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, $(n\text{Bu}_3\text{Sn})_2\text{O}$ with 2-cyano-3-ferrocenyl acrylic acid leads to the formation of $[(n\text{Bu}_3\text{SnOC}(\text{O})\text{CNCHFc})_n]$ polymeric structure. FT-IR, NMR, UV-Vis and emission spectroscopic techniques were performed for the characterization of $[(n\text{Bu}_3\text{SnOC}(\text{O})\text{CNCHFc})_n](\text{Fc} = \eta^5\text{C}_5\text{H}_4\text{-Fe-}\eta^5\text{C}_5\text{H}_4)$ 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 $(n\text{Bu}_3\text{Sn})_2\text{O}$ 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. $(n\text{Bu}_3\text{Sn})_2\text{O}$ is commercially available and it is purchased from Alfa-Aesar. $\text{FcCH}(\text{CN})\text{COOH}$ 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 $(4000\text{-}400\text{ cm}^{-1})$ 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 $[(n\text{Bu}_3\text{SnOC}(\text{O})\text{CNCHFc})_n]$: A stoichiometric mixture of $(n\text{Bu}_3\text{Sn})_2\text{O}$ (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 °C; ^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; $-\text{CH}=\text{C}=\text{N}$) ppm. ^{13}C NMR data (400 MHz, CDCl_3): δ = 117.5 ($\text{C}\equiv\text{N}$), 206.06 ($\text{C}=\text{O}$), 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.

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

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

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 $[E_{1/2} = (E_{pa} + E_{pc})/2]$, $E_{1/2} = 0.65 \text{ V}$ (vs. Ag/AgCl , $[(n\text{Bu}_3\text{SnOC}(\text{O})\text{CNCHFc})_n]$ (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 MTBAP 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, ^1H and ^{13}C NMR. It is further supported by absorbance spectra shows high-energy ligand-centred $\pi-\pi^*$ electronic transition and metal ligand charge transfer. Fluorescence spectra has dominated emission intensity of much stronger due to acceptor group ($-\text{C}\equiv\text{N}$) in the polymeric unit. Electrochemical data that clearly indicate a mutual donor-acceptor electronic influence between the electron releasing to organo-metallic 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	E_{pa} (V)	E_{pc} (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	$[(n\text{Bu}_3\text{SnOC}(\text{O})\text{Fc})_n]$	-	-	0.57	112	[13]
4	$[(n\text{Bu}_3\text{SnOC}(\text{O})\text{CNCHFc})_n]$	0.691	0.613	0.65	78	This work

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