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Supplementary Information

for

Hierarchical Chiral Amplification via Grafting and Co-assembly in Flexible Polymers for Full-Color Circularly Polarized Luminescence

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1. Materials

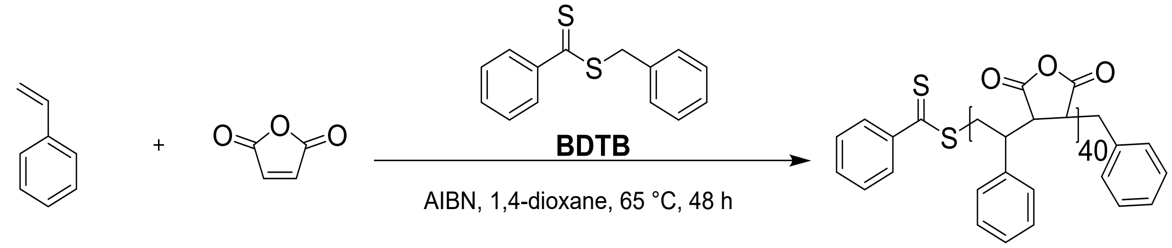
Maleic anhydride (**MA**) (>98%, Adamas), styrene (**ST**) (>99.5%, Aladdin), 2,2’-azobis(isobutyronitrile) (AIBN) (99%, Macklin), benzyl benzodithioate (BDTB) (98%, Leyan), *D*-phenylalanine (***D*-Phe**) (98%, Aladdin), *L*-phenylalanine (***L*-Phe**) (98%, Aladdin), triethylamine (TEA) (99.5%, Energy), 1,4-dioxane (super dry, Innochem), *N*,*N*-Dimethylformamide (DMF) (99.9%, Energy), concentrated hydrochloric acid (HCl) (36%-38%, Bohua), methanol (spectral grade, 99.9%, Alfa Aesar), water (Wahaha), 4,4'-bis(2-sulfostyryl)biphenyl disodium salt (**CBS**) (97%, Macklin), Berberine hydrochloride (**BCH**) (97%, Heowns), 2',7'-dichlorofluorescein sodium salt (**DCF**) (98%, Innochem), Rhodamine B (**RhB**) (97%, Bide), and tetra-(4-pyridylphenyl)ethylene (**TPY**) (98%, Mreda). **ST** was redistilled, **MA** was purified by sublimation and 2,2’-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol for three times before use.

2. Methods

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker spectrometers (400 MHz) at 25 °C. FT-IR spectra of samples were obtained between 4000 and 400 cm^{-1} with a Bruker FT-IR spectrometer (TENSOR II) using the KBr pellet method. SEM images were recorded on a Zeiss MERLIN Compact. UV-Vis absorption spectra was measured on an Agilent Cary 60 spectrophotometer. PL spectra, Luminescence quantum yield (Φ_{PL}) and fluorescence lifetime were measured on Edinburgh FS5. CD spectra were collected on MOS-450 at 25 °C. CPL measurements were performed at 25°C using a JASCO CPL-300 and measurements were taken every 90° to avoid the influence of linear dichroism. The GPC analysis for SMA was carried out using a Waters Alliance e2695 Separations Module equipped with a 2414 Refractive Index Detector. The mobile phase was tetrahydrofuran (THF) at a flow rate of 1.0 mL/min. The column oven temperature was maintained at 30 °C.

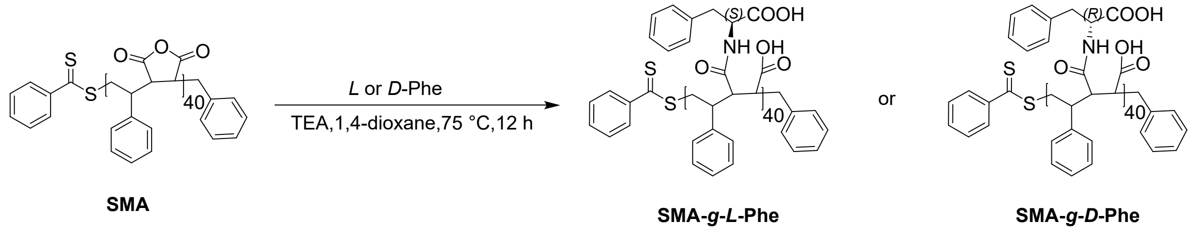
Three GPC columns were connected in series: WAT045920, WAT045935, and WAT045950, and polystyrene samples as the standards in the calibration of the molar masses. The molecular masses and their distribution for **SMA-*g*-*L*(*D*)-Phe** were determined by GPC in DMF solution at 50 °C with an elution rate of 1.0 mL/min on an Agilent Technologies 1260 Infinity II GPC system equipped with a refractive index detector. The apparent molecular weights were determined on a single Polargel-M column using linear poly(methyl methacrylate) as standards. Fluorescence images were measured by Spinning Disk Confocal Super Resolution Microscope SpinSR10 IXplore and analyzed using Image J.

3. Polymers synthesis



ST **MA** **SMA**

Synthesis of SMA. The synthesis of alternating copolymer **SMA** by RAFT polymerization was described as follows: a 20 mL 1,4-dioxane solution of **ST** (1.04 g, 10.0 mmol), **MA** (980.06 mg, 10.0 mmol), RAFT agent **BDTB** (61.09 mg, 0.25 mmol), and AIBN (7.38 mg, 0.045 mmol) was degassed by three freeze−pump−thaw cycles and backfilled with argon gas. The solution was stirred at 65 °C for 48 h and poured into anhydrous diethyl ether to precipitate the produced polymer. Then, the precipitated terpolymer was purified by repeated precipitations from THF into petroleum ether three times. Finally, the obtained polymer was dried under vacuum at 40 °C for 24 h, yielding **SMA** as a pink powder solid.



Synthesis of SMA-*g*-*L*(*D*)-Phe. The synthesis of grafting polymer **SMA-*g*-*L(D)*-Phe** are the same, taking **SMA-*g*-*L*-Phe** as an example, was described as follows: a mixture of copolymer **SMA** (202.2 21 mg,1.0 mmol), ***L*-Phe** (330.38 mg, 2.0 mmol) and 825 µL triethylamine (TEA) were added into a 100 mL Schlenk flask containing 20 mL 1,4-dioxane. The reaction mixture was stirred at 75 °C for 12 h. Then, the reaction system was evaporated to afford the mixture, and the residue was dissolved in DMF and filtrated. The filtrate was acidified with HCl aqueous solution (1 M, 6 mL), a white solid is obtained by filtration. Then, the solid was purified by repeated precipitations from acetone into *n*-Pentane. Finally, the obtained polymer was dried under vacuum at 40 °C for 24 h to afford **SMA-*g*-*L*-Phe** as a white powder solid.

4. General preparation methods for co-assembled (Dyes@*L*(*D*)-Phe/ SMA-*g*-*L*(*D*)-Phe) films

First, the **SMA-*g*-*L*(*D*)-Phe** (1.11 mg) was pretreated with trimethylamine in methanol solution and concentrated, then dissolved in methanol (0.9 mL) containing different concentrations of fluorescents (0.055 mg/mL for **CBS**, **BCH**, **RhB**, **TPY** and 0.11 mg/mL for **DCF**, respectively). After that, a 7 mg/mL aqueous solution of ***L*(*D*)-Phe** (0.1 mL) was added dropwise to the above solution and incubated at room temperature for 24 h. Finally, the co-assembly solution was spin-coated (250 rpm for 45 s) onto a 2 cm × 1 cm × 1 mm quartz substrate and allowed to evaporate-e at 13 °C with 30% RH.

5. Preparation methods for information encryption

The **TPY@*L*(*D*)-Phe/SMA-*g*-*L*(*D*)-Phe**-containing solution was poured into a stamp engraved with the emblem of "*Nankai University*". After the stamp was fully wetted, it was pressed onto medium-speed qualitative filter paper. Upon solvent evaporation, the system self-assembled to form a fluorescent logo exhibiting CPL emission. Subsequently, half of the fluorescent pattern was covered with paper, while the other half was exposed to HCl vapor for 60 s using a cotton swab soaked in HCl solution, producing a fluorescence pattern with a distinct yellow–green contrast.

6. Characterization results related to the co-assemblies

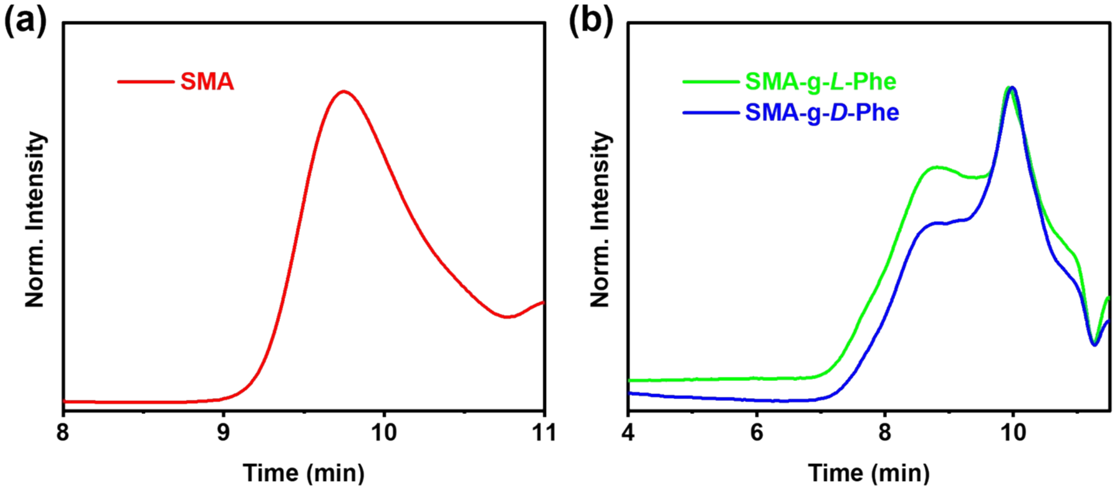


Figure S1. GPC spectra of (a) **SMA** and (b) **SMA-*g*-*L*(*D*)-Phe**.

Table S1. GPC results of prepared polymers

Sample	M_n (Daltons)	M_w (Daltons)	M_p (Daltons)	M_z (Daltons)	M_{z+1} (Daltons)	PDI
SMA	6129	7190	7536	8250	9251	1.17
SMA-*g*-*L*-Phe	586	5861	624	25108	44162	10.00
SMA-*g*-*D*-Phe	560	4706	567	21092	39052	8.40

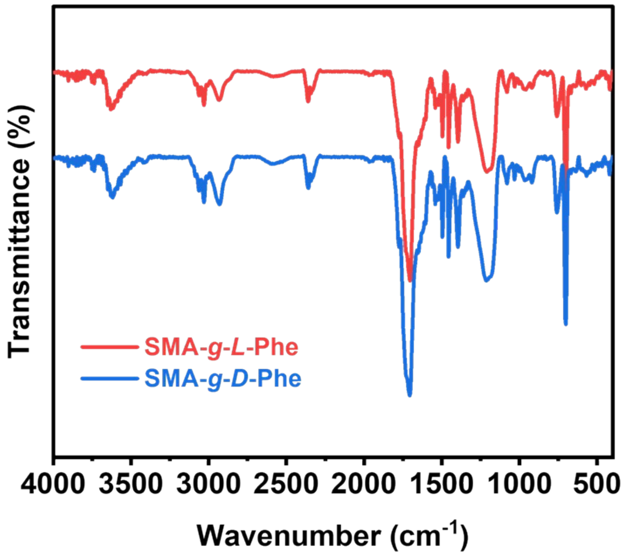


Figure S2. FT-IR spectra of **SMA** and **SMA-*g*-*L*(*D*)-Phe**.

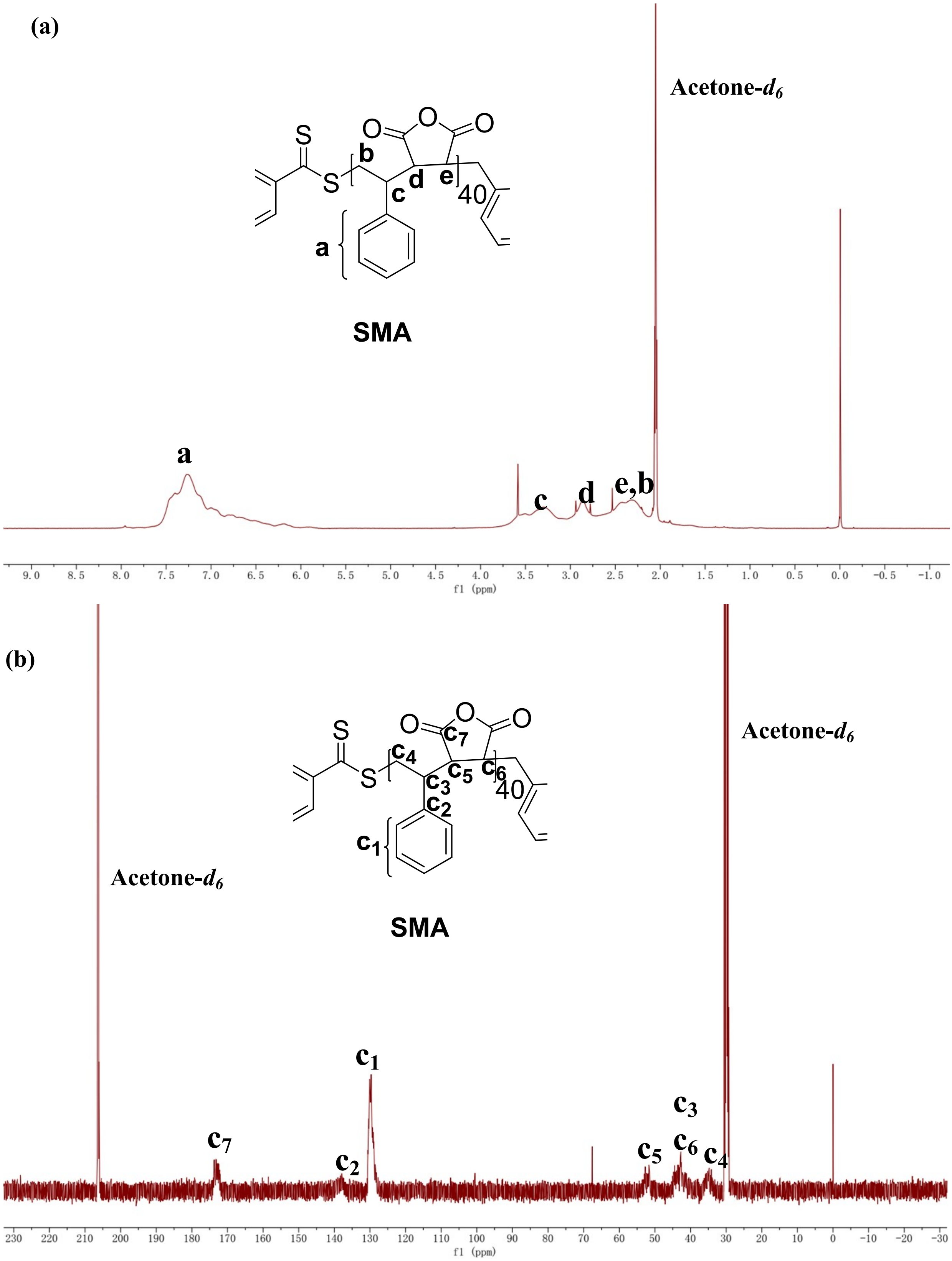


Figure S3. (a) ^{1}H NMR (400 MHz, Acetone-d_6, 298 K) and (b) ^{13}C NMR (121 MHz, Acetone-d_6, 298 K) of **SMA**.

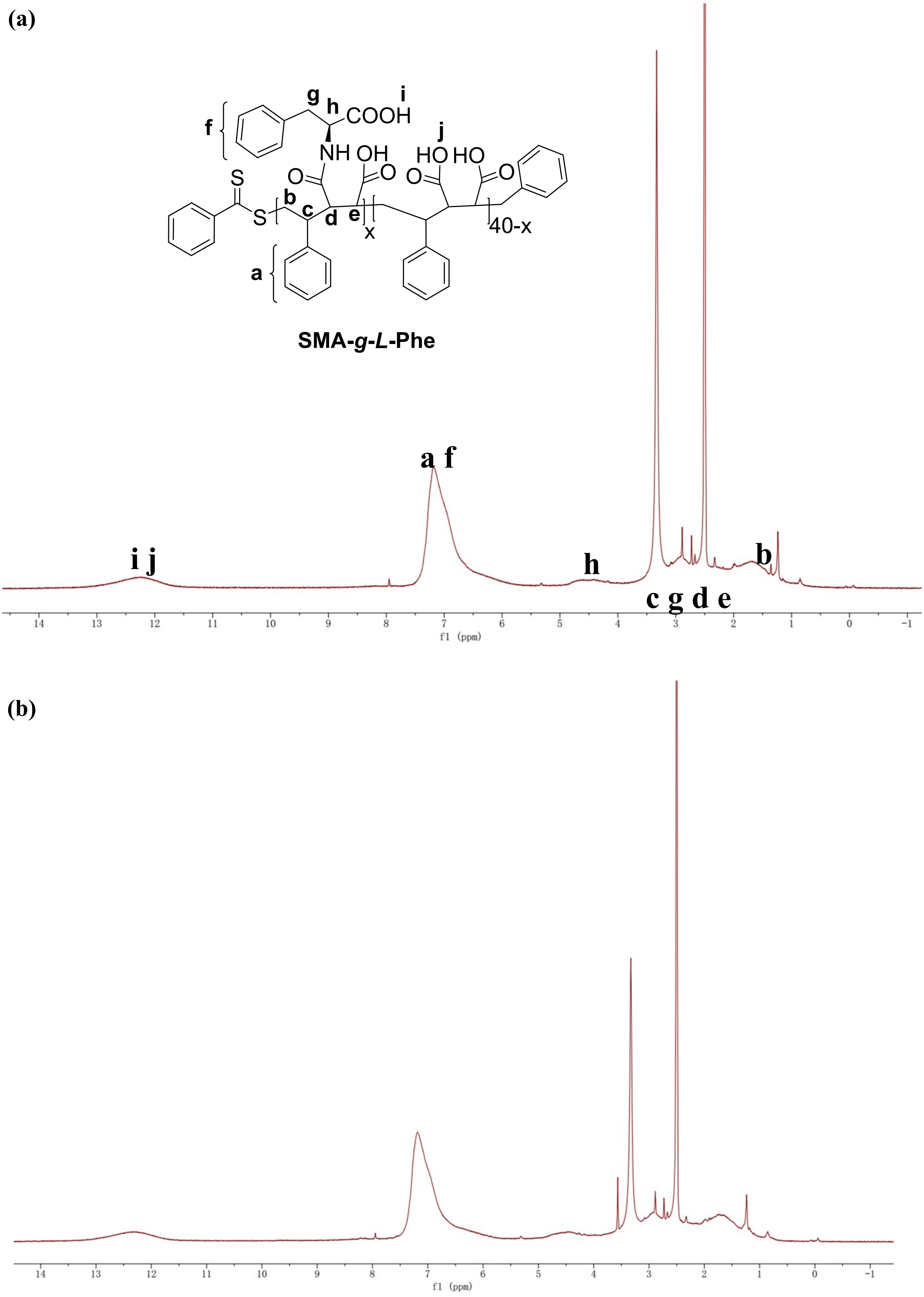


Figure S4.^{1}H NMR (400 MHz, DMSO-*d*, 298 K) of (a) **SMA-*g*-*L*-Phe** and (b) **SMA-*g*-*D*-Phe**.

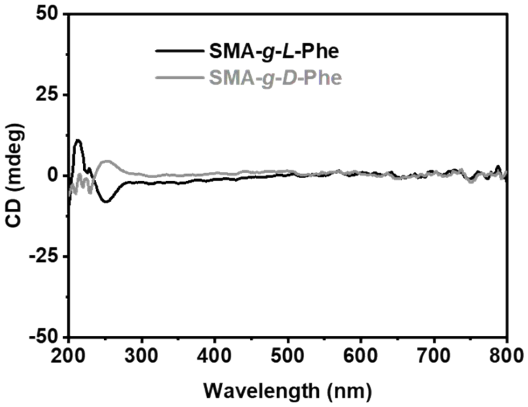


Figure S5. CD Spectra of **SMA-*g*-*L*(*D*)-Phe** films.

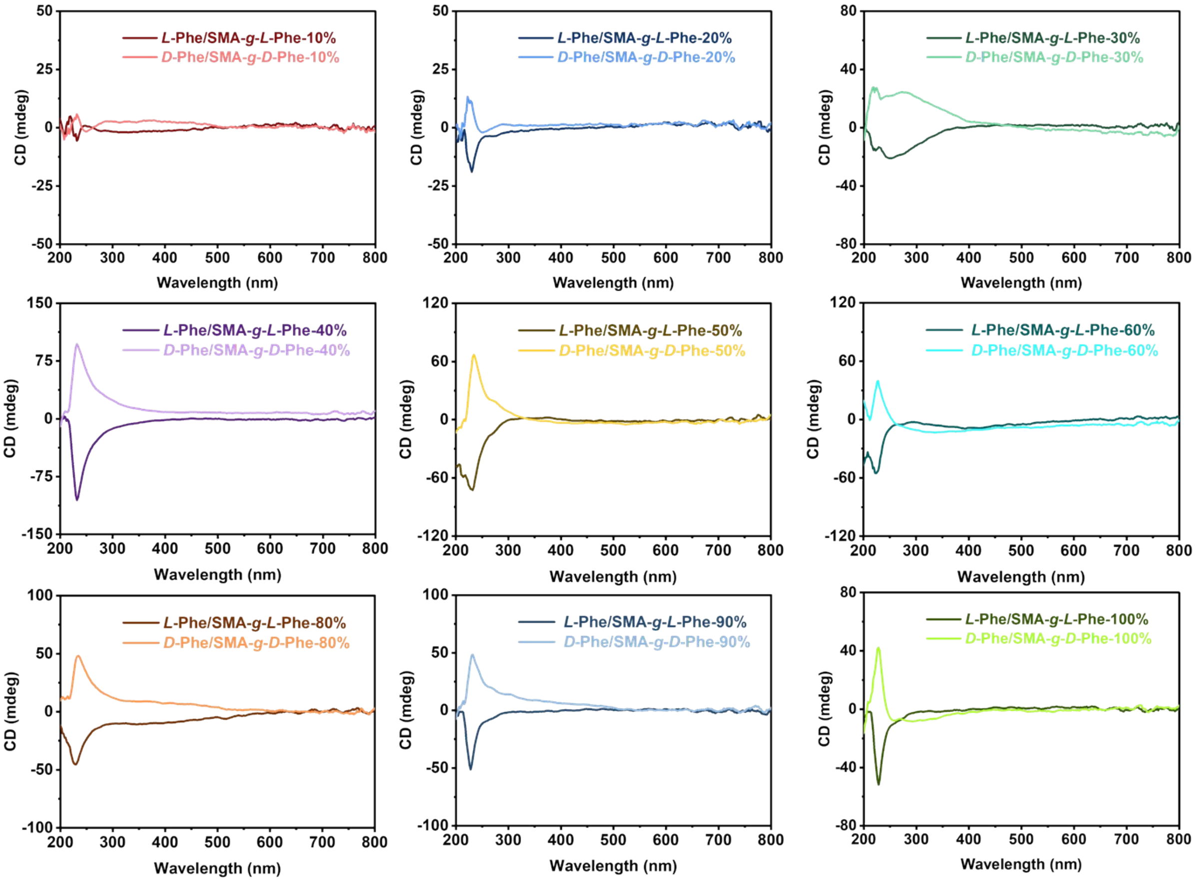


Figure S6. CD Spectra of ***L*(*D*)-Phe/ SMA-*g*-*L*(*D*)-Phe** films with gradient weight-doping ratios.

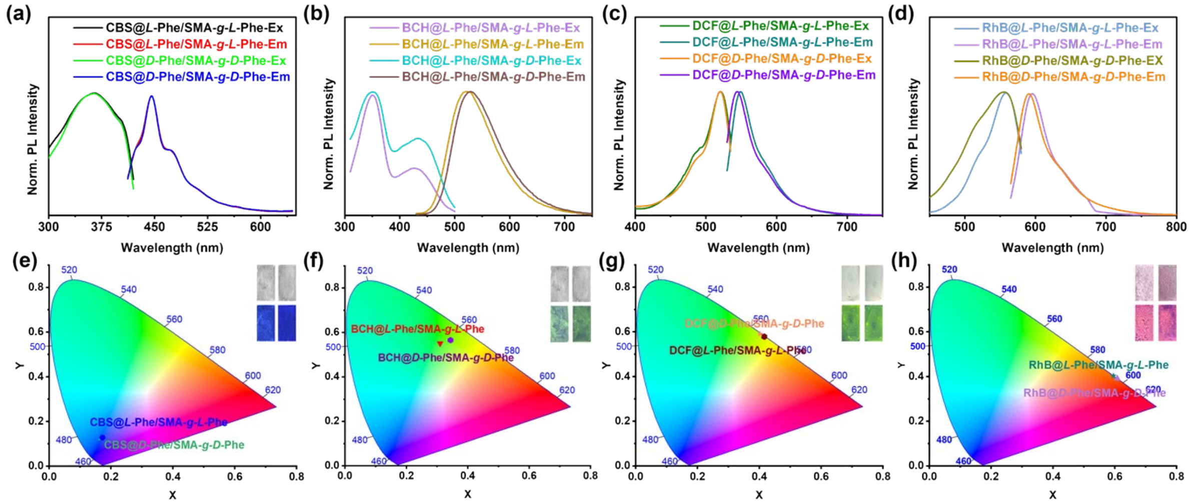


Figure S7. Normalized excitation (left) and emission (right) spectra of (a) **CBS@*L*(*D*)-Phe/SMA-*g*-*L*(*D*)-Phe**, (b) **BCH@*L*(*D*)-Phe/SMA-*g*-*L*(*D*)-Phe**, (c) **DCF@*L*(*D*)-Phe/SMA-*g*-*L*(*D*)-Phe** and (d) **RhB@*L*(*D*)-Phe/SMA-*g*-*L*(*D*)-Phe** films. CIE coordinate of (e) **CBS@*L*(*D*)-Phe/SMA-*g*-*L*(*D*)-Phe**, (f) **BCH@*L*(*D*)-Phe/SMA-*g*-*L*(*D*)-Phe**, (g) **DCF@*L*(*D*)-Phe/SMA-*g*-*L*(*D*)-Phe** and (h) **RhB@*L*(*D*)-Phe/SMA-*g*-*L*(*D*)-Phe** films. Insert: Images of assembled films taken under ambient light (top) and UV 365 nm irradiation (bottom).

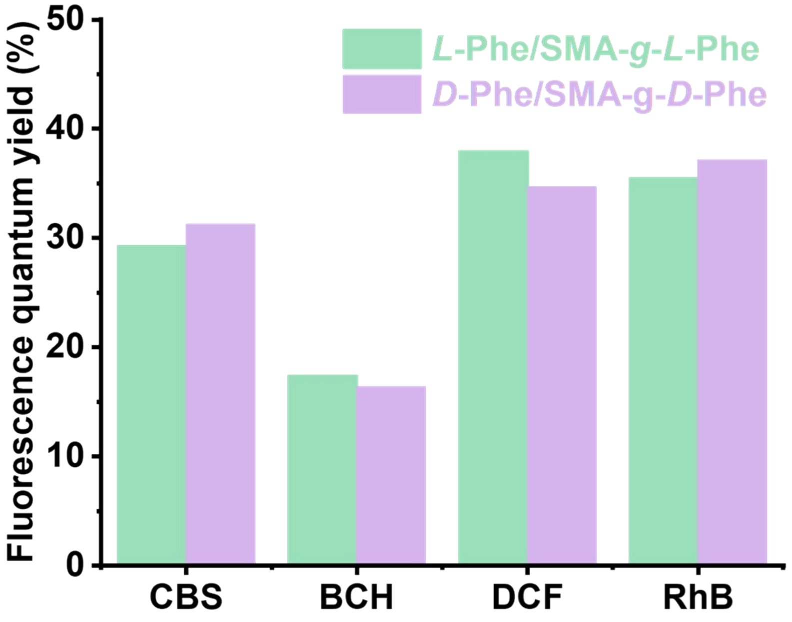


Figure S8. The fluorescence quantum yield (Φ_{PL}) of the co-assembled films

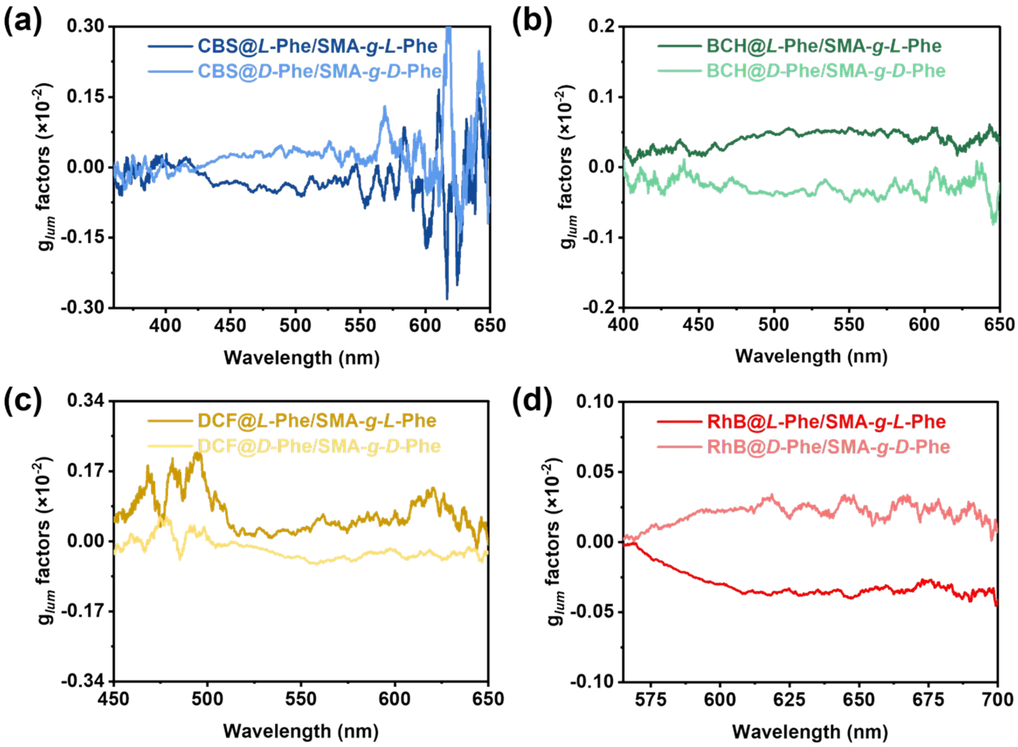


Figure S9. g_{lum} spectra of the co-assembled films. (a) **CBS@*L*(*D*)-Phe/SMA-*g*-*L*(*D*)-Phe**, (b) **BCH@*L*(*D*)-Phe/SMA-*g*-*L*(*D*)-Phe**, (c) **DCF@*L*(*D*)-Phe/SMA-*g*-*L*(*D*)-Phe** and (d) **RhB@*L*(*D*)-Phe/SMA-*g*-*L*(*D*)-Phe**.

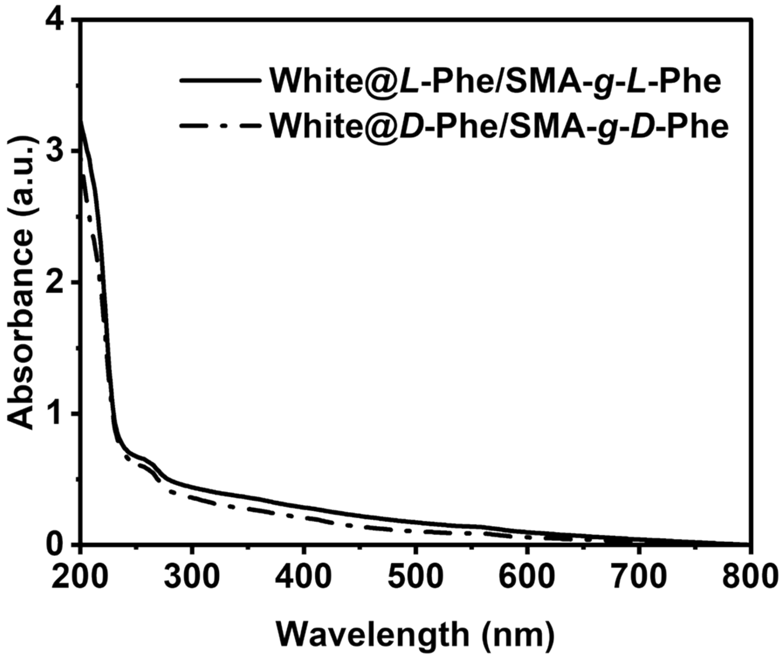


Figure S10. UV-vis absorption spectra of **White@*L*(*D*)-Phe/SMA-*g*-*L*(*D*)-Phe** films.

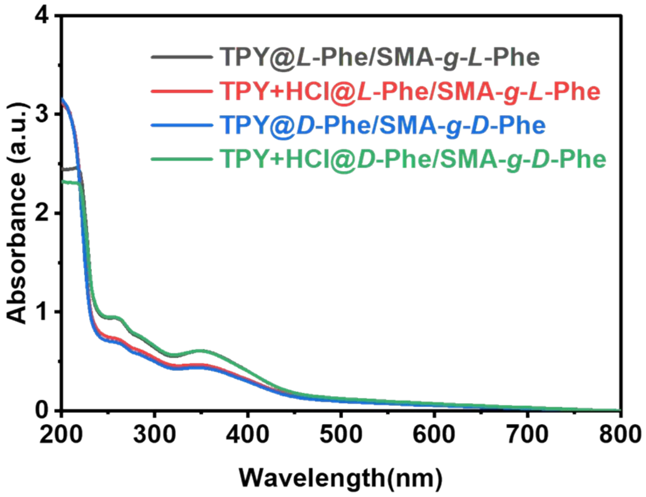


Figure S11. UV-vis absorption spectra of **TPY@*L*(*D*)-Phe/SMA-*g*-*L*(*D*)-Phe** films before and after treatment of HCl vapor.

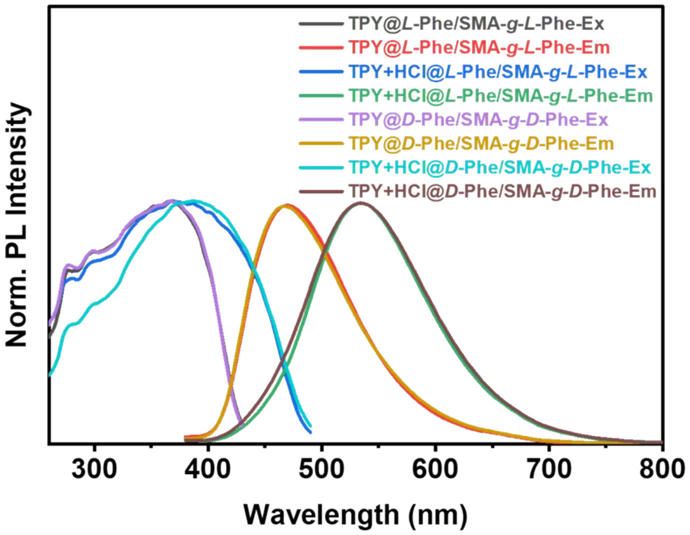


Figure S12. Normalized excitation (left) and emission (right) spectra of **TPY@*L*(*D*)-Phe/SMA-*g*-*L*(*D*)-Phe** films before and after treatment of HCl vapor.

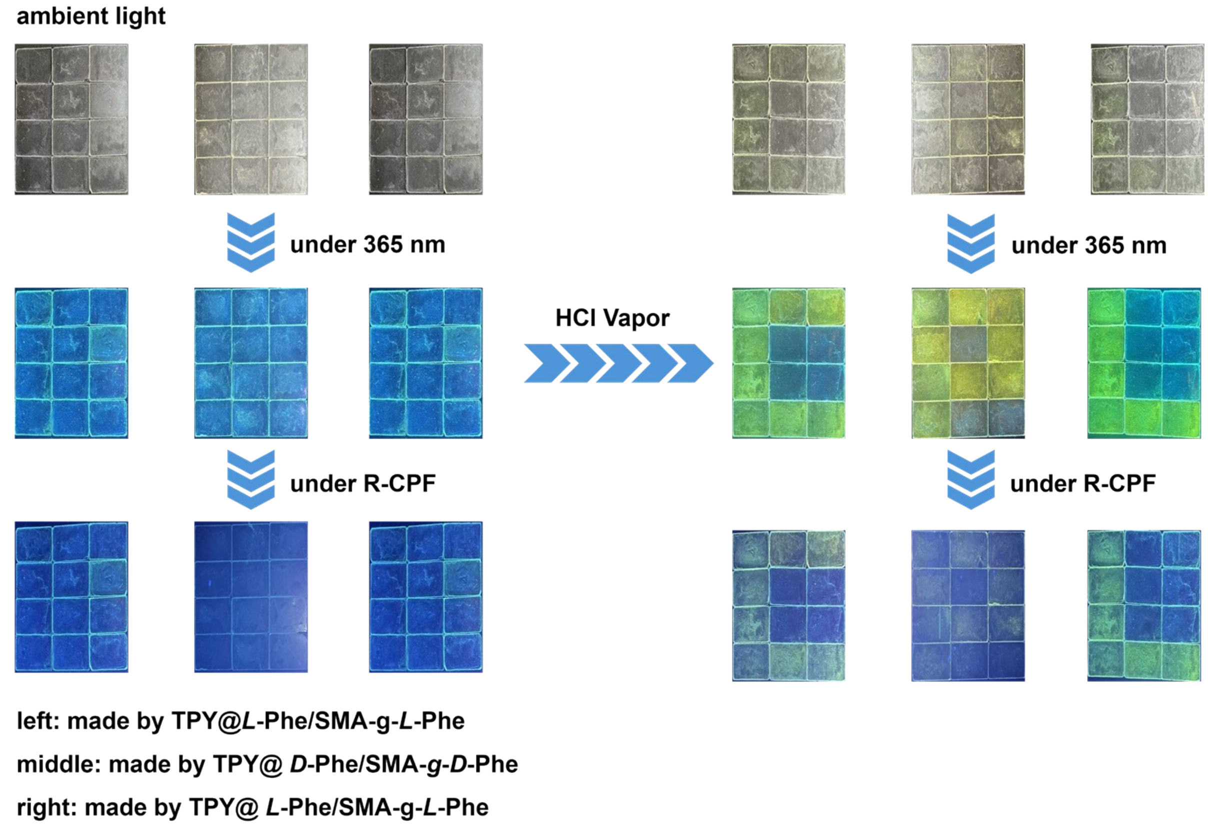


Figure S13. Fluorescence color change and information encryption demonstration of **TPY@*L*(*D*)-Phe/SMA-*g*-*L*(*D*)-Phe** films under HCl vapor.

Under ambient light, all films appeared nearly identical and under 365 nm excitation all films emitted blue fluorescence. When viewed through a right-handed circular polarizing filter (*R*-CPF), films derived from ***L*-Phe/SMA-*g*-*L*-Phe** (left and right) appeared brighter due to their preferential right-hand circularly polarized luminescence (*R*-CPL), while the ***D*-Phe/SMA-*g*-*D*-Phe** (middle) appeared darker. Upon exposure to HCl vapor, the emission color switched from blue to yellow, with distinct fluorescent patterns corresponding to the letters "C", "P" and "L". Subtle differences in film appearance emerged after treatment, likely reflecting variations in HCl vapor exposure time. Viewed through the *R*-CPF, the "C" and "L" patterns remained clearly discernible, whereas the "P" pattern was markedly dimmer, consistent with its preference in left-hand circularly polarized luminescence (*L*-CPL) character. Upon HCl vapor exposure, the film emission shifted from blue to yellow, revealing well-defined fluorescent patterns corresponding to the letters "C", "P" and "L". Minor variations in appearance were observed, likely arising from differences in vapor exposure time. When viewed through *R*-CPF, the "C" and "L" patterns remained clearly visible, whereas the "P" pattern appeared substantially dimmer, consistent with its left-handed CPL (*L*-CPL) preference.

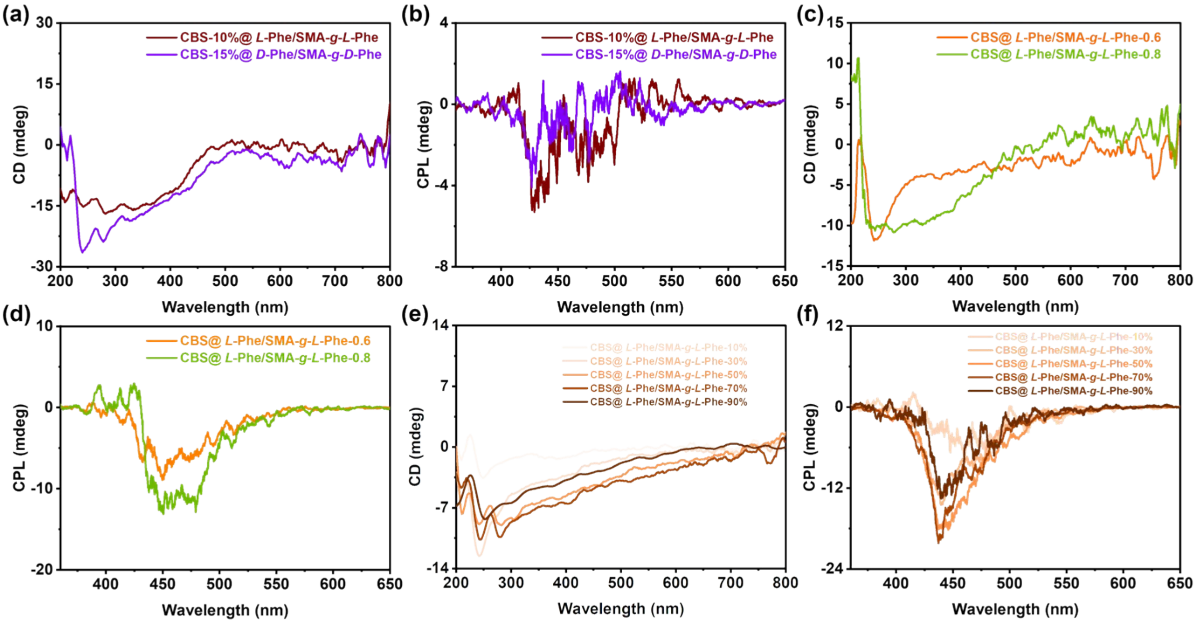


Figure S14. (a) CD and (b) CPL spectra of **CBS@*L*-Phe/SMA-*g*-*L*-Phe** films (the doping ratios of **CBS** were 10% and 15% wt, respectively); (c) CD and (d) CPL spectra of **CBS@*L*-Phe/SMA-*g*-*L*-Phe** films (the polymer concentrations were 0.6 and 0.8 mg/mL, respectively.); (e) CD and (f) CPL spectra of **CBS@*L*-Phe/SMA-*g*-*L*-Phe** films (the doping ratios of ***L*-Phe** were from 10% to 90% wt).Note: the doping percentages of **CBS** and ***L*-Phe** are defined as their mass ratios relative to **SMA-*g*-*L*-Phe**.