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Introduction

Nowadays, a large amount of waste water containing inorganic heavy metal ions and organic compounds is produced with the rapid development of modern industry.^{1,2} The wastewater has low biodegradability, which means the pollutants are easy to be concentrated in the environment and can enter living organisms through the food chain. Among the inorganic pollutants, Cr(vI) pollution is particularly critical. The toxicity of Cr(vI) is 100 times higher than that of Cr(m), which can cause serious health problems as certain classes of Cr(vI) are teratogenic and carcinogenic and can cause mutations.^{3,4} In contrast to Cr(vI), trivalent chromium Cr(m) is slightly toxic and can be easily precipitated or adsorbed in the solid phase.^{5,6} Therefore, the reduction of Cr(vI) to Cr(m) is considered an effective method for the remediation of Cr(vI)-contaminated waters. Moreover, organic dyes are notorious due to their low pen-

Two novel organic phosphorous-based MOFs: synthesis, characterization and photocatalytic properties[†]

Tianyu Zeng, Liwen Wang, Lu Feng, Hailong Xu, Qingrong Cheng ()* and Zhiquan Pan*

Two novel metal–organic framework (MOF) photocatalysts with different structures [(Cu(H₂L)(4,4'-bipy)_{0.5}(H₂O)] (**1**) and [Co(C₁₄H₁₄O_{6.5}P₂)(4,4'-bipy)_{0.5}(H₂O)₂]·H₂O (**2**) were synthesized using a hydrothermal method using a phosphonate ligand [H₄L = 1,1'-biphenylene-4,4'-bis(methylene)-bis(phosphonic acid)] and 4,4'-bipyridine ligand. All the samples were characterized by elemental analysis, thermal analysis, and single crystal X-ray diffraction. As novel porous materials, the two complexes showed active performance for the reduction of Cr(vi) to Cr(iii) and the photodegradation of methylene blue (MB) dye in aqueous solution under UV light. Control experiments showed that the pH value was vital for Cr(vi) reduction, meanwhile, the use of a hole scavenger of methanol promoted the photocatalytic reduction significantly. It was also demonstrated that complexes **1** and **2** were efficient for the degradation of MB. Moreover, the possible reaction mechanism of the reaction was also investigated in detail. Finally, the cyclic experiments indicated the two photocatalysts were stable and reusable, enabling them to be potential candidates for use in environment governance.

etrations, high toxicity, and high chemical oxygen demand, which make them toxic not only to human beings but also to plants in photosynthesis.⁷ Therefore, it is of great importance to develop effective and economical technologies to reduce $Cr(v_1)$ to Cr(m) and to degrade organic dyes in the treatment of wastewater.

Various methods, such as physical, chemical, and biological techniques, have been reported to deal with wastewater. Among these, photocatalytic technology has been broadly used in green wastewater treatment due to it being mild and environmentally friendly.⁸⁻¹⁰ Since the semiconductor TiO₂ was initially discovered to be useful for pollutants degradation in the photocatalytic system, many semiconductors, including ZnS, SnO₂, ZnO, and CdS, have been investigated as potential photocatalysts for eliminating contaminants in wastewater.¹¹⁻¹⁵ However, these semiconductor photocatalysts have several disadvantages, such as low surface area, easy photoelectron-hole recombination, and rapid deactivation.¹⁶ Consequently, it has become urgent to find new efficient photocatalysts for the reduction of Cr(vi) and for the degradation of organic pollutants.

Metal–organic frameworks (MOFs), an extensive class of multi-functional crystalline materials with novel structures, are made up of metal ions or metal clusters and organic ligands by self-assembly.¹⁷ Due to their ultrahigh porosity, enormous internal surface areas, diverse structural topologies, and rich

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Key Laboratory for Green Chemical Process of Ministry of Education, Wuhan Institute of Technology, Wuhan 430073, P. R. China. E-mail: chengqr383121@sina.com, zhiqpan@163.com

[†]Electronic supplementary information (ESI) available: More detailed information about the characterization of MOFs, as well as that for photocatalytic study as noted in the text (PDF). CCDC complex **1** 1872673 and complex **2** 1872661. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt04106g

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active site, MOFs have attracted considerable attention for their potential applications in gas storage and separation, luminescent, catalysis, and proton conductivity.18-23 Moreover, some MOFs have exhibited semiconducting properties under illumination, implying that they can be potentially used as photocatalysts.^{24,25} Compared with conventional inorganic semiconductors, the high porosity and desirable topology of MOFs would shorten the transport distance of charge carriers to the pore surface throughout the structure in reactions, which would extremely inhibit the recombination of electrons and holes. Garcia's team demonstrated that MOF-5 shows photocatalytic activity for phenol degradation, in which the lifetime of electrons and holes reached the microsecond level.^{16,26} Furthermore, some bridging ligands with conjugate structures provide channels for the transport of electrons, which provide the possibility to enhance the separation of photogenerated electrons and holes. In addition, the band gap in MOF systems is closely related to the HOMO-LUMO gap, which allows for the fine-tuning and rational design of these photocatalysts at the molecular level.²⁷ Recently, Gascon reported two Zn(II) MOFs, assembled by terephthalic acid or 1,4-naphthalene diacid, with energy band gaps $(E_{\rm g})$ of 3.4 eV and 3.3 eV, respectively.²⁸ Their results demonstrated that the E_{α} of MOFs can be adjusted by changing the length of ligands, without altering the topological structure, which make MOFs particularly suitable for photocatalysis. Up to now, many carboxylate-based MOFs and N-heterocycle-based MOFs have been reported as catalysts for photocatalysis. For example, Wang et al. disclosed Cr(vi) reduction by NH2-MIL-125(Ti) as the photocatalyst, which showed a relatively high efficiency.²⁹ Cheng et al. reported $[Cu(4,4'-bipy)Cl]_n$ and $[Co(4,4'-bipy)Cl]_n$ bipy)·(HCOO)₂]_n as photocatalysts using H_2O_2 on MB degradation to achieve considerable efficiency under visible light irradiation.³⁰ Zhao et al. demonstrated that NNU-36 ([Zn₂(BPEA)(BPDC)₂]·2DMF) could achieve the excellent photocatalytic reduction of Cr(vi) and the degradation of dyes (RhB, MB, R6G).³¹ It is well known that the stability and recyclability of a photocatalyst are crucial for its catalytic application. Wang and co-workers used carboxylate-based MOF (named BUC-21) in photocatalytic Cr(vi) reduction, and the results showed that the photocatalytic activity under the condition of pH = 1 was significantly lower than that under pH = 2 or 3, possibly because of destruction of the framework of BUC-21.32 In contrast to metal carboxylates, metal phosphonates show higher thermal stability and are harder to be soluble even in highly acidic media,33,34 which indicated that MOFs based on phosphonate might be more stable for the photocatalytic degradation of organic dyes and the reduction of Cr(vi) to Cr(iii) in acidic environments. However, investigations on the photocatalytic activities of phosphonate-based MOFs are limited.

Herein, an organic phosphorous ligand H₄L [1,1'-biphenylene-4,4'-bis(methylene)bis(phosphonic acid)] containing π - π conjugate structure was designed and synthesized, and two new MOF photocatalysts, [(Cu(H₂L)(4,4'-bipy)_{0.5}(H₂O)] (1) and [Co(C₁₄H₁₄O_{6.5}P₂)(4,4'-bipy)_{0.5}(H₂O)₂]·H₂O (2), with different band gaps and band positions were synthesized. As part of ongoing studies on the photocatalysis, the photocatalytic reactions of the new phosphonate-based MOFs were investigated under different experimental conditions, and the results showed that these new MOFs are highly efficient photocatalysts for aqueous Cr(vi) reduction and MB degradation under ultraviolet light. The possible mechanism of the reaction was also investigated by measuring the major active species in the catalytic process. Finally, the photocatalytic activity of these two photocatalysts showed high stability, and the activity did not decrease after five consecutive cycles.

Experimental

Preparation of the ligand (H₄L)

Chemical reagents were purchased commercially from Sinopharm Chemical Reagent Co., Ltd and used as received without further purification. The ligand 1,1'-biphenylene-4,4'-bis(methylene)bis(phosphonic acid) (H₄L, Scheme S1[†]) was prepared according to the literature method.³⁵

Preparation of complexes

 $[Cu(H_2L)(4,4'-bipy)_{0.5}(H_2O)]$ (1). The complex was hydrothermally synthesized by the reaction of Cu(CH₃COO)₂·H₂O (0.130 g, 0.650 mmol), 4,4'-bipyridine (0.101 g, 0.650 mmol), and H₄L (0.222 g, 0.650 mmol) dissolved in H₂O (40.0 g, 2.22 mol), then HCl (0.350 mL, 6.00 mol L^{-1}) was added. After stirring under air atmosphere for 30 min, the solution was transferred into a 150 mL Teflon-lined stainless-steel autoclave, sealed, and heated up to 140 °C for 72 h. By slow cooling of the reaction mixture to room temperature over 24 h, blue crystals of complex 1 were obtained and were washed with H₂O and ethanol several times for further use. Yield: 66.62% (based on Cu). Calcd for C19H20CuNO7P2 (499.85): C, 45.65; H, 4.03; N, 2.80. Found: C, 45.37; H, 4.24; N, 2.42. Selected IR data (KBr pellet cm⁻¹): 3442(s), 3033(w), 2909(w), 2370(w), 1607(m), 1494(m), 1417(m), 1251(w), 1132(s), 1067(s), 932(s), 807(m), 724(w), 642(w), 594(w), 558(m), 464(w).

 $[Co(C_{14}H_{14}O_{6.5}P_2)(4,4'-bipy)_{0.5}(H_2O)_2]\cdot H_2O$ (2). The same synthetic procedure was used to synthesize 2 as that for 1 except $Co(CH_3COO)_2 \cdot 4H_2O$ was used instead of $Cu(CH_3COO)_2 \cdot 4H_2O$ and the ratio was 1:1:1:3415 $[Co(CH_3COO)_2 \cdot 4H_2O:4,4'-bipy:H_4L:H_2O]$. Yield: 71.23% (based on Co). Calcd for $C_{19}H_{24}CoNO_{9.5}P_2$ (539.28): C, 42.32; H, 4.49; N, 2.60. Found: C, 42.45; H, 4.28; N, 2.72. Selected IR data (KBr pellet cm⁻¹): 3428(m), 3030(w), 2910(w), 2369(w), 1604(m), 1534(w), 1497(m), 1410(m), 1265(m), 1161(m), 1126(s), 1099(s), 1041(s), 958(s), 838(m), 806(m), 757(w), 714(w), 615(w), 592(w), 544(s), 498(w).

Photocatalytic experiments

The photocatalytic experiments for aqueous Cr(vI) to Cr(m) were carried out under 125 W UV irradiation with a 380 nm cut-off filter at ambient conditions in a 50.0 mL quartz reactor containing 4.00 mg MOFs-based photocatalysts which were dispersed into 40.0 mL Cr(vI) aqueous solution (30.0 ppm). The distance between the light source and the quartz reactor

containing the reaction mixture was fixed at 10.0 cm. Prior to irradiation, the suspension was magnetically stirred for 60 min in the dark to ensure an adsorption-desorption equilibrium and then 0.200 M H₂SO₄ was added to adjust the acidity in the reaction, with the pH values determined using a pH detector. During the reduction of aqueous Cr(vi), stirring was maintained to keep the mixture in suspension, 2.00 mL of suspension was withdrawn at regular intervals and the photocatalyst was separated by centrifugation. Then, the Cr(vi) content in the solution was determined colorimetrically by the diphenylcarbazide method (DPC) with a detection limit of 0.005 mg $L^{-1.36}$ The Cr(vi) content in the solution at different illumination times was monitored by measuring its maximum absorbance (centered at 540 nm) using a UV-visible spectrophotometer. The reduction ratio of Cr(vi) was calculated using the following expression: reduction ratio of $Cr(v_I) = (C_0 - C_t)/C_0 \times 100\%$.

The photocatalytic experiments for the degradation of dyes of MB were carried out under 125 W UV irradiation with a 380 nm cut-off filter at ambient conditions in a 50 mL quartz reactor containing 5.00 mg MOF-based photocatalysts, which were dispersed in 40.0 mL MB aqueous solution (10.0 ppm). Prior to irradiation, the suspension was magnetically stirred for 60 min in the dark to ensure adsorption–desorption equilibrium. During the photodegradation reaction, 2.00 mL of suspension was taken out each time from the reactor at scheduled intervals and the photocatalyst was separated by centrifugation. The MB concentration changes at different illumination times were monitored by measuring the absorption intensity at its maximum absorbance wavelength of $\lambda = 664$ nm using a UV-visible spectrophotometer.

Results and discussion

Crystal structure

Single-crystal X-ray diffraction data for complexes 1 and 2 were collected on a Bruker Smart CCD area-detector diffractometer

with graphite-monochromatic Mo/K α radiation ($\lambda = 0.71073$ Å) in ω -scan mode. The collected data were reduced using the software package SAINT,³⁷ and semi-empirical absorption correction was applied to the intensity data using SADABS program.³⁸ The structures of **1** and **2** were solved using direct methods, and all nonhydrogen atoms were refined anisotropically by least squares on F^2 using the SHELXTL-2014 program.³⁹ Hydrogen atoms were placed in calculated positions and refined isotropically using the riding model. Details of the crystallographic data of **1** and **2** are summarized in Table S1.† Selected bond lengths (Å) and angles (°) for **1** and **2** are listed in Table S2.†

Structure description of $[Cu(H_2L)(4,4'-bipy)_{0.5}(H_2O)](1)$

Single-crystal structure analysis revealed that complex 1 crystallizes in a space group $P\overline{1}$. The asymmetric unit in 1 contains one Cu(II) ion, one $[H_2L]^{2-}$ anion, 1/2 4,4'-bipy molecule and one coordination water molecule (Fig. 1a). Each Cu ion coordinates with an half 4,4'-bipy(N1), one water molecule (O7), and three oxygen atoms from the phosphonate ligand (O1, O2, O4), forming a slightly distorted square pyramidal type of geometry (Fig. 1b). The distances of Cu-O and Cu-N are in the range of 1.894(4)-2.323(5) Å and 2.072(5) Å, respectively. In the asymmetric unit, the H₂L anion acts as a tridentate ligand to chelate three Cu atoms, with each $\{CP(1)O3\}$ group chelating two Cu(II) sites through O1 and O2, respectively, while each {CP(2)O3} group is monodentate for O4. So, the coordination mode can be adopted as with $\mu_3 - \eta^1 \eta^1 \eta^0 \eta^1 \eta^0 \eta^0$ (Fig. S1[†]). As shown in Fig. 1c, two equivalent Cu²⁺ ions are bridged by two $[H_2L]^{2-}$ anion with the connection of $(P1-O2-Cu1-O4-P2)_2$, forming a 30-membered ring, then two Cu ions are connected with two nitrogen atoms in the 4,4'-bipy molecule, respectively, which separates the ring into the same two parts. The rings are further bridged by P1-O1-Cu1 through the coordination interactions, leading to a two-dimensional plane along the c-axis with Cu1...Cu1 separation of 4.9493 Å (Fig. 1d).



Fig. 1 (a) The asymmetric unit of complex 1; (b) the coordination environment of Cu(II) in complex 1; (c) two-membered Cu-dimer ring formed in complex 1; (d) 2D plane structure in complex 1; (e) hydrogen-bond interactions between the inorganic planes along the a-axis; (f) hydrogen-bond interactions between the inorganic planes along the *b*-axis.

Neighboring planes are further interlinked through hydrogen bond interactions along the a-axis (such as O3-H3A···O12, O7-H7A···O8 and O14-H14C···O3 etc.) and b-axis (O9-H9A···O5 and O10-H6A…O6), as shown in Fig. 1e and f. The hydrogen bonds are formed between the non-coordinated phophonate oxygen atoms and the coordinated water molecules, resulting in a 3D supramolecular assembly. To clearly understand the network, topological investigations were performed by using the software package TOPOS. The crystallographically independent metallic centers (Cu²⁺) with different coordination configurations were taken as network nodes, with the diphosphonic acid and 4,4'-bipy being ensured by the bridging ligands, and the simplified structure is shown in Fig. S2.† The point symbol for the network of complex 1 is described as a 3,4-connected network with the overall point symbol $\{3\cdot 4\cdot 5\}\{3^2\cdot 4^2\cdot 5.6\}$, of which the Cu²⁺ ions are two-connected nodes.

Structural description of $[Co~(C_{14}H_{14}O_{6.5}P_2)~(4,4'\text{-bipy})_{0.5}~(H_2O)_2]~\cdot H_2O~(2)$

Complex 2 crystallizes in the space group $P2_1/c$. The asymmetric unit in 2 contains two Co(II) ions, two $[C_{14}H_{14}O_{6.5}P_2]^{2-1}$ anions, one 4,4'-bipy molecule, four coordination water molecules, and two water molecules in the lattice (Fig. 2a). Each Co atom coordinates with two oxygen atoms from two water molecules (07, 08), three oxygen atoms from peroxyphosphonate (O1, O3', O10), one oxygen atom from phosphonate (O1), and a nitrogen atom from a pyridine molecule (N1), forming a slightly distorted monoctahedron coordination geometry (Fig. S3[†]). The distances of Co-O and Co-N are in the range 2.036(3)-2.208(4) Å and 2.277(4) Å, respectively. The $[C_{14}H_{14}O_{6.5}P_2]^{2-}$ anion acts as a tetradentate ligand to chelate three Co atoms, each peroxyphosphonate group chelates two Co(II) sites through O1, O3' and O10, respectively, while each phosphonate group chelates one Co(II) ion through O4. So the coordination mode can be adopted as with $\mu_3\text{-}\eta^1\eta^0\eta^1\eta^1\eta^0\eta^0$ (Fig. S4[†]). Similar to complex 1, two equivalent Co(II) ions are bridged by two $[C_{14}H_{14}O_{6.5}P_2]^{2-}$ anions with the connection of (P1'-O3'-Co1-O4-P2)₂, forming a 30-membered ring, and then two nitrogen atoms in the 4,4'-bipy molecule connect with two Co atoms, respectively, which separate the ring into approximately the same two parts (Fig. 2b). The rings are further connected by (Co1-O1-P1'-O3')2 leading to a 3D frame structure along the *b*-axis with a Co1...Co1 separation of 5.7443 Å (Fig. 2c). As shown in Fig. 2e, neighboring frames are further interlinked through hydrogen bond interactions along the a-axis (such as O8-H8A····O5, O5-H5A····O7 and O9-H9B…O10). Hydrogen bonds are formed between the non-coordinated phophonate oxygen atoms and the coordinated water molecules, resulting in a 3D supramolecular assembly (Fig. 2d). The simplified topological structure of 2 is shown in Fig. S5.† The point symbol for network of 2 can be described as a 3-connected network with overall point symbol $\{4^2.6\}$, in which the $Co(\pi)$ is a single node.

Physical characterizations

Thermal analyses and BET analysis of the samples. TGA curves were made under flowing N₂ for complexes 1 and 2 in the temperature range 30–900 °C (Fig. 3a). Complex 1 showed thermal stability up to 80 °C with a weight loss of 3.2%, attributed to the coordination water molecule (calcd. 3.6%). The second weight loss stage had a decomposition temperature range of 240–360 °C, with a weight loss of 21.9%, corresponding to the loss of 4,4'-bipyridine (calcd. 19.4%), and the third weight loss stage had a decomposition temperature range of 400–520 °C, with a weight loss of 55.9%, corresponding to the combustion of phosphonate (calcd. 55.2%). Upon further heating, the final product obtained at 900 °C could be attributed to Cu(PO₃)₂ (found 39.0%; calcd 44.4%). The difference in the weight was due to loss of P₂O₅ from the residual mass.

For complex 2, the first step of weight loss in the range of 40–105 °C is consistent with the removal of two coordination water molecules and one water molecule in the lattice (found 10.2%; calcd 10.0%). Then it undergoes continuous weight



Fig. 2 (a) Asymmetric unit of complex 2; (b) two-membered Cu-dimer ring formed in complex 2; (c) 3D frame structure along the *b*-axis; (d) and (e) hydrogen-bond interactions between the inorganic frames along the *b*-axis.

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Fig. 3 (a) TGA diagrams of complexes 1 and 2; (b) N_2 adsorption–desorption isotherms of complexes 1 and 2.

losses at the temperature from 290 °C to 560 °C due to the combustion of organic groups, showing a constant residual mass of 140.2 (26.0%) up to 900 °C. It is well known that $Co(PO_3)_2$ can convert into $Co_2P_2O_7$ by eliminating P_2O_5 ($Co(PO_3)_2 \rightarrow 1/2 Co_2P_2O_7 + 1/2 P_2O_5$) after heating at high temperature for a long time.⁴⁰ The final end product was supposed to be $1/2 Co_2P_2O_7$ with a formula weight of 145.9 (27.0%).

The specific surface areas and pore structures of complexes 1 and 2 were studied using nitrogen adsorption-desorption isotherms. As shown in Fig. 3b, both complexes 1 and 2 display type III isotherms with H3 hysteresis, indicating the nitrogen has a weak interaction with the materials and the materials are non-porous.⁴¹ The Brunauer-Emmett-Teller (BET) specific surface areas, pore volumes and adsorption/desorption average pore diameters of complexes 1 and 2 are listed in Table S3.[†]

UV-Vis diffuse reflectance spectroscopy (DRS) and X-ray photoelectron spectra (XPS). The optical properties of the MOF-based photocatalysts were investigated by DRS and XPS. The optical band gap energy of the samples were calculated according to the energy dependence relationship of $\alpha h\nu =$ $(h\nu - E_g)^{1/2}$, where α , ν , and E_g are the absorption coefficient, photon frequency, and energy gap of the semiconductor, respectively.⁴² The band gap of the samples could be calculated from the plot of $(\alpha h\nu)^2$ versus the energy of the absorbed light. The E_g value is determined by measuring the x-axis intercept of an extrapolated tangential line from the linear regime of the curve. As shown in Fig. 4a, both MOF-based photocatalysts showed strong ultraviolet light absorption in the range of 200–400 nm (Fig. 4a), which indicated the MOF-based photocata-



Fig. 4 UV-vis spectrum of complexes 1 (black) and 2 (red); the band gap of complexes 1 (b) and 2 (c); the valence band XPS pattern of complexes 1 (d) and 2 (e).

lysts had a strong ultraviolet light harvesting capacity for photocatalytic reactions. In addition, the band gaps of complexes **1** and **2** were 2.57 eV (Fig. 4b) and 3.23 eV (Fig. 4c), respectively.

Apart from the low band gap, the proper matching of the valence band (E_v) (*vs.* NHE) and conduction band (E_c) (*vs.* NHE) is also important for evaluating photocatalysis. The E_v positions of the complexes were determined by linear extrapolation of the leasing edges of VB-XPS spectra to the base lines. As shown in Fig. 4d and e, the valence band (E_v) positions of 1 and 2 were located at ~3.15 eV and ~1.94 eV, respectively. By combining the band gap result with the valence band (E_v) of the samples, we can get the conduction band levels (0.58 eV for 1, -1.29 eV for 2) from $(E_v - E_g)$.

Photocatalytic activities

Photocatalytic reduction of Cr(v1). The photocatalytic reduction of aqueous Cr(v1) over the MOF-based photocatalysts was performed under ultraviolet light since they showed broad-range UV light absorption. Fig. 5 shows the photocatalytic activities of complexes 1 and 2 in the reduction of aqueous Cr(v1) under different experimental conditions. Taking a view of the overall activities from Fig. 5a and b, it can be found that there was no significant reduction of Cr(v1) in the absence of complexes 1 or 2 in the dark. On the contrary, the Cr(v1) concentration decreased obviously in the presence of



Fig. 5 Control experiments for the reduction of $Cr(v_l)$ over complexes 1 (a) and 2 (b) under different conditions; photocatalytic reduction of Cr (v_l) over complexes 1 (c) and 2 (d) at different pH values; photocatalytic reduction of $Cr(v_l)$ complexes 1 (e) and 2 (f) with different methanol addition.

1 and **2** under ultraviolet light, and the reduction ratio of $Cr(v_1)$ was rapidly increased to 46.7% and 49.4% after 50 min, respectively. The effect of pH value on the photocatalytic reduction of $Cr(v_1)$ over **1** and **2** was also investigated under different H_2SO_4 concentrations. As shown in Fig. 5c and d, the reduction rate of $Cr(v_1)$ was remarkably pH-dependent in all the photocatalytic systems with **1** and **2**, and the reduction processes were greatly accelerated by decreasing the pH values (for **1–2**, 66.2%, 100% at about pH = 2.30 after 50 min, respectively). This phenomenon was consistent with other reports that the photocatalytic reduction of $Cr(v_1)$ was an acid-catalyzed behavior.^{43,44} Under acid conditions, the predominating species of chromium is $Cr_2O_7^{-2-}$, and the protons participated in the reduction reaction may be as follows (eqn (1)):

$$14H^{+} + Cr_{2}O_{7}^{2-} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_{2}O$$
(1)

Therefore, the reduction efficiency of $Cr(v_1)$ is relatively high at low pH because of the existence of abundant protons. In particular, complexes 1 and 2 could retain their highly catalytic activities at the pH value of 1.24, which indicated that these two catalysts have good stability in strong acid conditions.

To further investigate the charge transfer during the photocatalytic reaction, a hole scavenger was introduced in the experiments. As methanol could capture the photoinduced holes in the VB of MOF-based photocatalysts, it is able to suspend the hole–electron pair recombination, and more electrons are thus available to participate in the surface reaction. Thus, methanol was used as a hole scavenger. The temporal concentration variation of Cr(vi) reduction over different amounts of methanol is shown in Fig. 5e and f, and the reactions were all performed in acid conditions at the same pH value of 3.21. The experiments showed that the reductive rate of Cr(vi) was increased along with the amount of methanol. For complex 2, Cr(vi) in the photocatalytic reaction could be fully reduced after 30 min when 150 µL of methanol was added (Fig. 5f), while complex 1 need about 50 min to complete the reaction under the same conditions (Fig. 5e).

To gain a better understanding of the reaction kinetics of the reduction of aqueous $Cr(v_I)$, the experimental data were fitted by a first-order model as expressed by eqn (2) (Langmuir–Hinshelwood model), due to the fact that the value of the rate constant k commonly gives an indication of the activity of a photocatalyst,

$$-\mathrm{In}(C/C_0) = k \times t \tag{2}$$

where C_0 and C are the initial and apparent concentration of the Cr(vi), respectively, and k is the kinetic rate constant. The values of k were obtained from the slope and the intercept of the linear plot. Fig. 6a and b show a linear relationship between $\ln(C/C_0)$ and the irradiation time for the reduction of aqueous Cr(vi) on complexes 1 and 2, respectively. As shown in Fig. 6c, the kinetic rate constants for the photocatalytic reduction of Cr(vi) follow the order: complex 2 (0.0801 min⁻¹, pH = 3.15) > complex 1 (0.0470 min⁻¹, pH = 3.21). Compared with other photocatalysts, complexes 1 and 2 have high photocatalytic efficiency with small dosage and need only a short time. A comparison of photoreduction capacity of complexes 1 and 2 with other reported photocatalysts is shown in Table 1.

Furthermore, in the photocatalytic $Cr(v_1)$ reduction reaction, photogenerated electrons in the CB of the MOF photocatalyst are believed to have a strong reductive ability to attack stable $Cr_2O_7^{2-}$ under acidic conditions. To investigate the percentage of effective electrons at the surface of complexes 1 and 2, AgNO₃ was added as an electron scavenger in the system, where the reactions were carried out under the conditions of pH = 3.21 and the addition of 150 µL methanol (Fig. 7a). In contrast to the reaction without AgNO₃, the photocatalytic Cr(v1) reduction efficiencies were decreased by 35.0% (1) and 43.6% (2) within 50 min, and the apparent reaction rate constants of complexes 1 and 2 declined to 0.0135 min⁻¹ and 0.00777 min⁻¹, respectively (Fig. 7b).

To characterize the main mechanism of Cr(vi) removal in our experiment, the valence state of chromium bound to the MOF-based photocatalysts after catalytic reaction was confirmed by X-ray photoelectron spectroscopy analysis. As shown in Fig. 7c and d, there was a significant contribution of the Cr bound on the MOF-based photocatalysts. Significant bands of standard Cr(m) compounds appeared at binding energies of 577–579 and 586–588 eV, with the former corresponding to the Cr 2p_{3/2} orbital, while the latter corresponded to the Cr 2p_{1/2} orbital. Meanwhile, those of the standard Cr(vi) compound, K₂Cr₂O₇, appeared at binding energies of 579–581 and



Fig. 6 Pseudo-first-order kinetics curves of photocatalytic $Cr(v_1)$ reduction reactions over complexes 1 (a) and 2 (b) under different conditions; (c) comparison of the apparent reaction rate constants of $Cr(v_1)$ reduction reactions over complexes 1 and 2.



Fig. 7 (a) Photocatalytic reduction of Cr(vi) over complexes 1 and 2 with or without electron scavenger of AgNO₃ (0.1 mmol); (b) comparison of the apparent reaction rate constants for reactions; Cr 2p spectrum bound to complexes 1 (c) and 2 (d) after photocatalytic Cr(vi) reduction.

588–590 eV, respectively.^{48,49} The XPS result indicated $Cr(v_1)$ is indeed reduced to Cr(m).

The recyclability and stability of complexes 1 and 2 were tested by performing repeated usage cycles under identical reaction conditions (pH = 1.24). After each cycling experiment, the photocatalyst was recycled by filtration, followed by washing with deionized water and ethanol several times, respectively, to completely remove the absorbed Cr(III), and then drying under room temperature. As shown in Fig. 8a and b, complexes 1 and 2 retained their catalytic activities during the whole reaction process even after five cycles, with very little decrease in activity observed. In addition, the structures of the complexes were recorded by PXRD pattern before and after cycle reaction. The PXRD patterns revealed that the structures of the complexes showed no significant changes during the reaction process, which indicated that complexes 1 (Fig. 8c) and 2 (Fig. 8d) possessed good structural stability, with no structural transformation in MOFs occurring during the photocatalytic Cr(vi) reduction under an extremely acidic environment.

Photocatalytic degradation of dyes. MB was chosen as a representative dye to evaluate the capability of the MOF-based

| Table 1 Comparison of the Cr(vi) reduction capacity of complexes 1 and 2 with other photocatalysts | | | | | | | | | |
|---|------------------------|------------|------------|------------------------|-----------|--|--|--|--|
| Catalyst/mg | Pollutants/mg L^{-1} | Irrigation | Time (min) | Efficiency (%) | Ref. | | | | |
| Complex 1/4 | Cr(vi)/30 | UV | 50 | 100 | This work | | | | |
| Complex 2/4 | Cr(vi)/30 | UV | 30 | 100 | This work | | | | |
| Zn(bpy)L/15 | Cr(vi)/10 | UV | 30 | 86 ^{<i>a</i>} | 32 | | | | |
| AgSCN/200 | Cr(vi)/10 | UV | 120 | 100 | 45 | | | | |
| TiO ₂ nanocrystals/50 | Cr(vi)/10 | UV | 120 | 100 | 46 | | | | |
| Ni@graphene–ZnO/10 | Cr(vi)/10 | UV | 40 | 99 | 47 | | | | |

^{*a*} L = *cis*-1,3-dibenzyl-2-imidazolidone-4,5-dicarboxylic acid, bpy = 4,4'-bipyridine.



Fig. 8 The photocatalytic $Cr(v_i)$ reduction during five consecutive runs over complexes 1 (a) and 2 (b); the PXRD patterns for complexes 1 (c) and 2 (d).

photocatalysts for organic pollutions degradation. As shown in Fig. 9a, the degradation of MB occurred merely up to 13.5% after 90 min under UV irradiation in the absence of the MOFbased photocatalysts. The variation of MB concentration was 8.90% and 20.5% when complexes 1 and 2 were added in the dark after 60 min, respectively, suggesting that the MB molecule could be adsorbed on the surface of the MOF photocatalysts. For 1 and 2, about 55.9% and 84.3% degradation of MB



Fig. 9 (a) Control experiments for the photocatalytic degradation of MB over complexes **1** and **2**; (b) pseudo-first-order kinetics curves of the photocatalytic degradation of MB over complexes **1** and **2** under UV light.

was observed after 90 min under ultraviolet irradiation, respectively. Complex 2 had a comparative predominance for photocatalysis over complex 1, suggesting that the adsorption capacities for MB of the MOF-based photocatalysts should play a predominant role in their photocatalytic activities. Because the photocatalytic reactions are commonly believed to occur on the surface of the photocatalyst, the larger adsorption amounts of MB onto the photocatalysts may contribute to the faster degradation rate of MB.^{50,51} The values of the BET specific surface areas and pore volumes of complexes 1 and 2 exhibited the order of 2 > 1 (Table S3[†]). The rate constants for MB photodegradation over 1 and 2 under UV light were 0.00778 min^{-1} and 0.0174 min^{-1} (Fig. 9b). The satisfactory photocatalytic efficiencies might result from the relatively slow recombination of photogenerated electrons and holes, which is consistent with the studies of Cr(vi) reduction. Compared with other MOF photocatalysts, complexes 1 and 2 have high photocatalytic efficiency with small dosage and short time. A comparison of the photocatalytic performance with reported photocatalysts in recent years for the degradation of MB is listed in Table 2.

Mechanism

Based on the experimental results of $Cr(v_1)$ reduction and MB degradation, a plausible mechanism for complexes **1** and **2** mediated photocatalysis is proposed.³¹ As illustrated in Fig. 10, upon light irradiation, the photogenerated electronhole pairs separate through the ligand to enable a metal charge transfer (LMCT) process,⁵⁶ leaving a photoinduced electron (e⁻) in the conduction band and a positive-charged hole (h⁺) in the valence band of the MOF-based photocatalysts (eqn (3)).

$${\rm MOFs} + h\nu \rightarrow {\rm MOFs} ({\rm h}^+ + {\rm e}^-) \tag{3}$$

$$methanol + h^+ \rightarrow CO_2 + H_2O + others$$
(4)

Inorganic species with a reduction potential more positive than that of the conduction band of the semiconductor can consume the electrons and complete the redox reaction cycle.⁵⁷ The reduction potential of Cr(vi) to Cr(iii) is pH dependent, which is more positive than the position of conduction band of complexes 1 and 2 (0.58 V and -1.29 V vs. NHE) in acid conditions, indicating that the photogenerated electrons in the CB possess a strong reduction ability and can reduce the adsorbed $Cr(v_1)$ to Cr(m) (eqn (1)). Meanwhile, the thermodynamic driving force for Cr(vi) reduction decreases with increasing pH, showing that the photocatalytic reduction of $Cr(v_1)$ is beneficial at low pH. The photogenerated holes (h^+) could easily react with organic species (methanol) to produce CO₂, H₂O, and other minerals, thereby limiting the recombination between photoinduced electrons and holes to accelerate the target reaction (eqn (4)). The introduction of a hole scavenger, such as methanol, was proven to be effective for promot-

Table 2 Comparison of the MB degradation capacity of complexes 1 and 2 with other photocatalysts

| Catalyst/mg | Pollutants/mg L^{-1} | Irrigation | Time (min) | Efficiency (%) | Ref. |
|---|------------------------|------------|------------|-----------------|-----------|
| Complex 1/5 | MB/10 | UV | 90 | 55.9 | This work |
| Complex 2/5 | MB/10 | UV | 90 | 84.3 | This work |
| [Ni(bismip)(bpy)(H ₂ O)]·H ₂ O/40 | MB/10 | UV | 180 | 80^a | 52 |
| $[Cu_{3}(4-bpah)_{4}(1,3,5-btc)_{2}]\cdot 8H_{2}O/150$ | MB/10 | UV | 240 | 50^b | 53 |
| $[Cu(3-dpye)(1,3-bdc)]\cdot 3H_2O/150$ | MB/10 | UV | 240 | 80 ^c | 54 |
| ZIF-8/LDO/20 | MB/10 | UV | 180 | 58^d | 55 |
| Zn(bpy)L/15 | MB/10 | UV | 30 | 93 ^e | 32 |

^{*a*} Bismip = 5-(1*H*-benzoimidazol-2-ylsulfanylmethyl)-isophthalic acid, bpy = 2,2'-bipyridine. ^{*b*} 4-Bpah = N,N'-bis(4-pyridinecarboxamide)-1,2-cyclohexane, 1,3,5-H₃BTC = 1,3,5-benzenetricarboxylic acid. ^{*c*} 3-Dpye = N,N'-bis(3-pyridinecarboxamide)-1,2-ethane, 1,3-H₂BDC = 1,3-benzenedicarboxylic acid. ^{*d*} LDO = Zn-Al layered double oxides. ^{*e*} L = *cis*-1,3-dibenzyl-2-imidazolidone-4,5-dicarboxylic acid, bpy = 4,4'-bipyridine.



Fig. 10 A schematic illustration of the energy position and $Cr(v_i)$ reduction over complexes 1 and 2.

ing photocatalytic $Cr(v_1)$ reduction over complexes 1 and 2 in our experiments.

$$MB + h^+ \rightarrow CO_2 + H_2O + others$$
 (5)

$$h^+ + H_2O \rightarrow OH + H^+$$
 (6)

$$O_2 + e^- \rightarrow O_2^- \tag{7}$$

$$MB + OH + O_2 \rightarrow CO_2 + H_2O + others$$
(8)

The photocatalytic mechanism of complexes 1 and 2 in dye molecule degradation was similar to those of reported photocatalysts.⁵⁸ The photoexcited holes have a strong oxidation capacity to oxidize MB molecules directly (eqn (5)) or to react with water molecules to produce hydroxyl radicals ('OH) (eqn (6)). Meanwhile, the photoexcited electrons in the conduction band could be captured by O₂ to form superoxide radicals ('O₂⁻) (eqn (7)). Both of the resulting hydroxyl radicals ('OH) and superoxide radicals ('O₂⁻) have a strong oxidation capacity to decompose MB molecules into CO₂ and H₂O and others (eqn (8)). The process of photocatalytic reaction is as shown in eqn (5)–(8):

In order to explore the insights into the role of the reactive species during the MB degradation, several trapping experiments were performed. Triethanolamine (TEOA) was chosen as an effective hole scavenger for the photocatalysis system,

and tert-butyl alcohol (t-BuOH) was chosen as an 'OH scavenger because it reacts with 'OH radicals with a high rate constant $(k = 6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1})$.^{59,60} For complex 1, the degrading rate of MB increased to about 95.3% when TEOA (10.0 mM) was added into the reaction solution after 60 min under UV light irradiation (Fig. 11a). Compared with the system without a hole scavenger, the degrading rate of MB increased significantly in the system with TEOA. We suspected that the MB was not oxidized by the holes but by O_2^- radical anions, which were generated by the reaction of e⁻ and O₂. The TEOA would capture photoinduced holes in the VB of complex 1 and more electrons could escape from the pair recombination, which could then be captured by O_2 to form superoxide radicals (O_2) (eqn (6)). To confirm this conjecture, nitrotetrazolium blue chloride (NBT) was chosen as an effective superoxide radical scavenger for the system.⁶¹ There was only about a 13.5% degradation of MB observed after 90 min when NBT (10.0 mM) was added into the reaction solution. Compared with the system without an 'OH scavenger, the degrading rate of MB was scarcely increased in the system with t-BuOH (10.0 mM) (Fig. 11a). These results clearly suggest that the main active component was superoxide radicals (O_2) for complex 1 system. For complex 2, the addition of tert-butyl alcohol and triethanolamine led to 69.1% after 90 min and 89.9% after 70 min quenching in the system, respectively, and NBT could significantly inhibit the MB degradation (Fig. 11b). All being said, the main reactive species in the system with 2 were both 'OH radicals and ' O_2 ', which was consistent with the PL experiments⁶² (Fig. 11c).

To further confirm the presence of active radicals in the MB photocatalytic degradation over **1** and **2**, electron spin resonance (ESR) spin-trap technique was conducted by using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as the spin-trap reagent under UV light irradiation. Fig. 12 shows four ESR characteristic signals during light irradiation, attributable to the DMPO- O_2^- adducts.⁶³ Therefore, O_2^- radicals play a key role in the photocatalytic degradation of MB over **1** and **2**.

In order to determine whether the radicals lead to decomposition of the complexes, the removal of metal ions from the MOFs after the photoreaction experiments was quantified by inductively coupled plasma optical emission spectrometry (ICP-OES). The concentrations of $Cu(\pi)$ and $Co(\pi)$ in



Fig. 11 Effect of photocatalytic reaction as different trapping agents were added to the system, (a) and (b) are for **1** and **2**, respectively; (c) the photoluminescence spectra of TAOH formed by the reaction of TA with 'OH radicals generated from different photocatalytic systems under UV-light for 60 min.

MB aqueous solution after photocatalysis were 0.460 mg L^{-1} and 1.98 mg L⁻¹, respectively, and the results are listed in Table S4.† Accordingly, the removal rate of metal ions from complexes 1 and 2 was 0.360% and 1.80%, respectively. In addition, the metals and P components of complexes 1 and 2 after photocatalysis were checked by XPS analysis (Fig. S6[†]). All of the binding energies (BEs) in this XPS analysis were corrected for specimen charging by referencing them to the C 1s peak (set at 284.8 eV). For complex 1, the peaks of $2p_{3/2}$ (934.4 eV) and $2p_{1/2}$ (953.8 eV), and their shake-up satellite peaks at 943.1 and 962.7 eV, corresponding to Cu(II), were observed (Fig. S7a[†]).⁶⁴ For 2, in the Co 2p spectrum of Fig. S7b,[†] the two Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks located at 781.2 and 797.1 eV were accompanied by two prominent shake-up satellite peaks (786.5 and 803.8 eV), which distinctly verified the dominating presence of the Co(II).⁶⁵ All P2p spectra from complexes 1 and 2 revealed a single peak at 133.1 eV, corresponding to P-O-metal (Fig. S8[†]).⁶⁶ All of the test results indicated that the radicals have little effect on the decomposition of the complexes.



Fig. 12 ESR spectra of complexes 1 (a) and 2 (b) for DMPO- O_2^- .

Conclusions

In summary, two metal-organic frameworks based on phosphonate ligands were synthesized by a general hydrothermal method and were then structurally characterized. Both complexes demonstrated that they were highly efficient heterogeneous photocatalysts for aqueous Cr(vi) reduction and for the degradation of MB under UV light irradiation. The experimental results indicated that the photocatalytic reduction of Cr(vi) to Cr(iii) was highly pHdependent, and the addition of a hole scavenger of methanol significantly promoted the photocatalytic reaction. The high photocatalytic efficiency of the catalysts depends on the phosphorous ligands with conjugate structure, which enhances the separation of photogenerated electrons and holes. Moreover, for the degradation of MB, the superoxide radicals and hydroxyl radicals to be the main reactive species in the system with the complexes. The results also indicated that the two photocatalysts were stable and reusable, enabling them to be potential candidates for wastewater purification. The metal-organic frameworks based on phosphonate ligands were first applied for the photocatalytic reduction of Cr(vi) and the degradation of dyes as new photocatalysts. It is hoped that our current work could widen the application range of MOFs based on phosphonate ligands and provide new inroads into the exploration and utilization of MOFs for industrial wastewater treatment.

Conflicts of interest

There are no conflicts to declare.

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