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ARTICLE TYPE

Highly stable photoresponsive complex framework formation involves unusual selective hydrogenation of a pyridine derivative

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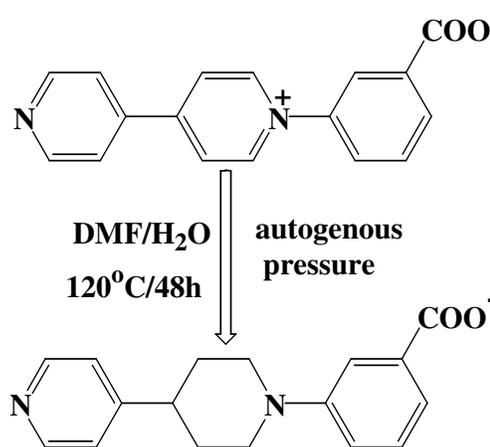
A unique hydrothermal selective hydrogenation process is carried out effectively in a simple and friendly way without adding any precious metal catalysts and hydrogen gas from outside. The self assembly of the hydrogenated product 3-(4-(pyridin-4-yl) piperidin-1-yl) benzoate (PYPDB) with the zinc ion produces a highly stable photoactive complex Zn(PYPDB)₂ displaying interesting long range electron transfer behavior in the conjugated ring system.

Metal-Organic Frameworks (MOF) are a class of complexes constructed by metal ions and organic bridging ligands through metal-ligand coordination bonds.¹ The structures together with the degree of variability for both the inorganic and organic components determine the characteristic properties of these species complexes.² Over the past decade, numerous functional MOF complexes, such as magnetic, nonlinear optical, microporous, hydrogen storage, and florescent materials, are built via careful selection of the connected blocks and structural control.³ The combination of building units provides endless possibilities to modify the characters of extended macromolecular networks. Recently, the synthesis strategy has also been used to construct new photoactive framework materials.⁴ Nowadays, organic photoresponsive materials are of special interest for their applications in solar energy technologies, optical computers, low-cost memory and display devices.⁵ However, their applicabilities are limited largely by the intrinsic thermal unstable characters of organic compounds. Light radiation exposure accompanied with the increase of surface temperature can typically induce thermal damage to a photoactive device. Comparing to traditional pure organic molecular systems, the merits of MOF complexes are not only in their highly thermal stabilities but also in their photoactive characters that can be easily perturbed and tuned by the connection of different metal centers and ligands.⁶ Porous and interpenetrating arranging modes are two common structural phenomena in molecular assemblies.⁷ In contrast with the topical research towards using porous channels in separation,⁸ less attention has been paid to the utilization of interpenetrating frameworks.⁹ The coordination networks in interpenetrating structures usually display high stability for their close space-filling packing modes of building units. Recognizing the potential of complex approach, we have embarked on a program aimed at utilization of suitable metal-ligand coordination to improve the thermal stability of the photoresponsive materials. Herein, we report an interesting example of highly stable photosensitive

complex framework with three-fold parallel interpenetrating architecture, Zn(PYPDB)₂ (**1** (PYPDB = 3-(4-(pyridin-4-yl) piperidin-1-yl) benzoate), of which its robust structure can be stabled up to 370 °C confirmed by TG and PXRD data. It contains a novel MOF based photoinduced electron transfer system exhibiting long-lived, long-distance charge separation behaviors. More interestingly, a unique selective hydrogenation of the pyridine ring is also first observed during the preparation of compound **1**.

Yellow crystals of compound **1** are obtained by a hydrothermal reaction of Zn(NO₃)₂·6H₂O, *N*-(3-carboxyphenyl)-4,4'-bipyridinium chloride, 2-aminoterephthalic acid, DMF, and water with a molar ratio of 1: 0.2: 0.4: 65: 277 at 120°C for 48h. It is interesting to observe that the *N*-(3-carboxyphenyl)-4,4'-bipyridinium chloride molecule is selectively hydrogenated to give a 3-(4-(pyridin-4-yl) piperidin-1-yl) benzoate ligand under a mild hydrothermal reaction condition (Scheme 1).

Analysis of ¹HNMR data shows that nine hydrogen atoms have been added selectively to one pyridine ring of the *N*-(3-carboxyphenyl)-4,4'-bipyridinium molecule (Fig. S1, see ESI[†]). As we known, hydrogenation reaction plays an important role in organic synthesis and industrial process.¹⁰ The traditional approaches for the hydrogenation of pyridine species are usually required working on the palladium supported catalyst, and need the hydrogen gas as reactant.¹¹ However, present case gives a successful approach that hydrogenation does not need to work in



Scheme. 1 The selective hydrogenation reaction.

the condition of any precious metal catalysts. The central ring has been hydrogenated with DMF and water as the hydride source. Labeling experiments indicate that two hydrogen atoms coming from the DMF molecule are added to the carbon atoms (C8, C10) next to the N2 atom (Fig. S2, see ESI[†]). The other seven hydrogen atoms for addition come from water solvent. The four original hydrogen atoms of the central ring are removed among the reductive process. The solvothermal in situ ligand reactions is very useful in the one-pot synthesis of some unusual organic molecules.¹² To our best knowledge, this is the first example to demonstrate that the pyridine ring can be converted to the piperidine ring at a simple and environment friendly way without the use of any precious metals as catalysts. A proposed hydrogenation mechanism is depicted for this reaction based on the experimental data (Fig. S3, see ESI[†]).

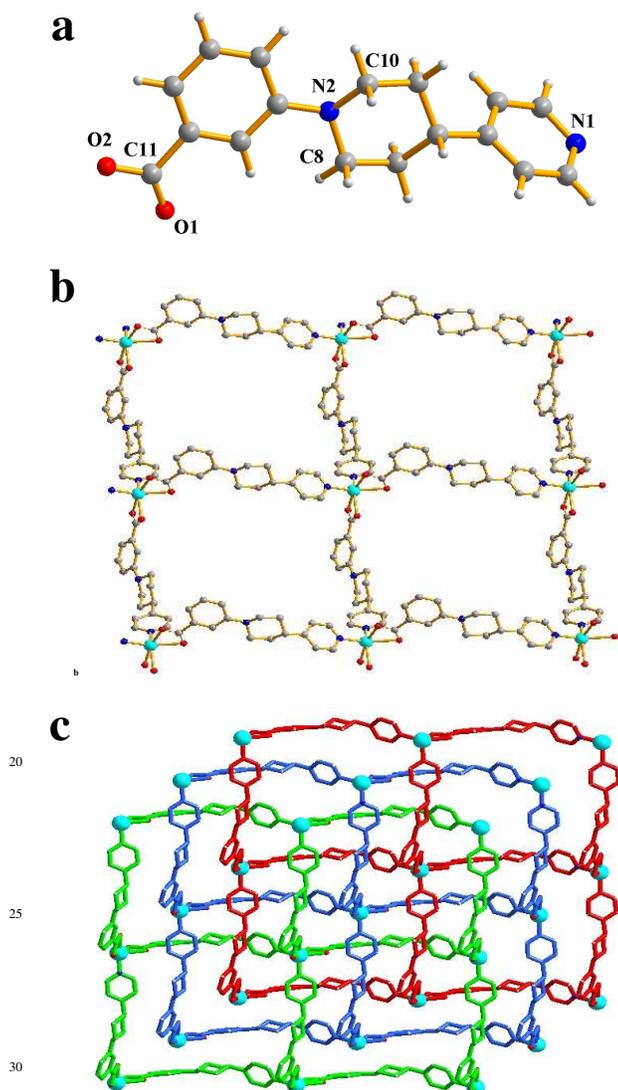


Fig. 1 a) Structure of the 3-(4-(pyridin-4-yl) piperidin-1-yl) benzoate ligand in compound **1**; b) view of the 2D layer framework linked together via the PYPDB ligands; c) view of the crystal packing down the *b* axis and the interpenetration model for complex **1**.

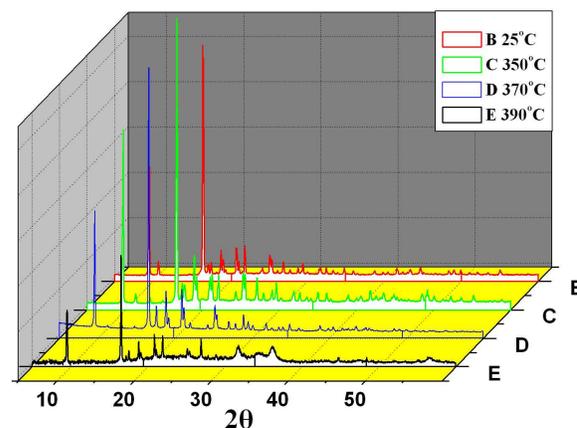


Fig. 2 Powder XRD patterns calcined at different temperatures.

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Single crystal data of **1** further confirm the formation of 3-(4-(pyridin-4-yl) piperidin-1-yl) benzoate (PYPDB) molecule, a new linear bridging ligand (Fig. 1a). Its middle piperidine ring adopts a typical chair conformation. Two carboxylate oxygen atoms and one nitrogen atom of the pyridine ring are coordinated to the octahedral zinc metal center. The linkages of them result in a square grid (4, 4) network (Fig. 1b). In the crystal packing, the 2D layer is interwoven with its neighbors. The independent equivalent networks are three-fold parallel interpenetrated within the structure. Each window of one sheet is filled by two adjacent parallel identical motifs (Fig. 1c). With this packing mode, the repeat arrangements result in a 3D array constructed by an infinite catenane of 2D architecture. The absence of any guests within the network prevents the possibility of structural collapse caused by the removal of small solvent molecules.

PXRD and TG data indicate that compound **1** is thermal robust. Fig. 2 shows the comparison of PXRD patterns of **1** obtained at different temperatures. The good agreement of the peaks in the patterns demonstrates that the crystalline phase and framework is stable up to 370 °C. A decrease in crystallinity is observed at 390 °C. The TG curve of **1** shows no change in weight up to 425 °C (Fig. S4, see ESI[†]), indicating the framework decomposition occurred at higher temperature (> 425 °C). Apparently, this is obvious better than that of the pure organic photosensitive materials. To our best knowledge, present compound **1** is the highest stable photosensitive metal-ligand framework so far.¹³

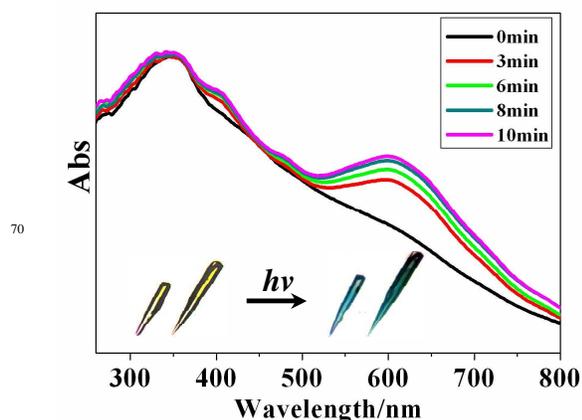


Fig. 3 UV-vis spectral changes of **1** upon photoirradiation.

Compound **1** shows an interesting photosensitive character. Its crystal color can be turned from yellow to blue under the UV-visible irradiation. The UV-vis spectrum (Fig. 3) give the difference between two colors of crystals that can be recognized in the absorption bands around 340 nm in the UV region for the either versus a new around 600 nm in the visible region for the blue only. The former may be assigned to the π - π^* and n - π^* charge-transfer transitions of the aromatic rings while the latter can be attributed to the generation of radicals that has also been confirmed by ESR spectra (Fig. S5, see ESI[†]). Moreover, the absorption intensity at 600 nm appears to be a clearly proportion to the irradiation time (Fig. 3). ESR measurement for the blue crystal gives a value of $g = 2.0024$, that is comparable to those free radicals in the previous reports,¹⁴ showing the generation of radicals during the photocoloration process. The spin density of the blue powdered sample is 1.29×10^{20} spins/mol (with 1, 1-diphenyl-2-picrylhydrazyl as reference).

Single crystal and XPS data before and after photoirradiation are collected to investigate structural characters of the hydrogenated piperidinium ring and mechanism of photoinduced color change in the metal-piperidinium-based molecular system (Fig. S6 and S7, see ESI[†]). The result of bond length analysis indicates that the N2 atom shares electrons with the adjacent 3-carboxyphenyl ring (N2-C11 = 1.402(5) Å), involving the formation of a p - π conjugation system for electron transfer. After light irradiation, there are structural variations occurred around the metal center. The largest change is the Zn1—O1 connection, which bond is shorted by ~ 0.03 Å, by comparison with all the bond lengths of the independent structural units. The XPS test is selective analysis on only the topmost surface where the photochemical process is prominent in the solid state. After light irradiation, the shifts to the higher binding energy in N1s and O1s core-level spectra suggest the N and O atoms involving in electron transfer as electron donor. In the Zn2p core-level spectra, the overall signal of Zn2p shifts to the lower binding energy after irradiation indicating that the Zn atom is the electron acceptor. All these above data suggest that the photoactive process of **1** is a typical long range electron transfer in the donor-bridge-acceptor complex as depicted in Fig. S8 (see ESI[†]).¹⁵ The conjugated organic components of the macromolecule act as the intervening bridge for electron transport. The development of solar energy conversion devices and molecule-based electronics inspire the design of donor-bridge-acceptor molecular systems.¹⁶ An important model for designing the functional systems is to achieve efficient, long-lived, long-distance charge separation.¹⁷ In this paper, we show for the first time that novel donor-bridge-acceptor complex with long-distance charge separation character can also be built based on the MOF framework via molecular design and supramolecular assembly.

In conclusion, a novel, practical, and efficient synthesis of N-substituted piperidine derivative has been achieved at mild hydrothermal condition. This process is distinguished by the fact that the hydrogenation is carried out in a simple and environmentally friendly way without the use of any precious metals as catalysts and hydrogen gas as reductant. The self assembly of the in-situ generated ligand 3-(4-(pyridin-4-yl)piperidin-1-yl) benzoate with the zinc ion creates a new sample of

photosensation metal-ligand system with N-substituted piperidinium as photoactive moiety. This new photoresponsive system based on interpenetrating coordination networks displays interesting long range electron transfer behavior and highly thermal stability. This work represents a new hydrogenation reaction and a route to stabilize organic photoactive components.

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Notes and references

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[†]Electronic Supplementary Information (ESI) available: Details of synthesis and general characterizations, crystal data, NMR data, additional figure, XPS spectra, ESR spectrum, TGA and IR data. See DOI: 10.1039/b000000x/

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