Supporting Information

Tartaric Acid-based Chiral Polyamides: Unraveling Intrinsic Multicolor Clusteroluminescence and Solvent-modulated Emission Mechanism

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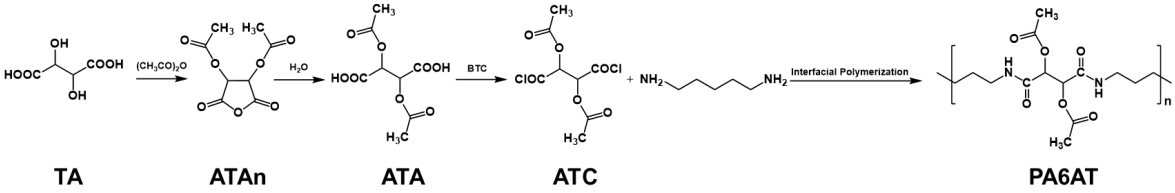
Part 1: Synthesis and Characterization of PA6ATs

The reaction strategy to polyamides is outlined in Scheme S1 and the procedure in detail is described as the follow.



Scheme S1. The synthesis route of PA6ATs

Tartaric acid (TA). TA was purchased from Aladdin reagent Co., Ltd. (Shanghai, China) and used with no further purification. ^{1}H NMR (DMSO, ppm): 4.31 (s, 2H, CH, b). FTIR (KBr): 3407, 3337 cm^{-1} (O-H alcohol) ; 1740 cm^{-1} (C=O carboxylic acid); 1750 cm-1. I_D:[a]$_D^{20}$ =-4.15° (ethanol). I_L:[a]$_D^{20}$ =+4.35° (ethanol). Purity: 99%.

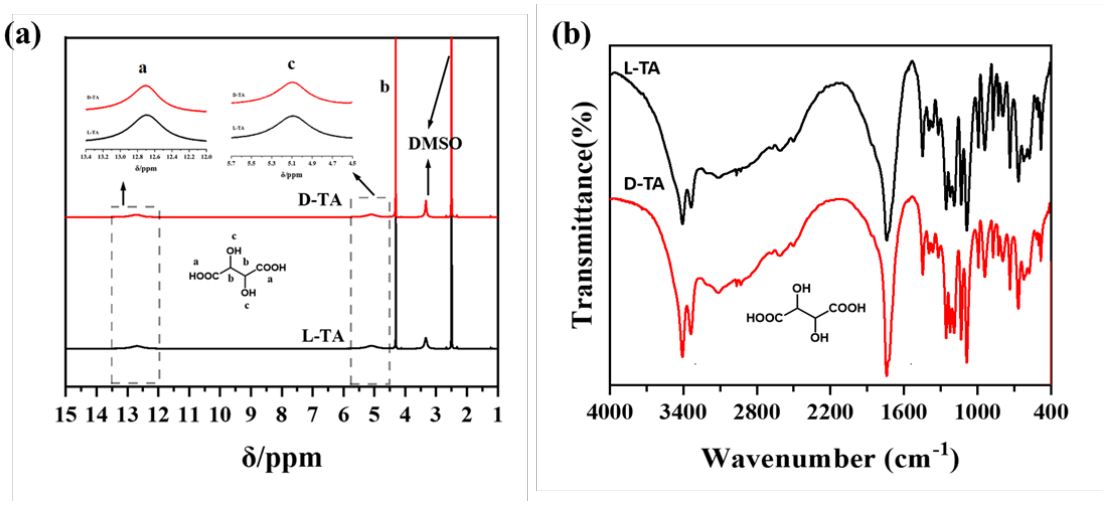


Figure S1. ^{1}H NMR (a) and FTIR (b) spectra of TA.

Synthesis of 2,3-di-O-acetyltartaric anhydride (ATAn). 10 g of tartaric acid (TA) was stirred in 50 mL of acetic anhydride for 2 hours at 60 ℃. The mixture was kept at 0 ℃ overnight and the precipitated 2,3-di-O-acetyltartaric anhydride was collected by filtration and washed with anhydrous ether.

^{1}H NMR (DMSO, ppm): 2.17 (s, 6H, CH_3, a) 6.27 (s, 2H, CH, b). FTIR (KBr): 2940,

1380 cm^{-1} (CH_3) ;1900, 1830 cm^{-1} (C=O anhydride); 1750 cm^{-1} (C=O ester). Yield: >96%; Purity: ~99%.

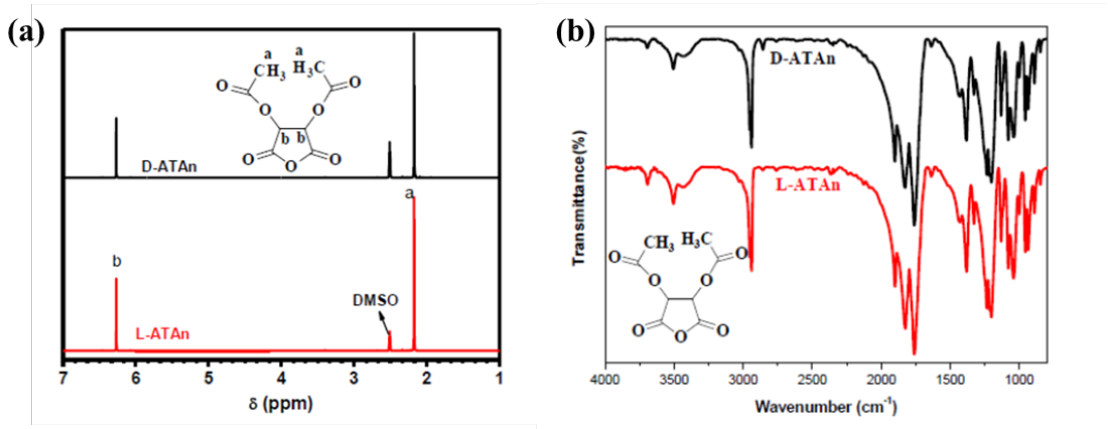


Figure S2. ^{1}H NMR (a) and FTIR (b) spectra of ATAn.

Synthesis of 2,3-di-O-acetyltartaric acid (ATA). The anhydride (6.5 g) was dissolved in 30 mL of water, stirred for 1 hour at 45 ℃, and then extracted with ethyl acetate (3×30 mL). The organic phase was dried over Na_2SO_4, filtered and the filtrate was concentrated under reduced pressure at 35 ℃ till silky white crystals present.

^{1}H NMR (DMSO, ppm): 2.10 (s, 6H, CH_3, c) 5.51 (s, 2H, CH, b). FTIR (KBr): 3100 cm^{-1} (OH carboxylic acid); 2940, 1380 cm^{-1} (CH_3); 1749 cm^{-1} (C=O ester); 1076, 1218 cm^{-1} (C-O-C ester). I_L:$[a]_D^{20}$ =-18.8° (ethanol); I_D:$[a]_D^{20}$ =+27.1° (ethanol). Yield: >92%; Purity: ~99.5%.

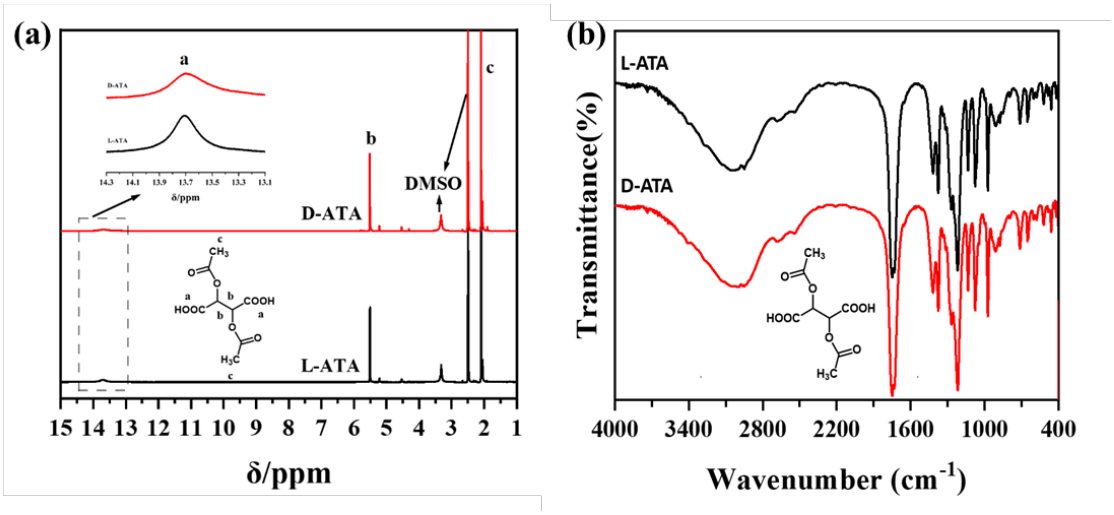


Figure S3. ^{1}H NMR (a) and FTIR (b) spectra of ATA.

Synthesis of 2,3-di-O-acetyltartaric Chloride (ATC). ATA (2.34g) and the equal mole BTC (triphosegene, 2.97g) were stirred in n-hexane (50 mL) and then DMF (3 mL, catalyst) was added dropwise. After the addition of DMF, stirring continued for 30 minutes in the ice-water bath to ensure complete decomposition of BTC. Then, the reaction system was slowly heated to 60 °C. A dark reddish-brown oily byproduct appeared in the lower layer of the phosgene solution. The reaction was maintained at 60 °C until no bubbles were observed. The upper layer became a clear and transparent phosgene solution, which was the L-ATC/n-hexane solution.

ATCs derived from D-ATA and L-ATA were hydrolyzed immediately when facing water in the air while evaporating n-hexane and characterized by FTIR and ^{1}H NMR spectra. So there are no characterizations of the 2,3-di-O-acetyltartaroyl chlorides inthis report. However, there are other reactive phenomena to determine the termination of reaction that the target products ATCs can be dissolved in n-hexane while ATAs couldn't.

Synthesis of TA derived Polyamide-PA6LAT&PA6DAT. To avoid the change of the configuration of the intermediates and obtain the high stereotactic polyamides, interfacial polycondensation was conducted between 1,6-hexanediamine aqueous and ATC hexane solution at 50 ℃. Take PA-6LAT for example, 1,6-hexamethylenediamine

(6.97g, 0.06mol) was completely dissolved in distilled water (50 mL) under stirring at 50 ℃. And acid acceptor triethylamine (0.01 mol) was added to the aqueous phase. The prepared L-ATC in n-hexane (50 mL) was poured into the beaker slowly and stirred for another 30 min at 50 ℃. The Polyamide was collected by filtration and washed well with anhydrous ethanol three times at 50℃. And then dried in a vacuum oven at 60 ℃ for 8h. The preparation of PA6DAT was the same as that of PA6LAT. Yield: >70%.

Table S1. The solubility of PA6LAT and PA6DAT.

Sample	Solvent					
	DMF	NMP	Methanol	DMSO	HFIP	TFA
PA6LAT	-	-	-	+	+	+
PA6DAT	-	-	-	+	+	+

(-) insoluble; (+) soluble. DMF: N,N-dimethylformamide; NMP: N-methylpyrrolidone; DMSO: dimethyl sulfoxide; HFIP: hexafluoroisopropanol; TFA: trifluoroacetic acid.

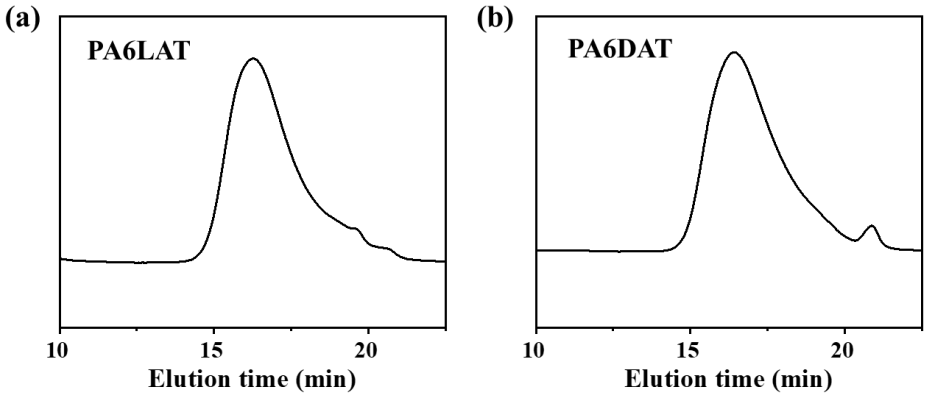


Figure S4. GPC elution profiles of (a) PA6LAT and (b) PA6DAT

Part 2: Photophysical Properties and Theoretical Simulation

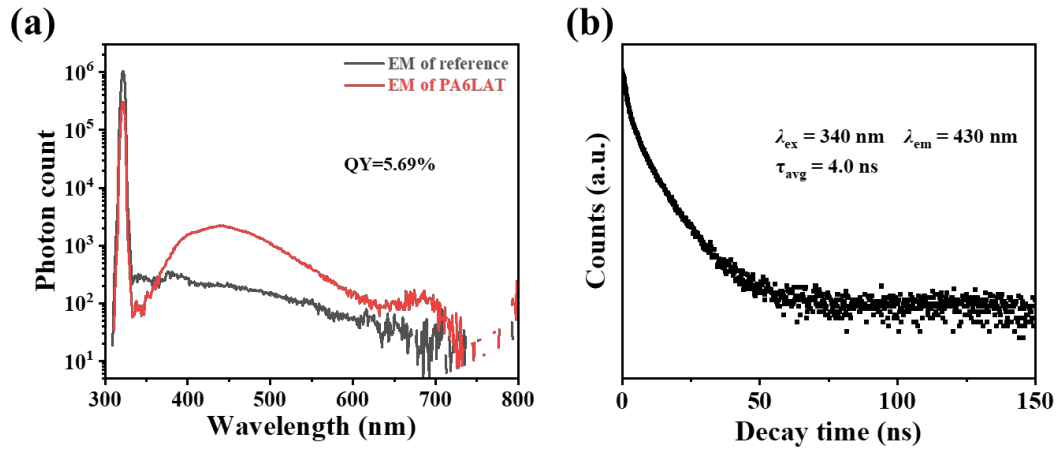


Figure S5. (a) Absolute fluorescence quantum yield and (b) fluorescence lifetime curve of PA6LAT powder.

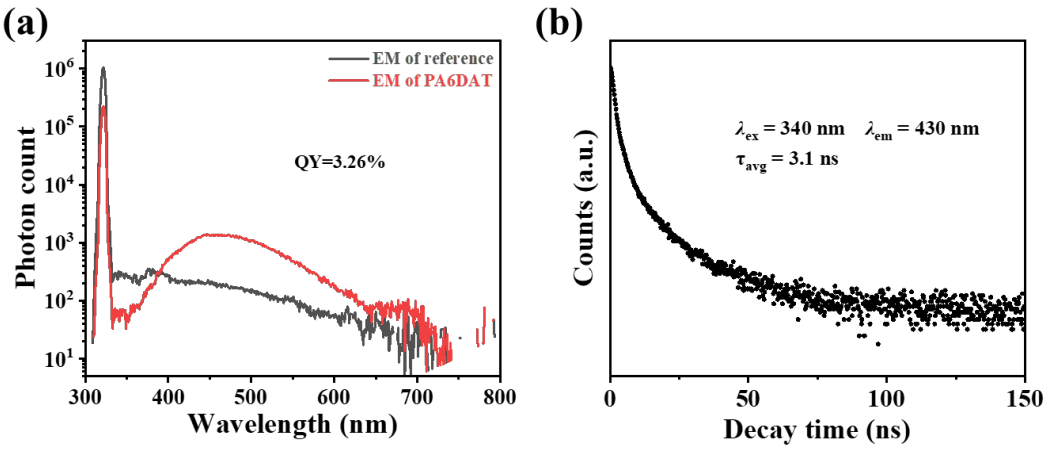


Figure S6. (a) Absolute fluorescence quantum yield and (b) fluorescence lifetime curve of PA6DAT powder.

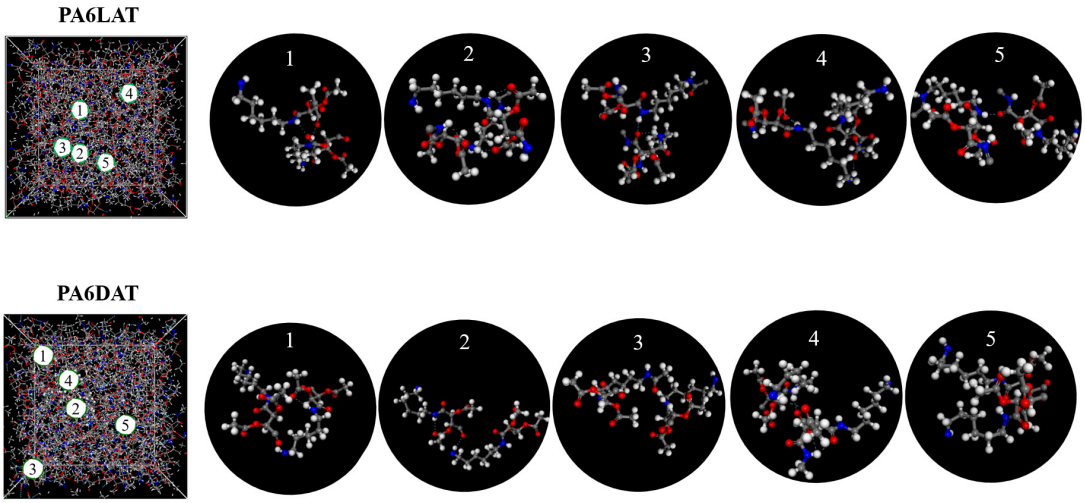


Figure S7 The diagrams of randomly picked five unit-structures with different conformations from the simulated clusters of PA6ATs

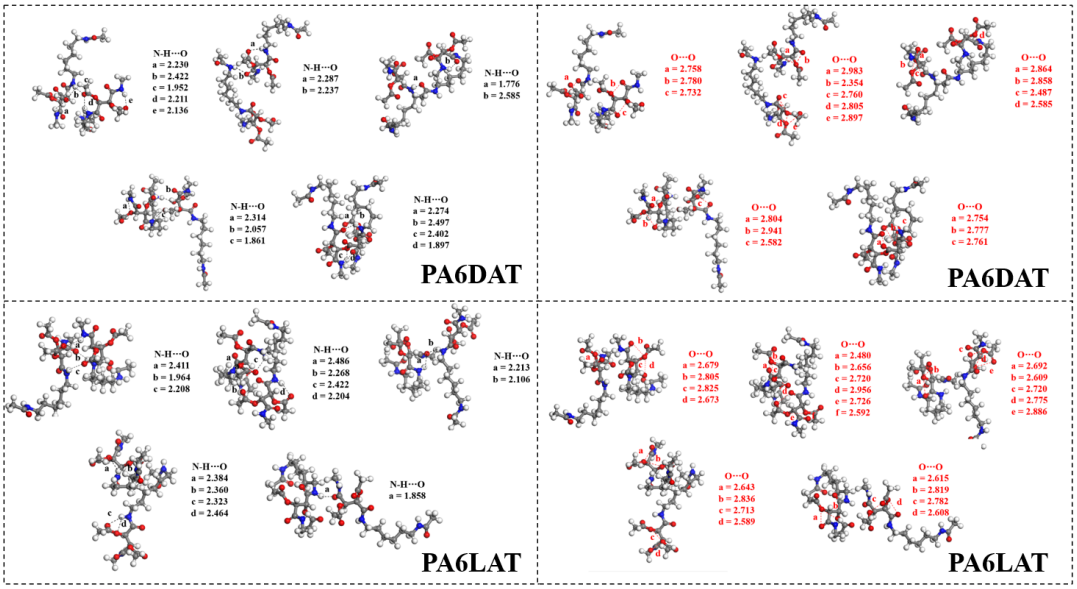


Figure S8 $d_{\text{N-H}\cdots\text{O}}$ and $d_{\text{O}\cdots\text{O}}$ of the randomly picked five unit-structures from the simulated clusters of PA6ATs.

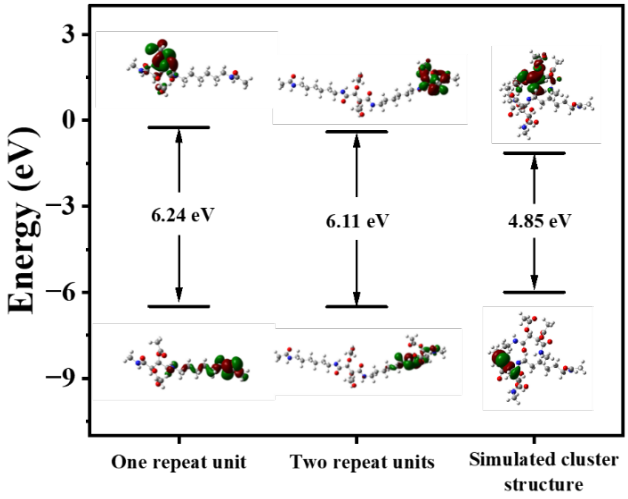


Figure S9. The HOMOs and LUMOs of PA6LAT one repeat unit, two repeat units and simulated cluster structure, and the corresponding energy gaps.

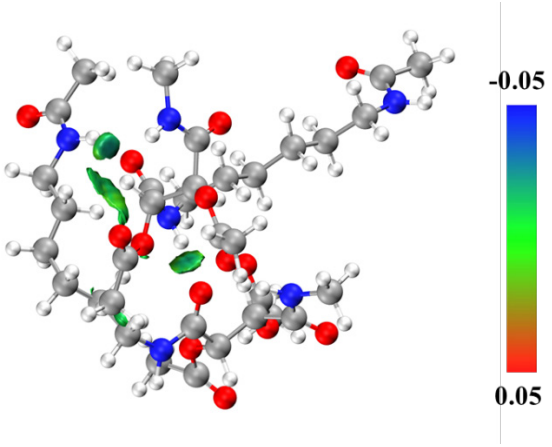


Figure S10. IGMH isosurface of PA6LAT simulated cluster. The blue and green region indicates strong interaction and van der Waals interaction, while the red region indicates prominent repulsive interaction.

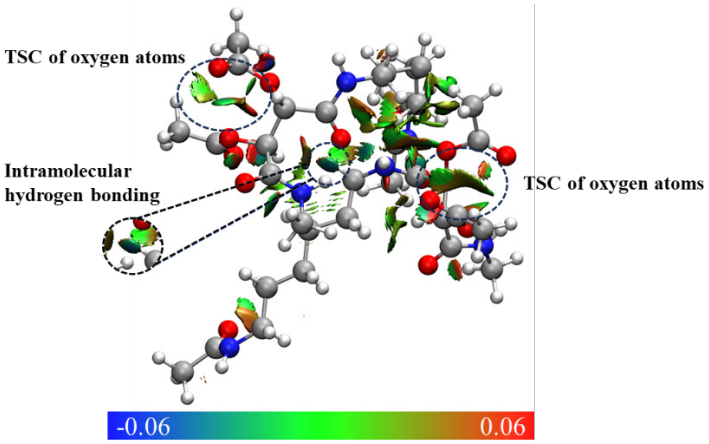


Figure S11. reduced density gradient (RDG) isosurface of PA6LAT simulated cluster. The blue and green region indicates strong interaction and van der Waals interaction, while the red region indicates prominent repulsive interaction.

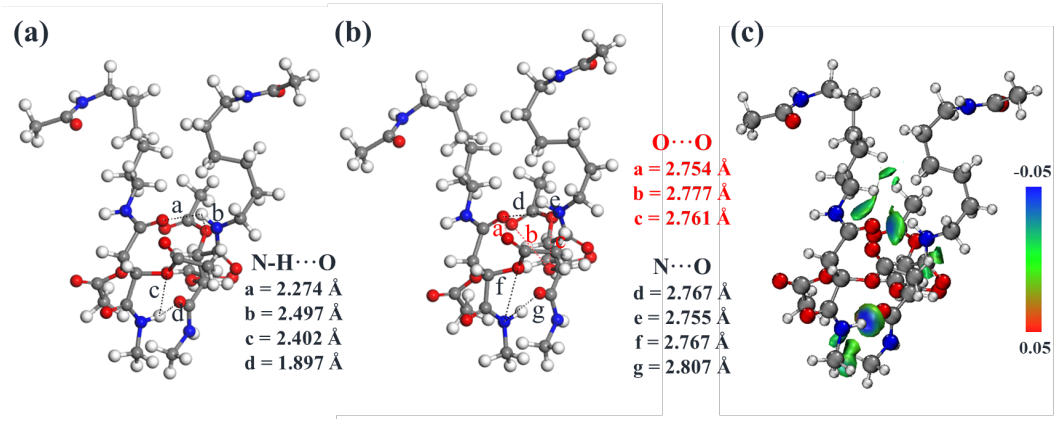


Figure S12. Theoretical calculation of PA6DAT. (a) $d_{\text{H bond}}$ and (b) $d_{\text{O···O}}$ and $d_{\text{N···O}}$ among the simulated cluster. (c) IGMH isosurface of PA6DAT simulated cluster.

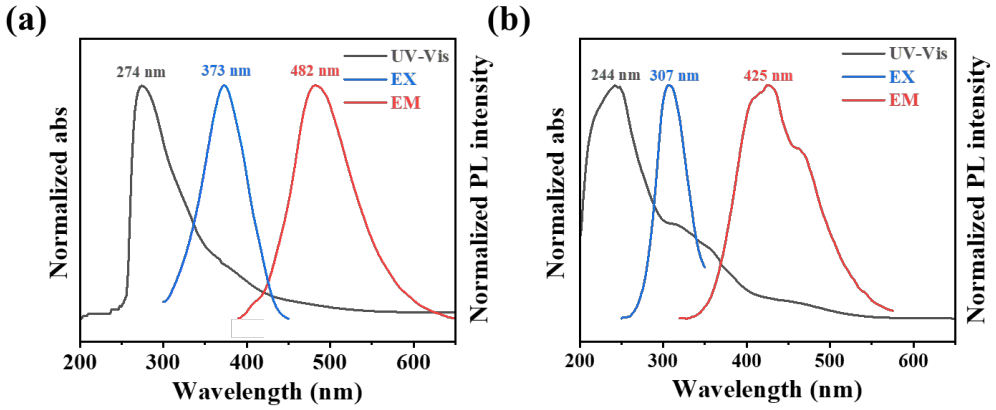


Figure S13. Normalized UV-Vis absorption, excitation and emission spectra of PA6DAT in (a) DMSO solution and (b) HFIP solution. (c = 10 mg/mL)

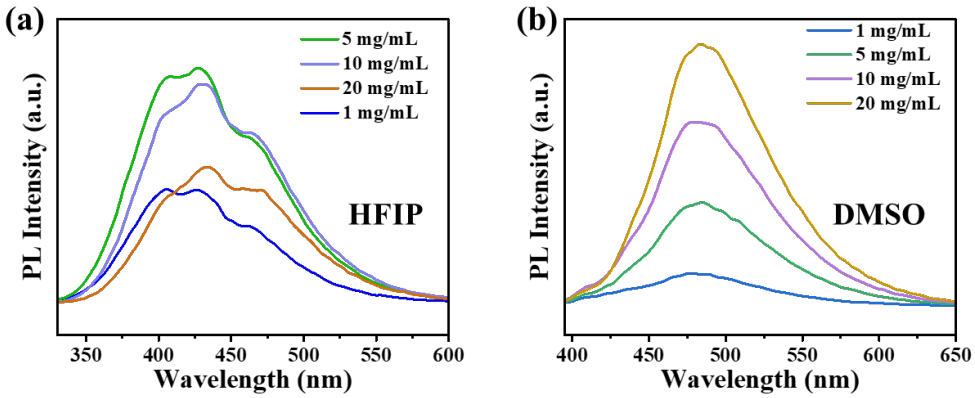


Figure S14. Emission spectra of PA6LAT in solution at high concentrations. (a) HFIP, (b) DMSO.

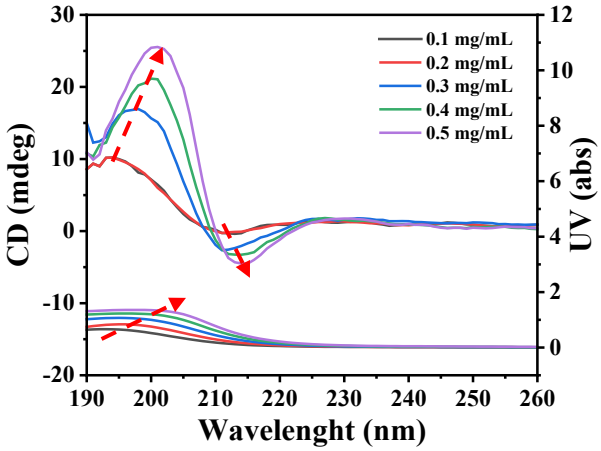


Figure S15. UV-CD spectra of PA6LAT in HFIP solution at different concentrations.

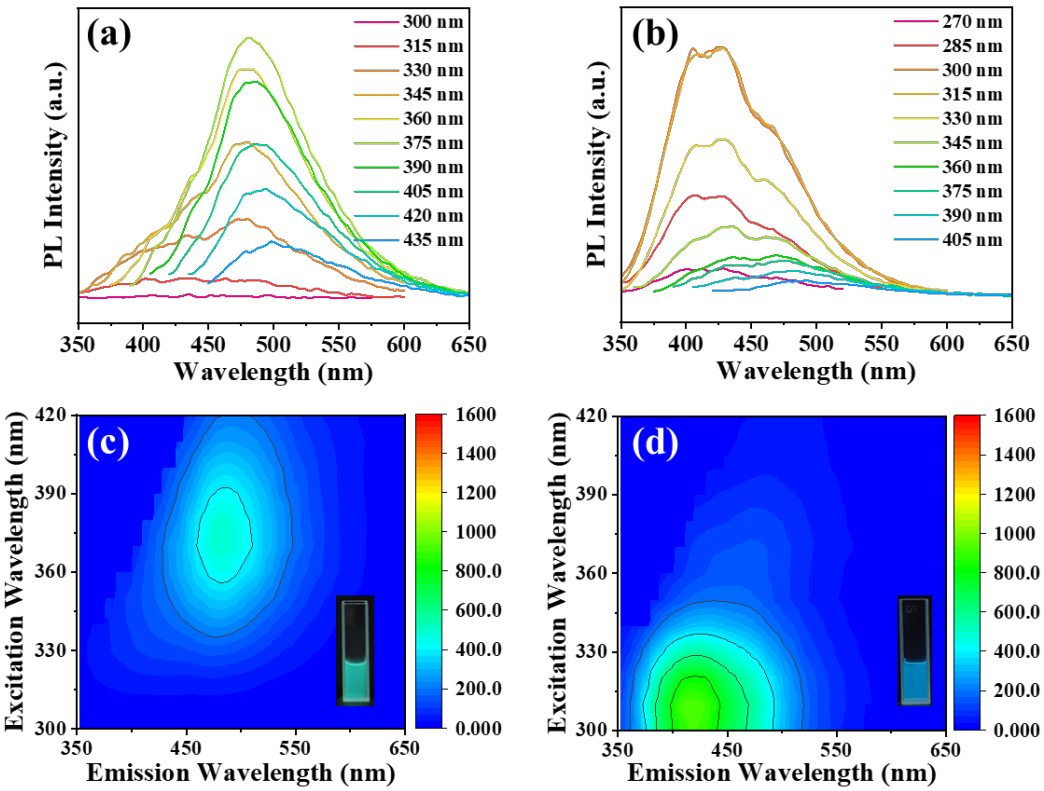


Figure S16. PL spectra at different excitation wavelengths and excitation-emission matrix of PA6DAT in (a,c) DMSO solution and (b,d) HFIP solution.

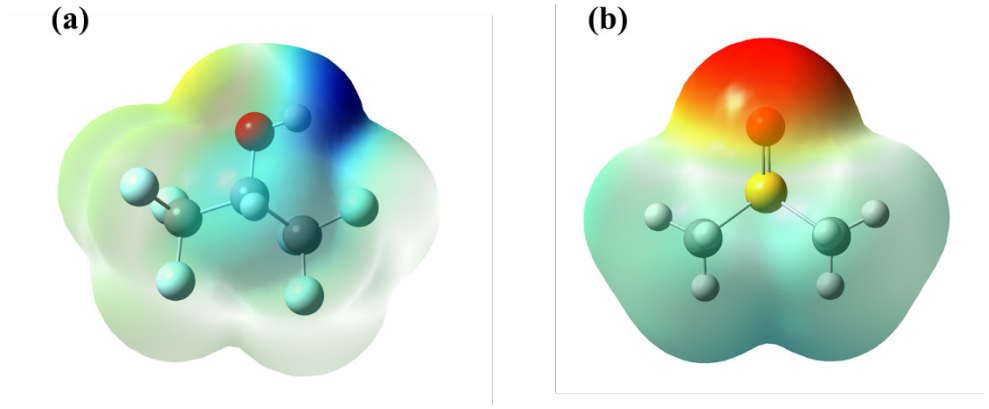


Figure S17. ESP of (a) HFIP and (b) DMSO mapped on the isosurface of electronic density.

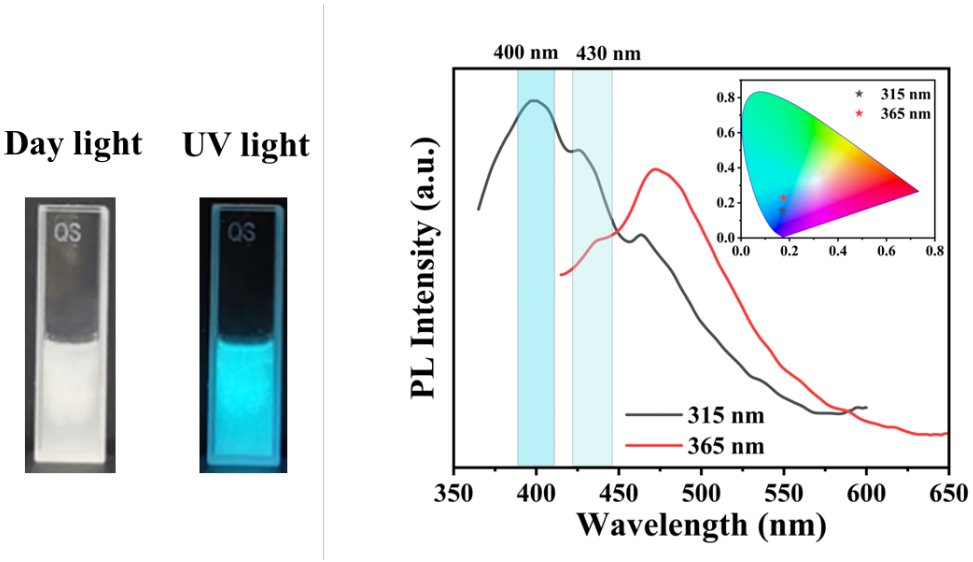


Figure S18. PL spectrum of mixed solution (λ_{ex} = 365 nm) and photographs of adding equimolar HFIP into PA6LAT DMSO solution token under day light and 365 nm UV light.

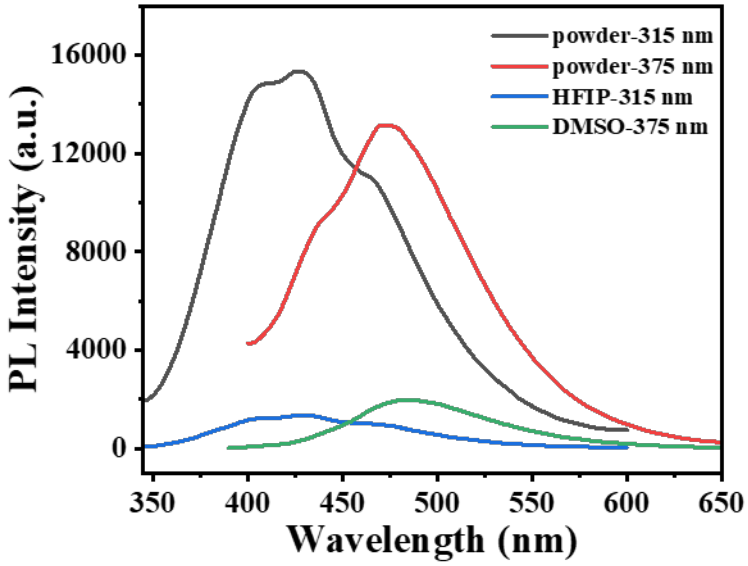


Figure S19. PL spectra of PA6LAT powder at λ_{ex}=315 nm and λ_{ex}=375 nm; the HFIP solution at λ_{ex}=315 nm; and the DMSO solution at λ_{ex}=375 nm.