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Cationic cyclopentadienyliron azo-complexes: Synthesis, spectroscopic characterization, and molecular structure

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ABSTRACT

Two novel cationic cyclopentadienyliron azo-complexes (Azo-Fc) were synthesized by the S_NAr reaction of (η^6-chlorobenzene) (η^5-cyclopentadienyl) iron hexafluorophosphate (Fc-Cl) with 1-phenylazo-2-naphthol and 4-(4-nitrophenylazo)carbazole. They were characterized by IR, ^{1}H NMR, ^{13}C NMR, and MS. The UV–vis spectral characteristics of the azo-complexes were investigated in four organic solvents of different degrees of polarity. These synthesized azo-complexes exhibited a bathochromic shift of the visible absorption maxima with the increase in conjugating skeleton. The study of photochemical properties reveals that the azo-complexes showed good photostability and that photolysis was difficult to realize. The geometric structures of the azo-complexes were optimized on the basis of density function theory at the B3PW91/Lanl2dz level. The energy levels of their frontier molecular orbitals were obtained.

1. Introduction

Azo compounds have drawn considerable attention in fundamental studies and applications, which include textile fiber dyeing, biomedical studies, photoelectronic applications, printing systems, optical storage technology, and photochemistry [1–5]. Azo compounds, which contain a metallic atom in their structures, possess the combined properties of the metal and azo groups, producing materials that can be processed with interesting magnetic, electronic, optic, and anisotropic properties [6,7]. Ferrocene containing the azo group have been reported. Literature showed that the reversible trans–cis photoisomerization of azo chromophores can be used to design and exploit novel photoactive materials [8–10].

A number of neutral and cationic iron-containing polymers with azo dyes either directly in the backbone or pendant to the polymer were reported by Abd-El-Aziz [11–14]. However, reports on the photochemical properties and geometric structure of mono-molecular cationic cyclopentadienyliron complexes containing the azo group remain limited. Given this backdrop, two cationic cyclopentadienyliron complexes containing the azo group (Azo-Fcs) were synthesized by the S_NAr reaction of Fc-Cl with 1-phenylazo-2-naphthol and 4-phenylazocarbazole. Research on the relationship between the photochemical properties and structure was carried out. The geometric structures of the azo-complexes were optimized and energy calculations were performed on the basis of density function theory (DFT).

2. Experimental

2.1. Materials

All the reagents and solvents in this experiment were of reagent-grade quality, which were obtained from commercial sources and used without further purification. (η^6-Chlorobenzene) (η^5-cyclopentadienyl) iron hexafluorophosphate (Fc-Cl) was prepared through the ligand exchange reaction of ferrocene and chlorobenzene according to the reference procedure [15].

2.2. Instrument and methods

The melting points of the compounds were determined using an XT-4 microscopic melting point apparatus. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV500 unity spectrometer

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operated at 500 MHz using acetone-d6 as deuterated solvent. FT-IR spectra were recorded on a Nicolet 5700 instrument (Thermo Electron Corporation, Waltham, MA). UV–vis absorption spectra were recorded on a Hitachi U2500 UV–vis spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan). Light intensity was recorded by the UV light radiometer (Photoelectric Instrument Factory, Beijing Normal University, China). A Pentium IV personal computer (CPU at 3.20 GHz) with the Windows XP operating system was used to calculate quantum chemistry. The initial geometry optimization was performed with ChemBio3D (Version 12.0). For all calculation, Gaussian 09 has been employed.

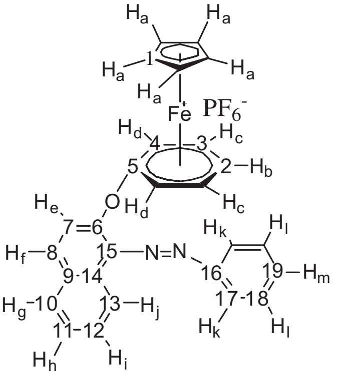
2.3. Synthesis of cationic cyclopentadienyliron azo-complexes

2.3.1. (η^6-1-phenylazo-2-naphthoxyl benzene) (η^5-cyclopentadienyl) iron hexafluorophosphate (Azo-Fc-1)

Aniline (3.72 g, 40 mmol) was dissolved in 20 ml hydrochloric acid (20%) at room temperature. The solution was then cooled to −5 to 0 °C in an ice-salt bath and maintained at this temperature. A solution of sodium nitrite (2.80 g, 40 mmol) in 10 ml water was added dropwise at below 5 °C under continuous stirring, and then the mixture was stirred at 0–5 °C for 1 h. The resultant diazonium solution was used directly in the coupling step.

2-Naphthol (5.84 g, 40 mmol) was dissolved in 40 ml sodium hydroxide solution (pH = 14). The mixture was cooled to −5 to 0 °C in an ice-salt bath. The diazonium solution was added to the stirred coupling component solution at −5 to 0 °C for 30 min, maintaining the pH at 8–10. The resultant mixture was vigorously stirred for another 4 h. The precipitate formed was filtered, washed repeatedly with water to remove any remaining reactants, and vacuum dried. The rough product 1-phenylazo-2-naphthol (Azo-1) was then purified by column chromatography and further recrystallized from ethanol/water (1:2).

The compounds Fc-Cl (3.78 g, 0.01 mol), Azo-1 (2.92 g, 0.02 mol), and K_2CO_3 (2.76 g, 0.02 mol) were stirred in 30 ml of *N, N*-dimethylformamide (DMF) in a 100 mL round bottom flask under a nitrogen atmosphere at 120 °C. Reactions were monitored by thin layer chromatography (TLC) using 0.25 mm aluminum-backed silica gel plates. After Fc-Cl was reacted thoroughly, the reaction mixture was transferred into a 15% (v/v) HCl solution, and a granular precipitate was formed. The obtained filtrate was washed by acetone resulting in the dissolution of the product. This solution was then concentrated by evaporating acetone and treated with sufficient KPF_6 in water to allow for the complete precipitation of Azo-Fc-1 as a granular solid. The rough product (Azo-Fc-1) was purified by column chromatography and further recrystallized from acetone/ether (1:5).

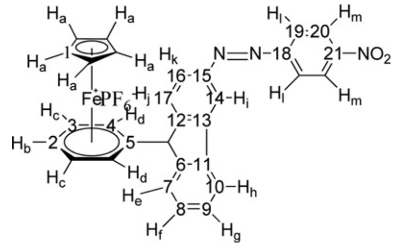


Yield: 56%. m.p. = 177–179 °C ^{1}H NMR (500 MHz, acetone-d_6): $\delta = 8.64$ (d, $1H_j$, $J_{HH} = 8.07$ Hz), 8.32 (d, $1H_g$, $J_{HH} = 8.63$ Hz), 8.18 (d, $1H_f$, $J_{HH} = 7.80$ Hz), 7.85 (d, $1H_i$, $J_{HH} = 8.91$ Hz), 7.75 (d, $2H_k$, $J_{HH} = 8.63$ Hz), 7.70 (d, $2H_l$, $J_{HH} = 7.10$ Hz), 7.57 (m, $1H_h$, $J_{HH} = 7.50$ Hz), 7.56 (m, $1H_m$, $J_{HH} = 6.94$ Hz), 7.54 (m, $1H_e$, $J_{HH} = 7.63$ Hz), 6.50 (t, $2H_c$, $J_{HH} = 5.52$ Hz), 6.44 (d, $2H_d$, $J_{HH} = 6.37$ Hz), 6.33 (t, $1H_b$, $J_{HH} = 5.52$ Hz), 5.27 (s, $5H_a$); ^{13}C NMR (500 MHz): $\delta = 77.45$ ($2C_3$), 78.05 ($5C_1$, Cp), 85.79 ($1C_2$), 87.67 ($2C_4$), 122.34($1C_5$), 123.37 ($2C_{17}$), 125.00 ($1C_7$), 127.97 ($1C_{11}$), 129.31 ($1C_{12}$), 129.43 ($1C_{10}$), 129.94 ($1C_9$), 130.35 ($2C_{18}$), 133.14 ($1C_{14}$), 133.55 ($1C_{13}$), 133.70 ($1C_{19}$) 135.75 ($1C_8$), 139.69 ($1C_6$), 141.43 ($1C_{15}$), 153.74 ($1C_{16}$); FT-IR spectra ν(cm^{-1}): 3104.9 (C–H, aromatic), 1590.5, 1527.3, 1505.7, 1453.7 (–C=C–), 1419.1 (–N=N–), 1150.5 (C–O–C), 825.5 ($-PF_6^-$). ESI-MS *m*/*z*: 444.77 (cation$^+$).

2.3.2. (η^6-4-(4-nitrophenylazo)-N-carbazole) (η^5-cyclopentadienyl) iron hexafluorophosphate (Azo-Fc-2)

4-Nitroaniline (2.76 g, 20 mmol) was dissolved in 20% hydrochloride solution (20 ml) at 0–5 °C. The reaction flask was immersed in an ice-bath for temperature control. Sodium nitrite (1.7 g, 25 mmol) was dissolved in cold water and added dropwise to the reaction mixture for 0.5 h under stirring. Freshly prepared 4-nitroaniline diazonium salt was added dropwise for 1 h to the solution of carbazole (1.95 g, 10 mmol) in 20 ml acetic acid and 20 ml DMSO under vigorous mechanical stirring. After stirring the mixture for a further 4 h, the mixture continues to react at 60–70 °C. After reacting further for 2 h, the mixture was added to 100 ml water. Then precipitate was filtered and was dried after repeatedly washed with water and ethanol. The crude product 4-(4-nitrophenylazo)carbazole (Azo-2) was recrystallized and the purified crystal was obtained.

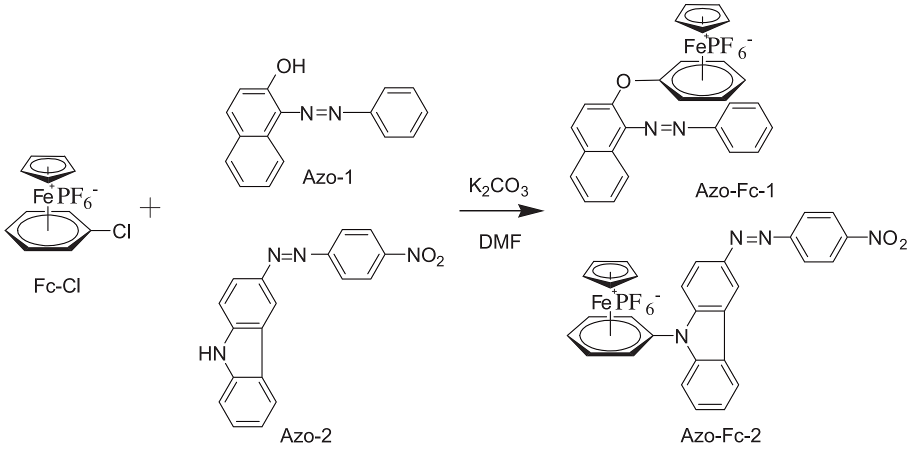
Azo-Fc-2 was prepared by the reaction of Fc-Cl with Azo-2 in a manner similar to Azo-Fc-1.



Yield: 38%. m.p. = 223–225 °C. ^{1}H NMR (500 MHz, acetone-d_6): $\delta = 9.00$ (s, $1H_i$), (d, $1H_b$, $J_{HH} = 6.14$ Hz), 8.52 (d, 1Hm, $J_{HH} = 8.17$ Hz), 8.40 (d, $1H_k$, $J_{HH} = 8.77$), 8.33 (d, $1H_j$, $J_{HH} = 8.77$), 8.24 (d, $1H_e$, $J_{HH} = 8.11$ Hz), 8.22 (d, $2H_l$, $J_{HH} = 8.17$ Hz), 7.73 (t, $1H_f$, $J_{HH} = 7.45$ Hz), 7.58 (t, 1H, $J_{HH} = 7.45$ Hz), 7.32 (d, $2H_d$, $J_{HH} = 6.41$ Hz), 6.98 (t, $2H_c$, $J_{HH} = 5.92$ Hz), 6.79 (t, $1H_b$, $J_{HH} = 5.92$ Hz), 5.51 (s, $5H_a$); ^{13}C NMR (500 MHz, acetone-d_6): $\delta = 78.94$ ($5C_1$), 84.31 ($2C_3$), 88.53 ($1C_2$), 89.01 ($2C_4$), 112.60 ($1C_5$), 112.92 ($1C_{13}$), 118.50 ($1C_7$), 122.37 ($1C_{16}$), 122.47 ($1C_{17}$), 124.05 ($1C_9$), 124.26 ($2C_{19}$), 125.83 ($2C_{20}$), 125.99 ($1C_{10}$), 126.13 ($1C_{14}$), 127.38 ($1C_8$) 128.10 ($1C_{12}$), 128.34 ($1C_{11}$), 128.82 ($1C_6$), 142.86 ($1C_{15}$), 155.51 ($1C_{18}$), 161.35 ($1C_{21}$); FT-IR spectra ν(cm^{-1}): 3106.4 (C–H, aromatic), 1589.2, 1519.3, 1470.4 (–C=C–), 1421.3 (–N=N–), 1170.5 (C–O–C), 837.0 ($-PF_6^-$). ESI-MS *m*/*z*: 513.18 (cation$^+$).

2.4. Photostability measurement

CH_3CN solution of Azo-Fc (1×10^{-4} M) in a quartz glass tube was irradiated with a 50 W halogen lamp (I = 1 mW/cm^2) at 25 °C in air. The UV–vis absorption spectra were measured and the stability of the Azo-Fc was calculated on the basis of absorbance at λ_{max}.



Scheme 1. Synthesis route of the cationic cyclopentadienyliron complexes containing azo group.

3. Results and discussion

3.1. Synthesis

The arene complexes of cyclopentadienyliron have been reported since the 1950s [16]. These complexes can be prepared by the ligand exchanging reaction of ferrocene and the nucleophilic aromatic substitution (S_NAr) reaction of Fc-Cl [17,18]. The chlorine atom of Fc-Cl is susceptible to attacks by nucleophiles because of the increased electrophilicity caused by the metallic moiety. In this study therefore, cationic cyclopentadienyliron complexes containing the azo group were synthesized from Fc-Cl and arylazo (see Scheme 1).

The reaction temperature in preparing cationic cyclopentadienyliron differs from the nucleophilic ability of nucleophiles. Azo is an electron-withdrawing group; thus, the nucleophilic abilities of azo-naphthoxide are weak. The S_NAr reactions of Fc-Cl with Azo-1 were carried out in the presence of potassium carbonate as a base in DMF at 120 °C; Fc-Cl was reacted with Azo-2 at 60 °C. The termination of S_NAr reaction was monitored by observing the disappearance of Fc-Cl via TLC.

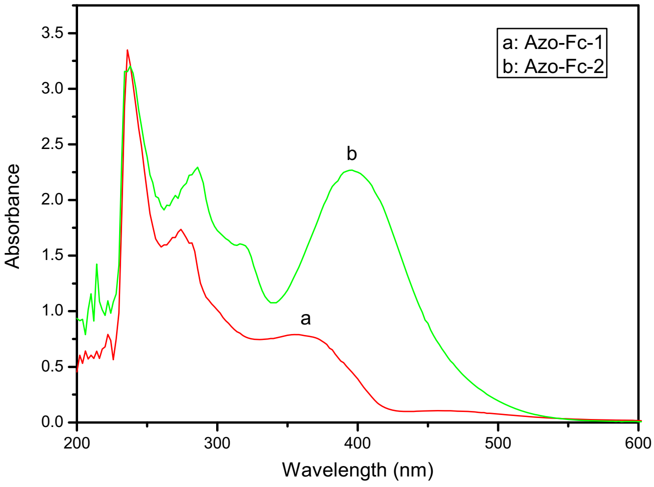


Fig. 1. UV–vis absorption spectra of Azo-Fcs in CH_3CN solution (1×10^{-4} M).

Table 1
UV–vis spectra of Azo-Fcs.

Dyes	CH_2Cl_2		CH_3CN		DMF		DMSO	
	λ_{max}	logε	λ_{max}	logε	λ_{max}	logε	λ_{max}	logε
Azo-Fc-1	352	3.83	356	3.90	364	3.85	370	3.86
Azo-Fc-2	–	–	394	4.36	408	4.34	412	4.35

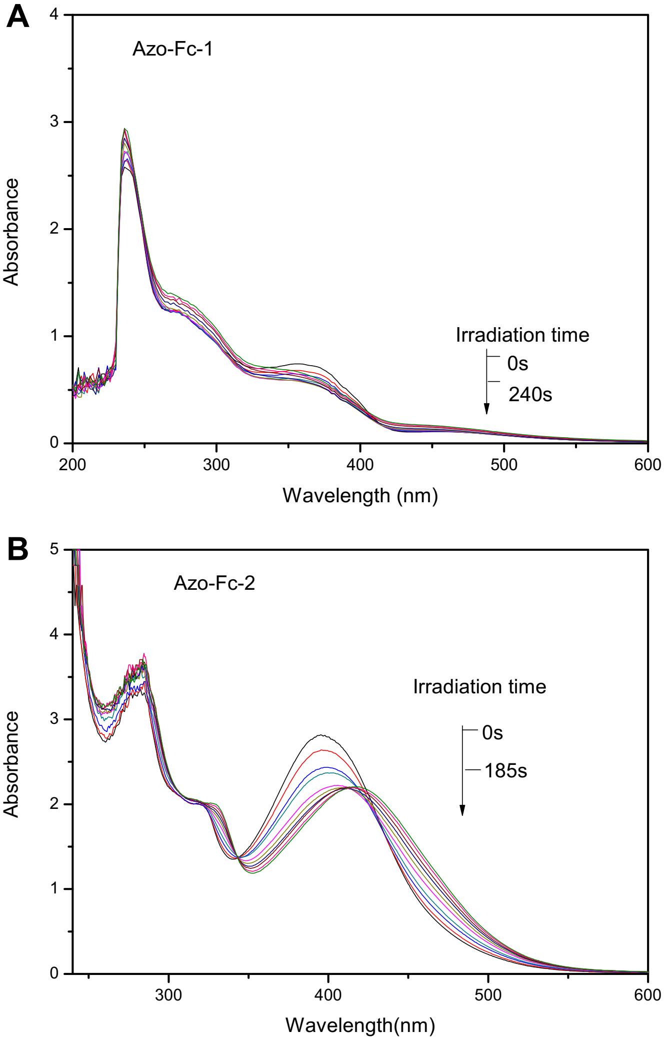


Fig. 2. UV–vis absorption spectral change of Azo-Fcs (1.0×10^{-4} M) in CH_3CN irradiated by halogen lamp without filter.

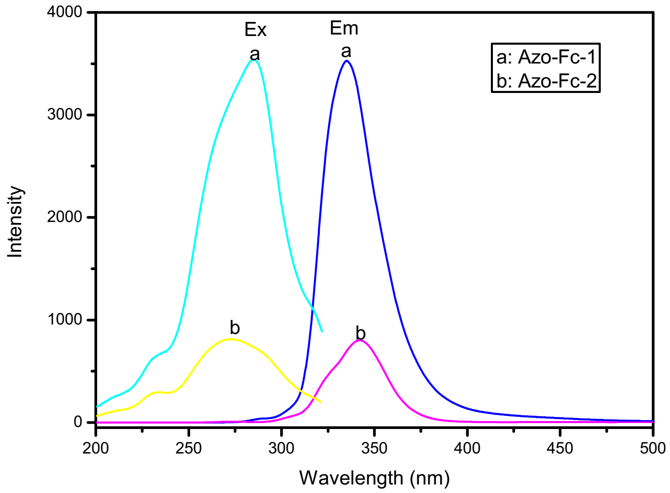


Fig. 3. Fluorescence emission and excition spectra of Azo-Fcs in CH_3CN solution.

The synthesized compounds were characterized on the basis of their physical data and spectral analysis. The IR spectra of Azo-Fcs showed a strong peak at about 820 cm^{-1} because of the P–F stretching vibration, indicating the existence of PF_6^-. In the IR spectra, the v (O–H) vibration did not exist at 3600 cm^{-1} to 3200 cm^{-1}, indicating the disappearance of –OH. The mass spectra showed that the cation was correctly identified. All the compounds showed ^1H NMR and ^{13}C NMR signals for different kinds of protons and carbon atoms at their respective positions. All the data on the compounds confirmed that the structures were correctly synthesized. The complete chemical shifts for all compounds are listed in Experimental part.

3.2. *UV–vis absorption spectra of Azo-Fc compounds*

The UV–vis absorption spectra of Azo-Fc-1 and Azo-Fc-2 in 10^{-4} M CH_3CN solution at 298 K are shown in Fig. 1 and Table 1. The electronic spectra of Azo-Fcs showed two strong absorption bands. The first band appearing below 250 nm is attributed to the π-π^* transition of the cyclopentadiene moiety, carbazole moiety, and naphthane ring, The second band appearing around 300–500 nm arose from a transition involving electron migration along the entire conjugate system of the ligand. The entire conjugate system includes both the aryl rings and azo groups.

Fig. 1 also shows that the maximal absorption peaks of Azo-Fcs are clearly different between Azo-Fc-1 and Azo-Fc-2. The increase in the degree of π delocalization caused by the coplanarity of the aromatic systems resulted in a bathochromic shift of the absorption peak wavelength. The absorption bands of Azo-Fc-1 from the entire conjugate system were at 330–420 nm. The absorption band of Azo-Fc-2 from the entire conjugate system was at 350–500 nm.

The electronic absorption spectra of the Azo-Fc compounds were studied in organic solvent with different polarities to investigate their solvatochromic behavior. The UV–visible bands in the electronic spectra of the Azo-Fc compounds in four organic solvents with different polarities, DMF, DMSO, dichloromethane, and acetonitrile, were recorded (see supplemental data). The degrees of polarity of the four solvents followed the order DMSO > DMF > CH_3CN > CH_2Cl_2. Table 1 shows that the absorption band corresponding to the UV–vis spectra of Azo-Fc showed positive solvatochromism (bathochromic shift) upon the increase in solvent polarity. This result indicates that a pronounced change in the position of an electronic absorption band accompanies the change in the polarity of the medium. This observed behavior suggests that a molecule in the ground and excitation state indicate different polarities.

3.3. *Photostability of Azo-Fc*

The study of the photostability of the synthesized Azo-Fcs was carried out by evaluating the UV–vis spectral changes of Azo-Fcs in CH_3CN upon irradiation with a halogen lamp (380–550 nm). The UV–vis spectral changes are shown in Fig. 2. The UV–vis spectra of Azo-Fcs changed only at the irradiation time of 0–30 s, after which no further changes were observed. The changes in the UV–vis spectra of Azo-Fcs in CH_2Cl_2 upon irradiation shows that Azo-Fcs did not undergo photolysis, a reaction that differs from the UV–vis spectral changes of other ferrocenium salts previously studied [19–21].

3.4. *Fluorescence*

The fluorescence emission and excitation spectra of Azo-Fc-1 and Azo-Fc-2 in CH_3CN solution are shown in Fig. 3. As can be seen, they exhibited broad structure emissions ranging from 300 to 450 nm. These two compounds had large Stoke's shifts ranging from 50 to 90 nm. Azo-Fcs showed two strong absorption bands confirming the absorption caused by the π-π^* transition of the whole molecule and the entire conjugate system of the ligand. However, the emission spectra of Azo-Fc shows that only one

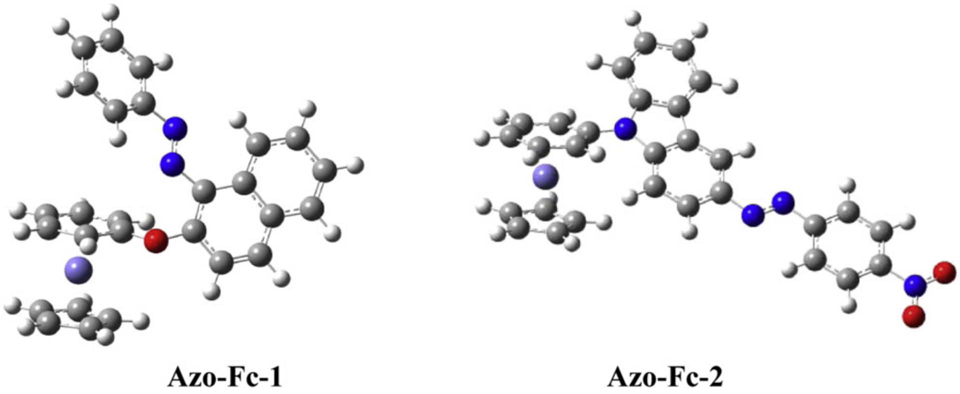


Fig. 4. Optimized structures of Azo-Fcs by DFT method.

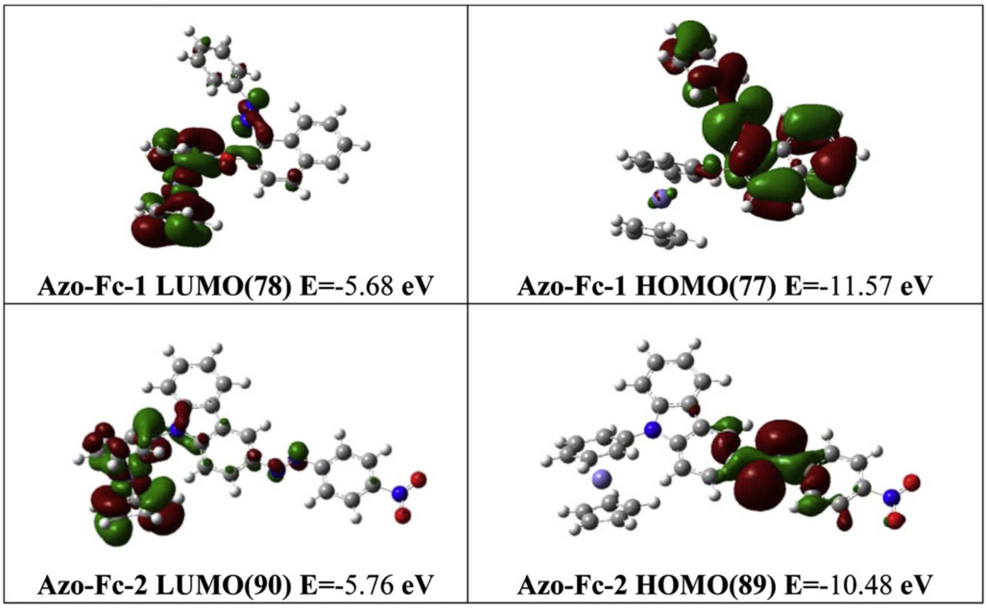


Fig. 5. Frontier molecular orbitals and energies of Azo-Fcs.

fluorescence emission of Azo-Fc caused by the π-π* transition of the cyclopentadiene moiety occurred. This result implies strong electron transfer from the ligand to the cyclopentadiene moiety. The quantum chemical calculations can explain this phenomenon (see Section 3.5).

3.5. *Quantum chemical calculations*

To gain insight into the electronic properties and geometries of Azo-Fc-1 and Azo-Fc-2, quantum chemical calculations were performed. Their geometric structure was optimized on the basis of DFT at the B3PW91/Lanl2dz level, and all structural optimizations and energy calculations were performed using the GAUSSIAN 09 program. The optimized structures and energies of the frontier molecular orbitals were obtained. The optimal structures of Azo-Fcs (Fig. 4) reveal that the azo framework contains two aryl rings and that the N=N linkage is nearly planar in the optimized structures of the compounds. This enables the π-electron conjugation to extend throughout the two aryl rings and N=N.

Fig. 5 shows the frontier orbitals of molecules. The calculations show that in their HOMO orbitals, the electron cloud delocalized over the −N=N− and aryl rings, while in their LUMO orbitals, the electron cloud delocalized over the cyclopentadienyliron cation and coordinated arene. This result suggests that electron transfer occurs from HOMO to LUMO in Azo-Fcs. Quantum chemical calculations indicate that Azo-Fc-2 showed the lower LUMO (−5.76 eV) and the higher HOMO (−10.48 eV).

Generally, the energy values of LUMO and HOMO and their energy gaps (the HOMO−LUMO energy) reflect the chemical activity of the molecule [22]. HOMO as an electron donor represents the ability to donate an electron, and LUMO as an electron acceptor represents the ability to obtain an electron. The smaller the LUMO and HOMO energy gaps, the easier it is for the HOMO electrons to be excited. The energies of the HOMO and LUMO for Azo-Fcs based on the optimized structure were computed. The HOMO−LUMO energy gaps followed the order Azo-Fc-2 (4.72 eV) < Azo-Fc-1 (5.89 eV). The result indicates that the HOMO−LUMO energy gap values decrease as the length of the π-conjugated system increases, a finding consistent with UV−vis absorption.

4. Conclusion

The synthesis, spectroscopic properties, and structures of two new cationic cyclopentadienyliron azo-complexes have been reported. The absorption spectra of these four molecules have been discussed. These Azo-Fc structures were confirmed by ^{1}H NMR, ^{13}H NMR, ESI-MS, and FT-IR spectroscopy. Azo-Fcs exhibited positive solvatochromic behaviors as determined by the investigation of four organic solvents of different degrees of polarity. Azo-Fcs showed good photostability. The molecular structures of Azo-Fcs were optimized on the basis of DFT at the B3PW91/Lanl2dz level, while the HOMO and LUMO levels of Azo-Fcs were deduced.

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Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.dyepig.2012.01.013.

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