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(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)ylidene]-2,2'-diones—from conspicuous blue impurities to "quasi-metallic" golden-bronze crystals†

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(*E*)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2*H*)-ylidene]-2,2'-dione (**1a**) has caught the eye of several chemists who have encountered it as a trace by-product in a variety of reactions. We report here the first deliberate synthesis of this intense blue dye (λ_{max} 635 nm; ε_{max} 32 400 L cm⁻¹ mol⁻¹). We prove on the basis of predictions made with TDDFT that **1a** has previously been misassigned as a structural isomer and we correct the visible absorption data that was reported. Derivatives of **1a** equipped with pentyl (**1b**) and butylsulfanyl (**1c**) groups are readily prepared with our divergent synthetic route (3–7% yield over five steps). Crystals of **1b** and **1c** exhibit an attractive "quasi-metallic" golden-bronze lustre. This effect is rare in molecular crystals and is observed only with the most intense dyes.

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Introduction

The blue dye **1a** first caught our eye as a trace but conspicuous by-product of the preparation of 2,2'-bithiophene-5-boronic acid (2) (Scheme 1).¹ Crude batches of 2 were coloured pale green to deep blue and we observed that spots of purified 2 on



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The lectronic supplementary information (ESI) available: Deconvoluted visible absorption spectra of the blue dyes (1). DFT-optimised geometries of the fully characterised compounds, structure 9 and blue dye 1 with R = OMe. TDDFT data for the blue dyes (1, including R = OMe) and structure 9. Thermal ellipsoid plots and other depictions of the crystal structures of blue dyes 1b and 1c. Proton and carbon-13 NMR spectra of the fully characterised compounds and the inseparable mixtures. CCDC 921750 and 921751. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ob40373d

silica TLC plates gradually turned deep blue in air but not under argon.¹ In a plausible mechanism boronic acid 2 is oxidised to 5-(thiophen-2-yl)thiophen-2(3H)-one (3) or a tautomer.² Oxidative coupling of ketone 3 yields dimer 4 (or a tautomer) which is oxidised further to blue dye 1a. This mechanism is supported by the earlier studies reviewed below. A similar mechanism was recently reported to be very efficient in the case of naphthalene-1-boronic acids.³

In 1964 Hörnfeldt reported that ketone 3 is the unstable product of reacting boronic acid 2 with hydrogen peroxide.² Ketone 3 rapidly oxidised in air to a blue dye that Hörnfeldt did not investigate further.²

In 1954 Kosak *et al.* had noted that 5-phenylthiophen-2-(3H)-one (5) degraded to tars and blue dye 6 when solutions or solid samples were exposed to air (Scheme 2).⁴ Kosak *et al.* hinted at the intensity of the dye by observing that "the



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amount of oxidized material responsible for the color must be very small."⁴ The structure of blue dye **6** was supported by the established oxidation of 5-phenylthiophen-3(2H)-one (7, a structural isomer of **5**) to dye **8** (a structural isomer of **6**).⁴

Structure **9**, analogous to that of dye **8**, was assigned to a blue by-product of the Friedel–Crafts acylation of thiophene with succinyl chloride (Scheme 3) by Merz and Ellinger in 1991.⁵ Despite observing that the blue by-product was not formed in the absence of succinyl chloride, Merz and Ellinger proposed that **9** was a result of oxidative oligomerisation of thiophene.⁵ We report here that the characterisation data for the blue by-product isolated by Merz and Ellinger is mostly consistent with our data for **1a**. Accordingly we propose that keto acid **10**, a product of the Friedel–Crafts acylation, underwent a Paal–Knorr thiophene synthesis⁴ to yield ketone **3** which was oxidised to blue dye **1a**.

Some observations inconsistent with our proposed mechanism were reported by Hörnfeldt in 1967.⁶ 5-*tert*-Butylthiophen-2(5H)-one (11) degrades in air to dimer 12 and not to red dye 13 (Scheme 4).⁶ Ketone 11 can be oxidised to red dye 13 with potassium ferricyanide yet dimer 12 is still not oxidised under these conditions.⁶ Hörnfeldt concluded that dimer 12 is not an intermediate in the oxidation of ketone 11 to dye 13 but



noted the potential complication of tautomerism in these reactions.⁶ We present here clear evidence that dimer 4 (or a tautomer) is a precursor to blue dye 1a (Scheme 1) under our reaction conditions.

We sought a rational synthesis of blue dye **1a** to prove the structure and study the intense visible absorption. Our divergent synthetic route was designed not only to facilitate the preparation of derivatives of **1a** with improved physical properties but also to be an improvement on earlier synthetic methods.^{6,7} We also sought to prove that **1a** has previously been misassigned⁵ as **9** and to correct the inaccurate characterisation data that was published.

Finally we note that the analogous blue dyes **14a**⁸ and **14b**⁹ were reported recently. The visible absorptions of **14a** and **14b** are similar to that of **1a** except the absorption maxima occur at shorter wavelengths.



Results and discussion

Our divergent synthetic route to the blue dyes (1) begins with making the key 3,3' C–C bond. 3,3'-Bithiophene (15) was prepared in 94% yield by using a Suzuki cross-coupling method.¹⁰ Lithiation of **15** is reasonably selective for the 2,2' positions over the 5,5' positions (Scheme 5).¹¹ The 2,2'-dilithio derivative was converted into the corresponding Grignard reagent and quenched with *tert*-butyl peroxybenzoate to give di-*tert*-butoxy **16**⁷ in 32% yield. Conversion to the Grignard reagent is necessary to prevent substitution at the peroxyester carbonyl. This route to **16** is a significant improvement on the previously published method.⁷

Functionalisation of 3,3'-bithiophenes is problematic in general because of the instability of derivatives with common synthetic handles.^{6,11} We were unable to isolate dibromide **17** from the reaction of **16** with NBS due to rapid decomposition of the product mixture (Scheme 6). Diboronic ester **18** is more stable and can be isolated in 73% yield after recrystallisation from hexane. Unfortunately **18** suffers from steady





Scheme 6 ^a2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

deboronation under any other conditions. For this reason it is more efficient not to isolate **18** but to use the crude product immediately in the next step.⁶

Suzuki cross-coupling¹² of crude **18** and 2-bromothiophene (**19a**) was undermined by the poor stability of **18** (Scheme 7). Chromatographic purification afforded the desired quaterthiophene (**20a**) as part of an inseparable mixture along with terthiophene **21a** and bithiophene **16**, the by-products of deboronation. Yields of the product and two by-products were estimated from the mass and proton NMR analysis of the mixture. Quaterthiophene **20a** was present in a disappointing 16% yield over two steps whereas terthiophene **21a** was the major species in 27% yield. Fortunately separation of the mixture did not prove to be necessary in order to successfully complete the synthesis.

Cleavage of the *tert*-butyl ethers in the mixture of **20a**, **21a** and **16** was achieved with TFA (Scheme 7). The reaction was performed open to the air to drive oxidation of dimer **4** (Scheme 1), which we expect to be the initial product of **20a** under these conditions, to blue dye **1a**. Chlorobenzene was found to be the optimum solvent for accomplishing these transformations cleanly and in a single step. Furthermore **21a**

and **16** deteriorated under these conditions to several highly coloured and markedly polar products that were easily washed out of **1a** with methanol and ethanol. In this way **1a** was isolated in 14% yield over three steps from **16**.

Unsurprisingly **1a** is very poorly soluble in common organic solvents. Consequently we put our divergent synthetic route to use in the preparation of derivatives equipped with 5-pentyl (**1b**) and 5-butylsulfanyl (**1c**) groups from 2-bromothiophenes **19b** and **19c** respectively (Scheme 7). The syntheses of **1b** and **1c** were similar to that of **1a** in all respects including comparable yields. **1b** and **1c** were also isolated in high purity simply by washing the crude products with methanol and ethanol because although **1b** and **1c** are quite soluble in chloroform they have poor solubility in these alcohols.

Our synthetic route enables preparation of the blue dyes (1) in 3–7% yield over five steps from inexpensive commercially available starting materials. One of the limitations on the efficiency of our route is the preparation of di-*tert*-butoxy **16** in 32% yield from 3,3'-bithiophene (**15**) (Scheme 5). The other and more significant limitation is the poor stability of the boronic ester groups during the second Suzuki cross-coupling reaction (Scheme 7). We have proven that diboronic ester **18** is prepared in good yield (Scheme 6). A comparison of the estimated yields of the quaterthiophenes (**20**) with the isolated yields of the subsequent blue dyes (**1**) indicates that the final transformation proceeds in 67% yield or better (Scheme 7).

Our characterisation data for blue dye **1a** is mostly consistent with that reported by Merz and Ellinger for structure **9**⁵ (Scheme 3). The infrared absorption and proton NMR spectroscopic data both match perfectly. (These data are in the Experimental section and ref. 5. **1a** is not sufficiently soluble for carbon-13 NMR analysis.) We were unable to reproduce any of the data from the reported positive-ion mass spectrum. However we did find that the negative molecular ion is readily detected, which is not surprising given the presence of carbonyl groups in **1a**. The wavelengths of the visible absorption maxima (λ_{max}) are in close agreement: for example 631⁵ nm and 635 nm for the lowest-energy electronic transitions of **9** and **1a** respectively (Table 1). Unfortunately the molar absorption coefficients of these same maxima (ε_{max}) disagree entirely: 253 000⁵ L cm⁻¹ mol⁻¹ and 32 400 L cm⁻¹ mol⁻¹



Scheme 7 ^aDicyclohexyl(2',6'-dimethoxybiphenyl-2-yl)phosphine.

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lable 1 Experimental and calculated visible absorption properties"								
	Experiment (chloroform solutions)					TDDFT^{b} (gas phase)		
Dye	$\lambda_{\rm max}/{\rm nm}$	$\tilde{\nu}_{\rm max}/{\rm cm}^{-1}$	$\varepsilon_{\rm max}/{\rm L~cm^{-1}~mol^{-1}}$	$\tilde{\nu}_{0-0}/\mathrm{cm}^{-1}$	f	$\tilde{\nu}_{0-0}/\mathrm{cm}^{-1}$	f	Scaled ^c f
9	631^d	15800^{d}	$253\ 000^{d}$	n/a ^e	n/a ^e	20 000	0.19	0.13
1a	635	15 700	32 400	15 500	0.45	15 800	0.67	0.45
1b	660	15 200	40 200	15000	0.53	15 500	0.77	0.51
1c	676	$14\ 800$	41 900	14400	0.59	14 900	0.90	0.61

^{*a*} Transitions from the ground electronic state to the first singlet excited state. ^{*b*} B3LYP/6-311++G**//B3LYP/6-31G*. The alkyl chains of **1b** and **1c** were truncated to methyl groups. ^{*c*} Scale factor 0.45/0.67. ^{*d*} DCM solution. ^{5 *e*} Not reported. ⁵

respectively. ε_{max} reported for 9 may have gained an order of magnitude due to a simple error but still the values do not agree with our data (although the two sets are proportional). Fortunately the visible absorption data for derivatives 1b and 1c and TDDFT predictions for the blue dyes (1) and structure 9 all support our data for 1a and our reassignment of the blue by-product isolated by Merz and Ellinger as 1a.

The impact of pentyl (1b) and butylsulfanyl (1c) groups on the electronic states of **1a** can be seen in the corresponding solution-phase visible absorption spectra (Fig. 1). Transitions from the ground electronic state (S_0) to the first singlet excited state (S_1) dominate the spectra at wavelengths longer than 500 nm.¹³ λ_{max} and ε_{max} of these transitions both increase in the order **1a** < **1b** < **1c** (Table 1). However a comparison of the spectra with predictions made with TDDFT requires the use of more fundamental measures of the transition energies and intensities. The absorption profiles are broad and with clearly discernible shoulders in the cases of 1a and 1b (Fig. 1) due to strong coupling of the electronic transition $S_1 \leftarrow S_0$ with a vibrational mode of S₁. Deconvolution of the absorption profiles provides us with the wavenumbers of $S_1 \leftarrow S_0$ without



Visible absorption spectra of the blue dyes (1) in chloroform solutions.

accompanying vibrational transitions (the experimentally determined $\tilde{\nu}_{0-0}$ in Table 1). (Details of the deconvolution of these spectra are in the ESI.[†]) $\tilde{\nu}_{0-0}$ are slightly lower than the corresponding wavenumbers of the maxima ($\tilde{\nu}_{max}$). The oscillator strength (f) is a measure of the intensity of an electronic transition that also takes broadening of the absorption profile into account. (Details of the calculation of f from the deconvoluted spectra are also in the ESI.⁺) These experimentally determined f are not quite proportional to the corresponding ε_{max} .

We chose to simplify our model chemistry by calculating the absorption properties of the blue dyes (1) and structure 9 in the gas phase rather than in a solvent reaction field. We evaluated a few functionals of the time-dependent densities with a large basis set (6-311++G**14-17) and found that B3LYP^{18,19} was the best at reproducing the experimental data for the blue dyes (1) (Table 1). (Details of DFT geometry optimisations and TDDFT calculations are in the ESI.[†]) The predicted $\tilde{\nu}_{0-0}$ for $S_1 \leftarrow S_0$ of the blue dyes (1) are overestimates of the experimental values by no more than 500 cm⁻¹. $\tilde{\nu}_{0-0}$ was not reported⁵ for **9** but the predicted value is 4200 cm⁻¹ greater than the reported $\tilde{\nu}_{max}$. This discrepancy is much larger than the maximum error of 500 cm⁻¹ found for the blue dyes (1). $\tilde{\nu}_{0-0}$ for $S_1 \leftarrow S_0$ (*i.e.* the lowest-energy vibronic transition) cannot normally be greater than $\tilde{\nu}_{max}$ so it is reasonable to conclude that the blue by-product isolated by Merz and Ellinger was 1a and not 9.

The predicted f for $S_1 \leftarrow S_0$ of the blue dyes (1) are much larger than the experimental values (Table 1). Fortunately the two sets are proportional and the predicted values can be scaled to agree well with the experimental values. This consistency between our predicted and experimental data confirms the accuracy of our experimental value for ε_{max} of **1a** over that reported by Merz and Ellinger.⁵ The predicted f for $S_1 \leftarrow S_0$ of structure 9 is less than a third of that for 1a. This gives us confidence that 1a is the superior dye of these two structural isomers.

We did not observe luminescence from any of the blue dyes (1) in solution or the solid state.²⁰ However crystals of **1b** and **1c** exhibited an attractive "quasi-metallic"²¹ golden-bronze lustre (Fig. 2). This effect is only observed in molecular crystals when f and the concentration of the molecules are both very high.²² 1b formed small aggregates of golden plates when a solution was allowed to evaporate very slowly (Fig. 2a). 1c is highly crystalline and always has a quasi-metallic lustre when



Fig. 2 True-colour micrographs of typical crystalline samples of blue dyes (a) 1b and (b and c) 1c.

not in solution. **1c** readily forms elongated bronze plates that are much larger and have fewer defects (Fig. 2b and 2c) than the aggregates of **1b**.

Crystal structures of 1b and 1c were determined by means of X-ray crystallographic analysis. At first glance, the structures appear to be approximately isomorphous, the largest differences in their unit cell dimensions being ca. 0.64 Å in the *a* axis and *ca.* 1.4° in the β angle; the difference in the unit cell volumes is less than 4% (these data are in the Experimental section). It is thus no surprise that the structures of both molecules look very similar (Fig. S2 and S3 in the ESI⁺), with each having a centre of symmetry in the middle of the C(3) = C(3A)bond linking the two thiophenone units, confirming the E geometry across the double bond.²³ The neighbouring thiophenone and thiophene rings have anti configurations in both structures, as do the terminal pentyl (1b) and butylsulfanyl (1c) sidearms, and the four sulfur-based rings are approximately coplanar in each case, the maximum deviations from planarity being ca. 0.06 Å and 0.05 Å in 1b and 1c respectively. Likewise, the packing of both structures features near identical sheets of molecules, formed by two unique pairs of C_i -related weak C-H···S contacts (Fig. S6 and S7 in the ESI⁺).

However, when considering the π - π stacking interactions (which form the dominant feature of the packing of both molecules) the distinct differences between the two solid state structures become clear. In the crystals of 1b, the unique thiophenone and thiophene rings pack with the centrosymmetrically related counterpart of the other (Fig. 3) with centroid---centroid and mean interplanar separations of ca. 3.77 Å and 3.45 Å respectively, the two rings being inclined by ca. 3°. This extends to form a staggered stack of molecules along the crystallographic b axis direction with adjacent molecules offset by ca. 8.34 Å (Fig. 4), the separation between the centroids of the C(3) = C(3A) double bonds in neighbouring molecules in the stack being *ca.* 9.02 Å.²⁴ The solid state structure of **1c** has a superficially similar arrangement (Fig. 5), but with important differences. Here the π - π stacking is between the C(3)=C(3A) double bond of one molecule and the thiophene ring of two adjacent molecules; the centroid ... centroid and mean interplanar separations are both ca. 3.36 Å, the two planes being inclined by ca. 3°.25 This three-part stack (in contrast to the



Fig. 3 Part of one of the stacks of molecules linked by π - π interactions between thiophene and thiophenone rings present in the crystal of **1b**. Interaction **a** has centroid---centroid and mean interplanar separations of *ca*. 3.77 Å and 3.45 Å respectively, with the two rings inclined by *ca*. 3°. Adjacent molecules are related by a unit cell translation along the crystallographic *b* axis direction.



Fig. 4 Part of one of the stacks of π - π linked molecules present in the crystal of **1b** viewed perpendicular to the mean plane of the four thiophene/thiophenone rings of the central molecule (drawn with dark bonds), showing the *ca.* 8.34 Å offset of adjacent molecules.

two-part stack seen in **1b**) generates a chain of molecules along the crystallographic *a* axis direction with a much greater degree of overlap between the adjacent molecules (Fig. 6), the offset here being *ca.* 5.40 Å *cf. ca.* 8.34 Å in **1b**; the separation



Fig. 5 Part of one of the stacks of molecules linked by π - π interactions between the central C==C double bond and the thiophene rings present in the crystal of **1c**. The centroid---centroid and mean interplanar separations for interaction **a** are both *ca.* 3.36 Å, with the two rings inclined by *ca.* 3°. Adjacent molecules are related by a unit cell translation along the crystallographic *a* axis direction.



Fig. 6 Part of one of the stacks of π - π linked molecules present in the crystal of **1c** viewed perpendicular to the mean plane of the four thiophene/thiophenone rings of the central molecule (drawn with dark bonds), showing the *ca.* 5.40 Å offset of adjacent molecules.

between the centroids of the C(3)=C(3A) double bonds in neighbouring molecules in the stack is *ca.* 6.36 Å *cf. ca.* 9.02 Å in **1b**.

It is interesting to note that despite the evidently closer packing within the π - π stacks in the structure of **1c** compared to **1b**, the packing efficiency for **1c** (*ca.* 70.6%) is slightly lower than that for **1b** (*ca.* 72.1%).²⁶

Conclusion

We have combined conventional organic synthesis with modern computational chemistry in our contemporary approach to resolving the assignment and characterisation of **1a**. We have capitalised on the predictive power of modern TDDFT in proving that **1a** has previously been misassigned as a structural isomer. The marked intensity of this new family of blue dyes (**1**) has been quantified with the accustomed experimental measurements and authenticated with modern TDDFT predictions yet is ultimately highlighted by the rare and attractive "quasi-metallic" golden-bronze lustre exhibited by crystals of **1b** and **1c**.

Experimental section

Et₂O was dried over 4 Å molecular sieves. Reactions were performed under nitrogen unless indicated otherwise. Reaction temperatures are bath temperatures. Silica gel was the stationary phase in dry flash chromatography (60 Å pore size; 40–63 µm particle size) and TLC (60 Å pore size; 9.5–11.5 µm particle size; 0.20 mm layer thickness; fluorescent under 254 nm light). Mp are uncorrected. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) data are for CDCl₃ solutions ($\delta_{\rm H}$ 7.26; $\delta_{\rm C}$ 77.0) unless indicated otherwise (CD₂Cl₂ $\delta_{\rm C}$ 53.8). *J* are given in Hz. IR data are for neat solid samples. IR absorptions were assigned by comparing the wavenumbers and intensities with those of the corresponding gas-phase B3LYP/6-31G* vibrational modes. (Details of DFT geometry optimisations are in the ESI.[†]) UV-vis data are for CHCl₃ solutions.

2,2'-Di-tert-butoxy-3,3'-bithiophene (16)

16 has previously been reported as the product of a different synthetic route and without complete characterisation.⁷ A solution of BuLi in hexane (1.6 M, 7.5 mL, 12 mmol, 2.0 equiv.) was added dropwise over 8 min to a stirred suspension of 3,3'-bithiophene¹⁰ (15) (1.00 g, 6.01 mmol, 1.00 equiv.) in Et₂O (30 mL) at 0 °C. The resultant solution was stirred for 5 min at 0 °C and 1 h at rt. MgBr₂·Et₂O (3.11 g, 12.0 mmol, 2.00 equiv.) was added to the reaction at 0 °C and the resultant mixture was stirred for 20 min at 0 °C. tert-Butyl peroxybenzoate (2.3 mL, 12 mmol, 2.0 equiv.) was added dropwise over 15 min and the mixture was stirred for 20 min at 0 °C. The reaction was quenched at 0 °C with water (8 mL) followed by aq HCl (1.0 M, 12 mL, 12 mmol, 2.0 equiv.). The mixture was diluted with CHCl₃ and the aq layer was neutralised with concd aq HCl before it was extracted with CHCl₃. The combined organic layers were washed with saturated NaHCO₃, dried with brine and Na₂SO₄ and evaporated under reduced pressure. Dry flash chromatography (hexane) of the crude product recovered some of the starting material (15) (80 mg, 8%). Repeated dry flash chromatography (hexane-DCM 1:0 changing to 4:1) and recrystallisation (hexane) eventually afforded 16 (604 mg, 32%) as colourless crystals. Mp 96–98 °C (from hexane) [lit.,⁷ 100 °C (from EtOH)]. R_f 0.3 (hexane-DCM 3:1). ν_{max}/cm^{-1} 3095vw (thienyl C-H), 2980w (methyl C-H), 1429 (C=C), 1140s (asymmetric C-O-C), 1086 (thienyl C-H in-plane bend), 842s $(O^{-t}Bu)$, 828 (C–S) and 698s (thienyl C–H out-of-plane bend). $\delta_{\rm H}$ 1.33 (18 H, s, 2 × O^tBu), 6.70 (2 H, d, J 6.0, 4-H and 4'-H or 5-H and 5'-H) and 7.40 (2 H, d, J 6.0, 4-H and 4'-H or 5-H and 5'-H). $\delta_{\rm C}$ 28.1 (OCMe₃), 82.3 (OCMe₃), 114.2 (5-C and 5'-C), 122.8 (3-C and 3'-C), 126.2 (4-C and 4'-C) and 154.2 (2-C and 2'-C). m/z (EI+) 310.1065 (M⁺, C₁₆H₂₂O₂S₂⁺ requires 310.1056), 310 (24%, M^+), 254 (20, $[M - {}^tBu + H]^+$), 198 (100, $[M - 2{}^tBu + H]^+$) $(2H)^+$ and 137 (76, $[M - 2^tBu - 2S + 5H]^+$).

2,2'-Di-*tert*-butoxy-5,5'-bis(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)-3,3'-bithiophene (18)

A solution of BuLi in hexane (1.6 M, 0.60 mL, 0.96 mmol, 3.0 equiv.) was added dropwise over 3 min to a stirred solution of 16 (100 mg, 322 µmol, 1.00 equiv.) in Et₂O (10 mL) at -78 °C. The solution was stirred for 2 min at -78 °C and 1 h at rt. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.30 mL, 1.5 mmol, 4.6 equiv.) was added to the solution at -78 °C and the resultant suspension was allowed to warm to rt overnight. The reaction was quenched with aq HCl (0.2 M, 10 mL, 2 mmol, 6 equiv.) and diluted with $CHCl_3$ and water. The aq layer was extracted with CHCl3 and the combined organic layers were dried with MgSO4 and evaporated under reduced pressure. The crude product was recrystallised twice from hexane to afford 18 (132 mg, 73%) as pale yellow needles. Mp 156 °C (from hexane) decomposition with gas evolution. $R_{\rm f}$ 0.5 (CHCl₃). $\nu_{\rm max}/{\rm cm}^{-1}$ 2979w (methyl C-H), 1536 (C=C), 1429s (C=C), 1349s (C-B), 1260 (asymmetric O-B-O), 1121vs (thienyl C-H in-plane bend), 853s (C-O) and 664s (C-B(-O)₂ out-of-plane deformation). $\delta_{\rm H}$ 1.32 (24 H, s, 8 × Me), 1.34 (18 H, s, 2 × O^tBu) and 7.91 (2 H, s, 4-H and 4'-H). $\delta_{\rm C}$ (125 MHz; CD₂Cl₂) 24.9 (OCMe₂CMe₂O), 28.3 (OCMe₃), 83.4 (OCMe₃), 84.2 (OCMe₂CMe₂O), 117.4 (br, 5-C and 5'-C), 124.4 (3-C and 3'-C), 137.5 (4-C and 4'-C) and 161.2 (2-C and 2'-C). m/z (CI+) 563.2865 ([M + H]⁺, C₂₈H₄₅B₂O₆S₂⁺ requires 563.2838), 563 (10%, $[M + H]^+$), 507 (59, $[M - {}^{t}Bu + 2H]^+$), 451 $(100, [M - 2^{t}Bu + 3H]^{+}), 381 (22, [M - {}^{t}Bu - BO_{2}C_{6}H_{12} + 3H]^{+})$ and 325 (24, $[M - 2^{t}Bu - BO_{2}C_{6}H_{12} + 3H]^{+}$).

(*E*)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2*H*)-ylidene]-2,2'-diones (1)

A solution of BuLi in hexane (1.6 M, 0.30 mL, 0.48 mmol, 3.0 equiv.) was added dropwise over 2 min to a stirred solution of **16** (50 mg, 0.16 mmol, 1.0 equiv.) in Et₂O (5 mL) at -78 °C. The solution was stirred for 3 min at -78 °C and 1 h at rt. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.15 mL, 0.74 mmol, 4.6 equiv.) was added to the solution at -78 °C and the resultant suspension was allowed to warm to rt overnight. The reaction was quenched with aq HCl (0.2 M, 5 mL, 1 mmol, 6 equiv.) and diluted with CHCl₃ and water. The aq layer was extracted with CHCl₃ and the combined organic layers were dried with MgSO₄ and evaporated under reduced pressure. The crude product (**18**) (89–95 mg) was used without further purification.

Water (0.2 mL) was added to a suspension of crude **18** (89–95 mg), a 2-bromothiophene (**19**) (0.20 mL), Pd(OAc)₂ (2.2 mg, 10 μ mol, 6.1 mol%), dicyclohexyl(2',6'-dimethoxybiphenyl-2-yl)phosphine (8.2 mg, 20 μ mol, 12 mol%) and K₃PO₄ (86 mg, 0.41 mmol, 2.5 equiv.) in THF (2 mL). The mixture was stirred vigorously for 3–5 d at rt before it was diluted with CHCl₃ and water. The aq layer was extracted with CHCl₃ and the combined organic layers were dried with MgSO₄ and evaporated under reduced pressure. The crude product was purified using dry flash chromatography (hexane–DCM 1:0 changing to 4:1) to afford an inseparable mixture of the desired quaterthiophene (20), a terthiophene by-product (21) and 16 that was used without further purification.

The reaction with 2-bromothiophene (**19a**) (0.20 mL, 2.1 mmol, 13 equiv.) afforded a pale green oil (37 mg. ¹H NMR: *ca.* 28 mol% **20a**, 47 mol% **21a**, 24 mol% **16**. Estimated yields over two steps from **16**: 16% **20a**, 27% **21a**, 14% **16**). $R_{\rm f}$ 0.4 (hexane-CHCl₃ 3 : 1).

2",5'-Di-tert-butoxy-2,2':4',3":5",2"'-quaterthiophene (20a) $\delta_{\rm H}$ 1.41 (18 H, s, 2 × O'Bu), 6.98–7.01 (2 H, m, 4-H and 4"'-H), 7.07 (2 H, dd, J 1.0 and 3.5, 3-H and 3"'-H), 7.15 (2 H, dd, J 1.0 and 5.0, 5-H and 5"'-H) and 7.61 (2 H, s, 3'-H and 4"'-H). *m*/*z* (EI+) 474.0823 (M⁺, C₂₄H₂₆O₂S₄⁺ requires 474.0810), 474 (4%, M⁺), 418 (3, [M - ^tBu + H]⁺), 362 (65, [M - 2^tBu + 2H]⁺) and 301 (15, [M - 2^tBu - 2S + 5H]⁺).

2",5'-Di-tert-butoxy-2,2':4',3"-terthiophene (**21a**) $\delta_{\rm H}$ 1.36 (9 H, s, O^tBu), 1.37 (9 H, s, O^tBu), 6.72 (1 H, d, *J* 6.3, 4"-H or 5"-H), 6.98–7.01 (1 H, m, 4-H), 7.07 (1 H, dd, *J* 1.0 and 3.5, 3-H), 7.14 (1 H, dd, *J* 1.0 and 5.1, 5-H), 7.41 (1 H, d, *J* 6.3, 4"-H or 5"-H) and 7.61 (1 H, s, 3'-H). *m/z* (EI+) 392.0944 (M⁺, C₂₀H₂₄O₂S₃⁺ requires 392.0933), 392 (4%, M⁺), 336 (5, [M - ^tBu + H]⁺), 280 (100, [M - 2^tBu + 2H]⁺) and 219 (29, [M - 2^tBu - 2S + 5H]⁺).

The reaction with 2-bromo-5-pentylthiophene²⁷ (**19b**) (0.20 mL, 1.1 mmol, 6.9 equiv.) afforded a green oil (50 mg. ¹H NMR: *ca.* 57 mol% **20b**, 37 mol% **21b**, 7 mol% **16**. Estimated yields over two steps from **16**: 33% **20b**, 22% **21b**, 4% **16**). $R_{\rm f}$ 0.3 and 0.4 (hexane–CHCl₃ 3 : 1).

2",5'-Di-tert-butoxy-5,5'''-dipentyl-2,2':4',3":5'',2'''-quaterthiophene (20b) $\delta_{\rm H}$ 0.90 (6 H, t distorted by virtual coupling, *J ca.* 7, 2 × pentyl 5-H₃), 1.31–1.42 (8 H, m, 4 × CH₂), 1.39 (18 H, s, 2 × O'Bu), 1.62–1.74 (4 H, m, 2 × CH₂), 2.77 (4 H, t, *J* 7.6, 2 × pentyl 1-H₂), 6.64 (2 H, d, *J* 3.3, 3-H and 3'''-H or 4-H and 4'''-H), 6.87 (2 H, d, *J* 3.3, 3-H and 3'''-H or 4-H and 4'''-H) and 7.51 (2 H, s, 3'-H and 4'''-H).

2",5'-Di-tert-butoxy-5-pentyl-2,2':4',3"-terthiophene (21b) $\delta_{\rm H}$ 0.90 (3 H, t distorted by virtual coupling, *J ca.* 7, pentyl 5-H₃), 1.31–1.42 (4 H, m, 2 × CH₂), 1.35 (9 H, s, O^tBu), 1.36 (9 H, s, O^tBu), 1.62–1.74 (2 H, m, CH₂), 2.77 (2 H, t, *J* 7.6, pentyl 1-H₂), 6.64 (1 H, d, *J* 3.3, 3-H or 4-H), 6.71 (1 H, d, *J* 6.0, 4"-H or 5"-H), 6.87 (1 H, d, *J* 3.3, 3-H or 4-H), 7.41 (1 H, d, *J* 6.0, 4"-H or 5"-H) and 7.51 (1 H, s, 3'-H). *m/z* (EI+) 462.1739 (M⁺, C₂₅H₃₄O₂S₃⁺ requires 462.1715), 462 (6%, M⁺), 350 (100, [M - 2^tBu + 2H]⁺) and 289 (17, [M - 2^tBu - 2S + 5H]⁺).

The reaction with 2-bromo-5-(butylsulfanyl)thiophene²⁸ (**19c**) (0.20 mL, 1.1 mmol, 6.9 equiv.) afforded a dark green oil (45 mg. ¹H NMR: *ca.* 20 mol% **20c**, 46 mol% **21c**, 35 mol% **16**. Estimated yields over two steps from **16**: 12% **20c**, 28% **21c**, 21% **16**). $R_{\rm f}$ 0.3 (hexane–CHCl₃ 3 : 1).

2",5'-Di-tert-butoxy-5,5"''-bis(butylsulfanyl)-2,2':4',3":5",2"''quaterthiophene (20c) $\delta_{\rm H}$ 0.91 (6 H, t, J 7.4, 2 × butyl 4-H₃), 1.37–1.48 (4 H, m, 2 × butyl 3-H₂), 1.40 (18 H, s, 2 × O^tBu), 1.57–1.66 (4 H, m, 2 × butyl 2-H₂), 2.80 (4 H, t, J 7.3, 2 × butyl 1-H₂),6.91 (2 H, d, J 3.8, 3-H and 3'''-H or 4-H and 4'''-H), 6.98 (2 H, d, J 3.8, 3-H and 3'''-H or 4-H and 4'''-H) and 7.56 (2 H, s, 3'-H and 4''-H).

2",5'-Di-tert-butoxy-5-(butylsulfanyl)-2,2':4',3"-terthiophene (21c) $\delta_{\rm H}$ 0.91 (3 H, t, J 7.4, butyl 4-H₃), 1.36 (9 H, s, O^tBu), 1.37 (9 H,

s, O^tBu), 1.37–1.48 (2 H, m, butyl 3-H₂), 1.57–1.66 (2 H, m, butyl 2-H₂), 2.80 (2 H, t, *J* 7.3, butyl 1-H₂), 6.71 (1 H, d, *J* 5.9, 4"-H or 5"-H), 6.91 (1 H, d, *J* 3.5, 3-H or 4-H), 6.98 (1 H, d, *J* 3.5, 3-H or 4-H), 7.40 (1 H, d, *J* 5.9, 4"-H or 5"-H) and 7.57 (1 H, s, 3'-H). *m*/*z* (EI+) 480.1289 (M⁺, C₂₄H₃₂O₂S₄⁺ requires 480.1280), 480 (5%, M⁺), 424 (6, $[M - {}^{t}Bu + H]^{+}$), 368 (100, $[M - 2{}^{t}Bu + 2H]^{+}$) and 307 (12, $[M - 2{}^{t}Bu - 2S + 5H]^{+}$).

TFA (10 drops every 30 min) was added to a stirred solution of an inseparable mixture of **20**, **21** and **16** (37–50 mg) in PhCl (5 mL) until the solution started to turn blue. The mixture was stirred vigorously for 2–3 d open to the air before it was concentrated under reduced pressure. The residue was successively washed with MeOH, EtOH and hexane. A CHCl₃ solution of the remaining solid was filtered and evaporated under reduced pressure to afford **1**.

(*E*)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2*H*)-ylidene]-2,2'-dione (1a)

(8 mg, 14% over three steps from **16**) as a black powder. **1a** has previously been reported but misassigned as structure **9**.⁵ **1a** is not sufficiently soluble for ¹³C NMR analysis. Mp > 250 °C. $R_{\rm f}$ 0.2 (hexane–CHCl₃ 3 : 1). $\lambda_{\rm max}$ /nm 635 (ϵ /L cm⁻¹ mol⁻¹ 32 400), 604sh (28 600), 440sh (2400), 403sh (4700), 386sh (6500), 357 (21 400), 346 (21 300) and 314sh (10 000). $\nu_{\rm max}$ /cm⁻¹ 3088w (thienyl C–H), 1658s (C=O), 1532s (C=C), 1409 (C=C), 1172s (thienyl C–H in-plane bend), 1053s (thienyl C–H in-plane bend), 835s (C–S) and 708s (thienyl C–H out-of-plane bend). $\delta_{\rm H}$ 7.14 (2 H, dd, *J* 3.9 and 5.1, 2 × thienyl 4-H), 7.39 (2 H, dd, *J* 1.0 and 3.9, 2 × thienyl 3-H), 7.54 (2 H, dd, *J* 1.0 and 5.1, 2 × thienyl 5-H) and 8.13 (2 H, s, 4-H and 4'-H). *m/z* (ESI–) 359.9394 (M⁻, C₁₆H₈O₂S₄⁻ requires 359.9413).

(*E*)-5,5'-Bis(5-pentylthiophen-2-yl)-3,3'-bi[thiophen-3(2*H*)-ylidene]-2,2'-dione (1b)

(18 mg, 22% over three steps from 16) as a black powder. Mp 171-173 °C (from CDCl₃) partial decomposition. R_f 0.3 (hexane-CHCl₃ 3:1). $\lambda_{\text{max}}/\text{nm}$ 660 (ϵ/L cm⁻¹ mol⁻¹ 40 200), 627sh (33 800), 445sh (3200), 416sh (5200), 367 (23 800), 355 (22 700) and 320sh (9800). $\nu_{\rm max}/{\rm cm}^{-1}$ 3083vw (thienyl C-H), 2926w (alkyl C-H), 1664 (C=O), 1506s (C=C), 1443 (C=C), 1172vs (thienyl C-H in-plane bend), 1093w (thienyl C-H inplane bend), 835 (C-S) and 788 (thienyl C-H out-of-plane bend). $\delta_{\rm H}$ 0.91 (6 H, t distorted by virtual coupling, J ca. 7, 2 × pentyl 5-H₃), 1.30-1.42 (8 H, m, 4 × CH₂), 1.66-1.77 (4 H, m, 2 × CH₂), 2.85 (4 H, t, J 7.6, 2 × pentyl 1-H₂), 6.81 (2 H, d, J 3.7, 2 × thienyl 3-H or 4-H), 7.19 (2 H, d, J 3.7, 2 × thienyl 3-H or 4-H) and 8.03 (2 H, s, 4-H and 4'-H). $\delta_{\rm C}$ 14.0 (pentyl 5-C), 22.4 (pentyl 4-C), 30.7 (pentyl 1-C or 2-C or 3-C), 31.0 (pentyl 1-C or 2-C or 3-C), 31.2 (pentyl 1-C or 2-C or 3-C), 116.5 (4-C and 4'-C), 126.2 (thienyl 3-C or 4-C), 129.6 (thienyl 3-C or 4-C), 134.5 (3-C or 5-C or thienyl 2-C or 5-C), 135.5 (3-C or 5-C or thienyl 2-C or 5-C), 142.2 (3-C or 5-C or thienyl 2-C or 5-C), 152.5 (3-C or 5-C or thienyl 2-C or 5-C) and 194.3 (2-C and 2'-C). m/z (ESI-) 500.0981 (M⁻, C₂₆H₂₈O₂S₄⁻ requires 500.0978). Crystal: $C_{26}H_{28}O_2S_4$, M = 500.72, triclinic, $P\bar{1}$ (no. 2), a = 5.7198(15), b =9.0209(19), c = 11.863(3) Å, $\alpha = 79.850(19)$, $\beta = 78.78(2)$, $\gamma =$

87.139(19)°, *V* = 590.9(3) Å³, *Z* = 1 [*C*_i symmetry], *D*_c = 1.407 g cm⁻³, μ (Cu-Kα) = 3.866 mm⁻¹, *T* = 173 K, lustrous bronze plates, Oxford Diffraction Xcalibur PX Ultra diffractometer; 2253 independent measured reflections (*R*_{int} = 0.0500), *F*² refinement,²⁹ *R*₁(obs) = 0.0689, w*R*₂(all) = 0.2082, 1864 independent observed absorption-corrected reflections [|*F*_o| > 4σ (|*F*_o|), $2\theta_{max} = 146^{\circ}$], 145 parameters; CCDC 921750.

(*E*)-5,5'-Bis[5-(butylsulfanyl)thiophen-2-yl]-3,3'-bi[thiophen-3(2*H*)-ylidene]-2,2'-dione (1c)

(8 mg, 9% over three steps from 16) as bronze crystals. Mp 153-154 °C (from hexane-CHCl₃) partial decomposition. Rf 0.3 (hexane–CHCl₃ 3 : 1). λ_{max} /nm 676 (ϵ /L cm⁻¹ mol⁻¹ 41 900) and 374 (17 800). $\nu_{\text{max}}/\text{cm}^{-1}$ 3085vw (thienyl C-H), 2925w (alkyl C-H), 1656 (C=O), 1525s (C=C), 1404s (C=C), 1171s (thienyl C-H in-plane bend), 830 (thienyl C-S) and 780 (thienyl C-H out-of-plane bend). $\delta_{\rm H}$ 0.94 (6 H, t, J 7.4, 2 × butyl 4-H₃), 1.46 $(4 \text{ H}, \text{ sextet}, J 7.4, 2 \times \text{butyl } 3-\text{H}_2), 1.69 (4 \text{ H}, \text{quintet}, J 7.4, 2 \times \text{L}_2)$ butyl 2-H₂), 2.97 (4 H, t, J 7.4, 2 × butyl 1-H₂), 6.99 (2 H, d, J 3.9, 2 × thienyl 3-H or 4-H), 7.19 (2 H, d, J 3.9, 2 × thienyl 3-H or 4-H) and 8.00 (2 H, s, 4-H and 4'-H). $\delta_{\rm C}$ 13.6 (butyl 4-C), 21.7 (butyl 3-C), 31.3 (butyl 2-C), 37.6 (butyl 1-C), 117.1 (4-C and 4'-C), 129.8 (thienyl 3-C or 4-C), 131.1 (thienyl 3-C or 4-C), 134.5 (3-C or 5-C or thienyl 2-C or 5-C), 138.5 (3-C or 5-C or thienyl 2-C or 5-C), 141.3 (3-C or 5-C or thienyl 2-C or 5-C), 144.1 (3-C or 5-C or thienyl 2-C or 5-C) and 193.9 (2-C and 2'-C). m/z (ESI-) 536.0109 (M⁻, C₂₄H₂₄O₂S₆⁻ requires 536.0106). Crystal: $C_{24}H_{24}O_2S_6$, M = 536.79, triclinic, $P\overline{1}$ (no. 2), a = 6.3559(4), b = 8.6356(3), c = 11.6399(6) Å, $a = 78.832(4), \beta =$ 77.408(5), $\gamma = 87.543(4)^{\circ}$, $V = 611.71(6) \text{ Å}^3$, $Z = 1 [C_i \text{ symmetry}]$, $D_{\rm c} = 1.457 \text{ g cm}^{-3}, \ \mu({\rm Cu-K\alpha}) = 5.330 \text{ mm}^{-1}, \ T = 173 \text{ K}, \ {\rm dark}$ bronze platy needles, Oxford Diffraction Xcalibur PX Ultra diffractometer; 2354 independent measured reflections (R_{int} = 0.0215), F^2 refinement,²⁹ R_1 (obs) = 0.0306, w R_2 (all) = 0.0801, 2103 independent observed absorption-corrected reflections $[|F_{o}| > 4\sigma(|F_{o}|), 2\theta_{max} = 145^{\circ}], 146 \text{ parameters; CCDC 921751.}$

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