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Supporting Information

Regulating the crystal and electronic structures and optical properties of hybrid bromoplumbates with alkylated N, S- or P-containing aromatic cations

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S1.1 Materials and characterization

All reagents were purchased commercially and used without further purification. Elemental analyses of C, H, and N were performed on an Elementar Vario EL III microanalyzer. Powder X-ray diffraction (PXRD) patterns were recorded on Bruker D8 Advance diffractometer using Cu $K\alpha$ radiation. CrystalExplorer21 software was used to quantitatively analyze the intermolecular interaction in the crystal structures. A Perkin-Elmer Diamond thermogravimetric analyzer was used to obtain thermogravimetric analyses (TGA) curves in N_2 with a flow rate of 20 mL·min^{-1} and a ramp rate of 10 °C·min^{-1} in the temperature range 30–800 °C. An empty Al_2O_3 crucible was used as the reference. The FT-IR spectra were obtained in the range 400-4000 cm^{-1} on a PerkinElmer FT-IR spectrometer using KBr pellets. Optical diffuse reflectance spectra were measured at room temperature with a Shimadzu UV-3101 PC UV-vis spectrophotometer. The instrument was equipped with an integrating sphere and controlled with a personal computer. The samples were ground into fine powder and pressed onto a thin glass slide holder. A $BaSO_4$ plate was used as a standard (100% reflectance). The absorption spectra were calculated from reflectance spectrum using the Kubelka-Munk function: $\alpha/S = (1-R)^2/2R$ where α is the absorption coefficient, S is the scattering coefficient (which is practically wavelength independent when the particle size is larger than 5 μm), and R is the reflectance. The solid-state fluorescence excitation and emission spectra were measured on an Edinburgh Instruments analyzer model FLS920 spectrofluorometer at room temperature with a wavelength increment of 1.0 nm and an integration time of 0.2 s.

The X-ray crystallographic data of **1**–**6** was used to calculate their electronic structures. The calculations of density of states (DOS) were carried out using density functional theory (DFT) with one of the three nonlocal gradient-corrected exchange-correlation functionals (GGA-PBE) and performed with the CASTEP code[1, 2], which uses a plane wave basis set for the valence electrons and norm-conserving pseudopotential for the core electrons[3]. The number of plane waves included in the basis was determined by a cutoff energy, E_c, of 280 eV for **1**–**6**. Pseudo-atomic calculations were performed for Pb $5d^{10}6s^26p^2$, Br $4s^24p^5$, P $3s^23p^3$, S $3s^23p^4$, C $2s^22p^2$, N $2s^22p^3$ and H $1s^1$. The parameters used in the calculations and convergence

criteria were set by the default values of the CASTEP code.

S 1.2 Preparations of 1–6

Preparations of 1–3. A mixture of $PbBr_2$ (0.092 g, 0.2 mmol), btz (0.2 mL, 1.84 mmol), concentrated HBr (1.0 mL, 45%) and 6.0 mL different alcohols, methanol for **1**, ethanol for **2** and n-propanol for **3** were sealed in a 25-mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heated at 120 °C for 3 days and finally cooled to room temperature. Colorless prismatic crystal for **1** and light yellow prismatic crystals for **2–3** were obtained and washed with ethanol. (Yields: 55%, 59% and 51% based on Pb for **1**–**3**, respectively).

Elemental analysis calcd. (%) for **1** $C_8H_8NSPbBr_3$: C 16.09, H 1.35, N 2.35; found: C 16.15, H 1.30, N 2.27. IR (KBr pellet, cm^{-1}) 3427(m), 3067(m), 2997(w), 2833(vw), 1606(s), 1517(m), 1441(s), 1397(m), 1360(m), 1277(vw), 1163(w), 1113(m), 1037(vw), 993(s), 891(m), 803(m), 759(vs), 569(w), 513(vw).

Elemental analysis calcd. (%) for **2** $C_9H_{10}NSPbBr_3$: C 17.69, H 1.65, N 2.29; found: C 17.36, H 2.23, N 2.50. IR (KBr pellet, cm^{-1}) 3427(vs), 3061(m), 2985(w), 2827(vw), 1606(s), 1499(m), 1423(s), 1391(m), 1366(m), 1252(vw), 1183(w), 1139(m), 1087(vw), 1005(s), 885(m), 853(m), 765(vs), 571(vw), 510(vw).

Elemental analysis calcd. (%) for **3** $C_{20}H_{24}N_2S_2Pb_3Br_8$: C 14.85, H 1.50, N 1.73; found: C 14.72, H 1.94, N 1.33. IR (KBr pellet, cm^{-1}) 3477(vs), 3067(m), 2972(w), 2871(vw), 1613(s), 1505(m), 1467(s), 1423(m), 1366(m), 1208(vw), 1139(w), 1087(m), 999(s), 911(m), 885(m), 841(w), 760(vs), 651(vw), 506(vw).

Preparations of 4–6. A mixture of $PbBr_2$ (0.092 g, 0.2 mmol), PPh_3 (0.066 g, 0.25 mmol), concentrated HI (1.0 mL, 45%) and 6.0 mL different alcohols, methanol for **4**, ethanol for **5** and n-propanol for **6** were sealed in a 25-mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure and then heated at 120 °C for 3 days and finally cooled to room temperature. Colorless prismatic crystals of **4–6** were obtained and washed with ethanol. (Yield: 66%, 60%, 55% based on Pb for **4–6**, respectively).

Elemental analysis calcd. (%) for **4** $C_{19}H_{18}PPbBr_3$: C 31.51, H 2.50; found: C 31.02, H 2.89. IR (KBr pellet, cm^{-1}) 3459(m), 3047(w), 2980(w), 2909(m), 2359(s), 1689(vw), 1581(vw),

1473(vw), 1435(vs), 1391(s), 1309(m), 1189(w), 1107(vs), 987(w), 885(vs), 753(vs), 683(vs), 487(vs).

Elemental analysis calcd. (%) for **5** $C_{20}H_{20}PPbBr_3$: C 32.54, H 2.73; found: C 32.47, H 3.14. IR (KBr pellet, cm^{-1}) 3453(vs), 2987(w), 2929(w), 2884(m), 2820(vw), 2346(s), 2065(vw), 1604(vs), 1476(m), 1431(m), 1374(m), 1309(m), 1169(m), 1118(vs), 990(w), 885(vs), 746(vs), 683(m), 523(m)

Elemental analysis calcd. (%) for **6** $C_{21}H_{22}PPbBr_3$: C 33.53, H 2.95; found: C 33.36, H 3.39. IR (KBr pellet, cm^{-1}) 3465(w), 3061(w), 2965(w), 2927(w), 2883(w), 2353(s), 1695(vw), 1581(vw), 1479(w), 1435(vs), 1391(m), 1315(w), 1170(m), 1113(vs), 987(w), 835(w), 740(vs), 683(vs), 531(vs)

S 1.3 Single-crystal structure determinations

The intensity data sets of **1**–**6** were collected on a Agilent Xcalibur, Eos, Gemini CCD diffractometer equipped with a graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) at 293 K. The data sets were reduced by the CrysAlisPro program.[4] An empirical absorption correction using spherical harmonics was implemented in SCALE3 ABSPACK scaling algorithm. The structures were solved by direct methods using the Siemens SHELXL package of crystallographic software. Difference Fourier maps were created on the basis of these atomic positions to yield the other non-hydrogen atoms. The structures were refined using a full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of **1**–**6** were located at geometrically calculated positions and refined as riding on their parent atoms with fixed isotropic displacement parameters [U_{iso}(H) = 1.2U_{eq}(C, N)]. Crystallographic data and structural refinements for **1**–**6** are summarized in Table 1. Important bond lengths and angles are listed in Table S1.

Table S1. Selected Bond Distances (Å) and Angles (°) for **1**–**6**.

1			
Bond	(Å)	Bond	(Å)
Pb(1)-Br(1)	2.955(5)	S(1)-C(7)	1.714(7)

Pb(1)-Br(1)#1	3.1078(5)	N(1)-C(1)	1.326(7)
Pb(1)-Br(2)	2.9673(6)	N(1)-C(7)	1.294(8)
Pb(1)-Br(2)#1	3.1767(6)	N(1)-C(8)	1.489(8)
Pb(1)-Br(3)#1	3.1493(5)	C(1)-C(2)	1.394(8)
Pb(1)-Br(3)	2.9519(5)	C(1)-C(6)	1.417(7)
Br(1)-Pb(1)#2	3.1078(5)	C(2)-C(3)	1.376(7)
Br(2)-Pb(1)#2	3.1767(6)	C(3)-C(4)	1.312(9)
Br(3)-Pb(1)#1	3.1494(5)	C(4)-C(5)	1.432(9)
S(1)-C(6)	1.709(6)	C(5)-C(6)	1.337(7)

Angle	(°)	Angle	(°)
Br(1)-Pb(1)-Br(1)#1	175.522(18)	Pb(1)-Br(3)-Pb(1)#1	78.645(12)
Br(1)-Pb(1)-Br(2)#1	95.942(15)	C(6)-S(1)-C(7)	89.6(3)
Br(1)#1-Pb(1)-Br(2)#1	80.659(14)	C(1)-N(1)-C(8)	124.8(5)
Br(1)-Pb(1)-Br(2)	86.747(15)	C(7)-N(1)-C(1)	116.4(5)
Br(1)#1-Pb(1)-Br(3)#2	99.271(15)	C(7)-N(1)-C(8)	118.7(5)
Br(1)-Pb(1)-Br(3)#2	84.105(15)	N(1)-C(1)-C(2)	129.1(5)
Br(2)-Pb(1)-Br(1)#1	96.479(15)	N(1)-C(1)-C(6)	110.8(5)
Br(2)-Pb(1)-Br(2)#1	175.719(18)	C(2)-C(1)-C(6)	120.0(4)
Br(2)-Pb(1)-Br(3)#2	84.366(15)	C(3)-C(2)-C(1)	116.4(5)
Br(3)-Pb(1)-Br(1)	91.875(16)	C(4)-C(3)-C(2)	124.4(5)
Br(3)-Pb(1)-Br(1)#1	84.900(15)	C(3)-C(4)-C(5)	119.6(6)
Br(3)-Pb(1)-Br(2)#1	84.133(15)	C(6)-C(5)-C(4)	118.1(5)
Br(3)#2-Pb(1)-Br(2)#1	99.201(15)	C(1)-C(6)-S(1)	110.5(4)
Br(3)-Pb(1)-Br(2)	92.465(16)	C(5)-C(6)-S(1)	128.6(4)
Br(3)-Pb(1)-Br(3)#2	175.006(16)	C(5)-C(6)-S(1)	120.9(5)
Pb(1)-Br(1)-Pb(1)#2	79.264(12)	N(1)-C(7)-S(1)	112.6(5)
Pb(1)-Br(2)-Pb(1)#2	77.982(12)		

Symmetry transformations used to generate equivalent atoms: #1 -1/2+*x*, 3/2-*y*, 1-*z*; #2 1//2+*x*,

3/2-*y*, 1-*z*.

2			
Bond	(Å)	Bond	(Å)
Pb(1)-Br(1)	2.9792(5)	N(1)-C(6)	1.405(5)
Pb(1)-Br(1)#1	3.1383(5)	N(1)-C(7)	1.303(6)
Pb(1)-Br(2)#1	3.1032(5)	N(1)-C(8)	1.485(4)
Pb(1)-Br(2)	2.9540(4)	C(1)-C(2)	1.412(6)
Pb(1)-Br(3)#1	3.0983(5)	C(1)-C(6)	1.367(5)
Pb(1)-Br(3)	3.0244(5)	C(2)-C(3)	1.321(7)
Br(1)-Pb(1)#2	3.1383(5)	C(3)-C(4)	1.448(5)
Br(2)-Pb(1)#2	3.1032(5)	C(4)-C(5)	1.378(6)
Br(3)-Pb(1)#2	3.0984(5)	C(5)-C(6)	1.360(6)
S(1)-C(1)	1.730(5)	C(8)-C(9)	1.498(6)
S(1)-C(7)	1.639(4)		
Angle	(°)	Angle	(°)
Br(1)-Pb(1)-Br(1)#1	171.286(14)	Pb(1)-Br(3)- Pb(1)#2	79.488(11)
Br(1)-Pb(1)-Br(2)#1	92.263(14)	C(7)-S(1)-C(1)	89.8(2)
Br(1)-Pb(1)-Br(3)#1	93.358(14)	C(6)-N(1)-C(8)	123.6(4)
Br(1)-Pb(1)-Br(3)	88.933(14)	C(7)-N(1)-C(6)	110.7(3)
Br(2)-Pb(1)-Br(1)#1	97.334(14)	C(7)-N(1)-C(8)	125.7(4)
Br(2)-Pb(1)-Br(1)	84.033(14)	C(2)-C(1)-S(1)	129.0(3)
Br(2)#1-Pb(1)-Br(1)#1	79.028(13)	C(6)-C(1)-S(1)	110.3(3)
Br(2)-Pb(1)-Br(2)#1	97.790(14)	C(6)-C(1)-C(2)	120.6(4)
Br(2)-Pb(1)-Br(3)	82.897(12)	C(3)-C(2)-C(1)	118.8(4)
Br(2)-Pb(1)-Br(3)#1	176.047(16)	C(2)-C(3)-C(4)	121.9(4)
Br(3)#1-Pb(1)-Br(1)#1	84.801(13)	C(5)-C(4)-C(3)	117.0(5)
Br(3)-Pb(1)-Br(1)#1	99.772(14)	C(6)-C(5)-C(4)	121.2(4)

Br(3)#1-Pb(1)-Br(2)#1	79.312(12)	C(1)-C(6)-N(1)	112.1(4)
Br(3)-Pb(1)-Br(2)#1	178.676(13)	C(5)-C(6)-N(1)	127.6(3)
Br(3)-Pb(1)-Br(3)#1	100.056(14)	C(5)-C(6)-C(1)	120.4(4)
Pb(1)-Br(1)- Pb(1)#2	79.534(14)	N(1)-C(7)-S(1)	117.1(3)
Pb(1)-Br(2)- Pb(1)#2	80.493(12)	N(1)-C(8)-C(9)	111.7(3)

Symmetry transformations used to generate equivalent atoms: #1 3/2-*x*, -1/2+*y*, +*z*; #2 3/2-*x*, 1/2+*y*, +*z*.

3			
Bond	(Å)	Bond	(Å)
Pb(1)-Br(1)	2.9820(7)	N(1)-C(1)	1.387(7)
Pb(1)-Br(1)#1	3.1004(7)	N(1)-C(7)	1.275(7)
Pb(1)-Br(2)	3.0370(7)	N(1)-C(8)	1.427(8)
Pb(1)-Br(3)	3.0281(7)	C(1)-C(2)	1.397(9)
Pb(1)-Br(3)#2	3.1123(7)	C(1)-C(6)	1.449(9)
Pb(1)-Br(4)	3.0952(7)	C(2)-C(3)	1.332(9)
Pb(2)-Br(2)#2	3.1556(7)	C(3)-C(4)	1.366(8)
Pb(2)-Br(4)	3.1338(7)	C(4)-C(5)	1.313(8)
Pb(2)-Br(5)	2.7949(7)	C(5)-C(6)	1.397(9)
Pb(2)-Br(6)	2.9871(7)	C(8)-C(9)	1.563(8)
Pb(2)-Br(8)#3	3.0594(7)	C(9)-C(10)	1.411(11)
Pb(3)-Br(2)#2	3.1523(7)	S(2)-C(16)	1.712(6)
Pb(3)-Br(4)#4	3.1369(7)	S(2)-C(17)	1.639(7)
Pb(3)-Br(6)	3.0308(7)	N(2)-C(11)	1.503(7)
Pb(3)-Br(7)	2.8097(7)	N(2)-C(17)	1.293(8)
Pb(3)-Br(8)	2.9915(7)	N(2)-C(18)	1.370(8)
Br(1)-Pb(1)#1	3.1004(7)	C(11)-C(12)	1.425(8)
Br(2)-Pb(2)#1	3.1556(7)	C(11)-C(16)	1.377(8)
Br(2)-Pb(3)#2	3.1522(7)	C(12)-C(13)	1.321(10)

Br(3)-Pb(1)#2	3.1122(7)	C(13)-C(14)	1.366(9)
Br(4)-Pb(3)#3	3.1369(7)	C(14)-C(15)	1.386(9)
Br(8)-Pb(2)#4	3.0594(7)	C(15)-C(16)	1.375(9)
S(1)-C(6)	1.753(6)	C(18)-C(19)	1.546(8)
S(1)-C(7)	1.611(6)	C(19)-C(20)	1.502(9)

Angle	(°)	Angle	(°)
Br(1)-Pb(1)-Br(1)#1	83.70(2)	Pb(1)-Br(4)-Pb(2)	97.740(19)
Br(1)-Pb(1)-Br(2)	93.859(19)	Pb(1)-Br(4)-Pb(3)#3	97.252(19)
Br(1)-Pb(1)-Br(3)#2	179.40(2)	Pb(2)-Br(4)-Pb(3)#3	89.885(18)
Br(1)-Pb(1)-Br(3)	89.81(2)	Pb(2)-Br(6)-Pb(3)	95.61(2)
Br(1)#1-Pb(1)-Br(3)#2	96.653(19)	Pb(3)-Br(8)-Pb(2)#4	94.11(2)
Br(1)-Pb(1)-Br(4)	86.822(19)	C(7)-S(1)-C(6)	87.0(3)
Br(2)-Pb(1)-Br(1)#1	88.821(19)	C(1)-N(1)-C(8)	120.3(5)
Br(2)-Pb(1)-Br(3)#2	85.661(19)	C(7)-N(1)-C(1)	110.7(5)
Br(2)-Pb(1)-Br(4)	177.66(2)	C(7)-N(1)-C(8)	128.8(5)
Br(3)-Pb(1)-Br(1)#1	173.50(2)	N(1)-C(1)-C(2)	131.6(6)
Br(3)-Pb(1)-Br(2)	91.187(19)	N(1)-C(1)-C(6)	109.2(5)
Br(3)-Pb(1)-Br(3)#2	89.829(19)	C(2)-C(1)-C(6)	119.3(6)
Br(3)-Pb(1)-Br(4)	86.572(19)	C(3)-C(2)-C(1)	116.0(6)
Br(4)-Pb(1)-Br(1)#1	93.483(19)	C(2)-C(3)-C(4)	125.8(6)
Br(4)-Pb(1)-Br(3)#2	93.642(19)	C(5)-C(4)-C(3)	120.3(6)
Br(4)-Pb(2)-Br(2)#2	84.797(18)	C(4)-C(5)-C(6)	119.4(6)
Br(5)-Pb(2)-Br(2)#2	94.292(19)	C(1)-C(6)-S(1)	110.4(4)
Br(5)-Pb(2)-Br(4)	94.81(2)	C(5)-C(6)-S(1)	130.3(5)
Br(5)-Pb(2)-Br(6)	91.63(2)	C(5)-C(6)-C(1)	119.0(6)
Br(5)-Pb(2)-Br(8)#3	91.35(2)	N(1)-C(7)-S(1)	122.6(5)
Br(6)-Pb(2)-Br(2)#2	87.023(19)	N(1)-C(8)-C(9)	109.9(5)
Br(6)-Pb(2)-Br(4)	169.94(2)	C(10)-C(9)-C(8)	110.1(6)

Br(6)-Pb(2)-Br(8)#3	100.287(19)	C(17)-S(2)-C(16)	90.5(3)
Br(8)#3-Pb(2)-Br(2)#2	170.64(2)	C(17)-N(2)-C(11)	107.5(5)
Br(8)#3-Pb(2)-Br(4)	87.301(19)	C(17)-N(2)-C(18)	129.3(5)
Br(4)#4-Pb(3)-Br(2)#2	95.075(18)	C(18)-N(2)-C(11)	123.0(5)
Br(6)-Pb(3)-Br(2)#2	86.335(19)	C(12)-C(11)-N(2)	125.1(5)
Br(6)-Pb(3)-Br(4)#4	173.32(2)	C(16)-C(11)-N(2)	110.6(5)
Br(7)-Pb(3)-Br(2)#2	90.46(2)	C(16)-C(11)-C(12)	124.2(5)
Br(7)-Pb(3)-Br(4)#4	88.58(2)	C(13)-C(12)-C(11)	112.9(6)
Br(7)-Pb(3)-Br(6)	97.94(2)	C(12)-C(13)-C(14)	124.8(6)
Br(7)-Pb(3)-Br(8)	95.24(2)	C(13)-C(14)-C(15)	122.4(6)
Br(8)-Pb(3)-Br(2)#2	173.38(2)	C(16)-C(15)-C(14)	115.7(6)
Br(8)-Pb(3)-Br(4)#4	88.438(19)	C(11)-C(16)-S(2)	111.5(4)
Br(8)-Pb(3)-Br(6)	89.543(19)	C(15)-C(16)-S(2)	128.6(5)
Pb(1)-Br(1)-Pb(1)#1	96.30(2)	C(15)-C(16)-C(11)	119.9(6)
Pb(1)-Br(2)-Pb(2)#2	99.65(2)	N(2)-C(17)-S(2)	119.6(5)
Pb(1)-Br(2)-Pb(3)#2	96.466(19)	N(2)-C(18)-C(19)	116.1(5)
Pb(3)#2-Br(2)-Pb(2)#2	89.955(18)	C(20)-C(19)-C(18)	113.2(5)
Pb(1)-Br(3)-Pb(1)#2	90.172(19)		

Symmetry transformations used to generate equivalent atoms: #1 -1-*x*, 1-*y*, 2-*z*; #2 -*x*, 1-*y*, 2-*z*; #3 -1+*x*, +*y*, +*z*; #4 1+*x*, +*y*, +*z*.

4			
Bond	(Å)	Bond	(Å)
Pb(1)-Br(1)#1	3.0689(3)	C(3)-C(4)	1.348(4)
Pb(1)-Br(1)	3.0506(3)	C(4)-C(5)	1.395(4)
Pb(1)-Br(2)	3.0409(3)	C(5)-C(6)	1.384(4)
Pb(1)-Br(2)#2	3.0584(3)	C(7)-C(8)	1.361(4)
Pb(1)-Br(3)	3.0366(3)	C(7)-C(12)	1.407(3)
Pb(1)-Br(3)#1	3.0533(3)	C(8)-C(9)	1.358(4)

Br(1)-Pb(1)#2	3.0690(3)	C(9)-C(10)	1.378(4)
Br(2)-Pb(1)#1	3.0585(3)	C(10)-C(11)	1.383(4)
Br(3)-Pb(1)#2	3.0533(3)	C(11)-C(12)	1.376(4)
P(1)-C(1)	1.787(2)	C(13)-C(14)	1.373(4)
P(1)-C(7)	1.823(2)	C(13)-C(18)	1.382(4)
P(1)-C(13)	1.797(2)	C(14)-C(15)	1.389(4)
P(1)-C(19)	1.790(3)	C(15)-C(16)	1.344(4)
C(1)-C(2)	1.391(3)	C(16)-C(17)	1.372(5)
C(1)-C(6)	1.374(4)	C(17)-C(18)	1.411(4)
C(2)-C(3)	1.362(4)		

Angle	(°)	Angle	(°)
Br(1)-Pb(1)-Br(1)#1	102.154(11)	C(2)-C(1)-P(1)	120.61(19)
Br(1)-Pb(1)-Br(2)#2	84.651(9)	C(6)-C(1)-P(1)	119.85(18)
Br(1)-Pb(1)-Br(3)#1	170.084(8)	C(6)-C(1)-C(2)	119.4(2)
Br(2)-Pb(1)-Br(1)#1	84.634(9)	C(3)-C(2)-C(1)	119.6(2)
Br(2)-Pb(1)-Br(1)	91.222(9)	C(4)-C(3)-C(2)	121.6(3)
Br(2)#2-Pb(1)-Br(1)#1	93.344(9)	C(3)-C(4)-C(5)	119.9(3)
Br(2)-Pb(1)-Br(2)#2	174.931(12)	C(6)-C(5)-C(4)	119.0(3)
Br(2)-Pb(1)-Br(3)#1	81.483(9)	C(1)-C(6)-C(5)	120.4(2)
Br(3)#1-Pb(1)-Br(1)#1	83.937(10)	C(8)-C(7)-P(1)	123.65(18)
Br(3)-Pb(1)-Br(1)#1	171.189(8)	C(8)-C(7)-C(12)	122.3(2)
Br(3)-Pb(1)-Br(1)	84.532(9)	C(12)-C(7)-P(1)	114.1(2)
Br(3)-Pb(1)-Br(2)	101.102(9)	C(9)-C(8)-C(7)	119.7(2)
Br(3)-Pb(1)-Br(2)#2	81.468(9)	C(8)-C(9)-C(10)	119.8(3)
Br(3)#1-Pb(1)-Br(2)#2	102.955(9)	C(9)-C(10)-C(11)	120.8(2)
Br(3)-Pb(1)-Br(3)#1	90.263(10)	C(12)-C(11)-C(10)	120.4(2)
Pb(1)-Br(1)-Pb(1)#2	79.275(9)	C(11)-C(12)-C(7)	117.0(3)
Pb(1)-Br(2)-Pb(1)#1	79.588(9)	C(14)-C(13)-P(1)	121.35(18)

Pb(1)-Br(3)-Pb(1)#2	79.738(9)	C(14)-C(13)-C(18)	121.4(2)
C(1)-P(1)-C(7)	111.74(12)	C(18)-C(13)-P(1)	117.1(2)
C(1)-P(1)-C(13)	108.79(10)	C(13)-C(14)-C(15)	119.3(2)
C(1)-P(1)-C(19)	108.91(11)	C(16)-C(15)-C(14)	119.7(3)
C(13)-P(1)-C(7)	108.20(10)	C(15)-C(16)-C(17)	122.2(3)
C(19)-P(1)-C(7)	108.99(11)	C(16)-C(17)-C(18)	119.0(3)
C(19)-P(1)-C(13)	110.21(13)	C(13)-C(18)-C(17)	118.2(3)

Symmetry transformations used to generate equivalent atoms: #1 1/2-*x*, 1/2+*y*, +*z*; #2 1/2-*x*, -1/2+*y*, +*z*.

5			
Bond	(Å)	Bond	(Å)
Pb(1)-Br(1)#1	3.1449(5)	C(4)-C(5)	1.372(8)
Pb(1)-Br(1)	3.0137(5)	C(5)-C(6)	1.338(7)
Pb(1)-Br(2)	2.9491(5)	C(7)-C(8)	1.382(6)
Pb(1)-Br(3)	2.9551(5)	C(7)-C(12)	1.406(6)
Pb(1)-Br(3)#1	3.1832(5)	C(8)-C(9)	1.360(7)
Br(1)-Pb(1)#2	3.1448(5)	C(9)-C(10)	1.377(7)
Br(3)-Pb(1)#2	3.1832(5)	C(10)-C(11)	1.327(7)
P(1)-C(1)	1.772(4)	C(11)-C(12)	1.371(6)
P(1)-C(7)	1.798(4)	C(13)-C(14)	1.386(6)
P(1)-C(13)	1.817(5)	C(13)-C(18)	1.382(6)
P(1)-C(19)	1.808(4)	C(14)-C(15)	1.390(6)
C(1)-C(2)	1.394(6)	C(15)-C(16)	1.355(6)
C(1)-C(6)	1.391(6)	C(16)-C(17)	1.371(6)
C(2)-C(3)	1.383(7)	C(17)-C(18)	1.369(6)
C(3)-C(4)	1.360(7)	C(19)-C(20)	1.518(6)
Angle	(°)	Angle	(°)

Br(1)-Pb(1)-Br(1)#1	102.149(14)	C(4)-C(3)-C(2)	118.9(5)
Br(1)-Pb(1)-Br(3)#1	172.580(14)	C(3)-C(4)-C(5)	122.1(5)
Br(1)#1-Pb(1)-Br(3)#1	79.400(12)	C(6)-C(5)-C(4)	118.8(5)
Br(2)-Pb(1)-Br(1)	90.225(14)	C(5)-C(6)-C(1)	122.1(4)
Br(2)-Pb(1)-Br(1)#1	85.993(14)	C(8)-C(7)-P(1)	121.6(3)
Br(2)-Pb(1)-Br(3)	96.208(14)	C(8)-C(7)-C(12)	117.6(4)
Br(2)-Pb(1)-Br(3)#1	82.622(13)	C(12)-C(7)-P(1)	120.4(3)
Br(3)-Pb(1)-Br(1)#1	172.300(13)	C(9)-C(8)-C(7)	120.7(4)
Br(3)-Pb(1)-Br(1)	85.250(13)	C(8)-C(9)-C(10)	119.8(5)
Br(3)-Pb(1)-Br(3)#1	93.536(14)	C(11)-C(10)-C(9)	121.4(5)
Pb(1)-Br(1)-Pb(1)#2	80.344(11)	C(10)-C(11)-C(12)	119.9(5)
Pb(1)-Br(3)-Pb(1)#2	80.600(11)	C(11)-C(12)-C(7)	120.5(4)
C(1)-P(1)-C(7)	107.8(2)	C(14)-C(13)-P(1)	124.0(3)
C(1)-P(1)-C(13)	109.7(2)	C(18)-C(13)-P(1)	116.6(3)
C(1)-P(1)-C(19)	111.8(2)	C(18)-C(13)-C(14)	119.4(4)
C(7)-P(1)-C(13)	112.98(19)	C(13)-C(14)-C(15)	119.4(4)
C(7)-P(1)-C(19)	107.8(2)	C(16)-C(15)-C(14)	120.0(4)
C(19)-P(1)-C(13)	106.8(2)	C(15)-C(16)-C(17)	120.8(4)
C(2)-C(1)-P(1)	123.1(3)	C(18)-C(17)-C(16)	120.0(4)
C(6)-C(1)-P(1)	118.6(3)	C(17)-C(18)-C(13)	120.3(4)
C(6)-C(1)-C(2)	118.0(4)	C(20)-C(19)-P(1)	114.7(3)
C(3)-C(2)-C(1)	120.1(4)		

Symmetry transformations used to generate equivalent atoms: #1 3/2-*x*, -1/2+*y*, +*z*; #2 3/2-*x*, 1/2+*y*, +*z*.

6			
Bond	(Å)	Bond	(Å)
Pb(1)-Br(1)#1	3.1728(4)	C(7)-C(8)	1.385(4)
Pb(1)-Br(1)	2.9364(4)	C(7)-C(12)	1.392(4)

Pb(1)-Br(2)	2.8326(4)	C(8)-C(9)	1.402(4)
Pb(1)-Br(3)	2.9062(4)	C(9)-C(10)	1.376(5)
Br(1)-Pb(1)#2	3.1728(4)	C(10)-C(11)	1.376(5)
P(1)-C(1)	1.777(3)	C(11)-C(12)	1.384(4)
P(1)-C(7)	1.799(3)	C(13)-C(14)	1.376(4)
P(1)-C(13)	1.786(3)	C(13)-C(18)	1.377(4)
P(1)-C(19)	1.801(3)	C(14)-C(15)	1.392(4)
C(1)-C(2)	1.370(4)	C(15)-C(16)	1.366(4)
C(1)-C(6)	1.374(4)	C(16)-C(17)	1.347(4)
C(2)-C(3)	1.366(4)	C(17)-C(18)	1.378(4)
C(3)-C(4)	1.380(5)	C(19)-C(20)	1.568(4)
C(4)-C(5)	1.360(5)	C(20)-C(21)	1.418(5)
C(5)-C(6)	1.370(4)		

Angle	(°)	Angle	(°)
Br(1)-Pb(1)-Br(1)#1	174.441(10)	C(5)-C(6)-C(1)	120.6(3)
Br(2)-Pb(1)-Br(1)	89.631(12)	C(8)-C(7)-P(1)	119.3(2)
Br(2)-Pb(1)-Br(1)#1	85.425(11)	C(8)-C(7)-C(12)	120.1(3)
Br(2)-Pb(1)-Br(3)	94.579(12)	C(12)-C(7)-P(1)	120.5(2)
Br(3)-Pb(1)-Br(1)#1	92.303(12)	C(7)-C(8)-C(9)	119.2(3)
Br(3)-Pb(1)-Br(1)	90.621(12)	C(10)-C(9)-C(8)	120.2(3)
Pb(1)-Br(1)-Pb(1)#2	83.846(11)	C(11)-C(10)-C(9)	120.5(3)
C(1)-P(1)-C(7)	111.07(12)	C(10)-C(11)-C(12)	120.0(3)
C(1)-P(1)-C(13)	108.12(12)	C(11)-C(12)-C(7)	120.1(3)
C(1)-P(1)-C(19)	109.09(13)	C(14)-C(13)-P(1)	122.2(2)
C(7)-P(1)-C(19)	109.74(13)	C(14)-C(13)-C(18)	119.3(2)
C(13)-P(1)-C(7)	108.93(13)	C(18)-C(13)-P(1)	118.5(2)
C(13)-P(1)-C(19)	109.86(12)	C(13)-C(14)-C(15)	120.3(3)
C(2)-C(1)-P(1)	124.6(2)	C(16)-C(15)-C(14)	119.0(3)

C(2)-C(1)-C(6)	118.3(3)	C(17)-C(16)-C(15)	121.0(3)
C(6)-C(1)-P(1)	117.0(2)	C(16)-C(17)-C(18)	120.6(3)
C(3)-C(2)-C(1)	121.7(3)	C(13)-C(18)-C(17)	119.9(3)
C(2)-C(3)-C(4)	119.1(3)	C(20)-C(19)-P(1)	112.37(19)
C(5)-C(4)-C(3)	119.9(3)	C(21)-C(20)-C(19)	113.4(3)
C(4)-C(5)-C(6)	120.4(3)		

Symmetry transformations used to generate equivalent atoms: #1 3/2-*x*, -1/2+*y*, 3/2-*z*; #2 3/2-*x*, 1/2+*y*, 3/2-*z*.

Table S2. Selected Hydrogen Bonds Data for **2**.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	∠DHA (°)
C7-H7···Br1[a]	0.930	2.912	3.786	157.00

Symmetry codes: a (-*x*+3/2, *y*+1/2, -*z*).

Table S3. Selected Hydrogen Bonds Data for **3**.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	∠DHA (°)
C17-H17···Br5[a]	0.930	2.944	3.516	121.16

Symmetry codes: a (-*x*+1, -*y*+1, -*z*+1).

Table S4. Selected Hydrogen Bonds Data for **5**.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	∠DHA (°)
C18-H18···Br3	0.930	2.907	3.775	155.97

Table S5. Selected Hydrogen Bonds Data for **6**.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	∠DHA (°)
C6-H6···Br2[a]	0.930	2.948	3.809	154.57

Symmetry codes: a (-*x*+1, -*y*+1, -*z*+1).

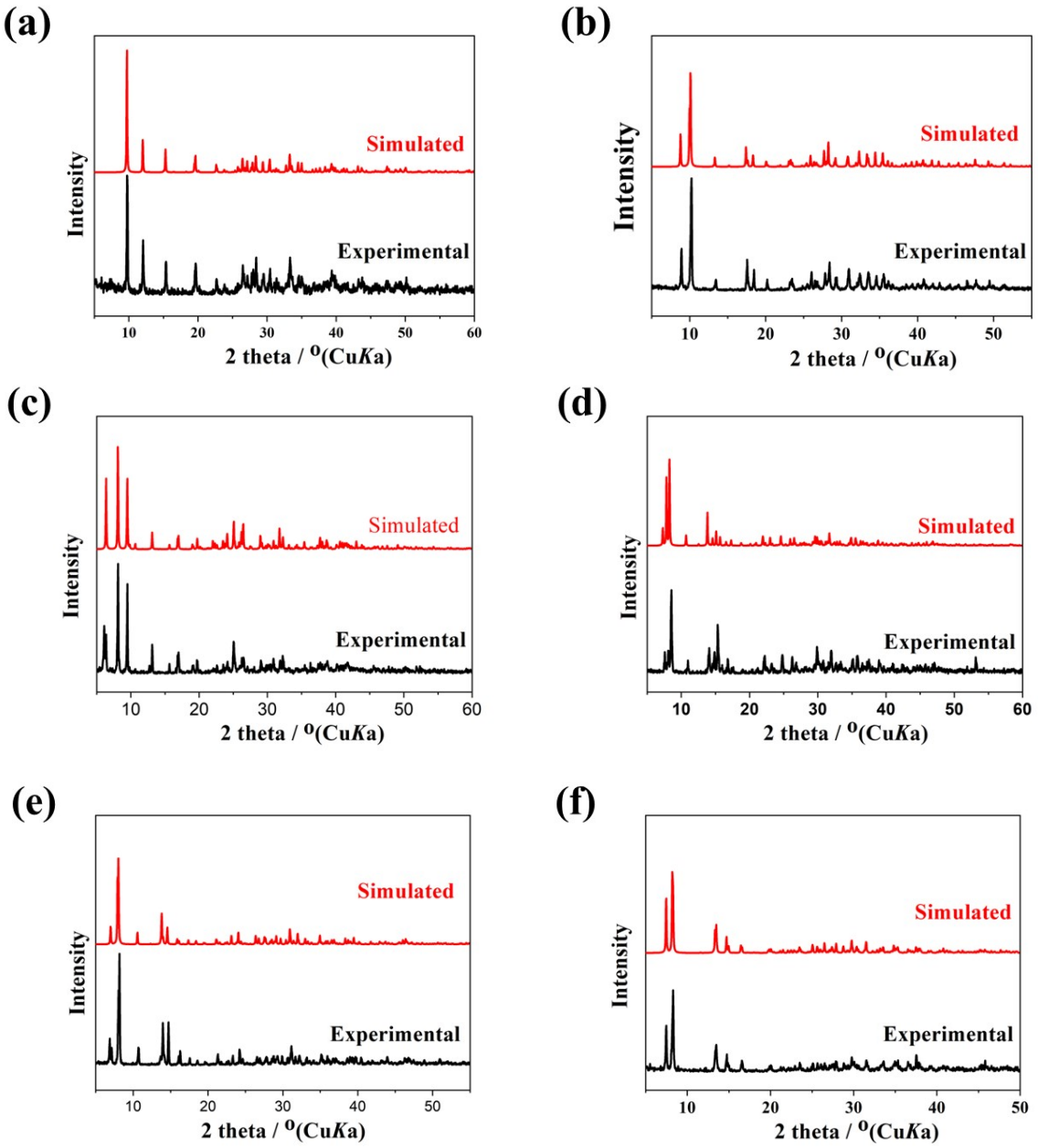

Fig. S1 The simulated and experimental PXRD patterns of **1** (a), **2** (b), **3** (c), **4** (d), **5** (e) and **6** (f).

(a)

(b)

RetTim	Width	Area	Height	Area%
0.59	0.05	350.35	107.90	4.42
0.64	0.06	809.62	199.12	10.22
0.88	0.04	21.62	5.97	0.27
1.32	0.01	104.32	111.57	1.32
1.48	0.04	5320.16	1806.32	67.15
1.59	0.02	24.35	16.12	0.31
1.63	0.02	57.75	45.23	0.73
1.68	0.02	83.45	78.24	1.05
1.71	0.02	23.92	23.09	0.30
1.76	0.02	501.47	430.32	6.33
1.82	0.02	25.83	22.73	0.33
1.90	0.02	229.45	197.15	2.90
1.93	0.02	130.68	99.50	1.65
2.03	0.02	52.18	47.68	0.66
2.08	0.02	25.10	17.57	0.32
2.15	0.03	28.62	15.91	0.36
2.22	0.02	112.44	83.00	1.42
2.34	0.03	20.93	11.69	0.26

(c)

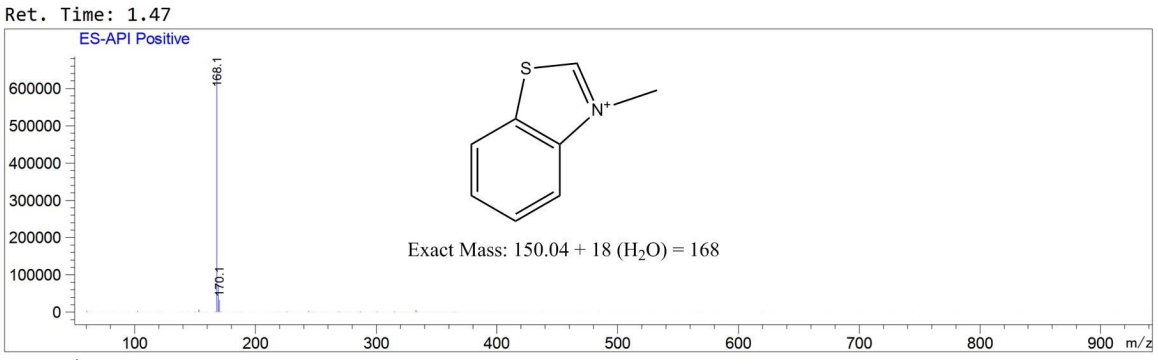

Fig. S2 (a) The reaction product of the blank reaction based on the btz reaction system. (b) Liquid chromatogram analysis report for the blank experiment. (c) Mass spectrometry analysis result for the blank experiment.

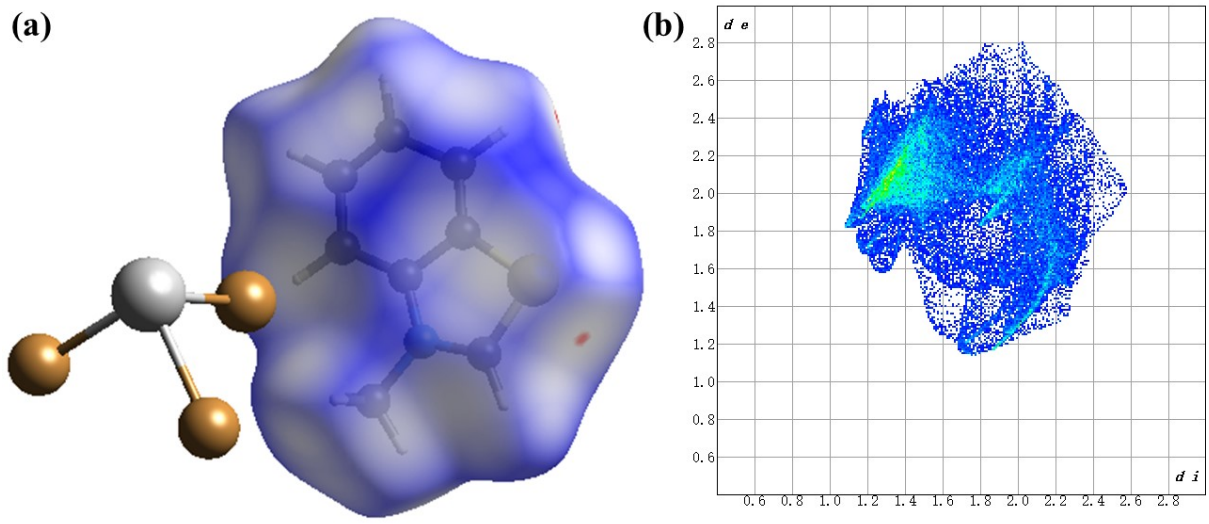

Fig. S3 (a) Hirshfeld surfaces mapped over d_{norm} for **1**. (b) Two dimensional fingerprint plot of **1**.

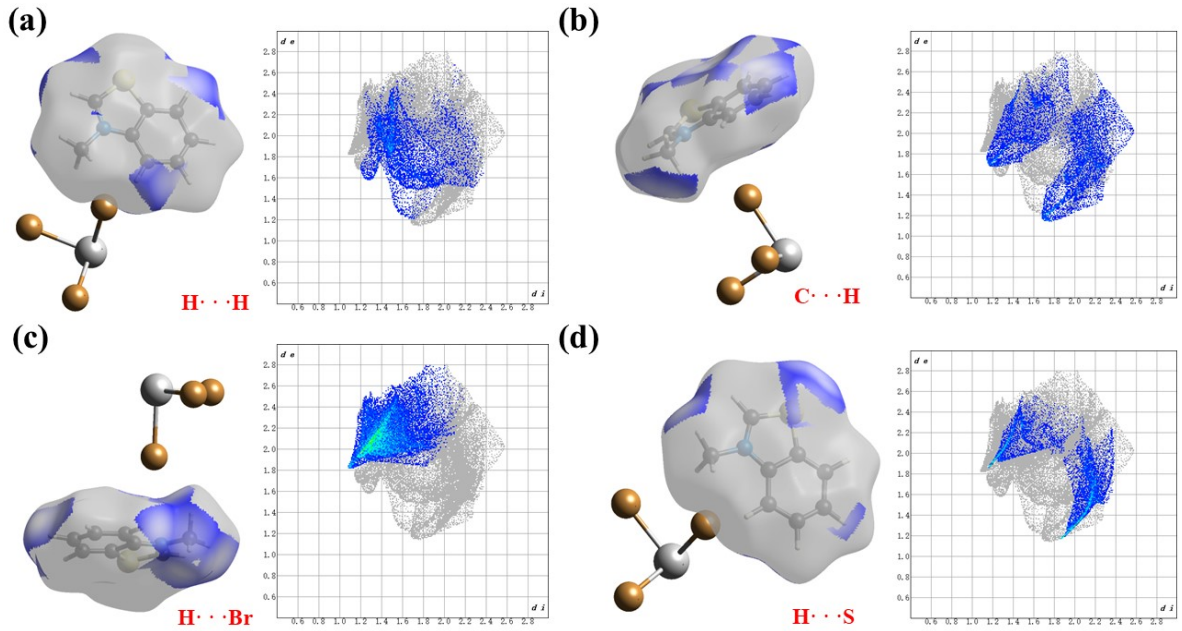

Fig. S4 The 2D fingerprint plots with a d_{norm} view of the H···H (15.2%) (a), C···H/H···C (20.0%) (b), H···Br/Br···H (36.1%) (c) and S···H/H···S (15.7%) (d) in **1**.

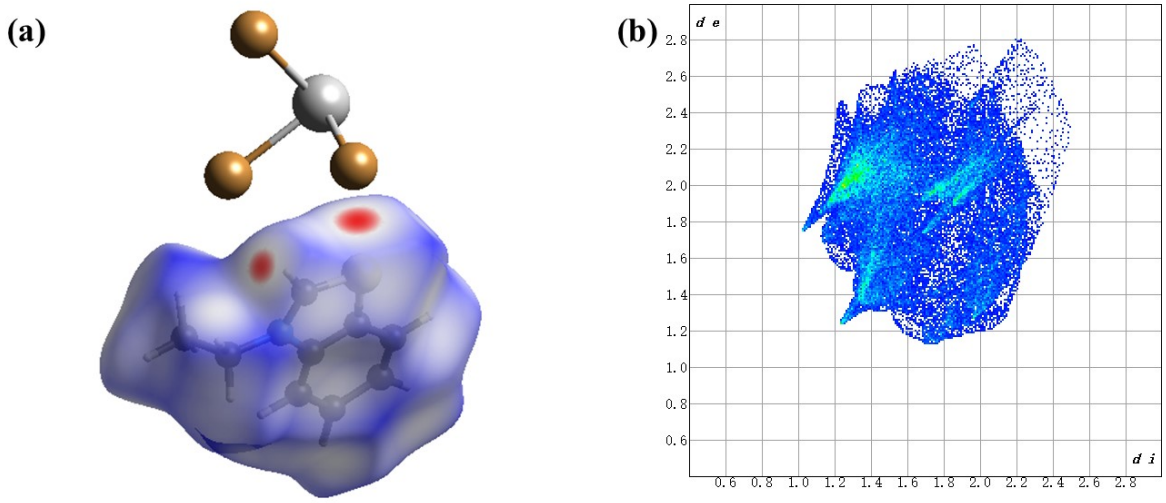

Fig. S5 (a) Hirshfeld surfaces mapped over d_{norm} for **2**. (b) Two dimensional fingerprint plot of **2**.

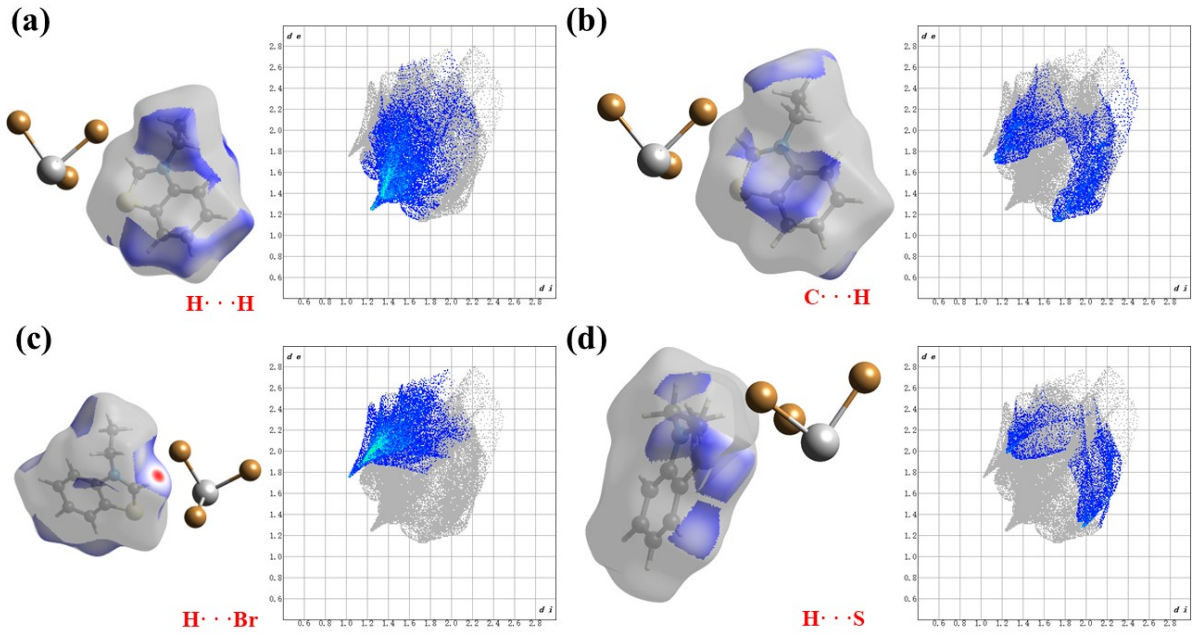

Fig. S6 The 2D fingerprint plots with a d_{norm} view of the H···H (32.4%) (a), C···H/H···C (17.7%) (b), H···Br/Br···H (25.7%) (c) and S···H/H···S (10.5%) (d) in **2**.

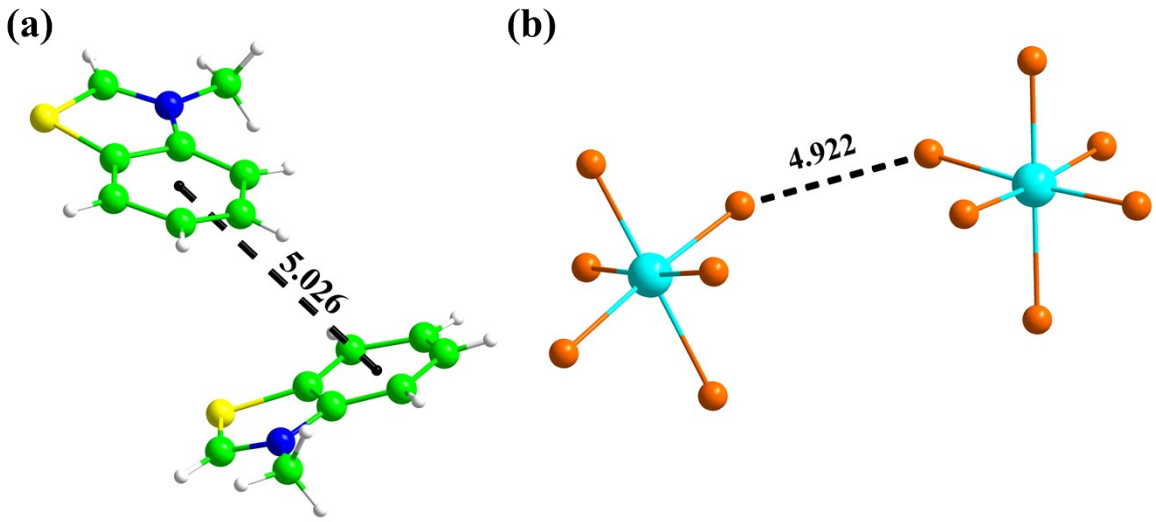

Fig. S7 (a) The nearest centroid to centroid distance between the neighboring benzene rings. (b) The nearest distance between Br atoms in **1**.

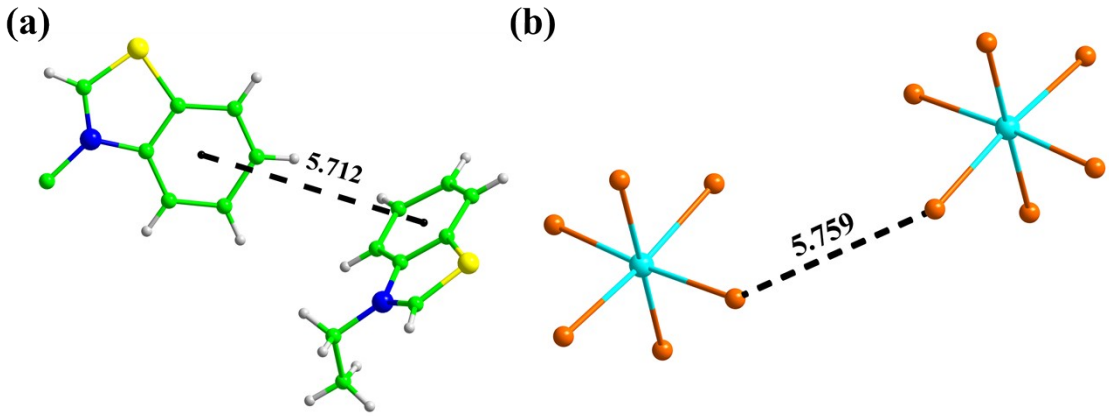

Fig. S8 (a) The nearest centroid to centroid distance between the neighboring benzene rings. (b) The nearest distance between Br atoms in **2**.

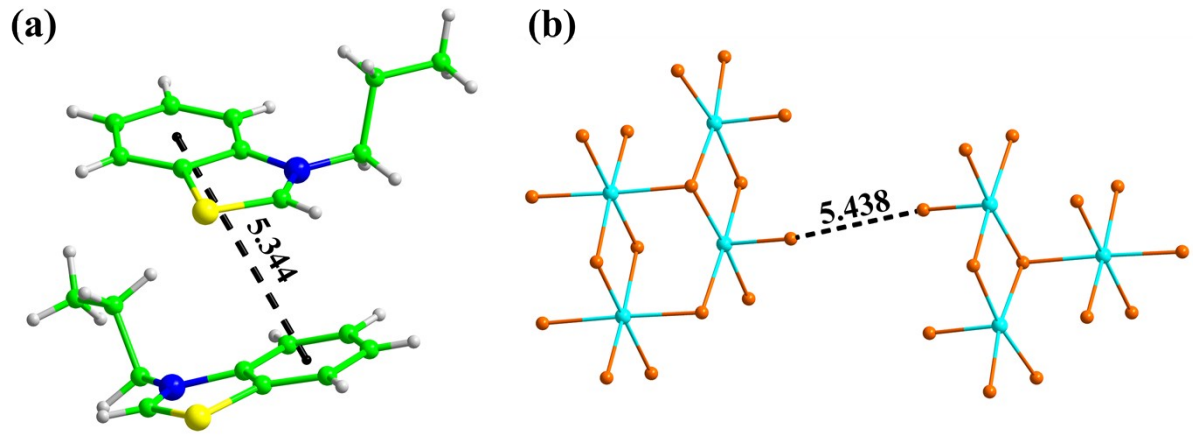

Fig. S9 (a) The nearest centroid to centroid distance between the neighboring benzene rings. (b) The nearest distance between Br atoms in **3**.

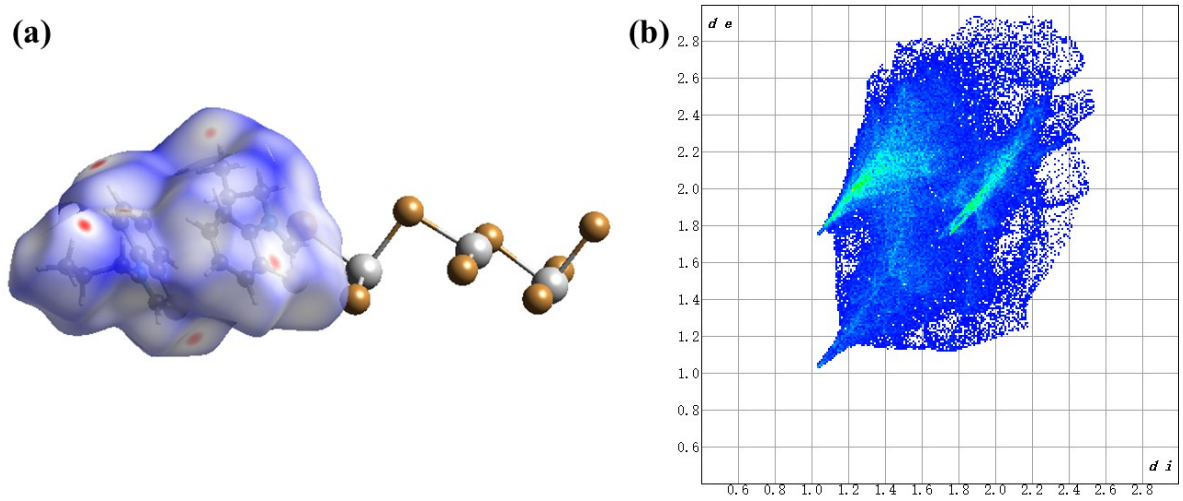

Fig. S10 (a) Hirshfeld surfaces mapped over d_{norm} for **3**. (b) Two dimensional fingerprint plot of **3**.

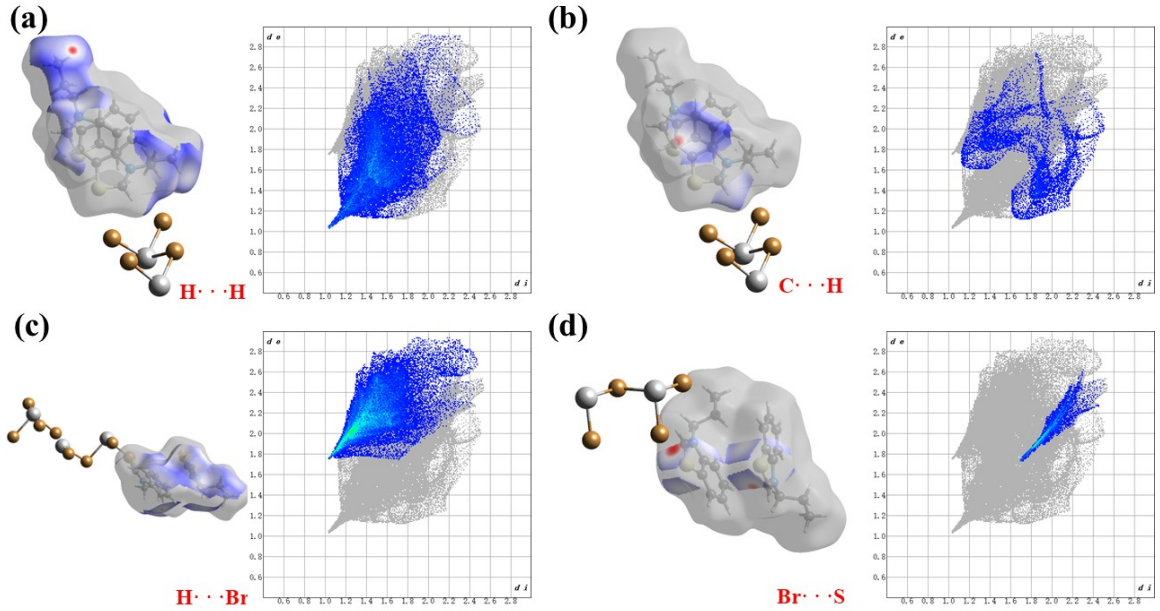

Fig. S11 The 2D fingerprint plots with a d_{norm} view of the H···H (32.7%) (a), C···H/H···C (9.0%) (b), H···Br/Br···H (40.2%) (c) and S···Br / Br···S (5.6%) (d) in **3**.

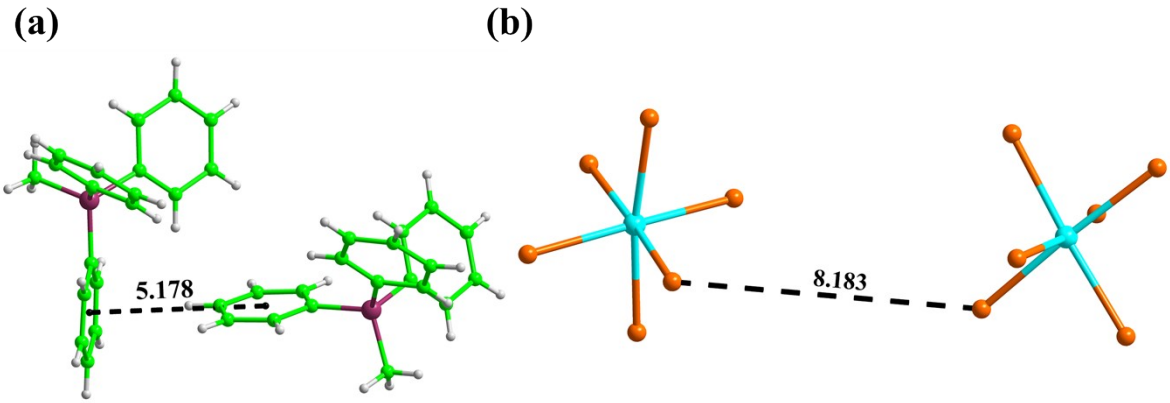

Fig. S12 (a) The nearest centroid to centroid distance between the neighboring benzene rings. (b) The nearest distance between I atoms in **4**.

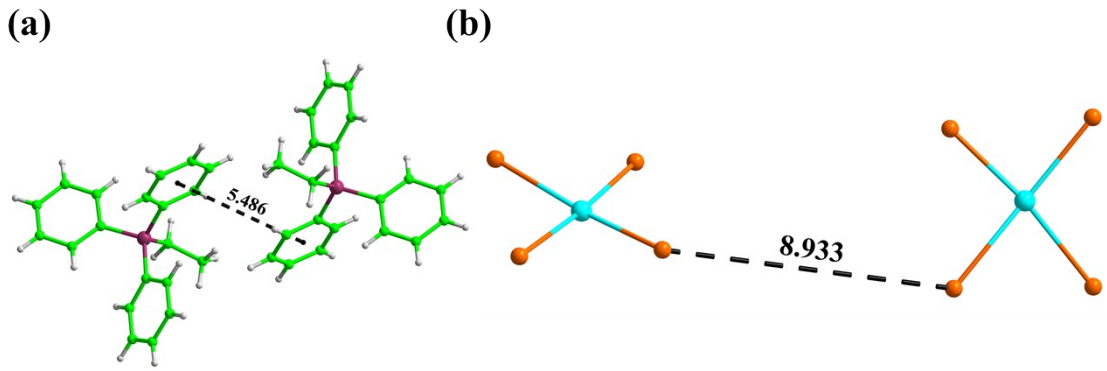

Fig. S13 (a) The nearest centroid to centroid distance between the neighboring benzene rings. (b) The nearest distance between Br atoms in **5**.

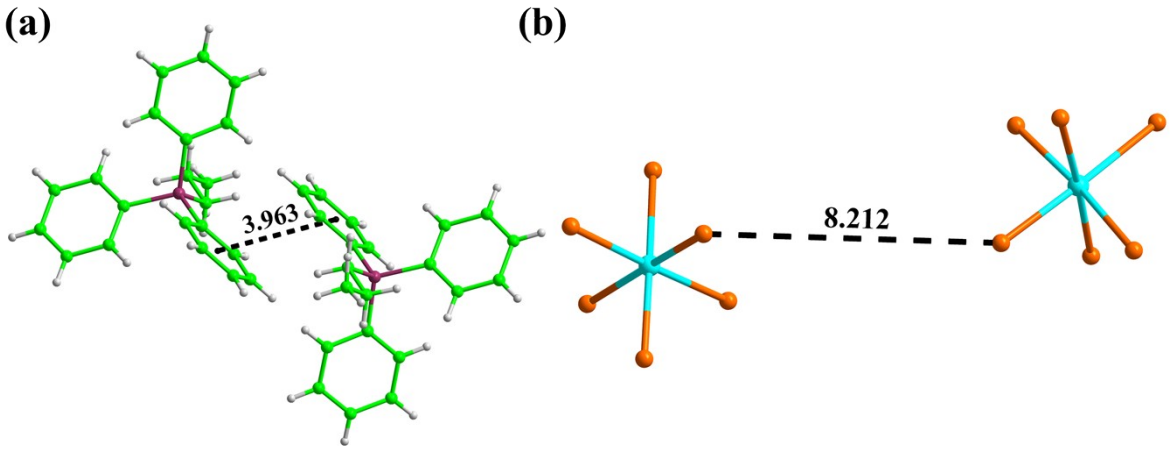

Fig. S14 (a) The nearest centroid to centroid distance between the neighboring benzene rings. (b) The nearest distance between Br atoms in **6**.

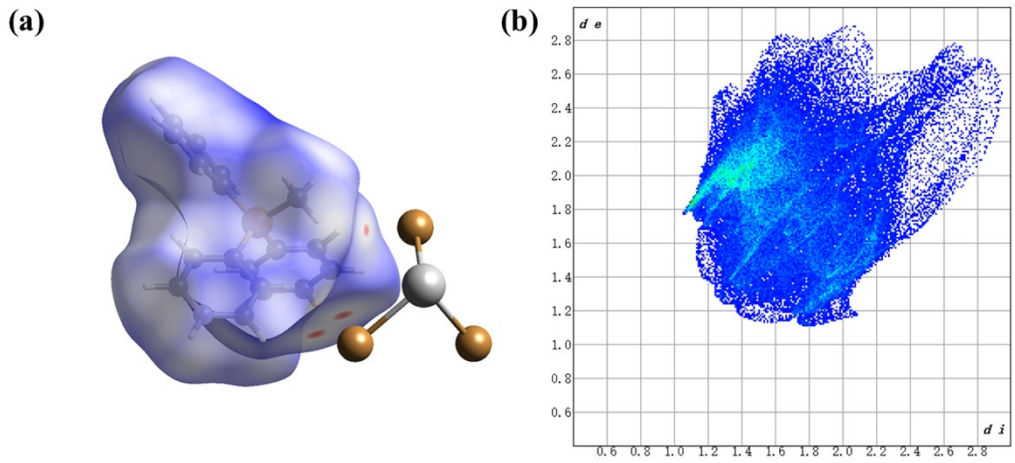

Fig. S15 (a) Hirshfeld surfaces mapped over d_{norm} for **4**. (b) Two dimensional fingerprint plot of **4**.

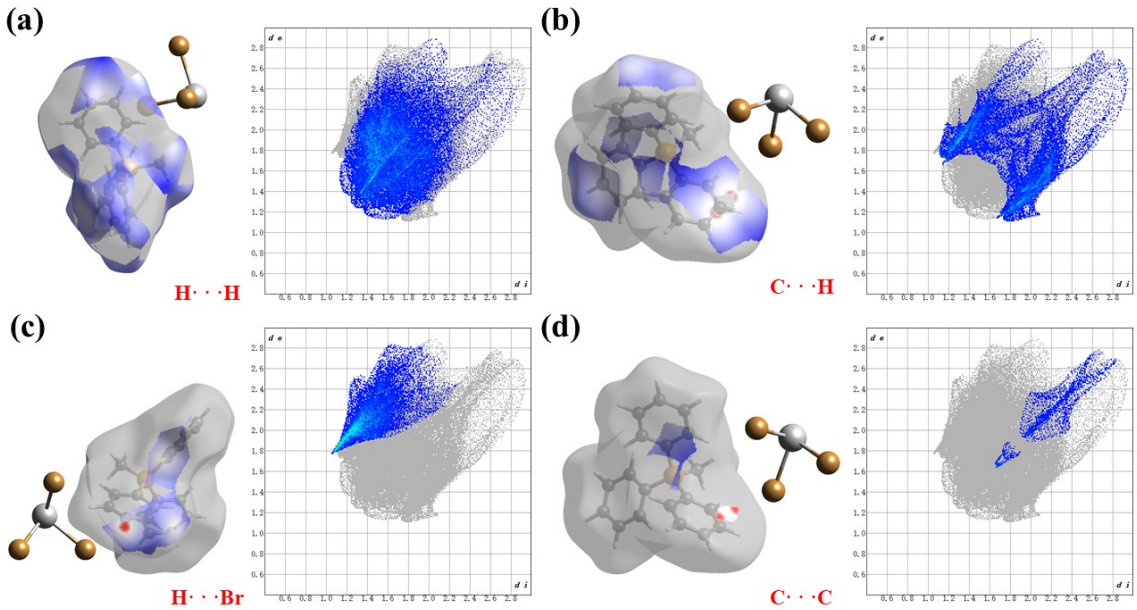

Fig. S16 The 2D fingerprint plots with a d_{norm} view of the H···H (48.6%) (a), C···H/H···C (27.6%) (b), H···Br / Br···H (20.2%) (c) and C···C (3.0%) (d) in **4**.

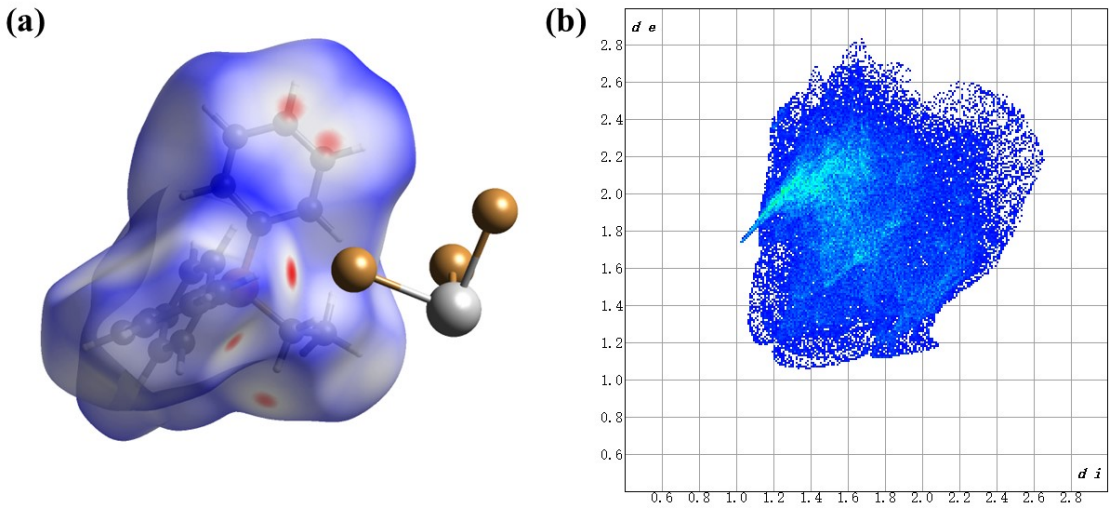

Fig. S17 (a) Hirshfeld surfaces mapped over d_{norm} for **5**. (b) Two dimensional fingerprint plot of **5**.

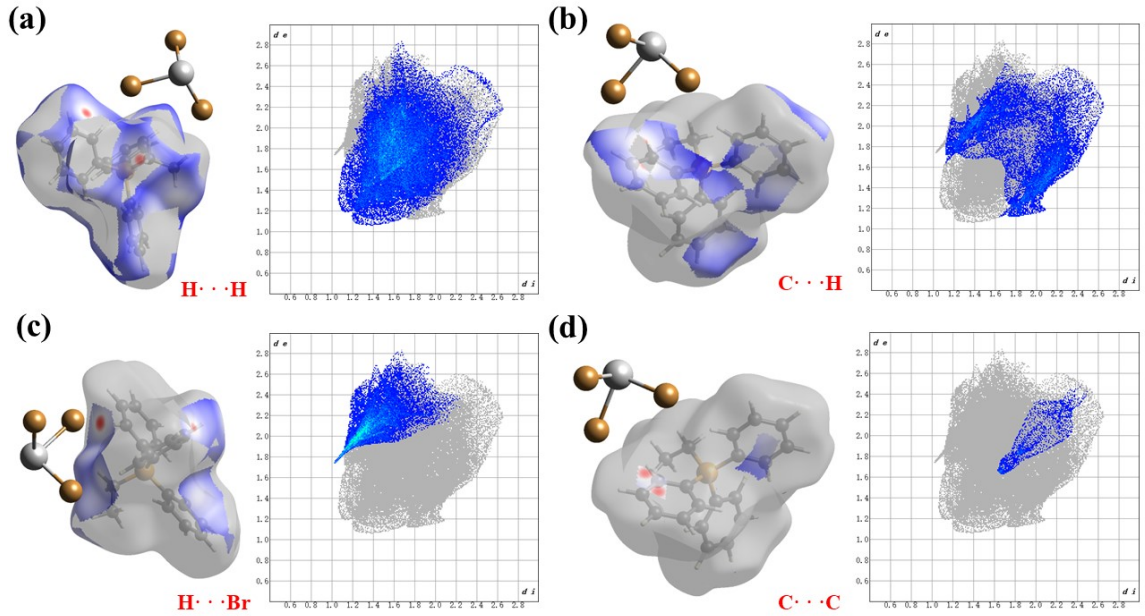

Fig. S18 The 2D fingerprint plots with a d_{norm} view of the H···H (52.7%) (a), C···H/H···C (23.8%) (b), H···Br / Br···H (20.1%) (c) and C···C (2.3%) (d) in **5**.

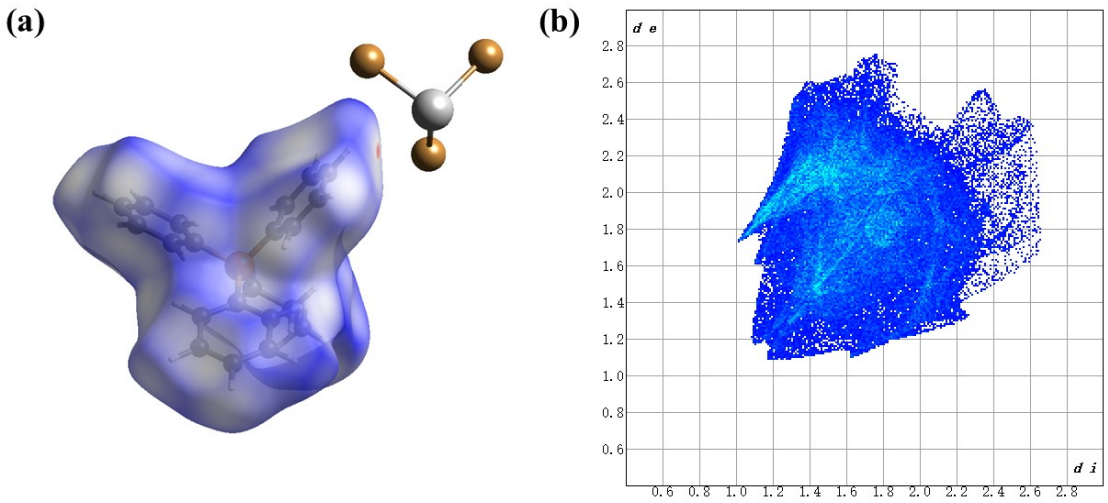

Fig. S19 (a) Hirshfeld surfaces mapped over d_{norm} for **6**. (b) Two dimensional fingerprint plot of **6**.

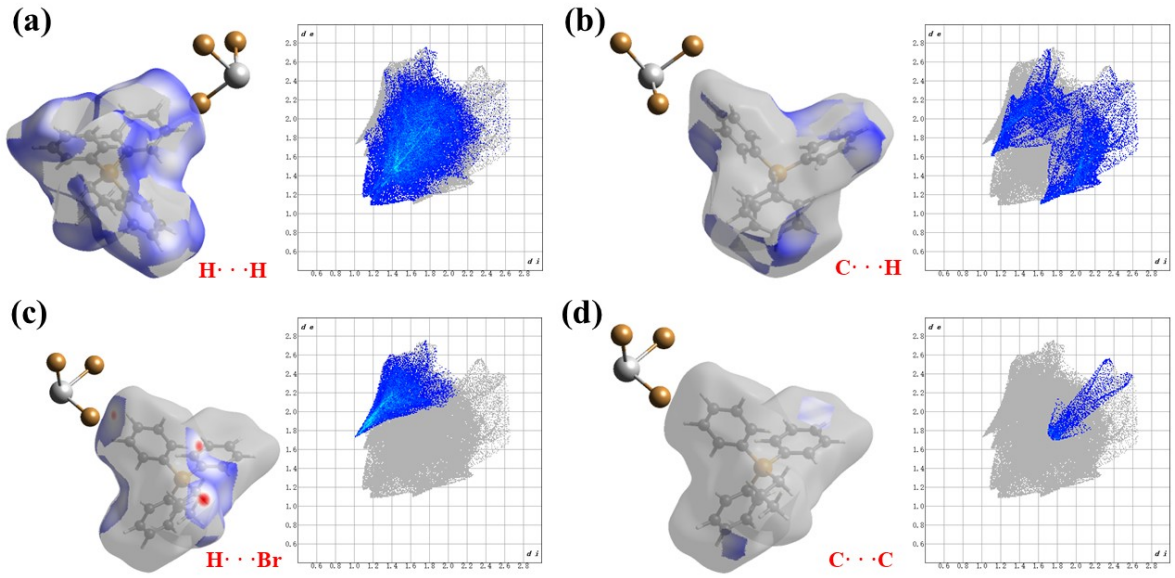

Fig. S20 The 2D fingerprint plots with a d_{norm} view of the H···H (55.3%) (a), C···H/H···C (22.2%) (b), H···Br / Br···H (18.1%) (c) and C···C (2.9%) (d) in **6**.

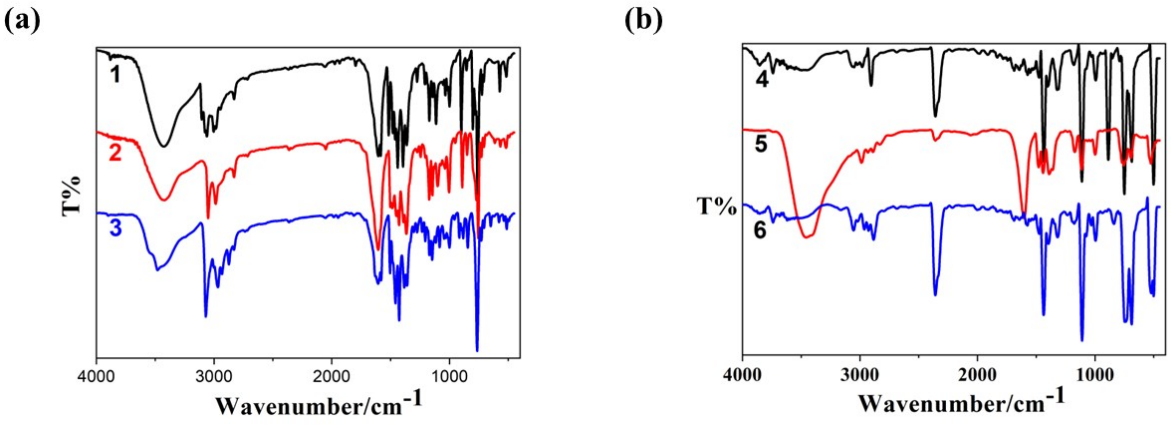

Fig. S21 IR spectra of **1**–**3** (a) and **4**–**6** (b).

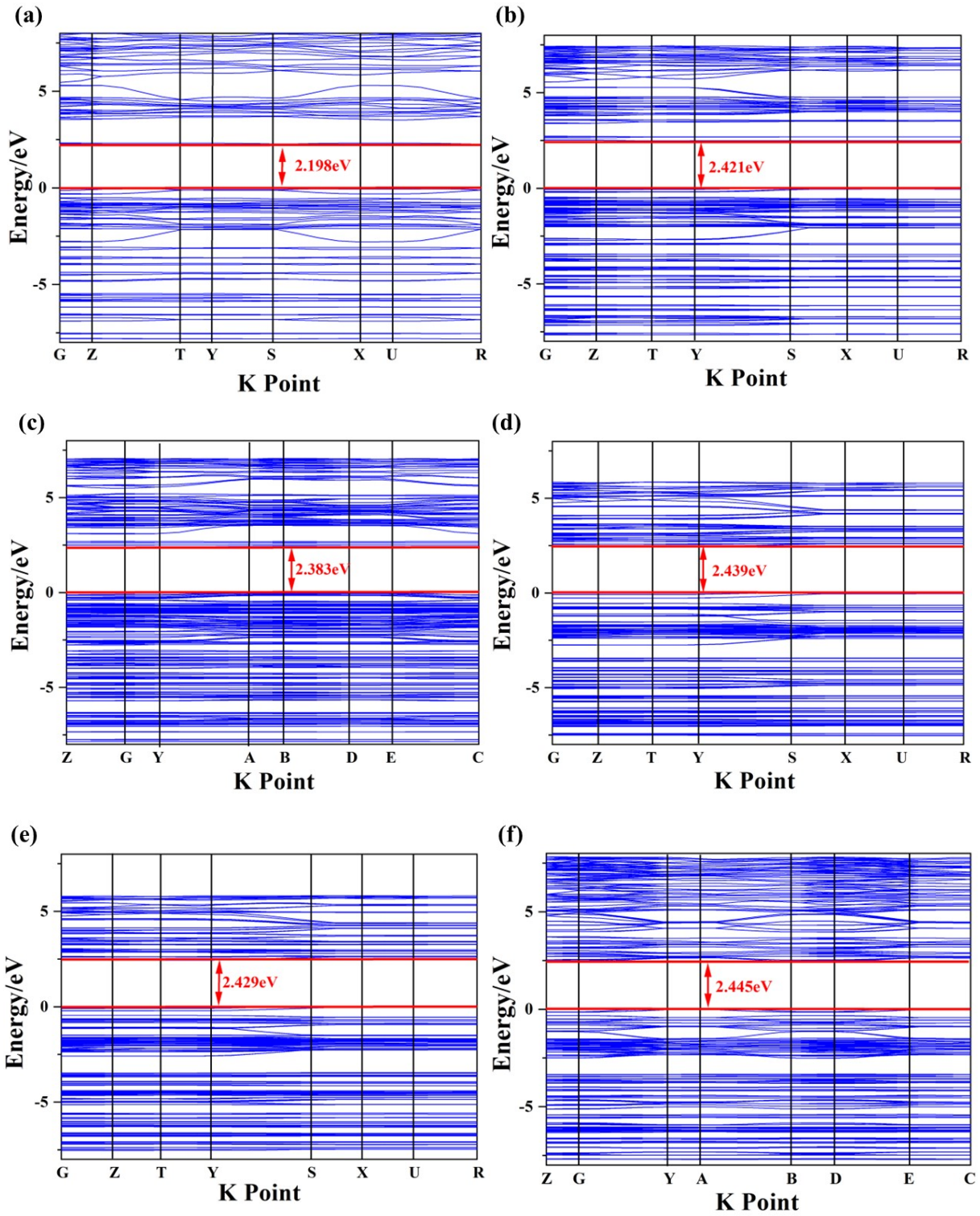

Fig. S22 Band structures of **1–6** (a–f). The Fermi level is set at 0 eV.

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