Electronic Supporting Information for:

A Combined Spectroscopic and TDDFT Study of Single-Double Anthocyanins for Application in Dye-Sensitized Solar Cell

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Figure S1. Dye absorbance comparison between Anthocyanin and N719 (left) and the dye extracts of anthocyanin and N719 (right)

Figure S2. Unpurified anthocyanin powder

Figure S3. UV-Vis spectra for anthocyanin concentration analysis

*The example of anthocyanin concentration calculation*

\[ A = (A_{512} - A_{700})_{pH \, 1.0} - (A_{524} - A_{700})_{pH \, 4.5} \]
\[ A = (3.0059 - 0.057934)_{pH \, 1.0} - (1.58637 - 0.281571)_{pH \, 4.5} \]
\[ A = 1.643167 \]

\[ \text{Anthocyanin concentration} = \frac{A \times 449.3 \times DF \times 1000}{26900 \times 1} \text{ mg/l} \]

**Anthocyanin concentration** = \[ \frac{1.643167 \times 449.3 \times 200 \times 1000 \text{ mg}}{26900 \times 1} \text{ l} \]
Anthocyanin concentration = 5489.03 mg l⁻¹
Anthocyanin concentration = 12.2 mM relative to the cyanidin – 3 – glucoside

Figure S4. Cyclic voltammetry of I/I₃⁻

Table S1
E₉ₓ, E₉ᵣₑᵈ, E₉_HOMO, E₉_LUMO, I₉₉ₚ₉, I₉₉ₚ₉ of I/I₃⁻ electrolyte estimated using cyclic voltammetry

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>E₉ₓ (V)</th>
<th>E₉ᵣₑᵈ (V)</th>
<th>E₉_HOMO (eV)</th>
<th>E₉_LUMO (eV)</th>
<th>E₉₉_hand overlap (eV)</th>
<th>I₉₉ₚ₉ (µA)</th>
<th>I₉₉ₚ₉ (µA)</th>
<th>n = I₉₉ₚ₉/I₉₉ₚ₉</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI-I₂</td>
<td>0.36</td>
<td>0.58</td>
<td>-4.768</td>
<td>-4.986</td>
<td>0.218</td>
<td>0.062</td>
<td>0.043</td>
<td>1.425</td>
</tr>
<tr>
<td>LiI-I₂</td>
<td>0</td>
<td>8</td>
<td>-4.760</td>
<td>-4.958</td>
<td>0.198</td>
<td>0.089</td>
<td>0.044</td>
<td>2.035</td>
</tr>
</tbody>
</table>

Figure S5. X-Ray diffraction pattern of TiO₂ nanoparticles (left) and the Crystallite Size analysis using Scherrer’s equation (right)

The grain size of TiO₂ is calculated by Scherrer’s equation as formulated in Eq. (1).

\[ D = \frac{K\lambda}{\beta \cos \theta} \]
Where $D$ is the average TiO$_2$ Crystallite Size, $K$ is the dimensionless shape factor (0.9 for the spherical particles), $\lambda$ is the Cu K$\alpha$ X-ray radiation wavelength, and $\beta$ is the full width at half-maximum height regarding the diffraction peaks.

**Table S2**

Parameters obtained by Scherrer’s equation

<table>
<thead>
<tr>
<th>$2\theta^\circ$</th>
<th>plane</th>
<th>K</th>
<th>$\lambda$ (nm)</th>
<th>FWHM</th>
<th>$\theta^\circ$</th>
<th>$\text{Cos } \theta^\circ$</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.3</td>
<td>101</td>
<td>0.9</td>
<td>0.15405</td>
<td>0.031151</td>
<td>12.75</td>
<td>0.975</td>
<td>4.56</td>
</tr>
</tbody>
</table>

Compared to standard anatase and rutile peaks from JCPDS 21-1272 and 21-1276, respectively, it can be seen that the TiO$_2$ photoelectrode results in the structure of mixed anatase and rutile. The analysis of Scherrer’s equation on the plane of (101) has the Crystallite size of 4.56 nm. The smaller crystallite size of particles will facilitate the higher number of dyes attaching the TiO$_2$ film. The Figure S6 showing the scanning electron microscope images of the TiO$_2$ film. According to the figure S6(a), the TiO$_2$ photoelectrode has the film thickness of 11.06 µm. The images show that the TiO$_2$ nanoparticles have the uniform mesoporous morphology. The grain size analysis based on the SEM image shows the average grain size of 20.47 nm. The surface analysis of TiO$_2$ nanoparticles is conducted using Brunauer–Emmett–Teller (BET) method resulting in the graph of the isotherm linear plot of adsorption-desorption of N$_2$ gas surrounding TiO$_2$ nanoparticles as seen in Fig. S7. The average surface area of TiO$_2$ nanoparticles is 52.0309 m$^2$/g.
Figure S6. Scanning electron microscope images of cross section film of TiO$_2$ nanoparticle (a), the surface of TiO$_2$ nanoparticle with the scale of 500 nm (b), 100 nm (d), and the grain size analysis of TiO$_2$ nanoparticles (c)

BET Data of TiO$_2$ nanoparticles

Analysis Adsorptive: N$_2$, Analysis Bath Temp.: 77.350 K, Sample Mass: 0.2021 g
Cold Free Space: 30.5800 cm$^3$, Surface Area: 52.0309 m$^2$/g

Figure S7. The isotherm linear plot of TiO$_2$ nanoparticle
Figure S8. The photochemical properties of DSSC using the N719 dyes with the same parameters as anthocyanin dyes resulting the efficiency of 6.25%.

Table S3

Vibration analysis of anthocyanin pigments

<table>
<thead>
<tr>
<th>No</th>
<th>Unpurified anthocyanin</th>
<th>Fraction 1 Anthocyanin</th>
<th>Fraction 2 Anthocyanin</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k (cm⁻¹)</td>
<td>T (%)</td>
<td>k (cm⁻¹)</td>
<td>T (%)</td>
</tr>
<tr>
<td>1</td>
<td>524.6</td>
<td>64.4</td>
<td>528.5</td>
<td>72.1</td>
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<tr>
<td>2</td>
<td>821.7</td>
<td>97.4</td>
<td>819.7</td>
<td>97.0</td>
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<tr>
<td>3</td>
<td>873.8</td>
<td>95.5</td>
<td>869.9</td>
<td>89.0</td>
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<tr>
<td>4</td>
<td>952.8</td>
<td>66.6</td>
<td>956.7</td>
<td>68.5</td>
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<tr>
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<td>26.9</td>
<td>1051.2</td>
<td>40.7</td>
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<td>6</td>
<td>1078.2</td>
<td>29.3</td>
<td>1085.9</td>
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<td>7</td>
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<td>26.3</td>
<td>1120.6</td>
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<td>35.1</td>
<td>1232.5</td>
<td>53.4</td>
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<td>1404.2</td>
<td>48.5</td>
<td>1404.2</td>
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<td>10</td>
<td>1456.3</td>
<td>61.6</td>
<td>-</td>
<td>-</td>
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<tr>
<td>11</td>
<td>1518.0</td>
<td>71.5</td>
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<tr>
<td>12</td>
<td>1656.9</td>
<td>38.6</td>
<td>1647.2</td>
<td>26.2</td>
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<tr>
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<td>1735.9</td>
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<td>2939.5</td>
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<td>15</td>
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<tr>
<td>16</td>
<td>3250.1</td>
<td>13.5</td>
<td>3190.3</td>
<td>20.9</td>
</tr>
<tr>
<td>17</td>
<td>3373.5</td>
<td>9.6</td>
<td>3333.0</td>
<td>23.7</td>
</tr>
</tbody>
</table>
Details of Dye-sensitized solar cell analysis

- **HOMO-LUMO analysis**

  Analysis The HOMO-LUMO levels are calculated using the following empirical Bredas equations as given in Eq. (2) and (3)

  \[
  E_{HOMO} = -e(E_{ox}^{onset} + 4.4) \\
  E_{LUMO} = -e(E_{RED}^{onset} + 4.4)
  \]

- **Electrochemical impedance spectroscopy analysis**

  The photoanode properties of capacitance and conductivity are quantified using the electrochemical impedance spectroscopy method. By using this method, the diffusion length \((L_n)\), the charge lifetime \((\tau_n)\), and the charge extraction time \((\tau_d)\) are analyzed from the equivalent circuit. Figure 9(b) displays the equivalent circuit element model simplifying the system due to the low current restriction in which the impedance of electrolyte diffusion \((Z_d)\) is vanishingly small. The Nyquist plot as seen in Fig. 9(a) explains the cell’s impedance characteristic features using anthocyanin dye-sensitized solar cell. A large arc in a low-frequency semicircle is assigned to the dye recombination resistance \((R_r)\) coupled with \(C_\mu\) explaining the electrolyte-solid interface total capacitance. The small arc of the high-frequency semicircle indicates the charge transport resistance \((R_d)\) through the semiconductor of TiO\(_2\) nanoparticles. At the bias potential of 0 V and the low-frequency condition, a large arc, which is resulted from the charge recombination and the back layer chemical capacitance, will lead to the higher impedance. The work is controlled as a diffusion-recombination transmission line under the reflecting boundary conditions. Therefore, the electrons will be injected at the interface between the film TiO\(_2\) semiconductor and the FTO. The electron will diffuse through the film or to the outer edge of the film where the electron transport is blocked.

  In a restricted condition displaying at least two impedance spectra domains as seen in Fig. 9, the domains of impedance are divided by the characteristic frequency \((\omega_d)\). The Warburg impedance happens in the high frequency regime \((\omega \gg \omega_d)\), which shows a short straight line in the impedance representation due to the diffusion. At the frequency
which is lower than $\omega_d$, the impedance behavior is commonly reflected or extracted at the end of the diffusion region. A large semicircle of lower frequency regime results in the longer electron lifetime and the faster electron transport through the TiO$_2$ film.

Equation (4) explains the transmission line impedance excluding the effects of the series resistance ($R_s$), the counter electrode resistance ($R_{pt}$), and the counter electrode chemical capacitance ($C_{pt}$) as described in Fig. 9(b). For the impedance at low frequencies, the vertical feature intercept with the real axis results in 1/3 of the transport resistance ($R_t$).

$$Z = \frac{1}{3} R_t + \frac{R_r}{1+i\omega/\omega_r}$$

(4)

When electrons diffuse through a material, the true driving force for the chemical diffusion has two components including the first term of $\partial \mu / \partial n$ indicating a gradient in concentration and a gradient in chemical potential, and the second phenomenological coefficient of film thickness $L$. The coefficient of chemical diffusion ($D_n$) is acquired from the EIS data as expressed in Eq. (5).

$$D_n = \frac{l^2}{\tau_d} = \frac{t_n^2}{\tau_n}$$

(5)

Furthermore, the effective diffusion length ($L_n$) is calculated using Eq. (6).

$$L_n = \sqrt{D_n \tau_n} = L \sqrt{\frac{\tau_n}{\tau_d}} = L \sqrt{\frac{R_r}{R_t}}$$

(6)

Figure 9 displays that $L_n$ exceeds the thickness of photoanode due to the $R_r \gg R_t$. The $\tau_d$ corresponds to the transient time for the diffusion of an electron through the film injected at $x = 0$ through a distance $L$ which is shown by Eq. (7)

$$\tau_d = R_t C_\mu = \frac{1}{\omega_d} = \frac{l^2}{D_n}$$

(7)

A rapid recombination commonly happens because the electrons react with tri-iodide ion $I_3^-$ in the redox electrolyte before they recapture each other at the current collector. The phenomenon is explained by the electron lifetime and it is represented by a large semicircle impedance as expressed in Eq. (8). A good cell performance should show the faster carrier extraction time ($\tau_d$) and the slower recombination time ($\tau_n$).
\[ \tau_n = R_r C_\mu = \frac{1}{\omega_r} = \frac{\nu_n^2}{b_n} \]  

Equation (9) describes the electron conductivity in the TiO\(_2\) calculated from the resistance of electron transport.

\[ \sigma_n = \frac{L}{A} R_t^{-1} \]  

where \( L \) is the film thickness, \( A \) is the photoanode projected area exposed through the Surlyn frame, and \( R_t \) is the macroscopic transport resistance.

- **Theoretical DFT-based DSSC modeling**

The theoretical DSSC analysis is obtained from the dyes’ DFT data. The charge transfer rate from dyes’ withdrawing group to the TiO\(_2\) surface is estimated using the General Marcus theory.

\[ k_{inj} = |V_{RP}| \frac{2}{\hbar} (\pi / \lambda k_B T)^{1/2} \exp \left[-(\Delta G^{inj} + \lambda)^2 / 4\lambda k_B T \right] \]  

In Eq.(10), \( |V_{RP}| \) is the coupling constant between the reagent and the product potential curves, \( k_{inj} \) (in \( S^{-1} \)) is the electron injection rate constant from dye to TiO\(_2\), \( \hbar \) is the Planck constant, \( \lambda \) is the reorganization energy of the system, \( k_B \) is the Boltzmann thermal energy, \( T \) is the temperature, and \( \Delta G^{inj} \) is the free energy of injection. Eq. (10) confirms that \( |V_{RP}| \) mostly indicates the sensitizer quality. The Generalized Mulliken-Hush formalism can be used to calculate \( |V_{RP}| \) for the electron transfer.

\[ |V_{RP}| = \Delta E_{RP} / 2 \]  

From Eq. (11), the electron injection can be improved along the increase of \( \Delta E_{RP} \). Therefore, the Koopmans approximation explains the driving force of electron injection.

\[ \Delta E_{RP} = [E_{HOMO}^{dye} + 2E_{LUMO}^{dye}] - [E_{LUMO}^{dye} + E_{HOMO}^{dye} + E_{CB}^{TiO_2}] \]  

Since the \( E_{HOMO}^{dye} \) describes the potential of first oxidation (\( E_{OX}^{dye} \)), the \( E_{LUMO}^{dye} \) indicates the dye’s reduction potential (\( E_{RED}^{dye} \)), and the \( E_{CB}^{TiO_2} \) is the TiO\(_2\) conduction band edge. Hence, the Eq.(12) can be stated as
\[ \Delta E_{RP} = \left[ -E_{HOMO}^{dye} + E_{CB}^{TiO_2} \right] = -\left[ E_{OX}^{dye} + E_{CB}^{TiO_2} \right] \]  \hspace{1cm} (13)

The Eq. (13) can also be modified as Eq. (14)

\[ \Delta E_{RP} = E_{0-0}^{dye} - \left[ 2E_{OX}^{dye} + E_{RED}^{dye} + E_{CB}^{TiO_2} \right] \]  \hspace{1cm} (14)

In Eq. (14), the free energy change (\( \Delta G^{\text{inject}} \)) for electrons injected from dyes to TiO\(_2\) surface is formulated as Eq. (15).

\[ \Delta G^{\text{inject}} = E_{OX}^{dye^*} - E_{CB}^{TiO_2} \]  \hspace{1cm} (15)

where \( E_{OX}^{dye^*} \) is the dye’s oxidation potential in the excited state condition. In this model, the first state electron injection happens because of the unrelaxed excited state. Therefore, the excited state oxidation potential is derived from the dye’s ground state redox potential and (\( E_{OX}^{dye} \)) is obtained from IEF-PCM(UAKS)-B3LYP-6-31+G(d,p) level of theory. Furthermore, the vertical transition energy indicates the photoinduced intramolecular charge transfer (ICT). The \( E_{OX}^{dye^*} \) is formulated as Eq. (16).

\[ E_{OX}^{dye^*} = E_{OX}^{dye} - \lambda_{\text{ICT}} \]  \hspace{1cm} (16)

where \( \lambda_{\text{ICT}} \) is the photoinduced intramolecular charge transfer energy. According to the electron injection which happens after relaxation, this phenomenon assumes that the entropy change during the light absorption can be ignored. In view of this condition, the Rehm and Weller equation shows that \( E_{OX}^{dye^*} \) is calculated as Eq. (17)

\[ E_{OX}^{dye^*} = E_{OX}^{dye} - \lambda_{0-0} \]  \hspace{1cm} (17)

where \( \lambda_{0-0} \) is the transition energy between the excited state and the ground state.

Moreover, the efficiency of DSSC is also influenced by the dye’s response to the incident light. In Eq.(18), the dye’s light harvesting efficiency (LHE) has to be as much as possible in order to maximize the photocurrent response.

\[ LHE = 1 - 10^{-A} = 1 - 10^{-f} \]  \hspace{1cm} (18)

where \( A(f) \) is the absorption (oscillator strength) corresponding to the absorption energy (\( \lambda_{\text{max}}^{\text{ICT}} \)) of the dye. The oscillator strength is directly obtained from the TDDFT calculations as shown in Eq. (19)
\[ f = \frac{2}{3} \lambda_{\text{max}}^{\text{ICT}} |\vec{\mu}_o - \text{ICT}|^2 \]  

where $|\vec{\mu}_o - \text{ICT}|$ is the dipolar transition moment regarding the electronic excitation. Thus, both \( \lambda_{\text{max}}^{\text{ICT}} \) and \( \vec{\mu}_o - \text{ICT} \) and must be improved in order to enhance the oscillator strength \( f \).

\[ J_{\text{SC}} = \int LHE(\lambda) \cdot \phi_{\text{injection}} \eta_{\text{injection}} \, d\lambda \]  

In Eq. (13), the \( J_{\text{sc}} \) is directly related to the LHE, and the \( \phi_{\text{injection}} \) concerning the free energy change \( (\Delta G_{\text{inject}}) \). It can be conclude theoretically that the greater LHE and \( \Delta G_{\text{inject}} \), the higher cell efficiency.

The theoretical open circuit voltage adopts the Misra’s equation, which is formulated as Eq. (21)\(^6\)

\[ eV_{\text{oc}} = E_{F,n} - E_{\text{red}} \]  

where \( E_{F,n} \) is TiO\(_2\) quasi-fermi level.

**References**