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Lower rim tetra-substituted and upper rim ferrocene amide calix[4]arenes: synthesis, conformation and anion-binding properties

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Abstract—Calix[4]arenes containing ferrocene amide at the upper rim and methoxy or ethoxycarbonylmethoxy (ethyl ester) groups at the lower rim (**5a**, **5b** and **5c**) have been synthesized. It was found that tetramethoxy **5a** and dimethoxy diethyl ester **5c** were conformationally labile and existed in both cone and partial cone conformation in solution. Anion-binding studies by ^{1}H NMR titration in $CDCl_3$ showed that **5b** bound Cl^- selectively with high stability. Compound **5c** formed complexes with Cl^- and $H_2PO_4^-$ where the former was more stable. The ratio of cone to partial cone conformation in compound **5a** was found to decrease upon binding Cl^- and $H_2PO_4^-$ and in a polar solvent.

Anion recognition and sensing is now an increasingly important research topic in supramolecular chemistry due to the entanglement of various anions in biological and environmental subjects. Chemists employ either electrostatic or hydrogen bonding interactions as binding tools for constructing anion receptors.[1] Beer and co-workers have been pioneers in making metallocene amide receptors for binding anions.[2] These types of compound can also be used as electrochemical sensors. In 1999, Beer et al. reported the anion recognition of upper rim cobaltocenium calix[4]arene receptors and found that they formed complexes with carboxylate anions, dihydrogen phosphate and halide anions to a different extent.[3] Recently, ion-pair recognition has been recognized by supramolecular chemists due to its potential applications in metal ion and anion attraction or metal-controlled anion sensing devices.[4] Beer and colleague have synthesized hetero ditopic ferrocene receptors containing two ethyl ester calix[4]arene units bridged by a ferrocene amide moiety.[5] It was found that the binding ability of this ligand toward halide anions increased in the presence of Na^+.

We have synthesized tripodal aza crown ether calix[4]arenes containing simultaneous cation- and anion-binding sites and found out that the binding ability toward Br^- is enhanced in the presence of K^+.[6] We are interested in constructing ion-pair receptors and sensors using calix[4]arene as building block and attaching the ferrocene amide functional group on the upper rim and ethyl ester groups on the lower rim.

Syntheses of ethyl ester ferrocene amide and methoxy ferrocene amide calix[4]arenes **5a**, **5b** and **5c** are summarized in Scheme 1. Dinitro derivatives of dimethoxy and diethyl ester calix[4]arenes, **1a**[7] and **1b**,[8] respectively were synthesized from a catalytic nitration reaction using $NaNO_3$ and HCl in H_2O as reagent and $La(NO_3)_3$ as catalyst. This reaction is appropriate for producing nitro substituents on the *para* position of phenol rings. The dinitro compounds **2a** and **2b** were obtained in 71 and 88% yields, respectively.[9] Compound **2a** hardly dissolves in CH_2Cl_2, but dissolves very well in DMF. Nucleophilic substitution reactions of **2a** with CH_3I in the presence of K_2CO_3 in DMF and ethyl bromoacetate in the presence of NaH in DMF yielded the tetra-substituted dinitrocalix[4]arenes, **3a**[10] (71%) and **3c**[11] (61%), respectively. Tetraethyl ester dinitrocalix[4]arene, **3b**, was obtained in 61% yield from the reaction of **2b** with ethyl bromoacetate in the presence of Na_2CO_3 in CH_3CN.[8] Reduction of **3a**, **3b** and **3c** with Raney Ni and $N_2H_4{\cdot}H_2O$ resulted in diamino compounds **4a** (98%), **4b** (95%) and **4c** (96%), respectively.[12] Upon coupling with freshly synthesized 1,1-bis(chlorocarbonyl)ferrocene[13] in the presence of NEt_3 in CH_2Cl_2, compounds **4a**, **4b** and **4c** gave the desired ferrocene amide calix[4]arenes **5a** (50%), **5b** (42%) and **5c** (40%), respectively.[14] All spectroscopic data and elemental analysis results support the existence of all synthesized compounds.

Keywords: ferrocene; calix[4]arene; conformation; anion binding.

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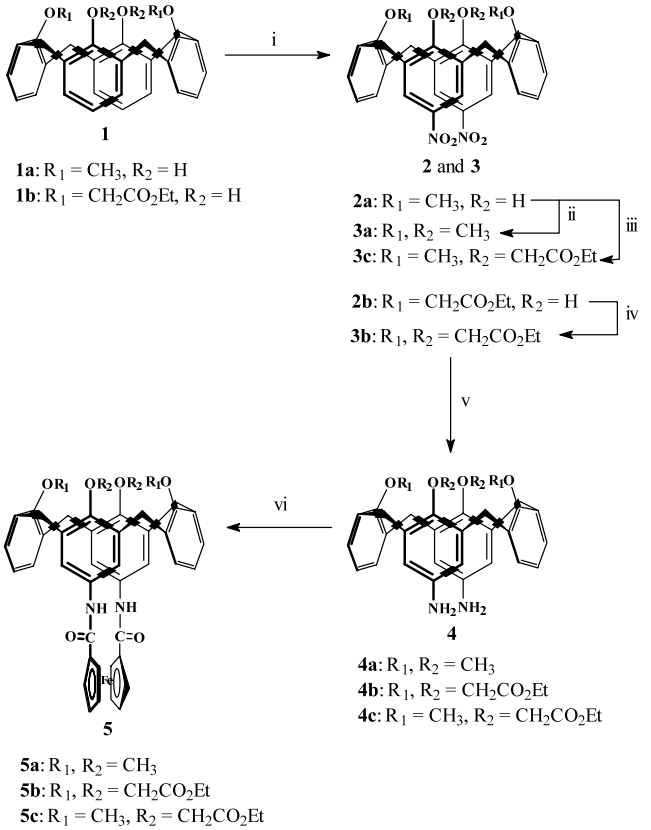

Scheme 1. *Reagents and conditions*: (i) $NaNO_3$, $La(NO_3)_3$, HCl, H_2O in CH_2Cl_2; (ii) CH_3I, K_2CO_3 in DMF; (iii) $BrCH_2CO_2Et$, NaH in DMF; (iv) $BrCH_2CO_2Et$, Na_2CO_3 in CH_3CN; (v) Raney Ni, $N_2H_4{\cdot}H_2O$, EtOAc in CH_3OH; (vi) 1,1-bis(chlorocarbonyl)ferrocene, NEt_3 in CH_2Cl_2.

The structure of calix[4]arene is usually classified into four basic conformations according to the possible 'up' and 'down' arrangement of phenol rings: cone, partial cone, 1,2-alternate and 1,3-alternate. Due to the lack of intramolecular hydrogen bonding among OH groups of the aryl rings, compounds **5a**, **5b** and **5c** should be conformationally labile at room temperature. However, **5b** is found to exist only in cone conformation in solution because four bulky ethyl ester groups at lower rim inhibit the phenyl ring rotation. Although **5a** and **5c** show complicated ^1H and ^{13}C NMR spectra at room temperature suggesting mixed conformations of the calix[4]arene unit, the upper rim connection to ferrocene limits possible conformations to be cone, partial cone and 1,3-alternate. Using NOESY, COSY and HMBC spectroscopy, we have found that **5a** and **5c** exist in both cone and partial cone conformations in an approximately 1:1 ratio in $CDCl_3$. ^1H NMR spectra (500 MHz, acetone-d_6) of **5a** and **5c** and the conformation assignment are shown in Fig. 1.

The methylene bridge protons in cone conformation appear as two sets of doublets at 4.04 and 3.06 ppm for **5a** and at 4.04 and 3.06 ppm for **5c** while partial cone conformation has 4 sets of doublets at 4.29, 3.98, 3.11 and 3.03 ppm for **5a** and at 4.09, 3.82, 3.32 and 3.19 ppm for **5c**. It should be noted that peaks due to methyl protons of the partial cone conformation shift more upfield than those of the cone conformation. This probably stems from the effect of ring currents from aryl units of calix[4]arene when one of the methoxy group points into the calix[4]arene cavity (Fig. 1). In addition, ^{13}C NMR spectra of compounds **5a** and **5c** show characteristic peaks of methylene bridge carbons at ca. 31 ppm for the cone conformation and at ca. 31 ppm and ca. 37 ppm for the partial cone conformation.[15]

We are interested in the binding ability of compounds **5a**, **5b** and **5c** toward anions. Halide anions and dihydrogen phosphate are quite interesting in terms of their relevance to the biological systems. ^1H NMR (200 MHz) titration has thus been employed in complexation studies of **5a**, **5b** and **5c** toward halide anions (Cl^-, Br^- and I^-) and $H_2PO_4^-$ using Bu_4N^+ as countercation in $CDCl_3$.[16] There is no displacement of any proton signals of **5a**, **5b** and **5c** observed upon addition of Br^- and I^-. The result suggests that **5a**, **5b** and **5c** do not form complexes with $Br^-$and I^-. Addition of Cl^- to **5a**, **5b** and **5c** results in the displacement of signals due to -OCN***H***-. Job plot analysis indicates that **5b** and **5c** bind Cl^- in a 1:1 ligand/anion ratio. However, in the presence of $H_2PO_4^-$, only signals due to -OCN***H***- of **5a** and **5c** shift downfield while those of **5b** do not move.

Unfortunately, due to the unconformity of the ratio of cone and partial cone conformation of **5a** during anion titration, vide infra, the stability constant of **5a** toward anions cannot be estimated. Association constants of **5b** and **5c** toward various anions calculated by the program EQNMR[17] are collected in Table 1. The result shows that **5b** binds Cl^- selectively with high stability. This is similar to the tetraethyl ester urea calix[4]arene that can bind Cl^- efficiently in the presence of Na^+.[18] Compound **5c** can bind both Cl^- and $H_2PO_4^-$ in which the former gives a more stable complex. As compared to **5b**, the flexibility of the calix[4]arene unit may reduce the anion-binding ability of **5c**.

Interestingly, the ratio of cone to partial cone conformation of **5a** in $CDCl_3$ changes upon addition of Cl^- and $H_2PO_4^-$. From the integration of signals of cp ring protons, we can estimate the ratio of cone to partial cone conformation as shown in Table 2. The result implies that the concentration of the partial cone conformation of **5a** increases upon increasing the concentration of Cl^- and $H_2PO_4^-$. Another example of conformational change of calix[4]arene from cone to partial cone upon binding anions has recently been found by us.[19] In addition, in a polar solvent such as acetone-d_6, the cone to partial cone ratio of compound **5a** becomes approximately 1:2 signifying the increase of partial cone conformation. This is opposite to that reported by Shinkai where the concentration of the cone conformation of tetramethoxy calix[4]arene was found to increase upon increasing solvent polarity.[20] Our results thus suggest that besides solvent polarity, the conformation ratio of the calix[4]arene unit in **5a** may depend upon the degree of hydrogen bond interactions between its -CONH- groups and solvents and anions.

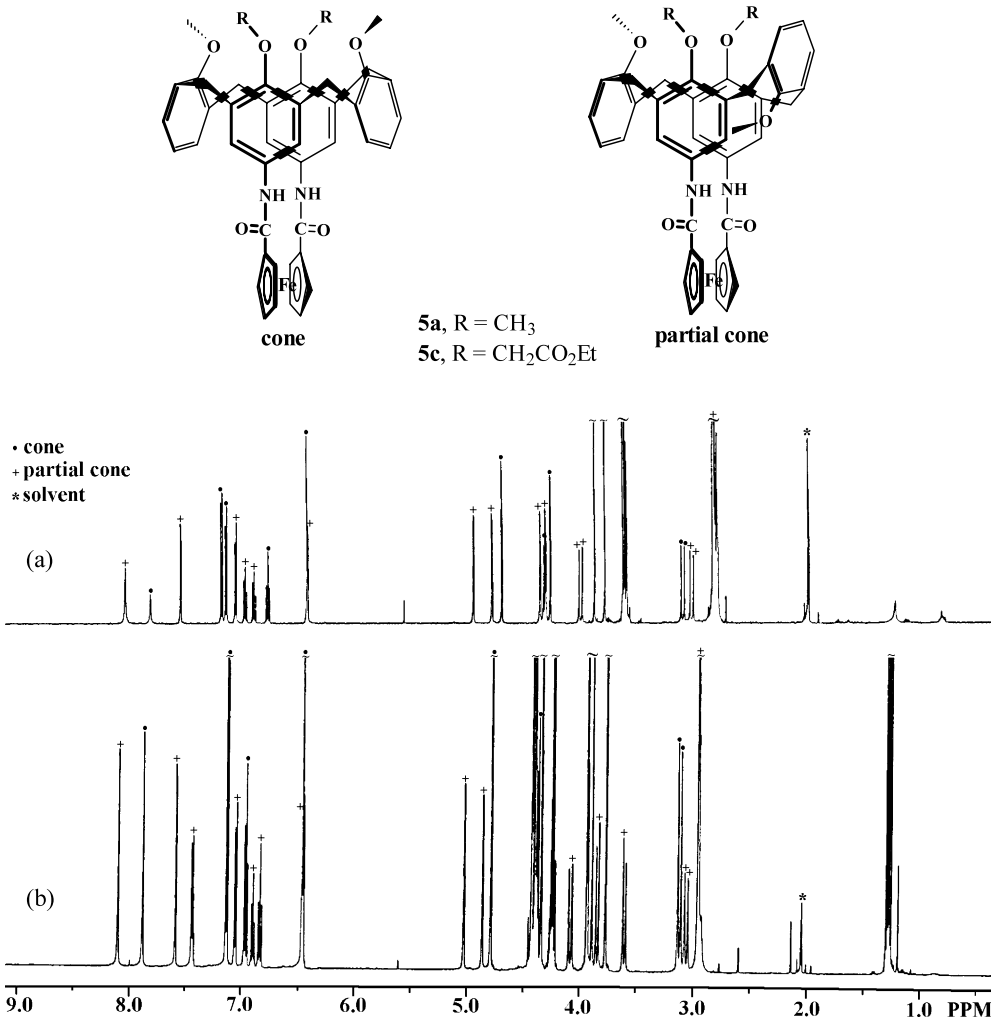

Figure 1. ^{1}H NMR spectra of (a) **5a** and (b) **5c** and their conformation assignment.

Table 1. Association constants of **5a**, **5b** and **5c** with various anions[a]

Anion[b]	K_{assoc} (M^{-1})		
	5a	**5b**	**5c**
Cl^-	[d]	1800.1	513.6
Br^-	[c]	[c]	[c]
I^-	[c]	[c]	[c]
$H_2PO_4^-$	[d]	[c]	244.0

[a] All experiment were carried out at 298 K; errors estimated to be less than 15%.
[b] Using Bu_4N^+ as countercation.
[c] No peak shift of -OCN*H* protons was observed.
[d] K_{assoc} cannot be calculated due to conformational unconformity.

Table 2. Mole fraction (X) of cone (c) and partial cone (pc) conformation when increasing the ratio of **5a** to anions

Anion	X_c/X_{pc} with various **5a**:anion ratios		
	1:0	1:1	1:4
Cl^-	0.452/0.548	0.427/0.573	0.395/0.605
$H_2PO_4^-$	0.452/0.548	0.448/0.552	0.427/0.573

In conclusion, we have synthesized three derivatives of calix[4]arene containing bifunctional substituents at both upper and lower rim (**5a**, **5b** and **5c**), and their preliminary anion-binding and conformational properties have been reported. We are investigating ion-pair binding ability of ligands **5a**, **5b** and **5c**, the detail of their conformational and redox properties. The results will be reported in due course.

Acknowledgements

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8. Rudkevich, D. M.; Verboom, W.; Reinhoudt, D. N. *J. Org. Chem.* **1994**, *59*, 3683. Compound **3b** was synthesized and characterized by the method described in this article.
9. Typical procedure: To a solution of **1** (22.1 mmol) in CH_2Cl_2 (494 mL) was added a solution of $NaNO_3$ (5.64 g, 66.3 mmol) and a catalytic amount of $La(NO_3)_3{\cdot}6H_2O$ in a mixture of H_2O (304 mL) and concentrated HCl (55 mL). The mixture was stirred overnight at room temperature. The color of the mixture changed to yellow. The aqueous layer was then separated and extracted with CH_2Cl_2 (2×250 mL). The organic layer was combined and washed with saturated aqueous NH_4Cl (2×250 mL) and dried over anhydrous Na_2SO_4. The solvent was removed by a rotary evaporator and the product was crystallized by adding hexane. Compound **2a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.93 (s, 2H, -O*H*), 8.04 (s, 4H, *H*Ar-NO_2), 6.94 (d $J=7.2$ Hz, 4H, *m*-*H*Ar-OCH_3), 6.85–6.77 (t $J=7.4$, 2H, *p*-*H*Ar-OCH_3), 4.28 and 3.52 (d each $J=13.3$ Hz, 8H, ArCH_2Ar), 4.02 (s, 6H, -OCH_3). Compound **2b**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.90 (s, 2H, -O*H*), 8.01 (s, 4H, *O*-Ar*H*-NO_2), 6.91 (d $J=8.3$ Hz, 4H, *m*-Ar*H*-OH), 6.84 (t $J=6.4$ Hz, 2H, *p*-Ar*H*-OR), 4.67 (s, 4H, OCH_2CO), 4.45, and 3.49 (d each $J=13.3$ Hz, 8H, ArCH_2Ar), 4.35 (q $J=7.1$ Hz, 4H, OCH_2CH_3), 1.39 (t $J=8.7$ Hz, 6H, -CH_2CH_3).
10. Compound **2a** (0.271 g, 0.500 mmol) in the presence of K_2CO_3 (0.695 g, 5.000 mmol) in DMF (10 mL) was stirred at room temperature for 1 h. CH_3I (0.500 mL, 8.000 mmol) was then added and the mixture was heated at 60°C for 7 days. After the mixture cooled to room temperature, the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (30 mL) and extracted with aqueous NH_4Cl (2×30 mL). The combined organic phase was washed with water and brine (2×30 mL) and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. Upon addition of CH_3OH, a white solid of **3a** precipitated. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.19–6.43 (m, 10H, Ar*H*), 4.37, 4.05, 3.28 and 3.17 (d each $J=13.3$ Hz, 8H, ArCH_2Ar), 3.85–3.72 (m, 12H, -OCH_3). ESI-TOF m/z 571.30 [M+H$^+$] (M, 570.30).
11. Compound **2c** (1.001 g, 1.840 mmol) and NaH (0.222 g, 9.250 mmol) in DMF (20 mL) were stirred at room temperature for 1 h and ethyl bromoacetate (1 mL) was then added. The mixture was stirred and heated at 60°C overnight. The work-up procedure is the same as for compound **3a**. Compound **3c** was obtained as white solid. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.83–7.08 (m, 10H, *H*Ar), 4.45 (s, 4H, -OCH_2CO-), 4.37 (q $J=7.2$ Hz, 4H, -OCH_2CH_3), 3.96–2.99 (m, 14H, -OCH_3 and ArCH_2Ar), 1.30 (t $J=7.1$, 6H, -CH_2CH_3). Anal. calcd for $C_{38}H_{38}N_2O_{12}$: C, 63.86; H, 5.36; N, 3.92. Found: C, 63.85; H, 5.29; N, 3.88.
12. Typical procedure: To a solution of **3** (1.950 mmol) and Raney Ni (2.095 g) in a mixture of ethyl acetate (80 mL) and CH_3OH (40 mL) was added $N_2H_4{\cdot}H_2O$ (4 mL). The mixture was refluxed for 2 h and allowed to cool to room temperature. The solvent was subsequently removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and extracted with several portions of H_2O. The organic layer was separated and dried over anhydrous Na_2SO_4. The solvent was then removed under reduced pressure to give **4** as white solid. In order to avoid the decomposition, **4** was used immediately (without further purification) for synthesizing compound **5**. Compound **4a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.04–6.43 (m br, 6H, Ar*H*), 6.09 (s br, 4H, *o*-Ar*H*-NH_2), 4.26–2.91 (m br, 20H, -OCH_3 and ArCH_2Ar); ES-TOF m/z 511.30 [M+H$^+$] (M, 510.63). Compound **4b**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.69–6.59 (m, 6H, m-Ar*H*-OR), 6.01 (s, 4H, *o*-Ar*H*-NH_2), 4.78 and 3.10 (d each $J=13.1$ Hz, 8H, ArCH_2Ar), 4.70 (s, 4H, ArOCH_2-), 4.61 (s, 4H, NH_2-Ar-OCH_2-), 4.18 (q $J=7.1$ Hz, 8H, -CH_2CH_3), 1.26 (t $J=7.2$ Hz, 12 H, -CH_2CH_3); ESI-TOF m/z 799.13 [M+H$^+$] (M, 798.89). Compound **4c**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.22 (d $J=6.9$ Hz, 4H, *m*-*H*Ar-OCH_3), 6.90 (t $J=7.2$ Hz, 2H, *p*-*H*Ar-OCH_3), 5.69 (s, 4H, *o*-*H*Ar-NH_2), 4.40 (d $J=13.1$ Hz, 4H, ArCH_2Ar, and s, 4H, -CH_2CO-), 4.25 (q $J=7.1$ Hz, 4H, -OCH_2CH_3), 3.96 and 3.46 (s, 6H, -OCH_3), 3.10 (d $J=12.8$ Hz, 4H, ArCH_2Ar), 1.30 (t $J=7.1$ Hz, 6H, -OCH_2CH_3); ESI-TOF m/z 655.70 [M+H$^+$] (M, 654.76); Anal. calcd for $C_{38}H_{42}N_2O_8$: C, 69.71; H, 6.47; N, 4.28 Found: C, 69.71; H, 6.25; N, 4.26.
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14. Typical procedure: Into a two-necked round-bottomed flask, compound **4** (1.54 mmol) and triethylamine in dichloromethane (30 mL) were stirred at room temperature under a nitrogen atmosphere. A solution of 1,1-bis-(chlorocarbonyl)ferrocene (0.6201g, 2.0 mmol) in dichloromethane (30 mL) was transferred into the mixture via cannula. The mixture was stirred continuously at room temperature under a nitrogen atmosphere for 4 h. It was washed with several portions of H_2O and the organic layer was dried with anhydrous $NaSO_4$. The solvent was removed under reduced pressure to afford a dark red residue which was then placed on a SiO_2 chromatography column. Compound **5** was eluted from the column using 10% EtOAc in CH_2Cl_2 as eluant. Compound **5a**: ^{1}H NMR (acetone-d_6, 500 MHz) δ 8.09 (s, 2H, -N*H*- (pc)), 7.86 (s, 2H, -N*H*- (c)), 7.59 and 6.46 (d $J=3.0$ Hz, 4H, -Ar*H*-NH- (pc)), 7.22 (d $J=8.0$ Hz, 4H, *m*-Ar*H* (c)) 7.18 and 7.10 (d $J=7.5$ Hz, 4H, *m*-Ar*H* (pc)), 7.01 (t $J=7.5$ Hz, 2H, *p*-Ar*H* (c)), 6.93 and 6.81 (t $J=7.5$ Hz, 2H, *p*-Ar*H* (pc)), 6.47 (s, 4H, -NH-Ar*H*- (c)), 5.00 and 4.83 (m, 4H, -Cp*H* (pc)), 4.75 (t $J=2.5$ Hz, 4H,

-Cp*H* (c)), 4.41 and 4.36 (m, 4H, *m*-Cp*H* (pc)), 4.36 and 3.14 (d $J=13.5$, 12H, ArCH_2Ar (c and pc)), 4.31 (t $J=2.0$ Hz, 4H, Cp*H* (c)), 4.04 and 3.06 (d each $J=14.0$ Hz, 4H, ArCH_2Ar (pc)), 3.92–3.65 (m, 21H, -OCH_3 (pc and c)), 2.86 (s, 3H, -OCH_3 (pc)); ESI-TOF m/z 749.50 [M+H$^+$] (M, 748.66); Anal. calcd for $C_{44}H_{40}FeN_2O_6\cdot 0.5CH_2Cl_2$: C, 67.56; H, 5.22; N, 3.54 Found: C, 67.72; H, 5.24; N, 3.55. Compound **5b**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.25 (s, 2H, -N*H*-), 7.20 (d $J=6.7$ Hz, 4H, *m*-Ar*H*-OR), 7.09 (t $J=6.4$ Hz, 2H, *p*-Ar*H*OR), 6.43 (s, 4H, *o*-Ar*H*-NH-), 4.87 and 3.22 (d each $J=13.0$ Hz, 8H, ArCH_2Ar), 4.90 (s, 4H, -NH-ArHOCH_2-), 4.77 (s br, 4H, Cp*H*), 4.45 (s, 4H, ArH-OCH_2-), 4.33 (s, br, 4H, Cp*H*), 4.17 (q $J=7.1$ Hz, 8H, -OCH_2CH$_3$), 1.33–1.22 (m, 12H, -OCH$_2$CH_3); ESI-TOF m/z 1037.20 [M+H$^+$] (M, 1036.91); Anal. calcd for $C_{56}H_{56}FeN_2O_{14}$: C, 64.87; H, 5.44; N, 2.70 Found: C, 64.84; H, 5.40; N, 2.63. Compound **5c**: ^{1}H NMR (acetone-d_6, 500 MHz) δ 8.10 (s, 2H, -N*H*- (pc)) and 7.88 (s, 2H, -N*H*- (c)), 7.58 and 6.45 (d $J=2.5$ Hz, 4H, -Ar*H*-NH- (pc)), 7.43 and 7.04 (d $J=7.5$ Hz, 4H, *m*-Ar*H* (pc)), 7.12 (d $J=7.5$ Hz, 4H, *m*-Ar*H* (c)), 6.95 (t $J=7.5$ Hz, 2H, *p*-Ar*H* (c)), 6.89 and 6.82 (t $J=7.5$ Hz, 2H, *p*-Ar*H* (pc)), 6.46 (s, 4H, -NH-Ar*H*- (c)) 5.03 and 4.86 (m, 4H, *o*-Cp*H* (pc)), 4.78 (t $J=2.0$ Hz, 4H, *o*-Cp*H* (c)), 4.39–4.37 (m, 4H, *m*-Cp*H* (pc) and 4H, *m*-Cp*H* (c) and 8H, -OCH_2-CO- (c and pc) and 8H, ArCH_2Ar (c)), 4.26–4.21 (m, 4H, -OCH_2CH$_3$), 4.07 and 3.05 (d $J=14.0$ Hz, 4H, ArCH_2Ar (pc)), 3.83 and 3.59 (d each $J=12.5$ Hz, 4H, ArCH_2Ar (pc)), 3.93–3.76 (m, 9H, -OCH_3 (c and pc)), 2.97 (s, 3H, -OCH_3 (pc)), 1.28 (m, 12H, -CH$_2$CH_3 (c and pc)); ESI-TOF m/z 893.51 [M+H$^+$] (M, 892.79); Anal. calcd for $C_{50}H_{48}FeN_2O_{10}\cdot 0.5CH_2Cl_2$: C, 64.85; H, 5.28; N, 3.00 Found: C, 65.28; H, 5.51; N, 3.19.

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16. Solutions of **5a**, **5b** and **5c** (0.01M) in $CDCl_3$ were prepared. To a solution of a ligand in each NMR tube was added 0.0–4.0 equiv. of 0.25 M tetrabutylammonium salt of an anion. Spectra were recorded every 24 h until the complexation reached the equilibrium. The result of the experiment was a plot of displacement in chemical shift as a function of the amount of added anion. The program EQNMR was then used to analyze the resulting titration curves and calculate stability constant values in M^{-1}. Titration experiments were repeated twice with at least 12 data points for each anion.
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