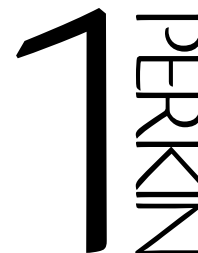


# The synthesis and structural characterization of the first bis(benzocrown ethers) with polyyne linkages †



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Bis(benzo-15-crown-5)buta-1,3-diyne and bis(benzo-15-crown-5)octa-1,3,5,7-tetrayne were successfully synthesized and characterized by X-ray crystallography. Experiments with poly[bis(benzocrown ethers)diacetylene] were also studied.

## Introduction

The pioneering work of Pedersen,<sup>1</sup> Lehn,<sup>2</sup> and Cram<sup>3</sup> on the syntheses of macrocyclic and macropolycyclic host systems such as crown ethers, cryptands and spherands, has generated a great amount of interest in host–guest and supramolecular chemistry. The construction of multisite molecular receptor molecules capable of binding two or more guest metal cations is one current area of interest in this field.<sup>4–7</sup>

Functionalized benzocrown ethers are good candidates for molecular receptor molecules because crown ether moieties are well known for their ability to form strong complexes with alkali metal, alkaline metal and organic cations. In addition, these compounds are also being studied for their applications in the analytical and pharmaceutical fields.<sup>8–10</sup> Specifically, synthetic and medicinal chemists apply the “biscrown effect” when constructing new organic and inorganic molecular receptors.<sup>11–14</sup> The “biscrown effect” occurs when two crown ether rings in one molecule bind a cation in a sandwich-type structure.<sup>15</sup> This enables the molecule to bind a cation that is larger than the ideal size for a particular crown ether unit. Therefore, the exploitation of this effect yields exceptional enhancement in the complexation properties and markedly changes the selectivity of a given crown ether system.

Our research group has studied and prepared one-dimensional carbon allotropes containing polyyne linkages by laser vaporization of carbon to produce a wide range of carbon chain lengths.<sup>16,17</sup> The ends of these chains are subsequently capped with trifluoromethyl or nitrile groups to enhance their stability. However, the products made using the laser technique must be carefully separated before they can be crystallized and completely characterized by X-ray crystallography. The creation of model compounds containing multiple acetylenic linkages, using standard wet synthesis techniques, has proven to be useful in the comparison of the spectroscopic properties for acetylenic molecules synthesized *via* the laser synthesis. We have successfully applied C≡C units as spacers in both organic and inorganic host molecules. Such compounds have been proven to be useful as molecular wires and chemosensors due to the rigidity of their linear structures and the excellent conductivity of their conjugated  $\pi$  systems.<sup>18–22</sup> Compounds of this nature have also generated interest in the biochemistry and materials research areas.<sup>23</sup> In addition to pure acetylenic systems, the syntheses of organic polymers with any form of extended

$\pi$ -conjugation are also of interest. Preparations of polydiacetylenes have been studied by Wegner.<sup>24–26</sup> Substituted 1,3-diacetylenes undergo smooth topochemical polymerization in their crystalline states by heat, UV-light,  $\gamma$ -ray irradiation or pressure. Each molecule is bonded with two adjacent neighbors along a particular crystallographic direction by a sequence of 1,4-addition reactions. The resulting polydiacetylene polymer has a quasi-one-dimensional structure with a long effective conjugation length.<sup>27</sup> In light of these findings, we have expanded our interest beyond acetylenic model compounds to include the design and synthesis of benzocrown ethers containing multiple acetylenic linkages as spacers between the two benzocrown ethers. We have also attempted to prepare and investigate the properties of polydiacetylenes by employing bis(benzocrown ethers)diacetylene as a monomer. The addition of the crown ether moiety to these architectures may enhance the ability to tune the electronic properties of a particular system by selective cationic complexation.

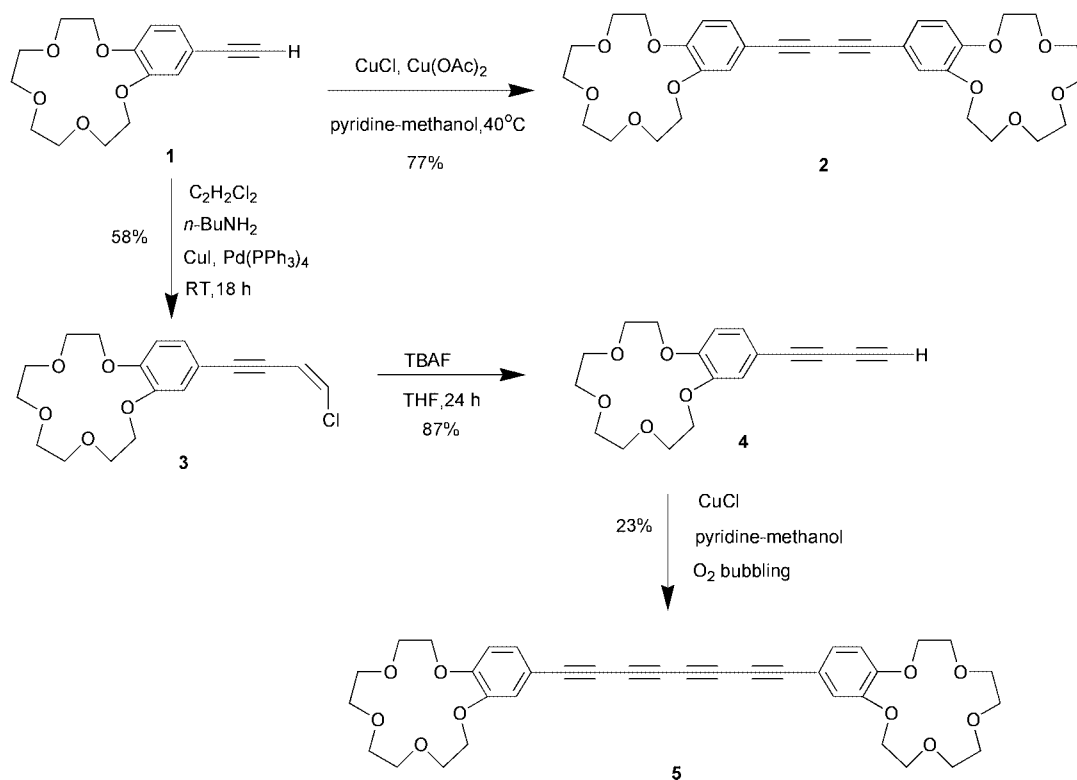
This article reports the syntheses and complete characterizations of two new compounds, bis(benzo-15-crown-5)buta-1,3-diyne **2** and bis(benzo-15-crown-5)octa-1,3,5,7-tetrayne **5**. The synthesis of poly[bis(benzocrown ethers)diacetylene] is also discussed.

## Result and discussion

The syntheses of **2** and **5** are described in Scheme 1. Bis(benzo-15-crown-5)buta-1,3-diyne **2** was prepared by self-coupling 4'-ethynylbenzo-15-crown-5 **1**<sup>1,10,11,28–30</sup> using Eglinton–Glaser coupling.<sup>31</sup> Recrystallization of **2** from chloroform formed white needles in 77% yield. Compound **2** was characterized *via* <sup>1</sup>H, <sup>13</sup>C NMR, IR, UV, mass spectrometry, melting point, elemental analysis, and X-ray crystallography.<sup>32</sup> The <sup>13</sup>C NMR of **2** showed C=C resonances at 81.2 and 72.6 ppm and the IR spectrum of **2** exhibited C≡C stretches at 2299 cm<sup>–1</sup>.

The step growth acetylenic chain methodology for **5** is different from the preparation of similar inorganic molecules. We did not add acetylenic units in this molecule by simply using the acetylene reagent, BrC≡CSiMe<sub>3</sub>, because the self-coupled compound would be formed instead of the desired product. Here, *cis*-1,2-dichloroethylene was introduced as the coupling reagent. Catalytic palladium(0) and CuI coupling of **1** and *cis*-1,2-dichloroethylene in a mixture of benzene–*n*-butylamine at room temperature for 18 hours under an argon atmosphere gave **3** as a yellow oil.<sup>33</sup> Compound **3** was then purified by flash column chromatography on silica gel (chloroform–methanol 40:1 as an eluent) to obtain pure compound in 58% yield. The two protons in the C=C bond of **3** were unambiguously

† Details of the characterization of **1–5** are available as supplementary data. For direct electronic access see <http://www.rsc.org/suppdata/p1/b0/b001856m/>



Scheme 1

assigned at 6.40 and 6.07 ppm respectively in  $^1\text{H}$  NMR. The IR spectrum of **3** also contained two  $\text{C}\equiv\text{C}$  stretches at 2250 and  $2196\text{ cm}^{-1}$ . The elimination of  $\text{HCl}$  from **3** using fluoride ion as a base produced **4** as a brown oil in 88% yield. The  $^{13}\text{C}$  NMR revealed four different acetylenic carbons at 75.6, 71.1, 70.9, 68.3 ppm and  $^1\text{H}$  NMR contained a peak at 2.44 ppm typical of a proton adjacent to  $\text{C}\equiv\text{C}$ . The IR spectrum showed two  $\text{C}\equiv\text{C}$  stretches at 2250 and  $2202\text{ cm}^{-1}$  and one strong  $\text{C}\equiv\text{CH}$  stretch at  $3305\text{ cm}^{-1}$ .

Hay coupling was used to couple **4** in the presence of  $\text{CuCl}$  and oxygen in methanol–pyridine (1:1 mixture) to yield compound **5**.<sup>31</sup> Compound **5** was further purified by column chromatography on silica (chloroform–methanol 40:1 as an eluent) and isolated in 23% yield. Recrystallization of **5** from biphasic chloroform and hexane yielded bright yellow crystals. Bis(benzo-15-crown-5)octa-1,3,5,7-tetraene was well characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, IR, UV, mass spectrometry, melting point, elemental analysis, and X-ray crystallography.<sup>32</sup> The  $^{13}\text{C}$  NMR presented four  $\text{C}\equiv\text{C}$  peaks at 78.1, 73.5, 67.1, 63.9 ppm and the IR spectrum showed  $\text{C}\equiv\text{C}$  stretches at  $2195\text{ cm}^{-1}$ .

Compounds which have uncomplexed benzocrown ethers are often too flexible to grow satisfactory crystals. Surprisingly, **2** and **5** form single crystals spontaneously without having to bind cations into the benzocrown ether cavities. The crystal structure of **2** has shown some disordered crown ether rings which were not shown in the crystal structure of **5** (shown in Fig. 1). This suggests that an increase in the number of acetylenic ( $\text{C}\equiv\text{C}$ ) units attaching molecules results in an increase in molecular rigidity, thereby allowing for easier solid state arrangements. The average values for the  $\text{C}\equiv\text{C}$  and  $\text{C}\text{--}\text{C}$  bond lengths are 1.211 and 1.366 Å, respectively. The sp hybridized carbons are clearly indicated in this structure.

The UV/Vis spectra of **2** and **5** are compared in Fig. 2. They show a red-shifted trend while **5** has more  $\pi$  conjugations than **2**. The colors of solutions range from clear to bright yellow due to different numbers of acetylenic units attached. In comparison, the solubilities of **2** and **5** drop sharply as the numbers of repeating  $\text{C}\equiv\text{C}$  units increase.

Based on the packing patterns of 1,3-dynes, solid state polymerization of monomers can result in polymers of two

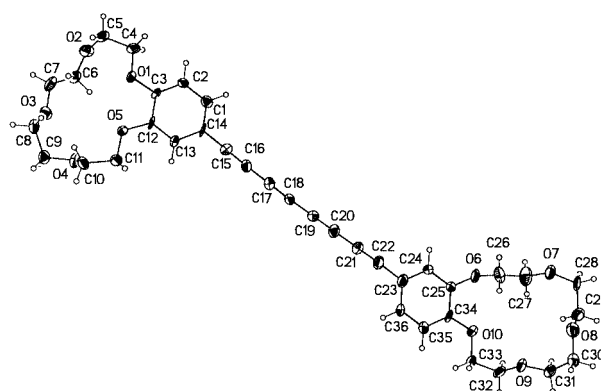


Fig. 1 View of the atom labeling scheme for  $\text{C}_{36}\text{H}_{38}\text{O}_{10}$ , **5**. Displacement parameters are scaled to the 30% probability level. Selected bond lengths (Å) and bond angles (deg): C14–C15 1.427 (12), C15–C16 1.220 (12), C16–C17 1.362 (13), C17–C18 1.211 (13), C18–C19 1.367 (13), C19–C20 1.210 (13), C20–C21 1.370 (13), C21–C22 1.204 (13), C22–C23 1.444 (13), C16–C15–C14 177.5 (10), C15–C16–C17 178.1 (11), C18–C17–C16 178.6 (12), C17–C18–C19 177.7 (10), C20–C19–C18 178.2 (12), C19–C20–C21 179.7 (9), C22–C21–C20 179.2 (11), C21–C22–C23 177.5 (11).

configurations. When 1,3-diyne monomers adopt tilted stacking, the center-to-center distance of two neighboring molecules is about 4.7–5.2 Å and the angle  $\Phi$  between the molecular and stacking axes is about  $45^\circ$ . After irradiation of the monomers, the molecules transform into diradical cumulene moieties and propagate through the molecular stacks by a 1,4-addition process, producing a conjugated enediyne polymer with a *trans* configuration. However, when the diacetylene monomers are packed in a ladder-type structure ( $\Phi = 90^\circ$ ) and the center-to-center distance of two neighboring molecules is about 3.4 Å, the topochemical polymerization is assumed to form *cis* enediyne polymers<sup>34</sup> (shown in Scheme 2).

Since the crystal structure of **2** has been determined by X-ray crystallography, its packing arrangement in the solid state was found. The center-to-center distance between two neighboring diynes was 5.141 Å within the range of 4.7–5.2 Å. The angle between the molecular and stacking axes was about  $49.4^\circ$  within

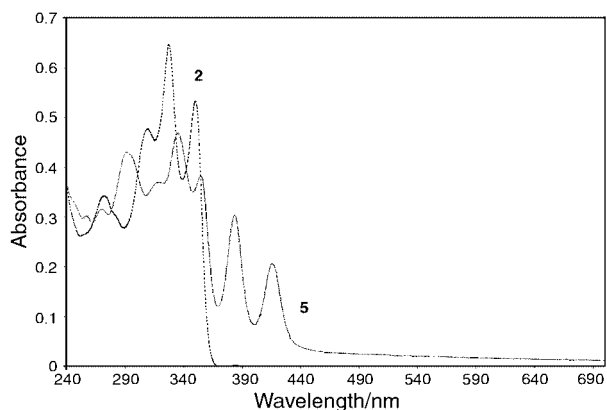
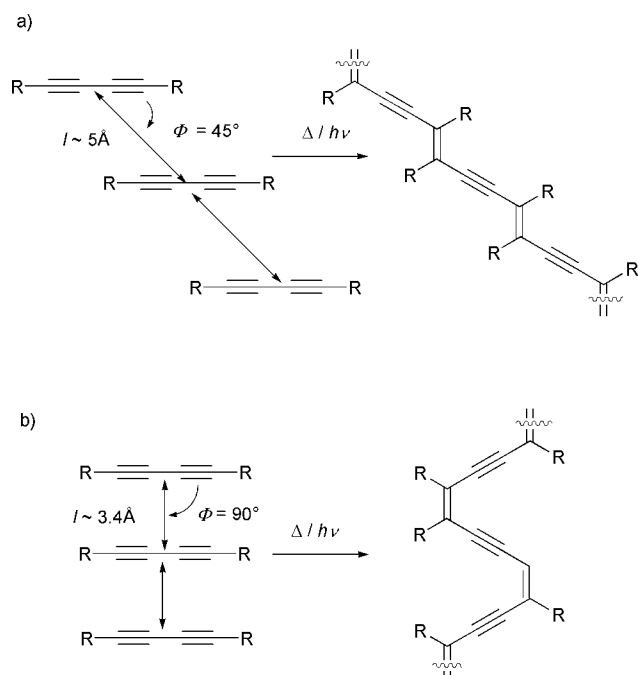


Fig. 2 UV/Vis spectra of **2** (dashed line) and **5** (solid line) in  $\text{CH}_2\text{Cl}_2$ .



Scheme 2 (a) *trans* configuration polymer; (b) *cis* configuration polymer.

the range of transformation from diynes to *trans* polymers. We thought **2** was a potential precursor for making polydiacetylene. Thus, these cross-linked polymers would consist of  $\text{=C-C}\equiv\text{C-C=}$  as the rigid backbone and benzocrown ethers as pendant groups. If guest cations were hosted by the benzocrown ethers, the conformations of the polymers would change, resulting in a shift in the UV/Vis spectrum. Hence, poly[(benzo-15-crown-5)diacetylene]s would be candidates for use as chemosensors. The solid state polymerizations of **2**, initiated with UV radiation, has been performed. The color of **2** deepened from clear to brown which indicated certain changes in the structures. The polymer solubility dropped sharply compared to the solubility of the monomer. The soluble parts of the polymer have been determined to be at least six ( $M^+ = 3497$ ) repeating units of **2** ( $M^+ = 583$ ), by low resolution mass spectroscopy in chemical ionization positive mode (shown in Fig. 3).

We were also interested in performing the solid-state polymerization using bis(benzo-15-crown-5)octa-1,3,5,7-tetrayne **5** as the monomer. According to the measurement by X-ray crystallography, the center-to-center distance was found to be about 4.5 Å and the angle between the molecular and stacking axes was shown to be about 69°. These results show that the packing arrangement of **5** in the solid state did not meet the criteria for the polymerization. Also, the color of **5** deepened from yellow to dark green after it was exposed to light for about one week.

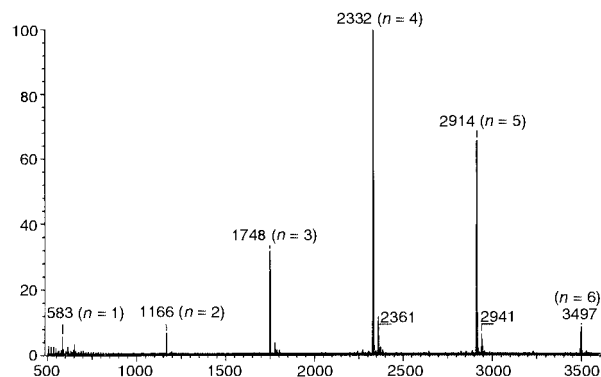


Fig. 3 Mass spectrum of poly[(benzo-15-crown-5)diacetylene].

We believed this color change indicates a transformation in the structure, but did not lead to the desired polymerization as evidenced by the mass spectrum.

As we mentioned earlier, the polymerization of **2** did not proceed very far and only trace amounts of samples were transformed. We believed the reason as to why the yield of the polymerization was so low is that the stacking factors (distance: 5.141 Å and angle: 49.4°) fell just within the edge of the criteria for topochemical polymerizations. Some disordered crown ether portions may affect the solid-state reactivity as well. Thus, we were not able to investigate the chemical and physical properties of polydiacetylenes due to the topochemical restrictions.

## Conclusion

In summary, we have prepared bis(benzo-15-crown-5)buta-1,3-diyne **2** and bis(benzo-15-crown-5)octa-1,3,5,7-tetrayne **5** successfully. Their crystal structures are reported as well. Their unusual properties and their applications will be reported in the near future.

## Experimental

### General

All reactions were carried out under argon except self-coupling reactions. Tetrahydrofuran (THF) and benzene were dried by distillation from sodium benzophenone ketyl. *N*-Butylamine was dried by distillation from  $\text{CaH}_2$ .  $^1\text{H}$  NMR spectra were recorded at either 500 or 300 MHz using Varian Utility Plus 300 or Bruker AMX 500 instruments.  $^{13}\text{C}$  NMR spectra were obtained at either 125 or 75 MHz using Varian Utility Plus 300 or Bruker AMX 500 instruments. High resolution mass spectra were performed on a ZAB2-E spectrometer. Infrared spectra were recorded using a Biorad FTS-40 instrument and UV/Vis spectra were obtained using a Beckman DU640 spectrometer. Elemental analyses were performed by Atlantic Microlab, Norcross, Georgia. All compounds were purified using silica gel 60, 230–400 mesh by liquid chromatography. Melting points were determined using a Mel-Temp capillary melting point apparatus and are uncorrected.

### 4'-(Ethyne)benzo-15-crown-5 (**1**)

4'-(2-Trimethylsilyleth-1-ynyl)benzo-15-crown-5 (12.33 g, 34 mmol) was dissolved in 300 mL of dry THF. The resulting solution was treated with tetrabutylammonium fluoride (50 mL, 1.0 M in THF, 50 mmol) at  $-10^\circ\text{C}$  for 2 h. After removal of THF under reduced pressure, the residue was purified by chromatography on silica (chloroform–methanol 40:1 as an eluent) to provide the compound (8.85 g, 30.3 mmol) as a brown oil in 89.5% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.04 (1 H, dd,  $J = 8.1, 1.8$  Hz), 6.95 (1 H, s), 6.74 (1 H, d,  $J = 8.1$  Hz), 4.11–3.72 (16 H, m), 2.96 (1 H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  149.95,

148.5, 125.8, 117.3, 114.5, 113.2, 83.7, 75.7, 71.0, 70.3, 69.3, 68.9, 68.7; IR 3308, 2934, 2876, 2255, 2199, 1511, 1264, 909, 734  $\text{cm}^{-1}$ ; HRMS-Cl ( $m/z$ ) calcd for ( $\text{C}_{16}\text{H}_{20}\text{O}_5 + \text{H}$ )<sup>+</sup> 293.1389. Found: 293.1389.

#### Bis(benzo-15-crown-5)buta-1,3-diyne (2)

4'-(Ethyne)benzo-15-crown-5 (8.73 g, 30 mmol) was dissolved in 40 mL of methanol, and then the mixture of copper(II) acetate hydrate (20.15 g) and copper(I) chloride (0.81 g) dissolved in an equal amount of pyridine and methanol (130 mL each) were introduced in the starting material solution. The reaction mixture was heated at 40 °C for 2 days. The reaction was quenched with concentrated hydrochloric acid and extracted with chloroform. The solvent was simply removed under vacuum and the residue was purified by flash chromatography and further purified by recrystallization in chloroform. The product was formed as white needles in 76.8% yield (6.68 g, 11.5 mmol). Mp 143–145 °C; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.02 (2 H, dd,  $J = 8.6, 2.0$  Hz), 6.91 (2 H, s), 6.70 (2 H, d,  $J = 8.4$  Hz), 4.05–3.66 (32 H, m); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  150.2, 148.3, 126.3, 116.99, 113.8, 112.9, 81.2, 72.6, 70.8, 70.1, 69.1, 69.0, 68.6; IR 2300, 1597, 1500, 1268, 1127, 734  $\text{cm}^{-1}$ ; HRMS-Cl ( $m/z$ ) calcd for ( $\text{C}_{32}\text{H}_{38}\text{O}_{10} + \text{H}$ )<sup>+</sup> 583.2543. Found 583.2532; UV/Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ) 350 (26744), 327 (32422), 310 (23980), 273 (17186) nm ( $\text{M}^{-1} \text{cm}^{-1}$ ). Elemental analysis: calcd C, 65.96; H, 6.57. Found: C, 65.81; H, 6.57%.

#### (Z)-1-Chloro-4-(benzo-15-crown-5)but-1-en-3-yne (3)

To a solution of 4'-(ethyne)benzo-15-crown-5 (1.81 g, 6.2 mmol) in 90 mL of dry benzene was added anhydrous *n*-butylamine (3.6 mL, 36.4 mmol), followed by *cis*-1,2-dichloroethylene (1.10 mL, 14.5 mmol). To this stirred reaction mixture was added copper(I) iodide (0.22 g, 1.2 mmol) and tetrakis-(triphenylphosphine)palladium(0) (0.43 g, 0.37 mmol). The mixture was stirred at room temperature for 18 hours under an argon atmosphere. Then the reaction was ceased by removal of solvent under reduced pressure. The residue was dissolved in chloroform and washed with brine 3 × 25 mL. The organic phase was dried over magnesium sulfate. This red extract was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica (chloroform–methanol 40:1 as an eluent) to obtain the title compound (1.27 g, 3.6 mmol) as a brown oil in 58.1% yield. <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.09 (1 H, dd,  $J = 8.4, 1.8$  Hz), 6.99 (1 H, d,  $J = 1.8$  Hz), 6.80 (1 H, d,  $J = 8.1$  Hz), 6.40 (1 H, d,  $J = 7.5$  Hz), 6.07 (1 H, d,  $J = 7.5$  Hz), 4.16–3.77 (16 H, m); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  149.98, 148.6, 127.4, 125.5, 116.8, 115.1, 113.2, 112.1, 97.6, 81.995, 71.0, 70.33, 70.29, 69.33, 69.28, 68.9, 68.7; IR 2949, 2868, 2254, 2196, 1707, 1511, 1134, 909, 733  $\text{cm}^{-1}$ ; HRMS-Cl ( $m/z$ ) calcd for ( $\text{C}_{18}\text{H}_{21}\text{O}_5\text{Cl}$ ) 352.1078. Found: 352.1079.

#### 4-(Benzo-15-crown-5)buta-1,3-diyne (4)

A stirred solution of (Z)-1-chloro-4-(benzo-15-crown-5)but-1-en-3-yne (2.695 mmol) in 60 mL dry THF was treated with tetrabutylammonium fluoride (6.8 mmol, 6.8 mL, 1.0 M in THF). This reaction mixture was stirred vigorously for 24 hours under argon. The solvent was removed *in vacuo*, then the residue was taken up by chloroform. This organic phase was washed with 20 mL of saturated ammonium chloride and 2 × 20 mL of brine, then dried over magnesium sulfate. The residue was formed by evaporation *in vacuo* and was purified by flash column chromatography on silica (chloroform as the eluent) to give 0.74 g (2.4 mmol) of product as a brown oil in 87.47% yield. <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.09 (1 H, dd,  $J = 8.3, 2.0$  Hz), 6.96 (1 H, d,  $J = 1.8$  Hz), 6.75 (1 H, d,  $J = 8.40$  Hz), 4.12–3.73 (16 H, m), 2.44 (1 H, s); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  150.7, 148.6, 126.9, 117.5, 113.15, 113.1, 75.6, 71.1, 70.9, 70.4, 69.3, 68.9, 68.7, 68.3; IR 3304, 2949, 2868, 2255, 2201, 1511, 1134,

909, 732  $\text{cm}^{-1}$ ; HRMS-Cl ( $m/z$ ) calcd for ( $\text{C}_{18}\text{H}_{20}\text{O}_5 + \text{H}$ )<sup>+</sup> 317.1389. Found: 317.1390.

#### Bis(benzo-15-crown-5)octa-1,3,5,7-tetrayne (5)

To a solution of 4-(benzo-15-crown-5)buta-1,3-diyne (1.9 mmol) in 10 mL methanol was added a green mixture of copper(I) chloride (40 mg) and 10 mL pyridine. The reaction mixture was stirred vigorously and oxygen was bubbled into the solution. After the reaction was completed, the pyridine and methanol were removed by reduced pressure. The residue was dissolved in 60 mL chloroform and this organic solution was washed with 60 mL of 2 M hydrochloric acid, followed by the equal amount of water. The extract was dried over magnesium sulfate and concentrated, then further purified by column chromatography on silica (chloroform and methanol 40:1 as an eluent). This tetrayne was obtained 0.28 g (0.45 mmol) in 23.19% yield. Recrystallization of tetraynes from the chloroform and hexane two phases were given as bright yellow crystals. Mp decomposition at 200 °C; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.13 (2 H, dd,  $J = 8.3, 1.9$  Hz), 6.98 (2 H, d,  $J = 1.9$  Hz), 6.76 (2 H, d,  $J = 8.5$  Hz), 4.13–3.73 (32 H, m); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  151.3, 148.7, 127.7, 117.8, 113.2, 112.7, 78.1, 73.5, 71.2, 70.5, 70.4, 69.4, 69.3, 69.0, 68.8, 67.2, 63.9; IR 2191, 1595, 1380, 1129, 1069  $\text{cm}^{-1}$ ; HRMS-Cl ( $m/z$ ) calcd for ( $\text{C}_{36}\text{H}_{38}\text{O}_{10} + \text{H}$ )<sup>+</sup> 631.2543. Found: 631.2543; UV/Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ) 416 (11747), 384 (17331), 354 (21879), 335 (26850), 319 (21168), 291 (24668), 271 (18087) nm ( $\text{M}^{-1} \text{cm}^{-1}$ ). Elemental analysis: calcd C, 68.55; H, 6.07. Found: C 67.51, H 6.05%.

#### X-Ray crystallographic analysis of compounds 2 and 5 ‡

X-Ray data were collected on a Siemens P4 diffractometer, equipped with a Nicolet LT-2 low-temperature device and using a graphite monochromator with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data reduction, decay correction, structure solution and refinement were performed using the SHELXTL/PC software package.<sup>35</sup>

#### Compound 2

Crystal data for  $\text{C}_{32}\text{H}_{38}\text{O}_{10}$ ,  $M = 582.62$ , monoclinic, space group  $P2_1/c$ ,  $a = 13.344(1)$ ,  $b = 5.1406(5)$ ,  $c = 21.862(3)$  Å,  $\beta = 100.95(1)^\circ$ ,  $V = 1472.3(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 198(2)$  K,  $\mu$  (Mo-K $\alpha$ ) = 0.097  $\text{mm}^{-1}$ , 2581 reflections measured, 1872 unique ( $R_{\text{int}} = 0.052$ ). Refinement on  $F^2$  using all data with  $wR(F^2) = 0.267$ ,  $R(F) = 0.114$  for 927 reflections with  $F_o > 4(\sigma(F_o))$ . The molecules lie on a crystallographic inversion center. A fragment of the crown ether portion of the molecule is disordered.

#### Compound 5 (Fig. 1)

Crystal data for  $\text{C}_{36}\text{H}_{38}\text{O}_{10}$ ,  $M = 630.66$ , triclinic, space group  $P-1$ ,  $a = 8.781(4)$ ,  $b = 8.807(4)$ ,  $c = 21.478(14)$  Å,  $\alpha = 79.22(4)$ ,  $\beta = 79.78(4)$ ,  $\gamma = 73.48(3)^\circ$ ,  $V = 1550.6(14)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 193(2)$  K,  $\mu$  (Mo-K $\alpha$ ) = 0.098  $\text{mm}^{-1}$ , 4261 reflections measured, 4001 unique ( $R_{\text{int}} = 0.11$ ). Refinement on  $F^2$  using all data with  $wR(F^2) = 0.206$ ,  $R(F) = 0.0933$  for 1558 reflections with  $F_o > 4(\sigma(F_o))$ .

#### Acknowledgements

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‡ CCDC reference number 207/447. See <http://www.rsc.org/suppdata/p1/b0/b001856m> for crystallographic files in .cif format.

#### References

- (a) C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017; (b) C. J. Pedersen, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1021.

- 2 (a) J. M. Lehn, *Struct. Bonding (Berlin)*, 1973, **16**, 1; (b) J. M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 59.
- 3 D. J. Cram, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1009.
- 4 J. M. Lehn, *Pure Appl. Chem.*, 1980, **52**, 2441.
- 5 A. Carroy and J. M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1986, 1232.
- 6 J. C. Chambron and J. P. Sauvage, *Tetrahedron Lett.*, 1986, **27**, 865.
- 7 P. D. Beer, *J. Chem. Soc., Chem. Commun.*, 1986, 1678.
- 8 H. Nakamura, H. Nishida, M. Takagi and K. Ueno, *Bunseki Kagaku*, 1982, **31**, E131.
- 9 G. R. Brown and A. J. Foubister, *J. Med. Chem.*, 1979, **22**, 997.
- 10 K. Kikukawa, A. Abe, F. Wada and T. Matsuda, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 961.
- 11 K. Kikukawa, G. He, A. Abe, T. Goto, R. Arata, T. Ikeda, F. Wada and T. Matsuda, *J. Chem. Soc., Perkin Trans. 2*, 1987, 135.
- 12 F. Wada, R. Arata, T. Goto, K. Kikukawa and T. Matsuda, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2061.
- 13 P. D. Beer and A. S. Rothin, *Polyhedron*, 1988, **7**, 137.
- 14 B. Konig and H. Rutters, *Tetrahedron Lett.*, 1994, **35**, 3501.
- 15 K. Kimura, H. Sakamoto, Y. Koseki and T. Shono, *Chem. Lett.*, 1985, 1241.
- 16 R. Eastmond and D. R. M. Walton, *Tetrahedron*, 1972, **28**, 4591.
- 17 R. J. Lagow, J. J. Kampa, H.-C. Wei, S. L. Battle, J. W. Genge, D. A. Laude, C. J. Harper, R. Bau, R. C. Stevens, J. F. Haw and E. Munson, *Science*, 1995, **267**, 362.
- 18 T. Bartik, B. Bartik, M. Brady, R. Dembinski and J. A. Gladysz, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 414.
- 19 J. S. Lindsey and R. W. Wagner, *J. Am. Chem. Soc.*, 1994, **116**, 9759.
- 20 V. S. Lin, S. G. DiMagno and M. J. Therien, *Science*, 1994, **264**, 1105.
- 21 T. M. Swager, *Acc. Chem. Res.*, 1998, **31**, 201.
- 22 P. D. Beer, O. Kocian, R. J. Mortimer and C. Ridgway, *J. Chem. Soc., Dalton Trans.*, 1993, 2629.
- 23 P. J. Stang and F. Diederich, *Modern Acetylene Chemistry*, New York, VCH, 1995.
- 24 G. Z. Wegner, *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.*, 1969, **24**, 824.
- 25 G. Wegner, *Makromol. Chem.*, 1970, **134**, 219.
- 26 G. Wegner, *Makromol. Chem.*, 1971, **145**, 85.
- 27 A. Sarkar and S. S. Talwar, *J. Chem. Soc., Perkin Trans. 1*, 1998, 4141.
- 28 E. M. Hyde, B. L. Shaw and I. Shepherd, *J. Chem. Soc., Dalton Trans.*, 1978, 1696.
- 29 S. Takahashi, Y. Kuroyama, K. Sonogashira and N. Hagihara, *Synth. Commun.*, 1980, 627.
- 30 J. L. Sessler, C. T. Brown, R. Wang and T. Hirose, *Inorg. Chim. Acta*, 1996, **251**, 135.
- 31 O. M. Behr, G. Eglinton, A. R. Galbraith and R. A. Raphael, *J. Chem. Soc.*, 1960, 3614.
- 32 The purities and structures of compound **2** and **5** were confirmed by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, IR, UV, mass spectrometry, melting point, elemental analysis, and X-ray crystallography. Details are provided as supplementary data.
- 33 A. S. Kende and C. A. Smith, *J. Org. Chem.*, 1988, **53**, 2655.
- 34 G. W. Coates, A. R. Dunn, L. M. Henling, D. A. Dougherty and R. H. Grubbs, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 248.
- 35 G. M. Sheldrick, SHELXTL/PC, Version 5.03, Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.