# Push-pull carbazole twin dyads as efficient sensitizers/co-sensitizers for DSSC application: Effect of various anchoring groups on photovoltaic performance

Kavya S. Keremane <sup>a,b</sup>, Islam M. Abdellah <sup>c,d,\*</sup>, Mohamed R. Eletmany <sup>d,e</sup>, Praveen Naik <sup>f</sup>, P. Anees <sup>g</sup>, and Airody Vasudeva Adhikari <sup>a,h,\*</sup>

<sup>a</sup> Organic Materials Laboratory, Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Mangalore-575025, India

<sup>b</sup> Materials Research Institute, The Pennsylvania State University, University Park, PA, 16802 USA <sup>c</sup> Chemistry Department, Faculty of Science, Aswan University, Aswan, 81528, Egypt

d TECS Department, Wilson College of Textiles, NC State University, Raleigh, 27606, USA

<sup>e</sup> Chemistry Department, Faculty of Science, South Valley University, Qena 83523, Egypt

<sup>f</sup> Department of Chemistry, Nitte Meenakshi Institute of Technology, Yelahanka, Bengaluru, 560064, Karnataka, India

<sup>g</sup> Materials Science Group, Indira Gandhi Centre for Atomic Research, A CI of Homi Bhabha National Institute, Kalpakkam, 603102, Tamilnadu, India

<sup>h</sup> Yenepoya Research Centre, Yenepoya (Deemed to be) University, Deralakatte, Mangalore, 575018, India

\*Corresponding author's e-mail: <u>avachem@gmail.com</u> (A. Vasudeva Adhikari), <u>islamabdellah2@gmail.com</u> (Islam M. Abdellah)

## **Experimental section**

#### 1. Materials and Methods

The starting materials such as carbazole, 1,6-dibromohexane, cyanoacetic acid, rhodanine-3-acetic acid, rhodanine, barbituric acid, 1,3-dimethylbarbituric acid, 1,3-diethyl-2-thiobarbituric acid, 2,4-thiazolidinedione, oxindole (2-indolone), and 4-nitrophenyl acetonitrile were procured from Sigma-Aldrich, Alfa Aesar, and Spectrochem companies. All the synthetic grade solvents used in the reactions (Merck, Loba Chemie, and Spectrochem companies) were purified by different processes such as drying and distillation. All the reactions were carried out under an inert atmosphere and the reaction completion was gradually monitored by the TLC technique. The standard synthesis protocol was used to synthesize the designed dyes. The final dye molecules and their intermediates were purified using recrystallization or column chromatographic separation techniques. The melting points of synthesized molecules were recorded using the Stuart SMP10 digital melting point apparatus. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of all the synthesized molecules were recorded on a Bruker Avance (III) 400 MHz instrument by using CDCl<sub>3</sub>/DMSO-d<sub>6</sub> as a solvent and TMS

as an internal standard. The mass spectra and elemental analysis of the synthesized dyes DCH<sub>1-9</sub> were obtained from LC-MS6410Q (Agilent Technologies) and Flash EA1112 CHNS elemental analyzer (Thermo Scientific), respectively. Further, ATR-FTIR spectra were obtained using Bruker FTIR Alpha spectrometer. Also, Thermogravimetric analysis (TGA) was carried out using a Perkin Elmer TGA4000 analyzer, at the heating rate of 10 °C min<sup>-1</sup> under the nitrogen atmosphere. Similarly, differential scanning calorimetry (DSC) studies were performed using NETZSCH DSC 404F1 analyzer at the heating rate of 10 °C min<sup>-1</sup>. The UV-Vis absorption spectra and photoluminescence spectra of DCH<sub>1-9</sub> in N,N-dimethyl formamide (DMF) solvent were recorded at room temperature by using Analytik Jena SPECORD S 600 and Jasco FP 6200 spectrophotometers, respectively. Furthermore, to calculate their experimental GSOP and ESOP values, the CV (cyclic voltammetry) measurements were performed in anhydrous acetonitrile solution with 0.1M tetrabutylammonium hexafluorophosphate [TBA] [PF<sub>6</sub>] as a supporting electrolyte at a scan rate of 100 mVs<sup>-1</sup>. The theoretical simulations, viz. density functional theory (DFT) and timedependent density functional theory (TD-DFT), were performed for all the final molecules using the Turbomole V7.2 software package.<sup>[1-5]</sup>

#### **Photoelectrochemical Measurements**

The DSSC devices sensitized with new **DCH**<sub>1-9</sub> dye molecules were fabricated by using the doctor blade technique. Similarly, DSSCs were constructed employing the dyes **DCH**<sub>1-9</sub> as co-sensitizers along with Ru-based **HD-2** dye and chenodeoxycholic acid (CDCA) as a co-adsorbent. Further, the Current-Voltage (J-V) characteristics of fabricated devices were measured using solar simulator Oriel SOL3A connected to Keithley 2400 source mete under the illumination of AM 1.5 G solar source. The intensity of incident light was calibrated using a reference Si solar cell (Newport Oriel, 91150V) to set 1 Sun (100 mWcm<sup>-2</sup>) and the corresponding measurement was fully controlled under Oriel IV test station software. Further, incident photon conversion efficiency (IPCE) spectra of all the fabricated devices with **DCH**<sub>1-9</sub> were recorded using the QEX10 PV measurement system. Finally, electrochemical impedance spectra (Nyquist and Bode plots) for the fabricated devices were measured with Bio-Logic SP-150 potentiostat over a frequency range of 100 mHz to 200 kHz at 298K using a solar simulator under the illumination of a standard 1.5 G light source. Further, the applied voltage was set at the V<sub>OC</sub> of the devices with AC amplitude fixed at 10 mV. The obtained plots were fitted *via Z*-Fit software (Bio-Logic).

#### 2. Synthetic Methods

The required intermediates and final target molecules were synthesized using standard synthetic methods and their detailed procedures along with structural characterization data are given below.

#### 2.1. Synthesis of 1,6-di(9H-carbazole-9-yl)hexane (1)

A mixture of carbazole (12 g, 71.70 mmol), and NaH (3.5 g, 143.35 mmol) was dissolved in 30 mL of DMF and stirred at 0 °C for half an hour under an argon atmosphere. Further, 1,6-dibromohexane (7 g, 28.69 mmol) was added to the reaction mixture and continued stirring at room temperature for 12 h. The reaction progress was monitored using thin-layer chromatography (TLC). After completion of the reaction, the reaction mixture was cooled and poured into crushed ice (250 mL) and neutralization was done using a saturated solution of ammonium chloride. The precipitate formed was filtered, washed with ice-cold water, and finally, it was recrystallized using ethanol to get an off-white solid as a product. Yield: 92%. Melting point: 108-110 °C.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 8.10-8.08 (d, 4H), 7.44-7.41 (m,4H), 7.33-7.23 (t, 4H, 7.21-7.20 (d, 4H), 4.25-4.22 (t, 4H), 1.83-1.81 (t,3H), 1.57-1.26 (m, 5H). Anal. Calcd. for C<sub>30</sub>H<sub>28</sub>N<sub>2</sub>: C, 86.50; H, 6.78; N, 6.72; and found C, 86.13; H, 6.49; N, 6.13. **FT-IR (ATR)**,  $\upsilon$  cm<sup>-1</sup>: 3063, 2956 (C-H), 1589, 1533, 1482 (C=C), 1191 (C-N).

# 2.2. Synthesis of 9,9'-(hexane-1,6-diyl)bis(9H-carbazole-3-carbaldehyde) (2)

In a cleaned two-neck round bottom flask, freshly distilled DMF (18.58 mL, 240.06 mmol) was taken and cooled at -3 to 4 °C. Then, phosphorous oxychloride, POCl<sub>3</sub> (22.4 mL, 240.06 mmol) was added drop-wise with constant stirring at the same temperature under an argon atmosphere to obtain a glassy white salt. To this mixture, 1,6-di(9*H*-carbazole-9-yl)hexane (1, 5 g, 12 mmol) dissolved in dichloroethane (10-12 mL) was added. The reaction mixture was refluxed at 110 °C for 2 h. After completion of the reaction, the reaction mass was cooled to room temperature, and poured into 200 mL crushed ice, and subsequently basified by using 5 M NaOH solution. The product formed was extracted with dichloromethane (50 mL x 4) and the organic layer was dried over sodium sulphate and evaporated under reduced pressure. The impure residue was later purified by column

chromatography on silica gel (100-200 mesh) to yield a pale brown solid (2). Yield: 69%. Melting point: 148-150 °C.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm): 10.07 (s, 2H), 8.58-8.58 (d, 2H), 7.95-7.93 (t, 2h), 7.49-7.48 (t, 2H), 7.47-7.46 (d, 2H), 7.36-7.28 (m,6H), 4.27-4.25 (t, 4H), 1.84-1.81 (t, 4H), 1.58-1.34 (m, 4H). Anal. Calcd. for C<sub>32</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>: C, 81.33; H, 5.97; N, 5.93; and found C, 81.46; H, 5.89; N, 5.13. **FT-IR (ATR)**, v cm<sup>-1</sup>: 2956, 2927 (C-H), 1681 (C=O), 1587, 1482 (C=C), 1193 (C-N).

2.3. Synthesis of (2*E*,2'*E*)-3,3'-(9,9'-(hexane-1,6-diyl)bis(9*H*-carbazole-9,3-diyl))bis(2-cyano acrylic acid) (**DCH**<sub>1</sub>)

A mixture of intermediate 9,9'-(hexane-1,6-diyl)bis(9*H*-carbazole-3-carbaldehyde) (**2**, 0.5 g, 1.058 mmol), cyanoacetic acid (0.1 g, 1.26 mmol), and ammonium acetate (0.89 g, 11.6 mmol) and glacial acetic acid (5 mL) were taken in a RB flask and refluxed for 12 h under argon atmosphere. The completion of the reaction was monitored using the TLC technique. After its completion, the reaction mixture was cooled to room temperature and poured into ice-cold water. The solid obtained was filtered, washed with cold water, and finally, dried. The crude product was recrystallized from absolute methanol to get the pure product **DCH**<sub>1</sub> as a bright yellow solid. Yield: 89%. Melting point: 280-282 °C.

<sup>1</sup>**H NMR** (400 MHz, DMSO-d<sub>6</sub>,  $\delta$  ppm): 10.05 (s, 1H), 8.85 (s, 1H), 8.75 (s, 1H), 8.45 (s, 1H), 8.29-8.26 (t, 2H), 8.15-8.14 (d, 1H), 7.96-7.95 (d, 1H), 7.77-7.76 (d, 1H), 7.72-7.71 (d, 1H), 7.64-7.63 (m, 2H), 7.52-7.51 (m, 3H), 7.32-7.29 (dd, 2H), 4.42-4.39 (t, 4H), 1.72-1.31 (m, 8H). <sup>13</sup>**C NMR** (400 MHz, DMSO-d<sub>6</sub>,  $\delta$  ppm): 192.27, 164.63, 155.66, 143.94, 143.11, 141.19, 141.12, 128.67, 128.12, 127.33, 127.15, 127.03, 126.06, 124.42, 122.92, 122.77, 122.69, 122.64, 122.41, 121.28, 120.99, 120.79, 120.56, 117.79, 110.67, 110.45, 110.15, 98.85, 31.15, 28.69, 26.42. Anal. Calcd. for C<sub>38</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub>: C, 75.23; H, 4.98; N, 9.24 and found C, 75.39; H, 4.12; N, 9.21. **FT-IR (ATR), v** cm<sup>-1</sup>: 2942, 2860 (C-H stretch), 2226 (C=N stretch), 1687 (C=O stretch), 1581, 1495 (C=C), 1156 (C-N stretch). **Mass (m/z):** 606.67; Obtained (M-H): 605.25.

2.4. Synthesis of 2-((E)-5-((9-(6-(3-((Z)-(3-(carboxymethyl)-4-oxo-2-thioxothiazolidin-5-ylidene) methyl)-9H-carbazole-9-yl)hexyl)-9H-carbazole-3-yl)methylene)-4-oxo-2-thioxo thiazolidin-3-yl)acetic acid (**DCH**<sub>2</sub>)

A mixture of intermediate 9,9'-(hexane-1,6-diyl)bis(9*H*-carbazole-3-carbaldehyde) (**2**, 0.5 g, 1.058 mmol), rhodanine-3-acetic acid (0.24 g, 1.26 mmol), and ammonium acetate

(0.89 g, 11.6 mmol) and glacial acetic acid (5 mL) were taken in a RB flask and refluxed for 12 h under argon atmosphere. The completion of the reaction was monitored using the TLC technique. After its completion, the reaction mixture was cooled to room temperature and poured into ice-cold water. The solid obtained was filtered, washed with cold water, and finally, dried. The crude product was recrystallized from absolute methanol to get the pure product **DCH<sub>2</sub>** as a pale yellow solid. Yield: 86%. Melting point: 330-332 °C.

<sup>1</sup>**H NMR** (400 MHz, DMSO-d<sub>6</sub>,  $\delta$  ppm): 10.05 (s, 1H), 8.74 (s, 1H), 8.49-8.48 (d, 1H), 8.29-8.27 (d, 2H), 8.06-8.05 (d, 1H), 7.96-7.94 (d, 1H), 7.74-7.71 (t, 4H), 7.64-7.62 (m, 2H), 7.53-7.51 (t, 2H), 7.31-7.28 (t, 2H), 4.75 (m, 3H), 4.40 (m, 5H), 1.72-1.31 (m, 8H). <sup>13</sup>**C NMR** (400 MHz, DMSO-d<sub>6</sub>,  $\delta$  ppm): 193.66, 192.29, 166.99, 143.95, 141.90, 141.20, 141.13, 129.03, 128.67, 127.30, 127.17, 127.04, 124.93, 124.46, 124.08, 123.45, 122.69, 122.64, 122.32, 121.38, 121.29, 120.57, 117.77, 110.99, 110.47, 110.18, 28.69, 26.43. Anal. Calcd. for C<sub>42</sub>H<sub>34</sub>N<sub>4</sub>O<sub>6</sub>S<sub>4</sub>: C, 61.59; H, 4.18; N, 6.84 and found C, 61.32; H, 4.12; N, 6.82. **FT-IR** (**ATR**), **v** cm<sup>-1</sup>: 2936 (C-H stretch), 2360 (C=N stretch), 1678 (C=O stretch), 1577, 1494 (C=C), 1189 (C-N stretch). **Mass (m/z):** 818.14; Obtained (M-H): 817.25.

2.5. Synthesis of (5Z,5'E)-5,5'-(9,9'-(hexane-1,6-diyl)bis(9H-carbazole-9,3-diyl))bis (methanylylidene))bis(2-thioxothiazolidin-4-one) (**DCH**<sub>3</sub>)

A mixture of intermediate 9,9'-(hexane-1,6-diyl)bis(9*H*-carbazole-3-carbaldehyde) (2, 0.5 g, 1.058 mmol), rhodanine (0.16 g, 1.26 mmol), and ammonium acetate (0.89 g, 11.6 mmol) and glacial acetic acid (5 mL) were taken in a RB flask and refluxed for 12 h under argon atmosphere. After the reaction completion, the reaction mixture was cooled to room temperature and was poured into ice-cold water. The solid obtained was filtered, washed with cold water, dried, and recrystallized using absolute methanol to get the pure product **DCH<sub>3</sub>** as a pale yellowish-orange solid. Yield: 83%. Melting point: 294-296 °C.

<sup>1</sup>**H NMR** (400 MHz, DMSO-d<sub>6</sub>, δ ppm): 10.05 (s, 1H), 8.75 (s, 1H), 8.41-8.40 (t, 1H), 8.33-8.25 (m, 3H), 7.96-7.94 (dd, 1H), 7.83-7.82 (d, 1H), 7.71-7.70 (t, 2H), 7.64-7.63 (m, 4H), 7.51-7.49 (m, 2H), 7.31-7.27 (m, 2H), 4.40-4.38 (t, 4H), 1.71-1.30 (m, 8H). <sup>13</sup>**C NMR** (400 MHz, DMSO-d<sub>6</sub>, δ ppm): 196.16, 192.28, 170.05, 141.19, 141.08, 128.67, 127.15, 124.17, 123.36, 122.69, 122.64, 122.30, 121.28, 120.55, 120.39, 110.82, 110.44, 110.13, 28.67, 26.42. Anal. Calcd. for  $C_{38}H_{30}N_4O_2S_4$ : C, 64.93; H, 4.30; N, 7.97 and found C, 64.90; H, 4.29; N, 7.96. **FT-IR (ATR), v** cm<sup>-1</sup>: 3033, 2845 (C-H stretch), 2360 (C=N stretch), 1678 (C=O stretch), 1572 (C=C), 1176 (C-N stretch). Mass (m/z): 702.13; Obtained (M-H): 701.10.

2.6. Synthesis of 5,5'-((9,9'-(hexane-1,6-diyl)bis(9*H*-carbazole-9,3-diyl))bis(methanyl ylidene))bis(1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione) (**DCH**<sub>4</sub>)

9,9'-(Hexane-1,6-diyl)bis(9*H*-carbazole-3-carbaldehyde) (**2**, 0.5 g, 1.058 mmol), was dissolved in 10 mL of absolute methanol and to this mixture 1.2 eq of an active methylene compound like 1,3-dimethylbarbituric acid (0.19 g, 1.26 mmol) was added under an argon atmosphere and heated at 60 °C with stirring for 10 h. After completion of the reaction, the content was cooled to room temperature, and precipitated solid was filtered, washed with cold methanol, and collected. It was further recrystallized from the CHCl<sub>3</sub>-hexane mixture to get the pure product **DCH<sub>4</sub>** as pale orange solid. Yield: 89%. Melting point: 202-204 °C.

<sup>1</sup>**H NMR** (400 MHz, DMSO-d<sub>6</sub>,  $\delta$  ppm): 9.27 (s, 2H), 8.75 (s, 1H), 8.61 (s, 1H), 8.33-8.28 (t, 2H), 7.96-7.95 (d, 2H), 7.73-7.64 (m, 3H), 7.52-7.50 (t, 3H), 7.31-7.30 (m, 2H), 4.41-4.37 (m, 12H), 4.05-4.01 (m, 4H), 1.99-0.83 (m, 8H). <sup>13</sup>**C NMR** (400 MHz, DMSO-d<sub>6</sub>,  $\delta$  ppm): 160.06, 142.28, 141.09, 127.61, 127.13, 127.08, 125.89, 123.06, 122.55, 119.14, 114.43, 109.82, 107.84, 77.36, 77.24, 77.04, 76.72, 55.46, 47.80, 39.51, 31.01, 28.82, 24.42, 23.02, 14.03, 10.09. Anal. Calcd. for C<sub>44</sub>H<sub>40</sub>N<sub>6</sub>O<sub>6</sub>: C, 70.57; H, 5.38; N, 11.22 and found C, 70.50; H, 5.39; N, 11.21. **FT-IR (ATR), v** cm<sup>-1</sup>: 2944 (C-H stretch), 2360 (C=N stretch), 1661 (C=O stretch), 1595, 1544, 1491 (C=C), 1158 (C-N stretch). **Mass (m/z):** 748.30; Obtained (M-H): 747.25.

2.7. Synthesis of 5,5'-((9,9'-(hexane-1,6-diyl)bis(9*H*-carbazole-9,3-diyl))bis(methanyl ylidene)) bis(pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione) (**DCH**<sub>5</sub>)

The intermediate 9,9'-(hexane-1,6-diyl)bis(9*H*-carbazole-3-carbaldehyde) (**2**, 0.5 g, 1.058 mmol), was dissolved in 10 mL of absolute methanol and to this mixture 1.2 eq of an active methylene compound like barbituric acid (0.16 g, 1.26 mmol) was added under an argon atmosphere and heated at 60 °C with stirring for 10 h. After completion of the reaction, the content was cooled to room temperature, and the precipitated solid was filtered, washed with cold methanol and collected. It was further recrystallized from the CHCl<sub>3</sub>-hexane mixture to get the pure product **DCH**<sub>5</sub> as a red solid. Yield: 91%. Melting point: 214-216 °C. <sup>1</sup>**H NMR** (400 MHz, DMSO-d<sub>6</sub>,  $\delta$  ppm): 11.31 (s, 2H), 11.19 (s, 2H), 9.29 (s, 2H), 8.75 (s, 1H), 8.62-8.60 (d, 1H), 8.52 (s, 1H), 8.33 (s, 1H), 8.18-8.17 (d, 2H), 7.72-7.64 (m, 5H), 7.52-

7.50 (t, 2H), 7.32-7.28 (m, 2H), 4.42-4.40 (t, 4H), 1.73-1.33 (m, 8H). <sup>13</sup>C NMR (400 MHz, DMSO-d<sub>6</sub>,  $\delta$  ppm): 164.70, 162.89, 157.33, 150.76, 143.53, 141.16, 133.76, 129.98, 127.17, 123.91, 122.84, 122.63, 120.98, 120.91, 114.55, 110.64, 109.66, 28.73, 26.44. Anal. Calcd. for C<sub>40</sub>H<sub>32</sub>N<sub>6</sub>O<sub>6</sub>: C, 69.35; H, 4.66; N, 12.13 and found C, 69.28; H, 4.60; N, 12.11. **FT-IR** (ATR),  $\upsilon$  cm<sup>-1</sup>: 3192 (N-H stretch), 3047, 2840 (C-H stretch), 2333 (C=N stretch), 1664 (C=O stretch), 1529, 1495 (C=C), 1183 (C-N stretch). Mass (m/z): 692.24; Obtained (M-H): 691.30.

2.8. Synthesis of 5,5'-((9,9'-(hexane-1,6-diyl)bis(9*H*-carbazole-9,3-diyl))bis(methanyl ylidene)) bis(1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione) (**DCH**<sub>6</sub>)

9,9'-(Hexane-1,6-diyl)bis(9*H*-carbazole-3-carbaldehyde) (**2**, 0.5 g, 1.058 mmol), was dissolved in 10 mL of absolute methanol and to this mixture 1.2 eq of 1,3-diethyl-2-thiobarbituric acid (0.25 g, 1.26 mmol) was added under argon atmosphere and heated at 60 °C with stirring for 10 h. After completion of the reaction, the content was cooled to room temperature, and the precipitated solid was filtered, washed with cold methanol, and collected. It was further recrystallized from the CHCl<sub>3</sub>-hexane mixture to get the pure product **DCH<sub>6</sub>** as a bright orange solid. Yield: 86%. Melting point: 290-292 °C.

<sup>1</sup>**H NMR** (400 MHz, DMSO-d<sub>6</sub>, δ ppm): 8.75 (s, 2H), 8.32-8.28 (d, 4H), 7.96-7.95 (m, 2H), 7.73-7.71 (m, 2H), 7.66-7.63 (m, 2H), 7.52-7.49 (t, 2H), 7.31-7.28 (t, 2H), 4.49-4.30 (m, 12H), 1.72 (m, 4H), 1.31-1.05 (m, 16H). <sup>13</sup>**C NMR** (400 MHz, DMSO-d<sub>6</sub>, δ ppm): 162.89, 157.33, 150.76, 143.53, 141.16, 133.76, 129.98, 127.17, 123.91, 122.84, 122.63, 120.98, 120.91, 114.55, 110.64, 109.66, 28.73, 26.44. Anal. Calcd. for C<sub>48</sub>H<sub>48</sub>N<sub>6</sub>O<sub>4</sub>S<sub>2</sub>: C, 68.87; H, 5.78; N, 10.04 and found C, 68.91; H, 5.72; N, 10.01. **FT-IR** (**ATR**),  $\nu$  cm<sup>-1</sup>: 3109 (N-H stretch), 2979, 2931 (C-H stretch), 2361 (C=N stretch), 1691 (C=O stretch), 1531, 1497 (C=C), 1143 (C-N stretch). **Mass (m/z):** 836.32; Obtained (M-H): 835.20.

2.9. Synthesis of (5Z,5'E)-5,5'-(9,9'-(hexane-1,6-diyl)bis(9H-carbazole-9,3-diyl))bis (methanyl ylidene))bis(thiazolidine-2,4-dione) (**DCH**<sub>7</sub>)

A mixture of intermediate 9,9'-(hexane-1,6-diyl)bis(9*H*-carbazole-3-carbaldehyde) (**2**, 0.5 g, 1.058 mmol), 2,4-thiazolidinedione (0.14 g, 1.26 mmol), and ammonium acetate (0.89 g, 11.6 mmol) and glacial acetic acid (5 mL) were taken in an RB flask and refluxed for 12 h under argon atmosphere. After the reaction completion, the reaction mixture was cooled to room temperature and was poured into ice-cold water. The solid obtained was filtered,

washed with cold water, dried, and recrystallized using absolute methanol to get the pure product **DCH**<sub>7</sub> as a pale yellow solid. Yield: 80%. Melting point: 328-330 °C.

<sup>1</sup>**H** NMR (400 MHz, DMSO-d<sub>6</sub>,  $\delta$  ppm): 10.05 (s, 2H), 8.75 (s, 2H), 8.33-8.27 (m, 3H), 7.96-7.94 (d, 2H), 7.71-7.62 (m, 5H), 7.52-7.49 (t, 2H), 7.31-7.28 (m, 2H), 4.40-4.38 (t, 4H), 1.70 (m, 4H), 1.49 (m, 4H). <sup>13</sup>**C** NMR (400 MHz, DMSO-d<sub>6</sub>,  $\delta$  ppm): 192.31, 143.94, 141.19, 127.17, 122.68, 121.30, 120.57, 110.48, 110.19, 69.91, 28.70, 26.43. Anal. Calcd. for C<sub>38</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>: C, 68.04; H, 4.51; N, 8.35 and found C, 68.21; H, 4.56; N, 8.32. **FT-IR** (ATR),  $\upsilon$  cm<sup>-1</sup>: 3143 (N-H stretch), 2943, 2902 (C-H stretch), 2360 (C=N stretch), 1678 (C=O stretch), 1586, 1467 (C=C), 1171 (C-N stretch). Mass (m/z): 670.17; Obtained (M-H): 669.25.

2.10. Synthesis of (3Z,3'Z)-3,3'-((9,9'-(hexane-1,6-diyl)bis(9H-carbazole-9,3-diyl))bis (methanylylidene))bis(indolin-2-one) (**DCH**<sub>8</sub>)

A mixture of 9,9'-(hexane-1,6-diyl)bis(9*H*-carbazole-3-carbaldehyde) (**2**, 0.5 g, 1.058 mmol), indolin-2-one (0.14 g, 1.26 mmol), and pipyridine (0.30 mL) were dissolved in ethanol (5-10 mL) and stirred at room temperature for half an hour. Further, the reaction mixture was refluxed at 80 °C for 12 h under an argon atmosphere. After the reaction completion, the reaction mixture was cooled to room temperature and was poured into ice-cold water. The solid obtained was filtered, washed with cold water, dried, and recrystallized using absolute methanol to get the pure product **DCH**<sub>8</sub> as a brownish-red solid. Yield: 79%. Melting point: 256-258 °C.

<sup>1</sup>**H NMR** (400 MHz, DMSO-d<sub>6</sub>, δ ppm): 10.62-10.58 (m, 2H), 10.05-10.03 (t, 1H), 9.36-9.33 (t, 1H), 8.75-8.69 (m, 1H), 8.56 (s, 1H), 8.32-8.28 (m, 4H), 8.20-8.19 (m, 1H), 8.14-8.11 (m, 1H), 7.98-7.95 (m, 1H), 7.86-7.83 (m, 2H), 7.78-7.76 (d, 1H), 7.72-7.69 (m, 2H), 7.65-7.61 (m, 1H), 7.49-7.46 (t, 1H), 7.24-7.20 (m, 3H), 6.91-6.81 (m, 3H), 4.42-4.39 (t, 4H), 1.75 (m, 4H), 1.36 (m, 4H). <sup>13</sup>C NMR (400 MHz, DMSO-d<sub>6</sub>, δ ppm): 148.66, 148.29, 141.32, 140.28, 126.92, 126.27, 124.80, 122.06, 121.49, 118.12, 117.77, 110.31, 108.83, 107.56, 107.01, 76.32, 76.00, 75.68, 55.08, 55.03, 46.79, 38.49, 29.98, 27.78, 23.39, 21.99, 12.99, 9.87. Anal. Calcd. for C<sub>48</sub>H<sub>38</sub>N<sub>4</sub>O<sub>2</sub>: C, 82.03; H, 5.45; N, 7.97 and found C, 81.98; H, 5.43; N, 7.98. **FT-IR (ATR), v** cm<sup>-1</sup>: 3061 (N-H stretch), 2359 (C≡N stretch), 1688 (C=O stretch), 1588, 1467 (C=C), 1139 (C-N stretch). **Mass (m/z):** 702.30; Obtained (M-H): 701.35.

2.11. Synthesis of (2Z,2'Z)-3,3'-(9,9'-(hexane-1,6-diyl)bis(9H-carbazole-9,3-diyl))bis(2-(4-nitrophenyl)acrylonitrile) (**DCH**<sub>9</sub>)

A mixture of 9,9'-(hexane-1,6-diyl)bis(9*H*-carbazole-3-carbaldehyde) (**2**, 0.5 g, 1.058 mmol) and potassium *tert*-butoxide (0.58 g, 5.25 mmol) was dissolved in dry methanol (15 mL) and stirred at room temperature under an argon atmosphere for 15 min. Later, 4-nitrophenyl acetonitrile (0.204 g, 1.26 mmol) was added while stirring and the reaction mixture was refluxed for 6 h. The precipitate formed was filtered, washed with absolute methanol, and finally, it was recrystallized from chloroform to obtain a brown solid. Yield: 89%. Melting point: 192-194 °C.

<sup>1</sup>**H** NMR (400 MHz, DMSO-d<sub>6</sub>,  $\delta$  ppm): 8.75 (s, 2H), 8.32-8.27 (m, 9H), 7.96-7.94 (dd, 2H), 7.72-7.62 (d, 5H), 7.52-7.49 (t, 3H), 7.31-7.28 (t, 3H), 4.41-4.38 (t, 4H), 1.71 (m, 4H), 1.38 (m, 4H). <sup>13</sup>**C** NMR (400 MHz, DMSO-d<sub>6</sub>,  $\delta$  ppm): 192.31, 143.94, 141.19, 128.66, 127.17, 122.63, 121.30, 120.57, 110.48, 110.19, 79.64, 42.84, 40.37, 40.23, 40.10, 39.96, 39.82, 39.68, 39.54, 28.70, 26.43. Anal. Calcd. for C<sub>48</sub>H<sub>36</sub>N<sub>6</sub>O<sub>4</sub>: C, 75.77; H, 4.77; N, 11.05 and found C, 75.70; H, 4.75; N, 11.03. **FT-IR (ATR)**, **v** cm<sup>-1</sup>: 2942, 2826 (C-H stretch), 2207 (C=N stretch), 1680 (C=O stretch), 1580, 1517 (C=C), 1172 (C-N stretch). Mass (m/z): 760.84; Obtained (M): 760.31.



3. Structural characterizations

Figure S1. <sup>1</sup>H-NMR spectrum of intermediate 1 recorded in CDCl<sub>3</sub>



Figure S2. <sup>1</sup>H-NMR spectrum of intermediate 2 recorded in CDCl<sub>3</sub>



Figure S3. FT-IR spectrum of intermediate 2



Figure S4. <sup>1</sup>H-NMR spectrum of DCH<sub>1</sub> recorded in DMSO-d<sub>6</sub>



Figure S5. <sup>13</sup>C-NMR spectrum of DCH<sub>1</sub> recorded in DMSO-d<sub>6</sub>



Figure S6. FT-IR spectrum of DCH<sub>1</sub>



Figure S7. LCMS spectrum of DCH<sub>1</sub>



Figure S8. <sup>1</sup>H-NMR spectrum of DCH<sub>2</sub> recorded in DMSO-d<sub>6</sub>



Figure S9. <sup>13</sup>C-NMR spectrum of DCH<sub>2</sub> recorded in DMSO-d<sub>6</sub>



Figure S10. FT-IR spectrum of DCH<sub>2</sub>



Figure S11. LCMS spectrum of DCH<sub>2</sub>



Figure S12. <sup>1</sup>H-NMR spectrum of DCH<sub>3</sub> recorded in DMSO-d<sub>6</sub>



Figure S13. <sup>13</sup>C-NMR spectrum of DCH<sub>3</sub> recorded in DMSO-d<sub>6</sub>



Figure S14. FT-IR spectrum of DCH<sub>3</sub>



Figure S15. LCMS spectrum of DCH<sub>3</sub>



Figure S16. <sup>1</sup>H-NMR spectrum of DCH<sub>4</sub> recorded in DMSO-d<sub>6</sub>



Figure S17. <sup>13</sup>C-NMR spectrum of DCH<sub>4</sub> recorded in DMSO-d<sub>6</sub>



Figure S18. FT-IR spectrum of DCH<sub>4</sub>



Figure S19. LCMS spectrum of DCH<sub>4</sub>



Figure S20. <sup>1</sup>H-NMR spectrum of DCH<sub>5</sub> recorded in DMSO-d<sub>6</sub>



Figure S21. <sup>13</sup>C-NMR spectrum of DCH<sub>5</sub> recorded in DMSO-d<sub>6</sub>



Figure S22. FT-IR spectrum of DCH<sub>5</sub>



Figure S23. LCMS spectrum of DCH<sub>5</sub>



Figure S24. <sup>1</sup>H-NMR spectrum of DCH<sub>6</sub> recorded in DMSO-d<sub>6</sub>



Figure S25. <sup>13</sup>C-NMR spectrum of DCH<sub>6</sub> recorded in DMSO-d<sub>6</sub>



Figure S26. FT-IR spectrum of DCH<sub>6</sub>



Figure S27. LCMS spectrum of DCH<sub>6</sub>



Figure S28. <sup>1</sup>H-NMR spectrum of DCH<sub>7</sub> recorded in DMSO-d<sub>6</sub>



Figure S29. <sup>13</sup>C-NMR spectrum of DCH<sub>7</sub> recorded in DMSO-d<sub>6</sub>



Figure S30. FT-IR spectrum of DCH<sub>7</sub>



Figure S31. LCMS spectrum of DCH<sub>7</sub>



Figure S32. <sup>1</sup>H-NMR spectrum of DCH<sub>8</sub> recorded in DMSO-d<sub>6</sub>



Figure S33. <sup>13</sup>C-NMR spectrum of DCH<sub>8</sub> recorded in DMSO-d<sub>6</sub>



Figure S34. FT-IR spectrum of DCH<sub>8</sub>



Figure S35. LCMS spectrum of DCH<sub>8</sub>



Figure S36. <sup>1</sup>H-NMR spectrum of DCH<sub>9</sub> recorded in DMSO-d<sub>6</sub>



Figure S37. <sup>13</sup>C-NMR spectrum of DCH<sub>9</sub> recorded in DMSO-d<sub>6</sub>



Figure S38. FT-IR spectrum of DCH9



Figure S39. LCMS spectrum of DCH<sub>9</sub>





Figure S40. Optimized geometries and frontier molecular orbitals (HOMO-5 to LUMO+5) of dyes DCH<sub>1-9</sub>

#### DFT studies on dye interaction with TiO<sub>2</sub> semiconductor



Figure S41. (a) Optimized geometry, (b) HOMO, and (c) LUMO levels of DCH<sub>1</sub>-TiO<sub>2</sub> (101) adduct; the isosurface value is 0.02045 e/Å<sup>3</sup>.

To understand the adsorption as well as charge transfer mechanism in the presence of a supporting substrate, density functional theory (DFT) calculations were performed using the Vienna Ab inito Simulation Package (VASP). (6) To compute the exchange correlation functional the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was used. (7) For geometry optimization we adopted an energy cut off of 450 eV. The sampling over the Brillouin zone was done using a gamma-centered K mesh of size  $5 \times 5 \times 1$ . The partial occupancy near the Fermi level was treated using a Gaussian smearing scheme. (8) An optimized bulk anatase  $TiO_2$  was cleaved along the (101) surface and made a supercell of size  $2 \times 2 \times 1$ . A vacuum separation of 15 Å was provided perpendicular to the surface to eliminate the unphysical periodic image interactions. The van der Waals (vdW) interaction between the DCH<sub>1</sub> and TiO<sub>2</sub>-(101) surface was modeled using the scheme of Tkatchenko et al. (TS-method). (9) The optimized geometry of TiO<sub>2</sub>-(101)-DDC is shown in Figure S41a. To analyze the charge transfer direction, we plotted the Kohn-Sham (KS) wave function for the HOMO and LUMO (Figure S41 b and c) using the methodology of Kamil et al. (10) In these simulations, the anchoring approach of  $DCH_1$  on  $TiO_2$  was selected as it is shown to be the most stable adsorption mode for the carboxylic acid anchoring group. (11-13) Typically, the electron transfer from the dye to the  $TiO_2$  depends on the relative symmetry, orientation of the orbitals, and electron density localized on the binding atoms. This possibly affects the rate and effectiveness of the recombination process. (14) In **Figure S41**, the yellowish region depicts the electron-rich area whereas the cyanish area corresponds to the electron deficit region. Careful observation of the HOMO level of the adduct shows that the anchored oxygen has electron deficient (cyan color) whereas the linked Ti atom has electron-rich (yellow) surroundings, indicating that, the electron transfer takes place from the dye to the Ti atoms. At the same time, in the LUMO there is still an appreciable charge density around the anchored oxygen atoms; hence, one can argue that the electron transfer occurs via the HOMO level.





Figure S42. Simulated electronic excitation spectra of DCH<sub>1-9</sub>





Figure S43. Theoretically obtained FT-IR spectra of DCH<sub>1-9</sub>





Figure S44. DOS plots of DCH<sub>1-9</sub>

#### Procedure for calculation of molar extinction coefficient

In the present study, the molar extinction coefficients of molecules  $DCH_{1-9}$  were determined according to Lambert-Beer law ( $A = \varepsilon c l$ , where, A is Absorbance,  $\varepsilon$  is molar absorption coefficient, c is molar concentration, l is optical path length and is usually 1 cm). The stock solutions of  $DCH_{1-9}$  were prepared in chloroform medium at a concentration of  $10^{-5}$  M and were further diluted to five different concentrations. The absorbance of the samples was recorded at their corresponding  $\lambda_{abs}$  (absorption maxima) using an Analytik Jena SPECORD S 600 spectrophotometer. The obtained absorbance values were plotted versus their molar concentrations. The slope of the graph indicates the molar extinction coefficient. <sup>[5]</sup>



Figure S45. DSC plots of dyes DCH<sub>1-9</sub>



Figure S46. CV plots of dyes DCH<sub>1-9</sub>



Figure S47. FTIR spectra of dyes  $DCH_{1-9}$  along with HD-2 adsorbed on TiO<sub>2</sub> surface

Table S1. Summary of dyes with similar molecular design along with their efficiency

Structure	η (%)	Reference			
	1.25	https://doi.org/10.1016/j.tet.2017.09.018			
R = -(CH <sub>2</sub> ) <sub>4</sub> -					
	1.63	https://doi.org/10.1016/j.tet.2017.09.018			
R = -(CH <sub>2</sub> ) <sub>8</sub> -					

HOOC NC NC NC NC NC NC NC NC NC NC NC NC NC	4.23	https://doi.org/10.1016/j.tet.2017.09.018
	5.68	https://doi.org/10.1016/j.electacta.2018.07.119
$HO_{2}C \xrightarrow{N} Ar \xrightarrow{N} CO_{2}H$ $HO_{2}C \xrightarrow{N} Ar \xrightarrow{N} CO_{2}H$ $n = 2, X = S, Ar = $	4.71	https://doi.org/10.1016/j.solener.2021.07.030



Figure S48. IPCE spectra of DSSCs sensitized with HD-2 alone and co-sensitized using DCH<sub>1-9</sub> and their integrated currents.



Figure S49. EIS spectra of devices sensitized with HD-2 alone (Nyquist plots, and Bode phase plots) along with equivalent circuit used for devices

Cell	S1+HD-2	S2+HD-2	S3+HD-2	S4+HD-2	S5+HD-2	S6+HD-2	S7+HD-2	S8+HD-2	S9+HD-2
$Rh/\Omega$ cm-2	21.18	28.46	20.28	18.52	23.81	21.6	19.83	21.2	19.71
RCT/Ω									
cm-2	3.858	4.103	3.63	3.164	2.691	11.63	3.338	14.79	13.55
n1	0.964 8	0.946	0.966 2	0.942 6	0.999 9	0.998 6	0.998 6	0.787 4	0.842 1
CPE1/Sn					1.15E-	0.354 7e-		0.809	
cm-2	1.43E-05	1.74E-05	1.60E-05	1.99E-05	05	3	9.16E-06	8e-3	0.606 4e-3
RPt/Ω									
cm-2	15.79	13.59	15.76	13.96	14.76	5.249	1.44E+01	3.967	3.915
					8.71E-			9.63E-	
n2	0.856 8	0.833 6	0.777 9	0.8196	01	0.796 6	0.831 3	01	0.973 4
CPE2/Sn		0.521 8e-		0.631 9e-	0.419		0.617 1e-	1.34E-	
cm-2	0.505 7e-3	3	0.504 1e-3	3	4e-3	8.28E-05	3	05	1.25E-05

Table S2. EIS parameters of devices co-sensitized with HD-2 using DCH<sub>1-9</sub>

# **Device fabrication procedures**

## TiO<sub>2</sub> electrode preparation and device fabrication using new dyes DCH<sub>1-9</sub> as sensitizers

Fluorine-doped tin oxide (FTO) coated glasses (thickness: 2.2 mm; sheet resistance: 8  $\Omega$ /cm<sup>2</sup>; from TEC, Pilkington) were gently washed with a soap solution, distilled water, acetone, and ethanol in that order. After washing, the FTO glasses were immersed in a 40 mM aqueous solution of TiCl4 (from Wako Pure Chemical Industries, Ltd) at 70 °C for 30 minutes. Once cooled, the glasses were rinsed with water and ethanol. Next, a thin layer of TiO<sub>2</sub> paste (Solaronix, Ti-Nanoxide D/SP) with a thickness of approximately 8-10 µm was coated onto the transparent substrates (active area: 0.18 cm<sup>2</sup>) using a screen printer. The coated substrates were then dried at 350 °C for 10 minutes and annealed at 500 °C for 30 minutes to serve as a seed layer. After the electrodes dried, a scattering layer of TiO<sub>2</sub> particles (5 µm thick) was screen-printed onto the previously deposited TiO<sub>2</sub> layer and subsequently annealed at 350 °C for 10 minutes, followed by another annealing at 500 °C for 30 minutes. Upon reaching room temperature, the TiO<sub>2</sub> electrodes were treated with a 40 mM aqueous TiCl<sub>4</sub> solution at 70 °C for 30 minutes, then rinsed with water and ethanol to fill in the defective "pinholes" present in the TiO<sub>2</sub> layer. Before immersing the electrodes in the dye solution, they were annealed once more at 500 °C for 30 minutes and allowed to cool to 80 °C. To prepare the dye solution, 0.2 mM solutions of  $DCH_{1-9}$  were made by dissolving the dye in a 10 mL mixture of acetonitrile, tert-butanol, and dimethyl sulfoxide (DMSO) in equal parts. Chenodeoxycholic acid (CDCA) was added to achieve a concentration of 20 mM. The hot electrodes were then immersed in the dye solutions and kept at room temperature for 20 hours to enhance adsorption onto the TiO<sub>2</sub> surface.

To prepare the counter electrode, pre-cut transparent conductive oxide (TCO) glass slides were first washed with distilled water, followed by a treatment with a 0.1 M HCl solution in ethanol. After this, the slides were sonicated in an acetone bath for 15 minutes. Once cleaned, the TCO glasses were dried at 400 °C for 15 minutes. Next, a thin layer of platinum paste (Solaronix, Plastisol T/SP) was uniformly applied to the TCO surface. The electrodes were then annealed at 450 °C for 10 minutes. Finally, the dye-sensitized TiO2 electrodes were sandwiched between the platinum counter electrodes. A liquid electrolyte (Solaronix, Iodolyte HI-30) was injected into the cell while the two electrodes were held together with clips.

#### $TiO_2$ electrode preparation and device fabrication using new dyes $DCH_{1-9}$ as co-sensitizers

Fluorine-doped tin oxide (FTO) coated glasses (thickness: 2.2 mm, sheet resistance: 8  $\Omega/cm^2$ , TEC, Pilkington) were gently washed with a soap solution, distilled water, acetone, and ethanol in that order. After washing, the FTO glasses were immersed in a 40 mM aqueous TiCl<sub>4</sub> solution (Wako Pure Chemical Industries, Ltd) at 70 °C for 30 minutes. Once cooled, the glasses were rinsed with water and ethanol. Next, a thin layer of TiO<sub>2</sub> paste (Solaronix, Ti-Nanoxide D/SP) approximately 8-10 µm thick was coated on the transparent substrates (active area: 0.18 cm<sup>2</sup>) using a screen printer. This was followed by drying at 350 °C for 10 minutes and annealing at 500 °C for 30 minutes to create a seed layer. After the electrodes had dried, a scattering layer of TiO<sub>2</sub> particles, 5 µm thick, was applied to the previously deposited TiO<sub>2</sub> layer and annealed first at 350 °C for 10 minutes and then at 500 °C for 30 minutes. Once at room temperature, the TiO2 electrodes were treated again with the 40 mM aqueous TiCl<sub>4</sub> solution at 70 °C for 30 minutes, followed by rinsing with water and ethanol. This treatment helps to fill the defective pinholes present in the TiO<sub>2</sub> layer. Before immersing the electrodes in the dye solution, they were annealed once more at 500 °C for 30 minutes and allowed to cool to 80 °C. The dye solutions were prepared by dissolving HD-2 (0.2 mM) and DCH1-9 (0.2 mM) in a 10 mL mixture of acetonitrile, tert-butanol, and dimethyl sulfoxide (DMSO) in a 1:1:1 ratio. Additionally, chenodeoxycholic acid (CDCA) was added at a concentration of 20 mM. The hot electrodes were immersed in the dye solutions and left at room temperature for 20 hours to enhance adsorption onto the TiO<sub>2</sub> surface.

To prepare the counter electrode, pre-cut TCO (Transparent Conductive Oxide) glasses were first washed with distilled water, then treated with a 0.1 M HCl solution in ethanol, and subsequently subjected to sonication in an acetone bath for 15 minutes. After cleaning, the TCO glasses were dried at 400 °C for 15 minutes. A thin layer of Pt-paste (Solaronix, Plastisol T/SP) was applied uniformly onto the TCO. The electrodes were then annealed at 450 °C for 10 minutes. Next, the dye-sensitized TiO2 electrodes were sandwiched between the Pt counter electrodes. Liquid electrolyte (Solaronix, Iodolyte HI-30) was injected into the cell while the two electrodes were held together with clips.

#### References

- (1) Becke, A. D. (1993) Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 98, 1372-1377.
- (2) Lee, C., W. Yang and R. G. Parr (1998) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **37**, 785-789.
- (3) Naik, P., R. Su, M. R. Elmorsy, D. D. Babu, A. V. Adhikari (2017) Molecular design and theoretical investigation of new metal-free heteroaromatic dyes with D-π-A architecture as photosensitizers for DSSC application. J. Photochem. Photobiol. A 345, 63-73.
- (4) Jin, R., X. Zhang and W. Xiao (2020) Theoretical Studies of Photophysical Properties of D-π-A-π-D-Type Diketopyrrolopyrrole-Based Molecules for Organic Light-Emitting Diodes and Organic Solar Cells. *Molecules* 25, 667.
- (5) Naik, P., R. Su, M. R. Elmorsy, D. D. Babu, A. V. Adhikari (2017) Molecular design and theoretical investigation of new metal-free heteroaromatic dyes with D- $\pi$ -A architecture as photosensitizers for DSSC application. *J. Photochem. Photobiol. A* **345**, 63-73.
- (6) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. Phys. Rev. B: Condens. Matter Mater. Phys. 1993, 47, 558.
- (7) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865.
- (8) De Vita, A. Energetics of Defects and Impurities in Metals and Ionic Materials from First Principles. Ph.D. Thesis, University of Keele, 1992.
- (9) Tkatchenko, A.; DiStasio, R. A., Jr; Car, R.; Scheffler, M. Accurate and Efficient Method for Many-Body van Der Waals Interactions. Phys. Rev. Lett. 2012, 108, 236402.
- (10) Czelej, K.; Ć wieka, K.; Ś piewak, P.; Kurzydlowski, K. J. Titanium-Related Color Centers in Diamond: A Density Functional Theory Prediction. J. Mater. Chem. C 2018, 6, 5261–5268.
- (11) Zhang, J.; Zhu, H.-C.; Zhong, R.-L.; Wang, L.; Su, Z.-M. Promising Heterocyclic Anchoring Groups with Superior Adsorption Stability and Improved IPCE for High-Efficiency Noncarboxyl Dye Sensitized Solar Cells: A Theoretical Study. Org. Electron. 2018, 54, 104–113.

- (12) Katono, M.; Bessho, T.; Meng, S.; Humphry-Baker, R.; Rothenberger, G.; Zakeeruddin, S. M.; Kaxiras, E.; Gratzel, M. D- π-A. Dye System Containing Cyano-Benzoic Acid as Anchoring Group for Dye-Sensitized Solar Cells. Langmuir 2011, 27, 14248–14252.
- (13) Prajongtat, P.; Suramitr, S.; Nokbin, S.; Nakajima, K.; Mitsuke, K.; Hannongbua, S. Density Functional Theory Study of Adsorption Geometries and Electronic Structures of Azo-Dye-Based Molecules on Anatase TiO2 Surface for Dye-Sensitized Solar Cell Applications. J. Mol. Graphics Modell. 2017, 76, 551–561.
- (14) Oprea, C. I.; Panait, P.; Lungu, J.; Stamate, D.; Dumbrava, A.; Cimpoesu, F.; Gîrtu, M. A. DFT Study of Binding and Electron Transfer from a Metal-Free Dye with Carboxyl, Hydroxyl, and Sulfonic Anchors to a Titanium Dioxide Nanocluster. Int. J. Photoenergy 2013, <u>https://doi.org/10.1155/2013/893850</u>