

## Supporting Information

### 1. Materials and methods

Sigma-Aldrich and Alfa Aesar supplied the chemicals, which were utilized exactly as directed. JEOL's NMR spectrometer was used to record  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra in  $\text{DMSO-}d_6$  and  $\text{CDCl}_3$  as solvents at 500 MHz. A Nicolet iS10 spectrometer from Thermo Scientific was used to produce Fourier transform IR spectra. UV-visible spectra were measured by using UV-Vis. spectrophotometer (T80 series). Thermo Scientific GC/MS model ISQ was used to record mass spectra. The Perkin Elmer 2400 analyzer was used to collect data for elemental analysis.

### 2. Spectral analysis:

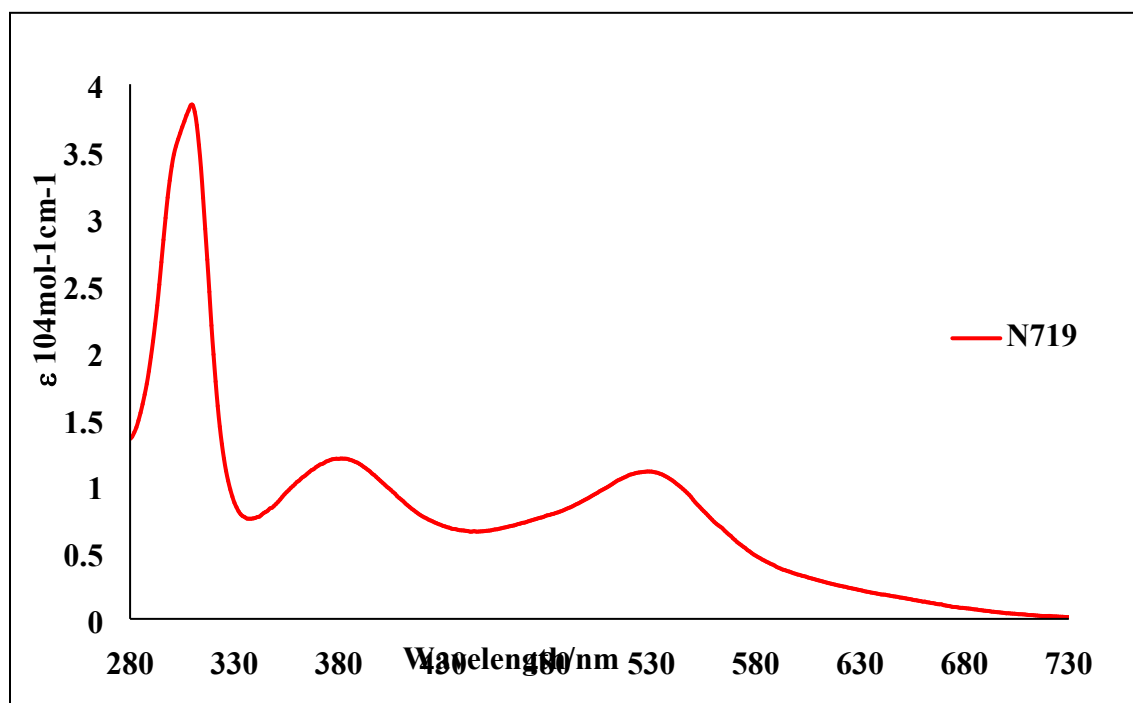
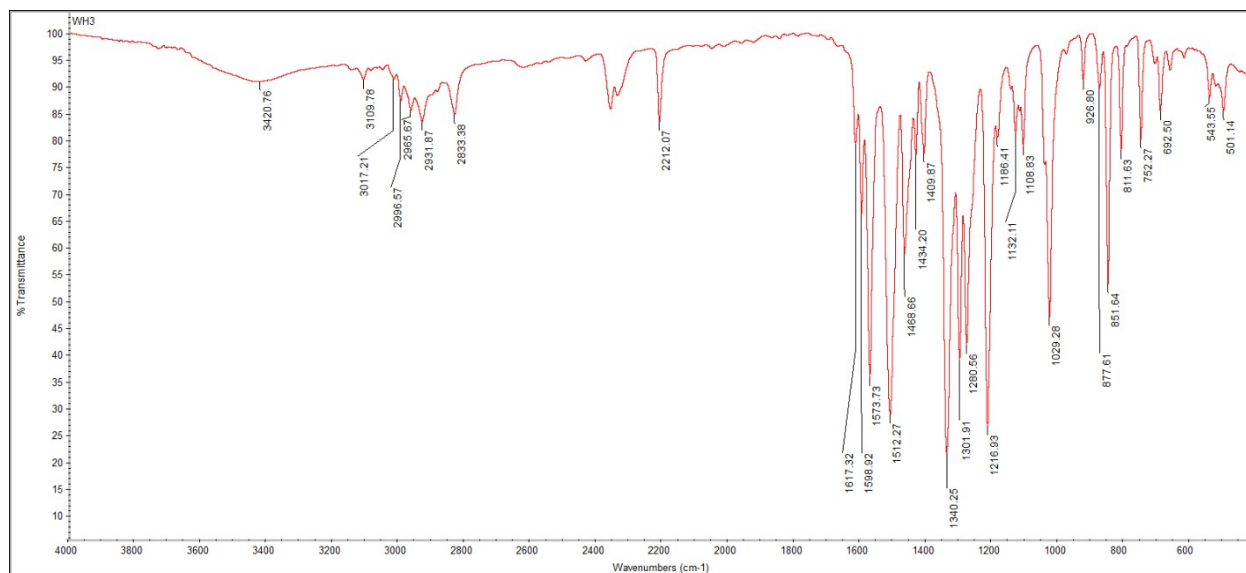


Fig. (S1): UV-Vis. absorption of N719

$\lambda_{\text{max}}$ (nm)	$\epsilon$ ( $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ )	$\lambda_{\text{onset}}$ / nm	$E_{0-0}$ (eV)
307, 384, 537	3.69, 1.18, 1.08	602	1.92



**Figure (S2): <sup>1</sup>H NMR spectrum of MSW-1.**

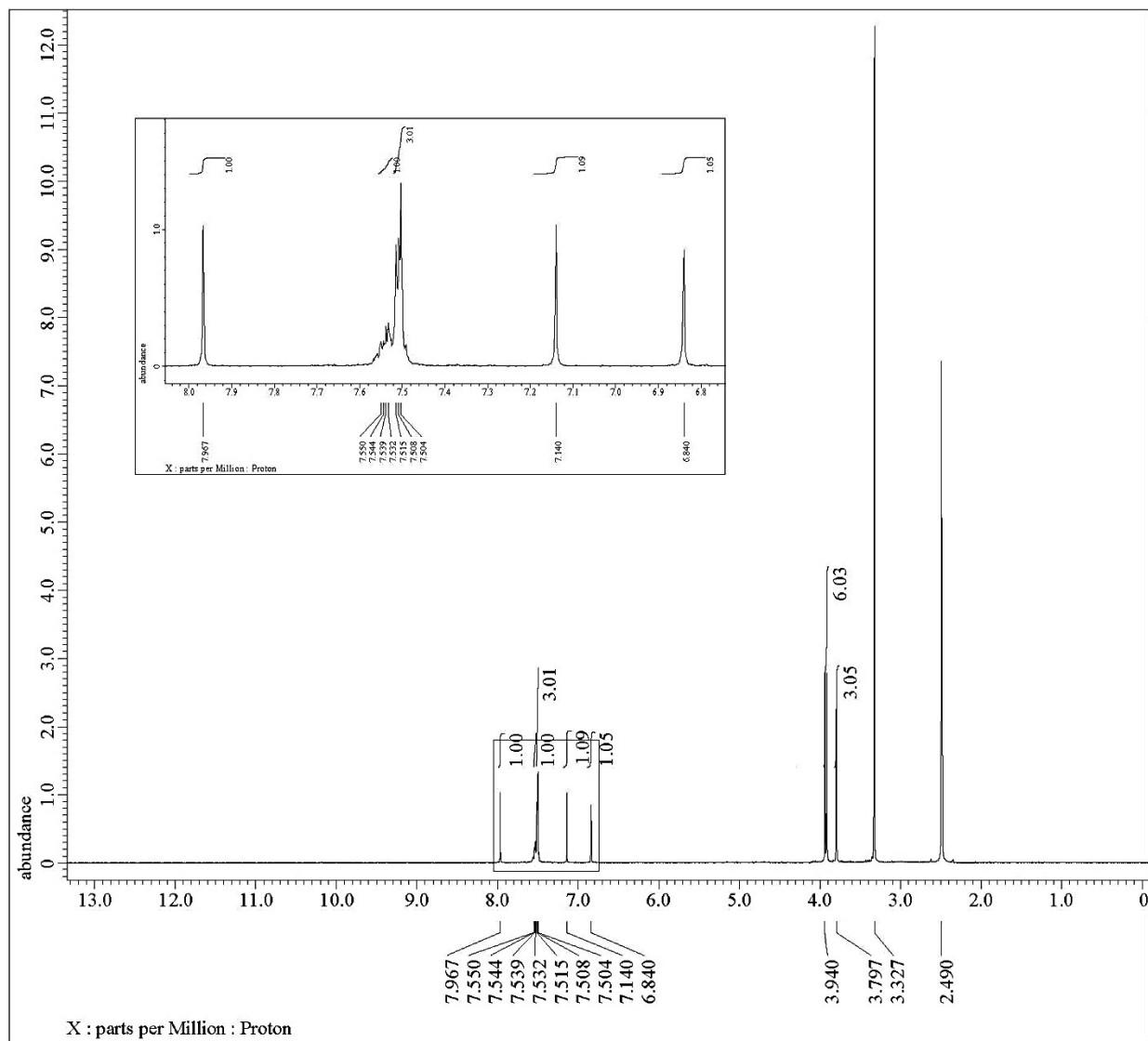
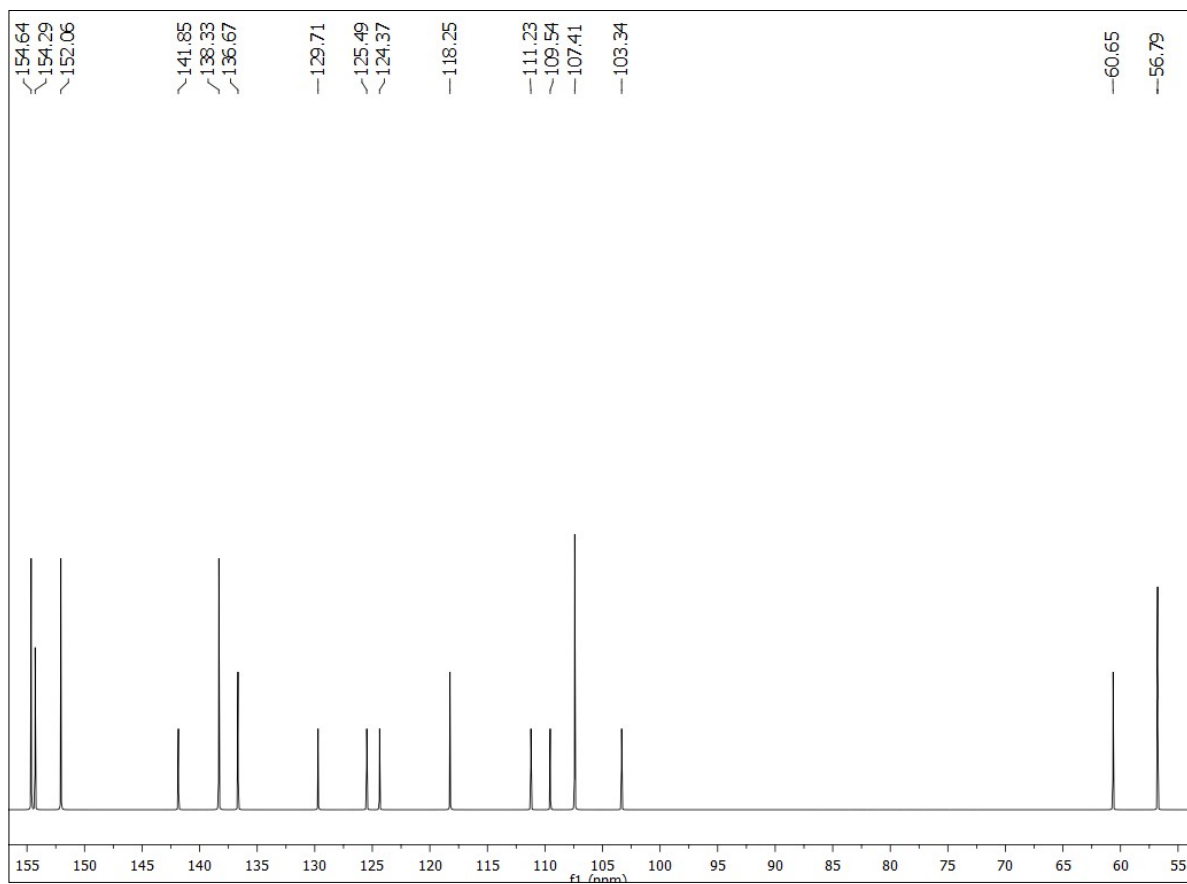
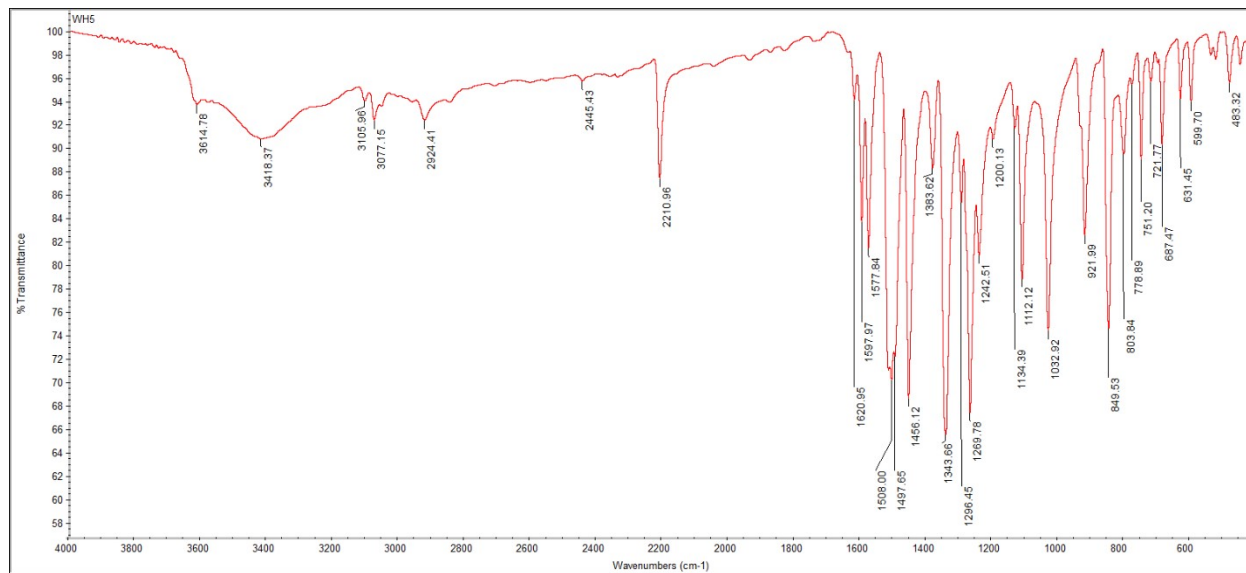


Figure (S3):  $^1\text{H}$  NMR spectrum of MSW-1.



**Figure (S4): <sup>13</sup>C NMR spectrum of MSW-1.**



**Figure (S5): IR spectrum of sensitizer MSW-2.**

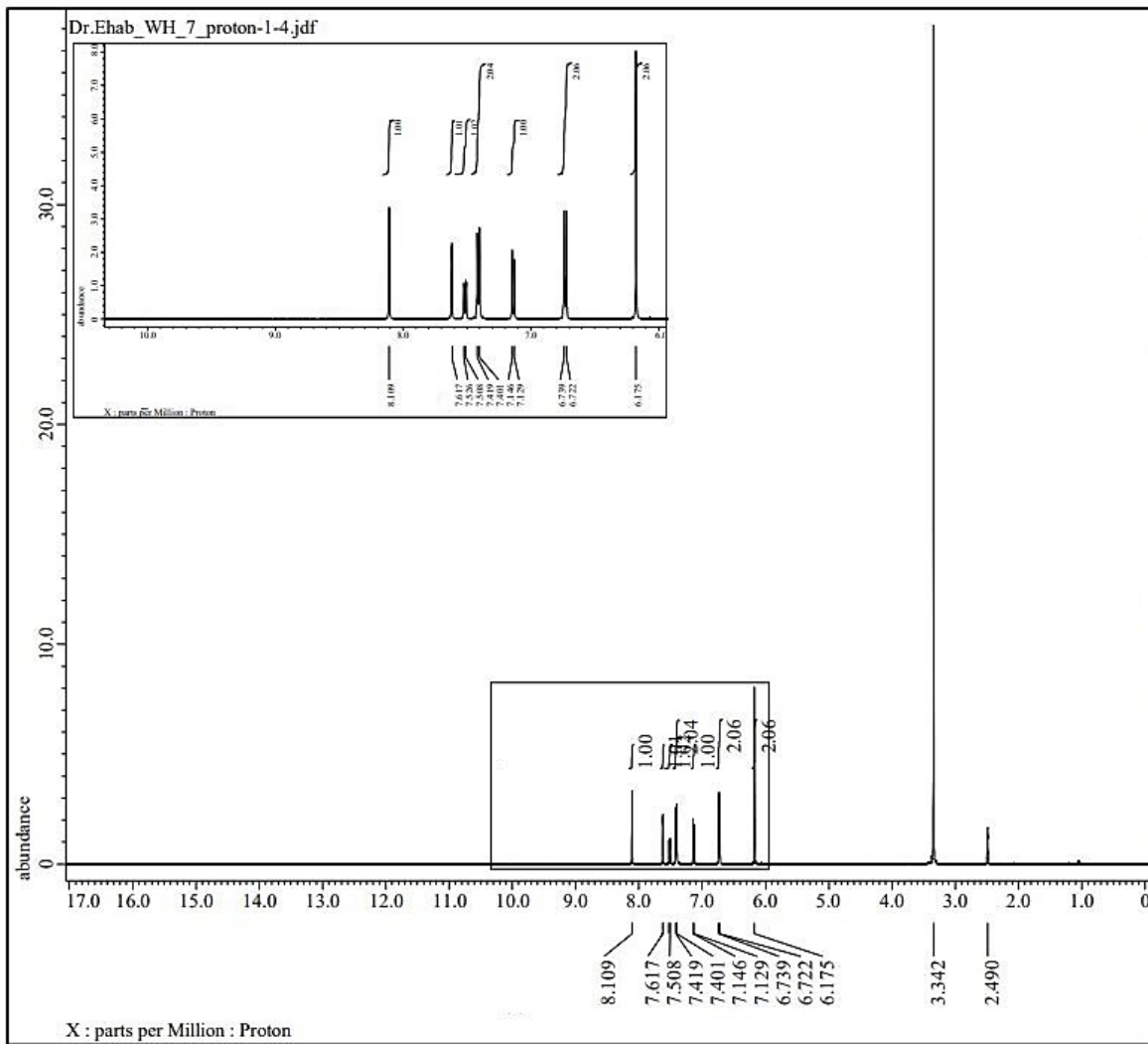
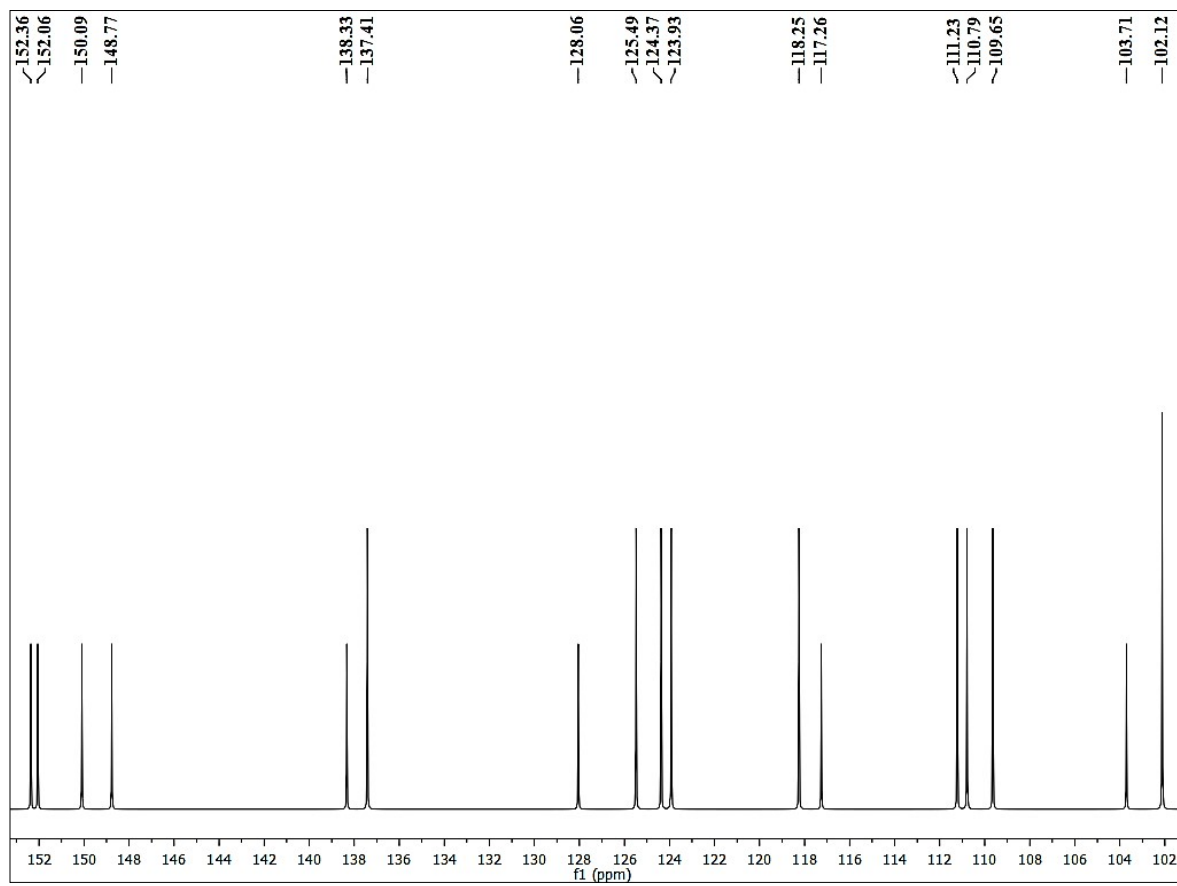
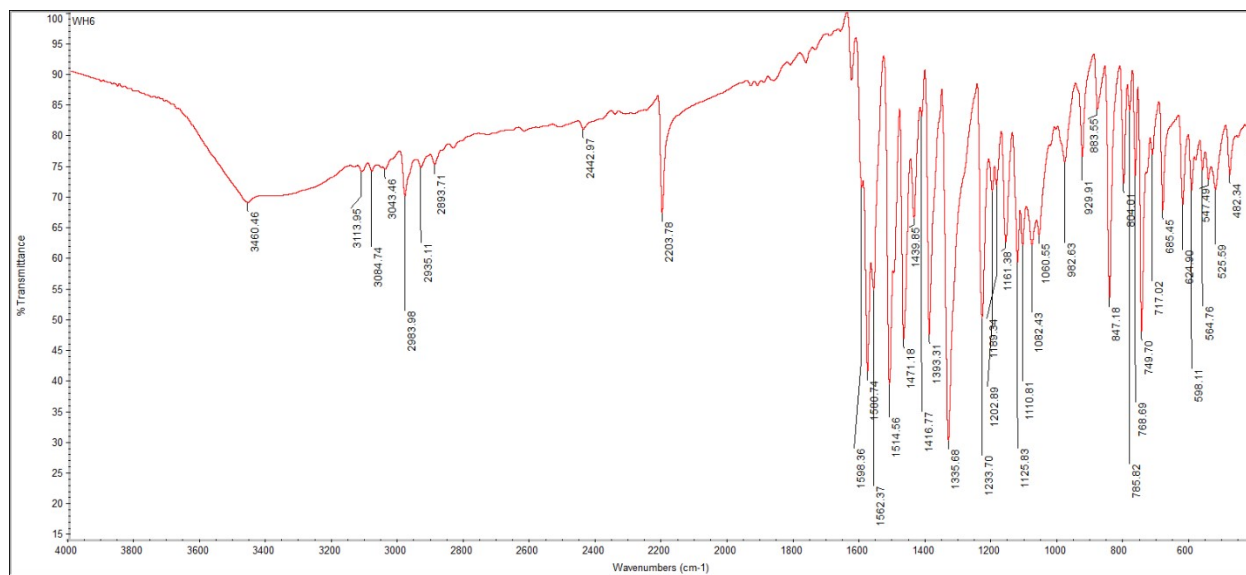


Figure (S6):  $^1\text{H}$  NMR spectrum of sensitizer MSW-2.



**Figure (S7):  $^{13}\text{C}$  NMR spectrum of sensitizer MSW-2**



**Figure (S8): IR spectrum of sensitizer MSW-3**



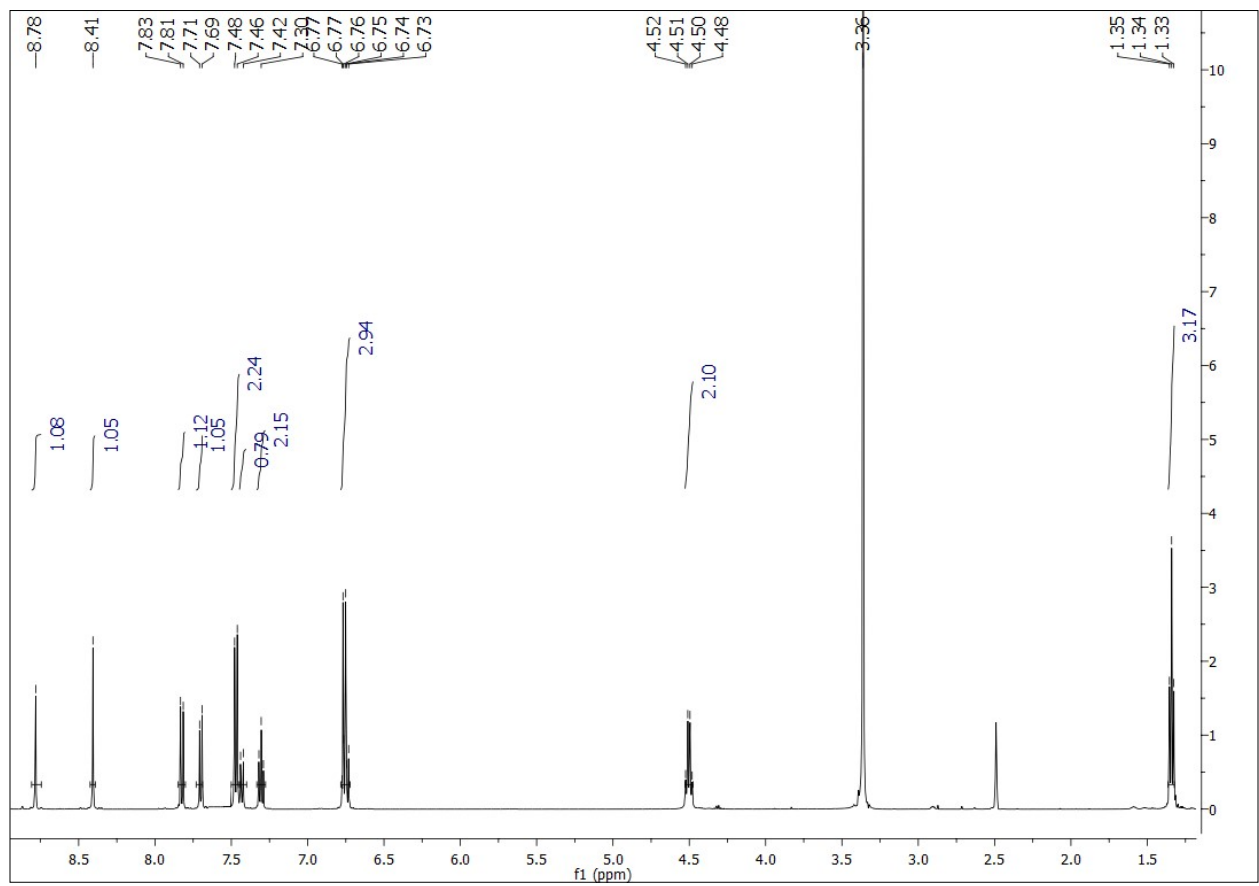
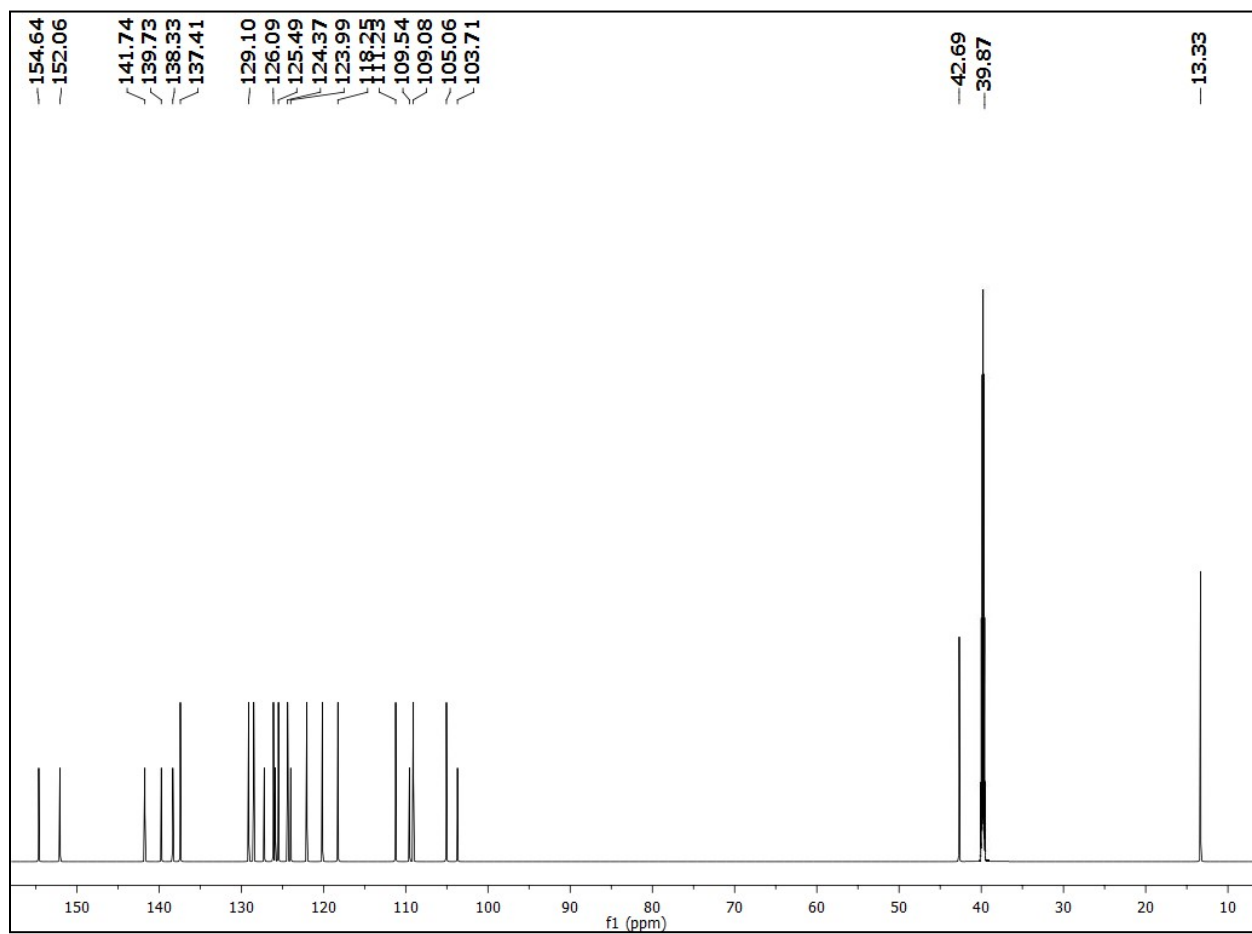
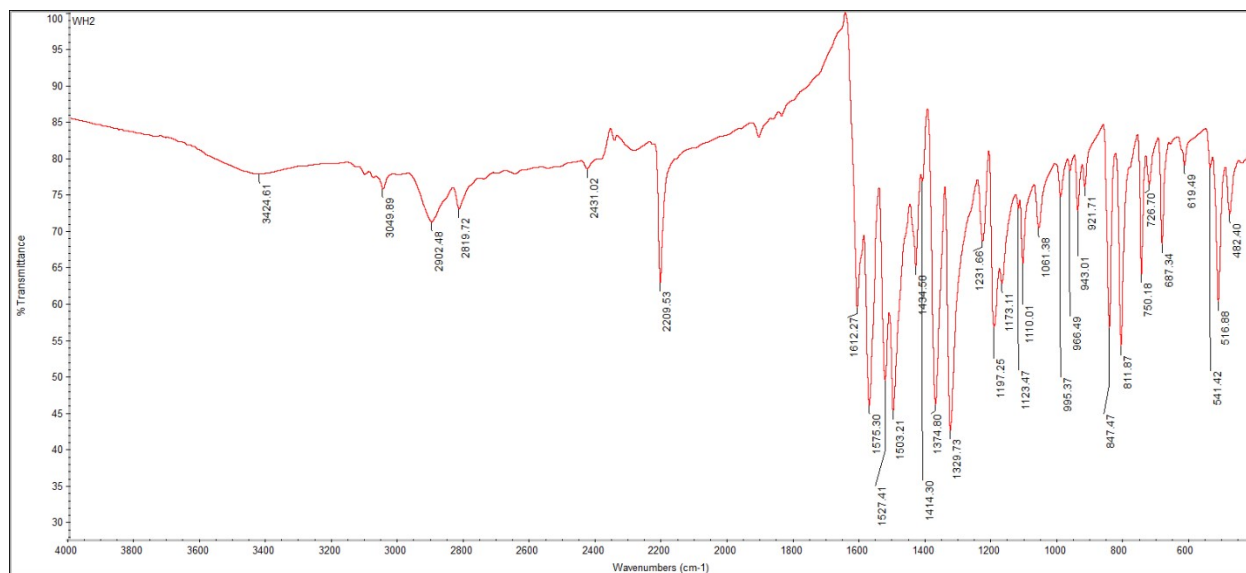


Figure (S9):  $^1\text{H}$  NMR spectrum of sensitizer MSW-3.



**Figure (S10):  $^{13}\text{C}$  NMR spectrum of sensitizer MSW-3.**



**Figure (S11): IR spectrum of MSW-4.**

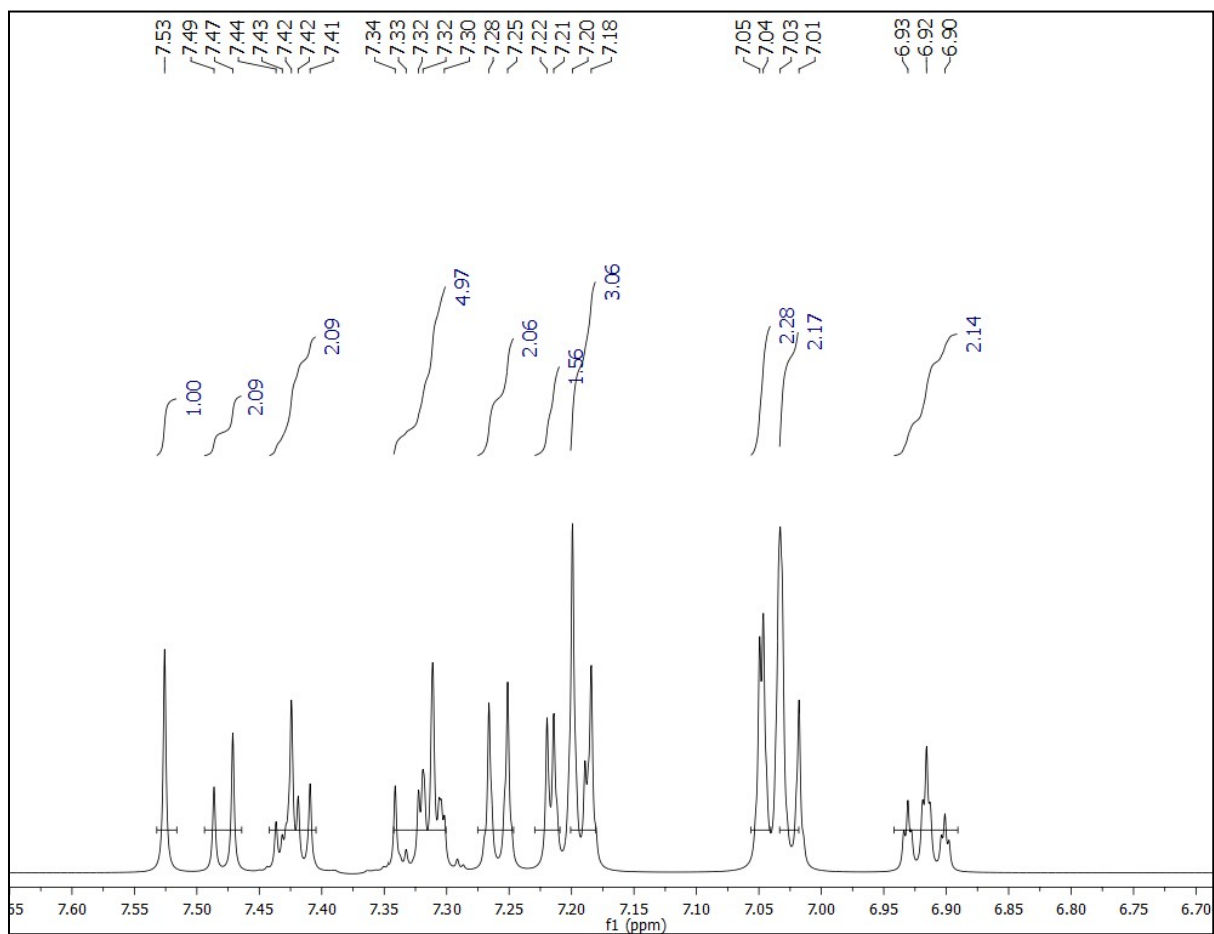
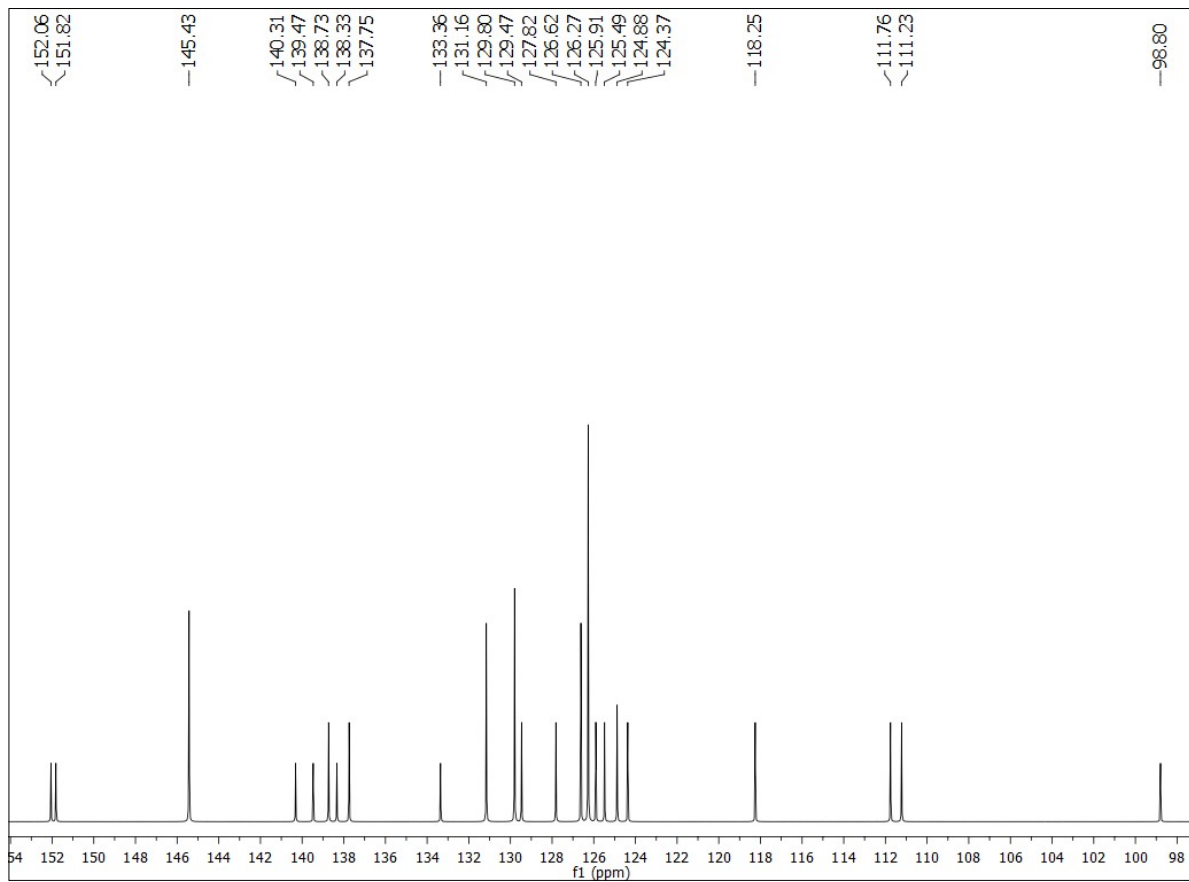
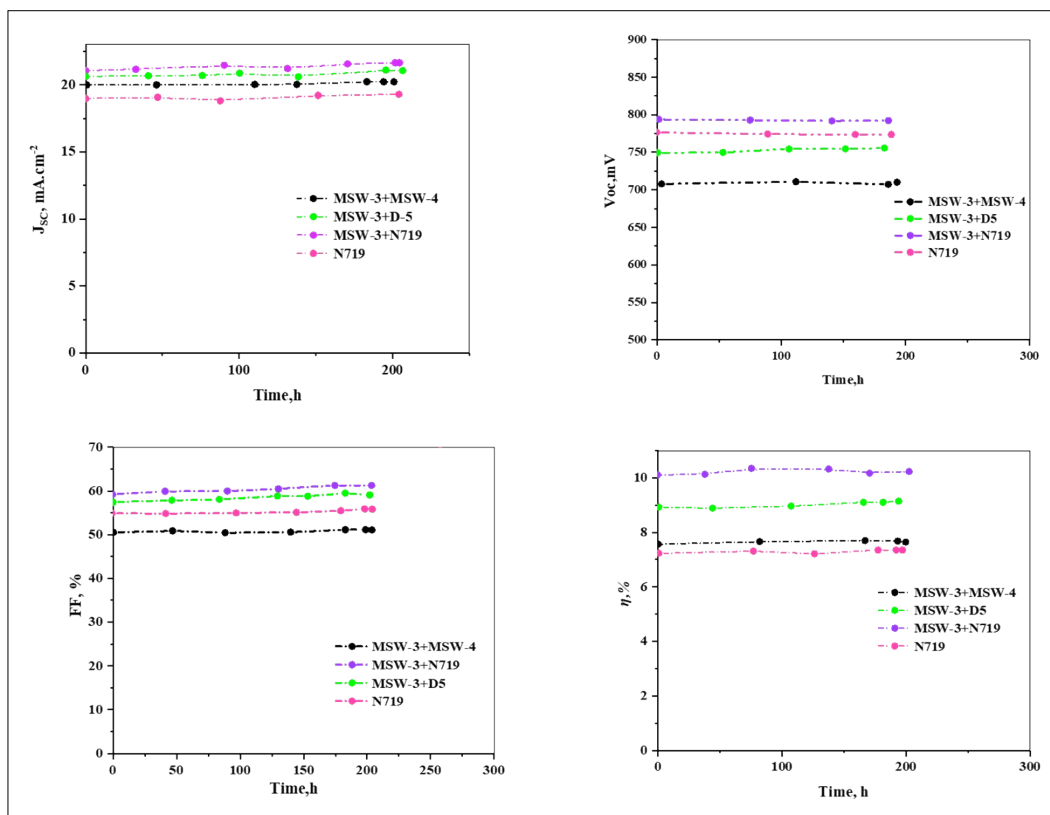


Figure (S12):  $^1\text{H}$  NMR spectrum of MSW-4.



**Figure (S13):  $^{13}\text{C}$  NMR spectrum of MSW-4.**

As shown in Fig. S14, the long-standing photostability of co-sensitizer of MSW-3 with N719, D-5 and MSW-4 dye within DSSCs applications is clear from the sustained performance of the cell. Notably, even after 200 h of illumination, there was no discernible degradation in the initial performance. The excellent stability of sensitizers can be attributed to the inherent stability of the TPA (MSW-4) and ethyl carbazole (MSW-3) unit, which significantly contributes to its superior stability over time



**Fig. S14.** Photovoltaic stability of the device of for co-sensitizers MSW-3, D-5, MSW-4, and N719 measured under sunlight illumination for 200 h.

## 2. Cell preparations and photovoltaic characterizations

### 2.1. TiO<sub>2</sub> electrode preparation

A double-layer TiO<sub>2</sub> photoelectrode (10 + 5)  $\mu\text{m}$  in thickness with a 10  $\mu\text{m}$  thick nanoporous layer and a 5  $\mu\text{m}$  thick scattering layer (area: 0.25 cm<sup>2</sup>) was prepared using a reported method. Fluorine-doped tin oxide (FTO) coated glasses (Nippon Sheet Glass Co., Japan) with a sheet resistance of 8-10 ohm-2 and an optical transmission of greater than 80% in the visible range were screen printed using anatase TiO<sub>2</sub> colloids (particle size  $\sim$  13 nm) obtained from commercial sources (Ti-Nanoxide D/SP, Solaronix). Nanocrystalline TiO<sub>2</sub> thin films were deposited onto the conducting glass by screen-printing, which was then sintered at 500  $^{\circ}\text{C}$  for 1 h. The film thickness was

measured with a Surfcom 1400A surface profiler (Tokyo Seimitsu Co. Ltd.). The electrodes were impregnated with a 0.05 M titanium tetrachloride solution and sintered at 500 °C. The films were further treated with 0.1 M HCl(aq) before examination. The dye solutions of the main sensitizers **MSW-1-4** were prepared in 1:1:1 mixture of acetonitrile, tert-butyl alcohol and dimethyl sulfoxide (DMSO).

For Co-sensitization we used two different concentration of **MSW-3** (0.2 mM) with the 0.2 mM **N719**, **D-5** and **MSW-4** and followed the same processing as above. The electrodes were immersed in the dye solutions and then kept at 25 °C for 20 h to adsorb the dye onto the TiO<sub>2</sub> 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.

## 2.2. Fabrication of dye-sensitized solar cell

Photovoltaic and incident photon-to-current efficiency (IPCE) measurements were made on sandwich cells, which were prepared using TiO<sub>2</sub> coated working electrodes and platinum coated counter electrodes and were sealed using a 40 µm Syrlyn spacer through heating of the polymer frame. The redox electrolyte (Solaronix, Iodolyte HI-30) consisted of a solution of 0.6 M DMPII, 0.05 M I<sub>2</sub>, 0.1 M LiI and 0.5 M TBP in acetonitrile.

## 2.3. Photovoltaic measurements

Photovoltaic measurements of sealed cells were made by illuminating the cell through the conducting glass from the anode side with a solar simulator (WXS-155S-10) at AM 1.5 illuminations (light intensity: 100 mW cm<sup>-2</sup>).

## 2.4. Incident photon to current efficiency (IPCE) conversion

IPCE measurements were made on a CEP-2000 system (Bunkoh-Keiki Co. Ltd.). IPCE at each wavelength was calculated using Equation 1, where  $I_{SC}$  is the short-circuit photocurrent density (mA. cm<sup>-2</sup>) under monochromatic irradiation,  $q$  is the elementary charge,  $\lambda$  is the wavelength of incident radiation in nm and  $P_0$  is the incident radiative flux in W/m<sup>2</sup>.

$$IPCE(\lambda) = 1240 \left( \frac{I_{SC}}{q\lambda P_0} \right) \quad (1)$$

## 2.5. Electrochemical impedance spectroscopy (EIS)

The electrochemical impedance spectra were measured with an impedance analyzer potentiostat (Bio-Logic SP-150) under illumination using a solar simulator (SOL3A, Oriel) equipped with a

450 W xenon lamp (91160, Oriel). EIS spectra were recorded over a frequency range of 100 mHz to 200 kHz at room temperature. The applied bias voltage was set at the  $V_{OC}$  of the DSSCs, with AC amplitude set at 10 mV. The electrical impedance spectra were fitted using Z-Fit software (Bio-Logic).

## 2.6. Cyclic voltammetry

Cyclic voltammetry (CV) was performed in DMF with the electrolyte 0.1 M [TBA][PF<sub>6</sub>] at a scan rate of 50 mV s<sup>-1</sup>. The working electrode used is the Glassy carbon, Pt wire represented the counter electrode and the reference electrode is Ag/Ag<sup>+</sup> in ACN. Fc/Fc<sup>+</sup> was introduced as internal reference.

## 4. Molecular Modeling

Equilibrium molecular geometries of AH-1-5 calculated using the Becke's three parameter hybrid functional, Lee–Yang–Parr's gradient corrected correlation functional (B3LYP) and (6-311g(d, p)) [1, 2, 3, 4]. The geometry optimization calculations were followed by energy calculations using time-dependent density functional theory (TD-DFT) utilizing the energy, functional B3lyp and the basis set 6-311g (d, p). The solvent (DMF) effect was accounted for by using the conductor-like polarizable continuum model (C-PCM), implemented in Gaussian 09.

## References

- [1] G. Melikian, F. Rouessac, C. Alexandre, Synth Commun. 1993, 23, 2631
- [2] A. D. Becke, Phys. Rev. A 1988, 38, 3098.
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- [4] N. Godbout, D.R. Salahub, J. Andzelm, E. Wimmer, Optimization of Gaussian-type basis-sets for local spin-density functional calculations .1. Boron through neon, optimization technique and validation. Can. J. Chem.-Rev. Can. Chim. 1992, 70, 560-571.