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Supplementary Information

Selenophene-containing benzodithiophene based donors with different alkyl chains in terminal groups for high-performance all-small-molecule organic solar cells

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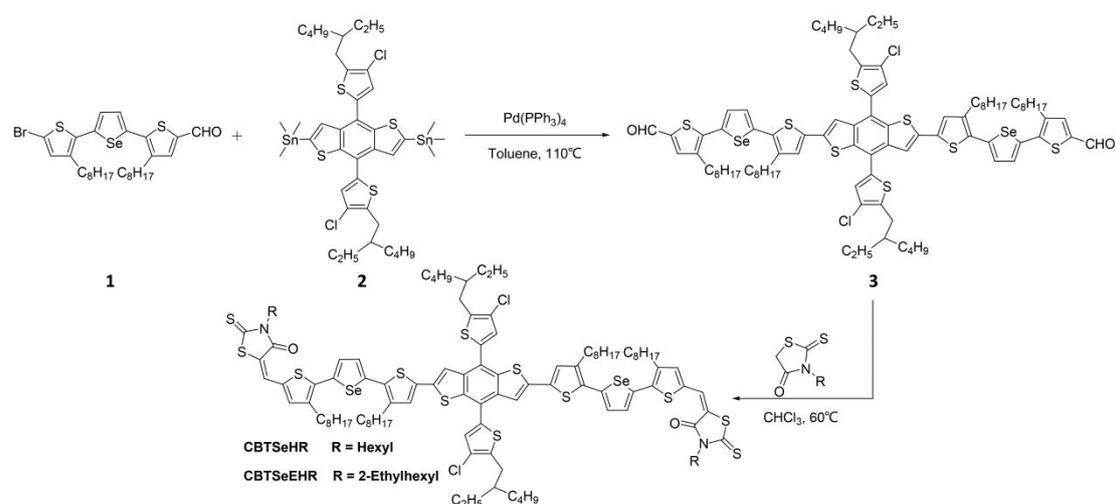
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Materials and synthesis

All reactions and manipulations were carried out by standard Schlenk techniques under nitrogen atmosphere. The solvents were purified and dried according to standard procedures. Non-fullerene acceptor FO-2Cl was prepared according to the reported literature.¹ The other materials were commercially available and used without further purification.



Scheme S1. Synthetic routes of CBTSeHR and CBTSeEHR.

Synthesis of compound **3**:

Under the protection of nitrogen, the weighed compound **1** (0.28 g, 0.45 mmol), compound **2** (0.20 g, 0.21 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (20 mg) were added into the dry toluene (15 mL). Then, the reaction was stirred at 110°C for 20 h under dark condition. After removing the solvent, the crude product was purified by silica gel chromatography using petroleum ether/dichloromethane (1:1.5, v/v) as the eluent. And the pure compound **3** was obtained as red solid (0.27 g, 76%). ^1H NMR (400 MHz, CD_2Cl_2), δ (ppm): 9.78 (s, 2H), 7.58 (s, 2H), 7.55 (s, 2H), 7.41-7.40 (d, 2H), 7.28-7.27 (d, 2H), 7.25 (s, 2H), 7.13 (s, 2H), 2.90-2.70 (m, 12H), 1.81-1.75 (m, 2H),

1.70-1.64 (m, 8H), 1.40-1.24 (m, 56H), 1.00-0.84 (m, 24H). MALDI-TOF MS: calcd for $C_{92}H_{116}Cl_2O_2S_8Se_2 [M]^+$, 1738.44; found: 1738.42.

Synthesis of **CBTSeHR**:

The compound **3** (120 mg, 0.069 mmol) and 3-hexylrhodanine (150 mg, 0.69 mmol) were dissolved in dry $CHCl_3$ (25 mL). Then, the solution was deoxygenated by nitrogen gas for 5 min. Subsequently, dry piperidine (0.15 mL) was added by syringe and the reaction solution was heated to 60 °C. After stirring for 16 h, the mixture was poured into water (130mL) and extracted using $CHCl_3$ (60 mL \times 2). The combined organic layer was washed twice with water and then dried by anhydrous Na_2SO_4 . The crude product was chromatographed by silica gel using petroleum ether/ $CHCl_3$ (2.5:1, v/v) as the eluent, obtaining dark purple solid (115.9 mg, 78.6%). 1H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.74 (s, 2H), 7.54 (s, 2H), 7.38-7.37 (d, 2H), 7.28-7.27 (d, 2H), 7.26 (s, 2H), 7.21 (s, 2H), 7.12 (s, 2H), 4.11-4.08 (t, 4H), 2.92-2.89 (d, 4H), 2.79-2.72 (m, 8H), 1.83-1.78 (m, 2H), 1.74-1.65 (m, 12H), 1.45-1.26 (m, 68H), 1.04-1.00 (t, 6H), 0.96-0.94 (t, 6H), 0.90-0.88 (m, 18H). HRMS: calcd for $C_{110}H_{142}Cl_2N_2O_2S_{12}Se_2 [M]^+$, 2136.5427; found: 2136.5399.

Synthesis of **CBTSeEHR**:

The synthesized process was same as compound **CBTSeHR** with 72.3% yield. 1H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.74 (s, 2H), 7.56 (s, 2H), 7.38-7.37 (m, 4H), 7.30-7.29 (d, 2H), 7.22 (s, 2H), 7.13 (s, 2H), 4.02-4.00 (d, 4H), 2.92-2.76 (m, 12H), 2.10-2.05 (m, 2H), 1.83-1.78 (m, 2H), 1.72-1.67 (m, 8H), 1.45-1.26 (m, 72H),

1.04-0.87 (m, 36H). HRMS: calcd for $C_{114}H_{150}Cl_2N_2O_2S_{12}Se_2 [M]^+$, 2192.6053; found: 2192.6128.

Measurements and Instruments

The 1H NMR spectra were obtained using a Bruker AV400 Spectrometer. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry were performed on a Bruker Autoflex III instrument. High resolution mass spectrometry (HRMS) data were recorded on Bruker solari X XR FTMS. The UV-*vis* spectra in dilute chloroform solution and films were tested on Agilent Technologies Cary 5000 spectrophotometer. GIWAXS measurement was conducted at the beamline of 7.3.3 at the Advanced Light Source (ALS), and the samples were prepared on Si/PEDOT:PSS substrates under the same conditions as those used for device fabrication. Cyclic voltammetry (CV) experiments were performed with a LK98B II Microcomputer-based Electrochemical Analyzer in acetonitrile solution. All measurements were carried out at room temperature with a conventional three-electrode configuration employing a glassy carbon electrode as the working electrode, Ag/AgCl as the reference electrode, and a platinum wire as the counter electrode. Tetrabutylammonium phosphorus hexafluoride ($n-Bu_4NPF_6$, 0.1 M) in acetonitrile was used as the supporting electrolyte, and the scan rate was 100 mV s^{-1} .

The current density-voltage ($J-V$) characteristics of all the devices were measured with a Keithley 2400 source-measure unit. Using a SAN-EI XES-70S1 AAA class solar simulator, photocurrent was performed under illumination with simulated 100

mW cm⁻² AM 1.5G irradiation. The external quantum efficiency (EQE) curve was obtained by a QE-R Solar Cell Spectral Response Measurement System.

Atomic force microscope (AFM) images were obtained on a Bruker MultiMode 8 in tapping mode. A FEI Tecnai G2 Spirit TWIN transmission electron microscope was used to obtain the transmission electron microscopy (TEM) images.

Space charge limited current (SCLC) mobility was performed by a diode configuration of ITO/ZnO/active layer/Ag for electron mobility and ITO/PEDOT:PSS/active layer/Ag for hole mobility, respectively. The results were fitted via a space charge limited form, being described as the equation:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu_0V^2}{8L^3} \exp\left(0.89\beta\sqrt{\frac{V}{L}}\right)$$

where J is the current density, ε_0 is the permittivity of free space (8.85×10^{-12} F m⁻¹), ε_r is the relative dielectric constant of the transport medium, μ_0 is the hole or electron mobility, V ($= V_{\text{appl}} - V_{\text{bi}}$) is the internal voltage in the device, where V_{appl} is the applied voltage to the device and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes, L is the film thickness of the active layer.

Fabrication of OSC devices

The ASM-OSC devices were fabricated with conventional structure of ITO/PEDOT:PSS/active layer/PDINO/Al as the following procedures. The ITO-coated glasses were cleaned using a detergent scrub, and subsequently subjected to ultrasonic treatment in soap water, deionized water, acetone and isopropyl alcohol for 15 min in each step. After drying by a nitrogen flow, the ITO substrates were treated by ultraviolet-ozone for 15 min and spin-coated with PEDOT:PSS solution at

4500 rpm for 20 s. Subsequently, the glasses were baked at 150 °C for 20 min under ambient conditions, and transferred into the glove box with nitrogen gas. Chloroform solution with small-molecule (SM) donor (8 mg/mL) and FO-2Cl (various concentration based on different D/A weight ratio) was spin-coated on the PEDOT:PSS at 1800 rpm for 30 s. Afterward, PDINO with the concentration of 1.0 mg/mL in C₂H₅OH was spin-coated on the active layer at 3000 rpm for 20 s. Finally, under the high vacuum, a cathode material Al was deposited onto PDINO layer. The work area of each device is ~0.04 cm², defined by the masks for all the solar cell devices discussed in this work.

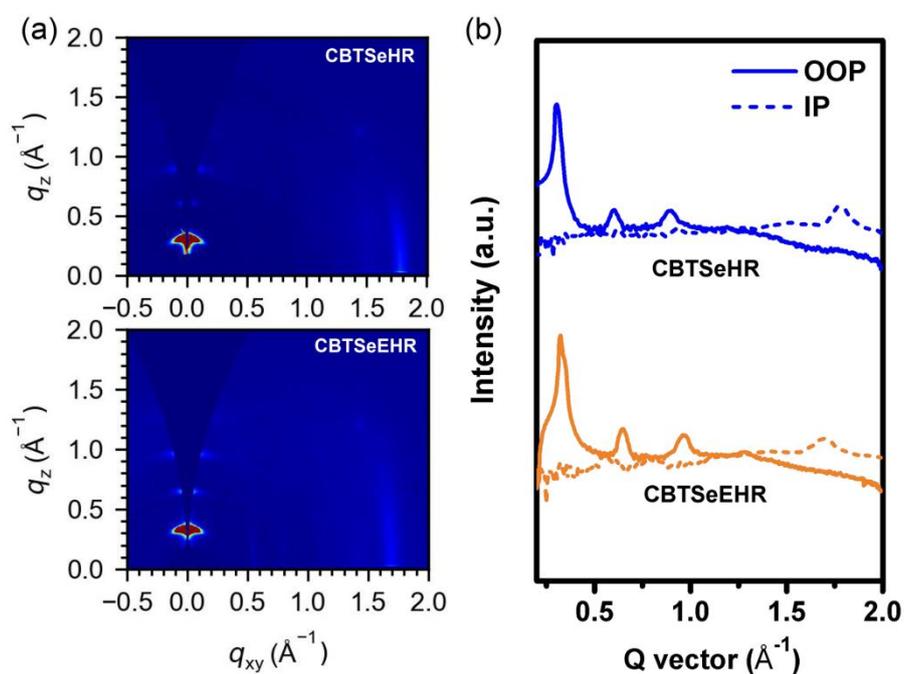


Fig. S1. (a) 2D GIWAXS diffraction patterns and (b) the out-of-plane (solid lines) and in-plane (dashed lines) line-cut profiles of the SM donor films.

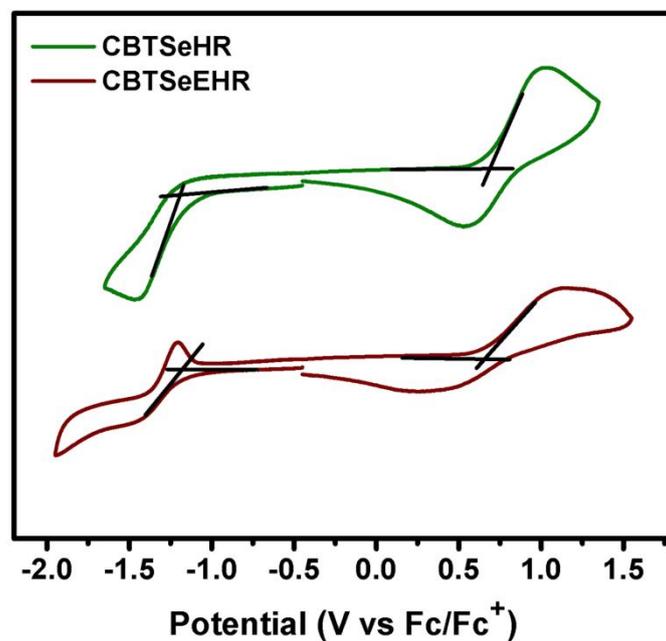


Fig. S2. Cyclic voltammogram of CBTSeHR and CBTSeEHR in acetonitrile solution with 0.1 mol L⁻¹ n-Bu₄NPF₆ and ferrocene as reference compound.

Table S1 Photovoltaic performances of the devices based on CBTSeHR (D):FO-2Cl (A) with different weight ratio under various optimization conditions.

D:A (w/w)	Treatment	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF(%)	PCE (%) ^a
1:0.9	As cast	0.935	6.24	0.308	1.80 (1.67 ± 0.13)
1:1.1	As cast	0.933	6.92	0.321	2.07 (1.88 ± 0.18)
1:1.2	As cast	0.930	7.48	0.342	2.38 (2.27 ± 0.15)
1:1.3	As cast	0.929	6.65	0.310	1.91 (1.80 ± 0.14)
1:1.2	TA(135 °C)	0.884	18.05	0.715	11.41 (11.25 ± 0.30)
1:1.2	TA(140 °C)	0.881	18.76	0.732	12.10 (11.75 ± 0.35)
1:1.2	TA(145 °C)	0.877	18.45	0.699	11.31 (11.12 ± 0.29)

^a Average PCE values obtained from 15 devices are shown in parentheses.

Table S2 Photovoltaic performances of the devices based on CBTSeHR (D):FO-2Cl (A) with different weight ratio under various optimization conditions.

D:A (w/w)	Treatment	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF(%)	PCE (%) ^a
1:1.0	As cast	0.933	5.01	0.282	1.32 (1.19 ± 0.15)
1:1.1	As cast	0.927	6.45	0.311	1.86 (1.73 ± 0.13)
1:1.0	As cast	0.926	5.15	0.287	1.38 (1.30 ± 0.11)
1:1.1	TA(130°C)	0.874	14.61	0.647	8.26 (8.05 ± 0.25)
1:1.1	TA(135°C)	0.871	15.28	0.698	9.30 (8.91 ± 0.39)
1:1.1	TA(140°C)	0.872	15.26	0.661	8.80 (8.58 ± 0.31)

^a Average PCE values obtained from 15 devices are shown in parentheses.

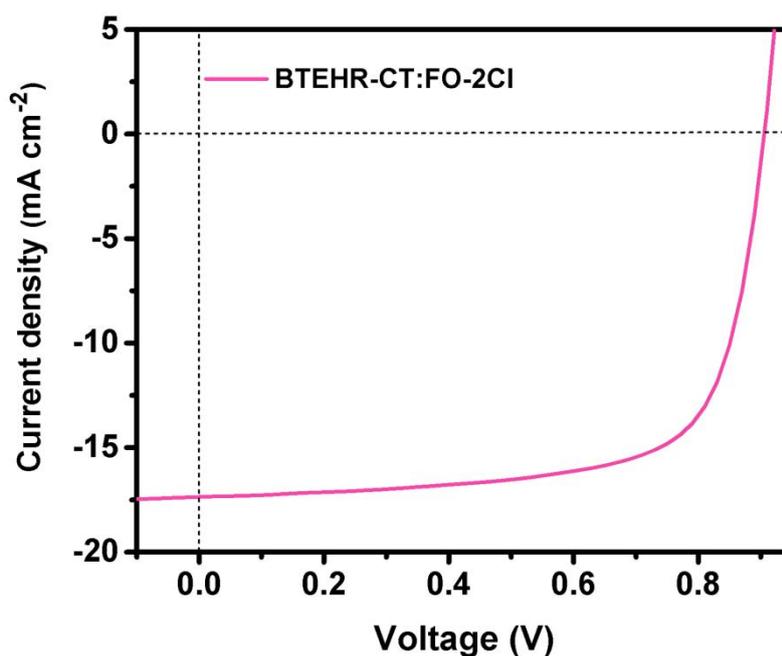


Fig. S3. Current density-voltage (J - V) curve of BTEHR-CT:FO-2Cl based device optimized by TA treatment at 130 °C for 5 min.

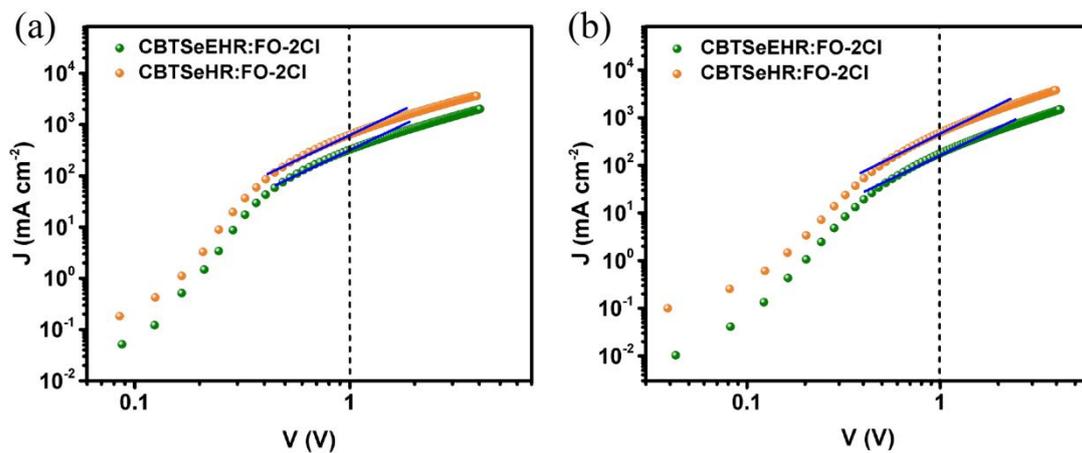


Fig. S4. The current density-voltage (J - V) plots for (a) hole-only and (b) electron-only devices based on SM donors:FO-2Cl.

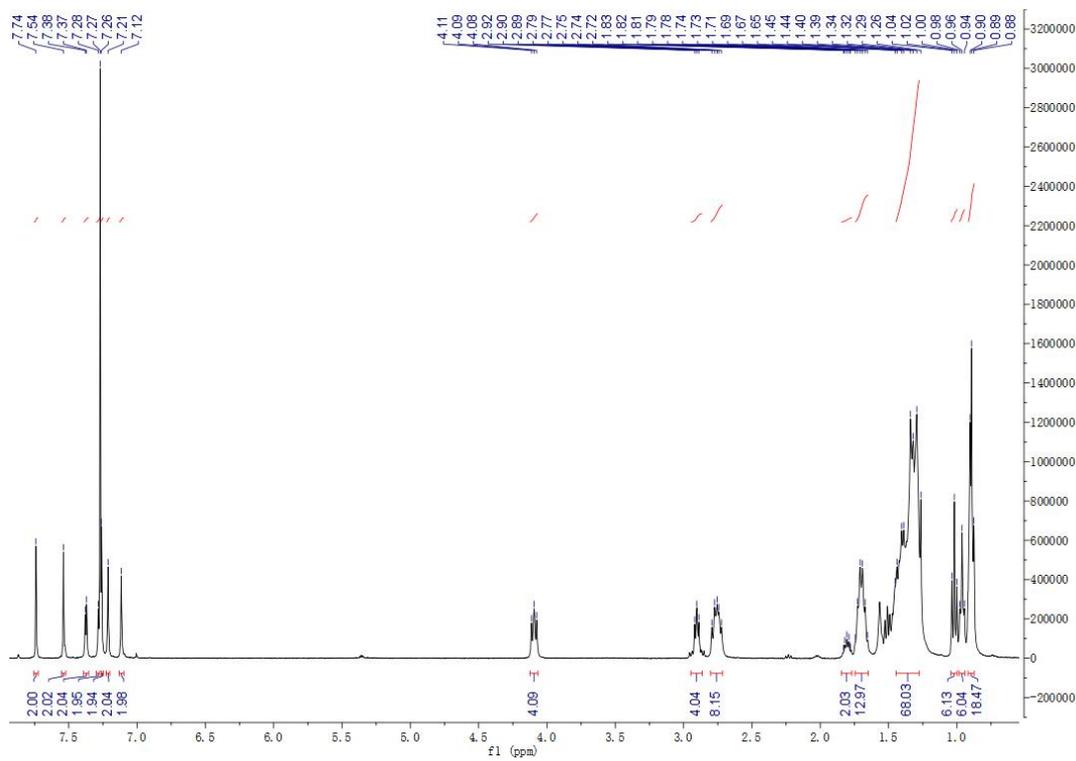


Fig. S5. ^1H NMR spectra of compound CBTSeHR at 300K in CDCl_3 .

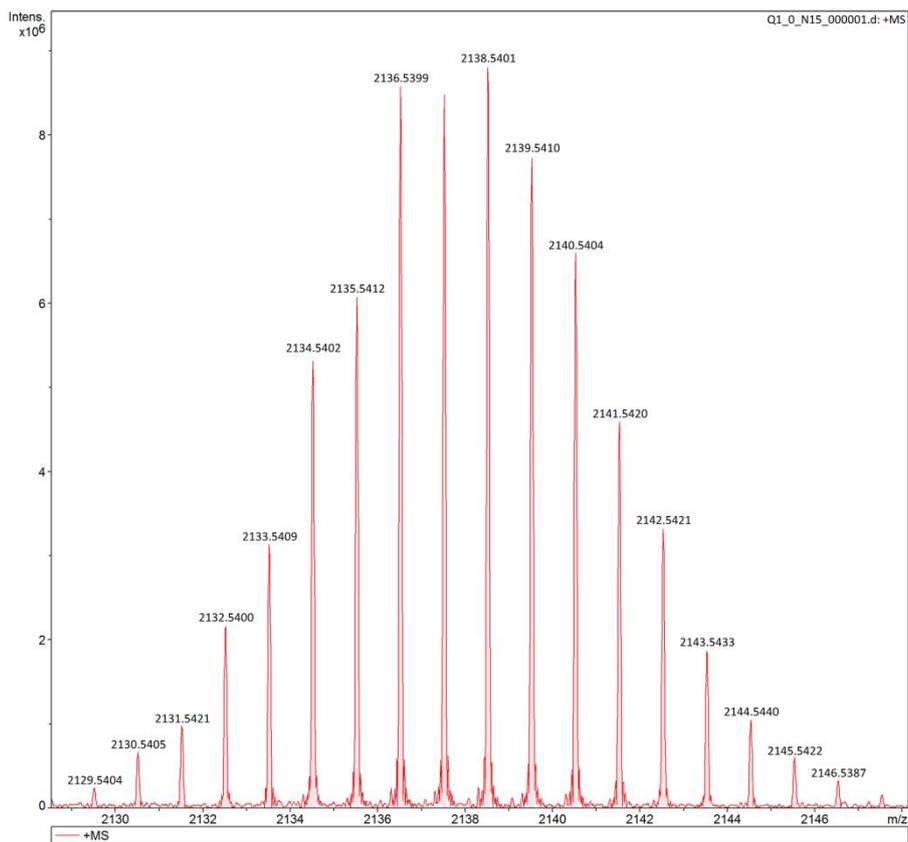


Fig. S6. HR-MS plot of compound CBTSeHR.

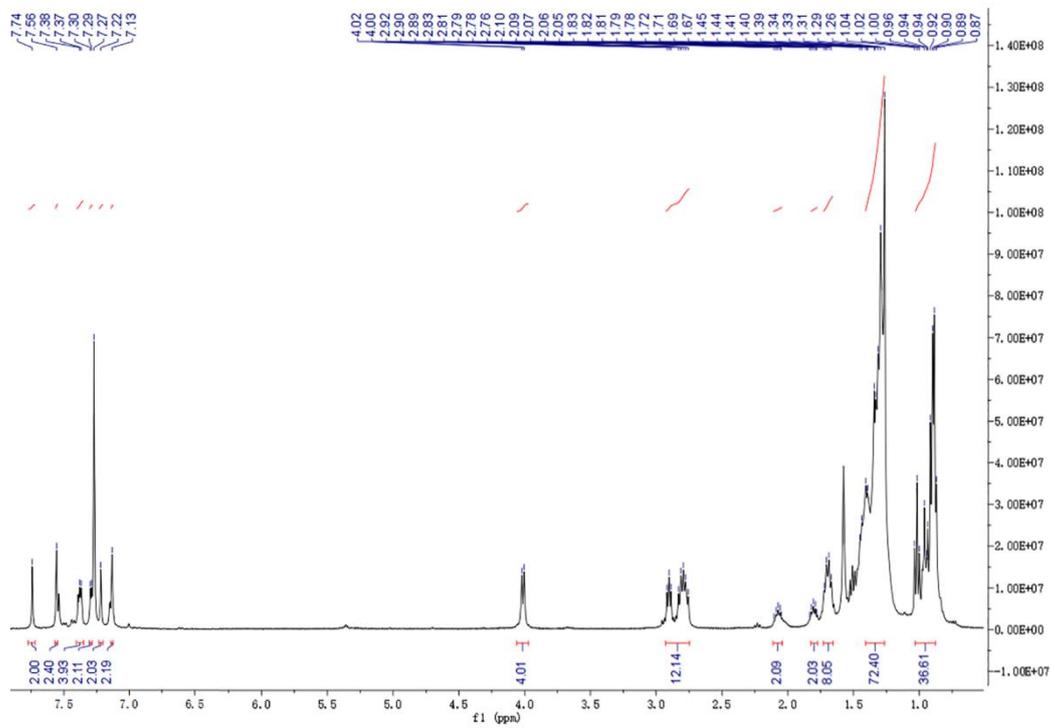


Fig. S7. ¹H NMR spectra of compound CBTSeHR at 300K in CDCl₃.

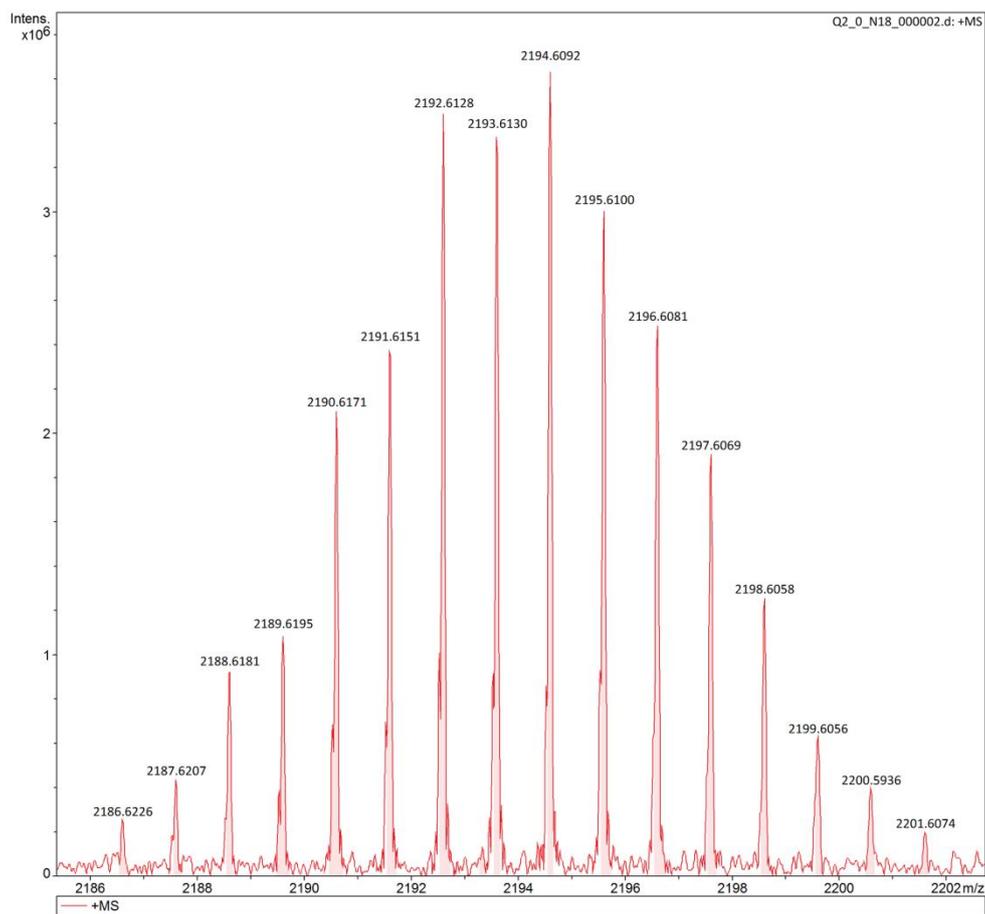


Fig. S8. HR-MS plot of compound CBTSeEHR.

References

1. L. Meng, M. Li, G. Lu, Z. Shen, S. Wu, H. Liang, Z. Li, G. Lu, Z. Yao, C. Li, X. Wan and Y. Chen, *Small*, 2022, **18**, e2201400.