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ARTICLE TYPE

Structures, photoluminescence and photocatalytic properties of two novel metal-organic frameworks based on tetrazole derivatives

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Two novel metal-organic frameworks, [Ag(ATZ)]_n (**1**) (ATZ = 5-amino-tetrazole) and [Ag₂(en)₂(AT)]_n (**2**) (en = ethylenediamine, AT = 5, 5'-azotetrazolate), are prepared from corresponding Ag(I) salts and have been structurally characterized by elemental analyses, Fourier transform infrared spectroscopy and single crystal and powder X-ray diffraction. The structures of both compounds consist of 2-D three-
10 connected layers that are linked by π - π overlap interactions between the tetrazolate fragments in the neighboring layers to form a 3-D supramolecular. The photoluminescent properties of solid samples of **1** and **2** at room temperature and photocatalytic performance of them have been also reported and discussed. The results indicate that **1** seems to be a good candidate for novel inorganic-organic photoactive materials with high quantum yield. Moreover, compounds **1** and **2** represent the first example of coordination polymers with a Ag ion that exhibit high efficient photocatalytic abilities for dye degradation under UV light and show good stability toward
15 photocatalysis.

Introduction

In recent years, considerable constructions have been made in the design and engineering of metal-organic frameworks (MOFs) because of their potential applications in gas sorption, separation,
20 and catalysis.¹⁻³ The continuing interest in this area is also due to intriguing aesthetic structures and many possible metal-ligand coordinations,⁴ as well as exploiting new properties through the variation of building blocks.⁵⁻⁷ Typically, MOFs are built from O-donor ligands, such as bridging multicarboxylate compounds.⁸
25 Recently, the use of tetrazolates and their derivatives as N-donor linkers is increasingly reported, since the tetrazolates heterocycle has versatile coordination fashions ranging from κ_1 to κ_4 and also has the ability to form various of different topological architectures. However, compared with the investigation for the
30 synthesis of tetrazolate-based MOFs with peculiar features, only few efforts have been devoted to explore new application of these materials. Therefore, searching the peculiar properties, discovering the practical application for tetrazolate-based MOFs and evaluating their performance are challenging but in high
35 demanded.

Photocatalysis, as a “green” technology, has been widely applied in the treatment of solar water splitting, purifying air, and eliminating the organic contamination of water.⁹ In past decade, the development of solid photocatalysts are mainly focus on the
40 semiconductor metal oxide, sulfide particles and so on. More recently, a few contributions about new photocatalytic materials based on MOFs are successively accomplished, which indicated that this area is a new application for MOFs materials and also an alternative strategy to develop novel photocatalysts.¹⁰ Because
45 MOFs could become to a versatile and potentially tunable photocatalyst, which is achieved by changing the organic linkers and transition metal centres to form different ligand-to-metal charge-transfer (LMCT) transitions. However, such kinds of applications of MOFs are just to emerge. And inexpensive, stable,
50 efficient novel photocatalysts based on MOFs still need to be continuously developed with great effort.

Motivated by the above-mentioned superiority of MOFs, a few pursuits of MOFs-based photocatalysts for the degradation of organic dyes have been reported.^{11,12} Most of them are
55 constructed by polycarboxylate acids, where the imidazole-based spacer also be used as a second ligand in some case. However, there is only one example built by N-donor tetrazolate ligands, but showing excellent property for decomposing organic dyes. So it is expected that this kind photocatalyst may show more
60 captivating performance by the optimization of tetrazolate ligands and metal centres.

On the other hand, one of the most popular metals employed in the construction of MOFs has been silver(I).¹³ This d¹⁰ metal is particularly versatile in its coordination number, geometry and
65 applied properties, but rarely emerging in the MOFs built by tetrazolates and its derivatives.¹⁴ Considering the above points, we design and synthesis two novel Ag(I)-based MOFs from 5-aminotetrazolate¹⁵ and 5, 5'-azotetrazolate¹⁶⁻¹⁸ and evaluate their performance as efficient photocatalysts in decomposing the
70 organic dye R6G. The thermal stabilities and photoluminescent properties of these two compounds are also investigated.

Experiment and details

Materials and Methods

Reagents and solvents employed were commercially available
75 and used as received. C, H and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. IR spectra were recorded on KBr discs on a Bruker 6700 spectrophotometer in the 50 - 3500cm⁻¹ region. Fluorescence measurements were recorded with a Hitachi 910 fluorescence spectrophotometer. The UV/vis
80 spectra for solution samples were obtained on a U-4100 Spectrophotometer (Solid).

Photocatalytic experiments: the UV light source was a 300 W high-pressure mercury lamp (main output 365 nm). A suspension of powdered catalyst (5 mg) in a fresh aqueous solution of

organic dye (10 mL, 1×10^{-5} mol/L) were first sonicated for 5 min, and shaken at a constant rate in the dark overnight (to establish an adsorption/desorption equilibrium of organic dye on the sample surface). At given irradiating intervals, a series of suspension of a certain volume were collected and filtered through a membrane filter (pore size, 0.022 mm) to remove suspended catalyst particles, and the filtrate was analyzed on the UV/vis spectrometer. The organic dye concentration was estimated by absorbance at 519 nm, which directly relates to the structure change of its chromophore.

Preparation of **1** and **2**

Sodium-5,5'-azotetrazolate and 5-amino-tetrazole was synthesized according to the reported method.^{15a, 17c, 17h}

Caution! The complex of sodium-5,5'-azotetrazolate or 5-amino-tetrazole and its deprotonated anions are potentially explosive and should be handled in small quantities. Appropriate safety precautions should be taken and larger scale syntheses are not recommended.

[Ag(ATZ)] (**1**)

1.13g (19.5 mmol) en was added to a solution of AgNO₃ (0.042g, 0.25mmol) in water (3ml) and stirred for 5 min. B: 2 ml water and methanol mixture with the same-size ratio. C: 5-amino-tetrazole (0.043 g, 0.5 mmol) in 5 ml methanol was stirred to clarification. Solution A was shifted in the bottom of a clean 1 centimeter diameter glass tube, then B and C was added onto the surface of previous solution slowly in turn to form a diffusion system. Colourless crystals were obtained in the diffused part after several days (yield : 67% based in Ag). Anal. Calcd For CH₂AgN₅: C, 6.26; H, 1.05; N, 36.50. Found: C, 6.21; H, 1.12; N, 36.47. IR spectrum (cm⁻¹): 3398m, 3296m, 2965w, 1598s, 1555s, 1458w, 1438w, 1264m, 1153w, 1082m, 735s, 459w.

[Ag₂(en)₂(AT)] (**2**)

Method One: A: 1.13g (19.5 mmol) en was added to a solution of AgClO₄ (0.056g, 0.25mmol) in water (3ml) and stirred for 5 min. B: 2 ml water and methanol mixture with the same-size ratio. C: 0.026g (0.125mmol) Sodium-5,5'-azotetrazolate in 5 ml methanol was stirred to clarification. Solution A was shifted in the bottom of a clean 1 centimeter diameter glass tube, then B and C was added onto the surface of previous solution slowly in turn to form a diffusion system. Brown crystals were obtained in the diffused part after several days (yield : 47% based in Ag).

Method Two: A mixture of AgClO₄ (0.056 g, 0.25 mmol) and 1.13g (19.5 mmol) en in 5ml water and 10ml methanol was stirred for 5 min, to the above solution, 0.026g(0.125mmol) sodium-5,5'-azotetrazolate was added then stirred for 10 min to be a brown solution. Brown crystals were obtained by slow evaporation of the solution for 2 days (yield : 58% based in Ag). Anal. Calcd For C₃H₈AgN₇: C, 14.41; H, 3.23; N, 39.23. Found: C, 14.39; H, 3.30; N, 39.27. IR spectrum (cm⁻¹): 3338w, 3248w, 3160w, 1598m, 1391w, 1052w, 1008w, 970w, 745w, 570w.

X-Ray crystallography and data collection

The crystals were filtered from the solution and immediately coated with a hydrocarbon oil on the microscope slide. Suitable crystals were mounted on glass fibers with silicone grease and placed in a Bruker Smart APEX(II) area detector using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 140(2) K.

Table 1. Crystal data and structure refinement for **1** and **2**.

Compound	1	2
Empirical formula	CH ₂ AgN ₅	C ₃ H ₈ AgN ₇
Formula weight	191.95	250.03
Crystal system	Monoclinic	Monoclinic
Space group	P 2 ₁ /c	P 2 ₁ /c
a/Å	3.4771(8)	4.5401
b/Å	10.671(2)	11.0469
c/Å	10.220(2)	14.585
α (°)	90	90
β (°)	94.143(4)	93.647(2)
γ (°)	90	90
V (Å ³)	378.22(15)	730.02(17)
Z	4	4
Dc/g cm ⁻³	3.371	2.275
F(000)	360	488
μ /mm ⁻¹	5.151	2.705
R ¹ (all data)	0.0382	0.0336
w R ² (all data)	0.0986	0.0750

Their structures were solved by direct methods and successive Fourier difference syntheses using the SHELXTL software suite. Hydrogen atoms were added theoretically and were riding on their parent atoms. Crystallographic data were deposited in the Cambridge Crystallographic Database Centre: CCDC-1004250 for **1**, 1004249 for **2**. Table 1 gives the crystals data and data collection parameters for **1** and **2**.

Results and discussion

Description of structures

The crystal structure of Compound [Ag(ATZ)]_n (**1**).

Compound **1** crystallizes in monoclinic space group P 2₁/c and consists of one 5-aminotetrazolate ligand and one Ag(I) ion in crystallographically independent unit. As shown in Fig. 1a. each Ag(I) ion features a trigonal geometry, coordinated by three nitrogen atoms from three different ATZ ligands. The Ag–N bond lengths are 2.207(5), 2.208(5) and 2.273(5) Å, and the N–Ag–N angles are 112.0(2), 113.79(19) and 134.16(19)°. And each ATZ ligand is bonded to three Ag(I) ions in μ_3 -1,2,4 bridging mode to give a 2-D three-connected (4,8) planar layer containing 6-membered rings (Ag₂N₄) and 16-membered rings (Ag₄N₁₂). The intramolecular Ag(I)⋯Ag(I) distance in Ag₂N₄ rings is 3.82 Å. The cavity of each Ag₄N₁₂ rings is filled up with two amino groups of ATZ ligands. This 2-D layer structure of **1** can be rationalized as a bimodal (4,8²)_{Ag}(4,8²)_{ATZ} topological network in which Ag(I) ion and ATZ ligand function as three-connected nodes. The adjacent layers are stacked in sequence to form a 3-D supramolecular framework (Fig. 1b). It should be noted that there is a Ag(I)⋯Ag(I) distances of 3.48 Å between different layers that is close to the sum of the van der Waals radii of two silver atoms,¹⁹ indicating weak ligand unsupported Ag(I)⋯Ag(I) interactions.

The crystal structure of Compound [Ag₂(en)₂(AT)]_n (**2**).

Complex **2** has the chemical formula [Ag₂(en)₂(AT)]_n and crystallizes in the monoclinic primitive space group P 2₁/c. The atomic labeling diagram of **2** is show in Fig. 1c. The building unit consists of two silver and one 5,5'-azotetrazolate ligand as well as two en ligands all of them located in general positions. Each silver (I) ion in **2** is coordinated within a strongly distorted tetrahedron by four nitrogen atoms from different ligands, two of which is from different μ_2 -en ligands and the others are provided

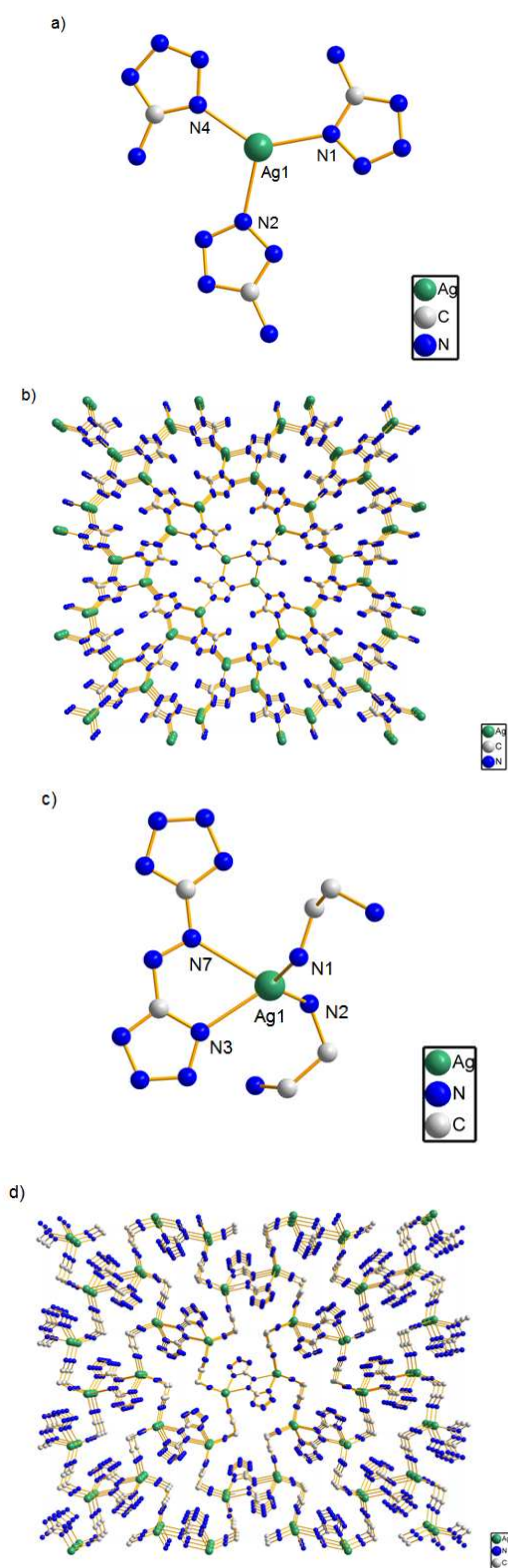


Figure 1. (a) Coordination environments of Ag atoms in **1** with hydrogen atoms omitted for clarity. (b) The complicated 3D structure of **1**. (c) Coordination environments of Ag atoms in **1** with hydrogen atoms omitted for clarity. (d) The complicated 3D structure of **2**.

by the tetrazolate ring and the azo group of μ_2 -AT ligand, respectively. The bond length of Ag–N range from 2.244(2)–2.572(2) Å, and the N–Ag–N angles are 128.85(8), 113.21(8), 112.09(8) and 122.59(8) °C. The en ligands behave as a bridging ligand using both amine N atoms. And the whole ligand is located on a polygonal line-shape. In the structure of **2**, the trans-AT²⁻ ligand chelates two Ag(I) ion in an unprecedented coordination modes, a novel bis-chelating mode, which is rarely found and reported in other metal-AT coordination polymer. Two five members chelate ring are formed by the interactions between Ag(I) ion and two different nitrogen atoms from azo group and the tetrazolate ring, respectively. Then this dinuclear Ag-AT unit are connected by the en ligands via μ -N,N'-coordination into a three-connected 6³ corrugated 2D layer structure (Fig. 1d). And these layers are stacked in the direction of the crystallographic a-axis via a π - π interaction.

Photoluminescence Properties

The luminescent properties of compounds **1** and **2** are investigated in the solid state at room temperature. As illustrated in dark line in Figure 2, it can be observed that maximum excitation wavelength of **1** is at 274 nm, while at 310 for **2**. And the emission spectra of this two compounds are also described in Figure 2 with red line. With excitation at 274 nm complex **1** exhibits two intense blue fluorescence bands around 441 and 468 nm, and the stock shift is as long as 194 nm. This significantly strong emission would originate from intra-ligand π_L - π_L^* transitions emission (LLCT), as the free HAT ligand presents a weak photoluminescence emission at 325 nm at ambient temperature.^{15d, 15g} Correspondingly, the

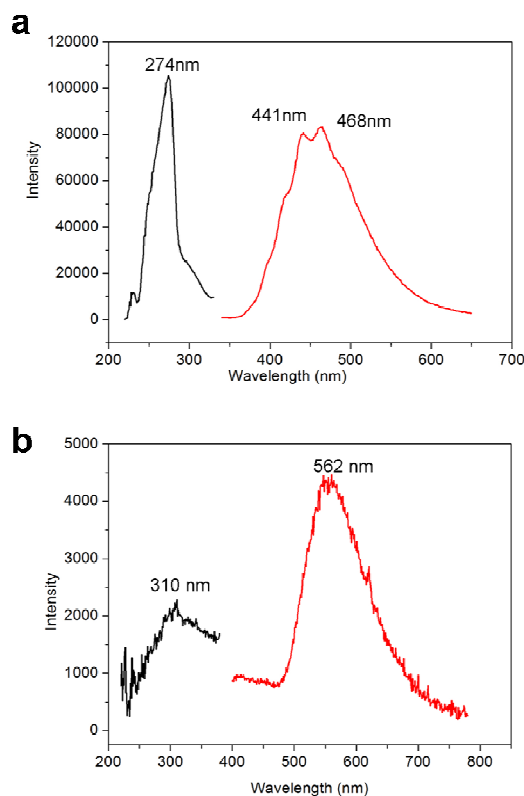


Figure 2. Emission and excitation spectra of (a) compound **1** and (b) compound **2** in the solid state at room temperature.

emission wavelength of the compound **2** is significantly red-shifted to 562 nm showing a green fluorescence, when the optimum excitation wavelength is 310 nm, and the stock shift of **2** is as long as 252 nm. According to the previously literatures about the weak emission of MOFs, the fluorescent emission of **2** is tentatively attributed to the metal-to-ligand charge transition (MLCT) and/or ligand-to-metal charge transition (LMCT). It is should be noted that the cause of significant red-shifts of the two compounds is the coordination interactions and the deprotonation of the ligands. In addition, Compared to **2**, the tetrazol rings in **1** are closely packed and show much stronger π - π interactions between adjacent layers. Such strong π - π interactions probably lower the π^* energy of the ATZ ligand and enhance the photoluminescence.²⁰ Therefore, the emission energy level of **2** is lowered, and longer wavelength emission is found.

Moreover, the different performance in photoluminescent lifetime of **1** and **2** also arise from the discrepancy of the structures. The photoluminescent lifetime of the polymer **1** is four times longer than that of the polymer **2** (4.065 ns vs 1.077 ns). Because compound **1** is constructed by the rigid HATZ ligand and Ag ion, which lead to reduce the loss of energy by radiationless decay of the intraligand emission excited state. In contrast, the en ligand make the structure of **2** more flexible. It is worth mentioning that the photoluminescent quantum yield of the coordination polymer **1** is as high as 0.12 and make compound **1** a potential blue fluorescence material along with the fact that compound **1** has high thermal stability and is virtually insoluble in most common solvents.

Photocatalytic Activities

The diffuse-reflectance UV-vis spectra reveal the absorption features of solid **1** and **2** in Figure 3, and this two spectra consist of absorption components in the ultraviolet and visible regions. In both cases, the peaks of absorption at 265 nm for **1** and 294 nm for **2** could be ascribed to π - π^* transitions of the ligands, while the main UV absorption bands at 379 nm and 392 nm (480 nm) for **1** and **2**, respectively, which could be attributed to ligand-to-metal charge transfer (LMCT). In order to acquire the precise values of band gap from the absorption edges, the point of inflection in the first derivatives of the absorption spectrum was used. The values of the band gap for **1** and **2** obtained from corresponding LMCT transitions are 3.29 eV and 2.12 eV (see Figure S1 and S2 in ESI). Such distinct band-gap sizes for **1** and **2** may result from the local coordination factors, such as the different coordination model of Ag ion and the discrepancy of the ligands. The presence of narrow band gaps motivated us to explore applications of **1** and **2** in heterogeneous photocatalysis. So the photocatalytic activities of both compounds were further studied.

Following, we selected the notorious organic dye R6G, as a target pollutant for degradation experiments in aqueous media to evaluate the photocatalytic performance of compounds **1** and **2**. After adsorption equilibrium between the photocatalysts and the dye in the dark achieved the photodegradation experiment under UV irradiation was carried out. Moreover, the control experiments of the photodegradation of R6G have also been accomplished. The result of control experiment in Figure 4 show that the concentration of R6G almost does not change in the dark condition or without catalyst by tracing the decrease in the main peak absorbance at 519nm as a function of irradiation time (see Figure S3-S7 in ESI). Therefore, the presence of both

illumination and catalyst **1** and **2** is necessary for the efficient degradation of R6G. Compared with the control experiments, the distinctly

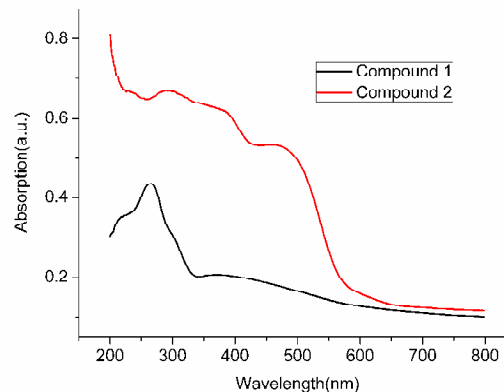


Figure 3. UV-vis diffuse-reflectance spectra of compounds **1** and **2** with BaSO₄ as background.

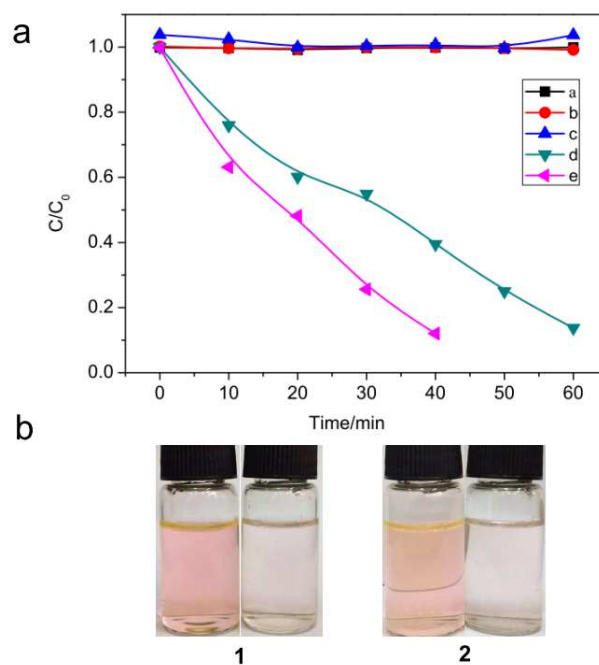


Figure 4. (a) Photodecomposition of R6G in solution over different condition with light irradiation: (—■—) a) R6G/UV light without catalysts, (—●—) b) R6G/in dark with **1**, (—▲—) c) R6G/in dark with **2**, (—▼—) d) R6G/**1**/UV light, (—□—) e) R6G/**2**/UV light; (b) Colour change photograph image of dye R6G solution before and after photodecomposition of compound **1** and **2**.

shortened degradation time indicates that **1** and **2** are effective to degrade the dye R6G under UV light irradiation. Figure 4a also shows the comparison of the photocatalytic activities of two polymers. It is obvious that **2** exhibits much higher activity. After 43 min of UV irradiation, 90.8 % of the R6G concentration was removed by **2**. In contrast, photocatalyst **1** has to take a little longer time for degradation of R6G, with the irradiation time increasing to 60 min the degradation of R6G could also reach 86.3%. In Figure 4b, excellent photocatalytic abilities of both compounds are indicated visually by the colour change of the solutions before and after photocatalytic process. In contrast with

the deep pink initial liquids without **1** and **2**, only a very weak pink is obtained in both catalytic systems with **1** and **2** after UV-light irradiation. To quantify the reaction, the kinetics is determined by Langmuir-Hinshelwood mechanism ($\ln C/C_0 = -kt$, where C is the R6G concentration as a function of photodegradation time, C_0 is the initial concentration, and k is the apparent reaction-rate constant). The rate constant for **2** under UV-light irradiation was found to be 3.321 h^{-1} , whereas the rate constant for **1** under UV-light irradiation was 1.989 h^{-1} , when pseudo-first-order kinetics was fitted with the experimental data. It is clear that polymer **2** possessed higher activity than **1**, which may attribute to the structural difference between polymer **1** and **2**. The structure of **2** contained more delocalized π electrons of ATZ ligands, compared with ATZ ligands in polymer **1**, may facilitate the LMCT transitions and decrease electronic band gap of the MOFs, which contribute greatly to the enhanced photocatalytic rate. Therefore, it could be concluded that the semiconductor properties of the obtained MOFs strongly depend on the resonance effects in the organic linker.²¹

In order to establish a fair appraisal of these two novel MOFs' true potential for photocatalytic application, we take commercial TiO₂ (Degussa P-25) as a reference photocatalyst, which is well known because of its excellent photocatalytic performance in the degradation of organic dyes. So in the same photocatalytic experimental conditions as that of compounds **1** and **2** the photocatalytic performance of Degussa P-25 is assessed. After 40 min of UV irradiation, 90.1 % of the R6G concentration is removed by Degussa P-25. And the rate constant for it under UV-light irradiation is found to be 3.29 h^{-1} . For purpose of making a more accurate comparison, the apparent rate constant calculated for the pseudo-first order kinetic should be expressed on a metal basis (per mmole of metal). So the rate constants are 0.765 h^{-1} for **1** (the amount of Ag in 5mg is 2.6 mmol), 1.661 h^{-1} for **2** (the amount of Ag in 5mg is 2.0 mmol) and 0.526 h^{-1} for P-25 (the amount of Ti in 5mg is 6.26 mmol), when the loading of the photocatalyst is 1 mmol/L based on the metal. It is thus clear that compounds **1** and **2** are more superior photocatalysts than Degussa P-25 (The experimental data of Degussa P-25 is found Figure S23-S24 in ESI).

To rule out the possibility that the photocatalytic activity of **1** and **2** arise from molecular or oligomeric fragments formed from through dissolution of solid catalysts in the photocatalytic reaction process, other control experiments are conducted (see Figure S8-S10 in ESI). After 30min of irradiation the solid catalyst is filtered from the reaction suspensions, and the filtrate is irradiated for another 30 min in UV light. Without the catalysts, the concentration of R6G is not change, suggesting that the solution contains no photocatalytically active species. Moreover, the measurement of total organic carbon is used to analyze the total organic carbon of the organic residues after photocatalysis process. The results reveal that the TOC decreases obviously, which indicate that the organic dye R6G is mineralized by the photocatalysts in the manner of being degraded into carbon dioxide. In addition, in order to investigate the stability of two compounds as visible light photocatalysts, we prepared the photocatalytic degradation of R6G three times. It is proved that the photocatalysts still keep similar photocatalytic efficiencies (see Figure S11-S17 in ESI). Moreover, the IR spectrum and power X-ray diffraction (PXRD) patterns of two polymers at the end of each repeated bleaching experiment are almost identical with that of the as-prepared sample (see Figure S18-S21 in ESI), which indicate that their stability towards photocatalysis are good.

Conclusions

In summary, we have synthesized and characterized two novel metal-organic framework photocatalysts based on silver salts and the tetrazolate derivatives for the first time, which have been characterized using a variety of techniques such as elemental analyses, Fourier transform infrared spectroscopy and single crystal and powder X-ray diffraction. X-ray single crystal structure analysis indicate that compound **1** has a 2-D three-connected layer structures formed by trigonal Ag ion and 5-amino-tetrazole, and compound **2** also show 2-D framework containing tetrahedrally Ag ion, 5,5'-zaotetrazolate and en ligand with a novel bis-chelating mode. The results of photoluminescent experiments reveal that compound **1** is a potential blue fluorescence material with high quantum yield. Considering the narrow band gaps of two compounds, the photocatalytic activities of them are also studied. In the photocatalytic studies, both compounds exhibit excellent light-driven photocatalytic efficiency for the degradation of organic dye R6G under UV light and show good stabilities toward photocatalysis. Considering their high efficiency and high stability on the photocatalytic degradation of organic dye, the successful synthesis of compounds **1** and **2** provides access to a promising way in the search for photocatalytic applications. Further studies into the photocatalytic reaction mechanism and systematic work on degradation of other organic dyes are in progress.

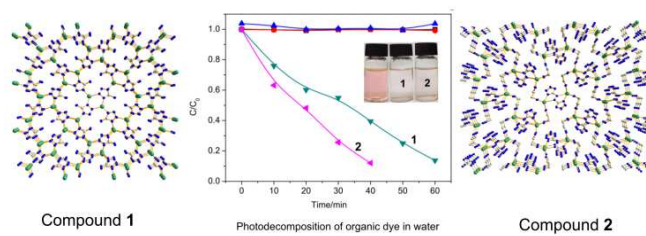
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Notes and references

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[†] Electronic Supplementary Information (ESI) available: Bond lengths and angles for **1** and **2**; Fig. S1-S21. See DOI:10.1039/b000000x/
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Two novel efficient metal organic framework photocatalysts based on silver salts and the tetrazolate derivatives have been successfully prepared and characterized.