Tetrahedron Letters 52 (2011) 2914–2917

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Topological and metal ion effects on the anion binding abilities of new heteroditopic receptors derived from *p-tert*-butylcalix[4]arene

Nisachol Nerngchamnong [a], Benjamas Chailap [a], Pannee Leeladee [a], Orawon Chailapakul [a], Chomchai Suksai [b,*], Thawatchai Tuntulani [a,*]

[a] *Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*
[b] *Department of Chemistry and Center for Innovation in Chemistry, Faculty of Science, Burapha University, Chonburi 20131, Thailand*

ARTICLE INFO

Article history:
Received 31 January 2011
Revised 21 March 2011
Accepted 1 April 2011
Available online 9 April 2011

ABSTRACT

Two derivatives of *p-tert*-butylcalix[4]arenes **1** and **2** containing diethyl ester and amidoferrocene units as cation and anion binding sites, respectively, have been synthesized. Both compounds were isomeric with different topology for accommodating ions. ^{1}H NMR spectroscopy, cyclic voltammetry, and square-wave voltammetry were used to study the binding abilities of receptors **1** and **2** toward anions. Both receptors were found to bind Br^- and I^- selectively in the presence of Na^+. The electrochemically oxidized ferrocenium form of *para*-isomer **2** in the free form was found to sense AcO^- selectively, but demonstrated a negative sensing in the presence of Na^+. In contrast, the electrochemically oxidized ferrocenium form of *meta*-isomer **1** was found to enhance sensing of AcO^- and Cl^- in the presence of Na^+.

For anion recognition, attention has been focused on the design and construction of anion receptors and sensors.[1] In general, simple anion receptors bind anions directly using noncovalent interactions, for example, hydrogen bonding and electrostatic interactions. Nevertheless, to gain high selectivity for a specific anion is quite a challenge. Sessler has shown in his recent review that heteroditopic receptors or ion-pair receptors can be designed to demonstrate co-operative binding of ion pairs with different binding modes.[2] Compared to simple anion receptors, ion-pair receptors generally display significantly enhanced affinities for anions as the result of allosteric effects that can strengthen electrostatic interactions between the bound cation and anion.[3]

In 2005, we reported a heteroditopic electrochemical anion sensor consisting of an azacrown ether unit for binding alkali metal cations and an amidoferrocene for hydrogen-bonding with anions.[4] Interestingly, this receptor was found to bind Br^- selectively with high stability in the presence of Na^+. We continued working on the synthesis of ditopic receptors and sensors using calix[4]arene as the building block. Our calix[4]arenes containing amidoferrocene at the wide rim were reported as electrochemical anion receptors and sensors.[5] To achieve heterditopic electrochemical anion receptors and sensors, we have modified *p-tert*-butylcalix[4]arene with ethyl ester and amidoferrocene units on the narrow rim. In this Letter, two isomers of bis-ethyl ester-calix[4]arene-capped amidoferrocene **1** (*meta*-**1**) and **2** (*para*-**2**) have been synthesized. The ethyl ester and amidoferrocene units were chosen as the cation and anion binding functionality, respectively. We expected that the unique topology of compounds **1** and **2** would provide different anion binding abilities. Furthermore, the anion binding abilities can be further affected by cations and electrochemical oxidation of the ferrocene unit.

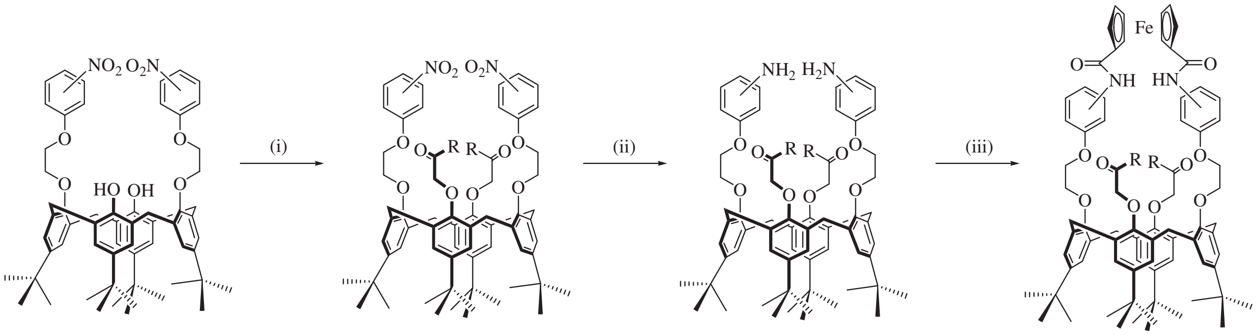
The synthetic route to amidoferrocene calix[4]arenes **1** and **2** is summarized in Scheme 1. Compounds **1a** and **2a** were synthesized by the procedure reported previously.[6] Nucleophilic substitution of bisnitrobenzene calix[4]arene with ethyl chloroacetate in THF afforded bis-esters **1a** and **2a**, which were then converted into the corresponding diamines **1b** and **2b** in almost quantitative yields with $NH_2NH_2{\cdot}H_2O$ using Pd/C as the catalyst. Finally, receptors **1** and **2** were obtained in 14% and 12% yields through treatment of the bisamines with chlorocarbonyl ferrocene[7] in the presence of triethylamine. These new calix[4]arene derivatives were characterized by ^{1}H and ^{13}C NMR spectroscopy, MALDI-TOF mass spectroscopy and elemental analysis.[8,9]

Receptors **1** and **2** exist in the cone conformation, as supported by their NMR spectra, possessing a pair of doublets around 3.24 and 4.43 ppm ($J \approx 13$ Hz) corresponding to the equatorial and the axial protons of the methylene bridging groups (Figs. S1–S4 in Supplementary data). Moreover, the chemical shift of the NH amide protons also appeared in the downfield region at 8.77 and 7.37 ppm for receptors **1** and **2**, respectively. This indicates that intramolecular hydrogen bonding interactions between the two amide groups could occur, as in the solid state structure of an amidoferrocene calix[4]arene reported previously.[10] Interestingly, the amide protons of **1** were shifted to a more downfield region than **2**, implying that intramolecular hydrogen bonding interactions in **1** were stronger than those in **2**, probably due to a shorter

---

* Corresponding authors. Tel.: +66 2 2187643; fax: +66 2 2187598 (T.T.).
E-mail addresses: jomjai@buu.ac.th (C. Suksai), thawatchai.t@chula.ac.th (T. Tuntulani).

0040-4039/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2011.04.014



R = OEt
1a, *meta* (24%)
2a, *para* (72%)

R = OEt
1b *meta*, **2b** *para* (quantitative yields)

R = OEt
1, *meta* (14%)
2, *para* (12%)

Scheme 1. Synthetic route to receptors **1** and **2**. Reagents and conditions: (i) ethyl chloroacetate, NaH, NaI (catalyst), THF, reflux; (ii) Ra/Ni, hydrazine, 40% v/v MeOH in EtOAc, reflux; (iii) chlorocarbonylferrocene, Et_3N, CH_2Cl_2, rt.

hydrogen bonding distance in the *meta*-isomer **1**. The MALDI-TOF mass spectra of the two receptors demonstrated intense peaks due to [Fe($C_{80}H_{92}N_2O_{12}$)] at m/z = 1351.45 [M+Na$^+$].

The ability of receptors **1** and **2** to bind metal salts in solution was studied by ^{1}H NMR spectroscopy in 5% $CD_3CN/CDCl_3$. Upon subjecting receptors **1** and **2** to titration with $NaClO_4$ and KPF_6 salts, two sets of resonances were observed for all the proton signals in the ^{1}H NMR spectra of **1** and **2**, resulting from strong binding interactions with slow complexation/decomplexation kinetics. Near complete conversions into what was presumed to be the bound form were observed upon the addition of ~1.0 equiv of M$^+$, which were consistent with a 1:1 binding mode. Binding constants were determined by direct integrations of the host and complex resonances in the ^{1}H NMR spectra as described by Macomber.[11] Binding constants (*K*) for compounds **1** and **2** with Na$^+$ (K$^+$) were calculated to be 760 (180) and 505 (236) M^{-1}, respectively. According to these binding constants, co-bound Na$^+$ complexes were chosen to study the co-operative binding of receptors **1** and **2** with anions. Moreover, the NH protons of co-bound receptors moved to a more downfield region, indicating that during metal co-ordination the two amide units probably moved into close proximity resulting in stronger intramolecular hydrogen bonding interactions. (Figs. S5 and S6 in Supplementary data). This preorganization upon adding the metal ion would influence the anion binding ability of the receptor.

In the absence of Na$^+$, upon adding aliquots of selected anions to solutions (5% CDCN/$CDCl_3$) of receptors **1** and **2**, small changes in the chemical shifts of the NH amide protons were observed indicating that these protons interacted with the added anions. Determination of the binding constants was performed on the basis of the data of the titration profiles using the EQNMR[12] nonlinear curve fitting program. Titration data analysis using a 1:1 binding model gave the stability constants displayed in Table 1. It should be noted that the unique topological arrangement of the ferrocene amide moieties of each isomer played a crucial role in anion selectivity. Receptor *meta*-**1** exhibited binding ability toward benzoate only. Strong intramolecular hydrogen bonding interactions between the amide protons in the structure of **1** may inhibit the binding of the receptor toward anions. In contrast, the *para*-isomer **2** could bind spherical iodide, Y-shaped acetate and benzoate and also tetrahedral dihydrogenphosphate because intramolecular hydrogen bonding interactions were weaker in *para*-**2** and the anion binding site of *para*-**2** was larger than that of *meta*-**1**. However, low values for the anion binding constants of both compounds suggested that they were poor receptors for anions.

Table 1
Binding constants (*K*) for receptors **1** and **2** with anionic guests in the presence and absence of Na$^+$ in 5% $CD_3CN/CDCl_3$

Receptor	*K* (M^{-1})					
	Cl$^-$	Br$^-$	I$^-$	BzO$^-$	AcO$^-$	$H_2PO_4^-$
1	—[a]	—[a]	—[a]	25	—[a]	—[a]
[**1**·**Na$^+$**]	—[b]	2096	1187	—[b]	—[b]	—[b]
2	—[a]	—[a]	25	66	64	32
[**2**·**Na$^+$**]	—[b]	1119	886	—[b]	—[b]	—[b]

[a] Values are very small and errors are more than 10%.

[b] Values cannot be calculated due to ion-pair formation between co-bound cations and added anions.

To improve the anion binding abilities, ^{1}H NMR titrations were carried out using co-bound Na$^+$ complexes to reveal the cation effect on the binding affinity of the receptors toward anions. A large downfield shift of the NH amide proton signals was observed upon progressive addition of aliquots of bromide and iodide to the co-bound Na$^+$ complex of **1**, [**1**·**Na$^+$**], Figure 1. The association constants of co-bound Na$^+$ with anions were calculated with the expression of a 1:1 binding isotherm and the results are summarized in Table 1. Interestingly, the complex formation constants of [**1**·**Na$^+$**] toward bromide and iodide were higher than [**2**·**Na$^+$**], suggesting that the electrostatic attraction of anions with positively charged [**1**·**Na$^+$**] was stronger than that in [**2**·**Na$^+$**]. This 'positive co-operative binding' of halide anions must be due to electrostatic interactions with Na$^+$ and preorganization of co-bound receptors when metal cations are encapsulated in the pseudo crown ether cavity.

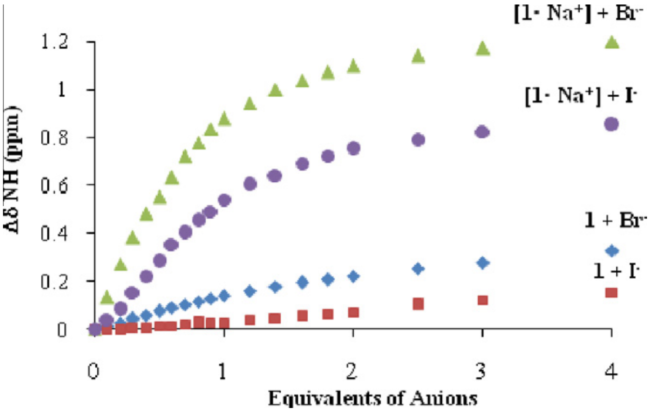


Figure 1. Change in the NH chemical shift (Δδ NH) of receptor **1** and its co-bound cation complex [**1**·**Na$^+$**] as a function of increasing equivalents of tetrabutylammonium (TBA) bromide and iodide in 5% $CD_3CN/CDCl_3$.

Since Na$^+$ can 'switch on' bromide and iodide binding in both receptors *meta*-**1** and *para*-**2**, we explored whether the positive charge of the oxidized forms of **1** and **2** could affect anion binding abilities. Furthermore, it was of interest to study the potential of these two cation complexes as ion-pair electrochemical sensors. The electrochemical properties of the free receptors were investigated by cyclic and square-wave voltammetries. The cyclic voltammograms of **1** and **2** underwent reversible one-electron transfer (Fig. S7 in Supplementary data). It was found that the redox potential of **1** (E_{pa} = 0.493 V, E_{pc} = 0.386 V) was higher than that of **2** (E_{pa} = 0.428 V, E_{pc} = 0.321 V), implying that *meta*-**1** was harder to oxidize than *para*-**2**. This may result from stronger intramolecular hydrogen bonding interactions in *meta*-**1** compared to those in *para*-**2**.

As reported previously, the binding of ferrocene-based receptors with cations generally resulted in an anodic shift of the Fc/Fc$^+$ redox couple.[13] Therefore, upon addition of increasing amounts of Na$^+$ to receptor solutions, an anodic shift of the wave was observed and the electrochemical response still remained reversible (Fig. S8 in Supplementary data), while no change was observed when K$^+$ was added, as expected from the increasing charge-to-size ratio of K$^+$.[14] The quantitative values of the reaction coupling efficiency, or RCEs,[15] for receptors **1** and **2** with Na$^+$ were calculated to be 0.19 and 0.76, respectively. The difference in ΔE of **1** with Na$^+$ (42 mV) was much higher than that of **2** (7 mV). Presumably, Na$^+$ resided in a larger crown ether like cavity of *para*-**2** resulting in a longer distance between the iron center and the bound cation as compared with *meta*-**1**, giving weaker electrostatic repulsions between Fc$^+$ and Na$^+$. This also implied that the preorganization of receptor **1** in the presence of Na$^+$ affected the anion recognizing ability of the receptor.

In the absence of alkali metal cations, interactions of the receptors with anions were investigated electrochemically. Cyclic voltammograms and square-wave voltammograms were recorded after progressively adding aliquots of anion guests to the electrolytic solutions of the receptors and the results are summarized in Table 2. When aliquots of selected anions were added to the receptor solutions, the initially observed Fc/Fc$^+$ redox couple underwent significant negative potential shifts. This cathodic shift could be attributed to hydrogen bonding interactions between the anions and NH protons of the amide groups, which facilitated the oxidation of Fc–Fc$^+$. Unfortunately, the redox process corresponding to iodide oxidation interfered with the Fc/Fc$^+$ redox wave. Therefore, the electrochemical behavior of the receptors upon adding iodide could not be monitored. Furthermore, the limited solubility of the anion adducts of the oxidized forms of **1** and **2** with bromide, benzoate, and dihydrogenphosphate did not allow complete electrochemical studies for these anions.

There were two types of voltammograms observed upon adding anions to the electrolytic solution of receptors **1** and **2**: one-wave and two-wave voltammograms.[16] The former corresponded to a gradual potential shift of the voltammetric curve. The latter demonstrated the emergence of a new voltammetric curve which developed at the expense of the original following progressive addition of anionic guests. Significant one-wave cathodic shifts of the respective Fc/Fc$^+$ redox couples of the receptors were observed with all anionic guest species (Fig. S9 in Supplementary data) except acetate anions. Changes in the Fc/Fc$^+$ redox couples of receptors **1** and **2** turned out to be almost identical, $\Delta E \approx -80$ mV, after adding 4 equiv of Cl$^-$ as shown in Table 2. In the presence of AcO$^-$, two-wave voltammograms were observed for the electrolytic solutions of free receptors **1** and **2**, Figure 2 and Figure S10. Interestingly, a significant perturbation was found in receptor **2** in which an unexpected negative shift of the Fc/Fc$^+$ redox couple was observed up to −180 mV. This phenomenon could be considered as an increase of the equilibrium constant for acetate binding by electrochemically-oxidized receptor **2$^+$**.[17] The binding enhancement factor (BEF)[15] was calculated to be 1100 with a ΔG of −17.36 kJ mol^{-1}. Therefore, the *para*-isomer **2** should be a good electrochemical sensor for acetate.[5b,18] The selective sensing properties of **2** toward acetate mainly stemmed from the fact that the oxidized Fc$^+$ species possessed more acidic NH amide protons to participate in hydrogen bonding with acetate anions as well as electrostatic attractions with the Fc$^+$ moiety.

Table 2
Cathodic shifts (ΔE) of the ferrocene redox couples of receptors **1** and **2** on addition of 4 equiv of Cl$^-$ and AcO^{-a}

Receptor	ΔE^b (mV)	
	Cl$^-$	AcO$^-$
1	−70	−80
[**1**·**Na$^+$**]	−100	−106
2	−80	−180
[**2**·**Na$^+$**]	−90	−120

[a] Experiments were carried out in 40% CH_3CN/CH_2Cl_2 using a Pt working electrode, $Ag/AgNO_3$ as the reference electrode and $TBAPF_6$ as the supporting electrolyte at a scan rate of 100 mV/s.

[b] ΔE is defined as E_{pa} (complex) – E_{pa} (receptor).

In all anion sensing studies, the cyclic voltammograms became quasi-reversible and completely irreversible after adding more than four equivalents of anions. This indicated an electrochemical–chemical (EC) mechanism causing product adsorption.[19] The oxidized forms of the receptors could form adducts with anions giving insoluble ion pairs that strongly adsorbed onto the electrode surface and could not be reduced in the reverse scan. Moreover, the difference in the diffusion coefficients of the reduced forms of the free receptors and their anion adducts resulted in the differences in the current intensity observed in the voltammograms.

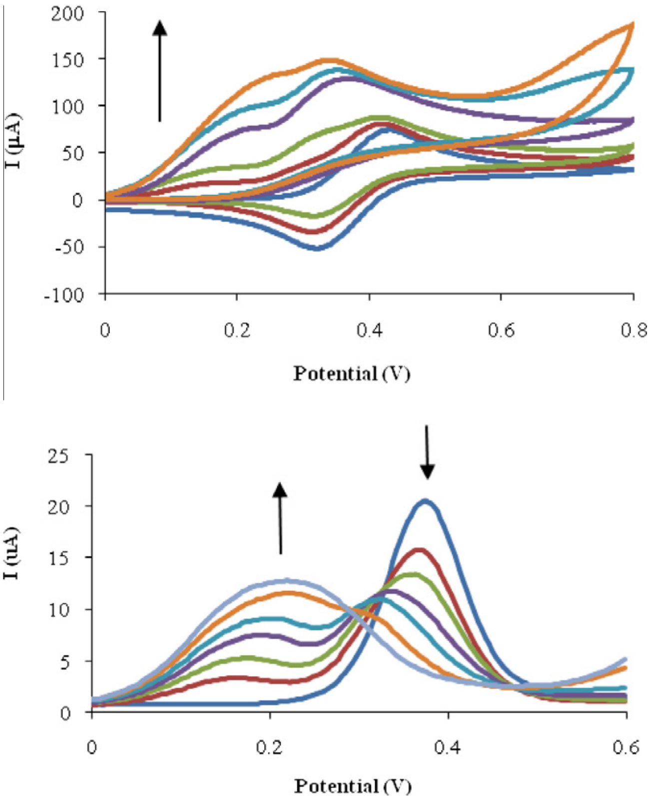


Figure 2. Cyclic voltammograms (top) and square-wave voltammograms (bottom) on titration of *para*-**2** with 0, 0.5, 1.0, 2.0, 3.0 and 4.0 equiv of acetate anions in 40% CH_3CN/CH_2Cl_2 with 0.1 M $TBAPF_6$ at a scan rate of 100 mV/s.

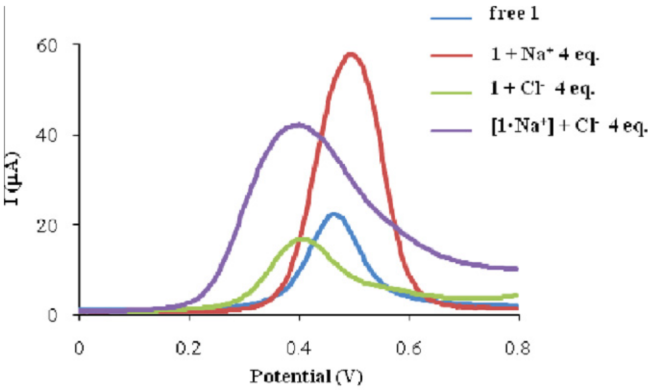


Figure 3. Square-wave voltammograms of free receptor **1** and [**1**·**Na**$^+$] with chloride anions in 40% CH_3CN/CH_2Cl_2 with 0.1 M $TBAPF_6$ at a scan rate of 100 mV/s.

The electrochemical sensing of Na$^+$ co-bound receptors was also investigated by voltammetry. Table 2 shows cathodic shifts of Fc/Fc$^+$ redox couples upon addition of chloride and acetate to the co-bound Na$^+$ complexes of **1** and **2**. It can be clearly seen from Figure 3 and Table 2 that the complex [**1**·**Na**$^+$] gave a larger ΔE than the free form **1** upon addition of Cl$^-$. Therefore, [**1**·**Na**$^+$] provided ‘positive co-operative electrochemical sensing’. We expected that the suitable distance between the two positive ions **1**$^+$ and Na$^+$ with the preorganization of the doubly positive charge [**1**$^+$·**Na**$^+$] and the electrostatic attraction of anions led to a greater shift in the potential of the Fc/Fc$^+$ redox couples. These results indicated that the degree of anion electrochemical sensing increases in the electrochemically-oxidized Na$^+$ co-bound receptor [**1**$^+$·**Na**$^+$] containing double positive charges as compared to reduced form [**1**·**Na**$^+$]. However, the co-bound [**2**·**Na**$^+$] complex demonstrated ‘negative co-operative electrochemical sensing’ for acetate anions. It can be seen that the longer distance between the two positive charges of co-bound Na$^+$ and Fc$^+$, resulting from the topology of the ligand, may decrease the anion association ability.

In conclusion, we have successfully synthesized heteroditopic receptors **1** and **2** derived from *p*-*tert*-butyl-calix[4]arene. Both compounds showed a ‘turn on’ binding with Br$^-$ and I$^-$ employing Na$^+$ as a ‘switch’. We also showed that the topology of compounds **1** and **2** played a crucial role in the electrochemical sensing abilities toward anions. The *meta*-isomer **1** possessed a suitable cationic cavity for Na$^+$ co-ordination, whereas the *para*-isomer **2** provided a larger cationic cavity in which Na$^+$ probably sat deeply in the cavity. Therefore, the incoming anion would interact with the positive charge of the co-bound cation complexes [**1**·**Na**$^+$] and [**2**·**Na**$^+$] to a different extent. Complex [**1**·**Na**$^+$] showed ‘positive co-operative electrochemical sensing’ for chloride and acetate anions, whereas complex [**2**·**Na**$^+$] gave a negative result for acetate. However, the free-form of *para*-isomer **2** was well-suited for electrochemical sensing of acetate anions. Therefore, the topology of the ligands and the presence of metal ions were able to differentiate the anion binding abilities of the heteroditopic receptors **1** and **2**.

Acknowledgment

Financial support from The Thailand Research Fund (RTA5380003) is gratefully acknowledged.

Supplementary data

Supplementary data (additional ^{1}H and ^{13}C NMR spectra of **1** and **2**, and results of electrochemical studies) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.04.014.

References and notes

1. (a) Beer, P. D. *Chem. Commun.* **1996**, 689–696; (b) Suksai, C.; Tuntulani, T. *Chem. Soc. Rev.* **2003**, *32*, 192–202; (c) Martínez-Máñez, R.; Sancenón, F. *Chem. Rev.* **2003**, *103*, 4419–4476.
2. Sessler, J. L.; Kim, S. K. *Chem. Soc. Rev.* **2010**, *39*, 3784–3809.
3. (a) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486–516; (b) Gale, P. A. *Coord. Chem. Rev.* **2003**, *240*, 191–221; (c) Beer, P. D.; Hayes, E. J. *Coord. Chem. Rev.* **2003**, *240*, 167–189; (d) Mahoney, J. M.; Nawaratna, G. U.; Beatty, A. M.; Duggan, P. J.; Smith, B. D. *Inorg. Chem.* **2004**, *43*, 5902–5907; (e) Gale, P. A.; García-Garrido, S. E.; Garric, J. *Chem. Soc. Rev.* **2008**, *37*, 151–190; (f) Lankshear, M. D.; Dudley, I. M.; Chan, K. M.; Cowley, A. R.; Santos, S. M.; Fejix, V.; Beer, P. D. *Chem. Eur. J.* **2008**, *14*, 2248–2263; (g) Kim, S. K.; Sessler, J. L.; Gross, D. E.; Lee, C.-H.; Kim, J. S.; Lynch, V. M.; Delmau, L. H.; Hay, B. P. *J. Am. Chem. Soc.* **2010**, *132*, 5827–5836.
4. Suksai, C.; Leeladee, P.; Jainuknan, D.; Tuntulani, T.; Muangsin, N.; Chailapakul, O.; Kongsaeree, P.; Pakavatchai, C. *Tetrahedron Lett.* **2005**, *46*, 2765–2769.
5. (a) Tomapatanaget, B.; Tuntulani, T. *Tetrahedron Lett.* **2001**, *42*, 8105–8109; (b) Tomapatanaget, B.; Tuntulani, T.; Chailapakul, O. *Org. Lett.* **2003**, *5*, 1539–1542.
6. Sukwattanasinitt, M.; Rojanathanes, R.; Tuntulani, T.; Sritana-Anant, Y.; Ruangpornvisuti, V. *Tetrahedron Lett.* **2001**, *42*, 5291–5293.
7. Knobloch, F. W.; Rauscher, W. H. *J. Polym. Sci.* **1961**, *54*, 651–656.
8. *Meta-isomer* **1**: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ, 8.77 (t, 2H, J = 6.4 Hz, ArNH), 7.72 (s, 2H, Ar*H*), 7.28 (s, 2H, ArH), 7.18 (t, 2H, J = 8.0 Hz, ArH), 7.08 (s, 4H, ArH), 6.63 (d, 2H, J = 8.0 Hz, ArH), 6.48 (s, 4H ArH), 4.64 (s, 8H, $-OCH_2CH_2O-$), 4.68 (s, 4H, FcH), 4.47 (s, 4H FcH), 4.37 (s, 4H, $-OCH_2COOR$), 3.96 (q, 4H, J = 7.2 Hz, CH_3CH_2O-), 4.53 (d, 4H, J = 12.8 Hz, $ArCH_2Ar$), 3.14 (d, 4H, J = 12.8 Hz, $ArCH_2Ar$), 1.30 (s, 18H, *tert*-butyl), 1.09 (t, 6H, J = 6.8 Hz, CH_3CH_2OCO-), 0.81 (s, 18H, *tert*-butyl); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.5, 170.0, 169.0, 159.8, 155.5, 152.2, 144.8, 139.7, 135.1, 131.7, 129.5, 125.6, 124.9, 112.3, 111.6, 105.3, 79.0, 73.2, 71.9, 71.0, 68.8, 60.6, 51.2, 33.8, 31.1, 13.9. Elemental analysis: Anal. Calcd for $C_{80}H_{92}FeO_{12}N_2$: C, 72.26; H, 6.98; N, 2.11. Found: C, 72.25; H, 6.94; N, 2.14; ESI *m*/*z*: calcd 1329.46; found 1351.187 [M+Na$^+$].
9. *Para-isomer* **2**: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.37 (s, 2H, ArNH), 7.21 (d, 4H, J = 8.8 Hz, ArH), 6.95 (s, 4H, ArH), 6.68 (s, 4H, ArH), 6.75 (d, 4H, J = 8.8 Hz, ArH), 4.89 (s, 4H, FcH), 4.69 (s, 4H, FcH), 4.46 (s, 4H, $-OCH_2COOR$), 4.39 (s, 8H, $-OCH_2CH_2O-$), 4.20 (q, 4H, J = 7.1 Hz, CH_3CH_2O-), 4.65 (d, 4H, J = 12.8 Hz, $ArCH_2Ar$), 3.24 (d, 4H, J = 12.8 Hz, $ArCH_2Ar$), 1.28 (t, 6H, J = 7.2 Hz, CH_3CH_2OCO-), 1.19 (s, 18H, *tert*-buyl), 0.99 (s, 18H, *tert*-buyl); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 170.2, 166.8, 155.6, 154.1, 152.3, 145.1, 134.3, 132.7, 130.7, 125.1, 122.0, 114.0, 79.2, 71.3, 69.7, 60.9, 34.0, 31.3, 14.4. Elemental analysis: Anal. Calcd for $C_{80}H_{92}FeO_{12}N_2$: C, 72.26; H, 6.98; N, 2.11. Found: C, 72.24; H, 6.97; N, 2.15; ESI *m*/*z*: calcd 1329.46; found 1351.452 [M+Na$^+$].
10. Suksai, C.; Leeladee, P.; Jennings, C.; Tuntulani, T.; Kongsaeree, P. *J. Chem. Crystallogr.* **2008**, *38*, 363–368.
11. Macomber, R. S. *J. Chem. Educ.* **1992**, *69*, 375–378.
12. Hynes, M. J. *J. Chem. Soc., Dalton Trans.* **1993**, 311–312.
13. Togni, A.; Hayashi, T. *Ferrocene*; VCH: New York, 1995.
14. (a) Medina, J. C.; Goodnow, T. T.; Bott, S.; Atwood, J. L.; Kaifer, A. E.; Gokel, G. W. *J. Chem. Soc., Chem. Commun.* **1991**, 290–292; (b) Hall, C. D.; Chu, S. Y. F. *J. Organomet. Chem.* **1995**, *498*, 221–228.
15. Beer, P. D.; Gale, P. A.; Chen, G. Z. *J. Chem. Soc., Dalton Trans.* **1999**, 1897–1910.
16. Miller, S. R.; Gustowski, D. A.; Chen, Z. H.; Gokel, G. W.; Echegoyen, L.; Kaifer, A. E. *Anal. Chem.* **1988**, *60*, 2021–2024.
17. Bourgel, C.; Boyd, A. S. F.; Cooks, G.; de Cremires, H. A.; Dulairoir, F. M. A.; Rotello, V. M. *Chem. Commun.* **2001**, 1954–1955.
18. Beer, P. D.; Hesek, D.; Nam, K. C. *Organometallics* **1999**, *18*, 3933–3943.
19. (a) Wopshall, R. H.; Shain, I. *Anal. Chem.* **1967**, *39*, 1514–1527; (b) Chen, Z.; Graydon, A. R.; Beer, P. D. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 97–102; (c) Beer, P. D.; Graydon, A. R.; Johnson, A. O. M.; Smith, D. K. *Inorg. Chem.* **1997**, *36*, 2112–2117; (d) Stone, D. L.; Smith, D. K. *Polyhedron* **2003**, *22*, 763–768.