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# Synthesis and applications of new triphenylamine dyes with donor-donor-(bridge)-acceptor structure for organic dye-sensitized solar cells<sup>†</sup>

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Four novel asymmetric triphenylamine dyes configured with donor-donor-acceptor (D–D–A) and donor-donor-bridge-acceptor (D–D– $\pi$ –A) structures were synthesized and applied to organic dye-sensitized solar cells. The terminal methoxy group in the donor part and the furane-bridge unit contributed to the wider absorption region and enhanced electron life time, resulting in a higher photocurrent density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), and overall conversion efficiency ( $\eta$ ). Among the synthesized dyes, the **SK2**-based DSSC showed the highest conversion efficiency of 5.57% ( $J_{sc} = 10.41 \text{ mA cm}^{-2}$ ,  $V_{oc} = 729 \text{ mV}$ , and FF = 0.73) caused by the synergetic effect of the methoxy group and the furane-bridge unit.

# Introduction

Dye-Sensitized Solar Cells (DSSCs) as some of the promising alternatives for the photovoltaic conversion of solar energy have attracted considerable attention because of their low production cost, easy preparation and relatively high solar-to-electricity conversion efficiency.<sup>1</sup> Sensitizers play a key role in the DSSCs' high conversion efficiency and have been studied extensively by researchers throughout the world. The most typical sensitizers used in DSSCs are the ruthenium(II) polypyridyl complex series, which are known as N3 and N719. These Ru-complex dyes have shown high conversion efficiencies (more than 11%) due to the broad absorption band and good long-term stability.<sup>2</sup> However, they have the disadvantages of a relatively high production cost and difficulties in purification.

In recent years, a range of organic dyes have been developed as alternatives to the Ru-complex dye due to the many advantages such as diversity of the molecular structures, high molar extinction coefficient, simple synthesis and low cost.<sup>3</sup> Most organic dyes have the push-pull structure of donor–conjugated bridge–acceptor (D– $\pi$ –A). Amine moieties are generally used as the electron donor, and cyanoacrylic acid or a rhodanine moiety is used as the electron acceptor and anchoring group. These two parts are linked by

 $\pi$ -conjugated bridge units, such as methine, furane and thiophene. Many groups have worked on the development of organic dyes with D– $\pi$ –A structure and published results on triphenylamine, indoline, coumarin, cyanine, perylene and phenothiazine.<sup>3,4</sup> Among them, indoline<sup>5</sup> and triphenylamine<sup>6</sup> based organic dyes showed good conversion efficiencies above 9%, which were close to those of the Ru complex dyes.

On the other hand, organic dyes with D–D–A or D– $D-\pi$ –A structure are reported by several groups.<sup>7</sup> They suggested that organic dyes based on D-D-n-A structure can achieve the enhanced photovoltaic performance through the modifications of molecular structure compared to the organic dyes with simple D-n-A structure. Furthermore, introducing an additional donor group into the dye molecule can increase the electron donating ability of the donor and enhance charge separation and electron injection, which resulted in high overall conversion efficiency.<sup>8</sup> Based on these strategies, we designed and synthesized four novel triphenylamine-based organic dyes with D-D-A and D-D- $\pi$ -A molecular structures. Additional electron donor groups, benzene and methoxy benzene, were connected by a methine chain (-CH=CH-) in order to increase the molar extinction coefficient. And furane and thiophene moieties were used as a  $\pi$ -conjugated bridge unit for the effective conjugation and red-shifted absorption spectrum. Photovoltaic cells were fabricated using the synthesized dyes and their photovoltaic properties were measured and analyzed.

# **Results and discussion**

# (1) Synthesis of the dyes

The molecular structures and synthetic routes of the triphenylamine dyes with an additional donor group are shown in Fig. 1

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Fig. 1 Molecular structures of synthesized dyes.

and Scheme 1, respectively. 4-((4-Bromophenyl)(phenyl)amino) benzaldehyde as a starting material was synthesized according to the published procedure.<sup>8d</sup> The triphenylamine donor was extended to the donor-donor intermediates 1-3 all in 75 to 85% yield, using the efficient Horner-Wadsworth-Emmons olefination methodology with the appropriate phosphonates, diethyl-4-methylbenzylphosphonate and diethyl-4-methoxybenzylphosphonate. The donor-donor intermediates 1 and 2 were formylated via Vilsmeier-Haack reaction in moderate yield to form intermediates 4 and 5. Subsequently, the carbaldehydes were condensed with cyanoacetic acid by the Knoevenagel reaction in the presence of piperidine and converted to SP1 and SK1. For the preparation of SK2–3, the intermediate 3 was allowed to react with appropriate boronic acids via Suzuki coupling to form intermediates 6 and 7. Subsequent reactions of the intermediates with cyanoacetic acid and piperidine afforded the desired compounds. The structures of all synthesized intermediates and dyes were characterized by NMR and mass spectrometry.

# (2) Photophysical properties of the dyes in solution and $TiO_2$ film

The absorption spectra of the synthesized dyes in a  $5 \times 10^{-6}$  M dichloromethane solution are shown in Fig. 2(a) and the corresponding data are collected in Table 1. All dyes exhibited



Fig. 2 Absorption spectra of the dyes in  $CH_2Cl_2$  (a) and adsorbed on  $TiO_2$  (b).

two major absorption bands, appearing at below 400 nm and 420–500 nm, respectively. The former is due to a localized  $\pi$ - $\pi$ \* transition and the latter is attributed to the intramolecular charge transfer transition (ICT) from the triphenylamine donor containing an additional donor group to the cyanoacrylic acid acceptor group.<sup>9</sup>

A comparative examination of the absorption spectra between SP1 and SK1 indicates that the maximum absorption



Fig. 3 Cyclic voltammograms (C-V curves) of the synthesized dyes.



Scheme 1 Synthetic routes; (a) BuO'K, THF, 0 °C  $\rightarrow$  room temp.; (b) DMF, POCl<sub>3</sub>, reflux; (c) cyanoacetic acid, piperidine, reflux; (d) Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, THF, 5-formyl-2-furylboronic acid or 5-formyl-2-thienylboronic acid, reflux.

wavelength is unaffected by the introduction of the methoxy group into the additional donor part. On the other hand, maximum absorption wavelengths of **SK2** and **SK3** showed a considerable red shift of 46 nm by the introduction of  $\pi$ -conjugated bridge units, furane and thiophene. This is due to the extension of  $\pi$ -conjugation length by the introduction of bridge units and the red shifts in the absorption spectra are desirable for light harvesting. The molar extinction coefficients,  $\varepsilon$ , of the synthesized dyes ranged from 23 000 to 55 880 M<sup>-1</sup> cm<sup>-1</sup> and were relatively higher than those of the conventional triphenylamine dyes due to methine chains. Such a red shift in the absorption spectrum and a higher molar extinction coefficient could increase the amount of light harvested and enhance the photocurrent generation of DSSCs.

The absorption spectra of the dyes adsorbed on transparent  $TiO_2$  films are shown in Fig. 2(b) and the corresponding data are collected in Table 1. All the dyes showed broad and blue-shifted absorption spectra on the  $TiO_2$  surface compared to those in solution. Either a polar interaction of the dyes with  $TiO_2$  through the deprotonation of carboxylic acid or H-aggregation of the dyes has been suggested accountable for such broadening and blue-shift of the absorption spectrum.<sup>10</sup>

## (3) Electrochemical properties of the dyes

The first oxidation potential  $(E_{\rm ox})$  corresponding to the HOMO level of the dye was measured in dichloromethane by cyclic voltammetry (CV), and the *C*-*V* curves of the dyes are shown in Fig. 3. The LUMO levels of the dyes were calculated by  $E_{\rm ox} - E_{0-0}$ , where  $E_{0-0}$  is the zeroth-zeroth

energy of the dyes estimated from the intersection between the normalized absorption and emission spectra. The electrochemical properties of the synthesized dyes are listed in Table 1 and the HOMO-LUMO level diagram is shown in Fig. 4. The HOMO levels of all synthesized dyes ranged from 1.15 eV to 0.96 eV (vs. NHE) and became more negative by the introduction of the methoxy group into the additional donating group and  $\pi$ -conjugated bridge units. The HOMO levels of the dyes were positive enough compared to the redox potential of the electrolyte, ca. 0.4 V (vs. NHE), indicating that the oxidized dyes could be regenerated effectively by the electrolyte. The LUMO levels of the dyes ranged from -1.29 eV to -1.43 eV (vs. NHE) and became more positive by the introduction of  $\pi$ -conjugated bridge units. The LUMO levels of the dyes were sufficiently more negative than the conduction band of TiO<sub>2</sub>, ca. -0.5 eV (vs. NHE), indicating that the excited electrons of the dyes could be effectively injected into the conduction band of TiO<sub>2</sub>.

# (4) Photovoltaic properties of DSSCs based on the synthesized dyes

DSSCs were fabricated using the synthesized dyes according to the methods described in Experimental section (3). The incident monochromatic photon-to-current conversion efficiencies (IPCEs) of the DSSCs are shown in Fig. 5. The DSSCs based on the synthesized dyes as sensitizers exhibited a high maximum IPCE value. The maximum IPCE value of the DSSC based on **SK2** reached 80.3% at 480 nm, and the values of DSSCs based on **SP1**, **SK1** and **SK3** reached 77.4%, 77.7%

 Table 1
 Photophysical and electrochemical properties of the synthesized dyes

				Potentials and energy levels		
Dye	$\begin{array}{l}\lambda_{max}{}^{a}\!/\!nm\\(\epsilon/M^{-1}~cm^{-1})\end{array}$	$\begin{array}{l} \lambda_{max} \text{ on } \\ TiO_2/nm \end{array}$	$\lambda_{ m emission}^a / nm$	${E_{ m ox}}^b/{ m V}$	${E_{0-0}}^c/{ m V}$	$\frac{E_{\mathrm{ox}}-}{E_{0-0}{}^c/\mathrm{V}}$
SP1	448 (50 950)	438	548	1.15	2.58	-1.43
SK1	448 (55880)	438	548	1.00	2.54	-1.54
SK2	494 (40 630)	456	593	0.97	2.27	-1.30
SK3	494 (23 000)	458	598	0.96	2.25	-1.29

<sup>*a*</sup> Absorption and emission spectra were measured in CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>*b*</sup> The oxidation potentials ( $E_{ox}$ ) of the dyes were obtained by cyclic voltammetry in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) with a scan rate of 100 mV s<sup>-1</sup> and converted to NHE. <sup>*c*</sup> The zeroth–zeroth transition  $E_{0-0}$  values were estimated from the intersection of the normalized absorption and emission spectra (Fig. S1, ESI).

and 78.7%, respectively. These high maximum IPCE values of the dyes may be tentatively attributed to efficient electron injection and charge separation due to the D–D–A and D–D– $\pi$ –A molecular structures.<sup>7,8</sup> The IPCE spectrum of the DSSC based on **SK1** was slightly broadened and red shifted compared to the spectrum of **SP1** due to the introduction of the methoxy group into the donor part. The IPCE spectra of the DSSCs based on **SK2–3** containing  $\pi$ -conjugated bridges remarkably red shifted and the onsets of the IPCE spectra were extended to 680 nm. Among the dyes, the onset of the IPCE spectrum of the DSSC based on **SK2** was 670 nm, and the best IPCE performance (>79%) was observed in the range from 420 nm to 500 nm. These higher and broader IPCE spectra of the DSSCs based on **SK2–3** are responsible for the higher  $J_{sc}$  and superior  $\eta$ .

The corresponding photocurrent density-voltage (J-V) curves of DSSCs based on the synthesized dyes are shown in Fig. 6 and the detailed photovoltaic parameters, including



**Fig. 5** Incident photon-to-current conversion efficiencies spectra for the DSSCs based on the synthesized dyes.

short-circuit photocurrent density  $(J_{sc})$ , open-circuit voltage  $(V_{oc})$ , fill factor (FF), and conversion efficiency  $(\eta)$ , are listed in Table 2. The  $J_{sc}$  of the DSSCs based on the synthesized dyes increased gradually in the order of SP1 < SK1 < SK2 < SK3. It could be attributed to the wider absorption spectra and the broadening of IPCE spectra towards a longer wavelength region by the introduction of the methoxy group into the donor part and  $\pi$ -conjugated bridge units.

The  $V_{\rm oc}$  of the DSSCs based on SP1 and SK1–2 increased in the order of SP1 < SK1 < SK2 as the methoxy group and the bridge unit were introduced. However, the  $V_{\rm oc}$  of the SK3-based DSSC is lower than all the other dyes, although it has both the methoxy group and the bridge unit. To elucidate the correlation of  $V_{\rm oc}$  with the dyes, electrochemical impedance spectroscopy (EIS) was measured in the dark under a forward bias of -0.70 V with a frequency range of 0.1 Hz to 100 kHz. The Nyquist plots and Bode phase plots of the DSSCs based on SP1 and SK1–3 are shown in Fig. 7.



Fig. 4 Energy diagrams of synthesized dyes and the frontier molecular orbitals of the HOMO and LUMO calculated with DFT on a B3LYP/6-31+G (d,p) level.

Table 2Photovoltaic performances of DSSCs based on SP1 andSK1-3

Dye	$J_{\rm sc}/{ m mA~cm^{-2}}$	$V_{\rm oc}/{ m mV}$	FF	$\eta^{a}$ (%)
SP1	6.85	696	0.74	3.54
SK1	7.40	718	0.73	3.89
SK2	10.41	729	0.73	5.57
SK3	10.67	689	0.73	5.37
N719	15.13	757	0.71	8.10

<sup>*a*</sup> The concentration was maintained at  $5 \times 10^{-4}$  M in CH<sub>2</sub>Cl<sub>2</sub>, with 0.5 M 1-methyl-3-propylimidazolium iodide (PMII), 0.2 M LiI, 0.05 M I<sub>2</sub> and 0.5 M 4-tert-butylpyridine (TBP) in ACN-VN (85:15) solution. The efficiencies of DSSCs were an average value obtained from measurements of three cells with a 0.24 cm<sup>2</sup> working area.



**Fig. 6** Photocurrent density–voltage (J-V) curves for the DSSCs based on the synthesized dyes under AM 1.5G simulated solar light (100 mW cm<sup>-2</sup>).

In the Nyquist plot, the large semicircle at the intermediated frequency is assigned to the charge transfer impedance at the TiO<sub>2</sub>-dye-electrolyte interface.<sup>11</sup> The charge recombination resistance at the TiO<sub>2</sub> surface,  $R_{rec}$ , can be estimated from the radius of the middle semicircle in the Nyquist plot and the larger  $R_{\rm rec}$  means a slower charge recombination rate. As shown in Fig. 7(a), the  $R_{\rm rec}$  values increased in the order of SK3 < SP1 < SK1 < SK2. These results are consistent with the tendency of  $V_{\rm oc}$  in the DSSCs based on the synthesized dyes. The increased  $R_{rec}$  values imply the retardation of charge recombination between the injected electron into the TiO<sub>2</sub> and oxidized species  $(I_3^{-})$  in the electrolyte. Correspondingly, the frequency of the characteristic frequency peaks in the Bode phase plots increased in the order of SK3 < SP1 < SK1 < SK2. The characteristic frequency in the Bode plot is related to the charge recombination rate, and its reciprocal is associated with the electron lifetime.<sup>12</sup> Therefore, these results suggest that the methoxy group in the donor part and furane-bridge unit contributes to the enhanced electron lifetime due to a slower recapture of the conduction band electrons by  $I_3^-$ , leading to a higher Voc. The DSSC based on SK2 consequently showed the highest  $V_{oc}$ , which is presumably caused by the synergetic effect of the methoxy group and the furane-bridge unit. On the other hand, the SK3-based DSSC showed a lower  $V_{\rm oc}$  compared to that based on SK2, although SK3 also had



Fig. 7 Electrochemical impedance spectra of DSSCs based on the synthesized dyes measured in the dark under -0.70 V bias; (a) Nyquist plots, (b) Bode phase plots.

the terminal methoxy group and the bridge unit (thiophene). This is consistent with published results for PTZ and TPAbased dyes,<sup>4g,12b,13</sup> but the reasons for the results were not explained clearly. We postulate that the thiophene-bridge unit can lead to an increased intermolecular  $\pi$ - $\pi$  interaction, which can explain the higher amount of **SK3** adsorbed on TiO<sub>2</sub> compared to the other dyes. The amounts of dye adsorbed increased in the order of **SP1**  $\approx$  **SK1** < **SK2** « **SK3** (**SP1**, 5.20 × 10<sup>-8</sup>; **SK1**, 5.24 × 10<sup>-8</sup>; **SK2**, 7.81 × 10<sup>-8</sup>; **SK3**, 1.12 × 10<sup>-7</sup> mol cm<sup>-2</sup>). This thiophene-bridge unit can increase the charge recombination due to the higher aggregation and result in a lower  $V_{oc}$  of **SK3**.<sup>8b,14</sup>

Among the synthesized dyes, the DSSC based on SK2 exhibited the best conversion efficiency of 5.57% with  $J_{sc} = 10.41$  mA cm<sup>-2</sup>,  $V_{oc} = 729$  mV, and FF = 0.73 under simulated AM 1.5G irradiation conditions.

# Conclusion

A new series of D–D–A and D–D– $\pi$ –A structured organic dyes containing additional donor groups connected by methine chains and heterocyclic  $\pi$ -conjugated bridge units were designed and synthesized to improve the  $J_{sc}$  and  $V_{oc}$ of DSSCs. The terminal methoxy group in the donor part and π-conjugated bridge units led to the higher and broader IPCE spectra of the DSSCs, resulting in an improved  $J_{sc}$  and η. An electrochemical impedance study was conducted to elucidate the correlation of  $V_{oc}$  with the dye structure. The result indicates that the terminal methoxy group and the furanebridge unit contribute to the enhanced electron lifetime due to the retardation of charge recombination between the injected electron into the TiO<sub>2</sub> and oxidized species in the electrolyte, leading to a higher  $V_{oc}$ . The DSSC based on **SK2** showed the highest conversion efficiency of 5.57% ( $J_{sc} = 10.41$  mA cm<sup>-2</sup>,  $V_{oc} = 729$  mV, and FF = 0.73) caused by the synergetic effect of the methoxy group and the furane-bridge unit.

# **Experimental section**

# (1) Materials and general procedures

4-(Diphenylamino)benzaldehyde, 4-bromo-N,N-diphenylaniline, diethyl-4-methylbenzylphosphonate, diethyl-4-methoxybenzylphosphonate and 5-formyl-2-furanylboronic acid purchased from Sigma-Aldrich, 5-formyl-2-thienylboronic acid from TCI were used without further purification. All chemicals used in this study were of synthesis-grade. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 500 at 500 MHz using CDCl<sub>3</sub> and DMSO- $d_6$  as the solvent and TMS as the internal standard. Mass spectra were measured using a JEOL JMS-600W Agilent 6890 Series. UV-Visible absorption spectra were measured with an HP 8452A spectrophotometer and emission spectra were recorded on a QuantaMaster<sup>™</sup> UV-VIS spectrofluorometer. Cyclic voltammetry (CV) was performed with a three-electrode electrochemical cell on a Potentostat/Gavanostat Model 273A. Glassy-carbon, platinum wire, and Ag/Ag+ were employed as the working, counter, and reference electrodes, respectively. Tetrabutylammonium tetrafluoroborate (TBATFB) was used as the supporting electrolyte and ferrocene was added as an internal reference for calibration.

# (2) Syntheses

(E)-4-(4-Methylstyryl)-N,N-diphenylaniline (1). A solution of potassium tert-butoxide (0.73 g, 6.5 mmol) in THF (5 mL) was slowly added to a mixture of 4-(diphenylamino)benzaldehyde (1.37 g, 5 mmol), diethyl-4-methylbenzylphosphonate (1.33 g, 5.5 mmol) and THF (60 mL) for 10 min at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 8 h. The mixture was quenched into water (50 mL) and then extracted with ethyl acetate. The organic layer was washed with water and brine, dried over anhydrous MgSO<sub>4</sub>. The solvent was removed by rotary evaporation and subsequently dried in a vacuum oven. The crude product was purified by column chromatography on silica gel using ethyl acetate: hexane (1:15, v/v) afforded compound 1 (1.48 g, 82%) as a pale yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz),  $\delta$ : 7.35 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H), 7.17 (t, J = 7.8 Hz, 4H), 7.01 (d, J =8.5 Hz, 4H), 6.98–6.92 (m, 4H), 6.85 (d, J = 6.4 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 2.29 (s, 3H).

(*E*)-4-(4-Methoxystyryl)-*N*,*N*-diphenylaniline (2). This compound was synthesized using the method established for compound 1. The crude product was purified by column chromatography on silica gel using ethyl acetate: hexane (1:10, v/v) afforded

compound **2** (1.43 g, 78%) as a pale yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz),  $\delta$ : 7.36 (d, J = 8.7 Hz, 2H), 7.29 (d, J = 8.6 Hz, 2H), 7.19 (t, J = 7.8 Hz, 4H), 7.04 (d, J = 8.5 Hz, 4H), 6.97–6.93 (m, 4H), 6.87 (d, J = 6.4 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 3.74 (s, 3H).

(*E*)-4-Bromo-*N*-(4-(4-methoxystyryl)phenyl)-*N*-phenylaniline (3). This compound was synthesized using the method established for compound 1. The crude product was purified by column chromatography on silica gel using ethyl acetate:hexane (1:12, v/v) afforded compound 3 (4.2 g, 80%) as a pale yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz),  $\delta$ : 7.43 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.7 Hz, 2H), 7.28 (t, J = 7.8 Hz, 2H), 7.09 (d, J = 7.8 Hz, 2H), 7.06–7.02 (m, 3H), 6.98–6.93 (m, 4H), 6.89 (d, J = 8.5 Hz, 2H), 3.82 (s, 3H).

(E)-4-((4-(4-Methylstyryl)phenyl)(phenyl)amino)benzalde-

hyde (4). POCl<sub>3</sub> (0.7 mL, 7.5 mmol) was added dropwise to icecold DMF (3 mL) and the mixture was stirred for 30 min at 0 °C. A solution of 1 (1.08 g, 3 mmol) in dichloroethane (20 mL) was added and the resulting mixture was stirred for 14 h at 80 °C. The reaction mixture was cooled to room temperature and poured into ice water. The mixture was neutralized with 20% NaOH aqueous solution and extracted with dichloromethane, washed with water and brine, and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed by rotary evaporation and subsequently dried in a vacuum oven. The crude product was purified by column chromatography on silica gel using dichloromethane: hexane (1:1, v/v) afforded compound 4 (0.63 g, 54%) as a yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz),  $\delta$ : 9.84 (s, 1H), 7.71 (d, J = 8.7 Hz, 2H), 7.46 (d, J = 8.0 Hz, 4H), 7.38 (t, J = 7.9 Hz, 2H), 7.21 (d, J = 7.6 Hz, 3H), 7.16 (d, J = 8.5 Hz, 2H), 7.09–6.94 (m, 4H), 6.92 (d, J =8.7 Hz, 2H), 2.30 (s, 3H).

(*E*)-4-((4-(4-Methoxystyryl)phenyl)(phenyl)amino)benzaldehyde (5). This compound was synthesized using the method established for compound 4. The crude product was purified by column chromatography on silica gel using dichloromethane: hexane (2:1, v/v) afforded compound 5 (0.69 g, 62%) as a yellow solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz),  $\delta$ : 9.82 (s, 1H), 7.69 (d, J = 8.7 Hz, 2H), 7.45 (d, J = 8.0 Hz, 4H), 7.36 (t, J = 7.9 Hz, 2H), 7.19 (d, J = 7.6 Hz, 3H), 7.13 (d, J = 8.5 Hz, 2H), 7.06–6.92 (m, 4H), 6.91 (d, J = 8.7 Hz, 2H), 3.83 (s, 3H).

(*E*)-2-Cyano-3-(4-((4-(*E*)-4-methylstyryl)phenyl)(phenyl)amino)phenyl) acrylic acid (SP1). A mixture of 4 (0.39 g, 1 mmol), cyanoacetic acid (0.21 g, 2.5 mmol) and piperidine (0.4 mL, 4 mmol) was dissolved in acetonitrile (80 mL) and refluxed for 6 h at 92 °C under nitrogen. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using dichloromethane : methanol (12:1, v/v). The product was dissolved in dichloromethane (150 mL) and then 0.1 M HCl aqueous solution (100 mL) was added to this solution. The solution was vigorously stirred for 2 h and the organic layer was dried over anhydrous MgSO<sub>4</sub>. The solvent was removed by rotary evaporation and subsequently dried in a vacuum oven afforded SP1 (0.35 g, 78%) as an orange solid. <sup>1</sup>H NMR (DMSO- $d_6$ , 500 MHz),  $\delta$ : 8.15 (s, 1H), 7.94 (d, J = 9.0 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.45–7.42 (m, 2H), 7.27 (t, J = 7.5 Hz, 1H), 7.22–7.16 (m, 8H), 6.93 (d, J = 9.0 Hz, 2H), 2.31 (s, 3H). <sup>13</sup>C NMR (DMSO- $d_6$ , 500 MHz),  $\delta$ : 163.99, 153.15, 151.50, 145.09, 144.32, 136.98, 134.32, 134.21, 132.79, 130.00, 129.24, 128.28, 127.76, 126.49, 126.33, 126.05, 125.65, 123.22, 118.74, 116.88, 98.16, 20.76. HR-MS: m/z (%) calcd for C<sub>31</sub>H<sub>25</sub>N<sub>2</sub>O<sub>2</sub>: 457.1916; found 457.1915 [FAB<sup>+</sup>].

(*E*)-2-Cyano-3-(4-((4-((*E*)-4-methoxystyryl)phenyl)(phenyl)amino)phenyl) acrylic acid (SK1). This compound was synthesized using the method established for compound SP1. The crude product was purified by column chromatography on silica gel using dichloromethane : methanol (10 : 1, v/v) afforded SK1 (0.33 g, 77%) as an orange solid. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz),  $\delta$ : 8.14 (s, 1H), 7.94 (d, J = 9.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 7.45–7.42 (m, 2H), 7.27 (t, J =7.5 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.18–7.10 (m, 4H), 6.96–6.91 (m, 4H), 3.77 (s, 3H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 500 MHz),  $\delta$ : 164.03, 158.97, 153.18, 151.55, 145.11, 144.06, 134.62, 132.83, 130.01, 129.65, 128.06, 127.73, 127.58, 126.33, 126.15, 125.66, 125.22, 123.15, 118.66, 116.92, 114.16, 98.07, 55.12. HR-MS: *m*/*z* (%) calcd for C<sub>31</sub>H<sub>25</sub>N<sub>2</sub>O<sub>3</sub>: 473.1865; found 473.1868 [FAB<sup>+</sup>].

#### (E)-5-(4-((4-(4-Methoxystyryl)phenyl)(phenyl)amino)phe-

nyl)furan-2-carbaldehyde (6). A solution of 3 (2 g, 4.4 mmol) in THF (120 mL) was stirred and purged with nitrogen gas for 10 min, and then tetrakis(triphenylphosphine)palladium(0) (0.25 g, 0.22 mmol) was added followed by 5-formyl-2furanylboronic acid (0.67 g, 4.8 mmol) and a 2 M K<sub>2</sub>CO<sub>3</sub> aqueous solution (6 mL). The reaction mixture was heated at 80 °C and stirred for 12 h. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was extracted with methylene chloride and water, washed with water and brine, and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed by rotary evaporation and subsequently dried in a vacuum oven. The crude product was purified by column chromatography on silica gel using dichloromethane: hexane (10:1, v/v) afforded compound 6 (0.87 g, 42%) as a yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz),  $\delta$ : 9.59 (s, 1H), 7.67 (d, J = 8.7 Hz, 2H), 7.45–7.40 (m, 4H), 7.32-7.29 (m, 3H), 7.16 (d, J = 7.7 Hz, 2H), 7.12-7.08(m, 5H), 7.6.98–6.89 (m, 4H), 6.71 (s, 1H), 3.83 (s, 3H).

(*E*)-5-(4-((4-(4-Methoxystyryl)phenyl)(phenyl)amino)phenyl)(thiophene-2-carbaldehyde (7). This compound was synthesized using the method established for compound 6. The crude product was purified by column chromatography on silica gel using dichloromethane : hexane (8 : 1, v/v) afforded compound 7 (0.75 g, 39%) as a yellow solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz),  $\delta$ : 9.85 (s, 1H), 7.71 (s, 1H), 7.53 (d, J = 8.6 Hz, 2H), 7.45–7.40 (m, 4H), 7.32–7.29 (m, 3H), 7.16 (d, J = 7.8 Hz, 2H), 7.12–7.08 (m, 5H), 6.98–6.88 (m, 4H), 3.83 (s, 3H).

(E)-2-Cyano-3-(5-(4-((4-((E)-4-methoxystyryl)phenyl)(phenyl)amino)phenyl)furan-2-yl)acrylic acid (SK2). This compound was synthesized using the method established for compound SP1. The crude product was purified by column chromatography on silica gel using dichloromethane : methanol (10:1, v/v) afforded **SK2** (0.26 g, 78%) as a red solid. <sup>1</sup>H NMR (DMSO- $d_6$ , 500 MHz),  $\delta$ : 8.02 (s, 1H), 7.81 (d, J = 8.5 Hz, 2H), 7.55–7.51 (m, 5H), 7.39 (t, J = 7.8 Hz, 2H), 7.22–7.01 (m, 10H), 6.95 (d, J = 8.5 Hz, 2H), 3.77 (s, 3H). <sup>13</sup>C NMR (DMSO- $d_6$ , 500 MHz),  $\delta$ : 163.96, 159.07, 158.84, 148.50, 147.06, 146.04, 145.13, 137.35, 133.23, 129.75, 127.58, 127.40, 127.33, 126.94, 126.33, 125.39, 125.17, 124.76, 124.35, 121.51, 116.62, 114.12, 108.78, 95.91, 55.09. HR-MS: m/z (%) calcd for C<sub>35</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub>: 539.1971; found 539.1973 [FAB<sup>+</sup>].

(*E*)-2-Cyano-3-(5-(4-((*4*-((*E*)-4-methoxystyryl)phenyl)(phenyl)amino)phenyl)thiophen-2-yl)acrylic acid (SK3). This compound was synthesized using the method established for compound SP1. The crude product was purified by column chromatography on silica gel using dichloromethane : methanol (8 : 1, v/v) afforded SK3 (0.22 g, 75%) as a dark red solid. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz),  $\delta$ : 8.45 (s, 1H), 7.98 (s, 1H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.64 (s, 1H), 7.54–7.51 (m, 4H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.17–7.01 (m, 9H), 6.95 (d, *J* = 8.5 Hz, 2H), 3.77 (s, 3H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 500 MHz),  $\delta$ : 163.65, 158.84, 152.99, 148.37, 146.33, 146.16, 145.25, 141.43, 133.57, 133.12, 129.78, 129.75, 127.60, 127.41, 127.28, 125.56, 125.41, 125.07, 124.65, 124.25, 123.97, 122.03, 116.61, 114.14, 97.61, 55.09. HR-MS: *m*/*z* (%) calcd for C<sub>35</sub>H<sub>27</sub>N<sub>2</sub>O<sub>3</sub>S: 555.1742; found 555.1746 [FAB<sup>+</sup>].

#### (3) Fabrication of dye-sensitized solar cells

FTO glass plates (Pilkington, TEC-8, 8 Ω per square, 2.3 mm thick) were cleaned with ethanol by ultrasonication for 10 min, and then treated in a UV-O<sub>3</sub> system for 20 min. The FTO layer was first covered with 7.5% Ti(IV) bis(ethyl acetoacetato)diisopropoxide solution by a spin-coating method. For the transparent nanocrystalline layer, TiO<sub>2</sub> paste (230(M2331)-2T) was coated on the FTO glass plates, which was followed by sintering at 500 °C for 30 min. TiO<sub>2</sub> paste (CCIC-1T) for the scattering layer was prepared using the same method. The resulting layer was composed of 9 µm thickness of transparent layer and 4 µm thickness of scattering layer. The active area of  $TiO_2$  films was approximately 0.26 cm<sup>2</sup>. The TiO<sub>2</sub> electrodes were immersed into the dye solution (0.5 mM in dichloromethane containing 10 Mm CDCA) and kept at room temperature for 24 h. Counter electrodes were prepared by dropping a 0.7 mM H<sub>2</sub>PTCl<sub>6</sub> solution on a FTO glass and heating at 400 °C for 20 min. The dye-adsorbed TiO<sub>2</sub> electrode and counter electrode were sealed using 25 µm-thick surlyn film (Dupont 1702). An electrolyte solution was introduced through a drilled hole on the counter electrode, where the electrolyte solution consisted of 0.5 M 1-methyl-3-propylimidazolium iodide (PMII), 0.2 M LiI, 0.05 M I<sub>2</sub>, and 0.5 M 4-tert-butylpyridine (TBP) in ACN/VN (85:15).

#### (4) Photovoltaic measurements

Photovoltaic measurements were performed using a Keithly model 2400 source measuring unit. A 1000 W Xe lamp (Spectra-physics) served as a light source and its light intensity was adjusted using a NREL-calibrated silicon solar cell equipped with a KG-5 filter to approximate AM 1.5G of sun light intensity. IPCE was measured

as a function of the wavelength from 300–800 nm using a specially designed IPCE system for dye-sensitized solar cells (PV Measurements, Inc.). A 75 W Xe lamp was used as the light source to generate a monochromatic beam. Calibrations were performed using a silicon photodiode, which was calibrated using NIST-calibrated photodiode G425 as a standard, and IPCE values were collected at a low chopping speed of 10 Hz.

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