Supporting Information

Exciton dynamics and charge transfer in polymer with effects of chlorine substituents

Xu Han,[a,b] Guangliu Ran,[a,b] Hao Lu,[c] Shumei Sun[*a,b]

1. School of Physics and Astronomy, Applied Optics Beijing Area Major Laboratory, Center for Advanced Quantum Studies, Beijing Normal University, Beijing 100875, China

2. Key Laboratory of Multiscale Spin Physics, Ministry of Education, Beijing Normal University, Beijing 100875, China

3. College of Materials Science and Engineering, Qingdao University, Qingdao, Shandong 266071, China

 *Corresponding author: sunshumei@bnu.edu.cn

1. Sample Preparation and Instruments

The details of molecular structures, design and synthesis methods of three polymer donors (PJ-1, PJ-2, PJ-3) can be seen in the literature[1]. The UV-vis spectra of the samples were obtained using the Cary 60 UV-vis spectrophotometer (Agilent Technologies, America). A quartz cuvette of 2 mm× 10 mm was used for the UV-vis spectra, and the baseline was corrected with pure solvent before the experiment. Single Cell Peltier accessory (Agilent Technologies, America) was used for the variable temperature UV-Vis absorption experiment. The PL spectra of three donors were measured using FLS980 Spectrometer produced by Edinburgh Instruments.

## 2. Femtosecond Transient absorption (fs-TA) measurements

The femtosecond TA measurements were got from an ultrafast TA spectrometer (Harpia-TA, Light Conversion). The output of a Yb:KWG laser (1030 nm, 54 kHz, Light Conversion) is split into multiple branches. One is focused on a sapphire window to produce continuum white light as a probe beam. Others are directed into an optical parametric amplifier to produce the specific wavelength for the pump beam. The time delay between the pump and probe is controlled by a motorized precision translation stage. For all TA experiments, a magic angle (54.7°) is used between the pump and probe beam. The pump and probe beam spatially overlapped at the sample.
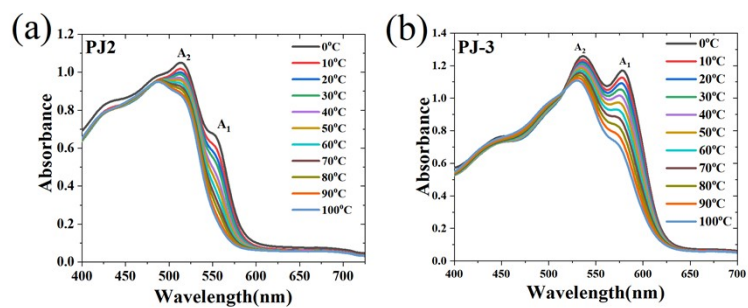

Figure S1. Energy level diagram of donors and acceptor.
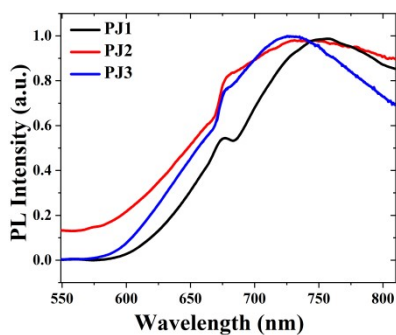
Figure S2. Steady-state fluorescence spectra of donor films.
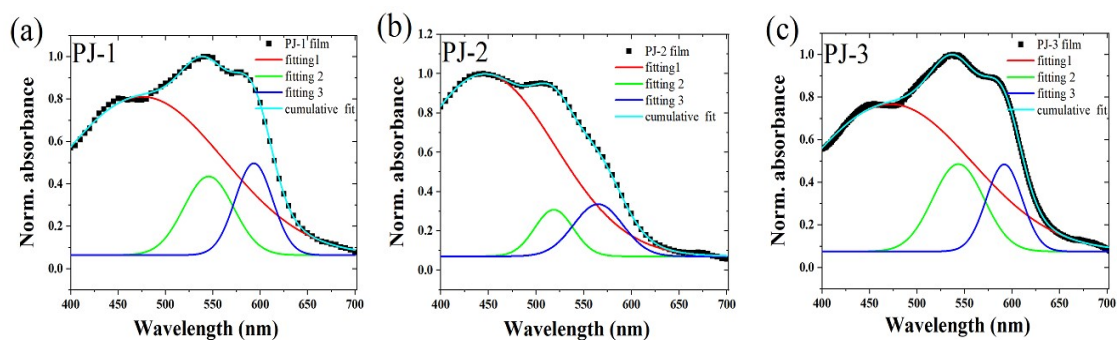
Figure S4. Gaussian multi-peak fitting of the steady-state absorption spectra of polymer films

Figure S3. Temperature-dependent UV–vis absorption spectra of PJ-2 and PJ-3 solution with a measurement interval of 10°C.

Table S1: the aggregation capacity (A_{agg}/A_{tot}) of the three polymers

sample	PJ-1	PJ-2	PJ-3
A_{agg}/A_{tot}	0.105	0.081	0.099

3. The detailed calculation processes of exciton diffusion length.

We measure the exciton diffusion length through the exciton-exciton annihilation (EEA) method. The diffusion length of excitons can be evaluated using $L_D = (D\tau)^{1/2}$, where τ is the intrinsic exciton lifetime ($\tau = 1/k$) and D is the exciton diffusion constant. Generally speaking, excitons have two main quenching channels, namely defect-assisted recombination and bimolecular exciton-exciton annihilation recombination corresponds to two decay parameters k and γ respectively：

$$-\frac{dn(t)}{dt} = kn(t) + \gamma n^2(t)$$

$$n(t) = \frac{n_0 exp(-kt)}{1 + \frac{\gamma}{k}n_0[1 - exp(-kt)]}$$

Where $n(t)$ is the exciton density, n_0 is the initial exciton density. Under the pump of lower pulsed light, EEA can be ignored：

$$-\frac{dn(t)}{dt} = kn(t)$$

But under the pump of high power pulsed light, the exciton annihilation effect occurs, which generally leads to faster decay dynamics, we can get:

$$t_{1/2} = \frac{\alpha \, ln2}{k}, \alpha < 1$$

$$\gamma = \frac{k(2exp(\alpha \, ln2) - 1)}{n_0(1 - exp(-\alpha \, ln2))}$$

Among them, $t_{1/2}$ is the half-life time representing the exciton concentration decays to the first half concentration; α is a correction factor that accounts for EEA and experimentally obtained by the ratio between the half-life times under high and low pump conditions Then the diffusion coefficient D can be calculated by the following formula:
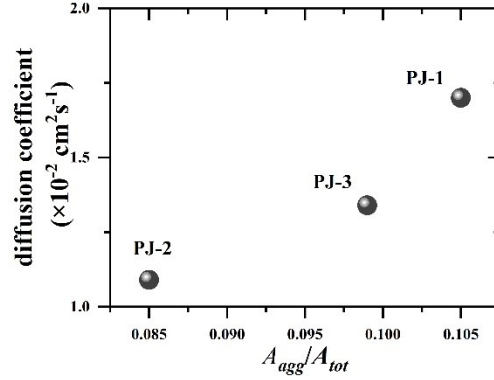
$$D = \frac{\gamma}{4\pi R}$$

Figure S5: aggregation capacity vs. diffusion coefficient for the three polymers of PJ-1, PJ-2 and PJ-3 respectively.

Where R is the annihilation radius of the singlet exciton, which is mainly driven by the dipole-dipole interaction and it can be estimated by the equation $R = a\left(\frac{R_e}{R_g}\right)^{\frac{3}{2}}$, where a, the average exciton hopping distance, was considered to be the stacking distance (0.37 nm) as determined from GIWAXS of neat films. R_e and R_g correspond to the Förster radii for exciton transfer onto an excited and a ground state segment of the polymer respectively. The upper estimation of $\frac{R_e}{R_g}$ is 4. Here, we set R to be 2 nm, which is a reasonable value and was widely adopted by many researchers.[2-4]

4. **The detailed calculation processes of hole transfer efficiency.**

The hole transfer in the blend is mainly derived from the ultrafast dissociation of boundary excitons and the diffusion-mediated transfer of domain excitons, which can be expressed as

$$\eta_{HT} = c_1\eta_1 + c_2\eta_2$$

where c_1 and c_2 represent the percentages of ultrafast hole transfer process and diffusion-mediated hole transfer process, respectively. Since the exciton dissociation at the boundary is very fast: PJ-1:BTP-eC9-4F ($\tau_1 = 0.88$ ps) and PJ-2:BTP-eC9-4F ($\tau_1 = 2.13$ ps), which is significantly shorter compared to the recombination time of acceptor

excitons (hundreds of picoseconds),[5] thus we assumed that all excitons on the boundary to be dissociated ($\eta_1 \approx 100\%$). While in the domain, only part of the excitons diffuse to the D-A interface for dissociation and hole transfer (k_{HT}) and the others return to the ground state (k_R) by exciton recombination. Therefore, the efficiency of diffusion-mediated hole transfer process can be expressed as the equation of $\eta_2 = \dfrac{k_{HT}}{k_{HT} + k_R}$.

Table S2: the efficiency of diffusion-mediated hole transfer process.

Samples	τ_R	τ_{HT}	η_2
pure BTP-eC9-4F	50.2 ps	--	
PJ-1:BTP-eC9-4F	--	18.9 ps	**72.6%**
PJ-2:BTP-eC9-4F	--	43.1 ps	**53.8%**

Note that τ_R is the exciton half-lifetime of BTP-eC9-4F and τ_{HT} is the diffusion-mediated hole transfer lifetime.

1.H. Lu, H. Wang, G. Ran, W. Liu, H. Huang, X. Jiang, Y. Liu, X. Xu and Z. Bo, Chlorinated Thiazole-Based Low-Cost Polymer Donors for High Efficiency Binary and Ternary Organic Solar Cells, *CCS Chem*, 2023, 1–10.

2. P. Bi, S. Zhang, Z. Chen, Y. Xu, Y. Cui, T. Zhang, J. Ren, J. Qin, L. Hong, X. Hao and J. Hou, Reduced non-radiative charge recombination enables organic photovoltaic cell approaching 19% efficiency, Joule, 2021, 5, 2408–2419.

3. S. Chandrabose, K. Chen, A. J. Barker, J. J. Sutton, S. K. K. Prasad, J. Zhu, J. Zhou, K. C. Gordon, Z. Xie, X. Zhan and J. M. Hodgkiss, High Exciton Diffusion Coefficients in Fused Ring Electron Acceptor Films, J. Am. Chem. Soc., 2019, 141, 6922–6929.

4. S. Cook, H. Liyuan, A. Furube and R. Katoh, Singlet Annihilation in Films of Regioregular Poly(3-hexylthiophene): Estimates for Singlet Diffusion Lengths and the Correlation between Singlet Annihilation Rates and Spectral Relaxation, J. Phys. Chem. C, 2010, 114, 10962–10968.

5. Y. Jia, X. Jiang, Y. Liang, Y. Peng, S. Fang, Y. Yang, C. Miao, Y. Lin and S. Zhang, Enhanced photocatalytic hydrogen evolution by extending exciton lifetime via asymmetric organic semiconductor, Dyes and Pigments, 2024, 224, 111982.