Supporting Information for

Promoted Exciton Transport in Organic Semiconductors by Triplet-State Manipulation

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1. Experimental Details

All chemicals are of analytical grade and used directly without further purification. The following anthracene derivatives were synthesized by a method reported by Jiang et al.¹

1.1. Synthesis of 5-btA. The synthesis of 5-btA starts with preparing the M5-1. In details, to a 250 mL flask charged with a magnetic bar, 5/6bromobenzo[b]thiophene (10 mmol), bis(pinacolato)diboron (20 mmol), Pd(OAc)₂ (0.5 mmol), S-phos (1 mmol), KOAc (30 mmol) were added under argon. Then 100 mL degassed DMF was added, and the whole system was heated at 80 °C for 20 h. Then the mixture was poured into water, extracted with ethyl acetate (50 mL×3), and separated. The organic layer was dried over anhydrous Na₂SO₄. The solvent was removed under vacuum. Further purification by column chromatography on silica gel using petroleum ether: CH₂Cl₂ (4 : 1) as eluent afforded the product of M5-1 as a white solid (2.39 g, 92% yield).

Then, to a 50 mL flask charged with a magnetic bar, M5-1 (1 mmol), 2bromoanthracene (1 mmol), and Pd(PPh₃)₄ (0.05 mmol) were added under argon. Then 10 mL toluene 2 mL ethanol and 2M K₂CO₃ 2 mL were added. The whole system was refluxed overnight. The crude product was obtained by filtration. And the filtrate was further purified by gradient sublimation, obtaining the final product as a yellow crystalline powder (~220 mg, 70%).

1.2. Synthesis of 5-bteA. The synthesis of 5-bteA starts with preparing the M5-0 and M5-3. Synthesis of M5-0: To a 100 mL flask charged with a magnetic bar,

5- bromobenzo[b]thiophene (10 mmol), CuI (0.6 mmol) and Pd(PPh₃)₂Cl₂ (0.3 mmol) were added under argon. Then 20 mL ethanolamine, 30 mL THF, and 2 mL 2methylbut-3-yn-2-ol were added. The whole system was warmed up to 80 °C and kept for 8 h. After cooling down to room temperature, the organic solvent was removed under vacuum. Then 50 mL water was added, and the extracted with dichloromethane (30 mL \times 3). The combined organic layer was dried over anhydrous Na₂SO₄. The solvent was removed under vacuum. Further purification by column chromatography on silica gel using petroleum ether: CH_2Cl_2 (1:1) as eluent afforded the product as a white solid (1.95 g, 90% yield). Synthesis of M5-3: To a 50 mL flask charged with a magnetic bar, M5-0 (5 mmol), and NaOH (25 mmol) were added under argon, then 15 mL anhydrous toluene was added, and the whole system was refluxed at 110 °C for 1h, then the solvent was vacuum evaporated. Further purification by column chromatography on silica gel using petroleum ether as eluent gives M5-3 as a white needle-like solid (0.75 g, 95% yield). The two compounds were used directly for the next reaction.

For the synthesis of 5-bteA, to a 50 mL flask charged with a magnetic bar, M5-3 (1 mmol), 2-bromoanthracene (1 mmol), $Pd(PPh_3)_2Cl_2$ (0.03 mmol), CuI (0.06 mmol) were added under argon, then 10 mL THF and 2 mL Et₃N was added, the mixture was stirred at reflux overnight, then filtrated. The filtrate was further purified by gradient sublimation, obtaining the final product as a yellow crystalline powder (~216 mg, 65%).

1.3. Synthesis of 5-btvA. The synthesis of 5-btvA starts with preparing the

M5-2. In details, in a 100 mL flask charged with a magnetic bar, a mixture of bis(pinacolato)diboron (6.6 mmol), sodium methoxide (1.2 mmol), triphenylphosphine (0.36 mmol), CuBr (0.3 mmol), and 30 mL THF was added under argon, the mixture was stirred for 30 min at room temperature. To the mixture, M5-3 (6 mmol) and methanol (12 mL) were added. The mixture was stirred at room temperature for another 8 h. Then the solvent was removed under vacuum, and further purification by column chromatography on silica gel using petroleum ether: dichloromethane (4:1) as eluent giving M5-2 as white solid (1.46 g, 85%).

Then, to a 50 mL flask charged with a magnetic bar, M5-2 (1 mmol), 2bromoanthracene (1 mmol), and Pd(PPh₃)₄ (0.05 mmol) were added under argon. Then 10 mL toluene 2 mL ethanol and 2M K₂CO₃ 2 mL were added. The whole system was refluxed overnight. The crude product was obtained by filtration. And the filtrate was further purified by gradient sublimation, obtaining the final product of 5btvA as a yellow crystalline powder (~230 mg, 70%).

1.4. Fabrication of Single-Crystalline Organic Semiconductors. The single-crystalline organic semiconductors are obtained via a physical vapor transport (PVT) method on octadecyltrimethoxysilane-modified SiO₂ substrates. The optimized temperatures for 5-BTA, 5-BTVA, and 5-BTEA are 150, 160–170, and 170–180 °, respectively, with Ar (20 sccm) for 1.5–2 hours.

1.5. PL Measurement. We used a home-built PL-scanned imaging microscope coupled with a time-correlated single photon counting (TCSPC) module (see Fig. S6 for the setup) to collect the time-resolved PL imaging and kinetics of the

samples. A 405 nm pulsed laser (35 ps pulse width, PIXEA-405, Aurea Technology, France) was focused by an oil objective ($100 \times$, NA = 1.45) to a near diffractionlimited spot to excite the samples. The excitation intensity is adjusted by a neutral density filter and measured with a power meter (PM100D S130VC, Thorlabs, USA). With the laser spot fixed at a selected position on the sample, the PL collection pathway was scanned over the sample by fast rotation of a pair of galvanometer mirrors. Each scanning image contains 256 × 256 pixels (19 nm/pixel). The PL kinetics at any positions in PL images are collected by a high-speed detector (HPM-100-50, Hamamatsu, Japan) with a 425 nm long-pass filter. Besides, a 1 mm pinhole was placed before the detector to ensure that only PL from a diffraction-limited spot was observed.

1.6. PL spectra Measurement. The steady state emission spectra were obtained by a monochromator (SpectraPro-HRS-300, Princeton Instruments, USA) coupled with a charge coupled device (CCD) camera (PIXIS 100B, Princeton Instruments, USA), sharing the same excitation source and microscope objective for signal collection.

1.7. Ultrafast TA Measurement. The ultrafast TA spectrometer is based on a Pharos laser (1030 nm, 10 kHz, 230 fs pulse-duration; Light Conversion Ltd.), nonlinear frequency mixing techniques and the Femto-TA100 spectrometer (Time-Tech Spectra LLC). Briefly, the fundamental 1030 nm laser pulse was split into two parts. One part was introduced to pump a TOPAS optical parametric amplifier (OPA) to generate wavelength-tunable pump beam pulses. The other was beam doubled to 515 nm then focused onto the sapphire crystal to generate continuum white light used as probe beam which was focused with a parabolic reflector onto the sample. The transmitted probe beam was collimated and then focused into a fiber-coupled spectrometer with CMOS sensors. The intensity of the pump pulse was adjusted by a neutral density filter. The time delay between the pump and probe pulses was achieved by a mechanical delay stage. The pump pulses were chopped by a synchronized chopper at 5 kHz and the absorbance change was calculated with two adjacent probe pulses (pump-blocked and pump-unblocked). For TA spectroscopy, a pump pulse at 350 nm was used to excite the sample, and the induced absorption change (DA), as functions of both wavelength and time, were recorded.

1.8. Linear absorption spectra measurement. The steady state absorption spectra are recorded by a UV-vis absorption spectrometer (Cary60, Agilent Technologies, USA).

2. Supplementary Note 1: Determination of exciton diffusion coefficient by PL microscopy

The PL kinetics at an examined position on the sample reflects the change of exciton population as a function of time, which can be described by a twodimensional diffusion model:

$$\frac{\partial \phi(x,y,t)}{\partial t} = D\left\{\frac{\partial^2 \phi(x,y,t)}{\partial x^2} + \frac{\partial^2 \phi(x,y,t)}{\partial y^2}\right\} - k_1 \phi(x,y,t) + f(\phi(x,y,t)) \#(S1)$$
$$f(\phi(x,y,t)) = -k_2 \phi(x,y,t)^2 - k_3 \phi(x,y,t)^3 \#(S2)$$

where $\phi(x, y, t)$ is the density of exciton at time t at the position (x, y); D is the

diffusion coefficient, k_1 is the first order recombination coefficient. $f(\phi(x, y, t))$ is high order recombination function, where k_2 is the bimolecular recombination coefficient and k_3 is the three-body recombination coefficient. Under a low excitation flux density, the higher order recombination (Equation S2) can be avoided because of the limited exciton density. The initial exciton population follows a two-dimensional Gaussian distribution as created by a Gaussian pump beam at position (x_0 , y_0); therefore Equation (S1) can be described by the Gaussian variance:

$$\emptyset(x,y,t) = Nexp\left[-\frac{(x-x_0)^2}{2\sigma_{t,x}^2} - \frac{(y-y_0)^2}{2\sigma_{t,y}^2}\right] \#(S3)$$

where the $\sigma_{t,x}^2$ and $\sigma_{t,y}^2$ are the time-dependent variances of the Gaussian profiles along x- and y-axis directions. Therefore, the diffusion coefficient of exciton can be

obtained by fitting $D = \frac{\sigma_t^2 - \sigma_{t0}^2}{2t}$. For this exciton transport imaging measurement, the spatial resolution of our setup is limited by signal-to-noise rather than diffraction limit.^{2, 3}

3. Supplementary Note 2: Electronic states calculation by density functional theory (DFT) and time-dependent DFT (TD-DFT)

All of the simulation calculations were carried out with Gaussian 09 program package. Density functional theory (DFT) calculations on the geometrical and electronic properties of the ground-state were performed based on B3LYP density functional method with basis set 6-31G(d). Time-dependent DFT (TD-DFT) calculations were also carried out by this method. The molecular configurations used here were determined in crystals by X-ray diffraction.

The SOCs between S_1 and T_n (n = 1, 2) states were calculated with PySOC by considering that the three T_n substrates (m = 1, 0, -1) are degenerate, *i.e.*,

$$\langle S_1 | \hat{H}_{soc} | T_1 \rangle = \sqrt{\sum_{m=0,\pm 1} \langle S_1 | \hat{H}_{so} | T_1^m \rangle^2},$$
 where The \hat{H}_{soc} represents the interaction of the SOC. All SOCs were obtained at the TD DET level of theory using

interaction of the SOC. All SOCs were obtained at the TD-DFT level of theory using the B3LYP functional and the def2svp basis set.

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
5-BTA	5.9681	7.52570	32.8655	86.5170	85.9290	89.8220
	0(10)	(10)	(3)	(10)	(10)	(10)
5-BTEA	5.8481 0(10)	7.49050 (10)	37.0770 (6)	90	94.2530 (10)	90
5-BTVA	5.9387	7.39720	36.9135	94.4240	93.435	90.2300
	0(10)	(10)	(8)	(10)	(2)	(10)

Table S1. The lattice parameters of 5-btA, 5-bteA, and 5-btvA.

Table S2. The fitting results of PL kinetics for 5-btA, 5-bteA, and 5-btvA.

	A ₁	A ₂	A ₃	$\tau_1(ns)$	$\tau_2(ns)$	τ ₃ (μs)
5-BTA	0.41	0.59	3.5×10 ⁻⁵	3.4	7.3	8.0
5-BTEA	0.82	0.18	9.4×10 ⁻⁴	3.3	14.0	3.5
5-BTVA	0.73	0.28	-	1.5	6.9	-

The τ_1 , τ_2 , and τ_3 can be assigned to carrier trapping by deep and shallow defects, and TADF, respectively. Herein, we ignore the influence of thermal quenching effect since the PL kinetics remained consistent in temperature-dependent TRPL measurements (see Fig. S13b).



Fig. S1. The optical images of typical 5-btA, 5-bteA, and 5-btvA crystals.



Fig. S2. Illustrated crystal structure of 5-btvA (a), 5-btA (b), and 5-bteA (c).



Fig. S3. PL spectra of 5-btA, 5-bteA, and 5-btvA crystals under widefield excitation at 405 nm.



Fig. S4. PL spectra of 5-btA, 5-bteA, and 5-btvA in dilute tetrahydrofuran solutions, excited at 405 nm.



Fig. S5. The UV-vis absorption spectra of 5-btA, 5-bteA, and 5-btvA in dilute tetrahydrofuran solutions.



Fig. S6. Schematic of the time-resolved and PL-scanned imaging microscopy for PL imaging measurements.



Fig. S7. Excitation intensity dependent PL kinetics of 5-btvA crystals, where these identical traces imply the absence of high-order recombinations with the pump density ≤ 1506 nJ cm⁻².



Fig. S8. The direction of $\theta = 0^{\circ}$ in lattice coordinates of 5-btvA crystals determined from the dipole moment (blue arrows) by DFT and TD-DFT calculations.



Fig. S9. Normalized time-dependent PL intensity profiles extracted of 5-btA (a) and 5-bteA (b), showing the spatial broadening of the PL distribution due to exciton transport. The plots are fitted by a Gaussian function (solid lines) for the determination of Gaussian variance (σ^2).



Fig. S10. The fs-TA spectra of 5-btA and 5-bteA in tetrahydrofuran solutions.



Fig. S11. ns-TA kinetics probed at the PIA band (~600 nm) of 5-btA, 5-bteA, and 5btvA solutions, where these microsecond-scale lived components are far beyond the lifetime limit of singlet-states, therefore the PIA bands located at ~600 nm could be assigned to the ESA signal of triplet-states.



Fig. S12. HOMO and LUMO of 5-series determined by DFT and TD-DFT calculation, where the evenly distributed wavefunctions suggest the absence of charge separation state.



Fig. S13. Temperature-dependent PL kinetics of 5-bteA (a) and 5-btvA (b) crystals.



Fig. S14. Molecular structures of 2-phA, 2-pheA, and 2-phvA.



Fig. S15. PL spectra collected from 2-phA, 2-pheA, and 2-phvA crystals.



Fig. S16. Optical images of typical 2-phA and 2-pheA and 2-phvA crystals.



Fig. S17. Schematic illustration diagrams of the singlet- and triplet-states in 2-phA, 2-pheA, and 2-phvA.



Fig. S18. The $\sigma_t^2 - \sigma_0^2$ as a function of delay time t, from which the exciton diffusion coefficients are determined by linear fit (solid lines).



Fig. S19. Normalized time-dependent PL intensity profiles extracted of 2-phA (a), 2-pheA (b) and 2-phvA (c), showing the spatial broadening of the PL distribution due to exciton transport. The solid lines show Gaussian fits.

Supplementary References:

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