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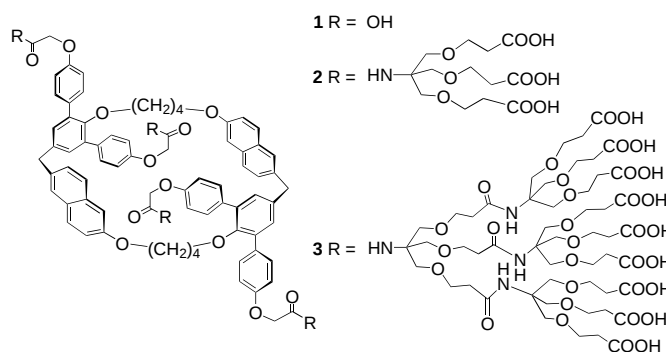
Supramolecular Aggregates of Dendritic Cyclophanes (Dendrophanes) Threaded on Molecular Rods with Steroid Termini**

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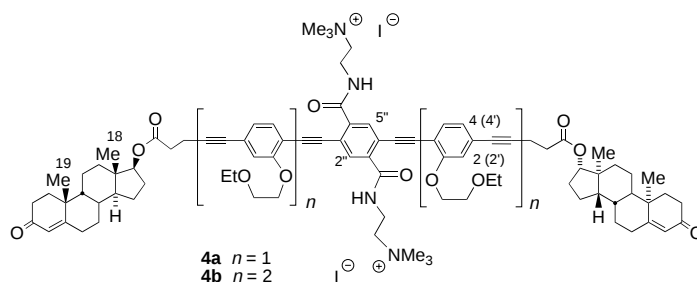
Noncovalent association of dendrimers^[1] promises to provide a rapid, efficient way to construct higher molecular architectures with properties and functions^[2] that are absent in the individual components. Whereas metal ion mediated assembly of dendritic branches (dendrons) to form higher generation compounds is well established,^[1a, 3] the noncovalent networking^[4a] of individual dendrimers to defined higher

order structures in the absence of metal ions has only been achieved in a few cases.^[4–7] A particularly intriguing example for dendritic self-association is the discrete hexameric assembly of dendritic wedges through directional COOH...COOH hydrogen-bonding interactions, which was reported by Zimmerman and co-workers.^[6] Hydrophobic nonstoichiometric association of dendrimers in aqueous solution has been observed on several occasions,^[5, 8] yet apolar bonding interactions and hydrophobic desolvation have not been previously employed to form structurally defined supramolecular aggregates containing two or more dendritic components. Here we report for the first time the formation of such assemblies in aqueous solution by hydrophobically driven threading of water-soluble dendrophanes (dendritic cyclophanes)^[9] onto the testosterone termini of suitably designed molecular rods.

The initiator core cyclophane **1** (generation zero, G-0) and the two dendrophanes of the first (**2**, G-1; M_r = 2486) and second generation (**3**, G-2; M_r = 6318) had previously been shown to form stable 1:1 complexes (ΔG° at 298 K between −3.9 and −4.3 kcal mol^{−1}) with testosterone in borate-buffered D₂O (pD 10.5)/CD₃OD (1/1).^[10] ¹H NMR investigation



of the bonding provided clear evidence that the steroid binds axially in the cyclophane cavity of **2** or **3** rather than in nonspecific fluctuating voids in the dendritic shells.^[11] The molecular rods **4a** and **4b** consist of rigid oligo(phenylacetylene) spacers with terminal testosterone units for dendro-phane complexation. Because of their different lengths, they



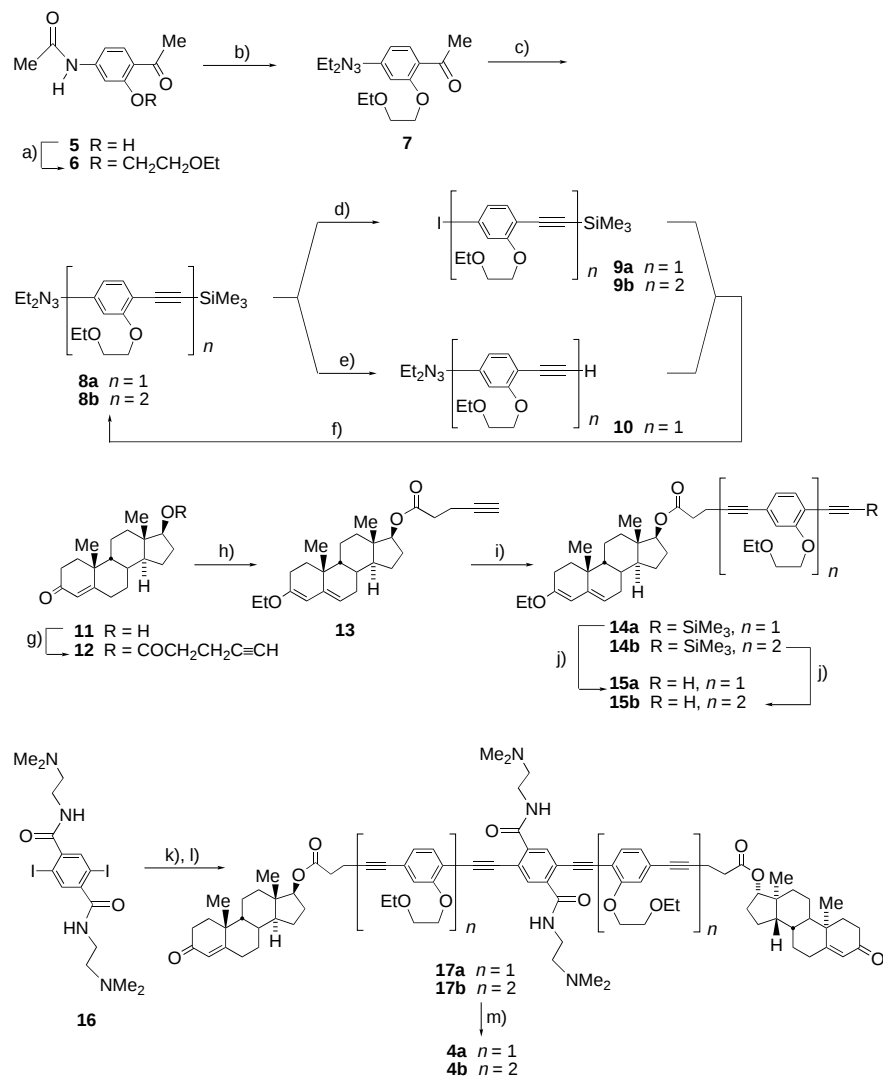
were expected to accommodate dendrophanes of different generation and size. Solubility of the rods in aqueous solutions represented a considerable challenge, which could be overcome with the attachment of both glycol ether groups and quaternary ammonium ions (to the central benzene ring). These ions were expected to undergo ion pairing with the

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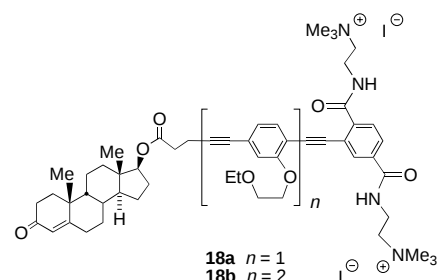
surface carboxylate residues in **1–3** and thus reduce the undesired electrostatic repulsion between two anionic dendrimers threaded onto one rod.

The synthesis of the novel molecular rods **4a** and **4b** utilizes in its key steps the elegant binomial strategy introduced by Moore and co-workers for the construction of oligo(phenylacetylene) sequences (Scheme 1).^[11, 12] The orthogonal doubly protected arylacetylene **8a**, which was obtained in three steps from **5**^[13] via **6** and **7**, was transformed into iodide **9a** and the deprotected alkyne **10**.^[14] Sonogashira cross-coupling between **9a** and **10** in pyrrolidine^[15] yielded **8b**, which was converted into aryl iodide **9b**.



Scheme 1. Synthesis of **4a** and **4b**. a) $\text{EtO}(\text{CH}_2)_2\text{OTos}$, K_2CO_3 , DMF, 20°C , 5 h, 75%; b) 10% aq HCl, 100°C , 81%, then NaNO_2 , 0°C , 15 min, then Et_2NH , 0°C , 15 min, 65%; c) lithium 2,2',6,6'-tetramethylpiperidide (1.1 equiv), THF, -78°C , 30 min, then $(\text{EtO})_2\text{POCl}$, THF, -78°C , then lithium 2,2',6,6'-tetramethylpiperidide (2.2 equiv), THF, $-78 \rightarrow 20^\circ\text{C}$, 1.5 h, then Me_3SiCl (2 equiv), THF, -78°C , 64%; d) MeI, 130°C , 17 h, 78% (**9a**), 97% (**9b**); e) K_2CO_3 , MeOH, 20°C , 1 h, 95%; f) $[\text{Pd}_2(\text{dba})_3]$ (5 mol %), CuI (10 mol %), pyrrolidine, 20°C , 97% (**8b**); g) pent-4-ynoic acid, N,N' -dicyclohexylcarbodiimide, 4-(dimethylamino)pyridine, CH_2Cl_2 , 20°C , 96%; h) $\text{H}(\text{COEt})_3$, TosOH, EtOH, 20°C , 1 h, 100%; i) **9a** or **9b**, $[\text{PdCl}_2(\text{PPh}_3)_2]$ (5 mol %), CuI (10 mol %), pyrrolidine, 20°C ; j) $n\text{Bu}_4\text{NF}$, THF, 0°C , 30 min; k) **15a** or **15b**, $[\text{PdCl}_2(\text{PPh}_3)_2]$ (5 mol %), CuI (10 mol %), PhMe/ Et_3N 1/1, 110°C , 6–17 h; l) 10% aq HCl/THF/MeOH 1/2/5, 0°C , 2 h, then 20°C , 1 h, 54% (**17a**) and 18% (**17b**) starting from **13**; m) MeI/ CH_2Cl_2 1/1, CaCO_3 (traces), 20°C , 2 h, 77% (**4a**), 95% (**4b**). Tos = *p*-toluenesulfonyl, dba = dibenzylideneacetone.

The attachment of testosterone (**11**) to **9a** and **9b** to yield **14a** and **14b**, respectively, was achieved by esterification with pent-4-ynoic acid ($\rightarrow$ **12**), protection of the steroid enone chromophore as dienol ether ($\rightarrow$ **13**),^[16] and Sonogashira coupling. Deprotection of the alkyne group afforded **15a** and **15b**, which were coupled^[17] to the 2,5-diiodoterephthalamide **16** (prepared in 30% yield by heating 2,5-diiodoterephthalic acid^[18] with SOCl_2 to 100°C for 4 h, followed by reaction with N,N -dimethyl-1,2-ethylenediamine in CH_2Cl_2 at 0°). Hydrolysis of the dienol ethers to give enones **17a** and **17b**, and quaternization of the tertiary amino groups led to the bis-steroid rods **4a** and **4b** (Table 1). Following a similar synthetic route, the mono-steroid rods **18a** and **18b** were prepared as controls.



The bis-steroid rods **4a** and **4b** are light yellow solids (Table 1) that fluoresce strongly ($\lambda_{\text{exc}} = 370 \text{ nm}$, $\lambda_{\text{em}} = 471 \text{ nm}$ (**4a**) and 482 nm (**4b**) in H_2O (0.15 M phosphate buffer, pH 6.9)/MeOH 1:1). Therefore, complexation by threading receptors **1–3** could not only be studied by ^1H NMR titrations in D_2O , but also by fluorescence titrations in H_2O ; all data were evaluated by nonlinear least-squares curve-fitting analysis (Table 2).^[19] Pure testosterone (**11**) forms 1:1 complexes with the G-0 receptor **1** ($\Delta G^\circ = -4.0 \text{ kcal mol}^{-1}$) and the G-1 receptor **2** ($\Delta G^\circ = -4.4 \text{ kcal mol}^{-1}$; entries 1 and 2 in Table 2).^[10] Apolar bonding interactions and hydrophobic desolvation provide the driving force for formation of these complexes.^[11] Much more stable 1:1 complexes are formed between **1–3** and the mono-steroid rods **18a** and **18b** (ΔG° between -5.9 and $-6.4 \text{ kcal mol}^{-1}$; entries 3–8 in Table 2). Since the complexation-induced shifts (CIS) of the resonances for the steroid methyl groups in the ^1H NMR titrations adopt similar values in complexes of **11** with both **18a** and **18b**, the inclusion geometries must be similar. Thus, the steroid A–D rings of **18a** and **18b**, rather than the phenylacetylene moiety, are axially included in the cyclophane cavities. Therefore, the significantly

Table 1. Selected physical data for the molecular rods **4a** and **4b**.

4a: M.p. 171 °C; IR (KBr): $\tilde{\nu}$ = 3288, 1727, 1666 cm⁻¹; ¹H NMR (CD₃OD, 500 MHz): δ = 7.93 (s, 2H; H(2'')), 7.50 (d, J = 8.0 Hz, 2H; H(5')), 7.13 (d, J = 1.6 Hz, 2H; H(2)), 7.06 (dd, J = 1.6, 8.0 Hz, 2H; H(4)), 5.74 (s, 2H; C=CHC=O), 4.74 (t, J = 8.1 Hz, 2H; CHOCO), 4.28 (t, J = 4.8 Hz, 4H; ArOCH₂), 3.95 (t, J = 6.5 Hz, 4H; N⁺CH₂), 3.88 (t, J = 4.78 Hz, 4H; ArOCH₂CH₂O), 3.67 (q, J = 7.0 Hz, 4H; OCH₂CH₃), 3.63 (t, J = 6.8 Hz, 4H; NHCH₂), 3.24 (s, 18H; NCH₃), 2.78 (m, 4H; OOCCH₂), 2.66 (m, 4H; OOCCH₂CH₂), 2.05–2.55 (m, 12H; steroid), 1.30–1.95 (m, 20H; steroid), 1.25 (s, 6H; CH₃(19)), 1.23 (t, J = 7.0 Hz, 6H; CH₃CH₂O), 0.92–1.20 (m, 6H; steroid), 0.92 (s, 6H; CH₃(18)); ESI-MS (MeOH): m/z = 1573 (1%, [M – I]⁺), 1431 (1%, [M – Me – 2I]⁺), 722 (100%, [M]²⁺)

4b: M.p. 88 °C; IR (KBr): $\tilde{\nu}$ = 3288, 1727, 1655 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz): δ = 8.50 (m, 2H; NH), 8.05 (s, 2H; H(2'')), 7.55 (d, J = 7.9 Hz, 2H; H(5')), 7.38 (d, J = 7.9 Hz, 2H; H(5')), 7.18 (dd, J = 1.3, 7.9 Hz, 2H; H(4')), 7.13 (d, J = 1.3 Hz, 2H; H(2'')), 6.96 (d, J = 1.3, 7.9 Hz, 2H; H(4)), 6.93 (d, J = 1.3 Hz, 2H; H(2)), 5.71 (s, 2H; C=CHC=O), 4.67 (t, J = 8.1 Hz, 2H; CHOOC), 4.30 (m, 4H; ArOCH₂), 4.19 (t, J = 4.2 Hz, 4H; ArOCH₂), 3.98–4.03 (m, 8H; NHCH₂CH₂N⁺), 3.86 (t, J = 4.2 Hz, 4H; ArOCH₂CH₂O), 3.81 (t, J = 4.2 Hz, 4H; ArOCH₂CH₂O), 3.66 (q, J = 7.0 Hz, 4H; OCH₂CH₃), 3.55 (q, J = 7.0 Hz, 4H; OCH₂CH₃), 3.36 (s, 18H; NCH₃), 2.74 (t, J = 6.2 Hz, 4H; OOCCH₂), 2.64 (t, J = 6.2 Hz, 4H; OOCCH₂CH₂), 1.20–2.50 (m, 32H; steroid), 1.22 (t, J = 7.0 Hz, 6H; CH₃CH₂O), 1.17 (s, 6H; CH₃(19)), 1.11 (t, J = 7.0 Hz, 6H; CH₃CH₂O), 0.89–1.10 (m, 6H; steroid), 0.84 (s, 6H; CH₃(18)); ESI-MS (MeOH): m/z = 1949 (0.5%, [M – I]⁺), 1807 (0.5%, [M – Me – 2I]⁺), 911 (100%, [M]²⁺)

enhanced association strength ($\Delta(\Delta G^\circ)_{11-18a/18b} \approx 2.0 \pm 0.2$ kcal mol⁻¹) measured for the complexes of **18a** and **18b**, as compared to complexes of pure testosterone (compare entries 1 and 2 with entries 3–8 in Table 2), is mainly a result of the additional ion pairing between the surface carboxylate residues of dendrophanes **1–3** and the quaternary ammonium ions of the mono-steroid rods. The extra stabilization of about 1 kcal mol⁻¹ provided by each of the two salt bridges is in good agreement with results from previous studies.^[20]

The binding of the G-0 derivative **1** to the bis-steroid rod **4a** was evaluated by fluorescence titrations, since precipitation of the formed complex occurred at the higher concentration ranges required for ¹H NMR titrations. An excellent fit of the titration data for a 2:1 binding model was obtained, with the threading of the two cyclophanes through **4a** occurring with nearly identical association strength ($\Delta G^\circ_{1:1} = -6.1$, $\Delta G^\circ_{2:1} = -5.9$ kcal mol⁻¹; entry 9 in Table 2). Clear evidence for the proposed 2:1 stoichiometry was also obtained by Job analysis.^[21] Each cyclophane in the 2:1 complex ($M_r = 4117$) independently binds to one steroid terminus with similar association strength to that measured for the 1:1 complexation of **1** to the mono-steroid rod **18a**.

In contrast to these findings, significant differences in the driving force for the first and second binding event were measured when the G-1 derivative **2** was threaded onto the shorter bis-steroid rod **4a** (entries 10 and 11 in Table 2). Again, clear evidence for formation of a supramolecular complex with 2:1 stoichiometry was obtained.^[21] In this case, however, the driving force for the second association step $\Delta G^\circ_{2:1}$ is between 2.1 (fluorescence) and 2.8 kcal mol⁻¹ (¹H NMR) smaller than for the first association step, which with $\Delta G^\circ_{1:1} = -6.7$ kcal mol⁻¹ has a driving force of similar magnitude to that for threading the G-0 derivative **1** on **4a**, **18a**, or **18b**. The two dendrophanes once again prefer inclusion of the tetracyclic steroid skeletons over the complexation of the phenylacetylene moieties of **4a**, as indicated by a comparison of the complexation-induced shifts of the ¹H NMR signals for steroid methyl groups CH₃(18) and CH₃(19). At saturation binding, these resonances in the 2:1 complex of **4a** with **2** (entry 10, Table 2) display strong upfield shifts similar to those observed in the 1:1 complexes of **11** (entry 2) and the mono-steroid rods **18a** and **18b** (entries 6 and 7). The considerable reduction in thermodynamic driving force for the second complexation step is undoubtedly a

Table 2. Association constants and binding free enthalpies for the complexes formed by dendrophanes **1–3** with testosterone (**11**) and the molecular rods **4a/4b** and **18a/18b** as well as complexation-induced shifts at saturation binding of signals monitored during ¹H NMR titrations.^[a]

Entry	Titration method	Steroid substrate	Dendro-phane	$K_{1:1}$ [L mol ⁻¹]	$\Delta G^\circ_{1:1}$ [b] [kcal mol ⁻¹]	$K_{2:1}$ [L mol ⁻¹]	$\Delta G^\circ_{2:1}$ [b] [kcal mol ⁻¹]	CH ₃ (18)	$\Delta\delta_{\text{sat}}$ [ppm] CH ₃ (19)	CH ₃ CH ₂ O
1	NMR ^[c]	11	G-0 (1)	900	-4.0	–	–	–	–	–
2	NMR	11	G-1 (2)	1600	-4.4	–	–	-0.41	-1.06	–
3	NMR	18a	G-0 (1)	21000	-5.9	–	–	-0.41	-1.19	-0.26
4	NMR	18b	G-0 (1)	30000	-6.1	–	–	-0.38	-1.06 ^[d]	-0.27, -0.28
5	fluor. ^[e]	18b	G-0 (1)	22000	-5.9	–	–	–	–	–
6	NMR	18a	G-1 (2)	47000	-6.4	–	–	-0.31	-1.50	-0.21
7	NMR	18b	G-1 (2)	38000	-6.2	–	–	-0.38	-1.02	-0.14, -0.20
8	fluor. ^[e]	18b	G-2 (3)	32000	-6.1	–	–	–	–	–
9	fluor. ^[f]	4a	G-0 (1)	29000	-6.1	23000	-5.9	–	–	–
10	NMR	4a	G-1 (2)	79000	-6.7	700	-3.9	-0.40	-1.39	-0.20
11	fluor.	4a	G-1 (2)	81000	-6.7	2300	-4.6	–	–	–
12	fluor.	4b	G-1 (2)	31000	-6.1	30000	-6.1	–	–	–
13	fluor. ^[g]	4a	G-2 (3)	15000	-5.7	–	–	–	–	–
14	fluor.	4b	G-2 (3)	91000	-6.8	4000	-4.9	–	–	–

[a] The thermodynamic data were determined by 500-MHz ¹H NMR titration in D₂O (0.15 M phosphate buffer, pD 7.3)/CD₃OD 1/1 at 300 K and/or by fluorescence titrations in H₂O (0.15 M phosphate buffer, pH 8.7)/CH₃OH 1/1 at 298 K.^[19] [b] Uncertainties: ± 0.1 kcal mol⁻¹ for $\Delta G^\circ_{1:1}$ and ± 0.3 kcal mol⁻¹ for $\Delta G^\circ_{2:1}$. [c] Titration at constant dendropane concentration; a titration at a constant concentration of **11** in D₂O (0.1 M borate buffer, pD 10.5)/CD₃OD 1/1 gave $K_2 = 1350$ L mol⁻¹ as well as $\Delta\delta_{\text{sat}} = -0.24$ (CH₃(18)) and -0.81 (CH₃(19)).^[10] [d] Maximum shift. [e] The hypsochromic shift of the emission of **18b** at saturation binding was -43 nm (entry 5) and -40 nm (entry 8). [f] In H₂O (0.15 M phosphate buffer, pH 6.9)/CH₃OH 4/6 for solubility reasons. [g] Formation of a 1:1 complex with the given stability was also confirmed by ¹H NMR titrations at constant concentration of **4a** [$\Delta\delta_{\text{sat}}$: -0.20 (CH₃(18)); -0.16 (CH₃CH₂O)].

consequence of the Coulombic repulsion between the surface carboxylate groups of the two threaded dendrophanes, which are positioned in too close proximity on the small rod.

Computer modeling^[22] suggests that the distance between the junctions of the B and C rings of the two testosterone termini is approximately 41 Å. When the rod size is extended in **4b** to about 55 Å, the driving forces for threading the first and second dendrophane become identical again (entry 12 in Table 2). Fluorescence titrations yielded for both 1:1 and 2:1 complexation between **4b** and **2** a free enthalpy of formation of $\Delta G^\circ = -6.1 \text{ kcal mol}^{-1}$, that is, nearly the same driving force as measured for the complexation of one dendrophane **2** by the mono-steroid rods **18a** and **18b**.^[23] Thus, a highly stable supramolecular aggregate with a molecular mass of 6642 is formed in which the two dendrophanes, through inclusion of the testosterone termini, are placed at sufficient distance to avoid charge repulsion.

The bulky G-2 dendrophane **3** ($M_r = 6318 \text{ D}$) only forms a 1:1 complex with the smaller rod **4a**, as evidenced by the curve fitting of fluorescence and ¹H NMR titration data and Job analysis; the fluorescence data gave a maximum at mole fraction $x(\mathbf{3}) = 0.5$ (entry 13 in Table 2). Formation of a stable 2:1 complex with a molecular mass of 14714 was, however, observed again by fluorescence titrations and Job analysis for the association between the longer rod **4b** and G-2 dendrophane **3** (entry 14 in Table 2). The threading of the first dendrophane is more favorable ($\Delta G^\circ = -6.8 \text{ kcal mol}^{-1}$) than that of the second ($\Delta G^\circ = -4.9 \text{ kcal mol}^{-1}$) owing to charge repulsion.^[21, 23] Further extension of the phenylacetylenic sequence in the bis-steroid rod is currently under way to accommodate two G-2 dendrophanes with similar binding free enthalpy. The successful threading of two third-generation dendrophanes ($M_r = 17813$), which are already available,^[10] to form 2:1 complexes with molecular weights approaching 40000 will require the construction of bis-steroid rods with even larger spacers.

We have demonstrated a novel, efficient dendrimer association process which takes advantage of apolar interactions, hydrophobic desolvation, and ion pairing to produce supramolecules of defined structures with molecular weights exceeding 14000. The experiments establish experimentally an optimal distance for threading two anionic dendrophanes in the thermodynamically most favorable way onto the steroid termini of molecular rods with rigid phenylacetylene spacers. For optimal binding, two G-0 dendrophanes **1** require an intramolecular steroid...steroid distance of about 41 Å, whereas in the case of the G-1 dendrophanes **2** this distance is about 55 Å. From these data, the extensions of the complexed dendrophanes, which are hard to obtain otherwise, can be estimated. Thus, the bis-steroid rods **4a** and **4b** serve as rulers on the molecular scale.

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with the program SPECFIT V.2.10 (R. A. Binstead, A. D. Hungerbühler, Spectrum Software Associates, Chapel Hill, NC, 1997). This program performs global least-squares fits which, in fluorescence titrations, include the entire measured wavelength region (multiple wavelength analysis). In the ^1H NMR titrations at constant concentration of the molecular rod ($c(\text{rod}) \approx 0.1\text{--}0.2\text{ mM}$, $c(\text{dendrophane}) \approx 0.05\text{--}1\text{ mM}$), the complexation-induced shifts of the steroid $\text{CH}_3(18)$ and $\text{CH}_3(19)$ resonances and the $\text{CH}_3\text{CH}_2\text{O}$ resonances were evaluated. In the fluorescence titrations at constant concentration of the molecular rod ($c(\text{rod}) \approx 0.01\text{--}0.02\text{ mM}$, $c(\text{dendrophane}) = 0.005\text{--}0.8\text{ mM}$), the emission intensity of the rod decreased upon addition of dendrophane and the emission maxima of **4a/4b** at saturation binding shifted by 5–16 nm to higher energy.

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Desolvation of a Novel Microporous Hydrogen-Bonded Framework: Characterization by In Situ Single-Crystal and Powder X-ray Diffraction**

Cameron J. Kepert, Dusan Heseck, Paul D. Beer,* and Matthew J. Rosseinsky*

Attention has recently focused on the use of the hydrogen bond,^[1] and also the coordinate bond,^[2] in the controlled assembly of porous molecular frameworks. Studies into the guest exchange and catalytic properties^[3] of these materials have led to a growing recognition of molecular frameworks as zeolite analogues, many retaining their structural integrity with desolvation or solvent exchange. Aware of these devel-

opments, and of the importance of redox centers to heterogeneous catalysis^[4] and molecular recognition by electrochemical sensing,^[5] we have synthesized an electrochemically active organic species suitable for forming novel extended molecular frameworks. Here we show how hydrogen bonding and $\pi \cdots \pi$ nonbonding interactions can produce a microporous framework of this species linked to a transition metal complex. The material described displays remarkable flexibility, and undergoes significant structural rearrangements with desolvation to leave an empty-channel material that shows selectivity to guest sorption.

By making use of slow diffusion in aqueous silica gels, we have synthesized crystals incorporating the diprotonated, redox-active tetra(carboxyl)tetrathiafulvalene anion $\text{H}_2(\text{TC-TTF})^{2-}$, hexaaquacobalt(II) cations, and solvent water molecules. $[\text{Co}(\text{H}_2\text{O})_6]\text{H}_2(\text{TC-TTF}) \cdot 2\text{H}_2\text{O}$ (**A**) consists of a three-dimensional hydrogen-bonded network of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $\text{H}_2(\text{TC-TTF})^{2-}$ ions (Figure 1).^[6] Short

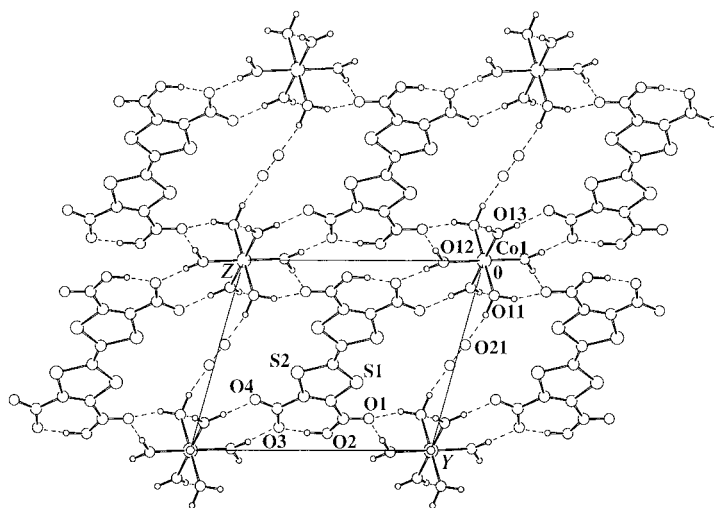


Figure 1. Projection of **A** down the a axis. For clarity, only one oxygen atom position of the disordered cavity water molecule is displayed. Selected bond lengths [Å] and angles [°] (a fixed value of 0.86 Å was used for O–H distances in the cation): O11 $\cdots$ O1* 2.715(4), O12 $\cdots$ O3* 2.773(4), O12 $\cdots$ O1* 2.802(4), O13 $\cdots$ O4* 2.685(4), O2 $\cdots$ O3 2.438(5), H2 $\cdots$ O3 1.47(8); O11–H11B $\cdots$ O1* 159(6), O12–H12B $\cdots$ O3* 173(8), O12–H12A $\cdots$ O1* 179(5), O13–H13A $\cdots$ O4* 174(6), O13–H13B $\cdots$ O11* 173(7), O3–H2 $\cdots$ O2 168(7).

hydrogen bonds exist between eight of the twelve protons in the hexaaquometal cation and six of the eight carboxyl oxygen atoms. The two protons of the doubly deprotonated acid form very short hydrogen bonds to neighboring carboxyl groups, giving this unit a rigid planarity. Running along the a axis, and lying parallel with slipped stacks of the TTF derivative and hydrogen-bonded chains of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions, are one-dimensional channels that are filled with zig-zag chains of disordered water molecules. The sites occupied by these molecules are defined by hydrogen bonding to the framework, primarily to a water molecule coordinated to Co^{2+} (O11) and to a lesser degree to O4 of the anion. Hydrogen bonding between solvent molecules occurs along the channels, the mean solvent separation being about 2.9 Å, compared with 2.8(1) Å for a typical hydrogen-bonded O $\cdots$ O distance.

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