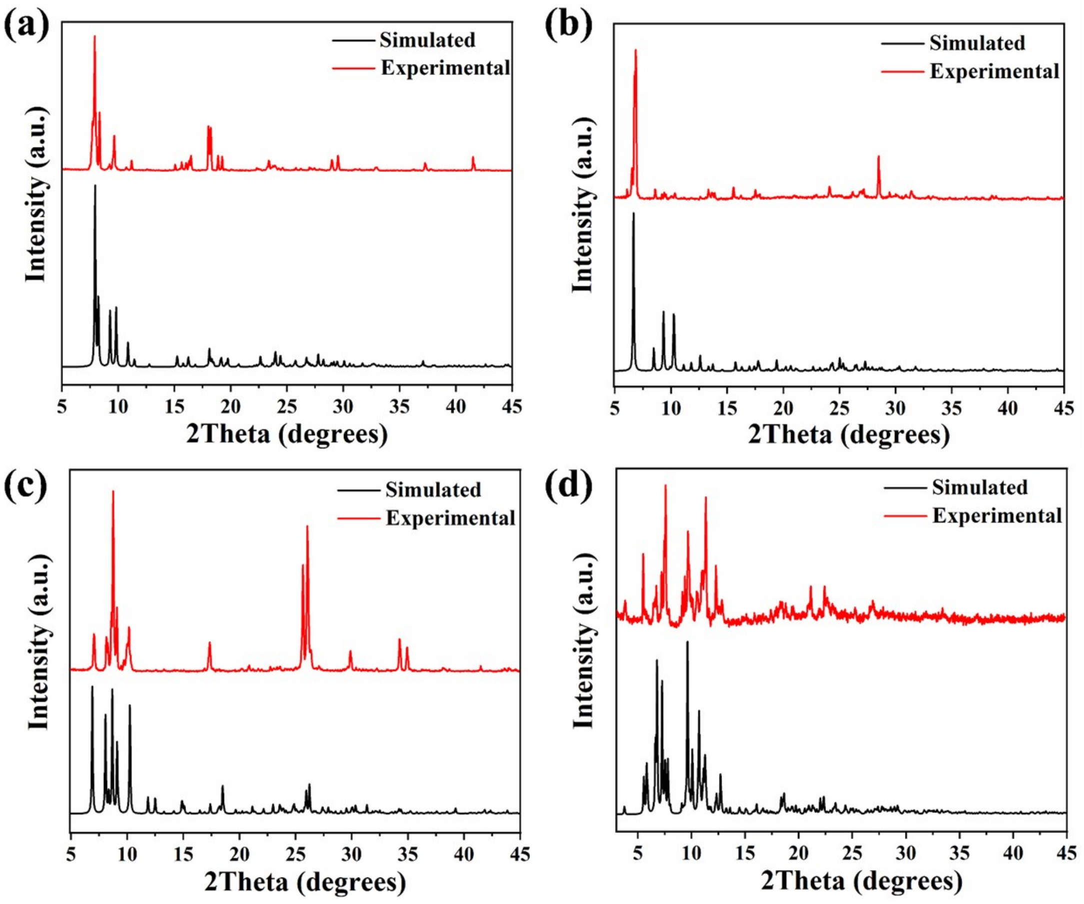

**Fig. S12** PXRD patterns of **1**-**4**.

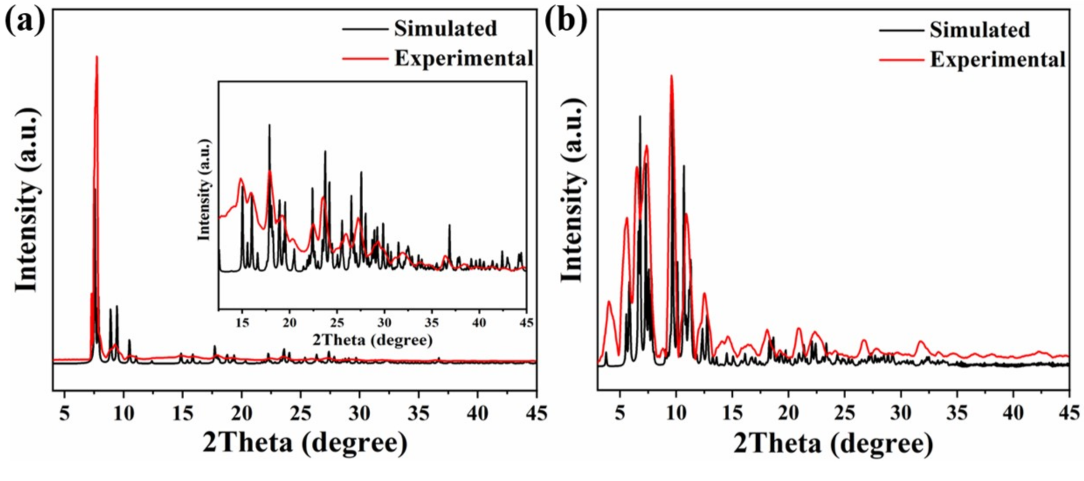

**Figure 13** PXRD patterns of **1** and **4** recorded on Single Crystal X-ray diffractometer.

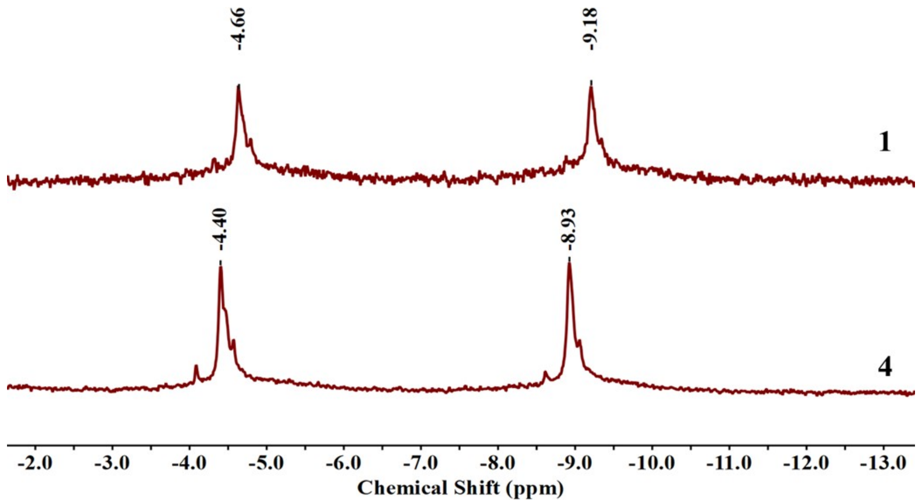

**Fig. S14** The $^{31}P$ NMR spectra of **1** and **4** in $DCl/D_2O$ at pH=3.

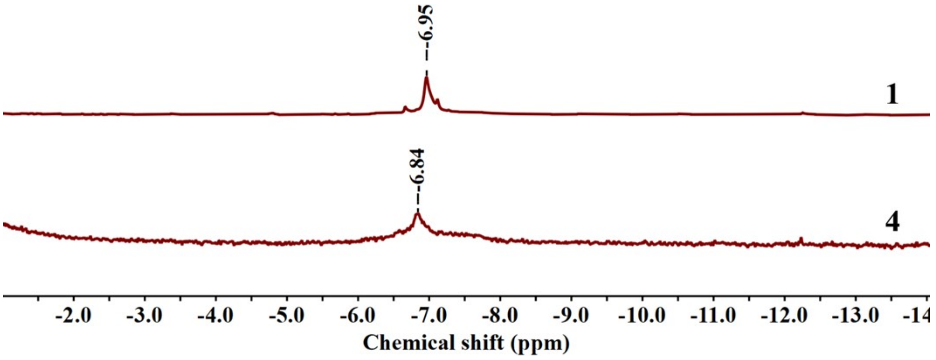

**Fig.S15** The decoupled $^{31}P$ NMR spectra of **1** and **4** in $DCl/D_2O$ at pH=3.

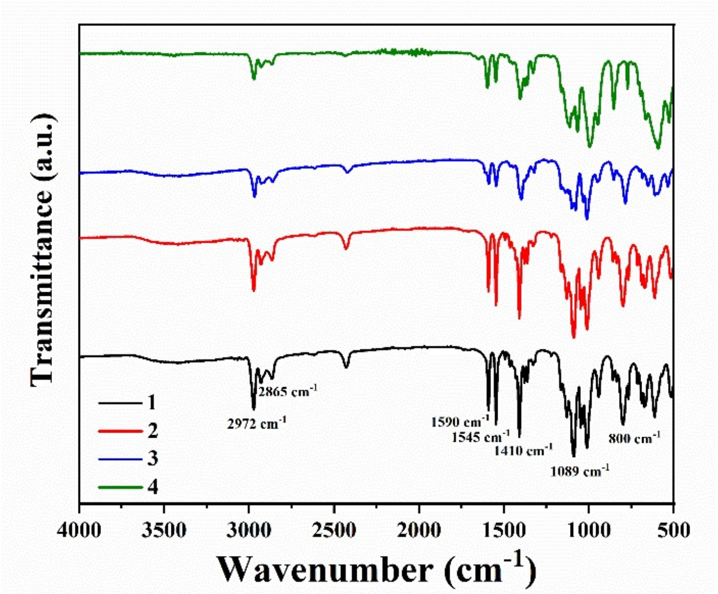

**Fig. S16** The FT-IR spectra of **1-4**. The absorption bands between 2972-2865 $cm^{-1}$ can be ascribed to the stretching vibrations of C-H bonds from isopropyl groups. The characteristic stretching vibrations of ν(C=O) from carboxylate are observed between 1590-1410 $cm^{-1}$. The intense absorption peaks between 1200-1000 $cm^{-1}$ are assigned to the stretching vibrations of ν(C-O) from isopropanol, the Ti-O vibrations peak are found at wavenumbers between 800-500 $cm^{-1}$.

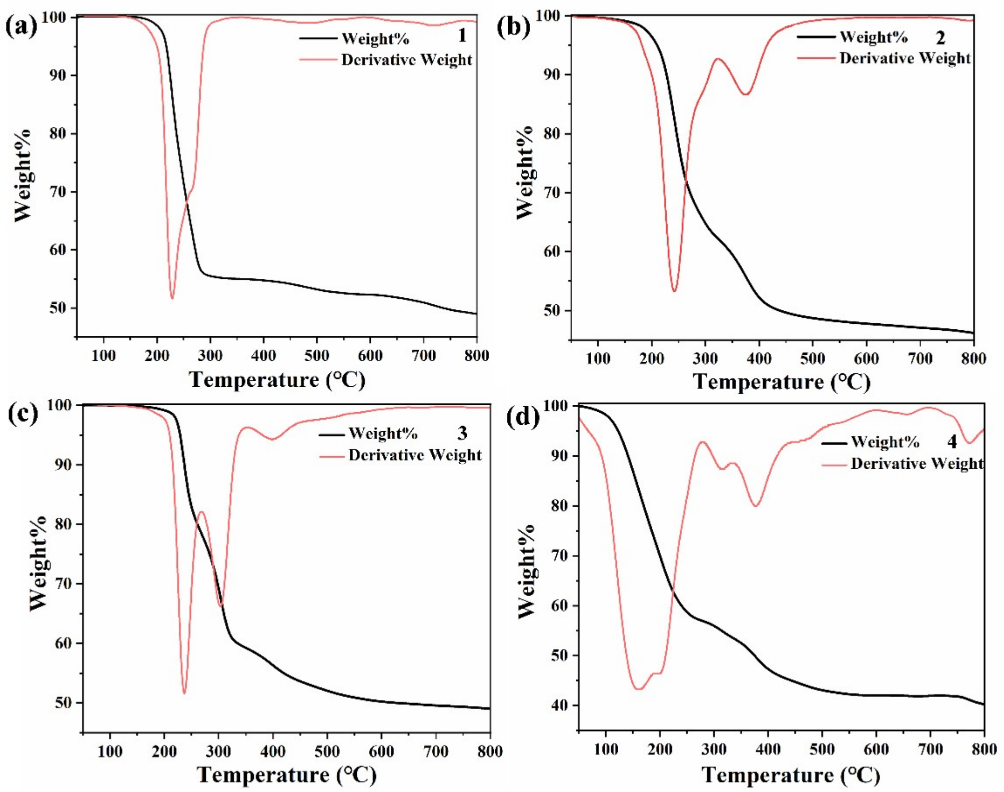

**Fig. S17** TGA curves of **1-4.** The TGA curve of **1** shows a steep decomposition step between 150 °C and 300 °C, the mass loss corresponds to the removal of ten isopropyl groups and two isonicotinate (45.57 %, calculated 45.37 %). Afterwards, the residual **1** gradually transforms into related oxides. The TGA curve of **2** shows two-step decomposition in the range of 120 °C to 330 °C, with a weight loss of calculated 35.19 % corresponding to the complete removal of ten isopropyl groups and partial elimination of 3-pyca. All the ligands are lost when the temperature increases to around 500 °C, corresponding to a further weight loss of 15.62 %. The skeleton of **2** is then entirely destroyed and gives rise to corresponding oxides. The same trend is observed for **3**. The two-step decomposition from 170 °C to 330 °C showing a weight loss of 40.11% is assigned to the depletion of ten isopropyl groups and one 4-pyca. The further removal of another 4-pyca is observed between 330 °C and 500 °C, equal to a mass loss of 12.21%. The latter calcination converts the residual into oxides. Compared with **1-3**, **4** is relatively unstable, which loses two guest isopropanol and five water molecules (4.10% in total, calculated 4.01%) before 120 °C. The subsequent mass loss of 38.28% during 120 °C and 270 °C corresponds to the removal of forty-two isopropyl groups and two isonicotinate. Afterwards, compound 4 gradually loses the remaining four ligands and three chlorine atoms from 270 °C to 400 °C, according to a weight loss of 10.12%. Finally, it completely transforms to titanium oxide and copper oxide..

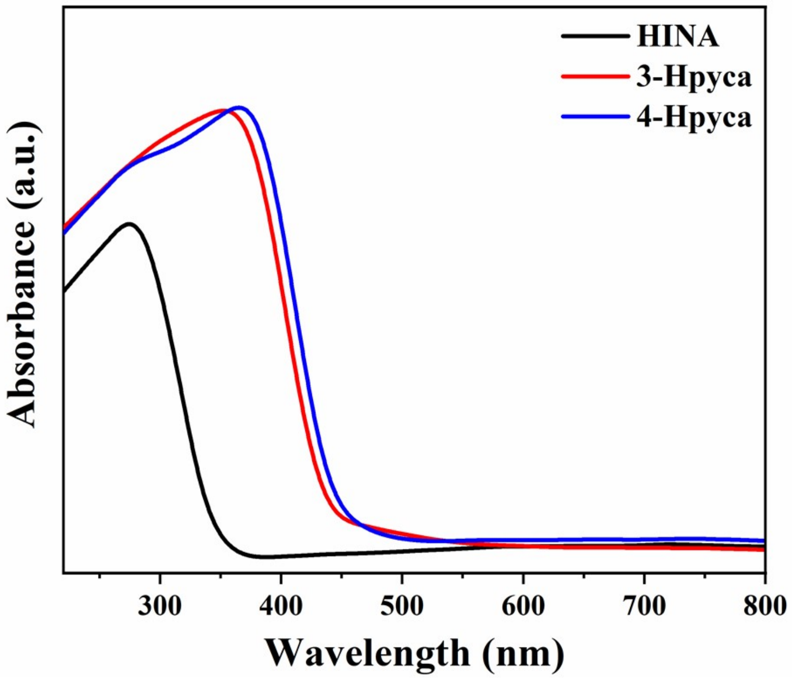

**Fig.S18** The UV-vis spectra of ligands in **1-4**.

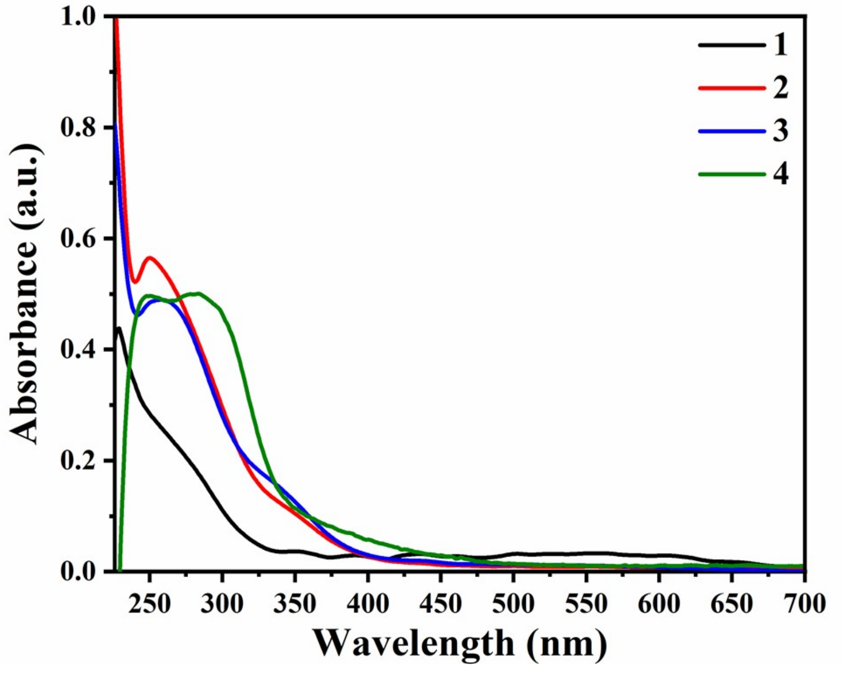

**Fig. S19** UV−vis spectra of compounds **1-4** in $CH_2Cl_2$.

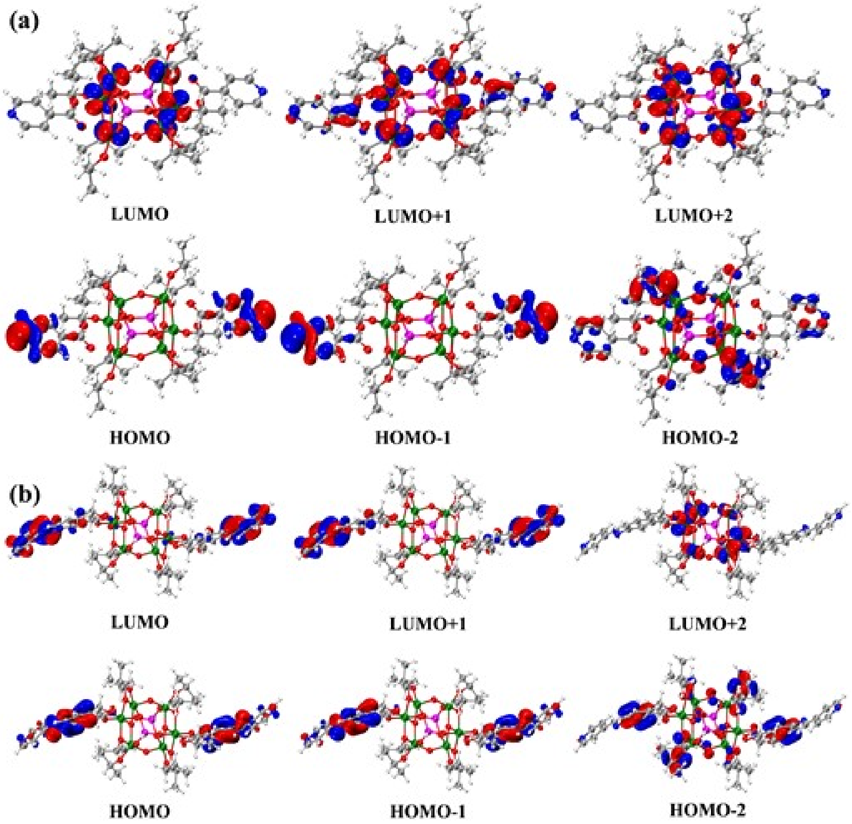

**Fig. S20** (a) Frontier molecular orbitals of **1** and (b) Frontier molecular orbitals of **2**.

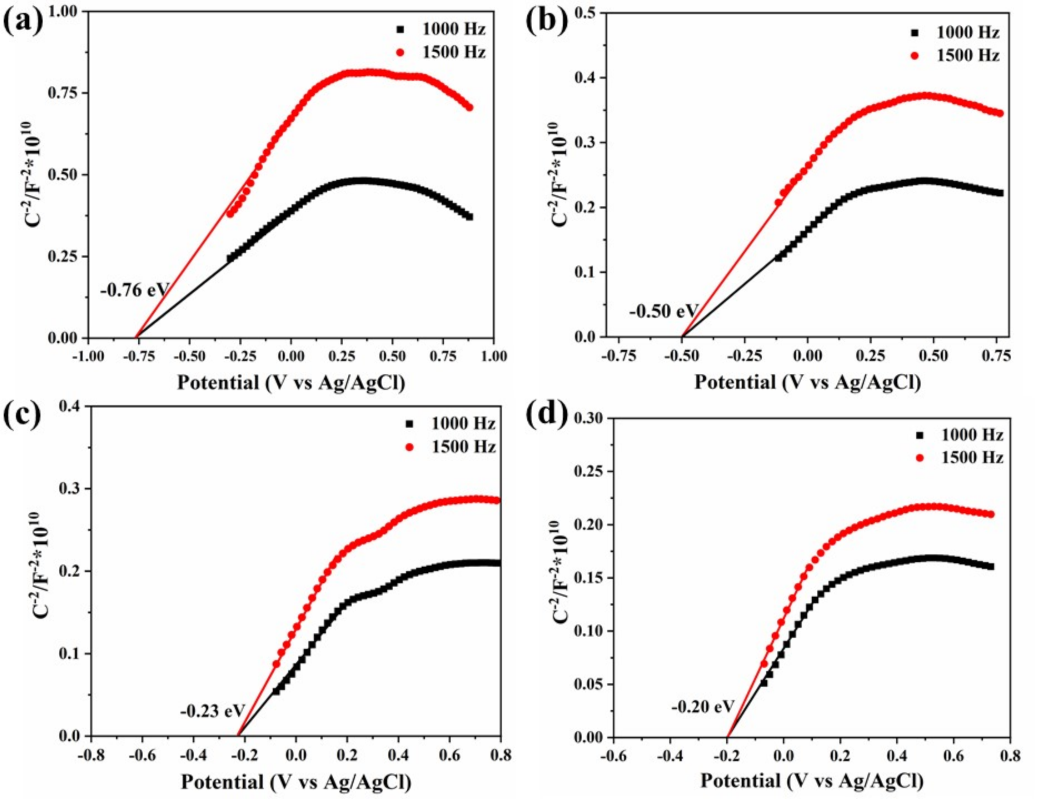

**Fig. S21** The Mott-Schottky curves of **1-4.**

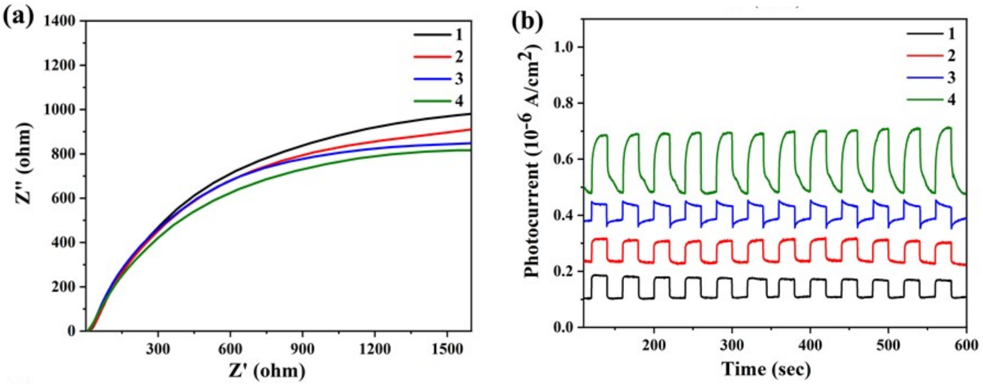

**Fig. S22** (a) The Electrochemical impedance spectra of **1**-4 and (b) The photocurrent responses of **1-4**.

**Table S2** Bond valence sum (BVS) analysis[a] of metal ions in **1**.

| Atom | Bond | Distance/Å | Bond Valence | Bond Valence Sum (BVS) |
|---|---|---|---|---|
| Ti(1) | O(3) | 1.7768(9) | 1.108 | 4.240 |
| | O(5)#1 | 2.0318(9) | 0.556 | |
| | O(6) | 1.9753(10) | 0.649 | |
| | O(7)#1 | 2.0041(9) | 0.602 | |
| | O(8) | 1.8507(10) | 0.907 | |
| | O(9)#1 | 2.1385(10) | 0.418 | |
| Ti(2) | O(2) | 1.9553(10) | 0.683 | 4.285 |
| | O(4) | 1.9552(10) | 0.685 | |
| | O(5) | 1.9638(9) | 0.670 | |
| | O(7) | 1.9667(9) | 0.663 | |
| | O(11) | 2.1063(10) | 0.455 | |
| | O(12) | 1.7698(10) | 1.129 | |
| Ti(4) | O(4) | 2.0365(9) | 0.549 | 4.204 |
| | O(7) | 1.9113(9) | 0.769 | |
| | O(8) | 1.7552(9) | 1.176 | |
| | O(10)#1 | 1.9820(10) | 0.637 | |
| | O(13) | 1.7890(10) | 1.073 | |

**Table S3** Bond valence sum (BVS) analysis[a] of metal ions in **3**.

| Atom | Bond | Distance/Å | Bond Valence | Bond Valence Sum (BVS) |
|---|---|---|---|---|
| Ti(1) | O(005)#1 | 1.9694(14) | 0.658 | 4.267 |
| | O(006) | 1.9883(16) | 0.626 | |
| | O(008)#1 | 2.0326(15) | 0.555 | |
| | O(00B) | 1.8254(14) | 0.971 | |

| | | | | |
|---|---|---|---|---|
| | O(00D)#1 | 2.1504(15) | 0.404 | |
| | O(00F) | 1.7970(15) | 1.053 | |
| Ti(2) | N(1)#2 | 2.4002(18) | 0.262 | 4.172 |
| | O(005) | 1.9629(14) | 0.672 | |
| | O(009) | 2.0613(15) | 0.514 | |
| | O(00A) | 1.9922(15) | 0.619 | |
| | O(00B) | 1.7782(14) | 1.105 | |
| | O(00E) | 1.8146(15) | 1.000 | |
| Ti(3) | O(005) | 1.9202(14) | 0.751 | 4.193 |
| | O(007) | 1.9586(15) | 0.679 | |
| | O(008) | 1.9658(15) | 0.665 | |
| | O(009) | 2.0034(15) | 0.538 | |
| | O(00C) | 2.0860(14) | 0.481 | |
| | O(00G) | 1.7868(16) | 1.079 | |

**Table S4** Bond valence sum (BVS) analysis[a] of metal ions in **4**.

| Atom | Bond | Distance/Å | Bond Valence | Bond Valence Sum (BVS) |
|---|---|---|---|---|
| Ti(1) | O(26) | 1.779(4) | 1.102 | 4.297 |
| | O(18) | 1.872(4) | 0.860 | |
| | O(6) | 1.953(4) | 0.687 | |
| | O(4) | 2.177(3) | 0.376 | |
| | O(32) | 2.019(4) | 0.576 | |
| | O(28) | 1.948(4) | 0.696 | |
| Ti(9) | O(18) | 1.984(4) | 0.633 | 4.281 |
| | O(21) | 2.062(5) | 0.513 | |
| | O(25) | 2.226(5) | 0.328 | |
| | O(30) | 1.983(5) | 0.637 | |
| | O(13) | 1.790(5) | 1.073 | |
| | O(33) | 1.781(5) | 1.096 | |
| Ti(7) | O(32) | 1.963(5) | 1.102 | 4.371 |
| | O(17) | 1.751(6) | 0.860 | |
| | O(27) | 1.748(6) | 0.687 | |
| | O(18) | 1.989(4) | 0.376 | |
| | O(21) | 1.956(5) | 0.576 | |
| Ti(6) | O(24) | 1.969(4) | 0.660 | 4.217 |
| | O(5) | 1.795(4) | 1.053 | |
| | O(22) | 1.998(4) | 0.611 | |
| | O(39) | 1.905(4) | 0.786 | |
| | O(1) | 2.146(3) | 0.409 | |
| | O(8) | 1.949(4) | 0.698 | |
| Ti(8) | O(22) | 2.019(5) | 0.576 | 4.229 |

| Atom | Bond | Distance/Å | Bond Valence | Bond Valence Sum (BVS) |
|---|---|---|---|---|
| | O(39) | 2.019(4) | 0.575 | |
| | O(38) | 2.188(4) | 0.366 | |
| | O(23) | 2.018(6) | 0.575 | |
| | O(3) | 1.783(5) | 1.087 | |
| | O(15) | 1.798(5) | 1.050 | |
| Ti(2) | O(39) | 1.908(5) | 0.778 | 3.735 |
| | O(23) | 1.983(6) | 0.638 | |
| | O(35) | 1.790(8) | 1.076 | |
| | O(29) | 1.926(6) | 0.741 | |
| | O(19A) | 2.07(3) | 0.502 | |
| Ti(4) | O(20) | 1.953(4) | 0.691 | 4.300 |
| | O(14) | 1.896(4) | 0.799 | |
| | O(16) | 1.986(4) | 0.630 | |
| | O(10) | 1.969(4) | 0.660 | |
| | O(34) | 1.773(4) | 1.120 | |
| | O(12) | 2.154(3) | 0.400 | |
| Ti(5) | O(30) | 2.168(4) | 0.385 | 4.314 |
| | O(14) | 2.029(4) | 0.559 | |
| | O(16) | 2.005(5) | 0.598 | |
| | O(7) | 2.021(6) | 0.575 | |
| | O(2) | 1.791(6) | 1.070 | |
| | O(31) | 1.772(6) | 1.126 | |
| Ti(3) | O(11) | 1.944(5) | 0.706 | 4.299 |
| | O(37) | 1.750(8) | 1.195 | |
| | O(14) | 1.920(4) | 0.757 | |
| | O(7) | 1.976(5) | 0.645 | |
| | O(9) | 1.751(6) | 1.192 | |
| Cu(1) | N(1)#1 | 1.986(13) | 0.265 | 0.925 |
| | Cl(2) | 2.423(3) | 0.173 | |
| | Cl(1) | 2.5071(14) | 0.217 | |
| | N(3) | 1.971(5) | 0.270 | |
| Cu(2) | Cl(2) | 2.587(3) | 0.139 | 0.886 |
| | N(2) | 1.960(6) | 0.272 | |
| | N(2A) | 1.980(1) | 0.260 | |
| | Cl(1) | 2.425(3) | 0.215 | |

[a]$V_i = \Sigma S_{ij} = \Sigma \exp[(r_0 - r_{ij})/B]$, where $r_0$ is the length of a single bond (here $r_0$=1.815 for $Ti^{iv}$–O; $r_0$=1.906 for $Ti^{iv}$–N; $r_0$=1.480 for $Cu^{I}$–N; $r_0$=1.858 for $Cu^{I}$–Cl;), $r_{ij}$ is the bond length between atoms i and j; B is a constant, the "universal parameter" ~0.37 Å; Sij is the valence of a bond between atoms i and j; $V_i$ is the sum of all bond valences of the bonds formed by a given atom i.[S5]

**Table S5** Bond valence parameters available from Brown .I .D's list for $P^{3+}$.

| Atom 1 | Atom 1 valence state | Atom 2 | Atom 2 valence state | Ro parameter |
|---|---|---|---|---|
| P | 3 | O | 2 | 1.63 |
| P | 3 | S | 2 | 2.12 |
| P | 3 | Se | 2 | 2.24 |
| P | 3 | F | 1 | 1.53 |

**Table S6** Bond valence sum (BVS) analysis[a] of P element in **1**.

| Atom | Bond | Distance/Å | Bond Valence | Bond Valence Sum (BVS) |
|---|---|---|---|---|
| P(1) | O(10) | 1.5191(10) | 1.350 | 4.027 |
| | O(6) | 1.5230(10) | 1.335 | |
| | O(2) | 1.5211(10) | 1.342 | |

**Table S7** Bond valence sum (BVS) analysis[a] of P element in **4**.

| Atom | Bond | Distance/Å | Bond Valence | Bond Valence Sum (BVS) |
|---|---|---|---|---|
| P(1) | O(30) | 1.513(5) | 1.373 | 4.065 |
| | O(6) | 1.526(4) | 1.324 | |
| | O(24) | 1.514(4) | 1.368 | |
| P(2) | O(8) | 1.509(5) | 1.390 | 4.062 |
| | O(10) | 1.518(4) | 1.351 | |
| | O(29) | 1.527(6) | 1.321 | |
| P(3) | O(28) | 1.507(4) | 1.394 | 4.134 |
| | O(20) | 1.508(4) | 1.390 | |
| | O(11) | 1.519(5) | 1.350 | |

[a] $V_i = \Sigma S_{ij} = \Sigma \exp[(r_0 - r_{ij})/B]$, where $r_0$ is the length of a single bond (here $r_0$=1.63 for $P^{III}$-O;), $r_{ij}$ is the bond length between atoms i and j; B is a constant, the "universal parameter" ~0.37 Å; Sij is the valence of a bond between atoms i and j; $V_i$ is the sum of all bond valences of the bonds formed by a given atom i.

## 5 Reference

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