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Oligo(*p*-Quinone Methide)s Bridged with Thiophene Rings. Novel Oligomeric, Quinonoid π-Systems with High Electron Affinity

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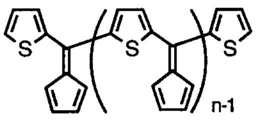
Abstract: Novel cross-conjugated oligomers composed of *p*-quinone methides and thiophenes, synthesized up to tetramer, possess substantially high electron affinity (CV). Alkali metal reduction of the dimer yields a stereoisomeric mixture of stable dianions, and protonation with trifluoroacetic acid generates the corresponding monocation and dication depending on acid strength. © 1997 Elsevier Science Ltd.

We have reported the synthesis of oligo-6-(2-thienyl)pentafulvenes **1** which show fairly low reduction potentials with good reversibility on cyclic voltammetry and form stable oligothienylenemethines attached with cyclopentadienide groups upon alkali metal reduction.[1,2] The thienyl groups in **1** serve to increase stability of the pentafulvene moiety by their electron-donating property as well as to extend the oligomer chain by their ready lithiation of thiophene. In spite of the favorable effect of the thienyl groups, **1** becomes less stable as the oligomer chain is extended. In search of stable oligomers of cross-conjugated π-systems with high electron affinity, we have designed and synthesized thiophene-extended oligomers of *p*-quinone methide, **2**. Although the parent *p*-quinone methide (4-methylene-2, 5-cyclohexadien-1-one) is unstable,[3] diaryl derivatives (fuchsones) such as **4** are stable and have been fairly extensively studied.[4] However, no oligomers of *p*-quinone methide have been described. In view of ready protonation of fuchsones forming triarylmethyl cations, oligomers **2** would also be transformed to polycationic oligothienylenemethines in acidic media. Here, we report the synthesis and properties of **2** up to tetramer.



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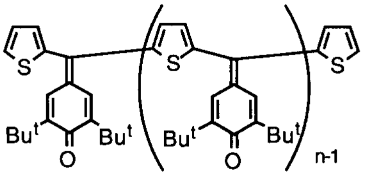

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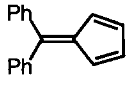
a: n = 1; **b**: n = 2; **c**: n = 3; **d**: n = 4



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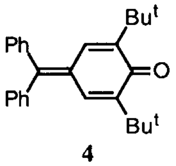


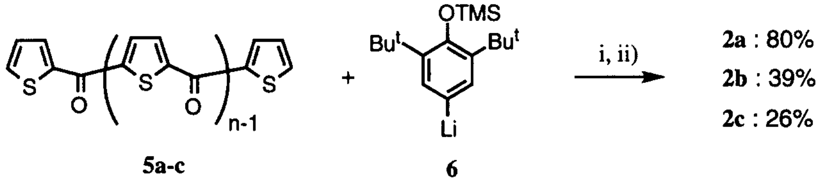
4

Quinone methide **4** ($^1E_{red}$ = -1.14 V[5]) is a stronger electron acceptor than fulvene **3** ($^1E_{red}$ = -1.50 V[5]), and hence oligomers **2** are expected to be superior electron acceptors than oligomers **1**. The *tert*-butyl groups in **2a**-

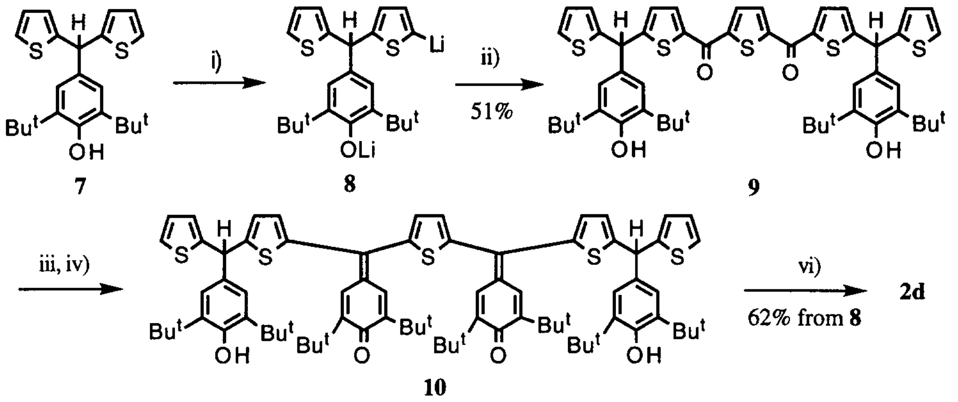
d were introduced to increase both their stability and solubility .

Monomer **2a** to trimer **2c** were obtained by the nucleophilic addition of 3, 5-di-*tert*-butyl-4-trimethylsiloxyphenyllithium **6**[6] to the corresponding 2-thienylketones **5a-c**[7] followed by acid treatment of the crude products in moderate to good yields (Scheme 1). However, this simple method could not be applied to the synthesis of tetramer **2d** because of extremely poor solubility of tetraketone **5d**.

As a possible alternative way, attempted use of **2a** as a building block for the higher oligomers through lithiation and functionalization at the thienyl part was unsuccessful because of high electron affinity of the quinone methide part. However, it was found that dihydro compound **7**,[8] obtained by reduction of **2a** with $NaBH_4$, can be used as a building block for the tetramer: treatment of **7** with 2 equiv of *t*-BuLi in THF selectively formed dianion **8** which could be converted to tetramer **2d** via **9** and **10** (Scheme 2).



Scheme 1: i) small excess of **6**/THF, 0 °C - r.t.; ii) 2M HCl/acetone



Scheme 2: i) 2 eq. ^{t}BuLi/THF, 0 °C; ii) 0.3 eq. *N, N, N', N'*-tetramethyl-2, 5-thiophenedicarbamide; iii) 5 eq. **6** / THF, 0 °C to r. t.; v) 2 M HCl/acetone, r.t.; vi) 2.5 eq. DDQ/benzene

Compounds **2a-d** are orange crystalline substances with good stability and solubility to common organic solvents. While dimer **2b** exhibits a large bathochromic shift (64 nm) compared to monomer **2a** in the visible region, trimer **2c** and tetramer **2d** show little change from **2b** probably due to the mode of cross conjugation and conformational mobility similar to oligomers **1** (Table 1).

Upon cyclic voltammetry, while monomer **2a** shows two poorly reversible reduction waves, oligomers **2b-d** show two or three reversible reduction waves with the first reduction potentials ($^1E_{red}$) approaching to that of *p*-benzoquinone (Table 2). The first reduction waves of **2b, c** and the first and second waves of **2d** appear to involve two-electron transfer,[9] thus forming the corresponding dianions and tetraanion, respectively. The fairly sharp drop of $^1E_{red}$ from **2a** to **2b** and rather small drop from **2b** to **2d** are in consonant with the observations in the absorption spectra.

Table 1. Selected spectral data of **2a-d**[a]

2a: MS (EI) m/z = 382 (M^+), ^{1}H-NMR (270 MHz, $CDCl_3$): δ 7.60 (dd, J = 5.0, 1.3 Hz, 2H), 7.44 (s, 2H), 7.23 (dd, J = 3.6, 1.3 Hz, 2H), 7.15 (dd, J = 5.0, 3.6 Hz, 2H), 1.28 (s, 18H); UV-Vis: λ_{max}/nm (log ε) 419 (4.48), 296 (4.25), 258 (4.30); IR (KBr): $\nu_{C=O}$ 1593 cm^{-1}.

2b: MS (FAB) m/z = 681 [$(M+H)^+$], ^{1}H-NMR: δ 7.66 (dd, J = 5.0, 1.1 Hz, 2H), 7.49 (d, J = 2.5 Hz, 2H), 7.45 (d, J = 2.5 Hz, 2H), 7.31 (s, 2H), 7.29 (dd, J = 3.6, 1.1 Hz, 2H), 7.19 (dd, J = 5.0, 3.6 Hz, 2H), 1.28 (s, 18H), 1.26 (s, 18H); UV-Vis: λ_{max}/nm (log ε) 483 (4.60), 411 (4.63), 364 sh (4.48), 312 sh (4.47), 286 sh (4.49), 255 sh (4.59); IR (KBr): $\nu_{C=O}$ 1605 cm^{-1}.

2c: MS (FAB) m/z = 980 [$(M+2)^+$]; ^{1}H-NMR: δ 7.66 (dd, J = 5.0, 1.1 Hz, 2H), 7.48 (s, 2H), 7.45 (s, 4H), 7.34 (d, J = 3.9 Hz, 2H), 7.32 (d, J = 3.9 Hz, 2H), 7.29 (dd, J = 3.6, 1.1 Hz, 2H), 7.19 (dd, J = 5.0, 3.6 Hz, 2H), 1.28 (s, 18H), 1.27 (s, 18H), 1.26 (s, 18H); UV-Vis: λ_{max}/nm (log ε) 475 (4.73), 414 (4.67), 372sh (4.60), 308sh (4.57), 291sh (4.59); IR (KBr): $\nu_{C=O}$ 1608 cm^{-1}.

2d: MS (FAB) m/z = 1280 [$(M+4)^+$]; ^{1}H-NMR: δ 7.62 (dd, J = 5.2, 1.1 Hz, 2H), 7.49 (d, J = 2.8 Hz, 2H), 7.46 (d, J = 2.8 Hz, 4H), 7.45 (m, 6H), 7.34 (s, 2H), 7.34 (d, J = 3.9 Hz, 2H), 7.32 (d, J = 3.9 Hz, 2H), 7.28 (dd, J = 3.6, 1.1 Hz, 2H), 7.16 (dd, J = 5.2, 3.6 Hz, 2H), 1.29 (s, 18H), 1.26 (s, 36H), 1.25 (s, 18H); UV-Vis: λ_{max}/nm (log ε) 477 (4.90), 411 sh (4.83), 293 sh (4.75), 261 (4.90); IR (KBr): $\nu_{C=O}$ 1608 cm^{-1}.

[a] ^{1}H NMR spectra were taken at 600 MHz in CD_2Cl_2, unless otherwise noted; UV-Vis spectra in CH_2Cl_2.

Reduction of dimer **2b** with 3% Na-Hg in degassed THF gave rise to a new strong absorption at 583 nm assignable to dianion **2b**$^{2-}$ (Fig. 1). Dianion **2b**$^{2-}$ was stable at room temperature in this solution and regenerated **2b** upon exposure to air. ^{1}H-NMR spectrum of **2b**$^{2-}$ shows the presence of all the three possible geometrical isomers, **2bA**$^{2-}$, **2bB**$^{2-}$ and **2bC**$^{2-}$, in a ratio of ca. 9 : 7 : 1.[10] The structures of the two major isomers are assignable from the NOESY spectrum to **2bA**$^{2-}$ and **2bB**$^{2-}$, respectively. This geometrical preference is largely different from the results of alkali metal reduction of **1b** where the one of the syn-isomers, **1b**$^{2-}$, was formed predominantly.[2] Greater steric bulkiness of the di-*tert*-butyl group than cyclopentadienyl group may be a reason for the geometrical preference.

Similar reduction of trimer **2c** suggests stepwise formation of dianion (λ_{max} = 546 and 905 nm),[11] trianion radical (754 nm),[12] and finally tetraanion (583 nm).[11]

Table 2. Reduction potentials of **2a-d**[a]

Compound	$^1E_{red}$	$^2E_{red}$	$^3E_{red}$
2a	-0.99	-1.58	
2b	-0.61	-2.01	
2c	-0.55	-1.00	-1.45
2d	-0.52	-0.72	-1.88
BQ[b]	-0.44	-1.29	

[a] V vs Ag/AgCl, 0.1 M nBu_4NClO_4 in DMF, sweep rate 100 mV/s, Ferrocene = +0.48 V. [b]p-Benzoquinone.

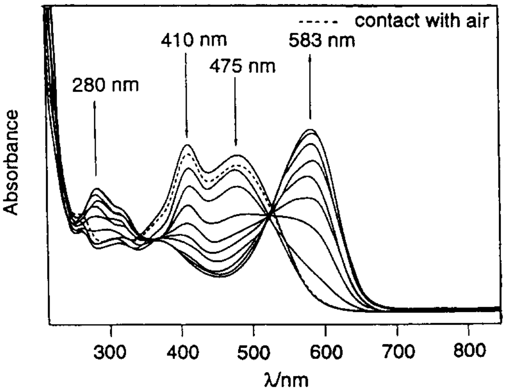
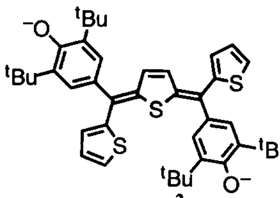
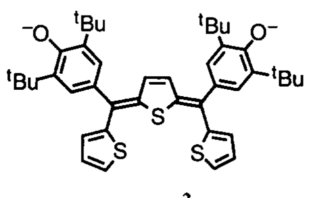


Fig. 1. UV-Vis spectral change of **2b** upon reduction with 3% Na-Hg in THF.

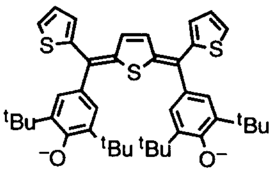
Dissolution of dimer **2b** in CF_3COOH produced dication **11** (523 and 564 nm) by double protonation.[13] Titrative addition of CF_3COOH to a dicholomethane solution of **2b**, however, at first showed rise of a new absorption at 651 nm to suggest the intermediate formation of monocation **10**.



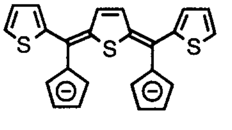
2bA^{2-}



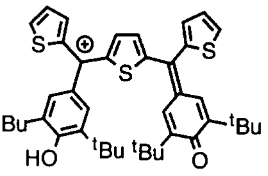
2bB^{2-}



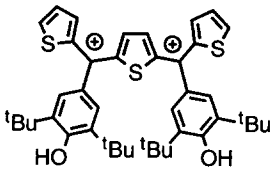
3bC^{2-}



1b^{2-}



10



11

In conclusion, the present results provide a good prospect for the synthesis of stable higher oligomers of quinone methide and thereby the corresponding polyanions or polycations by alkali metal reduction or protonation with acids. Further studies on oligomers **2** are in progress.

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References and Notes;

1. Kawase, T.; Kurata, H.; Morikawa, T.; Oda, M.*Tetrahedron Lett.*, **1993**, *34*, 3449.
2. Kurata, H.; Kawase T.; Oda, M.*Chem. Lett.*, **1994**, 2219.
3. For a review; *The Chemistry of the quinonoid compounds Vol. 2* (Patai, S.; Rappoport, Z. ed.) Wiley, New York (1988).
4. Wagner, H. -U.; Gompper, R. *The chemistry of the quinonoid compounds* (Patai, S. ed), Chapt. 18 Quinone Methide, p 1145-1178 (1974). b) Becker, H.-D., *J. Org. Chem.*, **1967**, *32*, 2115. c) Hünig S.; Schwarz, H. *Liebigs Ann. Chem.*, **1956**, *599*, 131.d) Musil, L; Koutek, B.; Verek, J.; Soucek, M. *Coll. Czech. Chem. Commun.*, **1984**, *49*, 1949, and references cited therein.
5. Data obtained in our laboratory under the same conditions for **2a-c**. See also Kawase, T.; Fujino, S.; Oda, M. *Chem. Lett.*, **1990**, 1683.
6. Gierke, W.; Harrer, W.; Kurreck, H.; Reusch, J. *Tetrahedron Lett.*, **1973**, 3681.
7. **5a**: Acheson, R. M.; MacPhee, K. E.; Philpott, D. G.; Barltrop, J. A. *J. Chem. Soc.*, **1956**, 698. **5b**: Miyahara, Y. *J. Heterocyclic. Chem.*, **1979**, 1147. **5c**: Ahmed, M.; Meth-Cohn, O. *J. Chem. Soc. (C)*, **1971**, 2104.
8. **7**: colorless needles, mp 104-105 ℃, ^{1}H-NMR (270 MHz, $CDCl_3$) δ 7.14 (dd, J = 5.3, 1.1 Hz, 2H), 7.13 (s, 2H), 6.89 (dd, J = 5.3, 3.6 Hz, 2H), 6.80 (dd, J = 3.6, 1.3 Hz, 2H), 5.74 (s, 1H), 5.10 (s, 1H), 1.39 (s, 18H).
9. The integral area of these waves are nearly twice of the third reduction wave of **2c,d**.
10. **2bA^{2-}**: ^{1}H-NMR (600 MHz, THF-d_8) δ 7.25 (dd, J = 5.2, 1.1 Hz, 1H), 7.24 (dd, J = 3.8, 1.1 Hz, 1H), 7.23 (s, 2H, phenyl), 7.12 (dd, J = 5.2, 1.1 Hz, 1H), 7.00 (dd, J = 3.6, 1.1 Hz, 1H), 6.96 (dd, J = 5.2, 3.6 Hz, 1H), 6.91 (s, 2H), 6.89 (dd, J = 5.2, 3.8 Hz, 1H), 6.76 (d, J = 6.0 Hz, 1H, thienoquinoid), 6.69 (d, J = 6.0 Hz, 1H, thienoquinoid), 1.41 (s, 18H), 1.40 (s, 18H). **2bB^{2-}**: ^{1}H-NMR (600 MHz, THF-d_8) δ 7.29 (dd, J = 3.8, 1.1 Hz, 2H), 7.19 (dd, J = 5.2, 1.1 Hz, 2H), 6.95 (dd, J = 5.2, 3.8 Hz, 2H), 6.92 (s, 2H), 6.81 (s, 2H), 1.40 (s, 36H). The phenyl and thienoquinoid protons of **2bC^{2-}** are observed at δ 7.14 and 6.55 as singlets.
11. ^{1}H NMR signal are observable, although very complex due to the isomeric mixture similar to **2b^{2-}**.
12. The preliminary measurement of ESR spectrum of **2c^{3-}** shows triplet with a_H = 1.50 G (20 ℃, THF).
13. **11**: ^{1}H-NMR (270 MHz, CF_3COOD) δ 8.89 (brd, J = 4.3 Hz, 2H), 8.05 (br. d, J = 4.4 Hz, 2H), 8.04 (s, 2H), 7.80 (s, 4H), 7.69 (br. t, J = 4.4 Hz, 2H), 1.39 (s, 36H). ^{13}C-NMR (67.8 MHz, CF_3COOD) δ 173.15, 170.93, 157.11, 156.94, 149.41, 145.28, 144.44, 143.38, 141.22, 135.51, 133.56, 35.92, 29.57.

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