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A New Dyad Based on C_{60} and a Conjugated Dimethylaniline-Substituted Dithienylethylene Donor

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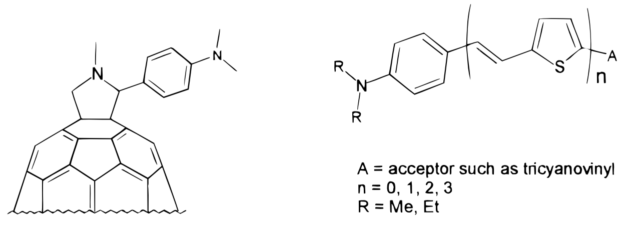
A facile synthesis of the title compound is described, and its optical and electrochemical properties are discussed.

In recent years, a number of electron donors have been covalently linked to the C_{60} cage by different synthetic procedures in an effort to obtain efficient intramolecular energy and electron or charge transfer and to generate long-lived charge-separated states in these donor−acceptor (D−A) molecular assemblies.[1−10] Diekers et al. recently pointed out that three types of dyads and triads involving a C_{60} moiety with various donor molecules have been developed.[11] Although spontaneous intramolecular charge-transfer interactions have been claimed in some cases, unequivocal evidences are still lacking.[7]

In an attempt to enhance intramolecular electron or charge transfer, we report here a novel donor−C_{60} involving dimethylaniline-substituted dithienylethylene (DADTE) as the donor part. This approach is based on the following rationale: (i) compound **1** (Chart 1), which contains a donating aniline group linked to the C_{60} cage by a saturated heterocyclic bridge, has been recently reported to show intramolecular photoinduced charge separation in polar solvents,[12] and (ii) push−pull chromophores based on the DADTE system, such as **2** (Chart 1), are known to exhibit high second-order nonlinear optical (NLO) susceptibilities due to, among other factors, an easily attainable charge-asymmetry thanks to the low aromatic stabilization energy of the thiophene ring.[13,14]

Chart 1



1 **2**

On this basis, we report here the synthesis of a new donor−C_{60} compound (**4c**) in which a DADTE donor group is linked to C_{60} through a pyrrolidine ring and we discuss some of its optical and electrochemical properties using the related compounds **4a** and **4b** as reference compounds.

The synthetic approach to prepare compounds **4a**−**c** relies upon the [3 + 2] 1,3-dipolar cycloaddition of azomethine ylides to C_{60} (Scheme 1).[15]

This methodology has proven to be one of the most powerful procedures for the functionalization of [60]-fullerene due to its versatility and the ready availability of the starting materials.[16] Thus, reaction of aldehydes **3a**−**c**[17] (0.273 mmol), with *N*-methylglycine (64 mg, 0.718

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(1) Recent reviews related to C_{60}-based donor−acceptor molecular assemblies: (a) Martin, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527−2547. (b) Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519−530.

(2) (a) Drovetskaya, T.; Reed, C. A.; Boyd, P. *Tetrahedron Lett.* **1995**, *36*, 7971−7974. (b) Linssen, T. G.; Dürr, K.; Hanack, M.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 103−104. (c) Qiu, W. F.; Liu, Y. Q.; Zhu, D. B. *Chin. Chem. Lett.* **1997**, *8*, 363−366.

(3) Maggini, M.; Karlsson, A.; Scorrano, G.; Sandonà, G.; Farnia, G.; Prato, M. *J. Chem. Soc., Chem. Commun.* **1994**, 589−590.

(4) Martín, N.; Sánchez, L.; Seoane, C.; Andreu, R.; Garín, J.; Orduña, J. *Tetrahedron Lett.* **1996**, *37*, 5979−5982.

(5) (a) Llacay, J.; Mas, M.; Molins, E.; Veciana, J.; Powell, D.; Rovira, C. *J. Chem. Soc., Chem. Commun.* **1997**, 659−660. (b) Llacay, J.; Veciana, J.; Vidal-Gancedo, J.; Bourdelande, J. L.; Gonzalez-Moreno, R.; Rovira, C. *J. Org. Chem.* **1998**, *63*, 5220−5225. (c) Boulle, C.; Rabreau, J. M.; Hudhomme, P.; Cariou, M.; Jubault, M.; Gorgues, A.; Orduna, J.; Garin, J. *Tetrahedron Lett.* **1997**, *38*, 3909−3910.

(6) Lawson, J. M.; Oliver, A. M.; Rothenfluh, D. F.; An, Y. Z.; Ellis, G. A.; Ranasinghe, M. G.; Khan, S. I.; Franz, A. G.; Ganaphthi, P. S.; Stephard, M. J.; Paddon-Row, M. N.; Rubin, Y. *J. Org. Chem.* **1996**, *61*, 5032−5054.

(7) Matsubara, Y.; Tada, H.; Nagase, S.; Yoshida, Z. *J. Org. Chem.* **1995**, *60*, 5372−5373.

(8) Nakamura, Y.; Minowa, T.; Tobita, S.; Shizuka, H.; Nishimura, J. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2351−2357.

(9) Williams, R. M.; Koeberg, M.; Lawson, J. M.; An, Y. Z.; Rubin, Y.; Paddon-Row, M. N.; Verhoeven, J. W. *J. Org. Chem.* **1996**, *61*, 5055−5062.

(10) Güldi, D. M.; Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1997**, *119*, 974−980.

(11) Diekers, M.; Hirsch, A.; Pyo, S.; Rivera, J.; Echegoyen, L. *Eur. J. Org. Chem.* **1998**, 1111−1121 and references therein.

(12) Williams, R. M.; Zwier, J. M.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 4093−4099.

(13) Rao, V. P.; Jen, A. K. Y.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1118−1120.

(14) (a) Jen, A. K. Y.; Rao, V. P.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 90−93. (b) Rao, V. P.; Jen, A. K. Y.; Wong, K. Y.; Drost, K. J. *Tetrahedron Lett.* **1993**, *34*, 1747−1750. (c) Drost, K. J.; Rao, V. P.; Jen, A. K. Y. *J. Chem. Soc., Chem. Commun.* **1994**, 369−371. (d) Jen, A. K. Y.; Rao, V. P.; Drost, K. J.; Wong, K. Y.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1994**, 2057−2058. (e) Shu, C. F.; Tsai, W. J.; Chen, J. Y.; Jen, A. K. Y.; Zhang, Y.; Chen, T. A. *J. Chem. Soc., Chem. Commun.* **1996**, 2279−2280.

(15) Xu, J. H.; Li, Y. L.; Zheng, D. G.; Yang, J. K.; Mao, Z.; Zhu, D. B. *Tetrahedron Lett.* **1997**, *38*, 6613−6616.

(16) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798−9799.

(17) **3c** was synthesized by the methodology developed by Jen et al. with a slight modification; see ref 14a.

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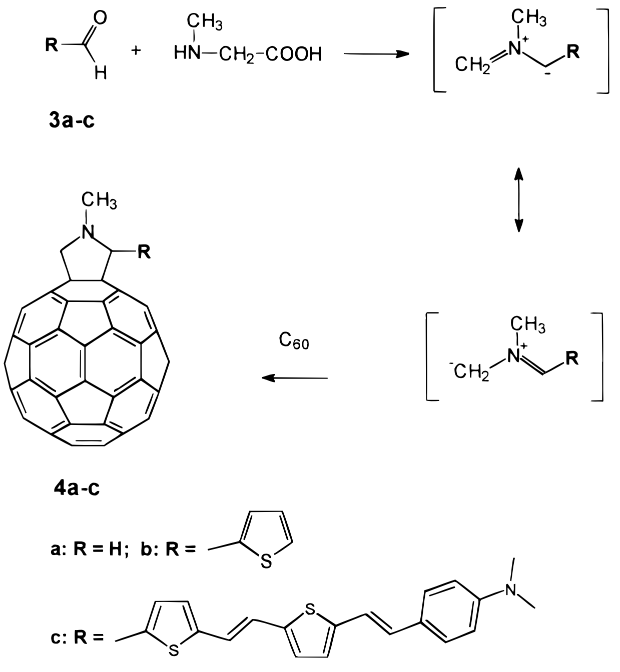
Scheme 1



mmol) and C_{60} (197 mg, 0.273 mmol) in toluene (75 mL) at reflux for 5−24 h, gave the corresponding fulleropyrrolidine **4a**−**c** in 10−40% overall isolated yield after two chromatographic separations (silica gel, CS_2 followed by toluene/CS_2 or CH_2Cl_2/cyclohexane).

The structures of compounds **4b**[18] and **4c** were fully supported by analytical and spectroscopic data. For example, in the case of **4c**, a parent ion at *m/e* 1114 (100%) is observed in the FAB^+ mass spectrum along with the $C_{60}^+ + 1$ (721, 30%) and a fragment at 394 ($M^+ - C_{60}$, 80%). High-resolution FABMS spectra completely agree with the theoretically predicted pattern of isotopic distribution (calcd for $C_{83}H_{24}S_2N_2$ 1112.1381, found 1112.1381). The ^1H NMR spectrum of **4c** in $CDCl_3$ solution exhibits the expected features with the correct integration ratios. The signals of the pyrrolidine protons appear at δ 4.97 and 4.26 ppm as doublets ($J = 9.2$ Hz; geminal hydrogens) and at δ 5.22 (CH, s), in good agreement with the results for similar derivatives.[4] Furthermore, all the double-bond linkages were confirmed to be all-trans by careful NMR analysis.[14a] The ^{13}C NMR spectrum shows two different NCH_3 groups at δ 40.24 (2 C) and 40.33 (1 C) ppm, the sp^3 carbons of the 6,6-ring junction and the remaining pyrrolidine carbons at δ 68.65, 77.04 and 69.99, 79.42 ppm, respectively,[4] and all the sp^2 carbons in both C_{60} and the donor moiety between 112.45 and 155.71 ppm.[19]

Figure 1 shows the electronic absorption spectra of compounds **4a**, **4b**, **3c**, and **4c**. The spectrum of compounds **4a** and **4b** is essentially dominated by the three characteristic absorption bands of C_{60} in the 200−350 nm region. Very weak absorption bands (not shown) around 430 and 703 nm, typical of C_{60} monoadducts, can be observed at higher magnification. Upon introduction of the DADTE moiety in the structure, a broad and intense absorption band develops in the 400−500 nm region with a λ_{max} around 440 nm in cyclohexane. This absorption band shows a well-resolved vibronic fine structure with three maxima equally spaced by ~25 nm (ca. 0.15 eV), which is consistent with the energy of a C=C stretching mode in the DADTE-conjugated system. The similarity of this spectrum with that of compound **3c** or that of other push−pull chromophores based on the dithienylethylene (DTE) system[20] clearly shows that this band is related to the $\pi-\pi^*$ transition of a DADTE conjugated system. The λ_{max} of **4c** (436 nm in cyclohexane) is substantially blue-shifted compared to that of related push−pull NLO chromophores containing acceptor groups such as formyl **3c** (467 nm), nitro (506 nm),[14b] dicyanovinyl (547 nm),[14a] and tricyanovinyl (653 nm)[13] but slightly red-shifted for ~12 nm relative to the unsubstituted analogue HR (424 nm, R was defined in Scheme 1 as that of **3c**). These data suggest that **4c** behaves as a push−pull system in which the C_{60}-pyrrolidine group acts as a weak electron acceptor.

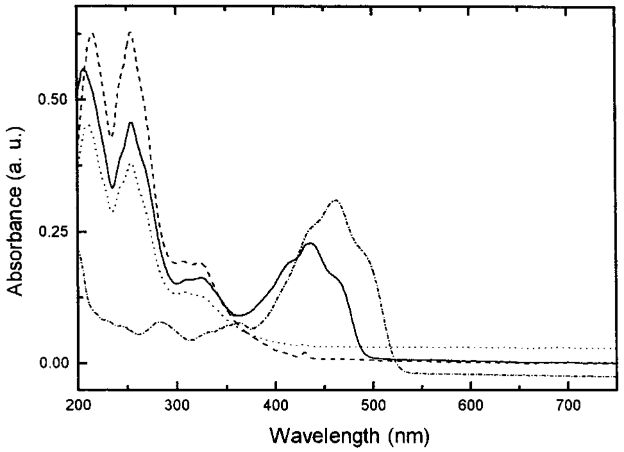


Figure 1. UV−vis spectra of **4a** (dashed), **4b** (dotted), **4c** (solid), and **3c** (−•−) in cyclohexane.

Cyclic voltammetric (CV) analysis of **4c** in THF shows four quasireversible reduction waves with cathodic peak potentials (E_{pc}) at −1.052, −1.594, −2.208, and −2.428 V versus Fc/Fc^+ and two irreversible reductions at −2.704 and −2.883 V (Figure 2a). In addition, two quasireversible oxidation processes occur with anodic peak potentials (E_{pa}^1 and E_{pa}^2) at 0.140 and 0.364 V. Comparison of these values with those for **3c** (0.219 and 0.475 V) suggests that the two oxidation processes are related to the DADTE system, the higher E_{pa}^1 and E_{pa}^2 values observed in the latter case reflecting the larger electron-withdrawing effect of the formyl group compared to the C_{60}-pyrrolidine one, in good agreement with the optical data.

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[18] Selected data for **4b**: HRFABMS calcd for $C_{67}H_9SN$ 859.0456, found 859.0455; ^{13}C NMR (in $CS_2/CDCl_3$ 1/1, one carbon for each piece of data unless otherwise indicated in parentheses) 40.27, 70.01, 79.14, 68.60, 125.31, 126.55 (2 C), 126.60 (2 C), 127.85 (2 C), 128.21, 128.97, 135.58, 135.81, 136.61, 136.97, 139.59, 139.87, 140.14, 140.67, 141.55, 141.62, 141.86, 141.92, 142.00, 142.07, 142.11 (2 C), 142.14, 142.23, 142.55 (2 C), 142.65, 142.94, 143.11, 144.31, 144.60, 144.66, 145.10, 145.19 (2 C), 145.21, 145.28, 145.32, 145.42, 145.53, 145.57, 145.71, 145.88 (2 C), 146.03, 146.06, 146.10, 146.15, 146.19, 146.22 (2 C), 146.30, 146.78, 147.25 (2 C), 153.00, 153.07, 153.75, 155.77.

[19] Careful ^{13}C NMR analysis ($CS_2/CDCl_3$ 1/1) of **4c** shows the total 76 sp^2 carbons in both C_{60} and the donor moiety listed as follows (one carbon for each piece of data unless otherwise indicated in parentheses): 112.45 (2 C), 117.59, 120.67, 122.28, 125.23, 125.29, 125.58, 127.53, 127.64 (2 C), 128.26, 128.59, 129.00, 129.37, 135.56, 135.78, 136.66, 137.03, 139.43, 139.79, 139.87, 139.94, 140.15 (2 C), 141.59, 141.62, 141.90 (2 C), 141.95, 142.01, 142.05, 142.10 (2 C), 142.15, 142.24, 142.55 (2 C), 142.66, 142.94, 143.12, 143.61, 143.98, 144.30, 144.33, 144.65 (2 C), 145.12, 145.17, 145.21 (2 C), 145.26, 145.34, 145.38, 145.41, 145.53, 145.60, 145.72, 145.88 (2 C), 146.03, 146.08, 146.12, 146.16, 146.19, 146.23, 146.26, 146.30, 146.77, 147.23, 147.26, 149.80, 152.91, 153.00, 153.72, 155.71 ppm.

[20] Chou, S. S. P.; Sun, D. J.; Huang, J. Y.; Yang, P. K.; Lin, H. C. *Tetrahedron Lett.* **1996**, *37*, 7279−7282.

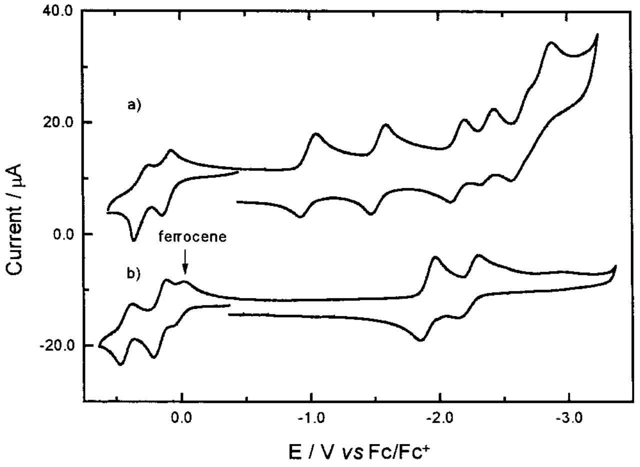

Figure 2. Cyclic voltammograms in THF at room temperature of compounds (a) **4c**, (b) **3c** (working conditions: 100 mV/s, 0.1 M TBAPF$_6$, ∅ 3 mm glassy carbon as the working electrode, ∅ 1 mm Pt wire as the counter electrode, internal ferrocene as the reference).

To assign the origin of the reduction processes, we carefully compared the CVs of compounds **4a**−**c** and **3c** recorded under essentially identical conditions. Figure 3 clearly shows that the first three successive and nearly equally spaced reductions and the fifth reduction are C_{60}-based. This is not only in good agreement with our previous work on the electrochemistry of fullerene derivatives[21] but also in good agreement with our ESR results measured for the corresponding mono-, di-, and trianion of **4c**.[22] On the basis of the observed *g* values for all of these species ($g_1 = 2.00067$, $g_2 = 2.00119$, $g_3 = 2.00138$), these reductions are all based on the fullerene core. The fourth and sixth reductions are centered on the conjugated donor part.

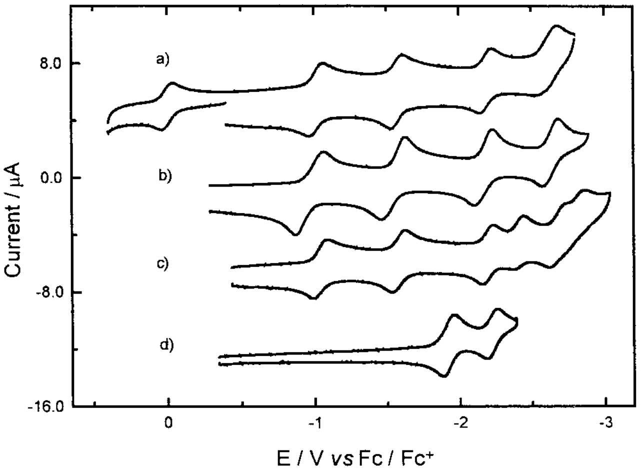

Figure 3. Cyclic voltammograms in THF at room temperature of compounds (a) **4a**, (b) **4b**, (c) **4c,** and (d) **3c**. All were recorded under identical conditions with a scan rate of 100 mV/s. Internal ferrocene was added as an internal reference in all cases but is not shown for b−d.

The electrochemical reduction of **3c** exhibits two reversible processes at $E_{1/2}$ −1.921 and −2.230 V vs Fc/Fc$^+$ with ΔE_p values of 75 and 61 mV, respectively. Obviously, these reductions in **3c** are more positive than those of the corresponding reductions in **4c** due to the stronger acceptor ability of the carbonyl group and also to its direct conjugation with the donor group, also in good agreement with the optical data.

In summary, a novel C_{60}-based thiophene-containing donor−acceptor compound has been synthesized and characterized. Work is now underway in order to analyze the possible charge-transfer interactions between the donor and acceptor parts of the molecule.

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(21) Arias, F.; Echegoyen, L.; Wilson, S. R.; Lu, Q.; Lu, Q. Y. *J. Am. Chem. Soc.* **1995**, *117*, 1422−1427.

(22) We performed the successive reductions from the neutral **4c** to its mono-, di-, and trianion species in THF under high vacuum. The ESR signals for these three different anions are C_{60}-based and are in accord with our previous work with C_{60} derivatives.