Aggregation-Free Organic Dyes Featuring Spiro[dibenzo[3,4:6,7]cyclohepta[1,2-b]quinoxaline-10,9′-fluorene] (SDBQX) for Dye-Sensitized Solar Cells

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Three novel organic dyes coded as FHD4-1, FHD4-2, and FHD4-3 featuring spiro[dibenzo[3,4:6,7]cyclohepta[1,2-b]quinoxaline-10,9′-fluorene] (SDBQX) moieties are designed to inhibit dye aggregation to improve the performance of dye-sensitized solar cells (DSSCs). The consistent absorption onsets of FHD4-1, FHD4-2, and FHD4-3 in solutions and adsorbed on TiO₂ films indicate that these dyes are aggregation-free dyes. Therefore, coadsorption with chenodeoxycholic acid (CDCA) of these three dyes reduces the performance of DSSCs because no inhibition effect for dye aggregation is needed, but, on the contrary, the dye loading amount is reduced after addition of CDCA.

Since it was first reported in 1991, dye-sensitized solar cells (DSSCs) have attracted wide attention and been well developed. Many chemists put their eyes on organic dyes because of their advantages such as low cost, low toxicity, easy structural modification and even efficiency predictable. Many kinds of excellent organic dyes have been developed, such as porphyrin dyes, N-annulated perylene dyes, and many different kinds of rigidified aromatics dyes. Dyes with D–π–A system is the main type organic dyes, which contains an electron donor (D), an electron acceptor (A), and a π-conjugated spacer (π) to link the donor and acceptor. Base on this, dyes with D–A–π–A system were developed by adopting an extra electron deficient spacer to decrease the bandgap and enlarge the absorption range to achieve high power conversion efficiency.

Dye aggregation is a common phenomenon especially for planar dyes and it is adverse for DSSC performance. We have reported a series of D–A–π–A organic dyes (FHD4, FHD5, and FHD6) featuring with spiro[dibenzo[3,4:6,7]cyclohepta[1,2-b]quinoxaline-10,9′-fluorene] (SDBQX) moieties to suppress dye aggregation in DSSCs considering about the fluorenyl moiety is perpendicular to the quinoxaline moiety of SDBQX and a 3D structure is realized. However, dye aggregation was still not be eliminated especially for FHD5 and FHD6. Thus, we designed three organic dyes (FHD4-1, FHD4-2, and FHD4-3) by replacing the electron donor of FHD4 with electron donor groups adopted long alkyl chains. We expected that thorough suppression of dye aggregation could be observed for these novel organic dyes. The molecular structures of FHD4-1, FHD4-2, and FHD4-3 are shown in Scheme 1. Their photophysical and electrochemical properties and photovoltaic parameters of DSSCs sensitized by these dyes were investigated systematically.

Scheme 2 depicts the synthetic routes for FHD4-1, FHD4-2, and FHD4-3. Intermediate 2 could be synthesized by Suzuki cross-coupling reaction between 1 and 3-formylfurural-2-yl boronic acid. Then Suzuki cross-coupling reactions between 2 and 4-(bis(4-((2-ethylhexyl)oxy)phenoxy)aminophenyl)boronic acid, 4-(bis(2-ethylhexyl)aminophenyl)boronic acid, or 9-(2-ethylhexyl)-9H-carbazol-3-yl)boronic acid would give the aldehyde 3a–3c, respectively. Finally, cyanoacrylic acid groups were introduced by Knoevenagel reactions between aldehyde...
3a–3c and cyanoacetic acid to afford FHD4-1, FHD4-2, and FHD4-3, respectively. FHD4-1, FHD4-2, and FHD4-3 were characterized with 1H NMR, 13C NMR, and HRMS.

Figure 1 shows the UV–vis absorption spectra of FHD4-1, FHD4-2, and FHD4-3 in CH2Cl2 solutions (2 × 10−5 M) and adsorbed on TiO2 films. The relevant photophysical data are summarized in Table 1. In the solution absorption spectra, all of the three dyes exhibited two prominent peaks at around 410–430 and 490–550 nm. The intense absorption bands in short wavelength region could be assigned to the π–π* transition.[21] The absorption peaks in long wavelength region corresponding to the intramolecular charge transfer (ICT) from the electron donor to the electron acceptor were observed at 531, 545, and 490 nm for FHD4-1, FHD4-2, and FHD4-3, respectively.[21] Broader spectral coverages were observed for FHD4-1 and FHD4-2 compared with FHD4-3. Similar molar extinction coefficients (ε) were observed for these three dyes, the high ε values guaranteed their good light harvesting capabilities.[22] Based on the molecular exciton theory, dye aggregation would lead to a shift of absorption spectrum.[20] As for FHD4, an obvious bathochromic shift was observed for absorption spectrum on TiO2 film compared with in solution, which suggested that the existence of J-aggregation for FHD4 molecules on the surface of TiO2.[21] The absorption onsets of FHD4-1, FHD4-2, and FHD4-3 in solutions and adsorbed on TiO2 films had good consistency and no apparent shifts were observed. It demonstrates that dye aggregation could be suppressed efficiently by adopting donors with long alkyl chains, and hence FHD4-1, FHD4-2, and FHD4-3 are confirmed to be aggregation free dyes and their well performance in DSSC could be expected due to aggregation is a key adverse factor for DSSC performance.
The redox potentials of FHD4-1, FHD4-2, and FHD4-3 were determined by cyclic voltammetry to evaluate the feasibilities of the electron injection and dye regeneration. The cyclic voltammograms are shown in Figure 2a and the corresponding data are summarized in Table 1. The first oxidation potentials ($E_{\text{ox}}$) of dyes FHD4-1 (0.86 V), FHD4-2 (0.97 V), and FHD4-3 (1.37 V) were more positive than the $I_3^-/I^-$ redox potential (0.4 V vs normal hydrogen electrode, NHE), so efficient dye regeneration of the oxidized dyes by the $I_3^-/I^-$ electrolyte could be expected.\(^{23}\) The energy band diagrams of the dyes between these dyes and the CB edge of TiO$_2$ are getting smaller (FHD4-3 0.67 V) were negative than the conduction band (CB) edge of TiO$_2$ (0.5 V vs NHE). The potential difference between these dyes and the CB edge of TiO$_2$ are getting smaller in the sequence of FHD4-1, FHD4-2, and FHD4-3. The latter one might not enough to guarantee the thermodynamic feasibility of charge injections from excited dye molecules to the CB of TiO$_2$, which might restrict the photovoltaic performances for DSSCs.\(^{24}\)

The optimized geometrical structures and electron distributions of FHD4-1, FHD4-2, and FHD4-3 were simulated by density functional theory (DFT) calculations with the B3LYP exchange correlation functional under the 6-31G (d,p) basis set implemented in the Gaussian 09 program. The simulated electron distributions in highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the dyes are shown in Figure 3, while the isodensity surface values were fixed at 0.02. As shown in their molecular orbital profiles, the electrons mainly distributed over the triphenylamine moiety with a little contribution over the quinoxaline core for the HOMO of FHD4-1, and distributed over the whole molecules for the HOMOs of FHD4-2 and FHD4-3. For the LUMOs, the electrons located on the quinoxaline core and electron acceptors (furanylacrylic acid moiety) for all of these three dyes. The bandgaps between HOMOs and LUMOs according to DFT calculations (2.14, 2.42, and 2.63 V for FHD4-1, FHD4-2, and FHD4-3, respectively) exhibited consistent trend with the $E_{\text{red}}$ values obtained from onsets of the absorption spectra. Figure 4 shows the calculated dihedral angles between quinoxaline of SDBQX moieties and the aromatic rings connected with quinoxalines in the optimized structures of FHD4-1, FHD4-2, and FHD4-3. It is clear that the dihedral angles between quinoxaline moieties and electron donating groups are very similar (39.6°, 38.5°, and 41.2° for FHD4-1, FHD4-2, and FHD4-3, respectively), and the dihedral angles between quinoxaline moieties and furan rings are almost same (6.3°, 6.4°, and 6.8° for FHD4-1, FHD4-2, and FHD4-3, respectively). Based on the dihedral angle data, quinoxaline moieties showed an approximate coplanar geometry with the furan rings for FHD4-1, FHD4-2, and FHD4-3. The big dihedral angles between quinoxaline moieties and electron donating groups is beneficial to ICT, and hence enlarging the absorption spectra range, which could enhance the light harvesting capabilities of these dyes.\(^{25,26}\)

The photovoltaic performances of the DSSCs based on FHD4-1, FHD4-2, and FHD4-3 with or without chenodeoxycholic acid (CDCA) were evaluated under illumination simulated AM 1.5G irradiation (100 mW cm$^{-2}$). Figure 5 shows the

![Figure 1. UV–vis absorption spectra of FHD4-1, FHD4-2, and FHD4-3 a) in solutions and b) adsorbed on TiO$_2$ films.](image1)

Table 1. Photophysical and electrochemical data of FHD4-1, FHD4-2, and FHD4-3.

| Dye   | $\lambda_{\text{max}}$ [nm]$^a$ | $\varepsilon$ [10$^4$ M$^{-1}$ cm$^{-1}$]$^b$ | $E_{\text{ox}}$ [V]$^c$ | $E_{0-0}$ [V]$^d$ | $E_{\text{red}}$ [V]$^e$ | Bandgap [eV]$^f$ |
|-------|-------------------------------|------------------------------------------|-------------------|-----------------|------------------|---------------- |
| FHD4-1 | 531                           | 2.02                                    | 0.86              | 1.76            | −0.90            | 2.14           |
| FHD4-2 | 545, 429                      | 2.36, 3.03                              | 0.97              | 1.78            | −0.81            | 2.42           |
| FHD4-3 | 490, 429, 411                 | 2.46, 3.35, 2.64                        | 1.37, 2.04        | 2.04, 2.63      | −0.67            | 2.63           |

$^a$In CH$_2$Cl$_2$ solution; $^b$First oxidation potentials ($E_{\text{ox}}$) vs NHE were calibrated with ferrocene (0.63 V vs NHE); $^c$Transition energy was calculated from optical absorption onset; $^d$Redox potential ($E_{\text{red}}$) vs NHE; $^e$$E_{0-0} = E_{\text{ox}} - E_{0-0}$; $^f$DFT/B3LYP calculated values.
photocurrent density–voltage ($J–V$) curves and the incident photon-to-current conversion efficiencies (IPCE) characteristic plots. The detailed corresponding photoelectrode chemical data of short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor (FF), and power conversion efficiency ($\eta$) are listed in Table 2. The DSSCs based on FHD4-1, FHD4-2, and FHD4-3 exhibited high short-circuit current density ($J_{sc} = 10.44, 12.94,$ and 11.00 mA cm$^{-2}$, respectively) as well as high open-circuit photovoltage ($V_{oc} = 0.72$, 0.68, and 0.71 V, respectively), and hence good power conversion efficiency ($\eta = 4.54\%, 5.16\%,$ and $4.87\%$, respectively) was observed for them. The high $J_{sc}$ value of DSSCs based on FHD4-2 guaranteed its highest power conversion efficiency among these three dyes even if a little lower $V_{oc}$ was observed for it. The IPCE plots were measured to
further study the $J_{sc}$ of the DSSCs based on FHD4-1, FHD4-2, and FHD4-3. As shown in Figure 5b, the devices based on these three dyes exhibited broad spectral responses, which were well consistent with the absorption spectra on TiO$_2$ films (Figure 1b). Low response intensity for FHD4-1 and narrow response range for FHD4-3 resulting in there lower $J_{sc}$ values compared with FHD4-2.

Typically, the addition of CDCA would improve the power conversion efficiency because it could obstruct the dye aggregation on TiO$_2$ film.[23] Similar effects were observed for FHD4, FHD5, and FHD6 in our previous work.[24] However, after coadsorption with CDCA, lower efficiencies were observed for analogues FHD4-1, FHD4-2, and FHD4-3 (4.17%, 5.08%, and 4.34%, respectively) featuring with long alkyl chains mainly due to the reduction of $J_{sc}$ values. As we discussed above, FHD4-1, FHD4-2, and FHD4-3 are aggregation free dyes which means no auxiliary additive such as CDCA is necessary to prevent the dye aggregation. Moreover, the addition of CDCA could reduce the chance of dye adsorption,[25] so lower $J_{sc}$ values could be expected which is well coincident with our study. It could also explain the lower response intensity of IPCE for the DSSCs coadsorbed with CDCA. To examine this guess, dye loading amount ($J$) on TiO$_2$ of FHD4-1, FHD4-2, and FHD4-3 with or without CDCA were measured. As shown in Table 2, the $\Gamma$ values of FHD4-1, FHD4-2, and FHD4-3 decreased from $1.41 \times 10^{-7}$, $1.31 \times 10^{-7}$, and $1.23 \times 10^{-7}$ cm$^{-2}$ (no CDCA) to $1.13 \times 10^{-7}$, $1.08 \times 10^{-7}$, and $1.22 \times 10^{-7}$ cm$^{-2}$ (with 3 × 10$^{-3}$ M CDCA), respectively. It is clear that dye loading amount reduced after coadsorption with CDCA for all of these three dyes as we expected above.

In summary, three novel organic dyes featuring with SDBQX moieties (FHD4-1, FHD4-2, and FHD4-3) were designed and synthesized. These dyes were characterized with $^1$H NMR, $^{13}$C NMR, and HRMS. The absorption onsets of FHD4-1, FHD4-2, and FHD4-3 in solutions and adsorbed on TiO$_2$ films had good consistency and no apparent shifts were observed. It demonstrates that FHD4-1, FHD4-2, and FHD4-3 are aggregation free dyes. Good power conversion efficiency was achieved for FHD4-1, FHD4-2, and FHD4-3 (4.54%, 5.16%, and 4.87%, respectively). Coadsorption with CDCA reduced the efficiency to 4.17%, 5.08%, and 4.34%, respectively. It was attributed to the reduce of dye loading amount and hence the $J_{sc}$ value after addition of CDCA. It was proved that no auxiliary additive such as CDCA is necessary for aggregation free dyes FHD4-1, FHD4-2, and FHD4-3 to prevent dye aggregation.

Table 2. Photovoltaic performance parameters of DSSCs based on FHD4-1, FHD4-2, and FHD4-3.

| Dye  | CDCA $[\times 10^{-3} \text{ M}]$ | $J_{sc}$ [mA cm$^{-2}$] | $V_{oc}$ [V] | FF [%] | $\eta$ [%] | $\Gamma$ [M cm$^{-2}$] |
|------|-------------------------------|--------------------------|-------------|--------|-----------|---------------------|
| FHD4-1 | 0                              | 10.44 ± 0.45             | 0.72 ± 0.01 | 60.86 ± 1.51 | 4.54 ± 0.06 | 1.41 ± 10$^{-2}$ |
|       | 3                              | 9.36 ± 0.47              | 0.72 ± 0.01 | 61.97 ± 0.77 | 4.17 ± 0.22 | 1.13 ± 10$^{-2}$ |
| FHD4-2 | 0                              | 12.94 ± 0.42             | 0.68 ± 0.01 | 59.06 ± 1.42 | 5.16 ± 0.03 | 1.31 ± 10$^{-2}$ |
|       | 3                              | 12.36 ± 0.36             | 0.67 ± 0.02 | 61.79 ± 1.21 | 5.08 ± 0.15 | 1.08 ± 10$^{-2}$ |
| FHD4-3 | 0                              | 11.00 ± 0.25             | 0.71 ± 0.02 | 62.67 ± 0.86 | 4.87 ± 0.02 | 1.79 ± 10$^{-2}$ |
|       | 3                              | 9.54 ± 0.24              | 0.71 ± 0.01 | 63.93 ± 0.87 | 4.34 ± 0.07 | 1.32 ± 10$^{-2}$ |

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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