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Metalloporphyrin-Capped Calix[4]pyrroles: Heteroditopic Receptor Models for Anion Recognition and Ligand Fixation

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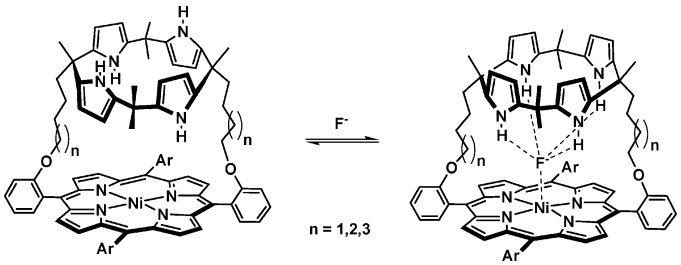

Diametrically strapped calix[4]pyrrole−metalloporphyrin conjugates, potential hosts for anionic guests, have been synthesized and characterized. The syntheses rely on the acid-catalyzed condensation of two dipyrromethane bearing Ni(II) porphyrins with acetone. An ^{1}H NMR spectroscopic titration experiment indicated that the resulting receptors selectively trapped fluoride anions in organic media but not other, larger halide anions. The experimental results from titration and Job plots indicated that the bound fluoride anion must reside inside the cavity. The current systems provide a well-defined illustration of how size-selective anion receptors may be synthesized by incorporating recognition functions, such as Lewis acidity, hydrogen bonding, and encapsulating moieties into established recognition motifs, calix[4]pyrrole in the present instance.

Introduction

The design and synthesis of neutrally charged anion receptors that possess high affinities and inherent selectivity for a variety of targeted anions represents a well-appreciated challenge issue in supramolecular chemistry. The interests in this problem reflects in part the significant role played by anions in many biological systems.[1−3] Unfortunately, anion recognition, as a general rule, has been found to be more difficult to achieve than cation recognition.[3] One of the more appealing neutral anion receptors prepared to date is calix[4]pyrrole. This species is easily synthesized via the acid-catalyzed condensation of pyrrole and acetone and is known to bind various anions in organic media. Since the anion recognition characteristics of calix[4]pyrroles were first reported by Sessler et al. in 1996,[4] various modifications have been put forward in an effort to fine-tune the anion binding characteristics of parent fascinating systems.[4−10] As a result of these efforts, some enhancements in inherent anion binding affinities and selectivities have been achieved.[11−17]

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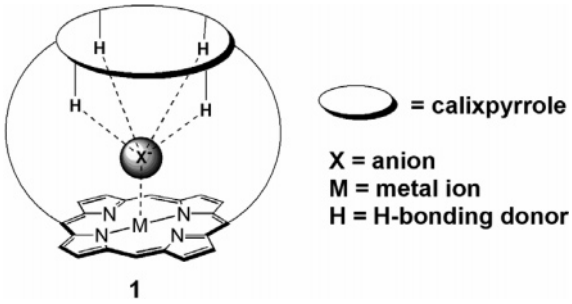
Noncovalent interactions (electrostatic, hydrophobic, or coordinative) serve as the driving force for the complexation and recognition of anions in both natural and synthetic anion recognition motifs. Most of the synthetic anion receptors designed so far have generally relied on only a single interaction. Indeed, receptor systems that recognize anions through combined noncovalent interactions are rare. On the other hand, systems that recognize anions by combined interactions such as hydrogen bonding, donor−acceptor interactions, and hydrophobic effects would be ideal in order to achieve higher sensitivity and selectivity.

Another attractive approach involves ion-pair recognition, wherein anions and cations are bound simultaneously. This approach is attractive for salt extraction. However, it is also appealing since the design and synthesis of receptors bearing both hydrogen bonding and coordination sites might lead to anion recognition systems with enhanced anion selectivities. Recently we reported[18] the synthesis and anion binding studies of a heteroditopic receptor based on this motif, in which a calix[4]pyrrole unit was doubly strapped to a Ni(II)−porphyrin in a diametrical fashion. In this report, we present a detailed account of the design and synthesis of ditopic anion receptors bearing both coordination sites and hydrogen-bonding sites. Our design relies on a combination of axial ligand binding to a metalloporphyrin and hydrogen-bonding interactions derived from calix[4]pyrrole. In systems of this type, which can be constructed by multiply bridging the two recognition parts, the extent of cooperation and hence the binding affinity can be controlled by modulating the separation distance and geometry.

Results and Discussion

We have for some time been interested in designing preorganized receptor systems for anion binding. In the context of this general goal, we considered that a preorganized system based on the combination of calix[4]pyrrole and metalloporphyrin would be of particular interest since simple changes in structure could be used to modulate the anion binding properties. Here, we report the synthesis and complete characterizations of ditopic receptors of general structure **1** and their preliminary binding properties. These systems are also of potential interest since they could be good models for various natural metalloporphyrin-catalyzed reactions including monooxygenation and electron-transfer reaction.



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System 1 contains both a calix[4]pyrrole and a metalloporphyrin. This construction provides for several unique features including ancillary hydrogen bonding donors and Lewis acidic metal center for anion coordination. The net result is a system designed in such a way that the anion can be coordinated as axial ligand while being tightly trapped inside the cavity by up to four hydrogen bond interactions provided by the calix[4]pyrrole moiety. The trapped anion may be strongly held inside the cavity by the metal ion and hydrogen-bond donor regardless of any intrinsic changes of oxidation state of the metal ion. Because of these cooperative effects and the potential ability to change the oxidation state of coordinated metal center, these system also could be a good model for studying the mechanism of metalloporphyrin-catalyzed reactions, such as monooxygenation and expoxidation reactions, provided the proper anion is placed inside the cavity. In the present instance, the simple alkyl groups were chosen as the connecting elements due to their ease of manipulation. In addition, it was thought that these straps would assist in the isolation of the binding site from the surrounding solvent, helping to impose size-based anion selectivity.

The synthesis of the desired receptors is shown in Scheme 1. Aldehydes **2a** and **2b** were reacted with the appropriate bromo-ketones ($n = 1-3$) to afford **3a**−**f** in high yield. Then, aldehydes **3a**−**f** were condensed with mesityldipyrromethane to afford the 5,15-dialkoxy-substituted free-base porphyrins **4a**−**f.** The two atropisomers of the free-base porphyrin **4a**−**c** could be separated on TLC and analytically pure compounds were obtained by preparative TLC. The trans isomer has a higher R_f value (reflecting an internal cancellation of dipole moment) than the cis isomer. In the case of **4b** and **4c**, the cis isomer showed three different aromatic methyl signals in the ^{1}H NMR spectrum, whereas two signals were detected (due to equivalent *o*-methyl substituents) for the trans isomer. As expected, the meta-substituted dialkoxyporphyrins did not show atropisomerism. Quantitative insertion of Ni(II) was possible by treating the free-base porphyrins with $Ni(OAc)_2$.

When the pure cis isomer of **4a** was treated with nickel(II) acetate in boiling DMF, slow atropisomerization to the trans isomer was observed as well as metalation. Thus, nickel(II) insertion was carried out by using isomeric mixtures of **4a**−**c**, respectively, rather than effecting a prepurification. Then, the resulting atropisomeric mixture of the two Ni(II) complexes **5a**−**c** were condensed with pyrrole in the presence of a catalytic amount of TFA, affording **6a**−**c** as mixtures of atropisomers in moderate overall yields. The optimal condition for the condensation involves using neat pyrrole in the presence of a catalytic amount of TFA. It is worthwhile to mention here that separation of the atropisomeric Ni complexes of the dialkoxyporphyrins **5a**−**c** and their corresponding bisdipyrromethanes **6a**−**c** was not possible due to the similarity of the R_f values for the various species involved. The meta isomeric free-base porphyrins **4d**−**f** were similarly converted to their corresponding bisdipyrromethanes **6d**−**f** via their respective Ni(II) complexes **5d**−**f**.

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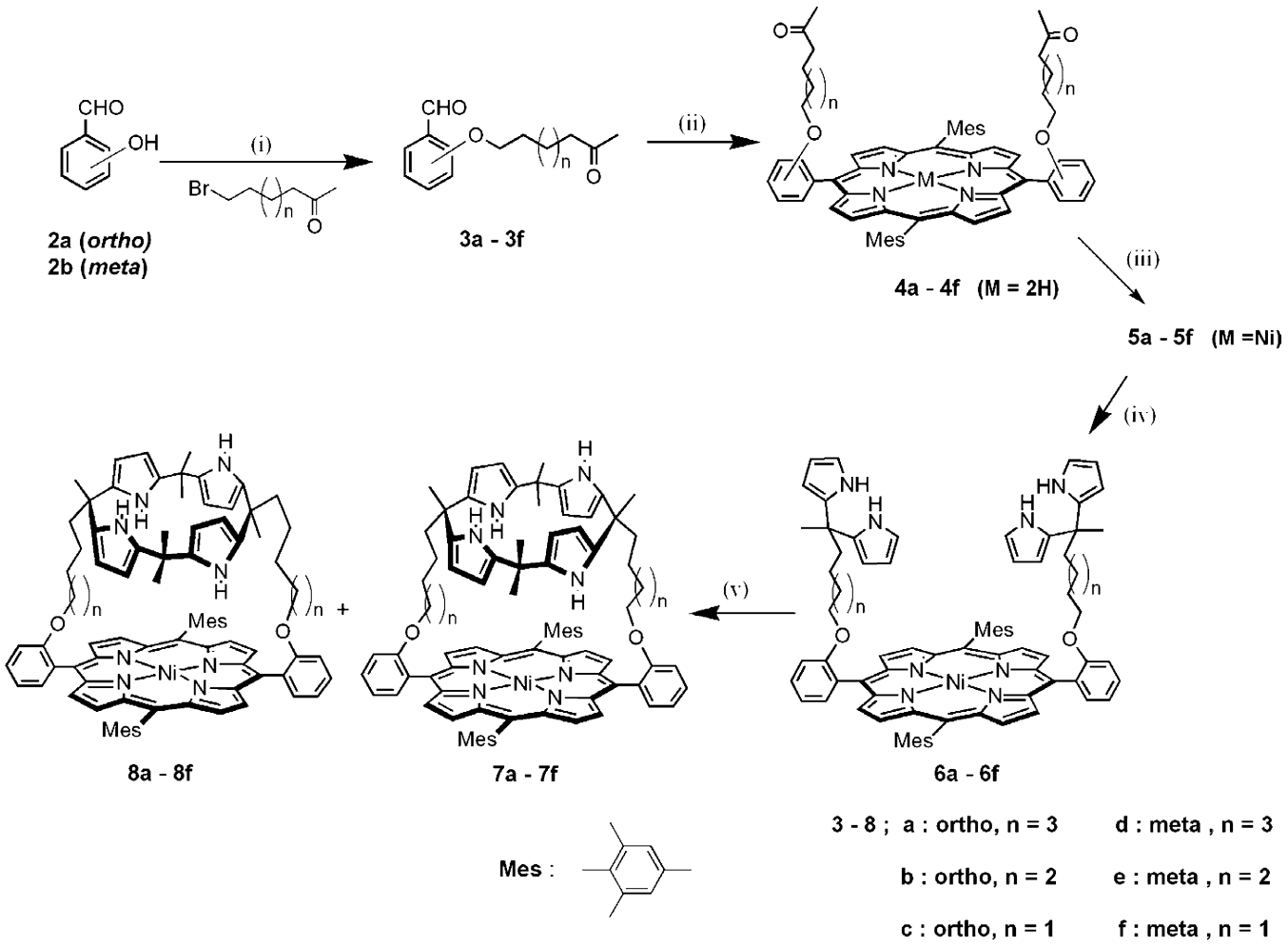
SCHEME 1[a]



[a] Reagents and conditions: (i) DMF, K_2CO_3, 60 °C, 18 h; (ii) (a) 5-mesityldipyrromethane, acetonitrile, NH_4Cl, $BF_3{\cdot}(OEt)_2$, 0 °C, 30 min, (b) DDQ, rt, 30 min; (iii) $Ni(CH_3COO)_2{\cdot}4H_2O$, DMF, reflux, 2 h; (iv) pyrrole, TFA, 50 °C, 24 h; (v) acetone, $BF_3{\cdot}(OEt)_2$, 30 min.

Our initial attempts to synthesize an analogue of **6a** starting with the free-base porphyrin **4a** yielded a highly polar mass that was sparingly soluble in ethyl acetate and could not be properly characterized. Unfortunately, the Zn(II) complex of **4a** did not give the desired product under similar conditions. Finally, acid-catalyzed condensation of **6a**−**f** with acetone under high dilution conditions (∼10 mM) afforded the desired products **7a**−**f** in low yields. Surprisingly, the twisted, 1,3-alternate forms of the calix[4]pyrrole-strapped metalloporphyrins **8a**−**f** were also isolated in about 4−11% yields each. Our attempt at the separation of the two sets of isomers, **7d/8d** and **7e/8e**, proved unsuccessful owing to the similarity of the R_f values involved. However, the identity of these products could be confirmed via FAB-MS, NMR spectroscopy (revealing a mixture of resonances), and UV−vis spectroscopy. It is interesting to note here that the polarity of the two isomers **7** and **8** becomes reversed after changing the connecting point of the strap from the ortho to the meta position of the *meso*-phenyl group. This is likely the result of compounds **8a**−**f** having three *meso*-methyl groups pointing toward the porphyrin plane while compounds of the series of **7a**−**f** have only two methyl groups.

The identity of the two isomeric compounds was confirmed unambiguously by temperature-dependent ^{1}H NMR spectroscopic analysis and via anion binding studies (vide infra).

The ^{1}H NMR spectra of **7a** obtained at room temperature show a single peak at 6.61 ppm corresponding to the calix[4]pyrrole NH resonance, as well as two multiplets, at 5.39 and 5.36 ppm (which happen to merge with the CD_2Cl_2 signal at room temperature), respectively, that are ascribed to the β-pyrrolic protons. Both sets of resonances are shifted upfield compared to those of simple octamethyl calix[4]pyrrole due to the diamagnetic ring current effect of the metalloporphyrin. The two *meso*-methyl groups of the calix[4]pyrrole are thought to be pointing in toward the porphyrin ring, as inferred from the fact that peaks assigned to these subunits appear at 1.01 ppm in the NMR spectrum. The singals for four of the bridging methylene groups appear as multiplets at 0.86 and 0.74 ppm, leading to the conclusion that all the hydrogens are in the proximity of the porphyrin core. The ^{1}H NMR spectra obtained at −50 °C did not show any significant changes in these resonances except for a general broadening of the signals and a downfield shift

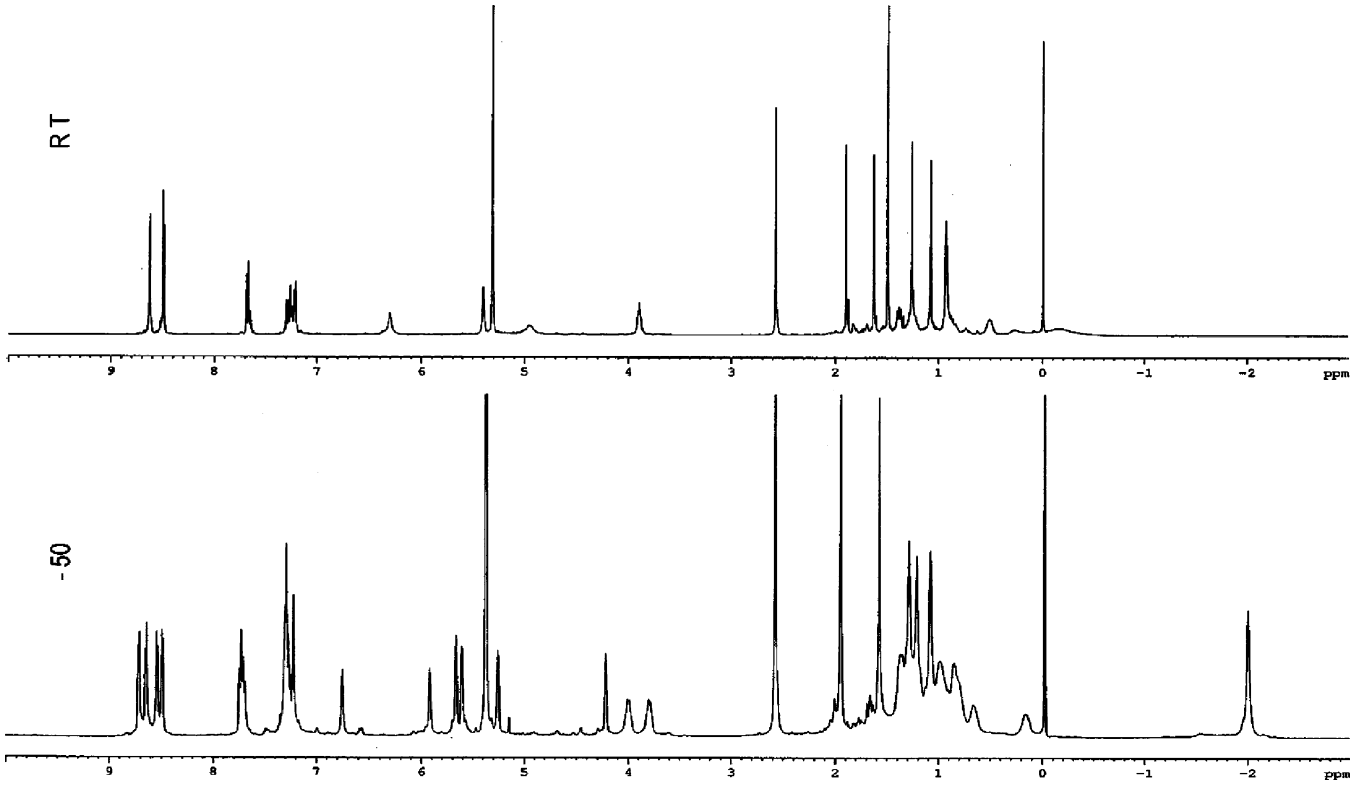


FIGURE 1. Proton NMR (CD_2Cl_2) spectra of compound **8a** at room temperature (top trace) and at −50 °C (bottom trace).

of the pyrrolic NH signal along with a slight rearrangement in the conformation of the methylene chain.

The ^{1}H NMR spectral characteristics of receptor **8a** were found to differ significantly from those of **7a**. In near analogy to what is seen in **7a**, at room temperature the spectrum of **8a** is characterized by an NH resonance at 6.37 ppm, which appears as a broad singlet, and two broad singlets at 5.41 and 4.91 ppm corresponding to the calix[4]pyrrole β-pyrrolic protons. On the other hand, the signals for the two methylene groups of the strap appeared at −0.15 and 0.51 ppm in the form of a very broad signal, which represents a dramatic upfield shift for this signal compared to what is seen in the case of **7a**.

Dramatic changes were also observed for all the resonances when the spectrum was acquired at −50 °C (Figure 1). For example, at this low temperature, the calix[4]pyrrole *NH* resonance becomes split into two distinct singlets that appear at 6.75 and 5.92 ppm. The β-pyrrolic protons of both the porphyrin and the calix[4]-pyrrole units are also split, appearing as four distinct doublets at 8.72, 8.65, 8.54, and 8.49 ppm and as singlets at 5.64, 5.60, 5.27, and 4.19 ppm, respectively. In addition, two sets of resonances were observed for most of the methylene protons in the bridging "strap", whereas the signal ascribed to one set of bridging methylene protons originally appearing at −0.15 ppm is shifted to higher field and is found to resonate at −2.01 ppm as a well-defined singlet. Similar trends were also observed in the case of **7b** and **8b**. The resulting analysis indicated the proximity of the methylene protons to the porphyrin skeleton in the case of the longer strap (n = 2 and 3). This stands in contrast to our earlier report[18] on the *meso*-methyl groups where the strap attached suffered the shielding effect of the porphyrin moiety due to its shorter strap length (n = 1). On this basis, we propose that the calix[4]pyrrole unit is much closer to the porphyrin plane when the strap is shorter. Consistent with this suggestion, the finding that **8f** has a shorter strap length shows similar behavior (Figure 2).

High-temperature proton NMR spectroscopic studies carried out in DMSO-d_6/$CDCl_3$ (3/1) revealed no evidence of interconversion of the two isomers, **7a** and **8a**, even at 120 °C. Moreover, all the resonance lines of **7a** remain unchanged upon heating to 100 °C while the structure of **8a** becomes more symmetrical at elevated temperature as judged from a sharpening of all the ^{1}H NMR signals including those ascribed to the β-pyrrolic protons. All the above experimental results when considered in concert lead us to conclude that the two compounds, **7a** and **8a**, are not conformational isomers of each other. Since the other shorter strapped compounds showed similar spectral features, this conclusion is considered to be general.

Preliminary solution-phase binding studies of receptor **7a** were made by using proton NMR spectroscopy in $CDCl_3$. When the tetrabutylammonium salt of fluoride ion (purchased commercially as the purported trihydrate and used without further purification) was added to a $CDCl_3$ solution of **7a**, a new set of signals was seen to grow in at the expense of those seen in the case of **7a** alone. The fact that two distinct sets of peaks were observed (as opposed to a single time averaged set) was considered reflective of strong binding with slow complexation/decomplexation kinetics. Near complete conversion to what was presumed to be the bound form was seen upon the addition of ∼1.2 equiv of fluoride anion. A Job plot analysis was performed and found to be consis-

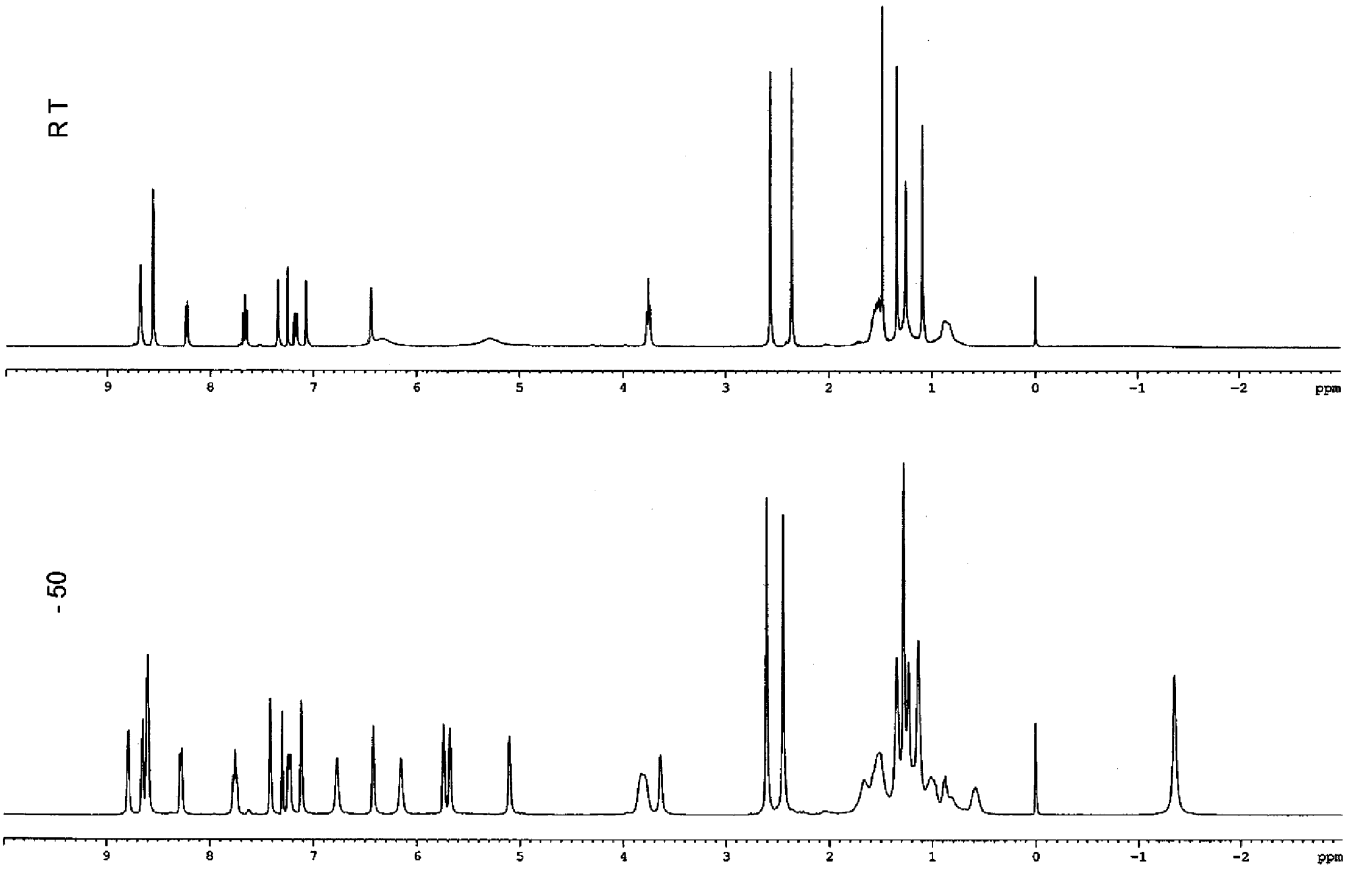


FIGURE 2. Proton NMR ($CDCl_3$) spectra of compound **8f** at room temperature (top trace) and at −50 °C (bottom trace).

tent with a 1:1 binding ratio. Further quantitative estimates of anion affinities could not be made on the basis of these studies due to strong binding. On the other hand, the fact that this kind of spectroscopic behavior was observed provides good qualitative evidence for fluoride anion binding. It also provided evidence for structural changes occurring during the course of binding. For example, titration of receptor **7a** with fluoride anion produced a new set of signals for the pyrrole NH protons at 12.78 ppm that were shifted to lower field than what was observed in the absence of anions (δ 6.61 ppm). Likewise, the β-pyrrolic *CH* signals shifted from 5.39 and 5.36 ppm to 5.42 ppm upon the addition of fluoride anion, which is a very minute change compared to what was seen in the case of **7c** as reported earlier.[18] Similar minor shifts in the resonances of the β-pyrrolic CH signals of **7b** were also observed upon the addition of fluoride anion. These findings bolster our earlier argument, made on the basis of low-temperature NMR study, that upon increasing the strap length the calix[4]pyrrole unit moves further away from the porphyrin and hence experiences a reversed shielding effect. Since anion binding to the pyrrole NH groups is expected to increase the electron density on the pyrrole ring and engender upfield shifts in the β-pyrrolic CH signals, the observed spectral shifts are consistent with structural changes that cause the respective protons to move away from the porphyrin plane upon binding to the fluoride ion. The exact nature of these structural changes, however, must await more detailed analysis, either in solution or in the solid state. Interestingly, the addition of fluoride anion to **7f** in this same solvent led to the appearance of new sets of signals for the calix[4]pyrrole *N*−*H* and β-pyrrolic *C*−*H* protons, respectively, that were shifted to lower field along with emergence of a new signal at very low field (∼13 ppm). The changes were apparent even upon the addition of only 0.6 equiv of TBAF. Upon addition of 1.3 equiv of this anion, signals associated with the unbound host completely disappeared while the new β-pyrrolic *C*−*H* signals were still apparent as two sets of singlets. This result stands in contrast to **7a**−**c** where the new signals appeared as a single resonance, presumably, to the molecular symmetry. Symmetrization could not be achieved in the case of **7f**, even upon the addition of 3 equiv of TBAF. Also, no significant change was observed for the resonance at 13 ppm. This behavior of **7f** could be attributed to its meta connectivity, which imparts greater conformational flexibility to the host and hence promotes secondary binding interactions in addition to those associated within cavity binding, thus precluding its ability to achieve the symmetrical conformation of the isomeric *o*-phenoxy strapped receptors.

Attempted solution-phase binding studies involving the tetrabutylammonium salts of chloride, bromide, and iodide anions did not reveal any evidence of appreciable binding, as judged from the absence of changes in the corresponding ^{1}H NMR spectra. While not a proof, these observations are consistent with the notion that only fluoride anion can fit readily into the cavity and that either the size of this cavity or the conformational flexibility of the calix[4]pyrrole−porphyrin receptor moi-

ety is sufficiently restricted so as to exclude the larger halide anions.

In accord with the notion that structural limitations can play a key role in regulating the anion affinities of strapped or capped calix[4]pyrroles, it was found that receptors **8a**−**c** showed almost no affinity for fluoride (or any other halide anion), as judged from the absence of observable changes in the ^{1}H NMR spectra when subjected to titration analogous to those described above. In this instance, it is inferred that the restriction imposed by the twisted junction of the two macrocycles somehow restricts the conformational changes needed to accommodate a bound fluoride anion. Analysis of the single-crystal structure of diester-strapped calix[4]pyrrole reported earlier[19] reveals that the most stable conformation of a strapped calix[4]pyrrole moiety, including those of the present series, is likely to be the twisted 1,3-alternate form in the absence of a bound anion as a result of presumed compensation between the conformational stability of the calix[4]pyrrole moiety and the strain induced by the bridging methylene chain. On the other hand, in analogy to what is seen in most anion-bound forms of calix[4]pyrrole, it is likely that the anion-bound form requires (or at least favors) the cone conformation. A system that is unable to adopt to such a conformation might thus show very high anion binding selectivity or, as in the case of **8a**−**c**, prove unable to bind any anionic substrate easily, at least within its central binding cavity.

In conclusion, we have demonstrated that Ni(II)−porphyrin-capped calix[4]pyrroles can be prepared readily by using a convergent approach. To the best of our knowledge, receptors **8a**−**c**, bearing a connecting strap with a trans junction relative to the porphyrin plane, are unique. Since they contain two different kinds of binding elements (calix[4]pyrrole and porphyrin), compounds such as those described here could find utility in the design and synthesis of heteroditopic receptors, as well as Lewis acid assisted anion receptors. Furthermore, these systems contain flexible straps that may be modified to incorporate additional anion recognition elements (e.g., amides, sulfamides, etc.) as such, additional fine-tuning of the anion binding properties may be envisioned. Finally, the use of the metalloporphyrin moiety as a spectroscopic probe for monitoring the anion binding can also be conceived. System **1** (compound **7a**) is rather unique in that it contains metalloporphyrins as ancillary coordination sites at a potentially proper distance from an anion recognition motif (calixpyrrole). This raises the appealing possibility that the anion being targeted could be one of the axial ligands trapped inside the cavity.[20] In principle, this trapped ligand will stay inside the cavity regardless of the changes in oxidation state of the metal ion. Receptors such as those described here could serve as models for studying metalloporphyrin-catalyzed reactions.

Experimental Section

Proton NMR spectra (400 MHz) were recorded with TMS as the internal standard. High- and Low-resolution FAB mass spectra were obtained on a high-resolution mass spectrometer. Column chromatography was performed over silica gel (230−400 mesh). Pyrrole was distilled at atmospheric pressure from CaH_2. Both CH_2Cl_2 and $CHCl_3$ (reagent grade) were distilled from K_2CO_3 to eliminate traces of acid. All other reagents were obtained from commercial sources and used as received unless noted otherwise.

2-(7-Oxooctyloxy)benzaldehyde (3a). To the solution of DMF (200 mL) and salicylaldehyde (2 mL, 18.77 mmol) was added K_2CO_3 (12.97 g, 93.85 mmol). The mixture was heated to 60 °C for 15 min then, 8-bromo-2-octanone (4.5 g, 21.73 mmol) was added and stirring continued for 24 h. The reaction mixture was cooled to room temperature and combined with water (200 mL). The mixture was extracted with dichloromethane and the organic layer was dried (anhyd Na_2SO_4). Solvent was removed in vacuo and the resulting black solid was purified by column chromatography on silica gel (CH_2Cl_2/EtOAc = 98/2). Yield 3.75 g (80%, light yellow oil). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 1H), 7.83 (m, 1H), 7.53 (m, 1H), 7.01 (t, 1H, J = 7.5 Hz), 6.97 (d, 1H, J = 8.5 Hz), 4.08 (t, 2H), 2.45 (t, 2H), 2.15 (s, 3H), 1.85 (m, 2H), 1.61 (m, 2H), 1.49 (m, 2H), 1.39 (m, 2H). MS (EI) Calcd for $C_{15}H_{20}O_3$ *m/z* 248.14, found (*m* + 1)/*z* 249.15.

2-(6-Oxoheptyloxy)benzaldehyde (3b). Yield 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 1H), 7.83 (m, 1H), 7.53 (m, 1H), 7.02 (t, 1H, J = 7.5 Hz), 6.97 (d, 1H, J = 8.4 Hz), 4.08 (t, 2H), 2.48 (t, 2H), 2.15 (s, 3H), 1.87 (m, 2H), 1.66 (m, 2H), 1.51 (m, 2H). MS (EI) calcd for $C_{14}H_{18}O_3$ *m/z* 234.13, found (*m* + 1)/*z* 235.14.

2-(5-Oxohexyloxy)benzaldehyde (3c). Yield 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 1H), 7.83 (m, 1H), 7.53 (m, 1H), 7.02 (t, 1H, J = 7.5 Hz), 6.97 (d, 1H, J = 8.4 Hz), 4.09 (t, 2H), 2.55 (t, 2H), 2.16 (s, 3H), 1.87 (m, 2H), 1.81 (m, 2H). MS (EI) calcd for $C_{13}H_{16}O_3$ *m/z* 220.11, found (*m* + 1)/*z* 221.10.

3-(7-Oxooctyloxy)benzaldehyde (3d). Yield 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.44 (m, 2H), 7.38 (d, 1H, J = 2.1 Hz), 7.17 (m, 1H), 4.01 (t, 2H), 2.45 (t, 2H), 2.14 (s, 3H), 1.81 (m, 2H), 1.61 (m, 2H), 1.49 (m, 2H), 1.32 (m, 2H). MS (EI) calcd for $C_{15}H_{20}O_3$ *m/z* 248.14, found (*m* + 1)/*z* 249.15.

3-(6-Oxoheptyloxy)benzaldehyde (3e). Yield 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.44 (m, 2H), 7.38 (d, 1H, J = 2.1 Hz), 7.17 (m, 1H), 4.01 (t, 2H), 2.48 (t, 2H), 2.15 (s, 3H), 1.82 (m, 2H), 1.65 (m, 2H), 1.49 (m, 2H). MS (EI) calcd for $C_{14}H_{18}O_3$ *m/z* 234.13, found (*m* + 1)/*z* 235.13.

3-(5-Oxohexyloxy)benzaldehyde (3f). Yield 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.45 (m, 2H), 7.38 (d, 1H, J = 2.0 Hz), 7.16 (m, 1H), 4.03 (t, 2H), 2.53 (t, 2H), 2.16 (s, 3H), 1.80 (m, 4H). MS (EI) calcd for $C_{13}H_{16}O_3$ *m/z* 220.11, found (*m* + 1)/*z* 221.11.

5,15-Bis[2-(7-oxooctyloxy)phenyl]-10,20-bis(2,4,6-trimethylphenyl)porphyrin (4a). The solution of **3a** (1.4 g, 5.65 mmol), 5-mesityldipyyromethane (1.5 g, 5.65 mmol), powdered ammonium chloride (1.5 g, 56.5 mmol), and acetonitrile (560 mL) was cooled to 0 °C in an ice bath. Then, BF_3·OEt_2 (72 μL, 0.57 mmol) was added and the stirring continued for another 30 min at 0 °C. The ice bath was removed, DDQ (1.9 g, 8.47 mmol) was added to the reaction mixture, and the solution was stirred for an additional 30 min. The solvent was removed in vacuo the resulting solid was purified by column chromatography on silica (CH_2Cl_2/EtOAc = 98/2) to afford the atropisomeric mixture of the product as a purple solid. Yield 280 mg (10%). Separation of the two atropisomers was possible by preparative TLC and each isomer was characterized as follow. Cis isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, 4H, J = 4.7 Hz), 8.63 (d, 4H, J = 4.7 Hz), 7.98 (m, 2H), 7.72 (m, 2H), 7.32 (m, 4H), 7.24 (s, 4H), 3.91 (t, 4H, J = 6.3 Hz), 2.62 (s, 6H), 1.84 (s, 12H), 1.51 (t, 4H, J = 7.4 Hz), 1.47 (s, 6H), 1.05 (m, 4H), 0.84 (m, 4H), 0.60 (m, 8H), −2.55 (br s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 208.8, 158.8, 139.5, 139.2, 138.6, 137.7, 136.0, 131.1, 129.7, 127.8, 127.7, 119.3, 117.5, 115.7, 111.9, 68.3, 42.8, 29.2, 28.3, 28.0, 27.9, 25.1, 22.9, 21.7, 21.6, 21.5. MS (FAB) calcd for $C_{66}H_{70}N_4O_4$ 982.54, found 983.53 (M^+

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+ 1). UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 418 (5.57), 514 (4.32), 548 (3.86), 591 (3.82), 645 (3.55). Trans isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, 4H, J = 4.7 Hz), 8.63 (d, 4H, J = 4.7 Hz), 7.98 (m, 2H), 7.73 (m, 2H), 7.32 (m, 4H), 7.25 (s, 4H), 3.89 (t, 4H, J = 6.2 Hz), 2.62 (s, 6H), 1.84 (s, 12H), 1.39 (s, 6H), 1.36 (t, 4H, J = 7.5 Hz), 1.00 (m, 4H), 0.69 (m, 4H), 0.50 (m, 4H), 0.43 (m, 4H), −2.56 (br s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 208.7, 158.8, 158.7, 139.5, 139.3, 139.2, 138.6, 137.6, 136.0, 135.8, 131.2, 131.1, 129.7, 127.7, 127.7, 119.4, 117.5, 115.7, 112.1, 68.4, 42.8, 29.2, 28.3, 27.9, 25.1, 22.8, 21.64, 21.5. MS (FAB) calcd for $C_{66}H_{70}N_4O_4$ 982.54, found 983.53 (m + 1)/z. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 419 (5.61), 514 (4.26), 548 (3.80), 591 (3.74), 645 (3.46).

5,15-Bis(2-(6-oxoheptyloxy)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (4b). Yield 15%. Cis isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, 4H, J = 4.7 Hz), 8.63 (d, 4H, J = 4.7 Hz), 7.99 (m, 2H), 7.73 (m, 2H), 7.30 (m, 8H), 3.91 (t, 4H, J = 6.2 Hz), 2.62 (s, 6H), 1.85 (s, 6H), 1.84 (s, 6H), 1.53 (t, 4H, J = 7.6 Hz), 1.48 (s, 6H), 1.05 (m, 4H), 0.90 (m, 4H), 0.56 (m, 4H), −2.55 (br s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 208.6, 158.7, 139.5, 139.2, 138.6, 137.6, 135.9, 131.1, 129.7, 127.8, 127.6, 119.4, 117.5, 115.7, 111.9, 67.9, 42.8, 29.3, 28.3, 24.7, 22.5, 21.7, 21.6, 21.5. MS (FAB) calcd for $C_{64}H_{66}N_4O_4$ m/z 954.51, found (m + 1)/z 954.50. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 418 (5.62), 514 (4.35), 548 (3.88), 591 (3.85), 646 (3.57). Trans isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, 4H, J = 4.7 Hz), 8.63 (d, 4H, J = 4.7 Hz), 7.99 (m, 2H), 7.74 (m, 2H), 7.32 (m, 4H), 7.25 (s, 4H), 3.89 (t, 4H, J = 6.1 Hz), 2.62 (s, 6H), 1.85 (s, 12H), 1.39 (s, 6H), 1.36 (t, 4H, J = 7.6 Hz), 0.99 (m, 4H), 0.79 (m, 4H), 0.42 (m, 4H), −2.56 (br s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 208.6, 158.8, 139.3, 138.6, 137.6, 135.8, 131.2, 129.8, 127.8, 119.5, 117.5, 115.7, 112.2, 68.1, 42.7, 29.2, 28.3, 24.6, 22.4, 21.7, 21.5. MS (FAB) calcd for $C_{64}H_{66}N_4O_4$ m/z 954.51, found (m + 1)/z 955.49. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 418 (5.64), 514 (4.33), 548 (3.89), 591 (3.85), 646 (3.56).

5,15-Bis(2-(5-oxohexyloxy)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (4c). Yield 17%. Cis isoner: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, 4H, J = 4.7 Hz), 8.63 (d, 4H, J = 4.7 Hz), 8.02 (m, 2H), 7.73 (m, 2H), 7.31 (m, 4H), 7.27 (s, 4H), 3.91 (t, 4H, J = 6.1 Hz), 2.62 (s, 6H), 1.85 (s, 6H), 1.83 (s, 6H), 1.39 (t, 4H, J = 7.1 Hz), 1.01 (m, 10H), 0.83 (m, 4H), −2.55 (br s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 208.3, 158.7, 139.5, 139.2, 138.5, 137.6, 135.8, 131.0, 129.8, 127.8, 127.67, 119.5, 117.6, 115.6, 111.8, 68.2, 42.2, 28.9, 27.9, 21.6, 21.5, 19.7. MS (FAB) calcd for $C_{62}H_{62}N_4O_4$ m/z 926.48, found (m + 1)/z 927.47. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 418 (5.57), 514 (4.23), 548 (3.90), 590 (3.88), 645 (3.54). Trans isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, 4H, J = 4.7 Hz), 8.64 (d, 4H, J = 4.7 Hz), 8.01 (m, 2H), 7.73 (m, 2H), 7.32 (m, 4H), 7.27 (s, 4H), 3.91 (t, 4H, J = 6.0 Hz), 2.62 (s, 6H), 1.84 (s, 12H), 1.29 (t, 4H, J = 7.0 Hz), 0.98 (m, 4H), 0.88 (s, 6H), 0.74 (m, 4H), −2.56 (br s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 208.4, 158.8, 139.3, 138.5, 137.6, 135.7, 131.1, 129.8, 127.7, 119.5, 117.6, 115.6, 111.9, 68.2, 42.1, 28.8, 27.9, 21.6, 21.5, 19.7. MS (FAB) calcd for $C_{62}H_{62}N_4O_4$ m/z 926.48, found (m + 1)/z 927.51. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 418 (5.65), 514 (4.34), 548 (3.95), 591 (3.89), 647 (3.66).

5,15-Bis(3-(7-oxooctyloxy)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (4d). Yield 8%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, 4H, J = 4.7 Hz), 8.68 (d, 4H, J = 4.7 Hz), 7.78 (m, 4H), 7.61 (m, 2H), 7.30 (d, 2H, J = 2.5 Hz), 7.28 (s, 4H), 4.14 (t, 4H, J = 6.4 Hz), 2.63 (s, 6H), 2.41 (t, 4H, J = 7.4 Hz), 2.01 (s, 6H), 1.84 (m, 16H), 1.59 (m, 4H), 1.51(m, 4H), 1.38 (m, 4H), −2.64 (br s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 209.2, 157.4, 143.3, 139.4, 138.4, 137.7, 127.7, 127.5, 121.0, 119.1, 118.2, 113.9, 68.0, 43.6, 32.1, 29.2, 28.9, 25.9, 23.7, 21.6, 21.5. MS (FAB) calcd for $C_{66}H_{70}N_4O_4$ m/z 982.54, found (m + 1)/z 983.54. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 418 (5.66), 514 (4.33), 548 (3.92), 590 (3.86), 645 (3.69).

5,15-Bis(3-(6-oxoheptyloxy)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (4e). Yield 10%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, 4H, J = 4.7 Hz), 8.68 (d, 4H, J = 4.7 Hz), 7.79 (m, 4H), 7.60 (m, 2H), 7.30 (d, 2H, J = 1.8 Hz), 7.28 (s, 4H), 4.14 (t, 4H, J = 6.4 Hz), 2.63 (s, 6H), 2.45 (t, 4H, J = 7.3 Hz), 2.11 (s, 6H), 1.84 (m, 16H), 1.66 (m, 4H), 1.52(m, 4H), −2.64 (br s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 208.9, 157.4, 143.3, 139.4, 138.4, 137.7, 127.7, 127.5, 121.0, 119.1, 118.2, 113.9, 67.9, 43.6, 29.9, 29.2, 25.8, 23.5, 21.6, 21.5. MS (FAB) calcd for $C_{64}H_{66}N_4O_4$ m/z 954.51, found (m + 1)/z 955.51. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 418 (5.68), 514 (4.34), 548 (3.93), 590 (3.84), 645 (3.61).

5,15-Bis(3-(5-oxohexyloxy)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin (4f). Yield 11%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, 4H, J = 4.7 Hz), 8.68 (d, 24, J = 4.7 Hz), 7.79 (m, 4H), 7.61 (m, 2H), 7.30 (d, 2H, J = 2.4 Hz), 7.28 (s, 4H), 4.15 (t, 4H, J = 5.8 Hz), 2.63 (s, 6H), 2.53 (t, 4H, J = 6.9 Hz), 2.13 (s, 6H), 1.84 (m, 20H), −2.64 (br s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 208.7, 157.3, 143.3, 139.4, 138.4, 137.7, 127.8, 127.6, 121.0, 119.1, 118.3, 113.9, 67.8, 43.3, 29.9, 28.8, 21.6, 21.5, 20.5. MS (FAB) calcd for $C_{62}H_{62}N_4O_4$ m/z 926.48, found (m + 1)/z 927.46. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 418 (5.64), 514 (4.33), 549 (3.90), 589 (3.81), 645 (3.59).

5,15-Bis(2-(7-oxooctyloxy)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinatonickel(II) (5a). 4a (200 mg, 0.2 mmol) and $(CH_3COO)_2Ni{\cdot}4H_2O$ (249 mg, 1 mmol) were dissolved separately in DMF (50 mL, each). The two solutions were mixed together and heated at reflux for 2 h. The mixture was cooled to room temperature and combined with water (200 mL). Then the mixture was extracted with dichloromethane and the organic layer was dried. Solvent was removed in vacuo and the remaining black solid was separated by column chromatography on silica (CH_2Cl_2:EtOAc = 98:2). The atropisomeric mixture was obtained as an orange solid (190 mg, 90% yield). MS (FAB) found (m + 1)/z 1039.45, calcd for $C_{66}H_{68}N_4NiO_4$ m/z 1038.46. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 414 (5.42), 526 (4.31), 556 (3.76).

5,15-Bis(2-(6-oxoheptyloxy)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinatonickel(II) (5b). Yield 92%. MS (FAB) calcd for $C_{64}H_{64}N_4NiO_4$ m/z 1010.43, found (m + 1)/z 1011.34. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 414 (5.47), 527 (4.36), 554 (3.77).

5,15-Bis(2-(5-oxohexyloxy)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinatonickel(II) (5c). Yield 93%. MS (FAB) calcd for $C_{62}H_{60}N_4NiO_4$ m/z 982.40, found (m + 1)/z 983.34. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 414 (5.55), 527 (4.44), 555 (3.87).

5,15-Bis(3-(7-oxooctyloxy)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinatonickel(II) (5d). Yield 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (m, 4H), 8.59 (d, 2H, J = 4.8 Hz), 7.62 (d, 2H, J = 7.5 Hz), 7.59 (s, 2H), 7.52 (t, 2H, J = 8.0), 7.21 (m, 6H), 4.06 (t, 4H, J = 6.4 Hz), 2.54 (s, 6H), 2.37 (t, 4H, J = 7.3 Hz), 2.06 (s, 6H), 1.81 (m, 16H), 1.55 (m, 4H), 1.47 (m, 4H), 1.32 (m, 4H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 209.6, 158.0, 143.1, 143.0, 142.8, 139.5, 138.1, 137.8, 133.0, 131.5, 128.2, 128.1, 127.1, 120.6, 118.8, 117.8, 114.5, 68.5, 44.1, 30.3, 29.7, 29.4, 24.2, 21.9, 21.8. MS (FAB) calcd for $C_{66}H_{68}N_4NiO_4$ m/z 1038.46, found (m + 1)/z 1039.45. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 414 (5.44), 526 (4.35), 554 (sh).

5,15-Bis(3-(6-oxoheptyloxy)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinatonickel(II) (5e). Yield 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (m, 4H), 8.59 (m, 4H), 7.63 (d, 2H, J = 7.2 Hz), 7.58 (s, 2H), 7.52 (t, 2H, J = 8.0), 7.21 (m, 6H), 4.06 (t, 4H, J = 6.4 Hz), 2.55 (s, 6H), 2.41 (t, 4H, J = 7.2 Hz), 2.08 (s, 6H), 1.81 (m, 16H), 1.62 (m, 4H), 1.47 (m, 4H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 209.4, 158.0, 143.1, 143.0, 142.8, 139.5, 138.1, 137.7, 132.9, 131.6, 128.2, 128.1, 127.1, 120.6, 118.8, 117.8, 114.5, 68.3, 44.0, 30.4, 29.6, 26.2, 24.0, 21.9, 21.8. MS (FAB) calcd for $C_{64}H_{64}N_4NiO_4$ m/z 1010.43, found (m + 1)/z 1011.33. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 414 (5.34), 526 (4.36), 553 (sh).

5,15-Bis(3-(5-oxohexyloxy)phenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrinatonickel(II) (5f). Yield 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, 4H, J = 4.9 Hz), 8.59 (d, 4H, J = 4.8 Hz), 7.64 (d, 2H, J = 7.5 Hz), 7.58 (s, 2H), 7.52 (t,

2H, J = 8.1), 7.21 (m, 6H), 4.07 (t, 4H, J = 5.8 Hz), 2.55 (s, 6H), 2.48 (t, 4H, J = 7.3 Hz), 2.09 (s, 6H), 1.78 (m, 20H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 208.6, 157.4, 142.6, 142.5, 142.4, 139.0, 137.6, 137.2, 132.4, 131.1, 127.7, 127.6, 126.6, 120.1, 118.2, 117.4, 113.9, 67.7, 43.2, 29.9, 28.7, 21.4, 21.3, 20.5. MS (FAB) calcd for $C_{62}H_{60}N_4NiO_4$ m/z 982.40, found (m + 1)/z 983.40. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 414 (5.45), 526 (4.35), 553 (sh).

Porphyrin 6a. 5a (200 mg, 0.19 mmol) was dissolved in neat pyrrole (2 mL) and TFA (20 μL, 0.26 mmol) was added. Then, the mixture was stirred for 24 h at 50 °C and cooled to room temperature. The reaction was quenched by addition of aqueous K_2CO_3 solution (10 mL) and extracted with dichloromethane. The organic layer was dried (anhyd Na_2SO_4) and the solvent was removed in vacuo. The resulting dark red solid was purified by column chromatography on silica (CH_2Cl_2). The collected red fraction contained the two atropoisomers. Yield 172 mg (70%). MS (FAB) calcd for $C_{82}H_{84}N_8NiO_2$ m/z 1270.61, found (m + 1)/z 1271.44. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 414 (5.40), 527 (4.32), 555 (3.81).

Porphyrin 6b. Yield 72%. MS (FAB) calcd for $C_{80}H_{80}N_8NiO_2$ m/z 1242.58, found (m + 1)/z 1243.60. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 414 (5.47), 526 (4.38), 555 (3.78).

Porphyrin 6c. Yield 74%. MS (FAB) calcd for $C_{80}H_{80}N_8NiO_2$ m/z 1214.54, found (m + 1)/z 1215.60. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 414 (5.47), 527 (4.36), 554 (3.80).

Porphyrin 6d. Yield 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, 4H, J = 4.9 Hz), 8.57 (d, 4H, J = 4.9 Hz), 7.68 (br s, 4H), 7.63 (d, 2H, J = 7.3 Hz), 7.54 (m, 4H), 7.22 (m, 6H), 6.56 (m, 4H), 6.08 (m, 4H), 6.04 (m, 4H), 4.04 (t, 4H, J = 6.5 Hz), 2.57 (s, 6H), 1.92 (m, 4H), 1.77 (m, 16H), 1.53 (s, 6H), 1.44 (m, 4H), 1.31 (m, 4H), 1.19 (m, 4H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 157.5, 142.6, 142.5, 142.3, 138.9, 138.1, 137.6, 137,3, 132.5, 131.0, 127.7, 127.6, 126.5, 120.1, 118.3, 117.3, 116.9, 114.1, 107.5, 104.5, 68.0, 41.0, 38.9, 29.8, 29.3, 26.2, 25.9, 24.3, 21.4. MS (FAB) calcd for $C_{82}H_{84}N_8NiO_2$ m/z 1270.61, found (m + 1)/z 1271.44. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 414 (5.44), 527 (4.32), 553 (sh).

Porphyrin 6e. Yield 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, 4H, J = 4.8 Hz), 8.57 (d, 4H, J = 4.9 Hz), 7.70 (br s, 4H), 7.63 (d, 2H, J = 7.5 Hz), 7.54 (m, 4H), 7.21 (m, 6H), 6.56 (m, 4H), 6.07 (m, 4H), 6.04 (m, 4H), 4.03 (t, 4H, J = 6.4 Hz), 2.57 (s, 6H), 1.96 (m, 4H), 1.81 (m, 16H), 1.53 (s, 6H, $-CH_3$), 1.45 (m, 4H), 1.25 (m, 4H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 158.0, 143.1, 143.0, 142.8, 139.5, 138.6, 138.1, 137.8, 133.0, 131.6, 128.2, 128.1, 127.1, 120.6, 118.8, 117.9, 117.5, 114.6, 108.1, 105.0, 68.6, 41.6, 39.4, 29.7, 27.1, 26.7, 24.7, 21.9. MS (FAB) calcd for $C_{80}H_{80}N_8NiO_2$ m/z 1242.58, found (m + 1)/z 1243.60. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 414 (5.44), 526 (4.31), 553 (sh).

Porphyrin 6f. Yield 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, 4H, J = 4.8 Hz), 8.57 (d, 4H, J = 4.8 Hz), 7.70 (br s, 4H), 7.63 (d, 2H, J = 7.5 Hz), 7.54 (m, 4H), 7.19 (m, 6H), 6.54 (m, 4H), 6.05 (m, 8H), 4.04 (t, 4H, J = 6.5 Hz), 2.57 (s, 6H), 2.02 (m, 4H), 1.83 (m, 16H), 1.56 (s, 6H), 1.39 (m, 4H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 157.9, 143.1, 143.0, 142.9, 139.5, 138.4, 138.2, 137.8, 133.0, 131.6, 128.3, 128.1, 127.1, 120.7, 118.8, 117.9, 117.5, 114.6, 108.1, 105.1, 68.4, 41.3, 39.5, 30.1, 26.7, 21.9, 21.6. MS (FAB) calcd for $C_{78}H_{76}N_8NiO_2$ m/z 1214.54, found (m + 1)/z 1215.50. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 414 (5.49), 526 (4.37), 554 (sh).

Porphyrin-Capped Calix[4]pyrroles 7a and 8a. BF_3·OEt_2 (10 μL, 0.08 mmol) was added to the solution of **6a** (150 mg, 0.12 mmol) dissolved in acetone (12 mL) and the mixture was stirred for 30 min at room temperature. The reaction was quenched with aqueous K_2CO_3 solution (10 mL) and was extracted with dichloromethane. The organic layer was dried (anhyd Na_2SO_4) and the solvent was removed in vacuo. The remaining dark solid was purified by column chromatography on silica (CH_2Cl_2 /hexanes = 70/30) to afford two fractions characterized as isomeric **7a** and **8a**. The fast moving fraction was **8a**: Yield 18 mg (11%). ^{1}H NMR ($CDCl_3$) δ 8.64 (d, 4H, J = 4.9 Hz), 8.52 (d, 4H, J = 4.9 Hz), 7.74 (m, 2H), 7.66 (m, 2H), 7.24 (m, 8H, Ms-H), 6.37 (br s, 4H), 5.41 (br s, 4H), 4.91 (br s, 4H), 3.87 (br s, 4H), 2.59 (s, 6H), 1.89 (s, 6H), 1.67 (s, 6H), 1.37 (m, 4H), 1.10 (s, 6H), 0.97 (s, 16H), 0.47 (br s, 4H), −0.15 (br s, 8H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 158.9, 144.0, 143.2, 139.8, 139.5, 138.4, 138.3, 137.8, 136.4, 132.3, 130.8, 130.4, 129.9, 128.1, 128.0, 119.6, 117.2, 115.8, 111.9, 103.7, 102.6, 69.2, 40.1, 38.8, 28.4, 27.7, 27.2, 23.9, 22.1, 22.0, 21.8, 21.8. MS (FAB) calcd for $C_{88}H_{92}N_8NiO_2$ m/z 1350.67, found (m + 1)/z 1351.89. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 414 (5.41), 526 (4.33), 558 (3.69). The slow moving fraction was **7a:** Yield 8 mg (5%). ^{1}H NMR ($CDCl_3$) δ 8.67 (d, 4H, J = 4.9 Hz), 8.55 (d, 4H, J = 4.8 Hz), 7.85 (m, 2H), 7.65 (m, 2H), 7.24 (m, 8H), 6.61 (s, 4H), 5.39 (m, 4H), 5.36 (m, 4H), 3.87 (t, 4H, J = 6.7 Hz), 2.58 (s, 6H), 1.85 (s, 6H), 1.80 (s, 6H), 1.29 (m, 10H), 1.22 (s, 10H), 1.06 (s, 6H), 0.85 (m, 8H), 0.70 (m, 4H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 158.6, 143.3, 142.6, 139.2, 138.5, 137.9, 137.7, 137.5, 136.6, 135.9, 132.1, 130.4, 130.4, 129.5, 127.7, 127.6, 119.4, 116.8, 115.3, 112.3, 103.6, 102.7, 69.2, 41.0, 38.6, 35.0, 30.3, 29.1, 28.4, 27.6, 24.7, 23.5, 21.4, 21.4, 21.4. MS (FAB) calcd for $C_{88}H_{92}N_8NiO_2$ m/z 1350.67, found (m + 1)/z 1351.73. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 414 (5.30), 527 (4.17), 556 (3.53).

Porphyrins 7b and 8b. First fraction **8b**: Yield 5.5%. ^{1}H NMR ($CDCl_3$) δ 8.63 (d, 4H, J = 4.9 Hz), 8.52 (d, 4H, J = 4.7 Hz), 7.75 (m, 2H), 7.64 (m, 2H), 7.24 (m, 8H), 6.08 (br s, 4H), 5.05 (br s, 4H), 4.75 (br s, 4H), 3.84 (br s, 4H), 2.57 (s, 6H), 1.91 (s, 6H), 1.72 (s, 6H), 1.24 (s, 6H), 1.13 (s, 6H), 1.09 (m, 4H), 1.02 (s, 6H), 0.88 (m, 8H), 0.68 (m, 4H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 158.6, 143.5, 142.8, 139.2, 139.2, 138.1, 137.7, 137.4, 135.8, 131.8, 130.7, 130.0, 129.5, 127.6, 127.5, 119.4, 116.9, 115.5, 112.0, 103.2, 101.8, 68.9, 38.3, 38.2, 29.7, 28.1, 25.1, 24.4, 22.3, 21.4, 21.4. MS (FAB) calcd for $C_{86}H_{88}N_8NiO_2$ m/z 1322.64, found (m + 1)/z 1323.96. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 414 (5.35), 526 (4.21), 558 (3.99).

Second fraction **7b**: Yield 4%. ^{1}H NMR ($CDCl_3$) δ 8.67 (d, 4H, J = 4.9 Hz), 8.56 (d, 4H, J = 4.9 Hz), 7.91 (m, 2H), 7.65 (m, 2H), 7.23 (m, 8H), 6.41 (s, 4H), 5.23 (m, 4H), 5.17 (m, 4H), 3.84 (t, 4H, J = 7.0 Hz), 2.58 (s, 6H), 1.85 (s, 6H), 1.80 (s, 6H), 1.29 (m, 10H), 1.22 (s, 10H), 1.06 (s, 6H), 0.85 (m, 8H), 0.70 (m, 4H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 158.4, 143.3, 142.8, 142.5, 139.2, 139.0, 137.9, 137.7, 137.4, 136.5, 135.9, 132.0, 131.8, 130.7, 130.4, 130.3, 129.5, 127.7, 127.6, 119.2, 116.8, 115.4, 111.7, 103.6, 102.6, 68.5, 39.3, 38.4, 34.9, 31.9, 29.7, 29.5, 28.1, 28.1, 24.9, 23.5, 21.6, 21.4, 21.3. MS (FAB) calcd for $C_{86}H_{88}N_8NiO_2$ m/z 1322.64, found (m + 1)/z 1323.65. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 414 (5.39), 527 (4.26), 556 (3.55).

Porphyrins 7c and 8c. First fraction (**8c**): Yield 7%. ^{1}H NMR ($CDCl_3$) δ 8.59 (d, 4H, J = 4.9 Hz), 8.54 (d, 4H, J = 4.7 Hz), 7.92 (m, 2H), 7.64 (m, 2H), 7.22 (m, 8H), 6.21 (br s, 4H), 5.30 (br s, 4H), 4.79 (br s, 4H), 3.60 (t, 4H, J = 7.9 Hz), 2.60 (s, 6H), 2.05 (s, 6H), 1.65 (s, 6H), 1.52 (br m, 4H), 1.49 (s, 6H), 1.06 (s, 6H), 0.90 (br m, 4H), 0.08 (br m, 4H), −0.43 (br s, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 158.9, 144.1, 143.3, 139.4, 138.6, 138.5, 137.8, 135.8, 135.1, 132.1, 130.6, 130.4, 129.8, 128.1, 128.0, 119.2, 117.5, 116.1, 111.5, 103.5, 102.4, 69.3, 39.5, 38.0, 34.4, 30.1, 29.3, 28.4, 26.2, 22.0, 21.9, 21.7, 21.2. MS (FAB) calcd for $C_{84}H_{84}N_8NiO_2$ m/z 1296.31, found (m + 1)/z 1297.25. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 411 (5.35), 524 (4.24), 555 (3.52).

Second fraction **7c**: Yield 5%. ^{1}H NMR ($CDCl_3$) δ 8.66 (d, 4H, J = 4.9 Hz), 8.54 (d, 4H, J = 4.9 Hz), 7.94 (m, 2H), 7.63 (m, 2H), 7.23 (m, 6H), 7.12 (s, 2H), 6.19 (s, 4H), 4.80 (m, 4H), 4.73 (m, 4H), 3.80 (t, 4H, J = 6.0 Hz), 2.56 (s, 6H), 1.92 (s, 6H), 1.53 (s, 6H), 1.10 (m, 14H), 1.03 (s, 6H), 0.76 (m, 4H), 0.69 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 158.6, 143.3, 142.6, 139.4, 138.9, 137.7, 137.4, 137.3, 136.4, 136.2, 132.2, 130.5, 130.4, 129.5, 127.6, 127.6, 119.4, 116.9, 115.6, 112.5, 103.2, 102.3, 69.3, 40.2, 38.2, 34.6, 30.2, 29.7, 29.6, 27.6, 26.9, 26.7, 25.3, 21.7, 21.4, 21.2, 21.2. MS (FAB) calcd for $C_{84}H_{84}N_8NiO_2$ m/z 1296.31, found (m + 1)/z 1297.52. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 415 (5.22), 527 (4.09), 557 (3.37).

Porphyrins 7d and 8d. Combined yield 12%. MS (FAB) calcd for $C_{88}H_{92}N_8NiO_2$ *m/z* 1350.67, found (*m* + 2)/*z* 1351.69. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 415 (5.23), 528 (4.07), 554 (sh).

Porphyrins 7e and 8e. Combined yield 10%. MS (FAB) calcd for $C_{86}H_{88}N_8NiO_2$ *m/z* 1322.64, found (*m* + 2)/*z* 1323.59. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 415 (5.23), 528 (4.07), 555 (sh).

Porphyrins 7f and 8f. First fraction **7f**: Yield 5%. ^{1}H NMR ($CDCl_3$) δ 8.75 (d, 4H, J = 4.9 Hz), 8.58 (d, 4H, J = 4.9 Hz), 8.31 (d, 2H, J = 7.4 Hz), 7.71 (t, 2H, J = 7.9 Hz), 7.34 (s, 2H), 7.17 (m, 2H), 7.04 (s, 2H), 6.66 (s, 2H), 6.43 (s, 4H), 5.21 (br s, 4H), 4.96 (br s, 4H), 3.74 (t, 4H, J = 7.3 Hz), 2.55 (s, 6H), 2.42 (s, 6H), 1.65 (m, 4H), 1.46 (s, 6H), 1.40 (br m, 4H), 1.24 (s, 6H), 1.17 (s, 6H), 0.96 (br m, 4H), 0.70 (s, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 156.8, 141.9, 141.8, 141.8, 139.1, 139.0, 138.4, 137.7, 137.6, 136.8, 136.6, 136.4, 132.6, 131.7, 128.1, 125.3, 119.3, 117.4, 117.0, 115.5, 103.4, 102.4, 67.7, 39.3, 38.4, 34.6, 29.0, 28.7, 27.8, 26.3, 21.9, 21.4, 21.1, 20.6. MS (FAB) calcd for $C_{84}H_{84}N_8NiO_2$ *m/z* 1294.61, found (*m* + 2)/*z* 1296.61. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 416 (5.21), 529 (4.05), 554 (sh).

Second fraction **8f**: Yield 4%. ^{1}H NMR ($CDCl_3$) δ 8.69 (d, 4H, J = 4.7 Hz), 8.56 (d, 4H, J = 4.8 Hz), 8.24 (d, 2H, J = 7.4 Hz), 7.68 (t, 2H, J = 7.8 Hz), 7.35 (s, 2H), 7.18 (m, 2H), 7.08 (s, 2H), 6.44 (s, 2H), 6.35 (br s, 4H), 5.30 (br s, 8H), 3.76 (t, 4H, J = 7.1 Hz), 2.57 (s, 6H), 2.37 (s, 6H), 1.54 (m, 4H), 1.48 (s, 6H), 1.34 (s, 6H), 1.26 (s, 6H), 1.09 (s, 6H), 0.88 (br m, 4H), −0.90 (br s, 4H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 157.0, 142.1, 142.0, 139.2, 138.9, 137.6, 137.1, 132.6, 132.4, 131.4, 129.4, 127.9, 127.7, 127.7, 125.8, 122.5, 121.5, 119.8, 117.6, 117.0, 116.2, 103.5, 102.2, 68.7, 64.0, 39.8, 38.5, 29.7, 28.5, 26.4, 21.8, 21.4, 21.1, 20.2. MS (FAB) calcd for $C_{84}H_{84}N_8NiO_2$ *m/z* 1294.61, found (*m* + 2)/*z* 1296.61. UV−vis λ_{max}/nm (log ϵ) (CH_2Cl_2) 416 (5.25), 528 (4.14), 554 (sh).

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Supporting Information Available: Spectroscopic data and binding experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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