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Synthesis and liquid crystal properties of some 2,6-disubstituted anthracenes

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The synthesis and liquid crystalline properties of some new 2,6-disubstituted anthracenes are described. Symmetrical alkylphenyl derivatives exhibit smectic mesophases, whereas simpler structures are non-mesogenic. One unsymmetrically substituted anthracene exhibits a narrow nematic phase. The potential for these molecules to act as phototriggers has been investigated but efficient photodimerisation cannot be achieved.

Keywords: anthracene derivative; phototrigger; cross-coupling

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1. Introduction

Benzenes (1,4-substituted) and naphthalenes (2,6-substituted) are frequently encountered as constituent units in liquid crystals. A much smaller number of reports describe liquid crystalline systems based on the anthracene or anthraquinone core (*1–4*). Indeed the latter anthraquinone-based materials are more widely reported and, depending on the number and nature of substituents, have been shown to exhibit either calamitic or discotic behaviour (*3, 4*). Anthracene and its derivatives are well known to show interesting spectroscopic behaviour, and most notably their fluorescence has been exploited (*5*).

Anthracene undergoes photodimerisation (Figure 1), which itself can be widely exploited in diverse applications (*6*). The dimerisation reaction has drastic effects on both spectroscopic properties and molecular shape. Importantly, the process is reversible (photochemically and thermally) so offers the potential to act as a trigger molecule in a liquid crystal host where the monomer supports mesophase stability but the dimer is anticipated to disrupt it. This potential has been previously recognised, most notably by Méry *et al.* (*2*), who synthesised a number of liquid crystalline anthracenes and examined their dimerisation. Unfortunately they were unable to induce significant dimerisation at the elevated temperature of the mesophases.

2. Results and discussion

This paper describes further examples of substituted anthracenes that were designed to investigate the effect of substituent on mesophase behaviour with a view to exploiting materials as photochemical triggers. Anthracene bistriflate **8** was recognised as a versatile intermediate for introduction of a variety of substituents. However, the previous synthesis of this intermediate used anthraflavic acid as starting material (*2, 7, 8*). The expense of this precursor made synthesis of reasonable quantities of **8** unattractive so an alternative was developed (Scheme 1). 3-Methoxybenzoic acid was converted to its corresponding acid chloride (using thionyl chloride) and aluminium chloride was then used to induce double Friedel–Crafts acylation and conveniently yield 2,6-dimethoxyanthraquinone **3** directly. Reduction (sodium borohydride) and hydrolysis (BBr_3) gave access to reasonable quantities of 2,6-dihydroxyanthracrene **7**. In some cases hydrolysis was incomplete. Triflation was achieved using triflic anhydride/triethylamine to give the ditriflate **8** (plus a trace of monotriflate **6** – the mixture was easily separated by column chromatography).

The first compounds investigated were alkylphenyl anthracenes (Scheme 2). Hexyl- and heptylphenyl derivatives were chosen (an odd and even numbered chain length). They were most conveniently prepared using a Suzuki coupling reaction (*9*) between anthracene bistriflate **8** and alkylphenylboronic acids **9** (themselves prepared from the corresponding bromides). The Suzuki reactions proved somewhat capricious, with the combination $Pd(PPh_3)_2Cl_2$/CsF in DME proving most effective, and often forcing conditions were required. The reactions gave sufficient materials for subsequent characterisation so were not further optimised. One coupling was also performed on monotriflate **6** to determine the properties of an unsymmetrical derivative (**13**). The thermal behaviour of the materials, as determined by polarising optical microscopy (POM) and differential scanning calorimetry (DSC), is also shown in Scheme 2. It can be seen that all derivatives exhibit

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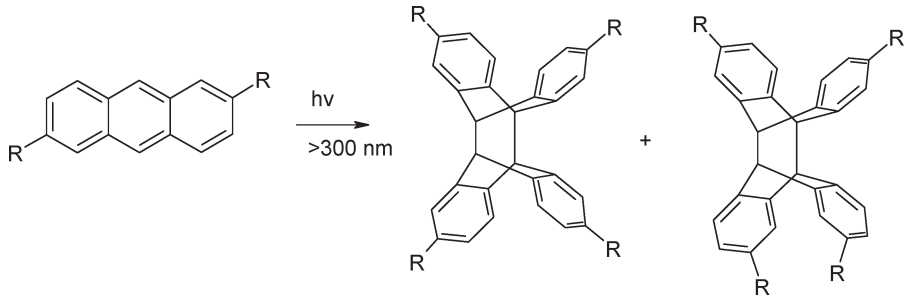
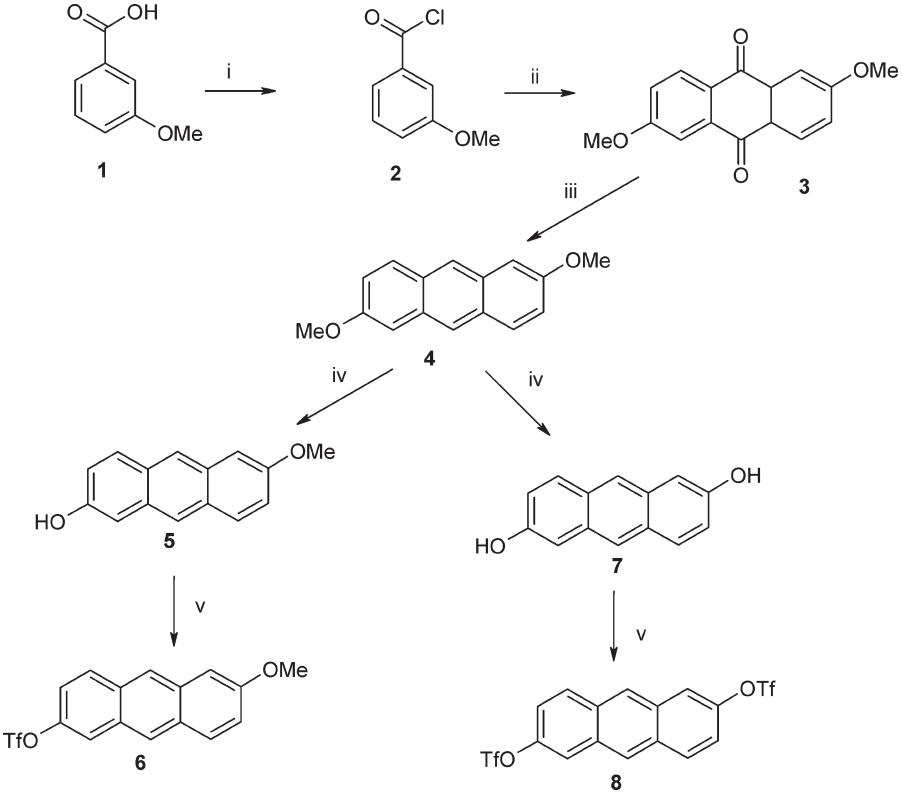


Figure 1. Photodimerisation of anthracenes.



Scheme 1. Synthesis of anthracene triflates. Reagents and conditions: (i) thionyl chloride, CH_2Cl_2; (ii) $AlCl_3$, CH_2Cl_2; (iii) $NaBH_4$, iPrOH, H_3O^+; (iv) BBr_3, CH_2Cl_2; (v) triflic anhydride, CH_2Cl_2, TEA.

high transition temperatures and melting points, and are comparable to the alkoxyphenyl anthracenes reported by Méry *et al.* (*2*). Unsymmetric anthracene **13** exhibits narrow nematic phase (it is the only example from both our work and that of Méry to show a nematic phase). Symmetrical 2,6-bishexylphenyl- (**10**) and 2,6-bisheptylphenylanthracene (**11**) exhibit smectic A phases (based on their textures) over comparable temperature ranges. Branched-chain analogue **12** (2-ethylhexyl-) was therefore synthesised in an attempt to lower the transition temperatures. This modification led to a lowering of the melting point, but no mesophase behaviour was observed.

Anthracene ditriflate **8** was recognised as a versatile intermediate allowing exploration of new 2,6-disubstituted derivatives. Two alternatives to phenyl substituents were investigated with a view to preparing mesogenic or promesogenic anthracenes with lower steric incumberance to dimerisation (the 2,6-phenyl substituents can twist out of the anthracene plane and disfavour dimerisation). Palladium-catalysed coupling (*10*) between ditriflate **8** and hexanethiol produced 2,6-bis(thiohexyl)anthracene (**14**) and Sonagashira coupling (*11*) with 1-hexyne produced the corresponding bisalkyne **15** (Scheme 3). Neither derivative, however, exhibited mesophase behaviour.

The solution absorption spectra for the three classes of symmetrical derivatives are shown in Figure 2. It can be seen that all spectra are broadly

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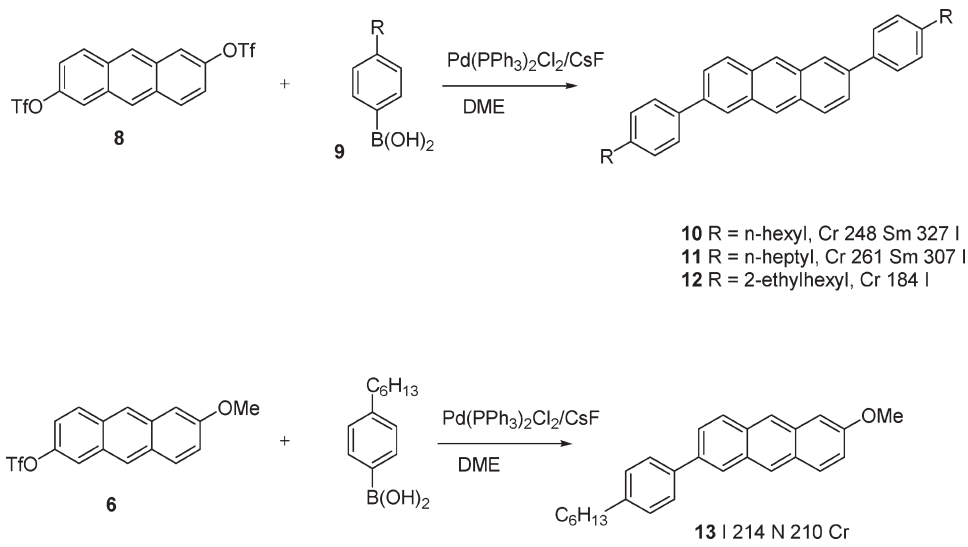
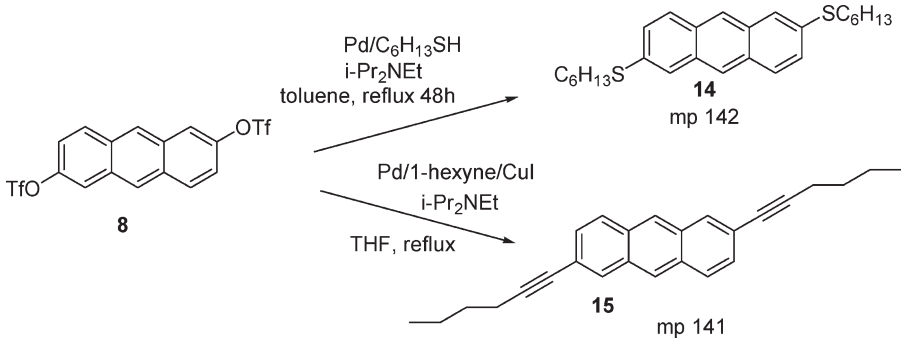


Scheme 2. Synthesis and liquid crystalline properties of novel alkylphenyl anthracenes.



Scheme 3. Synthesis and thermal behaviour of bis(hexylthio)anthracene **14** and dihexynylanthracene **15**.

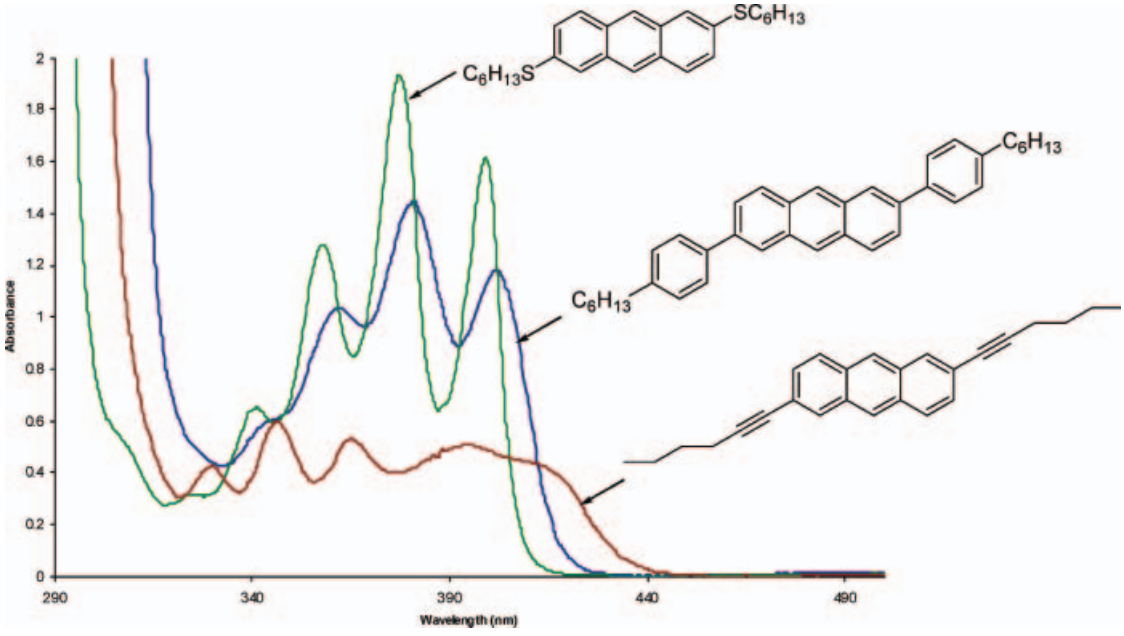


Figure 2. Solution-phase UV–visible spectra of anthracenes **10**, **14** and **15**.

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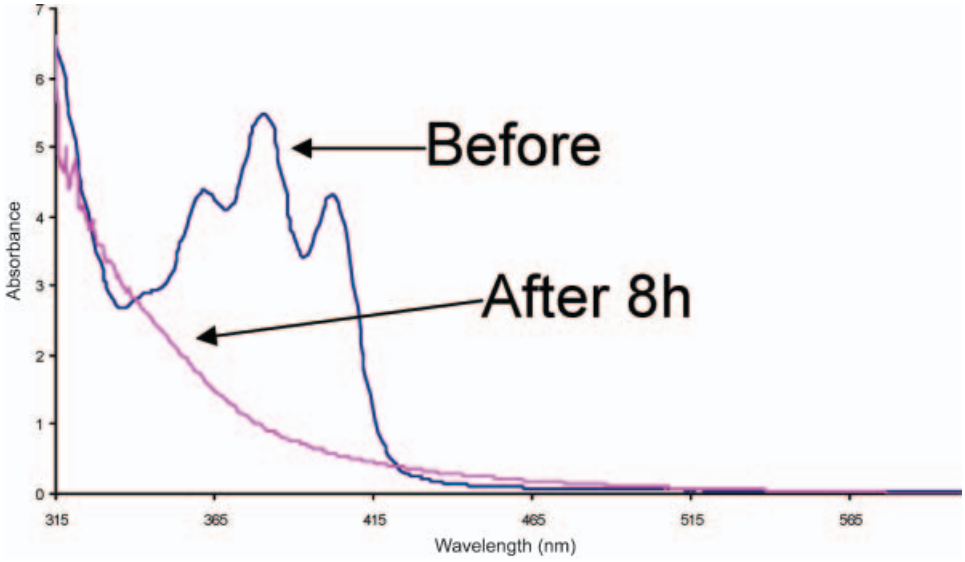

Figure 3. UV–visible spectra of compound **10** before and after irradiation at 365 nm.

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similar, suggesting that the anthracene chromophore is only minimally perturbed by substitution. Conjugation in dialkyne **15** broadens the spectrum and shifts absorptions to longer wavelengths, as expected. From these spectra, photodimerisation would be expected to proceed above 300 nm in all cases (the photodimer will not have significant absorption above ca 270 nm).

Solution-phase photodimerisation experiments were performed and employed irradiation at 365 nm produced by a Spot-Lite UV/light Wand System with a 400 W long wave light source and a wand with a 8 mm circumference. A sealed tube with a quartz cuvette fitted at one end was used and the sample, dissolved in chloroform, was degassed using a pump-freeze-thaw process. The samples were irradiated for a total of 8 h and monitored by UV–visible spectroscopy. All experiments produced similar results with the main anthracene absorption disappearing during irradiation. A representative example (**10**) is given in Figure 3 and shows the UV–visible spectra before irradiation and after 8 h of irradiation.

This change in the absorption spectrum is consistent with photodimerisation. However, further analysis of the reaction product mixtures (^{1}H NMR, LCMS) showed no evidence for photodimer products and, instead, slow decomposition of the starting materials was evident.

3. Conclusions

Further series of novel mono- and disubstituted anthracenes have been synthesised, using palladium catalysed cross-coupling procedures, to investigate their mesophase behaviour and potential for use as phototriggers. Alkylphenyl derivatives, like their alkoxyphenyl counterparts prepared by Méry *et al.* (*2*), show smectic mesophases and high transition temperatures; simple thioether and alkyne derivatives are non-mesogenic. The absorption spectra for all compounds indicated they were good candidates for photodimerisation. However, irradiation of solutions at 365 nm resulted only in photodecomposition with no evidence for production of the expected photodimer observed.

4. Experimental

Characterisation

NMR spectra were recorded on a Bruker EMX 400 instrument. Coupling constants are given in Hz. UV–vis spectra were recorded on a Hitachi U-3000-X spectrometer. Liquid crystalline properties were investigated using an Olympus BH-2 polarising optical microscope and Linkham TMS 92 hot stage.

Syntheses

4-Alkylphenylboronic acids (*12*), hydroxyanthracenes **5** and **7** and anthracene triflates **6** and **8** were prepared following previously reported methods (*2*).

*2,6-Dimethoxyanthraquinone (**3**)*

3-Methoxybenzoic acid (5.0 g, 32.86 mmol) and thionyl chloride (1.2 eq) were stirred in dichloromethane (10 ml) at reflux for 3 h. Excess thionyl chloride was removed under reduced pressure to give 3-methoxybenzoyl chloride **2** (93%), which was used

immediately without further purification. $AlCl_3$ (1.1 eq, 19.28 g) was stirred in dry dichloromethane (50 ml) and to this was added the acid chloride in 40 ml dry dichloromethane. The reaction was heated under reflux overnight, cooled and poured slowly onto 0.1M HCl. The mixture was extracted with dichloromethane, washed with water, brine and then dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was recrystallised twice from ethanol to give 2,6-dimethoxyanthraquinone **3** (3.47 g, 33%): m.p. 256°C [lit (*2*): 256–257°C].

*2,6-Bis(4-hexylphenyl)anthracene (**10**)*

Ditriflate **8** (0.3 g, 0.7 mmol), 4-hexylphenylboronic acid (0.6 g, 2.9 mmol) and CsF (0.6 g) were stirred under argon and dry DME (12 ml) was added. $Pd(PPh_3)_2Cl_2$ (48 mg, 0.05 eq/triflate) was then added and the reaction heated at reflux. After 8 h another portion of catalyst was conducted and the reaction refluxed for a further 48 h. Further boronic acid (0.15 g), CsF and $Pd(PPh_3)_2Cl_2$ was added and the reaction was heated under reflux for a further 12 h. The cooled reaction mixture was filtered through celite and washed with hot $CHCl_3$. The filtrate was reduced under vacuum and was recrystallised from $CHCl_3$ to give the desired compound as a yellow solid (111 mg, 31 %). ^{1}H NMR ($CDCl_3$): δ 0.91 (t, J=7.2 Hz, 6H), 1.25–1.42 (m, 12H), 1.68 (quin, J=7.2 Hz, 4H), 2.69 (t, J=8.0 Hz, 4H), 7.33 (d, J=8.0 Hz, 4H), 7.71 (d, J=8.0 Hz, 4H), 7.77 (d, J=8.0 Hz, 2H), 8.07 (d, J=8.0 Hz, 2H), 8.19 (s, 2H), 8.47 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 10.3, 18.8, 25.2, 27.6, 27.9, 31.8, 121.6, 122.0, 122.5, 123.5, 124.9, 125.3, 127.5, 128.3, 134.1, 134.7, 138.7. EIHRMS: m/z 498.3281 (expected 498.3281); λ_{max} 402 (log ε=4.43) nm, 381 (log ε=4.52) nm, 362 (log ε=4.37) nm, 343 (log ε=4.13) nm.

*2,6-Bis(4-heptylphenyl)anthracene (**11**)*

Ditriflate **8** (0.3 g, 0.7 mmol), 4-heptylphenylboronic acid (0.6 g, 2.72 mmol) and CsF (0.6 g) were stirred under argon and dry DME (12 ml) was added. $Pd(PPh_3)_2Cl_2$ (48 mg, 0.05 eq/triflate) was then added and the reaction heated at reflux for 4 days with an addition of further boronic acid, CsF and catalyst after 36 h. The reaction mixture was cooled, filtered through celite and washed with hot $CHCl_3$. The filtrate was concentrated under vacuum and was recrystallised from $CHCl_3$ to give the desired compound as a yellow solid (345 mg, 89%). ^{1}H NMR ($CDCl_3$): δ 0.90 (t, J=7.2 Hz, 6H), 1.20–1.40 (m, 16H), 1.70 (quin, J=7.0 Hz, 4H), 2.70 (t, J=8.0 Hz, 4H), 7.32 (d, J=8.0 Hz, 4H), 7.69 (d, J=8.0 Hz, 4H), 7.79 (d, J=8.0 Hz, 2H), 8.09 (d, J=8.0 Hz, 2H), 8.20 (s, 2H), 8.45 (s, 2H). ^{13}C ($CDCl_3$): δ 13.9, 22.5, 29.0, 29.2, 31.3, 31.7, 35.5, 125.3, 125.6, 126.2, 127.1, 128.6, 128.9, 131.2, 132.0, 137.7, 138.3, 142.4. EIHRMS: m/z 526.3593 (expected 526.3594); λ_{max} 402 (log ε=4.59) nm, 381 (log ε=4.68) nm, 361 (log ε=4.53) nm, 343 (log ε=4.30) nm.

*2,6-Bis(4-(2-ethylhexyl)phenyl)anthracene (**12**)*

Ditriflate **8** (0.447 g, 1 mmol), (2-ethylhexyl)phenyl boronic acid (1.02 g, 4 mmol) and CsF (0.248 g) were stirred under argon and dry DME (20 ml) was added. $Pd(PPh_3)_2Cl_2$ (7.6 mg, 0.005 eq/triflate) was then added and the reaction heated at reflux for 14 days (with addition of further boronic acid, catalyst and CsF after 7 days). The reaction mixture was cooled and filtered through celite and the filtrate was concentrated under vacuum. The mixture (which contained significant quantities of singly coupled product) was separated and purified by column chromatography DCM/hexane (1:4) and recrystallised from hexane to give **12** (50 mg, 9 %). ^{1}H NMR ($CDCl_3$): δ 0.88–0.92 (m, 12H), 1.25–1.39 (m, 16H), 1.59–1.65 (m, 2H), 2.59–2.63 (m, 4H), 7.30 (d, J=7.4 Hz, 4H), 7.70 (d, J=7.4 Hz, 4H), 7.78 (d, J=8.8 Hz, 2H), 8.10 (d, J=8.8 Hz, 2H), 8.20 (s, 2H), 8.48 (s, 2H). ^{13}C ($CDCl_3$): δ 10.3, 13.7, 22.6, 24.9, 28.4, 31.9, 39.3, 40.7, 124.8, 125.3, 125.9, 126.6 128.3, 129.4, 130.8, 131.7, 137.8, 137.9, 141.0. EIHRMS: m/z 554.3891 (expected 554.3907); λ_{max} 402 (log ε=4.34) nm, 380 (log ε=4.46) nm, 361 (log ε=4.32) nm, 343 (log ε=4.09) nm, 300 (log ε=5.45) nm.

*2-Methoxy-6-(4-hexylphenyl)anthracene (**13**)*

A mixture of the triflate **6** (0.1 g, 0.3 mmol), 4-hexylphenylboronic acid (95 mg, 0.46 mmol), KBr (40 mg, 0.33 mmol), K_3PO_4 (98 mg, 0.46 mmol) and $Pd(PPh_3)_4$ (9 mg, 2.5 mol%) were added to dry dioxane (4 ml) under argon. The mixture was degassed and heated at 85°C under vigorous stirring. After 8 h another portion of $Pd(PPh_3)_4$ (6 mg) was introduced and the mixture was heated for 24 h. The reaction mixture was cooled and the insoluble material was filtered off and washed with cold toluene. The filtrate was concentrated under vacuum and the residue purified by column chromatography (silica, ethyl acetate/hexane 1:4). The product was collected and recrystallised from hexane to give **13** (29 mg, 25%). ^{1}H NMR ($CDCl_3$): δ 0.90 (t, J=6.8 Hz, 3H), 1.25–1.43 (m, 6H), 1.70 (quin, J=7.0 Hz, 2H), 2.80 (t, J=8.0 Hz, 2H), 4.00 (s, 3H), 7.17 (dd,

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J=9.2 Hz, 2.4 Hz, 1H), 7.22 (s, 1H), 7.32 (d, J=8.0 Hz, 2H), 7.69 (d, J=8.0 Hz, 2H), 7.75 (dd, J=8.8 Hz, 2.4 Hz, 1H), 7.91 (d, J=9.2 Hz, 1H), 8.01 (d, J=8.8 Hz, 1H), 8.16 (s, 1H), 8.29 (s, 1H), 8.39 (s, 1H). λ_{max} 401 (log ε=4.03) nm, 380 (log ε=4.10) nm, 361 (log ε=4.11) nm, 342 (log ε=4.08) nm, 323 (log ε=4.02) nm.

*2,6-Bis(hexylthio)anthracene (**14**)*

A mixture ditriflate **8** (0.2 g, 0.48 mmol), i-Pr_2NEt (0.169 ml, 0.13 g, 0.947 mmol), and dry toluene (3 ml) was evacuated and filled with nitrogen (three cycles). Catalyst $Pd_2(dba)_3$ (11.1 mg, 0.0012 mmol), Xantphos (14.0 mg, 0.024 mmol) and hexylmercaptan (0.137 ml, 0.115 g, 0.974 mmol) were added and the mixture was degassed twice more. The mixture was heated to reflux overnight and TLC confirmed completion of the reaction. The reaction was cooled, filtered and concentrated. The crude product was purified by column chromatography (silica gel, DCM/hexane (1:4)) to afford the desired product as a yellow solid (0.17 g, 85%). ^{1}H NMR ($CDCl_3$): δ 0.90 (t, J=7.0 Hz, 6H), 1.28–1.35 (m, 8H), 1.45–1.55 (m, 4H), 1.75 (quin, J=6.8 Hz, 4H), 3.09 (t, J=8.0 Hz, 4H), 7.35 (d, J=8.0 Hz, 2H), 7.80 (s, 2H), 7.90 (d, J=8.0 Hz, 2H), 8.21 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 14.0, 22.6, 28.7, 29.1, 31.5, 33.2, 125.1, 125.4, 127.3, 128.6, 130.7, 131.9, 134.5. EIHRMS: m/z 410.2100 (expected 410.2096); λ_{max} 410 (log ε=1.93) nm, 394 (log ε=1.99) nm, 365 (log ε=2.00) nm, 346 (log ε=2.06) nm, 330 (log ε=1.91) nm.

*2,6-Dihexynylanthracene (**15**)*

Diisopropylamine (0.20 ml, 0.15 g, 1.46 mmol) was added to a stirred solution of ditriflate **8** (0.2 g, 0.49 mmol) and 1-hexyne (0.04 g, 0.97 mmol), CuI (9.2 mg, 0.05 mmol) and $PdCl_2(PPh_3)_2$ (18.9 mg, 0.027 mmol) in dry THF (30 ml) under an argon atmosphere. The mixture was refluxed overnight, cooled and then diluted with diethyl ether (20 ml). The resulting solution was washed with saturated aqueous NH_4Cl solution and dried over $MgSO_4$. The solvent was removed and the crude product (which contained significant quantities of singly coupled product) was purified by column chromatography (silica gel, DCM/hexane (1:4)) to give **15** as a yellow solid (43 mg, 26%). ^{1}H NMR ($CDCl_3$): δ 0.99 (t, J=8.0 Hz, 6H), 1.51–1.65 (m, 8H), 2.50 (t, J=8.0 Hz, 4H), 7.40 (d, J=8.2 Hz, 2H), 7.90 (d, J=8.2 Hz, 2H), 8.00 (s, 2H), 8.25 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 13.7, 19.4, 22.1, 30.9, 81.3, 91.9, 121.4, 126.0, 128.3, 128.6, 131.1, 131.5, 131.7. EIHRMS: m/z 338.2034 (expected 338.2029); λ_{max} 399 (log ε=4.38) nm, 377 (log ε=4.46) nm, 357 (log ε=4.28) nm, 340 (log ε=3.98) nm.

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