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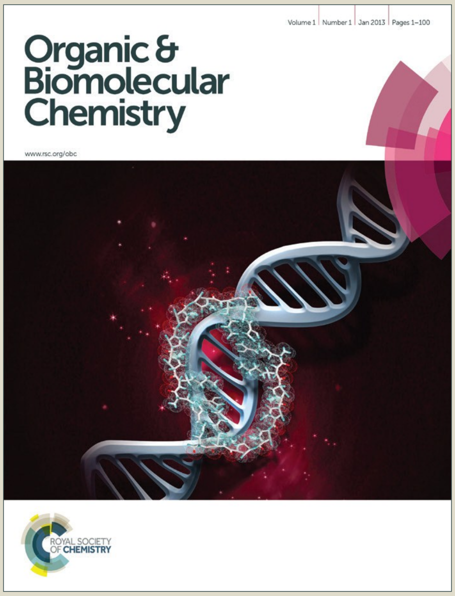

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Molecular Binding Behaviors and Thermodynamics of Ferrocenyl Dimethylaminium Derivatives by Anionic Pillar[5]arene

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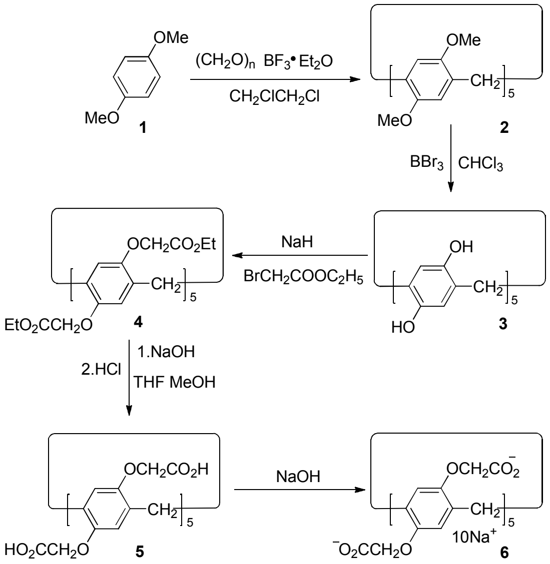
A novel anionic water-soluble pillar[5]arene (4C-WP5A) was synthesized via a convenient synthetic strategy of the direct cyclization of functionalized hydroquinone monomer. The alkyl chains dependent affinities of ferrocenyl aminiums (FC_n^+, n: carbon number) with 4C-WP5A are driven by hydrophobic interactions and desolvations with assisted C–H···π interactions and electrostatic interactions.

As a new class of cyclophanes,[1] pillar[n]arenes have received more attentions[2] in supramolecular chemistry due to their intrinsic characteristics and properties since reported by Nakamoto and Ogoshi.[3] Unlike other meta-bridged[4] and ortho-bridged[5] aromatic rings, pillar[n]arenes are para-bridged aromatic rings by methylene which make their shapes like cylinders rather than cones. Furthermore, pillar[n]arenes could be functionalized including monofunctionalization, difunctionalization, rim-differentiation, perfunctionalization, and phenylene substitution.[6] Benefiting from easy accessibility and versatile functionality of pillar[n]arenes, the first water-soluble pillar[n]arene (**WP[n]A**) with ten carboxylate ions at their rims was reported by Ogoshi in 2010,[6h] and then **WP[n]As** have been developed numerous applications[7] for molecular recognition and sensing, functional materials, biological applications and so on. Among those ionic water-soluble pillar[n]arenes, anionic series have attracted more popularity for their good biocompatibilities in chemical biology and good host–guest properties.[7b,8]

Based on the extensive studies of anionic carboxylatopillar[5]arenes, to find a facile way for preparing **WP[n]A** is vital for further applications. So far, the reported carboxylatopillar[5]arene was synthesized by means of cyclisation of 1,4-dialkoxybenzene precursor then removal of alkyl groups with BBr_3 to obtain pillar[5]arene, then functionalized the phenolic groups on both rims of pillar[5]arene with ethyl bromoacetate following by hydrolysis the ester groups to afford percarboxylatopillar[5]arene (Scheme 1).[6h,9]



Scheme 1. Former synthetic route of carboxylatopillar[5]arene

However, the corrosive and toxic BBr_3 was used for the deprotection of alkyl aryl ethers and the yield of functionalization of pillar[5]arene was relatively low. Meanwhile, the length of columnar conformation of the carboxylate **WP[n]A** was relatively shorter. In order to supplement the defect of the synthesis and extend the length of **WP[n]A**, we propose a convenient synthetic strategy for the preparation of a novel carboxylatopillar[5]arene with extended alkyl chains (Scheme 2). In this synthetic strategy, the direct cyclization of monomer precursor is in satisfactory yield for percarboxylatopillar[5]arene, and the BBr_3 is avoided because of no deprotection process involved in this strategy.

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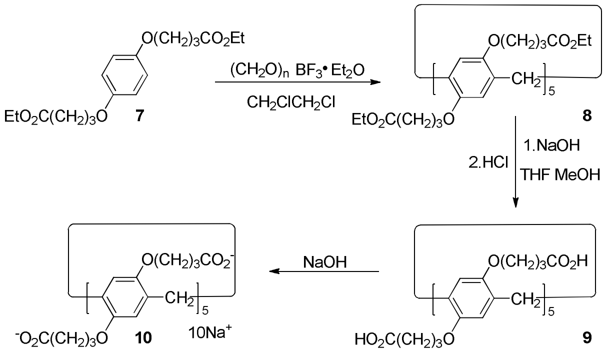
† Electronic Supplementary Information (ESI) available: Characterization of compound 8, 9 and 10 are by ^1H NMR and ^{13}C NMR spectra, high-resolution mass spectrometry. Job plots and association constants (Ka) values are measured by 1H NMR titration, ITC curves, as well as cyclic voltammetric curves. See DOI: 10.1039/x0xx00000x



Scheme 2. Synthesis of novel **4C-WP5A** with extended alkyl chains

As shown in Scheme 2, the synthesis of this **4C-WP5A** commenced from the direct cyclization of the monomer compound 7 with 3 equiv. paraformaldehyde in the presence of 1 equiv. boron trifluoride diethyl etherate ($BF_3{\cdot}Et_2O$) in 1, 2-dichloroethane to afford substituted pillar[5]arene **8** in 70% yield (ESI†), which was very efficient for further conversions. Then hydrolysis of ester groups in compound **8** obtained the corresponding sodium salt of **4C-WP5A**, which was verified by NMR spectroscopy, high-resolution mass spectrometry that could be seen in Figs. S1–S10†.

Despite the researches on the interactions of pillar[5]arene with various alkyl derivatives in organic media,[10,6f] a few effort has been invested in studying the complexation for the host **WP[5]A** and the guests possessed different alkyl chains in water, especially the complexation of the anionic carboxylatopillar[5]arene with different alkyl derivatives.[8a,h,9c,11] Based on our previous work about the β-Cyclodextrin inclusion with ferrocenyl dimethylaminium derivatives (**FC_n^+**, n: carbon number)[12] and the studies of inclusion complex between pillar[6]arenes and ferrocene,[13] we investigated the host–guest complexes of **FC_n^+** and **4C-WP5A** in water by comparative studies using ^{1}H NMR titrations and isothermal titration microcalorimetry (ITC), which would make some contributions to understand the binding behaviors of this novel carboxylatopillar[5]arenes with ferrocenyl aminiums derivatives(Fig. 1).

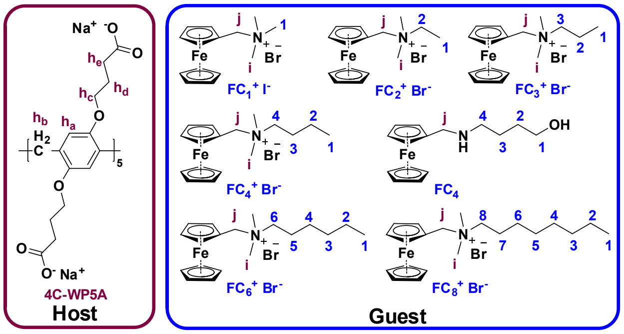


Fig. 1 Chemical structures of novel anionic **4C-WP5A** and guests **FC_n^+**

The host–guest complexation for **FC_8^+** and **4C-WP5A** was firstly investigated by ^{1}H NMR experiment in D_2O at 25°C. As shown in Fig. 2, the methylene proton signals of H-2–H-8 in **FC_8^+** are shifted upfield in the presence of 1 equiv. **4C-WP5A**, which is the consequence of the inclusion-induced shielding effects by the aromatic ring in **4C-WP5A**. Nevertheless, no obvious chemical shift changes is observed for methyl H-1, that indicates the methyl group at the end of alkyl chains thread out of the pillararene's cavity. On the other hand, all of the proton signals on the pillararene are shifted downfield attributes to deshielding effect of the guest **FC_8^+**. Interestingly, the single methylene proton (Hc) peak splits into multiple peaks when **FC_8^+** is in the presence of 1 equiv. **4C-WP5A**, but this phenomenon does not appear for **FC_n^+** of the short alkyl chain, which could be ascribed to obvious immobilization of the alkyl substituents[8a] in **4C-WP5A** after complexation with **FC_8^+**. And the other reason is that the protons of the upper or lower edges are in the different environment aroused by the asymmetry guest threading into the host.[8h,14] To find the binding stoichiometry of **4C-WP5A ⊃ FC_8^+**, the job plot was performed by monitoring the chemical shift of Hi on the **FC_8^+**. As shown in Fig. 3, the inflection point corresponds to the molar ratio of 0.5, which has revealed a 1:1 complexation.

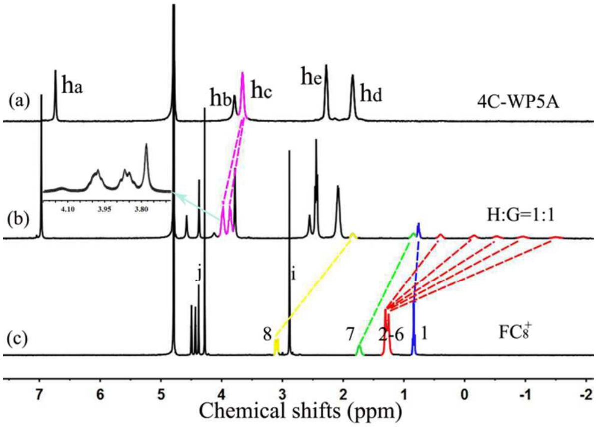


Fig. 2 ^{1}H NMR spectra (D_2O, 293 K, 400 MHz) of (a) 5 mM **4C-WP5A**; (b) 5 mM **4C-WP5A** + 5mM **FC_8^+**. (Insert: the chemical shifts of (b) zoom in from 3.70 ppm to 4.20 ppm.); (c) 5 mM **FC_8^+**.

The same ^{1}H NMR experiments were carried out for the different **FC_n^+** with **4C-WP5A**. Comparison of the chemical shift changes (Δδ) of methyl H-1 on the different **FC_n^+** in the absence / presence of the host **4C-WP5A** could find the different inclusion of **4C-WP5A ⊃ FC_n^+** (see Figs. S14–S17†). As shown in Table 1, for **FC_1^+**, the proton signal is shifted from 3.026 to 2.923. This slight change indicates the methyl group is not in the pillararene's cavity. For **FC_3^+** and **FC_4^+**, the proton signals are shifted from 0.902 to −0.408 and 0.920 to −0.334, respectively, which indicates the methyl group locates in pillararene's cavity. For **FC_6^+**, the signal is shifted from 0.747 to 0.446, the relative weak shielding effect partly because the methyl group threads out of the pillararene's cavity. Meanwhile, the signals of some methylene protons in **FC_n^+** are greatly upfield shifted to $\delta < 0$.

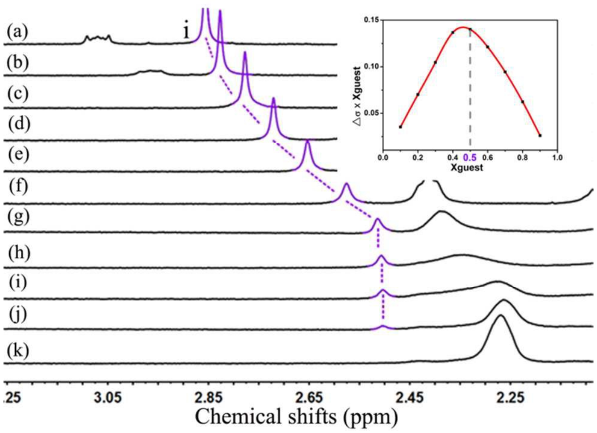


Fig. 3 ^{1}H NMR spectra ([**4C-WP5A**] + [$\mathbf{FC_8^+}$] = 2.0 mM, D$_2$O, 298 K, 400 MHz) of the chemical shift changes of Hi on FC$_8^+$ with the molar ratio of $\mathbf{FC_8^+}$ is: (a) individual $\mathbf{FC_8^+}$, (b) 0.9, (c) 0.8, (d) 0.7, (e) 0.6, (f) 0.5, (g) 0.4, (h) 0.3, (i) 0.2, (j) 0.1, and (k) individual **4C-WP5A**. Insert: Job plot showing the 1:1 stoichiometry of the complex between **4C-WP5A** and $\mathbf{FC_8^+}$ by ^{1}H NMR titration.

Table 1. Chemical shifts (δ) and chemical shift changes (Δδ) of hydrogen H-1 on $\mathbf{FC_n^+}$ before and after complexation with **4C-WP5A** .

Guests	H-1 (*δ*, ppm)	H-1 (Δ*δ*, ppm)
FC$_1^+$	3.026 → 2.923	0.093
FC$_3^+$	0.902 → −0.408	1.310
FC$_4^+$	0.920 → −0.334	1.254
FC$_6^+$	0.747 → 0.446	0.301
FC$_8^+$	0.839 → 0.757	0.082

As shown in the Fig. 4, the 1:1 stoichiometry was confirmed by the investigation of the job plot of $\mathbf{FC_6^+}$, $\mathbf{FC_4^+}$, $\mathbf{FC_3^+}$ with **4C-WP5A**. The binding stoichiometry and association constants for **4C-WP5A** ⊃ $\mathbf{FC_n^+}$ were listed in Table S1†. Nevertheless, the binding stoichiometry of **4C-WP5A** with $\mathbf{FC_1^+}$ was 1:2, but the average association constant for **4C-WP5A** ⊃ FC$_1^+$ was too small to calculate accurately.[10c] Concretely, the Ka values for these host–guest complexes became smaller followed the decreasing length of alkyl chains ($\mathbf{FC_8^+}$ > $\mathbf{FC_6^+}$ > FC$_4^+$ > $\mathbf{FC_3^+}$)[15] (see Figs. S25–S28†). The smaller binding affinity for $\mathbf{FC_1^+}$ and **4C-WP5A** was attributed to the single electrostatic interaction between quaternary ammonium salt in $\mathbf{FC_1^+}$ and carboxyl anions in **4C-WP5A**. The maximum C–H···π interactions were only up to quadruple owning to a fixed aromatic cavity in pillararene.[10c,f] So we rationalized the greater affinity of **4C-WP5A** ⊃ $\mathbf{FC_n^+}$ were mainly driven by the increasing hydrophobic interactions, and the C–H···π interactions and the electrostatic interactions made the minor contribution to the stability of these host-guest complexes. This speculation was supported by the investigation of complexation for **4C-WP5A** with the uncharged $\mathbf{FC_4}$. The ^{1}H NMR experiments showed that the proton signals of the alkyl chains in $\mathbf{FC_4}$ shifted upfield (see Fig. S18†) and the binding stoichiometry of **4C-WP5A** ⊃ $\mathbf{FC_4}$ is 1:1 (see Fig. S24†). The association constants for **4C-WP5A** ⊃ $\mathbf{FC_4}$ is (3.30 ± 0.35) × 10^4 M^{-1}, which is a little lager than that for **4C-WP5A** ⊃ $\mathbf{FC_4^+}$ because of the uncharged $\mathbf{FC_4}$ is more hydrophobic than $\mathbf{FC_4^+}$ (see Fig. S29†).

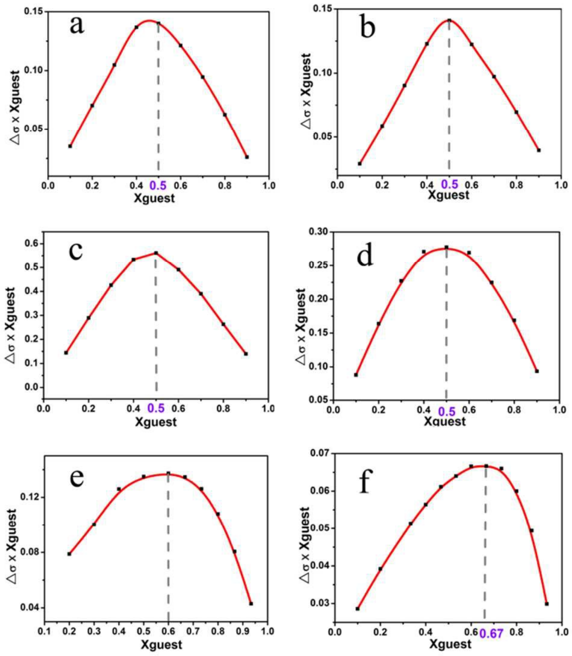


Fig. 4 Job plot for the complexation of (a) $\mathbf{FC_8^+}$, (b) $\mathbf{FC_6^+}$, (c) $\mathbf{FC_4^+}$, (d) $\mathbf{FC_3^+}$, (e) $\mathbf{FC_2^+}$, and (f) $\mathbf{FC_1^+}$, with **4C-WP5A** in D$_2$O.

Considering the Ka determined by ^{1}H NMR titration experiments have relatively big deviations, especially that the Ka values are larger than 10^5 M^{-1},[16] the microcalorimetric titration was used to ensure the quantitative accuracy of the titration data and gave a deep insight in thermodynamics for the host–guest complexation.[17] A typical titration curve is shown in Fig. 5a, the association constant for **4C-WP5A** ⊃ $\mathbf{FC_8^+}$ is up to (6.51 ± 0.29) × 10^5 M^{-1} with a good ''N'' value of 0.932 in the curve fitting by computer simulation using the "one set of binding sites" model and repeats as 1:1 complex formation. The host–guest complexation for **4C-WP5A** and $\mathbf{FC_n^+}$ except $\mathbf{FC_1^+}$ have been verified in the same ways which are shown in Figs. 5a–d. The Ka values and thermodynamic parameters (such as enthalpy change ΔH° and entropy change TΔS°) are listed in Table 2.

Table 2. Association constant (Ka), standard enthalpic (ΔH°), and entropic changes (TΔS°) for inclusion complexations of $\mathbf{FC_n^+}$ with **4C-WP5A** in deionized water at 298 K obtained by ITC.

Guests	Ka (M^{-1})	ΔH°($kJ\cdot mol^{-1}$)	TΔS($kJ\cdot mol^{-1}$)
FC_1^+	—[a]	—[a]	—[a]
FC_3^+	$(7.94 \pm 0.09) \times 10^3$	−8.27 ± 0.05	13.89 ± 0.17
FC_4^+	$(2.54 \pm 0.15) \times 10^4$	−16.27 ± 0.09	8.86 ± 0.23
FC_6^+	$(1.96 \pm 0.03) \times 10^5$	−21.55 ± 0.10	8.66 ± 0.14
FC_8^+	$(6.51 \pm 0.29) \times 10^5$	−26.8 ± 0.21	6.38 ± 0.32

(**a**. For **FC_1^+**, the exotherm of the complexation is too little to measure.)

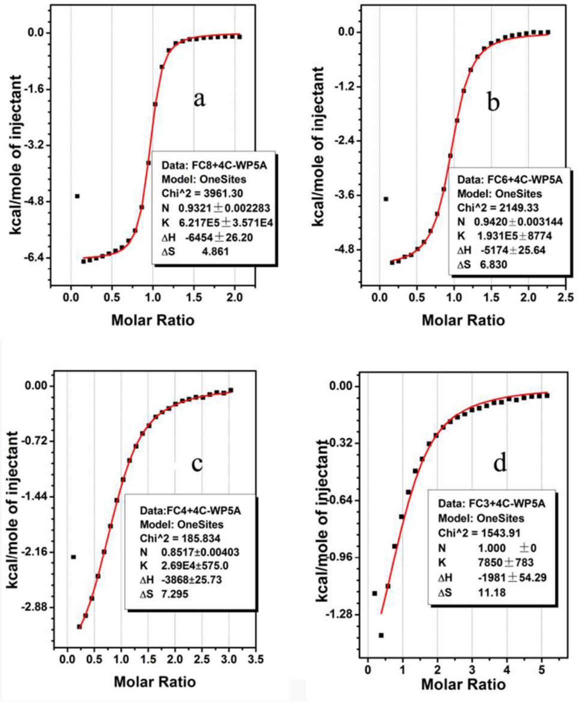


Fig. 5 ITC experiments on complexation of (a) **4C-WP5A** $\supset$ **FC_8^+**, (b) **4C-WP5A** $\supset$ **FC_6^+**, (c) **4C-WP5A** $\supset$ **FC_4^+**, and (d) **4C-WP5A** $\supset$ **FC_3^+**, respectively, in neat water at 25°C.

It is generally accepted that favorable enthalpic changes aroused by noncovalent interactions between host and guest including the vander Waals, ion-dipole, hydrogen bond, π-π, C−H···π and hydrophobic interactions.[18] For our cases, the increasing alkyl chains of **FC_n^+** result in the deeper inclusion by **4C-WP5A**, which could release more water molecules in the cavity of 4C-WP5A.[19] So the favorable alkyl-chains-dependent heat capacity changes are observed in the complexations for **4C-WP5A** $\supset$ **FC_n^+**, as a consequence of the release of those high-energy waters.[20] Interestingly, the $\Delta\Delta H°_{6\text{-}4}$ between the complexations of **FC_6^+** and **FC_4^+** with **4C-WP5A** is $\Delta H°_{4C\text{-}WP5A \supset FC6+} - \Delta H°_{4C\text{-}WP5A \supset FC4+} = -5.28\ kJ\cdot mol^{-1}$, and the $\Delta\Delta H°_{8\text{-}6}$ between the complexations of **FC_8^+** and **FC_6^+** with **4C-WP5A** is $\Delta H°_{4C\text{-}WP5A \supset FC8+} - \Delta H°_{4C\text{-}WP5A \supset FC6+} = -5.32\ kJ\cdot mol^{-1}$. Considering the C−H···π interactions and electrostatic interactions would be same in those complexations, the $\Delta\Delta H° = -5.30 \pm 0.02\ kJ\cdot mol^{-1}$ might be the neat contributions of increasing hydrophobic interactions owing to exclusion of water molecules by the increasing two methylenes in alkyl chains. So we conclude that increasing favorable enthalpic changes of **4C-WP5A** $\supset$ **FC_n^+** with growing n numbers are mainly driven by the more remarkable hydrophobic interactions.

Also as shown in Table 2, the positive entropy changes of **4C-WP5A** $\supset$ **FC_n^+** can be observed which hints the increased perplexity during the complexation process, and the values of TΔS° have followed the sequence of **FC_3^+** > **FC_4^+** > **FC_6^+** > **FC_8^+**. In general, the desolvation results in solvent liberation which makes the positive contributions to the entropy change, and immobilization of conformation makes the negative contributions. So especially for **4C-WP5A** $\supset$ **FC_3^+**, the feature of (|TΔS°| > |ΔH°|) indicates that the desolvation of inclusion for **4C-WP5A** $\supset$ **FC_3^+** makes more contributions than exothermic effect, while the declension of favorable entropic changes (TΔS° > 0) accompanied by the growing length of alkyl chains in **FC_n^+** can be rationalized in terms of the offset desolvation by the restricted conformations of alkyl chains in **4C-WP5A** $\supset$ **FC_n^+**, which is deduced from the aforementioned ^1H NMR experiments.

In conclusion, a novel anionic water-soluble pillar[5]arene (**4C-WP5A**) with extended alkyl chains was conveniently synthesized via the cyclization of functionalized precursor. The relatively high binding affinities of **4C-WP5A** with **FC_n^+** are attributed to the remarkable hydrophobic interactions with minor C−H···π interactions and electrostatic interactions, which is deduced by mutually supported investigations on ^1H NMR titrations and microcalorimetric titrations. Furthermore, the molecular binding affinity in the **4C-WP5A** $\supset$ **FC_8^+** is much greater than that in the **4C-WP5A** $\supset$ **FC_3^+**, which is $Ka_{,4C\text{-}WP5A \supset FC8+} / Ka_{,4C\text{-}WP5A \supset FC3+} = 82.0$. This facile synthesis of **4C-WP5A** and its increasing higher affinities with the growing length of alkyl chain aminiums would pave a way for investigating the supramolecular assemblies of different functions based on **4C-WP5A** in water. Further works on the aggregations of **4C-WP5A** with organic cations are in process in our laboratory.

Acknowledgements

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15 The job plot also revealed that the binding stoichiometry of **4C-WP5A** with **FC**$_2^+$ neither 1:1 nor 1:2 (Fig. S18 in the Supporting Information). We surmised that complexation forming by **4C-WP5A** with **FC**$_2^+$ in the transition from 1:1 to 1:2. Therefore, further discussion of the possible complexation of **4C-WP5A** with **FC**$_2^+$ was ignored in our research. Meanwhile, owing to the poor solubility of **FC**$_n^+$ with longer alkyl chain such as **FC**$_{18}^+$, the interactions of **4C-WP5A** and **FC**$_{18}^+$ in water did not only include the molecular binding but also include the molecular self-assembly. The related discussions can be seen in Figs. S30−S33†.

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

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