Electronic Supplementary Information for Dual Fluorescence in Strap ESIPT Systems: A Theoretical Study.

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Table S1: Difference between experimental and vertical theoretical (TD-DFT) fluorescence wavelengths calculated in nm and in eV using three solvent models (LR, cLR, and LR+cLR). The experimental values are taken from Refs. 1 and 2.

			Exp - Theo (nm)			**Exp - Theo (eV)**		
Compound	**Solvent**	**state**	**LR**	**cLR**	**LR+cLR**	**LR**	**cLR**	**LR+cLR**
1	cyclohexane	LE	-15	7	-17	0.08	-0.04	0.09
	acetone	LE	-50	7	-63	0.23	-0.03	0.29
		Z	3	65	-17	-0.01	-0.28	0.06
2	cyclohexane	LE	19	30	16	-0.10	-0.16	-0.08
	acetone	LE	10	33	-3	-0.05	-0.16	0.01
		Z	51	69	23	-0.19	-0.26	-0.08
3	cyclohexane	LE	-22	-9	-23	0.15	0.06	0.15
	acetone	LE	-51	-17	-55	0.32	0.11	0.34
		Z	9	42	0	-0.05	-0.23	0.00
4	cyclohexane	LE	12	28	9	-0.06	-0.13	-0.04
	acetone	LE	2	33	-23	-0.01	-0.13	0.08
		Z	65	97	22	-0.18	-0.28	-0.06
5a	cyclohexane	LE	-22	1	-23	0.11	-0.02	0.12
	acetone	LE	-46	12	-59	0.21	-0.06	0.27

Table S2: Difference between the fluorescence wavelengths of LE and Z forms for compounds **1**-**4** in acetone using three solvent models (LR, cLR, and LR+cLR). The experimental values are taken from Refs. 1 and 2. All values are given in nm.

Compound	**LR**	**cLR**	**LR+cLR**	**Exp[1,2]**
1	-25	-20	-32	-78
2	-41	-46	-56	-82
3	-10	-11	-15	-70
4	-60	-59	-78	-123

Table S3: Difference between LE fluorescence wavelengths computed in cyclohexane and acetone for compounds **1**-**5a** using three solvent models (LR, cLR, and LR+cLR). The experimental values are taken from Refs. 1 and 2. All values are given in nm.

	LE (cyclohexane) /LE(acetone)			
Compound	**LR**	**cLR**	**LR+cLR**	**Exp[1,2]**
1	-59	-24	-70	-24
2	-29	-17	-39	-20
3	-32	-11	-35	-3
4	-48	-33	-70	-38
5a	-57	-22	-69	-33

Table S4: Calculated ES dipole moments (in Debye) of the LE and Z forms of compound **1** in cyclohexane and acetone using the M06-2X functional and the 6-311+G(2d,p) atomic basis set.

Dipole moment			
Compound	**Solvent**	**LE**	**Z**
1	cyclohexane	10.6	15.1
	acetone	13.3	19.1

Table S5: Computed relative energies with respect to the GS (in eV) of compound **1** determined on the TD-DFT S_1 structure optimized in cyclohexane and acetone by correcting the total energies with CC2/aug-cc-pVDZ values following the same protocol as in Ref. 3.

		CC2
Solvent	**state**	**vertical energy**
cyclohexane	LE	2.80
	Z	2.78
acetone	LE	2.79
	Z	2.82

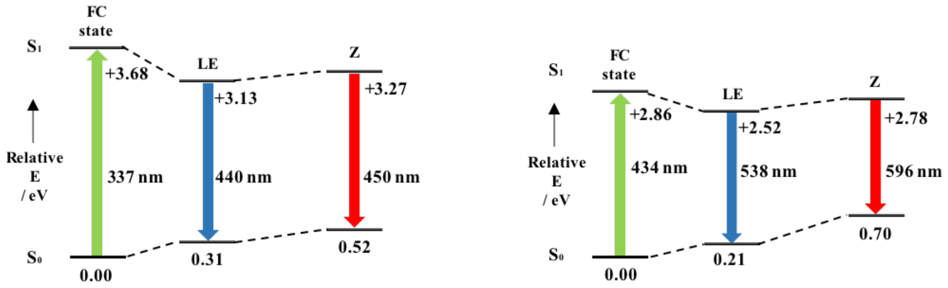
Table S6: Computed vertical emission energies in eV and corresponding fluorescence maximum wavelengths in nm obtained with the LR+cLR solvent model using the M06-2X functional and the 6-311+G(2d,p) atomic basis set. We consider both the locally excited state (LE) and the ESIPT (Z) structures.

			Emission						
			Vertical energy			λ_{fluo}			λ_{fluo}
Compounds	**Solvent**	**state**	**LR***	**cLR**	**LR+cLR**	**LR***	**cLR**	**LR+cLR**	**Exp[1,2]**
1	cyclohexane	LE	2.58	2.70	2.57	481	459	483	466
		Z	2.48	2.60	2.47	500	476	503	-
	acetone	LE	2.30	2.56	2.24	540	483	553	490
		Z	2.19	2.46	2.12	565	503	585	568
2	cyclohexane	LE	2.58	2.64	2.56	481	470	484	500
		Z	2.34	2.38	2.31	529	520	536	-
	acetone	LE	2.43	2.54	2.37	510	487	523	520
		Z	2.25	2.32	2.14	551	533	579	602
3	cyclohexane	LE	2.82	2.91	2.82	439	426	440	417△
		Z	2.76	2.85	2.76	448	435	450	-
	acetone	LE	2.63	2.84	2.61	471	437	475	420
		Z	2.58	2.76	2.53	481	448	490	490△
4	cyclohexane	LE	2.32	2.39	2.30	535	519	538	547
		Z	2.11	2.17	2.08	588	572	596	-
	acetone	LE	2.13	2.25	2.04	583	552	608	585
		Z	1.93	2.03	1.81	643	611	686	708
5a	cyclohexane	LE	2.56	2.69	2.55	485	462	486	463
		Z	2.34	2.47	2.33	530	501	533	-
	acetone	LE	2.29	2.56	2.23	542	484	555	496
		Z	2.07	2.36	2.00	597	525	621	-
5b	cyclohexane	LE	2.56	2.68	2.56	484	462	485	-
		Z	2.41	2.53	2.40	514	490	517	-
	acetone	LE	2.28	2.56	2.34	543	484	554	-
		Z	2.13	2.41	2.06	580	514	601	-

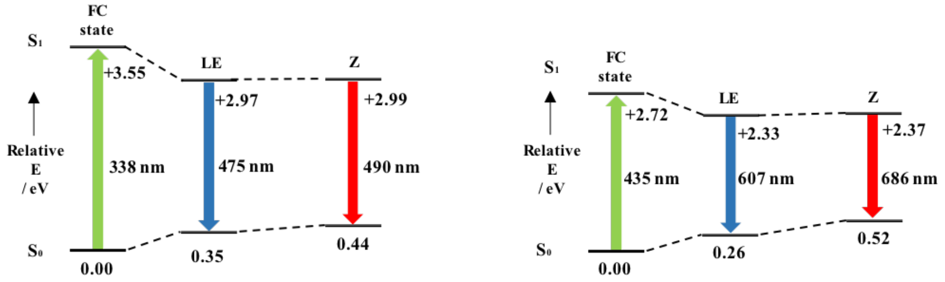
* in equilibrium

△ The peak maxima of the LE and Z bands in cyclohexane and acetone appear around 445 nm and 460 nm, respectively, in the spectrum of Fig. S2 in Ref. 2, the values 417 nm and 490 nm, that are taken from Table S1 of the same reference, might therefore be related to a misprint.

a) Cyclohexane



b) Acetone



3 **4**

Figure S1: Potential energy diagrams (E+ZPVE) in eV for compounds **3** and **4** in (a) in cyclohexane and (b) in acetone using the LR+cLR solvent model. All the theoretical energies and wavelengths have been obtained from TD-DFT calculations using the M06-2X functional and the 6-311+G(2d,p) atomic basis set.

Table S7: Distance between the two nitrogen atoms in the ground state of **1**, **2**, and **4** in cyclohexane and acetone. All values are given in Å.

	d(N-N)	
Compound	**cyclohexane**	**acetone**
1	2.84	2.82
2	3.25	3.23
4	3.24	3.23

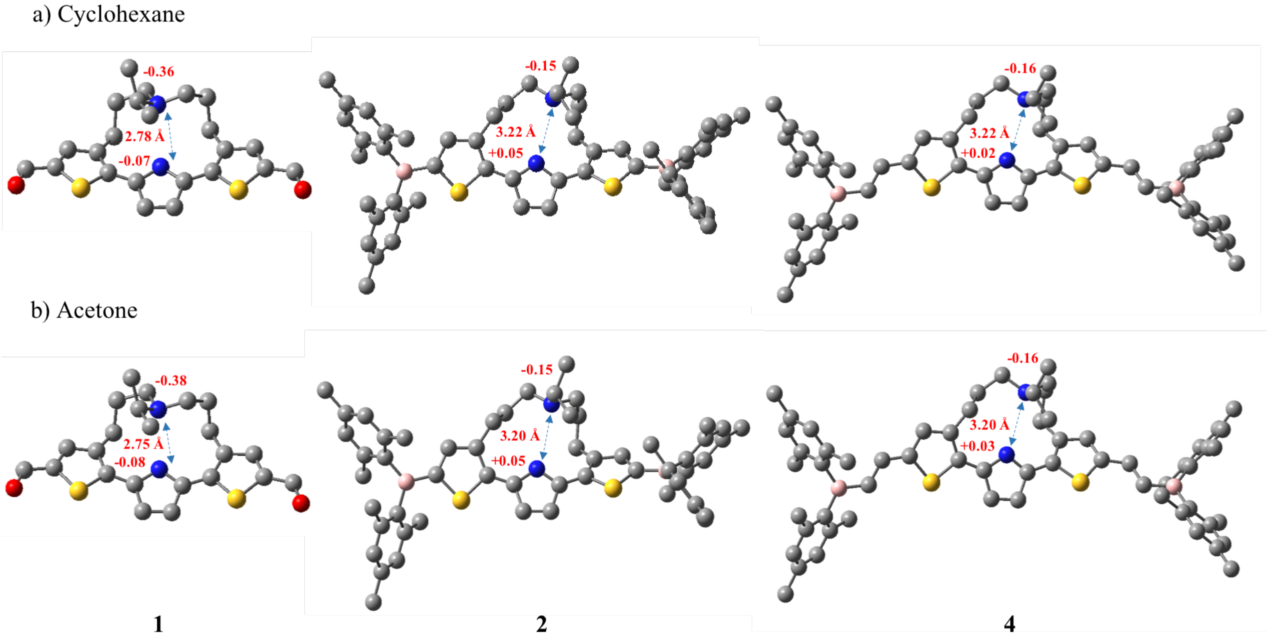


Figure S2: Distance between the two nitrogen atoms and partial atomic charges (Mulliken model) in Å for compounds **1**, **2**, and **4** in their LE forms in (a) cyclohexane and (b) acetone. All values are obtained on the optimal ES (LE) geometry.

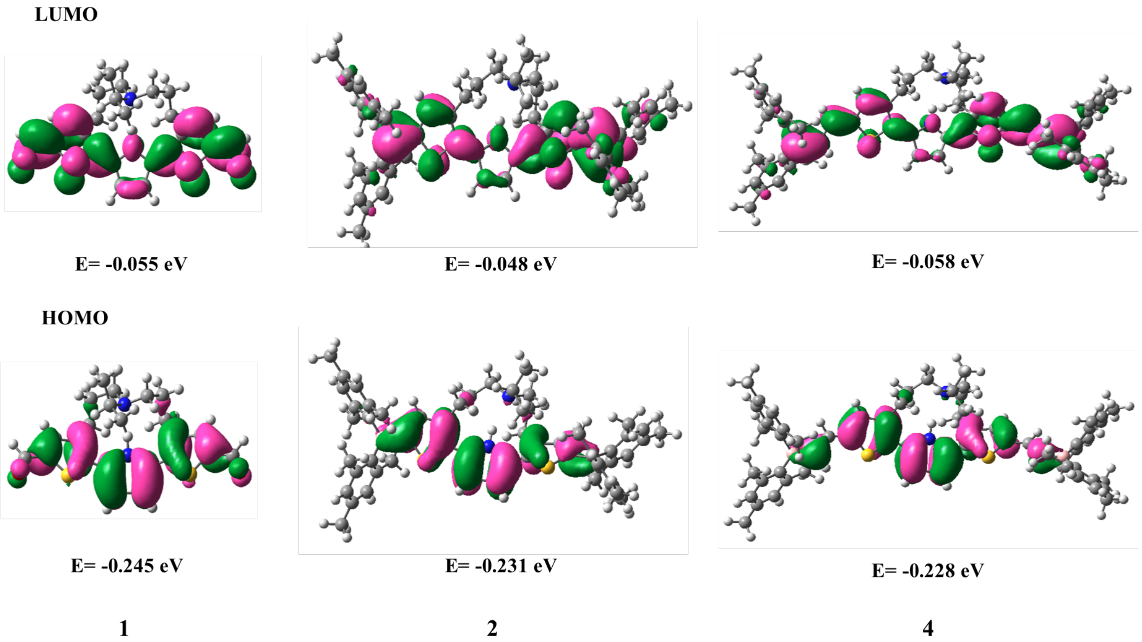


Figure S3: Representation of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) for **1**, **2**, and **4** in gas phase for the GS geometry. The energies are computed using the M06-2X functional and the 6-311+G(2d,p) atomic basis set. Contour threshold: 0.02 au.

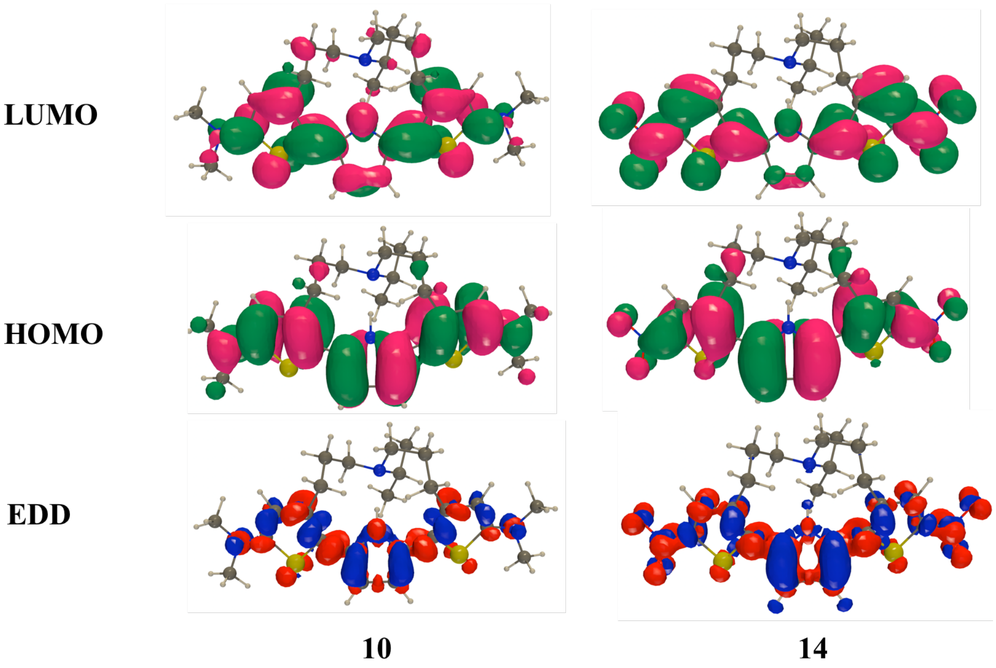


Figure S4: Representation of the highest occupied molecular orbitals (HOMO), lowest unoccupied molecular orbitals (LUMO) and Electron Density Difference (EDD) of **10** and **14** for the GS geometry in acetone. Contour threshold: 0.02 au (MOs) and 0.001 (EDDs).

Table S8: Energies (E+ZPVE) of the LE and Z forms as well as the ESIPT barrier (TS) for compounds **6-17**. The ground state energy at its optimal geometry and the LE excited state energy are taken as references. The LR+cLR solvent correction has been systematically applied. All values are given in eV.

		S_0 reference			**LE reference**		
Compound	**Solvent**	**LE**	**TS**	**Z**	**LE**	**TS**	**Z**
6	cyclohexane	2.93	3.01	3.06	0.00	0.08	0.13
	acetone	2.67	2.66	2.63	0.00	-0.01	-0.04
7	cyclohexane	2.68	2.73	2.79	0.00	0.05	0.11
	acetone	2.42	2.41	2.38	0.00	-0.01	-0.04
8	cyclohexane	3.10	3.20	3.26	0.00	0.10	0.16
	acetone	2.84	2.86	2.87	0.00	0.02	0.03
9	cyclohexane	3.14		[a]			
	acetone	3.00	3.21	3.27	0.00	0.21	0.27
10	cyclohexane	3.07		[a]			
	acetone	2.94	3.17	3.22	0.00	0.23	0.28
11	cyclohexane	3.24		[a]			
	acetone	3.12	3.24	3.30	0.00	0.12	0.18
12	cyclohexane	3.00	3.05	3.37	0.00	0.05	0.37
	acetone	2.79	2.78	2.76	0.00	-0.01	-0.03
13	cyclohexane	2.29	2.30	2.33	0.00	0.01	0.04
	acetone	2.02	1.97	1.90	0.00	-0.05	-0.12
14	cyclohexane	2.62	2.61	2.63	0.00	-0.01	0.01
	acetone	2.25	2.20	2.11	0.00	-0.05	-0.14
15	cyclohexane	3.21	3.29	3.35	0.00	0.08	0.14
	acetone	3.05	3.06	3.07	0.00	0.01	0.02
16	cyclohexane	3.21	2.90	3.39	0.00	-0.31	0.18
	acetone	3.07	3.11	3.13	0.00	0.04	0.06
17	cyclohexane	3.19	3.32	3.38	0.00	0.13	0.19
	acetone	3.05	3.10	3.13	0.00	0.05	0.08

[a] the Z conformer turned back to the LE form during geometry optimization process.

References

[1] N. Suzuki, A. Fukazawa, K. Nagura, S. Saito, H. Kitoh-Nishioka, D. Yokogawa, S. Irle and S. Yamaguchi, *Angew. Chem. Int. Ed.*, 2014, **53**, 8231–8235.

[2] N. Suzuki, K. Suda, D. Yokogawa, H. Kitoh-Nishioka, S. Irle, A. Ando, L. M. G. Abegão, K. Kamada, A. Fukazawa and S. Yamaguchi, *Chem. Sci.*, 2018, **9**, 2666–2673.

[3] D. Jacquemin, I. Duchemin and X. Blase, *J. Chem. Theory Comput.*, 2015, **11**, 5340–5359.