

Supporting Information

A Comparative study of the Influence of *N,N'*-dialkyl vs *N,N'*-diaryl based Electron Donors Ancillary Ligands on the Photocurrent and Photovoltage in Dye-Sensitized Solar Cells (DSSCs)

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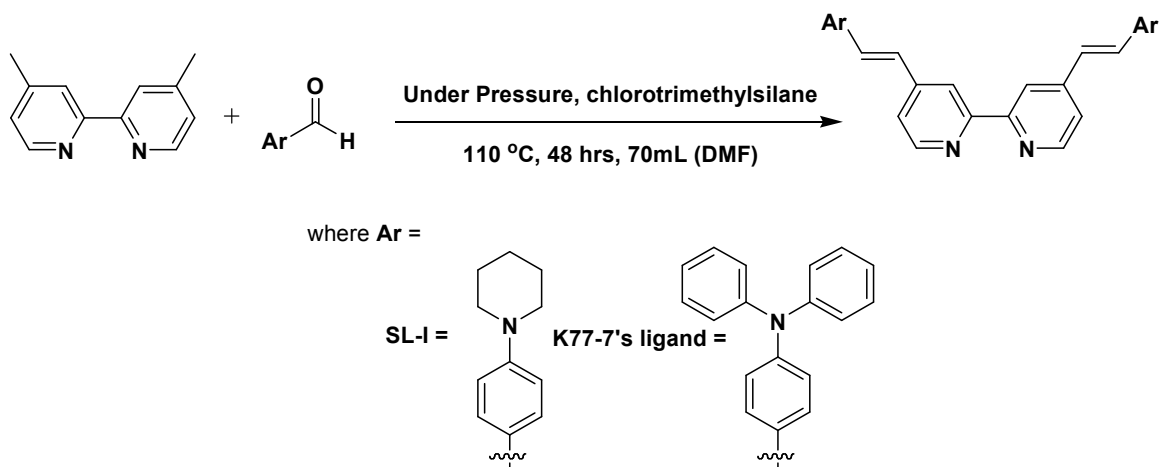
1. Materials:

All the chemicals and solvents were purchased either from Sigma-Aldrich, Fisher Scientific or TCI-America and were used as received. Sephadex LH-20 for purification of dyes was purchased from Fischer Scientific. ESI-MS was recorded on a high resolution mass spectrometer – the Thermo Fisher Scientific Exactive Plus MS, a benchtop full-scan Orbitrap™ mass spectrometer – using Heated Electrospray Ionization (HESI). FT-IR (ATR) spectra were recorded on a Nicolet Nexus 470 FTIR spectrometer (Thermo Scientific, USA) and UV-Visible spectra were measured by using Cary 300 spectrophotometer. Fluorescence and emission decay were recorded at room temperature on a Fluorolog-3 spectrofluorometer (HORIBA Jobin Yvon Inc.). ¹H-NMR spectra were recorded in a Bruker 500 MHz.

2. Synthesis

2.1. Synthesis of Ligands

General procedure for the synthesis of ligands is given in Scheme1. The antenna ligand LS-1 was synthesized in a pressure tube containing 4,4'-dimethyl-2,2'-bipyridine (0.5g, 5mmol), 4-piperidin-1-yl-benzaldehyde (1.05g, 10mmol), 2.5ml of chlorotrimethylsilane (30mmol), and a magnetic stirrer bar in 70ml of anhydrous DMF. Once the tube was closed with the cap the reaction temperature was raised to 110 °C and allowed to run for 48 hours with continuous stirring. During the course of the 48 hours, the color of the reaction mixture changed to dark red to black. At the end of the reaction, the pressure was released after cooling the tube and the solvent was removed using rotary evaporator, and the dark red product was precipitated by the addition of water. Finally vacuum filtration was performed to furnish the antenna ligand which was thoroughly washed with water and n-Haxane in sequence to obtain LS-1. It was then dried for overnight under vacuum to obtain 84% yield. LS-1 was used for next step without further purification.

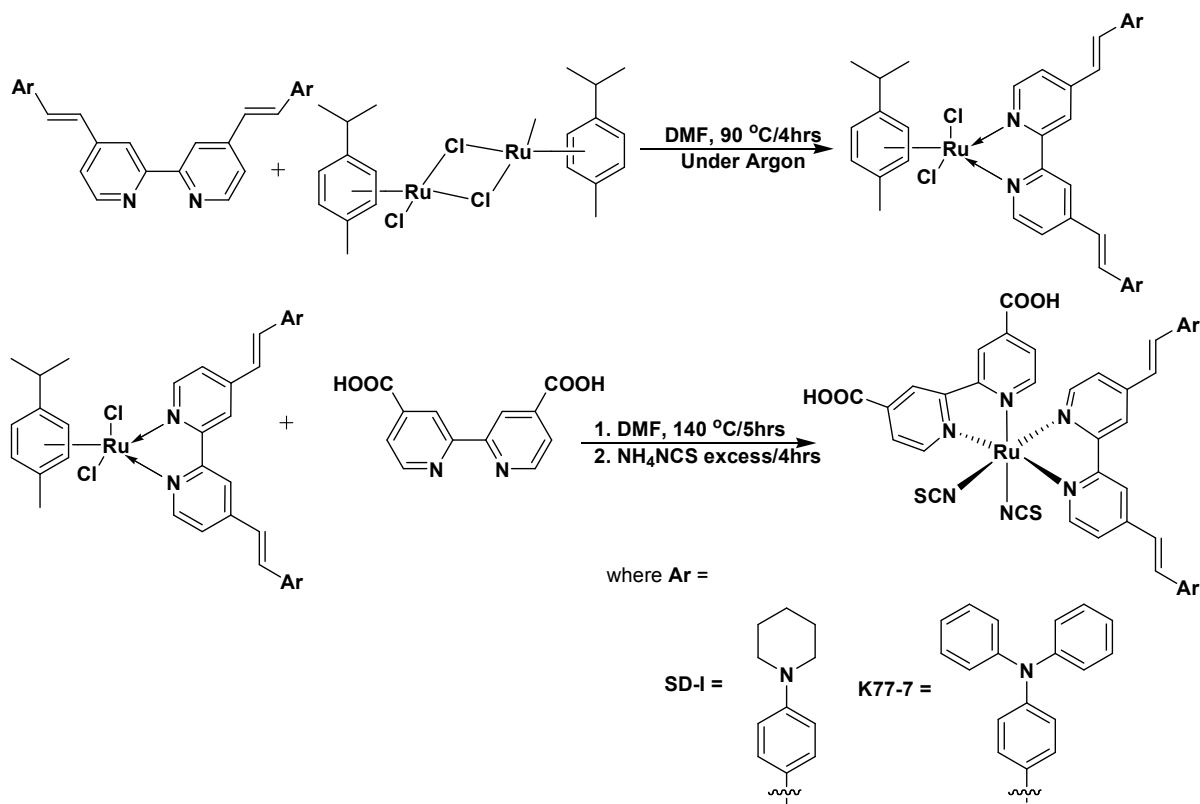


Scheme 1- Synthetic route *N,N'*-dialkyl (LS-1) vs *N,N'*-diaryl (K77-7) electron-donating ancillary ligands

2.2. Synthesis of Complexes

A general procedure for the synthesis of dyes is shown in Scheme 2. The synthesis of SD-1 was carried out according to one-pot three-step reaction procedure. The reactions were carried out in a 250 ml reaction flask equipped with a condenser and magnetic stirrer bar under argon atmosphere. The flask was charged with dry DMF, dichloro-(*p*-cymene)-Ruthenium (II) dimer (0.15g, 0.2mmol) and LS-1 (0.35g, 0.4mmol). The reaction mixture was stirred at 90°C for 4h. Then, 2,2'-bipyridyl-4,4'-dicarboxylic acid was added (0.1g, 0.4mmol) and the temperature was raised to 140°C and allowed to run for 5 hours, the color of reaction mixture changed from dark yellow to dark green in this step. After the 5 hours, excess of NH₄NCS (0.3g) was added to the reaction mixture, and the reaction mixture was allowed to run for extra 4h at 140°C. The reaction mixture was cooled down to room temperature and DMF was removed using a rotary evaporator. Ice was added to the flask and the insoluble solid was vacuum filtered and washed with de-ionized water and diethyl ether. The black color solid product was dried overnight and 0.5g (88%) of crude product was collected. After drying, SD-1 was dissolved in methanol with the addition of Tetrabutylammonium hydroxide (TBAOH). SD-1 was run through the column containing Sephadex LH-20 for three times. The main band was collected and acidified using 0.1M HCl to reduce the pH to 2.0 and allowed to precipitate for 20 hours in the refrigerator, precipitate was filtered, washed with plenty of de-ionized water to bring pH to neutral. The pure dye was then dried overnight and collected (0.25g, 45%). The pure dye was then further analyzed

by ATR/FT-IR, ^1H NMR and high resolution mass spectrometry. SD-1 was characterized by ESI high resolution MS and ^1H NMR, which is given in the coming sections.



Scheme 2- Synthetic route to sensitizers SD-1 and K77-7

2.3. Purification of Ru-complexes

SD-1 was purified on a column using Sephadex LH-20 as the stationary phase and pure methanol as the mobile phase. The crude dye of SD-1 was dissolved in a mixture of methanol and TBAOH and loaded on Sephadex LH-20, and the compound was eluted using clean methanol. The main band was collected and acidified using 0.1M HCl until the pH dropped to 2.0, and the acidified solution was kept in a refrigerator for 48 hours. Then, the precipitates were filtered, washed with plenty of de-ionized water to remove remaining HCl. The same purification procedure was repeated three times in order to obtain SD-1 in the pure form. Complexes K77-7 was also purified using the same procedure.

3. Analytical Measurements:

3.1 UV-Vis Spectra

UV-Visible spectra were measured by using Cary 300 spectrophotometer. A clean DMF solution of 2×10^{-5} M of each dye was prepared and spectra were recorded using 1 cm path length quartz cell. Molar absorptivity was measured by using Beer-lambert law:

$$\epsilon = A / c l$$

3.2. Fluorescence Spectra

Fluorescence and emission decay were recorded at room temperature on a Fluorolog-3 spectrofluorometer (HORIBA Jobin Yvon Inc).

3.3. Fourier-Transform Infra-Red Spectroscopy

Attenuated Total Reflectance-Fourier Transform Infra-Red (ATR/FT-IR) spectra were recorded on a Thermo Nicolet Nexus 470 FTIR Spectrophotometer (Thermo Scientific, USA) with Omnic 7.2 software. An average of 32 scans were used at a resolution of 4cm^{-1} . Fig. S1 shows FT-IR of **SD-1**: 2102.0 cm^{-1} (-NCS stretch, N-bonded isomer, very strong); 1719.3 cm^{-1} (C=O stretch of -COOH) SD-1.

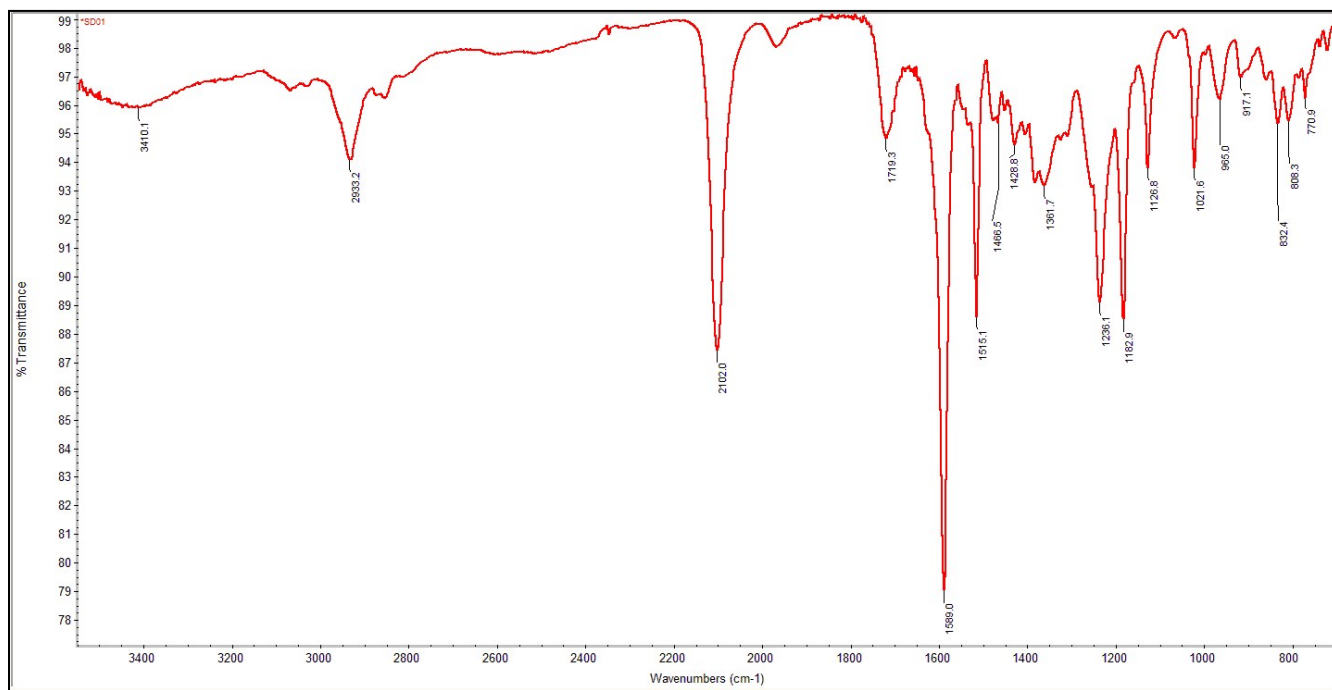


Figure S1. ATR/FTIR of SD-1

3.4. Mass Spectroscopy

The Mass Spectrometry Analysis was carried out on a high resolution mass spectrometer – the Thermo Fisher Scientific Executive Plus MS, a benchtop full-scan Orbitrap™ mass spectrometer – using Heated Electrospray Ionization (HESI). Samples were dissolved in methanol and analyzed via syringe injection into the mass spectrometer at a flow rate of 15 $\mu\text{L}/\text{min}$.

The sample was prepared in methanol and analyzed via syringe injection. The Spray voltage was set at 2.0 kV and results from 95 scans for SD-1 were averaged. The ESI-MS pattern for SD-1 is shown in Figure S2.

153064_SD-1 #2-96 RT: 0.01-0.43 AV: 95 NL: 1.19E7
T: FTMS - p ESI Full ms [500.00-1500.00]

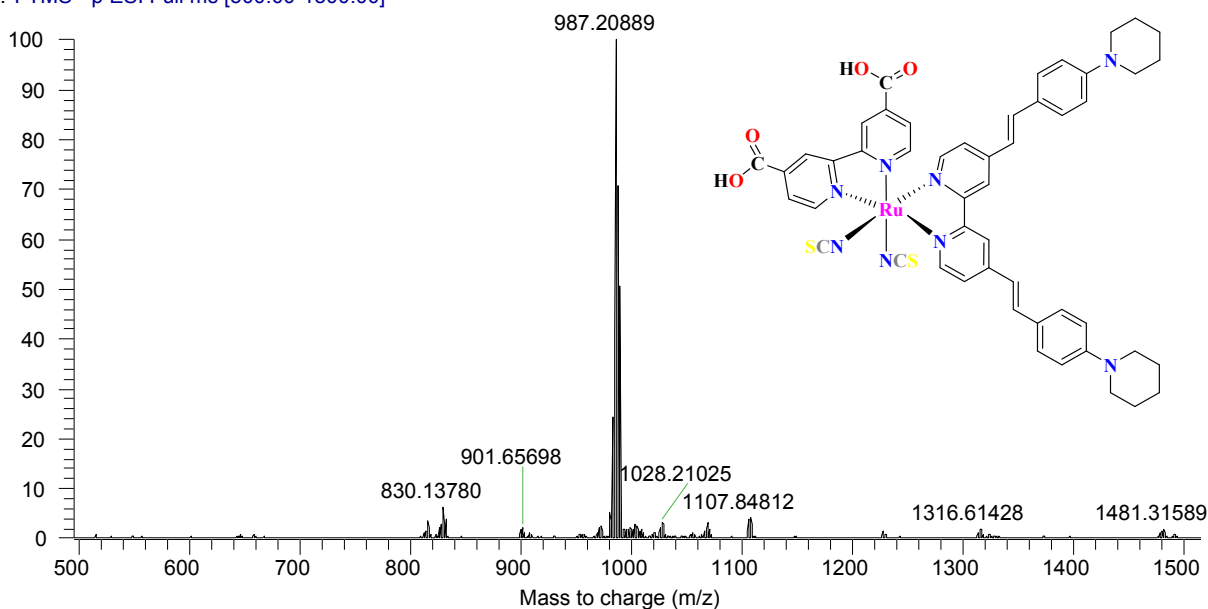


Figure S2 ESI mass spectrum of SD-1, $[\text{M} + \text{H}]^+$; Theo. $\text{M}/\text{Z} = 987.20542$, Found. $\text{M}/\text{Z} = 987.20889$, Error = 3.522 ppm.

3.5. ^1H -NMR spectroscopy

^1H -NMR spectra were recorded in a Bruker 700 MHz spectrometer. Splitting patterns reported here are: s (singlet), d (doublet), dd, (double-of-doublet), t (triplet) and m (multiplet). Chemical shifts (δ) and coupling constants (J) are reported in ppm and Hertz (Hz), respectively.

LS-1: ^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ 8.62 (d, $J=5.2$, 1H), 8.49 (s, 1H), 7.59 (d, $J=5.3$, 1H), 7.59 – 7.47 (m, 3H), 7.15 (d, $J=16.4$, 1H), 3.25 (t, $J=5.0$, 4H), 1.07 – 1.01 (m, 6H).

SD-1: ^1H NMR (500 MHz, DMSO-d_6): δ 8.98 – 8.93 (m, 2H), 8.63 (s, 1H), 7.61 (d, $J=10.5$, 2H), 7.52 (d, $J=15.3$, 2H), 7.13 – 7.04 (m, 3H), 6.99 (s, 1H), 6.88 – 6.81 (m, 1H), 3.23 – 3.12 (m, 4H), 1.31 – 1.25 (m, 6H).

3.6. Cyclic Voltammetry

The experimental HOMO and $E_{0,0}$ energy values for SD-1 and K77-7 were measured by cyclic voltammetry and the experimental absorption/emission point of overlap, respectively. The onset of oxidation were measured in DMF with 0.1 M [TBA][PF₆] and with a scan rate of 50 mV/s. Glassy carbon was used as the working electrode (WE), Pt wire as counter electrode and Ag/AgCl in acetonitrile was used as the reference electrode. It was calibrated with Fc/Fc⁺ as an internal standard and converted to NHE by addition of 0.63 V. Figures 3S (a,b) and 4S (a,b) show the HOMO energies of SD-1 and K77-7 respectively.

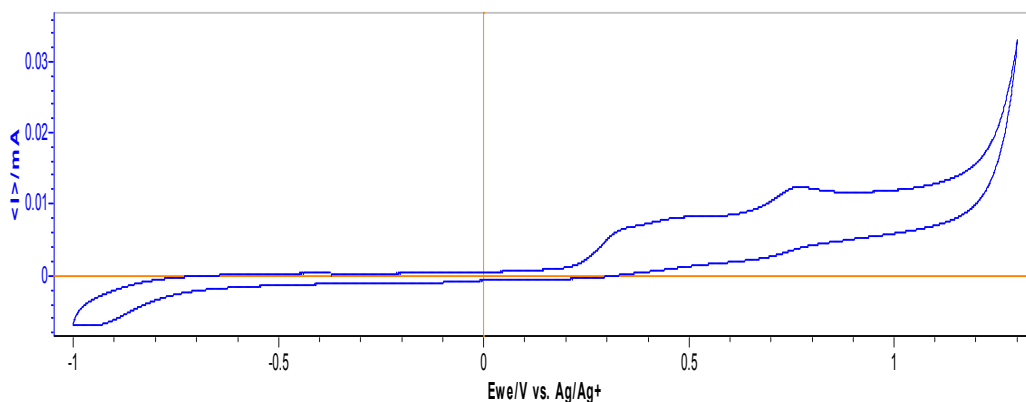


Fig. 3S: CV graph of SD-1

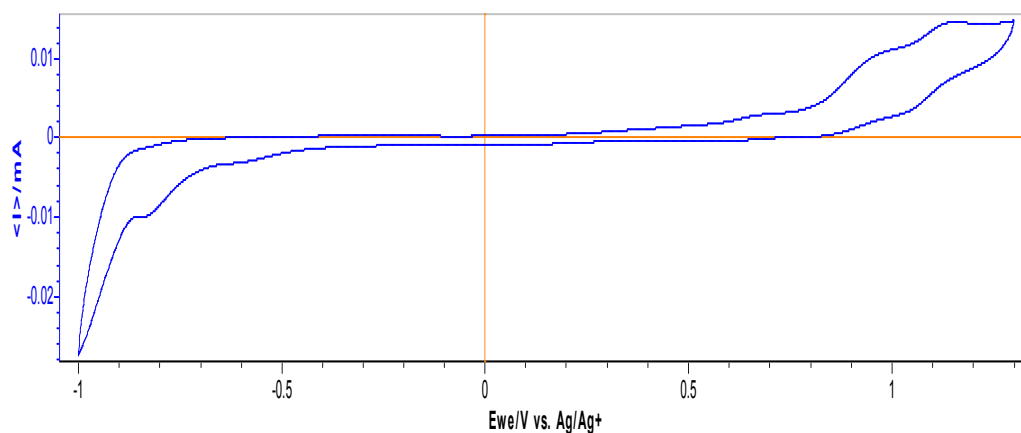


Fig. 4S: CV graph of K77-7

4. CELL PREPARATIONS AND PHOTOVOLTAIC CHARACTERIZATIONS

4.1. TiO₂ Electrode Preparation

The photo-anodes composed of nanocrystalline TiO₂ and counter electrodes were prepared using literature procedures. Fluorine-doped tin oxide (FTO) coated glasses (2.2 mm thickness, sheet resistance of 8 Ω/cm², TEC 8, Pilkington) were washed with detergent, water, acetone and ethanol, sequentially. After this FTO glass plates were immersed into a 40 mM aqueous TiCl₄ solution at 70 °C for 30 min and washed with water and ethanol. Thin layer (8-12 nm thick) of TiO₂ (Solaronix, Ti-Nanoxide T/SP) was deposited (active area, 0.18 cm²) on transparent conducting glass by squeegee printing. After drying the electrodes at 500 °C for 30 min, scattering layer (5 μm thick) TiO₂ particles (Solaronix, Ti-Nanoxide T/SP) were printed. The TiO₂ 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 TiO₂ electrodes were treated with 40 mM aqueous solution of TiCl₄ 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 into the dye solution. The dye solutions (0.3 mM) were prepared in 1:1:1 acetonitrile, tert-butyl alcohol and DMSO. Deoxycholic acid was added to the dye solution as a co-adsorbate at a concentration of 40 mM. The electrodes were immersed in the dye solutions with active area facing up and then kept at 25 °C for 20 h to adsorb the dye onto the TiO₂ surface.

For preparing the counter electrode, pre-cut TCO glasses were washed with water followed by 0.1 M 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 mins.

4.2. Fabrication of Dye-Sensitized Solar Cell

The dye sensitized TiO₂ electrodes were sandwiched with Pt counter electrodes and the electrolyte (Solaronix, Iodolyte AN-50) was then injected into the cell, while the two electrodes were held together with the clips.

4.3. 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 intensities: 100 mW cm⁻²).

4.4. Incident Photon to Current Efficiency (IPCE) Conversion

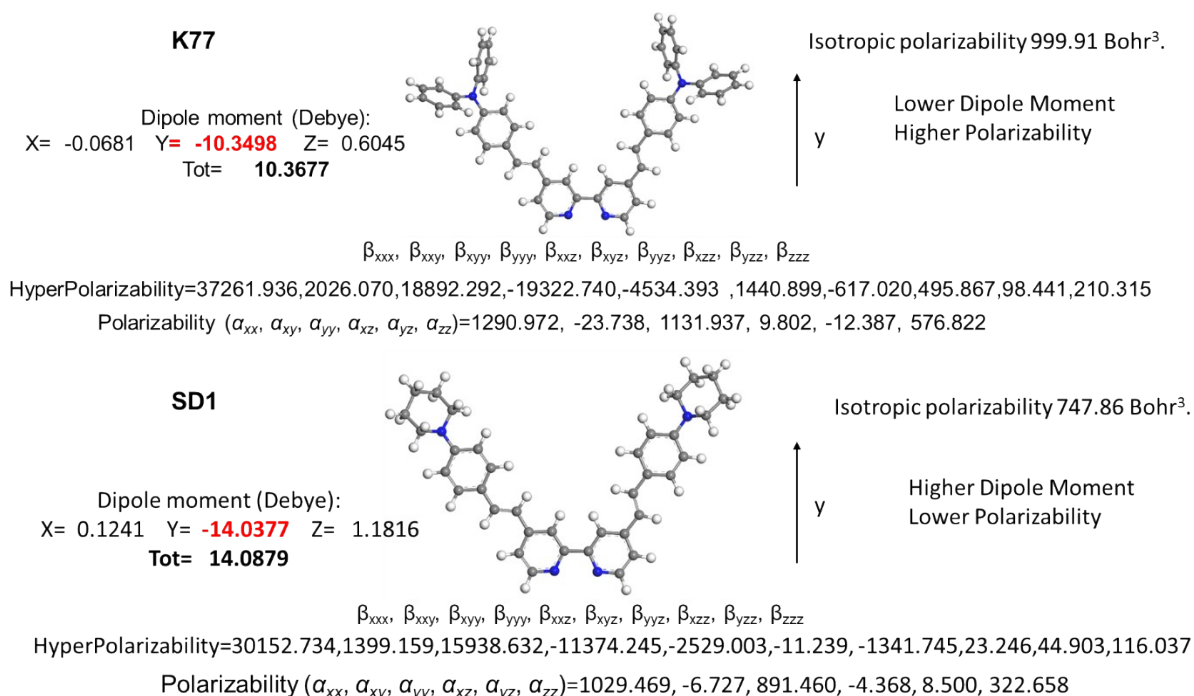
IPCE measurements were made on a CEP-2000 system (Bunkoh-Keiki Co. Ltd.). IPCE at each wavelength was calculated using Equation 1, where ISC is the short-circuit photocurrent density (mAcm⁻²) under monochromatic irradiation, q is the elementary charge, λ is the wavelength of incident radiation in nm and P₀ is the incident radiative flux in Wm⁻².

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

The incident photon-to-current conversion efficiency was plotted as a function of wavelength.

4.5. Dipole Moment and Polarizability

A



B

K77
Dipole moment (Debye):
X= **-12.4888** Y= 18.2623 Z= 20.8290 Tot= **30.3864**
 $\alpha_{xx}, \alpha_{xy}, \alpha_{yy}, \alpha_{xz}, \alpha_{yz}, \alpha_{zz}$
Polar=1974.130,27.467,1542.344,22.671,-19.169,1128.265
Isotropic polarizability 1548.25 Bohr³.

SD1
Dipole moment (field-independent basis, Debye):
X= **-17.5886** Y= 18.7709 Z= 21.7351 Tot= **33.6767**
 $\alpha_{xx}, \alpha_{xy}, \alpha_{yy}, \alpha_{xz}, \alpha_{yz}, \alpha_{zz}$
Polar=1679.250,76.065,1306.383,-58.2842,-4.395,882.571
Isotropic polarizability 1289.40 Bohr³.

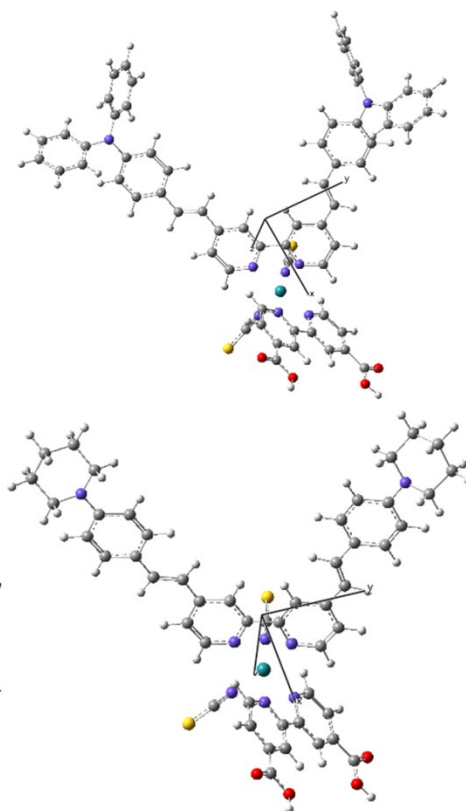
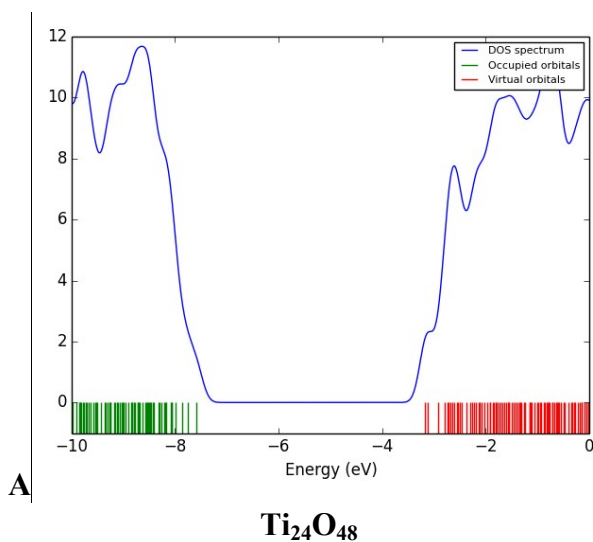


Fig. 5S. Dipole Moment, Polarizability and Hyperpolarizability for a)Electron Donating group of SD1 and K77 b) SD1 and K77.

4.7. Density of States (DOS)



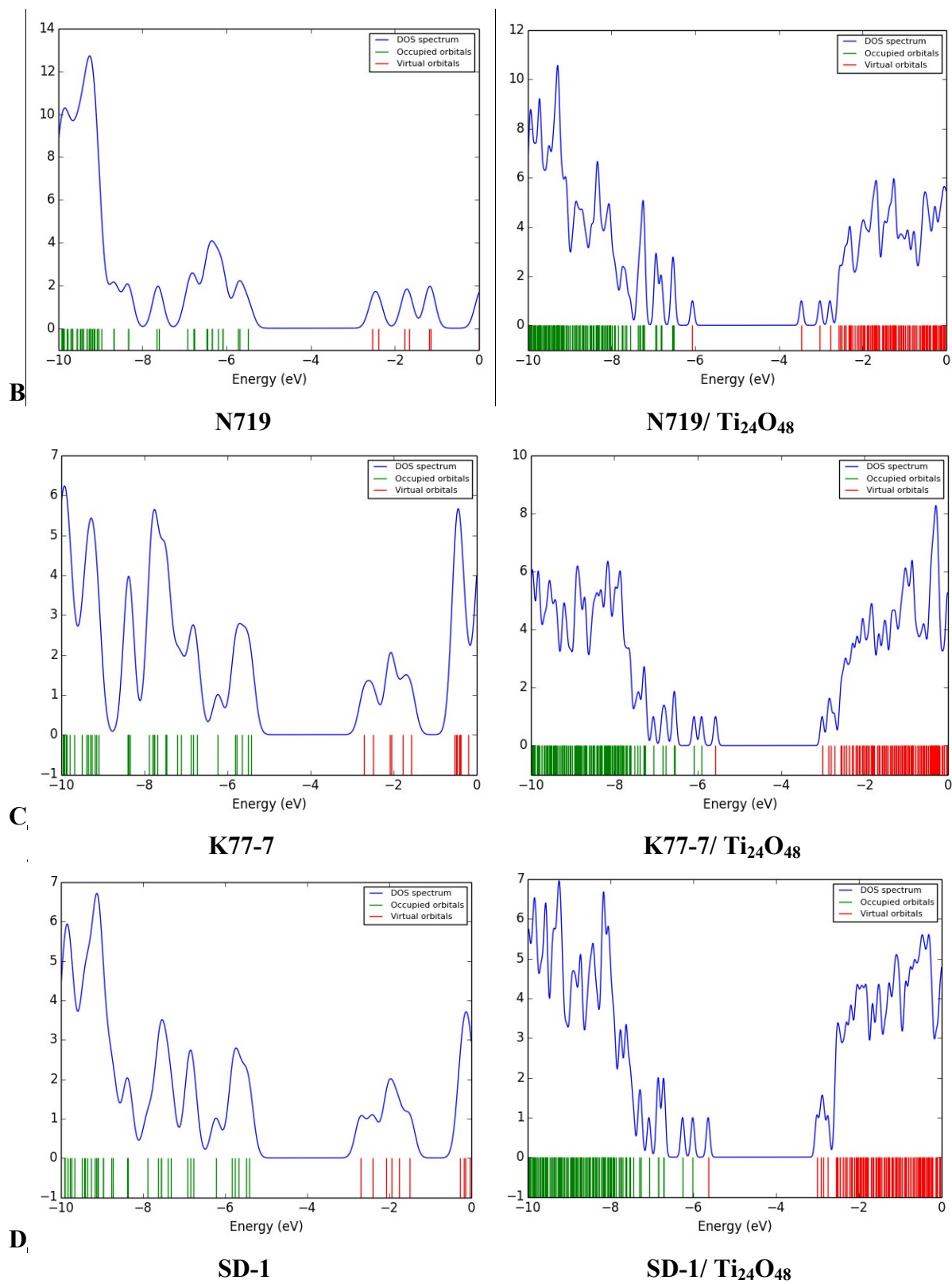


Figure S6. Density of states for **A)** TiO₂ cluster, **B)** N719 and its complex with Ti₂₄O₄₈ cluster, **C)** K77-7 and its complex with Ti₂₄O₄₈ cluster, **D)** SD-1 and its complex with Ti₂₄O₄₈ cluster.