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Synthesis and electropolymerization of fullerene–terthiophene dyads

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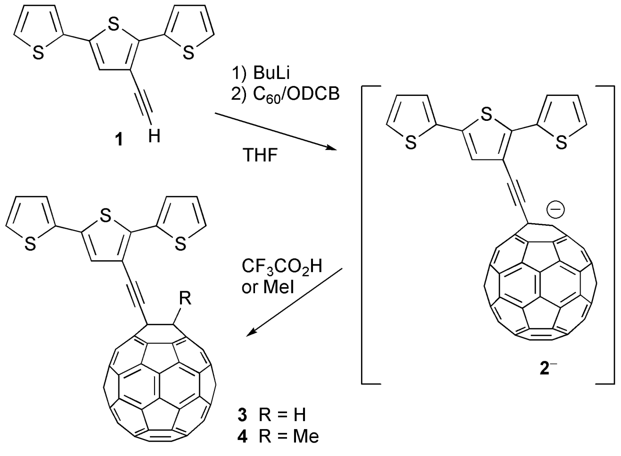
Fullerene derivatives having a terthiophene unit connected by a triple bond were newly synthesized and the electroactive polymers were obtained by electrolytic oxidation of the terthiophene moiety.

Materials consisting of fullerene C_{60} with high electron affinity and π-conjugated polymeric systems with electron donating ability have been attracting wide interest from the view point of fundamental science[1,2] as well as practical applications such as organic solar cells.[3] In this context, conjugated polymers bearing covalently connected C_{60} cages are more advantageous than a simple blend of the polymers and C_{60} since problems such as phase separation and/or aggregation of each component can be avoided in the thin film of the former.[4] Polythiophenes are typical π-donating polymers. Fullerene derivatives covalently linked to polythiophenes by the use of [2 + 1] or [2 + 3] cycloaddition reactions are reported to have unique properties.[5] The nucleophilic addition of lithium acetylide is another method for functionalising C_{60},[6] which has the advantage that the C_{60} cage can be further modified by attaching proton or alkyl groups in high yields.[7] Here we report the application of this method to synthesize novel dyads in which fullerene and terthiophene are connected by an acetylenic bond, together with their electrochemical properties. For the purpose of oxidative polymerisation in order to obtain the corresponding polythiophene, the terthiophene unit is expected to be a better monomer than bithiophene or thiophene itself because of the ready oxidizability.

As shown in Scheme 1, ethynylterthiophene **1**[8] was lithiated by BuLi in THF to generate the corresponding lithium acetylide, which was added to a solution of C_{60} in *o*-dichlorobenzene (ODCB) at room temperature. To the resulting dark green solution, in which fullereneyl anion $\mathbf{2}^-$ is considered to be present as a major species, was added either trifluoroacetic acid or iodomethane to afford fullerene–terthiophene dyad **3** or **4** in 46% or 35% yield, respectively, as brown powders after purification by flash chromatography over silica gel. The structure of **3** was fully characterized by spectroscopy as the 1,2-adduct of C_{60} at one of the 6,6-bonds.† The ^{1}H NMR spectrum of **3** showed a singlet at δ 7.22 ppm corresponding to a proton directly attached to the fullerene cage. The ^{13}C NMR spectrum displayed 42 signals in the sp^2 carbon region in addition to two signals for sp carbons and two signals for sp^3 carbons, in agreement with the structure of **3** having a C_s symmetry. The electronic spectrum in ODCB exhibited absorptions at 433 and 704 nm, which are typical for a 1,2-adduct of C_{60}.[9] Similarly, the structure of **4** was also determined as the 1,2-adduct with C_s symmetry.†



Scheme 1 Synthesis of fullerene–terthiophene dyads **3** and **4**.

The electorochemical properties of dyads **3** and **4** were investigated by cyclic voltammetry (CV) in ODCB (glassy carbon, 0.1 M Bu_4NBF_4, scan rate 0.1 V s^{-1}, V *vs.* Fc/Fc$^+$). One irreversible oxidation peak and three reversible reduction waves were observed upon a single scan: E_{pa} +0.85 and $E_{1/2}$ −1.13, −1.54 and −2.07 V for **3**; E_{pa} +0.82 and $E_{1/2}$ −1.15, −1.54 and −2.07 V for **4**. Thus, these dyads retain high electron affinity characteristic of the C_{60} cage as well as low oxidation potential ascribed to the terthiophene moiety.

Upon repetitive scanning over the potential range from +0.90 to −2.3 V (Fig. 1(a) and (b)), a new redox wave at

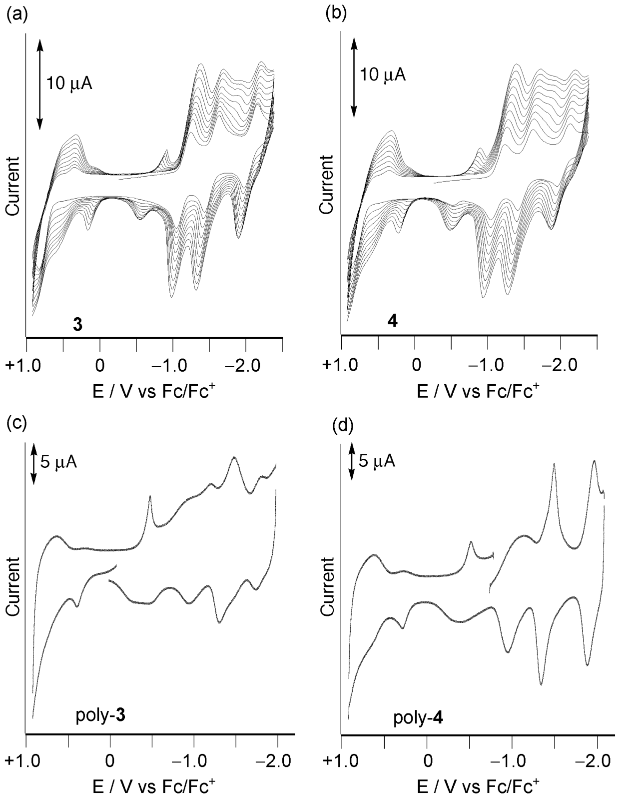


Fig. 1 Cyclic voltammograms (0.1 M Bu_4NBF_4, scan rate 0.1 V s^{-1}, V *vs.* Fc/Fc$^+$) of (a) dyads **3** in ODCB, (b) dyads **4** in ODCB, (c) poly-**3** on a glassy carbon electrode in acetonitrile and (d) poly-**4** on a glassy carbon electrode in acetonitrile.

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approximately +0.5 V was found to grow in intensity, together with the increase of three waves for reduction of the C_{60} cage. This indicates the formation of electrochemically active polymer film of **3** and **4** on the electrode surface. Small and remote redox peaks at E_{pa} +0.2 and E_{pc} −0.9 V are ascribed to a redox process involving transfer of electrolyte,[10] but the origin of the oxidation peak at approximately −0.5 V is not clear at the moment.

After 10 repetitive scans, the working electrodes covered with polymer films were thoroughly rinsed with $CHCl_3$, dried under vacuum and its CV studied in acetonitrile. As shown in Fig. 1(c), a single-sweep cyclic voltammogram (0.1 M Bu_4NBF_4, scan rate 0.1 V s^{-1}) of the polymer film obtained from dyad **3** exhibited rather complex waves, which were assumed to be due to chemically irreversible processes because the following repeated voltammograms were not identical to the first one. This is ascribed to irreversible chemical reactions of the anionic C_{60} cage of poly-**3**. It has been reported that deprotonation is induced by electrochemical reduction of hydrofullerenes[11] and that the fullerenyl anions dimerize to form a singly bonded fullerene dimer upon one-electron oxidation.[12] Similar chemical processes are considered to take place in the film of poly-**3** to form the fullerene dimers intramolecularly within the polythiophene chain and/or intermolecularly between the polythiophene chains.

On the other hand, the film obtained from dyad **4** (Fig. 1(d)) showed one oxidation wave and three reduction waves at $E_{1/2}$ +0.65, −1.03, −1.45, and −1.92 V *vs.* Fc/Fc$^+$, respectively, in addition to minor peaks descrived above (E_{pa} +0.28, E_{pa} −0.38 and E_{pc} −0.52 V). All waves exhibited high reproducibility upon repeated scans. Among three waves attibuted to the reduction of the C_{60} cage, the first wave is relatively broad, suggesting that a reorganization of the film structure takes place during the formation of the monoanionic species.[13]

When an ITO electrode was used as a working electrode for the CV of dyad **4**, repetitive scanning in the range of +1.3 to −0.2 V *vs.* Fc/Fc$^+$ resulted in formation of a transparent brown film of poly-**4** on the electrode, whose absorption spectrum is shown in Fig. 2. together with a spectrum of a film of dyad **4** coated on the ITO glass. A broad absorption extending to approximately 770 nm was observed for poly-**4**. The difference spectrum is also shown by subtracting the absorption of dyad **4** from that of poly-**4** normalized at 586 nm which corresponds to the absorption of the fullerene moiety. In the difference spectrum, the negative absorption at 385 nm is ascribed to consumption of the terthiophene monomer unit whereas the positive absorption at 464 nm is attributed to formation of the polythiophene chromophore. This absorption is more red-shifted than that of polythiophene obtained from a bithiophene monomer (440 nm),[5a] indicating that poly-**4** has a longer chain length than the polymer reported by Sannicoló and coworkers.[5a]

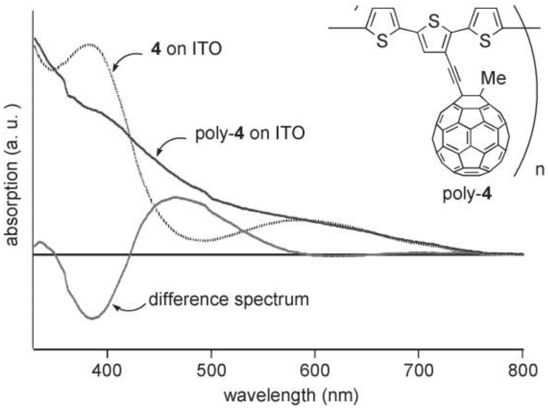

Fig. 2 UV-vis spectra of a cast film of dyad **4** on an ITO glass, poly-**4** on an ITO electrode and the difference spectrum.

In summary, we synthesized novel terthiophene–fullerene dyads **3** and **4** in which two electroactive moieties are connected by a triple bond. The electrochemical oxidation of dyads **3** and **4** gave corresponding polymers on the electrode upon repetitive CV. Poly-**3** was found to be unstable toward the electrochemical process because of the presence of a reactive hydrogen on the fullerene cage. However, poly-**4** was chemically stable and electroactive on both p-dope and n-dope states. A preliminary study indicated the presence of electrochromism[14] for poly-**4** on an ITO electrode, and further investigation on related compounds on this line are now in progress.

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Notes and references

† *Selected spectroscopic data.* For **3**: ^{1}H NMR (300 MHz, CS_2–CD_2Cl_2 = 3 : 1) δ 7.56 (1 H, dd), 7.36 (1 H, s), 7.35 (1 H, m), 7.26 (1 H, m), 7.22 (1 H, s), 7.22 (1 H, m), 7.08 (1 H, dd), 7.04 (1 H, dd); ^{13}C NMR (100 MHz, CS_2–CD_2Cl_2 = 3 : 1): δ 151.64, 150.98, 147.87, 147.60, 146.95, 146.69, 146.67, 146.51, 146.06, 145.99, 145.89, 145.79, 145.71, 145.63, 144.98, 144.79, 143.45, 143.15, 142.91, 142.88, 142.44, 142.35, 142.31, 142.18, 142.02, 141.92, 140.72, 140.68, 140.24, 136.38, 136.34, 135.89, 135.55, 135.09, 128.39, 127.75, 127.46, 126.52, 126.36, 125.72, 124.88, 117.41, 96.36, 80.11, 62.00, 55.98; UV-vis (ODCB) λ_{max} (log ε) 329 (4.72), 433 (3.66), 704 (2.52). HRMS calcd. for $C_{74}H_9S_3$: 992.9866. Found: 992.9826.

For **4**: ^{1}H NMR (300 MHz, CS_2–CD_2Cl_2 = 3 : 1): δ 7.52 (1 H, dd), 7.35 (1 H s), 7.27 (2 H, m), 7.21 (1 H, dd), 7.03 (2 H, m), 3.45 (3 H, s); ^{13}C NMR (100 MHz, CS_2–CD_2Cl_2 = 3 : 1): δ 157.09, 153.01, 148.09, 147.94, 146.75, 146.67, 146.52, 146.48, 146.12, 145.84, 145.74, 145.66, 145.62, 145.40, 145.26, 144.99, 144.89, 143.44, 142.88, 142.85, 142.43, 142.42, 142.37, 142.28, 141.91, 141.76, 140.57, 140.41, 139.96, 136.34, 135.74, 135.05, 134.84, 134.64, 129.27, 128.39, 127.76, 127.66, 126.49, 126.33, 125.71, 124.86, 117.63, 92.81, 81.52, 62.08, 60.58, 33.78; UV-vis (ODCB) λ_{max} (log ε) 331 (4.72), 434 (3.65), 704 (2.59). HRMS calcd. for $C_{75}H_{11}S_3$: 1007.0023. Found: 1006.9965.

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