Electronic Supplementary Information

Theoretical investigation of dihydroacridine- and diphenylsulphone-derivatives as thermally activated delayed fluorescence emitters for organic light-emitting diodes

Xiaguang Zhang, Wei Shen, Dongmei Zhang, Yongzhen Zheng, Rongxing He, Ming Li*

School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, P. R. China

* Corresponding author:

E-mail: liming@swu.edu.cn; Phone: +86-023-68253023

Supplementary data

Table S1. Calculated HOMO, E_T, and transition energies (S_1 and T_1) (in eV) by the different methods.

Table S2. Calculated HOMO and E_T values (in eV) at B3P86/6-31G(d) and M06/6-31G(d) levels.

Table S3. Calculated transition energies of the experiment molecules in vacuum and toluene by the different methods.

Table S4. Calculated emission wavelength (nm) of the experiment molecules in toluene on S_1 geometries optimized by different methods.

Table S5. Bonds lengths (nm) and dihedral angles (˚) of donor and acceptor in singlet state. All calculation is obtained by P3P86/6-31G(d) level.

Table S6. The wavelength (nm) transition assignment for $S_0 \rightarrow S_1$ of compounds 1-6 at the B3LYP/6-31G(d) level of theory.

Table S7. Transition energies (eV) of $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ at different dihedral angle (˚) for compounds 1, 2, 3 and 6. All calculation is obtained by B3LYP/6-31G(d) level.

Table S8. Calculated wavelength (λ/nm), oscillation strength (f), dipole moment (μ) and orbital assignment of $S_0 \rightarrow S_1$ transition for host molecules at the B3LYP/6-31G(d) level of theory.

Table S9. Calculated ionization potentials (eV), electron affinities (eV), reorganization energy (eV) and transfer integral (eV) of compounds 1-3 and host molecule DPEPO. All calculation is obtained by B3P83/6-31G(d) level.

Figure S1. The optimized geometry for compounds 1-6 in the ground state.

Figure S2. Total densities of states (DOS) and projected DOS (PDOS) for compounds 1-6.

Figure S3. Natural transition orbitals for compounds 1-6 in the singlet and triplet excited states

Table S1. Calculated HOMO, E_T, and transition energies (S_1 and T_1) (in eV) by the different methods.

	HF	6-31G(d)													6-311+G(d)		
	(%)	HOMO	LUMO	E_T	*E*r(H) %	Er(E_T) %	MAX (H, E_T)	MAD (H, E_T)	RMSD (H, E_T)	S_1	T_1	MAX	MAD	RMSD	HOMO	LUMO	*E*r(H) %
B3LYP	20	-5.25	-1.74	2.94	-11.32	1.03	0.67	0.35	0.474	2.91	2.90	0.09	0.09	0.09	-5.59	-2.13	-5.61
B3P86	20	-5.92	-2.41	2.92	0.00	0.34	0.01	0.00	0.007	2.91	2.89	0.09	0.09	0.09			
b3pw91	20	-5.35	-1.85	2.91	-9.63	0.00	0.57	0.29	0.403	2.90	2.89	0.10	0.10	0.10	-5.63	-2.16	-4.96
HSE06	25	-5.13	-2.02	2.82	-13.34	-3.09	0.79	0.44	0.562	2.92	2.90	0.08	0.08	0.08	-5.41	-2.35	-8.59
PBE0	25	-5.52	-1.65	2.95	-6.76	1.37	0.4	0.22	0.284	3.09	3.07	0.09	0.09	0.09	-5.79	-1.98	-2.18
M06	27	-5.60	-1.60	3.02	-5.41	3.78	0.32	0.22	0.239	3.16	3.15	0.17	0.17	0.17	-5.92	-2.00	0.00
b1b95	28	-5.53	-1.47	3.11	-6.59	6.87	0.39	0.30	0.310	3.18	3.17	0.19	0.19	0.19	-5.79	-1.78	-2.13
CAM	100	-6.60	-0.48	3.19	11.49	9.62	0.68	0.48	0.520	3.94	3.35	0.94	0.66	0.71	-6.93	-0.91	16.99
LC-WPBE	100	-7.87	0.41	3.26	32.94	12.03	1.95	1.15	1.401	4.62	2.99	0.62	0.82	1.15			
EXP[a]		-5.92	-2.92	2.91						3.00	2.98						

[a] experiment data, ref. 10

Table S2. Calculated HOMO and E_T values (in eV) at B3P86/6-31G(d) and M06/6-31G(d) levels.

	HOMO	E_T	MAX	RMSD
B3P86	-5.92	2.92	0.01	0.007
M06	-5.92	2.98	0.07	0.049

Table S3. Calculated transition energies of the experiment molecules in vacuum and toluene by the different methods.

	HF	in gas-phase						in toluene					
	(%)	S_1	T_1	LUMO	MAX	MAD	RMSD	S_1	T_1	LUMO	MAX	MAD	RMSD
BLYP	0	2.11	2.11	-3.81	0.89	0.880	0.880	2.14	2.14	-3.78	0.86	0.850	0.850
TPSSH	10	2.61	2.60	-3.31	0.39	0.384	0.384	2.64	2.63	-3.28	0.36	0.354	0.354
B3LYP	20	2.92	2.91	-3.00	0.08	0.074	0.074	2.95	2.94	-2.97	0.05	0.047	0.047
B3PW91	20	2.91	2.89	-3.01	0.09	0.091	0.091	2.94	2.92	-2.98	0.06	0.060	0.060
B3P86	20	2.91	2.89	-3.02	0.10	0.093	0.093	2.94	2.92	-2.98	0.06	0.063	0.060
HSE06	25	2.91	2.90	-3.01	0.09	0.083	0.083	2.95	2.93	-2.97	0.05	0.053	0.053
PBE0	25	3.09	3.07	-2.83	0.09	0.088	0.088	3.12	3.10	-2.80	0.12	0.119	0.119
M06	27	3.18	3.16	-2.74	0.18	0.178	0.178	3.20	3.18	-2.72	0.20	0.202	0.202
B1B95	28	3.14	3.12	-2.78	0.14	0.140	0.140	3.17	3.15	-2.75	0.17	0.169	0.169
BMK	42	3.59	3.56	-2.33	0.59	0.588	0.588	3.62	3.59	-2.30	0.62	0.614	0.614
M062X	54	3.80	3.78	-2.12	0.80	0.801	0.801	3.83	3.81	-2.09	0.83	0.827	0.827
LC-WPBE	100	4.56	2.90	-1.36	1.56	1.068	1.277	4.59	2.91	-1.33	1.59	1.083	1.229
CAM-B3LYP	100	3.92	3.31	-2.00	0.92	0.719	0.771	3.94	3.31	-1.98	0.94	0.738	0.792

Table S4. Calculated emission wavelength (nm) of the experiment molecules in toluene on S_1 geometries optimized by different methods.

	HF	λ	Er %
BLYP	0	699.38	52.04
TPSSH	10	542.42	17.92
B3LYP	20	471.08	2.41
B3P86	20	479.50	4.24
PBE0	25	445.19	-3.22
M06	27	424.73	-7.67
B1B95	28	431.02	-6.30
BMK	42	367.85	-20.03
M062X	54	392.06	-14.77
LC-WPBE	100	312.2	-32.13
CAM-B3LYP	100	330.49	-28.15
EXP[a]		460	

[a] experiment data, ref. 10

Table S5. Bonds lengths (nm) and dihedral angles (˚) of donor and acceptor in singlet state. All calculation is obtained by P3P86/6-31G(d) level.

compound		bond length		dihedral angle	
1	S_1	1.4312	1.4501	-78.5102	-89.1119
2	S_1	1.4630	1.4317	88.8228	76.3763
3	S_1	1.4538	1.4314	-78.2777	-69.7657
4	S_1	1.4716	1.4502	-36.1127	18.6782
5	S_1	1.4750	1.4804	-35.4452	35.2785
6	S_1	1.4843	1.4135	-55.6208	-24.5458

Table S6. The wavelength (nm) transition assignment for $S_0 \rightarrow S_1$ of compounds 1-6 at the B3LYP/6-31G(d) level of theory.

compounds	λ/nm	assignment
1	420.17	HOMO → LUMO (94%)
2	414.18	HOMO → LUMO (82%)
3	431.50	HOMO → LUMO (97%)
4	379.57	HOMO → LUMO (96%)
5	360.33	HOMO → LUMO (98%)
6	351.14	HOMO → LUMO (98%)

Table S7. Transition energies (eV) of $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ at different dihedral angle (˚) for compounds 1, 2, 3 and 6. All calculation is obtained by B3LYP/6-31G(d) level.

compound	dihedral angle	S_1	T_1	ΔE_{ST}
1	0	3.64	3.15	0.49
2	0	3.37	3.03	0.34
3	0	3.25	2.94	0.31
6	0	3.12	2.66	0.46
6	90	3.36	3.16	0.20

Table S8. Calculated wavelength (λ/nm), oscillation strength (f), dipole moment (μ) and orbital assignment of $S_0 \rightarrow S_1$ transition for host molecules at the B3LYP/6-31G(d) level of theory.

compound	λ/nm	f	μ	assignment
mcp	308.08	0.1414	1.4344	H-1 → L+1 (24%), HOMO → LUMO (69%)
dpepo	263.25	0.0504	0.4366	HOMO → LUMO (88%)
cbp	344.44	0.8793	9.9706	HOMO → LUMO (98%)

Table S9. Calculated ionization potentials (eV), electron affinities (eV), reorganization energy (eV) and transfer integral (eV) of compounds 1-3 and host molecule DPEPO. All calculation is obtained by B3P83/6-31G(d) level.

compound	IP(a)	EA(a)	λh	λe	λh/λe	Vh	Ve
1	6.72	-1.32	0.23	0.40	0.58	0.0030	0.3521
2	6.69	-1.26	0.24	0.44	0.55	0.0112	0.3454
3	6.63	-1.20	0.28	0.54	0.52	0.0035	0.3234
dpepo	7.42	-0.41					

The Marcus-Hush equation can expressed as

$$k = \frac{V^2}{\mathsf{h}} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{\lambda}{4 k_B T} \right) \tag{2}$$

Here λ is the reorganization energy, k_B is Boltzmann constant, T is the temperature, and V is the transfer integral between initial and final states, and the holes (electrons) transfer integral of organic materials is equal to the half the HOMO (LUMO+1) energy and HOMO-1 (LUMO) energy, as

$$V_{h/e} = \frac{E_{H(\mathrm{L}+1)} - E_{H-1(\mathrm{L})}}{2} \tag{3}$$

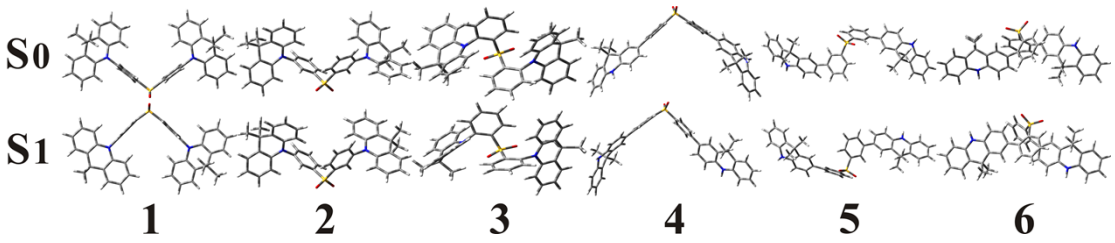

Figure S1. The optimized geometry for compounds 1-6 in the ground state.

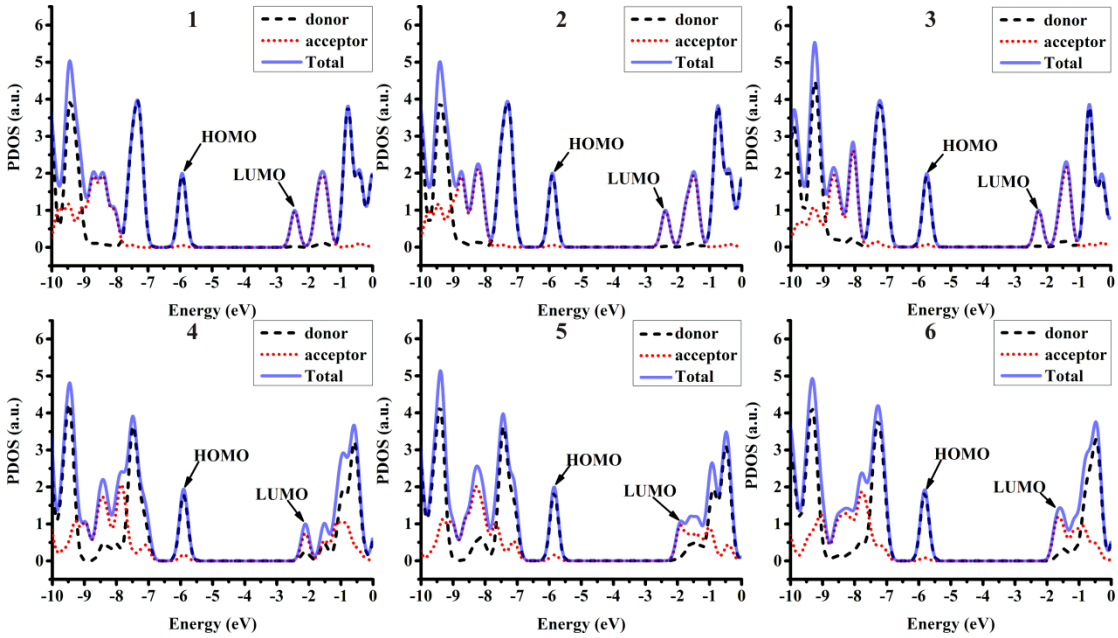

Figure S2. Total densities of states (DOS) and projected DOS (PDOS) for compounds 1-6.

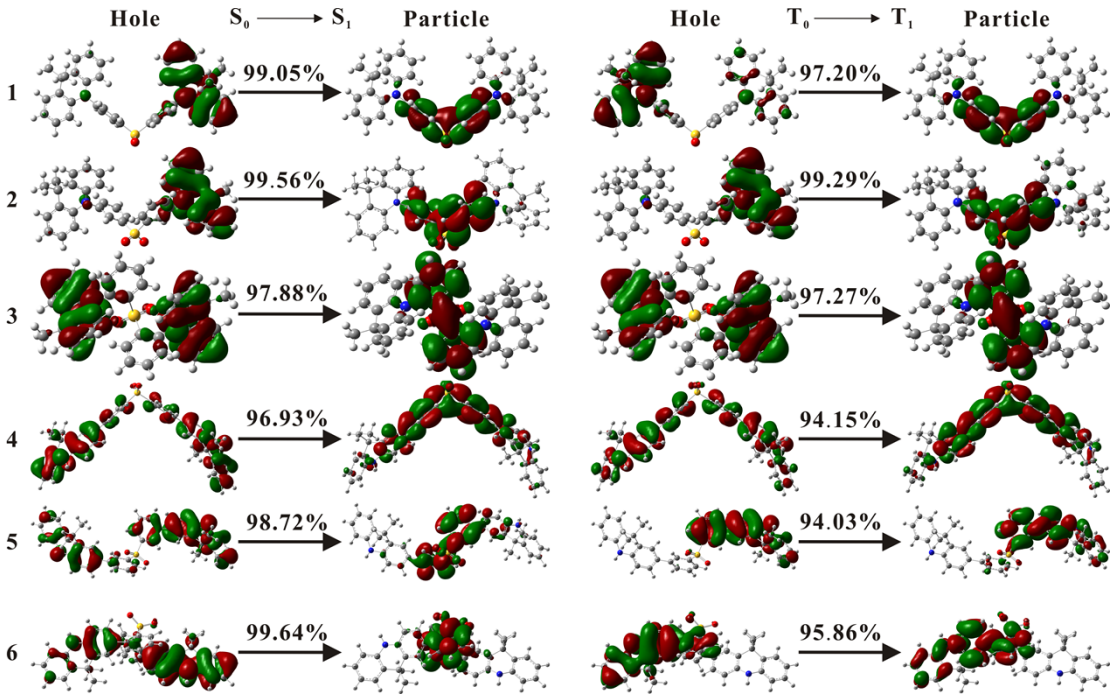

Figure S3. Natural transition orbitals for compounds 1-6 in the singlet and triplet excited states.