CrystEngComm



View Article Online

PAPER

Check for updates

Cite this: CrystEngComm, 2019, 21, 6423

Received 4th August 2019, Accepted 23rd September 2019

DOI: 10.1039/c9ce01218d

rsc.li/crystengcomm

Introduction

In the past few years, non-renewable energy consumption and environmental pollution have become the primary problems to be solved for the development of human society. For example, carbon dioxide can lead to the greenhouse effect, thus creating a disorder in the global ecosystem as a result of the combustion of most fossil fuels.¹⁻³ The utilization and development of CO₂ for the production of clean and energy-rich fuels have been a hot research area. This research area inreduction,4-9 cludes photocatalytic electrocatalytic reduction,10-12 and homogeneous catalytic hydrogenation.¹³⁻¹⁵ Among these, CO₂ photocatalytic reduction using solar light as a clean, abundant and renewable energy is an advanced technology to solve the above problems.16,17 Owing to the kinetic inertness and thermodynamic

Visible-light CO₂ photoreduction of polyoxometalate-based hybrids with different cobalt clusters[†]

Wei Yao, Chao Qin, 吵 * Na Xu, Jie Zhou, Chunyi Sun, Li Liu * and Zhongmin Su 吵

The photoreduction of carbon dioxide (CO₂) into a valuable energy gas (CO and H₂) is an efficient approach to address the fossil fuel crisis and mitigate the global warming effect. The development of effective photocatalysts for CO₂ reduction is still desirable and challenging. Herein, two novel polyoxometalatebased hybrids with multinuclear cobalt clusters, $[Co_{2.67}(SiW_{12}O_{40})(H_2O)_4(Htrz)_4]\cdot Cl_{1.33}$ (Htrz = 1,2,4-triazole) (1) with a binuclear cobalt cluster and $[Co_3(SiW_{12}O_{40})(H_2O)_3(Htrz)_6Cl] \cdot Cl \cdot 6H_2O$ (2) with a trinuclear cobalt cluster, were synthesized under hydrothermal conditions. Both of them were characterized by singlecrystal X-ray diffractions, PXRD, IR, TG and UV-vis spectra. Compound 1 exhibited a 3D structure with 4-connected [SiW₁₂O₄₀] and 3-connected [Co₂(Htrz)₃(H₂O)₃] secondary building units (SBUs). The 1D chain of compound 2 was constructed from $[SiW_{12}O_{40}]$ and $[Co_3(Htrz)_6(H_2O)_3Cl]$ SBUs. Furthermore, the photoreduction of CO₂ under visible light by the two cobalt-based POMs was investigated using [Ru(bpy)₃]Cl₂ $-6H_2O$ as a photosensitizer. The CO yields of compounds 1 and 2 were 15705 and 18501 μ mol g⁻¹ for the CO₂ photocatalytic reduction under three hour irradiation at 293 K, respectively. The difference in the photocatalytic performance of 1 and 2 was explained by comparing the energy of the valence band, band gaps and conduction band. The results showed that the photocatalysts incorporated with multinuclear Co clusters could effectively improve photocatalytic activities, thus providing a valuable view to design high performance and cost-acceptable molecular catalysts for CO₂ photoreduction.

stability of carbon dioxide, it is desirable to design and synthesize efficient catalysts for activating the CO_2 molecules.^{18–23}

Polyoxometalates (POMs) are typical metal oxygen cluster compounds and have definite particle sizes and shapes that render them highly potential in photochromism,²⁴⁻²⁶ redox activity,^{27,28} catalysts,²⁹⁻³¹ functional materials,³²⁻³⁷ etc. The terminal oxygen atoms of POMs can easily form chemical bonds with transition metals and various organic ligands; as a result, they have been widely employed as building blocks for assembling supramolecular structures.38-40 Keggin-type POMs, as the most common POMs, have caught worldwide attention because of their structural stability and excellent catalytic property.41 Impressive studies on the linking of Keggin-type polyoxometalate building blocks to generate related extended structures have been performed. Transition metals are usually used as the important linkers between POMs and organic ligands. Among them, cobalt metal captures our extra attention. In 2013, Wang et al. introduced cobalt species into g-C₃N₄ to accelerate the separation process of charge carriers of photocatalysis.⁴² Also, Co/PCN, which contains a single cobalt site, proved to deliver high selectivity and activity for CO₂ photoreduction.⁴³ Moreover, the CO₂ electroreduction performance of Co catalysts with different N

Key Laboratory of Polyoxometalate Science, Institute of Functional Material Chemistry, National & Local United Engineering Laboratory for Power Battery, Northeast Normal University, Changchun, Jilin, 130024, P. R. China. E-mail: qinc703@nenu.edu.cn

[†] Electronic supplementary information (ESI) available: Details of the PXRD, IR, TGA, UV-vis and photochemical performance data. CCDC 1915927 (1), 1915928
(2). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9ce01218d

coordination numbers was explored.⁴⁴ We thus expect to choose a suitable organic ligand containing nitrogen to design and synthesize new POM-based hybrids with different numbers of Co active sites and Co–N coordination, which might be used as catalysts to improve the CO₂ photocatalytic activities. Based on the crystal engineering work on polyoxometalate-based hybrids, Co metal is an important combining site, by which it is easy to combine with ligands bearing nitrogen atom to form multinuclear Co-based SBUs. For example, binuclear cobalt-containing $[Co_2(H_2O)_2(Htrz)_5]$ - $[SiW_{12}O_{40}]$ ·2.5H₂O and trinuclear cobalt-containing $[Co_3(dat)_4$ - $(datH)_2(H_2O)_6]$ Cl₃·9H₂O have been synthesized, where the rigid imidazole and triazole ligands are ideal ligands for constructing Co-based POMs.^{45,46}

Herein, we chose H4SiW12O40.2H2O as the molecular building block, Co ion as the linker and 1,2,4-triazole (1,2,4trz) as the organic ligand to construct new hybrid compounds. Two new POM-based organic-inorganic hybrids, $[Co_{2.67}(SiW_{12}O_{40})(H_2O)_4(Htrz)_4]$ ·Cl_{1.33} (1) with binuclear cobalt cluster and {Co₃[SiW₁₂O₄₀](H₂O)₃(Htrz)₆Cl}Cl·6H₂O (2) with trinuclear cobalt cluster, were synthesized under hydrothermal conditions. Compound 1 exhibited a 3D structure containing $[SiW_{12}O_{40}]$ and $[Co_2(Htrz)_3(H_2O)_3]$ as building blocks and compound 2 had a 1D chain structure, which was composed of [SiW₁₂O₄₀] and [Co₃(Htrz)₆(H₂O)₃Cl] as building blocks. It is noteworthy that compound 2 is the first example of trinuclear cobalt-based Keggin-type POM-based hybrids in the {POM/Co/trz} system. Compounds 1 and 2 can serve as heterogeneous photocatalysts in the photoreduction of CO₂ under visible light. The yields of CO and H₂ for 1 were 15705 and 14523 μ mol g⁻¹, and 18501 and 18199 μ mol g⁻¹ for 2, respectively. The inherent reason for the photocatalytic activity of 1 and 2 with different Co clusters was investigated by photochemical and electrochemical measurements.

Experimental

2.1 Materials

All the reagents were purchased from chemical suppliers without any further purification.

2.2 Instrument

The elemental analyses of C, H, and N were performed on a Perkin-Elmer 2400 CHN elemental analyzer. X-ray diffraction patterns (PXRD) were recorded on a Siemens D5005 diffractometer with graphite-monochromatized Cu K α (λ = 1.5418 Å) radiation. The Fourier transform infrared (FT-IR) spectra were recorded in the range of 4000–400 cm⁻¹ using a Matton Alpha-Centauri FT-IR spectrophotometer with KBr pellets. Thermogravimetric analyses (TGA) were performed using a Perkin-Elmer TG-7 analyzer heated from 25 °C to 600 °C under N₂ at a heating rate of 10 °C min⁻¹. The UV-vis absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer in the range of 200–800 nm.

2.3 Synthesis of [Co_{2.67}(SiW₁₂O₄₀)(H₂O)₄(Htrz)₄]·Cl_{1.33} (1)

A mixture of CoCl₂·6H₂O (110 mg, 0.5 mmol), 1,2,4-triazole (15 mg, 0.23 mmol) and H₄SiW₁₂O₄₀·2H₂O (30 mg, 0.01 mmol) was dissolved in 0.05 mol L⁻¹ HCl (5 mL) solution. The mixed solution was transferred into a 15 mL Teflon-lined autoclave and heated to 130 °C for one day. After being cooled to room temperature, the dark pink block crystals were filtered and washed with distilled water three times, yielding 67% based on Co. Elemental analysis calcd. for 1: C 2.49, H 0.76, N 5.05%; found: C 2.70, H 0.59, N 4.90%. IR (KBr, cm^{-1}): 3446(m), 1610(w), 1417(w), 1154(w), 1058(s), 973(s), 873(s), 788(s). Crystal data for 1: C₈H₂₀Co_{2.67}N₁₂O₄₄- $SiW_{12}Cl_{1.33}$, $F_w = 3427.06$, crystal system: cubic, space group: $I4\bar{3}d$, a = 25.1342(4) Å, b = 25.1342(4) Å, c = 25.1342(4) Å, $\alpha =$ $\beta = \gamma = 90^{\circ}, V = 15878.0(8) \text{ Å}^3, Z = 12, R_{(int)} = 0.0806, D_{cal} =$ 4.301 g cm⁻³, GOF = 1.017, R_1 = 0.0235, w R_2 = 0.0563 (I > $2\sigma(I)$).

2.4 Synthesis of [Co₃(SiW₁₂O₄₀)(H₂O)₃(Htrz)₆Cl]·Cl·6H₂O (2)

The same reaction condition and the stoichiometric ratio used for 1 were used to prepare compound 2, except that 0.05 mol L⁻¹ HCl was replaced by distilled water. The light pink crystals of 2 were obtained with about 50% yield based on Co. Elemental analysis calcd. for 2: C 4.12, H 1.15, N 7.13%; found: C 3.90, H 0.98, N 6.82%. IR (KBr, cm⁻¹): 3431(m), 1617(w), 1430(w), 1140(w), 1017(w), 973(s), 877(w), 791(s). Crystal data for 2: C₁₂H₃₆Co₃N₁₈O₄₉SiW₁₂, $F_w =$ 3698.57, crystal system: triclinic, space group: $P\bar{1}$, a =12.7994(10) Å, b = 13.1541(11) Å, c = 18.1961(15) Å, $\alpha =$ 92.8590°, $\beta = 90.2200°$, $\gamma = 95.7360°$, V = 3044.3(4) Å³, Z = 2, $R_{(int)} = 0.0365$, $D_{cal} = 4.035$ g cm⁻³, GOF = 0.980, $R_1 = 0.0406$, $wR_2 = 0.0940$ ($I > 2\sigma(I)$).

2.5 X-ray crystallography

Single-crystal diffraction data were recorded on a Bruker Apex CCD II diffractometer at 296 K, with graphitemonochromated Mo-K α radiation (λ = 0.71073 Å). The data frames were recorded and processed using the APEX 2 suite of programs.⁴⁷ The data were corrected for absorption and beam corrections based on the multi-scan technique as implemented in SADABS. The structures were solved by the direct method using SHELXS or SHELXT and refined by fullmatrix least-squares on F^2 using the SHELXL software.⁴⁸ Relevant crystal data, CCDC 1915927 (1) and CCDC 1915928 (2).

2.6 Photocatalytic test

The photocatalytic reaction was performed in a 50 mL quartz tube,⁴⁹ which was filled with CO₂. This system contained the title compounds (1.0 mg, 0.3 μ mol), [Ru(bpy)₃]Cl₂·6H₂O (10 mg, 0.013 mmol for 1, and 7 mg, 0.009 mmol for 2) as the photosensitizer, triethanolamine (TEOA) as the sacrificial agent, H₂O (1 mL), and acetonitrile (MeCN, 4 mL). The mixed solution was bubbled with CO₂ for 15 min, and the reaction temperature was maintained at 20 °C. The system was

irradiated by a 300 W Xe lamp ($\lambda \ge 420$ nm) for 3 h. After the completion of the photocatalytic reaction, the produced gases (CO and H₂) were analysed using a gas chromatography (GC) instrument with a molecular sieve column. In order to detect the produced CO, 500 µL gases from the tube were injected into a FID detector, and 1000 µL gases were injected into a TCD detector to detect H₂. Argon was used as the carrier gas, and the volume of certain products (CO and H₂) was calculated by comparing the integrated area of CO and H₂ with a calibration curve. The temperature of the injector and detector was kept to 80 °C. An isotopic test was performed under similar conditions, except that ¹³CO₂ (99% in purity) was used instead of ¹²CO₂.

2.7 Photocurrent measurements

The samples were mixed with graphite in a 3:2 mass ratio, and then put into a mixed solution containing 100 µL water, 100 µL ethanol, and 300 µL naphthol by ultrasonic dispersion for half an hour. The electrode was prepared by spreading 60 µL hybrid slurries on one side of the FTO glass substrate ($1 \times$ 1 cm²). A 300 W Xe lamp was used as the light source and 0.1 M Na₂SO₄ solution was used as the electrolyte. Photocurrent test was performed on a CHI760E electrochemical workstation with a three electrodes configuration. Platinum wire electrode, the sample electrode and Ag/AgCl electrode were employed as the counter, working and reference electrode, respectively.

Results and discussion

3.1 Synthesis

Compounds 1 and 2 were synthesized under hydrothermal conditions at 130 °C for 24 hours. The pH value of the reaction system played an important role in the synthesis of the products. In this study, compound 1 was obtained using 0.05 mol L^{-1} HCl solution, while compound 2 was synthesized in distilled water. When the pH value was higher than 5, only a clear solution without any crystals was obtained. Another key factor is the ratio of metal, POM and ligand. The results of a large number of parallel experiments show that their optimal molar ratio was 50:23:1 for 1 and 2.

3.2 Crystal structures

 $[Co_{2.67}(SiW_{12}O_{40})(H_2O)_4(Htrz)_4]\cdotCl_{1.33}$ (1). Single-crystal X-ray diffraction analysis displayed that 1 crystallized in the cubic space group $I4\bar{3}d$ (Table S1[†]). There are two Co cations with one third occupancy, one Htrz ligand, one fourth of Keggin $[SiW_{12}O_{40}]$ anion, one coordination water molecule and two free Cl ions in the asymmetric unit. Both the Co²⁺ cations have six-coordinated environments with octahedral coordination geometries. Co1 is coordinated with three nitrogen atoms from three different Htrz ligands and three oxygen atoms from three nitrogen atoms from three different [SiW₁₂O₄₀] polyoxoanions. Co2 is coordinated by three nitrogen atoms from three Mtrz ligands and three oxygen atoms from three nitrogen atoms from three Ntrz ligands and three nitrogen atoms from three nitrogen atoms from three Ntrz ligands and three Ntrz ligands and

bond distances of Co–N and Co–O are in the ranges of 2.121(14)–2.124(15) Å and 2.108(15)–2.131(12) Å, respectively, which are similar to the bond lengths reported before.⁵⁰ Two Co²⁺ are linked together by three Htrz ligands to form a binuclear $[Co_2(Htrz)_3(H_2O)_3]^{4+}$ secondary building unit (SBU) (Fig. 1). The adjacent binuclear $[Co_2(Htrz)_3(H_2O)_3]^{4+}$ clusters are further connected by $[SiW_{12}O_{40}]$ polyoxoanions to form a 3D structure, in which each $[SiW_{12}O_{40}]$ polyoxoanion connects with four $[Co_2(Htrz)_3(H_2O)_3]$ (Fig. 1a) and each $[Co_2(Htrz)_3(H_2O)_3]$ SBU links with three $[SiW_{12}O_{40}]$ (Fig. 1b). In order to better understand the structure, we consider $[Co_2(Htrz)_3(H_2O)_3]$ SBU as a 3-connected node and $[SiW_{12}O_{40}]$ acts as a 4-connected node, so the structure of 1 can be simplified into a 3,4-binodal net with the point symbol $\{8^3\}_4\{8^6\}_3$ (Fig. 1c).

[Co₃(SiW₁₂O₄₀)(H₂O)₃(Htrz)₆Cl]·Cl·6H₂O (2). Compound 2 crystallized in the triclinic space group P1 (Table S1⁺). The asymmetric unit of 2 consists of three Co2+ ions, six Htrz ligands, one [SiW₁₂O₄₀] polyoxoanion, three coordination water molecules, one coordinated Cl⁻ ion, six free water molecules and one free Cl^{-} ion (Fig. 2a). All the Co^{2+} ions exhibit sixcoordinated octahedral geometries, but have different coordination environments. As shown in Fig. 2b, Co1 cation is bridged by three nitrogen atoms from three different Htrz ligands, two coordinated water molecules and one oxygen atom from the terminal oxygen of [SiW₁₂O₄₀] polyoxoanion (Co-N 2.060(13)-2.091(13) Å, Co-O 2.107(9)-2.155(11) Å), Co2 cation is coordinated by six nitrogen atoms from six independent Htrz ligands with bond lengths ranging from 2.134(12) to 2.157(12) Å, and Co3 cation is linked by one Cl^{-} ion, one water molecule, another terminal oxygen of [SiW₁₂O₄₀] polyoxoanion and three nitrogen atoms form three Htrz ligands



Fig. 1 (a) Each $[SiW_{12}O_{40}]$ polyoxoanion links with four $[Co_2(Htrz)_3(H_2O)_3]$ SBUs. (b) Each $[Co_2(Htrz)_3(H_2O)_3]$ SBU connects with three $[SiW_{12}O_{40}]$ polyoxoanions. (c) Representation of the 3,4-connected $\{8^3\}_4\{8^6\}_3$ topology of 1, in which SiW_{12} acts as a 4-c node and $[Co_2(Htrz)_3(H_2O)_3]$ SBU as a 3-c node.



Fig. 2 (a) The coordination environment of $[SiW_{12}O_{40}]$ polyoxoanion in **2**. (b) The presentation of trinuclear Co clusters connected with six Htrz ligands. (c) A view of the one-dimensional chain constructed by $[SiW_{12}O_{40}]$ and $[Co_3(Htrz)_6(H_2O)_3Cl]$ SBUs. (d) The 3D supramolecular framework of **2** connected by multipoint hydrogen bonds.

(Co–N 2.102(12)–2.118 (14) Å, Co–O 2.172(10)–2.296(9) Å, Co– Cl 2.340(5) Å). Three Co atoms are bridged by six Htrz ligands into a trinuclear $[Co_3(Htrz)_6(H_2O)_3Cl]$ cluster with a Co···Co distance of 3.794–3.805 Å. As shown in Fig. 2c, the adjacent $[SiW_{12}O_{40}]$ polyoxoanions are connected by $[Co_3(Htrz)_6(H_2O)_3-$ Cl] clusters to form a one-dimensional chain running along [1 1 0] direction. The adjacent 1D chains are inter-connected through N–H···Cl hydrogen bonding and further extended into a 3D framework (Fig. 2d).

The powder X-ray diffraction (PXRD) patterns of the assynthesized 1 and 2 matched well with the simulated patterns, indicating the crystalline phase purities (Fig. S1 and S2[†]). The IR spectra of compounds 1 and 2 are shown in Fig. S3 and S4,† respectively, in which the broad peak at 3446 cm⁻¹ for 1 and 3431 cm⁻¹ for 2 correspond to the stretching and bending vibrations of lattice and coordinated water molecules. The terminal W=O vibrations appear at 1058 and 1017 cm⁻¹ for compound 1 and 2, respectively. The characteristic peaks at 973, 873, 788 and 973, 877, 791 cm⁻¹ are assigned to the Si-O, W=O and W-O-W vibrations, respectively. The TG and DTG (derivative thermogravimetric) curves of 1 are depicted in Fig. S5.† The weight loss of 2.2% of 1 from 25 to 250 °C corresponds to the loss of four water molecules (calcd 2.1%), followed by a multi-step weight loss from 330 to 570 °C assigned to the decomposition of 1. The TG and DTG curves of 2 display a weight loss of 4.5% from 25 °C to 170 °C, which corresponds to the nine water molecules (calcd 4.4%, Fig. S6†). After an obvious plateau, a weight loss from 325 to 550 °C is attributed to sample decomposition.

3.3 Photoreduction of CO₂

Before photocatalytic measurements, the UV-vis spectra of 1 and 2 were investigated (Fig. S7[†]). They have two similar absorption bands; the range from 200 to 430 nm is attributed to the charge migration of $O \rightarrow W$ from SiW₁₂ and the one from 450 to 700 nm originates from Co²⁺.^{51,52} Despite the same molar concentration of 1 as 2, it was obvious that 2 shows a stronger absorption intensity than 1, which means that the trinuclear cobalt cluster of 2 can absorb more visible light than the binuclear cobalt cluster of 1. The heterogeneous photocatalyst and [Ru(bpy)₃]Cl₂·6H₂O were put into a mixed solvent of TEOA, MeCN and H₂O in a ratio of 1:4:1. The photocatalytic system was filled with CO₂ atmosphere under visible light with a 420 nm cut off filter. The photocatalytic performance of 1 and 2 was investigated after 3 h of light exposure. The yields of CO₂ photoreduction are shown in Fig. 3, which are 15 705 $\mu mol~g^{-1}$ of CO and 14 523 μmol g^{-1} of H_2 for 1 and 18501 $\mu mol~g^{-1}$ of CO and 18199 μmol g^{-1} of H₂ for 2, respectively, both higher than that of g-C₃N₄ and its derivatives (Table S2[†]). After the reaction, the PXRD patterns and IR spectra of 1 and 2 confirmed that the photocatalysts are stable during the photoreduction process (Fig. S1-S4[†]).

As shown in Fig. 4, the yield of CO and H_2 increased almost linearly with reaction time and reached to a plateau after 3 h of irradiation, which indicated that the reduction reaction is almost complete after three hours. The same trend of hydrogen evolution was observed for 1 and 2. Interestingly, sample 2 showed a higher CO and H_2 evolution rate in 0.5 hours (87.60 and 56.53 h⁻¹, respectively) than 1 (TOF_{CO} of 51.81 h⁻¹ and TOF_{H₂} of 35.06 h⁻¹). The influence of the content of 1 and 2 on the photocatalytic performance is presented in Fig. 5. The TON of CO and H₂ first increased and then decreased with the increase in the photocatalyst



Fig. 3 The yield of CO and H_2 of CO_2 photoreduction using 1 and 2 as catalysts for 3 h.

Paper



Fig. 4 TONs of CO and H₂ evolution catalysed by 1 (a) and 2 (b) in the presence of CO₂-saturated CH₃CN/TEOA/H₂O (4:1:1, v:v:v) solvent mixture under irradiation using a 300 W Xe lamp at 293 K.

quantity. When the content of 1 and 2 was 0.5 mg, the TON_{CO} increased to 49.49 and 55.31, respectively, which was higher than that of the pure photosensitizer. The optimal performance of 1 and 2 was at 1 mg for the studied conditions. Further increasing the amount of 1 and 2 resulted in a decrease in the CO₂ photocatalytic performance. These results indicated that 1 and 2 can act as catalysts for CO₂ photoreduction, and the appropriate amount of the catalysts is crucial. It was interesting that the photocatalytic yield of 2 was always superior to that of 1, which indicated that the catalytic activity of the trinuclear cobalt cluster was higher than that of the binuclear Co cluster. Moreover, a comparison of the photocatalytic activities and cost of compounds 1 and 2 with those of the other reported heterogeneous materials demonstrated that they are potential highperformance and cost-acceptable molecular catalysts for CO₂ photoreduction (Tables S3 and S4[†]).

In order to investigate the CO_2 photocatalytic performance of 1 and 2 under different conditions, control experiments were performed, and the results are summarized in Table 1. When the system was short of visible light and photosensitizer [Ru(bpy)₃]Cl₂·6H₂O, CO was not detected (entries 2 and 4, Table 1), which suggested that the light and photosensitizer are indispensable for the CO_2 reduction system. When [Ru(bpy)₃]Cl₂·6H₂O was replaced by tris(2-phenylpyridinato)iridium(m), no gases were produced (entry 11, Table 1), which indicated that the formation of CO and H_2 needs a suitable photosensitizer. Without 1 and 2 in the photocatalytic system, only small amounts of CO and H_2 were detected, which confirmed the catalytic activities of 1 and 2 (entry 3, Table 1).

Without CO_2 , no CO was observed which excluded the degradation effect of TEOA and organic ligand Htrz (entry 5, Table 1). Replacing 1 atmospheric pressure CO_2 with CO_2 and Ar at a ratio of 1:8, the TON_{CO} of 1 and 2 were only 0.66 and 1.34, but the amount of H₂ was improved significantly (entry 12, Table 1). The results showed that light-induced electrons promoted H₂ generation under the reaction conditions with a small quantity of CO_2 .

On using pure CH₃CN or DMF/H₂O to replace CH₃CN/H₂O mixture, CO production was hindered slightly, which can be ascribed to the optimal reaction media of CH₃CN and DMF (entries 6 and 8, Table 1). Without CH₃CN during the photocatalytic experiment, no gases were formed (entry 7, Table 1), which indicated that excess water decreases the activity of the catalytic sites because H₂O covered on the surface of the photocatalyst decelerates the key kinetic step.⁵³ As the system was short of TEOA, only a small amount of H₂ but no CO was detected (entry 9, Table 1). These results showed that H₂O, MeCN and TEOA are indispensable to the CO₂ transformation. When catalysts 1 and 2 were replaced by mixtures of tungstosilicic acid hydrate and 1,2,4-trz, no gas was detected



Fig. 5 TONs of CO and H_2 production with different amounts of compounds 1 (a) and 2 (b) under 3 h of visible-light irradiation at 293 K.

from this reaction system. This study further showed that $H_4SiW_{12}O_{40}$ ·2H₂O has no catalytic activity and is unable to

promote carbon dioxide reduction in the photocatalytic system. Moreover, if catalysts 1 and 2 were replaced by the $CoCl_2$, the yields of CO and H_2 dramatically decreased (Table 1, entry 13). It indicated that the formation of the coordination compound is effective in improving the catalytic activity of Co^{2+} .⁵⁴

Isotope tracer experiment involving ${}^{13}\text{CO}_2$ was performed to verify the C origin of the generated CO from CO₂ reduction, and the product was detected by mass spectrometry (MS) in the presence of visible light for 3 h. The peaks at 2.0 and 13.5 min were assigned to ${}^{13}\text{CO}$ and ${}^{13}\text{CO}_2$ (Fig. S8 and S9†), respectively.⁴² The signals at *m*/*z* 29 and 45 were marked as ${}^{13}\text{CO}$ and ${}^{13}\text{CO}_2$, respectively, and no signal was found at *m*/*z* 28. These results confirmed that the generated carbonic oxide originated from CO₂ dissolved in the mixed solution.

For verifying the improved photocatalytic performance and the photogenerated charge carrier recombination of 1 and 2, the photoluminescence (PL) spectra and lifetime were investigated. As shown in Fig. S10 and S11,[†] [Ru(bpy)₃]Cl₂·6H₂O shows the same strong emission peaks at about 616 nm with an excitation wavelength of 452 nm. After 1 and 2 were added into the photosensitizer solution, the PL intensity decreased to a lower level relative to that of the pure photosensitizer, implying that the transfer recombination of photoexcited electrons is inhibited by 1 and 2. In addition, 2 showed a lower PL peak intensity, which means that 2 is more efficient for reducing the electronic recombination process.²⁸ Such a phenomenon was also demonstrated by transient emission spectroscopy (Fig. S12 and Table S5[†]). The analysis of the fit curves supported a single exponential decay model and revealed that the average PL lifetimes decreased from 1.21 ns (photosensitizer) to 1.08 ns for 1 and 1.01 ns for 2, suggesting that 2 has a higher photocatalytic activity and better photogenerated charge carrier separation performance than 1. To

Table 1Various experimental conditions of compounds 1^a and 2^b						
Entry	Compound 1 TON _{CO} ^c	Compound 1 $\text{TON}_{\text{H}_2}^{d}$	Compound 1 TON ^e	Compound 2 TON_{CO}^{c}	Compound 2 $\text{TON}_{\text{H}_2}^{d}$	Compound 2 TON ^e
1	52.35	51.37	100.72	61.67	60.66	122.33
2^{f}	n.d. ^g	n.d.	n.d.	n.d.	n.d.	n.d.
3^h	0.11	0.07	0.18	0.21	0.12	0.33
4^i	n.d.	10.59	10.59	n.d.	16.49	16.49
5^{j}	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
6^k	38.34	193.06	231.40	41.58	186.65	228.23
7^l	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8 ^{<i>m</i>}	34.00	43.78	77.78	39.68	118.61	158.29
9 ⁿ	n.d.	0.51	0.51	n.d.	0.43	0.43
10^{o}	14.46	36.77	51.23	51.13	72.29	120.42
11^p	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
12^q	0.66	105.56	106.22	1.34	106.07	107.41
13 ^r	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
14^s	15.33	13.57	28.90	19.70	17.71	37.41

Reaction conditions: compounds (1.0 mg, 0.3 µmol), triethanolamine (TEOA, 1 mL), H_2O (1 mL), acetonitrile (MeCN, 4 mL), $\lambda \ge 420$ nm, 20 °C, CO_2 (1 atm), 3 h. ^{*a*} [Ru(bpy)₃]Cl₂·6H₂O (0.013 mmol). ^{*b*} [Ru(bpy)₃]Cl₂·6H₂O (0.009 mmol). ^{*c*} Turnover number $(n_{CO}/n_{Compound})$. ^{*d*} Turnover number $(n_{H_2}/n_{Compound})$. ^{*e*} Turnover number $[(n_{CO} + n_{H_2})/n_{Compound}]$. ^{*f*} In the dark. ^{*g*} Not detectable. ^{*h*} Without 1 or 2. ^{*i*} Without [Ru(bpy)₃]Cl₂·6H₂O. ^{*j*} Using Ar to replace CO₂. ^{*k*} Without H₂O. ^{*i*} Without MeCN. ^{*m*} Using DMF to replace MeCN. ^{*n*} Without TEOA. ^{*o*} Using TEA to replace TEOA. ^{*p*} Using tris(2-phenylpyridinato)iridium(m) instead of [Ru(bpy)₃]Cl₂·6H₂O. ^{*q*} Using $c_{CO_2}/c_{Ar} = 1:8$ instead of CO₂. ^{*r*} Using SiW₁₂ (0.3 µmol) and Htrz (0.3 µmol) to replace 1 or 2. ^{*s*} Using CoCl₂ (0.3 µmol) to replace 1 or 2.

Paper



Fig. 6 Schematic of the CO₂ photocatalytic system using [Ru(bpy)₃]Cl₂·6H₂O as the light absorber and Co-POMs (1 and 2) as catalysts.

further confirm the charge carrier separation performance of 1 and 2, the transient photocurrent responses were recorded during five on/off cycles under visible-light irradiation (Fig. S13†). It can be clearly observed that the photocurrent density of 2 was higher than that of 1, which indicated that 2 had a superior performance to 1 for CO_2 photoreduction. Combining this with the crystal structures of 1 and 2, it can be concluded that the trinuclear Co cluster in 2 is more efficient in promoting separation and diffusion of photogenerated electron-hole pairs than the binuclear Co cluster in 1.

The suitable band gap and band energy are two key parameters to absorb visible light. First of all, the optical band gap (E_g) was measured by UV-vis diffuse reflection spectroscopy and the Tauc plots of $(\alpha hv)^{1/2}$ versus photon energy (*hv*). The values of $E_{\rm g}$ evaluated from the absorption edge were 2.90 eV for 1 and 2.64 eV for 2, demonstrating that 1 and 2 are underlying semiconductive materials (Fig. S14[†]).⁵⁵ Their valence band (VB) energy (E_{VB}) was determined by the VB XPS spectra (Fig. S15 and S16[†]). The conduction band (CB) energy (E_{CB}) for 1 and 2 was calculated by using the equation ($E_{CB} = E_{VB} - E_g$). The values of E_g , E_{CB} and E_{VB} are listed in Table S6.[†] It is shown that the E_{CB} of 2 with the trinuclear Co cluster is more negative than that of 1 with the binuclear Co cluster. According to the literature,⁵⁶ the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of [Ru(bpy)₃]Cl₂ are determined to be -5.68 and -3.19 eV (vs. vacuum level). The transformation of E_{HOMO} and E_{VB} values is given in Table S7.^{$†^{57}$} The result shows that the E_{LUMO} of 1 and 2 are lower than that of [Ru(bpy)₃]Cl₂. This indicates that the electrons in the LOMO of [Ru(bpy)₃]Cl₂ are preferentially transferred to the LUMO of 1 and 2 (Fig. S17 and S18[†]). The proposed mechanism of Co-POMs (1 and 2) in the CO₂ photocatalytic system is illustrated in Fig. 6. Under visible light irradiation,

the $[Ru(bpy)_3]^{2+}$ is excited from ground state to excited state. Then, the excited state combines with the sacrificial electron donor (TEOA) to form the reduced photosensitizer. Subsequently, the transfer process of the electron from the reduced photosensitizer to Co-POMs is effective in decreasing electron-hole pair recombination and active CO₂. In the end, carbon dioxide is reduced to carbon monoxide and released from the Co-POM surface.⁵⁸

Conclusions

In summary, two polyoxometalate-based hybrids based on cobalt cluster and trz ligand were successfully synthesized under hydrothermal conditions. Compound 1 was a 3,4-connected 3D network with $\{8^3\}_4\{8^6\}_3$ topology in which [SiW₁₂O₄₀] acted as a four-connected node and binuclear $[Co_2(Htrz)_3(H_2O)_3]$ cluster acted as a three-connected node. Compound 2 exhibited a 1D chain structure constructed from [SiW12O40] and [Co3(Htrz)6(H2O)3Cl] clusters. Both of them can act as catalysts for CO₂ photoreduction under visible-light irradiation. Interestingly, comparing the structures and photocatalytic performances of the two catalysts, we can conclude that the catalytic activity of the trinuclear Co cluster in 2 is superior to that of the binuclear Co cluster in 1. The inherent reason is that the trinuclear Co cluster can provide a more efficient recombination process for electronhole pairs and faster charge transfer than the binuclear Co cluster. This study might provide an innovative strategy for designing high-activity and cost-acceptable POM-based photocatalysts for CO₂ photoreduction.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the NSFC of China (no. 21771035, 21671034).

Notes and references

- C. C. Li, T. Wang, Z. J. Zhao, W. M. Yang, J. F. Li, A. Li, Z. L. Yang, G. A. Ozin and J. L. Gong, *Angew. Chem., Int. Ed.*, 2018, 57, 5278–5282.
- 2 Q. Zhang, M. Y. Mao, Y. Z. Li, Y. Yang, H. Huang, Z. K. Jiang, Q. Q. Hu, S. W. Wu and X. J. Zhao, *Appl. Catal.*, *B*, 2018, 239, 555–564.
- 3 X. Y. Liu, M. Ye, S. P. Zhang, G. C. Huang, C. H. Li, J. G. Yu, P. K. Wong and S. W. Liu, *J. Mater. Chem. A*, 2018, 6, 24245–24255.
- 4 P. Murugesan, S. Narayanan, M. Manickam, P. K. Murugesan and R. Subbiah, *Appl. Surf. Sci.*, 2018, **450**, 516–526.
- 5 A. Dhakshinamoorthy, S. Navalon, A. Corma and H. Garcia, *Energy Environ. Sci.*, 2012, 5, 9217–9233.
- 6 B. Tahir, M. Tahir and N. A. S. Amin, *Appl. Surf. Sci.*, 2017, **419**, 875–885.
- 7 Q. D. Truong, T. H. Le and H. T. Hoa, *CrystEngComm*, 2017, **19**, 4519.
- 8 T. Kimijima, K. Kanie, M. Nakaya and A. Muramatsu, *CrystEngComm*, 2014, 16, 5591.
- 9 P. Li, Y. Zhou, W. G. Tu, R. Wang, C. F. Zhang, Q. Liu, H. J. Li, Z. D. Li, H. Dai, J. J. Wang, S. C. Yan and Z. G. Zou, *CrystEngComm*, 2013, 15, 9855.
- 10 N. Han, Y. Wang, H. Yang, J. Deng, J. H. Wu, Y. F. Li and Y. G. Li, *Nat. Commun.*, 2018, 9, 1320.
- 11 K. Jiang, S. Siahrostami, T. T. Zheng, Y. F. Hu, S. Hwang, E. Stavitske, Y. D. Peng, J. Dynes, M. Gangisetty, D. Su, K. Attenkofer and H. T. Wang, *Energy Environ. Sci.*, 2018, 11, 893–903.
- 12 Y. Zhao, J. J. Liang, C. Y. Wang, J. M. Ma and G. G. Wallace, *Adv. Energy Mater.*, 2018, 8, 1702524.
- 13 S. Kar, J. Kothandaraman, A. Goeppert and G. K. S. Prakash, J. CO2 Util., 2018, 23, 212–218.
- 14 W. H. Bernskoetter and N. Hazari, Acc. Chem. Res., 2017, 50, 1049–1058.
- 15 J. Kothandaraman, A. Goeppert, M. Czaun, G. A. Olah and G. K. S. Prakash, *J. Am. Chem. Soc.*, 2016, 138, 778–781.
- 16 K. Garg, Y. Matsubara, M. Z. Ertem, A. Lewandowska-Andralojc, S. Sato, D. J. Szalda, J. T. Muckerman and E. Fujita, Angew. Chem., Int. Ed., 2015, 54, 14128–14132.
- 17 D. Zhang, Y. L. Guo and Z. K. Zhao, *Appl. Catal.*, *A*, 2018, 226, 1–9.
- 18 Y. F. Xu, M. Z. Yang, B. X. Chen, X. D. Wang, H. Y. Chen, D. B. Kuang and C. Y. Su, *J. Am. Chem. Soc.*, 2017, 139, 5660–5663.
- 19 S. Chu, P. F. Ou, P. Ghamari, S. Vanka, B. W. Zhou, I. Shih, J. Song and Z. T. Mi, *J. Am. Chem. Soc.*, 2018, 140, 7869–7877.
- 20 L. S. Guo, J. Sun, Q. J. Ge and N. Tsubaki, J. Mater. Chem. A, 2018, 6, 23244–23262.

- 21 D. Mukherjeea, S. E. Park and B. M. Reddya, J. CO2 Util., 2016, 16, 301–312.
- 22 Q. W. Song, Z. H. Zhou and L. N. He, *Green Chem.*, 2017, 19, 3707.
- 23 S. M. Xia, K. H. Chen, H. C. Fu and L. N. He, *Front. Chem.*, 2018, 6, 462.
- 24 J. J. Xu, H. Volfova, R. J. Mulder, L. Goerigk, G. Bryant, E. Riedle and C. Ritchie, *J. Am. Chem. Soc.*, 2018, 140, 10482–10487.
- 25 A. Kumar, A. K. Gupta, M. Devi, K. E. Gonsalves and C. P. Pradeep, *Inorg. Chem.*, 2017, 56, 10325–10336.
- 26 J. Z. Liao, L. Y. Meng, J. H. Jia, D. Liang, X. L. Chen, R. M. Yu, X. F. Kuang and C. Z. Lu, *Chem. – Eur. J.*, 2018, 24, 10498–10502.
- 27 J. S. Qin, D. Y. Du, W. Guan, X. J. Bo, Y. F. Li, L. P. Guo, Z. M. Su, Y. Y. Wang, Y. Q. Lan and H. C. Zhou, *J. Am. Chem. Soc.*, 2015, 137, 7169–7177.
- 28 Z. M. Zhang, T. Zhang, C. Wang, Z. K. Lin, L. S. Long and W. B. Lin, J. Am. Chem. Soc., 2015, 137, 3197–3200.
- 29 H. F. Shi, Y. C. Yu, Y. Zhang, X. J. Feng, X. Y. Zhao, H. Q. Tan, S. U. Khan, Y. G. Li and E. B. Wang, *Appl. Catal., A*, 2018, 221, 280–289.
- 30 X. X. Zhao, S. W. Zhang, J. Q. Yan, L. D. Li, G. J. Wu, W. Shi, G. M. Yang, N. J. Guan and P. Cheng, *Inorg. Chem.*, 2018, 57, 5030–5037.
- 31 X. B. Han, Y. G. Li, Z. M. Zhang, H. Q. Tan, Y. Lu and E. B. Wang, J. Am. Chem. Soc., 2015, 137, 5486–5493.
- 32 G. Paille, M. Gomez-Mingot, C. Roch-Marchal, B. Lassalle-Kaiser, P. Mialane, M. Fontecave, C. Mellot-Draznieks and A. Dolbecq, *J. Am. Chem. Soc.*, 2018, 140, 3613–3618.
- 33 T. Wei, M. Zhang, P. Wu, Y. J. Tang, S. L. Li, F. C. Shen, X. L. Wang, X. P. Zhou and Y. Q. Lan, *Nano Energy*, 2017, 34, 205–214.
- 34 S. Zhou, Y. G. Chen, B. Liu, Y. H. Xu and X. Y. Wang, J. Cluster Sci., 2018, 29, 417–423.
- 35 J. Song, Z. Luo, D. K. Britt, H. Furukawa, O. M. Yaghi, K. I. Hardcastle and C. L. Hill, *J. Am. Chem. Soc.*, 2011, 133, 16839–16846.
- 36 W. Yao, L. Liu, X. S. Wu, C. Qin, H. M. Xie and Z. M. Su, ACS Appl. Mater. Interfaces, 2018, 10, 35911–35918.
- 37 Y. C. Ji, L. J. Huang, J. Hu, C. Streb and Y. F. Song, *Energy Environ. Sci.*, 2015, 8, 776.
- 38 S. Y. Shi, Y. H. Sun, Y. Chen, J. N. Xu, X. B. Cui, Y. Wang, G. W. Wang, G. D. Yang and J. Q. Xu, *Dalton Trans.*, 2010, 39, 1389–1394.
- 39 H. Kumagai, M. Arishima, S. Kitagawa, K. Ymada, S. Kawata and S. Kaizaki, *Inorg. Chem.*, 2002, 41, 1989–1992.
- 40 X. L. Wang, C. Qin, E. B. Wang, Z. M. Su, Y. G. Li and L. Xu, Angew. Chem., Int. Ed., 2006, 45, 7411–7414.
- 41 H. F. Hao, W. Z. Zhou, H. Y. Zang, H. Q. Tan, Y. F. Qi, Y. H. Wang and Y. G. Li, *Chem. Asian J.*, 2015, **10**, 1676–1683.
- 42 J. L. Lin, Z. M. Pan and X. C. Wang, ACS Sustainable Chem. Eng., 2014, 2, 353–358.
- 43 Y. J. Cao, S. Chen, Q. Q. Luo, H. Yan, Y. Lin, W. Liu, L. L. Cao, J. L. Lu, J. L. Yang, T. Yao and S. Q. Wei, *Angew. Chem.*, *Int. Ed.*, 2017, 56, 12191–12196.

- 44 X. Q. Wang, Z. Chen, X. Y. Zhao, T. Yao, W. X. Chen, R. You,
 C. M. Zhao, G. Wu, J. Wang, W. X. Huang, J. L. Yang, X.
 Hong, S. Q. Wei, Y. E. Wu and Y. D. Li, *Angew. Chem., Int. Ed.*, 2018, 57, 1944–1948.
- 45 Y. Q. Jiao, C. Qin, H. Y. Zang, W. C. Chen, C. G. Wang, T. T. Zheng, K. Z. Shao and Z. M. Su, *CrystEngComm*, 2015, 17, 2176–2189.
- 46 L. Antolini, A. C. Fabretti, D. Gatteschi, A. Giusti and R. Sessoli, *Inorg. Chem.*, 1991, 30, 4858–4860.
- 47 Bruker, *APEX2, SAINT and SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA, 2008.
- 48 SHELXT and G. M. Sheldrick, Acta Crystallogr., Sect. C: Struct. Chem., 2015, 71, 3-8.
- 49 The control reactions indicate that the photocatalytic performance of 1 and 2 using quartz tube was higher than that of using pyrex tube (see Fig. S19[†]).
- 50 P. G. Lacroix, F. Averseng, I. Malfant and K. Nakatani, *Inorg. Chim. Acta*, 2004, 357, 3825–3835.
- 51 S. Himeno, M. Takamoto and T. Ueda, *J. Electroanal. Chem.*, 1999, 465, 129–135.

- 52 G. G. Gao, F. Y. Li, L. Xu, X. Y. Liu and Y. Y. Yang, J. Am. Chem. Soc., 2008, 130, 10838-10839.
- 53 Y. Xu, J. Mo, Z. C. Fu, S. Liu, Z. Yang and W. F. Fu, Chem. Eur. J., 2018, 24, 8596–8602.
- 54 T. Ouyang, C. Hou, J. W. Wang, W. J. Liu, D. C. Zhong,
 Z. F. Ke and T. B. Lu, *Inorg. Chem.*, 2017, 56, 7307–7311.
- 55 Z. C. Shao, C. Huang, X. Han, H. R. Wang, A. R. Li, Y. B. Han, K. Li, H. W. Hou and Y. T. Fan, *Dalton Trans.*, 2015, 44, 12832–12838.
- 56 C. Gao, Q. Q. Meng, K. Zhao, H. J. Yin, D. W. Wang, J. Guo, S. L. Zhao, L. Chang, M. He, Q. X. Li, H. J. Zhao, X. J. Huang, Y. Gao and Z. Y. Tang, *Adv. Mater.*, 2016, 28, 6485–6490.
- 57 J. Liu, Y. Liu, N. Y. Liu, Y. Z. Han, X. Zhang, H. Huang, Y. Lifshitz, S. T. Lee, J. Zhong and Z. H. Kang, Science, 2015, 347, 970.
- 58 J. Zhao, Q. Wang, C. Y. Sun, T. T. Zheng, L. K. Yan, M. T. Li, K. Z. Shao, X. L. Wang and Z. M. Su, *J. Mater. Chem. A*, 2017, 5, 12498.