Supporting Information

A novel 3-D lead-iodide polymer based on the linkage of rare binuclear $[Pb_2I]^{3+}$ cations and anionic bis(pyrazinyl)-trizole bridges

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General Remarks. All analytical grade chemicals were obtained commercially and used without further purification. Elemental analyses (C, N and H) were performed using a PE2400 II elemental analyzer. IR spectra were obtained from a powdered sample pelletized with KBr on an ABB Bomen MB 102 series IR spectrophotometer in the range of 400–4000cm^{-1}. PXRD patterns were obtained using a Bruker D8 Advance XRD diffractometer with Cu Kα radiation (λ = 1.54056 Å). The solide-state UV/Vis spectra were measured at room temperature using a PE Lambda 900 UV/Vis spectrophotometer. The photoluminescence spectra were recorded at room temperature with a modular double grating excitation spectrofluorimeter with a TRIAX 320 emission monochromator (Fluorolog-3, Horiba Scientific) coupled to an R928 Hamamatsu photomultiplier.

Crystal Structure Determinations

The intensity data of **1** were collected on a Bruker diffractometer-SMART-APEX II using a ω-scan method with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Data reduction and absorption corrections were performed using the SAINT and SADABS software packages, respectively. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 using the SHELXL-97 program. The non-hydrogen atoms were refined anisotropically. H atoms were placed in idealized locations and refined as riding. Technical details of data collections and refinement are summarized in Table S1.

Table S1 Crystallographic data for **1**.

	1
formula	$C_{30}H_{18}N_{21}IPb_2$
Fw	1213.95
crystal system	orthorhombic
space group	Pbcn

a, Å	13.065(4)
b, Å	15.691(5)
c, Å	16.493(5)
V, Å^3	3381.2(17)
Z	4
T, K	293(2)
Calcd density,Mg.m^{-3}	2.383
F(*000*)	2248
2θ(max), deg	50.996
Total reflns collected	15619
Unique reflns	3137
No. of param	245
*R*1[*I*>2σ(*I*)]	0.0378
*wR*2(all data)	0.0856

Table S2 Some important bond lengths (Å) and angles (°) of **1**.

Pb-N	2.467(6)-2.825(1)	Pb-I(weak bond)	4.153(1)
Pb-N (weak bond)	2.9617(7)-3.1333(7)	N-Pb-N	72.1(2)-140.5(2)

Electrode preparation and photocurrent measurement

The working electrodes for photocurrent measurements were prepared by following processes. 12 mg of microcrystal sample was dispersed into a mixed solution of ethanol (2 mL) and Nafion (50 μL), and followed by ultrasonic treatment for 0.5 h. Then, 80 μL of above slurry was coated onto the FTO glass (F-doped SnO_2) with an effective area of 1 cm^2 and dried naturally at room temperature. The photocurrent experiment was performed on a CHI650E electrochemistry work station in a three-electrode system, the sample coated FTO glass as the working electrode, a Pt slice as auxiliary electrode and a saturated calomel electrode (SCE) as reference electrode. The supporting electrolyte solution was 0.1 mol/L Na_2SO_4 aqueous solution (500 mL). A 450 W high

pressure Xe lamp with 420 nm was used as the illumination source. The lamp was kept on continuously, and a manual shutter was used to block exposure of the sample to the light. The sample was typically irradiated at intervals of 50 s.

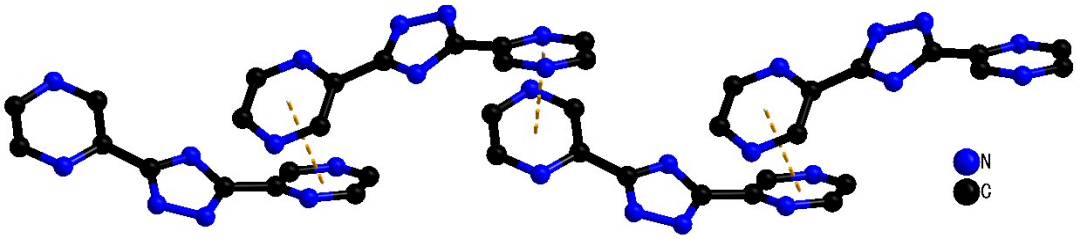

Fig. S1 The π···π stacking interactions between neighbor pyrazine groups.

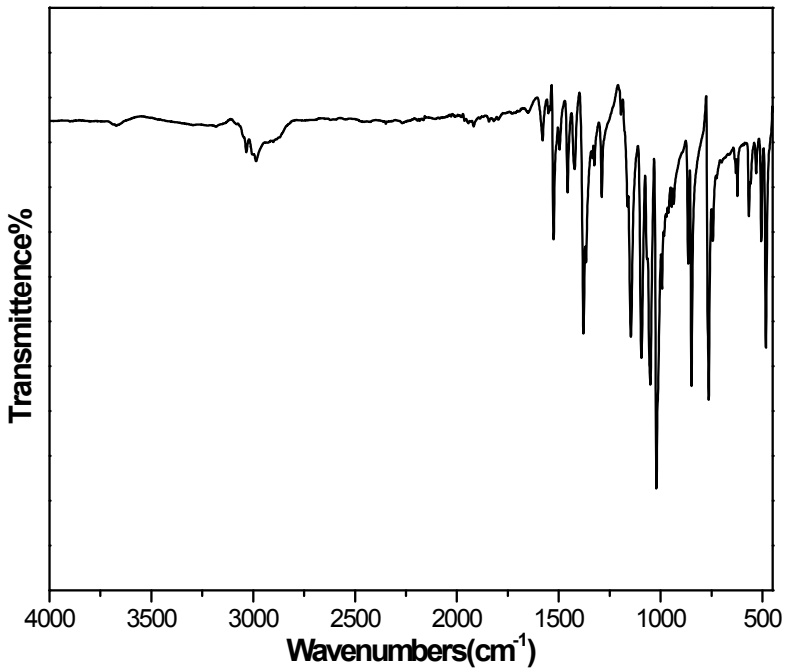

Fig. S2 The IR spectrum of **1**.

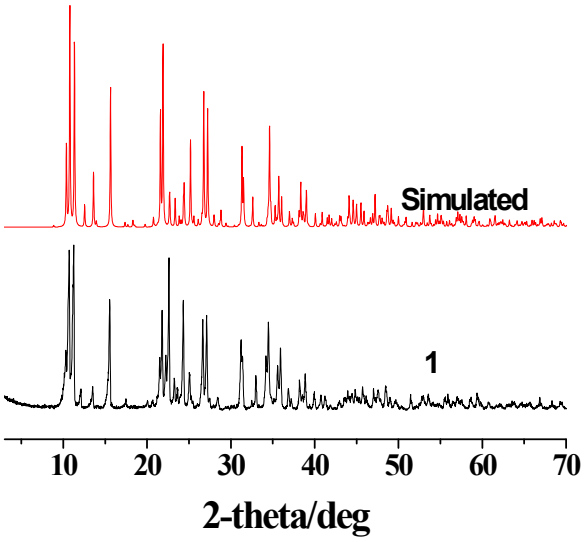

Fig. S3 Simulated and experimental powder XRD patterns of **1**.