Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Efficient Chirality Transfer from Chiral Amines to Oligo(*p*-phenylenevinylene)s to Fabricate Chiroptical Materials

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Experimental Section

Materials

(R)-2-Amino-1-butanol (^{R}B1), (S)-2-Amino-1-butanol (^{S}B1), (R)-(+)-α-Methylbenzylamine (^{R}B2), (S)-(-)-α-Methylbenzylamine (^{S}B2), R-Phenylglycinol (^{R}B3), S-Phenylglycinol (^{S}B3) (R)-1-(1-Naphthyl)ethylamine (^{R}B4), (S)-1-(1-Naphthyl)ethylamine (^{S}B4), hydroxyphenylacetonitrile, bromoacetate Diaza(1,3)bicyclo[5.4.0]undecane and terephthaldehyde with analytical quality are all bought commercially from Aladdin Biochemical Technology Co. Ltd. of Shanghai, China. Potassium carbonate, acetone, ethanol, sodium hydroxide, hydrochloric acid and dimethyl sulfoxide were purchased from Guoyao Chemical Reagent Co. Ltd of Shanghai, China. All chemicals were used without further purification while all water used in our experiments was deionized water.

Characterizations

^{1}H NMR and ^{13}C NMR were measured on a Bruker Advance DMX 400 MHz instrument with tetramethylsilane (TMS) as reference. ESI-MS spectrum was performed on API 4000 MS equipment. TEM (Transmission Electron Microscope) images were obtained with a JEM-100CX Ⅱelectron microscope (100 kV). TEM samples for detection were dropped in copper net, followed by air drying. AFM testing was conducted with a Veeco Nanoscope Multimode Ш SPM and operated in tapping contact mode at ambient temperature. The AFM sample was dropped on the smooth silicon wafer and dried in air. X-ray diffraction (XRD) was recorded on Advance D8 X-ray diffraction with copper Kα radiation. XRD measurement was divided into two parts comprising small angle (0.5-10 degree) and wide angle (10-50 degree) regions. The FT-IR (Fourier Transform Infrared Spectroscopy) spectrums were performed on an Avatar 370 FT-IR Spectrometer using the KBr pellet method at room temperature. For XRD and FT-IR, the samples were centrifuged to remove solvents and then the obtained aggregates were spread evenly on glass slide and dried in air at room temperature. UV-vis curves were obtained at room temperature with a TU-1800pc UV-vis spectrophotometer which was purchased from Purkinje General Co. Ltd. Fluorescence spectra were recorded by F-7000 fluorescence spectrophotometer from HITACHI (Japan). Circular dichroism (CD) and circularly polarized luminescence (CPL) spectra were measured with an Applied Photophysics Chirascan V100 (UK). In order to understand the self-assembly evolution of A2/B2R from the molecular level, the self-assembly process of A2/B2R in aqueous solution was investigated by molecular dynamics (MD) simulation with the Gromacs software package.

Synthesis

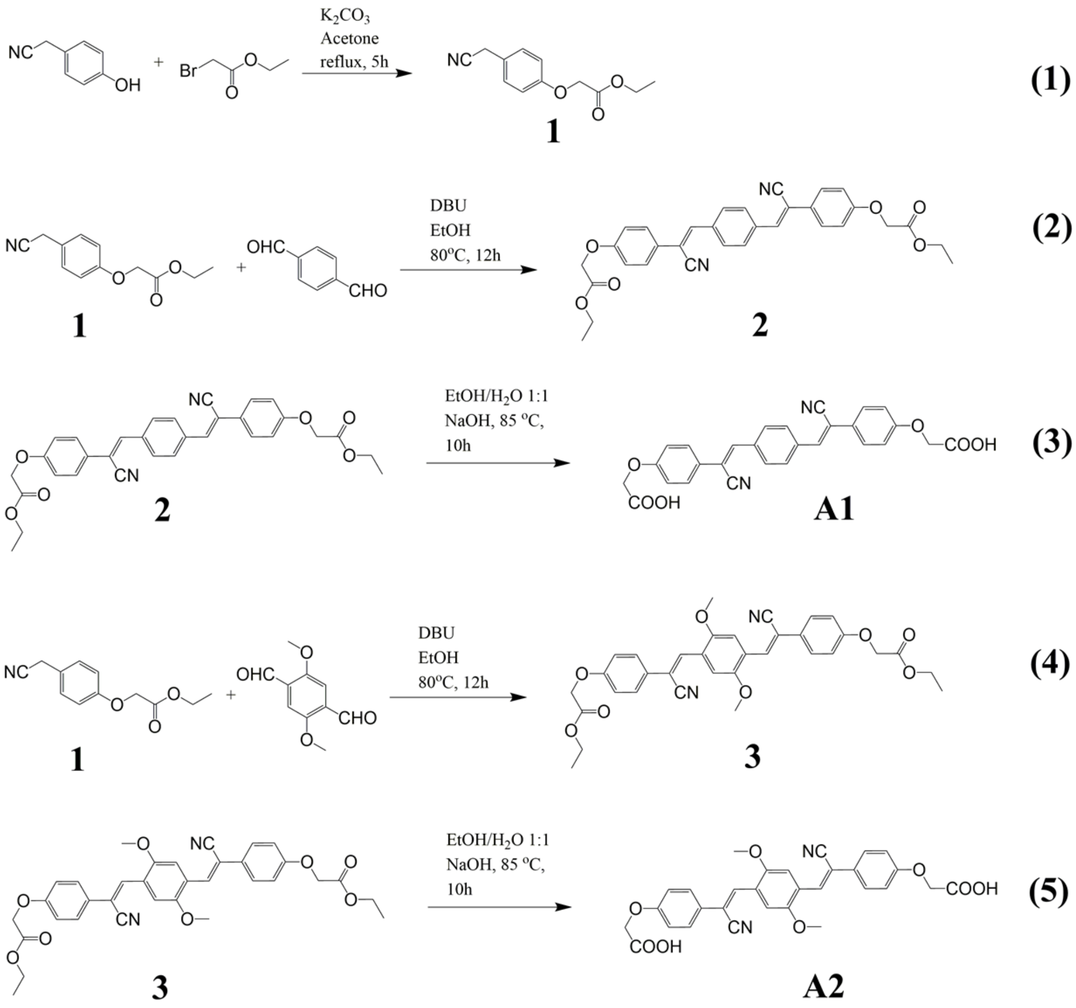

Fig. S1 The synthesis route of **A1** and **A2** molecules.

A1 and **A2** molecules were synthsized as below. 4-Hydroxyphenylacetonitrile (530 mg, 4 mmol), bromoacetate (734 mg, 4.4 mmol) and potassium carbonate (1.5 g, 12 mmol) were added in a single-neck flask, followed by the addition of 50 mL acetone. The mixture was refluxed at around 80 °C for 5 h under nitrogen protection. When the reaction was completed, the mixture was filtered to remove excess salts and the collected solution was subjected to rotary evaporator to remove acetone and excess bromoacetate. The resultant oil with slight yellow color was the product 1 (870 mg, yield 99%).

Compound 2 was synthesized according to a previous report (*Adv. Mater.* **2012**, *24*, 4020-4024). Compound 1 (722 mg. 3.3 mmol), terephthaldehyde (200 mg, 1.5

mmol), Diaza(1,3)bicyclo[5.4.0]undecane (DBU, 0.45 ml, 3 mmol) as well as EtOH (50 ml) were added into a 100 mL single-neck flask. The mixture was refluxed at 80 °C for 12 h. Yellow precipitates were generated quickly along with reaction process. After reaction, the precipitates were collected by reduced pressure filtration. The products were washed by EtOH for several times, followed by drying in oven (65 °C). Products show bright yellow color with a 50 % yield.

In this step, compound 2 shall undergo hydrolysis to form compound **A1**. In detail, 1.4 g of compound 2 (2.6 mmol) dispersed in 50 mL ethanol (EtOH), to which was added aqueous solution of sodium hydroxide (1.4 g, 35 mmol) in 50 ml deionized water. The mixture was stirred under nitrogen protection at 85 °C overnight. An emulsion-like solution was obtained. Then concentrated hydrochloric acid was added into the solution in ice bath to adjust the pH to about 1. A lot of yellow color precipitates appeared, which were collected by reduced pressure filtration. The crude product was dried in oven to generate pure compound **A1** (bright yellow color, 1.2 g, yield 98%). ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.01 (s, 4H), 7.94 (s, 2H), 7.72 (d, J = 12 Hz, 4H), 7.07 (d, J = 12 Hz, 4H), 4.74 (s, 4H). ^{13}C NMR (100 MHz, d_6-DMSO) δ 170.4, 159.3, 140.1, 135.9, 130.5, 129.8, 127.8, 127.0, 118.4, 115.7, 111.3. MS (ESI) calcd for $C_{28}H_{20}N_2O_6$ [MNa$^+$]: 503.1321; found: 503.1113.

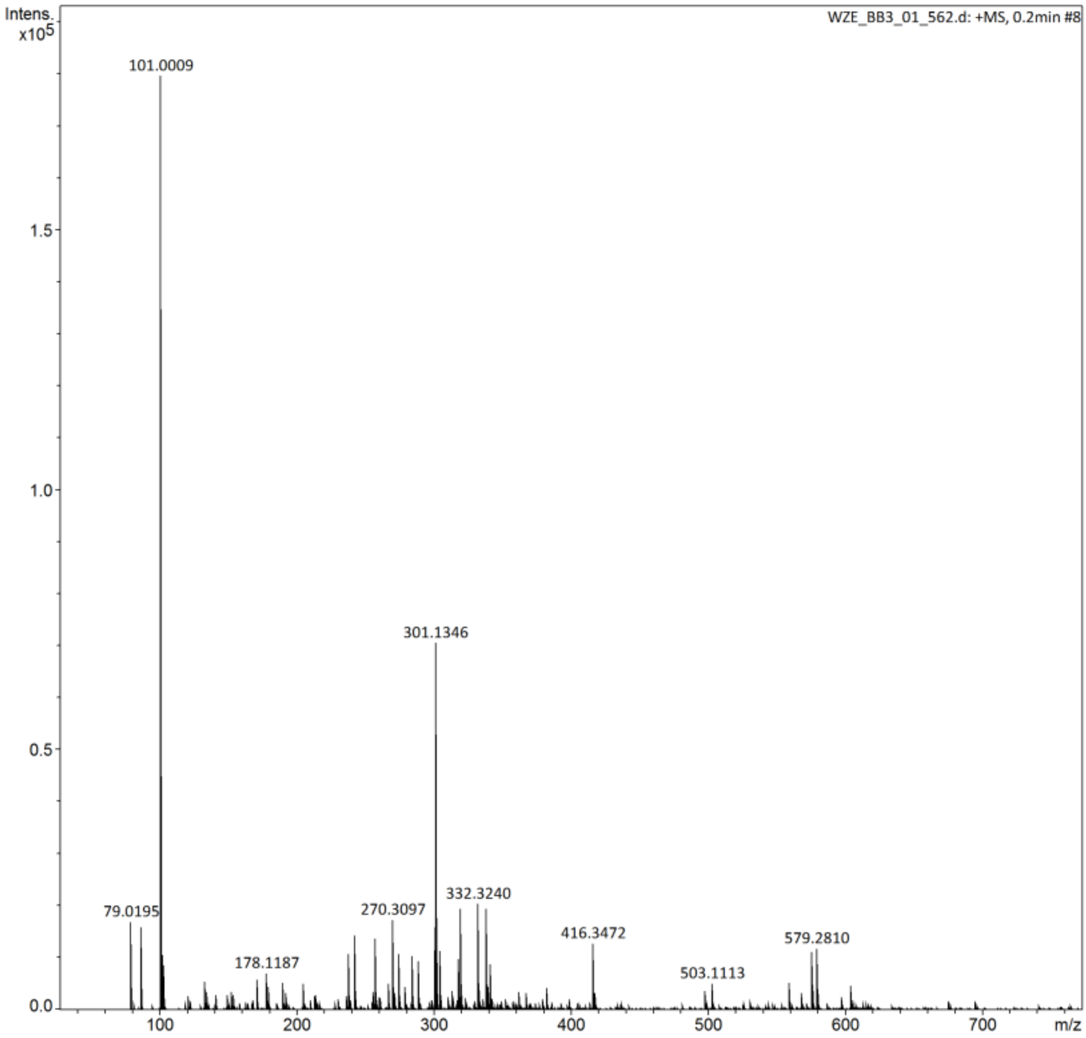

Fig. S2 MS (ESI) of compound **A1**.

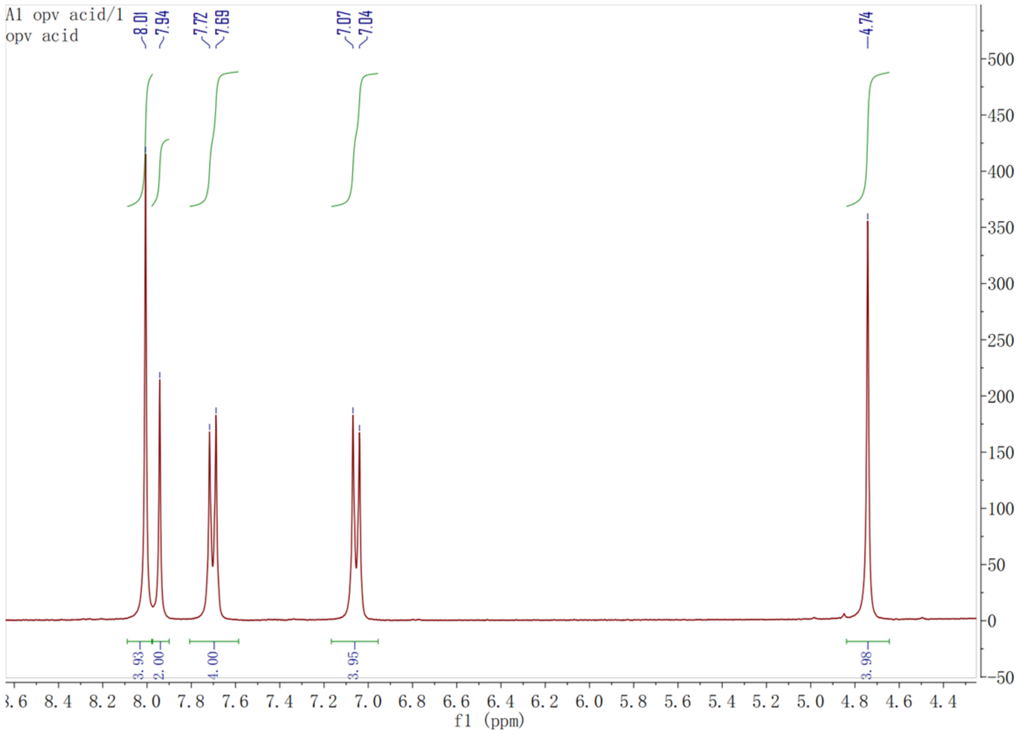

Fig. S3 ^{1}H NMR of compound **A1**.

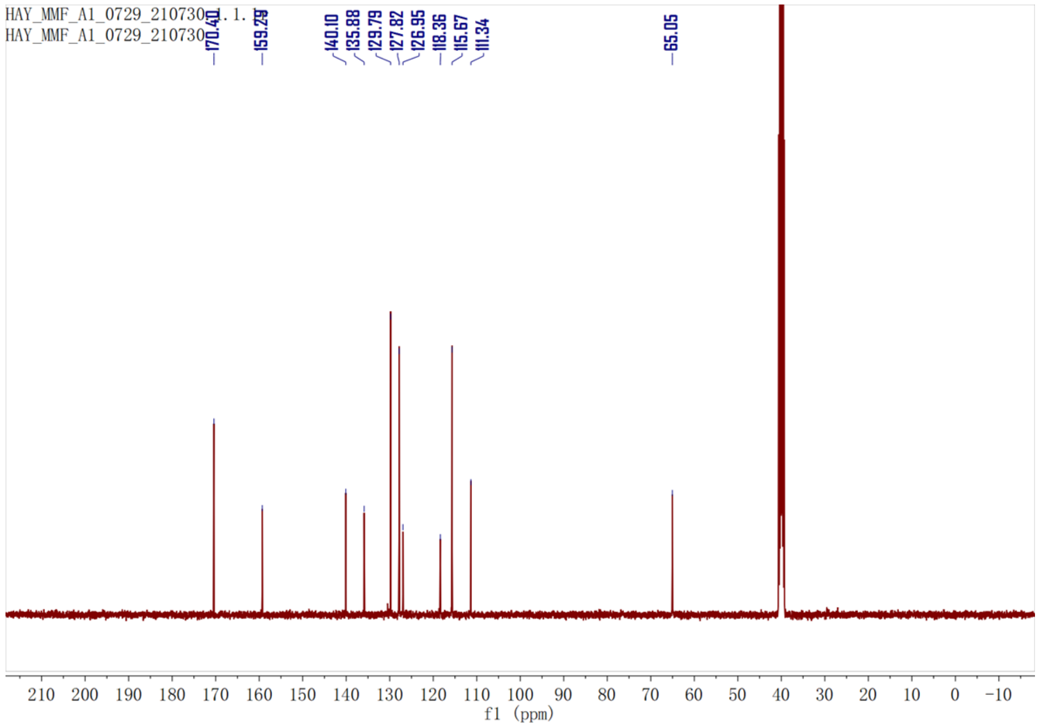

Fig. S4 ^{13}C NMR of compound **A1**.

The reaction (4) as well the yield of 3 is the same with the synthesis of compound 2. The reaction (5) as well the yield of **A2** is the same with the synthesis of compound **A1**. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.9 (s, 2H), 7.73 (s, 2H), 7.68 (d, J = 12 Hz, 4H), 7.06 (d, J = 12 Hz, 4H), 4.71 (s, 4H), 3.89 (s, 6H). MS (ESI) calcd for $C_{30}H_{24}N_2O_8$ [MNa$^+$]: 563.1398; found: 563.1420.

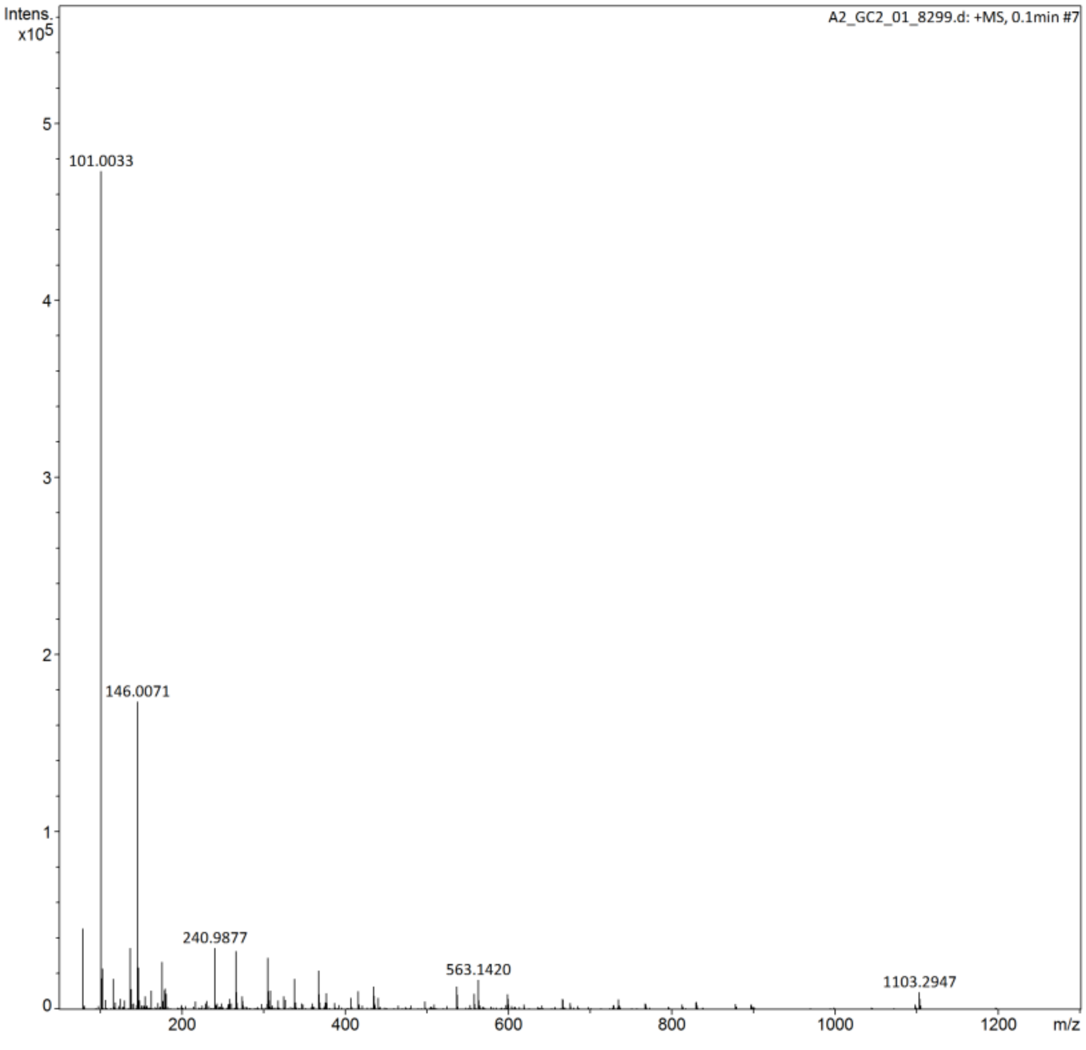

Fig. S5 MS (ESI) of compound **A2**.

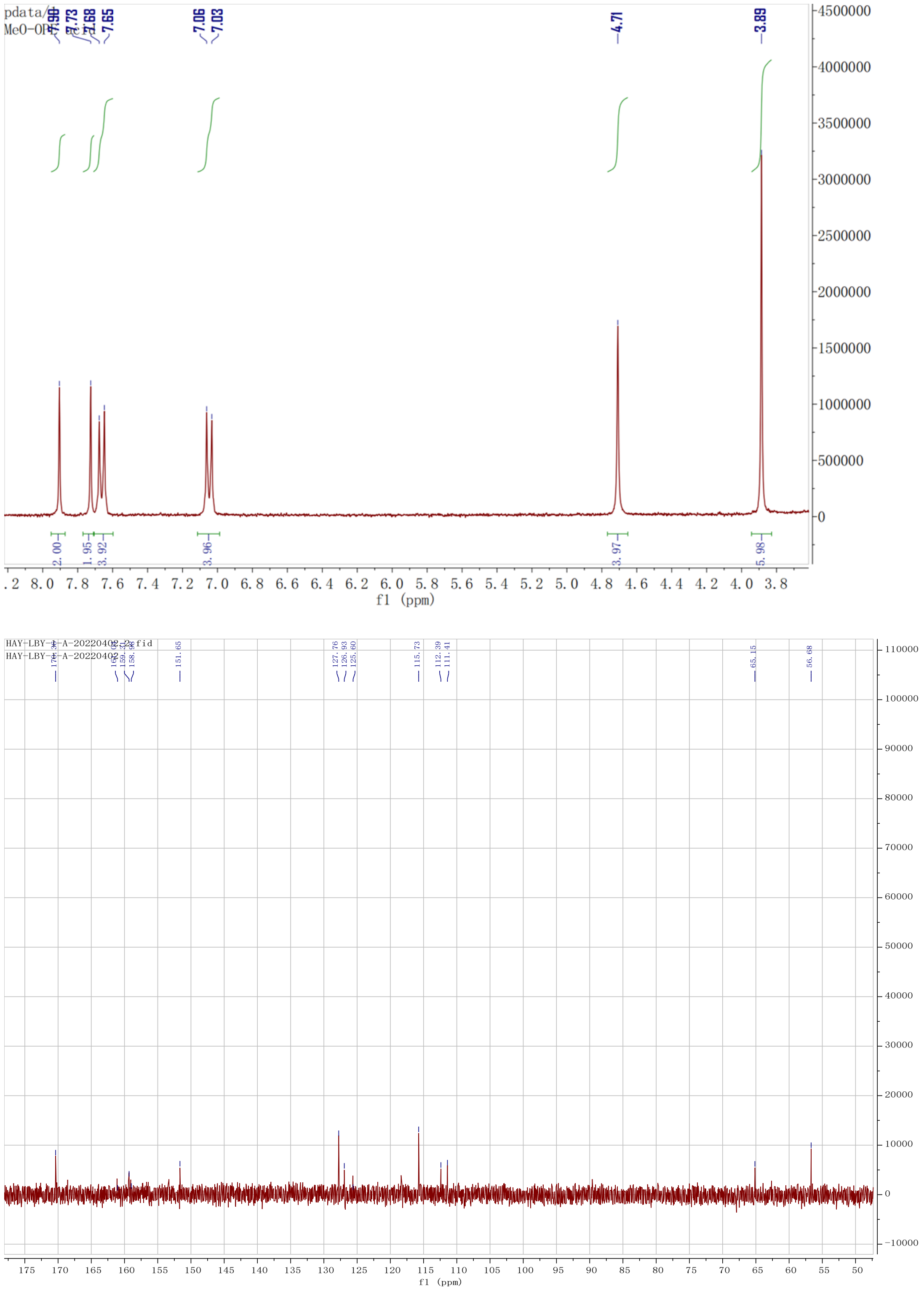

Fig. S6 ^{1}H and ^{13}C NMR of compound **A2**.

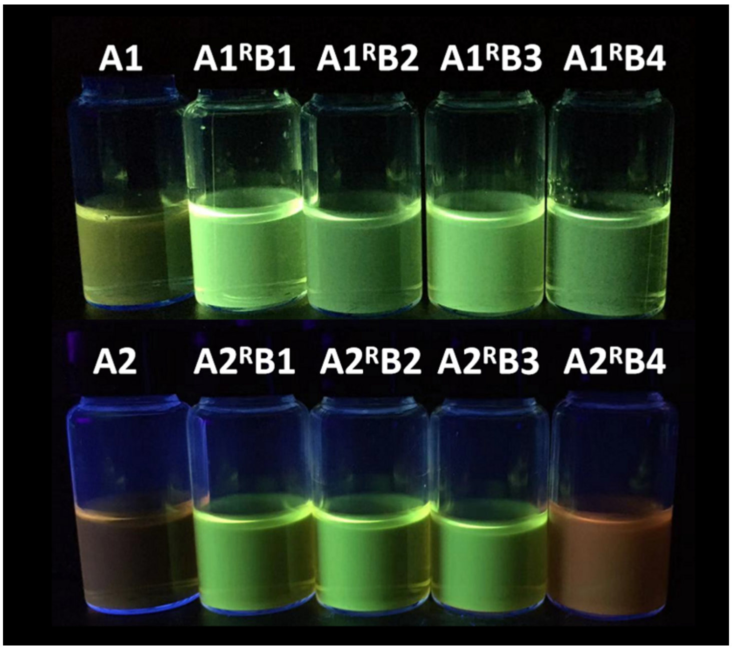

Fig. S7 Fluorescent images of A1, A2, A1/^{R}B1, A1/^{R}B2, A1/^{R}B3, A1/^{R}B4, A2/^{R}B1, A2/^{R}B2, A2/^{R}B3 and A2/^{R}B4 coassembled systems under 365 nm UV light, the concentration of those samples are all 1 mM .

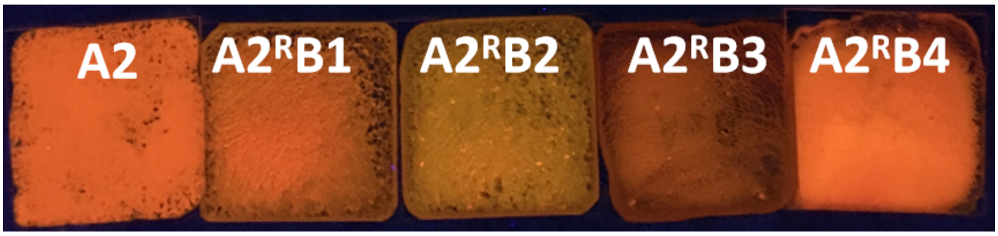

Fig. S8 Solid fluorescent images of A2, A2/^{R}B1, A2/^{R}B2, A2/^{R}B3 and A2/^{R}B4coassembled systems under 365 nm UV light .

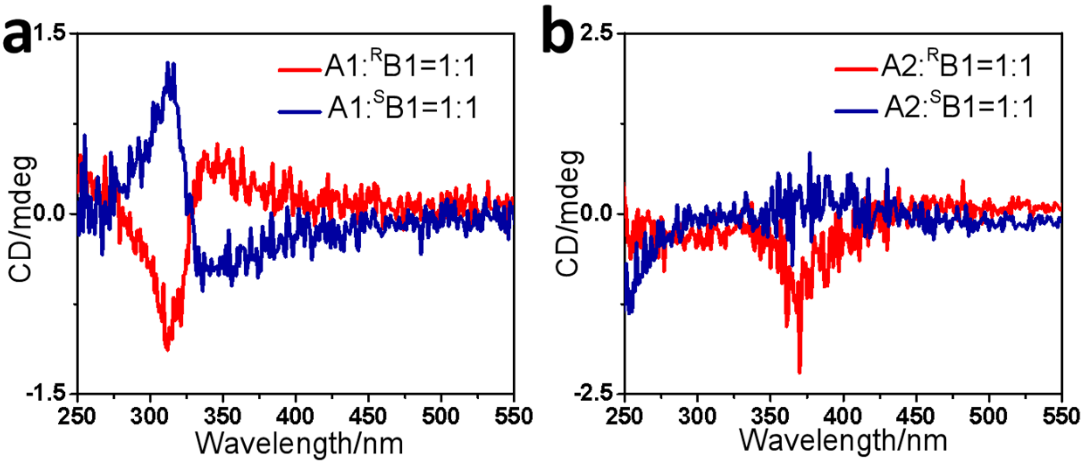

Fig. S9 CD spectra for A1/$^{R(S)}$B1 and A2/$^{R(S)}$B1 coassembled systems.

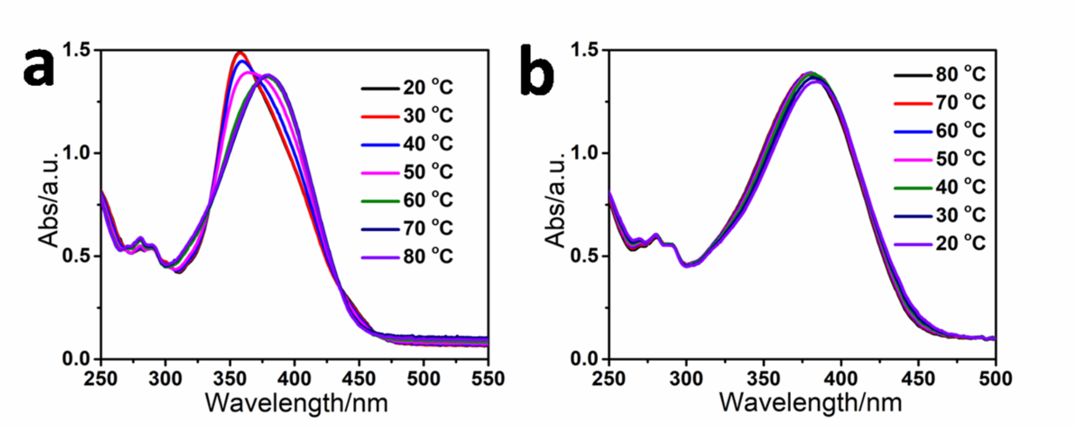

Fig. S10 (a) UV-vis spectra of A1/^{R}B4 (1:1 by molar, 1 mM) from 20 ^{o}C to 80 ^{o}C; (b) UV-vis spectra of A1/^{R}B4 (1:1 by molar, 1 mM) from 80 ^{o}C to 20 ^{o}C.

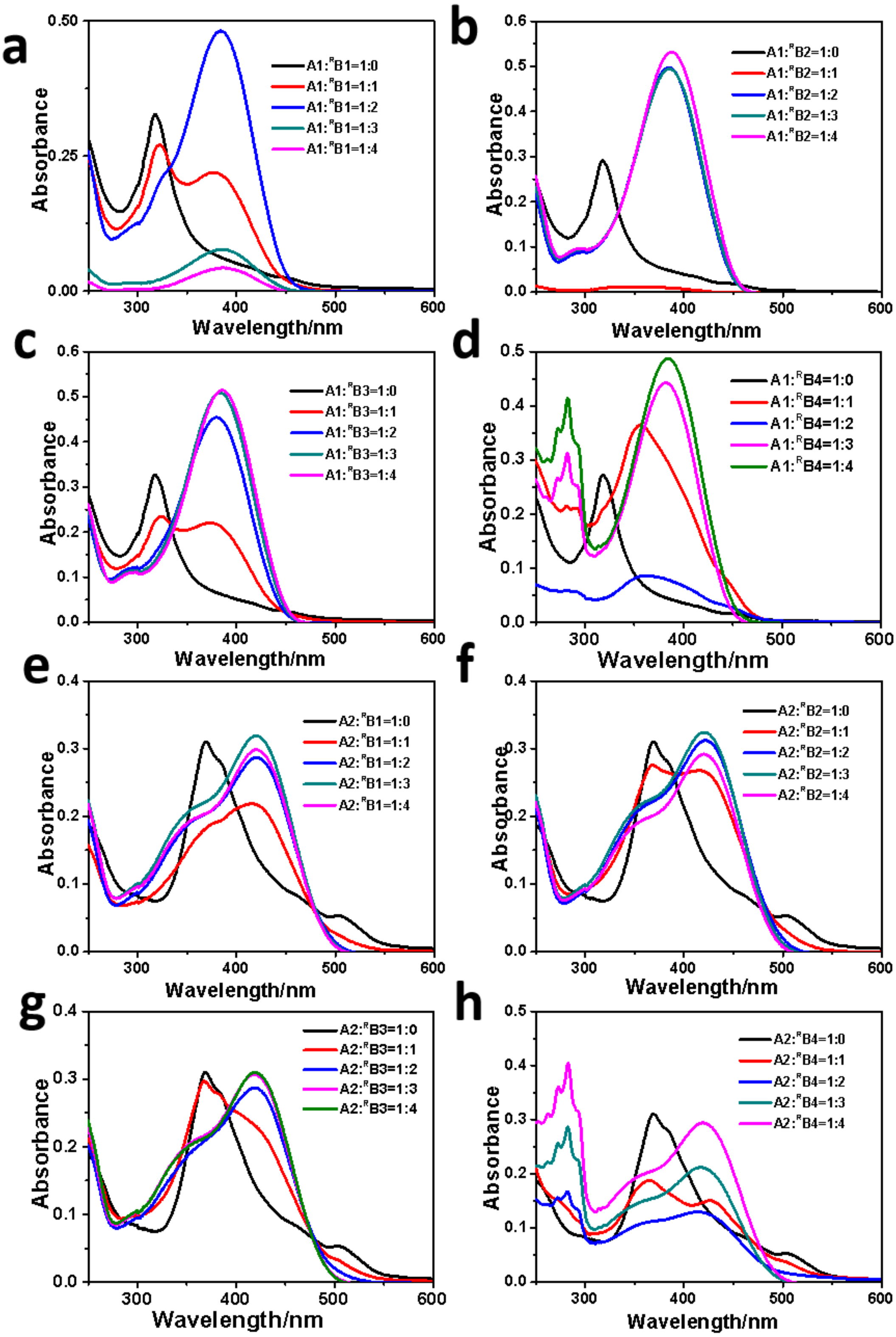

Fig. S11 UV-vis spectra comparison of different samples, (a) A1/^{R}B1; (b) A1/^{R}B2; (c) A1/^{R}B3; (d) A1/^{R}B4; (e) A2/^{R}B1; (f) A2/^{R}B2; (g) A2/^{R}B3 and (h) A2/^{R}B4 coassembled systems.

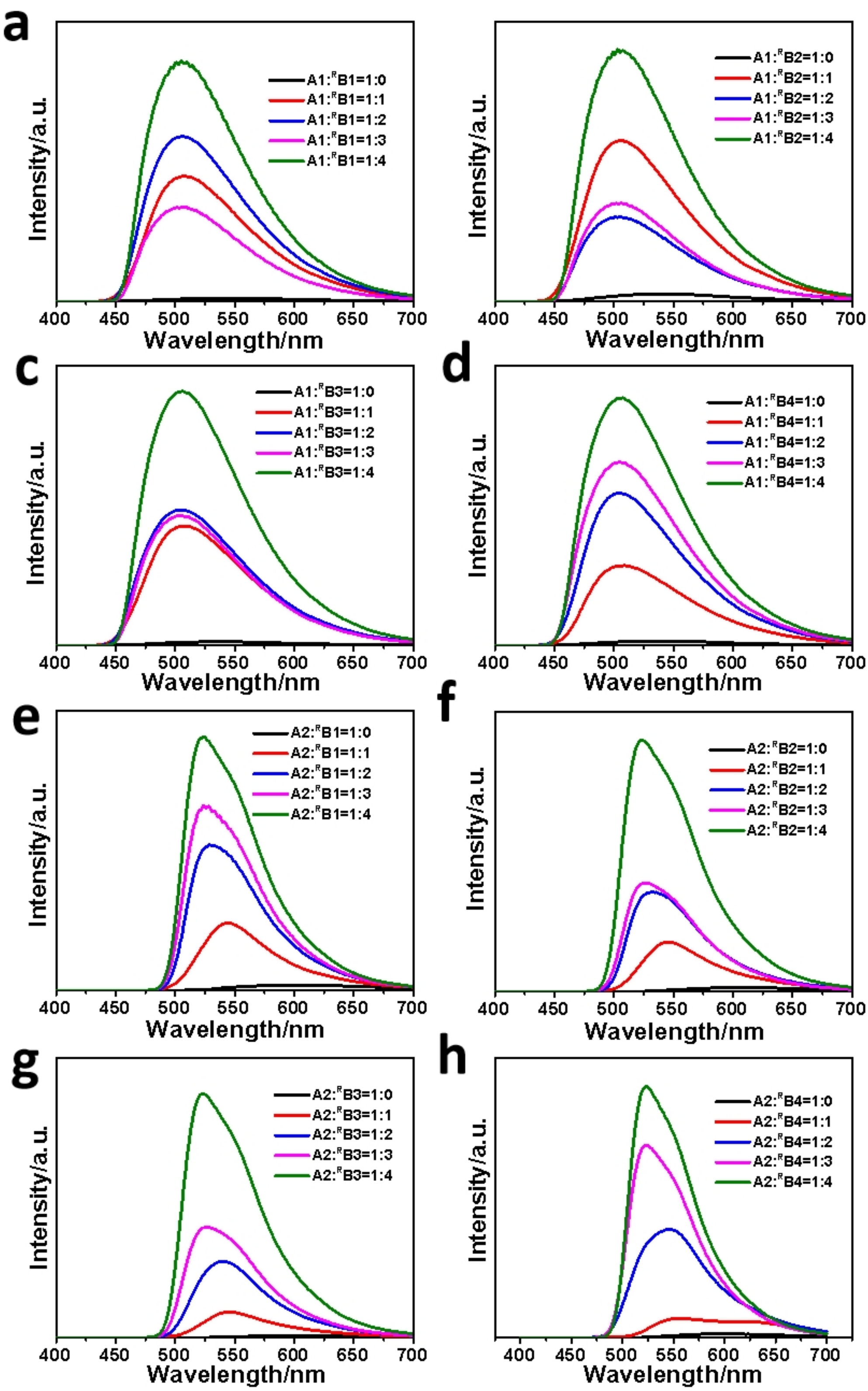

Fig. S12 Fluorescent spectra comparison of different samples, (a) A1/^{R}B1; (b) A1/^{R}B2; (c) A1/^{R}B3; (d) A1/^{R}B4; (e) A2/^{R}B1; (f) A2/^{R}B2; (g) A2/^{R}B3 and (h) A2/^{R}B4 coassembled systems.

Fig. S13 XRD pattern comparison of coassembled systems between A1 and different bases with 1: 1 ratio.

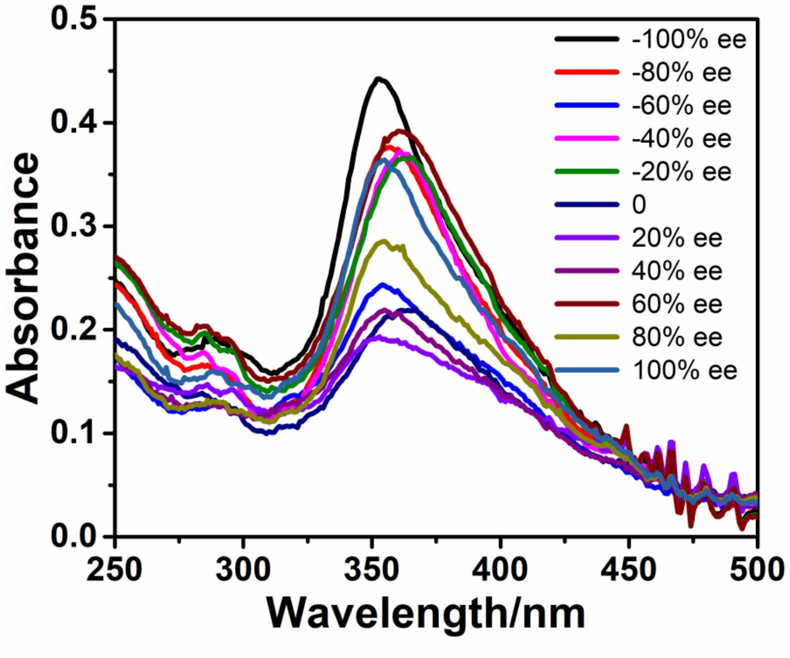

Fig. S14 UV-vis spectra comparison of A1/^{R}B4 coassembled system with different ee%.

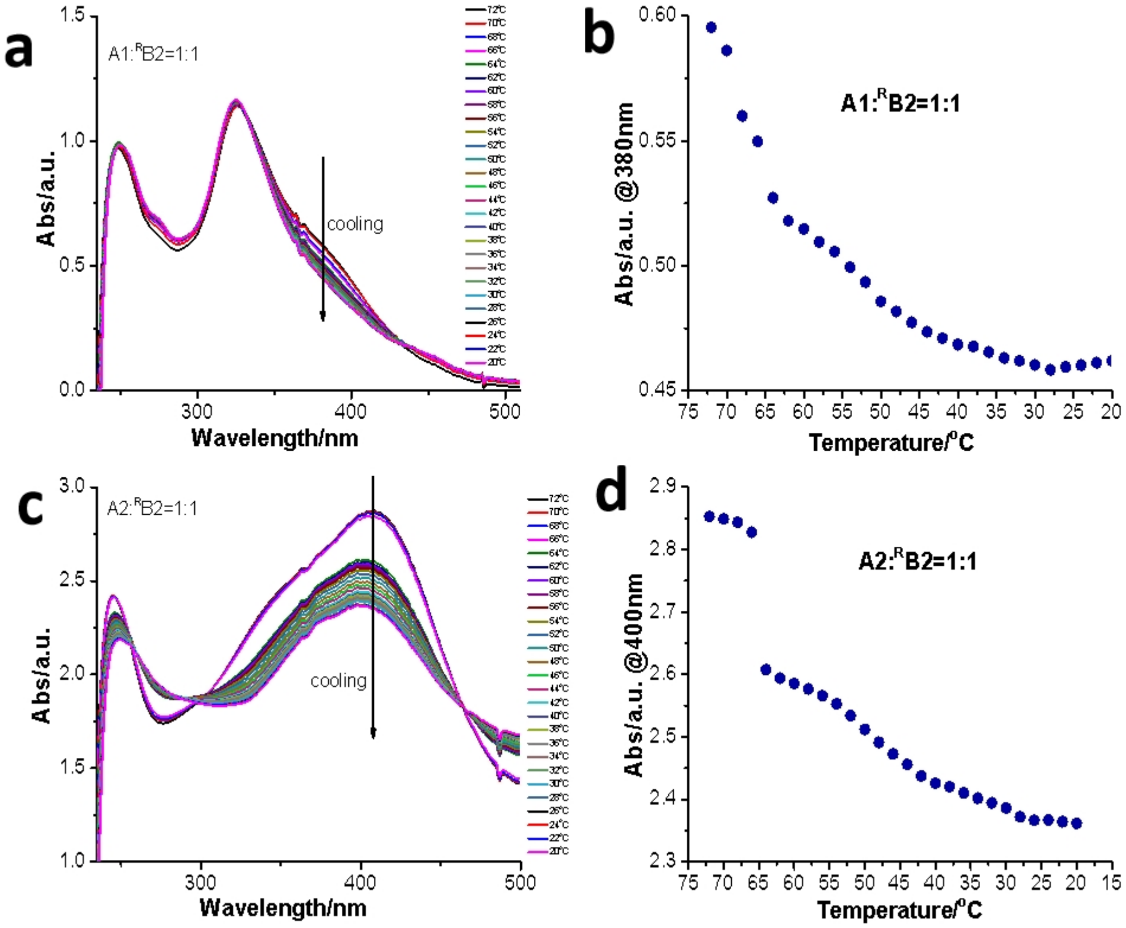

Fig. S15 UV-vis spectra comparison of A1/^{R}B2 and A2/^{R}B2 coassembled systems upon cooling from 72 °C to 20 °C.