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An hermaphroditic [*c*2]daisy chain

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Received (in Columbia, MO, USA) 5th July 2002, Accepted 16th September 2002
First published as an Advance Article on the web 12th November 2002

A cyclic dimeric daisy chain compound, which has been assembled from a difunctional [2]rotaxane in a sequence of noncovalent and covalent synthetic steps, the most important of which is a bis-Wittig reaction, has been characterised by X-ray crystallography.

Interlocked molecular compounds[1] are comprised of two or more mechanically linked components between which there are no covalent bonds. Rotaxanes—molecules in which one or more rings are trapped upon a dumbbell-shaped component by virtue of bulky terminal stoppers—represent a major subset[2] of such compounds. Interest in these compounds has been heightened by the fact that their noncovalently interacting constituent parts can be induced[1] to move with respect to one another—a functional property which has inspired the design and creation of numerous artificial molecular machines[3] that operate as molecular shuttles[4] and switches,[5] which have been incorporated[6] into memory and logic circuits.

Recently, we have become interested in fixing, by stoppering, supramolecular daisy chains[7] in which an NH_2^+ ion-containing arm is grafted, along with a second weaker recognition site, onto a macrocycle with either a [24]- or [25]-crown-8 constitution, *e.g.*, **I** in Fig. 1, to give (i) cyclic (**II**) and acyclic (**III**) daisy chain polymer molecules with potentially addressable components and (ii) molecular muscles[8] which can be controlled by pH to be either contracted (**IV**) or elongated (**V**). We have also demonstrated[9] that analogous NH_2^+ ion/crown ether-based [2]rotaxane monomers, *e.g.*, **VI** in Fig. 1—each incorporating a dumbbell-shaped component possessing an exchangeable benzylic triphenylphosphonium stopper as well as an aldehyde function—undergo a sequence of Wittig reactions in which the surrogate triphenylphosphonium stopper is exchanged for a ring either (i) in the *same* rotaxane molecule to give *cyclic* daisy chains by an *intramolecular* chain-terminating mechanism or (ii) in *another* rotaxane molecule to give *acyclic* daisy chains by an *intermolecular* chain-propagation mechanism, *cf.* **VI** in Fig. 1, giving **II** (≅ **IV**) and **III**, respectively.

More specifically, we have shown[9] that the [2]rotaxane **1**-H·$2PF_6$ undergoes (Scheme 1) a series of Wittig reactions to give, amongst numerous different products, the [*c*2]daisy chain as a mixture of stereoisomers containing (*E*) and (*Z*) olefinic

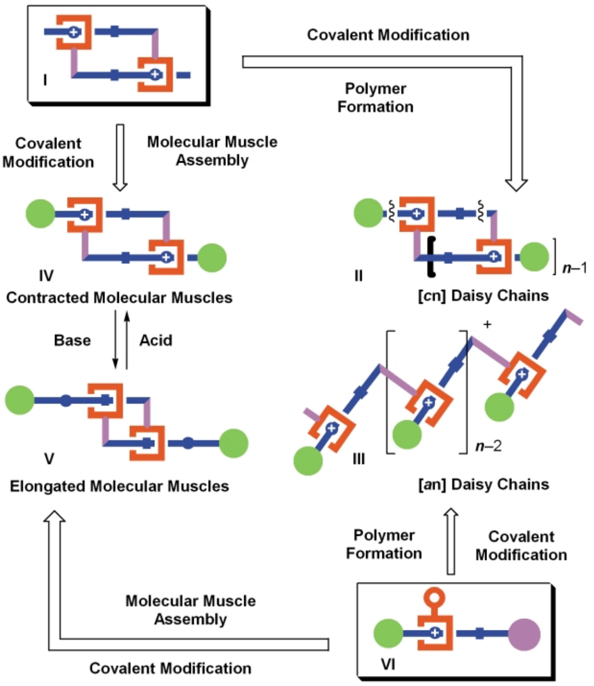
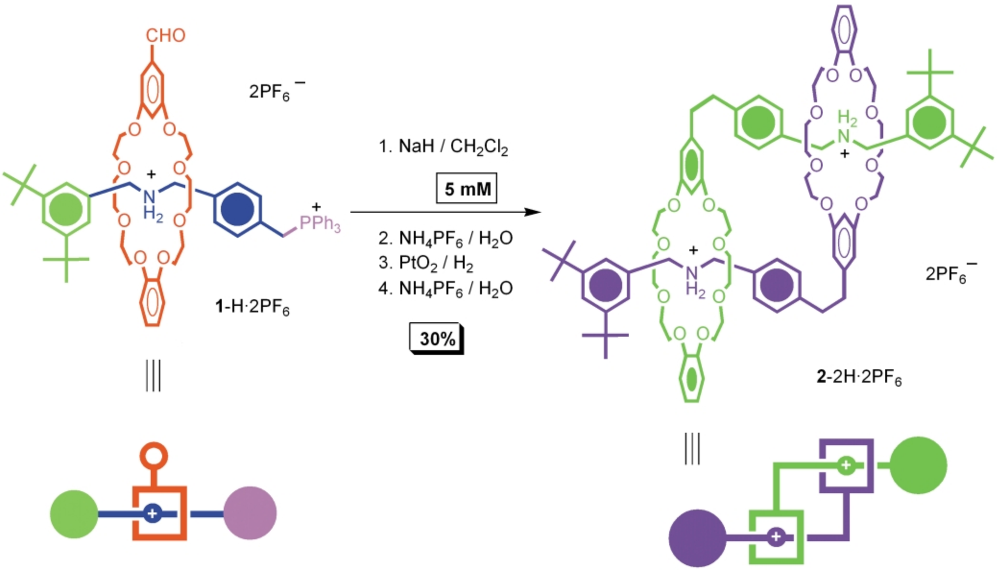


Fig. 1 Strategies for the template-directed syntheses of polymeric daisy chains and molecular muscles capable of actuation.



Scheme 1

DOI: 10.1039/b206675k

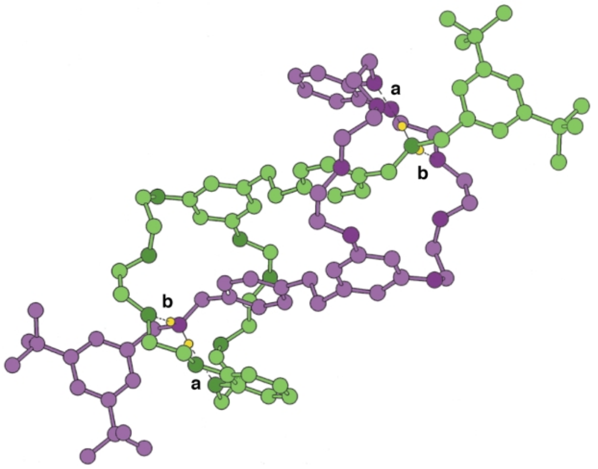


Fig. 2 The solid-state structure of the hermaphroditic [*c*2]daisy chain [**2**-2H]$^{2+}$. Hydrogen bonding geometries are [N$^{+}\cdots$O], [H$\cdots$O], [N^{+}–H$\cdots$O]: (a) 2.95, 2.06 Å, 168°; (b) 2.84, 1.95 Å, 176°.

units. Here, we report† that catalytic hydrogenation (PtO_2–H_2) of the crude product, obtained after reaction of **1**-H·2PF_6 with an excess of NaH under dilute conditions (5 mM) in CH_2Cl_2, followed by treatment with aqueous NH_4PF_6 solution, gives, in 30% yield overall, after further counterion exchange (NH_4PF_6–H_2O) and silica gel chromatography, the pure saturated [*c*2]daisy chain **2**-2H·2PF_6, as indicated by mass spectrometry, NMR spectroscopy and, above all, X-ray crystallography.[10]

Single crystals suitable for X-ray crystallography were grown by liquid diffusion of *i*-Pr_2O into a solution of **2**-2H·2PF_6 in a mixture of CH_2Cl_2 and MeCN. Single crystal X-ray analysis‡ of **2**-2H·2PF_6 shows it to have a [*c*2]daisy chain co-conformation containing crystal and molecular inversion symmetry with the NH_2^+ centre of one component being positioned within the macrocyclic polyether portion of the other component, and *vice versa*. The co-conformation is stablised by [N^{+}–H$\cdots$O] hydrogen bonds as illustrated in Fig. 2. The macrocyclic portion adopts a U-shaped geometry and its catechol and resorcinol rings sandwich the paraxylyl ring system within the "stem" of its symmetry-related counterpart. The ring centroid–ring centroid separations are long at 3.91 and 4.44 Å, respectively, precluding any significant stabilising [π–π] interaction. The catechol rings of symmetry-related molecules do enter into a parallel [π–π] arrangement with mean interplanar and centroid–centroid separations of 3.64 and 3.71 Å, respectively. There is also a weak intermolecular [C–H$\cdots$π] interaction ([H$\cdots$π], 2.99 Å, [C–H$\cdots$π], 159°) between one of the hydrogen atoms (H-2/6) on the 3,5-di-*tert*-butylphenyl 'flower' in one molecule and the resorcinol ring of another.

The characterisation of this [*c*2]daisy chain in the solid state, as well as in the solution state, is important in relation to the establishment of a synthetic strategy (as outlined in Fig. 1) that will allow us to template the formation of polymeric daisy chains and molecular muscles that are capable of undergoing actuation by altering the pH of the surrounding media. The post-assembly processing[11] of [2]rotaxanes, based on the recognition[7,9,12] by crown ethers of NH_2^+ centres, is affording access to a wide range of exotic, yet potentially useful, interlocked molecular compounds[13] containing interactive and reactive functional groups.

This research was supported by the National Science Foundation (CHE-9910199) and the Petroleum Research Fund, administered by the American Chemical Society.

Notes and references

† NaH (20 mg, 0.83 mmol) was added to a solution of **1**-H·2PF_6 (0.3 g, 0.22 mmol) in CH_2Cl_2 (50 mL). The mixture was stirred at ambient temperature for 5 d before MeOH (2 mL) was added to quench the reaction. After removing the solvent under reduced pressure, the residue was dissolved in MeCN (20 mL) and an aqueous solution (20 mL) of NH_4PF_6 (1 g) was added. The organic solvent was removed under reduced pressure and CH_2Cl_2 (30 mL) was added to dissolve the precipitate. The organic layer was then washed with H_2O (2 × 20 mL), dried ($MgSO_4$) and concentrated. PtO_2 (7 mg) and THF (3 mL) were added to the residue and the mixture was stirred for 1 h at room temperature under hydrogen. The solvent was evaporated and the crude product was dissolved in MeCN (20 mL) and an aqueous solution (20 mL) of NH_4PF_6 (1 g) was added. The organic solvent was removed under reduced pressure and CH_2Cl_2 (30 mL) was added to dissolve the precipitate. The organic layer was then washed with H_2O (2 × 20 mL), dried ($MgSO_4$) and concentrated. The residue was subjected to chromatography (SiO_2; MeCN–CH_2Cl_2, 1 : 9) to afford the [*c*2]daisy chain **2**-2H·2PF_6 as a white solid (60 mg, 30%). ^1H NMR (400 MHz, CD_3CN): δ 1.24 (s, 36H), 2.40–2.60 (m, 8H), 3.35–4.20 (m, 52H), 4.42 (m, 4H), 6.16 (d, J = 2 Hz, 4H), 6.24 (s, 2H), 6.70–6.90 (m, 12H), 6.91 (d, J = 8 Hz, 4H), 7.38 (d, J = 2 Hz, 4H), 7.50 (s, 2H), 7.65–7.80 (br, 4H); ^{13}C NMR (125 MHz, CD_3CN): δ 31.6, 35.6, 36.8, 37.5, 52.9, 53.6, 68.6, 68.9, 70.5, 70.8, 71.3, 72.0, 101.2, 108.6, 113.2, 122.4, 124.7, 124.8, 129.0, 129.3, 130.6, 131.8, 143.8, 145.5, 147.5, 152.7, 160.5; FAB-MS 1715 for $[M - PF_6]^+$, 1569 for $[M - H - 2PF_6]^+$.

‡ Crystal data for **2**-2H·2PF_6: $[C_{96}H_{132}N_2O_{16}](PF_6)_2\cdot 5CH_2Cl_2$, M = 2284.6, triclinic, $P1$ (no. 2), a = 14.447(1), b = 15.840(3), c = 15.965(2) Å, α = 60.65(1), β = 81.71(1), γ = 65.08(1)°, V = 2879.0(7) Å^3, Z = 1, D_c = 1.318 g cm^{-3}, μ(Cu-Kα) = 3.14 mm^{-1}, T = 203 K; 7894 independent measured reflections. F^2 refinement, R_1 = 0.091, wR_2 = 0.247, 5927 independent observed reflections [$|F_0| > 4\sigma(|F_0|)$, $2\theta \leqslant 120°$], 670 parameters. CCDC 189556. See http://www.rsc.org/suppdata/cc/b2/b206675k/ for crystallographic data in CIF or other electronic format.

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