Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information

Near Zero Singlet−Triplet Gap Through Nonfullerene Core Modification with Phenalene Derivatives Building Blocks

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S1. Complementary Computational Methods

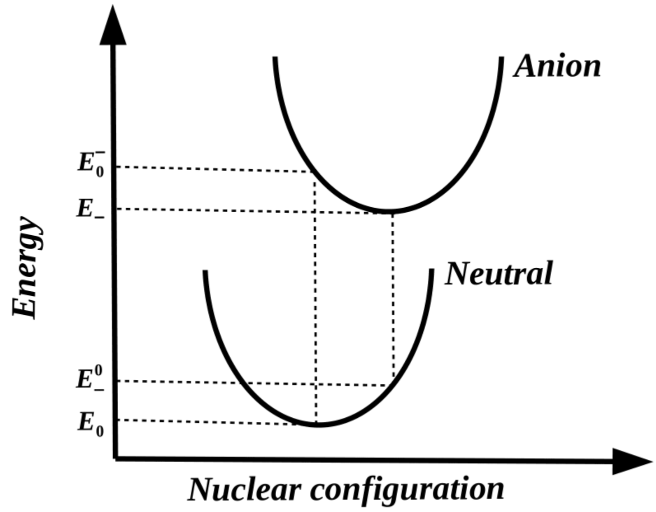


Figure S1: Schematic representation of the molecular potential energy surface as a function of the nuclear configuration in the neutral and charged state.

S2. Complementary Results

Table S1: Singlet and triplet vertical excitation energies [eV] calculated with different excited-state electronic structure methods, resulting singlet−triplet gaps, and the reference. Results for different phenalene derivatives and benzothiadiazole small molecules.

Molecule	Method	E_{S1}	E_{T1}	ΔE_{ST}	Reference
Phenalene derivative that constitutes the A1 molecule (cyc[3.3.3]azine)	ωB2PLYP’/def2-SVP	1.32	1.27	0.04	[1], This work
	ωB2PLYP’/def2-TZVP	1.29	1.24	0.05	This work
	ADC(2)/cc-pVDZ	1.04	1.20	−0.16	[1], [2]
	EOM-CCSD/cc-pVDZ	1.09	1.19	−0.10	[1], [2], This work
	EOM-CCSD/def2-SVP	1.04	1.17	−0.13	This work
	CIS(D)/cc-pVDZ	1.07	1.37	−0.30	[2], This work
	CIS(D)/def2-SVP	1.03	1.37	−0.34	This work
5AP (1,3,4,6,9b-pentaazaphenalene)	ωB2PLYP’/def2-SVP	2.481	2.436	0.045	This work
	ωB2PLYP’/def2-TZVP	2.558	2.473	0.085	This work
	ADC(2)/def2-TZVP	2.154	2.296	−0.142	[3]
	EOM-CCSD/cc-pVDZ	2.251	2.329	−0.078	[1], This work
	EOM-CCSD/def2-SVP	2.194	2.306	−0.112	This work
	CIS(D)/def2-SVP	2.086	2.623	−0.537	This work
	Experimental	1.957	2.003	−0.047	[4]
Phenalene derivative that constitutes the A1-5F molecule	ωB2PLYP’/def2-SVP	0.89	0.86	0.03	This work
	ωB2PLYP’/def2-TZVP	0.91	0.86	0.05	This work
	EOM-CCSD/def2-SVP	0.64	0.77	−0.13	This work
	CIS(D)/def2-SVP	0.61	0.95	−0.34	This work
Phenalene derivative that constitutes the B1 molecule	ωB2PLYP’/def2-SVP	2.33	2.23	0.1	This work
	ωB2PLYP’/def2-TZVP	2.27	2.17	0.1	This work
	EOM-CCSD/def2-SVP	2.13	2.17	−0.04	This work
	CIS(D)/def2-SVP	2.09	2.37	−0.28	This work
Benzothiadiazole that constitutes the Y6 molecule	ωB2PLYP’/def2-SVP	4.71	2.36	2.35	This work
	ωB2PLYP’/def2-TZVP	4.51	2.38	2.13	This work
	EOM-CCSD/def2-SVP	4.64	2.67	1.97	This work
	CIS(D)/def2-SVP	4.90	3.16	1.74	This work

Table S2: Excited-state energies calculated both in vacuum and with implicit solvent corrections using the conductor-like polarizable continuum model (C-PCM).

Method	Y6			A1			A1-5F		
	E_{S1}	E_{T1}	ΔE_{ST}	E_{S1}	E_{T1}	ΔE_{ST}	E_{S1}	E_{T1}	ΔE_{ST}
ωB2PLYP'/def2-SVP	2.451	1.66	0.791	1.635	1.325	0.31	1.22	1.195	0.025
ωB2PLYP'/def2-SVP/C-PCM[a]	2.413	1.689	0.727	1.534	1.23	0.295	1.236	1.189	0.047
ωB2PLYP'/def2-SVP/C-PCM-Chlo[b]	2.418	1.691	0.724	1.539	1.239	0.309	1.264	1.188	0.076

[a] Results assuming a dielectric constant of 4.0, and a refractive index of 1.8. [b] Results in chloroform medium.

Table S3: Singlet and triplet vertical excitation energies [eV] calculated with different excited-state electronic structure methods, and resulting singlet−triplet gaps.

Molecules	ωB2PLYP'/def2-SVP			CIS(D)/def2-SVP		
	E_{S1}	E_{T1}	ΔE_{ST}	E_{S1}	E_{T1}	ΔE_{ST}
Y6	2.451	1.66	0.791	2.327	2.139	0.188
A1	1.635	1.325	0.31	1.245	1.433	−0.188
A1-2F	1.462	1.285	0.177	1.113	1.399	−0.286
A1-3F	1.461	1.266	0.195	1.105	1.378	−0.273
A1-5F	1.22	1.195	0.025	0.874	1.283	−0.409
B1	2.173	1.641	0.532	1.822	1.908	−0.086
B1-5F	2.273	1.694	0.579	2.003	2.031	−0.028
C1	1.935	1.549	0.386	1.578	1.779	−0.201
C1-3F	1.729	1.476	0.316	1.431	1.681	−0.25

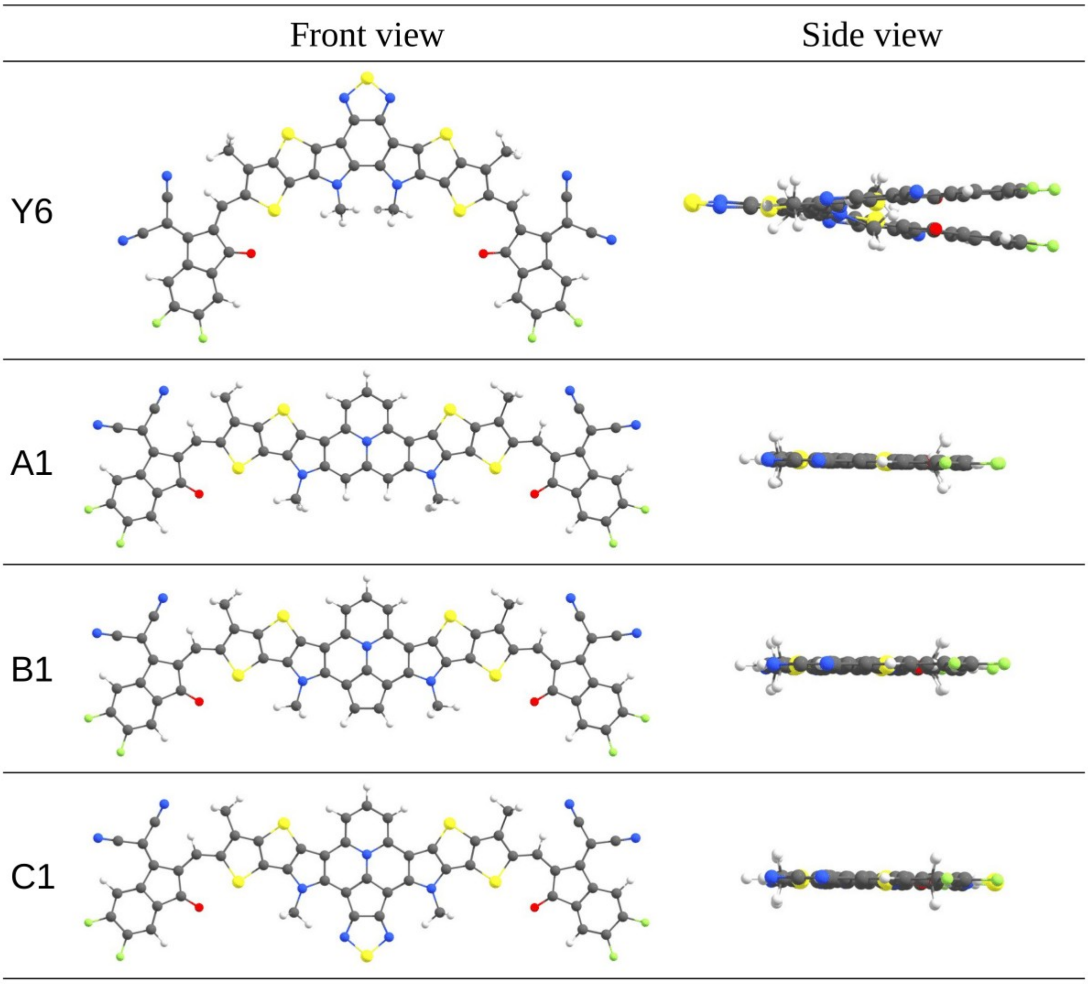


Figure S2: Optimized structure of molecules in front and side view.

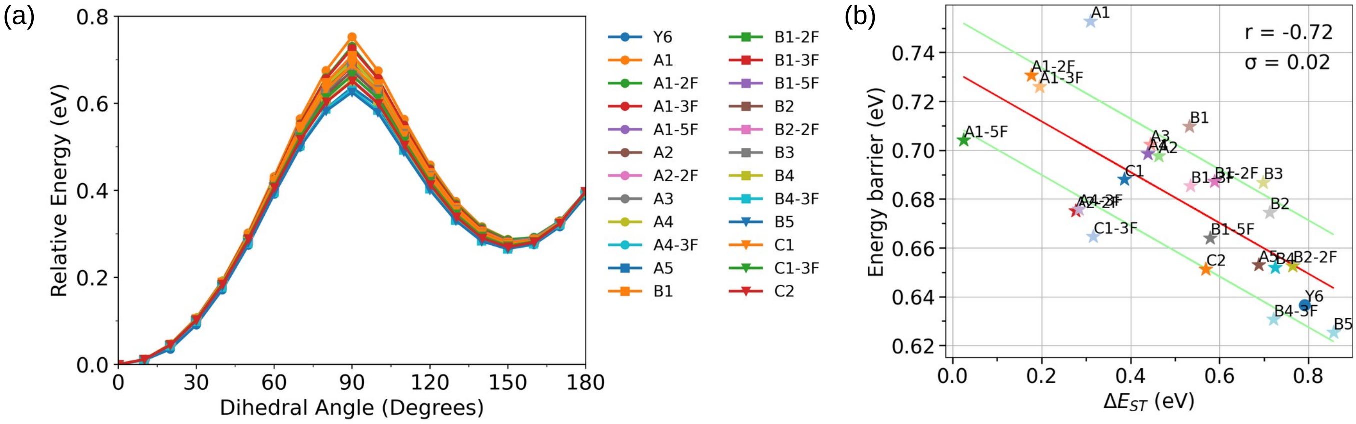


Figure S3: (a) Relative molecular energy vs the dihedral angle between central fused−ring core and acceptor end−group. (b) Correlation between ΔE_{ST} and the rotation energy barrier. The linear regression line is in red, where *r* is the Pearson’s correlation coefficient. The green lines are +/- one standard deviation (σ) around the linear regression.

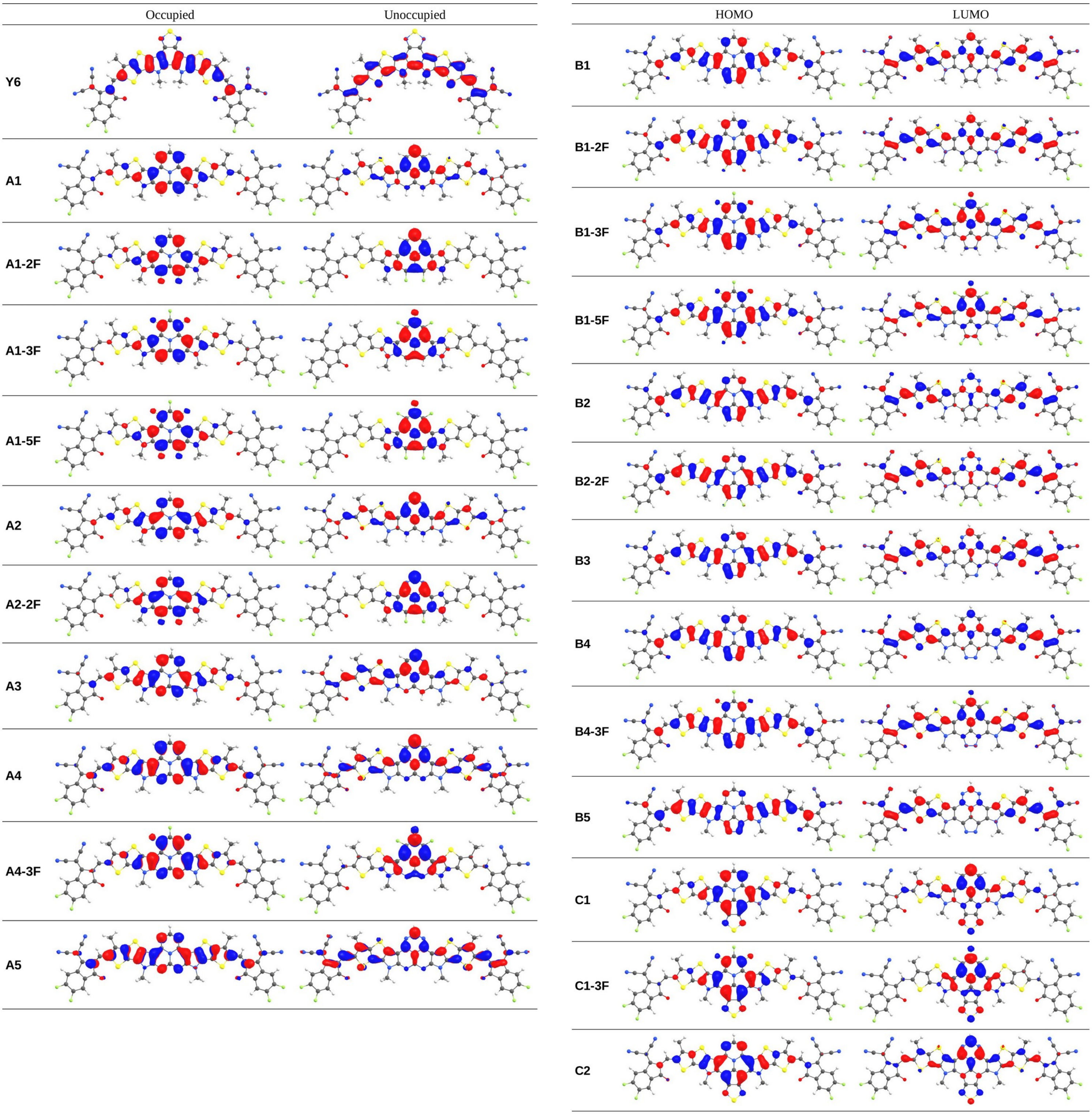
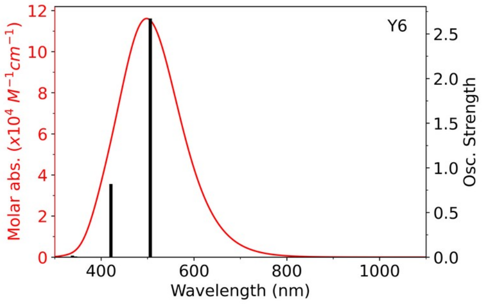


Figure S4: Natural transition orbitals of the first excited singlet state (S_1) (isovalues 0.03).


Y6
Molar abs. ($x10^4$ $M^{-1}cm^{-1}$)
0
2
4
6
8
10
12
Osc. Strength
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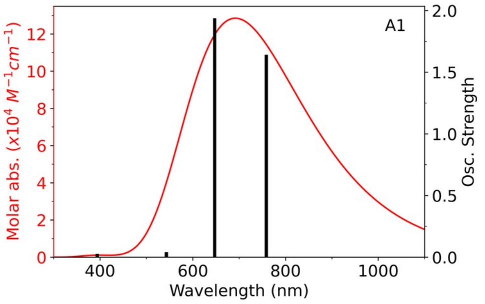
0.5
1.0
1.5
2.0
2.5
Wavelength (nm)
400
600
800
1000


A1
Molar abs. ($x10^4$ $M^{-1}cm^{-1}$)
0
2
4
6
8
10
12
Osc. Strength
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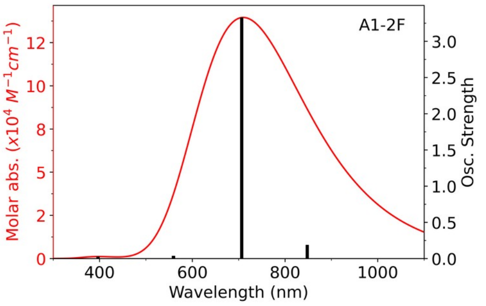
0.5
1.0
1.5
2.0
Wavelength (nm)
400
600
800
1000


A1-2F
Molar abs. ($x10^4$ $M^{-1}cm^{-1}$)
0
2
4
6
8
10
12
Osc. Strength
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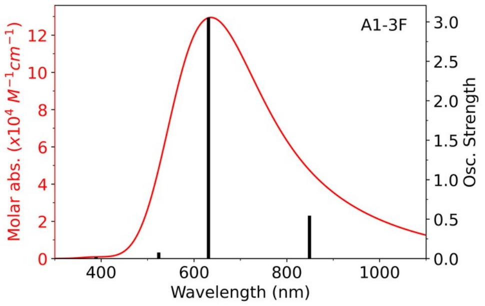
0.5
1.0
1.5
2.0
2.5
3.0
Wavelength (nm)
400
600
800
1000


A1-3F
Molar abs. ($x10^4$ $M^{-1}cm^{-1}$)
0
2
4
6
8
10
12
Osc. Strength
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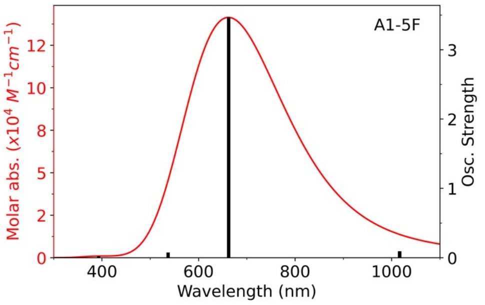
0.5
1.0
1.5
2.0
2.5
3.0
Wavelength (nm)
400
600
800
1000


A1-5F
Molar abs. ($x10^4$ $M^{-1}cm^{-1}$)
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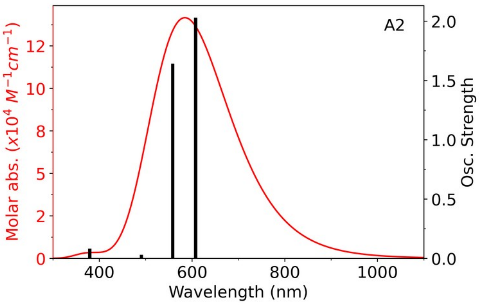
2
4
6
8
10
12
Osc. Strength
0
1
2
3
Wavelength (nm)
400
600
800
1000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Molar abs. ($x10^4$ $M^{-1}cm^{-1}$)
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2
5
8
10
12
Osc. Strength
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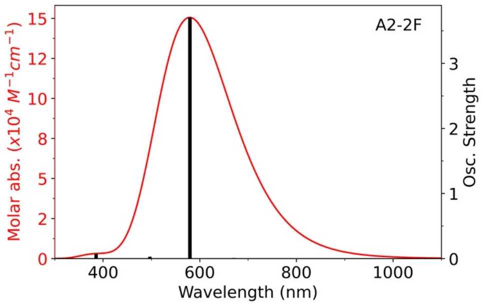
1.0
1.5
2.0
Wavelength (nm)
400
600
800
1000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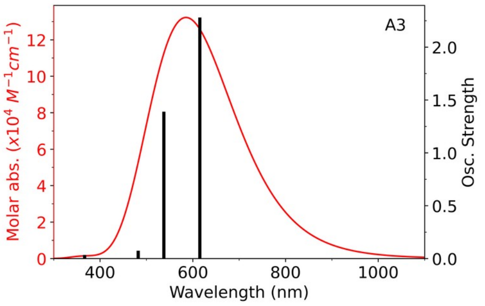
8
10
12
15
Osc. Strength
0
1
2
3
Wavelength (nm)
400
600
800
1000


A3
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2
4
6
8
10
12
Osc. Strength
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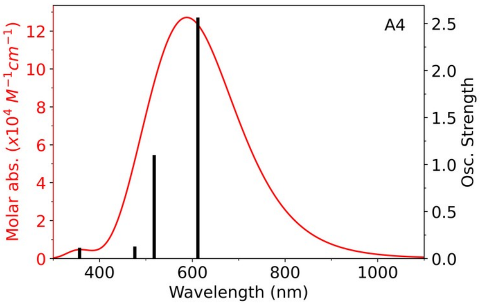
1.0
1.5
2.0
Wavelength (nm)
400
600
800
1000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Molar abs. ($x10^4$ $M^{-1}cm^{-1}$)
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2
4
6
8
10
12
Osc. Strength
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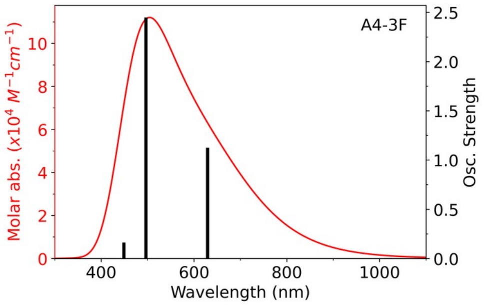
0.5
1.0
1.5
2.0
2.5
Wavelength (nm)
400
600
800
1000


A4-3F
Molar abs. ($x10^4$ $M^{-1}cm^{-1}$)
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2
4
6
8
10
Osc. Strength
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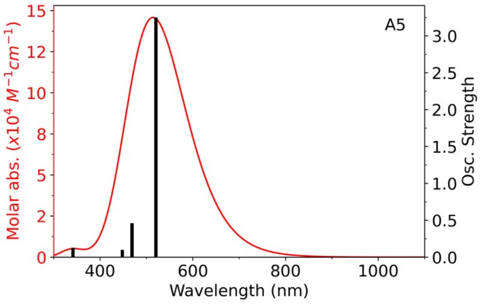
0.5
1.0
1.5
2.0
2.5
Wavelength (nm)
400
600
800
1000


A5
Molar abs. ($x10^4$ $M^{-1}cm^{-1}$)
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2
5
8
10
12
15
Osc. Strength
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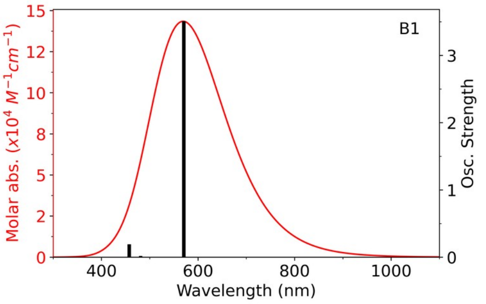
0.5
1.0
1.5
2.0
2.5
3.0
Wavelength (nm)
400
600
800
1000


B1
Molar abs. ($x10^4$ $M^{-1}cm^{-1}$)
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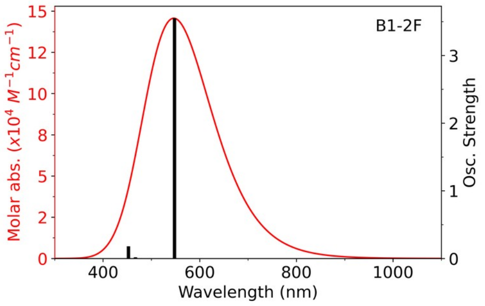
2
5
8
10
12
15
Osc. Strength
0
1
2
3
Wavelength (nm)
400
600
800
1000


B1-2F
Molar abs. ($x10^4$ $M^{-1}cm^{-1}$)
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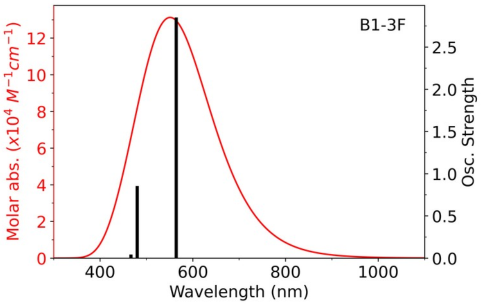
2
5
8
10
12
15
Osc. Strength
0
1
2
3
Wavelength (nm)
400
600
800
1000


B1-3F
Molar abs. ($x10^4$ $M^{-1}cm^{-1}$)
0
2
4
6
8
10
12
Osc. Strength
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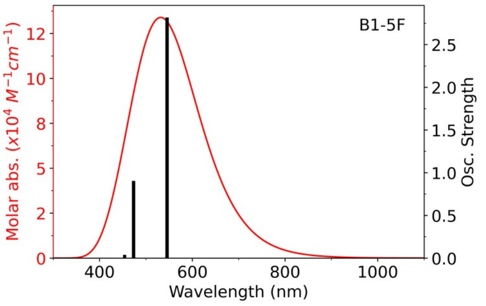
0.5
1.0
1.5
2.0
2.5
Wavelength (nm)
400
600
800
1000


B1-5F
Molar abs. ($x10^4$ $M^{-1}cm^{-1}$)
0
2
5
8
10
12
Osc. Strength
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0.5
1.0
1.5
2.0
2.5
Wavelength (nm)
400
600
800
1000

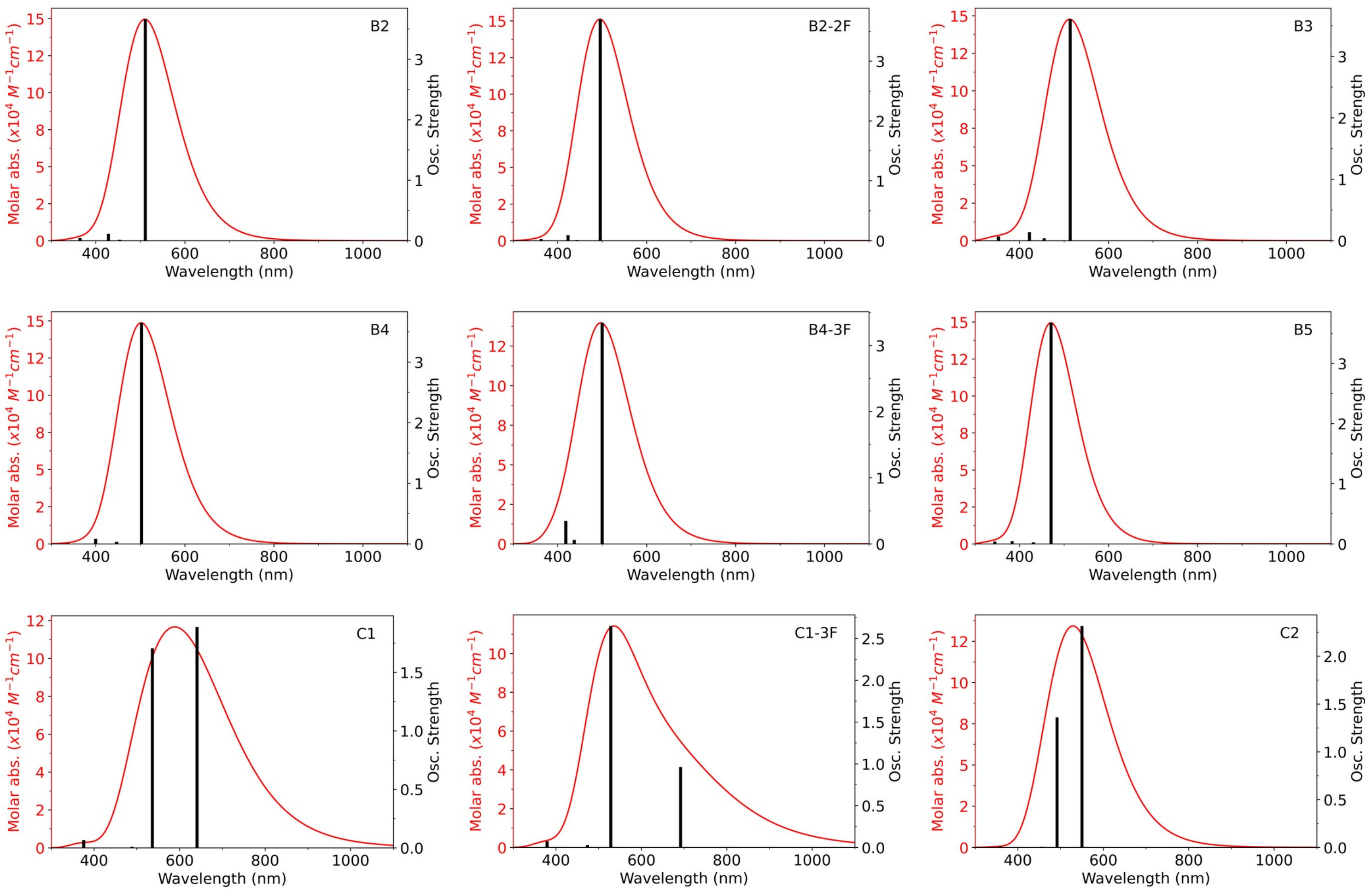

Figure S5: Absorption spectra and oscillator strength of the vertical electronic transitions.

Table S4: Summary of the correlation between ΔE_{ST} and some molecular properties. The correlation strength classification was also presented.

Molecular property	Correlation coefficient (r)	Correlation strength
Singlet excited-state energy (E_{S1})	0.98	Very Strong $|r| > 0.9$
Occupied−Unoccupied contribution to S_1	−0.95	
HOMO−LUMO gap	0.94	
Oscillator strength of the first lowest electronic transition (f_{S1})	0.91	
Oscillator strength of the second lowest electronic transition (f_{S2})	−0.91	
HOMO−LUMO contribution to S_2	−0.91	
Ionization Potential (IP)	0.91	
Triplet excited-state energy (E_{T1})	0.87	Strong $0.89 > |r| > 0.7$
Integrated absorption spectrum	−0.87	
Occupied−Unoccupied overlap (η_{OU})	0.84	
Triplet exciton binding energy ($E_{b,T1}$)	0.83	
HOMO−LUMO contribution to S_1	0.78	
Singlet exciton binding energy ($E_{b,S1}$)	−0.77	
Quadrupole moment (Q_{π})	−0.75	
Rotation energy barrier	−0.72	
Intramolecular reorganization energy for electron transfer (λ_{int})	−0.64	Moderate $0.69 > |r| > 0.4$
Internal charge transfer (ICT)	−0.63	
Dipole moment	−0.21	Weak $0.39 > |r| > 0.2$
Electron Affinity (EA)	0.19	

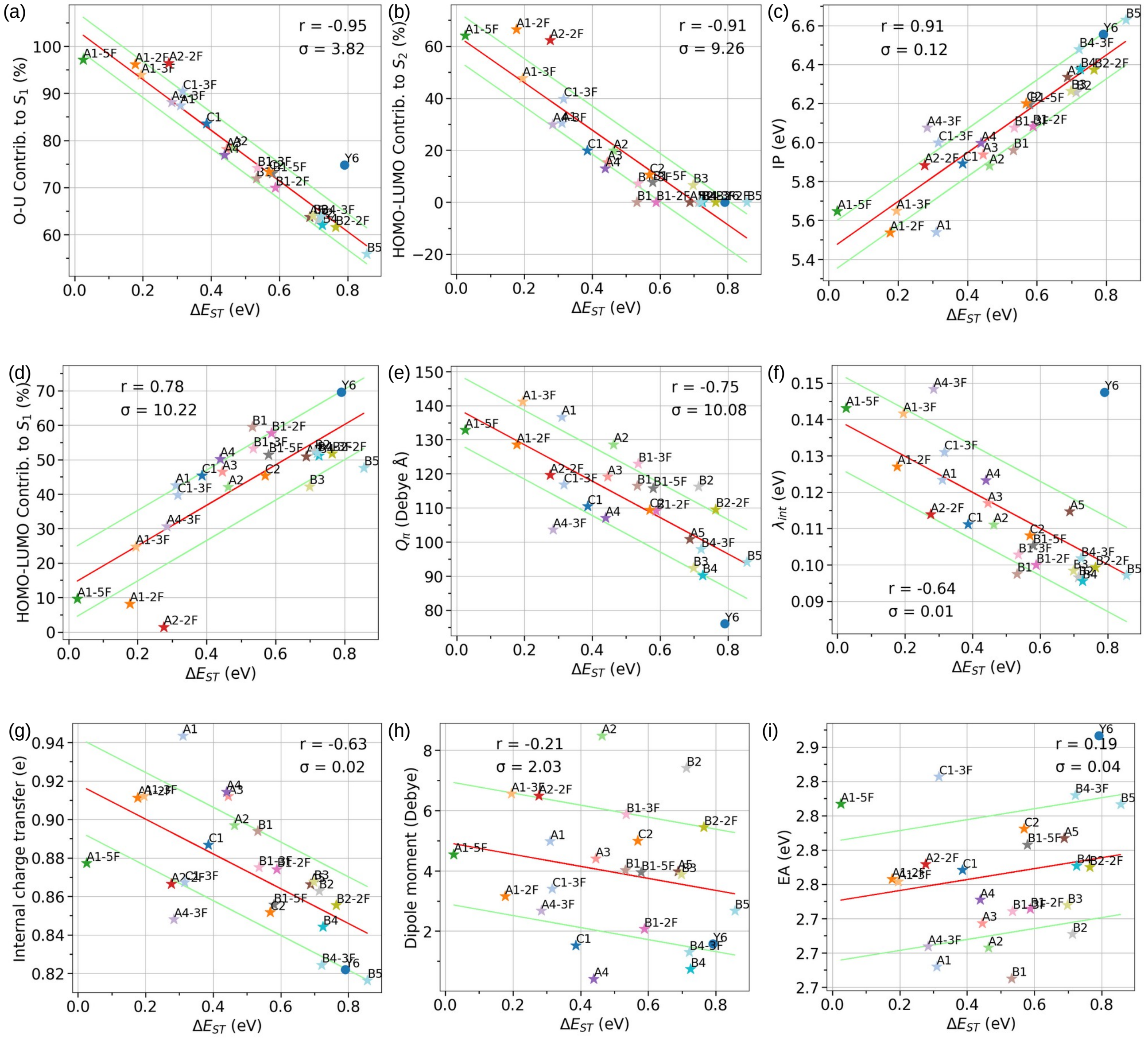

Figure S6: Correlation between ΔE_{ST} and some molecular properties. (a) Contribution of the Occupied and Unoccupied NTOs to the S_1 transition. (c) Ionization potential. (d) Contribution of the HOMO and LUMO to the S_1 transition. (e) Quadrupole component along the π-π stacking direction. (f) Intramolecular reorganization energy. (g) Internal Charge Transfer. (h) Dipole moment. (i) Electron affinity. The linear regression line is in red, where *r* is the Pearson's correlation coefficient. The green lines are +/- one standard deviation (σ) around the linear regression.

S3. References

[1] R. Pollice, P. Friederich, C. Lavigne, G. dos Passos Gomes, A. Aspuru-Guzik, Organic molecules with inverted gaps between first excited singlet and triplet states and appreciable fluorescence rates, Matter 4 (5) (2021) 1654–1682.

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[4] K. D. Wilson, W. H. Styers, S. A. Wood, R. C. Woods, R. J. McMahon, Z. Liu, Y. Yang, E. Garand, Spectroscopic quantification of the inverted singlet–triplet gap in pentaazaphenalene, Journal of the American Chemical Society.