

## Supporting Information for “Investigations on the charge transfer mechanism at donor/acceptor interfaces in quest of descriptors of organic solar cell performance”

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### (1) Calculation procedure of $\Delta Q$ , $d_{CT}$ , and $\Delta\mu_{D/A}$

The variation of density upon the electronic transition is written as

$$\Delta\rho(r) = \rho_e(r) - \rho_g(r) \quad (S1)$$

, where  $\rho_g(r)$  and  $\rho_e(r)$  are the densities of the ground and excited electronic states, respectively. If we define two factions,  $\rho_+(r)$  and  $\rho_-(r)$ , by the points in space where an increase or a decrease of the density upon electronic excitation is produced, ( $\Delta\rho(r)$ ),

$$\rho_+(r) = \begin{cases} \Delta\rho(r) & \text{if } \Delta\rho(r) > 0 \\ 0 & \text{if } \Delta\rho(r) < 0 \end{cases} \quad (S2)$$

$$\rho_{-}(r) = \begin{cases} \Delta\rho(r) & \text{if } \Delta\rho(r) < 0 \\ 0 & \text{if } \Delta\rho(r) > 0 \end{cases} \quad (\text{S3})$$

, the barycenters of the spatial regions of donor ( $R_{+}$ ) and acceptor ( $R_{-}$ ) are expressed as

$$R_{+} = \frac{\int r\rho_{+}(r)dr}{\int \rho_{+}(r)d} \quad (\text{S4})$$

$$\int r\rho_{+}(r)d$$

$$R_{-} = \frac{\int r\rho_{-}(r)dr}{\int \rho_{-}(r)d} \quad (\text{S5})$$

, respectively. The charge transfer distance,  $d_{CT}$ , is thus obtained as

$$d_{CT} = |R_{+} - R_{-}| \quad (\text{S6})$$

Then, the transferred charge,  $\Delta Q$ , is calculated by integrating  $\rho_{+}(r)$  and  $\rho_{-}(r)$  over all space:

$$\Delta Q = \int \rho_{+}(r)dr - \int \rho_{-}(r)dr \quad (\text{S7})$$

Finally, the variation of dipole moments between the ground and excited states upon charge transfer,  $\Delta\mu_{D/A}$ , is defined as

$$\Delta\mu_{CT} = d_{CT} \int \rho_{+}(r)dr - d_{CT} \int \rho_{-}(r)dr = d_{CT} \cdot \Delta Q \quad (\text{S8})$$

## (2) Reproducibility of the absorption spectra in Fig. 2

Comparing Fig. 2a of this paper and Fig. 1 b of [15], it is clear that the numerically calculated absorption spectrum and the experimentally observed absorption spectrum do not agree. In particular, Fig. 2a shows that PTB7 has the absorption maximum at the

wavelength of around 400 nm numerically while it has the absorption peak at round 690 nm experimentally [17]. To bridge the gap between the experimental and the calculation results, we have examined the relationship between the HOMO and LUMO energies and the unit number of several donor molecules.

Figure S1 shows the relationship between HOMO, LUMO, and excited energies and the unit number of the donor molecules. In these figures, (a) is the numerical result for *n*-PTB7, (b) is that for *n*-PTB1, and (c) is that for *n*-PTBF2, where *n* denotes the unit number. From Fig. S1, it can be seen that the HOMO energy increases and the LUMO energy decreases as *n* increases for all the cases. This is in accord with the general rule verified in other  $\pi$ -conjugated oligomers and polymers [S1]. As a consequence, the excitation energies decrease as *n* increases for all the cases. In addition, the excitation energies versus  $1/n$  extrapolated to the limit of large *n* coincide with the experimentally observed excitation energies for all the panels in Fig. S1. This phenomenon also agrees with the general trend found in other  $\pi$ -conjugated oligomers and polymers [S1]. From the above considerations, it can be concluded that the experimental absorption spectra of PTB7, PTB1, and PTBF2 donor molecules suggest that the measured molecules may be highly  $\pi$ -conjugated.

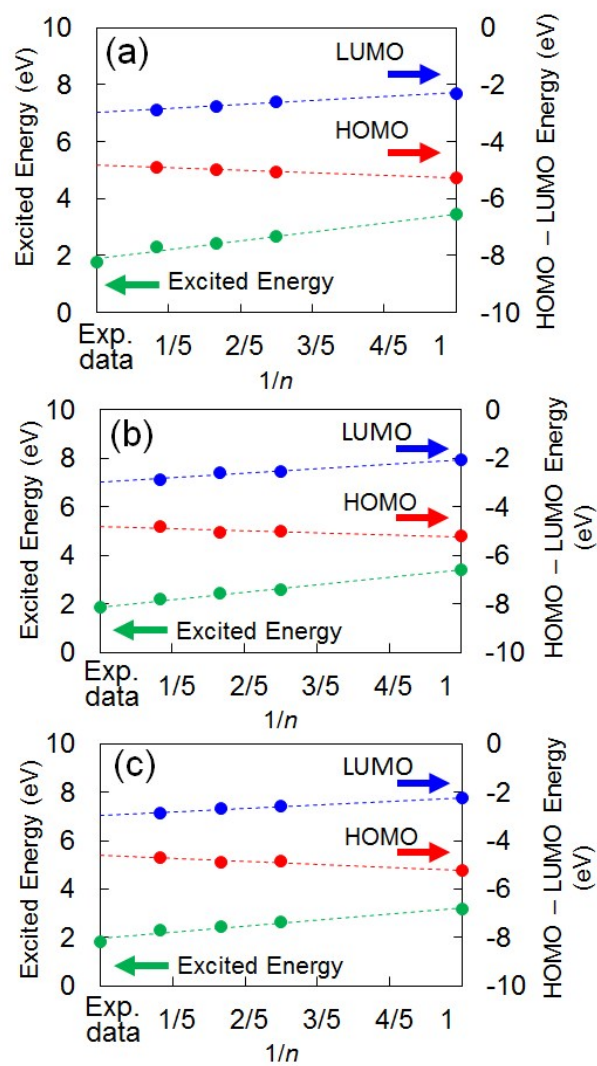


Fig. S1. Relationship between HOMO, LUMO, and excited energies and the unit number of the donor molecules. (a): *n*-PTB7, (b): *n*-PTB1, and (c): *n*-PTBF2, where *n* denotes the unit number.

[S1] S. S. Zade and M. Bendikov, *Org. Lett.*, **8**, (2006) 5243.