



Synthesis, photophysical properties and DFT studies of *N*-aryl-2-cyano-3-(4-(diphenylamino)phenyl)acrylamides for DSSCs

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Abstract: Herein, we report develop, synthesis of new co-sensitizers of D- π -A architected design containing triphenylamine core as an efficient donor attached to acrylamide moiety as an anchoring group and studies the ability of the novel co-sensitizers in the application of DSSC. From their UV-vis absorption spectra all the dyes **AR1-3** were red-shifted with maximum molar extinction co-efficient compared to standard **TPA** dye, which can be attributed to extended conjugation within the molecular structure. **AR-3** displayed the maximum molar extinction co-efficient of 9.29×10^5 M due to the favorable charge transfer between the donor and acceptor. Moreover, DFT / TD-DFT studies were performed for the dyes **AR1-3** and were in a good agreement with the experimental data. Finally, theoretical calculation confirmed the ability of new dyes as co-sensitizers for dye-sensitized solar cell (DSSC).

keywords: Co-sensitizers; Dye sensitized solar cells (DSSCs); acrylamide; DFT.

1. Introduction

Dye-sensitized solar cell (DSSC) is considered as a third generation of organic photovoltaic since discovered by O'Regan and Gratzel in 1991 [1]. The merits of using DSSC compared to another photovoltaics are low cost, simple preparation methods and multi-design structures [2]. Typical DSSC consist of five main components: working electrode, semiconductor (usually TiO₂), liquid electrolyte (Iodolyte), photosensitizer (dye molecule) and counter electrode [3]. The photosensitizer or the dye molecule plays a significant role for the cell as its responsible for absorption of the incident light to produce electrons. An ideal photosensitizer should have some requirements to be used as DSSC; (1) the lowest an occupied molecular orbital (LUMO level) should be above the conduction band of the electrolyte for electron injections. (2) The highest occupied molecular orbital (HOMO level) of the dye should be below the redox potential of the electrolyte for the dye regeneration. (3) The dye should have special anchoring moiety for strong binding to the TiO₂ edge, the most efficient anchoring moiety is carboxylic group [4-7]. DSSC can be classified in two main categories, first is metal free dye in which dye

structure consist of organic compound. The second category is metal dye where the dye structure contain metal. The most efficient metal DSSCs are those consist of Ru (II) complexes [8]. The main feature of metal dyes is a broad absorption spectrum so, they can absorb most of the incident light. Among sensitizers, **N719** and **N3** considered as a standard benchmark both in industry and academia with an overall efficiency of greater than 10 %. However, they have some drawback of the low molar extinction co-efficient [9]. On the other hand, organic metal free dyes characteristics with their high molar extinction coefficient but, low absorption spectrum. There were many design strategies for organic metal free dyes. One of the most common strategies is D- π -A architecture [10-12]. Interestingly, triphenylamine based dyes has been widely accepted as an efficient DSSC due to their thermal stability and superior photochemical properties [13]. Researcher over the globe focused on developed new techniques and methods for increasing the photovoltaic performance of the fabricated dyes.

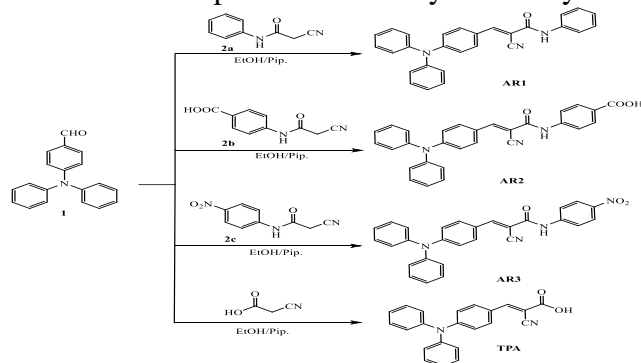
Among these, co-sensitization is an efficient technique with high harvesting ability which

depends on combining both Ru(II) dyes and metal free dyes in the same fabricated cell to have the merits of the two categories. Our group have design new dyes as a co-sensitizer with high photovoltaic performance compared to N-719 dye [14-20]. Herein, in this research we synthesis and design new co-sensitizer (**AR 1-3**) with D- Π -A architecture containing triphenylamine core as a donating group attached to acrylamide moiety as an anchoring group (**Scheme 1**).

2. Results and Discussion

2.1. Synthesis and structure characterization

The synthetic pathway of three novel metal free dyes **AR1-3** possessing triphenylamine moiety as a strong donating moiety was outlined in **Scheme 1**. In the first step, our starting compound 4-formyltriphenylamine (**1**) was synthesized in good yield by formylation of triphenylamine according to the reported Vilsmeier-Hack reaction protocol [13]. The cyanoacetanilides derivatives **2a-c** were prepared in a high yield *via* cyanoacetylation of their corresponding primary aromatic amines with 1-cyanoacetyl-3,5-dimethylpyrazole. Cyanoacetanilides **2a-c** has been synthesized according to literature procedure by refluxing aniline, 4-aminobenzoic acid and/or 4-nitroaniline with 1-cyanoacetyl-3,5-dimethylpyrazole in dioxane [21,22]. The target dyes **AR1-3** were obtained in good yield by application of Knoevenagel condensation between 4-formyltriphenylamine (**1**) with cyanoacetanilide compounds **2a-c**. The condensation reaction was carried out in boiling ethanol in the presence of drops piperidine as a basic catalyst to afford the corresponding cyanoacetanilide based-dyes **AR1-3** (**Scheme 1**). The skeleton of co-sensitizers **AR1-3** was secured based upon distinct analytical analyses.



Scheme 1: Synthesis of co-sensitizers **AR1**, **AR2** and **AR3**.

Firstly, IR spectrum of co-sensitizer **AR1** showed absorption bands due to N-H, C \equiv N and C=O at 3328 cm^{-1} , 2210 cm^{-1} , 1679 cm^{-1} , respectively. In ^1H NMR spectrum of **AR1**, we observed the expected signals of aromatic protons as doublet, triplet and multiplet in the range of δ 6.90 – 7.88 ppm, in addition the olefinic proton (C=CH) resonated δ 8.11 ppm. In addition, singlet signal due to NH proton at δ 10.19 ppm. Finally, the structure was confirmed by its mass spectroscopic data.

2.2. Photophysical properties

The UV-vis absorption spectra of the novel co-sensitizers (**AR1-3**) was recorded in DMF at standard concentration (2×10^{-5} M) compared to standard **TPA** dye (**Figure 1**).

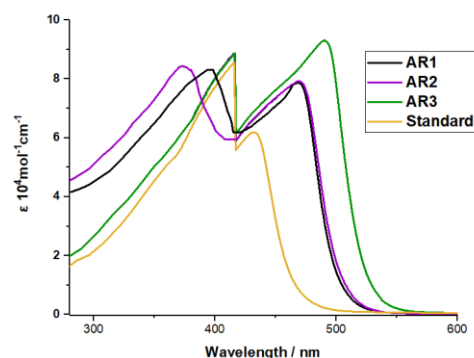


Fig. 1: Absorption spectra of **SA1-6** in DMF solution (2×10^{-5} M).

All the dyes **AR1-3** showed two distinctive absorption bands, at the range of 300-420 nm for π to π^* electronic transition, in addition to second peak at a region from 430 to 530 nm which are assigned for internal charge transfer from the donor moiety (triphenylamine) to the acceptor moiety (acrylamide). Interestingly, all novel co-sensitizers showed a bathochromic shift with maximum higher molar extinction co-efficient compared to standard dye (**TPA**) [23] that attributed to the higher conjugated system of **AR1-3** beside the superior accepting function of acrylamide moiety.

Among dyes **AR1-3**, **AR3** showed the highest molar extinction coefficient of 9.29×10^5 M because of the presence of Nitro (NO_2 group) which is considered as strong acceptor moiety compared to -H in **AR1** and -COOH group in **AR2**. Furthermore, band energy gap (E0-0) of all dyes **AR1-3** was measured from their absorption spectrum via determination of

the lowest energy onset and their corresponding data was summarized in **Table 1**.

Table 1: Optical Data for **AR1-3** and **TPA**

Dye	$\lambda_{\text{max}}/\text{nm}$	$\epsilon/10^4\text{M}^{-1}\text{cm}^{-1}$	$\lambda_{\text{onset}}/\text{nm}$	Experimental E_{0-0} (eV)
AR1	395,469	8.33, 7.88	521	2.38
AR2	374,470	8.41, 7.96	524	2.36
AR3	415,493	8.89, 9.29	553	2.24
TPA	415,432	8.41, 6.16	499	2.48

2.3. Theoretical calculations:

To gain inside the molecular structure of the new dyes **AR1-3** beside measuring HOMO / LUMO energy levels, DFT / TD-DFT studies were performed. Structure optimization and frontier molecular orbitals (FMO) of dyes were done using Gaussian 09 software using B3LYP as energy function and 6-311G (d, p) as a basis set. As shown in **Figure 2**, at the HOMO levels, the electron distribution concentrated at the donor part (triphenylamine), while in the LUMO levels, electron mainly presented in the acceptor moiety (acrylamide). Furthermore, the calculated HOMOs potentials were found to be below the redox potential of the electrolyte, while the LUMOs potentials were found to be above the conduction band of the semiconductor enabling the dyes to be used as DSSC co-sensitizers (**Figure 2**).

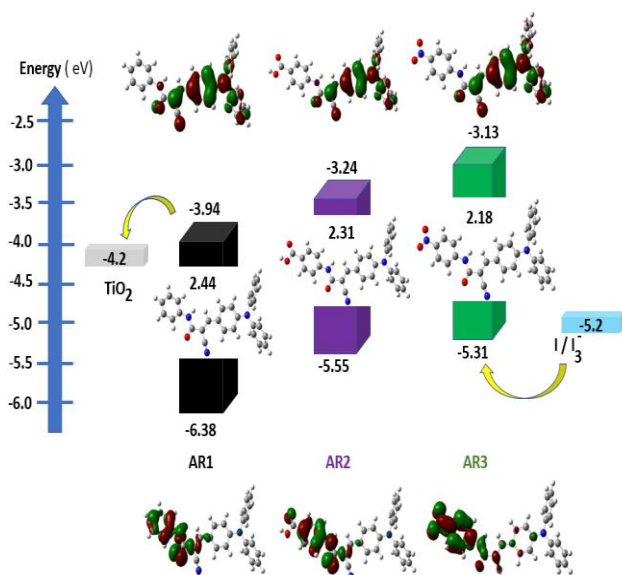


Fig. 2: Energy level diagram, optimized and FMO structures for **AR1-3**.

3. Conclusion:

We have synthesized novel metal free co-sensitizers **AR1-3** triphenylamine-based dyes. The structure of the target dyes **AR1-3** was

confirmed through different spectroscopic analysis. E_{0-0} of **AR1-3** was measured from their UV-vis spectra. Among the dyes **AR1-3**, **AR-3** showed the lowest band gap value with higher molar extinction co-efficient, which attributed to structure nature of the dye. Further, All the dyes possess the requirements for DSSC application as All HOMOs below the redox potential of electrolyte while, LUMOs above the conduction band of the semiconductor. Finally, DFT theoretical studies were in agreements with the experimental data.

4. Experimental section

4.1. Materials and instruments

Infrared (IR) spectra were obtained using Thermo Scientific Nicolet iS10 FTIR spectrometer in KBr pellets. ^1H NMR (500 MHz) and ^{13}C NMR (125MHz) spectra were obtained by JEOL's NMR spectrometer in $\text{DMSO-}d_6$. Mass analyses were obtained by a Shimadzu Qp-2010 Plus (GC-MS) spectrometer. Elemental analyses were performed using Perkin-Elmer 2400 analyzer.

4.2. General synthesis of co-sensitizers **AR1-3**:

In a 50 mL RBF, 4-(diphenylamino)benzaldehyde (0.55 g, 2 mmol) was dissolved in 20 mL of absolute ethanol. To this solution, (2 mmol) of cyanoacetanilide derivatives **2a-c** (namely, 2-cyanoacetanilide, 2-cyano-*p*-carboxyacetanilide and 2-cyano-*p*-nitroacetanilide) was added. The reaction mixture was refluxed for 3 hours. The resulting solid was filtered and recrystallized from EtOH to afford co-sensitizers **AR1-3**.

4.2.1.2-Cyano-3-(4-(diphenylamino)phenyl)-*N*-phenylacrylamide (**AR-1**):

Yellow crystals; yield = 62%; mp 208-210 °C. IR (ν , cm^{-1}): 3328 (N-H), 2210 ($\text{C}\equiv\text{N}$), 1679 ($\text{C}=\text{O}$). ^1H NMR: δ 6.90 (d, $J = 9.00$ Hz, 2H), 7.11 (t, $J = 7.25$ Hz, 2H), 7.19-7.24 (m, 6H), 7.34 (t, $J = 8.25$ Hz, 2H), 7.40-7.43 (m, 4H), 7.64 (d, $J = 7.50$ Hz, 2H), 7.88 (d, $J = 8.50$ Hz, 2H), 8.11 (s, 1H, C=CH), 10.19 ppm (s, 1H, N-H). MS, m/z (%): 415 (M^+ , 100.00), 323 (43.27), 295 (11.28). Analysis for $\text{C}_{28}\text{H}_{21}\text{N}_3\text{O}$ (415.50): Calculated: C, 80.94; H, 5.09; N, 10.11%. Found: C, 80.80; H, 5.05; N, 10.19%.

4.2.2.4(2Cyano3(4(diphenylamino)phenyl)acrylamido)benzoic acid (AR-2):

Orange crystals; yield = 48%; mp 289-291 °C. IR (v, cm⁻¹): 3333 (N-H), 2206 (C≡N), 1689 (C=O). ¹H NMR: δ 6.90 (d, 2H, J = 9.00 Hz), 7.20-7.25 (m, 6H), 7.41-7.44 (m, 4H), 7.78 (d, 2H, J = 9.00 Hz), 7.88-7.93 (m, 4H), 8.41 (s, 1H, C=CH), 10.48 (s, 1H, N-H), 12.79 (s, 1H, COOH). MS, m/z (%): 459 (M⁺, 100.00), 425 (20.56), 368 (23.19), 339 (20.93), 323 (2.48), 295 (39.03), 215 (20.77), 166 (34.39). Analysis for C₂₉H₂₁N₃O₃ (459.51): Calculated: C, 75.80; H, 4.61; N, 9.14%. Found: C, 75.70; H, 4.64; N, 9.08%.

4.2.3. 2-Cyano-3-(4-(diphenylamino)phenyl)-N-(nitrophenyl) acrylamide (AR-3):

Yellow crystals; yield = 60%; mp 239-241 °C. IR (v, cm⁻¹): 3314 (N-H), 2215 (C≡N), 1683 (C=O). ¹H NMR (DMSO-*d*₆): δ 6.90 (d, 2H, J = 9.00 Hz), 7.21-7.26 (m, 6H), 7.41-7.44 (m, 4H), 7.89-7.93 (m, 4H), 8.17 (s, H, C=CH), 8.26 (d, 2H, J = 8.50 Hz), 10.75 (s, 1H, N-H). MS, m/z (%): 460 (M⁺, 100.00), 323 (83.91), 295(89.71), 77 (35.70). Analysis for C₂₈H₂₀N₄O₃ (460.49): Calculated: C, 73.03; H, 4.38; N, 12.17%. Found: C, 73.18; H, 4.31; N, 12.10%.

4.3.(E)-2-cyano-3-(4-(diphenylamino)phenyl)acrylic acid (TPA)

The syntheses of TPA were conducted according to literature [23].

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