Surpporting information

Detection of *β*-transition in Polyesters via Clusteroluminescence

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Experimental Procedures

Section S1: Materials

All manipulations involving air- and/or water-sensitive compounds were carried out with the standard Schlenk and vacuum line techniques under an argon atmosphere or in a nitrogen-filled glovebox. Glutaric anhydride (GA), Paraldehyde, Benzaldehyde, Phenylacetaldehyde, Phenylpropyl aldehyde, 2-phenyl-propionaldehyde, Biphenylacetaldehyde were purchased from Macklin.

All the aldehydes were refluxed over CaH_2 for 24 h and vacuum-distilled prior before use. All the anhydrides were purified by vacuum sublimation for three times. The purified anhydride and aldehydes were collected under inert atmosphere and stored in the glovebox for use. Other organic reagents were used without purified.

Section S2: Characterization

The polyester samples were characterized by nuclear magnetic resonance (^1H NMR and ^{13}C NMR), gel permeation chromatograph (GPC), fluorescence-phosphorescence spectrophotometer, and UV-vis spectrophotometer and NMR spectra were recorded on a Bruker 400 MHz instrument in $CDCl_2$ (to avoid the interefere with H in phenyl group) or $CDCl_3$ by using tetramethylsilane (TMS) as an internal reference.

The number-averaged molecular weight (M_n) and polydispersity index (PDI) were obtained using a PL-GPC 220 chromatograph (Polymer Laboratories, Ltd., Santa Clara/United States) equipped with an HP 1100 pump from Agilent Technologies (Shanghai, China), using chromatographic purity THF as an eluent at 40 °C.

Differential scanning calorimetry (DSC) tests were conducted on a TA Instruments TA-Q200 instrument (New Castle, DE) with a heating rate of 10 °C min^{-1} under a N_2 atmosphere, and the data from the second heating curve were collected.

Photoluminescence spectra were collected from a FLS920 transient fluorescence spectrometer with an excitation source of xenon lamp. Absolute quantum yields were obtained by additional integrating sphere. UV-Vis absorption spectra were recorded on UV-vis spectrophotometer of Cary 100.

The Photos were recorded by a Cannon EOS 90D.

Dielectric spectrum was measured by broadband dielectric spectroscopy (Concept 40, Novocontrol Technologies). After drying, the sample was applied to electrode plates and placed into the instrument. Measurements commenced at 130 K, with the temperature increased in 10 K increments. At each set temperature, the system was stabilized within a ± 0.5 K range for 180 seconds before recording the storage modulus and loss modulus over a frequency range of 10^2 Hz to 1 Hz.

Section S3: Representative copolymerization procedures

Synthesis of P1. In a glovebox, Paraldehyde (0.19 mL, 1.47 mmol), GA (0.5 g, 4.4 mmol) and $InBr_3$ (15.6 mg, 0.044 mmol) with the feeding ratio of 33.3:100:1, were measured into a 10.0 mL vial equipped with a Teflon-coated stir bar and sealed with a Teflon-lined cap at 0 ℃. After 24 h reaction, the mixture was dissolved in 2 mL DCM and then precipitated into 50 mL analytical ethanol (without PL response) to precipitate the product. The dissolve-precipitation process was repeated for three times to remove unreacted monomers and catalysts. The white polymer was finally collected and dried in vacuum at 40 °C for 24 h. ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 6.83 (s, 1H), 2.38 (s, 4H), 1.91 (s, 2H), 1.46 (d, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 171.31, 88.81, 53.84, 33.25, 20.92, 19.76.The M_n, M_w from GPC Curves are 5.8 *KDa* and 6.8 *KDa*. PDI is 1.17.

Synthesis of P2. In a glovebox, Benzaldehyde (0.45 mL, 4.4 mmol), GA (0.5 g, 4.4 mmol) and $InBr_3$ (15.6 mg, 0.044 mmol) with the feeding ratio of 100:100:1, were measured into a 10.0 mL vial equipped with a Teflon-coated stir bar and sealed with a Teflon-lined cap at 0 ℃. After 12 h reaction, the mixture was dissolved in 2 mL DCM and then precipitated into 50 mL analytical ethanol (without PL response) to precipitate the product. The dissolve-precipitation process was repeated for three times to remove unreacted monomers and catalysts. The white polymer was finally collected and dried in vacuum at 40 °C for 24 h. ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.65 (s, 1H), 7.46 (s, 2H), 7.38 (s, 3H), 2.41 (s, 4H), 1.92 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.81, 135.46, 129.93, 128.76, 126.75, 89.89, 32.91, 19.60. The M_n, M_w from GPC Curves are 13.2 *KDa* and 17.9 *KDa*. PDI is 1.36.

Synthesis of P3. In a glovebox, Phenylacetaldehyde (0.50 mL, 4.4 mmol), GA (0.5 g, 4.4 mmol) and $InBr_3$ (15.6 mg, 0.044 mmol) with the feeding ratio of 100:100:1, were measured into a 10.0 mL vial equipped with a Teflon-coated stir bar and sealed with a Teflon-lined cap at 0 ℃. After 12 h reaction, the mixture was dissolved in 2 mL DCM and then precipitated into 50 mL analytical ethanol (without PL response) to precipitate the product. The dissolve-precipitation process was repeated for three times to remove unreacted monomers and catalysts. The white polymer was finally collected and dried in vacuum at 40 °C for 24 h. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.28 (s, 5H), 6.97 (s, 1H), 3.10 (s, 2H), 2.32 (s, 4H), 1.85 (s, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 171.15, 134.80, 130.41, 128.86, 127.51, 90.57, 40.08, 33.15, 19.89. The M_n, M_w from GPC Curves are 3.1 *KDa* and 4.0 *KDa*. PDI is 1.31.

Synthesis of P4. In a glovebox, Phenylpropyl aldehyde (0.58 mL, 4.4 mmol), GA (0.5 g, 4.4 mmol) and $InBr_3$ (15.6 mg, 0.044 mmol) with the feeding ratio of 100:100:1, were measured into a 10.0 mL vial equipped with a Teflon-coated stir bar and sealed with a Teflon-lined cap at 0 ℃. After 12 h reaction, the mixture was dissolved in 2 mL DCM and then precipitated into 50 mL analytical ethanol (without PL response) to precipitate the product. The dissolve-precipitation process was repeated for three times to remove unreacted monomers and catalysts. The white polymer was finally collected and dried in vacuum at 40 °C for 24 h. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.22 (d, J = 34.3 Hz, 5H), 6.81 (s, 1H), 2.69 (s, 2H), 2.34 (s, 4H), 2.09 (s, 2H), 1.87 (s, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 171.31, 141.13, 128.70, 126.53, 90.36, 35.14, 33.21, 19.95. The M_n, M_w from GPC Curves are 2.9 *KDa* and 3.4 *KDa*. PDI is 1.19.

Synthesis of P5. In a glovebox, Phenylacetaldehyde, Phenylpropyl aldehyde, 2-phenyl-propionaldehyde, Biphenylacetaldehyde (0.58 mL, 4.4 mmol), GA (0.5 g, 4.4 mmol) and $InBr_3$ (15.6 mg, 0.044 mmol) with the feeding ratio of 100:100:1, were measured into a 10.0 mL vial equipped with a Teflon-coated stir bar and sealed with a Teflon-lined cap at 0 ℃. After 12 h reaction, the mixture was dissolved in 2 mL DCM and then precipitated into 50 mL analytical ethanol (without PL response) to precipitate the product. The dissolve-precipitation process was repeated for three times to remove unreacted monomers and catalysts. The white polymer was finally collected and dried in vacuum at 40 °C for 24 h. ^{1}H NMR (400 MHz, METHYLENE-CHLORI) δ 7.27 (s, 5H), 6.89 (s, 1H), 3.14 (s, 1H), 2.27 (s, 4H), 1.75 (s, 2H), 1.29 (s, 3H). ^{13}C NMR (101 MHz, METHYLENE-CHLORI) δ 171.26, 140.60, 128.75, 127.55, 92.20, 43.44, 33.22, 19.88, 15.48. The M_n, M_w from GPC Curves are 4.2 *KDa* and 5.7 *KDa*. PDI is 1.35.

Synthesis of P6. In a glovebox, Biphenylacetaldehyde (0.78 mL, 4.4 mmol), GA (0.5 g, 4.4 mmol) and $InBr_3$ (15.6 mg, 0.044 mmol) with the feeding ratio of 100:100:1, were measured into a 10.0 mL vial equipped with a Teflon-coated stir bar and sealed with a Teflon-lined cap at 0 ℃. After 12 h reaction, the mixture was dissolved in 2 mL DCM and then precipitated into 50 mL analytical ethanol (without PL response) to precipitate the product. The dissolve-precipitation process was repeated for three times to remove unreacted monomers and catalysts. The white polymer was finally collected and dried in vacuum at 40 °C for 24 h. ^1H NMR (400 MHz, CD_2Cl_2) δ 7.50 (s, 1H), 7.27 (s, 10H), 4.36 (s, 1H), 2.00 (s, 4H), 1.58 (s, 2H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 170.95, 139.39, 128.99, 127.61, 90.22, 55.38, 33.00, 19.78. The M_n, M_w from GPC Curves are 2.0 *KDa* and 2.6 *KDa*. PDI is 1.30.

Section S4: Variable-temperature fluorescence experiments procedures

All samples were initially dried in a vacuum oven for a duration exceeding 24 hours. During testing, after evacuating the apparatus, the samples were heated to 310 K and maintained at this temperature for 20 minutes to eliminate any residual thermal history. This was followed by cooling to 80 K for 30 minutes to ensure complete thermal equilibration. Fluorescence spectra were subsequently recorded at 10 K intervals, with a stabilization period of at least 3 minutes at each temperature point prior to measurement.

Section S5: Computational Details

All the compounds were fully optimized with the density functional theory (DFT) method by using WB97XD density functional and 6-31G(d,p) basis set. Analytical frequency calculations were also performed at the same level of theory to confirm that the optimized structures were at a minimum point. Time dependent density functional theory (TD-DFT) was utilized at the same level of theory to calculate optimized excited (S1) geometries. The polymer-related calculations were replaced by the oligomers with three repeating units. The frontier molecular orbitals (FMO) and hole-electron analyses of **P1-P6** were displayed by Multiwfn 3.8 and Visual Molecular Dynamics (VMD) (Isovalue: 0.006).

The conformation with five repeated units was simulated using molecular dynamics (MD) simulations to study the conformational behavior of the system across different temperatures. The simulation involved cyclic heating and cooling processes, where the temperature was ramped from 77 K to 500 K and subsequently cooled to 77 K, repeated for 10 cycles at a time step of 4 ns per cycle. From all the cycles, we selected the conformations with the lowest energy at 77 K, 150 K and 298 K, respectively.

Gel Permeation Chromatography

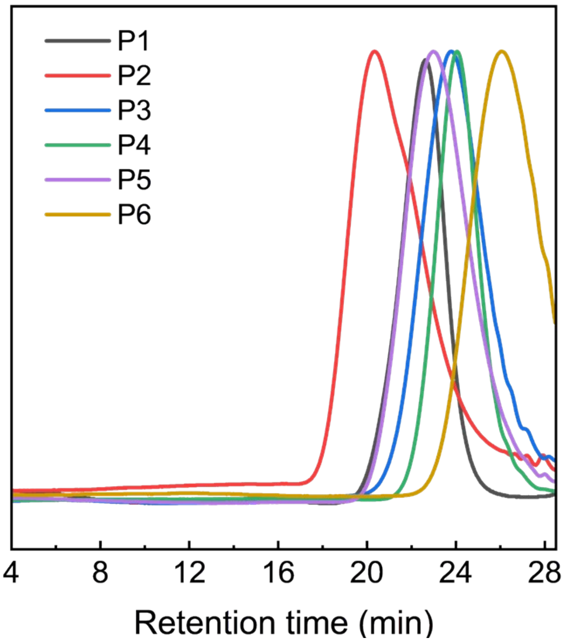
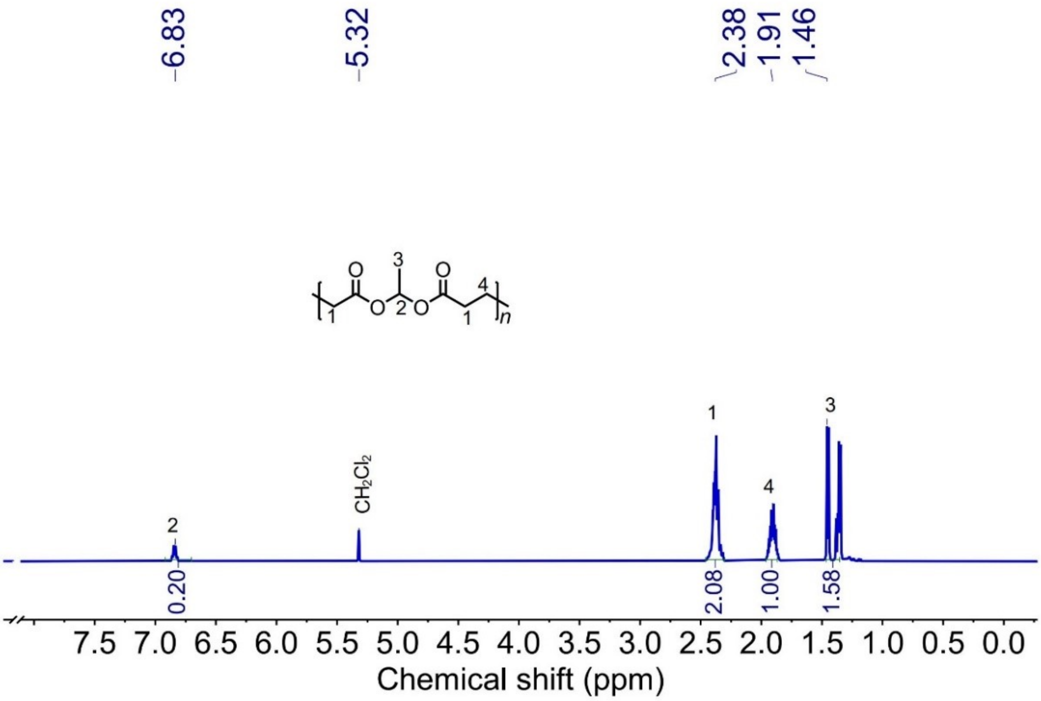


Figure S1. GPC curves of P1-6 with polystyrene was used as the standard sample using chromatographic purity THF as an eluent at 40 °C. The M_n of P1-6 from GPC Curves are 6.0 KDa, 10.8 KDa, 3.1 KDa, 2.9 KDa, 4.2 KDa and 2.7 KDa, respectively.

Nuclear Magnetic Resonance (NMR) Spectra



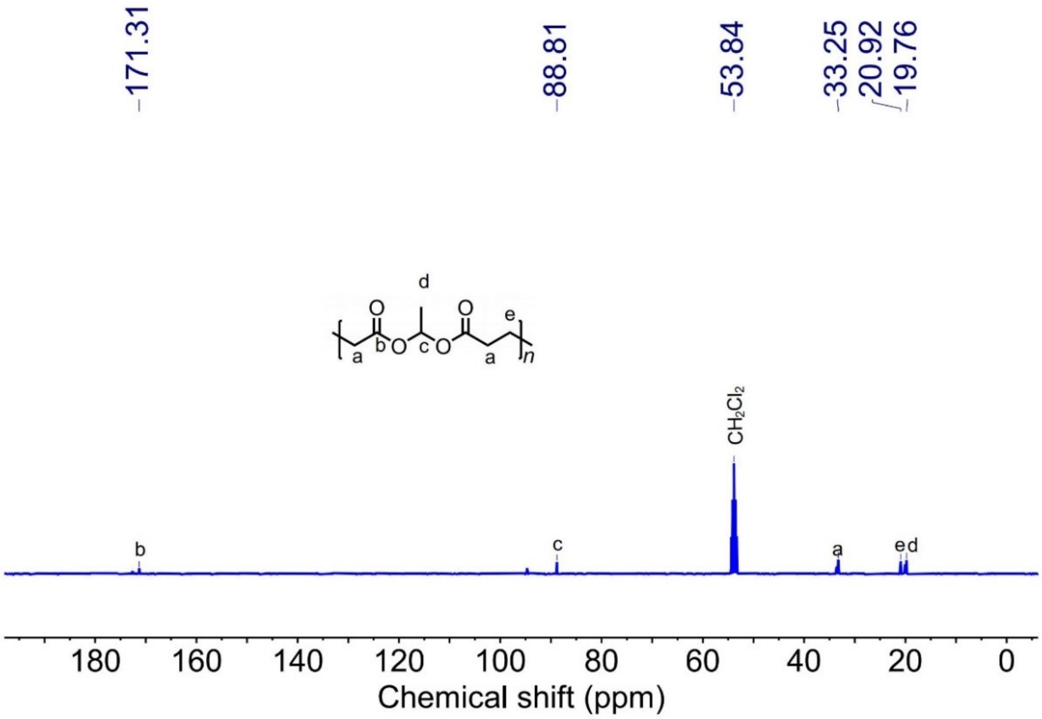


Figure S2. A)^{1}H NMR spectra and B)^{13}C NMR spectra of polyester P1 (400 MHz, $CDCl_2$).

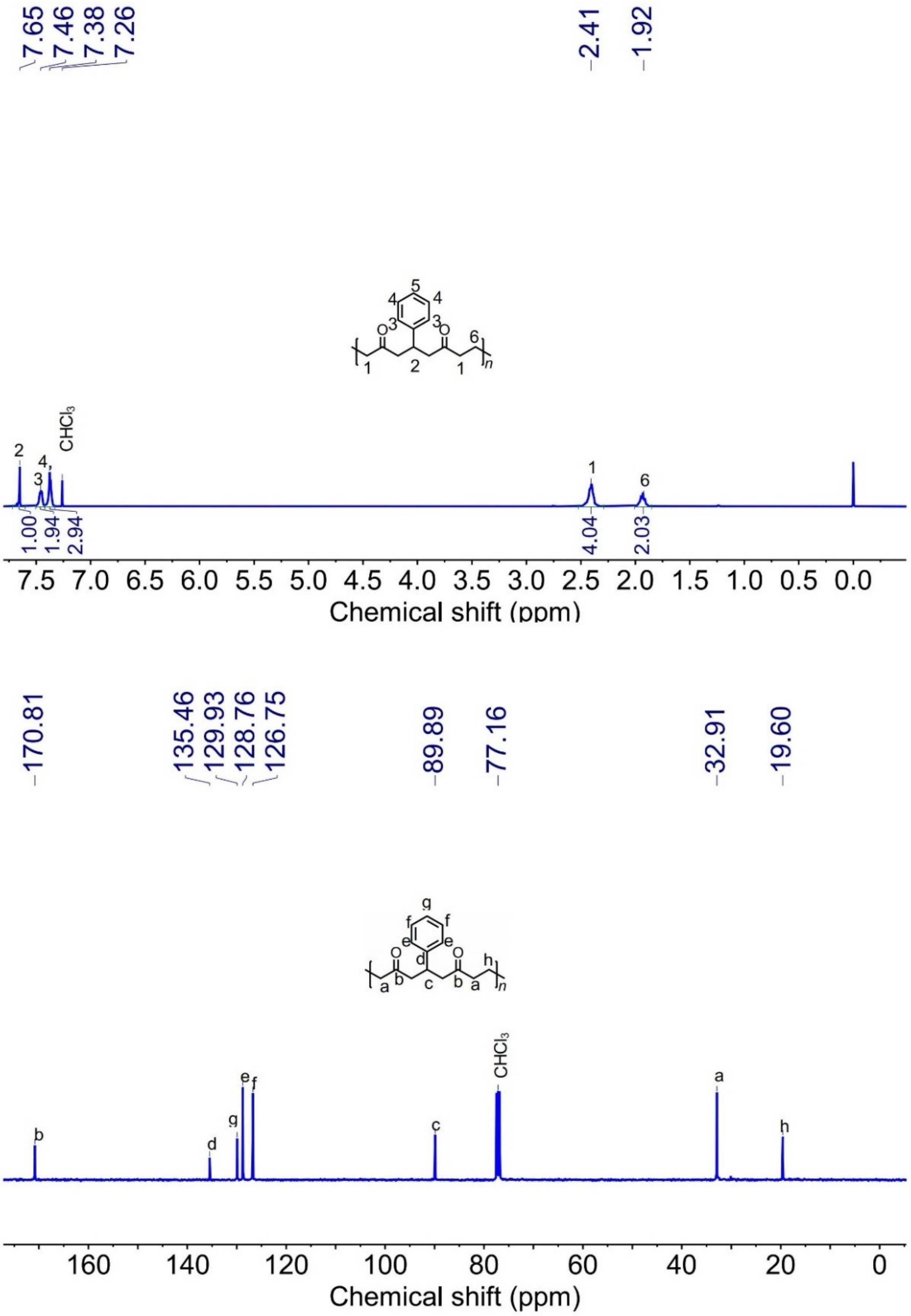


Figure S3. A)^{1}H NMR spectra and B)^{13}C NMR spectra of polyester P2 (400 MHz, $CDCl_3$).

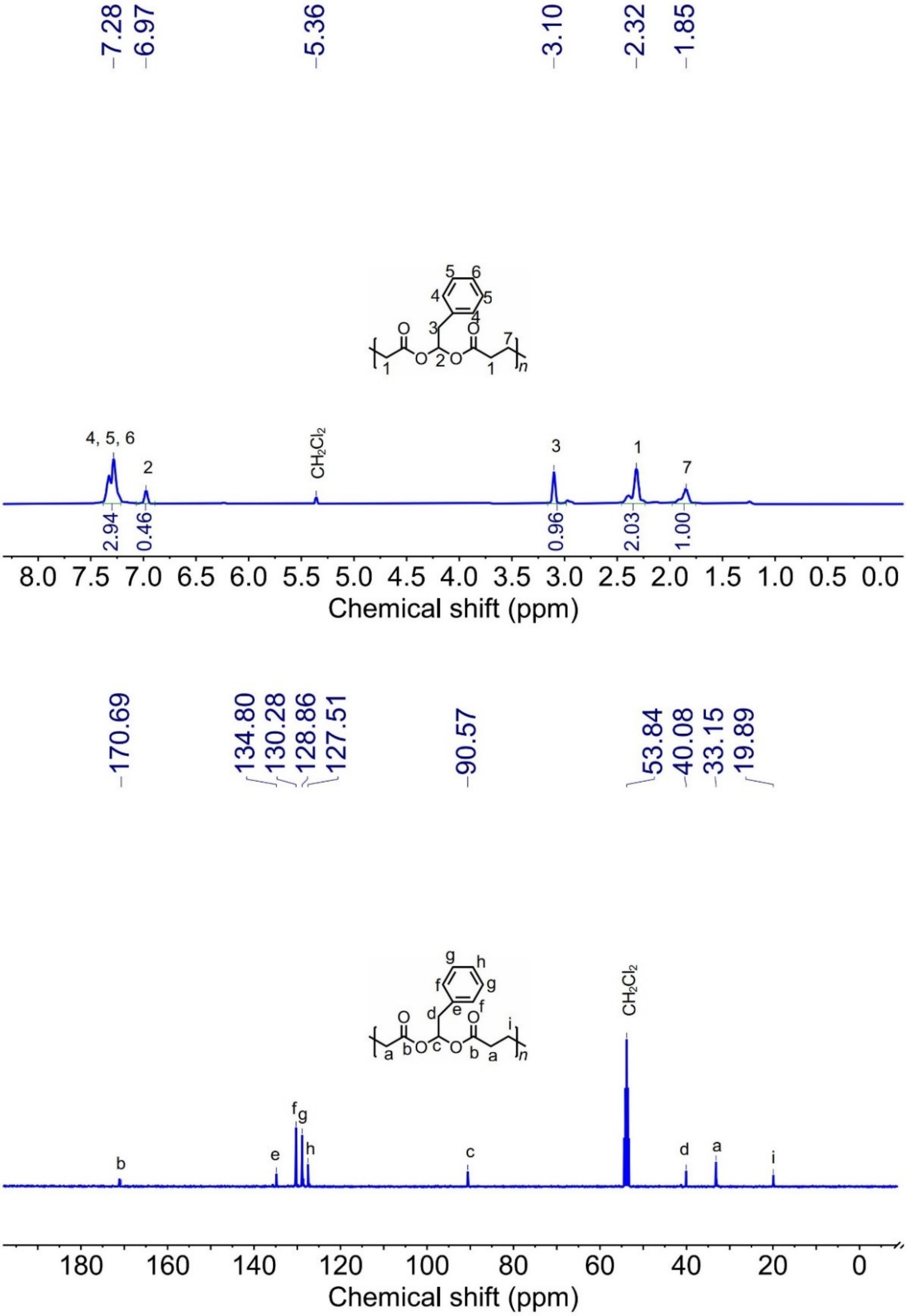


Figure S4. A)^{1}H NMR spectra and B)^{13}C NMR spectra of polyester P3 (400 MHz, $CDCl_2$).

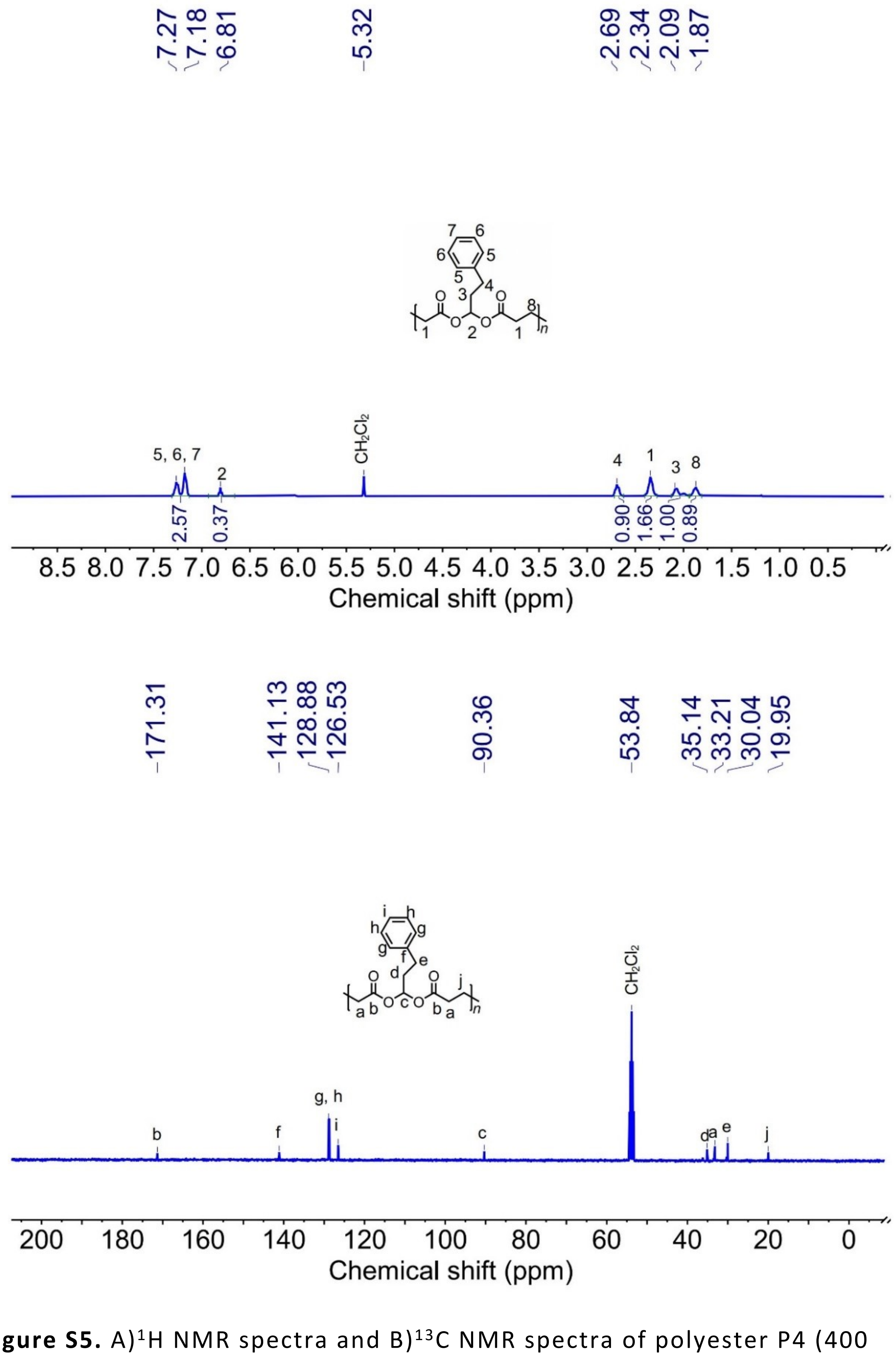


Figure S5. A)^{1}H NMR spectra and B)^{13}C NMR spectra of polyester P4 (400 MHz, $CDCl_2$).

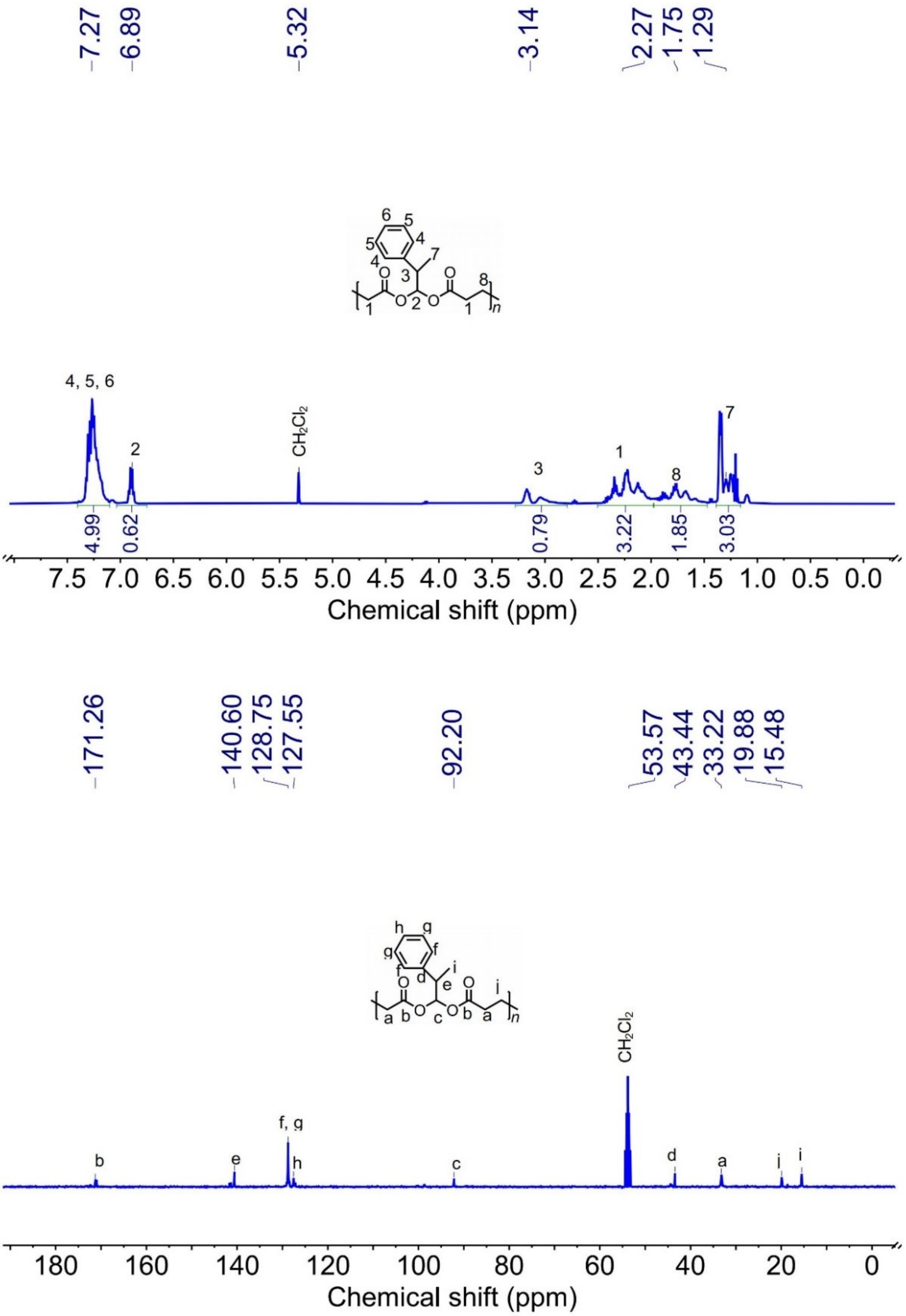


Figure S6. A)^{1}H NMR spectra and B)^{13}C NMR spectra of polyester P5 (400 MHz, $CDCl_2$).

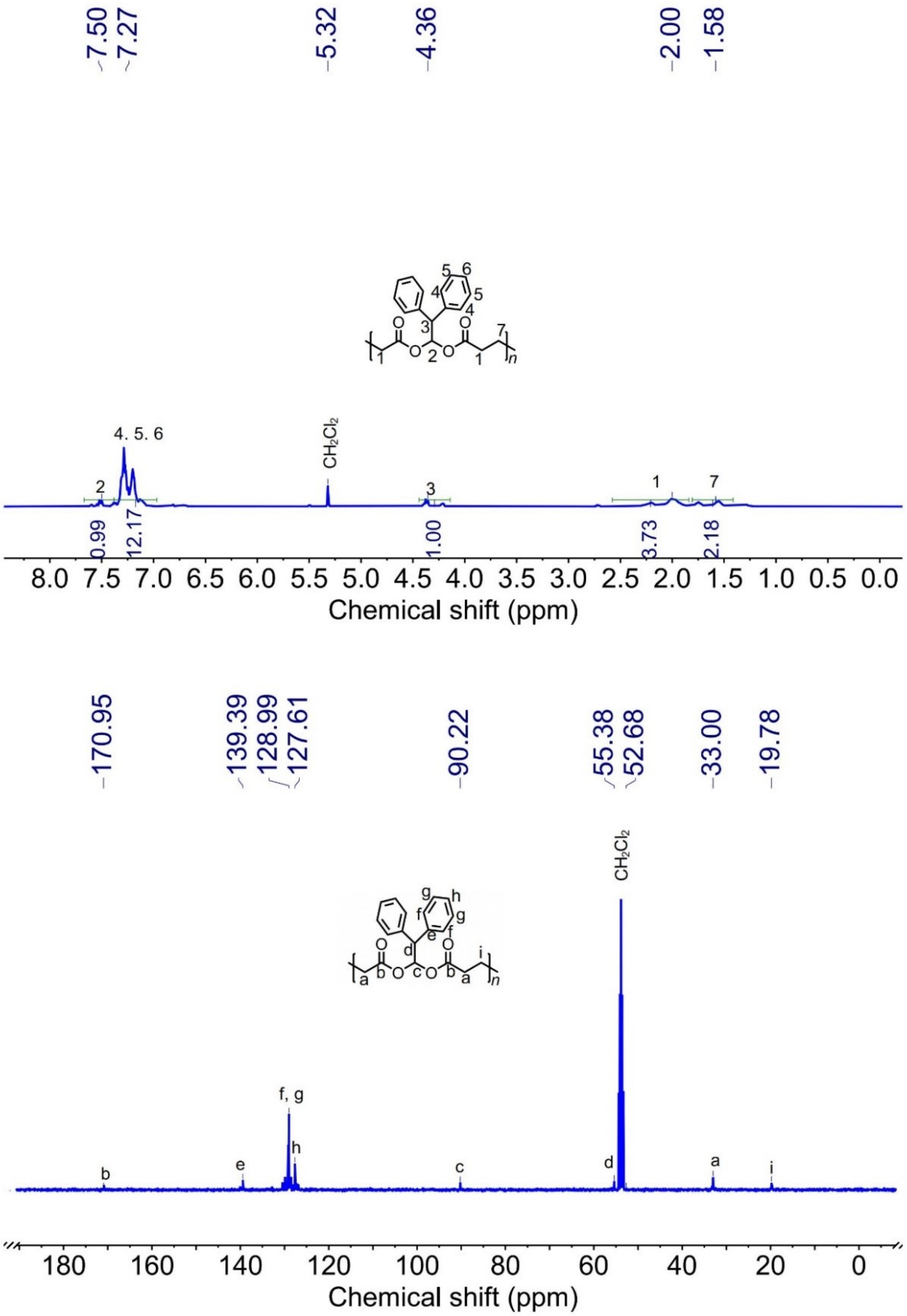


Figure S7. A)^{1}H NMR spectra and B)^{13}C NMR spectra of polyester P6 (400 MHz, $CDCl_2$).

Time-resolved PL decay curves

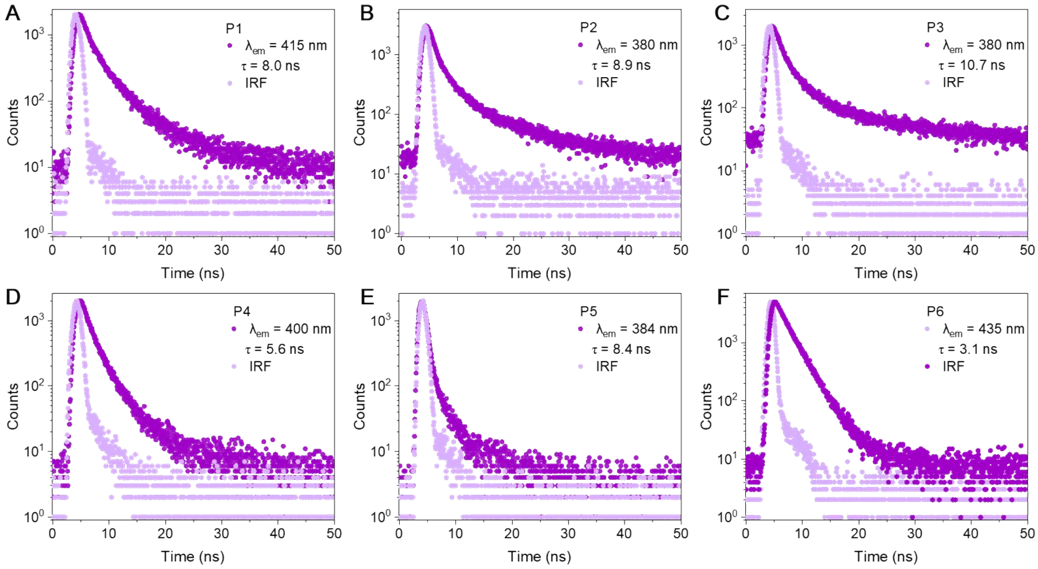


Figure S8. PL decay spectra of A)P1, B)P2, C)P3, D)P4, E)P5 and F)P6 in solid.

DSC curves of P1-P6

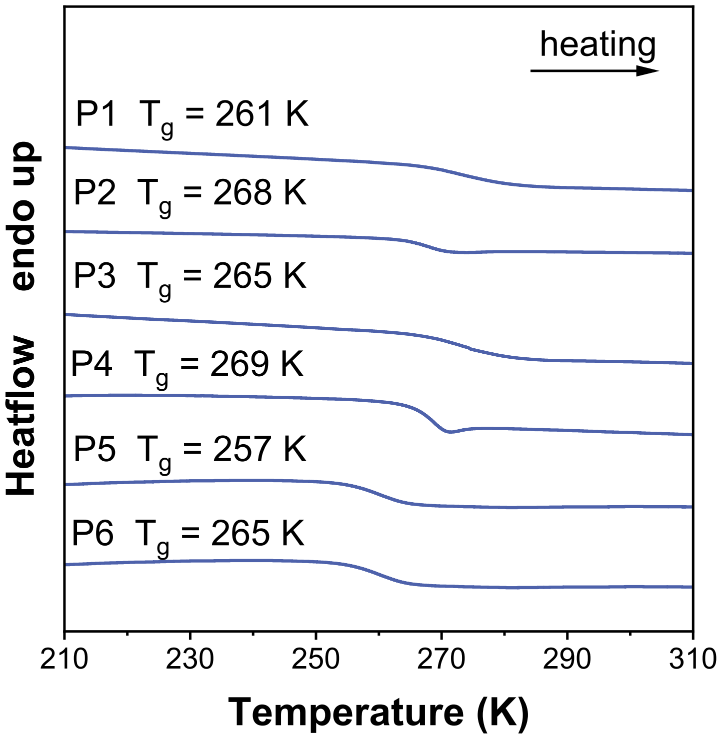


Figure S9. DSC Curves of P1-6 under nitrogen atmosphere of (heating rate: 10 K min^{-1}). The calculation of T_g is based on TA universal analysis method.

Theoretical calculation

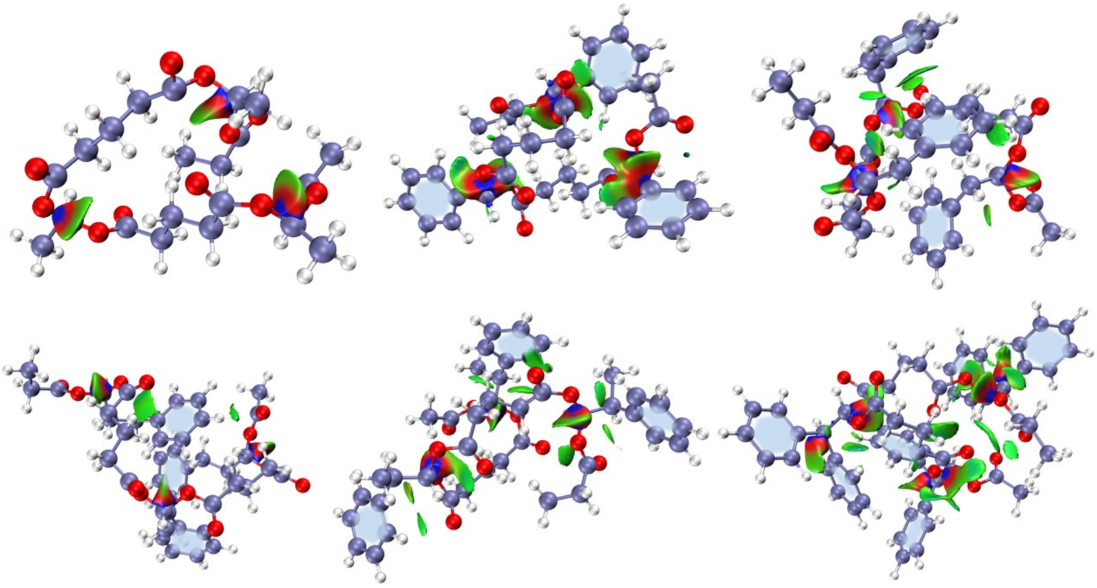


Figure S10. Visualization of non-covalent interactions in polymers. Blue regions indicate stronger interactions, red indicate repulsion, and green represent weak interactions. (Isosurface value: 0.06)

Variable-temperature fluorescence experiments

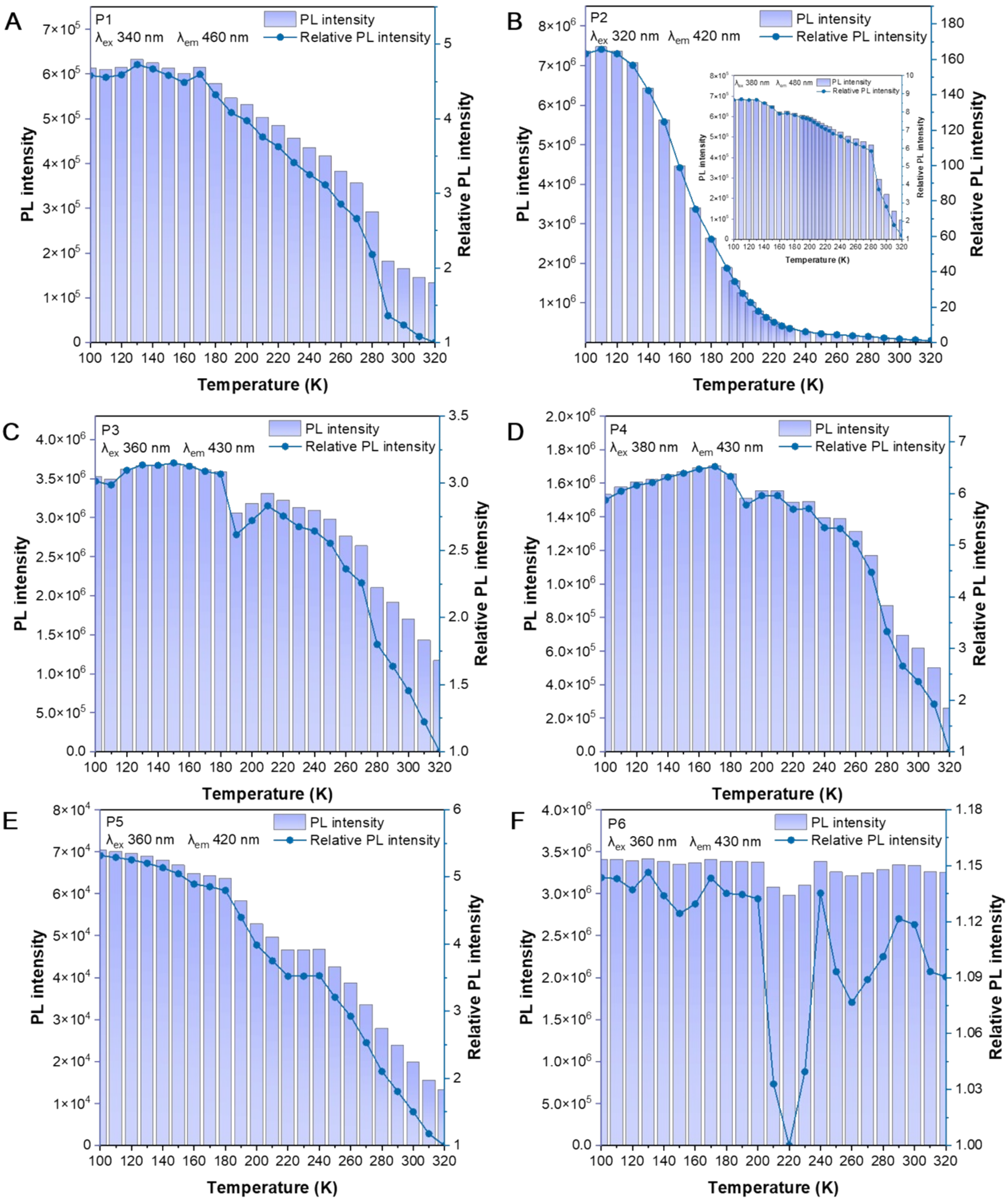


Figure S11. Bar chart of PL intensity and plot of relative PL intensity (I/I_0) of A) P1, B) P2, C) P3, D) P4, E) P5 and F) P6 in solid state heating from 80 K to 320 K.

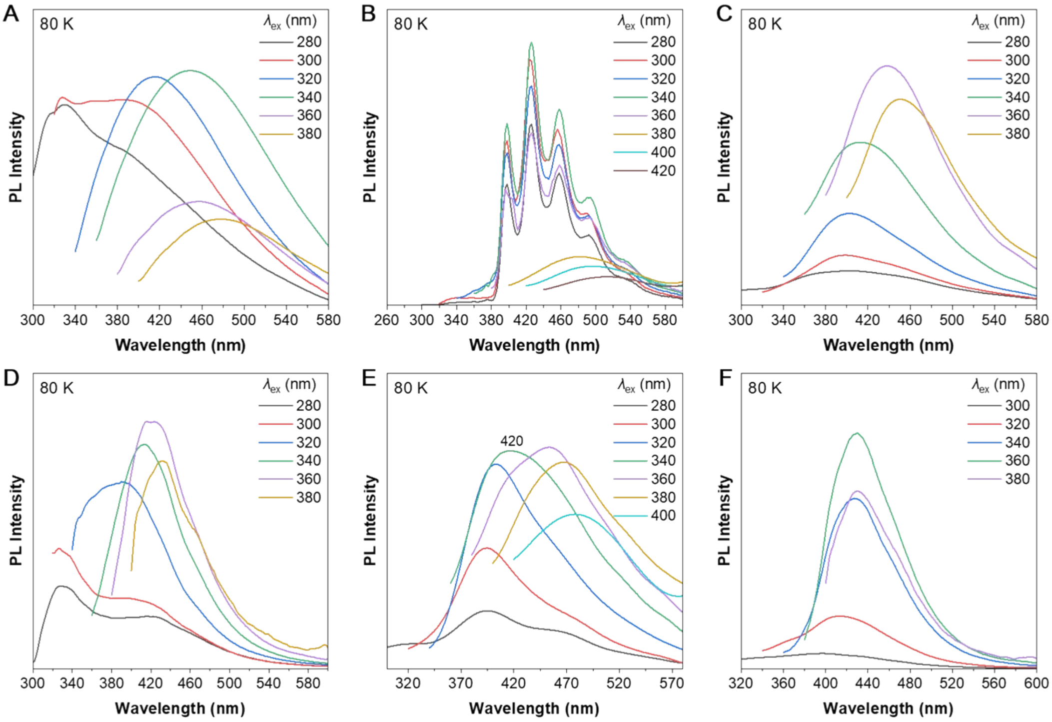


Figure S12. Solid-state PL spectra of A) P1, B) P2, C) P3, D) P4, E) P5 and F) P6 recorded at 80 K.

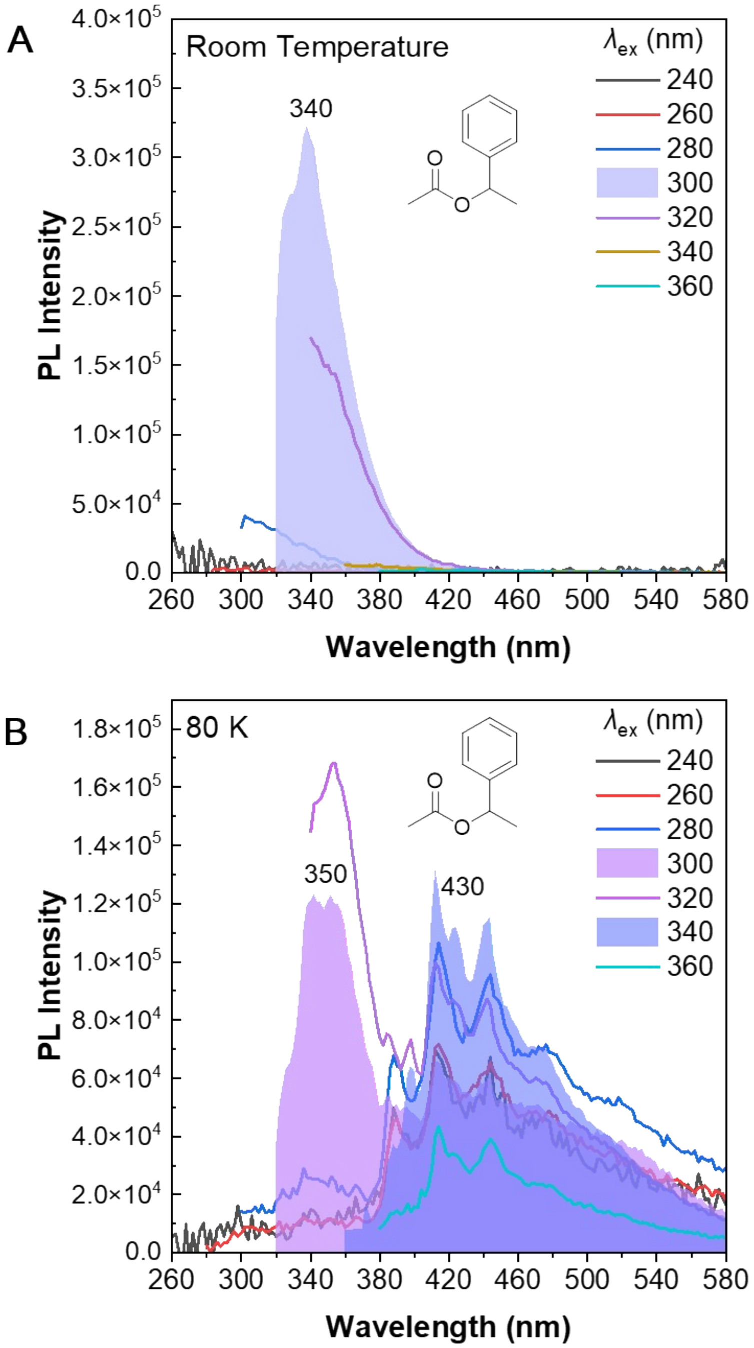


Figure S13. PL spectra of α-methylbenzyl ester under A) room temperature, B) 80 K.

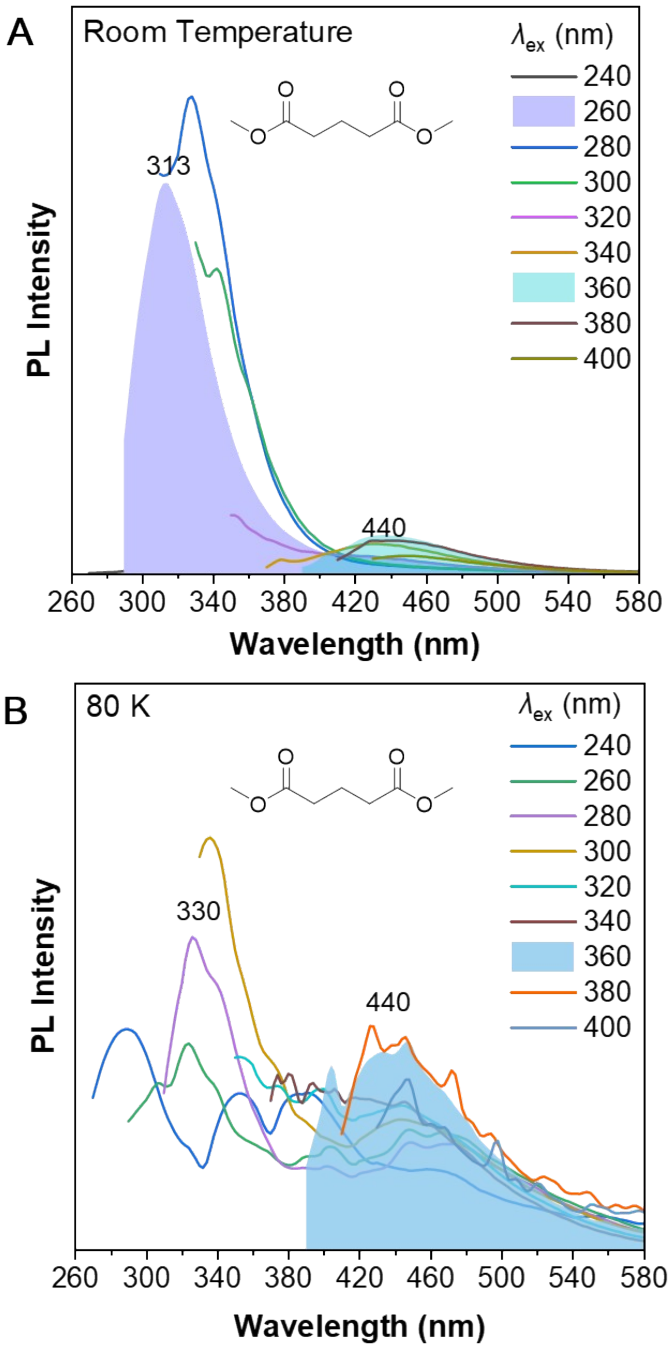


Figure S14. PL spectra of dimethyl glutarate under A) room temperature, B) 80 K.

Enlarged DSC curves of P2 heating from 160 K

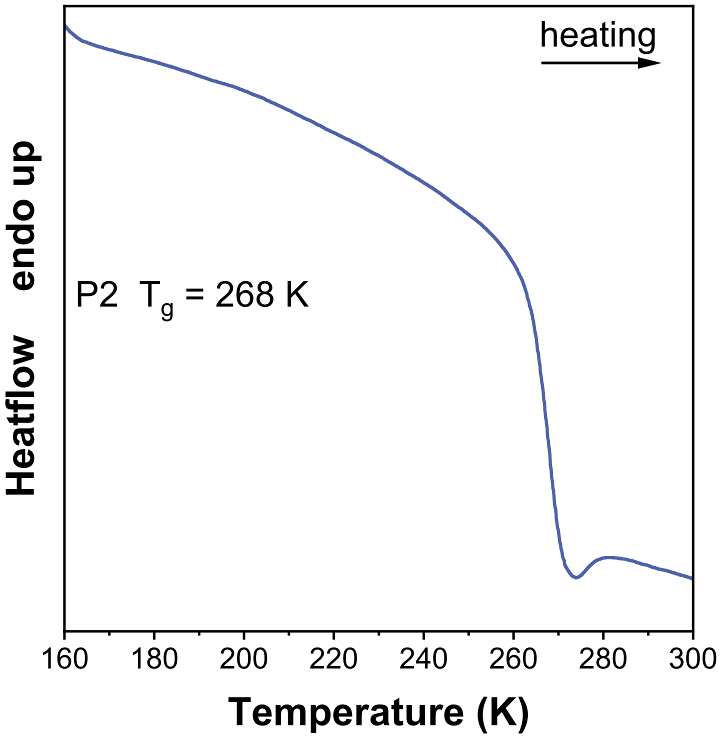


Figure S15. DSC curves of P2 under nitrogen atmosphere heating from 160 K to 300 K (heating rate: 10 K min^{-1}). The calculation of T_g is based on TA universal analysis method.

Validation of repeatability and accuracy

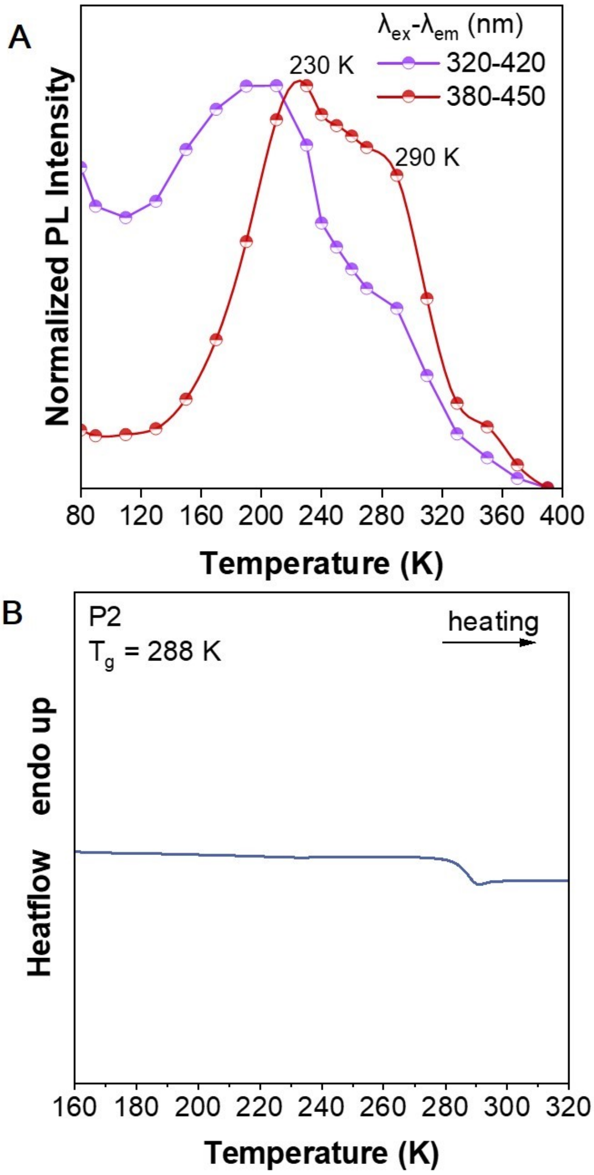


Figure S16 A) Temperature-dependent normalized PL intensity plots of P2-B (solid state, different batches) recorded during heating from 80 K to 380 K without prior annealing above its T_g, B) DSC curve of P2-B under nitrogen atmosphere heating from 160 K to 320 K (heating rate: 10 K min^{-1}).

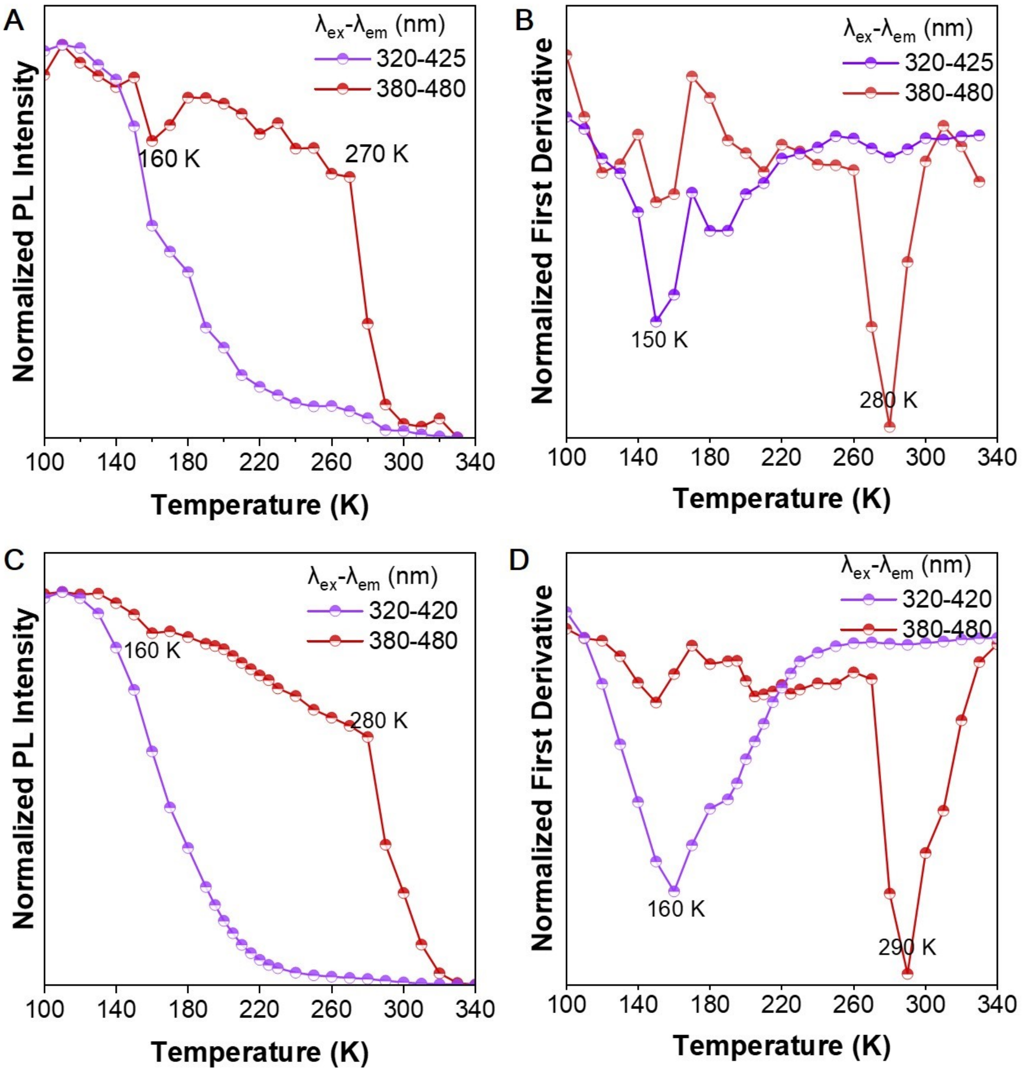


Figure S17 A) Replicated temperature-dependent normalized PL intensity of **P2** (T_g = 268 K, solid state, same batch) during heating from 100 K to 330 K, B) First derivative of PL intensity for **P2**, C) Temperature-dependent normalized PL intensity of **P2-B** (T_g = 288 K, solid state, different batch) during heating from 100 K to 340 K, D) First derivative of PL intensity for **P2-B**.