Supporting Information

Theoretical Study of Synergy Effect between Halogenation and Pyrazine Substitutions on Transport Properties of Silylethynylated Pentacenes

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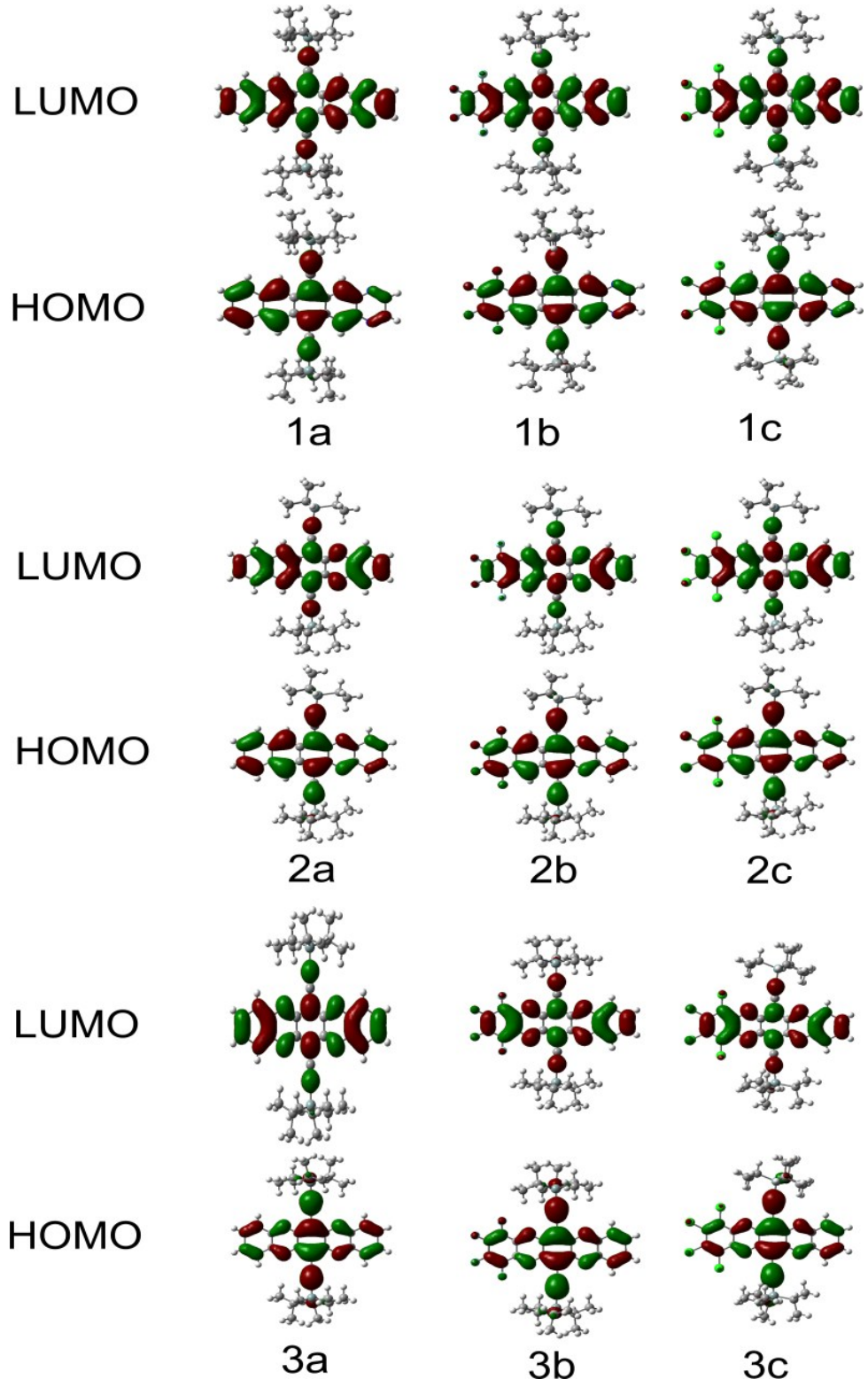

Fig. S1. Orbital composition distribution of the HOMO and LUMO for studied molecules. isovalue for orbitals is 0.02.

Table S1. Crystallographic parameters from experiments and optimized crystals at vdW-DF (revPBE) level for the TIPS-PEN derivatives.

compounds	Space group	a (Å)	b (Å)	c (Å)	α(deg)	β(deg)	γ(deg)	Cell Vol (Å^3)
1a	P1	7.569	7.947	16.860	78.24	89.30	79.54	976.021
1b	P1	7.662	7.788	17.071	77.76	88.81	83.90	989.850
1c	P-1	7.925	15.284	17.503	99.80	90.50	90.13	2089.032
2a	P1	7.660	7.721	16.983	78.23	88.76	81.78	973.193
3a	P-1	7.584	7.612	16.836	78.98	89.54	81.90	944.346
3b	P-1	7.646	7.673	16.941	89.46	78.56	84.13	968.969
1a(R*)	p1	7.805	7.684	16.520	81.06	89.85	81.84	968.602
2a(R*)	P1	7.818	7.635	16.758	78.80	89.32	82.42	972.598

* R represents optimization at vdW-DF (revPBE) level

Table S2. Crystallographic parameters from optimized crystals at vdW-DF (revPBE) level for the TIPS-PEN derivatives.

compounds	Space group	a (Å)	b (Å)	c (Å)	α(deg)	β(deg)	γ(deg)	Cell Vol (Å^3)
1a	P1	7.805	7.684	16.520	81.06	89.85	81.84	968.602
1b	p1	7.989	7.609	16.692	79.01	89.52	85.44	992.839
1c	p1	7.840	15.574	17.552	98.53	92.67	91.04	2116.243
2a	P1	7.818	7.635	16.758	78.80	89.32	82.42	972.598
2b	p1	7.569	7.995	16.735	89.01	79.26	85.56	992.080
2c	p1	7.838	15.688	17.584	99.05	92.86	91.26	2131.618
3a	P1	7.794	7.544	16.817	79.92	89.35	82.77	965.776
3b	P1	7.345	7.679	16.213	91.41	81.55	86.78	902.536
3c	P1	7.813	15.609	17.547	98.99	92.23	91.90	2110.415

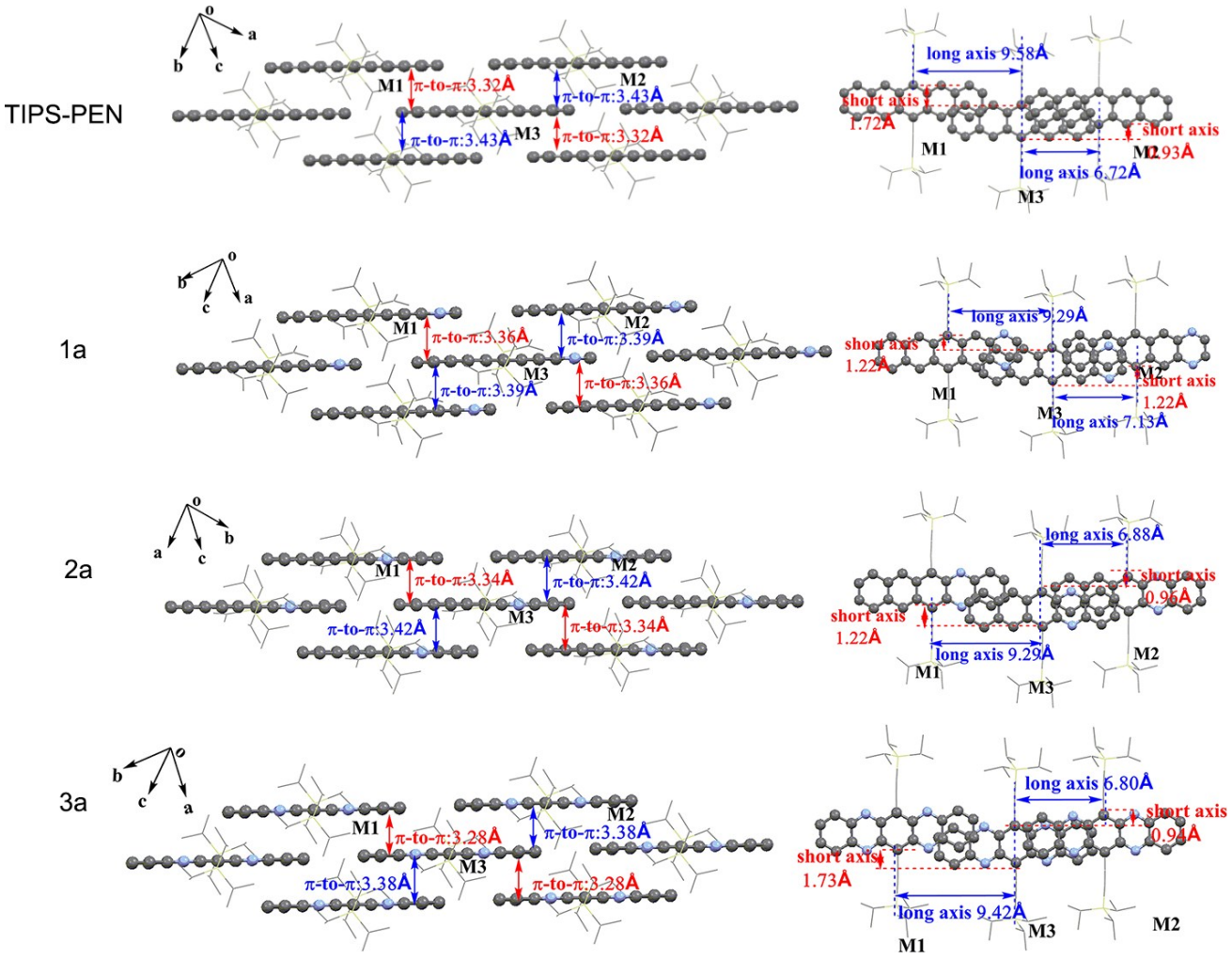

Fig. S2 Two dimensional π-stacking, π-π distance (left) and the displacements of π-stacking (right) for TIPS-PEN, **1a**, **2a,** and **3a** in their crystals. (Hydrogen atoms are removed for clarity, triisopropylsilyl groups are shown as wires)

The normalized contact distance (dnorm) described as $d_{norm} = \frac{d_i - r_i^{vdW}}{r_i^{vdW}} + \frac{d_e - r_e^{vdW}}{r_e^{vdW}}$, enables recognizing the regions of particular important intermolecular contacts, where r^{vdW} is the atomic van der Waals radius, d_e and d_i are the distances from the Hirshfeld surface to the nearest atoms outside and inside the surface, respectively.[1] The Hirshfeld surface could decode and quantify the intermolecular contacts in a crystal lattice by the combination of d_e and d_i in the form of a 2D fingerprint.[2]

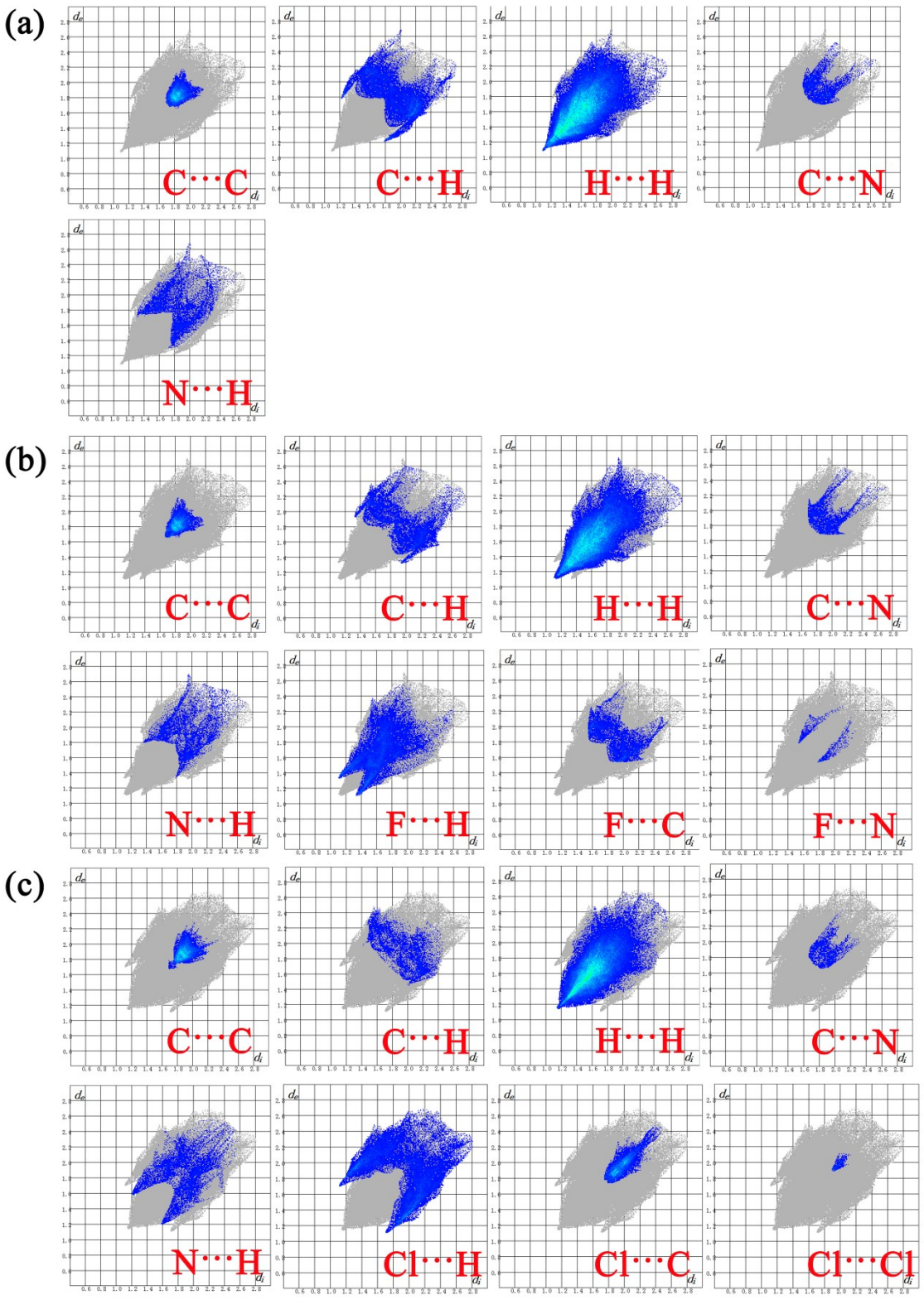

Fig. S3 Resolved 2D fingerprint plots for **1a** (a), **1b** (b) and **1c** compounds.

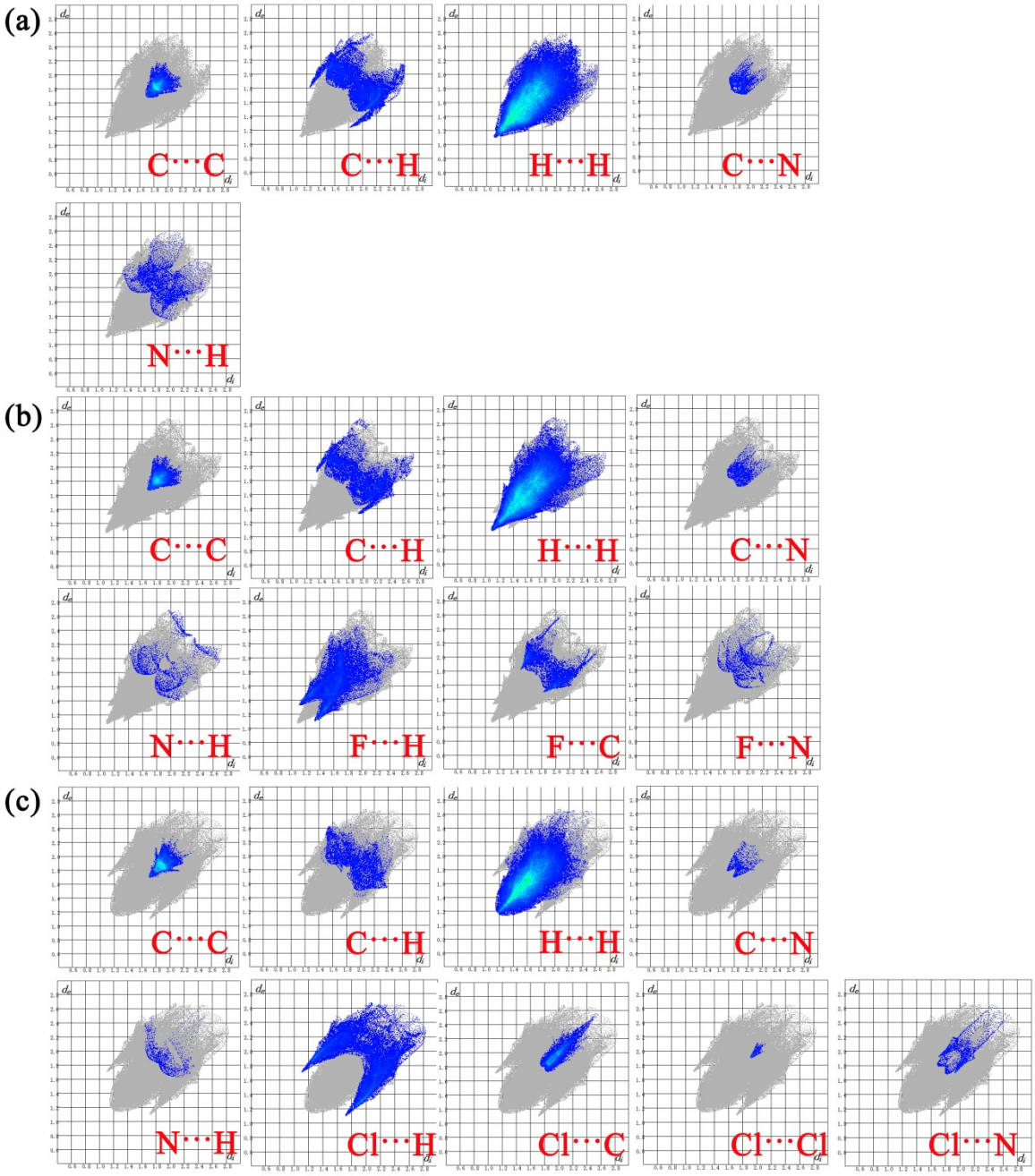

Fig. S4 Resolved 2D fingerprint plots for **2a** (a), **2b** (b) and **2c** (c) compounds.

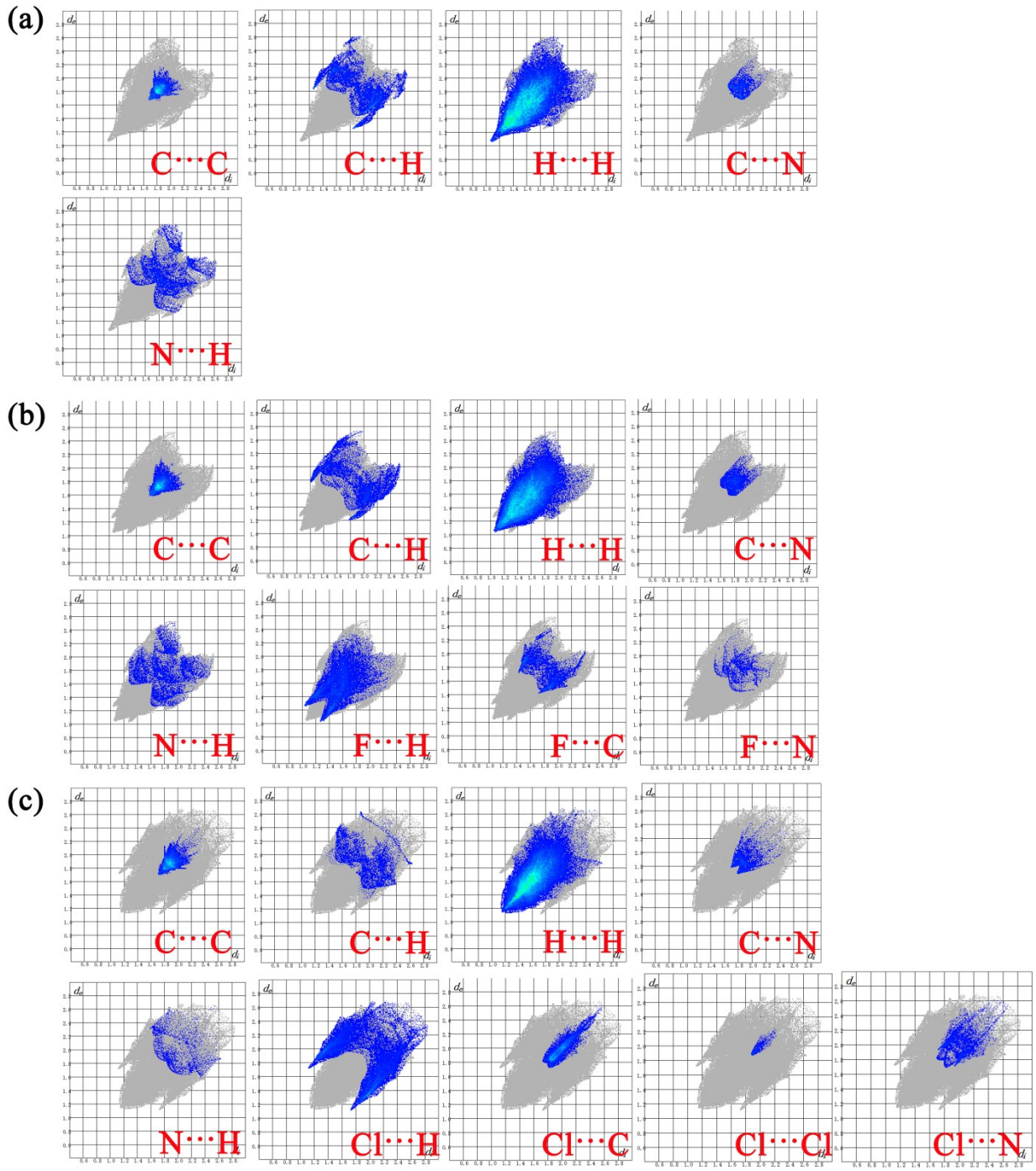

Fig. S5 Resolved 2D fingerprint plots for **3a** (a), **3b** (b) and **3c** (c) compounds.

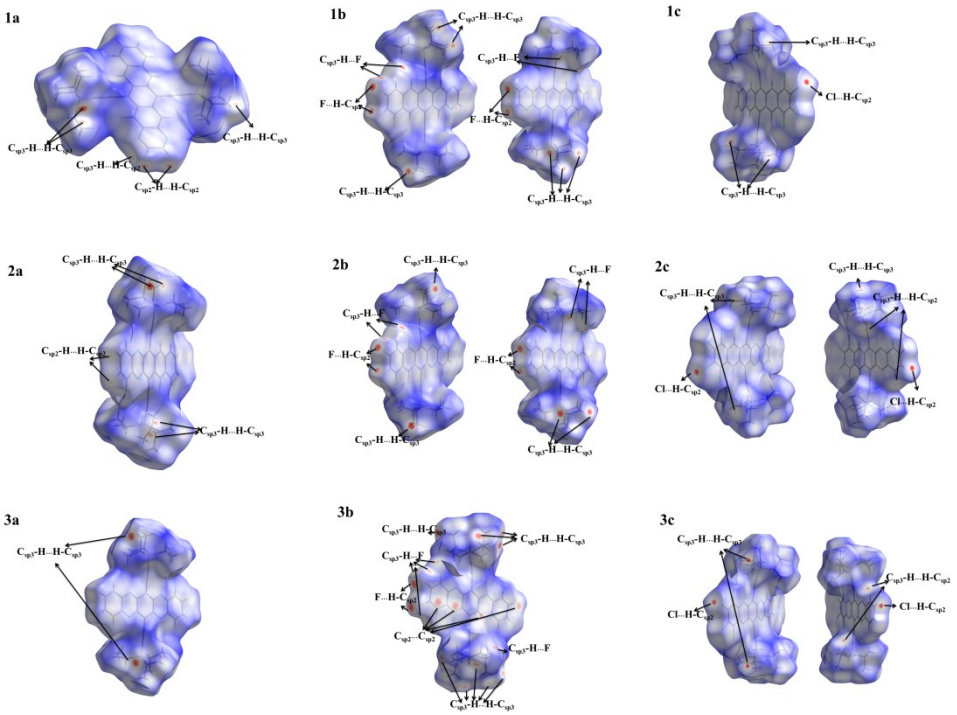

Fig. S6 Hirshfeld surfaces of molecules in single crystals mapped with d_{norm}.

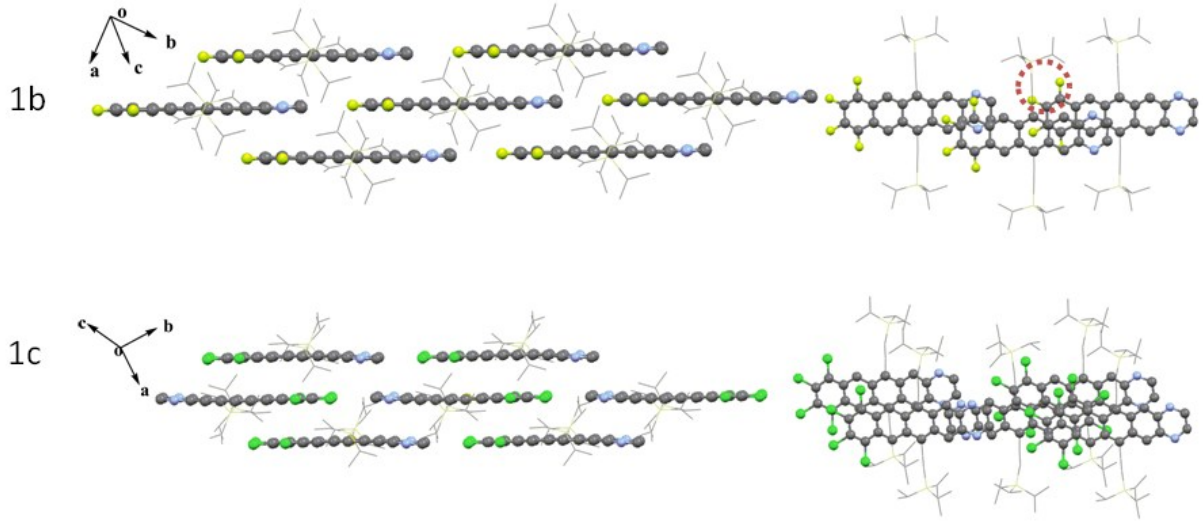

Fig. S7 Two dimensional π-stacking, (flat view, left; top view, right) for **1b** and **1c** in their optimized crystals (F…H-Csp3 contact is marked with a red circle, hydrogen atoms are removed for clarity, triisopropylsilyl groups are shown as wires).

Fig. S8 Representative MD snapshots of TIPS-PEN derivatives **1a-3c** morphologies equilibrated at 300K, TIPS parts are omitted for clarity.

1. J. J. McKinnon, D. Jayatilaka and M. A. Spackman, *Chem. Commun.*, 2007, DOI: 10.1039/b704980c, 3814-3816.
2. M. A. Spackman and J. J. McKinnon, *Crystengcomm*, 2002, **4**, 378-392.