

Supporting Information

Thiocyanate-free ruthenium(II) sensitizers with a bi-imidazole ligand in dye-sensitized solar cells (DSSCs)

Saba Ashraf^{a,b}, Javeed Akhtar^c, Humaira M. Siddiqi^a, Ahmed El-Shafei^{*b}

^a Department of Chemistry, Quaid-I-Azam University, Islamabad 45320, Pakistan

^b Department of Textile Engineering, Chemistry & Science, North Carolina State University, Raleigh, NC, 27695, USA

^c Department of Physics, Polymers & Materials Synthesis Lab (PMS), COMSATS, Institute of Information Technology, Chak Shahzad Islamabad, Pakistan

(* Corresponding Authors: Ahmed_El-Shafei@ncsu.edu)

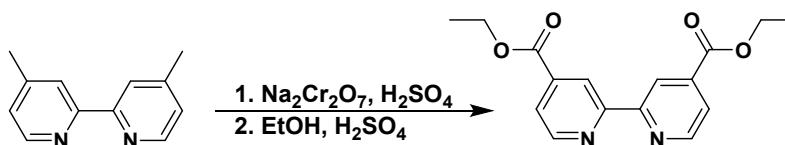
1. Materials:

All the chemicals and solvents were purchased either from Sigma-Aldrich, Fisher Scientific or TCI-America and were used as received. Silica gel (230-400 mesh, Grade 60 Å) for purification of dyes was purchased 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 Electrospray Ionization (ESI). 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 was 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 diethyl 2,2'-bipyridine-4,4'-dicarboxylate

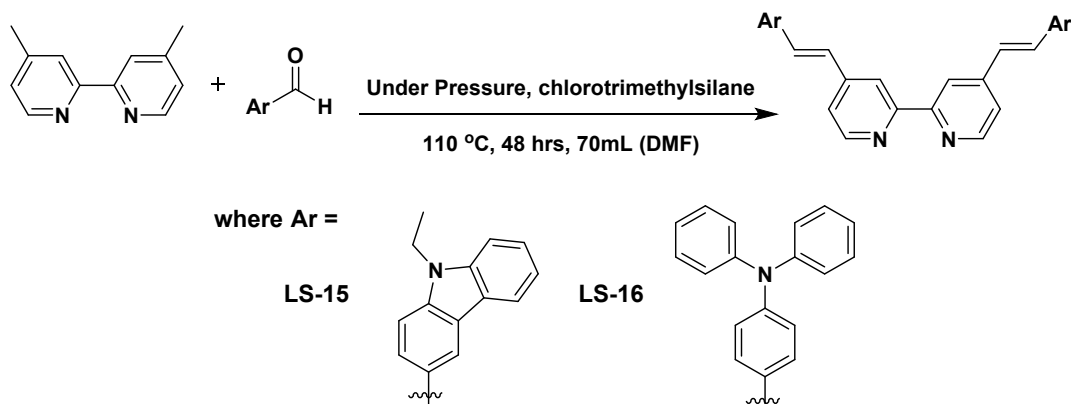
2,2'-Bipyridinyl-4,4'-dicarboxylic acid was synthesized according to literature.¹ In a three neck round bottom flask 4,4'-Dimethyl-2,2'-bipyridine (3 g, 16.3 mmol) was gradually added to a sodium dichromate (Na₂Cr₂O₇) solution (10.9g, 36.5 mmol) in conc. sulfuric acid (45 ml) and stirred for 30 min at 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. NaOH. The product was crystallized by slowly acidifying the solution with 10 % aq. HCl at a 2 pH. The precipitation and acidification process was repeated three times to obtain the white chromium free precipitates of 2,2'-Bipyridinyl-4,4'-dicarboxylic acid (2.56g, 90%). Esterification of 2,2'-Bipyridinyl-4,4'-dicarboxylic acid was carried out by dissolving 2.5g of 2,2'-bipyridinyl-4,4'-dicarboxylic acid and 60ml of absolute ethanol in 50g of conc. H₂SO₄ at 85 °C, for 10 hours., which was then cooled by pouring on ice cold water, which was further neutralized with 25% aq. NaOH and the precipitate was filtered out and thoroughly washed with deionized water which was used without further purification after drying overnight (2.59g, 84%).



Scheme S1. Synthetic route for diethyl 2,2'-bipyridine-4,4'-dicarboxylate

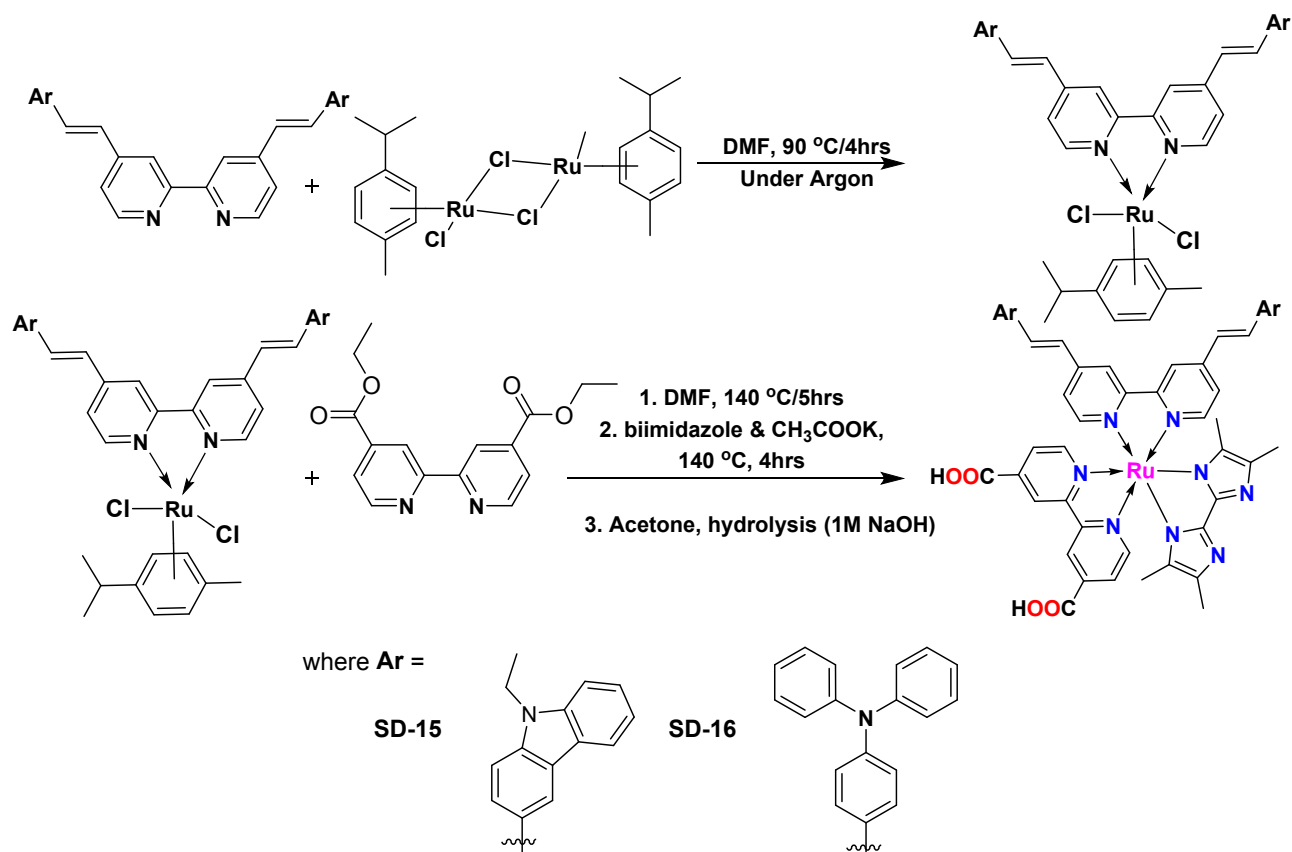
2.2 Synthesis of ligands and sensitizers (SD-15 & SD-16)

The antenna ligands were first synthesized by following the exact similar method reported previously in 75% yield as shown in scheme S2. These antenna ligands were further used for next step without further purification.



Scheme S2. Synthetic route for ligands

Schematic procedure for the synthesis of SD-15 and SD-16 is shown in Scheme S3 and synthesized according to already reported procedure.² All the reactions were carried out in the dark under argon. The synthesis was carried out in a one-pot three-step reaction. The reactions were carried out in a reaction flask equipped with a condenser and magnetic stirrer bar. The flask was charged with anhydrous DMF, dichloro-(p-cymene)-Ruthenium (II) dimer (0.13mmol) and antenna ligand (0.27mmol). The reaction mixture was stirred at 90 °C for 4h. Then, diethyl 2,2'-bipyridine-4,4'-dicarboxylate was added (0.08g, 0.26mmol) and the temperature was raised to 145°C and allowed to run for 4 hours. After the 4 hours, 0.175g (1.6mmol) of potassium acetate was added followed by excess (1.26mmol) of 4,4',5,5'-tetramethyl-1*H*,1'*H*-2,2'-*bi*-imidazole, 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 deionized water and diethyl ether. The black color solid product was dried overnight and the mixture of products was purified by silica gel column chromatography (ethyl acetate/CH₂Cl₂ 1:20) to give a black solid (70 mg, 42%).



Scheme S3. Synthetic route for SD-15 and SD-16

Next, the solid product (70 mg, 0.006 mM) was dissolved in acetone (40 mL) and 1 M NaOH solution (0.825 mL). The solution was heated to 60 °C under argon for 3 h. After completing the hydrolysis, the solvent was removed under vacuum and the residue was dissolved in deionized water (10 mL). The solution was acidified using 0.1M HCl to reduce the pH to 2.0 and allowed to precipitate for 48 hours in refrigerator, after that precipitate was filtered, and washed with plenty of de-ionized water to bring pH to neutral. The pure dye was then dried overnight and collected (58 mg, 86%).

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 spectra was 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} .

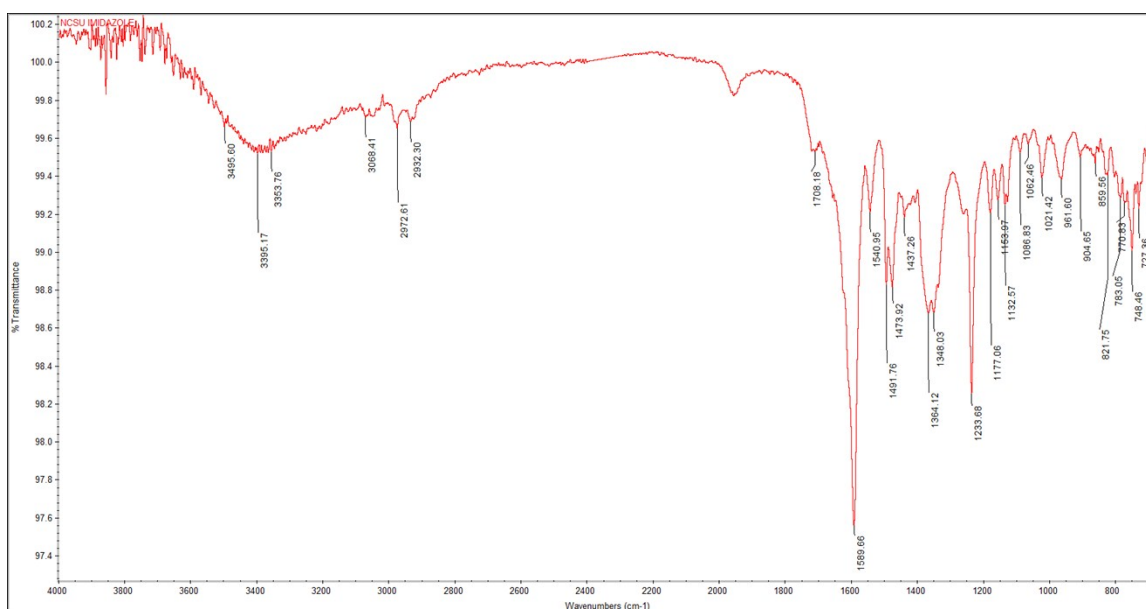


Fig. S1 FTIR of SD-15

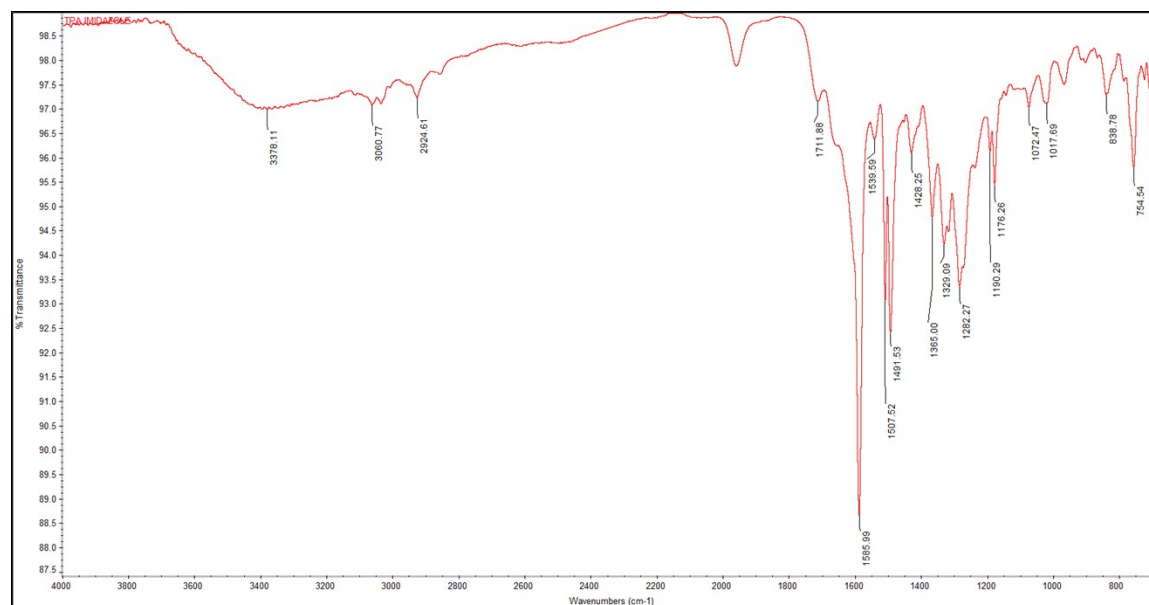


Fig. S2 FTIR of SD-16

3.4. $^1\text{H-NMR}$ spectroscopy

$^1\text{H-NMR}$ 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.

3.5. Cyclic Voltammetry

The experimental HOMO and E_{0-0} energy values for SD-15 and SD-16 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 and 4S show the HOMO energies of SD-15 and SD-16 respectively.

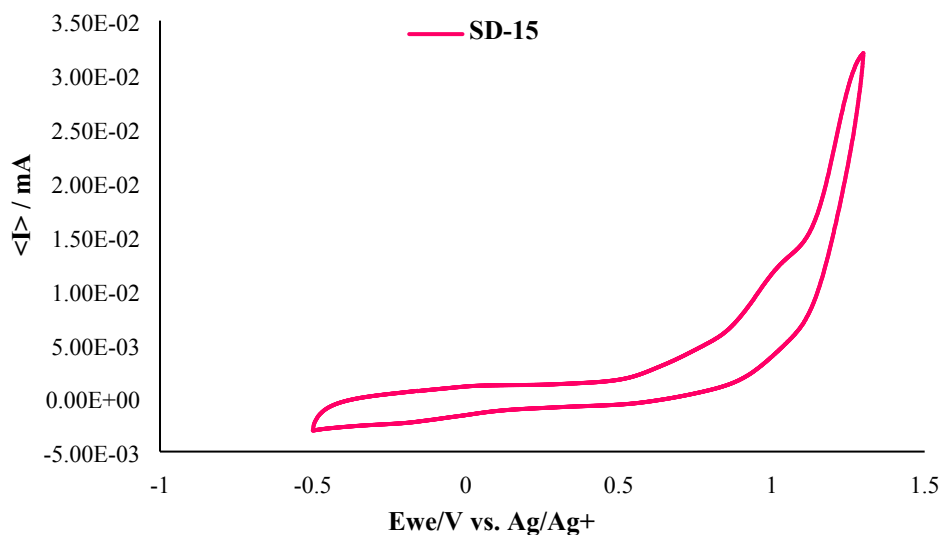


Fig. S3 CV graph of SD-15

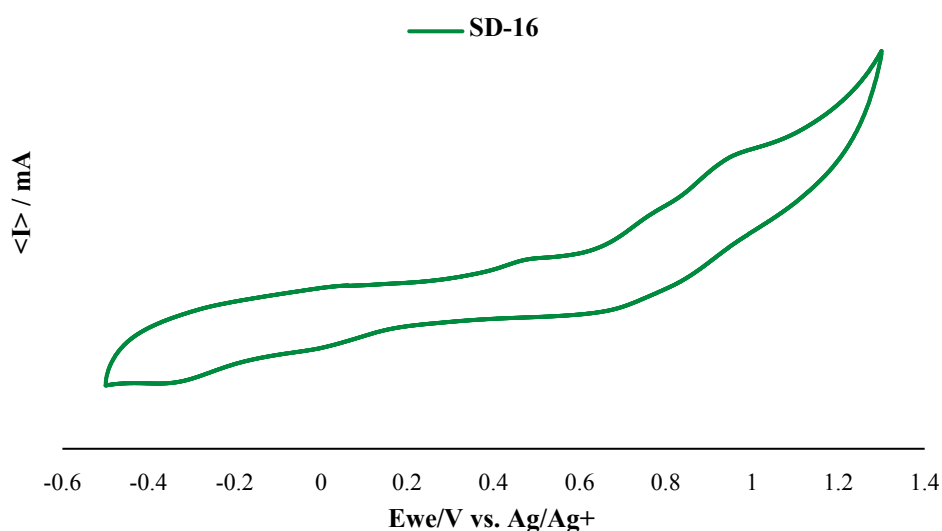


Fig. S4 CV graph of SD-16

4. CELL PREPARATIONS AND PHOTOVOLTAIC CHARACTERIZATIONS

4.1. TiO_2 Electrode Preparation

The photo-anodes composed of nanocrystalline TiO_2 and counter electrodes were prepared using literature procedures.^{3,4} Fluorine-doped tin oxide (FTO) coated glasses (2.2 mm thickness, sheet resistance of $8 \Omega/\text{cm}^2$, TEC 8, 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 deionized water and absolute ethanol. Thin layer (12 mm thick) of TiO_2 (Solaronix, Ti-Nanoxide T/SP) was deposited (active area, 0.18 cm^2) on transparent conducting glass by squeegee printing. After drying the electrodes at 500 °C for 30 min, scattering layer (5 mm thick) TiO_2 particles (Solaronix, Ti-Nanoxide T/SP) were printed. 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 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 TiO_2 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 TiO_2 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. Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance spectra were measured with an impedance analyzer (Solartron Analytical, 1255B) connected with a potentiostat (Solartron Analytical, 1287) under illumination using a solar simulator (WXS-155S-10: Wacom Denso Co. Japan). EIS spectra were recorded over a frequency range of 102 to 106 Hz at 298 K. The applied bias voltage and AC amplitude were set at the V_{oc} of the DSCs. The applied bias voltage and AC amplitude were set at the V_{oc} of the DSCs. The electrical impedance spectra were characterized using Z-View software (Solartron Analytical).

5. References

- 1 A. El-Shafei, M. Hussain, A. Islam and L. Han, *J. Mater. Chem. A*, 2013, **1**, 13679.
- 2 H. Cheema, A. Islam, L. Han and A. El-Shafei, *Dye. Pigment.*, 2015, **120**, 93–98.
- 3 M. Hussain, A. El-Shafei, A. Islam and L. Han, *Phys. Chem. Chem. Phys.*, 2013, **15**, 8401–8.
- 4 H. Cheema, L. Ogbose and A. El-Shafei, *Dye. Pigment.*, 2015, **113**, 151–159.