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Supporting Information

Enhancement of Solar Efficiency of Dye-Sensitized Solar Cell by Molecular Engineering of Organic Dye Incorporating N-alkyl Attached 1, 8-Naphthalamide Derivative

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Synthesis

Reagents and solvents were procured from Sigma Aldrich and TCI chemicals and used as such. Precursors 1,[1] 2,[2] 4,[2] 7,[2] and 8[3] were synthesized by known procedures from reported article. All oxygen- and moisture sensitive reactions were performed under nitrogen atmosphere. The other materials were of the common commercial level and used as received. PhMe was dried over Na/benzophenone ketyl and freshly distilled prior to use.

Synthesis of 5-bromo-3,4-dimethoxythiophene-2-carbaldehyde, 5: In a 100 mL single neck round bottom flask, N-bromosuccinimide (320 mg, 1.8 mmol) was dissolved in 20 mL of DMF. In another 250 mL of round bottom flask, 3,4-dimethoxythiophene-2-carbaldehyde (250 mg, 1.5 mmol) was dissolved in 20 mL of dry $CHCl_3$. After then NBS solution was added drop wise and stirred at 0 °C. After completion of NBS addition the reaction mixture was left for 16h. Reaction was monitored by TLC and reaction mixture was purified by column chromatography by using CH_2Cl_2 and hexane as an eluting agent. Yield was 62 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.91 (s, 3 H), 4.13 (s, 3 H), 9.91 (s, 1 H).

Synthesis of 5-(2-butyl-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6-yl)-3,4-dimethoxythiophene-2-carbaldehyde, 6: Precursor 1 (200 mg, 1.1 mmol), precursor (0.44g, 1.2 mmol) were dissolved in THF : H_2O (9:1) solvent ratio (20 mL) in a 100 mL round bottom flask. The reaction mixture was purging with nitrogen gas for 20 minutes. To this reaction mixture K_2CO_3 (0.75 g, 5.3 mmol) and Pd $(PPh_3)_4$ (10 mg) were added and the reaction mixture kept for 24 h under refluxing condition. The reaction was monitored by TLC. After completion of reaction the mixture was cooled down to room temperature and concentrated by reducing pressure. The mixture was washed with water (100 mL) and extracted by 150 mL of CH_2Cl_2. Organic layer was concentrated by reducing pressure and purified by column chromatography. Yield was 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.98 (t, J = 4 Hz, 3 H), 1.34-1.38 (m, 2 H), 1.59-1.62 (m, 2H), 3.88-4.01 (m, 6 H), 4.02 (t, J = 4 Hz, 2 H), 7.71-7.82 (m, 2 H), 8.2-8.43 (m, 1 H), 8.62-8.68 (m, 2 H), 10.03 (s, 1 H).

Synthesis of (E)-3-(5-(2-butyl-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6-yl)-3,4-dimethoxythiophen-2-yl)-2-cyanoacrylic acid, M-dye: A mixture of compound 6 (200 mg, 0.473 mmol), cyanoacetic acid (50 mg, 0.6 mmol), ammonium acetate (45 mg, 0.6 mmol) and glacial acetic acid (20 mL) was heated under reflux for 12 h during which time the aldehyde is completely consumed as indicated by TLC. After 12 h the reaction mixture was washed with water and di ethyl ether thoroughly. Compound was purified by washing and yield was 65 %. ^{1}H NMR (200 MHz, DMSO-d_6) δ : 1.02 (t, J = 4 Hz, 3 H), 1.47-1.54 (m, 2 H), 1.74-1.79 (m, 2 H), 3.92-4.0 (m, 4 H), 4.23(t, J = 4 Hz, 4 H), 7.84 (t, J = 2 Hz, 1 H), 8.29 (d, J = *4 Hz*, 1 H), 8.62 (s, 1 H), 8.66 (d, J = *4 Hz*, 2 H), 8.98 (d, J = *4 Hz*, 1 H). MALDI-TOF *m/z* calcd for $[M+H]^+$ $[C_{26}H_{22}N_2O_6SH]^+$ 491.1277, found 491.1264.

Synthesis of 6,6'-dibromo-2H,2'H,4H,4'H-3,3'-spirobi[thieno[3,4-b][1,4]dioxepine]-8,8'-dicarbaldehyde, 9: In a 100 mL round bottom flask, NBS (910 mg, 5.1 mmol) in DMF was added drop wise on the solution of compound 8 (600 mg, 1.7 mmol) in $CHCl_3$ by using a dropping funnel under nitrogen atmosphere under 0 °C. After addition of NBS solution the reaction mixture was stirred at room temperature for overnight. The reaction mixture was washed with water (100 mL) and extracted by CH_2Cl_2 (50 mL). The organic layer was concentrated by reducing pressure and purified by column chromatography using CH_2Cl_2, Yield was 71%. ^{1}H NMR (200 MHz, $CDCl_3$) δ : 4.11- 4.22 (m, 4 H), 4.29 (s, 4 H), 9.84 (s, 1 H).

Synthesis of 6'-bis(2-butyl-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6-yl)-2H,2'H,4H,4'H-3,3'-spirobi[thieno[3,4-b][1,4]dioxepine]-8,8'-dicarbaldehyde, 10: Compound 9 (0.250 g, 0.5 mmol), compound 2 (0.6 g, 1.5 mmol) and 2 M K_2CO_3 were dissolved in toluene and water solvent mixture (3:1) in a 100 mL round bottom flask equipped with reflux condenser under nitrogen atmosphere. The solution was degassed with nitrogen gas for 20 minutes. After then Pd $(PPh_3)_4$ (50 mg) added to that reaction mixture and refluxed the mixture for overnight under the same inert atmosphere. Reaction was monitored by TLC and concentrated the reaction mixture by reducing pressure. Purification of the reaction has been done by column chromatography using CH_2Cl_2 and hexane as an eluting agent. Yield was 65 %. ^{1}H NMR (200 MHz, $CDCl_3$) δ : 0.99 (t, J = 400Hz, 6H), 1.41-1.49 (m, 4 H), 1.71-1.75 (m, 4H), 3.93 (s, 8 H), 4.20 (t, J = 4 Hz, 4 H), 7.81 (t, J = 400Hz, 2H), 8.26 (d, J = 4 Hz, 2 H), 8.58 (d, J = 2Hz, 2 H), 8.63 (d, J = 2Hz, 2 H), 8.94 (d, J = 2 Hz, 2 H), 10.1 (s, 1 H).

Synthesis of 3,3'-((S)-6,6'-bis(2-butyl-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6-yl)-2H,2'H,4H,4'H-3,3'-spirobi[thieno[3,4-b][1,4]dioxepine]-8,8'-diyl)bis(2-cyanoacrylic acid), D-dye: A mixture of aldehyde precursor, 10 (100 mg, 0.12 mmol), cyanoacetic acid (30 mg, 0.3 mmol), ammonium acetate (24 mg, 0.3 mmol) and glacial acetic (10 mL) acid were taken in a 50 mL round bottom flask equipped with reflux condenser under nitrogen atmosphere. The reaction mixture was refluxed for 12 h. The reaction was monitored by thin layer chromatography. After completion of the reaction the reaction mixture was concentrated by reducing pressure and purified by column chromatography by using CH_2Cl_2 and MeOH as an eluting agent. Yield was 58%. ^{1}H NMR (200 MHz, DMSO-d_6) δ: 0.91 (t, *J = 2 Hz*, 6H), 1.31-1.33 (m, 4H), 1.57-1.64 (m, 4H), 3.99-4.55 (m, 12 H), 7.77-7.91 (m, 5H), 8.25 (s, 1H), 8.30 (s, 1H), 8.32-8.57 (m, 5H). MALDI-TOF *m/z* calcd for $[M]^+$ $[C_{53}H_{40}N_4O_{12}S_2]^+$ 988.2084, found 988.2264.

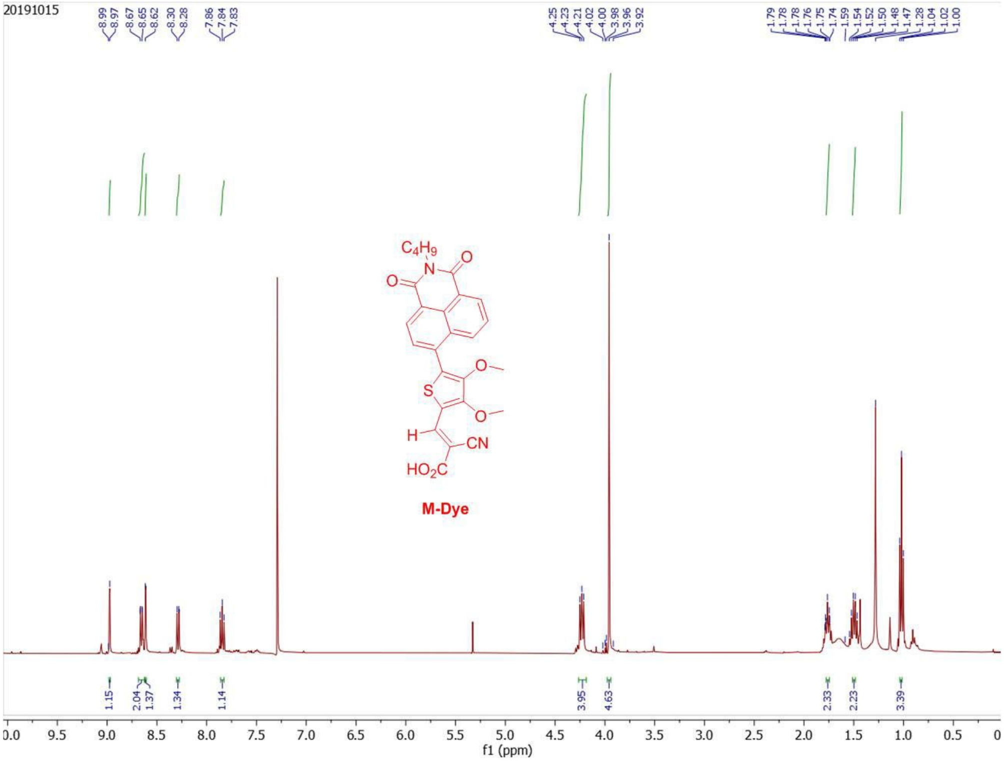

Figure S1. ^{1}H NMR spectrum of monomeric **M-Dye**.

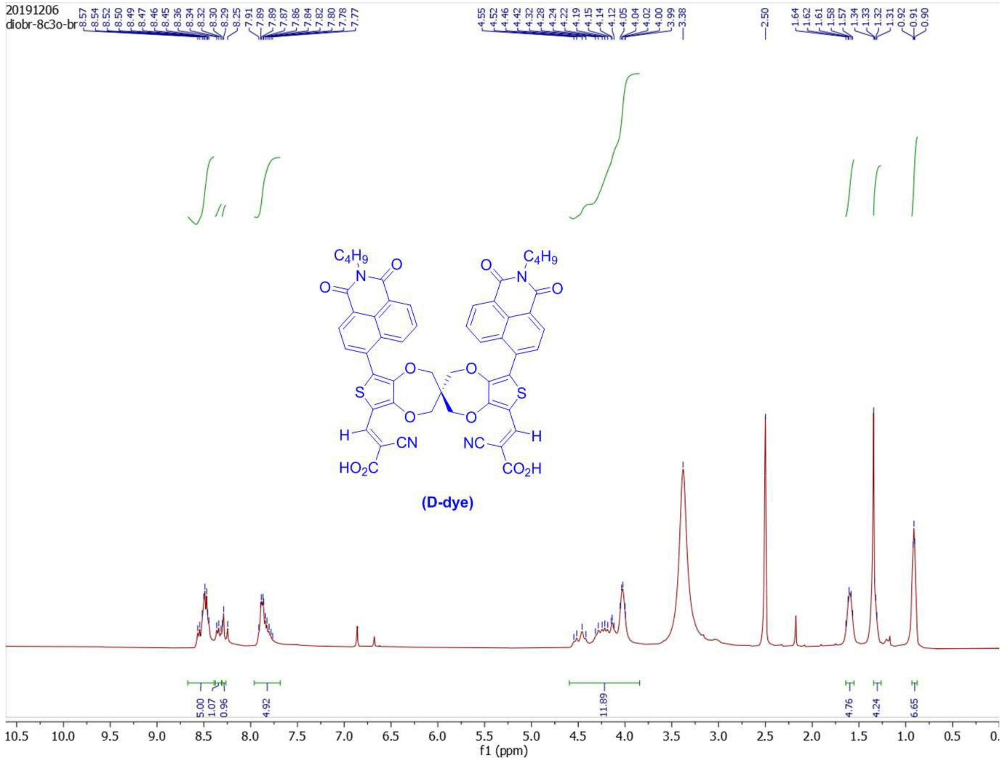

Figure S2. ^{1}H NMR spectrum of dimeric **D-Dye**.

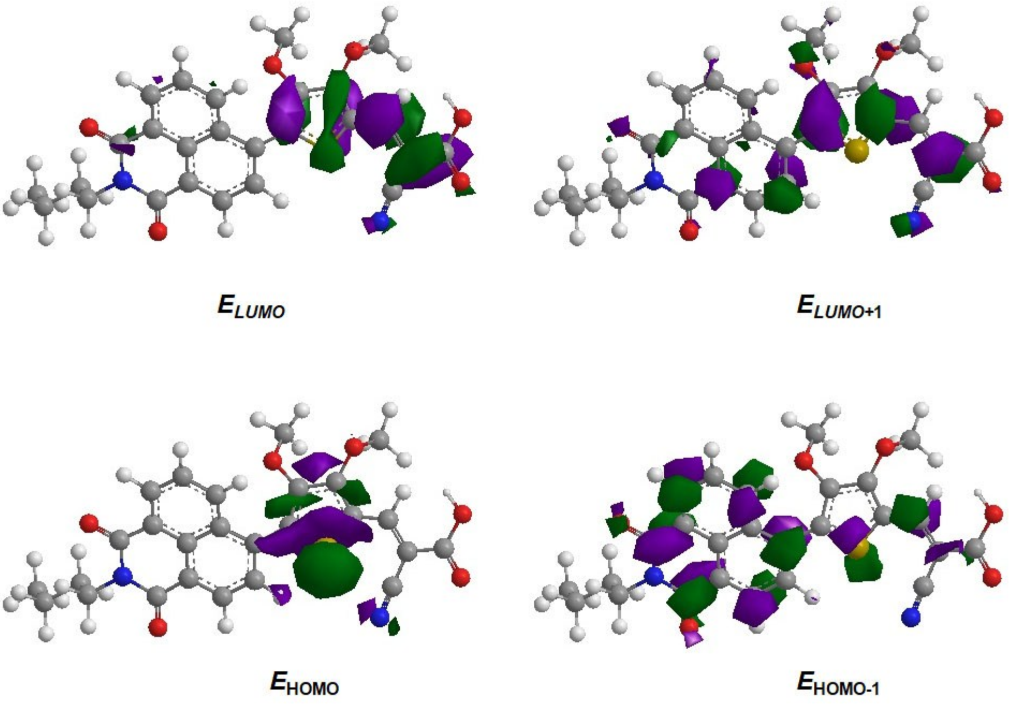

Figure S3. Electron distribution of **M-Dye** molecules in different energy states (white colour-hydrogen atom, grey- carbon, blue-nitrogen, red-oxygen, pale yellow-sulphur, violet-positive cloud and green-negative cloud).

References:

1. T. S. Reddy, J. Hwang and M. Choi, *Dyes and Pigments*, 2018, **158**, 412–419.
2. M. C. Sil, V. Sudhakar, M. F. Mele Kavungathodi, V. Punitharasu and J. Nithyanandhan, *ACS Appl. Mater. Interfaces*, 2017, **9**, 34875–34890.
3. M. C. Sil, M. F. M. Kavungathodi and J. Nithyanandhan, *Dyes and Pigments*, 2019, **161**, 313–323.