

Electronic Supplementary Information (ESI)

Novel benzodithiophene-based polymer acceptors for efficient organic solar cells

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Section S1. Computational Details about Marcus Rate Parameters

The charge transport is considered as a hopping process in the organic materials,¹ which can be evaluated by the Marcus model. The electron mobility (μ) was evaluated from the diffusion coefficient, D , with the Einstein equation² as follows

$$\mu = \frac{eD}{k_B T} \quad (S1)$$

where e represents the electronic charge, and D represents diffusion coefficient³ which can be approximately evaluated by²

$$D = \lim_{t \rightarrow \infty} \frac{1}{2d} \frac{\langle x(t)^2 \rangle}{t} \approx \frac{1}{2d} \sum_i r_i^2 k_i p_i \quad (S2)$$

where i is a given transfer pathway and r_i is defined as the charge hopping centroid-to-centroid distance, d ($d=3$) is defined as spatial dimensionality, and p_i ($p_i = \frac{k_i}{\sum k_i}$) is the relative probability for charge hopping to a particular i th neighbor.

Additionally, when considering only two adjacent molecular fragments, D is simply estimated by:⁴

$$D = \frac{1}{2} k_{CT} r^2 \quad (S3)$$

where k_{CT} and r are the charge transfer rate and intermolecular distance for dimer. Herein, the electron mobility is defined as:⁵

$$\mu = \frac{er^2}{2k_B T} k_{CT} \quad (S4)$$

The electron mobility is directly proportional to the electron transport rate (k_{CT}). According to the Marcus-Hush theory, the electron transport rate (k_{CT}) between the neighboring sites is expressed as:⁶

$$k_{CT} = \frac{4\pi^2 \nu^2}{h} \sqrt{\frac{1}{4\pi\lambda k_B T}} \exp\left(\frac{-\lambda}{4k_B T}\right) \quad (S5)$$

where h , ν , k_B , T , and λ are the Planck's constant, charge transfer integral between adjacent molecular segments, Boltzmann constant, temperature, and inner reorganization energy, respectively.

The inner reorganization energy (λ) was obtained by four-point method^{5, 7, 8}

$$\lambda = (E_0^- - E_-) + (E_-^0 - E_0) \quad (S6)$$

where E_0 and E_- represent the energies of neutral and anion segments in their lowest energy geometries, respectively. E_-^0 denotes the energy of neutral segment at anion state, and E_0^- is the energy of anion segment with the neutral optimized geometry.

The electron-transfer integral (ν) of the adjacent neutral optimized acceptor molecules is given by the following eq (7), which is equal to half of the energy difference between the LUMO+1 (L+1) and the LUMO (L) of the interactive segment pairs, respectively.⁵

$$\nu = \frac{E_{L+1} - E_L}{2} \quad (S7)$$

In addition, the electron transfer distance and the fraction of electron exchange for all trimer models were calculated.⁹ The total electron density difference ($\sum \partial_{i \rightarrow j}$) after photoexcitation between the starting and final

states could be expressed as the sum of all molecular orbital transitions including each participating excitation $i \rightarrow j$ (i and j are the starting and final molecular orbital, respectively.)^{7, 9}:

$$\delta_{i \rightarrow j} = \frac{C_{i \rightarrow j}^2}{\sum C_{i \rightarrow j}^2} (\rho_i - \rho_j) \quad (\text{S8})$$

$C_{i \rightarrow j}$ represents the orthogonal coefficient of the TD-DFT equation. ρ_i and ρ_j represent the electron densities of the each

participating molecular orbital with respect to the transitions^{5, 10}

$$\rho_r = \sum_i \eta_i |\varphi_i(r)|^2 = \sum_i \eta_i |C_{j,i} \chi_i(r)|^2 \quad (\text{S9})$$

where η_i , χ , and C represent the occupation number of orbital i , the basis function, and the coefficient matrix, respectively. And the factor of i th row j th column is equal to the expansion coefficient of orbital j with respect to basis function χ . The electron density differences between the starting and the final states are the linear combination of various electron transition models.¹⁰ All calculated results were gained using the *cubman* utility supplied by the Gaussian 09 and *Multwfn* programs. Moreover, the two functions $\rho_+(r)$ and $\rho_-(r)$ were used for defining the increase and decrease in the density owing to the electronic transition. The centroids of spatial regions defined by $\rho_+(r)$ and $\rho_-(r)$ are expressed as⁹

$$C_+ = (x_+, y_+, z_+) = \frac{\int r \rho_+(r) dr}{\int \rho_+(r) dr} \quad (\text{S10})$$

And

$$C_- = (x_-, y_-, z_-) = \frac{\int r \rho_-(r) dr}{\int \rho_-(r) dr} \quad (\text{S11})$$

The charge transfer distance (D), eq (12) was used

$$D = |C_+ - C_-| \quad (\text{S12})$$

The fraction (F) of electron exchange is evaluated as

$$F = \left| \int \rho_+(r) dr \right| = \left| \int \rho_-(r) dr \right| \quad (\text{S13})$$

Section S2. Figures

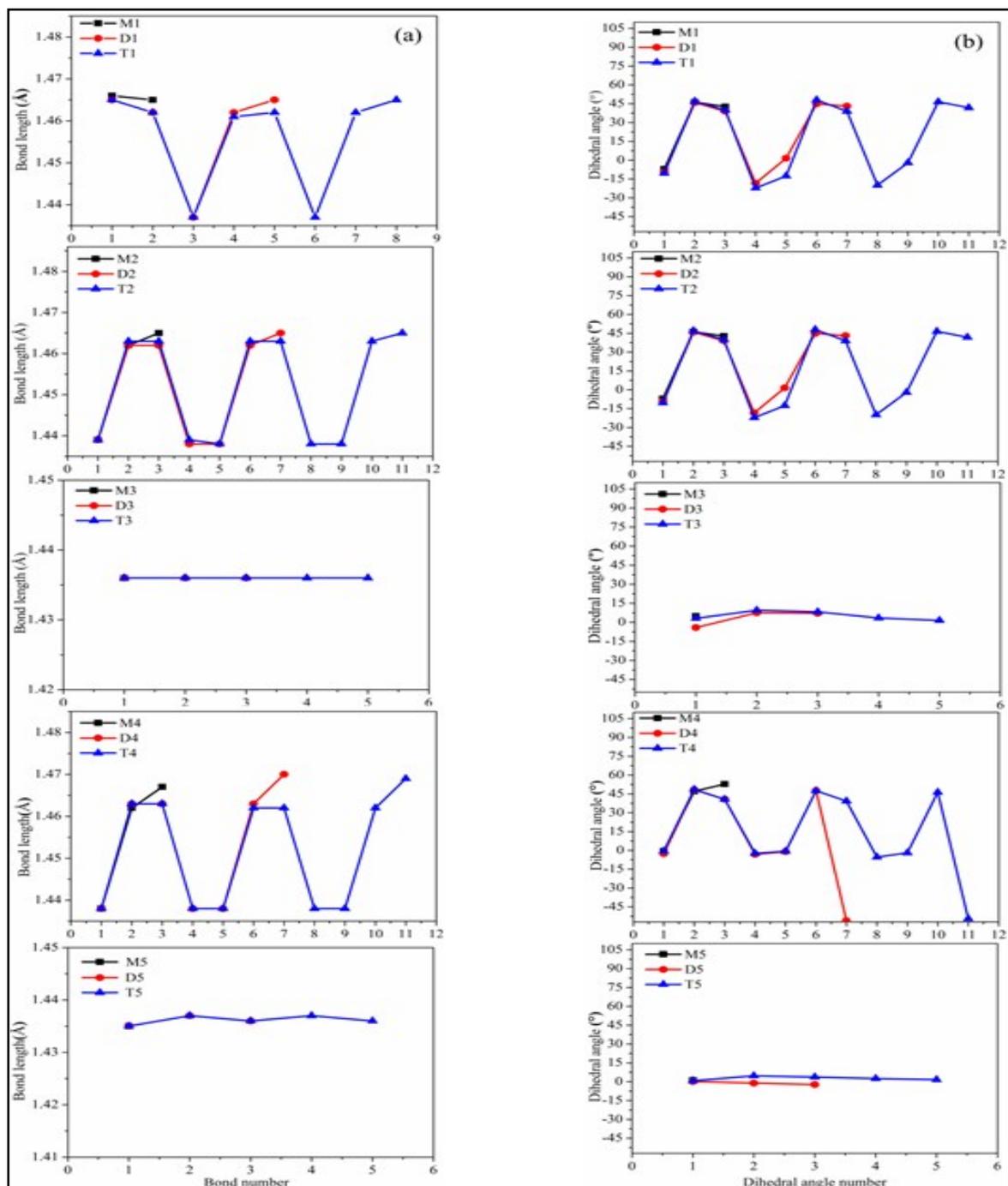
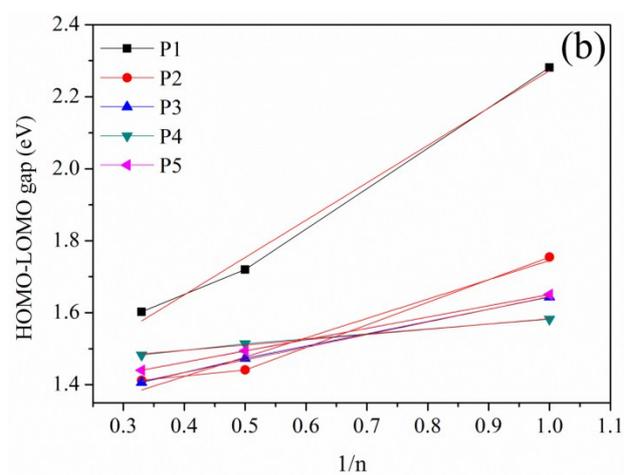
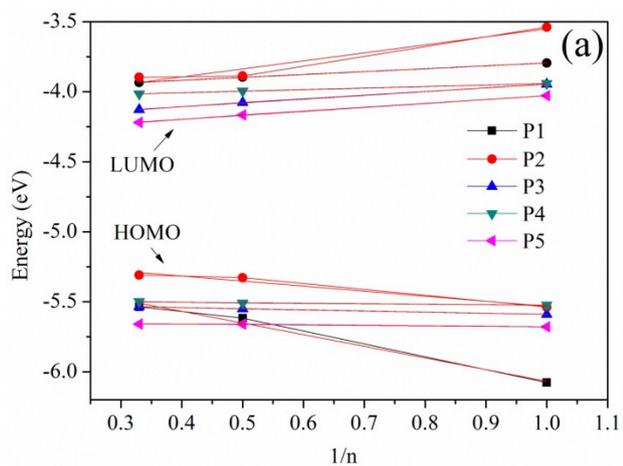
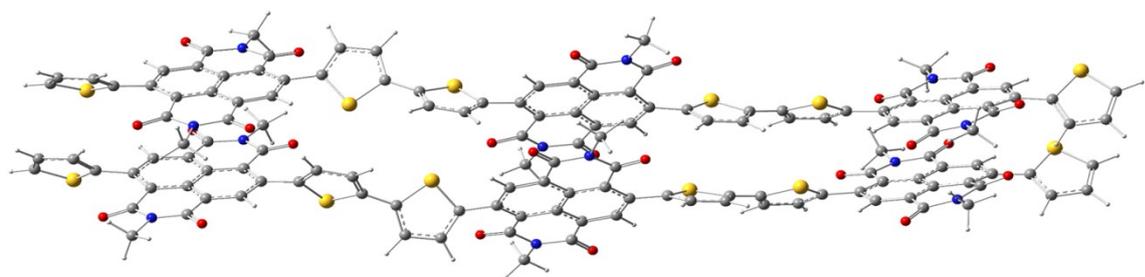


Fig. S1 Optimized bond lengths ($L_1, L_2...L_i$ in Fig. 1) and dihedral angles ($\vartheta_1, \vartheta_2... \vartheta_i$ in Fig. 1) of the oligomers in neutral states versus their numbers at HSE06/6-311G (d, p) level. (a) C-C bond lengths, (b) dihedral angles.

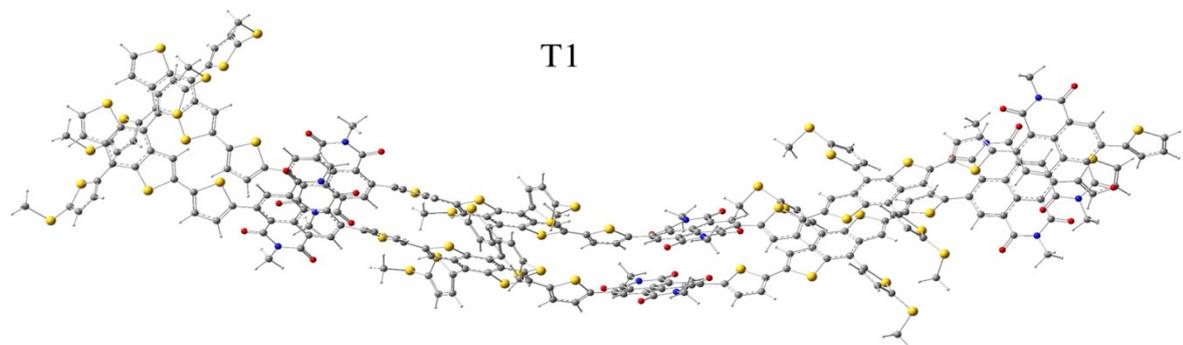


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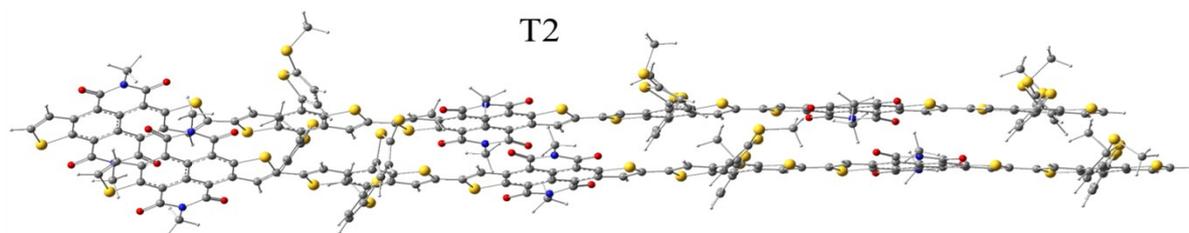
g. S2 (a) The HOMO/LUMO energies and (b) the HOMO-LUMO gaps by HSE06/6-311G(d,p) of the five series of reciprocal chain length n in oligomers.



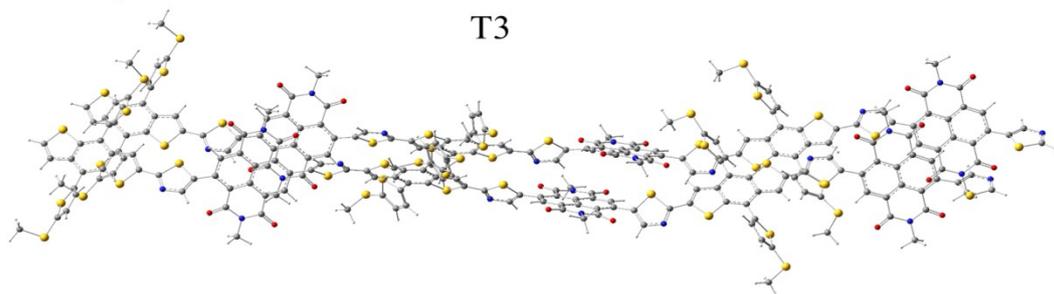
T1



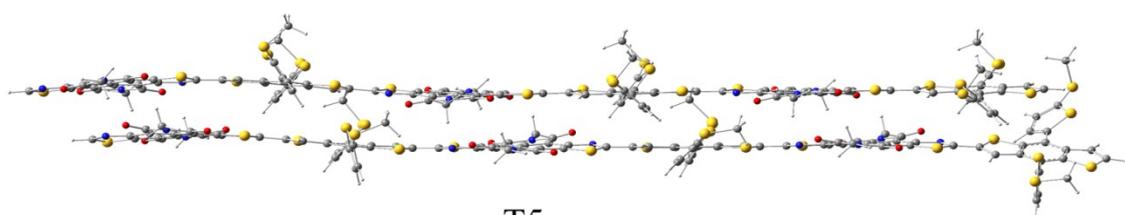
T2



T3



T4



T5

Fig. S3 3D models of two adjacent fragments of T1-T5.

Section S3. Spectral Properties of Monomers and Dimers

Table S1 The calculated maximum absorption wavelength (λ), excitation energy, largest oscillator strength (f), main configuration, and light absorption efficiency (η_λ) of the oligomers

<i>System</i>	<i>Electronic transitions</i>	<i>Excitation energy (eV, nm)</i>	<i>Main configurations</i>	<i>f</i>	<i>η_λ</i>
M1	$S_0 \rightarrow S_{12}$	4.08, 304	H \rightarrow L+2(64%)	0.7696	0.8300
D1	$S_0 \rightarrow S_1$	1.85, 669	H \rightarrow L (97%)	1.1683	0.9321
M2	$S_0 \rightarrow S_1$	1.85, 669	H \rightarrow L(96%)	0.3159	0.5168
D2	$S_0 \rightarrow S_1$	1.67, 740	H \rightarrow L (91%)	1.3768	0.9580
M3	$S_0 \rightarrow S_{12}$	3.49, 355	H-1 \rightarrow L +1(85%)	0.4685	0.6600
D3	$S_0 \rightarrow S_1$	1.72, 721	H \rightarrow L(89%)	2.1101	0.9922
M4	$S_0 \rightarrow S_1$	3.37, 368	H-1 \rightarrow L+1 (51%)	0.5910	0.7436
D4	$S_0 \rightarrow S_1$	1.78, 698	H \rightarrow L (87%)	1.0457	0.9100
M5	$S_0 \rightarrow S_{17}$	3.67, 338	H \rightarrow L (71%)	0.7458	0.8204
D5	$S_0 \rightarrow S_1$	1.79, 693	H \rightarrow L (72%)	1.2791	0.9474

From Table S1 we can see that the main electronic transition in the oligomers is assigned to the $\pi \rightarrow \pi^*$ type and the strongest absorption peak in the visible region are mainly dominated by the HOMO \rightarrow LUMO, HOMO-1 \rightarrow LUMO, HOMO-1 \rightarrow LUMO+1, and HOMO \rightarrow LUMO+2 transitions. In all cases, the oscillator strength (f) increases strongly when the repeat unit increases. With the increasing conjugation lengths, the strongest peaks are red-shifted.

References

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