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A bismuth-based fluorous metal-organic framework for efficient degradation of Congo red

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ABSTRACT

A new bismuth-based fluorous metal-organic framework, $[Bi(OOCC_6F_5)_3(C_{10}H_8N_2)(H_2O)_2]$, ($OOCC_6F_5$ = pentafluorobenzoate, $C_{10}H_8N_2$ = 2,2′-bipyridine)(1) is synthesized by a hydrothermal method. Compound 1 crystalizes in the $P2_1/c$ space group, exhibiting a two-dimensional supramolecular architecture by intermolecular C—H···F—C interactions between the hydrogen atoms in 2,2′-bipyridine and fluorine atoms in adjacent perfluorophenyl rings. In addition, compound 1 shows excellent properties of degradation Congo red in the absence of UV–vis radiation. Moreover, adsorption kinetics study suggested that the adsorption of Congo red belongs to first-order reaction kinetics. Our results indicated that bismuth-based FMOFs could be promising candidates for the development of efficient degradation of organic dye.

1. Introduction

Efficient removal of organic pollutants from wastewater has become a hot research topic due to its ecological and environmental importance. As one of the main pollutants in wastewater, organic dyes, not only reduce the water quality, but also significantly impact the health of human beings because they are toxic, mutagenic, and carcinogenic. A variety of efforts have been made to develop photocatalysts that work efficiently in the visible light [1–3]. In the research areas related to photocatslysts, the removal of hazardous compounds using metal-organic frameworks (MOFs) as adsorbent materials has been widely expanded [4–7]. Although photocatalytic degradation of organic dyes with MOFs would be one of the unique features of MOFs, co-relation between the efficiency and the porosity of MOFs has not been well discussed as compared with their other properties such as gas storage and separation, sensing, and drug delivery [8,9]. In this paper we report that a Bi-FMOF constructed with $[Bi(OOCC_6F_5)_3(C_{10}H_8N_2)(H_2O)_2]$, ($OOCC_6F_5$ = pentafluorobenzoate, $C_{10}H_8N_2$ = 2,2′-bipyridine) has high degradation properties for Congo red.

Despite the excellent catalytic properties of bismuth based MOFs reported so far, still studies on Bi-MOFs are rather limited [10,11]. Here, a novel bismuth-based FMOF, namely $[Bi(OOCC_6F_5)_3(C_{10}H_8N_2)(H_2O)_2]$, ($OOCC_6F_5$ = pentafluorobenzoate, $C_{10}H_8N_2$ = 2,2′-bipyridine) (1) was synthesized and its structure was determined by X-ray crystallographic analysis. To the best of our knowledge, it is the first example in which Bi^{3+} and pentafluorobenzoic acid were introduced to construct a FMOF and 2,2′-bipyridine was brought as secondary N-donor ligand.

2. Results and discussion

The new Bi-FMOF has been prepared by the combination of $Bi(NO_3)_3{\cdot}5H_2O$, pentafluorobenzoic acid and 2,2′-bipyridine ligand at 1:3:1 under suitable reaction conditions, affording pink crystals (see Section 4.2 the synthesis). Single crystal X-ray diffraction analysis reveals that compound 1 crystallizes in $P2_1/c$ space group, and contains one Bi^{3+} cation, three pentafluorobenzoate anoins, one 2,2′-bipyridine ligand and one water molecule (Fig. 1).

2.1. Crystal structure

Crystal structure analysis proved that the compound 1 belongs to the monoclinic, $P2_1/c$ space group with one molecule containing of one bismuth cation, three pentafluorobenzoate groups acting as bidentate μ–K^2O:O′ ligands, one 2,2′-bipyridine ligand and one lattice water. The bismuth center is nine-coordinated to two nitrogen atoms from 2,2′-bipyridine ligand with Bi-N distances of 2.475 Å and 2.425 Å, six oxygen atoms from three undependent

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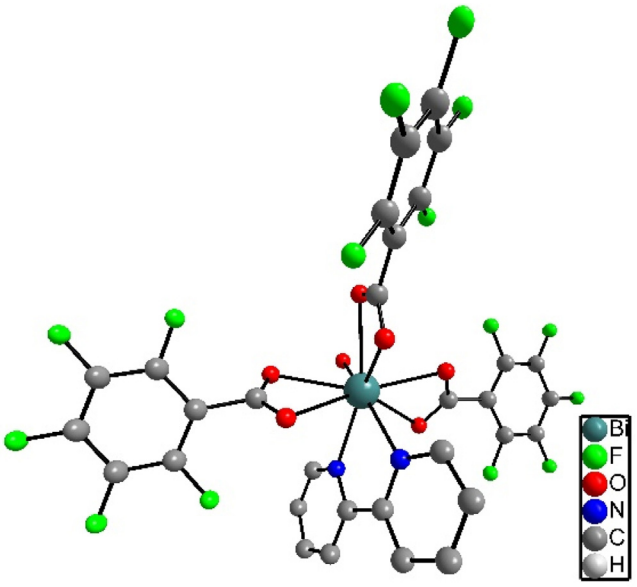

Fig. 1. Molecular structure of **1** (one solvent water molecule and all hydrogen atoms have been omitted for clarity).

pentafluorobenzoate groups with average Bi-O distance of 2.562 Å, and one oxygen atom from lattice water with the Bi—O distance of 2.578 Å. The selected bond lengths and angles are listed in Table 1, and data collection and refinement parameters are summarized in Table 2.

In the crystal structure of compound 1, a two-dimensional supramolecular architecture is formed by intermolecular C—H···F—C interactions (as shown by the orange dashed lines in Fig. 2). The C—H···F—C interactions happened between the hydrogen atoms in 2,2′-bipyridine rings and fluorine atoms in adjacent perfluorophenyl rings, where the H···F distances are 2.605 Å and 2.598 Å, and the corresponding C—H···F angles are 125.785° and 121.648° respectively, belonging to the strong intermolecular C—H···F—C interactions. For fluoroaromatic compounds, C—H···F—C interactions [12–15], although weak, contribute significantly to regulating the arrangement of organic molecules in the crystalline state and to stabilizing the secondary structure. The sum of the van der Waals radii of fluorine and hydrogen is about 2.67 Å. Consequently, the H···F distance up to 2.9 Å is considered as a C—H···F—C interactions.

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

Empirical formula	$C_{31}H_8BiF_{15}N_2O_8$
Formula weight	1030.37
Crystal color	pink
Crystal size (mm)	0.10 x 0.08 x 0.08
Crystal system	Monoclinic
space group	P2(1)/c
a (Å)	15.0574(7)
b (Å)	10.7187(5)
c (Å)	23.9801(9)
α (deg)	90
β (deg)	122.783(2)
γ (deg)	90
Volume (Å^3)	3253.9(2)
Z	4
d_{calcd} (g/cm^3)	2.103
μ (mm^{-1})	5.561
F (000)	1960
λ (Å)	0.71073
Temperature	293(2) K
θ range (deg)	1.61 to 25.00
h,k, l range	−9<=h<=17 −12<=k<=12 −28<=l<=18
Reflections collected / unique	15946 / 5720 [R(int) = 0.0271]
Completeness to θ	99.9 % (θ = 25.00)
Max. and min. transmission	0.847and 0.812
Data / restraints / parameters	5720 / 0 / 509
Goodness-of-fit on F^2	1.012
Final R indices [I>2σ(I)][a]	R_1 = 0.0234 wR_2 = 0.0479
R indices (all data)	R_1 = 0.0347 wR_2 = 0.0511
Largest diff. Peak and hole(e Å^{-3})	0.874 and −0.523

[a] $R_1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$; $wR_2 = [\Sigma w(Fo^2-Fc^2)^2/\Sigma wFo^4]^{1/2}$.

2.2. Degradation of Congo red experiments

To characterize the catalytic activities of the sample, measurements on degradation of Congo red (CR) chosen as a model pollutant to evaluate the adsorption capacity of the FMOFs were carried out at room temperature in the absence of UV–vis radiation. Fig. 3 presenting the structure of Congo red, CR was used as the dye model as it is one of the well-known azo dyes that are highly toxic and even carcinogenic to animals and human and are not readily degraded [16].

Table 1
Selected bond lengths (Å) and angles (°).

Bi(1)-N(1)	2.425(3)
Bi(1)-O(4)	2.443(3)
Bi(1)-N(2)	2.475(3)
Bi(1)-O(2)	2.488(3)
Bi(1)-O(5)	2.527(3)
Bi(1)-O(1S)	2.578(3)
Bi(1)-O(1)	2.624(3)
Bi(1)-O(6)	2.630(3)
Bi(1)-O(3)	2.664(3)
N(1)-Bi(1)-N(2)	66.79(10)
O(2)-Bi(1)-O(1)	50.67(9)
O(4)-Bi(1)-O(3)	50.61(10)
O(5)-Bi(1)-O(6)	50.38(9)

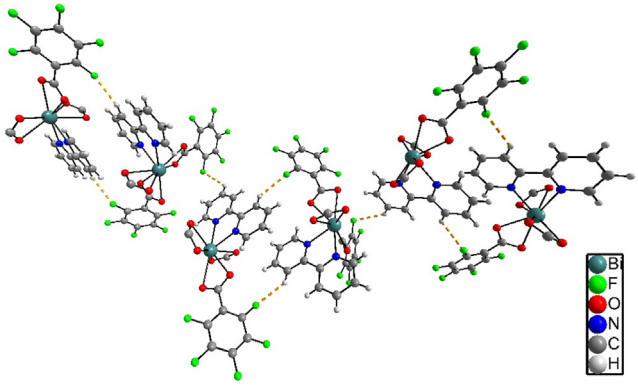

Fig. 2. Crystal structure of compound 1.