Supporting Information

Theoretical Investigation of the Singlet−Triplet Splittings for Carbazole-Based Thermally Activated Delayed Fluorescence Emitter

Ke Liang,[a] Caijun Zheng,[b,c] Kai Wang,[a,c] Wei Liu,[a,c] Zhenyu Guo,[a] Youyong Li,*[a] Xiaohong Zhang.*[a]*

[a]*Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou, Jiangsu, 215123, P.R. China,*

E-mail: xiaohong_zhang@suda.edu.cn, yyli@suda.edu.cn

[b]*School of Optoelectronic Information, University of Electronic Science and Technology of China (UESTC) Chengdu, 610054, P.R. China,*

E-mail: zhengcaijun@uestc.edu.cn

[c]*Nano-organic Photoelectronic Laboratory and Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, P.R. China.*

Contents

OHF method

OHF is determined by the relation OHF=42q. q is the CT amount which simplified in equation (1) below. $\Sigma_i a_i=1$, $\Sigma_i b_i=1$, and $q = q_+ = q_-$, where the index i represents the number of fragments; a_i and b_i are the contribution percentages of different molecular fragments in HOMO and LUMO, respectively. $E_{00}(S_1)$ is expressed by equation (2), in which 0.24 eV consists of two parts: Stokes-shift energy loss (0.09 eV) and vibrational energy level difference between the vertical transition (0.15 eV). In equation (3), $C = E_{VA}(S_1,OHF)/E_{VA}(S_1,B3LYP)$ where $E_{VA}(S_1,OHF)$ is the singlet vertical excitation energy from the E_{VA} and HF% curves according to OHF=42q, and $E_{VA}(S_1,B3LYP)$ is the singlet vertical excitation energy calculated by B3LYP functional. In equation (4), 0.09 eV is the Stokes-shift energy loss and $E_{00}(^3LE)$ is the average value calculated by BMK, M06-2X and M06-HF where C is 1.10, 1.18 and 1.30, respectively.

$$q_+ = e\,\Sigma_i|a_i-b_i|,\ a_i-b_i > 0;\ q_- = e\,\Sigma_i|a_i-b_i|,\ a_i-b_i < 0 \quad (1)$$

$$E_{00}(S_1) = E_{VA}(S_1,OHF) - 0.24 \quad (2)$$

$$E_{00}(^3CT) = E_{00}(S_1) - E_{VA}(S_1,OHF) + C \times E_{VA}(T_1,B3LYP), \quad (3)$$

$$E_{00}(^3LE) = E_{VA}(T_1)/C - 0.09 \quad (4)$$

Table S1. Calculated $E_{VA}(S_1)$ and $E_{VA}(T_1)$ using various XC functionals based on B3LYP optimized S_0 geometry (unit of all the data is eV).

Functional	TTO		AQ1		AQ2		DMD		MID	
	$E_{VA}(S_1)$	$E_{VA}(T_1)$	$E_{VA}(S_1)$	$E_{VA}(T_1)$	$E_{VA}(S_1)$	$E_{VA}(T_1)$	$E_{VA}(S_1)$	$E_{VA}(T_1)$	$E_{VA}(S_1)$	$E_{VA}(T_1)$
BLYP	2.327	2.181	1.568	1.414	1.558	1.377	2.226	2.042	2.145	1.958
MPWLYP1M	2.506	2.334	1.735	1.574	1.713	1.524	2.402	2.197	2.314	2.111
B3LYP*	2.861	2.620	2.083	1.891	2.040	1.824	2.762	2.490	2.658	2.402
B3LYP	3.037	2.740	2.266	2.045	2.214	1.971	2.943	2.611	2.834	2.529
PBE0	3.216	2.811	2.451	2.169	2.388	2.092	3.122	2.672	3.018	2.613
MPW1B95	3.353	2.972	2.620	2.334	2.549	2.255	3.236	2.805	3.165	2.783
BMK	3.650	3.176	2.952	2.582	2.868	2.506	3.353	2.893	3.466	2.992
M06-2X	3.860	3.374	3.146	2.763	3.112	2.731	3.3287	2.941	3.727	3.225
M06HF	4.404	3.785	2.805	2.492	2.808	2.495	2.883	2.568	3.816	3.492

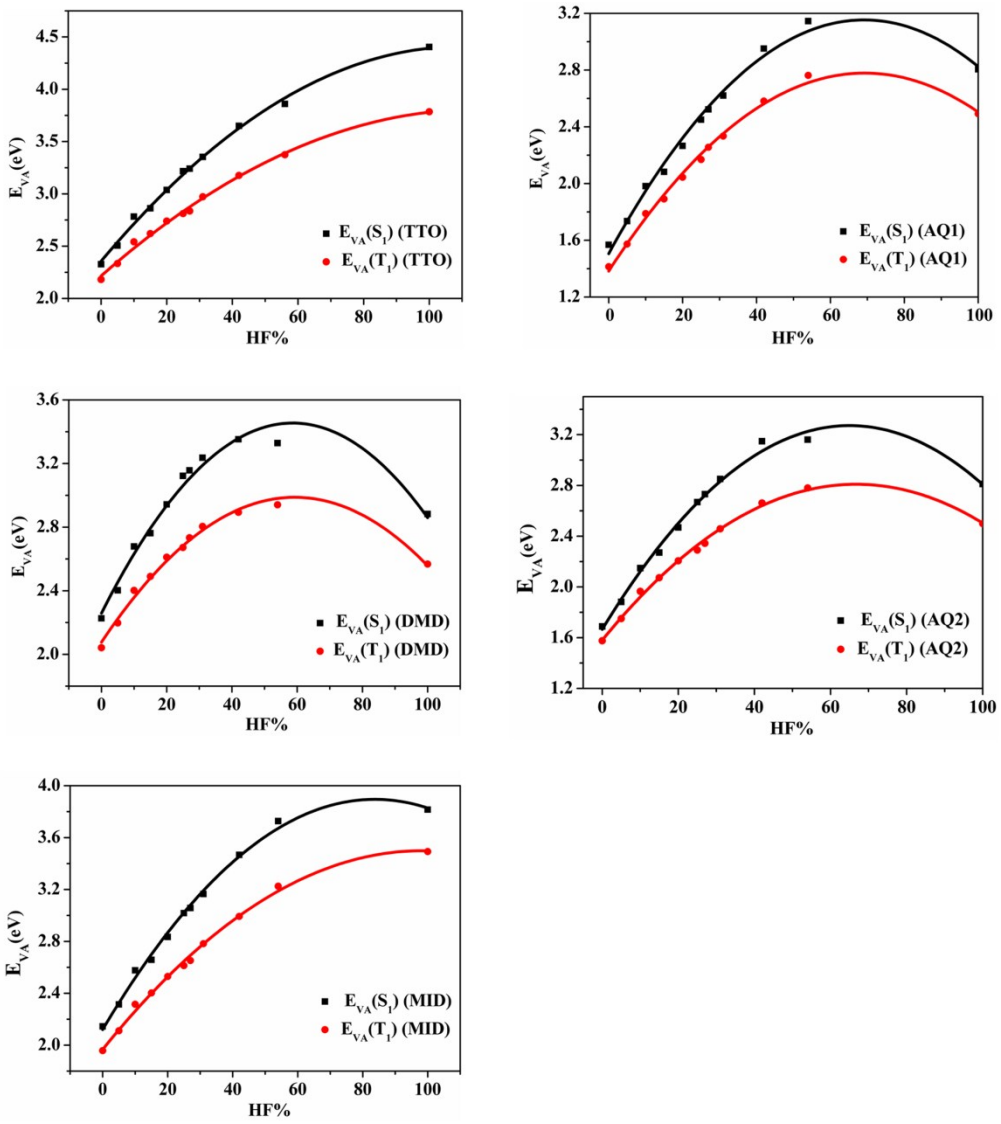

Figure S1. Dependence of $E_{VA}(S_1)$ and $E_{VA}(T_1)$ of the compounds investigated on the HF% in TD-DFT functionals.

Table S2. CI description of S_1 transition by B3LYP/6-31G* level and the amount of charge transfer.

Compound	CI coefficient	CI description of S_1	C_j %[a]	CT amount (q)
TTO	0.70106	HOMO→LUMO	98.3%	0.8609
AQ1	0.70404	HOMO→LUMO	99.1%	0.8614
AQ2	0.70383	HOMO→LUMO	99.1%	0.8283
DMD	0.68883	HOMO→LUMO	94.9%	0.8548
MID	0.70384	HOMO→LUMO	99.1%	0.8518

[a]C_j % = (CI coefficient)^2 × 2 × 100%.

Table S3. Calculated $E_{00}(^3LE)$ of the Cz-based compounds using OHF (unit of all the energy data is eV).

Compound	OHF%	$E_{VA}(S_1,OHF)$	$E_{00}(^3LE)$			
			BMK	M06-2X	M06-HF	Average
TTO	36	3.49	2.797	2.769	2.821	2.796
AQ1	36	2.78	2.347	2.251	1.827	2.142
AQ2	35	2.68	2.188	2.225	1.829	2.081
DMD	36	2.85	2.540	2.312	1.885	2.246
MID	36	3.32	2.630	2.643	2.596	2.623

Table S4. Calculated $E_{00}(S_1)$ and $E_{00}(T_1)$ and relaxation energies using various XC functionals based on the optimized excited states (unit of all the data is eV).

Functional		TTO	AQ1	AQ2	DMD	MID
BLYP	$E_{00}(S_1)$	1.734	0.977	0.957	1.572	1.493
	$E_{00}(T_1)$	1.730	0.974	0.952	1.565	1.487
MPWLYP1M	$E_{00}(S_1)$	1.953	1.203	1.180	1.800	1.717
	$E_{00}(T_1)$	1.948	1.199	1.174	1.792	1.710
B3LYP*	$E_{00}(S_1)$	2.34	1.64	1.60	2.24	2.15
	$E_{00}(T_1)$	2.33	1.635	1.59	2.23	2.14
B3LYP	$E_{00}(S_1)$	2.53	1.86	1.81	2.45	2.36
	$E_{00}(T_1)$	2.51	1.84	1.80	2.40	2.30
PBE0	$E_{00}(S_1)$	2.73	2.10	2.04	2.70	2.60
	$E_{00}(T_1)$	2.57	1.99	1.95	2.47	2.37
MPW1B95	$E_{00}(S_1)$	2.91	2.24	2.30	2.93	2.83
	$E_{00}(T_1)$	2.74	2.06	2.12	2.55	2.55
BMK	$E_{00}(S_1)$	3.26	2.66	2.68	3.09	3.18
	$E_{00}(T_1)$	2.86	2.27	2.32	2.69	2.67
CAM-B3LYP	$E_{00}(S_1)$	3.607	3.134	3.085	3.244	3.558
	$E_{00}(T_1)$	2.736	2.252	2.239	2.578	2.515
wB97X-D	$E_{00}(S_1)$	3.782	3.224	3.23	3.213	3.659
	$E_{00}(T_1)$	2.896	2.386	2.359	2.795	2.636
Experimental	$E_{00}(S_1)$	2.54	2.15	2.11	2.53	2.45
	$E_{00}(T_1)$	2.51	2.13	2.10	2.50	2.41

Table S5. Calculated relaxation energies (λ) using various XC functionals (unit of all the data is eV).

Functional		TTO	AQ1	AQ2	DMD	MID
B3LYP*	λ_S	0.52	0.44	0.44	0.52	0.51
	λ_T	0.29	0.26	0.23	0.26	0.26
B3LYP	λ_S	0.51	0.41	0.40	0.49	0.47
	λ_T	0.23	0.20	0.17	0.21	0.23
PBE0	λ_S	0.49	0.35	0.35	0.42	0.42
	λ_T	0.24	0.18	0.142	0.20	0.24
MPW1B95	λ_S	0.44	0.38	0.25	0.31	0.34
	λ_T	0.23	0.27	0.14	0.26	0.23
BMK	λ_S	0.39	0.29	0.19	0.26	0.29
	λ_T	0.32	0.31	0.19	0.20	0.32

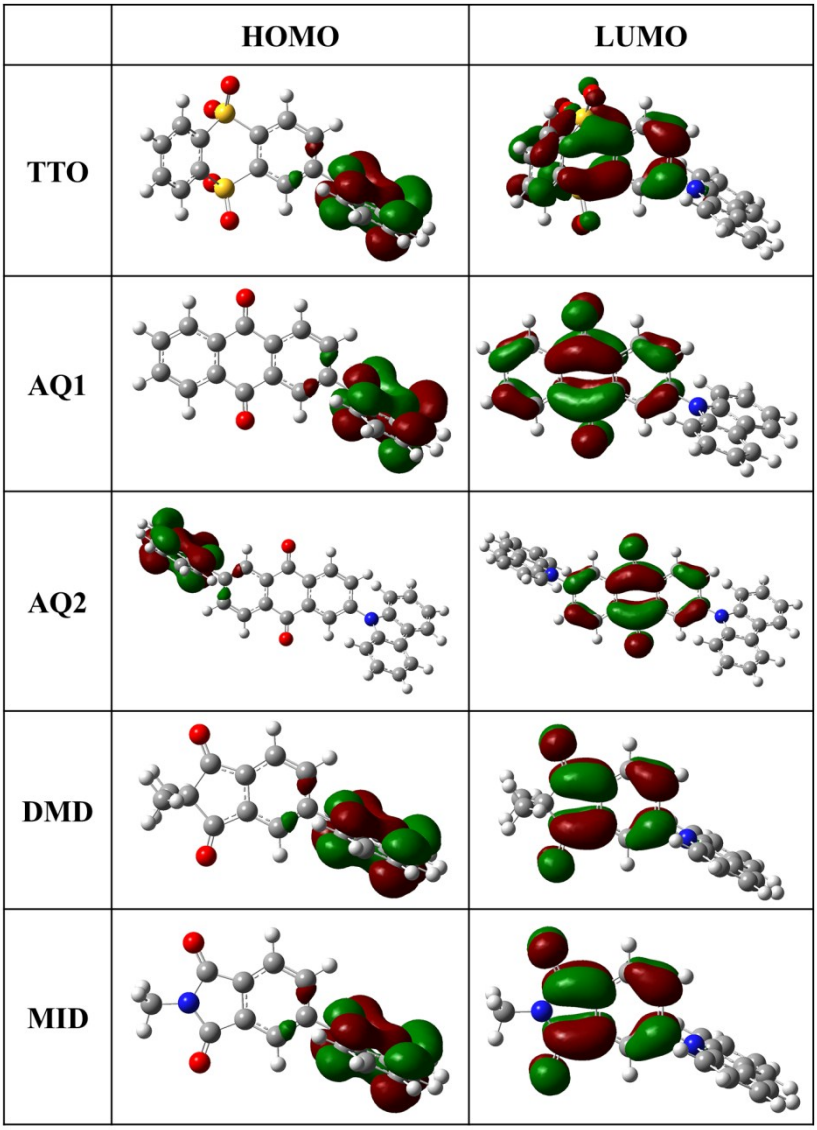

Figure S2. HOMO and LUMO of the S_1 state calculated at the B3LYP/6-31G* level.

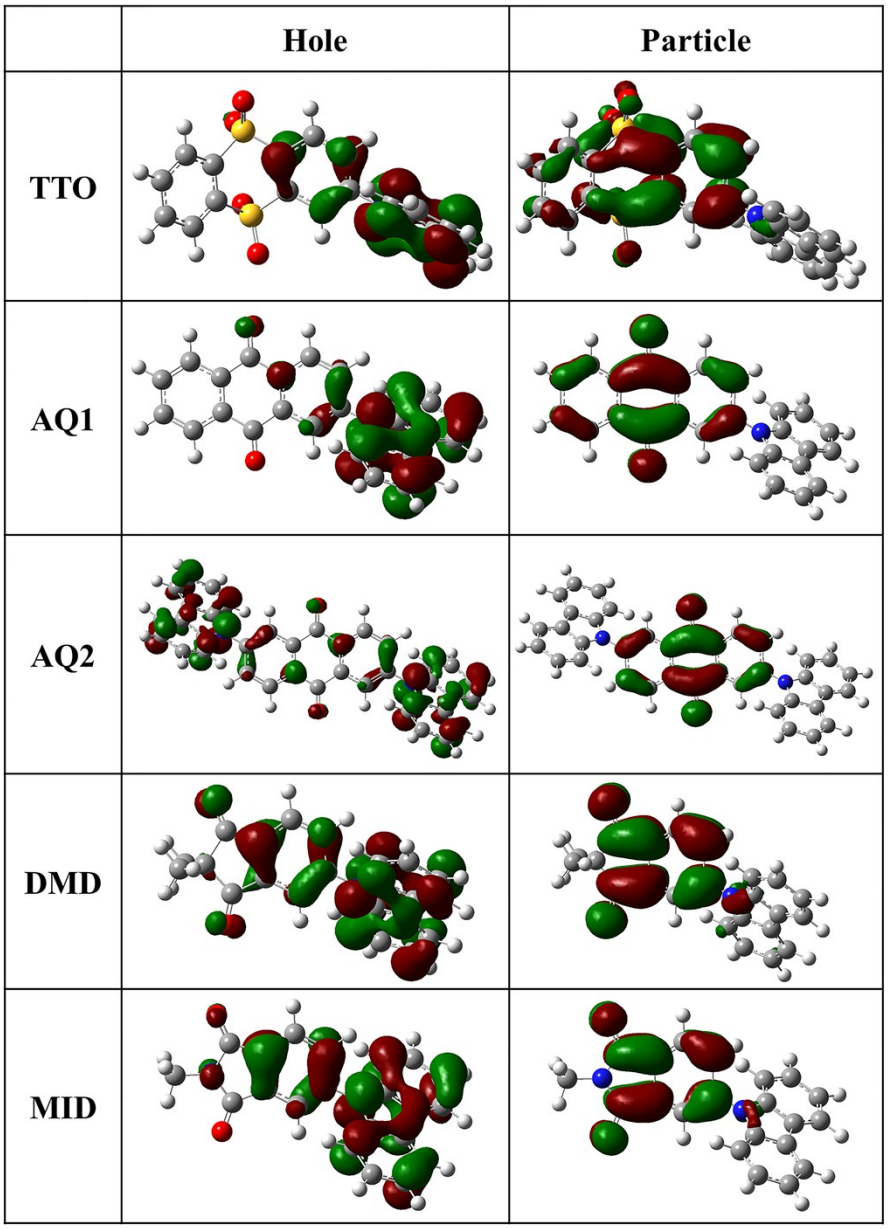

Figure S3. Hole-particle pairs of natural transition orbitals (NTO) of the optimized T_1 state for the Cz-based molecules.