

[2.2](2,7)-Fluorenophanediene, [2.2.2](2,7)-fluorenophanetriene, and their fluorenyl ions

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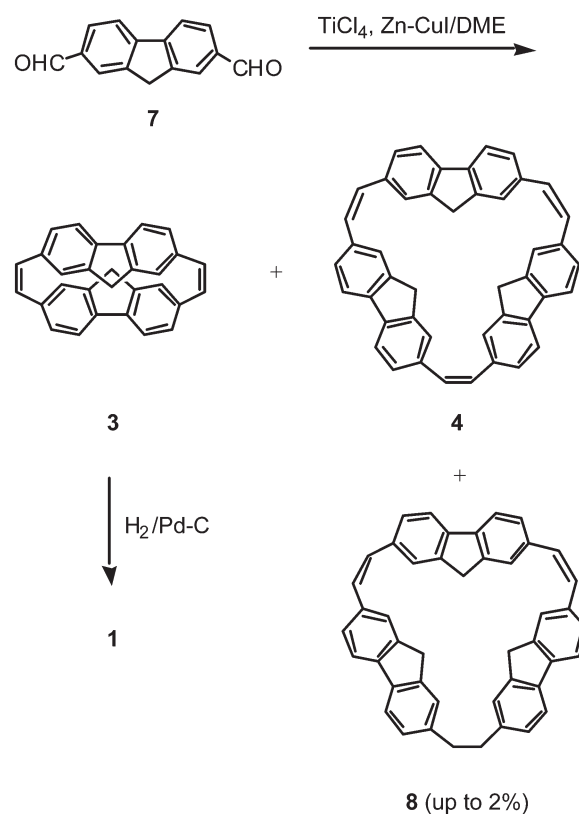
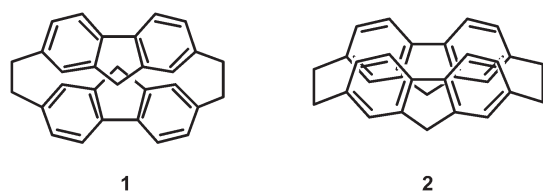
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The McMurry coupling of 2,7-diformylfluorene affords a dimer, *anti*-[2.2](2,7)-fluorenophanediene, and a trimer, [2.2.2](2,7)-fluorenophanetriene, as cyclic oligomers. X-Ray crystallography of the dimer establishes its strained, layered structure with *anti*-conformation. While the fluorenyl groups of the dimer do not show any sign of rotation in the variable temperature ^1H NMR spectra up to 120 $^\circ\text{C}$, those of the trimer are fast rotating even at -50 $^\circ\text{C}$. Treatment of the dimer and trimer with KH in DMSO furnished the respective dianion and trianion that are stable at room temperature in the solutions. While the trianion shows substantial conjugation through the etheno bridges, the dianion shows little conjugation through the etheno bridges and almost no proton–deuterium exchange of the fluorenyl C9-H with the solvent $\text{DMSO-}d_6$ probably due to stereospecific protonation–deprotonation associated with the tightly layered structure.

Introduction

Cyclophanes have been attracting continuing attention owing to their novel structures and properties.¹ Among them, fluorenophanes could be an interesting family because fluorene is readily transformed, by treatment with bases, to fluorenyl ion that in turn can be converted into fluorene derivatives functionalised at the 9-position. These potential transformations would widen the scope of study on the intramolecular interactions and host–guest chemistry of fluorenophanes. A few fluorenophanes such as *anti*- and *syn*-[2.2](2,7)-fluorenophane, **(1)** and **(2)**, their 9-oxo derivatives,² and (1,8)-fluorenophanes³ had been reported, and more recently the synthesis of fullerene(C60)-substituted [2.2](2,7)-fluorenophane has also been described.⁴ However, no fluorenophanepolyenes composed of fluorenes and alkenyl bridges have been reported. The known fluorenophanes have been synthesized through multi-step procedures by way of cyclic bis-sulfides.^{2–4} We have recently reported the synthesis of cyclic oligomers of phenylacetylene, *e.g.* cyclic *meta*-phenylacetylenes⁵ and cyclic *para*-phenylacetylenes,⁶ where the McMurry reaction of bis-aldehydes was used as the key reaction for the short-step construction of the precursor cyclic oligostyrenes. Here we report the synthesis of fluorenophanepolyenes, *anti*-[2.2](2,7)-fluorenophanediene (**3**) and [2.2.2](2,7)-fluorenophanetriene (**4**), and their anions (**5**) and (**6**) through the McMurry reaction of 2,7-diformylfluorene (**7**).



Scheme 1 McMurry coupling of bisaldehyde **7**.

Result and discussion

Treatment of **7** with low-valent titanium in DME under reflux for six hours afforded cyclic dimer **3** (3–5% yield) and trimer **4** (8–13%) (Scheme 1). The reactions in THF or DME–toluene resulted in poorer yields of these cyclophanes. Sometimes the reactions were accompanied with the formation of a small amount of dihydro-trimer **8** (up to 2%). The cyclophanes higher than the trimers were hardly detected. The major products were unidentifiable substances, probably acyclic higher oligomers, which did not come out from the silica gel column.

While cyclic dimer **3** is a colorless stable compound, trimer **4** is a yellow, somewhat labile compound slowly depositing scarcely soluble solids in solutions.⁸ Fig. 1 and 2 displays the ^1H NMR

spectra and Table 1 lists the ^1H chemical shifts of **3**, **4** and their polyanions. ^1H and ^{13}C NMR spectra of **3** show a C_2 symmetry of the molecule, exhibiting six kinds of proton and eight kinds of carbon signals (Fig. 1 upper). The methylene protons of the fluorenes (C9-H) are observed as an AB quartet at δ 3.26 and 2.35 ($J = 20.9$ Hz; in CDCl_3) similar to those of **1** (δ 3.10 and 2.31^{2a}). The doublet at higher field is assignable to the *endo* protons that are anisotropically somewhat shielded by the facing fluorene ring. The signals of C9-H remained almost unchanged up to 120 $^\circ\text{C}$ in bromobenzene- d_5 , indicating no tendency of the rotation of the fluorene rings. The etheno bridge protons are observed at relatively low field (δ 7.02) probably due to deshielding anisotropy effect of the nearby fluorene rings. Catalytic hydrogenation of **3** cleanly yielded the tetrahydro-dimer, namely **1**; thus, the present McMurry reaction of **7** provides a short step synthesis of **1**.

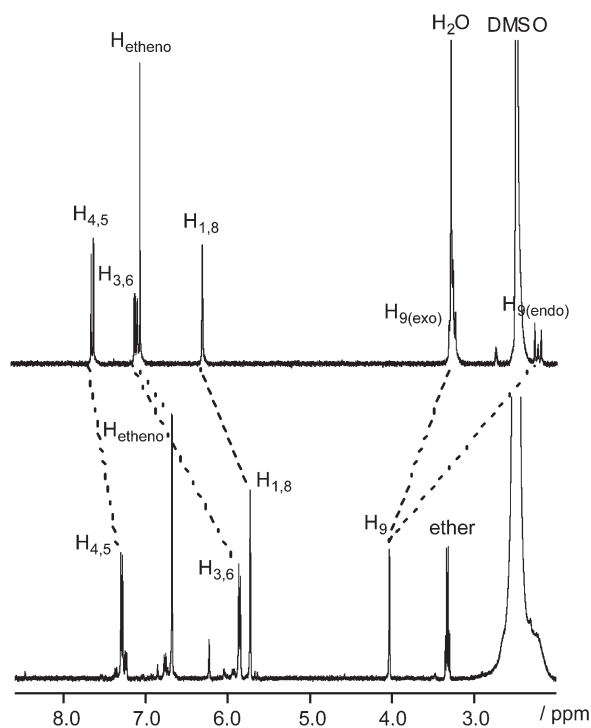


Fig. 1 ^1H NMR spectra of dimer **3** (upper) and dianion **5** (lower) (in $\text{DMSO-}d_6$).

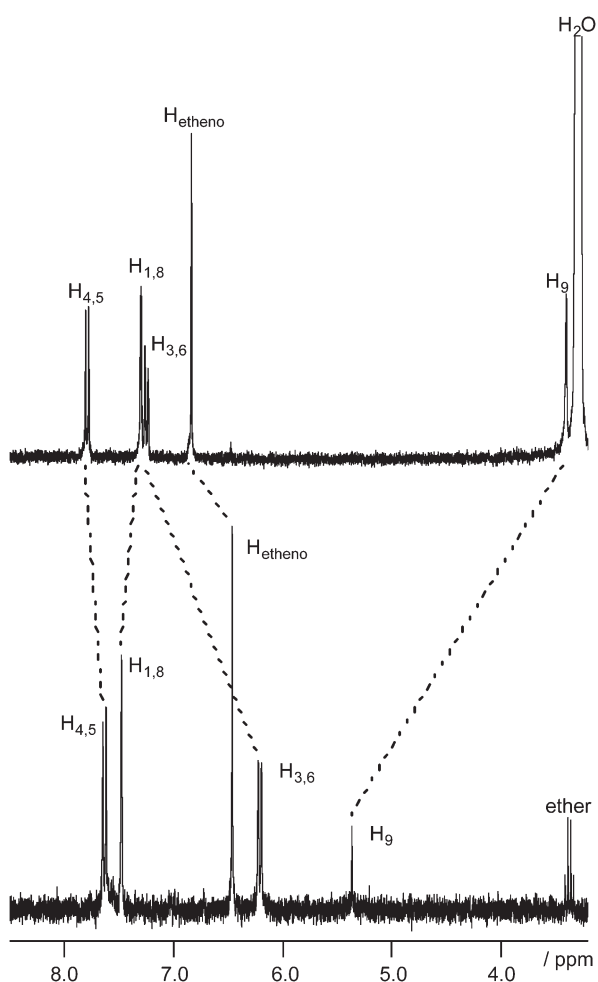


Fig. 2 ^1H NMR spectra of trimer **4** (upper) and trimer **6** (lower) (in $\text{DMSO-}d_6$).

The detailed molecular structure of **3** was established by X-ray structural analysis. Fig. 3 shows the molecular structure with the selected bond lengths and angles in the caption, and Table 2 lists crystallographic data and collection parameters. There are two

Table 1 ^1H chemical shifts of **3**, **4**, and anions **5**, **6** and **9**^a

Compound	H _{1,8}	H _{3,6}	H _{4,5}	H ₉	H _{etheno}
3	6.29	7.09	7.62	3.26, 2.23	7.04
4	7.31	7.25	7.79	3.39	6.84
5	5.72	5.85	7.29	4.03	6.68
6	7.48	6.21	7.63	5.36	6.46
9	7.17	6.33	7.78	5.80	—

^aMeasured in $\text{DMSO-}d_6$.

crystallographically independent molecules with structurally similar asymmetric units, and therefore, only one is shown here. The fluorene rings in **3** are a little more bent than those in **1**, carrying a higher strain: while the transannular distances between C2 (C7) and C2' (C7') of **3** (2.86 Å) are only slightly longer by 0.07 Å than those of **1**, the transannular distance between the central five-membered rings (3.8 Å in average) of **3** is 0.2 Å longer than that of **1**. No formation of the *syn*-dimer may be ascribed to higher steric repulsion between the methylene protons at the transition state for ring closure during the McMurry reaction.

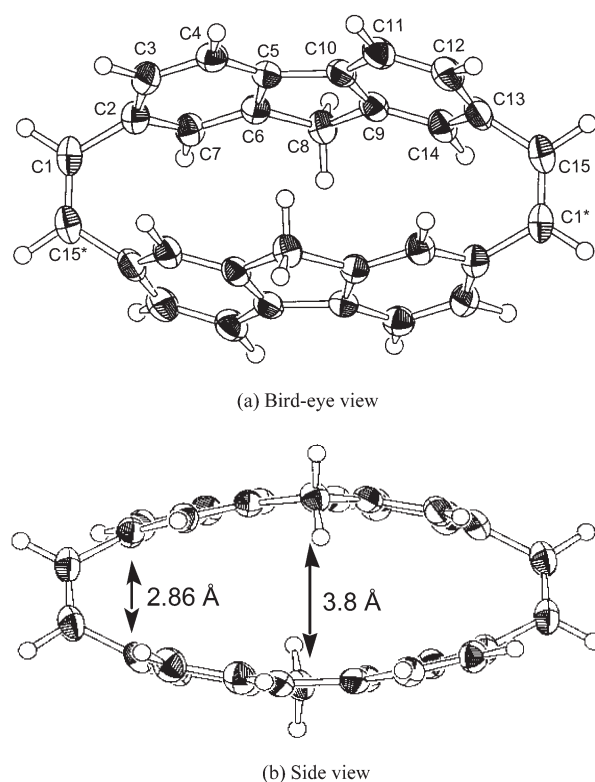


Fig. 3 ORTEP drawings of cyclic dimer **3** (50% probability). Selected bond lengths (Å) and angles ($^\circ$): C1–C2 1.485(3), C1–C15* 1.323(4), C2–C3 1.394(3), C2–C7 1.403(3), C3–C4 1.388(3), C4–C5 1.401(3), C5–C6 1.396(3), C5–C10 1.472(3), C6–C7 1.380(3), C6–C8 1.504(3), C2–C1–C15* 121.2(2), C1–C2–C3 122.1(2), C1–C2–C7 118.1(2), C3–C2–C7 118.9(2), C2–C3–C4 121.6(2), C3–C4–C5 118.5(2), C4–C5–C6 119.8(2), C6–C5–C10 108.5(2), C5–C6–C7 121.0(2), C5–C6–C8 110.3(2), C2–C7–C6 119.4(2), C6–C8–C9 102.5(2), C8–C9–C10 110.6(2).

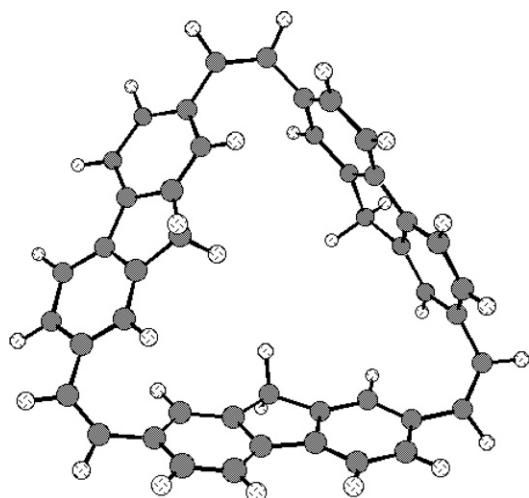
Trimer **4** shows C_3 symmetry in ^1H and ^{13}C NMR spectra at 30 $^\circ\text{C}$: the C9-H and etheno protons are observed as each singlet at δ 3.38 and 6.80 (in CDCl_3), respectively (Fig. 2 upper). The C9-H signal remained unchanged at low temperatures down to -50 $^\circ\text{C}$. Thus, while the fluorene rings in **3** do not rotate owing to steric congestion, those in **4** are fast rotating around room temperature. The vicinal coupling constant of the etheno protons of **4** was measured to be $J = 12.5$ Hz by observation of the ^{13}C satellite signals, indicating all *cis*-geometry of the etheno bridges.

According to a theoretical calculation (PM3), the structure of **4** is roughly triangular at the energy minimum with all *cis* etheno bridges and *anti,syn,syn*-conformation of the fluorene rings (Fig. 4). The three fluorene rings are oblique (47–57 $^\circ$) to the

Table 2 Crystallographic data and collection parameters for **3**

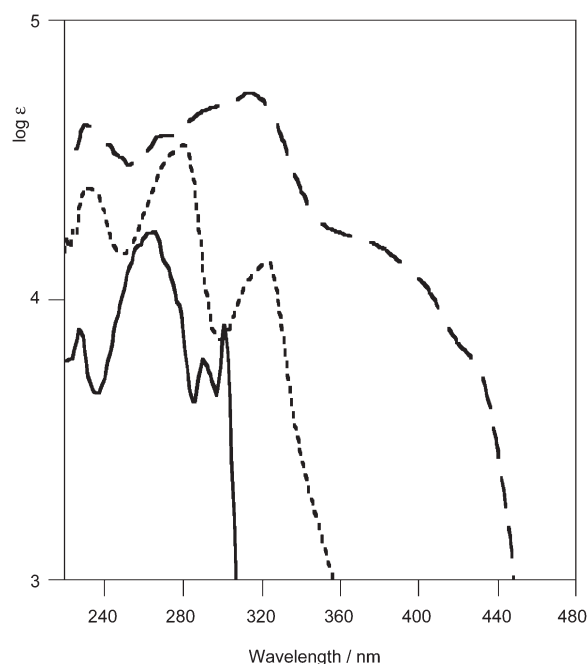
$C_{30}H_{20}$, $M = 380.49$, triclinic, $a = 11.322(2)$, $b = 11.979(4)$, $c = 8.130(2)$ Å, $\alpha = 105.49(2)^\circ$, $\beta = 98.75(2)^\circ$, $\gamma = 66.68(2)^\circ$, $U = 974.4(4)$ Å³, $T = 296$ K, space group $P\bar{1}$ (no. 2), $Z = 2$, $\mu(\text{Mo-K}\alpha) = 0.73$ cm⁻¹, 5476 reflections collected, 4492 unique ($R_{\text{int}} = 0.110$) which were used in all calculations. $R1 = 0.054$ (3004 data, $I > 2\sigma(I)$), $Rw = 0.072$ (all data). CCDC 239576.^a

^aSee <http://www.rsc.org/suppdata/ob/b4/b407582j/> for crystallographic data in .cif or other electronic format.

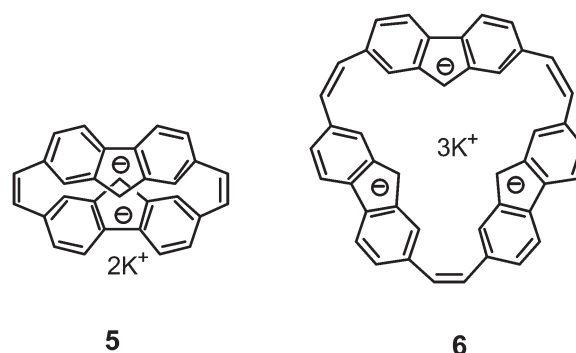
**Fig. 4** PM3 optimized structure of trimer **4**.

molecular plane in such direction that the C9-protons point inward. Differing from dimer **3**, trimer **4** is almost free of steric congestion and therefore a high energy-barrier is not expected for the rotation of fluorene rings in agreement with the NMR observation. For the dihydrotrimer **8**, ¹H and ¹³C NMR spectra indicate C_2 symmetry with the presence of two unsymmetrical etheno bridges of *cis* configuration ($J = 12.2$ Hz), one symmetrical ethano bridge and two kinds of fluorenyl groups.

While dimer **3** exhibits UV absorptions at a slightly longer wavelength ($\lambda_{\text{max}} = 280, 323$ nm) than those of fluorene (266, 301 nm) and **1** (314 nm), trimer **4** shows broad absorptions at appreciably longer wavelengths (314 and 385 nm), reaching the visible region, to indicate substantially effective conjugation (Fig. 5).

**Fig. 5** Absorption spectra of fluorene (solid line), dimer **3** (dotted line), and trimer **4** (dashed line) in CH_2Cl_2 .

Treatment of dimer **3** with excess KH in $\text{DMSO-}d_6$ (dimethyl potassium) afforded its dianion **5** in a red solution. Its ¹H NMR spectrum (Fig. 1 lower) shows the fluorene ring-protons at considerably higher field compared to those of the parent fluorene ion (**9**) ($\delta_{\text{av}} = 5.96$ vs. 6.91 for C1, 3, 4, 9-H of **9**). In particular, a remarkably high field shift is observed for C9-H (δ 4.03 vs. 5.80 of **9**). The stacking structure of two fluorene rings in close proximity would explain the observed high field shifts in terms of anisotropy effects. The etheno protons are also shifted to higher field relative to those of **3** (δ 6.68 vs. 7.04). Dianion **5** is stable in the DMSO solution in a sealed NMR tube at room temperature. Notably, the C9-H signal of **5** shows almost no decrease in intensity even after three months in contrast to the smooth disappearance of the C9-H of **6** and **9** through proton–deuterium (H–D) exchange with the solvent $\text{DMSO-}d_6$. The seemingly unusually slow H–D exchange in **5** can be explained in terms of highly stereospecific proton abstraction by the base as well as protonation by the solvent rather than the absence of abstraction–protonation process. Because of the tightly layered structures of **3** and **5**, bases and solvents would approach the C-9 from only the *exo*-side of the molecules, thus leaving the *endo*-protons intact.



Similar treatment of trimer **4** with KH in $\text{DMSO-}d_6$ also generated trianion **6** as a stable species in the solution (Fig. 2 lower). The fluorene protons ($\delta_{\text{av}} = 6.57$) are at slightly higher field than those of **5**. The etheno protons (δ 6.46) are observed at appreciably higher field than those of **5**, suggesting more effective delocalization of the negative charges throughout the molecule. However, as far as the ¹H chemical shifts are concerned, there seems little induction of peripheral ring current associated with aromaticity in **6**.

Conclusion

The McMurry reaction of 2,7-diformylfluorene (**7**) affords the expected fluorenophanepolyenes up to trimer, though the yields are poor. For higher fluorenophanepolyenes, therefore, use of extended precursors like *cis*-1,2-difluorenylethene derivatives would be necessary if the McMurry reaction is to be employed. It would be of interest to determine whether trianion **6** obtained from trimer **4** can be a suitable synthon for capped fluorenophanes by reactions with proper tripodal capping reagents and such an approach is to be attempted.

Experimental

General

The melting points were measured on a hot-stage apparatus and are uncorrected. EI or high resolution MS spectra were recorded with a SHIMADZU GCMS-QP5050A or JEOL JMS-SX 102 spectrometer. IR spectra were measured on a Perkin Elmer 1650 spectrophotometer in KBr disk. UV-Vis spectra were taken in CH_2Cl_2 solution on a JASCO V-570 spectrometer. ¹H and ¹³C NMR spectra were measured in CDCl_3 or $\text{DMSO-}d_6$ solution on a JEOL EX-270 (270 MHz) spectrometer, and were recorded in δ -value from TMS as an internal standard. Column chromatography was carried out with the use of Merck Art. 7734 Kieselgel 60, 70–230 mesh ASTM, or neutral alumina Merck Art. 1097 Aluminiumoxide

90, activity II–III, 70–230 mesh ASTM. Analytical thin layer chromatography (TLC) was performed on Merck Art. GF-254 silica gel plates (0.25 mm thick) prepared in this laboratory.

Materials

2,7-Diformylfluorene was prepared according to the literature.⁷ Tetrahydrofuran (THF) and dimethoxyethane (DME) was distilled from sodium–benzophenone before use. Zn and CuI were dried well before use. TiCl₄ was commercially available and used without further purification.

McMurry coupling reaction of 2,7-diformylfluorene

A well-dried three-necked, round bottomed flask equipped with a reflux condenser bearing a nitrogen inlet tube, a magnetic stirring bar, and a pressure-equalizing dropping funnel was charged with zinc powder (1.31 g, 20 mmol) and copper(I) iodide (130 mg, 0.68 mmol). Freshly distilled DME (60 ml) was added through a rubber septum by a syringe, followed by the addition of TiCl₄ (1.1 ml, 10 mmol) at 0 °C. The mixture was heated to reflux for 4 h under nitrogen atmosphere and cooled to room temperature. A solution of 2,7-diformylfluorene (222 mg, 1.0 mmol) in DME (60 ml) was added dropwise through the dropping funnel over 2 h under cooling in a water-bath. The mixture was stirred overnight at room temperature and then refluxed for 6 h. After cooling, the reaction mixture was filtered through a short alumina column (100 g) washed with benzene. The filtrate was concentrated and the residue was purified by column chromatography on silica gel eluted by *n*-hexane–benzene (2:1) to give dimer **3** (3–5%, *R*_f value: 0.5/hexane–benzene (2:1)), trimer **4** (8–13%, *R*_f: 0.35) and dihydrotrimer **8** (0–2%, *R*_f: 0.25). ¹H NMR data of **3** and **4** in DMSO-*d*₆ are listed in Table 1.

3. Colorless prisms; mp 302–303 °C; Found C, 94.49; H, 5.23. Calcd. for C₃₀H₂₀: C, 94.70; H, 5.30%. ν_{\max} (KBr)/cm⁻¹ 3002, 1613, 1460, 887, 836, 787 and 754; δ_{H} (270 MHz, CDCl₃, Me₄Si) 7.49 (d, *J* = 7.9 Hz, 4H), 7.06 (d, *J* = 7.9 Hz, 4H), 7.02 (s, 4H), 6.38 (s, 4H), 3.26 (d, *J* = 20.9 Hz) and 2.35 (d, *J* = 20.9 Hz, 2H); δ_{C} (67.8 MHz, CDCl₃, Me₄Si) 143.78, 139.83, 136.45, 135.07, 128.04, 127.49, 118.99, 36.45; λ_{\max} (CH₂Cl₂)/nm 280 (log ϵ 4.55), 323 (4.14); HRMS *m/z* 380.1595. C₃₀H₂₀ requires 380.1566. *m/z* (EI) 380 (M⁺, 100), 190 (M²⁺, 14).

4. Yellow needles; mp > 300 °C (decomp.); ν_{\max} (KBr)/cm⁻¹ 3005, 2921, 1607, 1467, 1016, 830; δ_{H} (270 MHz, CDCl₃, Me₄Si) 7.66 (d, *J* = 7.9 Hz, 6H), 7.31 (s, 6H), 7.21 (d, *J* = 7.9 Hz, 6H), 6.80 (s, 6H) and 3.38 (s, 6H); δ_{C} (67.8 MHz, CDCl₃, Me₄Si) 142.70, 140.25, 135.87, 131.14, 127.78, 125.71, 119.57 and 36.61; λ_{\max} (CH₂Cl₂)/nm 314 (log ϵ 4.74) and 380sh (4.10); HRMS *m/z* 570.2392. C₄₅H₃₀ requires 670.2349. *m/z* (EI) 570 (M⁺, 100), 285 (M²⁺, 21).

8. Yellow powder; mp > 300 °C (decomp.); δ_{H} (270 MHz, CDCl₃, Me₄Si) 7.65 (d, *J* = 7.7 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 2H), 7.57 (d, *J* = 7.7 Hz, 2H), 7.30 (s, 2H), 7.24–7.14 (m, 8H), 6.96 (s, 2H), 6.77 (d, *J* = 12.2 Hz, 2H), 6.65 (d, *J* = 12.2 Hz, 2H), 3.47 (s, 4H), 3.23 (s, 4H) and 3.08 (s, 2H); δ_{C} (67.8 MHz, CDCl₃, Me₄Si) 142.85, 142.76, 142.65, 142.58, 140.56, 139.98, 138.90, 135.98, 135.43, 130.71, 130.58, 128.16, 127.18, 127.06, 126.05, 125.51, 125.45, 119.67, 119.63, 119.50, 36.60, 34.57 and 29.79; λ_{\max} (CH₂Cl₂)/nm 281 (log ϵ 4.10), 310 (4.00), 337 sh (3.72) and 376 sh (3.41). MS(EI) *m/z* 572 (M⁺, 100), 286 (M²⁺, 63).

Hydrogenation of dimer 3

A solution of dimer **3** (13 mg, 3.4 × 10⁻⁵ mol) in benzene (10 ml) was stirred under H₂ in the presence of 10% Pd–C (10 mg) at room temperature overnight. The catalyst was removed by filtration and

the solvent was evaporated. Crystallisation of the colorless residue from benzene gave 12 mg (92%) of **1**.

1. Colorless crystals; mp 370–371 °C (lit.^{2a} 371–372 °C); δ_{H} (270 MHz, CDCl₃, Me₄Si) 7.35 (d, *J* = 7.8 Hz, 4H), 6.95 (d, *J* = 7.8 Hz, 4H), 6.10 (s, 4H), 3.20–3.10 (m, 6H including one doublet of C9-*Hexo*), 2.70–2.65 (m, 4H), 2.35 (d, *J* = 21.3 Hz, 2H, C9-*Hendo*).

General procedure for the preparation of polyanions 5 and 6

A reaction vessel bearing a NMR tube, nitrogen gas inlet tube, and a stopcock for attachment to the vacuum manifold was charged with KH (*ca.* 1.0 ml, 35% oil dispersion) washed with dry ether. After drying by evacuation, the vessel was purged with nitrogen. DMSO-*d*₆ (0.3 ml) was added to KH and the solution of the sample was charged in an NMR tube. The solution of dimsyl anion was transferred into the sample solution and the NMR tube was shaken for a minute to afford the brown solution of the corresponding anion. The reaction mixture was degassed by repeating freeze–thaw–pump method and the NMR tube was sealed off.

5. δ_{H} (270 MHz, DMSO-*d*₆) 7.29 (d, *J* = 7.9 Hz, 4H), 6.68 (s, 4H), 5.85 (d, *J* = 7.9 Hz, 4H), 5.72 (s, 4H), 4.03 (s, 2H).

6. δ_{H} (270 MHz, DMSO-*d*₆) 7.63 (d, *J* = 7.9 Hz, 6H), 7.48 (s, 6H), 6.46 (s, 6H), 6.21 (d, *J* = 7.9 Hz, 6H), 5.36 (s, <2H; soon disappeared).

Fluorenyl anion 9. δ_{H} (270 MHz, DMSO-*d*₆) 7.78 (d, *J* = 5.8 Hz, 2H), 7.17 (d, *J* = 5.8 Hz, 2H), 6.71 (bs, 2H), 6.33 (bs, 2H), 5.80 (s, <1H; soon disappeared).

Acknowledgements

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- This poorly soluble solid, though not pursued further, seems to contain oxidized compounds having fluorenone moiety(s), since its IR spectrum shows absorptions around 1720 cm⁻¹.