ELECTRONIC SUPPLEMENTARY INFORMATION

Efficient and Tunable Fluorescence Energy Transfer via Long-Lived Polymer Excitons

Wei Chen,¹ Xingxing Sun,¹ XijunWang,² Qishen, Huang,¹ Xinyang Li,¹ Qun Zhang,² Jun Jiang,² Guoqing Zhang¹*

¹CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, 230026, China.

E-mail: gzhang@ustc.edu.cn

²Innovation Center of Chemistry for Energy Materials, Department of Chemical Physics, University of Science and Technology of China, Hefei, 230026, China.

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Part I. Materials.

Materials. Rhodamine B(95%, Aladdin Reagent Co.), ethyl-2-bromoisobutanoate(98%, Aladdin Reagent Co.), 4-hydroxyacetophonone(98%, Aladdin Reagent Co.), methyl 4methoxybenzoate(99%, Aladdin Reagent Co.), decane-1,10-diol(98%, Aladdin Reagent Co.), hydrobromic acid(48%, Aladdin Reagent Co.), 3,4-Dihydro-2H-pyran(95%, Aldrich Reagent Co.), 4-methylbenzenesulfonic acid(99%, Aladdin Reagent Co.), ethylene glycol(99%, Aladdin Reagent Co.), methacryloyl chloride(95%, Aladdin Reagent Co.), 2-bromo-2methylpropanoyl bromide(95%, Aladdin Reagent Co.), sodium hydride (95%, Aldrich Reagent Co.), and Boron trifluoride diethyl etherate (Aldrich Reagent Co., purified by redistillation) were used as received. Water was deionized with a Milli-Q SP reagent water system (Millipore) to a specific resistivity of 18.2 M Ω .cm. All other solvents and reagents were purchased from Aladdin Reagent and were used as received or purified as previously described methods when preparing the corresponding published compounds.

Methods.

Methods. ¹H NMR (300 MHz) spectra were recorded on a Bruker AV300 NMR spectrometer operated in the Fourier transform mode. NMR chemical shifts were reported in standard format as values in ppm relative to deuterated solvents. Mass spectral data (ESI/MS) were obtained on a Micromass auto spectrometer. Dynamic laser light scattering (LLS) measurements were conducted on a commercial spectrometer (ALV/DLS/SLS-5022F) equipped with a multitau digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He-Ne laser ($\lambda_0 = 632$ nm) as the light source. Scattered light was collected at a fixed angle of 90° for duration of ~5 min. Distribution averages and particle size distributions were computed using cumulants analysis and CONTIN routines. UV/Vis absorption spectra were recorded on a Beijing Persee TU-1901 UV-Vis spectrometer. Excitation and steady-state fluorescence emission spectra and absolute quantum yield were recorded on a FluoroMax-4 spectrofluorometer (Horiba Scientific) and analyzed with an Origin integrated software FluoroEssence (v2.2). Fluorescence lifetime data were acquired with a 1MHz LED laser with the excitation peak at 370 nm (NanoLED-370). Lifetime data were analyzed with DataStation v6.6 (Horiba Scientific). Molecular weights and molecular weight distributions were

determined by gel permeation chromatography (GPC) equipped with Waters 1515 pump and Waters 2414 differential refractive index detector (set at 30 °C). The detection components used a series of two linear Styragel columns (HR2 and HR4) at an oven temperature of 45 °C. The eluent was DMF at a flow rate of 1.0 mL/min. Melting point was recorded on a SGW-X4 (Shanghai Precision and Scientific Instrument Co., Ltd.) illuminated microscope melting point apparatus.

DFT Calculations. Quantum chemistry calculations of molecular geometry optimizations and electronic structures were performed with density function theory (DFT) using the Gaussian 09 program, at the B3LYP/6-31G level. The dispersion effect in aggregated polymer has been examined with DFT B97D function calculations. The solvent effect was treated with water solution and the polarizable continuum model (PCM). Molecular photo absorption was simulated with time-dependent DFT (TDDFT) method.

Laser Spectroscopy. The femtosecond transient absorption data were recorded on a modified pump-probe spectrometer (ExciPro, CDP) in combination with an ultrafast amplified laser system (schematic of the optical layout in Supplementary Fig. SA). The pump pulses (center wavelength at 400 nm for this work; pulse energy $\sim 25 \ \mu$ J at the sample cell) were delivered by an optical parametric amplifier (TOPAS-800-fs, Coherent), which was excited by a Ti:sapphire regenerative amplifier (Legend Elite-1K-HE, Coherent; centre wavelength ~800 nm, pulse duration \sim 35 fs, pulse energy \sim 3 mJ) seeded with a mode-locked Ti:sapphire laser system (Micra 5, Coherent) and pumped with a 1-kHz Nd:YLF laser (Evolution 30, Coherent). The much weaker probe pulses (< 1 μ J/pulse at the sample cell) were provided by a stable white-light (WL) continuum (500–750 nm for this work) that was generated by focusing the 800-nm beam (split from the regenerative amplifier by a portion of $\sim 10\%$) in a rotating 4.55mm-thick CaF₂ crystal. The pump and probe beams were collinearly polarized. The instrument response function was determined to be \sim 50 fs by cross-correlating the pump and probe pulses at the sample cell.

Precise spatial overlap of the pump and probe beams (with diameters of ~ 1 mm and 300 µm, respectively) at the centre of the 1.2-mm-thick sample cell (quartz) was attained through optimizing the transient absorption signals with the aid of a laser beam analyzer (BG-USB-

SP620, Ophir-Spiricon). The time delay between the pump and probe pulses was varied by a motorized optical delay line (minimum step 1.56 fs; maximum delay 1.0 ns). A mechanical chopper operating at 500 Hz was used to modulate the pump pulse such that the transient absorption spectra with and without the pump pulses can be recorded alternately. The WL probe beam was first split into two tiny portions to synchronize the chopper and monitor the stability of the probe pulse using two separate photodiode detectors, and then separated into two parts (\sim 70/30 in percentage), with the 70% part focused on the sample cell and overlapped with the pump beam yielding a transmitted probe signal, while the 30% part focused onto another place of the sample cell to serve as a reference signal for achieving a best signal-to-noise ratio.

The sample cell was mounted on a rapidly rotating stage (5000 rpm) so as to ensure that the photo-excited volume of the sample was kept always fresh to avoid sample bleach during the course of the measurements. The temporal and spectral profiles of the pump-induced transient absorbance change were visualized by a 1024-pixel imaging spectrometer (CDP2022i).



Figure SA: Schematic optical layout of the femtosecond pump-probe experiment.

Part II. Sample synthesis.

RhBr (1) was synthesized according to a previously published procedure^[1]. Specially, Rhodamine B (0.720 g, 1.50 mmol), 2-hydroxyethyl 2-bromoisobutyrate (0.330 g, 1.56 mmol), EDC•HCl (0.287 g, 1.50 mmol), and dry CH₂Cl₂ (15 ml) were added to a round bottom flask equipped with a magnetic stir bar. After cooling to 0°C in an ice-water bath, DMAP (0.180 g, 1.50 mmol) was added. The reaction was conducted under 25°C for 12 h. Then the reaction mixture was sequentially extracted with 0.1 M HCl (50 mL×3), aqueous saturated NaHCO₃ (50 mL×3), and aqueous saturated NaCl solution (50 mL×3). After drying over anhydrous Na₂SO₄, CH₂Cl₂ was removed on a rotary evaporator. The crude product was purified by column chromatography (first THF/n-hexane = 4/1, v/v; then THF/methanol = 10/1, v/v), yielding a purple powder (0.640 g, 63%). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 8.26 (1H, -Ar*H*), 7.81 (1H, -Ar*H*), 7.71 (1H, -Ar*H*), 7.27 (1H, -Ar*H*), 7.03 (2H, -Ar*H*), 6.89 (2H, -Ar*H*), 6.79 (2H, -Ar*H*), 4.28 (4H, -CH₂CH₂-), 3.62 (8H, -CH₂CH₃), 1.68 (6H, -CH₃), and 1.30 (12H, -CH₂CH₃). UV/Vis (DMF): $\lambda_{max} = 561$ nm, $\varepsilon = 78,000$ M⁻¹cm⁻¹.

BAM (2) Synthesis. BF₂dbmOH was prepared according to a previously published procedure^[2]. Then BF₂dbmOH (2.00 g, 4.22 mmol), Et₃N (1.29 g, 12.7 mmol), and dry CH₂Cl₂ (50 ml) were added to a round bottom flask equipped with a magnetic stir bar. After cooling to 0° C in an ice-water bath, methacryloyl chloride (0.660g, 6.30mmol) was added dropwise over ~ 30 min. The reaction was completed after stirring for another 6 h at 25 °C. The mixture was quenched with 30 ml H₂O and extracted with CH₂Cl₂ (50 mL×3). After drying over anhydrous Na₂SO₄, CH₂Cl₂ was removed on a rotary evaporator. The crude product was purified by column chromatography (hexane/ethyl acetate = 2:1, v/v), yielding a green-yellow powder (2.03g, 88%). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 8.10 (d, J = 9.0 Hz, 4H, 2',6', 2", 6"-ArH), 7.02 (d, J = 9.0 Hz, 4H, 3', 5', 3", 5"-ArH), 7.00 (s, 1H, COCHCO), 6.09 (s, 1H, cis-OCC(CH₃)=CH₂), 5.54 (s, 1H, trans-OCC(CH₃)=CH₂), 4.14 (t, 2H, J= 6 Hz, ArOCH₂), 4.06 (t, 2H, CH₂OOCC(CH₃)=CH₂), 3.91 (s, 3H, -ArOCH₃), 1.94 (s, 3H. $OCC(CH_3)=CH_2)$, 1.84(m, 2H. -ArOCH₂CH₂CH₂), 1.68(m, 2H. $CH_2CH_2OOCC(CH_3)=CH_2),$ 1.50-1.25(m, 12H.-

nm, $\epsilon = 57,000 \text{ M}^{-1}\text{cm}^{-1}$. M.P.: 119-120 °C. MS: m/z calcd for $C_{30}H_{37}O_6BF_2$, [M+Na]⁺: 565.25435, found 565.25363.

Rh-(BA), (3a)(3b) was synthesized via atom transfer radical polymerization (ATRP). Firstly, for a typical example preparation, acrylate-functionalized $BF_2dbmC_2H_4OH$ monomer (0.160 g, 0.481 mmol), rhodamine B-based initiator (3.2 mg, 4.76 µmol), PMDETA (0.8 mg, 4.8 µmol), and dry DMF (0.400 ml) were charged into a tube. The mixture was degassed by two freezepump-thaw cycles, CuBr (0.7 mg, 4.8 µmol) was then added to the tube under N₂ protection. The tube was further degassed via three freeze-pump-thaw cycles, and then sealed under vacuum. After being stirred at 70°C for 12 h, the reaction mixture was unsealed and precipitated into an excess of cold methanol. However, the precipitate was barely soluable in any tested solvents, like DMF, DMSO, acetonitrile, DCM, THF, acetone, ethyl acetate, hexane, ether and toluene. To increase the solubility, we synthesize the acrylatefunctionalized BF2dbmC10H22OH monomer. The reaction steps were the same, and the reaction mixture was unsealed and precipitated into an excess of cold methanol. The dissolution-precipitation cycle was repeated for three times. The residue was dissolved in CH₂Cl₂, and passed through a silica gel column to remove the copper catalysts. After drying in a vacuum oven overnight at room temperature, sample **3a** and **3b** were obtained as maroon powders.¹H NMR (300 MHz, DMSO), δ(TMS, ppm): 8.20-8.10 (4H, 2',6', 2", 6"-ArH), 7.11-6.99 (5H, 3', 5', 3", 5"-ArH, COCHCO), 4.10-3.86 (7H, -ArOCH₂, CH₂OOCC(CH₃)CH₂, -1.84-1.20 $ArOCH_3$), (19H,- $ArOCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OOCC(CH_3)CH_2,OCC(CH_3)CH_2).$

BF₂**dbm-RhB** (4) Synthesis. BF₂dbmOH (100 mg, 0.276 mmol), rhodamine B (124 mg, 0.276 mmol), EDC•HCl (75 mg, 0.400 mmol), and dry CH₂Cl₂ (15 ml) were added to a round bottom flask equipped with a magnetic stir bar. After cooling to 0°C in an ice-water bath, DMAP (48 mg, 0.400 mmol) was added. The reaction was conducted under 25°C for 12 h, and CH₂Cl₂ was removed in vacuo, and the crude product was purified by silica gel column chromatography (first acetone, and then acetone/methanol 9/1), yielding a purple powder (160 mg, 73%). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 8.26 (1H, -Ar*H*), 8.10 (4H, -Ar*H*),

7.81 (1H, -Ar*H*), 7.71 (1H, -Ar*H*), 7.27 (1H, -Ar*H*), 7.03 (2H, -Ar*H*), 7.02 (4H, -Ar*H*), 7.00 (1H, COC*H*CO), 6.89 (2H, -Ar*H*), 6.79 (2H, -Ar*H*), 4.28 (4H, -OC*H*₂CH₂-), 3,91(s, 3H, -ArOCH3), 3.62 (8H, -C*H*₂CH₃), 1.84(m, 2H, -ArOCH₂C*H*₂C*H*₂), 1.50-1.25(m, 26H, -ArOCH₂CH₂C*H*₂C

Part III. Supplementary Figures.



Figure S1: a)-e): UV-Vis absorption spectra of RhB initiator 1, BF₂dbm monomer 2, EnT polymers 3a 3b and 4).



Figure S2: a)-c) Fluorescence decay profiles of **1**, **3a**, and **3b** at 587 nm; d) - f) Fluorescence decay profiles of **2**, **3a**, and **3b** at 447 nm.



Figure S3: Excitation spectra of polymer 3b in DMF and DCM solutions (5 μ g/mL) with emission wavelength monitored at 587 nm.



Figure S4. a) Steady-state emission spectra of polymers **3b** at different temperatures in DMSO $(\lambda_{ex} = 385 \text{ nm})$. b) data fitting of emission intensity ratio between 587 and 447 nm at different temperatures for 3b ($\lambda_{ex} = 385 \text{ nm}$). c) Steady-state emission spectra of **3b** as a function of polymer concentration in DMF and in the solid state ($\lambda_{ex} = 385 \text{ nm}$).

	$\Phi_{ m F,absolute}$
RhBr (1)	0.3504
BAM (2)	0.704
Rh - $(BA)_n$ (3a)	0.1401
Rh - $(BA)_n$ (3b)	0.1638
BF_2 dbm-RhB (4)	0.2703

Table S1. Absolute quantum yields of different compounds in DMF solutions.

 Table S2. Fluorescence lifetimes of different fluorescent compounds in DMF solution at room temperature.

	$\tau_1{}^ans/{}^b\!\!\!/_b$	$\tau_2{}^ans/{}^b\!\!\!/_{o}{}^b$	$\tau_3{}^ans/{}^b\!\!\!/_{\!0}{}^b$	$\tau_{pw0}{}^c$	χ^2
				ns	
1	1.53/			1.53	1.28
	100				
2	1.68/			1.68	0.94
	100				
3a 447 nm	1.54/	0.28/	10.8/	1.30	1.23
	22.37	70.63	7.00		
3a 550 nm	4.04/	22.9/	1.03/	9.40	1.23
	38.27	33.04	28.69		
3a 587 nm	1.78/	3.68/	18.8/	4.09	0.99
	51.85	38.92	9.23		
3b 447 nm	2.55/	15.6/	0.54/	2.23	1.18
	21.38	8.36	70.26		

3b 550 nm	6.93/	27.6/	1.87/	15.96	1.25
	24.64	42.12	33.24		
3b 587 nm	5.19/	2.12/	24.8/	7.26	1.08
	27.49	53.54	18.97		
4 447 nm	1.40/	0.13/	11.5/	1.13	1.06
	24.05	69.83	6.12		
4 587 nm	1.98/			1.98	0.97
	100				

a. fitted fluorescence lifetime component with triple exponential decay

b. percentage weight of each fitted lifetime component

c. pre-exponential weighted average fluorescence lifetime

		$\tau_1{}^a\!ns\!/$	τ_2^{a} ns/	$ au_3^{a}$ ns/	$\tau_{pw0}{}^c$	χ^2
		% ₀b	% ^b	% ^b	ns	
3 a	447	0.18/	1.49/	13.1/	1.06	0.91
nm		57.86	39.27	2.88		
3 a	550	9.26/	37.3/	2.82/	21.5	1.21
nm		27.4	49.22	23.38		
3 a	587	16.0/	4.71/	38/	11.1	0.97
nm		17.53	69.22	13.25		
3b	447	0.36/	1.55/	20.6/	1.68	1.17
nm		36.33	60.71	2.96		
3b	550	10.8/	43.2/	2.51/	34.1	1.12
nm		17.17	74.03	8.8		
3b	587	18.1/	41.4/	5.39/	19.1	1.04
nm		16.46	32.34	51.2		

 Table S3. Fluorescence lifetimes of different fluorescent compounds in CH₂Cl₂ solution at room temperature.

a. fitted fluorescence lifetime component with triple exponential decay;

b. percentage weight of each fitted lifetime component

c. pre-exponential weighted average fluorescence lifetime

Part IV. NMR, MS and GPC figures.



Figure Sa: ¹H-NMR spectrum of RhBr (1) (300 MHz, CDCl₃, 298 K).



Figure Sb: ¹H-NMR spectrum of BAM (2) (300 MHz, CDCl₃, 298 K).



Figure Sc: MS spectrum of BAM (2).



Figure Sd: ¹H-NMR spectrum of Rh-(BA)_n(3a) (300 MHz, DMSO-d₆, 298 K).



Figure Se: ¹H-NMR spectra for Rh-(BA)_n(3b) (300 MHz, DMSO-d₆, 298 K).



Figure Sf: ¹H-NMR spectrum of BF₂dbm-RhB (4) (300 MHz, CDCl₃, 298 K).



Figure Sg: MS spectrum of RhB-BF₂dbm(4).



Figure Sh: GPC elution profiles recorded for compounds 3a and 3b.

References.

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