Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2019

# Electronic Supplementary Information

## Molecular Engineering, Synthesis and Photovoltaic Studies of Novel Highly Efficient Ru (II) Complex Incorporating Bulky TPA Ancillary Ligand for DSSCs: Donor Versus π-Spacers Effect

*Islam M. Abdellah[1] and Ahmed El-Shafei[2, *]*

[1]*Department of Chemistry, Faculty of Science, Aswan University, Aswan, 81528, Egypt*
[2] *Polymer and Color Chemistry Program, North Carolina State University, Raleigh, 27606, USA*

***Corresponding Author**: Ahmed El-Shafei, NC State University, Department of TECS, Raleigh, NC, USA, E-Mail: Ahmed_El-Shafei@ncsu.edu.

## 1. Device fabrication

### 1.1. Electrode Preparation and Device Fabrication

Fluorine-doped tin oxide (FTO) coated glasses (2.2 mm thickness, sheet resistance of 8 Ω/cm$^2$, TEC, Pilkington) were washed with detergent, water, acetone and ethanol, sequentially. After this FTO glass plates were immersed into a 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min and washed with water and ethanol. Thin layer (8-12 µm thick) of $TiO_2$ (Solaronix, Ti-Nanoxide T/SP) was deposited (active area, 0.18 cm$^2$) on transparent conducting glass by squeegee printing followed by drying at 350 °C for 10 min and curing at 500 °C for 30 min. Next, after drying the electrodes, scattering layer (5 µm thick) $TiO_2$ particles (Solaronix, Ti-Nanoxide R/SP) were printed onto the already deposited $TiO_2$ layer. The $TiO_2$ electrodes were heated under an air flow at 350 °C for 10 min, followed by heating at 500 °C for 30 min. After cooling to room temperature, the $TiO_2$ electrodes were treated with 40 mM aqueous solution of $TiCl_4$ at 70 °C for 30 min and then washed with water and ethanol. The electrodes were heated again at 500 °C for 30 min and left to cool to 80 °C before dipping them into the dye solution. The dye solutions (0.2 and 0.3 mM) were prepared in 10 mL 1:1:1 acetonitrile, DMSO and *tert*-butanol. Chenodeoxycholic acid (CDCA) was added at a concentration of 20 mM. The electrodes were

immersed in the dye solutions and then kept at 25 °C for 20 hours to adsorb the dye onto the $TiO_2$ surface.

For preparing the counter electrode, pre-cut TCO glasses were washed with water followed by 0.1M HCl in EtOH, and sonication in acetone bath for 10 min. These washed TCO were then dried at 400 °C for 15 min. Thin layer of Pt-paste (Solaronix, Platisol T/SP) on TCO was printed and the printed electrodes were then cured at 450 °C for 10 min. The dye sensitized $TiO_2$ electrodes were sandwiched with Pt counter electrodes and the electrolyte (Solaronix, Iodolyte HI-30) was then injected into the cell, while the two electrodes were held together with the clips.

## 2. Synthesis

### 2.1. Synthesis of 2, 2'-Bipyridinyl-4, 4'-dicarboxylic acid

The 2, 2'-Bipyridinyl-4, 4'-dicarboxylic acid was synthesized according to published procedure [3]. In a three neck round bottom flask 4,4'-Dimethyl-2,2'-bipyridine (3 g, 16.3 mmol) was gradually added to a stirred solution of sodium dichromate ($Na_2Cr_2O_7$) (10.9g, 36.5 mmol) in concentrated sulfuric acid ($H_2SO_4$) (93%, 45 ml) and stirred for 30 min at 75°C. After 30 min, the dark green reaction mixture was poured into cold water forming a light-yellow precipitate. The precipitate was then filtered under vacuum and dissolved in 10 % aq. Sodium hydroxide. The product was crystallized by slowly acidifying the solution with 10 % aq. hydrochloric acid at a pH of 2. The precipitation and acidification process were repeated three times to obtain the white chromium free precipitates of 2, 2'-Bipyridinyl-4, 4'-dicarboxylic acid (2.56g, 90%).

## 3. Spectral Data

### 3.1. High Resolution Mass Spectral data

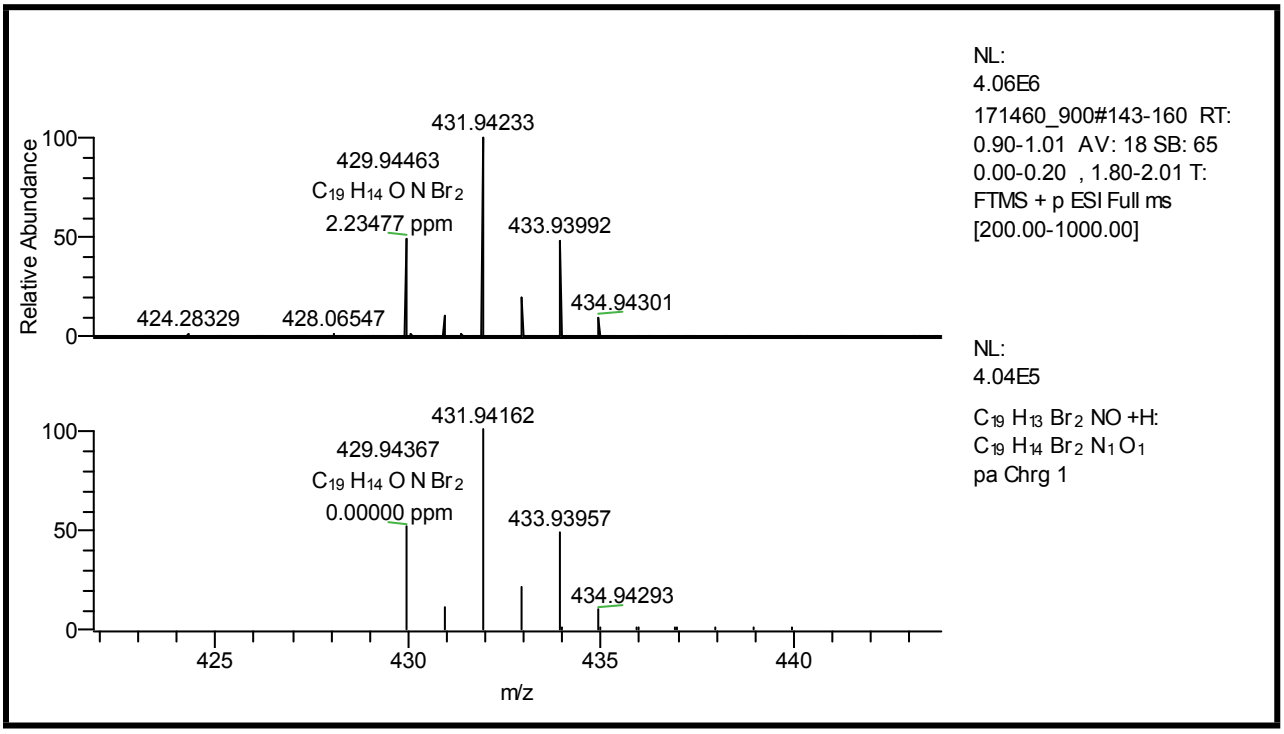


Fig. **S1.** Experimental and Theoretical Isotopic Distribution for **1**; **[M+H]**$^+$

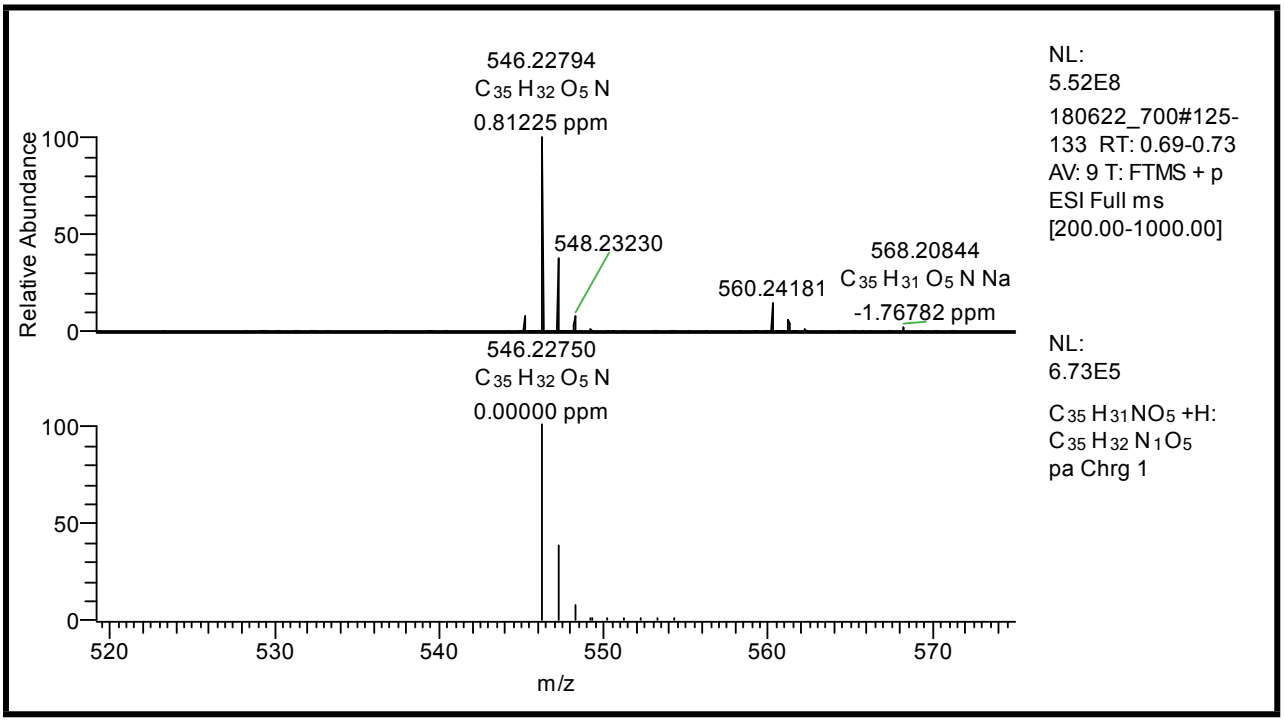


Fig. **S2.** Experimental and Theoretical Isotopic Distribution for **2**; **[M+H]**$^+$

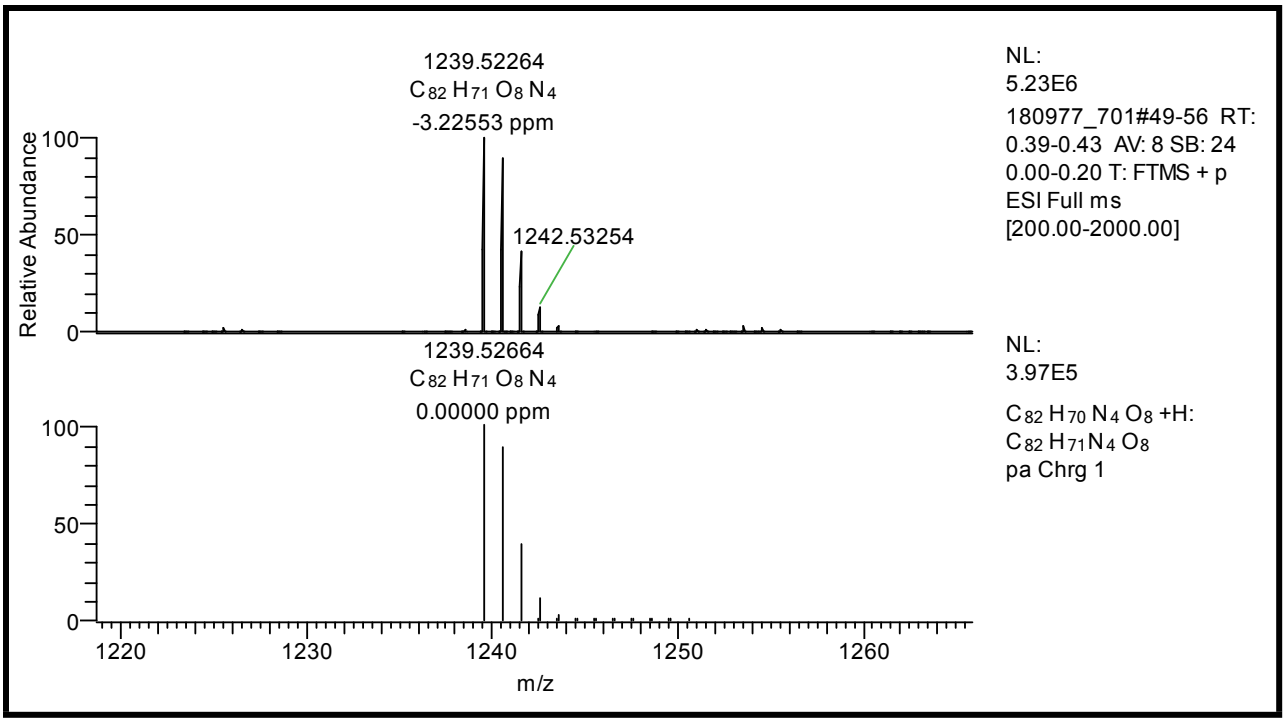


Fig. **S3.** Experimental and Theoretical Isotopic Distribution for **3**; **[M+H]**$^+$

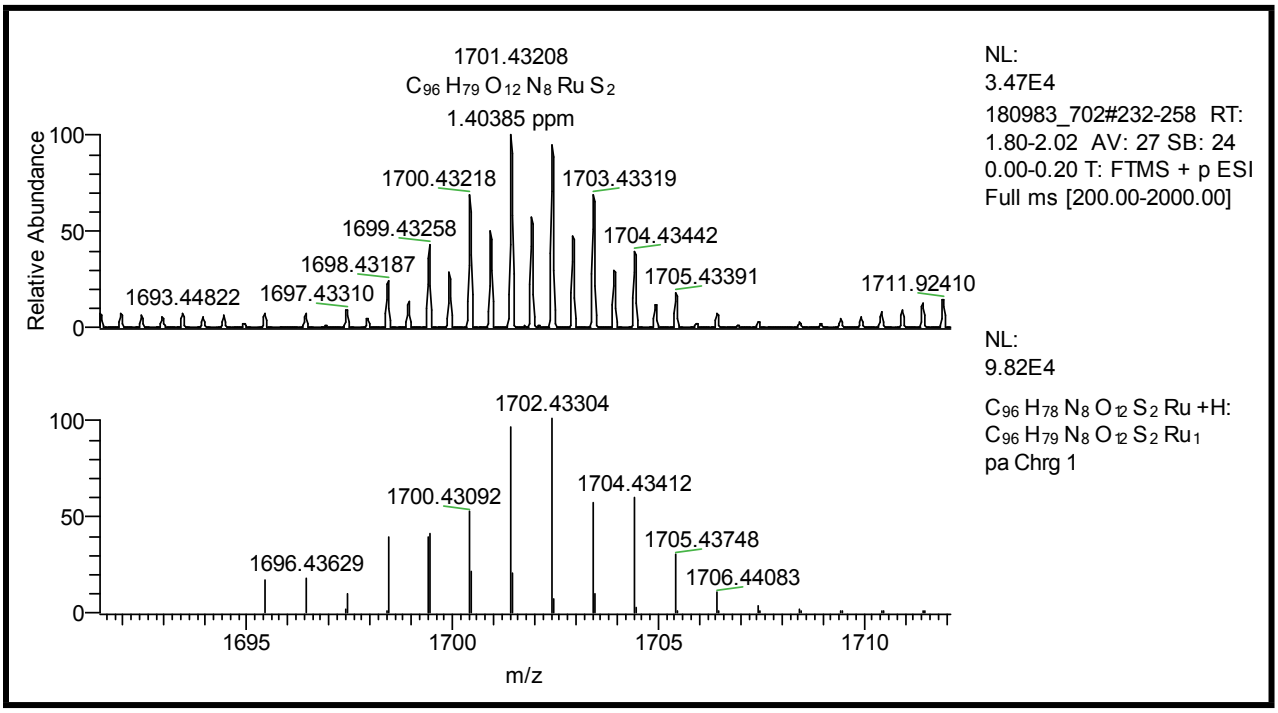


Fig. **S4.** Experimental and Theoretical Isotopic Distribution for **IA-7**; **[M+H]**$^+$

## 3.2. FT-IR Spectral Data

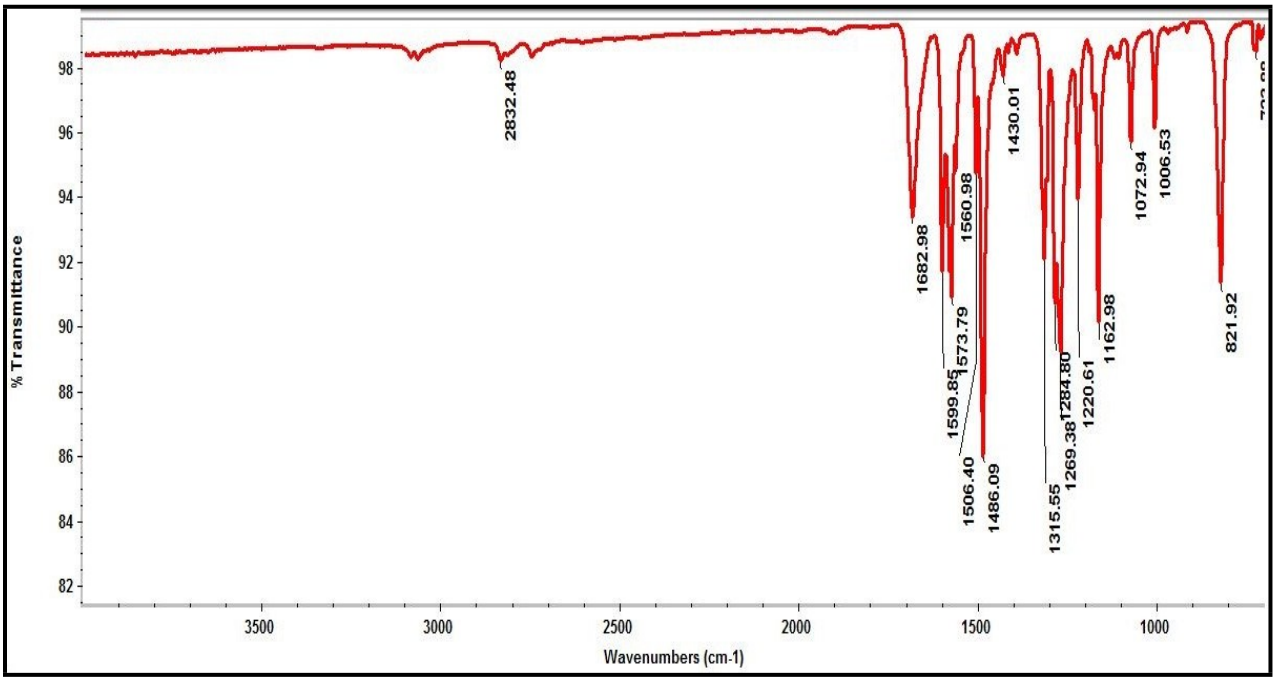


Fig. **S5.** FTIR spectra for compound **1**

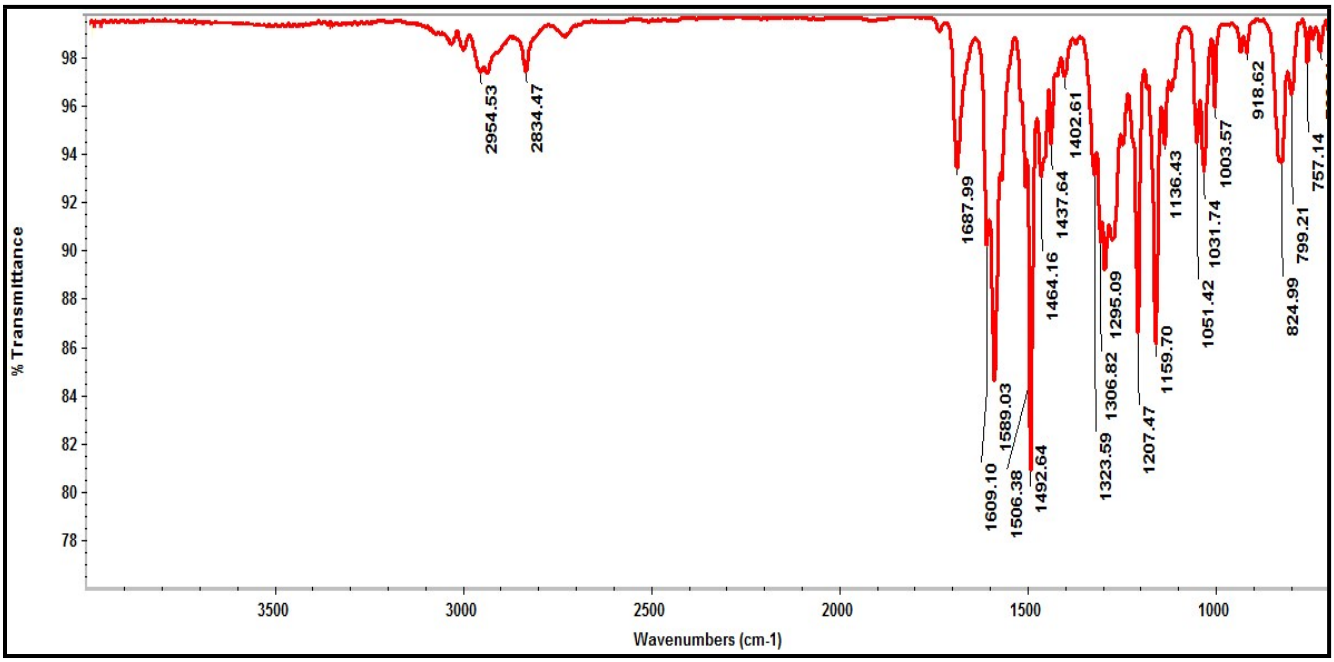


Fig. **S6.** FTIR spectra for compound **(2)**

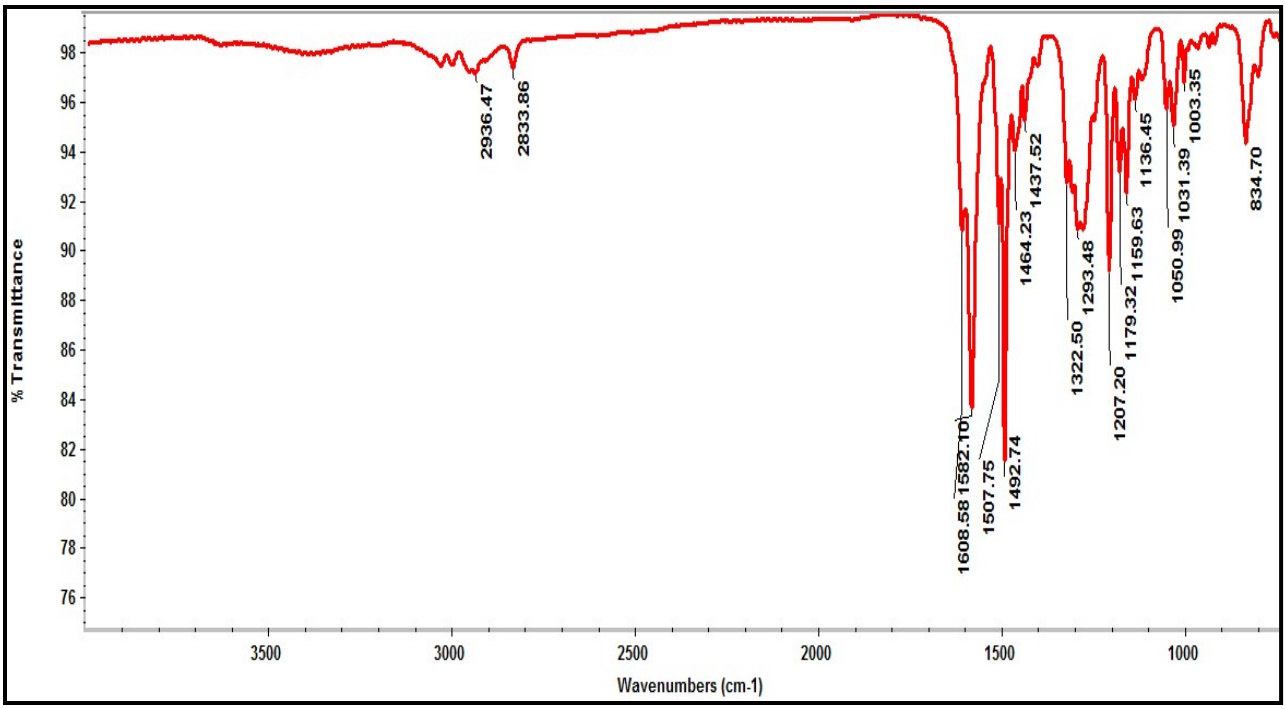


Fig. **S7.** FTIR spectra for compound **(3)**

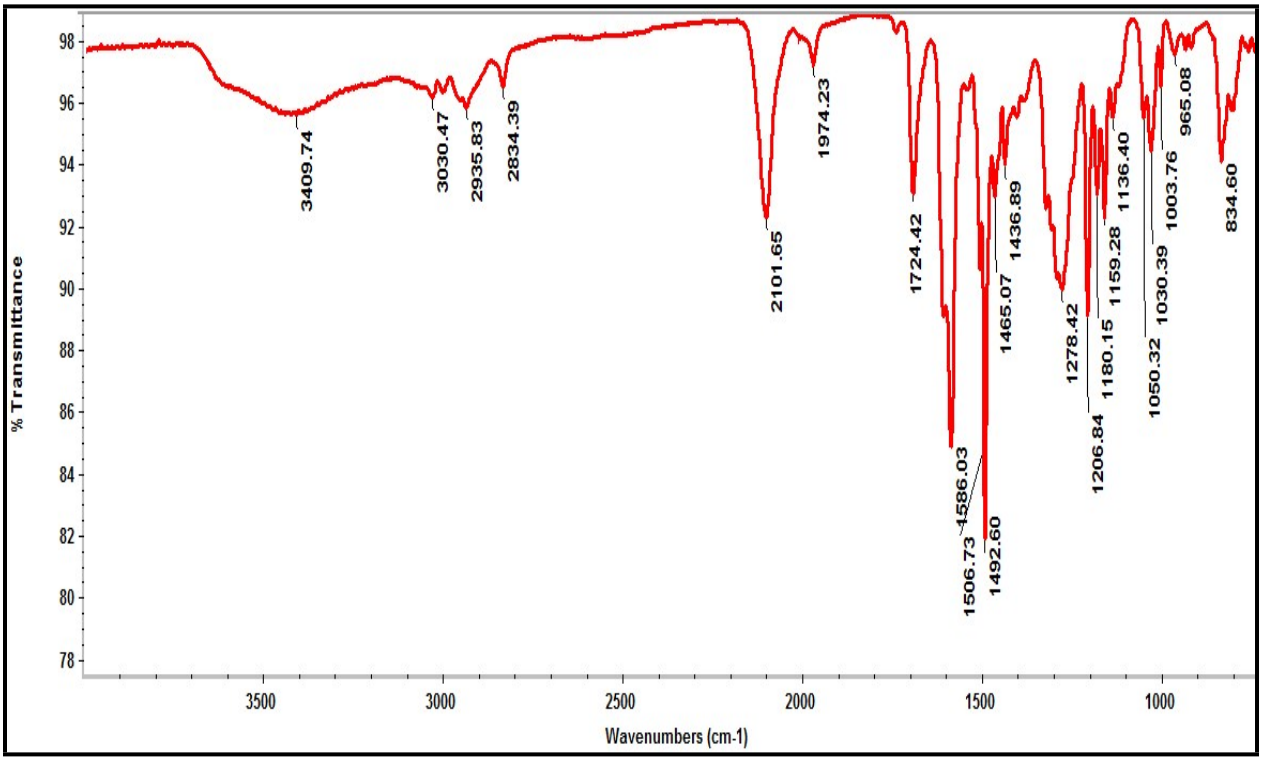


Fig. **S8.** FTIR spectra for dye **(IA-7)**

### 3.3. $^{1}$H-NMR Spectral Data

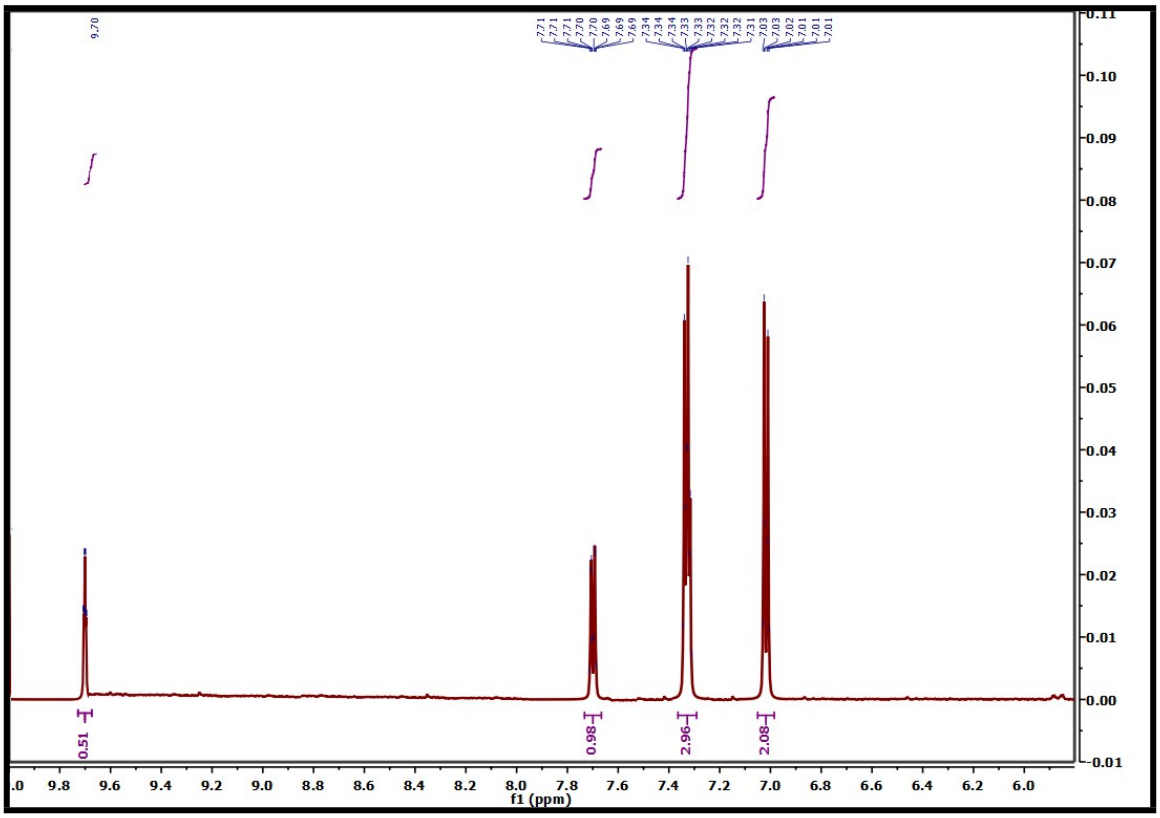


Fig. **S9.** $^{1}$H-NMR spectra of compound **1**

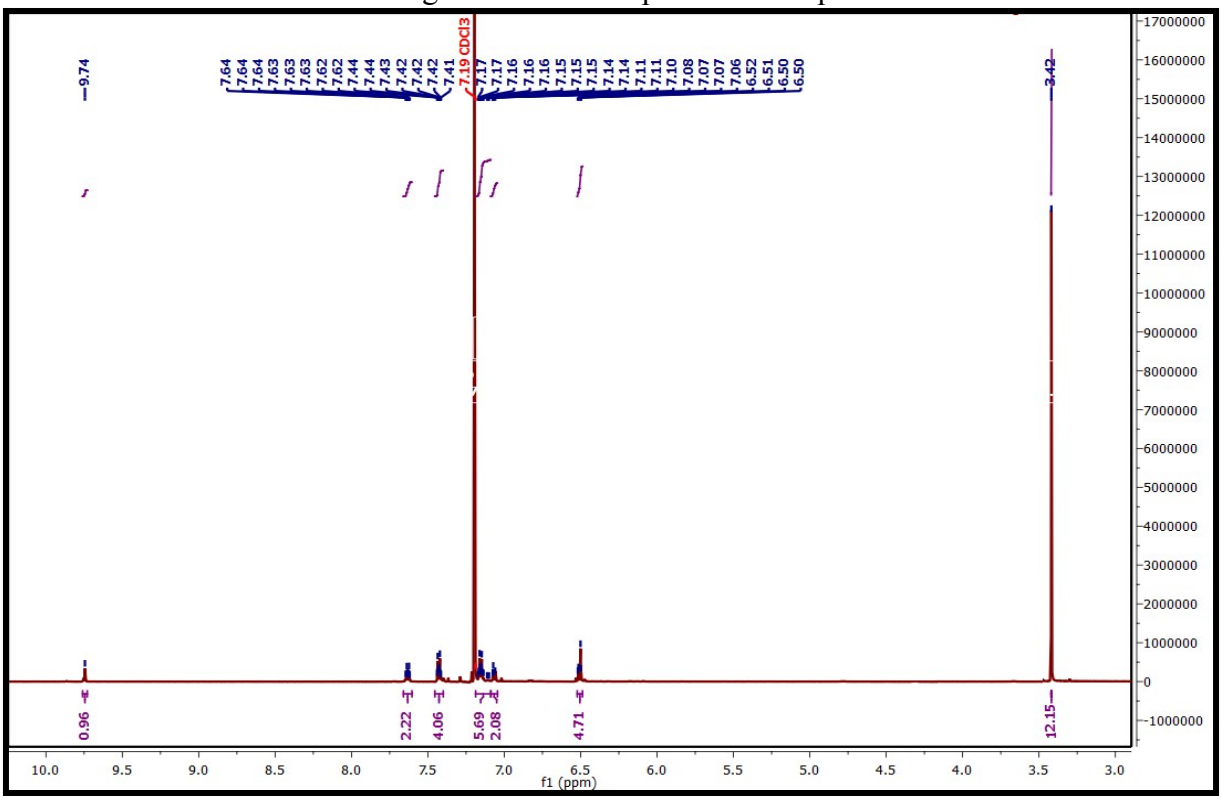


Fig. **S10.** $^{1}$H-NMR spectra of compound **2**

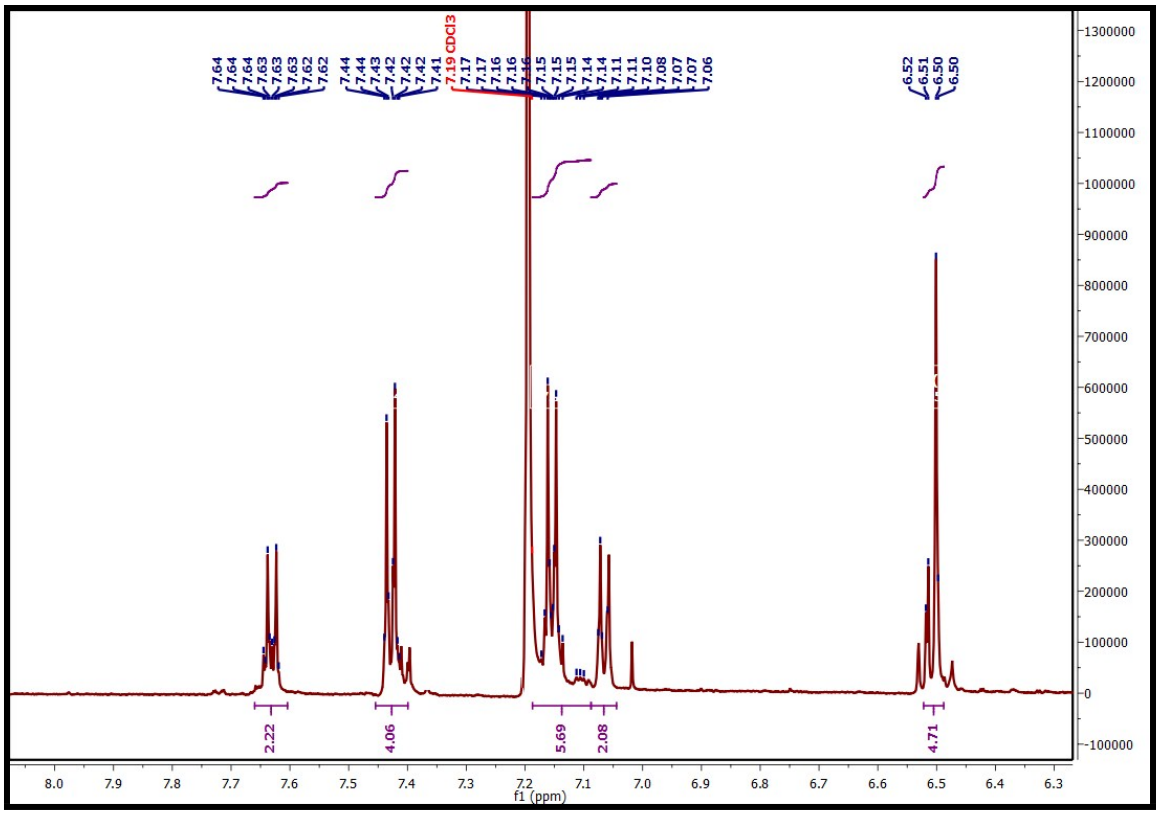


Fig. **S11**. [1]H-NMR spectra of compound **2 (Aromatic Zoom)**

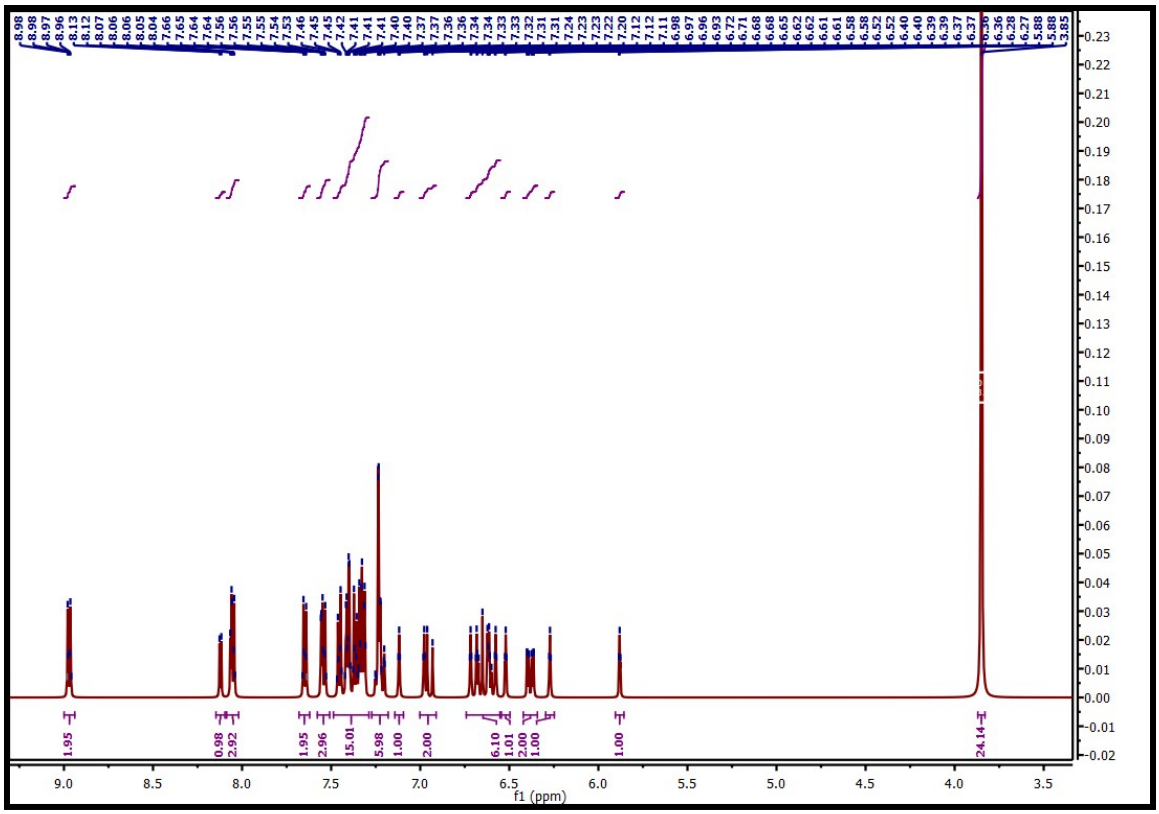


Fig. **S12**. [1]H-NMR spectra of compound **3**

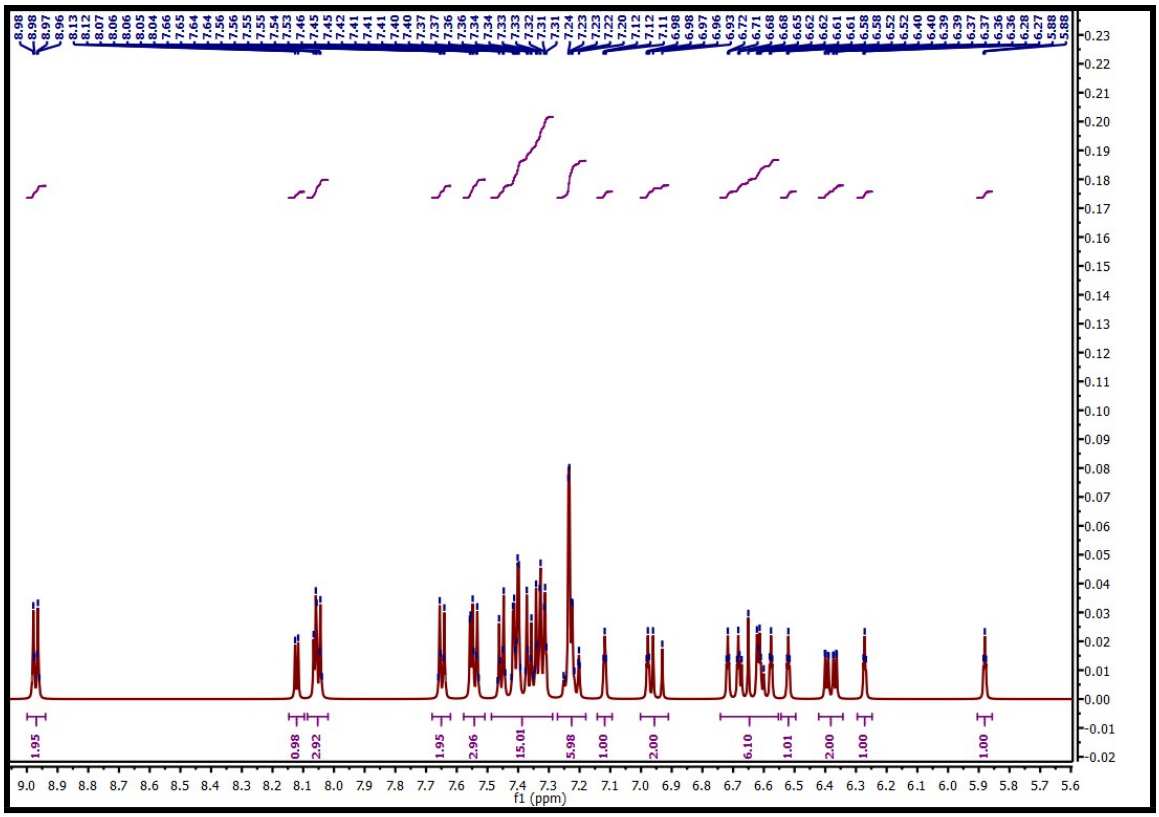


Fig. **S13.** [1]H-NMR spectra of compound **3 (Aromatic Zoom)**

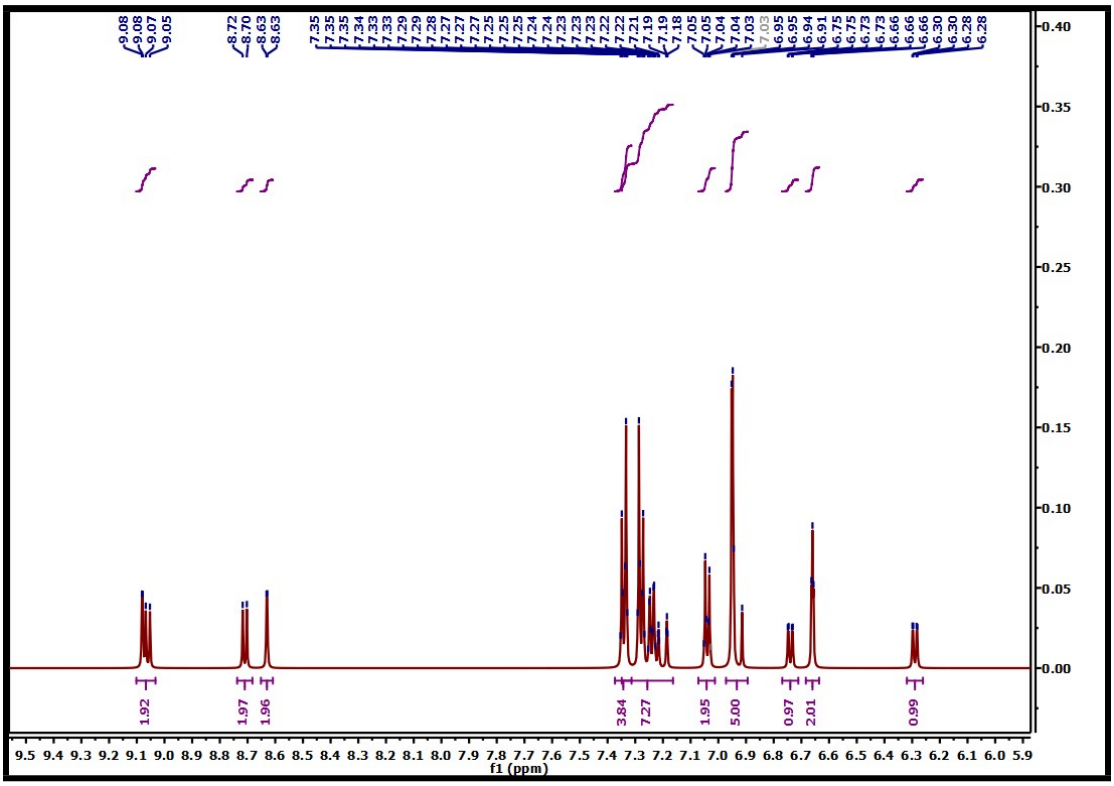


Fig. **S14.** [1]H-NMR spectra of dye **IA-7**

## 4. Cyclic Voltammograms for IA-7 complex

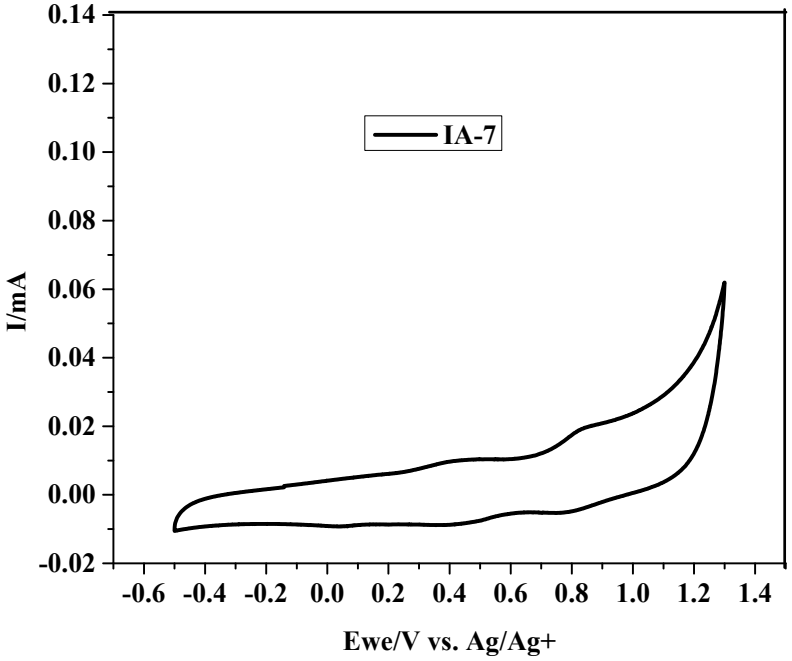


Fig. **S15.** Cyclic Voltammograms of **IA-7** complex