

Report on TrzCz1 molecule

Andriy Zhugayevych, ...

June 23, 2025

S1	Computational methodology and abbreviations	S1
S2	Molecular structure	S2
S3	Electronic structure	S3
S4	Excited states	S4

S1 Computational methodology and abbreviations

a3p	Ahlrichs triple- ζ basis Def2-TZVP	MO	Molecular Orbital
CIS	Configuration Interaction Singles	NO	Natural Orbital
CT	Charge-Transfer (state)	NTO	Natural Transition Orbital
CS	Charge-Separated (state)	PAW	Projector Augmented Wave
Cz	Carbazole	PES	Potential Energy Surface
DFT	Density Functional Theory	PCM	Polarizable Continuum Model
HOMO	Highest Occupied Molecular Orbital	p2p	Pople double- ζ polarized basis 6-31G*
LE	Local Excitation (triplet)	SCF	Self-Consistent Field
LMO	Localized Molecular Orbital	SCRf	Self-Consistent Reaction Field
LP	Lone Pair	TDDFT	Time Dependent DFT
LUMO	Lowest Unoccupied Molecular Orbital	Trz	Triphenyltriazine
MD	Molecular Dynamics	ZPE	Zero-Point Energy

For calculations of molecules and their multimers we use CAM-B3LYPp2p method as implemented in Gaussian 16 package [Gaussian]. The CAM-B3LYP functional [Yanai04] is chosen according to its proven reliability for π -conjugated molecules as in particular has been benchmarked in our previous publications [Tukachev19, Zhugayevych18, Zhugayevych16]. The basis 6-31G*, referred here as ‘p2p’, provides a reasonable trade off between accuracy and scalability.

For calculations of crystals we use PBE-D3/PAW900 method as implemented in VASP 6 package [VASP], here 900 means 900 eV plane wave energy cutoff. Despite PBE functional gives typically inaccurate electronic structure of π -conjugated systems, the combination PBE-D3 is robust for prediction of intermolecular packing [Zhugayevych23b]. Details of geometry optimization of crystals including experimental CIF refinement are described in <http://zhugayevych.me/CMS/protocols.htm>.

Excited state calculations are performed with TDDFT, CIS-DFT (Tamm–Dancoff approximation), and Δ SCF approaches. For the balanced description of both singlets and triplets, CIS-DFT is more accurate than TDDFT [Liang22]. The CAM-B3LYP is among the most reliable functionals for the calculation of excitation energies for valence and CT states of conjugated molecules [Liang22]. For reliable modeling of the solvation and relaxation of excited states and accurate estimation of the singlet-triplet gap Δ SCF is used [Froitzheim24, Valverde25]. For some states Gaussian program does not allow to perform Δ SCF calculation. In this case state-specific solvation within CIS-DFT approach is used. However, it overestimates the solvation energy of CT states (Table S2).

In all figures of the current work, the wave-function isovalue is 0.03. In case of comparison, all figures are plotted with the same isovalue.

S2 Molecular structure

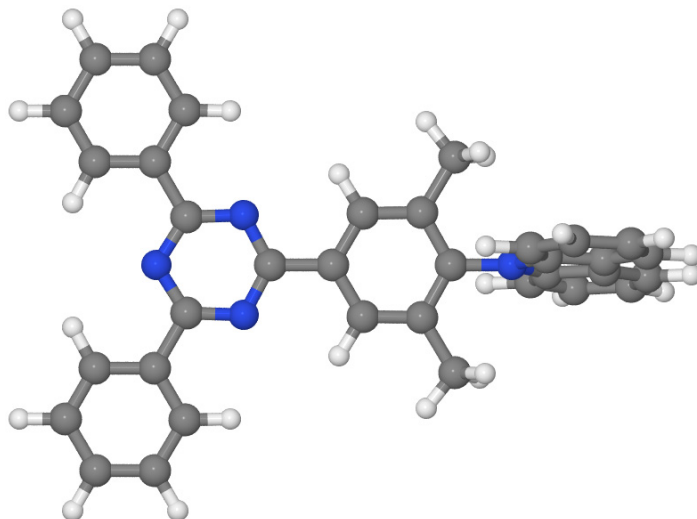


Figure S1: Lowest-energy conformer.

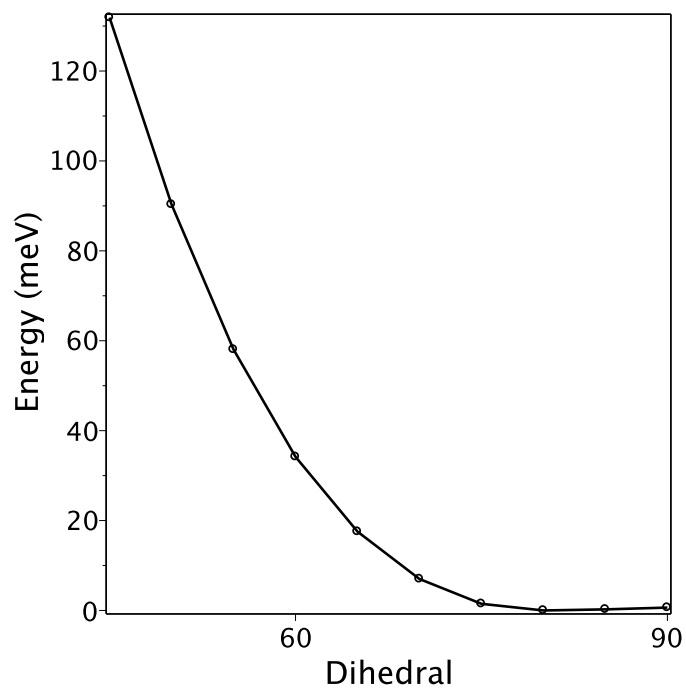


Figure S2: Relaxed PES for the flexible dihedral (32,36,45,46).

S3 Electronic structure

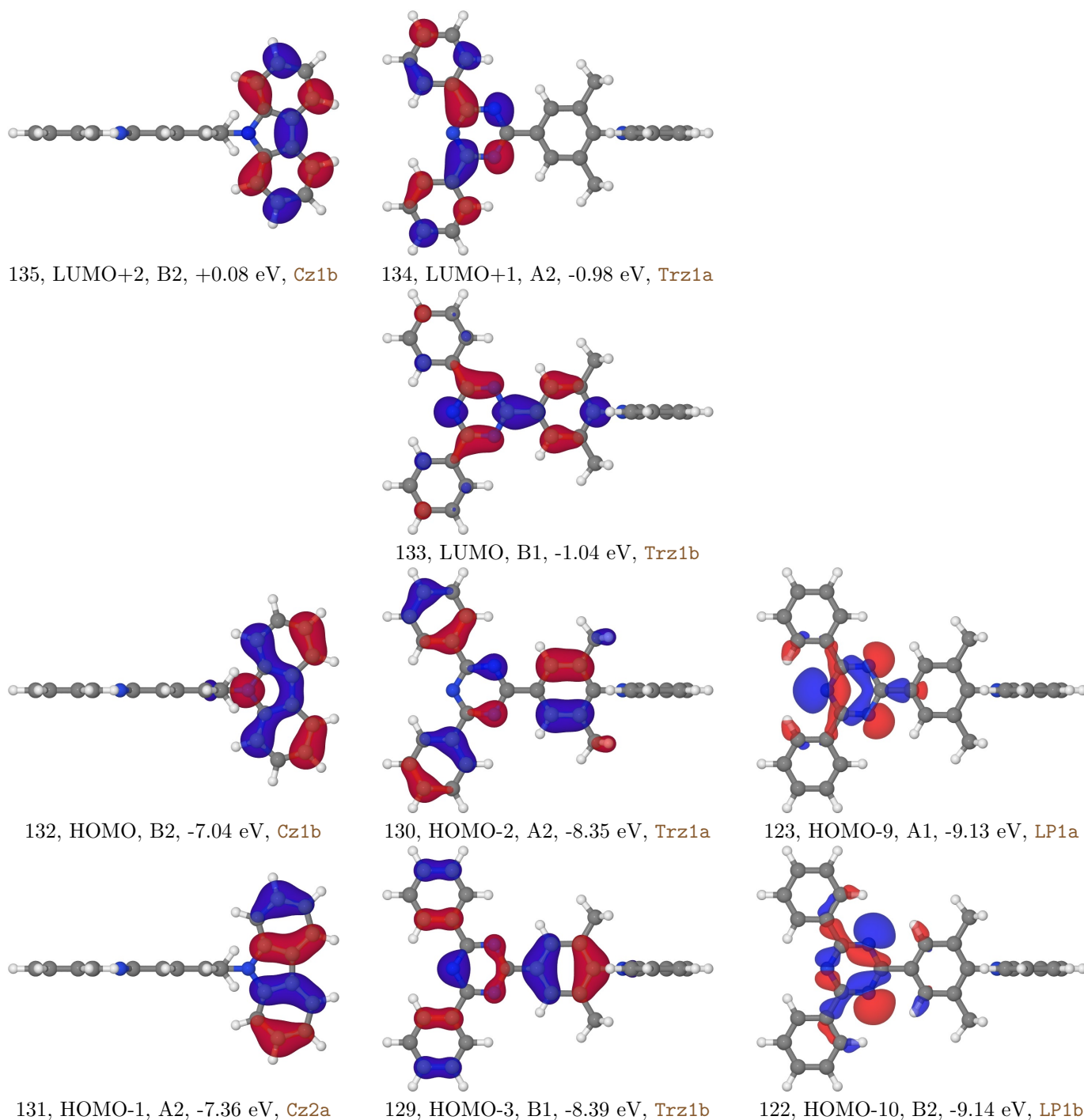


Figure S3: Frontier MOs. Listed are absolute and relative MO numbers, symmetry, CAM-B3LYP energy, and reference code. Two deep occupied MOs are included because their relative energy is sensitive to SCF and SCRF. Beyond the shown frontier MOs are HOMO-4 at -8.48 eV (**Trz1a2**) and LUMO+3 at +0.35 eV (**Trz1b3**).

S4 Excited states

Table S1: Lowest excited states by TDDFT (in vacuum) grouped by excitation type: CT, LE on Cz, and LE on Trz of π - π^* ('Trz') and LP- π^* ('LP') kinds. The first two columns list the numerical and symbolic codes of excited states. For example, **CT21b** encodes the excitation from MO **Cz2** \equiv **Cz2a** to **Trz1b**, **Trz11A** encodes any excitation between the frontier MO-bands of Trz (124,125,127-130) and (133,134) of the symmetry A1. The 'h-e' column interprets excited states in terms of single excitations in the MO basis whenever a meaningful assignment can be made, whereas ε gives the corresponding MO energy differences. The rest of columns are grouped in blocks of two columns corresponding to singlet and triplet excitations. The first block lists excitation energies. The table is ordered and contiguous (no missing states) in singlet energies per each excitation type and symmetry. The δw is the deviation of the weight of the dominant singly excited Slater determinant in the transition density from 100%. The next block gives the deviation of those hole and electron orbitals from the MOs given in 'h-e' column (whenever is meaningful). The last block lists order number of the excited state, so that the table is complete till 12 singlets and 8 triplets. Note that local π - π^* excitations on Trz have complex wave-function and substantial intermixing of MOs due to high density of nearly degenerate one-electron levels especially in the valence band. In particular, triplets corresponding to h-e pairs 130-134 and 129-134 are ill-defined. Nevertheless, the two lowest π - π^* triplets on Trz of each symmetry are included in the table. The lowest states of each kind are marked by asterisk: CT state 1 **CT11b**, CS state 2 **CT11a**, LE on the donor 25 **Cz21** (nearly degenerate with 35 **Cz11**), LE on the acceptor 31 **Trz11A**.

	code	sym	h-e	ε (eV)	E (eV)		δw (%)		$\delta w_{\text{MO}}^{\text{h,e}}$ (%)		#	
1*	CT11b	A2	132-133	6.01	4.22	4.17	1	18	13,4	38,7	1	8
4	CT21b	B2	131-133	6.33	4.90	4.89	4	0	4,7	1,8	10	24
2*	CT11a	B1	132-134	6.08	5.04	5.03	0	0	3,3	1,3	14	26
3	CT21a	A1	131-134	6.40	5.44	5.44	0	0	0,1	0,1	17	31
35	Cz11	A1	132-135	7.28	4.47	3.55	14	16	0,0	5,5	2	5
25*	Cz21	B1	131-135	7.60	4.91	3.09	20	31	2,0	8,1	11	2
31*	Trz11A	A1	129-133	7.39	4.88	2.97	27	59	39,4	7,4	9	1
	Trz11A	A1	129-133	7.39	—	3.23	—	55	—	51,25	—	3
	Trz11A	A1	125-134	7.76	5.03	4.23	47	44	0,2	7,8	13	12
32	Trz11A	A1	130-134	7.42	5.15	5.75	44	1	27,0	58,6	16	33
41	Trz11B	B2	130-133	7.35	4.73	3.92	22	1	15,6	47,23	7	6
42	Trz11B	B2	129-134	7.46	4.87	4.82	53	30	22,3	5,5	8	23
	Trz11B	B2	127-134	7.63	4.97	3.28	50	56	43,0	34,12	12	4
	Trz11B	B2	124-134	7.77	5.09	4.24	41	40	15,2	10,8	15	13
11	LP1b1b	A2	122-133	8.18	4.54	4.26	38	37	3,5	70,9	3	14
12	LP1a1a	A2	123-134	8.24	4.61	4.44	38	47	1,5	0,5	5	16
21	LP1a1b	B1	123-133	8.17	4.61	4.07	12	40	1,7	1,8	4	7
22	LP1b1a	B1	122-134	8.25	4.66	4.23	13	41	4,5	3,6	6	11

Table S2: Lowest excited states by CIS-DFT. See Table S1 for notations. The E^{water} is the excitation energy in water calculated using state-specific solvation such that the molecule is in its ground-state geometry and the PCM solvent is self-consistently polarized by the excited state density. Note that during SCRF iterations, states might change their identity in terms of ‘h-e’ classification, so that some states are marked with ‘-’. The $E^{\text{water}}_{\text{LR}}$ is obtained by the linear response (“CorrectedLR” keyword) with both zero- and high-frequency dielectric constants set to 80. Apparently, this approach gives meaningful results only for singlets. The table is complete till 17 singlets and 10 triplets.

	code	sym	h-e	$E(\text{eV})$		$E^{\text{water}}(\text{eV})$		$E^{\text{water}}_{\text{LR}}(\text{eV})$		#	
1*	CT11b	A2	132-133	4.22	4.18	1.97	1.98	3.54	4.07	1	8
4	CT21b	B2	131-133	4.89	4.89	1.91	1.91	3.98		8	24
2*	CT11a	B1	132-134	5.03	5.03	1.32	1.32	3.65		11	25
3	CT21a	A1	131-134	5.44	5.44	1.28	1.28	3.97		17	31
35	Cz11	A1	132-135	4.58	3.72	4.56	3.66	4.56	3.69	3	5
25*	Cz21	B1	131-135	5.04	3.57	5.03	3.61	5.04	3.59	12	2
31*	Trz11A	A1	129-133	5.01	3.45	5.29	3.45	4.85	3.45	10	1
	Trz11A	A1		5.10	3.66	4.71	3.64	5.04		14	3
32	Trz11A	A1	130-134	5.37	5.75	3.51	–	5.34	3.65	16	33
41	Trz11B	B2	130-133	4.79	3.99	–	3.65	4.72	3.85	7	6
	Trz11B	B2		4.93	3.70	4.84	3.67	4.92	3.69	9	4
42	Trz11B	B2	129-134	5.10	4.75	4.92	4.69	4.98	4.22	13	19
	Trz11B	B2		5.16	4.30		4.09	5.10		15	13
11	LP1b1b	A2	122-133	4.55	4.28	4.54	4.23	4.57	4.47	2	10
12	LP1a1a	A2	123-134	4.64	4.47	4.64	4.48	4.64	4.13	5	14
21	LP1a1b	B1	123-133	4.64	4.13	4.58	4.08	4.63	4.13	4	7
22	LP1b1a	B1	122-134	4.70	4.27	–	4.26	4.68	4.26	6	9

Table S3: Lowest excited states by ΔSCF . See Table S1 for notations. The CT21a triplet in vacuum is not in the table because it converges to Trz11A.

	code	sym	h-e	$E(\text{eV})$		$E^{\text{water}}(\text{eV})$		$\delta w_{\text{MO}}^{\text{h,e}}(\%)$	
1*	CT11b	A2	132-133	4.07	4.08	3.39	3.39	3,13	3,13
4	CT21b	B2	131-133	4.75	4.77	3.84	3.84	4,10	28,4
2*	CT11a	B1	132-134	4.87	4.85	3.62	3.62	28,2	3,14
3	CT21a	A1	131-134	–	–	–	4.00	–	–
35	Cz11	A1	132-135	–	3.89	–	3.86	–	1,0
25*	Cz21	B1	131-135	4.53	3.83	4.54	3.85	0,0	2,2
31*	Trz11A	A1	129-133	–	3.70	–	3.67	–	31,21
32	Trz11A	A1	130-134	–	4.07	–	4.07	–	50,3
41	Trz11B	B2	130-133	4.69	4.04	4.63	3.88	9,2	48,21
42	Trz11B	B2	129-134	4.66	4.52	4.61	4.48	31,1	34,1
11	LP1b1b	A2	122-133	4.36	4.33	4.35	4.31	5,7	5,7
12	LP1a1a	A2	123-134	4.43	4.42	4.42	4.41	1,5	1,5
21	LP1a1b	B1	123-133	4.30	4.19	4.27	4.15	2,9	2,10
22	LP1b1a	B1	122-134	4.37	4.27	4.34	4.24	3,7	3,7

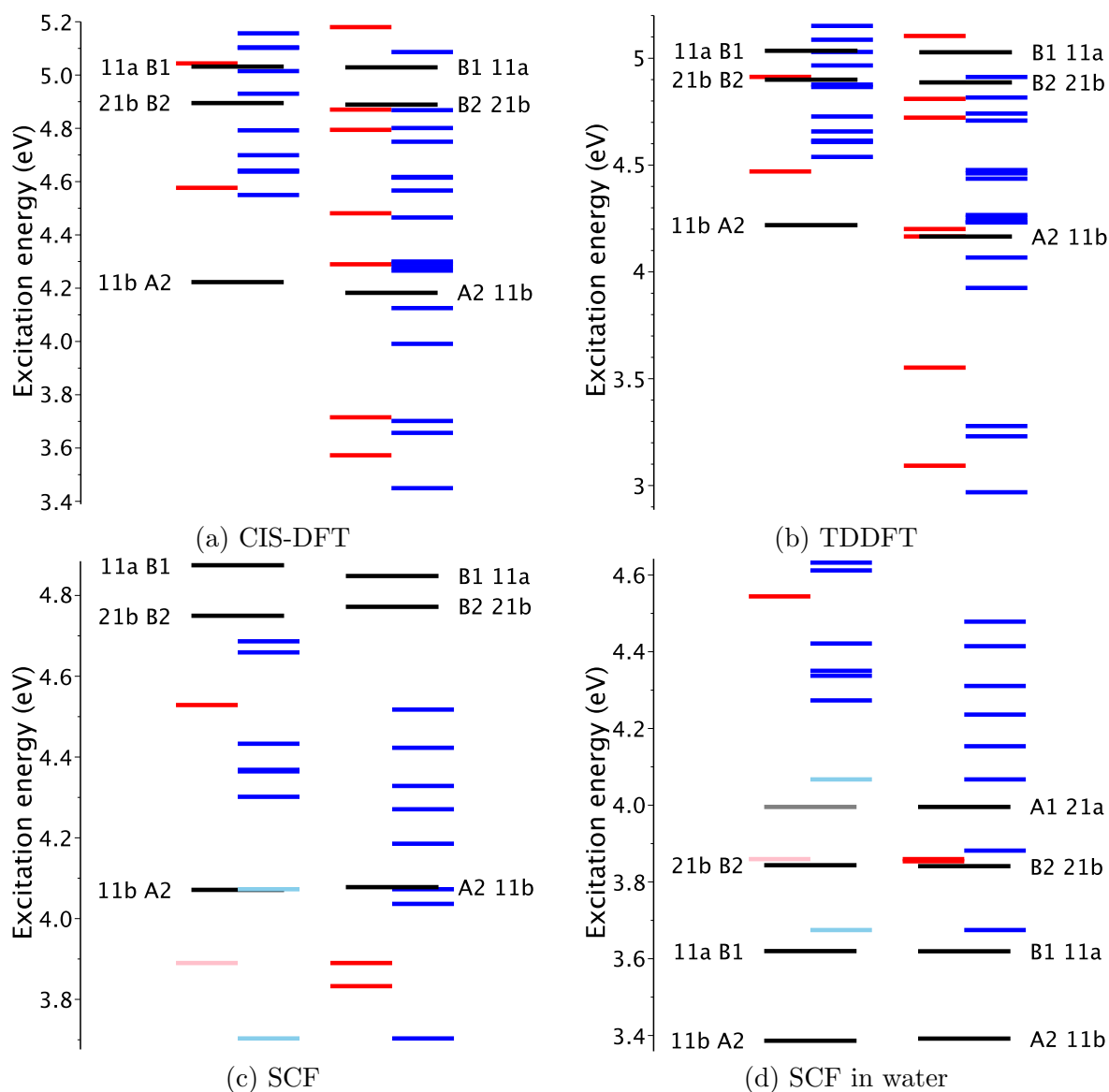
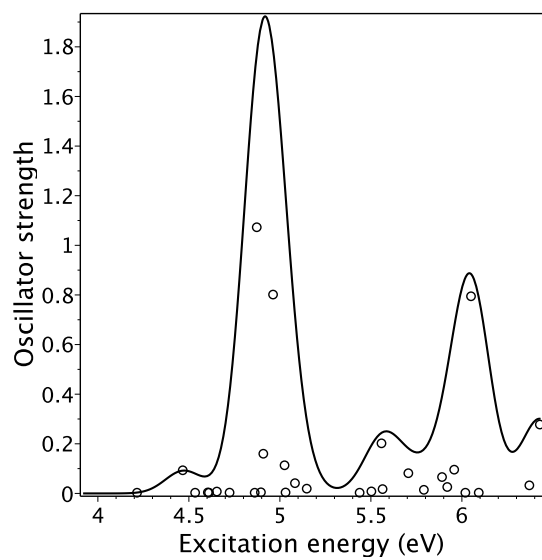
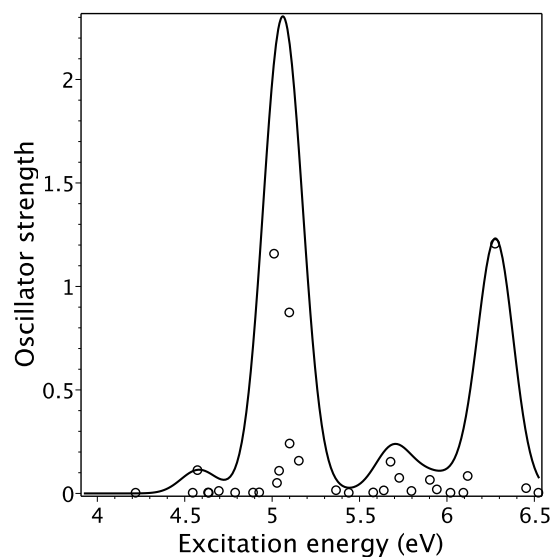


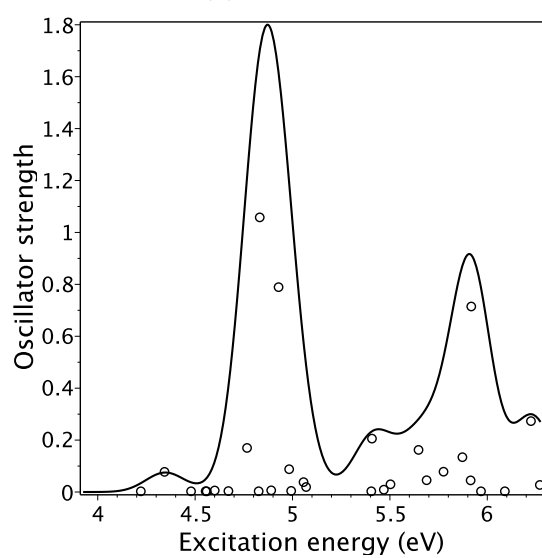
Figure S4: Excited states calculated by CAM-B3LYPp2p. In each panel, singlets are on the left and triplets are on the right. Local excitations on the donor and acceptor are colored in red and blue, charge transfer states are shown in black. In SCF approach, only a few lowest excitations per symmetry and localization type are calculated. Full symmetry singlets converge to the ground state, they are shown at the corresponding triplet energy in light color.



(a) TDDFT

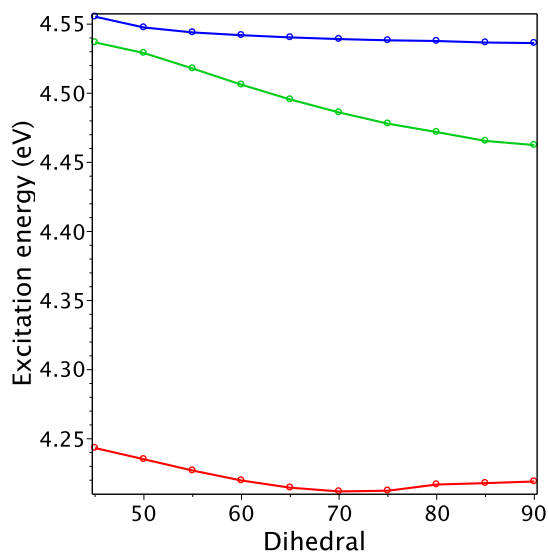


(b) CIS-DFT

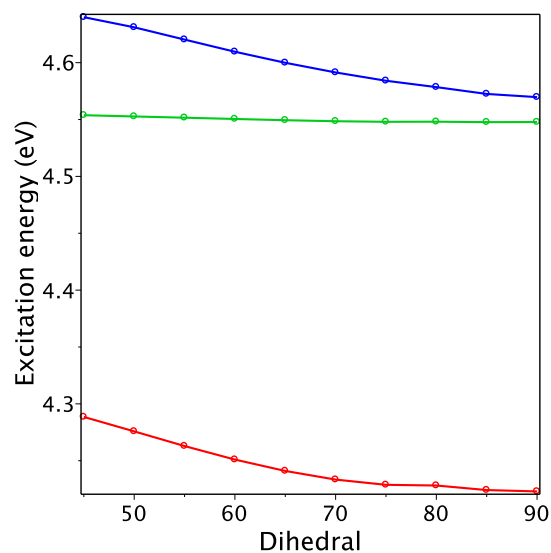


(c) TDDFT by CAM-B3LYPa3p

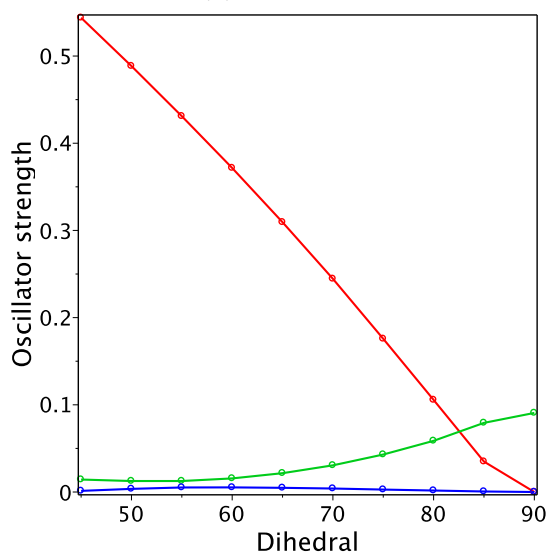
Figure S5: Oscillator strength of excited states.



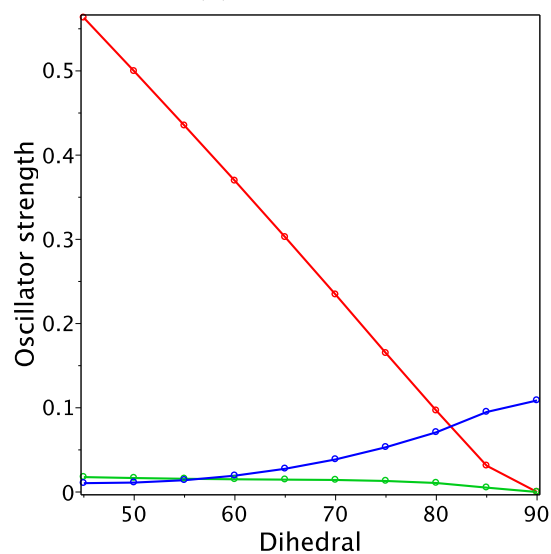
(a) TDDFT



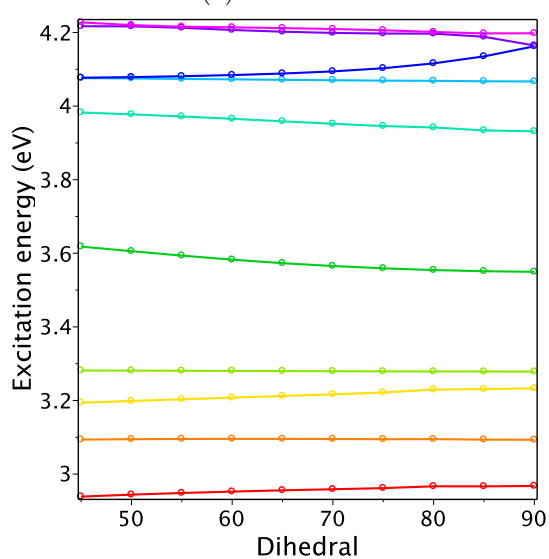
(b) CIS-DFT



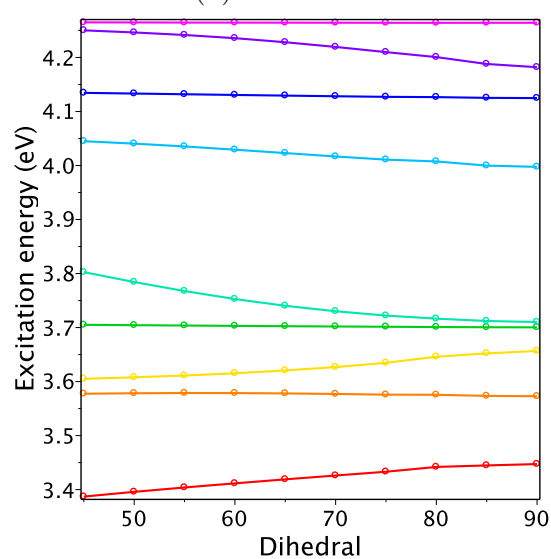
(c) TDDFT



(d) CIS-DFT

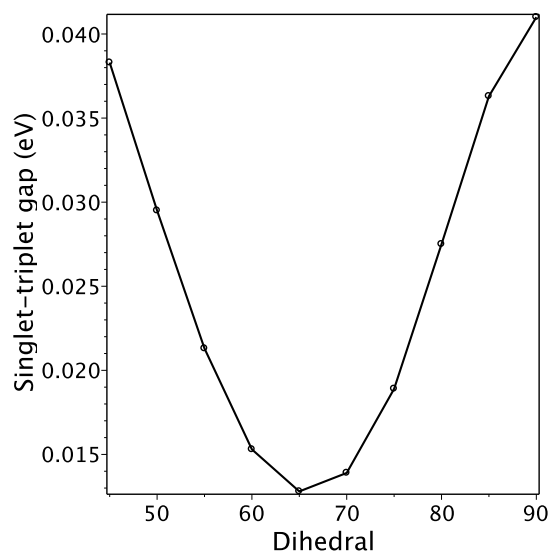


(e) TDDFT triplets

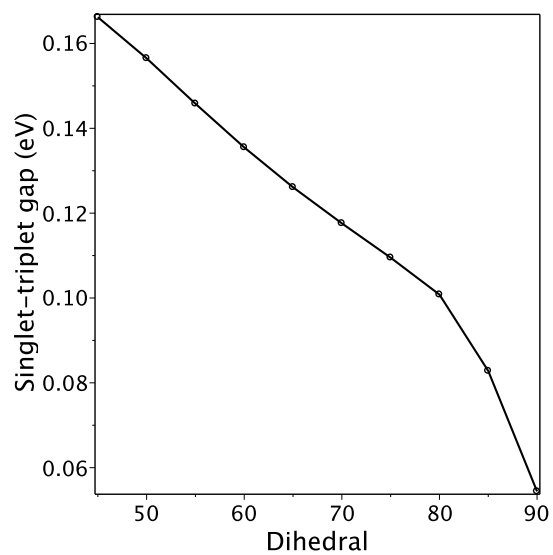


(f) CIS-DFT triplets

Figure S6: Dependence of energy and oscillator strength on dihedral angle. The CT state is the lowest for singlets (red color) and the next to the highest shown for triplets (violet color).



(a) CIS-DFT



(b) TDDFT

Figure S7: Singlet-triplet gap for CT-state.

References

- [Froitzheim24] T Froitzheim, L Kunze, S Grimme, J Herbert, J Mewes, Benchmarking Charge-Transfer Excited States in TADF Emitters: Delta-DFT Outperforms TD-DFT for Emission Energies, *JPCA* 128, 6324 (2024)
- [Gaussian] M J Frisch et al, Gaussian 16, Revision A.03 (Gaussian Inc, Wallingford CT, 2016)
- [Liang22] J Liang, X Feng, D Hait, M Head-Gordon, Revisiting the Performance of Time-Dependent Density Functional Theory for Electronic Excitations: Assessment of 43 Popular and Recently Developed Functionals from Rungs One to Four, *JCTC* 18, 3460 (2022)
- [Tukachev19] N V Tukachev, D R Maslennikov, A Y Sosorev, S Tretiak, A Zhugayevych, Ground state geometry and vibrations of polyphenylenevinylene oligomers, *J Phys Chem Lett* 10, 3232 (2019)
- [VASP] G Kresse, J Furthmuller, Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set, *Phys Rev B* 54, 11169 (1996)
- [Valverde25] D Valverde, G Ricci, J Sancho-Garcia, D Beljonne, Y Olivier, Can DeltaSCF and ROKS DFT-Based Methods Predict the Inversion of the Singlet-Triplet Gap in Organic Molecules?, *JCTC* 21, 2558 (2025)
- [Yanai04] T Yanai, D P Tew, N C Handy, A new hybrid exchange-correlation functional using the Coulomb-attenuating method (CAM-B3LYP), *Chem Phys Lett* 393, 51 (2004)
- [Zhugayevych16] A Zhugayevych, O Postupna, H L Wang, S Tretiak, Modification of optoelectronic properties of conjugated oligomers due to donor/acceptor functionalization: DFT study, *Chem Phys* 481, 133 (2016)
- [Zhugayevych18] A Zhugayevych, O Mazaleva, A Naumov, S Tretiak, Lowest-energy crystalline polymorphs of P3HT, *J Phys Chem C* 122, 9141 (2018)
- [Zhugayevych23b] A Zhugayevych, W Sun, T van der Heide, C Lien-Medrano, T Frauenheim, S Tretiak, Benchmark Data Set of Crystalline Organic Semiconductors, *J Chem Theory Comput* 19, 8481 (2023)