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Self-Assembly of Cucurbit[7]uril Based Triangular [4]Molecular Necklaces and Their Fluorescence Properties

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Abstract

Self-assembly of rigid-rod dipyrindine ligand **1** with $M(en)(NO_3)_2$ ($M = Pd, Pt$) affords triangular (3, 5) and square (4, 6) supramolecular coordination complexes (SCCs). The binding affinity of **1** toward CB[n]-type containers results in the formation of triangular [4]molecular necklaces ([4]MNs, 7 – 10) by either one-pot or post complexation approaches as evidenced by 1H NMR, diffusion ordered spectroscopy, and ESI-MS.

Pioneering work by the groups of Stoddart, Sauvage and Leigh have resulted in an in depth knowledge of the nature of the mechanical bond and utilisation of mechanically interlocked molecules (MIMs) to create functional molecular devices.¹ In the intervening years, these groups and others have used MIMs as the basis for advanced applications like molecular motors and machines, nanoscale devices and smart materials for drug delivery and imaging.² Whereas MIMs comprise at least one molecular ring threaded onto one molecular axle, a subset of MIMs known as [n]molecular necklaces ([n]MNs) comprise $n-1$ molecular rings threaded onto a macrocycle. The first example of a [3]MN, also known as a [3]catenane, was reported by Sauvage based on metal ion templation.³ In 1998, Stoddart reported the preparation of [4]MNs by templation based on aromatic donor-acceptor interactions.⁴ More recently, Kim, Stang and others synthesized [n]MNs ($n = 4, 5$) by utilising pairs of orthogonal (non)covalent interactions (e.g. metal-ligand coordination and host-guest complexation).⁵

Since the discovery of cucurbit[n]uril homologues (CB[n] ($n = 5, 6, 7, 8, 10$), Chart 1) in 2000, the supramolecular chemistry of CB[n]-type receptors has developed rapidly.⁶ In particular, the high binding affinities and selectivities that CB[n] display toward their guests along with the stimuli responsiveness (e.g. pH, chemical, photochemical, electrochemical) of CB[n] complexes have made them prime components for the preparation of complex functional systems.^{6a, 6b, 6c, 7} For example, CB[n] have been used to create chemical sensors, supramolecular materials, molecules and materials for drug solubilisation, delivery, and reversal, and as promoters of biological dimerisation events.⁸ Over the past two decades, the strategic combination of rigid ligands and metal-ions with well defined coordination

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Electronic Supplementary Information (ESI) available: Experimental procedures and characterization data and additional NMR, UV/Vis, Fluorescence, and ITC data.

geometries has lead to the creation of a variety of functional self-assemblies.⁹ Furthermore, some scientists have sought to extend the abilities of these systems by decorating them with molecular containers (e.g. crown ethers, pillarenes).^{5c, 10} However, the strategic merger of the structural features of macrocyclic metal-organic assemblies with the outstanding recognition properties of CB[n]-type receptors is relatively unexplored.¹¹ Very recently, we reported a Fujita-type metal organic cubooctahedron studded with 24 methyl viologen groups which non-covalently recruits CB[8] and doxorubicin prodrugs by heteroternary complexation and its ability to deliver doxorubicin to HeLa cells.¹² To make robust multivalent systems for imaging, delivery, and theranostic applications, namely those whose CB[n] components cannot dissociate, requires that CB[n] units be incorporated within MIMs. Herein, we report that ligand **1** self-assembles with M(en)(NO₃)₂ (M = Pd, Pt) and CB[n]-type receptors to form [4]MNs.

Chart 1 shows the structure of rigid-rod ligand **1** which features two terminal monocationic 4,4'-bipyridinium units and a central dicationic benzidinium unit.¹³ All three units constitute binding sites for CB[n]-type receptors, but the central dicationic benzidinium unit was expected to be preferred. The synthesis of **1** was accomplished in two steps (ESI). First, reaction of 4,4'-bipyridine with 2,4-dinitrochlorobenzene gave N-(2,4-dinitrophenyl)-4,4'-bipyridine (**2**).¹⁴ Next, the Zincke reaction¹⁵ of **2** with benzidine followed by anion exchange gave **1**•(NO₃⁻)₂ in 40% yield.

First, we studied the complexation behavior of **1** with CB[7] by ¹H NMR and UV/Vis spectroscopy. The ¹H NMR spectra recorded at various **1**:CB[7] stoichiometries (Fig. 1 and 2) established that two different complexes (**1**•CB[7] and CB[7]•**1**•CB[7]) coexist depending on the stoichiometry. When 1 equiv. of CB[7] is used, a single **1**•CB[7] complex is formed selectively. The ¹H NMR of **1**•CB[7] is shown in Fig. 2b and displays substantial upfield shifts for H_e & H_f (7.15 and 7.64 ppm) relative to free **1**. Conversely, the resonances for H_a – H_d of **1** shift slightly downfield upon complexation. The CB[7] cavity constitutes an NMR shielding region whereas the region just outside the C=O portals is slightly deshielding region,^{6c} which establishes that CB[7] binds to the benzidinium core of **1** whose geometry (**1**•CB[7]) is shown in Fig. 1. Addition of more CB[7] (1 equiv.) to [**1**•CB[7]] causes H_e and H_f to shift downfield whereas H_a – H_d shift upfield indicating translocation of CB[7] from benzidinium core to the terminal bipyridinium units to form **1**•CB[7]₂ (Fig. 1). UV/Vis titration of **1** (6.6 μM) with CB[7] (0–17.4 μM) results in a decreased absorbance at λ = 320 nm along with a bathochromic shift. A plot of A₃₂₀ versus [CB[7]] showed saturation at 2.0 molar ratio indicating tight 1:2 binding for the **1**/CB[7] system in agreement with the NMR results. ¹H NMR competition experiments between **1** and p-hexanediammonium ion for a limiting quantity of CB[7] allowed us to determine K_a = 8.6 × 10⁸ M⁻¹ for **1**•CB[7] (ESI, Fig. S36). Similarly, addition of **M2** to **1** initially gives **1**•**M2** followed by translocation to the terminal bipyridinium sites upon formation of **1**•**M2**₂ (ESI, Fig. S13 and S14).

Next, we studied the interaction between **1** and CB[8]. We hoped that CB[8] would bind in a 1:1 fashion to the central benzidinium unit which would leave cavity volume available for ternary complex formation. Unfortunately, the ¹H NMR titration at **1**:CB[8] ratios below 1:0.5 show the formation of the **1**₂•CB[8] (ESI, Fig. S8). Analysis of the complexation

induced chemical shifts for $H_a - H_f$ (all upfield) with $\mathbf{1}_2 \bullet \text{CB}[8]$ suggests that the benzidinium unit is the major binding site although other complex geometries may be populated as shown in Fig. 1. Further addition of CB[8] up to a 1:1 $\mathbf{1}:\text{CB}[8]$ ratio results in the disappearance of the resonances for $\mathbf{1} \bullet \text{CB}[8]_2$ and the presence of broadened resonances which suggests the formation of a $[\mathbf{1} \bullet \text{CB}[8]]_n$ oligomer based on CB[8]-induced homodimerisation of the bipyridinium binding sites.¹⁶ DOSY NMR measurements confirm that $[\mathbf{1} \bullet \text{CB}[8]]_n$ ($D = 7.94 \times 10^{-11} \text{ m}^2/\text{s}$) is substantially larger than $\mathbf{1}_2 \bullet \text{CB}[8]$ ($D = 3.16 \times 10^{-10} \text{ m}^2/\text{s}$). Our inability to obtain the 1:1 $\mathbf{1} \bullet \text{CB}[8]$ complex, suggested that the planned synthesis of $[n]\text{MNs}$ incorporating CB[8] might be challenging.

Next, we prepared the unthreaded SCCs¹⁷ by heating ligand **1** (5.5 mM) with an aqueous solution of $\text{Pd}(\text{en})(\text{NO}_3)_2$ (100 °C, 24 h). ^1H NMR displayed resonances for two SCC's (ratio = 86:14) that were of different size as determined by diffusion ordered spectroscopy (DOSY) analysis (Fig. 3 and ESI Fig. S18). Diagnostic downfield shifts of H_a were observed for **3** ($\delta = 0.09$ ppm) and for **4** ($\delta = 0.21$ ppm), which establishes that the Pd^{2+} center is bound to the terminal pyridine groups. We attribute the low magnitude of these shifts to the presence of the charged pyridinium substituent as previously observed by Quintela.^{17c} We hypothesised that two products are triangle **3** (most abundant, $D = 3.02 \times 10^{-10} \text{ m}^2/\text{s}$) and square **4** ($D = 2.18 \times 10^{-10} \text{ m}^2/\text{s}$). When **1** was reduced from 5.5 to 2.5 mM, the relative abundance of **3** with respect to **4** increased upon dilution from 86% to >99% (**4** is below NMR detection limit). When **3** was subjected to ESI-MS, molecular ion peaks at 466.2 ($[\text{Pd}_3\mathbf{1}_3](\text{NO}_3)_7^{5+}$), 615.2 ($[\text{Pd}_3\mathbf{1}_3](\text{NO}_3)_8 + 4\text{H}_2\text{O}]^{4+}$) and 815.8 ($[\text{Pd}_3\mathbf{1}_3](\text{NO}_3)_9^{3+}$) were observed corresponding to triangle **3**. Similar phenomena were observed during the preparation of platinum complexes **5** and **6**. A concentrated solution of **1** (5.6 mM) and $\text{Pt}(\text{en})(\text{NO}_3)_2$ afforded a mixture **5** and **6** in a 80:20 ratio, whereas a dilute solution of **1** (2.3 mM) afforded only triangle **5** as evidenced by ^1H NMR and DOSY (ESI).

The kinetically labile nature of the $\text{Pd} \bullet \bullet \text{pyridine}$ interaction suggested that CB[7] could be threaded postsynthetically to give the desired $[n]\text{MN}$. Addition of CB[7] (3.0 equiv.) to **3** followed by refluxing at 100 °C for 24 h gave only $[4]\text{MN}$ **7** ($[\text{Pd}_3(\mathbf{1} \bullet \text{CB}[7])_3](\text{NO}_3)_{12}$) as evidenced by ^1H , DOSY NMR and ESI-MS. Diagnostically, H_e and H_f undergo significant upfield shift ($\delta = 0.55$ and 0.86 ppm compared to **1**) reflecting their inclusion in the anisotropic shielding region of CB[7] (Fig. 4a,b). DOSY NMR shows the formation of a single species ($D = 2.24 \times 10^{-10} \text{ m}^2/\text{s}$) that diffuses slower than free its components CB[7] ($D = 5.0 \times 10^{-10} \text{ m}^2/\text{s}$) and triangle **3** ($D = 3.02 \times 10^{-10} \text{ m}^2/\text{s}$). ESI-MS provided final evidence of the formation of $[4]\text{MN}$ **7**. A molecular ion peak at $m/z = 813.7$ was assigned to $[\text{Pd}_3(\mathbf{1} \bullet \text{CB}[7])_3](\text{NO}_3)_5^{7+}$. One pot self-assembly of **1**, CB[7] and $\text{Pd}(\text{en})(\text{NO}_3)_2$ or $\text{CB}[7] \bullet \mathbf{1}$ and $\text{Pd}(\text{en})(\text{NO}_3)_2$ also successfully delivered $[4]\text{MN}$ **7**. The postsynthetic threading approach was not successful for $[4]\text{MN}$ **8** due to the kinetically inert $\text{Pt} \bullet \bullet \text{pyridine}$ interaction. However, a one pot process involving the self-assembly of equimolar quantities **1**, CB[7], and $\text{Pt}(\text{en})(\text{NO}_3)_2$ in aq. NaNO_3 (1.0 M) afforded $[4]\text{MN}$ **8** (reflux, 5d) as evidenced by ^1H NMR (Fig. 4e). DOSY NMR showed that **8** ($D = 1.58 \times 10^{-10} \text{ m}^2/\text{s}$) diffuses at similar rate as **7** (*vide supra*). ESI-MS also exhibited peaks for $[4]\text{MN}$ **8**. Acyclic CB[n]-type container **M2** was also able to self assemble with equimolar amounts of **1** and

M(en)(NO₃)₂ (M = Pd, Pt) to give the analogous clipped [4]MN **9** (for Pd) and **10** (for Pt) as shown in Fig. 3.¹⁸

Next, we set out to synthesize [4]MNs incorporating CB[8]. Unfortunately, the direct self-assembly of **1**, CB[8], and M(en)(NO₃)₂ was unsuccessful likely due to the preferred formation of [**1**•CB[8]]_n as described above. Attempts to form 1:1:1 heteroternary complexes between CB[8], **1**, and second guests (e.g. 2,6-dihydroxynaphthalene, 1,4-dihydroxynaphthalene, indole, 4,4'-diaminoazobenzene) as building blocks for [4]MN formation were not successful as monitored by ¹H NMR. Nevertheless, we attempted the direct self-assembly of **1**, CB[8], second guest, and M(en)(NO₃)₂ but did not observe [n]MN formation. We conclude that **1** with its central benzidinium unit must be redesigned to disfavor ternary complexation and promote [n]MN formation.

It is known that conformational restriction (e.g. rotational, geometrical) of chromophores by inclusion within metal-organic frameworks (MOFs) or SCCs or by host-guest binding can slow down non-radiative decay of the excited state and thereby enhance luminescence.^{15a, 19} Accordingly, we next turned our attention to the photophysical properties of the [4]MNs and their components. Rigid-rod ligand **1** exhibits a high fluorescence quantum yield (Φ = 20%) in water. Addition of 1 equiv. of CB[7] results in a 20 nm blue shift of the fluorescence emission band to λ_{max} = 526 nm and the fluorescence emission intensity of **1**•CB[7] at this wavelength increases $\approx$ 2-fold due to the higher molar extinction coefficient of **1**•CB[7]. The quantum yield measured for **1**•CB[7] (Φ = 31%) is significantly higher than free **1** presumably due to restricted rotation upon complexation. Triangular SCC **3** and triangular [4]MN **7** display broad absorption bands centered at ca. 260 nm and 320 nm. As expected, platinum analogues **5** and **8** show red shifted absorption bands (303 and 351 nm) relative to **3** and **7**.²⁰ The quantum yield measured for triangle **3** (Φ = 22%) is similar to that measured for free ligand **1**. In contrast, the quantum yield of **5** is dramatically decreased (Φ = 1.6%) due to the heavy atom effect of Pt which promotes the intersystem crossing leading to nonradiative decay.²⁰ Threading of CB[7] onto the ligands comprising **3** and **5** to give [4]MNs **7** and **8** conformationally restrict the chromophore and lead to 1.5-fold and 8.8-fold (**5** to **8**) higher quantum yields (**7**: Φ = 32%; **8**: Φ = 14%). Interestingly, the fluorescence emission was quenched in **9** and **10** due to charge-transfer interaction between the electron rich dialkoxynaphthalene walls of **M2** and ligand **1**.

In conclusion, we prepared rigid rod ligand **1** which forms stable inclusion complexes with CB[7], CB[8], and **M2**. An equimolar mixture of **1** and M(en)(NO₃)₂ (M = Pd, Pt) gave triangular and square SCCs. Under more dilute conditions, assembly of **1** and M(en)(NO₃)₂ afforded only triangles **3** and **5**. Threading of CB[7] onto the SCCs to give [4]MNs **7** and **8** occurs by postsynthetic transformation or by a one-pot approach for kinetically labile Pd triangle **3** but only by the one-pot process for kinetically inert Pt triangle **5**. Attempts to form MNs incorporating CB[8] were unsuccessful due to ternary complex formation. The fluorescence and quantum yields of **1**, SCCs, and [4]MNs were quite different due to complexation induced conformational restriction and charge transfer processes. For this reason, we believe that CB[n] derived MNs will perform well as components of sensing arrays. Furthermore, when MNs incorporating larger CB[n] (e.g. n = 8) become available we

believe they will constitute robust plug-and-play scaffolds for imaging, targeted drug delivery, and theranostic application. We will report on these possibilities in due course.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1.
Complexation of **1** with CB[7] and CB[8].

Fig. 2.

^1H NMR recorded (400 MHz, D_2O , RT) for a) **1** (0.3 mM) and b-g) with various equiv. of CB[7] – b) 1.0, c) 1.25, d) 1.50, e) 1.75, f) 2.0, g) 3.0.

Fig. 3. Synthesis of [4]MNPs from **1** with $Pd(en)(NO_3)_2$ and $Pt(en)(NO_3)_2$ to afford mixture of triangle and square. Using CB[7] or **M2** give [4]MNPs or pseudo [4]MNPs in water.

Fig. 4. Partial ^1H NMR (D_2O , 600 MHz) recorded for a) **1**, b) **3**, c) **5**, d) [4]MN **7**, and e) [4]MN **8**.

Chart 1.
Molecular structures of compounds used in this study.