

## Supporting Information

### Two highly crystalline coordination polymers with two-dimensional PbS networks for photocatalytic synthesis of imines

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### **General Information.**

4-Hydroxybenzenethiol and *p*-benzoquinone (BQ) were purchased from J&K Scientific Ltd. 1,4-Benzenedithiol, benzylamine, 4-methylbenzylamine, 4-methoxybenzylamine, 4-tert-butylbenzylamine, 4-bromobenzylamine, 4-fluorobenzylamine, 4-trifluoromethylbenzylamine, 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), 2,2,6,6-tetramethylpiperidine (TEMP) and beta-carotene were purchased from Innochem Science & Technology Co., Ltd.  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$  was purchased from Acros Organic of Thermo Fisher Scientific Co., Ltd.

### **Synthesis of Pb-HBT.**

4-Hydroxybenzenethiol (0.2524 g, 2 mmol) was dissolved in 40 mL degassed  $\text{H}_2\text{O}$  under argon atmosphere. Then,  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$  (0.3793 g, 1 mmol) was added. The mixture was heated at 120 °C for 24 h. The solid was collected by filtration and washed with  $\text{H}_2\text{O}$ , methanol, diethyl ether. After drying under vacuum at 60 °C for 12 h, the product was obtained as black brown solid (> 90% yield).

### **Synthesis of Pb-BDT.**

1,4-Benzenedithiol (0.142 g, 1 mmol) was suspended in 40 mL degassed  $\text{H}_2\text{O}$  under argon atmosphere. Then,  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$  (0.19 g, 0.5 mmol) was added. The mixture was heated at 85 °C for 24 h. The solid was collected by filtration and washed with  $\text{H}_2\text{O}$ , methanol, diethyl ether. After drying under vacuum at 60 °C for 12 h, the product was obtained as brown solid (40-50% yield).

### **Photocatalytic oxidation of benzylamine.**

5 mg photocatalyst was added to a 50 mL round-bottom flask, then 5 mL acetonitrile and 0.5 mmol substrate were added in sequence. The mixture was stirred in air for 30 min. After sealed by a rubber stopper, the reaction system was irradiated by a 300 W Xe lamp ( $350 < \lambda < 780$  nm, Aulight CEL-HX, Beijing) for desired time while cooling with circulating water device. The mixed product was analyzed by  $^1\text{H}$  nuclear magnetic resonance ( $^1\text{H}$  NMR). The conversion (conv.), selectivity (select.) and production rate were calculated from the integration of  $^1\text{H}$ -NMR peaks using 1,3,5-trioxane as an internal standard.

### **Photoelectrochemical test.**

3 mg of the photocatalyst was suspended in a mixture of 140  $\mu\text{L}$  ethanol and 10  $\mu\text{L}$  5 % Nafion solution. The mixture system was sonicated for 30 min and transferred to a piece of 1  $\text{cm}^2$  indium-tin oxide (ITO) in batches to prepare working electrodes. The photoelectrochemical measurement was carried out at electrochemical workstation (CHI660E, Chenhua Instrument, Shanghai, China). A three-electrode system with the photocatalyst-coated ITO as the working electrode, 1  $\text{cm}^2$  Pt net as the counter electrode and saturated Ag/AgCl as a reference electrode was used. 0.5 M  $\text{Na}_2\text{SO}_4$  solution was used as electrolyte to conduct the photoelectrochemical test.

### **Quenching experiment.**

The quenching experiment was the same as photocatalytic oxidation of benzylamine experiment in addition to 2 equivalents of scavengers (beta-carotene and *p*-benzoquinone) were added.

### **Electron spin resonance (ESR) experiment.**

2 mg of catalyst was added to 2 mL acetonitrile in a 50 mL round-bottom flask under dark condition. After stirring in air for 30 min, the mixture was mixed with 10  $\mu$ L trapping agent of TEMP or DMPO. Then the mixture was light-illuminated at room temperature and analyzed by Bruker ELEXSYS II E500.

#### **Structure solving and refinement method.**

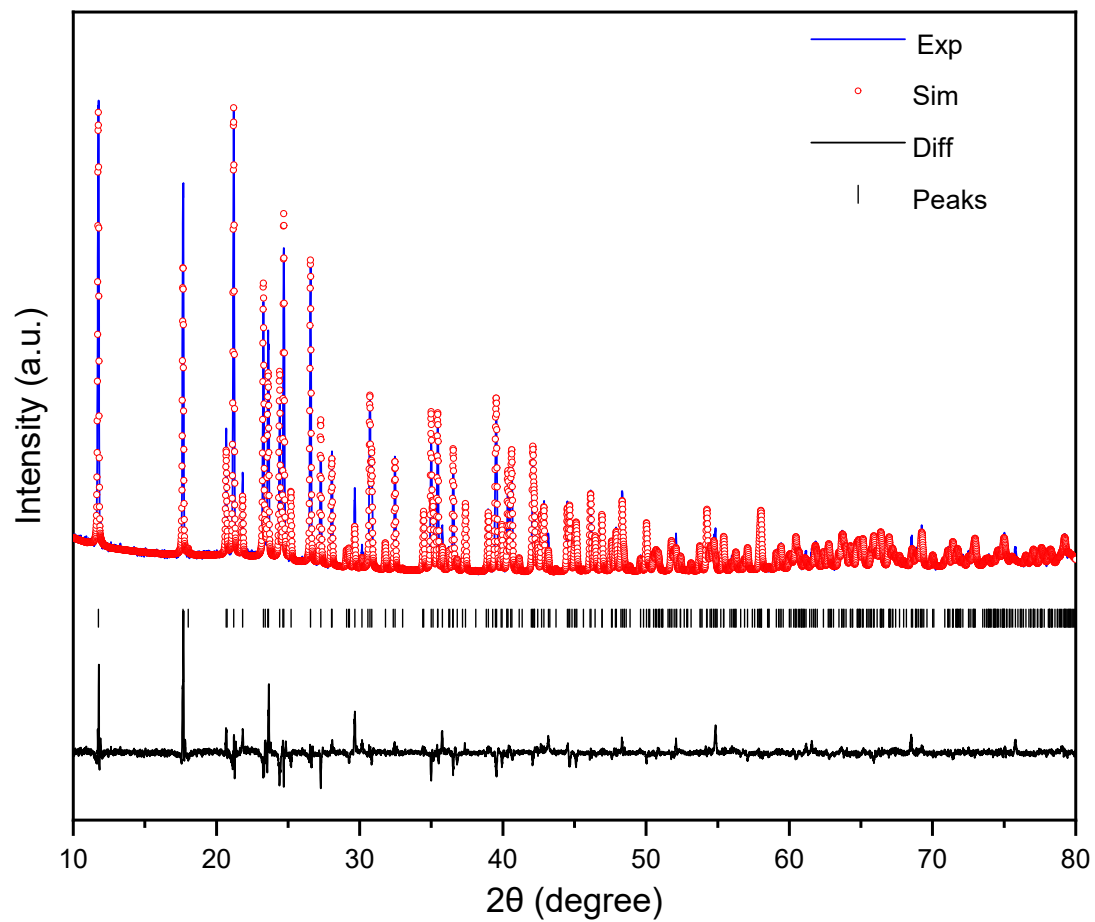
The Pb-HBT (HBT = 4-hydroxybenzenethiol) structure was solved from powder XRD pattern of the as prepared sample, recorded on a high-resolution X-ray powder diffractometer (Rigaku SmartLab 9KW,  $\lambda$  (Cu K $\alpha$ 1) = 1.540593 Å) with Debye-Scherrer transmission geometry in  $2\theta$  ranging from 4° to 120°. The indexing process was performed by EXPO2014<sup>1</sup> using the program N-TREOR09.<sup>2</sup> A monoclinic unit cell with  $a = 15.12$  Å,  $b = 5.20$  Å,  $c = 7.63$  Å,  $\beta = 95.54^\circ$ ,  $V = 597.37$  Å<sup>3</sup> was obtained with figure of merit  $M_{20} = 76.0$  from the first 23 XRD peaks in the  $2\theta$  range of 3° to 40°. The initial lattice parameters were refined by le Bail algorithm using Jana2006.<sup>3</sup> Background, zero-point, profile shape and asymmetry parameters were refined together to get the profile fitting converged with GOF = 0.76, Rp = 4.99, Rwp = 6.78. The space group was determined as P2<sub>1</sub>/c based on symmetric extinction calculation. The structure was solved with direct method using Super flip program.<sup>4</sup> The final Rietveld refinement with involving the coordination parameters and thermal factors of Pb, S, O and C atoms was performed with Jana2006<sup>3</sup> and converged with GOF = 1.00, Rp = 6.85%, Rwp = 9.52%.

The Pb-BDT (BDT = benzene-1,4-dithiol) structure was solved from powder XRD pattern of the as prepared sample, recorded on a Debye-Scherrer transmission geometry by high resolution X-ray powder diffractometer (Rigaku SmartLab 9KW,  $\lambda$  (Cu K $\alpha$ 1) = 1.540593 Å) with  $2\theta$  ranging from 5° to 120°. The indexing process was performed by EXPO2014<sup>1</sup> using the program N-TREOR09.<sup>2</sup> A monoclinic unit cell with  $a = 7.48$  Å,  $b = 5.21$  Å,  $c = 17.46$  Å,  $\beta = 93.38^\circ$ ,  $V = 678.83$  Å<sup>3</sup> was obtained with figure of merit  $M_{20} = 49.0$  from the first 23 XRD peaks in the  $2\theta$  range of 5° to 40°. The initial lattice parameters were refined by le Bail algorithm using Jana2006.<sup>3</sup> Background, zero-point, profile shape and asymmetry parameters were refined together to get the profile fitting converged with GOF = 0.73, Rp = 2.23, Rwp = 2.98. The space group was determined as P2<sub>1</sub>/c based on symmetric extinction calculation. The structure was solved with direct method using Super flip program.<sup>4</sup> The final Rietveld refinement with involving the coordination parameters and thermal factors of Pb, S, and C atoms was performed with Jana2006<sup>3</sup> and converged with GOF = 0.88, Rp = 2.69%, Rwp = 3.58%.

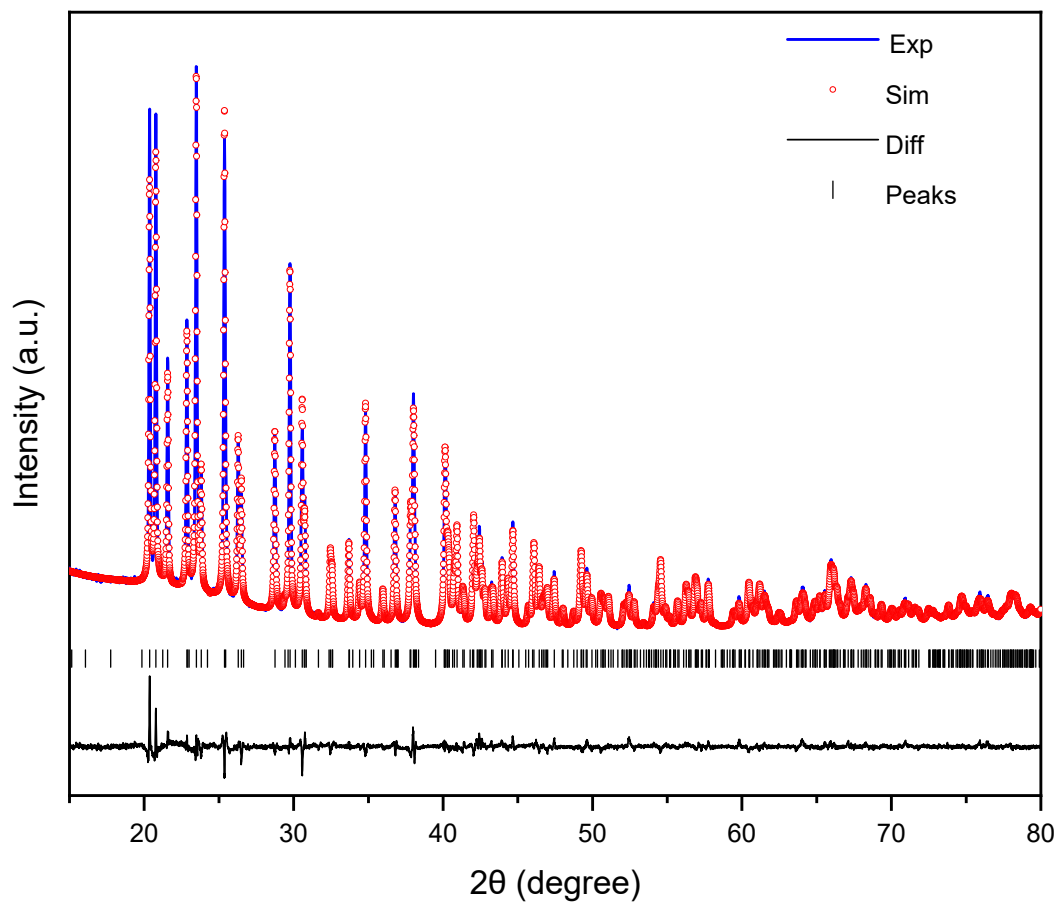
#### **Characterizations.**

The scanning electron microscopy (SEM) and SEM-Energy-dispersive X-ray spectroscopy (SEM-EDS) images were obtained by Toshiba SU8020 SEM. High-resolution transmission electron microscopy (HRTEM) images were obtained by Themis 300. TEM-EDS images were obtained by JEM 2100F (JEOL) TEM with an accelerated voltage of 200 kV. The contents of C, H and S were analyzed by Flash EA 1112 (Thermo Fisher Scientific). The S/Pb ratio was confirmed by EPMA (JEOL, JXA-8,100). Fourier transform infrared spectroscopy (FT-IR) was obtained at a TENSOR-27 spectrometer (Bruker). Raman spectra were recorded using a LabRAM HR Evolution

(HORIBA) Raman spectrometer with the excitation wavelength of 532 nm at room temperature. X-ray photoelectron spectroscopy (XPS) was performed by AXIS Ultra-DLD ultrahigh vacuum photoemission spectroscopy system (Kratos Co.). Thermogravimetric analysis (TGA) was carried out by a TGA Q500 instrument with a heating rate of 10 °C·min<sup>-1</sup> under a nitrogen flow. Ultraviolet-visible diffused reflectance spectra (UV-Vis DRS) were collected with an UV-2000 (SHIMADZU) spectrophotometer at room temperature. Photoluminescence (PL) spectra were recorded at room temperature with a Hitachi F-4600 fluorescence spectrophotometer with the excitation wavelength of 390 nm. ESR spectra were collected on a Bruker ELEXSYS II E500 spectrometer.

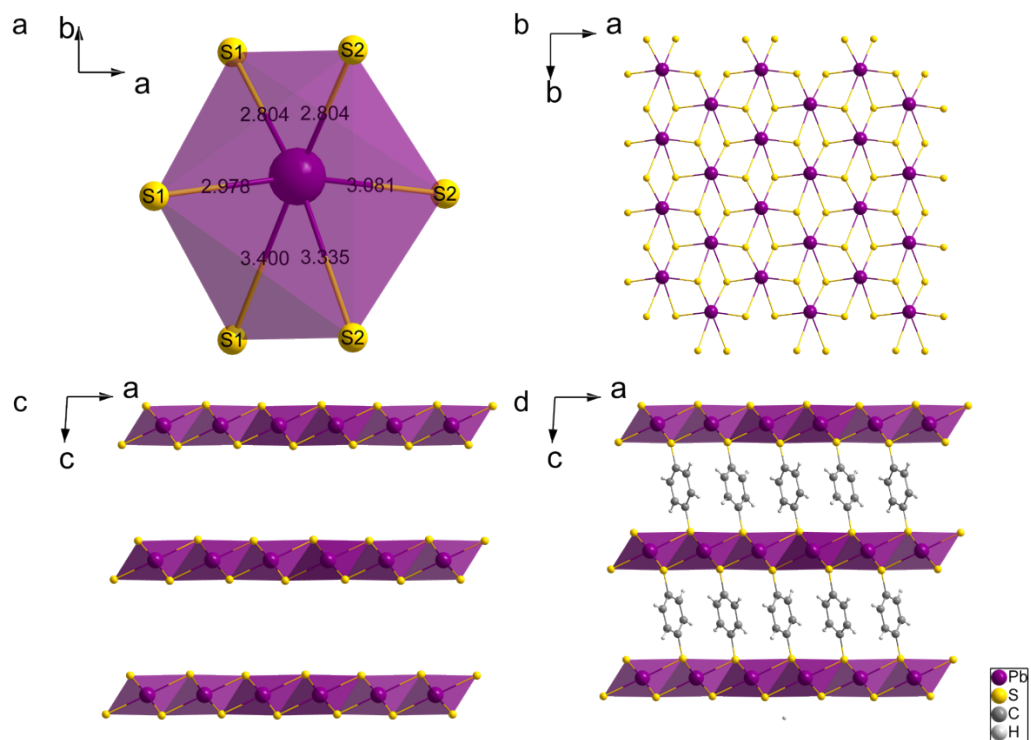


**Fig. S1** Amplified image of PXRD pattern of Pb-HBT in the  $2\theta$  range of  $10^\circ$  to  $80^\circ$ .

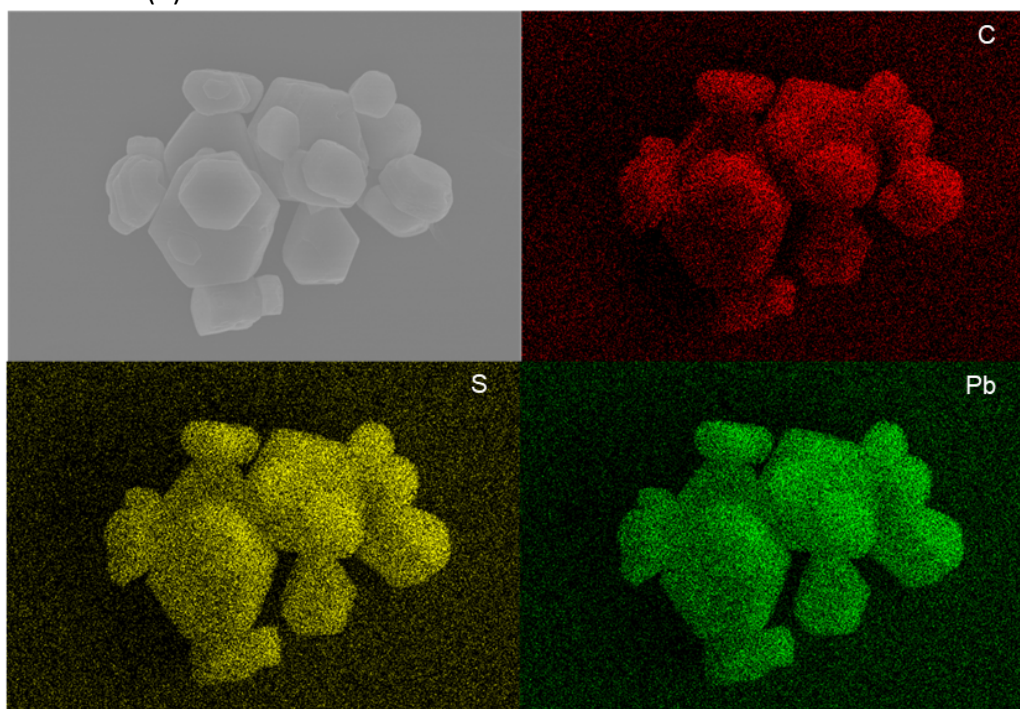


**Fig. S2** Amplified image of PXRD pattern of Pb-BDT in the  $2\theta$  range of  $15^\circ$  to  $80^\circ$ .

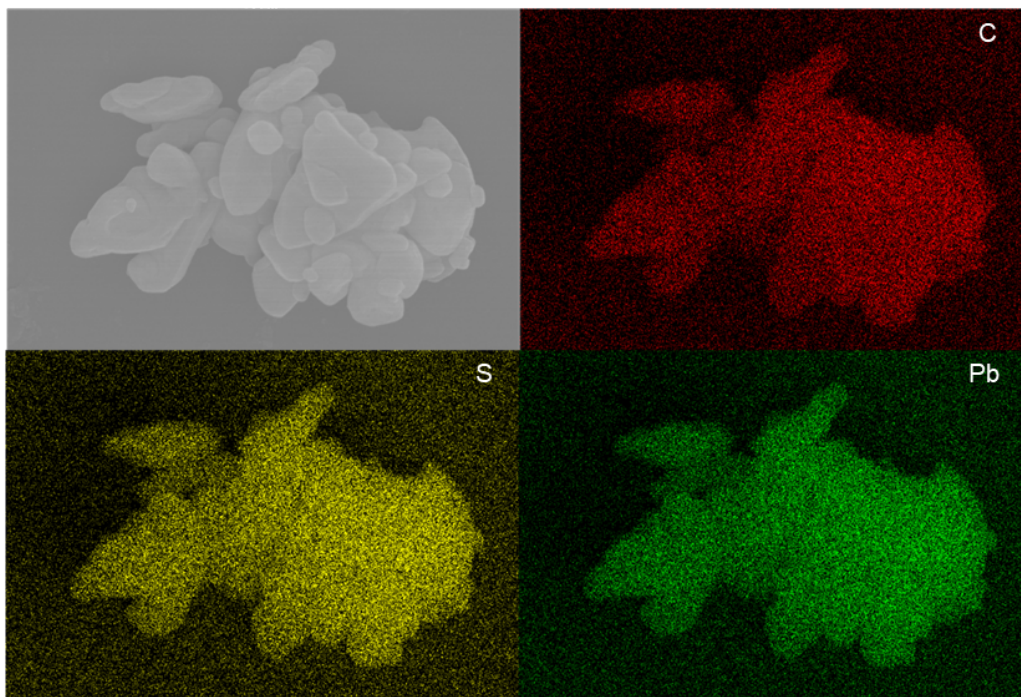




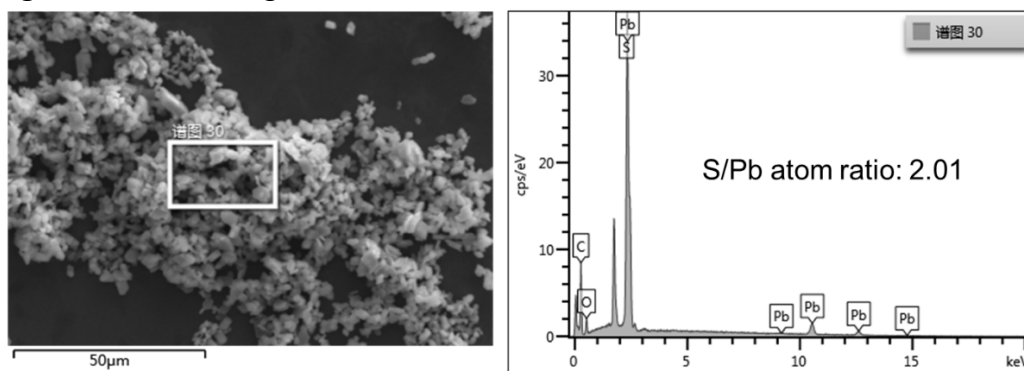
**Fig. S3** Crystal structure of Pb-BDT: (a) Coordination environments of Pb. (b, c) Pb-S 2D networks. (d) Extended structure of Pb-BDT.



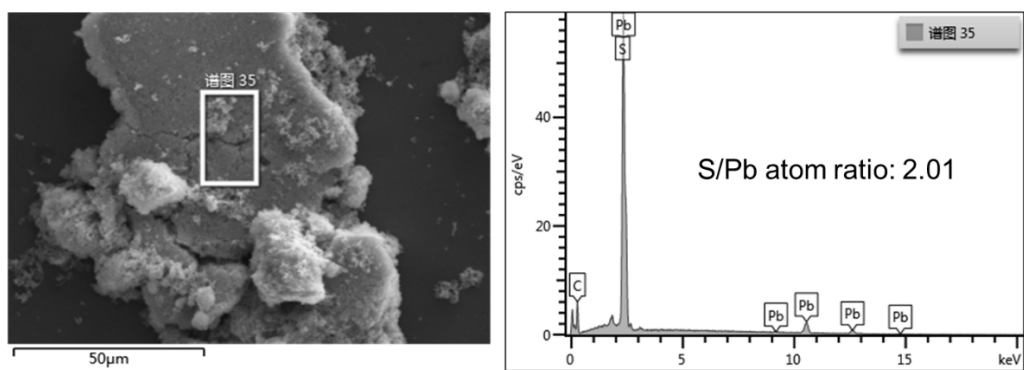
**Fig. S4** SEM-EDS images of Pb-HBT.



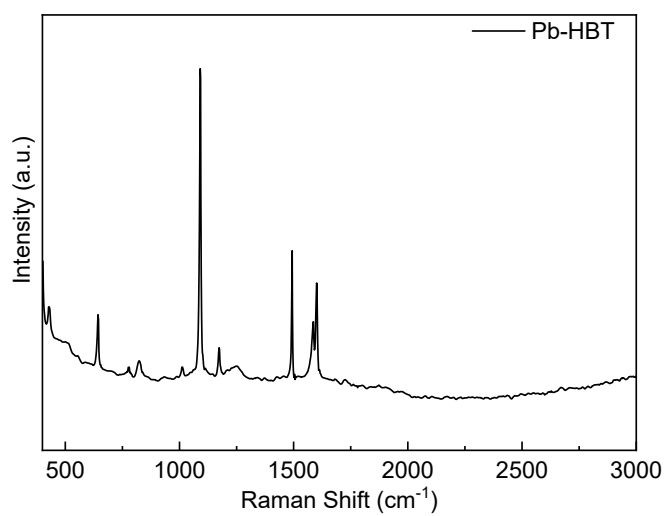
**Fig. S5** SEM-EDS images of Pb-BDT.



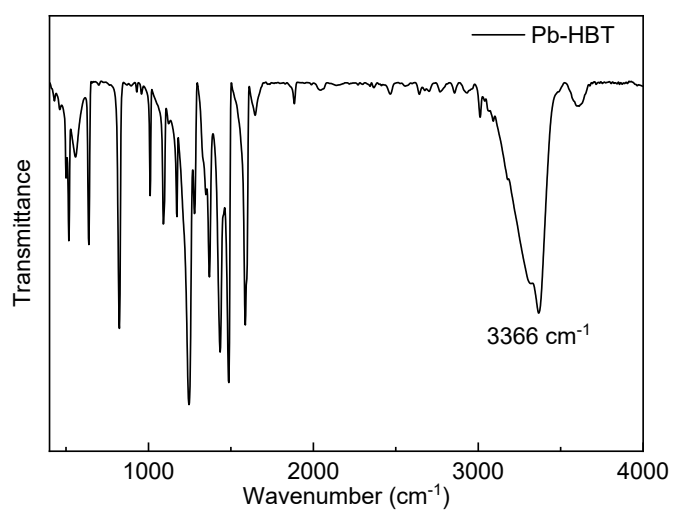
**Fig. S6** EPMA data of Pb-HBT.



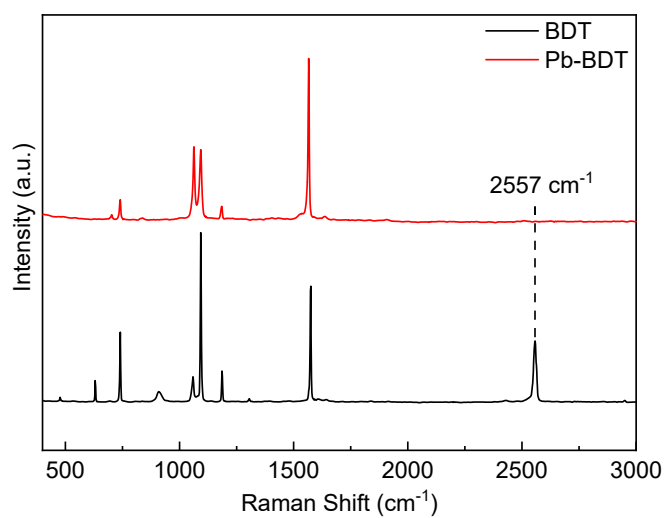
**Fig. S7** EPMA data of Pb-BDT.



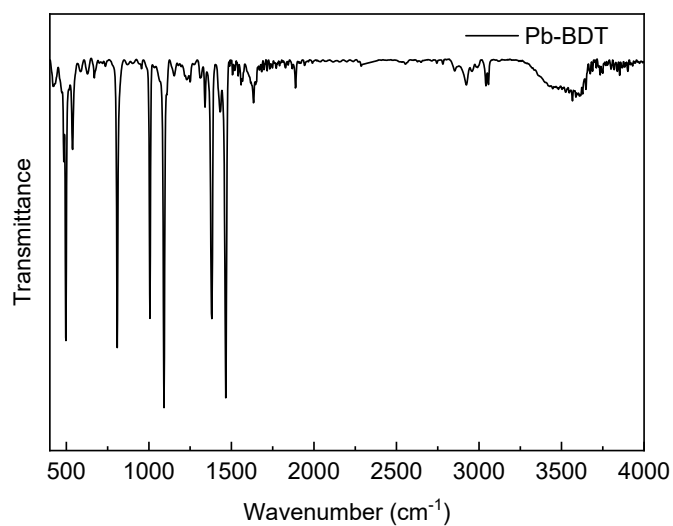
**Fig. S8** Raman spectrum of Pb-HBT.



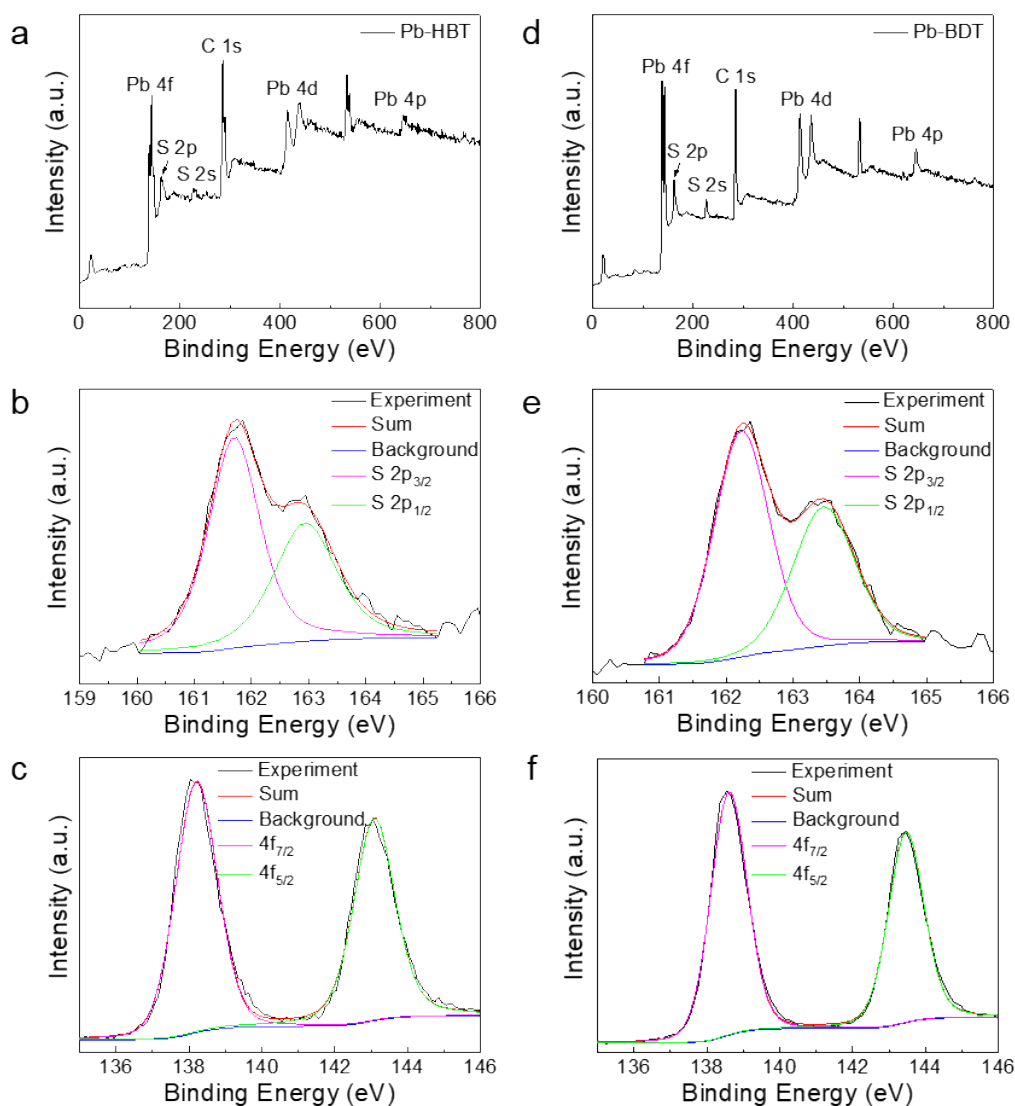
**Fig. S9** FT-IR spectrum of Pb-HBT.



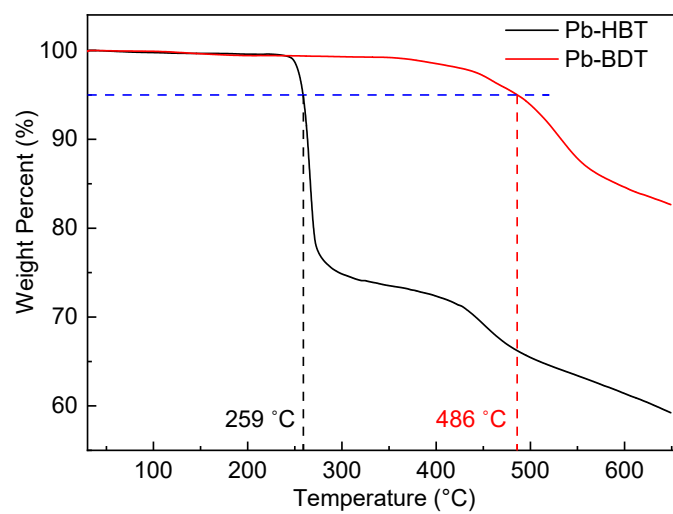
**Fig. S10** Raman spectra of BDT and Pb-BDT.



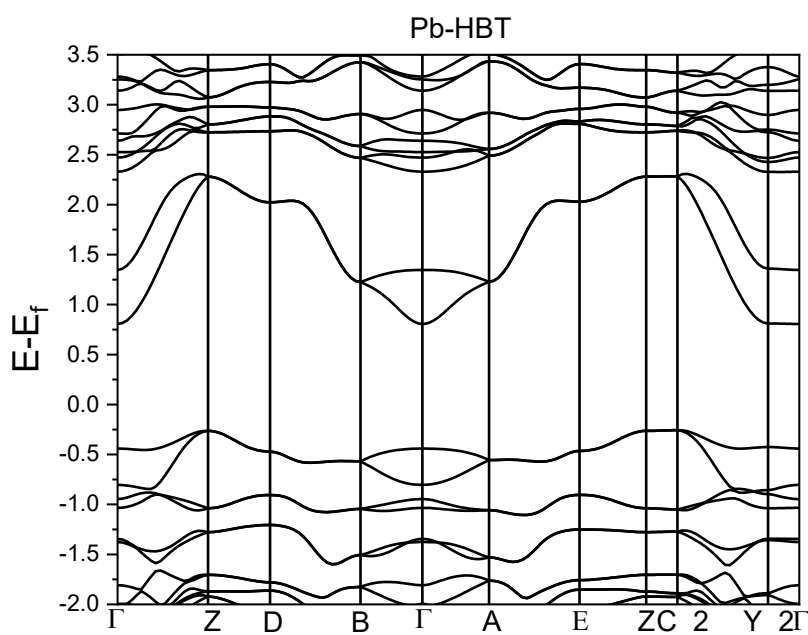
**Fig. S11** FT-IR spectrum of Pb-BDT.



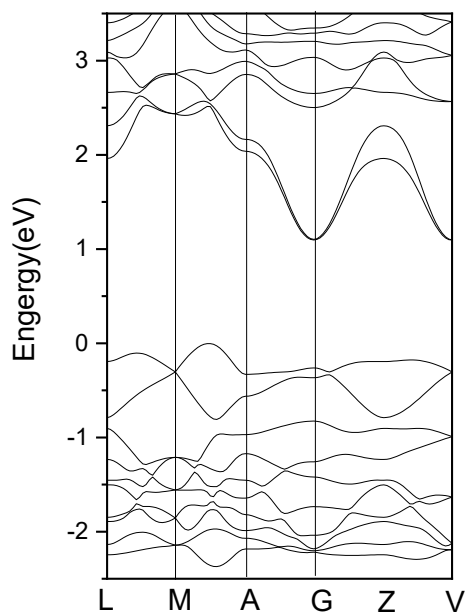
**Fig. S12** (a) The full XPS spectrum, (b) S 2p XPS spectrum and (c) Pb 4f XPS spectrum of Pb-HBT. (d) The full XPS spectrum, (e) S 2p XPS spectrum and (f) Pb 4f XPS spectrum of Pb-BDT.



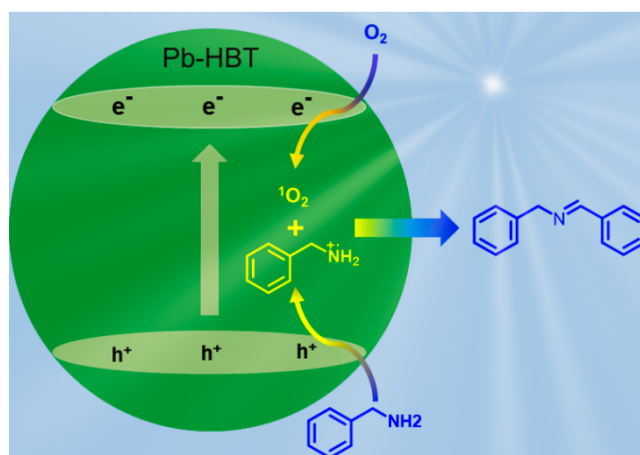
**Fig. S13** TGA curves of Pb-HBT and Pb-BDT.



**Fig. S14** Calculated band structure of Pb-HBT.



**Fig. S15** Calculated band structure of Pb-BDT.



**Scheme S1** Proposed reaction mechanism for the photocatalytic oxidation of benzylamine over the Pb-HBT.

**Table S1** Crystallographic data of Pb-HBT and Pb-BDT.

Empirical formula	PbC <sub>12</sub> S <sub>2</sub> O <sub>2</sub> H <sub>10</sub>	PbC <sub>6</sub> S <sub>2</sub> H <sub>4</sub>
Formula weight	457.52	347.41
Temperature, K	293	293
Wavelength, Å	1.540593	1.540593
Crystal system	Monoclinic	Monoclinic
space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c
<i>a</i> , Å	15.1207	7.4789(7)
<i>b</i> , Å	5.2004	5.2068(5)
<i>c</i> , Å	7.6325	17.4623(16)
$\beta$ , °	95.5358	93.3828(19)
Volume, Å <sup>3</sup>	597.367	678.83(11)
Z	2	4
Calculated density, Mg/m <sup>3</sup>	2.544	3.399
$\theta$ range for data collection, °	4 to 120	5 to 120
Refinement method	Rietveld	Rietveld
GOF	1.00	0.88
R <sub>p</sub> , %	6.85	2.69
R <sub>w</sub> p, %	9.52	3.58



**Table S2** Element analysis data of Pb-HBT and Pb-BDT.

	Elements	C (wt%)	H (wt%)	S (wt%)
Pb-HBT	Found	31.44	2.23	14.13
	Calculated	31.50	2.20	14.01
Pb-BDT	Found	21.00	1.26	18.98
	Calculated	20.74	1.16	18.46

**Table S3** Catalytic performances of various photocatalysts.

Catalysts	Conditions	Time (h)	Conv. (%)	Select. (%)	Production rate of <i>N</i> -benzylbenzaldimine ( $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ )	Ref.
TiO <sub>2</sub> (Degussa P25) (10 mg)	benzylamine (0.1 mmol), CH <sub>3</sub> CN (5 mL), air (1 atm). 100 W Hg lamp ( $\lambda \geq 300$ nm)	9	99	85	467.5	5
HNb <sub>3</sub> O <sub>8</sub> NS (20 mg)	benzylamine (0.25 mmol), CH <sub>3</sub> CN (10 mL), air, 300 W Xe lamp ( $\lambda > 420$ nm)	6	95.0	98.9	978.7	6
NH <sub>2</sub> -MIL-125(Ti) (5 mg)	benzylamine (0.1 mmol), CH <sub>3</sub> CN (2.0 mL), saturated O <sub>2</sub> , 300 W Xe lamp ( $420 < \lambda < 800$ nm)	12	73.0	86.0	523.2	7
n-NH <sub>2</sub> -MIL-125 (10 mg)	benzylamine (0.2 mmol), MeCN (4 mL), air, 25 °C, 300 W Xe lamp ( $350 < \lambda < 780$ nm).	9	98.5	99	1083.5	8
Cd(dcbpy) (10 mg)	benzylamine (0.48 mmol), DMF (5 ml), air, 300 W Xe lamp ( $350 < \lambda < 780$ nm)	7	99.1	>99	3397.7	9
PCN-222 (Zr-MOF) (5 mg)	benzylamine (0.1 mmol), CH <sub>3</sub> CN (3 mL), air, 100 mW cm <sup>-2</sup> Xe lamp ( $\lambda \geq 420$ nm).	1	100	100	10000.0	10
Pb-BDT (5 mg)	benzylamine (0.5 mmol), CH <sub>3</sub> CN (10 mL), air, 300 W Xe lamp ( $350 < \lambda < 780$ nm)	10	100	96.8	4838.0	This work
Pb-HBT (5 mg)	benzylamine (0.5 mmol), CH <sub>3</sub> CN (10 mL), air, 300 W Xe lamp ( $350 < \lambda < 780$ nm)	9	100	90.2	5010.6	This work

**Table S4** Effect of scavengers on benzylamine oxidation catalyzed by Pb-HBT.<sup>[a]</sup>

Scavengers	Quenching group	Conv. (%) <sup>[b]</sup>	Select. (%) <sup>[b]</sup>
beta-carotene	$^1\text{O}_2$	67.5	100.0
BQ	$\text{O}_2^{\bullet-}$	94.6	98.5

<sup>[a]</sup>Reaction conditions: 5 mg catalyst, 5 mL acetonitrile, 0.5 mmol benzylamine, 2 equivalents of scavenger, 9 h, 300 W Xe lamp ( $350 < \lambda < 780$  nm). <sup>[b]</sup> Conv. and Select. were determined by  $^1\text{H}$  NMR.

The conversion of benzylamine at 9 h decreases from 100% to 67.5% with beta-carotene as a scavenger to capture  $^1\text{O}_2$ , revealing that  $^1\text{O}_2$  is a reactive oxygen species (ROS) for the photocatalytic oxidation of benzylamine. In contrast, the conversion of benzylamine at 9 h only decreases to 94.6% when BQ as a scavenger to capture  $\text{O}_2^{\bullet-}$ . These results suggest that the main ROS in the photocatalytic reactions is  $^1\text{O}_2$ .

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