

Article



A Three-Component Hybrid Templated by Asymmetric Viologen Exhibiting Visible-Light-Driven Photocatalytic Degradation on Dye Pollutant in Maritime Accident Seawater

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Abstract: The increasing dangerous chemical pollutants led by shipping accidents call for the new pollutant treatment strategy. In this work, a new three-component hybrid $\{[(BiI_6)I_{13}] \cdot 2I_3 \cdot (H-BPA)_4\}_n$ (1) can be used in dye degradation in seawater. The highly interesting feature of **1** lies in its unique 1-D Z-shape $[(BiI_6)I_{13}]_n^{6-}$ infinite chain constructed from the I···I contacts between mono-nuclear $(BiI_6)^{3-}$ anions and I_{13}^{3-} polyiodide anions. Finally, the hydrogen bonds between $[(BiI_6)I_{13}]_n^{6-}$ polyanions and H-BPA²⁺ cations contribute to the formation a quasi-3-D network. Specifically, **1** exhibits the wide absorption zone from ultraviolet to visible regions and high charge-separation efficiency, hinting its application in visible-light catalysis. As expected, **1** represents photocatalytic activity for the degradation of rhodamine B in seawater with degradation ratio of 90%, and the photocatalytic performance is stable. This work might provide new photocatalytic material for pollutant treatment in shipping accidents.

Keywords: organic–inorganic hybrid; iodobismuthate; asymmetric viologen; photocatalytic degradation; photocurrent response

1. Introduction

With the rapid development of the global economy, dangerous chemicals have become an important part in sea transportation, which increases sea safety uncertainty because of shipping accidents [1]. In the last decade, the increasing dangerous chemical pollutants led by shipping accidents call for the new pollutant treatment strategy. Among the dangerous chemicals, organic dyes such as rhodamine types are the most commonly observed, which have been extensively used in printing, biological staining, textiles, etc. [2]. This kind of pollutant possesses chronic toxicity not only to humans but also to animals and aquatic life, which are hard to be degraded [3]. Thus far, various treatment technologies on dye pollutants in wastewater have been executed, including biological, physical, and chemical methods [4,5]. As a green technology, photocatalysis method is popular in the complete mineralization of organic dyes in wastewater. Researchers have already developed numerous photocatalysts, including the traditional TiO₂ semiconductor materials [6], nano particles (ZnO, CdS, PbMoO₄) [7,8], g-C₃N₄ or its composites [9], and inorganic/organic hybrids [10,11]. Among these photocatalysts, inorganic/organic hybrids are good photocatalysts because they are stable, efficient, and band-gap tunable [12,13], which can be achieved by the structural modification on their inorganic/organic moieties or their interactions. The Pb-based hybrids have demonstrated their photocatalysis activities on organic dyes, which stem from the synergism of all moieties [13,14]. Iodobismuthate-based photocatalysts such as BiOI have also illustrated the visible light activities for removal of methylene blue [15–18]. However, most of the degradation reactions were applied in



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). fresh water, and the studies about the removal of dye pollutants in seawater are still in its infancy, because the Na⁺, Mg²⁺, and Ca²⁺ ions in seawater will affect the degradation efficiency [19–21]. In this work, a three-component hybrid containing iodobismuthate $(BiI_6)^{3-}$ anion, polyiodides $(I_3^- \text{ and } I_{13}^{3-})$, and asymmetric viologen cation (protonized 4,4'-bipyridinium-N-pentanoic acid, (H-BPA)²⁺), i.e., {[(BiI_6)I_{13}]·2I_3·(H-BPA)_4}_n (1) was used as photocatalyst to degrade RhB in seawater, because all components are photoactive [14]. Interestingly, efficient photocatalytic degradation performances on RhB have been observed and the mechanism was discussed.

2. Results and Discussion

2.1. Structure Description

The hybrid 1 crystallizes in monoclinic space group $P2_1/c$, which is composed of a 1-D Z-shape $[(BiI_6)I_{13}]_n^{6-}$ infinite chain constructed from the I…I contacts between mono-nuclear $(BiI_6)^{3-}$ anion, the I_{13}^{3-} polyiodide anion, two I_3 ions, and one and four protonized 4,4'-bipyridinium-N-pentanoic acid (H-BPA²⁺). Hydrogen bonds between $[(BiI_6)I_{13}]_n^{6-}$ polyanions and H-BPA²⁺ cations contribute to the formation a 3-D network. The $(BiI_6)^{3-}$ anion is commonly observed in halobismuthate system [22], which is an ideal octahedron with nearly identical equator Bi-I length and linear axial I-Bi-I angle (Figure 1a, Table 1). Polyiodides display a very rich structural chemistry ranging from I_2^- to I_{29}^{3-} , whose orientation, aggregation, and dimensionality can be controlled by the counteractions [23]. Three crystallographically independent I_3^- anions can be found in the lattice, among which I(4)–I(5)–I(6) anion is I-I2 adducts with un-symmetrical I-I distances (Table 1). The other two (I(7)–I(8)–I(9), I(10)–I(11)–I(10)^b) are symmetrical and can be treated as molecular triiodide [10]. A I_2 molecule (I(12)–I(13)) with typical I-I length of 2.741(2) Å can be found, which interacts with adjacent I_3^- anions via short I···I interactions (I(9)–I(12) 3.361(4) Å; I(10)–I(13) 3.30(3)Å, I(11)–I(10)–I(13) angle 144.42(5) $^{\circ}$) to generate a Z-shape I_{13}^{3-} polyiodide anion (Figure 1a, Table 1). Furthermore, Z-shape I_{13}^{3-} interacts with $(BiI_6)^{3-}$ cluster via additional secondary I···I contacts (I(4)–I(4)^a 3.776(3) Å) to generate a unique $[(BiI_6)I_{13}]_n^{6-}$ 1-D infinite chain (Figure 1a). Besides, two isolated I_3^- anions are connected into a I_6^{2-} dimmer through weak I…I contact (I(3)–I(7) 3.727(3)Å). These I...I distances are definitively shorter than the sums of the Van der Waal's radii of I (3.92 Å) [24], which verify the presence of secondary I…I contacts [25]. In H-BPA²⁺ cation, the C-O bond distances in carboxyl groups (C(15)-O(1) 1.309(18) Å, C(15)-O(2) 1.220(14)Å; C(30)-O(3) 1.303(18)Å, O(4)-C(30)-O(4) 1.240(19)Å) hint the maintenance of protons, and the protonization on N atoms are deduced from the charge balance. The dihedral angles between two pyridine rings in two independent H-BPA²⁺ cations are 9.88 and 11.73°, suggesting a slight distortion. Two H-BPA²⁺ cations are combined into a $(H-BPA)_2^{4+}$ dimer via O(2)–H(2W)···O(3) hydrogen bonds, which are captured in the cavities defined by $[(BiI_6)I_{13}]_n^{6-}$ chains and I_6^{2-} anions through N/C-H…I hydrogen bonds (Figure 1b, Table 2). Consequently, based on these I...I contacts and hydrogen bonds, a quasi-3-D network is generated (Figure 2).

2.2. Absorption Spectrum and Photocurrent Response Behavior

The purity of crystalline sample of 1 has been proved by powder X-ray diffraction (PXRD), as shown in Figure 3. The good agreement between experimental and simulated patterns indicates its good phase purities. In order to determine its photo-responsive domains, the solid-state diffuse reflectance spectrum of the newly prepared crystalline sample of **1** was conducted at room temperature (Figure 4a). Interestingly, **1** exhibits a wide absorption zone from ultraviolet to visible regions (250–800 nm), suggesting its application in visible-light catalysis. No such absorption behavior is observed for viologen compounds [26]. The presence of visible and near-infrared absorptions in this work could be attributed to charge or partial electron transfers between the $[(BiI_6)I_{13}]_n^{6-}$ anions and H-BPA²⁺ cations induced by short contacts such as hydrogen bonding. The peaks at about 247 and 345 nm can be attributed to the n/π - π * charge transfer of H-BPA²⁺ cation [10], the

broad band around 534 nm might relate to a mixed metal/halide-ligand charge transfer processing between the I-5p/5s to the π^* orbital of H-BPA²⁺ cations [27]. As the absorptions locate in visible regions, the photocatalytic activity was further driven by visible light.



Figure 1. (a) The 1-D $[(BiI_6)I_{13}]_n^{6-}$ infinite chain constructed from the I···I contacts between $(BiI_6)^{3-}$ ion and Z-shape I_{13}^{3-} polyiodide anions; (b) hydrogen bonds between $[(BiI_6)I_{13}]_n^{6-}$ chains, I_6^{2-} anions and H-BPA²⁺ cations.

Bond	Dist.	Bond	Dist.	Dist.	Dist.
Bi(1)–I(1)	3.0568(11)	Bi(1)–I(1) ^a	3.0568(11)	Bi(1)–I(2)	3.1094(12)
$Bi(1)-I(2)^{a}$	3.1094(12)	Bi(1)–I(3)	3.0761(10)	$Bi(1)-I(3)^{a}$	3.0760(10)
I(4)–I(5)	2.970(2)	I(5)–I(6)	2.888(2)	I(7)–I(8)	2.9226(17)
I(8)–I(9)	2.9316(19)	I(10)–I(11)	2.9024(13)	I(9)–I(12)	3.361(4)
I(10)–I(13)	3.30(3)	I(12)–I(13)	2.741(2)	I(3)–I(7)	3.727(3)
Angle	(°)	Angle	(°)	Angle	(°)
I(1) ^a –Bi(1)–I(2) ^a	87.53(3)	I(1)–Bi(1)–I(2) ^a	92.47(3)	I(3) ^a -Bi(1)-I(2) ^a	89.43(3)
$I(3)-Bi(1)-I(2)^{a}$	90.57(3)	$I(1)^{a}-Bi(1)-I(2)$	92.47(3)	I(1)-Bi(1)-I(2)	87.53(3)
I(3) = Bi(1) - I(2)	90.57(3)	I(3)-Bi(1)-I(2)	89.43(3)	$I(2)^{a}-Bi(1)-I(2)$	180.0
I(6)–I(5)–I(4)	176.62(6)	I(7)–I(8)–I(9)	176.31(6)	I(10)–I(11)–I(10) ^b	180.00(4)
I(9)–I(12)–I(13)	164.87(7)	I(11)–I(10)–I(13)	144.42(5)	/ . /	

Table 1. Selected Bond Lengths (Å) and Bond Angles (°).

Symmetry transformation: ^a: -x, -y + 2, -z + 1; ^b: -x - 1, -y + 2, -z + 1.

Table 2. Hydrogen Bond Lengths (Å) and Bond Angles (°).

D-H A	d(D–H)	d(H A)	d(D A)	∠DHA	Symmetry Codes
N(1)–H(1N) I(2)	0.86	2.84	3.597(13)	149	-1 - x, 2 - y, -z
N(3)–H(3N) I(2)	0.86	2.79	3.578(13)	153	-1 + x, y, $-1 + z$
C(5)–H(5) I(6)	0.93	3.04	3.84(2)	146	-1 - x, 2 - y, -z
O(2)–H(2W) O(3)	0.82	2.10	2.640(14)	123	-1 - x, $1/2 + y$, $1/2 - z$

To estimate the charge separation efficiency of **1**, the crystalline sample-coated ITO electrode was prepared. A 150 W xenon lamp was used as light resource, and the electrode was irradiated using an ON–OFF cycle with intervals of 20 s, and sensitive photocurrent response can be monitored (Figure 4b). When the electrode was illuminated, repeatable and steady photocurrents with rapid response with the photocurrent density of 2.35 μ A·cm⁻² can be achieved. This result clearly demonstrates the charges in this electrode can be separated efficiently. The good photocurrent density can be explained as the wide absorption band in visible zone or narrow optical gap [28].



Figure 2. Quasi-3-D network of 1 based on I…I contacts and hydrogen bonds.



Figure 3. Powder X-ray diffraction (PXRD) patterns under different conditions for 1.

2.3. Photocatalytic Degradation of RhB in Seawater

The photocatalytic degradation of RhB in seawater using this three-component hybrid as catalyst was conducted. Before irradiation by visible light, the absorption-desorption equilibrium must be achieved by stirring the suspension magnetically in the dark for 30 min. As shown in Figure 5a, $\{[(BiI_6)I_{13}] \cdot 2I_3 \cdot (H-BPA)_4\}_n$ exhibits a high photocatalytic performance for the degradation of RhB in seawater. The time-dependent UV-Vis spectra of RhB showing its wavelength/absorption intensity changes under the irradiation of xenon-lamp are revealed in Figure 5a, and the concentrations of RhB (C) versus the irradiation time (t) of **1** are plotted in Figure 5b. As expected, with the lengthening of irradiation time, the absorption spectra of RhB decrease gradually, implying the occurrence of degradation reactions of RhB. The degradation rates of two catalysts are 90% after the irradiation time of 120 min. This degradation data are higher than that of $(PBPY-H_2)_2[PbI_4(I_3)_2]$ [10]. Comparably, the blank experiment without the presence of a catalyst among the same time scope shows that the photolysis rate of RhB is very low (about 5.0%). Therefore, we can conclude that **1** is vigorous for the decomposition of RhB under visible light irradiation in seawater. The stability and reusability of photocatalyst was verified by recovering the sample from reaction solution after 12 h. As the degradation reaction is heterogeneous, the catalyst can be recovered by a centrifugal method. The recovered sample was washed with ethanol and vacuum-dried at 55 °C. To our interest, the recovered amount is 38.6 mg

(the recovered ratio is 96.50%). The PXRD pattern of recovered catalyst is nearly identical with that of the as-prepared sample (Figure 3), hinting that the catalyst is stable in seawater. Moreover, as seen in Figure 5c, the catalyst can maintain its original activity after repeating the photocatalytic degradation of RhB three cycles, indicating good photochemical stabilities of **1**. According to the reported literatures, the degradation process of RhB under the visible light irradiation involves N-de-ethylation, chromophore cleavage, and mineralization, which leads to the final products of CO₂, H₂O, NO^{3–}, and NH⁴⁺ [29]. TOC analysis on degradation solution suggests that the removal ratio is 88.3%, indicating that most of RhB has been degraded. However, there is only slightly TOC decrease (about 1.2%) without irradiation of visible light.



Figure 4. (a) Solid state electronic spectrum and (b) photocurrent response behavior of 1.



Figure 5. (a) Time-dependent UV–Vis spectra of RhB with the presence of **1** as catalyst; (b) Degradation ratio of RhB different irradiation time with or without the presence of catalyst; (c) Recycling tests of **1** for RhB photodegradation under light irradiation.

3. Experimental

3.1. Materials and Methods

The chemicals including inorganic salts and organic solvents involved in the synthesis process were purchased from commercial sources with AR quality. 4,4'-bipyridinium-N-pentanoic acid (BPA·Br) was self-prepared according to literature [30]. IR spectrum was executed on a JASCO FT/IR-4100 FTIR spectrophotometer (Jasco, Easton, MD, USA) (4000–400 cm⁻¹). The solid-state diffuse reflectance spectrum was measured on a UV-Visible Spectrometer (Thermo SCIENTIFIC, Waltham, MA, USA, EVLUTION 220). The optical gap was evaluated from diffuse reflectance data based on Kubelka–Munk function: $\alpha/S = (1 - R)^2/(2R)$, in which the absorption coefficient (α), scattering coefficient (S), and reflectance (R) are adopted [31]. Elemental analysis for C, H, and N was carried out on a Vario MICRO elemental analyzer (Frankfurt, Elementar, Germary). The crystalline purity of the catalyst was characterized by powder X-ray diffraction (XRD, D8-advanced, Bruker, Karlsruhe, Germany, CuK α radiation). The photocurrent data was obtained using a CHI650 electrochemistry workstation (Shanghai, Chenghua, China) with three-electrode system. Total organic carbon (TOC) was determined on a Shimadzu TOC-L_{CPH-CPN} equipment (Kyoto, Shimadzu, Japan).

3.2. Synthesis

Synthesis of BPA·Br

BPA·Br was self-prepared based on the literature process (Scheme 1). 4,4'-bipyridine (4.7000 g, 0.03 mol) and 5-bromo-pentanoic acid (3.6000 g, 0.02 mol) were dissolved in 50 mL CH₃CN, the mixture was heated to 40 °C for 24 h. Afterwards, the yellow solids can be obtained after removal of solvents by rotary evaporation. The raw product was washed with ethyl acetate four times (25 mL) and dried at 60 °C for 1 h (4.721 g, yield: 70%).



Scheme 1. Synthesis of BPA·Br.

• Synthesis of $\{[(BiI_6)I_{13}] \cdot 2I_3 \cdot (H-BPA)_4\}_n$ (1)

BPA·Br (0.1120 g, 0.33 mmol), BiI₃ (0.1900 g, 0.33 mmol), and I₂ (0.0600 g, 0.33 mmol) were dissolved in 5 mL HI (concentration: 50%) and stirred magnetically for 90 min. Then, a typical hydrothermal reaction was executed under 120 °C for 72 h. Finally, after cooling the autoclave to room temperature in 24 h, black block single crystals can be separated and washed with ether (0.2913 g, yield 20% based on Bi.). Elemental analysis calculated for $C_{60}H_{72}BiI_{25}N_8O_8$ (4414.74): C, 16.33; H, 1.64; N, 2.54%. Found: C, 16.45; H, 1.72; N, 2.63%. IR (KBr, cm⁻¹): 3589(w), 3036(w), 2933(w), 1703(w), 1610(m), 1580(m), 1540(m), 1416(m), 1225(m), 1062(s), 610(s), 812(s), 720(m), 500(m), 403(w).

3.3. Photocurrent Measurements

Solution method was adopted in the fabrication of electrode in the photocurrent measurement [32]. In detail, the newly prepared crystalline sample of 1 (5 mg) was dispersed into 0.5 mL DMF, and the resultant solution was spread on an indium tin oxide glass (ITO, 0.36 cm²), which was precleaned by acetone. Epoxy resin was used to cover the uncoated parts of ITO. After evaporating the solvent under an ambient atmosphere, the electrode can be obtained. A 150 W xenon lamp equipped with a cutoff filter (>420 nm) was used as light resource to determine its photo-responsive behavior. Photocurrent data was plotted by electrochemical workstation in a typical three-electrode system in NaSO₄ aqueous solution (0.2 M): the 1-coated electrode as working electrode, the platinum plate

as counter electrode, and a Ag/AgCl electrode as reference electrode. The lamp was turn on throughout the measurement, and the irradiation was blocked by a manual shutter at intervals of 10 s.

3.4. Photodegradation of RhB

The photocatalytic degradation of RhB in seawater was executed under normal condition. The visible light was simulated by a A 300W xenon lamp equipped with a cutoff filter (>420 nm). Artificial seawater was prepared according to the literature amounts, i.e., 3.4 wt% containing NaCl (77.9%), MgCl₂ (9.6%), MgSO₄ (6.1%), CaSO₄ (4.0%), and KCl (0.07%) [33]. Then, rhodamine B was added into seawater solution with concentration of 0.01 mM. The crystalline sample of **1** (40 mg) was directly scattered into the above solution (80 mL). Before light irradiation, the absorption equilibrium must be formed by stirring the mixture in dark for 2 h. Afterwards the light resource was turned on. The initial concentration of RhB was marked as C₀ at the absorption equilibrium, which was determined by the absorption band maximum in the UV–Vis spectra. Aliquots (3 mL) in the degradation mixture were extracted to monitor the RhB concentration change with intervals of 30 min, which were labelled as C. The percentage of degradation is reported as C/C₀, which is a typical method in photocatalytic degradation [34].

3.5. X-ray Crystallography

The single crystal structure of **1** was determined at room temperature by X-Ray diffraction method using a Bruker APEX II diffractometer equipped with graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). Afterwards, direct method and Fourier technique in the SHELXTL-97 program package were adopted to visualize its structure [35,36]. For all non-hydrogen atoms, anisotropical refinements were carried out, and hydrogen atoms attached to carbon/oxygen atoms were geometrically placed. Crystal data: monoclinic, space group $P2_1/c$ with M_r = 4414.74, *a* = 14.859(2), *b* = 14.340(2), *c* = 24.718(4) Å, β = 103.264(3)°, V = 5126.3(14)Å³, Z = 2, $D_c = 2.857$ g/cm³, *F* (000) = 3920, μ (MoK α) = 9.293 mm⁻¹, the final *R* = 0.0642 and w*R* = 0.1884, *S* = 1.070, (Δ/σ)_{max} = 0.000, ($\Delta\rho$)_{max} = 2.413 and ($\Delta\rho$)_{min} = -2.028e/Å³. Important bond lengths and angles are given in Table 1, C–H··· π interactions are shown in Table 2. (See the Supplementary Materials).

4. Conclusions

In summary, a three-component hybrid containing $[(BiI_6)I_{13}]_n^{6-}$ infinite chain, I_3^- ions, and one and protonized 4,4'-bipyridinium-N-pentanoic acid (H-BPA²⁺) has been synthesized and structurally determined. Specifically, its unique 1-D Z-shape $[(BiI_6)I_{13}]_n^{6-}$ chain is constructed from the I…I contacts between mono-nuclear $(BiI_6)^{3-}$ anion and I_{13}^{3-} polyiodide anion, and hydrogen bonds between $[(BiI_6)I_{13}]_n^{6-}$ polyanions and H-BPA²⁺ cations contribute to the formation a quasi-3-D network. The wide absorption zone from ultraviolet to visible regions (250–800 nm) and high charge-separation efficiency suggest its application in visible-light catalysis. As expected, 1 can be used as a good photocatalyst in the photo-degradation of rhodamine B in seawater with degradation ratio of 90%. This work might provide new photocatalytic material for pollutant treatment in shipping accidents.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10 .3390/catal11050640/s1, Data S1 for publication: Crystal structure data, Report S2 for review only: Crystal structure correctness report.

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Data Availability Statement: Data available on request due to restrictions, e.g., privacy or ethical.

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