N-(2,4-Dinitrophenyl)-2-phenylfulleropyrrolidine: an electroactive organofullerene dyad

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Using Sanger's method, an electroactive organofullerene dyad, N-(2,4-dinitrophenyl)-2-phenylfulleropyrrolidine, is synthesized and its spectral and electrochemical characterization is reported.

Studies on C_{60}-based electroactive organofullerene dyads[1] are of current interest due to the interesting electronic and optical properties they display. Such electroactive fullerenes are considered to be useful in the development of molecular electronic devices[2] and non-linear optical materials[3] as well as in the design of artificial photosynthetic systems.[4,5] Two types of electroactive organofullerene dyads are known, namely, (i) C_{60} covalently linked to a donor entity (C_{60}–Donor type dyads) and (ii) C_{60} bearing an electron-deficient entity (C_{60}–Acceptor type dyads). A number of studies have reported electroactive fullerene dyads of the former type, while only a few systems of the latter type are known in the literature,[1] even though the potential for such double electron acceptor systems as precursors for the formation of multichromophoric systems with well-defined gradient of redox potentials has been realized.[5]

Among the different types of electron deficient compounds that could be utilized to form C_{60}–Acceptor dyads, nitroaromatic compounds are one of the attractive candidates. This is because the reduction potential of this acceptor molecule can be easily tuned by choosing appropriate numbers of nitro groups and other substituents on the aromatic ring.[6] However, no nitroaromatic acceptor molecule-linked fullerene dyad is known to date, although several donor–acceptor type molecules involving nitroaromatic compounds are known in the literature.[7] This has been achieved in the present study where we report the first synthesis and electrochemical characterization of a nitroarene appended fullerene dyad.

The strategy adopted for the synthesis of nitroarene appended fullerene is shown in Scheme 1. This involves the initial synthesis of 2-phenylfulleropyrrolidine **1**[8] followed by treatment with 1-fluoro-2,4-dinitrobenzene in the presence of NaH according to Sanger's reaction.[9] The secondary nitrogen on the pyrrolidine ring reacts with 1-fluoro-2,4-dinitrobenzene to yield the desired N-(2,4-dinitrophenyl)-2-phenylfulleropyrrolidine **2**.† The molecular integrity of the newly synthesized compound is established from mass, UV–visible and ^{1}H NMR spectroscopy. In addition to the fullerene absorption bands, the UV–

visible spectrum of the product in hexane exhibited an absorption band at 274 nm indicating the presence of the dinitrophenyl entity.[6] It is also observed that the proton resonance peaks of the N-dinitrophenyl entity are shielded by *ca.* 0.5 ppm as compared to the peaks of the starting material, 1-fluoro-2,4-dinitrobenzene, while the protons of the 2-phenylpyrrolidine group experienced a small deshielding upon forming the N-(2,4-dinitrophenyl)-2-phenylfulleropyrrolidine (Fig. 1).

The redox behavior of the newly synthesized compound has been investigated using cyclic voltammetry.‡ Fig. 2 shows the cyclic voltammograms of 2-phenylfulleropyrrolidine and N-(2,4-dinitrophenyl)-2-phenylfulleropyrrolidine in PhCN with 0.1 M Bu_4NPF_6. In the investigated solvent, the first three reductions of 2-phenylfulleropyrrolidine are found to be reversible one-electron processes with an anodic to cathodic peak separation, ΔE of *ca.* 80 mV. These processes are located at $E_{1/2}$ = -1.05, -1.48 and -2.01 V *vs.* Fc/Fc⁺, respectively, and are negatively shifted by 120 to 190 mV compared to the corresponding electroreductions of C_{60} (Table 1). The redox behavior of N-(2,4-dinitrophenyl)-2-phenylfulleropyrrolidine is found to be more complicated due to the overlapping reductions of the dinitrophenyl entity [Fig. 2(*b*)]. Only the first reduction process is reversible and is located at $E_{1/2}$ = -1.01 V *vs.* Fc/Fc⁺. Spectroelectrochemical studies have indicated that this reduction occurs at the C_{60} macrocycle resulting in the formation of a C_{60} anion radical. The observed positive shift of 40 mV for the first reduction of N-(2,4-dinitrophenyl)-2-phenylfulleropyrrolidine as compared to the first reduction of the starting material, 2-phenylfulleropyrrolidine, indicates small electronic interactions between the C_{60} and dinitrobenzene entities, consistent with the ^{1}H NMR results discussed above.
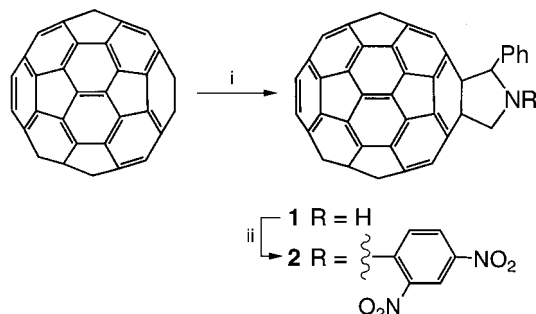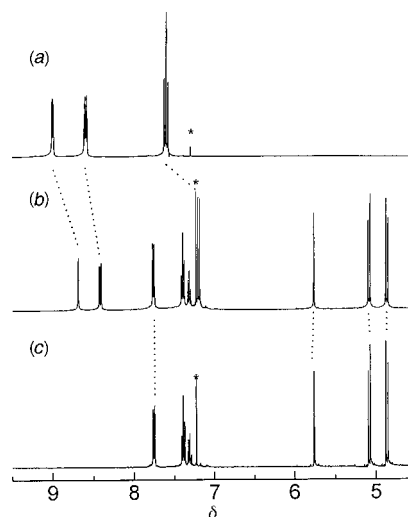

Fig. 1 ^{1}H NMR spectrum of (*a*) 1-fluoro-2,4-dinitrobenzene, (*b*) N-(2,4-dinitrophenyl)-2-phenylfulleropyrrolidine and (*c*) 2-phenylfulleropyrrolidine, in CS_2–$CDCl_3$ (1:1).

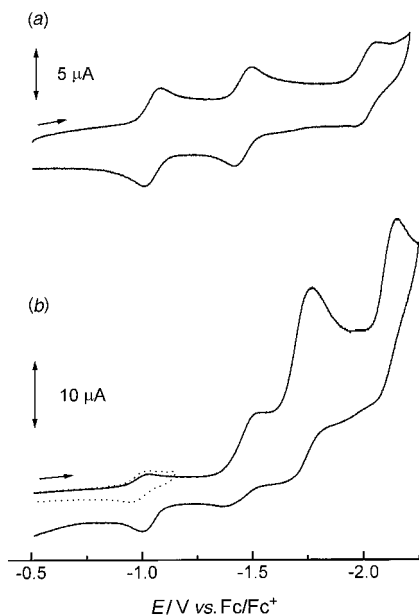**Scheme 1**

1 R = H
2 R = (2,4-dinitrophenyl, –NO₂, O₂N–)

Fig. 2 Cyclic voltammogram of (*a*) 2-phenylfulleropyrrolidine and (*b*) *N*-(2,4-dinitrophenyl)-2-phenylfulleropyrrolidine in PhCN with 0.1 M Bu$_4$NPF$_6$. Scan rate = 100 mV s^{-1}.

Table 1 Half-wave potentials for the reduction of C$_{60}$ and fulleropyrrolidine derivatives in PhCN with 0.1 M Bu$_4$NPF$_6$

| Compound | *E*/V *vs.* Fc/Fc$^+$ | | |
	1st	2nd	3rd
C$_{60}$	−0.92	−1.34	−1.83
2-phenylfulleropyrrolidine	−1.05	−1.48	−2.01
N-Dinitrophenyl-2-phenylfulleropyrrolidine^a	−1.01		

^{a} Additional peaks corresponding to the reduction of C$_{60}$ and the dinitrobenzene entities are observed. See Fig. 2 and text for details.

The first reduction of the appended dinitrophenyl entity is found to be irreversible and is located at E_{pc} = −1.56 V *vs.* Fc/Fc$^+$, that is, the potential where the second reduction of C$_{60}$ occurs. Control experiments performed by using a model compound, 1-morpholino-2,4-dinitrobenzene, synthesized by reacting morpholine and 1-fluoro-2,4-dinitrobenzene, confirmed the reduction of the dinitrophenyl entity in this potential range. When the potential is scanned to more negative potentials, additional reductions of the C$_{60}$ and the dinitrophenyl entities are also observed. A comparison between the potentials corresponding to the first reduction of C$_{60}$ and the first reduction of dinitrophenyl entities in the synthesized compound reveal a large potential separation of nearly 500 mV.

In summary, we are able to synthesize an *N*-dinitrobenzene-appended fulleropyrrolidine *via* Sanger's reaction using a simple one step procedure. The electrochemical and spectroelectrochemical results indicate that the reduction of C$_{60}$ in the newly synthesized compound is easier by 40 mV than the starting fulleropyrrolidine. Both ^{1}H NMR and the cyclic voltammetric results indicate the existence of weak interactions between the C$_{60}$ and dinitrophenyl entities in the synthesized compound. Owing to a potential separation of nearly 500 mV between the first reductions of the C$_{60}$ and dinitrobenzene entities in the synthesized compound, utilization of this dyad as a precursor for developing multichromophoric supramolecular systems is envisioned.

Notes and references

† To a solution of 2-phenylfulleropyrrolidine (22.5 mg) in dry THF (15 ml), NaH (2 mg) was added and the resulting suspension was stirred. After the evolution of hydrogen had ceased, 1-fluoro-2,4-dinitrobenzene (20 μl) was added and the solution was stirred for another 6 h. At the end, water (1 ml) was added and the solution was evaporated under reduced pressure. The crude product was adsorbed on silica and separated on a silica gel column using 1:1 toluene–hexane as eluent (68% yield). Negative ion electrospray mass spectrum of the product in either a toluene or MeOH matrix revealed peaks at *m/z* 963.7 and 838.2 corresponding to the molecular ion minus nitro and dinitrobenzene units respectively. A control experiment performed using ^{19}F NMR of the product revealed the complete absence of the fluorine resonance peak that was present in the starting material, 1-fluoro-2,4-dinitrobenzene, at δ 221.5 (C$_6$F$_6$ at δ 166); δ_H[CS$_2$–CDCl$_3$ (1:1) 8.69 (s, 1H, dinitrophenyl-H), 8.42 (m, 1H, dinitrophenyl-H), 7.76 (d, 1H, phenyl-H), 7.39 (m, 2H, phenyl-H), 7.31 (m, 2H, phenyl-H), 7.19 (d, 1H, dinitrophenyl-H), 5.77 (s, 1H, pyrrolidine-H), 5.09 (d, 1H, pyrrolidine-H), 4.87 (d, 1H, pyrrolidine-H); λ_{max}(hexane)/nm 429, 307(sh), 274, 252, 213.

‡ Cyclic voltammograms were obtained on a EG & G Model 263 A potentiostat using a three-electrode system. A glassy carbon electrode was used as the working electrode. A platinum wire served as the counter electrode, while a Ag/AgCl electrode was used as the reference electrode. All the potentials are referenced against an internal Fc/Fc$^+$ redox couple. Analysis of the peak current and peak potentials from the voltammetric data was carried out using EG&G M270 electrochemical software. All the experiments were carried at 22 ± 1 °C.

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