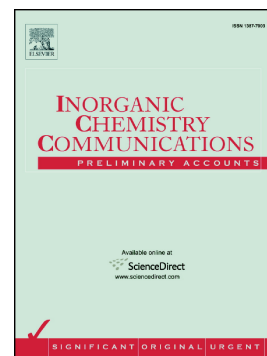


## Accepted Manuscript

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PII: S1387-7003(18)30635-X  
DOI: doi:[10.1016/j.inoche.2018.08.006](https://doi.org/10.1016/j.inoche.2018.08.006)  
Reference: INOCHE 7072  
To appear in: *Inorganic Chemistry Communications*  
Received date: 8 July 2018  
Revised date: 2 August 2018  
Accepted date: 3 August 2018

Please cite this article as: Ya-Nan Sun, Li Li, Chen Fu, Hai-Yu Wang, Hong Zhang , Two cases of bipyridinium-based metal-organic frameworks: Syntheses, structures, photochromic behaviors. *Inoche* (2018), doi:[10.1016/j.inoche.2018.08.006](https://doi.org/10.1016/j.inoche.2018.08.006)

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## Two cases of bipyridinium-based metal-organic frameworks :syntheses,structures, photochromic behaviors

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**Abstract:** Two novel bipyridinium-based metal-organic frameworks  $Zn[(pbpy)_{0.5}(m-BDC)Cl] \cdot 1.5H_2O(1)$  and  $Cd[(pbpy)_{0.5}(m-BDC)Cl] \cdot H_2O(2)$ . ( $pbpyCl_2=1,1'$ -[1,4-phenylenebis-(methylene)]bis(4,4'-bipyridinium)-dichloride) have been synthesized and structurally characterized by single crystal X-ray crystallography. Both of them show 2D layered window structures. When they are irradiated by 300 W Xenon lamp, both of them exhibit photochromic behaviors which are attributed to the process of intermolecular electron transfer to generate  $pbpyCl_2$  free radicals. These processes have been demonstrated by UV-Vis absorption characterization analysis, electron spin resonance (ESR). The photoproduct of compound 1 is more stable than compound 2 in air. Photochromic mechanisms and the relationships between structures and properties have been discussed adequately.

**Keywords:** Zinc(II) complex, Cadmium(II) complex, Crystal structure, Photochromism, Decolorization.

photochromism is a reversible color change between two states of chemical substances induced by light irradiation[1]. photochromic materials can be used in inkless and erasable printing[2], colorimetric detection[3], optical memory storage device[4], and so on. there are many pure organic photochromic materials, such as schiff base, azobenzene, diarylethene and so on[5], the complicated procedures of organic syntheses, the poor thermal stabilities of photoproducts make their applications limited, however, inorganic components can overcome these disadvantages. When combining with each other, their properties can be preserved, and even be able to produce more excellent characteristics. About how to design and assemble these organic-inorganic hybrid photochromic materials at molecular level in order to improve their photochromic behaviors is still the issue that material scientists focused on. MOFs have been recognized as a promising class of switchable materials[6], when they are stimulated, a MOF conformation can turn to another conformation by phase transition[7], redox reaction[8], and so on, thus result in reversible transformations of their physical properties[9]. This inspires us to explore the syntheses of photochromic MOF materials. The basic synthetic strategy in the construction of photochromic MOF materials is to introduce photoinduced bistable systems based on electron-transfer mechanism, which is seen as donor-acceptor-type photochromic materials[10]. There are five organic compounds are generally selected as electron acceptors,  $N,N'$ -disubstituted-4,4'-bipyridiniums (viologens),  $N,N'$ -disubstituted-1,4,5,8-naphthalene diimide (NDIs), tris(4-pyridiniumyl)-1,3,5-triazine, 4,4'-Bis(1-imidazolyl)biphenyl, 3,5-Bis(pyridine-2-yl)-1,2,4-triazole[11]. Among them, mono- or bis-substituted 4,4'-bipyridiniums (viologens) derivatives possess excellent electron-accepting abilities, therefore, they are widely used in the construction of crystalline photochromic materials. In the past few years, viologen-based crystalline photochromic materials have been from single metachromatism developing into multifunctional materials, such as using a photoactive asymmetric viologen-based ligand to obtain a bulk with intrinsic photoswitchable second-order NLO characteristic material[12], detecting ammonia vapours accompanied by sensitive fluorescent response[13], serving as a fluorescence probe to detect  $CrO_4^{2-}$  and  $Cr_2O_7^{2-}$  anions selectively[14], adsorbing  $H_2O$ ,  $CO_2$ , and  $NH_3$  utilizing its properties of porous coordination polymers[15], and so on. These viologen-based photochromic materials are moving to more practical value directions, so, the

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