

Research Letter

Photoinduced Change of UV-Absorption and Redox Potential of Alkyne-Bridged Diferrocenyl Azobenzene Derivative

Limin Han, Jianchen Bai, Quanling Suo, Meihua Luo, and Lifeng Zhang

Chemical Engineering College, Inner Mongolia University of Technology, Hohhot 010051, China

Correspondence should be addressed to Quanling Suo, szj@imut.edu.cn

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An alkynyl-coupled diferrocenylpropane and azobenzene derivative has been synthesized. Photoinduced change of UV-absorbance and shifts of redox potential of synthesized compound were elucidated by time-dependent density function theory (TD-DFT) calculations, indicating that isomerization of trans to cis configuration occurs by UV irradiation.

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1. Introduction

Since the structures and properties of intelligent azo molecules are facilely and reversibly changeable by the application of external physical and chemical stimuli, they have attracted much attention relative to the development of new molecule-based devices [1]. One category of such molecules comprises transition metal complexes with conjugated spacers to azo unit, in which the combination of flexibility of metal *d*- and azo π -orbitals can yield unique optical, magnetic, and electronic properties [2–4]. For example, when the ferrocene is covalently bound to an azobenzene, the isomerization of azo functional group may lead to change of intrinsic redox potential of ferrocene [5]. Inversely, isomerization behavior of azo-structure can also be influenced by the connected metal complex [6].

Though attention has been focused on photoisomerization of metal complexes-azobenzene systems, there are no reports on the alkynyl-bridged diferrocene and azo system, especially, for the interpretation of absorbency change of UV-spectrum and electrochemical redox potential shift in this system. In this paper, we synthesized an alkynyl-bridged diferrocenyl azobenzene derivatives by using documental methods [7–10], and investigated the photoinduced azo isomerization and redox potential shift of ferrocene.

2. Experimental

2.1. Material Preparation. Diferrocenylpropane and diferrocenylpropanyl acetylene (DFA) were prepared by previous methods [11], the Diferrocenylpropanyl acetylene azophenol (DFAA) was synthesized by the Sonogashira coupling reaction of DFA with iodic azophenol (see Scheme 1). Under N_2 atmosphere DFA (165 mg, 0.51 mmol) and iodic azophenol (162 mg, 0.5 mmol) were stirred in diisopropylamine (20 mL) with $Pd(PPh_3)_2Cl_2$ (6.4 mg, 0.009 mmol) and CuI (5.3 mg, 0.0275 mmol) for 20 hours under reflux. The solvent of the resulting orange mixture was removed in vacuum. The residue was dissolved in a minimal amount of CH_2Cl_2 . The filtrate was concentrated and subjected to chromatographic separation on a neutral alumina column. Elution with hexane-dichloromethane (4:1, v/v) afforded a yellow band and red band, the red band product was obtained by recrystallizing from hexane-dichloromethane at $-20^\circ C$. Yield, 55.1%. Anal. Calc: C, 70.28; H, 5.10; N, 4.14. Found: C, 69.79; H, 5.42; N, 4.43%. IR(KBr): 3088 [Cp $\nu C-H$]; 2197 [$C\equiv C$, $\nu C\equiv C$]; 1593, 1495, [C₆H₄, $\nu C=C$]; 1424 [N=N, $\nu N=N$]; 1265 [OH $\delta O-H$]; 1101, 1029 [Cp $\gamma C-H$]; 820 [Cp $\delta C-H$] cm^{-1} . 1H NMR 10.3 (m, 1H, -OH); 6.9–7.8 (m, 8H, -C₆H₄-N=N-C₆H₄-); 4.0–4.5 (m, 9H, -Cp)·1.5–1.6 (m, 6H, -C(CH₃)₂) ppm. ^{13}C NMR(CDCl₃, δ): 161.2, 150.9, 145.3, 132.0, 124.9, 122.5, 116.0 (-C₆H₄-N=N-C₆H₄-);

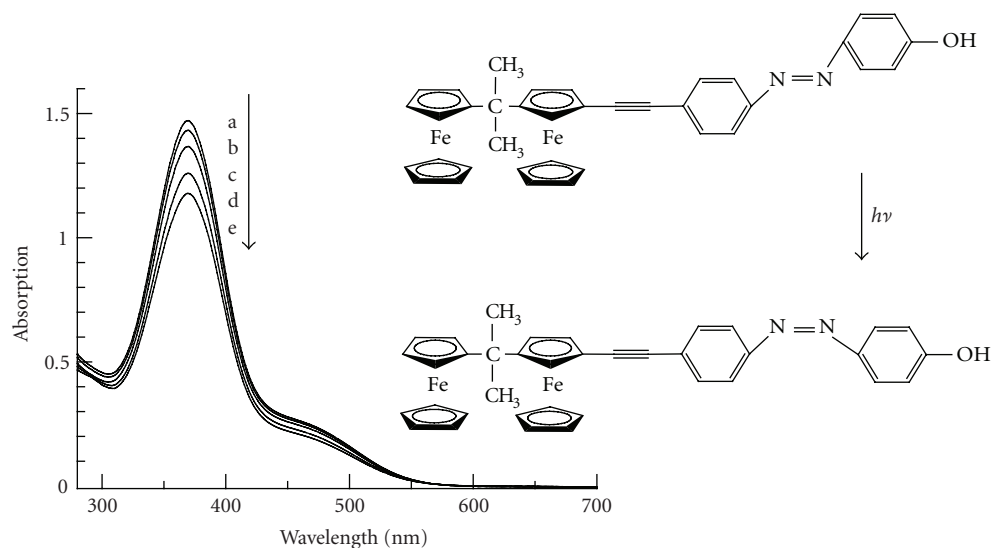


FIGURE 1: UV-vis absorption spectral change of DFAA (2 mM) in THF solution upon irradiation with UV light at 365 nm for (a) 30 minutes, (b) 50 minutes, (c) 70 minutes, (d) 90 minutes, (e) 100 minutes.

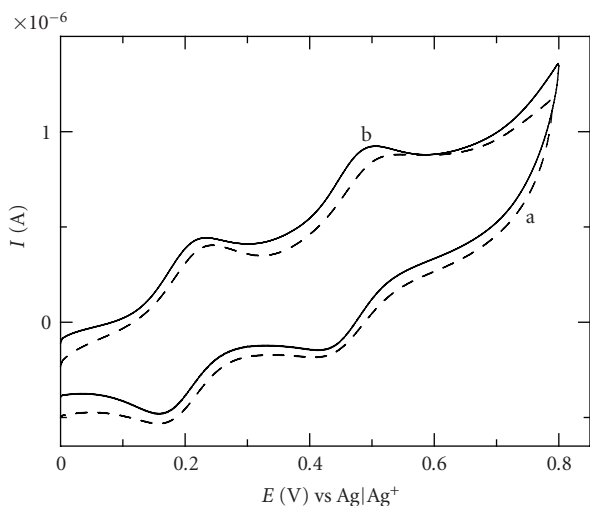


FIGURE 2: Cyclic voltammogram of DFAA in solution of CH_2Cl_2 - Bu_4NClO_4 (0.1 M) (a) before irradiation and (b) after irradiation.

91.4, 85.3($\text{C}\equiv\text{C}$); 71.2, 69.8, 69.2, 63.9 (Cp) ppm. MS(EI) 632(M⁺).

2.2. Characterization. IR spectra were recorded on a Nicolet FTIR spectrometer as KBr discs. Elemental analysis was carried out on an Elementar var III-type analyzer. ^1H and ^{13}C NMR spectra in CDCl_3 were recorded on an Inova 500 FT-MHz spectrometer. The mass spectra were determined using a Polaris QMS and a Micromass Autospec Ultima-TOF instrument. The electrochemical properties were determined with a CHI760C type analyzer. UV spectra were recorded on a Shimadzu UV-3150 spectrometer.

The quantum calculations were performed using Gaussian03 program [12]. The geometries of DFAA and the frequencies were evaluated using the DFT level of the three-

parameter compound functional of Becke (B3LYP) [13]. The 6-31G(d) basis set was used for all atoms. The geometry structures of neutral molecules were optimized under no constraint.

3. Results and Discussions

The synthesized DFAA was characterized using FT-IR, NMR, MS, and elemental analysis data. However, because there was an azo group in the molecule, the product may be a mixture of trans and cis configuration, it was very difficult to obtain a single crystal of DFAA.

3.1. UV Absorption Change. The UV-vis spectra of DFAA in tetrahydrofuran (THF) showed an intense azo π - π^* band at $\lambda_{\text{max}} = 364 \text{ nm}$ and a weak visible band at 450 nm, the latter was primarily ascribable to a transition from the e_{1g} of ferrocene to the π^* of azo group [14]. The irradiation of DFAA solution with 365 nm UV light led to a decrease in the absorbance of azo π - π^* band, which indicated the trans-to-cis isomerization of DFAA (Figure 1), and the photostationary state (PSS) of DFAA at a nonradiation condition should be transconfiguration, or transform was a main configuration in mixture of trans and cis product.

3.2. Redox Potential Shift. The cyclic voltammogram of DFAA in THF solution containing a supporting electrolyte of Bu_4NClO_4 in a sealed thin quartz cell shows that there are two reversible $1e^-$ oxidation waves at $E = 0.24$ and 0.51 V versus Ag/Ag^+ reference electrode (Figure 2(a)). $E = 0.24 \text{ V}$ was ascribed to the oxidation of ferrocene unit at position B, and 0.51 V was the oxidation of ferrocene unit at position A because the withdrawing electron azo group and alkyne were connected to it [15] (see Scheme 1). The potential difference between ferrocene unit A and B is 270 mV, which is similar to that of diferrocenyl propane derivatives [16]. After the

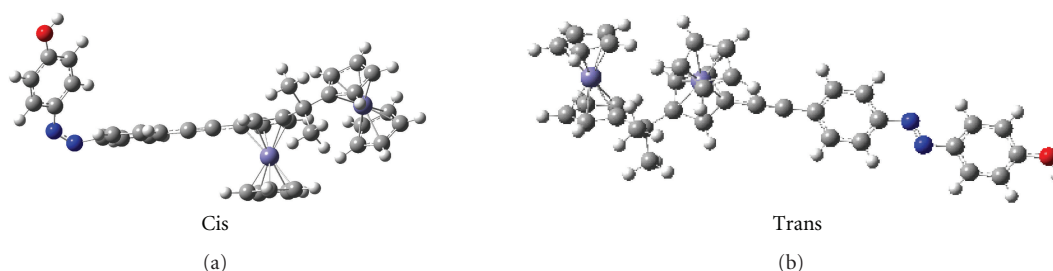
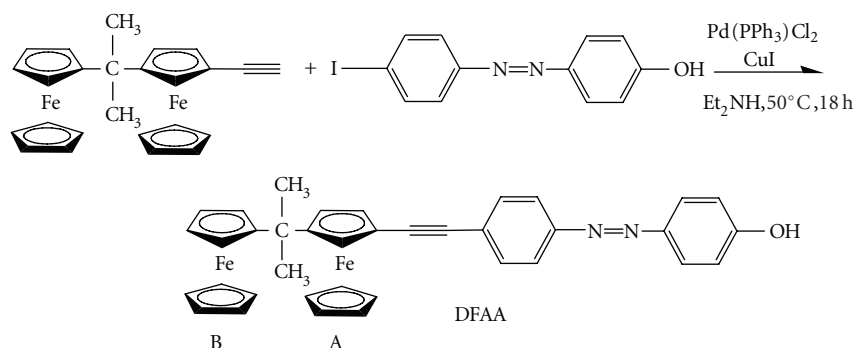


FIGURE 3: Optimized molecular structure of cis and trans DFAA.



SCHEME 1: Synthesis procedure of DFAA.

cell was irradiated with UV at 365 nm for 1.5 hours, we repeated the cyclic voltammetric measurement, oxidation potential at 0.51V of ferrocene unit A negatively shifted to 0.48 V (Figure 2(b)), and there was no clear potential shift of ferrocenyl unit B in curve a and b.

3.3. Calculations. In order to understand the change of absorbency and oxidation potential, the geometry of trans-DFAA was optimized by three parameterized Becke-Lee-Yang-Parr (B3LYP) hybrid exchange-correlation function [17]. In transoptimized structure (see Figure 3(b)), the azo and phenyl groups are located nearly on a plane in optimized molecular structure, the dihedral angle of Ph-N=N-Ph was near to 0°, the N=N bond length was 1.282 Å, and others structural data were consistent with documented reported [18]. Comparing to trans structural datas, cis-DFAA was also optimized by B3LYP/DFT (see Figure 3(a)), the resulted N=N bond length was 1.265 Å, shorter than that of trans, and Ph-N=N-Ph dihedral angle of cis-DFAA was 12°, similar to other cis-azobenzene derivatives [19, 20]. Because two phenyls lose their coplanarity in the cis configuration, the π electrons prefer to localize in N=N bond compared to the large conjugated system of trans configuration. The bond length was shortened and electron withdrawing function of N=N was reduced. Therefore, in the optimized structure of trans DFAA, the Mulliken charge numbers of Fe(II) in ferrocene units A and B (see Scheme 1) were 0.6210 and 0.6005, respectively, and those of cis were 0.6110 and 0.6003. For the ferrocene unit in position A, charge difference was 0.0100 between trans and cis configuration, with no apparent difference exhibited between trans and cis configuration in

position B. This phenomenon may give us a possible reason for the oxidation potential of ferrocene A being slightly shifted negatively after irradiated by 365 nm light.

Calculated excitation energies in the trans and cis forms were in reasonable agreement with the experimental values. For the trans DFAA, molecular orbitals contributing to the main UV absorption at 364 nm was the excitation of electron from orbital 160 to 165, not the excitation from the HOMO (164) to LUMO (165), and the oscillator strengths (f_{trans}) contributed to this excitation was 0.8396. For the cis DFAA, molecular orbitals contributing to the main UV absorption at 364 nm was the excitation of electron from orbitals of 160, 159, 158 to 165, not from HOMO (164) to LUMO (165). The oscillator strengths (f_{cis}) contributed to excitation was 0.4072. Comparing the calculated results, the excitation energy of trans and cis form was 3.4193 and 3.4173 eV, no apparent difference existed. However, the difference of oscillator strengths (f) was obvious, Δf value between the trans and cis was 0.4324, this helped us to understand why the absorbance of trans-DFAA decreased with the irradiation of UV light at 365 nm and to identify the isomerization of trans to cis DFAA. MLCT (from Fe d orbital to azo π orbital) band of DFAA in experimental and calculated results was not very obvious in the calculations of trans configuration; excitation at 462 nm with oscillator strengths (f) 0.2698 can be attributed to MLCT, but we did obtained the similar data in the calculations of cis form. The reason might be derived from the optimized structure of cis form, in which the ferrocene unit lost the conjugated plane, and the avenue of electron transfer from Fe d orbital to azo π orbital is interdicted partially.

4. Conclusions

In summary, the DFAA was synthesized by Sonogashira coupling reaction, and the phenomena of absorbance change and redox potential shift of DFAA were interpreted in terms of the optimization of structures and the singlet excitation calculations of DFAA, which indicated that the synthesized DFAA was mainly in trans configuration, but it could isomerize to a cis form by the irradiation of UV light with wavelength of 365 nm.

Acknowledgments

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