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Exploring the Chemistry of a Double-Stranded Cycle with the Carbon Skeleton of the Belt Region of the C_{84} Fullerene

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Intense scale-up efforts greatly improved the availability of the known double-stranded cycle **2** with two bridging ether units. The chemistry of **2** towards Bronsted and Lewis acids could, therefore, be investigated quite comprehensively. It was discovered that the reactivity of **2**, whose carbon framework resembles the belt region of the C_{84} (D_2) fullerene, is rather unusual as compared with acyclic model compounds. Whereas the latter could easily be dehydrated to the corresponding planar arenes, the former gave rise to a bouquet of unexpected reactions, which all avoided the aromatization of **2** to its still-elusive, fully conjugated congener **B**. Intermediates generated from **2** under acidic conditions attack the solvent (e.g. toluene) to give **4**, form bridging lactones to give **11** or close back to starting material **2** (e.g. from **16**) rather than dehydrate to more highly conjugated structures on the way to the fully unsaturated target cycle **B**. The structure of compound **4** was solved by X-ray diffraction. Through the reactions of **2** with Lewis acids, derivatives **14** and **15** became accessible. They are candidates for future attempts to achieve the desired aromatization under basic conditions or by thermal treatment.

Introduction

Fully unsaturated, double-stranded hydrocarbon cycles have been a dream of chemists for several decades.[1–3] Besides their aesthetic appeal, they could be important to the study of host/guest interactions including hydrogen bonding between weak donors and π-systems, the formation of polyrotaxanes, the *endo*/*exo* selectivity of reactions, the dynamics of transition-metal fragments complexed to a π-system and redox behaviour such as maximum chargeability. They could also serve as models for their open-chain linear analogues, the ladder polymers.[4] Furthermore, they are expected to exhibit an unprecedented electron density distribution, may show superconductivity[5] and could be developed into novel shape-persistent constituents for molecular constructions. Though there has been significant synthetic progress, a breakthrough has not yet been achieved. Several double-stranded cycles with the appropriate carbon skeletons were synthesized and even a few chemical modifications were accomplished with the aim of expanding the conjugated parts of the compound.[6] However, attempts to generate a fully unsaturated structure like belt **A**, which consists of linearly annulated six-membered rings, or belt **B**, which combines five- and six-membered rings, failed altogether. Reasons for this are target specific but, by and large, have something to do with the compound's curvature, rendering a fully conjugated structure energetically less favourable compared to uncurved flat analogues. This energy price will make the final "aromatization" step more difficult to achieve. Additionally, the target structure, once accomplished, will be more prone to follow-up reactions, which may not render it isolable. With this consideration in mind, we decided that [*n*]cyclacenes (**A**) (Figure 1) may not be the optimum choice to start with. They resemble curved oligoacenes, the uncurved representatives of which have exhibited an extreme reactivity.[7] We rather started a project aimed at target structures like **B** (Figure 1), which can be considered the belt region of buckyballs. Here the conjugated system contains five-membered rings, a structural feature which ought to render these targets more persistent.[8] Recently, the syntheses of compound **1** and its dehydration product **2** (Figure 1), which contain the required carbon skeleton and are potential precursors of **B** were reported.[1d] Unfortunately, the synthetic sequence leading to them comprises several steps and does not provide sufficient quantities of **1** or **2** to reasonably explore their chemistries. Based on a successful scale-up process, the present contribution describes the first substantial investigation into the reactivity of compound **2**, always with the intention to convert it either directly into **B** or into novel intermediates from which **B** may be eventually accessible. The focus of this report is on electrophilic reagents and conditions (proton and

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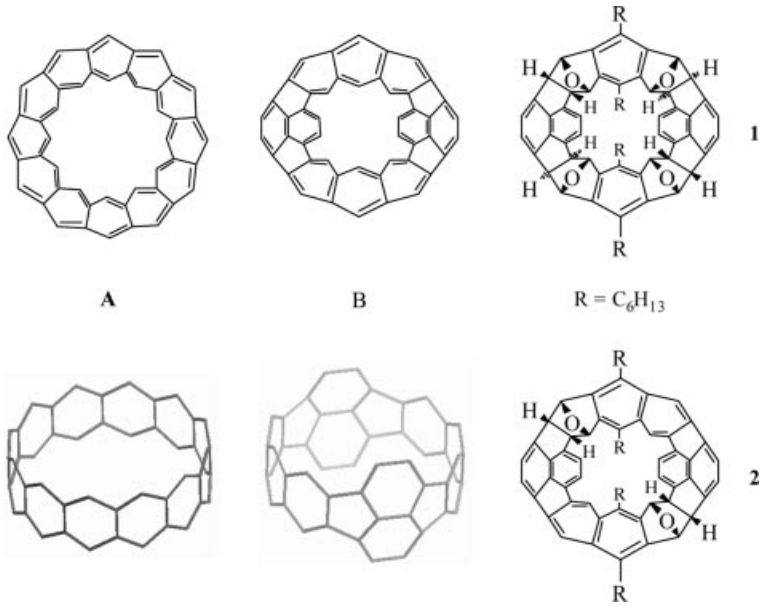


Figure 1. Chemical and spatial structures of a [*n*]cyclacene **A**, the targeted buckybelt **B** and chemical structures of compounds **1** and **2**.

Lewis acids). Whenever appropriate, the curvature of starting materials or products is invoked to rationalize the outcome of model reactions.

Results and Discussion

Treatment with Proton Acids

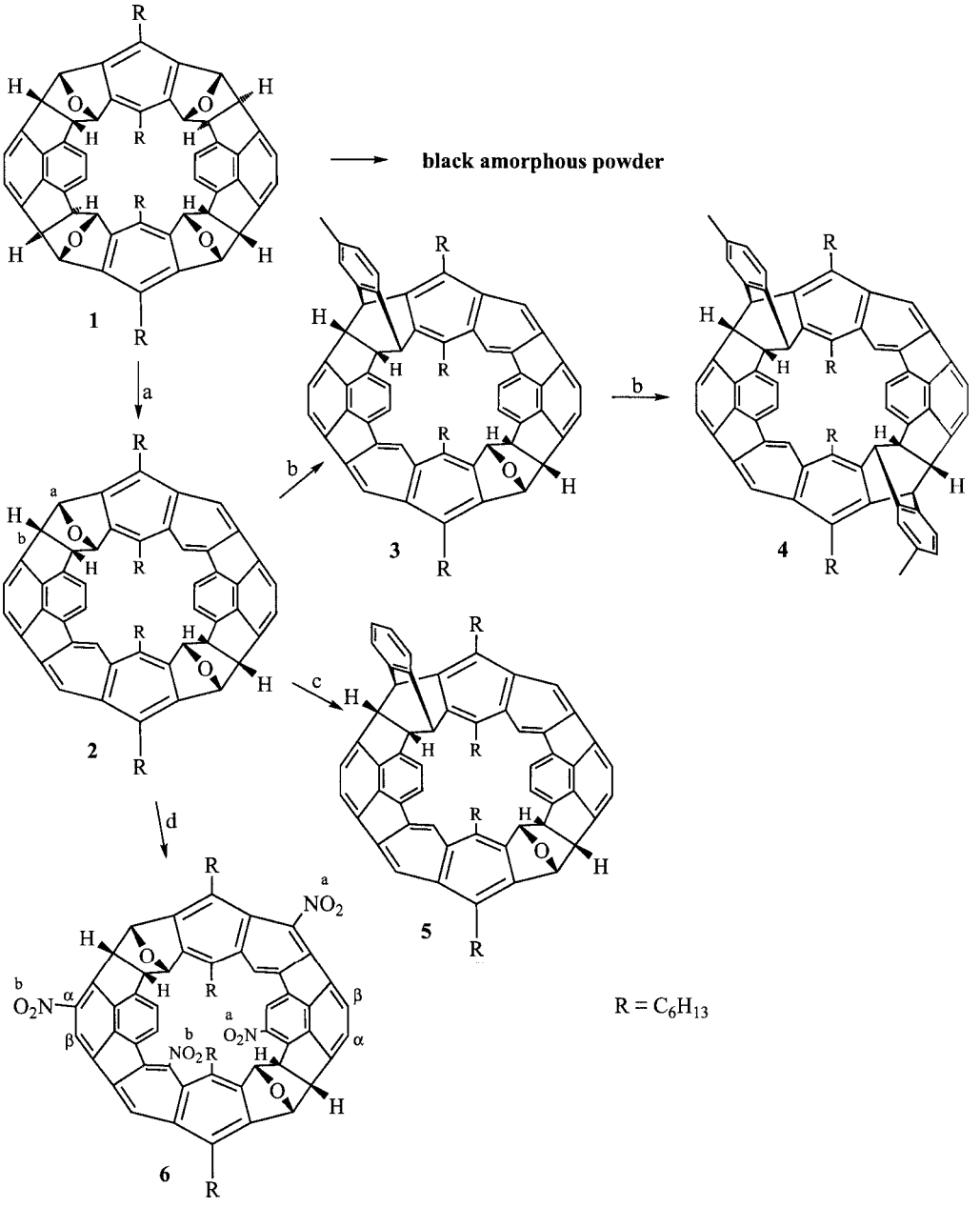
As has already been reported,[1d] compound **1**, upon acidic treatment, suffers loss of only two of its four "waters" to give compound **2** (a "water" is an oxygen bridge plus two adjacent hydrogen atoms). We reasoned that the removal of the remaining "waters" would be associated with a change of the almost strainless oval structure of **2** into the strained round structure of **B** and that this build up of strain may hinder facile follow-up reactions of **2**. Compound **2** was, therefore, considered a key compound in the entire enterprise, and its limited availability (10–20 mg) needed to be overcome first. Since there was not much to be optimized in the synthetic sequence leading to it, we decided to try to scale the sequence up considerably so as to provide at least 500 mg of **1**, the direct precursor of **2**. Consequently, dihydropyracylene (**12**) and the isobenzofuran precursor **13** of ref.[1d] (the original scheme from this reference is given in the Supporting Information; compounds **12**–**17** in this paragraph refer to the compounds in this scheme) were prepared on a 15 g and 100 g scale, respectively. In typical experiments, 7 g of **12** and 33 g of **13** were reacted with one another to give a raw 3:1 mixture of *endo*- and *exo*-**14**[1d] on a 30 g scale. This mixture was separated by column chromatography, as reported, but now with loadings as high as 25 g. Most of the material could be obtained in fractions containing the pure isomers; there was, however, always a fraction containing a mixture. This typically amounted to 1–3 g and was subjected to a second separation. The pure isomers *endo*- and *exo*-**14** were obtained on a 22 g scale and then dehydrogenated with DDQ to give the corresponding isomers *endo*- and *exo*-**15**[1d] in amounts of up to 5 and 20 g, respectively. The reaction time for this step was pro

Table 1. Conditions and products of compounds **1** and **2** in reaction with proton acids.

Entry	Starting compound	Solvent	Acid	Reaction conditions			Products
				T [°C]	Reaction time [h]	[**1**] or [**2**]/[acid]	
1	**1**	toluene	*p*-$CH_3C_6H_4SO_3H$	90–100	48	0.25	**1**+**2**
2	**1**	toluene	*p*-$CH_3C_6H_4SO_3H$	reflux	12	0.25	**4**
3	**1**	toluene	CF_3COOH	reflux	48	0.17	**1**+**2**
4	**1**	toluene	CH_3SO_3H	reflux	4	0.17	**4**
5	**1** or **2**	toluene	CH_3SO_3H	reflux	2	0.17	**1**+**2**+**3**+**4**
6	**1**	benzene	CH_3SO_3H	reflux	48	0.25	**2**
7	**1**	*o*-dichlorobenzene	CH_3SO_3H	140	10	0.25	**2**
8	**1**	nitrobenzene	CH_3SO_3H	130	0.5	0.25	**2**
9	**1**	nitrobenzene	CH_3SO_3H	130	2–3	0.25	black material
10	**1**	CCl_4	CH_3SO_3H	110	36	0.50	**2**
11	**2**	neat	H_2SO_4 (concd.)	150	24	excess of acid	**2**
12	**2**	neat	P_2O_5/CH_3SO_3H	r.t.	24	excess of acid	**2**
13	**2**	benzene	CH_3SO_3H	150	12	0.33	**5**
14	**2**	*o*-dichlorobenzene	HNO_3 (concd.)	100	0.5	0.17	**6**

longed by a factor of 2 relative to that reported in the literature procedure. The obtained quantities were directly employed in the next step, which after column chromatographic separation, led to the four diastereomers **16**[1d] in quantities of up to 2.5 g, 2.3 g, 7.2 g and 3.1 g for *exo*,*syn*-**16**, *exo*,*anti*-**16**, *endo*,*syn*-**16** and *endo*,*anti*-**16**, respectively. These amounts were then directly subjected to the next step, which gave the cycle precursors **17**[1d] in the following amounts: 2.2 g, 2.3 g, 7.6 g and 3.1 g for *exo*,*syn*-**17**, *exo*,*anti*-**17**, *endo*,*syn*-**17** and *endo*,*anti*-**17**, respectively. Finally, these precursors were converted in separate experiments[9] into starting material **1**, through which it became accessible as analytically pure material in amounts of up to 3 g.

In the next step, the conversion of **1** to **2** was explored in some detail to find improved conditions. Initially, this conversion had been performed with *p*-toluenesulfonic acid (*p*TsOH) in hot toluene and proceeded in an unsatisfactory 47% yield. The optimization was performed with different proton acids under varying conditions. During this investigation, it became clear that, under certain conditions, compound **2** undergoes follow-up reactions. Table 1 summarizes the attempts that led from **1** to **2** and those where other products formed. Additionally, it contains representative cases in which **2** was used as a starting material in attempted dehydrations with proton acids. The corresponding synthetic sequences can be found in Scheme 1. Reaction of



Scheme 1. Reagents and conditions. a) $CH_3SO_3H/C_6H_5NO_2$, 130 °C, b) CH_3SO_3H/C_7H_8, reflux, c) CH_3SO_3H/C_6H_6, 150 °C, d) HNO_3/*o*-$C_6H_4Cl_2$, 100 °C.

2 with reagents other than proton acids will be treated below and in subsequent publications.[10]

All experiments starting from **1** were carried out either in flasks or in NMR tubes. For screening purposes, the flask experiments were performed on a 10–40 mg scale. The reaction progress was monitored by TLC and/or NMR integration. The best results for the generation of **2** as the only product in the shortest time were achieved with methanesulfonic acid in nitrobenzene at 130 °C (Table 1, Entries 1–10). Under these conditions, the double dehydration of **1** to **2** proceeded very cleanly and gave the product virtually quantitatively, if the reaction was quenched after approximately 30 min (see below). Also, the workup was very simple. The raw product just needed to be taken up in ethanol and cooled to 0 °C, whereupon compound **2** crystallized out. When the same acid was applied in benzene, *o*-dichlorobenzene or carbon tetrachloride (Table 1, Entries 6, 7 and 10), the reaction also went very cleanly but required more time. A more complex situation was encountered when toluene was used as solvent (Table 1, Entries 1–5). In the case of *p*TsOH in toluene, a relatively small difference in temperature changed the products significantly. Whereas for up to 100 °C (Table 1, Entry 1), a mixture of **1** and **2** was observed (with an increasing proportion of **2** with increasing time), refluxing the mixture at 115 °C led to a new and single product (**4**), isolated in a yield of 70%. The same product also formed with methanesulfonic acid (Table 1, Entry 4) in virtually quantitative yield, and its structure was established by single-crystal X-ray diffraction and MALDI TOF mass spectrometry (Figure 2).

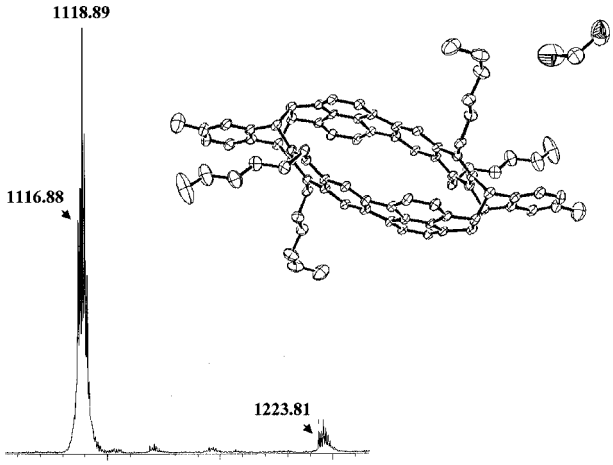


Figure 2. Molecular structure (ORTEP,[11] 50% probability scale) of compound **4** with one molecule of CH_2Cl_2 in the crystal (left) (symmetry operation to form the complete molecule: $2 - x$, $1 - y$ and $1 - z$) and MALDI TOF mass spectrometric molecular ion peak of **4** (right) (Dithranol matrix, $Ag^+BF_4^-$). The molecular weight of **4** is 1117.59 g/mol. The signal at m/z = 1223.8 corresponds to the Ag^+ adduct.

Compound **4** contains two toluene molecules, which bridge the cycle's two strands at the positions where the oxygen bridges of **2** had been. The methyl groups of the "toluene" units are oriented *anti* to one another. No indication of a *syn* isomer was obtained. Even in a 700 MHz raw NMR spectrum, only one signal for the methyl groups was observed. Thus, a preferential crystallization of the *anti* isomer seems unlikely.

Compound **4** crystallizes in the monoclinic space group $P2_1/n$ with half a molecule of **4** and one molecule of CH_2Cl_2 forming the asymmetric unit. Thus, **4** possesses crystallographic C_i symmetry, as necessary for the *anti* orientation of the toluene units. The atomic numbering scheme (Figure 3) shows the molecule with side chains and hydrogen atoms omitted. The molecule has an elliptical shape with long and short axes of about 11.6 Å and 4.5 Å, respectively. The unsaturated part of the molecule differs strongly from planarity resulting in an angle of the planes defined by C2, C3, C29 and C21 and C1′, C11, C12 and C22' (symmetry operation to create C1′ and C22′: $2 - x$, $1 - y$ and $1 - z$) of 125.9(1)°. Thus, C2, C21, C11 and C12 lie 1.14 Å, 1.17 Å, 0.96 Å and 0.97 Å, respectively, below the least-square plane defined by C6, C8, C15 and C17. Bond lengths within the unsaturated part of the molecule vary between 1.35 Å and 1.48 Å with the longest bonds found in the central five-membered ring. Very large [C5–C6–C7: 137.2(6)° and C16–C17–C18: 137.9(6)°] and small [C7–C6–C24: 104.5(5)°, C16–C17–C24: 104.7(6)°] bond angles were observed at C6 and C17, respectively. The longest bond of 1.61(1) Å was between C2 and C21.

A plausible mechanism for this somewhat unexpected formation of **4** is that on the way to dehydration a protonated oxygen bridge opened to a carbenium ion, which then attacked the solvent toluene in an electrophilic aromatic substitution reaction. A subsequent protonation at the same oxygen, followed by extrusion of the preformed water molecule, generated a second carbenium ion on the other

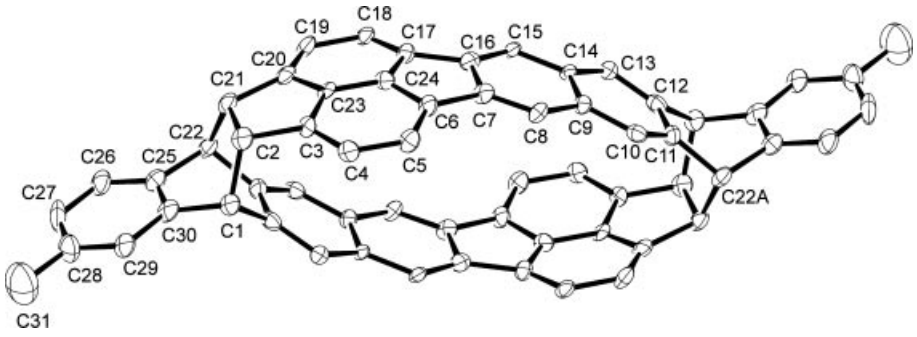


Figure 3. Atomic numbering scheme (ORTEP[11]). Side chains and hydrogen atoms are omitted.

side, which attacked the toluene already connected to the opposite side, leading to the bridged structure shown in Figure 2.

As one would expect, the incorporation of the two toluene molecules proceeded in a stepwise fashion (Table 1, Entry 5). If the reaction was quenched after about 2 h, a mixture of **1**, **2** and **4** was found plus a small quantity of compound **3** (TLC), in which only one of the oxygen bridges suffered replacement by toluene. Entry 13 of Table 1 shows that benzene can also participate in such undesired reactions. Under harsh enough conditions, a few percent of the benzene-containing compound **5** were found when benzene was used as the solvent. Refluxing of **1** with methanesulfonic acid in benzene, however, did not lead to any follow-up reaction of **2** (Table 1, Entry 6). Additionally, with concentrated nitric acid, the oxygen bridges of **2** stayed intact, but the cycle underwent four-fold nitration to derivative **6**, which was obtained in a yield of 80%. Through an investigation of CH long-range couplings in the NMR spectra of **6**, the *anti* positioning of the two pairs of nitro groups (denoted as *a* and *b* in Scheme 1) was established; the relative orientation of these two pairs, however, is still not known. Note that the nitro groups at the naphthalene moieties vertical to the cycle's perimeter are always located at the C atom near the oxygen bridge (position α). The alternative position β was ruled out by the NMR coupling experiments. Compound **6** is crystalline. Unfortunately, crystals large enough for X-ray diffraction could not be obtained. Finally, it should be noted that even when heated to 150 °C in concentrated sulfuric acid (H_2SO_4), compound **2** remained completely unchanged (Table 1, Entry 11)!

After this screening phase, compound **2** was also prepared in a synthetically useful quantity of 200 mg.[12] In several independent runs, the isolated yields were between 80–90% after purification by column chromatography. This represents a considerable advance over the 47% yield, which had been achieved previously. As was mentioned above, it was important to quench the reaction of **1** with methanesulfonic acid in nitrobenzene (Table 1, Entry 8) immediately after the starting material had been consumed (as determined by TLC). Only then were the reported high yields obtained. If compound **2** was treated for a longer time under these conditions, a black insoluble material precipitated, leaving only a trace of **2** in solution (Table 1, Entry 9). Thus, this material is a follow-up product of **2** and, as such, of potential interest in the context of the present investigation. Some effort was, therefore, invested to unravel its structure. Unfortunately, all attempts to solubilise it failed. Refluxing of the black material in toluene, benzene or *o*-dichlorobenzene, or treating it with concentrated H_2SO_4 at 150 °C or carbon disulfide at 40 °C did not lead to any extraction. The solutions stayed colourless. By visual inspection, it also seemed that the material did not swell. Therefore, we concluded that it was densely cross-linked. Some insight into its structure could nevertheless be gained by solid-state ^{13}C NMR spectroscopy, whereby the most striking feature observed was the loss of much of the remaining "water" molecules while the main carbon structure seemed to be retained. This proposal is based on a comparison of the solid-state ^{13}C NMR spectra of the black product and the starting material **2**.[13] This comparison shows that the intensity of the signals of the carbon atoms carrying the "water" hydrogens and oxygens, which for **2** absorb at δ = 55 ppm and δ = 80 ppm, respectively, is reduced for the black product relative to that of compound **2** (Figure 4). Also, the remaining signals became much broader. At the same time, the intensity of the carbon atoms absorbing in the aromatic region seems to have increased, and the alkyl chains are clearly still present. It would be tempting to propose that dehydration to the aromatic target compound **B** had actually taken place to some degree, and that the product then suffered a follow-up reaction involving cross-linking. A plausible pathway for cross-linking could be the dimerization of the anthracene units of **B**. Pericyclic anthracene dimerizations through their 9,10-positions have been intensely studied but are not thermally allowed by orbital symmetry rules.[14] For anthracene dimmers, one would, however, expect chemical shifts for the bridgehead positions to be in the range of δ = 50–60 ppm,[15] and the signal present in this range is of low intensity (Figure 4). An alternative mechanism for cross-linking could be based on proton-catalyzed intermolecular ether formation at hydroxy groups resulting from opened ether bridges of **2**. This would require significant amounts of carbon–oxygen bonds to still be present. The corresponding ^{13}C NMR signals ought to have very similar chemical shifts to the ones in starting compound **2**. However, there are only relatively low-intensity signals in this range. The data from combustion analysis are not fully convincing either but may support this mechanistic assumption. The carefully dried black material (7 d at 20 °C, followed by 3 d at 150 °C both under high vacuum) was analyzed repeatedly for C, H, N, O and S, and the following average values in % were found: C 82.35, H 6.66, N 0.80, O 7.52 and S 1.63 (total: 98.96%). Taking into account that the material had contact to nitrobenzene and methanesulfonic acid, approximately 4.4% of the 7.5% of oxygen content could be rationalized by assuming that the samples still contained these two compounds, which had somehow adhered despite the rigorous drying procedure. However, even if one accepts this assertion, it remains unclear to which structural element the remaining oxygen content of 3.1% could be assigned, since the NMR spectrum shows that the amount of oxygen-carrying carbons was reduced. Please note the intensity of the carbon atoms bound to oxygen in the starting compound **2**, which has an oxygen content of 3.3%.

Powder X-ray diffractometry proved the black material to be completely amorphous, and MALDI TOF mass spectrometric analyses did not furnish any conclusive results. At this point, it has to be concluded that the structure of the black material remains unclear. Research in this direction is ongoing.

From the results in Table 1 it becomes clear that compound **2** is amazingly stable towards protic conditions. As mentioned above, even when concentrated H_2SO_4 is applied at 150 °C, the compound survives unchanged. It will not be

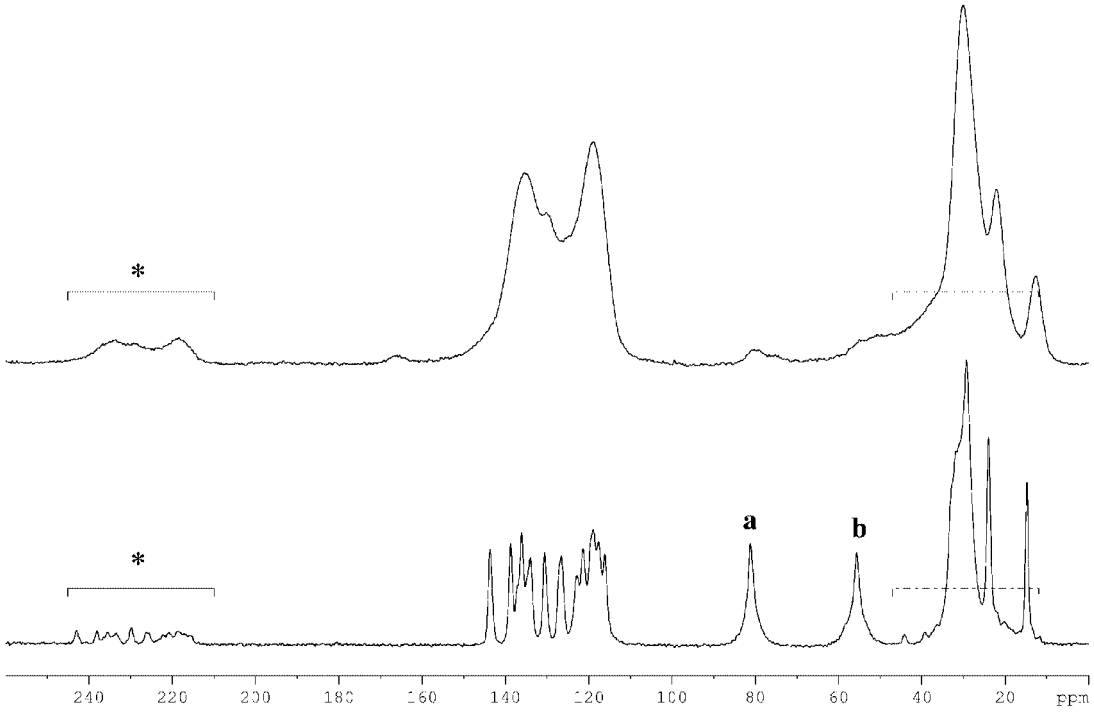
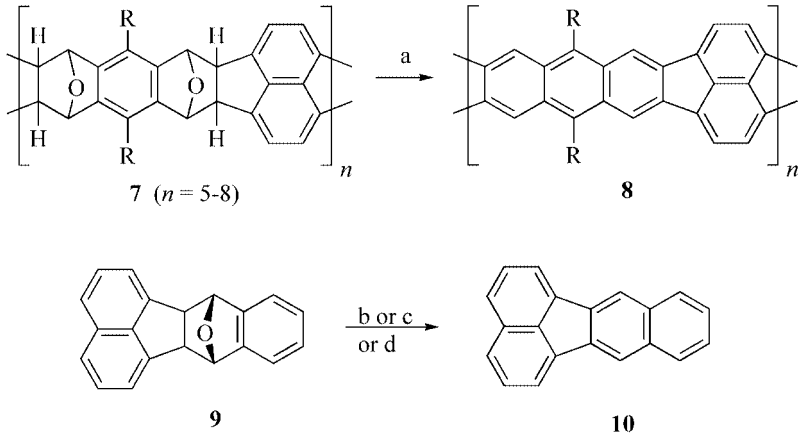


Figure 4. CPMAS ^{13}C NMR spectra of compound **2** (bottom) and the black amorphous powder obtained from **1** with methanesulfonic acid in nitrobenzene (top). For the assignment of the signals marked a and b, consult structure **2** in Scheme 1. Spinning side bands are marked by an asterisk *. The origin of the signal at approximately δ = 170 ppm is unclear.



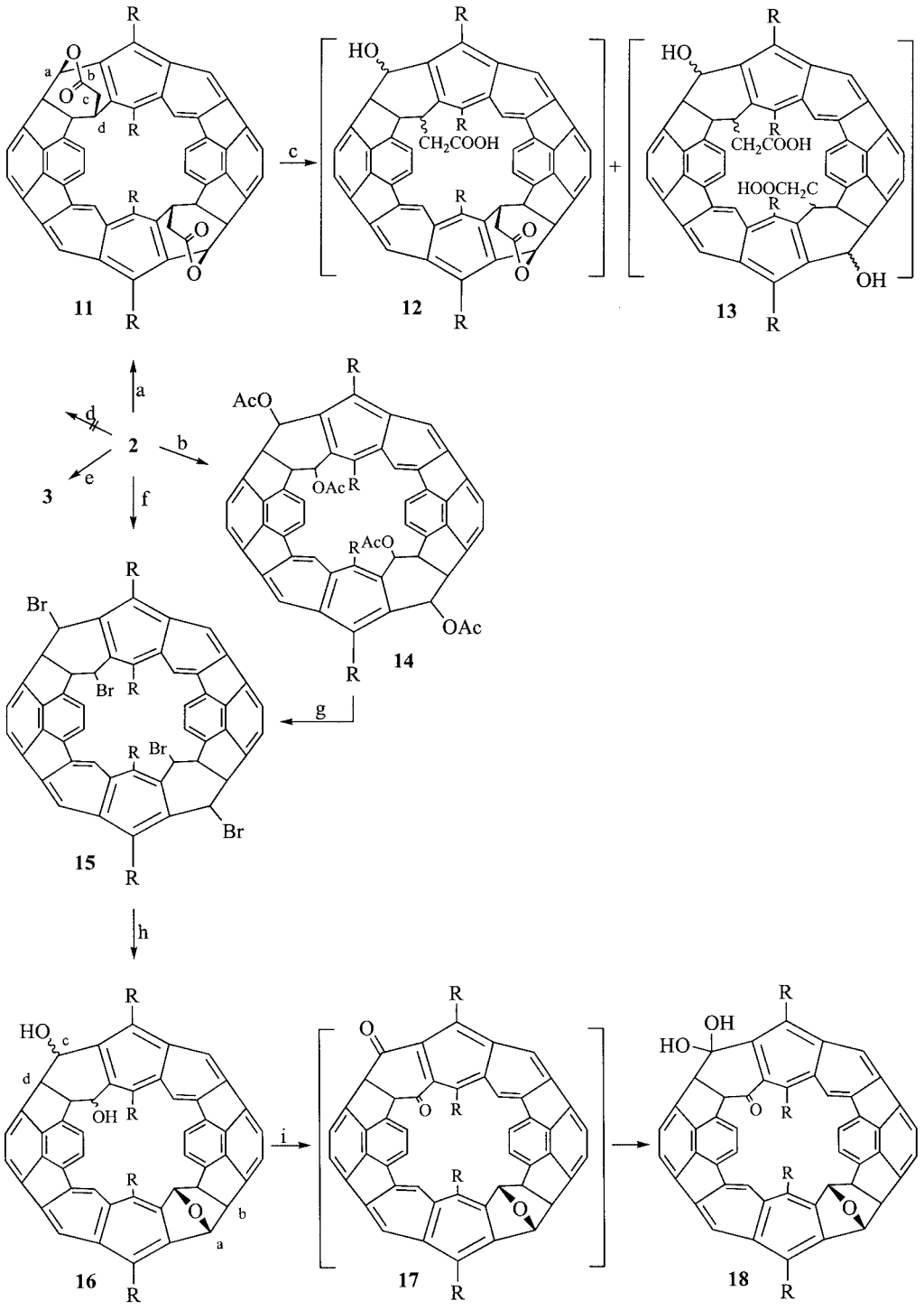
Scheme 2. Reagents and conditions. a) *p*TsOH/C_7H_8, b) H_2SO_4/P_2O_5, c) $ZnCl_2/Ac_2O$, d) $TiCl_4/Et_3N/CH_2Cl_2$.

too surprising, therefore, that application of similar conditions as those in Table 1 to model compounds like **7** and **9** led to their immediate dehydration with aromatization and furnished **8** and **10**, respectively, in very high yields (Scheme 2). This comparison underlines the rather peculiar properties of compound **2** (see below).

Treatment with Lewis Acids

Cycle **2** was treated with various Lewis acids including $ZnCl_2$, BBr_3, $TiCl_4$ and γ-Al_2O_3, which have been used in the literature for the dehydration of bridged ether fragments of the kind dealt with here.[16] Representative reactions are summarized in Scheme 3 and Table 2. The cleanest reaction courses were observed with $ZnCl_2$ and Ac_2O as the solvent (Table 2, Entries 1 and 2). Depending on the ratio of **2** to $ZnCl_2$ and the reaction temperature, either compound **11** (as a mixture of isomers, which differ by the relative orientation of the lactone units) or **14** (as a single isomer) was obtained in yields above 80%. For a **2**/$ZnCl_2$ of 1:2 at 130 °C, compound **11** was obtained. No trace of **14** could be detected. However, if the Lewis acid was applied in trace amounts only and the temperature was kept at 60 °C, compound **14** was obtained, and no **11** found. As expected, if the former conditions were applied to model compound **9** (Scheme 2), clean dehydration to **10** took place (80% yield).

No bridged compound analogous to **11** was found. The structure of the isomers of **11** rests upon ^{1}H and ^{13}C NMR analysis. Especially informative is the appearance of the bridging methylene unit (H^c) as an ABX spin system at δ = 3.56 ppm and δ = 3.29 ppm in the ^{1}H NMR spectrum and the carbonyl carbon, which absorbs at δ = 171.58 ppm, typical for lactones. Additional support comes from an analysis of the long-range couplings, which can be observed between H^a and C^b as well as H^d and C^b. For further information regarding this long-range coupling see the Supporting Information. The ratio of the two isomers of **11** was determined as approximately 50:50 by ^{1}H NMR integration of some of the signals in the aromatic region, which were clearly resolved. The IR spectrum of **11** shows a stretching vibration at $\tilde{\nu}$ = 1726 cm^{-1}, and the high-resolution MALDI mass spectrum gives the molecular ion at *m*/*z* =



Scheme 3. Reagents and conditions. a) $Ac_2O/ZnCl_2$ (1:2), 130 °C, b) $Ac_2O/ZnCl_2$ (traces), 60 °C, c) KOH/THF, d) $TiCl_4/Et_3N$/DCM, e) Al_2O_3/C_7H_8, reflux temp., f) BBr_3/DCM, r.t., g) $PBr_3/CDCl_3$, h) H_2O, i) PCC/DCM, r.t.

Table 2. Conditions and products of compound **2** in reactions with Lewis acids.

Entry	Starting compound	Solvent	Acid	Reaction conditions			Products
				T [°C]	Reaction time [h]	[**2**]/[acid]	
1	**2**	acetic anhydride	$ZnCl_2$	130	0.5	0.5	**11**
2	**2**	acetic anhydride	$ZnCl_2$	60	1	traces of acid	**14**
3	**2**	CH_2Cl_2	$TiCl_4/Et_3N$	r.t.	3	0.1	**2**
4	**2**	toluene	γ-Al_2O_3	150	24	excess of acid	**2**+**3**
5	**2**	CH_2Cl_2	BBr_3	r.t.	48	0.25	**15**

1053.5738. Crystals of **11** were obtained; however, their size was insufficient for X-ray structure analysis. The lactone unit in **11** was also chemically proved. Upon basic treatment of the isomeric mixture of **11**, a mass spectrometric analysis of the raw product showed molecular ion peaks corresponding to the partially and fully saponified products **12** and **13**, respectively. Attempted isolation of these compounds by column chromatography on silica gel caused ring closure, and only lactone **11** was obtained.

The structure of **14** was clarified mainly by NMR spectroscopy. The most striking point is the fact that the acetate methyl groups appear isochronously at δ = 2.29 ppm (500 MHz). This indicates that only one isomer has formed because the methyl groups should sense whether they are inside or outside of the double-stranded ring. The acetates most likely are pointing outwards. This is supported by the finding that compound **14** closes back to the starting material **2** upon treatment with concentrated H_2SO_4. A possible mechanism involves acid-catalyzed hydrolysis of the acetates, followed by an transannular dehydration to give the bridging ethers. This transannular dehydration obviously proceeds faster than a potentially competing dehydration to the fully unsaturated target **B**, which was not observed (by mass spectrometry).

The role of $ZnCl_2$ in the formation of **11** and **14** can be rationalized. As an oxophilic compound, it can dock both to the oxygen bridges of **2** and the carbonyl oxygen atoms of Ac_2O and also catalyze the enolization of Ac_2O. At high concentrations of $ZnCl_2$, we suggest that the oxygen bridges of **2** are attacked and either opened directly to give a benzylic carbenium ion or rendered sensitive to such a process. The enolized Ac_2O could then act as a nucleophile to quench the carbenium ion, formed as a result of the opening process. If the concentration of $ZnCl_2$ relative to the oxygen bridge is low, it activates the abundantly available Ac_2O to become a strong enough acylation agent so as to attack the oxygen bridges of **2** giving acetylation. This process furnishes the same carbenium ion as above, which we now propose is quenched by acetate rather than enolate. The former is available from the acylation process. Given the NMR evidence that all the acetates of **14** are equivalent, the quenching process must take place from the same side of the cycle at which the acetate, formed by the acetylation of the ether bridge, is positioned. It is reasonable to assume that an attack from the opposite side will be disfavoured because of the steric shielding imposed by the rigid double-stranded cycle on its rear side.

A main motivation behind all the transformations described here is to find the best precursor for the ultimate target structure **B**. The tetraacetate **14** was considered interesting in this respect because it may open non-acidic avenues to **B**. Both the thermal and basic treatment[17] of **14** could lead to **B** and, this observation broadens the synthetic repertoire considerably. Additionally, **14** may serve as a starting point for the corresponding tetrabromide **15**, which would also be an interesting precursor of **B**. Therefore, we decided to investigate the reaction of **14** with phosphorus tribromide (PBr_3). Exposing **14** to a large excess of PBr_3 at room temperature afforded the corresponding tetrabromide **15** in an almost quantitative yield. From the simplicity of the ^1H NMR spectrum of **15**, we concluded that, like **14**, it consists of one isomer only. For steric reasons, we propose that the four bromides point outwards, though there is no proof for this. Stimulated by this finding, we also tried to obtain the same tetrabromide directly from compound **2** (Table 2, Entry 5). In fact, if this compound was treated with boron tribromide, the tetrabromo compound **15** was obtained in virtually quantitative yield. This latter route had the advantage of an easier purification and was, therefore, selected for a 100 mg-scale synthesis of **15**. The ^1H NMR spectra of the tetrabromides **15**, prepared according to these different routes, were superimposable. The workup of the tetrabromide was somewhat delicate because of its relatively high sensitivity towards aqueous hydrolysis. If an aqueous workup was chosen, it had to be carried out very quickly. If a CH_2Cl_2 solution of **15** at room temperature was washed with water and quickly dried with $MgSO_4$, whereby this procedure took some 15 min, then the organic phase did not contain **15** but only a mixture of the hydrolysis products **16** and **2**. Alternatively, the workup could be performed non-aqueously by filtering the precipitated **15**, washing it, and drying it.

Obviously, the hydrolysis products of both **14** and **15** have the same tendency to re-form the starting material **2**. This process of a transannular ether formation could also be monitored by NMR-tube experiments with the intermediate **16**. Figure 5 shows the NMR spectra of the raw compound **16** before and 20 min after the addition of methanesulfonic acid (Figure 5 bottom and centre spectra, respectively). For comparison purposes, Figure 5 also contains the spectrum of pure compound **2** (Figure 5, top spectrum). As can be seen, compound **16** was virtually quantitatively converted into **2**. As already observed above, a competitive dehydration associated with aromatization did not occur.

With a few milligrams of diol **16** we explored whether or not two additional sp^2-hybridized carbon atoms could be incorporated into the double-stranded structure of the cy-

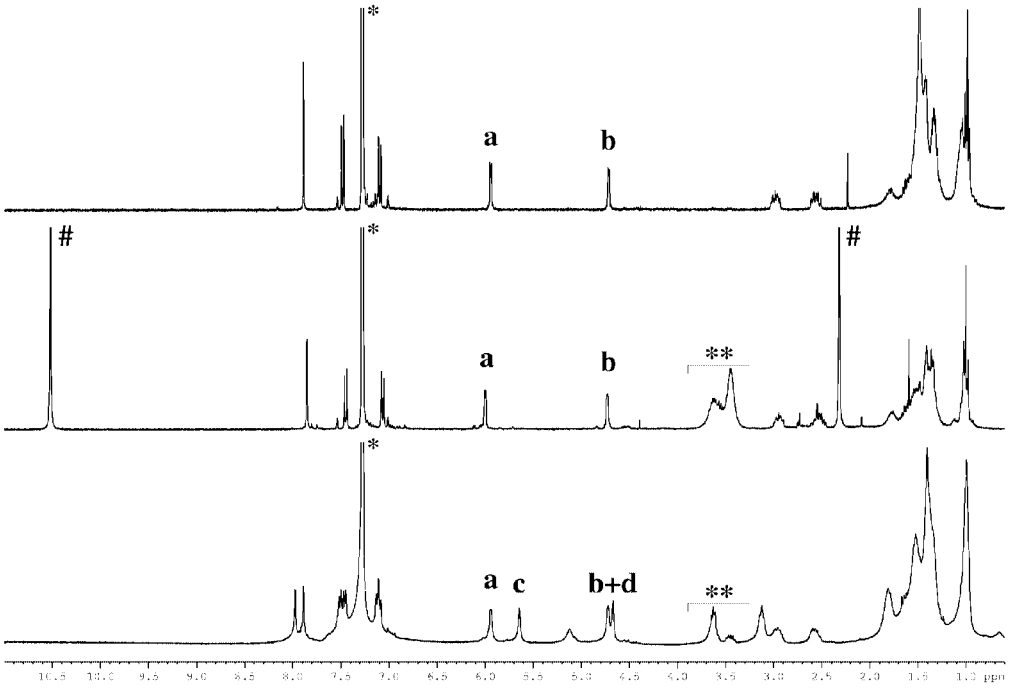


Figure 5. The ^{1}H NMR spectra of raw compound **16** before (bottom) and after the addition of methanesulfonic acid (center). The spectrum of compound **2** (top) is shown for comparison purposes. For a signal assignment (a, b, c, and d) see structures **2** and **16** in Scheme 1 and Scheme 3, respectively. The solvent (C_6D_6) is marked by an asterisk *, a uninvestigated impurity by ** and signals caused by methanesulfonic acid by #.

cle. For this purpose, **16** was oxidized in an NMR-tube experiment by pyridinium chlorochromate (PCC) at room temperature, and the heterogeneous mixture obtained was analyzed by MALDI mass spectrometry. The mass spectrum showed the molecular ion peak of the corresponding diketone **17** prominently. The formation of this compound was further substantiated by isolating its monohydrate **18** after aqueous workup on a few mg scale. The structure of **18** was unequivocally proven by long-range homo- and heteronuclear NMR correlation experiments (see the Supporting Information).

Finally, the reactivity of starting compound **2** towards $TiCl_4$ and γ-Al_2O_3 was tested (Table 2, Entries 3 and 4). There is considerable evidence in the literature that $TiCl_4$ can dehydrate and deoxygenate bridged ethers. In agreement with this, model compound **9**, when treated with $TiCl_4/NEt_3$ in CH_2Cl_2 at room temperature, furnished the dehydrated product **10**, which by analysis of a raw high-field NMR spectrum, was the only product formed. Under the same conditions, compound **2** did not show any reaction. Only starting material could be isolated in yields exceeding 90%. γ-Al_2O_3 was activated by heating it to 300 °C under high vacuum for 2 d. A solution of **2** in dry toluene was then added, and the mixture was heated to 150 °C for 1 d in a sealed high-pressure tube. Upon analysis, most of the starting material was still present; some had been converted to compound **3**. No other product was found.

Experimental Section

General: Compounds **7** and **9** were prepared according to literature procedures;[1d] all other compounds are new. For the known compound **10**,[18] analytical data are given here because they are not fully available in the literature. None of the new compounds was characterized by combustion analysis because of the small scale in which they were prepared. The structures were nevertheless proven unequivocally by high-resolution mass spectrometry and both homo- and heteronuclear long-range NMR correlation experiments. For an evaluation of the compounds' purity, representative NMR spectra are provided in the Supporting Information for all compounds. All commercial reagents were used without further purification. Solvents were purified and dried by standard procedures. The small amounts of acid used were added with Eppendorf pipettes. Column chromatography was carried out on silica gel 60 M (Macherey–Nagel, 0.04–0.063 mm/230–400 mesh) as the stationary phase. Reactions were monitored by thin layer chromatography (TLC) with TLC silica gel-coated aluminium plates (60 UV_{254}, Macherey–Nagel) and visualized by ultraviolet (UV) light (λ = 254 nm and λ = 366 nm). ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AVANCE (^{1}H: 300 MHz and ^{13}C: 75 MHz), Bruker AVANCE (^{1}H: 500 MHz and ^{13}C: 125 MHz) or Bruker AVANCE (^{1}H: 700 MHz) spectrometer at room temperature with $CDCL_3$, CD_2Cl_2, [D_6]benzene or [D_8]tetrahydrofuran as solvents. High-resolution mass spectra (HRMS) analyses were performed by the MS service of the Laboratorium für Organische Chemie at ETH Zürich. MALDI MS spectra were recorded with an IonSpec Ultra Instrument. 2-[(2*E*)-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene] malonitrile (DCTB) and 3-hydroxypyridine-2-carboxylic acid (3-HPA) served as the matrix, if not otherwise stated.

Crystal Sructure: Monoclinic crystals of **4**, suitable for X-ray structure analysis, were obtained by slow diffusion of ethanol into a solution of **4** in CH_2Cl_2. A platelet crystal ($0.31 \times 0.21 \times 0.03$ mm) was mounted on top of a glass fibre at –150 °C and brought into the cold gas stream of a Bruker-AXS SMART CCD diffractometer. To avoid loss of the intercalated solvent, the data collection was performed at –120 °C. A total of 1800 frames were collected [Mo-

K_α radiation (λ = 0.71073 Å), a graphite monochromator, a scan width of 0.3° in ω and exposure time of 30 s/frame and a detector–crystal distance of 4.00 cm] and integrated with the Bruker SAINT software package with a narrow-frame integration algorithm.[19] Results: space group $P2_1/n$, a = 16.710(5), b = 11.630(3), c = 19.055(5) Å, β = 108.137(7)°, V = 3519.2(17) Å^3, Z = 2, 2 θ_{max} = 46.5°, 5057 crystallographically unique reflections (2872 observed with $I \geq 2\sigma(I)$). The structure was solved by direct methods and refined by full-matrix least-squares refinement based on F^2 with anisotropic thermal displacement parameters for the non-hydrogen atoms.[20] The hydrogen atoms were included with geometrically calculated positions and refined according to the "riding model"; 418 parameters, R_1 = 0.1073, wR_2 = 0.3328 and GOF = 0.998. The highest residual electron density of 1.73 e·Å^{-3} is located 1.95 Å from C1L of the CH_2Cl_2 molecule, indicating that the solvate molecule may be disordered. In addition, the chlorine atoms of the intercalated CH_2Cl_2 molecule exhibited large temperature factors.

CCDC-617868 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

***rel*-(1*R*,4*S*,4a*S*,9*S*,9a*S*,17b*R*,18*R*,22b*R*)-8,19,23,24-Tetrahexyl-1,4,4a,9,9a,17b,18,22b-octahydro-1,4:9,18-diepoxy-2,14:3,13-dimethenodiindeno[1,2,3-*c*,*d*:1′,2′,3′-*c*′,*d*′]benzo[2,3-*j*:5,6-*j*′]difluoranthene (2):** To a solution of compound **1** (100 mg, 0.99 mmol) in nitrobenzene (20 mL), methanesulfonic acid (20 μL, 0.3 mmol) was added all at once, and the mixture was heated to 130 °C. The reaction course was followed by TLC (hexane/CH_2Cl_2, 1:2). Upon completion (30 min), the reaction was quenched with aqueous $NaHCO_3$, and the phases were separated. The organic phase was poured into ethanol (500 mL) and cooled to 0 °C, whereupon a precipitate formed. The precipitate was filtered off, washed with ethanol and dried to give compound **2** as a yellow solid (88 mg, 90% yield). Occasionally, it was necessary to pretreat compound **2** by column chromatography on silica gel (hexane/CH_2Cl_2, 1:3, R_f = 0.41). For analytical data, see ref.[1d]

8,19,23,24-Tetrahexyl-1,4,4a,9,9a,17b,18,22b-octahydro-1,4-epoxy-2,14:3,13-dimetheno-9,18-tolueno[3,4]diindeno[1,2,3-*c*,*d*:1′,2′,3′-*c*′,*d*′]benzo[2,3-*j*:5,6-*j*′]difluoranthene (3): To a solution of compound **1** (57 mg, 0.056 mmol) in toluene (5 mL) was added methanesulfonic acid (0.03 mL, 43 mg, 0.150 mmol) all at once, and the reaction mixture refluxed. The reaction course was followed by TLC, as described for compound **4**. As soon as compound **4** started to form, the reaction was quenched with aq $NaHCO_3$. The two phases were separated, and the organic one was washed once with water (10 mL). After drying over $MgSO_4$, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 1:3, R_f = 0.56) to give compound **3** as a yellow powder (13 mg, 22% yield). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.6 (s, 2 H, H-7, H-20), 7.59 (d, ^3J = 7.0 Hz, 2 H, H-11, H-16), 7.55 (s, 2 H, H-12, H-15), 7.50 (d, ^3J = 6.9 Hz, 2 H, H-6, H-21), 7.46 (d, ^3J = 7.0 Hz, 2 H, H-10, H-17), 7.43 (d, ^3J = 7.4 Hz, 1 H, H-27) 7.38 (s, 1 H, H-25), 7.32 (d, ^3J = 6.9 Hz, 2 H, H-5, H-22), 7.12 (d, ^3J = 7.4 Hz, 1 H, H-26), 5.92 (m, 2 H, H-1, H-4), 5.05 (s, 1 H, H-9 or H-18), 5.03 (s, 1 H, H-9 or H-H-18), 4.8 (m, 2 H, H-4a, H-22b), 4.3 (s, 2 H, H-9a, H-17b), 3.01 (m, 2 H, CH_2(CH$_2$)$_4$CH$_3$), 2.88 (m, 2 H, CH_2(CH$_2$)$_4$CH$_3$), 2.80 (m, 2 H, CH_2(CH$_2$)$_4$CH$_3$), 2.56 (m, 2 H, CH_2(CH$_2$)$_4$CH$_3$), 2.44 (s, 3 H, *tol*-CH$_3$), 1.25–1.65 (m, 32 H, CH$_2$(CH_2)$_4$CH$_3$), 0.92 (t, ^3J = 4.2 Hz, 6 H, CH$_2$(CH$_2$)$_4$CH_3), 0.86 (m, 6 H, CH$_2$(CH$_2$)$_4$CH_3) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 145.95, 145.92, 142.73, 142.33, 139.75, 138.15, 137.72, 137.37, 136.64, 136.03, 135.98, 134.74, 134.70, 134.55, 133.93, 133.92, 133.91, 133.55, 131.77, 131.72, 130.88, 129.67, 129.65, 128.77, 126.75, 125.08, 123.94, 121.56, 121.47, 120.23, 119.26, 116.34, 116.13, 81.56, 56.03, 46.41, 45.98, 31.82, 31.77, 31.73, 31.71, 31.59, 31.43, 31.32, 31.09, 29.69, 29.59, 29.34, 28.18, 28.14, 22.67, 22.65, 22.62, 22.61, 22.59, 21.09, 13.90, 13.87, 13.81 ppm. HR MALDI MS: calcd. For $C_{79}H_{78}O$ 1042.6047; found 1042.6061 [M]$^+$, HR EI MS: calcd. for [$^{12}C_{79}{}^1H_{78}{}^{16}O_1$]$^+$ 1042.60522; found 1042.6027.

8,19,23,24-Tetrahexyl-1,4,4a,9,9a,17b,18,22b-octahydro-2,14:3,13-dimetheno-1,4:9,18-ditolueno[3,4]diindeno[1,2,3-*c*,*d*:1′,2′,3′-*c*′,*d*′]benzo[2,3-*j*:5,6-*j*′]difluoranthene (4): To a solution of **1** (0.150 g, 0.149 mmol) in toluene (9 mL) methanesulfonic acid (0.08 mL, 0.114 g, 1.19 mmol; or the equivalent amount of *p*TsOH) was added all at once, and the reaction mixture was refluxed for 4 h (1 d, in the case of *p*TsOH). The reaction course was followed by TLC (hexane/CH_2Cl_2, 1:3), whereby compounds **1**, **2**, **3** and **4** eluted at the following R_f values: 0.18, 0.41, 0.56 and 0.88, respectively. After the conversion into compound **4** was completed, the reaction was quenched with aq $NaHCO_3$ and washed once with water (10 mL). The organic layer was dried with $MgSO_4$ and the solvent was removed. Compound **4** was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 1:3, R_f = 0.88) to give a yellow solid (120 mg, 70% yield). Single crystals of **4** for X-ray diffraction were obtained by slow diffusion of ethanol into CH_2Cl_2. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (s, 4 H, H-7, H-12, H-15, H-20), 7.53 (d, ^3J = 7.0 Hz, 4 H, H-6, H-11, H-16, H-21), 7.4 (d, ^3J = 6.5 Hz, 2 H, H-27, H-30), 7.38 (d, ^3J = 7.0 Hz, 4 H, H-5, H-10, H-17, H-22), 7.34 (s, 2 H, H-25, H-28), 7.09 (d, ^3J = 6.6 Hz, 2 H, H-26, H-29), 5.01 (s, 2 H, H-1, H-9 or H-4, H-18), 5.00 (s, 2 H, H-1, H-9 or H-4, H-18), 4.28 (s, 4 H, H-4a, H-9a, H-17b, H-22b), 2.85 (m, 4 H, CH_2(CH$_2$)$_4$CH$_3$), 2.98 (m, 4 H, CH_2(CH$_2$)$_4$CH$_3$), 2.43 (s, 6 H, *tol*-CH$_3$), 1.23–1.42 (m, 32 H, CH$_2$(CH_2)$_4$CH$_3$), 0.85 (m, 12 H, CH$_2$(CH$_2$)$_4$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.80, 142.84, 139.86, 138.27, 136.09, 135.92, 134.39, 134.33, 134.31, 134.24, 134.07, 131.46, 131.42, 129.56, 129.53, 126.80, 125.12, 123.96, 121.25, 119.84, 116.08, 77.20, 53.33, 53.16, 46.42, 46.00, 31.72, 31.23, 29.69, 29. 44, 28.25, 22.61, 22.58, 21.41, 14.04, 14.02 ppm. MALDI-TOF MS: (dithranol, $Ag^+BF_4^-$): calcd. for $C_{86}H_{84}$ 1116.66; found 1116.88 [M]$^+$, 1223.81 [M + Ag]$^+$.

8,19,23,24-Tetrahexyl-1,4,4a,9,9a,17b,18,22b-octahydro-9,18-benzeno[1,2]-1,4-epoxy-2,14:3,13-dimethenodiindeno[1,2,3-*c*,*d*:1′,2′,3′-*c*′,*d*′]benzo[2,3-*j*:5,6-*j*′]difluoranthene (5): A solution of compound **2** (50 mg, 0.051 mmol) in benzene (3 mL) was prepared in a high-pressure tube. Methanesulfonic acid (14 μL, 0.206 mmol) was added all at once, and the mixture was heated to 150 °C. After 3 h at this temperature, the reaction was cooled to room temperature and was then quenched with water (3 mL). The two layers were separated, and the organic solvent was removed under reduced pressure. The reaction mixture was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 1:1, R_f = 0.47) to give compound **5** as a yellow solid (2 mg, 3% yield). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.48–7.64 (overlapped signals, 12 H), 5.95 (m, 2 H, H-1, H-4), 5.13 (s, 2 H, H-9 or H-18), 4.83 (m, 2 H, H-4a, H-22b), 4.35 (s, 2 H, H-9a, H-17b), 3.06 (m, 2 H, CH_2(CH$_2$)$_4$CH$_3$), 2.68–2.96 (m, 4 H, CH_2(CH$_2$)$_4$CH$_3$), 2.60 (m, 2 H, CH_2(CH$_2$)$_4$CH$_3$), 1.30–1.70 (m, 32 H, CH$_2$(CH_2)$_4$CH$_3$), 0.95 (m, 6 H, CH$_2$-(CH$_2$)$_4$CH_3), 0.88 (m, 6 H, CH$_2$(CH$_2$)$_4$CH_3) ppm. HR MALDI MS: calcd. For $C_{78}H_{76}O$ 1028.5896; found 1028.591 [M]$^+$.

***rel*-(1*R*,4*S*,4a*S*,9*S*,9a*S*,17b*R*,18*R*,22b*R*)-8,19,23,24-Tetrahexyl-1,4,4a,9,9a,17b,18,22b-octahydro-6,11,15,20-tetranitro-1,4:9,18-diepoxy-2,14:3,13-dimethenodiindeno[1,2,3-*c*,*d*:1′,2′,3′-**

***c′*,*d′*]benzo[2,3-*j*:5,6-*j′*]difluoranthene (6):** To a solution of compound **2** (0.012 g, 0.012 mmol) in *o*-dichlorobenzene (5 mL) at room temp. was added concentrated nitric acid (10 μL, 0.154 mmol), and the reaction mixture was heated to 90 °C. Upon addition of the acid, the colour changed instantaneously to orange and then red, and a brown gas developed within a few minutes. After 1 h at this temperature, the reaction mixture was cooled to room temp., and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 2:5, R_f = 0.31) to give compound **6** a red-orange solid (11 mg, 78% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.73 (s, 4 H, H-7, H-12), 8.27 (2 H, H-5, H-10), 7.43 (d, ^3J = 7.3 Hz, 2 H, H-17, H-22 or H-16, H-21), 7.38 (d, ^3J = 7.3 Hz, 2 H, H-17, H-22 or H-16, H-21), 6.03 (m, 4 H, H-1, H-4, H-9, H-18), 4.90 (m, 4 H, H-4a, H-9a, H-17b, H-22b), 2.80 (m, 2 H, CH_2(CH$_2$)$_4$CH$_3$) 2.52 (m, 6 H, CH_2(CH$_2$)$_4$CH$_3$) 1.76–1.28 (m, 32 H, CH$_2$(CH_2)$_4$CH$_3$), 0.90 (m, 12 H, CH$_2$(CH$_2$)$_4$CH_3) ppm. HR MALDI MS: calcd. for $C_{72}H_{68}N_4O_{10}$ 1118.4961 [M – NO$^-$]$^+$; found 1118.494.

Polymer 8: To a solution of polymer **7** (0.100 g) in toluene (100 mL), *p*TsOH (0.038 g, 0.20 mmol) was added, and the mixture was refluxed for 10 h. The colour changed from red to green and, towards the end, a dark precipitate formed. The reaction mixture was cooled to room temp., washed three times with water (50 mL), and the solvent was removed to give material **8** as a dark insoluble solid, which was recovered and carefully dried under high vacuum. For the structure assignment, see the main text, Scheme 2, and the Supporting Information.

Benzo[*k*]fluoranthene (10). Route A: To methanesulfonic acid (5 g, 0.052 mol), phosphorus pentoxide (P_2O_5, 0.5 g, 3.52 mmol) was added in one portion. The mixture was stirred at room temp. until all the P_2O_5 had dissolved (1.5–2 h). To this mixture, compound **9** (0.100 g, 0.370 mmol) was added in small portions, and stirring was continued at room temp. for 10 h. The mixture was poured onto crushed ice and neutralized with aq $NaHCO_3$. The aq solution was extracted with CH_2Cl_2 (3 × 100 mL). The organic phases were combined and dried with $MgSO_4$ and the solvent was removed. The residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 1:1, R_f = 0.62) to give compound **10** as a pale yellow solid (80 mg, 86% yield). **Route B:** Compound **9** (0.100 g, 0.370 mmol) was dissolved in dry CH_2Cl_2 (5 mL), and $TiCl_4$ (0.224 g, 0.129 mL, 1.181 mmol) was added. The resulting red solution was stirred at room temp. for 1 h, and dry Et_3N (1 mL) was added, which resulted in a darkening of the colour. The solution was stirred for an additional 2 h at room temp. and then quenched with water (10 mL). The aqueous phase was extracted with CH_2Cl_2 (5 × 20 mL). The combined organic phases were dried with $MgSO_4$, and the solvent was removed. The raw product was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 1:1, R_f = 0.62) to give compound **9** as a pale yellow solid (70 mg, 80% yield). **Route C:** To a solution of compound **9** (0.100 g, 0.370 mmol) in Ac_2O (10 mL) was added at room temp. zinc chloride (0.050 g, 0.370 mmol) all at once, and the reaction mixture was heated to 130 °C for 30 min. The reaction was then cooled to room temp., the solvent was removed, and the raw mixture was purified by column chromatography on silica gel (hexane/CH_2Cl_2, 1:1, R_f = 0.62) to give compound **10** as a pale yellow solid (82 mg, 88% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.33 (s, 2 H, H-7, H-12), 7.98 (d, ^3J = 7.0 Hz, 2 H, H-1, H-6), 7.91 (dd, ^3J = 6.0 Hz, ^4J = 3.4 Hz, 2 H, H-8, H-11), 7.82 (d, ^3J = 8.1 Hz, 2 H, H-3, H-4), 7.64 (dd, ^3J = 7.0 Hz, ^3J = 7.9 Hz, 2 H, H-2, H-5), 7.46 (dd, ^3J = 6.0 Hz, ^4J = 3.4 Hz, 2 H, H-9, H-10) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 137.82, 136.90, 135.28, 133.48, 130.54, 128.74, 128.20, 126.20, 126.02, 120.22, 119.18 ppm.

8,19,23,24-Tetrahexyl-1,4,4a,9,9a,17b,18,22b-octahydro-2,14:3,13-dimetheno-1,4:9,18-bis(methylenecarbonyloxy)diindeno[1,2,3-*c*,*d*:1′,2′,3′-*c′*,*d′*]benzo[2,3-*j*:5,6-*j′*]difluoranthene (11): To a solution of **2** (50 mg, 0.051 mmol) in Ac_2O (10 mL) was added at room temp. zinc chloride (0.104 g, 0.103 mmol) all at once, and the reaction mixture was heated to 130 °C for 30 min. After a few minutes of heating, the solution became transparent for a short time before the product started to precipitate. The reaction was cooled to room temp., and the precipitate was filtered, washed with ethanol and dried in vacuo to give compound **11** as a yellow solid (49 mg, 92% yield). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.69 (s, 2 H, C_i: H-7, H-12 or H-15, H-20; C_2: H-7, H-15 or H-12, H-20), 7.68 (s, 2 H, C_i: H-7, H-12 or H-15, H-20; C_2: H-7, H-15 or H-12, H-20), 7.66 (s, 2 H, C_i: H-7, H-12 or H-15, H-20; C_2: H-7, H-15 or H-12, H-20), 7.65 (s, 2 H, C_i: H-7, H-12 or H-15, H-20; C_2: H-7, H-15 or H-12, H-20), 7.61 (d, ^3J = 7.0 Hz, 2 H, C_i: H-5, H-17 or H-10, H-22; C_2: H-5, H-10 or H-17, H-22), 7.60 (d, ^3J = 7.0 Hz, 2 H, C_i: H-5, H-17 or H-10, H-22; C_2: H-5, H-10 or H-17, H-22), 7.58 (d, ^3J = 7.0 Hz, 2 H, C_i: H-5, H-17 or H-10, H-22; C_2: H-5, H-10 or H-17, H-22), 7.57 (d, ^3J = 7.0 Hz, 2 H, C_i: H-5, H-17 or H-10, H-22; C_2: H-5, H-10 or H-17, H-22), 6.02 (2d, ^3J = 2.6 Hz, ^3J = 2.9 Hz, 2 H, C_i: H-1, H-9; C_2: H-4, H-9), 4.98 (dd, ^3J = 6.1 Hz, ^3J = 1.7 Hz, 2 H, C_i: H-4a, H-18b; C_2: H-1b, H-18b), 4.59 (d, ^3J = 6.1 Hz, 2 H, C_i: H-9a, H-1b; C_2: H-4a, H-9a), 4.00 (d, ^3J = 1.7 Hz, 2 H, C_i: H-4, H-18; C_2: H-1, H-18) 3.56 (dd, ^2J = 18.8 Hz, ^3J = 3.2 Hz, 2 H, bridge -OCOC*H*H-), 3.29 (dd, ^2J = 18.8 Hz, ^3J = 3.2 Hz, 2 H, bridge -OCOCH*H*-), 2.86 (m, 8 H, CH_2(CH$_2$)$_4$CH$_3$) 1.69–1.27 (m, 32 H, CH$_2$(CH_2)$_4$CH$_3$), 0.88 (m, 12 H, CH$_2$(CH$_2$)$_4$CH_3) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 171.58, 146.85, 146.75, 144.31, 144.08, 137.42, 137.34, 137.30, 136.58, 136.54, 136.46, 136.43, 134.68, 134.65, 134.63, 134.61, 134.57, 134.55, 134.34, 134.32, 133.26,131.54, 131.40, 130.32, 130.16, 129.00, 128.97, 121.76, 121.64, 121.34, 121.26, 121.10, 121.04, 116.86, 116.72, 116.42, 116.27, 77. 35, 52.70, 50.85, 41.00, 40.96, 37.52, 37.46, 31.80, 31.75, 31.70, 31.58, 29.63, 29.52, 28.18, 28.14, 28.10, 28.05, 22.70, 22.67, 13.99, 13.91 ppm. HR MALDI MS: calcd. for $C_{76}H_{76}O_4$ 1052.5743; found 1053.5738 [M]$^+$, 981.4888 [M – C_5H_{11}]$^+$, 897.4122 [M – C_5H_{11}–C_6H_{13}]$^+$.

Compounds 12 and 13: A solution of compound **11** (34 mg, 0.032 mmol) and potassium hydroxide (27 mg, 0.484 mmol) in tetrahydrofuran/water (3:1, 8 mL) was heated to 80 °C for 10 h. The reaction mixture was cooled to room temp., and the solvent was removed to give a raw mixture, which by HR MALDI MS analysis showed a mixture of **11**, **12** and **13** (see the Supporting Information). Attempts to isolate these compounds by column chromatography on silica gel (hexane/ethyl acetate, 1:1) gave starting material only.

1,4,9,18-Tetraaceto-8,19,23,24-tetrahexyl-1,4,4a,9,9a,17b,18,22b-octahydro-2,14:3,13-dimethenodiindeno[1,2,3-*c*,*d*:1′,2′,3′-*c′*,*d′*]-benzo[2,3-*j*:5,6-*j′*]difluoranthene (14): To a solution of compound **2** (0.050 g, 0.051 mmol) in Ac_2O (10 mL) was added a trace of zinc chloride at room temp., and the mixture was heated to 60 °C for 1 h. The reaction was cooled to room temp., and stirring was continued for 10 h, during which time a precipitate formed. The precipitate was recovered by filtration, washed with ethanol and dried under vacuum to give compound **14** as a yellow solid (54 mg, 90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63 (s, 4 H, H-7, H-12, H-15, H-20), 7.57 (d, ^3J = 7.1 Hz, 4 H, H-5, H-10, H-17, H-22), 7.46 (d, ^3J = 7 Hz, 4 H, H-6, H-11, H-16, H-21), 6.76 (s, 4 H, H-1, H-4, H-9, H-18), 4.63 (s, 4 H, H-4a, H-9a, H-17b, H-22b), 3.06 (m, 4 H, CH_2(CH$_2$)$_4$CH$_3$), 2.83 (m, 4 H, CH_2(CH$_2$)$_4$CH$_3$), 2.29 (s, 12 H, CH$_3$, OCOCH_3) 1.57–1.27 (m, 32 H, CH$_2$-(CH_2)$_4$CH$_3$), 0.88 (m, 12 H, CH$_2$(CH$_2$)$_4$CH_3) ppm. ^{13}C NMR

(125 MHz, $CDCl_3$): δ = 171.02, 145.07, 137.97, 137.47, 137.38, 134.64, 131.55, 128.15, 122.29, 121.33, 116.82, 72.14, 49.76, 31.75, 31.64, 29.73, 28.60, 22.73, 21.96, 14.17 ppm. HR MALDI MS: calcd. for $C_{80}H_{84}O_8$ 1172.6161; found 1172.6140 $[M]^+$, 1114 $[M - (OCOCH_3)]^+$, 1072 $[M - (OCOCH_3)–(COCH_3)]^+$, 1054 $[M - 2(OCOCH_3)]^{+\cdot}$, 995 $[M - 3(OCOCH_3)]^{+\cdot}$.

1,4,9,18-Tetrabromo-8,19,23,24-tetrahexyl-1,4,4a,9,9a,17b,18,22b-octahydro-2,14:3,13-dimethenodiindeno[1,2,3-*c*,*d*:1′,2′,3′-*c*′,*d*′]-benzo[2,3-*j*:5,6-*j*′]difluoranthene (15). Route A: To a solution of compound **2** (0.200 g, 0.206 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise at room temp. BBr_3 (1 M solution in CH_2Cl_2, 1.1 mL, 1.3 mmol) over a period of 30 min, whereupon the colour changed slowly to brown. After 4 h stirring at room temp., the reaction was quenched with water (2 mL) whereupon a precipitate formed. The precipitate was recovered by filtration, washed with ethanol and dried in vacuo to give compound **15** as a yellow solid (160 mg, 62% yield). If the precipitate was dissolved in CH_2Cl_2 and washed with water, a mixture of compounds **2** and **16** was obtained. **Route B:** A solution of **14** (10 mg) in $CDCl_3$ (0.5 mL) was prepared in an NMR tube, and a drop of PBr_3 was added. The transformation of **14** into **15** was followed by NMR spectroscopy, which showed that the reaction was complete within 3 h. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.70 (s, 4 H, H-7, H-12, H-15, H-20), 7.63 (d, ^3J = 7.2 Hz, 4 H, H-6, H-11, H-16, H-21), 7.44 (d, ^3J = 7.2 Hz, 4 H, H-5, H-10, H-17, H-22), 6.15 (s, 4 H, H-1, H-4, H-9, H-18), 5.05 (s, 4 H, H-4a, H-9a, H-17b, H-22b), 2.91 (m, 8 H, $CH_2(CH_2)_4CH_3$) 1.66–1.38 (m, 32 H, $CH_2(CH_2)_4CH_3$), 0.96 (m, 12 H, $CH_2(CH_2)_4CH_3$) ppm. ^{1}H NMR (500 MHz, [D$_8$]THF): δ = 7.76 (s, 4 H, H-7, H-12, H-15, H-20), 7.61 (d, ^3J = 7.2 Hz, 4 H, H-6, H-11, H-16, H-21), 7.55 (d, ^3J = 7.2 Hz, 4 H, H-5, H-10, H-17, H-22), 6.25 (s, 4 H, H-1, H-4, H-9, H-18), 4.97 (s, 4 H, H-4a, H-9a, H-17b, H-22b), 2.99 (m, 4 H, $CH_2(CH_2)_4CH_3$), 2.90 (m, 4 H, $CH_2(CH_2)_4CH_3$), 1.60–1.33 (m, 32 H, $CH_2(CH_2)_4CH_3$), 0.91 (t, ^3J = 6.6 Hz, 12 H, $CH_2(CH_2)_4CH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.18, 146.26, 138.09, 137.68, 134.96, 128.59, 122.36, 121.86, 116. 88, 53.67, 44.54, 39.09, 31.63, 30.77, 29.79, 28.06, 22.57, 14.10 ppm. HR MALDI MS: calcd. for $C_{72}H_{72}Br_4$; found 1093.379 $[M - Br–HBr]^+$, 1015.477 $[M - 3Br]^+$, 936.5611 $[M - 4Br]^+$, 851.4120 $[M - 4Br–C_6H_{13}]^+$.

8,19,23,24-Tetrahexyl-9,18-dihydroxy-1,4,4a,9,9a,17b,18,22b-octahydro-1,4-epoxy-2,14:3,13-dimethenodiindeno[1,2,3-*c*,*d*:1′,2′,3′-*c*′,*d*′]benzo[2,3-*j*:5,6-*j*′]difluoranthene (16): To an ice-cooled solution of compound **2** (0.130 g, 0.164 mmol) in dry CH_2Cl_2 (15 mL), BBr_3 (1 M solution in CH_2Cl_2, 0.402 mL, 0.402 mmol) was added dropwise. After the completed addition, a colour change from yellow to brown was observed. Stirring was continued for 1 h under ice cooling while the colour disappeared, and a yellow precipitate formed. The reaction was allowed to stir for another 2 h at room temp. and quenched with water (5 mL). Additional CH_2Cl_2 was added until all the precipitate dissolved. The organic phase was washed twice with water, dried with $MgSO_4$, and the solvent was removed. The residue was purified by column chromatography on silica gel (CH_2Cl_2). After the first compound (**2**) had eluted, the polarity of the solvent was increased by the addition of 10% acetone, whereupon the second compound (**6**) eluted. The solvent was removed, and compound **6** was obtained as a yellow solid (38 mg, 28% yield). ^{1}H NMR: (300 MHz, C_6D_6): δ = 7.98 (s, 2 H, H-7, H-20), 7.89 (s, 2 H, H-12, H-15) 7.51 (d, ^3J = 7.0 Hz, 2 H, H-11, H-16), 7.46 (d, ^3J = 7.0 Hz, 2 H, H-6, H-21), 7.14 (d, ^3J = 7.1 Hz, 2 H, H-10, H-17), 7.10 (d, ^3J = 7.1 Hz, 2 H, H-5, H-22) 5.94 (m, 2 H, H-1, H-4), 5.68 (s, 2 H, H-9, H-18), 4.72 (m, 42 H, H-4a, H-9a, H-17b, H-22b), 3.13 (t, ^3J = 7.4 Hz, 4 H, $CH_2(CH_2)_4CH_3$), 2.96 (m, 2 H, $CH_2(CH_2)_4CH_3$), 2.57 (m, 2 H, $CH_2(CH_2)_4CH_3$) 1.81–1.33 (m, 32 H, $CH_2(CH_2)_4CH_3$), 0.99 (m, 12 H, $CH_2(CH_2)_4CH_3$) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 148.81, 146.09, 143.57, 142. 76,139.74, 139. 27, 138. 38, 137.82, 137.39, 137.33, 136.93, 136.80, 135.94, 135.83, 134.96, 134.66, 134. 61, 134.41, 133.40, 133.09, 132.25, 131.42, 132.31, 130.03, 128.67, 121.66, 121.50, 120.95, 120.67, 120.45, 120.39, 120.04, 119.49, 116.47, 116.32, 81. 48, 81.35, 72.36, 56.37, 53.54, 31.92, 31.87, 31.84, 31.81, 31.44, 31.08, 30.85, 29.97, 29.82, 29.67, 22.93, 22.80, 22.79, 14.13, 14.10, 14.07 ppm. HR MALDI MS: calcd. for $C_{72}H_{74}O_3$ 1986.5633; found 1986.5616 $[M]^+$.

8,19,23,24-Tetrahexyl-9,9-dihydroxy-18-oxo-1,4,4a,9,9a,17b,18,22b-octahydro-1,4-epoxy-2,14:3,13-dimethenodiindeno[1,2,3-*c*,*d*:1′,2′,3′-*c*′,*d*′]benzo[2,3-*j*:5,6-*j*′]difluoranthene (18): A solution of **16** (3 mg) in CD_2Cl_2 (0.5 mL) was prepared in an NMR tube, and pyridinium chlorochromate (PCC, 15 mg) was added. After 1 h at room temp., the reaction mixture was washed through a short silica gel column with CH_2Cl_2. ^{1}H NMR: (700 MHz, $CDCl_3$): δ = 7.83 (s, 1 H), 7.80 (d, ^3J = 6.8 Hz, 1 H), 7.70 (s, 1 H), 7.69 (d, ^3J = 6.9 Hz, 1 H), 7.66 (d, ^3J = 2.0 Hz, 1 H), 7.64 (d, ^3J = 1.9 Hz, 1 H), 7.62 (d, ^3J = 6.9 Hz, 1 H), 7.61 (s, 1 H), 7.56 (d, ^3J = 7.0 Hz, 1 H), 7.53 (s, 1 H), 7.40 (dd, ^3J = 6.8 Hz, ^3J = 1.1 Hz, 1 H), 7.39 (dd, ^3J = 6.8 Hz, ^3J = 1.1 Hz, 1 H), 6.35 (d, ^3J = 8.4 Hz, 1 H, H-9a), 6.01 (d, ^3J = 5.9 Hz, 1 H, H-1 or H-4), 5.98 (d, ^3J = 5.9 Hz, 1 H, H-1 or H-4), 4.87 (m, 2 H, H-4a, H-22b), 4.79 (d, ^3J = 8.2 Hz, 1 H, H-17b), 3.38 (m, 1 H, $CH_2(CH_2)_4CH_3$), 2.97 (m, 3 H, $CH_2(CH_2)_4CH_3$), 2.72 (m, 2 H, $CH_2(CH_2)_4CH_3$) 2.61 (m, 1 H, $CH_2(CH_2)_4CH_3$) 2.52 (m, 1 H, $CH_2(CH_2)_4CH_3$) 1.67–1.28 (m, 32 H, $CH_2(CH_2)_4CH_3$), 0.91 (m, 12 H, $CH_2(CH_2)_4CH_3$) ppm. HR MALDI MS: calcd. for $C_{72}H_{72}O_4$ 1000.5430 $[M]^+$ 998.5269; found 998.5263 $[M - 2H]^+$, 999.5341 $[M - H]^+$, 1000.5380 $[M]^+$, 1021.521 $[M - 2H + Na]^+$, 1021.521 $[M - 2H + K]^+$.

Supporting Information (see also the footnote on the first page of this article): The original reaction scheme for the synthesis of compound **1**. Representative NMR spectra for all compounds. HR-MALDI MS of a mixture of compounds **11**, **12**, and **13**.

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