

Synthesis and Electrochemical Properties of 1,4-Dithiafulvenyl-Substituted Bianthrone Molecules with Potential Application as Molecular Switches

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Four new 1,4-dithiafulvenyl substituted bianthrone **3** have been prepared with the aim of making a light-activated "molecular switch". Acylation of 10,10'-dimethoxy-9,9'-bianthracene (**2**) could be controlled to give 3-acyl- or 3,3'-diacyl-10,10'-dimethoxy-9,9'-bianthracenes **4** and **5**, respectively. Demethylation and oxidation yielded 2-acylbianthrone **7**. Horner-Emmons-type coupling of **4** and **5** with substituted 1,3-dithiole-2-phosphonate esters **8** and **11** gave 1,4-dithiafulvenyl-substituted bianthrone **9** and **12**. Demethylation and oxidation finally gave the 1,4-dithiafulvenyl-substituted bianthrone **3**. The electrochemical properties and absorption spectra of these new molecules (**3**) have been investigated and compared to bianthrone.

Introduction

In recent years considerable attention has been directed toward molecular structures which may serve as constituents in molecular electronic devices.¹ Molecules undergoing reversible conformational changes between two states stable within an appropriate time scale may serve as possible switch units in such devices.²⁻⁹ A candidate for such a molecular system is the bianthrone molecule grafted with electron-donor molecules.^{10,11} The rationale behind this strategy is to try to couple a charge-transfer process (CT) to a large conformational change of the molecule in order to delay the charge recombination process.

The bianthrone molecule (**1**) exists in two conformationally different forms, denoted the **1_A** and the **1_B** form (see Figure 1). In the **1_A** form¹² the molecule has a quasi planar conformation around the central double bond while the anthracene parts are bent into a puckered conformation due to an unfavorable steric interaction between the hydrogen atoms in the 4,4' and 5,5' positions. In the **1_B** form¹³ the steric strain is released by rotation of the central

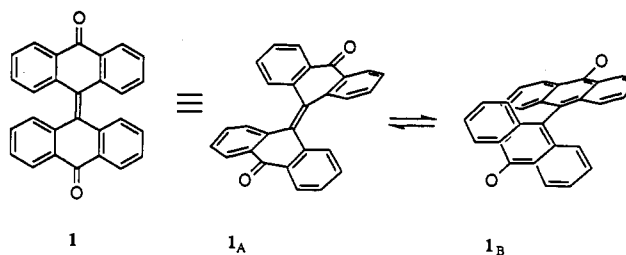


Figure 1. Conformations of the A and B forms of bianthrone.

double bond at the expense of electronic delocalization energy. In unsubstituted bianthrone the A to B transformation can be triggered by photoexcitation,¹⁴⁻¹⁷ heating,^{13,17-22} pressure,^{18,19,23} and electrochemical redox cycles.²⁴⁻²⁹

The present approach for obtaining a switch action was to combine bianthrone (an electron acceptor) with a suitable electron donor moiety (D) to form molecules denoted D-1 (Figure 2). Upon charge-transfer photoexcitation we expect to form $[D^+ \cdot 1_A^-]^*$. Subsequently, the conformational change followed by relaxation may yield $D^+ \cdot 1_B^-$ which is expected to be a stable (or metastable) charge-separated state.

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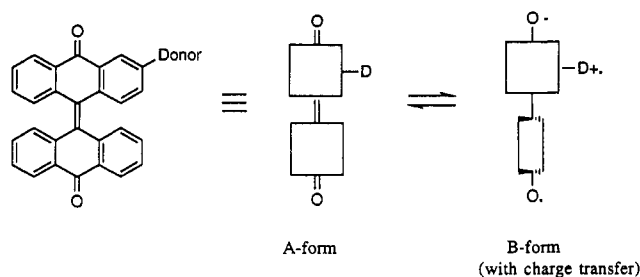


Figure 2. Schematic representation of the switching action of donor-substituted bianthrone molecules.

The present paper describes the synthesis of donor-substituted bianthrone (D-1) together with data from optical and electrochemical measurements of selected structures. The photochemical results as well as a detailed theoretical treatment of the phenomena occurring will be published in forthcoming papers.

Ultimately, the intention is to incorporate "molecular switches" in materials used in simple devices. To reach this goal it is essential to be able to control the orientation of the molecules in the solid or semisolid phase. One possibility is to use the Langmuir-Blodgett technique, by which polar molecules substituted with long alkyl chains can be transferred from an air-water interface to a substrate as an ordered monomolecular layer. With this in mind derivatives of D-1 molecules (3b and 3c) substituted with long alkyl chains have been prepared.

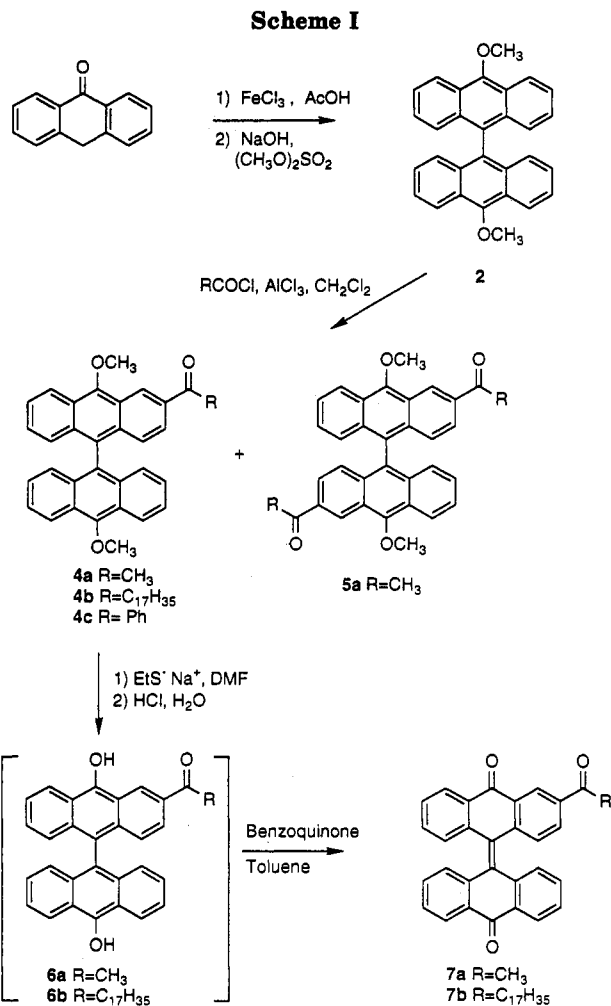
Results and Discussion

Monosubstituted Bianthrone. The synthesis of bianthrone coupled to a donor can be realized either by so-called cross-coupling of a substituted anthrone with an unsubstituted one or by direct substitution of 1.

The cross-coupling route seemed to be the more attractive because the synthesis of bianthrone-2-carboxylic acid using this approach has been reported in the literature.³⁰ Utilization of the carboxylic acid function as a linker to the donor moiety would provide a route to the desired compound. However, separation of the reaction mixture, which contains two symmetric and one unsymmetrical bianthrone structure (the target), proved highly impractical and irreproducible in our hands. Since the desired product, bianthrone-2-carboxylic acid, was only an intermediate in the synthetic strategy, this route was abandoned.

The second route was not immediately attractive because the quinoid character of the bianthrone makes the aromatic rings very unreactive toward electrophilic substitution. However, a protected precursor 10,10'-dimethoxy-9,9'-bianthracene (2), obtained by oxidative coupling of anthrone to 10,10'-bi-9(10*H*)-anthracenone³¹ followed by methylation with dimethyl sulfate,³² has been prepared earlier (Scheme I).

Friedel-Crafts acylation of 2 with acetyl chloride, stearoyl chloride, or benzoyl chloride could be controlled to give mono- or disubstituted products. Using a slight excess of acyl chloride and aluminum chloride gave good yields of mono 3-acyl-substituted products 4. The monoacylated compounds could be separated from unreacted



starting material and small amounts of disubstituted product 5 by flash chromatography on silica. When 2.5 equiv of acetyl chloride and aluminum chloride were used, an excellent yield of diacetylated product 5 was obtained. A larger excess gave more complex mixtures presumably containing di-, tri-, and tetrasubstituted derivatives.

The keto functions of compounds 4 and 5 were used to introduce the donor groups by a Horner-Emmons reaction as described below. Demethylation of 4a and 4b with sodium ethanethiolate in DMF³³ followed by acidification with aqueous hydrochloric acid precipitated the 3-acyl-10,10'-dihydroxy-9,9'-bianthracenes 6. Oxidation with benzoquinone in hot toluene gave 2-acetylbianthrone (7a) and 2-stearoylbianthrone (7b), respectively (Scheme I).

The position of the acyl substituent was established by ¹H-NMR spectroscopy. The results are listed in the Experimental Section and are summarized for 4a in Figure 3. Among the aromatic signals in the spectrum two groups of signals appear at 9.14 and 8.5 ppm, corresponding to one and three hydrogen atoms, respectively. The signal at 9.14 ppm is a doublet with a coupling constant of 1.3 Hz, and since it has no ortho coupling it can be assigned to a hydrogen atom in one of the peri positions (1, 4, 5, or 8), with the acyl substituent occupying the ortho position. The signals at ≈ 8.5 ppm show broadened doublets with $J = 8.7$ Hz. They can then be assigned to the hydrogen atoms in the equivalent positions of the remaining three unsubstituted benzo groups. Furthermore, a nuclear Overhauser effect is observed between the 9.14 ppm signal and the methoxy group signal (4.4 ppm). This indicates

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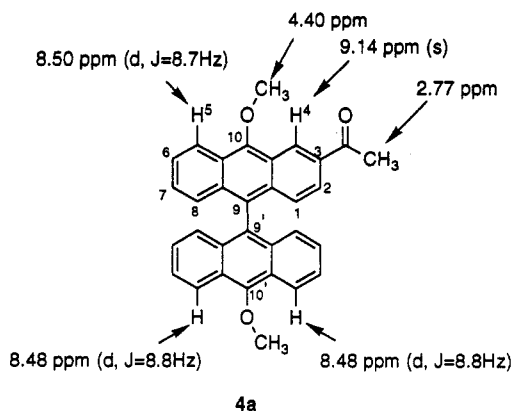


Figure 3. Chemical shift values of 4a.

that the proton giving rise to the 9.14 ppm signal is in the 4-position and that the acyl substituent therefore must occupy the 3-position. The spin-spin coupling patterns of the other aromatic signals substantiated this assignment.

The presence of a second acetyl substituent as in 5a simplifies the spectrum significantly. Only one methoxy and one acetyl group signal appear in the spectrum indicating a symmetrical substitution in each of the two halves of the molecule. Similarly, the pattern in the aromatic region is also simplified compared to 4a, showing that the second acetyl group occupies the 3'-position.

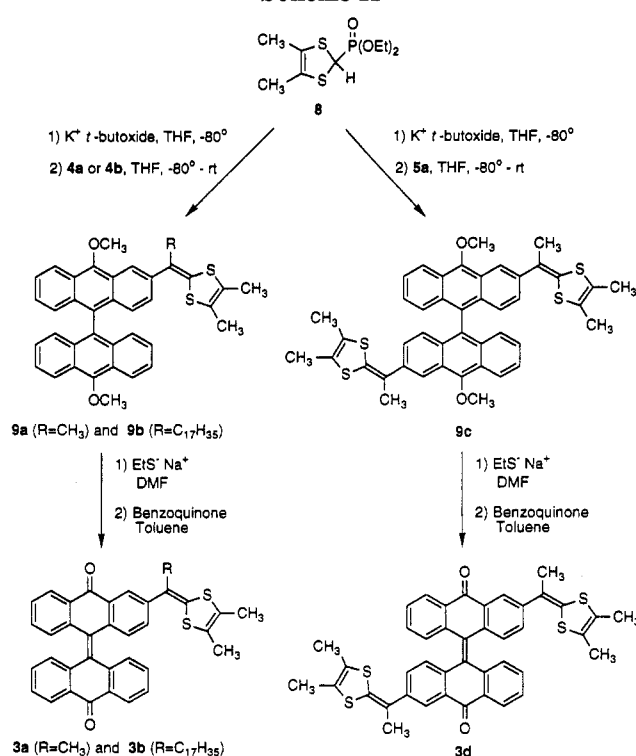
Bianthrone Coupled to 1,4-Dithiafulvenyl Donors.

As described above, the keto function in compounds 4 or 5 was used for introduction of the donor group. Since the following step involves an oxidation, the donor group must be stable enough to survive this treatment. At the same time it must be a strong enough donor to stabilize the charge-transferred state. The 1,4-dithiafulvenyl group was chosen for this purpose. Recently, synthetic procedures leading to 1,3-dithiole-2-phosphonate ester reagents, like 8 (Scheme II), have been developed.³⁴ The phosphonate esters can be coupled to keto functions³⁴ or 2-(dialkylamino)-1,3-dithiolium compounds³⁵ in Horner-Emmons-type reactions and were thus suited for our purpose. The phosphonate ester 8 was deprotonated with potassium *tert*-butoxide and allowed to react with 4a, 4b, or 5a in THF at low temperature. The resulting 3-(1,4-dithiafulven-6-yl)bis-10,10'-dimethoxy-9,9'-bianthracenes (9a, 9b, or 9c) were demethylated and oxidized as described for compound 7 yielding the desired 2-(1,4-dithiafulven-6-yl)bianthrone 3a, 3b, and 3d (Scheme II).

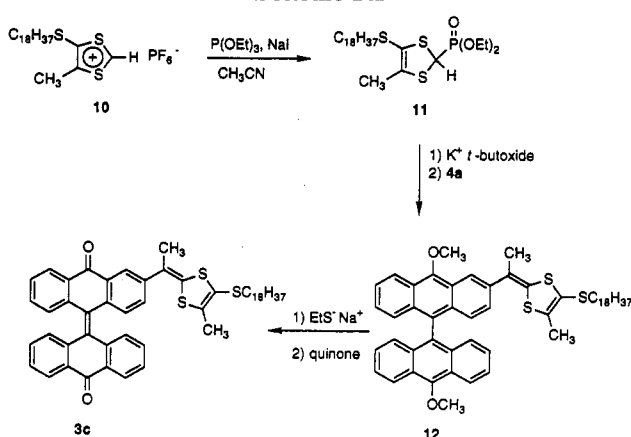
A long alkyl chain, needed for LB-film formation, could also be introduced via the 1,4-dithiafulvenyl donor, by employment of the octadecylthio-substituted 1,3-dithiole-2-phosphonate ester 11 as outlined in Scheme III. Compound 11 was prepared from the 1,3-dithiolium salt 10³⁵ by reaction with triethyl phosphite and sodium iodide as described for 8. Deprotonation of 11 and subsequent reaction with 4a provided 12, which was converted to 3c as described for 3a and 3b (Scheme III).

UV-vis Spectra. The UV-vis spectra of bianthrone (1), the donor 13 (prepared as outlined in Scheme IV) and of the "switch molecules" 3a (1-D) and 3d (D-1-D) are shown together in Figure 4. The spectrum of 3a is similar to that of 1, except for the additional absorption peak at

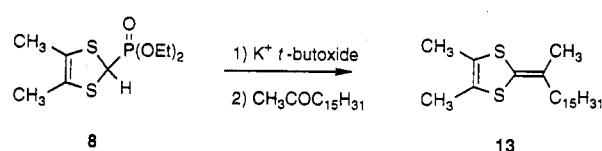
Scheme II



Scheme III



Scheme IV



480 nm. Quantum mechanical calculations³⁶ and solvatochromic investigations³⁶ support that this absorption is indeed due to charge transfer from the "donor" to the "acceptor" part of the molecule. The spectrum of the double donor substituted bianthrone compound (3d) also exhibits this feature (Figure 4).

Electrochemistry. The electrochemical properties of the "switch molecules" 3 and reference compounds (bianthrone (1) and donor 13) were determined by cyclic voltammetry in CH₂Cl₂ solution against a saturated calomel electrode. The investigation gave preliminary

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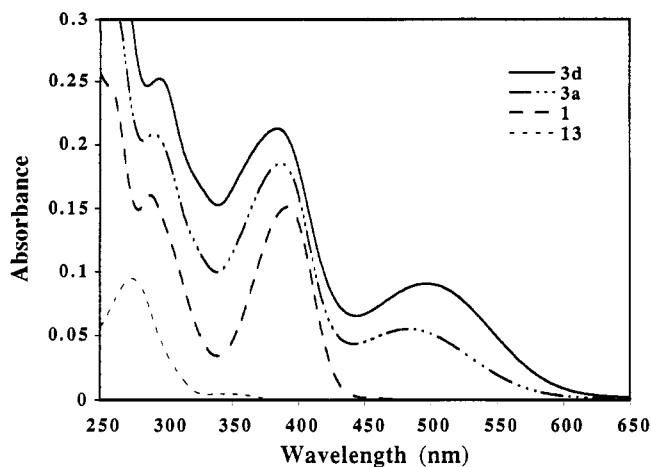


Figure 4. Absorbance in the UV-vis region of CH_2Cl_2 solutions (1.0×10^{-5} M) of 2,3,6-trimethyl-6-hexadecyl-1,4-dithiafulvene (13), 2-(2,3,6-trimethyl-1,4-dithiafulven-6-yl)-bianthrone (3a), 2,2'-bis(2,3,6-trimethyl-1,4-dithiafulven-6-yl)bianthrone (3d), and bianthrone (1). The band at 480 nm is a charge-transfer band.

Table I. Cyclic Voltammetry of the "Switch Compounds" 3a-d Together with Bianthrone (1) and Donor 13 as Reference Compounds vs SCE in CH_2Cl_2 with 0.10 M nBu_4NPF_6 . Scan Speed (800 mV/s)

compd no.	E_1	E_2	E_3	E_4	E_5
3a	0.62	0.44	-0.36	-0.57	-1.47 ^a
3b	0.57	0.38	-0.44	-0.61	-1.37 ^a
3c	0.64	0.48	-0.42	-0.63	-1.39 ^a
3d	0.62	0.33	-0.40	-0.56	-1.37 ^a
1			-0.43	-0.61	-1.38 ^a
13		+0.63 ^a			

^a Irreversible peak potentials.

insight into the "switch processes" which may occur in the molecule, and the results are listed in Table I.

The behavior of bianthrone (1) upon electrochemical reduction and reoxidation is well documented in the literature.²⁴⁻²⁹ In agreement with previously reported experiments, we find that a two-electron irreversible reduction occurs at -1.38 V (vs SCE) to produce the dianion of the B-form, which can be oxidized successively in one-electron steps, at -0.61 and -0.43 V, to the mono anion and neutral state B-form, respectively. The latter reverts to the neutral A-form.

The redox behavior of the "switch molecule" 3a is more complicated as shown by the cyclic voltammograms in Figure 5a and b. In the cyclic voltammogram shown in Figure 5a, 3a is first scanned in the positive direction and a single reversible redox couple is observed with at $\text{O}_1\text{-R}_1$ ($E^{1/2} = +0.62$ V). This corresponds to the oxidation of the 1,4-dithiafulvenyl (donor) part of the molecule to the cation radical. Upon subsequent reduction, an irreversible peak R_2 is observed at $E = -1.27$ V. This can be ascribed to irreversible two-reduction of the bianthrone part to the dianion of 3a in the B-form. As in bianthrone, when the potential is moving toward positive values, this species exhibits two reversible one-electron couples $\text{O}_2\text{-R}_3$ and $\text{O}_4\text{-R}_4$ ($E^{1/2} = -0.57$ and -0.36 V) to the monoanion and neutral B-form of 3a, respectively. If the oxidation is carried further (see Figure 5b) the molecule in the B-form yields an extra reversible couple at $\text{O}_1^{\text{B}}\text{-R}_1^{\text{B}}$ (together with the usual $\text{O}_1\text{-R}_1$ couple). The new redox wave occurring at $E^{1/2} = +0.44$ V is interpreted as arising from the donor part of 3a with the bianthrone moiety still present in the B-form. Experiments were performed at different scan rates. It was found that the neutral and charged B-forms

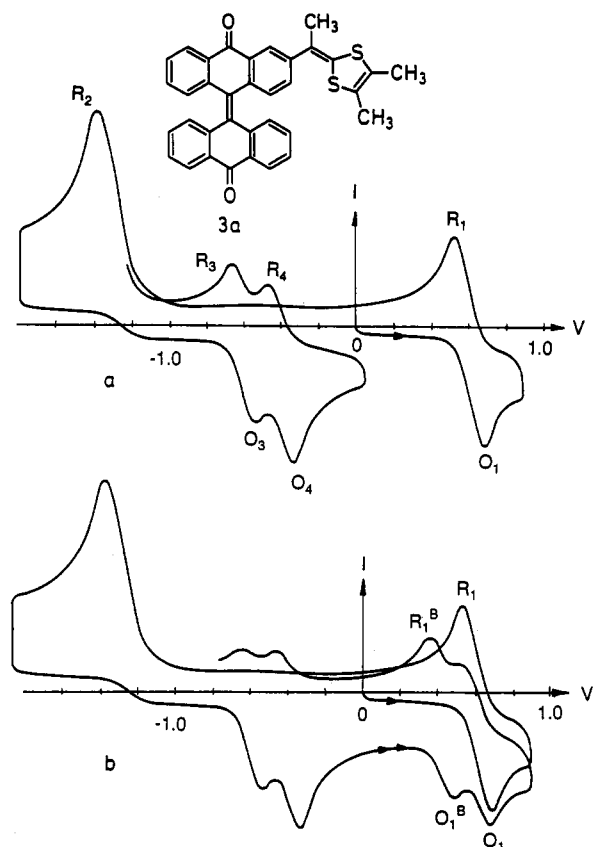
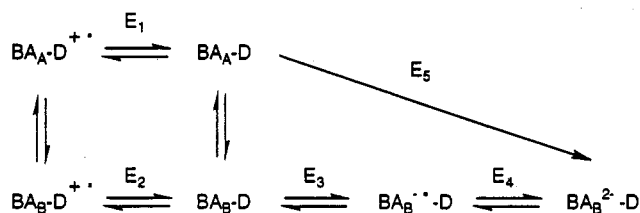


Figure 5. Cyclic voltammograms of 2-(2,3,6-trimethyl-1,4-dithiafulven-6-yl)bianthrone (3a).

revert slowly (seconds) to the A-forms, and the appearance of the voltammograms therefore depends strongly on the scan rate (in this case 800 mV/s).



BA-D: Bianthrone-1,4-Dithiafulvene compounds 3a - 3d.

The double-donor bianthrone compound 3d exhibits similar features. In the positive scan, two redox couples corresponding to $\text{O}_1^{\text{B}}\text{-R}_1^{\text{B}}$ and $\text{O}_1\text{-R}_1$ appear at $E^{1/2} = +0.33$ and $+0.62$ V. The $\text{O}_1^{\text{B}}\text{-R}_1^{\text{B}}$ couple is at first a few percent of the size of the second. On reduction to the dianion and reoxidation the integrated intensity of the couple increases. The results demonstrated that for compound 3d already on dissolution at ambient temperature some B-form is present.

Conclusion

A method for synthesizing various donor-substituted bianthrone derivatives has been developed.

The electrochemical properties of the donor-substituted bianthrone derivatives appears as a combination of the intrinsic properties of the donor and bianthrone, respectively. It is also noted that the redox potential of the donor part of the molecule depends on the conformation of the bianthrone moiety.

The UV-vis absorption spectrum of the new derivatives exhibits a characteristic absorption (around 500 nm) due to weak coupling between the donor moiety and the bianthrone moiety. This is similar to what is found in intermolecular charge-transfer transitions. The results demonstrate that an intramolecular optical charge-transfer process (crucial for the switching process) can be facilitated by grafting a donor moiety to bianthrone.

Experimental Section

Elemental microanalysis were performed on a Perkin-Elmer 240 elemental analyzer. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-250 instrument (250 MHz) with tetramethylsilane as internal standard and a digitalization precision of 0.3 Hz. Melting points were obtained on a Büchi melting point apparatus. Cyclic voltammetry was performed using a standard three-electrode cell configuration, employing a platinum-button working electrode, a platinum count electrode, and a K901 Calomel reference electrode (Radiometer Copenhagen).

3-Acetyl-10,10'-dimethoxy-9,9'-bianthracene (4a). 10,10'-Dimethoxy-9,9'-bianthracene (**2**)^{31,32} (8.20 g, 19.8 mmol) was dissolved in 100 mL of CH_2Cl_2 together with 2.0 mL (2.20 g, 28.0 mmol) of acetyl chloride. Aluminum chloride (2.80 g, 21 mmol) was added in portions, and the reaction mixture was stirred for 1 h at ambient temperature and 1 h at reflux. After being cooled to 10 °C, the mixture was hydrolyzed by addition of 30 g of ice followed by 30 mL of concd hydrochloric acid and stirred vigorously for 10 min. The layers were separated, and the water phase was extracted once with 24 mL of CH_2Cl_2 . The combined organic phases were dried over MgSO_4 , filtered, and evaporated under vacuum to yield 10.6 g of yellow-green oil. TLC on silica gel with CH_2Cl_2 as eluent showed four components: starting material **2** (R_f 0.95); unidentified material (R_f 0.90); monoacylated product **4a** (R_f 0.60); and diacylated product **5a** (R_f 0.15). The oil was dissolved in 25 mL of CH_2Cl_2 and separated by "flash" chromatography on a silica gel column (70-mm \times 100-mm inside diameter) with CH_2Cl_2 as eluent. Evaporation under vacuum of the fraction containing **4a** gave 6.32 g yellow-green oil that could be crystallized from 150 mL of heptane. Yield of **4a**: 4.71 g (52.1%). Mp: 231–3 °C. ^1H -NMR (CDCl_3) δ : 2.77 (s, 3 H), 4.34 (s, 3 H), 4.40 (s, 3 H), 7.05–7.3 (multiplet, 7 H), 7.4–7.6 (multiplet, 3 H), 7.69 (q, 1 H, $J_1 = 1.8$ Hz, $J_2 = 7.4$ Hz), 8.48 (d, 2 H, $J = 8.8$ Hz), 8.50 (d, 1 H, $J = 8.7$ Hz), 9.14 (d, 1 H, $J = 1.3$ Hz) ppm. ^{13}C -NMR (CDCl_3) δ : 26.53, 63.47, 64.19, 122.58, 123.30, 124.34, 124.86, 125.18, 125.77, 126.03, 126.42, 126.81, 127.20, 127.33, 127.79, 129.21, 132.47, 133.25, 133.70, 134.35, 152.95, 154.90, 197.69. Anal. Calcd for $\text{C}_{32}\text{H}_{24}\text{O}_3$: C, 84.19; H, 5.30; Found: C, 84.48; H, 5.77.

Evaporation of the fraction containing **5a** provided an oil that could be crystallized from heptane. Yield: 0.653 g (6.6%). The material was identical to the compound prepared by the following procedure.

3,3'-Diacyl-10,10'-dimethoxy-9,9'-bianthracene (5a). Compound **2** (4.20 g, 10 mmol) was dissolved in 100 mL of CH_2Cl_2 together with 2.35 mL (2.1 mL, 30 mmol) of acetyl chloride. Aluminum chloride (2.8 g, 21 mmol) was added and the deep red reaction mixture heated to reflux for 1 h. A further 0.50 g (4 mmol) of aluminum chloride was added and reflux continued for 40 min to complete the conversion. After cooling, the reaction mixture was poured into 150 mL of ice-water containing 20 mL of concd HCl and stirred vigorously a few minutes. The organic phase was separated, washed with brine, dried over MgSO_4 , filtered, and evaporated to dryness under vacuum. The residue was triturated with 50 mL of boiling ethanol for a few minutes, cooled, and filtered. The yellow crystalline product was washed on the filter with ethanol followed by petroleum ether to provide 4.60 g of the desired compound **5a** (92.2%). Mp: 267–8 °C. ^1H NMR (CHCl_3) δ : 2.77 (s, 6 H), 4.40 (s, 6 H), 7.05–7.73 (multiplet, 10 H), 8.49 (d, 2 H, $J = 8.9$ Hz), 9.12 (d, 2 H, $J = 1.7$ Hz) ppm. Anal. Calcd for $\text{C}_{34}\text{H}_{26}\text{O}_4$: C, 81.91; H, 5.26. Found: C, 81.68; H, 5.41.

3-Stearoyl-10,10'-dimethoxy-9,9'-bianthracene (4b) was prepared from **2** and octadecanoyl chloride as described above for **4a**. The compound was purified by flash chromatography on

silica gel using petroleum ether changing to toluene as eluents. Yield: 1.89 g (27.8%) of yellow crystals. Mp: 75–6 °C. ^1H NMR (CDCl_3) δ : 0.87 (t, 3 H, $J = 6.2$ Hz), 1.25 (unresolved, 30 H), 3.13 (t, 2 H, $J = 7.3$ Hz), 4.33 (s, 3 H), 4.38 (s, 3 H), 7.1–7.6 (m, 11 H), 8.46 (d, 3 H, $J = 8.9$ Hz), 9.12 (d, 1 H, $J = 1.2$ Hz). ^{13}C NMR (CDCl_3) δ : 14.13, 22.70, 24.75, 29.38, 29.57, 29.70, 31.94, 38.61, 63.57, 64.26, 122.62, 122.76, 123.48, 124.41, 124.86, 125.21, 124.73, 126.10, 126.92, 127.16, 127.41, 127.82, 128.07, 129.20, 132.49, 133.32, 133.64, 134.30, 152.99, 154.85, 200.39. Anal. Calcd for $\text{C}_{48}\text{H}_{56}\text{O}_3$: C, 84.66; H, 8.29. Found: C, 84.71; H, 8.43.

3-Benzoyl-10,10'-dimethoxy-9,9'-bianthracene (4c) was prepared and purified as described above for **4a**. Yield: 1.95 g (37.6%) yellow crystals. Mp: 230–1 °C. ^1H NMR (CDCl_3) δ : 4.30 (s, 3 H), 4.34 (s, 3 H), 7.1–7.3 (m, 14 H), 7.5–7.6 (m, 2 H), 7.57 (d, 3 H, $J = 2.4$ Hz), 8.48 (m, 1 H). ^{13}C NMR (CDCl_3) δ : 63.58, 64.15, 122.62, 122.75, 123.10, 124.41, 124.96, 125.23, 125.76, 126.97, 127.18, 127.41, 127.73, 127.80, 128.06, 128.35, 129.25, 130.15, 132.43, 133.15, 133.95, 134.29, 137.86, 153.00, 154.80, 196.48. Anal. Calcd for $\text{C}_{37}\text{H}_{26}\text{O}_3$: C, 85.69; H, 5.05. Found: C, 85.02; H, 5.32.

2-Acetylbianthrone (7a). Ethanethiol (0.40 mL) was dissolved in DME, and 0.15 g of NaH (80% in mineral oil) was added under argon. When the hydrogen evolution ceased, 0.50 g (1.10 mmol) of 3-acetyl-10,10'-dimethoxy-9,9'-bianthracene (**4a**) was added and the reaction mixture heated to 100 °C, and the color of the reaction mixture changed rapidly to dark red as the dianion of **6a** formed. After 1 h the mixture was cooled to ambient temperature and poured into 100 mL of ice-water containing 5 mL of concd HCl. The orange precipitate (**6a**) was filtered, washed with water, and dried on the filter. Without further purification the compound was dissolved in 30 mL of toluene, 0.50 g of benzoquinone was added, and the mixture was heated to reflux for 5 min. The black-brown reaction mixture was evaporated to dryness under vacuum and the residue treated with 50 mL of hot ethanol to remove hydroquinone and the excess of benzoquinone. Purification of flash chromatography on silica gel with CH_2Cl_2 as eluent provided 0.28 g (60%) **7a** as a green-yellow powder. Mp: 235–6 °C. ^1H NMR (CDCl_3) δ : 2.66 (s, 3 H), 7.02–7.20 (m, 7 H), 7.38–7.45 (m, 3 H), 7.74 (dd, 1 H, $J_1 = 8.2$ Hz, $J_2 = 1.8$ Hz), 8.08–8.12 (m, 3 H), 8.62 (d, 1 H, $J = 1.8$ Hz). ^{13}C NMR (CDCl_3) δ : 26.73, 127.01, 128.70, 128.89, 129.41, 129.74, 130.13, 130.32, 134.22, 134.42, 134.62, 136.36, 138.64, 138.84, 143.32, 185.98, 189.83, 196.78. Anal. Calcd for $\text{C}_{30}\text{H}_{18}\text{O}_3$: C, 84.49; H, 4.25. Found: C, 84.20; H, 4.32.

2-Stearoylbianthrone (7b) was prepared as described above for **7a** and recrystallized from 2-propanol. Yield: 0.82 g (84.4%) of yellow-green crystals. Mp: 127–9 °C. ^1H NMR (CDCl_3) δ : 0.88 (t, 3 H), 1.25 (unresolved, 30 H), 3.03 (t, 2 H, $J = 6.5$ Hz), 7.05–7.20 (multiplet, 10 H) ppm. ^{13}C NMR δ : 14.11, 22.70, 24.19, 29.65, 31.93, 38.82, 126.94, 128.70, 128.83, 129.41, 129.74, 130.13, 130.32, 134.35, 138.65 ppm. Anal. Calcd for $\text{C}_{46}\text{H}_{50}\text{O}_4$: C, 84.88; H, 7.74. Found: C, 84.70; H, 7.91.

3-(2,3,6-Trimethyl-1,4-dithiafulven-6-yl)-10,10'-dimethoxy-9,9'-bianthracene (9a). Phosphonate ester **8³⁴** (0.50 g, 2.0 mmol) was dissolved in 50 mL of dry THF (distilled from sodium ketyl) kept under argon and cooled to –80 °C on a dry ice-acetone bath. Potassium *tert*-butoxide (0.25 g, 2.2 mmol) dissolved in 5 mL of THF was added dropwise and the mixture stirred for 5 min. 3-Acetyl-10,10'-dimethoxy-9,9'-bianthracene (**4a**) (0.89 g, 2 mmol) was added in one portion and the cooling bath removed. After 1 h a homogeneous orange solution had formed, it was poured into 100 mL of water, and the mixture was extracted twice with 100-mL portions of CH_2Cl_2 . The organic phase was washed with 100 mL of water, dried over MgSO_4 , filtered, and evaporated to dryness. Purification by "flash" chromatography on silica gel with toluene as eluent yielded 0.43 g (38%) of an orange oil that could be crystallized by treatment with hot ethanol (25 mL). Mp: 203–4 °C. ^1H NMR (CDCl_3) δ : 1.86 (s, 3 H), 1.95 (s, 3 H), 2.13 (s, 3 H), 4.32 (s, 3 H), 4.33 (s, 3 H), 7.06–7.40 (m, 7 H), 7.44–7.55 (m, 4 H), 8.39 (d, 1 H, $J = 1.2$ Hz), 8.44 (d, 3 H, $J = 9.2$ Hz), 8.50 (d, 1 H, $J = 1.0$ Hz) ppm. ^{13}C NMR (CDCl_3) δ : 13.38, 13.48, 22.60, 63.49, 63.94, 118.27, 119.55, 121.33, 122.43, 124.33, 124.73, 125.16, 125.32, 125.67, 125.87, 127.25, 127.33, 128.65, 128.89, 131.23, 132.53 ppm. Anal. Calcd for $\text{C}_{37}\text{H}_{30}\text{O}_2\text{S}_2$: C, 77.86; H, 5.30; S, 11.23. Found: C, 77.94; H, 5.46; S, 11.40.

3-(2,3-Dimethyl-6-heptadecyl-1,4-dithiafulven-6-yl)-10,10'-dimethoxy-9,9'-bianthracene (9b) was prepared from **4b** as described above for **9a** as yellow-orange crystals that could be

recrystallized from ethanol. Yield: 0.85 g (73.9%). Mp: 55–7 °C (changes to glass). $^1\text{H NMR}$ (CDCl_3) δ : 0.87 (t, 3 H, $J = 5.9$ Hz), 1.20 (unresolved, 30 H), 1.84 (s, 3 H), 1.94 (s, 3 H), 2.51 (t, 2 H, $J = 3.5$ Hz), 4.32 (s, 3 H), 4.33 (s, 3 H), 7.06–7.3 (m, 7 H), 7.35–7.6 (m, 4 H), 8.36 (d, 1 H, $J = 1.2$ Hz), 8.44 (d, 1 H, $J = 8.6$ Hz), 8.46 (d, 2 H, $J = 8.7$ Hz) ppm. $^{13}\text{C NMR}$ (CDCl_3) δ : 13.46, 22.69, 29.39, 29.72, 31.93, 37.19, 63.47, 64.05, 122.45, 125.18, 125.71, 125.84, 127.39, 132.59, 152.69 ppm. Anal. Calcd for $\text{C}_{52}\text{H}_{82}\text{O}_2\text{S}_2$: C, 79.75; H, 7.98; S, 8.19. Found: C, 79.87; H, 8.08; S, 8.42.

3,3'-Bis(2,3,6-trimethyl-1,4-dithiafulven-6-yl)-10,10'-dimethoxy-9,9'-bianthracene (9c) was prepared as described above for **9a** from **5a** and 2 equiv of the phosphonate ester and a corresponding amount of base. TLC of the reaction mixture (silica gel/ CH_2Cl_2) showed the presence of three compounds: unchanged starting material and mono- and disubstituted products with R_f values of 0.16, 0.36, and 0.87, respectively. The product mixture was purified by flash chromatography on silica gel with CH_2Cl_2 as eluent, and the first fraction was collected. Evaporation of the solvent yielded 0.573 g (20%) of **9c** as an orange solid. Mp: 130–40 °C (glass-like transition). $^1\text{H NMR}$ (CDCl_3) δ : 2.95 (s, 12 H), 2.15 (s, 6 H), 4.35 (s, 6 H), 7.0–7.4 (m, 8 H), 7.35–7.5 (m, 2 H), 8.40 (d, 1 H, $J = 1.5$ Hz), 8.43 (d, 3 H, $J = 8.8$ Hz) ppm. $^{13}\text{C NMR}$ (CDCl_3) δ : 13.35, 22.49, 30.18, 63.78, 119.44, 122.23, 124.04, 124.58, 125.08, 125.55, 127.19, 128.47, 131.08, 132.30, 138.76, 152.28 ppm.

3-(2,6-Dimethyl-3-(octadecylthio)-1,4-dithiafulven-6-yl)-10,10'-dimethoxy-9,9'-bianthracene (12). Phosphonate ester **11** (1.60 g, 3.10 mmol) was dissolved in 100 mL of dry THF under N_2 and the mixture cooled to –30 °C with a dry ice–acetone bath. Potassium *tert*-butoxide (0.50 g, 4.5 mmol) in 5 mL of THF was added dropwise, and after 1 min 3-acetyl-10,10'-dimethoxy-9,9'-bianthracene (**4a**) (1.00 g, 2.2 mmol), was added. The cooling bath was removed, and the reaction mixture was allowed to warm to ambient temperature, and the stirring was continued for 1.5 h. The orange solution was then poured into 100 mL of dilute HCl and extracted with 100 mL of CH_2Cl_2 . The organic phase was washed with 100 mL of dilute HCl, dried over MgSO_4 , filtered, and evaporated to dryness. The dark orange residue was purified by flash chromatography on silica gel with toluene–petroleum ether (1:1) as eluent, and the orange band was collected. TLC on silica gel of the product showed one yellow spot (R_f 0.40), which turned green on exposure to iodine vapor. Yield: 1.68 g (96.5%) orange-yellow oil. $^1\text{H NMR}$ (CDCl_3) δ : 0.87 (unresolved, 3 H), 1.25 (unresolved, 32 H), 2.04 (s, 3 H), 2.12 (s, 3 H), 2.62 (2 H, unresolved), 4.31 (s, 3 H), 4.32 (s, 3 H), 7.07–7.15 (multiplet, 7 H), 7.49 (multiplet, 4 H), 8.39 (1 H, d, $J = 1.0$ Hz), 8.44 (d, 3 H, $J = 8.4$ Hz) ppm. $^{13}\text{C NMR}$ (CDCl_3) δ : 14.12, 15.09, 22.19, 22.51, 22.64, 28.50, 29.15, 29.34, 29.67, 30.32, 31.03, 31.94, 35.85, 63.43, 63.95, 117.76, 119.45, 119.71, 122.44, 123.09, 124.20, 124.33, 124.78, 125.17, 125.88, 127.25, 128.23, 128.75, 129.01; 131.29, 132.52, 133.44, 138.64, 152.56, 152.76 ppm. Anal. Calcd for $\text{C}_{53}\text{H}_{84}\text{O}_2\text{S}_3$: C, 76.76; H, 7.78; S, 11.60. Found: C, 76.36; H, 8.14; S, 11.67.

2-(2,3,6-Trimethyl-1,4-dithiafulven-6-yl)bianthrone (3a). Ethanethiol (2.2 g, 2.5 mL) was dissolved in 100 mL of DMF, and 1.05 g of NaH (80% in mineral oil) was added, under N_2 , with stirring. When the hydrogen evolution subsided, **9a** (1.55 g, 2.72 mmol) was added in one portion and the mixture heated to 120 °C for 1.5 h. After cooling, the red solution was poured into 250 mL of ice-cold 4 M HCl and the orange product collected by filtration (TLC on silica gel with CH_2Cl_2 as eluent showed one spot at R_f 0.56, while the starting material had R_f 0.94). The material was dissolved in 100 mL of toluene together with 1.0 g of 1,4-benzoquinone and the mixture heated to reflux for 5 min. The solvent was removed under vacuum and the brown residue treated with 50 mL of boiling ethanol to remove excess quinone and hydroquinone. The red crystals were purified by chromatography on silica gel with CH_2Cl_2 as eluent to provide 1.23 g of **3a** (83.3%). Mp: 225 dec. $^1\text{H NMR}$ (CDCl_3) δ : 1.95 (s, 3 H), 2.00 (s, 3 H), 2.13 (s, 3 H), 7.0–7.3 (m, 7 H), 7.4–7.5 (m, 4 H), 8.1–8.16 (m, 4 H) ppm. $^{13}\text{C NMR}$ (CDCl_3) δ : 13.30, 22.54, 124.27, 126.61, 127.86, 128.18, 129.42, 129.56, 129.87 ppm. MS (EI) m/z 540 (M^+ , 55), 350 (25). HRMS: 540.1198, $\text{C}_{35}\text{H}_{24}\text{O}_2\text{S}_2$ requires 540.122.

2,2'-Bis(2,3,6-trimethyl-1,4-dithiafulven-6-yl)bianthrone (3d). Prepared from **9c** as above. Yield: 0.30 g (42%) of red crystals. Mp: 321–2 °C. $^1\text{H NMR}$ (CDCl_3) δ : 1.89 (s, 3

H), 1.96 (s, 3 H), 2.09 (s, 3 H), 6.98–7.2 (m, 10 H), 7.39 (t, 2 H, $J = 7.2$ Hz), 8.07 (s, 2 H) ppm. $^{13}\text{C NMR}$ (CDCl_3) δ : 13.38, 22.58, 121.45, 124.27, 126.67, 127.85, 128.13, 129.49, 129.88, 134.34, 142.32 ppm. MS (EI) m/z 696 (M^+ , very small), 350 (30), 236, 165. HRMS could not be obtained due to the small intensity of M^+ .

2-(2,3-Dimethyl-6-heptadecyl-1,4-dithiafulven-6-yl)bianthrone (3b). Prepared from **9b** as above. Yield: 0.73 g (32%). Mp: 138–140 °C. $^1\text{H NMR}$ (CDCl_3) δ : 0.89 (t, 3 H, $J = 6.0$ Hz), 1.21 (unresolved, 30 H), 1.82 (s, 3 H), 1.95 (s, 3 H), 7.1–7.2 (m, 8 H), 7.4–7.5 (m, 3 H), 8.0–8.1 (m, 4 H) ppm. $^{13}\text{C NMR}$ (CDCl_3) δ : 15.69, 16.92, 25.82, 30.44, 32.40, 32.56, 32.87, 35.12, 40.12, 124.17, 124.29, 126.12, 128.30, 129.80, 129.85, 130.06, 131.50, 131.87, 132.87, 132.99, 133.15, 134.30, 134.92, 135.35, 137.82, 137.95, 140.43, 142.49, 142.54, 142.64, 145.11, 188.42, 188.65. Anal. Calcd for $\text{C}_{51}\text{H}_{56}\text{O}_2\text{S}_2$: C, 80.06; H, 7.38; S, 8.38. Found: C, 80.04; H, 7.50; S, 8.30.

2-(2,6-Dimethyl-3-(octadecylthio)-1,4-dithiafulven-6-yl)bianthrone (3c). Prepared from **12** as above. Yield: 0.46 g (26%) as a yellow-orange oil. $^1\text{H NMR}$ δ : 0.87 (3 H, t, unresolved), 1.25 (32 H, s), 2.08 (3 H, s), 2.15 (3 H, s), 7.02–7.1 (11 H, m), 8.05 (3 H, s), 8.13 (1 H, s). $^{13}\text{C NMR}$ (CDCl_3) δ : 13.94, 14.81, 14.96, 22.12, 22.48, 28.29, 28.98, 29.15, 29.48, 31.71, 35.70, 117.33, 117.69, 117.76, 124.13, 124.29, 126.55, 127.80, 128.12, 129.34, 129.42, 129.79, 130.03, 130.12, 131.56, 131.67, 133.43, 133.49, 134.12, 136.37, 138.87, 138.92, 141.91, 141.98, 186.27, 186.35. Anal. Calcd for $\text{C}_{52}\text{H}_{58}\text{O}_2\text{S}_3$: C, 76.99; H, 7.21. Found: C, 76.75; H, 7.10.

4-Methyl-5-(octadecylthio)-1,3-dithiole-2-diethylphosphonate Ester (11). 4-Methyl-5-(octadecylthio)-1,3-dithiolium hexafluorophosphate (5.50 g, 10 mmol)⁸⁶ was dissolved in 50 mL of acetonitrile and 1.50 g (10 mmol) of sodium iodide added. The orange mixture was heated to reflux, and 1.3 mL (1.35 g, 11 mmol) of trimethylphosphite was added over a few min. After cooling, 100 mL of ether and 100 mL of dilute aqueous HCl were added. The layers were separated, and the organic phase was dried over MgSO_4 , filtered, and evaporated in vacuum. The residue was taken up in 50 mL of petroleum ether and adsorbed on silica gel. A yellow impurity was removed by elution with petroleum ether–ether (5:3), and the product was obtained by elution with ether. After evaporation the residue was taken up in methanol (25 mL) and crystallized by cooling to –20 °C. Yield: 3.80 g (74.4%). Mp: 40–2 °C. $^1\text{H NMR}$ (CDCl_3) δ : 0.72 (t, 3 H, $J = 5.7$ Hz), 1.26 (unresolved, 32 H), 2.01 (s, 3 H), 2.73 (unresolved, 2 H), 3.87 (dd, 6 H, $J_1 = 8.9$ Hz, $J_2 = 1.6$ Hz), 4.73 (d, 1 H, $J = 4.5$ Hz). $^{13}\text{C NMR}$ (CDCl_3) δ : 14.12, 15.42, 22.71, 28.56, 29.21, 29.41, 29.73, 31.94, 35.78, 37.08, 44.17, 54.39, 54.78, 55.10, 117.56, 131.55. Anal. Calcd for $\text{C}_{24}\text{H}_{47}\text{O}_3\text{PS}_3$: C, 56.43; H, 9.27; S, 18.83. Found: C, 56.68; H, 9.32; S, 19.12.

2,3,6-Trimethyl-6-hexadecyl-1,4-dithiafulvene (13). Phosphonate ester **8** (1.0 g, 4.2 mmol) and 2-heptadecanone (1.0 g, 4 mmol) were dissolved in 25 mL of dioxane and cooled on an ice bath to 5 °C, and 0.50 g of potassium *tert*-butoxide, dissolved in a minimum amount of dioxane, was added. The reaction mixture was stirred for 0.5 h at room temperature until a nearly homogeneous yellow-orange solution was obtained. The mixture was diluted with CH_2Cl_2 (60 mL), and water (30 mL) was added, and the layers were separated. The water phase was extracted with 30 mL of CH_2Cl_2 , and the combined organic phases were dried over MgSO_4 . After filtration, the solvents were removed under vacuum and the residual oil crystallized from ethanol. Yield: 1.20 g (77.5%) as white crystals. Mp: 48–9 °C. $^1\text{H NMR}$ (CDCl_3) δ : 0.83 (t, 3 H, $J = 5.8$ Hz), 1.23 (unresolved, 28 H), 1.62 (s, 3 H), 1.84 (s, 6 H). Anal. Calcd for $\text{C}_{22}\text{H}_{40}\text{S}_2$: C, 71.67; H, 10.94; S, 17.39. Found: C, 71.59; H, 11.04; S, 17.40.

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