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Noncovalent Catch and Release of Carboxylates in Water

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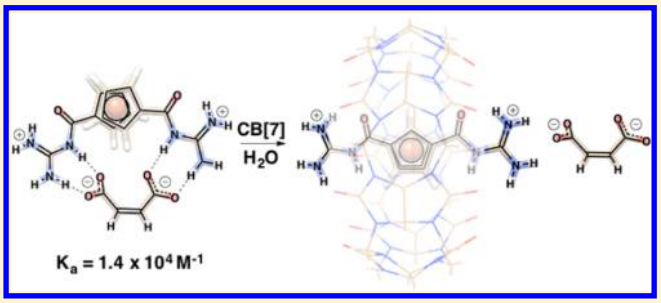
Supporting Information

ABSTRACT: Association constants of a bis-(acetylguanidinium)ferrocene dication to various (di)carboxylates were determined through UV−vis titrations. Association constant values greater than 10^4 M^{-1} were determined for both phthalate and maleate carboxylates to the bis-(acetylguanidinium)ferrocene salt in pure water. Density functional theory computations of the binding enthalpy of the rigid carboxylates for these complexes agree well with the experimentally determined association constants. Catch and release competitive binding experiments were done by NMR for the cation−carboxylate ion-pair complexes with cucurbit[7]uril, and they show dissociation of the ion-pair complex upon addition of cucurbit[7]uril and release of the free (di)carboxylate.



INTRODUCTION

The design of strong host−guest complexes from small molecules in aqueous solutions continues to be a challenge in supramolecular chemistry.[1−9] In particular, there is considerable interest in developing suitable hosts for monocarboxylates and dicarboxylates because there are numerous examples of (di)carboxylates of biological importance within living systems.[6,10−21] Strongly binding, selective receptors to carboxylates with a reporting mechanism could find use as biological sensors.[4,6,16,19,22−29] Additionally, numerous pharmaceuticals contain carboxylate groups,[30−36] and tightly binding receptors could eventually find use in drug delivery[37] by transporting encapsulated carboxylate pharmacophores to the site of a disease.[34−36,38,39]

While there have been numerous studies of receptors that can bind to carboxylates,[13,40−46] there are fewer examples that retain strong complex affinities in water that rely on electrostatic interactions because these interactions are diminished by competitive interactions with solvent.[18,19,47−49] However, rigid molecules bearing a guanidinium moiety have been shown to bind carboxylates even in polar solutions,[17,19,50,51] but associations strong enough to mimic those in biology are far from realized for these particular systems.[52,53] The self-assembly of noncovalent structures in polar solvents, such as water or DMSO, relies on electrostatic interactions between the building blocks.[14,17,54−56] These electrostatic forces, coupled with hydrogen bonding, lead to aggregates in nonpolar solvents;[46,57−63] however, many of these complexes fall apart or have low association constants in polar solvents like water because of competitive interactions with the solvent.[7,43,64−66]

Previous work from our lab indicated that a dicationic pincher bis-(acetylguanidinium)ferrocene salt (**1**) could bind to monocarboxylates in aqueous DMSO.[49] Here, we show that **1** forms tight complexes to dicarboxylates in pure water and that additional electrostatic interactions as well as the size and shape complementarity of the carboxylate to the ferrocene salt dramatically increase the stability of the complex. Through NMR studies, we find that upon addition of cucurbit[7]uril (CB[7], **10**) the ferrocene cation−carboxylate complex dissociates, releasing the carboxylate to the bulk solvent, which demonstrates a noncovalent catch and release process.

RESULTS AND DISCUSSION

The (di)anionic guests used in this study are shown in Figure 1. With one exception, the binding constants for these guests were determined in neat H_2O by UV−vis titrations. We have demonstrated the binding of **1** to monocarboxylates in water,[49] and the binding constants and stoichiometry determination of guest **2**, found via NMR titrations, were previously reported in the literature.[49] The binding of bis-(acetylguanidinium)-ferrocene to acetate **2** in water was used as a comparison for the carboxylates discussed in this article. Guest **2** was found in previous studies to bind **1** as strongly as 850 M^{-1} (K_{a1}) in neat water by NMR titrations.[49] UV−vis titrations were performed to determine the association constants of cation **1** bound to carboxylates **3**−**9**. A 1:1 binding stoichiometry for carboxlates **3**−**9** was determined from Job plots (Figure 2). Representative binding isotherms can be seen in Figure 3, and these were fit to a 1:1 binding equation. (See the Supporting Information for complete binding data and Job plots for each carboxylate discussed.)

Importance of Complementary Structure on Association Strength. The association constants for binding of **1** with (di)carboxylates **2**−**9** can be seen in Table 1. Not

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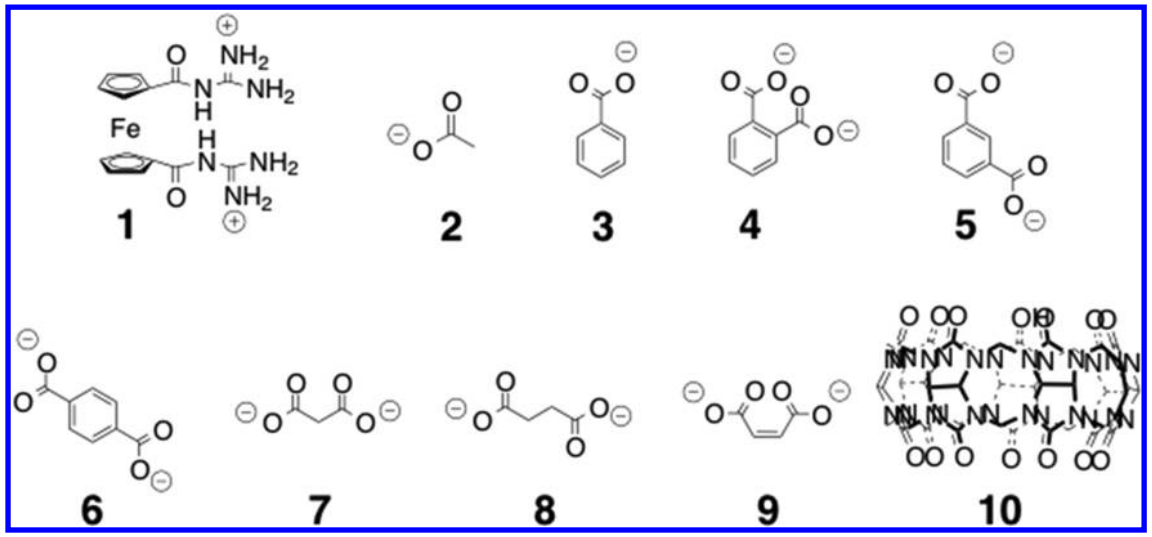

Figure 1. Compounds described in this study.

surprisingly, dicarboxylates bind ferrocene host **1** better than monocarboxylates because of the increased number of electrostatic interactions. Most remarkably, association constants greater than 10^4 M^{-1} in pure water are shown for two of the ferrocene/carboxylate complexes: **1·4** and **1·9**.

Table 1 shows a summary of experimentally determined association constants and the computationally determined changes in binding enthalpy. The binding curve of the ferrocene host with (di)carboxylates as well as the density functional theory (DFT) enthalpy calculations show that the rigid dicarboxylates with the size and shape complementary to the ferrocene host have stronger association constants. For example, **1·5** and **1·6** do not position the carboxylates ideally to allow for binding without strain and, as a result, have diminished association constants. Complexes **1·7** and **1·8** show weaker binding, presumably because the more flexible linker connecting the dicarboxylate groups leads to a greater entropic penalty upon binding. Complementary carboxylates **1·4** and **1·9** that have the ability to exploit the maximum number of electrostatic interactions were found to have the highest associations in water (Figure 4).

Computational Results. With the exception of the binding of **1** with **8**, the computed binding enthalpies of the cation−(di)carboxylate ion pairs (Figure 4) correlate well with experimentally determined binding constants (Figure 5). Note that these computations do not incorporate entropic effects or explicit solvent (a PCM water solvation model was employed), so they are likely only valid for obtaining trends within a class of host−guest complexes such that the errors cancel out (i.e., change in entropy of solvation).[68−70] One exception to this generally good agreement is the binding of **1** to succinate ion **8**. The calculated enthalpy does not correlate well with its experimentally determined association constant. In this case, there is anticipated to be a larger entropic penalty of binding for the conformationally flexible linker than for the other hosts. Given that this entropic penalty is omitted from our computations, it is perhaps not surprising that our computations overestimate the stability of this complex relative to the other complexes.

CATCH AND RELEASE STUDIES

Ferrocene compounds and cucurbit[*n*]urils have been found to have association constants as high as 10^{15} M^{-1} in water.[52,71−81] Therefore, we thought it might be possible to release the carboxylates from their complexes with the bis-(acetylguanidinium)ferrocene cation **1** via addition of CB[7]. It was anticipated that CB[7] would bind ferrocene compound **1** more tightly than any of the carboxylates used in the study. We exploited the strength of the association of the ferrocene compound to CB[7] to allow us to monitor the release of the carboxylate guests via NMR. Figure 6d shows the NMR spectra of ferrocene compound **1** mixed with **10**. The large upfield shift of the ferrocene protons is indicative of binding inside the cavity of **10**.

It was a concern that the part of the guanidine substrates could potentially protrude from the CB[7] portals and thus would be able to bind the carboxylate even when bis-(acetylguanidinium)ferrocene **1** and CB[7] **10** are bound. Hartree−Fock computations (RHF/STO-3G) suggest that part of the guanidine moiety does protrude from the portal cavity (see the Supporting Information). Thus, an NMR titration of the CB[7]−ferrocene complex to maleate **9** was done by NMR in neat D_2O to determine the extent of binding of the guanidinium substrate to the carboxylate **9**. The association constant determined for the interaction between the guanidine substrate and carboxylate **9** was estimated to be 185 M^{-1} (see the Supporting Information for binding details and Cartesian coordinates), which is much weaker than the complexes to the unbound **1**. A possible explanation for this weak association is unfavorable ion−dipole interactions between the carboxylate anion and the carbonyl electrons at the portal of the CB[7].[71]

Ferrocene compound **1** was mixed with 1 equiv of succinate **8**. A downfield shift of the succinate protons was observed, indicating formation of the complex **1·8** (Figure 7). Upon addition of 1 equiv of **10**, an upfield shift of the succinate protons was observed, returning the NMR signal to near the unbound chemical shift, indicating release of the dicarboxylate ion. Additionally, the upfield shift of the ferrocene protons indicates incorporation of this dication within the cavity of CB[7].

Figure 8 shows ferrocene compound **1** bound to 1 equiv of maleate **9**. Similar to the results found with succinate, a

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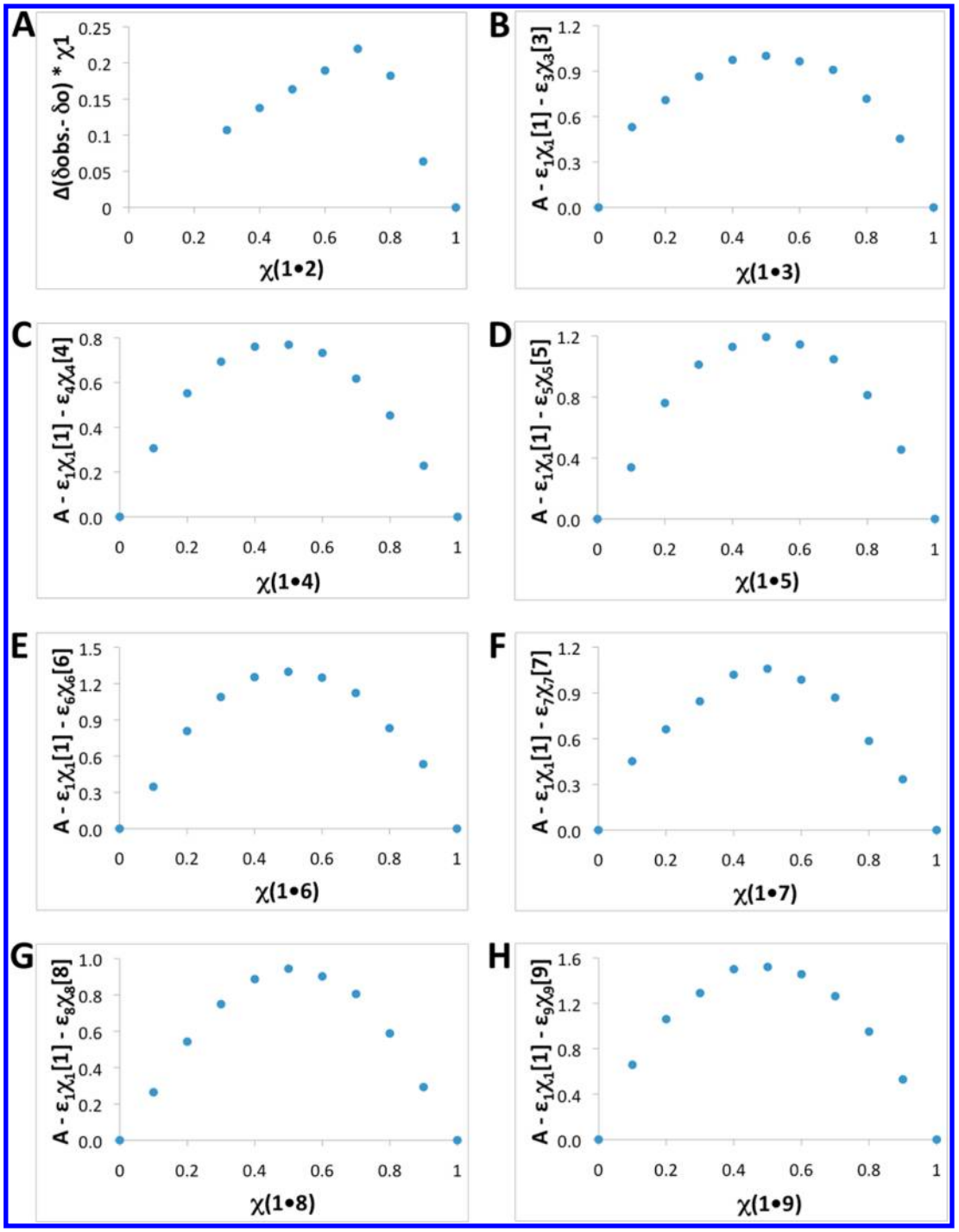

Figure 2. Determination of stoichiometry using Job's Method of Continuous Variation[67] indicating a 1:1 binding stoichiometry for complexes of cation **1** with carboxylates **3**–**9** at concentrations for UV–vis titration experiments. A stoichiometry of 1:2 was determined for the complex of cation **1** with carboxylate **2** (previously reported) at concentrations for NMR titration experiments. Mole fraction in the plots is denoted by the symbol χ.

downfield shift was observed upon binding of **9** to **1**. Upon addition of 1 equiv of CB[7], the maleate protons shift back upfield, nearly restoring its original, unbound signal shift and indicating release of the dicarboxylate.

■ CONCLUSIONS

We have shown the binding of a bis-(acetylguanidinium)-ferrocene cation **1** to seven carboxylates in water by UV–vis titrations. The effects of recruiting an additional carboxylate group play a major role in increasing the association constant. Two of these carboxylates, phthalate **4** and maleate **9**, achieve binding greater than 10^4 M^{-1} in neat water. DFT computations of the binding enthalpy of the rigid carboxylates were in good agreement with the experimentally determined association constants. We have also shown competitive binding experiments by NMR, which show that the carboxylate guest is released to the bulk solvent upon addition of cucurbit[7]uril to the system. This is due to the strong interactions between the ferrocene compound and the hydrophobic pocket of the CB[7]. Although two of the complex association constants

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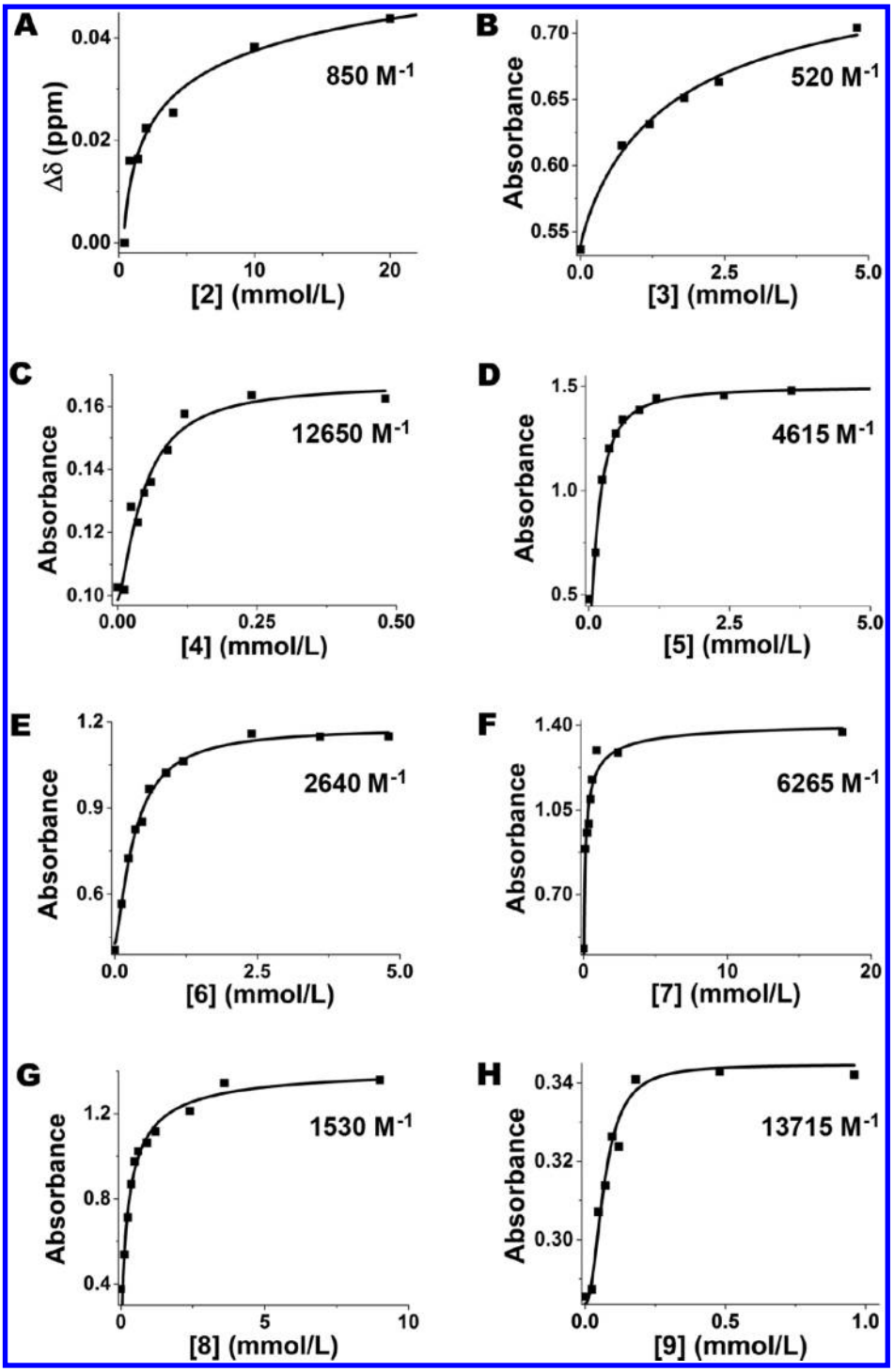

Figure 3. Representative binding isotherms for compound **1** with (di)carboxylate **2** (A), **3** (B), **4** (C), **5** (D), **6** (E), 7 (F), **8** (G), and **9** (H). All absorbances are measured at 425 nm. Data for panel A was previously reported.[49] Each binding titration was repeated three times, and the association constant was reported as the average of the three runs (full data for each binding can be found in the Supporting Information).

reported in this article are greater than 10^4 M^{-1}, their strength is still insufficient for practical biological applications, but these studies may provide the basis for preparing new ligands for carboxylates that also include hydrophobic interactions to maximize the binding constants.

EXPERIMENTAL SECTION

Computational Methods. All of the computations were computed with Gaussian03/09.[82] For all other structures, the lowest-energy molecular geometries of the complexed and non-complexed structures were all optimized using the DFT 6-31G(d) basis set with the hybrid B3LYP functional, which consists of the Becke three-parameter exchange functional[83] with the correlation functional of Lee, Yang, and Parr.[84] All DFT geometries were found to have zero imaginary frequencies, and all of the reported enthalpies contain a correction for the zero-point energy. An effort was made to find the global minima for both the complexed and noncomplexed structures by optimizing numerous input geometries. A PCM water solvation model was employed for the DFT computations.

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Table 1. Binding Constants of 1 with 2−9 in Water and Computed Changes in Binding Enthalpy for Complexes (B3LYP/6-31G(d))

substrate	K_a (M^{-1})[a]	Log(K_a)	Δ enthalpy (kcal/mol)
2	8.5×10^2	2.9	−45.1
3	5.2×10^2	2.7	−40.9
4	1.3×10^4	4.1	−62.0
5	4.6×10^3	3.7	−55.9
6	2.6×10^3	3.4	−45.9
7	6.3×10^3	3.8	−62.4
8	1.5×10^3	3.2	−66.5
9	1.4×10^4	4.1	−64.2

[a]Estimated error in K_a < ±25%.

Experimental Procedures. Bis-(acetylguanidinium)ferrocene **1** was synthesized following a reported literature procedure.[49] Cucurbit[7]uril, D_2O, potassium benzoate, and dicarboxylic acids were purchased and used without further purification. Dicarboxylates were synthesized by adding 2 equiv of potassium hydroxide to the dicarboxylic acid in water. Removal of the water in vacuo afforded the dicarboxylates as white solids. NMR competitive binding experiments for Figures 6 and 7 were performed at a field of 400 MHz. NMR competitive binding experiments for Figure 8 were performed at a field strength of 600 MHz. The catch and release was shown for both maleate **9**, which has an association constant in neat water of 1.4×10^4 M^{-1}, and for succinate **8**, which has an association constant of 1.5×10^3 M^{-1}. These particular carboxylates were chosen for the catch and release study because of their complex solubility, complex strength, and the magnitude of the change in signal shift when bound and unbound. At the concentrations used for typical NMR experiments, all of the cation-carboxylate complexes, with the exception of succinate **8**, precipitate out of solution. Because of this, much less concentrated solutions were made for maleate **9**. Even at these dilute concentrations, precipitation of the complex was observed for malonate **7**. For aromatic carboxylates **3**−**5**, monitoring the shift change by NMR was difficult because of precipitation. Terephthalate **6** catch and release studies were inconclusive because of the small magnitude of change in the proton signal when bound and unbound.

Determination of Association Constants and Complex Stoichiometry. Binding constants were determined through NMR or UV−vis titration experiments. The association constants determined through UV−vis titrations were calculated using the global fit in Pall Thordarson's titration fitting software for Matlab, and the association constant determined through NMR titrations was calculated using the individual fit.[85] Job plots were used to determine the complex stoichiometry (see the Supporting Information). For carboxylates **3**−**9**, a maximum in the Job plot corresponded to a 1:1 stoichiometry. Procedures and data for each NMR or UV−vis titration experiment performed can be found in the Supporting Information. With the exception of the K_a determination of maleate **9** bound to the **1**·**10** complex, all binding constant titrations were run a minimum of three times, with the association constant being the average of the

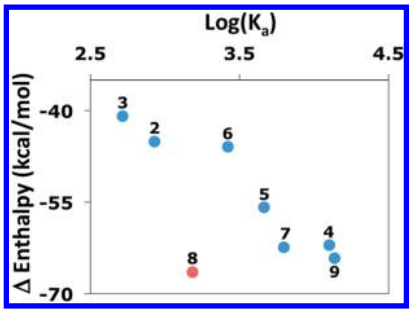

Figure 5. Plot of computed enthalpy change in binding (B3LYP/6-31G(d)) versus Log(K_a).

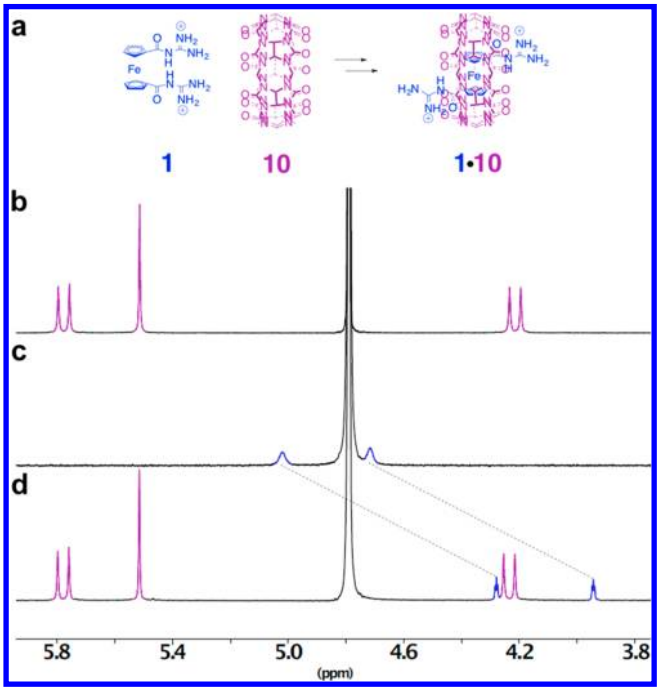

Figure 6. Stacked ^{1}H NMR spectra in D_2O (4.79 ppm) for verification of **1** binding to **10** (**1** is blue and **10** is purple). (a) Proposed scheme of binding, (b) ^{1}H NMR spectra of **10**, (c) spectra of **1**, and (d) complex of **1**·**10**.

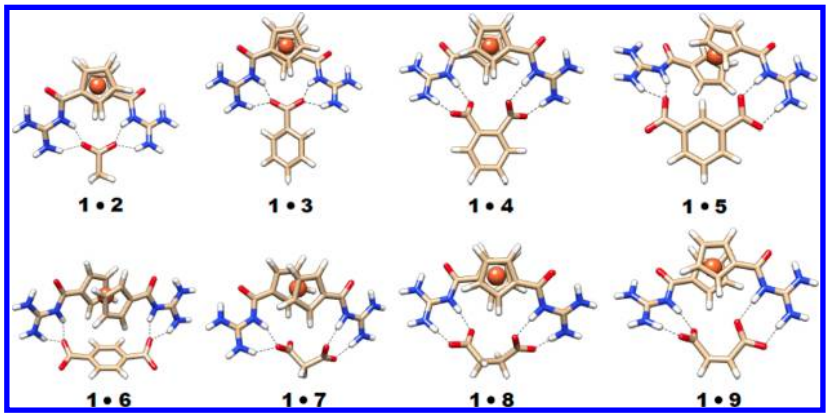

Figure 4. Computed structures of the 1:1 association complexes (B3LYP/6-31G(d)). Lowest minima found are shown.

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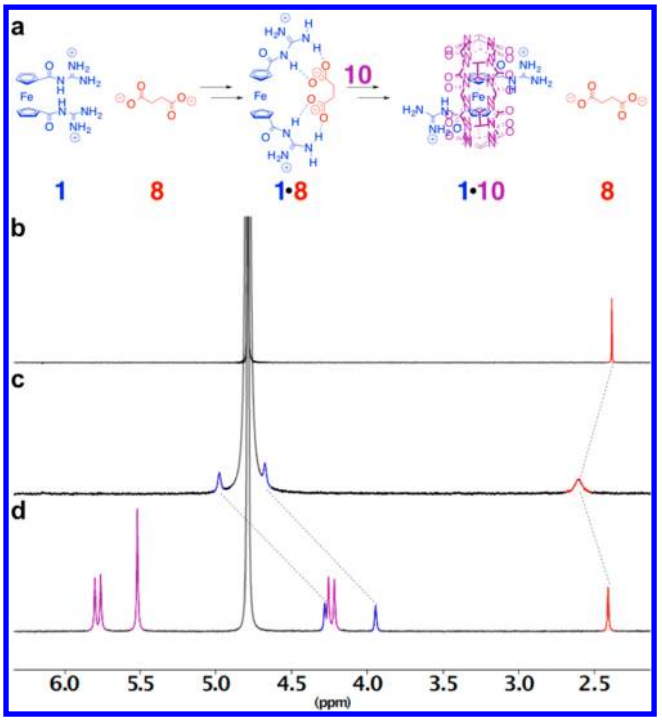

Figure 7. Stacked ^{1}H NMR spectra in D_2O (4.79 ppm) for competitive binding study of **8** (**1** is blue, **8** is red, and **10** is purple). (a) Proposed scheme of binding and release, (b) ^{1}H NMR spectra of **8**, (c) spectra of the complex of **1·8**, and (d) complex of **1·10** showing the dissociation of **8**.

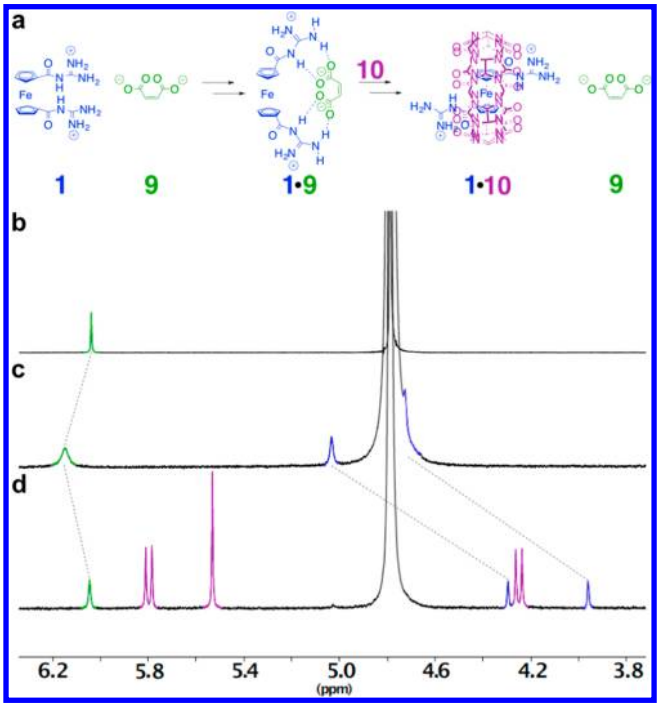

Figure 8. Stacked ^{1}H NMR spectra in D_2O (4.79 ppm) for competitive binding study of **9** (**1** is blue, **9** is green, and **10** is purple). (a) Proposed scheme of binding and release, (b) ^{1}H NMR spectra of **9**, (c) spectra of the complex of **1·9**, and (d) complex of **1·10** showing the dissociation of **9**.

three runs. The K_a's shown in Table 1 represent the average value of all of the fits. Thus, a typical binding constant represents the average value of at least three global fits consisting of four sets of data for each trial. One representative fit for each carboxylate is shown in Figure 2 at an absorbance of 425 nm. (All raw binding data can be found in the Supporting Information.) Error in the K_a is estimated to be <25%.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Raw binding and stoichiometry determination data. Absolute energies and Cartesian coordinates for computed complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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