Electronic Supplementary Information

General Techniques

All chemicals and solvents were purified according to the standard procedure.¹ HBT and HET were synthesized according to literature.² The ultrasonic equipment is POGSON-1000D (Najing Pogson Instrument Co., LTD) with the power of 50–1000 W and frequency of 22 ± 1 kHz. Melting points (Mp) 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 and TMS as internal standard. The HRMS was carried out on a maXis 4G mass spectrometer (Bruker Daltonic Inc.). UV-Vis spectra were measured on Shimadazu UV-2600 spectrometer. For the UV-Vis in CH_2Cl_2 , $c = 10^{-5}$ mol L⁻¹. For the UV-Vis in solid state, the sample was dispersed in KBr with a concentration of 5% in weight, and compressed to a round pellet under a pressure of 16 MPa. Fluorescence excitation and emission spectra were recorded with an F-7000 FL spectrophotometer, and the measurements were conducted in CH₂Cl₂ solution ($c = 10^{-5} \text{ mol } \text{L}^{-1}$) at 20°C. The IR spectra were record on the PerkinElmer Spectrum 400 spectrometer with the resolution of 2 cm⁻¹. The cyclic voltammery (CV) and differential pulse voltammetry (DPV) analyses were recorded on a RST 5000 electrochemical workstation at a scan rate of 50 mV s^{-1} , with glassy carbon discs as working electrode, Pt wire as counter electrode, and SCE electrode as reference electrode. The concentration was 1×10^{-4} mol L⁻¹ in CH₂Cl₂, and the supporting electrolyte was $(n-Bu)_4N \cdot PF_6$ (0.1 mol L⁻¹). The measurement was performed at 20 °C after bubbling the solution with N₂ gas for 15 min. The X-ray diffraction was carried out on SuperNova (Agilent) type diffractometer. The crystal structures were solved by a direct method $SIR2004^3$ and refined by full-matrix least-square method on F^2 by means of SHELXL-97.⁴ The calculated positions of hydrogen atoms were included in the final refinement.

References

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Synthesis



Scheme S1. Synthesis of tritellurasumanene 3a from HBT. Reaction conditions: i) *n*-BuLi, hexane, TMEDA, 60 °C, 3h; ii) Te powder, ultrasound, r.t., 12 h.

To a hexane (25 mL) solution of 2,3,6,7,10,11-hexabutoxytriphenylene (**HBT**) (3.37 g, 5 mmol) was added TMEDA (7.5 mL) and *n*-BuLi (2.4 M in hexane, 31.3 mL, 75 mmol) at 60 °C for 4 hours. The resulting solution was cooled to -30° C and diluted with 60 mL THF. Tellurium powder (9.57 g, 75 mmol) was added in one portion. The resulting black mixture was slowly warmed to room temperature and allowed to stir under ultrasound for 12 hours. The reaction was quenched by adding distilled water and then extracted with CH₂Cl₂ (3 × 50 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: 5, *v*/*v*) to afford **3a** as a yellow solid (1.57 g, 30%), **4a** as a yellow solid (0.458 g, 10%).

For compound **3a**: Mp, 89.6–91.8 °C; ¹H NMR (400 MHz, CDCl₃): δ 4.34 (*t*, *J* = 6.5 Hz, 12H), 1.91–1.84 (*m*, 12H), 1.67–1.57 (*m*, 12H), 1.05 (*t*, *J* = 7.4 Hz, 18H); ¹³C NMR (100 MHz, CDCl₃): δ 151.98, 136.69, 117.37, 73.05, 32.70, 19.55, 14.01; HRMS (*m/z*): [M]⁺ calculated for C₄₂H₅₄O₆Te₃, 1038.1055; found 1038.1080.

For compound **4a**: Mp, 113.4–115.7°C; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (*s*, 2H), 4.33–4.28 (*m*, 12H), 2.00–1.93 (*m*, 4H), 1.88–1.81 (*m*, 8H), 1.70–1.57 (*m*, 12H), 1.05 (*dt*, *J* = 14.6, 7.4 Hz, 18H). ¹³C NMR (100 MHz, CDCl₃) δ 151.20, 150.85, 149.24, 136.83, 133.84, 127.46, 122.03, 115.40, 106.14, 73.15, 72.82, 69.45, 32.82, 32.78, 31.70, 19.55, 19.51, 14.02, 14.00, 13.96; HRMS (*m/z*): [M+H]⁺ calculated for (C₄₂H₅₆O₆Te₂ + H), 915.2256; found, 915.2239.



Scheme S2. Synthesis of tritellurasumanene 3b from HET. Reaction conditions: i) *n*-BuLi, hexane, TMEDA, 60 °C, 3h; ii) Te powder, ultrasound, r.t., 12 h.

To a hexane (50 mL) solution of 2,3,6,7,10,11-hexaethoxytriphenylene (**HET**) (5.16 g, 10 mmol) was added TMEDA (15 mL) and *n*-BuLi (2.4 M in hexane, 41.6 mL, 100 mmol) at 60 °C for 3 hours. The resulting solution was cooled to -30° C and diluted with 60 mL THF. Tellurium powder (12.8 g, 100 mmol) was added in one portion. The resulting black mixture was slowly warmed to room temperature and allowed to stir under ultrasound for 12 hours. The reaction was quenched by adding distilled water and then extracted with CH₂Cl₂ (3 × 50 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 **3b** as a yellow solid (2.17 g, 25%), **4b** as a yellow solid (0.74 g, 10%).

For compound **3b**: Mp, 136.6–138°C; ¹H NMR (400 MHz, CDCl₃): δ 4.45–4.40 (*q*, 12H), 1.53–1.50 (*t*, *J* = 4 Hz, 18H); ¹³C NMR (100 MHz, CDCl₃): δ 151.70, 136.74, 117.70, 68.83, 16.33; HRMS (*m/z*): [M]⁺ calculated for C₃₀H₃₀O₆Te₃, 874.9284; found, 874.9325.

For compound **4b**: Mp, 127 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.87 (*s*, 2H), 4.43–4.32 (*m*, 12H), 1.61–1.57 (*t*, *J* = 4 Hz, 6H), 1.52–1.47 (*m*, 12H); ¹³C NMR (100 MHz, CDCl₃): δ 150.82, 150.52, 148.98, 136.82, 133.79, 127.42, 122.29, 115.66, 106.26, 68.84, 68.64, 65.29, 16.41, 16.36, 15.10; HRMS (*m*/*z*): [M]⁺ calculated for C₃₀H₃₂O₆Te₂, 746.0300; found, 746.0295.



Scheme S3. Bromination 3a to form 3a•Br₆.

Compound **3a** (50 mg, 0.048 mmol) was dissolved in CH₂Cl₂ (5 mL), and a solution of bromine (75.6 mg, 0.48 mmol) in CH₂Cl₂ (5 mL) was added introduced slowly. After stirred at room temperature for 15 min, and *n*-hexane (100 mL) was added. The resulting mixture was kept in a refrigerator for 2 hours (-20 °C) to give orange precipitate. The precipitate was collected by suction, washed with n-hexane, and dried in air to give **3a**•**Br**₆ as orange miro-crystals (72.8 mg, 100% yield). **3a**•**Br**₆: Mp, 221.2–223.1 °C; ¹H NMR (400 MHz, CDCl₃) δ 4.65 (*t*, *J* = 6.3 Hz, 12H), 2.07–2.00 (*m*, 12H), 1.73–1.63 (*m*, 12H), 1.10 (*t*, *J* = 7.4 Hz, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 151.81, 134.60, 133.40, 73.52, 32.10, 19.29, 13.86.



Scheme S4. Bromination 3b to form 3b•Br₆.

Compound **3b** (30 mg, 0.034 mmol) was dissolved in CH₂Cl₂ (5 mL), and a solution of bromine (54 mg, 0.34 mmol) in CH₂Cl₂ (5 mL) was added introduced slowly. After stirred at room temperature for 15 min, and *n*-hexane (100 mL) was added. The resulting mixture was kept in a refrigerator for 2 hours (-20 °C) to give orange precipitate. The precipitate was collected by suction, washed with n-hexane, and dried in air to give **3b**•**Br**₆ as orange miro-crystals (45 mg, 100% yield). **3b**•**Br**₆: Mp > 300 °C; ¹H NMR (400 MHz, CDCl₃) δ 4.72 (*q*, *J* = 7.0 Hz, 12H), 1.68 (*t*, *J* = 6.9 Hz, 18H); ¹³C NMR (100 MHz, DMSO) δ 151.87, 136.60, 135.25, 70.35, 15.84.

Crystal structures

The single crystals of **3b** (clear light yellow) and **4b** (clear light yellow) were obtained by slow evaporation of their CH₂Cl₂-ethyl acetate (v/v = 1 : 1) solution at room temperature. The single crystals of the **3b**•**Br**₆ were obtained by slowly evaporation of the mixed solution of **3b** and bromine in CH₂Cl₂-AcOEt (v/v = 1 : 1) at room temperature. The X-ray diffraction measurement of **3b**•**Br**₆ was conducted at room temperature. Due to the relatively poor quality of the single crystal of **3b**•**Br**₆, the completeness of the diffraction analysis is not fairly satisfactory. During the structure analysis of of **3b**•**Br**₆, the residue peaks are relatively high, which is ascribable to the existence of two kinds of heave atoms, the Br and Te. The selected crystallographic data are shown in Table S1.

	3b	4b	3b•Br ₆
CCDC number	1409047	1409048	1409049
Empirical formula	$C_{30}H_{30}O_{6}Te_{3}$	$C_{30}H_{32}O_6Te_2$	$C_{30}H_{30}O_6Te_3Br_6$
Formula weight	869.34	743.76	1348.85
Temperature [K]	150(2)	293(2)	293(2)
λ [Å]	0.71073	1.5418	0.71073
Crystal size [mm ³]	$0.32 \times 0.10 \times 0.06$	$0.34 \times 0.22 \times 0.21$	$0.25 \times 0.20 \times 0.07$
Crystal system	Monoclinic	Monoclinic	Triclinic
space group	$P2_{1}/n$	$P2_1/n$	<i>P</i> -1
<i>a</i> [Å]	15.5616(4)	8.3225(3)	10.889(2)
<i>b</i> [Å]	24.9422(5)	15.0760(6)	10.890(2)
<i>c</i> [Å]	15.8574(5)	23.2305(10)	18.299(4)
α [°]	90	90	86.12(3)
β[°]	104.681(3)	95.20(4)	86.29(3)
γ [°]	90	90	71.19(3)
V[Å ³]	5954.0(3)	2902.7(2)	2047.2(7)
Ζ	8	4	2
$d_{\rm calc} [\rm g \cdot \rm cm^{-3}]$	1.738	1.702	2.276
$\mu [\mathrm{mm}^{-1}]$	2.961	16.179	8.025
$2\theta_{\rm max}$ [°]	57.04	151.48	50.02
Data/restraints/parameters	13674/16/703	5536/0/343	6147/1698/493
GooF	1.022	1.0481	1.052
$R[I \ge 2\sigma(I)]$	0.0705	0.0664	0.0936
wR_2	0.1794	0.1805	0.1958

Table S1. Selected crystallographic data for 3b and 4b.

Compound **3b** crystallizes in the monoclinic $P2_1/n$ space group. The asymmetric unit contains two molecules *A* and *B*. Regarding the bond lengths on the central polycyclic cores and the side views, these two molecules have almost the same geometries (Fig. S1). The packing structure of compound **3b** is shown in Fig. S2, which indicates that the **3b** molecules form columnar array along the *c*-axis.



Fig. S1 Comparison of molecular geometries of molecule A and B in the crystal structure of compound 3b. The bond lengths are shown in unit of Å.



Fig. S2 Packing structure of **3b** viewed along the *c*-axis. The brown dashed lines represent the intermolecular Te^{...}Te atomic close contacts in unit of Å. The ethyl groups are omitted for clarity.

Compound **4b** crystallizes in the monoclinic $P2_1/n$ space group. The asymmetric unit contains one molecule. Fig. S3 depicts the crystal structure of compound 4b. The central benzene ring in **4b** is significantly distorted, *i.e.*, the longest and the shortest C=C bond lengths are 1.48 and 1.37 Å respectively, which makes this ring deviate from the aromatic system. Consequently, the flank benzene rings also show the bond alternation. Similar to tritellurasumanene **3b**, the C-Te bond length in **4b** is 2.10 Å. Compound **4b** possess planar conjugated skeleton and forms the columnar arrays.



Fig. S3 Crystal structure of compound **4b**. (a) Top view of a molecule with the bond lengths shown in unit of Å; (b) packing structures with the inter-planar distances shown in unit of Å, and the hydrogen atoms and oxyalkyl chains are omitted for clarity. The grey, pale cyan, red, and orange balls represent carbon, hydrogen, oxygen, and tellurium atoms respectively.

Electrochemical properties



Fig. S4 Differential pulse voltammetry (DPV) analyses for compounds HBT, 1, 2, and 3a. The dashed lines are guide for eyes to recognize the oxidation peaks. The oxidation potentials were recorded versus SCE.



Fig. S5 Differential pulse voltammetry (DPV) analyses for compounds **HBT**, **3a**, and **4a**. The dashed lines are guide for eyes to recognize the oxidation peaks. The oxidation potentials were recorded versus SCE.



Fig. S6 Cyclic voltammetry (CV) analyses for compounds HBT, 1, 2, and 3a. The redox potentials were recorded versus SCE.

Absorption and emission spectra



Fig. S7 The UV-Vis absorption spectra for compounds **HBT**, **3a**, and **4a** in the (a) CH_2Cl_2 solution ($c = 10^{-5} \text{ mol } L^{-1}$) and (b) solid state.



Fig. S8 The UV-Vis absorption spectra for compounds **3a**, **3b**, **3a**•**Br**₆, and **3b**•**Br**₆ in the (a) CH₂Cl₂ solution ($c = 10^{-5} \text{ mol } L^{-1}$) and (b) solid state.



Fig. S9 The emission spectra for compounds **3a**, **4a**, and **HBT** in CH_2Cl_2 solution ($c = 10^{-5} \text{ mol } L^{-1}$). The excitation wavelengths for **3a**, **4a**, and **HBT** are 273, 281, and 280 nm, respectively.

Theoretical calculation

All calculations were carried out with the Gaussian 09 programs. For DFT calculations, we used the hybrid gradient corrected exchange functional of Lee, Yang, and Parr. A standardized 6-31G basis set was used together with polarization (d) and (p) functions. In the calculation, the terminal butyl groups of **1**, **2**, and **3a** on each molecule were replaced with methyl groups, because the butyl groups have almost no contribution to the HOMO and LUMO orbitals. The molecular orbitals for **1** and **2** have been reported in our previous work (X. Li, et al., *Angew. Chem., Int. Ed.*, 2014, **53**, 535), therefore they are not shown herein.

compounds	$E_{\rm HOMO-1}$ / eV	$E_{\rm HOMO}$ / eV	$E_{ m LUMO}$ / eV	$E_{\rm LUMO+1}$ / eV	E_{g} / eV
1	-4.715	-4.618	-1.163	-1.115	3.45
2	-4.310	-4.235	-0.781	-0.774	3.45
3a	-4.038	-4.038	-0.681	-0.681	3.36
HBT	-5.071	-4.886	-0.969	-0.872	3.90

Table S2. Calculated energy levels for the frontier orbitals of trichalcogenasumanenes and HBT

 $E_{\rm g} = E_{\rm LUMO}$ - $E_{\rm HOMO}$



Fig. S10 a) The calculated frontier orbitals for compounds 3a; b) comparison of the energy levels of the HOMO and LUMO orbitals for 1, 2, 3a, and HBT

IR spectra



Fig. S11 IR spectra for the oxidation products of compounds 1, 2, and 3a upon oxidation by Oxone. The peaks marked with star are the vibrational frequencies ($v = 1707 \text{ cm}^{-1}$) of carbonyl groups in the ring-opening products of 1 and 2 upon oxidation by Oxone.





Fig. S12 ¹³C NMR for compounds 3a, 3a•Br₆, and 3a•I₆ in the aromatic region.



Fig. S13 ¹³C NMR for compounds 3b, 3b•Br₆, and 3b•I₆ in the aromatic region.

Thermogravimetry analysis (TGA)

The thermogravimetry analyses (TGA) for compounds **3a**, **3b**, **4a**, and **4b** were performed on an Netzsch STA 449 C instrument. The TGA for **3a**•**Br**₆ and **3b**•**Br**₆ were not performed owing to the decomposition of these two species under high vacuum.

Tuble Set Therman Statistics of the products.							
	3 a	3 b	4a	4b			
$T_d(^{\circ}\mathrm{C})$	330	125	336	329			



Table S3. Thermal stability of the products.

Fig. S14 Thermogravimetric analyses of compounds 3a, 3b, 4a, and 4b.



Original ¹H NMR, ¹³C NMR, and IR Spectra for the new compounds













S23

$$\begin{array}{c} -7.27 \\ 4.53 \\ 4.51 \\ 4.50 \\ 1.06 \\ 1.68 \\ 1.66 \\ 1.60 \\ 1.60 \\ 1.07 \\ 1.00 \\ 1.07 \end{array}$$















