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Electronic Supplementary Information

Theoretical Study on the Optoelectronic Properties of Fluorinated Phenylpyrrole-based Hole Transport Materials for Perovskite Solar Cells

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Computational details

The hole mobility of the investigated molecules was calculated based on the Einstein relation[1]:

$$\mu = \frac{eD}{k_B T}$$

where e, D, k_B, and T represent the elementary charge, the charge diffusion coefficient, Bolztmann's constants, and the temperature in Kelvin, respectively. For isotropic systems, D can be expressed as[2]

$$D = \frac{1}{2d}\sum_i r_i^2 k_i p_i$$

where i represents the hole hopping pathway, r_i is the centroid to centroid distance, d is the spatial dimensionality (usually $d = 3$) and p_i ($p_i = k_i \Big/ \sum_i k_i$) is the hopping probability.

The Marcus theory with the hopping model was employed to describe the hole transport behavior.[3] The charge hopping rate (k) can be evaluated as[3, 4]

$$k = \frac{4\pi^2}{h}|V|^2 \frac{1}{\sqrt{4\pi k_B T \lambda}} exp[-\frac{\lambda}{4k_B T}]$$

where h denotes Planck's constant, λ represents the reorganization energy, and V is the transfer integral.

In this work, only internal reorganization energy was considered. It can be estimated by the adiabatic potential energy surface approach,[5]

$$\lambda = (E_0^* - E_0) + (E_+^* - E_+)$$

where E_+^* and E_0^* represent the total energies of cationic and neutral species with the geometries of the neutral and cationic species, respectively. E_+ and E_0 are the total energies of the cationic and neutral molecules in their lowest energy geometries, respectively.

The transfer integral can be obtained by a direct electronic coupling method,[6]

$$V = < \psi_i^{HOMO} | F | \psi_f^{HOMO} >$$

where ψ_i^{HOMO} and ψ_f^{HOMO} represent the HOMOs of the isolated molecules 1 and 2, and F is the Fock operator.

Table S1. Energies of the studied molecules optimized by B3LYP/6-31G(d,p) in dichloromethane.

Molecule	Absolute Energy (Hartree)	Relative Energy (eV)
T3-pF	-2495.87756	0.000
T3-mF	-2495.87758	-0.001
T3-oF	-2495.87617	0.038
T3-2F-A	-2595.10668	0.000
T3-2F-B	-2595.10216	0.123
T3-2F-C	-2595.10795	-0.035
T3-2F-D	-2595.10298	0.101
T3-2F-E	-2595.10584	0.023
T3-2F-G	-2595.10543	0.034
T3-3F-A	-2694.33474	0.000
T3-3F-B	-2694.32562	0.248

Table S2. The maximum absorption wavelength (λ_{abs}, nm) of T3-pF, and the difference from the experimental value ($\Delta\lambda_{ads}$, nm) under 7 different functionals with different Hartree-Fock (HF) ratios within the 6-31G(d,p) basis set.

Functional	Hartree-Fock ratio (%)	λ_{ads} (nm)	$\Delta\lambda_{ads}$ (nm)
Experimental value		347	0
B3LYP	20	387	40
PBE0	25	372	25
MPW1B95	31	362	15
PBE33	33.3	352	5
PBE38	37.5	344	3
BMK	42	340	7
M06-2X	54	330	17

Table S3. Selected bond length, bond angle and dihedral angle of the studied molecules [a].

Molecule	$R_{\text{C-F}}$ [b]	N1-C6	C6-C7-C8	C7-C8-C9	C8-C9-C10	C9-C10-C11	C10-C11-C6	C11-C6-C7	C5-N1-C6-C11	C2-N1-C6-C7	N1-C5-C12-C14	C4-C5-C12-C13	N1-C2-C15-C17	C3-C2-C15-C16
T3-pF	1.35	1.42	120	119	122	119	120	120	60	60	40	41	40	41
T3-mF	1.35	1.42	120	121	118	123	118	121	58	58	41	42	40	41
T3-oF	1.35	1.42	120	120	120	119	122	119	62	61	41	41	41	41
T3-2F-A	1.35	1.42	121	118	123	117	122	118	62	61	41	41	41	41
T3-2F-B	1.35	1.42	120	119	120	121	119	121	58	58	41	42	41	41
T3-2F-C	1.35	1.42	118	123	117	123	118	121	57	57	41	43	41	43
T3-2F-D	1.35	1.42	120	121	119	121	120	119	60	57	48	52	40	41
T3-2F-E	1.35	1.42	119	122	119	119	122	119	61	59	41	41	41	42
T3-2F-G	1.35	1.41	122	119	121	119	122	117	63	63	42	41	42	41
T3-3F-A	1.34	1.41	123	117	123	117	123	117	63	63	43	42	43	42
T3-3F-B	1.34	1.42	119	121	119	121	119	121	57	57	42	43	42	43

[a] Distances are in Å and angles in degrees; [b] $R_{\text{C-F}}$ is the average C-F bond length.

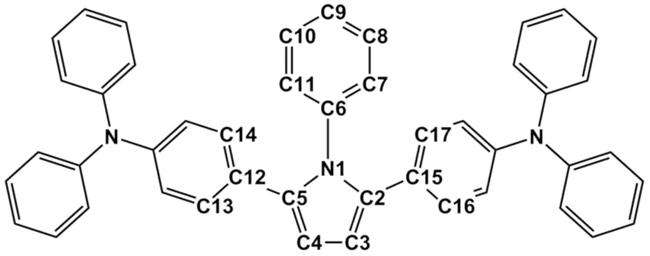


Table S4. The Max negative molecular electrostatic potentials (ESP), the Max positive ESP, the difference between positive and negative ESP of the investigated molecules, and the ESP average value of the studied molecules, units are expressed in kcal/mol.

Molecule	Max negative ESP (kcal/mol)	Max positive ESP (kcal/mol)	ESP difference (kcal/mol)	ESP average (kcal/mol)
T3-pF	-26.41	21.54	47.95	-1.63
T3-mF	-26.64	23.49	50.13	-1.78
T3-oF	-31.57	23.75	55.32	-2.08
T3-2F-A	-29.47	23.44	52.91	-1.66
T3-2F-B	-26.24	24.27	50.51	-1.39
T3-2F-C	-26.10	23.27	49.37	-1.50
T3-2F-D	-27.85	28.69	56.54	-1.40
T3-2F-E	-29.11	25.69	54.80	-1.78
T3-2F-G	-30.58	27.40	57.98	-2.08
T3-3F-A	-28.54	25.47	54.01	-1.65
T3-3F-B	-25.71	20.80	46.51	-1.14

Table S5. Specific data for crystal structure analysis, including Space group, Z, Cell volume (cm^3), Density (g/cm^3), Total energy (eV), Van der Waals energy (eV), Electrostatic energy (eV), Length a (Å), b (Å), c (Å), and Angle α, β, γ (°).

Molecule	Space group	Cell volume	Density	Total energy	Van der Waals energy	Length a	Length b	Length c	α	β	γ
T3-pF	P-1	2.19×10^3	1.17	159.77	41.02	14.30	11.34	13.87	101	86	84
T3-mF	P-1	2.17×10^3	1.18	128.79	39.94	15.12	10.10	18.38	70	58	69
T3-oF	P-1	2.13×10^3	1.20	168.31	33.76	9.33	20.08	16.18	90	119	121
T3-2F-A	P-1	2.19×10^3	1.19	115.08	41.14	11.35	17.22	13.94	79	101	124
T3-2F-B	P-1	2.22×10^3	1.18	196.02	41.62	13.42	11.37	19.53	49	88	81
T3-2F-C	P-1	2.21×10^3	1.18	100.13	41.78	16.69	15.35	10.12	68	93	70
T3-2F-D	P-1	2.09×10^3	1.25	180.34	35.84	13.22	14.04	12.34	85	113	89
T3-2F-E	P-1	2.21×10^3	1.18	174.08	39.53	14.70	11.30	16.46	74	69	108
T3-2F-G	P-1	2.23×10^3	1.17	127.96	38.58	14.64	16.45	11.37	105	106	111
T3-3F-A	P-1	2.19×10^3	1.22	-17.18	35.85	21.57	10.00	14.90	80	58	54
T3-3F-B	P-1	2.21×10^3	1.21	192.76	40.81	19.91	10.09	15.35	112	96	123

Table S6. The reorganization energy λ (eV), centroid to centroid distance (d, Å), hole transfer integral V (eV), hole hopping rate k_i (s^{-1}), and hole mobility (μ, $cm^2V^{-1}s^{-1}$) based on the predicted crystalline structures of the studied molecules.

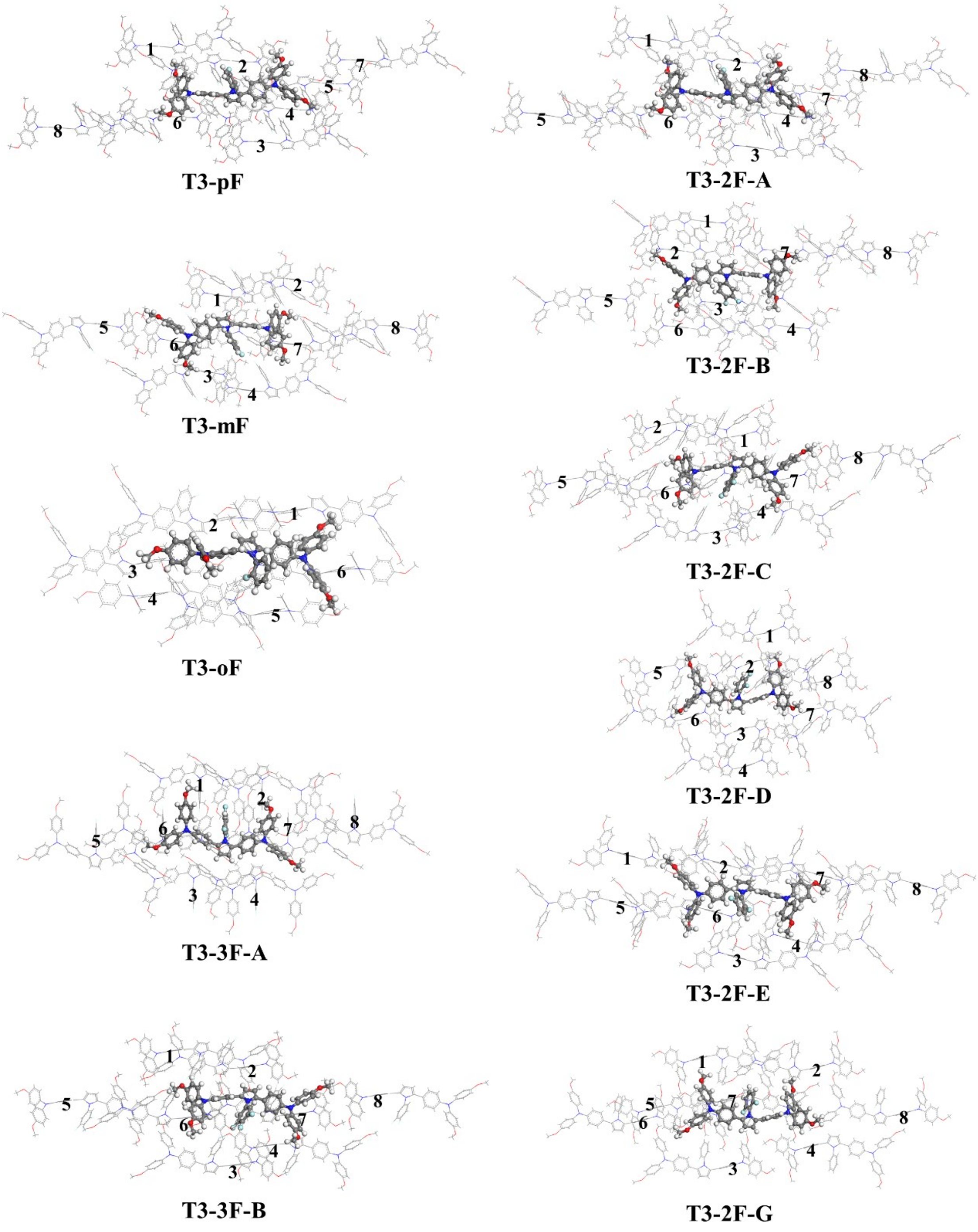
Molecules	λ (eV)	Path	r_i (Å)	V (eV)	k_{ij} (s^{-1})	μ ($cm^2V^{-1}s^{-1}$)
T3-pF	0.296	1	11.342	-7.23×10^{-3}	9.19×10^{10}	1.30×10^{-2}
		2	5.831	-4.81×10^{-3}	4.08×10^{10}	
		3	11.342	-7.23×10^{-3}	9.19×10^{10}	
		4	9.711	-1.05×10^{-2}	1.94×10^{11}	
		5	12.565	1.71×10^{-3}	5.14×10^{9}	
		6	13.218	1.05×10^{-2}	1.96×10^{11}	
		7	24.074	-2.65×10^{-4}	1.23×10^{8}	
		8	24.074	-2.65×10^{-4}	1.23×10^{8}	
T3-mF	0.295	1	9.805	-1.66×10^{-2}	4.92×10^{11}	2.93×10^{-2}
		2	10.100	-2.07×10^{-3}	7.59×10^{9}	
		3	10.100	-2.06×10^{-3}	7.59×10^{9}	
		4	10.888	-1.28×10^{-3}	2.93×10^{9}	
		5	23.814	2.80×10^{-4}	1.40×10^{8}	
		6	6.694	8.60×10^{-4}	1.32×10^{9}	
		7	13.660	3.70×10^{-4}	2.43×10^{8}	
		8	23.814	2.80×10^{-4}	1.40×10^{8}	
T3-oF	0.325	1	9.326	-2.39×10^{-3}	7.27×10^{9}	1.37×10^{-3}
		2	9.270	-5.34×10^{-3}	3.61×10^{10}	
		3	15.228	-2.40×10^{-3}	7.28×10^{9}	
		4	9.326	-2.39×10^{-3}	7.25×10^{9}	
		5	7.364	-1.66×10^{-3}	3.51×10^{9}	
		6	7.375	1.18×10^{-3}	1.76×10^{9}	
T3-2F-A	0.283	1	11.346	-6.88×10^{-3}	9.64×10^{10}	1.61×10^{-2}
		2	5.895	-4.37×10^{-3}	3.89×10^{10}	
		3	11.346	-6.87×10^{-3}	9.64×10^{10}	
		4	9.731	-1.02×10^{-2}	2.12×10^{11}	

Molecules	λ (eV)	Path	r_i (Å)	V (eV)	k_ij (s^{-1})	μ (cm^{2}V^{-1}s^{-1})
		5	24.153	-2.62×10^{-4}	1.40×10^{8}	
		6	13.304	1.10×10^{-2}	2.45×10^{11}	
		7	12.466	1.97×10^{-3}	7.88×10^{9}	
		8	24.153	-2.62×10^{-4}	1.40×10^{8}	
T3-2F-B	0.293	1	11.367	-4.74×10^{-3}	4.10×10^{10}	4.92×10^{-3}
		2	9.923	-7.78×10^{-3}	1.10×10^{11}	
		3	5.519	-1.02×10^{-2}	1.88×10^{11}	
		4	11.367	-4.74×10^{-3}	4.09×10^{10}	
		5	23.384	3.89×10^{-4}	2.76×10^{8}	
		6	10.635	7.06×10^{-4}	9.08×10^{8}	
		7	13.942	5.62×10^{-3}	5.76×10^{10}	
		8	23.384	3.89×10^{-4}	2.75×10^{8}	
T3-2F-C	0.291	1	10.011	-1.50×10^{-2}	4.20×10^{11}	2.49×10^{-2}
		2	10.122	-3.17×10^{-3}	1.87×10^{10}	
		3	10.969	-8.74×10^{-4}	1.42×10^{9}	
		4	10.122	-3.17×10^{-3}	1.87×10^{10}	
		5	23.854	3.40×10^{-4}	2.15×10^{8}	
		6	13.760	-8.31×10^{-5}	1.29×10^{7}	
		7	6.835	-1.27×10^{-4}	3.02×10^{7}	
		8	23.854	3.40×10^{-4}	2.15×10^{8}	
T3-2F-D	0.267	1	12.336	8.80×10^{-5}	1.90×10^{7}	2.32×10^{-2}
		2	8.334	4.58×10^{-3}	5.14×10^{10}	
		3	10.288	-7.30×10^{-3}	1.31×10^{11}	
		4	12.336	8.78×10^{-5}	1.89×10^{7}	
		5	12.200	-3.31×10^{-3}	2.68×10^{10}	
		6	13.225	5.31×10^{-3}	6.90×10^{10}	
		7	17.305	9.92×10^{-3}	2.41×10^{11}	
		8	13.225	5.31×10^{-3}	6.91×10^{10}	
T3-2F-E	0.279	1	16.403	7.74×10^{-4}	1.28×10^{9}	1.16×10^{-3}

Molecules	λ (eV)	Path	r_{i} (Å)	V (eV)	k_{ij} (s^{-1})	μ (cm^{2}V^{-1}s^{-1})
		2	5.842	-4.92×10^{-3}	5.17×10^{10}	
		3	10.636	-5.63×10^{-4}	6.76×10^{8}	
		4	12.643	2.68×10^{-3}	1.54×10^{10}	
		5	22.349	1.50×10^{-3}	4.79×10^{9}	
		6	11.305	-2.16×10^{-3}	9.98×10^{9}	
		7	11.305	-2.16×10^{-3}	9.95×10^{9}	
		8	22.349	1.50×10^{-3}	4.80×10^{9}	
T3-2F-G	0.275	1	10.659	-7.33×10^{-4}	1.20×10^{9}	3.61×10^{-3}
		2	11.370	-2.40×10^{-3}	1.29×10^{10}	
		3	11.370	-2.40×10^{-3}	1.29×10^{10}	
		4	16.382	8.42×10^{-4}	1.59×10^{9}	
		5	22.287	1.37×10^{-3}	4.17×10^{9}	
		6	12.812	5.21×10^{-3}	6.08×10^{10}	
		7	5.846	-3.37×10^{-3}	2.54×10^{10}	
		8	22.287	1.37×10^{-3}	4.18×10^{9}	
T3-3F-A	0.273	1	8.626	-5.78×10^{-3}	7.65×10^{10}	5.45×10^{-3}
		2	9.075	-1.11×10^{-4}	2.84×10^{7}	
		3	9.749	2.81×10^{-3}	1.81×10^{10}	
		4	10.210	-7.65×10^{-3}	1.34×10^{11}	
		5	22.775	1.30×10^{-3}	3.88×10^{9}	
		6	9.998	-4.05×10^{-3}	3.76×10^{10}	
		7	9.998	-4.05×10^{-3}	3.76×10^{10}	
		8	22.775	1.30×10^{-3}	3.89×10^{9}	
T3-3F-B	0.290	1	10.089	-3.13×10^{-3}	1.84×10^{10}	2.54×10^{-2}
		2	10.175	-1.48×10^{-2}	4.14×10^{11}	
		3	10.877	-9.24×10^{-4}	1.61×10^{9}	
		4	10.089	-3.13×10^{-3}	1.84×10^{10}	
		5	23.813	3.61×10^{-4}	2.45×10^{8}	
		6	13.673	-1.51×10^{-4}	4.32×10^{7}	

Molecules	λ (eV)	Path	r_i (Å)	V (eV)	k_ij (s^{-1})	μ (cm^{2}V^{-1}s^{-1})
		7	6.961	-1.75×10^{-4}	5.79×10^{7}	
		8	23.813	3.60×10^{-4}	2.45×10^{8}	

Figure S1. Main transfer pathways (marked by numbers) in the obtained crystal structures.



T3-pF **T3-2F-A**

T3-mF **T3-2F-B**

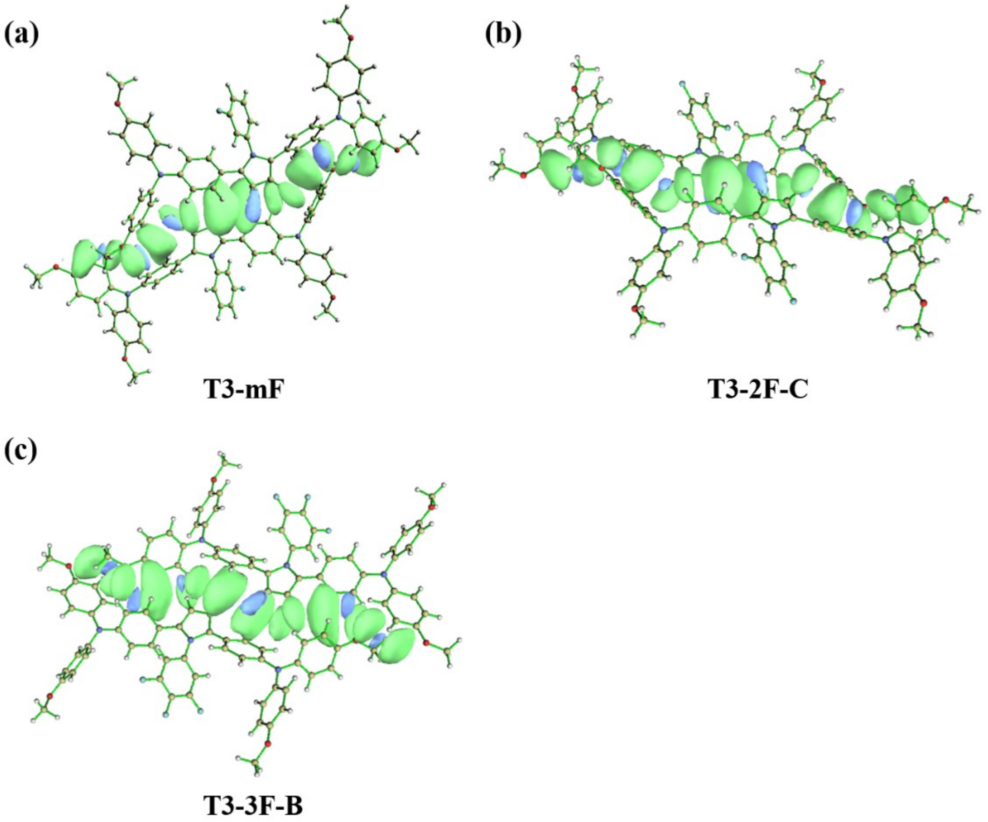
T3-oF **T3-2F-C**

T3-2F-D

T3-3F-A **T3-2F-E**

T3-3F-B **T3-2F-G**

Figure S2. HOMO-HOMO overlaps of dimers for the transfer routes with the largest transfer integral in the proposed crystal structures of (a) T3-mF, (b) T3-2F-C, and (c) T3-3F-B, respectively.



T3-mF

T3-2F-C

T3-3F-B

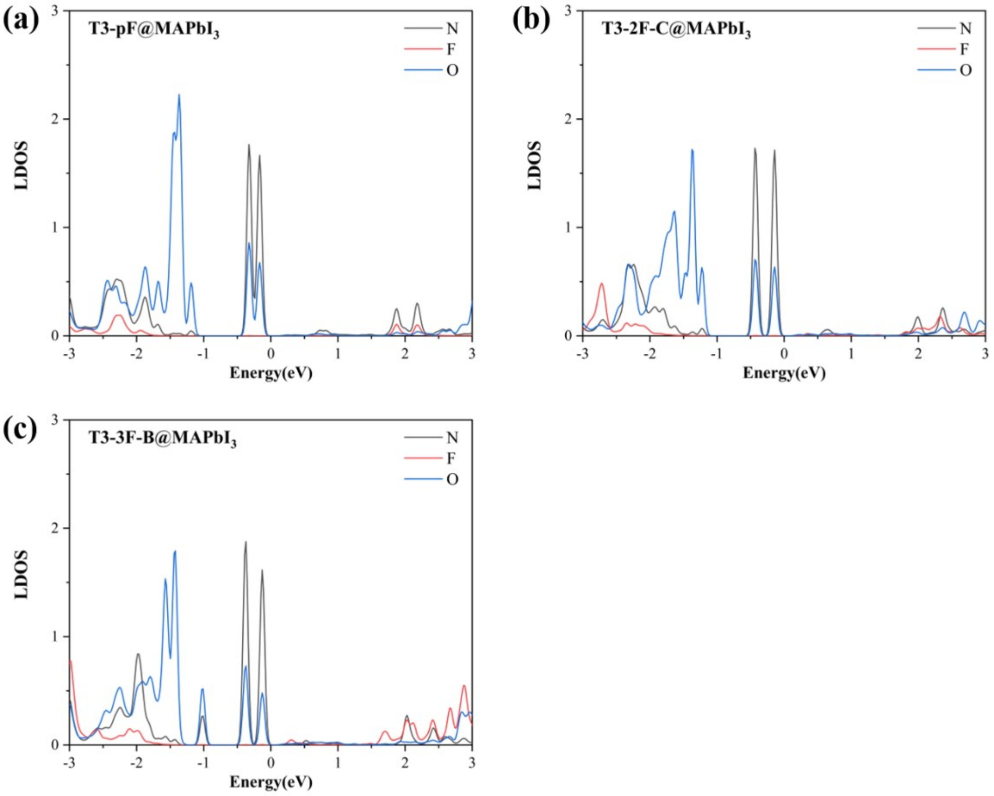
Table S7. Calculated oscillator strength *f*, transition energy E_g(eV) of absorption, maximum wavelengths λ_{abs}(nm), and transition energy E_1(eV) of emission, maximum wavelengths λ_{em}(nm) and Stokes shifts (nm).

Molecule	*f*	E_g (eV)	λ_{abs} (nm)	Major configuration	E_1 (eV)	λ_{em} (nm)	Stokes shifts (nm)
T3-pF	1.74	3.61	344	HOMO→LUMO (87%)	2.77	448	104
T3-mF	1.63	3.59	345	HOMO→LUMO (85%)	2.73	454	109
T3-oF	1.67	3.60	344	HOMO→LUMO (85%)	2.74	452	108
T3-2F-A	1.69	3.61	344	HOMO→LUMO (85%)	2.75	451	107
T3-2F-B	1.66	3.60	344	HOMO→LUMO (85%)	2.74	453	108
T3-2F-C	1.50	3.57	347	HOMO→LUMO (84%)	2.69	462	115
T3-2F-D	1.27	3.64	340	HOMO→LUMO (80%)	2.72	456	116
T3-2F-E	1.46	3.57	347	HOMO→LUMO (79%)	2.70	459	112
T3-2F-G	1.58	3.60	344	HOMO→LUMO (83%)	2.72	455	111
T3-3F-A	1.62	3.62	342	HOMO→LUMO (84%)	2.73	454	111
T3-3F-B	1.53	3.59	345	HOMO→LUMO (84%)	2.70	459	114

Table S8. The adiabatic ionization potentials (IP_a, eV), adiabatic electron affinities (EA_a, eV), the absolute hardness (η) and solvation free energy (ΔG_{solv}, kcal/mol) of the studied molecules.

Molecule	IP_a (eV)	EA_a (eV)	η (eV)	ΔG_{solv} (kcal/mol)
T3-pF	4.41	1.24	1.59	-11.16
T3-mf	4.42	1.28	1.57	-11.53
T3-oF	4.42	1.26	1.58	-11.65
T3-2F-A	4.43	1.27	1.58	-11.33
T3-2F-B	4.43	1.29	1.57	-11.22
T3-2F-C	4.44	1.34	1.55	-11.77
T3-2F-D	4.48	1.29	1.60	-11.46
T3-2F-E	4.44	1.33	1.55	-11.88
T3-2F-G	4.44	1.29	1.57	-11.94
T3-3F-A	4.46	1.29	1.58	-11.47
T3-3F-B	4.46	1.34	1.56	-11.99

Figure S3. Local density of states (LDOS) of the (a) T3-pF interfaced surface, (b) T3-2F-A interfaced surface, and (c) T3-3F-B interfaced surface.



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