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Convenient Regioselective Syntheses of Isomeric Bis(tetrathiafulvalenylethenyl)naphthalene π-Donors

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Abstract: Novel highly soluble isomeric tetrathiafulvalene (TTF) dimers with unusual divinylnaphthalene spacers have been prepared from Wittig reactions. The cyclic voltammetry of the new TTF dimers reveals an independent behaviour of the two TTF units which show different oxidation potential values depending upon the substitution pattern.

Following the idea of Haddon and Wudl who suggested that systems containing two or more linked donor units might afford to highly conducting charge transfer (CT) complexes of high dimensionality,[1] a great deal of work has been devoted during the last years to the preparation of dimeric TTF molecules,[2] higher oligomers,[3] polymers[4] and dendrimers[5] in which the TTF units are linked by one or more spacer groups.

Mizutani[6] and Otsubo[2,7] have studied dimeric TTF systems with different divinylarene and divinylheteroarene spacers such as *p*-xylene, thiophene or bithiophene, obtaining radical anion salts with room temperature conductivities as high as 80-140 S cm^{-1}, while keeping the metallic behaviour down to about 180 K. The high electrical conductivities are ascribable to the extensive π-conjugation of the donors, which efficiently reduces on-site Coulombic repulsion and increases dimensionality. On the basis of this concept, we present in this communication the synthesis and study of novel dimeric systems of TTF with divinylnaphthalene spacers **1** and **2** (Figure 1). Due to the rigid symmetrical structure of the naphthalene ring, it has been the building block of choice in different materials for improvement of thermal properties and for the introduction of liquid crystalline properties.[8] Moreover, with the eventual aim of examining the interaction between both TTF moieties in this type of systems, naphthalene units might be useful provided that different regioisomeric dimers can be synthesized.

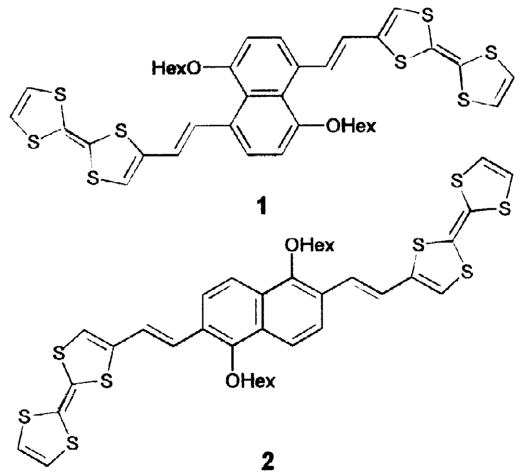

Figure 1

Thus, in this communication the naphthalene units are incorporated regioselectively as spacers either through the 2,6 or the 1,5 positions.

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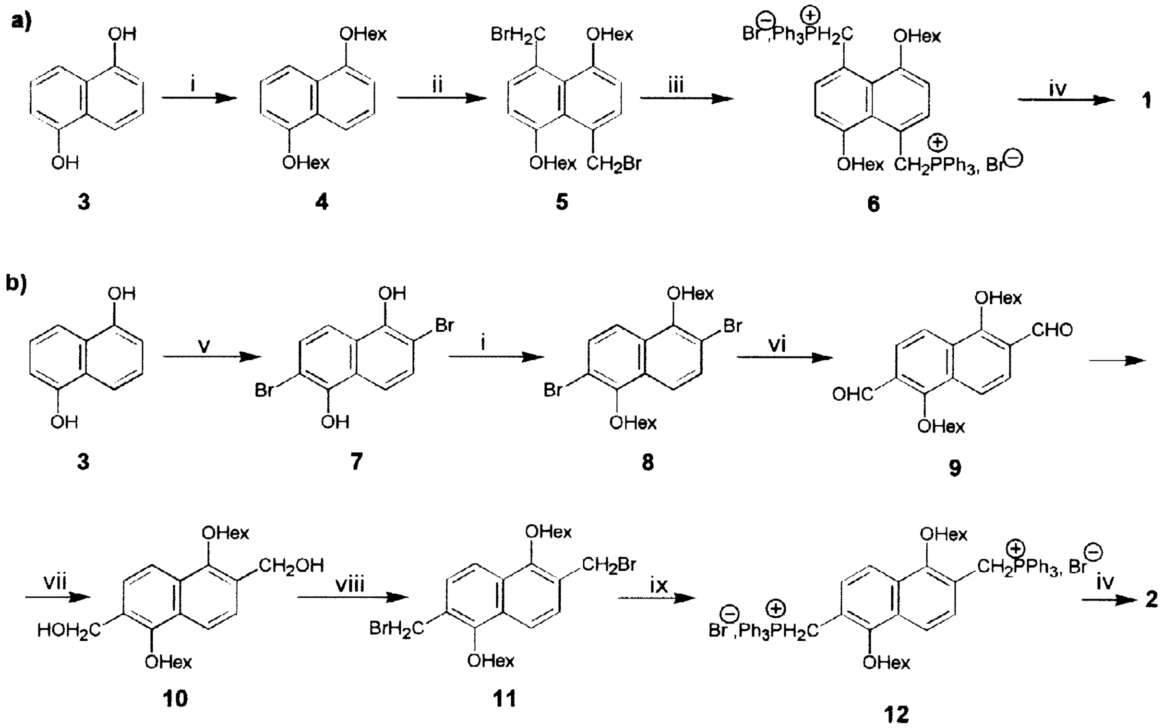
Two long alkoxy chains are introduced in the naphthalene units in order to increase the solubility of the final dimeric TTF derivatives. The syntheses of 1 and 2 were carried out by conventional Wittig reactions[9] of 2-formyltetrathiafulvalene[10] with phosphonium salts 6 and 12, respectively. The isomeric phosphonium salts were prepared by using multistep synthetic routes in order to obtain the desired substitution pattern (Scheme).



Scheme. i , KOH , DMSO, BrHex ; ii, HCHO, HBr, HOAc ; iii, PPh_3, xylene, Δ ; iv, TTF-CHO, EtOLi, EtOH ; v, Br_2, HOAc, 80 °C ; vi, n-BuLi, DMF ; vii, $NaBH_4$, CH_2Cl_2, MeOH ; viii, BF_3Et_2O, Et_4NBr, CH_2Cl_2, ix, PPh_3, DMF

The key steps that allow different substitution patterns on the naphthalene are the aromatic electrophilic substitution steps (dibromomethylation of 4 and dibromination of 3). Thus, when the 1,5-dihydroxynaphthalene 3 is first hexylated with bromohexane to yield 4 and then bromomethylated with paraformaldehyde and a (commercially available) 30 wt % solution of HBr in acetic acid,[11] the corresponding 4,8-dibromomethyl derivative 5 is obtained. Treatment of 5 with triphenylphosphine in boiling *p*-xylene gave the corresponding 1,5-dihexyloxy-4,8-bis[(triphenylphosphonium)methyl]naphthalene dibromide 6. The alternative route towards the isomeric 2,6-disubstituted phosphonium salt 12 starts with bromination under acidic conditions[12] of the 1,5-dihydroxynaphthalene 3 to yield the corresponding 2,6-dibromoderivative 7. Subsequent hexylation of 2,6-dibromoderivative 7 gave the dihexyloxyderivative 8, which on treatment with n-butyllithium and dimethylformamide afforded dialdehyde 9. Reduction with sodium borohydride and treatment with boron trifluoride etherate and tetraethylammonium bromide in dichloromethane[13] yielded the 2,6-

dibromometylderivative **11** which was finally reacted with triphenylphosphine (DMF, reflux) to give the corresponding 1,5-dihexyloxy-2,6-bis[(triphenylphosphonium)methyl]naphthalene **12**.

The isomeric triphenylphosphonium salts **6** or **12** were afterwards suspended in anhydrous ethanol together with formyl-TTF. To the mixture, a solution of lithium ethoxide was added dropwise and the mixture was stirred under argon overnight. The resulting red crude product was treated with water to precipitate a red solid which was filtered, washed with methanol and chromatographed to afford the new isomeric TTF derivatives **1** and **2** respectively.[14] In both cases the Wittig reaction afforded solely to the *all-trans* configuration products, according to the coupling constants data (J =15 Hz). The presence of the hexyloxy chains in the naphthalene moieties of **1** an **2** results in highly soluble TTF dimers contrary to that observed for other dimeric[6h] and trimeric[15] TTF analogues.

The cyclic voltammograms of these new donors show two reversible redox waves, each one of them involving a two-electron transfer process ($E^1_{1/2}$ = 0.369 V and $E^2_{1/2}$ = 0.766 V for **1** and $E^1_{1/2}$ = 0.380 V and $E^2_{1/2}$ = 0.831 V for **2** compared with $E^1_{1/2}$ = 0.372 V and $E^2_{1/2}$ = 0.672 V for TTF under the same conditions).[16] The two TTF units are thus oxidized independently to form bis(radical-cation) and tetracation species. The slightly more positive first oxidation potential of **2** in comparison with **1**, which is quite similar to that of TTF, could indicate a less effective conjugation of the TTF moieties with the divinylnaphthalene moiety in donor **1**, thus resulting in an almost independent behaviour of the two TTF units in this molecule.

To gain some understanding of the experimental observations reported above, the geometric structures of the new donors **1** and **2** were investigated by performing semiempirical calculations at the PM3 level.[17] The minimum energy structures found for the new donors are depicted in Figure 2 showing that the conjugated system in **1** is not totally planar, the dihedral angle between the TTF and the naphthalene moieties being of 26.35 ° (much higher than that observed for compound **2** which is of 4.14 °). The higher distortion of planarity observed for donor **1** might cause a decrease of the conjugation, thus supporting the above experimental observations.

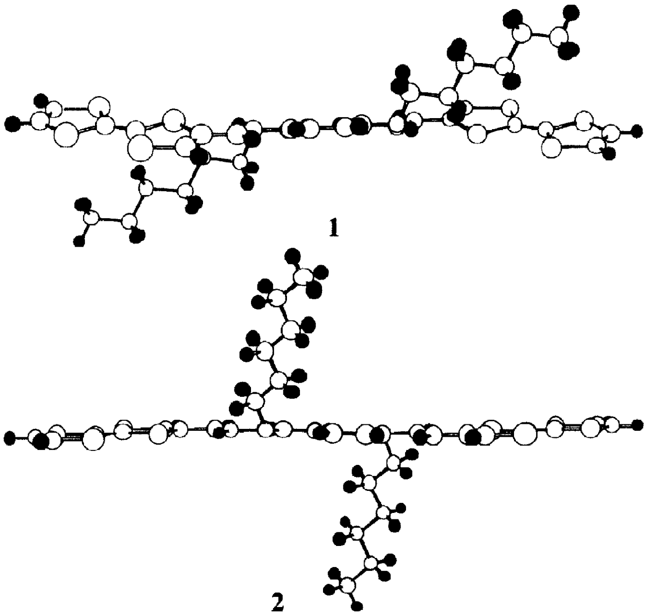


Figure 2. PM3 stereoview of the minimum energy structures of **1** and **2**

In summary, we have developped a new procedure for the preparation of novel TTF-dimers with divinylnaphthalene spacers **1** and **2**, showing different interaction of the TTF moieties with the divinylnaphthalene core depending upon the position of the tetathiafulvalenevinyl substituents on the naphthalene system. Preliminary attempts of complexation of **1** and **2** gave black charge transfer complexes with TCNQ and DDQ as well as radical ion salts with counter ions such as I_3^-. X-ray structures as well as the study of the solid state properties of the new resulting charge transfer salts are under study in our laboratory.

Acknowledgments.

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14. Compounds **1** and **2** gave satisfactory analytical data. Selected spectroscopic data for compound:

    1: IR (NaCl) : ν = 2945, 2875, 1725, 1530, 1480, 1385, 1025, 945 cm^{-1}. ^{1}H-NMR (300 MHz, CDCl$_3$) : δ = 7.60 (d, J = 15 Hz, 2H), 7.34 (d, J = 8 Hz, 2H), 6.82 (d, J = 8 Hz, 2H), 6.42 (d, J = 15 Hz, 2H), 6.32 (s, 4H), 6.23 (s, 2H), 4.05 (t, 4H), 2.00 (m, 4H), 1.45 (m, 4H), 1.28 (m, 8H), 0.86 (t, 6H). UV-Vis (HCCl$_3$, λ_{max}) : 398, 348, 336, 246 nm.

    2: IR (KBr) : ν = 2940, 1535, 1380, 1350, 1175, 1150, 950 cm^{-1}. ^{1}H-NMR (300 MHz, CDCl$_3$) : δ = 7.82 (d, J = 9 Hz, 2H), 7.60 (d, J = 9 Hz, 2H), 7.00 (d, J = 15 Hz, 2H), 6.86 (d, J = 15 Hz, 2H), 6.42 (d, 2H), 6.34 (s, 4H), 3.97 (t, 4H), 1.95 (m, 4H), 1.67 (m, 4H), 1.44 (m, 8H), 0.96 (t, 6H). UV-Vis (HCCl$_3$, λ_{max}) : 446, 398, 358, 341, 324, 293, 254 nm.
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16. Cyclic voltammetry measurements were carried out at 200 mV/s in dichloromethane by using SCE, platinum and glassy carbon as reference, counter and working electrodes respectively and tetrabutylammonium perchlorate as the supporting electrolyte.
17. Semiempirical calculations (PM3) were performed using the program Hyperchem (version 3.0) from Hypercube Inc. on a PC compatible Pentium at 133 MHz. For each structure, the minimum energy was determined after reminimization.