Self-assembly of metallomacrocycles with dipyrazole ligands and anion sensing of [Pd$_4$Fe$_2$] macrocycle with ferrocene-based dipyrazole ligand†

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By employing dipalladium corners [(bpy)$_2$Pd$_2$(NO$_3$)$_2$]([NO$_3$])$_2$ or [(phen)$_2$Pd$_2$(NO$_3$)$_2$][NO$_3$])$_2$ (where bpy = 2,2'-bipyridine and phen = 1,10-phenanthroline) to bridge ferrocene-based dipyrazole ligand (L$^1$) and m-phenylene-based dipyrazole ligands (L$^{2-4}$) in aqueous solution, a series of positively-charged [M$_4$L$_2$][NO$_3$]$_4$ metallomacrocycles were obtained. Their structures were characterized by $^1$H NMR, electrospray ionization mass spectrometry (ESI-MS), elemental analysis, and single crystal X-ray diffraction analysis for 1-4NO$_3$ ((([(bpy)Pd]$_4$L$_2$)[NO$_3$])$_4$ and 4-4NO$_3$ ((([(phen)Pd]$_4$L$_2$)[NO$_3$])$_4$. In their single crystal structures, NO$_3^-$ anions are located at the dipalladium corners by C–H⋯O hydrogen bonds. Importantly, the anion-sensing properties of ferrocene functionalized [Pd$_4$Fe$_2$] hetero-metallomacrocycle 1 were investigated in acetonitrile by SWV, CV and NMR analysis, showing promise for Br$^-$ sensing.

Introduction

Anions exist ubiquitously in nature and play important roles in both biological and environmental processes. However, in contrast to the coordination chemistry of cations, the anion coordination chemistry (i.e., supramolecular chemistry of anions) pioneered by Lehn in the late 1970s has received little attention until the last decade.1,2 As the understanding of the crucial roles that anions play in biology, medicine, catalysis, and environment has accumulated, the emerging field of anion coordination chemistry3,4 has attracted increasing interest with regard to these exciting topics such as anion recognition,5 anion-templated assembly and synthesis,6 chemosensors for anions,7 as well as the anion-switched molecular devices and machines.8

Over the last decade, considerable research attention has been directed towards the design and synthesis of receptors for a range of different anionic species.9 So far, a large number of the artificial anion receptors have been reported and most of them were neutral or positively charged organic or organometallic compounds. However, much less attention has been paid to the use of metal ions to assemble anion receptors.10 With the rapid development of coordination-driven self-assembly,11-13 metal-assembled anion receptors have gradually attracted research interest in recent years, owing to their ease of synthesis, water solubility, potential multi-functionalization with redox, luminescence, and magnetism.

Recently, we have become interested in the design and self-assembly of metallo-supramolecular entities that show promise in anion binding, sensing and switching.14,15 Those positively charged coordination hosts featured with mobile cone conformation are capable of binding inorganic or organic anions through electrostatic and/or hydrogen bonding interactions. In particular, heterometal-assembled anion receptors exhibit unusual properties. Accordingly, we have begun to study the programmable self-assembly of heterometallomacrocycles.15 Herein, by employing ferrocene-functionalized redox-active or m-phenylene-based dipyrazole ligands and dimetal corners [(bpy)$_2$Pd$_2$(NO$_3$)$_2$][NO$_3$])$_2$ or [(phen)$_2$Pd$_2$(NO$_3$)$_2$][NO$_3$])$_2$ as constructing units, a series of positively-charged homo- or hetero-metallomacrocyclic complexes were synthesized via a coordination-driven self-assembly approach. Several ferrocene-containing anion receptors with unique organic frameworks have been reported previously by Beer.16,19 However, to our knowledge, metal-assembled macrocycles with ferrocene-based ligands utilized as anion redox sensors are very rare to date.14i Moreover, the pyrazolate-bridged dinuclear...
Pd(II) connected macrocyclic receptors are dynamically stable in solution and thus are capable of interacting with a wide range of anions. The structures of the di-Pd(II)-assembled macrocycles were established by $^1$H NMR, ESI-MS, elemental analysis, and single crystal X-ray diffraction studies. The anion-sensing properties of ferrocene-functionalized redox-active hetero-metallomacrocycle 1 in acetonitrile were investigated via square wave voltammetry (SWV), cyclic voltammetry (CV) titration, and $^1$H NMR analysis, which indicates that complex 1 possesses a favorable sensory capability towards Br$^-$. 

**Results and discussion**

**Synthesis and characterizations of the heterometallomacrocycles with ferrocene-based ligand L$^1$**

As shown in Scheme 1, [(bpy)$_2$Pd$_2$(NO$_3$)$_2$](NO$_3$)$_2$ or [(phen)$_2$Pd$_2$(NO$_3$)$_2$](NO$_3$)$_2$ was added to a suspension containing 1 equiv. of H$_2$L$^1$ in H$_2$O/acetone, and the mixture was stirred at 80 °C over 12 h. The resulting clear solution was cooled to room temperature, leading to the formation of positively charged metallomacrocycles [M$_4$L$_2$](NO$_3$)$_4$ [M = bpyPd$^{II}$, $^1$; M = phenPd$^{II}$, $^2$] as a gray precipitate. The $^1$H NMR analysis clearly indicated the formation of a single product. The assignments of [M$_4$L$_2$]$_{4+}$-type macrocycles were based on ESI-MS studies, where multiple charged molecular ions corresponding to intact cyclic dimers were observed. X-Ray single-crystal structural studies of 1-4NO$_3$ confirmed the formation of the metal-organic macrocycles.

The $^1$H NMR spectrum of 1-4NO$_3$ in Fig. 1 clearly shows that a symmetrical single product is formed. Signals at 8.72–8.70 (doublet), 8.45–8.41 (triplet), 8.22–8.21 (doublet), and 7.77–7.73 (triplet) ppm correspond to a, c, d, and b protons of the bpy, respectively. Signals of Fe at 3.99 and 3.89 ppm stand as two singlets. The corresponding resonances of the methylene and methyl groups of the ligand L$^1$ appear in the upfield region, which reveals two singlets each at 3.46 and 2.35 ppm. The proportion of these peaks indicates the formation of a 2 : 1 bpyPd$^{II}$ to the dipyrazole ligand complex. The NMR analysis of metallomacrocycle 2-4NO$_3$ was similar to that of 1-4NO$_3$ (Fig. S1$^\dagger$).

The formation of the ferrocene-based metallomacrocyclic structure was further confirmed by an ESI-MS study in methanol. ESI-MS of 1-4NO$_3$ and 2-4NO$_3$ in methanol allowed the unambiguous assignment of [(bpy)Pd]$_4$L$^1_2$ and [(phen)Pd]$_4$L$^1-2$. As shown in Fig. 2, the multiple charged molecular ions of 1-4NO$_3$ were observed at m/z = 987.6, 637.7, and 462.8, assignable to [1-2NO$_3$]$_2^+$, [1-NO$_3$]$^3+$, and [1]$^4+$, respectively. Similarly, the molecular ions of 2 were at m/z = 669.3 [2-NO$_3$]$^2+$ and 487.1 [2]$^4+$ (Fig. S2$^\dagger$).

Finally, the configuration of the ferrocene-based metallomacrocycle was confirmed by the X-ray single-crystal diffraction study of 1-4NO$_3$. The ORTEP diagram of 1 is shown in

![Scheme 1 Synthesis of ferrocene-based organometallic macrocycles.](image-url)
Fig. 3. By slow vapor diffusion of ether, complex 1·4NO$_3$ in methanol crystallizes in the tetragonal space group I4/m. The crystal structure reveals a Pd$_4$Fe$_2$ hetero-metallomacrocyclic structure with two ferrocene-based dipyrazolate ligands doubly bridged by two dipalladium corners. Within each corner, two (bpy)Pd$^{II}$ planes display an “open clip” disposition. The Pd1⋯Pd1A separation of 3.273 Å indicates the existence of weak metal–metal interaction. The dihedral angle between the two pyrazolate (N3–N3A and N4–N4A) planes at the corner is 86.6°, which is smaller than the angles of N1–Pd1–N3 (96.6°), N2–Pd1–N4 (95.8°). The sizes of this supramolecule and its inner square-shape cavity are approximately 14 × 15 and 6 × 11 Å, respectively. Separation of Pd–N is around 2 Å, and the average distance between Fe and C is about 1.9 Å. The most interesting feature of the structure is the trapping of NO$_3^-$ near the clips (formed by (bpy)Pd1 and (bpy)Pd1A planes) through hydrogen bonding of C9–H9⋯O2 (118.0°, 2.030 Å). In the crystal packing diagram, every four macrocycles surround eight nitrate anions, leading to the formation of a larger square with hydrogen bonds (2.030 Å), C–H⋯O weak interaction (2.666 and 2.705 Å) and C–H⋯π interaction (average 2.90 Å) (Fig. S3†). In the needle shape crystal, molecules of complex 1·4NO$_3$ tend to pack along the c-axis with molecules alternately overlapped (Fig. S4†).

Synthesis and characterizations of metallomacrocycles based on ligands L$_2$ and L$_3$

As seen from Scheme 2, [[(bpy)$_2$Pd$_2$(NO$_3$)$_2$](NO$_3$)$_2$] or [[(phen)$_2$Pd$_2$(NO$_3$)$_2$](NO$_3$)$_2$] was simply mixed with a suspension containing one equiv. of H$_2$L$^2$ or H$_2$L$^3$ in H$_2$O at 80 °C over 12 h, resulting in positively-charged metallomacrocycles [M$_4$L$^2_2$]·(NO$_3$)$_4$ [M = bpyPd$^{III}$, L = L$^2$, 3·NO$_3$; M = phenPd$^{III}$, L = L$^2$, 4·NO$_3$; M = bpyPd$^{II}$, L = L$^3$, 5·NO$_3$; M = phenPd$^{II}$, L = L$^3$, 6·NO$_3$]

Scheme 2 Synthesis of square-type metallomacrocycles.
in quantitative yield. Several characterization methods, including NMR, ESI-MS, X-ray single crystal diffraction, and elemental analysis, were employed to confirm the formation of these metallomacrocycles.

The NMR analysis of these complexes clearly showed that symmetrical 1:1 (bpy)_{2}Pd^{II} or (phen)_{2}Pd^{II} corners to the dipyrazole ligand complexes were formed. From the \(^1\)H NMR spectrum of 4-4NO\(_3\) shown in Fig. 4, the signals at 9.00–8.98 (doublet), 8.72–8.70 (doublet), 8.27 (singlet), and 8.07–8.04 (doublet–doublet) ppm correspond to the a, c, d, and b protons of the phen, respectively, while other signals belong to the organic ligand \(L_2\). The signals of phenyl stand at 7.43–7.25 ppm as one doublet and two triplets. The corresponding resonances of the methylene and methyl groups of the ligand \(L_1\) appear in the upfield region, which reveals singlets each at 5.18 and 2.45 ppm, respectively. The NMR analysis of metallomacrocycles 3-4NO\(_3\), 5-4NO\(_3\), and 6-4NO\(_3\) represent similar results to that of 4-4NO\(_3\) (Fig. S5–S7†).

The assignments of \([M_4L_2]^{4+}\)-type metallomacrocycles were based on ESI-MS analysis, where multiple charged molecular ions assignable to intact cyclic complexes were observed. ESI mass spectra of 3-4NO\(_3\) and 4-4NO\(_3\) in methanol suggested the unambiguous assignment of the \([\{(bpy)Pd\}L_2^2\] and \([\{(phen)\}Pd\]L_2\) products, respectively. As shown in Fig. 5, the multiple charged molecular ions of 4 at \(m/z = 1005.6, 649.8,\) and 471.8 were ascribed to \([4\cdot2NO_3]^{2+}\), \([4\cdot3NO_3]^{3+}\), and \([4\cdot4NO_3]^{4+}\). Similarly, the multiple charged molecular ions of 3 were at \(m/z = 957.7\) \([3\cdot2NO_3]^{2+}\), 617.8 \([3\cdot3NO_3]^{3+}\), and 447.82 \([3\cdot4NO_3]^{4+}\) (Fig. S8†). In addition, the molecular ions of 5-4NO\(_3\) were at \(m/z = 631.9\) \([5\cdot3NO_3]^{3+}\) and 458.6 \([5\cdot4NO_3]^{4+}\), and those of 6-4NO\(_3\) were at \(m/z = 1027.3\) \([6\cdot2NO_3]^{2+}\), 665.1 \([6\cdot3NO_3]^{3+}\), and 482.4 \([6\cdot4NO_3]^{4+}\) (Fig. S9–S10†).

Single-crystal X-ray structural study of 4-4NO\(_3\) was carried out. The ORTEP diagram of 4-4NO\(_3\) is shown in Fig. 6. Complex 4-4NO\(_3\) crystallizes in the monoclinic space group \(C2/c\). The square-shape hybrid metallomacrocycle consists of two dipyrazole ligands doubly bridged by \([\{(phen)\}Pd^{II}\] corners. Within each corner, the dihedral angle of the clips between the two \(\{(phen)\}Pd^{II}\) planes is 72.7°. The Pd⋯Pd separation of 3.182 Å indicates typical Pd⋯Pd interactions. Separations of Pd–N are around 2.0 Å. The dihedral angle between the two pyrazole (N5–N6 and N7–N8) planes at the corner is 66.5°. The angles of N1–Pd1–N2 and N6–Pd1–N8 are 81.9 and 86.3°, which are smaller than those of N1–Pd1–N8 (96.2°), N2–Pd1–N6 (95.6°). This molecule is nearly 22 × 25 Å, while the size of the inner cavity is about 3 × 6 Å. Interestingly, all the NO\(_3^-\) anions are located beside the clips formed by the two phen planes via multiple C–H⋯O hydrogen bonds. In the crystal, molecules of complex 4-4NO\(_3\) pack with C–H⋯O hydrogen bonds and weak intermolecular C–H⋯π and π⋯π
interactions involving phen and benzene rings between the neighboring molecules (Fig. S11†).

Anion sensing for redox-active metallomacrocycles

For the hetero-metallomacrocyles employed with redox-active ferrocene, cyclic voltammetry (CV) experiments of 1-4PF6 (the PF6− salt of 1) were carried out in CH3CN containing 0.1 M (n-Bu)4NPF6 as the supporting electrolyte. The macrocycle exhibited a reversible one-electron redox wave that is typical for ferrocene derivatives.16

The anion sensing properties of receptor 1-4PF6 (5.0 × 10−4 M) were investigated by SWV and CV in CH3CN. The electrochemical behaviors of the receptor with and without various concentrations of anions (Br−, Cl−, F−, CF3SO3−, CH3COO−, H3PO4−, HSO4−, and NO3−) were analyzed.

Firstly, SWV was employed to make a good estimation about the E1/2 values and obtain well-resolved potential information (Fig. 7a) upon addition of various anions. Each test shows a highest current peak in the region of 0–0.1 V. The presence of H3PO4− resulted in few changes on the SWV.

Addition of NO3−, CF3SO3−, CH3COO−, and F− led to a current decrease, while addition of HSO4−, Br−, and Cl− resulted in a current increase. Few changes of the Ep values were observed upon addition of these anions. Most interestingly, compared to other anions, Br− provokes a second wave at more positive potential (around 0.4 V) significantly, which could be attributed to the formation of a receptor–anion complex.17

To further investigate the Br− sensing property of receptor 1-4PF6, the CV titrations of Br− were carried out in 0.1 M (n-Bu)4NPF6-CH3CN solution (Fig. 7b). From Fig. 7b, it can be seen that another anodic peak appeared at approximately 0.45 V and the current decreased constantly upon the continuous addition of Br− to the CH3CN solution containing receptor 1-4PF6. These behaviors on CV could be attributed to the formation of a receptor–anion complex, which agrees with the SWV experiment results obtained previously. Job’s plot analysis suggested the 1 : 4 stoichiometry of the receptor–anion complex (Fig. S12†).

NMR was employed to study the mechanism of Br− sensing. Upon addition of 4 equiv. of (n-Bu)4NBr, the signal of Ha in bpy of 1 exhibits remarkable downfield shift (δ ≈ 0.08 ppm), while other signals remain unchanged or change slightly (Fig. 8), indicating Ha in bpy as the interacting sites.18

Based on the above results and in view of the fact that these metallomacrocyles could bond NO3− anions through hydrogen bonds on bpy or phen in solid state single crystals, the possible mechanism for Br− sensing can be explained as that, in CH3CN solution, macrocycle 1 could trap four Br− at Ha via C–H⋯Br hydrogen bonds19 to form a new receptor–anion complex ([1-4Br]), which could be detected and reported by CV, SWV, and NMR analysis.

Experimental

Materials

All chemicals and solvents were of reagent grade and were purified according to conventional methods.20 The metal–diimine complexes [(bpy)2Pd2(NO3)2]2(NO3)2 and [(phen)2Pd2(NO3)2]2(NO3)2 (where bpy = 2,2′-bipyridine and phen = 1,10-phenanthroline) (Chart 1) were prepared according to literature procedures.21
Correction for all complexes was performed using SADABS.22 Chromated Mo Kα radiation (α = 0.71073 Å). The absorption correction for all complexes was performed using SADABS. The organic ligand, 1,1′-bis(1H-pyrazol-4-yl)methylferrocene (H2L1), was synthesized according to the published methods.24

The other two bipyrazole ligands, 4,4″-(5-benzoxyl)-1,3-phenylene)bis(3,5-dimethyl-1H-pyrazole) (H2L2), and 4,4″-(5-octyloxy)-1,3-phenylene)bis(3,5-dimethyl-1H-pyrazole) (H2L3), are new compounds and were synthesized using a method similar to that employed for other known ligands20 (Chart 2).

**Synthesis**

The authors describe the synthesis of various complexes. They start with the organic ligand, 1,1′-bis(1H-pyrazol-4-yl)methylferrocene (H2L1), which they synthesize according to published methods. They also synthesize other bipyrazole ligands, 4,4″-(5-benzoxyl)-1,3-phenylene)bis(3,5-dimethyl-1H-pyrazole) (H2L2) and 4,4″-(5-octyloxy)-1,3-phenylene)bis(3,5-dimethyl-1H-pyrazole) (H2L3), which are new compounds.

**Crystallographic data for complexes 1-4NO3 and 4-NO3_H2O**

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<th>Formula</th>
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<td>12.601(18)</td>
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ρcalc (g cm⁻³): 1.244 (1.372)
μ (mm⁻¹): 0.935 (0.727)
F(000): 4224 (4504)
2θmax (°): 50.2 (52.00)
No. unique data: 5177 (10 593)

Parameters: 312 (640)

GOF (P(2)²): 1.01 (1.09)
R [P(2)² > 2σ(P(2)²)] wR[P(2)²]: 0.0413, 0.0833 (0.0651, 0.1372)

Δρmax | Δρmin (e Å⁻³): 0.62, -0.24

ρcalc = (|Fo|² − |Fp|²)/2N, where n and p denote the number of data points and the number of parameters, respectively.

**Table 1 Crystallographic data for complexes 1-4NO3 and 4-NO3_H2O**

**Chart 1 All dipalladium complexes.**

**Chart 2 All organic ligands.**

**In instrumentation**

1H NMR experiments were performed on a Bruker Avance DMX400 spectrometer. ES-MS measurements were performed with an HP5989B mass spectrometer. Elemental analyses were performed on a Thermoquest Flash EA 1112 instrument.

Cyclic voltammetry (CV) and square wave voltammetry (SWV) studies were performed on a CHI620b electrochemical analyzer in 0.1 M ([n-Bu]4N)PF6-CH3CN solution with a platinum electrode as the working electrode at 25 °C (scan rate: 100 mV s⁻¹). A 0.01 M Ag/AgNO3 electrode (in 0.1 M ([n-Bu]4N)PF6-CH3CN) was employed as reference electrode and a Pt electrode (d = 0.3 mm) was used as the supporting electrode. Redox titration experiments were obtained after addition of anions as their ([n-Bu]4N)⁺ salts to the solution of receptors 1-4PF6 in CH3CN (5.0 × 10⁻⁴ M) containing 0.1 M ([n-Bu]4N)PF6.

**X-Ray structural determinations**

X-Ray diffraction measurements were carried out on a Bruker Smart Apex CCD area detector equipped with a graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The absorption correction for all complexes was performed using SADABS.22 All the structures were solved by direct methods and refined employing full-matrix least-squares on F² by using SHELXTL (Bruker, 2000) program and expanded using Fourier techniques.23 All non-H atoms of the complexes were refined with anisotropic thermal parameters. The hydrogen atoms were included in idealized positions. Final residuals along with the unit cell, space group, data collection, and refinement parameters are presented in Table 1.

**Synthesis**

The ligand 1,1′-bis(1H-pyrazol-4-yl)methylferrocene (H2L1), was synthesized as described in the literature.24 The other two bipyrazole ligands were synthesized using a similar method to that employed for other known ligands.20 (Chart 2).

4,4″-(5-Benzyloxy)-1,3-phenylene)bis(3,5-dimethyl-1H-pyrazole) (H2L1). 1H NMR (CDCl3, 300 MHz): δ 6.75 (s, 3 H, Ar-H-2,4,6), 4.01 (t, J = 6 Hz, 2 H), 2.37 (s, 12 H, -CH3), 1.80-1.82 (m, 2 H), 1.48 (m, 2 H), 1.29 (m, 8 H), 0.88 (br s, 3 H), 13C NMR (CDCl3, 150.91MHz): δ 159.17, 141.94, 135.02, 128.59, 118.09, 113.57, 70.03, 11.69; Mass spectrum (MALDI-TOF): m/z = 373.1 [M + H]; Anal. Calcd for C23H24N4O (%): C, 74.17, H, 6.49, N, 15.04; Found: C, 73.72, H, 6.76, N, 14.96.

4,4″-(5-Octyloxy)-1,3-phenylene)bis(3,5-dimethyl-1H-pyrazole) (H2L2). 1H NMR (CDCl3, 300 MHz): δ 8.63 (s, 2 H, -NH), 7.37-7.16 (m, 5 H, Ar-H), 6.73 (s, 2 H, Ar-H-2,4,6), 6.71 (s, 1 H, Ar-H-6), 5.03 (s, 2 H, -CH2), 2.26 (s, 12 H, -CH3); 13C NMR (CDCl3, 100 MHz): δ 158.68, 141.76, 137.01, 135.08, 128.59, 127.91, 127.33, 122.99, 118.09, 113.57, 70.03, 11.82; Mass spectrum (MALDI-TOF): m/z = 373.1 [M + H]; Anal. Calcd for C23H24N4O (%): C, 74.17, H, 6.49, N, 15.04; Found: C, 73.72, H, 6.76, N, 14.96.

4,4″-(5-Benzoxyl)-1,3-phenylene)bis(3,5-dimethyl-1H-pyrazole) (H2L3). 1H NMR (CDCl3, 300 MHz): δ 8.63 (s, 2 H, -NH), 7.37-7.16 (m, 5 H, Ar-H), 6.73 (s, 2 H, Ar-H-2,4,6), 6.71 (s, 1 H, Ar-H-6), 5.03 (s, 2 H, -CH2), 2.26 (s, 12 H, -CH3); 13C NMR (CDCl3, 100 MHz): δ 158.68, 141.76, 137.01, 135.08, 128.59, 127.91, 127.33, 122.99, 118.09, 113.57, 70.03, 11.82; Mass spectrum (MALDI-TOF): m/z = 373.1 [M + H]; Anal. Calcd for C23H24N4O (%): C, 74.17, H, 6.49, N, 15.04; Found: C, 73.72, H, 6.76, N, 14.96.

 [(bpy)2Pd(NO3)4] (1-4NO3). [(bpy)2Pd2(NO3)4] (23.2 mg, 0.03 mmol) was added to a suspension of H2L1 (12.2 mg, 0.03 mmol) in H2O (1 mL), and the mixture was stirred for 2 h at room temperature. Then acetone (0.5 mL) was added and the mixture was placed under 80 °C for 12 h. The resulting clear green solution was cooled to room temperature, leading to the formation of pure 1-4NO3 as a gray precipitate. The precipitate was collected and dried under vacuum.

Chart 1 All dipalladium complexes.

Chart 2 All organic ligands.
conditions. Yield: 24.2 mg (77%). 1H NMR (400 MHz, DMSO-d6, 25 °C, Si(CH3)4, ppm): 8.72–8.70 (d, J = 7.8 Hz, 8H, bpy-H), 8.45–8.41 (t, J = 7.8 Hz, 8H, bpy-H), 8.22–8.21 (d, J = 5.3 Hz, 8H, bpy-H), 7.77–7.73 (t, J = 6.7 Hz, 8H, bpy-H), 3.99 (s, 8H, Fc-H), 3.88 (s, 8H, Fc-H), 3.46 (s, 8H, –CH2), 2.35 (s, 24H, –CH3). ESI-MS (methanol) m/z: 987.1 [2-NO3]15, 637.1 [NO3]15, and 462.8 [1]15. Elemental analysis calec (%) for C45H40Fe2N20O12P2C3: H, 3.96; C, 52.87; H, 3.59; N, 13.12; found: C, 52.63; H, 3.74; N, 12.79.

X-Ray quality crystals were obtained by the slow vapor diffusion of diethyl ether into a solution of 4-NO3 in methanol at room temperature.

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\{\text{[bpy]Pd}_2L^2\text{[NO}_3\text{]}_4\} \quad (5\text{-NO}_3)\]

The same procedure as employed for 3-NO3 was followed for the synthesis of 5-NO3, except that H2L4 (11.8 mg, 0.03 mmol) was used as the starting material. Yield: 30.1 mg (96%). 1H NMR (400 MHz, DMSO-d6, 25 °C, Si(CH3)4, ppm): 8.76–8.74 (d, J = 7.1 Hz, 8H, bpy-H), 8.48 (s, 8H, bpy-H), 8.41 (s, 8H, bpy-H), 7.80 (s, 8H, bpy-H), 6.78 (s, 4H, Ar-H), 5.98 (s, 2H, Ar-H), 4.04 (s, 4H, –OCH2), 2.46 (s, 24H, –CH3), 1.74 (s, 4H, –CH2), 1.43–1.25 (m, 20H, –CH2), 0.84 (s, 6H, –CH3). ESI-MS (methanol): m/z 613.9 [5(NO3)]15 and 458.6 [5]15. Elemental analysis calec (%) for C39H36N20O12P2C3: C, 50.73; H, 4.64; N, 13.45; found: C, 50.57; H, 4.94; N, 13.31.

\[
\{\text{[phen]Pd}_2L^2\text{[NO}_3\text{]}_4\} \quad (6\text{-NO}_3)\]

The same procedure as employed for 3-NO3 was followed for the synthesis of 6-NO3, except that \{[phen]Pd(NO3)2\}(NO3) (24.6 mg, 0.03 mmol) and H2L4 (11.8 mg, 0.03 mmol) were used as the starting material. Yield: 31.1 mg (95%). 1H NMR (400 MHz, DMSO-d6, 25 °C, Si(CH3)4, ppm): 9.07–9.05 (d, J = 8.2 Hz, 8H, phen-H), 8.79–8.78 (d, J = 4.7 Hz, 8H, phen-H), 8.34 (s, 8H, phen-H), 8.15–8.11 (dd, J1 = 8.2 Hz, J2 = 5.3, 8H, phen-H), 6.87 (s, 4H, Ar-H), 6.07 (s, 2H, Ar-H), 4.10–4.07 (t, J = 6.3 Hz, 4H, –OCH2), 2.56 (s, 24H, –CH3), 1.79–1.75 (t, J = 7.2 Hz, 4H, –CH2), 1.46–1.26 (m, 20H, –CH2), 0.85–0.82 (t, J = 6.7 Hz, 6H, –CH3). ESI-MS (methanol): m/z 1027.3 [6-NO3]15, 665.1 [6(NO3)]15, and 482.4 [6]15. Elemental analysis calec (%) for C42H36N20O12P2C3: C, 52.90; H, 4.44; N, 12.85; found: C, 52.79; H, 4.72; N, 12.65.

Conclusions

Redox-active and m-phenylene-based dipyrrozolate-bridged metallomacrocycles with dipalladium(u) corners can be assembled from \{[bpy]Pd(NO3)2\} or \{[phen]Pd(NO3)2\} and dipyrrozole ligands in a 1:1 molar ratio in water. The assemblies have been characterized by various methods, such as, 1H NMR, ESI-MS, elemental analysis, and single-crystal X-ray diffraction. As known from their crystal structures, the receptors could bond NO3- via C–H···O hydrogen bonds in the solid state. In addition, the anion sensing properties of metallomacrocycle 1 in CH3CN (or CD3CN) for NMR solution were investigated via square wave voltammetry, cyclic voltammetry titration, and NMR analysis, which shows that macrocycle 1 can sense Br- effectively. These positively-charged hetero-metallomacrocycles provide an alternative choice for potential novel anion receptors.

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