PAPER

Donor-acceptor dyes incorporating a stable dibenzosilole π -conjugated spacer for dye-sensitized solar cells[†]

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Four novel organic dyes including three based on dibenzosilole (YS01-03) and one based on fluorene (YS04) were synthesized, and their photophysical properties and dye-sensitized solar cell (DSC) performances were characterized. The silicon-containing dibenzosilole-based dves (YS01-03) were superior to the carbon analogue fluorene-based dye YS04 in incident-photon-to-current conversion efficiency (IPCE), and total solar-to-electric conversion efficiency (η), with **YS03**, which has the bulkiest and most branched electron donor group, achieving the highest η of 5.07% compared to 2.88% of **YS04**. To better understand how silicon influences the excited state oxidation potentials $(S^{+/*})$ and absorption maxima (λ_{max}), the equilibrium molecular geometries of dyes **YS01–04** were calculated using density functional theory (DFT) utilizing B3LYP energy functional and DGDZVP basis set. It was shown that the torsion angles ($\theta 1$ and $\theta 2$) across the biphenyl linkages of dyes containing silicon (**YS01–03**) were less twisted than that of the silicon-free dye (YS04), which enhanced the π - π * overlap, and that translated into photocurrent enhancements in the silicon-containing dyes YS01-03. Moreover, the vertical electronic excitations and S^{+/*} of dyes YS01-04 were studied using different long-range corrected time-dependent DFT methods, including CAM-B3LYP, LC-BLYP, WB97XD, and LC-wPBE at the basis set level DGDZVP. Excellent agreement between the calculated, using CAM-B3LYP/DGDZVP, and experimental results was found.

Introduction

In recent years, the molecular design and realization of metalfree organic sensitizers have attracted considerable attention in the academia and industry for applications in dye-sensitized solar cells (DSCs), owing to their high molar extinction coefficients, flexible molecular structural modulations, facile synthesis, and low costs.¹ Currently, the most popular design of organic sensitizers is based on D– π –A systems, in which the electron-donating (D) and accepting (A) moieties are linked by π -conjugated spacers such as polyene, oligophenylenevinylene, oligothiophene and their derivatives.² The overall DSC performances of these organic sensitizers are lower than Ru-based dyes because they do not absorb across a wide range of the solar radiation spectrum.³ Furthermore, they have inferior photostability and tend to aggregate on the semiconductor TiO₂ surface, which precludes efficient electron injection into the semiconductor.⁴ It was reported that the E_{0-0} energy gap of dyes for DSCs is one of the key thermodynamic parameters that can be used effectively to significantly increase the efficiency of DSCs up to 33% if and only if the ground-state oxidation potential, S+/0, and excited-state oxidation potential, S+/*, were maintained thermodynamically favorable for replenishing the hole and electron injection, respectively, while maintaining the E_{0-0} energy gap ~1.4 eV.⁵ Therefore, proper design of organic sensitizers with small E_{0-0} energy-gap that extends to the NIR region up to 880 nm while maintaining the $S^{+/0}$ and $S^{+/*}$ thermodynamically favorable is highly desirable for furnishing panchromatic sensitizers with efficient electron injection and dye regeneration.⁶ Hence, the systematic molecular design of the D and A moieties along with the π -conjugation linker is paramount for achieving the enviable E_{0-0} energy-gap and the energy locations of the S^{+/0} and S^{+/*} that

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lead to sensitizers that can harvest energetic photons across a wide range of the solar spectrum, and the desirable molecular geometry that precludes dye aggregations.

Silicon-based dyes have been considered to have very promising chemistry for DSCs due to their photostability and thermal stability, and the ability to effectively tune their HOMO-LUMO energy levels.⁷ Polymers and copolymers containing a silole unit were recently investigated for organic photovoltaics (OPV). organic field-effect transistors (OFETs) and sensors because of their low-lying LUMO arising from the strong $\sigma^*-\pi^*$ conjugation between the σ^* orbital of the exocyclic two Si–C bonds and the π^* orbital of the butadiene moiety.⁸ However, the silole chemistry has not been investigated extensively for the molecular design of organic sensitizers for DSC applications. From the open literature, very few examples have been found based on dithienosilole heterocyclic aromatic motifs with an electron donor at one end of the molecule and an electron acceptor at the other end for DSCs application.9 In the present paper, novel D- π -A sensitizers (Fig. 1) based on silole chemistry were successfully designed and synthesized, containing indolized analogs as the electron donor, and cyanoacrylic acid as the electron acceptor moiety, and both are connected with a dibenzosilole π -conjugated unit to furnish dyes **YS01–03**, to study and better understand the photophysical and photoelectrochemical properties of silole-containing dves for DSCs. YS01 had the simplest structure, with methyl substituted indoline as the electron donor. Two different indoline derivatives, methoxy in YS02 and di-tert-butyl in YS03, were also introduced to further increase the electron-donating strength of the donor moiety and to generate the bulkiest group for precluding dye aggregations, respectively. To study the influence of non-silicon containing sensitizers on photovoltaic performance in DSCs, dye YS04, a fluorene-based one was synthesized. The photophysical properties, equilibrium molecular geometry calculations and the performance of DSCs based on these organic dyes are reported.

Experimental section

General information for materials synthesis

¹H NMR and ¹³C NMR spectra were recorded on JEOL JMTC-270/54/SS (JASTEC, 400 MHz) and BRUKER (600 MHz) spectrometers. ¹H NMR spectra are reported as follows: chemical shift in ppm (δ), integration, multiplicities (s = singlet, d = doublet and m = multiplet), and coupling constants (Hz). ¹³C NMR spectra are reported in ppm (δ). High-resolution mass



Fig. 1 Chemical structures of dyes **YS01–04** where θ 1 and θ 2 refer to the torsion angles across the biphenyl linkages.

spectra were obtained on a BRUKER APEXIII spectrometer. Column chromatography was carried out employing Silica Gel 60N (spherical, neutral, 40–100 μ m, 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 noted.

Synthesis of compounds YS01-04

To a mixture of intermediates **8a–c**, **11** (0.14 mmol), 2-cyanoacetic acid (0.448 mmol) and ammonium acetate (0.08 mmol) in acetonitrile (5 mL) was added 10 mL of glacial acetic acid, and the mixture was refluxed for 3 h under Ar. After evaporation of the solvent, the crude solid was dissolved into CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4 . After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography to give compounds **YS01–04**.

Dye YS01. Yield 73%; ¹H NMR (400 MHz, DMSO- d_6 , δ) 8.42 (s, 1H), 8.20 (d, J = 8.4 Hz, 2H), 8.14 (d, J = 1.6 Hz, 1H), 8.09–7.93 (m, 5H), 7.88 (dd, J = 8.0 Hz, J = 1.6 Hz, 1H), 7.69 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 7.53 (brs, 1H), 7.41 (dd, J = 8.4 Hz, J = 1.6 Hz, 1H), 7.25 (d, J = 8.8 Hz, 4H), 7.21 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.4 Hz, 1H), 4.94–4.85 (m, 1H), 3.94–3.86 (m, 1H), 2.32 (s, 3H), 2.18–1.61 (m, 6H), 1.45–1.14 (m, 12H), 1.12–0.97 (m, 4H), 0.85–0.69 (m, 6H); ¹³C NMR (100 MHz, DMSO- d_6 , δ) 163.2, 153.5, 148.1, 146.6, 145.0, 144.3, 139.7, 139.5, 138.22, 138.20, 136.6, 135.4, 131.5, 131.3, 130.26, 130.22, 130.17, 129.96, 128.9, 127.6, 126.9, 125.6, 122.7, 121.7, 121.3, 119.0, 116.2, 107.2, 102.9, 68.2, 44.7, 34.79, 34.77, 33.2, 24.0, 23.1, 21.5, 20.4, 13.8, 11.6. HRMS (ESI positive): [M + H]⁺ calcd for C₅₀H₅₃N₂O₂Si, 741.3871; found, 741.3867%.

Dye YS02. Yield 85%; ¹H NMR (400 MHz, CDCl₃, δ) 8.33 (s, 1H), 8.12 (d, J = 8.4 Hz, 2H), 7.95–7.77 (m, 6H), 7.71 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.41 (s, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.81 (d, J = 8.0 Hz, 1H), 4.83–4.74 (m, 1H), 3.95–3.86 (m, 1H), 3.83 (s, 3H), 2.15–1.56 (m, 6H), 1.49–1.19 (m, 12H), 1.05–0.95 (m, 4H), 0.87–0.76 (m, 6H); ¹³C NMR (100 MHz, DMSO, δ) 163.2, 154.5, 153.2, 148.1, 147.7, 144.9, 144.2, 139.6, 138.20, 138.17, 136.6, 135.4, 135.0, 131.5, 131.2, 130.3, 130.2, 129.5, 128.9, 127.5, 126.9, 125.6, 122.7, 121.9, 121.7, 121.3, 116.4, 114.5, 106.4, 103.4, 68.8, 55.2, 44.7, 34.9, 34.8, 33.1, 24.0, 23.1, 21.5, 13.8, 11.6. ESI-MS: *m*/*z* calcd for [M (C₅₀H₅₂N₂O₃Si) – H]: 755.37; found, 755.1%.

Dye YS03. Yield 81%; ¹H NMR (400 MHz, DMSO- d_6 , δ) 8.09 (brs, 1H), 8.07–7.93 (m, 6H), 7.89 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.52 (brs, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.18 (brs, 1H), 6.93 (d, J = 8.4 Hz, 1H), 4.88–4.82 (m, 1H), 3.92–3.85 (m, 1H), 3.69 (s, 3H), 2.20–1.15 (m, 18H), 1.45 (s, 18H), 1.10–1.00 (m, 4H), 7.83–0.71 (m, 6H). FAB-MS (EI positive): m/z calcd for C₅₈H₆₈N₂O₃Si, 868.5; found, 868.5%.

Dye YS04. Yield 83%; ¹H NMR (400 MHz, DMSO- d_6 , δ) 8.42 (s, 1H), 8.21 (d, J = 8.0 Hz, 2H), 8.05 (d, J = 8.4 Hz, 2H), 7.97–7.92 (m, 2H), 7.89 (d, J = 7.6 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H),

Downloaded by University of Hong Kong Libraries on 22 February 2013 Published on 26 March 2012 on http://pubs.rsc.org | doi:10.1039/C2JM30978E 7.72 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.57 (s, 1H), 7.45 (d, J = 8.8 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 6.98 (d, J = 8.4 Hz, 1H), 4.94–4.88 (m, 1H), 3.97–3.89 (m, 1H), 2.33 (s, 3H), 2.20–1.36 (m, 10H), 1.13–0.99 (m, 8H), 0.73–0.55 (m, 10H); ¹³C NMR (100 MHz, DMSO- d_6 , δ) 163.3, 153.5, 151.3, 146.6, 144.6, 141.1, 139.8, 137.9, 136.8, 135.4, 131.3, 130.4, 130.3, 130.1, 129.6, 129.0, 127.1, 126.9, 125.9, 125.8, 124.6, 122.9, 121.1, 120.5, 120.1, 119.8, 119.1, 116.3, 107.3, 103.0, 68.2, 54.9, 44.7, 34.8, 33.3, 31.51, 31.5, 24.0, 23.2, 21.7, 20.4, 13.8. HRMS (ESI positive): [M + H]⁺ calcd for C₅₁H₅₃N₂O₂, 725.4107; found, 725.4084%.

Molecular modelling

The ground state equilibrium molecular geometry of dye **YS01** was calculated by generating an energy search map in molecular mechanics using augmented MM3 parameters implemented in Scigress Workspace Version 7.7.0.47. To generate the energy search map, a conformation search was performed using MM3 parameters by varying the torsion angles across the two peripheral biphenyl linkages (θ 1 and θ 2) from -180° to $+180^{\circ}$ using 120 steps of 3° each, which furnished a potential energy map of a total of 14 641 conformers.

Ground state equilibrium molecular geometries of **YS01–04** were calculated using the hybrid DFT energy functional B3LYP^{15,16} and the basis set 3-21G* or DGDZVP (density Gauss double- ζ with polarization functions).^{17,18} Subsequently, a single point energy calculation was performed on the optimized geometry using different long-range corrected time-dependent

DFT energy functional methods including CAM-B3LYP,¹⁹ LC-BLYP,²⁰ WB97XD,²¹ or LC-wPBE²² with the basis set DGDZVP, and the electronic absorption spectra were extracted. The MM3 calculations were performed on a desktop computer equipped with four processors at 2.6 GHz and 8 GB of RAM. The TD-DFT calculations were performed in DMF using the polarizable conductor calculation model (PCM). The DFT calculations were performed on the East Carolina University's Super Computer Jasta using 8 processors and 4 GB 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

A double-layer TiO₂ photoelectrode $(10 + 5) \mu m$ 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 a conducting glass substrate. A dye solution of 3×10^{-4} M concentration in acetonitrile–*tert*-butyl alcohol (1/1, v/v) was used to uptake the dye onto 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 sandwich type solar cell in conjunction with an electrolyte consisting of a solution of 0.6 M dimethylpropyl-imidazolium iodide (DMPII), 0.05 M I₂, 0.1 M LiI and 0.5 M *tert*-butylpyridine (TBP) in acetonitrile (AN). The dye-deposited TiO₂ film and a platinum-coated



Scheme 2 Synthesis routes of dye YS04.

conducting glass were separated by a Surlyn spacer (40 µm thick) and sealed by heating the polymer frame. Photocurrent 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 (V_{oc}), fill factor (FF), and power conversion efficiency (η) were estimated from *I–V* characteristics under illumination.

Results and discussions

The synthesis routes of compounds **YS01–04** are shown in Schemes 1 and 2. The intermediate compounds **2a**, **2b**, **5** and **10** were synthesized according to the published methods.^{10,11} Other intermediate compounds (**2–8**, **10**, **11**) were obtained in high yields following standard reaction conditions as described in the ESI[†]. The target compounds **YS01–04** were prepared *via* condensation of their corresponding aldehyde derivatives and cyanoacetic acid in the presence of ammonium acetate in high yields as described in the Experimental section.

The photophysical properties of dyes **YS01–04** are summarized in Table 1. Their wavelengths of absorption maxima (λ_{max}) were in the range of 385–391 nm, shown in Fig. 2a. The low-lying absorption bands, due to the π – π * transition, for **YS01**, **YS02 YS03**, and **YS04** exhibited λ_{max} at 386, 390, 391, and 385 nm, respectively. When absorbed on a transparent thin TiO₂ film, all dyes exhibited broad absorption spectra similar to those in solution, due to the interaction between the carboxylate group and TiO₂ (Fig. 2b). Upon adsorption on the TiO₂ film, the tail of the absorption spectrum of all dyes extended up to 550 nm, which is highly desirable for harvesting more of the solar spectrum and translates into greater photocurrent.

The ionization potential (IP) of **YS01–04** bound to the nanocrystalline TiO₂ film was measured using the photoemission yield spectrometer (Riken Keiki, AC-3E). The IP values of **YS01–04** were found in the range of -5.59 to -5.68 eV (Fig. S2, ESI†). The IP values of **YS01–04**, which correspond to S^{+/0}, were sufficiently lower than the redox potential of I⁻/I₃⁻ (-5.20 eV),¹² which ensured favorable thermodynamic ground states for efficient regeneration of the dye through the reaction of the oxidized dye with iodide. The IP value of the silyl containing sensitizers (**YS01–03**) was shifted anodically compared to the fluorene-based dye (**YS04**) (Table 1). This anodic shift is because silicon is more electropositive than carbon, exhibiting more electron donation relative to carbon (β -silicon effect), which furnished more charge transfer from D to A in silicon-based dyes than that of the fluorene-based dye (**YS04**). Moreover, the anodic shift increased the negative free energy of electron injection, which explained why **YS01–03** furnished more photocurrent than **YS04**. The onset of the optical energy gap (E^{0-0}) of **YS01–04** dyes was in the range of 2.43–2.53 eV (Table 1).¹³ The excited-state oxidation potential, S^{+/*}, of sensitizers **YS01–04** was in the range of -3.15 to -3.18 eV (Table 1) and lay above the conduction band edge (-4.2 eV)^{1c} of the nanocrystalline TiO₂ ensuring that the excited states of these dyes are thermodynamically driven for efficient electron injection into the conduction band edge of TiO₂.

A key factor in predicting accurately the electronic and thermodynamic properties of any compound is to obtain first the correct molecular geometry. Hence, to gain more insights and



Fig. 2 Absorption spectra of YS01–04 (a) in DMF and (b) on a transparent TiO_2 film.

 Table 1
 Photophysical properties and DSCs performance parameters of dyes YS01–04

Dye	$\lambda_{max}/nm^a~(\epsilon \times 10^4/M^{-1}~cm^{-1})$	$\lambda_{\rm max}/{\rm nm}^b$ on TiO ₂	$IP^{c} (eV)$	$E^{0-0} \left(\mathrm{eV} \right)^d$	$\mathbf{S}^{\scriptscriptstyle +/*}\left(\mathbf{eV} ight)^{e}$	$J_{\rm sc}~({\rm mA~cm^{-2}})$	$V_{\rm oc}$ (V)	FF	η (%)
YS01	386(4.5)	382	-5.66	2.48	-3.18	8.23	0.767	0.735	4.64
YS02	390(4.5)	379	-5.60	2.46	-3.15	7.69	0.798	0.740	4.55
YS03	391(4.8)	392	-5.59	2.43	-3.16	9.14	0.778	0.712	5.06
YS04	385(5.4)	396	-5.68	2.53	-3.15	5.10	0.772	0.732	2.88

^{*a*} Absorption measured in DMF 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 the dye loaded on a TiO₂ film. ^{*e*} The excited-state oxidation potential (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; FF, fill factor; η , conversion efficiency.



Fig. 3 Potential energy map generated by varying two torsion angles. The black ball at the bottom of the map represents the global energy minimum conformer.

better understanding into the electronic and thermodynamic properties of dyes **YS01–04**, the equilibrium molecular geometry for each dye was calculated first followed by an energy calculation, and the $S^{+/*}$, $S^{+/0}$, vertical electronic excitation values, and the delocalization of the HOMO and LUMO were extracted for each dye.

To identify an accurate and reliable molecular modelling method for the prediction of the equilibrium molecular geometry, different geometry optimization methods were performed first on dye **YS01**. First, a conformation search was performed on dye **YS01** in molecular mechanics using augmented MM3 parameters, which generated an energy map of 14 641 conformers, shown in Fig. 3. Fig. 4 shows the lowest conformational energy structure, the global energy minimum conformer, in which the two terminal torsion angles $\theta 1$ and $\theta 2$ were twisted by 36.05° ($\theta 1$) and 36.26° ($\theta 2$), respectively.

To determine the accuracy of the global energy minimum conformer calculated using MM3 parameters, the ground state equilibrium molecular geometry of dye **YS01** was calculated using high level DFT calculations utilizing the hybrid energy functional B3LYP at two different basis sets, $3-21G^*$ and DGDZVP.¹⁴ In the case of the basis set $3-21G^*$, the two torsion angles (θ 1 and θ 2) of the equilibrium molecular geometry were twisted by 38.67° and 40.67° while in the case of the basis set DGDZVP the twist was slightly less showing 34.42° and 36.11° , respectively, which was comparable to those obtained using MM3 calculations.



Fig. 4 Global energy conformer extracted from the potential energy map shown in Fig. 3, calculated using augmented MM3 parameters. The terminal torsion angles are twisted by 36.05° (θ 1) and 36.26° (θ 2), from left to right.

 Table 2
 Calculated absorption spectra for YS01 using different starting optimized geometries and long range corrected DFT methods

λ_{\max} (nm)								
	Long-range corrected energy functional/basis set							
Geometry optimization	CAM-B3LYP/ DGDZVP	LC-BLYP/ DGDZVP	WB97XD/ DGDZVP	LC-wPBE/ DGDZVP	Expt.			
B3LYP/ 3-21G*	371	328	355	329				
B3LYP/ DGDZVP	376	332	359	333	386			

Table 2 shows a comparison between the calculated and experimental λ_{max} for **YS01**. These data clearly demonstrate that the geometry optimization of **YS01** using the energy functional B3LYP and the basis set DGDZVP, coupled with TD-DFT CAM-B3LYP energy functional and the basis set DGDZVP furnished the closest λ_{max} (376 nm) to the experimental result (386 nm). These findings are vital because they clearly demonstrate the high sensitivity of the λ_{max} to the twist across the biphenyl linkage. Hence, a novel generation of these dyes that absorbs at much longer wavelength can be achieved if the twist across the biphenyl is prevented.

Based on the data presented in Table 2, it was deemed that the aforementioned DFT and TD-DFT methods will be the methods of choice for the prediction of the optimized geometries and λ_{max} , respectively, for **YS02–04**. Table 3 shows the calculated *versus* experimental λ_{max} and S^{+/*} for dyes **YS01–04**. It also shows the

Table 3 A comparison between the experimental and calculated $S^{+\prime*}$ and λ_{max} of YS01--04

	Torsion angles (°)		S+/* (eV)		λ_{\max} (nm)		
Dye	$\theta 1$	θ2	Calcd	Expt.	Calcd	Expt.	
YS01	34.42	36.11	-3.361	-3.18	376	386	
YS02	34.51	37.57	-3.228	-3.15	377	390	
YS03	35.29	36.12	-3.229	-3.16	377	391	
YS04	35.05	39.07	-3.263	-3.15	376	385	



Fig. 5 Calculated absorption spectra of **YS01–YS04**, using the energy functional CAM-B3LYP and the basis set DGDZVP.

calculated torsion angles (θ 1 and θ 2). The calculated λ_{max} and S^{+/*} are in excellent agreement with experimental results, which demonstrates the high level of accuracy of the DFT/TD-DFT methods used for this class of dyes. Moreover, **YS04** exhibited the largest twist across the biphenyl linkage for θ 2 (39.09°), which reduced the π - π overlap across the quarterphenyl, and furnished the weakest charge transfer from the D to A in the series.

Fig. 5 shows the calculated absorption spectra of **YS01–YS04**, using time-dependent DFT long-range corrected energy functional CAM-B3LYP and the basis set DGDZVP. The comparison between calculated (Fig. 5) and experimental absorption spectra (Fig. 2a) showed excellent agreement between the calculated and experimental λ_{max} . Moreover, the shapes of

calculated absorption peaks are also identical to the experimental spectra. Fig. 6 shows the HOMO (left) and LUMO (right) of dyes **YS01–04**. It can be seen clearly that the HOMO is delocalized mainly on the electron donor regime where the auxochrome (indole analog) resides, which facilitates the reduction of the oxidized dye through the reaction with I⁻, making the dye regeneration more efficient. On the other hand, the LUMO was mainly delocalized on the π^* cyanuric unit and has sizable contributions from the carboxylic groups, facilitating electron injection from the photoexcited sensitizer into the TiO₂ semiconductor. This clearly confirms that this structural motif is an excellent design for efficient charge transfer in DSCs. Moreover, it can be seen from Fig. 6 that the torsion angle $\theta 2$ across the



HOMO (YS04)

LUMO (YS04)

a)

biphenyl linkage for **YS04** is the largest, which diminished the π - π^* overlap, and this is why its photocurrent and total conversion efficiency were the lowest compared to dyes **YS01-03**.

Fig. 7 shows the monochromatic IPCE and photocurrentvoltage (I-V) characteristics for DSCs based on YS01-04 demonstrating excellent sensitization of nanocrystalline TiO₂ from 350 to 650 nm with a maximum quantum efficiency of 85% in the plateau region. Dve YS03 showed the highest solar to power conversion efficiency (η) (5.06%) among the four dyes with the short-circuit current (J_{sc}) , the open circuit voltage (V_{oc}) and the fillfactor (FF) of 9.14 mA cm⁻², 0.778 V and 0.712, respectively. Under the same conditions the overall power conversion efficiencies (η) of dyes **YS01** and **YS02** were 4.64 and 4.55%, respectively. Silyl-containing dyes (YS01-03) showed higher power conversion efficiency compared to the fluorene-based dye YS04 (2.88%), as shown in Table 1 due to the strong electron donation of silicon relative to carbon and the less twist across the biphenyl linkages of $\theta 1$ and $\theta 2$, and the anodic shift of S^{+/*} in dyes YS01-03 compared to dye YS04. The overall power conversion efficiency of these dyes was in the range 2.88-5.06% owing to the lack of absorption of the energetic photons from the blue, red and NIR regions. Therefore, work is underway in our laboratory to develop a novel generation of more efficient dyes that have the



Fig. 7 (a) Photocurrent action spectra (IPCE) of nanocrystalline TiO_2 film sensitized by **YS01–04**. (b) Photocurrent–voltage (*I–V*) characteristics of dyes **YS01–04**. The redox electrolyte solution was a mixture of 0.6 M DMPII, 0.05 M I₂, 0.1 M LiI and 0.5 M TBP in acetonitrile.

potential to exhibit significant increase in the extinction coefficient and simultaneously harvest more energetic photons across a wider range of the solar radiation spectrum.

Conclusions

Four novel D- π -A sensitizers, **YS01-04**, were designed, synthesized, and characterized for DSCs. It was demonstrated that dyes with a π -conjugated-silvl unit linker (YS01–03) furnished better charge separation and more photocurrent, resulting in higher total conversion efficiency than the silicon-free dye (YS04). Among dyes YS01-YS03, the photovoltaic properties of YS03 showed the greatest light harvesting ability, suppressed dye aggregation owing to the highly branched donor group, which led to the highest overall conversion efficiency of 5.06%. Moreover, DFT calculations showed that the torsion angles across the biphenyl linkage in dyes containing silicon (YS01-YS03) are less than in the silicon-free dye (YS04), which contributed to better charge separation, and enhancements in the total efficiency of dyes YS01-03 compared to YS04. Results from this work strongly indicate that the application of this class of organic dyes as panchromatic sensitizers for DSCs is promising, and opens new avenues for the design of more efficient organic dyes based on the silvl moiety for DSCs. With the aid of molecular modeling, work in our laboratory is underway for the synthesis of novel silicon-based sensitizers that can harvest solar energy across a wider range of the solar spectrum up to 900 nm.

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