

Hybrid Benzidinium Lead Iodide Perovskite with 1D structure as Photoinduced Electron Transfer Photocatalyst

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Experimental section

Materials

Milliq water was obtained using a IQ 7000 purifying system. Ethanol absolute (analytical grade), tetrahydrofurane anhydrous 99.99 % (THF), diethyl ether (puriss. p.a. ACS reagent dried 00.5 % GC 0.0075 % water), hexane (HPLC grade), toluene (chromasolvr for HPLC 99.9 %) and N,N-dimethylformamide anhydrous 99.8 % (DMF) were purchased from Scharlau. Hydrazobenzene (< 10 % azobenzene), tetradecane (≥ 99 %), aqueous hydriodic acid (HI, 55 wt%), aqueous hydrochloric acid (HCl, 37 wt%), lead iodide (99.999 % trace metals basis) (PbI₂), cis-stilbene (96 %) and trans-stilbene (96 %) were purchased from Sigma Aldrich. Perfluoropolyether was purchased from Chemos GmbH % Co. KG. NaOH micropearls (98 %) were purchased from ACROS. All solvents and reagents were used without further purification.

Synthesis

Benzidine (1) preparation

Commercial hydrazobenzene (1 g) was dissolved in ethanol/water (60 mL/40 mL) solution with stirring, followed by adding 10 mL concentrated HCl (~37 wt%). After 10 mins reaction, the solution was concentrated under reduced pressure evaporation by about one third of the initial volume and benzidine precipitate was obtained by neutralizing the solution with 1 M NaOH. The final obtained product was isolated by filtration and washed with H₂O/EtOH. The purity of benzidine was confirmed by ¹H NMR and IR spectroscopy.

Benzidinium Diiodide (2) preparation.

The Benzidinium diiodide was obtained by protonation of benzidine. Specifically, 0.92 g of benzidine (5 mmol) was dissolved in 20 mL THF under stirring at 0 °C (ice bath), then 1.6 mL concentrated HI aqueous solution (55 wt%) was added to the solution drop by drop. After 2 hours of reaction, the benzidinium diiodide salt was precipitated by

adding 20 mL of cold diethyl ether into the solution. The final product was filtered and washed with diethyl ether and characterized by IR spectroscopy and combustion elemental analysis.

Benzidinium lead iodide perovskite (Material 3) preparation

Perovskite either as a fine powder or as single macro crystal were both synthesized in this work. The preparation method for fine powder is as follow. PbI_2 (184 mg, 0.4 mmol) and benzidinium diiodide **2** (88 mg, 0.2 mmol) were dissolved in 4 mL DMF under stirring. Then 10 mL toluene were added to the precursor solution to precipitate the perovskite. The obtained hybrid benzidinium lead perovskite **3** as a fine powder was isolated by filtration and washed with diethyl ether, then, dried under vacuum.

The single crystal was obtained by slow diffusion of toluene vapor into the perovskite precursor solution. Specifically, the aforementioned perovskite precursor solution was diluted to 0.05 M in a vial, and then put into a sealed bottle which was filled with some amount of toluene. The single crystal can be formed in the vial within 1 day.

Characterization

Single-crystal X-ray structure analysis.

One crystal of **3** of suitable size for X-ray diffraction analysis was coated with dry perfluoropolyether and mounted on glass fibers and fixed in a cold nitrogen stream ($T = 193 \text{ K}$) to the goniometer head. Data collection was performed on a Bruker-Nonius X8Apex-II CCD diffractometer, using monochromatic radiation $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$, by means of ω and ϕ scans with a width of 0.50 degree. The data were reduced (SAINT) [1] and corrected for absorption effects by the multi-scan method (SADABS) [2]. The structures were solved by direct methods (SIR-2002) [3] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12) [4] minimizing $w[F_o^2 - F_c^2]^2$. All the non-hydrogen atoms were refined anisotropically, while C-H hydrogen atoms were placed in geometrically calculated positions using a riding model. The asymmetric unit of the structure contains a set of independent PbI_3 , formed in turn by two independent half lead-atoms that match an inversion center, both metals being separated by half of crystallographic a -axis, i.e. $4.041(2) \text{ \AA}$. By symmetry and translation of the unit cell this motif forms a chain-link of the 1D anionic polymer that develops along the crystallographic a -axis. In addition, the asymmetric unit has half a molecule of dication [1,1'-biphenyl-4,4'-diyl]diammonium, which appear positionally disordered in two halves with the same occupancy factors. These halves are close to an inversion center at the end of the phenyl group in such a way that by symmetry the entire molecule of the dication is generated. Two molecules of crystallization of DMF complete the asymmetric unit, one of which appears disordered with the ratio of occupancy factors of 57:43. Some

geometric restraints (DFIX command), the ADP restraint SIMU and the rigid bond restraint DELU were used to make the geometric and ADP values of the disordered atoms more reasonable. A summary of cell parameters, data collection, structure solution, and the refinement of this crystal structure is provided below (Table S2, Fig. S9 and Fig. S10). The corresponding crystallographic data were deposited with the Cambridge Crystallographic Data Centre as supplementary publications. CCDC 1902819. The data can be obtained free of charge *via*: <https://www.ccdc.cam.ac.uk/structures/>

Powder X-ray diffraction (XRD) patterns were collected with a Shimadzu XRD-7000 diffractometer by using $\text{Cu}_{\text{K}\alpha}$ radiation ($\lambda=1.5418\text{\AA}$), operation at 40 kV and 40 mA at a scanning speed of 10° per min in the $2-90^\circ$ 2θ range.

Optical microscopy images were obtained with a Leica DM4000 microscope coupled with an Avantes AvaSpec-2048 Fiber Optic Spectrometer and SEM images were acquired with a JEOL JSM 6300 apparatus equipped with an X-MAX detector of OXFORD INSTRUMENTS

ICP-OES were acquired on an Agilent Esquire 6000 instrument. Combustion Elemental analyses were measured on an Euro EA Elemental AnaSlyser Eurovector.

Diffuse reflectance UV/Vis spectra (DRS) in the range of 200 - 800 nm were collected in a Varian Cary 5000 spectrophotometer from Varian. Steady-state fluorescence measurements were carried out using a Photon Technology International (PTI, Germany) LPS-220B spectrofluorometer, equipped with a monochromator in the range of 200–700 nm. The excitation wavelength was 390 nm and emission was recorded from 420–650 nm by 1 nm steps with an integration time of 0.1 s, averaging three measurements. Time-resolved fluorescence measurements were performed with an Easylife X Filter Fluorescence Lifetime Fluorometer (PTI, Canada) using a 380 nm filter.

X-ray photoelectron spectra (XPS) were measured on a SPECS spectrometer equipped with a Phoibos 150 9MCD detector using a non monochromatic X-ray source (Al) operating at 200 W. The samples were evacuated in the prechamber of the spectrometer at 1×10^{-9} mbar. The measured intensity ratios of the components were obtained from the area of the corresponding peaks after nonlinear Shirley-type background subtraction and corrected by the transition function of the spectrometer.

Gas chromatography (GC) analysis were performed with a Varian CP-3800 apparatus equipped with an Carbowax column (15m x 0.32 mm x 0.25 μm).

^1H NMR a Bruker AV300 (300 MHz) spectrometer, Chemical shifts of ^1H signals are reported in ppm using the solvent peak as internal standard (CD_2Cl_2 : 5.27 ppm, Ethanol- D_6 : 5.29 ppm). Data are reported as follows: chemical

shift, integral, multiplicity (s = singlet, br = broad, d = doublet, t = triplet, sept = septuplet, m = multiplet), coupling constants (Hz) and assignment.

Benzidine ^1H NMR: (300MHz, Ethanol- D_6) δ =6.75-6.79 (d, 4H; CH-Ph), 7.26-7.30(d, 4H; CH-Ph).

Trans-stilbene ^1H NMR: (300MHz, CD_2Cl_2) δ =7.10 (s, 2H; CH-C=C), 7.17-7.26 (t, 2H; CH-Ph), 7.27-7.37 ((t, 4H; CH-Ph), 7.45-7.55 (d, 4H; CH-Ph).

Photoinduced isomerization reactions

The photoinduced isomerization reactions were performed under visible light irradiation ($\lambda > 450$ nm) using a 300 W Xe lamp equipped with 450 nm filter. Specifically, cis-stilbene (0.25 mmol) was dissolved in 1.5 mL of toluene and 0.15 mL tetradecane was added to the above solution as the internal standard to quantify the amount of cis-stilbene. 2 wt% (4.1 mg) PbI_3 Benzidinium perovskite was added as photocatalyst. Prior to irradiation, the reactor was purged with argon. The course of cis-stilbene conversion was followed periodically by injecting aliquots of the reaction mixture in the GC. The final products were isolated and characterized by ^1H NMR spectroscopy.

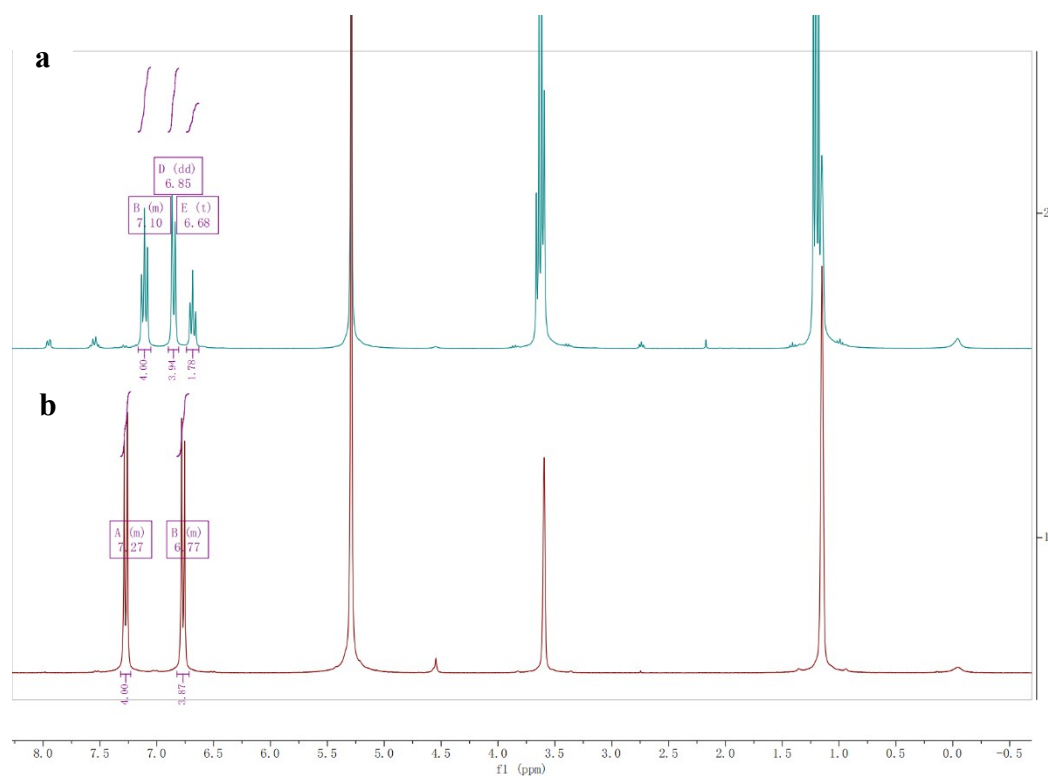


Fig. S1. ^1H NMR results of hydrazobenzene (a) and benzidine (b).

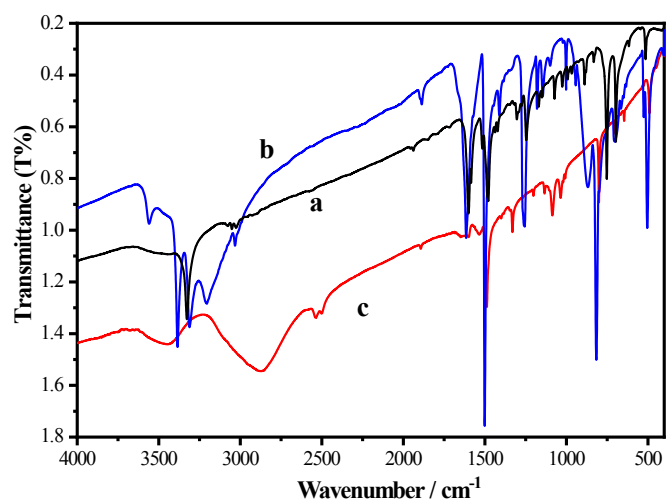


Fig. S2. Infrared spectra of Hydrazobenzene (a), Benzidine (b), and Benzidinium diiodide (c)

Table S1. Combustion Elemental analysis results and theoretic proportion of Benzidinium iodide

Type	N %	C %	H %	Rest %	Weight (mg)
Experimental proportion	6.483	33.038	3.298	57.181	1.673
Theoretic proportion	6.360	32.709	3.180	57.696	-

Table S2. Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) and Combustion Elemental analysis results of hybrid perovskite 3

Element	Combustion Elemental analysis				ICP-OES
	N (wt%)	C (wt%)	H (wt%)	Rest (wt%) (Pb, I, O)	Pb(wt%)

Proportion	2.574	11.366	1.453	84.607	28.4
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Detailed Calculation process for experimental formula of hybrid perovskite **3** :

The Atomic proportion of each element $\text{Atom}\% = \text{Weight proportion}/\text{Molecular weight}$, then

Pb (Atom %) = 0.137, N (Atom %) = 0.184, C (Atom %) = 0.947, H (Atom %) = 1.453

Normalizing the number of Pb to be 1, then,

$n(\text{Pb}) = 1$, $n(\text{N}) = 1.343$, $n(\text{C}) = 6.9$, $n(\text{H}) = 10.6$

Assuming each Hybrid perovskite **3** contains half benzidinium, of which the formula is $\text{C}_6\text{H}_7\text{N}$, the ratio of the rest carbon ($\text{C}_{0.9}$) and Nitrogen ($\text{N}_{0.343}$) is $\sim 2.6 : 1$, which is coincidence with the C, N ratio of DMF. So, the number of DMF in this molecular is ~ 0.3 , and the weight proportion of oxygen in hybrid perovskite **3** could then be obtained as 0.66 %. After taking out of the weight proportion of O and Pb, the rest weight proportion is from iodine, and the value of which is 55.5 %. Based on that value and Repeat the calculation process we can get the number of I in the formula is ~ 3 .

So, the experimental formula of Hybrid perovskite **3** is $\text{PbI}_3(\text{Benzidinium})_{0.5} \text{DMF}_{0.3}$

Table S3: Crystal data and structure refining for **3**.

Empirical formula	$\text{C}_{12}\text{H}_{21}\text{I}_3\text{N}_3\text{O}_2\text{Pb}$	
	[I_3Pb , $\text{C}_6\text{H}_7\text{N}$, $2(\text{C}_3\text{H}_7\text{NO})$]	
Formula weight	827.21	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$\text{P}\bar{1}$	
Unit cell dimensions	$a = 8.0816(8)$ Å	$\alpha = 97.876(4)^\circ$.
	$b = 12.3906(12)$ Å	$\beta = 106.389(4)^\circ$.
	$c = 12.9013(11)$ Å	$\gamma = 104.083(4)^\circ$.
Volume	1172.40(19) Å ³	
Z	2	
Density (calculated)	2.343 Mg/m ³	
Absorption coefficient	11.151 mm ⁻¹	

F(000)	742
Crystal size	0.400 x 0.100 x 0.050 mm ³
Theta range for data collection	2.676 to 25.248°.
Index ranges	-9<=h<=9, -14<=k<=14, -15<=l<=15
Reflections collected	15886
Independent reflections	4246 [R(int) = 0.0306]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.4715
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4246 / 352 / 307
Goodness-of-fit on F ²	1.070
Final R indices [I>2sigma(I)]	R1 = 0.0374, wR2 = 0.1253
R indices (all data)	R1 = 0.0415, wR2 = 0.1303
Extinction coefficient	n/a
Largest diff. peak and hole	2.484 and -1.683 e.Å ⁻³

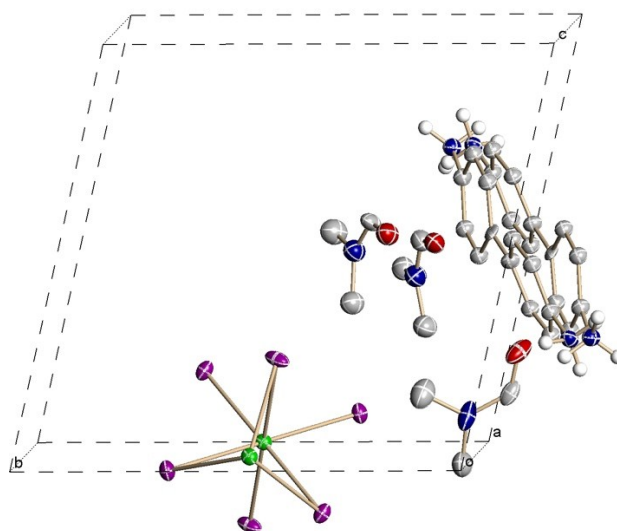


Fig. S3: ORTEP drawing of the crystal asymmetric unit of **3** view along a-axis with thermal ellipsoids set at a 30% probability level, hydrogen atoms and one part of modelling of a disordered DMF solvent molecule are omitted for clarity.

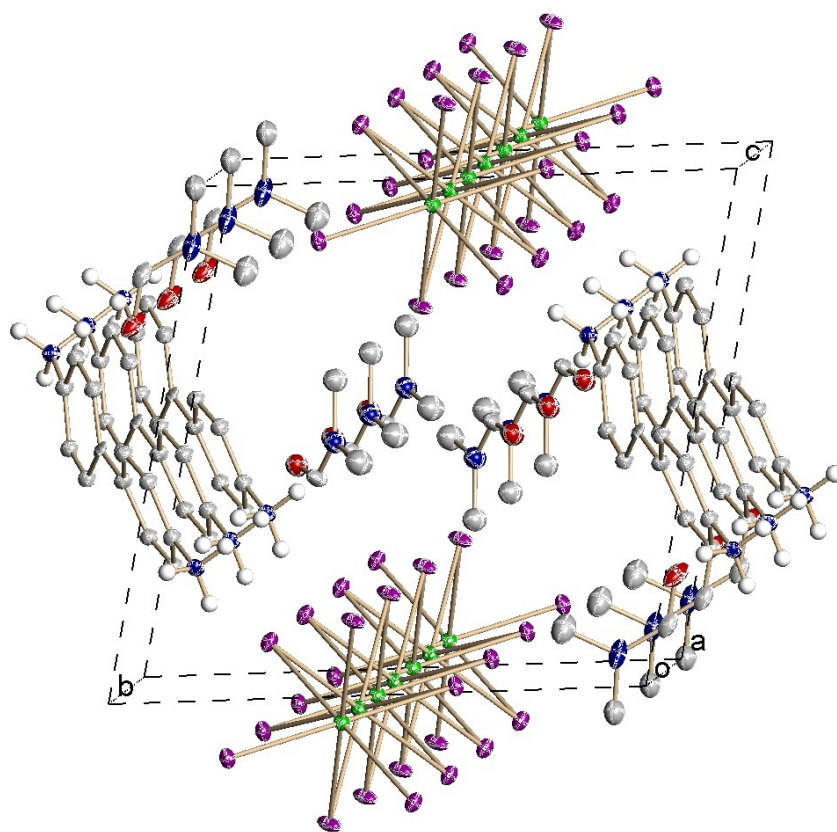


Fig. S4: Partial packing diagram of **3** view along a-axis with thermal ellipsoids set at a 30% probability level, hydrogen atoms are omitted for clarity.

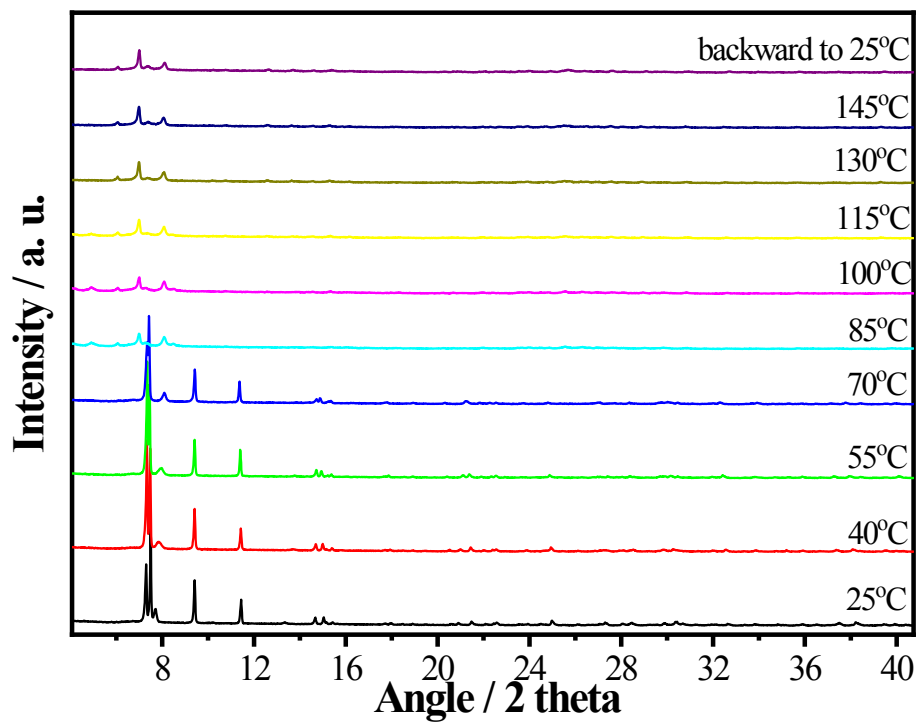


Fig. S5. Thermo-stability results of hybrid perovskite 3 by in-situ XRD monitoring.

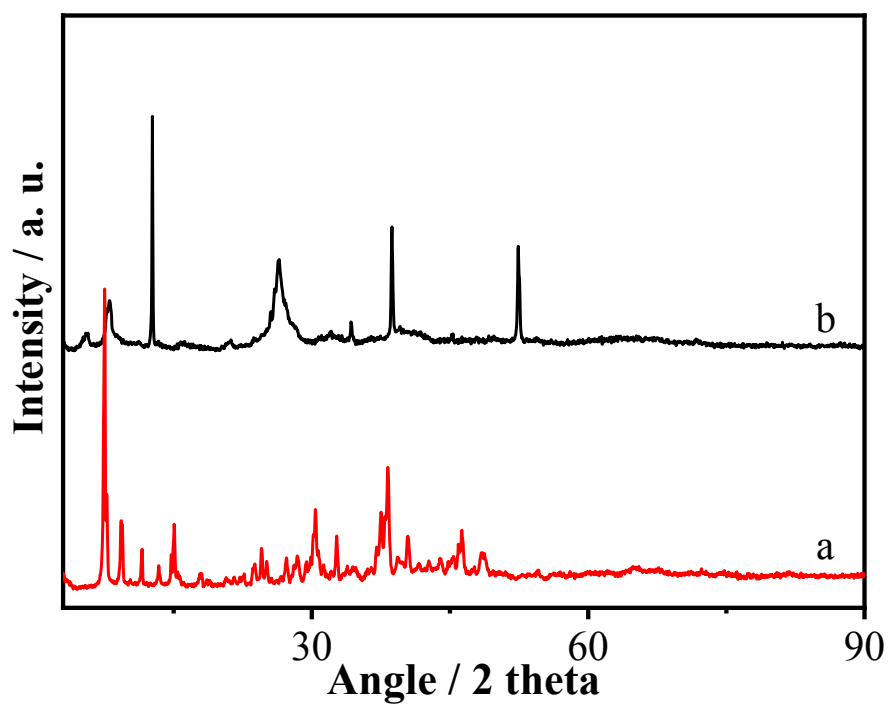


Fig. S6. XRD patterns of hybrid perovskite 3 (a) and perovskite 3 after disperse in acetonitrile for 3 h (b).

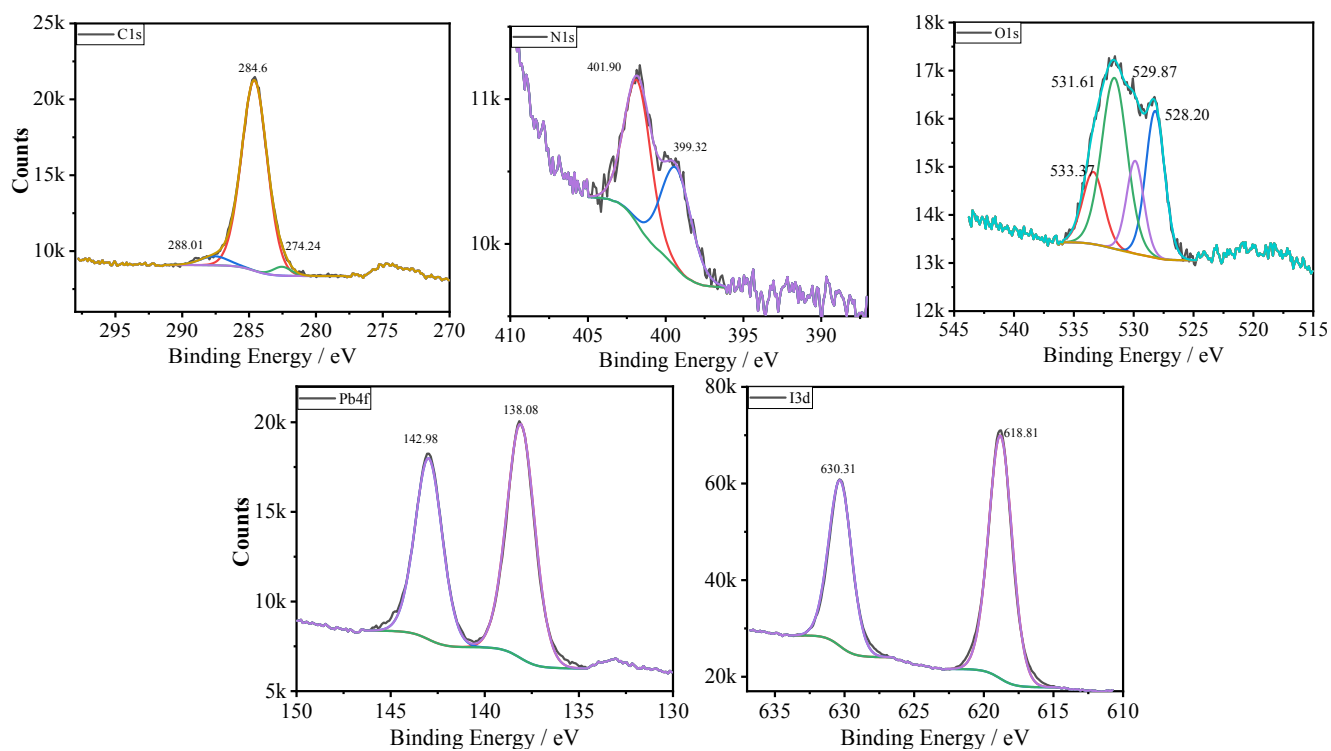


Fig. S7 XPS results of hybrid perovskite 3.

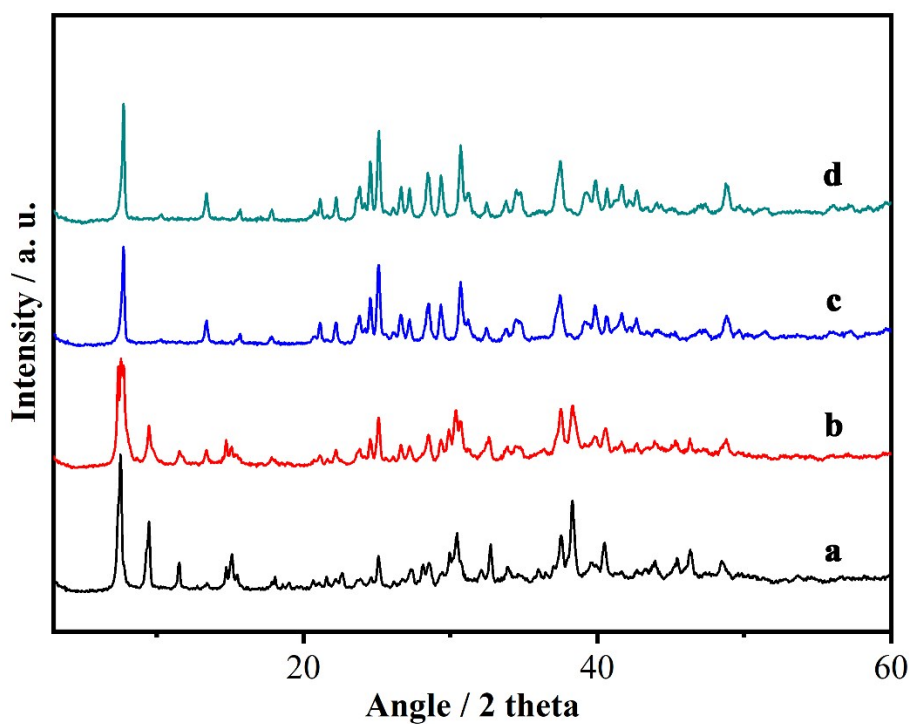


Fig. S8 XRD Patterns of Hybrid perovskite 3 before disperse in hexane (a) and after dispersed in hexane with 4 h (b), 7 h (c), 18 h (d).

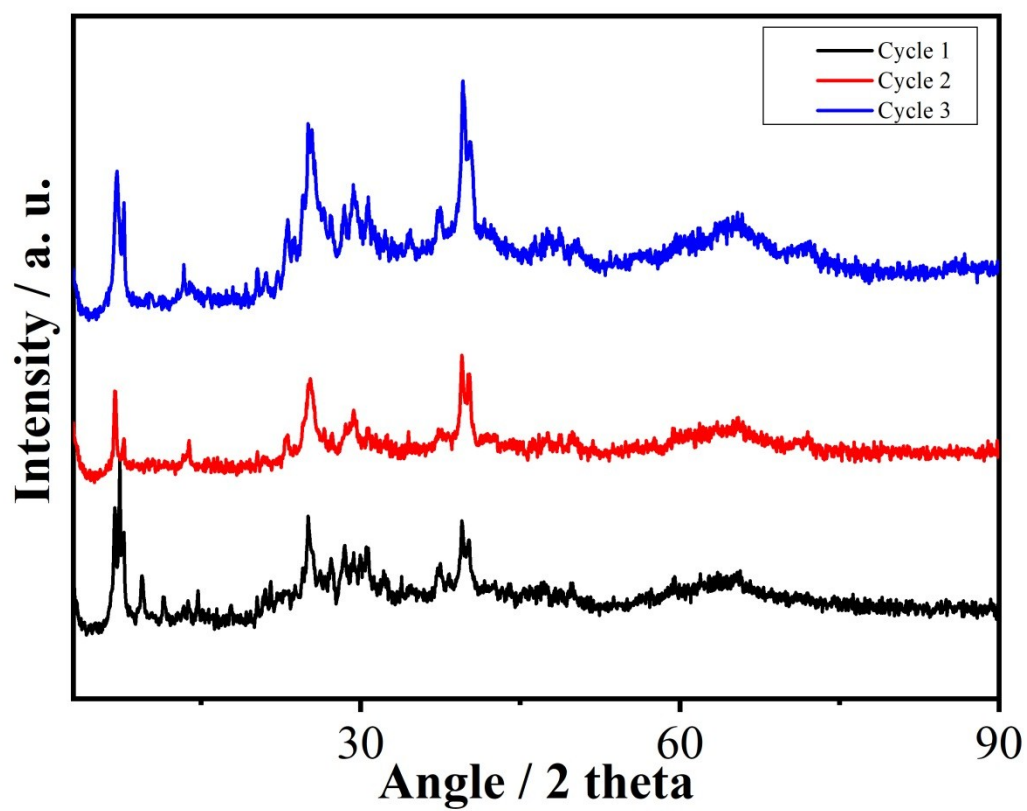


Fig. S9 XRD Patterns of Hybrid perovskite **3** after each use as photocatalyst for cis-to-trans stilbene isomerization reaction.

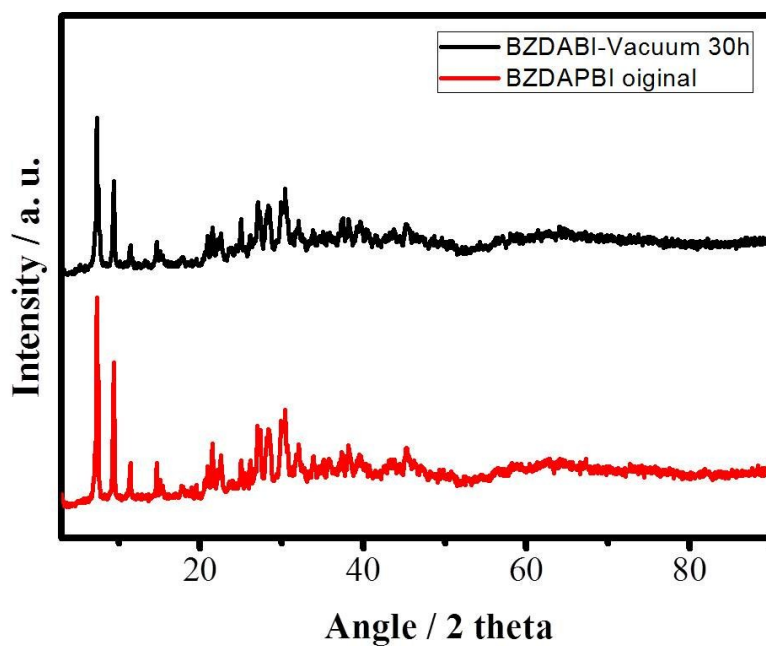


Fig. S10 XRD Patterns of Hybrid perovskite **3** after and before 30 h vacuum at 50 °C

Table S4. Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) and Combustion Elemental analysis (EA) results of fresh hybrid perovskite **3**, after hexane exposure and after photocatalytic reaction.

Element	EA			ICP-OES
	N (wt%)	C (wt%)	H (wt%)	Pb(wt%)
Before in Hexane	2.574	11.366	1.453	28.4
After in hexane	2.51	12.5	1.52	31.80

After reaction	2.07	11.96	1.32	33.39
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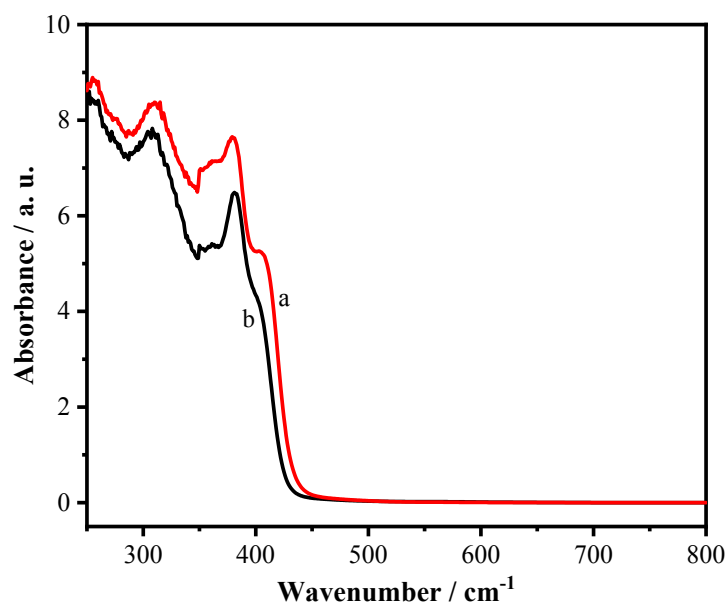


Fig. S11 Diffuse reflection spectrum of hybrid perovskite **3** before disperse in hexane (a), and after disperse in hexane for 18h (b).

[1] Bruker (2007). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.

[2] Bruker (2001). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.

[3] C. M. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Poliori, R. Spagna, *SIR2002*: the program; (2003). *J. Appl. Cryst.* **36**, 1103–1103.

[4] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, **2008**, 64, 112-122.