

Synthesis and Characterizations of New Ferrocenyl Schiff Base with NLO Responses

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Abstract: A series of new stable (thermal and photochemical) ferrocenyl derivatives containing C=N bond and benzene ring in long conjugated chains have been synthesized and characterized by ¹HNMR(400MHz), IR, and elemental analysis. Pull-push ferrocenyl complexes that we have prepared have strong NLO responses identified by electronic absorption spectrum.

Keywords: Ferrocenyl, Schiff base, NLO, C=N.

Introduction

There is considerable interest in materials with NLO (nonlinear optics) properties in the past ten years^{1,2}. It has stated that the use of organometallic compounds with NLO has a wide fan of advantages³ that make them appropriate in the field of nonlinear optics. It is possible to be used as promising material because of stability of ferrocenyl complexes to heat and optics.

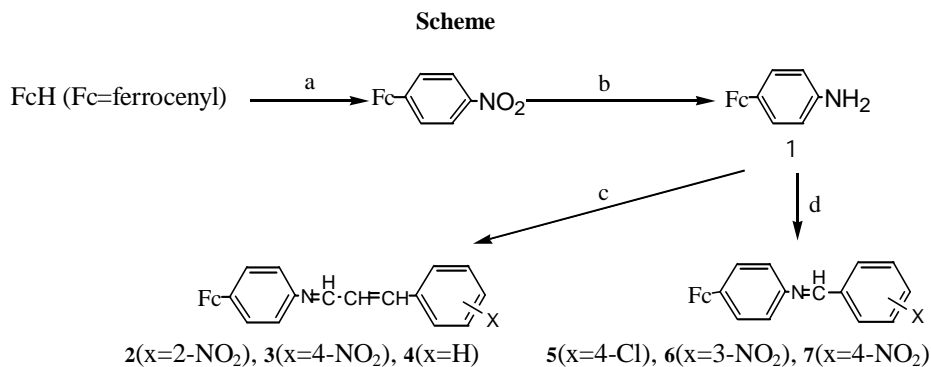
Recently, K.R.J. Thomas *et.al*⁴ have investigated new ferrocene based donor-acceptor complexes containing thiophene and furan in the conjugation chain. In these case, the importance of the push-pull structure skeleton has been stressed as one of the factors allowing for cooperative NLO properties.

We report here in the facile synthesis of novel push-pull ferrocenyl Schiff base containing benzene ring, C=N and C=C bond. We have obtained six new compounds containing a typical electron-donor moiety (ferrocene) and a electron-acceptor fragment (-NO₂, -Cl) without center of symmetry. C=N bond and benzene ring which are seemed as conjugated chains deliver electronic effects.

Experimental

The procedures of synthesis are listed in **scheme**. Compound **1** was obtained according to literature methods⁵. Aromatic aldehydes were obtained according to literature methods^{6,7}, too. Typical procedure for synthesis of **2**, **3**, **4**, **5**, **6** and **7**: 0.005mol *p*-ferrocenyl phenylamine was dissolved in 10 mL ethanol, many drops of acetic acid was added. Aromatic aldehyde (in 10 mL dried ethanol) was added dropwise during 10 min. The precipitate was formed in 5 min, then the mixture was continued to stir for 3 hr at

room temperature. The product was filtered, washed with 10 mL ethanol, dried in vacuum. The mp., yield, elemental analysis of products are listed in **Table 1**.



Reagents and conditions: a) *p*-NO₂-Ph-NH₂, HCl, NaNO₂, 0-5°C; b) Sn, HCl/EtOH, reflux; c) *x*-Ph-CH=CH-CHO, EtOH, r.t.; d) *x*-Ph-CHO, EtOH, r.t.

Table 1 The data of product 2, 3, 4, 5, 6 and 7

	Formula	mp. ^o C	yield%	Elemental analysis %			
2	C ₂₅ H ₂₀ FeN ₂ O ₂	198-200	98	Caclcd.	C68.82	H4.62	N6.42
				Found.	C68.94	H4.39	N6.53
3	C ₂₅ H ₂₀ FeN ₂ O ₂	219-221	98.5	Caclcd.	C68.82	H4.62	N6.42
				Found.	C68.59	H4.63	N6.40
4	C ₂₅ H ₂₁ FeN	172-174	97	Caclcd.	C76.72	H5.41	N3.58
				Found.	C76.68	H5.67	N3.53
5	C ₂₃ H ₁₈ ClFeN	202-204	98	Caclcd.	C69.10	H4.54	N3.51
				Found.	C68.87	H4.57	N3.53
6	C ₂₃ H ₁₈ FeN ₂ O ₂	134-136	96.5	Caclcd.	C67.32	H4.43	N6.83
				Found.	C67.18	H4.71	N6.93
7	C ₂₃ H ₁₈ FeN ₂ O ₂	244-246	99	Caclcd.	C67.32	H4.43	N6.83
				Found.	C66.98	H4.78	N6.83

Results and discussion

The reactions were carried out at room temperature because all products are stable conjugated system. Acetic acid was added as catalyst in order to make the reactions easy.

The Chemical shift⁸ of the five protons on the unsubstituted cyclopentadienyl ring of ferrocenyl is observed at 4.05-4.06. The protons signal of substituted cyclopentadienyl ring appears at 4.33-4.36(2H) and 4.66-4.68(2H), which have considerable downfield chemical shifts. And the coupling constant of *trans*- isomer

equals 14-18Hz, it is predominant in molecule. The *trans*- isomers may have nonlinear responses². No attempt was made to separate the isomer. But the isomeric mixtures were mainly converted into *trans*- isomer by heating in toluene for 4 hr⁴.

The important IR⁸ absorption of the compounds **2**, **3**, **4**, **5**, **6** and **7** at 1604.9, 1597.9, 1618.0, 1620.0, 1635.0, 1589.7cm⁻¹, respectively, are assigned to ν (-C=N-).

Table 2 Electronic absorption data for **2-7***

compound	λ max(nm)	ϵ max(M ⁻¹ cm ⁻¹ ×10 ³)
2	377	18.32
	485	4.48
3	359	10.00
	481	2.44
4	361	16.44
	461	2.92
5	367	13.00
	465	3.24
6	359	17.56
	458	2.72
7	352	15.92
	454	2.64

*Data measured for dichloromethane solution of concentration 5×10⁻⁵M.

Table 3 Solvatochromic data for **2-7**

Sol.	Et ₂ O	MeCN	Me ₂ CO	THF	MeOH	CH ₂ Cl ₂	DMF	DMSO
2	356	362	364	366	373	377	382	427
	448	462	474	475	485	485	491	595
3	309	337	341	347	359	360	353	443
	437	454	466	470	476	481	477	599
4	330	338	349	359	360	361	366	488
	429	439	443	454	458	461	473	536
5	333	347	355	363	366	367	372	434
	423	429	443	449	463	465	449	538
6	320	329	344	351	355	359	358	406
	422	426	438	449	457	458	451	529
7	317	332	337	340	350	352	358	426
	431	438	447	448	455	454	461	537

The solution electronic absorption spectral studies of compounds are designed to possess NLO properties. Firstly, it is necessary to know the transparency region. Secondly, the solvatochromic behavior of the products is generally considered as indicative of high molecular hyperpolarisability and potential NLO properties. The electronic absorption data and solvatochromic data were listed in **Table 2** and **Table 3**. The compounds **2-7** have absorption data in transparency region listed in **Table 2**. In **Table 3**, prominent solvatochromic effects were observed, too. All these data indicate the compounds have NLO response.

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References and notes

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8. **Compound 2**: IR (KBr) cm^{-1} : 3099w, 1604.9s, 1524.7vs, 846.23s, 822.35m. ^1H NMR (CDCl_3 , 400MHz) δ ppm: 4.06(s, 5H, C_5H_5), 4.35(s, 2H, C_5H_4), 4.67(s, 2H, C_5H_4), 7.13(t, 1H, CH=CH), 7.6(d, 1H, CH=CH), 7.19(d, 2H, Fc- C_6H_4 -), 7.51(d, 2H, Fc- C_6H_4 -), 7.54(t, 1H, C_6H_4 - NO_2), 7.67(t, 1H, C_6H_4 - NO_2), 7.71(d, 1H, C_6H_4 - NO_2), 8.04(d, 1H, C_6H_4 - NO_2), 8.42(d, 1H, CH=N).
Compound 3: IR (KBr) cm^{-1} : 3079w, 1597.9s, 1512.8vs, 856.2s, 820.0s. ^1H NMR(CDCl_3 , 400MHz) δ ppm: 4.05(s, 5H, C_5H_5), 4.36(s, 2H, C_5H_4), 4.66(s, 2H, C_5H_4), 7.21(t, 1H, CH=CH), 7.24(d, 1H, CH=CH), 7.26(d, 2H, Fc- C_6H_4 -), 7.51(d, 2H, Fc- C_6H_4 -), 7.70(d, 2H, C_6H_4 - NO_2), 8.27(d, 2H, C_6H_4 - NO_2), 8.43(d, 1H, CH=N).
Compound 4: IR (KBr) cm^{-1} : 3091m, 1618.0vs, 1518.1vs, 844.7s, 815.44m. ^1H NMR(CDCl_3 , 400MHz) δ ppm: 4.06(s, 5H, C_5H_5), 4.33(s, 2H, C_5H_4), 4.67(s, 2H, C_5H_4), 7.17(t, 1H, C_6H_5), 7.19(t, 2H, C_6H_5), 7.36(d, 1H, CH=CH), 7.40(t, 1H, CH=CH), 7.40(d, 2H, Fc- C_6H_4 -), 7.49(d, 2H, Fc- C_6H_4 -), 7.58(d, 2H, C_6H_5), 8.36(d, 1H, CH=N).
Compound 5: IR (KBr) cm^{-1} : 3087w, 1620.0m, 846.6s, 818.0m. ^1H NMR(CDCl_3 , 400MHz) δ ppm: 4.05(s, 5H, C_5H_5), 4.53(s, 2H, C_5H_4), 4.66(s, 2H, C_5H_4), 7.20(d, 2H, Fc- C_6H_4 -), 7.52(d, 2H, Fc- C_6H_4 -), 7.47(d, 2H, C_6H_4 -Cl), 7.86(d, 2H, C_6H_4 -Cl), 8.50(s, 1H, CH=N).
Compound 6: IR (KBr) cm^{-1} : 3079m, 1635.0m, 849.5s, 816.3m. ^1H NMR(CDCl_3 , 400MHz) δ ppm: 4.06(s, 5H, C_5H_5), 4.35(s, 2H, C_5H_4), 4.68(s, 2H, C_5H_4), 7.22(d, 2H, Fc- C_6H_4 -), 7.53(d, 2H, Fc- C_6H_4 -), 7.67(t, 1H, C_6H_4 - NO_2), 8.27(d, 1H, C_6H_4 - NO_2), 8.32(d, 1H, C_6H_4 - NO_2), 8.62(s, 1H, CH=N), 8.76(s, 1H, C_6H_4 - NO_2).
Compound 7: IR (KBr) cm^{-1} : 3079s, 1589.7s, 858.6s, 848.8s. ^1H NMR(CDCl_3 , 400MHz) δ ppm: 4.06(s, 5H, C_5H_5), 4.36(s, 2H, C_5H_4), 4.68(s, 2H, C_5H_4), 7.24(d, 2H, Fc- C_6H_4 -), 7.53(d, 2H, Fc- C_6H_4 -), 8.10(d, 2H, C_6H_4 - NO_2), 8.33(d, 2H, C_6H_4 - NO_2), 8.63(s, 1H, CH=N).

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