Electronic Supplementary Information

Tetraphenylene-based semiconductive metal–organic framework crystals for direct X-ray detection and imaging

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Experimental

Materials

The organic ligand tetrakis(4-carboxyphenyl)ethylene (H_4TCPE, 98%) was purchased from Zhengzhou Ruke Biotech Co., Ltd. Metal ion salt $PbCl_2$ (99.999%) was purchased from Aladdin. N,N-Dimethylformamide (DMF, AR) was purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized water was self-prepared and used for all experiments. All of the chemicals were purchased from commercial sources and were used without further purification.

Synthesis of Pb_2(TCPE)$(DMF)_2 \cdot H_2O$ (Pb-TCPE)

$PbCl_2$ (33.4 mg, 0.12 mmol) and H_4TCPE (30.5 mg, 0.06 mmol) were added to 6 mL mixed solvent of DMF/H_2O (5:1, V/V). The resultant solution was sealed in a 20 mL Pyrex scintillation vial and sonicated in an ultrasonic cleaner for 10 minutes to mix well. The reaction mixture was slowly heated to 100 °C, kept at 100 °C for 72 h, and cooled to room temperature. Colourless transparent plate crystals of Pb-TCPE were formed, then collected and washed with DMF several times, and finally dried in a drying oven at 65 °C for 6 h. Anal. calcd (%) for $C_{36}H_{32}N_2O_{11}Pb_2$: C 39.92, H 2.98, N 2.59. Found (%): C 39.61, H 2.93, N 2.49. FT-IR (KBr pellet, cm^{-1}): ν = 3350 (m), 2929 (w), 1716 (w), 1668 (s), 1583 (m), 1533 (s), 1390 (s), 1226 (m), 1172 (w), 1105 (w), 1055 (s), 958 (w), 839 (w), 765 (m), 713 (w), 611 (m), 513 (w).

Preparation of Pb-TCPE microcrystalline wafer

An appropriate amount of Pb-TCPE microcrystalline powder was weighed and molded under pressure at 5 MPa to prepare microcrystalline wafer with a diameter of 6 mm and a thickness of about 0.7 mm. The silver paste was evenly coated on both sides of the wafer to form Ag electrodes, and then the gold wires were fixed on the electrodes and connected to the electrical testing equipment. The schematic diagram of the simple Ag/Pb-TCPE/Ag detector with a symmetrical structure is shown in Fig. 3b in the text.

Physical characterization and fluorescence testing

Elemental analyses were obtained with a German Elementar vario MICRO cube elemental analyzer. The FT-IR spectrum was measured by Bruker Optics VERTEX70 fourier transform infrared spectrometer using KBr pellets in the range of 4000-400 cm^{-1}.

X-ray diffraction patterns were recorded on a Rigaku Miniflex 600 system at 40 kV and 40 mA using a graphite-monochromated Cu-K_α radiation source with a step size of 0.02°, the data were collected within a 2θ range of 5–55°. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a METTLER TOLEDO analyzer at a heating rate of 10 K min^{-1} under nitrogen atmosphere. The UV–Vis absorption spectrum was obtained at room temperature on a PerkinElmer Lambda 950 spectrophotometer and with $BaSO_4$ as a reference. The photoluminescence spectra were recorded on a fluorescence spectrophotometer (Edinburgh FLS 1000) using a 450 W xenon lamp as the excitation source. Luminescence lifetimes were measured using the same fluorescence spectrophotometer with a nanosecond lamp.

Single crystal X-ray crystallography testing

Single-crystal X-ray diffraction data of Pb-TCPE were performed using a Rigaku MetalJet D2+ CCD diffractometer equipped with a micro-focus metaljet Ga-K_α radiation (λ = 1.3405 Å) at 293 K. The intensity data sets were collected using the ω scan technique and reduced using the CrysAlisPro software. The structure was solved by direct methods and refined by full-matrix least square on F^2 using the Olex2-1.2 software. All atoms except hydrogen were refined anisotropically. The hydrogen atoms were calculated in idealized positions and refined using the riding model. Crystal data for Pb-TCPE is summarized in Table S1.

X-ray detection and imaging testing

The tungsten target X-ray excitation source (10W) is used to generate X-rays, and the Keithley 2450 sourcemeter is used to test various electrical properties of the sample under X-rays. The X-ray detection and imaging test platform is built under the condition of ensuring safety.

Theoretical calculations

The calculation model of Pb-TCPE was imported from single crystal X-ray diffraction data, and then established through geometry optimization. The calculation of Band structure and Density of states were carried out by the CASTEP code and the GGA-PBE functional in the Materials Studio 2017 software package.

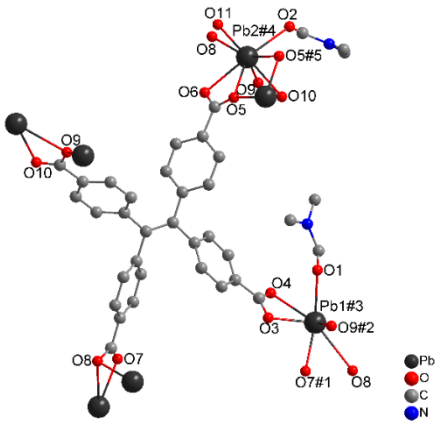

Fig. S1 The asymmetric unit of Pb-TCPE. The symmetric codes for compound: #1 1/2 - x, 1/2 + y, 3/2 - z; #2 1 - x, 1 - y, 1 - z; #3 1 - x, 1 - y, 2 - z; #4 - 1/2 + x, 1/2 - y, - 1/2 + z; #5 3/2 - x, - 1/2 + y, 1/2 – z.

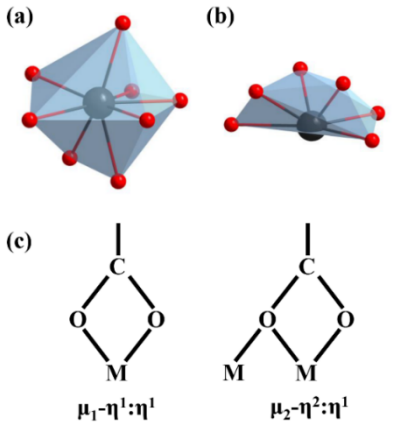

Fig. S2 (a) The holo-directed coordination structure of Pb2(II) (eight coordinated). (b) The hemi-directed coordination structure of Pb1(II) (six coordinated). (c) The coordination modes of carboxylate group with Pb^{2+}.

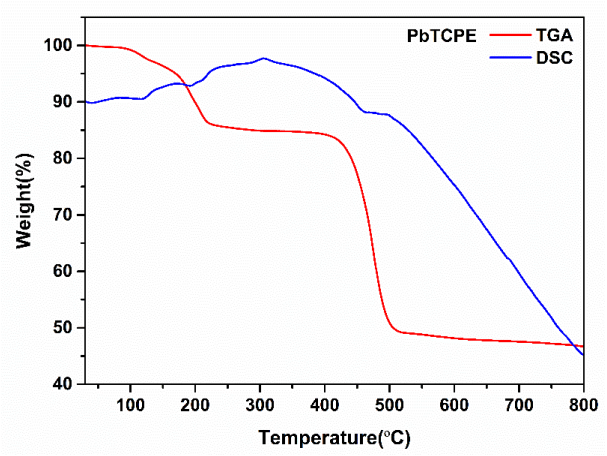

Fig. S3 The TGA and DSC curves of Pb-TCPE.

As shown in Fig.S3, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a METTLER TOLEDO analyzer at a heating rate of 10 K·min^{-1} under nitrogen atmosphere. Starting temperature is room temperature.

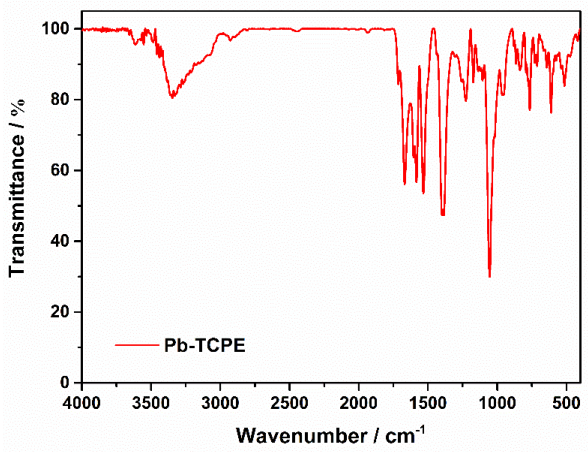

Fig. S4 The FT-IR spectrum of Pb-TCPE.

As shown in Fig. S4. The peak at 3529.6 cm^{-1} corresponds to O-H bonds in water molecules. This is due to the fact that the KBr used in the test is susceptible to deliquescence. It's hard to avoid this in testing. As the Pb^{2+} replaces the oxygen atom of the carboxyl group in tetrakis(4-carboxyphenyl)ethene, the C=O stretching vibrational peak is usually shifted, appears at 1674.7 cm^{-1}. C=C (benzene ring) stretching vibration, similar to tetrakis(4-carboxyphenyl)ethylene, the C=C stretching vibration peaks usually appear in the range of about 1600-1500 cm^{-1}. C-H (benzene ring) bending vibration, similar to tetrakis(4-carboxyphenyl)ethylene, the peak at 757.8 cm^{-1}. The C-H (vinyl) bending vibration caused a peak at 1056.6 cm-1. As for the peak

at 571 cm^{-1}, this peak corresponds to the stretching vibration of the Pb-O bond.

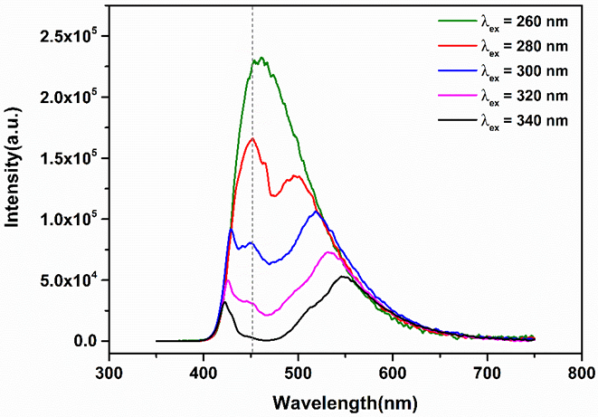

Fig. S5 Photoluminescence spectra of Pb-TCPE at different excitation wavelengths.

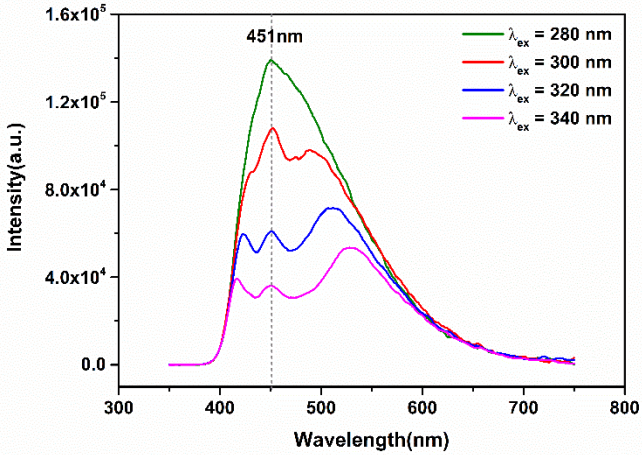

Fig. S6 Photoluminescence spectra of H_4TCPE at different excitation wavelengths.

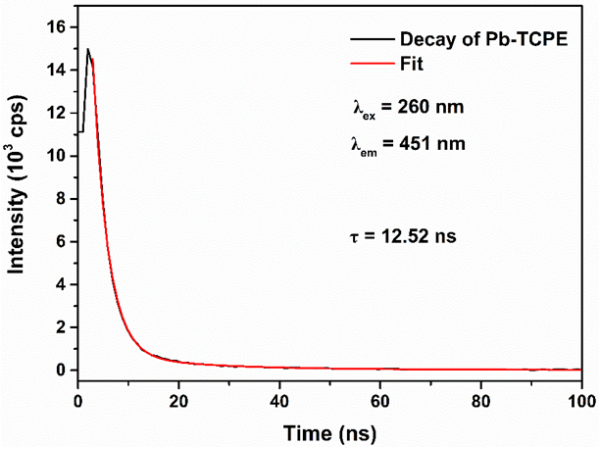

Fig. S7 TRPL decay curve of Pb-TCPE

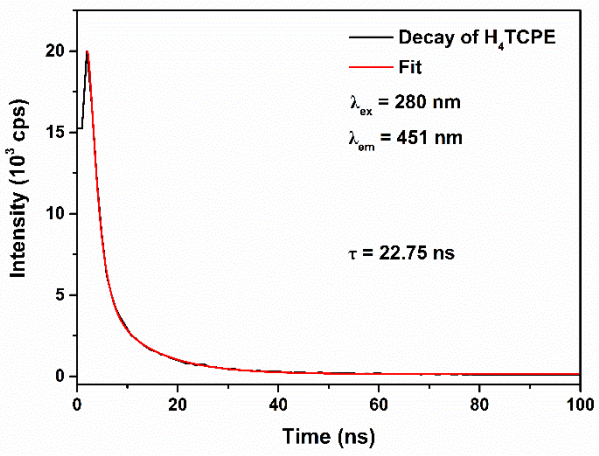

Fig. S8 TRPL decay curve of H_4TCPE.

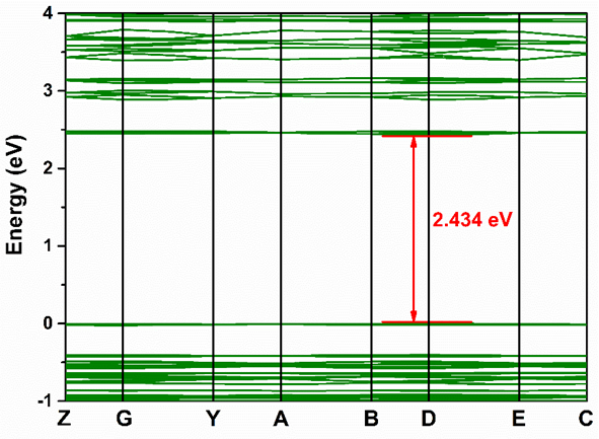

Fig. S9 The energy band structure of Pb-TCPE.

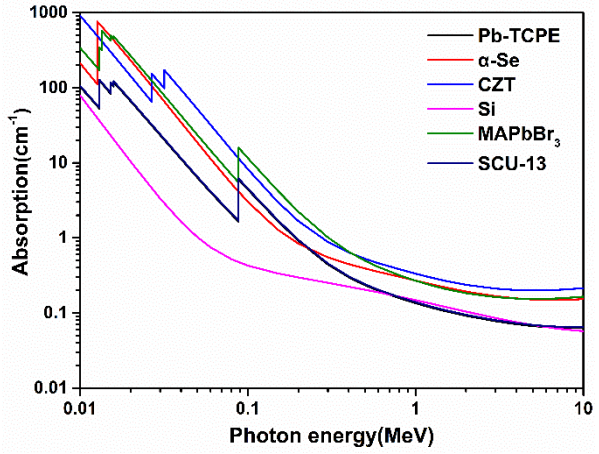

Fig. S10 The absorption coefficients of Pb-TCPE and several semiconductors for X-rays.

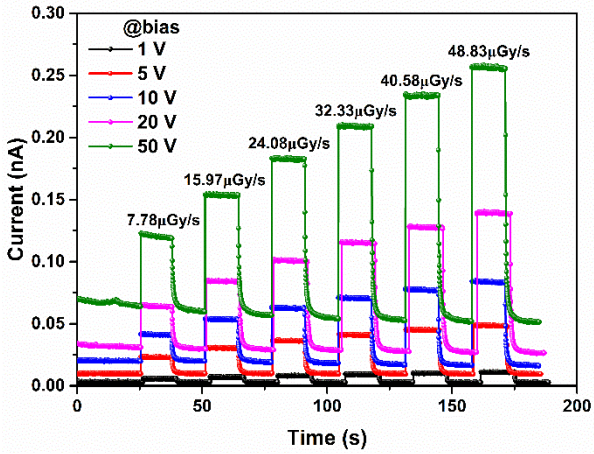

Fig. S11 Photocurrent responses of detector based on Pb-TCPE single crystal to X-rays, I-t curves were recorded by turning X-rays on and off at different dose rates and different bias voltages.

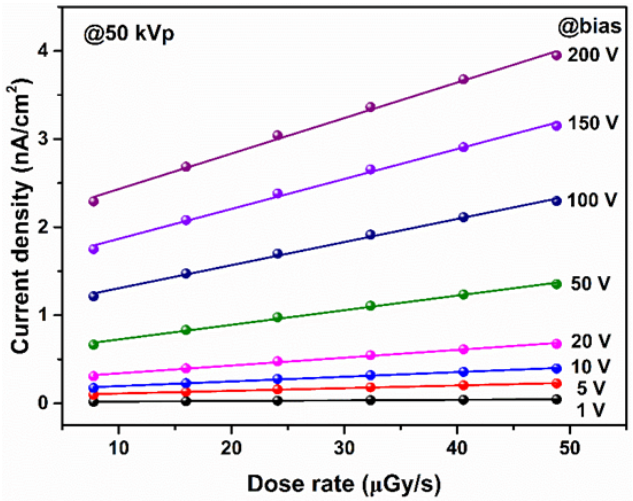

Fig. S12 X-ray-generated photocurrent density versus dose rate in Pb-TCPE microcrystalline wafer

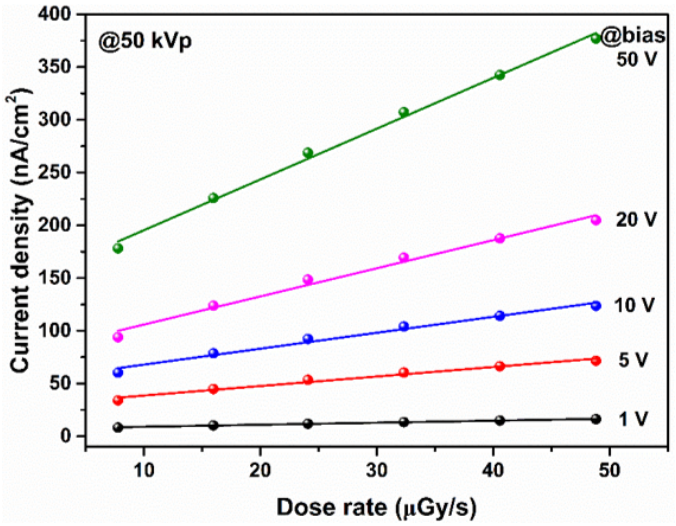

Fig. S13 X-ray-generated photocurrent density versus dose rate in Pb-TCPE single crystal detectors.

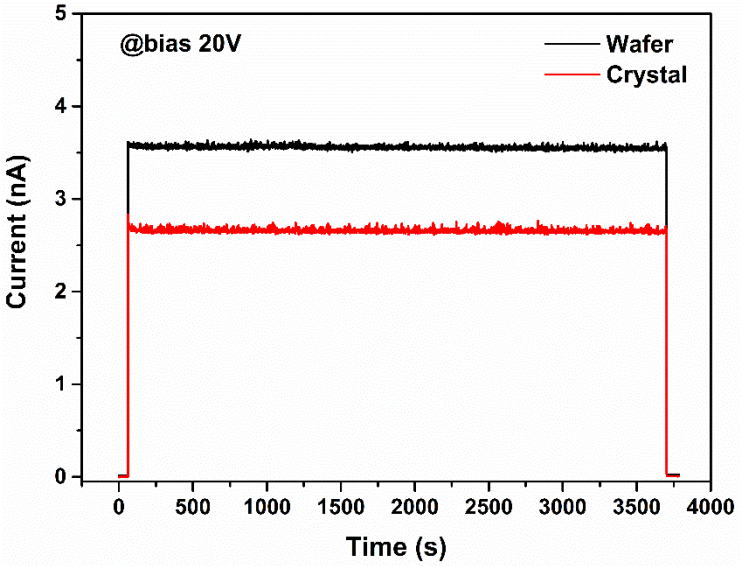

Fig. S14 Tability of Pb–TCPE X-ray detectors. Photocurrent response was measured for 1 h under X-ray with a tube voltage of 50 kV and tube current of 60 μA.

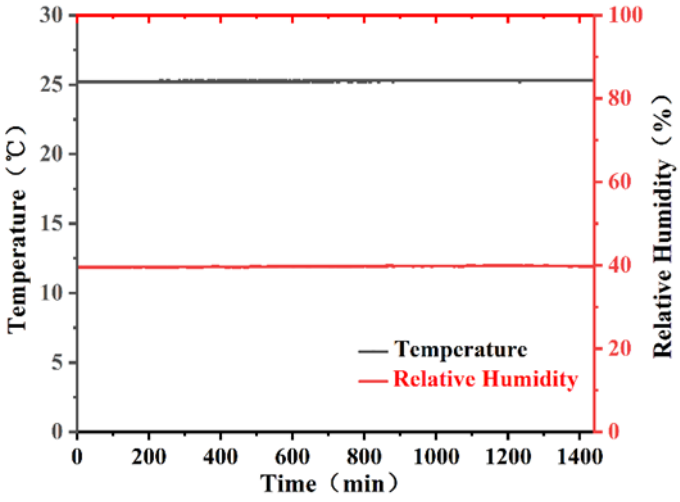

Fig.S15 Temperature and relative humidity in the laboratory

Table. S1 Crystallographic data of compound Pb-TCPE.

Crystal data	Pb-TCPE
CCDC number	2339838
Empirical formula	$C_{36}H_{32}N_2O_{11}Pb_2$
Formula weight	1083.04

Temperature	293(2)
Wavelength (Å) /MoK_α	1.3405
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	16.4600(6)
b (Å)	11.3441(5)
c (Å)	19.5207(6)
α (°)	90
β (°)	94.325(3)
γ (°)	90
V (Å^3)	3634.6(2)
Z	4
Calcd. density (g cm^{-3})	1.979
Absorption coefficient (mm^{-1})	9.314
F(000)	2056
Reflections collected	47011
Completeness to θ = 53.54°	96.9%
Data/restraints/parameters	8189/264/527
Goodness-of-fit on F^2	1.052
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0446
	wR_2 = 0.1300

[a]$R_1 = \sum(F_o - F_c)/\sum F_o$. [b]$wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\ ]^{1/2}$.

Table. S2 Luminescence lifetime parameters of H_4TCPE ligand and Pb-TCPE.

	τ_1(ns)	$A_{1(}$%)	τ_2(ns)	A_2(%)	τ_3(ns)	A_3(%)	τ(ns)
H_4TCPE	2.17	33.84	10.78	44.72	103.95	16.44	22.75
Pb-TCPE	2.97	74.62	18.68	19.85	119.56	5.52	12.52

Table. S3 The performance comparison of some reported MOFs and Pb-TCPE.

Sample	Operating field (V mm^{-1})	Sensitivity ($\mu C\ Gy_{air}^{-1}\ cm^{-2}$)	Detection limit ($\mu Gy_{air}/s$)	Ref.
SCU-12 (Microcrystalline wafer)	43	23.8	0.705	22
SCU-13 (Membrane)	NA	65.86	6.553	23
Ni-DABDT (Film)	20	98.6	7.2	24
Pb-TPCE (Microcrystalline wafer)	72	16.6	0.0446	This work
Pb-TPCE (Single crystal)	1440	4812.6	0.0933	This work