



# Novel fullerene-based ferrocene dyad and diferrocene triad: Synthesis and effects of introduction of fullerene[60] and phenyl linker on the thermodynamic stability, the magnetic properties and the band structure

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## ARTICLE INFO

### Article history:

Received 6 December 2016

Received in revised form

22 March 2017

Accepted 8 April 2017

Available online 10 April 2017

### Keywords:

Fullerene-based ferrocene dyad  
Fullerene-based diferrocene triad  
Thermodynamic stability  
Magnetic properties  
Band structure

## ABSTRACT

In this paper, two nanoscale fullerene[60]-based compounds, *N*-methyl-2-(ferrocenyl) (phenyl) fulleropyrrolidine (C<sub>60</sub>-ph-Fc) and *N*-methyl-2-(diferrocenyl propane) fulleropyrrolidine (C<sub>60</sub>-diFc) were synthesized and characterized. The effects of the covalent linkage of fullerene[60] and the insertion of a phenyl group between fullerene[60] and diferrocenyl propane (diFc) moiety on the thermodynamic stability, the magnetic properties and the band structure were studied through measurements of the temperature-dependent magnetic susceptibility and cyclic voltammetry. The results show that both the covalent linkage of fullerene[60] and the insertion of a phenyl linker between fullerene[60] and diferrocenyl propane moiety lead to a weakness in the antiferromagnetic interaction between the two ferrocenyl entities. The introduction of C<sub>60</sub> leads to an increase in the thermodynamic stability of the diferrocenyl propane moiety. The insertion of phenyl group between C<sub>60</sub> and diFc or between C<sub>60</sub> and Fc decreases the thermodynamic stability, and result in an increase in the HOMO orbital energies, but lead to a decrease in the HOMO-LUMO gap. The above experimental results lay the foundation for the future design of novel functional materials that can be applied to molecular devices.

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## 1. Introduction

Ferrocene is an electron-rich aromatic complex with sandwich structure. It has the characteristics of good thermal stability, high reactivity, reversible single-electron redox in most common solvents. The polarized ferrocene derivatives formed by the ferrocene and electron-withdrawing groups have unique electrochemical and optical properties, and shows a larger second order optical nonlinear response. Their photochemical properties can be tuned to achieve redox switch effect by the reversible redox properties of the ferrocene moiety. Therefore, the ferrocene-based materials have broad applications in the fields of the molecular electronic devices, molecular catalysis, magnetic, nonlinear optical materials and other fields, which have aroused people's interest from both industry and academia.

Two ferrocenyl units can covalently bonded together by a

suitable bridging group to form a diferrocene-containing compound. There are a variety of the electron-coupling channels between the ferrocenyl (Fc) entities in such ferrocenyl derivatives [1–4]. Cyclic voltammetry studies have shown that electronic coupling are highly correlated with the properties of the bridge [5], the type of the substituent [6], the molecular space configuration, the planarity of the central molecule, and the heteroatom bridge. Recent studies by Lang et al. [7] show that the electronic properties of the bridging system have a significant effect on the electron interaction between the two ferrocenyl entities. The electronic interaction increases from thiophene over furan to pyrrole [8]. The introduction of electron-withdrawing groups on the bridging system will result in a reduction in redox splittings  $\Delta E_{1/2}$  between the redox active ferrocenyls, while the introduction of electron-withdrawing groups leads to a decrease in  $\Delta E_{1/2}$  [6]. An increase in the electron withdrawing nature of the ferrocenyls functional group linearly increases the redox splitting and therefore the thermodynamic stability of mixed-valent compounds.

Fullerene[60] has a diameter of 0.78 Å and has a remarkable electron-withdrawing property [9,10], and it can accommodate 6

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electrons in the solution [11]. As an electron acceptor, Fullerene[60] can construct the nanoscale photo-active donor-bridge-acceptor molecules in the covalent bond form with various types of chromophores, such as ferrocene [12,13], porphyrin [14–16], phthalocyanine [17–19] and ruthenium complexes [20–22]. Due to the quantum size effect, these nanoscale molecules have unique properties which are significantly different from those of the corresponding bulk materials. Such nanomolecules can be used as building blocks to fabricate nanomaterials [23]. Owing to the significant electron-donating properties of chromophores, light-induced intramolecular electron transfer can take place over large distances in such donor-bridge-acceptor molecules constructed by chromophores and fullerene[60]. Therefore, fullerene-based D-A systems have potential applications in molecular wires [24], nonlinear optical materials [25], molecular switches [26] and other molecular devices.

In this paper, we report the preparation of new fullerene-based dyad *N*-methyl-2-(ferrocenyl) (phenyl)fulleropyrrolidine (**C<sub>60</sub>-ph-Fc**) and triad *N*-methyl-2-(diferrocenyl propane) fulleropyrrolidine (**C<sub>60</sub>-diFc**) (Fig. 1) and focus on effects of the covalent linkage of fullerene[60] and the insertion of phenyl group between fullerene [60] and diferrocenyl propane moiety on the thermodynamic stability, the magnetic properties and the band structure.

## 2. Results and discussion

**C<sub>60</sub>-ph-Fc** and **C<sub>60</sub>-diFc** have been synthesized according to the procedure depicted in Fig. 2. The precursor of **C<sub>60</sub>-ph-Fc**, *p*-formylphenylferrocene, was prepared by using the literature method [27,28], that is, the coupling reaction of a benzoyl diazonium salt of sulfuric acid with cyclopentadienyl group of a ferrocenes. And precursor of **C<sub>60</sub>-diFc**, 1-formyl-2,2-diferrocenylpropane, was produced by using the vilsmeier reaction, namely, covalently bonding formyl group to the cyclopentadienyl ring of diferrocenyl propane (**diFc**, for synthesis, see Refs. [29,30]). Both *p*-formylphenylferrocene and 1-formyl-2,2-diferrocenylpropane are very easily oxidized in air and must avoid long air exposure. Thus, it is desirable to use them to prepare **C<sub>60</sub>-ph-Fc** and **C<sub>60</sub>-diFc** as soon as possible after they are synthesized. The synthesis of **C<sub>60</sub>-ph-Fc** and **C<sub>60</sub>-diFc** are based on the 1,3-dipolar cycloaddition of the corresponding azomethine ylide. For example, **C<sub>60</sub>-diFc** was prepared in 42.5% by mixing 1-formyl-2,2-diferrocenylpropane, with fullerene[60] in 1:1.14 and refluxing for 18 h in the presence of sarcosine under nitrogen atmosphere (Fig. 2). The crude product was purified by column chromatography using toluene:acetonitrile = 6: 1 as the eluent. Both **C<sub>60</sub>-ph-Fc** and **C<sub>60</sub>-diFc** are easily soluble in toluene, *o*-dichlorobenzene and carbon disulfide.

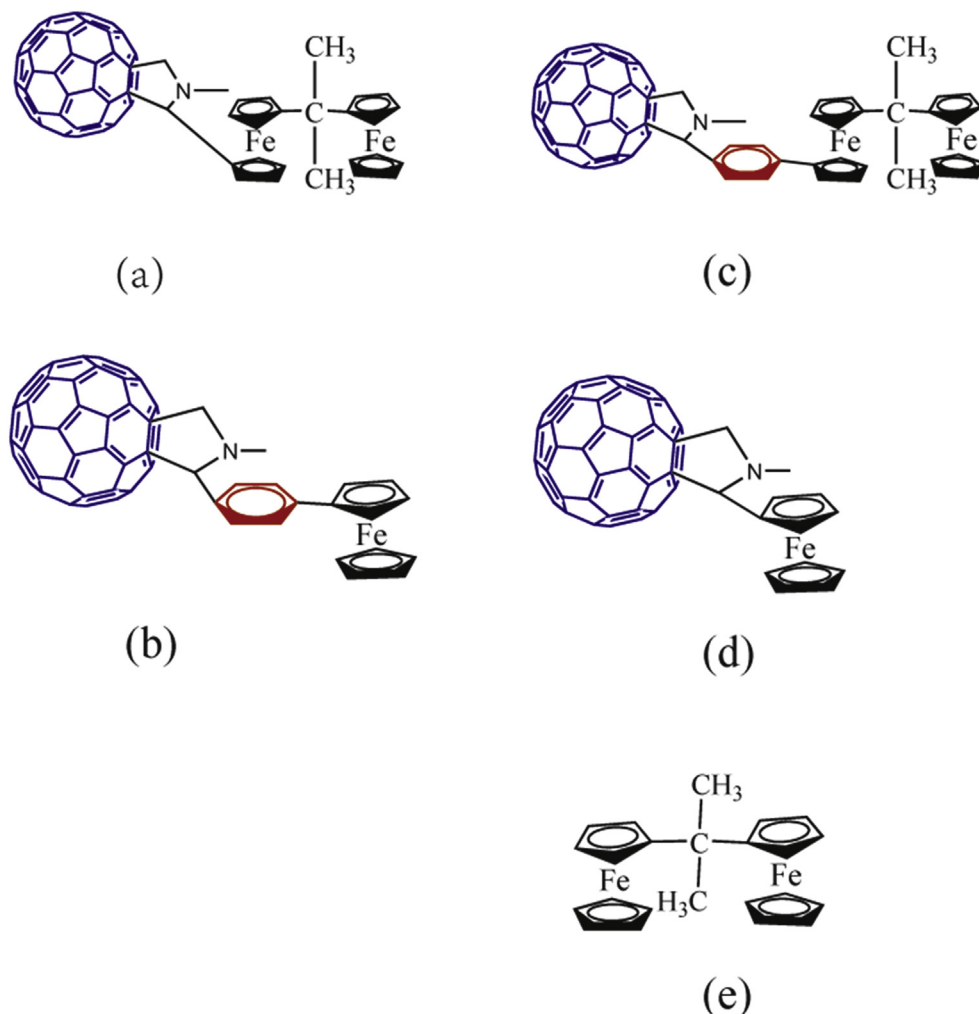


Fig. 1. Structures of (a) **C<sub>60</sub>-diFc**, (b) **C<sub>60</sub>-ph-Fc**, (c) analogue **C<sub>60</sub>-ph-Fc-Fc**, (d) analogue **C<sub>60</sub>-Fc** and (e) parent **Fc-Fc**.

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