Supplementary Information (SI) for CrystEngComm.

Supporting Information

Tetraphenylethylene-based blue light-emitting organic salt crystals

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Section 1 Experimental Materials and Methods

1.1 Materials

The chemicals listed below, 1,1,2,2-tetrakis(4-(pyridin-3-yl)phenyl)ethene (T3PPE, 97%), [1,1'-biphenyl]-4,4'-disulfonic acid (BPDS, 98.0%), naphthalene-1,5-disulfonic acid (1,5-NDS, 98.0%), 4,4',4'',4'''-methanetetrayltetrabenzenesulfonic acid (TPMS, 95%), 4,4',4'',4'''-(adamantane-1,3,5,7-tetrayl)tetrabenzenesulfonic acid (TPADS, 95%) The purchase links for these compounds are provided in Table S1. These chemicals are utilized following the confirmation of their chemical structures via NMR analysis. The solvents utilized in this study include deionized water, anhydrous methanol, N,N-dimethylformamide (DMF), dimethyl sulfoxide-d6 (DMSO-d_6), all of which were obtained from Aladdin Chemicals.

1.2 Chemical Reagents

Table S1. Website of purchased compounds

Compound	Accessible link
T4PPE (CAS 1227195-24-5)	https://www.leyan.com/1227195-24-5.html?bd_vid=8292957862413068324
BPDS (CAS 5314-37-4)	https://www.chem960.com//offer/25845042/ or https://www.fishersci.com/shop/products/4-4-biphenyldisulfonic-acid-98-0-tci-america/B16645G
1,5-NDS (CAS 211366-30-2)	https://www.labgogo.com/product/productnew_61328.html or https://www.sigmaaldrich.com/HK/zh/product/aldrich/276375
TPMS CAS 1042222-34-3)	http://www.chemextension.com/en/product-YSZC042
TPADS (CAS 1607013-23-2)	http://www.chemextension.com/en/product-YSZC1488

All of chemicals were used as purchased without further purification. These compounds are directly used after their structures have been confirmed by NMR(Figure S1 and Figure S3-6).

1.3 Methods

1.3.1 Theoretical Calculation of ESPMs and Fukui Function

Density functional theory (DFT) calculations were conducted using the CASTEP code.[1] The generalized gradient approximation (GGA) method with the Fukui, Becke, Lee, Yang and Parr (BLYP) function was employed to describe the electronic structure and properties of the studied systems.[2-8] The coordinates of all atoms were constrained to the same positions as those in the single crystal structure.

In the context of DFT, among the various local properties, the Fukui function can be used to describe the extent of change in the electron density of individual atoms when the total electron count of the system changes, according to eqn (1) and (2):

$$f^{+}(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^{+} = \rho_{N+1}(r) - \rho_{N}(r) \quad (1)$$

$$f^{-}(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^{-} = \rho_{N}(r) - \rho_{N-1}(r) \quad (2)$$

Where $\rho_N(r)$, $\rho_{N+1}(r)$, $\rho_{N-1}(r)$ are the electron densities of the neutral species (N electrons), its anion ($N+1$ electrons), and its cation ($N-1$ electrons), respectively. f^{+} describes the change in electron density when the molecule gains an electron, identifying stronger electrophilic reactivity. f^{-} describes the change in electron density when the molecule loses an electron, identifying stronger nucleophilic reactivity.

Notes and References

1. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson and M. C. Payne, *Z*, *Kristallogr*, 2005, **220**, 567–572.
2. N. F. Frazão, E. L. Albuquerque, U. L. Fulco, P. W. Mauriz and and D. L. Azevedo, *J Nanosci Nanotechnol*, 2016, **16**, 4825-4834.
3. A. D. Becke, *J. Chem. Phys*, 1988, **88**, 2547-2553.
4. A. D. Corso, A. Pasquarello, A. Baldereschi, and R. Car, *Phys. Rev. B*, 1996, **53**, 1180-1185.
5. A. D. Becke, *J. Chem. Phys*, 1988, **88**, 2547-2553.
6. R. G. Parr and W. Yang, *J. Am. Chem. Soc*, 1984, **106**, 4049-4050.
7. K. Fukui, Science, 1982, **218**, 747-754.
8. W. Yang and W. J. Mortier, *J. Am. Chem. Soc*, 1986, **108**, 5708-5711.

Section 2 NMR Spectra of Compounds

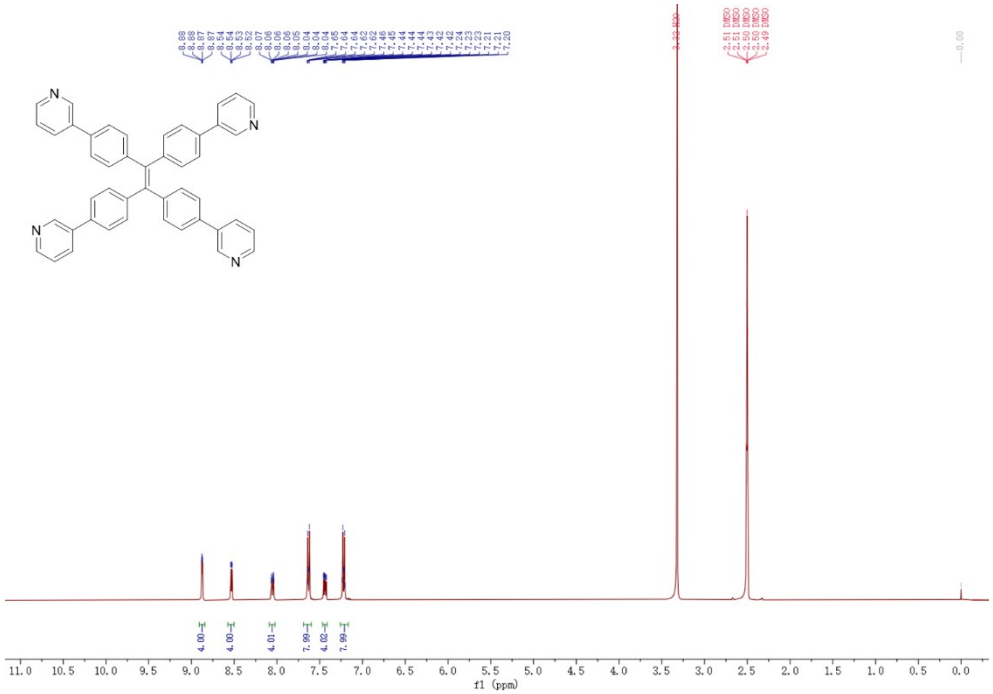

Figure S1. ^{1}H NMR (400 MHz) spectrum of T3PPE in DMSO-d_6.

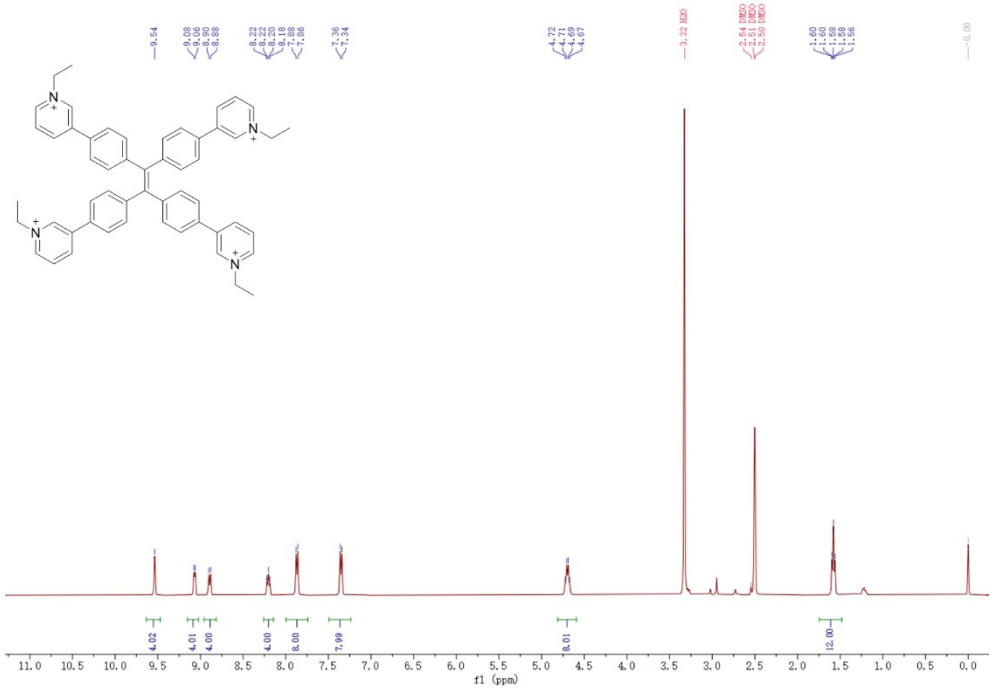

Figure S2. ^{1}H NMR (400 MHz) spectrum of T3Py-TPEBr$_4$ in DMSO-d_6.

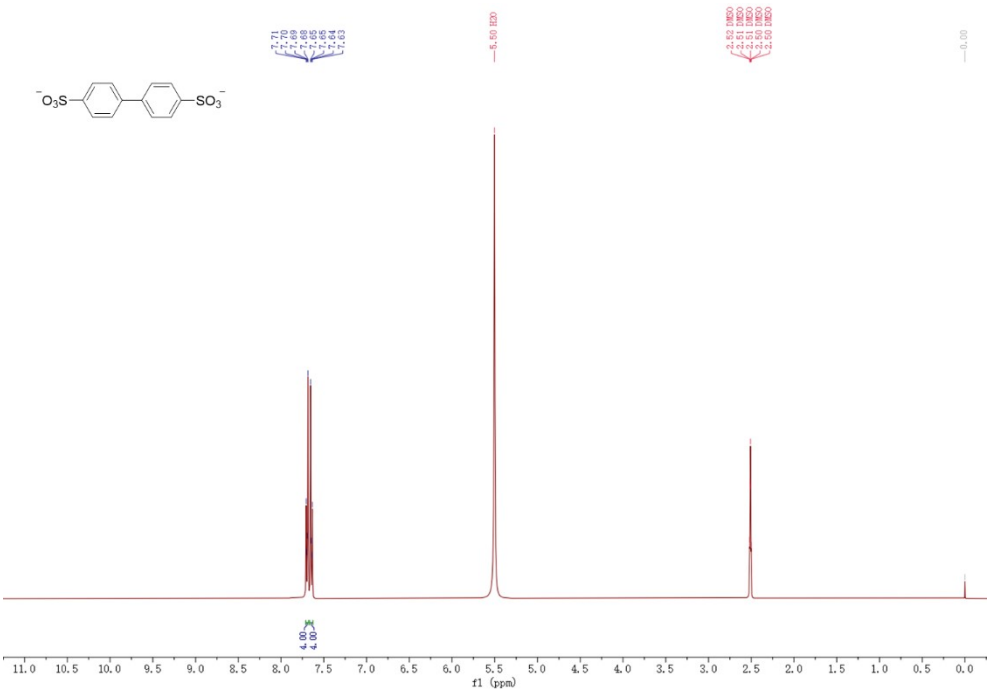

Figure S3. ^{1}H NMR (400 MHz) spectrum of BPDS in DMSO-d_6.

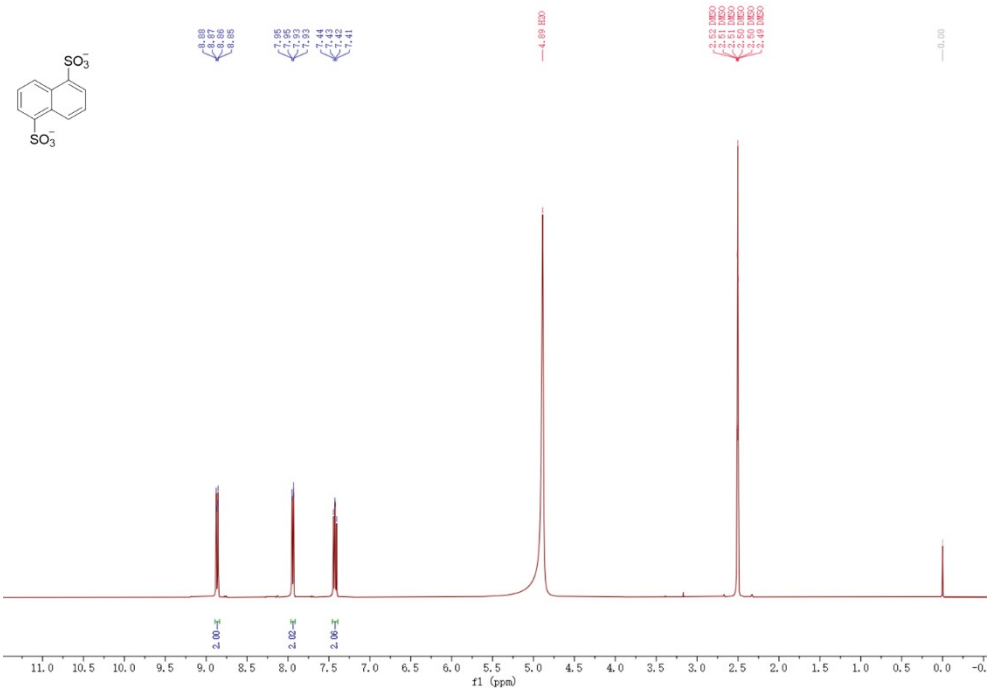

Figure S4. ^{1}H NMR (400 MHz) spectrum of 1,5-NDS in DMSO-d_6.

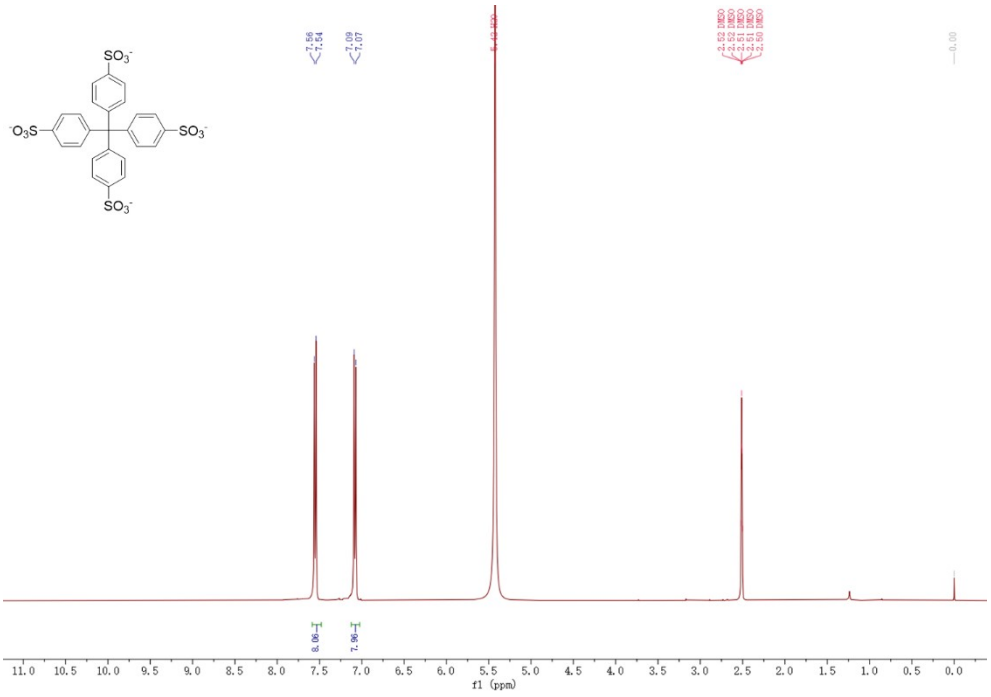

Figure S5. ^{1}H NMR (400 MHz) spectrum of TPMS in DMSO-d_6.

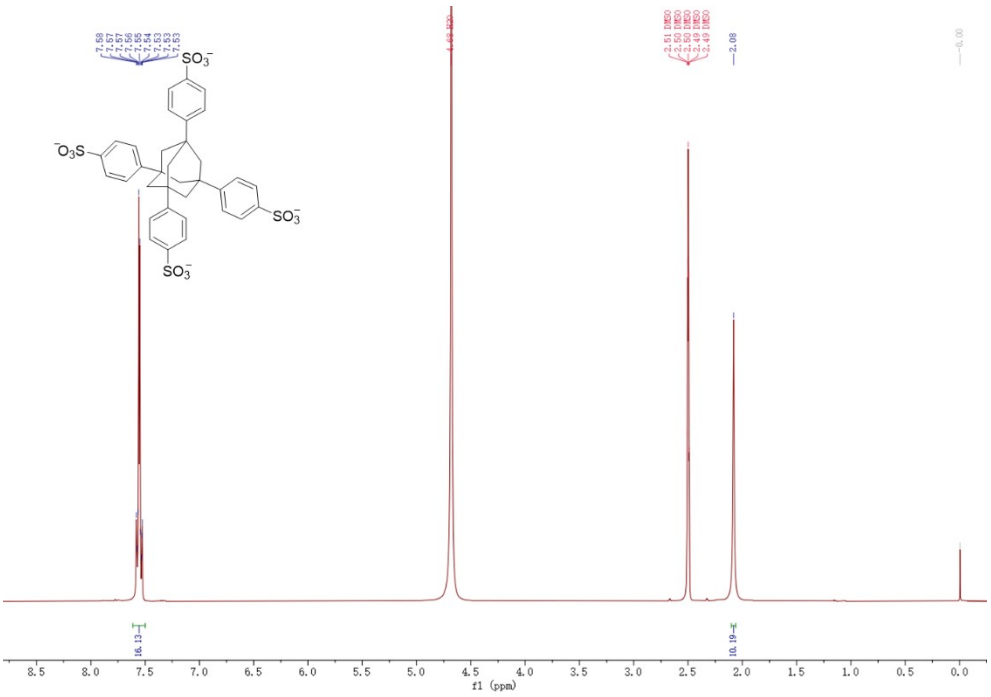

Figure S6. ^{1}H NMR (400 MHz) spectrum of TPADS in DMSO-d_6.

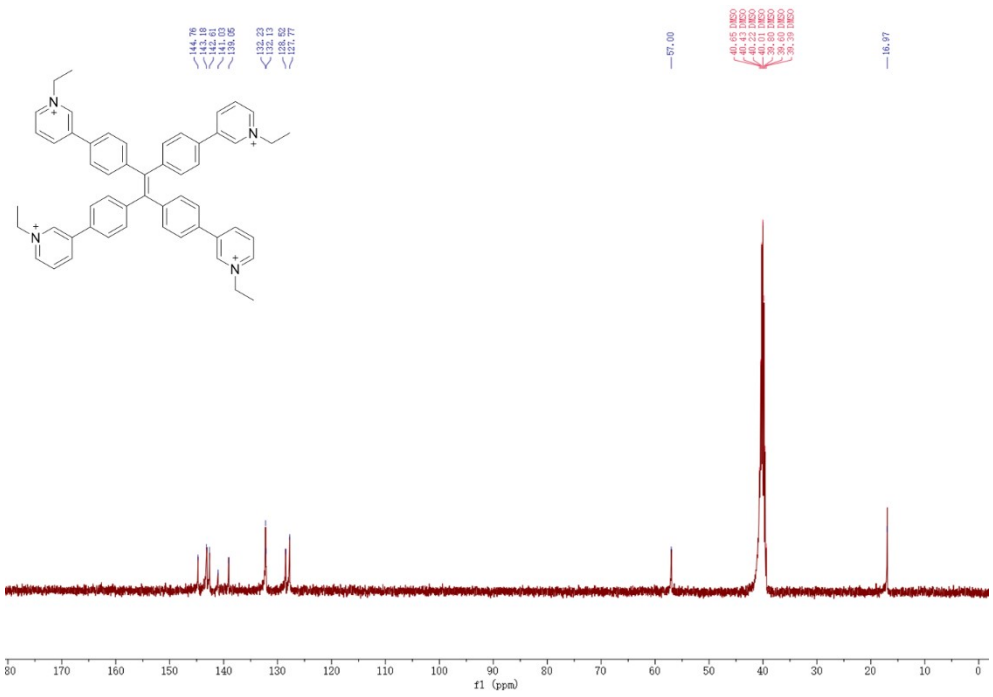

Figure S7. ^{13}C NMR (101 MHz) spectrum of T3Py-TPEBr$_4$ in DMSO-d_6.

Section 3 Optical Microscope Image of Crystals

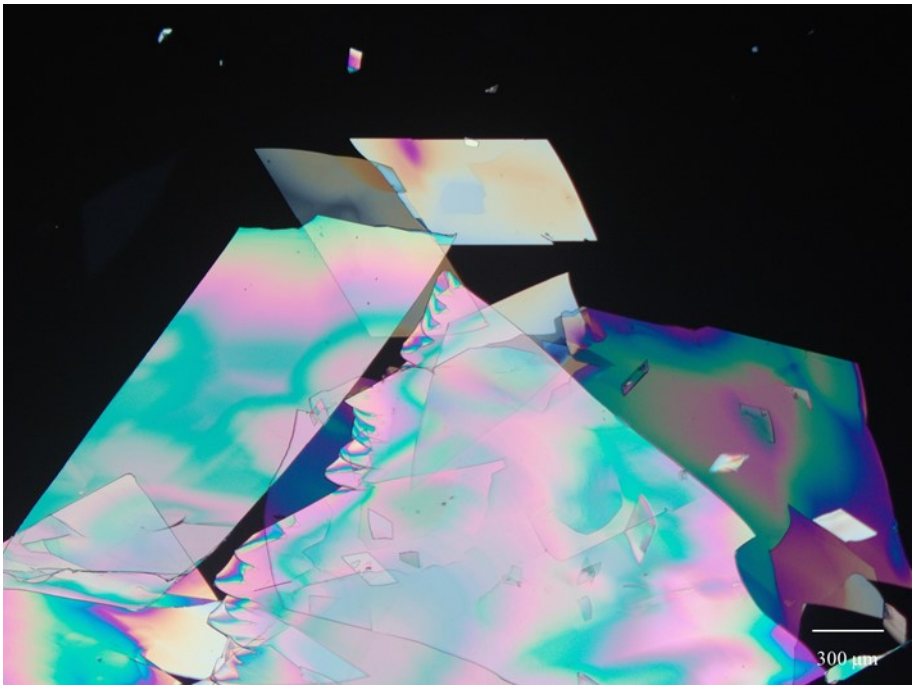

Figure S8. POM image of the T3Py-TPE⋓BPDS$_2$ crystal.

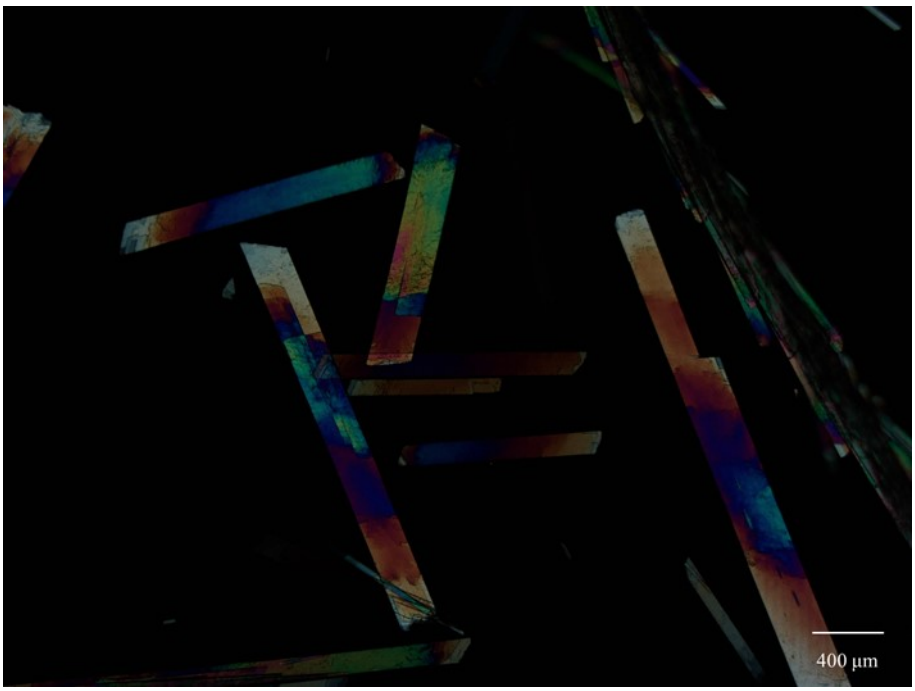

Figure S9. POM image of the T3Py-TPE⋓1,5-NDS_2 crystal.

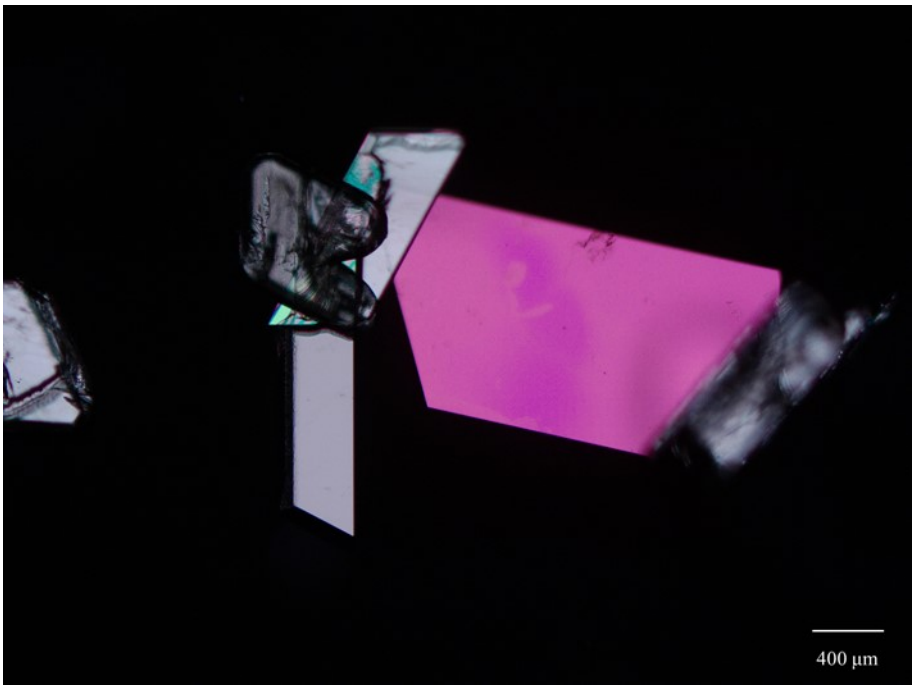

Figure S10. POM image of the T3Py-TPE⋓TPMS crystal.

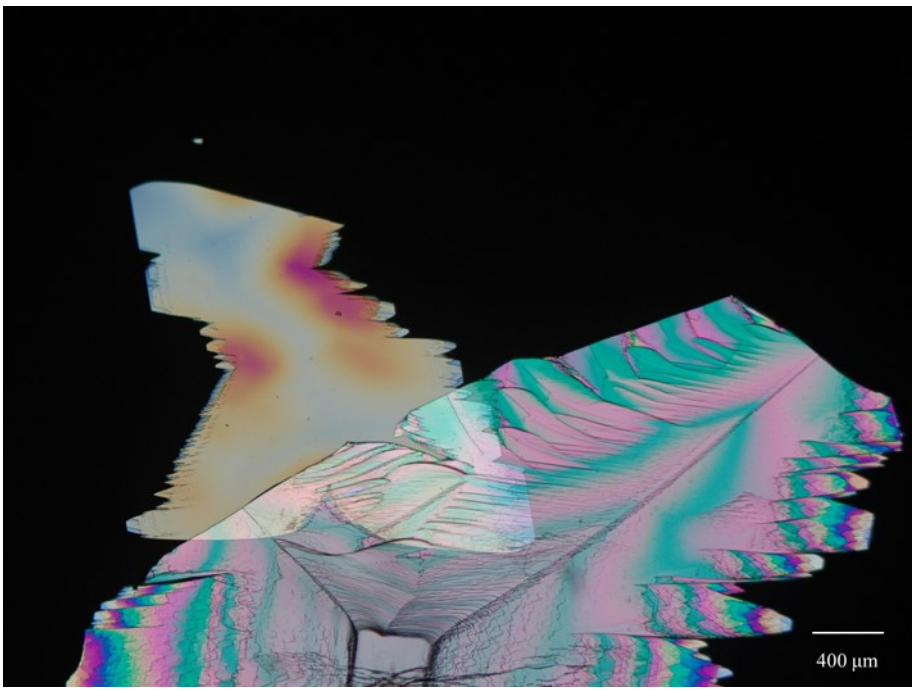

Figure S11. POM image of the T3Py-TPE⋓TPADS crystal.

Section 4 Crystal Structures and Dihedral Angles (α and β)

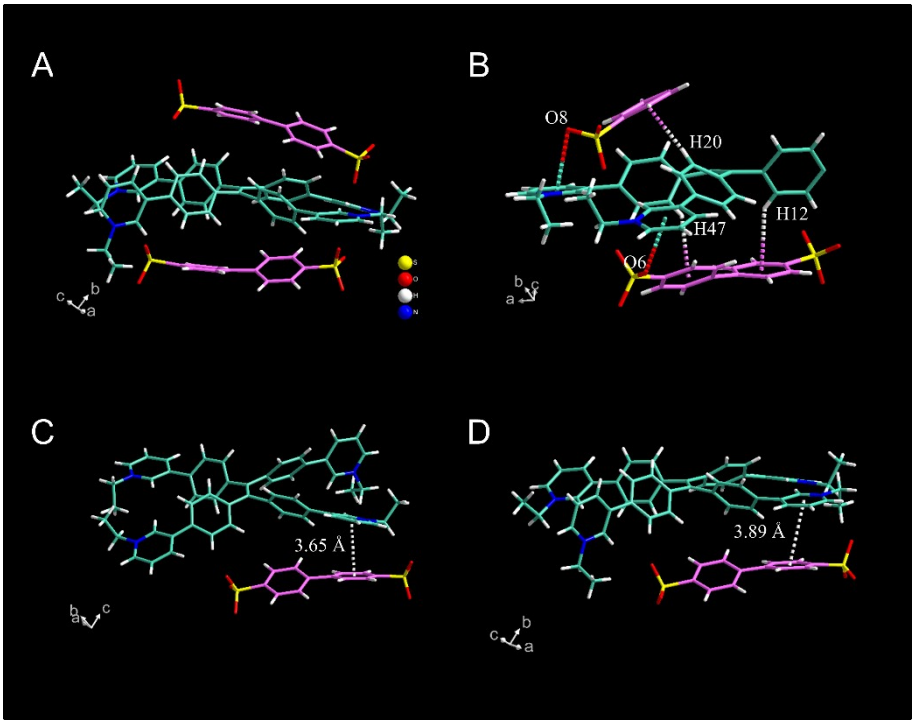

Figure S12. (A) Asymmetric unit of T3Py-TPE⋓$BPDS_2$. (B) C-H…π and S-O…π interaction in the crystal structure. (C-D) π–π stacking interactions in the crystal structure.

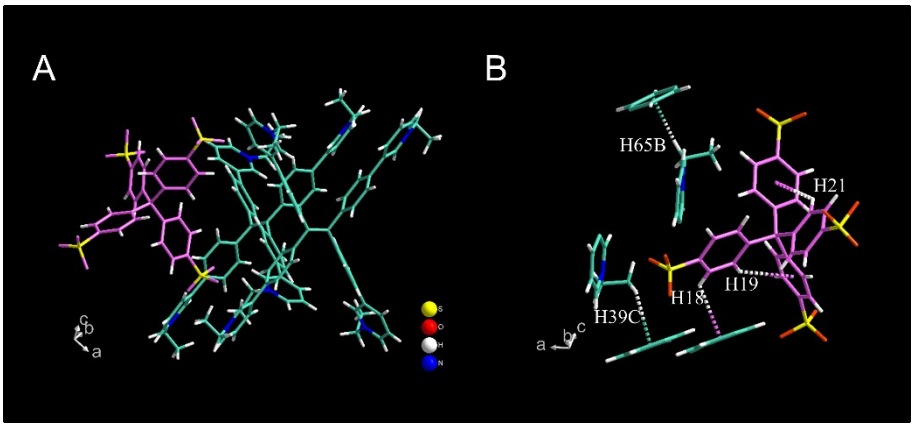

Figure S13. (A) Asymmetric unit of T3Py-TPE⋓TPMS. (B) C-H…π interaction in the crystal structure.

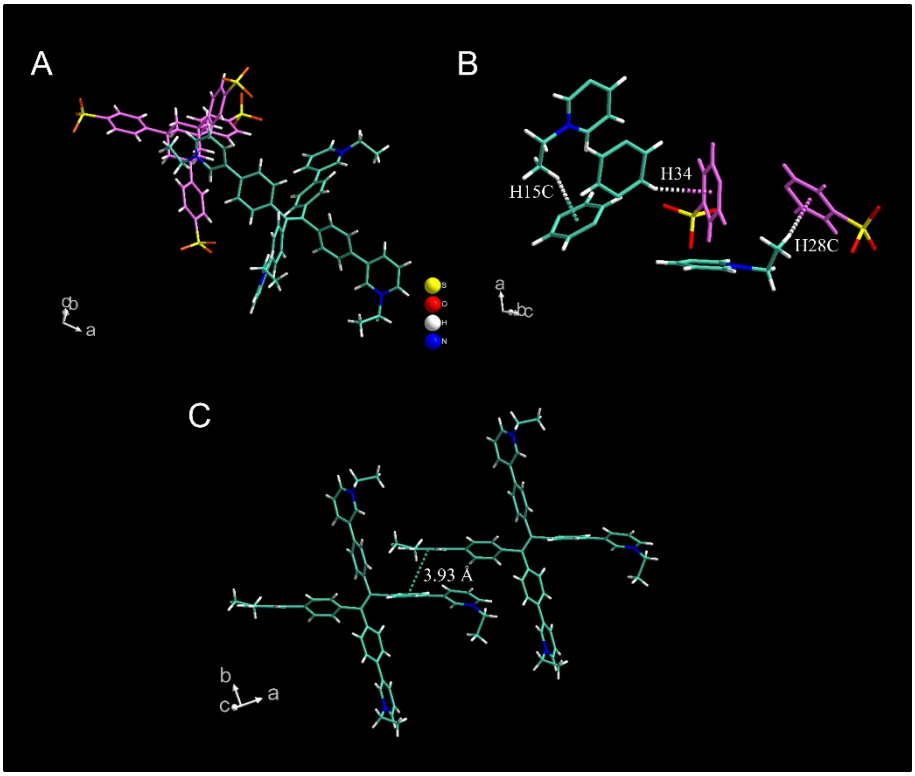

Figure S14. (A) Asymmetric unit of T3Py-TPE₪TPADS. (B) C-H…π interaction in the crystal structure. (C) π–π stacking interactions in the crystal structure.

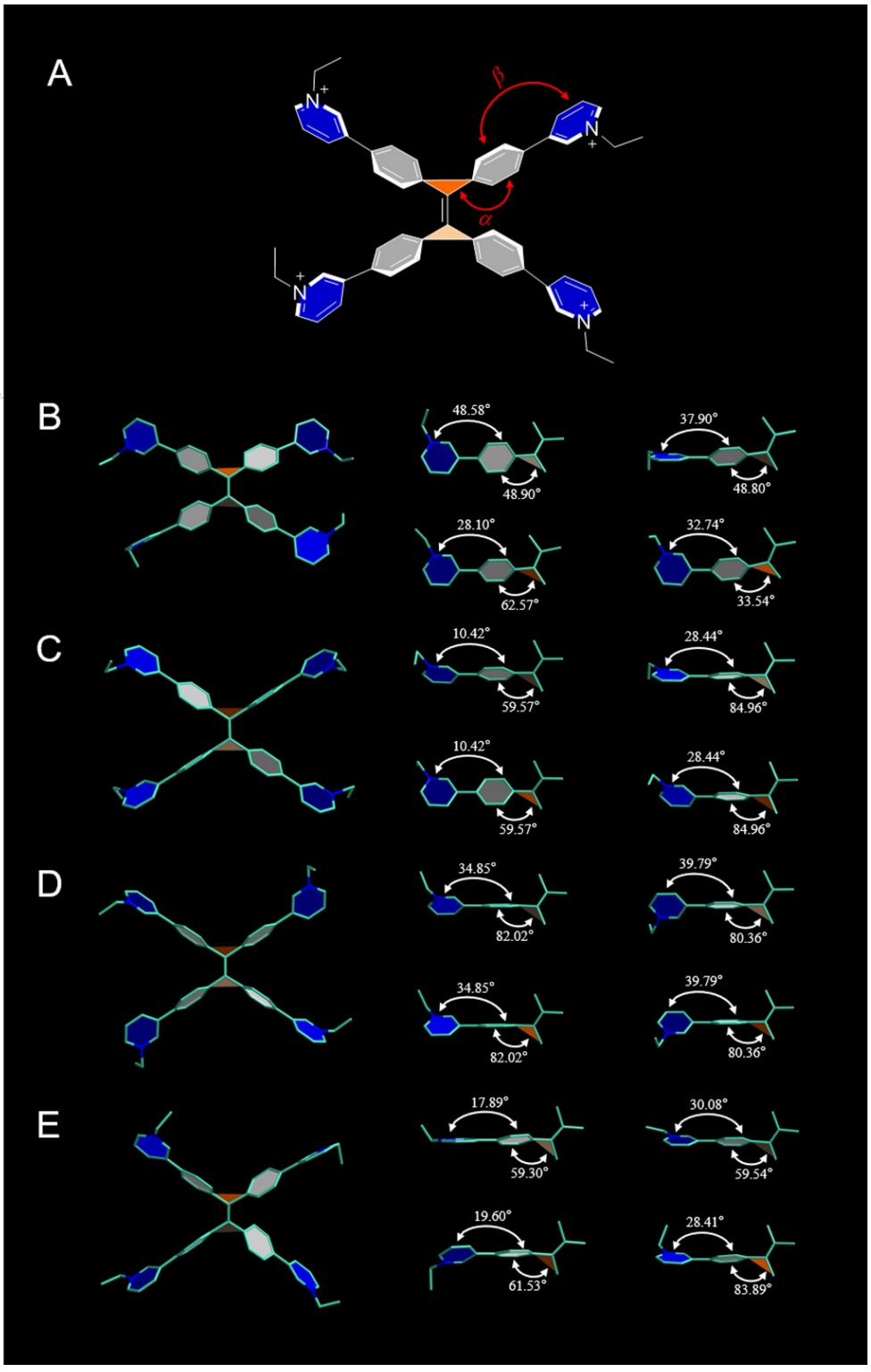

Figure S15. (A) Schematic illustration of dihedral angles α and β of T3Py-TPE^{4+}. Conformations and the dihedral angles of the arms of T3Py-TPE^{4+} in crystals of T3Py-TPE⋓BPDS$_2$ (B), T3Py-TPE⋓1,5-NDS$_2$ (C), T3Py-TPE⋓TPMS (D) and T3Py-TPE⋓TPADS (E).

Table S2. Dihedral angles (α) and emission wavelength (λ_{em})

Name	λ_{em} (nm)	α (°)				
T3Py-TPE⋓BPDS$_2$	470	48.9	48.80	62.57	33.54	48.45±11.86
T3Py-TPE⋓1,5-NDS$_2$	465	59.57	84.96	59.57	84.96	72.27±14.66
T3Py-TPE⋓TPMS	471	82.02	80.36	82.02	80.36	81.19±0.96
T3Py-TPE⋓TPADS	483	59.3	59.54	61.53	83.89	66.07±11.93

Table S3. Dihedral angles (β) and emission wavelength (λ_{em}).

Name	λ_{em} (nm)	β (°)				
T3Py-TPE⋓BPDS$_2$	470	48.58	37.9	28.10	32.74	36.83±8.80
T3Py-TPE⋓1,5-NDS$_2$	465	10.42	28.44	10.42	28.44	19.43±10.40
T3Py-TPE⋓TPMS	471	34.85	39.79	34.85	39.79	37.32±2.85
T3Py-TPE⋓TPADS	483	17.89	30.08	19.6	28.41	23.40±6.14

Section 5 Fukui Function

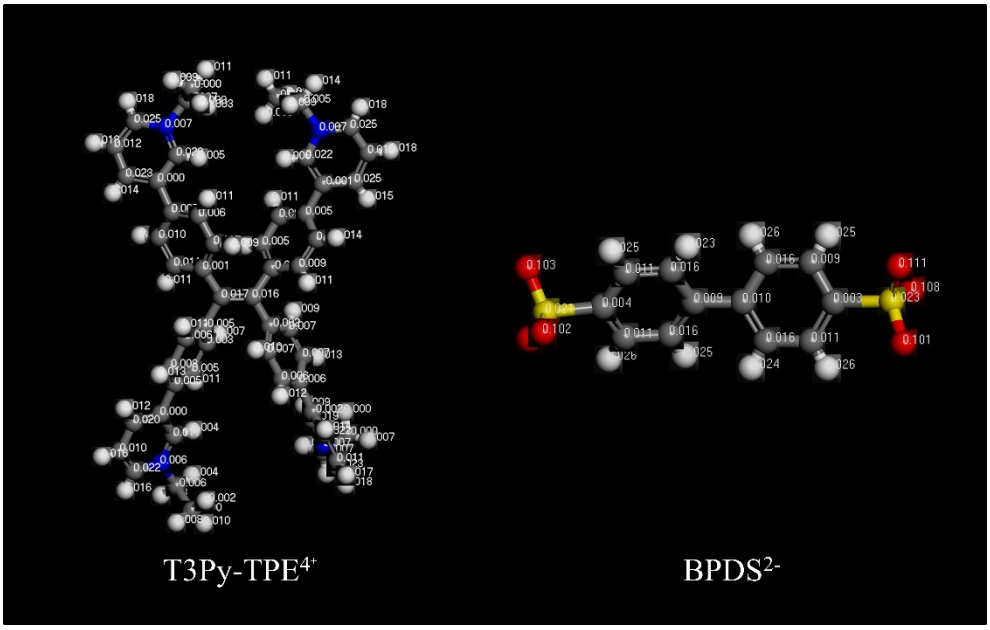

Figure S16. Fukui function of T3Py-TPE^{4+} and BPDS^{2-} in the fine crystals.

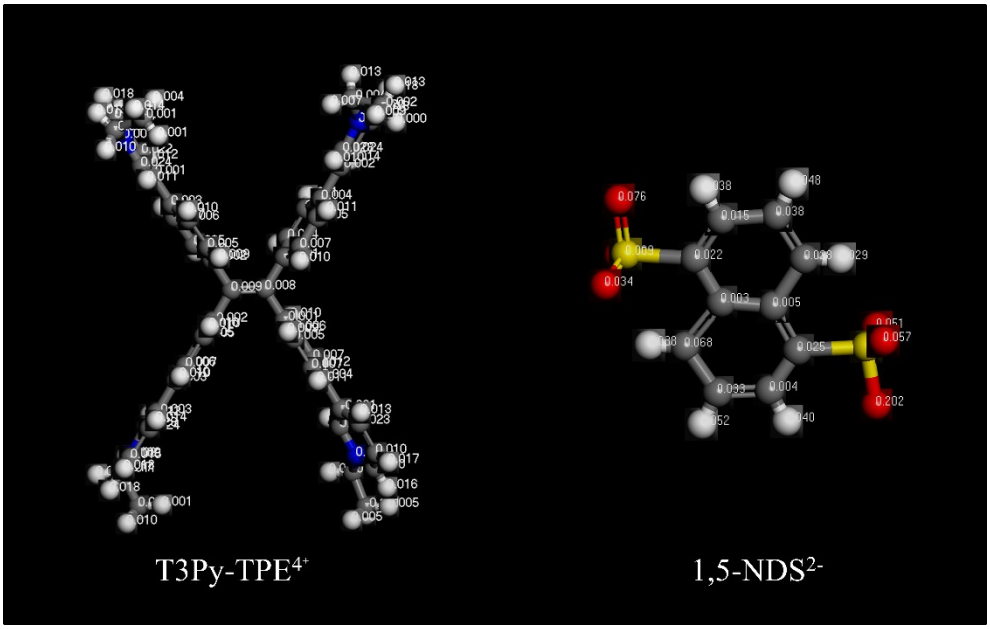

Figure S17. Fukui function of T3Py-TPE^{4+} and 1,5-NDS^{2-} in the fine crystals.

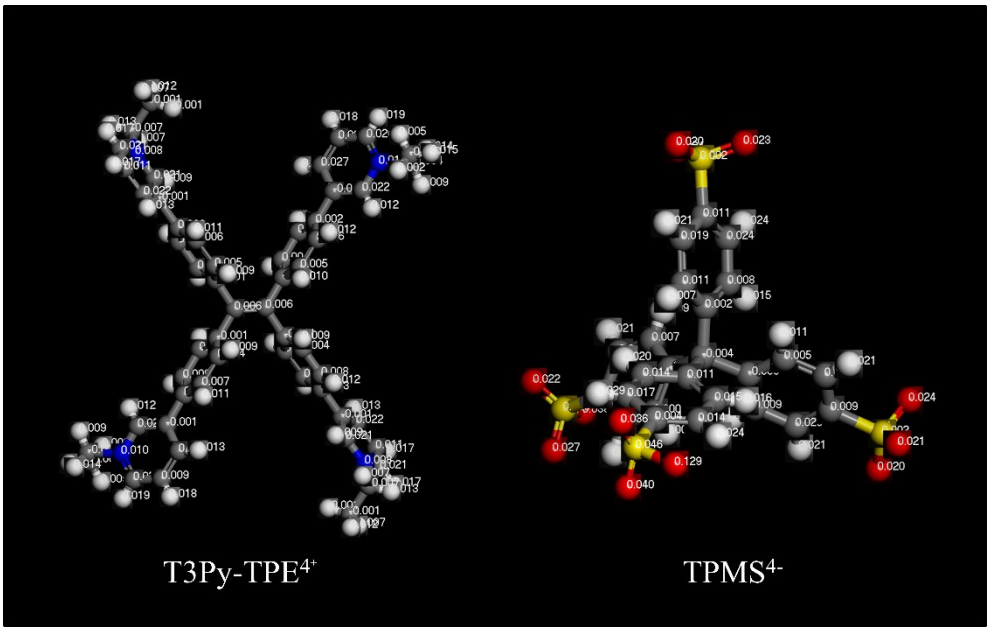

Figure S18. Fukui function of T3Py-TPE^{4+} and TPMS^{4-} in the fine crystals.

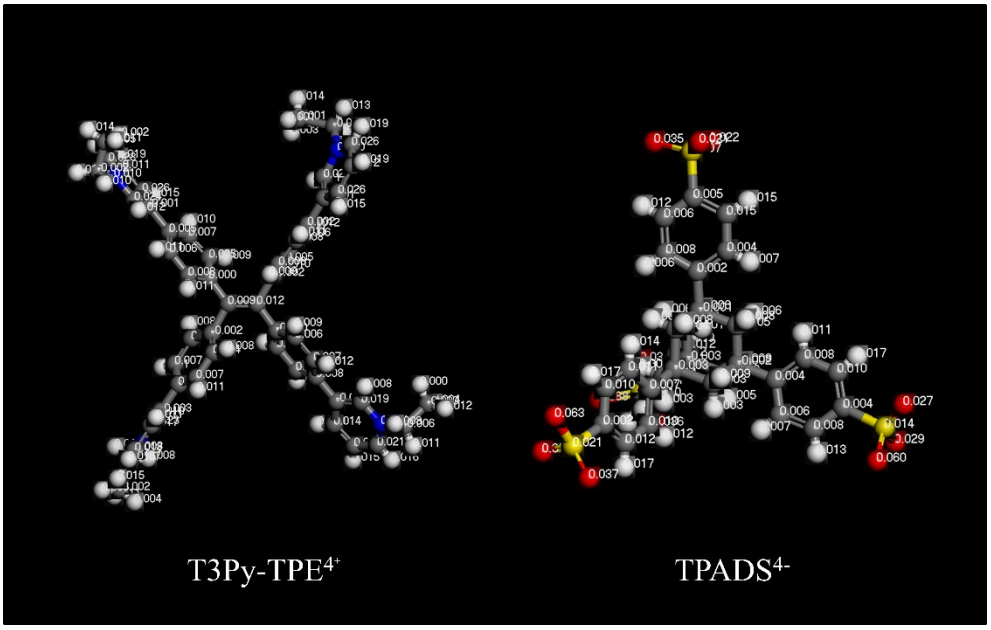

Figure S19. Fukui function of T3Py-TPE^{4+} and TPADS^{4-} in the fine crystals.

Table S4. Fukui function corresponding to cations and anions in the fine crystals

Crystals	Atoms	Cations		Anions	
		f^+	f^-	f^+	f^-
T3Py-TPE⋒$BPDS_2$	C27	0.025	0.023	/	/
	O14	/	/	0.060	0.111
T3Py-TPE⋒1,5-NDS_2	C73	0.028	0.017	/	/
	O2	/	/	0.052	0.076
T3Py-TPE⋒TPMS	C23	0.027	0.014	/	/
	O41	/	/	0.035	0.040
T3Py-TPE⋒TPADS	C61	0.026	0.018	/	/
	O1	/	/	0.069	0.088

Section 6 Absolute Fluorescence Quantum Yields

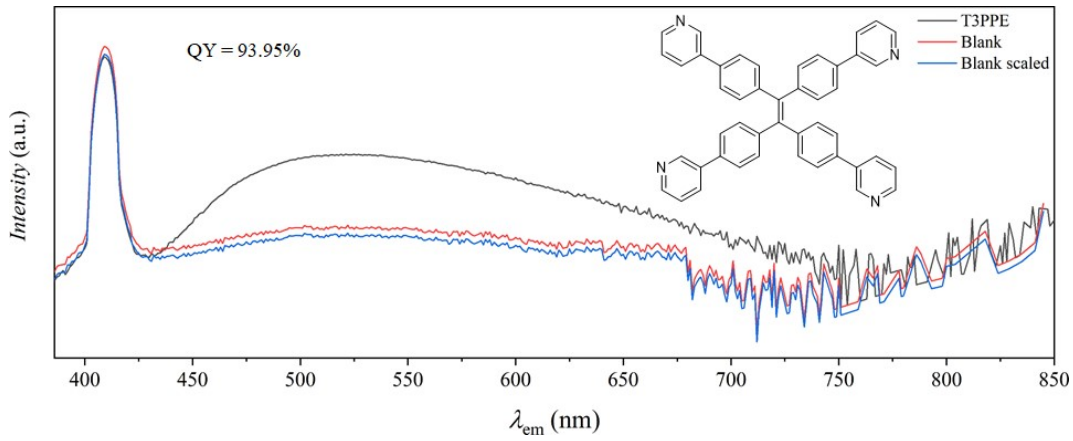

Figure S20. Absolute fluorescence quantum yield of the T3PPE precipitate.

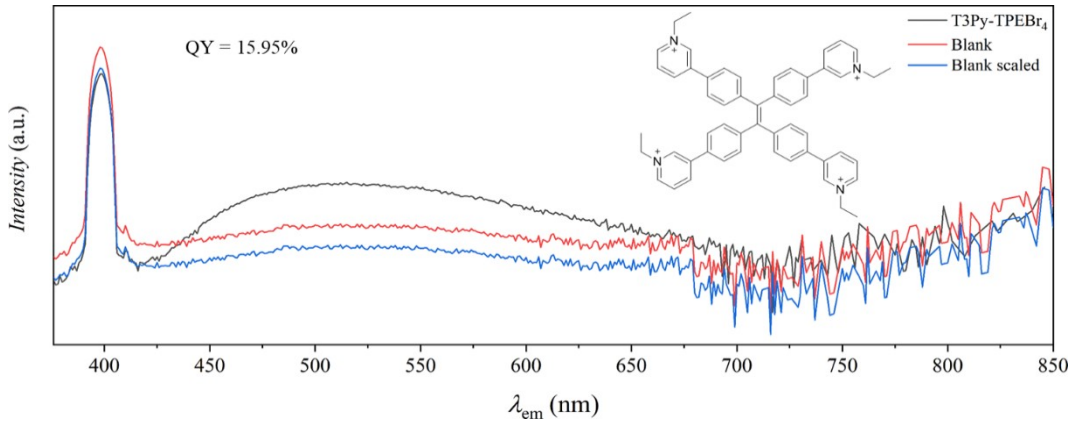

Figure S21. Absolute fluorescence quantum yield of the T3Py-TPEBr_4 precipitate.

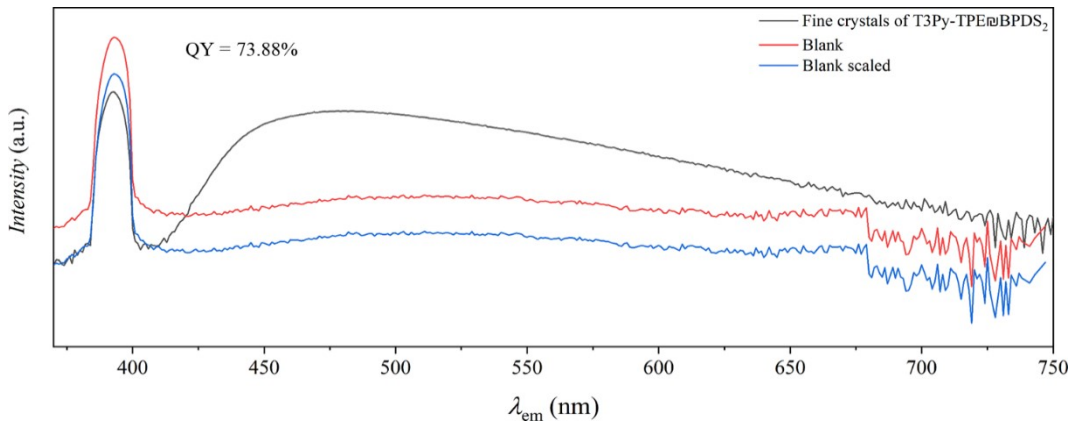

Figure S22. Absolute fluorescence quantum yield of the T3Py-TPE⋓BPDS_2 fine crystal.

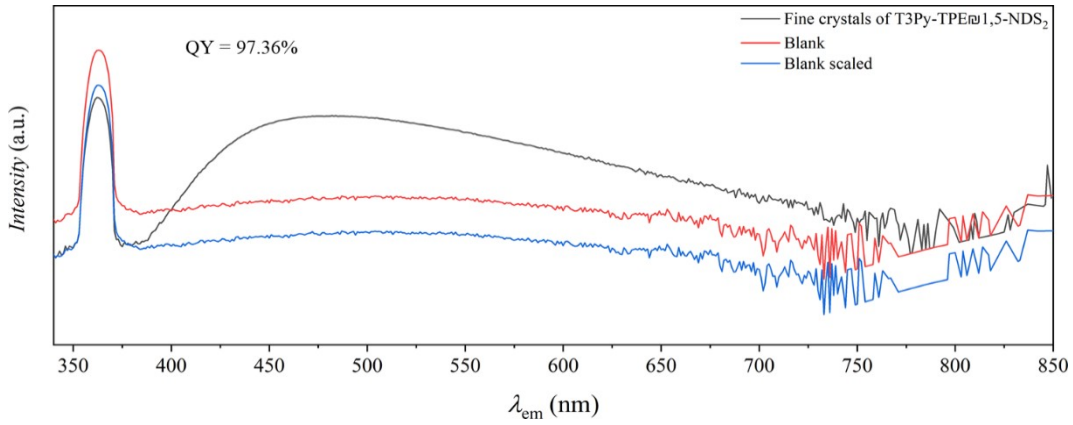

Figure S23. Absolute fluorescence quantum yield of the T3Py-TPE⋓1,5-NDS_2 fine crystal.

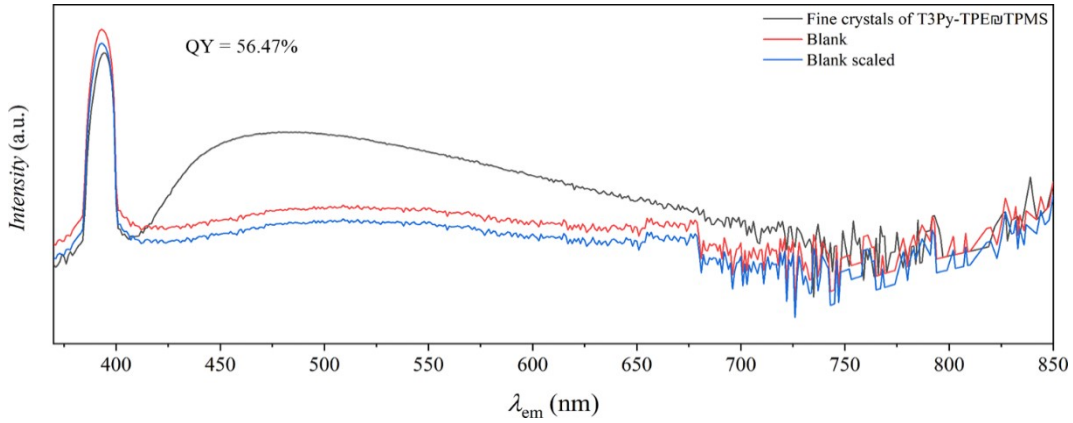

Figure S24. Absolute fluorescence quantum yield of the T3Py-TPE⋓TPMS fine crystal.

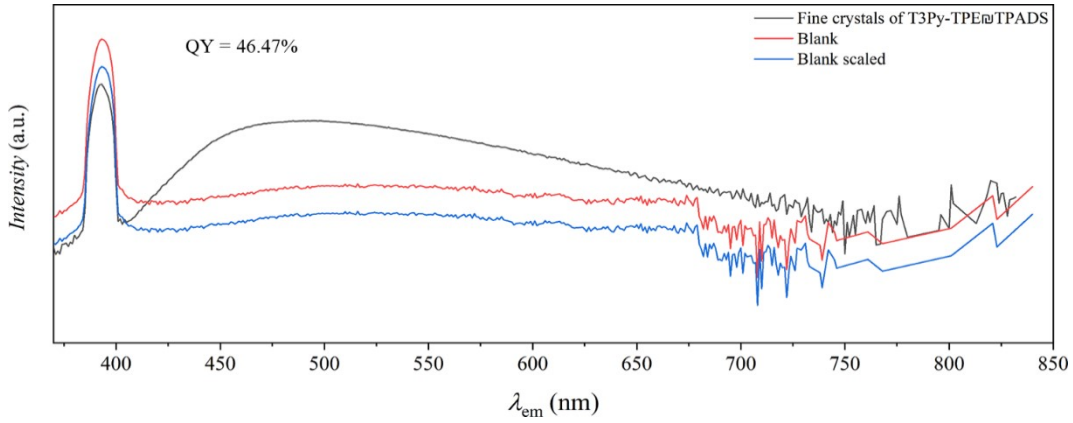

Figure S25. Absolute fluorescence quantum yield of the T3Py-TPE⋓TPADS fine crystal.

Section 7 SEM Image of The Film

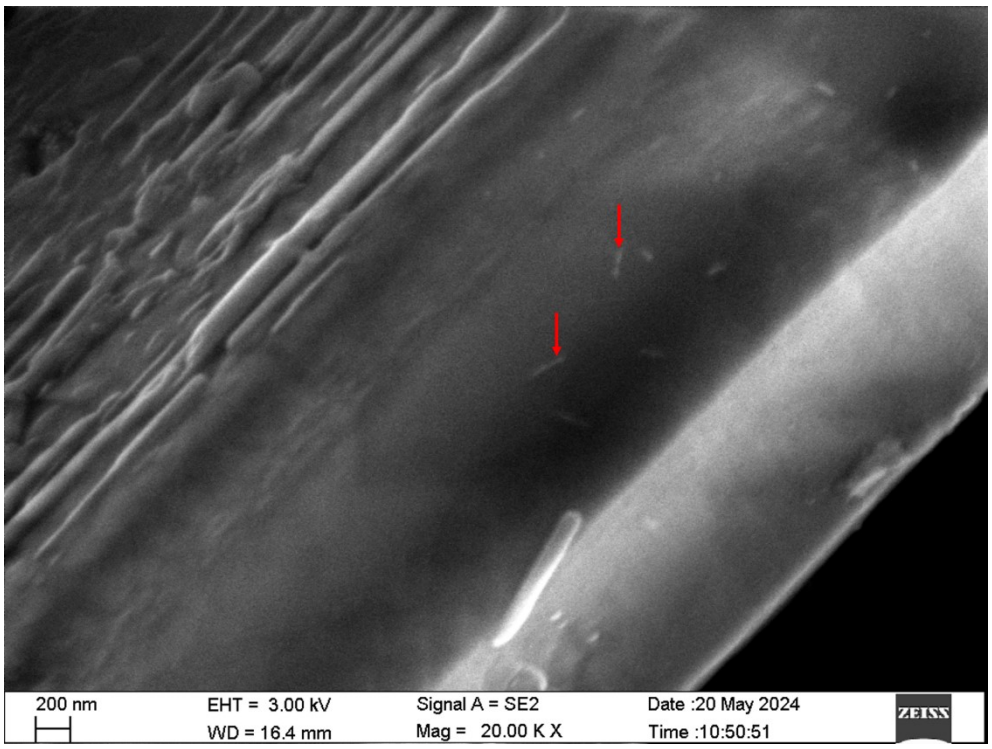

Figure S26. SEM image of the cross section of the film sample of the PVA/T3Py-TPE₪1,5-NDS2. The film was prepared from the aqueous solution of PVA/T3Py-TPE₪1,5-NDS2 with a mass fraction of 0.02%. The SEM sample was prepared by breaking the film in liquid nitrogen. The thin columnar objects pointed by the red arrows are fine crystals of the salts with a size of approximately 30 nm $\times$ 200 nm.