

Supporting Information

A theoretical study on the donor ability adjustment of tris(2,4,6-trichlorophenyl)methyl- triarylamine (TTM-TPA) radicals aiming to develop better organic luminescent materials

Hai-Ping Zhou,^{a,b} Shui-Xing Wu,^{*a} Ying-Chen Duan,^b Feng-Wei Gao,^b Qing-Qing Pan,^{*b} Yu-He Kan,^{*c} and Zhong-Min Su^{b,d}

^a Key Laboratory of Electrochemical Energy Storage and Energy Conversion of Hainan Province, School of Chemistry & Chemical Engineering, Hainan Normal University, Haikou 571158, China. E-mail: sxwu@live.com

^b School of Chemistry and Environmental Engineering, Changchun University of Science and Technology, 7989 Weixing Road, Changchun 130012, China. E-mail: panqq349@nenu.edu.cn

^c Address here Jiangsu Province Key Laboratory for Chemistry of Low-Dimensional Materials, School of Chemistry and Chemical Engineering, Huaiyin Normal University, Huai'an 223300, China. E-mail: kyh@hytc.edu.cn

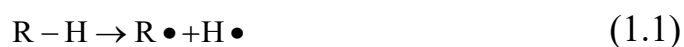
^d Institute of Functional Material Chemistry, Faculty of Chemistry & National & Local United Engineering Laboratory for Power Battery, Northeast Normal University, Changchun 130024, China

Content

Details on computational methodology	3
Figure S1. Absorption energies (eV) of TTM computed with various methods using the 6-311G(d,p) basis set with PCM solvent models (solvent=cyclohexane).	5
Figure S2. D_1 state excitation energies (eV) of TTM computed with various methods using the 6-311G(d,p) basis set with PCM solvent models (solvent=cyclohexane).	5
Figure S3. Spin density of D-A radical molecules at PBE0-D3(BJ)/6-311G (d, p) level with Becke theory. Yellow and white surfaces represent α and β spin density distributions with 0.0001 a.u. isosurfaces, respectively.	6
Figure S4. Molecule structure of D-A monoradical molecules. Dihedral C1-C2-C3-C4 is marked in orange.....	6
Figure S5. Energies and FMOs of monoradical molecules 1-8.	7
Table S1. Excitation wavelengths (nm) of TTM computed with various methods using the 6-311G(d,p) basis set with PCM solvent models (solvent=cyclohexane).	8
Table S2. Spin population of the central carbon atom of TTM-TPA in the D_0 -state with selected dihedral angles.	8
Table S3. Electron coupling values (V/eV) of radical molecules 1-8 between Ground and Excited States.	9
Table S4. The bond distance (\AA) and dihedral angles ($^\circ$) between donor and acceptor at optimized D_0 - and D_1 - states, respectively, together with their difference (Δ) at the PBE0-D3(BJ)/6-311G(d,p) level.....	9
References.....	10

Details on computational methodology

It is generally known that the stability of the relevant radical with C-center has a generally bearing on the C-H BDE,¹⁻² and a smaller BDE signifies better thermodynamic stability of the corresponding radical. Commonly speaking, BDE can be described and calculated by eqn (1.1) and eqn (1.2).



$$\text{BDE}(\text{R-H}) = H(\text{R}\bullet) + H(\text{H}\bullet) - H(\text{R-H}) \quad (1.2)$$

where R•, H• and R-H denote the TTM-Based radical, hydrogen radical, and precursor of the relevant radical, respectively.

The stability of carbon-centered radicals can expediently be indicated by the transfer reaction as shown in eqn (1.3), whose energy of the reaction is normally known as the radical stabilization enthalpy (RSE)² of the freshly shaped TTM-Based radical relative to the TTM, can be calculated using eqn (1.4).



$$\begin{aligned} \text{RSE}(\text{R}\bullet) &= H(\text{R-H}) + H(\text{TTM}) - H(\text{R}\bullet) - H(\text{TTM-H}) \\ &= \text{BDE}(\text{TTM-H}) - \text{BDE}(\text{R-H}) \end{aligned} \quad (1.4)$$

In general, the more positive the RSE, the better the thermodynamic stability of the corresponding radical. When RSE is positive, the radical is steadier than TTM.

The reorganization energy (λ) related to non-radiative transitions was

obtained from the adiabatic potential energy surfaces of the D_0 and D_1 states,³ which can be proximately predicted by:

$$\lambda = \left[E(D_0)^E - E(D_0) \right] + \left[E(D_1)^G - E(D_1) \right] \quad (1.5)$$

where $E(D_0)$ and $E(D_0)^E$ are the energy of the D_0 -state calculated at the minimal ground-state structure and minimal excited state structure, respectively. $E(D_1)^G$ and $E(D_1)$ are the energy of the D_1 -state calculated at the minimal ground-state structure and minimal excited state structure, respectively.

The electronic coupling (V) between the CT state and ground state can be evaluated immediately from the 2-state Generalized Mulliken–Hush (GMH)⁴⁻⁷ approximation:

$$V = \frac{\mu_{12} \Delta E_{12}}{\Delta \mu_{12}^D} = \frac{\mu_{12} \Delta E_{12}}{\left(\Delta \mu_{12}^2 + 4 \mu_{12}^2 \right)^{1/2}} \quad (1.6)$$

where μ_{12} , $\Delta \mu_{12}$, ΔE_{12} and $\Delta \mu_{12}^D$ denote the transition dipole moment between the two adiabatic states, the difference between the dipole moments of the adiabatic states, the energy difference between the adiabatic states, and the difference between the dipole moments of the diabatic states, respectively.

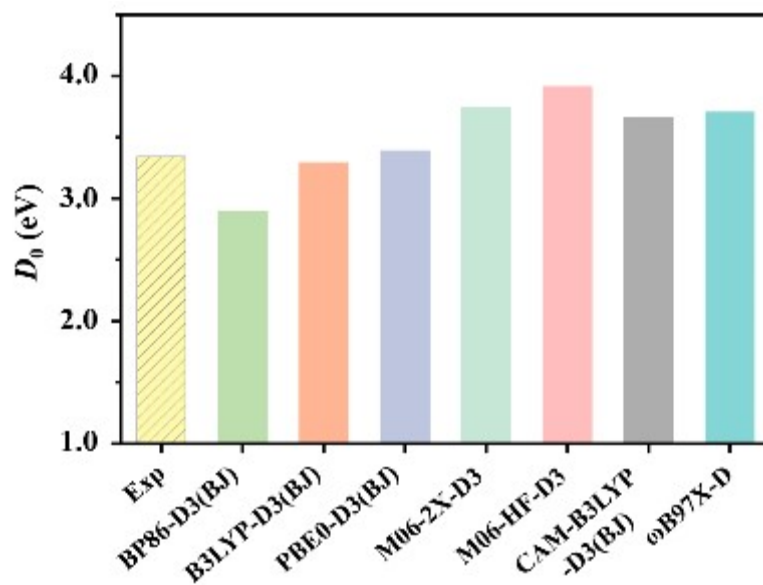


Figure S1. Absorption energies (eV) of TTM computed with various methods using the 6-311G(d,p) basis set with PCM solvent models (solvent=cyclohexane).

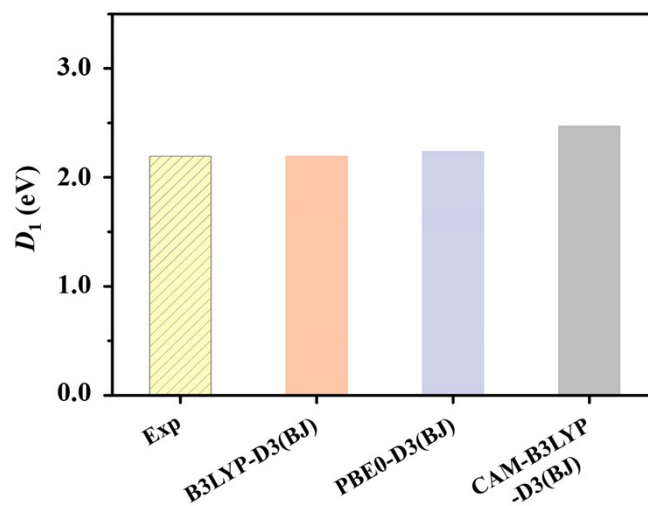


Figure S2. D_1 state excitation energies (eV) of TTM computed with various methods using the 6-311G(d,p) basis set with PCM solvent models (solvent=cyclohexane).

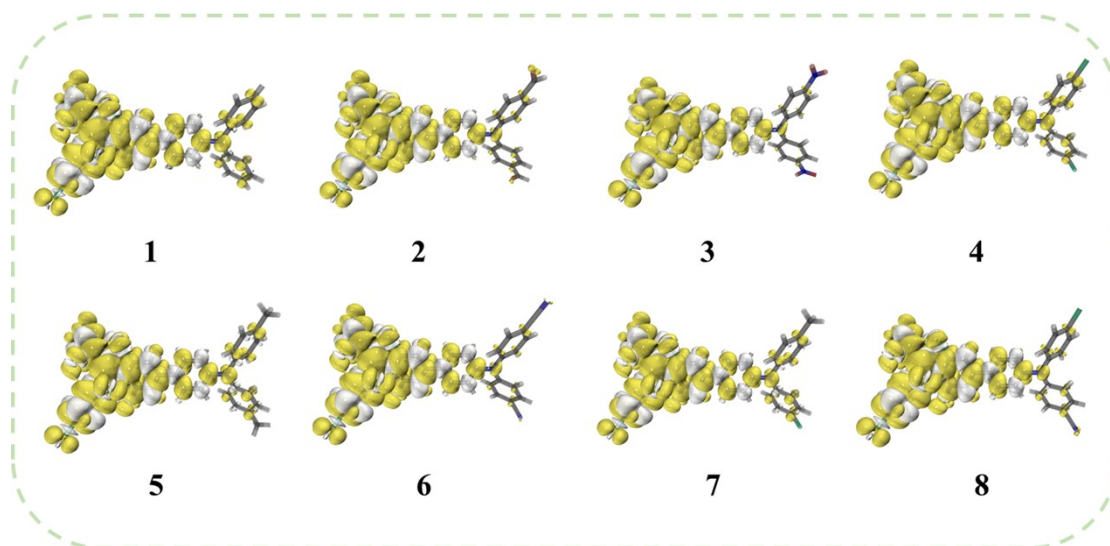


Figure S3. Spin density of D-A radical molecules at PBE0-D3(BJ)/6-311G (d, p) level with Becke theory. Yellow and white surfaces represent α and β spin density distributions with 0.0001 a.u. isosurfaces, respectively.

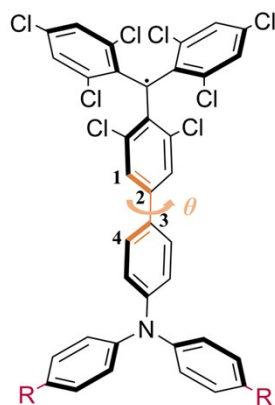


Figure S4. Molecule structure of D-A monoradical molecules. Dihedral C1-C2-C3-C4 is marked in orange.

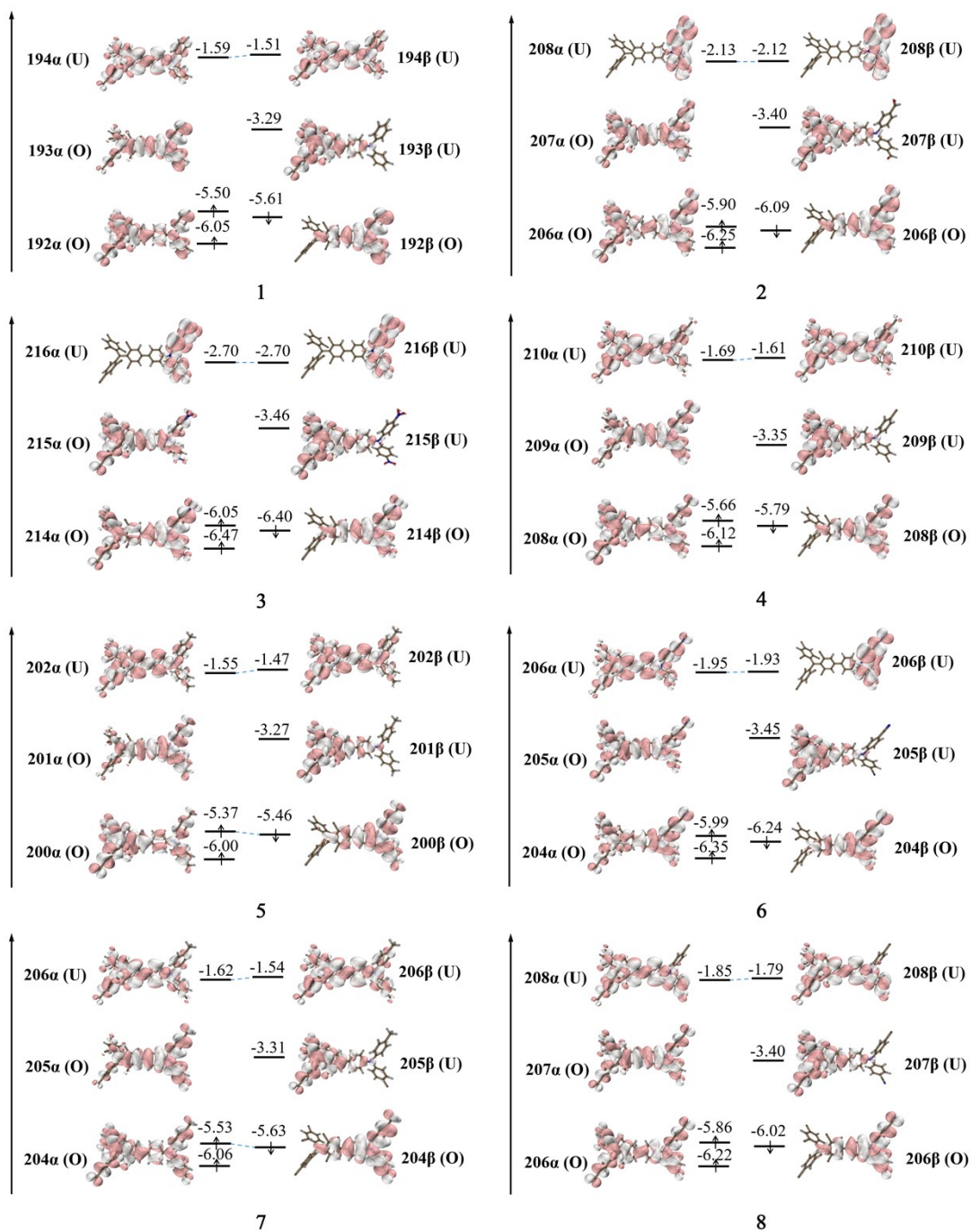


Figure S5. Energies and FMOs of monoradical molecules 1-8.

Table S1. Excitation wavelengths (nm) of TTM computed with various methods using the 6-311G(d,p) basis set with PCM solvent models (solvent=cyclohexane).

Method	HF%^a	λ_{abs}(nm)	λ_{emi}(nm)
Expt.	/	371	565
BP86-D3(BJ)	0%	428.50	
B3LYP-D3(BJ)	20%	376.63	564.59
PBE0-D3(BJ)	25%	365.84	553.05
M06-2X-D3	54%	331.38	/
M06-HF-D3	100%	316.79	/
CAM-B3LYP-D3(BJ)	19%/65%, $\omega = 0.33$	339.16	501.60
ωB97X-D	22.2%/100%, $\omega = 0.2$	334.85	/

^a HF% is percentage of Hartree-Fock (HF) exchange energy. For the range-separated methods, ω is the partitioning of the interelectronic distance.

Table S2. Spin population of the central carbon atom of TTM-TPA in the D_0 -state with selected dihedral angles.

Dihedral angles	0°	15°	30°	32.5°	45°	60°	75°	90°
Spin population	0.5380	0.5387	0.5413	0.5434	0.5451	0.5489	0.5518	0.5530

Table S3. Electron coupling values (V/eV) of radical molecules 1-8 between Ground and Excited States.

GMH Couplings (V/eV)								
States	1	2	3	4	5	6	7	8
0-1	0.23	0.25	0.32	0.23	0.22	0.26	0.22	0.24
0-2	0.49	0.05	0.05	0.46	0.46	0.24	0.46	0.51
0-3	0.98	0.51	0.87	0.93	1.00	0.84	0.96	0.89
0-4	0.95	0.88	0.69	1.07	0.82	0.41	0.93	1.00
0-5	0.19	1.23	0.72	0.20	0.18	1.34	0.20	0.20

Table S4. The bond distance (\AA) and dihedral angles ($^\circ$) between donor and acceptor at optimized D_0 - and D_1 - states, respectively, together with their difference (Δ) at the PBE0-D3(BJ)/6-311G(d,p) level.

	C1-C2-C3-C4 ($^\circ$)			C2-C3 (\AA)		
	D_0	D_1	$\Delta(D_1-D_0)$	D_0	D_1	$\Delta(D_1-D_0)$
1	-32.500	-29.620	2.881	1.468	1.462	-0.006
2	-34.839	-20.927	13.913	1.471	1.442	-0.029
3	-35.610	-16.452	19.158	1.472	1.433	-0.039
4	-34.016	-27.038	6.978	1.469	1.457	-0.012
5	-31.949	-32.004	-0.055	1.467	1.467	0.000
6	-34.532	-17.607	16.925	1.471	1.437	-0.034
7	-32.920	-30.505	2.414	1.468	1.463	-0.006
8	-34.367	-22.318	12.049	1.470	1.447	-0.024

References

- Blanksby, S. J.; Ellison, G. B., Bond Dissociation Energies of Organic Molecules. *Accounts of*

Chemical Research **2003**, *36* (4), 255-263.

2. Hioe, J.; Zipse, H., Radical stability and its role in synthesis and catalysis. *Organic & Biomolecular Chemistry* **2010**, *8* (16), 3609-3617.
3. Coropceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Brédas, J.-L., Charge Transport in Organic Semiconductors. *Chemical Reviews* **2007**, *107* (4), 926-952.
4. Rust, M.; Lappe, J.; Cave, R. J., Multistate Effects in Calculations of the Electronic Coupling Element for Electron Transfer Using the Generalized Mulliken–Hush Method. *The Journal of Physical Chemistry A* **2002**, *106* (15), 3930-3940.
5. Cave, R. J.; Newton, M. D., Generalization of the Mulliken-Hush treatment for the calculation of electron transfer matrix elements. *Chemical Physics Letters* **1996**, *249* (1), 15-19.
6. Hsu, C.-P., The Electronic Couplings in Electron Transfer and Excitation Energy Transfer. *Accounts of Chemical Research* **2009**, *42* (4), 509-518.
7. Voityuk, A. A., Estimation of electronic coupling in π -stacked donor-bridge-acceptor systems: Correction of the two-state model. *The Journal of Chemical Physics* **2006**, *124* (6), 064505.