Electronic Supporting Information (ESI)

Tris(*S*,*S*-dioxides)-trithiasumanene: Strong Fluorescence and Cocrystal with 1,2,6,7,10,11-Hexabutoxytriphenylene (HBT)

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1. Synthesis

All chemicals and solvents were purified according to the standard procedure.^[1] Compounds 2,3,6,7,10,11-hexabutoxytriphenylene (HBT) and trithiasumanene (**1**) was synthesized according to literature.^[2] Melting points were determined on WRS-2 melting point apparatus. ¹H and ¹³C NMR spectra were recorded on a Bruker Advance III 400MHz (100 MHz for ¹³C) spectrometer using CDCl₃ as solvent. High resolution mass spectral analysis (HRMS) was carried out on Brucker APEX II type mass spectrometer.



Compound **1** (750 mg, 1 mmol) and hydrogen peroxide (H₂O₂ aqueous 30%, 20 mL) were dissolved in the mixed solvent of dichloromethane (CH₂Cl₂, 10 mL) and glacial acetic acid (AcOH, 20 mL). The resulting mixture was stirred at 60 °C for 15 h. The reaction mixture was then diluted by adding distilled water (25 ml) and then extracted with CH₂Cl₂ (3 × 20 mL). The organic layers were combined and dried over anhydrous Na₂SO₄, then concentrated under reduced pressure. The crude product was further purified by column chromatography on silica (eluent, CH₂Cl₂: petro ether, 1:1, v/v) to afford compound **3** as a yellow power (787 mg, yield 93%). mp: 210-212 °C. ¹H NMR (400 MHz, CDCl₃) δ =4.72 (t, *J*=6.1 Hz, 12H), 1.98 (m, 12H), 1.68 (m, 12H), 1.07 (t, *J*=7.4 Hz, 18H); ¹³C NMR(100 MHz, CDCl₃): δ =149.79, 127.18, 114.62, 74.65, 31.66, 19.10, 13.76; HRMS: calculated for C₄₂H₅₄S₃O₁₂+ H⁺, 847.2850; found, 847.2885.



Compound 4 (690 mg, 1 mmol) and H_2O_2 (20 mL) were dissolved in the mixed solvent of CH_2Cl_2 (10 mL) and AcOH (20 mL). The resulting mixture was stirred at 60 °C for 15 h. The reaction mixture was then diluted by adding distilled water (25 ml) and then extracted with CH_2Cl_2 (3 × 20 mL). The

organic layers were combined and dried over anhydrous Na₂SO₄, then concentrated under reduced pressure. The crude product was further purified by column chromatography on silica (eluent, CH₂Cl₂: Petro ether, 1:1, v/v) to afford compound **5** (red solid, 671 mg, yield 93%). Mp:116-117 °C. ¹H NMR (400 MHz, CDCl₃) δ =7.74 (4H), 4.57 (t, *J*=6.5Hz, 4H), 4.26 (m, 8H), 1.98(m, 12H), 1.67 (m, 12H), 1.08 (m, 18H); ¹³C NMR (100 MHz CDCl₃): δ =152.97, 149.05, 144.97, 126.22, 122.42, 121.15, 118.32, 109.60, 106.48, 74.31, 69.62, 68.92, 32.21, 31.50, 31.42, 19.41, 19.34, 19.11, 14.00, 13.97, 13.95. HRMS (m/z): [M]+ calculated for C₄₂H₅₈O₈, 723.3925; found, 723.3939.



Compound **6** (720 mg, 1 mmol) and H₂O₂ (20 mL) were dissolved in the mixed solvent of CH₂Cl₂ (10 mL) and AcOH (20 mL). The resulting mixture was stirred at 60 °C for 15 h. The reaction mixture was then diluted by adding distilled water (25 ml) and then extracted with CH₂Cl₂ (3 × 20 mL). The organic layers were combined and dried over anhydrous Na₂SO₄, then concentrated under reduced pressure. The crude product was further purified by column chromatography on silica (eluent, CH₂Cl₂: Petro ether, 1:1, v/v) to afford compound **7** as a pale yellow powder (627 mg, yield 80%). Mp:224-225 °C. ¹H NMR (400 MHz, CDCl₃) δ =7.71 (s, 2H), 4.72 (t, *J*=6.1 Hz, 4H), 4.59 (t, *J*=6.4 Hz, 4H), 4.22 (t, *J*=6.3 Hz, 4H), 1.98 (m, 12H), 1.69 (m, 12H), 1.08 (m, 18H); ¹³C NMR (100 MHz CDCl₃): δ =153.52, 148.94, 145.74, 126.67, 124.97, 119.55, 117.10, 114.50, 110.26, 74.27, 74.05, 69.84, 32.11, 31.75, 31.36, 19.35, 19.16, 19.05, 13.89, 13.84; HRMS (m/z): [M]+ calculated for C₄₂H₅₆O₁₀, 785.3388; found, 785.3421.

2. Theoretical calculation

All calculations were carried out with the Gaussian 09 programs.^[3] For DFT calculations, we used the hybrid gradient corrected exchange functional of Lee, Yang, and Parr.^[4a, b] A standardized 6-311G basis set^[4c] was used together with polarization (d) and (p) functions. The calculation of frontier orbitals for compounds **1**, **3**, and HBT were based on their optimized structures. The calculated frontier orbitals are summarized in Table S1.

Compounds	$E_{ m HOMO-1}$ [eV]	<i>E</i> _{HOMO} [eV]	<i>E</i> _{LUMO} [eV]	$E_{ m LUMO+1}$ [eV]	$\Delta E_{ m HOMO-LUMO}^{[a]}$ [eV]
1	-4.76	-4.67	-1.20	-1.14	3.47
3	-5.98	-5.50	-2.43	-2.01	3.07
HBT	-4.93	-4.93	-0.94	-0.94	3.98

Table S1.	The calculated	energy	level fo	r the	frontier	orbitals
						01010000

^[a] $\Delta E_{\text{HOMO-LUMO}} = E_{\text{LUMO}} - E_{\text{HOMO}}$



Fig. S1 Comparison of the optimized structure of compounds **1** and **3**; the numeric data indicates the bond lengths (top panels) and bowl depth (bottom panels) in the unit of Å.



Fig. S2 Calculated molecular orbitals of compound 3.



Fig. S3 Calculated molecular orbitals of compound 1.

Table S2. Comparison of bond lengths and angles for the central core of compound 3.^[a]



Ring A

Bond length	Optimized ^[b]	Cocrystal ^[c]
C1–C2, C9–C10, C15–C16	1.46 Å	1.48 Å
C1-C6, C2-C3, C8-C9, C10-C11, C14-C15, C16-C17	1.39 Å	1.39 Å
C5-C6, C3-C4, C7-C8, C11-C12, C13-C14, C17-C18	1.39 Å	1.40 Å
Angle		
C1-C2-C3, C2-C1-C6, C8-C9-C10, C9-C10-C11, C14-C15-C16, C15-C16-C17	119.3°	120.1°
C2-C3-C4, C1-C6-C5, C7-C8-C9, C10-C11-C12, C13-C14-C15, C16-C17-C18	119.1°	117.5°
C3-C4-C5, C4-C5-C6, C8-C7-C12, C7-C12-C13, C14-C13-C18, C13-C18-C17	121.5°	122.5°

Ring B

Bond length	Optimized ^[b]	Cocrystal ^[c]
C4–C5, C7–C12, C13–C18	1.39 Å	1.38 Å
C5–C7, C4–C13, C12–C18	1.42 Å	1.42 Å
Angle		
C4–C5–C7, C5–C4–C13	119.8°	120.1°
C5–C7–C12, C4–C13–C18	120.4 [°]	119.9°
C7–C12–C18, C13–C18–C12	119.8°	120.0°
	Ping C	

Kilig C					
Bond length	Optimized ^[b]	Cocrystal ^[c]			
S1-C6, S1-C8, S2-C3, S2-C14, S3-C11, S3-C17	1.86 Å	1.84 Å			
Angle					
C6-S1-C8, C3-S2-C14, C11-S3-C17	93.0°	95.0°			
S1-C6-C5, S1-C8 -C7, S2-C3-C4, S2-C14-C13, S3-C11-C12, S3-C17-C18	106.0 [°]	105.0°			
C6–C5–C7, C5–C7–C8, C11–C12–C18, C12–C18–C17, C3–C4–C13, C4–C13–C14	117.3°	117.5°			

^[a] The calculated reversion energy from bowl-shaped to planar for compound **3** is 5.36 Kcal mol⁻¹;

^[b] The optimized structure of compound **3** by averaging the bond lengths and angles for the same positions on rings **A**, **B**, and **C**.

^[c] Structure of compound **3** in the cocrystal **3**•(HBT) by averaging the bond lengths and angles for the same positions on rings **A**, **B**, and **C**.

3. Optical properties

UV/Vis spectra were measured on Lambda 35 spectrometer (Varian). Fluorescence excitation and emission spectra were recorded with an FLS920 (Edinburgh Instruments) combined fluorescence lifetime and steady state spectrometer. For the emission spectra in solution, the compounds were dissolved in the distilled CH_2Cl_2 with $c = 10^{-5}$ mol L⁻¹, and the measurement were conducted at 20 °C. The solid state emission spectra were measured by dispersing the samples on the KBr pellet. The solid state circulardichroism (CD) spectra of cocrystal **3**•(HBT) were measured for each single crystal on a JASCO J-815 spectrometer.

Table S3. Emission properties of compounds 1 and 3 in CH₂Cl₂ solution (10⁻⁵ mol L⁻¹) at 20 °C

compounds	$\lambda_{ex} [nm]$	$\lambda_{em} [nm]$	Stokes shift [cm ⁻¹]	Quantum yield [%]
1	315	418	7823	6.9
3	313	463	10351	5.8

Table S4. The emission and excitation properties of compounds in solid state at 20 °C

	λ_{ex}	λ_{em}	Stokes shift	Quantum yield	Fluorescence
	[nm]	[nm]	$[cm^{-1}]$	[%]	lifetime [ns]
3	313	478	11028	2.9	1.62
HBT	292	404	9494	9.9	9.09
3•(HBT)	320	572	13767	2.9	22.17

4. X-ray diffraction analysis

The single crystals of cocrystal $3 \cdot (HBT)$ was obtained by slow evaporation of the mixed solution of compound 3 and HBT (molar ratio, 1 : 1) in CH₂Cl₂-CH₃OH (v/v, 1 : 1) at room the temperature. After about one week, the pale yellow needle-like single crystals were obtained. The thin layer chromatography (TLC) investigation revealed that the resulting crystals contained both compound 3and HBT, and also the resulting cocrystals exhibited the distinctly different emissions from HBT and compound 3.

Because the size of the cocrystals **3**•(HBT) was very small (typical, $0.40 \times 0.03 \times 0.02 \text{ mm}^3$), the X-ray diffraction measurement on an Agilent SuperNova diffractometer failed to afford enough reflections for the structure analysis. Thus, the diffraction analysis of the cocrystal **3**•(HBT) was conducted at 3W1A beam line of Beijing Synchrotron Radiation Facility (BSRF) at Institute of High Energy Physics, Chinese Academy of Science, Beijing. The crystal structure was solved by direct methods *SIR2004*^[5] and refined by full-matrix least-squares on *F*² by means of *SHELXL-97*.^[6] The calculated positions of the hydrogen atoms were included in the final refinement.

It should be noted that compound **3** also could form the tiny single crystals, whereas the quality of the crystal was not enough good for the diffraction analysis by either Agilent SuperNova diffractometer or 3W1A beam line of Beijing Synchrotron Radiation Facility (BSRF).

The selected crystallographic data of cocrystal **3**•(HBT) are as following: empirical formula, $C_{84}H_{114}O_{18}S_3$; formula weight, 1507.93; crystal size, $0.40 \times 0.03 \times 0.02$ mm³; measurement temperature, 77(1) K; irradiation wavelength, 0.95382 Å; crystal system, triclinic; space group, *P*1; a = 10.542(2) Å, b = 12.791(3) Å, c = 15.052(3) Å, $a = 97.91(3)^{\circ}$, $\beta = 98.81(3)^{\circ}$, $\gamma = 96.16(3)^{\circ}$, V = 1969.4(7) Å³; Z = 1; absorption coefficient $\mu = 0.163$ mm⁻¹; F(000) = 810; $2.42 \le \theta \le 27.54$; total reflections, 6954; refinement parameters, 959; restraints, 3 (for the non-centrosymmetric space group *P*1); Flack parameter, 0.05(6); Goodness-of-fit on F^2 , 1.171; final *R* indices for $I > 2\sigma(I)$], $R_1 = 0.0795$, $wR_2 = 0.1831$; largest differential peak and hole, 1.029 and -0.936 e A⁻³.

The bond lengths of the central polycyclic skeletons for molecule **3** and HBT are shown in Figs. S4 and S5, respectively. As mentioned in the main manuscript, molecules **3** and HBT are slightly dimerized in the columnar stacks with alternating inter-planar distances of 3.55 and 3.63 Å. The intermolecular overlap modes between molecule **3** and HBT are also different for the intra-dimer and inter-dimer ones, as shown in Fig. S6.



Fig. S4 Top view of molecule **3** in the cocrystal **3**•(HBT) with bond lengths (in unit of Å) of the central polycyclic ring and bond lengths C-O of the butoxy groups.



Fig. S5 Top view of molecule HBT in the cocrystal **3**•(HBT) with bond lengths (in unit of Å) of the central polycyclic ring and bond lengths C-O of the butoxy groups.



Fig. S6 The intermolecular overlap modes HBT and molecule **3** in the cocrystal **3**•(HBT): a) intra-dimer and b) inter-dimer. The figures are drawn along the direction perpendicular to the mean plane of HBT molecule. Molecule **3** and HBT are painted in blue and grey, respectively.

5. Thermogravimetric Analyses (TGA)

To elucidate the thermal stability of compound **3**, we have carried out the thermogravimetric analyses (TGA) of compounds **1** and **3**. The TGA measurements were conducted on 1090B type thermal analyzer (Dupont Engineering Polymers) as shown in Fig. S7. The degradation temperature (T_d) of compound **1** is 320 °C. As for compound **3**, the weight lost about 8% was observed in the temperature region of 170–228 °C. Concerning the molecular formula weight of compound **3** (M_w = 847.2850), the lost of the formula weight (8%) is about 68, which reflects to the loss of one SO₂ unit (64). The massive degradation of compound **3** occurs above 328 °C.



Fig. S7 Thermogravimetric analyses of compounds 1 and 3

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7. ¹H NMR and ¹³C NMR Spectra











