Supplementary Information (SI) for Nanoscale.

Supporting Information

Multicolor and Sign-Invertible Circularly Polarized Luminescence from Nonchiral Charge-Transfer Complexes Assembled with *N*-Terminal Aromatic Amino Acids

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Experimental section

Materials

All reagents and solvents were used as received without further purification. *N*,*N*-dimethylformamide (DMF), Fmoc-*L*-alanine (**^{L}Ala**), Fmoc-*D*-alanine (**^{D}Ala**), Fmoc-*L*-phenylalanine (**^{L}Phe**), Fmoc-*D*-phenylalanine (**^{D}Phe**), Fmoc-*L*-tyrosine (**^{L}Tyr**) and Fmoc-*L*-tyrosine (**^{D}Tyr**) were purchased from Macklin. Naphthalene (**D1**), anthracene (**D2**), phenanthrene (**D3**), benzo[*a*]phenanthrene (**D4**), triphenylene (**D5**) and 1,2,4,5-tetracyanobenzene (**TCNB**) were purchased from Bore. All water used in this work was deionized water which obtained from Titan.

Preparation of assemblies

Self-assembly of different samples were triggered by a nanoprecipitation method. Taking the **^{L}Phe**/**D1**/**TCNB** assemblies as an example, **^{L}Phe** (2.17 mg, 5.6 mmol), **D1** (0.72 mg, 5.6 mmol) and **TCNB** (1 mg, 5.6 mmol) were dissolved in DMF (50 μL) by vigorous shaking in a septum-capped 5 mL glass vial. Then, by adding water (950 μL) into the mixture, followed by aging at room temperature for at least 24 h, a colloidal suspension was eventually obtained.

Characterization

UV–vis spectra were recorded on a Shimadzu UV-2600i spectrometer (Shimadzu, Japan) at room temperature in a 10 mm quartz cell. Fluorescence spectra were measured using a Perkin Elmer LS 55 spectrometer (Perkin Elmer, America). Circular dichroism (CD) and circularly polarized luminescence (CPL) spectra of the suspension and solution samples were measured in quartz cuvettes (light path length 1 mm) on JASCO J-810 and JASCO CPL-300 spectrophotometers (JASCO, Japan), respectively. Scanning electron microscopy (SEM) was performed on a S-4800 microscope (Hitachi, Japan) with an accelerating voltage of 10 kV. One drop of the as-prepared suspension samples was deposited on a polished silicon wafer, followed by drying and coating with a thin layer of Au to enhance the contrast. Fourier transform infrared (FTIR) spectra were measured on IRAffinity-1 Fourier infrared spectrometer (Shimadzu, Japan). Powder X-ray diffraction (XRD) data were measured on an Ultima IV X-ray diffractometer (Rigaku, Japan) operated in 2θ range from 3° to 30.0° at room temperature.

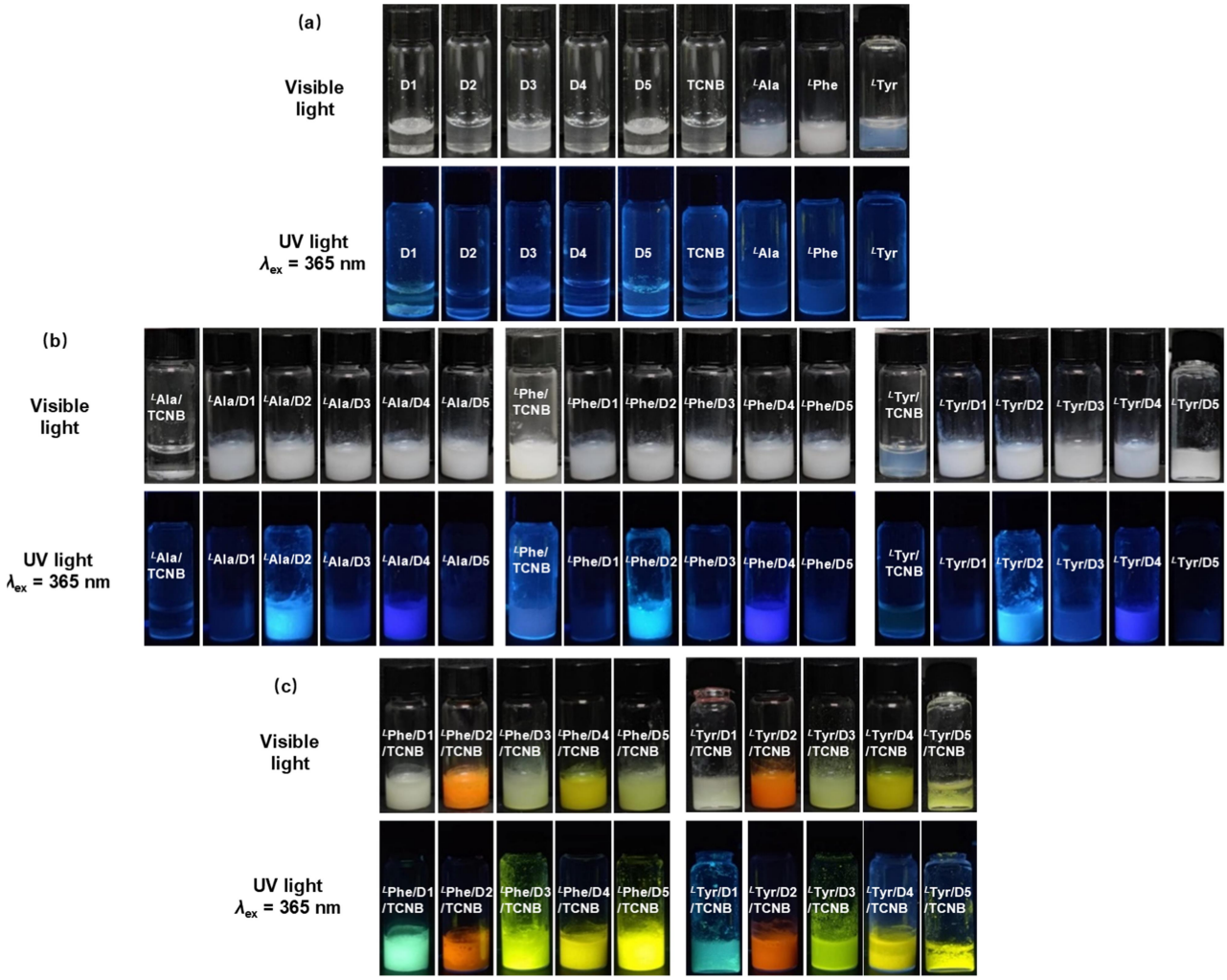

Fig. S1 Photographs of (a) individual **D1-5**, **TCNB**, **^{L}Ala**, **^{L}Phe** and **^{L}Tyr** (5.6 mM) assemblies, (b) binary assemblies of **^{L}Ala/TCNB**, **^{L}Ala/D1-5**, **^{L}Phe/TCNB**, **^{L}Phe/D1-5**, **^{L}Tyr/TCNB** and **^{L}Tyr/D1-5** (5.6 mM:5.6 mM), and (c) ternary assemblies of **^{L}Phe/D1-5/TCNB** and **^{L}Tyr/D1-5/TCNB** (5.6 mM:5.6 mM:5.6 mM) formed in DMF/H_2O (1/19, *v*/*v*) under visible light and UV light (λ_{ex} = 365 nm).

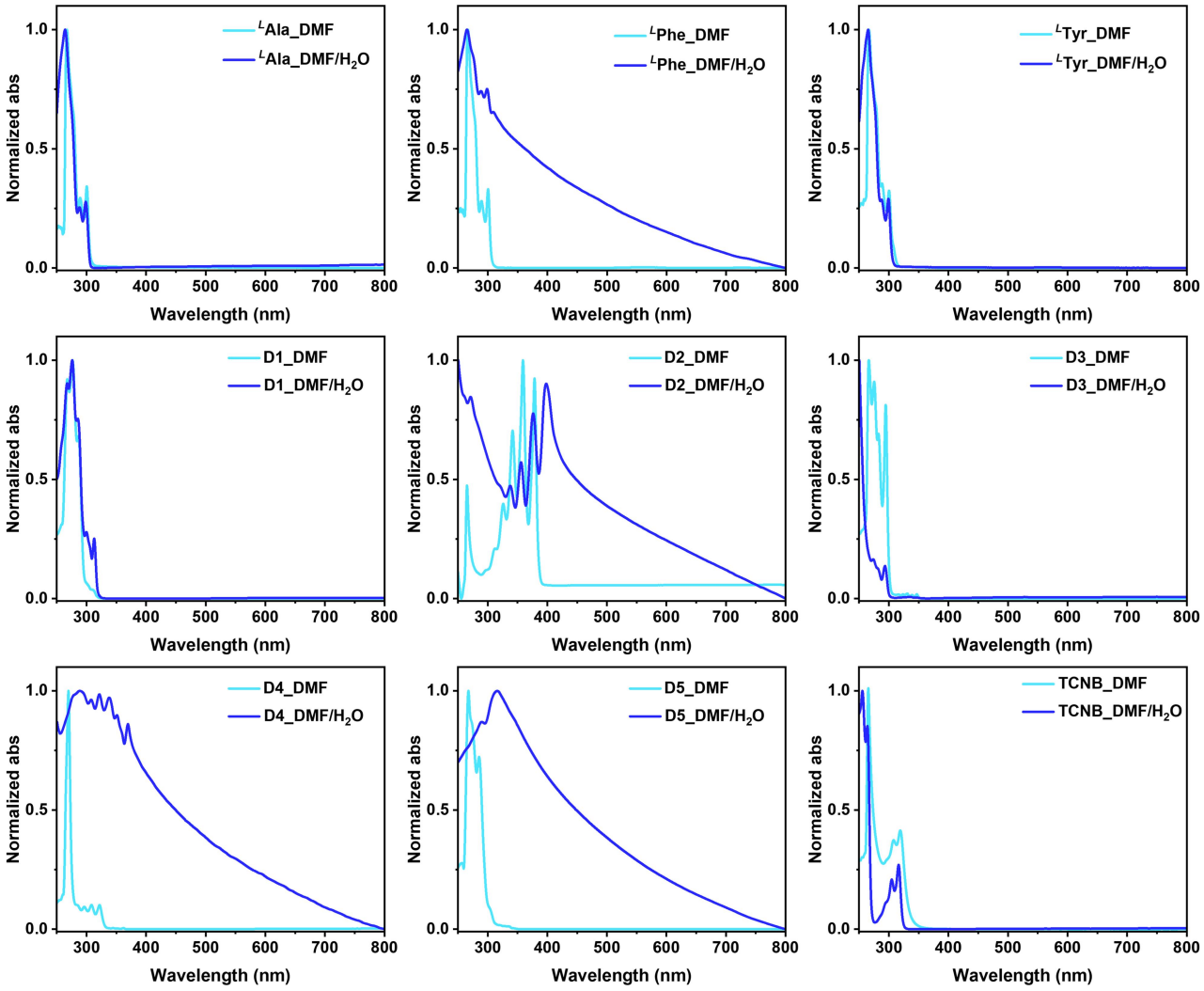

Fig. S2 Normalized UV–vis spectra of individual **^{L}Ala**, **^{L}Phe**, **^{L}Tyr**, **D1-5** and **TCNB** (5.6 mM) in DMF and DMF/H_2O (1/19, *v*/*v*).

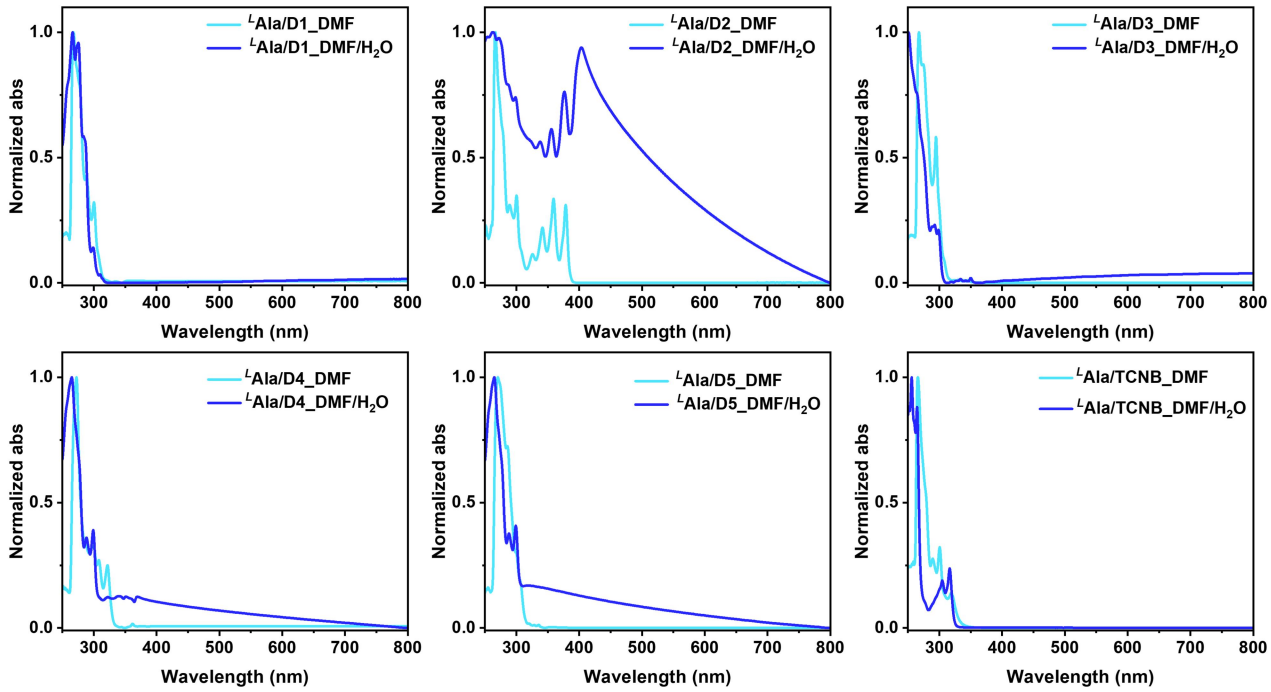

Fig. S3 Normalized UV–vis spectra of **^{L}Ala/D1-5** and **^{L}Ala/TCNB** (5.6 mM:5.6 mM) in DMF and DMF/H_2O (1/19, *v*/*v*).

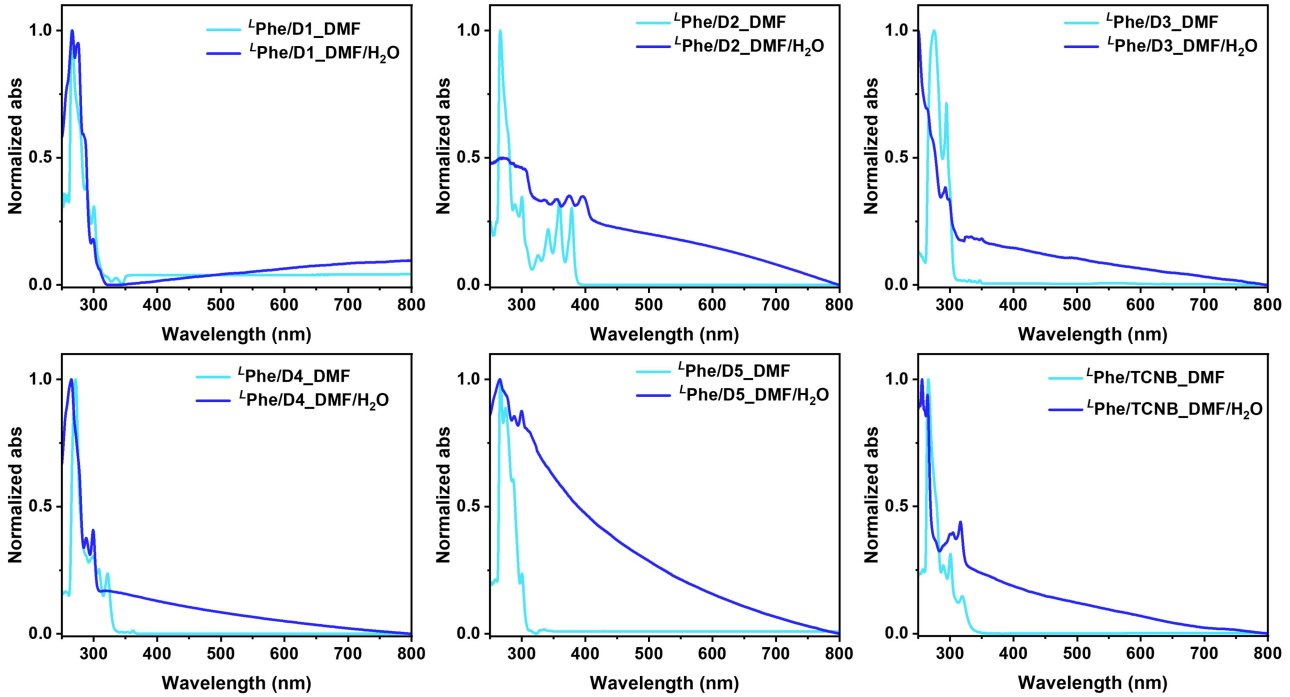

Fig. S4 Normalized UV–vis spectra of **^{L}Phe/D1-5** and **^{L}Phe/TCNB** (5.6 mM:5.6 mM) in DMF and DMF/H_2O (1/19, *v*/*v*).

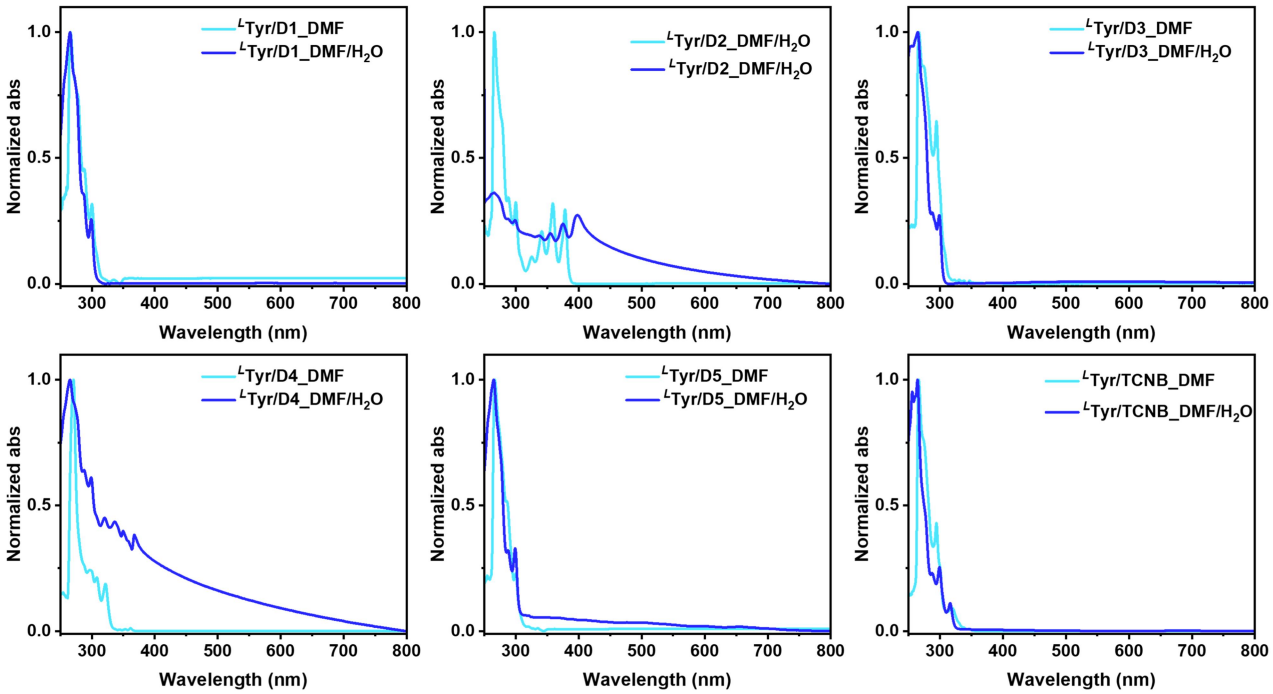

Fig. S5 Normalized UV–vis spectra of **^{L}Tyr/D1-5** and **^{L}Tyr/TCNB** (5.6 mM:5.6 mM) in DMF and DMF/H_2O (1/19, *v*/*v*).

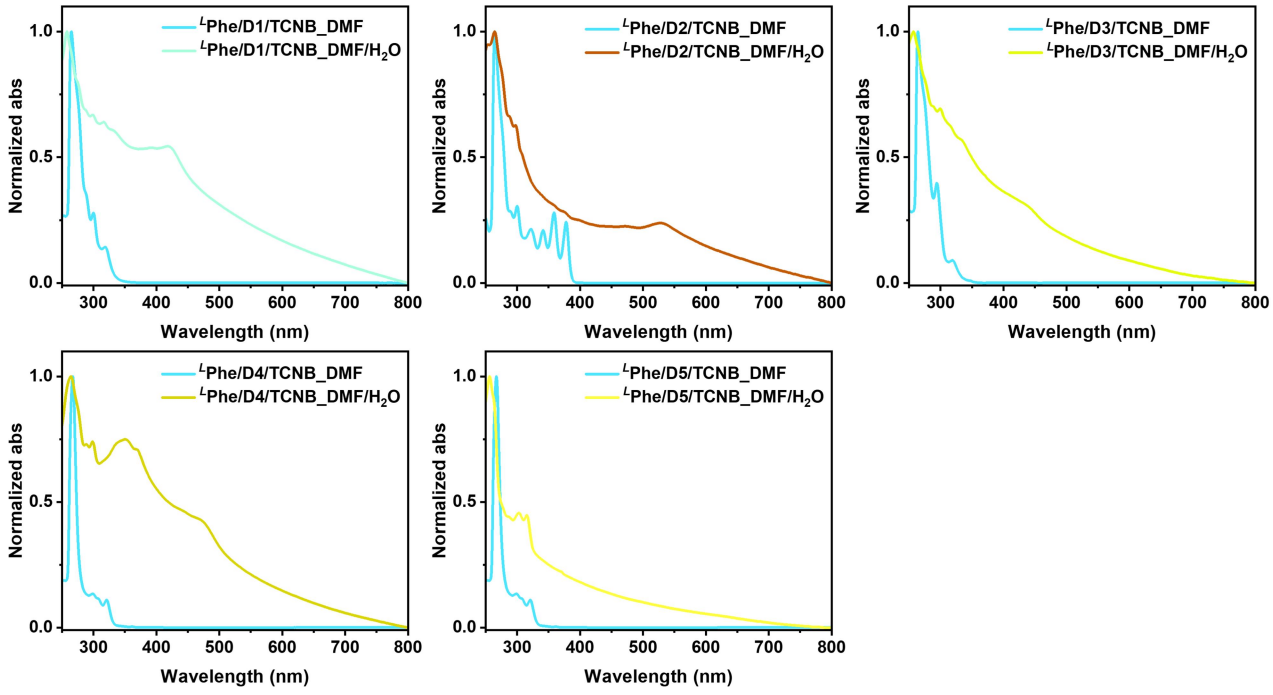

Fig. S6 Normalized UV–vis spectra of **^{L}Phe/D1-5/TCNB** (5.6 mM:5.6 mM:5.6 mM) in DMF and DMF/H_2O (1/19, *v*/*v*).

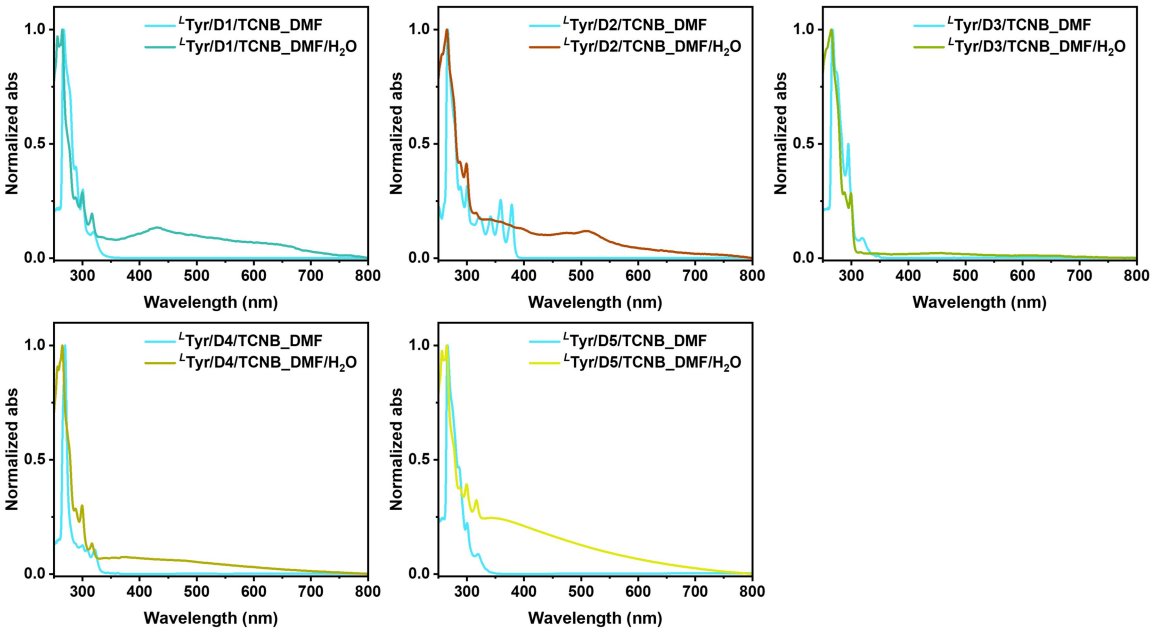

Fig. S7 Normalized UV–vis spectra of **^{L}Tyr/D1-5/TCNB** (5.6 mM:5.6 mM:5.6 mM) in DMF and DMF/H_2O (1/19, *v*/*v*).

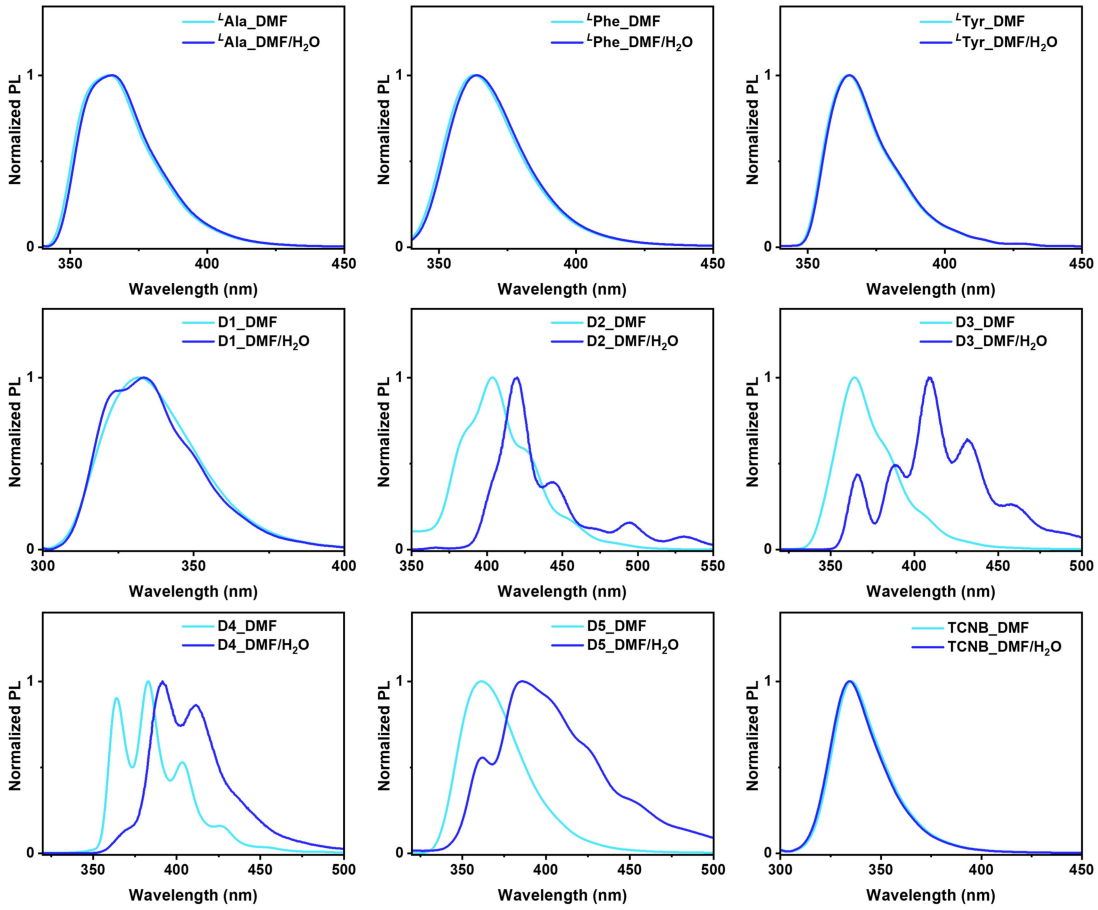

Fig. S8 Normalized PL spectra of individual **^{L}Ala**, **^{L}Phe**, **^{L}Tyr**, **D1-5** and **TCNB** (5.6 mM) in DMF (λ_{ex} = 280 nm) and DMF/H_2O (λ_{ex} = 280 nm, 1/19, *v*/*v*).

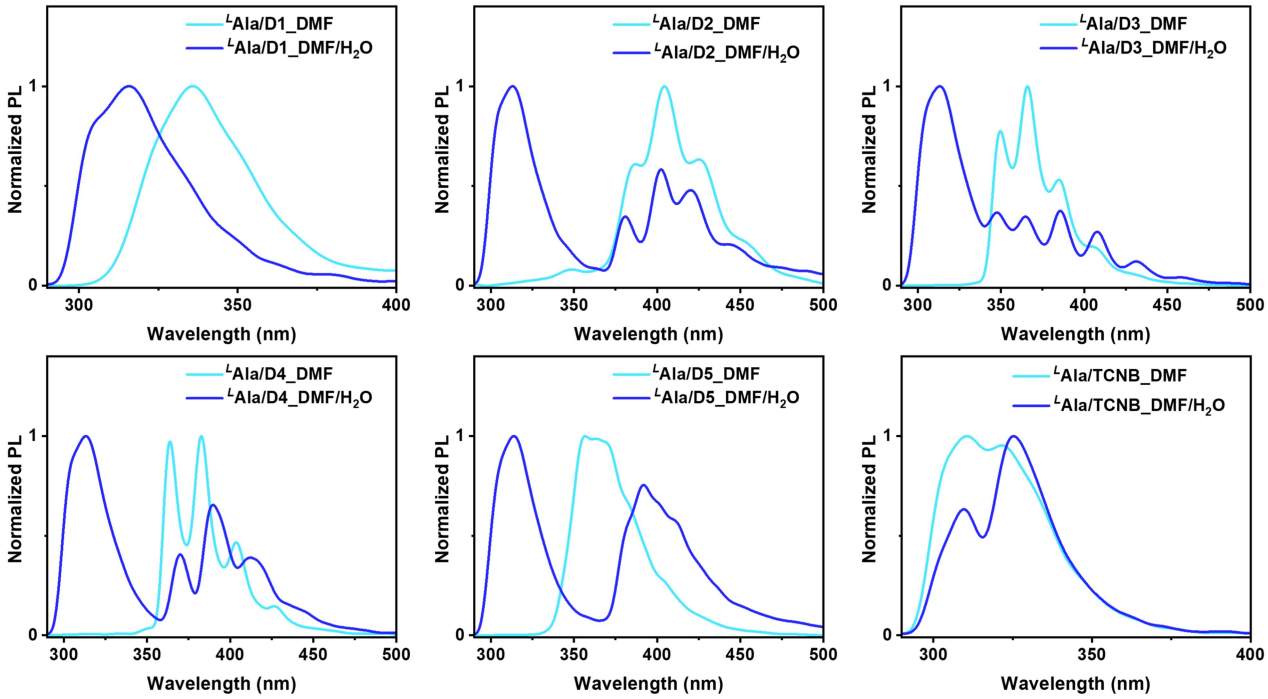

Fig. S9 Normalized PL spectra of **^{L}Ala/D1-5** and **^{L}Ala/TCNB** (5.6 mM:5.6 mM) in DMF (λ_{ex} = 280 nm) and DMF/H_2O (λ_{ex} = 280 nm, 1/19, *v*/*v*).

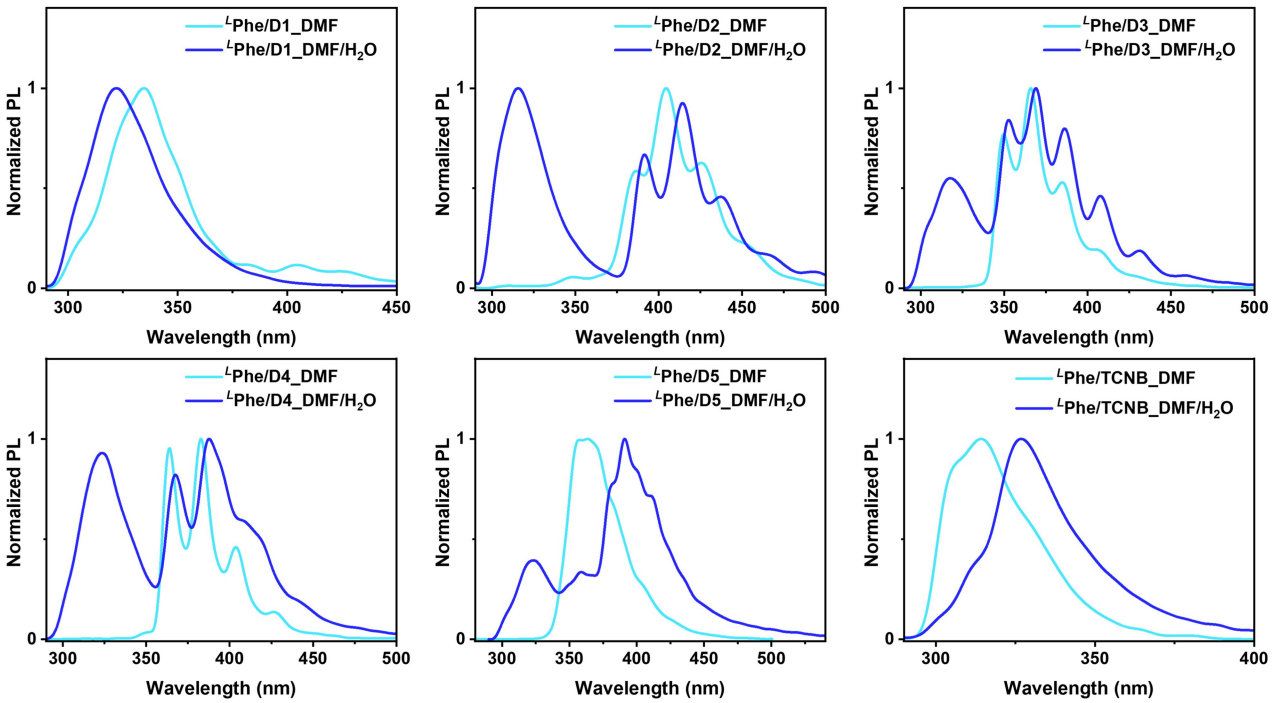

Fig. S10 Normalized PL spectra of **^{L}Phe/D1-5** and **^{L}Phe/TCNB** (5.6 mM:5.6 mM) in DMF (λ_{ex} = 280 nm) and DMF/H_2O (λ_{ex} = 280 nm, 1/19, *v*/*v*).

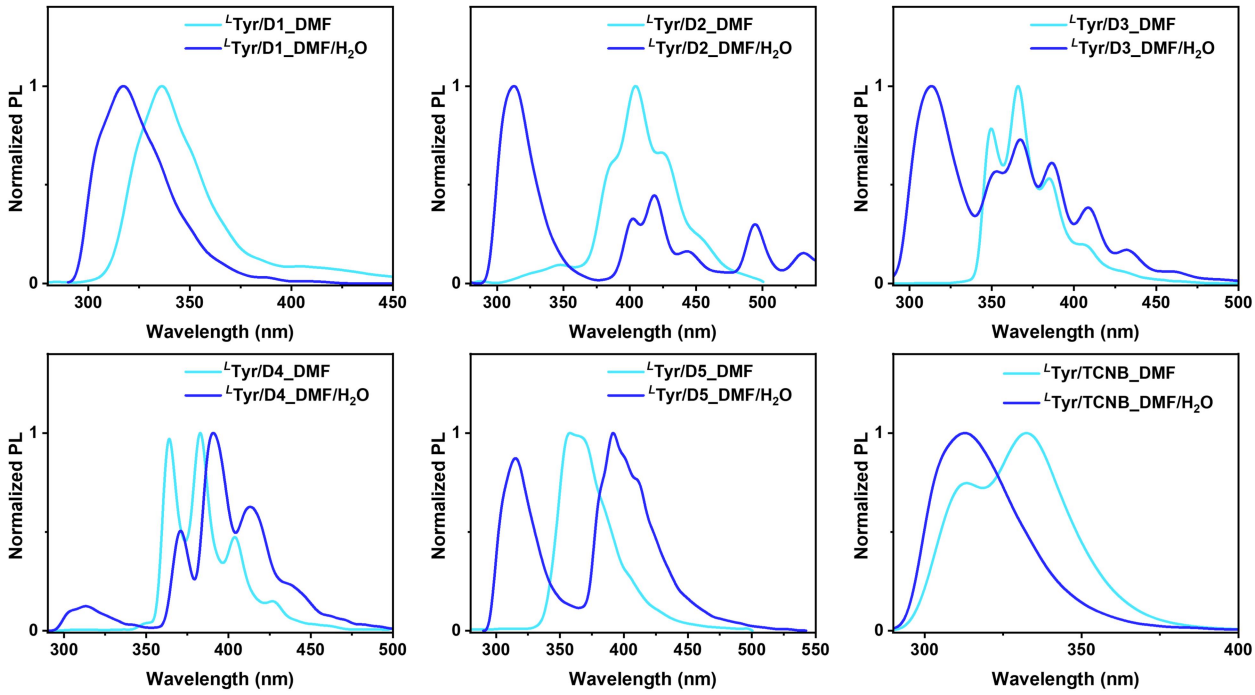

Fig. S11 Normalized PL spectra of **^{L}Tyr/D1-5** and **^{L}Tyr/TCNB** (5.6 mM:5.6 mM) in DMF (λ_{ex} = 280 nm) and DMF/H_2O (λ_{ex} = 280 nm, 1/19, *v*/*v*).

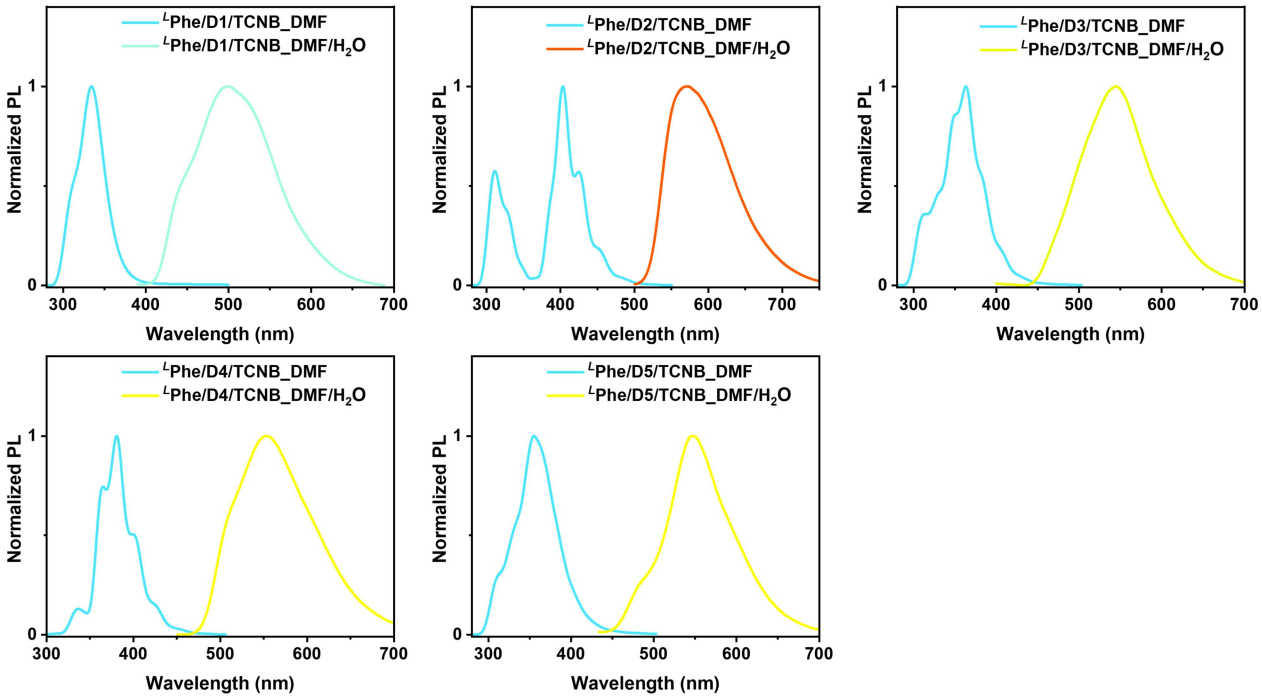

Fig. S12 Normalized PL spectra of **^{L}Phe/D1-5/TCNB** (5.6 mM:5.6 mM:5.6 mM) in DMF (λ_{ex} = 280 nm) and DMF/H_2O (λ_{ex} = 360 nm, 1/19, *v*/*v*).

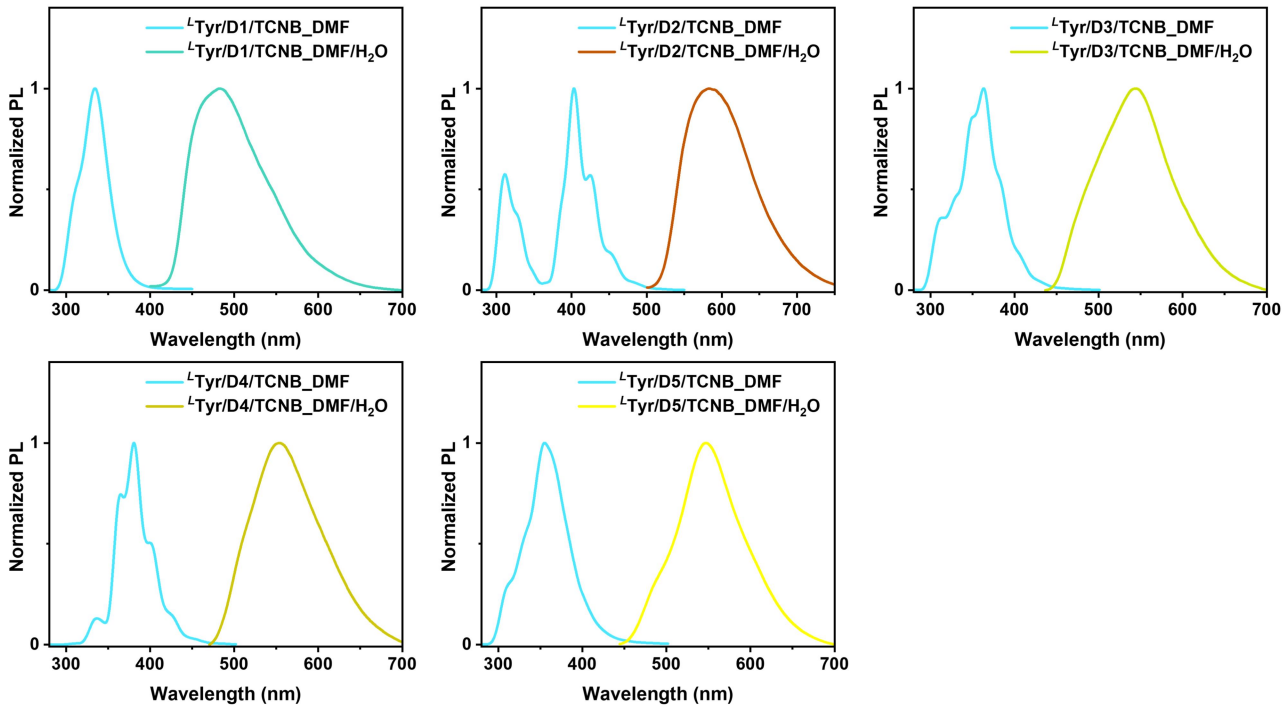

Fig. S13 Normalized PL spectra of **^{L}Tyr/D1-5/TCNB** (5.6 mM:5.6 mM:5.6 mM) in DMF (λ_{ex} = 280 nm) and DMF/H_2O (λ_{ex} = 360 nm, 1/19, *v*/*v*).

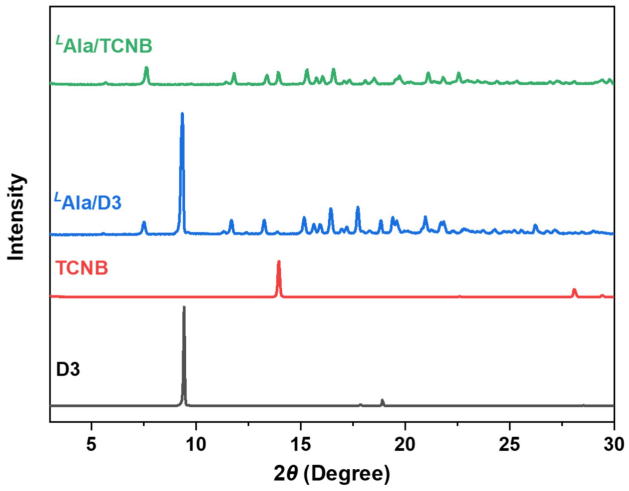

Fig. S14 Powder XRD patterns of assemblies of **D3** and **TCNB** (5.6 mM), and assemblies of **^{L}Ala/D3** and **^{L}Ala/TCNB** (5.6 mM:5.6 mM) formed in DMF/H_2O (1/19, *v*/*v*).

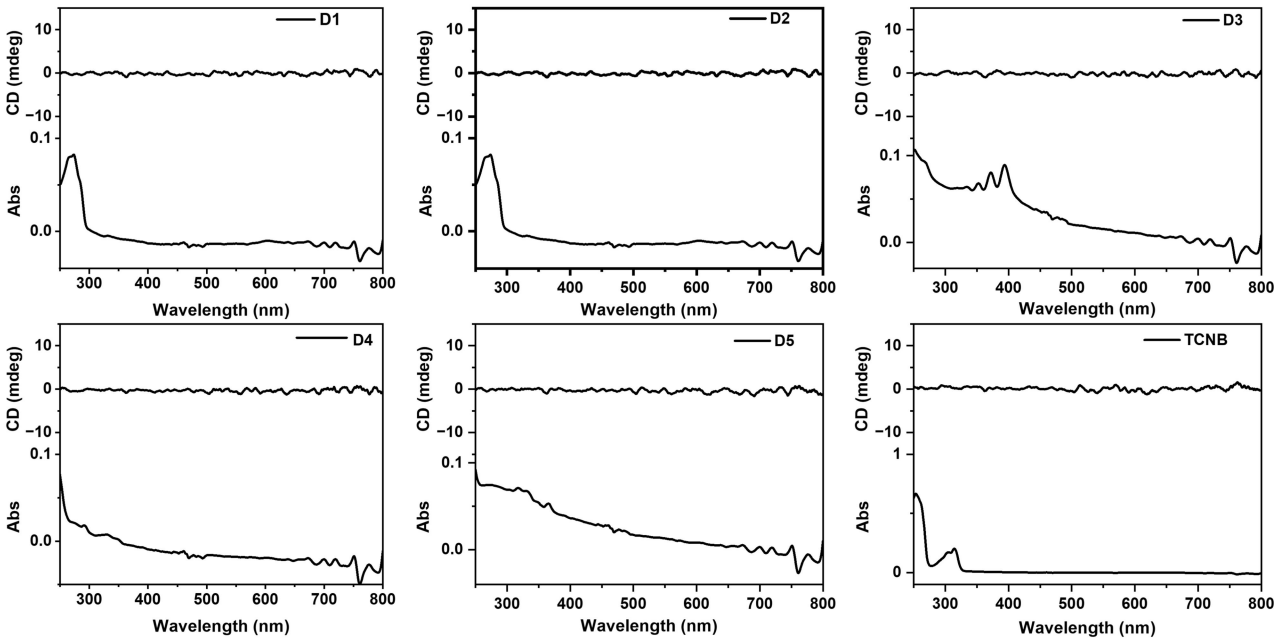

Fig. S15 CD and UV–vis spectra of individual **D1-5** and **TCNB** (5.6 mM) assemblies formed in DMF/H_2O (1/19, *v*/*v*)

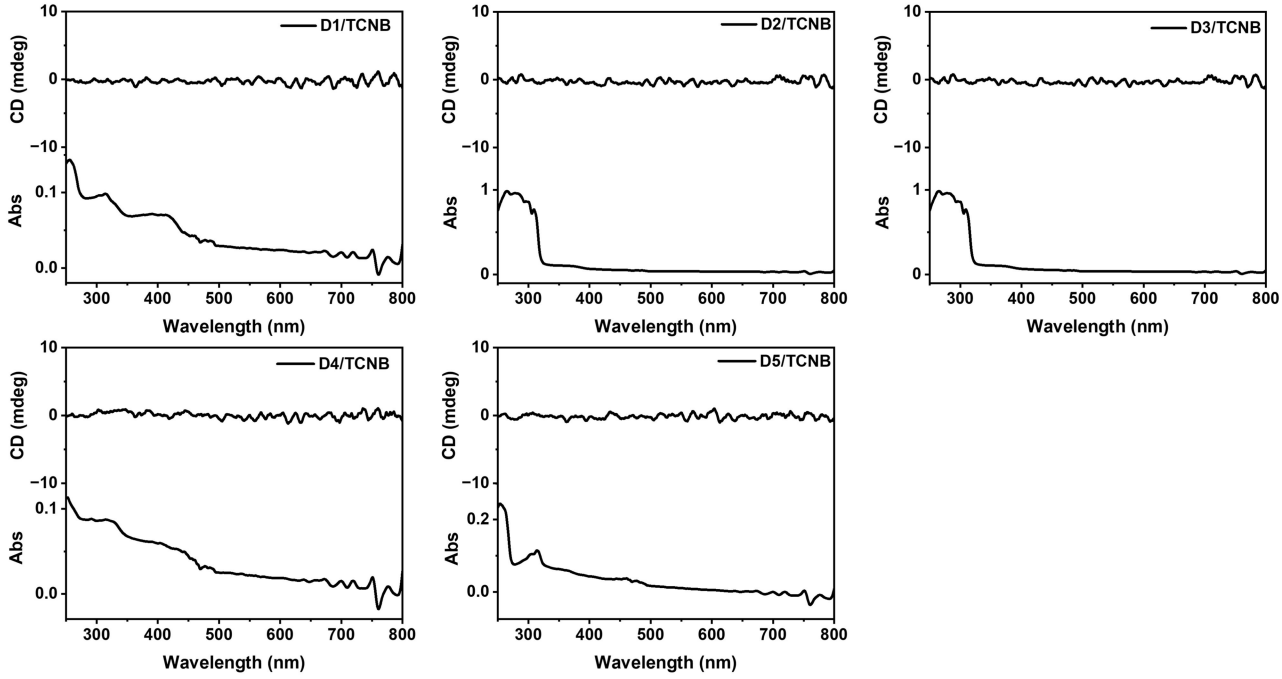

Fig. S16 CD and UV–vis spectra of **D1-5**/**TCNB** (5.6 mM:5.6 mM) assemblies formed in DMF/H_2O (1/19, *v*/*v*).

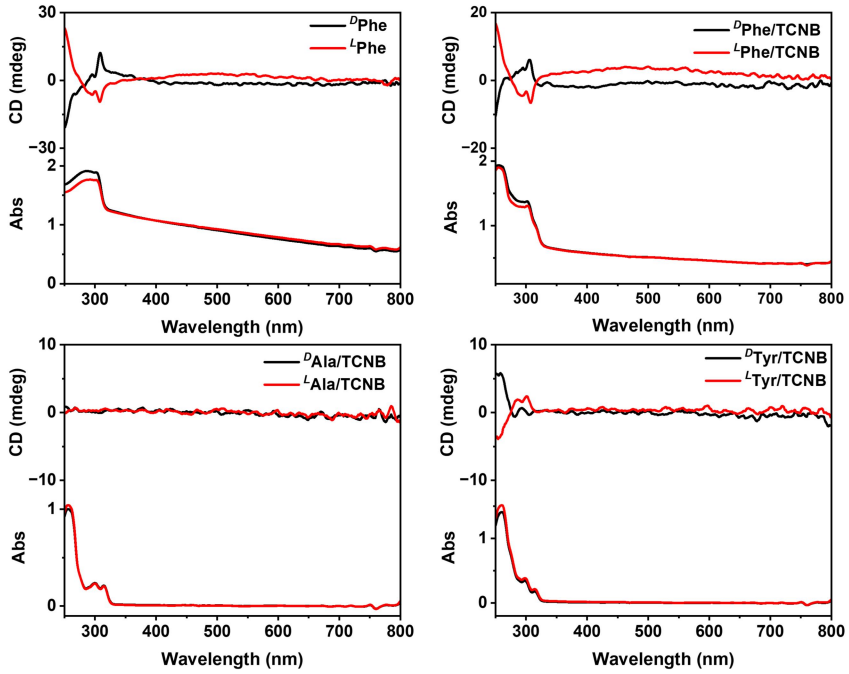

Fig. S17 CD and UV–vis spectra of individual $^{L\text{ or }D}$**Phe** (5.6 mM) assemblies and $^{L\text{ or }D}$**Phe/TCNB**, $^{L\text{ or }D}$**Ala/TCNB** and $^{L\text{ or }D}$**Tyr/TCNB** (5.6 mM:5.6 mM) assemblies formed in DMF/H_2O (1/19, *v*/*v*).

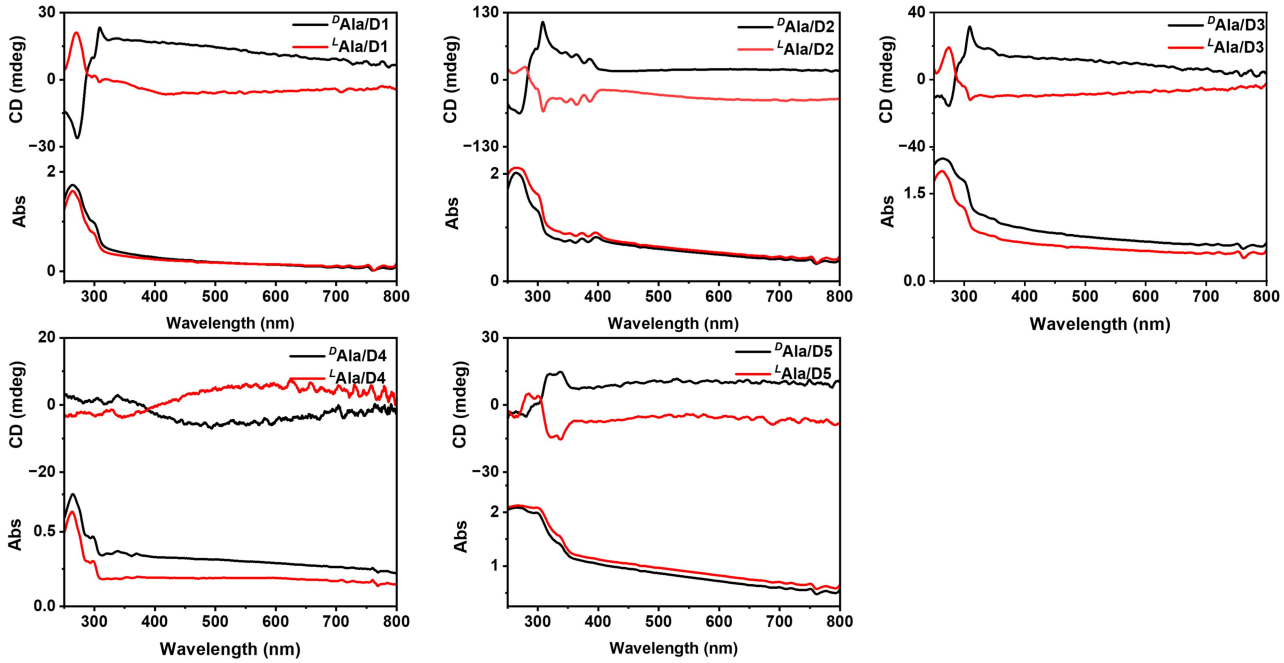

Fig. S18 CD and UV–vis spectra of $^{L\text{ or }D}$**Ala/D1-5** (5.6 mM:5.6 mM) assemblies formed in DMF/H_2O (1/19, *v*/*v*).

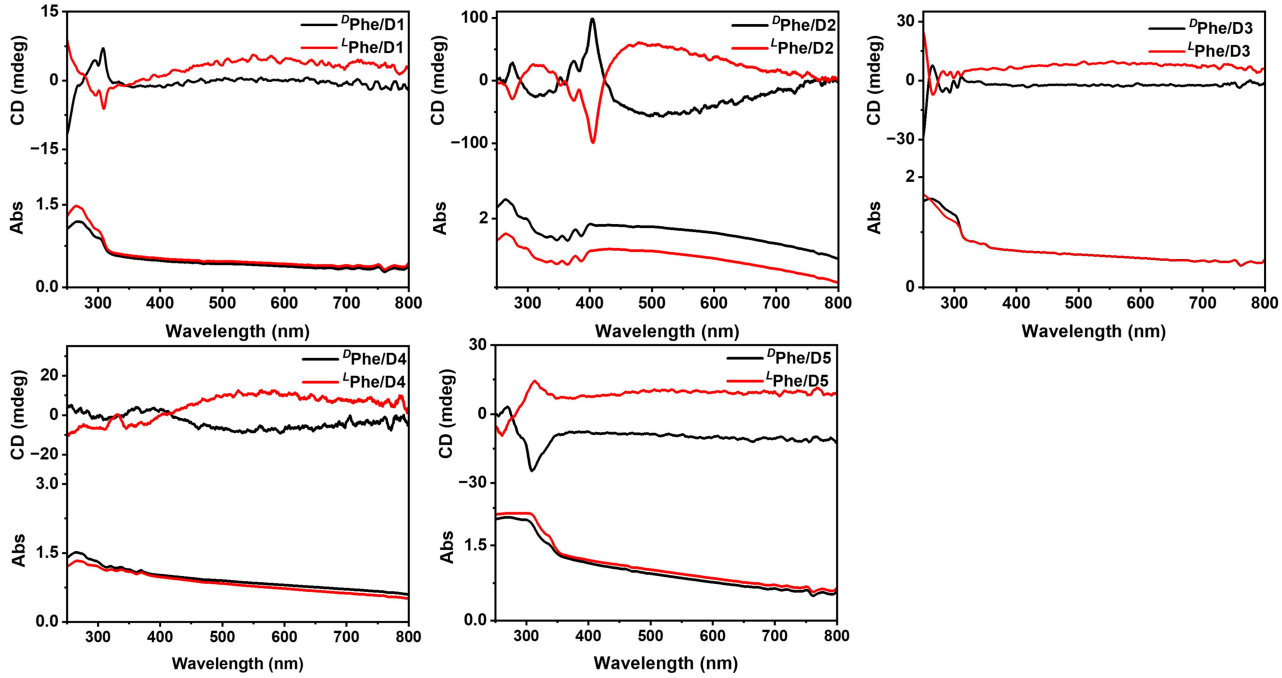

Fig. S19 CD and UV–vis spectra of $^{L\text{ or }D}$**Phe/D1-5** (5.6 mM:5.6 mM) assemblies formed in DMF/H_2O (1/19, *v*/*v*).

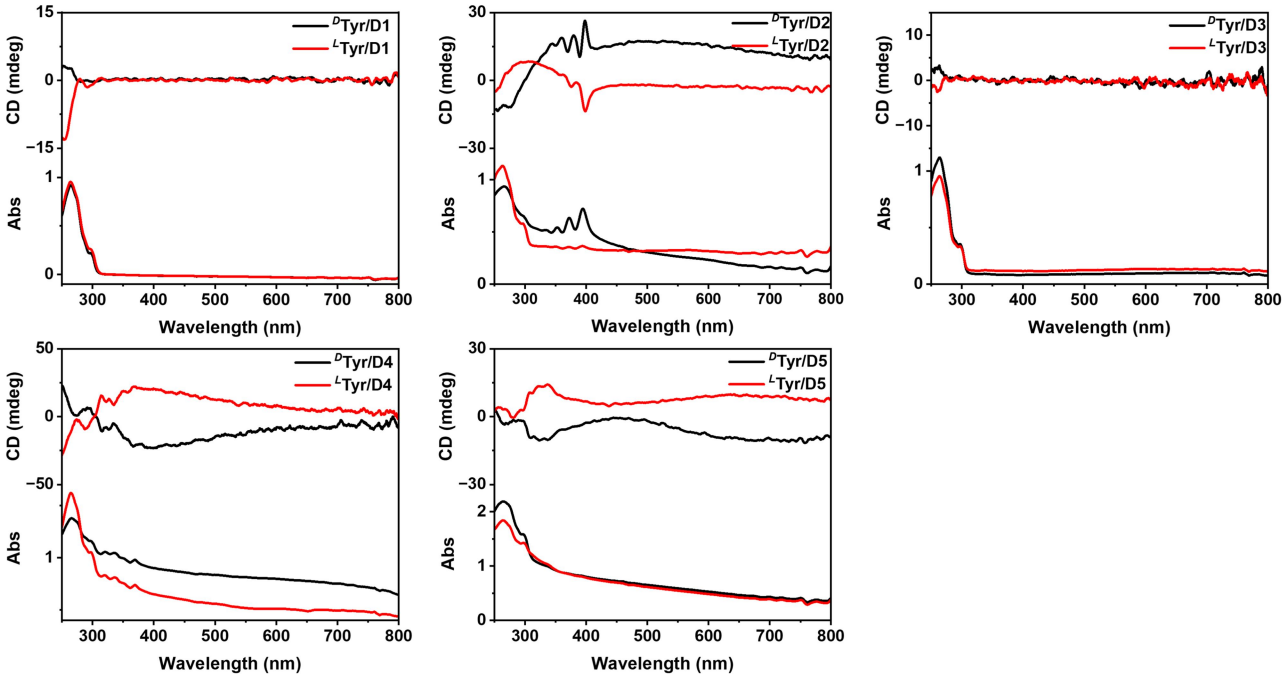

Fig. S20 CD and UV–vis spectra of $^{L\text{ or }D}$**Tyr/D1-5** (5.6mM:5.6 mM) assemblies formed in DMF/H_2O (1/19, *v*/*v*).

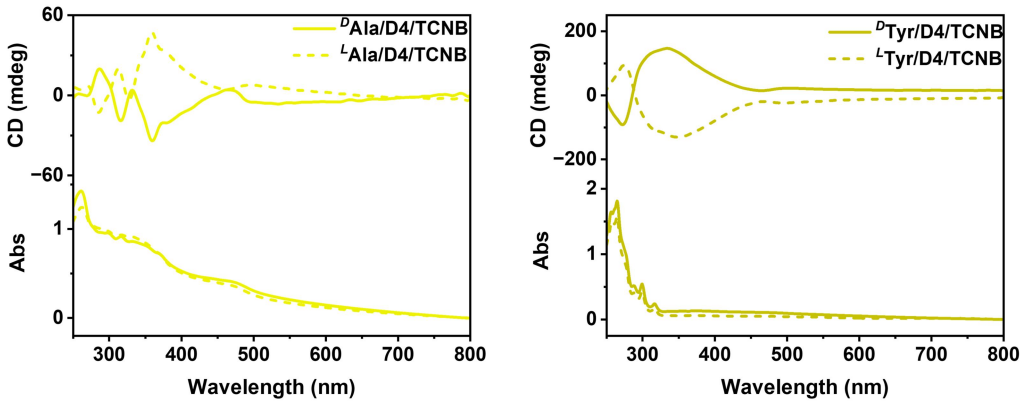

Fig. S21 CD and UV–vis spectra of $^{L\text{ or }D}$**Ala/D4/TCNB** and $^{L\text{ or }D}$**Tyr/D4/TCNB** (5.6 mM:5.6 mM:5.6 mM) assemblies formed in DMF/H_2O (1/19, *v*/*v*).

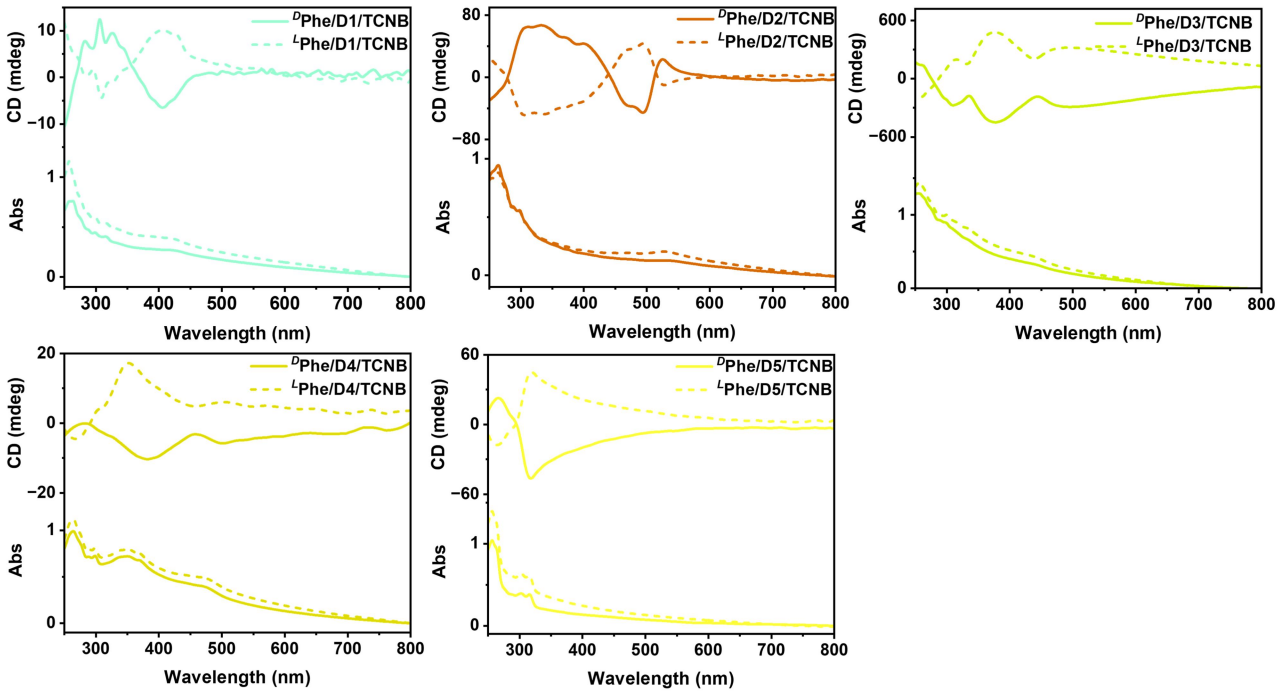

Fig. S22 CD and UV–vis spectra of $^{L\text{ or }D}$**Phe/D1-5/TCNB** (5.6 mM:5.6 mM:5.6 mM) assemblies formed in DMF/H_2O (1/19, *v*/*v*).

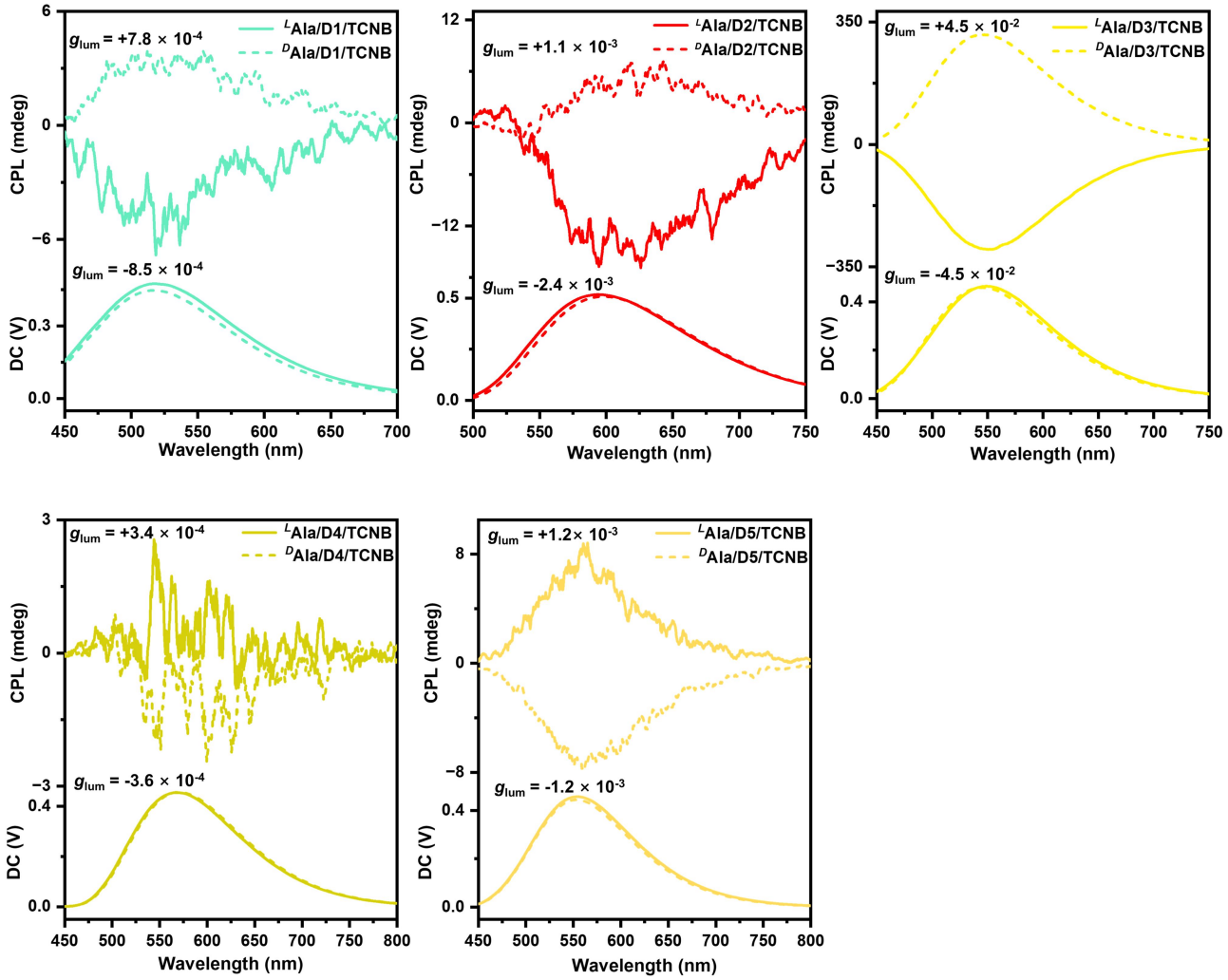

Fig. S23 CPL spectra of ^{L} or ^{D}**Ala/D1-5/TCNB** (5.6 mM:5.6 mM:5.6 mM) assemblies formed in DMF/H_2O (1/19, *v*/*v*) excited by 360 nm UV light.

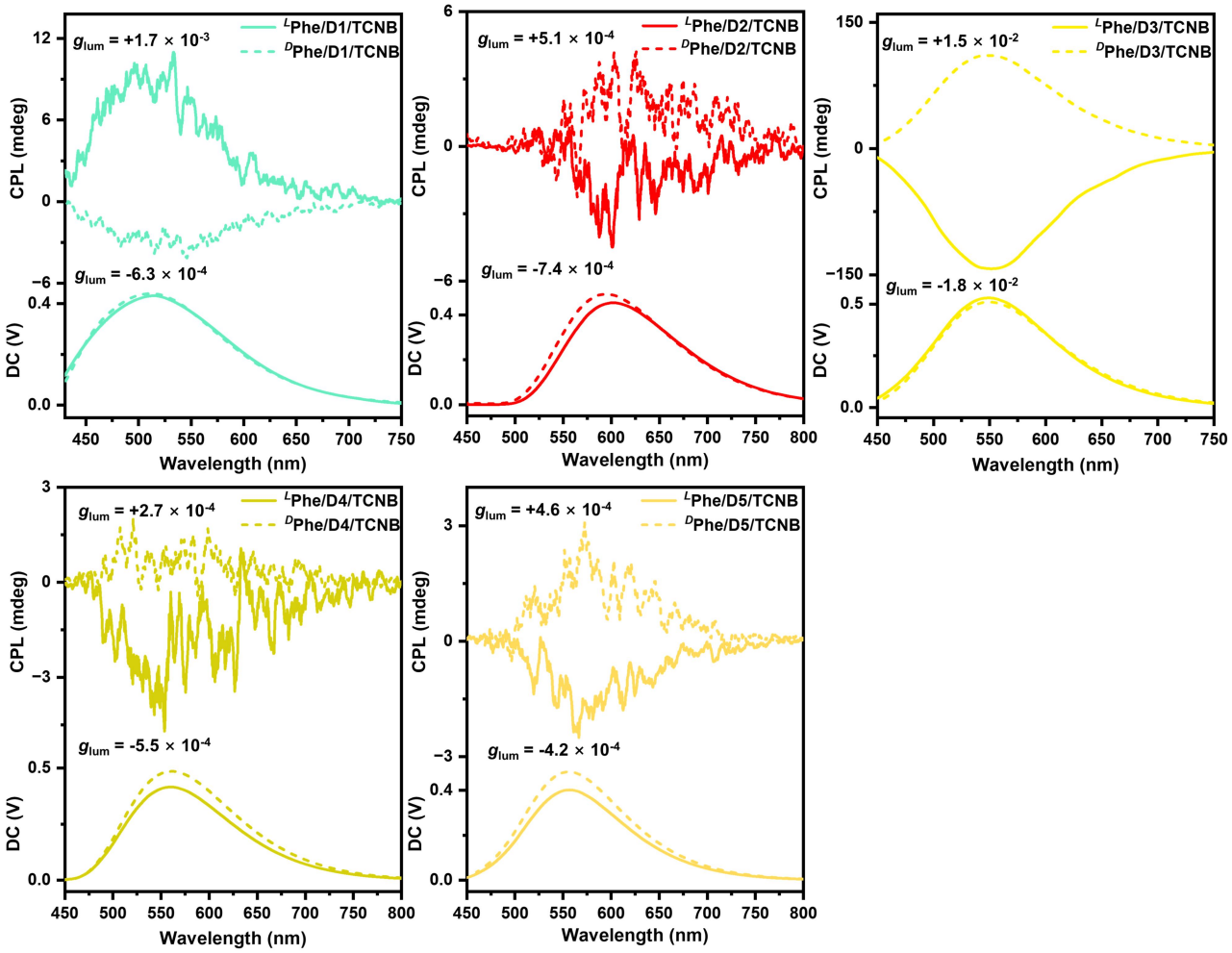

Fig. S24 CPL spectra of $^{L\text{ or }D}$**Phe/D1-5/TCNB** (5.6 mM:5.6 mM:5.6 mM) assemblies formed in DMF/H_2O (1/19, *v*/*v*) excited by 360 nm UV light.

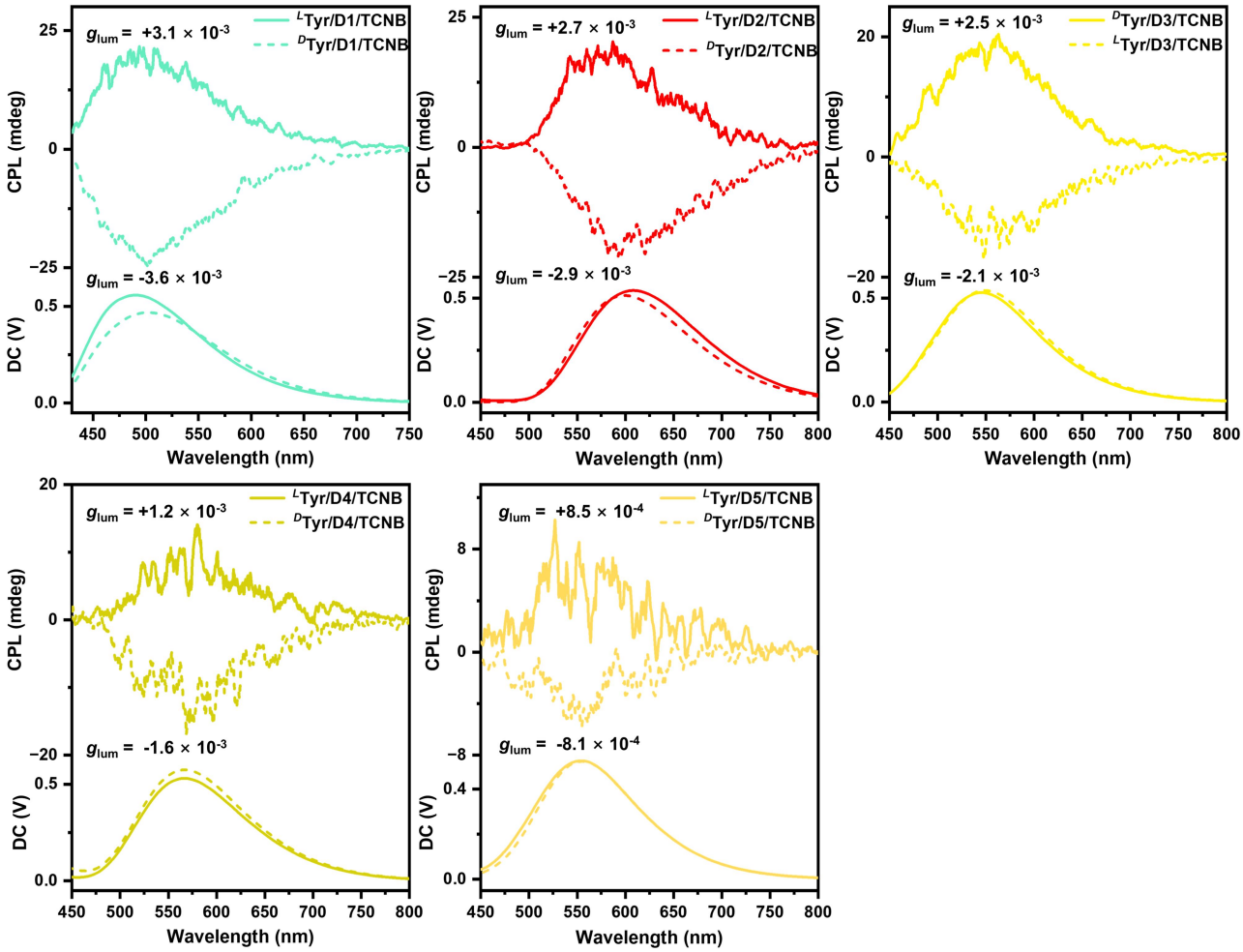

Fig. S25 CPL spectra of ^{L} or ^{D}**Tyr/D1-5/TCNB** (5.6 mM:5.6 mM:5.6 mM) assemblies formed in DMF/H_2O (1/19, *v*/*v*) excited by 360 nm UV light.

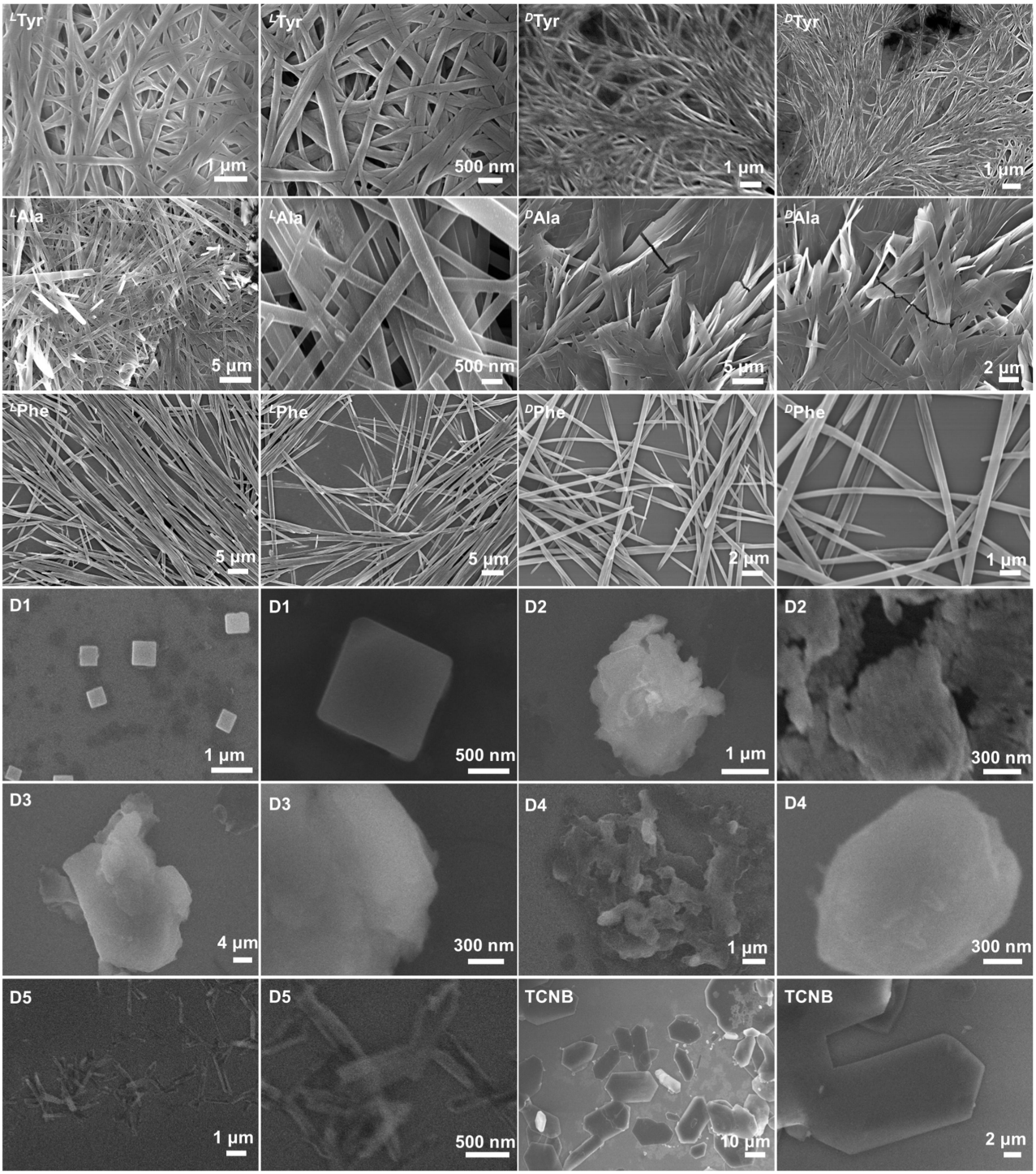

Fig. S26 SEM images of individual $^{L\text{ or }D}$**Tyr**, $^{L\text{ or }D}$**Ala**, $^{L\text{ or }D}$**Phe**, **D1-5** and **TCNB** (5.6 mM) assemblies formed in DMF/H_2O (1/19, *v*/*v*).

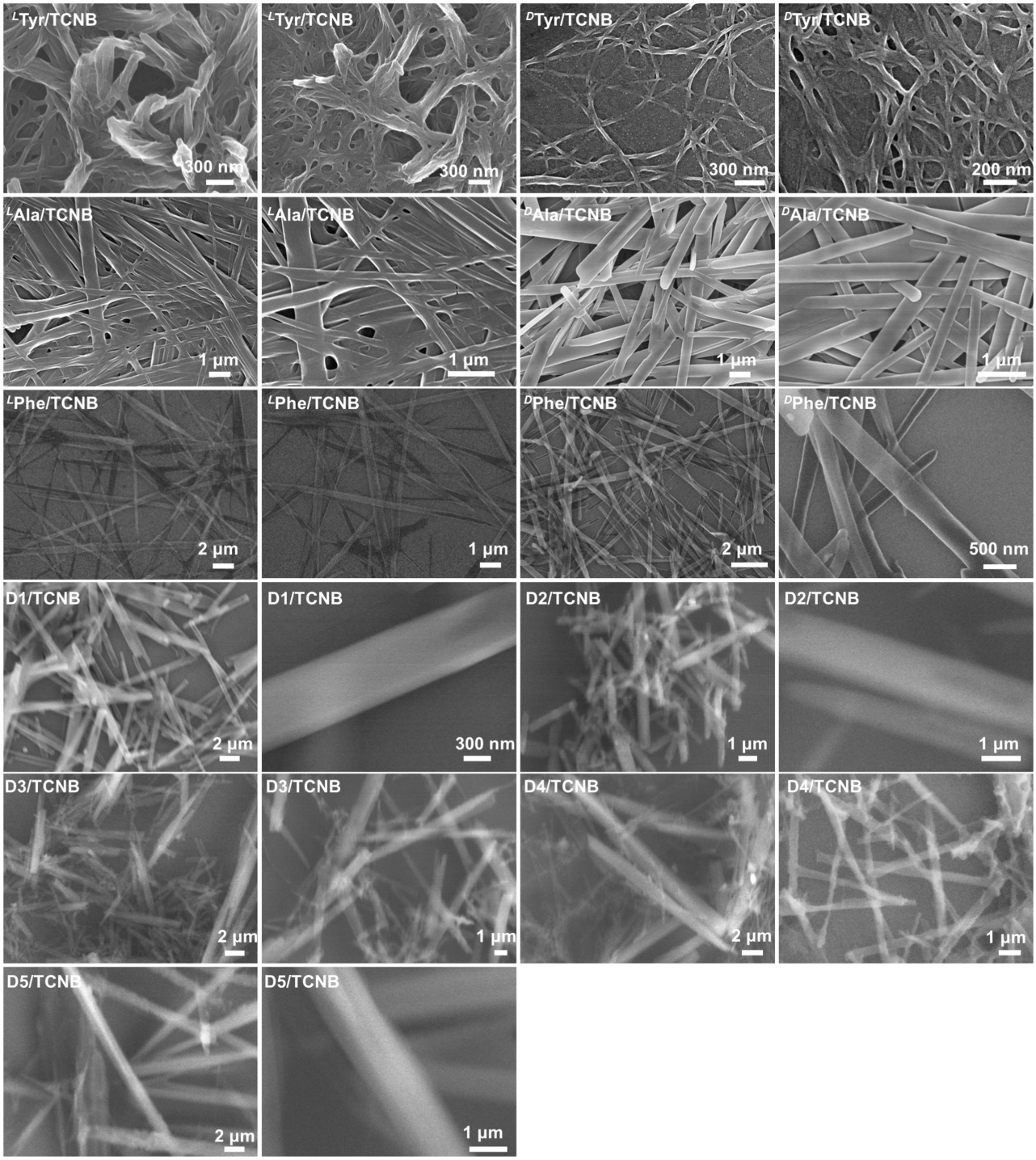

Fig. S27 SEM images of assemblies of $^{L\text{ or }D}$**Ala**/**TCNB**, $^{L\text{ or }D}$**Phe**/**TCNB**, $^{L\text{ or }D}$**Tyr**/**TCNB** and **D1-5**/**TCNB** (5.6 mM:5.6 mM) formed in DMF/H_2O (1/19, *v*/*v*).

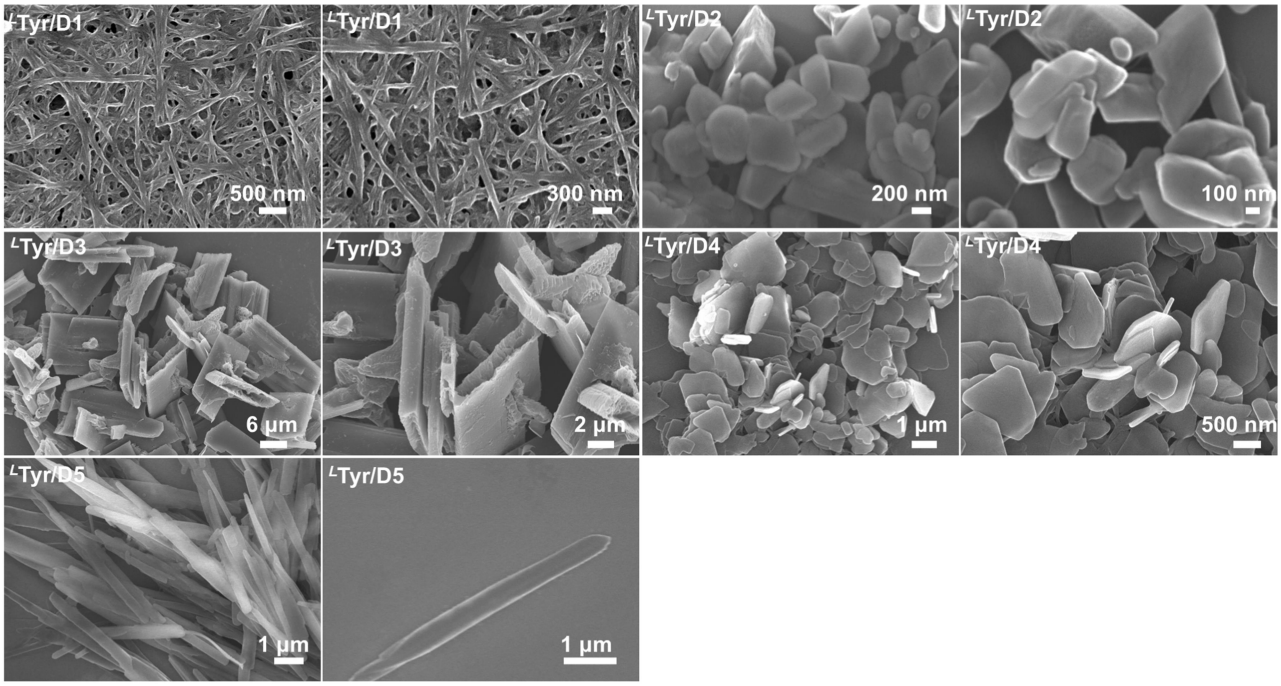

Fig. S28 SEM images of **^{L}Tyr/D1-5** (5.6 mM:5.6 mM) assemblies formed in DMF/H_2O (1/19, *v*/*v*).

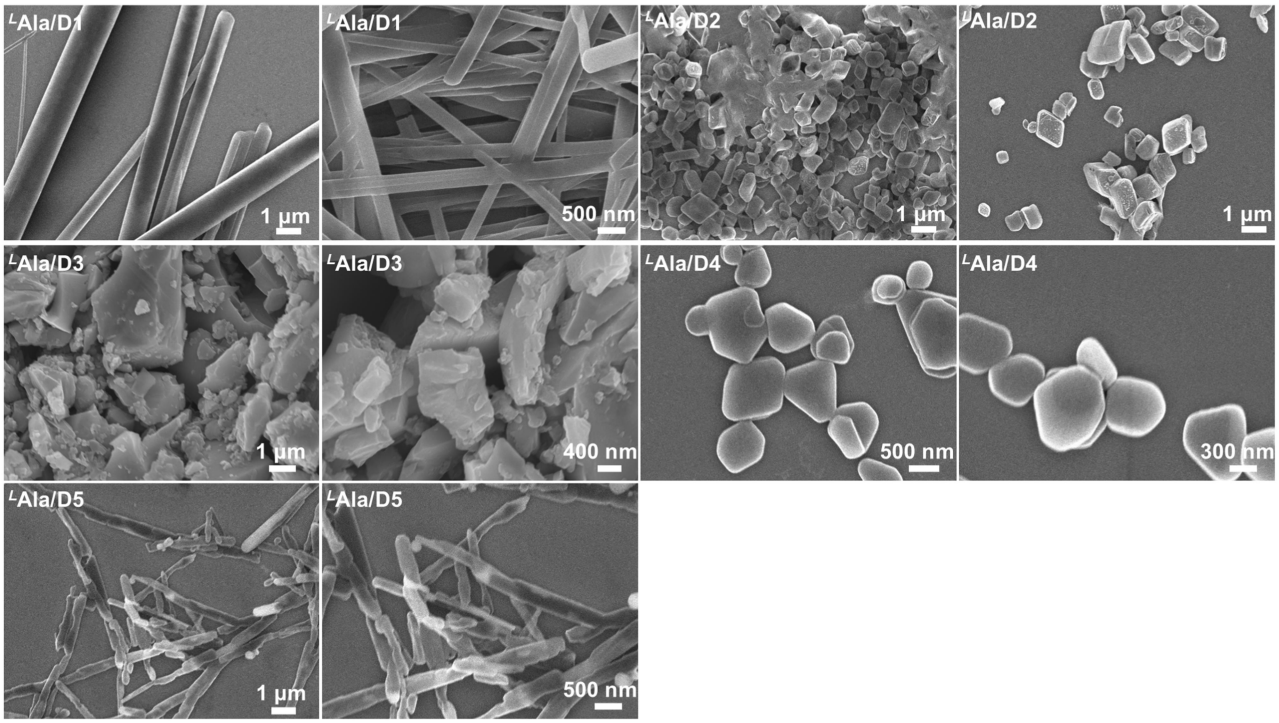

Fig. S29 SEM images of **^{L}Ala/D1-5** (5.6 mM:5.6 mM) assemblies formed in DMF/H_2O (1/19, *v*/*v*).

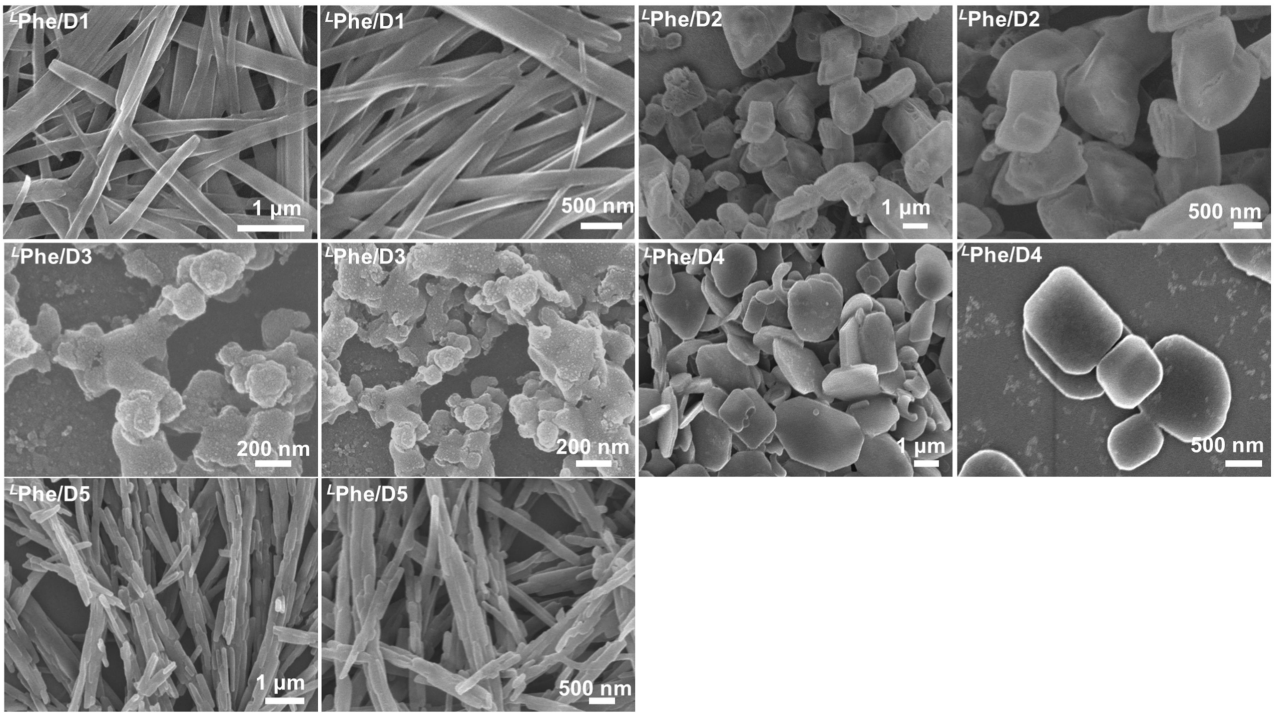

Fig. S30 SEM images of **^{L}Phe/D1-5** (5.6 mM:5.6 mM) assemblies formed in DMF/H_2O (1/19, *v*/*v*).

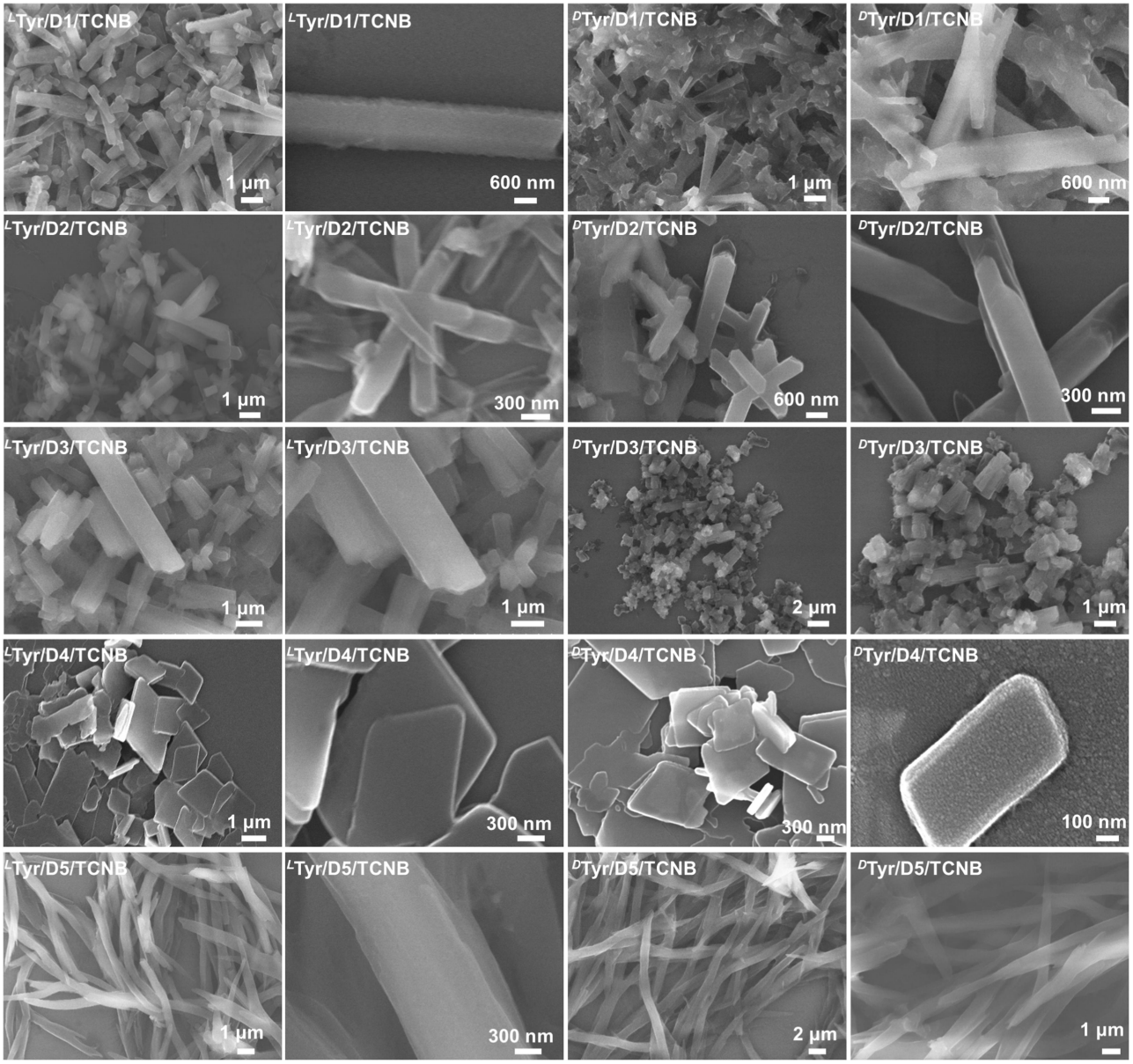

Fig. S31 SEM images of ternary assemblies of ^{L} or ^{D}**Tyr/D1-5/TCNB** (5.6 mM:5.6 mM:5.6 mM) formed in DMF/H_2O (1/19, *v*/*v*).

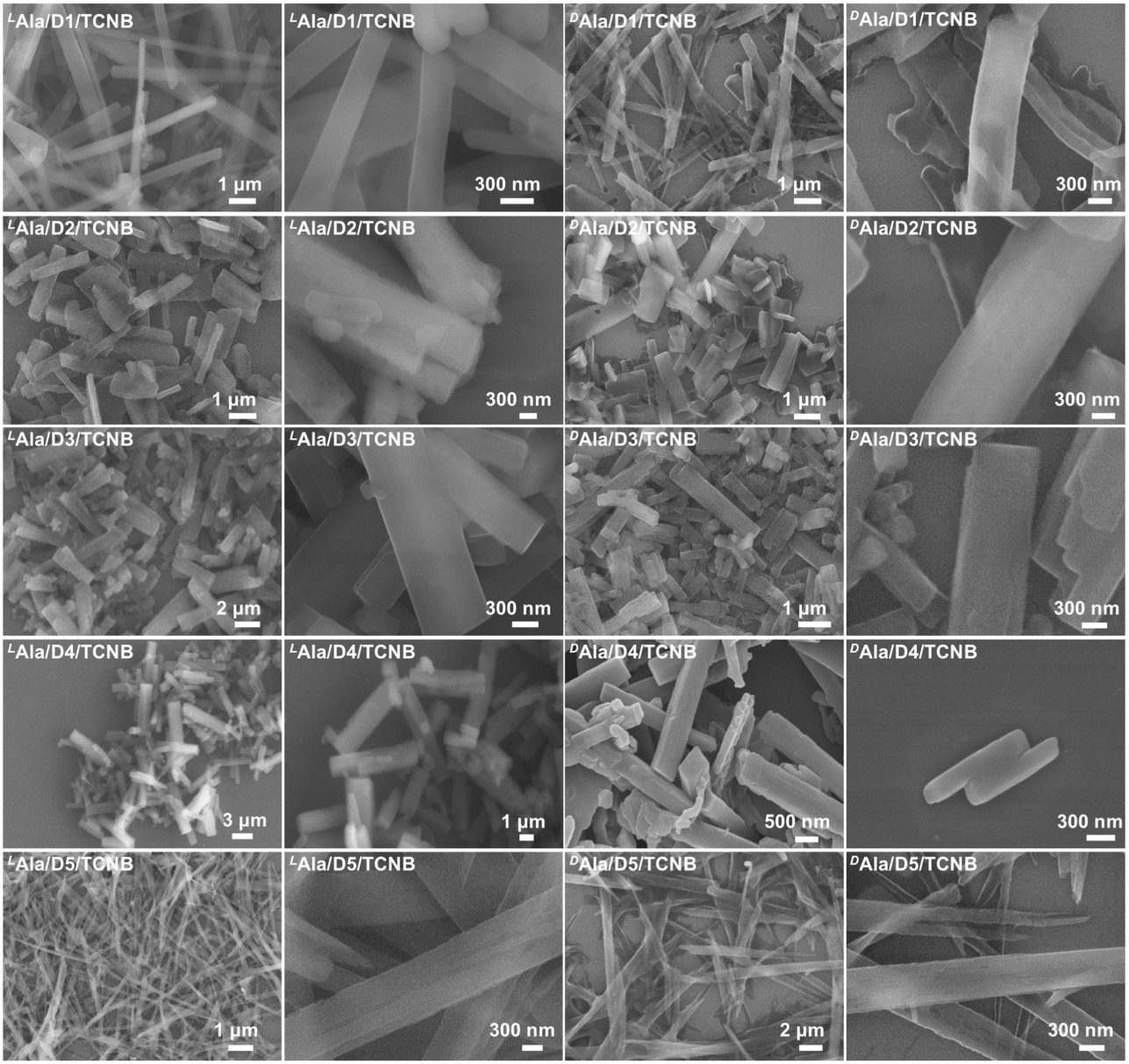

Fig. S32 SEM images of ternary assemblies of ^{L} or ^{D}**Ala/D1-5/TCNB** (5.6 mM:5.6 mM:5.6 mM) formed in DMF/H_2O (1/19, *v*/*v*).

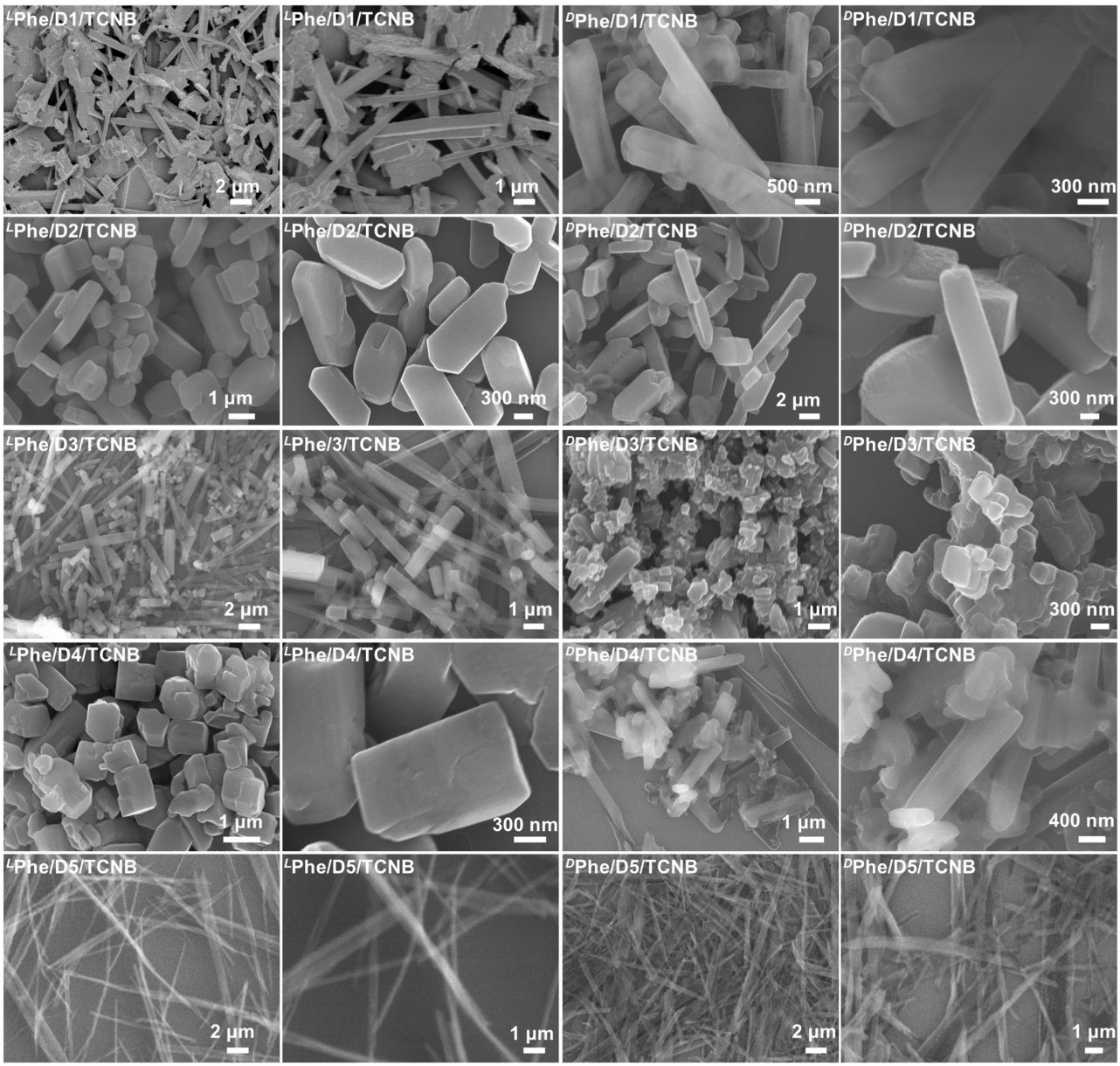

Fig. S33 SEM images of ternary assemblies of $^{L\text{ or }D}$**Phe/D1-5/TCNB** (5.6 mM:5.6 mM:5.6 mM) formed in DMF/H_2O (1/19, *v*/*v*).

Tab. S1 Diameters of the supramolecular nano- or micro-structures obtained in different assemblies of **^{L}Tyr**, **^{L}Ala**, **^{L}Phe**, **^{L}Tyr/TCNB**, **^{L}Ala/TCNB**, **^{L}Phe/TCNB**, **D1-5/TCNB**, **^{L}Tyr/D1**, **^{L}Tyr/D5**, **^{L}Ala/D1**, **^{L}Ala/D5**, **^{L}Phe/D1**, **^{L}Phe/D5**, **^{L}Tyr/D1-5/TCNB**, **^{L}Ala/D1-5/TCNB**, **and ^{L}Phe/D1-5/TCNB**.

Sample	Diameter/nm	Sample	Diameter/nm
^{L}Tyr	230	**^{L}Tyr/D3/TCNB**	750-910
^{D}Tyr	230	**^{D}Tyr/D3/TCNB**	670-920
^{L}Ala	690	**^{L}Tyr/D4/TCNB**	1070-1730
^{D}Ala	690	**^{D}Tyr/D4/TCNB**	850-1740
^{L}Phe	410	**^{L}Tyr/D5/TCNB**	940-1160
^{D}Phe	410	**^{D}Tyr/D5/TCNB**	960-1100
^{L}Tyr/TCNB	45	**^{L}Ala/D1/TCNB**	260-690
^{D}Tyr/TCNB	50	**^{D}Ala/D1/TCNB**	230-620
^{L}Ala/TCNB	400	**^{L}Ala/D2/TCNB**	310-760
^{D}Ala/TCNB	400	**^{D}Ala/D2/TCNB**	350-630
^{L}Phe/TCNB	350	**^{L}Ala/D3/TCNB**	540-910
^{D}Phe/TCNB	380	**^{D}Ala/D3/TCNB**	320-770
D1/TCNB	570	**^{L}Ala/D4/TCNB**	370-960
D2/TCNB	360-780	**^{D}Ala/D4/TCNB**	410-680
D3/TCNB	340-890	**^{L}Ala/D5/TCNB**	450-870
D4/TCNB	470-790	**^{D}Ala/D5/TCNB**	550-920
D5/TCNB	460-820	**^{L}Phe/D1/TCNB**	460
^{L}Tyr/D1	120	**^{D}Phe/D1/TCNB**	500
^{L}Tyr/D5	480	**^{L}Phe/D2/TCNB**	580
^{L}Ala/D1	400-860	**^{D}Phe/D2/TCNB**	530
^{L}Ala/D5	330	**^{L}Phe/D3/TCNB**	310-580
^{L}Phe/D1	230	**^{D}Phe/D3/TCNB**	490-670
^{L}Phe/D5	140	**^{L}Phe/D4/TCNB**	580-660
^{L}Tyr/D1/TCNB	320-980	**^{D}Phe/D4/TCNB**	420-710
^{D}Tyr/D1/TCNB	470-810	**^{L}Phe/D5/TCNB**	210-590
^{L}Tyr/D2/TCNB	270-880	**^{D}Phe/D5/TCNB**	310-660
^{D}Tyr/D2/TCNB	450-890		

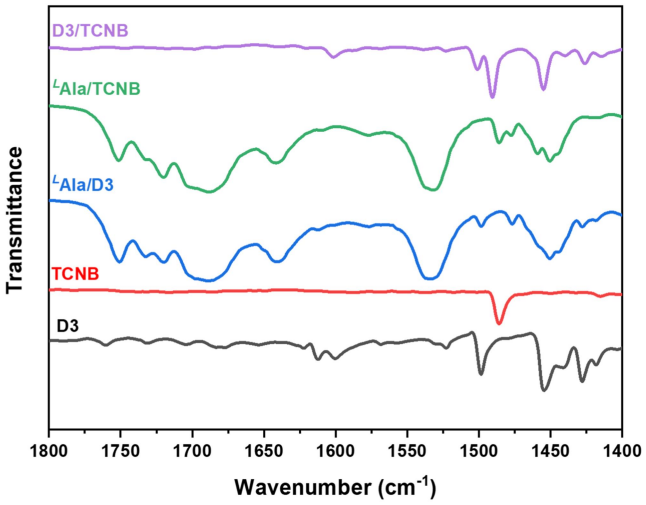

Fig. S34 FTIR spectra of individual **D3** and **TCNB** assemblies (5.6 mM), and assemblies of **^{L}Ala/D3**, **^{L}Ala/TCNB** and **D3/TCNB** (5.6 mM:5.6 mM) formed in DMF/H_2O (1/19, *v*/*v*).