Theoretical Investigation of Photoelectronic Properties in Symmetric and Asymmetric A-DA'D-A Non-Fullerene Acceptors with Diverse Central Cores

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Supplementary Notes

Supplementary Note1. The imaging principle of STM.

STM images by measuring the tunneling current (I) between the probe and the sample, which is directly related to the local density of states (LDOS) of the sample surface and the bias voltage (V):

$$I \propto \int_{E_F}^{E_F} \rho\,(r, E)\, dE$$

Here, $\rho\,(r, E)$refers to the LDOS at position r and energy E. Imaging with negative bias targets the HOMO and below occupied states, while positive bias images the LUMO and above unoccupied states. The contrast in STM images directly reflects the spatial distribution of the molecular surface LDOS, i.e., the electron cloud density at specific energies.

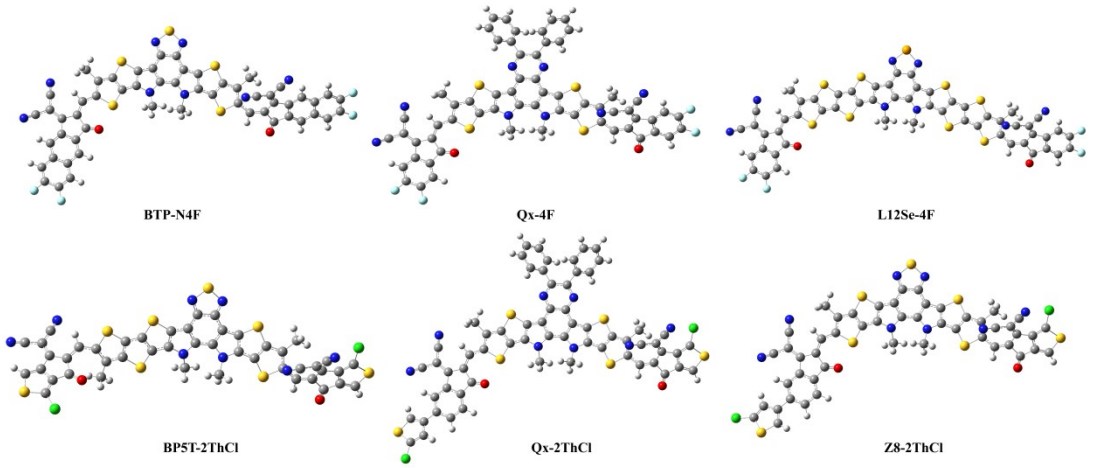
Supplementary Note2. Density difference (Δρ).

The difference in electron density between the excited state and the ground state reflects the spatial redistribution of charge when electrons transition from the ground state to the excited state. That is:

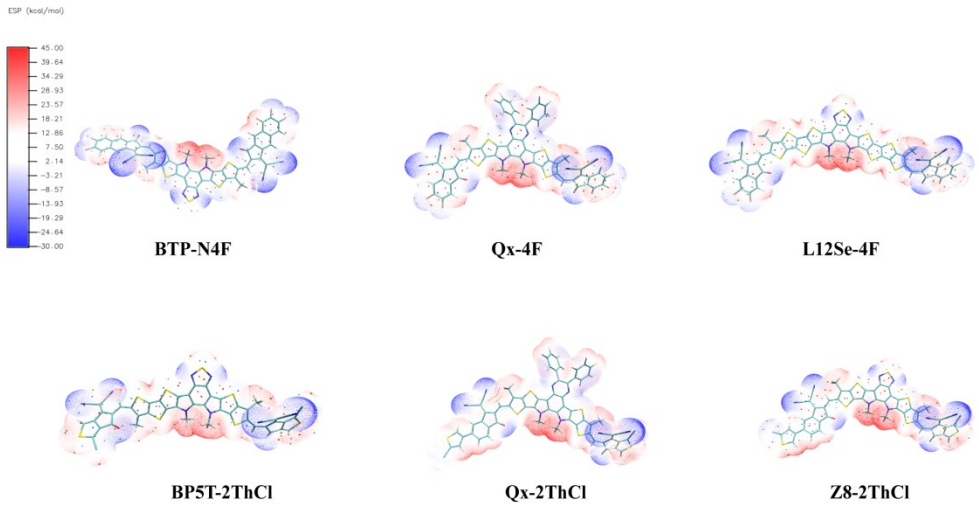
$$\Delta\rho = \rho_{ex} - \rho_{gs}$$

where ρ_{ex} and ρ_{gs} are the electron densities of the excited state and ground state, respectively.

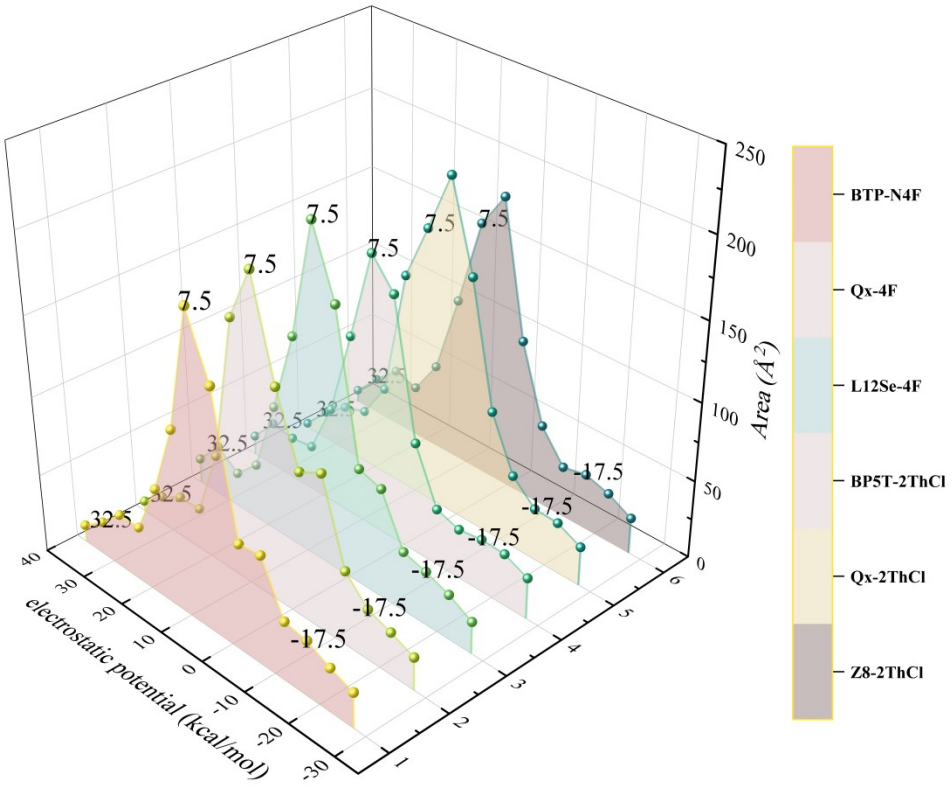
Supplementary Figures



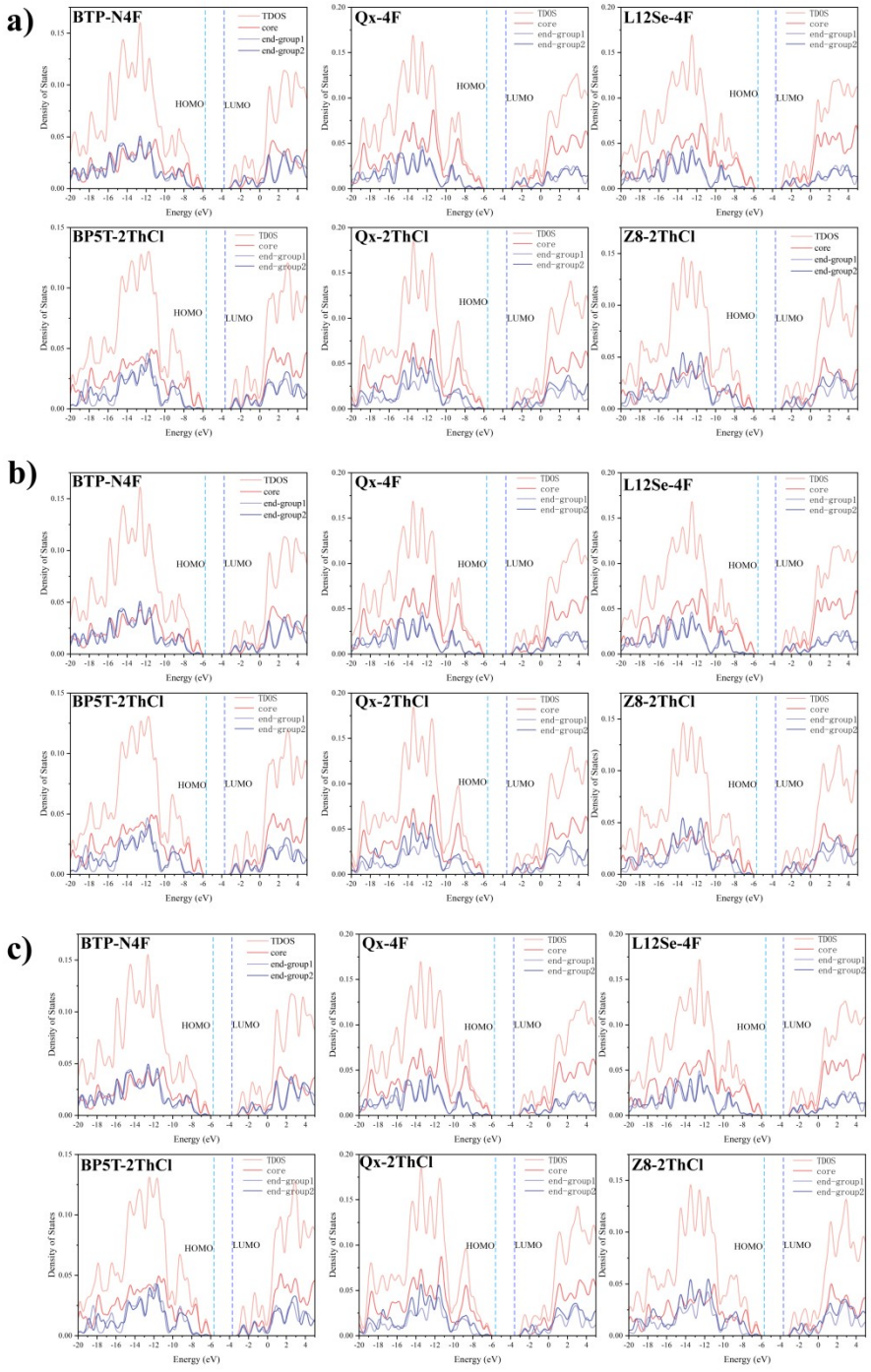
Supplementary Figure 1. Geometry optimization of BTP-N4F, Qx-4F, L12Se-4F, BP5T-2ThCl, Qx-2ThCl, and Z8-2ThCl



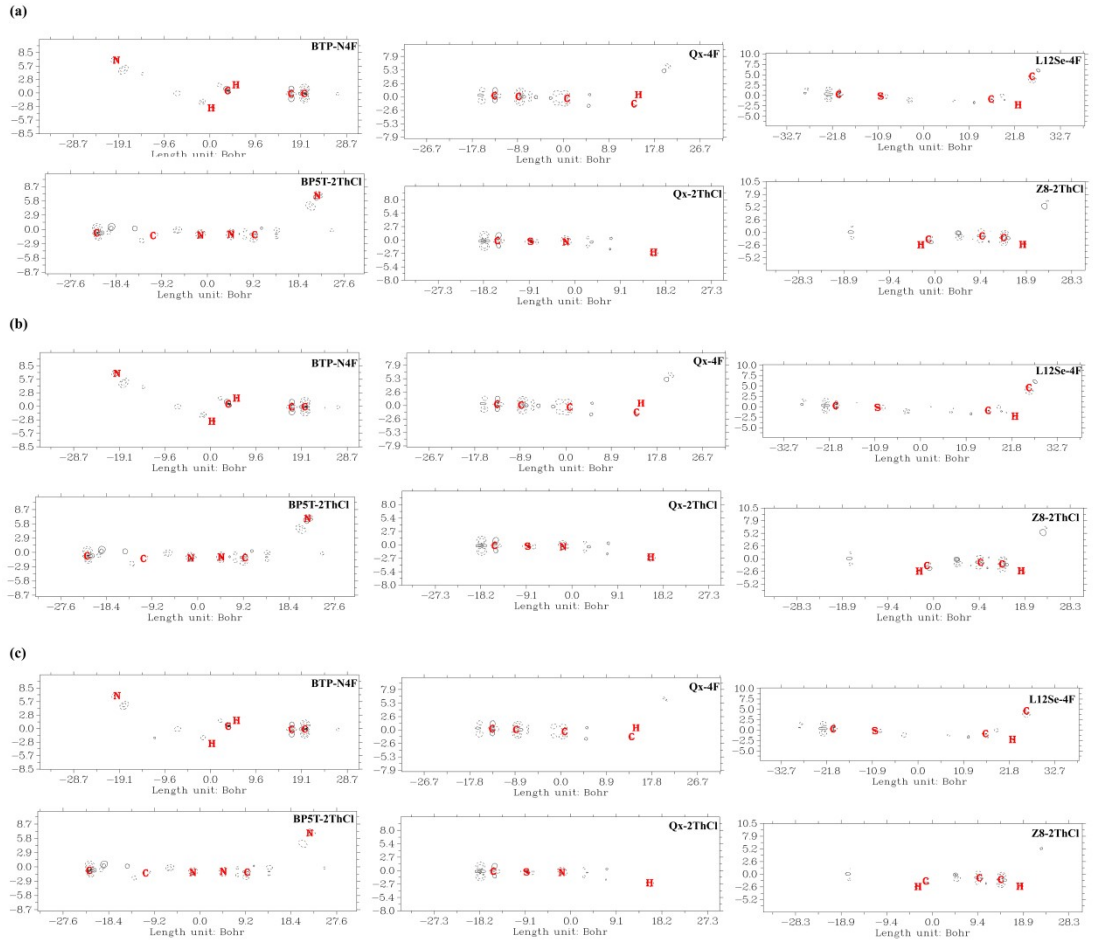
Supplementary Figure 2. Diagram of ESP for BTP-N4F, Qx-4F, L12Se-4F, BP5T-2ThCl, Qx-2ThCl, and Z8-2ThCl



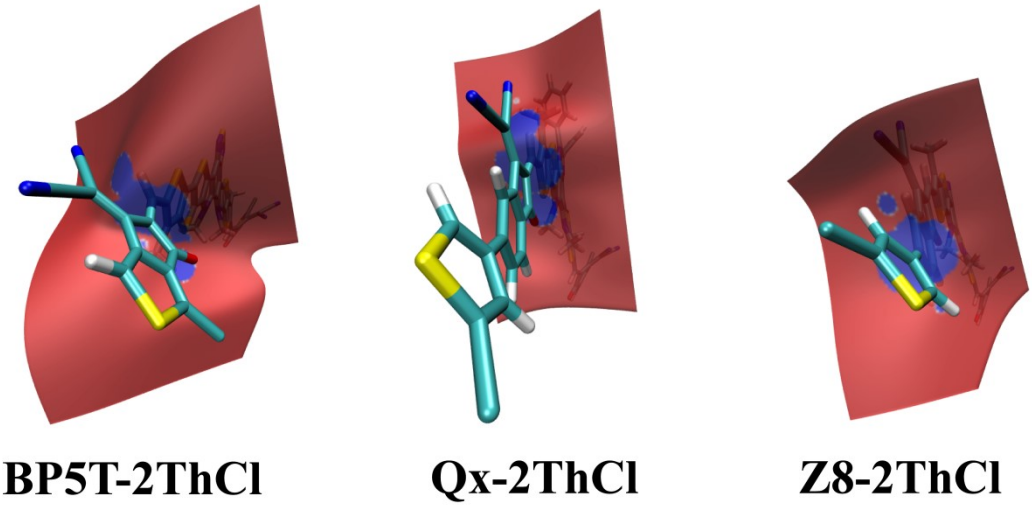
Supplementary Figure 3. Quantitative distribution map of electrostatic potential of BTP-N4F, Qx-4F, L12Se-4F, BP5T-2ThCl, Qx-2ThCl, and Z8-2ThCl[1, 2]



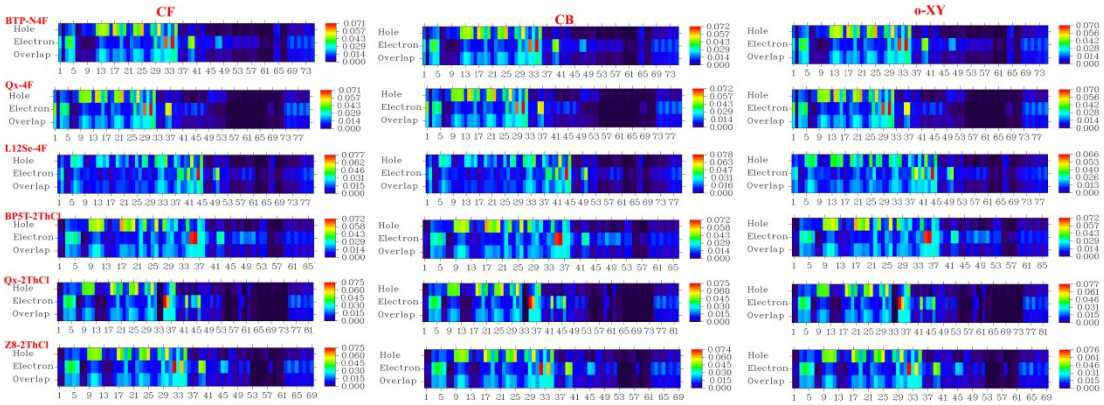
Supplementary Figure 4. DOS diagram in excited states of BTP-N4F, Qx-4F, L12Se-4F, BP5T-2ThCl, Qx-2ThCl, and Z8-2ThCl



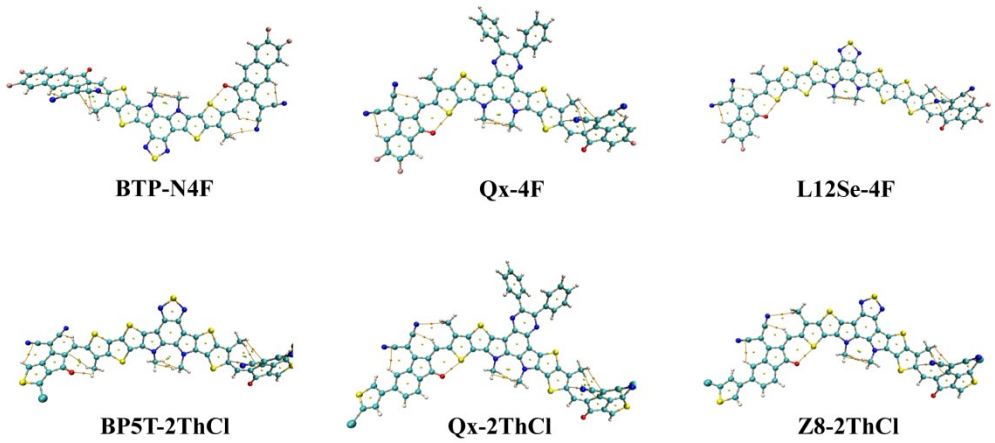
Supplementary Figure 5. Isosurface density difference maps before and after electronic excitation for a) CF, b) CB, and c) o-XY solvent environments



Supplementary Figure 6. Schematic Diagram of Hirshfeld Analysis for the -ThCl Group



Supplementary Figure 7. Diagram for the contribution of non-hydrogen atoms to holes, electrons, and hole-electron overlap



Supplementary Figure 8. Chart of the intramolecular topological analysis

Supplementary Tables

Supplementary Table 1. Calculated values of HOMO, LUMO, and band-gap of BTP-N4F, Qx-4F, L12Se-4F, BP5T-2ThCl, Qx-2ThCl, and Z8-2ThCl

Molecules	HOMO (eV)	LUMO (eV)	Eg (eV)
BTP-N4F	-5.75	-3.76	1.99
Qx-4F	-5.71	-3.68	2.03
L12Se-4F	-5.54	-3.66	1.88
BP5T-2ThCl	-5.66	-3.70	1.97
Qx-2ThCl	-5.60	-3.59	2.01
Z8-2ThCl	-5.69	-3.67	2.02

Supplementary Table 2. Calculated values of HOMO/LUMO energy shift and E_b for BTP-N4F, Qx-4F, L12Se-4F, BP5T-2ThCl, Qx-2ThCl, and Z8-2ThCl

Molecule	HOMO shift（eV）			LUMO shift（eV）			E_b (eV)		
	CF	CB	o-XY	CF	CB	o-XY	CF	CB	o-XY
BTP-N4F	-0.82	-0.82	-0.86	1.04	1.04	1.01	0.08	0.07	0.08
Qx-4F	-0.85	-0.90	-0.88	1.03	0.93	1.00	0.08	0.08	0.08
L12Se-4F	-0.79	-0.78	-0.83	1.04	1.04	1.00	0.22	0.21	0.22
BP5T-2ThCl	-0.83	-0.82	-0.86	1.05	1.02	1.02	0.15	0.14	0.14
Qx-2ThCl	-0.91	-0.91	-0.92	0.98	0.98	0.97	0.11	0.10	0.10
Z8-2ThCl	-0.86	-0.85	-0.89	1.04	1.04	1.01	0.10	0.09	0.09

Supplementary Table 3. Calculated parameters of surface analysis for BTP-N4F, Qx-4F, L12Se-4F, BP5T-2ThCl, Qx-2ThCl, and Z8-2ThCl[3]

Molecules	Minimal value (kcal/mol)	Maximal value (kcal/mol)	Balance of charges (nu)	Internal charge separation (Pi) (a.u.)	Molecular polarity index (MPI) (eV)
BTP-N4F	-34.12	40.17	0.25	0.017	0.508
Qx-4F	-34.78	39.02	0.25	0.016	0.478
L12Se-4F	-34.67	41.11	0.25	0.016	0.508
BP5T-2ThCl	-36.01	40.22	0.25	0.017	0.526
Qx-2ThCl	-36.66	37.21	025	0.016	0.441
Z8-2ThCl	-35.73	39.27	0.25	0.017	0.487

Supplementary Table 4. Calculated D index, Sr index, HCT index, t index, HDI, and EDI of BTP-N4F, Qx-4F, L12Se-4F, BP5T-2ThCl, Qx-2ThCl, and Z8-2ThCl in CB solvent

Molecules	D (Å)	S_r	H_{CT} (Å)	t (Å)	HDI	EDI
BTP-N4F	1.37	0.59	2.02	-0.65	4.33	3.93
Qx-4F	1.16	0.59	2.14	-0.97	4.32	4.14

L12Se-4F	1.68	0.63	7.38	-5.70	3.86	3.77
BP5T-2ThCl	1.21	0.59	4.68	-3.47	4.32	3.78
Qx-2ThCl	1.77	0.58	4.60	-2.82	4.25	4.02
Z8-2ThCl	1.83	0.58	4.93	-3.10	4.30	3.97

Supplementary Table 5. Calculated D index, Sr index, HCT index, t index, HDI, and EDI of BTP-N4F, Qx-4F, L12Se-4F, BP5T-2ThCl, Qx-2ThCl, and Z8-2ThCl in o-XY solvent

Molecules	D (Å)	S_r	H_{CT} (Å)	t (Å)	HDI	EDI
BTP-N4F	1.43	0.60	2.57	-1.14	4.33	3.90
Qx-4F	1.17	0.60	1.96	-0.79	4.33	4.12
L12Se-4F	1.70	0.61	7.63	-5.93	3.72	3.50
BP5T-2ThCl	1.22	0.60	4.78	-3.56	4.32	3.76
Qx-2ThCl	1.98	0.58	4.96	-2.98	4.24	3.99
Z8-2ThCl	2.07	0.58	5.29	-3.22	4.29	3.94

Reference

1. T. Lu and S. Manzetti, *Structural Chemistry*, 2014, **25**, 1521-1533.
2. S. Manzetti and T. Lu, *Journal of Physical Organic Chemistry*, 2013, **26**, 473-483.
3. Z. Liu, T. Lu and Q. Chen, *Carbon*, 2021, **171**, 514-523.