Electronic supplementary information for

Effects of Aromatic Substituents on Electronic Structure and Excited State Energy Levels of Diketopyrrolopyrrole Derivatives for Singlet Fission

Li Shen, Zhaofeng Tang, Xuemin Wang, Heyuan Liu, Yanli Chen, Xiyou Li*

College of science, China University of Petroleum (East China), Qingdao, 266580, China.

To whom correspondence should be addressed: E-mail: xiyouli@upc.edu.cn

1. Functional and solvation effects on SF relevant excited states of DPP derivatives.

The vertical excitation energies of DPPs have been tested with different functionals to evaluate the effect of potential Charge-transfer state. These functionals include B3LYP, Cam-B3LYP, ωB97XD and tuned-LC-BLYP. The range separating parameters μ were tuned for each DPP derivatives (Table 1S) in vacuum condition with Quantum program optDFTw.[1] The vertical excitation energies are calculated based on the optimized S_0 geometries B3LYP/6-311G* level. The side chains on 2, 5-positions were replaced with methyl groups. The solvation effect was evaluated by polarizable continuum model (PCM).[2] The long-range-separated functionals Cam-B3LYP and ωB97XD overestimate $E(S_1)$ but underestimate $E(T_1)$ (Table 2S). Compared to the tuned-LC-BLYP, the calculated results with functional B3LYP are more close to the experimental results. The three DPP derivatives with/without solvents give quite similar results both for $E(S_1)$ and $E(T_1)$, the maximum error of which is ~0.15 eV (Table 3S). These results show that the solvation effects are negligibly small for the calculations of vertical excitation energies $E(S_1)$ and $E(T_1)$.

Table 1S. Tuned range separating parameters μ^{tuned} [bohr^{-1}] in LC-BLYP/6-311G* for DPP derivatives.

Molecule	PhDPP	TDPP	PhTDPP
μ	0.1981	0.1994	0.1660

Table 2S. Vertical excitation energies [eV] of DPPs with different functionals based on S_0 geometries.

		B3LYP	Cam-B3LYP	ωB97XD	Tuned-LC-BLYP	Exp.
PhDPP	S_1	2.619	2.864	2.879	2.701	2.667
	T_1	1.205	0.927	1.018	1.203	
TDPP	S_1	2.408	2.616	2.635	2.504	2.263
	T_1	1.007	0.648	0.760	1.012	
PhTDPP	S_1	2.162	2.408	2.443	2.256	2.081
	T_1	0.929	0.552	0.665	0.996	

Table 3S. Solvation effects on vertical excitation energies [eV] of S_1 and T_1 states for DPPs.

	vacuum	toluene	dichloromethane	Exp
PhDPP	2.619/1.205	2.552/1.233	2.587/1.253	2.667
TDPP	2.408/1.007	2.294/1.023	2.314/1.034	2.263
PhTDPP	2.162/0.929	2.044/0.942	2.056/0.952	2.081

Table 4S. Basis set effects on the energies [eV] of the S_1 and T_1 states of the three model compounds.

	6-311G*	6-311G**	cc-pVTZ	Exp
PhDPP	2.619/1.205	2.613/1.202	2.589/1.196	2.667
TDPP	2.408/1.007	2.406/1.009	2.388/1.009	2.263
PhTDPP	2.162/0.929	2.157/0.929	2.144/0.931	2.081

2. Calculation procedure of multiple diradical character using the PUHF method

The multiple diradical characters (y_i) are calculated by the spin-projected spin-unrestricted Hartree-Fock (PUHF) method as proposed by Yamaguchi.[3,4] This method is simple and reliable, and has been extensively used in evaluating diradical character of open-shell-character molecules by Nakano and co-workers.[5] The explicit formula is given by[4]

$$y_i = 1 - \frac{2T_i}{1 + T_i^2} \qquad (1)$$

$$T_i = \frac{n_{HONO-i} - n_{LUNO-i}}{2} \qquad (2)$$

Where n_i is the occupation number of the i-th natural orbitals (i=0, 1, $\cdots\cdots$). The HONO and LUNO correspond to the highest occupied natural orbital and lowest unoccupied natural orbital, respectively.

3. Molecular structures of nTz-DPPs.

1Tz-DPP
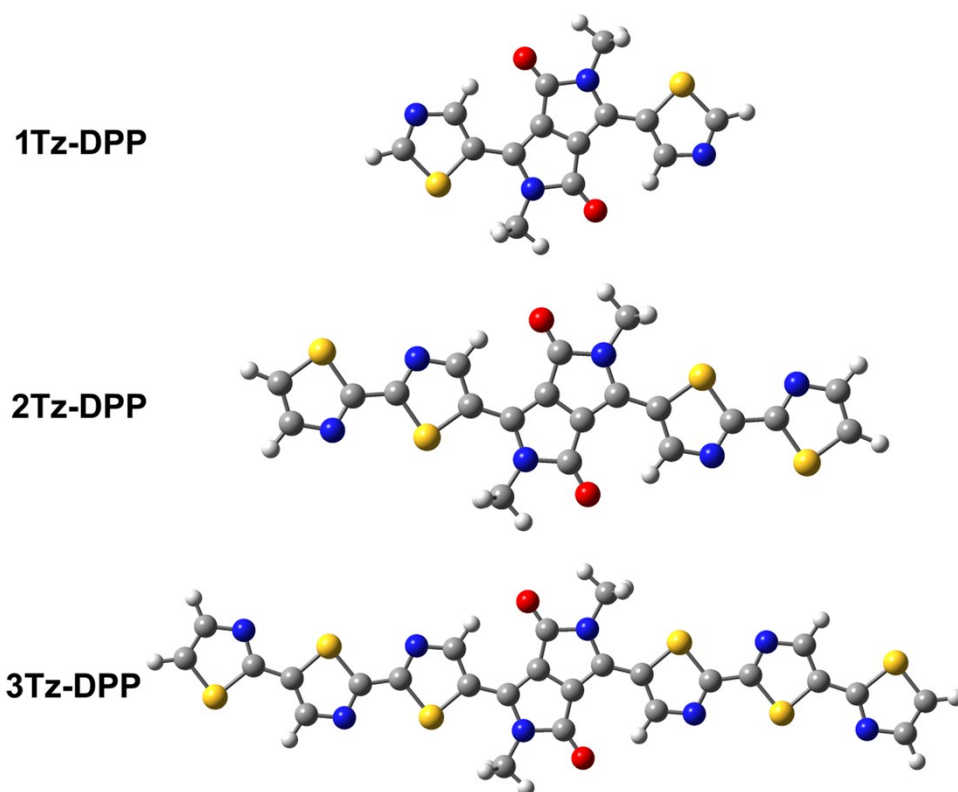
2Tz-DPP

3Tz-DPP

Figure S1. Molecular structures of n**Tz-DPPs**.

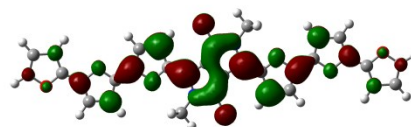**4. Electron density distributions of HOMO, LUMO for nF-DPP, nT-DPP and nTz-DPP.**
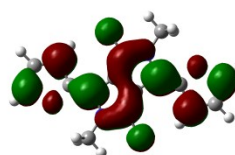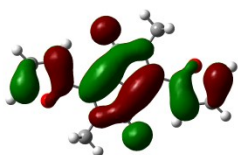
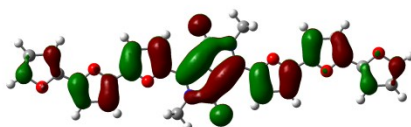|	**HOMO**	**LUMO**
1F-DPP		
2F-DPP		
3F-DPP		
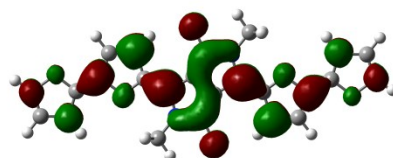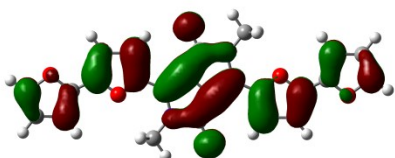
	HOMO	**LUMO**
1T-DPP		
2T-DPP		
3T-DPP		
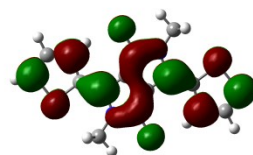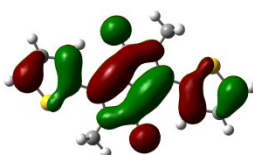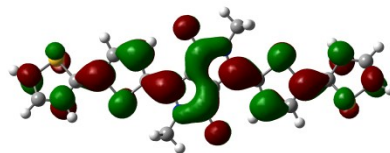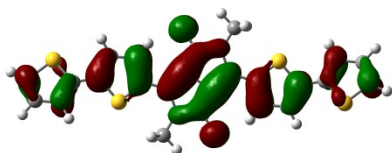
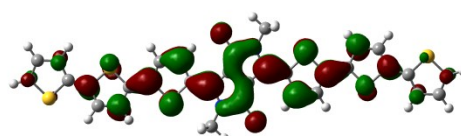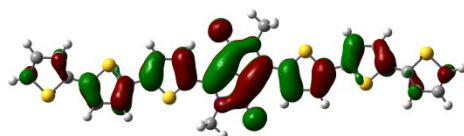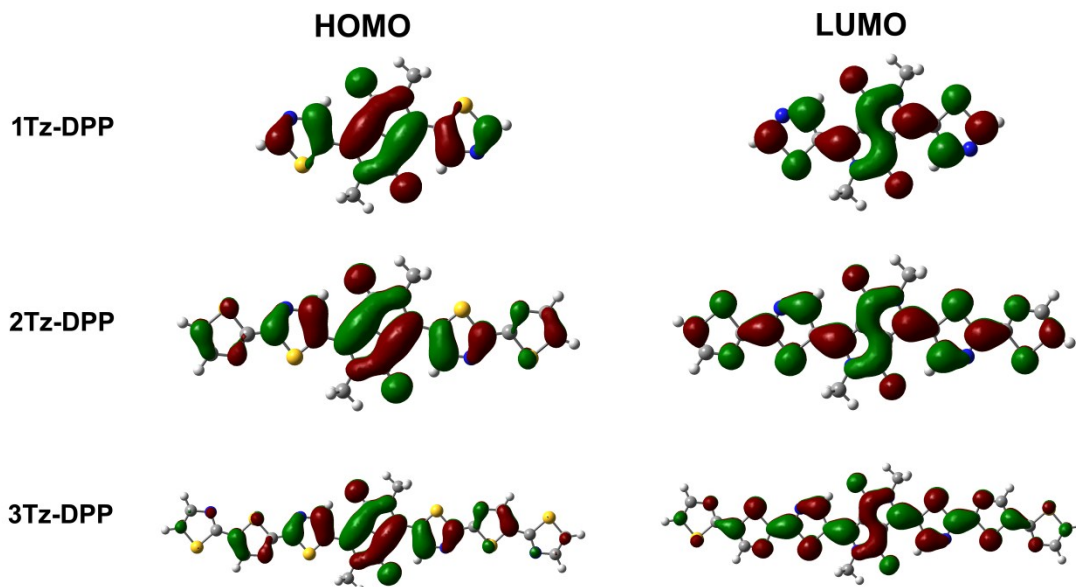|	HOMO	LUMO
1Tz-DPP		
2Tz-DPP		
3Tz-DPP		

Figure S2. Electron density distributions of HOMO, LUMO for nF-DPP, nT-DPP, nTz-DPP.

5. The twist energy for T-T, F-T and T-T with respect to the inter-ring twist angle. The twist energy is calculated as relative energy with respect to the twist of 180° .
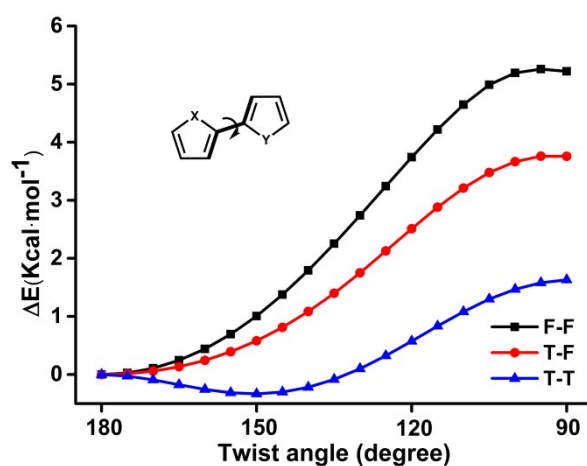

Figure S3. Calculated (B3LYP/6-311G*) relative energy versus twist angle for F-F, F-T and T-T (F-F: X=Y=O; T-F: X=S, Y=O; T-T: X=Y=S).

5. Tetraradical character indicator y_1 and y_1/y_0 of DPP derivatives in the second part.
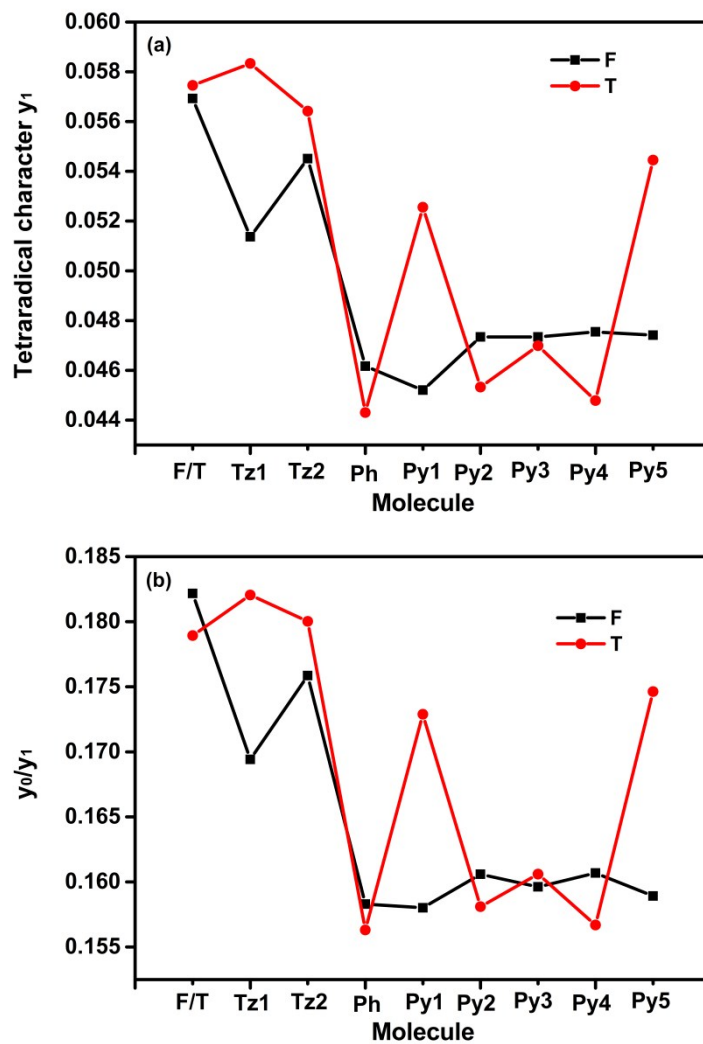

Figure S4. Tetraradical character indicator y_1 (a) and y_1/y_0 (b) of DPP derivatives in category 2 with respect to the end-capped aromatic groups (Ar2).

6. The frontier molecular orbital energies and diradical character indicator y₀ of 1F-DPP derivatives in the third part.
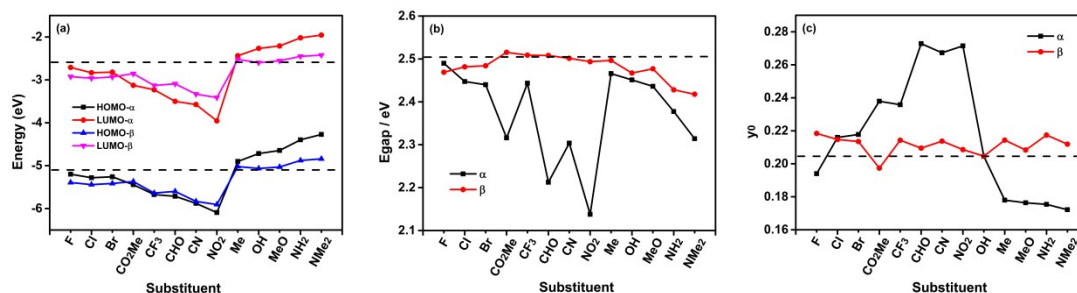

Figure S5. HOMO, LUMO energy levels (a) and corresponding Egap (b), as well as diradical character indicator y_0 (c) of 1F-DPP derivatives with respect to the introduced side-substituents and positions. (The solid lines are only guides for the eyes and the dash lines indicate the corresponding values of 1F-DPP).

7. The calculated excitation energies E(S₁), E(T₁), E(T₂) and energy changes of ΔE_SF, ΔE_TTA (d) with respect of the introduced side-substituents.

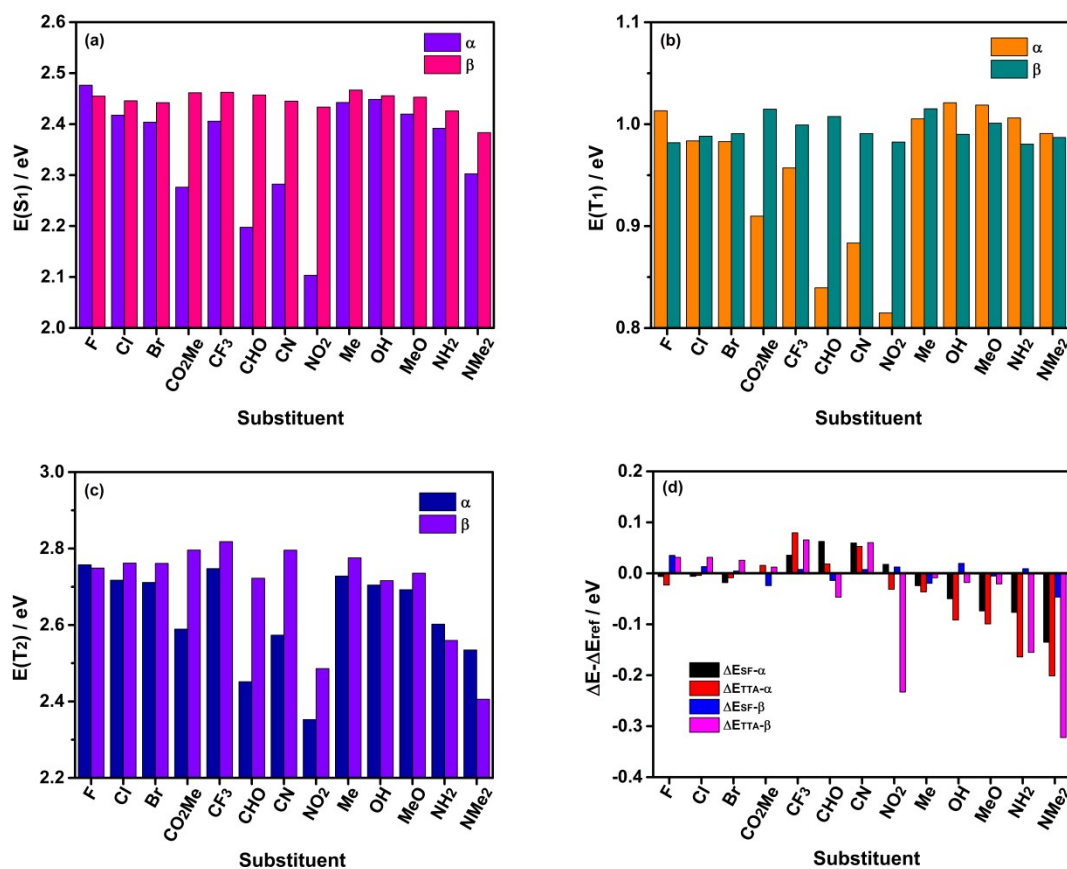**Figure S6**. E(S_1) (b), E(T_1) (b) and E(T_2) (c) of 1F-DPP derivatives with respect to the

introduced side-substituents. The energy changes of ΔE_{SF}, ΔE_{TTA} (d) upon attaching side-substituents. ΔE_{ref} denotes the corresponding ΔE_{SF}, ΔE_{TTA} values of 1F-DPP.

References

(1) T. Lu, optDFTw program v1.0, webpage: http://sobereva.com/346.

(2) G. Scalmani, M. J. Frisch, *J. Chem. Phys*, 2010, **132**, 114110.

(3) K. Yamaguchi, *Chem. Phys. Lett.* 1975, **33**, 330.

(4) K. Yamaguchi, In Self-Consistent Field: Theory and Applications; Carbo, R., Klobukowski, M., Eds.; *Elsevier: Amsterdam, The Netherlands,* 1990; pp 727.

(5) M. Nakano, *Chem. Rec*. 2017, **17**, 27.