Synthesis and oxidative polymerization of dialkyl fluorene-9,9-dicarboxylates

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ABSTRACT

Novel long-chain dialkyl fluorene-9,9-dicarboxylates were synthesized by treating fluorene with lithium diisopropylamide followed by alkyl chloroformates. The fluorene derivatives were readily electro-oxidized to form electroactive films on the surface of a glassy carbon electrode. From the viewpoint of suitable potential window (from −2.5 to 1.5 V vs Ag/Ag+), cyclic voltammograms of the films indicated the electroactive properties of the fluorene derivatives that make them good candidates for electrochemical capacitor materials.

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Electrochemical capacitors with redox-active electrode materials have recently attracted increasing attention because of their higher power density as compared to the secondary batteries and their higher specific energy as compared to electric double-layer capacitors. They can also be used as charge-storage devices to complementary conventional batteries.[1,2] Energy density, power density and cycle life are three main characteristics of capacitor materials. In general, activated carbons have low capacity because of their low energy density; however, they have high power density and long cycle life. Electroactive metal oxides such as RuO_2 exhibited a narrow potential window because they are generally used with aqueous electrolytes. Conductive polymers can be modified more easily by chemical methods and they have high capacity resulting in high energy density. Furthermore, their electroactive potentials are key characteristics that affect both the energy density and the power density. Therefore, the development of conducting polymers for electrochemical capacitors has become popular.[3,4] There is a strong requirement for the conductive polymers with suitable electroactive potential windows and energy density.[5,6]

We have been interested in the development of electrochemical capacitors and had recently reported on the electrooxidation behaviour of several 9,9-dialkylfluorenes. We found that 9,9-dialkylfluorenes bearing long alkyl chains such as octyl and decyl groups could be readily electropolymerized to afford polyfluorene derivatives; these are good candidates for active electrode materials in electrochemical capacitors.[7] The cyclic voltammetry (CV) analysis of these polyfluorenes showed that the working voltage of the conducting polymer would be around 4.0 V,[2,5] which was higher than that of conventional polymers.[8] However, their elec-

troactive potential ranged from −3.0 to 1.2 V. It is known that when using an eletrochemically stable non-aqueous electrolyte solution, it is desirable for the redox potential caused by p- and n-doping to be as far apart in the potential range as possible. (e.g., $CH_3CN/0.1$ M $TEABF_4$: −3.0 to +2.0 V). Moreover, because organic electrolyte solutions are intolerant of such negative reduction voltage, conductive polymers with more positive range of n-doping/undoping reaction potential were desirable.[9] The situation prompted us to reinvestigate a novel conducting polymer for electrochemical capacitor materials. In this study, we focused on dialkyl 9,9-fluorene-dicarboxylates, which are fluorene derivatives bearing two ester groups at the 9-position. While several fluorene derivatives have been reported, only a few fluorene dicarboxylates have been known[10] although these have not been used to the capacitor materials. We assumed that the polymers of dialkyl 9,9-fluorenecarboxylates should have more positive electroactive potential windows than poly-9,9-n-dioctylfluorenes because of their electron-withdrawing ester moieties.

On the basis of our previous study, we predicted that the electrooxidation of fluorenecarboxylates bearing long alkyl chains would proceed smoothly to give conducting polymers in a manner similar to the electrooxidation of 9,9-dialkylfluorenes.[7a] From this point of view, we recently designed dialkyl fluorene-9,9-dicarboxylates 2a–b (Scheme 1). In this Letter, we report the synthetic procedure of dialkyl fluorene-9,9-dicarboxylates and the electrochemical properties of their electropolymerized polymer film.

First, we synthesized diethyl fluorene-9,9-dicarboxylate according to the literature (Table 1, entry 1).[11] Using 2 mol of n-butyl lithium (BuLi) as a lithiating agent, fluorene was deprotonated at −78 °C and subsequently reacted with ethyl chloroformate ($ClCO_2Et$) to give diethyl fluorene-9,9-dicarboxylate (2c) in 54% yield. We then applied the procedure to the preparation of dihexyl fluorene-9,9-dicarboxylate (2a). However, the product was
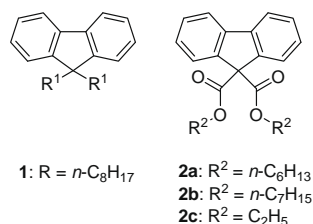
Scheme 1. 9,9-Dialkylfluorene **1** and dialkyl fluorene-9,9-dicarboxylates **2**.

Table 1
Synthesis of dialkyl fluorene-9,9-dicarboxylates

Entry	Lithiating agent	R	2	Yield[a] (%)
1	BuLi	C_2H_5	**2c**	54
2	BuLi	n-C_6H_{13}	**2a**	44
3	LDA	n-C_6H_{13}	**2a**	78
4	LDA	n-C_7H_{15}	**2b**	76

[a] Isolated yield.

obtained in a low yield as a mixture with by-products (44% of GC yield, entry 2). On modifying the reaction conditions, we found that lithium diisopropylamide (LDA) was an effective lithiating re-agent for the reactions. A solution of n-butyllithium in hexane (1.6 M, 15 mmol) was added dropwise to a solution of diisopropyl-amine (16 mmol) in THF (20 mL) at -78 °C. The mixture was stir-red at -78 °C for 45 min and at 0 °C for 20 min and cooled again to -78 °C. To the LDA solution prepared thus, a solution of fluorene (7.0 mmol) in THF (20 mL) was added dropwise and stirred at -78 °C for 30 min. Hexyl chloroformate (33 mmol) was added to the mixture. The solution was allowed to warm to room tempera-ture, and it was stirred for 3 h. Then, the mixture was poured into water (100 mL) and extracted with Et_2O (3 × 50 mL). The com-bined organic phase was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (hexane/Et_2O 20:1) to afford dihexyl fluorene-9,9-dicarboxylate (**2a**) in 78% yield (entry 3). Diheptyl fluorene-9,9-dicarboxylate (**2b**) was obtained in 76% yield (entry 4) in a similar manner.

Next, the electropolymerization of dialkylfluorene-9,9-dicar-boxylates **2a** and **2b** was carried out. The electrochemical oxidation processes for dialkyl fluorene-9,9-dicarboxylates with different lengths of alkyl chain in the ester groups were investigated using CVs in a CH_3CN-based electrolyte. The CVs of dialkyl fluorene-9,9-dicarboxylates **2a**, **2b** and 9,9-n-dioctylfluorene (**1**) are shown in Figure 1a, b and c, respectively.

The voltammograms during potential cycles in Figure 1c exhib-ited an oxidative current peak in the potential range around 1.2 V versus Ag/Ag$^+$ and electrochemically reversible redox waves with some peaks and shoulders in the range of 0.7–1.2 V. These waves were previously reported to ascribe a formation of radical cation species for the 9,9-n-dioctylfluorene monomers and the redox reactions of the resulted oligomer/polymer.[7] Similar to Figure 1c, each voltammogram in Figure 1a and b indicated an oxidative cur-rent increase from 1.5 V and redox waves in the range of 1.0–1.4 V; this can be attributed to the formation of radical cation species of the corresponding monomers, and the redox reactions of the oligo-mer/polymer.

On comparing the CV shapes of dialkyl fluorene-9,9-dicarboxyl-ates **2a** and **2b** with that of 9,9-n-dioctylfluorene (**1**) during elec-tropolymerization, marked positive potential shifts were observed for the monomer oxidation and for the redox reactions of the oligo-
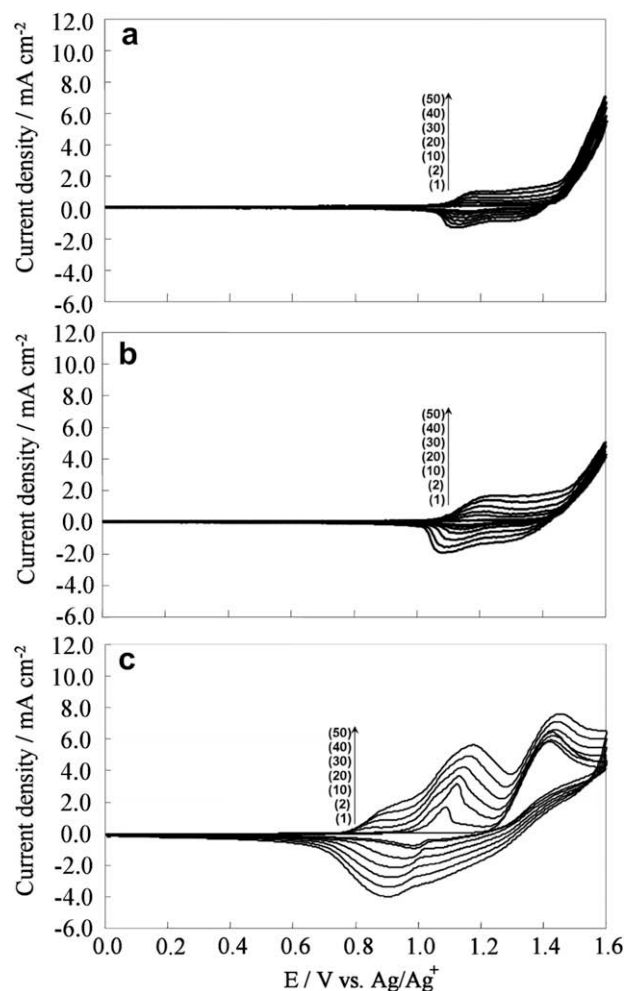
Figure 1. Multiple cyclic voltammograms for 0.1 mol dm^{-3} tetraethylammonium tetrafluoroborate (TEABF$_4$) + CH_3CN including **2a** (a), **2b** (b) and **1** (c) at a concentration of 10 mmol dm^{-3} on glassy carbon disk electrode in a potential range from 0 to 1.6 V versus Ag/Ag$^+$ at a scan rate of 100 mV s^{-1}. Each number in the parentheses corresponds to a cycling number.

mer/polymer, indicating that the introduced esters work as elec-tron-withdrawing groups (EWGs). We also observed that the current densities of the redox waves of **2b** with longer alkyl chain exhibited a slightly higher growing rate than those of **2a**. The appearance and sequential increase of the reversible waves in the potential range from 1.0 to 1.4 V during multiple cycles is
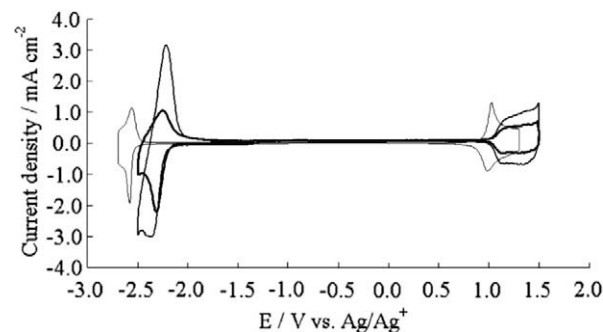
Figure 2. CVs for the resulted electroactive films based on **2a** (thick black line), **2b** (thick gray line) and **1** (thin gray line) formed on glassy carbon electrode in 0.1 mol dm^{-3} TEABF$_4$ + propylene carbonate at a scan rate of 100 mV s^{-1}.

characteristic of the formation of an electroactive and conductive polymer layer on the electrode.

The CV analyses of the fluorene polymers thus obtained were carried out to evaluate their electrochemical properties (Fig. 2). In Figure 2, each CV of the films based on **2a**, **2b** and **1** (poly**2a**, poly**2b** and poly**1**, respectively) exhibited two redox waves, which appeared in the potential ranges from −3.0 to −2.0 V and from 0.5 to 1.5 V. These two waves were considered as the redox reactions accompanying the *n*-doping and *p*-doping processes, respectively. On comparing the potential shifts of poly**2a** and poly**2b** with that of poly**1**, both *n*- and *p*-doping lead to ca. 0.3 V positive potential shifts. These positive shifts can be attributed to the EWG effects produced by the introduction of ester moieties, and make dialkyl fluorene-9,9-dicarboxylates **2a** and **2b** have more suitable potential window to avoid the decomposition of electrolytes. Fluorene derivatives **2a** and **2b** bearing ester groups with alkyl chains have better potential windows and are thus promising materials for application in electrochemical capacitors; these not only have wide working voltage but also more positive potential windows from −2.5 V to 1.5 V, where the electrolyte is electrochemically stable.

In summary, we have synthesized novel electroactive materials **2a** and **2b** as potential candidates for electrochemical capacitors having more positive potential windows than dialkylfluorenes. Further studies on polyfluorenes-based composite electrode materials for capacitors are ongoing in our research group.

Acknowledgments

References and notes

1. (a) Kalpana, D.; Omkumar, K. S.; Kumar, S. S.; Renganathan, N. G. *Electrochim. Acta* **2006**, *52*, 1309–1315; (b) Song, H.-K.; Palmore, G. T. R. *Adv. Mater.* **2006**, *18*, 1764–1768.
2. Toupin, M.; Brousse, T.; Bélanger, D. *Chem. Mater.* **2004**, *16*, 3184–3190.
3. (a) Rudge, A.; Davey, J.; Raistrick, I.; Gottesfeld, S. *J. Power Sources* **1994**, *47*, 89–107; (b) Martin, B.; Zdenek, S. Patent WO2007020458, Aug 18, 2006.
4. (a) Best, A. S.; Viale, S. M. J.; Picken, S. J. Patent WO2005117188A1.; (b) Nakamura, M.; Saito, H. Patent JP2003168437.; (c) Yoshinari, T.; Kamisuke, H.; Shinoda, T.; Nishiyama, T.; Mitani, K. Patent JP2004355823.; (d) Matsumoto, S.; Itaya, H. Patent JP 2001040108.
5. Fusalba, F.; Mehdi, N. El.; Breau, L.; Bélanger, D. *Chem. Mater.* **1999**, *11*, 2743–2753.
6. Conway, B. E. *Electrochemical Supercapacitors Scientific Fundamentals and Technological Applications*, Kluwer Academic/Plenum Publishers, NY, 1999.
7. (a) Suematsu, S.; Mitsudo, K.; Katagiri, F.; Tanaka, H. *Electrochemistry* **2007**, *75*, 54–57; (b) Leclerc, M. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 2867–2873.
8. (a) Suematsu, S. Patent JP 2006049386.; (b) Suematsu, S. Patent JP2006049387.; (c) Suematsu, S. Patent JP2006048973.; (d) Suematsu, S. Patent JP2006048974.; (e) Suematsu, S. Patent JP2006048975.; (f) Suematsu, S.; Tamamitsu, K.; Uchi, H.; Hata, K.; Hatori, H.; Yumura, M. Patent JP 2007234346.
9. Aida, T.; Murayama, I.; Yamada, K.; Morita, M. *J. Electrochem. Soc.* **2007**, *154*, A798–A804.
10. (a) Guo, L.-N.; Duan, X.-H.; Liu, X.-Y.; Hu, J.; Bi, H.-P.; Liang, Y.-M. *Org. Lett.* **2007**, *9*, 5425–5428; (b) Zhang, D.; Liu, Z.; Yum, E. K.; Larock, R. C. *J. Org. Chem.* **2007**, *72*, 251–262; (c) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **1997**, *30*, 7686–7691; (d) Schafer, G. *Z. Kristallogr.* **1932**, *82*, 472–473; (e) Adickes, F.; Brunnert, W.; Lucker, O.; Schafer, G. *J. Prakt. Chem.* **1932**, *133*, 305–327; (f) Wislicenus, W.; Mocker, W. *Ber. Dtsch. Chem. Ges.* **1914**, *46*, 2772–2793.
11. Cipens, G.; Slavinskaya, V. A. *Latv. Kim. Zur.* **1991**, *5*, 623–625.