Supporting Information

Revisit anti-heavy-atom effect: no halogen-based bond, no enhanced aggregation induced emission for bromine substituted tetraphenylethylene derivatives

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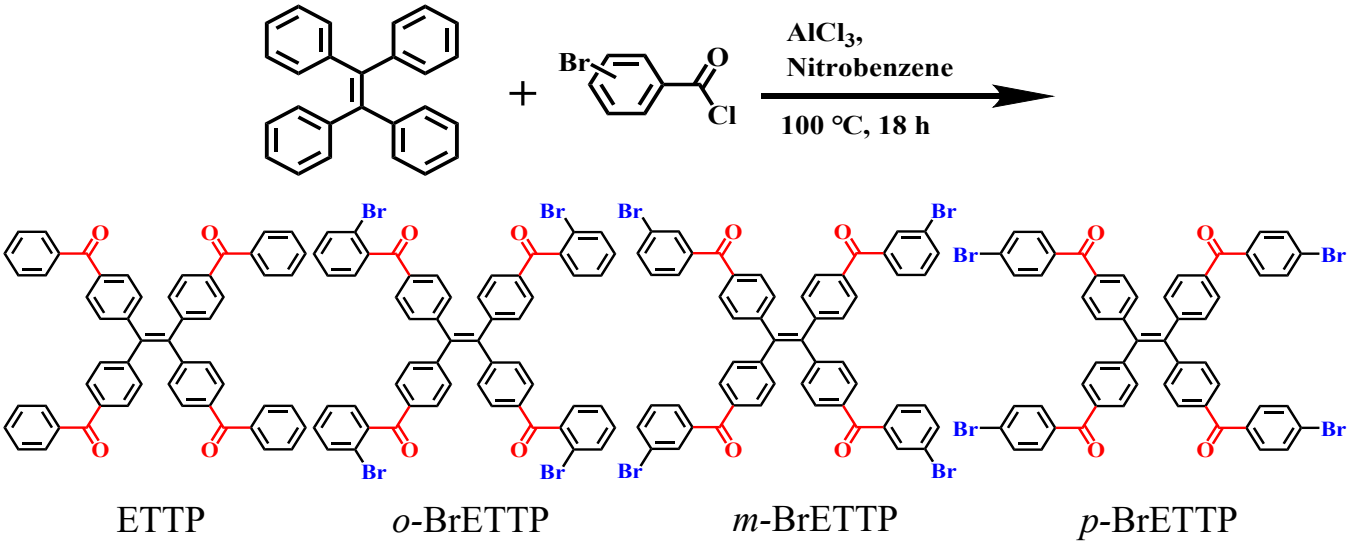
Synthesis: All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to the standard procedures.



Scheme S1. Synthetic route of ETTP derivatives.

ETTP: TPE (1.00 g, 3 mmol) and $AlCl_3$ (4.00 g, 30 mmol) were add to a 100 ml round-bottom flask. Subsequently, dissolve the solid completely by adding 10 ml of nitrobenzene solution. Weigh benzoyl chloride (4.22 g, 3.48 ml, 30 mmol) and mix it with 10 ml of nitrobenzene before dropping the mixture into the round-bottom flask. Seal the flask and heat it to 100℃ for a reaction period of 18 hours while monitoring progress periodically. Upon completion of the reaction, quench with dilute NaOH solution and extract the organic layer using dichloromethane; repeat this extraction process three times. Concentrate the organic layer via rotary evaporation to obtain a crude product which can be further purified through silica gel column chromatography resulting in yellow solid powder (1.08 g) yield after recrystallization with ethanol at a yield of 48.1%. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.76 (d, J = 6.8 Hz, 8H), 7.65 (d, J = 8.3 Hz, 8H), 7.58 (t, J = 7.4 Hz, 4H), 7.47 (t, J = 7.7 Hz, 8H), 7.20 (d, J = 8.2 Hz, 8H). ^{13}C NMR (126 MHz, Chloroform-d) δ 196.01, 146.50, 141.88, 137.43, 136.32, 132.52, 131.16, 130.03, 129.94, 128.34. HRMS (ESI, m/z): [M]+ calcd for $C_{54}H_{36}NaO_4$, 771.2506, found 771.2503.

***o*-BrETTP:** The synthetic/ purified methods and dosage of raw materials are the same as ETTP, but benzoyl chloride is replaced by 2-bromobenzoyl chloride. The yellow powder (1.30 g) is obtained with

yields of 40.8%. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.62 (dd, J = 7.8, 1.2 Hz, 4H), 7.59-7.55 (m, 8H), 7.41 (td, J = 7.5, 1.1 Hz, 4H), 7.36-7.31 (m, 8H), 7.12-7.08 (m, 8H). ^{13}C NMR (126 MHz, Chloroform-d) δ 195.17, 147.26, 142.22, 140.37, 135.11, 133.24, 131.44, 131.32, 130.02, 129.10, 127.29, 119.59. HRMS (ESI, m/z): [M]+ calcd for $C_{54}H_{32}Br_4NaO_4$, 1082.8926, found 1082.8921.

***m*-BrETTP:** The synthetic/ purified methods and dosage of raw materials are the same as ETTP, but benzoyl chloride is replaced by 3-bromobenzoyl chloride. The yellow powder (1.37 g) is obtained with yields of 42.5%. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.62 (dd, J = 7.8, 1.2 Hz, 4H), 7.59-7.55 (m, 8H), 7.41 (td, J = 7.5, 1.1 Hz, 4H), 7.36-7.31 (m, 8H), 7.12-7.08 (m, 8H). ^{13}C NMR (126 MHz, Chloroform-d) δ 195.17, 147.26, 142.22, 140.37, 135.11, 133.24, 131.44, 131.32, 130.02, 129.10, 127.29, 119.59. HRMS (ESI, m/z): [M]+ calcd for $C_{54}H_{32}Br_4NaO_4$, 1082.8926, found 1082.8990.

***p*-BrETTP:** The synthetic/ purified methods and dosage of raw materials are the same as ETTP, but benzoyl chloride is replaced by 4-bromobenzoyl chloride. The yellow powder (1.46 g) is obtained with yields of 45.7%. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.62 (dd, J = 7.8, 1.2 Hz, 4H), 7.59-7.55 (m, 8H), 7.41 (td, J = 7.5, 1.1 Hz, 4H), 7.36-7.31 (m, 8H), 7.12-7.08 (m, 8H). ^{13}C NMR (126 MHz, Chloroform-d) δ 195.17, 147.26, 142.22, 140.37, 135.11, 133.24, 131.44, 131.32, 130.02, 129.10, 127.29, 119.59. HRMS (ESI, m/z): [M]+ calcd for $C_{54}H_{32}Br_4NaO_4$, 1082.8926, found 1082.8907.

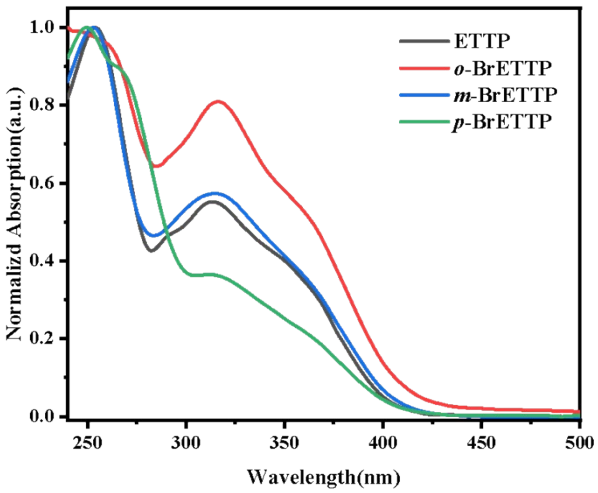


Fig. S1 UV-visible spectra of ETTP derivatives in the dilute THF solution (1.0×10^{-5} M).

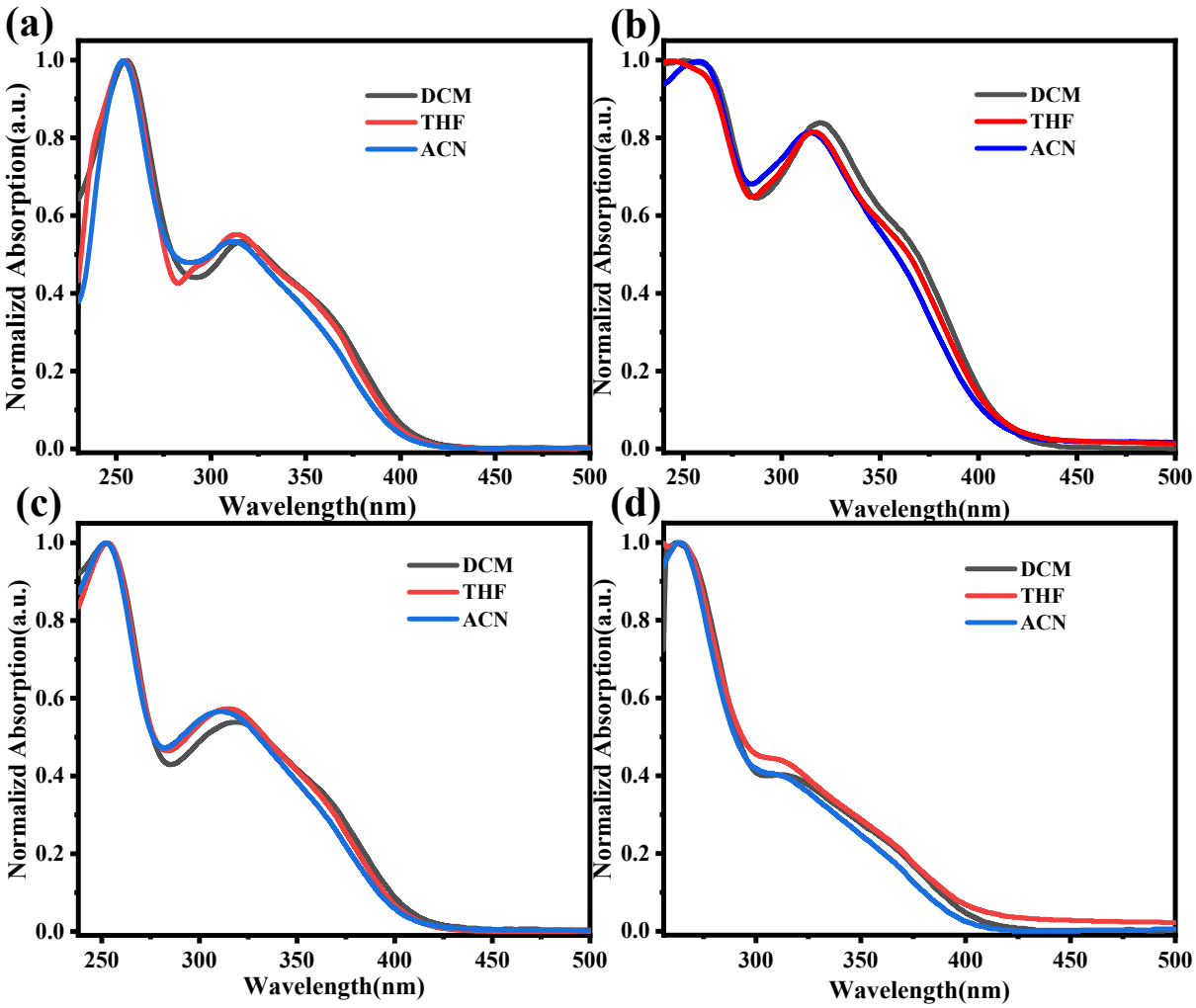


Fig. S2 UV-visible spectra of ETTP derivatives in different solvents (1.0×10^{-5} M). (a) ETTP, (b) *o*-BrETTP, (c) *m*-BrETTP, (d) *p*-BrETTP.

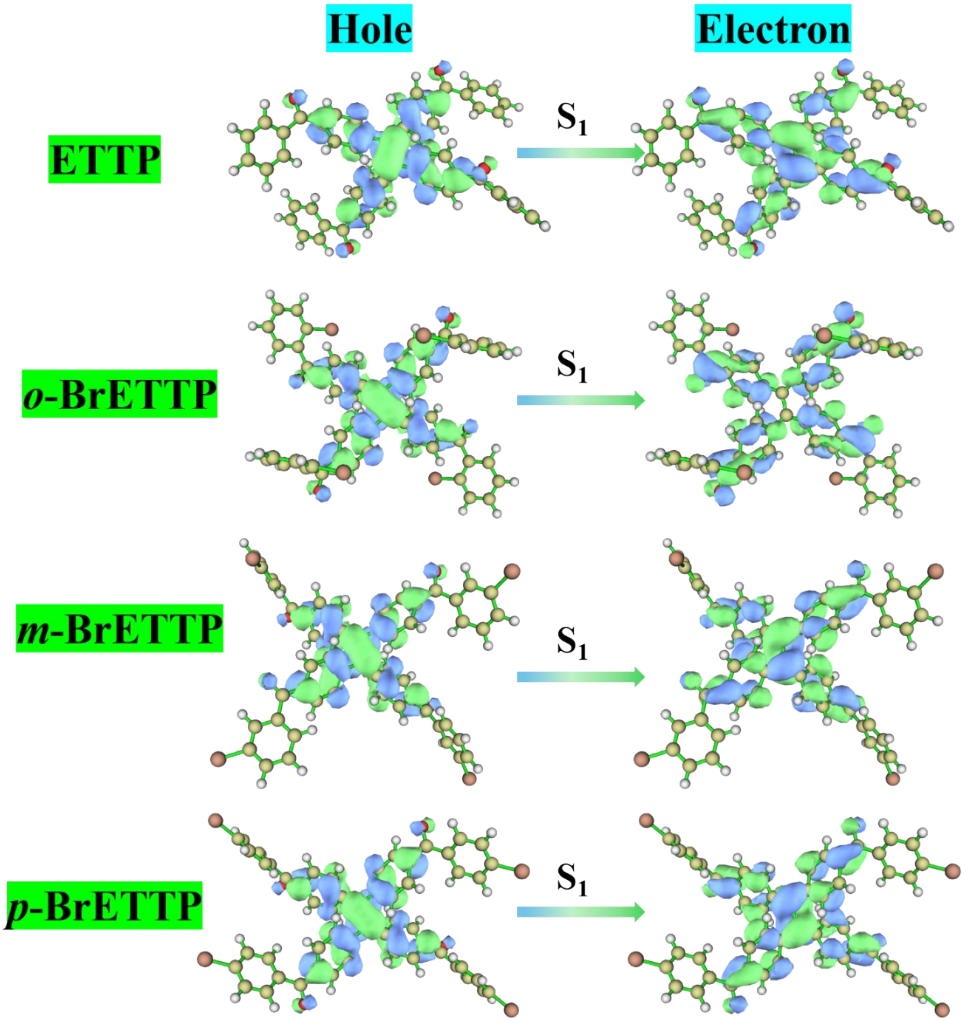


Fig. S3 Hole-particle pairs of natural transition orbitals (NTO) of the optimized S1 state for ETTP derivatives.

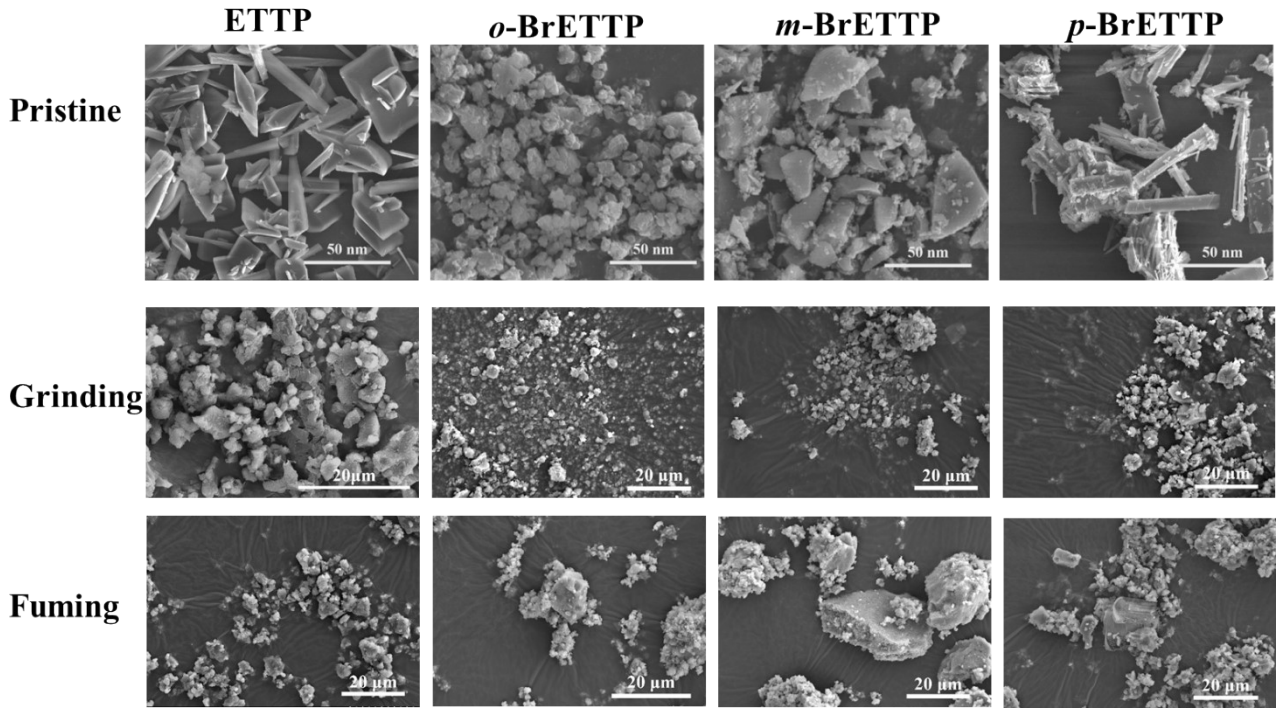


Fig. S4 SEM morphology images of ETTP derivatives in pristine , ground and fuming with DCM vapors.

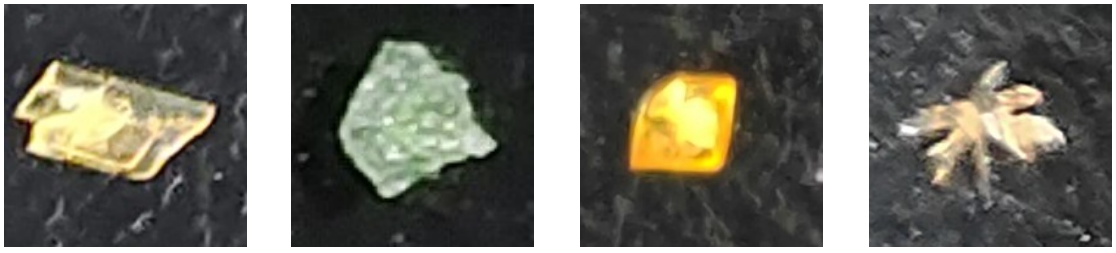


Fig. S5 Images of ETTP derivatives crystals upon visible light.

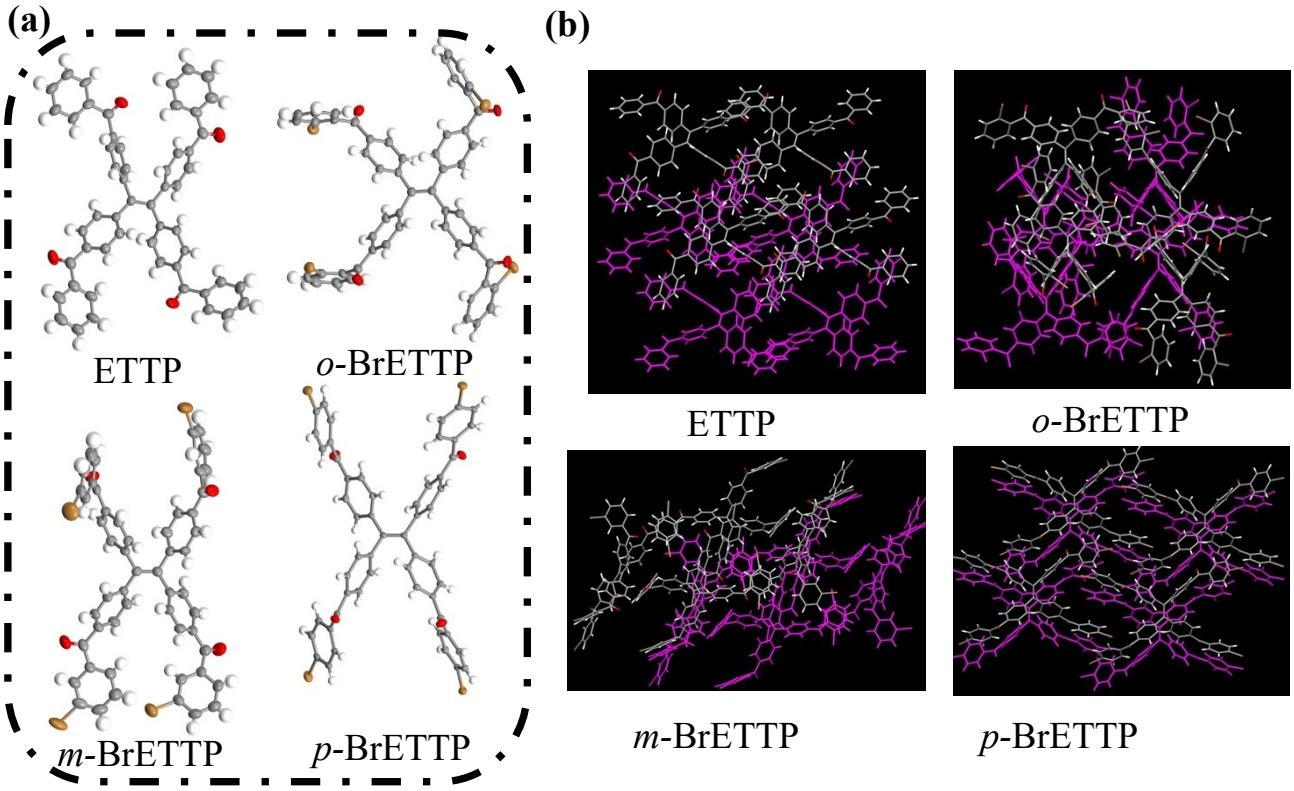
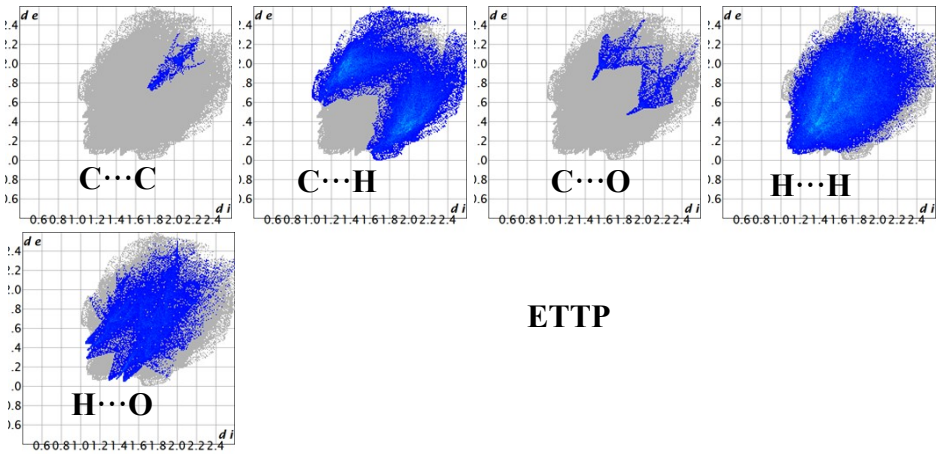


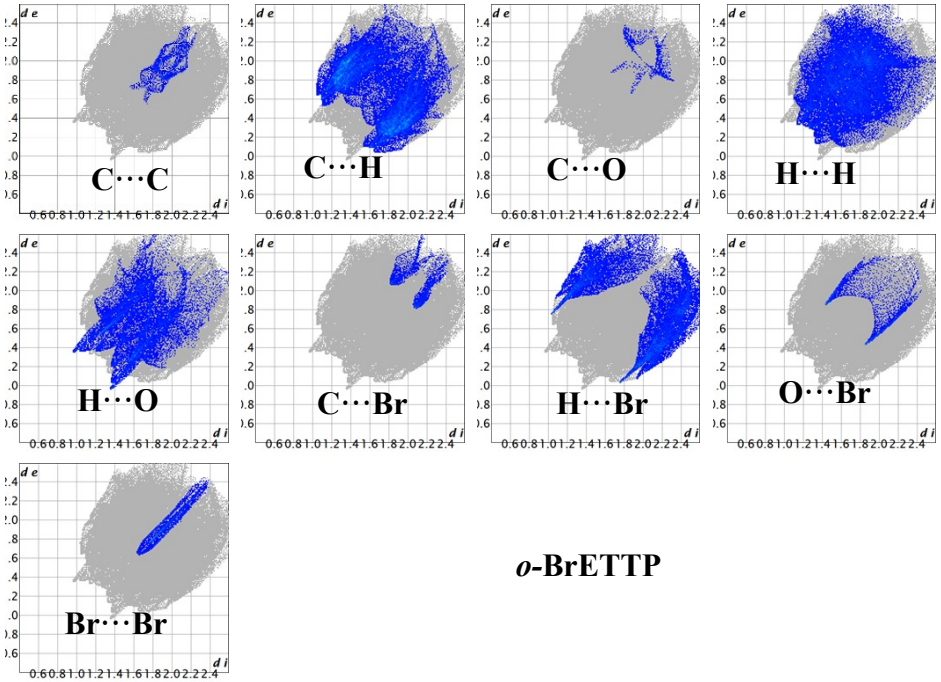
Fig. S6 (a) Molecular conformation in the crystal lattices. Carbon atoms (grey), Hydrogen atoms (white), oxygen atom (red), Br atoms (yellow); (b) Two planes of ETTP derivatives exhibiting different packing modes.

Table S1. Structures determination summary for ETTP derivatives

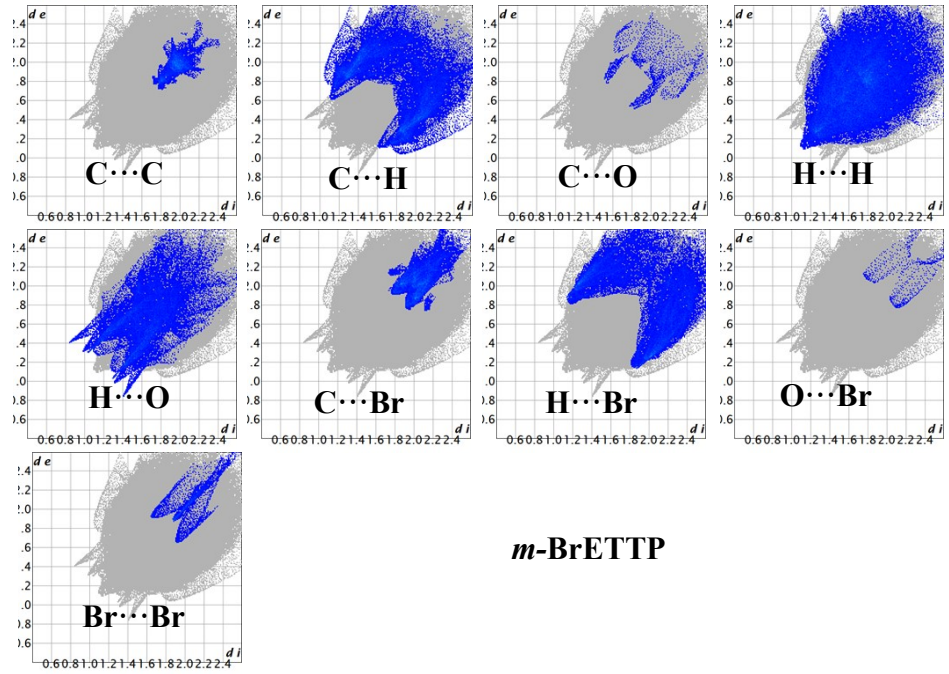
Parameters	**ETTP**	***o*-BrETTP**	***m*-BrETTP**	***p*-BrETTP**
CCDC number	2380072	2380073	2380074	2380075
Empirical formula	$C_{54}H_{36}O_4$	$C_{54}H_{32}O_4Br_4$	$C_{54}H_{32}O_4Br_4$	$C_{54}H_{32}O_4Br_4$
Formula weight	748.83	1064.43	1064.43	1064.43
Temperature/K	296 K	150 K	296 K	150 K
Crystal system	triclinic	tetragonal	monoclinic	triclinic
Space group	*P*-1	$I4_1/a$	$P\ 2_1/n$	*P*-1
a/Å	10.9821(8)	22.8748(3)	14.4094(17)	11.5486(2)
b/Å	12.2279(8)	22.8748(3)	13.0437(15)	=12.2225(2)
c/Å	15.9810(11)	16.3836(2)	24.170(3)	16.1992(3)
α/°	78.157(2)	90	90	79.244(1)
β/°	85.725(2)	90	97.358(3)	74.581(1)
γ/°	72.994(2)	90	90	83.774(1)
Volume/Å^3	2008.3(2)	8572.8(2)	4505.4(9)	2161.35(7)
Z	2	8	4	2
$D_{calcd.}$/ g cm^{-3}	1.238	1.649	1.569	1.635
Reflections collected	51079	20653	81880	41492
Independent reflections	9208	4399	7696	8843
R_{int}	0.0901	0.0318	0.1538	0.0320
GOF on F^2	1.001	1.056	1.154	1.062
Final R indexes [all data]	R_1 = 0.0528 wR_2 = 0.1340	R_1 = 0.0526 wR_2 = 0.1663	R_1 = 0.1022 wR_2 = 0.1837	R_1 = 0.0309 wR_2 = 0.0853



ETTP



***o*-BrETTP**



***m*-BrETTP**

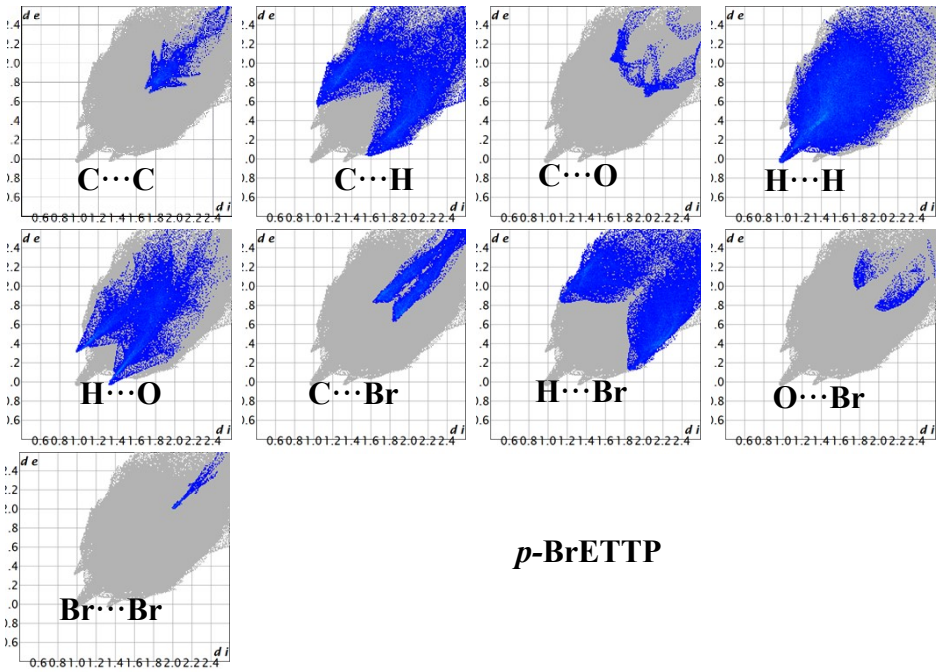


Fig. S7 2D fingerprint plots quantifying the contributions of intermolecular interactions to Hirshfeld surface.

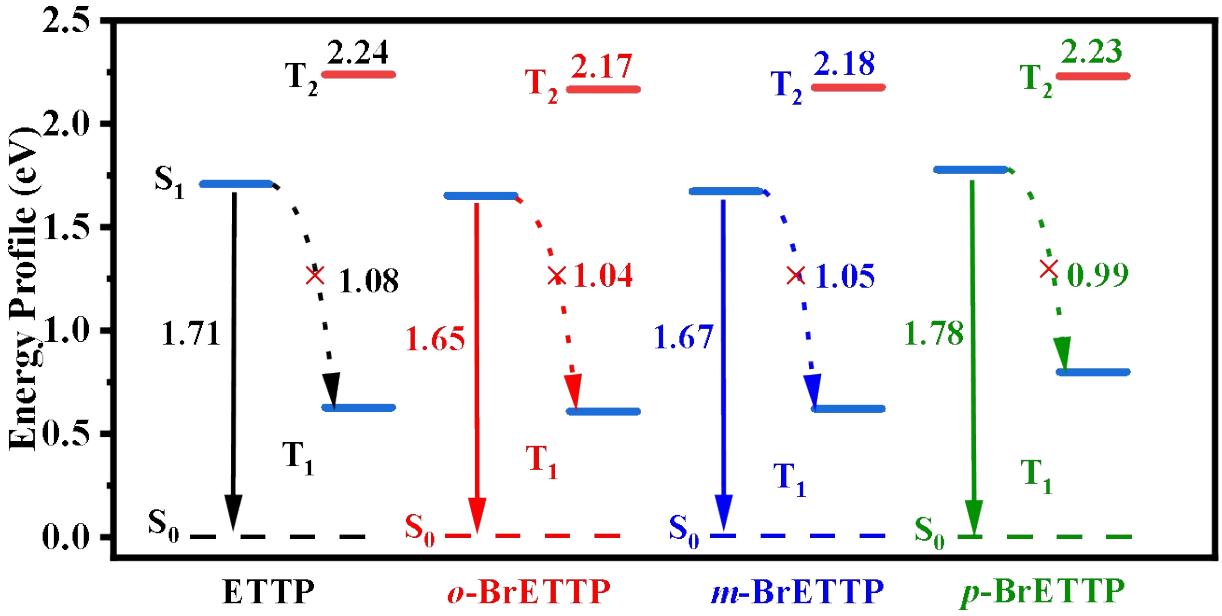


Fig. S8 Energy profiles of the excited states of ETTP derivatives calculated using time-dependent density functional theory (TDDFT).

Table S2. Contribution ratio of different atoms to HOMOs and LUMOs of ETTP derivatives

Compound	Group	Contribution to HOMO (%)	Contribution to LUMO (%)
ETTP	TPE	89.73	66.04
	benzoyl group	10.27	33.96
o-BrETTP	TPE	89.41	69.18
	benzoyl group	8.92	29.71
	Br	1.67	1.11
m-BrETTP	TPE	90.39	63.30
	benzoyl group	9.57	36.52
	Br	0.04	0.18
p-BrETTP	TPE	90.31	61.94
	benzoyl group	9.60	37.15
	Br	0.09	0.91

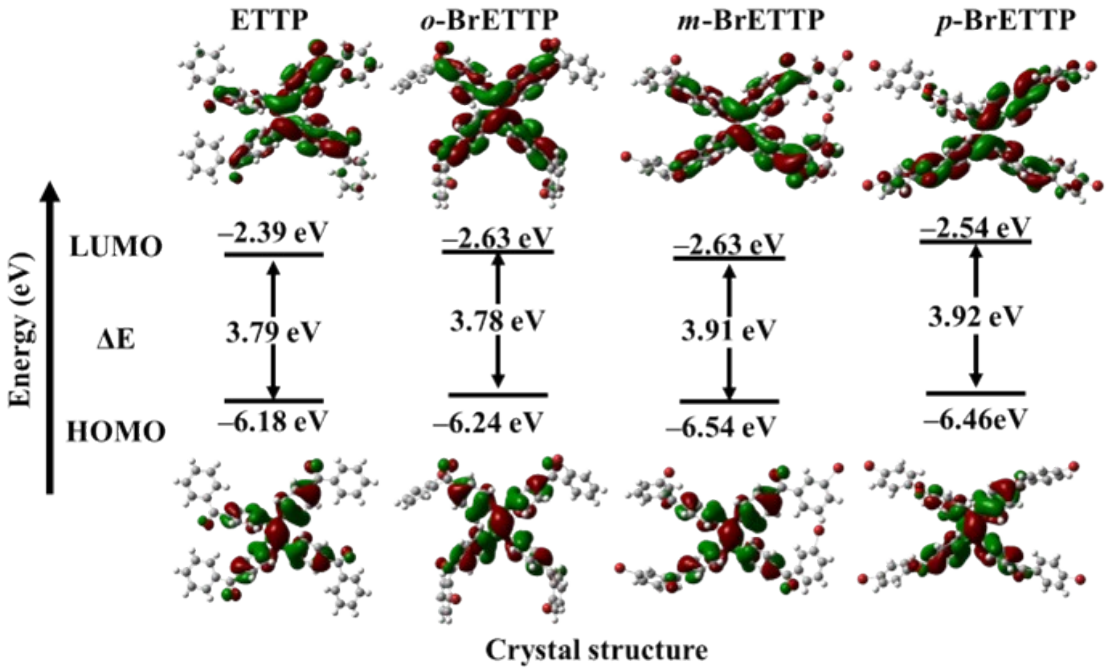


Fig. S9 HOMOs and LUMOs and their band gaps for the molecular conformation in the crystal of ETTP

derivatives.

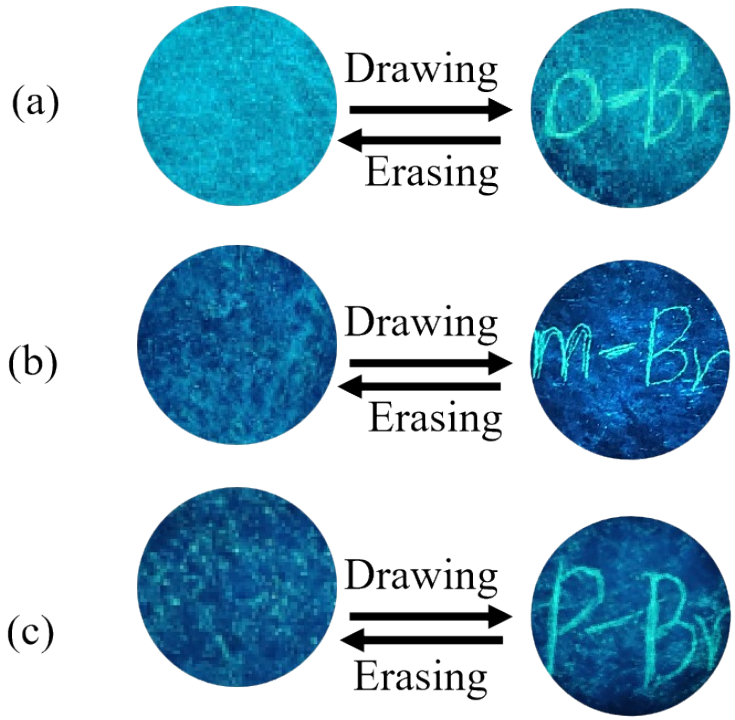
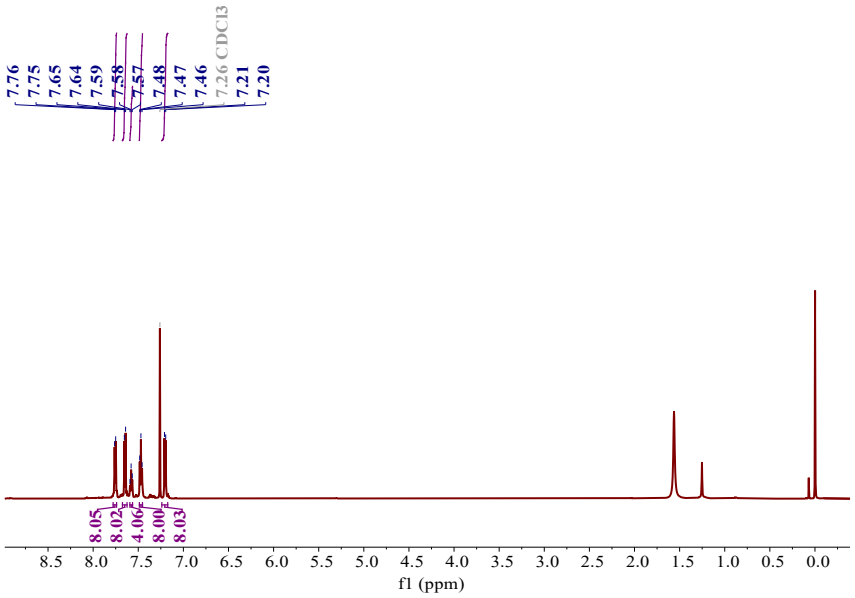


Fig.S10 Photographs of the drawing/erasing cycle for (a) *o*-BrETTP, (b) *m*-BrETTP, and (c) *p*-BrETTP under 365 nm UV.

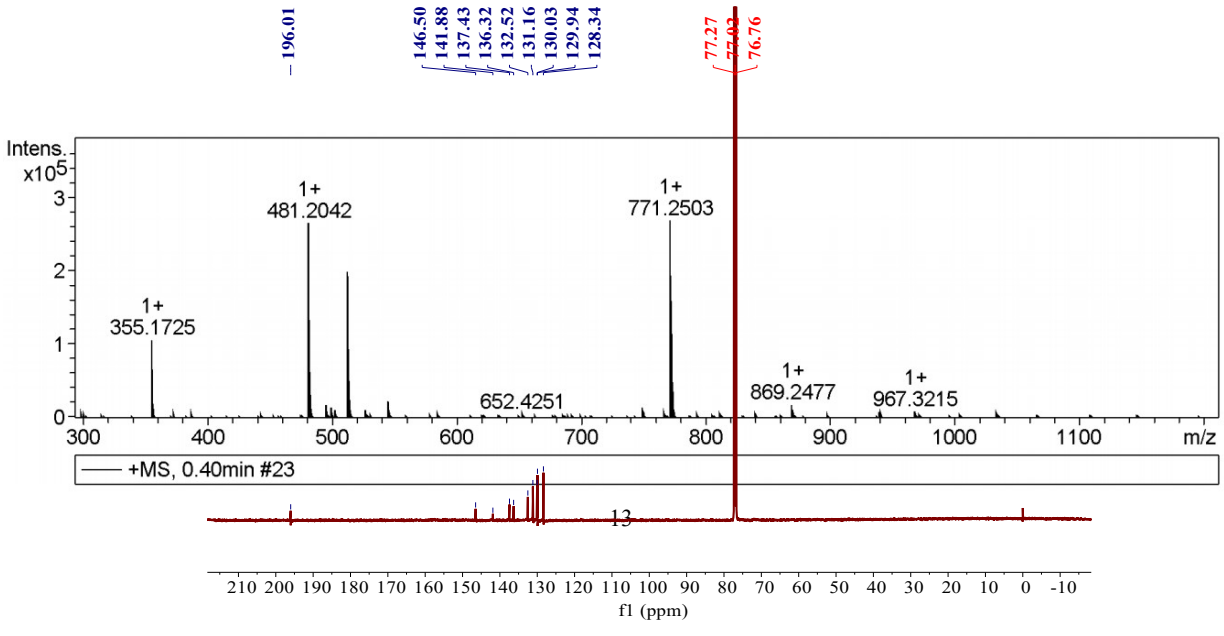


NMR spectra and HRMS spectra of target compounds

Fig. S11 ^{1}H NMR spectrum of ETTP in $CDCl_3$.

Fig. S12 ^{13}C NMR spectrum of ETTP in $CDCl_3$.

Fig. S13 HRMS spectrum of ETTP.



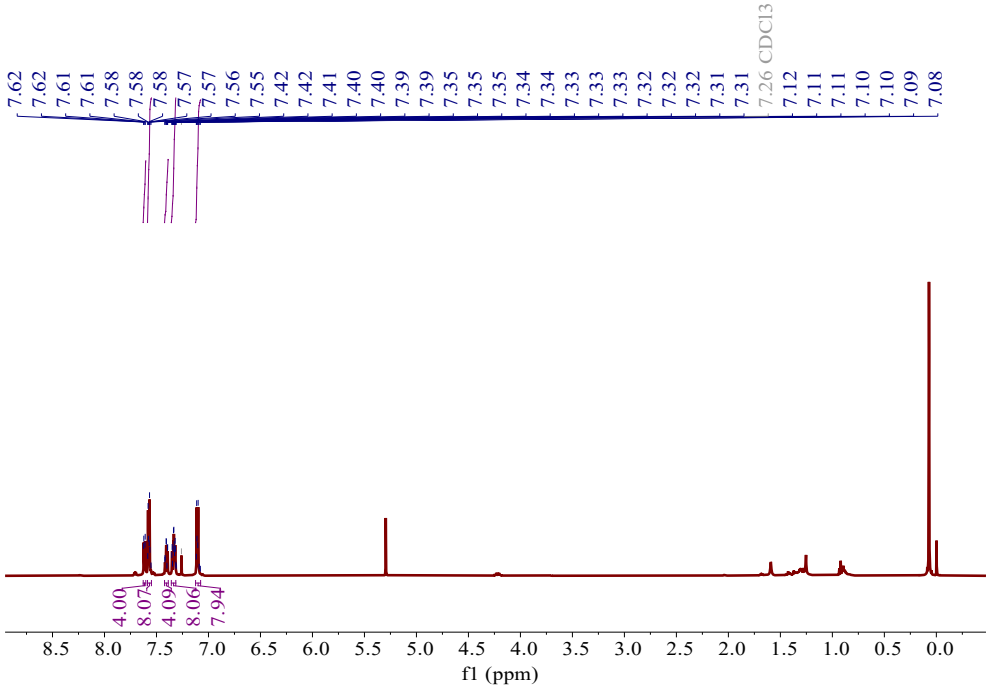
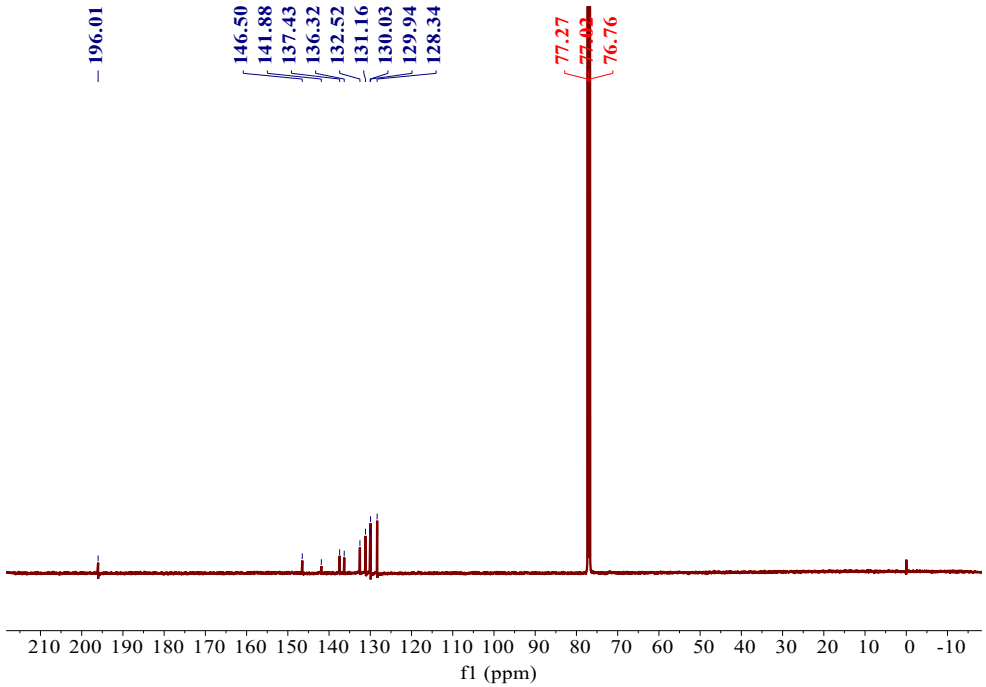


Fig. S14 ^{1}H NMR spectrum of *o*-BrETTP in $CDCl_3$.



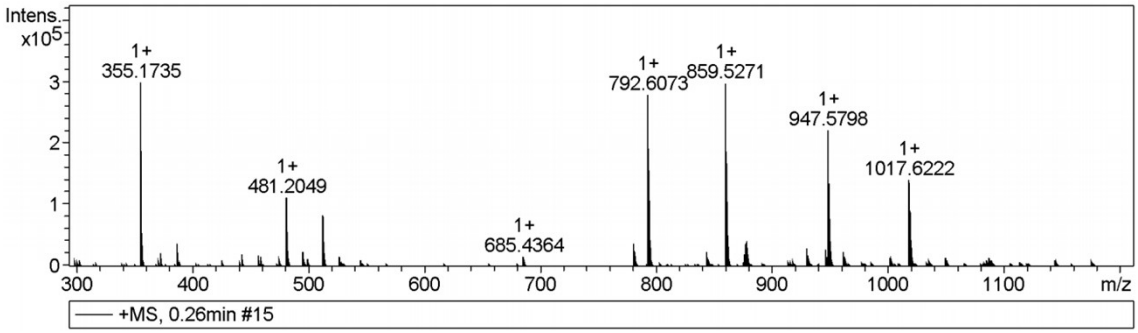


Fig. S15 ^{13}C NMR spectrum of *o*-BrETTP in $CDCl_3$.

Fig. S16 HRMS spectrum of *o*-BrETTP.

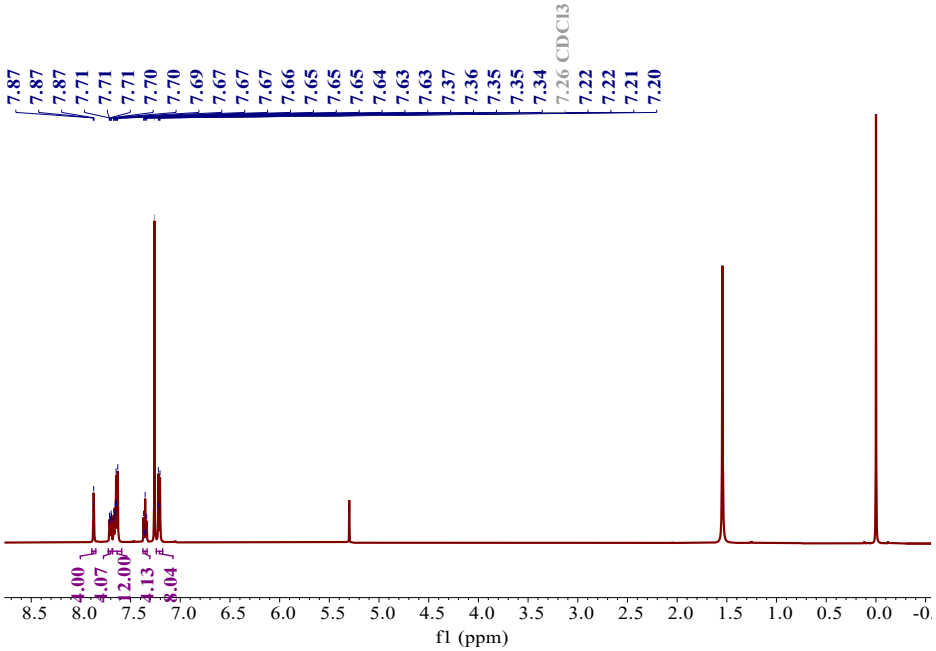


Fig. S17 ^{1}H NMR spectrum of *m*-BrETTP in $CDCl_3$.

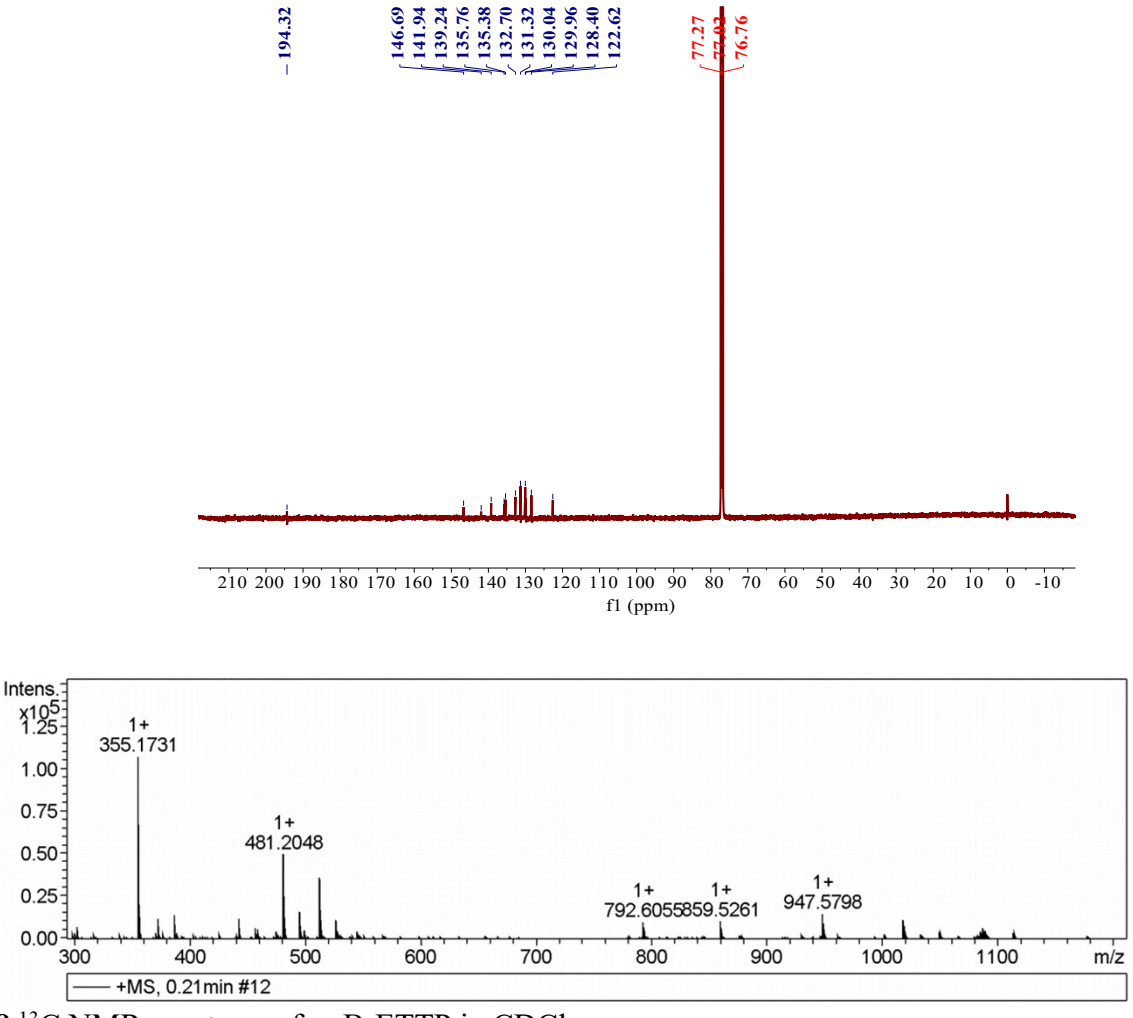


Fig. S18 ^{13}C NMR spectrum of *m*-BrETTP in $CDCl_3$.

Fig. S19 HRMS spectrum of *m*-BrETTP.

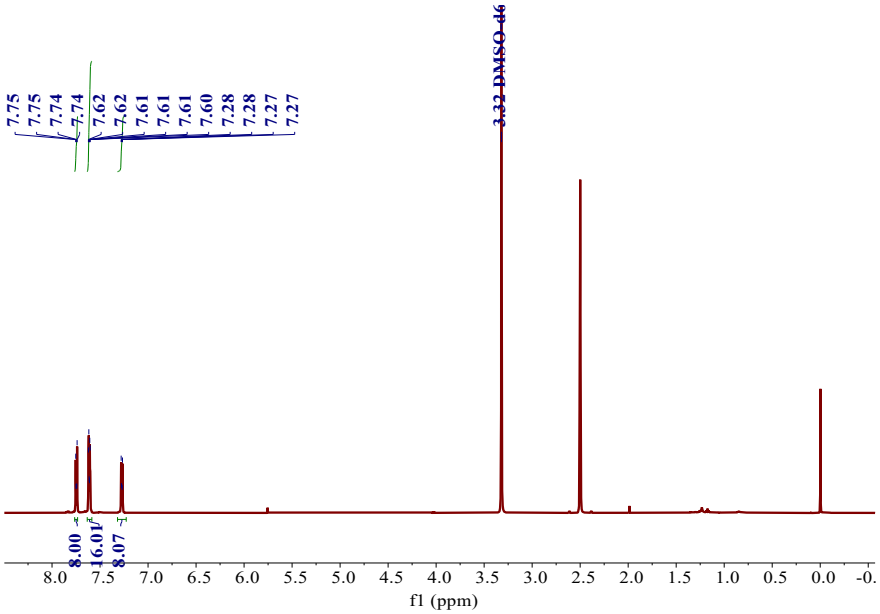


Fig. S20 ^{1}H NMR spectrum of *p*-BrETTP in DMSO.

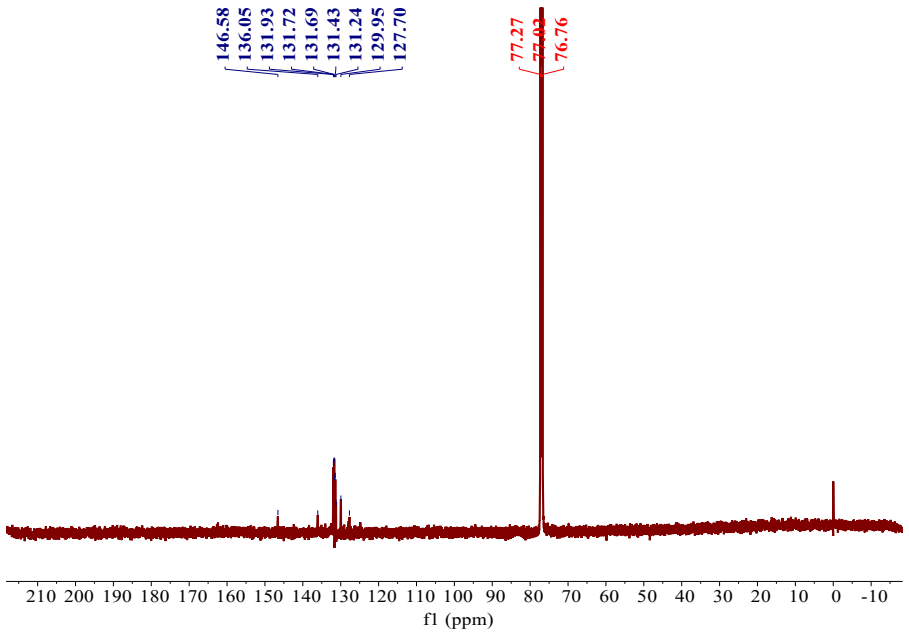


Fig. S21 ^{13}C NMR spectrum of *p*-BrETTP in $CDCl_3$.

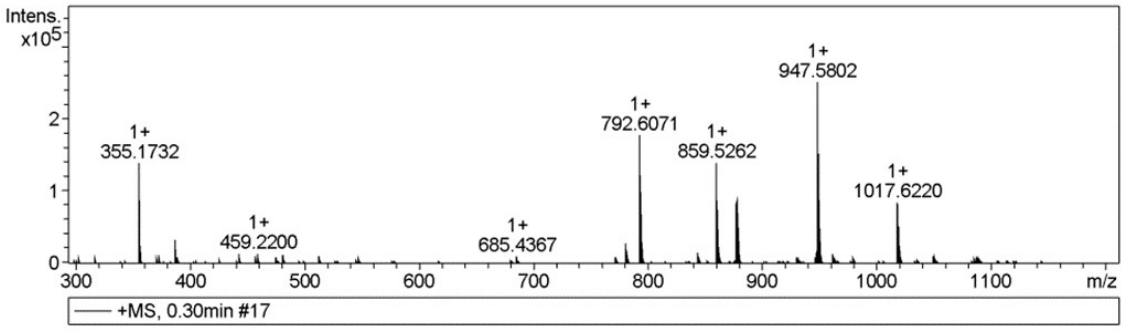


Fig. S22 HRMS spectrum of *p*-BrETTP.