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Supporting Information

Coupling an Organic Photosensitizer and Inorganic Framework into a Single-Phase Material that Shows Visible-Light Photocurrent Response

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1. Experimental Section

General Consideration.

All chemicals were commercially available and were used as received. All solvents were used without any further treatments. All manipulations were performed in air. Powder X-ray diffractometry spectroscopy (PXRD) data were collected on a Rigaku Smartlab X-ray diffractometer with CuKα radiation (λ = 1.5418 Å). Infrared spectra were collected on a Thermo Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. Cyclic voltammetry (CV) and Mott-Schottky measurements were performed using AutoLab PGSTAT302N equipment. The diffuse reflection spectrum of **1** was measured by UV−vis−NIR spectrophotometer PE Lambda950 at Instrument Analysis Center of Xi'an Jiaotong University.

Single crystal X-ray diffraction.

Crystal data was collected on a Bruker Apex CCD area-detector diffractometer using MoKα (λ = 0.71073 Å) radiation. The structures were solved using direct methods and refined with a full-matrix least-squares technique using OLEX2 programpackage.[1] Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. CCDC-1843769 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $[Ru(bpy)_3](PF_6)_2$. The two-step synthesis procedure is according to a reported method.[2]

Firstly, preparation of *cis*-$Ru(bpy)_2Cl_2\cdot 2H_2O$: $RuCl_3\cdot 3H_2O$ (3.9 g, 15 mmol), 2,2'-Bipyridine (4.7 g, 30 mmol), and LiCl (4.2 g, 100 mmol) were added to 100 mL DMF, affording a dark slurry. The mixture was heated at 170 °C and refluxed for 8 hours. After cooling down to room temperature, 250 mL acetone was added and the solution was stored at 0 °C overnight, which gave dark green product. The solid was washed with water and diethyl ether and dried in air, yields 63 % based on Ru.

Finally, synthesis of $[Ru(bpy)_3](PF_6)_2$: under argon atmosphere, *cis*-$Ru(bpy)_2Cl_2\cdot 2H_2O$ (3.0 g, 5.8 mmol), 2,2'-Bipyridine (1.5 g, 10 mmol) were added to the 100 mL degased mixture of H_2O/EtOH (1:1 in v/v), generating a dark suspension. Then the mixture was heated at 130 °C for 6 hours, the suspension became clear solution and a color change from dark green to wine red was observed. Subsequently, the solution was concentrated and NH_4PF_6 (3.3 g, 20 mmol) was added, which afforded light orange precipitate as product. The solid was filtrated and washed with water and diethyl ether, dried in air (*ca*. 50 % based on Ru).

Synthesis of 1.

In a 15 mL Teflon-lined stainless steel reactor, slurry of tin (100 mg, 1.6 mmol), selenium (200 mg, 2.5 mmol), $[Ru(bpy)_3](PF_6)_2$ (0.5 mmol), glycol (3 mL), water (3 mL) and en (1 mL) was heated at 190 °C for 14 days, and then cooled down to room temperature in 48 h. Dark red crystals of **1** were washed with DMF and dried in vacuum (Yield: *ca*. 60 % based on Sn).

Two-point probe conductivity measurements.

The powder sample of **1** was pressed into pellet with diameter 1.3 cm and thickness 0.11 cm, which was painted with silver paste and further connected to a combination of a picoameter (Keithley 6485) and a source meter (Keithley 2400) with platinum wires. Current-coltage (*I-V)* were canned at various voltage ranges according to the resistance of the samples and the sensitivity of the instrument. The conductivity was obtained by the Ohm's law. The photocurrent measurement was performed under irradiation of Xe lamp with power of 350 W.

Optical absorption measurement.

Solid-state UV-Vis diffusion reflectance spectra were measured on a PE Lambda950 UV-Vis-NIR spectrophotometer using $BaSO_4$ powder as the reflectance reference. The absorption spectra were calculated from reflectance spectra by the Kubelka-Munk function: $F(R) = \alpha/S = (1\text{-}R)^2/2R$, where R, α, and S are the coefficients for the reflection, the absorption and the scattering, respectively.

Cyclic voltammetry (CV) measurement.

A three-electrode system was used to invest the electrochemical property of **1**. The reference electrode was Ag/AgCl in saturated KCl, and the counter electrode was platinum wire. The powder sample of **1** (5 mg), acetylene black (5 mg) were dispersed in the mixture of 1 mL of CH_3CH_2OH and 50 μL Nafion and subsequently loaded on the glassy cabon and dried under the infrared light source, which was used as the working electrode. The CV measurement was conducted in 0.1 M NBu_4PF_6 in degassed CH_3CN with scan rate 100 mV/s.

Mott-Schottky measurement.

Powder sample of **1** (5 mg) together with acetylene black (5 mg) were dispersed in the mixture of 1 mL of CH_3CH_2OH and 50 μL Nafion and subsequently loaded on the glassy cabon and dried under the infrared light source, which was used as the working electrode. Pt worked wire as counter electrode and Ag/AgCl worked as reference electrode. The measurements were conducted 0.1 M NBu_4PF_6 in degassed CH_3CN. The working frequencies were 1, 10, 100, and 1000 Hz from 0 to 2.0 V.

2. X-Ray Crystallography Structure and Data

Table S1. Crystal data and structure refinement for **1**.

	1
formula	$C_{30}H_{24}N_6RuSe_9Sn_4$
M/g mol^{-1}	1755.02
crystal system	trigonal
space group	$R3c$
a, Å	27.2403(10)
b, Å	27.2403(10)
c, Å	31.010(2)
V, Å^3	19927(2)
Z	18

d_{cal}/g cm^{-3}	2.632
temperature, K	296.15
2θ range	4.338 to 49.626
completeness	0.96
residual map, e Å^{-3}	2.22/-1.27
Goodness-of-fit on	1.031
final indices	$R_1 = 0.0293$, $wR_2 = 0.0711$
R indices (all data)	$R_1 = 0.0317$, $wR_2 = 0.0726$
Flack parameter	0.742(11)

[a] $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obc} - n_{param})]^{1/2}$.

[b] $R_1 = ||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(Fo^2)^2]^{1/2}$.

3. Theoretical calculation

The DFT calculation was carried out using CASTEP module[4] in Material Studio software package. The structure information was taken from the data from single-crystal diffraction. Considering the large unit cell and number of atoms, the conventional cell was transformed into a primitive cell for calculation. The general gradient approximation (GGA) in PBE form[3] was used during the calculation and the SCF tolerance was set to be 10^{-6} Ha. The TS method[5] was applied for van der Waals dispersion correction. The plane wave basis set was used in the calculation. The 1 × 1 × 1 Monkhorst-Pack *k*-point grids[6] were used to sample the Brillouin zone for the material.

4. Photograph of single-crystal sample of 1

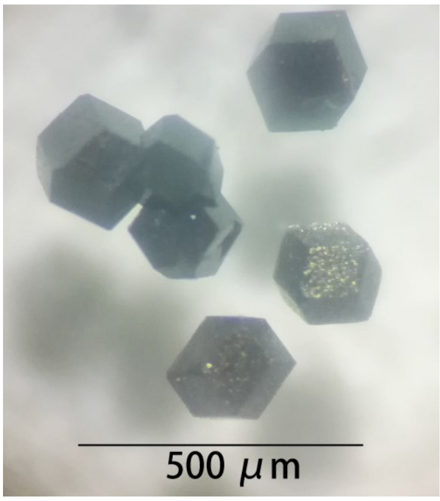

Figure S1. Photograph of single-crystal sample of **1**.

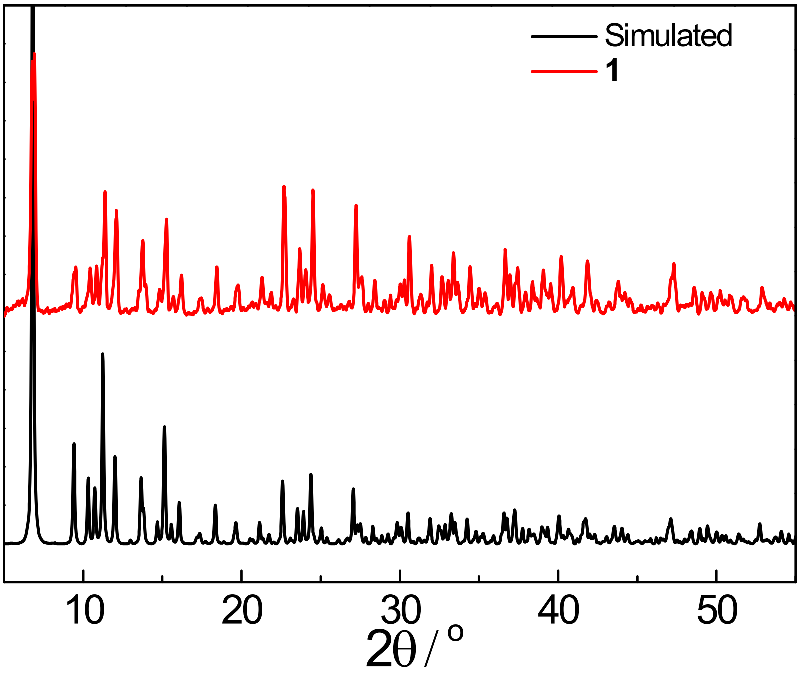

Figure S2. PXRD pattern of powder sample of **1**.

5. FT-IR

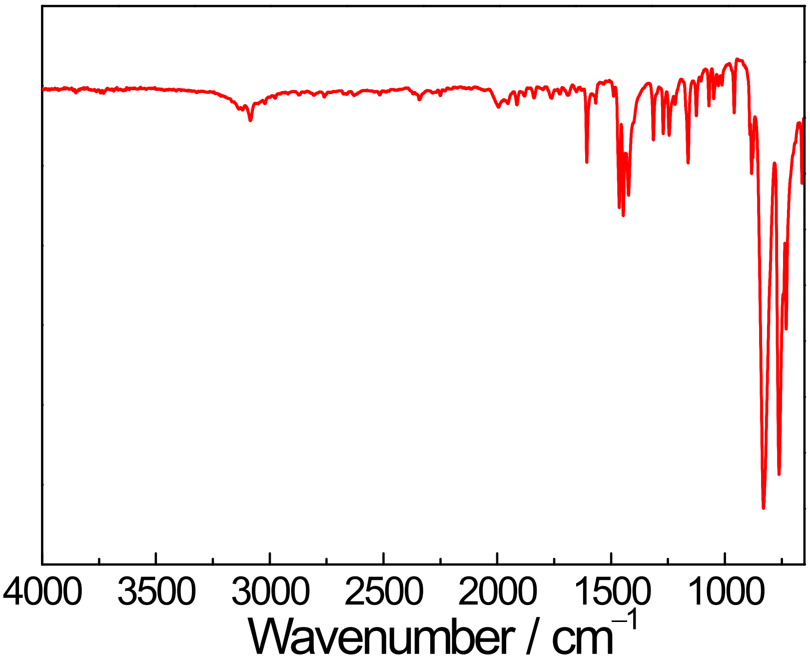

Figure S3. FT-IR of **1**.

6. TG

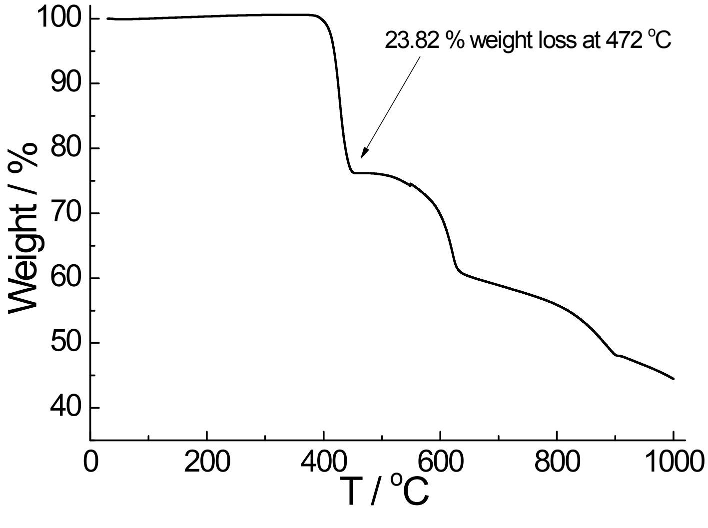

Figure S4. TG curve of **1**

7. CV curve

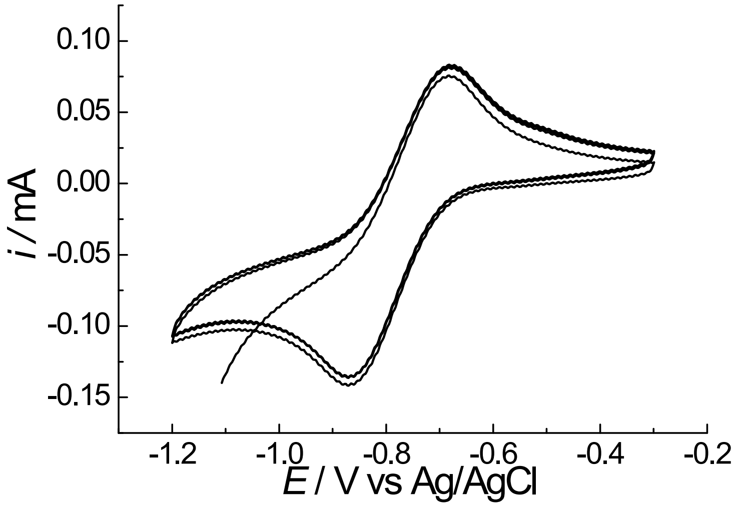

Figure S5 . CV curve of **1**

8. Reference

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