Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.


# Supporting Information

## 3D electropolymerized thin film based on a thiophene-functionalized Ru(II) complex: electrochemical and photoelectrochemical insights

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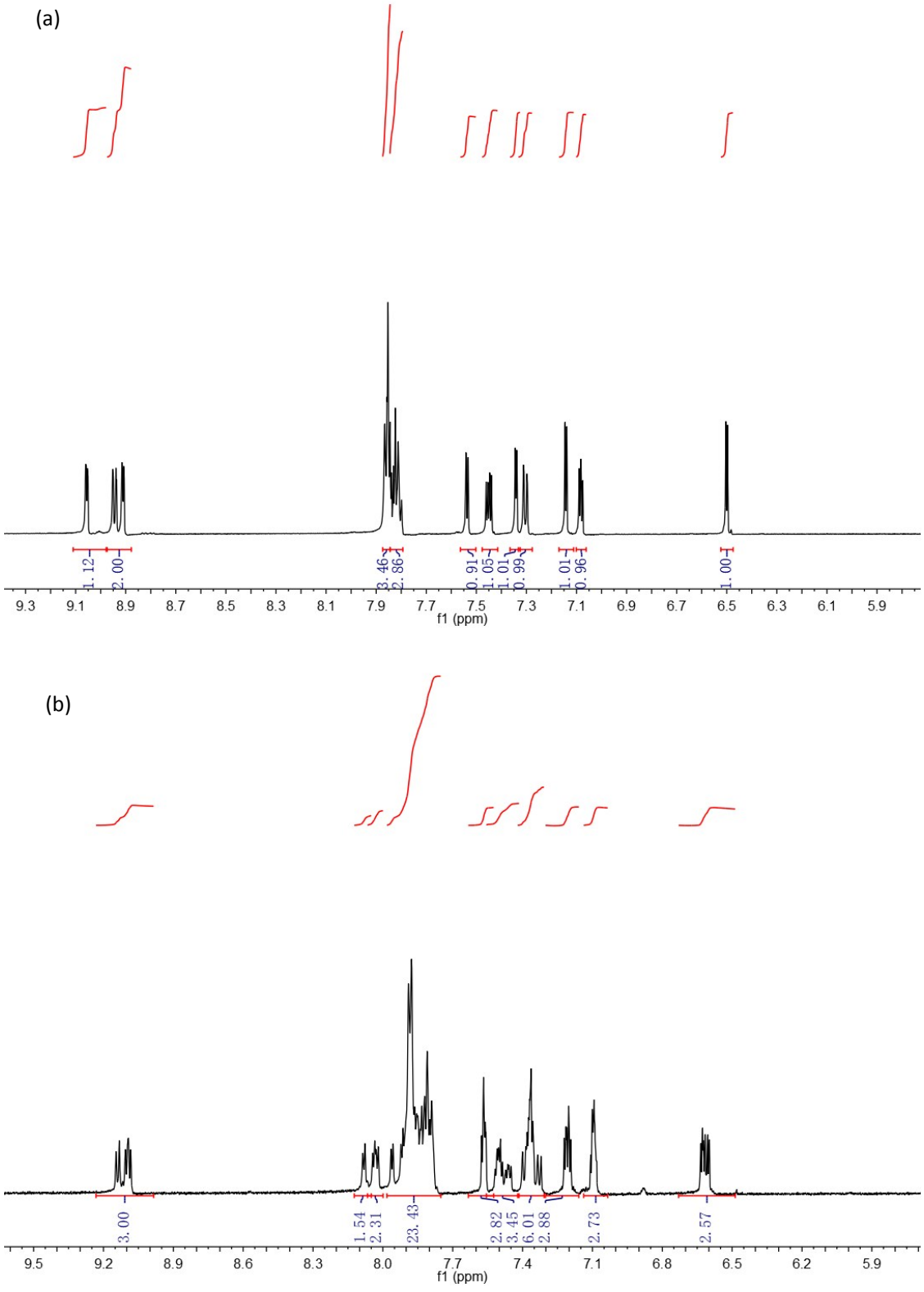


**Fig. S1** $^{1}$H NMR spectra of L (a) and $RuL_3(ClO_4)_2$ (b).

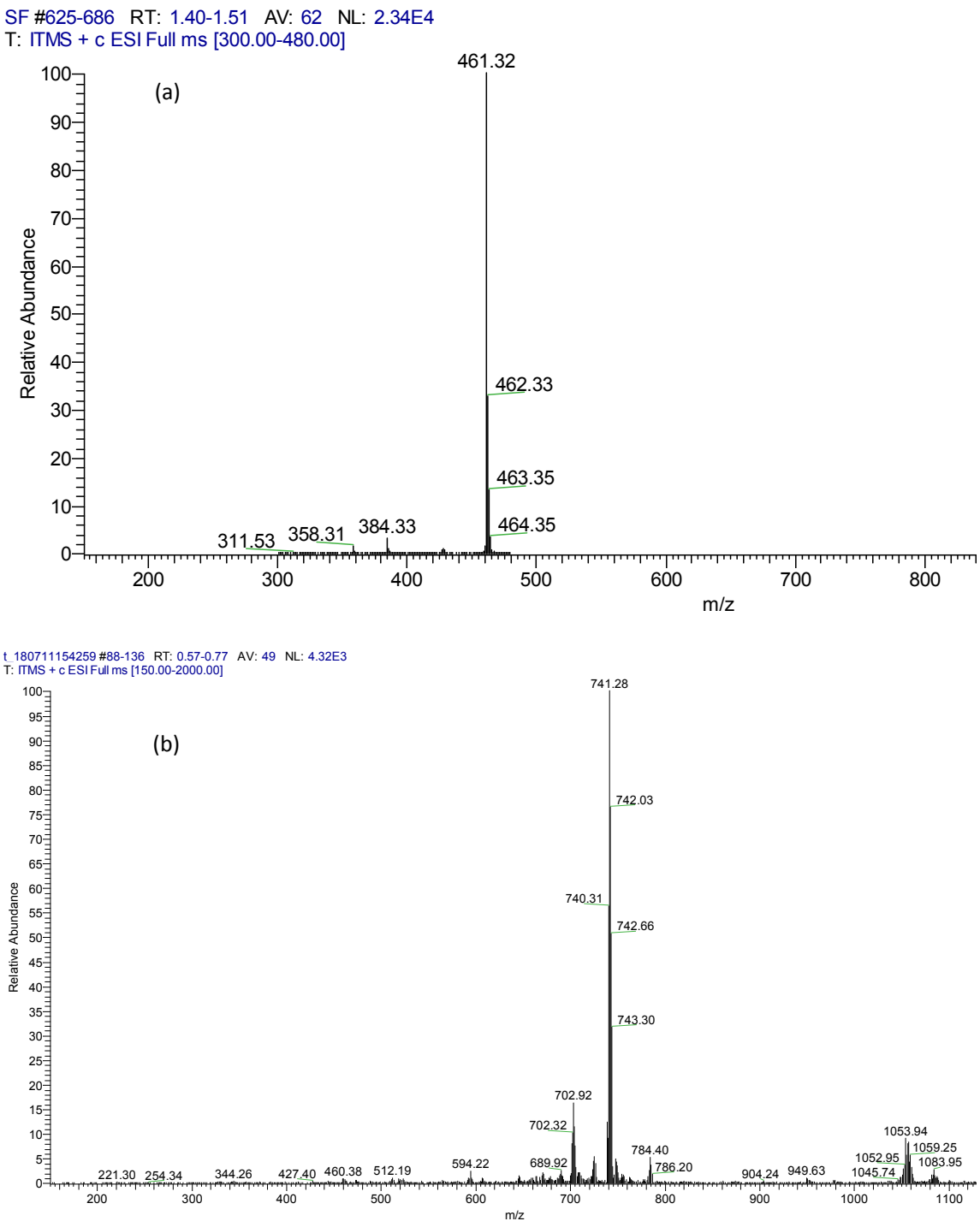


**Figure S2.** Mass spectra of L (a) and $RuL_3(ClO_4)_2$ (b).

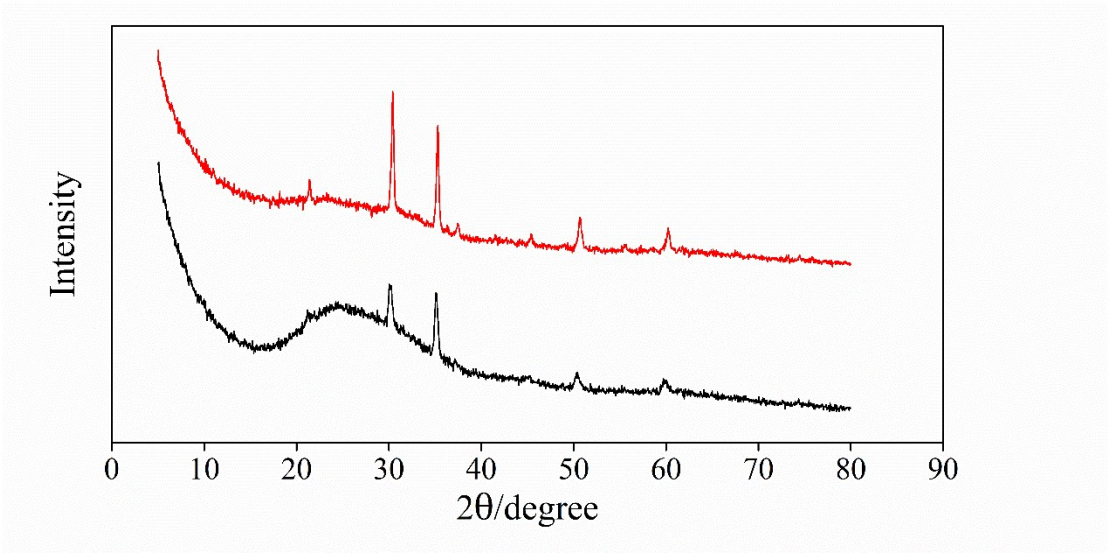


**Figure S3.** XRD profiles of poly($RuL_3$)$_5$ film on ITO (top) and bare ITO (bottom).

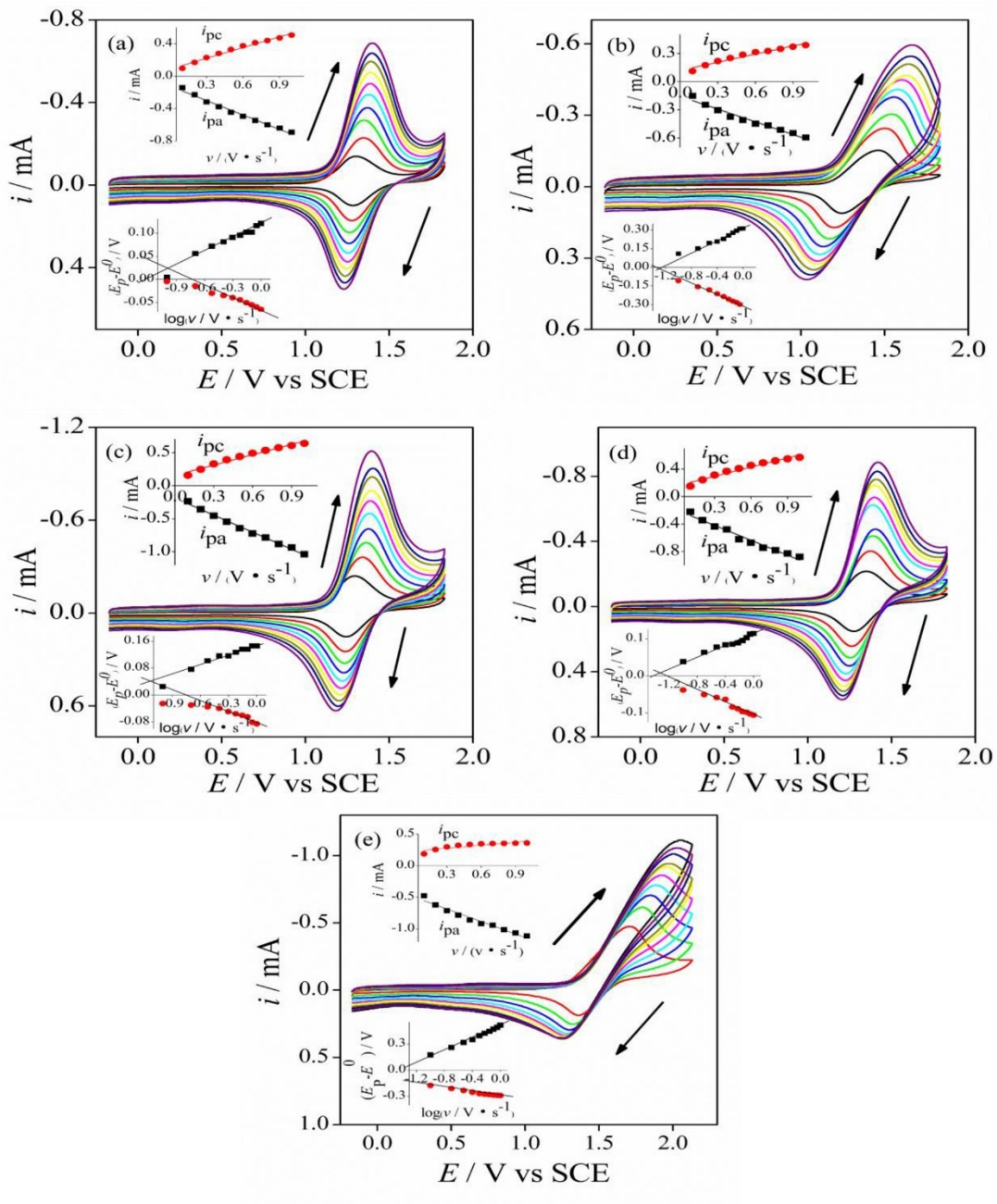


**Figure S4.** Electrochemical scan rate behaviors of (a) poly($RuL_3$)$_2$, (b) poly($RuL_3$), (c) poly($RuL_3$)$_4$, (d) poly($RuL_3$)$_5$, and (e) poly($RuL_3$)$_6$ film in $CH_2Cl_2$ solution containing 0.1M $TBAPF_6$; top inset: linear relationship of peak current versus scan rate (0.1-1 v/s); bottom inset: dependence of the overpotentials on the scan rates (0.1-1 v/s).

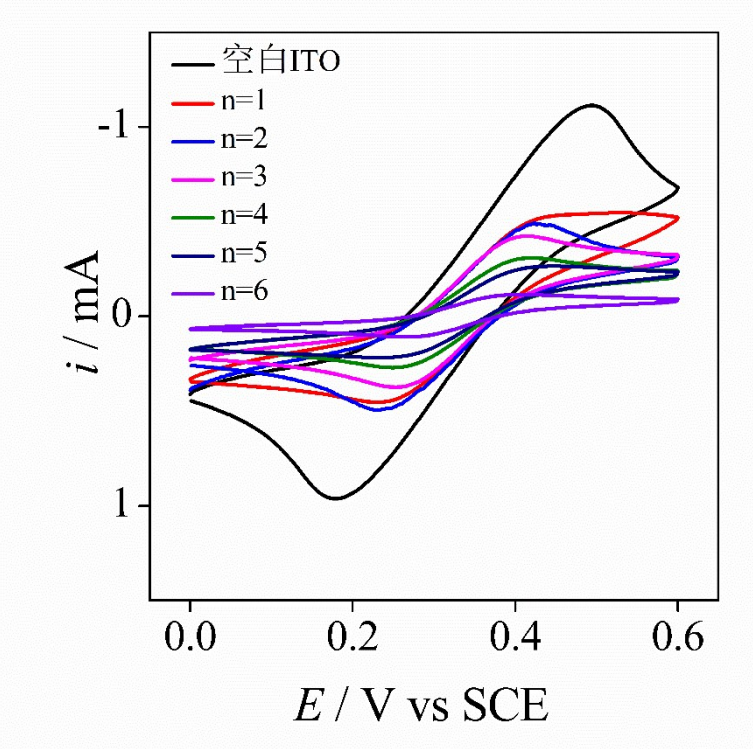


**Figure S5.** Cyclic voltammetry of blank ITO and poly($RuL_3$)$_n$ (n = 1-6) film in 0.1 M HCl aqueous solution containing 1mM $[Fe(CN)_6]^{3-/4}$ at the scan rate of 500 mV/s.

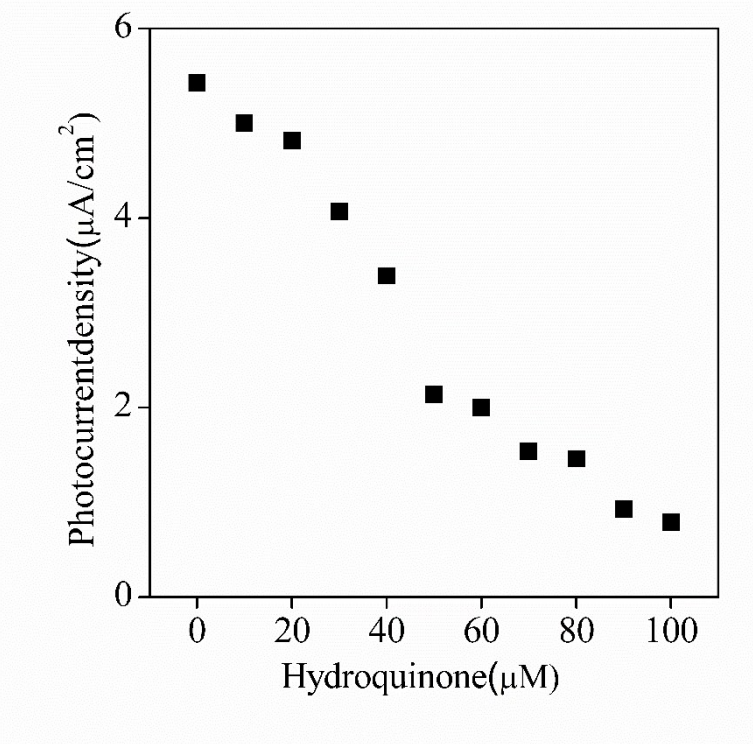


**Figure S6.** Dependence of photocurrent density of poly($RuL_3$)$_2$ film on the different concentrations of the electron donor of hydroquinone in degassing 0.1 M $Na_2SO_4$ aqueous solution at an applied potential of -0.4 V vs. SCE under 100 mW/cm$^2$ white light irradiation.

**Table S1.** The parameters obtained by fitting the data according to the equivalent electrical circuit of Fig. 6 (b)

| poly($RuL_3$)$_n$ | $R_S$/Ω cm$^2$ | $C$/μF S$^{n-1}$ | $n$ | $R_{ct}$/Ω cm$^2$ |
|---|---|---|---|---|
| n = 1 | 55.94 | 271.05 | 0.68864 | 41.41 |
| n = 2 | 40.79 | 286.1 | 0.71038 | 51.52 |
| n = 3 | 43.59 | 580.15 | 0.60534 | 52.42 |
| n = 4 | 35.24 | 473.99 | 0.63145 | 106.8 |
| n = 5 | 68 | 333.04 | 0.67344 | 86.37 |
| n = 6 | 88.61 | 75.784 | 0.87101 | 2670 |

**Table S2.** Electron transfer rate constant $k_s$ and surface converage $\Gamma$ of poly($RuL_3$)$_n$ (n = 1-6) in $CH_2Cl_2$ solution containing 0.1 M $TBAPF_6$

| poly($RuL_3$)$_n$ | $v_a$ (V/s) | $v_c$ (V/s) | $\alpha$ | $k_s$ (s$^{-1}$) | $\Gamma$ (mol/cm$^2$) |
|---|---|---|---|---|---|
| n = 1 | 0.02630 | 0.1778 | 0.1289 | 0.9077 | 1.182×10$^{-10}$ |
| n = 2 | 0.05888 | 0.1862 | 0.2403 | 1.773 | 2.066×10$^{-10}$ |
| n = 3 | 0.05495 | 0.4571 | 0.5459 | 0.9886 | 1.577×10$^{-10}$ |
| n = 4 | 0.02630 | 0.1738 | 0.1315 | 0.9064 | 2.995×10$^{-10}$ |
| n = 5 | 0.03715 | 0.05888 | 0.3869 | 0.9023 | 2.524×10$^{-10}$ |
| n = 6 | 0.03846 | 0.04571 | 0.8938 | 0.1618 | 2.299×10$^{-10}$ |