Calix[8]arene-constructed stable polyoxo-titanium clusters for efficient CO₂ photoreduction†

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It is still rare for coordination complexes to achieve CO₂ reduction reaction in water. Demonstrated here is the self-assembly and CO₂ photoreduction performance of two thermodynamically reversibly-converted polyoxo-titanium clusters (PTCs), Ti₄-C₈A and Ti₇-C₈A, using calix[8]arene with high molecular degrees of freedom and variable conformations as an organic “functional armor”. Because of the rich coordination sites and bridging modes of calix[8]arene, the obvious electron transfer effect generated between the titanium–oxo core and calix[8]arene ligand extended the light absorption of the two PTCs from the traditional ultraviolet to the visible region. Moreover, the hydrophobic benzene groups in calix[8]arene endowed the two clusters with high structural and chemical stability in aqueous solutions with different pH values. On this foundation, these two stable and photosensitive clusters were used as heterogeneous molecular photocatalysts for efficient CO₂ reduction in water (with triethanolamine as a sacrificial agent) and they exhibited very high CO₂-to-HCOO⁻ conversion activity and selectivity. Most importantly, this is the first report of molecular coordination complexes in water containing a sacrificial agent to perform heterogeneous CO₂ reduction reaction.

Introduction

The large amount of CO₂ emission from fuel combustion has created serious environmental burden and energy crisis. By imitating natural photosynthesis, solar energy-driven artificial CO₂ reduction reaction (CO₂RR) performed in water (H₂O) is considered the most energy-efficient and eco-friendly means to achieving CO₂ recycling, since it can reduce CO₂ into value-added carbon-based chemicals under the action of a photocatalyst.1–4 Thus, as the crucial factor of CO₂RR, the fundamental design requirements of photocatalyst structures are usually water-stability, photosensitivity, and recyclability. Although many stable and efficient nanostructured photocatalyst materials have been explored to perform CO₂RR,1,4–9 in most cases the identification of catalytically active sites is limited by their complicated hybrid or composite structures.

In this context, the development of efficient, photosensitive, and heterogeneous photocatalysts with well-defined structures is highly important.10–12

In recent years, the exploration of photocatalysts for CO₂RR has targeted structurally adjustable coordination complexes including metal–organic frameworks (MOFs) and metal–organic molecules/clusters (MOMs/MOCs),13–26 because their clear structure information can provide a visual platform for the study of catalytically active sites and reaction mechanisms. However, the poor water stability and photosensitivity of these crystalline materials make them mostly used as homogeneous or heterogeneous photocatalysts to perform CO₂RR in toxic organic solvents containing an auxiliary photosensitizer.2,25,27 In this regard, effectively increasing the light absorption and H₂O stability of crystalline coordination complexes is the most fundamental and significant design requirement for them to perform heterogeneous photocatalytic CO₂RR in eco-friendly H₂O. In recent years, some well-defined, conjugated organic polymer/covalent-organic framework/single-atom catalyst materials have been developed to reduce CO₂ in pure H₂O.28–33 However, coordination complexes that can achieve CO₂RR in H₂O containing/excluding a sacrificial agent are still very rare.16,34

Polyoxo-titanium clusters (PTCs), due to their intrinsic low-toxicity and photosensitivity, have been widely used in many photocatalytic applications.35,36 Importantly, these PTCs under the modification of specifically functionalized organic ligands can display high water and chemical stability, and their photo-
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two stable and photosensitive PTCs applied in artificial CO2RR.

This work provides a new strategy toward developing
heterogeneous photocatalysts to perform CO2RR in H2O con-
water-stable and photosensitive PTCs were further used as
the C8A ligand. In consideration of these advantages, two
were extended to the visible light region through strong charge
absorption ranges
CO2RR in H2O in the presence of

Consequently, the selection of suitable functionalized organic
ligands to construct water-stable and light absorption-
extended PTCs is the key to solving these problems.

In this work, we designed and synthesized two calix[8]arene
(H4C8A)-modified PTCs, ellipse-shaped [Ti7O4(C8A)(OiPr)4(HOiPr)]
(Ti7-C8A), HOiPr = isopropanol) and bowknot-shaped
[Ti4O2(C8A)(CH3O)12] (Ti4-C8A), and their crystallographic
structures can achieve thermodynamic interconversion under
different solvent and temperature conditions (Scheme 1). Because of the hydrophobic benzene group of C8A,43 these two
PTCs displayed high structural and chemical stability in aqueous
solutions. Moreover, their light absorption ranges
were extended to the visible light region through strong charge
transfer between the titanium-oxo core and hydroxyl groups of
the C8A ligand. In consideration of these advantages, two
water-stable and photosensitive PTCs were further used as
heterogeneous photocatalysts to perform CO2RR in H2O contain-
ing sacrificial triethanolamine (TEOA). We found that both
could reduce CO2 to HCOOH with very high activity (253.88 ±
1.29 and 488.35 ± 21.41 μmol g⁻¹ h⁻¹) and selectivity (96.0% and
99.7%) under ultraviolet light, which is even comparable
to the reported superior coordination complex photocatalysts
for CO2-to-HCOO⁻ conversion in organic solvents under visible
light irradiation.13,15,16,21,44–46 Significantly, this is the first case of a
crystalline molecular coordination system as heterogeneous
photocatalysts to perform CO2RR in H2O in the presence of
TEOA. This work provides a new strategy toward developing
more stable and photosensitive PTCs applied in artificial CO2RR.

Synthetic materials, procedures, and
the methods

All reagents and solvents employed in this work were commer-
cially available and used without further purification. Infrared

spectra using KBr pellets were measured on a Bruker Tensor
27 in a range of 4000–400 cm⁻¹. Thermogravimetric (TG) ana-
ysis was performed on a Netzch STA449F3 analyzer at a
heating rate of 10 °C min⁻¹ from ambient temperature to
800 °C under a nitrogen gas atmosphere. Room-temperature
powder X-ray diffraction (PXRD) spectra were recorded on a
Rigaku D/Max 2500/PC diffractometer at 40 kV and 200 mA
with a Cu-target tube and a graphite monochromator. UV-Vis
absorption spectra were acquired on a Varian Cary 5000 UV-Vis
spectrophotometer in a wavelength range of 250–800 nm. The
photocatalytic liquid products were analyzed by ion chromato-
graphy (LC-2010 PLUS). Gas chromatography was performed
on GC-7920A (Aultight Co.) equipped with a flame ionization
detector (FID) with a methanizer and a thermal conductivity
detector (TCD). 13CNMR spectra were measured using chromo-
tagraphy–mass spectrometry (7890A and 5975C, Agilent).
Inductively coupled plasma-atomic emission spectroscopy
(ICP-AES) measurements were performed using Agilent 720.

Synthesis of Ti4-C8A

A mixture of C8A (0.01 mmol, 8.5 mg) and phosphoric acid
(10.0 mg) in isopropanol (5.0 mL) was ultrasonically dissolved,
and then titanium isopropoxide (0.6 mL) was added into the
above solution. After stirring for 10 min, this solution was
transferred into a 15 mL Teflon-lined stainless steel autoclave
for 72 h at 100 °C under autogenous pressure. After cooling
down to room temperature, yellow crystals were collected by fil-
tration and fully washed several times with isopropanol. Yield:
ca. 89%.

Synthesis of Ti7-C8A

The mixture of C8A (8.5 mg), phosphoric acid (30.0 mg) in iso-
propanol (2 mL), and CH3OH (3 mL) was ultrasonically dis-
solved. After stirring for 10 min, titanium isopropoxide (1.2 mL) was added into the resultant solution and stirred for
another 10 min for dissolution. This solution was transferred
into a 15 mL Teflon-lined stainless steel autoclave for 72 h at
120 °C under autogenous pressure. After cooling down to
room temperature, reddish brown crystals were collected by fil-
tration and fully washed several times with isopropanol. Yield:
ca. 76%.

Thermodynamic conversion of Ti4-C8A to Ti7-C8A

5.0 mg of Ti4-C8A crystals was added into 3 mL CH3OH and
then transferred into a 15 mL Teflon-lined stainless steel autoclave
for 72 h at 150 °C under autogenous pressure. After
cooling down to room temperature, reddish brown crystals of
Ti7-C8A were obtained and collected by filtration.

Thermodynamic conversion of Ti7-C8A to Ti4-C8A

5.0 mg of Ti7-C8A crystals was dissolved in 3 mL isopropanol
and then transferred into a 15 mL Teflon-lined stainless steel autoclave for 96 h at 100 °C under autogenous pressure. After
cooling down to room temperature, yellow crystals of Ti4-C8A
and a few co-crystals of Ti7-C8A were obtained and collected by filtration.
X-ray crystallography

The single-crystal diffraction analysis of Ti₄-C₈A and Ti₇-C₈A were performed using a Bruker AXS smart Apex CCD diffractometer at 296 K. The X-ray generator was operated at 50 kV and 35 A using Mo Kα (λ = 0.71073 Å) radiation. The crystal structures were solved and refined by full matrix methods against F² using the SHELXL-2014 program package and Olex2 software. All non-hydrogen atoms were refined with anisotropic temperature parameters, and hydrogen positions were fixed at calculated positions and refined isotropically. The selected bond lengths and angles of the compounds are listed in Table S1b.† The crystal structures of the two clusters have been deposited, and CCDC numbers are 1999136 and 1999137† for Ti₄-C₈A and Ti₇-C₈A, respectively.

Crystal structures

Single-crystal X-ray diffraction analysis reveals that Ti₄-C₈A crystallizes in a monoclinic system with the space group P₂₁/n (Table S1a†) and is composed of four independent Ti atoms, one C₈A ligand, two μ₃-O atoms, and five isopropanol molecules. Within the cluster structure, five-coordinated Ti₁, Ti₂, and Ti₃ atoms all exhibit a distorted tetragonal pyramid geometry, except six-coordinated Ti₄ that exhibits a slightly distorted octahedral geometry (Fig. 1a). Ti₂ and Ti₃ atoms are linked by two μ₃-O atoms, which are further connected with Ti₁ and Ti₄ atoms to constitute a tetranuclear titanium–oxo (Ti₄O₂) core. Then, the overall metal–oxo core of small size (ca. 5.27 × 2.16 Å) is firmly fixed into the cavity (ca. 8.17 × 4.99 Å) of the C₈A ligand by coordinating its eight hydroxyl groups (Fig. 1b and c). Interestingly, when the Ti₄-C₈A crystals are soaked in methanol solution undergoing solvothermal reaction at 150 °C for 72 hours, they can be thermodynamically converted into another more stable neutral cluster, Ti₇-C₈A. The crystal structure of Ti₇-C₈A is different from that of Ti₄-C₈A, and the originally coordinated isopropanol groups in Ti₄-C₈A are all replaced and coordinated by more methoxy (OCH₃) groups. Crystallographic structure analysis shows that Ti₇-C₈A crystallizes in the orthogonal Cmca space group with relatively high symmetry (Table S1a†). The asymmetric unit contains three and a half Ti atoms, one half of the C₈A ligand, six OCH₃ groups, one μ₂-O atom, and one μ₄-O atom. There are four independent Ti atoms within the cluster, and all of them display a slightly distorted octahedral geometry constructed by six O atoms from μ₂-O, μ₄-O, and μ₃-OCH₃ groups and/or the C₈A ligand. The main difference is that the coordination environment of the Ti₄ atom includes two terminal methoxy groups, which may be easily substituted by other small molecules in solution. Among these Ti atoms, the Ti₃ atom is

![Fig. 1 Schematic of the crystal structures of Ti₄-C₈A and Ti₇-C₈A. (a) The metal–oxo core, (b) C₈A ligand (cavity of ca. 8.17 × 4.99 Å), and (c) overall cluster structure of Ti₄-C₈A. (d) The metal–oxo core, (e) C₈A ligand (cavity of ca. 8.17 × 5.50 Å), and (f) overall cluster structure of Ti₇-C₈A. Except for the protonated –OiPr group (blue ball), all the hydrogen atoms are omitted for clarity.](image-url)
located at the intersection of the symmetric elements of glide and mirror planes, and thus it is the center of the metal–oxo core (Fig. S1†). The central Ti3 atom is connected by two sets of symmetric Ti1, Ti2, and Ti4 atoms through two μ2-O atoms, two μ2-O atoms, and two μ2-OCH3 groups to form a heptanuclear titanium–oxo (Ti7O16) core (Fig. 1d). The two sets of Ti1, Ti2, and Ti4 atoms on the periphery communicate with each other by six μ2-OCH3 groups. Analogously, the overall metal–oxo core is also captured by the cavity of the C8A ligand in which eight hydroxyl groups are coordinated to two Ti1 and two Ti2 atoms. However, the shared Ti3 atom and two Ti4 atoms are exposed above the cavity (ca. 8.17 × 5.50 Å) of the C8A ligand due to the larger size (ca. 11.12 × 5.98 Å) of the heptanuclear metal–oxo core (Fig. 1e and f). It should be noted that different morphologies of Ti7–C8A crystals can be obtained through slight changes in the synthetic protocol (Table 1 and Fig. 2a). Furthermore, the Ti7–C8A crystals can also be converted into Ti4–C8A by further soaking them in isopropanol at 100 °C for one week. More details about the supramolecular stacking, main bond lengths and bond angles of Ti7–C8A and Ti4–C8A are provided in Table S1b and Fig. S2, S3.† The phase purity and thermal stability of Ti7–C8A and Ti4–C8A were first confirmed by well-matched powder X-ray diffraction (PXRD) patterns and thermogravimetric analysis, respectively (Fig. S4–S6†). It should be noted that the hydrophobic benzene group modification of the C8A ligand endows these two PTCs with high structural and chemical stability in aqueous solutions with different pH values, which is essential and important for them to be used in water-dependent applications. Besides, it is well recognized that Ti-based nanostructured or crystalline materials generally exhibit intrinsic photocactivity and extensive photocatalytic applications, in which their light harvesting capability plays a key role in determining their photocatalytic performance. Therefore, ultraviolet-visible (UV-vis) absorption spectroscopy was performed to estimate the photosensitivity and optical bandgaps of Ti7–C8A and Ti4–C8A. In Fig. 2b, it can be observed that both the clusters coordinated with the C8A ligand exhibited better visible light collecting ability than the traditional UV-responsive PTCs and free C8A ligand, indicating that an obvious charge transfer occurred between the C8A ligand and titanium–oxo core. The optical bandgaps were thus calculated to be 1.86 (Ti7–C8A) and 1.64 eV (Ti4–C8A) from their Tauc plots (Fig. 2c), which means that these two water-stable PTCs also can display semiconductor-like properties. On this basis, the corresponding HOMO and LUMO energy levels of Ti7–C8A and Ti4–C8A were further determined by ultraviolet photoelectron spectroscopy (UPS) (Fig. 2d and e) and Mott–Schottky measurements (Fig. S7†), and they were converted to electrochemical energy potentials in volts vs. normal hydrogen electrode (NHE). It can be found that the Ti7–C8A and Ti4–C8A clusters have very negative LUMO levels; therefore, they are expected to serve as catalysts for photocatalytic reduction reactions.

### CO2 photoreduction

Based on the abovementioned advantages, we conducted UV and visible light-driven photocatalytic CO2RR over Ti7–C8A and Ti4–C8A, with TEOA and H2O as the electron donor and reaction solvent (H2O/TEOA = 4/1), respectively. As we can see from Fig. 3a and b, the yield of HCOO− for these two PTC clusters shows a continuous growth with the extended irradiation time. After 17 hours, the HCOO− production of Ti7–C8A under UV light irradiation (200–400 nm) reaches up to 41.51 ± 1.87 μmol (488.35 ± 21.41 μmol g−1 h−1), which is nearly two times higher than that of Ti7–C8A (21.58 ± 1.13 μmol; 253.88 ± 1.32 μmol g−1 h−1).

### Table 1

<table>
<thead>
<tr>
<th>Ti(OiPr)4</th>
<th>C8A ligand</th>
<th>H2PO4</th>
<th>HOiPr:MeOH</th>
<th>Crystal morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 mmol</td>
<td>0.01 mmol</td>
<td>30.0 mg</td>
<td>1:4 (mL)</td>
<td>Polygon</td>
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<tr>
<td>4 mmol</td>
<td>0.01 mmol</td>
<td>30.0 mg</td>
<td>0:5 (mL)</td>
<td>Ball</td>
</tr>
<tr>
<td>4 mmol</td>
<td>0.01 mmol</td>
<td>30.0 mg</td>
<td>2:3 (mL)</td>
<td>Spindle</td>
</tr>
<tr>
<td>4 mmol</td>
<td>0.01 mmol</td>
<td>30.0 mg</td>
<td>3:2 (mL)</td>
<td>Long pyramid</td>
</tr>
</tbody>
</table>
13.29 μmol g⁻¹ h⁻¹). The photocatalytic results revealed that HCOO⁻ is the only liquid product detected by ion chromatography (IC; Fig. S8†), while a small amount of competitive H₂ and CO was observed by gas chromatography (GC; Fig. S9† and Fig. 3c). According to the reductive product distribution (Fig. 3c), the photocatalytic selectivity of CO₂-to-HCOO⁻ conversion for Ti₄-C₈A and Ti₇-C₈A was determined to be 96.0% and 99.7%, respectively. The higher photocatalytic activity of Ti₄-C₈A is probably related to its four potentially catalytically active sites with naked coordination space (five-coordinated Ti₁, Ti₂, and Ti₃ atoms) or a coordinated isopropanol molecule (Ti₄ atom), which are easily available sites for CO₂ attack. For Ti₇-C₈A, however, only two Ti₄ atoms coordinated with two terminal methoxy groups can function as catalytically active sites for CO₂ reduction. Additionally, when an identical photocatalytic reaction was carried out under visible-light irradiation (420–800 nm), the HCOO⁻ yield (8.25 ± 1.06 μmol; 97.06 ± 12.47 μmol g⁻¹ h⁻¹) of Ti₄-C₈A was slightly higher than that of Ti₇-C₈A (6.19 ± 1.32 μmol; 72.82 ± 15.53 μmol g⁻¹ h⁻¹). This is mainly because Ti₄-C₈A has a better visible-light absorption ability compared with Ti₇-C₈A. Moreover, no gaseous or liquid reductive by-products were detected by IC and GC during the reaction process, which suggested that both the PTC clusters displayed a relatively higher selectivity (~100%) for CO₂-to-HCOO⁻ conversion under visible light. From the structural viewpoint, we assume that the potentially active sites (Ti₁, Ti₂, Ti₃, and Ti₄ atoms) in Ti₄-C₈A are twice those (two Ti₄ atoms) in Ti₇-C₈A. Consequently, we compared the catalytic activity of active sites in Ti₄-C₈A and Ti₇-C₈A using the turnover number (TON). As shown in Table S2,† each potential Ti⁴⁺ catalytic site (TON_TI) in Ti₇-C₈A is more active than that in Ti₄-C₈A under UV or visible light irradiation, whereas the Ti₄⁺ C₈A cluster has a higher overall TON. Therefore, the higher photocatalytic activity of Ti₄-C₈A compared with that of Ti₇-C₈A is mainly attributed to its more potentially active Ti⁴⁺ sites. To know the reasons behind the different photocatalytic activities of Ti₄-C₈A and Ti₇-C₈A, we first explored the charge separation efficiencies by their transient photocurrent responses to UV and visible light irradiation. It was revealed that Ti₄-C₈A had a slightly higher photocurrent than Ti₇-C₈A under UV or visible light irradiation (Fig. S10–S13†). However, the photocurrent is usually affected by the resistance of the material (both within a crystallite and at grain boundaries), conductivity between the ITO and the material, as well as the homogeneous distribution and connectivity among ITO, the material and Nafion used as a binder. All these factors affect the current that is measured. The photocurrent measured thus describes the complete electrode and not one particular component of the electrode. Our electrode consisting of ITO, Nafion, and Ti₄-C₈A shows a more efficient charge separation which does not mean that Ti₄-C₈A itself has a more efficient charge separation than Ti₇-C₈A, because the fabricated electrodes were not used in photocatalysis. To further confirm the charge separation efficiency, we also conducted electrochemical impedance spectroscopy (EIS) measurements. As shown in Fig. S14,† the size of the Nyquist plot of Ti₄-C₈A is clearly smaller than that of Ti₇-C₈A, which indicates that the interfacial charge transfer process of Ti₇-C₈A is faster than that of Ti₄-C₈A. Therefore, Ti₇-C₈A does have a higher charge separation efficiency than Ti₄-C₈A. To further validate the exciton separation (or charge separation) efficiency of Ti₄-C₈A and Ti₇-C₈A, we also calculated the electron–hole Coulomb attraction energies (E_c) in the first excited state. In general, a small E_c results in high exciton separation efficiency. Density functional theory (DFT) and time-dependent DFT (TD-DFT) were employed in this work. The calculated E_c values are 3.42 and 2.16 eV for Ti₄-C₈A and Ti₇-C₈A, respectively (Fig. S15†). This result also suggested that Ti₄-C₈A has higher exciton separation efficiency than Ti₇-C₈A, which is consistent with our experimental data. The difference in the charge separation of these two clusters is mainly derived from their structural distinction, which results in different activities for photocatalytic CO₂RR. Moreover, the apparent quantum efficiency (QE) for HCOO⁻ evolution was measured using different monochromatic light (365/420/450/500 nm), and the corresponding results indicate that Ti₄-C₈A has higher QE than Ti₇-C₈A (see the QE Calculation section in the ES†). It is worth noting that Ti₄-C₈A and Ti₇-C₈A not only showed high HCOOH production under UV light irradiation (Table S3†), but also they are the first crystalline coordination molecular system to perform heterogeneous photocatalytic CO₂RR in H₂O containing TEOA.

After the reaction, the photocatalyst solids were removed from the reaction solution. The Ti⁴⁺ residual ions in the resultant filtrate were evaluated to be 0.082% (Ti₄-C₈A) and 0.054% (Ti₇-C₈A) by inductively-coupled plasma analysis. At the same time, the UV-vis absorption spectra of the filtrates did not show any obvious signal (Fig. S16 and S17†), which excludes
the influence of the decomposed active components from catalysts on the photocatalytic activity. Moreover, nearly unchanged solid IR spectra and PXRD patterns obtained before and after photocatalytic CO2RR also confirmed the heterogeneous catalysis nature of the Ti4-C8A and Ti7-C8A clusters (Fig. S18–S21†). A series of deletional control experiments were conducted to verify the photocatalytic activity of these two PTCs, in the absence of photocatalysts, CO2, TEOA, the C8A ligand or light irradiation. The results revealed that no detectable products were observed by IC and GC in the reaction system (Table S4†), corroborating the photocatalytic potential of these two PTC clusters for reducing CO2 into HCOO−.

Subsequently, recycling experiments were performed for checking photocatalytic durability, in which Ti4-C8A and Ti7-C8A can maintain their initial activities for at least six cycles (Fig. 3d). The slightly reduced HCOO− yield was probably due to the mass loss of the photocatalysts in the recovery process. Since the catalysts had undergone centrifugation, washing, and redispersion processes, the quality was inevitably lost in the circulation process; therefore, it is relatively reasonable that the product yield slightly decreases. To further confirm the photocatalytic activities of Ti4-C8A and Ti7-C8A, an isotopic 13CO2 experiment under identical photocatalytic reaction conditions was performed to identify the carbon source origin of the produced HCOO−, and the products were identified by 13C NMR spectroscopy. As shown in Fig. S22–S24†, the 13C NMR spectrum gives very clear and strong signals corresponding to HCOO−, CO2, CO3−, and HCO3−, which are consistent with other previous important works.15,16,21 Also, these signals disappeared when using 13CO2 instead of 13CO2, except for the additional peaks corresponding to DMSO and TEOA. This fact unambiguously establishes that the produced HCOO− indeed originates from CO2. Therefore, Ti4-C8A and Ti7-C8A are indeed active for reducing CO2 to HCOO− under UV and visible-light irradiation.

Additionally, we further conducted electron spin-resonance spectroscopy (ESR) measurement to study the reaction mechanism behind CO2 photoreduction over Ti4-C8A and Ti7-C8A. As shown in Fig. S25†, the reaction systems including Ti4-C8A/Ti7-C8A and TEOA under a N2 atmosphere without light irradiation did not show any ESR signal. When the reaction systems were irradiated with a light source under identical conditions, a clear signal of Ti3+(g = 1.948) could be observed from their ESR spectra. This means that the Ti4+ ions within the Ti4-C8A and Ti7-C8A clusters were reduced into Ti3+ ions by receiving photoexcited electrons transferred from the C8A ligand, while the corresponding photo-generated holes were quenched by TEOA. Moreover, the intensity of the Ti3+ signal increased with the extended irradiation time. When the reaction system was exposed to a CO2 atmosphere, the ESR signal of Ti3+ disappeared, indicating that the photogenerated Ti3+ ions indeed involved in the CO2 reduction reaction. Besides, a sharp and narrow ESR signal (g = 2.002) of light-induced radical formation of the ligand also can be observed. The ESR results revealed that the Ti4+ ions within Ti4-C8A and Ti7-C8A were the photocatalytically active sites for the CO2-to-HCOOH reduction (Fig. S25†). Based on the above-mentioned experimental results and a deep understanding of the previously reported PTC-based photocatalysts (including Ti-MOFs and PTC clusters in our group) used for photocatalytic CO2RR,15,23 a proposed reaction mechanism for CO2 reduction is illustrated as shown in Fig. 4. Upon UV/visible-light irradiation, photo-excited electron–hole pairs are generated in the titanium–oxo cluster. Then, the Ti4+ ions within the cluster accept photo-generated electrons transferred from the C8A ligand and turn into Ti3+ ions, whereas the TEOA molecules in the reaction system act as electron donors to consume the produced photo-generated holes. Subsequently, the generated Ti3+ ions offer photo-excited electrons to the absorbed CO2 molecules for activation, and then go back to the Ti4+ ions. In this way, a complete CO2-to-HCOO− photosynthesis cycle can be achieved by Ti3+–Ti4+ intervacency charge transfer in Ti4-C8A and Ti7-C8A, in the presence of TEOA (as an electron and proton donor) and H2O.

Conclusions

In conclusion, two water-stable and photosensitive PTCs were constructed by using the “functional armor” C8A with high molecular degrees of freedom and variable conformations, and they can be converted thermodynamically into each other under different solvothermal conditions. Thanks to the strong charge transfer generated from the intimate coordination effect between the titanium–oxo core and the C8A ligand, the
light absorption range of these two PTCs is effectively extended from the traditional ultraviolet to the visible region. Moreover, the overall titanium–o xo core was surrounded by the hydrophobic benzene ring of C8A, resulting in high structural and chemical stability of the two PTCs in aqueous solutions. Based on these advantages, Ti4-C8A and Ti7-C8A were treated as heterogeneous photocatalysts to carry out CO2RR in H2O containing TEOA, and they finally exhibited very high photocatalytic activity and selectivity for CO2-to-HCOO− conversion. Significantly, this is the first time that a coordination molecular complex system performed heterogeneous photocatalytic CO2RR in H2O in the presence of TEOA. This work not only expanded the photocatalytic application of traditional PTCs, but also provided more insights into the design and preparation of heterogeneous molecular photocatalysts to achieve efficient CO2RR in H2O as the reaction solvent.

Conflicts of interest
There are no conflicts to declare.

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Notes and references