

## Supplementary information

**Strategy to modulate the electron-deficiency  $\pi$ -bridged units in bis(4-methoxyphenyl)amine-based hole-transporting materials for improvement of the perovskite solar cell performances**

*Hongyuan Liu, Xiaorui Liu\**

<sup>a</sup>Key Laboratory of Luminescent and Real-Time Analytical Chemistry (Southwest University), Ministry of Education, School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China

**\*Corresponding Authors**

**E-mail:** liuxiaorui@swu.edu.cn (X. Liu)

## The theoretical details of hole transport

The Marcus theory is a widely used method to estimate the charge transfer rate:<sup>1-3</sup>

$$k = \frac{2\pi}{h} \frac{1}{\sqrt{4\pi\lambda K_B T}} t^2 \exp\left[-\frac{\lambda}{4K_B T}\right] \quad (S1)$$

Where  $h$ ,  $t$ ,  $K_B$ ,  $T$  and  $\lambda$  are the Planck's constant, charge transfer integral, Boltzmann constant, temperature and total reorganization energy, respectively. Hence,  $k$  is governed by the two important parameters: the total reorganization energy  $\lambda$  and intermolecular charge transfer integral.

In equation (1S), for an optimal transport system, transfer integral should be maximized and  $\lambda$  should be minimized. The total reorganization energy which reflects on the ability of vibration structure change due to the electron gaining/losing process of the segment consists of two components:<sup>2,4</sup> (i) the inner reorganization energy  $\lambda_{in}$  that accounts for the changes in the geometry of the two molecules upon electron transfer and (ii) the outer reorganization energy  $\lambda_{out}$  of the surrounding medium. When the medium contribution to the relaxation energy in virtue of the polarization in the medium is neglected (such as in thin film), the inner reorganization energy should be dominated. In the paper, inner reorganization is the studied object and can be obtained by calculating the individual relaxation process energies for the neighboring segments. According to the theory, we obtained the total hole reorganization energy  $\lambda$  by calculating the optimized geometries in neutral, cationic states, the total energy of cation state in the optimized neutral geometry, and the total energy of neutral state in the optimized geometry of cation. The inner reorganization energy  $\lambda_i$  for holes could be calculated as follows:

$$\lambda_{\text{hole}} = \lambda_1 + \lambda_2 = E_+ - E_+^* + E^* - E \quad (S2)$$

here we use  $E$  and  $E_+^*$  to represent the energies of the neutral segment and the cation segment, respectively. Both of them lie in the lowest energy geometries, while  $E_+$  and  $E^*$  denote the energies

of the neutral segment and the cation segment with the geometries of the cation segment and the neutral segment, respectively.<sup>5</sup> The other important parameter of the electronic coupling ( $v$ ) can be written as:<sup>6, 7</sup>

$$v = \frac{J - S(H_1 + H_2) / 2}{1 - S^2} \quad (\text{S3})$$

where  $S$  is the spatial overlap,  $J$  is charge transfer integral, and  $H$  is site energies. The calculation of  $J$  can be obtained from<sup>[6, 7]</sup>

$$J = \langle \phi_{\text{HOMO}}^1 | h_{\text{ks}} | \phi_{\text{HOMO}}^2 \rangle \quad (\text{S4})$$

where  $h_{\text{ks}}$  is the Kohn-Sham Hamiltonian of the dimer system which includes two fragments, and  $\phi_{\text{HOMO}}^1$  and  $\phi_{\text{HOMO}}^2$  are the HOMO of two fragments.

. In order to obtain the hole mobility, we adopt Einstein relation in the low field limit as follows:

$$\mu = \frac{eD}{K_B T} \quad (\text{S5})$$

Where  $e$  is the electron charge and  $D$  is the charge diffusion coefficient. For a  $d$ -dimensional system,

$D$  is defined as the ratio between the mean-square displacement and the diffusion time: <sup>8</sup>

$$D = \lim_{t \rightarrow \infty} \frac{1}{2d} \frac{\langle x(t)^2 \rangle}{t} \quad (\text{S6})$$

For a spatially isotropic system, the homogeneous diffusion constant  $D$  can be approximately evaluated by: <sup>9</sup>

$$D = \frac{1}{2d} \sum_i r_i^2 k_i p_i \quad (\text{S7})$$

where  $d$  is the spatial dimensionality,  $i$  runs over all nearest adjacent molecules and  $r_i$ ,  $k_i$  and  $p_i$  are the corresponding centre-to-center hopping distance, charge transfer rate ( $k$ ), and hopping probability ( $p_i = \frac{k_i}{\sum_i k_i}$ ), respectively.

**Table S1** The LUMO energy levels of theoretical calculation and experimental values for HTMs.

	LUMO( Exp.)	References	LUMO (Cal.)
TPD	-2.2	10	0.46
AS37	-1.99	11, 12	0.51
AS44	-1.93	11, 12	0.58
H101	-2.40	13, 14	0.25
EDOT-OMeTPA	-3.3	14	-0.72
BTT-1	-1.98	15	0.71
H-Di	-2.22	16	0.36
Z25	-2.44	17	0.11
FDT	-2.28	18	0.22
X59	-2.10	19	0.49

**Table S2** The absorption wavelengths  $\lambda_{\text{abs}}$  (nm) and emission wavelengths  $\lambda_{\text{em}}$  (nm) of molecules pDPA-DBTP and X59 in the  $S_0$ - $S_1$  states together with the Stokes shift at TD-B3LYP/6-31g(d) levels in toluene solvent.

	Absorption				Emission	
	$\lambda_{\text{abs}}$	$f$	Assignments	$\lambda_{\text{abs}}(\text{Exp.})$	$\lambda_{\text{em}}$	Shift(nm)
pDPA-DBTP	422	1.77	H $\rightarrow$ L (97%)		479	57
X59	398	1.29	H $\rightarrow$ L (90%)	387 <sup>17</sup>	468	70

**Table S3** The adiabatic ionization potential ( $IP_a$  in eV), electron affinities ( $EA_a$  in eV), absolute hardness ( $\eta$  in eV), exciton binding energy ( $E_b$  in eV) and solvation free energy ( $\Delta G$  in kcal  $\cdot$  mol<sup>-1</sup>) of the molecules pDPA-DBTP and X59.

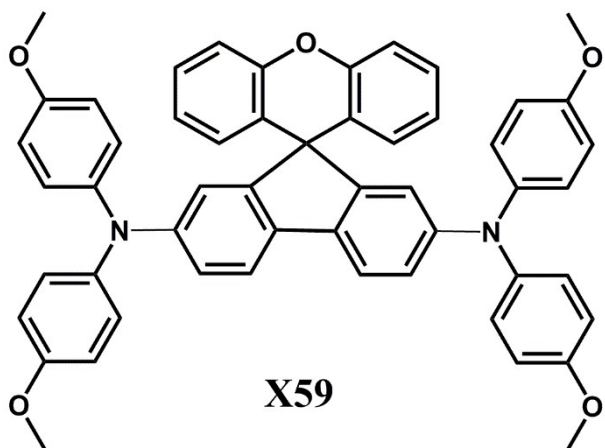
	$E_b$	$IP_a$	$EA_a$	$\eta$	$\Delta G$
pDPA-DBTP	0.46	5.13	-0.24	2.69	-5.93
X59	0.50	5.14	-0.10	2.62	-5.79

**Table S4** Predicted crystal data of investigated molecules.

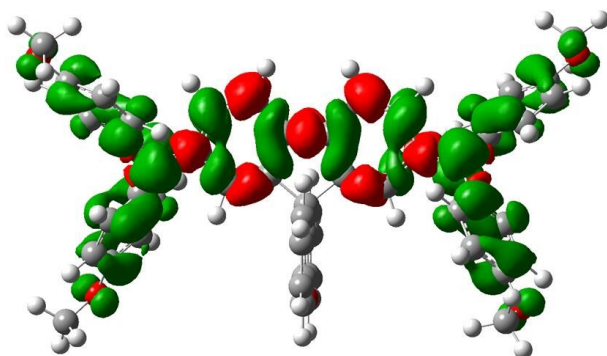
Molecules	Space group	$\rho$	$Z$	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\alpha$	$\beta$	$\gamma$
pDPA-DBTP	$P2_12_12_1$	1.026	4	9.55	21.33	25.99	90°	90°	90°
S1	$P2_12_12_1$	1.192	4	7.29	26.71	18.50	90°	90°	90°
S2	$P2_12_12_1$	1.114	4	20.80	17.93	12.71	90°	90°	90°
S3	$Pbca$	0.987	8	6.87	64.52	27.17	90°	90°	90°

**Table S5** The reorganization energy  $\lambda_h$  (eV), hole coupling  $v_h$  (eV), hole transport rate  $k_h$  ( $s^{-1}$ ), center-of-mass distance  $D$  ( $\text{\AA}$ ) and hole mobility  $u_h$  ( $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ ) of main hopping pathway selected on basis of the predicted crystal structure for molecules pDPA-DBTP.

Compounds	Pathways	$\lambda_h$	$v_h$	$k_h$	$D$	$u_h$	$u_h(\text{Exp.})^{20}$
pDPA-DBTP	1	0.595	$5.983 \times 10^{-5}$	$2.46 \times 10^5$	9.553	$6.92 \times 10^{-4}$	$3.10 \times 10^{-4}$
	2		$9.395 \times 10^{-3}$	$6.08 \times 10^9$	14.064		
	3		$1.063 \times 10^{-3}$	$7.78 \times 10^7$	11.868		
	4		$1.867 \times 10^{-4}$	$2.40 \times 10^6$	16.783		
	5		$3.416 \times 10^{-3}$	$8.03 \times 10^8$	13.648		

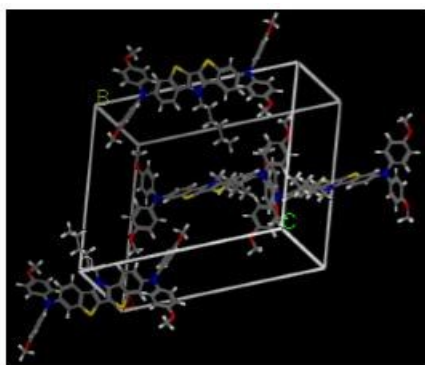


**Figure S1** The chemical structures of the molecules X59.

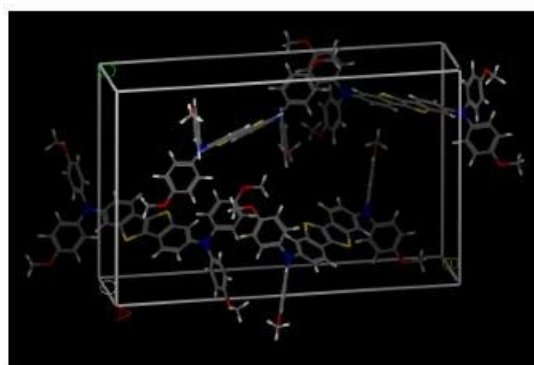


$$\Delta q = 0.83 |e^-|$$

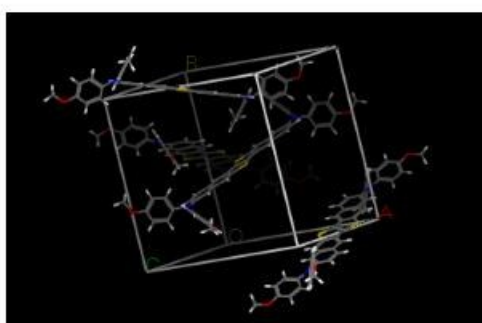
**Figure S2** Electron density difference plots of electronic transition  $S_0 \rightarrow S_1$  for X59 (isovalue:  $4 \times 10^{-2} \text{ e au}^{-3}$ ),  $\Delta q$  in e is transferred charge amount ( $|e^-|$ ).



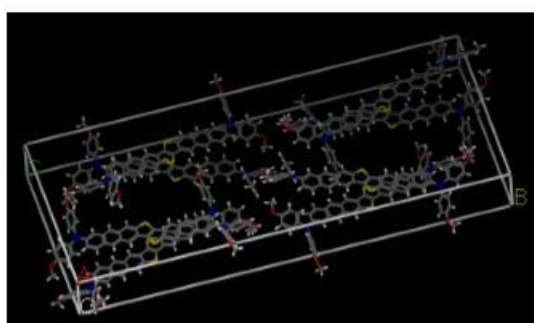
**pDPA-DBTP**



**S1**

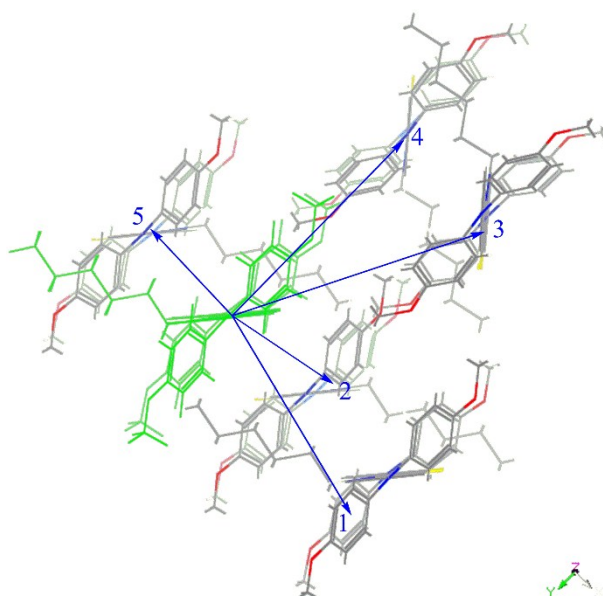


**S2**



**S3**

**Figure S3** The predicted crystal structures of the investigated molecules pDPA-DBTP and S1-S3.



**Figure S4** Main hole hopping pathways selected on basis of the predicted crystal structures for the molecule pDPA-DBTP.

## References

1. R. A. Marcus, *Angew. Chem. Int. Ed.*, 1993, **32**, 1111-1121.
2. L. Wang, G. Nan, X. Yang, Q. Peng, Q. Li and Z. Shuai, *Chem. Soc. Rev.*, 2010, **39**, 423-434.
3. C. Leng, H. Qin, Y. Si and Y. Zhao, *J. Phys. Chem. C*, 2014, **118**, 1843-1855.
4. C. Wang, F. Wang, X. Yang, Q. Li and Z. Shuai, *Org. Electron.*, 2008, **9**, 635-640.
5. B. C. Lin, C. P. Cheng and Z. P. M. Lao, *J. Phys. Chem. A*, 2003, **107**, 5241-5251.
6. S.-H. Wen, A. Li, J. Song, W.-Q. Deng, K.-L. Han and W. A. Goddard III, *J. Phys. Chem. B*, 2009, **113**, 8813-8819.
7. K. Senthilkumar, F. Grozema, F. Bickelhaupt and L. Siebbeles, *J. Chem. Phys.*, 2003, **119**, 9809-9817.
8. J. Bisquert, *Phys. Chem. Chem. Phys.*, 2008, **10**, 3175-3194.
9. W. Q. Deng and W. A. Goddard III, *J. Phys. Chem. B*, 2004, **108**, 8614-8621.
10. M. Aonuma, T. Oyamada, H. Sasabe, T. Miki and C. Adachi, *Appl. Phys. Lett.*, 2007, **90**, 183503.
11. T. Leijtens, I. K. Ding, T. Giovenzana, J. T. Bloking, M. D. McGehee and A. Sellinger, *ACS Nano*, 2012, **6**, 1455-1462.
12. T. Leijtens, T. Giovenzana, S. N. Habisreutinger, J. S. Tinkham, N. K. Noel, B. A. Kamino, G. Sadoughi, A. Sellinger and H. J. Snaith, *ACS Appl. Mater. Inter.*, 2016, **8**, 5981-5989.
13. H. Li, K. Fu, A. Hagfeldt, M. Gratzel, S. G. Mhaisalkar and A. C. Grimsdale, *Angew. Chem. Int. Ed.*, 2014, **53**, 4085-4088.
14. M. L. Petrus, T. Bein, T. J. Dingemans and P. Docampo, *J. Mater. Chem. A*, 2015, **3**, 12159-12162.
15. A. Molina-Ontoria, I. Zimmermann, I. Garcia-Benito, P. Gratia, C. Roldán-Carmona, S. Aghazada, M. Graetzel, M. K. Nazeeruddin and N. Martín, *Angew. Chem. Int. Ed.*, 2016, **55**, 6270-6274.
16. X. Liu, F. Kong, S. Jin, W. Chen, T. Yu, T. Hayat, A. Alsaedi, H. Wang, Z. a. Tan, J. Chen and S. Dai, *ACS Appl. Mater. Inter.*, 2017, **9**, 27657-27663.
17. F. Zhang, Z. Wang, H. Zhu, N. Pellet, J. Luo, C. Yi, X. Liu, H. Liu, S. Wang, X. Li, Y. Xiao, S. M. Zakeeruddin, D. Bi and M. Grätzel, *Nano Energy*, 2017, **41**, 469-475.
18. M. Saliba, S. Orlandi, T. Matsui, S. Aghazada, M. Cavazzini, J.-P. Correa-Baena, P. Gao, R. Scopelliti, E. Mosconi, K.-H. Dahmen, F. De Angelis, A. Abate, A. Hagfeldt, G. Pozzi, M. Graetzel and M. K. Nazeeruddin, *Nature Energy*, 2016, **1**, 15017.
19. D. Bi, B. Xu, P. Gao, L. Sun, M. Grätzel and A. Hagfeldt, *Nano Energy*, 2016, **23**, 138-144.
20. R. Azmi, S. Y. Nam, S. Sinaga, Z. A. Akbar, C.-L. Lee, S. C. Yoon, I. H. Jung and S.-Y. Jang, *Nano Energy*, 2018, **44**, 191-198.