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ARTICLE TYPE

Structure-Activity Relationship of Naphthalene Based Donor-π-Acceptor Organic Dyes for Dye-Sensitized Solar Cells: Remarkable Improvement of Open-Circuit Photovoltage

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Four new donor- π -acceptor organic dyes (**YF01-04**) containing naphthalene-substituted amines as an ¹⁰ electron donor and cyanoacrylic acid as an electron acceptor were designed and synthesized, and their photophysical properties and dye-sensitized solar cells (DSCs) performances were characterized. Dyes **YF02** and **YF04** with 2,6-disubstituted naphthalene framework were superior to their analog dyes **YF03** and **YF01** having 1,2-disubstituted naphthalene moiety in incident-photo-to-current conversion efficiency (IPCE) and total solar-to-electric conversion efficiency (η). The DSCs based on **YF02** comprised of ¹⁵ diphenylamine moiety as the donor produced the highest η of 5.29% compare to 4.03% of the analog dye **YF04** which has pyrrolidine as the donor. Remarkably, a high open-circuit photovoltage (V_{oc}) of 0.799-0.807 V was achieved in the case of **YF02-03**, which has diphenylamine-donor. To better understand the structure-activity relationship for DSCs application, molecular modelling were performed on **YF01-04** and vertical electronic excitations were calculated using long-range corrected energy functional WB97XD ²⁰ and CAM-B3LYP at the basis set level DGDZVP, which were in excellent agreement with the experimental results. Moreover, the equilibrium molecular geometries of dyes **YF01-04** were calculated

at the DFT level using the hybrid energy functional B3LYP and basis set DGDZVP. The torsion angles (θ) between the naphthalene moiety and diphenylamine donor in **YF02** and **YF03** were more twisted than that of the pyrrolidine-donor dyes **YF01** and **YF04**, precluding efficient intermolecular π - π charge ²⁵ transfer, which translated into high V_{oc} . Compared to the reference dye **TA-St-CA**, which is based on diphenylamine as an electron donor linked to a phenyl ring, **YF02** achieved higher V_{oc} , which indicated that naphthalene substituted with diphenylamine is more efficient in retarding charge recombinations.

Introduction

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- Dye-sensitized solar cells (DSCs) are one of the most promising ³⁰ next-generation photovoltaic cells due to their versatile, energysaving, and environmentally friendly nature in comparison with the traditional silicon-based solar cells.¹ At present, the state-ofthe-art DSCs based on ruthenium(II)–polypyridyl complexes as the active material have an overall power conversion efficiency
- 35 (η) approaching 12% under standard (Global Air Mass 1.5) illumination.² However, the rarity and high cost of the ruthenium metal may limit their development for large-scale applications. Metal free organic dyes have attracted considerable attention in recent years due to their high molar extinction coefficients,
- ⁴⁰ flexible structural modifications and low costs. In the past few years, many researchers have focused on developing metal-free organic sensitizers, and some of these endeavours have achieved decent efficiencies.³ Among them, the donor-(π -spacer)-acceptor (D- π -A) conjugated system is the basic structure for designing the ⁴⁵ organic sensitizers due to their effective photo-induced

intramolecular charge-transfer characteristics. Recently, tremendous research efforts have been invested to improve the efficiency of solar energy conversion. In principle, high performance DSCs require organic dyes to produce high short-50 circuit photocurrent (J_{sc}), high open-circuit photovoltage (V_{oc}), and high fill factor (FF).⁴ Generally, the efficiency of the DSC is mainly determined by J_{sc} and V_{oc} . J_{sc} is usually correlated to the absorption ability and electron injection efficiency of organic dyes, while the effect of $V_{\rm oc}$ is considered to be more complicated 55 than $J_{\rm sc}$. Therefore, in order to further improve the efficiency of fundamental understanding of structure-activity DSCs. relationship is needed to reduce the charge recombination and increase the electron injection efficiency.⁵ In addition, charge recombination and electron injection efficiency are closely 60 correlated with the $V_{\rm oc}$, which means that $V_{\rm oc}$ becomes the key factor among many factors responsible for enhancing the performance of DSCs. One strategy to improve the $V_{\rm oc}$ is to decrease the molecular π -stacked aggregation of dyes on the TiO₂ surface because strong dye aggregation can lead to self-

80

90

Page 2 of 8



Figure 1. Organic dyes TA-St-CA and AK01.

quenching and reduction of electron injection resulting in a low $V_{\rm oc}$ ^{3b,6} In our recent DSCs study based on **AK01** dye⁷ compared 5 to TA-St-CA dye (Figure 1),⁸ it was demonstrated that AK01 showed higher overall conversion efficiency (η) than TA-St-CA (6.20% vs 5.41%). The $V_{\rm oc}$ of AK01 was much lower than TA-St-CA (0.64 V vs 0.718 V),⁷ the higher efficiency of AK01 was mainly ascribed to the higher J_{sc} . Considering the structures of 10 triphenyl amine (TA-St-CA) and indoline moiety (AK01), it is likely that the higher V_{oc} of TA-St-CA is due to large torsion angels in the molecular structure of TA-St-CA. In an extension to our continuous effort for enhancing the V_{oc} ,⁹ we report herein a novel series of D- π -A sensitizers **YF** based on naphthalene-linked 15 pyrrolidine or diphenylamine as an electron donor, oligophenylenevinylene as a π -linkage, and the cyanoacrylic acid as an electron acceptor/anchor group (Figure. 2) for nanocrystalline TiO₂ solar cells. DSCs based on the novel dyes YF02 and YF04 comprised of a naphthalene-linked diphenylamine as a donor $_{20}$ showed a high $V_{\rm oc}$ of ~0.8 V. To study the influence of naphthalene-amine moiety and its substitution position on the photophysical, photoelectrochemical properties, and solar-cell performance, the pyrrolidine-naphthalene based dyes, YF01 and YF03, were also synthesized. Molecular orbital calculations at 25 the DFT level were performed, and the equilibrium molecular geometries of the YF and TA-St-CA were calculated to better understand the structure-activity relationship, and in particular the interrelationship between the torsion angels (θ 1-6) and V_{oc}. Figure 2 shows the molecular structures of dyes **YF01-04**, where $\theta 1 - \theta 6$ 30 refer to the locations of torsion angels of interest.



Experimental Section

35 General information for materials synthesis

¹H NMR and ¹³C NMR spectra were recorded on JEOL JMTC-270/54/SS (JASTEC, 400 MHz) spectrometers. ¹H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of CDCl₃ at 7.26 ppm, integration, multiplicities (s ⁴⁰ = singlet, d = doublet, t = triplet, q = quartet and m = multiple), and coupling constants (Hz). ¹³C NMR spectra reported in ppm (δ) relative to the central line of triplet for CDCl₃ at 77.00 ppm. High-resolution mass spectra were obtained on a BRUKER APEXIII spectrometer. Column chromatography was carried out ⁴⁵ employing Silica gel 60N (spherical, neutral, 40~100 µm, KANTO Chemical Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck). All other reagents and solvents commercially available were used without further purification unless otherwise ⁵⁰ noted.

Synthesis of compounds YF01-04

A mixture of the corresponding aldehyde derivatives (1.2 mmol), 2-cyanoacetic acid (306 mg, 3.6 mmol) and ammonium acetate (46 mg, 0.6 mmol) was dissolved in 10 mL acetonitrile and 10 ⁵⁵ mL acetic acid, and the mixture was stirred for 12 hours in Ar under reflux condition. After evaporation of the solvent, the residue was purified by silica-gel column chromatography to give compounds **YF01-04**.

Dye YF01. Yield 92%; ¹H NMR (400 MHz, CDCl₃) δ 13.94 (s, 1H), 8.31 (s, 1H), 8.06 (d, J = 8.4 Hz, 3H), 7.90-7.84 (m, 3H), 7.77-7.72 (m, 2H), 7.40-7.37 (m, 1H), 7.31-7.23 (m, 2H), 6.70 (d, J = 16.8 Hz, 1H), 3.30 (bs, 4H), 1.86 (bs, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 163.34, 153.49, 145.83, 142.46, 132.90, 131.22

 $_{65}$ (2C), 130.17, 130.08, 128.29, 127.91, 127.37, 126.62, 126.31, 122.82, 122.01, 116.97, 116.78, 102.300, 51.83, 25.30. HRMS (ESI positive): $[M+H]^+$ calcd for $C_{26}H_{22}N_2O_2H$, 395.17540; found, 395.17546.

Dye YF02. Yield 75%; ¹H NMR (400 MHz, CDCl₃) δ 8.29 (s, 1H), 8.06 (d, *J* = 8.8 Hz, 2H), 7.96 (s, 1H), 7.82-7.77 (m, 4H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.60 (d, *J* = 16.4 Hz, 1H), 7.42 (d, *J* = 16.4 Hz, 1H), 7.34-7.30 (m, 5H), 7.18 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 7.10-7.06 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 163.30, 75 153.33, 146.85, 145.39, 141.95, 133.89, 132.58, 131.88, 131.21, 130.21, 129.53, 129.32, 129.27, 127.24, 127.01, 126.87, 126.71, 124.21, 124.04, 123.79, 123.36, 118.56, 116.38, 102.27. HRMS (ESI positive): [M+Na]⁺ calcd for C₃₄H₂₄N₂O₂Na, 515.17300; found, 515.17291.

Dye YF03. Yield 70%; ¹H NMR (400 MHz, CDCl₃) δ 13.94 (s, 1H), 8.26 (s, 1H), 8.19-8.16 (m, 1H), 7.96-7.92 (m, 4H), 7.54-7.49 (m, 4H), 7.39 (d, J = 16.4 Hz, 1H), 7.28 (d, J = 8.8 Hz, 1H), 7.20-7.16 (m, 4H), 6.92-6.86 (m, 7H). ¹³C NMR (100 MHz, 85 CDCl₃) δ 163.22, 153.44, 146.92, 141.90, 141.56, 132.86, 132.33, 131.53, 130.93, 130.64, 130.42, 129.54, 129.13, 128.28, 127.47, 126.81, 126.76, 125.64, 124.70, 121.77, 121.68, 116.22, 102.58. HRMS (ESI positive): [M+Na]⁺ calcd for C₃₄H₂₄N₂O₂Na, 515.17300; found, 515.17256.

Dye YF04. Yield 76%; ¹H NMR (400 MHz, CDCl₃) δ 8.20 (s,

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Scheme 1. Synthesis of new organic dyes YF01-04.

⁵ 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.83 (s, 1H), 7.77-7.69 (m, 4H), 7.62 (d, J = 8.8 Hz, 1H), 7.53 (d, J = 16.4 Hz, 1H), 7.29 (d, J = 16.4 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 6.75 (s, 1H), 3.35 (bs, 4H), 1.99 (bs, 4H). ¹³C NMR (100 MHz, THF-d₈) δ 163.00, 152.94, 146.42, 143.08, 135.66, 132.80, 131.40, 130.34, 129.65, 128.96, 10 127.83, 126.49, 126.32, 126.30, 126.08, 124.57, 123.42, 115.79, 104.70, 101.98, 47.55, 25.45. HRMS (ESI positive): [M+H]⁺ calcd for C₂₆H₂₂N₂O₂H, 395.17540; found, 395.17547.

Molecular modeling

- Ground state equilibrium molecular geometries of YF01-04 were ¹⁵ calculated using the hybrid DFT energy functional B3LYP^{10,11} and the basis set DGDZVP (density Gauss double-ζ with polarization functions).^{12,13} Subsequently, a single point energy calculation was performed on the optimized geometry using different long-range corrected time-dependent DFT energy ²⁰ functional methods including CAM-B3LYP¹⁴ or WB97XD¹⁵ with
- ²⁰ functional methods including CAM-B3LYP or WB97XD with the basis set DGDZVP, and the electronic absorption spectra were extracted. The TD-DFT calculations were performed in ethanol using the polarizable conductor calculation model (PCM). The DFT/TD-DFT calculations were performed on the East
- ²⁵ Carolina University's Super Computer Jasta using 8 processors and 4GB of RAM. The solvent effect was accounted for using the polarizable conductor calculation model (PCM), implemented in Gaussian 09. All calculations were performed using Gaussian 09.

Fabrication of dye sensitized solar cells

³⁰ A double-layer TiO₂ photoelectrode (10 + 5) µm in thickness with a 10 µm thick nanoporous layer and a 5 µm thick scattering layer (area: 0.25 cm²) was prepared by screen printing on conducting glass substrate. A dye solution of **YF04-01** with 3 x 10^{-4} M concentration in acetonitrile/*tert*-butyl alcohol (1/1, v/v) ³⁵ was used to up take the dye on to the TiO₂ film. Deoxycholic acid (DCA) (20 mM) as a co-adsorbent was added into the dye solution to prevent aggregation of the dye molecules. The TiO₂ films were immersed into the dye solution and then kept at 25 °C for 30 h. Photovoltaic measurements were performed in a ⁴⁰ sandwich type solar cell in conjunction with an electrolyte consisting of a solution of 0.6 M dimethylpropyl-imidazolium iodide (DMPII), 0.05M I₂, 0.1M LiI and 0.5M *tert*-butylpyridine (TBP) in acetonitrile (AN). The dye-deposited TiO₂ film and a platinum-coated conducting glass were separated by a Surlyn ⁴⁵ spacer (40 µm thick) and sealed by heating the polymer frame.

Potocurrent density-voltage (*I-V*) of sealed solar cells was measured under AM 1.5G simulated solar light at a light intensity of 100 mW cm⁻² with a metal mask of 0.25 cm². The photovoltaic parameters, *i.e.* short circuit current (J_{sc}), open circuit voltage ⁵⁰ (V_{oc}), fill factor (*FF*), and power conversion efficiency (η) were estimated from *I-V* characteristics under illumination.

EIS and IMVS measurements

The intensity-modulated photovoltage spectra (IMVS) were measured with a potentiostat (Solartron1287) equipped with a ⁵⁵ frequency response analyzer (Solartron1255B) at an open-circuit condition based on a monochromatic illumination (420 nm) controlled by Labview system to obtain the photovoltaic response induced by the modulated light. The modulated light was driven with a 10% AC perturbation current super imposed on a DC ⁶⁰ current in a frequency range from 0.1 to 10⁶ Hz. The charge extraction method (CEM) was performed with the same monochromatic light source. The solar cell was illuminated at an open-circuit condition for 5 s to attain a steady state and then the light source was switched off when the device simultaneously ⁶⁵ switched to a short-circuit condition to extract the charges generated at that light intensity. The electrochemical impedance spectra were measured with an impedance analyzer (Solartron Analytical, 1255B) connected with a potentiostat (Solartron Analytical, 1287) under illumination using a solar simulator (WXS-155S-10: Wacom Denso Co. Japan). EIS spectra were recorded over a frequency range of 10⁻²-10⁶ Hz at 298 K. The 5 applied bias voltage and AC amplitude were set at Voc of the DSCs. The electrical impedance spectra were characterized using

Z-View software (Solartron Analytical).

Results and discussion

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The synthesis routes of compounds **YF01-04** are shown in ¹⁰ Scheme 1. The 2-amino-substituted 1-naphthaldehydes were prepared according to the reported methods (Scheme S1, ESI).^{16-¹⁸ The substituted (*E*)-4-(2-(naphthalenyl)vinyl)benzaldehydes were synthesized in high yield by using the Vilsmeier-Haack, Wittig-Horner and Buchwald-Hartwig reactions which were ¹⁵ described in ESI. The target compounds **YF01-04** were obtained via Knoevenagel condensation from the corresponding aldehydes with cyanoacetic acid in the presence of ammonium acetate in high yields as described in the experimental section.}

The photophysical properties of dyes YF01-04 in ethanol 20 solution and on TiO₂ film are summarized in Table 1. The wavelengths of absorption maxima (λ_{max}) are in the range of 404-423 nm due to the similar π - π * electron transition of **YF** dyes as shown in Figure 3a. The absorption maxima of pyrrolidine based sensitizers YF01 and YF04 were observed at a slightly longer 25 wavelength region compared to diphenylamine based sensitizers due to the stronger donor ability of pyrrolidine than diphenylamine. The molar extinction coefficients (ε) at the maximum absorption wavelength for these dyes are in the range of 1.1-3.2 x 10^4 M⁻¹ cm⁻¹, where **YF02** exhibits the highest ε 30 value. When absorbed on transparent thin TiO₂ film, YF01-04 showed broad absorption spectra similar to that in solution, while the absorption peaks are slightly blue-shifted due to the interaction between the carboxylic group and TiO₂ (Figure 3b). Upon dye adsorption on TiO₂ film, the tails of the absorption 35 spectra of all sensitizers are red-shifted compared to that of the absorption spectra in solution. It is worth mentioning that the tail of the absorption spectrum of dye YF04 extended up to 650 nm, which is highly desirable for harvesting more of the solar



spectrum and leads to a large photocurrent.

Figure 3. Absorption spectra of **YF01-04** in ethanol (a) in EtOH and (b) on a transparent TiO_2 film.

The Ionization potential (IP) of **YF** dyes bound to nanocrystalline TiO₂ film was measured using the photoemission ⁴⁵ yield spectrometer (Riken Keiki, AC-3E) (Fig. S1, ESI[†]). The IP values which correspond to ground-state oxidation potentials ($S^{+/0}$) were found to be -5.71, -5.70, -5.91 and -5.54 eV for the sensitizers **YF01-04**, which were sufficiently lower than the redox potential of Γ/Γ^{3-} (-5.20 eV),¹⁹ ensuring the favourable ⁵⁰ thermodynamic ground states for efficient regeneration of the dye through the reaction of the oxidized dye with iodide. The IP value of **YF04** was shifted positively compared to the other **YF** dyes due to the stronger electron donation of pyrrolidine moiety at the 6-position of naphthalene, which furnished more charge transfer

⁵⁵ from D to A. Moreover, the positive shift increased the negative free energy of electron injection, which furnishs more favorable thermodynamic excited state for electron injection, which can lead to more photocurrent (see Table 1, J_{sc}). The onset of the optical energy gap ($E^{0.0}$) of **YF** dyes was in the range of 1.91-⁶⁰ 2.39 eV (Table 1).²⁰ The excited-state oxidation potential ($S^{+/*}$) of sensitizers **YF01-04** was in the range of -3.45 to -3.63 eV, which lay above the conduction band edge (-4.2 eV)^{1c} of the nanocrystalline TiO₂ (Table 1), ensuring the efficient electron injection into the conduction band edge of TiO₂ from the ⁶⁵ adsorbed **YF** sensitizers.

Incident photon-to-current conversion efficiencies (IPCEs) for DSCs based on **YF** dyes are plotted in Figures 4a. The IPCEs of **YF02** and **YF03** are relatively blue-shifted compared to the dyes **YF04** and **YF01**, consistent with the UV-Vis absorption spectra ⁷⁰ of dye adsorbed on TiO₂ film (Figure 3b). Dyes **YF02** and **YF04** comprised of a donor moiety at the 6-position of naphthalene showed higher maximum IPCEs than that of dyes with the donor moiety at the 2-position of naphthalene (**YF01** and **YF03**). The maximum quantum efficiency of **YF02** and **YF04** reached up to 75 86% in the plateau region. These results implied that the rod-like D-π-A structure should be favorable for efficient electron injection quantum yield.



Figure 4. (a) Photocurrent action spectra (IPCE) of nanocrystalline TiO₂ ⁸⁰ film sensitized by **YF 01-04**. (b) Photocurrent voltage (*I-V*) characteristics of dyes **YF01-04**. The redox electrolyte solution was a mixture of 0.6 M DMPII, 0.05 M I₂, 0.1 M LiI and 0.3 M TBP in acetonitrile.

The solar cell performance for the DSCs based on the **YF** dyes is listed in Table 1, and the corresponding photocurrent-voltage scurves are shown in Figure 4b. Dye **YF02** showed the highest solar to power conversion efficiency (η) (5.29%) among the four dyes with the short-circuit current (J_{sc}), the open-circuit voltage (V_{oc}) and the fillfactor (*FF*) of 9.19 mA cm⁻², 0.799 V and 0.721, respectively. Under the same conditions, the overall power ⁹⁰ conversion efficiencies (η) of dyes **YF01**, **YF03**, and **YF04** were 3.57%, 3.67%, and 4.03%, respectively. DSCs based on the rodlike dyes, **YF02** and **YF04**, produced higher J_{sc} than **YF01** and **YF03**, which may be attributed to the more efficient electron transfer from donor to acceptor moiety of the formers. ⁹⁵ Remarkably, the V_{oc} of the diphenyl(naphthyl)amine based dyes, **YF02** and **YF03**, reach about 0.8 V, which is much higher than

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Table 1. Photophysical properties and DSCs performance parameters of dyes YF01-04.

Dye	$\lambda_{\text{max}}/\text{nm}^a$ ($\varepsilon \times 10^4 \text{M}^{-1} \text{cm}^{-1}$)	λ_{onset} /nm ^b on TiO ₂ film	$(IP)^{c} (eV)$	$\mathrm{E}_{0-0}(\mathrm{eV})^d$	$\mathbf{S}^{\scriptscriptstyle{+/*c}}\left(\mathbf{eV} ight)^{e}$	$J_{\rm sc}$ [mA cm ⁻²]	$V_{ m oc}[{ m V}]$	[<i>ff</i>]	η [%]
YF01	309, 407 (1.1)	575	-5.71	2.16	-3.55	8.33	0.574	0.747	3.57
YF02	298, 406 (3.2)	550	-5.70	2.25	-3.45	9.19	0.799	0.721	5.29
YF03	324 (2.7), 404	520	-5.91	2.39	-3.52	6.494	0.807	0.700	3.67
YF04	316, 422 (2.1)	650	-5.54	1.91	-3.63	10.24	0.552	0.712	4.03

^a Absorption maxima, measured in ethanol at room temperature; ^b Absorption measured on a transparent 4 μ m TiO₂ film. ^c Ionization potential (IP) of absorbed dyes on the nanocrystalline TiO₂ film was determined by using the photoemission yield spectrometer (Riken Keiki, AC-3E). ^d E_{0.0} was estimated from the absorption onset of dye loaded on TiO₂ film; ^e The excited-state oxidation potential, S^{+/*} levels were calculated from the expression of S^{+/*} = IP - E_{0.0}. Measurements were performed under AM 1.5 irradiation on the DSC devices with 0.25 cm² active surface area defined by a metal mask. J_{sc}: short circuit current; V_{oc}: open circuit voltage; <u>ff</u>: fill factor; η : conversion efficiency.

the naphthalene-substituted pyrrolidine based dyes, **YF01** and ⁵ **YF04**. This can be rationalized by the increased intermolecular π - π interaction of the pyrrolidine based dyes (**YF04** and **YF01**) which have less twisted structures compared to the diphenylamine based dyes (**YF02** and **YF03**), which are more twisted due to large torsion-angels. The strong intermolecular π - π ¹⁰ interactions on the TiO₂ surface may cause self-quenching process, resulting in a low V_{oc} , and hence, poor device performance.



Figure 5. (a) V_{∞} as a function of electron density and (b) electron lifetime 15 (τ_e) as a function of V_{∞} for DSCs sensitized with YF dyes.

The generation of V_{oc} is related to the energy level of the TiO₂ conduction band (E_{CB}) and the charge recombination rate in DSCs.²¹ To clarify the effect of molecular planarity on V_{oc} , the charge extraction and lifetime (τ_e) of YF dyes based DSCs were ²⁰ measured. As shown in Figure 5a, the measurement of the E_{CB} with the charge extraction method (CEM) shows that all of the dyes have almost same effect on the conduction band of TiO₂. Therefore, the improvement of V_{oc} of YF-dyes based DSCs should be attributed to the suppression of charge recombination, ²⁵ which is related to the τ_e . The τ_e was measured by means of

intensity modulated photovoltage spectroscopy (IMVS) as shown in Figure 5b. The τ_e values for the DSCs based on **YF02** and **YF03** dyes are much larger than that of **YF01** and **YF04** dyes, which suggests that the **YF02** and **YF03** dyes having a low ³⁰ planarity are favourable for the blocking I₃⁻ ions approaching the TiO₂ surface for charge recombination, and thus show an improvement in V_{oc} .



Figure 6. The EIS (a) Nyquist plots and (b) Bode plots for DSCs ³⁵ sensitized with YF dyes.

Electrochemical impedance spectroscopy (EIS) was employed to study the influence of electron recombination and interfacial charge transfer process on V_{oc} .²¹ Figure 6 shows the EIS Nyquist and Bode plots for the DSCs based on YF dyes. The values of the 40 first semicircles in Nyquist plots corresponding to the series resistance and electrolyte resistance in all YF-DSCs are almost same. The reciprocal of the peak frequency for the left-frequency peak in the Bode plot is regarded as the electron lifetime which represents the charge transfer process at the dye/TiO₂/electrolyte 45 interface. The **YF02** and **YF03** dyes afford the higher lifetimes and charge transfer resistances at the dye/TiO₂/electrolyte interface (R_{rec}) than that of **YF01** and **YF04** dyes. This trend is in

Page 6 of 8

accordance with the $\tau_e vs V_{oc}$ results, implying that the decrease of molecular aggregation of dyes by introduction of naphthalene linked diphenylamine donor moiety may suppress the electron recombination rate between the TiO₂ film and the electrolyte.

- ⁵ In order to gain more insights and better understanding into the electronic and molecular geometry of **YF** dyes, equilibrium molecular geometry, vertical electronic excitation values, delocalization of HOMO and LUMO, and torsion angels θ 1- θ 6 were calculated.
- ¹⁰ The calculated HOMOs and LUMOs isodensity superimposed on the molecular structures of dyes are shown in Figure 7. The HOMOs are delocalized considerably on the electron donor synthon where the auxochrome (pyrrolidine or diphenylamine) resides, which facilitates the reduction with Γ, making the dye
- ¹⁵ regeneration more efficient. On the other hand, the LUMO was mainly delocalized on the π^* cyanuric unit and has significant contributions from the carboxylic groups, which facilitates the electron injection from the photoexcited sensitizer into the TiO₂ semiconductor. This confirms that the D- π -A structural motif is ²⁰ an excellent design for efficient charge transfer and separation in DSCs.

Results of the equilibrium molecular geometry demonstrated that the pyrrolidine ring at position 6 in dye **YF04** is coplanar with the rest of the dye molecule furnishing strong intermolecular 25π - π overlap in the D- π -A motif. In the case of dye **YF01**, however,

the location of the pyrrolidine ring is at position 2, which is twisted out of the plane by 33.99 (θ 1) and also forces the stilbene

moiety out of the plane by 44.04 (θ 2) (Table 2). This explains why dye **YF04** is bathochromically shifted compared to dye

- 30 **YF01**. On the other hand, in the case of dye **YF02**, the diphenylamine is at position 6 and it is twisted by 33.33 out of the plane. While in the case of dye **YF03**, the diphenylamine is at position 2, therefore it is more twisted out of the plane by 62.16° (θ4) and also forces the stilbene moiety out of the plane by 46.66°
- ³⁵ (θ 5). Considering the strength of pyrrolidine compared to biphenyl amine as an electron-donor auxochorme and the more twist in the torsion angles generated by the introduction of the latter at position 2, one should expect that in the case of dye **YF03**, the π - π overlap and π - π * charge transfer should be weaker ⁴⁰ than that of dye **YF01** because of the more twist in the case of the former, which would significantly enhance the V_{oc} but decrease the intermolecular charge transfer within the molecule. Therefore, it should be expected that the electron injection and hence in theory the J_{sc} of dye **YF03** should be weaker than that of dye **45 YF01**, and the V_{oc} of dye **YF03** should be higher than **YF01**,
- which is consistent with the experimental results. Moreover, by the same analogy, the torsion angle $\theta 6$ (4.01) in dye **YF04** is significantly less twisted compared to $\theta 3$ (33.33) in dye **YF02**, which produces stronger π - π overlap and π - π * charge transfer in so the case of the former, and that explains why dye **YF04** produced
- the higher J_{sc} and lower V_{oc} compared to dye **YF02**. Because of the introduction of diphenylamine at position 2 in dye **YF03**, the twist in the torsion angles θ 4- θ 5 were the largest among all dyes,



Figure 7. The calculated HOMO and LUMO isodensity of YF01-04 showing the regions of delocalization.

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Figure 8. The calculated torsion angles of YF02 and TA-St-CA.

which significantly reduced the π - π * charge transfer. This s explains why **YF03** produced the most inferior J_{sc} and highest V_{oc} (0.807 V) among all dyes. In comparison to **YF03**, **YF02** shows a much higher J_{sc} and a comparably high V_{oc} (0.799), which are the important parameters for dye **YF02** to produce the highest solar to electric efficiency of 5.29%.

¹⁰ The calculated and the experimental λ_{max} of **YF** dyes are shown in Table 3. Excellent correlation between the experimental and calculated λ_{max} values was founded by using the energy functional B3LYP and the basis set DGDZVP for geometry optimization, and the TD-DFT energy calculations utilizing the long-range ¹⁵ corrected energy functional WB97XD and basis set DGDZVP, which was found superior to the long-range corrected energy functional CAM-B3LYP.

04

Dyes	YF	701	YF02	YF	703	YF04
Dihedral	θ1	θ2	θ3	θ4	θ5	θ6
angles (°)	31.99	44.04	33.33	62.16	46.66	4.01

20 Table 3. Calculated versus experimental λmax of YF01-04.

	λmax					
Calculated Energy caculations						
Dyes	WB97XD/DGDZVP	CAM-B3LYP/DGDZVP				
YF01	410	446	407			
YF02	413	433	406			
YF03	401	420	404			
YF04	429	453	422			

Although the dyes containing triarylamine unit as donors always show high V_{oc} compared to other organic dyes,²² the V_{oc} of dyes up to 0.8 V have been rarely reported.²³ To better understand the ²⁵ relationship between the high V_{oc} and molecular geometry, the equilibrium molecular geometries of dyes **YF02** and **TA-St-CA** were further calculated using the hybrid energy functional B3LP and basis set DGDZVP. As shown in Figure 8, **YF02(a)** and **(b)** torsion angles are 33.33 and 40.81, while **TA-ST-CA(a)** and **(b)** ³⁰ torsion angles are 34.33 and 35.44, respectively. The overall twist around diphenylamine in **YF02** is greater than that of **TA-ST-CA**, supporting our experiment results that DSCs based on the new dye **YF02** with a diphenyl(naphthyl)amine as a donor, showed a higher V_{oc} than the DSC based on **TA-ST-CA** which has a ³⁵ triphenylamine as a donor.

Conclusion

We have synthesized a series of new organic dyes YF01-04 based on naphthylamine moiety as a donor unit in the D- π -A system for nanocrystalline TiO₂ solar cells. The dyes YF02 and YF04 40 having amine donors substituted at 6-position of naphthalene moiety furnished better charge separation and more photocurrent than the dyes YF01 and YF03 which have amine donors at 2position of naphthalene moiety. Moreover, the dyes YF02 and **YF03** with diphenylamine as a donor showed a very high V_{oc} 45 about 0.8 V due to their highly twisted geometry, which led to the highest overall conversion efficiency of 5.29% for YF02. The EIS and electron lifetime measurements indicated that the DSCs sensitized with YF02 and YF03 dyes have a larger τ_e and R_{rec} than that of **YF01** and **YF04** dyes, which resulted in higher V_{oc} s. 50 DFT calculations indicated that the torsion angels around naphthalene in the phenylamine based dyes (YF02 and YF03) are more twisted than the pyrroline based dyes (YF01 and YF04), which contributed to less dye aggregation on TiO₂, resulting in a high Voc. Further molecular geometry calculation of the 55 triphenylamine based dye TA-St-CA and the result that a higher $V_{\rm oc}$ of **YF02** than that of **TA-St-CA**, indicated that the existence of naphthalene moiety linked to diphenylamine is favourable for retarding the charge recombination. The introduction of naphthalene moiety in D- π -A dyes might be a promising way to 60 inhibit the molecular aggregation of dyes and hence enhance the solar cell performance. With the aid of molecular modelling, molecular engineering and synthesis in our laboratory is

Page 8 of 8

underway to develop a novel generation of more efficient naphthalene-based dyes that have the potential to exhibit significant increase in DSC performance across a wider range of the solar spectrum.

5 Notes and references

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and 25 spectral data, and crystallographic data.

References

- (a) B. Oregan and M. Gratzel, *Nature*, 1991, **353**, 737; (b) A. Hagfeldt and M. Gratzel, *Chem. Rev.*, 1995, **95**, 49; (c) A. Hagfeldt and M. Gratzel, *Acc. Chem. Res.*, 2000, **33**, 269.
- 30 2 (a) Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide and L. Y. Han, *Jpn. J. Appl. Phys.*, 2006, **45**, L638; (b) L. Y. Han, A. Islam, H. Chen, C. Malapaka, B. Chiranjeevi, S. F. Zhang, X. D. Yang and M. Yanagida, *Energy Environ. Sci.*, 2012, **5**, 6057.
- 3 (a) N. Robertson, Angew. Chem., Int. Ed., 2006, 45, 2338; (b) A.
 ⁵ Mishra, M. K. R. Fischer and P. Bäuerle, Angew. Chem., Int. Ed., 2009, 48, 2474; (c) A. Hagfeldt, G. Boschloo, L. C. Sun, L. Kloo and H. Pettersson, Chem. Rev., 2010, 110, 6595.
- 4 M. Gratzel, Acc. Chem. Res., 2009, 42, 1788.
- 5 Z. J. Ning, Y. Fu and H. Tian, Energy Environ. Sci., 2010, 3, 1170.
- ⁴⁰ 6 Z. Ning and H. Tian, *Chem. Commun.* 2009, 5483.
 7 M. Akhtaruzzaman, A. Islam, F. Yang, N. Asao, E. Kwon, S. P. Singh, L. Y. Han and Y. Yamamoto, *Chem. Commun.*, 2011, **47**, 12400.
- 8 S. Hwang, J. H. Lee, C. Park, H. Lee, C. Kim, C. Park, M. H. Lee, W.
- M. Akhtaruzzaman, Y. Seya, N. Asao, A. Islam, E. Kwon, A. El-Shafei, L. Yuan and Y. Yamamoto, *J. Mater. Chem.*, 2012, 22, 10771.
 A. D. Barder, *Phys. Rev. A*, 1088, 29, 2008.
- 10 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.
- C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
 N. Godbout, D. R. Salahub, J. Andzelm and E. Wimmer, *Can. J. Chem.*, 1992, **70**, 560.
- 13 C. Sosa, J. Andzelm, B. C. Elkin, E. Wimmer, K. D. Dobbs and D. A. Dixon, J. Phys. Chem., 1992, 96, 6630.
- ⁵⁵ 14 T. Yanai, D. Tew and N. Handy, *Chem. Phys. Lett.*, 2004, **393**, 51.
 ¹⁵ J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615.
- 16 T. N. Jin, F. Yang and Y. Yamamoto, Org. Lett., 2010, 12, 388.
- 17 B. A. Reinhardt, L. L. Brott, S. J. Clarson, A. G. Dillard, J. C. Bhatt,
- 60 R. Kannan, L. X. Yuan, G. S. He and P. N. Prasad, *Chem. Mater.*, 1998, **10**, 1863.
 - 18 D. J. Li, B. P. Zhao and E. J. LaVoie, J. Org. Chem., 2000, 65, 2802.
 - 19 G. Oskam, B. V. Bergeron, G. J. Meyer and P. C. Searson, J. Phys. Chem. B, 2001, 105, 6867.
- $_{65}$ 20 $\,E_{0.0}$ value was estimated from the 5% intensity level of the absorption spectrum of YF-series adsorbed onto transparent TiO_2 film.

- 21 (a) H. Tian, I. Bora, X. Jiang, E. Gabrielsson, K. M. Karlsson, A. Hagfeldt and L. Sun, *J. Mater. Chem.* 2011, **21**, 12462; (b) S. Qu, C. Qin, A. Islam, Y. Wu, W. Zhu, J. Hua, H. Tian and L. Han, *Chem. Commun.* 2012, **48**, 6972; (c) C. Qin, A. Islam and L. Han, *J. Mater. Chem.* 2012, **22**, 19236; (d) S. Haid, M. Marszalek, A. Mishra, M. Wielopolski, J. Teuscher, J.-E. Moser, R. Humphry-Baker, S. M. Zakeeruddin, M. Grätzel and P. Bäuerle, *Adv. Funct. Mater.* 2012, **22**, 1291.
- 75 22 (a) D. P. Hagberg, J.-H. Yum, H. J. Lee, F. De Angelis, T. Marinado, K. M. Karlsson, R. Humphry-Baker, L. Sun, A. Hagfeldt, M. Grätzel and M. K. Nazeeruddin, *J. Am. Chem. Soc.*, 2008, **130**, 6259; (b) Z. Ning, Q. Zhang, H. Pei, J. Luan, C. Lu, Y. Cui and H. Tian, *J. Phys. Chem. C*, 2009, **113**, 10307; (c) J. S. Song, F. Zhang, C. H. Li, W. L.
- Liu, B. S. Li, Y. Huang and Z. S. Bo, J. Phys. Chem. C, 2009, 113, 13391; (d) R. Li, X. Jv, D. Shi, D. Zhou, Y. Cheng, G. Zhang and P. Wang, J. Phys. Chem. C, 2009, 113, 7469; (e) S.-H. Lin, Y.-C. Hsu, J. T. Lin, C.-K. Lin and J.-S. Yang, J. Org. Chem., 2010, 75, 7877; (f) B.-S. Chen, D.-Y. Chen, C.-L. Chen, C.-W. Hsu, H.-C. Hsu, K.-L.
- Wu, S.-H. Liu, P.-T. Chou and Y. Chi, J. Mater. Chem., 2011, 21, 1937; (g) S.-B. Ko, A.-N. Cho, M.-J. Kim, C.-R. Lee and N.-G. Park, Dyes Pigm., 2012, 94, 88.
- 23 (a) G. L. Zhang, H. Bala, Y. M. Cheng, D. Shi, X. J. Lv, Q. J. Yu and P. Wang, *Chem. Commun.*, 2009, 2198; (b) L. Y. Lin, C. H. Tsai, K. T. Wong, T. W. Huang, L. Hsieh, S. H. Liu, H. W. Lin, C. C. Wu, S.
- H. Chou, S. H. Chen and A. I. Tsai, *J. Org. Chem.*, 2010, **75**, 4778.

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