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Theoretical investigation of triscarbazole derivatives as host materials for blue electrophosphorescence: Effects of topology

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Comparison of computational methods

We address the accuracy of a range of quantum-chemical techniques to compute the singlet and triplet excitation energies in organic conjugated molecules. The calculated S_1 and T_1 energies along with the available experimental data are shown in Tables S1 and S2. Although INDO calculations predict the S_1 energies well, they largely underestimate the T_1 energies; the mean absolute and maximum errors amount to 0.99 and 1.12 eV, respectively. At the ab initio level, while CIS significantly overestimates the S_1 energies (the mean absolute and maximum errors correspond to 1.55 and 1.80 eV, respectively), it leads to the best prediction of the T_1 energies. DFT/B3LYP calculations, on the other hand, reproduce T_1 energies that are in very good agreement with experiment and S_1 energies that are comparable with experiment; the mean absolute and maximum errors correspond to 0.50 and 0.63 eV, respectively. Note that these calculations do not account for geometry relaxations in the excited state.

Table S1. Energies (in eV) of the S_1 state in monomers calculated at various level of theory.

X	INDO/CI	HF/CIS	TD-DFT[a]	Exp.	Ref.
NH	3.91	5.33	4.15	3.53	1
O	4.17	5.43	4.53	3.90	2
S	4.23	5.37	4.20	3.78	3
CH_2	4.30	5.34	4.40	4.08	4
$C(CH_3)_2$	4.29	5.29	4.39		
$C(CH_3)(CF_3)$	4.30	5.30	4.41		
$C(CF_3)_2$	4.32	5.29	4.42		

[a]TD-DFT is applied with the B3LYP functional and 6-31G* basis set.

Table S2. Energies (in eV) of the T_1 state in monomers calculated at various level of theory.

X	INDO/CI	HF/CIS	TD-DFT[a]	Exp.	Ref.
NH	2.03	3.03	3.19	3.05	5
O	2.00	3.01	3.21	3.12	2
S	2.06	2.93	3.16	3.01	6
CH_2	1.94	2.88	3.09	2.94	7
$C(CH_3)_2$	2.04	2.87	3.06	2.92	7
$C(CH_3)(CF_3)$	2.02	2.85	3.05		
$C(CF_3)_2$	2.02	2.85	3.03		

[a]TD-DFT is applied with the B3LYP functional and 6-31G* basis set.

Table S3. Vertical singlet (S1) and triplet (T1) excitation energies of the core molecules and their triscarbazole-like derivatives, and their energy difference ΔE_{ST} evaluated at the TD-DFT level of theory using the ωB97X exchange-correlation functional and the 6-31G* basis set.[a]

X	Core			TCz		
	$E (S_1)$	$E (T_1)$	ΔE_{ST}	$E (S_1)$	$E (T_1)$	ΔE_{ST}
NH	4.27	3.12	1.15	3.11	3.08	0.03
O	4.43	3.14	1.29	3.62	3.10	0.53
S	4.14	3.06	1.08	3.58	3.00	0.58
CH_2	4.67	3.02	1.65	3.61	2.96	0.65
$C(CH_3)_2$	4.84	2.99	1.85	3.61	2.94	0.67
$C(CH_3)(CF_3)$	4.64	2.98	1.66	3.61	2.99	0.62
$C(CF_3)_2$	4.64	2.96	1.68	3.58	2.90	0.68

[a] All the energies are in eV.

Table S4. Dominant transitions for the lowest singlet (S_1) and triplet (T_1) states of the core molecules and their 3(6),9'-triscarbazole-like derivatives.[a]

X	Core		TCz	
	S_1	T_1	S_1	T_1
NH	H→L	H-1→L	H→L	H-5→L
O	H-1→L	H→L	H-1→L+2, H→L+1	H-4→L
S	H→L	H-1→L	H→L	H-5→L
CH$_2$	H→L	H→L	H-1→L+2, H→L+1	H-4→L
C(CH$_3$)$_2$	H→L	H→L	H-1→L+2, H→L+1	H-4→L
C(CH$_3$)(CF$_3$)	H→L	H→L	H-1→L+2, H→L+3	H-4→L
C(CF$_3$)$_2$	H→L	H→L	H-1→L+3, H→L+2	H-4→L

[a] H and L denote HOMO and LUMO, respectively.

Table S5. B3LYP/6-31G* calculated adiabatic T_1 energies of the core molecules and their 3(6),9'-triscarbazole-like derivatives.[a]

	Core	TCz
NH	3.44	3.01
O	3.81	3.08
S	3.63	3.05
CH_2	3.03	2.94
$C(CH_3)_2$	2.99	2.90
$C(CH_3)(CF_3)$	2.98	2.87
$C(CF_3)_2$	2.96	2.83
FIrpic		2.69

[a] All the energies are in eV.

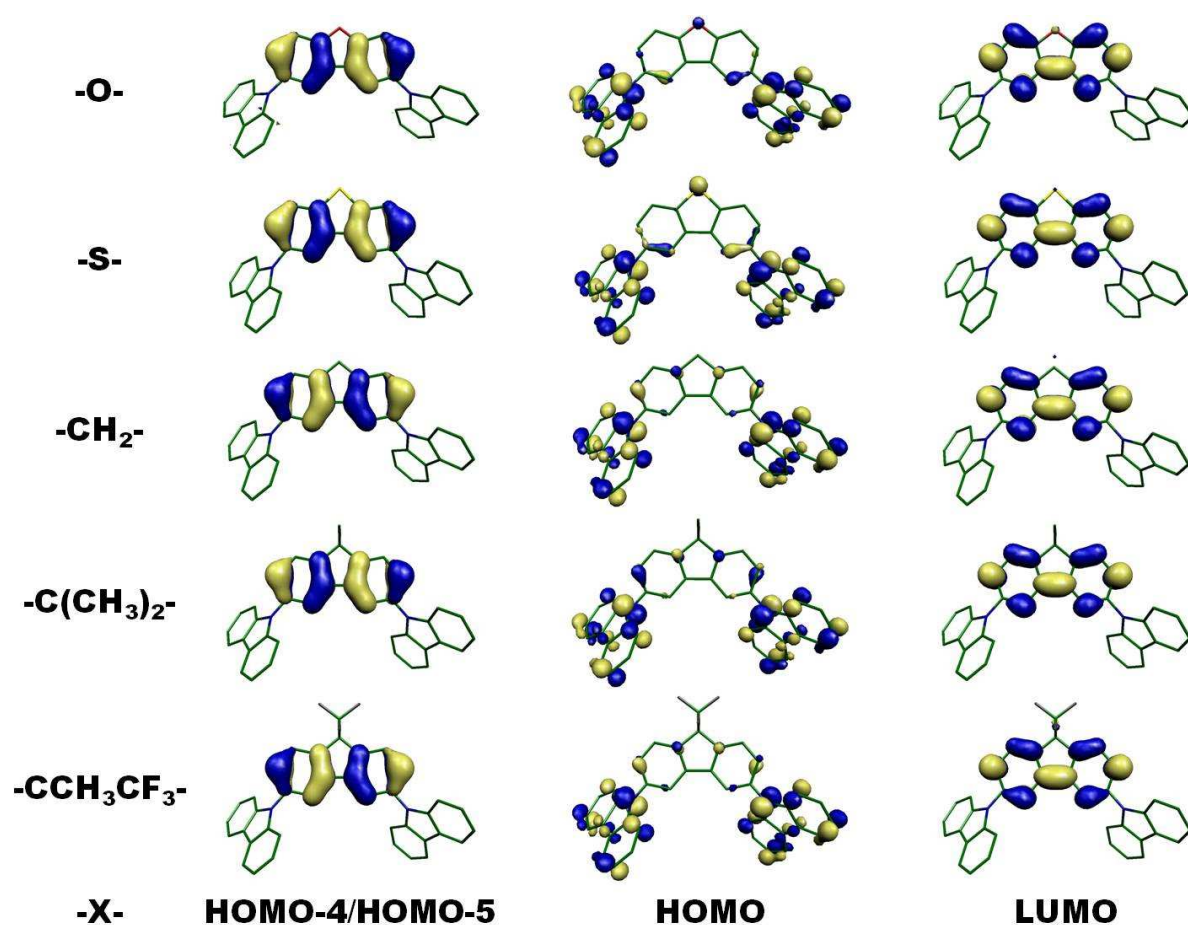|	**HOMO-4/HOMO-5**	**HOMO**	**LUMO**
-O-			
-S-			
-CH$_2$-			
-C(CH$_3$)$_2$-			
-CCH$_3$CF$_3$-			
-X-			

Figure S1. Frontier molecular orbitals in the triscarbazole-like derivatives with varying X groups (X=O, S, CH$_2$, C(CH$_3$)$_2$, C(CH$_3$)(CF$_3$)). The HOMOs are delocalized on the side carbazoles and the HOMO-4 or HOMO-5 and LUMOs are localized on the core units. In the case of X=S, the occupied orbital localized on the core unit is HOMO-5, and for the others, HOMO-4.

References

1. Tsai, M. H.; Hong, Y. H.; Chang, C. H.; Su, H. C.; Wu, C. C.; Matoliukstyte, A.; Simokaitiene, J.; Grigalevicius, S.; Grazulevicius, J. V.; Hsu, C. P., *Adv. Mater.* **2007,** *19,* 862.

2. Vecchi, P. A.; Padmaperuma, A. B.; Qiao, H.; Sapochak, L. S.; Burrows, P. E., *Org. Lett.* **2006,** *8,* 4211.

3. de Melo, J. S.; Pina, J.; Rodrigues, L. M.; Becker, R. S., *J. Photochem. Photobio. A-Chem.* **2008,** *194,* 67.

4. Wasserberg, D.; Dudek, S. P.; Meskers, S. C. J.; Janssen, R. A. J., *Chem. Phys. Lett.* **2005,** *411,* 273-277.

5. Bonesi, S. M.; Erra-Balsells, R., *J. Luminesc.* **2001,** *93,* 51.

6. Terada, T.; Koyanagi, M.; Kanda, Y., *Bull. Chem. Soc. Jpn.* **1980,** *53,* 352.

7. Padmaperuma, A. B.; Sapochak, L. S.; Burrows, P. E., *Chem. Mater.* **2006,** *18,* 2389.