# A New Iodiplumbate-based Hybrid Constructed from Asymmetric Viologen and Polyiodides: Structure, Properties and Photocatalytic Activity for the Degradation of Organic Dye Postprint

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## Abstract

A new iodiplumbate/organic hybrid constructed from asymmetric viologen and polyiodides, (PBPY-H2)2[PbI4(I3)2] (1, PBPY = N-(propionate)-4,4 -bipyridinium), has been synthesized via solvothermal reaction and structurally determined by X-ray diffraction method. Compound 1 crystallizes in monoclinic system, space group P21/c with Mr = 1936.72, a = 11.622(2), b = 14.839(3), c = 13.372(2) Å,  = 109.447(3)°, V = 2174.6(7) Å3, Z = 2, Dc = 2.958 g/cm3, F(000) = 1712,  (MoK ) = 11.011 mm-1, the final R = 0.0389 and wR = 0.0854 for 3866 observed reflections with I > 2 (I). [PbI4(I3)2]4- mononuclear cluster of 1 features a seldom example of coordinated I3- donors for the lead center. Intermolecular hydrogen bonds between [PbI4(I3)2]4- clusters and (PBPY-H)24+ dimmers contribute to the formation of a 2-D layer. Its absorption spectrum was investigated, and lower energy band gap of 1.42 eV was explained by DFT calculation. Interestingly, 1 exhibits photocatalytic activity for the degradation of rhodamine B.

## Full Text

### A New Iodiplumbate-based Hybrid Constructed from Asymmetric Viologen and Polyiodides: Structure, Properties and Photocatalytic Activity for the Degradation of Organic Dye

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## ABSTRACT

A new iodiplumbate/organic hybrid constructed from asymmetric viologen and polyiodides, (PBPY-H ) [PbI (I ) ] (1, PBPY = N-(propionate)-4,4 -bipyridinium), has been synthesized via solvothermal reaction and structurally determined by X-ray diffraction. Compound 1 crystallizes in the monoclinic system, space group P2 /c with M = 1936.72, a = 11.622(2), b = 14.839(3), c = 13.372(2) Å, = 109.447(3)°, V = 2174.6(7) Å$^3$, Z = 2, Dc = 2.958 g/cm$^3$, F(000) = 1712, (MoK ) = 11.011 mm $^1$, with final R = 0.0389 and wR = 0.0854 for 3866 observed reflections with I > 2 (I). The [PbI (I ) ] mononuclear cluster of 1 features a rare example of coordinated I donors for the lead center. Intermolecular hydrogen bonds between [PbI (I ) ] clusters and (PBPY-H) dimers contribute to the formation of a 2-D layer. Its absorption spectrum was investigated, and the lower energy band gap of 1.42 eV was explained by DFT calculation. Interestingly, 1 exhibits photocatalytic activity for the degradation of rhodamine B.

**Keywords:** organic-inorganic hybrid; iodiplumbate; asymmetric viologen; photocatalytic degradation

## INTRODUCTION

Over the last decade, great attention has been paid to the design and synthesis of main group metals (for example, Ge(II), Sn(II), Pb(II), Sb(III) and Bi(III)) and halide-based hybrid materials, owing not only to their versatile structure types but also to their potential applications in various fields such as semiconductivity [**?**, **?**], luminescence [**?**, **?**], photo/thermochroism [**?**], and especially the emerging visible-light sensitizers for photovoltaic cells [**?**, **?**]. The main group metal centers exhibit electronic configurations of $d^1$ $ns^2np^2$ or 3, so they present stereochemical activities with or without the presence of $ns^2$ lone pairs in their coordination spheres, from which many interesting properties can stem [**?**, **?**]. Up to now, regarding the anion structures of iodiplumbate, versatile structural dimensions have been observed ranging from isolated anions, infinite chains, layered perovskites to three-dimensional polymeric networks constructed from face-, edge-, or vertex-sharing PbI octahedra [**?**]. Among mononuclear cases, only PbI and PbI $^2$ have been reported [**?**, **?**].

More recently, viologens (N,N -disubstituted 4,4 -bipyridinium) have become attractive materials due to their excellent electron-accepting nature, and they have been incorporated into haloplumbate systems to realize photo/thermochroism functions [**?**]. Although symmetrical viologens have been widely studied in previous work, asymmetric viologens and their corresponding metal-halide hybrids have been rarely explored [**?**]. N-(propionate)-4,4 -bipyridinium is a neutral inner salt with an electron-donating carboxylate group and an electron-accepting 4,4 -bipyridinium group. In this work, we introduced asymmetric viologens and polyiodides into the haloplumbate system to generate a new hybrid, (PBPY-H ) [PbI (I ) ], whose adsorption, band gap and photocatalytic activity were investigated.

## EXPERIMENTAL

### Materials and Methods

All reactants were of reagent grade and used as purchased. PBPY was self-synthesized. Elemental analyses for C, H and N were performed on a Vario MICRO elemental analyzer. IR spectra were recorded on a Perkin-Elmer Spectrum-2000 FTIR spectrophotometer (4000–400 cm $^{1}$). UV-Vis spectrum was measured on a Perkin-Elmer Lambda 900 UV/Vis spectrophotometer equipped with an integrating sphere at 293 K, and BaSO plates were used as reference.

### Synthesis of PBPY

PBPY was synthesized according to a similar procedure reported in the literature [**?**], using 4,4 -bipyridine and bromopropionic acid as starting materials in CH CN solvent.

### Synthesis of (PBPY-H ) [PbI (I ) ] (1)

PBPY (0.2280 g, 1 mmol) and PbI (0.2305 g, 0.5 mmol) were dissolved in 10 mL HI (55%) and stirred for 30 minutes. The resultant solution was transferred and sealed in a 25 mL Teflon-lined stainless-steel reactor, which was heated at a rate of 5 °C/h to 120 °C under autogenous pressure. After being maintained for 3 days, the reaction vessel was cooled to room temperature at a rate of 4 °C/h. Black block crystals with a yield of 45.2% (0.437 g, based on Pb) were obtained and washed with ether. Anal. Calcd. for C H I N O Pb (1936.72): C, 16.12; H, 1.45; N, 2.89%. Found: C, 16.59; H, 1.58; N, 2.68%. IR (KBr, cm $^{1}$): 3391(s), 3047(s), 2922(s), 1708(m), 1610(s), 1580(s), 1458(m), 1390(s), 1120(m), 796(s), 765(m), 550(w). Due to the higher I concentration in HI solution, I anions can be observed in the product.

### Computational Details

The band structure calculation was based on density functional theory (DFT) [**?**], in which wave functions were expanded in a plane wave basis set, and the spin-polarized version of the PW-91 GGA was employed for the exchange-correlation functional in the CASTEP code [**?**]. The number of plane waves included in the basis was determined by a cutoff energy E_c of 550 eV. Pseudoatomic calculations were performed for Pb ($5d^{1}$ $6s^{2}6p^{2}$), I ($5s^{2}5p$ ), O ($2s^{2}2p$ ) and N ($2s^{2}2p^{3}$).

### Photocatalytic Testing

In the degradation experiment, a 300 W Xe arc lamp equipped with a 420 nm cutoff filter and an IR filter was used as the visible light source, with an output light intensity of 110 mW/cm$^2$. During the photodegradation experiment of RhB, 40 mg of catalyst powder was suspended in 80 mL of RhB solution (concentration: 10 ppm). To achieve adsorption-desorption equilibrium of the organic contaminants on the catalyst surface before irradiation, the suspensions were magnetically stirred in the dark for 2 h until no change occurred in the UV/Vis absorption of the RhB solution. The photocatalytic performance of the catalysts was estimated by monitoring the visible absorbance ( = 555 nm) characteristic of the target (RhB) by UV/Vis spectroscopy. Sample solutions (3 mL) were taken out at given time intervals and separated through filtration. The residual pollutant concentrations were analyzed by the maximum absorption band in the UV-Vis spectra of the organics. The percentage of degradation was reported as C/C . Here, C is the absorption of RhB at each irradiated time interval with the main peak at 553 nm, and C is the absorption of the starting solution when adsorption-desorption equilibrium was achieved.

### X-ray Crystallography

A red block crystal of 1 with dimensions of 0.35 mm × 0.30 mm × 0.25 mm was mounted on a glass fiber. Intensity data were collected on a Bruker APEX II diffractometer using graphite-monochromated MoK radiation ( = 0.71073 Å) at 293(2) K by an -2 scan mode. In the range of 2.44 31.05°, out of 9936 total reflections, 5548 were independent with R_int = 0.0258, of which 3866 were considered observed (I > 2 (I)) and used in subsequent refinement. Multi-scan absorption correction was applied. The structure was solved by direct methods using the SHELXS-97 program and refined on F$^2$ by full-matrix least-squares techniques using the SHELXL-97 program [?]. Hydrogen atoms of C-H were generated geometrically. The final R = 0.0389 and wR = 0.0854 (w = 1/[ $^2$(F $^2$) + (0.0426P)$^2$ + 2.0266P], where P = (F $^2$)/3), S = 1.014, (Δ/ )_max = 0.000, (Δ )_max = 1.466 and (Δ )_min = -1.264 e/Å$^3$. Important bond lengths are listed in Table 1 , and hydrogen bond details are given in Table 2 .

## RESULTS AND DISCUSSION

### Structure Description

The organic-inorganic hybrid structure of 1 is composed of [PbI (I ) ] mononuclear clusters and protonated (PBPY-H)$^2$ cations, with intermolecular hydrogen bonds between them contributing to the formation of a 2-D layer. In the [PbI (I ) ] mononuclear cluster, the lead center adopts a normal octahedral geometry coordinated by four iodide ions and two I anions. In this slightly distorted PbI octahedron, four iodide ions occupy the equatorial plane and two iodine atoms from I occupy the axial positions (Fig. 1a [Figure 1: see original paper]). The Pb-I_equatorial distances range from 3.1246(6) to 3.1732(6) Å, and the Pb-I_axial distance is 3.3177(10) Å. The I-Pb-I angles (89.836(17)-90.164(17) and 180.000(11)°) deviate slightly from ideal octahedral values of 90° and 180° (Table 1). Based on the Pb-I distances, we can conclude that the lead center is stereochemically inactive according to Brown' s model [?]. The I anion is slightly bent with the I(5)-I(4)-I(3) angle of 176.43(3)°, and the I-I distances of 2.9618(10)/2.8811(10) Å indicate a slightly asymmetrical triiodide. Cases of I anion coordination to metal centers have been observed in Cu, Pt, Ir, Ni and Hg systems [?, ?], but its coordination to Pb centers is very rare [?]. Because the synthesis environment is strongly acidic, the carboxyl group and N atom on PBPY are protonated. The C-C, C-N and C-O bonds in the (PBPY-H)$^2$ cation are normal. Two pyridine rings are nearly coplanar with a dihedral angle of 11.87°. Intermolecular hydrogen bonds between two carboxyl groups of (PBPY-H)$^2$ cations with an O ⋯ O distance of 2.662(8) Å can be observed (Fig. 1b, Table 2). Based on these intermolecular hydrogen bonds, a (PBPY-H) dimer is formed (Fig. 1b). N-H ⋯ I_equatorial hydrogen bonds between [PbI (I ) ] clusters and (PBPY-H) dimers contribute to the formation of a 1-D chain along the b axis, which is further linked into a 2-D plane along the bc plane via C-H ⋯ I_equatorial hydrogen bonds (Table 2, Fig. 2 [Figure 2: see original paper]).

## Adsorption Spectrum, Linear Absorption Optical Property and Band Structure

To determine the photo-response regions, solid-state diffuse-reflectance UV/Vis measurements were conducted on the as-synthesized compound, as shown in Fig. 3a [Figure 3: see original paper]. Compound 1 exhibits broad absorption ranging from 250 to 800 nm, indicating its absorption in the visible region and potential application in visible-light catalysis. The broad absorption range in the visible (400-600 nm) and near-infrared (600-800 nm) regions is unusual, and no such band is observed for MVI [?]. The presence of visible and near-infrared absorption is attributed to charge transfer (CT) or partial electron transfer between the [PbI (I ) ] anion and (PBPY-H)$^2$ cation. Overall, the intense CT bands of 1 stem from cation-anion interactions and short contacts, such as hydrogen bonding. Absorption peaks at 320 and 366 nm can be observed. Compared with the UV-Vis absorption spectra of bipyridine, bulk PbI and related compounds, the peak at 320 nm can be assigned to - * and n- * transitions of pyridine, while the peak at 366 nm originates from the PbI octahedral center [?, ?].

The optical gap of 1 was assessed from its optical diffuse reflectance data, and the Kubelka-Munk functions converted from the diffuse reflectance data are plotted in Fig. 3b [?, ?]. As shown in Fig. 3b, E_g of 1.41 eV indicates a narrow band gap. Compared with bulk PbI (2.47-2.49 eV) [?], the gap of 1 is significantly narrower, which may be caused by the introduction of conjugated organic cations and the presence of various weak interactions. The lower band gap of 1 can be explained by theoretical calculations. Band structure and density of states (DOS) of 1 are shown in Fig. 4 [Figure 4: see original paper]. The calculated band-gap value is 0.95 eV, which is generally consistent with the experimental value of 1.41 eV, considering the underestimation of band gaps using generalized-gradient approximation in Kohn-Sham DFT function [**?**]. The DOS diagram indicates that the tops of the valence bands are mostly formed by -bonding orbitals of (PBPY-H)$^2$ , while the bottoms of the conduction bands are almost entirely contributed by I-5p states of I anion (Fig. 4b). This situation differs from that of viologen/metal halide systems, whose conduction bands are generally p- * antibonding orbitals of the viologens. In other words, the introduction of I anion results in a lower band gap, which is beneficial for photocatalytic activity.

### Photocatalytic Degradation of Organic Pollutant

Here, the N-containing dye rhodamine B (RhB) was selected as a model pollutant for degradation experiments. The wavelength and absorption intensity changes of RhB under xenon lamp irradiation in the presence of catalysts are shown in Fig. 5a [Figure 5: see original paper]. As illustrated in Fig. 5a, with the catalyst present, the absorption spectra of RhB decrease to different extents with increasing irradiation time, indicating that degradation reactions of RhB have occurred. Importantly, the characteristic absorption of RhB (555 nm) shifted to 497 nm, suggesting that dye degradation proceeded in the presence of the catalyst [**?**]. The peaks at 555 nm exhibited only slight shifts, indicating that deethylation of RhB has occurred. Fig. 5b shows the rate of RhB degradation (measured as RhB concentration versus irradiation time) in aqueous solution in the presence of 1. After irradiation for 180 min, the degradation ratio reached approximately 82.4%.

## CONCLUSION

In summary, a new iodiplumbate/organic hybrid constructed from asymmetric viologen and polyiodide has been synthesized and structurally characterized. The [PbI (I ) ] mononuclear cluster of 1 represents a rare example with I coordinated to the lead center. Strong hydrogen bonds between [PbI (I ) ] clusters and (PBPY-H) dimers lead to the formation of a 2-D layer. Its absorption spectrum was investigated, and the lower energy band gap of 1.42 eV was explained by DFT calculation. Interestingly, 1 exhibits photocatalytic activity for the degradation of rhodamine B with a degradation ratio of 82.4%.

## REFERENCES

(1) Wang, G. E.; Xu, G.; Liu, B. W.; Wang, M. S.; Yao, M. S.; Guo, G. C. Semiconductive nanotube array constructed from giant [PbII18I54(I2)9] wheel clusters. Angew. Chem. Int. Ed. 2016, 55, 514–518.

(2) Dammak, H.; Yangui, A.; Triki, S.; Abid, Y.; Feki, H. Structural characterization, vibrational, optical properties and DFT investigation of a

new luminescent organic-inorganic material: (C6H14N)3Bi2I9. J. Lumin. 2015, 161, 214-220.

(3) Adonin, S. A.; Rakhmanova, M. E.; Smolentsev, A. I.; Korolkov, I. V.; Sokolov, M. N.; Fedin, V. P. Binuclear Bi(III) halide complexes with 4,4 -ethylenepyridinium cations: luminescence tuning by reversible salvation. New J. Chem. 2015, 5529-5533.

(4) Xu, G.; Guo, G. C.; Guo, J. S.; Guo, S. P.; Jiang, X. M.; Yang, C.; Wang, M. S.; Zhang, Z. J. Photochromic inorganic-organic hybrid: a new approach for switchable photoluminescence in the solid state and partial photochromic phenomenon. Dalton Trans. 2010, 39, 8688-8692.

(5) Xu, G.; Guo, G. C.; Wang, M. S.; Zhang, Z. J.; Chen, W. T.; Huang, J. S. Photochromism of a methyl viologen bismuth(III) chloride: structural variation before and after UV irradiation. Angew. Chem. Int. Ed. 2007, 46, 3249-3251.

(6) Wang, M. S.; Xu, G.; Zhang, Z. J.; Guo, G. C. Inorganic-organic hybrid photochromic materials. Chem. Commun. 2010, 46, 361-376.

(7) Gagor, A.; Weclawik, M.; Bondzior, B.; Jakubas, R. Periodic incommensurately modulated phases (2-methylimidazolium)tetraiodobismuthate(III) thermochromic organic-inorganic hybrid. CrystEngComm. 2015, 27, 3286-3296.

(8) Goforth, A. M.; Tershansy, M. A.; Smith, M. D.; Peterson Jr., L.; Kelley, J. G.; DeBenedetti, W. J.; zur Loye, H. C. Structural diversity and thermochromic properties of iodobismuthate materials containing d-metal coordination cations: observation of a high symmetry [Bi3I11]2- anion and of isolated I- anions. J. Am. Chem. Soc. 2011, 133, 603-612.

(9) Christians, J. A.; Fung, R. C. M.; Kamat, P. V. An inorganic hole conductor for organo-lead halide perovskite solar cells improved hole conductivity with copper iodide. J. Am. Chem. Soc. 2014, 136, 758-764.

(10) Mosconi, E.; Amat, A.; Nazeeruddin, M. K.; Grätzel, M.; De Angelis, F. First-principles modeling of mixed halide organometal perovskites for photovoltaic applications. J. Phys. Chem. C 2013, 117, 13902-13913.

(11) Zhang, Z. J.; Guo, G. C.; Xu, G.; Fu, M. L.; Zou, J. P.; Huang, J. S. [(H2en)7(C2O4)2]n(Pb4I18)n · 4nH2O, a new type of perovskite cotemplated by both organic cations and anions. Inorg. Chem. 2006, 45, 10028-10030.

(12) Aragoni, M. C.; Arca, M.; Caltagirone, C.; Devillanova, F. A.; Demartin, F.; Garau, A.; Isaia, F.; Lippolis, V. Inorganic-organic hybrid materials: construction of the first polymeric channelled halometallate(II) system. CrystEngComm. 2005, 7, 544-547.

(13) Wu, L. M.; Wu, X. T.; Chen, L. Structural overview and structure-property relationships of iodoplumbate and iodobismuthate. Coord. Chem. Rev. 2009, 253, 2787-2804.

(14) Wakamiya, A.; Endo, M.; Sasamori, T.; Tokitoh, N.; Ogomi, Y.; Murata, Y. Reproducible fabrication of efficient perovskite-based solar cells: X-ray crystallographic studies on the formation of CH3NH3PbI3 layers. Chem. Lett. 2014, 43, 711-713.

(15) Louvain, N.; Mercier, N.; Luc, J.; Sahraoui, B. Example of disulfide conformational change in the solid state: preparation, optical properties, and X-ray studies of a cystamine-based iodoplombate hybrid. Eur. J. Inorg. Chem. 2008, 3592-3596.

(16) Lin, R. G.; Xu, G.; Wang, M. S.; Lu, G.; Li, P. X.; Guo, G. C. Improved photochromic properties on viologen-based inorganic-organic hybrids by using -conjugated substituents as electron donors and stabilizers. Inorg. Chem. 2013, 52, 1199-1205.

(17) Phillips, A. D.; Fei, Z.; Ang, W. H.; Scopelliti, R.; Dyson, P. J. A crystallographic story of snakes and ladders: encapsulated water polymers and rigid metal complexes based on mono-N-substituted carboxylate 4,4 -bipyridine. Cryst.Growth Des. 2009, 9, 1966-1978.

(18) Perew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. Phy. Rev. Lett. 1996, 77, 3865-3868.

(19) Segall, M.; Probert, M.; Pickard, C.; Hasnip, P.; Clark, S.; Refson, K.; Payne, M. Materials Studio CASTEP version 4.1 2006.

(20) Sheldrick, G. M. SHELXS97 and SHELXL97. University of Göttingen, Germany 1997.

(21) Brown, D. J. Bond valence as an aid to understanding the stereochemistry of O and F complexes of Sn(II), Sb(III), Te(IV), I(V) and Xe(VI). J. Solid. State. Chem. 1974, 11, 214-233.

(22) Svensson, P. H.; Kloo, L. Metal iodides in polyiodide networks: synthesis and structure of binary metal iodide-iodine compounds stable under ambient conditions. Inorg. Chem.1999, 38, 3390-3393.

(23) Zhao, S. B.; Wang, R. Y.; Wang, S. N. Dinuclear Cu(I) complexes of 1,2,4,5-tetra(7-azaindolyl)benzene: persistent 3-coordinate geometry, luminescence, and reactivity. Inorg. Chem. 2006, 45, 5830-5840.

(24) Wang, G. E.; Xu, G.; Liu, B. W.; Wang, M. S.; Yao, M. S.; Guo, G. C. Semiconductive nanotube array constructed from giant [Pb18I54(I2)9] wheel clusters. Angew. Chem. Int. Ed. 2016, 55, 514-518.

(25) Tong, Z.; Pu, S.; Xiao, Q.; Liu, G.; Cui, S. Synthesis and photochromism of a novel water-soluble diarylethene with glucosyltriazolyl groups. Tetra. Lett. 2013, 54, 474-477.

(26) Sourisseau, S.; Louvain, N.; Bi, W.; Mercier, N.; Rondeau, D.; Boucher, F.; Buzare, J. Y.; Legein, C. Reduced band gap hybrid perovskites resulting from combined hydrogen and halogen bonding at the organic-inorganic interface. Chem. Mater. 2007, 19, 600–607.

(27) Zhu, X. H.; Mercier, N.; Frere, P.; Blanchard, P.; Roncali, J.; Allain, M.; Pasquier, C.; Riou, A. Effect of mono- versus di-ammonium cation of 2,2 -bithiophene derivatives on the structure of organic-inorganic hybrid materials based on iodo metallates. Inorg. Chem. 2003, 42, 5330–5339.

(28) Wendlandt, W. W.; Hecht, H. G. Reflectance Spectroscopy. Interscience Publishers: New York 1966.

(29) Kotiim, G. Reflectance Spectroscopy. Springer-Verlag: New York 1969.

(30) Baibarac, M.; Preda, N.; Mihut, L.; Baltog, I.; Lefrant, S.; Mevellec, J. Y. On the optical properties of micro- and nanometric size PbI2 particles. J. Phys. Condens. Matter. 2004, 16, 2345–2356.

(31) Yang, J.; Dolg, M. First-principles electronic structure study of the monoclinic crystal bismuth triborate BiB3O6. J. Phys. Chem. B 2006, 110, (32) Horikoshi, S.; Saitou, A.; Hidaka, H.; Serpone, N. Environmental remediation by an integrated microwave/UV illumination method. V. Thermal and nonthermal effects of microwave radiation on the photocatalyst and on the photodegradation of rhodamine-B under UV/Vis radiation. Environ. Sci. Technol. 2003, 37, 5813–5822.

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

| Bond/Angle | Distance/Value |
|---|---|
| Pb(1)-I(1)#1 | 3.124(6) |
| Pb(1)-I(2) | 3.173(2) |
| I(3)-I(4) | 2.961(8) |
| Pb(1)-I(1) | 3.124(6) |
| Pb(1)-I(3)#1 | 3.317(7) |
| I(4)-I(5) | 2.881(1) |
| Pb(1)-I(2)#1 | 3.173(2) |
| Pb(1)-I(3) | 3.317(7) |
| I(5)-I(4)-I(3) | 176.4(3) |
| I(1)#1-Pb(1)-I(2)#1 | 90.1(6) |
| I(1)-Pb(1)-I(2)#1 | 89.8(3) |
| I(1)#1-Pb(1)-I(2) | 89.8(3) |
| I(1)-Pb(1)-I(2) | 90.1(6) |
| I(3)#1-Pb(1)-I(3) | 180.0(0) |

Symmetry code: #1 -x+1, -y, -z

**Table 2.** Hydrogen Bond Details in 1

| D-H ⋯ A | d(D-H) | d(H ⋯ A) | d(D ⋯ A) | Symmetry code |
|---|---|---|---|---|
| O(2)-H(2C) ⋯ O(1) | - | - | 2.662(8) | 2-x, 2-y, 1-z |
| N(2)-H(2) ⋯ I(2) | 0.73(7) | 2.89(8) | 3.557(7) | 153(8) |
| C(12)-H(12) ⋯ I(1) | - | - | 3.788(8) | x, 1/2-y, 1/2+z |

**Fig. 1.** (a) Structure of [PbI (I ) ]  mononuclear cluster; (b) (PBPY-H) dimer constructed from hydrogen bonds

**Fig. 2.** (PBPY-H ) [PbI (I ) ] 2-D layer based on O-H ⋯ O, N-H ⋯ I and C-H ⋯ I hydrogen bonds

**Fig. 3.** Room temperature UV-Vis absorption spectrum (a) and diffuse reflectance spectrum in Kubelka-Munk unit (b) of 1

**Fig. 4.** (a) Band structure and (b) density of states based on DFT calculation

**Fig. 5.** (a) Time-dependent UV-Vis spectra of RhB in the presence of 1 under xenon lamp irradiation; (b) Concentration change of RhB. C_t and C_0 stand respectively for the RhB concentrations after and before irradiation

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