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Synthesis, photophysics and molecular structures of luminescent 2,5-bis(phenylethynyl)thiophenes (BPETs)

Jamie S. Siddle,^a Richard M. Ward,^a Jonathan C. Collings,^a Simon R. Rutter,^a Laurent Porrès,^a Lucas Applegarth,^a Andrew Beeby,^a Andrei S. Batsanov,^a Amber L. Thompson,^a Judith A. K. Howard,^a Abdou Boucekine,^b Karine Costuas,^b Jean-François Halet^b and Todd B. Marder^{*a}

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The Sonogashira cross-coupling of two equivalents of *para*-substituted ethynylbenzenes with 2,5-diiodothiophene provides a simple synthetic route for the preparation of 2,5-bis(*para*-R-phenylethynyl)thiophenes (R = H, Me, OMe, CF₃, NMe₂, NO₂, CN and CO₂Me) (**1a–h**). Likewise, 2,5-bis(pentafluorophenylethynyl)thiophene (**2**) was prepared by the coupling of 2,5-diiodothiophene with pentafluorophenylacetylene. All compounds were characterised by NMR, IR, Raman and mass spectroscopy, elemental analysis, and their absorption and emission spectra, quantum yields and lifetimes were also measured. The spectroscopic studies of **1a–h** and **2** show that both electron donating and electron withdrawing *para*-substituents on the phenyl rings shift the absorption and emission maxima to lower energies, but that acceptors are more efficient in this regard. The short singlet lifetimes and modest fluorescence quantum yields (*ca.* 0.2–0.3) observed are characteristic of rapid intersystem crossing. The single-crystal structures of 2,5-bis(phenylethynyl)thiophene, 2,5-bis(*para*-carbomethoxyphenylethynyl)thiophene, 2,5-bis(*para*-methylphenylethynyl)thiophene and 2,5-bis(pentafluorophenylethynyl)thiophene were determined by X-ray diffraction at 120 K. DFT calculations show that the all-planar form of the compounds is the lowest in energy, although rotation of the phenyl groups about the C≡C bond is facile and TD-DFT calculations suggest that, similar to 1,4-bis(phenylethynyl)benzene analogues, the absorption spectra in solution arise from a variety of rotational conformations. Frequency calculations confirm the assignments of the compounds' IR and Raman spectra.

Introduction

Conjugated systems, such as 1,4-bis(phenylethynyl)benzenes (BPEBs)^{1–15} and 9,10-bis(phenylethynyl)anthracenes (BPEAs),^{16–18} show interesting structural, electronic and luminescent properties, and have been well studied; however, there are far fewer examples of 2,5-bis(phenylethynyl)thiophenes (BPETs). The few BPETs that have been reported are of interest due to their luminescence^{19–24} and non-linear optical^{25–27} properties, as well as their liquid crystalline phase behaviour, which they owe to the bent nature of the thiophene moiety.^{28–31} An optically active (axially chiral) bis-BPET derivative has been described,³² as well as transition metal π -complexes containing BPETs as ligands.^{33a} Closely related to the BPETs are 2,5-bis(pyridylethynyl)thiophenes,^{33b–d} which have the capacity to coordinate to transition metal atoms (*via* nitrogen), and thus can be used to create photo-conducting solids or molecular wires.

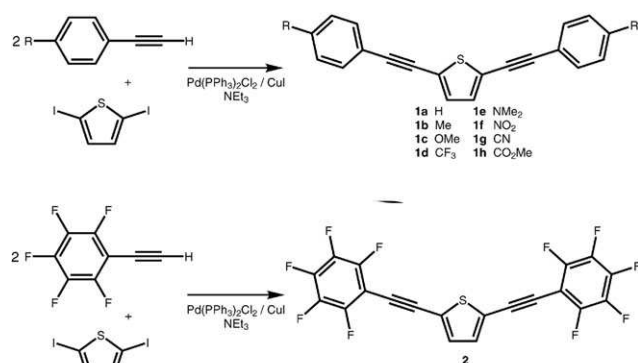
There are a number of routes for the synthesis of BPETs. The most straightforward methods utilise the catalytic cross-

coupling of terminal alkynes^{19–23} or alkynyl Grignard reagents³⁴ with 2,5-halothiophenes, giving BPETs in good yields. Pd-catalysed cross-coupling has also been used to produce BPETs in good yields from triorganoindium compounds and 2,5-dibromothiophene.³⁵ Other methods include longer reaction sequences involving elimination reactions. A one-pot synthesis using benzyl sulfone derivatives and 2-formyl-5-phenylethynylthiophene, incorporating two sequential eliminations from the reaction intermediates, has been developed, forming symmetrical or unsymmetrical BPETs in good yields.³⁶ The compound 1,8-diphenyl-1,7-octadiyne-3,6-dione, synthesised in nine steps from 1,4-butanediol, can also be converted to a BPET by a reaction with bis(triphenyl)tin sulfide in the presence of BCl₃.³⁷

To complement our current work on luminescent *mer,cis*-[tris(trimethylphosphine)-trimethylsilylethynyl-2,5-bis(*para*-R-phenylethynyl)-3,4-(*para*-R-phenyl)rhodacyclopenta-2,4-dienes],³⁸ we have synthesised a number of structurally related 2,5-bis(*para*-R-phenylethynyl)thiophenes with the aim of evaluating the role of the heteroatom on the optical properties of heterocyclopentadienes. Herein, we report the synthesis and optical properties of 2,5-bis(*para*-R-phenylethynyl)thiophenes, R = H (**1a**), Me (**1b**), OMe (**1c**), CF₃ (**1d**), NMe₂ (**1e**), NO₂ (**1f**), CN (**1g**) and CO₂Me (**1h**), 2,5-bis(pentafluorophenylethynyl)thiophene (**2**) and the crystal and molecular

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Scheme 1

structures of selected examples. A more detailed study of the photophysical behaviour of the parent compound **1a** is given in a companion paper.³⁹

Results and discussion

Syntheses

Compounds **1a–h** and **2** were synthesised *via* the Sonogashira cross-coupling reaction of 2,5-diiodothiophene with two equivalents of the appropriate substituted ethynylbenzene at room temperature for 24–96 h, except for **1h**, which was stirred at room temperature for 24 h and then heated to 80 °C for 2 h, catalysed by 2 mol% Pd(PPh₃)₂Cl₂ and CuI in triethylamine or diethylamine,⁴⁰ as shown in Scheme 1. Reactions were monitored by GC-MS or TLC, and the compounds were isolated after passage through a short silica gel column eluting with hexane, hexane/CH₂Cl₂ or hot toluene. Compounds **1a**,^{22,34–37} **1c**^{33,41} and **1e**^{19,20} have previously been reported, although no synthetic or characterisation details were given for **1c**. Analogues of **1c**, containing longer alkoxy substituents, have been reported very recently, along with their liquid crystal phase behaviour and optical properties.^{30b} Compound **1e** is reported to have been synthesised in almost quantitative yield; however, the procedure, surprisingly, used a 1 : 1 ratio of 4-*N,N*-dimethylaminophenylacetylene to 2,5-diiodothiophene with 10 mol% of a Pd(II) catalyst precursor, which should:

generate no more than 50% yield based on 2,5-diiodothiophene, and (b) generate a significant amount (10%) of the 4-Me₂N-C₆H₄-C≡C-C≡C-C₆H₄-4-NMe₂ diyne, further consuming 20% of the starting alkyne during the catalyst activation step.^{1,42} Both of these factors should significantly reduce the overall yield of **1e** obtained. We have prepared compound **1e** in moderate yield using 2 mol% Pd catalyst and did not observe a significant amount of diyne formation (*i.e.* beyond that required for catalyst precursor reduction). We also note that analytically pure samples of several of the compounds showed melting ranges that were slightly broader than expected, possibly an indication of transient liquid crystal phase behaviour,^{30b} but this aspect was not investigated further.

Optical properties

The optical properties (absorption and fluorescence maxima, fluorescence quantum yields and lifetimes) for compounds **1a–h** and **2** are presented in Table 1. All compounds show an intense absorption band in the UV region (Fig. 1 and Fig. 2). With the exception of the nitro derivative, **1f**, these chromophores are also fluorescent in the UV-vis region with moderate quantum yields of 0.19–0.33 (Fig. 3 and Fig. 4). It is apparent that the presence of both electron donating and electron withdrawing groups at the *para*-position of the phenyl rings shifts the absorption as well as the emission maxima bathochromically from 350 nm for **1a** to 386 and 387 nm for **1e** and **1f**, respectively, in absorption, and from 382 nm for **1a** to 434 and 402 nm for **1e** and **1h**, respectively, in emission. Compound **1f** is very weakly emissive in toluene, resulting from the presence of the NO₂ groups, which lead to non-radiative deactivation of the excited state, meaning its quantum yield could not be determined accurately. This presumably results from the fact that the $\pi \rightarrow \pi^*$ transition is higher in energy than the nitro $n \rightarrow \pi^*$ transition, as is often the case for such compounds. However, a quantum yield of 0.17 was measured in the more polar CH₂Cl₂ solvent. The excited state lifetimes of these compounds are short compared to those of related BPEA and BPEB systems,^{3b,15a,b,16a} and this is mirrored in the lower quantum yields. This observation can be attributed to the excited singlet state, S₁, undergoing more

Table 1 Spectroscopic data for compounds **1a–h** and **2** in toluene, unless otherwise noted.

Compound	R	λ_{\max} abs/nm	ϵ/mol^{-1} $\text{cm}^{-1} \text{dm}^3$	f_{calc}^a	λ_{\max} em/nm	Observed S ₁ –S ₀ energy/cm ^{-1b}	Calculated S ₁ –S ₀ energy/cm ^{-1a}	Φ	Stokes shift/cm ⁻¹	Lifetime τ/ps
1a	H	350	33 000	1.56	382	26 200	25 600	0.20	2400	240
1b	Me	353	40 000	1.72	386	25 900	25 200	0.23	2400	240
1c	OMe	345	39 000	1.76	394	25 400	24 800	0.22	2500	270
			40 000							
1d	CF ₃	354	40 000	1.72	387	25 800	25 000	0.22	2400	230
1e	NMe ₂	386	52 000	1.99	434	23 000	23 300	0.33	2900	400
1f	NO ₂	387	44 000	1.69	435	23 500	22 100	—	2900	—
		394 ^c	42 000		547 ^c			0.17 ^c	7100 ^c	930 ^c
1g	CN	365	49 000	1.93	401	24 900	23 800	0.31	2500	320
1h	CO ₂ Me	365	48 000	1.89	402	24 900	23 700	0.29	2500	310
2	F ^d	351	39 000	1.60	383	26 100	25 300	0.19	2400	210

^a From gas phase TD-DFT calculations; f = oscillator strength. ^b Estimated from λ_{\max} em (see text). ^c Measurements in CH₂Cl₂. ^d F at the 2, 3, 4, 5 and 6 positions of the phenyl ring.

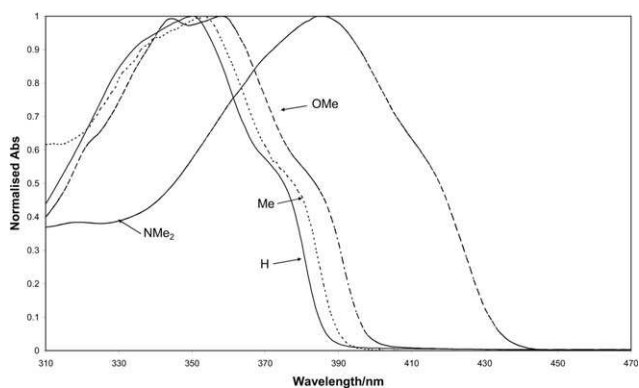


Fig. 1 Absorption spectra of compounds **1a–c** and **1e**.

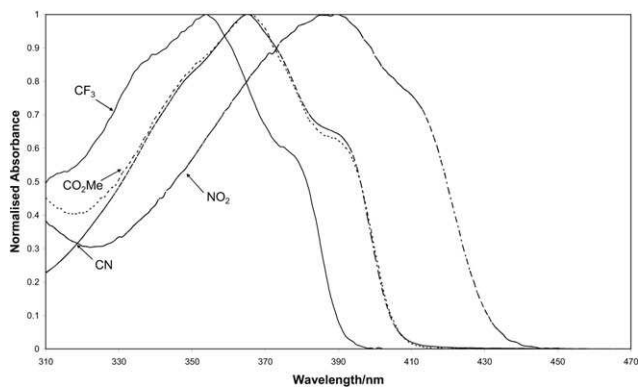


Fig. 2 Absorption spectra of compounds **1d** and **1f–h**.

rapid intersystem crossing (ISC) to the triplet state, T_1 , for the BPETs compared to their BPEB and BPEA analogues.³⁹ ISC is faster due to the introduction of the sulfur, a moderately heavy atom which enhances spin–orbit coupling in the molecule.

A plot of the absorbance maxima against the Hammett constant⁴³ for the *para*-substituent (σ_p), shown in Fig. 5, displays a similar trend to those that we have observed for the analogous BPEBs¹ and BPEAs.¹⁶ The absorption maxima for the BPETs are intermediate between the values for BPEBs and BPEAs, with the BPEAs being the most red-shifted of these series. The graph shows a shift of absorbance maxima to lower energy with both stronger electron withdrawing and electron donating *para*-substituents on the phenyl ring, signifying a reduced energy gap between the S_0 ground state and S_1 excited state in each case. This is the result of the fact that electron donors raise the HOMO more than the LUMO while electron acceptors lower the LUMO more than the HOMO (*vide infra*). However, in each of the series, the effect of acceptor substituents is greater than that of donor substituents, as can be seen from the gradients of each plot. The difference in gradient between the acceptor series and the donor series increases from BPEBs to BPETs to BPEAs, demonstrating that the photophysical properties for these related compounds, as well as being influenced by the *para*-substituents, are also dependent on the nature of the central core. Finally, we note that the optical data for the MeO derivative, **1c**, reported herein is, as expected, essentially

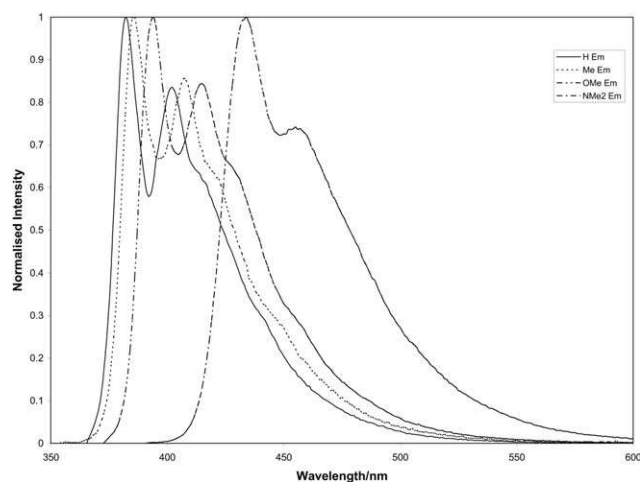


Fig. 3 Emission spectra of compounds **1a–c** and **1e**.

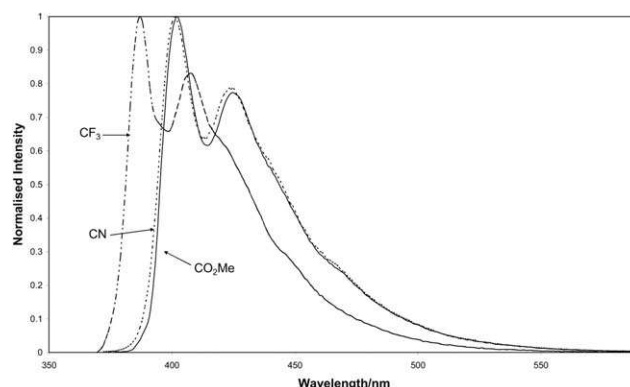


Fig. 4 Emission spectra of compounds **1d**, **1f** and **1h**.

identical to that reported very recently for the EtO derivative,^{30b} confirming the accuracy of our data.

Crystal structures

The structures of **1a**, **1b**, **1h** and **2** each contain one independent molecule (Fig. 6) possessing neither crystallographic symmetry nor local symmetry, except for **1b**, which has an approximate C_2 axis. Selected geometric parameters are listed in Table 2. The geometry of the planar thiophene ring is very similar in all four structures, but differs significantly from that of unsubstituted thiophene. The latter proved undeterminable in the solid state due to rotational disorder, complicated polymorphism and an incommensurate structure,⁴⁴ but was recently established (with much difficulty) in the gas phase by a combination of electron diffraction, NMR, rotational and microwave spectroscopy, and *ab initio* and DFT calculations,⁴⁵ giving equilibrium (r_e) bond lengths C–S 1.704(2), C=C 1.372(3) and C–C 1.421(4) Å. Longer C–S bonds in **1** and **2** probably indicate increased conjugation with the C≡C bonds. Indeed, the intervening C(2)–C(6) and C(5)–C(8) bonds are marginally shorter than the corresponding $C_{sp}-C_{sp^2}$ bonds in tolan⁴⁶ (mean 1.433(3) Å) or 1,4-bis(phenylethynyl)benzene^{4b,12} (mean 1.430(3) Å). Comparison of the C≡C bond lengths is inconclusive, as these distances are not very sensitive

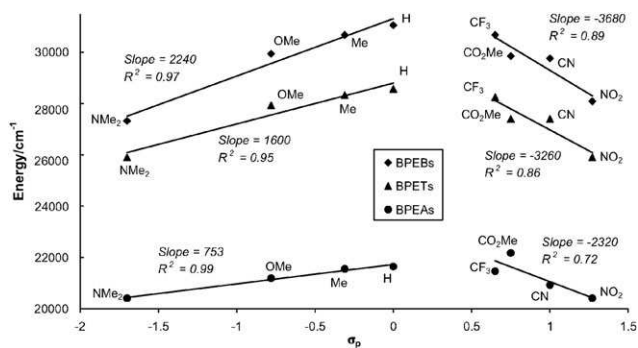


Fig. 5 Plots of absorption maxima vs. Hammett Constant (σ_{p+}/σ_{p-}) for the BPETs, **1a–h**, and the analogous 1,4-bis(*para*-R-phenylethynyl)benzenes (BPEBs) and 9,10-bis(*para*-R-phenylethynyl)anthracenes (BPEAs).

to changes in electronic structure, whilst being rather sensitive to the experimental procedure used to determine them, such as the availability of high-angle reflections.^{46a} DFT calculations (see Table 2) predict much stronger conjugation.

Molecules **1b** and **1h** are nearly planar, as found for the DFT optimised geometries, *vide infra*; the carboxylate groups in **1h** have a mutually *anti*-orientation and are nearly coplanar with the adjacent benzene rings, ii and iii, the dihedral angles being 3.3 and 5.7°, respectively (Fig. 7).

The central thiophene ring inevitably makes the molecular rod non-linear. Indeed, the exocyclic bonds C(2)–C(6) and C(5)–C(8) are not continuations of the bisector lines of the angles S(1)–C(2)–C(3) and S(1)–C(5)–C(4), but deviate from the latter towards the sulfur atom by several degrees. Thus, the

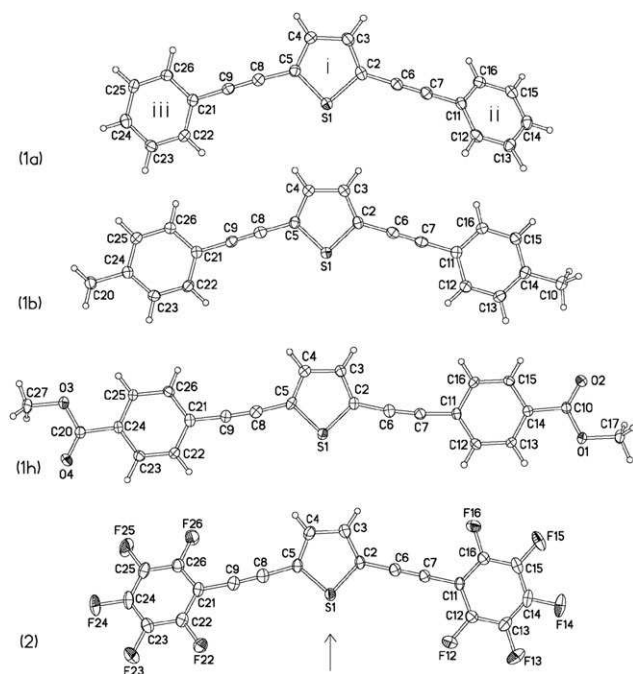


Fig. 6 Molecular structures of **1a**, **1b**, **1h** and **2** (50% thermal ellipsoids). The arrow indicates the approximate 2-fold axis (see Fig. 7).

Table 2 Mean bond distances (Å) and angles (°) between ring planes^a and/or vectors. Calculated distances (DFT, B3LYP, 6-31G*) are italicised

	1a	1b	1h	2
C–S	1.733(3)	1.727(2)	1.729(2)	1.723(2)
C=C	1.758	1.758	1.757	1.758
C(3)–C(4)	1.380(4)	1.378(2)	1.380(3)	1.374(3)
C(2,5)–C≡	1.386	1.386	1.387	1.387
C≡C	1.410(4)	1.405(2)	1.402(3)	1.401(3)
≡C–C(Ph)	1.411	1.411	1.409	1.409
i/ii	1.422(3)	1.422(2)	1.418(3)	1.418(3)
i/iii	1.403	1.403	1.402	1.402
ii/iii	1.204(4)	1.183(2)	1.207(3)	1.192(3)
C(6)≡C(7)/ii	1.219	1.219	1.219	1.217
C(8)≡C(9)/iii	1.443(3)	1.444(2)	1.426(3)	1.425(3)
C(2)–C(6)/C(5)–C(8)	1.422	1.422	1.426(3)	1.425(3)
C(11)–C(14)/C(21)–C(24)	141.1(2)	147.0(2)	175.5(2)	158.7(2)
	33.6	5.8	2.8	4.5
	9.7	5.7	3.4	23.5
	39.2	10.2	3.4	21.9
	9.1	0.9	6.6	0.7
	3.8	0.6	0.8	0.4
	148.6(2)	147.9(2)	153.9(3)	151.6(3)
	141.1(2)	147.0(2)	175.5(2)	158.7(2)

^a For the definition of planes i–iii, see Fig. 6.

angles between the C(2)–C(6) and C(5)–C(8) bonds (148–154°, see Table 2) are considerably smaller than between the bisector lines (*ca.* 157°) mentioned above. Note that this effect is also observed in *unsubstituted* thiophene, where the S(1)–C(2)–H and C(3)–C(2)–H angles are very different (119.9(3) and 128.5(3)°) and the C(2)–H and C(5)–H bonds form an angle of 147.4(3)°.

In **1b**, the acetylenic (–C≡C–) moieties are practically linear, whereas in **1h** they are substantially bent, which results, paradoxically, in the overall *straightening* of the molecule, making the C(11)··C(14) and C(21)··C(24) vectors more co-linear (Table 2). In **1a**, the acetylenic groups are bent to a similar extent but, in contrast with **1h**, out of the thiophene plane, so that no overall straightening occurs. In **1a** and **2**, the phenyl rings adopt considerably unsymmetrical orientations.

The crystal packing motif of **1b** is a longitudinally-slanted infinite stack, in which the adjacent molecules are related by the *b* translation, with a mean interplanar separation of *d* = 3.57 Å. The so-called ‘aromatic slip angle’, θ , between the translation and the normal to the molecular plane, equals 45.5°, so that the C≡C bonds of one molecule overlap with

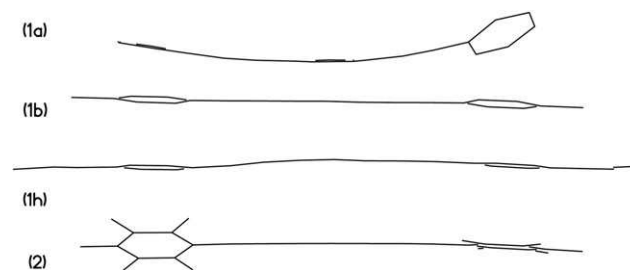


Fig. 7 Molecular structures of **1a**, **1b**, **1h** and **2** viewed down the approximately 2-fold axis of the thiophene ring (→ in Fig. 6). Hydrogen atoms are omitted for clarity.

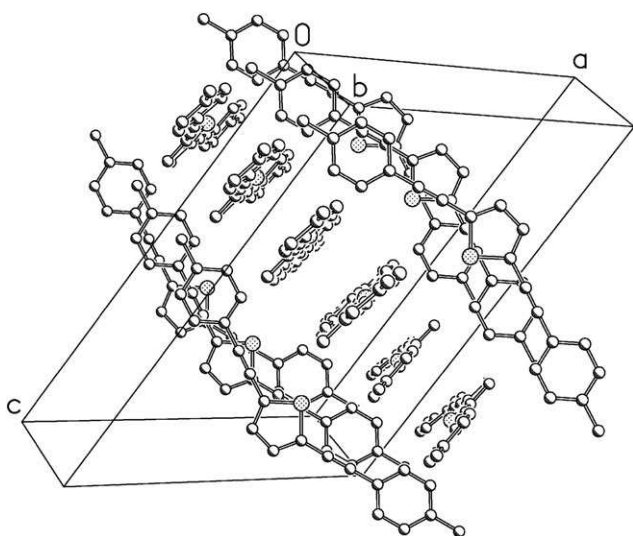


Fig. 8 Crystal packing of **1b** (hydrogen atoms are omitted).

the phenyl and thiophene rings of the next. The stacks are arranged into a layer parallel to the (1 0 $\bar{2}$) plane (Fig. 8). The adjacent layers, related by the screw axis, are obviously parallel, and the directions of the stacks in these layers, [1 0 0], are also parallel. However, both the mean planes and the long axes of the molecules belonging to adjacent layers are practically perpendicular (angles 89 and 88°, respectively). The packing of **2** is similar, albeit that in this case, the stacked molecules are related by the *a* translation, with $d = 3.49$ Å and $\theta = 45.0^\circ$. The planes of molecules belonging to adjacent layers form an angle of 75°, and their long axes are staggered by 85°. In **1a**, the corresponding angles are 70 and 85°, but the intra-stack slip is larger ($\theta = 54.9^\circ$) and more laterally directed. Thus, the overlap of molecules within a 'stack' (generated, as in **1b**, by the *b* translation) is actually slight, even though *d* is as short as 3.30 Å. In contrast, the more linear molecules of **1h** pack in a slanted herringbone manner into a layer, in which the planes of contacting molecules meet at a 45° angle (Fig. 9). The long axes of all molecules within a layer are parallel to one another and inclined by *ca.* 24° to the crystallographic axis *a*, which is normal to the mean plane of the layer.

DFT calculations on **1a–h** and **2**

We have performed DFT and TD-DFT calculations on all of the BPETs using the B3LYP functional and the 6-31G* basis

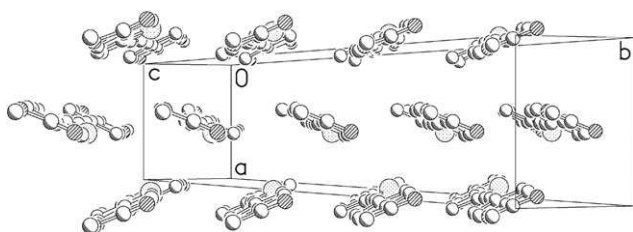


Fig. 9 Crystal packing of **1h**, viewed down the long axis of the molecule.

set, as defined in Gaussian03,⁴⁷ for all atoms. Geometries were optimised for all compounds, and in all cases, a coplanar arrangement of the aryl and thiophene rings was found to be the lowest in energy, as has been observed previously for BPEBs.^{13,15b} Details of the computed bond distances for compounds **1a,b,h** and **2** are given in Table 2, for comparison with the experimental values determined from the X-ray diffraction experiments. All of the computed distances are within 1.5% of their experimental counterparts, and most are within 1%. We also performed vibration frequency calculations on all of the optimised geometries, indicating that they are indeed minima. The frequency calculations also allowed us to assign the compounds' absorptions in their IR and Raman spectra, especially the symmetric stretching mode of the two C≡C units, which gives rise to a strong band in each of the Raman spectra, and its asymmetric counterpart, which leads to a strong band in the IR spectra. We note that the correction factor for the calculated frequencies in both the IR and Raman spectra is 0.96 in all cases, in excellent agreement with that normally observed for DFT calculations with this combination of functional and basis set.⁴⁸ Even though the compounds all have C_{2v} geometries, and thus lack inversion centres, due to the nature of the angles that the C≡C vectors make with the thienyl rings, there is clearly little change in dipole moment for the symmetric C≡C stretching mode and little change in polarisability for the asymmetric C≡C stretching mode, as these bands are predicted to be very weak in the IR and Raman spectra, respectively, and are not observed experimentally. Also of interest is the fact that the two bands are calculated to be *ca.* 10 cm⁻¹ apart, with the IR-active asymmetric stretching mode always being predicted to be at a slightly higher energy. However, in the experimental spectra, these bands are almost coincident in energy, within experimental error. Although we have not computed barriers to rotation about the C_{aryl}–C_{alkynyl} bonds, these are expected to be quite small in both solution and the gas phase, again, in line with what has been found previously for BPEBs,¹³ and consistent with the fact that various torsion angles (up to 33.6°, see Table 2) are observed in the solid-state structures, *vide supra*. The frequency calculations show very low energy modes corresponding to this rotational motion, as well as to a bending mode which changes the angle between the two C≡C vectors.

Gas phase TD-DFT calculations permitted assignment of the lowest energy allowed $S_1 \leftarrow S_0$ electronic absorptions in the UV-vis spectra to the HOMO–LUMO transition in all cases, and these are predicted to have large oscillator strengths ($f = ca.$ 1.5–1.9), corresponding to the observed large extinction coefficients, which are in the range *ca.* 33 000–52 000 mol⁻¹ cm⁻¹ dm³ (Table 1). The calculated $S_1 \leftarrow S_0$ absorptions are 41–45 nm red-shifted from the observed values of λ_{max} for **1a–e** and **2**, and 65, 55 and 56 nm red-shifted for **1f–h**, respectively, which is a result of the increased π -conjugation in the planar structures found in the calculations. In solution, nearly free rotation around the C≡C bonds leads to Frank–Condon absorption arising from a weighted average of all rotamers.^{13,15b} Thus, it is known^{13,15b} that at ambient temperature, the observed absorption profile is blue-shifted due to the presence of rotational isomers, in which the $S_1 \leftarrow S_0$

transition energies increase with the torsion angle between adjacent rings. Note that π -conjugation falls off with $\cos^2\theta$. However, the positions of the 0,0 transitions can be estimated from the absorption and emission spectra. Low temperature spectra of **1a** reveal the presence of an intense 0,0 transition of the planar conformation, which is virtually coincident with the emission maximum; in non-polar solvents, the 0,0 bands show a negligible Stokes shift.³⁹ Thus, in Table 1, we collect the observed transition energies in solution (using the emission maxima), along with those calculated from the TD-DFT studies in the gas phase. The observed and calculated values are generally in good agreement, with the observed values typically being 600–900 cm^{-1} (ca. 3–4%) higher in energy than the calculated ones. The notable exceptions are the NMe_2 compound, **1e**, for which the observed value is actually 300 cm^{-1} lower in energy than the calculated one, and the NO_2 compound, **1f**, for which the observed value is 1400 cm^{-1} higher in energy than the observed value. These larger discrepancies could well be a result of solvation effects, which are more important for the cases wherein there is a larger degree of charge transfer, *vide infra*. We note that a TD-DFT calculation on **1f**, in which both nitrophenyl groups have been rotated by 45° (in the same direction), leads to a 10 nm blue shift in the absorption energy, along with a reduction in the oscillator strength. In contrast, rotating one of the nitrophenyl groups by 90° leads to a 44 nm blue shift. Interestingly, when both nitrophenyl groups are rotated by 90°, effectively decoupling their π -systems from the diethynylthiophene core, the HOMO–LUMO transition has an oscillator strength of 0 and the lowest energy absorption is shifted by 133 nm. The conjugation effect is smaller for the donor-substituted and weakly acceptor-substituted systems than it is for the strong acceptor compounds, increasing with acceptor strength. This is also in keeping with the steeper slopes of the Hammett plots for the acceptors compared to the donors shown in Fig. 6. There is no significant charge transfer evident in the $S_1 \leftarrow S_0$ transition of the parent compound **1a** (see HOMO and LUMO in Fig. 10). In contrast, some degree of charge transfer is evident for the donor cases, wherein the HOMO has a significant contribution from the *para*-substituent, whereas the LUMO is more localised in the centre of the molecule (e.g. NMe_2 compound **1e** in Fig. 10). Likewise, for the acceptors (e.g. NO_2 compound **1f** in Fig. 10), we see the inverse charge transfer, with the HOMO being more localised at the centre of the molecule and the LUMO having significant NO_2 character. We confirmed the charge transfer by computing the contributions of each moiety (thienylene, ethynyl, phenylene and *para*-substituent) to the HOMO and LUMO. Consistent with this is the small red shift (7 nm) in the absorption maximum for **1f** when the solvent is changed from toluene to CH_2Cl_2 , although the emission maximum red-shifts by 112 nm, giving rise to a large Stokes shift of 7100 cm^{-1} in CH_2Cl_2 , indicating a substantial electronic/structural reorganisation in the singlet excited state prior to emission, especially in more polar solvents, which are capable of better stabilising the accompanying charge redistribution. Further details on the structure of the excited state of **1a** and its photophysics (in both singlet and triplet states) can be found in a companion paper.³⁹

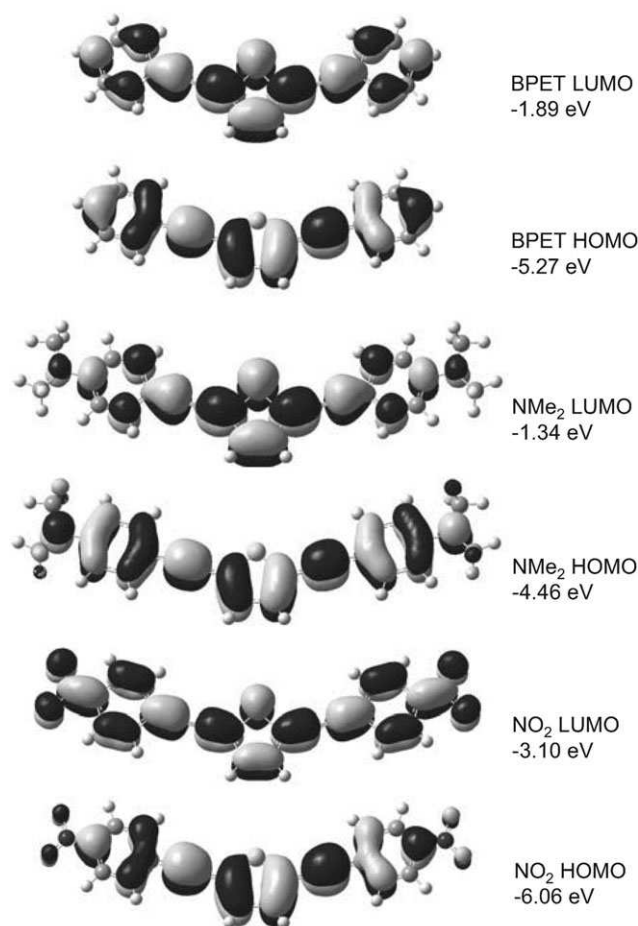


Fig. 10 Plots of the HOMO and LUMO for compounds **1a** (BPET), **1e** (NMe_2) and **1f** (NO_2), and their respective energies.

Conclusions

We have shown that the Pd/Cu-catalysed Sonogashira cross-coupling methodology provides a convenient route to a series of *para*-substituted 2,5-bis(phenylethynyl)thiophenes. These chromophores show interesting photophysical properties, which have been studied in solution at room temperature. The presence of strong donors or acceptors is found to red-shift both the absorption and emission bands. The compounds have the moderate quantum yields and short singlet lifetimes characteristic of rapid intersystem crossing to the triplet state.³⁶

Experimental

General

All reactions were performed under dry nitrogen using standard Schlenk techniques. The amine solvents used in syntheses were dried over CaH_2 and distilled under dry nitrogen. Reagents purchased from commercial suppliers were tested for purity by GC-MS before use. Ethynylbenzenes were synthesised by literature methods,⁴⁹ except for phenylacetylene, which was purchased from Aldrich. Crude yields of ca. $80 \pm 15\%$ were typical. As we required high purities for

spectroscopic measurements, the yields reported here are of analytically pure material, obtained after one or more recrystallisations.

Reactions were monitored *in situ* by GC-MS or by TLC to assure the complete disappearance of 2,5-diiodothiophene prior to workup. GC-MS analyses were performed on an Agilent Technologies 6890 N gas chromatograph equipped with a 5973 inert mass selective detector and a 10 m fused silica capillary column (5% cross-linked phenylmethylsilicone) under the following operating conditions: injector temperature 250 °C, detector temperature 300 °C, the oven temperature was ramped from 70 to 280 °C at 20 °C min⁻¹. UHP helium was used as the carrier gas. NMR spectra were recorded in CDCl₃ on Varian Mercury-200, Unity-300 and Inova-500, and Bruker Avance-400 spectrometers at the following frequencies: ¹H: 200, 300 and 400 MHz, ¹³C{¹H}: 100 and 126 MHz, ¹⁹F{¹H}: 188 MHz. ¹³C NMR assignments were made with the assistance of HSQC and HMBC experiments. Mass spectra for compounds **1a–d**, **1g** and **2** were obtained on a Thermo Finnigan Trace MS spectrometer operating in EI mode. Spectra for **1e**, **1f** and **1i** were obtained on a Thermo Finnigan DSQ spectrometer operating in EI mode. Elemental analyses were performed using an Exeter Analytical E440 machine by departmental services at Durham University. Melting point values were measured on a Stuart Scientific SM3 apparatus. IR spectra were recorded as KBr disks using a Perkin-Elmer Spectrum 100 series FT-IR spectrometer. Raman spectra were recorded on solid samples using a Horiba Jobin Yvon Lab-RamHR Raman microscope with the laser set at 785 nm.

UV-vis, fluorescence spectra, lifetime and quantum yield measurements were recorded in toluene if not indicated otherwise. UV-vis absorption spectra and extinction coefficients were obtained on a Hewlett-Packard 8453 diode array spectrophotometer using standard 1 cm width quartz cells. Fluorescence spectra and quantum yield measurements were recorded on a Horiba Jobin Yvon Fluorolog FL 3-22 Tau spectrophotometer. The spectra of dilute solutions, with absorbance maxima of less than 0.1, were recorded using a conventional 90° geometry. The emission spectra were fully corrected using the manufacturer's correction curves for the spectral response of the emission optical components. The quantum yield of each compound was estimated by comparing it with standards of known quantum yield. The absorbance of the sample was kept below 0.12 to avoid inner filter effects, and all measurements were carried out at room temperature. The fluorescence quantum yields of compounds **1a–d**, **1g**, **1i** and **2** were measured against 1,4-di-(5-phenyl-1,3-oxazole-2-yl)-benzene (PO-POP) in cyclohexane ($\Phi = 0.97$)⁵⁰ and quinine sulfate in 0.1 M H₂SO₄ ($\Phi = 0.54$)⁵⁰ and that of **1e** and **1f** were measured against norharmane in 0.1 M H₂SO₄ ($\Phi = 0.58$)⁵¹ and 9,10-diphenylanthracene in C₆H₁₂ ($\Phi = 0.9$)⁵⁰. The fluorescence lifetimes of **1a–e**, **1g**, **1i** and **2** were measured by time-correlated single photon counting (TCSPC) using either a 396 nm pulsed laser diode or the 3rd harmonic of a cavity-dumped, mode-locked Ti-sapphire laser (Coherent MIRA, 300 nm). The fluorescence emission was collected at right angles to the excitation source, with the emission wavelength selected using a monochromator and detected by a single photon avalanche diode (SPAD). The instrument response function was mea-

sured using a dilute LUDOX[®] suspension as the scattering sample, setting the monochromator at the emission wavelength of the laser, giving an instrument response function (IRF) of 200 or 100 ps at 396 or 300 nm, respectively. The resulting intensity decay was a convolution of the fluorescence decay with the IRF, and iterative deconvolution of the IRF with a decay function and non-linear least-squares analysis were used to analyse the convoluted data.^{50,52,53}

Syntheses

2,5-Bis(phenylethynyl)thiophene (1a). The compounds 2,5-diiodothiophene (0.67 g, 2.00 mmol), Pd(PPh₃)₂Cl₂ (0.03 g, 0.04 mmol) and CuI (0.008 g, 0.04 mmol) were added to a Schlenk flask that had been evacuated and refilled with nitrogen three times. Dry, de-gassed NEt₃ (50 mL) was added *via* a cannula. Phenylacetylene (0.43 g, 4.20 mmol) was then added under a positive pressure of nitrogen and the reaction mixture was stirred at room temperature for 72 h. The NEt₃ solvent was then removed *in vacuo*. The residual solid was applied to the top of a 5 cm silica gel column eluted with hot toluene. The toluene was removed *in vacuo* and the product was recrystallised from a toluene/hexane solution. Yield of analytically pure material 0.15 g (26%), m.p. 83.9–84.5 °C. IR (/cm⁻¹) 1595 (arene ring), 2199 (C≡C, asym). Raman (/cm⁻¹) 1445, 1595 (arene ring), 2198 (C≡C, sym). ¹H NMR (400 MHz): δ 7.54 (m, 4 H, CH_{arom}), 7.36 (m, 6 H, CH_{arom}), 7.17 (s, 2 H, CH_{thiophene}). ¹³C{¹H} NMR (100 MHz): δ 131.82 (C_{thio}), 131.50 (C_{arom}), 128.67 (C_{arom}), 128.42 (C_{arom}), 124.68 (C_{thio}), 122.63 (C_{arom}), 94.07 (C≡C), 82.28 (C≡C). MS (EI): *m/z* 284. Anal. calc. for C₂₀H₁₂S: C, 84.47; H, 4.25. Found: C, 84.09; H, 4.14%.

2,5-Bis(para-methylphenylethynyl)thiophene (1b). The compounds 2,5-diiodothiophene (0.67 g, 2.00 mmol), Pd(PPh₃)₂Cl₂ (0.03 g, 0.04 mmol) and CuI (0.008 g, 0.04 mmol) were added under nitrogen to a Schlenk flask. Dry, de-gassed NEt₃ (50 mL) was added *via* a cannula. 4-Methylphenylacetylene (0.49 g, 4.20 mmol) was then added under a positive pressure of nitrogen. The reaction mixture was stirred at room temperature for 24 h and the NEt₃ was then removed *in vacuo*. The residual solid was applied to the top of a 5 cm silica gel column eluted with 1 : 1 CH₂Cl₂/hexane, and the solvent was removed *in vacuo*. Analytically pure product was obtained as a red crystalline solid after recrystallisation from a hot hexane/toluene solution. Yield 0.17 g (27%), m.p. 167.9–168.2 °C. IR (/cm⁻¹) 1530 (arene ring), 2192 (C≡C, asym). Raman (/cm⁻¹) 1438, 1604, (arene ring), 2195 (C≡C, sym). ¹H NMR (200 MHz): δ 7.43 (d, *J* = 8 Hz, 4 H, CH_{arom}), 7.17 (d, *J* = 8 Hz, 4 H, CH_{arom}), 7.14 (s, 2 H, CH_{thiophene}), 2.38 (s, 6 H, CH₃). ¹³C{¹H} NMR (100 MHz): δ 138.89 (C_{arom}), 131.56 (C_{thio}), 131.39 (C_{arom}), 129.18 (C_{arom}), 124.69 (C_{thio}), 119.57 (C_{arom}), 94.19 (C≡C), 81.71 (C≡C), 21.54 (CH₃). MS (EI): *m/z* 312. Anal. calc. for C₂₂H₁₆S: C, 84.57; H, 5.16. Found: C, 84.68; H, 5.16%.

2,5-Bis(para-methoxyphenylethynyl)thiophene (1c). The compounds 2,5-diiodothiophene (0.67 g, 2.00 mmol), Pd(PPh₃)₂Cl₂ (0.03 g, 0.04 mmol) and CuI (0.008 g, 0.04 mmol) were added under nitrogen to a Schlenk flask. Dry,

de-gassed NEt_3 (50 mL) was added *via* a cannula and 4-methoxyphenylacetylene (0.55 g, 4.20 mmol) was then added under a positive pressure of nitrogen. The reaction mixture was stirred at room temperature for 72 h and the NEt_3 was then removed *in vacuo*. The residual solid was added to the top of a 5 cm silica gel column eluted with 1 : 1 CH_2Cl_2 /hexane. The solvents were removed *in vacuo*. Recrystallisation of the crude product from hot toluene/ CH_2Cl_2 gave a bright yellow, analytically pure solid. Yield: 0.23 g, (34%), m.p. 119.6–122.4 °C. IR (cm^{-1}) 1602 (arene ring), 2198 ($\text{C}\equiv\text{C}$, asym). Raman (cm^{-1}) 1441, 1607 (arene ring), 2197 ($\text{C}\equiv\text{C}$, sym). ^1H NMR (200 MHz): δ 7.46 (d, $J = 9$ Hz, 4 H, CH_{arom}), 7.11 (s, 2 H, $\text{CH}_{\text{thiophene}}$), 6.88 (d, $J = 9$ Hz, 4 H, CH_{arom}), 3.84 (s, 6 H, OCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz): δ 159.95 (C_{arom}), 133.03 (C_{arom}), 131.33 (C_{thio}), 124.64 (C_{thio}), 114.75 (C_{arom}), 114.10 (C_{arom}), 93.95 ($\text{C}\equiv\text{C}$), 81.11 ($\text{C}\equiv\text{C}$), 55.33 (OCH_3). MS (EI): m/z 344. Anal. calc. for $\text{C}_{22}\text{H}_{16}\text{O}_2\text{S}$: C, 76.72; H, 4.68. Found: C, 76.52; H, 4.65%.

2,5-Bis(*para*-trifluoromethylphenylethynyl)thiophene (1d).

The compounds 2,5-diiodothiophene (0.67 g, 2.00 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.03 g, 0.04 mmol) and CuI (0.008 g, 0.04 mmol) were added under nitrogen to a Schlenk flask. Dry, de-gassed NEt_3 (50 mL) was added *via* a cannula and 4-trifluoromethylphenylacetylene (0.72 g, 4.20 mmol) was then added under a positive pressure of nitrogen. The reaction mixture was stirred at room temperature for 94 h and the NEt_3 was then removed *in vacuo*. The residual solid was added to the top of a 5 cm silica gel column eluted with hexane and the solvent was removed *in vacuo*. The solid was recrystallised from a small amount of hot hexane to give a yellow, analytically pure, crystalline solid. Yield: 0.50 g (60%), m.p. 107.8–112.2 °C. IR (cm^{-1}) 1609 (arene ring), 2197 ($\text{C}\equiv\text{C}$, asym). Raman (cm^{-1}) 1442, 1617 (arene ring), 2202 ($\text{C}\equiv\text{C}$, sym). ^1H NMR (200 MHz): δ 7.62 (s, 8 H, CH_{arom}), 7.23 (s, 2 H, $\text{CH}_{\text{thiophene}}$). $^{19}\text{F}\{^1\text{H}\}$ NMR (188 Hz): δ -63.28 (s, 6 F, CF_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz): δ 132.88 (C_{thio}), 131.91 (C_{arom}), 130.57 (q, $J_{\text{CF}} = 33$ Hz, C_{arom}), 126.53 (C_{arom}), 125.62 (q, $J_{\text{CF}} = 3$ Hz, C_{arom}), 124.83 (C_{thio}), 124.10 (q, $J_{\text{CF}} = 272$ Hz, CF_3), 92.95 ($\text{C}\equiv\text{C}$), 84.41 ($\text{C}\equiv\text{C}$). MS (EI): m/z 420. Anal. calc. for $\text{C}_{22}\text{H}_{10}\text{F}_6\text{S}$: C, 62.86; H, 2.40. Found: C, 62.65; H, 2.39%.

2,5-Bis(*para-N,N*-dimethylaminophenylethynyl)thiophene (1e).

The compounds 2,5-diiodothiophene (0.58 g, 1.72 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.024 g, 0.034 mmol) and CuI (0.006 g, 0.034 mmol) were added under nitrogen to a Schlenk flask. Dry, de-gassed NEt_3 (50 mL) was added *via* a cannula and 4-*N,N*-dimethylaminophenylacetylene (0.53 g, 3.62 mmol) was then added under a positive pressure of nitrogen. The reaction mixture was stirred at room temperature for 96 h and the NEt_3 was then removed *in vacuo*. The residual solid was added to the top of a 5 cm alumina pad, which was first eluted with hexane (150 ml) to remove any unreacted starting materials. The column was eluted with 1 : 4 CH_2Cl_2 /hexane and the solvents were then removed *in vacuo*. The product was recrystallised from CH_2Cl_2 /hexanes to yield a bright yellow solid. Yield 0.25 g (39%), m.p. 194.4–198.0 °C. IR (cm^{-1}) 1531, 1605 (arene ring), 2194 ($\text{C}\equiv\text{C}$, asym). Raman (cm^{-1}) 1257,

1452, 1609 (arene ring), 2192 ($\text{C}\equiv\text{C}$, sym). ^1H NMR (300 MHz): δ 7.39 (d, $J = 9$ Hz, 4 H, CH_{arom}), 7.05 (s, 2 H, $\text{CH}_{\text{thiophene}}$), 6.65 (d, $J = 9$ Hz, 4 H, CH_{arom}), 3.00 (s, 12 H, $\text{N}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz): δ 150.46 (C_{arom}), 132.89 (C_{arom}), 130.98 (C_{thio}), 124.90 (C_{thio}), 111.98 (C_{arom}), 109.52 (C_{arom}), 95.29 ($\text{C}\equiv\text{C}$), 80.78 ($\text{C}\equiv\text{C}$), 40.41 ($\text{N}(\text{CH}_3)_2$). MS (EI): m/z 370. Anal. calc. for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{S}$: C, 77.80; H, 5.98; N, 7.56. Found: C, 77.29; H, 5.91; N, 7.57%.

2,5-Bis(*para*-nitrophenylethynyl)thiophene (1f). The compounds 2,5-diiodothiophene (1.34 g, 4.00 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.056 g, 0.08 mmol) and CuI (0.015 g, 0.08 mmol) were added under nitrogen to a Schlenk flask. Dry, de-gassed NEt_3 (50 mL) was added *via* a cannula and 4-nitrophenylacetylene (1.24 g, 8.40 mmol) was then added under a positive pressure of nitrogen. The reaction mixture was stirred at room temperature for 72 h and the NEt_3 was then removed *in vacuo*. The residual solid was added to the top of a 5 cm silica gel column eluted with 1 : 1 CH_2Cl_2 /hexane and the solvents were removed *in vacuo*. Analytically pure product was obtained as a gold coloured solid after two recrystallisations from hot toluene. Yield: 0.84 g (56%), m.p. 193.9–195.6 °C. IR (cm^{-1}) 1333 (NO_2 , asym), 1511, 1591 (arene ring), 2200 ($\text{C}\equiv\text{C}$, asym). Raman (cm^{-1}) 1329 (NO_2 , sym), 1589 (arene ring), 2195 ($\text{C}\equiv\text{C}$, sym). ^1H NMR (200 MHz): δ 8.25 (d, $J = 9$ Hz, 4 H, CH_{arom}), 7.68 (d, $J = 9$ Hz, 4 H, CH_{arom}), 7.28 (s, 2 H, $\text{CH}_{\text{thiophene}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz): δ 147.30 (C_{arom}), 133.23 (C_{thio}), 132.14 (C_{arom}), 129.25 (C_{arom}), 124.72 (C_{thio}), 123.75 (C_{arom}), 92.83 ($\text{C}\equiv\text{C}$), 87.10 ($\text{C}\equiv\text{C}$). MS (EI): m/z 374. Anal. calc. for $\text{C}_{20}\text{H}_{10}\text{N}_2\text{O}_4\text{S}$: C, 64.16; H, 2.69; N, 7.48. Found: C, 64.19; H, 2.63; N, 7.35%.

2,5-Bis(*para*-cyanophenylethynyl)thiophene (1g). The compounds 2,5-diiodothiophene (0.67 g, 2.00 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.03 g, 0.04 mmol) and CuI (0.008 g, 0.04 mmol) were added under nitrogen to a Schlenk flask. Dry, de-gassed NHET_2 (50 mL) was added *via* a cannula and 4-cyanophenylacetylene (0.53 g, 4.20 mmol) was then added under a positive pressure of nitrogen. The reaction mixture was stirred at room temperature for 63 h and the NHET_2 was removed *in vacuo*. The residual solid was added to the top of a 5 cm silica gel column eluted with 1 : 1 CH_2Cl_2 /hexane and the solvents were removed *in vacuo*. Analytically pure product was obtained as a tan solid after two recrystallisations from hot toluene. Yield: 0.23 g (34%), m.p. 250.6–252.6 °C. IR (cm^{-1}) 1597 (arene ring), 2202 ($\text{C}\equiv\text{C}$, sym), 2226 ($\text{C}\equiv\text{N}$, sym). Raman (cm^{-1}) 1436, 1602 (arene ring), 2197 ($\text{C}\equiv\text{C}$, asym). ^1H NMR (200 MHz): δ 7.63 (m, 8 H, CH_{arom}), 7.24 (s, 2 H, $\text{CH}_{\text{thiophene}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz): δ 132.99 (C_{thio}), 132.13 (C_{arom}), 131.90 (C_{arom}), 127.31 (C_{arom}), 124.63 (C_{thio}), 118.33 ($\text{C}\equiv\text{N}$), 112.03 (C_{arom}), 92.89 ($\text{C}\equiv\text{C}$), 86.24 ($\text{C}\equiv\text{C}$). MS (EI): m/z 334. Anal. calc. for $\text{C}_{22}\text{H}_{10}\text{N}_2\text{S}$: C, 79.02; H, 3.01; N, 8.38. Found: C, 78.77; H, 2.98; N, 8.16%.

2,5-Bis(*para*-carbomethoxyphenylethynyl)thiophene (1h).

The compounds 2,5-diiodothiophene (0.67 g, 2.00 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.03 g, 0.04 mmol) and CuI (0.008 g, 0.04 mmol) were added under nitrogen to a Schlenk flask. Dry, de-gassed NEt_3 (50 mL) was added *via* a cannula and 4-carbomethoxyphenylacetylene (0.67 g, 4.20 mmol) was then

Table 3 Crystal data^a

Compound	1a	1b	1h	2
CCDC no.	641166	641167	641168	641169
Formula	C ₂₀ H ₁₂ S	C ₂₂ H ₁₆ S	C ₂₄ H ₁₆ O ₄ S	C ₂₀ H ₂ F ₁₀ S
Formula weight	284.38	312.41	400.43	464.28
T/K	120	120	120	120
Symmetry	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group (no.)	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>Pca</i> 2 ₁ (#29)	<i>P</i> 2 ₁ / <i>n</i> (#14)
<i>a</i> /Å	14.752(1)	16.072(2)	7.1798(8)	4.9212(7)
<i>b</i> /Å	5.7461(2)	5.0902(5)	45.453(4)	31.274(4)
<i>c</i> /Å	17.339(1)	21.234(2)	5.8879(4)	11.3413(15)
β /°	90.87(1)	112.22(1)	90	101.83(1)
<i>V</i> /Å ³	1469.6(1)	1608.1(3)	1921.5(3)	1708.4(4)
<i>Z</i>	4	4	4	4
μ /mm ⁻¹	0.21	0.20	0.20	0.30
Reflections collected	9135	17948	19478	16756
Unique reflections	3365, 2098 ^b	4255, 3243 ^b	4881, 4505 ^b	3921, 3129 ^b
<i>R</i> _{int}	0.067	0.048	0.033	0.039
<i>R</i> (<i>F</i>) ^b	0.050	0.046	0.046	0.047
<i>wR</i> (<i>F</i> ²)	0.127	0.109	0.116	0.110

^a For crystallographic data in CIF or other electronic format see DOI: 10.1039/b701172e ^b Reflections with $F^2 > 2\sigma(F^2)$.

added under a positive pressure of nitrogen. The reaction mixture was stirred at room temperature for 66 h and then heated at 80 °C for 2 h. The NEt₃ was then removed *in vacuo*. The residual solid was added to the top of a 5 cm silica gel column eluted with 1 : 1 CH₂Cl₂/hexane and the solvents were removed *in vacuo*. Analytically pure product was isolated as a pale yellow solid after recrystallisation from hot toluene/hexane solution. Yield: 0.40 g (50%), m.p. 201.5–202.5 °C. IR (/cm⁻¹) 1602 (arene ring), 1717 (C=O, asym), 2191 (C≡C, asym). Raman (/cm⁻¹) 1448, 1607 (arene ring), 1717 (C=O, sym), 2197 (C≡C, sym). ¹H NMR (200 MHz): δ 8.03 (d, *J* = 8 Hz, 4 H, CH_{arom}), 7.58 (d, *J* = 8 Hz, 4 H, CH_{arom}), 7.21 (s, 2 H, CH_{thiophene}), 3.94 (s, 6 H, CO₂Me). ¹³C{¹H} NMR (100 MHz): δ 166.42 (CO₂), 132.54 (C_{thio}), 131.35 (C_{arom}), 129.91 (C_{arom}), 129.59 (C_{arom}), 127.16 (C_{arom}), 124.73 (C_{thio}), 93.66 (C≡C), 85.02 (C≡C), 52.26 (CH₃). MS (EI): *m/z* 401. Anal. calc. for C₂₄H₁₆O₄S: C, 71.98; H, 4.03. Found: C, 71.77; H, 3.96%.

2,5-Bis(pentafluorophenylethynyl)thiophene (2). The compounds 2,5-diiodothiophene (0.67 g, 2.00 mmol), Pd(PPh₃)₂Cl₂ (0.03 g, 0.04 mmol) and CuI (0.008 g, 0.04 mmol) were added under nitrogen to a Schlenk flask. Dry, de-gassed NEt₃ (50 mL) was added *via* a cannula and pentafluorophenylacetylene (0.81 g, 4.20 mmol) was then added under a positive pressure of nitrogen. The reaction mixture was stirred at room temperature for 24 h and the NEt₃ was then removed *in vacuo*. The residual solid was added to the top of a 5 cm silica gel column eluted with 1 : 1 CH₂Cl₂/hexane and the solvents were removed *in vacuo*. The product was recrystallised from a hot hexane/toluene solution to give the analytically pure material as large yellow crystals. Yield 0.39 g, (42%), m.p. 153.7–156.1 °C. IR (/cm⁻¹) 1532 (arene ring), 2218 (C≡C, asym). Raman (/cm⁻¹) 1424 (arene ring), 2217 (C≡C, sym). ¹H NMR (200 MHz): δ 7.32 (s, 2 H, CH_{thiophene}). ¹⁹F{¹H} NMR (188 MHz): δ -135.70 (m, 4 F, CF_{arom}), -151.64 (t, ³*J*_{FF} = 21 Hz, 2 F, CF_{arom}), -161.66 (m, 4 F, CF_{arom}). ¹³C{¹H} NMR (126 MHz): δ 147.21

(d, *J*_{CF} = 242 Hz, C_{arom}), 142.08 (d, *J*_{CF} = 258 Hz, C_{arom}), 140.90 (d, *J*_{CF} = 252 Hz, C_{arom}), 133.85 (C_{thio}), 124.51 (C_{thio}), 99.87 (t, *J* = 13 Hz, C_{arom}), 93.67 (C≡C), 78.70 (C≡C). MS (EI): *m/z* 464. Anal. calc. for C₂₀H₂F₁₀S: C, 51.74; H, 0.43. Found: C, 51.55; H, 0.48%.

X-Ray crystallography

Single-crystal diffraction experiments (Table 3) were carried out on Bruker three-circle diffractometers with CCD area detectors SMART 1 K or, for **1h**, SMART 6 K, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) and Cryostream (Oxford Cryosystems) open-flow N₂ cryostats. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 on all data using SHELXTL software.⁵⁴ Non-hydrogen atoms were refined in anisotropic and hydrogen atoms in isotropic approximations.

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