

Super-bridged thiophene-based conjugated systems with enhanced π -electron delocalization, photoluminescence efficiency and stability

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Letter

Multiple covalent bridging of 1,6-dithienyl-1,3,5-hexatriene produces a dramatic enhancement in effective conjugation, photoluminescence efficiency and thermal stability.

Linear π -conjugated systems (LCSs) are the focus of growing interest owing to their use as conjugating spacers in chromophores for nonlinear optics,¹ active components in electronic devices,² or as luminophores in light-emitting diodes (LEDs).³ Since the relevant electronic properties underlying these applications such as π -electron delocalization, charge-carrier concentration or absorption and emission spectra are related to the HOMO and LUMO levels and to their energy difference,⁴ the molecular engineering of these parameters appears as a prerequisite for future technological development.

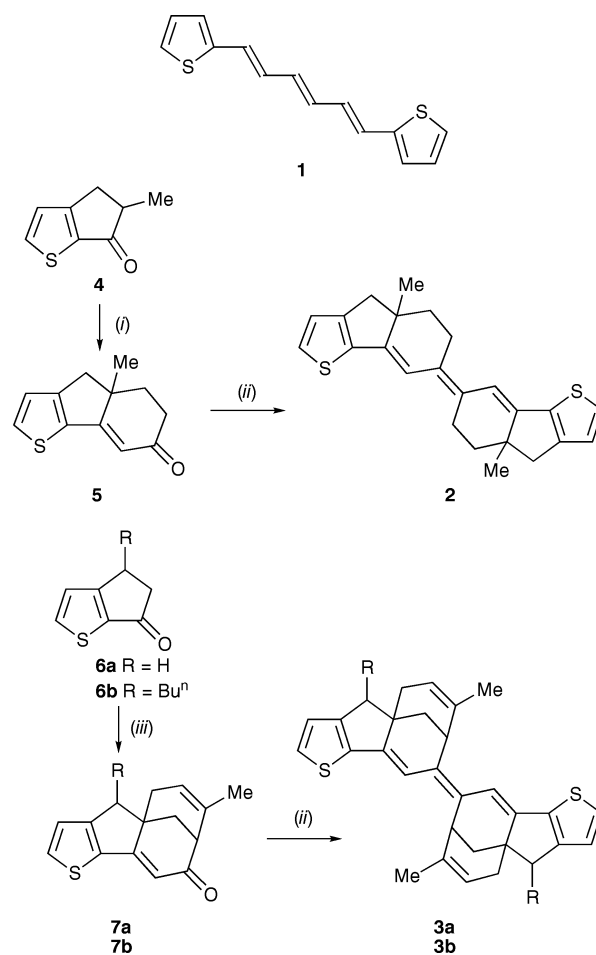
In this context, thiophene-based LCSs have received special attention as a trade-off between the efficient but unstable polyenes and the more stable but less efficient benzenic- or acetylenic-based LCSs.⁵

As shown in recent work, rigidification of the LCS is an efficient method for controlling the electronic properties of molecular or polymeric LCSs.⁶ However, further progress in this direction is still desirable and in particular, rigid LCSs with a lesser degree of overall aromaticity can be expected to present improved π -electron delocalization.

To this end we report here preliminary results on the synthesis and characterization of super-bridged 1,6-dithienylhexa-1,3,5-trienes (**3a** and **3b**). Comparison of the electrochemical and optical properties of these novel LCSs with those of the unbridged compound **1**⁷ or simply bridged system **2**, shows that in addition to a significant decrease in oxidation potential and HOMO–LUMO gap observed for **2** and **3**, super-bridged systems exhibit a dramatic enhancement of photoluminescence efficiency and thermal stability.

Whereas compounds **2** and **3** have been prepared by McMurry dimerization⁸ of ketones **5** and **7**, the synthesis of these bridged-precursor ketones has required a thorough analysis of the Robinson annulation⁹ of cyclopenta[*b*]thiophen-6-ones (**4** and **6**).^{6,10} Thus, whereas formation of the doubly bridged ketones **7a** and **7b** is observed even with a sub-stoichiometric amount of reagent, the selective preparation of ketone **5** required the substitution of the α -position of the carbonyl group in order to prevent a second annulation (Scheme 1).

Owing to the presence of two (**2**), four (**3a**) and six (**3b**) chiral centres, and to the possible *Z* and *E* configuration of the central double bond, the target compounds were obtained as mixtures of diastereomers that are quite difficult to separate. Thus, attempts to separate the diastereomers of **2** by column chromatography remained unsuccessful. Separation was not attempted for compound **3b** which contains six asymmetric carbons. Column chromatography of **3a** gave a first fraction (F1) containing two diastereomers, one being pre-



Scheme 1 Reagents and conditions: (i) 1 equivalent of methyl vinyl ketone, KOH–MeOH, Δ then EtONa–EtOH Δ ; (ii) $TiCl_4$ –Zn–THF; (iii) 2 equivalents of methyl vinyl ketone, KOH–MeOH, then H_2SO_4 , toluene, Δ

dominant (>90%), and a second one (F2) which contained a single diastereomer.[†] The crystal structure of this latter compound (*Z*-**3a**) (Fig. 1), shows that the central C=C bond adopts a *Z* configuration. The second bridging groups lie above and below the main plane of the molecule leading to a double locking of the π -conjugated system within two perpen-

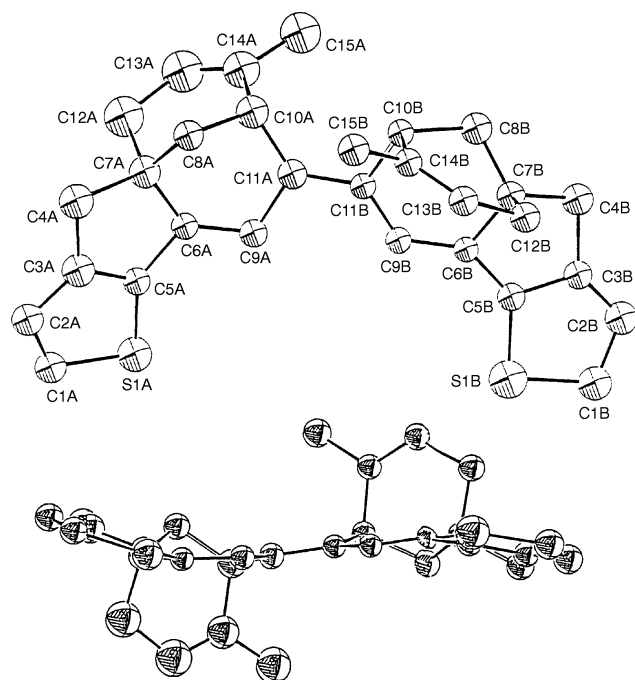
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[†] All new compounds were fully characterized by mass and NMR spectroscopies and elemental analyses giving satisfactory results.

Table 1 Electrochemical^a and optical data for dithienylhexatrienes

| Compound | E_{pa1}/V | E_{pa2}/V | λ_{max}^b/nm | $\log \epsilon$ | λ_{em}^b/nm | SS^c/eV | ϕ_{em}^d |
|----------------------|-------------|-------------|----------------------|-----------------|---------------------|-----------|---------------|
| 1 | 0.95 | 1.25 | 381 | 4.84 | 519 | 0.86 | 0.20 |
| 2 | 0.51 | 0.80 | 411 | 4.67 | 525 | 0.65 | 0.38 |
| <i>E</i> - 3a | 0.63 | 0.90 | 398 | 4.84 | 471 | 0.48 | 0.70 |
| <i>Z</i> - 3a | 0.65 | 0.90 | 392 | 4.70 | 483 | 0.59 | 0.54 |
| 3b | 0.66 | 0.95 | 398 | 4.49 | 470 | 0.48 | 0.40 |

^a 10^{-4} M substrate in 0.10 M $Bu_4NPF_6-CH_2Cl_2$, Pt electrodes, reference SCE, scan rate 100 mV s^{-1} . ^b In CH_2Cl_2 . ^c Stokes shift between the maxima of emission and absorption bands. ^d Determined using anthracene in 95% EtOH as standard.

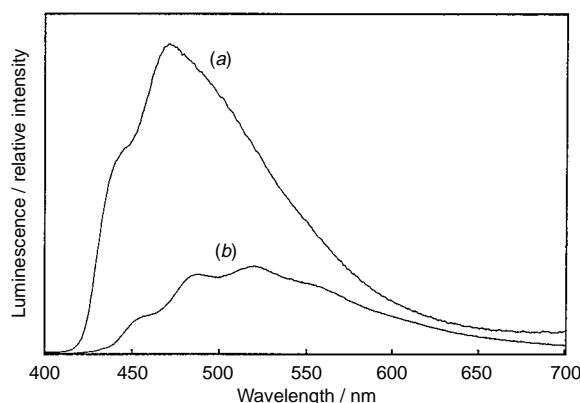
**Fig. 1** ORTEP view of *Z*-**3a**

dicular planes. The conjugated system is essentially planar except for the two thiophenes which exhibit a slight departure from planarity in the direction of the outer plane bridge.[‡]

The UV/VIS data in Table 1 show that all bridged compounds absorb at longer wavelengths than **1** indicating an extension in the effective conjugation. The most red-shifted λ_{max} observed for **2** can be attributed to a geometry more planar than that of the slightly curved super-bridged compounds **3**. For compound **3a**(F1), the red shift of λ_{max} , the higher ϵ value and the disappearance of the *cis* band¹¹ at 312 nm observed for *Z*-**3a** suggest an *E* configuration for the central double bond.

The cyclic voltammetric results are in close agreement with the optical data and they show that for all bridged compounds, the anodic peak potentials corresponding to the successive generation of the radical cation and dication (E_{pa1} and E_{pa2}) undergo a considerable negative shift (up to 0.44 V for **2**) compared to compound **1**. Furthermore, whereas **1** shows irreversible anodic waves, all bridged compounds exhibit fully reversible oxidation processes characteristic of stable cationic species.

[‡] Crystal data for *Z*-**3a**: $C_{30}H_{28}S_2$, MW 452.67, monoclinic, $P2_1/c$, $Z = 4$, $a = 14.444(20)$, $b = 10.943(6)$, $c = 15.198(17)$ Å, $\beta = 100.05(10)^\circ$, $U = 2365.33(45)$ Å³, $\rho_{calc} = 1.268\text{ g cm}^{-3}$, $\mu = 2.304\text{ cm}^{-1}$. Data collection: Enraf-Nonius Mach III diffractometer, Mo-K α , $\lambda = 0.71073$ Å, decay of standard 2%, 6940 reflections measured, $2 < \theta < 30^\circ$; h , 0–20; k , 0–15; l , –21 to 21. 2360 Reflections observed with $I > 3\sigma(I)$, Lorentz polarization and absorption corrections applied, Molen computer program, 289 variables, R 0.070, R_w 0.086. CCDC reference number 440/029.

**Fig. 2** Relative fluorescence emission spectra of (a) *Z*-**3a** and (b) **1** in CH_2Cl_2 , optical density 0.10, λ_{exc} 392 nm

The fluorescence emission data show that rigidification of the molecule produces a noticeable decrease of the Stokes shift and a large enhancement of the emission quantum yield (ϕ_{em}). Thus, whereas the bridged compound **2** shows a ϕ_{em} value twice that of **1**, ϕ_{em} reaches a value of 0.70 for the super-bridged compound *E*-**3a** which represents an increase by a factor of 3.5 compared to **1** (Fig. 2). This value, which is to our knowledge the highest ever reported for a thiophene-based LCS, is comparable to that of many laser dyes.¹²

Preliminary stability tests by differential scanning calorimetry ($10^\circ\text{C min}^{-1}$, ambient atmosphere) show that compound **1** melts at $212\text{--}213^\circ\text{C}$ and decomposes at 250°C . Compound *Z*-**3a** has a sharp melting point at 255°C whereas due to the presence of two diastereomers *E*-**3a** shows a broad peak ($275\text{--}305^\circ\text{C}$) with a maximum at 301°C . No decomposition was observed for either of the super-bridged compounds up to 340°C , the highest temperature investigated so far.

In summary a detailed analysis of the Robinson annulation of cyclopenta[*b*]thiophen-6-ones has led to the synthesis of super-bridged 1,6-dithienyl-1,3,5-hexatrienes. The dramatically enhanced π -electron delocalization, photoluminescence efficiency and thermal stability of these compounds make their incorporation as conjugating spacers in NLO-phores, or as fluorophores into polymeric structures, particularly attractive. Work in these directions is now in progress and will be reported in future publications.

References

- 1 S. R. Marder and J. W. Perry, *Adv. Mater.*, 1993, **5**, 804; N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 21.
- 2 S. Tasaka, H. E. Katz, R. S. Hutton, J. Orenstein, G. H. Frederickson and T. T. Wang, *Synth. Met.*, 1986, **16**, 17; F. Garnier, R. Hajlaoui, A. Yassar and P. Srivastava, *Science*, 1994, **265**, 1684; A. Dodabalapur, L. Torsi and H. E. Katz, *Science*, 1995, **268**, 270.
- 3 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn and A. B. Holmes, *Nature (London)*, 1990, **347**, 539; G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri and A. J. Heeger, *Nature (London)*, 1992, **357**, 477.
- 4 J. Roncali, *Chem. Rev.*, 1997, **97**, 173.

- 5 V. P. Rao, A. K.-Y. Jen, K. Y. Wong and K. J. Drost, *J. Chem. Soc., Chem. Commun.*, 1993, 1118; V. P. Rao, Y. M. Cai and A. K.-Y. Jen, *J. Chem. Soc., Chem. Commun.*, 1994, 1689.
- 6 J. Roncali, C. Thobie-Gautier, E. Elandalousi and P. Frère, *J. Chem. Soc., Chem. Commun.*, 1994, 2249; J. Roncali and C. Thobie-Gautier, *Adv. Mater.*, 1994, **6**, 846; P. Blanchard, H. Brisset, B. Illien, A. Riou and J. Roncali, *Chem. Commun.*, 1997, 569; P. Blanchard, H. Brisset, B. Illien, A. Riou and J. Roncali, *J. Org. Chem.*, 1997, **62**, 2401.
- 7 R. E. Miller and F. F. Nord, *J. Org. Chem.*, 1951, **16**, 1380.
- 8 J. E. McMurry, *Chem. Rev.*, 1989, **89**, 1513.
- 9 W. S. Rapson and R. Robinson, *J. Chem. Soc.*, 1935, 1285.
- 10 D. W. H. Mac Dowell, T. B. Patrick, B. K. Frame and D. L. Ellison, *J. Org. Chem.*, 1967, **32**, 1227; J. H. Burckhalter and J. Sam, *J. Am. Chem. Soc.*, 1951, **73**, 4460.
- 11 H. H. Jaffé and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, Wiley, New York, 1962.
- 12 F. P. Schäfer, *Dye Lasers*, Springer, Berlin, 1973.

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