SUPPLEMENTARY INFORMATION

The effect of torsion-inducing methyl substituents on the delayed luminescence of star-shaped emitters

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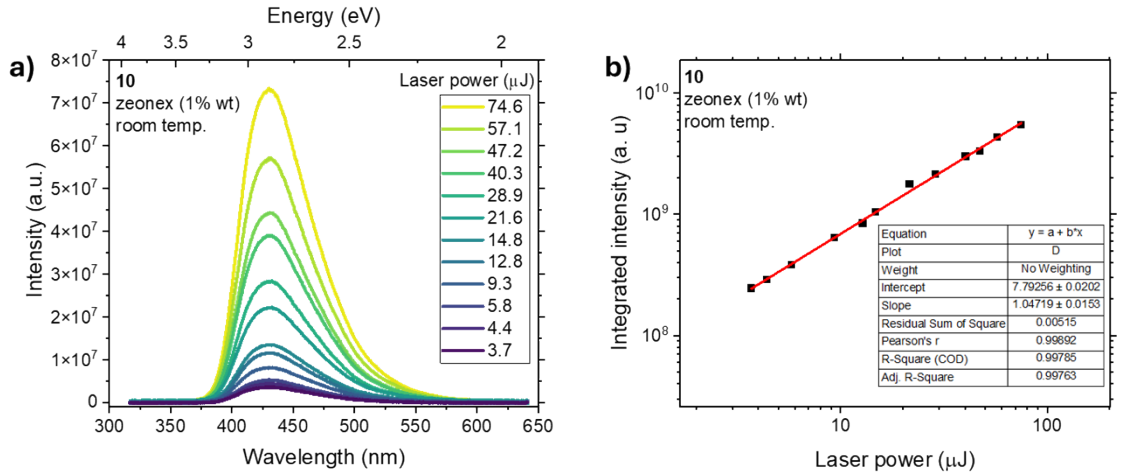


Figure S1 – PL of **10** doped into zeonex host (1% wt/wt) at room temperature. Curves were collected with 100 µs of delay time and 100 µs of integration time (a). Dependence of integrated PL to laser power (b).

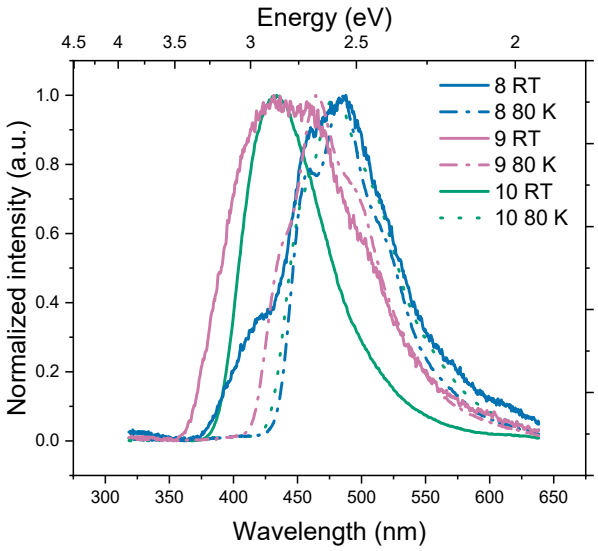


Figure S2 – TRPL in solid dispersion in zeonex (1% wt). Curves were acquired with a 10 ms delay time and 40 ms integration time at room temperature (solid) and 80 K (dashed). $\lambda_{excitation}$ = 355 nm.

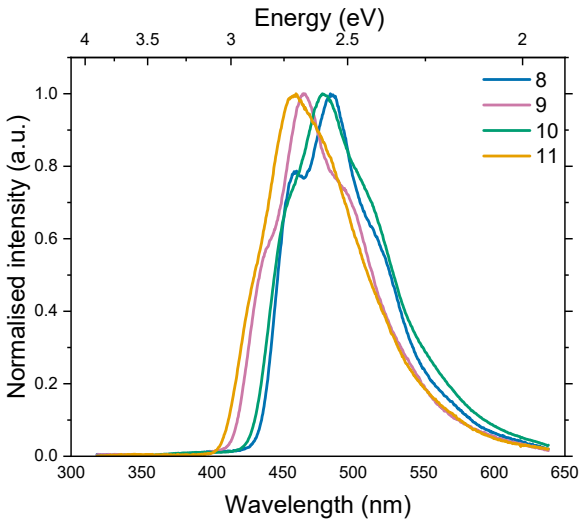


Figure S3 - TRPL in solid dispersion in zeonex (1% wt). Curves were acquired with a 10 ms delay time and 40 ms integration time at 80 K. $\lambda_{excitation}$ = 355 nm.

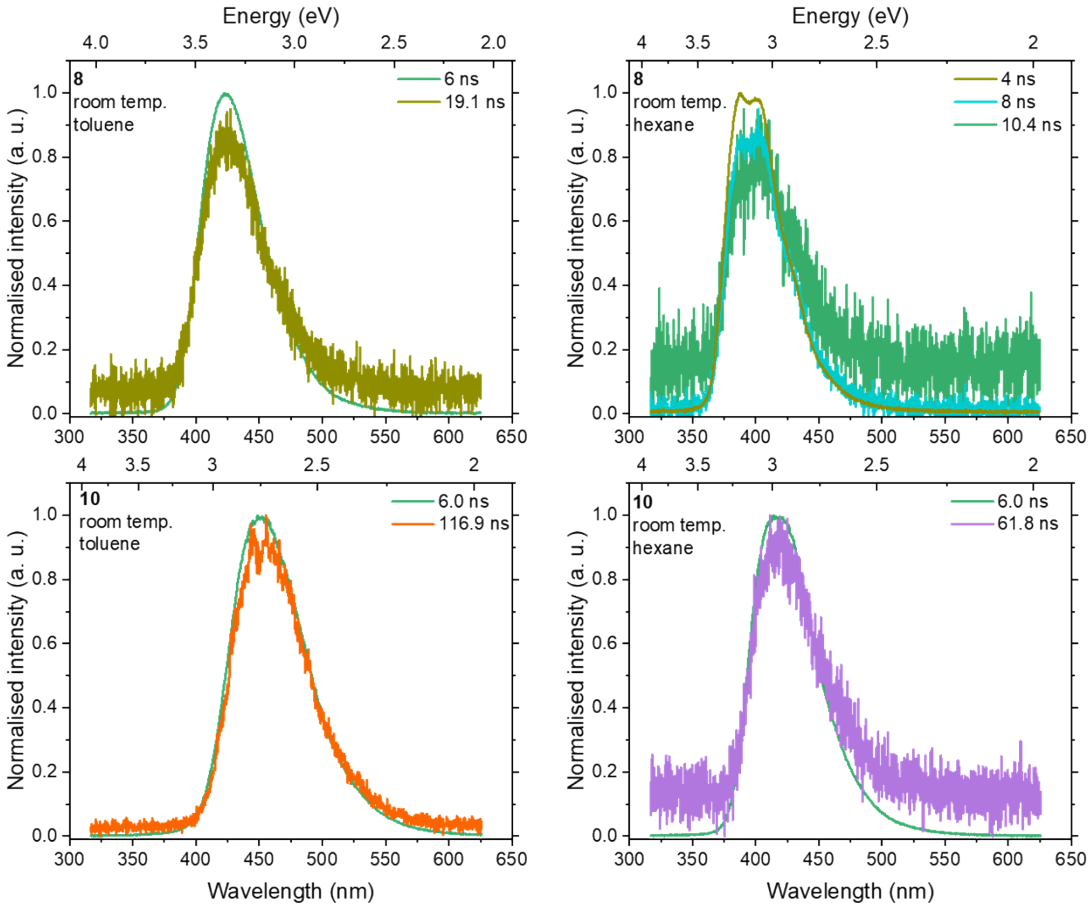


Figure S4 - TRPL in solution in toluene 10 µM (left) and hexane 10 µM (right) at room temperature. $\lambda_{excitation}$ = 355 nm.

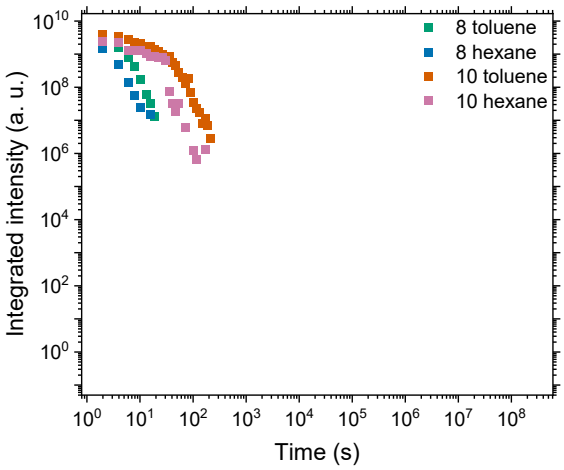


Figure S5 - Decay curves in toluene 10 µM and hexane 10 µM at room temperature. $\lambda_{excitation}$ = 355 nm.

Table S1 – Prompt fluorescence lifetime of **8** and **10** in solution. Decay curves were fitted with a monoexponential function.

	8		***10***	
	Hexane	*Toluene*	*Hexane*	*Toluene*
$\tau_{PF}(ns)$	1.8	3.2	11.5	21.0

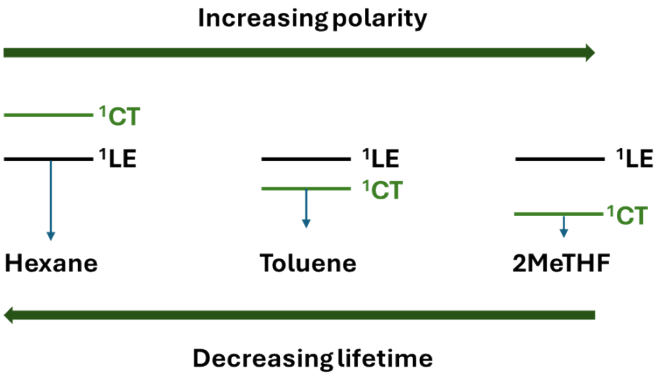


Figure S6 – Diagram depicting impact of solvent polarity on the energy levels of ^{1}LE and ^{1}CT.

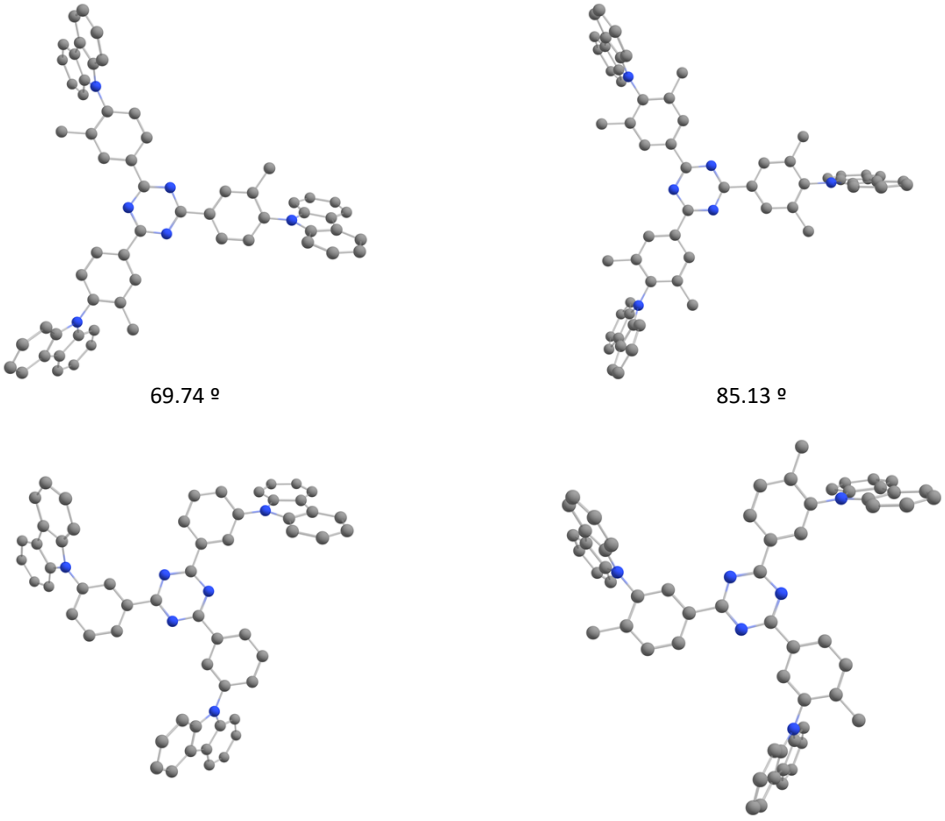


Figure S7 - Ground state optimized geometry and the average dihedral angle for compounds **8**-**11** obtained at the D3BJ-B3LYP/def2-TZVP(-f) level of theory. Hydrogen atoms omitted for clarity.

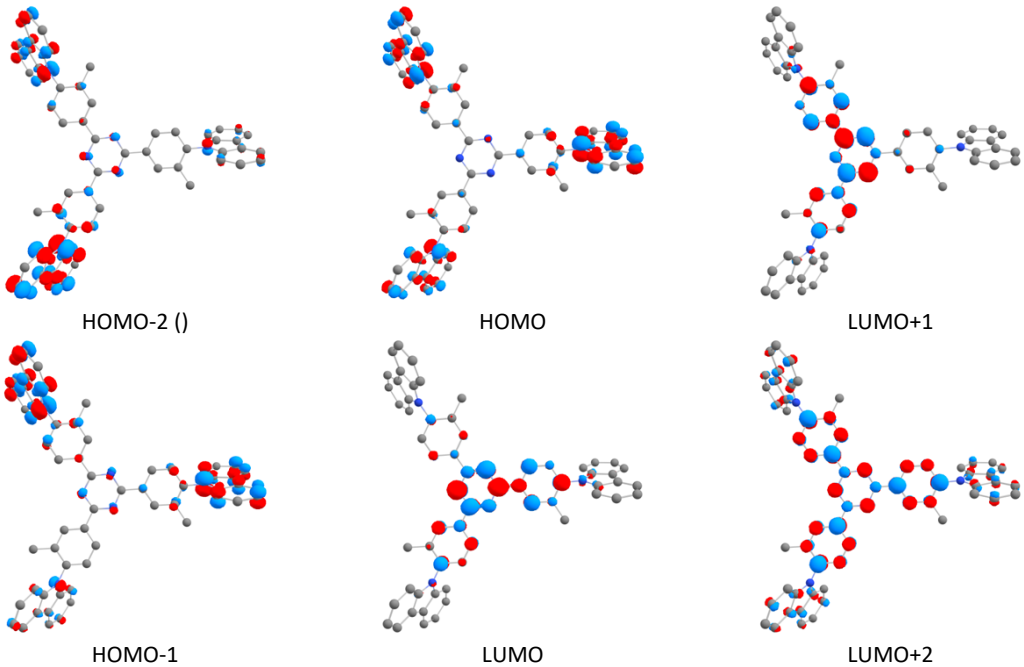


Figure S8 - Frontier molecular orbitals for compound **8** obtained at the D3BJ-B3LYP/def2-TZVP(-f) level of theory. Hydrogen atoms omitted for clarity.

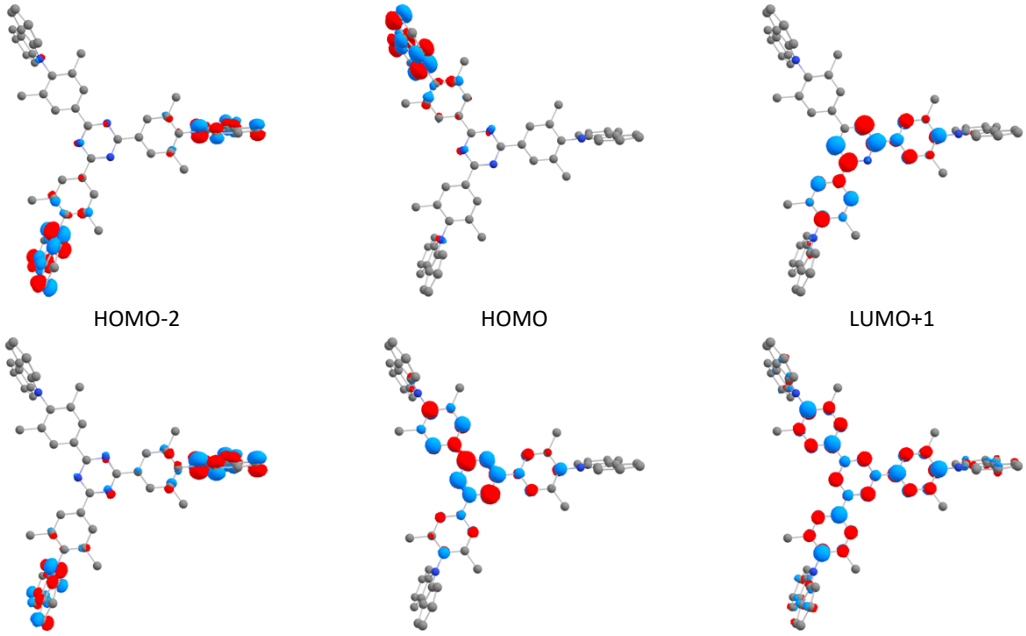


Figure S9 - Frontier molecular orbitals for compound **9** obtained at the D3BJ-B3LYP/def2-TZVP(-f) level of theory. Hydrogen atoms omitted for clarity.

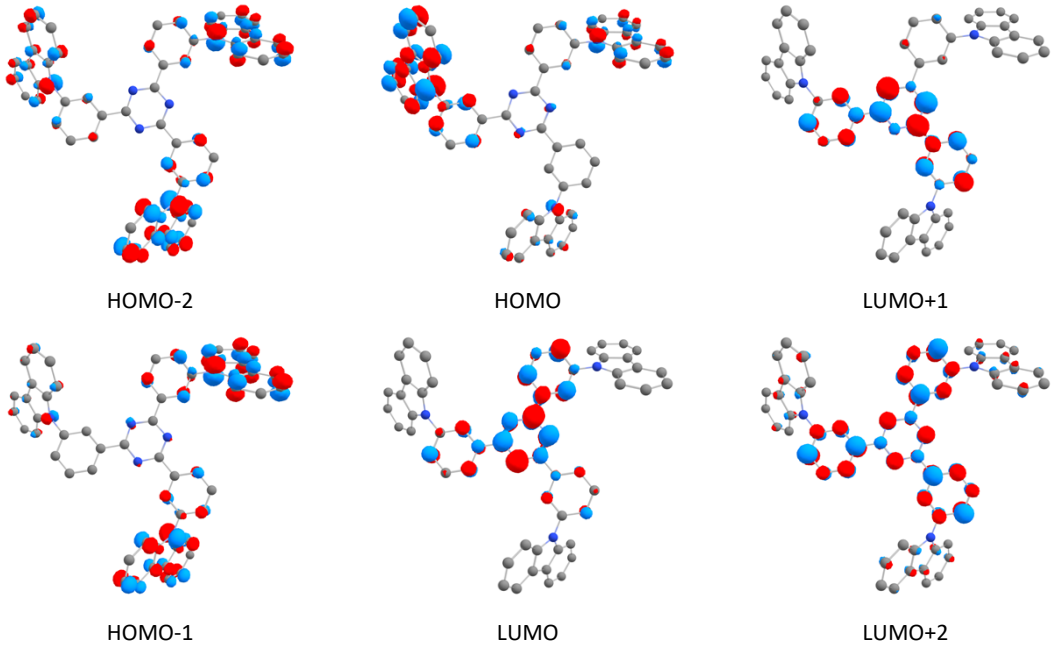


Figure S10 - Frontier molecular orbitals for compound **10** obtained at the D3BJ-B3LYP/def2-TZVP(-f) level of theory. Hydrogen atoms omitted for clarity.

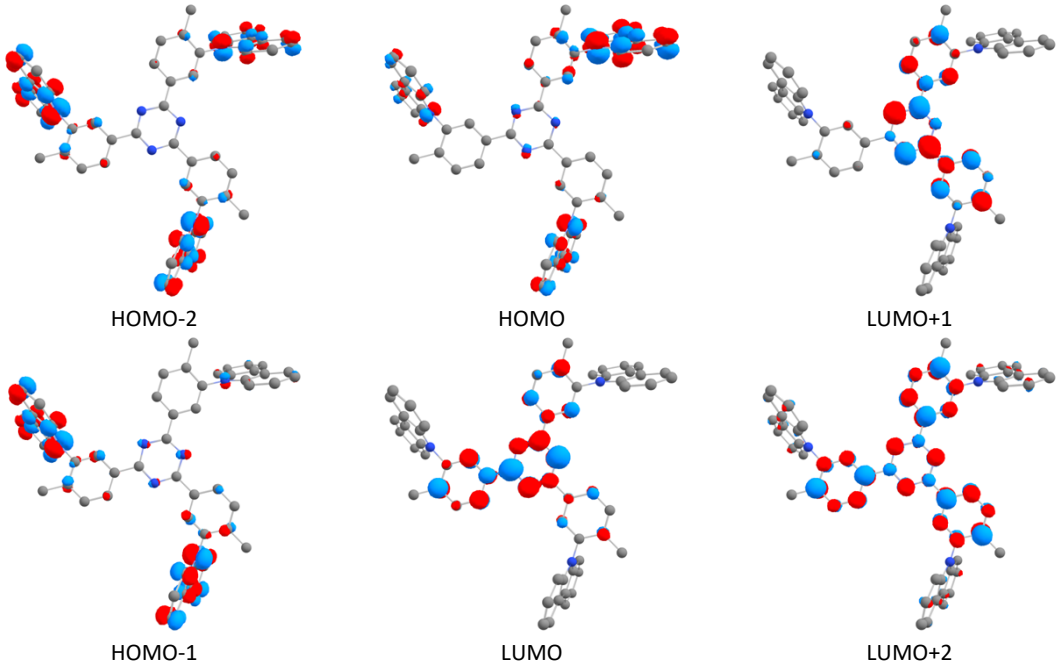


Figure S11 - Frontier molecular orbitals for compound **11** obtained at the D3BJ-B3LYP/def2-TZVP(-f) level of theory. Hydrogen atoms omitted for clarity.

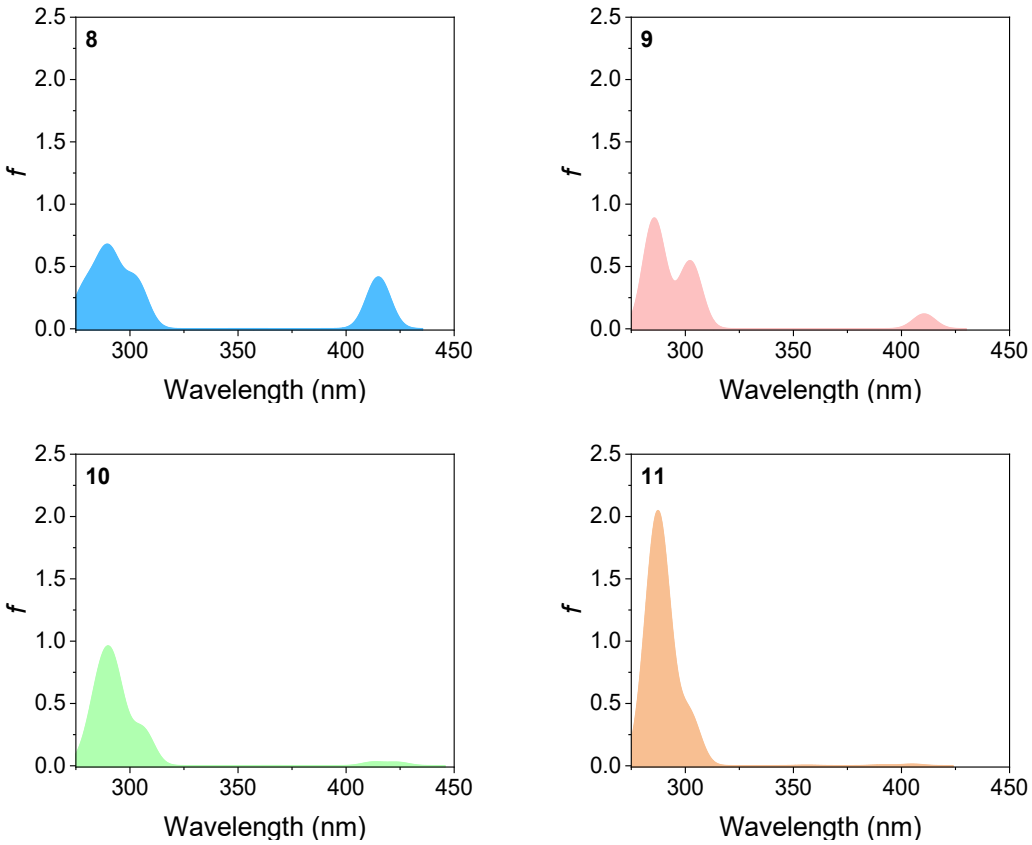
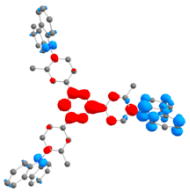
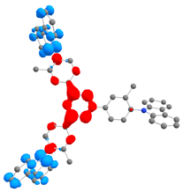
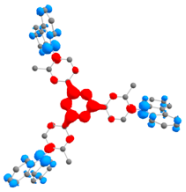
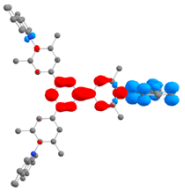
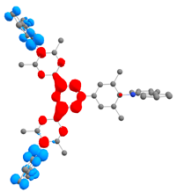
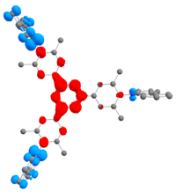
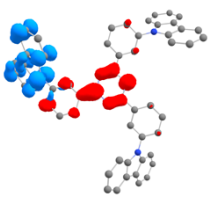


Figure S12 - Theoretical absorption spectra convoluted with Gaussians of 20 nm width for compounds **8**-**11** obtained at the D3BJ-B3LYP/def2-TZVP(-f) level of theory and 2-MeTHF as solvent.

Table S2 - Data for the TD-DFT/TDA excitations (>10%) obtained at the D3BJ-B3LYP/def2-TZVP(-f) level of theory and 2-MeTHF as solvent. For CIS-DD, blue indicates depletion, and red indicates increased electronic density. Hydrogen atoms omitted for clarity.

State	Energy (nm)	Energy (eV)	*f*	Configuration	CIS-DD
			8		
S_1	415	2.987	0.2069	H → L (45) H-2 → L (19) H-1 → L (15)	
S_2	415	2.988	0.2079	H → L+1 (52) H-1 → L (16) H-2 → L+1 (15)	
S_3	409	3.031	0.0004	H-1 → L (44) H → L+1 (52)	
			9		
S_1	411	3.015	0.0366	H → L (81)	
S_2	410	3.020	0.0712	H-1 → L+1 (45) H-2 → L (25) H → L+1 (16)	
S_3	409	3.032	0.0108	H-2 → L+1 (65) H-1 → L (32)	
			10		
S_1	424	2.921	0.0062	H-1 → L (81)	

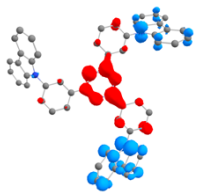
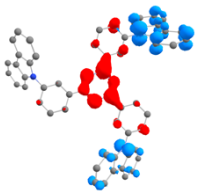
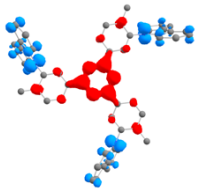
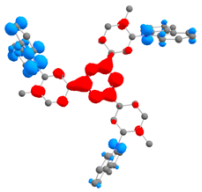
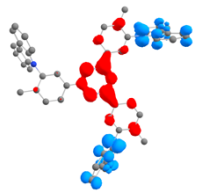
S_2	424	2.924	0.0073	H-2 → L (32) H → L+1 (30) H-2 → L+1 (23)	
S_3	424	2.924	0.0126	H → L+1 (50) H-2 → L (25)	
			11		
S_1	405	3.058	5.3×10^{-4}	H-1 → L (32) H → L+1 (45)	
S_2	405	3.060	0.0062	H-1 → L+1 (29) H-2 → L (23) H → L (18)	
S_3	405	3.060	0.0061	H-2 → L (50) H-1 → L+1 (27)	

Table S3 - Data for the TD-DFT/TDA and SOC-TD-DFT excitations (>10%) for **8** obtained at the D3BJ-B3LYP/def2-TZVP(-f) level of theory and 2-MeTHF as solvent. For CIS-DD, blue indicates depletion, and red indicates increased electronic density. Hydrogen atoms omitted for clarity.

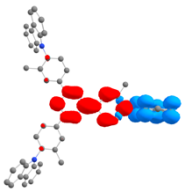
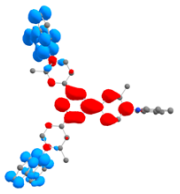
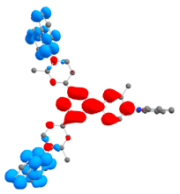
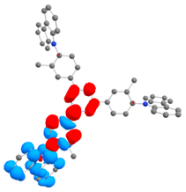
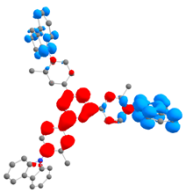
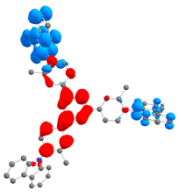
State	Energy (nm)	Energy (eV)	f	Configuration[a]	CIS-DD
S_1 geometry					
S_1	482	2.573	2.6×10^{-5}	H → L (99)	
S_2	442	2.806	0.0446	H-2 → L (87)	
S_3	441	2.814	0.0175	H-1 → L (88)	
T_1 geometry					
S_1	512	2.421	7.3×10^{-8}	H → L (77)	
S_2	440	2.816	1.7×10^{-7}	H-1 → L (75)	
S_3	439	2.823	1.8×10^{-7}	H-2 → L (86)	

Table S4 - Data for the TD-DFT/TDA and SOC-TD-DFT excitations (>10%) for **9** obtained at the D3BJ-B3LYP/def2-TZVP(-f) level of theory and 2-MeTHF as solvent. For CIS-DD, blue indicates depletion, and red indicates increased electronic density. Hydrogen atoms omitted for clarity.

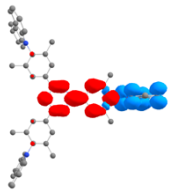
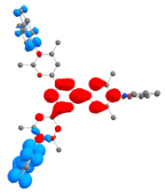
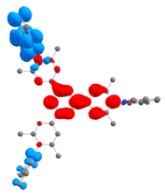
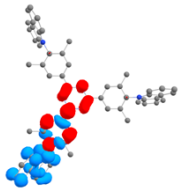
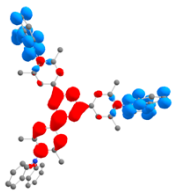
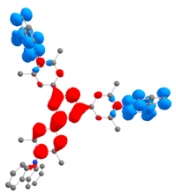
State	Energy (nm)	Energy (eV)	*f*	Configuration[a]	CIS-DD
S_1 geometry					
S_1	476	2.606	0.0002	H → L (99)	
S_2	437	2.839	0.0139	H-1 → L (49) H-2 → L (47)	
S_3	436	2.840	0.0095	H-1 → (47) H-2 → L (49)	
T_1 geometry					
S_1	496	2.499	> 1×10^{-9}	H → L (65)	
S_2	433	2.866	> 1×10^{-9}	H-1 → L (64)	
S_3	432	2.872	> 1×10^{-9}	H-2 → L (83)	

Table S5 - Data for the TD-DFT/TDA and SOC-TD-DFT excitations (>10%) for **10** obtained at the D3BJ-B3LYP/def2-TZVP(-f) level of theory and 2-MeTHF as solvent. For CIS-DD, blue indicates depletion, and red indicates increased electronic density. Hydrogen atoms omitted for clarity.

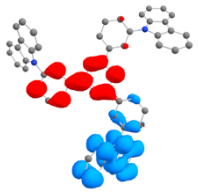
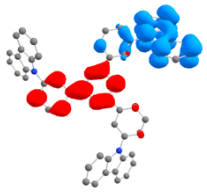
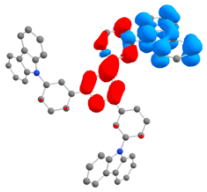
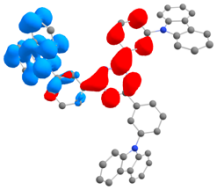
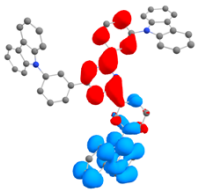
State	Energy (nm)	Energy (eV)	f	Configuration*	CIS-DD
			S_1 geometry		
S_1	492	2.519	0.0069	H → L (99)	
S_2	464	2.673	0.0039	H-2 → L (97)	
S_3	462	2.688	0.0106	H-1 → L (98)	
			T_1 geometry		
S_1	520	2.384	> 1×10^{-9}	H → L (93)	
S_2	470	2.636	> 1×10^{-9}	H-2 → L (88)	
S_3	466	2.658	> 1×10^{-9}	H-1 → L (88)	

Table S6 - Data for the TD-DFT/TDA and SOC-TD-DFT excitations (>10%) for 11 obtained at the D3BJ-B3LYP/def2-TZVP(-f) level of theory and 2-MeTHF as solvent. For CIS-DD, blue indicates depletion, and red indicates increased electronic density. Hydrogen atoms omitted for clarity.

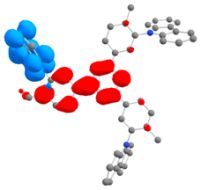
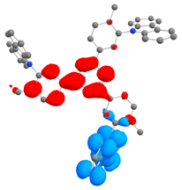
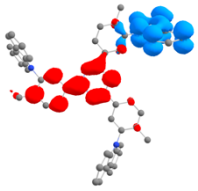
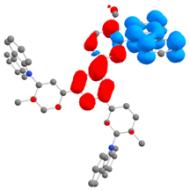
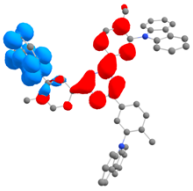
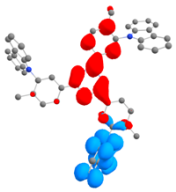
State	Energy (nm)	Energy (eV)	*f*	Configuration*	CIS-DD
			S_1 geometry		
S_1	474	2.617	0.0047	H → L (99)	
S_2	442	2.806	0.0029	H-2 → L (96)	
S_3	440	2.818	0.0030	H-1 → L (96)	
			T_1 geometry		
S_1	489	2.535	> 1×10^{-9}	H → L (94)	
S_2	440	2.814	> 1×10^{-9}	H-2 → L (90)	
S_3	437	2.839	> 1×10^{-9}	H-1 → L (91)	

Table S7 - SOCME data for compounds 8-11 obtained at optimized S1 and T1 geometries and their energies obtained at the D3BJ-B3LYP/def2-TZVP(-f) level of theory and 2-MeTHF as solvent.

	8	**9**	**10**	**11**
S_1 (eV)	2.573	2.606	2.519	2.617
T_1 (eV)	2.421	2.499	2.384	2.535
$\Delta E_{singlet\text{-}triplet}$ (eV)	0.152	0.107	0.135	0.082
			S_1 geometry	
$\langle T_1 \mid H_{SOC} \mid S_1 \rangle_a$ (cm^{-1})	0.00	0.02	0.22	0.18
$\langle T_2 \mid H_{SOC} \mid S_1 \rangle_a$ (cm^{-1})	0.10	0.15	0.02	0.05
$\langle T_3 \mid H_{SOC} \mid S_1 \rangle_a$ (cm^{-1})	0.07	0.05	0.01	0.03
$\Sigma \langle T_{1-3} \mid H_{SOC} \mid S_1 \rangle$ (cm^{-1})	0.18	0.23	0.26	0.26
			T_1 geometry	
$\langle T_1 \mid H_{SOC} \mid S_1 \rangle_a$ (cm^{-1})	0.38	0.46	0.25	0.28

[a] $\sqrt{\sum_{MS} \langle T_{j\,(MS=0,\pm 1)} \mid H_{SOC} \mid S_n \rangle^2}$.