

Supporting Information

IoT-enabled dye sensitized solar cells: an effective embedded tool toward monitoring the outdoor device performance

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Materials and methods

The ^1H and ^{13}C NMR spectra were recorded in 400 MHz and 100 MHz respectively. High Resolution Mass Spectrophotometer (HR-MS) was utilized for recording mass spectrum of ICA dye. UV-Visible absorption spectra of ICA and ICA/TiO₂ samples were recorded using Shimadzu UV-1800 spectrophotometer. Electrochemical analysis was carried out in Metrohm Autolab 302N potentiostat controlled by NOVA1.11 software. The experiments were executed in a tri-electrode set up with a glassy carbon disc electrode (GCE), Pt mesh and Ag/AgNO₃ (0.01 M) in 0.1 M TBAPF₆ in CH₃CN solvent as working, counter and reference electrodes respectively. The glassy carbon electrode was polished using alumina powder prior to use. 1mM of ICA dye was prepared in dry tetrahydrofuran (THF) solvent with addition of 0.1 M TBAPF₆ as a supporting electrolyte (dye: electrolyte ratio of 1:100). The solution was further purged with nitrogen gas for 10 min to get rid of dissolved oxygen. The cyclic voltammogram (CV) and differential pulse voltammogram (DPV) were recorded at 25°C with a scan rate of 100 mVs⁻¹. The density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods were employed to theoretically verify the experimental results as implemented in Gaussian 09 program.

Synthesis and characterization

3-[1-(4-Butyl-phenyl)-4,5-bis-(4-methoxy-phenyl)-1H-imidazol-2-yl]-9-ethyl-9H-carbazole (1).

Mixtures of 4-butylaniline, 4,4'-dimethoxybenzil, 9-ethyl-9H-carbazole-3-carbaldehyde, ammonium acetate were dissolved in 30 ml glacial acetic acid. The mixture was then place on oil bath maintaining 120°C under inert atmosphere. After 20 h, the mixture was the cooled, poured into crushed ice and the solid obtained was filtered. The crude product was purified on column chromatography using silica gel and ethyl acetate and hexane (2:3) yielding white crystalline solid. Yield 62 %; ^1H NMR (400 MHz, CDCl₃) δ 8.09-8.08 (d, 1H, $J = 4$ Hz), 7.87-7.86 (d, 1H, $J = 4$ Hz), 7.64-7.59 (m, 3H), 7.46-7.43 (t, 1H, $J = 6$ Hz), 7.39-7.37 (d, 1H, $J = 4$ Hz), 7.28-7.26 (t, 1H, $J = 4$ Hz), 7.20-7.16 (t, 1H, $J = 8$ Hz), 7.09-7.06 (m, 4H), 7.01-6.99 (d, 2H, $J = 4$ Hz), 6.85-6.83 (d, 2H, $J = 8$ Hz), 6.79-6.77 (d, 2H, $J = 8$ Hz), 4.36-4.30 (m, 2H), 3.81 (s, 3H), 3.79 (s, 3H), 2.61-2.57 (t, 2H, $J = 8$ Hz), 1.61-1.54 (m, 2H), 1.44-1.40 (t, 3H, $J = 8$ Hz), 1.35-1.26 (m, 2H), 0.93-0.89 (t, 3H, $J = 8$ Hz); ESI-MS 605 [M⁺]

6-[1-(4-Butyl-phenyl)-4,5-bis-(4-methoxy-phenyl)-1H-imidazol-2-yl]-9-ethyl-9H-carbazole-3-carbaldehyde (**2**).

To the stirring ice-cooled solution of **1** (1.1 g, 1.72 mmol) in 10 ml anhydrous dimethyl formamide, phosphorus oxychloride (0.66 g, 4.3 mmol) was added drop wise and the resulting mixture was allowed to stir under nitrogen atmosphere. After 1h, the reaction temperature was slowly raised to 90 °C and further stir overnight. Finally the mixture was cooled, poured into water and neutralized by NaHCO₃. The mixture was then extracted with dichloromethane and the organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated. The crude product was purified by column chromatography on silica gel (hexane: ethyl acetate 2:1) to give yellow solid. Yield 67%; ¹H NMR (400 MHz, CDCl₃) δ 10.08 (s, 1H), 8.38 (s, 1H), 8.16 (s, 1H), 8.05-8.03 (d, 1H, *J* = 8 Hz), 7.79-7.77 (d, 1H, *J* = 8 Hz), 7.63-7.61 (d, 2H, *J* = 8 Hz), 7.50-7.48 (d, 1H, *J* = 8 Hz), 7.40-7.38 (d, 1H, *J* = 8 Hz), 7.16-7.11 (m, 4H), 7.07-7.05 (d, 2H, *J* = 8 Hz), 6.90-6.88 (d, 2H, *J* = 8 Hz), 6.84-6.82 (d, 2H, *J* = 8 Hz), 4.42-4.37 (m, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 2.65-2.62 (t, 2H, *J* = 6 Hz), 1.62-1.58 (m, 2H), 1.51-1.47 (t, 3H, *J* = 8 Hz), 1.34-1.29 (m, 2H), 0.93-0.88 (t, 3H, *J* = 10 Hz); ESI-MS 633.7 [M⁺].

3-{6-[1-(4-Butyl-phenyl)-4,5-bis-(4-methoxy-phenyl)-1H-imidazol-2-yl]-9-ethyl-9H-carbazol-3-yl}-2-cyano-acrylic acid (**3**, **ICA dye**).

The mixture of compound **2** (0.15 g, 0.22 mmol), cyanoacetic acid (0.03 g, 0.45 mmol) and ammonium acetate (0.05 g, 0.67 mmol) were dissolved in 10 ml glacial acetic acid. The mixture was stirred at 120 °C in oil bath under argon atmosphere for 12 h, diluted with water and extracted from dichloromethane. The organic layer was dried in anhydrous Na₂SO₄ and concentrated. The final orange colored compound was obtained by purification through column chromatography (silica gel, hexane: ethyl acetate, 3:1). Yield 86%; ¹H NMR (400 MHz, CDCl₃) δ 8.54 (s, 1H), 8.32 (s, 1H), 8.17-8.15 (d, 1H, *J* = 8 Hz), 7.96 (s, 1H), 7.76-7.74 (d, 1H, *J* = 8 Hz), 7.64-7.62 (d, 1H, *J* = 8 Hz), 7.58-7.56 (d, 1H, *J* = 8 Hz), 7.46-7.44 (d, 2H, *J* = 8 Hz), 7.17-7.12 (m, 7H), 6.85-6.82 (m, 4H), 4.44-4.42 (m, 2H), 3.71 (s, 3H), 3.70 (s, 3H), 2.53-2.48 (m, 3H), 1.50-1.41 (m, 2H), 1.31-1.27 (t, 2H, *J* = 8 Hz), 1.16-1.09 (m, 2H), 0.74-0.7 (t, 3H, *J* = 8 Hz); ¹³C NMR (100 MHz, DMSO-d₆): δ 164.5, 159.3, 158.3, 146.6, 143.2, 142.9, 140.2, 136.9, 135.2, 132.9, 130.3, 129.5, 129.1, 127.9, 127.8, 127.7, 124.6, 123.3, 123.2, 122.9, 122.0, 120.6, 114.3,

114.0, 110.7, 110.1, 55.4, 38.0, 33.2, 21.9, 14.2, 14.0. HR-MS: m/z Calcd. for (C₄₅H₄₀N₄O₄): 700.30; Found: [M+H] 701.3076.

Surface coverage calculations

The surface coverage (Γ) values can be calculated by the following equations.

$$\Gamma = A(\lambda)/\sigma(\lambda)$$

where $A(\lambda)$ is absorbance and $\sigma(\lambda)$ is the optical cross section at a given wavelength.

$$\sigma(\lambda) = \varepsilon(\lambda) \times 1000 \text{ (cm}^3 \text{ L}^{-1}\text{)}$$

Device Fabrication

FTO glasses were cleaned in detergent solution, distilled water, acetone and isopropyl alcohol under ultrasonic bath, further it was subjected for UV treatment. The blocking layer of TiO₂ was deposited by spin coating of TiO₂ complex (TiO₂ complex was prepared by taking 20 μ l of titanium isopropoxide in 1:1 ratio ethanol and DI water (20ml) on FTO glasses at 4000 rpm and sintered at 500 °C for half an hour. Then, TiO₂ paste of \approx 8 μ m was coated by doctor blade technique and sintered at 500 °C for half an hour. Further TiCl₄ treatment was carried out and calcined at 500 °C for an hour. The TiO₂ coated glasses were immersed in 0.3 mM of ICA dye for overnight and unadsorbed dye molecules was washed with THF and dried over the N₂ flow. PEO-PEG/alkali iodide gel electrolyte (0.5 M DMPII, 0.05 M iodine, and 0.5 M TBP in acetonitrile) droplet was dropped on the dye coated TiO₂ film and sandwiched with platinum coated counter electrode (platinum coated counter electrode glass was prepared as followed, 0.05 M solution of chloroplatinic acid in isopropyl alcohol was spin coated on cleaned FTO glass and heated at 420 °C for half an hour). In order to avoid shorting the two electrodes were separated by hot melt polymer film (thickness 25mm) (Meltonix-1170-25) with an active area of 0.19 cm².

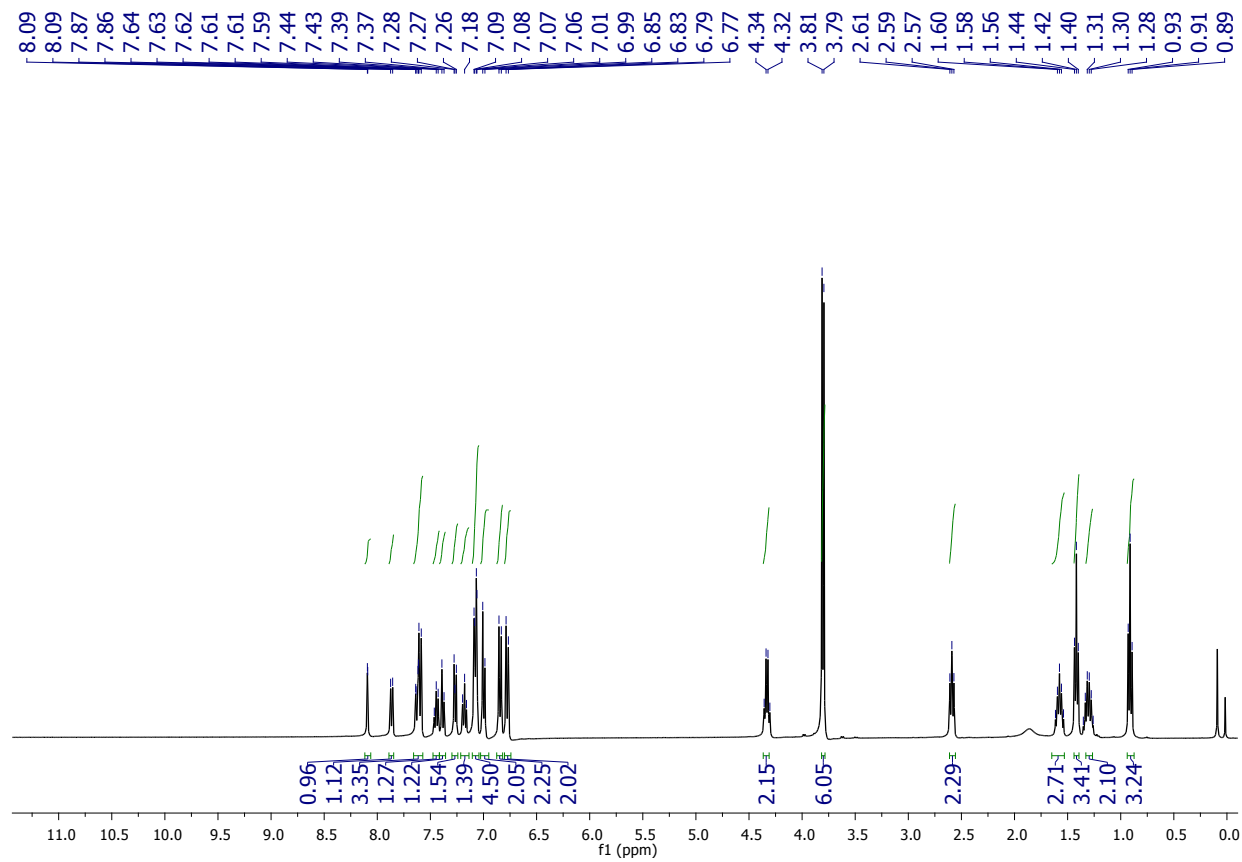


Figure S1: ¹H NMR spectrum of 3-[1-(4-Butyl-phenyl)-4,5-bis-(4-methoxy-phenyl)-1H-imidazol-2-yl]-9-ethyl-9H-carbazole(**1**) in CDCl₃.

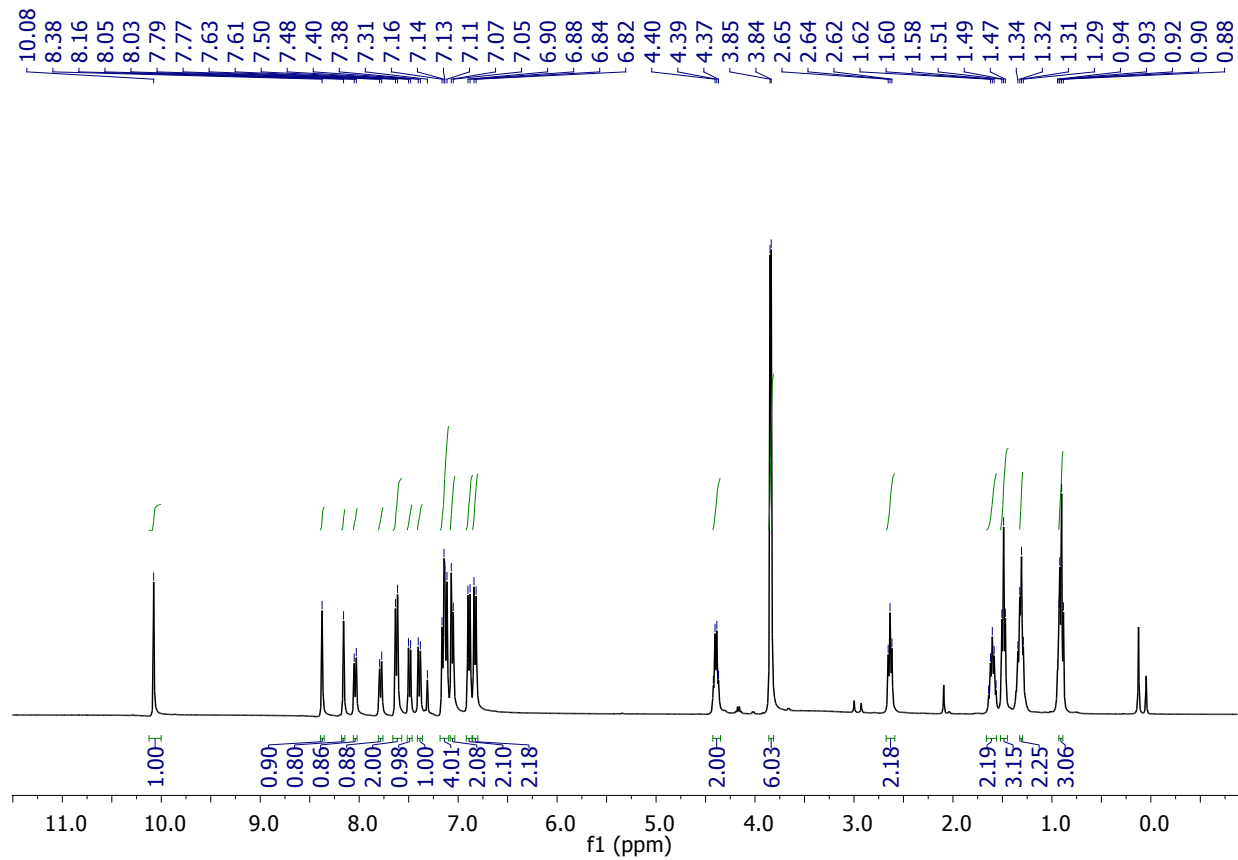


Figure S2: ¹H NMR spectrum of 6-[1-(4-Butyl-phenyl)-4,5-bis-(4-methoxy-phenyl)-1H-imidazol-2-yl]-9-ethyl-9H-carbazole-3-carbaldehyde (**2**).

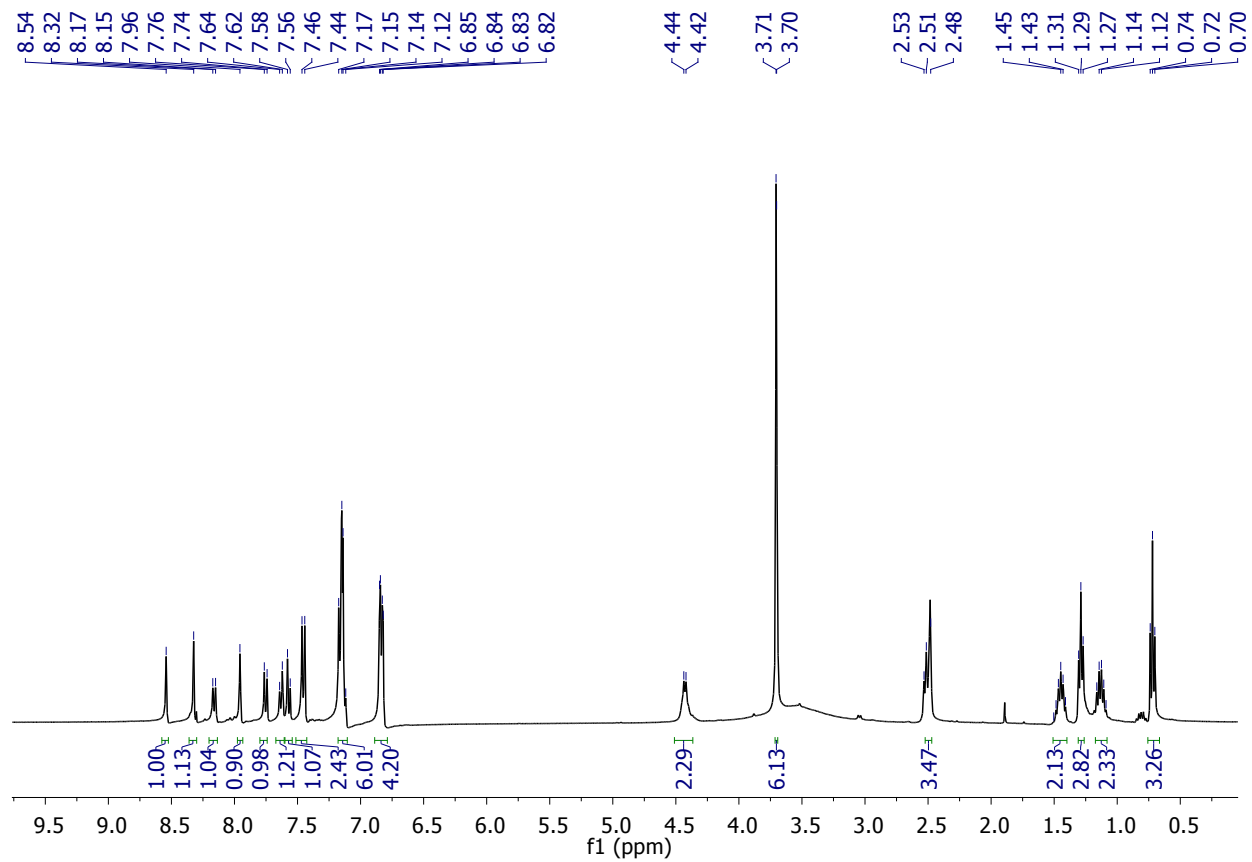


Figure S3: ^1H NMR spectrum of 3-{6-[1-(4-Butyl-phenyl)-4,5-bis-(4-methoxy-phenyl)-1H-imidazol-2-yl]-9-ethyl-9H-carbazol-3-yl}-2-cyano-acrylic acid (**3**) in DMSO-d_6 .

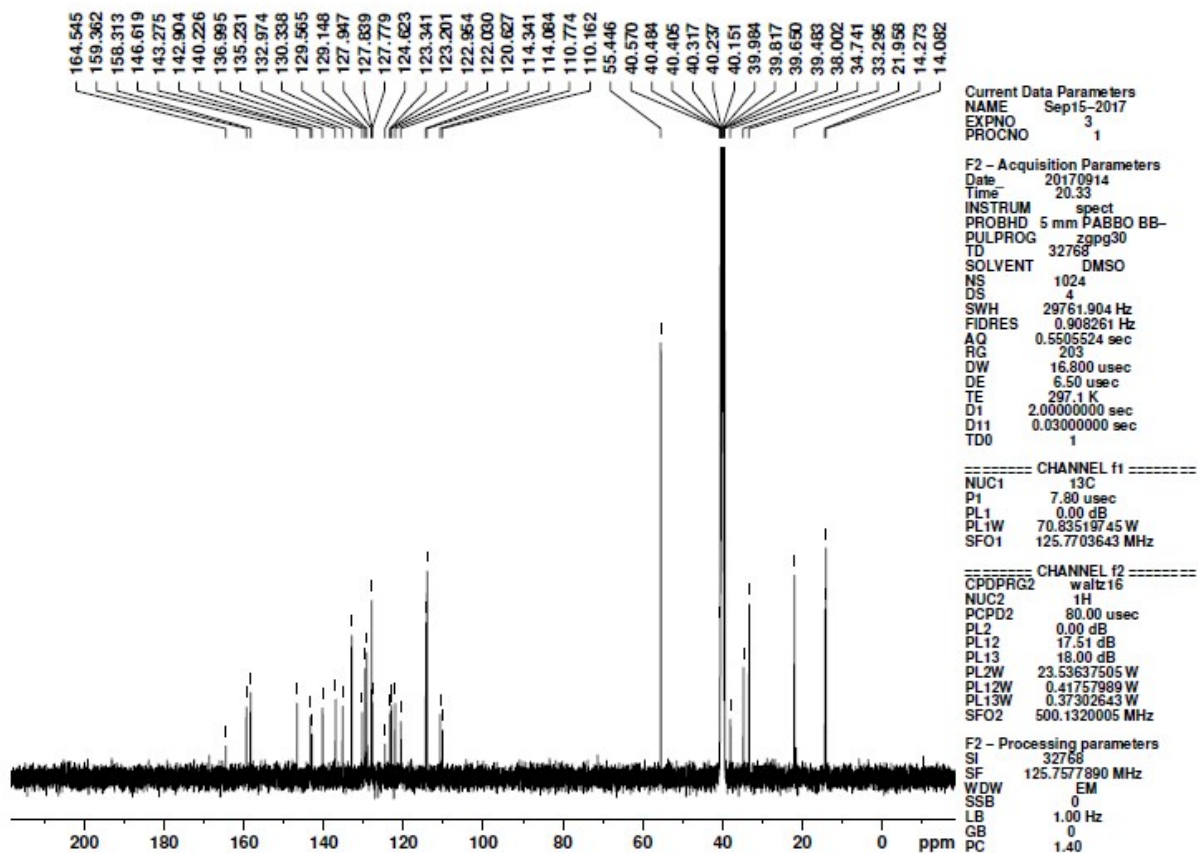


Figure S4: ^{13}C NMR spectrum of 3- $\{6-[1-(4\text{-Butyl-phenyl})-4,5\text{-bis-(4-methoxy-phenyl)-1H-imidazol-2-yl}]$ -9-ethyl-9*H*-carbazol-3-yl $\}$ -2-cyano-acrylic acid (**3**) in $\text{DMSO-}d_6$.

Cpd. 1: C₄₅ H₄₀ N₄ O₄

Compound Spectra (overlaid)

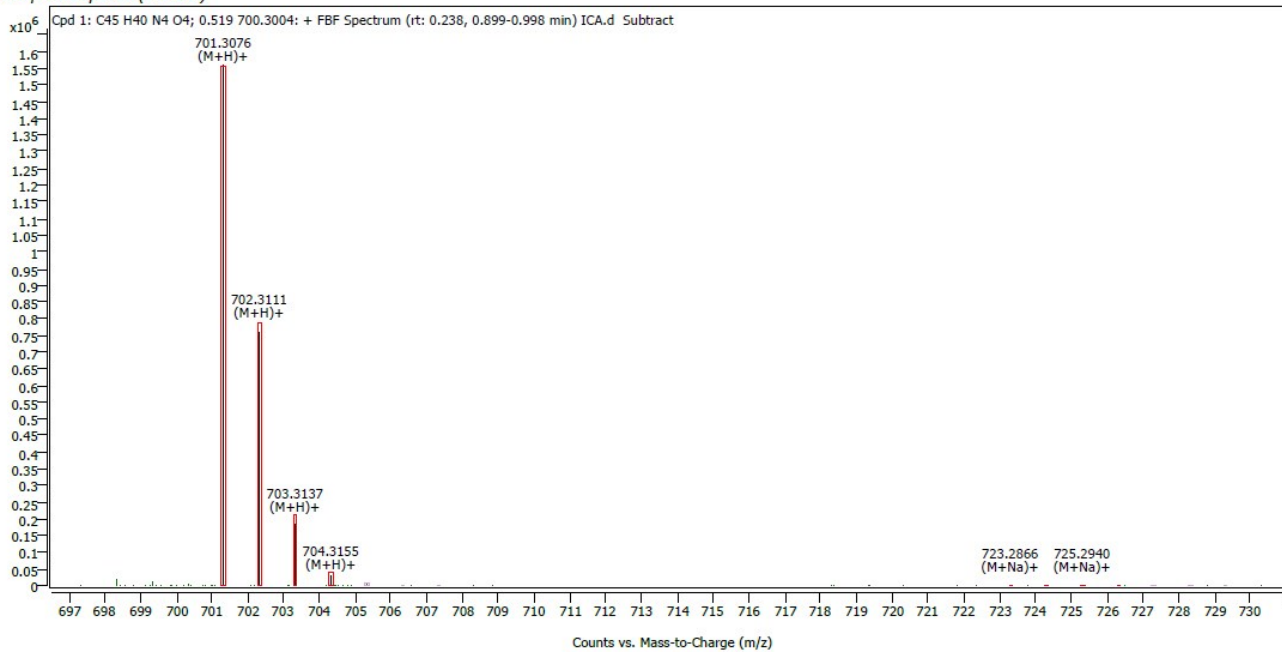


Figure S5: ESI mass spectroscopy of 3- $\{6$ -[1-(4-Butyl-phenyl)-4,5-bis-(4-methoxy-phenyl)-1H-imidazol-2-yl]-9-ethyl-9*H*-carbazol-3-yl}-2-cyano-acrylic acid (**3**)

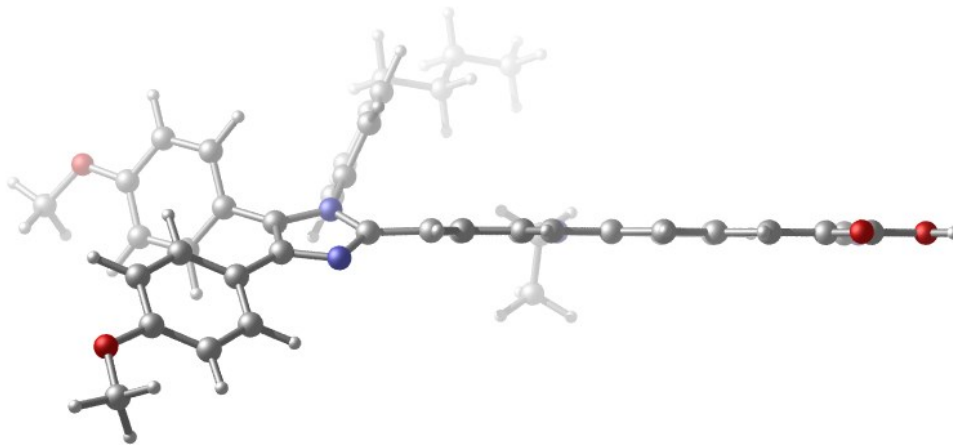


Figure S6: Optimized geometry of ICA dye (Side view).

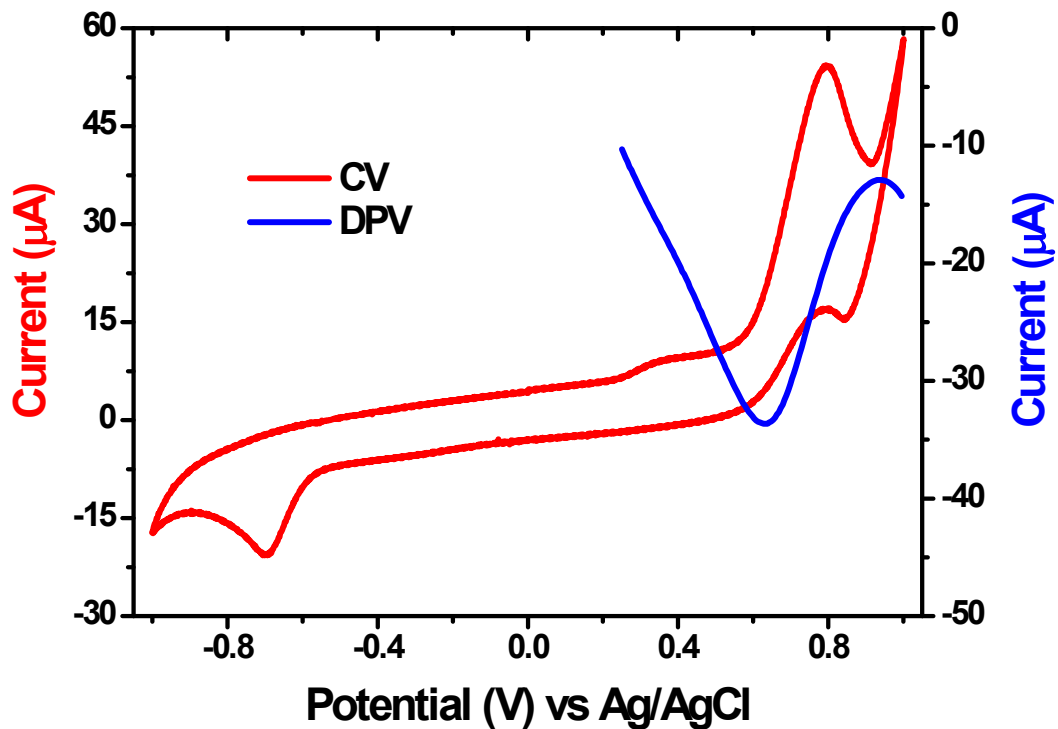


Figure S7: CV and DPV of ICA dye.

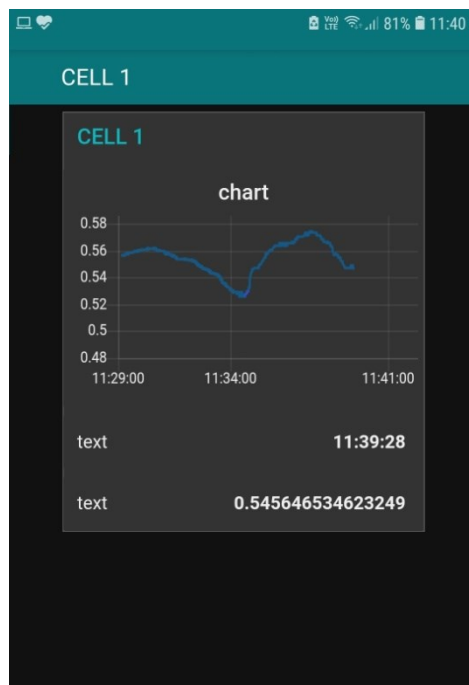


Figure S8: Screenshot of live data from the DSSC through cloud interface

Table S1: Computed absorption wavelength of maximum (λ_{\max} in nm) of ICA in THF solvent using different functionals using **6-311G**** basis set.

| Functional | λ_{\max}(nm) |
|-------------------|--|
| B3LYP | 398 |
| CAM-B3LYP | 346 |
| M06 | 381 |
| Wb97x | 340 |
| M06-2x | 347 |
| PBE0 | 382 |
| Experiment | 396 |

Table S2: Photovoltaic characteristics of ICA/TiO₂ electrode.

| Parameters | ICA dye | ICA dye + CDCA |
|---------------------------------------|----------------|-----------------------|
| J _{SC} (mA/cm ²) | 5.26 | 4.15 |
| V _{OC} (V) | 0.58 | 0.59 |
| FF | 0.66 | 0.66 |
| η (%) [#] | 2.04 | 1.65 |

[#] The average values of the four devices.

Table S3: The power conversion efficiency values reported in the literature

| Dyes | η/η_{N719} (%) | References |
|-------------|---|-------------------|
| MK-2 | 56 | 1 |
| CPTAA-1 | 48 | 2 |
| RA-199-Zn | 58 | 3 |
| ICA | 51 | This work |

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(2) K. Stalindurai, A. Karuppasamy, J.D. Peng, K.C. Ho, A. Tamilselvan and C. Ramalingan, *Tetrahedron*, 2017, 73, 278.

(3) R. Kumar, V. Sudhakar, K. Prakash, K. Krishnamoorthy and M. Sankar, *ACS Appl. Energy Mater.*, 2018, 1, 2793.