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Metal-Organic Frameworks with Organogold(III) Complexes for Photocatalytic Amine Oxidation with Enhanced Efficiency and Selectivity

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Abstract: Luminescent organogold(III) complex (Au^{III}) with highly emissive triplet excited states is encapsulated into two metal-organic frameworks with different porous size and structure, named MOF1 and ZJU-28. Contrast to Au^{III} complex in solution, the resultant composites, Au^{III}@MOF1 and Au^{III}@ZJU-28, exhibit enhanced emission intensity, lifetime and quantum yield. Under irradiation, Au^{III}@MOFs are efficient, selective, and recyclable catalysts for lightinduced aerobic C-N bond formation. When using Au^{III}@ZJU-28 as heterogeneous catalysts for oxidizing secondary amines to corresponding imines, high TONs of 876 - 1548 is achieved which is around 2.8 - 3.5 folds higher than that of homogenous Au^{III} complex. In addition, different selectivity to oxidize mixture substrates is realized based on different host MOFs which demonstrate that encapsulating active Au^{III} complex into an appropriate MOF could obtain the needed product. Inherent shortage of homogeneous catalyst in cyclic issue is also overcome by using composite catalysts and a high conversion of Au^{III}@ZJU-28 catalyst is still observed after ten cycles.

Introduction

Metal–organic frameworks (MOFs) constructed from metal ions and organic linkers via covalent bonds have emerged as a class of highly promising porous materials with appealing applications in gas storage/separation, heterogeneous catalysis, biomedicines, sensing, and proton/electrical conductivity.^[1] Taking advantage of tremendous choices of traditional inorganic and organic materials with active catalytic sites, catalytic properties of MOF materials can be engineered.^[2] For example, Lin and co-worker introduced mono(phosphine)–M (M–PR3; M = Rh and Ir) complexes into triaryIphosphine-based MOF through postsynthetic metalation and the resultant material exhibited

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activity in the hydrosilylation of ketones and alkenes.^[3] Jiang et al. reported PCN-777 ($Zr_6O_4(OH)_{10}(H_2O)_6(TATB)_2$) and Pt/PCN-777 composite which showed high activity and selectivity in hydrogen production and benzylamine oxidation.^[4] The catalytic activity of MOF materials can not only be generated from skeletons but also arise from by guest species.^[5] Pore size of MOF materials varied from a few angstroms to several nanometers, making them ideal for incorporating species ranging from small gas molecules^[6] to large inorganic^[7] and organic species.^[8] Encapsulation of guest catalytic species into the pores of MOFs provides an attractive avenue to realize MOF functionalization. The defined pore conditions in MOFs provide a unique platform to confine and stabilize guest species. What's more, the impossible size selective catalysis in homogeneous catalyst can be expected after it was encapsulated into MOFs.

Transition metal complexes with high-energy and highly emissive triplet excited states have been well documented to make enormous impact on the development of material science and photochemistry.^[9] Especially, the photocatalytic properties of heavy-metal materials have been extensively explored. Among them, gold(III) complexes with long-lived excited states, up to several hundreds of microseconds, have exhibited photocatalytic capability in various reaction for example C/C, C/N and C/O bond formation.^[5] However, the photocatalytic application is largely restricted by the poor stability of gold(III) complexes as well as recycling for long-term use.

Encapsulation of functional quest species into the pores of MOFs by cation exchange approach has been a facile and convenient post-synthetic method to realize MOF functionalization. Via this approach metal catalysts and luminescent metal ions/complexes have been successfully incorporated into the pore of MOFs.^[5, 10] In 2015, Che's group described the photocatalytic activity of luminescent gold(III) complexes@MOF composites, but the selectivity of them didn't obtain enough attention.^[5] In this regard, we are attracted to employ the cation exchange method to synthesize luminescent gold(III) complexes@MOF composited materials and investigate their emission properties so as to develop the selective heterogeneous photocatalysis applications. Thus, in this work, one gold(III) complex with C^N^C ligand^[11] was employed as photocatalytic quest species being incorporated into two MOFs with different porous structures. The resultant Au^{III}@MOF composites displayed phosphorescent emission between 400 nm and 750 nm with lifetimes around 4 µs in the presence of air at room temperature. Comparing with gold(III) complex in solution, emission intensity, lifetime and quantum yield of Au^{III}@MOFs were enhanced obviously and exhibited host

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FULL PAPER

depend behaviours. Furthermore, Au^{III}@MOFs are efficient, selective, and recyclable catalysts for light-induced aerobic amine oxidation.

Results and Discussion

Syntheses and structures of MOFs

Two MOF materials. MOF1 and ZJU-28, were chosen in this work to investigate the effect of MOF material porous structure on the photochemical properties of complex Au^{III} (Figure 1a). MOF1 was synthesized with CdCl₂ and H₆TATPT ligand under solvothermal condition as described in the literature.^[10a] MOF1 has a three-dimensional mesoporous anionic structure with two types of nanocages (Figure 1b), truncated tetrahedral cage (window size: 5.5 \times 5.5 Å²) and truncated octahedral cage (window size: $15.5 \times 15.5 \text{ Å}^2$).^[10a] The truncated octahedron was surrounded by four truncated tetrahedrons. Through sharing the truncated tetrahedrons a 3D non-interpenetrated network is formed. The pore structure can be considered as three crossing 1D channels (window size 15.5 × 15.5 Å²).^[10a] The nano-scale cages were occupied by disordered solvent molecules and $[Me_2NH_2]^+$ cations (the $[Me_2NH_2]^+$ cations came from decarbonylation of DMF).^[10a, 12]



Figure 1. (a) Complex Au^{III} used in this work; (b) Crystal structure of MOF1, viewed along the c axis; (c) Crystal structure of ZJU-28, viewed along the c axis.

ZJU-28 was synthesized with InCl₃ and H₃BTB ligand under solvothermal condition according to the literature.^[10c] ZJU-28 has two types of 1D channels along *c*-axis (Figure 1c) including planar triangular channel (window size: 9.5 × 9.5 Å²) and tetrahedral channel (window size: 9.8 × 14.7 Å²).^[10c, 13] Every tetrahedral channel is surrounded by two tetrahedral channels and two triangular channels through sharing the edge and vertex. The solvent molecules and cationic Me₂NH₂⁺ molecules reside in channels and void spaces, and the effective free volume of ZJU-28 is 64.7% of the total volume.^[13]

Syntheses and characterization of Au^{III}@MOF composites

Au^{III}@MOFs including Au^{III}@MOF1 and Au^{III}@ZJU-28 were synthesized via ion-exchange method. The Au^{III} complex was

incorporated into the corresponding framework materials by immersing MOFs in acetonitrile solutions, which contains the CF₃SO₃ salt of the Au^{III}. After 1 day, the light yellow solids were obtained (Figure S1).^[5] Contents of Au^{III} in Au^{III}@MOFs are determined by inductively coupled plasma (ICP) spectroscopy. There are indications that Au^{III} may reside in the channels/cages of the corresponding framework materials according to the following points: (i) the window sizes of MOF1 and ZJU-28 larger than the size of the complex Au^{III} (6.1 × 11.1 × 12.1 Å³), to have the possibility to incorporate Au^{III} into the pore of MOFs; (ii) photographs of the corresponding materials irradiated by 365 nm UV light revealed the distinctive green emission of Au^{III}@MOF1, congruent with Au^{III} and different from MOF1 (Figure S2); (iii) the scanning electron microscopy (SEM, Figure S3) and electron dispersive X-ray spectroscopy (EDX, Figure S4) studies for cross section of Au^{III}@MOF1 crystal revealed that Au^{III} was random location at the section, and F element was no detected in Au^{III}@MOF1 by EDX, to further confirm that Au^{III} incorporated into the MOF hosts.



Figure 2. Emission spectra of Au^{III} @MOFs in N2 (black) and air atmosphere (color) upon excitation at λ = 340 nm at room temperature. (a) Au^{III} @MOF1; (b) Au^{III} @ZJU-28.

Table 1. Emission data of the Au ^{III} complexes and Au ^{III} @MOFs.							
Compound	Conditions	τ ₀ (μs) ^[a]	$\Phi_{em}(\%)^{[b]}$	k _r (10 ³ s ⁻ 1) ^[c]	k _{nr} (10 ⁵ s⁻ ¹) ^[d]		
Au ^{III} solid ^[e]	Air	0.20					
Au ^{III} (DMF solution) ^[e]	Air	0.32	0.06	1.88	31.23		
	N ₂	0.59	0.09	1.53	16.93		
Au ^{III} @MOF1	Air	4.0	4.0	10.00	2.40		
	N ₂	6.4	6.2	9.69	1.47		
Au ^{III} @ZJU-28	Air	3.8	2.0	5.26	2.58		
	N ₂	5.3	2.8	5.28	1.83		

[a] Emission lifetime. [b] Emission quantum yield. [c] Radiative decay rate constant estimated by $k_r = \Phi/\tau$. [d] Non-radiative decay rate constant estimated by $k_{nr} = (1 - \Phi)/\tau$. [e] Reprinted with permission from ref. 5. Copyright 2015 Royal Society of Chemistry.

The UV-vis diffuse reflectance spectra (Figure S5) of Au^{III} at room temperature display two broad absorption band between 200-500 nm including an intense absorption band peaking at 250 nm and a moderately intense vibronic-structured band

FULL PAPER

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peaking at 385 nm.^[14] Au^{III}@MOF1 has a broad absorption band peaking at 289 nm and a shoulder peaking at 411 nm, the shoulder peak is corresponding to the absorption band of Au^{III}. Au^{III}@ZJU-28 has two broad absorption bands peaking at 250 nm and 385 nm, was similar to Au^{III}.

The emission spectra (Table 1, Figure 2 and Figure S6) of Au^{III}@MOFs solid were measured with the excitation of 340 nm at room temperature under air and nitrogen atmosphere. Under N₂ condition, Au^{III}@MOF1 exhibit structured emission between 400-750 nm peaking at 450 nm, 478 nm and 511 nm (Figure 2a). The first emission band belongs to MOF1 and the left peaks are the characteristic emission peaks of Au^{III} (Figure S6a and b). In this condition, the lifetime of Au^{III}@MOF1 at 478 nm is 6.4 μ s which is around 10 folds higher than Au^{III} in degassed solution (0.59 μ s), and the quantum yield is 6.2% which is ~69 folds higher than that of Au^{III} complex solution (0.09%). Under air condition, all the above peaks are maintained but with 68% decrease in the intensity. The lifetime of Au^{III}@MOF1 at 478 nm is 4.0 μ s which is 20 times longer than that of Au^{III} in the solid state (0.20 μ s) and around 10 folds higher than Au^{III} solution in air condition. The quantum vield in air condition is 4.0% which is ~66 fold higher than that of Au^{III} complex solution (0.06%). For Au^{III}@ZJU-28, in nitrogen atmosphere, the emission spectra of it displayed emission band peaking at 450 nm, 478 nm and 511 nm (Figure 2b). The first emission band is ascribed to ZJU-28 and other peaks are owing to the characteristic emission peaks of Au^{III} (Figure S6a and c). The lifetime of Au^{III}@ZJU-28 at 478 nm is 5.3 µs with the quantum yield of 2.8%. Under aerobic condition, all the above peaks are retained but with 78% reduction in the intensity, the lifetime of Au^{III}@ZJU-28 at 478 nm is 3.8 μ s with the quantum yield of 2.0% (Table 1). Compared with Au^{III} in DMF solution, the emission lifetimes of Au^{III}@MOF1 and Au^{III}@ZJU-28 are longer and the non-radiative decay rate constants (k_{nr}) of them are smaller (Table 1). This might result from restrictions of molecular motion by MOF framework. What's more, with steady state, oxygen concentration in the inner pores of Au^{III}@MOFs is probably lower than the oxygen dissolved in the solvent and in the atmosphere.^[15] This may reduce oxygen quenching effect of Au^{III}@MOFs emission under aerobic conditions. If the matrix and the surrounding environment are in equilibrium, the activity of oxygen in the matrix would be equal to in the external environment.^[5] When using oxygen as an oxidant in photocatalytic reactions (see the section below on the photocatalytic properties of the Au^{III}@MOF composites), a large-scale transport of oxygen would go through the matrix and the abovementioned equilibrium may reach.

Photocatalytic properties of Au^{III}@MOF composites

It is recently reported that the cyclometalated alkynylgold(III) complexes can produce ${}^{1}O_{2}$ upon light excitation which could induce amine oxidation. Using the previous reaction as an example, we studied the photo-catalytic activities of Au^{III}@MOF composites in oxidizing secondary amines to imines.^[16] The photochemical reactions were carried out in acetonitrile. The reaction mixture was implemented taking Au^{III}@MOFs as photocatalysts under light irradiation ($\lambda > 300$ nm) with bubbling of oxygen gas. As a control, homogeneous Au^{III} solution was employed as catalyst.

Experimental results for the reaction with N-(tertbutyl)benzylamine as substrate showed as following: (i) free Au^{III} gave imine product with TONs of 453 while Au^{III}@MOF1 and Au^{III}@ZJU-28 exhibited TONs of 75 and 1548 respectively; (ii) the photo-reaction activity of free Au^{III} showed a dramatically decrease after 1 h and almost no product was observed after 5h, whereas Au^{III}@ZJU-28 exhibited high reactivity over 10 hours' catalysis (Figure 3b); (iii) the Au^{III}@MOFs catalyst could be reused by washing with acetonitrile several times and after ten cycles, the conversion using Au^{III}@ZJU-28 as catalyst maintained 43% (Figure 3c); (iv) control experiments using bare MOFs as catalyst exhibited few product (Figure 3b); (v) As affirmed by the ICP measurements, the content of gold in Au^{III}@MOFs after reaction was nearly the same as before reaction (see Table S1); (vi) As revealed by PXRD data (see Figure S7), both Au^{III}@MOF1 and Au^{III}@ZJU-28 are stable after the photocatalytic reactions. These results above reveal that the photo-catalytic activity of Au^{III}@MOF1 and Au^{III}@ZJU-28 is significant different which may root in the difference in host MOF structures. For oxidative reaction of N-isopropylbenzylamine. around 1443 TONs was achieved by Au^{III}@ZJU-28 within 10 hours' irradiation (Figure 4). In general, this catalytic reactivity is comparable to the reactivity of used N-(tert-butyl)benzylamine as substrate.







Figure 4. (a) Photo-catalytic oxidation of N-isopropylbenzylamine to imine; (b) Turn over number of the oxidation by Au^{III}, MOFs, and Au^{III}@MOFs; (c) substrate conversion in recycling stability experiments using the Au^{III}@ZJU-28 catalyst.

Selective oxidation of secondary amines to corresponding imines is a significant area in organic synthesis.^[17] The

FULL PAPER

Au^{III}@MOFs as catalysts in the photocatalysis depicted above show beneficial effects of encapsulating the Au^{III} complex into the pores of the MOFs. Based on the mechanism suggested for the Au^{III} system, Au^{III} used as the catalyst and O₂ acted as the oxidant along with the light irradiation.^[16a] ¹O₂ sensitized from the triplet state of Au^{III} is suggested to be a terminal oxidant in this reaction. Therefore, a similar mechanism is suggested for the Au^{III}@MOF system. The improvement of photocatalytic activity upon the formation of Au^{III}@MOF might be attributed to the enhanced stability and reduced non-radiative decay of the MOFs results in triplet excited state.

From the porous structure of ZJU-28, we could find that, every tetrahedral channel is surrounded by three planar triangular channels. The window size of the two channel is larger than the size of N-(tert-butyl)benzylamine and N-isopropylbenzylamine. As for MOF1, the large truncated octahedral cage is encircled by four small truncated tetrahedrons and the N-(tert- 5butyl) benzylamine or N-isopropylbenzylamine can't access the truncated tetrahedral cages. Therefore, the oxidation reactivity of MOF1 is largely restricted. The extended catalytic lifetime of ZJU-28 might result from the enhanced stability of Au^{III} in the pores of ZJU-28.

Similar photocatalytic reactivity among Au^{III}@MOFs and Au^{III} solution emerged in oxidize dibenzylamine (Figure 5) which has large size than N-(tert-butyl)benzylamine. Around 1122 TONs was achieved by Au^{III}@ZJU-28 within 10 hours' irradiation. with the oxidizina reaction Comparing of N-(tertbutyl)benzylamine, this catalytic reactivity decrease around 27%. However, for using Au^{III}@MOF1 as catalyst, the decrease in reactivity reached 41%. As for homogeneous catalysis, around 322 TONs of dibenzylemine was obtained by Au^{III}. Compared to N-(tert-butyl)benzylamine substrate, this reactivity is reduced 28% which is similar to that of Au^{III}@ZJU-28 system. The reaction with R-(+)-N-Benzyl-1-phenylethylamine as substrate showed that the TONs of the product catalyzed by free Au^{III}, Au^{III}@MOF1 and Au^{III}@ZJU-28 were 310, 36 and 876, respectively (Figure 6). When substrate was changed into N,Nbis (4-methoxybenzyl)amine, only 224 TONs was achieved by Au^{III}@ZJU-28 within 10 hours' reaction and around 261 TONs was obtained by Au^{III} (Table 2). It can be make a rough conjecture that with the raise of substrate size, the reactivity of heterogeneous catalyst becomes low, because of the larger size of the substrate was more difficult to enter the channel. The



Figure 5. (a) Photo-catalytic oxidation of dibenzylamine; (b) Turn over number of the oxidation by Au^{III}, MOFs, and Au^{III}@MOFs; (c) substrate conversion in recycling stability experiments using the Au^{III}@ZJU-28 catalyst.

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Figure 6. (a) Photo-catalytic oxidation of R-(+)-N-Benzyl-1-phenylethylamine; (b) Turn over number of the oxidation by Au^{III} , MOFs, and Au^{III} @MOFs; (c) substrate conversion in recycling stability experiments using the Au^{III} @ZJU-28 catalyst.

Table 2. Photo-catalytic oxidation of N,N-bis(4-methoxybenzyl)amine using Au^{III}, Au^{III}@MOF1 and Au^{III}@ZJU-28 as catalysts. ^[a]

MeO		Light -> 300 nm) O ₂ , MeCN	→ N MeO	OMe
Catalyst	Time(h)	TON	Conversion (%)	Yield (%)
Au ^{III}	10	261	48.7	46.5
Au ^{III} @MOF1	10	43	30.5	29.2
Au ^{III} @ZJU-28	10	224	89.0	87.5

[a] Control experiment using MOF1 and ZJU-28 as catalysts resulted in < 10% conversion (reaction time: 10 h).

substrates entered into channels difficultly, however, the bigger size Au(III) complexes can encapsulated into the channels are attributed to the followings: (i) Au^{III} occupied the channel made substrates hard to enter the channel; (ii) When the anionic MOFs were accommodating the guest species, besides the strict size selectivity, they also exhibited remarkable selectivity of charge characteristics. Au^{III} was easier to be incorporated into MOFs via ion-exchange method.



Figure 7. (a) Photo-catalytic oxidation of 1,2,3,4-Tetrahydroisoquinoline; (b) Turn over number and mole quantity of product within 10 hours' reation; (c) substrate conversion in recycling stability experiments using the $Au^{III}@ZJU-28$ and $Au^{III}@MOF1$ catalysts.

FULL PAPER

Au^{III}@MOFs can also catalyze the photoinduced oxidation of 1,2,3,4-tetrahydroisoquinoline. Homogeneous catalysis gave two kinds of products, isoquinoline and 3,4-dihydroisoquinoline with TONs of 200 and 2090, respectively (Figure 7b). For heterogeneous catalysis, Au^{III}@MOF1 and Au^{III}@ZJU-28 also exhibited the two types of products. Around 40 TONs of isoquinoline and 1059 TONs of 3,4-dihydroisoquinoline was achieved by Au^{III}@MOF1. The total yield of Au^{III}@ZJU-28 is 1.2-fold enhancement than Au^{III}@MOF1 and the mole ratio of isoquinoline and 3,4-dihydroisoquinoline is 1:15. Recycle experiment demonstrate the photoactivity of Au^{III}@MOF1 and Au^{III}@MOF1 and Au^{III}@IDF1 and Au^{III}@IDF1 and Field Au^{III}@IDF1 and Au^{II}@IDF1 and Au^{II}@IDF1 and Au^{II}@IDF1 and Au^{II}@IDF1 and Au^{II}@IDF1 and Au^{III}@IDF1 and Au^{III}@IDF1 and Au^{II}@I



Scheme 1. Size selective photocatalysis of S1 and S2.

The presented different reactivity above inspires us to study the selective photocatalysis of Au^{III}@MOF1 and Au^{III}@ZJU-28. The research using Au^{III}@MOF1 or Au^{III}@ZJU-28 as catalyst actualized by adding the same amount substrates of S1 (1,2,3,4tetrahydroisoquinoline) and S2 (a slightly larger size substrate, N-(tert-butyl)benzylamine) in a reaction (Scheme 1).^[1b, 1c] With Au^{III}@MOF1 as photocatalyst, oxidative product of S1 (P1) was detected after 1 hour's irradiation while only tiny amounts of product of S2 (P2) was detected, the P1/P2 yield ratio is around 38:1. These results illuminate that the selectivity towards the oxidation of S1 is almost 97.4%. However, when employing Au^{III}@ZJU-28 as catalyst, the yield ratio of P1/P2 is 1.9/1 (Scheme 1). Homogeneous Au^{III} solution exhibited non-selective, with the yield ratio is around 1:1 (Scheme 1). When choose S2 (N-(tert-butyl)benzylamine) and large size S3 (bis(2naphthalenylmethyl)amine) as substrates (Scheme 2), P2 was detected after 1 hour's irradiation with Au^{III}@ZJU-28 as photocatalyst while no product of S3 was detected. Therefore, the selectivity of Au^{III}@ZJU-28 towards oxidation of S2 is almost 100%. Given the low reactivity of Au^{III}@MOF1 in oxidizing S2 and large substrates, the selective photocatalysis of Au^{III}@MOF1 didn't carry out. Contrast to the heterogeneous catalyst, homogeneous Au^{III} solution could trigger the oxidation reaction of both S2 and S3 and the yield ratio is around 1.8 : 1 (Scheme 2) corresponding to a 64.3% selectivity to S2 oxidation. These results indicate that encapsulating active catalysis

species $\mathrm{Au}^{\mathrm{III}}$ in an appropriate pore of MOF could obtain the needed product.



Scheme 2. Size selective photocatalysis of S2 and S3.

Conclusions

In conclusion, the luminescent Au^{III} was encapsulated into two MOFs with different porous size and structure via cation exchange. Comparing with Au^{III} in solution, the resultant Au^{III}@MOFs composites, Au^{III}@MOF1 and Au^{III}@ZJU-28, display enhanced emission lifetimes and quantum yield in both aerobic and N₂ conditions. In addition, Au^{III}@MOFs are efficient, selective, and recyclable catalysts for light-induced aerobic amine oxidation. Au^{III}@MOF1 provide an equivalent oxidizing ability to homogeneous Au^{III} solution while Au^{III}@ZJU-28 present high reactivity in oxidizing secondary amines to corresponding imines with TONs of 876 - 1548 which is around 2.8 - 3.5 folds higher than that of homogenous Au^{III} complex. Different selectivity to oxidize mixture substrates is realized based on different host MOFs. Around 97.4% selectivity of oxidizing 1,2,3,4-tetrahydroisoquinoline is achieved by Au^{III}@MOF1 with the solution containing N-(tert-butyl)benzylamine simultaneously. Very low selectivity is obtained by Au^{III}@ZJU-28 and Au^{III} complex in solution under the same condition. For large sized substrates, N-(tert-butyl)benzylamine and bis(2naphthalenylmethyl)amine mixture, Au^{III}@ZJU-28 shows almost 100% selectivity of oxidizing N-(tert-butyl)benzylamine while homogeneous reaction only exhibits 64.3% selectivity. What's more, the composite catalyst also present advantage in recycling and a high conversion of Au^{III}@ZJU-28 catalyst is still observed after ten cycles. In conclusion, the facile method of incorporating the transition complexes with long-lived emissive excited state into MOF materials provides a way to develop novel category of useful heterogeneous photo-catalysts.

Experimental Section

Synthesis of Au^{III}@MOFs composites.

MOF1 (10 mg) and ZJU-28 were immersed in 2 mL of acetonitrile solutions containing 1×10^{-6} mol of Au^{III} complex, respectively. After shaking for 1 day, the sample were taken out of the solutions and washed with acetonitrile several times to

FULL PAPER

remove residual Au^{III} complex on the surface. The concentrations of Au^{III} complex in Au^{III}@MOF1 and Au^{III}@ZJU-28 composites were confirmed by ICP spectroscopy and shown in Table S1.

Photocatalytic activity of Au^{III}@MOFs.

Complex Au^{III} (2 × 10⁻⁷ mol), MOF1 (20 mg), Au^{III}@MOF1 (20 mg, 0.75 wt% Au^{III}), ZJU-28 (20 mg) or Au^{III}@ZJU-28 (20 mg, 0.42 wt% Au^{III}) was added into acetonitrile (1.6 mL) solution containing dibenzylamine (0.107 mmol). The mixture was bubbled with oxygen gas during the entire process of experiment and irradiated by a 300 W Xe-lamp (λ > 300 nm) at room temperature. After irradiated for 1 h, 0.4 μ L of the solution was taken out and injected into a gas chromatography (GC) with FID and a HP-FFAP column. The yield of organic products was calculated based on GC. The recycle of catalyst Au^{III}@MOF1 or Au^{III}@ZJU-28 was carried out by washing the catalyst several times with acetonitrile, and then fresh substrate (0.107 mmol) and acetonitrile (1.6 mL) was added in the test tube. For oxidative reaction of other substrates, the same experimental condition was employed, except replacing dibenzylamine with other amine. And for oxidative reaction using N,N-bis(4methoxybenzyl)amine as substrate, the product yield was confirmed by 1H NMR spectroscopy using 4,4' -dimethyl-2,2' bipyridine as internal standard.

Size selective catalysis.

The selective oxidation reaction was carried out using Au^{III} (1 × 10⁻⁶ mol), Au^{III}@ZJU-28 (10 mg, 0.42 wt% Au^{III}) or Au^{III}@MOF1(10 mg, 0.75 wt% Au^{III}) as catalysts and adding two kinds of substrates with equimolar quantity (0.053 mmol). The mixture was bubbled with oxygen gas and irradiated under 300 W Xenon lamp (λ > 300 nm) at room temperature for 1 h. The yield ratio was calculated based on GC and ¹H NMR spectroscopy.

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a) J. R. Long, O. M. Yaghi, *Chem. Soc. Rev.* 2009, *38*, 1213-1214; b) A. Corma, H. Garcia, F. Xamena, *Chem. Rev.* 2010, *110*, 4606-4655; c) H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* 2013, *341*, 1230444; d) J. P. Zhang, Y. B. Zhang, J. B. Lin, X. M. Chen, *Chem. Rev.* 2012, *112*, 1001; e) F. A. Paz, J. Klinowski, S. M. Vilela, J. P. Tomé, J. A. Cavaleiro, J. Rocha, *Chem. Soc. Rev.* 2012, *41*, 1088; f) H. C. Zhou, J. R. Long, O. M. Yaghi, *Chem. Rev.* 2012, *112*, 673; g) D. Farrusseng, S. Aguado, C. Pinel, *Angew. Chem., Int. Ed.* 2009, *48*, 7502-7513; h) M. C. Das, S. Xiang, Z. Zhang, B. Chen, *Angew. Chem., Int. Ed.* 2011, *50*, 10510-10520; i) C. Xu, H. Liu, D. Li, J. H. Su, H. L. Jiang, *Chem. Sci.* 2018, *9*, 3152-3158.

- a) Y. Cui, Y. Yue, G. Qian, B. Chen, *Chem.Rev.* 2012, *112*, 1126; b) Q.
 Yang, Q. Xu, H. L. Jiang, *Chem. Soc. Rev.* 2017, *46*, 4774-4808; c) L.
 Li, Q. Yang, S. Chen, X. Hou, B. Liu, J. Lu, H.-L. Jiang, *Chem. Commun.* 2017, *53*, 10026-10029; d) J. Zhao, Q. Wang, C. Sun, T.
 Zheng, L. Yan, M. Li, K. Shao, X. Wang, Z. Su, *J. Mater. Chem. A* 2017, *5*, 12498-12505.
- [3] T. Sawano, Z. Lin, D. Boures, B. An, C. Wang, W. Lin, J. Am. Chem. Soc. 2016, 138, 9783-9786.
- [4] H. Liu, C. Xu, D. Li, H. L. Jiang, Angew. Chem. Int. Ed. 2018, 57, 5379-5383.
- [5] C.-Y. Sun, W.-P. To, X.-L. Wang, K.-T. Chan, Z.-M. Su, C.-M. Che, *Chem. Sci.* 2015, 6, 7105-7111.
- [6] a) O. K. Farha, A. Ö. Yazaydın, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr, J. T. Hupp, *Nat. Chem.* 2010, 2, 944-948; b) J. R. Li, H. C. Zhou, H. C. Zhou, *Nat. Chem.* 2010, 2, 893-898; c) X. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw, M. J. Rosseinsky, *Science* 2004, *306*, 1012-1015.
- a) H. Wu, Q. Gong, D. H. Olson, J. Li, *Chem. Rev.* 2012, *112*, 836-868;
 b) Z. Jin, H. Y. Zhao, X. J. Zhao, Q. R. Fang, J. R. Long, G. S. Zhu, *Chem. Commun.* 2010, *46*, 8612-8614.
- [8] a) Y. Liu, K. Vch, R. Larsen, M. Eddaoudi, *Chem. Commun.* 2006, 14, 1488-1490; b) H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gandara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O'Keeffe, O. Terasaki, J. F. Stoddart, O. M. Yaghi, *Science* 2012, 336, 1018-1023; c) G. Férey, C. Mellotdraznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* 2005, 309, 2040-2042; d) X. Zhao, X. Bu, T. Wu, S. T. Zheng, L. Wang, P. Feng, *Nat. Commun.* 2013, 4, 2344.
- [9] a) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* 2007, 107, 174-238; b) L. Murphy, J. A. G. Williams, *Top. Organomet. Chem.* 2010, 28, 75-111; c) J. Kalinowski, V. Fattori, M. Cocchi, J. A. G. Williams, *Coordin. Chem. Rev.* 2011, 255, 2401-2425; d) J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.* 2011, 40, 102-113; e) C. Y. Sun, W. P. To, F. F. Hung, X. L. Wang, Z. M. Su, C. M. Che, *Chem. Sci.* 2018, 9, 2357-2364.
- [10] a) C. Y. Sun, X. L. Wang, X. Zhang, C. Qin, P. Li, Z. M. Su, D. X. Zhu, G. G. Shan, K. Z. Shao, H. Wu, J. Li, *Nat. Commun.* **2013**, *4*, 2717-2024; b) Y.-Q. Lan, H.-L. Jiang, S.-L. Li, Q. Xu, *Adv. Mater.* **2011**, *23*, 5015-5020; c) D. T. Genna, A. G. Wong-Foy, A. J. Matzger, M. S. Sanford, *J. Am. Chem. Soc.* **2013**, *135*, 10586-10589.
- [11] J. J. Yan, A. L. Chow, C. H. Leung, R. W. Sun, D. L. Ma, C. M. Che, *Chem. Commun.* 2010, 46, 3893-3895.
- [12] J. Muzart, Tetrahedron 2009, 65, 8313-8323.
- [13] J. Yu, Y. Cui, C. Wu, Y. Yang, Z. Wang, M. O'Keeffe, B. Chen, G. Qian, Angew. Chem., Int. Ed. 2012, 51, 10542-10545.
- [14] V. K. Au, K. M. Wong, N. Zhu, V. W. Yam, J. Am. Chem. Soc. 2009, 131, 9076-9085.
- [15] a) P. Duan, N. Yanai, N. Kimizuka, J. Am. Chem. Soc. 2013, 135, 19056-19059; b) J.-H. Kim, F. Deng, F. N. Castellano, J.-H. Kim, Chem. Mater. 2012, 24, 2250-2252.
- [16] a) W. P. To, G. S. Tong, W. Lu, C. Ma, J. Liu, A. L. Chow, C. M. Che, Angew. Chem., Int. Ed. 2012, 51, 2654-2657; b) W. P. To, K. T. Chan, G. S. Tong, C. Ma, W. M. Kwok, X. Guan, K. H. Low, C. M. Che, Angew. Chem., Int. Ed. 2013, 52, 6648-6652; c) Q. Xue, J. Xie, H. Jin, Y. Cheng, C. Zhu, Org. Biomol. Chem. 2013, 11, 1606-1609; d) T. N. Zehnder, O. Blacque, K. Venkatesan, Dalton Trans. 2014, 43, 11959-11972.
- [17] a) K. Yamaguchi, N. Mizuno, Angew. Chem. Int. Ed. 2003, 42, 1480-1483; b) M. H. So, Y. Liu, C. M. Ho, C. M. Che, Chem. Asian. J. 2009, 4, 1551-1561; c) T. Naota, H. Takaya, S. I. Murahashi, Chem. Rev. 1998, 98, 2599-2660; d) A. G. Condie, J. C. González-Gómez, C. R. J. Stephenson, J. Am. Chem. Soc. 2010, 132, 1464-1465; e) L. Z, C. J. Li, J. Am. Chem. Soc. 2005, 127, 3672-3673; f) G. Jiang, J. Chen, J. S. Huang, C. M. Che, Org. Lett. 2009, 11, 4568-4571.

Entry for the Table of Contents

FULL PAPER

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Luminescent Au^{III} complex with longlived emissive excited state was encapsulated into MOFs and enhanced reactivity and selectivity were achieved when employing Au^{III}@MOFs as heterogeneous photocatalysts in amine oxidation reaction.



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Page No. – Page No.

Metal-Organic Frameworks with Organogold(III) Complexes for Photocatalytic Amine Oxidation with Enhanced Efficiency and Selectivity