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Luminescence and Electrochemical Properties of Organostannoxane Coordination Polymer Based on Ferrocenyl-2-Cyano Carboxylate Ligand

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Organostannoxane-based multiredox assemblies containing ferrocenyl peripheries have been readily synthesized by a simple one-pot synthesis, with quantitative yields. The reaction of triorganotin oxides, $(n\text{BuSn})_2O$ with 2-cyano-3-ferrocenyl acrylic acid leads to the formation of $[(n\text{Bu}_3\text{SnOC(O)CNCHFc})_n]$ polymeric structure. FT-IR, NMR, UV-Vis and emission spectroscopic techniques were performed for the characterization of $[(n\text{Bu}_3\text{SnOC(O)CNCHFc})_n]$(Fc = $\eta^5C_5H_4$-Fe-$\eta^5C_5H_4$) polymeric structure. Electrochemical studies on these hybrid organotin/ferrocene systems reveal that most of them exhibit a single quasi-reversible oxidation peak.

Keywords: Ferrocene, Organostannoxane, Electrochemistry.

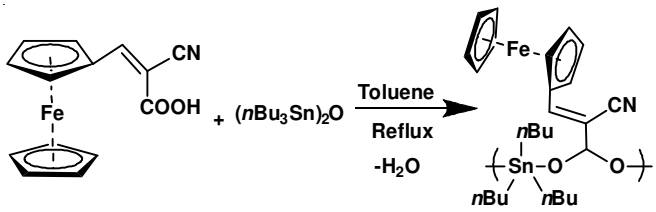
INTRODUCTION

Organometallic polymers have been attracting considerable attention in recent years with a view to generating new materials with interesting electrochemical, electronic and magnetic properties [1,2]. In particular, the ferrocene appended stannoxane frameworks are interest due to electrochemically inertness and do not interfere with the electrochemical properties of the peripheral ferrocene moiety [3-5]. Also, these molecules possess good electric, optical and magnetic properties [6-8]. On the other hand, cyanoacrylic acid based molecules used as a dyes in dye-sensitized solar cells [9]. In general, organotin compounds are traditionally synthesized by the use of high boiling solvents under reflux conditions and the structural diversity is depends on the reaction conditions [10,11]. In this study, we used simple one pot reaction between organotin $(n\text{Bu}_3\text{Sn})_2O$ precursor and 2-cyano-3-ferrocenyl acrylic acid which leads polymeric compound. The spectroscopic and electrochemical were investigated.

EXPERIMENTAL

All the starting materials and the products were found to be stable towards moisture and air. Solvents were freshly distilled over suitable drying agents. $(n\text{Bu}_3\text{Sn})_2O$ is commercially available and it is purchased from Alfa-Aesar. FcCH(CN)COOH was prepared based on literature procedure [9]. UV-visible spectra were obtained on a JASCO-V-670 spectrophotometer and emission spectra were obtained on a fluorescence spectrophotometer (HITACHI F7000). Infrared spectra were obtained using KBr disks on a SHIMADZU (4000-400 cm^{-1}) FT-IR spectrometer, ^1H and ^{13}C NMR spectra were recorded using a BRUKER-FT-NMR-400 MHZ spectrometer $CDCl_3$ solvent and tetramethylsilane as an internal standard. The electrochemical analysis was done by CH-instruments (CHI760E). In all electrochemical measurements, 0.1 M Bu_4NClO_4 (TBAP) was used as a supporting electrolyte. The working electrode was a glassy carbon and the counter electrode was a platinum wire. The operating reference electrode was a non-aqueous Ag/AgCl.

Synthesis of $[(n\text{Bu}_3\text{SnOC(O)CNCHFc})_n]$: A stoichiometric mixture of $(n\text{Bu}_3\text{Sn})_2O$ (0.6 mmol) and 2-cyano-3-ferrocenyl acrylic acid (1.2 mmol) were dissolved in dry toluene (50 mL) and the reaction mixture was heated to reflux and azeotropic removal of water was achieved *via* as Dean-Stark apparatus. After 6 h, the reaction mixture was filtered and evaporated to dryness. The corresponding residue was washed with petroleum ether and dried in air to give the polymeric compound (**Scheme-I**). Yield: 670 mg (96.5 %), m.p. 188 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ = (t, *J* = 7.42 Hz, 9H; butyl CH_3), 2.10 (m, 18H; butyl CH_2), 4.16 (s, 5H; ferrocenyl), 4.60, 2H; ferrocenyl), 4.91 ppm (t, *J* = 1.95 Hz, 2H; ferrocenyl); 8.09 (1H; -CH-C=C≡N) ppm. ^{13}C NMR data (400 MHz, $CDCl_3$): δ = 117.5 (C≡N), 206.06 (C=O), 129.40, 130.44, 136.94,158.88, 168.45, 98.52, 74.43, 73.75, 71.65, 70.50, 30.97 ppm. UV-visible (CH_3CN, nm): 264, 314, 380, 515. Fluorescence: (λ_{ex} = 314 nm, CH_3CN): 412 nm.



Scheme-I: Synthesis of ferrocenylorganostannoxane

RESULTS AND DISCUSSION

The polymeric compound [(nBu$_3$SnOC(O)CNCHFc)$_n$] was obtained in an analytically pure state was characterized by FT-IR, FT-NMR, UV-visible absorption and emission spectroscopy. The ^{1}H and ^{13}C NMR spectra of ferrocenylorganostannoxane is displayed in Figs. 1 and 2. The singlet from 4.16 ppm is due to cyclopentadienyl ring protons of ferrocene. The singlet at 4.60 and 4.91 ppm are assigned to substituted cyclopentadienyl ring protons. The singlet at 8.09 ppm is due to the (N≡C=CH) protons [12]. The two doublets at 7.42 ppm were observed due to the aliphatic methyl protons. The singlet at 8.58 ppm is due to aromatic proton. The ^{1}H NMR spectrum of ferrocenylorganostannoxane compared in litreature [13]. The ^{13}C NMR spectrum of the compound showed at 70.5 ppm is corresponding to the unsubstituted carbon of cyclopentadienyl ring in ferrocene moiety whereas substituted cyclopentadienyl ring carbon appears at 73.7 and 76.3 ppm, respectively. Aliphatic CH_3 appear 30.9 ppm and corresponding n-butyl (CH_2-CH_2-CH-) carbon appear at 128-137 ppm due to bulky organostannoxane.The nitrile group of (C≡N) appears at 117.5 ppm and carbonyl group appears at 207.0 ppm.

The IR spectra of compound shows strong peaks at 1743 cm^{-1} which is attributable to the $\nu_{asym}(COO)^-$ stretch. The corresponding $\nu_{sym}(COO)^-$ stretch is found 1368 cm^{-1}. In general, $\nu_{asym}(COO)^-$ for esters are lower than for free carboxylic acids; correspondingly the $\nu_{sym}(COO)^-$ for esters moves up in comparison to carboxylic acids [14]. The C-H bending of ferrocene ring appeared at 806 cm^{-1} and band due to Cp-Fe-Cp stretching vibration of ferrocenyl moiety occurs in the range 476-518 cm^{-1} (Fig. 3).

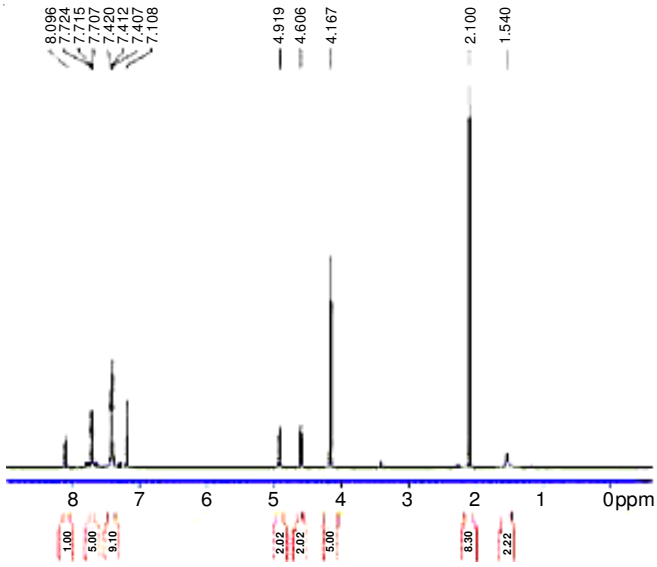


Fig. 1. ^{1}H NMR spectrum of ferrocenylorganostannoxane in $CDCl_3$

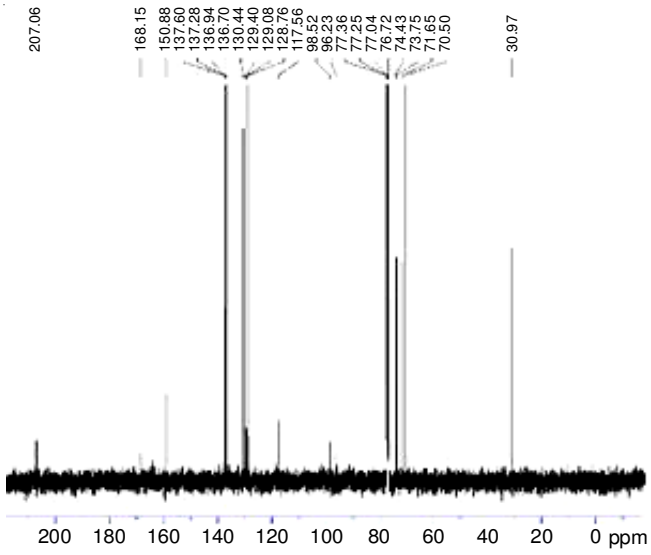


Fig. 2. ^{13}C NMR spectrum of ferrocenylorganostannoxane in $CDCl_3$

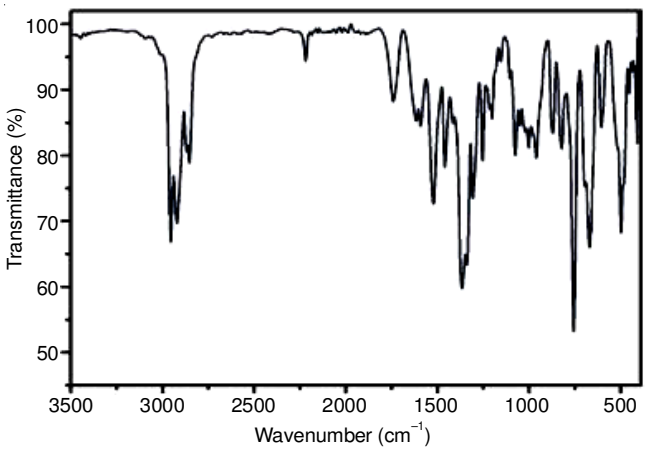


Fig. 3. FT-IR spectrum of ferrocenylorganostannoxane

The UV-visible absorption spectrum of a compound in CH_3CN (5×10^{-5} M) are stable with closely ferrocenyl chromophores in which they disclose two charge-transfer bands. The spectra control a prominent absorption bandwidth a restraint at 264 and 314, 380 nm respectively (Fig. 4), which bounce be deferring a high-energy ligand-centred π-π^* electronic transition. In initiation, a weaker absorption band in the visible region was observed at 515 nm respectively, which is to be found another localized excitation formed by two roughly degenerated transitions, and Fe(II) *d-d* transition or metal-ligand charge transfer (MLCT) process [15,16].

Fluorescence spectral studies: The fluorescence spectra of compound was investigated at room temperature in CH_3CN solution. The polymeric structure (Fig. 5) showed broad emission bands indicating charge transfer nature of the transitions. The polymeric structure exhibit one broad emissions at 412 nm with excitation wavelength value of 314 nm (Fig. 4). The emission of 412 nm wavelength is either due to MLCT or LMCT [17]. In addition, emission intensity of much stronger due to increased electronic energy population that take place through polymeric structure in spite of its considerable conjugated π-electron nature in the system [18].

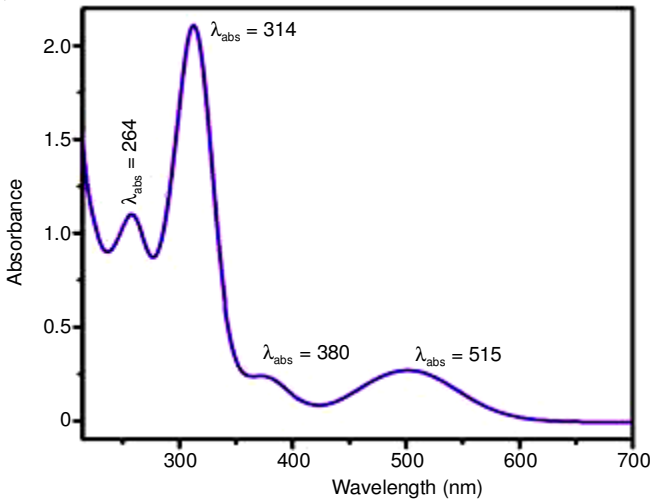


Fig. 4. UV-visible absorption spectrum of ferrocenylorganostannoxane in CH_3CN solution (5×10^{-5} M)

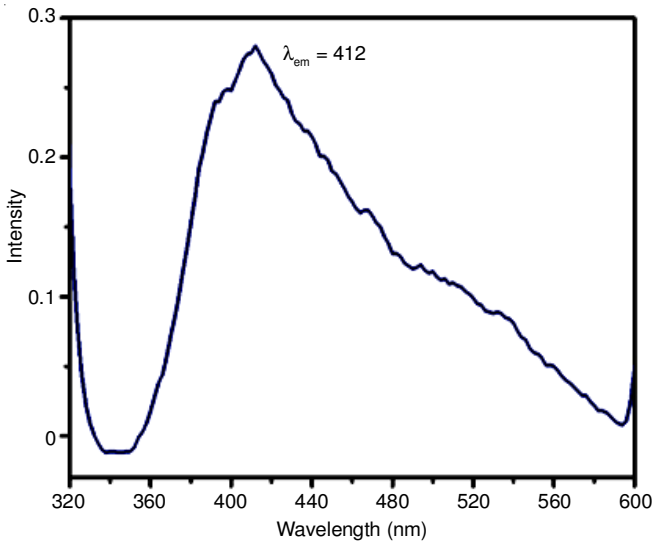


Fig. 5. Fluorescence emission and excitation spectra of ferrocenylorganostannoxane in CH_3CN solution (5×10^{-5} M)

Electrochemistry: The redox potential of ferrocene derivatives changes within wider limits. The redox potential depends on the electron-donating or electron withdrawing ability of the substituents. Thus, the redox properties can be rather strongly affected by altering the substituent nature [19]. The redox-potential for ferrocene-ferricenium couple ranges from 0 to 1 V. The single oxidation and reduction was observed with a [$E_{1/2} = (E_{pa} + E_{pc})/2$], $E_{1/2} = 0.65$ V (*vs.* Ag/AgCl, [(nBu$_3$SnOC(O)CNCHFc)$_n$] (Fig. 6). It clearly indicates that the redox potential of polymeric compound is in the range of ferrocene unit and the value is compared with literature compounds as shown in Table-1. The electrochemical property ($E_{1/2}$) of molecule mainly depends on the

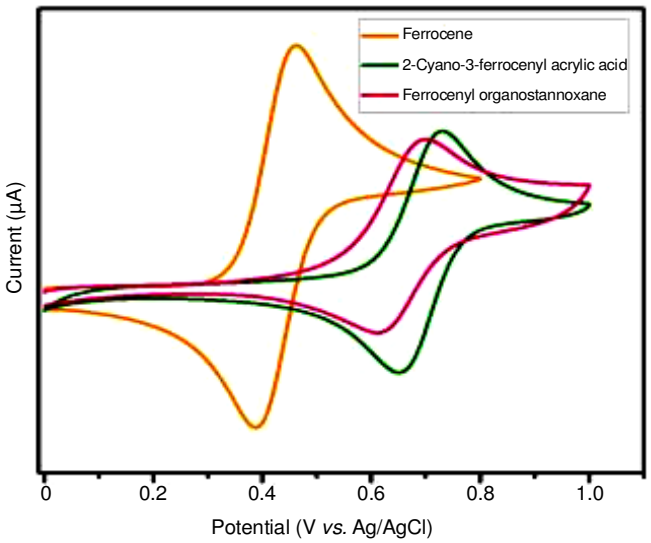


Fig. 6. Cyclic voltammogram obtained to 1-3 in the presence of 0.1 M TBAP in solution (0.1 V/s) in 10^{-3} M CH_3CN solution

substitution, which is suggested that electron withdrawing property of the carboxylate from cyclopentadienyl rings and the coordination bond between carboxylate and Sn atom, the effectiveness of cyclic voltammetry results from its capability for rapidly observing the redox behaviour over a wide potential range [20].

Conclusion

The organostannoxane polymer was synthesized based on 2-cyano-3-ferrocenyl acrylic acid. The compound was characterized by FT-IR, ^{1}H and ^{13}C NMR. It is further supported by absorbance spectra shows high-energy ligand-centred π-π^* electronic transition and metal ligand charge transfer. Fluorescence spectra has dominated emission intensity of much stronger due to acceptor group (-C≡N) in the polymeric unit. Electrochemical data that clearly indicate a mutual donor-acceptor electronic influence between the electron releasing to organometallic units. This enhanced donor-acceptor properties of the molecule can be utilized in dye synthesized solar cell (DSSC).

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TABLE-1
ELECTROCHEMICAL DATA FOR COMPOUNDS

S. No.	Compound	Ep_a (V)	Ep_c (V)	$E_{1/2}$ (V)	ΔE (mV)	Ref.
1	Ferrocene	0.459	0.389	0.42	70	[13]
2	2-Cyano-3-ferrocenyl acrylic acid	0.732	0.653	0.69	79	[9]
3	[(nBu$_3$SnOC(O)Fc)$_n$]	-	-	0.57	112	[13]
4	[(nBu$_3$SnOC(O)CNCHFc)$_n$]	0.691	0.613	0.65	78	This work

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