

SOLUTION PROCESSABLE C₆₀ FULLERENE-HYDRAZONE DYADS FOR OPTOELECTRONICS

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Introduction

Since their discovery and isolation, the fullerenes have attracted attention of an increasing number of scientists. Due to its fascinating physical and chemical properties, C₆₀ and its derivatives have been extensively applied in areas such as supramolecular materials, nano sciences [1,2], and medicine [3].

One of the most used methods for C₆₀ functionalization is the 1,3-cycloaddition of azamethine ylides with the C₆₀[6,6] bond [4], which leads to selective formation of usually solution processable fulleropyrrolidine derivatives. Among them, particular attention has been devoted to donor-acceptor interactions, utilizing dyads containing fullerene as the electron acceptor and various donors, such as tetracene, tetrathiafulvalene, chlorines, amine, and ferrocenes. A variety of C₆₀-bridge-donor dyads have been synthesized in the search for systems with improved charge separation properties.

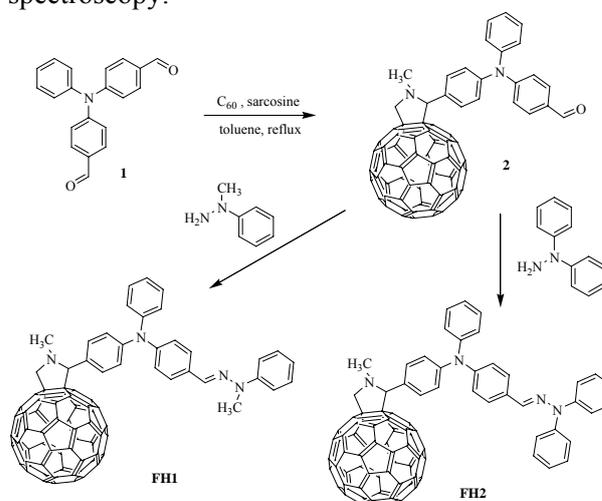
It is unexpected that simple fullerene-bridge-hydrazone dyads were not studied. Most probably because all attention was focused on the 1,3-dipolar cycloaddition between C₆₀ and the corresponding nitrile imine, generated in situ from the appropriate hydrazones, to yield corresponding pyrrolidino[60]fullerenes [5].

Here we report two new hydrazone-C₆₀ dyads, *N*-methyl-2-[4-(1-methyl-1-phenylhydrazone-2-methyl)diphenylamino]phenyl-3,4-fulleropyrrolidine (**FH1**) and *N*-methyl-2-[4-(1,1-diphenylhydrazone-2-methyl)diphenylamino]-phenyl-3,4-fulleropyrrolidine (**FH2**), whose structures are shown in Scheme 1.

Results and discussion

The fullerene-hydrazone dyads **FH1** and **FH2** were synthesized in two steps from 4-(diphenylamino)benzaldehyde (**1**) as shown in Scheme 1. First, in a typical Prato-Maggini-Scorrano reaction [6], according to the procedure described in [7], toluene solution of C₆₀ was refluxed with dialdehyde **1** and *N*-methylglycine (sarcosine). The fulleropyrrolidinetriphenylamine-adduct (**2**), possessing a free aldehyde group, was isolated after column chromatography. Subsequent

condensation of adduct **2** with *N*-methyl-*N*-phenylhydrazine or *N,N*-diphenylhydrazine gives target fullerene-hydrazone dyads **FH1** and **FH2**. The new dyads were characterized by MS as well as by ¹H, ¹³C NMR, FT-IR and UV-Vis spectroscopy.



Scheme 1. Synthesis route to **FH1** and **FH2**

The light absorption spectra of **FH1** and **FH2** recorded in CHCl₃ are shown in Fig.1, together with spectra of three reference compounds: 4-(diphenylamino)benzaldehyde *N*-methyl-*N*-phenylhydrazone (**3**), 4-(diphenylamino)benzaldehyde *N,N*-diphenylhydrazone (**4**), and fullerene C₆₀ (**Ful**).

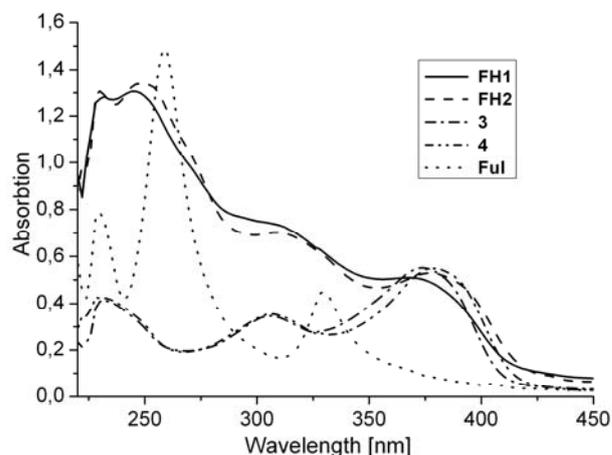


Fig. 1. Absorption spectra of the investigated and referred compounds in THF solutions ($c = 10^{-4}$ M).

The spectra of dyads **FH1** and **FH2** are the sum of the spectra of the separate components; this indicates that there is no interaction at the ground state between the fulleropyrrolidine and hydrazone moieties.

The ionization potential (I_p) was measured by the photoemission in air method (Figure 2). The I_p values are 5.29 eV and 5.36 eV for **FH1** and **FH2** accordingly.

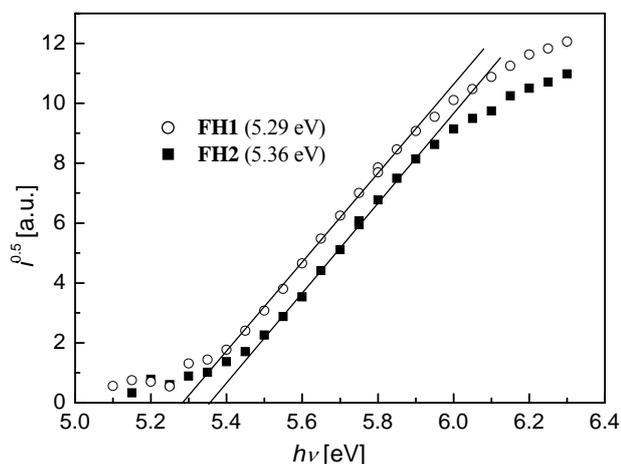


Fig. 2. Photoemission in air spectra of the investigated dyads **FH1** and **FH2**.

Obtained dyads are soluble in common organic solvents such as chloroform, THF, toluene, etc. Films of **FH1**, **FH2** and their compositions with polycarbonate (1:1) were prepared by the casting technique.

Charge transport properties were studied by the xerographic time-of-flight (XTOF) technique, charge carriers were generated at the layer surface by illumination with 1 ns pulses of nitrogen laser.

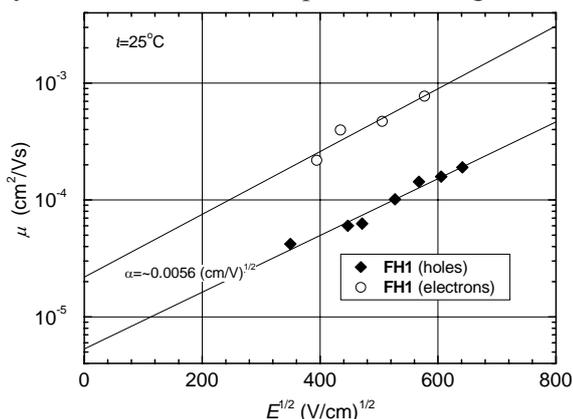


Fig. 3. Electric field dependencies of electron and hole drift mobilities in charge transport layer of **FH1**.

The **FH1** and **FH2** were found to be effective bipolar charge carrier transporters. Room temperature electron and hole mobilities exceed $10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at strong electric fields. Fig. 3 shows the room temperature dependencies of hole

and electron drift mobilities on electric field in the neat **FH1**.

Figure 4 shows good xerographic photosensitivity of **FH2** in composition with polycarbonate.

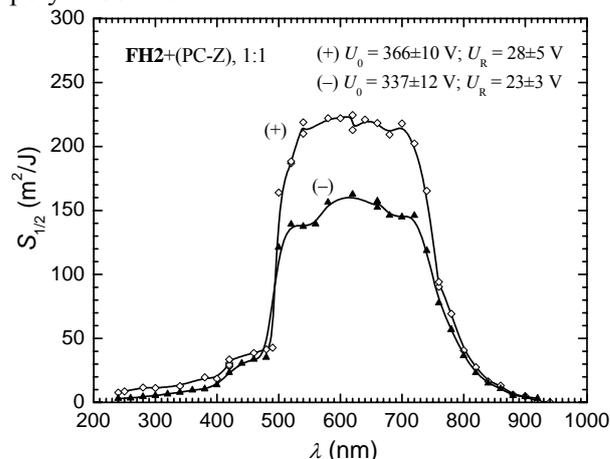


Fig. 4. Spectrums of the xerographic photosensitivity of 1:1 composition of **FH1** with polycarbonate Z.

Conclusions

In conclusion, novel fullerene-donor dyads have been synthesized. Good electron and hole drift mobility, good photosensitivity, solubility in common organic solvents makes them attractive materials for various optoelectronic applications.

References

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