Electronic Supporting Information

Enhanced Photovoltaic Performance of Meso-porous SnO₂ Based Solar Cells utilizing 2D MgO Nanosheets Sensitized by a Metal Free Carbazole Derivative

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1. Synthesis of Cobalt complexes

The cobalt(II) and cobalt(III) metal complexes with 2,2'-bipyridyl (bpy) ligand were used as a redox couple and synthesized by following reported method by Liu et al.¹ For the synthesis of $[Co(bpy)_3](PF_6)_2$, $CoCl_2 \cdot 6H_2O$ (0.25 g) was dissolved in 5.0 mL of distilled water with stirring, followed by the dropwise addition of 2,2'-bipyridyl (0.55 g) solution (prepared in methanol) and then the reaction mixture was stirred for another 10 min. For the precipitation of Co(II) complex, an aqueous solution of KPF₆ (1.2 g) was added into above reaction mixture. After precipitation, the obtained solid product was filtered, washed with water, and dried in vacuum to obtain the $[Co(bpy)_3](PF_6)_2$ solid. The complex $[Co(bpy)_3](PF_6)_3$ was synthesized via same procedure which is used for the synthesis of $[Co(bpy)_3](PF_6)_2$ complex through little modification. For the synthesis of $[Co(bpy)_3](PF_6)_3$ complex, $CoCl_2 \cdot 6H_2O$ (0.25 g) was dissolved in 5.0 mL of distilled water and then a methanolic solution of 2,2'bipyridyl (0.55 g)was added slowly under magnetic stirring. Now an equivalent molar concentration of methanolic Br₂ solution was added dropwise after 10 min of stirring, and then the reaction mixture was allowed to stir for another 10 min. After that an orange colored precipitate appeared in the reaction mixture which was then removed by filtering to get a clear solution and the solvent was evaporated by distillation under reduced pressure. After evaporation, the obtained residue was dissolved in methanol (15.0 mL) and then for the precipitation of Co(III) complex, an aqueous solution of KPF₆ (1.2 g) was added into above reaction mixture under magnetic stirring. Finally the product was filtered, washed with water, and dried in vacuum to yield the $[Co(bpy)_3](PF_6)_3$ solid.



2. 400 MHz ¹H NMR Spectrum of Metal-Free Carbazole SK1 Dye

Figure S1: ¹H NMR spectrum of SK1 dye recorded in CDCl₃ as the solvent.

3. 400 MHz ¹³C-NMR Spectrum of Metal-Free Carbazole SK1 Dye



Figure S2: ¹³C-NMR spectrum of SK1 dye recorded in CDCl₃ as the solvent.



4. Mass Spectrum for the Metal-Free Carbazole SK1 Dye

Figure S3: Mass spectrum of SK1 dye.

5. Electrochemical analysis of SK1 Dye.

The electrochemical analysis of metal-free carbazole dye (SK1) was carried out by performing cyclic voltammetry (CV). Highest-occupied molecular orbital (HOMO) level of SK1 dye was estimated in the anhydrous acetonitrile by using 0.1 M tetra-n-butyl ammoniumhexafluorophosphate (TBAP) electrolyte. The oxidation half-potential for SK1 is

found to be +1.37 V (vs NHE) (Figure S4). HOMO energy level of SK1 dye can be calculated by using following expression $E_{HOMO} = -[E_{onset(Fc/Fc^+)} + 5.1] eV$, and it is found to be at -5.62 eV (vs Fc/Fc⁺), which is more positive than the redox potentials of I^{3–}/I[–] (-4.8eV) and Co^{3+/2+} (-5.1 eV) electrolyte. From the optical energy band gap (E_g) value and HOMO level of SK1 dye, lowest unoccupied molecular orbital (LUMO) energy level was calculated by using the following expression i.e. $E_g = E_{HOMO} - E_{LUMO}$. The value of E_g for SK1 is found to be 2.25 eV from absorption onset (Figure 4). The LUMO energy level for SK1 is estimated at -3.37 eV (vs Fc/Fc⁺), which is higher than the CB energy level of SnO₂ (-4.53 eV). Electron transfer from the LUMO of the dye to the CB of SnO₂ is favorable due to fine matching of their band positions.



Figure S4: Cyclic voltagram of SK1 dye recorded at a scan rate of 50 mVs⁻¹ acetonitrile solvent by using TBAP as an electrolyte

6. Density Functional Theory (DFT) Study of SK1 Dye

We have reported the DFT analysis in our previous work.² In order to obtain the information regarding various parameters of frontier molecular orbitals of the SK1 dye such as geometric

configuration, electronic density distribution and minimal energy, density functional theory (DFT) calculations were carried out by using Accelrys Materials Studio 4.0. From the DFT calculations, we can easily predict the theoretical behavior of molecular orbitals of SK1 dye. The optimization of molecular geometries of SK1 was carried out in DMol3 program package using generalized gradient approximation (GGA) with BLYP as the basis set. These simulations were f4 carried out in a vacuum for the single molecule. Figure shows the optimized geometry of the molecule along with electron density map for HOMO and LUMO energy levels.



Figure S5: HOMO and LUMO frontier molecular orbitals of SK1 as calculated from the density functional theory (DFT) at a B3LYP/6-31+G(d) level showing the electronic distributions in its ground and excited states

Figure S5 represents the electronic density at the HOMO energy level of SK1 is consistently distributed over the donor and π -conjugated units i.e. carbazole and oligo-phenylenevinylene respectively. On the other hand, the LUMO energy level of SK1 represents the photoinduced electronic excitation of the molecule resulting in the intramolecular charge transfer leading to an electron migration from the donor unit to the cyanoacrylic acceptor unit. This clearly represents the transfer of excited electron from carboxylic group attached to the carbon atom bonded with cyano group to the CB of SnO₂. Moreover, the energy levels of HOMO and LUMO are separated remarkably which allow a long-lived excited state. Due to more life

time of excited electron, facilitate the charge transfer process which enhances performance parameters of photovoltaic devices. Further this process can be well understood from the energy level diagram of SnO_2 and SK1 dye (Scheme 2).

- 7. TEM images and selected area electron diffraction pattern (SAED) of 3D MgO

Figure S6: TEM images [(A), (B) and (C)] and selected area electron diffraction pattern (D) of 2D MgO nanosheets obtained after ultrasonication for 1h in ethanol.

8. Schematic of SnO₂-MgO photoanode fabrication process



Scheme S1. Step-by-step SnO₂-MgO photoanode fabrication process





Figure S7: Cyclic Voltagram of pristine SnO_2 electrode (black line) and SnO_2 -MgO electrode (red line) in 0.1 M NaClO₄ in dry acetonitrile.

10. (J-V) curves for optimization of SnO₂-MgO device by varying the amount of MgO



Figure S8: Optimization of SnO₂-MgO devices by varying the weight percentages of MgO

Table S1. Short-circuit current density (J_{sc}) , open-circuit voltage (V_{oc}) , fill factor (*FF*), and power conversion efficiency (η) for the fabricated solar cells with different weight percentage of MgO

Devices	J _{sc} (mA/cm ²)	V _{oc} (mV)	FF (%)	PCE (η%)	Active area (cm ²)	Redox couple
(20 wt %)						
SnO ₂ -MgO	9.21	550	49	2.48	0.25	I ⁻ /I ₃ -
(15 wt %)						
SnO ₂ -MgO	8.25	493	42	1.71	0.25	I-/I ₃ -
(10 wt %)						
SnO ₂ -MgO	7.47	395	43	1.30	0.25	I ⁻ /I ₃ -
(5 wt %)						
SnO ₂ -MgO	7.2	357	38.2	0.98	0.25	I ⁻ /I ₃ -
(0 wt %)						

REFERENCES

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- 2. D. Barpuzary, A. S. Patra, J. V. Vaghasiya, B. G. Solanki, S. S. Soni and M. Qureshi, *ACS Appl. Mater. Interfaces*, 2014, **6**, 12629.