SUPPLEMENTARY MATERIAL

The Conversion of Donor to Acceptor and Rational Design for Diketopyrrolopyrrole-Containing Small Molecule Acceptors by Introducing Nitrogen-Atoms for Organic Solar Cells

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CONTENTS

List of Tables

List of Figures

Section S.1. Computational Details of Marcus Rate Parameters

S.1.1 Reorganization Energy

In general, λ is consist of the internal (λ_{int}) and external (λ_{ext}) reorganization energy.[1] The internal component of the reorganization energy originates from the changes in the equilibrium geometries of D and A when they gain or lose charge upon electron transfer, can be obtained by four energies in eq S1 for the interface model.[2]

$$\lambda_{\text{int}} = \left[E\left(\text{A}^-\right) - E\left(\text{A}\right)\right] + \left[E^+\left(\text{D}\right) - E^+\left(\text{D}^+\right)\right] \tag{S1}$$

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

However, the external component of the reorganization energy is caused by the electronic and nuclear polarization from the surrounding medium.[3]Although it is calculated with more error than the other terms appearing in eq S2, first because of the intrinsic approximations of the continuum model and then because of the uncertainty in the measurement of ε_{op} and ε_0 caused by different conditions and experimental facility, it can be computed approximately by the following formula:[3]

$$\lambda_{ext} = \frac{1}{4\pi\varepsilon_0}\Delta e^2\left(\frac{1}{2a_1}+\frac{1}{2a_2}-\frac{1}{R}\right)\left(\frac{1}{\varepsilon_{op}}-\frac{1}{\varepsilon_0}\right) \tag{S2}$$

Where a_1, a_2, R, ε_{0P}, and ε_0 is donor radii, acceptor radii, the distance between the centers of the donor and acceptor, optical and zero-frequency dielectric constants of the surrounding media, respectively. Moreover, ε_{0P} can be calculated by $\varepsilon_{0P} = n^2$, which n is the refractive index of **PDPP5T/ 1-10**.

S.1.2 Gibbs Free Energy

In the exciton dissociation and charge recombination, The Gibbs free energy difference (ΔG_{CS} and ΔG_{CR}) was calculated as follows:[4, 5]

$$\Delta G_{\mathrm{CT}} = -\Delta G_{\mathrm{CR}} - \Delta E_{0\text{–}0} - E_{\mathrm{b}} \tag{S3}$$

$$\Delta G_{\mathrm{CR}} = E_{\mathrm{IP}}(\mathrm{D}) - E_{\mathrm{EA}}(\mathrm{A}) \tag{S4}$$

For eq S4, the $E_{\mathrm{IP}}(\mathrm{D})$ and $E_{\mathrm{EA}}(\mathrm{A})$ are the ionization potential of the donor and electron affinity of the acceptor that can be estimated by the HOMO energy of the donor and the LUMO energy of the acceptor, respectively.[6] While the $\Delta E_{0\text{–}0}$ and E_{b} of eq S3 represent the lowest excited state energy of free-base donor and the exciton binding energy, defined as the energy difference between the electronic and optical band-gap energy, respectively.

Section S.2. Formulation of the Open Circuit Voltage

$$V_{\mathrm{OC}} = (1/e)(|E^{\mathrm{D}}_{\mathrm{HOMO}}| - |E^{\mathrm{A}}_{\mathrm{LUMO}}|) - 0.3\ \mathrm{V} \tag{S5}$$

where e is the elementary charge, $E^{\mathrm{D}}_{\mathrm{HOMO}}$ is the HOMO energy level of the donor, $E^{\mathrm{A}}_{\mathrm{LUMO}}$ is the LUMO energy level of the acceptor, and 0.3 V is the empirical factor for efficient charge separation.[7]

Tables

Table S1 The energy levels value (eV) for the original structure of **PDPP2TzT**，the methyl- and hydrogen- substituted **PDPP2TzT** at B3LYP/6-31G (d) level.

	PDPP2TzT	**methyl-substituted PDPP2TzT**	**hydrogen-substituted PDPP2TzT**
HOMO	-5.08	-4.70	-5.27
LUMO	-2.67	-2.39	-3.03

Table S2 The energy levels value (eV), $\Delta E_{\mathrm{L\text{-}L}}$ (eV) and V_{OC} (eV), for **PDPP2TZT** and **PDPP5T** calculated by different functionals with the 6-31G(d) basis set compared with experimental value.

	PDPP2TZT		**PDPP5T**			
	HOMO	**LUMO**	**HOMO**	**LUMO**	$\Delta E_{\mathrm{L\text{-}L}}$	V_{OC}
Exp.[a]	-5.63	-4.00	-5.23	-3.63		
B3LYP/6-31G (d)	-5.27	-3.03	-4.83	-2.80	0.23	1.50
PBE0/6-31G (d)	-5.49	-3.00	-5.07	-2.73	0.27	1.77
B3P86/6-31G (d)	-5.93	-3.68	-5.5	-3.44	0.24	1.52
B3PW91/6-31G (d)	-5.37	-3.12	-4.95	-2.89	0.23	1.53

[a] Ref.[8]

Table S3 The difference of energy values (eV) between the stable conformation and filtered conformations along different distances of X axis (Å) for **PDPP5T/b1**, where the distance Y and Z is at 0 Å and 3.5 Å, respectively.

	-10	**-8**	**-4.5**	**-4**	**0**	**3.4**	**4**	**8**	**8.2**
Energy	0.0130	0.0108	0.0107	0.0107	0	0.0107	0	0.0130	0.0130

Table S4 The difference of energy values (eV) between the stable conformation and filtered conformations along different distances of Y axis (Å) for **PDPP5T/b1**, where the distance X and Z is at 0 Å and 3.5 Å, respectively.

	-4	**-3**	**-2**	**-1**	**0**	**1**	**2**	**3**	**4**
Energy	0.0004	0.0004	0.0004	0.0004	0.0049	0.0004	0	0	0

Table S5 The difference of energy values (eV) between the stable conformation and filtered conformations along different distances of Z axis (Å) for **PDPP5T/b1**, where the distance X and Y is at 0 Å and 2 Å, respectively.

	3.0	**3.1**	**3.2**	**3.3**	**3.4**	**3.5**	**3.6**	**3.7**	**3.8**
Energy	0.0004	0	0.0004	0.0004	0	0.0004	0.0004	0.0004	0.0004

Table S6 Calculated energy level values (eV), E_g (eV), $\Delta E_{\text{L-L}}$ (eV), V_{OC} (V), $k_{\text{inter-CR}}$ (s^{-1}), $k_{\text{inter-CT}}$ (s^{-1}) for **PDPP3T** and **PDPP2TzT** at B3P86/6-31G (d) level.

	$\boldsymbol{\Delta E_{\text{L-L}}}$	$\boldsymbol{V_{\text{oc}}}$	$\boldsymbol{E_g}$	$\boldsymbol{k_{\text{inter-CR}}}$	$\boldsymbol{k_{\text{inter-CT}}}$
PDPP5T/PDPP2TzT (b1)	2.26	1.13	0.74	2.67×10^{7}	1.10×10^{15}

Table S7 Calculated maximum absorption wavelength λ_{max} (nm), onset absorption wavelength λ_{onset} (nm), oscillator strengths f, and dominant excitation characters of **b1-b10** (n=1) of S_1 at B3P86/6-31G (d) level.

Molecules	λ_{max}	λ_{onset}	f	Configurations[a]
b1	597.0	259.0	1.256	H→L (100%)
b2	607.4	257.8	1.125	H→L (100%)
b3	609.7	269.6	1.401	H→L (100%)
b4	561.0	252.8	1.036	H→L (100%)
b5	583.6	258.2	1.150	H→L (100%)
b6	563.3	268.0	1.005	H→L (100%)
b7	585.1	273.1	1.226	H→L (100%)
b8	620.4	272.4	1.307	H→L (100%)
b9	581.8	291.9	1.430	H→L (100%)
b10	578.7	246.8	1.072	H→L (99%)

[a] H denotes HOMO and L denotes LUMO.

Figures

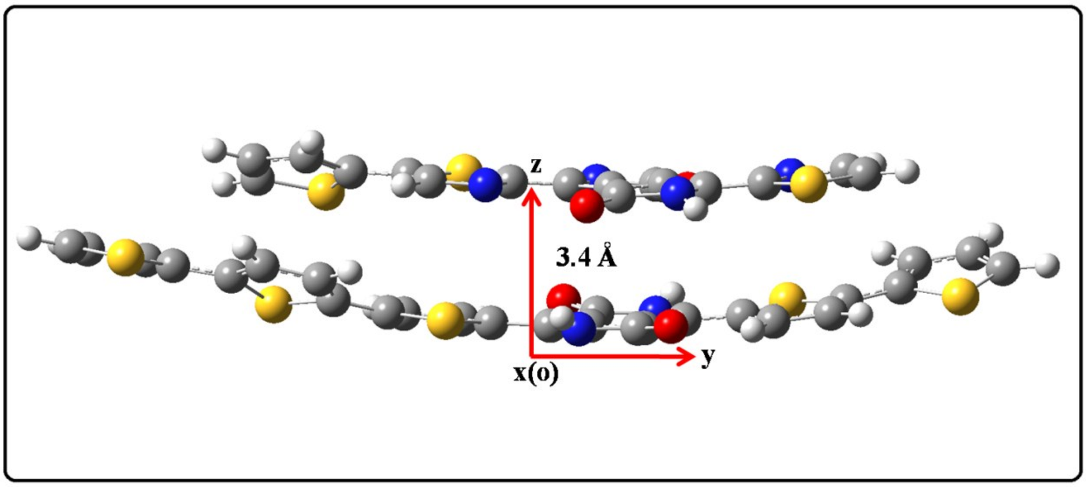

Figure S1. Optimized geometries of **PDPP5T/b1** obtained by B3LYP/6-31G(d) method.

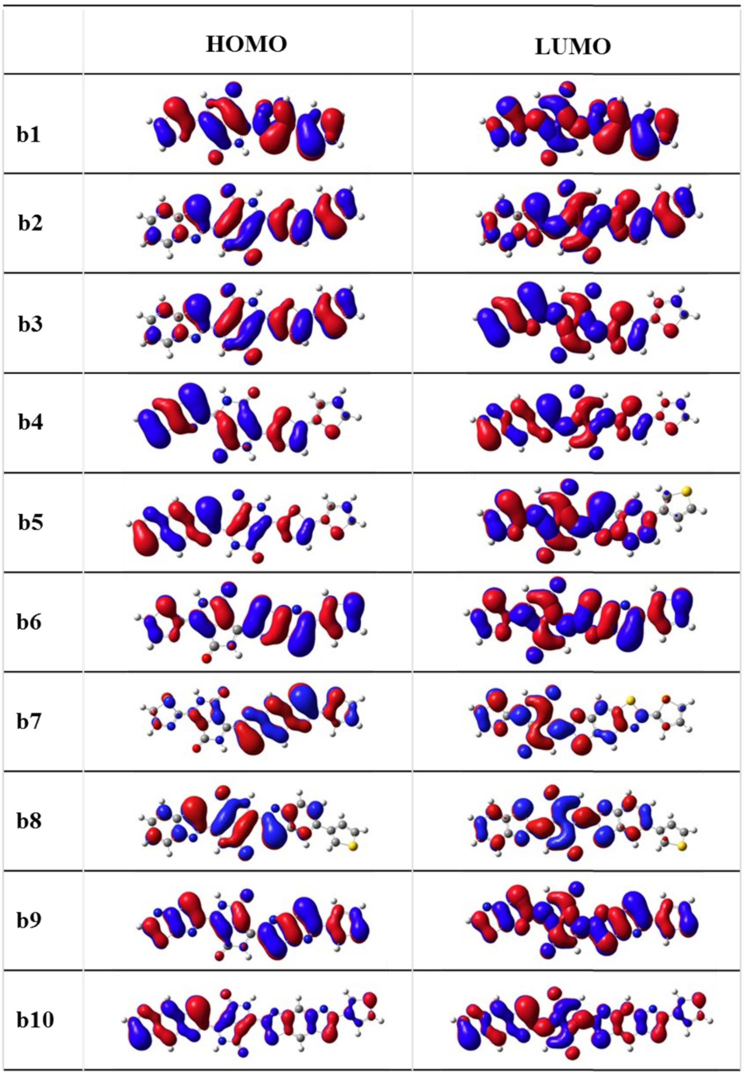

Figure S2. The frontier molecular orbital of all designed molecules **b1-b10** at the B3P86/6-31G (d) level with an isodensity surface of 0.02 in the chloroform solvent.

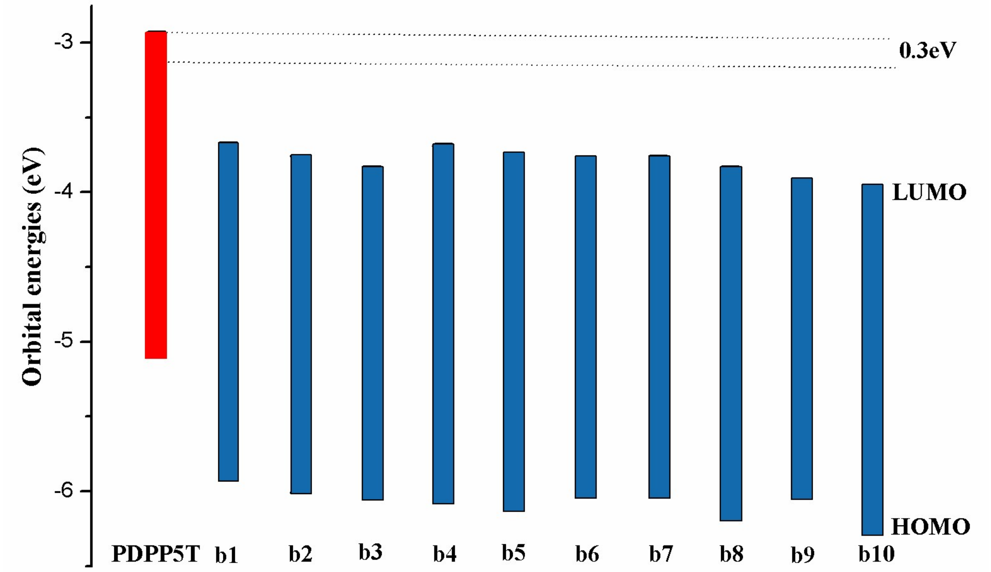

Figure S3. The energy levels of **b1-b10** and **PDPP5T** evaluated at the B3P86/6-31G (d) level in the chloroform solvent.

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