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Synthesis and characterization of oligo(heteroarylene vinylene)s incorporating furan and thiophene moieties

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This article describes the synthesis and characterization of a series of homologous conjugated dimers and trimers bearing alkenyl moieties between furan and/or thiophene heterocycles, linked through their 2,5- positions, and a terminal aldehyde group. A tetramer was also isolated and characterized. These oligomers constitute (i) useful model compounds for the corresponding conjugated homo- and co-polymers, (ii) interesting molecular structures for electroluminescence and other optoelectronic applications, and (iii) potential precursors to more specific compounds (e.g. liquid crystals or photosensitive species) thanks to the terminal aldehyde function. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Conjugated polymers and oligomers have attracted considerable scientific interest for their potential use as electronic, optical, optoelectronic and electroluminescent devices[1,2]. After much research on various *first-generation* polymers, such as polyacetylene and polyaniline, heterocyclic moieties were also investigated, viz. mostly polypyrrole and polythiophene. More recently, a new generation based on poly(arylene vinylene) moieties has been investigated of which poly(phenylene vinylene) is the parent structure. The synthesis of this polymer has been optimized, but problems related to processability have stimulated the search for similar, but more stable structures based on heterocyclic units[1,2] and again most of this work was concentrated upon thiophene and pyrrole derivatives. Conjugated polymers bearing furan rings have received much less attention[3], probably because of their supposedly less well-defined structures and poor stability.

In a previous investigation in our laboratory[4,5], a new synthetic route to linear low molecular weight poly(furylene vinylene) (**PVF**) was proposed, which involved the base-catalysed polycondensation of 5-methylfuraldehyde (**MF**) using *t*-BuOK as a nucleophile. According to the experimental conditions, reactions provided access either to the dimer **1**, or to the corresponding polymer **2**. The condensation of 5-methyl-2-thiophene carboxaldehyde (**MTC**) also led to the corresponding dimer **3** and polymer **4**.

In this preliminary study, little attention was devoted to the possibility of preparing well-defined single oligomeric structures from each precursor and from both, i.e. homo- and co-oligomers except for **1** and **3**.

The present article aims at filling this gap and describes the preparation and characterization of three series of conjugated dimers and trimers, namely:

(1) fully furanic,
(2) furanic–thiophenic
(3) fully thiophenic structures.

One tetramer was also isolated and characterized.

EXPERIMENTAL

Dimer **5** was first reported as a red oil[6], but unfortunately it was not fully characterized. More recently, Elandaloussi *et al.*[7] prepared it in two steps from furfural through the intermediate formation of 1,2-difurylethylene. Dimer **6** was prepared photochemically by D'Auria and Piancatelli[8] as a mixture of *cis* and *trans* isomers. The experimental conditions providing access to dimers **5**–**8** and trimers **9**–**12** are given here.
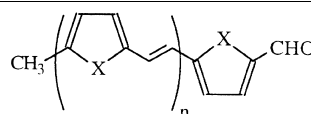
Preparation of dimer 5

t-BuOK (2.2 g) was added to dioxane (30 mL) with magnetic stirring under a nitrogen atmosphere. This
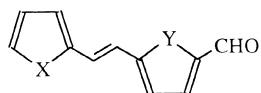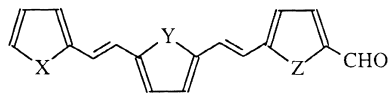

1: X = O

3: X = S

2: X = O

4: X = S
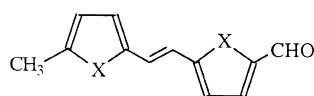
5: X = Y = O

6: X = S, Y = O

7: X = O, Y = S

8: X = Y = S

9: X = Y = Z = O

10: X = Y = O, Z = S

11: X = S, Y = Z = O

12: X = Z = O, Y = S

suspension was brought to reflux and then a mixture of an excess of furfural (**F**) (20.7 mL, 5 eq.) and **MF** (5 mL) was added dropwise over 30 min. The stirred reaction mixture was maintained for 3 h under reflux and for a further 20 h at room temperature. The addition of reagents such as CaH_2 during the course of this reaction further improved the yield by eliminating the water formed and thus avoiding the Cannizzaro dismutation. The reaction mixture was finally filtered, neutralized with concentrated acetic acid and shaken with water and methylene chloride. The organic phase was dried over anhydrous sodium sulfate and concentrated by evaporating under vacuum. Dimer **5** was isolated as yellow crystals (50% yield) either by high-vacuum distillation at 80–100°C, or by flash chromatography on silica gel (eluent: hexane–ethyl acetate 90:10).

Other dimers

Using the same procedure, **6** was obtained from monomers 2-thiophene carboxaldehyde (**TC**) (5 eq.) and **MF**, **7** from **F** (5 eq.) and **MTC** and **8** from **TC** (5 eq.) and **MTC**. The yields were in range of 30 to 40% and all purified products were crystalline materials.

Preparation of trimer **9**

A solution of dimer **5** (2.25 g; 2.6 eq) in dioxane (5 mL) was brought to reflux with magnetic stirring under a nitrogen atmosphere. *t*-BuOK (60 mg) was introduced and

a solution of **MF** (0.5 mL) in dioxane (5 mL) was added dropwise over 30 min. During the addition of the monomer, a further quantity of *t*-BuOK (100 mg) was introduced in the reacting medium. After maintaining the reflux for 1 h, the reaction was stirred overnight at room temperature. The resulting mixture was diluted with methylene chloride, neutralized with concentrated acetic acid and shaken with water. The organic phase was dried over anhydrous sodium sulfate and concentrated under vacuum to give a brown liquid crude product which was purified by flash chromatography on silica gel. The first fraction, eluted with hexane–ethyl acetate 90:10, contained the excess of dimer **5**. The second fraction, eluted with hexane–ethyl acetate 85:15, was precipitated into an excess of hexane to give trimer **9** as a microcrystalline orange powder (30% yield).

Others trimers

Using the same procedure, **10** was obtained from dimer **5** (excess) and monomer **MTC; 11** from **7** and **MF** and **12** from **6** and **MF**. All these compounds were purified to give crystalline red powders.

The characterization of all these products called upon u.v.–visible spectroscopy (in spectroscopic-quality CH_2Cl_2, Beckman DU-64 spectrometer), *FT*i.r. spectroscopy (KBr pellets, Perkin–Elmer Paragon 1000 spectrometer) and ^1H n.m.r. spectroscopy (CD_2Cl_2, Bruker AC300 instrument at 300 MHz), elemental analysis (carried out at the Central
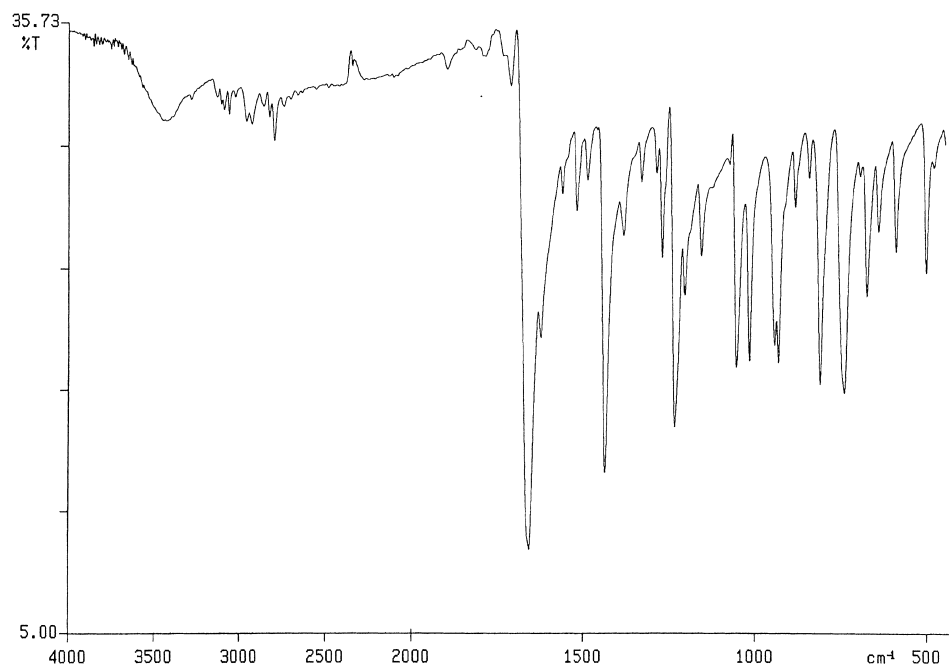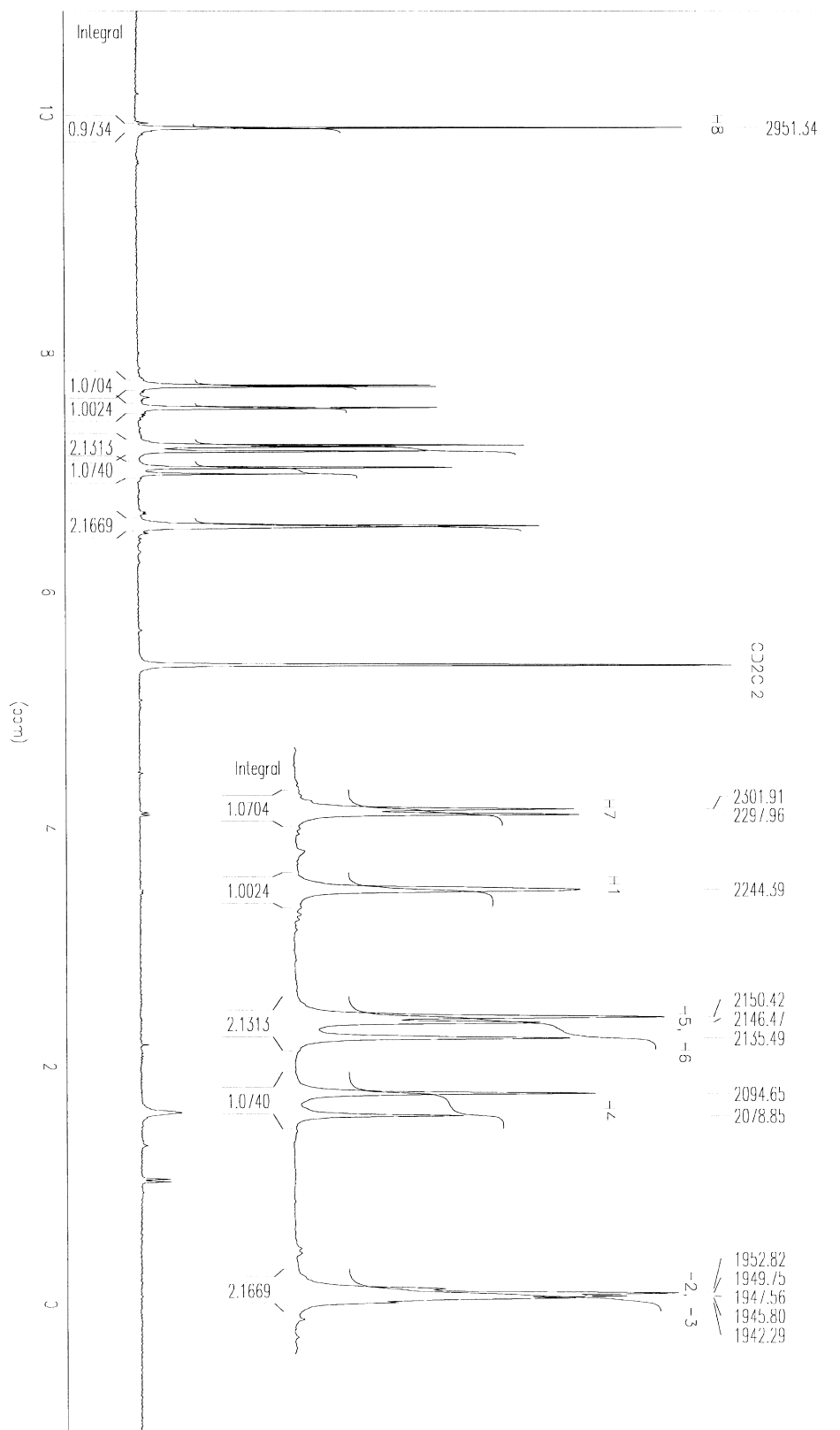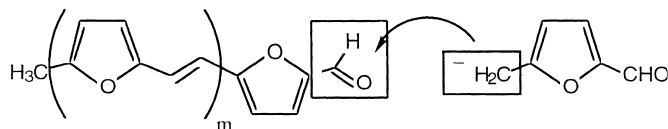

Figure 1 FTIR spectrum of dimer **7** (KBr pellet)

Figure 2 ^{1}H NMR spectrum of dimer **7** (CD$_2$Cl$_2$, 300 MHz)

Analysis Laboratory of the National Research Council of France), mass spectrometry (EI: 70 eV, Nermag R10-10C spectrometer) and melting points (determined by d.s.c. with a Setaram DSC-92 instrument).

## RESULTS AND DISCUSSION

Appendix A, B and C give the essential data related to the

characterization of dimers, trimers and the tetramer, respectively. The results of these thorough analyses gave clear confirmation of the validity of each postulated structure. The ^{1}H n.m.r. and *FT*i.r. spectra of these compounds, of which *Figures 1* and *2* are typical examples, were clearly indicative of the *trans* conformation of all external unsaturations with coupling constants of about 16.0 Hz for the alkenyl protons and typical peaks at 930–960 cm^{-1}. The expected batochromic shift of the u.v.–visible spectra was observed when going from the dimers ($\lambda_{max} = 370$–380 nm) to the trimers ($\lambda_{max} = 430$–440 nm) and to the tetramer ($\lambda_{max} = 470$ and 495 nm) as a function of the growing degree of conjugation. This trend suggests that up to four units, the molecular structures remain essentially planar. This planarity is then progressively lost as the DP increases as indicated by a limiting value of $\lambda_{max} = 510$ nm above about 10.

Contrary to our previous study[4,5] which was mostly aimed at preparing polymeric structures **2** and **4**, we wished here to orient the reactions towards the synthesis of specific oligomeric structures. For this purpose, we built the dimers and trimers by calling upon the indispensable methylated monomer and a unmethylated partner. This avoided the self-condensation of the latter. In order to avoid the self-dimerization of monomers **MF** or **MTC** leading respectively to dimers **1** and **2**, a large excess of **F** or **TC** was used to favour the desired condensations leading to the unmethylated dimers **5–8**. With molar ratios up to about 3, some methylated dimers were still encountered among the producers, whereas with the selected ratio of 5 the unmethylated homologue was the exclusive product. The same considerations were applied to the trimerizations except that the molar excess of the dimers in relation to the monomer to form only trimers such as **9–11** was threefold since possible traces of methylated dimers were easy to separate in this context.

The purification by flash chromatography on silica gel, of the crude product arising from the condensation reaction leading to dimer **5** gave a second fraction which was analysed and identified as trimers **9** (10% yield). Also, the crude product from the corresponding condensation leading to **6** gave a second fraction identified as trimer **11** (10% yield) and a third fraction identified as tetramer **13**.
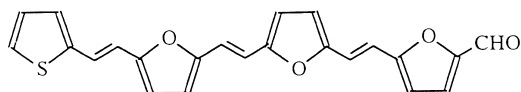
13

Attempts to synthesize the methylated tetramer arising from the direct self-condensation of **1** failed.

The behaviour of all the systems studied here confirms the fact that the only possible condensation reaction is that involving the methyl group of the monomer and the aldehyde function of the monomer, the dimer, or trimer added initially or formed in situ. This mechanism was postulated earlier[5] to explain the growth of polymers chain **2** and **4**, viz.:

This stepwise growth involving in-situ products was not observed in the condensations leading respectively to dimers **7** and **8**, because no traces of the corresponding trimers or tetramers were isolated. Thus these dimers which bear a thiophene ring attached to the aldehyde function appear to be less reactive towards monomer **MTC**, than their furanic-aldehyde homologues **5** and **6**. The condensations of dimer **8** with **MF** or **MTC** did not give any appreciable yields of the corresponding trimers. Although dimers **6** and **7** condensed readily with **MF**, they did not react with **MTC** under a rather wide range of experimental conditions, since they were recovered intact after the purification of the respective crude products. All these results point to the difficulty of preparing trimers containing at least two thiophene cycles. The reason for this diminished reactivity is probably related to the stronger aromatic character of that heterocycle, compared with the more pronounced dienic properties of the furan ring. This is in tune with previous observations related to the lower reactivity of **MTC** in the preparation of polymer **4**, compared with the synthesis of **2** from **MF**[5]. The preparation of thienylene vinylene oligomers via the Wittig reaction is an alternative route which has been explored by Kossmehl's group[9].

CONCLUSION

The possibility of preparing well-defined oligofurylene vinylenes and oligothienylene vinylenes bearing a terminal aldehyde function opens the way to their study either as such, in terms of, e.g., electroluminescence, electrochemical reactivity and photochemical properties, or as precursors to novel structures (e.g. liquid crystals and chromophore-bearing polymers) through the exploitation of the reactivity of the aldehyde group. Both types of investigation are currently in progress.

APPENDIX A: CHARACTERISTICS OF DIMERS **5–8**
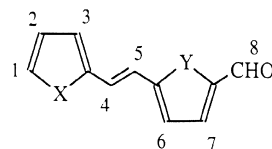

5: X = Y = O.

6: X = S, Y = O.

7: X = O, Y = S.

8: X = Y = S.

5: *FT*i.r. (ν_{max}/cm^{-1}): Fu: 3120 (νCH), 1455 and 1399 (νFu),

1249 (δCH), 1027 (νFu) and 1011 (ring breathing Fu), 820, 797 and 740 (γCH Fu). C=O: 1674 (νC=O). –CH: 2835 (νCH). CH=CH: 1624 (νC=C), 958 (ωCH *trans*).[1]H n.m.r. (δ/ppm): 9.54 (s, 1H: H8); 7.36 (s, 1H: H1); 7.24 (d, $J = 3.6$ Hz, 1H: H7); 7.14 (d, $J = 16.0$ Hz, 1H *trans*: H5); 6.84 (d, $J = 16.0$ Hz, 1H *trans*: H4); and 6.54–6.48 (m, 3H: H2, H3 and H6).u.v.–vis. (λ_{max}/nm): 370 and 380 (sh).$T°$m (°C): 56.MS (*m/z*): 188 (M$^+$), 159, 131, 103, 77, 51.Elemental anal. for $C_{11}H_8O_3$: calcd.: C: 70.23, H: 4.25, O: 25.52%; found: C: 70.24, H: 4.18, O: 25.22%.**6**: *FT*i.r. (ν_{max}/cm^{-1}): Fu–Th: 3105 (νCH), 1486 and 1398 (νAryls), 1247 (δCR Fu), 1024 (ring breathing Fu), 797 (γCH Fu), 714 (δCH Th). C=O: 1667 (νC=O). –CH: 2818 (νCH). CH=CH: 1623 (νC=C), 956 (ωCH *trans*). [1]H n.m.r. (δ/ppm): 9.54 (s 1H: H8); 7.50 (d, $J = 16.0$ Hz, 1H *trans*: H5); 7.32 (d, $J = 5.0$ Hz, 1H: H1); 7.25 (d, $J = 3.7$ Hz, 1H: H7); 7.20 (d, $J = 3.6$ Hz, 1H: H3); 7.05 (m, 1H: H2); 6.77 (d, $J = 15.9$ Hz, 1H *trans*: H4) and 6.53 (d, $J = 3.7$ Hz, 1H: H6).u.v.–vis. (λ_{max}/nm): 375.$T°$m (°C): 74.MS (*m/z*): 204 (M$^+$), 175, 147, 121, 105, 69, 57, Elemental anal.: calcd. for $C_{11}H_8O_2S$: C: 64.71, H: 3.92, O: 15.67, S: 15.70%; found: C: 65.38, H: 4.08, O: 16.51, S: 13.77%.**7**: *FT*i.r. (ν_{max}/cm^{-1}): Fu–Th: 3127 (νCH), 1437 (νAryls), 1232 (δCH), 1054 (ring breathing Th), 1016 (ring breathing Fu), 811 and 738 (δCH Th), 738 (γCH Fu). C=O: 1652 (νC=O). –CH: 2794 (νCH). CH=CH: 1623 (νC=C), 931 (ωCH *trans*).[1]H n.m.r. (δ/ppm): 9.84 (s, 1H: H8); 7.67 (d, $J = 3.9$ Hz, 1H: H7); 7.48 (s, 1H: H1); 7.17–7.12 (m, 2H: H5 *trans* and H6); 6.96 (d, $J = 15.8$ Hz, 1H *trans*: H4) and 6.52–6.47 (m, 2H: H2 and H3).u.v.–vis. (λ_{max}/nm): 380 and 395 (sh).$T°$m (°C): 38.5.MS (*m/z*): 204 (M$^+$), 175, 147, 131, 103, 69, 57.Elemental anal.: calcd. for $C_{11}H_8O_2S$: C: 64.71, H: 3.92, O: 15.67, S: 15.70%; found: C: 64.78, H: 3.99, O: 15.83, S: 15.12%.**8**: *FT*i.r. (ν_{max}/cm^{-1}): Th: 3100 (νCH), 1453 and 1420 (νTh), 1229 (δCH), 1046 (ring breathing Th), 817, 796 and 703 (δCH Th). C=O: 1655 (νC=O). –CH: 2855 (νCH). CH=CH: 1610 (νC=C), 948 (ωCH *trans*).[1]H n.m.r. (δ/ppm): 9.84 (s, 1H: H8); 7.67 (d, $J = 3.6$ Hz, 1H: H7); 7.32 (d, $J = 5.0$ Hz, 1H: H1); 7.31 (d, $J = 15.8$ Hz, 1H *trans*: H5); 7.18–7.14 (m, 2H: H3 and H6); 7.06 (d, $J = 15.6$ Hz, 1H *trans*: H4) and 7.06–7.04 (m, 1H: H2).u.v.–vis. (λ_{max}/nm): 380 and 395 (sh).$T°$m (°C): 80.1.MS (*m/z*): 220 (M$^+$), 191, 147, 121, 115, 69.Elemental anal.: calcd. for $C_{11}H_8OS_2$: C: 60.00, H: 3.63, O: 7.26, S: 29.11%; found: C: 60.66, H: 4.03, O: 8.32, S: 27.39%.

APPENDIX B: CHARACTERISTICS OF TRIMERS 9–12
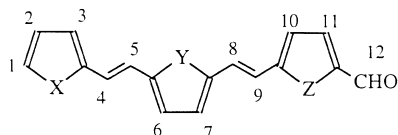
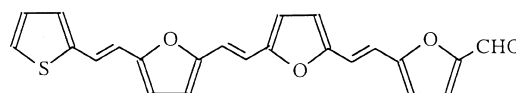
9: X = Y = Z = O.

10: X = Y = O, Z = S.

11: X = S, Y = Z = O.

12: X = Z = O, Y = S.

9: *FT*i.r. (ν_{max}/cm^{-1}): Fu: 3136 (νCH), 1450 and 1399 (νFu), 1256 (δCH), 1032 and 1016 (ring breathing Fu), 775, 752 and 737 (γCH Fu). C=O: 1679 (νC=O). –CH: 2824 (νCH). CH=CH: 1613 (νC=C), 958 (ωCH *trans*).[1]H n.m.r. (δ/ppm): 9.55 (s, 1H: H12); 7.44 (s, 1H: H1); 7.25 (d, $J = 3.5$ Hz, 1H: H11); 7.10 (d, $J = 15.8$ Hz, 1H alkenyl *trans*); 6.96 (d,

$J = 15.7$ Hz, 1H alkenyl *trans*); 6.92 (d, $J = 15.8$ Hz, 1H alkenyl *trans*); 6.79 (d, $J = 16.0$ Hz, 1H alkenyl *trans*) and 6.56–6.43 (m, 5H: H2, H3, H6, H7 and H10).u.v.–vis. (λ_{max}/nm): 430 and 440 (sh).$T°$m (°C): 143.MS (*m/z*): 280 (M$^+$), 165, 131, 77, 51, 39.Elemental anal.: calcd. for $C_{17}H_{12}O_4$: C: 72.88, H: 4.28, O: 22.84%; found: C: 71.62, H: 4.28, O: 22.92%.**10**: *FT*i.r. (ν_{max}/cm^{-1}): Fu–Th: 3116 (νCH), 1430 (νAryls), 1225 (δCH), 1043 (ring breathing Th), 1013 (ring breathing Fu), 803 (δCH Th), 731 (γCH Fu). C=O: 1655 (νC=O). –CH: 2832 (νCH). CH=CH: 1604 (νC=C), 951 (ωCH *trans*).[1]H n.m.r. (δ/ppm): 9.84 (s, 1H: H12); 7.68 (d, $J = 3.9$ Hz, 1H: H11); 7.45 (s, 1H: H1); 7.25–7.18 (m, 2H: 1H alkenyl *trans* and H10); 7.0–6.89 (m, 2H alkenyl *trans*); 6.79 (d, $J = 15.8$ Hz, 1H alkenyl *trans*) and 6.54–6.42 (m, 4H: H2, H3, H6 and H7).u.v.–vis. (λ_{max}/nm): 440.$T°$m (°C): 114.8.MS (*m/z*): 296 (M$^+$, 178, 121, 77, 65, 51, 39.Elemental anal.: calcd. for $C_{17}H_{12}O_3S$: C: 68.93, H: 4.05, O: 16.20, S: 10.82%; found: C: 68.27, H: 4.00, O: 16.95, S: 10.78%.**11**: *FT*i.r. (ν_{max}/cm^{-1}): Fu–Th: 3107 (νCH), 1458 and 1397 (νAryls), 1252 (δCH), 1030 (ring breathing Th), 1016 (ring breathing Fu), 784 (γCH Fu), 750 (δCH Th). C=O: 1674 (νC=O). –CH: 2854 (νCH). CH=CH: 1604 (νC=C), 958 (ωCH*trans*).[1]H n.m.r. (δ/ppm): 9.56 (s, 1H: H12); 7.33–7.25 (m, 3H: H1, 1H alkenyl *trans* and H11); 7.14–7.02 (m, 3H: H2, H3 and 1H alkenyl *trans*); 6.94 (d, $J = 15.8$ Hz, 1H alkenyl *trans*); 6.72 (d, $J = 16.2$ Hz, 1H alkenyl *trans*); 6.57–6.54 (m, 2H: H6 and H7) and 6.43 (d, $J = 3.5$ Hz, 1H: H10).u.v.–vis. (λ_{max}/nm): 435 and 450 (sh).$T°$m (°C): 129.1.MS (*m/z*): 296 (M$^+$), 148, 109, 77, 65, 51, 39.Elemental anal.: calcd. for $C_{17}H_{12}O_3S$: C: 68.93, H: 4.05, O: 16.20, S: 10.82%; found: C: 68.41, H: 4.03, O: 16.77, S: 09.96%.**12**: *FT*i.r. (ν_{max}/cm^{-1}): Th: 3115 (νCH), 1495 and 1396 (νTh), 1250 (δCH), 1021 (ring breathing Th), 800 and 754 (δCH Th). C=O: 1665 (νC=O). –CH: 2813 (νCH). CH=CH: 1609 (νC=C), 943 (ωCH *trans*).[1]H n.m.r. (δ/ppm): 9.55 (s, 1H: H12); 7.44 (s, 1H: H1); 7.43 (d, $J = 15.8$ Hz, 1H alkenyl *trans*); 7.25 (d, $J = 3.5$ Hz, 1H: H11); 7.13–7.08 (m, 2H: H7 and 1H alkenyl *trans*); 6.99 (d, $J = 3.5$ Hz, 1H: H6); 6.76 (d, $J = 16.2$ Hz, 1H alkenyl *trans*); 6.72 (d, $J = 15.8$ hz, 1H alkenyl *trans*); 6.54 (d, $J = 3.5$ Hz, 1H: H10) and 6.46–6.40 (m, 2H: H2 and H3).u.v.–vis. (λ_{max}/nm): 435.MS (*m/z*): 296 (M$^+$), 178, 149, 115, 71, 57, 43.Elemental anal.: calcd. for $C_{17}H_{12}O_3S$: C: 68.93, H: 4.05, O: 16.20, S: 10.82%; found: C: 68.80, H: 4.01, O: 16.62, S 10.53%.

APPENDIX C: CHARACTERISTICS OF TETRAMER 13

13: *FT*i.r. (ν_{max}/cm^{-1}): Fu–Th: 3108 (νCH), 1444 and 1397 (νAryls), 1249 (δCH Fu), 1017 (ring breathing Fu), 791 (γCH Fu), 754 (δCH Th). C=O: 1667 (νC=O). –CH: 2822 (νCH). CH=CH: 1614 (νC=C), 959 and 945 (ωCH *trans*).[1]H n.m.r. (δ/ppm): 9.54 (s, 1H: CHO); 7.97 (d, $J = 3.7$ Hz, 1H); 7.91 (s, 1H); 7.81 (d, $J = 4.8$ Hz, 1H); 7.30–7.23 (m, 3H); 7.14–6.90 (m, 5H); 6.71 (d, $J = 16.0$ Hz, 1H alkenyl *trans*); 6.57 (d, $J = 3.6$ Hz, 1H) and 6.48–6.40 (m, 2H).u.v.–vis. (λ_{max}/nm): 450 (sh), 470 and 495 (sh).$T°$m (°C): 196.3.MS (*m/z*): 388 (M$^+$), 194, 165, 137, 77, 51. Elemental anal.: calcd. for $C_{23}H_{16}O_4S$: C: 71.14, H: 4.12, O: 16.48, S: 8.26%; found: C: 68.93, H: 4.04, O: 16.21, S: 8.80%.

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