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Quantitative Chiral Sensing of Organic Acids by Benzimidazole Derivatives though H-bond Coassembly

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Experimental Section

Materials

All chiral acids were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Dimethylsulfoxide (DMSO), Tetrahydrofuran (THF), Ethyl alcohol, Chloroform-D ($CDCl_3$), Methanol-D (CD_4O) were purchased from Jinan Saibo Instrument Co., Ltd. All water used in this work was deionized (DI) water.

Characterizations

If not particularly indicated, all characterizations were carried out at room temperature. Scanning electron microscope (SEM) images were recorded using a Zeiss scanning electron microscope. The samples for SEM detection were dropped in the silicon pellet, sucking most of solvents by a filter paper and air dried, followed by gold spraying. X-ray diffraction (XRD) patterns were recorded on a German Bruker/D8 Advanced diffractometer with Cu Ka radiation (l = 0.15406 nm, voltage 40 kV, current 40 mA). It should be noted that the whole measurement was divided into two parts comprising small angle (0.5–10 degree) and wide angle (10–50 degree) regions. For XRD, assembled systems were centrifuged to remove solvents and non-assembled species, and the obtained aggregates were spread evenly on glass slide and air-dried at room temperature. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a Bruker Advance 400 MHz instrument. The samples of ^{1}H NMR were prepared as follows. Firstly, **BI-4**, *L*-**A-9**, *L*-**A-10** and *L*-**A-11** dissolved in THF as concentrated stock solutions (10 mM). Then, **BI-4** stock solution (100 μL) in the absence and presence chiral acids stock solution (500 μL) were taken out by pipettes into a 5 mL vial and

dried in oven. Finally, 500 μL (90% $CDCl_3$+10% CD_4O) were added into vial. Circular dichroism (CD) spectra were measured with Applied Photophysics Chirascan.

Computational details

The geometries of **BI-4** and *L*-**A-9** were optimized by Gaussian View06 program, which were initially optimized, and the electrostatic potential (ESP) was simultaneously calculated by Hartree–Fork method at the B3LYP/6-31G (d) basis. The Antechamber program was used to fit the restrained electrostatic potential (RESP) charge, and then the general Amber force field (GAFF) was adopted to parameterize the for subsequent MD simulations. MD was performed using GROMACS and the details as following. The initial configuration was obtained by equilibration of SPC water in a triclinic simulation box with a length (x), width (y) and height (z) of 10, 10, 50 nm, respectively. Then, a cylindrical cavity with 2 nm radius was carved in the center of the simulation box along the z axis. The molecules of 100 **BI-4** and 500 *L*-**A-9** with a length of 45 nm were placed randomly inside the cavity using PACKMOL. The MD simulations of **BI-4**/*L*-**A-9** coassembled system were carried out for 40 ns with a time step of 0.001 ps per integration step under the ensemble conditions of T = 298 K and 1 bar.

Sample preparation

All benzimidazole derivatives (**BI-1** to **BI-4**) and chiral acids (**A-1** to **A-16**) dissolved in DMSO as different concentration concentrated stock solutions. In order to trigger the coassembly, a certain amount of stock solutions of imidazole probes and chiral acids were added into 5 mL bottle, followed by the addition the DI water. Taking the preparation of **BI-4**/***L*-A-9** (**BI-4**: ***L*-A-9** = 0.5mM: 2.5mM) coassembly as an example, **BI-4** (42.6 mg, 0.1 mmol) and ***L*-A-9** (16.6 mg, 0.1 mmol) were dissolved in 1 mL DMSO (100 mM). Then, **BI-4** and ***L*-A-9** stock solution (5 μL and 25μL, respectively) were taken out by pipettes into different 5 mL vial, following adding the DI water (970 μL) by a pipette into the vials. The vial was sealed by a cap, and an aging period at least for 8 h at room temperature was applied.

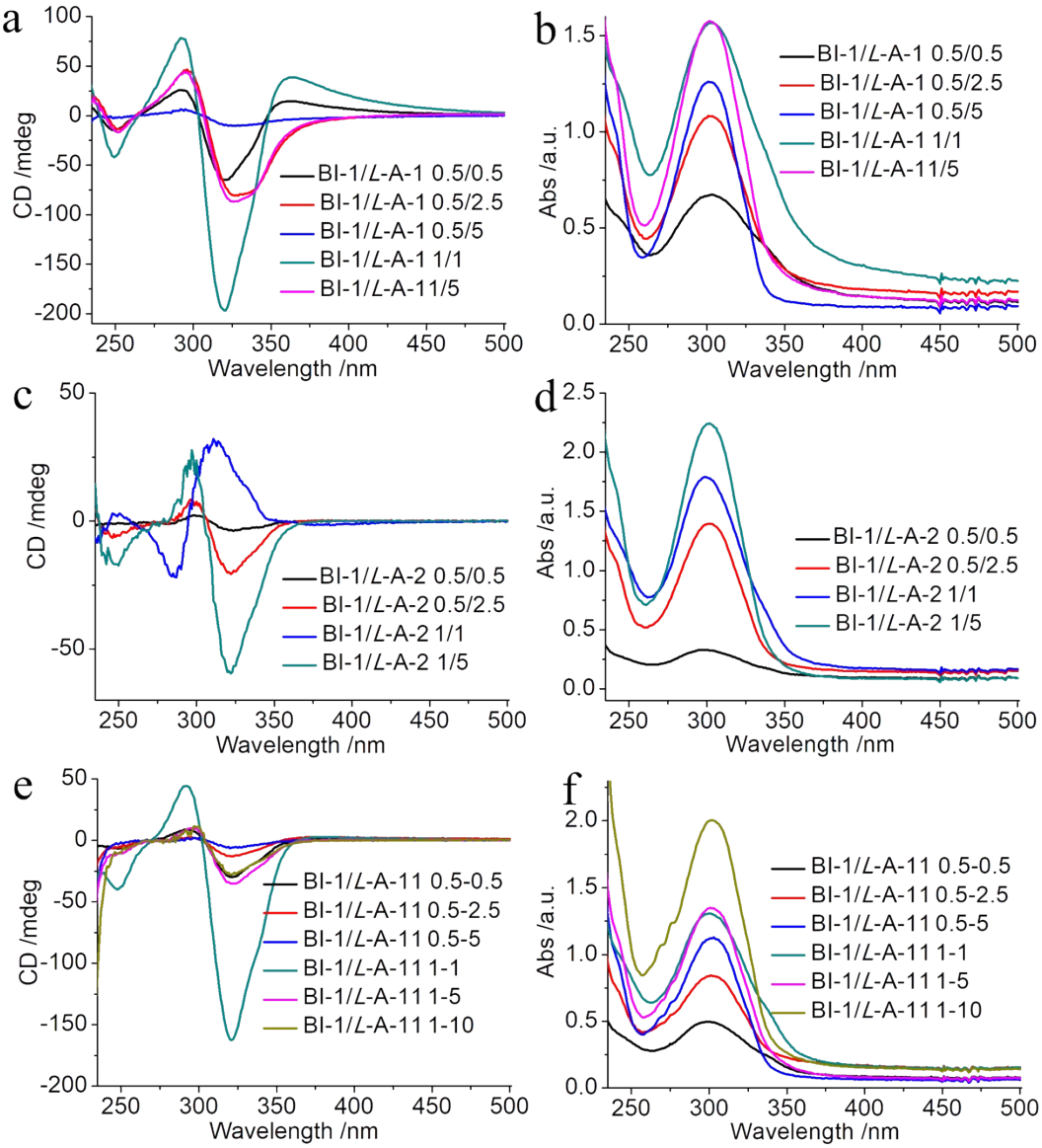

Figure S1. CD and UV-vis spectra of BI-1 coassembled with A-1 (a, b), A-2 (c, d) and A-11 (e, f) at different concertrations.

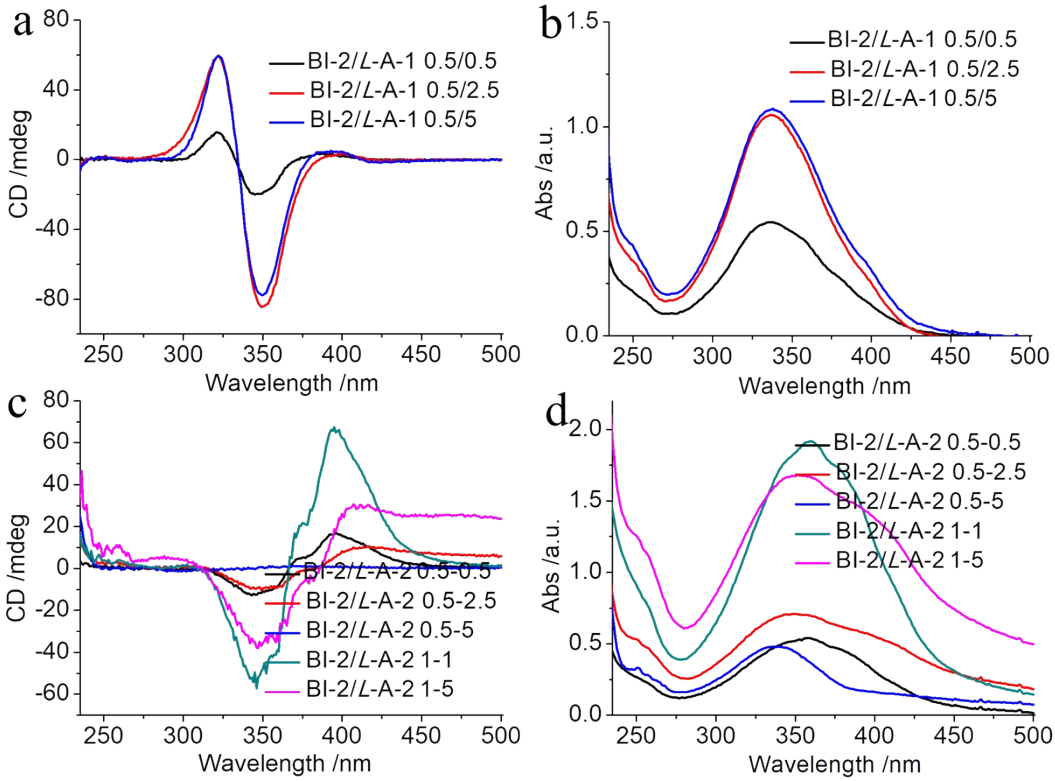

Figure S2. CD and UV-vis spectra of BI-2 coassembled with A-1 (a, b) and A-2 (c, d) at different concertrations.

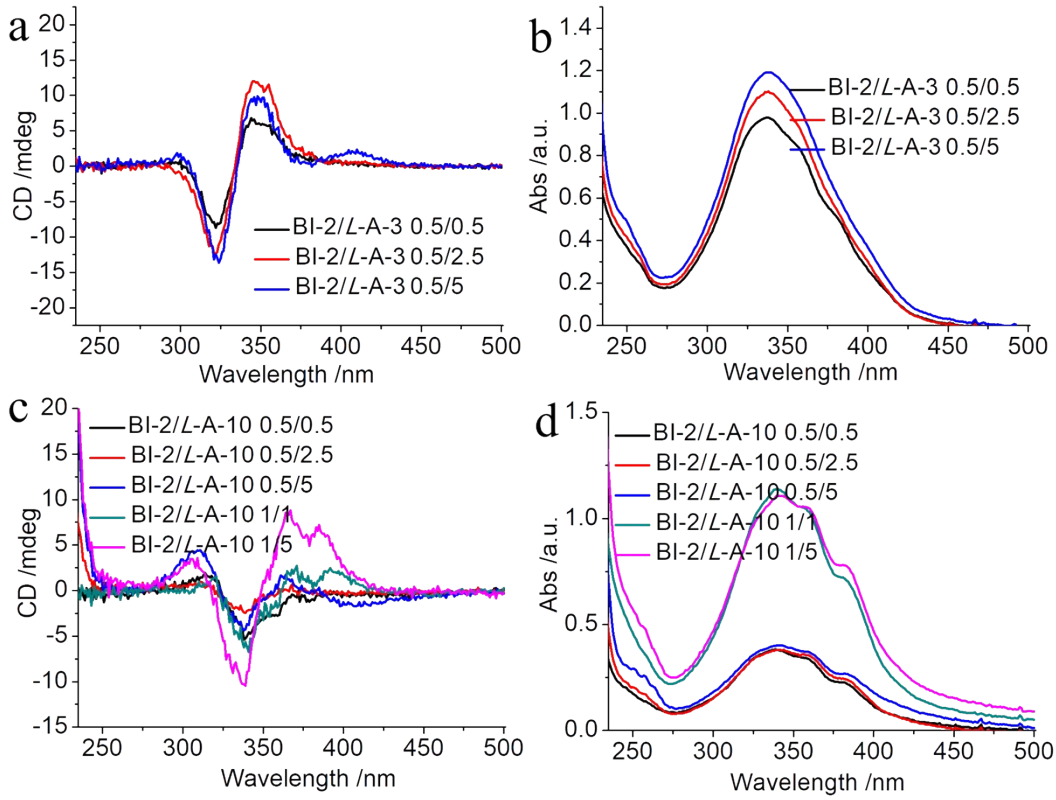

Figure S3. CD and UV-vis spectra of BI-2 coassembled with A-3 (a, b) and A-11 (c, d) at

different concertrations.

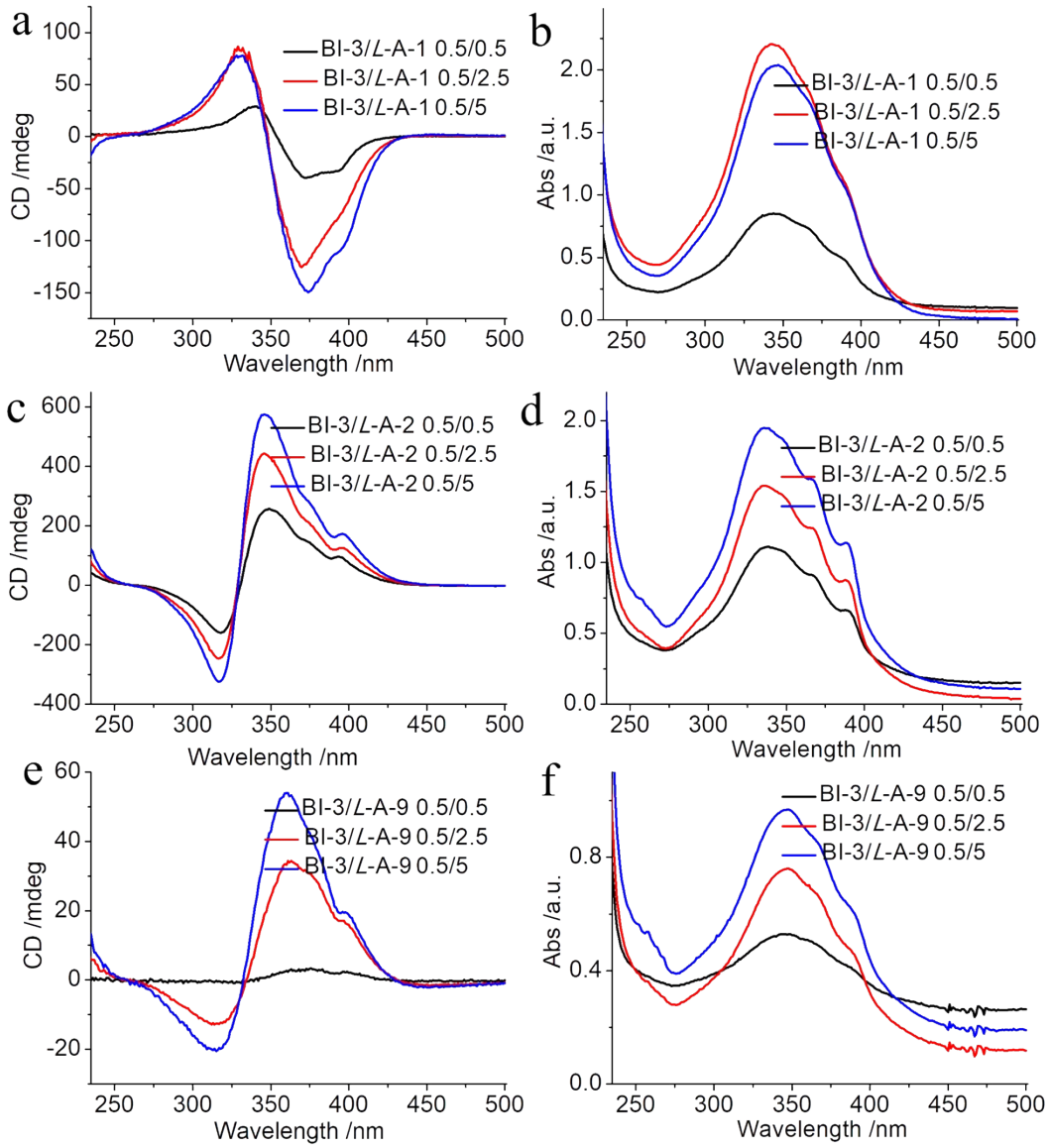

Figure S4. CD and UV-vis spectra of BI-3 coassembled with A-1 (a, b), A-2 (c, d) and A-9 (e, f) at different concertrations.

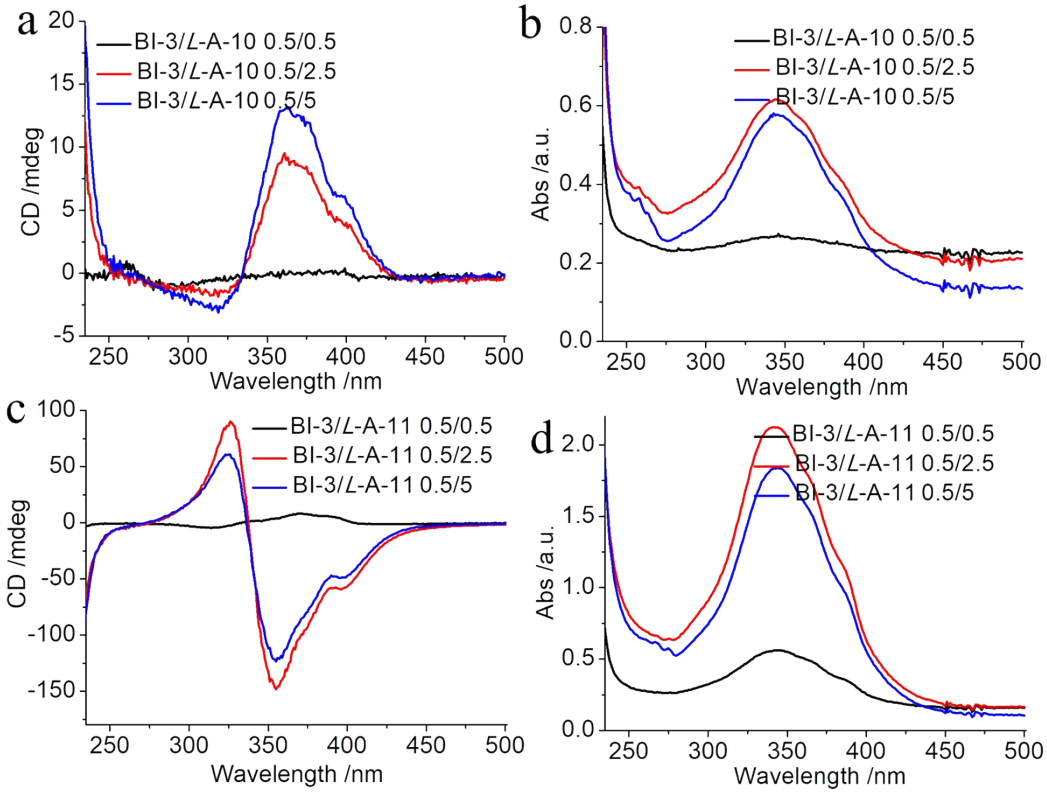

Figure S5. CD and UV-vis spectra of BI-3 coassembled with A-10 (a, b) and A-11 (c, d) at different concertrations.

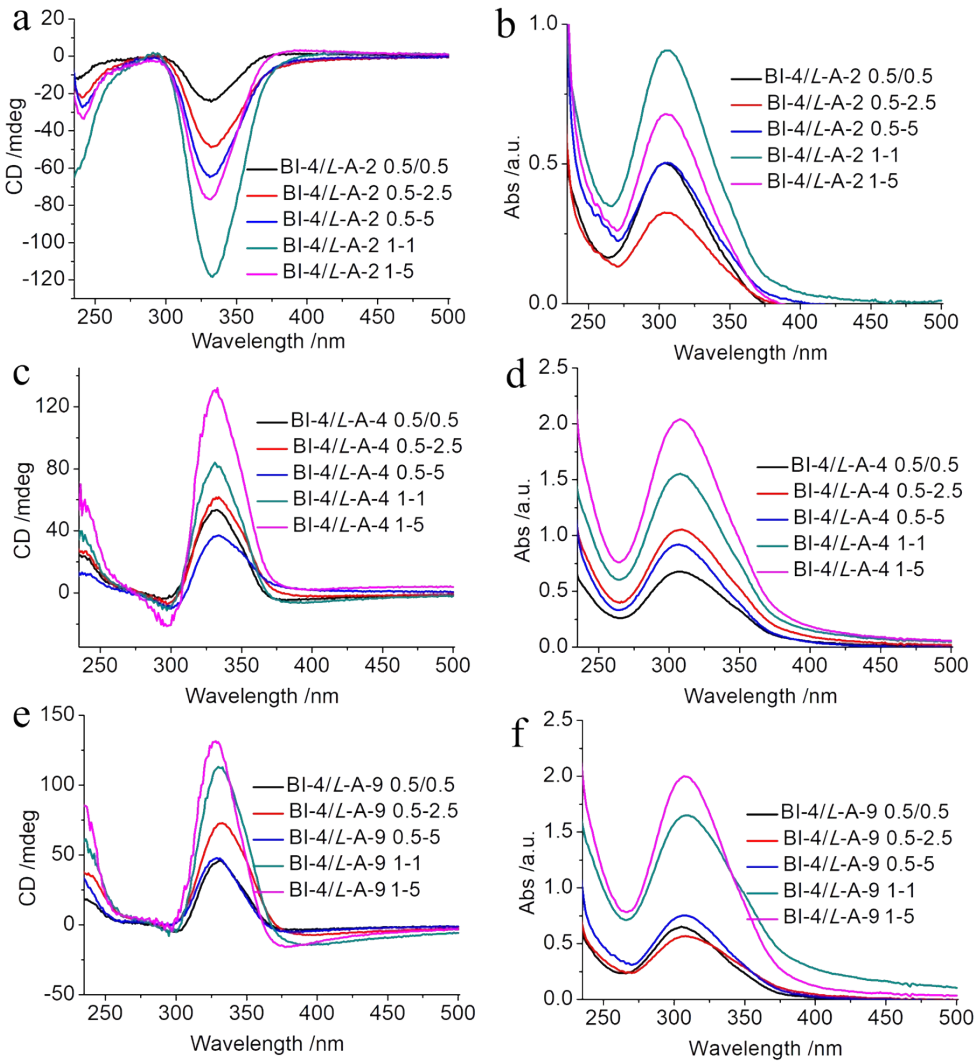

Figure S6. CD and UV-vis spectra of BI-4 coassembled with A-2 (a, b), A-4 (c, d) and A-9 (e, f) at different concertrations.

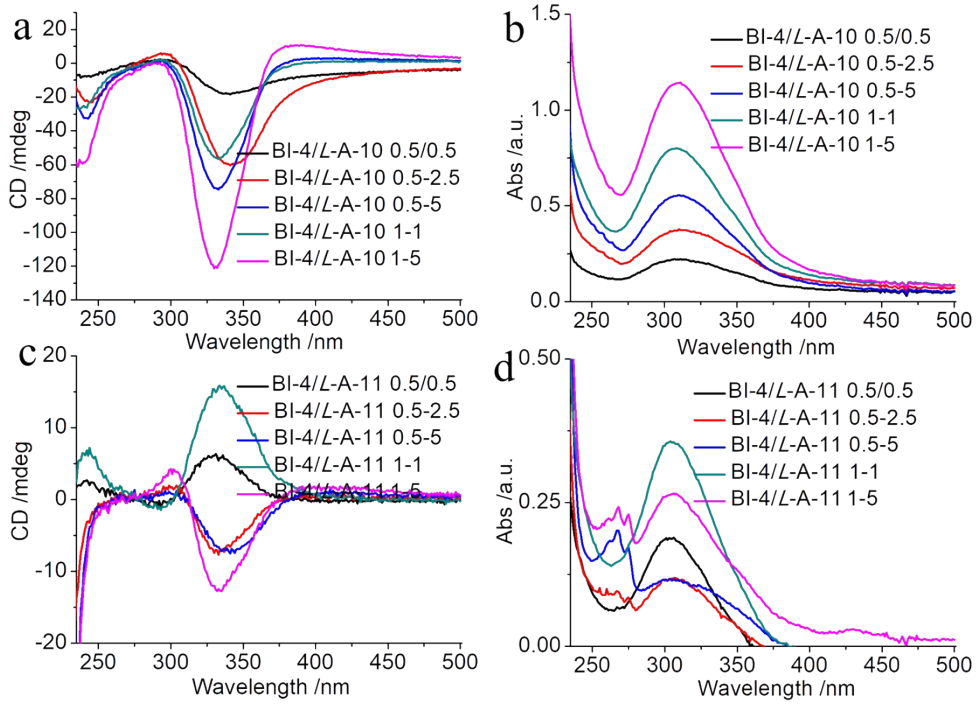

Figure S7. CD and UV-vis spectra of BI-4 coassembled with A-10 (a, b) and A-11 (c, d) at different concertrations.

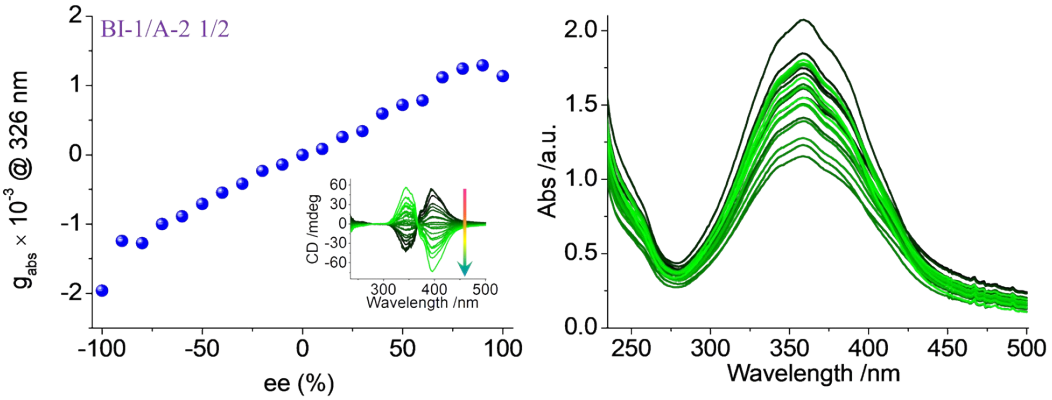

Figure S8. CD spectra, gabs values versus the ee% values and UV spectra of BI-1/A-2 (1 mM:2mM).

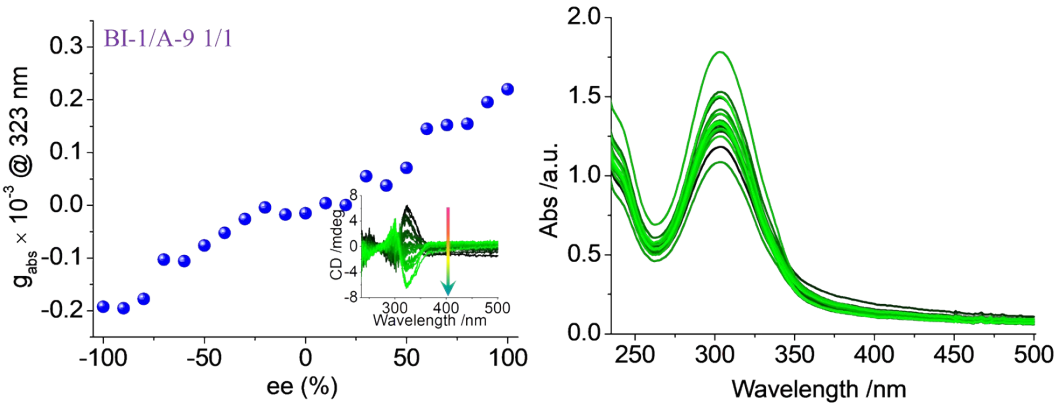

Figure S9. CD spectra, gabs values versus the ee% values and UV spectra of BI-1/A-9 (1 mM:1mM).

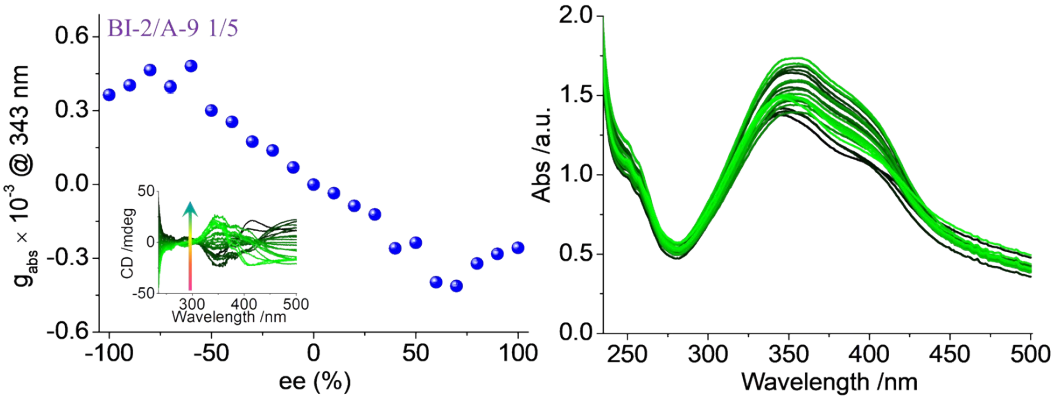

Figure S10. CD spectra, gabs values versus the ee% values and UV spectra of BI-2/A-9 (1 mM:5mM).

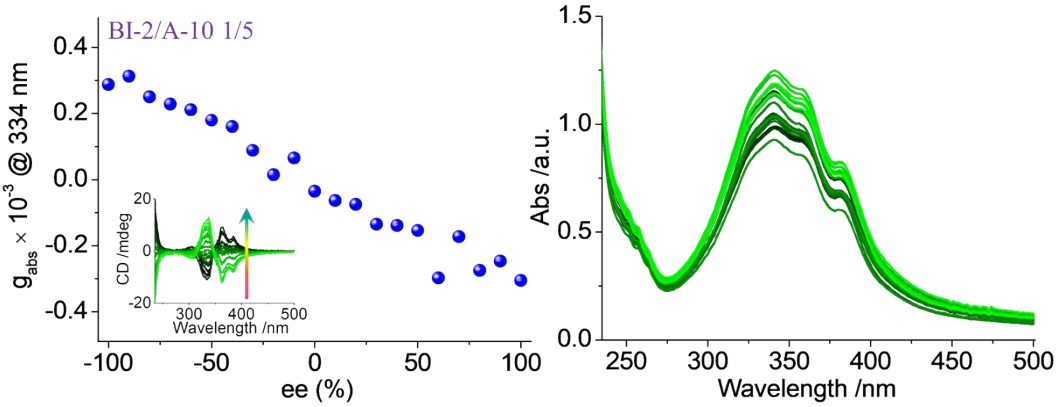

Figure S11. CD spectra, gabs values versus the ee% values and UV spectra of BI-2/A-10 (1 mM:5mM).

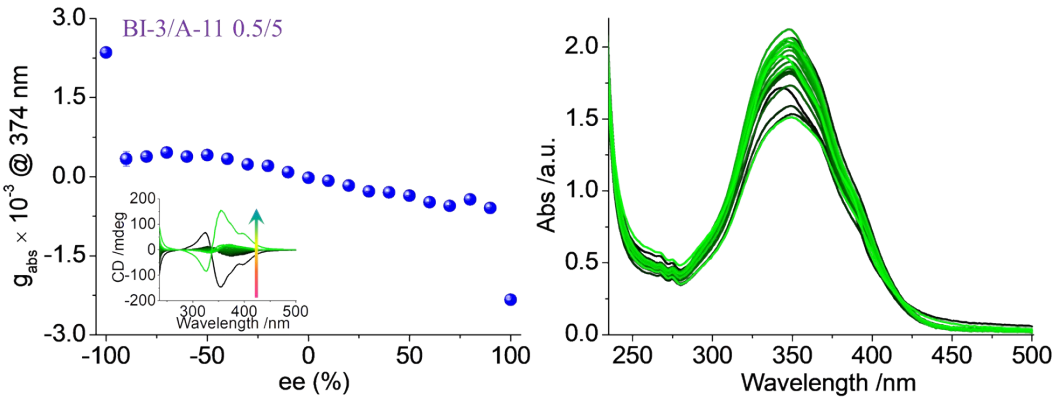

Figure S12. CD spectra, gabs values versus the ee% values and UV spectra of BI-3/A-11 (0.5 mM:5mM).

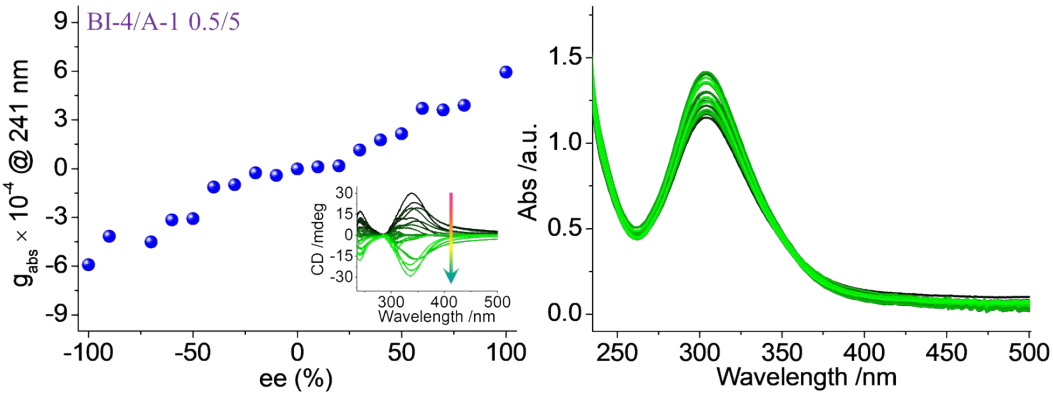

Figure S13. CD spectra, gabs values versus the ee% values and UV spectra of BI-4/A-1 (0.5 mM:5mM).

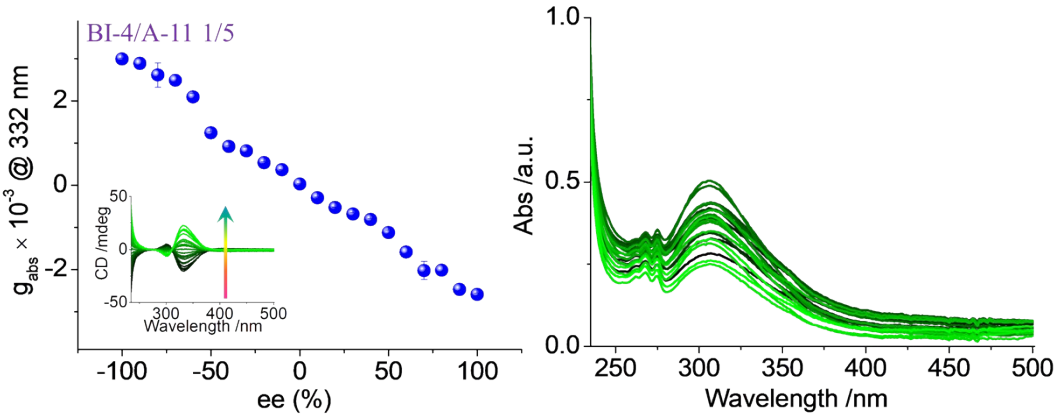

Figure S14. CD spectra, gabs values versus the ee% values and UV spectra of BI-4/A-11 (1 mM:5mM).

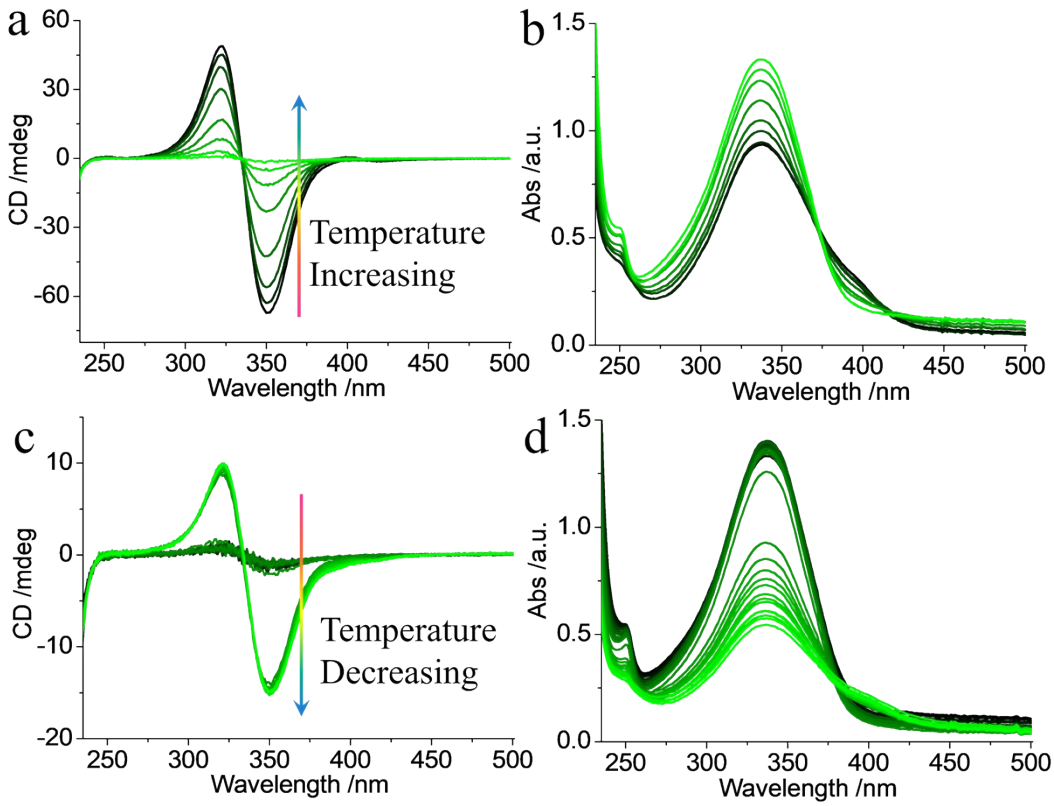

Figure S15. CD and UV spectra of temperature increasing (a, b) and decreasing (c, d) process of BI-2/A-1 (0.5 mM:5mM).

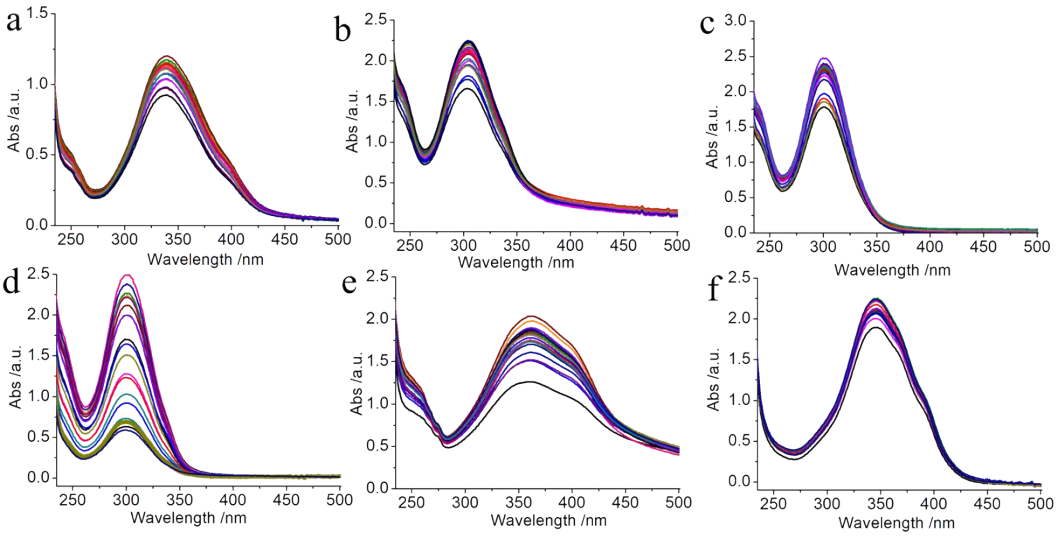

Figure S16. UV spectra of BI-2/A-1 (0.5 mM:5mM), BI-1/A-1 (1 mM:1mM), BI-2/A-2 (1 mM:5mM), BI-1/A-11 (1 mM:2mM), BI-2/A-11 (1 mM:5mM) and BI-3/A-1 (0.5 mM:5mM), respectively.

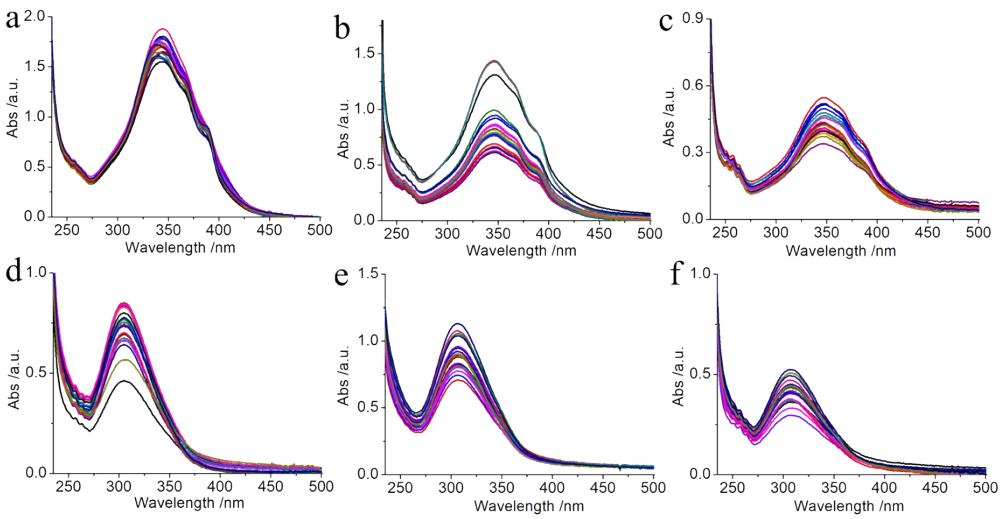

Figure S17. UV spectra of BI-3/A-2 (0.5 mM:5mM), BI-3/A-9 (0.5 mM:5mM), BI-3/A-10 (0.5 mM:5mM), BI-4/A-2 (0.5 mM:5mM), BI-4/A-9 (0.5 mM:2.5mM) and BI-2/A-10 (0.5 mM:5mM), respectively.

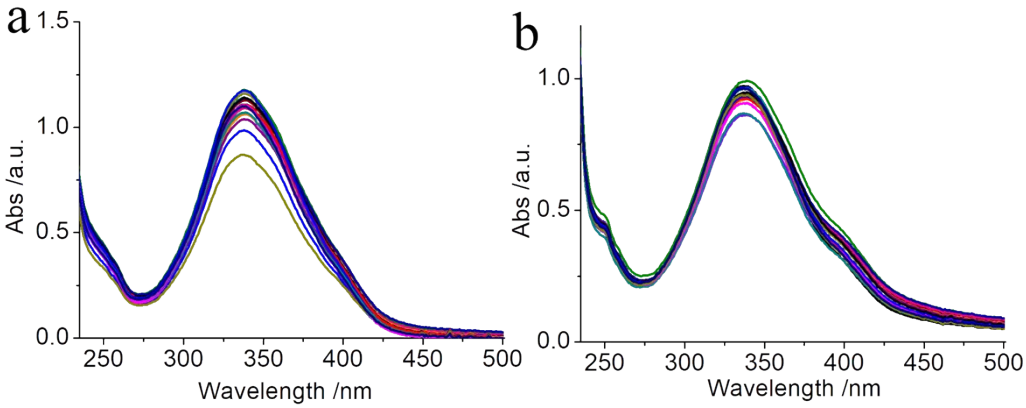

Figure S18. UV spectra of BI-2/A-1 (0.5 mM:2mM) and BI-2/A-1 (0.5 mM:8mM).

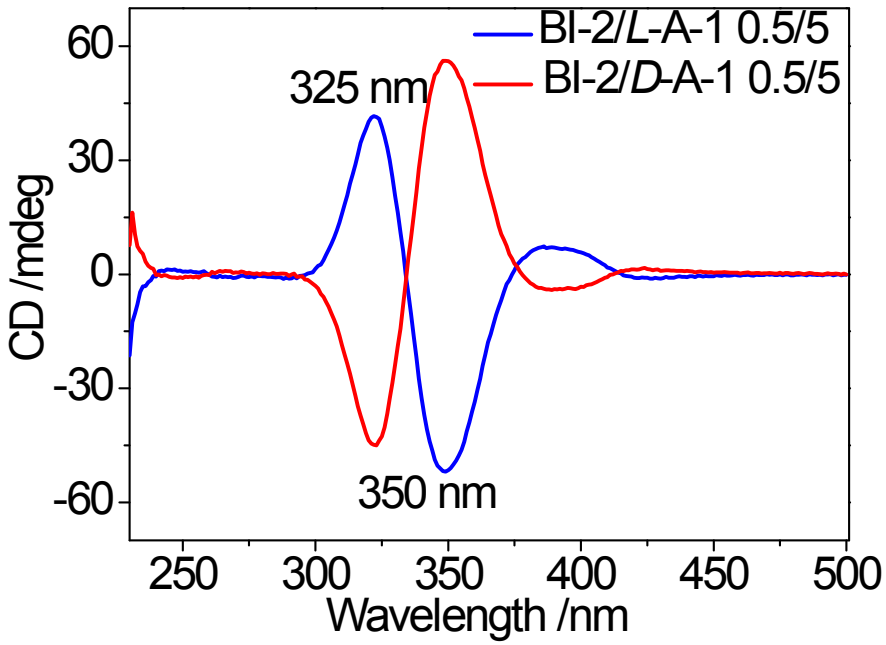

Figure S19. CD spectra of **BI-2** coassembled with **A-1**.

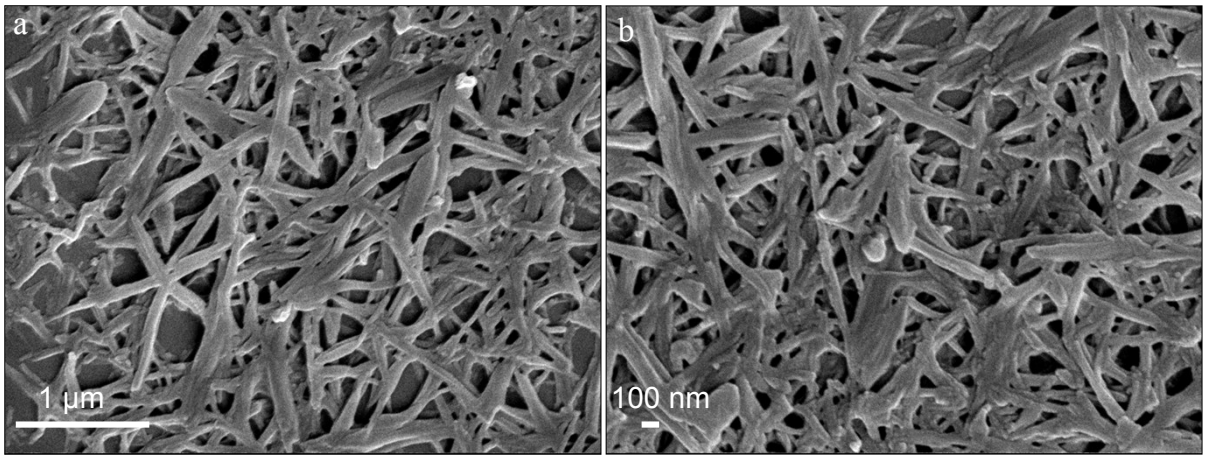

Figure S20. (a, b) SEM images of **BI-4** (1 mM).

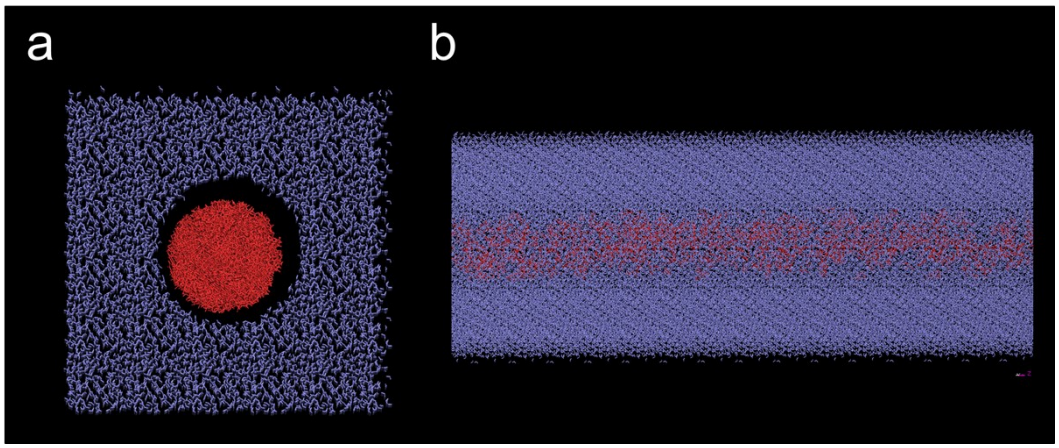

Figure S21. (a, b) MD simulations of **BI-4**/***L*-A-9** coassembled system (red) assembled in water (pale blue) in axial and lateral views, respectively.

Table S1. The fitted equations and R^2 of coassembled systems (Figure 1a-l).

Coassembled Systems	**Fitted Equations**	**R^2**
BI-1/A-1 1/1	$y = -0.2414 - 0.1991x - 3.5595\times10^{-5}x^2 + 1.8195\times10^{-5}x^3 + 6.0637\times10^{-9}x^4 - 4.3446\times10^{-10}x^5$	0.998
BI-1/A-2 1/2	$y = -0.1368 + 0.0518x - 3.5695\times10^{-5}x^2 - 1.0419\times10^{-5}x^3 + 2.2722\times10^{-8}x^4 + 1.2048\times10^{-9}x^5 - 2.0762\times10^{-12}x^6 - 6.1787\times10^{-14}x^7$	0.993
BI-1/A-11 1/5	$y = 0.2141 - 0.2384x + 6.9700\times10^{-5}x^2 + 4.6606\times10^{-5}x^3 - 2.1627\times10^{-8}x^4 - 4.9759\times10^{-9}x^5 + 1.3667\times10^{-12}x^6 + 2.1486\times10^{-13}x^7$	0.999
BI-2/A-11 1/5	$y = -1.3203\times10^{-4} - 0.0043x - 2.7537\times10^{-6}x^2 + 3.7643\times10^{-7}x^3 + 2.9769\times10^{-10}x^4 - 5.8898\times10^{-11}x^5$	0.998
BI-3/A-1 0.5/5	$y = -0.0169x - 0.0611$	0.993
BI-3/A-2 0.5/5	$y = 0.0212 + 0.0099x + 1.2547\times10^{-6}x^2 + 7.0293\times10^{-7}x^3$	0.995
BI-3/A-9 0.5/5	$y = -0.0195 + 0.0198x + 6.4320\times10^{-5}x^2 + 3.3359\times10^{-7}x^3$	0.999
BI-4/A-2 0.5/5	$y = 0.0602 - 0.0242x - 2.7198\times10^{-4}x^2 - 2.8455\times10^{-6}x^3 + 1.2770\times10^{-7}x^4 + 1.0693\times10^{-9}x^5 - 2.0705\times10^{-11}x^6 - 7.4679\times10^{-14}x^7 + 1.0310\times10^{-15}x^8$	0.992