Supporting Information

Transition from Dispersed RTP to Aggregated TADF in Single-Chromophore Polymers

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Experimental Section

Materials. 2 - (4,4,5,5-tetramethyl-1,3,2-dioxabicyclopentane-2-yl)-9H-carbazole (97%), 4-(4,4,5,5-tetramethyl-1,3,2-dioxabicyclopentane-2-yl) -9H-carbazole (97%), 4,7-dibromobenzo [c] [1,2,5] selenidazole (97%) was obtained from Leyan, 4-bromo-2,3-benzothiadiazole (95%) was obtained from Bidepharm, and tetra (triphenylphosphine) palladium (99%) was obtained from Energy Chemical 1,4-Dibromobutane (99%), methacrylic acid (99%) and anhydrous N, N-dimethylformamide (DMF) was obtained by Shanghai Yishi Chemical Co., Ltd., and TBAB was obtained by Aladdin. Toluene is refluxed with metallic sodium and distilled before use.

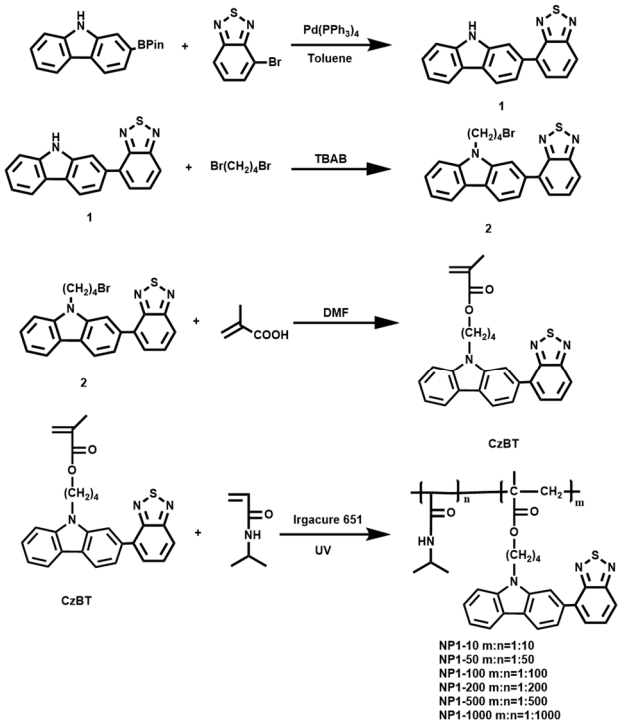
Instruments and Measurements.

^{1}H and ^{13}C NMR spectra were obtained from Bruker ARX 400 MHz spectrometer, tetramethylsilane (TMS) and $CDCl_3$ or DMSO as internal standard and solvent, respectively. Matrix assisted laser desorption ionization tandem flight time mass spectrometry (MALDI-TOF) were determined on a Bruker Daltonics BIFLEX Ⅲ MALDI-TOF analyzer. Elemental analyses were carried out on Elementary Vario EL (Germany). Fourier transform infrared spectroscopy (FTIR) spectra and Temperature-variable FTIR spectra were determined by a PE Spectrum on FTIR spectrometer under the powder state. High performance liquid chromatography (HPLC) was carried out by SHIMADZU IC-20A with C18 column, the running buffer was acetonitrile and water solution. Thermogravimetric analysis (TGA) was obtained on TA SDT 2960 instrument with the heating rate of 20 ºC/min and under nitrogen atmosphere. Differential scanning calorimetry (DSC) curves were measured by TA-Q10 calorimeter in nitrogen atomsphere with the rate of 10 °C/min. The refractive index of the polymers is measured by spectroscopic ellipsometer (HORIBA France SAS 520-600 nm).

UV-vis absorption spectra were measured by Cary 60 with the Flashing xenon lamp as the photosource. Emission spectra were obtained using spectrofluorometer F-4600 with 1 cm quartz cuvettes. The UV irradiation light source is a hand-held ultraviolet lamp of 365 nm UV LED (FUWO, FUV-6BK 800 Wm^{-2}).

Phosphorescence lifetime data were obtained on Horiba Deltaflex equipped with a microsecond flash-lamp and analyzed by DAS6 Analysis. The absolute fluorescent and phosphorescent quantum yields in the solid state were determined using an integrating sphere on a Nanolog FL3-2iHR fluorescence spectroscopy equipped with R928 photomultiplier as detector.

Synthesis.



Scheme S1. The synthetic routes of monomer CzBT, and polymers NP1-10~NP1-1000.

Synthesis of 4-(9H-carbazol-2-yl) benzo[c] [1,2,5] thiadiazole (compound 1). 4-bromo-2,3-benzothiadiazole (0.5 g, 2.33 mmol, 1eq), 2 - (4,4,5,5-tetramethyl-1,3,2-dioxabicyclopentane-2-yl) - 9H-carbazole, (0.75g, 2.56mmol, 1.1eq) 3.75mL KHCO3 aqueous solution (2.5 mol/L) and 40mL of toluene were added to a 100 mL three-necked flask, and refluxed at 110 °C for 24h under argon atmosphere. Then dichloromethane extraction, petroleum ether and dichloromethane as eluents, column chromatography purification, to obtain 0.325 g of compound 1, yield 46.4%.

^{1}H NMR (400 MHz, DMSO-d6, δppm): δ 11.41 (s, 1H, C-NH), 8.23 (d, 1H, Ar-H), 8.18-8.11 (d, 2H, Ar-H), 8.08 (d, 1H, Ar-H), 7.94 (d, 1H, Ar-H), 7.83 (t, 1H, Ar-H), 7.72 (d, 1H, Ar-H), 7.50 (d, 1H, Ar-H), 7.40 (t, 1H, Ar-H), 7.21-7.13 (m, 1H, Ar-H).

Synthesis of 4-(9-(4-bromobutyl)-9H-carbazol-2-yl) benzo[c] [1,2,5] thiadiazole (compound 2). Compound 1 (0.2g, 0.66mmol, 1eq), 1,4-dibromobutane (0.76mL, 6.6mmol, 10eq), TBAB (0.04g, 0.13mmol, 0.2eq), 50% NaOH aqueous solution (5gNaOH+5gH2O) and 50mL toluene were added to a 250mL round bottom flask, and stirred at 45 °C for 10h. Then, dichloromethane was used for extraction, petroleum ether and dichloromethane were used as eluents, and column chromatography was used for purification to obtain 0.219 g of compound 2, yield 76.3%.

^{1}H NMR (400 MHz, DMSO-d6, δppm): δ 8.27 (d, 1H, Ar-H), 8.19 (d, 2H, Ar-H), 8.10 (d, 1H, Ar-H), 7.98 (d, 1H, Ar-H), 7.89-7.78 (m, 2H, Ar-H), 7.66 (d, 1H, Ar-H), 7.47 (t, 1H, Ar-H), 7.21 (t, 1H, Ar-H), 4.50 (t, 2H, -N-CH2), 3.55 (t, 2H, -CH2-Br), 1.91 (m, 4H, -CH2-CH2-).

Synthesis of 4-(2-(benzo[c][1,2,5]thiadiazol-4-yl)-9H-carbazol-9-yl)butyl methacrylate (Monomer CzBT). Compound 2 (0.2 g, 0.46 mmol, 1 eq), methacrylic acid (0.12mL, 1.38mmol, 3eq), KHCO3 (1.38g, 1.38 mmol, 3eq) and 50mL DMF were added into a 250 mL round bottom flask, and reacted for 24h at 100 °C. After dichloromethane extraction, petroleum ether and dichloromethane were used as eluents and purified by column chromatography to obtain 0.136g monomer 1 ,yield 67.1%.

^{1}H NMR (400 MHz, DMSO-d6, δppm): δ 8.27 (d, 1H, Ar-H), 8.22-8.16 (d, 2H, Ar-H), 8.09 (d, 1H, Ar-H), 7.97 (d, 1H, Ar-H), 7.88-7.76 (m, 2H, Ar-H), 7.64 (d, 1H, Ar-H), 7.51-7.42 (t, 1H, Ar-H), 7.21 (t, 1H, Ar-H), 5.88 (s, 1H, -C=C-H), 5.52 (s, 1H, -C=C-H), 4.50 (t, 2H, -N-CH2-), 4.10 (t, 2H, O=C-CH2), 1.91 (m, 2H, -CH2-), 1.77-1.68 (s, 3H, -CH3), 1.66 (m, 2H, -CH2-).

^{13}C NMR (400 MHz, Chloroform-d, δppm): δ 167.44 (O=C-), 155.73-141.03 (aromatic-C), 140.52 (C-C=C), 136.23-134.87 (aromatic-C), 129.76 (CH2=C-), 128.01-108.72 (aromatic-C), 64.10 (O-CH2-C-), 42.62 (N-CH2-C-), 26.42 (C-CH2-C-), 25.62 (C-CH2-C-), 18.35 (C=C-CH3).

Synthesis of polymers.

The copolymer film of NP1-50~NP1-1000 were prepared by photo initiator radical polymerization. Monomer CzBT (1 eq), monomer NIPAM (50~1000 eq), UV photoinitiator Irgacure-651 (1wt%) and dichloromethane solvent were added to the vial and then ultrasonically dissolved, wrapped with tin foil. The mixed solution was placed in a dark environment to allow the solvent evaporate naturally. Then, the remaining mixtures were placed on a hot stage and heated to 85 °C for melting and then capillary-filled into the liquid crystal cells with PTFE spacer film of 100 μm. The reaction was completed and the polymers film obtained after irradiation with a UV lamp for half an hour. Finally, the liquid crystal cell was soaked in a hydrofluoric acid solution for 10 min, and the glass sheet was completely etched to obtain a thin film.

Device Fabrication: The patterned ITO conductive glass substrates were ultrasonic cleaned with deionized water and anhydrous ethanol consecutively, and then dried with nitrogen gas. Then the substrates were treated with ultraviolet ozone for 15 min to remove surface contaminants and then transferred to the nitrogen glove box for subsequent operation. Then PEDOT:PSS solution was spin-coated on the substrates at 3000 rpm for 30 s and then annealed at 150 °C for 15 min. After that, the emitting materials CzBT were doped into PVK dissolved in chlorobenzene with a concentration of 7.5 mg mL-1 and spin-coated at 4000 rpm for 40 s, followed by annealing at 75 °C for 10 min. After that, the devices were transferred into the vacuum chamber for depositing TPBI, LiF and Al cathode with thickness of 40 nm, 1.4 nm and 100 nm, respectively.

Results

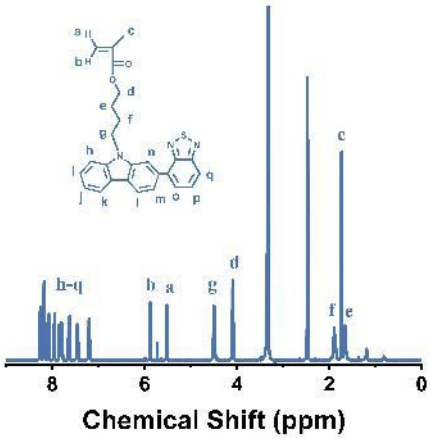


Figure S1. ^{1}H NMR spectra of monomer CzBT.

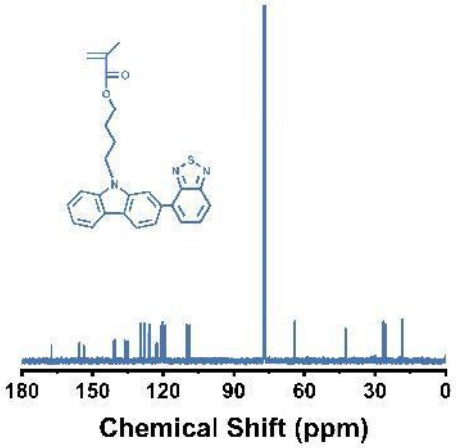


Figure S2. ^{13}C NMR spectra of monomer CzBT.

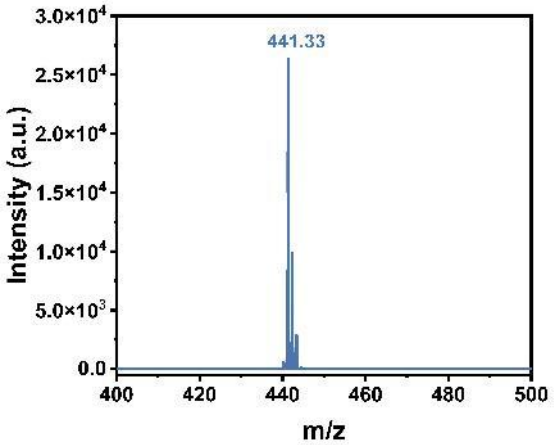


Figure S3. MALDI-TOF MS spectra of monomer CzBT.

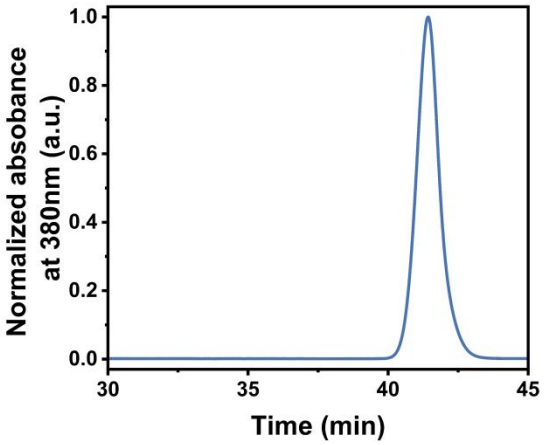


Figure S4. HPLC spectra of the monomer CzBT.

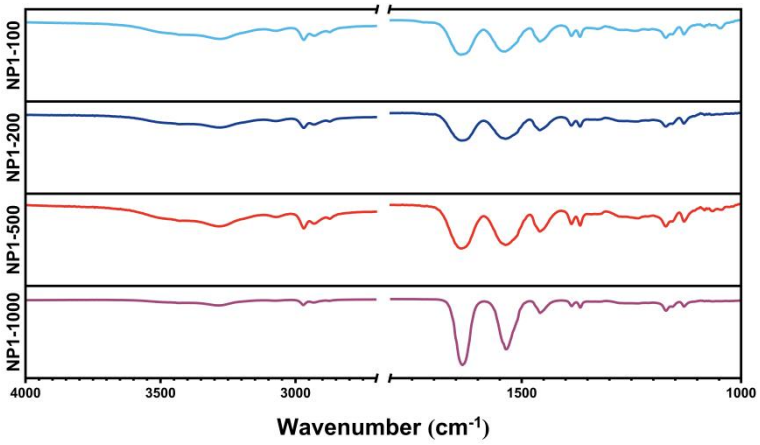


Figure S5. FTIR spectra of the polymers NP1-100~NP1-1000.

Table S1. Molecular weight of polymers.

Polymers	M_n g/mol	M_w g/mol	PDI
NP1-50	3.9×10^4	2.1×10^5	5.49
NP1-100	3.6×10^5	7.4×10^5	2.04
NP1-200	1.9×10^4	4.7×10^4	2.55
NP1-500	9.8×10^4	3.0×10^5	3.05
NP1-1000	1.2×10^4	1.6×10^4	1.36

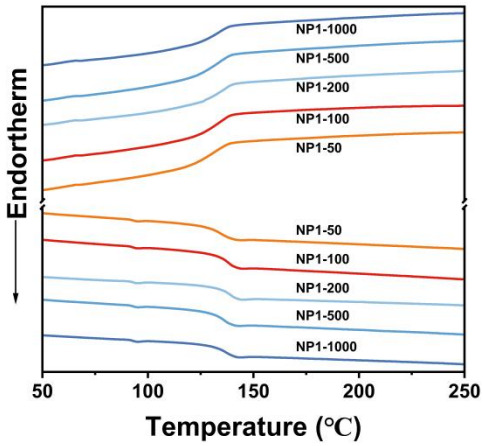


Figure S6. DSC curves of polymers NP1-50~NP1-1000.

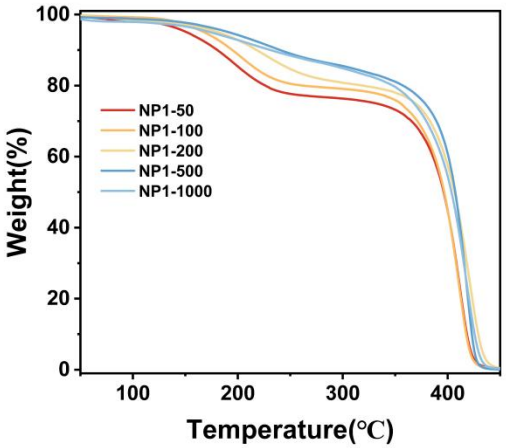


Figure S7. TGA curves of polymers NP1-50~NP1-1000.

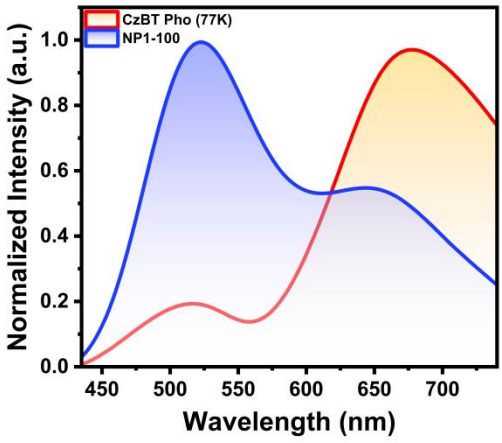


Figure S8. Delayed spectra (77K) of monomer CzBT and polymer NP1-100 at room temperature.

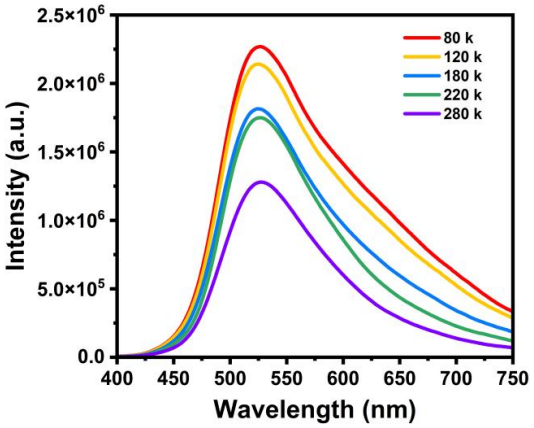


Figure S9. Temperature-dependent delay spectra of NP1-50.

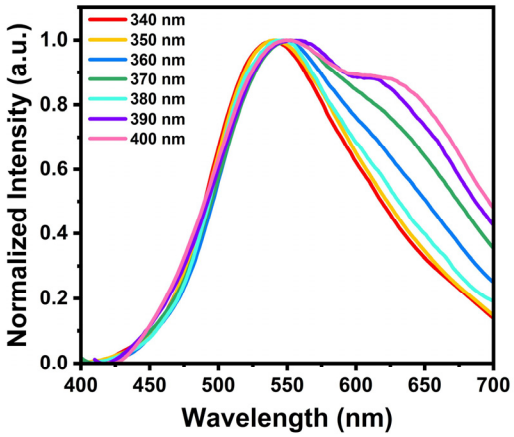


Figure S10. Excitation-dependent delay spectra of NP1-50.

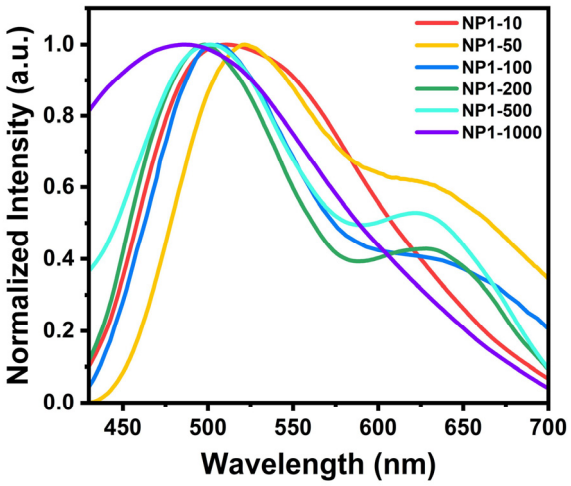


Figure S11. Delay spectra of polymers NP1-10~NP1-1000 with different concentrations under 380 nm excitation.

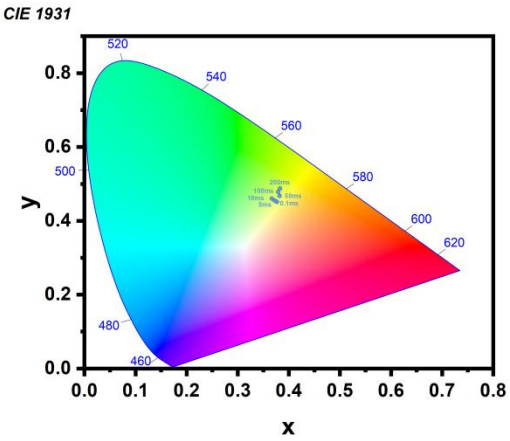


Figure S12. CIE coordinate spectra of NP1-200 at different delay times.

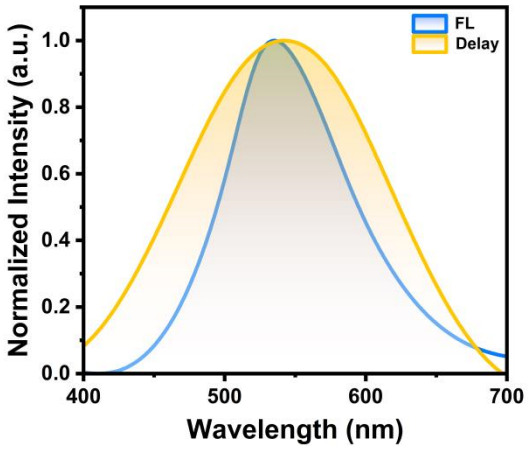


Figure S13. The fluorescent and delayed fluorescent spectra of CzBT:PVK (1:10).

Table S2. Photophysical properties of polymers.

	$\tau_{F\ (ns)}$	τ_{DF} (μs)[a]	τ_{RTP} (ms)[b]	τ_{RTP} (ms)[b]	Φ_{PL} %	FL λ_{max} nm	DF λ_{max} nm	Phos λ_{max} nm
NP1-10	\	14	\	\	15.5	510	511	\
NP1-50	7.30		37 (530)	32 (635)	16.4	520		535, 629
NP1-100	7.03		234(510)	211(630)	17.4	510		511, 633
NP1-200	6.67		268(510)	240(631)	20.4	502		505, 632
NP1-500	6.56		176(510)	171(640)	14.1	505		510, 630
NP1-1000	5.52		241(510)	227(630)	5.0	486		540

[a] The detection wavelength of delayed fluorescent lifetime was according to the maximum emission; [b] The detection wavelength of phosphorescent lifetime was according to the maximum phosphorescence emission.