Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Dynamic nature of excited states of donor-acceptor TADF materials for OLEDs: how theory can reveal structure-property relationships.

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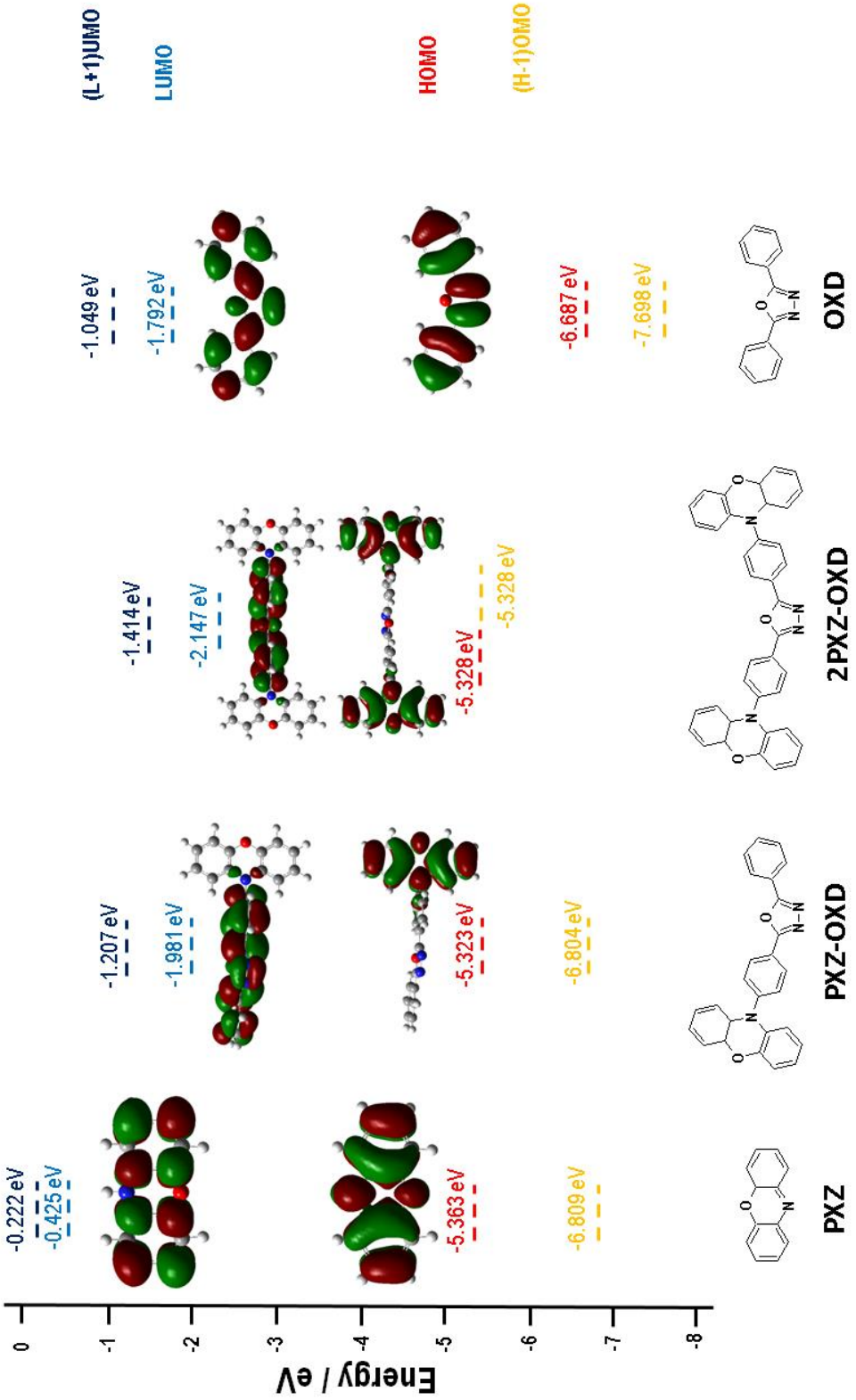


Figure S1: Isocontour plots (cutoff=0.02 a.u.) and energies of the frontier orbitals (HOMO and LUMO), calculated at the PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene), where the PXD donor (left) is combined with the OXD acceptor (right) giving rise to the PXZ-OXD and 2PXZ-OXD equatorial conformers (center). The size and color describe the amplitude and sign, respectively, of the lobes of orbitals.

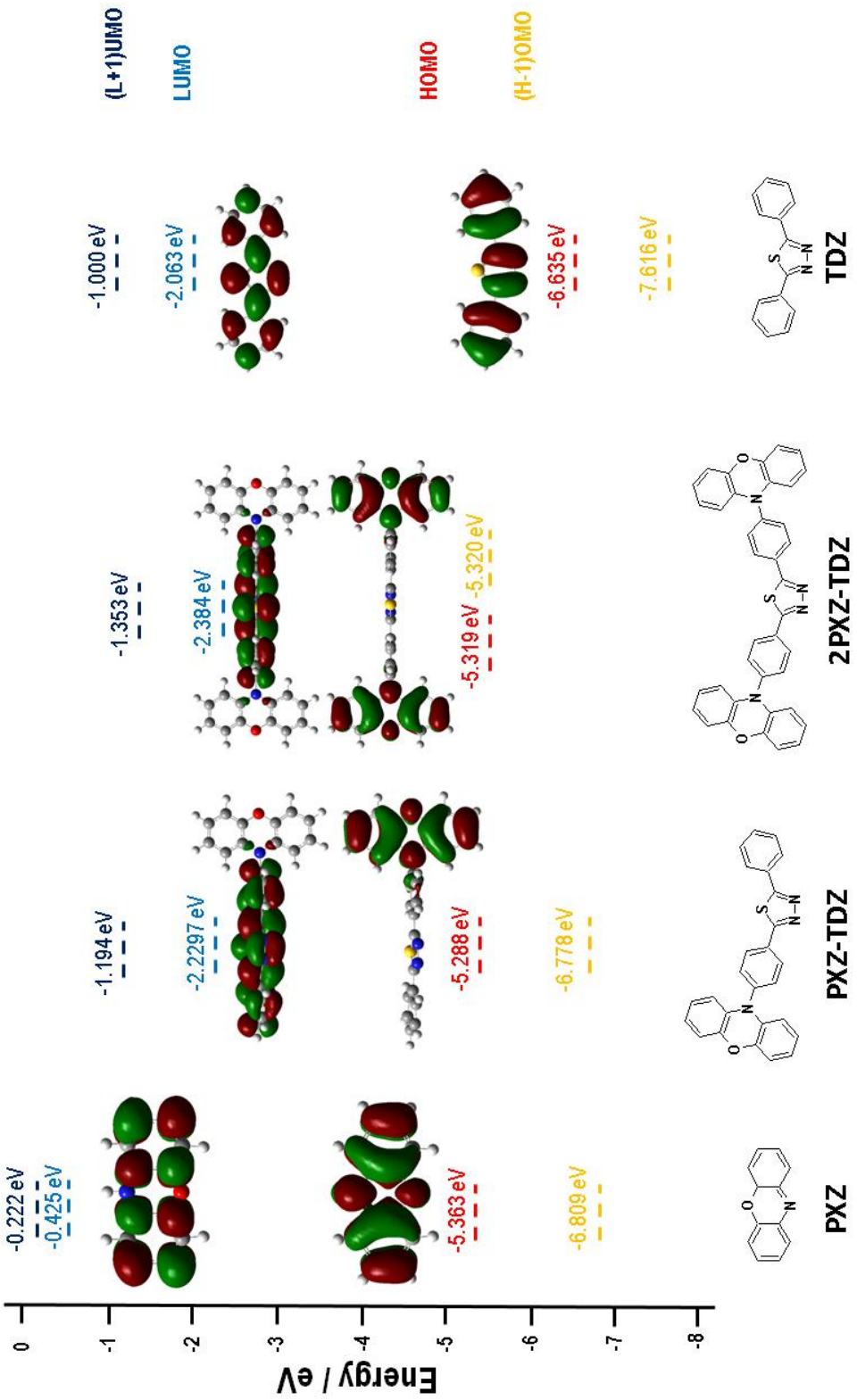


Figure S2: Isocontour plots (cutoff= 0.02 a.u.) and energies of the frontier orbitals (HOMO and LUMO), calculated at the PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene), where the PXZ donor (left) is combined with the TDZ acceptor (right) giving rise to the PXZ-TDZ and 2PXZ-TDZ equatorial conformers (center). The size and color describe the amplitude and sign, respectively, of the lobes of orbitals.

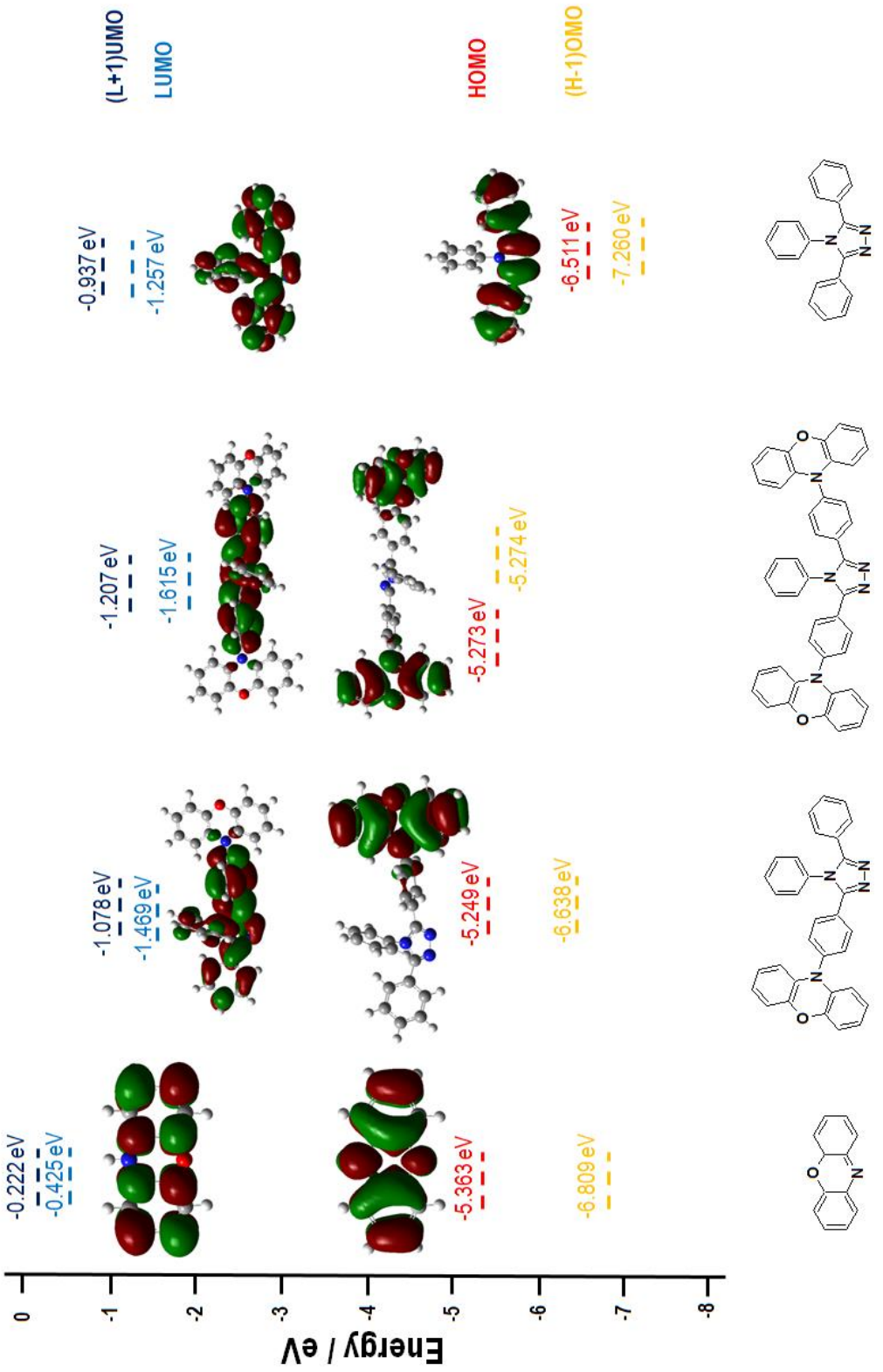


Figure S3: Isocontour plots (cutoff= 0.02 a.u.) and energies of the frontier orbitals (HOMO and LUMO), calculated at the PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene), where the PXZ donor (left) is combined with the TAZ acceptor (right) giving rise to the PXZ-TAZ and 2PXZ-TAZ equatorial conformers (center). The size and color describe the amplitude and sign, respectively, of the lobes of orbitals.

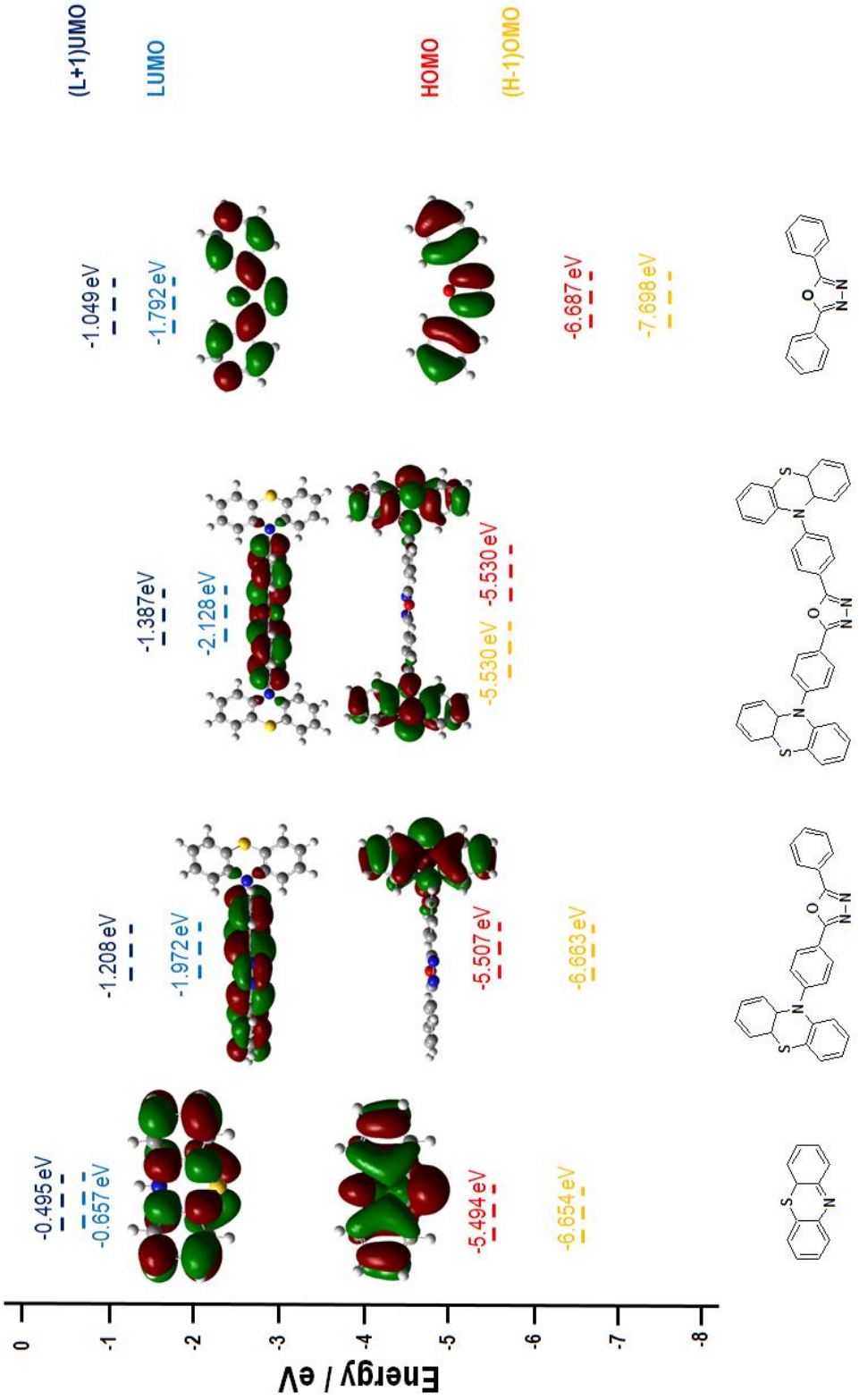


Figure S4: Isocontour plots (cutoff= 0.02 a.u.) and energies of the frontier orbitals (HOMO and LUMO), calculated at the PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene), where the PTZ donor (left) is combined with the OXD acceptor (right) giving rise to the PTZ-OXD and 2PTZ-OXD equatorial conformers (center). The size and color describe the amplitude and sign, respectively, of the lobes of orbitals.

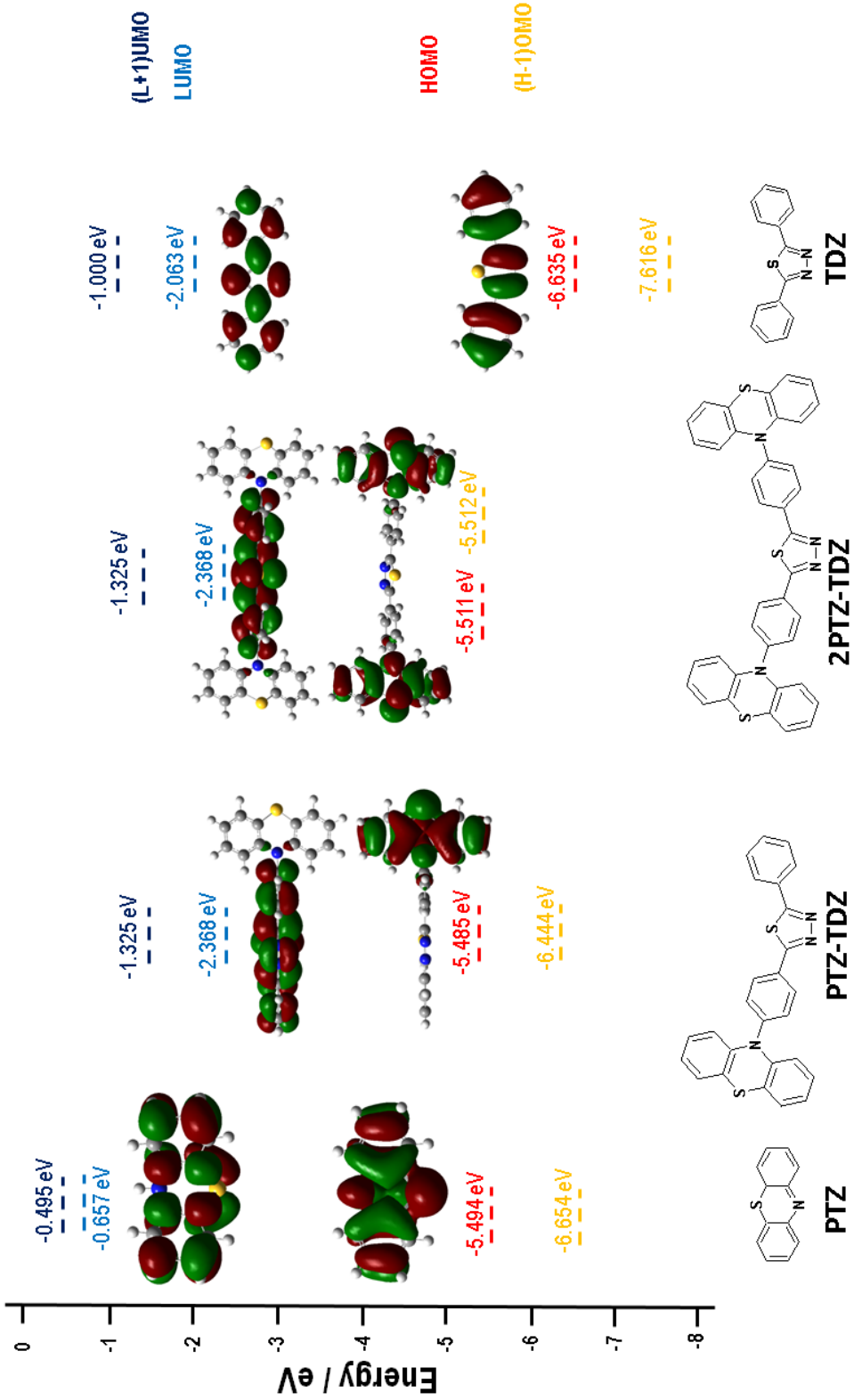


Figure S5: Isocontour plots (cutoff= 0.02 a.u.) and energies of the frontier orbitals (HOMO and LUMO), calculated at the PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene), where the PTZ donor (left) is combined with the TDZ acceptor (right) giving rise to the PTZ-TDZ and 2PTZ-TDZ equatorial conformers (center). The size and color describe the amplitude and sign, respectively, of the lobes of orbitals.

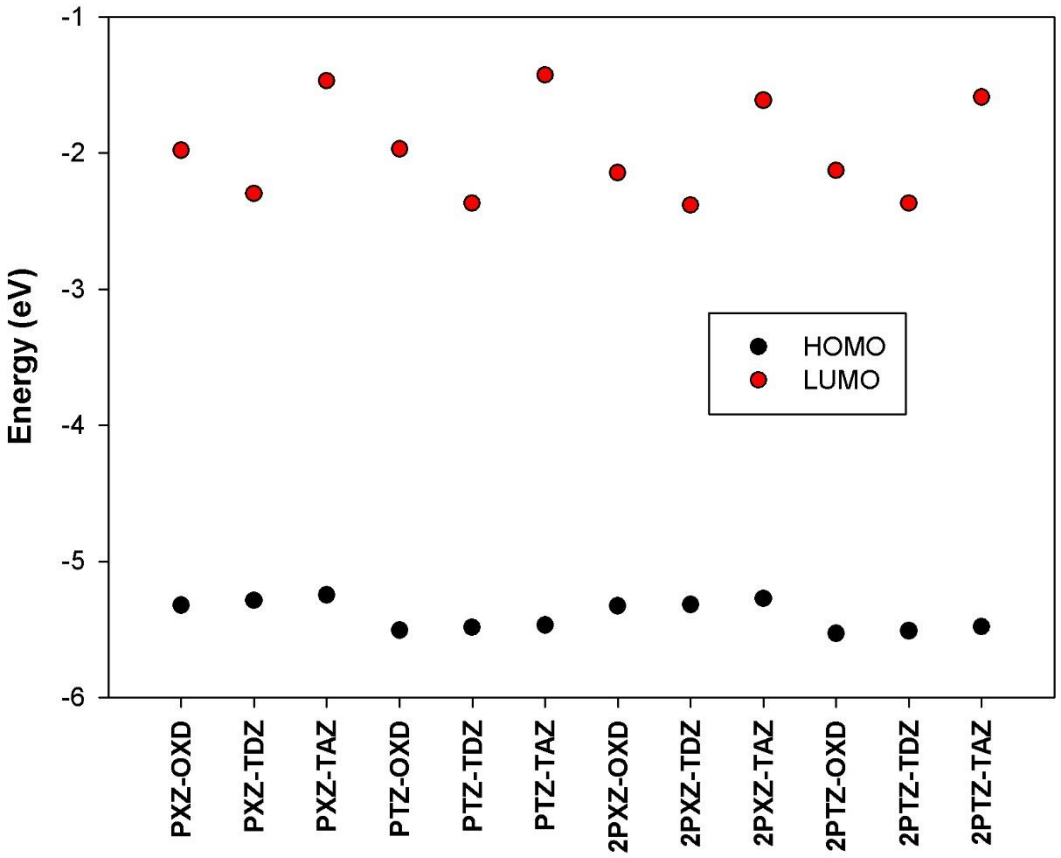


Figure S6: Comparison between the HOMO and LUMO energies of all compounds studied computed at the PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene).

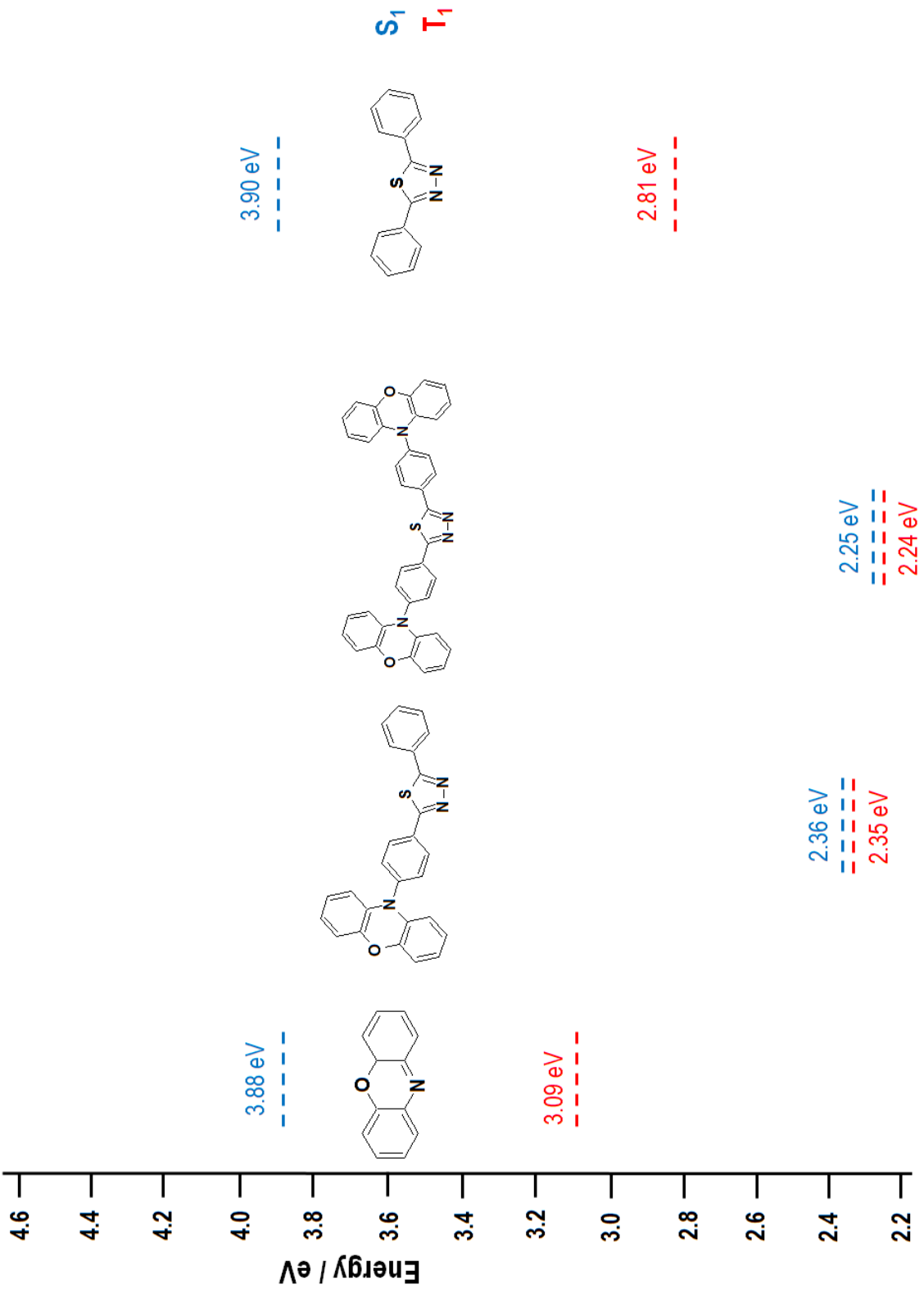


Figure S7: Excited states energy diagram, computed at the TDA-PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene), for the case where PXZ donor (left) is combined with TDZ acceptor (right) moieties giving rise to the PXZ-TDZ and 2PXZ-TDZ equatorial conformers (center).

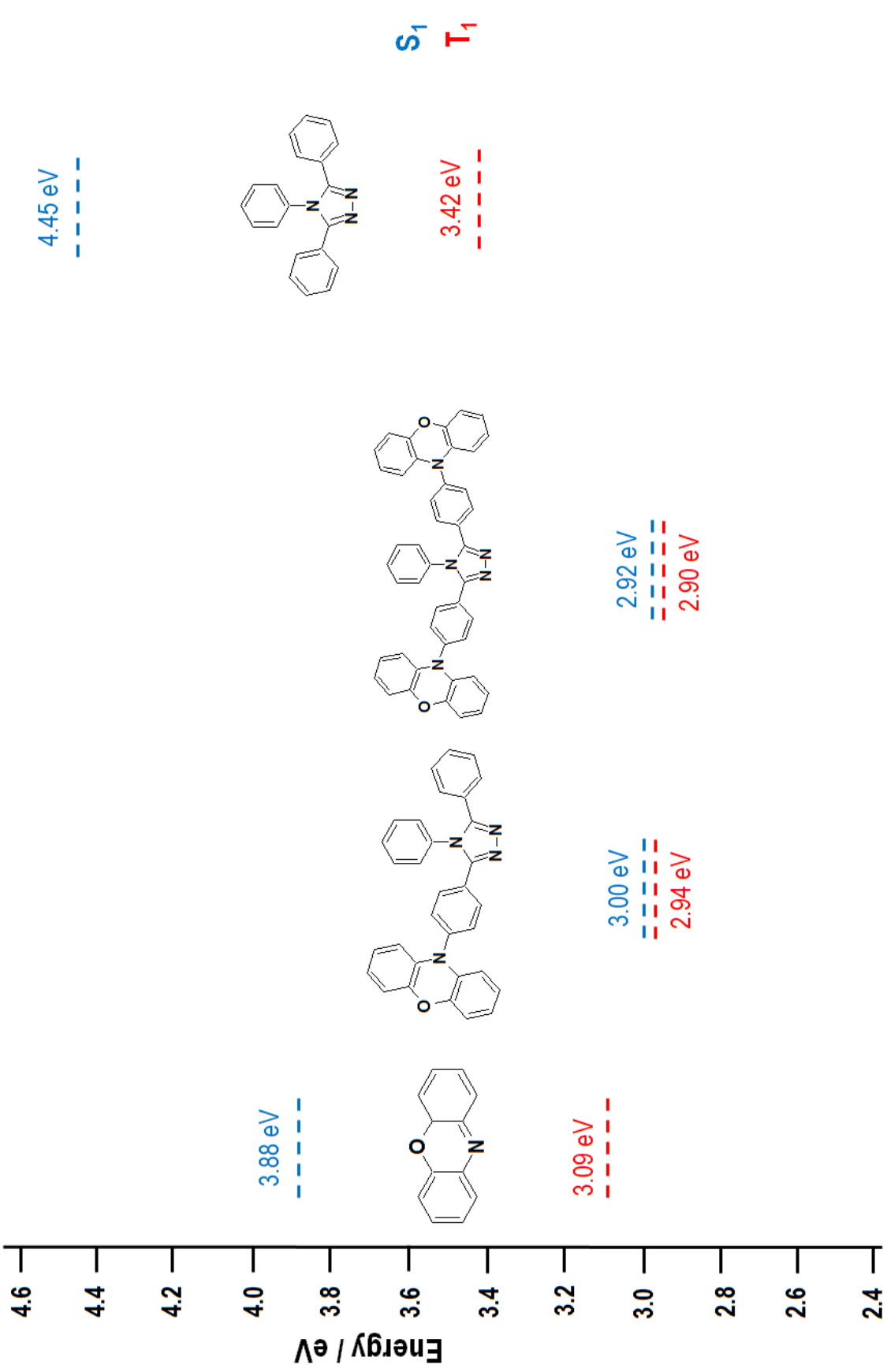


Figure S8: Excited states energy diagram, computed at the TDA-PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene), for the case where PXZ donor (left) is combined with TAZ acceptor (right) moieties giving rise to the PXZ-TAZ and 2PXZ-TAZ equatorial conformers (center).

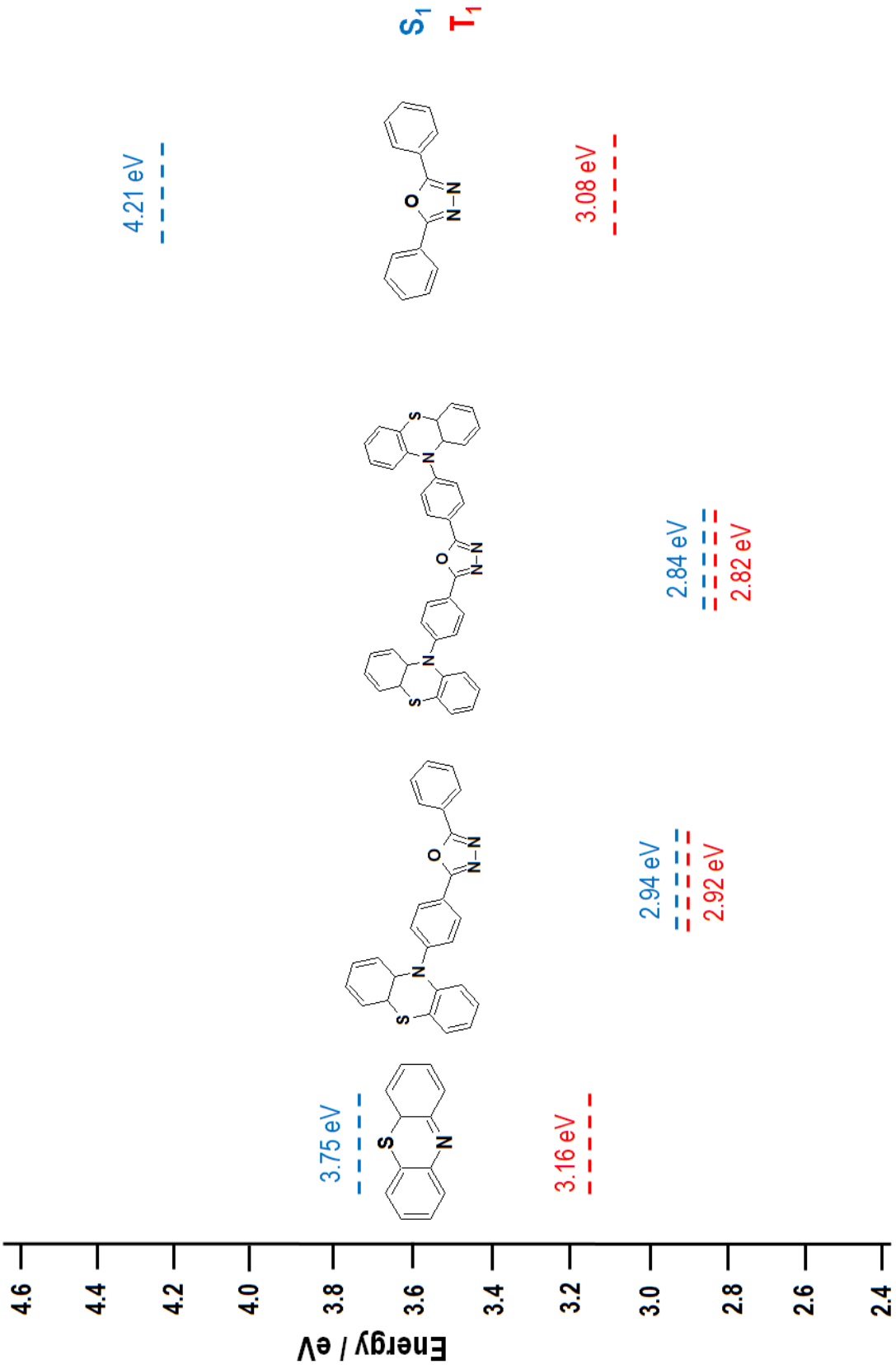


Figure S9: Excited states energy diagram, computed at the TDA-PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene), for the case where PTZ donor (left) is combined with OXD acceptor (right) moieties giving rise to the PTZ-OXD and 2PTZ-OXD equatorial conformers (center).

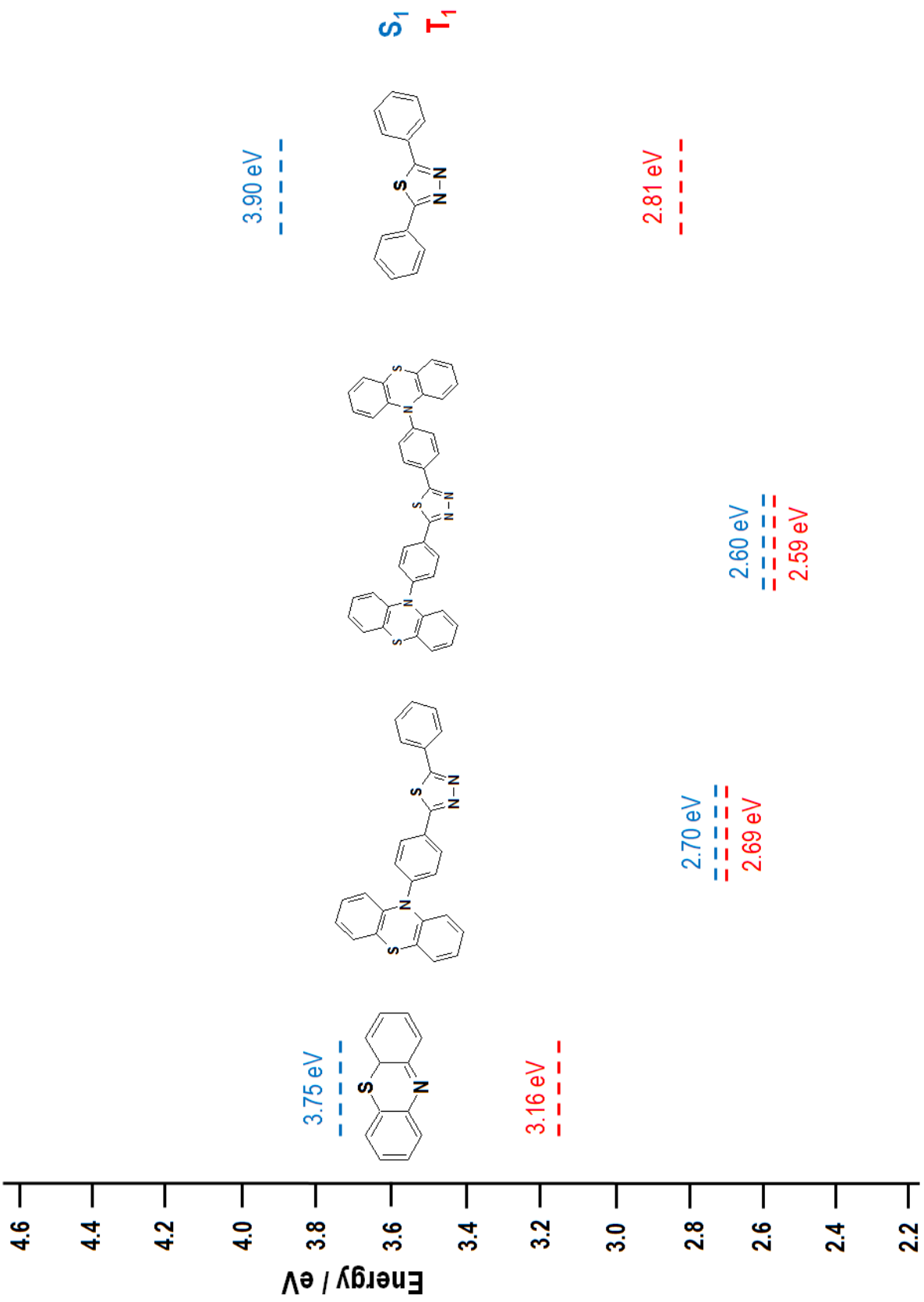


Figure S10: Excited states energy diagram, computed at the TDA-PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene), for the case where PTZ donor (left) is combined with TDZ acceptor (right) moieties giving rise to the PTZ-TDZ and 2PTZ-TDZ equatorial conformers (center).

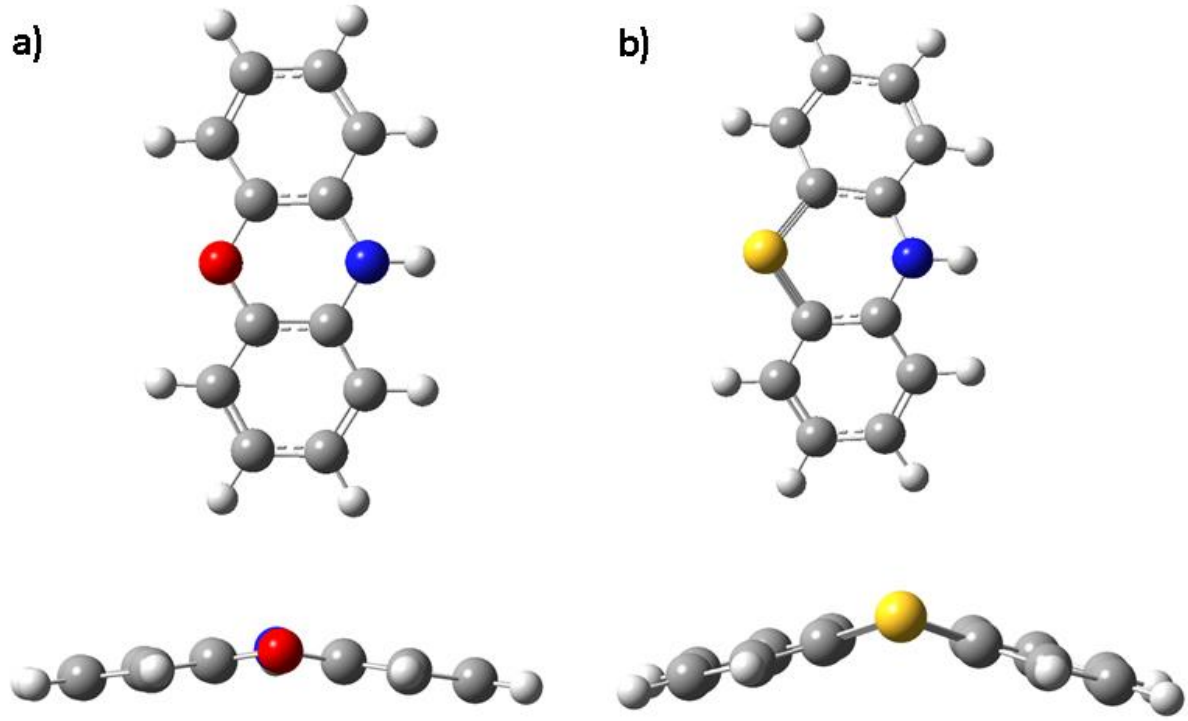
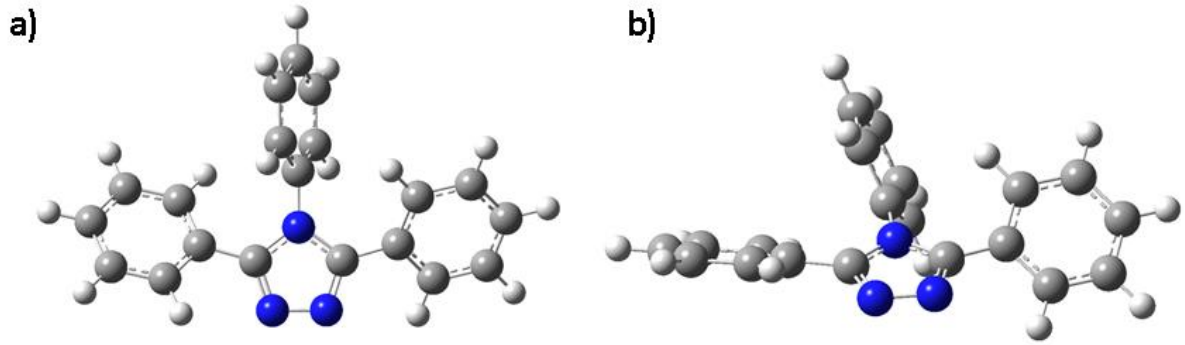


Figure S11: Front and side views of **a)** PXZ and **b)** PTZ electron donors.



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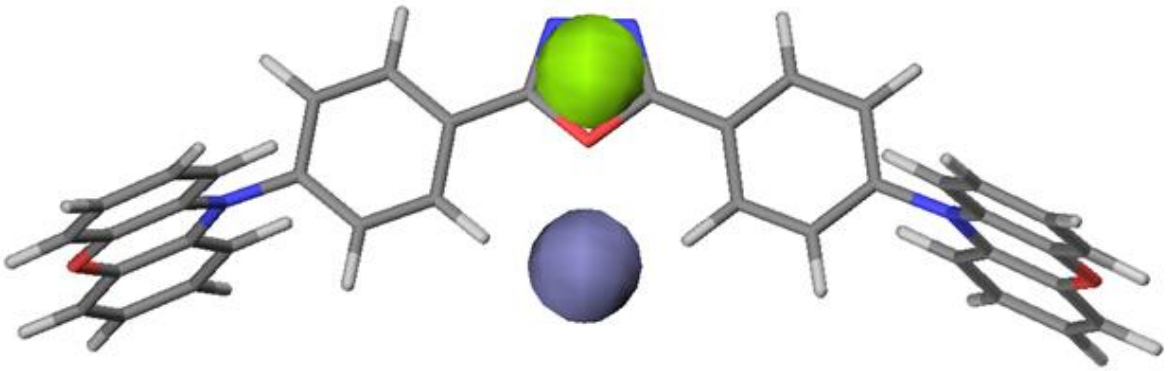

Figure S13: Hole (in blue) and electron (in green) density centroids of 2PXZ-OXD calculated in the attachment/detachment formalism

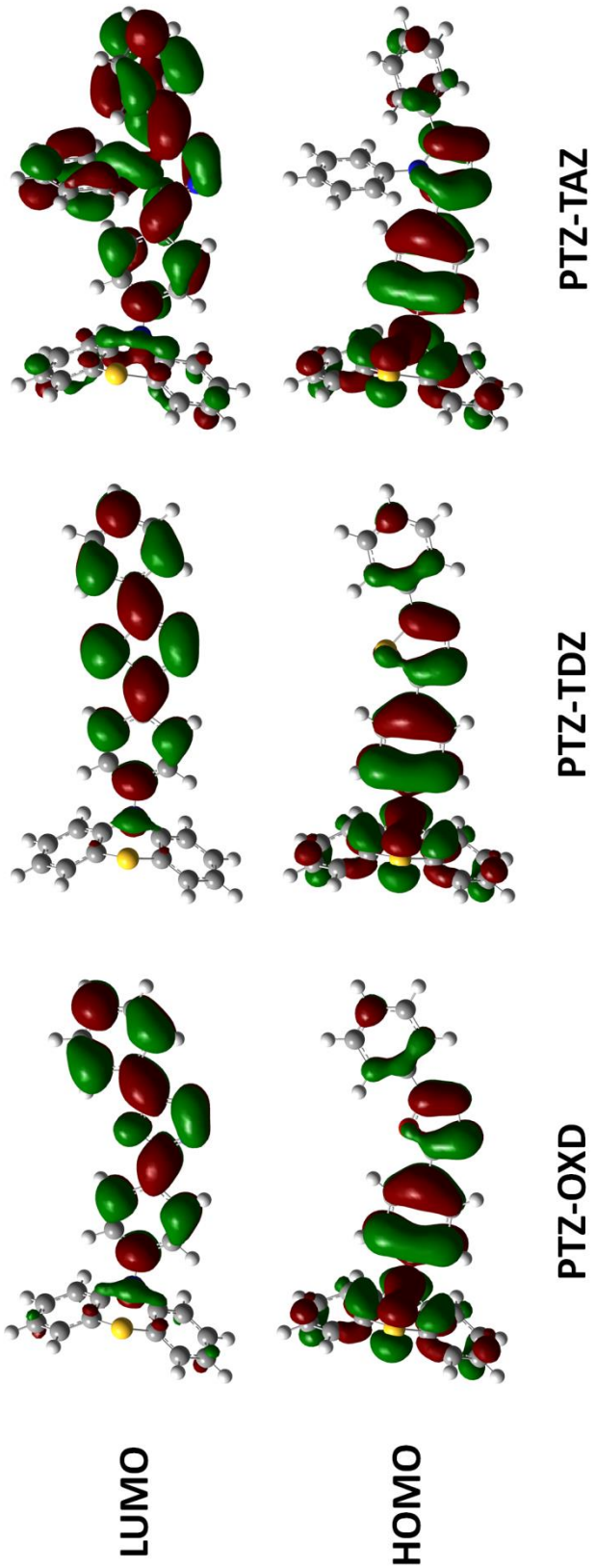

Figure S14: Isocontour plots (cutoff= 0.02 a.u.) of the frontier orbitals (HOMO and LUMO), computed at the PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene), for the case of PTZ-OXD, PTZ-TDZ and PTZ-TAZ axial conformers (center). The size and color describe the amplitude and sign, respectively, of the lobes of orbitals.

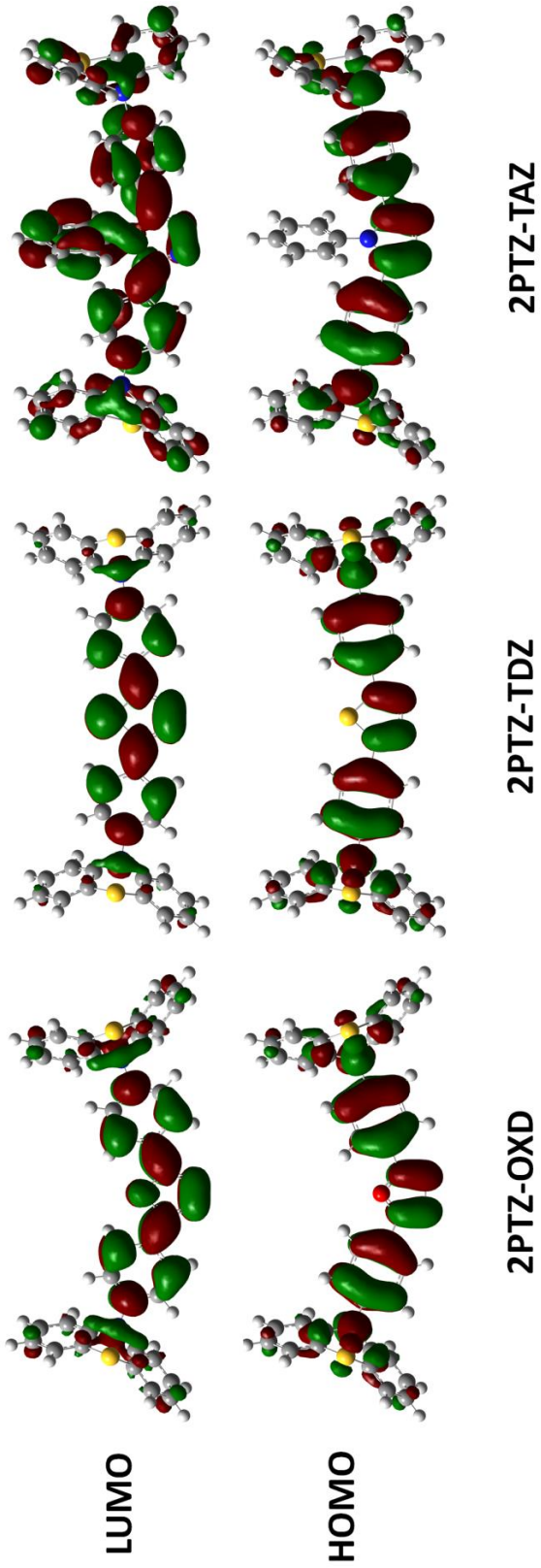

Figure S15: Isocontour plots (cutoff= 0.02 a.u.) of the calculated frontier orbitals (HOMO and LUMO), computed at the PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene), for the case of 2PTZ-OXD, 2PTZ-TDZ and 2PTZ-TAZ axial conformers (center). The size and color describe the amplitude and sign, respectively, of the lobes of orbitals.

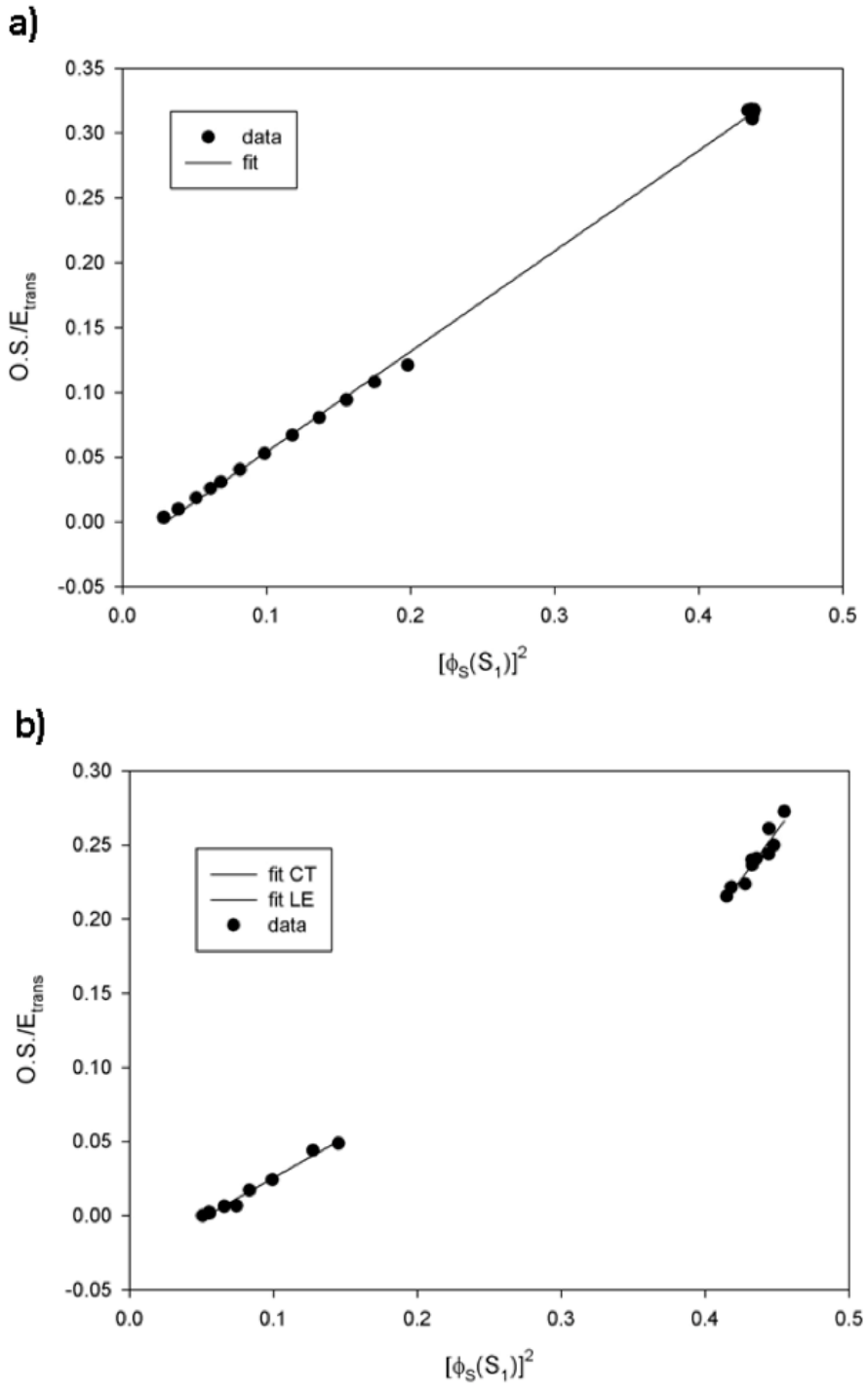

Figure S16: Oscillator strength normalized to the S_1 excitation energy as a function of $\phi_S^2(S_1)$ for **a)** PXZ-OXD and **b)** PTZ-TAZ. The straight lines represent linear fits of the data. For PTZ-TAZ, two different linear fits are required in order to interpolate the data corresponding to CT- and LE-dominated excitations.

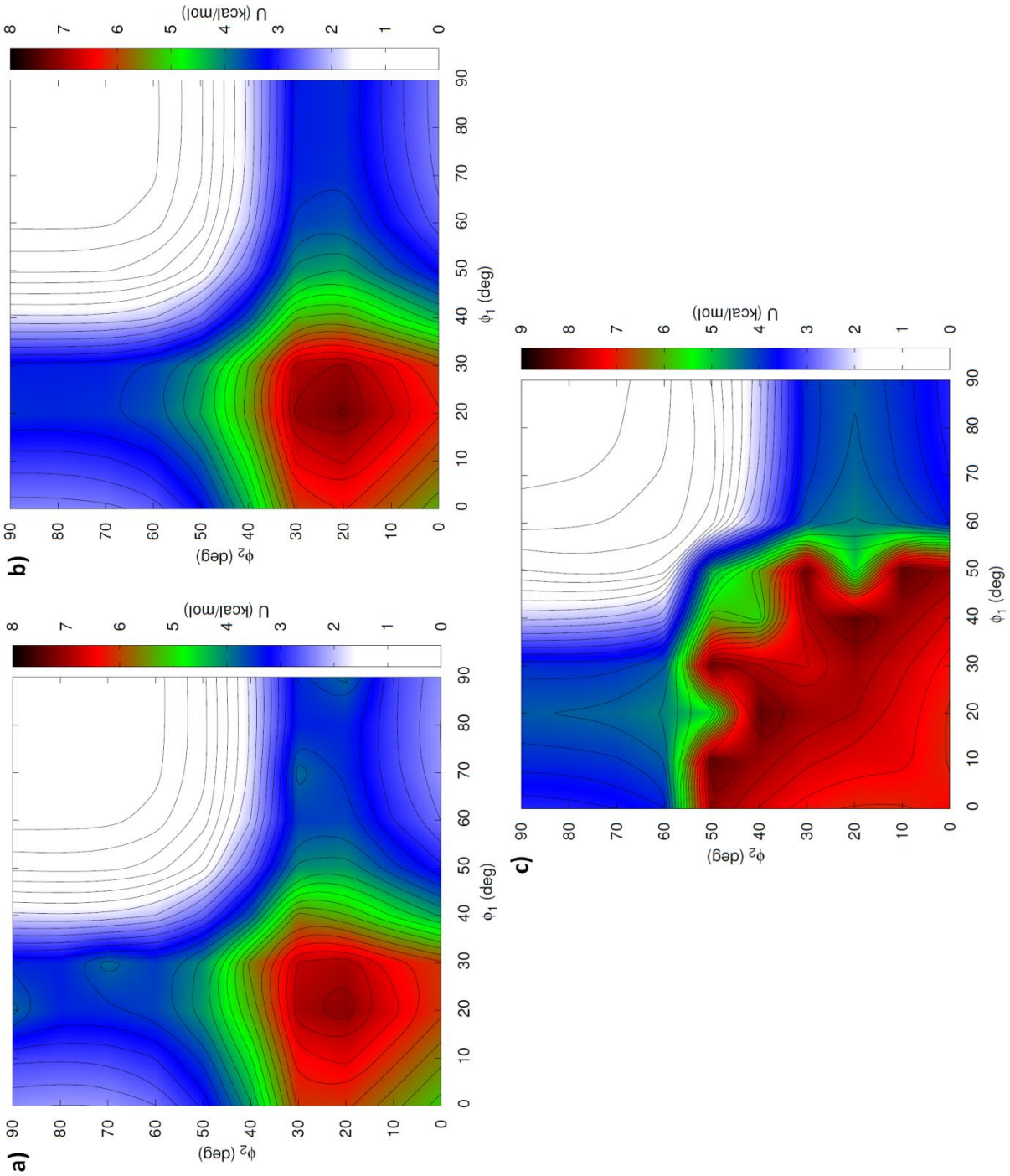

Figure S17: Two-dimensional torsion energy profiles (in kcal/mol), calculated at the PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene), as a function of the two D-A dihedral angles ϕ_1 and ϕ_2 between the PXZ donors and the three different acceptors (**a)** OXD, **b)** TDZ and **c)** TAZ).

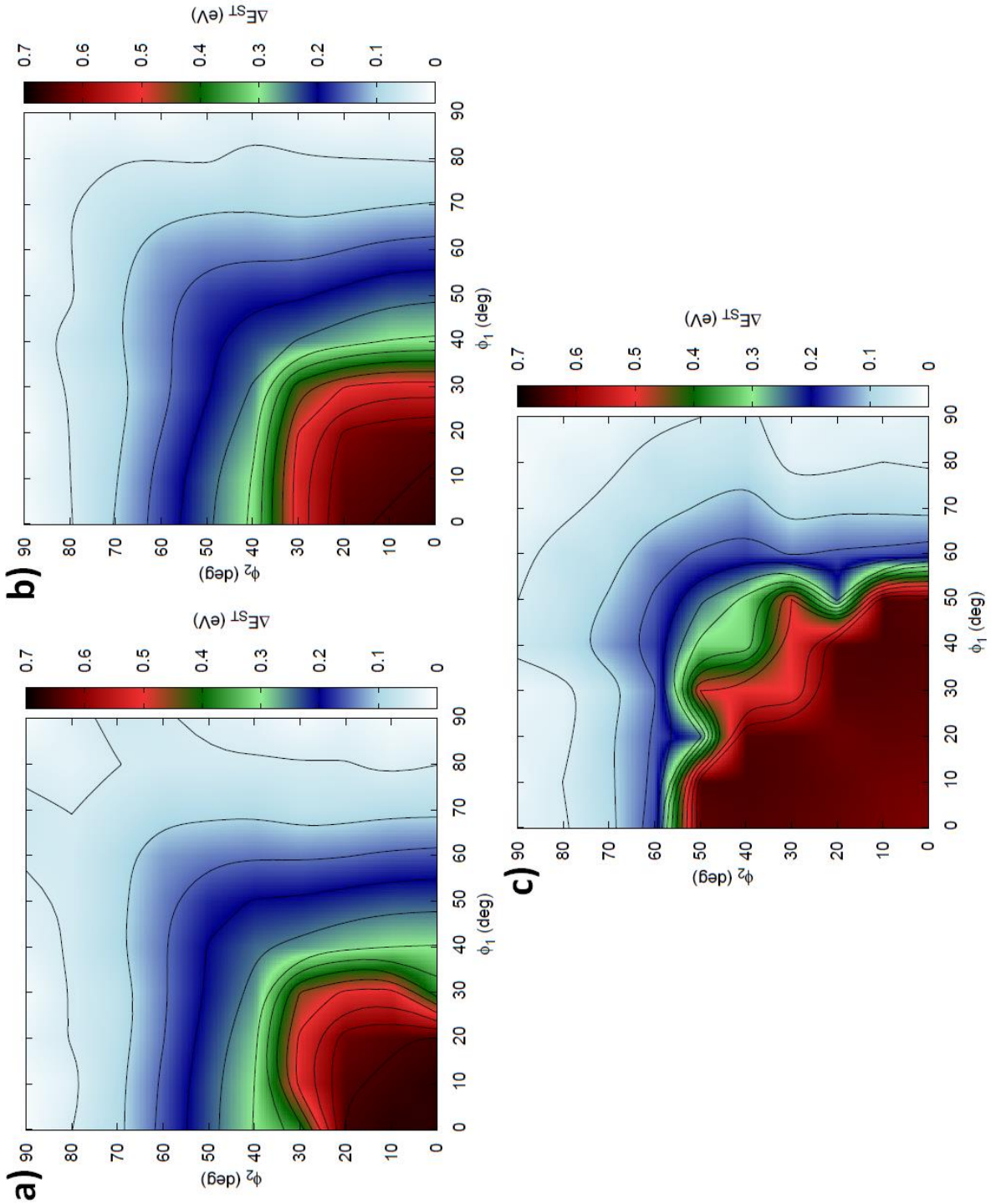

Figure S18: Evolution of the singlet-triplet energy gap ΔE_{ST} (in eV), calculated at the TDA-PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene), as a function of the two D-A dihedral angles ϕ_1 and ϕ_2 between the PXZ donors and the three different acceptors (**a)** OXD, **b)** TDZ and **c)** TAZ).

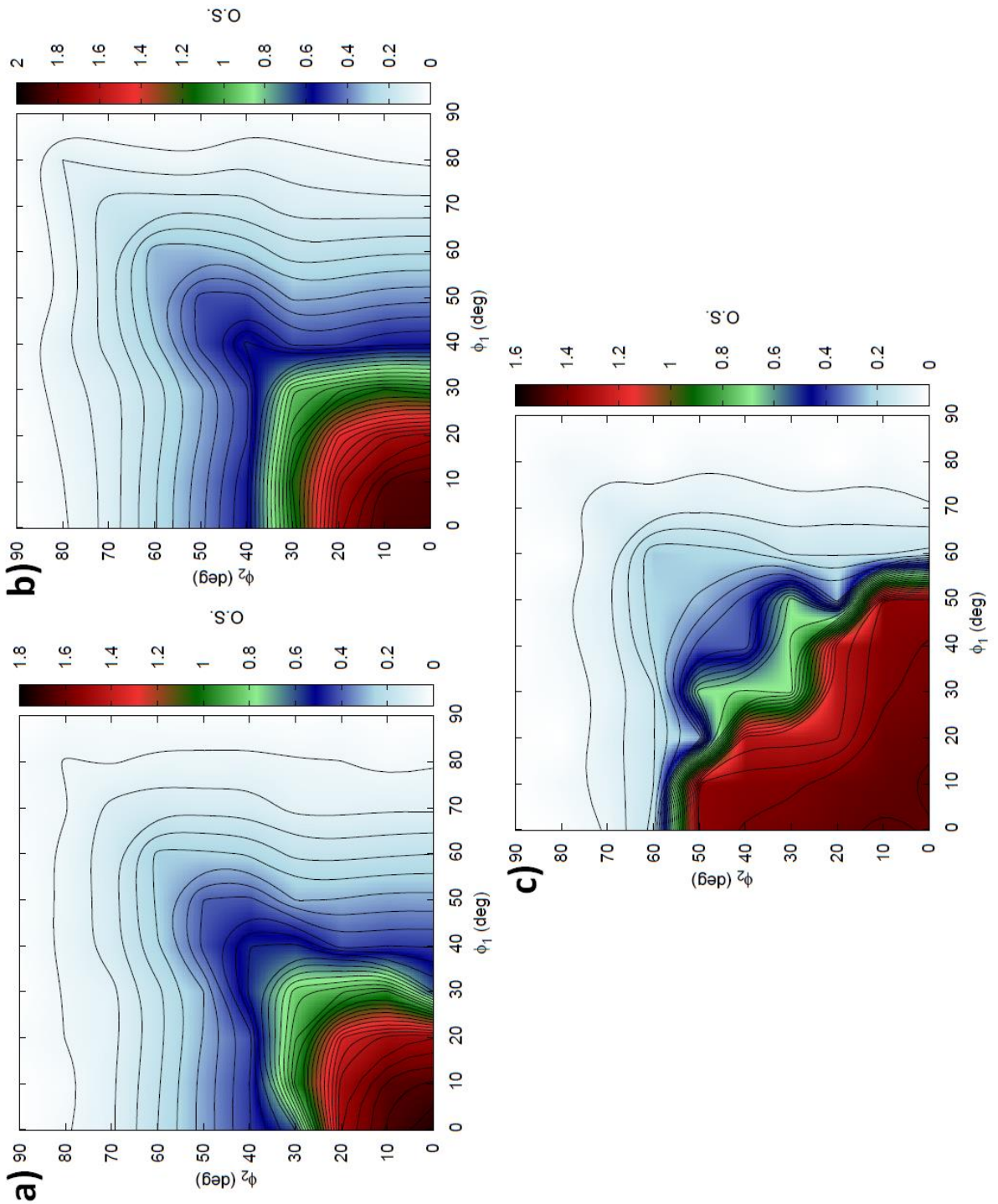

Figure S19: Evolution of the oscillator strength (O.S.), calculated at the TDA-PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene), as a function of the two D-A dihedral angles ϕ_1 and ϕ_2 between the PXZ donors and the three different acceptors (**a)** OXD, **b)** TDZ and **c)** TAZ).

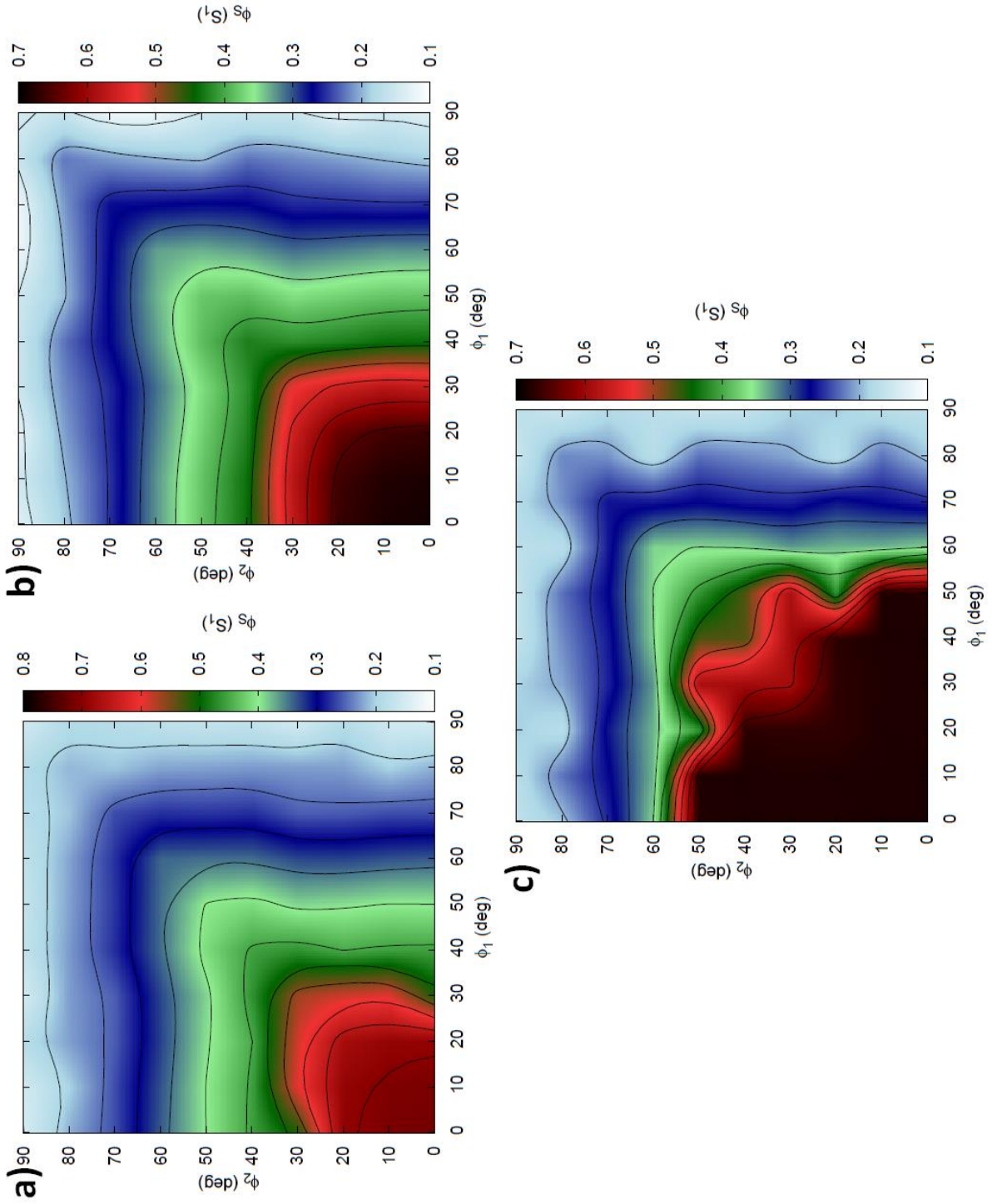

Figure S20: Evolution of the overlap between the hole and electron densities related to the electronic transition to S_1 (ϕ_S (S_1)), calculated at the TDA-PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene), as a function of the two D-A dihedral angles ϕ_1 and ϕ_2 between the PXZ donors and the three different acceptors (**a)** OXD, **b)** TDZ and **c)** TAZ).

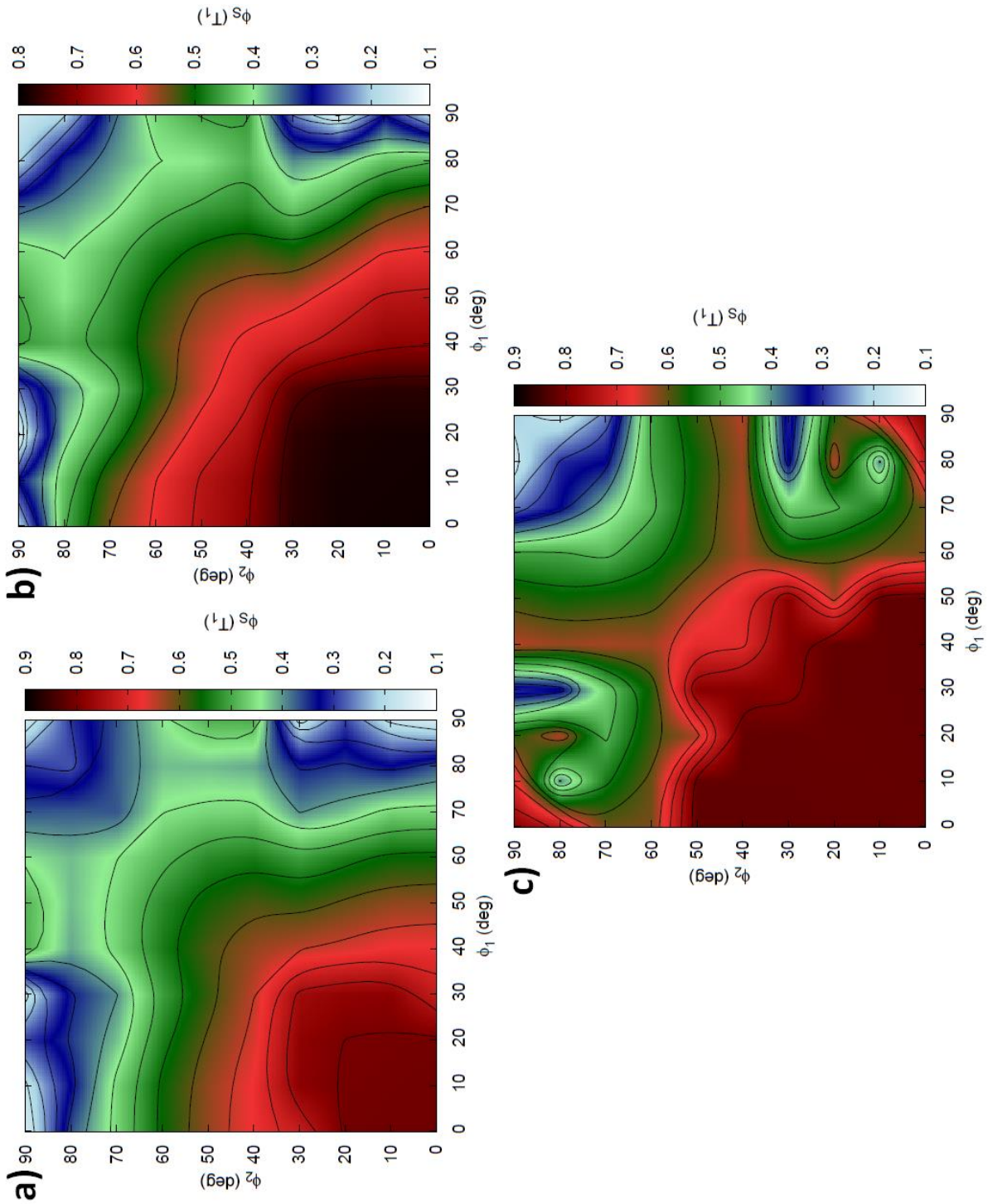

Figure S21: Evolution of the overlap between the hole and electron densities related to the electronic transition to T_1 (ϕ_S (T_1)), calculated at the TDA-PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene), as a function of the two D-A dihedral angles ϕ_1 and ϕ_2 between the PXZ donors and the three different acceptors (**a)** OXD, **b)** TDZ and **c)** TAZ).

Compound	Conformer	ΔE (kcal/mol)	Compound	Conformer	ΔE (kcal/mol)
PXZ-OXD	axial	2.24	**2PXZ-OXD**	axial	4.46
	equatorial	-		equatorial	-
PXZ-TDZ	axial	2.36	**2PXZ-TDZ**	axial	4.79
	equatorial	-		equatorial	-
PXZ-TAZ	axial	3.29	**2PXZ-TAZ**	axial	6.59
	equatorial	-		equatorial	-
PTZ-OXD	axial	-	**2PTZ-OXD**	axial	-
	equatorial	0.84		equatorial	1.54
PTZ-TDZ	axial	-	**2PTZ-TDZ**	axial	-
	equatorial	0.65		equatorial	1.24
PTZ-TAZ	axial	0.14	**2PTZ-TAZ**	axial	0.73
	equatorial	-		equatorial	-

Table S1: Relative energies between axial and equatorial (in kcal/mol) conformers for D-A and D-A-D compounds calculated at the PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene).

Compound	Conformer	ΔE (kcal/mol)	Compound	Conformer	ΔE (kcal/mol)
PXZ-OXD	axial	2.51	2PXZ-OXD	axial	5.03
	equatorial	-		equatorial	-
PXZ-TDZ	axial	2.75	2PXZ-TDZ	axial	5.54
	equatorial	-		equatorial	-
PXZ-TAZ	axial	3.53	2PXZ-TAZ	axial	7.14
	equatorial	-		equatorial	-
PTZ-OXD	axial	-	2PTZ-OXD	axial	-
	equatorial	0.64		equatorial	1.11
PTZ-TDZ	axial	-	2PTZ-TDZ	axial	-
	equatorial	0.35		equatorial	0.60
PTZ-TAZ	axial	0.36	2PTZ-TAZ	axial	1.08
	equatorial	-		equatorial	-

Table S2: Relative energies between axial and equatorial (in kcal/mol) conformers for D-A and D-A-D compounds calculated at the PBE0-D3(BJ)/def2TZVP level of theory with the PCM module for solvent (toluene).

	PXZ-OXD (Cs)				PXZ-TDZ (Cs)				PXZ-TAZ (C1)			
	Energy (eV)	**O.S.**	**ϕ_S**	**Δr (Å)**	**Energy (eV)**	**O.S.**	**ϕ_S**	**Δr (Å)**	**Energy (eV)**	**O.S.**	**phi_S**	**Δr (Å)**
T_1	2.5927	-	0.15	5.58	2.3523	-	0.13	6.52	2.9434	-	0.38	4.39
S_1	2.604	0	0.15	5.62	2.36	0	0.12	6.56	3.0079	0.0425	0.19	4.95
ΔE^{ST}	**0.0113**				**0.0077**				**0.0645**			

	PTZ-OXD (Cs)				PTZ-TDZ (Cs)				PTZ-TAZ (C1)			
	Energy (eV)	**O.S.**	**ϕ_S**	**Δr (Å)**	**Energy (eV)**	**O.S.**	**ϕ_S**	**Δr (Å)**	**Energy (eV)**	**O.S.**	**ϕ_S**	**Δr (Å)**
T_1	2.9193	-	0.23	5.48	2.6952	-	0.17	6.62	3.1769	-	0.72	0.85
S_1	2.9388	0	0.17	5.75	2.7062	0	0.14	6.73	3.3453	0.0004	0.23	4.98
ΔE^{ST}	**0.0195**				**0.011**				**0.1684**			

	2PXZ-OXD (C2V)				2PXZ-TDZ (C2V)				2PXZ-TAZ (C2)			
	Energy (eV)	**O.S.**	**ϕ_S**	**Δr (Å)**	**Energy (eV)**	**O.S.**	**ϕ_S**	**Δr (Å)**	**Energy (eV)**	**O.S.**	**ϕ_S**	**Δr (Å)**
T_1	2.4777	-	0.16	1.85	2.2459	-	0.14	0.56	2.897	-	0.24	0.85
S_1	2.4876	0	0.15	1.86	2.2529	0	0.14	0.56	2.9174	0	0.19	0.87
ΔE_{ST}	**0.0099**				**0.007**				**0.0204**			

	2PTZ-OXD (Cs)				2PTZ-TDZ (C2V)				2PTZ-TAZ (C2)			
	Energy (eV)	**O.S.**	**ϕ_S**	**Δr (Å)**	**Energy (eV)**	**O.S.**	**ϕ_S**	**Δr (Å)**	**Energy (eV)**	**O.S.**	**ϕ_S**	**Δr (Å)**
T_1	2.8207	-	0.25	1.73	2.5909	-	0.17	0.71	3.165	-	0.64	0.46
S_1	2.8376	0.002	0.18	1.78	2.6	0	0.15	0.72	3.2663	0	0.22	0.93
ΔE_{ST}	**0.0169**				**0.0091**				**0.1013**			

Table S3: S_1 and T_1 excitations energies and their associated singlet-triplet energy gap (ΔE_{ST}) for the equatorial conformer as well as the attachment and detachment densities overlap and distance difference between attachment and detachment densities centroids of the different compounds calculated at the TDA-PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene). Oscillator strengths (O.S.) for S_1 electronic transitions as well as the symmetry point group of the ground state optimized geometries (in parenthesis next to the molecule names) are also reported.

	PXZ-OXD (Cs)		PXZ-TDZ (Cs)		PXZ-TAZ (C1)	
	Energy (eV)	**O.S.**	**Energy (eV)**	**O.S.**	**Energy (eV)**	**O.S.**
T_1	2.6347	-	2.437	-	3	-
S_1	2.6465	0	2.4453	0	3.02	0.0112
ΔE^{ST}	**0.0118**		**0.0083**		**0.02**	

	PTZ-OXD (Cs)		PTZ-TDZ (Cs)		PTZ-TAZ (C1)	
	Energy (eV)	**O.S.**	**Energy (eV)**	**O.S.**	**Energy (eV)**	**O.S.**
T_1	2.8528	-	2.6647	-	3.05	-
S_1	2.872	0	2.676	0	3.3	0.0019
ΔE^{ST}	**0.0192**		**0.0113**		**0.25**	

	2PXZ-OXD (C2V)		2PXZ-TDZ (C2V)		2PXZ-TAZ (C2)	
	Energy (eV)	**O.S.**	**Energy (eV)**	**O.S.**	**Energy (eV)**	**O.S.**
T_1	2.4985	-	2.2874	-	2.949	-
S_1	2.5081	0	2.2944	0	2.9644	0
ΔE_{ST}	**0.0096**		**0.007**		**0.0154**	

	2PTZ-OXD (Cs)		2PTZ-TDZ (C2V)		2PTZ-TAZ (C2)	
	Energy (eV)	**O.S.**	**Energy (eV)**	**O.S.**	**Energy (eV)**	**O.S.**
T_1	2.7885	-	2.5634	-	3.0473	-
S_1	2.8038	0.0025	2.572	0	3.225	0
ΔE_{ST}	**0.0153**		**0.0086**		**0.1777**	

Table S4: S_1 and T_1 excitations and their associated singlet-triplet energy gap (ΔE_{ST}) for the equatorial conformer of the different compounds calculated at the TDA-PBE0-D3(BJ)/def2TZVP level of theory with the PCM module for solvent (toluene). Oscillator strengths (O.S.) for S_1 electronic transitions as well as the symmetry point group of the ground state optimized geometries (in parenthesis next to the molecule names) are also reported.

	PXZ-OXD (C1)		PXZ-TDZ (C1)		PXZ-TAZ (C1)	
	Energy (eV)	**O.S.**	**Energy (eV)**	**O.S.**	**Energy (eV)**	**O.S.**
T_1	2.878	-	2.607	-	3.237	-
S_1	3.598	1.156	3.299	1.204	3.867	0.834
ΔE^{ST}	**0.720**		**0.693**		**0.630**	

	PTZ-OXD (C1)		PTZ-TDZ (C1)		PTZ-TAZ (C1)	
	Energy (eV)	**O.S.**	**Energy (eV)**	**O.S.**	**Energy (eV)**	**O.S.**
T_1	2.871	-	2.610	-	3.225	-
S_1	3.604	1.186	3.334	1.242	3.842	0.908
ΔE_{ST}	**0.733**		**0.724**		**0.617**	

	2PXZ-OXD (Cs)		2PXZ-TDZ (Cs)		2PXZ-TAZ (C1)	
	Energy (eV)	**O.S.**	**Energy (eV)**	**O.S.**	**Energy (eV)**	**O.S.**
T_1	2.799	-	2.543	-	3.158	-
S_1	3.470	1.730	3.211	1.807	3.750	1.439
ΔE_{ST}	**0.671**		**0.668**		**0.592**	

	2PTZ-OXD (Cs)		2PTZ-TDZ (Cs)		2PTZ-TAZ (C1)	
	Energy (eV)	**O.S.**	**Energy (eV)**	**O.S.**	**Energy (eV)**	**O.S.**
T_1	2.811	-	2.529	-	3.142	-
S_1	3.505	1.691	3.207	1.410	3.716	1.947
ΔE_{ST}	**0.693**		**0.678**		**0.574**	

Table S5: S_1 and T_1 excitations and their associated singlet-triplet energy gap (ΔE_{ST}) for the axial conformer of the different compounds calculated at the TDA-PBE0-D3(BJ)/def2TZVP level of theory with the PCM module for solvent (toluene). Oscillator strengths (O.S.) for S_1 electronic transitions as well as the symmetry point group of the ground state optimized geometries (in parenthesis next to the molecule names) are also reported.

	PXZ-OXD (Cs)			PXZ-TDZ (Cs)			PXZ-TAZ (C1)		
	S_0	S_1	T_1	S_0	S_1	T_1	S_0	S_1	T_1
Angle (°)	83.08	90.31	89.69	85.60	89.74	89.74	101.66	89.42	122.31

	PTZ-OXD (Cs)			PTZ-TDZ (Cs)			PTZ-TAZ (C1)		
	S_0	S_1	T_1	S_0	S_1	T_1	S_0	S_1	T_1
Angle (°)	79.33	89.82	90.16	79.67	89.91	89.94	101.83	89.34	90.55

	2PXZ-OXD (C2V)			2PXZ-TDZ (C2V)			2PXZ-TAZ (C2)		
	S_0	S_1	T_1	S_0	S_1	T_1	S_0	S_1	T_1
Angle (°)	84.60	89.65	90.35	84.67	89.57	89.57	91.51	89.63	118.33

	2PTZ-OXD (Cs)			2PTZ-TDZ (C2V)			2PTZ-TAZ (C2)		
	S_0	S_1	T_1	S_0	S_1	T_1	S_0	S_1	T_1
Angle (°)	81.18	88.38	89.54	79.37	88.56	88.51	80.75	88.23	88.02

Table S6: Equilibrium D-A torsion angles (in degrees) for ground state (S_0) and, singlet (S_1) and triplet (T_1) excited state (Tamm-Dancoff) optimization at PBE0-D3(BJ)/6-31G(d,p) level of theory with the PCM module for solvent (toluene).

	PXZ-OXD	PXZ-TDZ	PXZ-TAZ
State	**% HONTO to LUNTO**	**% HONTO to LUNTO**	**% HONTO to LUNTO**
T_1	99.9	99.9	99.3
S_1	99.9	99.9	99.8
T_2	92.9	92.1	93.0

	PTZ-OXD	PTZ-TDZ	PTZ-TAZ
State	**% HONTO to LUNTO**	**% HONTO to LUNTO**	**% HONTO to LUNTO**
T_1	99.6	99.8	93.0
S_1	99.9	99.9	99.8
T_2	88.4	92.0	96.3

	2PXZ-OXD	2PXZ-TDZ	2PXZ-TAZ
State	**% HONTO to LUNTO**	**% HONTO to LUNTO**	**% HONTO to LUNTO**
T_1	92.2	96.4	86.0
T_2	92.2	96.4	85.9
S_1	92.6	96.6	87.0
S_2	92.6	96.6	87.1
T_3	46.9	91.9	47.0
T_4	46.9	47.3	47.0

	2PTZ-OXD	2PTZ-TDZ	2PTZ-TAZ
State	**% HONTO to LUNTO**	**% HONTO to LUNTO**	**% HONTO to LUNTO**
T_1	92.1	96.5	69.7
T_2	92.1	96.5	69.6
S_1	93.2	96.9	87.4
S_2	93.2	96.9	87.3
T_3	88.1	91.9	61.6
T_4	45.5	45.5	61.7

Table S7: Composition of the excited states transitions in terms of the HONTO to LUNTO transitions.