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Synthesis, Spectroscopy of New Push-Pull Ferrocene Complexes Containing Different Conjugation Bridge Between Ferrocenyl Donor and Pyridinium Acceptor

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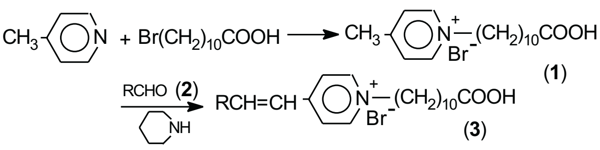
New materials with large optical non-linearities are of considerable interest, due to the variety of application such as optical information processing, optical computing and telecommunications [1–3]. Much effort was devoted to the synthesis of organic materials with large second-order optical nonlinearities. It revealed that molecular structure with both large differences between ground state and excited state dipole moments and large transition dipole moments would have large second-order optical non-linearities [4–7]. Molecules that possess π-donor acceptor interactions suitably fulfil these requirements. In contrast to the extensive study of organic materials with non-linear optical (NLO) properties, organometallic compounds have received less attention. Few ferrocenyl compounds for NLO properties have been examined [8–10].

We report a kind of novel ferrocene derivatives, which exhibit potential optical non-linearities. In these compounds ferrocenyl moiety is strong donor and pyridinium moiety can provide low-lying π* acceptor orbital. The previous work had proved that ferrocenyl ethylene pyridinium compounds had excellent NLO properties [11]. We initiated the research to study the influence of enlarging conjugation system to the NLO properties. Detailed solvatochromic and electrochemical researches have been performed on these organometallic compounds to assess the π-donor acceptor interactions. The synthesis procedure is shown in Scheme 1.

Scheme 1



R = Fc(**3a**), p-FcC$_6$H$_4$-(**3b**), FcC≡C-(**3c**), FcCH=CH-(**3d**); Fc = Ferrocenyl

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All commercially available reagents were purchased from market. ^{1}H NMR spectra were recorded in DMSO-d$_6$ solution using TMS as an internal standard on a Bruker DRX-200 instrument (Bruke Co. Ltd). Mass spectra were recorded by a ZAB-HS (VG Co. Ltd.) mass spectrometer by fast atom bombardment (FAB, MASPEC II data base). FTIR were measured by a Nicolet Avatar 360 FTIR spectrometer with potassium bromide windows and the elemental analyses were performed on a Carlo-Erba 1106 elemental analyzer. Melting points are uncorrected. **2b, 2c** and **2d** were prepared according to [12–14].

1-(10-Carboxydecyl)-4-methyl pyridinium bromide (1): A mixture of 4-methyl pyridine (0.93 g, 10 mmol), 11-bromoundecanoic acid (2.65 g, 10 mmol) and 5 mL ethanol was refluxed for 8 h. The solvent was removed *in vacuo*. The white solid precipitate was washed with ether and recrystallized from alcohol to give white crystals **1,** 2.91 g, yield 81%, m.p. 154°C (Lit m.p. 153°C) [15].

General procedure of synthesizing (**3**): A mixture of 1 mmol **1** with 1 mmol **2** in 5 mL methanol in the presence of a 2 drops of piperidine was stirred at room temperature overnight under argon. The methanol was removed under reduced pressure. The residue was chromatographed on silica gel with ether separated **2**. Further elution with acetone-methanol (5:1, v/v) afforded the purple product **3**. The results are listed below.

1-(10-Carboxydecyl)-4-(2-ferrocenyl-1-ethenyl) pyridinium bromide (3a): Yield 85%, m.p. 170°C (dec.). ^{1}H NMR (DMSO-d$_6$, 200 MHz), δ ppm, 8.81 (d, J = 6.4, 2H, C*H*N); 8.06 (d, J = 6.4, 2H, C*H*CHN); 7.89 (d, J = 16.0, 1H, (η-C$_5$H$_4$)C*H*); 6.96 (d, J = 16.0, 1H, (η-C$_5$H$_4$)CHC*H*); 4.73, 4.59 (each s, 2H, η-C$_5$H$_4$); 4.20 (s, 5H, η-C$_5$H$_5$); 4.41 (t, 2H, C$_5$H$_4$NC*H$_2$*); 1.0–2.2 (m, 18H). Anal. Calcd. for C$_{28}$H$_{36}$BrFeNO$_2$: C, 60.67; H, 6.55; N, 2.53. Found: C, 60.42; H, 6.12; N, 2.32. IR (KBr) cm^{-1} 2919s, 2848s (ν_{C-H}), 1718s ($\nu_{C=O}$), 1642s ($\nu_{C=N}$), 1613vs ($\nu_{C=C}$), 1518m, 1470m, 1102w, 814w (ferrocenyl group). MS (FAB, m/z): 474, (M-Br)$^+$.

1-(10-Carboxydecyl)-4-[2-(*p*-ferrocenylphenyl)-1-ethenyl]pyridinium bromide (3b): Yield 70%, m.p. 200°C (dec.). ^{1}H NMR (DMSO-d$_6$, 200 MHz), δ ppm, 8.94 (d, J = 6.0, 2H, C*H*N); 8.23 (d, J = 5.8, 2H, C*H*CHN); 8.02 (d, J = 16.2, 1H, (η-C$_5$H$_4$)C*H*); 7.51 (d, J = 16.2, 1H, (η-C$_5$H$_4$)CHC*H*); 7.67 (s, 4H, Fc-C$_6$*H$_4$*); 4.91, 4.49 (each s, 2H, η-C$_5$H$_4$); 4.05 (s, 5H,η-C$_5$H$_5$); 4.45 (s, 2H, C$_5$H$_4$NC*H$_2$*), 1.0–2.2 (m, 18H). Anal. Calcd. for C$_{34}$H$_{40}$BrFeNO$_2$: C, 63.86; H, 6.30; N, 2.19. Found: C, 63.58; H, 6.59; N, 2.32. IR (KBr) cm^{-1} 2919s, 2850s (ν_{C-H}) 1725s ($\nu_{C=O}$), 1640s ($\nu_{C=N}$), 1620vs ($\nu_{C=C}$), 1525m, 1468m, 1105w, 819w (ferrocenyl group). MS (FAB, m/z): 550 (M-Br)$^+$.

1-(10-Carboxydecyl)-4-[2-(2-ferrocenyl-1-ethynyl)-1-ethenyl]pyridinium bromide (3c): Yield 82%, m.p. 140°C (dec.). ^{1}H NMR (DMSO-d$_6$, 200 MHz,), δ ppm, 8.96 (d, J = 6.2, 2H, C*H*N); 8.02 (d, J = 5.82, 2H, C*H*CHN); 7.25 (m, 2H, C*H*C*H*C$_5$H$_4$N); 4.63, 4.52 (each s, 2H, η-C$_5$H$_4$); 4.30 (s, 5H, η-C$_5$H$_5$); 4.48 (s, 2H, C$_5$H$_4$NC*H$_2$*); 1.0–2.2 (m, 18H). Anal. Calcd. for C$_{30}$H$_{36}$BrFeNO$_2$: C, 62.30; H, 6.27; N, 2.42. Found: C, 62.95; H, 6.43; N, 2.57. IR (KBr) cm^{-1} 2921s, 2851s (ν_{C-H}), 1712s

($\nu_{C=O}$), 1636s ($\nu_{C=N}$), 1600vs ($\nu_{C=C}$), 1512m, 1467m, 1107m, 821m (ferrocenyl group). MS (FAB, m/z): 498 $(M-Br)^+$.

1-(10-Carboxydecyl)-4-[2-(2-ferrocenyl-1-thenyl)-1-ethenyl]pyridinium bromide (3d): Yield 83%, m.p. 150°C (dec.). ^{1}H NMR (DMSO-d_6, 200 MHz,) δ ppm, 8.84 (d, J = 5.4, 2H, C*H*N); 8.08 (d, J = 5.4, 2H, C*H*CHN); 7.75 (m, 1H); 6.98 (d, J = 15.4, 1H), 6.77 (m, 2H); 4.68, 4.50 (each s, 2H, η-C_5H_4); 4.18 (s, 5H, η-C_5H_5); 4.44 (s, 2H, $C_5H_4NCH_2$); 1.0–2.2 (m, 18H). Anal. Calcd. for $C_{30}H_{38}BrFeNO_2$: C, 62.08; H, 6.60; N, 2.41. Found: C, 61.73; H, 6.80; N, 2.53.IR (KBr) cm^{-1} 2919s, 2850s (ν_{C-H}), 1717s ($\nu_{C=O}$), 1641s ($\nu_{C=N}$), 1598vs ($\nu_{C=C}$) 1511m, 1467m, 1105w, 816w (ferrocenyl group). MS (FAB, m/z): 500 $(M-Br)^+$.

The products are easy to obtain by condensation of ferrocenyl substituted aldehydes and **1** in the presence of piperidine. However, excess of piperidine will combine with material **1** and products, so it will reduce the yields of the products. Other organic or inorganic base, such as KOH, EtOK, Et_3N, cannot catalyze the reaction. The ferrocenyl derivatives were characterized by IR and ^{1}H NMR spectroscopy, FAB MS and elemental analyses. The results are in accord with the proposed formulation. All of the compounds exhibit ^{1}H NMR signals associated with the ferrocenyl fragments. The ethylene bridge signals appear as doublets with a coupling constant of *ca*. 16 Hz, in accord with the expected *trans* stereochemistry. The ferrocenyl groups give rise to three separate signals as expected for the unsubstituted C_5H_5 (C_p) ring giving a sharp singlet around 4.20 ppm. The mono substituted C_5H_4 (C_p) ring exhibits an unsymmetrical pair of triplets corresponding to the spectrum of an A_2B_2 system. These signals appear at low field of the unsubstituted C_5H_5 singlet, showing that all the four ring protons are deshielded by the pyridinium rings.

Electronic absorption spectra: The solvatochromic behavior of the sample is generally considered as indicative of high molecular hyperpolarizability and hence of potential bulk NLO properties [16]. Therefore, the solution electronic absorption spectral studies of compounds designed to possess NLO properties are important. As regards metal-organic compounds, relationship has been drawn between solvatochromism and metal to ligand charge transfer (MLCT) excitations [17]. The compound (*cis*)-[1-ferrocenyl-2-(4-nitrophenyl)ethylene] provides an example of a species, which displays marked solvatochromism and also a high powder second harmonic generation (SHG) [8]. In general, ferrocenyl compounds show two prominent bands. The band in the UV region is described to possess d-d character, while the visible band is believed to be due to MLCT excitation [7,9]. The electronic absorption spectra of the present complexes were recorded in dichloromethane and data are presented in Table 1. The solvatochromism of the complexes were investigated in detail in six solvents of differing dielectric properties and the data are presented in Table 2. Solvatochromism arises from dipolar interactions between solvent and solute molecules, so that the greatest changes in absorption spectra are observed between solvents of largely differing polarity. Higher bathochromic shift is observed in dichloromethane (except **3d**). A drastic change in the spectral pattern is noticed when the spectrum of **3d** is recorded in both dimethyl formamide and dimethyl sulfoxide, in which the MLCT band of **3d** is shifted to higher wavelength and located at around 650 nm, implying large resonance interactions between ferrocenyl and pyridinium *via* conjugation bridge [9].

Table 1. UV-visible excitation maximum for the ferrocenyl compounds[a].

Compounds	λ_{max} (nm)	ε ($cm^{-1} M^{-1} \times 10^3$)
3a	575	2.5
	373	10.7
3b	540	3.91
	393	17.9
3c	538	2.4
	382	7.9
	317	9.20
3d	581	6.90
	414	23.9

[a]Spectra measured for dichloromethane solutions of concentration 5×10^{-5} M.

Table 2. Solvatochromic data for the ferrocenyl compounds.

Solvent	**3a**		**3b**		**3c**			**3d**	
MeCN	552	363	506	379	516	363	318	553	398
Me_2CO	553	362	507	379	518	363	323	553	397
MeOH	558	364	512	383	524	364	323	559	401
CH_2Cl_2	575	373	540	393	538	382	317	581	414
DMF	548	380	513	381	509		317	651	359
DMSO	552	364	510	381	519		319	646	429

Electrochemistry: The electrochemical properties of the ferrocenyl compounds were investigated in dichloromethane solution by cyclic voltammetry and the results obtained are presented in Table 3. The E_f values of ferrocenyl derivatives are almost similar because they are analogues (except **3c**). Comparison of the oxidation potential of **3a** and **3c** shows 50 mV cathodic shift when ethynyl is added to the vinyl bridge. The ΔE_p values of the ferrocenyl compounds show that ferrocene oxidation in all the compounds may be termed as reversible or quasi-reversible.

Table 3. Cyclic voltammetric data[a].

Compound	E_f (mV)	ΔE_p (mV)
3a	600	100
3b	580	100
3c	550	70
3d	580	100

[a]Conditions: sample concentration, 10^{-3} M; electrolyte, NBu_4ClO_4 (0.1 M); solvent, dichloromethane; scan rate, 60 mV s^{-1}.

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