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Supporting Information

Molecular Binding Behaviors and Thermodynamics of Ferrocenyl Dimethylaminiun Derivatives by Anionic Pillar[5]arene

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Guest molecules FC\textsubscript{n+} were synthesized according to the literature procedure\textsuperscript{S1}. The monomer diethyl 4,4\textsuperscript{1}-(1,4-phenylenebis(oxy))dibutanoate (compound 7) was prepared according to reported procedures\textsuperscript{S2}. Solvents were either employed as purchased or dried according to procedures described in the literature. Column chromatography was performed on silica gel (200–300 mesh). All of experiments were performed at room-temperature unless noted otherwise. \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra were recorded on a Bruker AVANCE AV400 (400 MHz and 100 MHz). Signal positions were reported in part per million (ppm) relative to the residual solvent peaks used as an internal standard with the abbreviations s, t, q, and m, denoting singlet, triplet, quartet and multiplet, respectively. The residual \textsuperscript{1}H peak of deuterated solvent appeared at 7.26 ppm in CDCl\textsubscript{3}, at 4.79 ppm in D\textsubscript{2}O and at 2.50 ppm in (CD\textsubscript{3})\textsubscript{2}SO, while the \textsuperscript{13}C peak of CDCl\textsubscript{3} at 77.1 ppm and (CD\textsubscript{3})\textsubscript{2}SO at 39.5 ppm. All coupling constants J are quoted in Hz. Mass spectra were performed on Varian 7.0TFTICR-MS with MAIDI resource and on an Agilent 6520 Q-TOF LC/MS with ESI ionization.

A thermostatted and fully computer-operated isothermal calorimetry (VP-ITC) instrument was used for all the microcalorimetric experiments. The ITC experiments were performed at 25 °C in aqueous solution, giving the association constants (Ka) and the thermodynamic parameters of guests upon complexations. In each run, a solution of guest in a 0.250 mL syringe was sequentially injected with stirring at 300
rpm into a solution of host in the sample cell (1.4227 mL volume). A control experiment to determine the heat of dilution was carried out for each run by performing the same number of injections with the same concentration of guest compound as used in the titration experiments into a same solution without the host compound. The dilution enthalpies determined in control experiments were subtracted from the enthalpies measured in the titration experiments to obtain the net reaction heat. All thermodynamic parameters reported in this work were obtained by using the “one set of binding sites” model. Two titration experiments were independently performed to give the averaged values with reasonable errors.
2. Synthetic procedure

a. The synthesis of compound 8

\[
\begin{align*}
\text{EtO}_2\text{C(H}_2\text{C}_3\text{O}) & \quad \text{O(CH}_2\text{)}_3\text{CO}_2\text{Et} \\
(\text{CH}_2\text{O})_n & \quad \text{BF}_3\text{O(C}_2\text{H}_5)_2 \\
\text{CH}_2\text{ClCH}_2\text{Cl} & \quad \text{EtO}_2\text{C(H}_2\text{C}_3\text{O}) \\
\text{O(CH}_2\text{)}_3\text{CO}_2\text{Et} & \quad \text{EtO}_2\text{C(H}_2\text{C}_3\text{O}) \\
\end{align*}
\]

To a solution of compound 7 (676 mg, 2 mmol) in 1,2-dichloroethane (10 mL) was added paraformaldehyde (186 mg, 6 mmol). Then, 0.25 mL (2 mmol) boron trifluoride diethyletherate BF$_3$·Et$_2$O was added to the solution, and the mixture was stirred at room temperature for 30 min. Then the mixture was quenched with water and the organic layer was washed with water, saturated aqueous NaHCO$_3$ solution and brine, dried over Na$_2$SO$_4$ and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether /ethyl acetate, 4:1 → 2:1) to get a white powder (490 mg, 70 %). $^1$H NMR (400 MHz, CDCl$_3$, 25 °C) $\delta$: 6.79 (s, 10H), 4.10 (q, 20H, $J = 8$ Hz), 3.90 (m, 20H), 3.72 (s, 10H), 2.57 (t, 20H, $J = 8$ Hz), 2.09–2.15 (m, 20H), 1.17(t, 30H, $J = 8$ Hz). $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C) $\delta$: 170.6, 147.2, 125.8, 112.4, 65.1, 57.9, 28.8, 26.8, 22.7, 11.6. MALDI-FTMS for C$_{95}$H$_{130}$O$_{30}$: calcd. [M + Na]$^+$: 1773.8542, found: 1773.8542.

b. The synthesis of compound 9
NaOH (334 mg, 8.34 mmol) was dissolved in the 10 mL deionized water. Then aqueous NaOH solution was added to a solution of compound 8 (731 mg, 0.42 mmol) dissolved in the 10 mL THF : MeOH = 1:1. After stirred for 6 h at room temperature, the reaction mixture was concentrated and the residue was acidified with 1M HCl. The white precipitate was collected by filtration, washed with H$_2$O for several times, dried under vacuum to obtain the compound 9 of corresponding acid. Yield: 580 mg, 94%. $^1$H NMR (400 MHz, (CD$_3$)$_2$SO, 25 °C) $\delta$: 12.18 (s, 10H), 6.83 (s, 10H), 4.07 (s, 10H), 3.83 (s, 10H), 3.67 (s, 10H), 2.51 (s, 20H), 2.02 (s, 20H). $^{13}$C NMR (400 MHz, (CD$_3$)$_2$SO, 25 °C) $\delta$: 174.7, 149.5, 128.3, 114.5, 67.7, 31.1, 29.2, 28.4. MALDI-FTMS for C$_{75}$H$_{90}$O$_{30}$: calcd. [M + Na]$^+$: 1493.5413, found: 1493.5412.

c. The synthesis of compound 10

198 mg (4.96 mmol) NaOH was added to the suspension of 9 (730 mg, 0.496 mmol) in 100 mL deionized water. After stirred overnight, the solvent was removed under reduced pressure to obtain the 10 (4C-WP5A) as white solid. Yield: 814 mg, 97%.
Purity: 93% (see Figures S10). $^1$H NMR (400 MHz, D$_2$O, 25 °C) $\delta$: 6.69 (s, 10H), 3.73 (s, 10H), 3.61 (s, 20H), 2.23 (s, 20H), 1.81 (s, 20H). $^{13}$C NMR (100 MHz, D$_2$O, 25 °C) $\delta$: 182.2, 150.1, 129.4, 116.2, 69.3, 34.1, 29.7, 26.0. ESI-HRMS for C$_{75}$H$_{80}$O$_{30}$: calcd. [M−10Na+8H]$^{2-}$/2: 734.2679, found: 734.2655.

d. The synthesis of compound FC$_4$

\[ \text{FeCHO} + \text{H}_2\text{N-CH(OH)CH}_2\text{OH} \rightarrow \text{a) THF 1.5h} \rightarrow \text{b) NaBH}_4 \]

A mixture of ferrocenecarboxaldehyde (1 mmol, 214.0 mg) and 4-Amino-1-butanol (7 mmol, 623.98 mg) in 20 ml tetrahydrofuran was stirred 1.5 h at room temperature. Then at 0°C added NaBH$_4$ (10mmol, 380mg) to this mixture. After stirred 1h, the solvent was removed under reduced pressure, a mixture of water (50 mL) and ethyl acetate (50 mL) was added to the crude product. After extraction, the organic layer was dried over Na$_2$SO$_4$ and concentrated, then the residue was purified by column chromatography on silica gel (dichloromethane / Methanol, 20:1 → 10:1) to get a yellow solid (172 mg, 60 %). $^1$H NMR (400 MHz, D$_2$O, 25 °C) $\delta$: 4.27 (s, 2H), 4.20 (s, 2H), 4.15 (s, 4H), 3.86 (t, 2H, $J = 9.6$ Hz), 3.47 (s, 2H), 2.38 (t, 2H, $J = 10.8$ Hz), 1.52 (m, 2H), 1.45 (m, 2H). $^{13}$C NMR (100 MHz, D$_2$O, 25 °C) $\delta$: 85.6, 68.5, 68.4, 68.0, 62.6, 49.1, 48.5, 32.6, 28.9. MALDI-FTMS for C$_{15}$H$_{21}$FeNO: calcd. [M]$^+$: 287.0972, found: 287.0970.
3. \(^1\text{H NMR}, \text{^13C NMR} \) spectra and mass spectra of compound 8, 9, 10 and FC\(_4\)

![Figure S1. \(^1\text{H NMR} \) spectrum (400 MHz, CDCl\(_3\), 25 °C) of compound 8.](image)

![Figure S2. \(^{13}\text{C NMR} \) spectrum (100 MHz, CDCl\(_3\), 25 °C) of compound 8.](image)
Figure S3. MALDI- FTMS spectrum of compound 8 (C₉₅H₁₃₀O₃₀). The peak at m/z 1773.8542 is assigned to [M + Na]⁺, calcd.: 1773.8542.

Figure S4. ¹H NMR spectrum (400 MHz, (CD₃)₂SO, 25 °C) of compound 9.
Figure S5. $^{13}$C NMR spectrum (100 MHz, (CD$_3$)$_2$SO, 25 °C) of compound 9.

Figure S6. MALDI-FTMS spectrum of compound 9 (C$_{75}$H$_{90}$O$_{30}$). The peak at $m/z$ 1493.5412 is assigned to [M + Na]$^+$, calcd.: 1493.5413.
Figure S7. $^1$H NMR spectrum (400 MHz, D$_2$O, 25 °C) of 10.

Figure S8. $^{13}$C NMR spectrum (100 MHz, D$_2$O, 25 °C) of 10.
Figure S9. ESI-HRMS spectrum of compound 10 (C$_{75}$H$_{80}$O$_{30}$). The peak at $m/z$ 734.2655 is assigned to [M–10Na + 8H]$^2$/2, calcd.: 734.2679.
Figure S10. Purity determination of the compound 10 by $^1$H NMR spectrum (400 MHz, D$_2$O, 25 °C) with DSS (3-(trimethylsilyl)-1-propanesulfonic acid sodium salt) as internal standard substance. The (*) express the proton peaks of DSS.

Figure S11. $^1$H NMR spectrum (400 MHz, D$_2$O, 25 °C) of FC$_4$. 
Figure S12. $^{13}$C NMR spectrum (100 MHz, CD3Cl, 25 °C) of FC$_4$. The (*) express the carbon peaks of grease.
Figure S13. MALDI-FTMS spectrum of compound $\text{FC}_4$ ($\text{C}_{15}\text{H}_{21}\text{FeNO}$). The peak at $m/z$ 287.0970 is assigned to $[\text{M}]^+$, calcd.: 287.0972.

4. $^1\text{H}$ NMR spectra of $\text{FC}_n^+$ and $\text{FC}_4$ in the absence and presence of 4C-WP5A

Figure S14. $^1\text{H}$ NMR spectra ($\text{D}_2\text{O}$, 293 K, 400 MHz) of (a) 5 mM 4C-WP5A; (b) 5
mM 4C-WP5A + 5 mM FC₆⁺; (c) 5 mM FC₆⁺.

Figure S15. ¹H NMR spectra (D₂O, 293 K, 400 MHz) of (a) 5 mM 4C-WP5A; (b) 5 mM 4C-WP5A + 5 mM FC₄⁺; (c) 5 mM FC₄⁺.
Figure S16. $^1$H NMR spectra (D$_2$O, 293 K, 400 MHz) of (a) 5 mM 4C-WP5A; (b) 5 mM 4C-WP5A + 5 mM FC$_3^+$; (c) 5 mM FC$_3^+$. 
Figure S17. $^1$H NMR spectra (D$_2$O, 293 K, 400 MHz) of (a) 2.5 mM 4C-WP5A; (b) 2.5 mM 4C-WP5A + 5 mM FC$_1^+$; (c) 5 mM FC$_1^+$. 
Figure S18. $^1$H NMR spectra (D$_2$O, 293 K, 400 MHz) of (a) 1 mM 4C-WP5A; (b) 1 mM 4C-WP5A + 1 mM FC$^4$; (c) 1 mM FC$^4$. 
5. Job plot of G with 4C-WP5A by $^1$H NMR titration.

Figure S19. $^1$H NMR spectra ([4C-WP5A] + [FC$_6^+$] = 2.0 mM, D$_2$O, 298 K, 400 MHz) of the chemical shift changes of H-1 on FC$_6^+$ with the molar ratio of FC$_6^+$ is:
(a) individual FC$_6^+$, (b) 0.90, (c) 0.80, (d) 0.70, (e) 0.60, (f) 0.50, (g) 0.40, (h) 0.30, (i) 0.20, (j) 0.10. Insert: Job plot showing the 1:1 stoichiometry of the complex between 4C-WP5A and FC$_6^+$ by $^1$H NMR titration.
Figure S20. $^1$H NMR spectra ([4C-WP5A] + [FC$_4^+$] = 3.2 mM, D$_2$O, 298 K, 400 MHz) of the chemical shift changes of H-1 on FC$_4^+$ with the molar ratio of FC$_4^+$ is: (a) individual FC$_4^+$, (b) 0.90, (c) 0.80, (d) 0.70, (e) 0.60, (f) 0.50, (g) 0.40, (h) 0.30, (i) 0.20, (j) 0.10. Insert: Job plot showing the 1:1 stoichiometry of the complex between 4C-WP5A and FC$_4^+$ by $^1$H NMR titration.
Figure S21. $^1$H NMR spectra ([4C-WP5A] + [FC$_3^+$] = 5 mM, D$_2$O, 298 K, 400 MHz) of the chemical shift changes of Hi on FC$_3^+$ with the molar ratio of FC$_3^+$ is: (a) individual FC$_3^+$, (b) 0.90, (c) 0.80, (d) 0.70, (e) 0.60, (f) 0.50, (g) 0.40, (h) 0.30, (i) 0.20, (j) 0.10. Insert: Job plot showing the 1:1 stoichiometry of the complex between 4C-WP5A and FC$_3^+$ by $^1$H NMR titration.
Figure S22. $^1$H NMR spectra ([4C-WP5A] + [FC$_2^+$] = 4.8 mM, D$_2$O, 298 K, 400 MHz) of the chemical shift changes of H-1 on FC$_2^+$ with the molar ratio of FC$_2^+$ is: (a) individual FC$_2^+$, (b) 0.93, (c) 0.87, (d) 0.80, (e) 0.73, (f) 0.67, (g) 0.60, (h) 0.50, (i) 0.40, (j) 0.30, (k) 0.20, (l) 0.10. Insert: Job plot showing neither 1:2 nor 1:1 stoichiometry of the complex between 4C-WP5A and FC$_2^+$ by $^1$H NMR titration.
Figure S23. $^1$H NMR spectra ([4C-WP5A] + [FC$_1^+$] = 4.8mM, D$_2$O, 298 K, 400 MHz) of the chemical shift changes of Hi on FC$_1^+$ with the molar ratio of FC$_1^+$ is: (a) individual FC$_1^+$, (b) 0.93, (c) 0.87, (d) 0.80, (e) 0.73, (f) 0.67, (h) 0.60, (i) 0.53, (j) 0.47, (k) 0.40, (l) 0.33, (m) 0.20, (n) 0.10. Insert: Job plot showing the 1:2 stoichiometry of the complex between 4C-WP5A and FC$_1^+$ by $^1$H NMR titration.
Figure S24. $^1$H NMR spectra ($[4C-WP5A] + [CF_4] = 1$ mM, D$_2$O, 298 K, 400 MHz) of the chemical shift changes of Ha on 4C-WP5A with the molar ratio of FC$_4$ is: (a) individual 4C-WP5A, (b) 0.1, (c) 0.20, (d) 0.30, (e) 0.40, (f) 0.50, (g) 0.60, (h) 0.70, (i) 0.80, (j) 0.90, (j) 1.0. Insert: Job plot showing the 1:1 stoichiometry of the complex between 4C-WP5A and FC$_4$ by $^1$H NMR titration.

6. Association constants determination for the complexation for G and 4C-WP5A by $^1$H NMR titration

Association constants of 4C-WP5A + FC$_n^+$ involved were measured by $^1$H NMR spectroscopic titrations using a nonlinear curvefitting analysis. The non-linear curvefitting was based on the equation$^{S3}$:
\[ \Delta \delta = (\Delta \delta_{\infty}/[G]_0) (0.5[H] + 0.5([G]_0 + 1/Ka) - (0.5 ([H]^2 + (2[H] (1/Ka - [G]_0)) + (1/Ka + [G]_0)^2)^{0.5})). \]

Where \( \Delta \delta \) is the chemical shift change of proton on G at [H], \( \Delta \delta_{\infty} \) is the chemical shift change of proton on G when the guest is completely complex, \([G]_0 \) is the fixed initial concentration of the guest, and [H] is the varying concentrations of 4C-WP5A.

Association constants of \( 4C-WP5A \bowtie FC_4 \) involved was also measured by \(^1\)H NMR spectroscopic titrations using a nonlinear curvefitting analysis. The non-linear curve-fitting was based on the equation\(^{S3}\):

\[ \Delta \delta = (\Delta \delta_{\infty}/[H]_0) (0.5[G] + 0.5([H]_0 + 1/Ka) - (0.5 ([G]^2 + (2[G] (1/Ka - [H]_0)) + (1/Ka + [H]_0)^2)^{0.5})). \]

Where \( \Delta \delta \) is the chemical shift change of proton on H at [G], \( \Delta \delta_{\infty} \) is the chemical shift change of proton on H when the host is completely complex, \([H]_0 \) is the fixed initial concentration of the \( 4C-WP5A \), and [G] is the varying concentrations of \( FC_4 \).
Figure S25. $^1$H NMR spectra (D$_2$O, 293 K, 400 MHz) of FC$_8^+$ at a concentration of 0.75 mM upon different concentrations of 4C-WP5A: (a) 0.00 mM, (b) 0.15 mM, (c) 0.30 mM, (d) 0.45 mM, (e) 0.60 mM, (f) 0.75 mM, (g) 0.90 mM, (h) 1.20 mM, (i) 1.50 mM, (j) 1.80 mM, (k) 2.10 mM, (l) 2.70 mM. Insert: The chemical shift changes of Hi on FC$_8^+$ upon addition of 4C-WP5A. The red solid line was obtained from the non-linear curve-fitting.
Figure S26. $^1$H NMR spectra (D$_2$O, 293 K, 400 MHz) of at FC$_6^+$ a concentration of 0.75 mM upon different concentrations of 4C-WP5A: (a) 0.00 mM, (b) 0.15 mM, (c) 0.30 mM, (d) 0.45 mM, (e) 0.60 mM, (f) 0.75 mM, (g) 0.90 mM, (h) 1.20 mM, (i) 1.50 mM, (j) 1.80 mM, (k) 2.25 mM. Insert: The chemical shift changes of H-1 on FC$_6^+$ upon addition of 4C-WP5A. The red solid line was obtained from the non-linear curve-fitting.
Figure S27. $^1$H NMR spectra (D$_2$O, 293 K, 400 MHz) of FC$_4^+$ at a concentration of 0.8 mM upon different concentrations of 4C-WP5A: (a) 0.00 mM, (b) 0.16 mM, (c) 0.32 mM, (d) 0.48 mM, (e) 0.64 mM, (f) 0.80 mM, (g) 1.20 mM, (h) 1.60 mM, (i) 2.40 mM, (j) 3.20 mM, (k) 4.00 mM. Insert: The chemical shift changes of H-1 on FC$_4$ upon addition of 4C-WP5A. The red solid line was obtained from the non-linear curve-fitting.
Figure S28. $^1$H NMR spectra (D$_2$O, 293 K, 400 MHz) of FC$_3^+$ at a concentration of 0.8 mM upon different concentrations of 4C-WP5A: (a) 0.00 mM, (b) 0.16 mM, (c) 0.32 mM, (d) 0.48 mM, (e) 0.64 mM, (f) 0.80 mM, (g) 1.20 mM, (h) 1.60 mM, (i) 2.40 mM, (j) 3.20 mM, (k) 4.00 mM, (l) 4.80 mM, (m) 5.60 mM. Insert: The chemical shift changes of H-1 on FC$_3^+$ upon addition of 4C-WP5A. The red solid line was obtained from the non-linear curve-fitting.
Figure S29. $^1$H NMR spectra (D$_2$O, 293 K, 400 MHz) of 4C-WP5A at a concentration of 0.2mM upon different concentrations of FC$_4$: (a) 0.00 mM, (b) 0.04 mM, (c) 0.08 mM, (d) 0.12 mM, (e) 0.16 mM, (f) 0.24 mM, (g) 0.32 mM, (h) 0.40 mM, (i) 0.50 mM, (j) 0.60 mM, (k) 0.70 mM, (l) 0.80 mM, (m) 0.90 Mm, (m) 1.00 mM. Insert: The chemical shift changes of Ha on 4C-WP5A upon addition of FC$_4$. The red solid line was obtained from the non-linear curve-fitting.
Table S1. Association constants (Ka) values and binding stoichiometry for inclusion complexations of G with host 4C-WP5A in deuterium water at 298 K obtained by $^1$H NMR titrations. The binding stoichiometry and the magnitude of Ka values are consistent with the ones measured by ITC.

<table>
<thead>
<tr>
<th>Guest</th>
<th>Stoichiometry (H: G)</th>
<th>Ka</th>
</tr>
</thead>
<tbody>
<tr>
<td>FC$_1^+$</td>
<td>1:2</td>
<td>$-$</td>
</tr>
<tr>
<td>FC$_3^+$</td>
<td>1:1</td>
<td>$(6.70 \pm 0.45) \times 10^3$</td>
</tr>
<tr>
<td>FC$_4^+$</td>
<td>1:1</td>
<td>$(1.89 \pm 0.21) \times 10^4$</td>
</tr>
<tr>
<td>FC$_4$</td>
<td>1:1</td>
<td>$(3.30 \pm 0.35) \times 10^4$</td>
</tr>
<tr>
<td>FC$_6^+$</td>
<td>1:1</td>
<td>$(2.33 \pm 1.06) \times 10^5$</td>
</tr>
<tr>
<td>FC$_8^+$</td>
<td>1:1</td>
<td>$(3.18 \pm 1.41) \times 10^5$</td>
</tr>
</tbody>
</table>

a. For 2:1 complexes 4C-WP5A $\supset$ FC$_1^+$, the Kav values are very small and cannot be calculated accurately.
7. The investigations of the complexation for FC$_{18}^+$ and 4C-WP5A

FC$_{18}^+$ is an amphiphilic surfactant, which is easily dissolved in CH$_2$Cl$_2$ but not well dissolved in water. The $^1$H NMR spectra in CDCl$_3$ and D$_2$O were shown as following:

Figure S30. $^1$H NMR spectrum (400 MHz, CDCl$_3$, 25 °C) of 5mM FC$_{18}^+$. 
Figure S31. $^1$H NMR spectrum (400 MHz, D$_2$O, 25 °C) of 0.4mM (the maximum solubility) FC$_{18}^+$. 

Figure S32. 0.4mM FC$_{18}^+$ (left) and 0.4mM FC$_{18}^+$ + 0.08mM 4C-WP5A (right) in NMR tubes. According to literatures, the critical aggregation concentration of guest would be decreased in the presence of WP5A.$^{54,55}$ Similarly, the obvious turbidity can be observed in our case, so it is difficult to study the binding behavior of 4C-WP5A ⊃ FC$_{18}^+$ by $^1$H NMR experiment.
Figure S33. UV-Vis spectra ([4C-WP5A] + [FC\textsubscript{18}+] = 25\mu M) with the molar ratio of 4C-WP5A is: 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0. The lower transmittance in these UV-Vis spectra indicates that 4C-WP5A and FC\textsubscript{18}+ were still aggregated at these dilute concentrations. So it is difficult to study the binding behavior because the interactions of 4C-WP5A and FC\textsubscript{18}+ in water did not only include the molecular binding but also include the molecular self-assembly.
8. Reference


