A Practical Synthesis of 1,4,5,8-Tetramethoxyanthracene from Inexpensive and Readily Available 1,8-Dihydroxyanthraquinone

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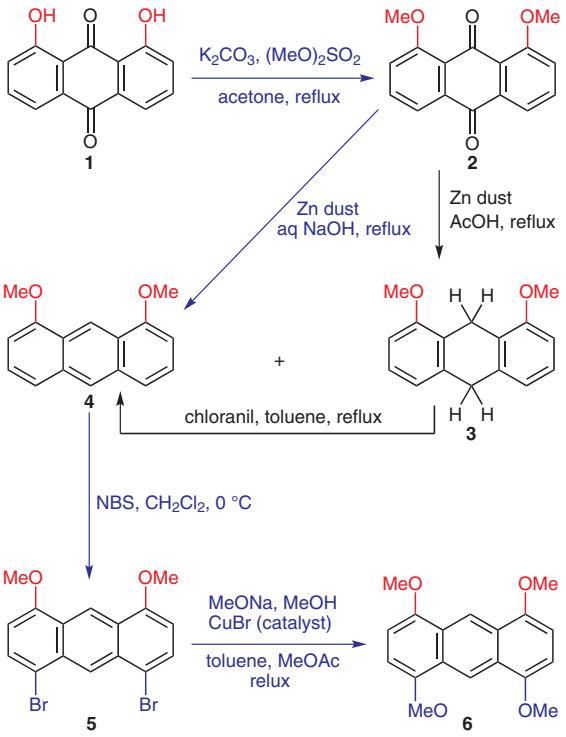
Abstract: The preparation of gram quantities of 1,4,5,8-tetramethoxyanthracene from commercially available and inexpensive 1,8-dihydroxyanthraquinone is described. The key steps in the synthesis involve bromination of 1,8-dimethoxyanthracene to form 1,8-dibromo-4,5-dimethoxyanthracene followed by Cu(I) catalyzed replacement of bromo substituents with methoxy groups. The contrasting reports concerning the preparation of 1,8-dimethoxyanthracene from 1,8-dimethoxyanthraquinone using zinc dust in refluxing acetic acid are also discussed.

Key words: anthraquinones, polycyclic aromatic hydrocarbons, copper(I) bromide, bromination, zinc

Our continued interest in the design and synthesis of polycyclic aromatic hydrocarbons (such as substituted benzenes, naphthalenes, anthracenes, pyrenes, poly *p*-phenylenes, polyfluorenes, and hexa-*peri*-hexabenzo-coronenes),[1] which form stable cation radicals (or hole carriers) prompted us to examine the redox characteristics of the well-know 1,4,5,8-tetramethoxyanthracene (**6**).[2] Unfortunately, the existing syntheses of **6** proved to be rather tedious and difficult, despite the fact that it has been extensively utilized for the preparation of novel belt-like iptycenes,[3] iptycene quinones,[4] triptycenes,[5] and liquid crystalline materials.[6]

None of the existing synthetic strategies for the preparation of **6** are amenable to access large quantities of **6** because they involve expensive starting materials and reagents and suffer from low yields. For example, the first synthesis of **6** was carried out using diaminoanthrarufin in six steps in rather poor yield.[7] The tedious nature and irreproducibility of this route[7] led Miller and co-workers[8] to devise an alternative strategy that involved a cycloaddition reaction of 1,4-dimethoxybenzocyclobutanol with benzoquinone. Unfortunately, the Miller synthesis[8] is accomplished in nine steps and a number of these steps require chromatographic separations and are rather low yielding. A single-step synthesis of **6** is known;[9] however, this synthesis uses a strong base, generated from 2,2,6,6-tetramethylpiperdine and methyllithum and requires careful chromatography to produce a relatively low yield (15–25%) of **6**.

Herein, we report a facile preparation of 1,4,5,8-tetramethoxyanthracene (**6**) on a gram scale from inexpensive and commercially available 1,8-dihydroxyanthraquinone (**1**) and inexpensive reagents (e.g., zinc dust, NBS, and CuBr) in four high-yielding steps without the need for chromatographic separations (Scheme 1).



Scheme 1 Synthetic route for the preparation of multi-gram quantities of **6**

Thus, methylation of dihydroxyanthraquinone **1** was performed in refluxing acetone using anhydrous potassium carbonate as a base and dimethyl sulfate as the methylating reagent for 24 hours. The isolation of **2** in a large-scale synthesis (50–100 mmol) was significantly improved by avoiding an aqueous workup (see the experimental section).

The next step in our synthesis required reduction of quinone **2** to anthracene **4**. A search of the literature revealed the existence of contrasting reports[10,11] for the direct transformation of **2** into **4**. For example, Müller and co-workers[10] reported that reduction of **2** with a large excess of zinc dust in refluxing acetic acid produced dihydroanthracene **3**. However, a recent report by Chen and co-workers[11] claimed that reduction of **2**, under the same conditions reported by Müller, did not produce **3** but, instead,

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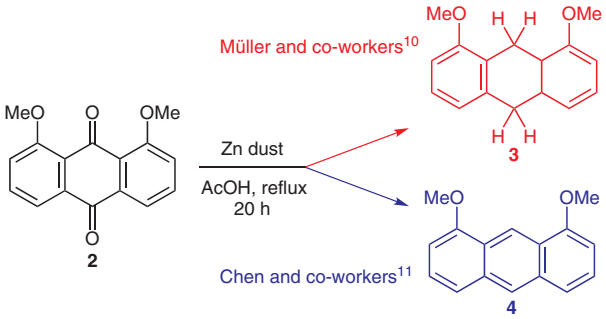


Scheme 2 Contrasting reports concerning the preparation of **4**

generated the corresponding dimethoxyanthracene **4** (Scheme 2).

In order to resolve these conflicting reports, we carefully examined the reduction of **2** with zinc dust in acetic acid. For example, a mixture of **2** (10 mmol), zinc dust (15 equivalent, 150 mmol) and acetic acid (50 mL) was heated at reflux under an argon atmosphere. Subsequently, 2-mL aliquots of the above reaction mixture were removed every 10 min and quenched with water. The aqueous layer was extracted with dichloromethane and the organic layers were dried over anhydrous magnesium sulphate and evaporated in vacuo. ^{1}H NMR analysis of these aliquots, collected during a course of approximately three hours, showed that they contained a mixture of starting anthraquinone **2**, dihydroanthracene **3**, and only small amounts of anthracene **4**. A plot of the formation **3** and **4** and the disappearance of starting anthraquinone **2** with time is shown in Figure 1. It is important to note that when the reduction of **2** with zinc dust and acetic acid was repeated under an air atmosphere, it produced similar ratios of **2**, **3**, and **4** throughout the course of the reaction to those observed from the reaction performed under an argon atmosphere (Figure 1).

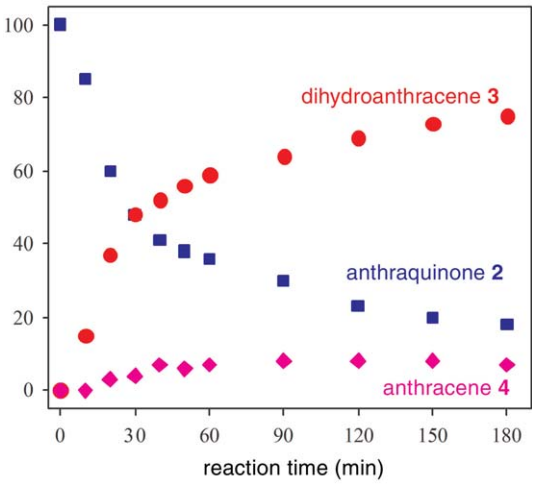


Figure 1 A plot of consumption of anthraquinone **2** (blue squares) and concomitant formation of dihydroanthracene **3** (red circles) and anthracene **4** (pink diamonds) in the presence of zinc dust in refluxing acetic acid during three hours

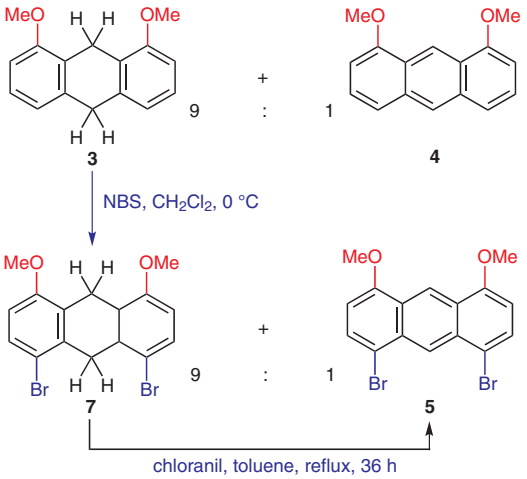
Figure 1 clearly demonstrates that anthracene **4** is a relatively minor product (<8%) while the major product (>92%) is dihydroanthracene **3** under these reaction conditions. It is also important to note that anthracene **4** does not undergo reduction to dihydroanthracene **3** under these reaction conditions. For example, when a purified sample of anthracene **4** (1 mmol) and zinc dust (15 mmol) in acetic acid (10 mL) was heated at reflux for 24 hours, no change was observed, and **4** was recovered quantitatively after aqueous workup. Moreover, a timely reduction of **2** to a mixture of **3** and **4** (ca. 9:1), in nearly quantitative yield, could be accomplished in approximately eight hours in refluxing acetic acid in the presence of approximately 15 equivalents of zinc dust (see the experimental section).

A mixture of **3** and **4**, obtained above, could be cleanly converted into the corresponding anthracene **4** by reaction with chloranil in refluxing toluene during the course of two to three hours.[12] It is also noteworthy that anthracene **4** can be prepared directly from **2** by reaction with zinc dust (6 equiv) in 10% aqueous NaOH solution at reflux for 24 hours in quantitative yield.[13]

Generally, the electrophilic aromatic substitution reactions of anthracene and various anthracene derivatives occur at the highly reactive 9,10-positions. We, however, conjectured that electron-donating methoxy groups at the 1,8-positions may activate sufficiently the 4,5-positions in **4** to carry out a selective bromination at the desired sites using a mild brominating agent. Indeed, bromination of **3** with two equivalents of NBS in dichloromethane at ~0 °C afforded the desired dibromoanthracene **5** in excellent yield. Pure dibromoanthracene **5** was easily obtained by simple crystallization from a mixture of dichloromethane and methanol.

Interestingly, **5** could also be prepared from a 9:1 mixture of dihydroanthracene **3** and anthracene **4**, obtained above. For example, bromination of a 9:1 mixture of **3** and **4** using *N*-bromosuccinimide (NBS) in dichloromethane afforded the crude dihydrodibromo derivative **7**, which was subjected, without further purification, to a dehydrogenation reaction with chloranil in refluxing toluene for 18 hours. The resulting anthracene **5** was purified by crystallization from a mixture of dichloromethane and methanol to afford pure **5** in a 79% yield (Scheme 3).

The availability of large quantities of dibromodimethoxyanthracene **5** through two different routes (Scheme 1 and Scheme 3), allowed us to develop a simple procedure for the conversion of its bromo substituents into methoxy groups. After some experimentation,[14] it was found that heating a mixture of **5** to reflux in toluene containing a large excess of sodium methoxide, a catalytic amount of Cu(I)Br, and methyl acetate (5% with respect to toluene) for 24 hours afforded clean tetramethoxyanthracene **6** in excellent yield. The resulting crude tetramethoxyanthracene **6** was sufficiently pure; however, if needed, an analytical sample of **6** could be obtained by simple recrystallization from a mixture of chloroform and toluene. The



Scheme 3 Alternative synthesis of dibromodimethoxyantharene **5**

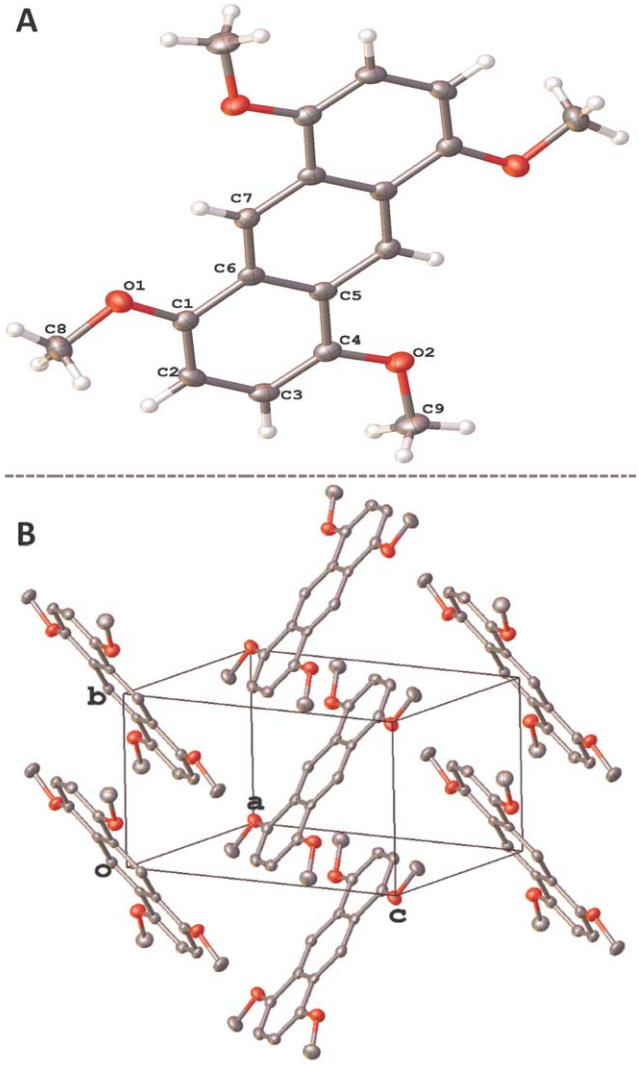


Figure 2 (A) An ORTEP diagram of tetramethoxyanthracene **6** with the thermal ellipsoid at 50% probability; (B) A packing diagram of **6** in its crystals

structure of **6** was established by $^{1}H/^{13}C$ NMR spectroscopy, mass spectrometry, and further confirmed by X-ray crystallography (Figure 2). Anthracene **6** crystallizes in a centrosymmetric space group and makes stacks along the y-axis where parallel terminal rings of the neighboring molecules overlap with an interplanar separation of 3.46 Å. These stacks of **6** are arranged in a herringbone fashion in its crystal with numerous edge-to-face contacts between the molecules from the different stacks. The packing of **6** in crystals is governed by both π,π-stacking (i.e., within each stack of **6**) and by CH···O interactions between the adjacent stacks.[15]

In summary, we have demonstrated that commercially available 1,8-dihydroxyanthraquinone (**1**) can be successfully utilized for an efficient four-step synthesis of 1,4,5,8-tetramethoxyanthracene (**6**) in excellent overall yield. The molecular structure of **6** was confirmed by X-ray crystallography. The ready availability of **6** will facilitate an evaluation of its redox properties and help in explorations of its use in photovoltaic applications.

Melting points are uncorrected. IR spectra were recorded using KBr disks with a Nicolet 560 Magna infrared spectrometer. NMR spectra were obtained with a Varian NMR spectrometer (300 MHz) as $CDCl_3$ solutions using TMS as an internal standard reference. GC-MS spectra were obtained with a Fisons 8000 Trio instrument at an ionization potential of 70 eV. TLC experiments were carried out on pre-coated silica gel plates (hexanes–EtOAc, 4:1). Solvents and reagents such as dimethyl sulfate, NBS, tetrachloro-*p*-benzoquinone (chloranil), zinc dust, and sodium metal were purchased from commercial sources.

1,8-Dimethoxy-9,10-anthraquinone (2)

A suspension of 1,8-dihydroxy-9,10-anthraquinone (15.5 g, 65 mmol) and K_2CO_3 (22.0 g, 162 mmol) in anhydrous acetone (400 mL) under an argon atmosphere was gently heated at reflux. A solution of dimethyl sulfate (20.5 g, 162 mmol) in acetone (~50 mL) was added dropwise over 30 min with the aid of a dropping funnel and the resulting mixture was heated at reflux for an additional 24 h. After cooling to r.t., the reaction mixture was filtered and the dark-colored K_2CO_3 residue was washed with CH_2Cl_2 (3 × 150 mL). The combined organic solvent was then passed through a short pad of silica gel and the pad was washed with CH_2Cl_2 (3 × 80 mL). The collected organic filtrate was then evaporated under reduced pressure. Note: Aqueous workup should be avoided because this complicates the isolation of **2** due to formation of an emulsion.

Yield: 15.6 g (90%); yellow solid; mp 222–224 °C (Lit.[11] 223–224 °C).

IR (KBr): 1664, 1587, 1434, 1318, 1239, 1061, 977, 743 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 4.01 (s, 6 H), 7.30 (dd, *J* = 8.4, 1.0 Hz, 2 H), 7.61–7.66 (t, *J* = 8.0 Hz, 2 H), 7.83 (dd, *J* = 7.7, 1.0 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 56.60, 118.12, 118.95, 124.05, 133.98, 134.79, 159.49, 182.98, 184.09.

MS (70 eV): *m*/*z* = 268 [M^+], 253 [$M^+ - CH_3$], 236, 225, 209, 180, 164, 152, 139, 76.

1,8-Dimethoxyanthracene (4)

To a suspension of **2** (8.0 g, 30 mmol) in 10% aq NaOH (150 mL) was added zinc powder (11.8 g, 180 mmol). The mixture was heated for 24 h with vigorous stirring, then vacuum filtered. The filtered cake was washed with H_2O (3 × 100 mL) and dried under vacuum.

The resulting pale-yellow solid was dissolved in CH_2Cl_2 (100 mL) and the solution was passed through a short pad of silica gel. The filtrate was evaporated in vacuo to afford **4**.

Yield: 7.0 g (88%); pale-yellow solid; mp 198–200 °C (Lit.[11] 198–200 °C).

IR (KBr): 1625, 1567, 1464, 1440, 1321, 1265, 1126, 1058, 1070, 789, 737 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 4.08 (s, 6 H), 6.73 (d, *J* = 7.3 Hz, 2 H), 7.37 (t, *J* = 8.0 Hz, 2 H), 7.56 (d, *J* = 8.6 Hz, 2 H), 8.30 (s, 1 H), 9.23 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 55.68, 101.72, 115.86, 120.37, 124.61, 125.32, 125.82, 133.06, 156.09.

MS (70 eV): *m*/*z* = 238 [M^+], 223 [$M^+ - CH_3$], 209 [$M^+ - CH_3 - CH_2$], 195, 180, 163, 152, 119.

1,8-Dibromo-4,5-dimethoxyanthracene (5)

To a pre-chilled solution of **4** (4.0 g, 16.8 mmol) in CH_2Cl_2 (200 mL) in an ice-salt bath (~0 °C) was added NBS (5.98 g, 33.6 mmol) in small portions over a 15 min period. After the addition, the temperature was slowly allowed to rise to r.t. and the mixture was stirred for an additional 3 h. The resulting reaction mixture was diluted with CH_2Cl_2 (150 mL) and washed with 5% HCl (50 mL) followed by H_2O (3 × 150 mL). The organic layer was separated, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure to afford **5**.

Yield: 6.1 g (92%); pale-green solid; mp 272–274 °C.

IR (KBr): 1613, 1461, 1386, 1318, 1263, 1221, 1148, 1091, 1073, 806, 610, 600 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 4.06 (s, 6 H), 6.62 (d, *J* = 8.1 Hz, 2 H), 7.72 (d, *J* = 8.1 Hz, 2 H), 9.0 (s, 1 H), 9.25 (s, 1 H).

^{13}C NMR ($CDCl_3$): δ = 55.97, 102.97, 113.62, 117.77, 125.53, 125.89, 130.07, 131.54, 155.82.

MS (70 eV): *m*/*z* = 396 [M^+], 381 [$M^+ - CH_3$], 353, 338, 310, 198, 150, 75.

1,4,5,8-Tetramethoxyanthracene (6)

Freshly cut sodium metal (11.0 g, 500 mmol) was added portionwise to a 500-mL Schlenk flask containing anhydrous MeOH (100 mL) under an argon atmosphere at 22 °C and the resulting mixture was heated at reflux until complete dissolution of the sodium metal was observed. To this solution was added 4,5-dibromo-1,8-dimethoxyanthracene (2.0 g, 5.0 mmol), toluene (100 mL), MeOAc (5.0 mL), and copper(I) bromide (0.70 g, 5.0 mmol), successively. The reaction mixture was then heated at reflux with rapid stirring for 24 h, after which time, solvent was evaporated under reduced pressure and the residue was dissolved in CH_2Cl_2 (ca. 300 mL) and washed with 10% HCl (100 mL) followed by H_2O (2 × 100 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure to afford a yellow-green solid, which was triturated with cold CH_2Cl_2 to afford 1,4,5,8-tetramethoxyanthracene as a yellow solid. An analytically pure sample could be obtained by recrystallization using a 1:1 mixture of chloroform/toluene.

Note that in above reaction a catalytic amount of CuBr (1 mmol, 20 mol%) can be employed, however, the reaction required ~72 h to reach completion.

Yield: 1.40 g (93%); yellow solid; mp 296–298 °C (Lit.[9] 298–300 °C).

IR (KBr): 1631, 1471, 1327, 1258, 1129, 1083, 806 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 4.03 (s, 12 H), 6.63 (s, 4 H), 9.10 (s, 2 H).

^{13}C NMR ($CDCl_3$): δ = 55.83, 101.47, 115.37, 125.39, 150.00.

MS (70 eV): *m*/*z* = 298 [M^+], 283 [$M^+ - CH_3$], 268 [$M^+ - 2CH_3$], 253 [$M^+ - 3CH_3$], 237, 225, 149, 134.

Synthesis of 1,8-Dimethoxy-9,10-dihydroanthracene (3) Contaminated with 4

To a suspension of **2** (12.0 g, 45 mmol) in glacial acetic acid (200 mL) was added zinc dust (44.0 g, 675 mmol) in one portion. The reaction mixture was heated at reflux for 3–4 h. When the reaction was complete, the mixture was cooled to r.t. and vacuum filtered to remove the zinc dust. The solid cake was washed with CH_2Cl_2 (5 × 80 mL) and the collected filtrate was washed with H_2O (200 mL), $NaHCO_3$ (2 × 100 mL) and again with H_2O (100 mL). The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure to afford a mixture containing 1,8-dimethoxy-9,10-dihydroanthracene (**3**) and 1,8-dimethoxyanthracene (**4**) in ca. 9:1 ratio. Note: The dihydroanthracene **3**, contaminated with ~10% anthracene **4**, was used for the next step without further separation or purification.

Yield: 10.0 g (94%; **3** + **4**); yellow solid.

^1H NMR ($CDCl_3$): δ = 3.90 (s, 6 H), 3.94 (t, *J* = 3.0 Hz, 2 H), 4.03 (t, *J* = 3.0 Hz, 2 H), 6.77 (d, *J* = 8.30 Hz, 2 H), 6.90 (d, *J* = 7.5 Hz, 2 H), 7.19 (t, *J* = 8.1 Hz, 2 H); remaining small signals were assigned to **3**.

^{13}C NMR ($CDCl_3$): δ = 22.14, 35.27, 55.59, 107.63, 120.07, 124.29, 126.67, 137.05, 157.07; remaining small signals were assigned to **3**.

MS (70 eV): *m*/*z* = 240 [M^+], 225 [$M^+ - CH_3$], 209, 194, 178, 165, 152, 139, 112.

4,5-Dibromo-1,8-dimethoxy-9,10-dihydroanthracene (7)

To a solution containing a 9:1 mixture of 1,8-dimethoxy-9,10-dihydroanthracene and 1,8-dimethoxy-anthracene (9.4 g, 39.0 mmol) in anhydrous CH_2Cl_2 (200 mL) was added NBS (13.90 g, 78.0 mmol) in small portions over 15 min at 0 °C under an argon atmosphere. After the addition, the temperature was slowly allowed to rise to r.t. and the mixture was stirred for an additional 3 h. The reaction mixture was diluted with CH_2Cl_2 (200 mL) and washed with 5% HCl (100 mL) followed by H_2O (3 × 150 mL). The organic layer was separated, dried over $MgSO_4$ and evaporated under reduced pressure to afford a mixture containing 4,5-dibromo-1,8-dimethoxy-9,10-dihydroanthracene and 4,5-dibromo-1,8-dimethoxyanthracene in a 9:1 ratio. Note: The dihydroanthracene **7**, contaminated with ~10% anthracene **5**, was used for the next step without further separation or purification.

Yield: 14.0 g (90%; **7** + **5**); greenish-yellow solid.

^1H NMR ($CDCl_3$): δ = 3.86 (s, 6 H), 3.92 (t, *J* = 3.04 Hz, 2 H), 4.05 (t, *J* = 3.04 Hz, 2 H), 6.65 (d, *J* = 8.7 Hz, 2 H), 7.43 (d, *J* = 8.7 Hz, 2 H); remaining small signals were assigned to **5**.

^{13}C NMR ($CDCl_3$): δ = 24.01, 26.63, 55.77, 109.30, 115.11, 125.23, 130.34, 134.28, 156.21; remaining small signals were assigned to **5**.

MS (70 eV): *m*/*z* = 398 [M^+], 383 [$M^+ - CH_3$], 367, 302, 286, 238, 223, 195, 152, 119.

Alternate Synthesis of 4,5-Dibromo-1,8-dimethoxyanthracene (5)

A mixture of 4,5-dibromo-1,8-dimethoxy-9,10-dihydroanthracene and 4,5-dibromo-1,8-dimethoxyanthracene (9.0 g, 22.6 mmol) and *p*-chloranil (5.9 g, 24.0 mmol) in toluene (200 mL) was heated at reflux for 18 h under an argon atmosphere. The solvent was evaporated to obtain a green residue, which was diluted with CH_2Cl_2 (ca. 400 mL) and washed with 10% NaOH (3 × 100 mL) followed by H_2O (2 × 100 mL). The separated organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure to afford a green solid that was further purified by tituration with CH_2Cl_2 to

give **5** (7.1 g, 79%), the analytical data of which were identical to those of the sample obtained above.

Alternate Synthesis of 1,8-Dimethoxyanthracene (4)

A 9:1 mixture of dihydroanthracene **3** and anthracene **4** (4.0 g, 16.6 mmol) and chloranil (4.1 g, 16.6 mmol) in toluene (100 mL) was heated at reflux for 2 h under an argon atmosphere. The solvent was evaporated under reduced pressure to afford a yellow-green residue, which was diluted with CH_2Cl_2 (200 mL) and washed with 10% aq NaOH (3 × 100 mL) followed by H_2O (2 × 100 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed under reduced pressure to afford pure **4** as a light-yellow solid (3.7 g, 93%). The sample of anthracene **4** obtained herein was identical to that obtained above by reduction of **2** by zinc dust in aqueous NaOH.

X-ray Crystal Structure Analysis of 6

All diffraction intensity data were collected with a Bruker Smart Apex CCD diffractometer operating at 173(2) K using Cu-radiation (1.54178 Å). All structures were solved using direct methods, completed by difference Fourier syntheses, and refined by full matrix least-squares procedures. Crystallographic data, details for data collections, and refinement methods for each structure are summarized below.

Yellow crystals of **6** were grown from a mixture of chloroform and toluene. A shiny crystal with dimensions ($0.28 \times 0.035 \times 0.03$ mm^3) was selected for data collection. Empirical formula: $C_{18}H_{18}O_4$; Formula weight: 298.32; Crystal system: monoclinic; Space group: $P2_1/n$; $Z = 2$; Unit cell dimensions: a = 10.9438(13) Å, b = 5.9802(5) Å, c = 11.6812(14) Å; $\alpha = 90°$, $\beta = 110.272(14)°$, $\gamma = 90°$; V = 717.14(13) Å^3; D (calculated) = 1.382 g cm^{-3}; m = 0.097 mm^{-1}. The total number of reflections measured was 4234, of which 1739 reflections were symmetrically nonequivalent. Final residuals were $R_1 = 0.0470$ and $wR_2 = 0.1034$ for 1452 reflections with $I > 2\sigma(I_0)$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-865141. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E-mail: deposit@ccdc.-cam.ac.uk; Fax: +44(1223)336033 or via www.ccdc.-cam.ac.uk/conts/retrieving.html].

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