Supplementary Material (ESI) for Energy & Environmental Science

Supplementary Data

High Molar Extinction Coefficient Amphiphilic Ruthenium Sensitizers for Efficient and Stable Mesoscopic Dye-Sensitized Solar Cells

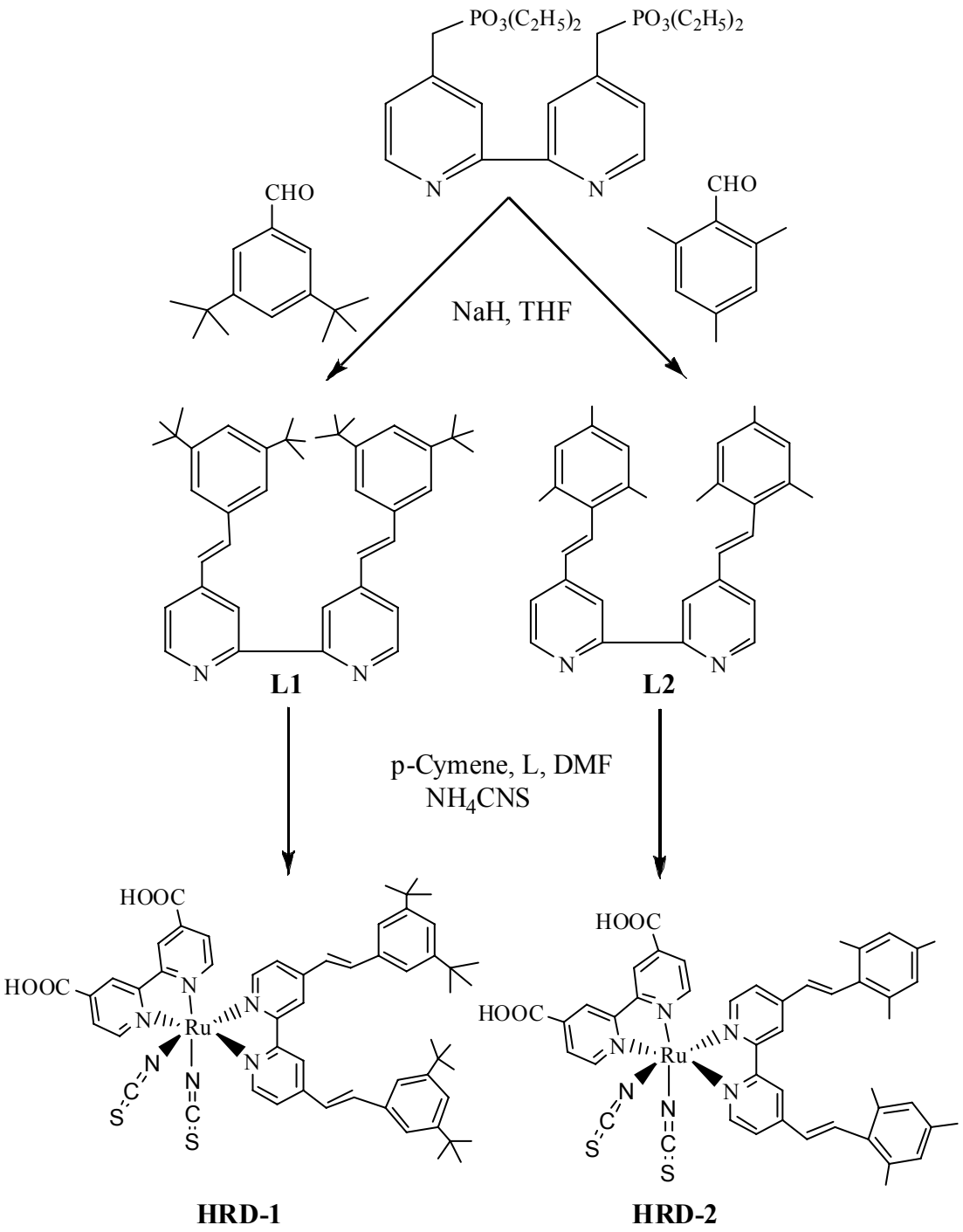
L. Giribabu,*[a] Ch. Vijay Kumar,[a] Ch. Srinivasa Rao,[a] V. Gopal Reddy,[a] P. Yella Reddy,[a] M. Chandrasekharam[a] and Y. Soujanya[b]

[a]Nanomaterials Laboratory, Inorganic & Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India.

[b]Molecular Modeling Group, Indian Institute of Chemical Technology, Hyderabad 500007, India.

*Author for correspondence E-mail: giribabu@iict.res.in, **Phone:** +91-40-27193186, Fax: +91 40-27160921

2.1 Synthesis



Synthetic Scheme for HRD-1 and HRD-2

2,2'-bipyridine-4,4'-dicarboxylic acid (**L**), 4,4'-diethyl ester phosphonate-2,2'-bipyridine ligand, and K-77 complex was synthesized and purified as per literature reported procedures.[1]

Synthesis of 4,4'-Bis-[2-(3,5-di-tert-butyl-phenyl)-vinyl]-[2,2']bipyridinyl, (L1): This ligand was synthesized by using Wittig reaction. NaH (360 mg, 15 mmol) was added to a solution of 2,2'-bipyridine-4,4'-diphosphonate (1.5 g, 3.5 mmol) and 3,5-di-*tert*-butyl benzaldehyde (1.7 g, 7.8 mmol) in 150 ml of dry tetrahydrofuran (THF). The resulting mixture was refluxed overnight under nitrogen atmosphere. The reaction mixture was allowed to cool to room temperature and filtered the compound. The filtrate is concentrated and the solid is washed with methanol and dried to obtain the desired product in pure form of 75% yield. Elemental analysis of $C_{42}H_{52}N_2$ (calculated mass % in parentheses) C, 86.20 (86.25); H, 9.00 (8.96); N, 4.75 (4.79). ^{1}H NMR (300 MHz, 25 ^{o}C, $CDCl_3$) 1.34 (m, 36H), 6.97 (d, 1H), 7.13-7.25 (m, 8H), 7.29 (d, 1H), 8.63 (s, 2H), 8.71 (d, 2H).

Synthesis of 4,4'-Bis-[2-(2,4,6-trimethyl-phenyl)-vinyl]-[2,2']bipyridyl (L2): NaH (360 mg, 15 mmol) was added to a solution of 2,2'-bipyridine-4,4'-diphosphonate (1.5 g, 3.5 mmol) and 2,4,6-trimethyl benzaldehyde (1.2 g, 7.8 mmol) in 150 ml of dry tetrahydrofuran (THF). The resulting mixture was refluxed overnight under nitrogen atmosphere. The reaction mixture is allowed to cool to room temperature and filtered the compound. The filtrate is concentrated and the solid is washed with methanol and dried to obtain the desired product in pure form of 77% yield. Elemental analysis of $C_{32}H_{32}N_2$ (calculated mass % in parentheses) C, 86.35 (86.44); H, 7.20 (7.25); N, 6.25 (6.30). ^{1}H NMR (300 MHz, 25 ^{o}C, $CDCl_3$) 2.35 (s, 18H), 6.58 (d, 1H), 6.62 (s, 4H), 7.25 (s, 2H), 7.31 (d, 1H), 8.63 (d, 2H), 8.71 (d, 2H).

General Procedure for p-cymene Complex

Ru(L1)(p-cymene)(Cl)$_2$ and Ru(L2)(p-cymene)(Cl)$_2$: A mixture of either **L1** (0.53 g, 1.25 mmol) or **L2** (0.55 g, 1.25 mmol) and [Ru(Cl)$_2$-(p-cymene)]$_2$ in ethanol:chloroform (8:2 v/v) was refluxed for 4 hours under nitrogen atmosphere. Evaporation of the solvent under reduced pressure afforded the pure complexes as orange solid.

General Procedure for Complex Preparation

The above p-cymene complex (1.24 mmol) and 4,4'-dicarboxy-2,2'-bipyridine, (**L**) (0.303 g, 1.24 mmol) in anhydrous DMF (75 ml) were heated to 140 ^{o}C for 4 hours under nitrogen atmosphere and in the dark. NH_4CNS (1,5 g, 19.7 mmol) was then added to the mixture and heating was continued for 4 h. After cooling to room temperature, DMF was evaporated and water was added. The resulting purple solid was filtered and washed with water. The crude complex in basic methanol [with tetrabutyl ammonium hydroxide (TBAOH)] and further purified on a Sephadex LH-20 column with methanol as eluent. The main band was collected, concentrated, and precipitated with dilute acidic methanol to obtain pure desired complex.

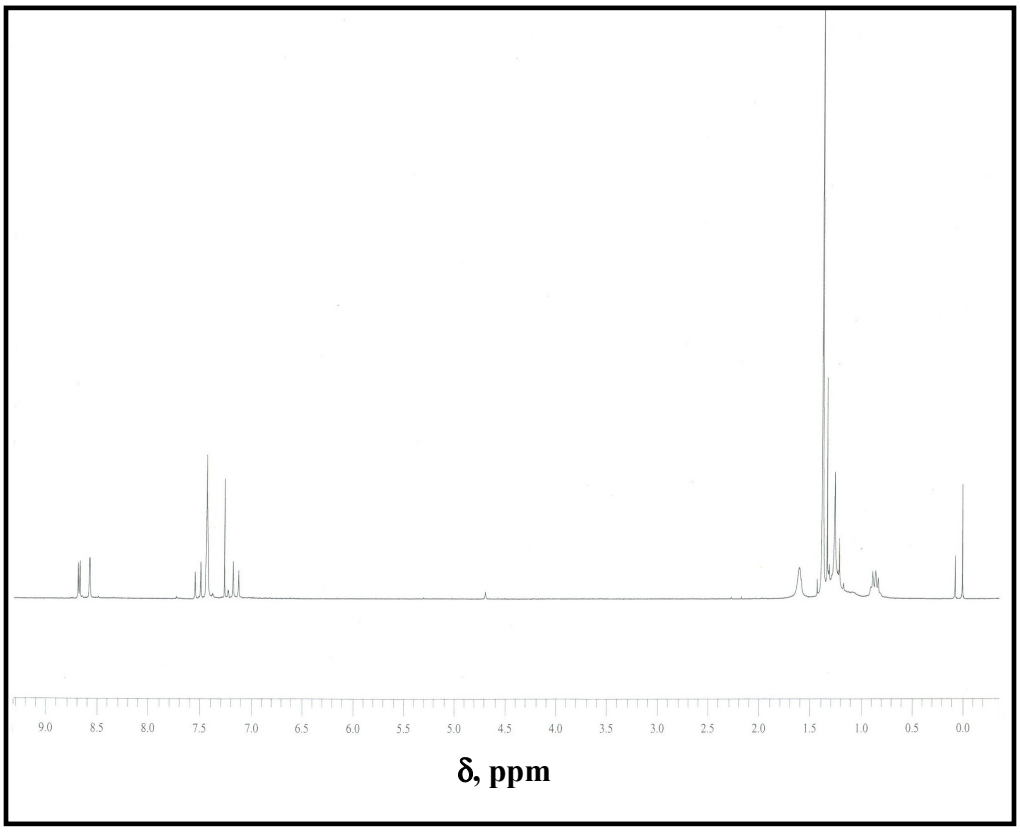
Ru(L)(L1)(NCS)$_2$ [HRD-1]: Elemental analysis of $RuC_{88}H_{130}N_8O_4S_2$ 2(TBA): (calculated mass % in parentheses) C, 67.00 (69.12); H, 8.60 (8.75); N, 7.25 (7.33). ESI-MS: $RuC_{88}H_{130}N_8O_4S_2 - C_{16}H_{36}N$ = 1529 - 242 = 1286 (2%); $RuC_{88}H_{130}N_8O_4S_2 - (C_{16}H_{36}N)_2$ = 1529 – 484 = 1045 (10%). ^{1}H NMR (300 MHz, 25 ^{o}C, CD_3OD) δ [ppm]: 9.10 (d, 4H), 8.75 (s, 2H), 8.70 (s, 2H), 8.40 to 6.90 (s, 8H), 3.50 to 0.90 (m, 108H).

Ru(L)(L2)(NCS)$_2$ [HRD-2]: Elemental analysis of $RuC_{78}H_{110}N_8O_4S_2$ 2(TBA): (calculated mass % in parentheses) C, 67.15 (67.45); H, 7.90 (7.98); N, 8.00 (8.07). ESI-MS: $RuC_{78}H_{110}N_8O_4S_2 - C_{16}H_{36}N$ = 1389 – 242 = 1147 (5%), $RuC_{78}H_{110}N_8O_4S_2 - (C_{16}H_{36}N)_2$ = 1382 – 484 = 905 (12%). ^{1}H NMR (300 MHz, 25 ^{o}C, CD_3OD) δ [ppm]: 9.47 (d, 1H), 9.35 (d, 1H), 8.98 (s, 1H), 8.83 (s, 1H), 8.55 (s, 1H), 8.40 (s, 1H), 8.10 to 6.60 (m, 8H), 3.50 to 0.90 (m, 90H).

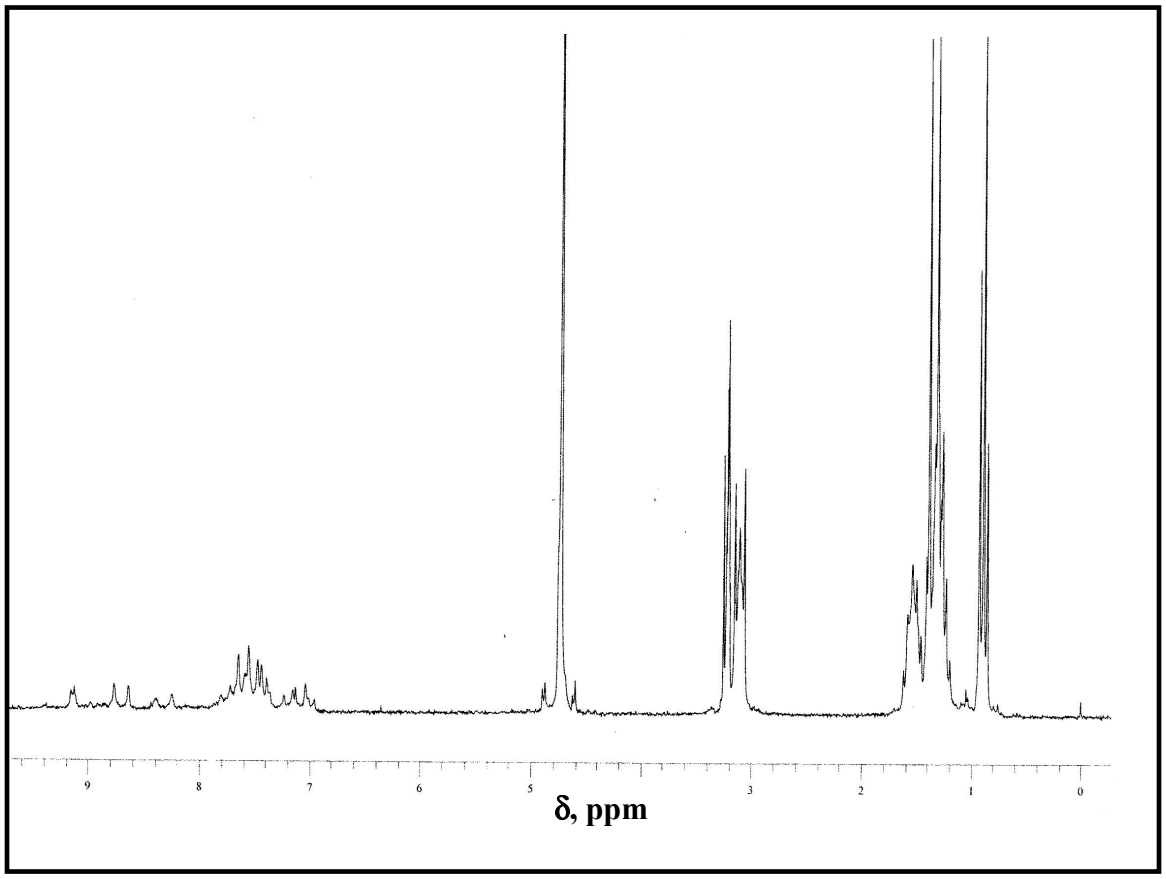
References:

1. B. O'Regan and M. Gratzel, *Nature*, 1991, **353**, 737; H. Zabri, I. Gillaizeau, C. A. Bignozzi, S. Caramori, M. F. Chariot, J. Cano-Boquera and F. Odobel, *Inorg. Chem*. 2003, **42**, 6655; D. Kaung, C. Klein, Z. Zhang, S. Ito, J. –E. Moser, S. M. Zakeeruddin and M. Gratzel, *Small*, 2007, **3**, 2094.

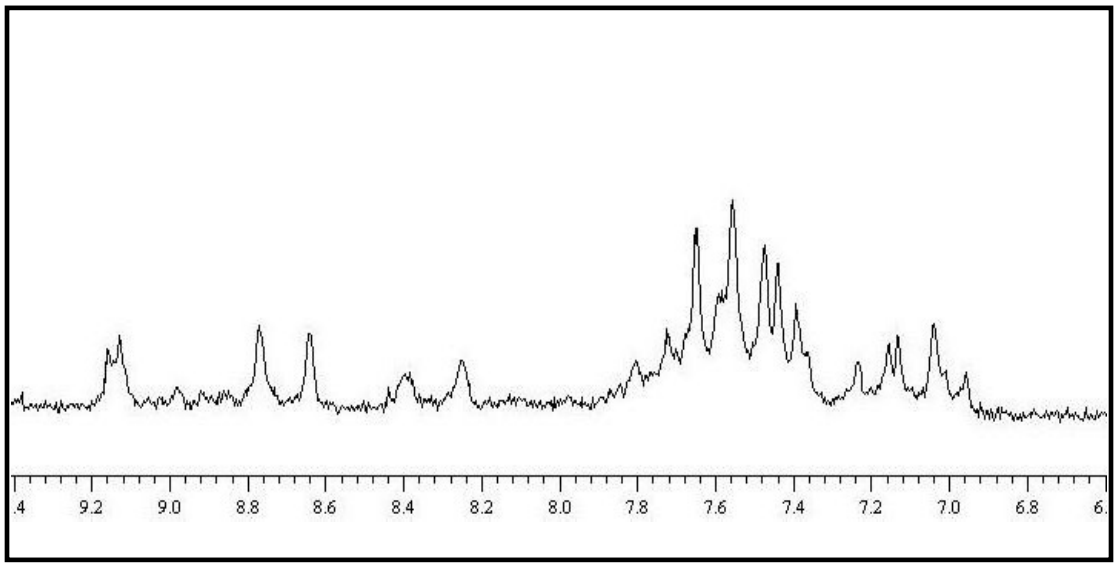
^{1}H NMR Spectrum of L1 in $CDCl_3$



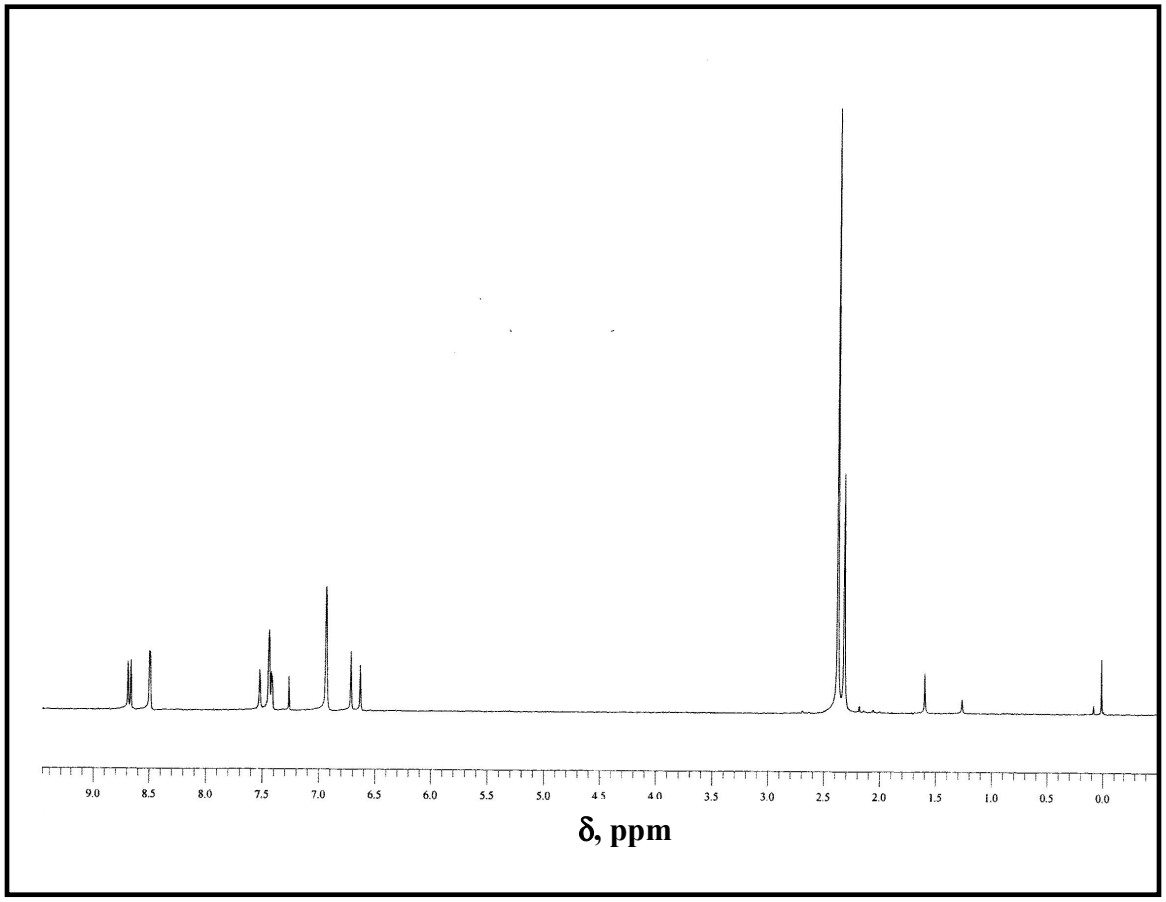
^{1}H NMR Spectrum of HRD-1 in CD_3OD



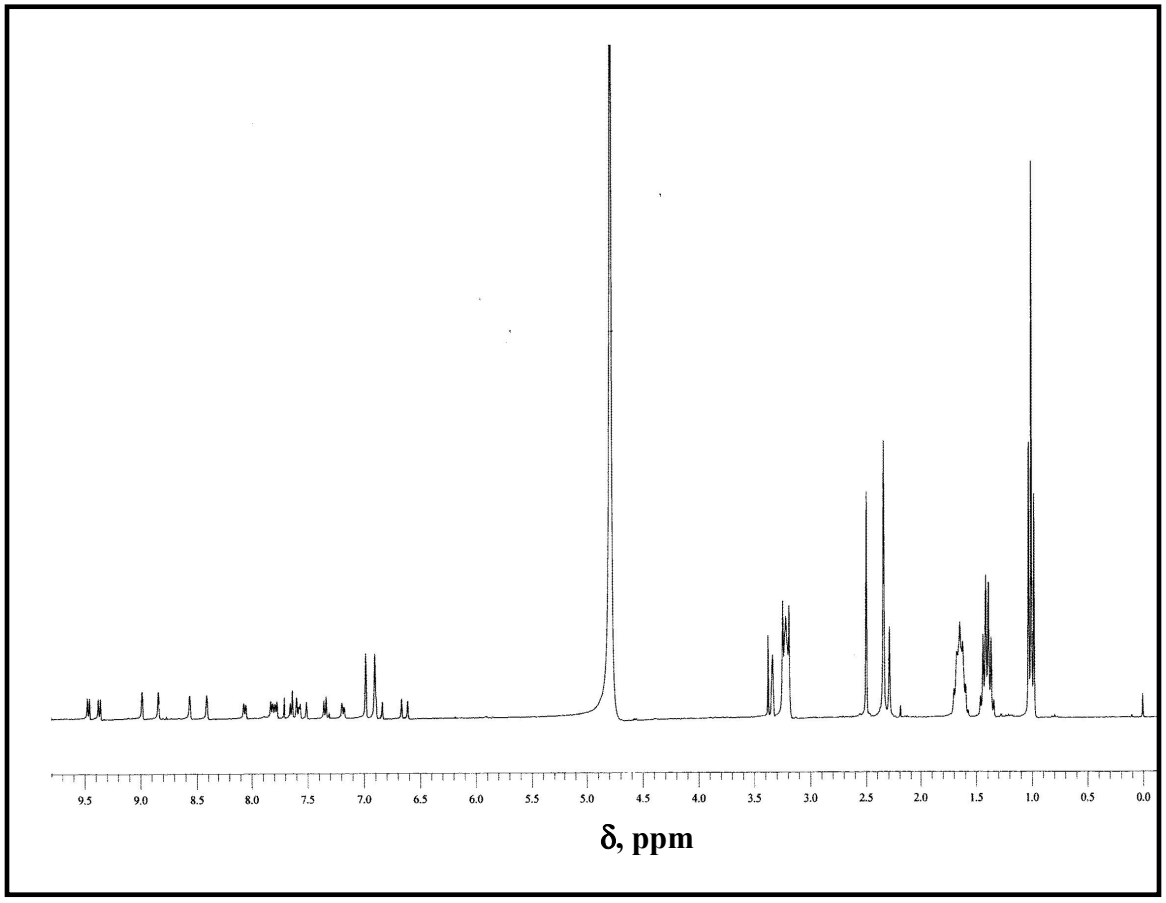
^{1}H NMR Spectrum of HRD-1 in CD_3OD in Aromatic Region



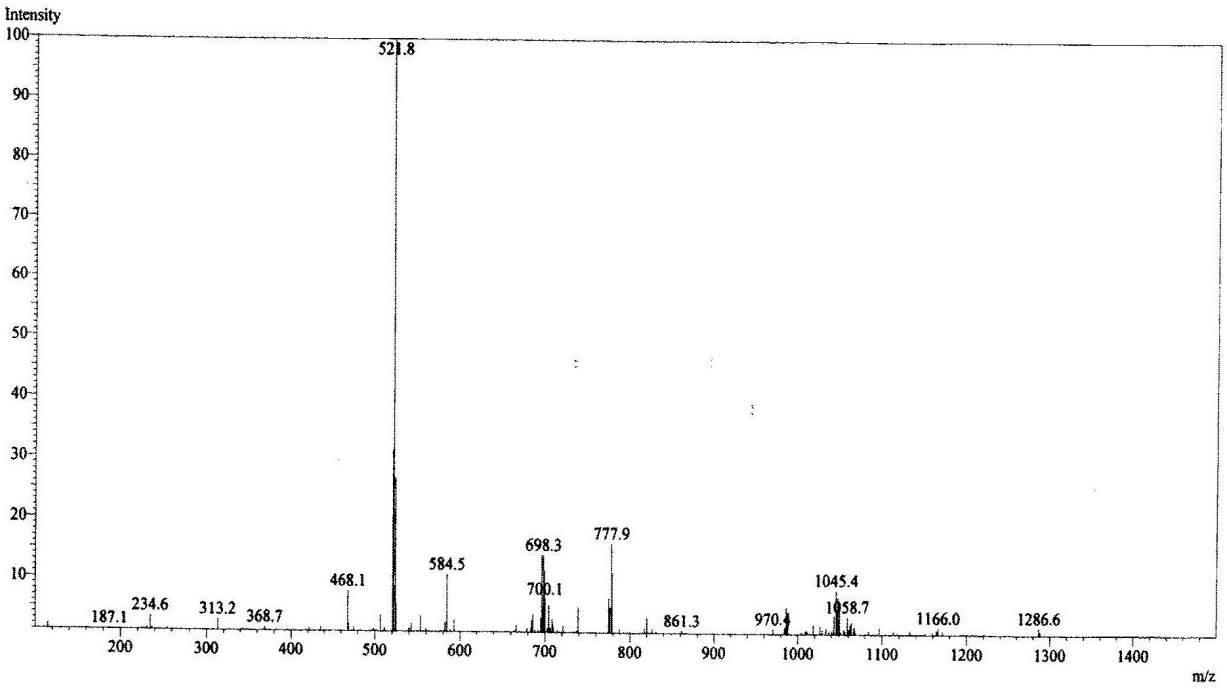
^{1}H NMR Spectrum of L2 in $CDCl_3$

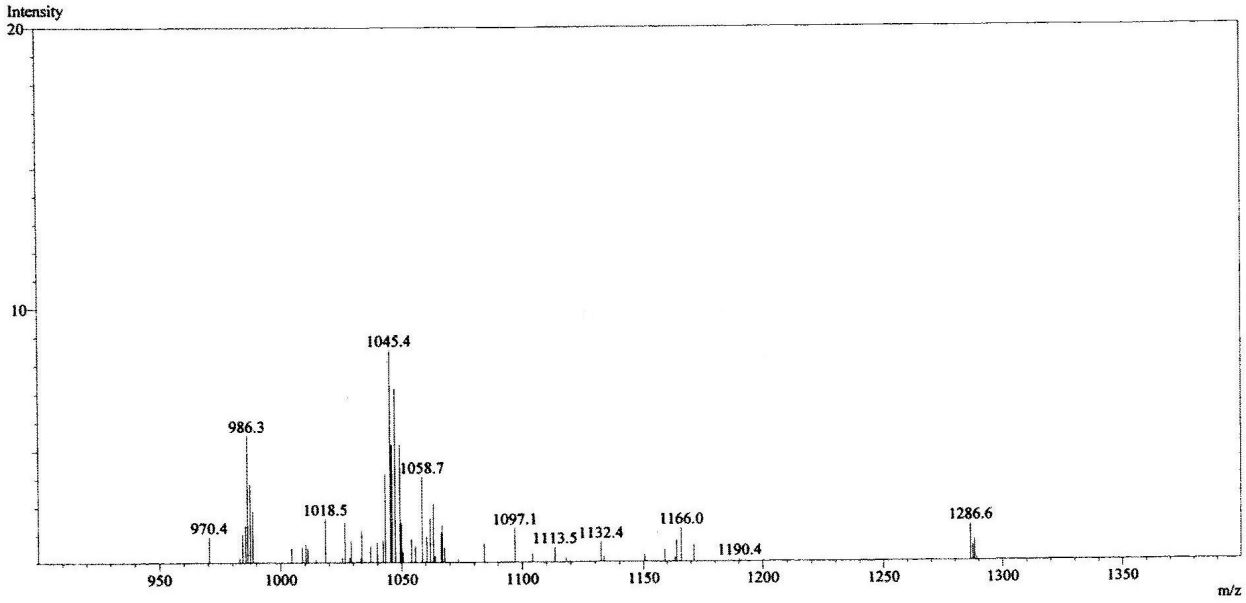


^{1}H NMR Spectrum of HRD-2 in CD_3OD

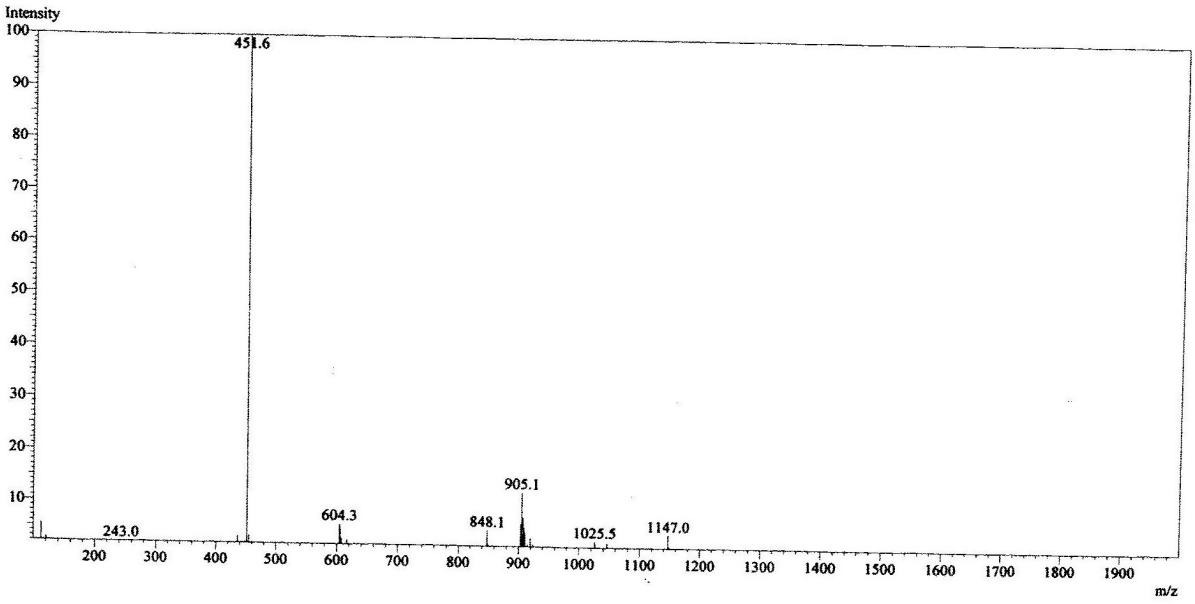


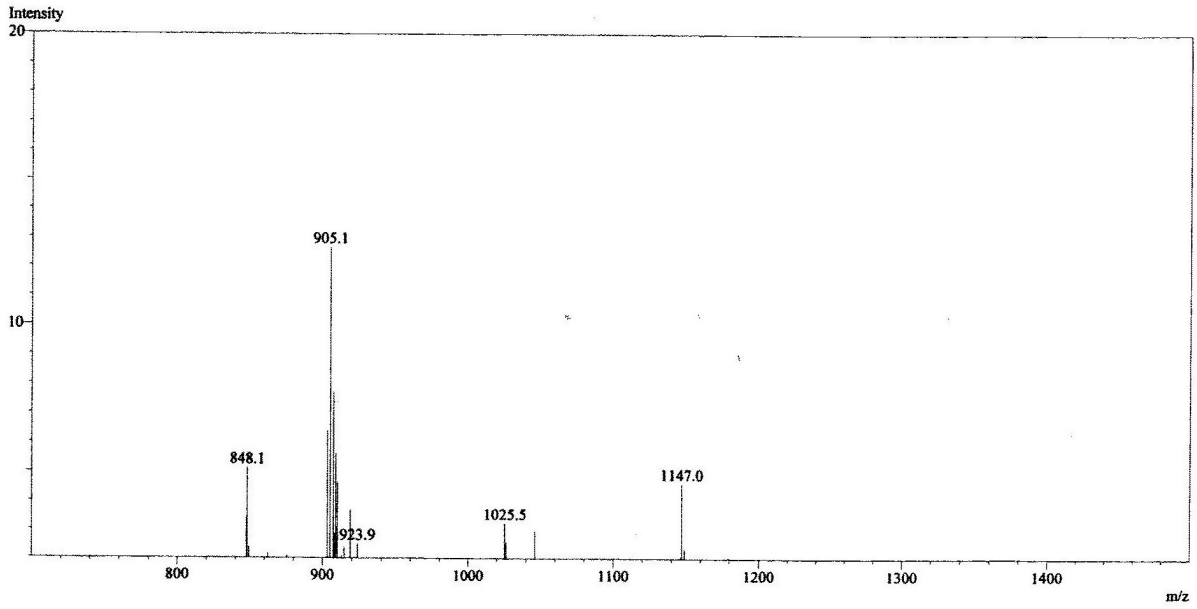
ESI-MS Spectra of HRD-1



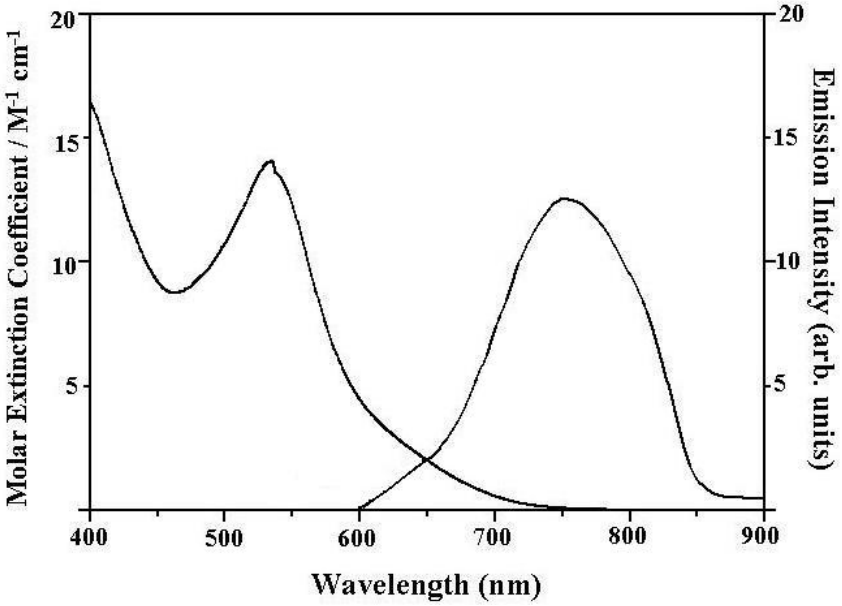


ESI-MS Spectra of HRD-2

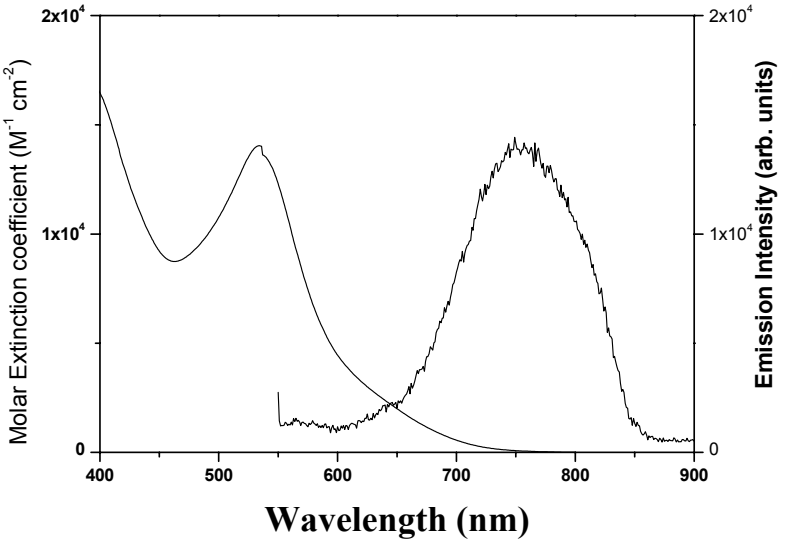




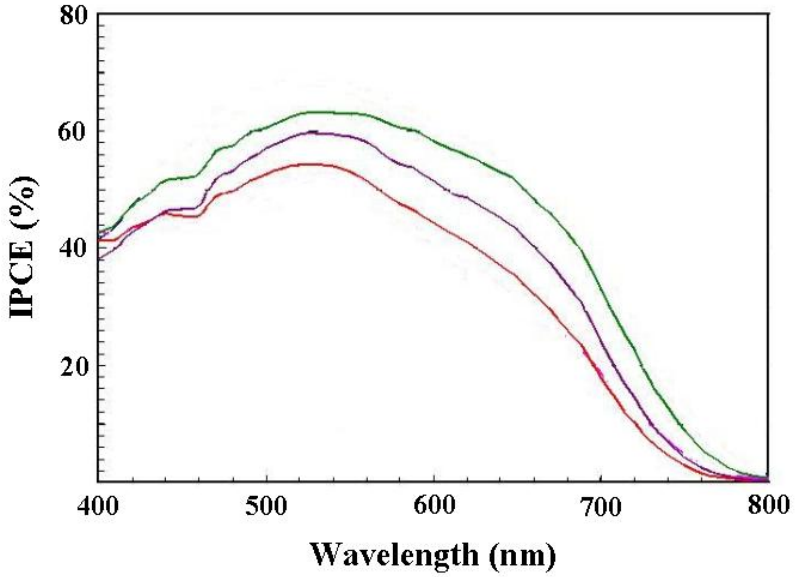
Electronic Absorption and Emission Spectra of HRD-1 in Ethanol



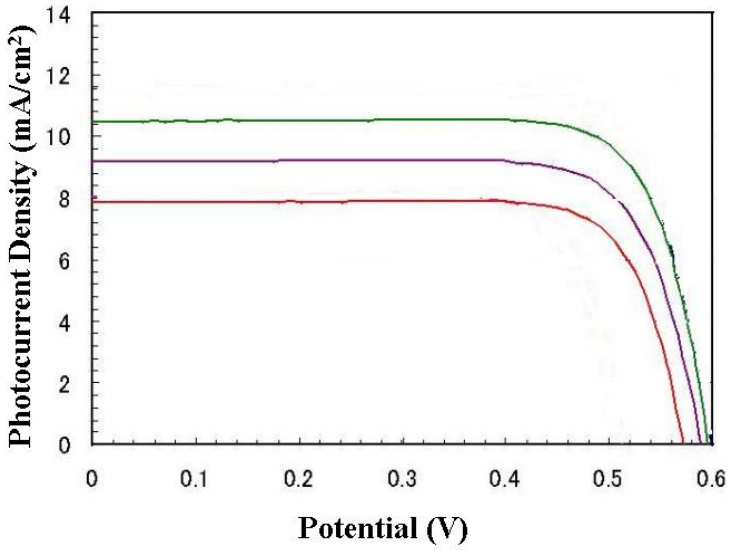
Electronic Absorption and Emission Spectra of HRD-2 in Ethanol



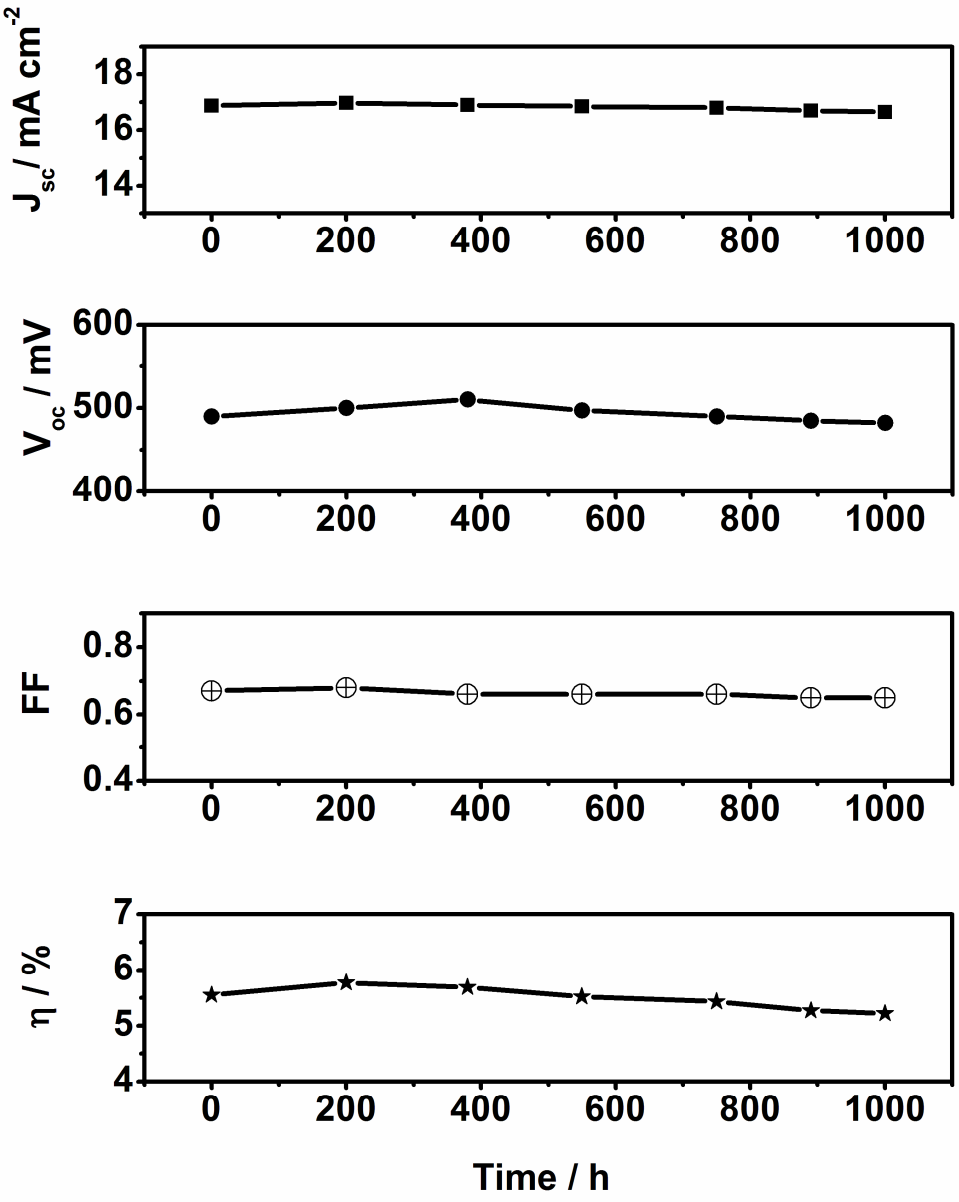
Photocurrent action spectra of (——) HRD-1, (——) HRD-2 and (——) K-77 in Z580 redox electrolyte.



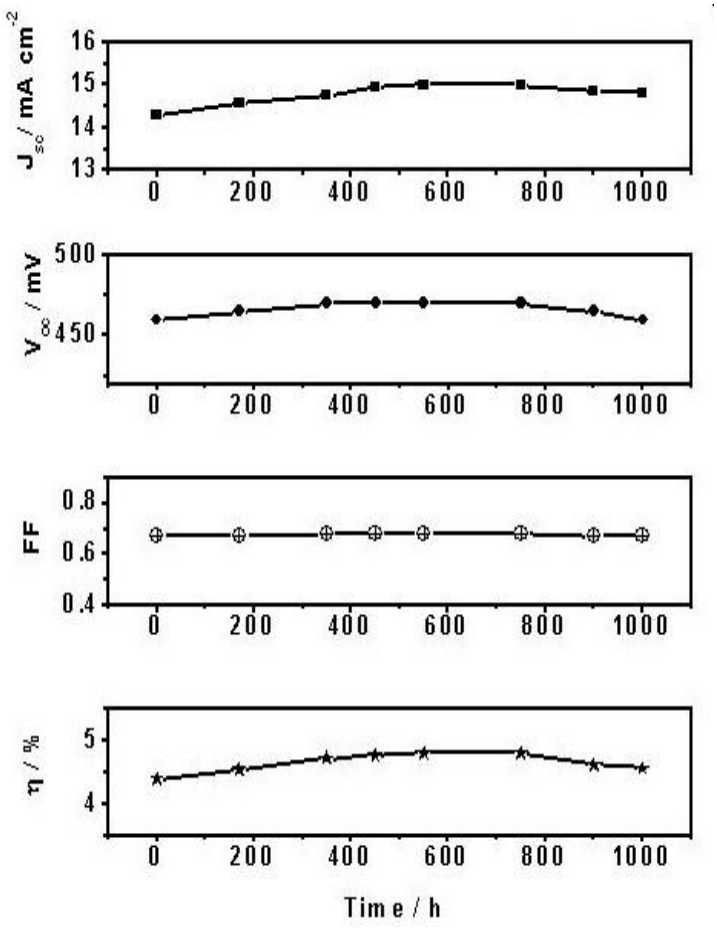
Current-voltage characteristics of (——) HRD-1, (——) HRD-2 and (——) K-77 in Z580 redox electrolyte.



Variations in photovoltaic parameters (J_{SC}, V_{OC}, FF and η) with aging time for the device based on HRD-1 and non-volatile electrolyte (Ei301) under light soaking



Variations in photovoltaic parameters (J_{SC}, V_{OC}, FF and η) with aging time for the device based on HRD-2 and non-volatile electrolyte (Ei301) during successive aging at 80 ^{o}C in the dark.



Variations in photovoltaic parameters (J_{SC}, V_{OC}, FF and η) with aging time for the device based on HRD-1 and non-volatile electrolyte (Ei301) under light soaking