Heteroaryl functionalised diacetylenes: preparation and solid-state reactivity

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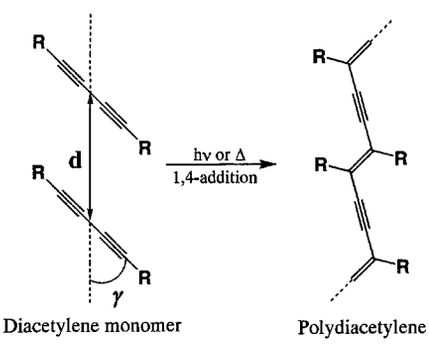
Diacetylenes are known to undergo solid-state topochemical polymerisation to give polydiacetylenes. The reactivity of the monomer is controlled by the arrangement of the molecules in the crystal lattice wherein certain parametric conditions must be met for 1,4-addition to proceed. In the present paper, we investigated the structure–reactivity relationship of a class of diacetylene monomers. Heteroaryl moieties such as thiophene, benzo[*b*]thiophene and quinoline as one or both directly bound side groups of a diacetylene backbone were used. Thus various symmetrical as well as unsymmetrical diacetylenes were prepared and characterised. The solid-state polymerisation behaviour of these diacetylenes was studied in the light of their single-crystal X-ray structure. It was found that in order to react in the solid state, the diacetylenes must have the required lattice parameters. However, even when the required lattice parameters are met, the diacetylene monomers do not necessarily undergo solid-state 1,4-addition polymerisation, implying the existence of further controlling factors to determine reactivity.

Introduction

Substituted diacetylenes (DAs) undergo 1,4-addition reaction in the solid state to give polydiacetylenes (PDAs).[1] The reaction can be initiated thermally, photochemically or by γ-irradiation. The reaction is topochemically controlled wherein the packing arrangements of the molecules in the monomer crystal lattice must satisfy the requirements for solid-state polymerisation (Scheme 1).[2] The polymer PDA has a quasi-one-dimensional structure with long effective conjugation length. This, in turn, makes it a potential candidate for nonlinear optical material with high and fast $\chi^{(3)}$ response.[3] The long conjugated backbone also gives them excellent thermochromic properties.[4] Consequently, solid-state polymerisation is an area of research interest for many scientists around the world. There have been a lot of studies, both theoretical as well as experimental, to predict the solid-state polymerisation of diacetylenes.[5–8] However, the biggest hurdle in this area of research is to get monomers which can be obtained in proper crystal lattice geometry suitable for polymerisation to PDAs. Numerous diacetylenes have been prepared but only a few of them undergo 1,4-addition reaction. Moreover, even when they do react, the polymer formed may not exhibit the desired properties. For example, the polymer may not be able to maintain crystallinity while transforming from the monomer.

Since the packing arrangement of a diacetylene monomer is the determining factor for its solid-state reactivity, manipulation of this to promote reactivity is most desired. In disubstituted diacetylenes, the only possible variations which can be effected, as far as molecular engineering is concerned, are manipulation of the side groups. We have been investigating the aspect of structure–reactivity relationships of diacetylenes toward solid-state polymerisation. One class of diacetylenes, which we have been investigating, consists of aryl and heteroaryl moieties directly bound to the diacetylene backbone.[9,10] The synthesis of diacetylene monomers with conjugated side groups has attracted interest for a long time and a few reports are also available in the literature.[11–14] The design of such diacetylenes has been based on the premise that the aromatic side group will, in suitable cases, help the backbone conjugation to extend further to provide longer effective conjugation length. The heteroaryl moiety, by virtue of its aromatic interactions with adjacent molecules, enhances the probability that the monomer would stack appropriately in the crystal for topochemical polymerisation. As will be discussed in the following sections, this strategy led us to obtain reactive as well as unreactive diacetylenes. Reactivity or lack of it has been examined in relation to molecular packing arrangements in the diacetylene crystals using the crystal-packing information obtained from X-ray single-crystal structure analysis of the monomer diacetylenes.



Scheme 1 Topochemical solid-state polymerisation of diacetylene by 1,4-addition. When the monomer in the crystal has the appropriate geometry, where the distance *d* and angle *γ* are about 5 Å and 45°, respectively, it can be polymerised *via* topochemical 1,4-addition.

Results and discussion

The monomers were prepared following Scheme 2 and Scheme 3. The solid-state reactivity of all seven monomers synthesised are summarised in Table 1. As can be seen, compound **4d** shows solid-state reactivity and undergoes 1,4-addition reaction to give blue coloured PDA. The rest of the monomers do not undergo 1,4-addition reaction in the solid state.

The X-ray diffraction studies of single crystals of five diacetylenes, namely compounds **4a**,[15] **4c**,[16] **4d**,[17] **6a**[18] and **7a**[19] have been carried out in order to probe the reactivity or unreactivity of the DAs towards topochemical 1,4-addition. The results of single-crystal X-ray structure analysis are summarised in Tables 2 and 3. While Table 2 lists the lattice parameters

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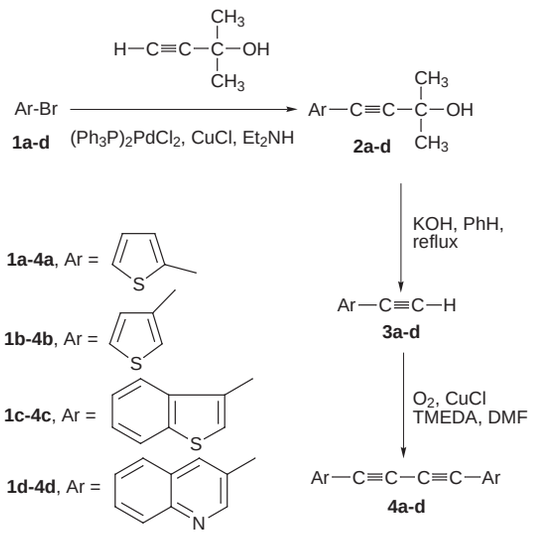
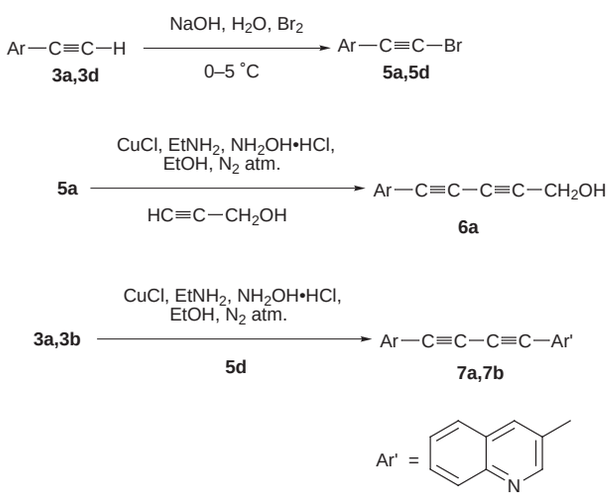
Table 1 Reactivity of diacetylenes towards solid-state 1,4-addition polymerisation

	Solid-state reactivity		
Diacetylene	γ	UV	heat
4a	×	×	×
4b	×	×	×
4c	×	×	×
4d	○	○	○
6a	×	×	×
7a	×	×	×
7b	×	×	×

○: reactive, ×: unreactive.



Scheme 2 Synthetic route for symmetrical diacetylenes.



Scheme 3 Synthetic route for unsymmetrical diacetylenes.

for the monomers, Table 3 summarises the packing parameters (d_1 and γ) relevant for topochemical 1,4-addition polymerisation.‡ Most of the monomers adhere to the established principles of topochemical 1,4-addition with the exception of compound **4a**.

‡ Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/271.

Table 2 Lattice parameters of diacetylene monomers

Diacetylene	Space group	*a*	*b* (in Å)	*c*	*α*	*β* (in degrees)	*γ*
4a	$P2_1/n$ monoclinic	5.89	5.97	13.15	90	102.59	90
4c	$P2_1/n$ monoclinic	13.28	3.96	14.12	90	92.11	90
4d	$P2_1/n$ monoclinic	4.81	13.69	11.91	90	95.34	90
6a	$P2_1/n$ orthorhombic	22.66	7.48	9.38	90	90	90
7a	$P2_1/n$ orthorhomic	6.98	28.76	12.49	90	90	90

Table 3 Distance d_1 and angle γ of diacetylenes[a]

Diacetylene	d_1 (Å)	γ (degrees)
4a	5.887	40.5
4c	3.958	62.3
4d	4.807	47.5
6a	7.482	70.0
7a	6.980	64.0

[a] Variables *d* and *γ* are defined in Scheme 1.

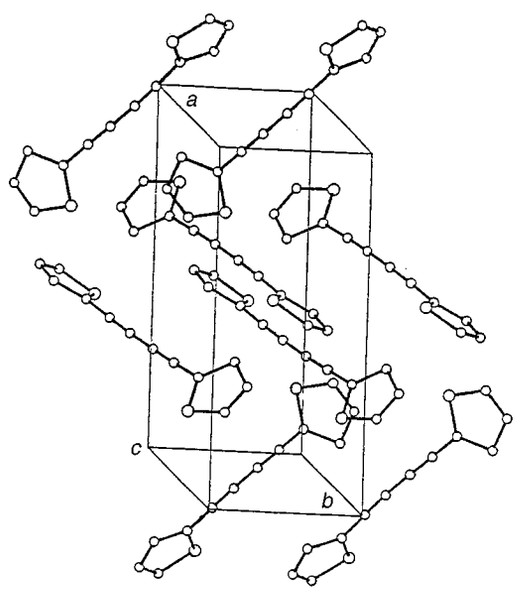


Fig. 1 Unit-cell packing diagram of compound **4a**.

Fig. 1 shows the unit-cell packing diagram of compound **4a**. In this crystal, both the thiophene rings are disordered. Thus the position of sulfur and carbon atoms in thiophene rings, adjacent to the diacetylenic backbone, are interchangeable but with unequal occupations. The thiophene rings are planar and the dihedral angle between them is 65.6°. The diacetylene chains are inclined to the shortest axis, *i.e.* the *a*-axis, by 40.5° and the perpendicular distance between the adjacent chains is 3.823 Å, as against the respective values of 45° and $3.4 < S_1 < 4.0$ Å, required for solid-state polymerisation.[2] Thus, it is surprising that compound **4a** is unreactive even though it has favourable packing arrangements. The disordered structure of compound **4a**, may partially explain its non-reactivity in the solid state.

Preliminary X-ray diffraction data of compound **4b** indicate that this diacetylene also has a disordered structure in its crystal state.[20]

It is possible that each of the diacetylenes **4a** and **4b** exists in a more ordered phase at a temperature below ambient, which could be a reactive phase. In order to confirm this view, low-temperature differential scanning calorimetry (DSC) was

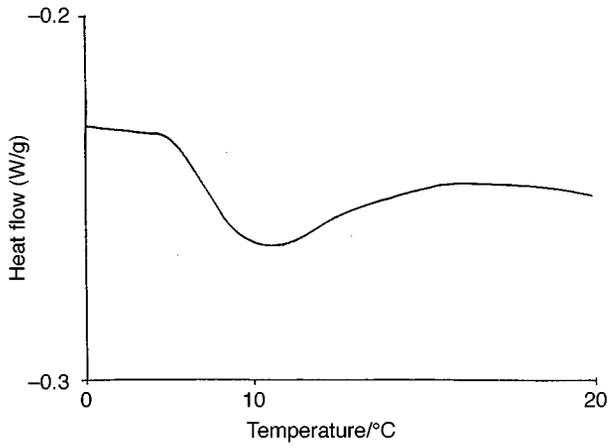


Fig. 2 DSC of compound **4a** at low temperature (0–20 °C).

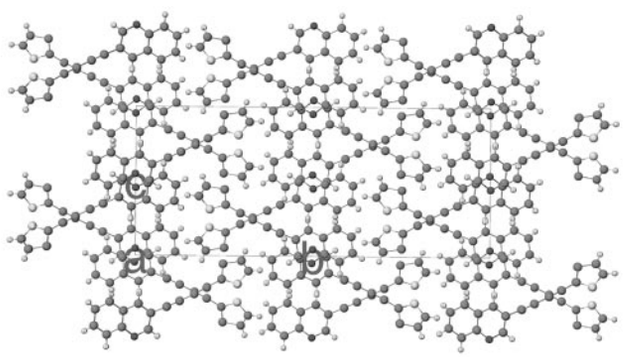


Fig. 3 Unit-cell packing diagram of compound **7a** down the *a*-axis.

carried out. As a typical case, the result for **4a** is shown in Fig. 2. Endotherms were observed at 10 °C for compound **4a** and at 6.5 °C for compound **4b** with ΔH of 0.037 kcal mol^{-1}§ and 0.014 kcal mol^{-1}, respectively. Following this result, solid-state polymerisation of compounds **4a** and **4b** was attempted at temperatures below −20 °C using high-power UV radiation. Even after several hours of exposure, neither of the two monomers showed any reactivity. Therefore, this suggests that even though the diacetylene crystals were in more ordered forms at the lower temperatures, enhanced order is not enough to induce reactivity. In other words, the disordered structure of compounds **4a** and **4b** is just one factor, among others, responsible for their lack of solid-state reactivity.

The crystal structure of compound **7a** also revealed that it has a disordered structure (Fig. 3). In the thiophene ring within each molecule of compound **7a**, the position of the sulfur atom and the carbon atom flanking the diacetylenic backbone are interchangeable. Moreover, the stacking of the molecules of compound **7a** is not parallel. These factors make this monomer unreactive towards solid-state polymerisation despite a short C(sp)–C(sp) distance of adjacent molecules. However, it may be noted that polymerisation has been observed in diacetylene crystals in which diacetylene molecules are packed in non-parallel stacks.[21]

For crystals **4c** and **6a**, the distance between adjacent molecules in a stack as well as the angle between the molecular axis and the stack axis are not suitable for 1,4-addition reaction to occur.

Diacetylene **4d** undergoes topochemical 1,4-addition.[9] The crystal structure of this compound reveals that the molecules have parallel stacking along the *b*-axis (Fig. 4). The quinoline rings are almost parallel to each other within a molecule as well as among adjacent molecules in the stack. The d_1- and γ-values are 4.8 Å and 47.5°, respectively. These values are almost

§ 1 cal = 4.184 J.

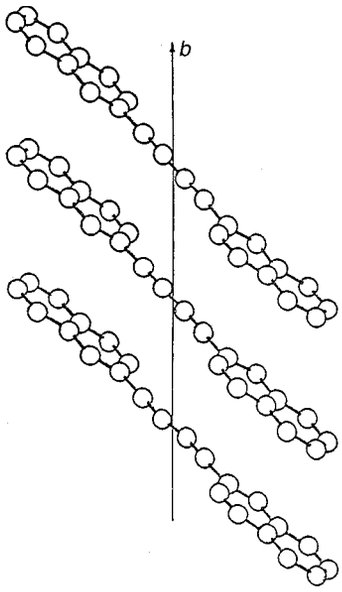


Fig. 4 Stacking of compound **4d** molecules along *b*-axis.

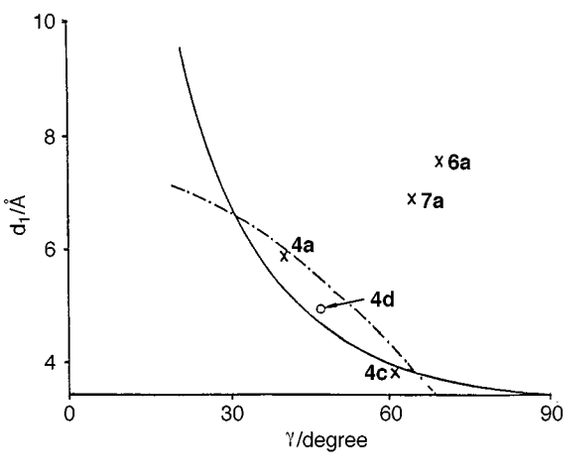


Fig. 5 Plot showing monomer-packing requirements for solid-state 1,4-addition. To be reactive, the diacetylene (DA) should fall inside the contour formed by the solid curve and the dotted curve. Experimental data obtained in the present study for reactive DAs (○) and unreactive DAs (×) are plotted in the graph.

the same as the ideal values proposed for topochemical 1,4-addition. The percentage polymer conversion, however, was low (25%). The $\chi^{(3)}$-value for this polymer has been estimated to be in the order of 10^{-11} esu by third-harmonic generation measurement.[10] The PDA obtained from compound **4d** is blue in colour and shows a high absorption λ_{max} of 715 nm. This is in line with our postulation that directly bound heteroaryl groups contribute favourably towards the conjugation length of the PDA chain.

The topochemical reaction criteria can be expressed by drawing contours for 1,4-carbon separation of 4.0 Å and an arbitrarily chosen r.m.s. displacement of 1.0 Å in the space with coordinates equal to the separation of the centres of gravity between the axes of the diacetylene units and the stack (Fig. 5).[6] Not all values of d_1 and γ are allowed since the diacetylene units cannot approach closer than twice the van der Waals radii of the acetylenic carbons. This limit is shown by the solid-line curve in Fig. 5. Values of d_1 and γ obtained from X-ray structure analysis of the diacetylenes reported here are plotted in Fig. 5. It is observed that, except for compounds **4a** and **4d**, all other diacetylenes tested do not fulfil the requirements for topochemical reactivity. It is noteworthy that even compound **4a**, falling within the contour, does not show topochemical reactivity.

There are reports on diacetylenes with aromatic side groups which are unreactive towards solid-state polymerisation. The crystal structures of these diacetylenes reveal that they do not fulfil the packing requirements for 1,4-addition reaction.[22,23] It has been a general contention that a methylene group next to the diacetylene backbone acts as a mechanical tuner and eases out the strain developed in the crystal during polymerisation and facilitates higher polymer conversion.[24] A recent study reported good topochemical reactivity of a diacetylene containing a tetrathiafulvalene side group attached to the backbone through an alkyl chain.[25] None of the diacetylenes reported in this study, except for compound **6a**, possesses such a methylene group. This could be a major contributing factor towards non-reactivity of the monomers.

Some of the monomers were used to determine their third-order nonlinear properties by the Z-scan technique.[26] The second molecular hyperpolarisability γ $(-\omega, \omega, \omega, -\omega)$ was found to be large (0.66 to 11.20×10^{-32} esu) for these small molecules. Thus, the study indicates that the symmetrical substitution with conjugated heterocyclic end-groups is the contributing factor for enhancement of their γ-values.

Conclusions

In conclusion, we have successfully synthesised a series of diacetylenes which are functionalised with heteroaryl moieties. The heteroaryl side groups were linked directly to the diacetylene backbone in order to get maximum π-conjugation effect. These DAs were prepared with the aim of probing the structure–solid-state reactivity relationship with respect to 1,4-addition. We have based our investigation on the single-crystal X-ray structure of the monomers because the above polymerisation reaction is highly dependent on the molecular-packing arrangement in monomer crystals. Our investigation has revealed that although the criteria proposed for topochemical 1,4-addition are necessary, they are not sufficient for reactivity. Other factors, like disordered crystal structure, may also play a role in controlling reactivity. The diacetylene **4d**, on the other hand, reacts to give polydiacetylene with high effective conjugation length as expected from such a type of PDA.

Experimental

Solvents and reagents used in this work were purified according to standard literature techniques and stored under nitrogen. Solvents were freshly distilled prior to use. Commercially available 2-bromothiophene **1a**, 3-bromothiophene **1b** and 3-bromoquinoline **1c** (Aldrich) were used as obtained. 3-Bromobenzo[*b*]thiophene **1c** was prepared from benzo[*b*]thiophene according to the literature procedure.[27] KCl and CuI were used as obtained. 2-Methylbut-3-yn-2-ol (Fluka or Aldrich) and diethylamine were distilled before use. Cuprous [copper(I)] chloride was purified before use. Petroleum spirit refers to the fraction with distillation range 40–60 °C.

Purification of the synthesised compounds was by crystallisation from suitable solvents. Column chromatography was done using 100–200 mesh silica gel. TLC was used to monitor the reactions. Mps were determined by the capillary method using a Veeco melting point apparatus model MP-5 and are uncorrected. IR spectra were taken in a Perkin-Elmer 681 IR spectrophotometer. Proton NMR spectra were recorded on either a 60 MHz Hitachi-600 of a 400 MHz Varian VXR-400 spectrometer. ^{13}C NMR spectra were recorded on a 400 MHz Varian VXR-400 spectrometer. Elemental analysis was done using a Carlo Erba Model 1106 elemental analyser. The single-crystal X-ray diffraction and analysis were carried out on a Philips X-ray diffractometer PW 1140.

Preparation of 2-methyl-4-(2′-thienyl)but-3-yn-2-ol 2a

To bis(triphenylphosphine)palladium(II) chloride (0.175 g) and CuI (0.05 g) was added dry, distilled diethylamine (90 ml) followed by 2-methylbut-3-yn-2-ol (4.13 g, 0.049 mol) and 2-bromothiophene **1a** (8.1 g, 0.049 mol). The reaction mixture was stirred for 8 h at rt under dry N_2. Diethylamine was removed under reduced pressure, water was added to the reaction mixture, and then it was extracted with diethyl ether. After drying of the extract over $MgSO_4$ and removal of ether, a brown slurry was obtained, which was chromatographed through a silica gel column using petroleum spirit–ethyl acetate (80:20) as eluent. Yellowish solid alcohol **2a** was obtained, which was further purified by recrystallisation from petroleum spirit to afford needles (80%), mp 54 °C; ν_{max}(KBr)/cm^{-1} 3300 (OH), 3030 (arom. C–H), 2960 (aliph. C–H), 2200 (C≡C) and 1370 and 1380 (*gem* dimethyl); ^{1}H NMR (60 MHz; $CDCl_3$) δ_H 1.60 (s, 6H), 2.20 (s, 1H), 6.94–6.98 (dd, 1H), 7.18 (d, 1H) and 7.24 (d, 1H); ^{13}C NMR (100 MHz; $CDCl_3$) δ_C 31.20, 64.98, 78.02, 81.42, 121.91, 125.43, 129.99 and 134.02 (Found: C, 64.9; H, 6.5; S, 19.25. Calc. for $C_9H_{10}OS$: C, 65.02; H, 6.71; S, 19.29%).

Preparation of 2-methyl-4-(3′-thienyl)but-3-yn-2-ol 2b

The procedure followed was similar to that given for isomer **2a** above. However, the time required for completion of the reaction was much longer (12 h) in the present case. After work-up, the crude product was recrystallised from methanol to give pure title alcohol **2b** as crystals (81%), mp 115–116 °C; ν_{max}(KBr)/cm^{-1} 3300 (OH), 3030 (arom. C–H), 2965 (aliph. C–H), 2215 (C≡C) and 1370 and 1380 (*gem* dimethyl); ^{1}H NMR (60 MHz; $CDCl_3$) δ_H 1.54 (s, 6H), 2.15 (s, 1H) and 7.18–7.34 (m, 3H); ^{13}C NMR (100 MHz; $CDCl_3$) δ_C 31.41, 65.20, 79.46, 80.15, 121.10, 125.84, 130.19 and 134.02 (Found: C, 65.0; H, 6.5; S, 19.1. Calc. for $C_9H_{10}OS$: C, 65.02; H, 6.71; S, 19.29%).

Preparation of 4-(3′-benzo[*b*]thienyl)-2-methylbut-3-yn-2-ol 2c

The procedure followed was similar to that given for compound **2a** above. The reaction was complete in 6 h. After work-up, column chromatography and crystallisation, pure title alcohol **2c** was obtained as needles (50%), mp 71 °C; ν_{max}(KBr)/cm^{-1} 3300 (OH), 3030 (arom. C–H), 2980 (aliph. C–H), 2210 (C≡C), 1640 (arom. C–H) and 1370 and 1380 (*gem* dimethyl); ^{1}H NMR (60 MHz; $CDCl_3$) δ_H 1.65 (s, 6H), 2.81 (s, 1H) and 7.18–8.00 (m, 5H); ^{13}C NMR (100 MHz; $CDCl_3$) δ_C 31.52, 65.11, 76.98, 78.44, 117.00, 127.02, 127.31, 128.21, 129.45, 130.48, 139.73 and 143.42 (Found: C, 72.0; H, 5.5; S, 14.6. Calc. for $C_{13}H_{12}OS$: C, 72.19; H, 5.59; S, 14.82%).

Preparation of 2-methyl-4-(3′-quinolyl)but-3-yn-2-ol 2d

The procedure followed was similar to that given for compound **2a** above. After work-up, column chromatography and crystallisation, pure title alcohol **2d** was obtained as needles (60%), mp 115–116 °C; ν_{max}(KBr)/cm^{-1} 3250 (OH), 3030 (arom. C–H), 2965 (aliph. C–H), 2215 (C≡C) and 1370 and 1380 (*gem* dimethyl); ^{1}H NMR (60 MHz; $CDCl_3$) δ_H 1.62 (s, 6H), 2.54 (s, 1H), 7.58–8.24 (m, 4H), 8.32–8.41 (d, 1H) and 9.0 (br s, 1H); ^{13}C NMR (100 MHz; $CDCl_3$) δ_C 31.39, 65.27, 78.21, 85.25, 116.05, 127.01, 127.63, 127.66, 129.04, 130.81, 140.44, 146.52 and 152.22 (Found: C, 79.3; H, 6.1; S, 6.5. Calc. for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63%).

Preparation of 2-thienylacetylene 3a

A solution of alcohol **2a** (3 g, 0.018 mol) in dry benzene (30 ml) containing potassium hydroxide (1.2 g) and methanol (5 ml) was refluxed in a flask equipped with a Dean–Stark trap. The reaction was found to be complete after 9 h. The reaction product was carefully distilled under reduced pressure to obtain pure title compound **3a** (90%), bp 129–131 °C (lit.,[28] bp_{20} 54–60 °C).

Preparation of 3-thienylacetylene 3b

The procedure followed was similar to that given for isomer **3a**.

The refluxing was continued for 14 h in order to let the reaction go to completion. Yield 81%, bp 129 °C (lit.,[29] bp_{15} 48–50 °C).

Preparation of (3-benzo[*b*]thienyl)acetylene 3c

The procedure followed was similar to that given for compound **3a**. The reaction took only 3 h to finish. Pure title compound **3c** was obtained as a yellowish liquid (55%), bp 146 °C; ν_{max}(KBr)/cm^{-1} 3300 (C≡C–H), 2100 (C≡C) and 1600 (arom. C–C); ^{1}H NMR (60 MHz; $CDCl_3$) δ_H 3.6 (s, 1H) and 7.18–8.13 (m, 5H); ^{13}C NMR (100 MHz; $CDCl_3$) δ_C 77.95, 78.92, 117.25, 127.09, 127.42, 128.39, 129.55, 130.57, 139.82 and 143.51 (Found: C, 75.5; H, 3.75; S, 20.0. Calc. for $C_{10}H_6S_2$: C, 75.91; H, 3.82; S, 20.27).

Preparation of 3-quinolylacetylene 3d

In a round-bottom flask, fitted with a magnetic stirrer was placed a mixture of 2-methyl-4-(3′-quinolyl)but-3-yn-2-ol **2d** (18 g, 0.085 mol) in benzene (400 ml). A mixture of powdered KOH (3 g) and 18-crown-6 ether (0.5 g) in benzene (50 ml) was added to the stirred mixture. The mixture was stirred for 24 h at rt until the reaction was complete. The mixture was filtered and the filtrate was concentrated under reduced pressure. Pure compound **3d** was obtained by filtration column chromatography with 4 : 1 petroleum spirit–ethyl acetate. Shining crystals of compound **3d** were obtained by recrystallisation from petroleum spirit (84%), mp 80 °C [lit.,[30] mp 81 °C]; ν_{max}(KBr)/cm^{-1} 3300 (C≡C–H) and 2110 (C≡C), 1600 (arom. C–C); ^{1}H NMR (60 MHz; $CDCl_3$) δ_H 3.55 (s, 1H), 7.49–8.20 (m, 4H), 8.31–8.41 (d, 1H) and 9.0 (br s, 1H); ^{13}C NMR (100 MHz; $CDCl_3$) δ_C 81.01, 85.33, 116.95, 127.64, 127.99, 128.10, 129.50, 131.12, 140.68, 146.75 and 152.25 (Found: C, 86.2; H, 4.6; N, 9.0. Calc. for $C_{11}H_7N$: C, 86.25; H, 4.61; N, 9.14%).

Preparation of 1,4-bis(2-thienyl)buta-1,3-diyne 4a

To a magnetically stirred suspension of CuCl (190 mg) in DME (10 ml) was added TMEDA (0.5 ml). After 10 min at rt the mixture was treated with 2-thienylacetylene **3a** (1 g, 0.009 mol) and the solution was stirred while O_2 was bubbled through it. The colour of the reaction mixture turned from blue to yellowish green. The reaction was found to be complete after 2 h. The mixture was poured into water and was extracted with ether. The ether layer was dried over $MgSO_4$ and then concentrated under reduced pressure to obtain a crude product as a yellowish solid. This was passed through a silica gel column, using petroleum spirit as eluent. Diyne **4a** was obtained as a solid, which was further purified by crystallisation to obtain needles (40%), mp 89 °C; ν_{max}(KBr)/cm^{-1} 2130 (C≡C) and 1620 (arom. C–C); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.02 (d, 2H), 7.34 (dd, 2H) and 7.37 (d, 2H); ^{13}C NMR (100 MHz; $CDCl_3$) δ_C 76.74, 77.86, 121.93, 127.30, 129.02 and 134.49 (Found: C, 67.16; H, 2.8; S, 29.6. Calc. for $C_{12}H_6S_2$: C, 67.76; H, 2.82; S, 29.92%).

Preparation of 1,4-bis(3-thienyl)buta-1,3-diyne 4b

Compound **4b** was synthesised using the same Glasser's coupling method as was used for the synthesis of isomer **4b**. The starting material in this case was 3-thienylacetylene **3b**. Yield of diyne **4b** was 40%, mp 111 °C; ν_{max}(KBr)/cm^{-1} 2140 (C≡C) and 1600 (arom. C–C); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.18 (d, 2H), 7.30 (dd, 2H) and 7.60 (d, 2H); ^{13}C NMR (100 MHz; $CDCl_3$) δ_C 73.52, 76.58, 120.90, 125.84, 130.19 and 131.28 (Found: C, 67.11; H, 2.82; S, 29.63. Calc. for $C_{12}H_6S_2$: C, 67.76; H, 2.82; S, 29.92%).

Preparation of 1,4-bis(3-benzo[*b*]thienyl)buta-1,3-diyne 4c

Compound **4c** was synthesised using the same method as was used for the synthesis of compound **4a**. The starting material in this case was (3-benzo[*b*]thiophenyl)acetylene **3c**. Yield of product was 42%, mp 165 °C; ν_{max}(KBr)/cm^{-1} 2120 (C≡C) and 1600 (arom. C–C); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.01 (dd, 2H), 7.07 (dd, 2H), 7.51 (d, 2H), 7.54 (d, 2H) and 7.66 (s, 2H); ^{13}C NMR (100 NHz; $CDCl_3$) δ_C 75.94, 76.31, 117.00, 127.22, 127.51, 128.43, 129.66, 130.67, 139.86 and 143.55 (Found: C, 76.3; H, 3.3; S, 20.0. Calc. for $C_{20}H_{10}S_2$: C, 76.40; H, 3.21; S, 20.40%).

Preparation of 1,4-bis(3-quinolyl)buta-1,3-diyne 4d

Compound **4d** was synthesised using the same method as was used for the synthesis of compound **4a**. The starting material in this case was 3-quinolylacetylene **3d**. Yield of product was 42%, mp 165 °C; ν_{max}(KBr)/cm^{-1} 2120 (C≡C) and 1600 (arom. C–C); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.60 (dd, 2H), 7.75 (dd, 2H), 7.80 (dd, 2H), 8.10 (d, 2H), 8.31 (s, 2H) and 8.95 (s, 2H); ^{13}C NMR (100 MHz; $CDCl_3$) δ_C 78.22, 80.01, 116.95, 127.41, 127.53, 127.62, 129.00, 130.85, 140.50, 146.67 and 152.35 (Found: C, 87.4; H, 3.3; N, 9.3. Calc. for $C_{22}H_{12}N_2$: C, 87.10; H, 3.57; N, 9.23%).

Preparation of 1-bromo-2-(2′-thienyl)ethyne 5a

Bromine (320 mg, 0.004 mol) was added to aq. KOH (0.01 mol in 10 ml) stirred at 0–5 °C. 2-Thienylacetylene **3a** as a solution in 1,4-dioxane (108 mg, 0.001 mol/20 ml) was added dropwise to the above mixture over a period of 15 min. The reaction mixture was stirred for another 15 min without further cooling and poured into 50 ml of ice-cold water. The product was extracted with diethyl ether. Upon drying over $MgSO_4$ and removal of solvent, **5a** was obtained as a yellow oil (82%), bp (at 5 mmHg) 40 °C; ν_{max}(KBr)/cm^{-1} 2190 (C≡C); ^{1}H NMR (60 MHz; $CDCl_3$) δ_H 6.80–7.50 (m, 3H); ^{13}C NMR (100 MHz; $CDCl_3$) δ_C 80.92, 81.83, 121.17, 125.92, 130.30 and 132.22 (Found: C, 38.45; H, 1.58; S, 17.0. Calc. for C_6H_3BrS: C, 38.53; H, 1.62; S, 17.14%).

Preparation of 1-bromo-2-(3′-quinolyl)ethyne 5d

Bromine (320 mg, 0.004 mol) was added to aq. KOH (0.01 mol in 10 ml) stirred at 0–5 °C. 3-Quinolylacetylene **3d** as a solution in 1,4-dioxane (153 mg, 0.001 mol/20 ml) was added dropwise to the above mixture over a period of 15 min. The reaction mixture was stirred for another 15 min without further cooling. Then the reaction mixture was poured into 50 ml of ice-cold water, when a solid precipitated out. The precipitate was filtered off, dried, and recrystallised from methanol (82%), mp 118–119 °C; ν_{max}(KBr)/cm^{-1} 2200 (C≡C); ^{1}H NMR (60 MHz; $CDCl_3$) δ_H 7.50–9.00 (m, 6H); ^{13}C NMR (100 MHz; $CDCl_3$) δ_C 81.01, 85.33, 116.95, 127.64, 127.99, 128.10, 129.50, 131.12, 140.68, 146.75 and 152.25 (Found: C, 57.5; H, 2.6; N, 5.9. Calc. for $C_{11}H_6BrN$: C, 56.92; H, 2.60; N, 6.03%).

Preparation of 1-(2′-thienyl)penta-1,3-diyn-5-ol 6a

A catalytic slurry of CuCl (100 mg), 70% aq. ethylamine (30 ml), $NH_2OH{\cdot}HCl$ (300 mg in 20 ml of water) and ethanol (60 ml) was prepared in a three-neck flask under argon. Propargyl alcohol (prop-2-ynol) (1 g, 0.01 mol) was added dropwise to the above slurry. The colour of the solution turned greenish yellow. The flask was maintained at a temperature of 40–45 °C and a solution of 1-bromo-2-(2′-thienyl)ethyne **5a** in ethanol (1.03 g, 0.0068 mol/40 ml) was added dropwise to the above mixture. The reaction mixture was stirred for another 3 h until completion of the reaction. The mixture was then poured into vigorously stirred ice-cold water (150 ml). A solid slowly precipitated out, and was filtered off, and extracted with ether. The ether layer was washed with saturated aq. ammonium chloride. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated. After column chromatography through a silica gel column, pure diynol **6a** was obtained as a crystalline solid

(45%), mp 81 °C; ν_{max}(KBr)/cm^{-1} 3400 (OH), 3000 (arom. C–H), 2962 (aliph. C–H) and 2150 (C≡C); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 1.76 (br s, 1H), 4.42 (s, 2H), 6.98 (dd, 1H), 7.31 (d, 1H) and 7.33 (d, 2H); ^{13}C NMR (100 MHz; $CDCl_3$) δ_C 66.25, 70.34, 71.70, 80.12, 82.58, 121.64, 127.10, 128.80 and 134.75 (Found: C, 66.3; H, 3.7; S, 19.6. Calc. for C_9H_6OS: C, 66.64; H, 3.73; S, 19.77%).

Preparation of 1-(3′-quinolyl)-4-(2′-thienyl)buta-1,3-diyne 7a

To a suspension of CuCl (12 mg), ethylamine (1 ml) and hydroxylamine hydrochloride (100 mg) in ethanol (5 ml) was added dropwise a solution of 2-thienylacetylene **3a** (250 mg, 0.023 mol) in *N*,*N*-dimethylacetamide (DMA) (11 ml). Afterwards, (bromoethynyl)quinoline **5d** (300 mg, 0.013 mol) as a solution in 71 ml of DMA was added at 30 °C. The reaction was carried out under nitrogen. After being stirred for 1.5 h the mixture was poured into 50 ml of ice-cold water; the precipitate was filtered off, and recrystallised from methanol. The pure diyne **7a** was obtained as needles (60%), mp 126 °C; ν_{max}(KBr)/cm^{-1} 3100 (arom. C–H), 2133 (C≡C), 1640, 1600 and 1580 (arom. C–C); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.02 (dd, 1H), 7.36 (d, 1H), 7.39 (d, 1H), 7.60 (dd, 1H), 7.75 (dd, 1H), 7.80 (d, 1H), 8.10 (d, 1H), 8.30 (s, 1H) and 8.95 (s, 1H); ^{13}C NMR (100 MHz; $CDCl_3$) δ_C 75.90, 77.03, 77.62, 80.80, 116.59, 121.10, 125.44, 127.01, 127.45, 127.66, 129.04, 129.99, 130.81, 132.71, 140.54, 146.51 and 153.12 (Found: C, 82.2; H, 2.8; N, 4.4; S, 9.9. Calc. for $C_{22}H_9NS$: C, 82.73; H, 2.84; N, 4.39; S, 10.04%).

Preparation of 1-(3′-quinolyl)-4-(3′-thienyl)buta-1,3-diyne 7b

The preparation of compound **7b** was achieved using a similar method to that for isomer **7a**. The starting materials used were 3-thienylacetylene **3b** and (bromoethynyl)quinoline **5d**. Pure compound **7b** was obtained as needles (48%), mp 133 °C; ν_{max}(KBr)/cm^{-1} 3100 (arom. C–H), 2133 (C≡C), 1640, 1600 and 1580 (arom. C–C); ^{1}H NMR (400 MHz; $CDCl_3$) δ_H 7.21 (d, 1H), 7.30 (d, 1H), 7.61 (dd, 1H), 7.66 (dd, 1H), 7.75 (dd, 1H), 7.80 (dd, 1H), 8.10 (d, 1H), 8.30 (s, 1H) and 8.90 (s, 1H); ^{13}C NMR (100 MHz; $CDCl_3$) δ_C 73.91, 77.16, 78.08, 78.62, 116.18, 120.54, 125.82, 127.01, 127.45, 127.66, 129.04, 129.99, 130.81, 134.02, 140.44, 146.51 and 153.01 (Found: C, 82.7; H, 2.8; N, 4.2; S, 9.9. Calc. for $C_{22}H_9NS$: C, 82.73; H, 2.84; N, 4.39; S, 10.04%).

Solid-state polymerisation

Polymerisation behaviour of the DA monomers was examined using UV and γ-rays as well as anealing. Freshly prepared monomer crystals were used for exposure to the above stimuli. Only compound **4d** turned blue by all three modes of stimuli, indicating that it is solid-state reactive. The rest of the monomers turned from colourless to brown, suggesting that 1,4-addition is not occurring for these DAs. γ-Radiation was used to polymerise compound **4d** in bulk. The percentage conversion of the reactive monomer to polymer was obtained by extracting out the unchanged monomer after solid-state polymerisation. The weight of the monomer before polymerisation and the weight of the extracted polymer were used to calculate the percentage polymer conversion.

Single crystal X-ray data

Single crystals of **4a**, **4c**, **4d**, **6a** and **7a**, that were suitable for X-ray crystallographic analyses, were obtained by slow evaporation from suitable organic solvents. The structure solution and refinement details for the compounds have been published elsewhere,[16–19] and so will only be briefly discussed here. Lattice parameters at 25 °C or 27 °C were determined by least-squares fit to the setting parameters of 25 independent reflections. Data were measured on an Enraf-Nonius CAD4F four-circle diffractometer with Mo-Kα radiation. Data reduction and application of Lorentz and polarisation corrections were carried out using the Enraf-Nonius Structure Determination Package.

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