

Supporting Information for

Multi-mode supermolecular polymerization driven by host–guest interactions

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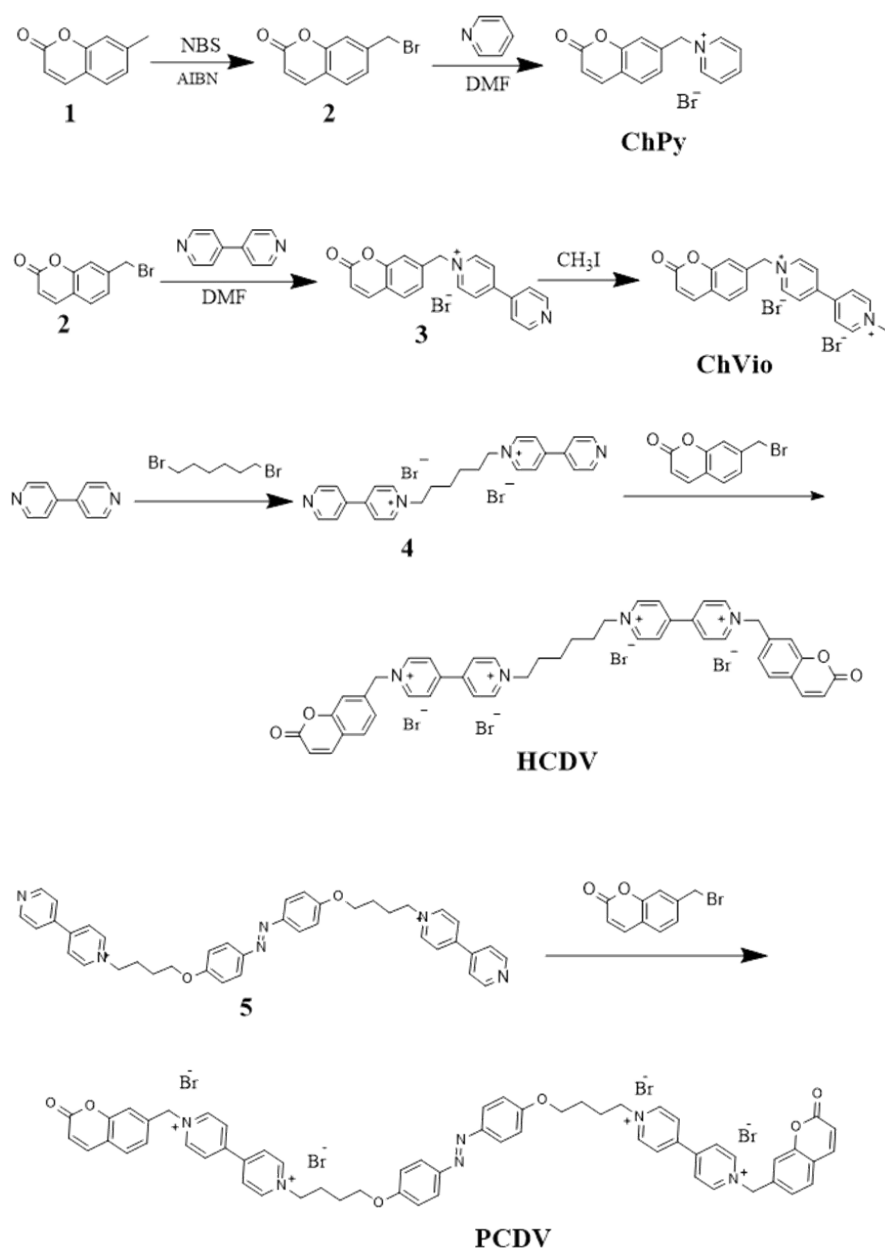
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1. Materials and methods

Materials were obtained from commercial suppliers, and were used directly without further purification. ^1H , ^{13}C and 2D ROESY spectra were measured on a Bruker AV-400 spectrometer. High resolution mass spectra (HRMS) were recorded on a Waters LCT Premier XE spectrometer using standard conditions (ESI, 70 eV). All UV-vis absorption spectra were measured on a Varian Cary 500 UV-vis spectrophotometer. Dynamic light scattering (DLS) was carried out on a Horiba LB-550 Dynamic Light Scattering Nano-Analyzer. TEM images were recorded on a JEOL JEM-1400 apparatus. The samples (1×10^{-4} M) were dropped on a perforated copper grid (200 mesh) covered with a carbon film. The photoirradiation was carried on a UV lamp of 6 W in a $1 \text{ mm} \times 1 \text{ cm}$ quartz cell.

2. Synthesis and characterization



Scheme S1. Synthesis route of all compounds.

Compound 2 This compound was synthesized according to literature procedure.³ A mixture of 7-methyl-2H-chromen-2-one (3.5 g, 22 mmol), NBS (3.88g, 22 mmol) and AIBN (5 mg, 0.22 mmol) in CCl₄ (100 mL) was refluxed for 1 h under an atmosphere of nitrogen, to the solution was added NBS (0.4 g, 2.51 mmol) and AIBN (5mg, 0.0306 mmol), and refluxed for another 1 h. The resulting was concentrated by evaporation and diluted with water and stirred for 1 h, collected by filtration, dried in vacuum and obtained the crude product. The crude product was used in further experiments without additional purification.

ChPy Compound 2 (1 g, 4.2 mmol) was dissolved in a mixture of N,N-dimethylformamide (20 mL) and pyridine (1.5 mL). The solution was stirred at 80 °C under argon for 24 h and cooled to

room temperature. The reaction solution was then poured into 150 mL ethyl acetate. The precipitate was collected by filtration and washed with ethyl acetate and dried in vacuo to provide compound ChPy as pale yellow powder (1.14g, 85.5% yield). ¹H NMR (400MHz, D₂O) δ 8.86 (d, 2H), 8.50(t, 1H), 8.01 (t, 2H), 7.93 (d, 1H), 7.64 (d, 1H), 7.35 (s, 1H), 7.32 (d, 1H), 6.44 (d, 1H), 5.85 (s, 2H). ¹³C NMR (400MHz, D₂O) δ 159.5, 153.5, 143.6, 137.8, 124.7, 119.3, 117.1, 116.8, 62.5. HRMS (ESI)(m/z): (M-Br)⁺ calcd for 238.0863; found 238.0864.

ChVio 4,4'-bipyridine (3g, 19.2 mmol) was dissolved in N,N-dimethylformamide (60 ml) and heated to 80 °C under argon. The solution of compound 2 (1.14g, 4.8 mmol) dissolved in N,N-dimethylformamide (5 ml) was added dropwise into the above solution and stirred at 80 °C for 24 h. After cooling to room temperature, the clear filtrate was collected by filtration and then poured into 300 mL ethyl acetate. Then the precipitate was collected by filtration and washed with ethyl acetate and dried in vacuo to obtain compound 3 (0.9g) as pale yellow powder. The compound 3 (0.9g) and CH₃I (0.4 ml) were dissolved in N,N-dimethylformamide (30 ml) and stirred at 80 °C under argon for 5 h and cooled to room temperature. The precipitate was collected by filtration and washed with ethyl acetate and dried in vacuo to provide compound ChVio (1.06g, 45.3%) as pale yellow powder. ¹H NMR (400MHz, D₂O) δ 9.11 (d, 2H), 8.95(d, 2H), 8.49 (d, 2H), 8.48 (d, 2H), 7.95 (d, 1H), 7.69 (d, 1H), 7.43 (s, 1H), 7.38 (d, 1H), 6.45 (d, 1H), 5.97 (s, 2H), 4.40 (s, 3H). ¹³C NMR (400MHz, D₂O) δ 163.6, 146.3, 145.0, 136.2, 129.7, 127.3, 126.7, 125.3, 120.0, 117.2, 116.6, 68.9, 48.4. HRMS (ESI)(m/z): (M-Br)⁺ calcd for 409.0546; found 409.0552.

Compound 4 1,6-dibromohexane (1g, 4.13mmol) and 4,4'-bipyridine (3.87g, 24.78mmol) were dissolved in 20 mL of DMF. The solution was stirred at 80 °C under argon for 12 h and cooled to room temperature. The precipitate was collected by filtration and washed with a small amount of DMF and ethyl acetate and dried in vacuo to obtain compound 4 as a pale yellow powder (1.2g, 52.4%). ¹H NMR (400MHz, DMSO-d₆) δ 9.29 (d, 4H), 8.87(d, 4H), 8.66 (d, 4H), 8.05 (d, 4H), 4.65 (t, 4H), 1.98 (m, 4H), 1.36 (m, 4H). ¹³C NMR (400MHz, DMSO-d₆) δ 153.7, 149.9, 144.7, 142.4, 125.9, 122.4, 61.4, 30.2, 24.9. HRMS (ESI)(m/z): (M-2Br)²⁺/2 calcd for 198.1152; found 198.1139.

HCDV compound 4 (1g, 1.8mmol) and compound 2 (0.52g, 2.16mmol) were dissolved in 20 mL of DMF. The solution was stirred at 80 °C under argon for 8 h and cooled to room temperature. The precipitate was collected by filtration and washed with a small amount of DMF

and ethyl acetate and dried in vacuo to obtain compound 4 as a pale yellow powder (1.38g, 74.2%). ^1H NMR (400MHz, D_2O) δ 9.08 (d, 4H), 8.97(d, 4H), 8.42 (m, 8H), 7.92 (d, 2H), 7.65 (d, 2H), 7.36 (m, 4H), 6.43 (d, 2H), 5.94 (s, 4H), 4.59 (t, 4H), 1.95 (s, 4H), 1.25 (s, 4H). ^{13}C NMR (400MHz, D_2O) δ 163.6, 153.5, 150.7, 149.8, 145.8, 145.4, 145.0, 136.2, 129.7, 127.3, 127.0, 125.3, 120.0, 117.1, 116.6, 63.9, 62.0, 30.4, 24.8. HRMS (ESI)(m/z): (M-Cl) $^+$ calcd for 819.2266; found 819.2275.

PCDV The synthetic route follows the previous literature¹. ^1H NMR (400MHz, D_2O) δ 9.06 (d, 4H), 8.92(d, 4H), 8.29 (d, 8H), 7.90 (d, 2H), 7.56 (d, 2H), 7.42 (d, 4H), 7.03-7.05 (m, 4H), 6.77 (d, 4H), 6.45 (d, 2H), 5.68 (s, 4H), 4.72 (t, 4H), 3.98 (t, 4H), 2.27 (m, 4H), 1.89(m, 4H). HRMS (ESI)(m/z): (M-3Br) $^{3+}/3$ calcd for 344.4424; found 344.4423.

3. Supplementary information for ^1H NMR data.

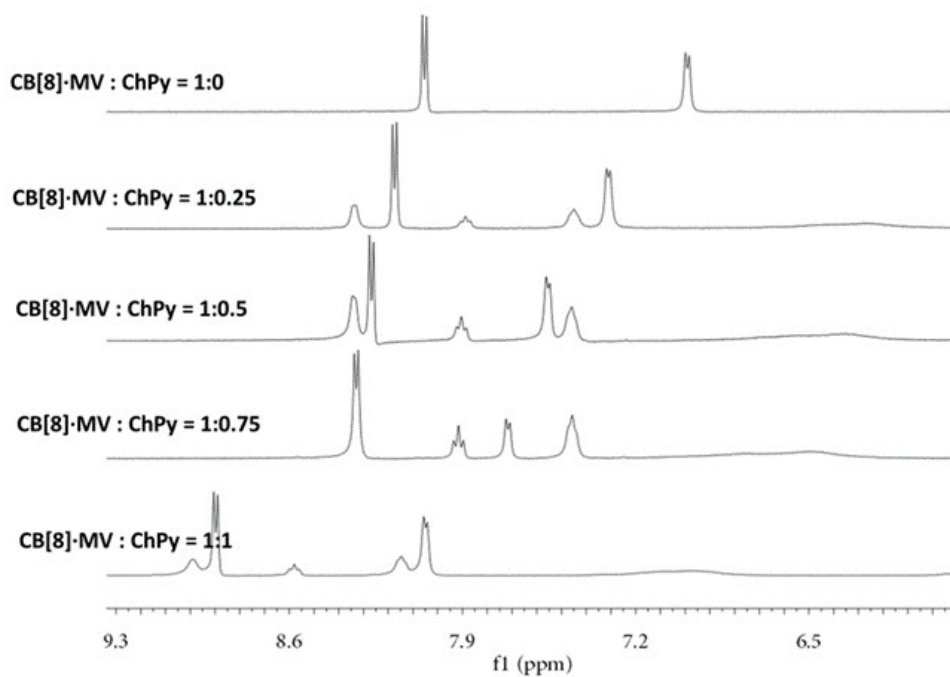


Figure S1. Partial ^1H NMR spectra (400 MHz, D_2O , 298 K) of CB[8]·MV with increasing ratio of ChPy.

With the increase of molar ratio of ChPy/ CB[8]·MV, all peaks gradually shift downfield due to the deshielding effect. But compared with the monomers ChPy and MV, the ^1H NMR signals of complex CB[8]·MV/ChPy with ratio of 1:1 shifted to upfield.

4. ITC experiments.

The ITC experiments was performed using a Microcal VP-ITC apparatus. The measurements were performed in ultrapure water at 298.15 K. The CB[8]•MV (0.05mM) was in the sample cell and ChPy (1mM) was in the injection. The data was analyzed using Origin software and fits well to the 1:1 binding model. Other thermodynamic data was showed in theFigure S2.

5. ^1H NMR data of supramolecular polymerization for HCDV and CB[8], PCDV and CB[8].

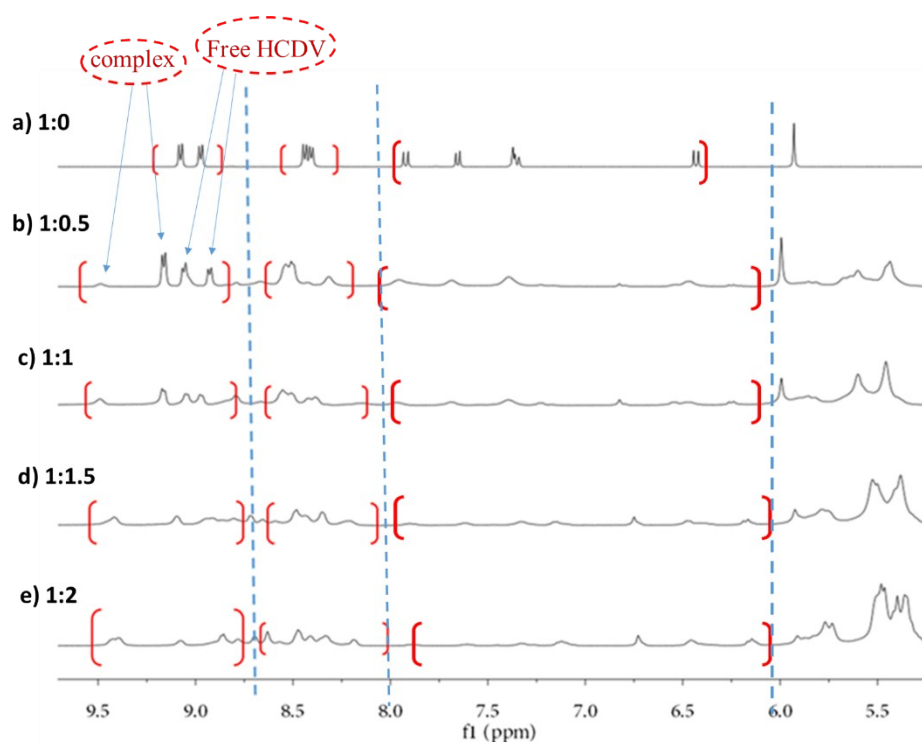


Figure S2. Partial ^1H NMR spectra (400 MHz, D_2O , 298 K) of HCDV with increasing ratio of CB[8].

As the addition of CB[8], ^1H NMR signals of free HCDV gradually decreased and disappeared eventually when the molar ratio of HCDV/CB[8] was 1:2. And all peaks broaden, indicating the formation of supramolecular polymers.

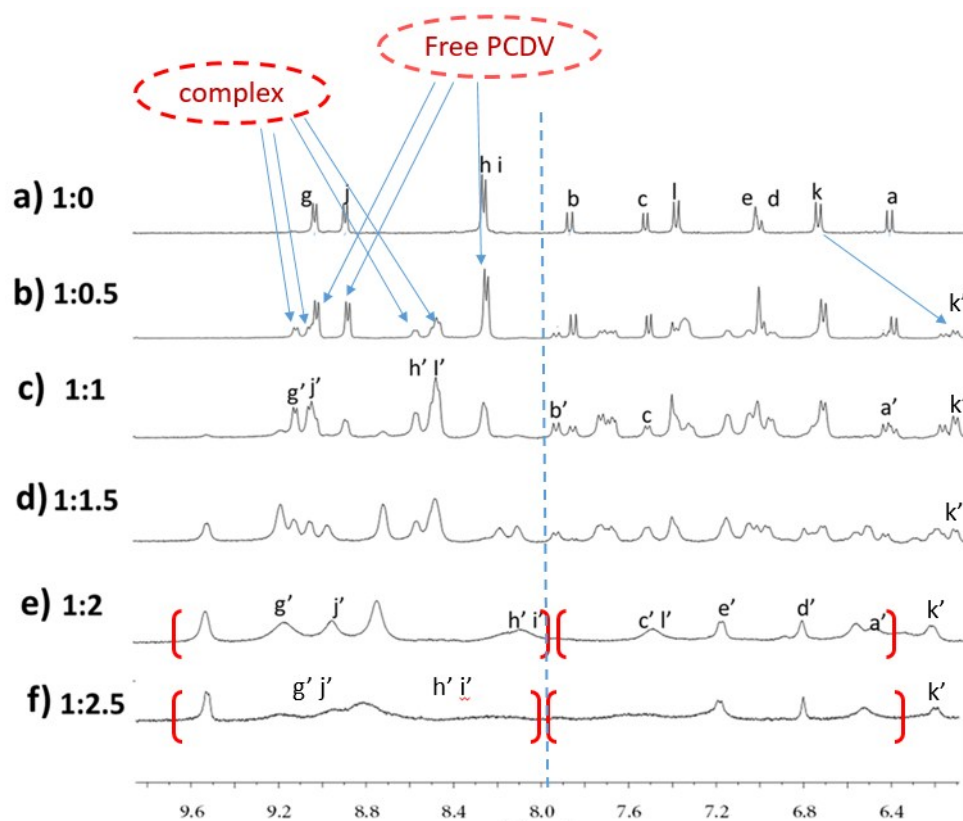


Figure S3. Partial ^1H NMR spectra (400 MHz, D_2O , 298 K) of PCDV with increasing ratio of CB[8].

As the addition of 0.5 equivalent CB[8], the new complex peaks occurred, and the signals H_k in azobenzene began to shift upfield, which showed that partial azobenzene moiety had been bounded in the cavity of CB[8]. The peaks of free PCDV broadened when the ratio of CB[8]/PCDV increased to 1:1, indicating the existence of supramolecular polymers. When the ratio of CB[8]/PCDV was 1.5:1, the peaks of free PCDV disappeared, which suggested that all free PCDV monomers took the assemble for supramolecular polymerization. When the molar ratio of CB[8]/PCDV was 2:1, the number of sharp peak reduce, and all peaks broadened, indicating the formation of supramolecular polymers. When the molar ratio of CB[8]/PCDV was 2.5:1, the peaks of viologen and coumarin were further broadened, especially the coumarin moiety, which suggested that further supermolecular polymerization occurred.

6. 2D ROESY NMR data of HCDV-2CB[8] and PCDV-2CB[8]

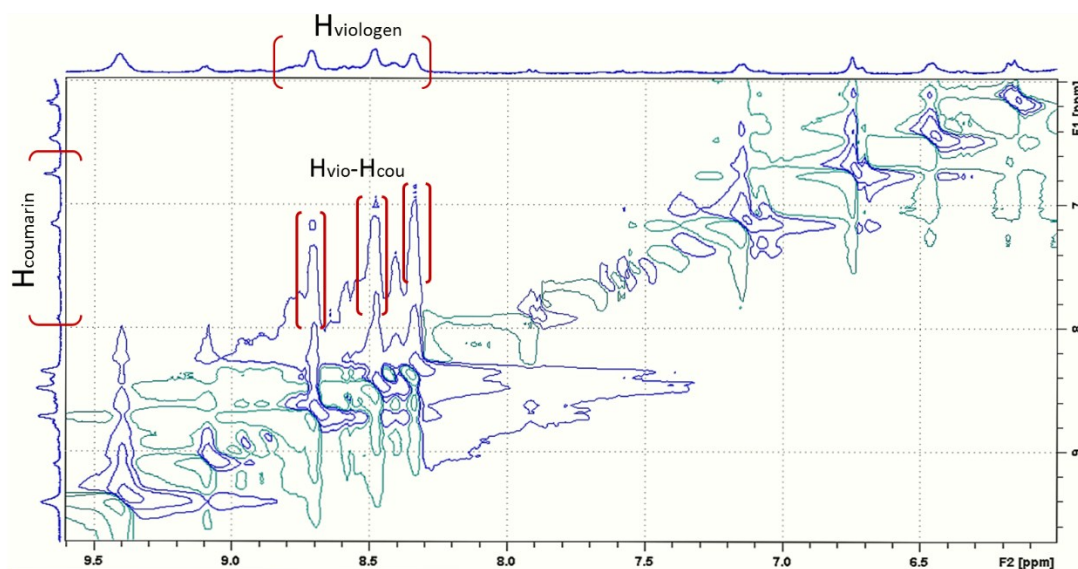


Figure S4. Partial 2D ROESY NMR spectrum (400 MHz, D₂O, 298 K) of HCDV and CB[8] with ratio of 1:2.

As shown in Figure S4, 2D ROESY NMR spectrum of HCDV-2CB[8] displayed that correlation signals were observed between the bulge peak in viologen and coumarin moiety, which suggested viologen moiety and coumarin moiety closed each other for encapsulation in the cavity of CB[8] clearly.

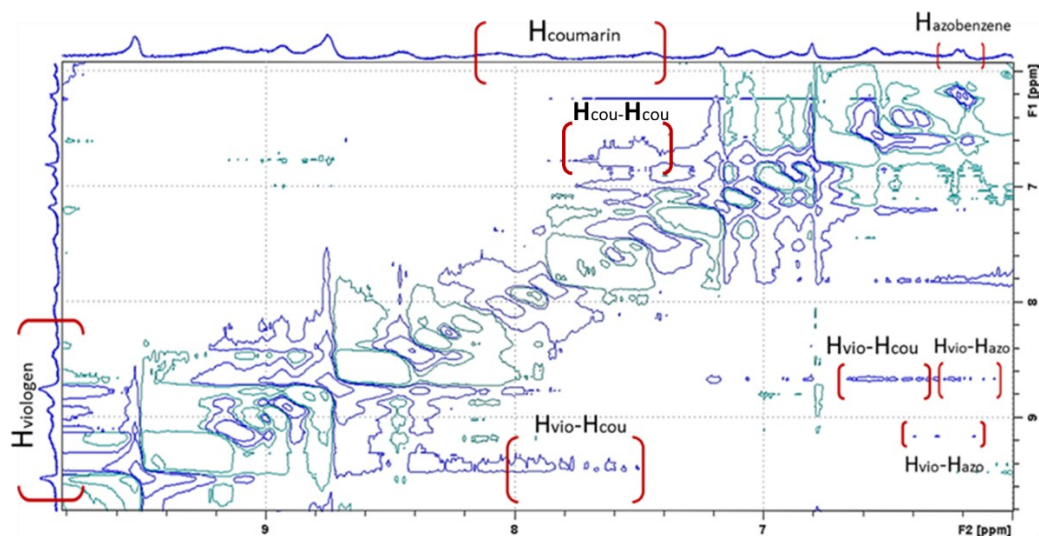


Figure S5. Partial 2D ROESY NMR spectrum (400 MHz, D₂O, 298 K) of PCDV and CB[8] with ratio of 1:2.

As shown in Figure S5, 2D ROESY NMR spectrum of PCDV-2CB[8] displayed that correlation signals were observed between the bulge peak in viologen and coumarin moiety, viologen and azobenzene moiety, even two coumarin moieties, respectively, suggesting viologen moiety and coumarin moiety, viologen and azobenzene, two coumarin moieties closed each other for encapsulation in the cavity of CB[8].

7. The stoichiometry between CB[8] and ChVio, between HCDV and CB[8] and PCDV and CB[8]

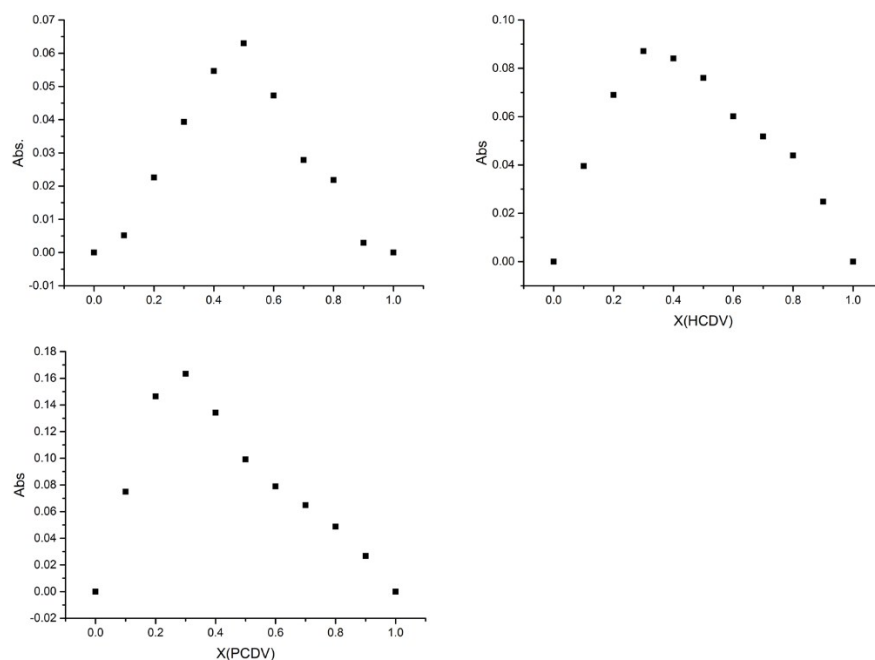


Figure S6. Job's plots of a) ChVio and CB[8], b) HCDV and CB[8], c) PCDV and CB[8].

The total concentration of CB[8] and guest molecule ChVio, HCDV and PCDV was fixed at 0.1mmol/L. The data of UV/Vis absorption at 319 nm (ChVio and HCDV) and 323nm (PCDV) was recorded for the calculation of Job's plots every time when changing the ratio of CB[8] and guest molecule. As shown in Figure S6a, the absorption changing of coumarin moiety in 319 nm reached its maximum when the molar ratio was around 0.5, indicating that combining stoichiometry between ChVio and CB[8] was 1:1. Similarly, as shown in Figure S6b, it could be considered that the absorption changing reached its maximum when the molar was 0.35, and the combining stoichiometry between CB[8] and HCDV was 2:1. As shown in Figure S6c, it could be considered that the absorption changing reached its maximum when the molar was around 0.3, and the combining stoichiometry between CB[8] and PCDV was about 2.33. This data is close to our prediction.

8. Supplementary schematic diagram of assembly method of PCDV/CB[8]

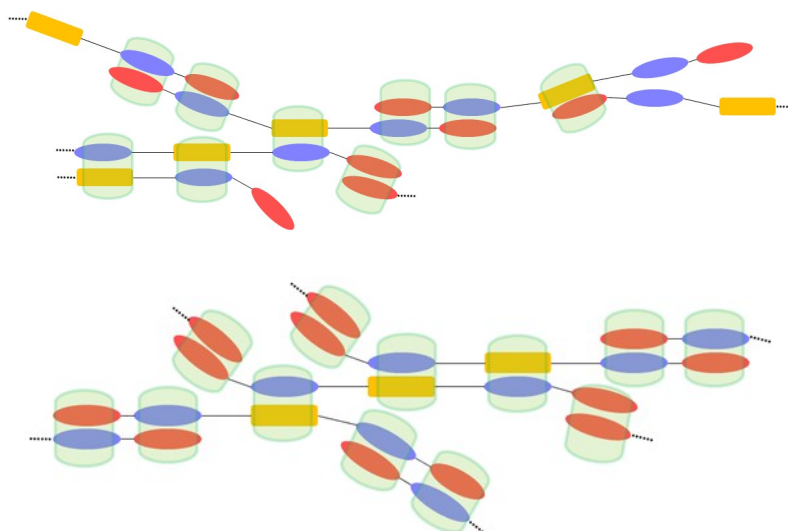


Figure S7. Schematic diagram of assembly method of PCDV/CB[8]

9. Supplementary TEM images of HCDV-2CB[8] and PCDV-2CB[8]

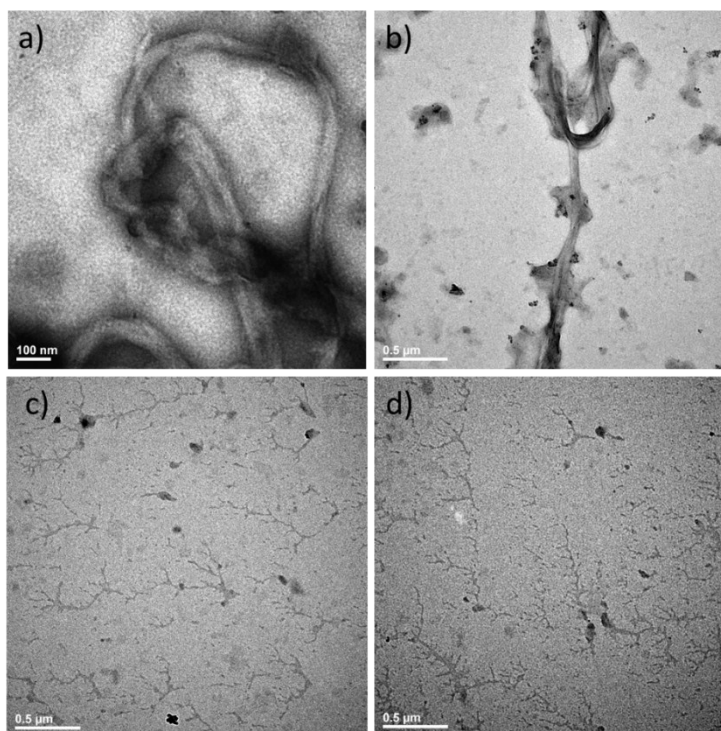


Figure S8. TEM images of the supramolecular polymer (a,b) HCDV-2CB[8] negative stained by Phosphotungstic acid and (c,d) PCDV-2CB[8] (40 μ M) in water.

10. DLS results of PCDV-CB[8] and PCDV-2CB[8]

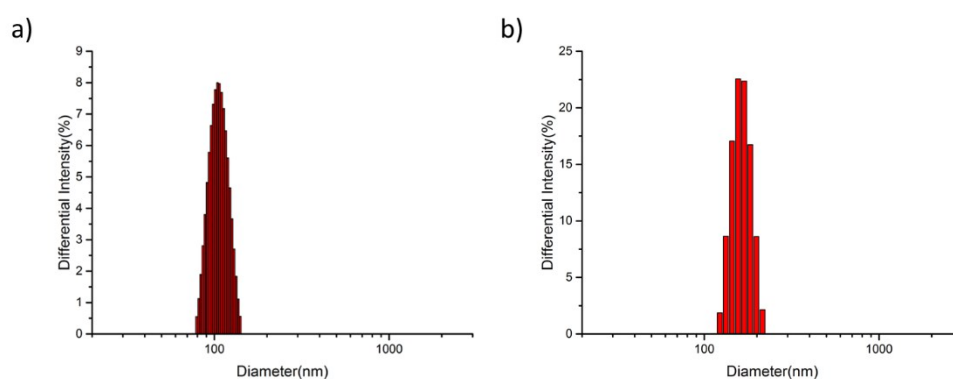


Figure S9. DLS results of (a) PCDV-CB[8] and (b) PCDV-2CB[8] (0.5 mM) in water.

As shown in Figure S9a, the DLS results showed that hydrodynamic radius of PCDV-CB[8] was around 120 nm, which suggested the existence of supramolecular polymer. However, with the increase of the ratio of CB[8]/PCDV, the hydrodynamic radius of PCDV-2CB[8] increased to around 180 nm and degree of concentration was higher, which was consistent with the assemble process we put forward.

11. UV/Vis spectra of different ratio of PCDV/CB[8]

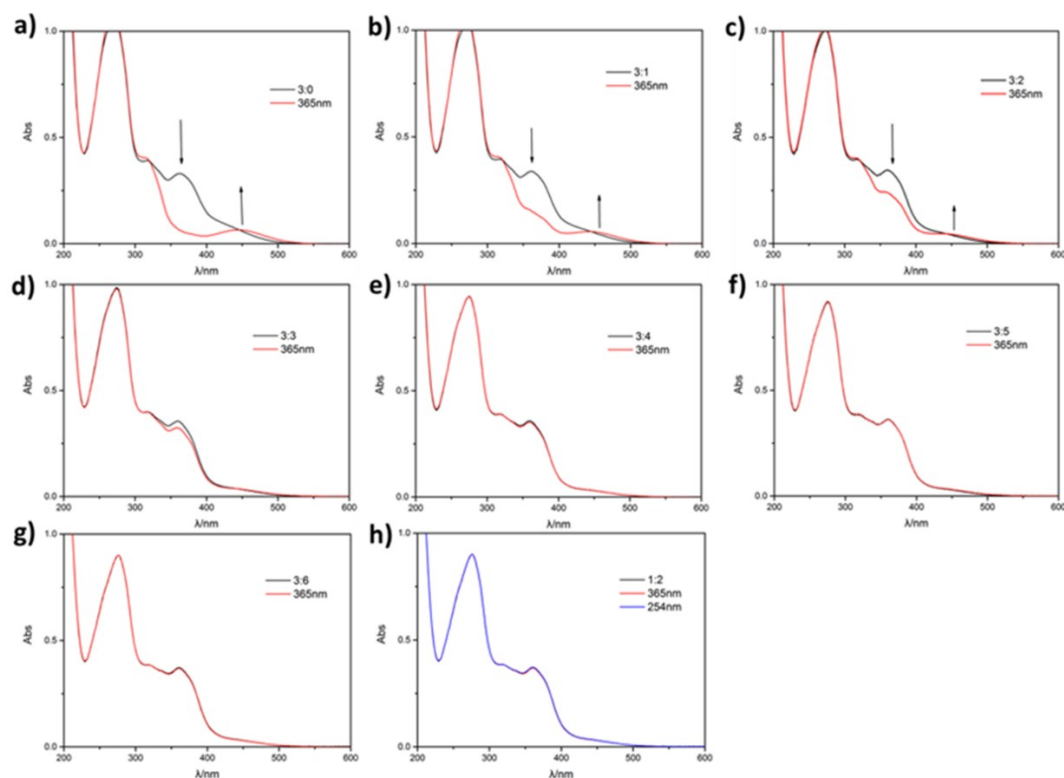


Figure S10. UV/Vis spectra of PCDV/CB[8] = (a)3:0, (b)3:1, (c)3:2, (d)3:3, (e)3:4, (f)3:5, (g)3:6 (0.02 mM) and under 365 nm UV irradiation; (h) UV/Vis spectra of PCDV/CB[8] =1:2 under 365

and 254 nm UV irradiation.

The experimental operation was conducted by the methods: Configured the solution of PCDV and CB[8] proportionally and tested the UV/Vis data, then tested it irradiated sufficiently with 365 nm UV for 10 min.

As shown in figure S10a, the monomer PCDV could be isomerized under UV for 10 min. As shown in figure S10b, when 0.5 equivalent CB[8] was added into PCDV, the degree of photoisomerization decreases, then carried on. Until the molar ratio of CB[8]/PCDV exceeded 1.0, the UV/Vis data had no response under UV irradiation. Contrast with previous NMR analysis, when the molar ratio of CB[8]/PCDV exceeded 1.0, there were no free monomer PCDV in aqueous solution, which suggested the assemble of CB[8] and PCDV inhibited the isomerization of PCDV under UV irradiation.

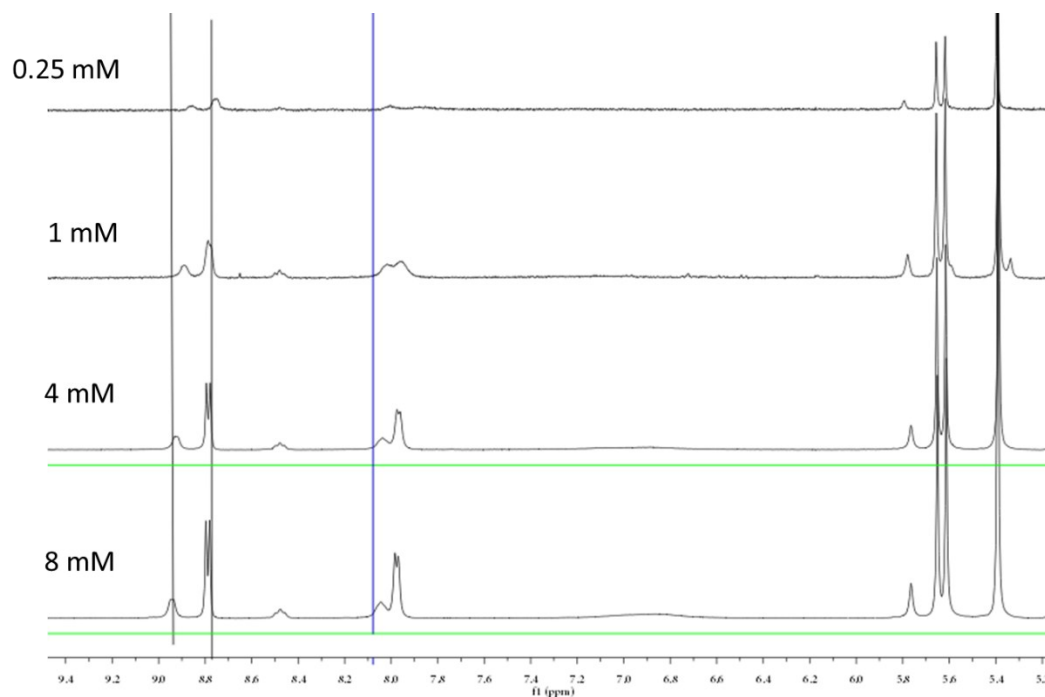
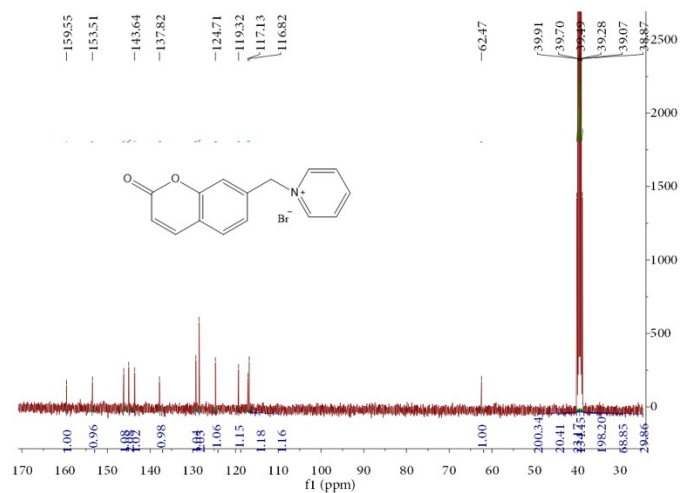
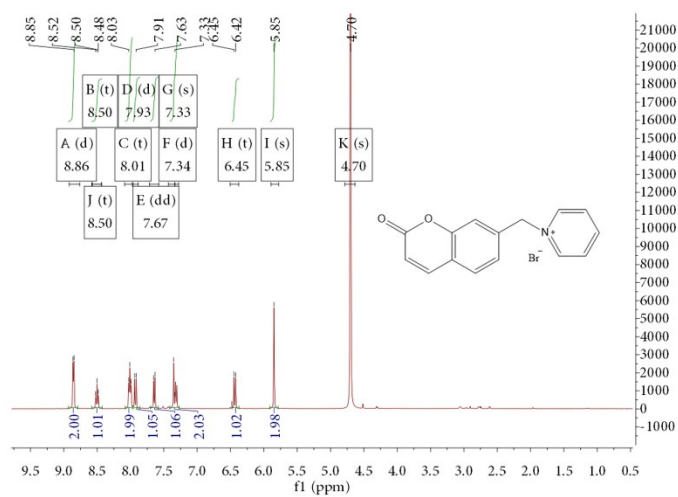
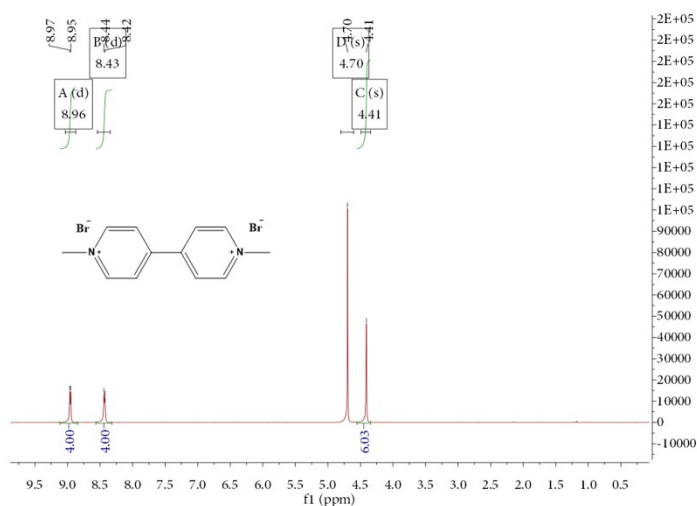


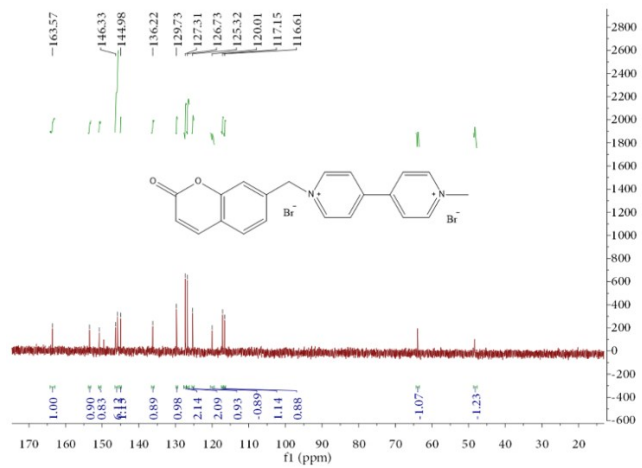
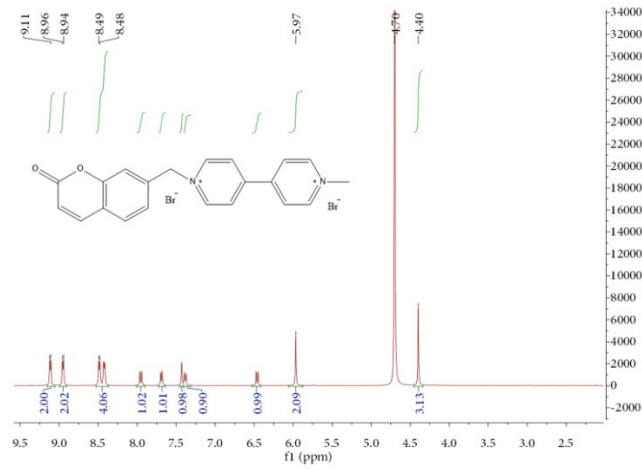
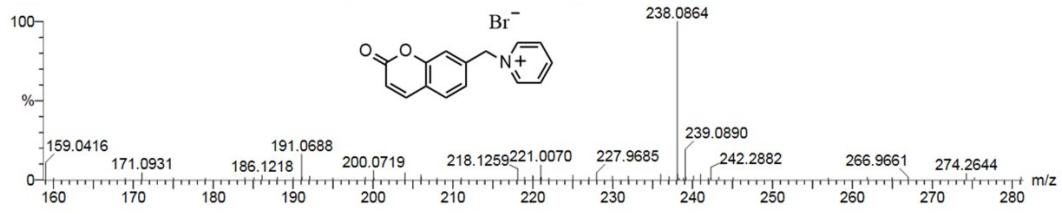
Figure S11. Partial ^1H NMR spectra (400 MHz, D_2O , 298 K) of CB[8]-MV-ChPy with the concentration of 0.25, 1, 4, 8 mmol/L.

Reference

- 1 D. Chang, W. Yan, D. Han, Q. Wang, L. Zou and X. Ma, *Dyes and Pigments*. 2018, 149, 188–192.

Additional spectrum of ^1H , ^{13}C and HRMS.





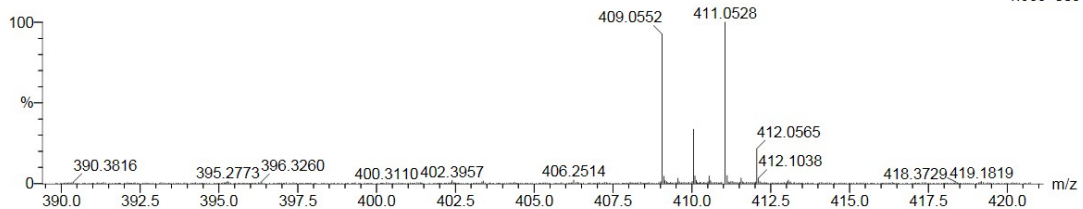
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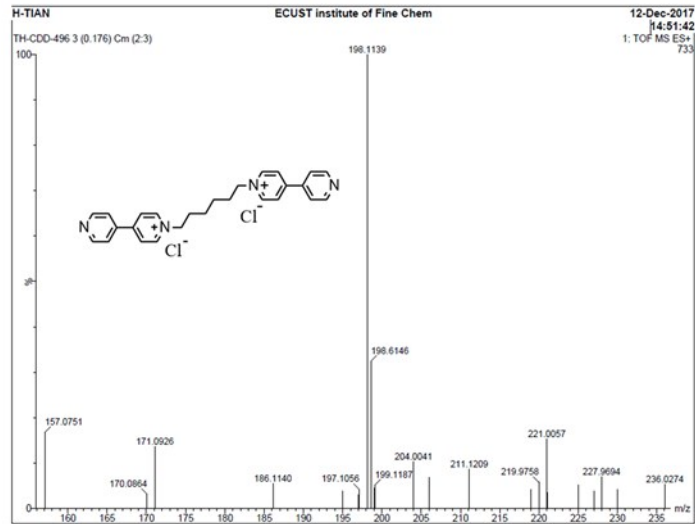
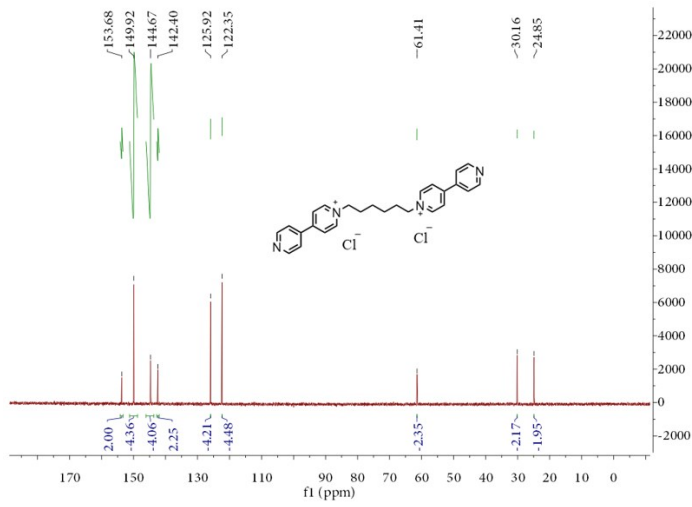
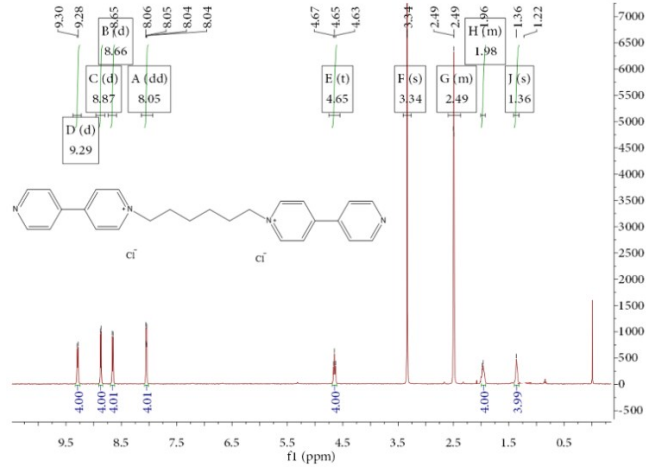
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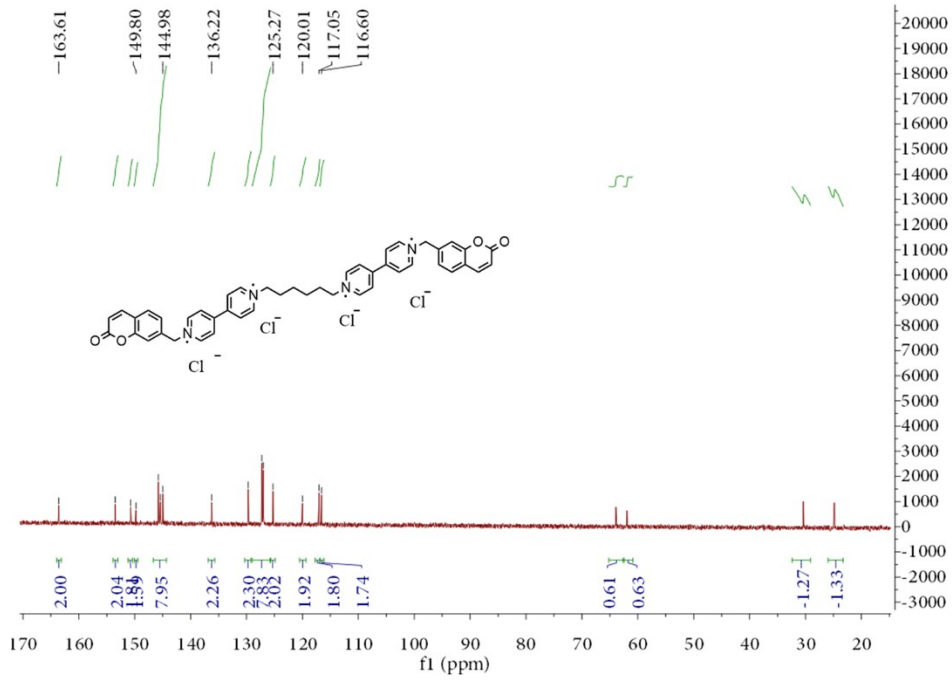
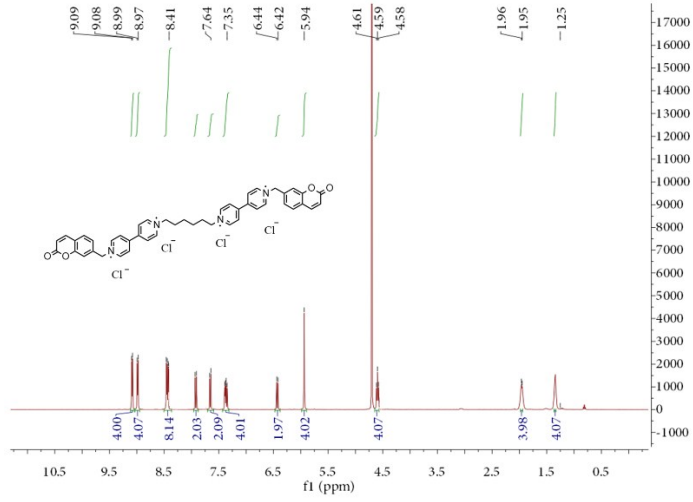
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Monoisotopic Mass, Even Electron Ions

187 formula(e) evaluated with 4 results within limits (up to 1 best isotopic matches for each mass)

Elements Used:

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