

ARTICLE

Photoinduced Electron Transfer in Dumbbell-type Fullerene Dyad

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1,3-Dipolar cycloaddition of DTE-azomethine ylides (DTE: dithienyl-ethene) to C_{60} in refluxed toluene was used to synthesize novel dumbbell-type fullerene dimer **1**. For the sake of comparison, the monoadduct **2** were also synthesized. The molecular geometries of these two compounds were determined by theoretical calculations with HF-3/21G method. UV-Vis and fluorescence experiments were carried out in solvents with different polarity at the room temperature. All the results indicated the existence of a photoinduced intramolecular electron transfer process between the donor and acceptor moieties.

Key words: Fullerene, Photophysical properties, Photoinduced intramolecular electron transfer

I. INTRODUCTION

The discovery of the facile methods for preparation and purification of gram-quantities of fullerenes has generated a growing interest in the chemical and physical properties of these systems [1-4]. And many novel derivatives with interesting properties have been synthesized and characterized in recent years [5,6]. In principle, because of their electronic properties and their great chemical stability, fullerene could be used to accomplish photoinduced charge separation in supramolecular system, and to initialize the first step of artificial photosynthesis [7,8]. For this purpose, a molecular architecture is required in which at least one additional chromophore or redox-active center is located in close proximity to the fullerene itself [9]. The relative orientation as well as the distance between the chromophores determines the energy- and charge-transfer properties of such artificial model photosynthetic systems. So far, four types of dyads and triads, i.e., C_{60} -donor, C_{60} -acceptor, C_{60} -donor¹-donor² (monoadduct with respect to C_{60}) and C_{60} -donor-acceptor (bisadduct with respect to C_{60}), involving a C_{60} moiety have been developed. However, much less is known about the covalently attached C_{60} -donor system. A variety of donor moieties such as porphyrin [10], phthalocyanine [11], ferrocene [12], ruthenium complexes [13], carotenoid polyenes [14], and aniline [15] derivatives were bound to the C_{60} cage, but only weak or negligible charge-transfer interactions were observed.

Fullerene dimers and their large assemblies (fullerodendrimers) [16,17] form a new class of molecular system with potential applications in molecular electronic devices and supramolecular chemistry. In spite of their interesting properties, the synthesis and characterization of dimers and oligomers containing two or more

C_{60} units has received much less attention compared to the [60]fullerene chemistry [5]. Only a quite limited number of organofullerenes with more than one cage have been reported so far, and most of the synthetic procedures involved with an oxidation coupling reactions [18,19] or cycloaddition reactions [20-22]. Oxo- and methylene-bridged [60]fullerene dimers containing fullerene-fullerene bonds were also reported by thermal treatment of $C_{60}O$ [23]. The former strategies also allow one to incorporate photo- or electroactive chromophores into these molecular systems.

1,3-dipolar cycloadditions represent a powerful tool to prepare fullerene derivatives. Azomethine ylides [24,25], diazoalkanes [26], azides [27], or nitrile oxides [28] all can afford the fulleroheterocycles. Among these different types of cycloadditions, the 1,3-dipolar cycloaddition of azomethine ylides to C_{60} has been widely used, because it is relatively easy to prepare, and there are several methods to generate the reactive intermediates from a wide series of available starting materials [24,29]. In the simplest case, the reaction of sarcosine, formaldehyde and C_{60} in toluene yields the parent N-methyl fulleropyrrolidine [29]. The scope of the reaction is very broad. For instance, when an aldehyde other than formaldehyde is used, 2-substituted N-methyl-3, 4-fulleropyridines can be synthesized. In addition, the condensation of N-functionalized glycines with aldehydes can lead to N-substituted fulleropyrrolidines. This offers opportunity for simultaneously introducing two functional chains in a single step. In addition, the third chain can also be introduced to the system using an additional reaction of corresponding fulleropyrrolidines with a halogenated compound (e.g. CH_3I), yielding fulleropyrrolidinium salts, which show enhanced electron-accepting properties compared with both the parent pyrrolidine derivatives and the C_{60} [30].

To date, a broad spectrum of intriguing fulleropyrrolidine derivatives, bearing electro- and/or photoactive addends, have been synthesized via the 1,3-dipolar cycloaddition procedure [31]. Therefore, we targeted at a dumbbell-type donor-acceptor organofullerene **1** in

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which the dithienylethene (DTE) donors are covalently linked to the C₆₀ cage, acting as an electron-accepting moiety, through a pyrrolidine ring. And for the sake of comparison, the monoadduct **2** is also synthesized. The synthesis, spectroscopy and theoretical calculations have been performed for the understanding of these C₆₀-donor dyads.

II. EXPERIMENTAL INSTRUMENTATION

¹H and ¹³C NMR was recorded with a Bruker DMX-300 spectrometer with CDCl₃ as the solvent, and the chemical shift was given downfield from TMS. IR spectra were recorded with a Bruker Vector 220 infrared spectrometer. The fluorescence spectra were measured by a CRT970 fluorescent spectrometer at the room temperature. UV absorption spectra were measured with a Perkin-Elmer lambda 45 UV-Vis spectrophotometer. MALDI-TOF mass spectra were recorded with a BIFLEX III instrument.

III. RESULTS AND DISCUSSION

A. Synthesis

The target molecules **1** and **2** were prepared by 1,3-dipolar cycloaddition reactions of the azomethine ylide, formed from sarcosine (N-methylglycine) and the respective bisaldehyde to C₆₀ by following the Prato's procedure. The starting aldehyde was synthesized following the literature [32].

The structure of the novel compounds was supported by their analytical and spectroscopic data. Good resolution was achieved for **1** and **2** by recording the ¹H NMR spectra at the room temperature. The signals of the pyrrolidine protons appear, for instance, at around 5.1 (CH) as a singlet and a set of two doublets (CH₂) with coupling constant around $J=9.6$ Hz, integrating for one hydrogen. On the other hand, the ¹³C NMR spectra showed, in addition to the N-Me group at around 40.1 ppm, the signals between 63.1 to 79.3 for the sp³ carbons of the pyrrolidine ring and those at the 6,6-junction of the C₆₀ cage, in accordance with the previous observations for other related fulleropyrrolidine derivatives [29]. The UV-Vis spectrum of **1** showed the presence of a band around 420 nm, in addition to the typical weak absorption band at 430 nm of the dihydrofullerenes, thus confirming the [6,6]-closed character of the dimer. The FTIR spectra showed the presence of both the donor and the acceptor fragments. Thus, a very strong C₆₀ band was observed at 527 cm⁻¹ and also the C-H stretching bands at 2841 cm⁻¹ and the aromatic vibrations at around 1630 and 1450 cm⁻¹. The mass spectroscopy of the molecular ions was observed using the MALDI-TOF techniques for **1** and **2** at m/z 1089.0 [M⁺-2H-C₆₀] and 1062.8 [M⁺-H], respectively.

B. HF-3/21G-optimized structures

To determine the geometries of the DTE donor and the C₆₀ acceptor framework, we performed *ab initio* calculation with the HF-3/21G method. The optimized structures of **1** and **2** are shown in Fig.1. In both dyads the thiophene rings are distorted from the planer cyclopentene. The bond numbers between the C₆₀ moiety and the closest sulfur atoms are both three, which lead to a through bond distances of 4.8 Å. In addition, the interchromophore distance from the closet sulfur atoms of the DTE moiety to the C₆₀ surface is 3.6 and 4.5 Å in dyads **1** and **2**, respectively.

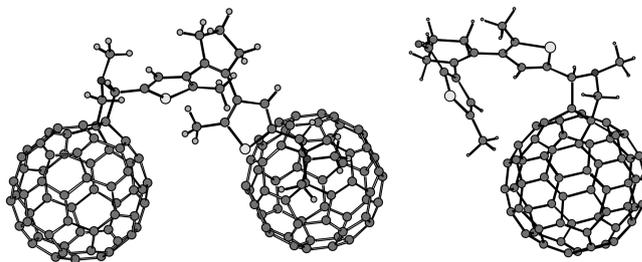


FIG. 1 Geometries for dyads **1** and **2** optimized by HF/3-21G method.

C. Absorption spectra

The UV-Vis spectra of **1** and **2** together with reference **3** in cyclohexane at the room temperature, shown in Fig.2, are very similar to those reported earlier for the 6,6-closed, monofunctionalized C₆₀ derivatives [33,34]. While the **1** and **2** shared the common absorption bands, the absorption peak at 430 nm, characteristic of [6,6]-bridged monoadducts, appeared only as a shoulder in the spectrum of **1**. In addition to this shoulder,

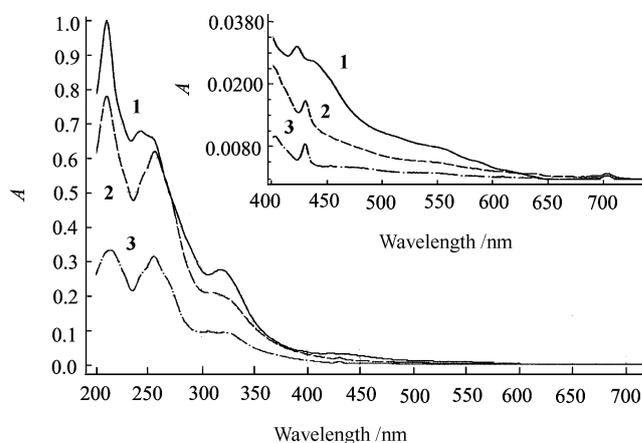


FIG. 2 UV-Vis spectra of **1**, **2** and **3** in cyclohexane measured at the room temperature. Insert: multiplied by factor of 50.

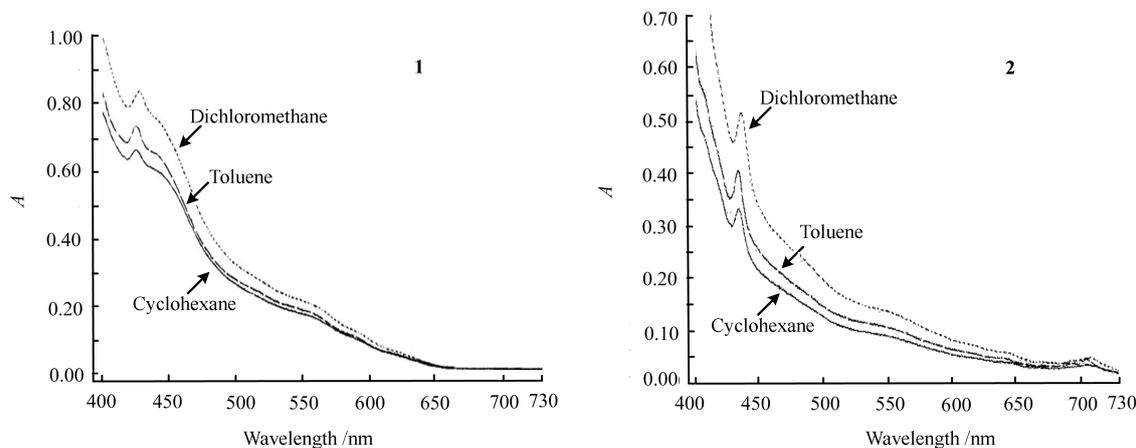


FIG. 3 UV-Vis spectra of **1** and **2** in cyclohexane, toluene and dichloromethane recorded at the room temperature.

1 also showed a peak at 422 nm. And in the dyads **1** and **2**, the transition band at 215 nm, presented in the spectrum of model N-methylfulleropyrrolidine **3**, exhibited an enhanced oscillator strength and a noticeable blue shift (215→209 nm). The blue shift and enhanced absorption may suggest electronic interaction between the DTE donor and the C₆₀ acceptor. Furthermore, another weak, broad absorption is observed in the region of 450-650 nm, similar broad bands were attributed to weak electronic interactions between the donor and the acceptor moieties, and were reported for intramolecular electron transfer in other C₆₀-based dyads [35-38] or intermolecular electron transfer interactions with other donors [39].

The broad absorptions of these compounds were red shifted with increasing solvent polarity (Fig.3), suggesting the formation of weak charge transfer (CT) complexes in the ground state in those dyads where this band was present. The weaker intensity of this band in cyclohexane compared with that of dichloromethane was shown by their ϵ values, and this supported the formation of CT complex in more polar or polarizable solvents (Table I).

TABLE I Absorption of dyads **1** and **2** in different solvents ($C=0.1$ mmol/L)

| Compounds | Cyclohexane | | Toluene | | Dichloromethane | |
|---------------|-------------|----------------|-----------|----------------|-----------------|----------------|
| | λ | $\lg \epsilon$ | λ | $\lg \epsilon$ | λ | $\lg \epsilon$ |
| Dyad 1 | 421 | 3.76 | 425 | 3.80 | 427 | 3.85 |
| Dyad 2 | 433 | 3.55 | 434 | 3.64 | 436 | 3.75 |
| | 705 | 2.62 | 705 | 2.50 | 708 | 2.54 |

λ in nm, ϵ in L/mol cm

D. Fluorescence spectra

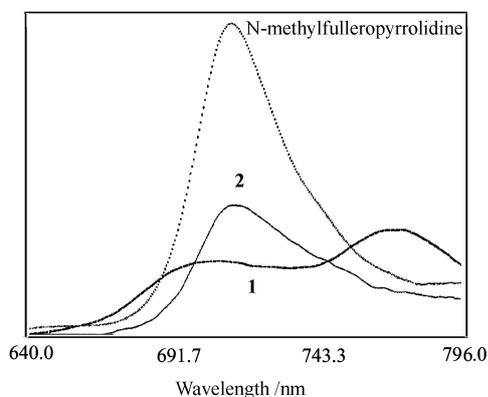
In the donor-spacer-acceptor systems, the fluorescence of the donor and/or the acceptor chromophores is generally strongly quenched [40] due to electron transfer. In general, the electron transfer character of the emissive state is reflected by a strong dependence of the emission wavelength on solvent polarity. A convenient way to probe such electron transfer events, involving, the fullerene singlet excited state and the covalently attached electron donor in dyads **1**, **2**, is the steady-state fluorescence at the ambient temperature or in frozen matrixes.

Considering its simplicity, the model N-methylfulleropyrrolidine **3** was chosen as an internal reference. Previous studies on the photochemical properties of this compound indicated that nitrogen of the pyrrolidine ring does not engage in electron-donating to the fullerene core [12,41]. Thus, the noticeably higher fluorescence quantum yield of this fullerene reference ($\Phi=6.0 \times 10^{-4}$) relative to the pristine [60]fullerene ($\Phi=1.5 \times 10^{-4}$) has been related to the partially broken symmetry of the former [42].

The fluorescence spectra of dyads **1** and **2** at the room temperature in cyclohexane solution by 430 nm excitation, together with the aforementioned fullerene reference, are shown in Fig.4. The spectra of the pyrrolidinofullerenes showed an emission peak at about 710 nm, similar to that of the unsubstituted reference compound; while the molecule **1** exhibited an additional shoulder about 770 nm which is likely to arise from the intramolecular interactions between the two excited fullerene moieties [43]. In addition, the similarity of the emission spectra confirmed the selective excitation of the fullerene core in both dyads. Under identical scanning conditions, all the dyads showed lower emission yields relative to the reference compounds. On the other hand, the lowest singlet excited state of DTE (2.45 eV) is higher than that of the fullerene (1.76 eV). So the

TABLE II Photophysical data of dyads **1** and **2** in different solvents (nm)

| Compounds | Solvent | Fluorescence max/nm | $\Phi \times 10^{-4}$ | Relative $\Phi/\%$ | k_{et}/s^{-1} |
|---------------|-----------------|---------------------|-----------------------|--------------------|--------------------|
| Dyad 1 | Toluene | 707, 765 | 2.73 | 46 | 9.36×10^8 |
| | Dichloromethane | 705, 772 | 1.64 | 27 | 2.08×10^9 |
| | Benzonitrile | 709, 772 | 0.75 | 13 | 5.47×10^9 |
| Dyad 2 | Toluene | 707 | 5.43 | 91 | 8.20×10^7 |
| | Dichloromethane | 715 | 4.15 | 69 | 3.48×10^8 |
| | Benzonitrile | 720 | 2.78 | 46 | 9.05×10^8 |

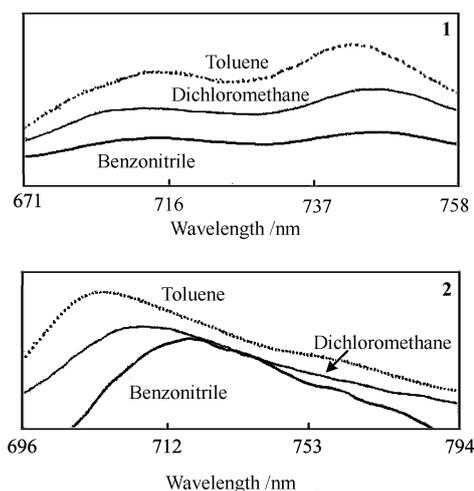
FIG. 4 Fluorescence spectra of dyads **1**, **2** and N-methylfulleropyrrolidine in cyclohexane at room temperature.

singlet energy transfer from the singlet excited fullerene state to the DTE moiety is impossible. Thus, we tentatively ascribe the observed emission quenching to the following photoinduced electron transfer (ET) event:



When using solutions with the same absorbance, the fluorescence intensities were found to be different, indicating that the quantum yields should be unequal. Solvent effects and the fluorescence quantum yields were examined in toluene, dichloromethane, and benzonitrile solutions. Ref.[3] shows a similar emission pattern in toluene and benzonitrile. Nevertheless, in benzonitrile the fluorescence intensities of compounds **1** and **2** were reduced to 28% and 51% of that in toluene (Fig.5), respectively. An intermediate situation was observed in dichloromethane in accordance with its intermediate polarity. The experiments in these solvents engender the expected trend, namely, the stepwise increase of the quenching efficiency on progressing solvent polarity (Table II). This quenching of the fluorescence is ascribed to the electron-transfer interactions in the excited state between the C_{60} moiety and the thiophene ring. This result clearly supports an intramolecular electron transfer mechanism. It is interesting to note that the fluorescence quantum yields of dyads **1** and **2** reveal a good correlation with their spacer length, which is 3.6 and

4.5 Å between the electron donor and acceptor moiety of dyads **1** and **2**, respectively. It is also in agreement with other N-methylfulleropyrrolidine derivatives [44].

FIG. 5 fluorescence spectra of **1** and **2** in toluene, dichloromethane and benzonitrile at room temperature.

From the relative fluorescence quantum yields in Table II and the fluorescence lifetime of **3** [44], an estimate of the electron transfer rate constant (k_{et}), assuming that the natural rate constants are the same as that of the reference compound, can be calculated according to the following expression,

$$k_{et} = \frac{1}{\tau_{ref}} \times \frac{\phi_{ref}}{\phi - 1} \quad (2)$$

The results of this estimate are compiled in the last column of Table II. Earlier reports on intramolecular electron transfer in donor-acceptor dyads demonstrated the dependence of the rate of electron transfer upon the solvent dielectric constant [45]. Accordingly, increasing the solvent polarity from toluene ($\epsilon=2.38$) to benzonitrile ($\epsilon=25.2$) resulted in a substantial enhancement of the quenching rate constant of both dyads.

IV. CONCLUSION

Novel C_{60} -based dyads, in which the C_{60} moiety was covalently linked to the electron donor dithienylethene

(DTE) through a pyrrolidine ring, were synthesized by 1,3-dipolar cycloaddition of *in situ*-generated DTE-containing azomethine ylides to C₆₀. Theoretical calculations showed the spatial interchromophore distance, and revealed a configuration in which the thiophene rings of the DTE moiety deviated from the planar form of the cyclopentene. Steady-state absorption spectra indicated that there were weak interactions between the DTE donor and C₆₀ acceptor in the ground state. And the fluorescence study revealed that the fullerene singlet excited states in dyads **1** and **2** were subject to rapid intramolecular electron transfer events yielding a short lived charge-separated radical pair, namely, (C₆₀^{•-})-(DTE^{•+}). These results were rationalized by the close distance of the coupled donor-acceptor structure.

V. ACKNOWLEDGMENTS

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