Supporting information

Impact of Polymer Rigidity on Thermoresponsive Luminescence and Electron Spin Resonance of Polyester-Tethered Single Radicals

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2. Materials and Characterization

All reagents and solvents were purchased from Sigma-Aldrich and Energy Chemicals (China) and used without further purification unless otherwise stated. Ultradry anisole, Tetrahydrofuran (THF) and N,N-Dimethylformamide (DMF) were purchased from Energy Chemicals (China). δ-Valerolactone (δ-VL) and ε-Caprolactone (ε-CL) were dried over CaH₂ overnight, followed by vacuum distillation. The dried monomers were then stored under a nitrogen atmosphere over 4 Å molecular sieves. D,L-Lactide (DLLA) and L-Lactide (LLA) were recrystallized from ethyl acetate (EtOAc). Flash chromatography was performed using silica gel (200-300 & 300-400 meshes). Tris(2,4,6-trichlorophenyl)methane (HTTM) and tris(2,4,6-trichlorophenyl)methyl (TTM) were synthesized according to a literature procedure.¹¹H NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer at 298 K. Chemical shifts are calibrated using the residual solvent peak as the internal reference (deuterated dimethyl sulfoxide (DMSO–d₆)=2.50 ppm, CDCl₃=7.26 ppm). The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets. Number-average molecular weight ($M_n$), weight average molecular weight ($M_w$) and polydispersity index (PDI) of the polymer samples were determined by gel permeation chromatography (GPC) using a Waters ACQUITY Advanced Polymer Chromatography™ system equipped with a refractive index (RI) and UV detector. THF (HPLC grade) and THF/Et₃N (2 vol%) were used as eluents with a flow rate of 0.5 mL/min. Calibration curve was achieved using a series of monodispersed polystyrene (PS) standards. Electrospray ionization-mass spectrometry (ESI-MS) spectra were obtained on a Waters Xevo G2-XS Tof using acetonitrile (ACN) as solvent. Differential scanning calorimeter (DSC) was performed on a calorimeter (DSC 2500, TA Instruments) under a nitrogen flow, where the samples were placed in alumina crucibles and calibrated with an indium standard. The samples were heated from room temperature to 200 °C and an isotherm for 5 min to erase thermal history and then cooled down to -40 °C at a rate of 10 °C/min, and heated again from -40 to 200 °C at a rate of 10 °C min⁻¹. Glass transition temperature ($T_g$) was determined by the mid-point of the glass
transition. UV/Vis spectra were recorded using a UV/Vis spectrophotometer (UV 1900, Shimadzu). Steady-state photoluminescence (PL) spectra were recorded on a SPEX Fluorolog spectrofluorometer (Jobin Yvon/SPEX, Edison, New Jersey). Film samples were prepared by drop-coating a chloroform solution on quartz substrates. Temperature-dependent PL and time-resolved PL spectra were recorded using a spectrometer (Andor SR-750). Temperature-dependent PL spectra were excited at 325 nm using a continuous-wave (CW) He-Cd gas laser and time-resolved PL spectra were excited at 375 nm using a pulsed ultraviolet picosecond diode laser as excitation source. Electron spin resonance (ESR) spectra (298 K, 100 K) measurement were done on a Bruker, EMXPlus-10/12 spectrometer using powder samples. Dynamic light scattering (DLS) was performed on Malvern Zetasizer Nano ZS90. The crystalline structures of the radical polymers were determined by powder X-ray diffraction (PXRD, Rigaku SmartLab X-ray diffractometer) using Cu Kα radiation (λ = 1.54 Å) at a voltage of 40 KV covering 20 angles 5~80°, a scanning rate of 20° min⁻¹. Powder samples of RPE1, RPE4, REP6 and a film sample of RPE2 were used for the PXRD.

3. Synthetic Procedure

3.1 Synthesis of radical initiator

The stepwise synthetic methods for the radical initiator, TTM-CZ-OH are outlined in Scheme 1a.

**Synthesis of Compound 1**

3,6-dibromo-9H-carbazole (3.25 g, 10 mmol), (4-(hydroxymethyl)phenyl)boronic acid (3.66 g, 30 mmol), powdered K2CO3 (13.8 g), toluene (100 mL), deionized (DI) water (20 mL) and ethanol (20 mL) were combined in an two-neck 250 mL round bottom flask containing a magnetic stir bar and topped with a water-cooled condenser. The contents were deaerated by N2 bubbling through the solution for 20 minutes. Pd(PPh3)4 (1% by weight) was added under N2. The flask was sealed and submersed in a 100 °C oil bath. After completion (~8 h) of the reaction as monitored by TLC, the reaction mixture was washed with water three times, dried over anhydrous MgSO4, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (petroleum ether/EtOAc, 1:1) to yield 2.30 g (6.06 mmol, 61%) 1 as a white solid. 1H NMR (500 MHz, DMSO-d6) δ 11.33 (s, 1H), 8.57 (s, 2H), 7.74 (dd, J=16.3, 8.1 Hz, 6H), 7.56 (d, J=8.4 Hz, 2H), 7.42 (d, J=7.8 Hz, 4H), 5.18 (t, J=5.6 Hz, 2H), 4.56 (d, J=5.2 Hz, 4H).
Synthesis of Compound 2

3,4-dihydro-2H-pyran (DHP, 2.74 mL, 30 mmol) was added dropwise to a stirred solution of compound 1 (3.80 g, 10 mmol) and p-toluenesulfonic acid monohydrate (1.52 g, 8 mmol) in 20 mL THF. After completion (1~2 h) of the reaction as monitored by TLC, the reaction was neutralized with aqueous solution of NaHCO₃ and washed with DI water three times. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. Flash chromatography (petroleum ether/EtOAc 8:1) afforded a white solid (2.74 g, 5 mmol, 50%). ¹H NMR (500 MHz, DMSO-d₆) δ 11.36 (s, 1H), 8.57 (s, 2H), 7.76 (dd, J=23.7, 8.1 Hz, 6H), 7.57 (d, J=8.4 Hz, 2H), 7.45 (d, J=7.8 Hz, 4H), 4.74 (d, J=11.8 Hz, 4H), 4.51 (d, J=12.1 Hz, 2H), 3.84 (t, J=8.8 Hz, 2H), 3.51 (d, J=11.3 Hz, 2H), 1.97-1.38 (m, 12H).

Synthesis of Compound 3

To a dry Schlenk tube equipped with a magnetic stir bar was charged compound 2 (1.4 g, 2.55 mmol), TTM (1 g, 1.82 mmol), anhydrous Cs₂CO₃ (950 mg, 1.6 mmol) and DMF (10 mL) in the dark. The solution was degassed by three freeze-thaw-pump cycles, filled with N₂ and sealed. The tube was submersed in a 160 °C oil bath for 2 h under N₂ atmosphere in the dark. The solution was cooled to room temperature and poured into an excess of diluted aqueous HCl acid (0.5M). The precipitate was filtered off and washed with DI water. The solid was dissolved in dichloromethane (CH₂Cl₂), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. Flash chromatography (petroleum ether/EtOAc 4:1) afforded a green solid (250 mg, 0.235 mmol, 26%). ¹H NMR (500 MHz, CDCl₃) δ 8.37 (d, J=1.5 Hz, 2H), 7.71 (d, J=8.0 Hz, 6H), 7.66 (d, J=2.2 Hz, 1H), 7.53-7.49 (m, 7H), 7.44 (d, J=2.2 Hz, 1H), 7.42 (d, J=2.2 Hz, 1H), 7.32 (d, J=2.2 Hz, 1H), 7.29 (d, J=2.2 Hz, 1H), 6.88 (s, 1H), 4.87 (d, J=12.0 Hz, 2H), 4.78 (t, J=3.5 Hz, 2H), 4.59 (d, J=12.0 Hz, 2H), 3.98 (ddd, J=11.5, 8.5, 3.0 Hz, 2H), 3.59 (dt, J=10.4, 4.9 Hz, 2H), 1.97-1.45 (m, 12H).

Synthesis of HTTM-CZ-OH

Compound 3 (900 mg, 0.84 mmol), THF and methanol (9:1, v/v, 50 mL), HCl (250 µL, 12 M) were combined in a 100 mL round-bottom flask. The reaction mixture was stirred at 60 °C for around 30 min until the deprotection reaction was complete (monitored by TLC). The resulting solution was concentrated under reduced pressure. The crude product was dissolved by EtOAc and washed with DI water three times. The organic layer was separated, dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. Flash chromatography (petroleum ether/EtOAc 2:1 to 1:1) afforded a green solid (562 mg, 0.63 mmol, 75%). ¹H NMR (500 MHz,
DMSO-\textsuperscript{d6} \( \delta \) 8.74 (s, 2H), 8.01 (m, \( J=2.0 \text{ Hz} \), 1H), 7.91-7.78 (m, 9H), 7.70-7.62 (m, 2H), 7.48 (dd, \( J=27.9, 8.2 \text{ Hz} \), 6H), 6.82 (s, 1H), 5.24 (t, \( J=5.6 \text{ Hz} \), 2H), 4.57 (d, \( J=5.1 \text{ Hz} \), 4H); MS (ES+) calcd 892.9550 [M]+, found \( m/z \) 892.9544 [M]+.

**Synthesis of TTM-CZ-OH**

To a solution of HTTM-CZ-OH (500 mg, 0.56 mmol) in THF (20 mL) was added tetrabutylammonium hydroxide solution in methanol (420 \( \mu \text{L} \), 2.0 M) under nitrogen atmosphere and in the dark. The reaction mixture was stirred for 5 h at room temperature. Then tetrachloro-\( p \)-benzoquinone (410 mg, 1.68 mmol) was added and react for another 2 h. The reaction was concentrated under reduced pressure, and the obtained crude was purified by flash chromatography (petroleum ether/EtOAc 4:1) to afford a green solid (375 mg, 0.42 mmol, 75%); MS (ES+) calcd 891.9472 [M]+, found \( m/z \) 891.9469 [M]+.

**3.2 Typical polymerization procedure for radical polymers**

Polymerization in solution was performed in a dry Schlenk tube with a stir-bar. Take RPE1 as an example. Initiator (TTM-CZ-OH 0.03 mmol, 27 mg), catalyst Sn(Oct)\(_2\) (0.01 mmol) and monomer (\( \delta \)-VL, 3 mmol, 300 mg) were added under nitrogen. The tube was sealed and the whole was stirred at 130 °C for 12 h. The tube was cooled to room temperature, the product polymer was precipitated by dripping the contents into vigorously stirring methanol. The solid was redissolved in a minimum amount of CH\(_2\)Cl\(_2\) and reprecipitated again into MeOH twice more. The resulting polymer was separated by centrifugation and dried under reduced pressure (yield, 60–90%). The final radical polymers were named RPE1, RPE2 …to RPE7.
Scheme S1. Synthetic routes to radical polymers via ring-opening polymerization.

3.3 General nanoparticles preparation procedure

5 mL DI water was quickly injected into the 1 mL mixture of RPE5 or RPE6 or RPE7 (2~5 mg) and Pluronic®127 (F127) (~70 mg) in THF under sonication. THF was removed by dialysis against water over two days. The external water was changed every several hours.

3.4 Photostability experiment

Photostability experiment were carried out using a white-light LED strip (lumen: 80ml/W, colour rendering index: 80 Ra, frequency: 60 Hz) as continuous irradiation source. Physically blended TTM-CZ-OH with pure PLLA ($M_n = 4500$, $M_w/M_n = 1.08$) are used as control. The films were prepared by drop-coating from chloroform solution on quartz slides (1 cm × 1 cm). In physically blended film, the ratio of TTM-CZ-OH versus pure PLLA (repeat unit) was kept consistent with RPE6 which is ~1:50 by moles. The slides were placed directly at the centre of LED. Digital photographs were taken after light irradiation.
4. Supporting Figures

**Figure S1.** $^1$H NMR (DMSO-$d_6$, 500 MHz) spectrum of Compound 1.

**Figure S2.** $^1$H NMR (DMSO-$d_6$, 500 MHz) spectrum of Compound 2.
Figure S3. $^1$H NMR (CDCl$_3$, 500 MHz) spectrum of Compound 3.

Figure S4. $^1$H NMR (DMSO-$d_6$, 500 MHz) spectrum of HTM-CZ-OH.
Figure S5. $^1$H NMR (CDCl$_3$, 500 MHz) spectrum of RPE1.

Figure S6. $^1$H NMR (CDCl$_3$, 500 MHz) spectrum of RPE2.
Figure S7. $^1$H NMR (CDCl$_3$, 500 MHz) spectrum of RPE4.

Figure S8. $^1$H NMR (CDCl$_3$, 500 MHz) spectrum of RPE6.
Figure S9. ESI-MS spectrum of HTTM-CZ-OH.

Figure S10. ESI-MS spectrum of TTM-CZ-OH.
Figure S11. GPC traces of RPE1-7 polymers as monitored by both refractive index (RI) and UV (375 nm) detectors.
Figure S12. DSC curves of four RPEs (second heating, 10 °C min⁻¹).

Figure S13. PXRD profiles of four RPEs.
**Figure S14.** Digital photographs of four RPEs in toluene under room light and UV light (365 nm).

**Figure S15.** Digital photographs of all synthesized radical polymers in bulk solid state under irradiation of room light (top) and UV (365 nm) light (bottom).
Figure S16. Digital photographs of RPE3 under irradiation of room light and UV (365 nm) light: (a) bulk solid state, (b) films on quartz plates at room temperature (RT: top row) and immediately after being chilled in liquid N\textsubscript{2} (bottom row).

Figure S17. (a) Normalized temperature-dependent PL emission spectra of RPE2 at different temperatures (80~240 K). Excitation: $\lambda_{\text{ex}} = 325$ nm. Some spectra (T > 240 K) are not shown for accurate normalization because of their weak emission. (b) Changes in the maximal emission wavelength with increase of temperature.
Figure S18. Normalized UV/Vis absorption and PL emission spectra of RPE2 and RPE3: (a), (b) in toluene; and (c), (d) in thin films (frozen by liquid nitrogen). The insets of Figures a and c magnify the absorption peaks in the region of 500-800 nm.

Figure S19. Optical properties of RPE5, RPE6 and RPE7 (3 mg/mL) in toluene. (a, c) UV/Vis absorption (a : non-normalized ; c : normalized): (b, d) Steady-state PL emission spectra (b :
Figure S20. Optical properties of RPE5, RPE6 and RPE7 in thin films. (a) Digital photographs. Top: under room light. Bottom: UV (365 nm) light. (b), (c) Non-normalized and normalized UV/Vis absorption. (d-e) Non-normalized (d) and normalized (e) PL emission spectra.

Figure S21. Digital photographs (under UV light, 365 nm) of PCL-DPP-PCL at different temperatures.
**Figure S22.** Characterization of radical polymer nanoparticles (NPs): (a) Digital photographs of RPE5, RPE6 and RPE7 NPs (1.25 mg/mL) in aqueous media under ambient and UV (365 nm) light. (b) Dynamic light scattering (DLS) histograms of the NPs in aqueous solution. (c) UV/Vis absorption of NPs (1.25 mg/mL). (d-e) Steady-state PL emission ($\lambda_{ex}=325$ nm) spectra of RPE5-6 NPs at RT (d) and RPE6 NPs at different temperatures (e). (f) PL intensity monitored at 665 nm during 5 heating-cooling cycles of RPE6 NPs.
**Figure S23.** ESR spectra of RPE3 in powdered state at different temperatures.

**Figure S24.** Molecular structure of branched PCL plasticizer$^{[S2]}$. 
**Figure S25.** Digital photographs of RPE6 films under room light and UV (365 nm) light as a function of temperature before and after addition of plasticizers: (a) diethyl phthalate and (b) branched PCL.

**Figure S26.** Digital photographs (under room light and UV light (365 nm)) show the photostability of RPE6 in thick films (a) relative to a physically blended mixture of TTM-CZ-OH and pure PLLA (b) before (0 h) and after different times of LED light irradiation as specified in Experimental Section.
Table S1. Estimated $T_g$ of plasticized RPE6.

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</table>

*Experimental $T_g$. *b* Values for diethyl phthalate are taken from Reference S3. *c* Values for branched PCL are taken from Reference S2.

5. References

