Synthesis of Functionalized Anthraquinones via Coupling Reactions of 2,6-Diiodo-1,5-dioctyloxy-9,10-anthraquinone

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Abstract: The synthesis of 2,6-bifunctionalized 9,10-anthraquinones bearing two alkoxy groups in the 1- and 5-positions is performed via transition-metal-catalyzed coupling reactions of 2,6-diiodo-1,5-dioctyloxy-9,10-anthraquinone, here reported for the first time.

Key words: anthraquinone, functionalization, Suzuki, cross-coupling

The anthraquinone moiety is a recurrent structural motif in a large number of organic molecules, biological compounds and supramolecular systems with application in several fields. In fact, various 9,10-anthraquinone derivatives have been investigated and used as antibiotics,[1]anticancer agents,[2] DNA photocleaving oxidants[3] or DNA intercalators,[4] as well as algicides,[5] organogelators,[6]pigments in the dyestuff and textile industry,[7] or organic stabilizers against photodegradation of polymers.[8]

Furthermore, molecular, polymeric, and supramolecular 9,10-anthraquinone-based systems have recently attracted considerable interest for their potential use as liquid crystals,[9] redox switches[10] for molecular electronics, chelating agents[11] or ionophores[12] for selective cation sensing, heterobifunctional reagents for preparation of biochips,[13] near infrared absorbing dyes[14] for optical data storage, or guest nonlinear optical dyes.[15]Recently, donor–anthraquinone acceptor[16] dyads or triads with photoinduced charge transfer properties have also been reported for applications in photovoltaic cells. Finally, 9,10-anthraquinone derivatives are important precursors in the synthesis of various compounds such as functionalized anthracenes.[17] Based on these grounds, the search for efficient and versatile synthetic methodologies leading to variously substituted 9,10-anthraquinones deserves great attention.

Many synthetic routes to these molecules have been developed so far, the most common being based on annulation reactions, such as Diels–Alder cycloadditions[18] of substituted dienes and quinones, Friedel–Crafts condensation[19] of benzene derivatives with functionalized phthalic anhydrides or phthaloyl dichlorides, and tandem directed ortho-metalation/metal–halogen exchange processes involving substituted *N*,*N*-diethylbenzamides and *o*-bromobenzaldehydes.[20] Aryne annulations,[21] thermolysis and subsequent oxidation of appropriate benzocyclobutenones,[22] or ring closing metathesis of 2,3-diallyl-1,4-naphthoquinones[23] have also been explored. However, some annulation processes are poorly efficient and incompatible with many functional groups on reagents, or they require several synthetic steps, harsh reaction conditions, or substrates that are synthetically demanding.

9,10-Anthraquinones functionalized with amide-, alkyamino-, arylamino-, and alkoxy-type groups have been also obtained by reactions involving easily available 9,10-anthraquinones bearing amino[4b,e,8] or hydroxyl[9c,24] groups, or derivatives of these substrates bearing halogen atoms,[2b,4a,d,7a,25] or tosyloxy[26] reactive sites.

Transition-metal-catalyzed cross-coupling processes of organometallic compounds with 9,10-anthraquinones bearing suitable leaving groups represent the most versatile methods for anthraquinone functionalization involving new C–C bond formation. Furthermore, these processes enable the synthesis of polymers with 9,10-anthraquinone units. Sonogashira coupling processes of terminal alkynes and 9,10-anthraquinoyl bromides or iodides have been recently investigated.[10,27] On the other hand, few examples of organometallic synthesis of mono- or disubstituted anthraquinones via palladium-catalyzed coupling reactions of anthraquinoyl triflates or halides with arylboronic esters,[28] organostannanes,[29] and substituted olefins[30] have been reported in the literature so far.

In the framework of our studies dealing with the development of organometallic routes to organic materials for photonics and electronics,[31] we report herein a straightforward methodology for the synthesis of the 2,6-diiodo-1,5-dioctyloxy-9,10-anthraquinone (**1**) (Scheme 1) together with an investigation of the reactivity of this useful building block in a series of cross-coupling reactions leading to novel symmetrically 2,6-di(aryl)-9,10-anthraquinones with alkoxy groups in the 1- and 5-positions (Schemes 2 and 3).

Indeed, compound **1** appears to be a very promising building block for the synthesis of novel processable oligomeric and polymeric systems for applications in electronics and optoelectronics. In fact, the introduction of the two *n*-octyloxy groups in the 1- and 5-positions should guarantee the resulting materials solubility in common organic solvents.[32] Moreover, the presence of iodine atoms in the 2- and 6-positions of intermediate **1** was considered par-

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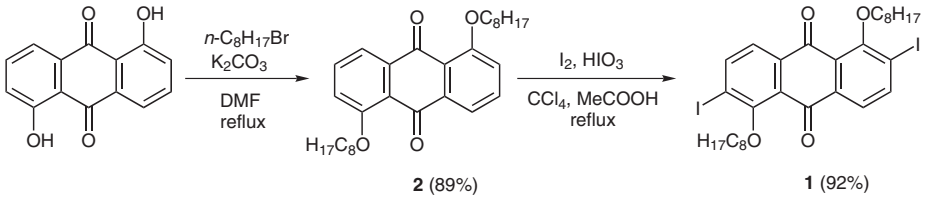


Scheme 1

ticularly interesting. Actually, it has been demonstrated that connections through the 2- and 6-positions lead to the highest planarity and conjugation in oligo- and polyanthracenes.[33]

Compound **1** was obtained in almost quantitative yield via nucleophilic substitution of the commercially available 1,5-dihydroxy-9,10-anthraquinone with *n*-octyl bromide, in the presence of potassium carbonate as a base and refluxing DMF as a solvent, followed by a double iodination of the resulting product **2** with iodine and iodic acid in acetic acid and CCl_4 as solvents (Scheme 1). The iodination reaction was performed following a protocol reported in the literature for the 1-hydroxy- and the 1,8-dihydroxy-9,10-anthraquinone leading to the 1-hydroxy-2-iodo- and the 1,8-dihydroxy-2,7-diiodo-9,10-anthraquinone in 48% and 61% yield, respectively.[34] In our case, the iodination reaction yielded regioselectively the 2,6-diiodo derivative **1** that can be easily isolated in 92% yield by crystallization from ethanol.

With the aim of exploring the reactivity of **1** in C–C bond-forming reactions with unsaturated substrates, various types of coupling processes were carried out using a series of commercially available reagents (Scheme 2). The results and experimental conditions of the coupling reactions are summarized in Table 1. The Suzuki cross-coupling of **1** with phenylboronic acid **3** performed in ethanol/toluene at 90 °C, using $Pd(PPh_3)_4$ as a catalyst and sodium carbonate as a base, afforded the 2,6-diphenylanthraquinone **10** in 91% yield. The 2,6-di(2′-thienyl)anthraquinone **11** was prepared in 81% yield via Stille cross-coupling using commercially available 2-(tributylstannyl)thiophene (**4**) in anhydrous toluene at 100 °C, in the presence of $Pd(PPh_3)_4$ as a catalyst. Sonogashira and Heck reactions with phenylacetylene (**5**) and methyl acrylate (**6**) (Scheme 2) were carried out in mild experimental conditions, as reported in Table 1, to afford **12** and **13** in 77% and 87% yield, respectively. Compound **1** is also reactive toward pentafluorophenylcopper (**7**). The reaction was performed at 110 °C in anhydrous THF–dioxane–toluene, leading to **14** in 81% yield.

Having verified the versatility of **1** as a substrate in the most important Pd-catalyzed coupling reactions, we investigated the possibility of using **1** as a building block for the preparation of more extended 2,6-bifunctionalized anthraquinones.

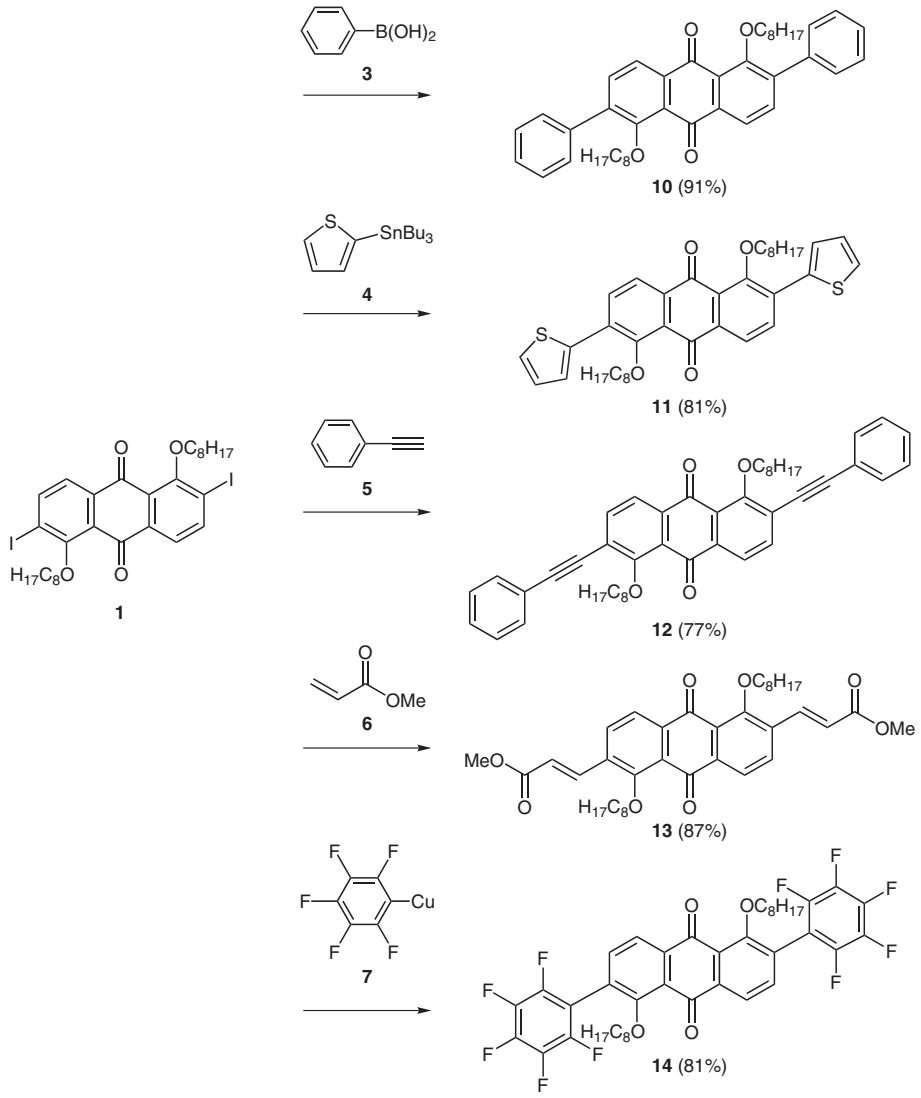
For this purpose, Suzuki cross-coupling processes appeared convenient because of the wide variety of commercially available arylboronic derivatives. Therefore, symmetrically dithienyl or terthienyl substituted anthraquinones **15** and **16** with extended π conjugation could be obtained by cross-coupling of **1** with the arylboronic esters **8** and **9** in 70% and 65% yield, respectively (Scheme 3 and Table 1).

Table 1 Coupling Reactions of **1** with **3**–**9**

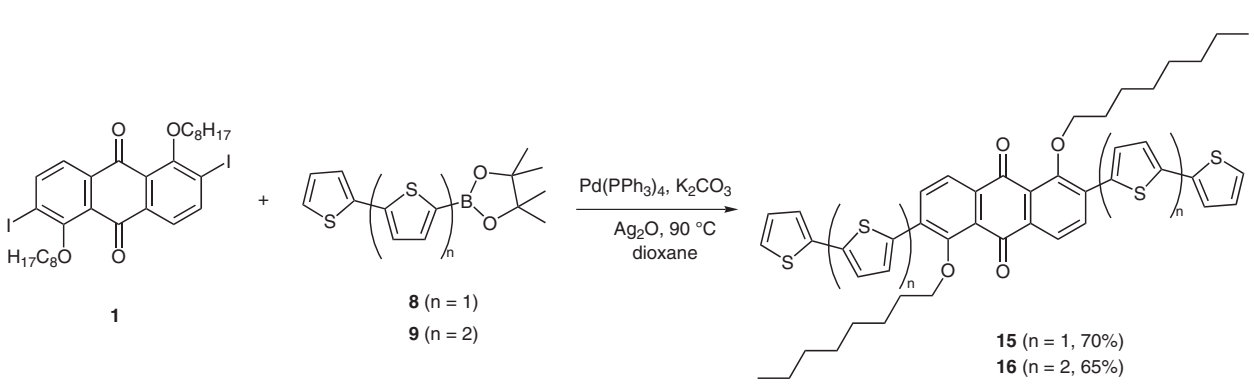
Entry	Reagent	Reaction conditions	Product	Yield %
1	**3**	$Pd(PPh_3)_4$, Na_2CO_3, EtOH–toluene, 90 °C	**10**	91
2	**4**	$Pd(PPh_3)_4$, toluene, 100 °C	**11**	81
3	**5**	$Pd(PPh_3)_4$, CuI, *i*-Pr_2NH, DMF, 80 °C	**12**	77
4	**6**	$Pd(OAc)_2$, PPh_3, Et_3N, DMF, 80 °C	**13**	87
5	**7**	THF, dioxane, toluene, 110 °C	**14**	81
6	**8**	$Pd(PPh_3)_4$, Na_2CO_3, Ag_2O, dioxane, 90 °C	**15**	70
7	**9**	$Pd(PPh_3)_4$, Na_2CO_3, Ag_2O, dioxane, 90 °C	**16**	65

Close scrutiny of the data reported in Table 1 reveals that 2,6-diiodo-1,5-dioctyloxy-9,10-anthraquinone (**1**) opens the access, with good to excellent yields, to various functionalized anthraquinones with interesting structural features such as the extended π-conjugation and the presence of electron-donating or electron-withdrawing groups. Besides being interesting in their own right, many of these compounds appear as suitable precursors for the synthesis of new functionalized anthracenes.

In conclusion, we have reported a straightforward synthetic route to the new 2,6-diiodo-1,5-dioctyloxy-9,10-anthraquinone (**1**). This compound is shown to be a useful substrate in many coupling processes allowing the synthesis in high yields of a variety of novel symmetrically 2,6-difunctionalized 9,10-anthraquinones with alkoxy groups in the 1- and 5-positions. Besides the results reported herein, on this basis it can be easily stated that compound **1** is a likely candidate for polymerization reactions that, due to the presence of the two alkoxy groups should lead to soluble materials of special interest at least in optoelectronics.



Scheme 2



Scheme 3

All the chemicals were purchased from Sigma Aldrich and used without further purification. THF, dioxane, and toluene were freshly distilled from sodium and benzophenone under N_2, immediately prior to use. DMF and Et_3N were distilled over CaH_2 at reduced pressure and stored with molecular sieves 4 Å, under N_2. The pentafluorophenylcopper (**9**) was prepared according to the literature.[35] Petroleum ether (PE) used refers to the fraction boiling in the range 40–60 °C. Column chromatography was performed using silica gel 60, 40–63 μm from Merck. Merck Silica gel 60 F254 aluminum sheets were used for analytical TLC analysis. FT-IR spectra were measured on a PerkinElmer Spectrum BX spectrophotometer using dry KBr pellets. ^1H, ^{13}C NMR, and ^{19}F NMR spectra were recorded at 400 MHz, 100 MHz, and 376 MHz on Varian Inova 400 spectrometer, respectively, or at 500 MHz (^1H NMR) and 125 MHz (^{13}C NMR) on Bruker AM 500 spectrometer, using the residual proton peaks of $CDCl_3$ at 7.26 ppm, CD_2Cl_2 at 5.36 ppm, as references for

^{1}H spectra and the signal of $CDCl_3$ at 77.0 ppm for ^{13}C NMR spectra. ^{19}F signal of trichlorofluoromethane was also used as internal standard at 0.0 ppm. Elemental analyses were done using a Carlo Erba CHNS-O EA1108-Elemental Analyzer.

1,5-Dioctyloxy-9,10-anthraquinone (2)

A suspension of 1,5-dihydroxy-9,10-anthraquinone (5.0 g, 20.8 mmol) and K_2CO_3 (0.632 g, 45.8 mmol) in anhyd DMF (130 mL) was heated at 130 °C under N_2. Then, *n*-octyl bromide (88.4 g, 458 mmol) was added dropwise and the mixture was stirred overnight at 130 °C. After cooling to r.t., the solvent was distilled at reduced pressure and the yellow liquid product was dissolved in Et_2O (30 mL). After washing with H_2O (5 × 100 mL), the organic layer was dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. The yellow-orange solid product **2** (8.59 g, 18.5 mmol) was isolated in 89% yield by column chromatography over silica gel, using PE–EtOAc (9:1); mp 96–97 °C (EtOH).

FTIR (KBr): 2950, 2920, 2850, 1670, 1580, 1470, 1450, 1440, 1280, 1250, 1070, 953, 804, 715 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.0 Hz, 6 H), 1.26–1.43 (m, 16 H), 1.56 (quint, *J* = 7.0 Hz, 4 H), 1.94 (quint, *J* = 7.0 Hz, 4 H), 4.14 (t, *J* = 7.0 Hz, 4 H), 7.24 (dd, *J* = 8.1, 1.0 Hz, 2 H), 7.65 (t, *J* = 8.1 Hz, 2 H), 7.88 (dd, *J* = 8.1, 1.0 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 22.6, 25.9, 29.0, 29.2, 29.3, 31.8, 69.6, 117.7, 119.4, 120.9, 134.7, 137.4, 159.3, 182.5.

Anal Calcd for $C_{30}H_{40}O_4$: C, 77.55; H, 8.68. Found: C, 77.60; H, 8.61.

2,6-Diiodo-1,5-dioctyloxy-9,10-anthraquinone (1)

H_2SO_4 (30%, 20 mL), I_2 (6 g, 23.6 mmol) and HIO_3 (2.75 g, 15.5 mmol) were added to a solution of 1,5-dioctyloxy-9,10-anthraquinone (**2**; 12 g, 25.8 mmol) in AcOH (300 mL) and CCl_4 (35 mL). The mixture was refluxed for 6 h and, after cooling to r.t., it was diluted with Et_2O (150 mL) and washed with sat. aq soln of $NaHCO_3$ (4 × 150 mL) and H_2O (4 × 150 mL). The organic layer was dried (Na_2SO_4) and the solvent removed at reduced pressure. Purification of the crude red product by crystallization from EtOH yielded a yellow solid **1** (16.99 g, 92%); mp 174–175 °C (EtOH).

FTIR (KBr): 2950, 2920, 2850, 1680, 1560, 1450, 1380, 1310, 1290, 1220, 1180, 1140, 955, 821, 647 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.4 Hz, 6 H), 1.20–1.38 (m, 16 H), 1.51 (quint, *J* = 6.4 Hz, 4 H), 1.85 (quint, *J* = 6.4 Hz, 4 H), 4.07 (t, *J* = 6.4 Hz, 4 H), 6.83 (d, *J* = 9.0 Hz, 2 H), 8.00 (d, *J* = 9.0 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 22.6, 25.8, 28.9, 29.2, 31.8, 69.7, 79.1, 118.4, 124.6, 137.9, 146.5, 158.1, 182.6.

Anal Calcd for $C_{30}H_{38}I_2O_4$: C, 50.29; H, 5.35. Found: C, 50.28; H, 5.31.

1,5-Dioctyloxy-2,6-diphenyl-9,10-anthraquinone (10)

The catalyst, $Pd(PPh_3)_4$ (0.127 g, 0.11 mmol), and aq 2 M Na_2CO_3 (7 mL) were added to a solution of **1** (0.716 g, 1.0 mmol) in a mixture of EtOH (8 mL) and anhyd toluene (40 mL) under N_2. After addition of phenylboronic acid (**3**; 0.268 g, 2.2 mmol), the mixture was stirred at 90 °C for 3 h and, then, cooled to r.t. The mixture was extracted with Et_2O (3 × 20 mL), the combined Et_2O layers were dried (Na_2SO_4), and the solvent was distilled at reduced pressure. The pale yellow solid **10** was isolated by column chromatography over silica gel using PE and EtOAc (8:2) as the eluent (0.566 g, 91%); mp 157–159 °C (hexane).

FTIR (KBr): 2950, 2920, 2850, 1690, 1480, 1470, 1280, 1210, 822, 754, 706 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 6.4 Hz, 6 H), 1.22–1.40 (m, 16 H), 1.42–1.51 (m, 4 H), 1.80 (quint, *J* = 6.4 Hz, 4 H), 4.09 (t, *J* = 6.4 Hz, 4 H), 7.15 (d, *J* = 8.8 Hz, 2 H), 7.31–7.41 (m, 10 H), 7.46 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 22.7, 25.8, 29.1, 29.2, 29.4, 31.9, 69.4, 116.3, 124.7, 126.8, 128.0, 129.2, 133.3, 136.4, 137.0, 140.2, 156.6, 185.6.

Anal Calcd for $C_{42}H_{48}O_4$: C, 81.78; H, 7.84. Found: C, 81.83; H, 7.82.

1,5-Dioctyloxy-2,6-di(2-thienyl)-9,10-anthraquinone (11)

The diiodoanthraquinone **1** (0.716 g, 1 mmol), 2-(tributylstannyl)thiophene (**4**; 0.820 g, 2.20 mmol) and the catalyst, $Pd(PPh_3)_4$ (0.127 g, 0.11 mmol), were dissolved in anhyd toluene (25 mL) under N_2. The mixture was refluxed for 4 d. After cooling to r.t., the solvent was distilled at reduced pressure and the crude product was purified by column chromatography over silica gel using PE–EtOAc (9:1) as the eluent to give a red solid (0.508 g, 81%); mp 113–115 °C (EtOH–H_2O, 8:2).

FTIR (KBr): 2950, 2920, 2850, 1680, 1480, 1460, 1390, 1290, 1260, 1240, 1210, 1040, 819, 693 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6.2 Hz, 6 H), 1.27–1.38 (m, 16 H), 1.30–1.54 (m, 4 H), 1.80 (quint, *J* = 6.2 Hz, 4 H), 4.07 (t, *J* = 6.2 Hz, 4 H), 7.03 (dd, *J* = 5.1, 3.6 Hz, 2 H), 7.05–7.09 (m, 2 H), 7.11 (d, *J* = 8.8 Hz, 2 H), 7.32 (dd, *J* = 5.1, 1.1 Hz, 2 H), 7.55 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3, 22.8, 26.0, 29.2, 29.4, 29.5, 32.0, 69.4, 116.4, 124.8, 125.4, 125.6, 127.1, 127.2, 137.2, 137.3, 141.2, 151.2, 185.0.

Anal Calcd for $C_{38}H_{44}O_4S_2$: C, 72.57; H, 7.05; S, 10.20. Found: C, 72.61; H, 6.98; S, 10.16.

2,6-Bis(phenylethynyl)-1,5-dioctyloxy-9,10-anthraquinone (12)

The co-catalyst CuI (0.016 g, 0.084 mmol) was dissolved under N_2 in a solution of **1** (0.300 g, 0.42 mmol) in anhyd toluene (15 mL). Then, *i*-Pr_2NH (15 mL), phenylacetylene (**5**; 0.095 g, 0.93 mmol) and $PdCl_2(PPh_3)_2$ (0.029 mg, 0.042 mmol) were added under N_2 and the mixture was refluxed for 2 h. After cooling to r.t., the solvent was distilled at reduced pressure and the crude product was purified by column chromatography over silica gel using PE–EtOAc (7:3) as the eluent. The product **12** was isolated as a yellow solid (0.214 g, 77%); mp 141–144 °C (hexane).

FTIR (KBr): 2950, 2920, 2850, 1680, 1670, 1650, 1560, 1460, 1280, 1210, 1110, 1030, 828, 754, 690, 668 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.0 Hz, 6 H), 1.20–1.38 (m, 16 H), 1.56 (quint, *J* = 7.0 Hz, 4 H), 1.91 (quint, *J* = 7.0 Hz, 4 H), 4.12 (t, *J* = 7.0 Hz, 4 H), 7.14 (d, *J* = 8.8 Hz, 2 H), 7.33–7.38 (m, 6 H), 7.62–7.67 (m, 4 H), 7.74 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 22.6, 25.9, 29.2, 29.4, 29.7, 31.8, 69.7, 88.3, 92.4, 113.5, 116.8, 123.5, 123.7, 128.2, 131.8, 139.2, 157.8, 182.4.

Anal Calcd for $C_{46}H_{48}O_4$: C, 83.10; H, 7.20. Found: C, 83.16; H, 7.15.

Methyl (2*E*)-3-{6-[(1*E*)-3-Methoxy-3-oxoprop-1-enyl]-1,5-dioctyloxy-9,10-dioxo-9,10-dihydroanthracen-2-yl}acrylate (13)

The diiodoanthraquinone **1** (0.200 g, 0.28 mmol), methyl acrylate (**6**; 0.072 g, 0.84 mmol), $Pd(OAc)_2$ (0.063 g, 0.028 mmol), Et_3N (0.028 g, 0.28 mmol) and PPh_3 (0.029 g, 0.11 mmol) were suspended in anhyd DMF (10 mL) under N_2 and the mixture was refluxed for 3 h. After cooling to r.t., the solvent was distilled at reduced pressure affording a dark yellow solid that was purified by column chromatography with hexane–EtOAc (9:1) as the eluent. The final

product **13** was isolated as an orange solid (0.152 g, 87%); mp 139–142 °C (hexane).

FTIR (KBr): 2950, 2920, 2850, 1720, 1700, 1670, 1400, 1300, 1280, 1160, 1120, 976, 826, 668 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.7 Hz, 6 H), 1.20–1.42 (m, 16 H), 1.54 (quint, *J* = 6.7 Hz, 4 H), 1.92 (quint, *J* = 6.7 Hz, 4 H), 3.82 (s, 6 H), 4.15 (t, *J* = 6.7 Hz, 4 H), 6.29 (d, *J* = 15.7 Hz, 2 H), 7.18 (d, *J* = 8.8 Hz, 2 H), 7.74 (d, *J* = 8.8 Hz, 2 H), 8.29 (d, *J* = 15.7 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3, 22.9, 26.0, 29.0, 29.5, 32.0, 51.9, 69.9, 117.5, 119.7, 123.5, 126.9, 134.2, 136.6, 143.7, 159.3, 167.3, 184.7.

Anal Calcd for $C_{38}H_{48}O_8$: C, 72.13; H, 7.65. Found: 72.18; H, 7.58.

2,6-Bis(pentafluorophenyl)-1,5-dioctyloxy-9,10-anthraquinone (14)

A solution of iodopentafluorobenzene (0.262 g, 0.89 mmol) in anhyd THF (3 ml) was slowly added dropwise to a refluxing suspension of Mg turnings (0.026 g, 1.07 mmol) in anhyd THF (1.5 mL) under N_2. The refluxing mixture was stirred for 2 h until the complete disappearance of iodopentafluorobenzene. Then, it was cooled to r.t. under N_2, and anhydrous CuBr (0.256 g, 1.8 mmol) was added. The resulting brown suspension was stirred at r.t. for 1 h, then anhyd dioxane (l.5 ml) was added and the mixture stirred at r.t. for 1 h. A solution of the dihalide **1** (0.158 g, 0.22 mmol) in anhyd toluene (10 ml) was introduced using a syringe at r.t. under N_2, and the resulting suspension was stirred at 90 °C for 24 h. After cooling to r.t., the mixture was diluted with Et_2O (10 mL) and filtered to remove inorganic salts and insoluble by-products. The organic solution was dried (Na_2SO_4) and the solvent distilled at reduced pressure. The purification of the crude product was carried out by column chromatography over silica gel using PE–CH_2Cl_2 (6:4) as the eluent to give a pale yellow solid (0.143 g, 81%); mp 118–122 °C (EtOH).

FTIR (KBr): 2960, 2930, 2860, 1680, 1520, 1490, 1480, 1290, 1260, 1230, 1070, 986, 827, 800 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.80 (t, *J* = 6.7 Hz, 6 H), 1.16–1.30 (m, 16 H), 1.36 (quint, *J* = 6.7 Hz, 4 H), 1.73 (quint, *J* = 6.7 Hz, 4 H), 4.03 (t, *J* = 6.7 Hz, 4 H), 7.15 (d, *J* = 8.7 Hz, 2 H), 7.37 (d, *J* = 8.7 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0, 22.6, 25.7, 28.8, 29.1, 29.2, 31.8, 69.5, 115.0 (td, $^2J_{C,F}$ = 19 Hz, $^3J_{C,F}$ = 5 Hz), 115.9, 116.7, 123.4, 137.0, 137.7, 137.7 (m, $^1J_{C,F}$ = 253 Hz), 140.5 (m, $^1J_{C,F}$ = 252 Hz), 143.9 (m, $^1J_{C,F}$ = 245 Hz), 159.0, 183.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –142.8 (dd, *J* = 22.3, 7.6 Hz, 2 F), –156.6 (t, *J* = 22.3 Hz, 1 F), –163.4 (td, *J* = 22.3, 7.6 Hz, 2 F).

Anal Calcd for $C_{42}H_{38}F_{10}O_4$: C, 63.31; H, 4.81. Found: C, 63.30; H, 4.80.

2,6-Bis[2,2′-Dithien-5-yl]-1,5-dioctyloxy-9,10-anthraquinone (15)

The diiodoanthraquinone **1** (0.716 g, 1 mmol), Ag_2O (0.510 g, 2.20 mmol), Na_2CO_3 (0.233 g, 2.20 mmol), and the catalyst $Pd(PPh_3)_4$ (0.127 g, 0.11 mmol) were added in sequence to a solution of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithiophene (**8**; 0.642 g, 2.20 mmol) in anhyd dioxane (50 mL) under N_2. The mixture was stirred overnight at 90 °C. After cooling to r.t., the solvent was distilled at reduced pressure. Column chromatography over silica gel of the resulting black crude product using PE–EtOAc (6:4) as the eluent gave **15** as a red solid (0.554 g, 70%); mp 145–148 °C (hexane).

FTIR (KBr): 2910, 2850, 1690, 1460, 1450, 1390, 1290, 1200, 802, 686 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 6.4 Hz, 6 H), 1.20–1.34 (m, 16 H), 1.41–1.50 (m, 4 H), 1.83 (quint, *J* = 6.4 Hz, 4 H), 4.10 (t, *J* = 6.4 Hz, 4 H), 7.00 (d, *J* = 3.6 Hz, 2 H), 7.02 (dd, *J* = 5.2, 3.6 Hz, 2 H), 7.12 (d, *J* = 3.6 Hz, 2 H), 7.13 (d, *J* = 8.7 Hz, 2 H), 7.18 (dd, *J* = 3.6, 1.2 Hz, 2 H), 7.21 (dd, *J* = 5.2, 1.2 Hz, 2 H), 7.59 (d, *J* = 8.7 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2, 22.7, 25.9, 29.1, 29.2, 29.3, 31.9, 69.5, 116.4, 123.5, 123.8, 124.2, 124.7, 124.9, 127.7, 127.9, 136.9, 137.0, 137.5, 137.7, 140.0, 157.1, 185.0.

Anal Calcd for $C_{46}H_{48}O_4S_4$: C, 69.66; H, 6.10; S, 16.17. Found: C, 69.72; H, 6.04; S, 16.13.

2,6-Bis[(2,2′;5′,2″)terthien-5-yl]-1,5-dioctyloxy-9,10-anthraquinone (16)

The diiodoanthraquinone **1** (0.358 g, 0.5 mmol), Ag_2O (0.255 g, 1.10 mmol), Na_2CO_3 (0.117 g, 1.10 mmol), and the catalyst $Pd(PPh_3)_4$ (0.064 g, 0.06 mmol) were added in sequence to a solution of **9** (0.412 g, 1.1 mmol) in anhyd dioxane (50 mL) under N_2. The mixture was stirred overnight at 90 °C. After cooling to r.t., the solvent was distilled at reduced pressure. The crude product was chromatographed over silica gel using PE–CH_2Cl_2 (4:6) as the eluent and then crystallized from CH_2Cl_2–MeOH to afford **16** as a red solid (0.311 g, 65%); mp 211–213 °C (CH_2Cl_2–MeOH).

FTIR (KBr) 2920, 2849, 1686, 1560, 1455, 1284, 1204, 792, 688 cm^{-1}.

^1H NMR (500 MHz, CD_2Cl_2): δ = 0.85 (t, *J* = 6.5 Hz, 6 H), 1.18–1.35 (m, 16 H), 1.44–1.51 (m, 4 H), 1.84 (quint, *J* = 7.5 Hz, 4 H), 4.13 (t, *J* = 6.3 Hz, 4 H), 7.00 (d, *J* = 3.5 Hz, 2 H), 7.05 (t-like, *J* ~ 3 Hz, 2 H), 7.11–7.14 (m, 4 H), 7.15 (d, *J* = 3.5 Hz, 2 H), 7.19 (d, *J* = 8.4 Hz, 2 H), 7.21–7.23 (m, 2 H), 7.25–7.28 (m, 2 H), 7.62 (d, *J* = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2, 22.7, 25.9, 29.1, 29.3, 29.4, 32.0, 69.5, 116.4, 123.6, 123.8, 124.0, 124.3, 124.4, 124.6, 124.8, 127.9, 128.0, 136.0, 136.3, 136.9, 137.0, 137.2, 137.4, 140.2, 157.2, 185.0.

Anal Calcd for $C_{54}H_{52}O_4S_6$: C, 67.74; H, 5.47; S, 20.10. Found: C, 67.80; H, 5.42; S, 20.02.

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