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Metal Cation Controlled Supramolecular Assembly of 1-Butyl-4,4′-bipyridinium and Cucurbit[8]uril

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Three supramolecular assemblies $[(C_{14}H_{17}N_2)_2{\subset}C_{48}H_{48}N_{32}O_{16}]Cl_2{\cdot}23H_2O$ (**1**), $\{[C_{14}H_{17}N_2Cu(H_2O)_5]_2{\subset}C_{48}H_{48}N_{32}O_{16}\}[(C_{14}H_{17}N_2)_2{\subset}C_{48}H_{48}N_{32}O_{16}]Cl_4(NO_3)_4{\cdot}32H_2O$ (**2**), and $\{[C_{14}H_{17}N_2Ni(H_2O)_5]_2{\subset}C_{48}H_{48}N_{32}O_{16}\}[(C_{14}H_{17}N_2)_2{\subset}C_{48}H_{48}N_{32}O_{16}]Cl_2(NO_3)_6{\cdot}22H_2O$ (**3**) were synthesized in aqueous solution and characterized by X-ray diffraction. The crystal structures of these supramolecular assemblies show that Q[8] can selectively encapsulate either the bipyridinium or butyl moiety of the 1-butyl-4,4′-bipyridinium guest in its hydrophobic cavity to form ternary complexes through the influence of metal–ligand coordination. The main driving force of the selective formation of these supramolecular assemblies may be due to ion–dipole interactions.

Introduction

The inclusion of two or more guest molecules into a same host structures has attracted great interest over the past two decades.[1–7] This interest has been stimulated by the potential applications of these supramolecular assemblies in many areas such as molecular recognition,[5] molecular reactive devices,[6] supramolecular polymers,[7] and so on. Owing to their internal hydrophobic cavities that are available for the encapsulation of many kinds of guest molecules in aqueous solution, cucurbit[*n*]urils (*n* = 5–8, 10, hereafter abbreviated as Q[*n*], Figure 1) are the most fascinating macrocyclic host systems.[8] Q[8], which has a cavity comparable to that of γ-cyclodextrin, is particularly attractive because it is large enough to accommodate simultaneously two aromatic molecules within the cavity to form a 1:2 ternary complex.[4] For example, a series of supramolecular architectures in which Q[8] encapsulates 1 equiv. of an electron-donor molecule and 1 equiv. of an electron-acceptor molecule inside the cavity to form a stable 1:1:1 ternary complex have been synthesized and studied by Kim and co-workers.[9] Kaifer and co-workers reported the recognition of neurotransmitters such as dopamine by using host-stabilized charge-transfer interactions.[10] Urbach examined the potential for Q[8]·MV (methyl viologen) to recognize N-terminal tryptophan in aqueous solution.[5] Ramamurthy and co-workers[11] found that Q[8] mediates intermolecular photodimerization of cinnamic acid, *trans*-1,2-bis(*n*-pyridyl)ethylenes, and stilbazoles. In the above-mentioned work, we noticed that at least one aromatic group of each guest molecule was situated in the cavity of Q[8].

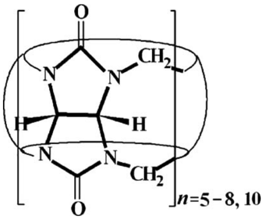

Figure 1. Molecular structure of cucurbit[*n*]urils (*n* = 5–8 and 10).

Recently, the Kim group discovered that alkyl chains adopt a U-shaped conformation when bound in the cavity of Q[8].[12] The results of Kim prompted us to wonder whether two alkyl groups could be encapsulated in the same Q[8] host instead of two aromatic groups. With this idea in mind, we wished to address three specific questions: (1) Is it possible to have two alkyl groups residing in the internal cavity of Q[8]? (2) Is it possible to demonstrate the competitive encapsulation of alkyl groups and aromatic groups? (3) Is it possible to control effectively and selectively the encapsulation.

Thus, we designed and synthesized 1-butyl-4,4′-bipyridinium (see the Experimental Section), a molecule with an alkyl (butyl) group and an aromatic (bipyridinium) group. In the present work, we report that Q[8] can interact with 1-butyl-4,4′-bipyridinium, forming highly stable 1:2 ternary complexes in aqueous solution and that the encapsulated group of 1-butyl-4,4′-bipyridinium in Q[8] is controlled by metal–ligand coordination.

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Results and Discussion

Description of the Crystal Structures of Three Supramolecular Assemblies 1–3

The reaction of Q[8] with 1-butyl-4,4′-bipyridinium resulted in the formation of supramolecular assembly **1**. The X-ray crystal structure of assembly **1** (Figure 2) clearly reveals that two 1-butyl-4,4′-bipyridinium guests, each situated in opposite positions, are included inside the cavity of the Q[8] host. Interestingly, there are two inclusion conformations, although both host–guest inclusion complexes in assembly **1** have the same 1:2 stoichiometry between the host and the guest. In one of the two host–guest inclusion complexes (Figure 2, **1a**), two bipyridinium moieties of two 1-butyl-4,4′-bipyridinium guests are parallel and separated by less than 3.801 Å (Figure 3, left). The axis of the parallel guest pair is almost vertical to the plane formed by eight carbonyl oxygen atoms of the Q[8] host. Two 1-butyl-4,4′-bipyridinium guests are stabilized by both the hydrophobic cavity interaction and the π···π stacking interaction between two bipyridinium rings. In the other host–guest inclusion complex (Figure 2, **1b**), the centrosymmetric guest pair, separated by 3.634 Å (Figure 3, right), interact with each other by forming π···π interactions between two bipyridinium rings, similar to that found in the fore-mentioned host–guest inclusion complex. It is noteworthy that the parallel guest pair lean toward the carbonyl groups of the Q[8] host, which is different from host–guest inclusion complex **1a**. The most remarkable feature of the two host–guest inclusion complexes in assembly **1** is that aromatic (bipyridinium) moieties, rather than alkyl (butyl) moieties, are located in the cavity of Q[8]. This result suggests that the aromatic moiety is more favorable than the alkyl moiety to the hydrophobic cavity of Q[8]. In the crystal structure of assembly **1**, each host–guest molecule is surrounded by six neighbors, and they interact to form a hydrogen-bonded layer structure. Naturally, the space between the layers is filled with water molecules and chloride anions.

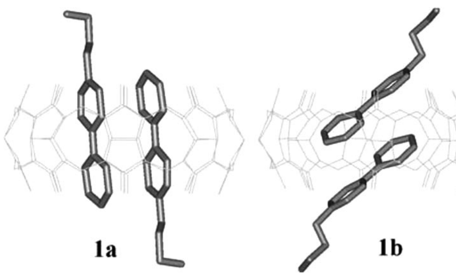

Figure 2. X-ray crystal structure of the two host–guest inclusion complexes in assembly **1**; solvate water molecules and anions are omitted for clarity.

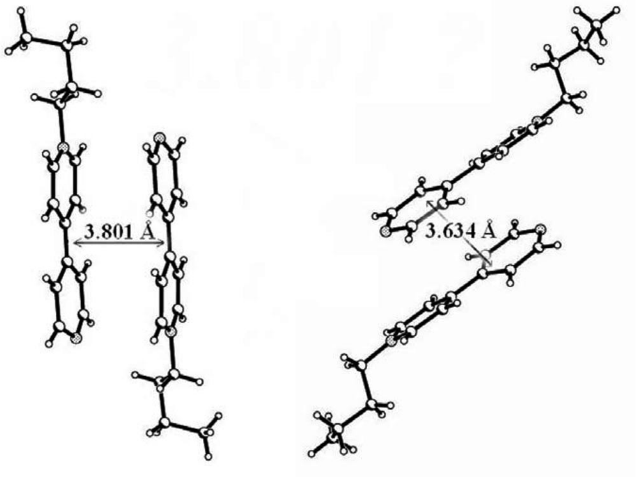

Figure 3. The π···π interactions between the two bipyridinium moieties of two 1-butyl-4,4′-bipyridinium guests in Q[8] in assembly **1**.

Because metal coordination on the pyridyl nitrogen atom is likely to increase the size of the aromatic moiety, we envisioned that Q[8] might be able to selectively capture two butyl moieties into its hydrophobic cavity to form a 1:2 inclusion complex. Thus, cupric nitrate was added to the reaction mixture, which led to the formation of supramolecular assembly **2**. Its crystal structure analysis (Figure 4) revealed that the Cu^{2+} atom is a six-coordinate center and that it is coordinated to five water molecules and one pyridyl nitrogen from the 1-butyl-4,4′-bipyridinium unit. The bond lengths of $Cu–O_{water}$ and $Cu–N_{bipyridinium}$ are 1.973(6)–2.414(7) and 2.013(6) Å, respectively. As anticipated, in one of two host–guest inclusion complexes in assembly **2** (Figure 4, **2a**), the copper-coordinated bipyridinium moieties reside outside and the butyl moieties are located inside the hydrophobic cavity of Q[8]. It should be noted that the two 1-butyl-4,4′-bipyridinium molecules are held together by C–H···π interactions[16] between the bipyridinium and butyl groups (Figure 5). In the other host–guest inclusion complex (Figure 4, **2b**), the uncoordinated bipyridinium moieties were encapsulated inside the hydrophobic cavity of the Q[8] host and the butyl groups reside outside, demonstrating the importance of metal coordination.

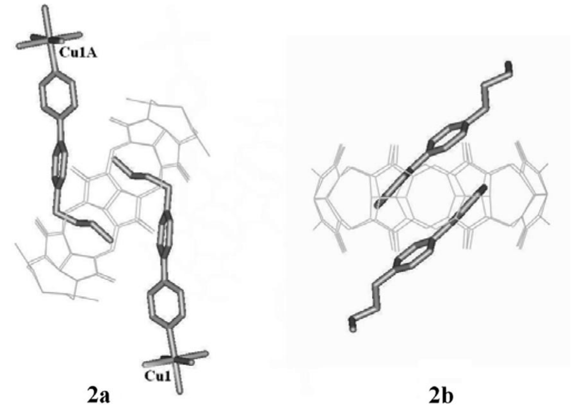

Figure 4. X-ray crystal structure of the two host–guest inclusion complexes in assembly **2**; solvate water molecules and anions are omitted for clarity.

Supramolecular assembly **3** was prepared by the same method used for the preparation of **2** but nickel salt was used instead. It crystallizes in space group $P\bar{1}$.[15] Single-crystal structural analysis revealed that the asymmetric unit

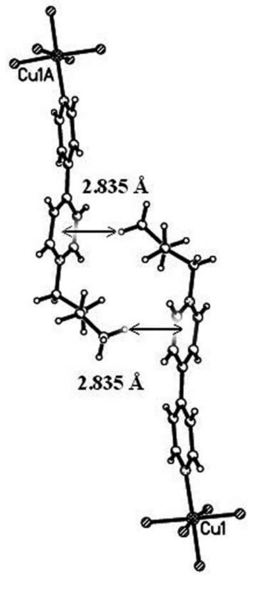

Figure 5. The C–H···π interaction between the bipyridinium and butyl moieties of 1-butyl-4,4′-bipyridinium in Q[8].

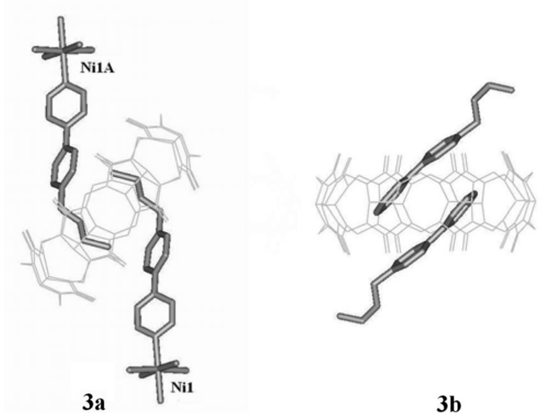

Figure 6. X-ray crystal structure of the two host–guest inclusion complexes in assembly **3**; solvate water molecules and anions are omitted for clarity.

of assembly **3** consists of 1 Q[8] molecule, 2 nitrate anions, 11 water molecules, and 2 1-butyl-4,4′-bipyridinium (one is coordinated to Ni^{2+}) molecules. Although assemblies **2** and **3** have different unit parameters, these two complexes have almost the same inclusion conformation. As shows in Figure 6, the inclusion architecture of the host–guest inclusion complex in assembly **3** is quite similar to that in assembly **2**, and the only difference is that Ni^{2+} ions are present instead of Cu^{2+} ions. The bond lengths of Ni–O_{water} and Ni–$N_{bipyridinium}$ in the six-coordinate geometry are 2.040(6)–2.094(5) and 2.090(6) Å, respectively. In one of the two host–guest inclusion complexes (Figure 6, **3a**), the nickel-coordinated bipyridinium moieties reside outside and the butyl moieties are located inside the hydrophobic cavity of Q[8]. C–H···π interactions[16] also appeared to exist between the bipyridinium and butyl moieties. In the other host–guest inclusion complex (Figure 6, **3b**), the uncoordinated bipyridinium moieties were encapsulated inside the cavity of Q[8] in a manner similar to that found in assembly **1**.

It must be mentioned that the 1-butyl-4,4′-bipyridinium salt was prepared as its bromide salt but that the three structures contain chloride. Without doubt, Q[8] is a source of chloride, as Q[8] is synthesized under hydrochloric conditions.

The host Q[8] macrocycle has significant steric rigidity and D_{8h} symmetrical conformation. However, a severe ellipsoidal deformation of the Q[8] macrocycle was observed in all these inclusion complexes. In the inclusion complexes of assembly **1**, the O···O diameters of the carbonyl portals of the Q[8] host range from 9.348 to 10.735 Å, whereas in the inclusion complexes of assembly **2**, the Q[8] portal diameters range from 8.765 to 11.131 Å. The deformation of the host Q[8] in assembly **2** is much more pronounced than that in assembly **1**. The same phenomenon was observed in the inclusion complexes of assembly **3**. To accommodate different guest pairs and to provide a best shape complementarity, all Q[8] hosts modulate their conformation spontaneously in the inclusion process.

Description of the ^1H NMR Spectra of the 1-Butyl-4,4′-bipyridinium Guest and the Q[8] Host

For better understanding of the orientations of the 1-butyl-4,4′-bipyridinium guest and the Q[8] host in solution, we carried out a ^1H NMR spectroscopy study in the absence of metal ions. The ^1H NMR spectra of 1-butyl-4,4′-bipyridinium and the guest bound to Q[8] are shown in Figure 7. Most of the signals for the bipyridinium protons (b′–d′) of the guest are shifted to higher field by $\delta = 0.2$ ppm relative to those of the free guest (Figure 7a), whereas no significant change in the chemical shifts are observed for the terminal part (e′–f′) of the aliphatic chain and one bipyridinium proton (a′). These findings indicates that the bipyridinium moiety is deeply encapsulated within the cavity of the Q[8] host and that the a′ proton is almost at the portal of the Q[8] host. Of course, the alkyl moiety of the guest is still outside the Q[8] host. Furthermore, the calculation of signal areas suggests that the large cavity of Q[8] can accommodate two bipyridinium guest molecules to form 1:2 host–guest inclusion complexes, which was confirmed by X-ray crystallography of assembly **1**.

Metal Ion Controlled Supramolecular Assembly

It is well known that aromatic moieties are favorable to the cavity of the Q[8] host, which is further confirmed by the X-ray crystal structure and ^1H NMR spectroscopic analysis of the host–guest inclusion complexes. To force the alkyl moiety to be selectively included in the cavity of Q[8], protective measures were taken to shield the bipyridinium moiety in the 1-butyl-4,4′-bipyridinium guest. Herein, Cu^{2+} and Ni^{2+} ions were introduced to coordinate the pyridyl nitrogen atoms. As shown in the host–guest inclusion complexes in assemblies **2** and **3**, the hydrated metal cations

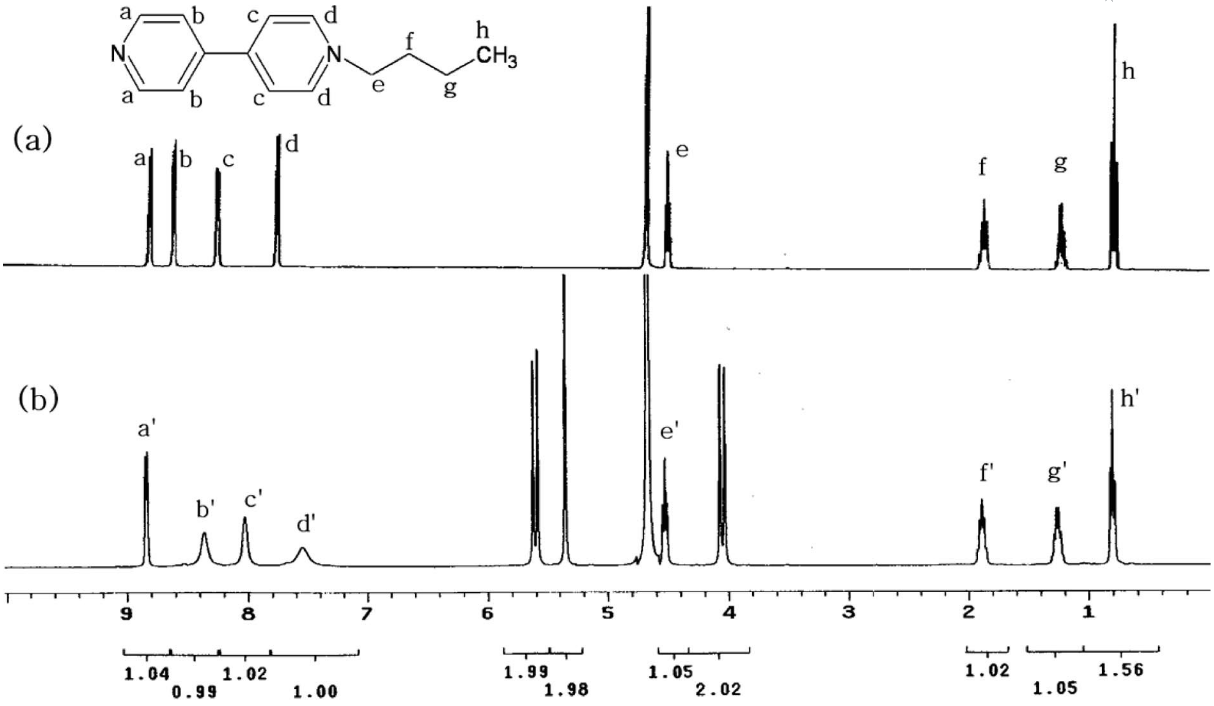

Figure 7. ^{1}H NMR spectra obtained in D_2O of (a) 1-butyl-4,4′-bipyridinium and (b) a 1:2 mixture of Q[8] and 1-butyl-4,4′-bipyridinium.

coordinated by the bipyridinium moiety were not encapsulated in the cavity of Q[8] as a result of hydrophobic effects and steric strain. Thus, the butyl moieties were encapsulated selectively by the Q[8] cavity. The metal–ligand coordination influenced which moiety of the 1-butyl-4,4′-bipyridinium guest was encapsulated in the hydrophobic cavity of the Q[8] host.

The driving force for the selective formation of the ternary complexes may due to the interactions between the ion–dipoles of the quaternary nitrogen atoms in the guest and the carbonyl oxygen atoms at the portals of the Q[8] host, rather than the host-stabilized charge-transfer interactions in other supramolecular assemblies that Kim et al. reported previously.[4] Additionally, several other reasons may be taken into account. The significant π···π stacking interaction induced by partial overlap between the aromatic rings may facilitate the stability of the guest pairs. Complementarity between the host and the guest is clearly crucial in determining selectivity.

Conclusions

As has been mentioned, we have synthesized three supramolecular assemblies of two 1-butyl-4,4′-bipyridinium guests and one Q[8] host in aqueous solution under different conditions. The three ternary complexes are stable and were isolated and characterized by X-ray crystallography. By comparing their structural differences, it was suggested that ion–dipole interactions were the driving force for the assembly of these ternary complexes and that the metal ion is key. In conclusion, for the first time, we successfully forced two alkyl groups to be included in the hydrophobic cavity of Q[8] through metal–ligand coordination. More importantly, this method offers new opportunities to construct supramolecular assemblies.

Experimental Section

General: Chemicals such as $Cu(NO_3)_2 \cdot 3H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ and solvents were commercially available and used as received without further purification. Cucurbit[8]uril was prepared by a published procedure.[13] The 1-butyl-4,4′-bipyridinium guest ($C_{14}H_{17}N_2$) was prepared by heating a mixture of 4,4′-bipyridine (1.0 equiv.), butyl bromide (1.0 equiv.), and polyethylene glycol (0.02 equiv.) at reflux for 5 h. The resulting precipitate was filtered and then loaded onto a silica gel (G 200) column, eluting with acetone/acetic acid (3:1). The second major species that was eluted was collected. The eluate was reduced in vacuo to a small volume, separated, and recrystallized from ethanol/diethyl ether (1:2). The crystals were collected, washed with diethyl ether, and air dried. The end product was obtained in 46.3% yield based on 4,4′-bipyridine. 1-butyl-4,4′-bipyridinium guest was characterized by ^{1}H NMR spectroscopy [^{1}H NMR (D_2O, 400 MHz): δ = 8.80 (d, J = 6 Hz, 2 H), 8.59 (d, J = 6 Hz, 2 H), 8.23 (d, J = 6 Hz, 2 H), 7.73 (d, J = 6 Hz, 2 H), 4.49 (t, J = 7 Hz, 2 H), 1.86 (m, J = 8 Hz, 6 H), 1.24 (m, J = 8 Hz, 2 H), 0.81 (t, J = 7 Hz, 3 H) ppm].

Crystal Structure Determination: Preliminary examination and data collection were performed with Mo-K_α radiation with the Bruker Smart Apex CCD diffractometer equipped with a graphite crystal incident beam monochromator (λ = 0.71073 Å) in $\omega/2\theta$ scan mode. Data were collected at 173 K. Absorption corrections were applied by using the multiscan program SADABS. Structural solution and full-matrix least-squares refinement based on F^2 were performed with the SHELXS-97 and SHELXL-97 program package,[14] respectively. All non-hydrogen atoms were refined with anisotropic displacement parameters. Carbon-bound hydrogen atoms were introduced at calculated positions. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. For all complexes, no hydrogen atoms are given for all isolated water molecules, as it is difficult and unnecessary. A summary of the crystallographic data, data collection, and refinement parameters for supramolecular assemblies **1**–**3** can be found in ref.[15]

$[(C_{14}H_{17}N_2)_2\subset C_{48}H_{48}N_{32}O_{16}]Cl_2\cdot 23H_2O$ (1): To an aqueous solution of 1-butyl-4,4′-bipyridinium (50 mL, 0.008 M) was added cucurbit[8]uril (0.27 g, 0.20 mmol). The mixture was stirred and heated at 80 °C for 20 min and then filtered. The filtrate solution was set aside for three weeks to allow colorless crystals of **1** to deposit. $C_{76}H_{128}Cl_2N_{36}O_{39}$ (2240.96): calcd. C 40.73, H 5.76, N 22.50; found C 40.47, H 5.92, N 22.36.

$\{[C_{14}H_{17}N_2Cu(H_2O)_5]_2\subset C_{48}H_{48}N_{32}O_{16}\}[(C_{14}H_{17}N_2)_2\subset C_{48}H_{48}N_{32}O_{16}]Cl_4(NO_3)_4\cdot 32H_2O$ (2): To an aqueous solution of 1-butyl-4,4′-bipyridinium (80 mL, 0.005 M) was added cucurbit[8]uril (0.27 g, 0.20 mmol) and $Cu(NO_3)_2\cdot 3H_2O$ (0.097 g, 0.40 mmol). The mixture was stirred and heated at 80 °C for 20 min and then filtered. The filtrate solution was set aside for two weeks to allow light blue crystals of **2** to deposit. $C_{152}H_{248}Cl_4Cu_2N_{76}O_{86}$ (4784.96): calcd. C 41.56, H 5.69, N 15.31; found C 41.33, H 5.82, N 15.17.

$\{[C_{14}H_{17}N_2Ni(H_2O)_5]_2\subset C_{48}H_{48}N_{32}O_{16}\}[(C_{14}H_{17}N_2)_2\subset C_{48}H_{48}N_{32}O_{16}]Cl_2(NO_3)_6\cdot 22H_2O$ (3): To an aqueous solution of 1-butyl-4,4′-bipyridinium (50 mL, 0.008 M) was added cucurbit[8]uril (0.27 g, 0.20 mmol) and $Ni(NO_3)_2\cdot 6H_2O$ (0.116 g, 0.40 mmol). The mixture was stirred and heated at 80 °C for 20 min and then filtered. The filtrate solution was set aside for two weeks to allow light green colorless crystals of **3** to deposit. $C_{152}H_{228}Cl_2N_{78}Ni_2O_{82}$ (4648.21): calcd. C 39.28, H 4.94, N 23.50; found C 39.03, H 5.11, N 23.36.

CCDC-726616 (for **1**), -726617 (for **2**), and -726618 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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[15] a) $[(C_{14}H_{17}N_2)_2\subset C_{48}H_{48}N_{32}O_{16}]Cl_2\cdot 23H_2O$: Monoclinic, a = 41.797(4) Å, b = 20.8588(14) Å, c = 27.7570(19) Å, β = 117.195(4)°, V = 21525(3) Å^3, Z = 4, $D_{calcd.}$ = 1.384 g cm^{-3}, reflns measured = 113313, unique reflns = 20472, R(int)= 0.0986, $R_1[I>2\sigma(I)]$ = 0.1112, $wR_2[I>2\sigma(I)]$ = 0.2808,

R_1(all data) = 0.1112, wR_2(all data) = 0.2808, *GOF* = 1.167; b) $\{[C_{14}H_{17}N_2Cu(H_2O)_5]_2{\subset}C_{48}H_{48}N_{32}O_{16}\}[(C_{14}H_{17}N_2)_2{\subset}C_{48}H_{48}N_{32}O_{16}]Cl_4(NO_3)_4{\cdot}32H_2O$: Triclinic, a = 16.6070(13) Å, b = 17.0928(13) Å, c = 20.5091(16) Å, α = 66.003(2)°, β = 77.568(3)°, γ = 89.155(3)°, V = 5176.5(7) Å^3, Z = 2, $D_{\mathrm{calcd.}}$ = 1.536 g cm^{-3}, reflns measured = 58186, unique reflns = 19564, R(int)= 0.1013, $R_1[I>2\sigma(I)]$ = 0.1068, $wR_2[I>2\sigma(I)]$ = 0.2770, R_1(all data) = 0.1857, wR_2(all data) = 0.3465, *GOF* = 1.041; c) $\{[C_{14}H_{17}N_2Ni(H_2O)_5]_2{\subset}C_{48}H_{48}N_{32}O_{16}\}$-$[(C_{14}H_{17}N_2)_2{\subset}C_{48}H_{48}N_{32}O_{16}]Cl_2(NO_3)_6{\cdot}22H_2O$: triclinic, a = 16.6706(18) Å, b = 16.6781(17) Å, c = 20.442(2) Å, α = 112.772(3)°, β = 101.844(4)°, γ = 90.102(3)°, V = 5108.1(9) Å^3, Z = 1, $D_{\mathrm{calcd.}}$ = 1.448 g cm^{-3}, reflns measured = 51161, unique reflns = 19232, R(int)= 0.1006, $R_1[I>2\sigma(I)]$ = 0.1128, $wR_2[I>2\sigma(I)]$ = 0.3140, R_1(all data) = 0.1946, wR_2(all data) = 0.3788, *GOF* = 1.130.

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