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Supporting Information

Design of Single-Porphyrin Donors toward High Open-Circuit Voltage for Organic Solar Cells via Energy Level Gradient-Distribution Screening Strategy of Fragments: A Theoretical Study

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Section S.1 Screening Functional

In this work, the molecule 5-bis(2,5-bis-(2-ethylhexyl)-3,6-dithienyl-2-yl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione-5'-ylethynyl)-10,20-bis(5-(2-ethylhexyl)-thienyl)-porphyrin zinc(II) (DPPEZnP-THE)[1] was used to perform functional screening, in order to ensure the accuracy of calculation. According to the HF content, five different functionals (B3LYP, M06, M06-2X, PBE0, PBE38) were selected, respectively. Because a linear relationship exist between the highest occupied molecular orbital (HOMO) level of the donor and open circuit voltage (V_{OC}), the calculation method closest to the experimental HOMO level was selected for optimizing molecule ground state geometry. The calculation results showed the M06/6-31G** was closer to the experimental values than other methods, so ground state geometry of all the molecules in this paper were optimized by using this method. Similarly, as for the absorption spectra and excited state energy, the TD-B3LYP/6-31G** method was used.

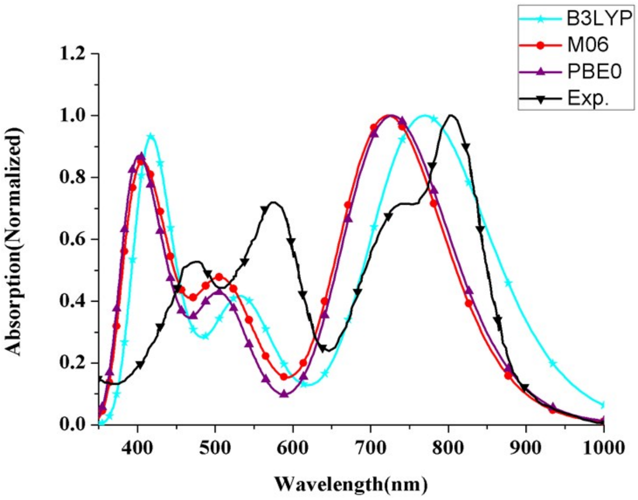


Fig. S1 Experimental spectra of DPPEZnP-TEH and absorption spectra were obtained by different calculation methods.

Table S1 The frontier molecular orbital (FMO) energy levels of DPPEZnP-THE were calculated and absorption spectrum were simulated by using five different methods with the 6-31G** basis set compared with experimental value

	B3LYP	M06	M06-2X	PBE0	PBE38	Exp.[1]
HOMO/eV	-4.74	-5.02	-5.78	-4.95	-5.35	-5.14

LUMO/eV	-3.13	-3.30	-3.76	-3.25	-3.44	-3.76
λ_{max}/nm	770	722	615	727	647	802

Section S.2 Computational Details of Marcus Semi-classical Model

S.2.1 Gibbs Free Energy Change

During the charge transfer process between the donor and acceptor interfaces, the Gibbs free energy change of charge recombination (ΔG_{CR}) could be obtained under thermodynamic conditions by the following formula[2]:

$$\Delta G_{\text{CR}} = E_{\text{IP(D)}} - E_{\text{EA(A)}} \tag{1}$$

Among them, E_{IP} (D) is the ionization potential of the donor, and E_{IP} (A) is the electron affinity of the acceptor, which could were approximated by the donor HOMO levels and the acceptor LUMO levels, respectively; the Gibbs free energy change of charge transfer (ΔG_{CT}) could was obtained from the Rehm-Weller equation[2]:

$$\Delta G_{\text{CT}} = -\Delta G_{\text{inter-CR}} - \Delta E_{\text{0-0}} - E_{\text{b}} \tag{2}$$

where $\Delta E_{\text{0-0}}$ is the lowest excited state energy of the free-base donor, and E_{b} is the exciton binding energy, which is the energy difference between electronic and optical band-gap energy.

S.2.2 Reorganization Energy

The reorganization energy λ include an internal reorganization energy (λ_{int}) and an external reorganization energy (λ_{ext}), with the following relation:

$$\lambda = \lambda_{\text{int}} + \lambda_{\text{ext}} \tag{3}$$

Among them, the λ_{int} originated from the change toward equilibrium geometries of donor (D) and acceptor (A) when they loss or gain charge upon charge transfer, could be obtained by four energies in eq 4 for the interface model[3]:

$$\lambda_{\text{int}} = \left[E\left(\text{A}^-\right) - E\left(\text{A}\right)\right] + \left[E\left(\text{D}\right) - E\left(\text{D}^+\right)\right] \tag{4}$$

where E(A$^-$) and E(A) are the energies of the neutral acceptor A at the anionic and optimal ground-state geometries, respectively. E(D) and E(D$^+$) are the energies of the cation donor D at the neutral and optimal cation geometries, respectively.

External reorganization energy mainly was affected by environmental factors and could was calculated according to the classical dielectric continuous model[4]:

$$\lambda_{\text{ext}} = \frac{1}{4\pi\varepsilon_0}\Delta e^2\left(\frac{1}{2\text{a}_1}+\frac{1}{2\text{a}_2}-\frac{1}{R}\right)\left(\frac{1}{\varepsilon_{\text{op}}}-\frac{1}{\varepsilon_0}\right) \tag{5}$$

where a_1 is the donor radii, a_2 is the acceptor radii, and R is the distance between the center of donor and acceptor, ε_{op} and ε_0 refer to optical and zero-frequency dielectric constants of the surrounding media, respectively. ε_{op} and ε_0 are estimated to be 2.56 and 3.4 by Troisi[4] and Jérôme[5], respectively. e is the elemental charge.

Table S2 The value of donor radii (a_1)， acceptor radii (a_2) and the distance between the center of the donor and acceptor (R)

	1	**2**	**3**	**4**	**5**
a_1	18.74	20.26	20.72	19.73	20.09
a_2	3.68	3.68	3.68	3.68	3.68
R	25.22	26.74	27.20	26.21	26.57
$1/2\text{a}_1+1/2\text{a}_2-1/R$	0.12	0.12	0.12	0.12	0.12
$\boldsymbol{\lambda}_{\textbf{ext}}$	0.17	0.17	0.17	0.17	0.17

S.2.3 Electronic Coupling

In this paper, the electronic coupling (V_{DA}) value was calculated by using time dependent-density functional theory within the Tamm–Dancoff approximation (TDDFT/TDA)[6] method based on the generalized Mulliken-Hush (GMH) model, the formula is as follows[7-10]:

$$V_{\text{DA}} = \frac{\mu_{\text{tr}}\Delta E}{\sqrt{(\Delta\mu)^2+4(\mu_{\text{tr}})^2}} \tag{6}$$

where μ_{tr} represents the transition dipole moment, $\Delta\mu$ represents the dipole moment difference between initial states to the final states. ΔE represents the excitation energy in the vertical direction. The excitation energy of the D/A complex could was calculated by the TDDFT theory. The coupling values between the excited state and the ground state (V_{CR}), and the coupling values between different excited states (V_{CT}) were calculated by Q-chem software, respectively.

Section S.3 Characterization of Photoelectric Properties of Research System Molecule

S.3.1 Formulation of the Open Circuit Voltage

$$V_{OC}=(1/e)(|E^{D}_{HOMO}|-|E^{A}_{LUMO}|)-0.3\ \mathrm{V} \tag{7}$$

where *e* is the elementary charge, $E^{D}{}_{HOMO}$ and $E^{A}{}_{LUMO}$ represent the HOMO energy level of the donor and LUMO energy level of the acceptor, and 0.3 V is the empirical factor for efficient charge separation[11-12]

Table S3 The FMO energy levels of all molecules with A-π-D-π-A (**1~9**) and A-D-A (**X-1**) configuration at M06/6-31G** level in the vacuum

Molecules	HOMO (eV)	LUMO (eV)	V_{OC} (V)	$\Delta E_{L\text{-}L}$ (eV)
1	-5.36	-3.61	1.15	0.30
2	-5.27	-3.55	1.06	0.36
3	-5.25	-3.60	1.04	0.31
4	-5.30	-3.57	1.09	0.34
5	-5.24	-3.49	1.03	0.42
6	-5.33	-3.85	1.12	0.06
7	-5.09	-3.44	0.88	0.47
8	-5.14	-3.49	0.93	0.42
9	-5.12	-3.43	0.91	0.48
X-1	-5.70	-3.61	1.49	0.30

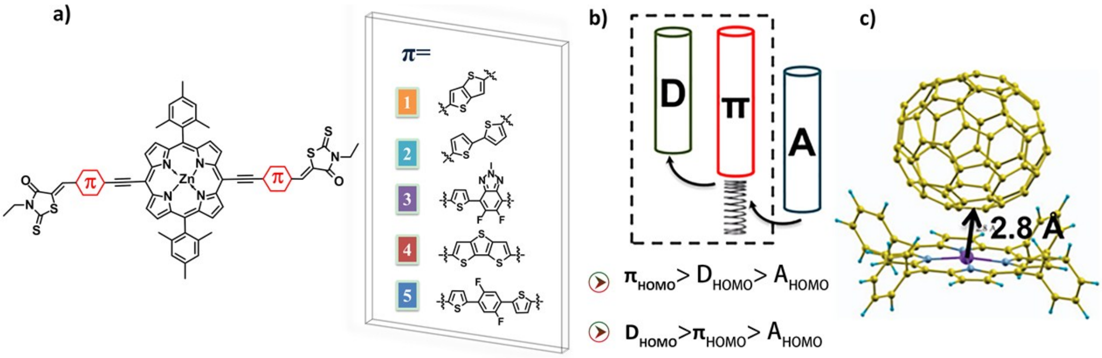


Fig. S2 a) Molecule structures of **1~5**; b) energy level gradient-distribution strategy and two distribution ways for the HOMO energy level of π bridges; c) the starting interface geometry of the porphyrins/fullerene complexes.

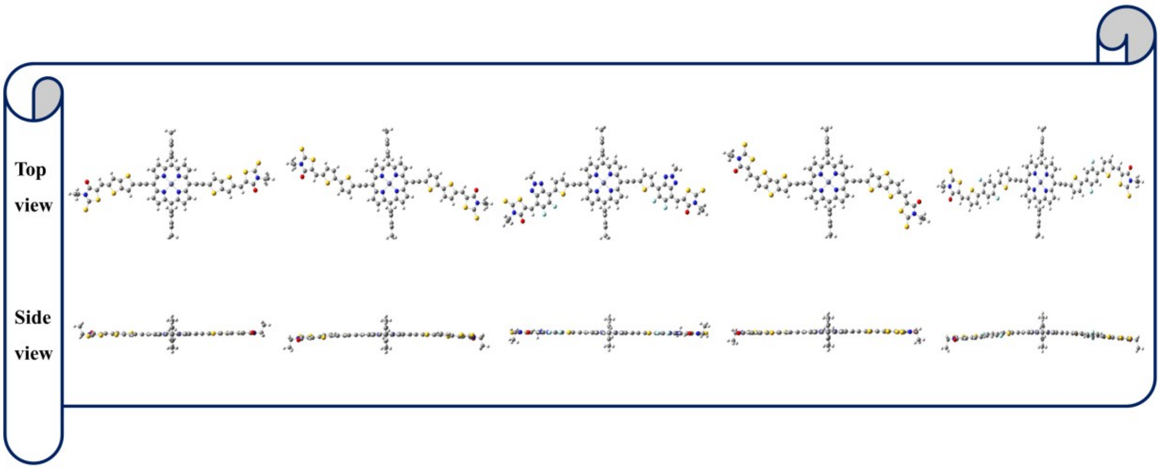


Fig. S3 Ground state optimized geometry of the research system **1**~**5**.

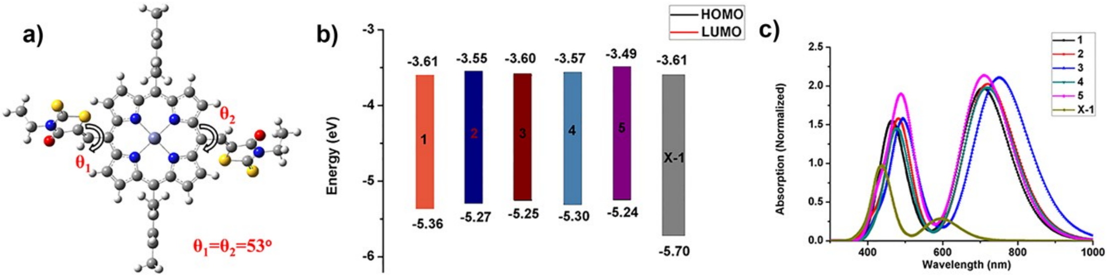


Fig. S4 a) Ground state optimized geometry of the **X-1**; b) HOMO and LUMO energy levels of **1**~**5** and **X-1**; c) absorption spectrum of **1**~**5** and **X-1** were calculated in vacuum using TD-B3LYP/6-31G** method.

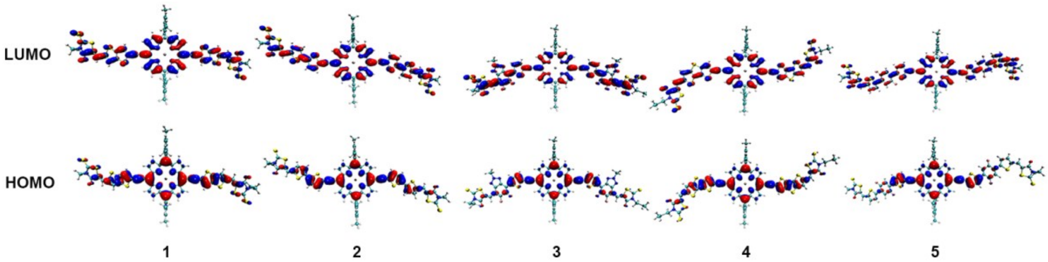


Fig. S5 The FMOs of the **1**~**5** molecules at the M06/6-31G** level.

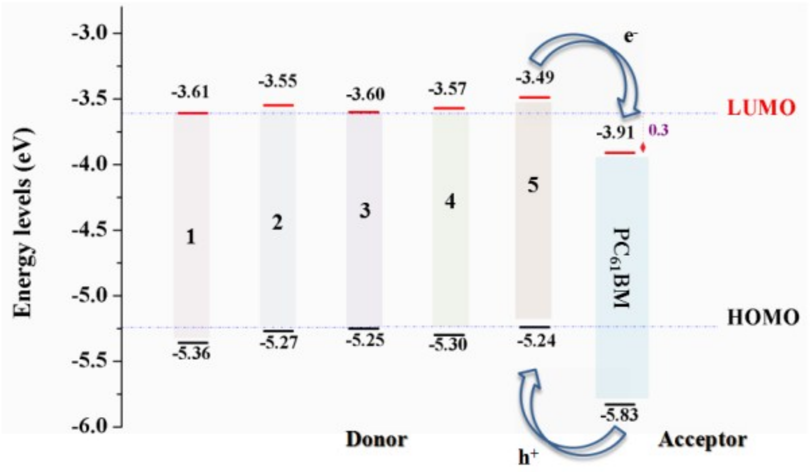
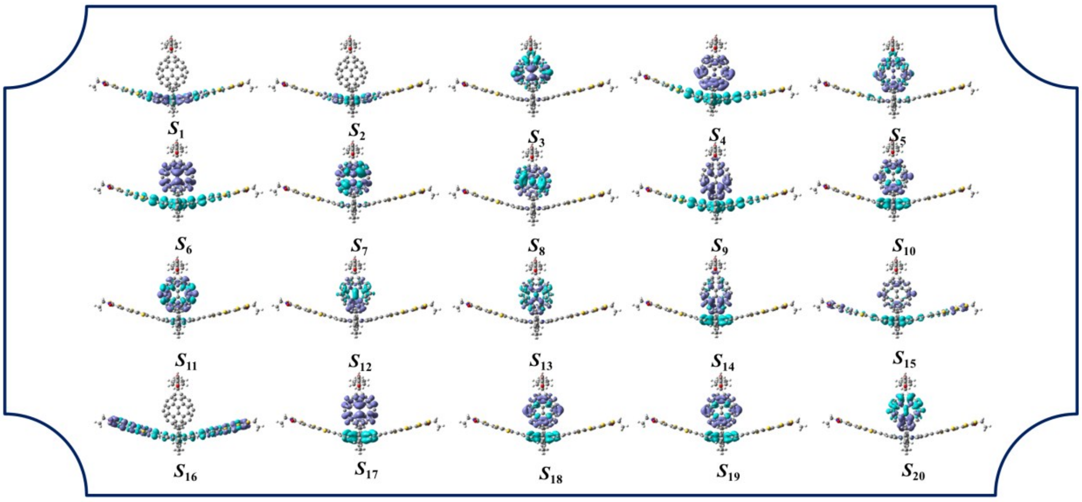
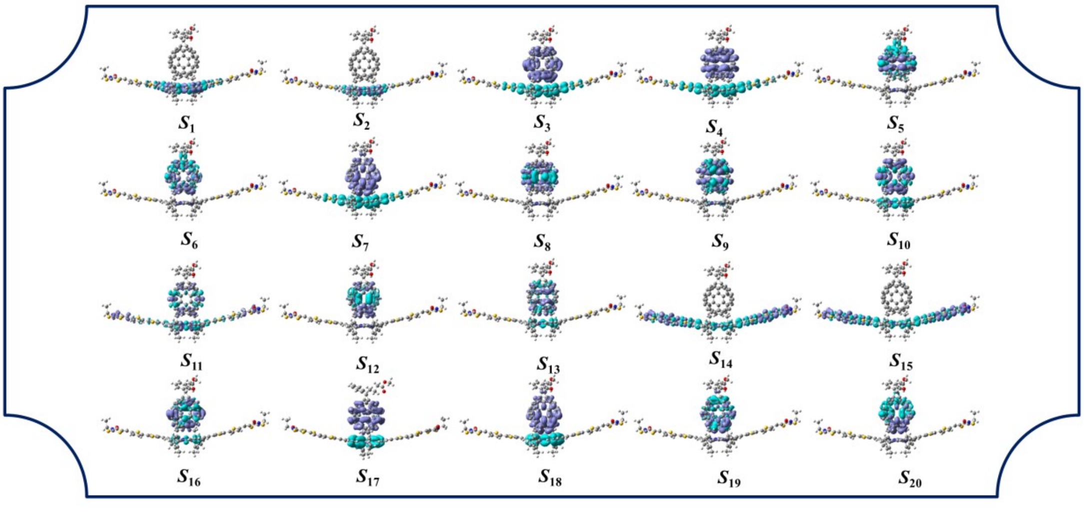
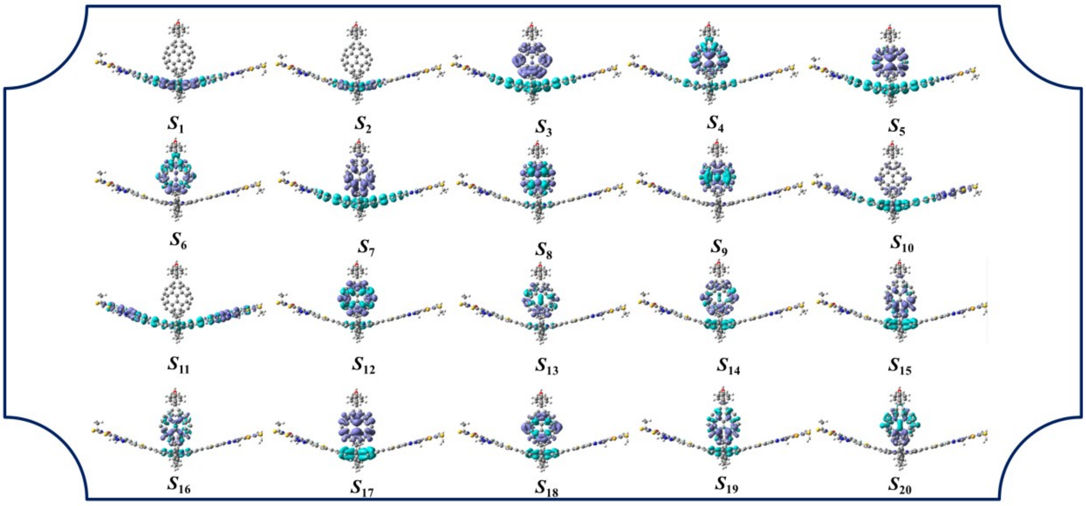


Fig. S6 Illustration of FMO level values of **1**~**5** and $PC_{61}BM$ were evaluated at M06/6-31G** level in the vacuum.



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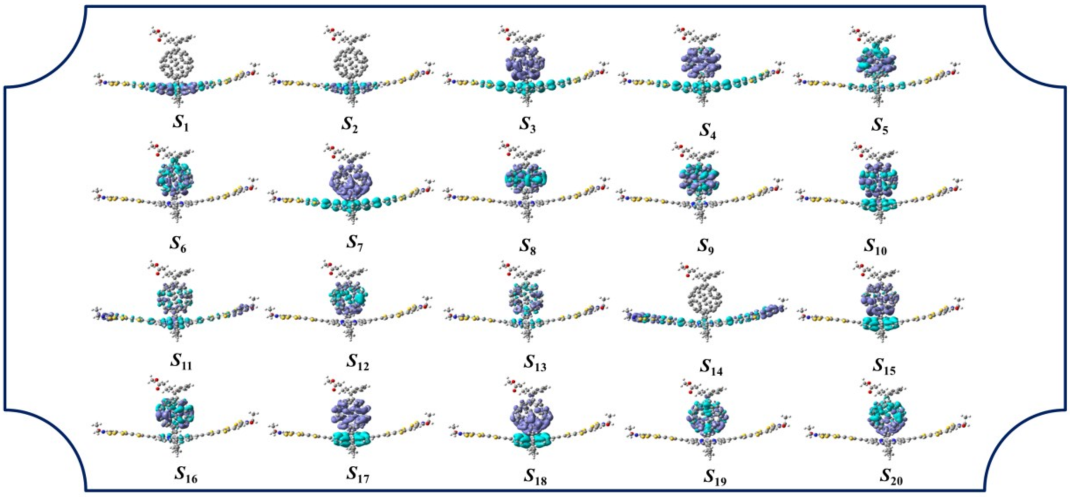
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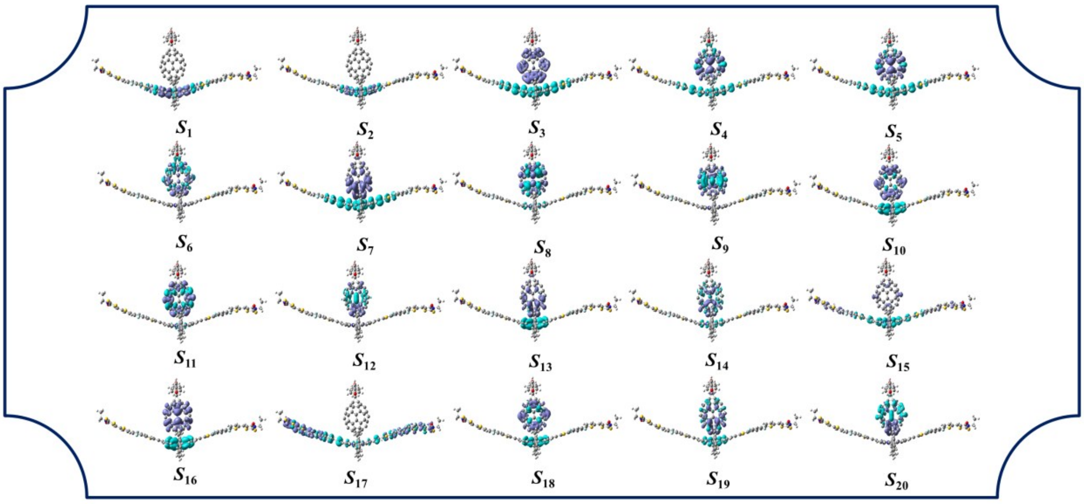
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Fig. S7 Charge density difference maps of **1~5**/$PC_{61}BM$ complex for finding charge transfer excited states were simulated at TD-CAM-B3LYP/6-31G** level (0.02 for isosurface values), where the violet and turquoise colors stand for the increase and decrease in electron density, respectively[13].

Table S4 Calculated internal reorganization energy λ_{int} (eV), external reorganization energy λ_{ext} (eV), total reorganization energy λ (eV), Gibbs free energy change ΔG (eV) of the **1~5**/$PC_{61}BM$ and **X-1**/$PC_{61}BM$

	λ_{int}	λ_{ext}	λ	ΔG_{CR}	ΔG_{CT}
1/$PC_{61}BM$	0.126	0.171	0.297	-1.450	-0.303
2/$PC_{61}BM$	0.127	0.171	0.298	-1.361	-0.362
3/$PC_{61}BM$	0.120	0.171	0.291	-1.337	-0.315
4/$PC_{61}BM$	0.126	0.171	0.297	-1.386	-0.341
5/$PC_{61}BM$	0.121	0.171	0.292	-1.328	-0.418
X-1/$PC_{61}BM$	0.132	0.173	0.305	-1.793	-0.295

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