Linear acenes such as tetracene and pentacene have been, among other organic materials, at the center of recent developments in semi-conducting materials, in view of the realization of low-cost electronic devices. Since tetracene and pentacene display a very low solubility in organic solvents, the study of their application is largely restricted to the solid state. By substituting tetracene in diverse positions, a significant solubility has been achieved in common organic solvents as reported in recent publications. This solubility is of particular advantage for deposition on surfaces, introduction into matrices, or formation of self-assembled networks. The substitution in the 2- and 3-positions of anthracene and tetracene with long alkoxy chains was shown to confer supergelating properties onto these aromatic nuclei, presumably because of their mutual organization along the long molecular axis. It seemed appropriate to prepare 2,3-substituted pentacenes to extend the molecular length in order to increase the solubility and induce the aggregation properties of this acene. Having described the synthesis and some properties of the homologous series beginning with the soluble anthracene diether in Scheme 1 and 2,3-di-n-hexadecyloxytetracene, we now present the preparation of the title compound, 2,3-di-n-hexadecyloxypentacene (3, Scheme 1) and the preliminary results of its organogel formation.

As shown in Scheme 2 the synthesis of the diether 3 started with a Diels–Alder addition between 2,3-dimethoxy-1,3-butadiene (4) and p-benzoquinone (5) in toluene. The resulting [2+4] cycloadduct 6 was reduced to the hydroquinone 7, which, on condensation with naphthalene-2,3-dicarboxaldehyde (8) furnished the quinone 9 with the complete carbon framework of the title compound, the two last steps occurring in excellent yield. For the replacement of the two methoxy groups, 9 was first cleaved to the catechol intermediate 10 which on alkylation with n-hexadecyl bromide provided the long-chain bisether 11. From various reduction methods the Meerwein–Ponndorf–Verley approach with tris(cyclohexyloxy)aluminium in cyclohexanol turned out best. Although the overall yield from benzoquinone was only ca 6.5%, gram amounts of 3 can be prepared by this route. The structures of 3 as well as its different precursors (Scheme 2) were derived from their spectroscopic and analytical data given in the experimental section.

Despite the presence of two long chains, the solubility in common organic solvents was not found to be as high as that of the tetracene analog. This is probably the reason why the chemical yield of the last step is only fair (24%). 1,1,1,2-Tetrachloroethane was used to record the spectra. The gelation properties of 3 were assessed using the inverted tube method. At 1.3 × 10⁻² M, in a capped tube 3 was dissolved in the Ar-saturated solvent at ca 80 °C (red color). After cooling down to ambient temperature a dark blue gel was formed.

The spectroscopic, thermodynamic and other physical properties of the pentacene gels are under current investigation.

Melting points were taken with a ‘Meltemp’ melting point apparatus and are uncorrected. ¹H and ¹³C NMR spectra were measured on a Bruker AC 200 (¹H: 200.2 MHz; ¹³C: 50.3 MHz) and a Bruker DRX 400 spectrometers (¹H: 400.1 MHz; ¹³C: 100.6 MHz) in CDCl₃ with TMS as internal standard. The coupling constant for AA'XX'-spin systems were analyzed by iterative calculation, using the WinDaISy® 4.1 software (Bruker, Rheinstetten). R-factors are generally better than 0.85%. In the cases where the spin system was not calculated, the distance between the outer signals is given in Hz (V-values). Mass spectra were measured on a Finnigan MAT 8430 instrument at 70 eV via electron impact (EI) ionization. IR spectra were recorded on a Nicolet 320 FT-IR spectrometer or a Diamond ATR Bruker Tensor 27, as KBr pellets. UV–Vis spectral data were measured with a Beckman UV 5200 spectrometer.

1,4-Dihydroxy-6,7-dimethoxynaphthalene (7) 6,7-Dimethoxynaphtho-1,4-quinone (6, 3.6 g, 16.5 mmol) was suspended in glacial AcOH (108 mL). Zn dust (2.15 g, 33 mmol) was
1,4-Dihydroxy-6,7-dimethoxynaphthalene (4) and 2,3-Dimethoxypentacene-5,14-quinone (9)

HRMS: naphthalene-2,3-dicarboxaldehyde (8) [M+ – CH₃], 177 (12) [M+ – CH₃ – CO].

MS (70 eV): m/z (%) = 368 (100) [M⁺], 353 (4) [M⁺ – CH₃], 325 (8) [M⁺ – CH₃ – CO].

Scheme 2 Synthesis of 2,3-di-n-hexadecyloxypentacene

added in four portions and after each addition the suspension was sonicated for 20 min in a 130 W ultrasound bath. The reaction was complete when the product was dissolved totally and the solution above the Zn residue was only slightly brownish. The mixture was diluted with EtOAc (100 mL) and the Zn/Zn(OAc)₂ precipitate was removed by filtration and washed with EtOAc. The solvent was removed under vacuum, the solid product washed with pentane and dried in high vacuum. The crude product (3.47 g, 95%) was directly used for further reaction; mp 178–182 °C (decomp.).

The mixture was heated to reflux for 4 h, diluted with water (10 mL) and the precipitate was filtered off. After washing with water, MeOH and Et₂O, the product was obtained as an orange solid (0.52 g, 89%); mp 340 °C (decomp.). Due to the poor solubility in the common deuterated solvents no ¹³C NMR spectrum could be measured.

IR (ATR): 3083 (w), 3044 (w), 3019 (w), 2967 (w), 2947 (w), 1664 (s), 1582 (s), 1535 (w), 1501 (m), 1469 (m), 1446 (m), 1418 (m), 1376 (m), 1307 (m) cm⁻¹.

HRMS: m/z [M⁺] calcd for C₂₄H₁₆O₄: 368.1049; found: 368.1039.

UV (CH₂Cl₂): λmax (log ε) = 262 (4.91), 309 (4.49), 325 (4.63), 340 (4.75), 409 (3.88), 456 (3.95) nm.

IR (ATR): 3044 (w), 2917 (s), 2849 (s), 1668 (m), 1573 (s), 1508 (m), 1466 (m), 1449 (m), 1421 (w), 1376 (m), 1318 (s), 1274 (m) cm⁻¹.


UV (CH₂Cl₂): λmax (log ε) = 262 (4.88), 325 (4.62), 339 (4.74), 455 (3.93) nm.

2,3-Dihydroxypentacene-5,14-quinone (10)

2,3-Dimethoxypentacene-5,14-quinone (9, 1.39 g, 3.77 mmol) was suspended in aq HBr (48%, 75 mL). The suspension was heated to reflux for 4 d, diluted with glacial AcOH (75 mL) and again heated for 2 d. The mixture was diluted with water, filtered and the residue was washed with water, MeOH and Et₂O. The crude product was directly alkylated without further purification.

2,3-Di-n-hexadecyloxypentacene-5,14-quinone (11)

2,3-Dihydroxypentacene-5,14-quinone (10; 0.80 g, 2.35 mmol) was dissolved in DMF (15 mL) and K₂CO₃ (0.97 g, 7.05 mmol) was added to the solution. After 1 h, n-hexadecylbromide (2.15 g, 7.05 mmol) was added over a period of 1 h. The reaction mixture was kept under reflux for 3 h and then cooled to r.t. The solvent was removed in vacuo and the raw product was purified by column chromatography (silica gel, CH₂Cl₂–pentane); orange solid (1.05 g, 57%); mp 170–172 °C (EtOAc).

IR (ATR): 3044 (w), 2917 (s), 2849 (s), 1668 (m), 1573 (s), 1508 (m), 1466 (m), 1449 (m), 1421 (w), 1376 (m), 1318 (s), 1274 (m) cm⁻¹.


UV (CH₂Cl₂): λmax (log ε) = 262 (4.88), 325 (4.62), 339 (4.74), 455 (3.93) nm.

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IR (ATR): 3044 (w), 2917 (s), 2849 (s), 1668 (m), 1573 (s), 1508 (m), 1466 (m), 1449 (m), 1421 (w), 1376 (m), 1318 (s), 1274 (m) cm⁻¹.

HRMS: m/z [M⁺] calcd for C₂₄H₁₆O₄: 368.1049; found: 368.1039.

UV (CH₂Cl₂): λmax (log ε) = 262 (4.91), 309 (4.49), 325 (4.63), 340 (4.75), 409 (3.88), 456 (3.95) nm.

2,3-Dihydroxypentacene-5,14-quinone (10)

2,3-Dimethoxypentacene-5,14-quinone (9, 1.39 g, 3.77 mmol) was suspended in aq HBr (48%, 75 mL). The suspension was heated to reflux for 4 d, diluted with glacial AcOH (75 mL) and again heated for 2 d. The mixture was diluted with water, filtered and the residue was washed with water, MeOH and Et₂O. The crude product was directly alkylated without further purification.
off and washed with EtOH and Et₂O. To separate the raw product from remaining Al, it was hot-extracted using Ar-saturated CHCl₃. The product was obtained as a dark blue solid (94 mg, 24%); mp 199–205 °C (decomp., CHCl₃).

IR (ATR): 3048 (w), 2917 (s), 2849 (s), 1672 (w), 1633 (w), 1555 (w), 1463 (s), 1380 (w), 1306 (m), 1253 (s), 1211 (m) cm⁻¹.

¹H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d₂, 81 °C): δ = 8.83 (s, 2 H, 13-H, 6-H), 8.63 (s, 2 H, 12-H, 7-H), 8.40 (s, 2 H, 14-H, 5-H), 7.94 (complex m, N = 9.8 Hz, 2 H, 11-H, 8-H), 7.33 (complex m, N = 9.9 Hz, 2 H, 10-H, 9-H), 7.11 (s, 2 H, 4-H, 1-H), 4.18 (t, J = 6.5 Hz, 4 H, 2×OCH₂), 1.98–1.91 (m, 4 H, chain), 1.63–1.56 (m, 4 H, chain), 1.48–1.31 (m, 48 H, chain), 0.92 (t, J = 6.8 Hz, 6 H, 2×CH₃).

¹³C NMR (100 MHz, 1,1,2,2-tetrachloroethane-d₂, 81 °C): δ = 150.8 (s, C-3, C-2), 131.2 (s, C-11a, C-7a), 129.7 (s, C-13a, C-5a or C-12a, C-6a), 129.5 (s, C-14a, C-4a), 128.2 (d, C-11, C-8), 125.9 (d, C-12, C-7), 125.1 (d, C-13, C-6), 124.7 (d, C-10, C-9), 122.9 (d, C-14, C-5), 105.8 (d, C-4, C-1), 68.9 (t, 2 × OCH₂), 31.7, 29.5, 29.4, 29.2, 29.1, 29.0, 26.0, 22.4 (t, chain, not all C-atoms resolved), 13.8 (q, 2 × CH₃).

MS (70 eV): m/z (%) = 758 (100) [M⁺], 534 (10) [M⁺ – C₁₆H₃₂], 310 (45) [M⁺ – C₁₃H₃₄], 281 (16) [M⁺ – C₁₂H₄₆ – CHO].

HRMS: m/z [M⁺] calcd for C₅₄H₇₈O₂: 758.6002; found: 758.6022.

UV (1,1,2,2-tetrachloroethane): λₘₐₓ = 309, 321, 348, 433, 498, 536, 580 nm. The UV/Vis spectrum was only measured qualitatively for a saturated solution.

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References


(9) Gelation test: Solvent (1 mL) was added to a weighed amount of gelator in a septum-capped test tube (ca 6 cm length and 0.7 cm diameter) in order to obtain the desired concentration. The mixture was warmed (to the bp) until the solid dissolved. Then the mixture was allowed to cool to r.t. When a gel was formed (ca several min), the sample did not flow when the tube was inverted.