

Synthesis and Properties of New Fullerene-Tetrathiafulvalene Dyads

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In the last few years fullerene-based donor and acceptor dyads have attracted increasing attentions, not only because of their remarkable photophysical properties such as photoinduced energy and/or electron-transfer processes, but because of their potentials for the application to molecular electronic devices.¹ Several C₆₀ dyads bearing tetrathiafulvalene (TTF) units as a donor part have been synthesized and intramolecular electron-transfer processes were observed for some C₆₀-TTF systems.² We report here the synthesis and electrochemical properties of new methano-bridged C₆₀ derivatives covalently linked with a TTF unit (**1a-c**).

The synthesis of **1a** (ortho), **1b** (meta), and **1c** (para) was carried out as shown in Scheme 1. Treatment of TTF derivative protected by cyanoethyl group with sodium methoxide and followed by reaction with compounds **3a-c** afforded TTF derivatives (**4a-c**). Deprotection of dioxane group of **4a-c** by *p*-toluenesulfonic acid gave aldehyde derivatives **5a-c**, which were converted into tosylhydrazone derivative **7a-c**. Treatment of **7a-c** with sodium methoxide generated diazo derivatives **8a-c** in situ, which were readily reacted with C₆₀ in toluene to give C₆₀-TTF dyads **1a-c** in 1.2-6.5 % yield after purification by HPLC (buckyprep/toluene).³

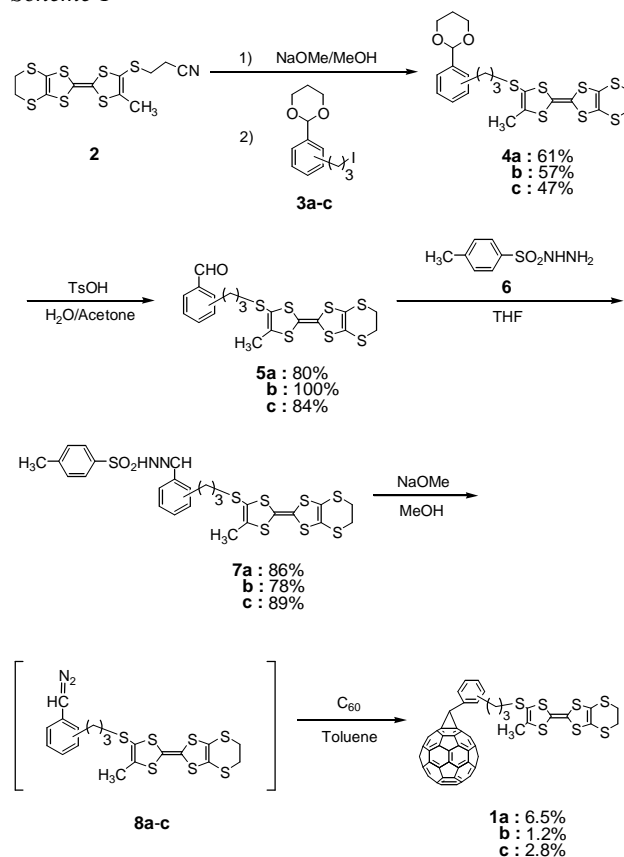
The redox potentials of **1a** were investigated by cyclic voltammetry. Cyclic voltammogram showed two pairs of reversible waves on the oxidation side, and three pairs of reversible waves and one irreversible wave on the reduction side, which correspond to the redox waves from TTF part and those from C₆₀ part, respectively (Table 1).

Fig 1. shows UV-Vis spectra of **1a-c** in cyclohexane. A broad absorption band was observed from 700 to 800nm for **1a**, which is attributable to charge transfer band from TTF to C₆₀ part. The absorption intensity of this band decreases in the order of **1a**, **1b**, and **1c**. The measurement of transient absorption spectra suggested the existence of intramolecular photoinduced charge separation process.

References

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Scheme 1



Compound	E_1^{ox}	E_2^{ox}	E_1^{red}	E_2^{red}	E_3^{red}	E_4^{red}
1a	0.52	0.84	-0.54	-0.95	-1.44	-2.00 ^a
C ₆₀			-0.49	-0.92	-1.39	-1.89
2	0.45	0.83				

Table 1. Redox potentials of **1a**, C₆₀, and **2** in PhCN at 25°C. V vs SCE, 0.1M nBu₄NClO₄, 50mV/sec, Pt electrode. ^aIrreversible step.

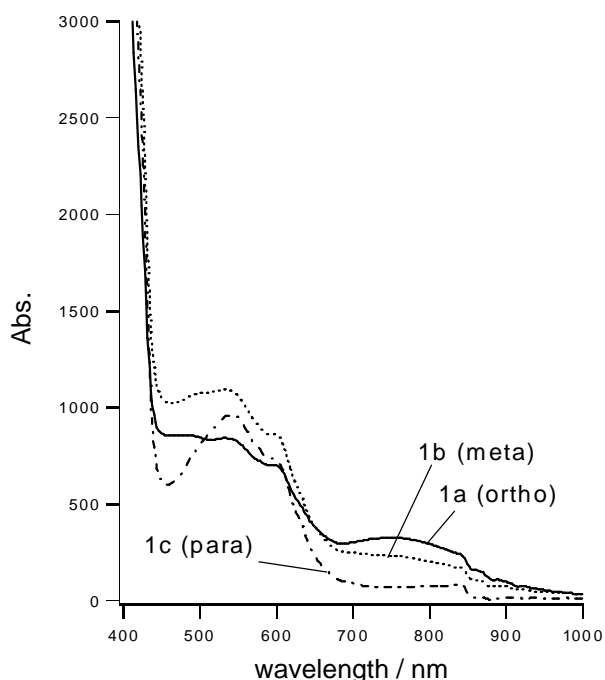


Fig. 1. UV-Vis spectra of **1a-c** in cyclohexane.