

Synthesis of Polyynes

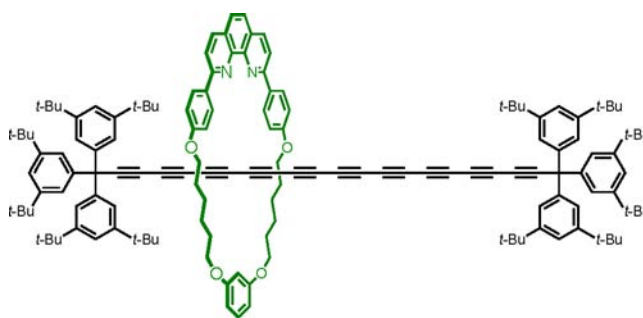
Levon D. Movsisyan,[†] Dmitry V. Kondratuk,[†] Michael Franz,[‡] Amber L. Thompson,[†]
Rik R. Tykwinski,^{*,‡} and Harry L. Anderson^{*,†}

Oxford University, Department of Chemistry, Chemistry Research Laboratory,
Oxford OX1 3TA, U.K., and Department of Chemistry and Pharmacy and
Interdisciplinary Center of Molecular Materials (ICMM), University of
Erlangen-Nuremberg, Henkestrasse 42, 91054 Erlangen, Germany

harry.anderson@chem.ox.ac.uk; rik.tykwinski@chemie.uni-erlangen.de

Received May 20, 2012

ABSTRACT



Active-metal templating has been used to synthesize rotaxanes consisting of a phenanthroline-based macrocycle threaded around a C8, C12, or C20 polyynes chain. The crystal structure of the C12 rotaxane has been determined. In the rhenium(I) carbonyl complex of this rotaxane, with $\text{Re}(\text{CO})_3\text{Cl}$ coordinated to the phenanthroline macrocycle, the proximity of the polyynes chain quenches the luminescence of the rhenium. These rotaxanes offer a new approach to controlling the environment and interactions of a polyynes chain.

Polyynes, with the formula $\text{R}-(\text{C}\equiv\text{C})_n-\text{R}$ where $n > 2$, have long attracted attention as oligomeric analogues of carbyne, the elusive one-dimensional allotrope of carbon.¹ Polyynes with up to 32 *sp*-carbon atoms, such as $\text{Et}_3\text{Si}-(\text{C}\equiv\text{C})_{16}-\text{SiEt}_3$, were synthesized by Walton and co-workers during the 1970s, but these long polyynes could only be studied in dilute solution; they polymerize rapidly when the solvent is removed.² Recently it has been discovered that long polyynes can be stable both in solution and in the solid state if they are terminated with bulky capping groups, such as platinum phosphine complexes³ and dendrimers.⁴ The longest polyynes to be isolated, with 44 *sp*-carbon atoms, has ‘super trityl’

tris(3,5-di-*tert*-butylphenyl)methyl (Tr*) terminal moieties.⁵ While still offering a stabilizing effect, the influence of the terminal groups on the properties of a polyynes is expected to decrease as the polyynes becomes longer. Thus, noncovalent strategies are required for controlling the interactions of an acetylenic thread, so that the unusual nonlinear optical properties⁶ and charge-transport behavior⁷ of polyynes can be exploited to create functional carbon-rich materials. Previously polyynes have been encapsulated by forming double-helical ‘bean-pole’ complexes,⁸ by cocrystallization with planar mercury(II) complexes,⁹ and by threading inside carbon nanotubes.¹⁰

[†] Oxford University.

[‡] University of Erlangen-Nuremberg.

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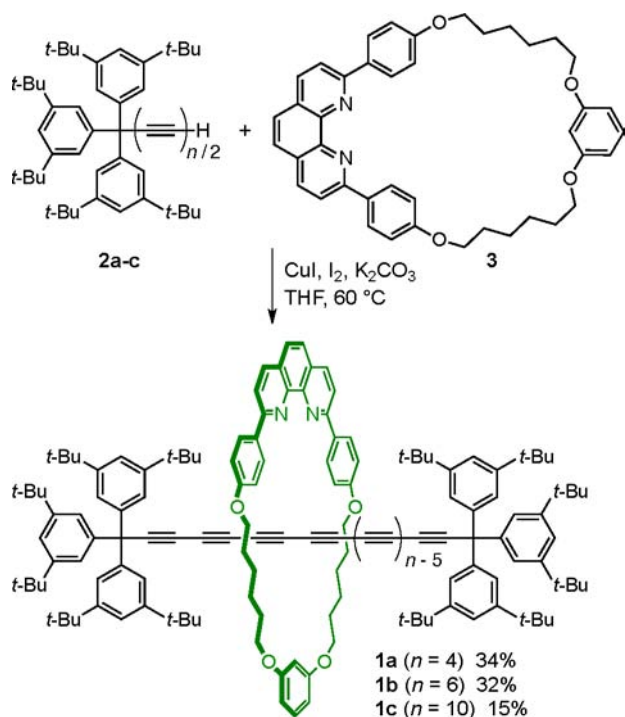
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Scheme 1. Synthesis of Rotaxanes **1a–c**



Several authors^{1a,11,12} have suggested that polyynes could be stabilized by threading them through macrocycles to form rotaxanes or polyrotaxanes, as a type of insulated molecular wire;¹³ however polyynes with more than two conjugated triple bonds in the axle unit have not been reported.¹⁴ Here we present the synthesis of a family of polyyne rotaxanes with 8, 12, and 20 *sp*-carbon atoms in the axle, **1a–c**, via active copper-templated coupling.^{12,15,16} We also show that the coordinating ability of the phenanthroline macrocycle can be exploited to position a transition metal in close proximity to the threaded polyyne chain.

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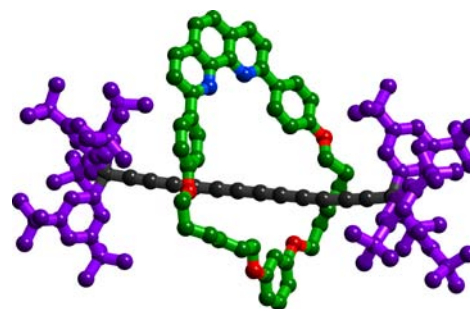


Figure 1. Structure of rotaxane **1b** in the crystal, with the macrocycle in green, the super trityl end groups in purple, and the C12 polyyne chain in gray (hydrogen atoms and solvent molecules omitted for clarity).¹⁷

Rotaxanes **1a–c** were synthesized in yields of up to 34% by copper-mediated coupling of alkynes **2a–c**⁵ in the presence of the phenanthroline-based macrocycle **3** (Scheme 1), using similar reaction conditions to those reported recently for preparation of a rotaxane with a butadiyne-linked porphyrin dimer axel.¹² Initially the reaction was performed in toluene at 110 °C; however, changing the solvent to THF and decreasing the temperature to 60 °C gave higher yields of rotaxane. Attempts at preparation of the corresponding C4 rotaxane ($n = 2$) were not successful; it seems that, with these bulky super trityl end groups, the polyyne chain needs at least eight *sp*-carbon atoms to accommodate the macrocycle. Polyyne rotaxanes **1a–c** were fully characterized by ¹H NMR, ¹³C NMR, mass spectrometry, IR, and UV spectroscopy (see Supporting Information). The crystal structure of

(17) Crystals of rotaxane **1b**·(4CH₃OH) were grown by vapor diffusion of methanol into a solution of **1b** in THF. X-ray diffraction data were collected at 100 K (Cosier, J.; Glazer, A. M. *J. Appl. Crystallogr.* **1986**, *19*, 105–107) with synchrotron radiation using I19 (EH1) at Diamond Light Source ($\lambda = 0.6889$ Å; Nowell, H.; Barnett, S. A.; Christensen, K. E.; Teat, S. J.; Allan, D. R. *J. Synchrotron Rad.* **2012**, *19*, 435–441). Cell parameters were determined and refined, and raw frame data were integrated using CrysAlisPro (Agilent Technologies, 2010). The structure was solved with SuperFlip (Palatinus, L.; Chapuis, G. *J. Appl. Crystallogr.* **2007**, *40*, 786–790) and refined by full-matrix least-squares on F^2 using CRYSTALS (Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Crystallogr.* **2003**, *36*, 1487). Disorder was identified in the stopper and macrocycle and was modeled appropriately, but copious restraints were necessary to maintain the sensible geometries, and residuals remained near the macrocycle. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were generally visible in the difference map and treated in the usual manner (Cooper, R. I.; Thompson, A. L.; Watkin, D. J. *J. Appl. Crystallogr.* **2010**, *43*, 1100–1107). The structure contained large solvent accessible voids comprising weak, diffuse electron density. The discrete Fourier transforms of the void regions were treated as contributions to the A and B parts of the calculated structure factors using PLATON/SQUEEZE (Spek, A. *J. Appl. Crystallogr.* **2003**, *36*, 7–13; van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194–201) integrated within the CRYSTALS software. *Single Crystal Data*: C₁₄₄H₁₈₄N₂O₈, $M_r = 2071.01$, triclinic, PT , $a = 13.3026(6)$ Å, $b = 19.4275(9)$ Å, $c = 26.7908(10)$ Å, $\alpha = 97.176(3)^\circ$, $\beta = 102.427(3)^\circ$, $\gamma = 92.395(3)^\circ$, $V = 6691.7(5)$ Å³, data/restraints/parameters: 18295/776/1507, $R_{\text{int}} = 5.20\%$, final $R_1 = 9.50\%$, $wR_2 = 25.15\%$ ($I > 2\sigma(I)$), $\Delta\rho_{\text{min,max}} = -0.78, +1.29$ e Å⁻³. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre (CCDC 885635), and copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

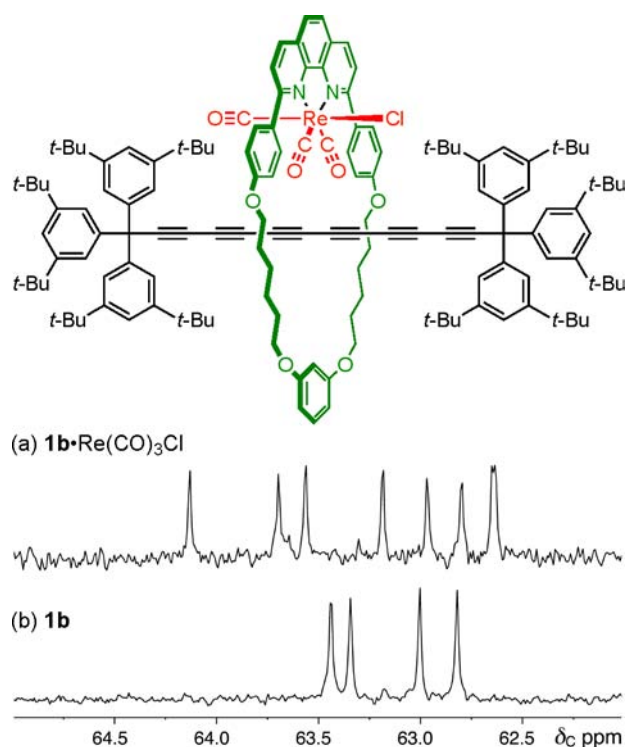


Figure 2. Structure of **1b**·Re(CO)₃Cl and comparison of its ¹³C NMR spectrum with that of **1b**, showing only the resonances of the eight central carbons of the C12 polyynyl chain (125 MHz, CD₂Cl₂, 298 K).

rotaxane **1b** shows that the macrocycle is threaded around the polyynyl unit (Figure 1).¹⁷ In the crystal, the rotaxanes associate into pairs by π -stacking of the phenanthroline units, as in the analogous porphyrin dimer rotaxane.¹² The mean bond length alternation in the C12 chain of **1b** is $0.142 \pm 0.008 \text{ \AA}$, which is slightly less than that reported in

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(20) Addition of the hexayne Tr*–C₁₂–Tr* dumbbell of **1b** to **3**·Re(CO)₃Cl does not alter the luminescence of the rhenium complex, demonstrating that the polyynyl needs to be in close proximity to quench the luminescence.

the crystal structure of the corresponding C12 dumbbell ($0.158 \pm 0.008 \text{ \AA}$).⁵

The presence of the phenanthroline unit in rotaxanes **1a–c** should allow the environment around the polyynyl chain to be modified by coordinating a wide variety of metals. To test this hypothesis, rotaxane **1b** was treated with Re(CO)₅Cl in toluene to give the rhenium(I) carbonyl chloride complex **1b**·Re(CO)₃Cl in 70% yield.¹⁸ The ¹H and ¹³C NMR spectra of **1b**·Re(CO)₃Cl show that the symmetry of the rhenium center is imposed on the polyynyl, splitting the resonances of the dumbbell component, as illustrated in Figure 2: **1b**·Re(CO)₃Cl exhibits twice as many *sp* ¹³C resonances as **1b**. Rhenium(I) carbonyl complexes are often studied because of their luminescence.^{18,19} The complex of the macrocycle, **3**·Re(CO)₃Cl, shows normal luminescence behavior (emission $\lambda_{\text{max}} = 550 \text{ nm}$, quantum yield $\phi = 0.033$ in toluene under air). Surprisingly, no luminescence is detected from **1b**·Re(CO)₃Cl under these conditions. Evidently the proximity of the C12 polyynyl chain quenches the emission from the rhenium center; further work will be required to elucidate the mechanism of this quenching process.²⁰

In conclusion, we have demonstrated that polyynyl rotaxanes, up to C20, can be prepared by active-metal templating using a phenanthroline-based macrocycle and that rhenium can be coordinated to these rotaxanes, positioning the metal center close to the polyynyl chain. This chemistry should be a powerful approach for controlling the environment around polyynyl chains.

Acknowledgment. This work was supported by an Oxford University Raffy Manoukian Scholarship (to L.D.M.) and an Oxford University Clarendon Fund Scholarship (to D.V.K.). We also thank the EPSRC Mass Spectrometry Service (Swansea) for mass spectra and Diamond Light Source for an award of beamtime (MT1858). R.R.T. thanks the Deutsche Forschungsgemeinschaft (DFG - SFB 953, Project A4 “Synthetic Carbon Allotropes”) for financial support.

Supporting Information Available. Experimental details and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.