Electronic Supporting Information

From Molecular Tweezers to Pliers: A Significant Enhancement of Fullerene Grasping Capability

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General Information

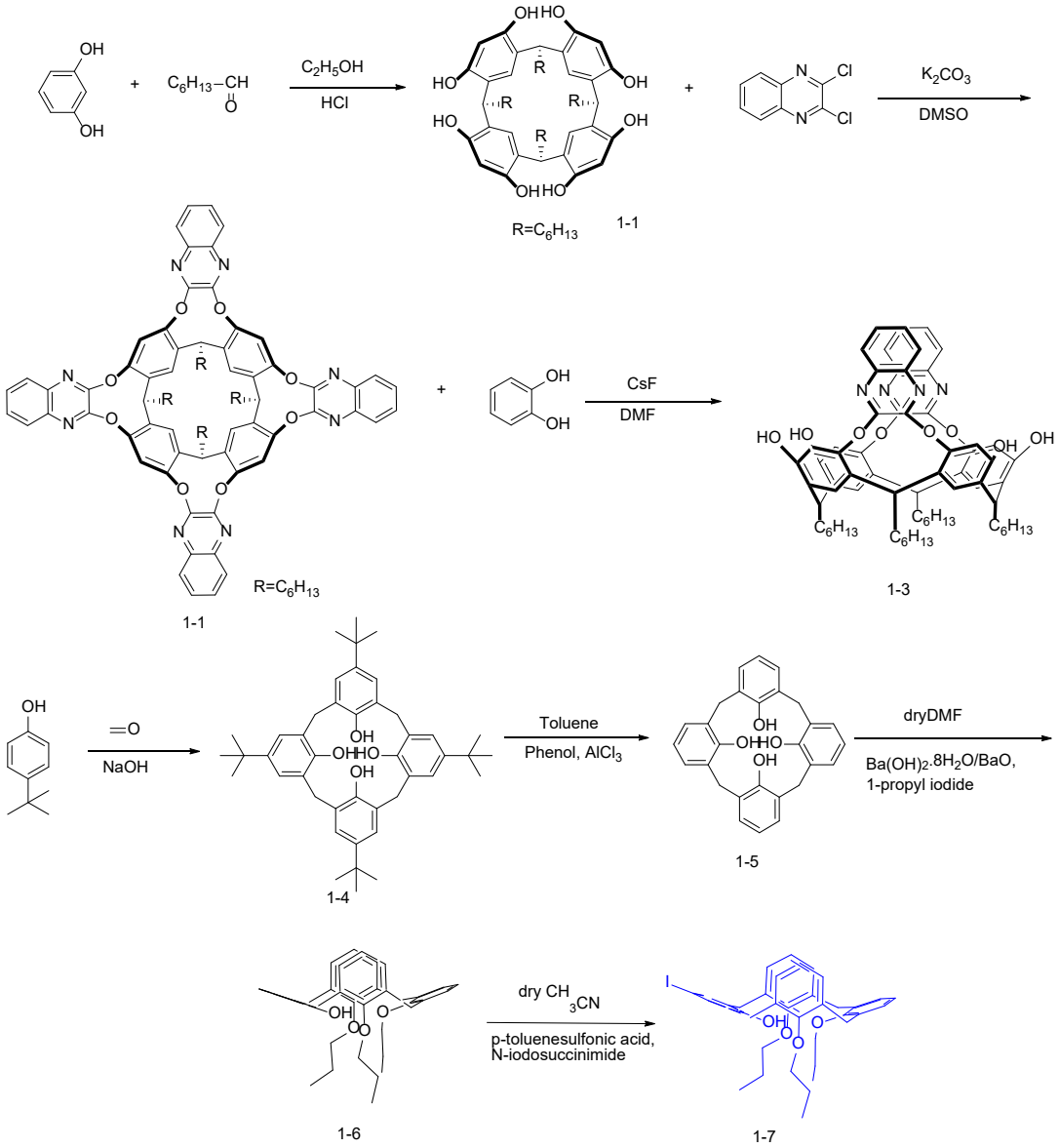
All solvents were purified and dried according to standard procedures. Commercially available reagents (Adamas-Beta, Energy Chemical, J&K Scientific Ltd.) were used without further purification unless specified. Column chromatography was performed on 200-300 mesh silica gel, and reactions were monitored by thin-layer chromatography (TLC). ^{1}H and ^{13}C NMR spectra were acquired on a Bruker DRX 400 MHz spectrometer at 298 K, with chemical shifts reported relative to tetramethylsilane

(TMS). Electronic absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer. UV-Vis absorption spectra were recorded on a Shimadzu UV2600 spectrophotometer, and all absorption spectra were recorded at room temperature.

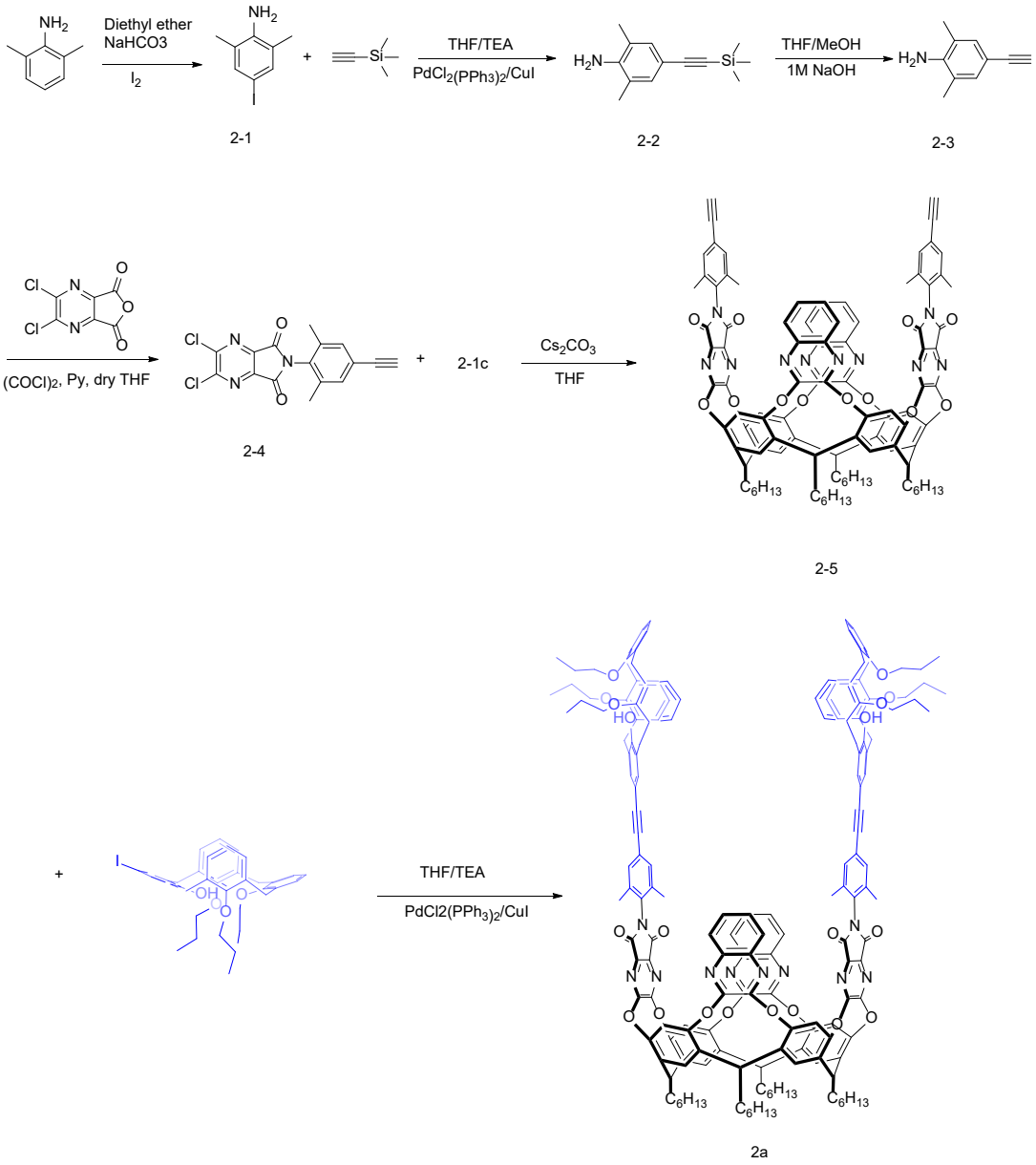
Experimental Procedures

Compound **1-7**, rigid **2a** and flexible **2b** calix(4)arene cavitands were synthesised according to literature procedures.[1-8]

Synthetic Schemes



Scheme S1. Synthesis of **1-7**.



Scheme S2. Synthesis route of **2a.**

Synthesis of 2a

In a dry 50 mL three-necked flask, compound **1-7** (0.2 g, 0.3 mmol) was dissolved in a mixture of anhydrous tetrahydrofuran (THF, 20 mL) and anhydrous triethylamine (10 mL). The mixture was stirred under an argon atmosphere at room temperature for 30 minutes. Compound **2-5** (0.16 g, 0.1 mmol), bis(triphenylphosphine)palladium(II) dichloride (10 mg, 0.015 mmol), and copper(I) iodide (6 mg, 0.032 mmol) were added, and the reaction was heated to 60 °C for 3 hours. The mixture was filtered, and THF and triethylamine were removed under reduced pressure. The crude product was

purified by column chromatography using a petroleum ether (PE): dichloromethane (DCM): ethyl acetate (EA) mixture (3:1:0.5, v/v/v) as the eluent, yielding compound **2a** as a brown solid (0.054 g, 0.019 mmol, 19.0% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 5.5 Hz, 4H), 7.89 (dd, J = 6.4, 3.4 Hz, 4H), 7.47 (d, J = 4.4 Hz, 4H), 7.36 (s, 4H), 7.27 (s, 4H), 7.18 (d, J = 7.6 Hz, 4H), 7.00 (d, J = 7.3 Hz, 2H), 6.47–6.36 (m, 12H), 5.67 (t, J = 7.9 Hz, 2H), 5.60 (t, J = 7.5 Hz, 2H), 5.29 (s, 2H), 4.40 (d, J = 13.0 Hz, 4H), 4.32 (d, J = 13.8 Hz, 4H), 3.87–3.81 (m, 4H), 3.71 (t, J = 6.7 Hz, 8H), 3.30 (d, J = 14.3 Hz, 4H), 3.21 (d, J = 13.0 Hz, 4H), 2.33–2.24 (m, 12H), 2.20 (s, 6H), 1.94–1.86 (m, 8H), 1.56–1.43 (m, 38H), 1.11 (t, J = 7.4 Hz, 12H), 0.96–0.91 (m, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 158.7, 154.2, 153.0, 152.0, 141.4, 139.7, 137.0, 136.7, 135.6, 133.4, 132.0, 131.8, 130.8, 129.5, 129.1, 128.3, 128.1, 127.8, 123.7, 123.2, 118.7, 112.9, 77.6, 77.2, 32.7, 32.1, 31.8, 30.7, 29.4, 27.9, 26.9, 25.8, 23.4, 22.7, 22.4, 18.1, 17.9, 14.1, 10.8, 9.6, -11.5.

$C_{174}H_{170}N_{10}O_{20}$ **HRMS** $[M + H]^+$ Exp.: 2720.26 Cal.: 2720.25.

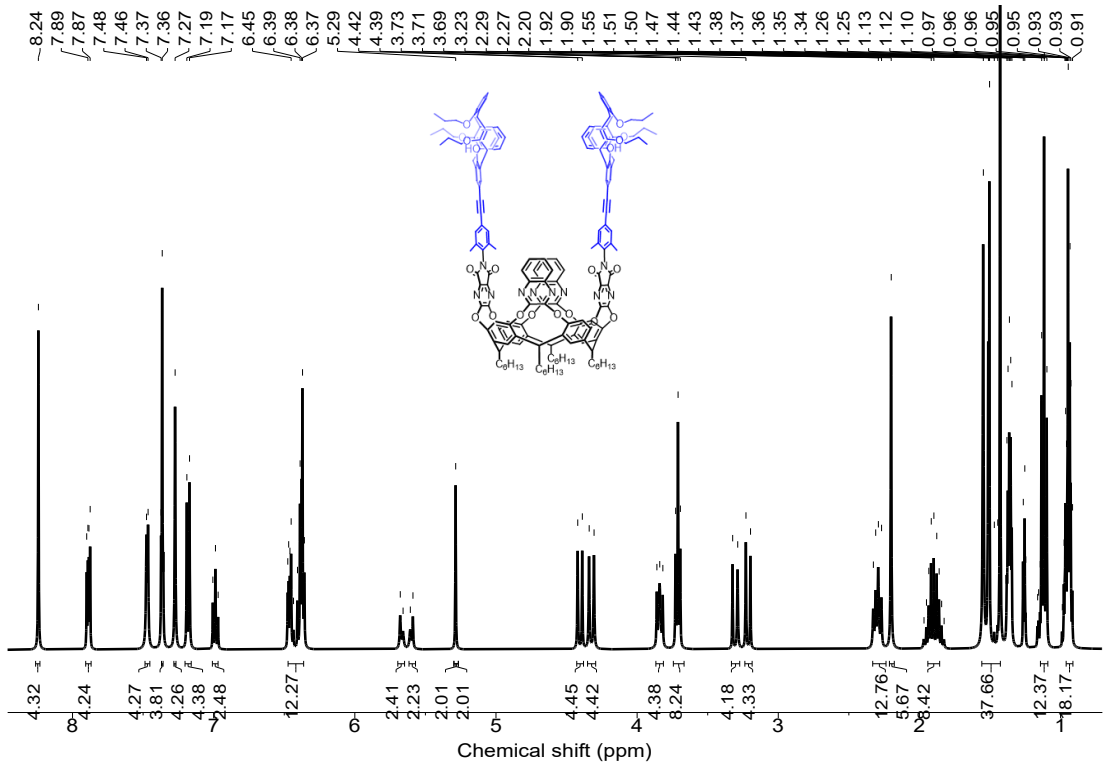


Figure S1. ^{1}H NMR spectrum of **2a** (400 MHz, $CDCl_3$, 298K).

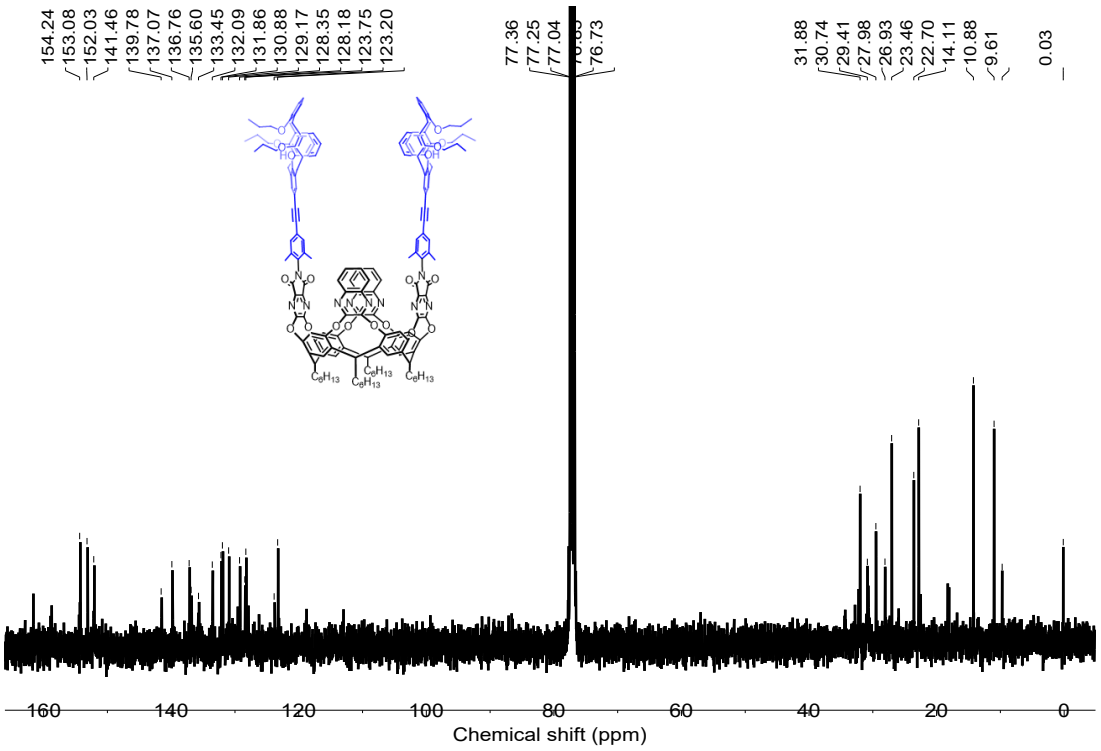


Figure S2. ^{13}C NMR spectrum of **2a** (100 MHz, $CDCl_3$, 298K).

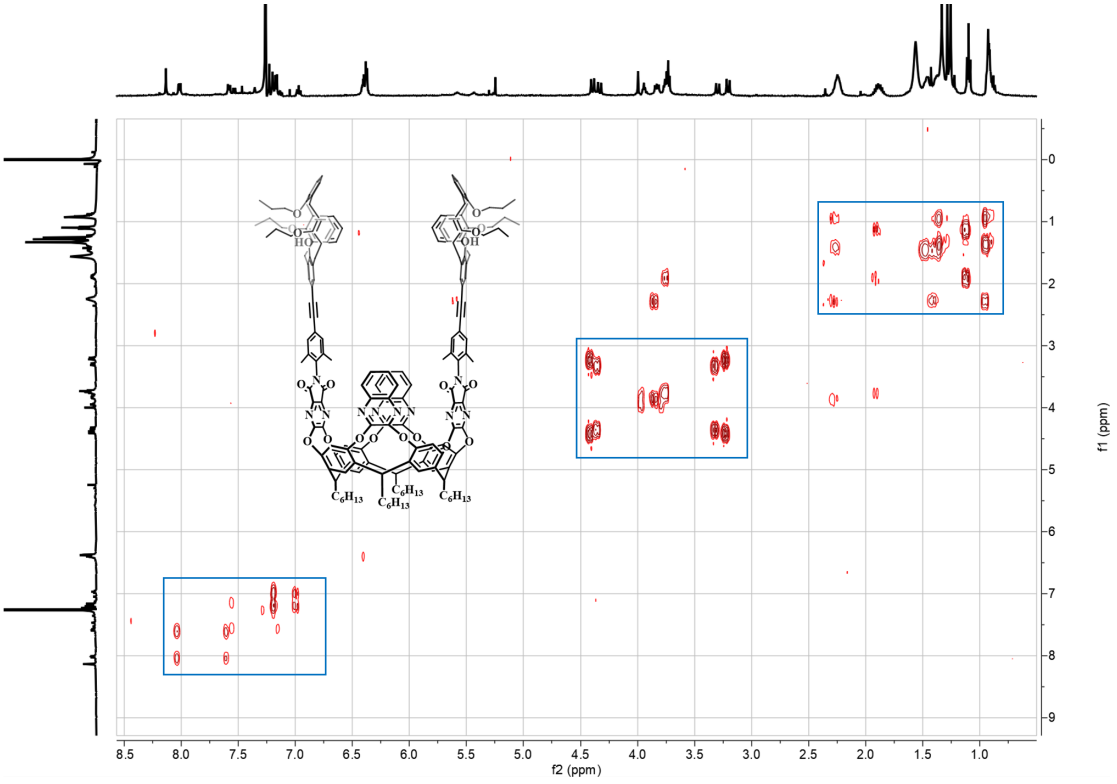


Figure S3. COSY NMR spectrum (500 MHz) of compound **2a**. Data collected in $CDCl_3$ at room temperature.

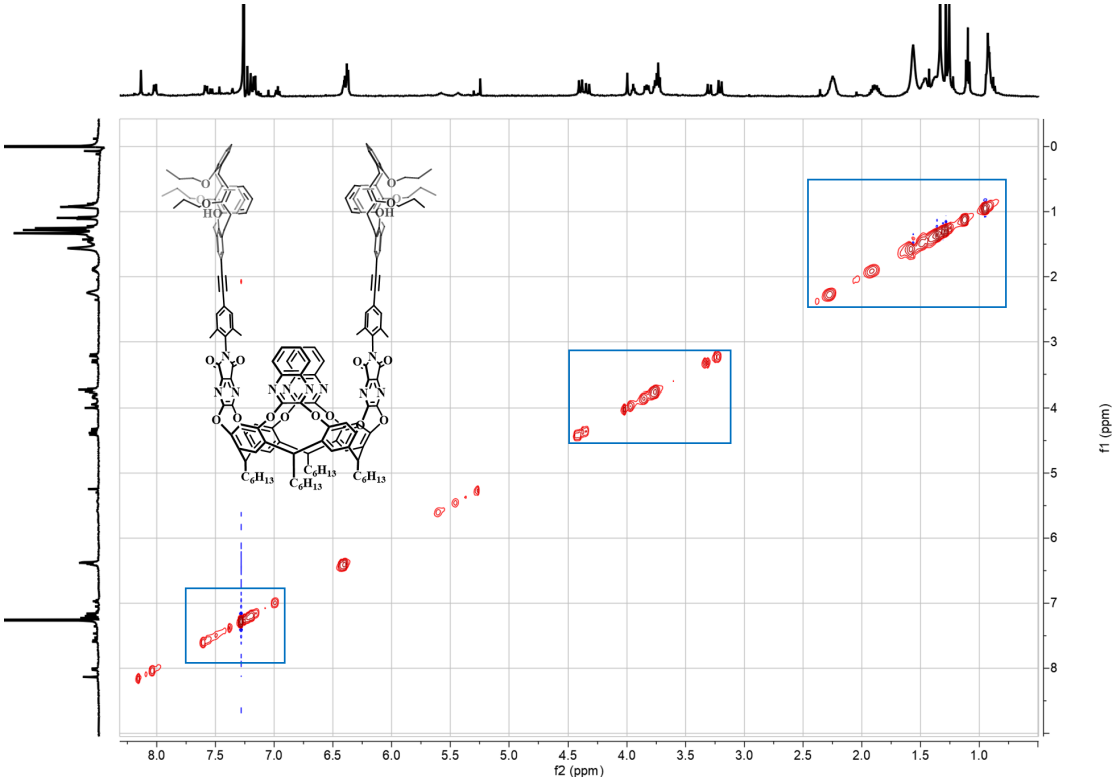


Figure S4. NOESY NMR spectrum (500 MHz) of compound **2a**. Data collected in $CDCl_3$ at room temperature.

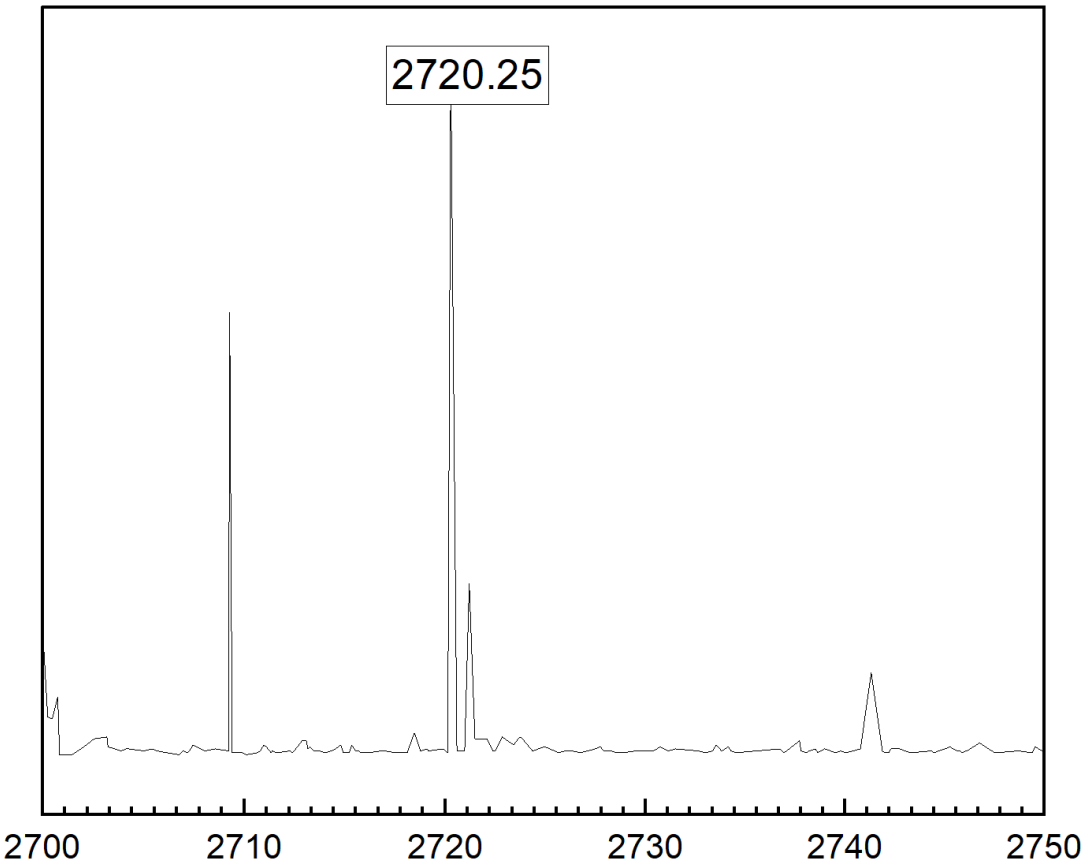
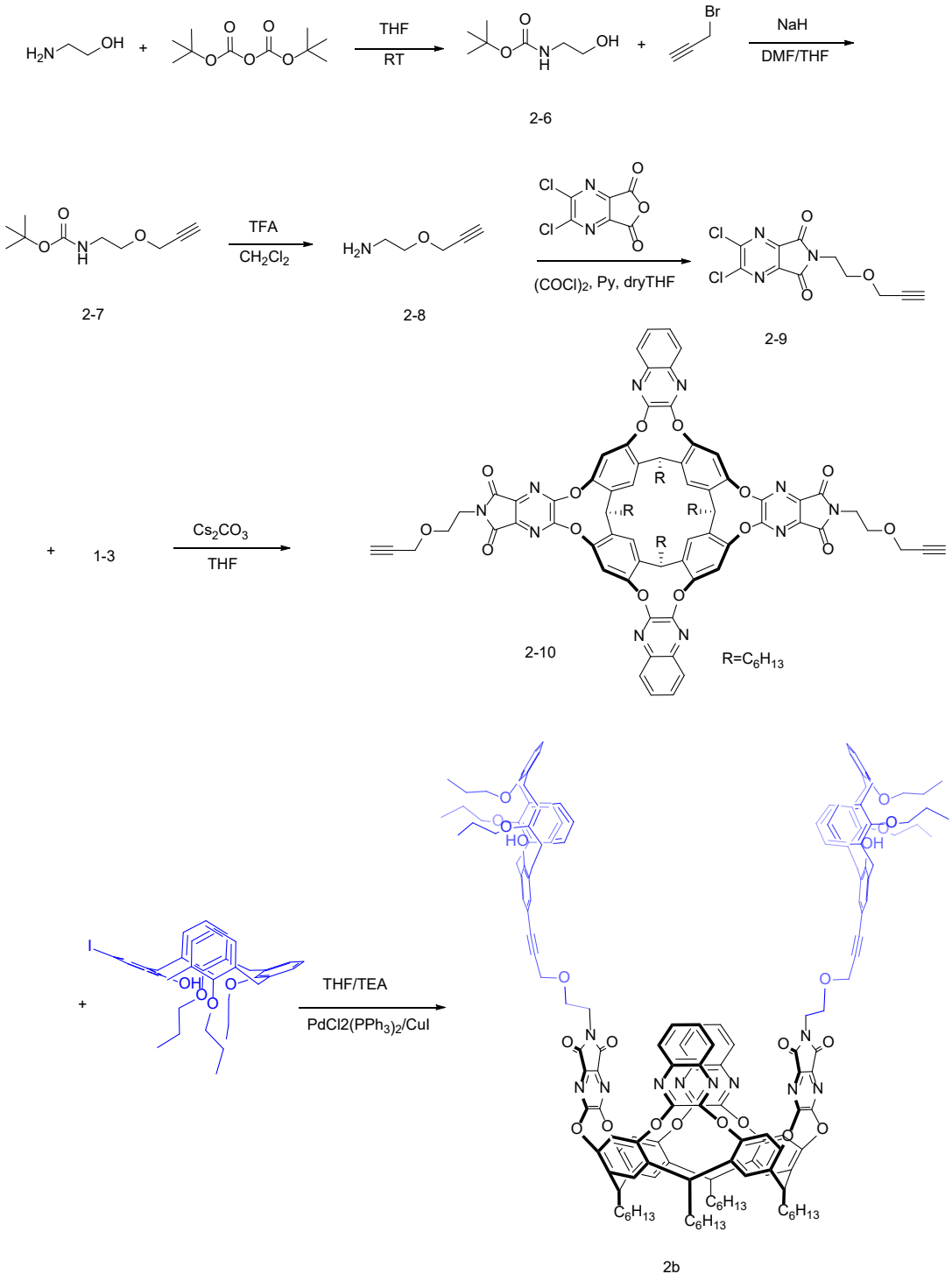


Figure S5. HRMS (MALDI) of compound 2a $[M+H]^+$, Exp.: 2720.26 Cal.: 2720.25 for $C_{174}H_{170}N_{10}O_{20}$.



Scheme S3. Synthesis route of **2b**.

Synthesis of 2b

In a dry 50 mL three-necked flask, compound **1-7** (0.2 g, 0.3 mmol) was dissolved in a mixture of anhydrous tetrahydrofuran (THF, 20 mL) and anhydrous triethylamine (10

mL). The mixture was stirred under an argon atmosphere at room temperature for 30 minutes. Compound **2-1** (75 mg, 0.12 mmol), bis(triphenylphosphine)palladium(II) dichloride (10 mg, 0.015 mmol), and copper(I)iodide (6 mg, 0.032 mmol) were added, and the reaction was heated to 60 °C for 3 hours. The mixture was filtered, and THF and triethylamine were removed under reduced pressure. The crude product was purified by column chromatography using a petroleum ether (PE): dichloromethane (DCM): ethyl acetate (EA) mixture (4:1:0.5, v/v/v) as the eluent, yielding compound **2b** as an orange-yellow solid (0.13 g, 0.05 mmol, 41.7% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 4H), 8.02 (dd, J = 6.3, 3.5 Hz, 4H), 7.59 (dd, J = 6.3, 3.5 Hz, 4H), 7.35 (d, J = 2.6 Hz, 2H), 7.23 (s, 4H), 7.21 (s, 4H), 7.17 (d, J = 7.5 Hz, 4H), 6.99–6.96 (m, 2H), 6.40 (ddd, J = 12.7, 6.1, 3.6 Hz, 12H), 5.59 (t, J = 8.0 Hz, 2H), 5.49–5.41 (m, 2H), 5.24 (s, 2H), 4.40 (d, J = 13.0 Hz, 4H), 4.34 (d, J = 13.8 Hz, 4H), 4.00 (s, 4H), 3.95 (t, J = 5.5 Hz, 4H), 3.86–3.81 (m, 5H), 3.78–3.71 (m, 12H), 3.30 (d, J = 13.8 Hz, 4H), 3.21 (d, J = 13.1 Hz, 4H), 2.26 (q, J = 8.0 Hz, 14H), 1.89 (dt, J = 14.3, 7.1 Hz, 8H), 1.40–1.31 (m, 42H), 1.10 (t, J = 7.4 Hz, 14H), 0.93 (dq, J = 7.1, 3.1 Hz, 20H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 156.7, 155.7, 153.3, 153.1, 151.9, 151.1, 150.8, 140.5, 138.6, 136.0, 135.3, 134.2, 132.4, 131.0, 130.8, 129.8, 128.5, 128.1, 127.4, 127.1, 126.7, 122.6, 122.1, 122.0, 117.5, 111.2, 86.6, 81.3, 76.6, 75.4, 64.8, 57.7, 37.0, 33.6, 33.4, 33.3, 31.4, 31.2, 30.8, 29.6, 29.4, 28.3, 28.3, 26.8, 26.8, 25.8, 24.2, 22.3, 21.6, 21.3, 13.0, 9.7, 8.5.

$C_{164}H_{166}N_{10}O_{22}$ **HRMS** $[M + H]^+$ Exp.: 2628.22 Cal.: 2628.022.

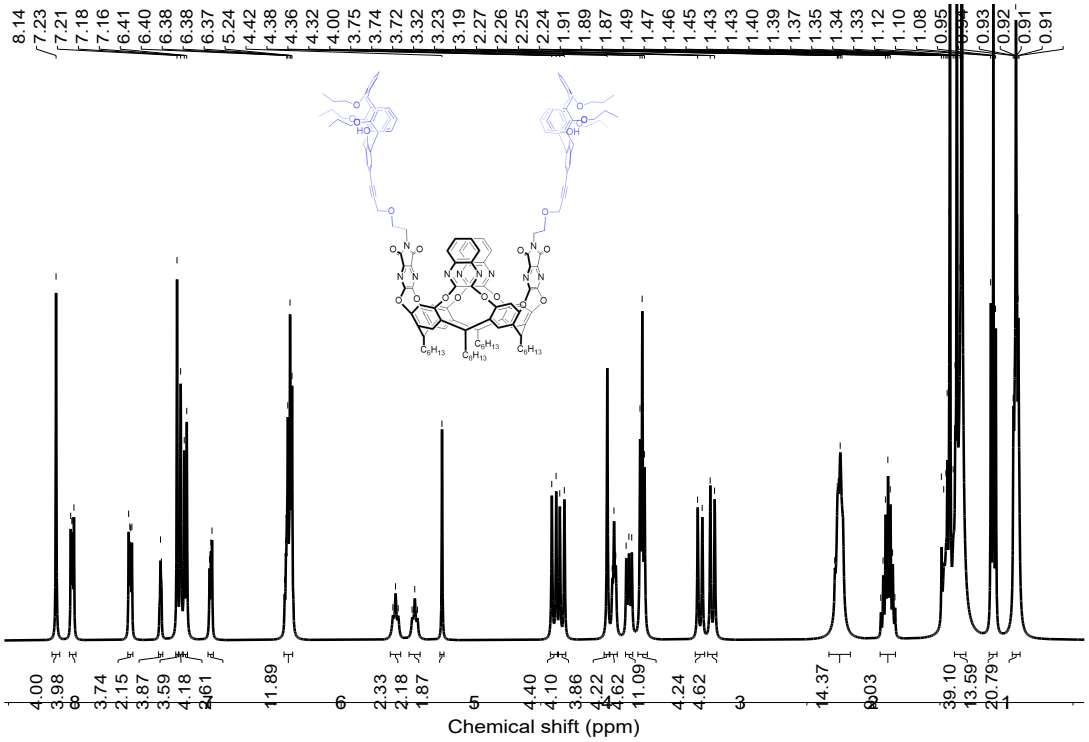


Figure S6. ^{1}H NMR spectrum of **2b** (400 MHz, $CDCl_3$, 298K).

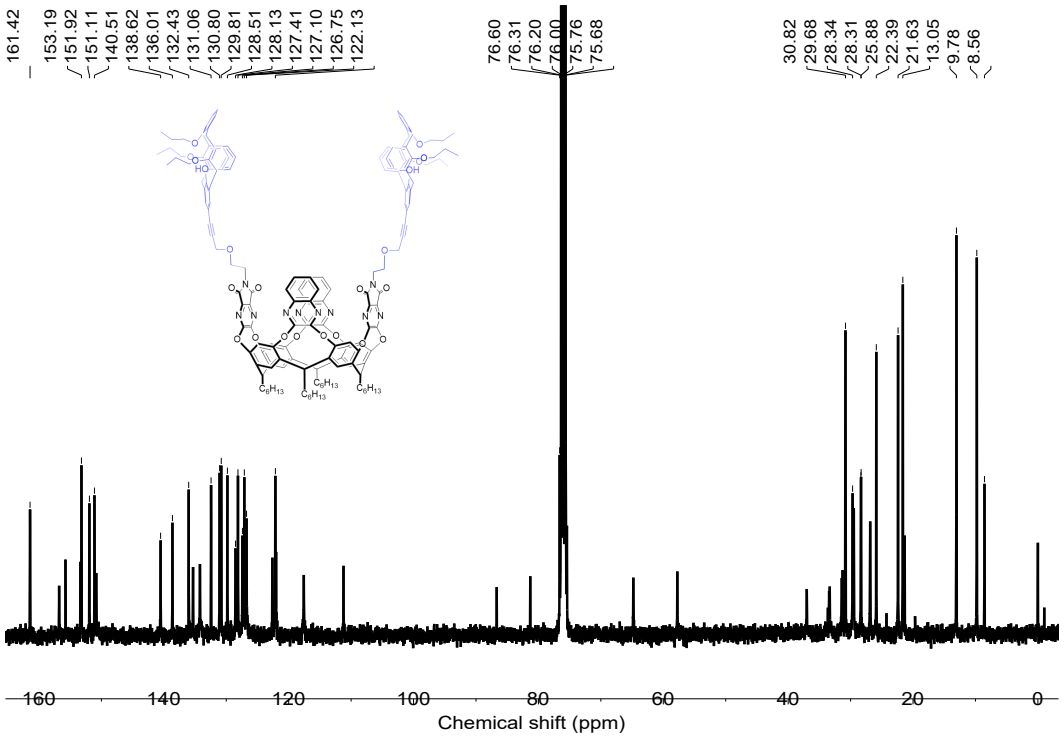


Figure S7. ^{13}C NMR spectrum of **2b** (100 MHz, $CDCl_3$, 298K).

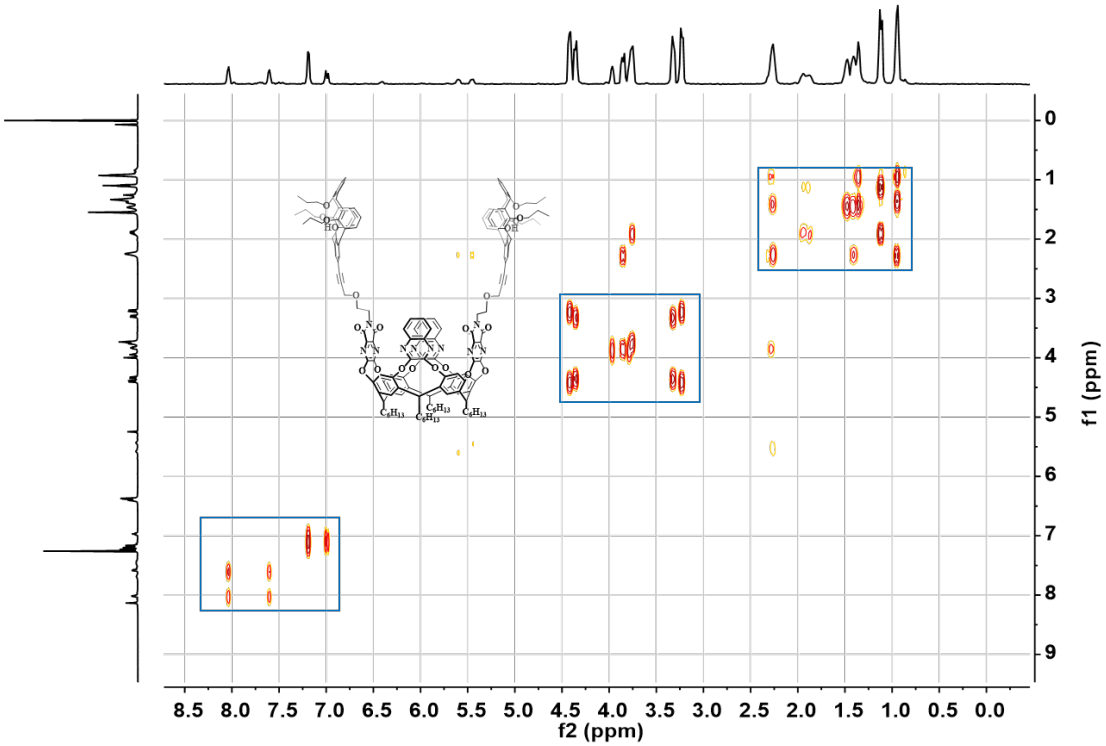


Figure S8. COSY NMR spectrum (600 MHz) of compound **2b**. Data collected in $CDCl_3$ at room temperature.

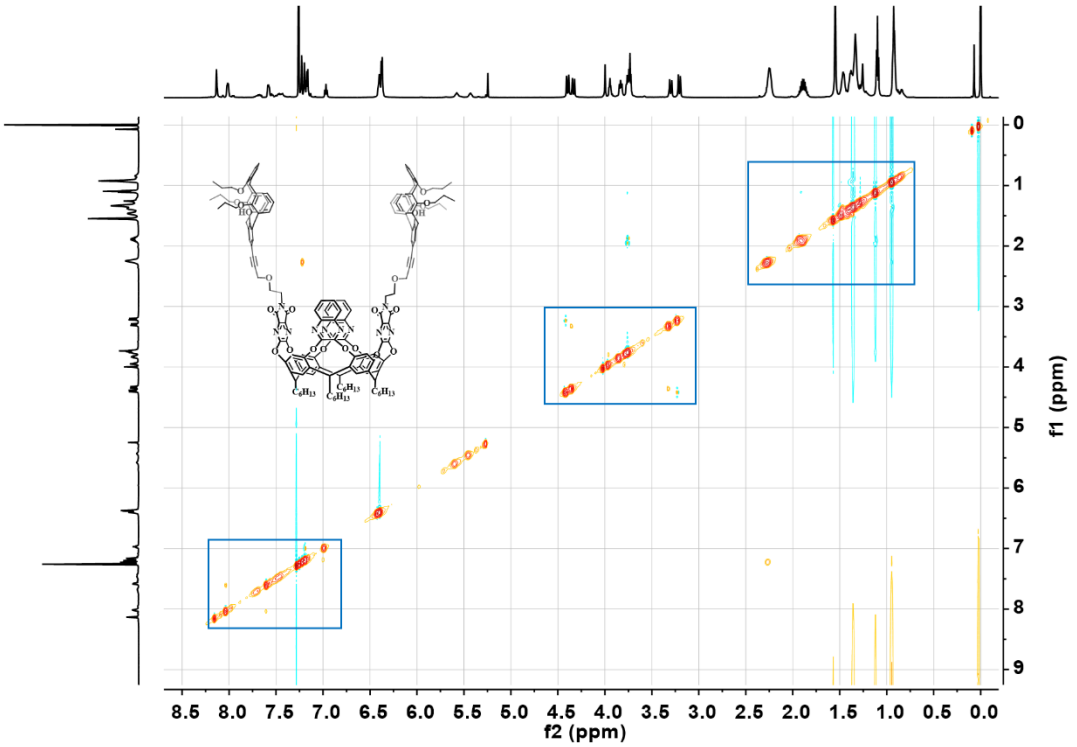


Figure S9. NOESY NMR spectrum (600 MHz) of compound **2b**. Data collected in $CDCl_3$ at room temperature.

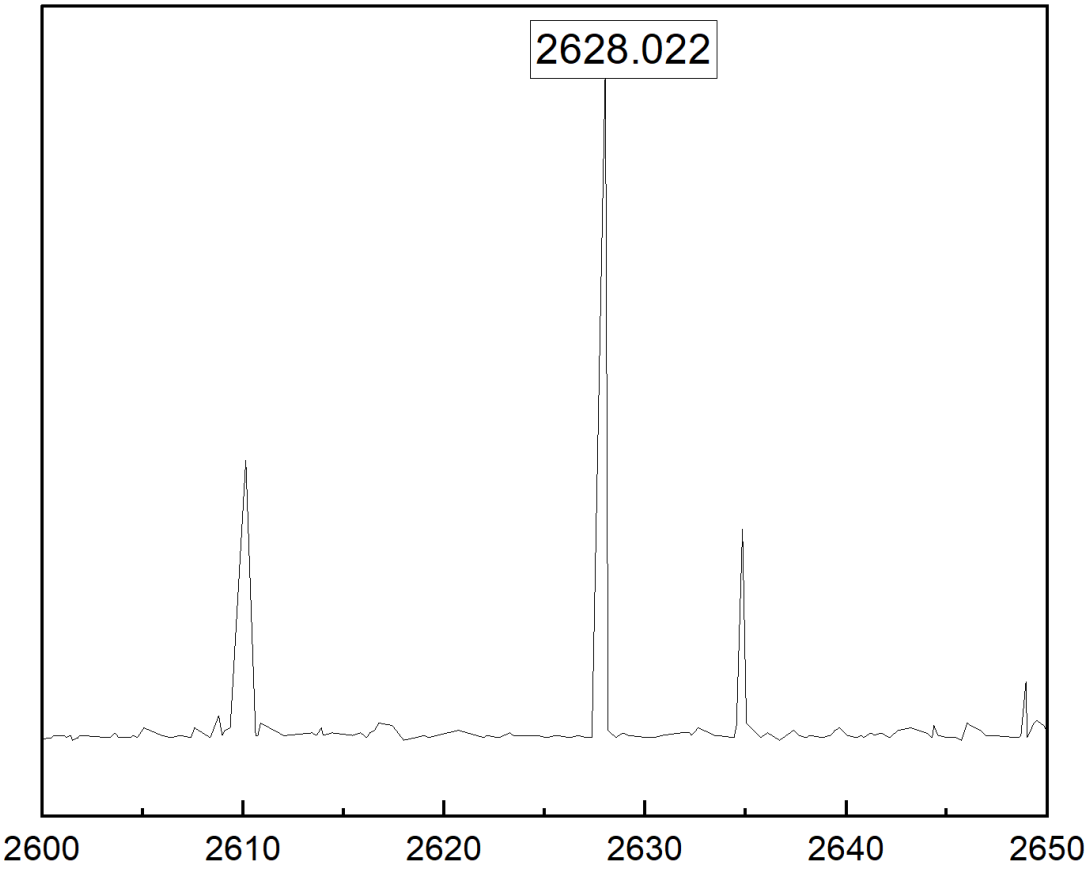


Figure S10. HRMS (MALDI) of compound **2b** $[M+H]^+$, Exp.: 2628.22 Cal.: 2628.022 for $C_{164}H_{166}N_{10}O_{22}$.

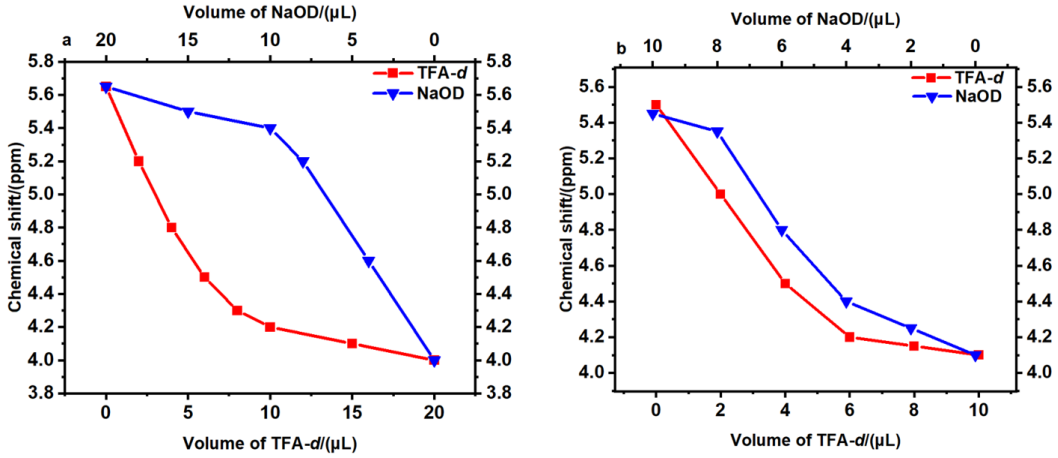


Figure S11. Variation of the chemical shift of the methylene proton H_a under different pH conditions for (a) **2a** and (b) **2b.**

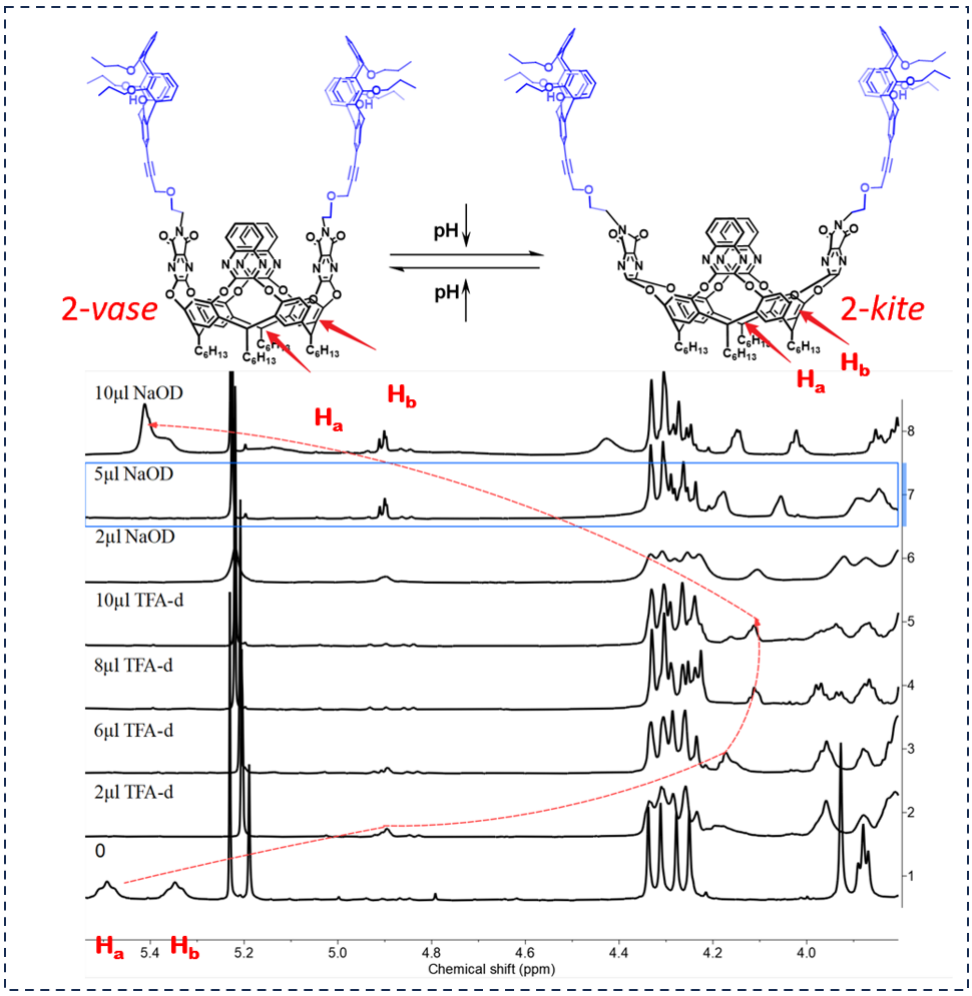


Figure S12. ^{1}H NMR spectra of **2b** (*vase*-to-*kite*) (400MHz, $CDCl_3$, 298K) under acid-base conditions.

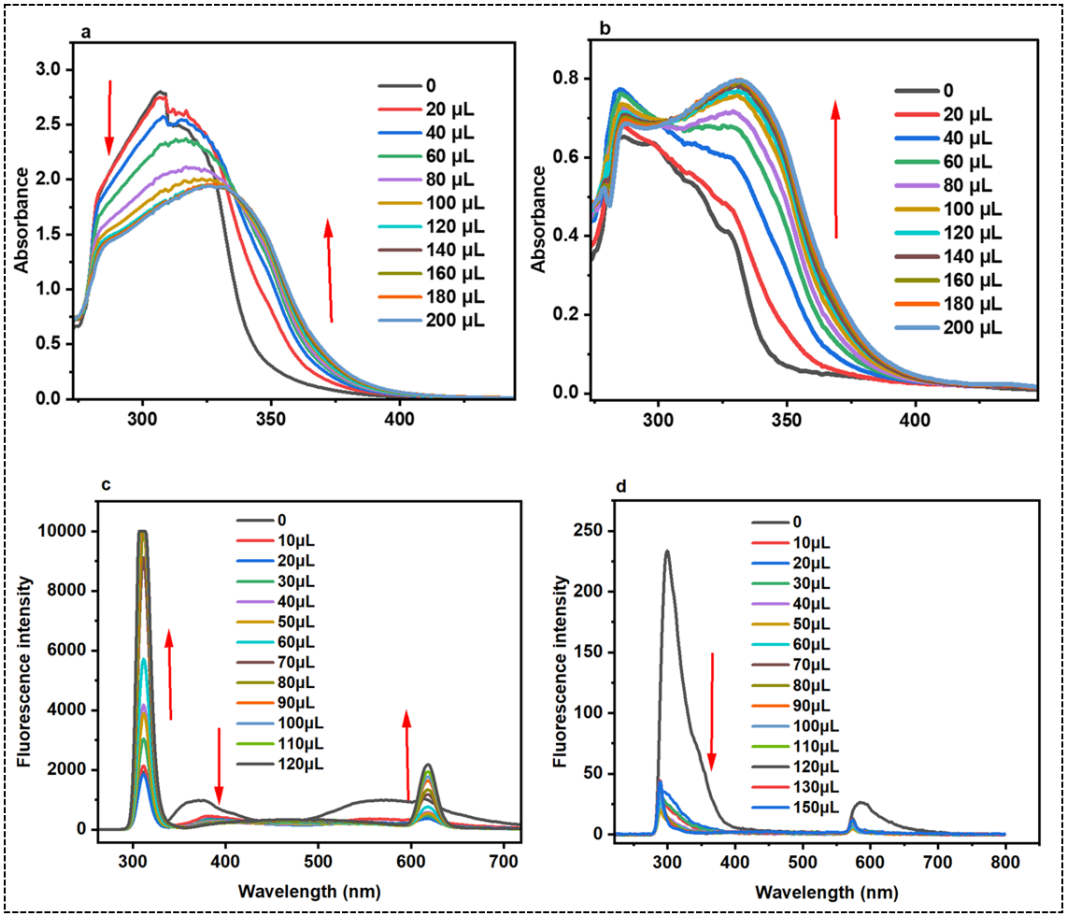


Figure S13. UV-Vis absorption spectral changes of (a) **2a**, (b) **2b**, and fluorescence emission spectral changes of (c) **2a** (3×10^{-5} M^{-1}, λex= 292 nm); (d) **2b** (3×10^{-5} M^{-1}, λex= 306 nm) upon addition of TFA-d.

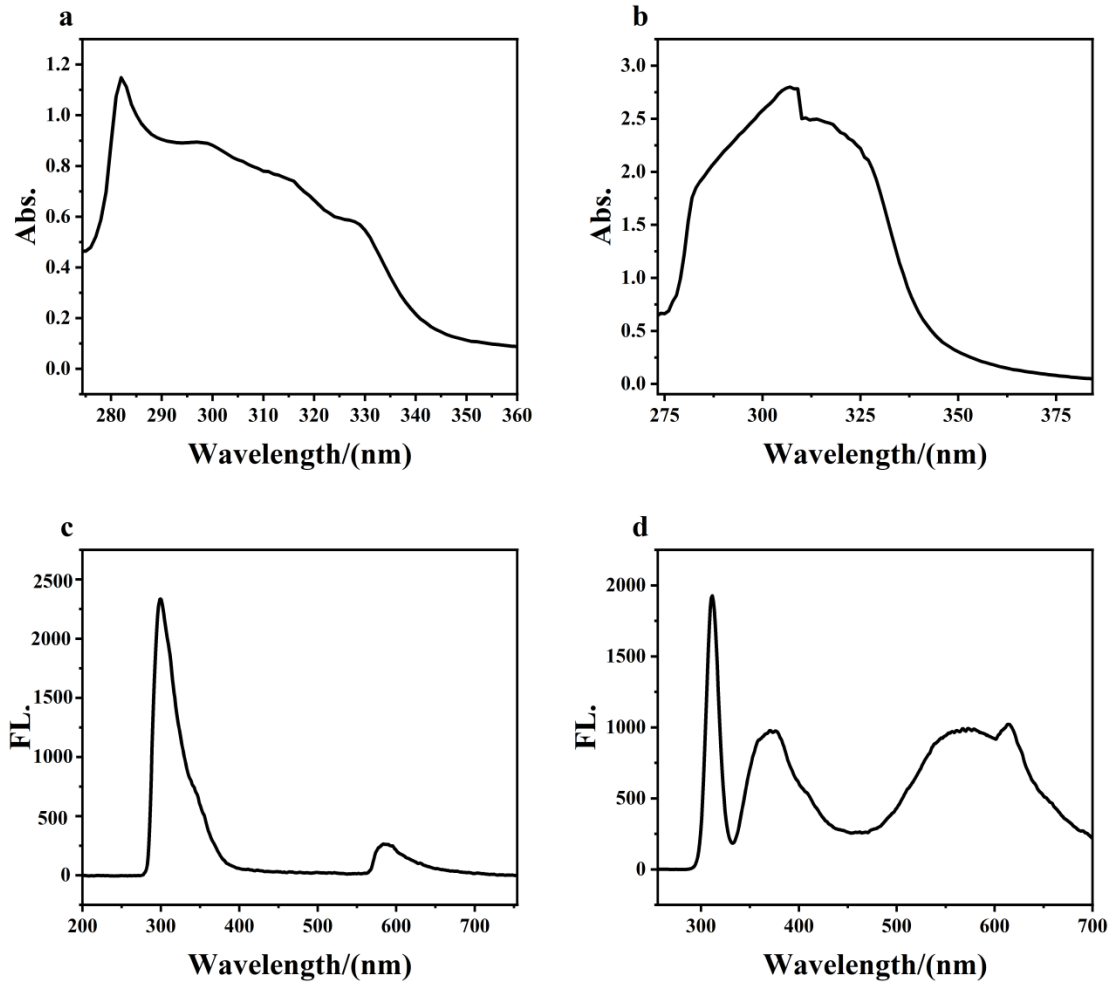


Figure S14. UV-Vis absorption spectra: (a) **2b,** (b) **2a**; Fluorescence emission spectra: (c) **2b** (3×10^{-6} M^{-1}, λ_{ex}= 292 nm), (d) **2a** (3×10^{-6} M^{-1}, λ_{ex}= 306 nm)

Host-Guest Interactions

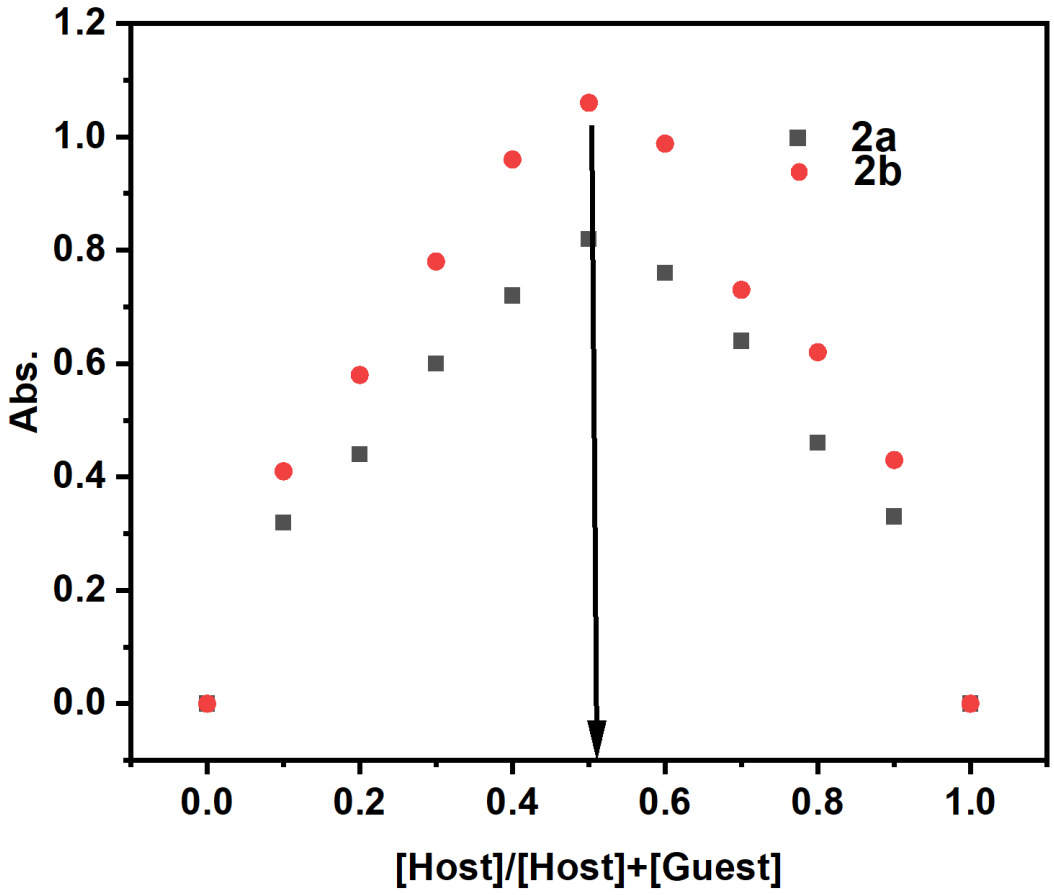


Figure S15. Job-plot curve of **2a, 2b** and C_{60}.

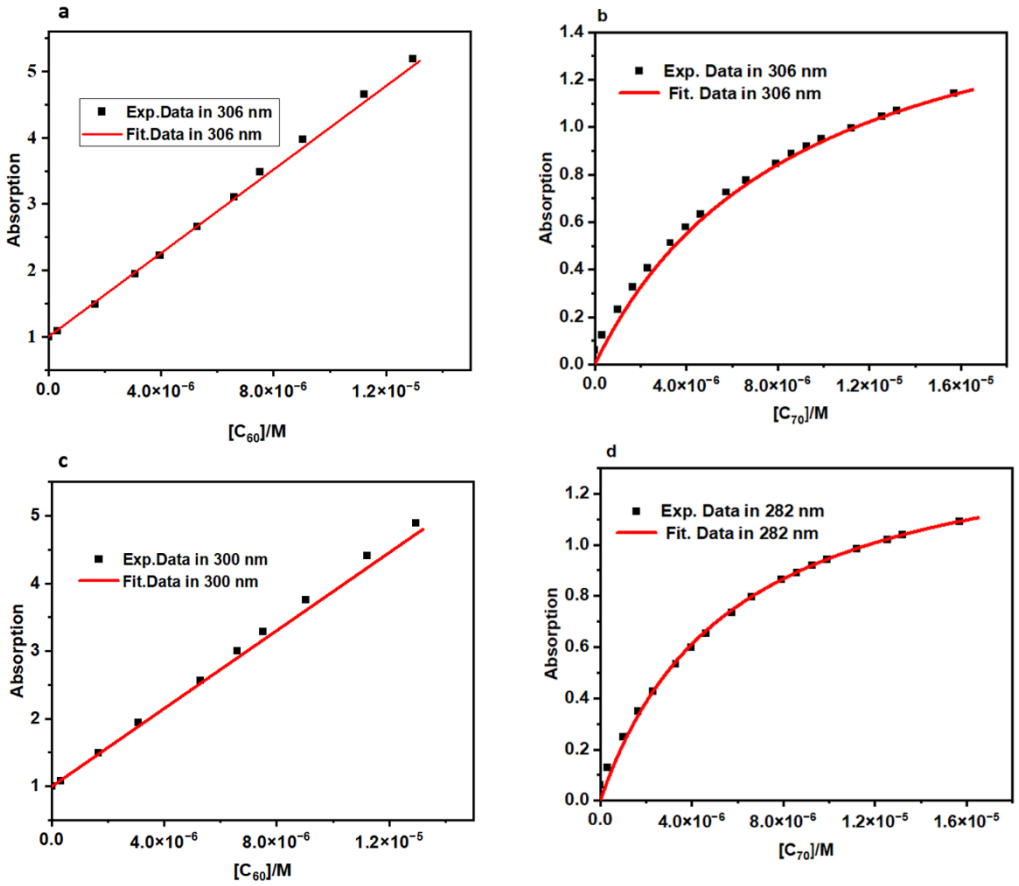


Figure S16. Nonlinear fitting of (a, b) **2a** and **2b** for C_{60} at 306 nm and (c, d) for C_{70} at 300 nm and 282 nm.

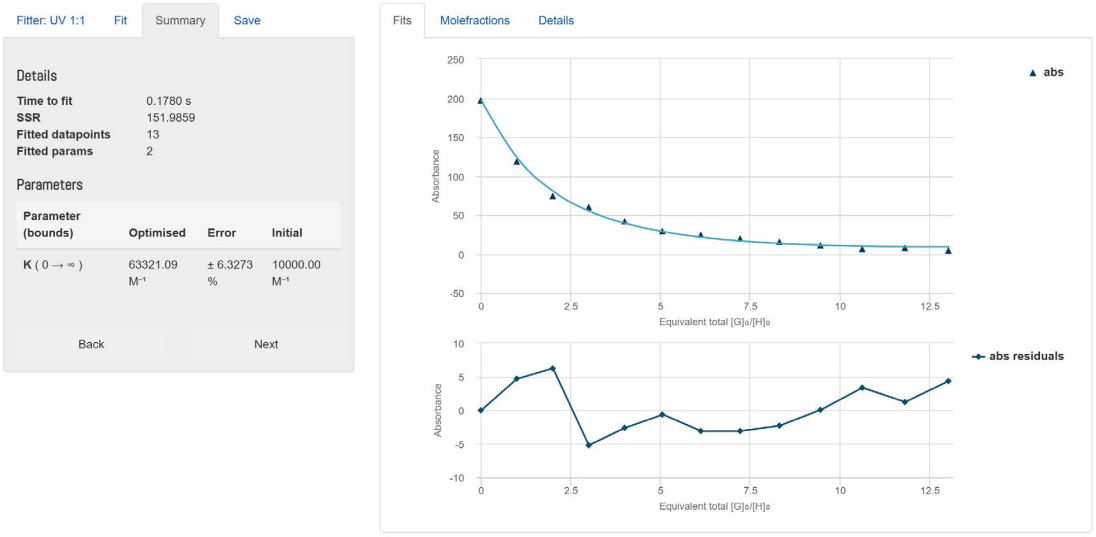


Figure S17. Fittings of the data by BindFit program for calculating binding constants (K_a) based on ultraviolet titration experiments of **2a** with C_{60}. Screenshot from the result window of supramolecular.org from data archived at the unique URL:

https://app.supramolecular.org/bindfit/view/fabbba28-42de-451e-a91a-502d21571448 based on a 1:1 binding model, the K_a value was calculated as 6.33×10^4 M^{-1}.

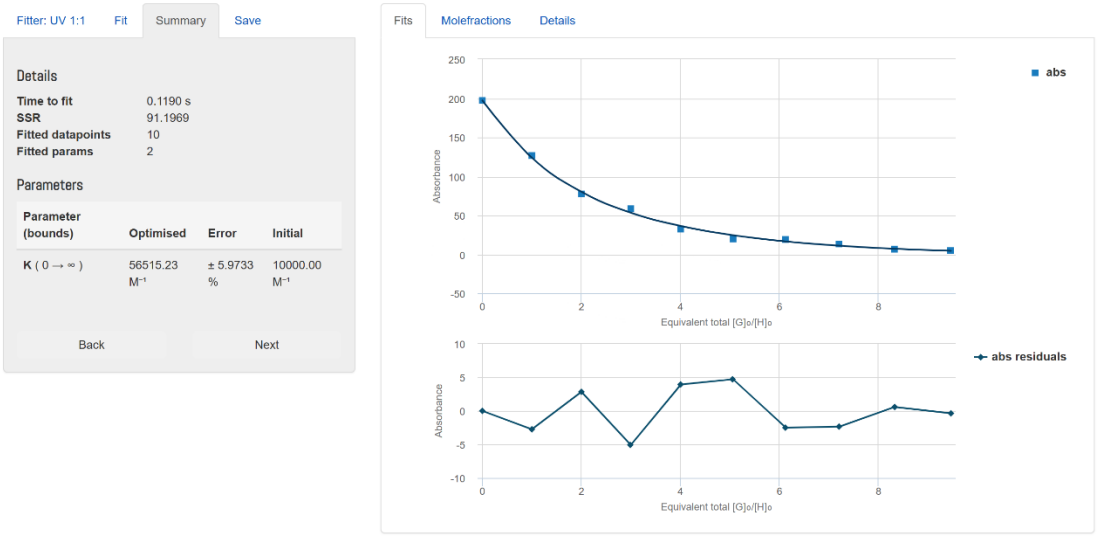


Figure S18. Fittings of the data by BindFit program for calculating binding constants (K_a) based on fluorescence titration experiments of **2b** with C_{60}. Screenshot from the result window of supramolecular.org from data archived at the unique URL: https://app.supramolecular.org/bindfit/view/506c52c0-1c65-4660-bbdb-2bab08749f2d based on a 1:1 binding model, the K_a value was calculated as 5.65×10^4 M^{-1}.

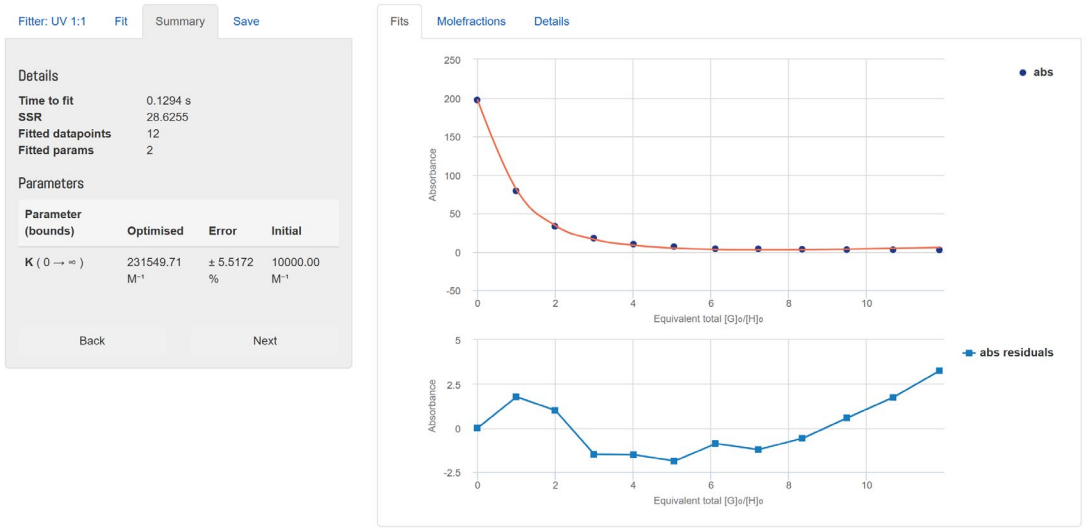


Figure S19. Fittings of the data by BindFit program for calculating binding constants (K_a) based on ultraviolet titration experiments of **2a** with C_{70}. Screenshot from the result window of supramolecular.org from data archived at the unique URL: https://app.supramolecular.org/bindfit/view/7d766f48-beb0-44e4-a583-095d18db5d4a based on a 1:1 binding model, the K_a value was calculated as 2.31×10^5 M^{-1}.

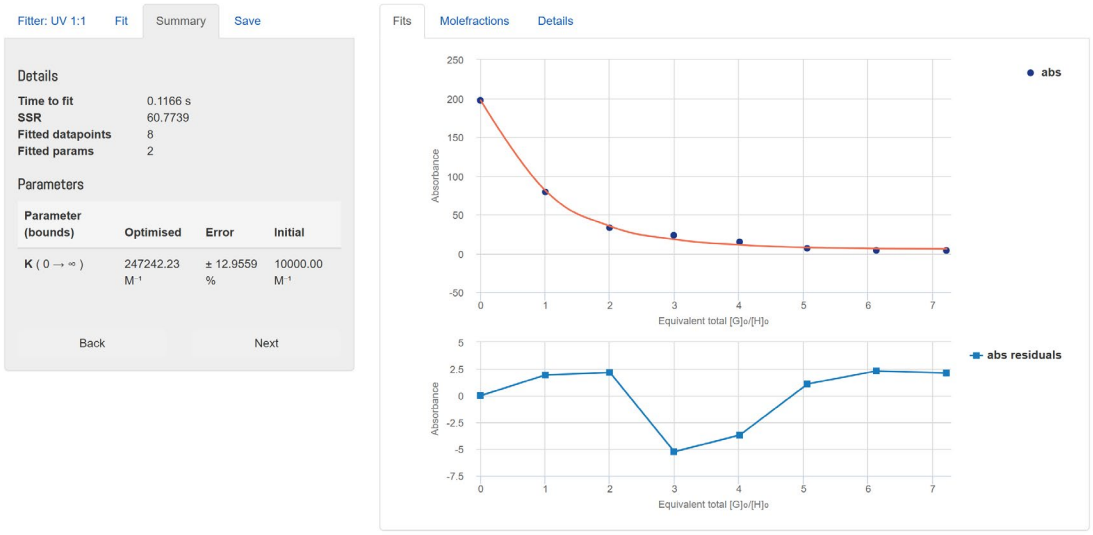


Figure S20. Fittings of the data by BindFit program for calculating binding constants (K_a) based on ultraviolet titration experiments of **2b** with C_{70}. Screenshot from the result window of supramolecular.org from data archived at the unique URL: https://app.supramolecular.org/bindfit/view/5c53730e-ead1-472b-9169-a4acf97730b6 based on a 1:1 binding model, the K_a value was calculated as 2.47×10^5 M^{-1}.

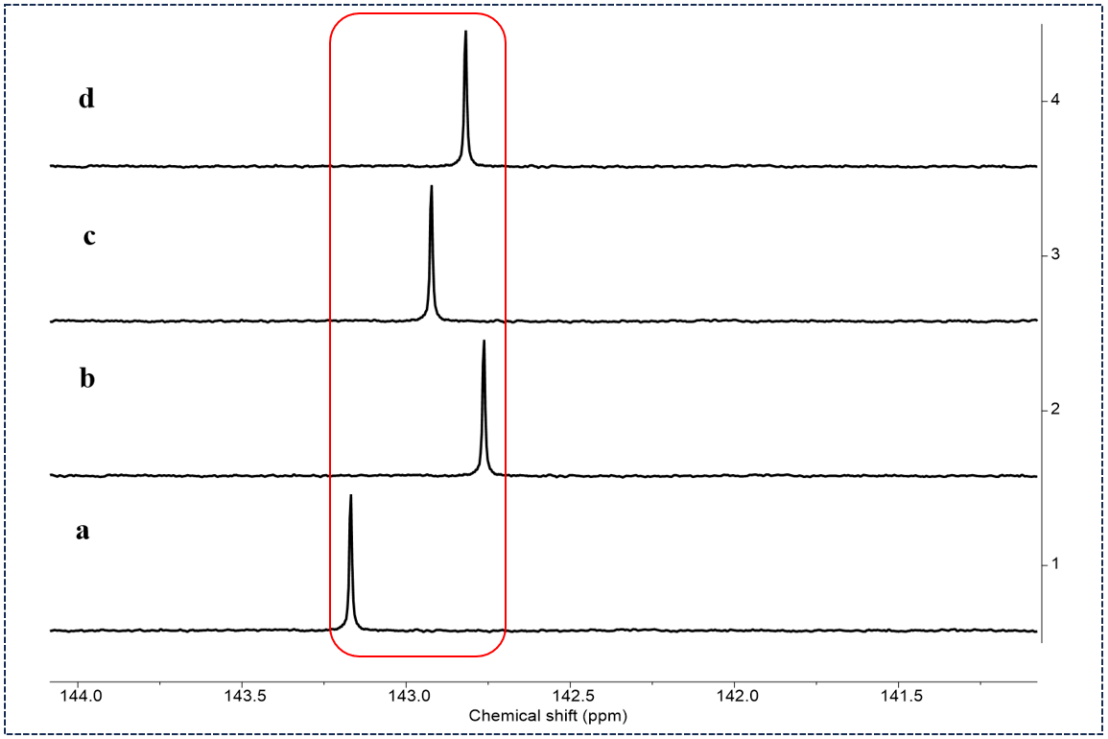


Figure S21. Partial ^{13}C NMR Spectra (150 MHz) (Solvent: $CDCl_3/CS_2$ = 1:1) (a) C_{60} (b) 1.0 equiv C_{60} + 1.0 equiv **2a** (c)1.0 equiv C_{60} + 1.0 equiv **2a** + TFA-d (d) 1.0 equiv C_{60} + 1.0 equiv **2a** + TFA-d + NaOD.

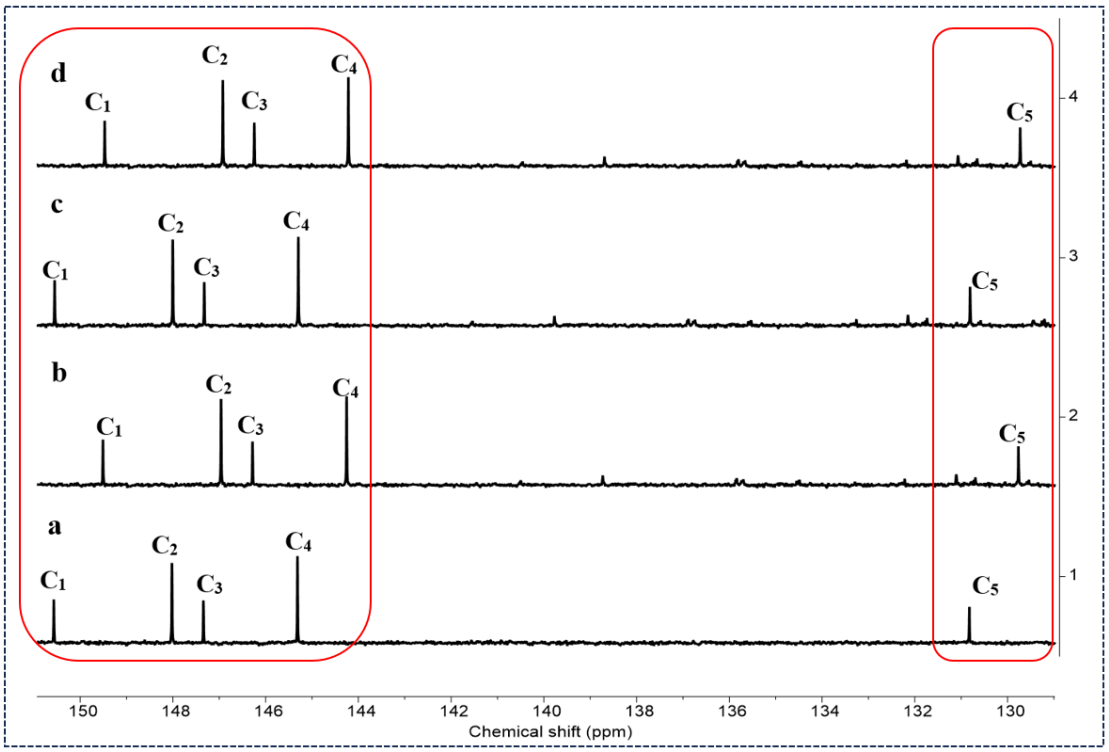


Figure S22. Partial ^{13}C NMR Spectra (150 MHz) (Solvent: $CDCl_3/CS_2$ = 1:1) (a) C_{70} (b) 1.0 equiv C_{70} + 1.0 equiv **2b** (c) 1.0 equiv C_{70} + 1.0 equiv **2b** + TFA-d (d) 1.0 equiv C_{70} + 1.0 equiv **2b** + TFA-d + NaOD.

Table S1. The binding constants of **2a** and **2b** with C_{60} and C_{70}.

Compound	C_{60}	C_{70}
2a	6.33×10^4 M^{-1}	2.31×10^5 M^{-1}
2b	5.66×10^4 M^{-1}	2.47×10^5 M^{-1}

Comparison of the binding affinity of C4A with C_{60} and C_{70}

The binding constant of flexible 2b for C_{70} is higher than that for C_{60}, and is often dominated by elongated shape cavities of both C4A and C_{70}, as summarized in (Table S1†). X-ray crystallography, molecular dynamics, and DFT calculations support this improved binding. This dramatic enhancement is attributed to a powerful synergistic effect wherein the cooperation of the two C4A units creates a much larger, three-dimensional cavity compared to a single unit; this larger volume is better suited to accommodate bulky fullerenes and provides multiple binding sites, which simultaneously enhance both the binding constant and the selectivity toward the guest.

Flexible-chain C4A can enhance interactions through minor conformational adjustments, such as cavity tilting, to better accommodate C_{70}. In low-polarity solvents such as toluene, hydrophobic effects are predominant. The larger surface area of C_{70} more efficiently excludes solvent molecules from the cavity, facilitating its encapsulation within the C4A cavity and reducing the system's free energy. The binding of C_{70} results in a considerable entropic gain due to the release of ordered solvent molecules.

References

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