Supplementary Information

Exploring Structure–Function Synergy in Multi-Fused A-D-A Systems for Advanced Organic Electronics

Contents

Fig. S1. Optimized GaussView geometries of non-selected designs for structural overview

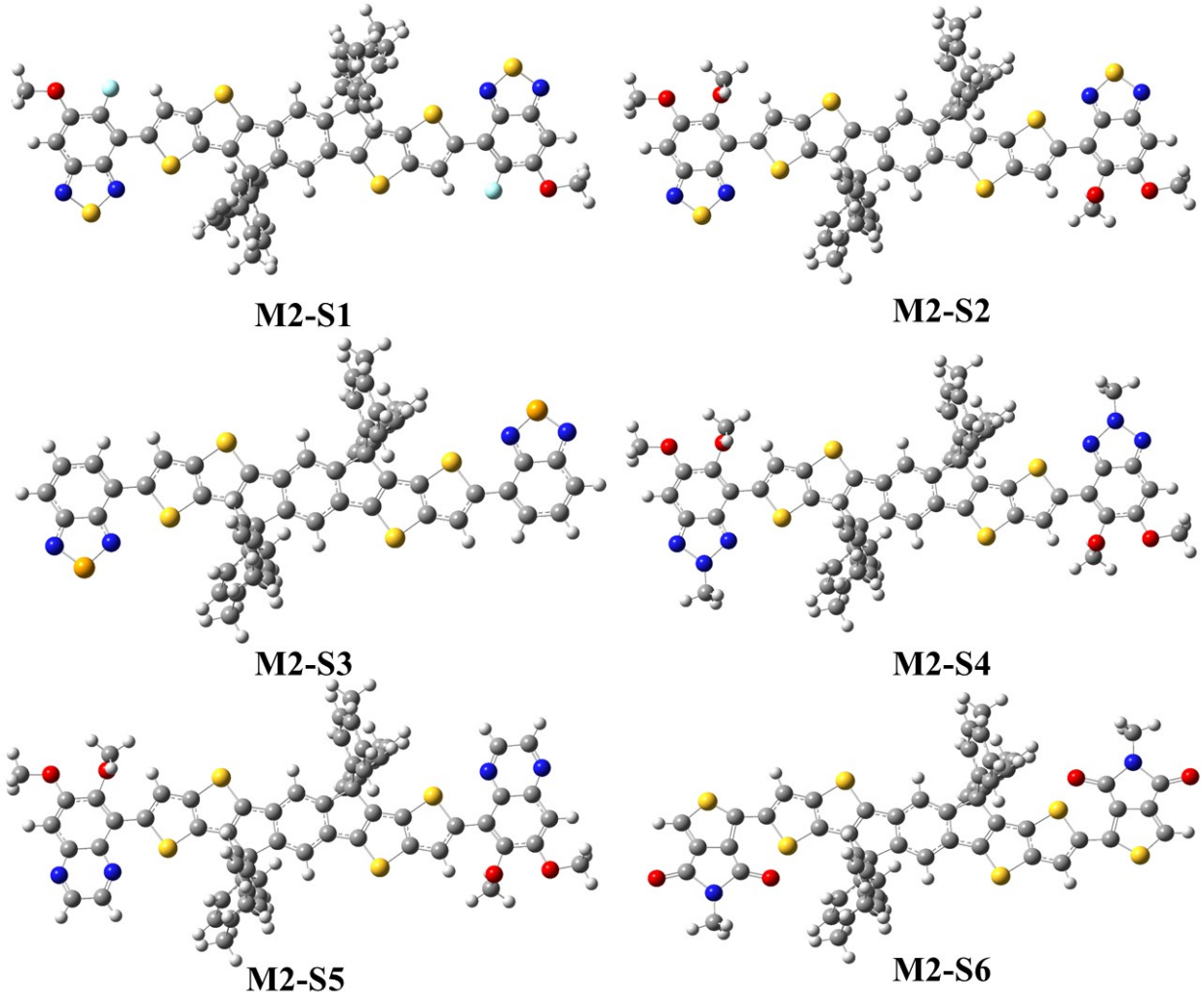


Table S1. Theoretically computed absorbance wavelength values of non-selected designs

Molecules	Gas λ_{max} (nm)	Solvent λ_{max} (nm)
M2-R	636	641
M2-S1	603	605
M2-S2	594	595
M2-S3	600	601
M2-S4	505	516
M2-S5	557	533
M2-S6	536	558

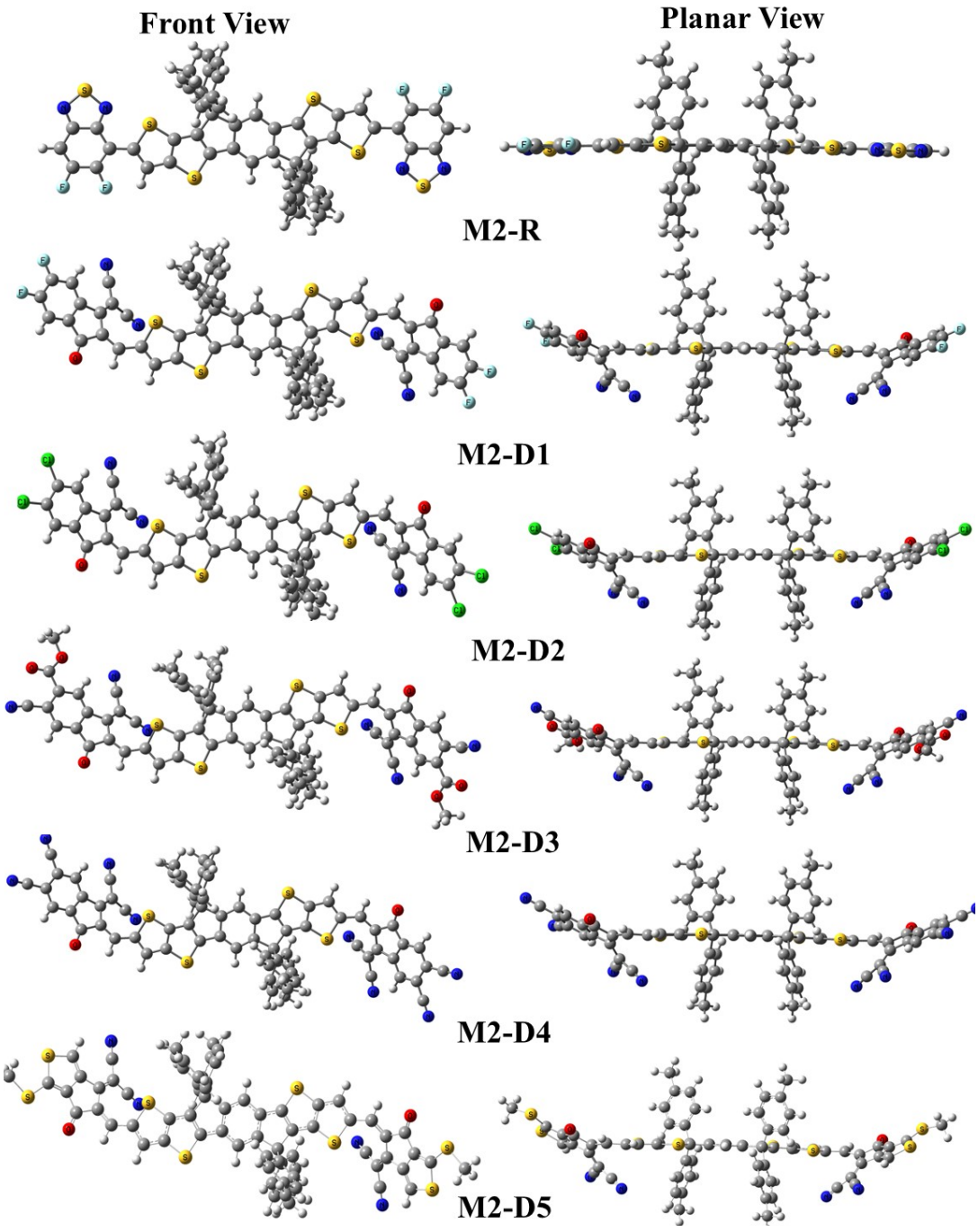


Fig. S2. Optimized GaussView geometries of all the studied molecules (**M2-R** and **M2-D1-M2-D5)** in the front and planar view

Table S2. Structural parameters like bond length L_{D-A}, dihedral angle θ_{D-A}, SDP, and MPP between different parts of reference **M2-R** and tailored **M2-D1-M2-D5**.

Molecules	L_{D-A} (Å)	θ_{D-A} (°)	SDP (Å)	MPP (Å)
M2-R	1.456	1.098	0.2665	0.0833
M2-D1	1.420	13.62	0.1762	0.0524
M2-D2	1.420	13.06	0.1720	0.0512
M2-D3	1.417	12.53	0.1728	0.0516
M2-D4	1.416	11.96	0.1688	0.0503
M2-D5	1.422	14.48	0.1906	0.0569

Table S3. Different optical parameters of the reference **M2-R** and tailored **M2-D1-M2-D5** in gaseous and chloroform solvent states.

Molecules	Gaseous			Chloroform		
	λ_{max}	f_o	LHE	λ_{max}	f_o	LHE
M2-R	636	1.0857	0.9180	641	1.3665	0.9570
M2-D1	675	1.8029	0.9843	722	2.0473	0.9910
M2-D2	686	1.9171	0.9879	736	2.1448	0.9928
M2-D3	700	1.8773	0.9868	758	2.0298	0.9907
M2-D4	719	1.9851	0.9897	778	2.2521	0.9944
M2-D5	684	1.9768	0.9894	729	2.2359	0.9942

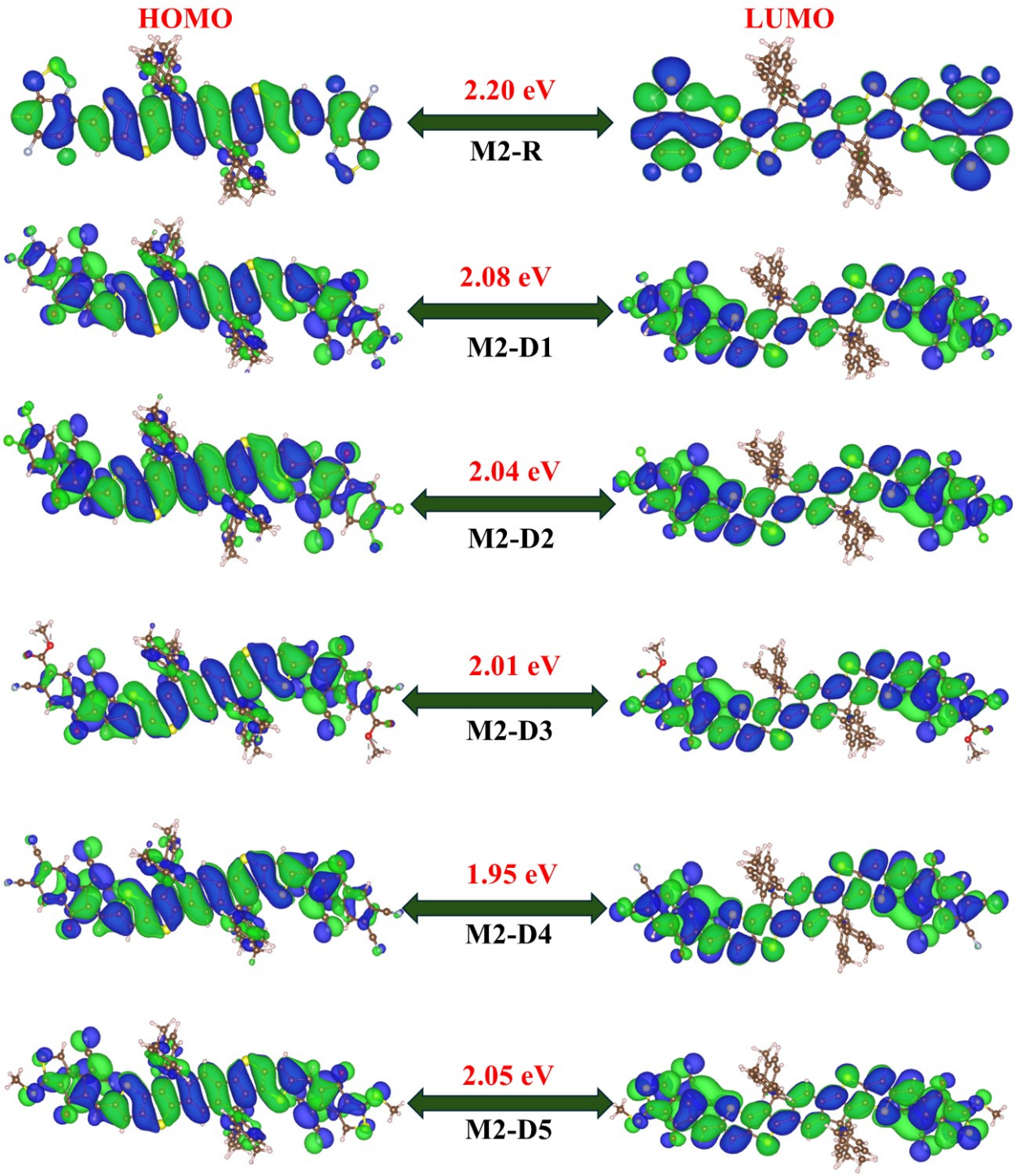


Fig. S3. FMOs of **M2-R** and **M2-D1-M2-D5** molecules

Table S4. The calculated LUMO energy (E_L), HOMO energy (E_H), energy gap (E_{H-L}), and Fermi level (E_{FL}) of **M2-R** and **M2-D1-M2-D5** molecules.

Molecules	E_L (eV)	E_H (eV)	E_{H-L} (eV)	E_{FL} (eV)
M2-R	-2.783	-4.936	2.20	-3.837
M2-D1	-3.484	-5.557	2.08	-4.521
M2-D2	-3.569	-5.614	2.04	-4.591
M2-D3	-3.752	-5.757	2.01	-4.755
M2-D4	-3.979	-5.928	1.95	-4.954
M2-D5	-3.314	-5.364	2.05	-4.339

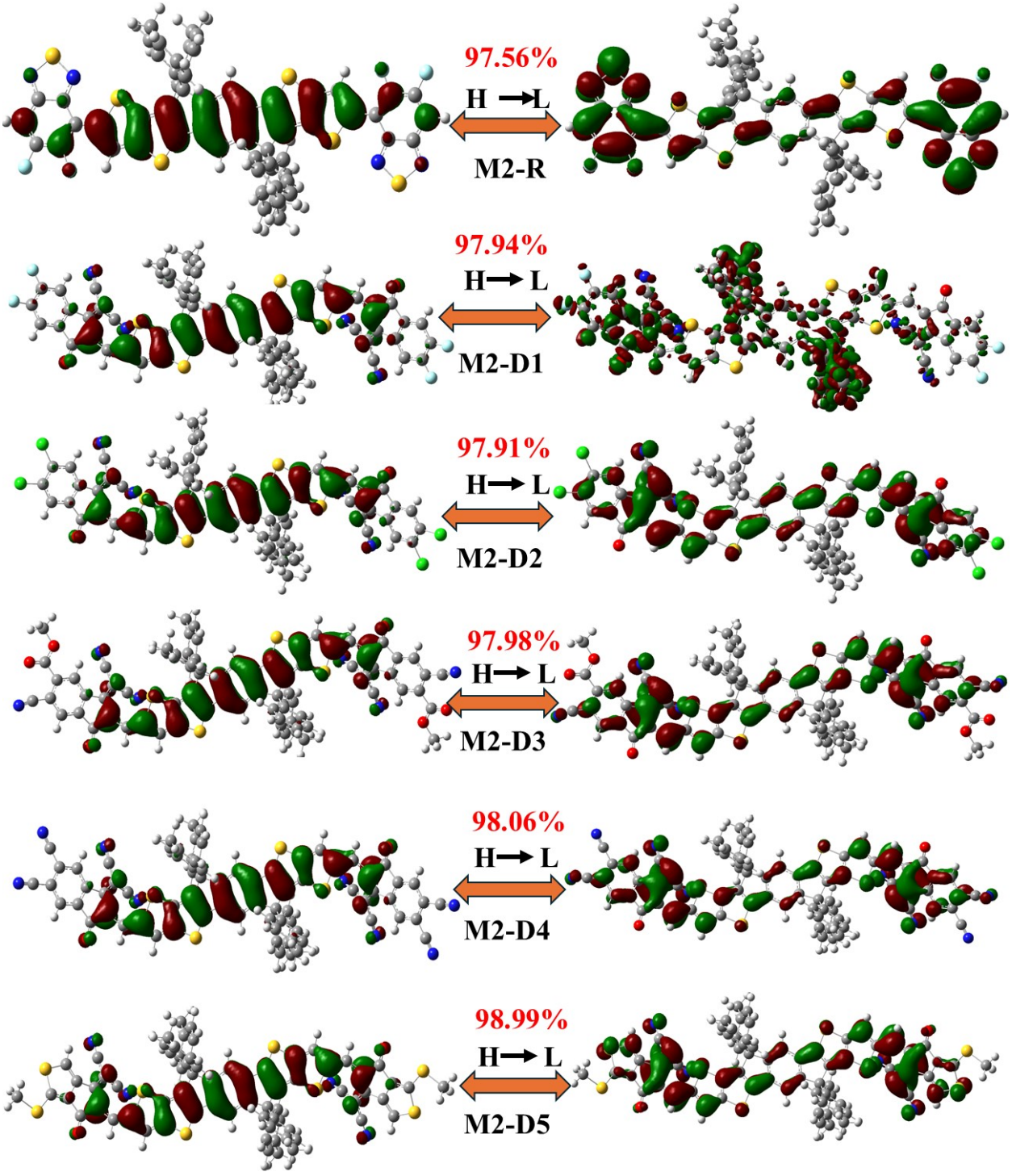
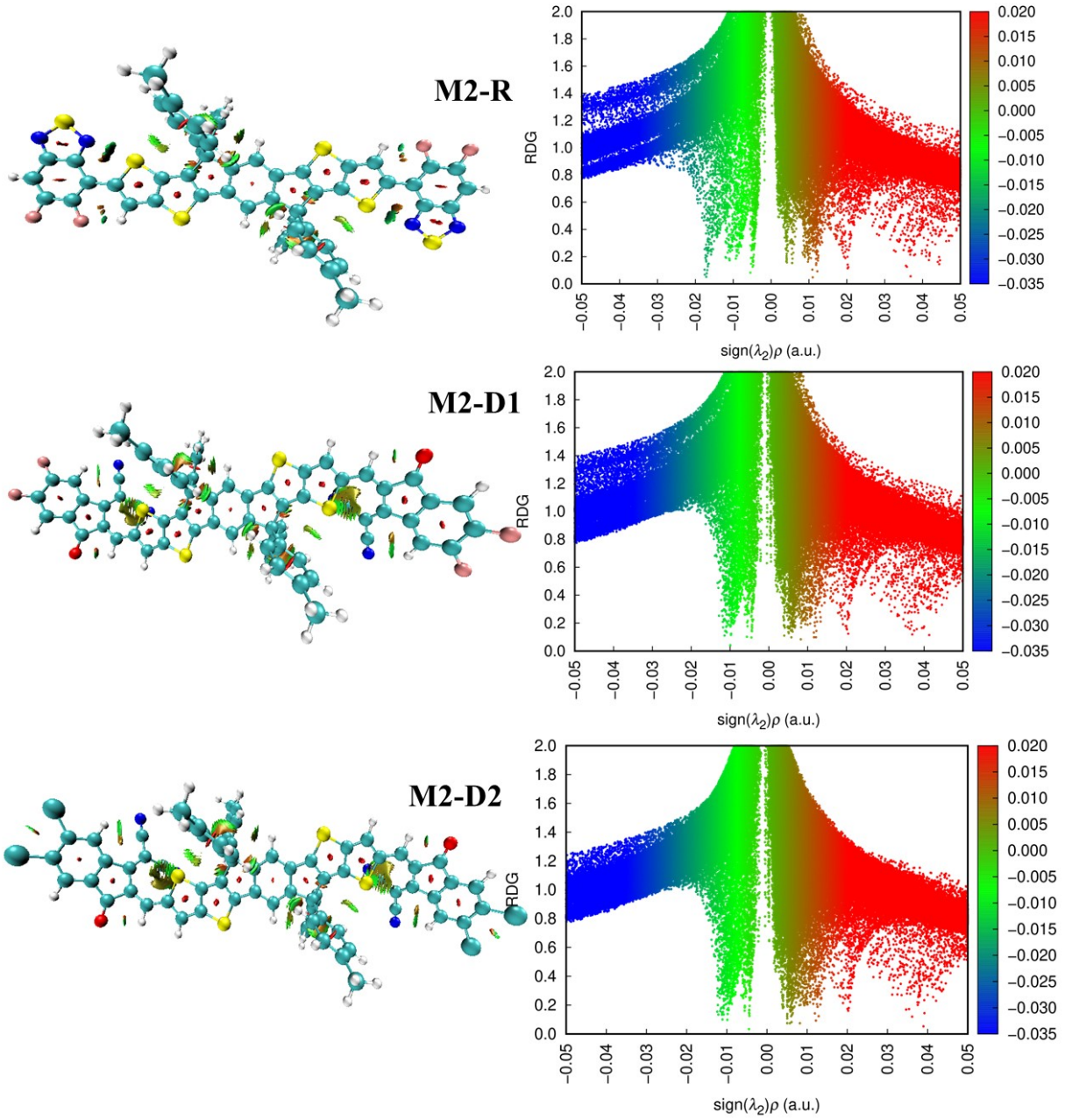


Fig. S4. The NTO mapped on the surface along with HOMO to LUMO transition percentage contribution of **M2-R** and **M2-D1-M2-D5** molecules


M2-R
M2-D1
M2-D2
RDG
sign(λ2)ρ (a.u.)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
−0.05
−0.04
−0.03
−0.02
−0.01
0.00
0.01
0.02
0.03
0.04
0.05
0.020
0.015
0.010
0.005
0.000
−0.005
−0.010
−0.015
−0.020
−0.025
−0.030
−0.035

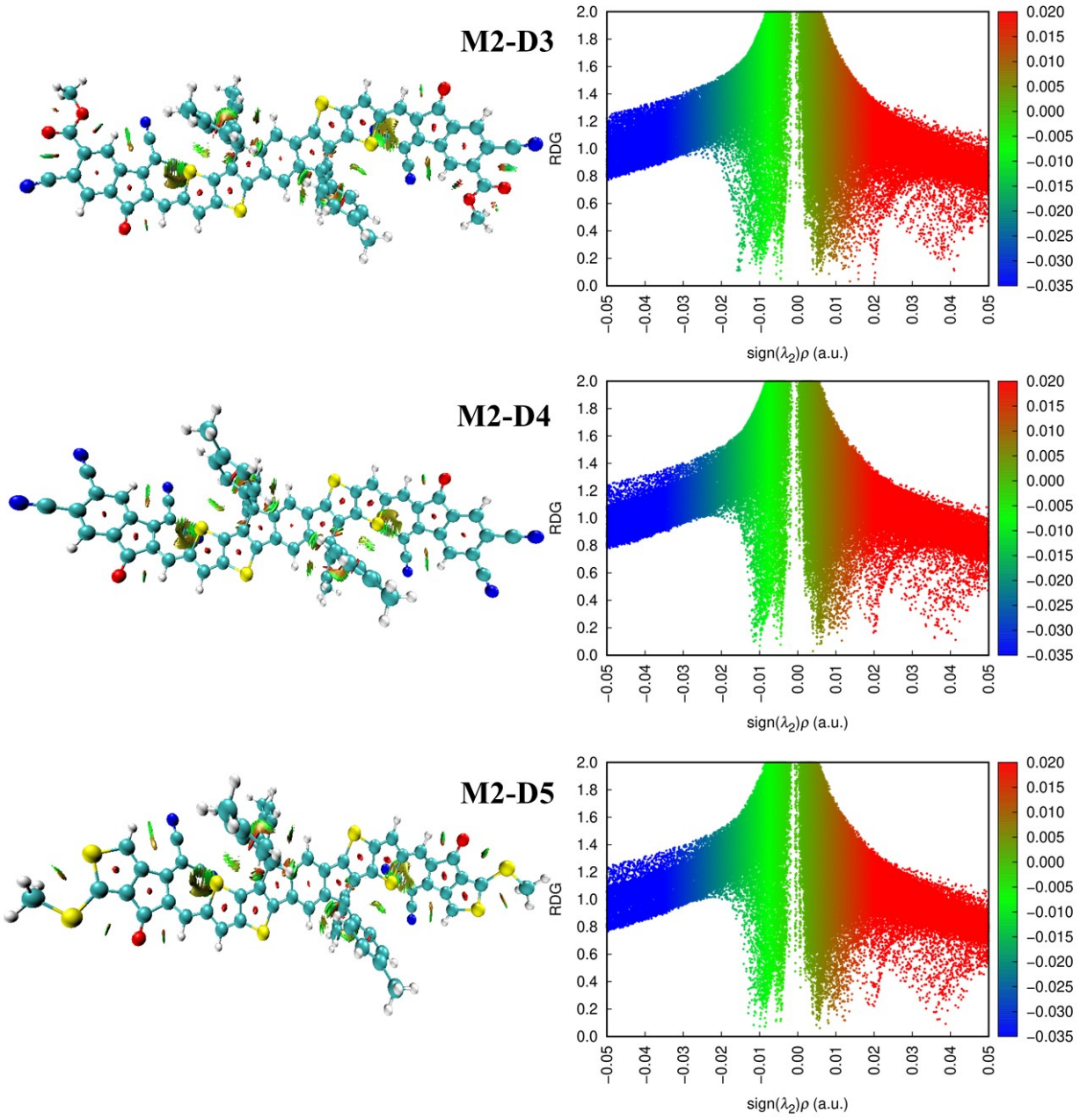


Fig. S5. The NCI maps and iso-surfaces of **M2-R** and **M2-D1-M2-D5** molecules

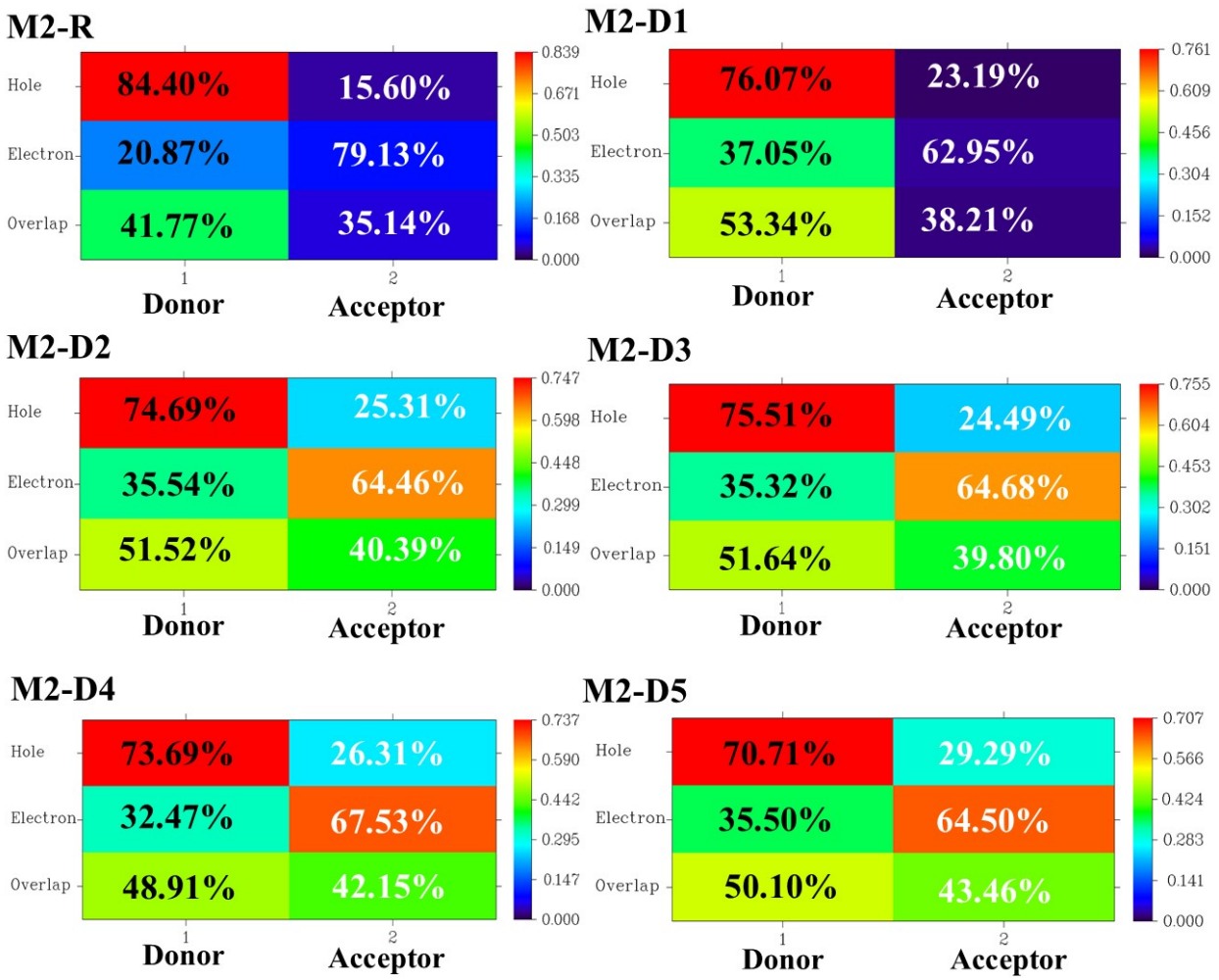


Fig. S6. Heat maps along with hole-electron and overlap percentage contributions of **M2-R** and **M2-D1-M2-D5** molecules.

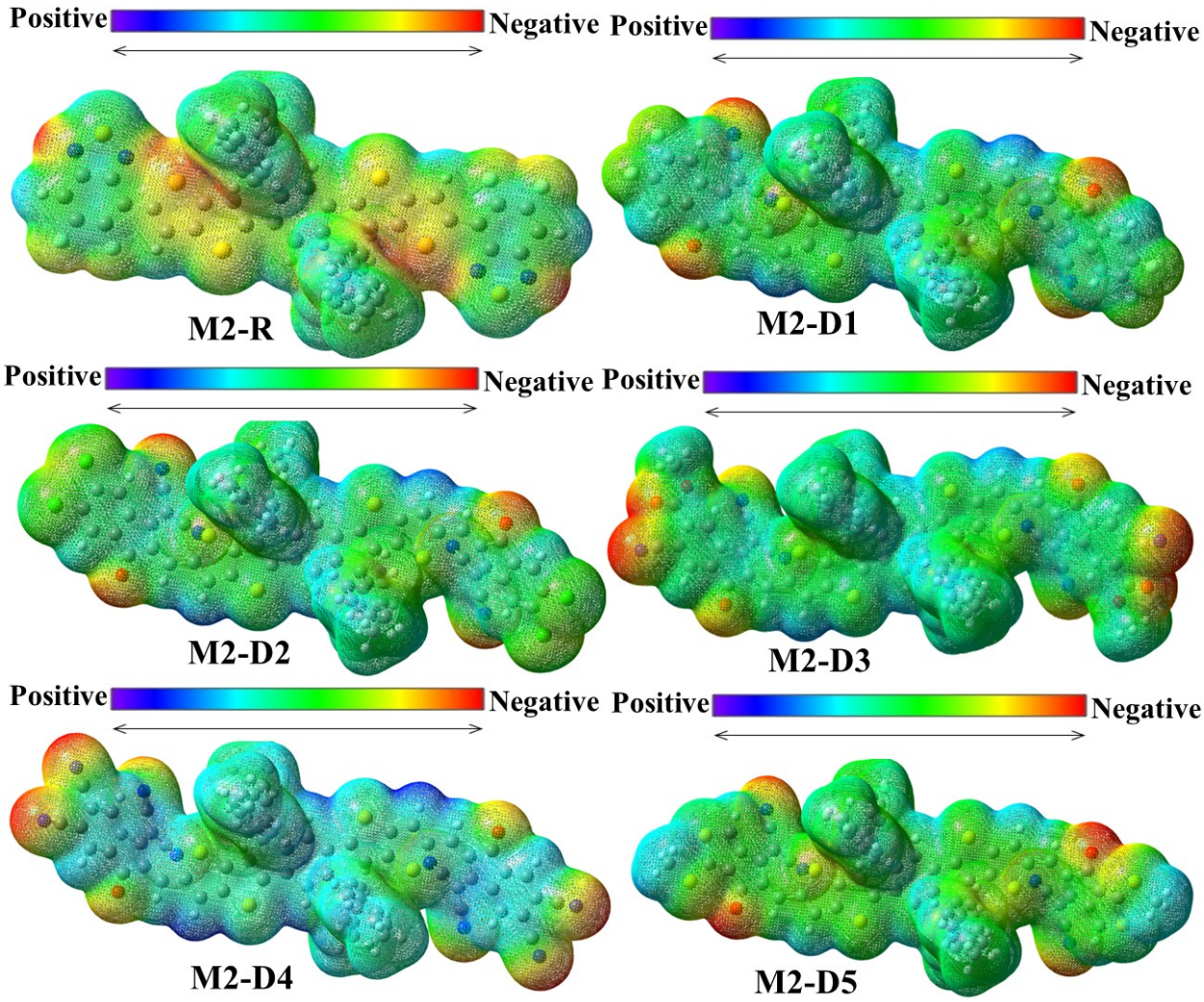


Fig. S7. Molecular electrostatic potential (MESP) images of **M2-R** and **M2-D1-M2-D5** molecules

Table S5. V_{oc}, Fill factor (FF %), and normalized (NV_{oc}) of **M2-R** and **M2-D1-M2-D5.**

Molecules	V_{oc} (V)	Normalized V_{oc} (NV_{oc})	FF %
M2-R	2.97	114.7826	95.03
M2-D1	2.27	87.7295	93.82
M2-D2	2.18	84.2512	93.62
M2-D3	2.00	77.2947	93.16
M2-D4	1.77	68.4058	92.46
M2-D5	2.44	94.2995	94.17

Table S6. Different NLO parameters calculated for **M2-R** and **M2-D4** molecules.

Parameters	M2-R	M2-D4	Parameters	M2-R	M2-D4
μ (D)	0.7882	3.5616	**β_{zyz} (esu)**	0.21×10^{-32}	-9.93×10^{-32}
α_{xx} (esu)	2.63×10^{-22}	4.27×10^{-22}	**β_{yyz} (esu)**	-0.56×10^{-30}	-1.39×10^{-30}
α_{yy} (esu)	1.16×10^{-22}	1.34×10^{-22}	**β_{yxz} (esu)**	-0.74×10^{-30}	8.63×10^{-30}
α_{zz} (esu)	0.84×10^{-22}	1.13×10^{-22}	**β_{x} (esu)**	0.71×10^{-30}	0.13×10^{-30}
α_{xy} (esu)	-0.68×10^{-24}	-7.21×10^{-24}	**β_{y} (esu)**	-0.15×10^{-30}	-3.65×10^{-30}
α_{xz} (esu)	-0.55×10^{-26}	-0.19×10^{-23}	**β_{z} (esu)**	26.0×10^{-30}	-2.75×10^{-30}
α_{yz} (esu)	0.85×10^{-27}	0.69×10^{-26}	**⟨β⟩ (esu)**	2.60×10^{-29}	4.57×10^{-29}
⟨α⟩ (esu)	1.54×10^{-22}	2.25×10^{-22}	**γ_{xxxx} (esu)**	0.41×10^{-31}	0.82×10^{-31}
Δα (esu)	1.65×10^{-22}	3.05×10^{-22}	**γ_{yyyy} (esu)**	0.47×10^{-34}	0.67×10^{-34}
α (esu)	1.54×10^{-22}	2.25×10^{-22}	**γ_{zzzz} (esu)**	0.54×10^{-34}	0.59×10^{-34}
β_{xxx} (esu)	0.22×10^{-30}	0.04×10^{-30}	**γ_{xxyy} (esu)**	0.16×10^{-33}	1.19×10^{-33}
β_{yyy} (esu)	0.31×10^{-32}	-0.15×10^{-32}	**γ_{xxzz} (esu)**	0.25×10^{-34}	3.39×10^{-34}
β_{zzz} (esu)	-0.23×10^{-30}	2.25×10^{-30}	**γ_{yyzz} (esu)**	0.27×10^{-34}	0.25×10^{-34}
β_{yxy} (esu)	0.01×10^{-30}	0.07×10^{-31}	**⟨γ⟩ (esu)**	9.25×10^{-33}	1.74×10^{-32}
β_{xxy} (esu)	-5.55×10^{-30}	-9.02×10^{-32}	**⟨α⟩∗ (PNa) (esu)**	0.22×10^{-22}	-
β_{xxz} (esu)	8.96×10^{-30}	-92.3×10^{-30}	**⟨β⟩* (PNa)(esu)**	1.5×10^{-31}	-
β_{zxz} (esu)	0.11×10^{-32}	-0.49×10^{-32}	**⟨γ⟩** (PNa) (esu)**	1.36×10^{-36}	-

Table S7. Different emission parameters with singlet(S_1)-triplet(T_1) splitting (ΔE_{ST}) of the **M2-R** and **M2-D4** molecules.

Molecules	λ_f (nm)	f_{em} (eV)	E_f (eV)	ΔE_{ST} (eV)
M2-R	724	0.8281	1.714	1.441
M2-D4	783	1.6063	1.583	1.274

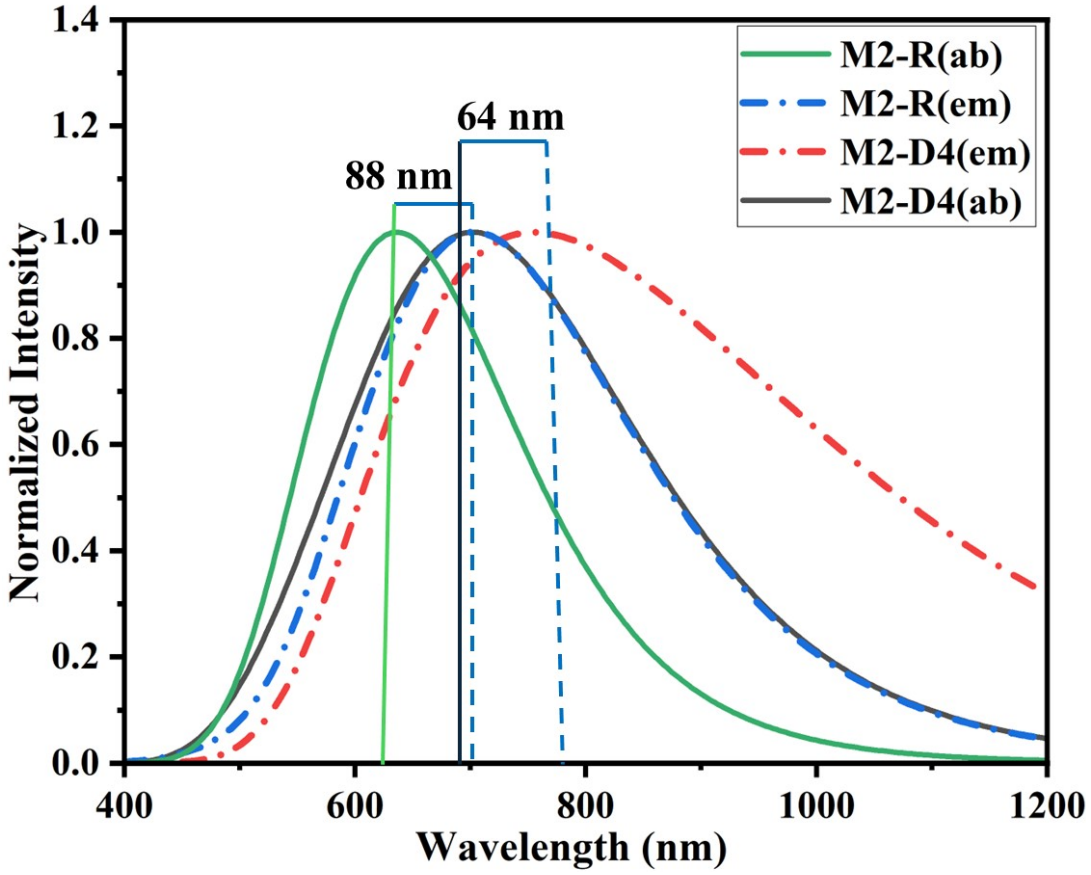


Fig. S8. UV-Vis absorption and emission comparison of **M2-R** and **M2-D4**

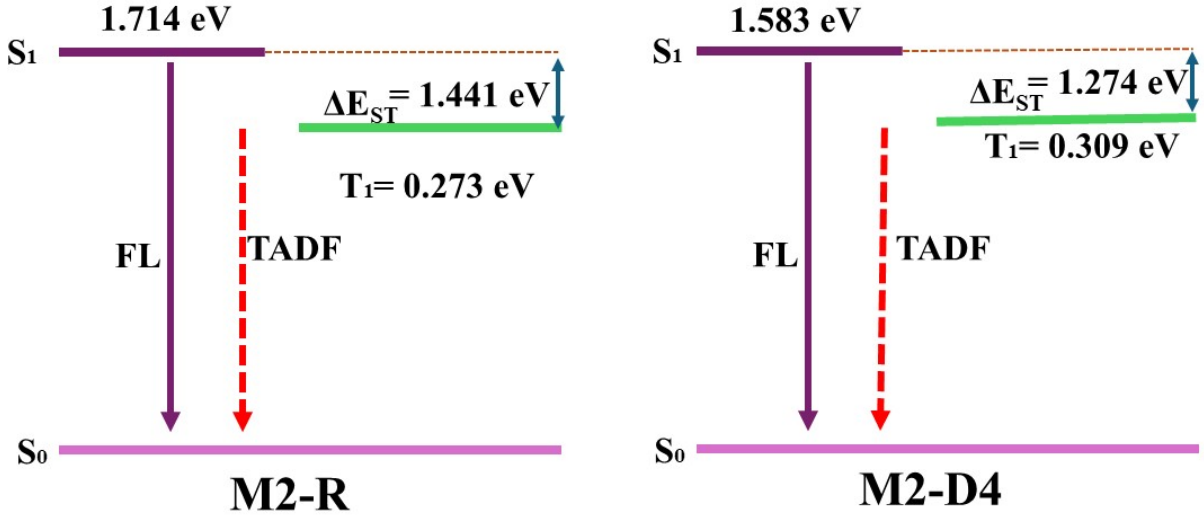


Fig. S9. Singlet(S_1)-triplet(T_1) splitting diagram of **M2-R** and **M2-D4**