Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information For:

Self-Sorting Behavior in Supramolecular Fullerene Polymerization Directed by Host-Guest Complexation between Calix[5]arene and C_{60}

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Contents

General:

All solvents were commercial reagent grade and were used without further purification. UV/vis absorption spectra were recorded on a JASCO V-560 spectrometer. DOSY experiments were carried out on JEOL JNM-ECA500 spectrometer, and chemical shifts were reported on the delta scale in ppm relative to residual chloroform (δ = 7.26 for ^{1}H). Circular dichroism (CD) spectra were recorded on a JASCO J-1500 spectrometer. Previously synthesized (*S*)-**1**,[1] (*R*)-**1**,[1] **2**,[1] **3**,[2] (*S*)-**4**,[3] and **5**[3] were used for this work.

Method:

*Determination of affinity constants corresponding to the interaction between the calix[5]arene moiety of (rac)-**1** and the fullerene moiety of **2**.*

A hyperbolic curve was obtained by plotting the total concentrations of 1:1 mixtures of (*rac*)-**1** and **2** against the extinction coefficients (*ε*). Curve fitting analysis was carried out using Igor pro program. The fitting functions are given by eq. S1,

$$\varepsilon(C_t) = \frac{KC_t + 1 - \sqrt{2KC_t + 1}}{K^2 {C_t}^2}(\varepsilon_1 - \varepsilon_a) + \varepsilon_a \#(S1)$$

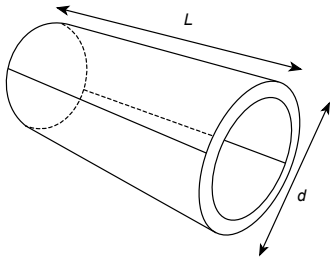
where C_t, K, ε_1, and ε_a indicate the total concentration of the compound, the affinity constant, the *ε* of the monomer, the *ε* of the aggregates, respectively.[4]

Determination of diffusion coefficients of the existing molecular species in solutions.

Chloroform-*d* solutions of a 1:1 mixture of (*rac*)-**1** and **2** were placed in an NMR sample tube (3 mm*Φ*). The pulse-field gradient diffusion NMR spectra were recorded using a bipolar pulse pair stimulated echo pulse sequence on a JEOL JNM-ECA500 spectrometer with a three mm inverse H3X/FG probe at 24 °C. The resulting DOSY data were analyzed using a MestReNova program to obtain the diffusion coefficient values shown in Table 1 and Fig. S10. The signal decay of selected aliphatic protons was fit to fitting functions given by eq. S2, where I and I_0 indicate the NMR signal intensities in the presence and absence of gradient pulses, respectively. D is the diffusion coefficient value.

$$I = I_0 e^{-xD} \#(S2)$$

The x denotes $[-\gamma^2 g^2 \delta^2 (\Delta - \delta/3)]$, where γ, g, δ, and Δ represent the gyromagnetic ratio, gradient strength, its duration, and separation between the edges of the gradient pulses, respectively.[5]



Determination of degree of polymerization (DP) by a cylindrical model.[6]-[11]

According to a cylindrical mode, diffusion coefficient (*D*) can be expressed by eq. S3.

$$D = \frac{k_B T}{3\pi\eta L}(\ln p + \nu) \#(S3)$$

k_B, T, η, and L are the Boltzmann constant, temperature, solvent viscosity, and length of the cylinder. p indicates the axial ratio of the cylinder ($p = L/d$). ν is the end-effect correction term, which was approximated as follows:

$$\nu = 0.312 + 0.565p^{-1} - 0.100p^{-2} \#(S4)$$

We previously estimated the *d* value of the supramolecular polymers from the molecular model to be 3.6 nm.[1] The eqs. S3 and S4 allowed to calculate the *L* values of the supramolecular polymers using the *D* values obtained experimentally (Fig. S10). Finally, the DP values were estimated based on a length of 5.1 nm for one helix turn (Table 1).

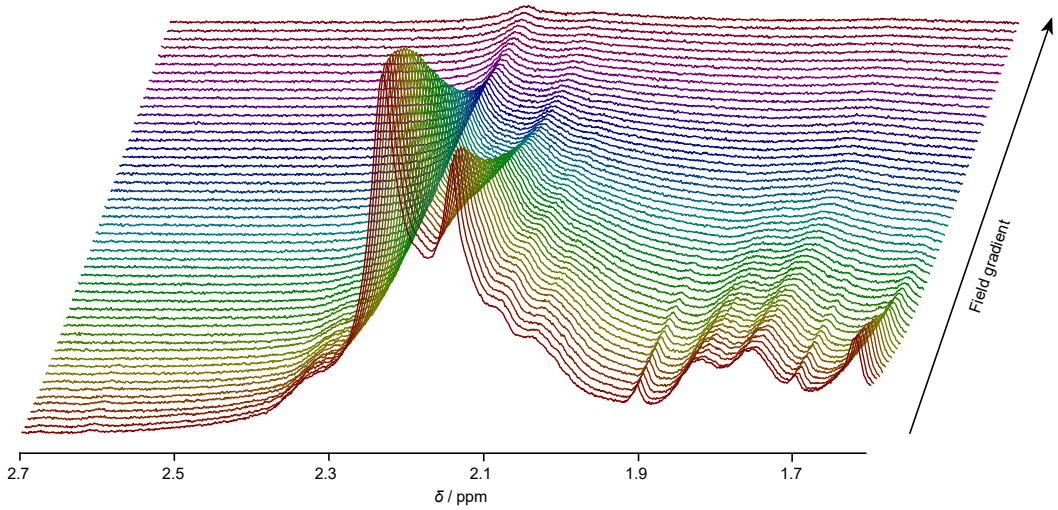


Figure S1. Stack plot of ^{1}H NMR spectra obtained from the diffusion experiment for a 1:1 mixture of (*rac*)-**1** and **2** in chloroform-*d* at the concentration of 30 mmol L^{-1}, showing the methyl protons of calix[5]arene moieties of (*rac*)-**1**.

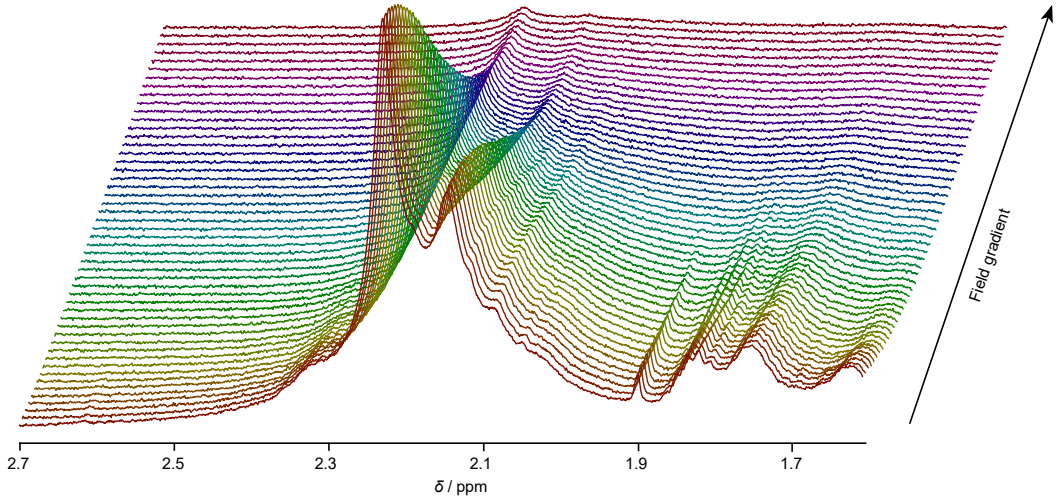


Figure S2. Stack plot of ^{1}H NMR spectra obtained from the diffusion experiment for a 1:1 mixture of (*rac*)-**1** and **2** in chloroform-*d* at the concentration of 25 mmol L^{-1}, showing the methyl protons of calix[5]arene moieties of (*rac*)-**1**.

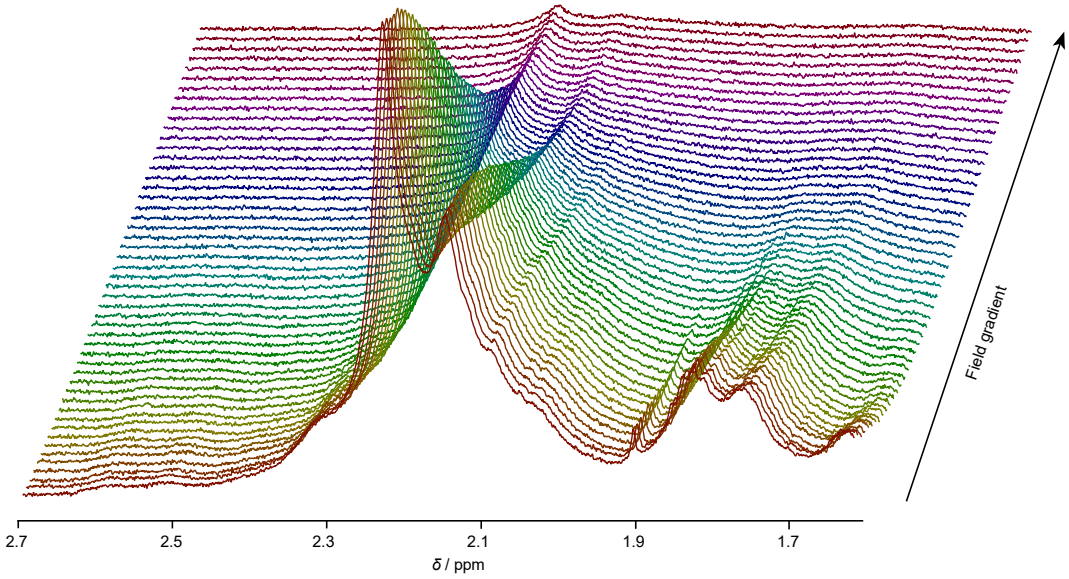


Figure S3. Stack plot of ^{1}H NMR spectra obtained from the diffusion experiment for a 1:1 mixture of (*rac*)-**1** and **2** in chloroform-*d* at the concentration of 20 mmol L^{-1}, showing the methyl protons of calix[5]arene moieties of (*rac*)-**1**.

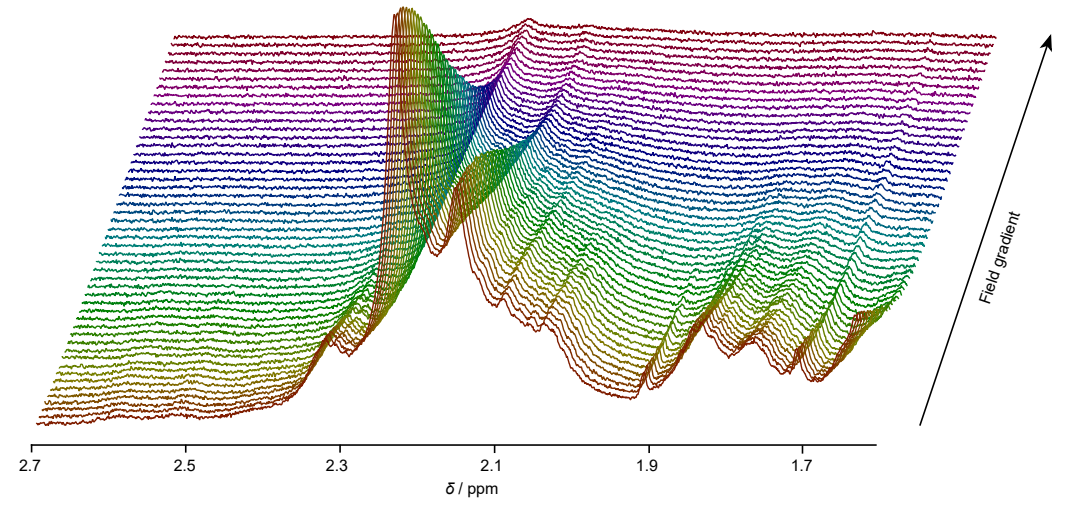


Figure S4. Stack plot of ^{1}H NMR spectra obtained from the diffusion experiment for a 1:1 mixture of (*rac*)-**1** and **2** in chloroform-*d* at the concentration of 15 mmol L^{-1}, showing the methyl protons of calix[5]arene moieties of (*rac*)-**1**.

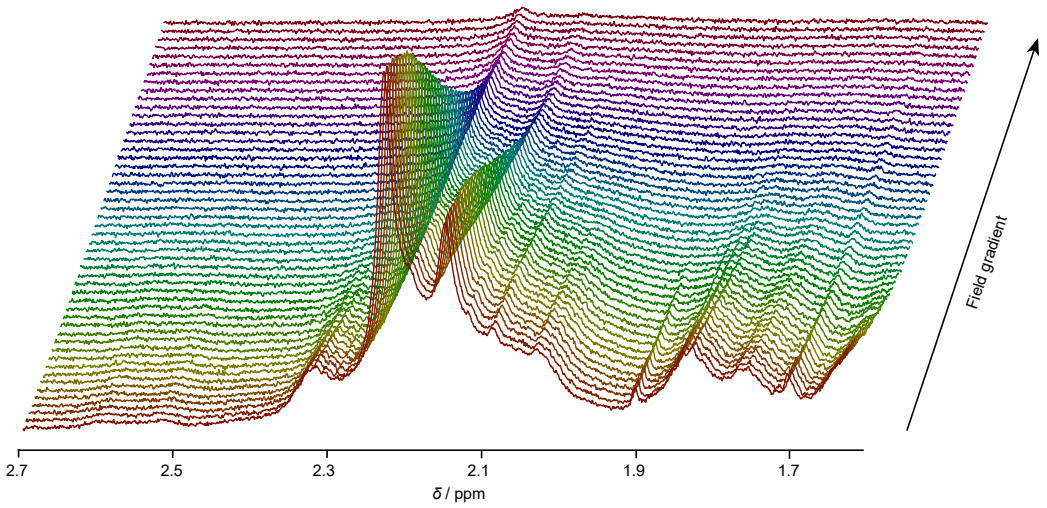


Figure S5. Stack plot of ^{1}H NMR spectra obtained from the diffusion experiment for a 1:1 mixture of (*rac*)-**1** and **2** in chloroform-*d* at the concentration of 10 mmol L^{-1}, showing the methyl protons of calix[5]arene moieties of (*rac*)-**1**.

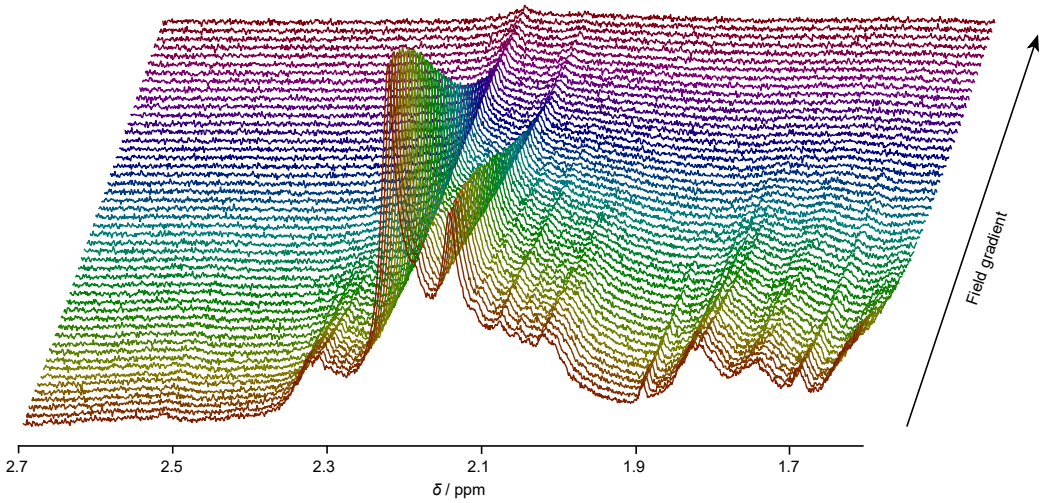


Figure S6. Stack plot of ^{1}H NMR spectra obtained from the diffusion experiment for a 1:1 mixture of (*rac*)-**1** and **2** in chloroform-*d* at the concentration of 7.0 mmol L^{-1}, showing the methyl protons of calix[5]arene moieties of (*rac*)-**1**.

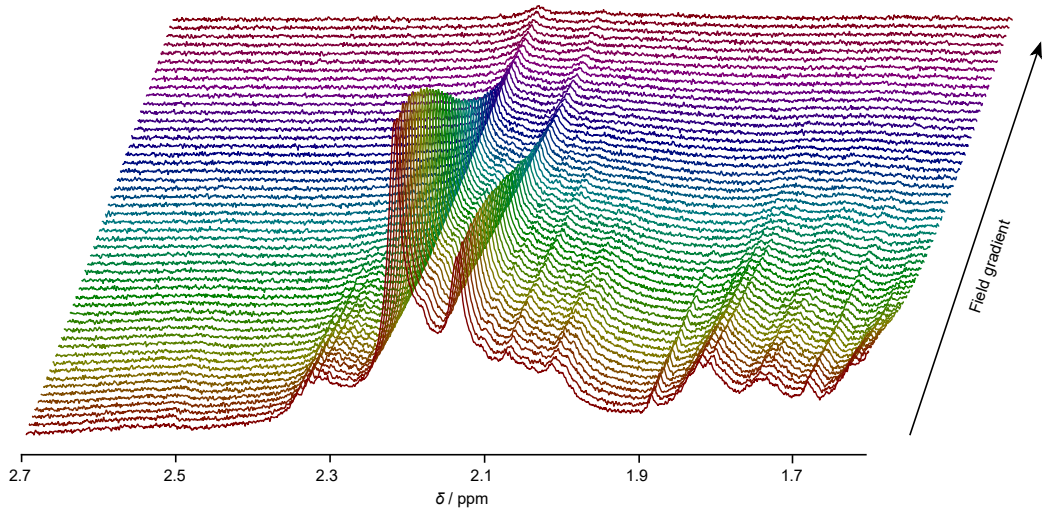


Figure S7. Stack plot of ^{1}H NMR spectra obtained from the diffusion experiment for a 1:1 mixture of (*rac*)-**1** and **2** in chloroform-*d* at the concentration of 5.0 mmol L^{-1}, showing the methyl protons of calix[5]arene moieties of (*rac*)-**1**.

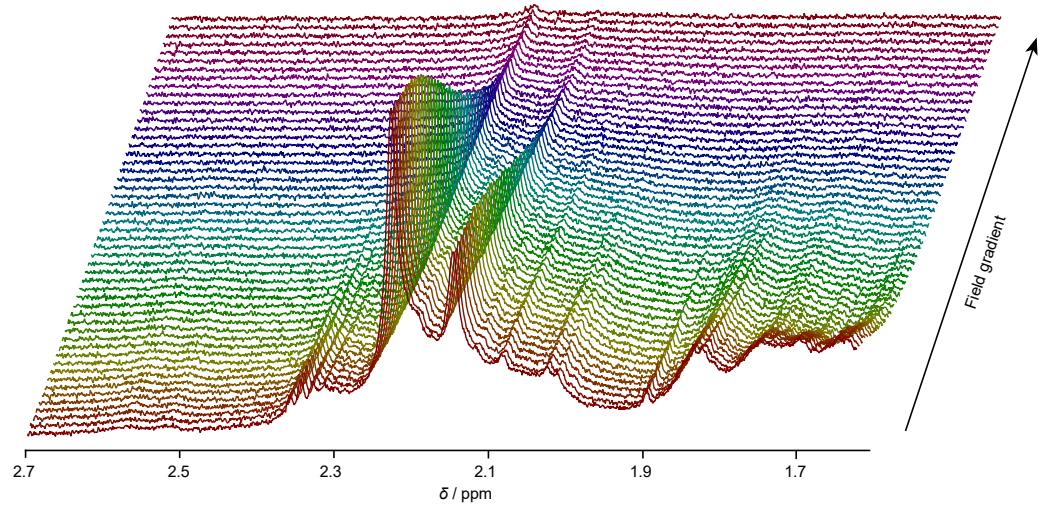


Figure S8. Stack plot of ^{1}H NMR spectra obtained from the diffusion experiment for a 1:1 mixture of (*rac*)-**1** and **2** in chloroform-*d* at the concentration of 2.5 mmol L^{-1}, showing the methyl protons of calix[5]arene moieties of (*rac*)-**1**.

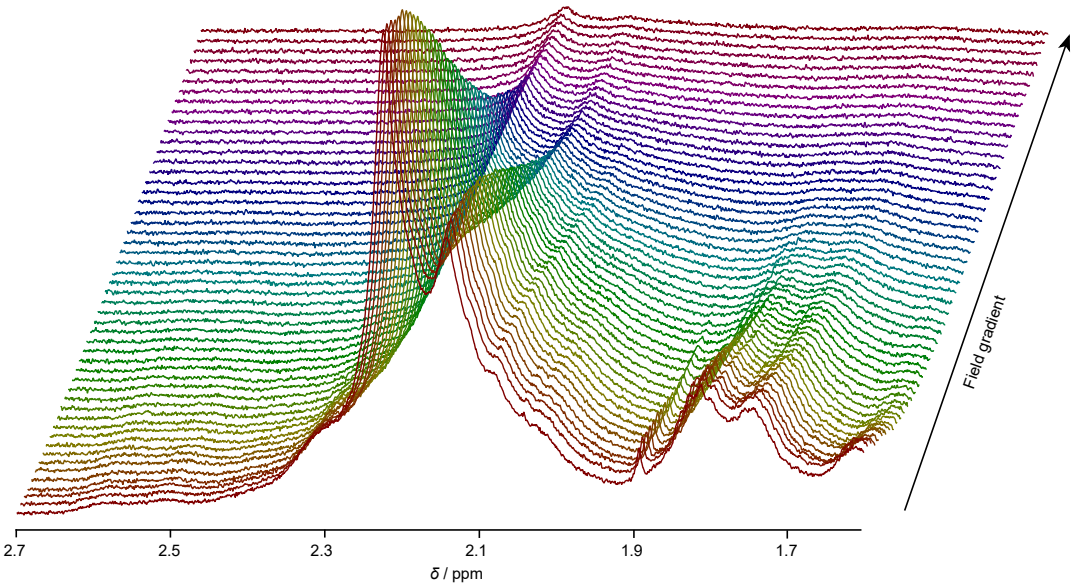


Figure S9. Stack plot of ^{1}H NMR spectra obtained from the diffusion experiment for a 1:1 mixture of (*rac*)-**1** and **2** in chloroform-*d* at the concentration of 1.0 mmol L^{-1}, showing the methyl protons of calix[5]arene moieties of (*rac*)-**1**.

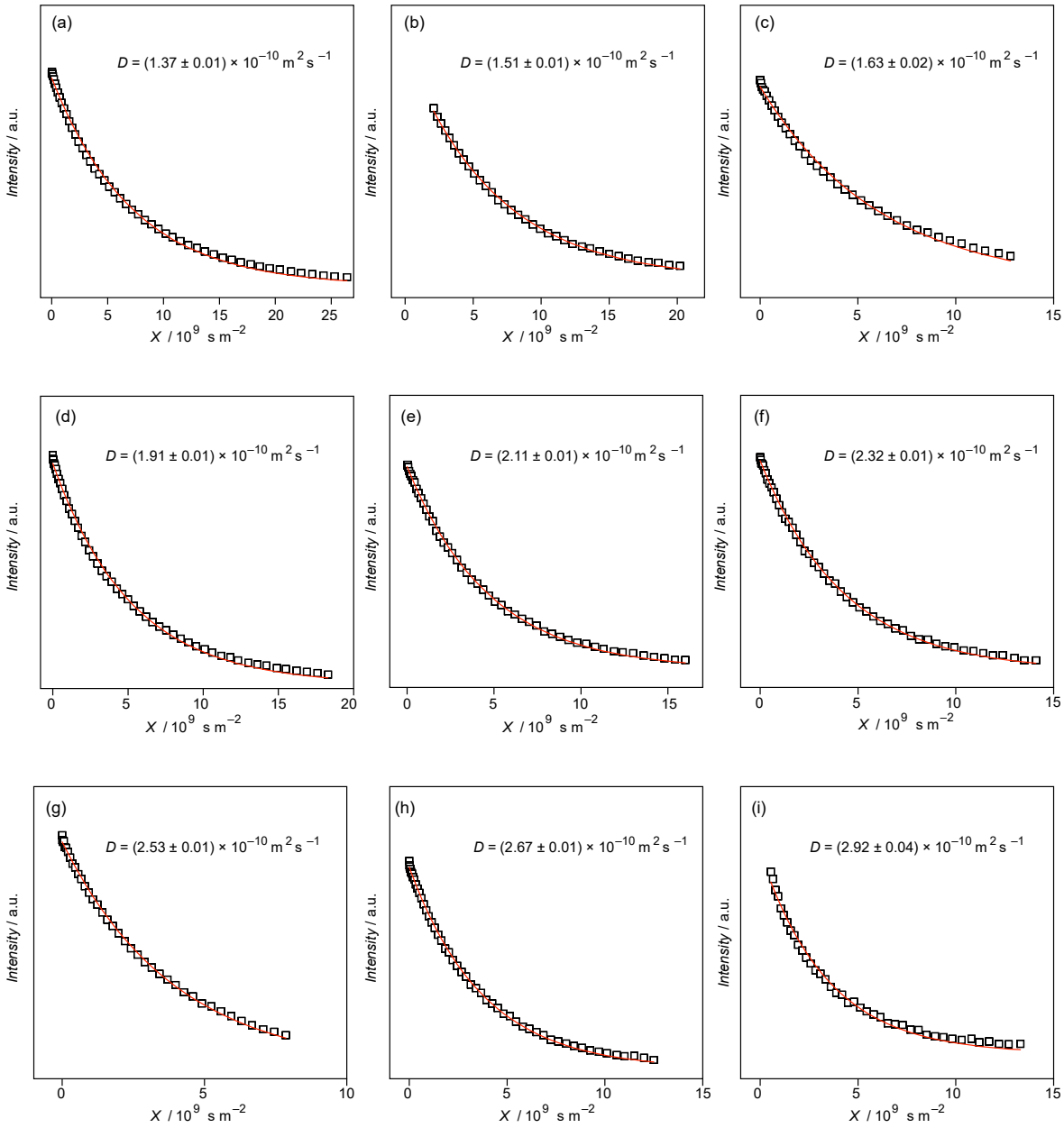


Figure S10. Plot of ^{1}H NMR signal intensities obtained from the diffusion experiments (Figs. S1-S9) and their fitting curves (red lines) for a 1:1 mixture of (*rac*)-**1** and **2** in chloroform-*d* at the concentrations of (a) 30, (b) 25, (c) 20, (d) 15, (e)10, (f) 7.0, (g) 5.0, (h) 2.5, and (i) 1.0 mmol L^{-1}.

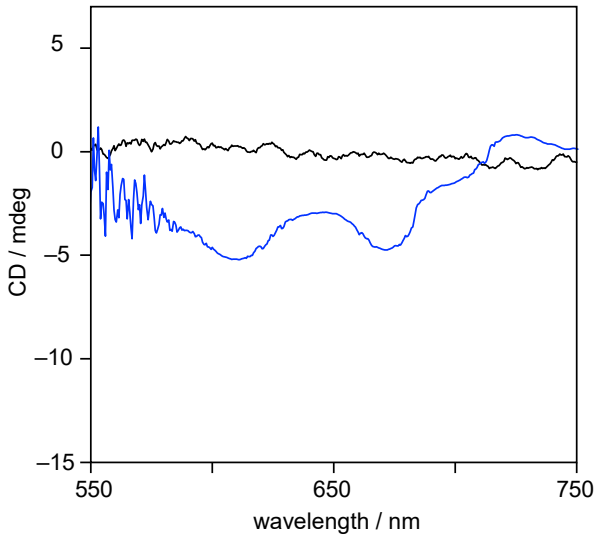
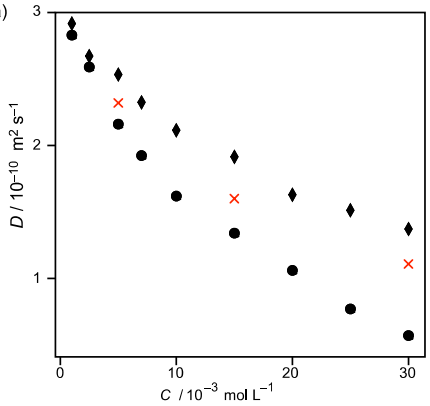


Figure S11. CD spectra of (blue line) a 1:1 mixture of (*S*)-**1** (1.0×10^{-2} mol L^{-1}) and **2** (1.0×10^{-2} mol L^{-1}), and (solid line) a 1:1 mixture of (*S*)-**1** (1.0×10^{-2} mol L^{-1}) and **2** (1.0×10^{-2} mol L^{-1}) with (*R*)-**1** (0.50×10^{-2} mol L^{-1}) in toluene at 5 °C. The spectrum shown in blue line is from Ref. [1] with permission of the publisher.

(a)



(b)

	C (mmol L^{-1})	5.0	15	30
(*R*)-**1** and **2**	*D* (10^{-10} m^2 s^{-1})[a]	2.16	1.34	0.57
	DP[b]	---[c]	7	32
(*R:S = 1:3*)-**1** and **2**	*D* (10^{-10} m^2 s^{-1})[a]	2.37	1.59	1.11
	DP[b]	---[c]	4	10
(*rac*)-**1** and **2**	*D* (10^{-10} m^2 s^{-1})[a]	2.67	1.91	1.37
	DP[b]	---[c]	---[c]	7

Figure S12. (a) Plot of diffusion coefficients (*D*s) of a 1:1 mixture of (*R*)-**1** and **2** (circle), a 0.25:0.75:1 mixture of (*R*)-**1**, (*S*)-**1** and **2** (cross), and a 1:1 mixture of (*rac*)-**1** and **2** (rhombus) in chloroform-*d* at 25 °C. The *D* values of a 1:1 mixture of (*R*)-**1** and **2** are from Ref.[1] with permission of the publisher. (b) Summary of diffusion coefficient (*D*) and the degree of polymerization (DP) values at various concentrations. The spectra and fitting analysis are shown in Figs. S1-S10, S13-S16. [a]Observed at 25 °C. Estimated error in $D < 10\%$. The error values are shown in Figs. S10 and S16. [b]Estimated by a cylindrical model. [c]Shorter than one-helix turn (DP < 4).

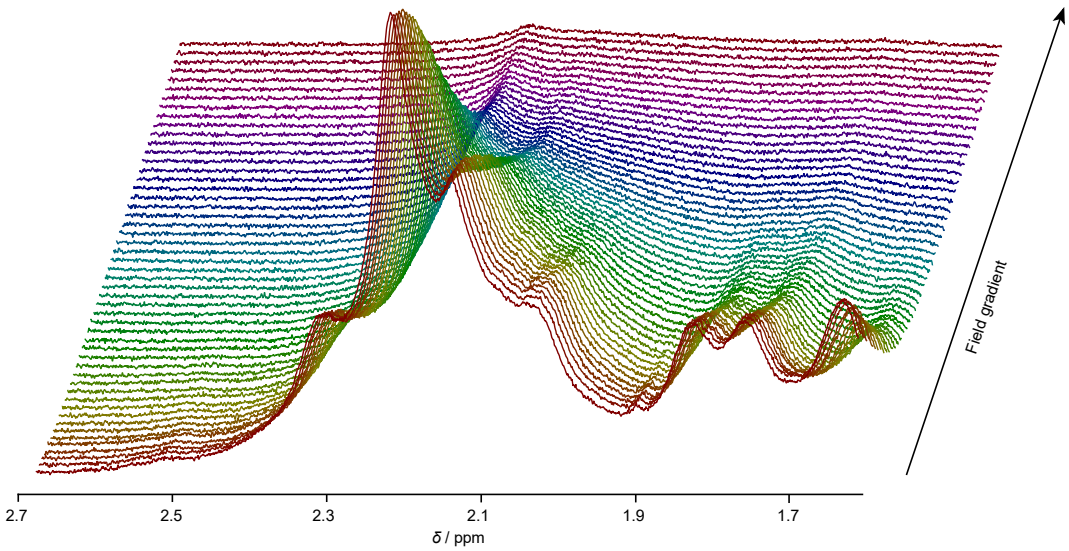


Figure S13. Stack plot of ^{1}H NMR spectra obtained from the diffusion experiment for a 0.25:0.75:1 mixture of (*R*)-**1**, (*S*)-**1** and **2** in chloroform-*d* at the concentration of 30 mmol L^{-1}, showing the methyl protons of calix[5]arene moieties of (*R*),(*S*)-mixture of **1**.

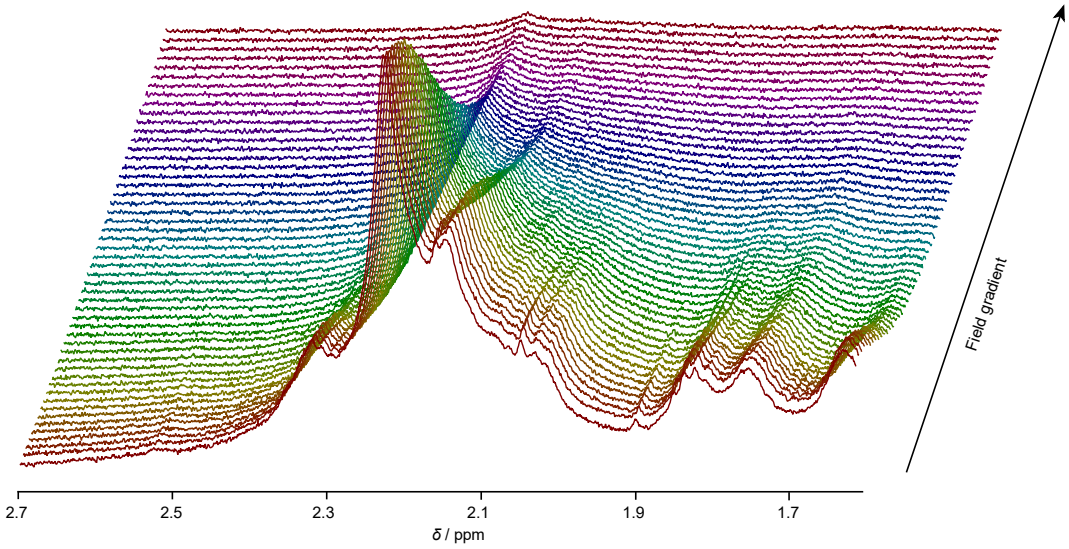


Figure S14. Stack plot of ^{1}H NMR spectra obtained from the diffusion experiment for a 0.25:0.75:1 mixture of (*R*)-**1**, (*S*)-**1** and **2** in chloroform-*d* at the concentration of 15 mmol L^{-1}, showing the methyl protons of calix[5]arene moieties of (*R*),(*S*)-mixture of **1**.

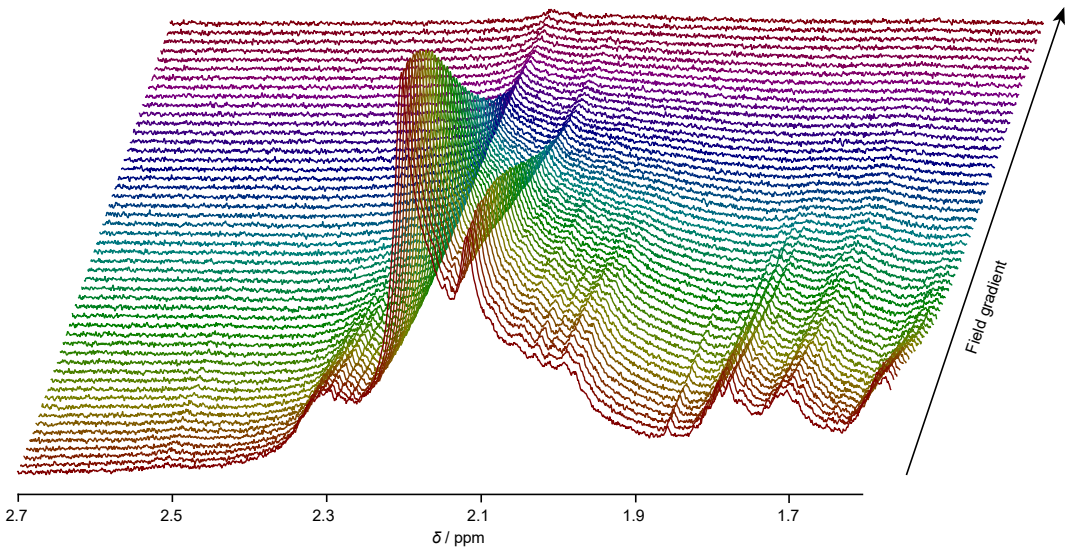


Figure S15. Stack plot of ^{1}H NMR spectra obtained from the diffusion experiment for a 0.25:0.75:1 mixture of (*R*)-**1**, (*S*)-**1** and **2** in chloroform-*d* at the concentration of 5.0 mmol L^{-1}, showing the methyl protons of calix[5]arene moieties of (*R*),(*S*)-mixture of **1**.

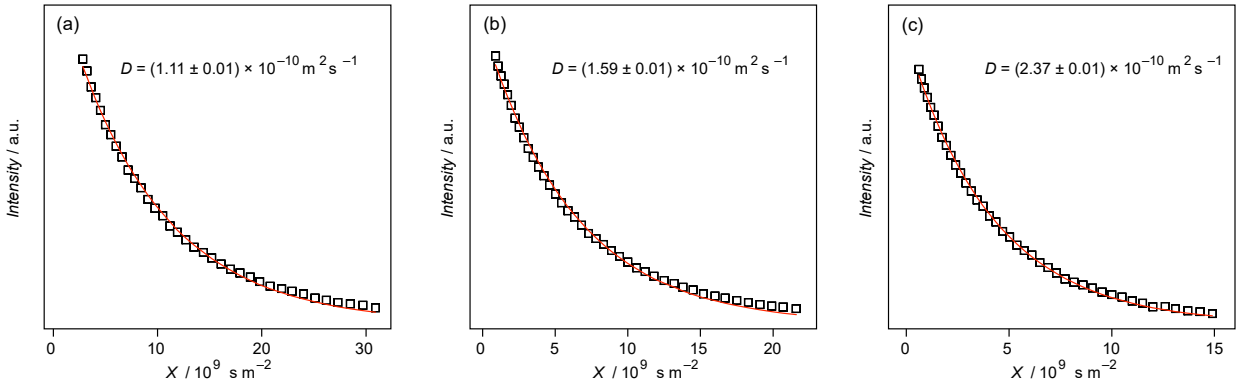


Figure S16. Plot of ^{1}H NMR signal intensities obtained from the diffusion experiments (Figs. S13-S15) and their fitting curves (red lines) for a 0.25:0.75:1 mixture of (*R*)-**1**, (*S*)-**1** and **2** in chloroform-*d* at the concentrations of (a) 30, (b) 15, and (c) 5.0 mmol L^{-1}.

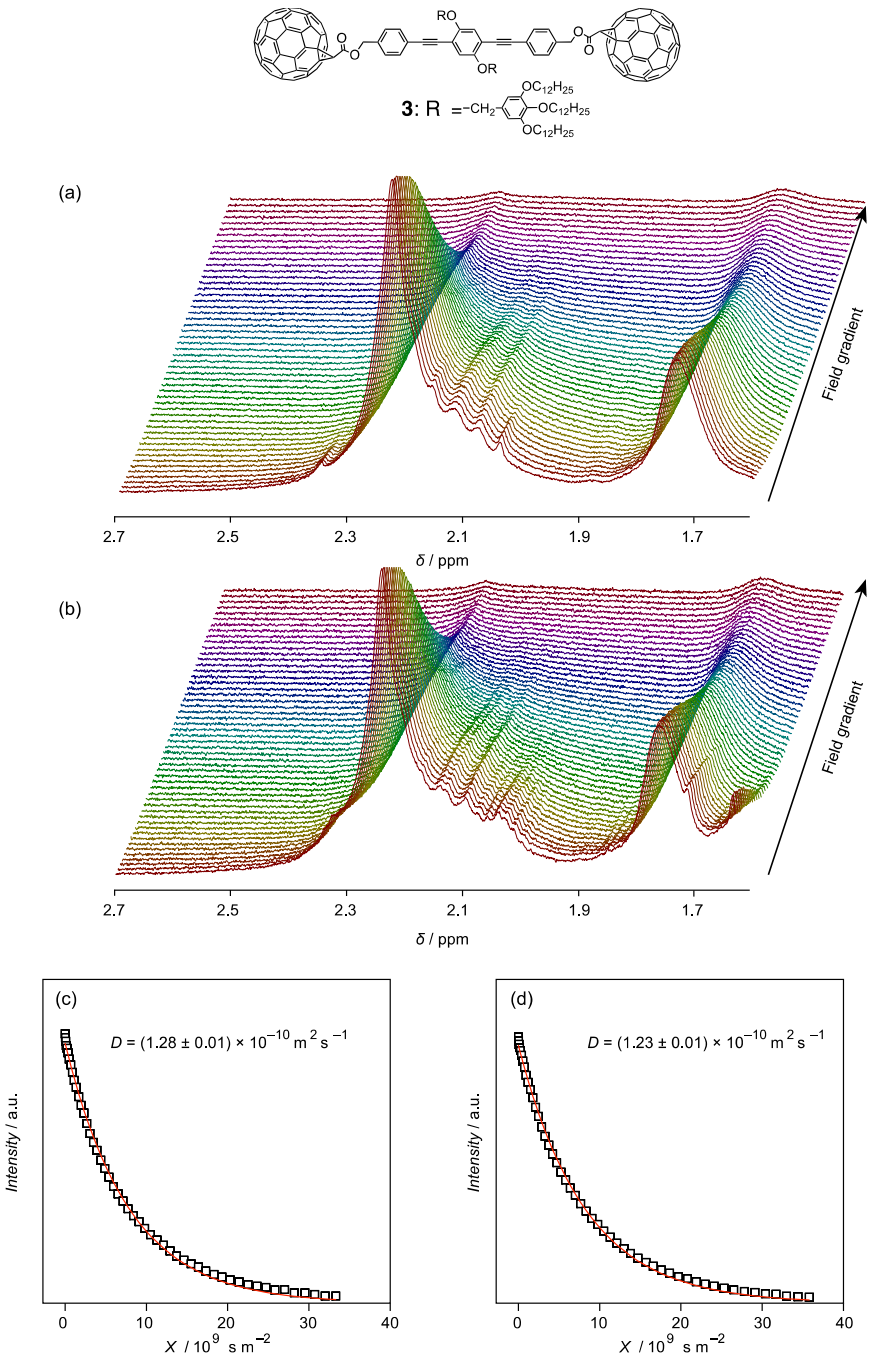


Figure S17. Stack plot of ^{1}H NMR spectra obtained from the diffusion experiment for 1:1 mixtures of (a) (*rac*)-**1** and **3** and (b) (*R*)-**1** and **3** in chloroform-*d* at the concentration of 15 mmol L^{-1}, showing the methyl protons of calix[5]arene moieties of (*rac*)-**1** and (*R*)-**1**, respectively. Plots of ^{1}H NMR signal intensities obtained from the diffusion experiments (panel a and b) and their fitting curves (red lines) for 1:1 mixtures (c) (*rac*)-**1** and **3** and (d) (*R*)-**1** and **3**.

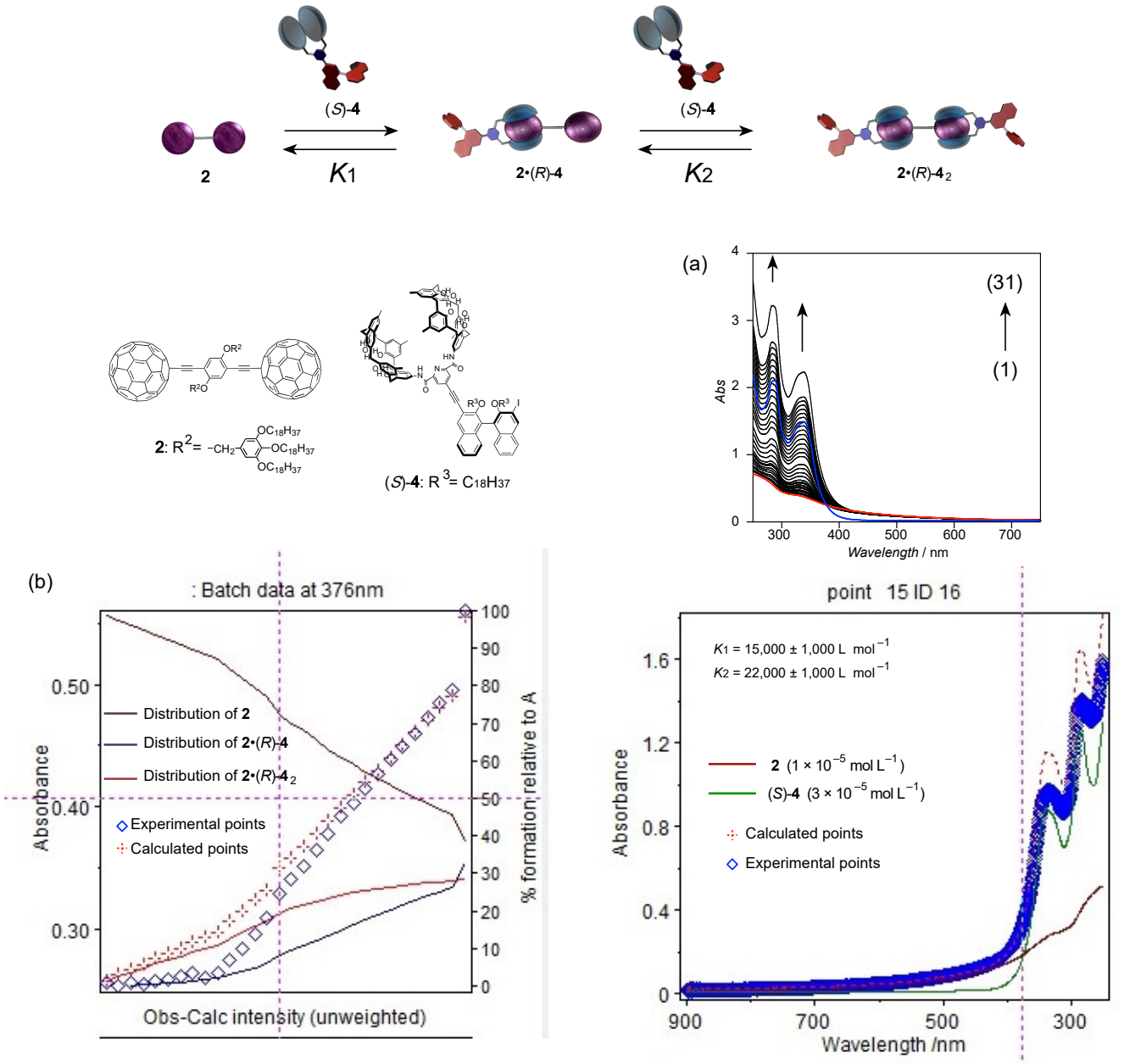


Figure S18. (a) Changes in the UV/vis absorption spectrum of **2** (1.0×10^{-5} mol L^{-1}) seen upon the addition of (*S*)-**4**. Concentrations of (*S*)-**4** are (1-31): 0.00, 0.10, 0.20, 0.30, 0.40, 0.51, 0.61, 0.70, 0.82, 0.91, 1.0, 1.2, 1.4, 1.6, 1.8, 2.2, 2.4, 2.6, 2.8, 3.1, 3.3, 3.5, 3.7, 3.9, 4.1, 4.3, 4.5, 4.7, 4.8, 5.0, 6.0×10^{-5} mol L^{-1}. The red and blue lines correspond to the UV/vis absorption spectra of **2** (3.1×10^{-5} mol L^{-1}) and (*S*)-**4** (1.0×10^{-5} mol L^{-1}), respectively. (b) Images exported from HypSpec Graphs[12] showing the fitting over the whole spectrum.

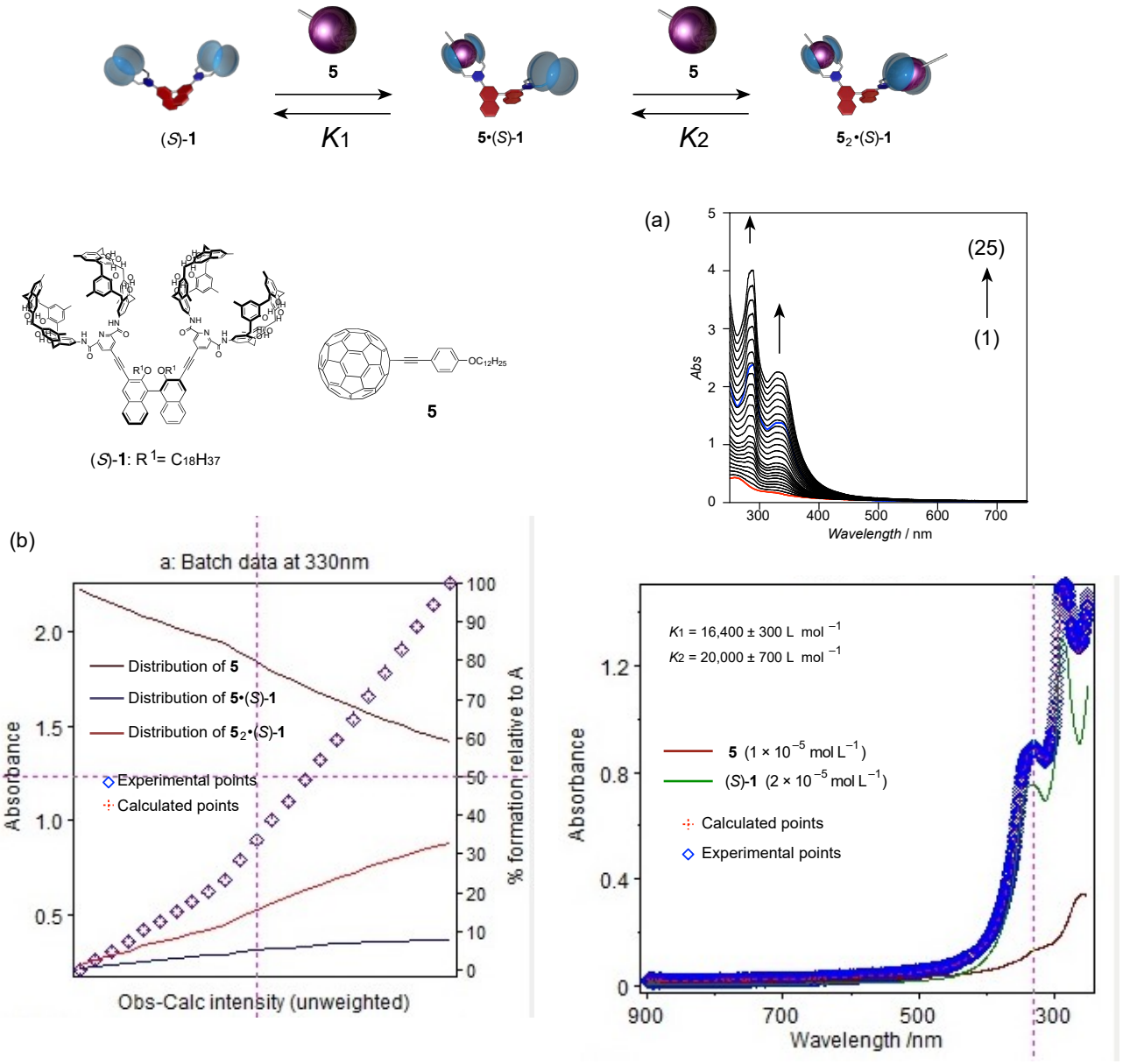


Figure S19. (a) Changes in the UV/vis absorption spectrum of **5** (1.0×10^{-5} mol L^{-1}) seen upon the addition of (*S*)-**4**. Concentrations of (*S*)-**1** are (1-25): 0.00, 0.10, 0.19, 0.29, 0.38, 0.49, 0.59, 0.68, 0.79, 0.87, 0.98, 1.2, 1.4, 1.6, 1.8, 2.0, 2.1, 2.3, 2.5, 2.7, 3.0, 3.2, 3.4, 3.6, 3.8 × 10^{-5} mol L^{-1}. The red and blue lines correspond to the UV/vis absorption spectra of **5** (2.2×10^{-5} mol L^{-1}) and (*S*)-**1** (1.0×10^{-5} mol L^{-1}), respectively. (b) Images exported from HypSpec Graphs[12] showing the fitting over the whole spectrum.

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