(5 units, NEB) for 1 h at 37 °C. Unincorporated ATP was removed by using Micro Bio-Spin columns (Bio-Rad). For nonradioactive phosphorylation, TFO (300 pmol) was incubated in T4 DNA ligase buffer (50 µL—50 mM Tris–HCl, 10 mM $MgCl_2$, 10 mM DTT, 1 mM ATP, and 25 $\mu g\,mL^{-1}$ BSA, pH 7.8 at 25 °C) with T4 PNK (10 units), for 1.5 h at 37 °C. The oligonucleotide was used without any further purification.

To assemble the radiolabeled oligonucleotide and the plasmid, the 5′-labeled TFO (20 nM) was incubated with plasmid (1 µg, 50 nM final) and BQQ (20 µM) in T4 DNA ligase buffer. The sample was heated to 75 °C and slowly cooled down to 37 °C. The 17-mer oligonucleotide template (100 nM) and T4 DNA ligase (40 units) were added to achieve circularization of the oligonucleotide. The reaction products were analyzed by using a 1% agarose gel containing ethidium bromide. The gels were visualized on a UV lamp, then dried and autoradiographed by using a phosphorimager system (Molecular Dynamics).

For the unlabeled oligonucleotides, the process was the same, except that different amounts of plasmid (100 nM, 4 µg in 20 µL), TFO (1 µM), template (2 µM), and DNA ligase (400 units) were used. To remove BQQ from the triplex, the sample was diluted to 50 µL so that final buffer concentration was 50 mM Tris–HCl pH 8.0, 100 mM NaCl, 20 mM $MgCl_2$, and 20 µM trap oligonucleotide. The sample was heated to 80 °C and then slowly cooled to 37 °C. Spermidine (50 µL, 40 mM) was then added, and the samples were left at room temperature for 30 min with frequent vortex-mixing in order to allow plasmid compaction. After centrifugation, the pellet was washed with a solution (200 µL) containing isopropanol (50%), $MgCl_2$ (10 mM), NaCl (300 mM), and EDTA (25 mM), as described by Murphy et al.[11] The plasmid was resuspended in TE buffer (40 µL, 10 mM Tris pH 8.0, 0.1 mM EDTA).

The restriction enzyme inhibition assay was carried out in the following way: the plasmid (0.2 µg) was incubated in NEB 3 buffer (40 µL—50 mM tris–HCl, 10 mM $MgCl_2$, 100 mM NaCl, 1 mM DTT, pH 7.9 at 25 °C) containing BQQ (2 µM). The samples were heated to 75 °C and slowly cooled to 37 °C. The cleavage reaction was performed at 37 °C for 60 min with *Eco*NI (30 units), then stopped by the addition of SDS 2%/EDTA 0.2 M (5 µL). The samples were precipitated with ethanol (200 µL), resuspended in TE buffer (10 µL), and analyzed by agarose gel electrophoresis.

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Selective Inclusion of a Hetero-Guest Pair in a Molecular Host: Formation of Stable Charge-Transfer Complexes in Cucurbit[8]uril**

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The inclusion of two or more guest molecules in a molecular host is attractive because it provides unique opportunities to study new forms of stereoisomerism,[1] bimolecular reactions,[2] and molecular recognition[3] in microenvironments. Although the inclusion of two different types of guest molecules in a host has been reported,[4–6] the resulting complexes have been characterized only by spectroscopy. For example, the formation of pyrene-cyclodextrin-alcohol ternary complexes has been studied extensively by emission spectroscopy, but they are not stable enough to be isolated or structurally characterized.[5] Thus, the selective inclusion of two different guests in a molecular host which leads to an isolable ternary complex is still difficult to achieve.

Cucurbituril (CB[6]), a macrocycle comprising six glycoluril units, has a cavity that is accessible through two identical carbonyl-fringed portals.[7] The polar carbonyl groups at the portals and the hydrophobic cavity allow the cavitand to form stable host–guest complexes with small molecules such as protonated aliphatic and aromatic amines.[7, 8] We recently reported new cucurbituril homologues, namely cucurbit[*n*]uril (CB[*n*]; $n = 5$, 7, and 8), that contain five, seven, and eight glycoluril units.[9] The largest member of the cucurbituril family, CB[8], which has a cavity comparable to that of γ-cyclodextrin, can accommodate two molecules of a naphthalene derivative to form a 1:2 host–guest complex.[9] The capability of CB[8] to form 1:2 host–guest complexes prompted us to study the inclusion of two different guests within CB[8]. Here we report the selective inclusion of a hetero-guest pair in CB[8] that is driven by a charge-transfer interaction between the guests. The resulting ternary complexes are highly stable, which enables them to be isolated and characterized by X-ray crystallography.

Host–guest interactions between redox-active viologens and cyclodextrins has been extensively studied.[10] While methylviologen (**MV**$^{2+}$) shows little interaction with β- or γ-cyclodextrin,[10a] it readily forms a 1:1 host–guest complex with CB[8], as evidenced by ^{1}H NMR spectroscopy and mass

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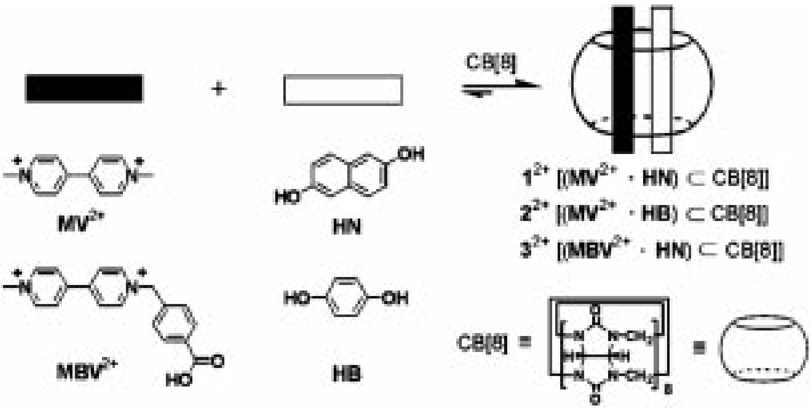
spectrometry. The chemical shifts of the pyridinium protons of **MV**$^{2+}$ are shifted to higher field upon the formation of the complex (Figure 1a, b). The major driving force for the formation of the 1:1 complex appears to be ion–dipole interactions between the positive charge of the guest and the portal oxygen atoms of CB[8]. It is interesting to note that although CB[8] has a cavity large enough to accommodate two **MV**$^{2+}$ molecules, the formation of a 1:2 host–guest complex with this guest is not observed. Presumably, electrostatic repulsion between two **MV**$^{2+}$ ions in the cavity disfavors the formation of the ternary complex.[11]



Scheme 1. Inclusion of a hetero-guest pair in cucurbit[8]uril.

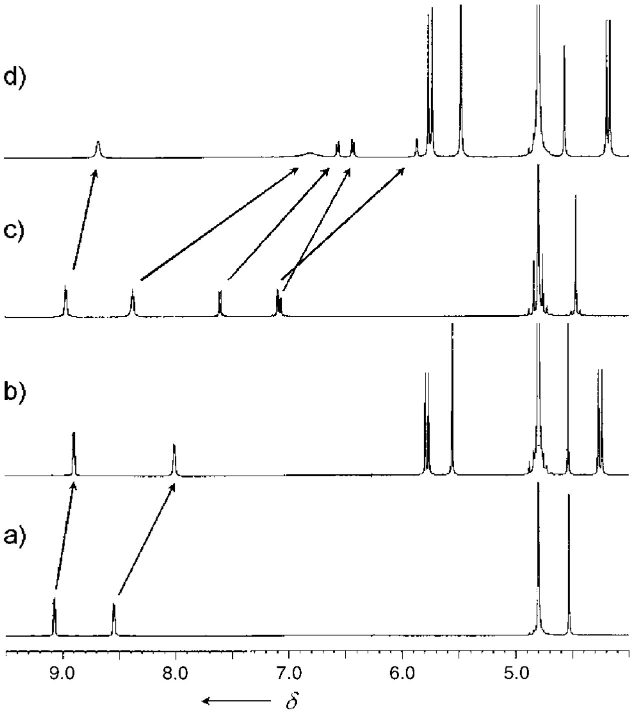


Figure 1. ^{1}H NMR spectra obtained in D_2O of a) **MV**$^{2+}$, b) 1:1 mixture of **MV**$^{2+}$ and CB[8], c) 1:1 mixture of **MV**$^{2+}$ and **HN**, and d) **1**.

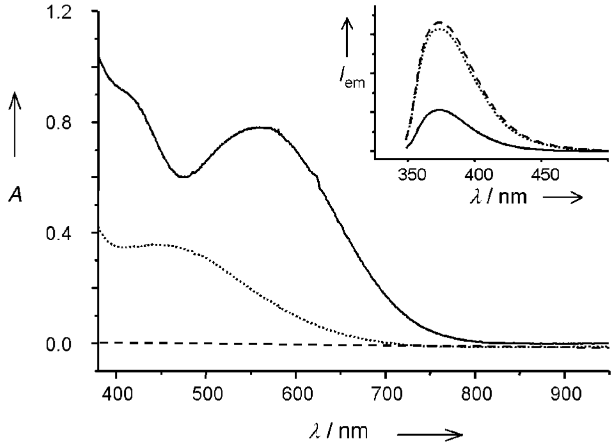


Figure 2. Absorption and emission (inset) spectra obtained in H_2O of **HN** (dashed line), a 1:1 mixture of **HN** and **MV**$^{2+}$ (dotted line), and **1** (solid line). The absorption spectra of **HN** and **1** were taken with 5 mM solutions whereas that of the 1:1 mixture of **HN** and **MV**$^{2+}$ was taken with a 0.5 M solution. All emission spectra were recorded with 5 μM solutions.

The exclusive formation of the 1:1 complex between CB[8] and **MV**$^{2+}$ prompted us to study the inclusion of a second guest into the 1:1 complex. Indeed, instantaneous and quantitative formation of the inclusion complex **1** or **2** containing a hetero-guest pair is observed upon addition of one equivalent of an electron-rich aromatic guest, such as 2,6-dihydroxynaphthalene (**HN**) or 1,4-dihydroxybenzene (**HB**), to the 1:1 complex of **MV**$^{2+}$ and CB[8]. The ternary complexes **1** and **2** are also formed exclusively when their components are mixed in a 1:1:1 ratio (Scheme 1). It should be noted that the electron-rich guest molecules themselves do not bind CB[8] in the absence of **MV**$^{2+}$. Therefore, the major driving force for the inclusion of the second guest appears to be a charge-transfer interaction between the electron-rich guest and the electron-deficient **MV**$^{2+}$, as evidenced by UV/Vis spectroscopy. The 1:1:1 ternary complex **1** exhibits a charge-transfer absorption at 580 nm which is greatly red-shifted ($\Delta\lambda = 120$ nm) and with a concomitant high increase in the intensity relative to that of a 1:1 mixture of **MV**$^{2+}$ and **HN** in the absence of CB[8] (Figure 2). The highly enhanced charge-transfer interaction between the two guests arises from their close contact within the cavity of CB[8], which is confirmed by NMR and emission spectroscopy. All the aromatic proton signals of the guest molecules are significantly shifted to higher field in the ^{1}H NMR spectra upon the formation of the inclusion complexes containing a pair of hetero guests (Figure 1c, d). While little fluorescence quenching is observed when only **MV**$^{2+}$ and **HN** are present in solution, the fluorescence intensity of **HN** decreases by 70% upon formation of **1**. A similar decrease in fluorescence intensity requires more than 500 equivalents of **MV**$^{2+}$ in the absence of CB[8]. To the best of our knowledge, this is the first example of the selective inclusion of a hetero-guest pair in a molecular host that is driven by a charge-transfer interaction between guests.[12, 13]

Attempts to determine the structure of **1** or **2** by X-ray crystallography were hampered by severe disorders in the guest molecules that arises from the high symmetry of their space groups. We therefore decided to use a dissymmetric bipyridinium derivative (**MBV**$^{2+}$) as the electron-deficient guest to lower the symmetry of the crystal system. The X-ray crystal structure of the resulting inclusion complex (**3**, Figure 3) shows the hetero-guest pair is included inside the cavity of CB[8]. While the carboxybenzylated pyridinium ring resides outside, the methylated pyridinium ring is located inside the cavity. The methylated pyridinium ring and the naphthalene ring of the donor are almost parallel, with a dihedral angle of 1.8° and a mean separation of 3.4 Å, which is consistent with the strong charge-transfer interaction observed by spectroscopy. This is probably the first example of inclusion of a hetero-guest pair in a molecular host that has been confirmed by X-ray crystallography.

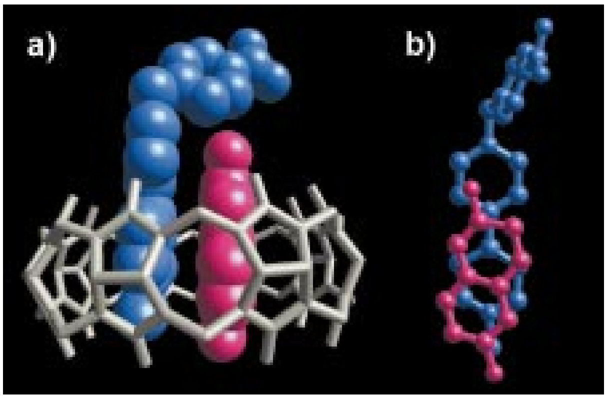


Figure 3. X-ray crystal structure of **3**$^{2+}$: a) full view, b) alternative view without the host. CB[8] = grey, **MBV**$^{2+}$ = blue, **HN** = magenta.

In summary, we have demonstrated the selective inclusion of a hetero-guest pair in a molecular host which is driven and stabilized by a charge-transfer interaction between electron-rich and electron-deficient guests. We expect that these ternary complexes will display rich spectroscopic and electrochemical properties, which are currently being investigated. Furthermore, such selective inclusion of a hetero-guest pair provides new opportunities for studying bimolecular reactions between selected reaction partners in molecular chambers, for developing chemical sensors for biomolecules with aromatic residues,[14, 15] and for creating elaborated supramolecular assemblies.[16, 17]

Experimental Section

Typical procedure: 2,6-dihydroxynaphthalene (2.5 mg, 15.7 µmol) and CB[8]$\cdot(H_2SO_4)\cdot 16H_2O$ (25.7 mg, 15.0 µmol) were added to methylviologen dichloride trihydrate (5.2 mg, 16.7 µmol) in water (3 mL). The violet suspension was stirred with occasional heating until all the solid materials had dissolved. The solution was then allowed to stand in a refrigerator. Dark violet crystals of **1** were obtained after 3 days (28.9 mg, 96 %). **1**: ^{1}H NMR (500 MHz, D_2O): δ = 8.67 (s, 4H), 6.80 (brs, 4H), 6.55 (d, 2H), 6.41 (d, 2H), 5.86 (s, 2H), 5.73 (d, 16H), 5.48 (s, 16H), 4.57 (s, 6H), 4.20 (d, 16H); UV/Vis (H_2O): λ_{CT} (lgε) = 580 nm (2.52); MS (electrospray ionization (ESI)): *m*/*z* (%): 837.37 (100) [M^{2+}]; elemental analysis calcd for $[(C_{48}H_{48}N_{32}O_{16})\cdot(C_{12}H_{14}N_2)\cdot(C_{10}H_8O_2)]\cdot SO_4\cdot 13H_2O$: C 41.92, H 4.82, N 23.74, S 1.60; found: C 41.72, H 4.63, N 23.96, S 1.98.

2: ^{1}H NMR (500 MHz, D_2O): δ = 8.75 (d, 4H), 7.08 (d, 4H), 5.74 (d, 20H), 5.49 (s, 16H), 4.53 (s, 6H), 4.20 (d, 16H); UV/Vis (H_2O): λ_{CT} (lgε) = 470 nm (2.41); MS (ESI): *m*/*z* (%): 812.10 (100) [M^{2+}]; elemental analysis calcd for $[(C_{48}H_{48}N_{32}O_{16})\cdot(C_{12}H_{14}N_2)\cdot(C_6H_6O_2)]\cdot SO_4\cdot 12H_2O$: C 40.91, H 4.79, N 24.58, S 1.65: found: C 40.60, H 4.43, N 24.49, S 2.05.

3: ^{1}H NMR (500 MHz, D_2O, 4 °C): δ = 8.48 (d, 2H), 7.96 (s, 2H), 7.73 (d, 2H), 7.43 (d, 2H), 6.48 (s, 2H), 6.21 (brs, 2H), 6.16 (d, 1H), 6.02–5.98 (dd, 2H), 5.90 (d, 1H), 5.64 (s, 2H), 5.41 (s, 1H), 5.37 (s, 1H), 5.25 (t, 16H), 4.99 (s, 16H), 4.04 (s, 3H), 3.72–3.67 (dd, 16H); UV/Vis (H_2O): λ_{CT} (lgε) = 578 nm (2.50); MS (ESI): *m*/*z* (%): 850.4 (100) [M^{2+}]; elemental analysis calcd for $[(C_{48}H_{48}N_{32}O_{16})\cdot(C_{19}H_{17}N_2O_2)\cdot(C_{10}H_8O_2)]\cdot 0.5SO_4\cdot 10H_2O$: C 45.72, H 4.63, N 23.54, S 0.79; found: C 45.93, H 4.48, N 23.36, S 0.86.

Crystal data for **3**: $[(C_{48}H_{48}N_{32}O_{16})\cdot(C_{19}H_{17}N_2O_2)\cdot(C_{10}H_8O_2)]\cdot 0.5SO_4\cdot 25.5H_2O$, M_r = 2302.13, monoclinic, $P2_1/c$, a = 15.1505(5), b = 20.7282(6), c = 33.4305(1) Å, β = 100.74(1)°, V = 10314.8(6) Å^3, Z = 4, ρ_{calcd} = 1.482 g cm^{-3}, T = 223 K, Siemens SMART CCD diffractometer, $Mo_{K\alpha}$ radiation (λ = 0.71073 Å), μ = 1.33 cm^{-1}. The structure was solved by the Patterson method (SHELXS-86). All non-hydrogen atoms were refined anisotropically (SHELXL-93). Final block-diagonal matrix least-squares refinement on F^2 with all 16038 reflections and 1452 variables converged to $R1$ ($I > 2\sigma(I)$) = 0.112, $wR2$ (all data) = 0.321, and GOF = 1.133. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-154114. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Template and Guest Effects on the Self-Assembly of a Neutral and Homochiral Helix**

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Dedicated to Professor Manfred Regitz
on the occasion of his 65th birthday

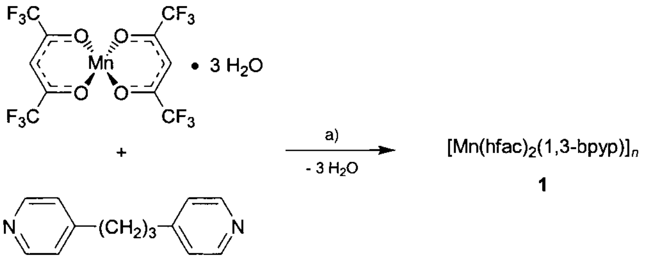
Over the past decade, the principles of recognition-driven, spontaneous self-assembly have become further elucidated. In such processes, the overall structure of the product is controlled by the combination of binding constraints and geometrical requirements. These intriguing discoveries have led to the development of general strategies for the design of abiotic, supramolecular entities, both discrete and infinite, that use coordination as a motif.[1]

The coordination paradigm pioneered by Lehn and Sauvage, and as developed in the groups of Fujita, Raymond, Stang, and others for closed systems, has allowed for the synthesis of a large assortment of supramolecular polygons and polyhedra through "rational design". This approach utilizes rigid subunits that have been pre-coded with the proper bonding and angular information, leading to highly predictable products.[2] Concurrently, a variety of solid-state coordination polymers and infinite-network lattices have been synthesized along similar lines.[1b, 3]

By incorporating a higher degree of flexibility into the building blocks, the amount of predefined information is reduced, and two or more different structures can arise from identical metal–ligand combinations. This strategy yields largely unpredictable products that depend mostly upon minor, experimental variations.[4] The iron-based circular helicates made by Lehn's group[5] and the cadmium-based, flexible coordination networks from Fujita's group,[6] are dependent upon the anion or guest employed, respectively, and serve as impressive examples of this methodology.

The work presented here is concerned with tuning the assembly of a new, neutral, solid-state system and serves as a step toward bridging the gap between discrete and infinite supramolecular structures. Such work may also have implications in crystal engineering.[7] In this study, the solid-state assembly of the highly flexible 1,3-bis(4-pyridyl)propane (1,3-bpyp) ligand and the neutral [Mn(hfac)$_2$(H$_2$O)$_3$] (hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) acceptor complex was probed under various reaction conditions.

By slow evaporation of the solvent from a previously heated 1:1 mixture of [Mn(hfac)$_2$(H$_2$O)$_3$] and 1,3-bpyp in acetone/methanol, crystals of **1** were obtained (Scheme 1).



Scheme 1. a) MeOH / (CH$_3$)$_2$CO / Δ.

As determined by single-crystal X-ray analysis,[8] the coordination polymer **1** exhibits a helical architecture in the solid state (Figure 1). This system crystallized in the chiral space group C_2, with two independent manganese centers per repeating asymmetric unit. Both pseudo-octahedral metal centers show *cis* coordination of the pyridine moieties and are enantiomeric. Each set of two crystallographically equivalent manganese centers constitutes a single revolution of the helix with a distance of 19.18 Å between them.

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