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## **Supporting Information**

Phenothiazine-Based Donor-Acceptor Covalent-organic Frameworks with Keto-enol Irreversible Tautomerism as a Promising Third-order Nonlinear Optics Material

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#### 1. Materials and methods

1,3,5-Triformylbenzene (TF) and 2,4,6-trihydroxybenzene-1,3,5-trialdehyde (TFP) were bought for BIDE PHARMATECH CO., LTD., and used without further purification. The 4,4'-(10-(4'-amino-[1,1'-biphenyl]-4-yl)-10H-phenothiazine-3,7-diphenyl)diamine) (BPTZ) was synthesized by the method reported in the literature (See Synthesis and general procedures), and the structure was verified by <sup>1</sup>H nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR), <sup>13</sup>C nuclear magnetic resonance spectroscopy (<sup>13</sup>C NMR) and Fourier transform infrared (FT-IR) spectra. [1,1'-Bis(diphenylphosphino)ferrocene] dichloropalladium (II) (PdCl<sub>2</sub>(dppf)<sub>2</sub>), Tetrahydrofuran (THF), Potassium carbonate, Phenothiazine, Copper acetate monohydrate, N-Bromosuccinimide (NBS), Triethylamine, Toluene, Methanol, Pyrrolidine, Chloroform-d, Dimethyl sulfoxide-d<sub>6</sub>, Sodium sulfate anhydrous, N,N-dimethylacetamide (DMAC), odichlorobenzene (o-DCB), n-butyl alcohol (n-BuOH), acetic acid, Phenylboric acid, dichloromethane, Petroleum ether, Ethyl acetate and acetone were purchased by chemical reagent manufacturers. All solvents were dried and distilled according to conventional methods. Glass block from NeVid S27105, size 25.0 × 75.0 mm, thickness 1.0~1.2 mm. Cut into a 1.0×0.8 cm rectangle with a glass knife before use.

**Power X-ray diffraction (PXRD):** PXRD patterns were collected on an X-ray diffraction system (DX-27mini, China) using Cu K $\alpha$  radiation.

**Crystal structure modeling:** Structural modeling of COFs was generated using the BIOVIA Materials Studio<sup>1</sup> program employing the Building (Crystal) module, and the lattice model was geometrically optimized using force-filed based method (Forcite molecular dynamics module) and SCC-DFTB (DFTB + module). The Pawley fitting (Reflex module) was performed to optimize the lattice parameters iteratively until the Rwp value converges and the overlay of the observed with refined profiles shows good agreement. Powder indexing and Rietveld refinement were performed using EXPO2014<sup>2</sup> various topology structures were illustrated by VESTA software<sup>3</sup>.

**Fourier transform infrared (FT-IR):** IR spectrum was measured on an IR spectrometer (Nicolet 6700) between the ranges of 4000 to 400 cm<sup>-1</sup>.

**Solution nuclear magnetic resonance spectroscopy (NMR):** Liquid state <sup>1</sup>H NMR spectroscopy was collected on a Varian Mercury Plus 400 NMR Spectrometer.

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Solid-state nuclear magnetic resonance spectroscopy (ssNMR): Solid-state NMR spectrum were performed on a Bruker 400M spectrometer with cross-polarization magic-angle-spinning (CP/MAS) at a resonance frequency of 150.9 MHz. <sup>13</sup>C CP/MAS NMR spectra were recorded using a 4 mm MAS probe and a spinning rate of 10 kHz. A contact time of 4 s and a recycle delay of 6.5  $\mu$ s were used for the <sup>13</sup>C CP/MAS NMR measurement. The chemical shifts of <sup>13</sup>C were externally referenced to tetramethylsilane (TMS).

**X-Ray Photoelectron Spectroscopy (XPS):** The XPS work was performed on a Thermo Scientific K-Alpha XPS system fitted with a monochromatic Al k $\alpha$  X-ray source (hv = 1486.6 eV). The binding energies in all of the obtained XPS spectra were calibrated using C 1s peak at 284.8 eV.

Thermogravimetric analysis (TGA): TGA was performed using a NETZSCH TG 209 F1 Libra under flowing N<sub>2</sub> with a 20 K min<sup>-1</sup> ramp rate. Samples were heated in a crucible (800 °C, 20 °C min<sup>-1</sup>).

**Sorption isotherm for N<sub>2</sub>:** The Brunauer-Emmett-Teller (BET) surface areas were calculated from N<sub>2</sub> sorption isotherms at 77 K using a Micromeritics ASAP 2460 3.01 system surface area and pore size analyzer.

Scanning electron microscopy (SEM): SEM images were collected using a GeminiSEM 500 system.

**Transmission electron microscope (TEM):** TEM images were obtained with a Tecnai G2 F30 S-Twin.

**Solid-state ultraviolet-visible (UV-Vis) absorption spectra:** The UV-vis absorption of the sample was recorded using the Shimadzu UV-2600i UV-visible absorption spectrum. The band gap width of the material is calculated using the Tauc plot method and extrapolating the straight-line part to the intersection of the abscissa.

**DFT calculation:** The structure optimizations were performed using the Gaussian 16 package,<sup>4</sup> and the density functional theory (DFT) method B3LYP-D3 (with the default D3 dispersion correction proposed by Grimme)<sup>5-7</sup> with the 6-31G(d) basis-set.<sup>8-10</sup> To perfrom the quantum mechanics calculation for COF material, the model was constructed by extracting a unit from the COF material, and the boundaries of the truncated unit were capped with hydrogen atoms. Hybrid DFT methods, such as B3LYP, predict many of the electronic properties correctly, and

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it performs well for different properties of conjugated polymers, such as geometries and band gaps<sup>11-14</sup> The HOMO/LUMO and their energies were computed at the B3LYP-D3/6-31G(d) level.

**Z-scan technology:** The laser used in the experiment was A mode-locked Nd: The YAG 532 nm laser, the ENERGY probe is Rj-7620 ENERGY RATIOMETER, the detection wavelength is 532 nm, the pulse width is 4 ns, the laser pulse energy is 5-20  $\mu$ J, the focal spot beam waist radius is 30  $\mu$ m. After passing through the attenuator, the incident light is divided by a beam splitter and focused by a lens with a focal length of 300 mm before hitting the sample. The sample moves along the optical path near the focal point of the lens and the transmittance is monitored by two energy detectors.

#### 2. Synthesis and general procedures

#### 2.1 Synthesis of monomers



Scheme S1. Synthetic scheme for BPTZ.

#### Synthesis of 10-phenyl-10H-Phenothiazine (A) :

10-phenyl-10H-phenothiazine (A) was synthesized by referring to the method reported in the literature<sup>15</sup>. Phenothiazine (3.00 g, 15.1 mmol), phenylboric acid (3.64 g, 29.8 mmol) and copper monohydrate acetate (2.82 g, 15.5 mmol) were placed into a 250 mL flask. 50 mL dichloromethane was added and then triethylamine (4.2 mL) was added drop by drop. Avoid light and inject oxygen, stirring at room temperature for 24 h, stop the reaction. The reaction solution was extracted with methylene chloride/water for 3 times, and the organic layer was spin dried. The crude product was purified by column chromatography (pure petroleum ether), and 1.98 g pure white solid A was obtained. The yield was 47.8%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 7.59-7.62 (t, *J* = 7.64 Hz, 2H), 7.46-7.50 (t, *J* = 7.39 Hz, 1H), 7.38-7.40 (t, *J* = 7.61 Hz, 2H), 7.01-7.03 (d, *J* = 8.97 Hz, 2H), 6.82-6.86 (m, 4H), 6.19-6.21 (d, *J* = 7.95 Hz, 2H).

#### Synthesis of 3,7-dibromo-10-(4-bromo-phenyl)-10H-Phenothiazine (B):

3,7-dibromo-10-(4-bromo-phenyl)-10H-phenothiazine (B) was synthesized by referring to the method reported in the literature<sup>15</sup>. Compound A (2.00 g, 7.3 mmol) was placed in a 250 mL flask, 50 mL tetrahydrofuran ice bath (0-5 °C) was added and stirred for 30 min. NBS (4.15 g, 23.3 mmol) was dissolved in about 100 mL tetrahydrofuran. A tetrahydrofuran solution of NBS was slowly dripped into the reaction flask (within 2 h). Continue the ice bath for 2 h, rise to room temperature for 6 h, and monitor the reaction endpoint. The reaction solution was extracted with methylene chloride/water for 3 times, and the organic layer was spin dried. The crude product was purified by silica gel column chromatography (eluent was pure petroleum ether), and 2.9983 g white powder B was obtained. The yield was 81.0%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 7.73-7.75 (d, *J* = 8.46 Hz, 2H), 7.21-7.23 (d, *J* = 8.32 Hz, 2H), 7.11 (s, 2H), 6.93-6.95 (d, *J* = 8.80 Hz, 2H), 6.01-6.04 (d, *J* = 8.86 Hz, 2H).

# 4,4'-(10-(4'-amino-[1,1'-biphenyl]-4-yl)-10H-phenothiazine-3,7-diphenyl)diamine (BPTZ) synthesis:

Compound B (0.50 g, 0.98 mmol), 4-aminophenylboronic acid pinacol ester (1.30 g, 5.86 mmol), PdCl<sub>2</sub>(dppf)<sub>2</sub> (0.12 g, 0.15 mmol) and potassium carbonate (0.81 g, 0.856 mmol) were added to the flask. Toluene: methanol (1:1 v/v) solution (20 mL) was then added to the above mixture and heated at 110 °C nitrogen for about 48 h. The mixture is cooled to room temperature. The organic layer is extracted with saturated brine and then dried with sodium sulfate anhydrous. The crude product was purified by column chromatography (eluent was petroleum ether: ethyl acetate = 1:1), and 0.535 g of light-yellow solid was obtained with a yield of 74.8%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  ppm): 7.83 (d, *J* = 8.46 Hz, 2H), 7.49 (d, *J* = 8.55 Hz, 2H), 7.41 (d, *J* = 8.44 Hz, 2H), 7.24-7.28 (m, 6H), 7.11 (m, 2H), 6.70 (d, *J* = 8.51 Hz, 2H), 6.60 (d, *J* = 8.53 Hz, 2H), 6.22 (d, *J* = 8.58 Hz, 2H), 5.25 (s, 6H, NH<sub>2</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>,  $\delta$  ppm): 114.64, 114.76, 116.67, 119.86, 123.55, 124.47, 126.56, 126.59, 126.96, 127.87, 128.11, 131.06, 135.62, 138.47, 141.06, 141.90, 148.56, 149.25; FT-IR (KBr pellet): v~ = 3460 (w), 3370 (m) cm<sup>-1</sup>, 1616 (s) cm<sup>-1</sup>, 1495 (vs) cm<sup>-1</sup>, 1470 (vs) cm<sup>-1</sup>, 1282 (s) cm<sup>-1</sup>, 1243 (s) cm<sup>-1</sup>, 1180 (m) cm<sup>-1</sup>, 816 (s) cm<sup>-1</sup>.



150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 £1 (read)

Figure S1. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum of BPTZ.

### 2.2 Synthesis and characterization of COFs

(1) **TF-TZ:** BPTZ (70.0 mg, 0.128 mmol) and benzaldehyde (TF, 20.6 mg, 0.128 mmol) were added into 5 mL glass bottles, 2.5 mL *o*-dichlorobenzene (*o*-DCB) and 2.5 mL *n*-butanol (*n*-BuOH) were added, and the mixture was treated with ultrasound for 5 min. The mixture was

then transferred to a 25 mL glass ampere bottle and placed into a pre-treated clean glass sheet base. Then add 0.5 mL of 6 M acetic acid to the reaction bottle. After sealing, it was subjected to three freezing-vacuum-thawing cycles under 77 K liquid nitrogen. Then the reaction was heated at 120°C for 72 h. After the reaction was cooled to room temperature, the glass sheet was washed with DMAC and acetone to obtain TF-TZ film. The remaining solids were filtered and washed 3 times with DMAC and acetone respectively. The obtained powder was extracted with THF and acetone as detergent for 48 h. Finally, after vacuum activation at 90°C for 24 h, TF-TZ was obtained as yellow powder (81 mg, 89% yield).



Scheme S2. Synthetic procedure for TF-TZ.

(2) TFP-TZ: BPTZ (62.8 mg, 0.299 mmol) and 2,4, 6-trihydroxybenzene-1,3, 5-triformaldehyde (TFP, 24.0 mg, 0.299 mmol) were added to a 5 mL glass bottle with 2.0 mL *o*-DCB and 2.0 mL *n*-BuOH. The mixture was treated with ultrasound for 5 minutes. The mixture was then transferred to a 25 mL glass ampere bottle and placed into a pre-treated clean glass sheet base. Then add 0.4 mL of pyrrolidine to the reaction bottle. The reaction system was sealed and then subjected to three freezing-vacuum-thawing cycles at 77 K liquid nitrogen. Then the reaction was heated at 120 °C for 72 h. After cooling to room temperature, the glass sheet was washed with DMAC and acetone to obtain TFP-TZ film. The residual reaction system solution was filtered, and the cake was washed with DMAC and acetone for 3 times. The obtained solids were extracted with THF and acetone as detergents for 48 h. Finally, after vacuum activation at 90 °C for 24 h, the obtained TFP-TZ was yellow powder (72 mg, 84% yield).



Scheme S3. Synthetic procedure for TFP-TZ.



**Figure S2.** XPS analysis of COF films: (a) Survey XPS spectrum, (b) Ratio of the element, (c) C 1s and (d) S 2p High-resolution XPS spectrum.

To further explore the elemental composition and chemical state of the two COFs, X-ray photoelectron spectroscopy (XPS) characterization measurement are cognized. Two similar element compositions of TF-TZ and TFP-TZ are observed in XPS spectra ensuring that all

samples mainly contained C, N, O and S elements from the wide scan region (**Figure S2** and **Table S1**). Furthermore, the C 1s, N 1s, O 1s and S 2p high-resolution XPS spectra of TF-TZ and TFP-TZ are fitted (**Table S2**). The high-resolution C 1s XPS spectrum of TF-TZ can be deconvoluted into three peaks with binding energies of 285.7, 285.0, and 284.8 eV, which are attributed to the C–S, C=N/C–N, and C=C/C–C bonds, respectively (Figure S2).<sup>16</sup> As shown in **Figure S2d**, the high-resolution S 2p XPS spectrum of TF-TZ and TFP-TZ observed a major S  $2p_{3/2}$  peak of about 163.8 eV and S  $2p_{1/2}$  peak of about 165.0 eV corresponding to the C–S–C bond in the phenothiazine structure of about 166.4 eV.<sup>17</sup> Furthermore, the C 1s, N 1s, O 1s and S 2p high-resolution XPS spectra of TF-TZ and TFP-TZ are fitted (**Table S2**).

Table S1. Summary of the proportions of different elements in COFs by XPS analysis.

Sample	C (wt%)	N (wt%)	O (wt%)	S (wt%)
TF-TZ	84.71	7.14	6.47	1.81
TFP-TZ	82.92	7.14	8.32	1.59

**Table S2.** High resolution spectrogram fitting results of different elements.

High resolution		TF-TZ	TFP-TZ
spectrum	Chemical bond	binding energy (eV)	binding energy (eV)
	C=C/C-C	284.8	284.7
C 1s	C = N	285.0	285.4
	C–S	285.7	285.7
	C = N	399.2	-
N 15	C-N	400.0	400.1
2.4	C=O	-	531.0
0 1s	Adsorbed O	532.3	532.7
	S 2p <sub>3/2</sub>	163.8	163.9
S 2p	S 2p <sub>1/2</sub>	164.9	165.1
	C–S–C	166.4	166.5



Figure S3. TGA curves of TF-TZ and TFP-TZ.

The weight loss of two kinds of COFs powder was recorded by TGA analysis method in the temperature range of 30~800  $^{\circ}$ C under N<sub>2</sub> atmosphere and temperature rise rate of 20  $^{\circ}$ C min<sup>-1</sup>. As shown in **Figure S3**, almost no weight loss occurred in TF-TZ within the range of 30~300  $^{\circ}$ C, indicating that there was no residue of solvent molecules on the surface and pores of TF-TZ and TFP-TZ after activation. When the temperature is higher than 450  $^{\circ}$ C, the skeleton of TF-TZ and TFP-TZ begins to collapse and gradually decompose,<sup>18</sup> which indicates that TF-TZ and TFP-TZ have high thermal stability. When the temperature is higher than 450  $^{\circ}$ C, the weight loss of TF-TZ is faster than that of TFP-TZ, indicating that TFP-TZ has higher thermal stability.



**Figure S4.**  $N_2$  adsorption-desorption isotherms measured at 77 K of TF-TZ (a) and TFP-TZ (b) powders. (c,d) the pore size distributions of TF-TZ (a) and TFP-TZ (b) powders.



**Figure S5.** The top and side views of the structural model of COFs with AA and AB stacking (Gray: C; Blue: N; White: H). (a) Eclipsed (AA) stacking of TF-TZ, (b) staggered (AB) stacking of TF-TZ, (c) AA stacking of TFP-TZ, (d) AB stacking of TFP-TZ, and (e) stacking of TFP-TZ as serrated with 1/4 an offset along the *a*-axi.

Possible crystal structures with various offset along a axis (0–1 a, where 0 and 1/2 a represent the AA and AB packing mode, respectively).<sup>19</sup>



Figure S6. (a-b) SEM images of TF-TZ powder, (c-d) SEM images of TFP-TZ powder.



**Figure S7.** Morphology of COF powders: (a-b) SEM images of TF-TZ, (c) TEM image of TF-TZ, (d-e) SEM images of TFP-TZ, and (f) TEM image of TFP-TZ.



Figure S8. Morphology of COF films: (a-b) SEM images of TF-TZ and (c-d) TFP-TZ.

**Table S3.** Calculated HOMO, LUMO, and  $E_{gt}$  values of COF films in B3LYP/6-31G(d).

Sample	E <sub>HOMO</sub> (eV)	E <sub>LUMO</sub> (eV)	E <sub>g</sub> t (eV)
TF-TZ	-4.84	-1.80	3.04
TFP-TZ	-4.97	-2.76	2.21

#### 2.3 NLO performance

The third-order nonlinear optical (NLO) properties of TF-TZ and TFP-TZ films were investigated by used open and closed aperture Z-scan techniques (Figure S7a). The laser used in the experiment was A mode-locked Nd: The YAG 532 nm laser, the ENERGY probe is Rj-7620 ENERGY RATIOMETER, the detection wavelength is 532 nm, the pulse width is 4 ns, the laser pulse energy is 5-20  $\mu$ J, the focal spot beam waist radius is 30  $\mu$ m. The glass sheet attached to the sample is placed on a mobile platform and is directly used for testing. All testing procedures are conducted at room temperature. The sample moves in the direction of optical path propagation near the focal point of the lens, and the transmittance is monitored by two

energy detectors. In the open aperture Z-scan curve, a normalized transmittance of 1.0 indicates no NLO absorption behavior. Normalized transmittance higher than 1.0 will be observed when the sample exhibits saturable absorption (SA). In contrast, a normalized transmittance lower than 1.0 indicates that the sample has reverse saturated absorption (RSA)<sup>20</sup>. Closed aperture Z-scan measurement of TF-TZ and TFP-TZ were performed only at 15  $\mu$ J. In the closed aperture Z-scan curve, the normalized transmittance of 1.0 indicates that the material has no NLO refraction behavior, and the curve presents the shape of trough before peak, indicating self-focusing phenomenon. On the contrary, the curve shows the shape of first peak and then valley, which is a self-defocusing phenomenon<sup>21</sup>.



**Figure S9.** (a) Schematic representation of the Z-scan setup, (b) Open-aperture Z-scan curve of the blank glass pane

The blank glass without COF films was tested by open hole Z-scan, as shown in **Figure S9b**. When the pulse energies were 5  $\mu$ J, 10  $\mu$ J, 15  $\mu$ J and 20  $\mu$ J, the linear transmittance of the blank glass was 0.97, and the normalized transmittance was all 1, the fitting curve was a straight line. The results show that the blank glass has no NLO absorption response under these pulse energies.

In addition, the nonlinear absorption coefficients ( $\beta$ ) of TF-TZ and TFP-TZ films at 10  $\mu$ J were fitted by the formula.

$$T = \frac{1}{\sqrt{\pi} \left[\frac{\beta I_0 L_{eff}}{\left|\frac{\beta I_0 L_{eff}}{\left|\frac{1 + Z^2}{Z_0^2}\right|}\right]^{-\infty}} \ln \left[1 + \frac{\beta I_0 L_{eff}}{\left(1 + \frac{Z^2}{Z_0^2}\right)^{-\infty}} \exp(-t^2)\right] dt$$

Where T is normalized transmittance,  $I_0$  is the input peak intensity at the focal point, and  $Z_0$  is the Rayleigh diffraction length which can be calculated by  $Z_0 = \pi \omega_0^2 / \lambda$ .  $\lambda$  is the wavelength, 532 nm.  $\omega_0$  is is the radius of the beam at the focal point, 30000 mm.  $L_{eff} = (1 - e^{-\alpha_0}L)/\alpha_0$ . The thickness (L) in the fitting formula uses the COF films thickness measured by SEM, and the TF-TZ and TFP-TZ films are 289 nm and 67 nm, respectively. Since COF films are attached to both sides of the glass sheet during the preparation of COF films, the L used in the calculation of COFs  $\theta$  is twice the thickness of the film measured by the actual SEM. In addition,  $\alpha_0$  is the linear absorption coefficient. The linear transmittance ( $e^{-\alpha_0}L$ ) of TF-TZ and TFP-TZ films at 10  $\mu$ J is 56% and 61%, respectively.



**Figure S10.** Open-aperture Z-scan curves of (a) TF-TZ and (b) TFP-TZ films at different pulse energies.

As shown in **Figures S10**, the TF-TZ and TFP-TZ films all exhibit SA behavior at different pulse energies, and the corresponding NLO values are shown in **Table S4** by fitting.



**Figure S11.** (a) Schematic diagram of irreversible *keto-enol* tautomerization. (b) Proposed charge transfer mechanism of TFP-TZ.

COF	$e^{-\alpha_0}L$	Pulse energy (nJ)	E (nJ)	I <sub>(0)</sub> (10 <sup>-6</sup> GW cm <sup>-2</sup> )	Fit depth values	ıL (nm)	α <sub>0</sub> (× 10 <sup>-3</sup> )	L <sub>eff</sub> (nm)	<i>6</i> (× 10 <sup>-7</sup> m W <sup>-1</sup> )
TF-TZ	0.52	5000	48077	4.79	0.22	578	1.13	424.2	-1.08
	0.56	10000	89286	8.91	0.45	578	1.00	438.6	-1.15
	0.56	15000	133929	1.34	0.60	578	1.00	438.6	-1.02
	0.56	20000	178571	1.78	0.88	578	1.00	438.6	-1.13
	0.53	5000	47170	4.71	0.40	134	4.74	99.2	-8.57
	0.61	10000	81967	8.18	0.90	134	3.69	105.7	-10.40
TFP-TZ	0.65	15000	115385	1.15	0.85	134	3.21	108.9	-6.78
	0.67	20000	149254	1.49	1.00	134	2.99	110.4	-6.08

**Table S4.** Third order nonlinear optical refraction parameters of the COF films obtained with different pulse energies by open-aperture Z-scan.

 $e^{-\alpha_0}L$ : The linear transmittance. E: The incoming laser energy. I<sub>(0)</sub>: The instantaneous intensity of the laser at the focal point. L: Sample thickness.  $\alpha_0$ : the linear absorption coefficient. L<sub>eff</sub> : Effective thickness.  $\beta$ : nonlinear absorption coefficient.

In addition, the third-order nonlinear refraction coefficient  $(n_2)$  and third-order nonlinear polarizability  $(\chi^{(3)})$  of TF-TZ and TFP-TZ films are further fitted according to the following formula.

Nonlinear index of refractive index:

$$n_2 = \frac{\lambda \Delta T_{P-V}}{0.812\pi (1 - S)^{0.25} I_0 L_{eff}}$$

As the  $\lambda$  as the laser wavelength, 532 nm,  $\Delta T_{P-V}$  for obturator scanning the difference between peaks and troughs, S for small aperture linear transmittance;

 $\chi^{(3)}$  is a complex quantity:

$$\chi^{(3)} = \chi^{(3)}_{R} + i \chi^{(3)}_{I}$$

Among them, the real component  $\chi_R^{(3)}$  the corresponding nonlinear refractive index:

$$\chi_R^{(3)} = \frac{n_0 c n_2}{80\pi}$$

Imaginary part  $\chi_{I}^{(3)}$  Corresponding to the nonlinear absorption coefficient:

$$\chi_{I}^{(3)} = \frac{n_0^2 \varepsilon_0 c^2 \beta}{\omega}$$

 $n_0$  is the linear refractive index of the blank glass substrate, which is 1.5,  $\varepsilon_0$  for the vacuum dielectric constant, 8.854187 × 10<sup>-12</sup> F m<sup>-1</sup>,  $\omega$  is the frequency of light, 5.63534 × 10<sup>14</sup> s<sup>-1</sup>. c is the speed of light, 3 × 10<sup>8</sup> m s<sup>-1</sup>.

The third-order nonlinear polarizability value is obtained by the following formula:

 $|\chi^{(3)}| = \sqrt{|\chi^{(3)}_R|^2 + |i\chi^{(3)}_I|^2}$ 

**Table S5.** Third-order nonlinear optical refraction parameters of COF films at 15  $\mu$ J pulse energies by closed-aperture Z-scan.

COF	<i>в</i> (10 <sup>-7</sup> m W <sup>-1</sup> )	$\Delta T_{P-V}$	n <sub>2</sub> (10 <sup>-13</sup> m <sup>2</sup> W <sup>-1</sup> )	χ <sup>(3)</sup> (10 <sup>-7</sup> esu)	χ <sup>(3)</sup> (10 <sup>-7</sup> esu)	χ <sup>(3)</sup> (10 <sup>-7</sup> esu)
TF-TZ	-1.02	2.10	-0.92	-2.46	-2.33	2.48
TFP-TZ	-6.78	0.67	-1.67	-4.47	-1.55	4.73

**Table S6.** A list of the third-order nonlinear optical parameters of different saturated absorption (SA) materials.

Number	Name	Measurement condition	Measured NLO parameter	Ref.
1	TF-TZ	Z-scan, 532 nm, 4 ns.	$\beta = -1.02 \times 10^4 \text{ cm GW}^{-1}$ $n_2 = -0.92 \times 10^{-13} \text{ m}^2 \text{ W}^{-1}$ $\chi^{(3)} = 2.48 \times 10^{-7} \text{ esu}$ $\beta = -6.78 \times 10^4 \text{ cm GW}^{-1}$	This work
2	TFP-TZ	5-20 μJ	$n_2 = -1.67 \times 10^{-13} \text{ m}^2 \text{ W}^{-1}$ $\chi^{(3)} = 4.73 \times 10^{-7} \text{ esu}$	
3	РТ-РА РВ-РА	Z-scan, 532 nm, 7 ns, 1 μJ	$b = -1.83 \times 10^{6} \text{ cm GW}^{-1}$ $b = -1.69 \times 10^{6} \text{ cm GW}^{-1}$	22
4	G/MoSe <sub>2</sub>	Z-scan, 532 nm	eta = -0.646 cm GW <sup>-1</sup> $\chi^{(3)}$ = 8.00 × 10 <sup>-8</sup> esu	23
5	RGO	Z-scan, 532 nm	$\beta = -7.5 \text{ cm GW}^{-1}$ $\chi^{(3)} = 1.31 \times 10^{-11} \text{ esu}$	24

6	MAPbBr <sub>3</sub> /ITO composite film	2 ps, 100 MHZ, 1550 nm	$\beta$ = -1.04 × 10 <sup>4</sup> cm GW <sup>-1</sup>	25
7	CsPbBr₃	340 fs, 1 KHZ, 515 nm	<i>β</i> = –0.35 cm GW <sup>-1</sup>	26
8	(AB/PMo <sub>10</sub> V <sub>2</sub> ) <sub>35</sub>	Z-scan, 532 nm 10 μJ	$\beta = -2.70 \times 10^5 \text{ cm GW}^{-1}$	27
9	Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub>	1550 nm, 95 fs	$\beta = -0.30 \text{ cm GW}^{-1}$ $n_2 = -4.89 \times 10^{-7} \text{ cm}^2 \text{ GW}^{-1}$	28
10	Graphene Oxide (GO) film	1560 nm, 67 fs	$\theta = -6.30 \times 10^3 \text{ cm GW}^{-1}$ $n_2 = 4.5 \text{ cm}^2 \text{ GW}^{-1}$	29
11	InN	1560 nm, 250 fs	$\theta$ = -3 × 10 <sup>4</sup> cm GW <sup>-1</sup>	30
12	MoS <sub>2</sub> /graphene	Z-scan, 800 nm, I <sub>0</sub> ~ 123 GW cm <sup>-2</sup>	<i>β</i> = −1217.76 cm GW <sup>-1</sup> FOM: 5.8 × 10 <sup>−14</sup> esu cm	31
13	PtSe <sub>2</sub>	Z-scan,	$\beta = -9.94 \times 10^3 \ cm \ GW^{-1}$	32
14	De-4.8	Z-scan, 800 nm	$\theta$ = -1578 ± 49 cm GW <sup>-1</sup>	33
15	Cu–Al–O thin films	Z-scan, 1550 nm	$\theta$ = -6.29 × 10 <sup>-5</sup> cm W <sup>-1</sup>	34
16	L3	Z-scan, 400 nm	$\theta$ = -80.63 cm GW <sup>-1</sup>	35
17	GaS	Z-scan, 800 nm & 1066 nm	$beta = -9.3 \times 10^3 \text{ cm GW}^{-1}$ (800 nm); $beta = -91 \text{ cm GW}^{-1}$ (1066 nm)	36
18	BTFA nanofilm COF	Z-scan, 800 nm;	$\beta = -10.1 \times 10^3 \mathrm{cm} \mathrm{GW}^{-1}$	37

19	MoS <sub>2</sub> film	Z-scan,	$\beta$ = -11.4 cm GW <sup>-1</sup>	38
20	WS <sub>2</sub> film	Z-scan,	$\theta$ = -5.25 × 10 <sup>2</sup> cm GW <sup>-1</sup>	
21	Bi <sub>2</sub> O <sub>2</sub> Se	Z-scan,	$\beta$ = -2.9 × 10 <sup>3</sup> cm GW <sup>-1</sup>	39
22	Ti <sub>3</sub> C <sub>2</sub> T <sub>x</sub> (=O rich)	Z-scan, 525 nm	$\theta$ = -1020 ± 136.2 cm GW <sup>-1</sup>	40
23	HgL2-1.0-150	Z-scan, 532 nm, 11 μJ	$\theta$ = –134 cm GW <sup>-1</sup>	41
24	GO	Z-scan,	$\beta$ = -40 cm GW <sup>-1</sup>	42
25	MOFs@CeO₂	Z-scan, 532 nm	$\beta = -80 \text{ cm GW}^{-1}$ $n_2 = -3.2 \times 10^{-19} \text{ m}^2 \text{ W}^{-1}$	43
26	(PEA) <sub>2</sub> Cs <sub>4</sub> Pb <sub>5</sub> Br <sub>1</sub>	Z-scan, 800 nm,	$\beta$ =-13.83 cm GW <sup>-1</sup> $n_2$ = 4.1× 10 <sup>-11</sup> cm <sup>2</sup> W <sup>-1</sup>	44
27	PTC-296	Z-scan, 532 nm,	$\theta$ = –193.7 cm GW <sup>-1</sup>	45
28	ZIF-67	Z-scan, 1064 nm, 4 ns	$\beta = -0.85 \pm 0.06 \text{ cm GW}^{-1}$ $n_2 = -9.3 \times 10^{-4} \text{cm}^2 \text{ GW}^{-1}$ $\chi^{(3)} = 8.2 \times 10^{-11} \text{ esu}$	46
29	Polymers (p2)	Z-scan	$\beta = -0.102 \text{ cm GW}^{-1}$ $\chi^{(3)} = 1.04 \times 10^{-13} \text{ esu}$	47
30	1-PMMA	Z-scan, 532 nm, 0.4μJ	$\beta = -4.58 \text{ cm GW}^{-1}$ $n_2 = 5.9 \times 10^{-18} \text{ m}^2 \text{ W}^{-1}$ $\chi^{(3)} = 50.2 \times 10^{-13} \text{ esu}$	48
31	DAST–PVA film	Z-scan, 520 nm;	$\beta$ = -7.57 cm GW <sup>-1</sup>	49

## 2.4 Unit cell parameters and fractional atomic coordinates

Space group				P1				
	Calculate	ad unit call		a = 23.3177 Å, b = 7.2529 Å, c = 23.3177 Å				
	Calculate				$\alpha = \gamma = 90^\circ$	°, β = 120°.		
Atoms	Х	Y	Z	Atoms	Х	Y	Z	
C1	0.85492	0.19015	0.47264	C51	1.22087	0.60188	0.19378	
N2	0.89292	0.15725	0.53519	N52	1.25887	0.56897	0.25633	
C3	0.96337	0.15966	0.56583	C53	1.32932	0.57138	0.28697	
C4	0.0018	0.12997	0.63406	C54	0.36774	0.5417	0.3552	
C5	0.07076	0.14269	0.66554	C55	0.43671	0.55441	0.38668	
C6	0.10179	0.18593	0.62893	C56	0.46773	0.59766	0.35007	
C7	0.0629	0.21309	0.56041	C57	0.42885	0.62481	0.28155	
C8	0.99439	0.20018	0.52909	C58	1.36033	0.61191	0.25023	
C9	0.7832	0.19552	0.44286	C59	1.14914	0.60725	0.164	
C10	0.75338	0.16821	0.48136	C60	1.11933	0.57993	0.2025	
C11	0.17412	0.2088	0.66138	C61	0.54007	0.62052	0.38252	
C12	0.21594	0.15841	0.72744	C62	0.58188	0.57014	0.44858	
C13	0.28422	0.18299	0.75647	C63	0.65016	0.59472	0.4776	
C14	0.3123	0.26031	0.72077	C64	0.67825	0.67203	0.44191	
C15	0.26972	0.30792	0.65408	C65	0.63567	0.71965	0.37522	
C16	0.20184	0.28283	0.62548	C66	0.56778	0.69455	0.34662	
S17	0.29758	0.40189	0.60104	S67	0.66353	0.81362	0.32218	
C18	0.63363	0.29625	0.27682	C68	0.99958	0.70797	-0.00204	
N19	0.65887	0.33186	0.23961	N69	1.02481	0.74358	-0.03925	
C20	0.61885	0.36926	0.17045	C70	0.98479	0.78099	-0.10841	
C21	0.6493	0.38688	0.13219	C71	1.01525	0.7986	-0.14667	
C22	0.61095	0.40631	0.06357	C72	0.9769	0.81804	-0.21529	
C23	0.54156	0.40927	0.03236	C73	0.90751	0.82099	-0.2465	
C24	0.51135	0.39692	0.07127	C74	0.87729	0.80865	-0.2076	
C25	0.54957	0.37712	0.13971	C75	0.91552	0.78885	-0.13915	
C26	0.6755	0.252	0.34687	C76	1.04144	0.66373	0.068	
C27	0.74433	0.23787	0.37574	C77	1.11027	0.64959	0.09688	
C28	0.50075	0.4042	0.95943	C78	0.8667	0.81592	0.68056	
C29	0.53056	0.38823	0.92036	C79	0.8965	0.79996	0.6415	

**Table S7.** Unit cell parameters and fractional atomic coordinates for TF-TZ were calculated based on the AB stacking.

C30	0.49205	0.35631	0.85249	C80	0.85799	0.76804	0.57363
C31	0.42292	0.33672	0.82162	C81	0.78887	0.74844	0.54276
C32	0.39351	0.36423	0.86084	C82	0.75945	0.77595	0.58198
C33	0.43163	0.39605	0.92869	C83	0.79758	0.80777	0.64983
C34	0.65594	0.16228	0.49514	C84	1.02189	0.574	0.21628
N35	0.59296	0.18144	0.47152	N85	0.9589	0.59316	0.19266
C36	0.5634	0.17362	0.51221	C86	0.92934	0.58535	0.23335
C37	0.49582	0.20929	0.48342	C87	0.86176	0.62101	0.20455
C38	0.46641	0.21697	0.52266	C88	0.83235	0.6287	0.2438
C39	0.50422	0.18892	0.59131	C89	0.87016	0.60065	0.31245
C40	0.5719	0.14973	0.61996	C90	0.93784	0.56146	0.3411
C41	0.60141	0.14252	0.58072	C91	0.96735	0.55424	0.30186
C42	0.68494	0.1815	0.45279	C92	1.05089	0.59323	0.17393
C43	0.64593	0.22378	0.38543	C93	1.01187	0.6355	0.10657
C44	0.47336	0.20867	0.63276	C94	0.8393	0.6204	0.3539
C45	0.40979	0.28265	0.60547	C95	0.77573	0.69437	0.32661
C46	0.37968	0.30743	0.64345	C96	0.74563	0.71915	0.36459
C47	0.41337	0.25977	0.71103	C97	0.77932	0.67149	0.43217
C48	0.47693	0.18202	0.73792	C98	0.84287	0.59374	0.45906
C49	0.50689	0.15777	0.69957	C99	0.87284	0.5695	0.4207
N50	0.38317	0.28781	0.75162	N100	0.74912	0.69954	0.47276

	Spac	e group		P1						
	Calculat	ed unit coll		a = 23.3177 Å, b = 7.2529 Å, c = 23.3177 Å						
	Calculat	eu unit tell			$\alpha = \gamma = 90^\circ$ , $\beta = 120^\circ$ .					
Atoms	Х	Y	Z	Atoms	Х	Y	Z			
C1	0.85286	0.15646	0.47524	C54	1.23473	0.45687	0.19359			
N2	0.89569	0.11601	0.54371	N55	1.27756	0.41641	0.26206			
C3	0.96566	0.13698	0.57388	C56	1.34754	0.43738	0.29223			
C4	0.00578	0.10804	0.64195	C57	0.38766	0.40844	0.3603			
C5	0.07426	0.13375	0.67227	C58	0.45613	0.43416	0.39062			
C6	0.10309	0.18901	0.63466	C59	0.48496	0.48942	0.35302			
C7	0.06241	0.21643	0.56636	C60	0.44429	0.51683	0.28471			
C8	0.99436	0.19078	0.53621	C61	1.37624	0.49118	0.25457			
С9	0.78677	0.15412	0.44572	C62	1.16865	0.45452	0.16407			
C10	0.75122	0.1077	0.48172	C63	1.1331	0.4081	0.20007			
C11	0.17505	0.21989	0.66575	C64	0.55693	0.52029	0.38411			
C12	0.21834	0.17251	0.73181	C65	0.60022	0.47292	0.45016			
C13	0.28626	0.20108	0.75947	C66	0.66813	0.50149	0.47783			
C14	0.3127	0.27925	0.72243	C67	0.69458	0.57965	0.44078			
C15	0.26876	0.32413	0.65574	C68	0.65063	0.62454	0.3741			
C16	0.20109	0.29517	0.62844	C69	0.58296	0.59558	0.3468			
017	0.77784	0.23401	0.34462	070	1.15972	0.53442	0.06298			
S18	0.29477	0.41801	0.60112	S71	0.67664	0.71841	0.31947			
C19	0.63943	0.29147	0.27953	C72	1.02131	0.59188	-0.00211			
N20	0.66686	0.3404	0.23891	N73	1.04874	0.6408	-0.04274			
C21	0.626	0.38046	0.17016	C74	1.00788	0.68086	-0.11148			
C22	0.65526	0.40429	0.13104	C75	1.03714	0.70469	-0.15061			
C23	0.61571	0.42614	0.06259	C76	0.99759	0.72654	-0.21905			
C24	0.54638	0.4254	0.03254	C77	0.92826	0.7258	-0.2491			
C25	0.51747	0.40677	0.07248	C78	0.89935	0.70718	-0.20917			
C26	0.5569	0.38445	0.14071	C79	0.93878	0.68485	-0.14093			
C27	0.67577	0.23247	0.34211	C80	1.05765	0.53287	0.06047			
C28	0.74868	0.20848	0.37525	C81	1.13056	0.50888	0.0936			
C29	0.50435	0.42275	0.95967	C82	0.88622	0.72315	0.67803			
C30	0.53284	0.40989	0.91933	C83	0.91471	0.7103	0.63769			
C31	0.49319	0.37941	0.85146	C84	0.87507	0.67982	0.56982			

**Table S8.** Unit cell parameters and fractional atomic coordinates for TFP-TZ were calculatedbased on the AB stacking.

C32	0.42421	0.35818	0.82183	C85	0.80609	0.65859	0.54018
C33	0.3961	0.38308	0.86235	C86	0.77798	0.68348	0.58071
C34	0.43534	0.41341	0.93018	C87	0.81722	0.71381	0.64854
O35	0.58058	0.19763	0.35012	088	0.96245	0.49803	0.06848
C36	0.65082	0.11877	0.48739	C89	1.0327	0.41918	0.20575
N37	0.58197	0.1486	0.46272	N90	0.96385	0.449	0.18107
C38	0.55438	0.15903	0.50503	C91	0.93625	0.45943	0.22339
C39	0.48728	0.20024	0.47744	C92	0.86916	0.50064	0.19579
C40	0.45976	0.22018	0.51812	C93	0.84164	0.52058	0.23647
C41	0.49901	0.19895	0.58698	C94	0.88089	0.49936	0.30534
C42	0.5663	0.15559	0.61441	C95	0.94817	0.45599	0.33277
C43	0.5939	0.13617	0.57371	C96	0.97578	0.43658	0.29207
C44	0.67897	0.13539	0.44977	C97	1.06085	0.43579	0.16812
C45	0.64097	0.18913	0.37881	C98	1.02284	0.48953	0.09717
C46	0.46982	0.22555	0.62975	C99	0.85169	0.52596	0.3481
C47	0.40617	0.29888	0.60326	C100	0.78805	0.59928	0.32162
C48	0.37731	0.32583	0.64239	C101	0.75918	0.62623	0.36075
C49	0.41237	0.28097	0.71022	C102	0.79425	0.58137	0.42858
C50	0.476	0.20439	0.73626	C103	0.85788	0.5048	0.45462
C51	0.50466	0.17793	0.69683	C104	0.88654	0.47833	0.41519
052	0.78142	0.04686	0.53807	0105	1.1633	0.34726	0.25643
N53	0.38335	0.3095	0.75187	N106	0.76522	0.6099	0.47023

## 3. References

- 1. Materials Studio; Accelrys: San Diego.
- 2. http://www.ba.ic.cnr.it/softwareic/expo/.
- 3. http://www.jp-minerals.org/vesta/en/.
- 4. *Gaussian 16, Revision C.01, Gaussian, Inc., Wallingford, CT*, 2019.
- 5. A. D. Becke, J. Chem. Phys., 1993, **98**, 1372-1377.
- 6. A. D. Becke, J. Chem. Phys., 1993, 98, 5648-5652.
- 7. P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623-11627.
- 8. R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724-728.
- 9. W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257-2261.
- 10. S. Manzetti and T. Lu, *RSC Adv.*, 2013, **3**, 25881-25890.
- 11. Z. Qiao, H. Han, X. Li, X. Wang, T. Lan, R. Wang and W. Ji, ACS Appl. Nano Mater., 2022, **5**, 11465-11473.
- 12. X. Chen, H. Zhang, C. Ci, W. Sun and Y. Wang, *ACS Nano*, 2019, **13**, 3600-3607.
- 13. C. Zhang, S. Zhang, Y. Yan, F. Xia, A. Huang and Y. Xian, ACS Appl. Mater. Interfaces, 2017, **9**, 13415-13421.
- 14. R. Xia, X. Zheng, C. Li, X. Yuan, J. Wang, Z. Xie and X. Jing, *ACS Nano*, 2021, **15**, 7638-7648.
- 15. J. Jia, J. Wang, M. Li, C. Gong, G. Liang, Y. Song and Y. She, *Dyes Pigm.*, 2022, **205**, 110398.
- Y. Jiang, I. Oh, S. H. Joo, O. Buyukcakir, X. Chen, S. H. Lee, M. Huang, W. K. Seong, J. H. Kim, J. U. Rohde, S. K. Kwak, J. W. Yoo and R. S. Ruoff, *ACS Nano*, 2019, **13**, 5251-5258.
- S. Haldar, M. Wang, P. Bhauriyal, A. Hazra, A. H. Khan, V. Bon, M. A. Isaacs, A. De, L. Shupletsov, T. Boenke, J. Grothe, T. Heine, E. Brunner, X. Feng, R. Dong, A. Schneemann and S. Kaskel, *J. Am. Chem. Soc.*, 2022, **144**, 9101-9112.
- 18. C. Yin, X. Liang, G. Hu, X. Hu, X. Chen, P. Li and W. Xiang, *Materials Characterization*, 2017, **126**, 96-103.
- L. Zhang, Y. Zhou, M. Jia, Y. He, W. Hu, Q. Liu, J. Li, X. Xu, C. Wang, A. Carlsson, S. Lazar, A. Meingast, Y. Ma, J. Xu, W. Wen, Z. Liu, J. Cheng and H. Deng, *Matter*, 2020, *2*, 1049-1063.

- L. Xu, J. Sun, T. Tang, H. Zhang, M. Sun, J. Zhang, J. Li, B. Huang, Z. Wang, Z. Xie and W. Y. Wong, *Angew. Chem. Int. Ed.*, 2021, **60**, 11326-11334.
- 21. G.-J. Zhou and W.-Y. Wong, *Chem. Soc. Rev.*, 2011, **40**, 2541-2566.
- 22. M. Li, C. Gong, J. Du, D. Ding, D. Du, D. Wang, J. Jiang, T. Li, C. Zheng, Y.-F. Yang, Y. She and J. Jia, *ACS Materials Lett.*, 2023, **5**, 694-703.
- G. Liu, S. Dai, B. Zhu, P. Li, Z. Wu and Y. Gu, *Opt. Laser Technol.*, 2019, 120, 105746.
- 24. Y. Yuan, B. Zhu, F. Cao, J. Wu, Y. Hao and Y. Gu, *Results Phys.*, 2021, **27**, 104568.
- J. Wang, P. Lu, Y. Shuai, Z. Fan, Y. Li, X. Li, R. Hong, C. Tao, Q. Wang, H. Lin, Z. Han and D. Zhang, ACS Appl. Nano Mater., 2023, 6, 13421-13430.
- 26. J. Li, H. Dong, B. Xu, S. Zhang, Z. Cai, J. Wang and L. Zhang, *Photon. Res.*, 2017, **5**, 457-460.
- 27. H. M. Asif, N. Qu, Y. Zhou, L. Zhang, F. K. Shehzad, Z. Shi, Y. Long and S. U. Hassan, *Inorg. Chem. Front.*, 2017, *4*, 1900-1908.
- X. Jiang, S. Liu, W. Liang, S. Luo, Z. He, Y. Ge, H. Wang, R. Cao, F. Zhang, Q. Wen, J. Li, Q. Bao, D. Fan and H. Zhang, *Laser Photonics Rev.*, 2018, 12, 1700229.
- X. Xu, X. Zheng, F. He, Z. Wang, H. Subbaraman, Y. Wang, B. Jia and R. T. Chen, *Sci. Rep.*, 2017, 7, 9646.
- 30. L. Monroy, M. Jiménez-Rodríguez, E. Monroy, M. González-Herráez and F. B. Naranjo, *Appl. Sci.*, 2020, **10**, 7832.
- 31. M. He, C. Quan, C. He, Y. Huang, L. Zhu, Z. Yao, S. Zhang, J. Bai and X. Xu, *J. Phys. Chem. C*, 2017, **121**, 27147-27153.
- 32. G. Wang, Z. Wang, N. McEvoy, P. Fan and W. J. Blau, *Adv. Mater.*, 2021, **33**, 2004070.
- 33. Y. Sun, H. Li, X. Gao, M. G. Humphrey, C. Zhang and Z. Huang, *Mat. Today Phys.*, 2023, **32**, 101024.
- 34. J. Xu, Q. Liu, X. Li, R. Hong, C. Tao, Q. Wang, H. Lin, Z. Han and D. Zhang, *Opt. Mater.*, 2023, **136**, 113466.
- 35. X. Xiao, M. Liu, J. Zhou, H. Zhu, C. Wang, Z. Chen, Y. Wang, S. Xiao and J. He, *Opt. Mater.*, 2022, **132**, 112773.
- S. Ahmed, P. K. Cheng, J. Qiao, W. Gao, A. M. Saleque, M. N. Al Subri Ivan, T. Wang, T. I. Alam, S. U. Hani, Z. L. Guo, S. F. Yu and Y. H. Tsang, *ACS Nano*, 2022, **16**, 12390-12402.
- 37. Y. Luo, M. Li, J. Tang, J. Zang, Y. Wang, T. Liu and Y. Fang, J. Colloid

Interface Sci., 2022, **627**, 569-577.

- S. Zhang, N. Dong, N. McEvoy, M. O'Brien, S. Winters, N. C. Berner, C. Yim, Y. Li, X. Zhang, Z. Chen, L. Zhang, G. S. Duesberg and J. Wang, ACS Nano, 2015, 9, 7142-7150.
- 39. X. Tian, H. Luo, R. Wei, C. Zhu, Q. Guo, D. Yang, F. Wang, J. Li and J. Qiu, *Adv. Mater.*, 2018, **30**, 1801021.
- 40. H. Li, S. Chen, D. W. Boukhvalov, Z. Yu, M. G. Humphrey, Z. Huang and C. Zhang, *ACS Nano*, 2022, **16**, 394-404.
- L. Xu, J. Sun, T. Tang, H. Zhang, M. Sun, J. Zhang, J. Li, B. Huang, Z. Wang, Z. Xie and W.-Y. Wong, *Angew. Chem. Int. Ed.*, 2021, 60, 11326-11334.
- 42. S. Kumar, M. Anija, N. Kamaraju, K. S. Vasu, K. S. Subrahmanyam, A. K. Sood and C. N. R. Rao, *Appl. Phys. Lett.*, 2009, **95**, 191911.
- 43. J. Huang, F. Lang, Y. Cui, L. Xie, K. Geng, Y. Zhao and H. Hou, *Adv. Optical Mater.*, 2022, **10**, 2201872.
- 44. A. Mushtaq, B. Pradhan, D. Kushavah, Y. Zhang, D. Naumenko, H. Amenitsch, J. Hofkens and S. K. Pal, *Mater. Adv.*, 2022, **3**, 8211-8219.
- 45. G.-H. Chen, Y.-P. He, Z.-R. Wang, Q.-H. Li, Z.-Z. Ma and J. Zhang, *Inorg. Chem. Front.*, 2022, **9**, 1984-1991.
- 46. H. Pan, H. Chu, X. Wang, Y. Li, S. Zhao, G. Li and D. Li, *Mater. Chem. Front.*, 2020, **4**, 2081-2088.
- 47. Z. Li, D. Wang, D. Ramella, H. Gao, H. Cao, Y. Zhao, Z. Miao, Z. Yang and W. He, *Polym. Chem.*, 2020, **11**, 3046-3053.
- 48. K. Geng, Q. Xie, Y. Zhao, L. Yang, Y. Song and H. Hou, *Chem. Asian J.*, 2021, **16**, 981-987.
- 49. M. Zhang, X. Xu, W. Hu, Y. Jiang, C. Chen, N. Dong, J. Wang, Y. Liang, B. Zhu, H. Zhang and J. Xu, *Adv. Optical Mater.*, 2023, **11**, 2202241.