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,1–4,5 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.23,25,27 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-
Because of the hydrophobic benzene group of C8A,43 these two structures can achieve thermodynamic interconversion under more stable and photosensitive PTCs applied in artificial CO2RR. This work provides a new strategy toward developing heterogeneous photocatalysts to perform CO2RR in H2O containing sacrificial triethanolamine (TEOA). We found that both Ti7-C8A and Ti4-C8A could reduce CO2 to HCOOH with very high activity (253.88 ± 13.29 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 methods**

All reagents and solvents employed in this work were commercially 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) analysis 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 chromatography (LC-2010 PLUS). Gas chromatography was performed on GC-7920A (Agilent Co.) equipped with a flame ionization detector (FID) with a methanizer and a thermal conductivity detector (TCD). 13CNMR spectra were measured using chromatography–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 filtration 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 isopropanol (2 mL), and CH3OH (3 mL) was ultrasonically dissolved. 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 filtration 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.

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Scheme 1 Simplified structures of ellipse-shaped Ti4-C8A and bowknot-shaped Ti7-C8A. Their crystallographic structures can undergo thermodynamic interconversion.
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 μ₁-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. 1a 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 Cmc₂ 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](https://example.com/fig1.png)

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.
that dinuclear metal charge transfer occurred between the C8A ligand and tita-
sive PTCs and free C8A ligand, indicating that an obvious visible light collecting ability than the traditional UV-respon-
be 1.86 (Fig. 2a). Furthermore, the through slight changes in the synthetic protocol (Table 1 and
through PXRD patterns and thermogravimetric analysis, respect-
tion (PXRD) patterns and thermogravimetric analysis, respect-
structured or crystalline materials generally exhibit intrinsic
cations. Besides, it is well recognized that Ti-based nano-
and important for them to be used in water-dependent appli-
benzene group modification of the C8A ligand endows these
which eight hydroxyl groups are coordinated to two Ti1 and
and visible light-driven photocatalytic CO2RR over
Based on the abovementioned advantages, we conducted UV
and visible light-driven photocatalytic CO2RR over Ti7-C8A and
Ti7-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 ±

**Table 1** The synthesis protocol of different Ti7-C8A crystal morphologies

<table>
<thead>
<tr>
<th>Ti(OiPr)4</th>
<th>C8A ligand</th>
<th>H3PO4</th>
<th>HOiPr : MeOH</th>
<th>Crystal morphology</th>
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<tbody>
<tr>
<td>4 mmol</td>
<td>0.01 mmol</td>
<td>30.0 mg</td>
<td>1 : 4 (mL)</td>
<td>Polygon</td>
</tr>
<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>

Fig. 2 (a) Different morphologies of Ti4-C8A and Ti7-C8A crystals. (b) UV/vis spectra of the C8A ligand, Ti4-C8A, and Ti7-C8A. (c) Tauc plots of Ti4-C8A and Ti7-C8A. (d and e) Ultraviolet photoelectron spectroscopy (UPS) spectra of Ti4-C8A and Ti7-C8A. The intersections of the tangents with the baseline give the edges of the UPS spectra from which the UPS width is determined. UPS is used to determine the ionization potentials [equivalent to the HOMO energy] of Ti4-C8A and Ti7-C8A. Their HOMO levels are determined to be 5.97 (1.12 V vs. NHE) and 5.51 eV (0.66 V vs. NHE) by subtracting the width of the He I UPS spectra from the excitation energy (21.22 eV). The LUMO levels of Ti4-C8A and Ti7-C8A are thus calculated to be −0.74 V (vs. NHE) and −0.98 V (vs. NHE), respectively.

Ti7-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 Ti4-C8A and Ti7-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 Ti4-C8A and Ti7-C8A, which display semiconductor-like properties. On this basis, the corresponding HOMO and LUMO energy levels of Ti4-C8A and

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terminal methoxy groups can function as catalytically active sites 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 ESI†). 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 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 effective 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 Ti₄-C₈A is faster than that of Ti₇-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 (Eₕ) in the first excited state. In general, a small Eₕ results in high exciton separation efficiency. Density functional theory (DFT) and time-dependent DFT (TD-DFT) were employed in this work. The calculated Eₕ values are 3.42 and 2.16 eV for Ti₄-C₈A and Ti₇-C₈A, respectively (Fig. S15†). This result also suggested that Ti₇-C₈A has higher exciton separation efficiency than Ti₄-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 ESI†). 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.

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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 CO$_2$RR also confirmed the heterogeneous catalysis nature of the Ti$_7$-C8A and Ti$_7$-C8A clusters (Fig. S18–S21†). A series of deletion control experiments were conducted to verify the photocatalytic activity of these two PTCs, in the absence of photocatalysts, CO$_2$, 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 CO$_2$ into HCOO$^-$. Subsequently, recycling experiments were performed for checking photocatalytic durability, in which Ti$_4$-C8A and Ti$_7$-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 Ti$_4$-C8A and Ti$_7$-C8A, an isotopic $^{13}$CO$_2$ experiment under identical photocatalytic reaction conditions was performed to identify the carbon source origin of the produced HCOO$^-$, and the products were identified by $^{13}$C NMR spectroscopy. As shown in Fig. S22–S24, the $^{13}$C NMR spectrum gives very clear and strong signals corresponding to HCOO$^-$, which are consistent with other previous important works.$^{15,16,21}$ Also, these signals disappeared when using $^{13}$CO$_2$ instead of $^{13}$CO$_2$, except for the additional peaks corresponding to DMSO and TEOA. This fact unambiguously establishes that the produced HCOO$^-$ indeed originates from CO$_2$. Therefore, Ti$_4$-C8A and Ti$_7$-C8A are indeed active for reducing CO$_2$ to HCOO$^-$ under UV and visible-light irradiation.

Additionally, we further conducted electron spin-resonance spectroscopy (ESR) study to reaction systems including Ti$_4$-C8A/Ti$_7$-C8A and TEOA under a N$_2$ 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 Ti$^{3+}$ ($g = 1.948$) could be observed from their ESR spectra. This means that the Ti$^{4+}$ ions within the Ti$_4$-C8A and Ti$_7$-C8A clusters were reduced into Ti$^{3+}$ 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 Ti$^{3+}$ signal increased with the extended irradiation time. When the reaction system was exposed to a CO$_2$ atmosphere, the ESR signal of Ti$^{3+}$ disappeared, indicating that the photogenerated Ti$^{3+}$ ion is involved in the CO$_2$ 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 Ti$^{4+}$ ions within Ti$_4$-C8A and Ti$_7$-C8A were the photocatalytically active sites for the CO$_2$-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 CO$_2$RR$^{15,23}$ a proposed reaction mechanism for CO$_2$ 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 Ti$^{4+}$ ions within the cluster accept photo-generated electrons transferred from the C8A ligand and turn into Ti$^{3+}$ ions, whereas the TEOA molecules in the reaction system act as electron donors to consume the produced photo-generated holes. Subsequently, the generated Ti$^{3+}$ ions offer photo-excited electrons to the absorbed CO$_2$ molecules for activation, and then go back to the Ti$^{4+}$ ions. In this way, a complete CO$_2$-to-HCOO$^-$ photosynthesis cycle can be achieved by Ti$^{3+}$–Ti$^{4+}$ intervalence charge transfer in Ti$_4$-C8A and Ti$_7$-C8A, in the presence of TEOA (as an electron and proton donor) and H$_2$O.

**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 Ti8-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