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Eight metal-free organic dyes **(YH-1–YH-8)** containing olefin or acetylene as the π -spacer linkage in the triarylene bridge were synthesised. Two dyes **(1N-PPP** and **1N-PPS)** without the olefin and triple bonds as π -spacer linkages were used as references. The photophysical and electrochemical properties of the dyes were characterised, and the dyes were then to fabricate dye-sensitised solar cells (DSSCs). We demonstrated the use of the D– π –A dipolar system by employing arylamine derivatives as an electron donor, triarylene with iterative olefin or acetylene as a π -bridge, and cyanoacrylic acid as an electron acceptor. **YH-1** had olefin as a repeat unit in the triarylene bridge and had broad absorption, favourable short-circuit photocurrent density (J_{sc}), and favourable open-circuit voltage (V_{oc}) when used in film morphology with DCA as a coabsorbent. The optimal device exhibited a J_{sc} of 16.23 mA·cm⁻², a V_{oc} of 650 mV, and a fill factor of 0.67, corresponding to an overall conversion efficiency of 7.08%. The photophysical properties of the DSSCs were analysed using time-dependent density functional theory with the B3LYP functional.

1 Introduction

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Very recently, under limited stocks of fossil fuels and CO₂ emission issue in global which is urged to investigate and develop renewable and environmental friendly energy source. Solar energy is generally acknowledged as a potential alternative energy source. In the past two decades, dyesensitised solar cells (DSSCs) based on nanocrystalline TiO_2 and photosensitisers have received considerable attention because they are easy to fabricate, colourful and transparent devices, low-cost devices, and can be scaled up.¹⁻⁴ DSSC devices utilising ruthenium-based polypyridyl complexes exhibit a power conversion efficiency of more than 11% under AM 1.5 conditions.⁵⁻⁸ Diau and Yeh et al. used a porphyrin dye (YD2-o-C8) and achieved a maximal performance of 13% with Y123 in a cocktail system.9 However, one previous report on a metal complex sensitiser reported a complicated synthesis route, difficult purification, low yield, and source-limited metal. Metalfree organic dyes are environmental friendly, have a high molar extinction coefficient, can be synthesised at a low cost, have high structural flexibility, and have sensitiser variety. Most organic sensitisers with high efficiency have dye molecules with linearly shaped structures comprising a strong D- π -A dipole with an electron donor D, a π -bridge, and an electron acceptor A. Numerous metal-free organic dyes have been investigated and demonstrated to exhibit a high performance level similar to that of ruthenium-based complexes.¹⁰⁻¹⁷ Yano and Hanaya used an alkoxysilyl anchor dye (**ADEKA-1**) as a cosensitiser and achieved the highest performance yet reported (i.e., 14%) with **LEG-4** in metal-free organic dyes.¹⁸

To achieve an optimal D– π –A photosensitiser for DSSCs, it is critical to improve the cell's power conversion efficiency. The πbridge is a crucial factor in DSSCs not only because it connects D and A in the electron channel, but also because a conjugated chromophore with light harvesting ability improves the shortcircuit current (J_{sc}). Numerous studies have focused on conjugated π -bridges, with the π -bridge unit in the sensitiser mainly composed of anthracene,^{15, 19-23} benzene,²⁴⁻²⁵ benzothiadiazole,²⁶⁻²⁹ furan,³³⁻³⁴ diketopyrrolopyrrole,³⁰⁻³² pyrrole,³⁵⁻³⁶ and thiophene,³⁷⁻³⁸ all of which exhibit C–C linkages. However, some π -spacers exhibit a low degree of π -conjugation along the main chromophore through the C-C linkage, which may reduce their electron injection efficiency.^{20, 39} In previous studies, the expansion of π -conjugated chromophores has yielded higher J_{sc}, which is often accompanied by a lower opencircuit voltage (V_{oc}). The effect of V_{oc} on device performance has mostly been attributed to the electron lifetime, which is the time taken for electrons from the excited state of the photosensitiser that have been injected into the nanoporous TiO₂ to recombine.⁴⁰⁻⁴¹ The V_{oc} results of previous reports can be summarised as follows: (i) The conduction band edge of TiO₂ is downshifted by electron acceptor species. (ii) Bulky triarylamine donors and alkyl substituents result in higher $V_{\rm oc}$ and a longer electron lifetime because of the enhanced surface blocking effect. (iii) The dye structures yield interactions between electrolyte and dye, hence producing numerous electrolyte acceptor species at the interface and enhancing electron recombination. (iv) Dye structures that exhibit favourable film morphology cover the TiO₂ surface more

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⁺⁺ Electronic Supplementary Information (ESI) available: Experimental data of compound **1**°**11**, and **YH-1°8**, the ¹H and ¹³C NMR spectra, theoretical calculation, UV/vis spectra, CV spectra, EIS spectra, and the devices in cooperating DCA. See DOI: 10.1039/b000000x/

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completely, thus preventing direct contact with the electron acceptor of the electrolyte.

Although some report showed fancy dye skeleton and good performance, it also has complicated synthetic route, and a low totally yield. ^{15-17, 42} We previously reported a simplify triarylene $\pi\text{-bridge}$ using C–C single bond linkage (1N-PPP and 1N-PPS) possessed different π -conjugated chromophores that (phenylene/thiophene) and a slight twist in the bridge moiety.²⁵ And rare report to discuss the Influence by double and triple bonds linkage in triarylene Bridge for DSSCs. In this study, we designed and synthesised eight YH-series dyes (YH-1-YH-8) containing olefin or acetylene as the π -spacer linkage in the triarylene bridge. To focus the effect of different dye structures on the charge recombination rate and the electron lifetime was investigated, and we also evaluated how the film morphology with the co-absorbent enhanced the performance of the resultant DSSC devices. We also discovery the thiophene moieties can enhance light harvesting, but the sensitisers with thiophene spacer exhibited lower $V_{\rm oc}$ than dyes with phenylene $\pi\text{-bridges},$ and discuss in the section of Photovoltaic performance of DSSCs. The synthesis procedures are described in Scheme 1, and all structures were confirmed using spectroscopy.



2 Experimental

2.1 Characterization and reagents

All reactions and manipulations were performed under a nitrogen atmosphere, and solvents were freshly distilled according to standard procedures. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded using a Bruker (AVIII HD 400) spectrometer with $CDCl_3$, THF- d_8 , or DMSO- d_6 as the solvent. Chemical shifts (δ) were reported downfield from the peak with respect to tetramethylsilane. Absorption spectra were recorded using a Shimadzu UV-1800 spectrophotometer, and emission spectra were obtained using a Hitachi F-4500 spectrofluorometer. Redox potentials were measured through cyclic voltammetry on a CHI 620 analyser. All measurements were performed in tetrahydrofuran solutions containing 0.1 M tetrabutylammonium hexaflourophosphate as the supporting electrolyte under ambient conditions after purging for 10 min with N₂. Furthermore, the conventional three-electrode configuration was employed, comprising a glassy carbon working electrode, a platinum counter electrode, and an Ag/Ag⁺ reference electrode calibrated using ferrocene/ferrocenium as an internal reference. Mass spectra were recorded using a JEOL JMS-700 double-focusing mass spectrometer.

n-Butyllithium (1.6 M in hexane), N,N-Dimethylformamide, sodium hydride (NaH), Palladium(II) acetate 1(Bg/(CAc)))415-Bromothiophene-2-carbaldehyde, 4-Bromobenzaldehyde, Triethylamine, Diisopropylamine, Copper (I) iodide (Cul), Trimethylsilylacetylene, 1-lodo-4-bromobenzene, Tri(otolyl)phosphine, Tetrakis(triphenylphosphine) palladium (0) (Pd (PPh₃)₄), Piperidine, Cyanoacetic acid, Ammonium acetate, and Acetic acid glacial were purchased from ACROS, Alfa, Merck, Lancaster, TCI, Sigma-Aldrich, Showa, respectively. Chromatographic separations were performed using Merck Kieselgel silica gel 60 (40–63 μm).

(E)-2-cyano-3-(5-((E)-4-((E)-4-(naphthalen-1-yl(phenyl)amino)

-styryl)styryl)thiophen-2-yl)acrylic acid (YH-1). A mixture of 4a (1.05 g, 1.96 mmol), cyanoacetic acid (168 mg,1.96 mmol), and piperidine (1 mL, 10 mmol) in acetic acid was placed in a three-necked flask with 15 mL chloroform and stirred at 70 °C for 6 h. After cooling, the reaction was quenched by adding distilled water, and extracted with CH₂Cl₂. The organic layer was dried over anhydrous MgSO₄ and evaporated under vacuum. The product was purified by silica gel column chromatograph eluted with CH₂Cl₂/acetic acid (19/1). The black solid was isolated in 77% yield (904 mg, 1.51 mmol). $\delta_{\rm H}$ (400 MHz, THF-d₈) 8.35 (s, 1H), 7.96 (d, 1H, J = 8.4 Hz), 7.94 (d, 1H, J = 8.04 Hz), 7.84 (d, 1H, J = 8.16 Hz), 7.79 (d, 1H, J = 3.92 Hz), 7.61 (d, 2H, J =8.36 Hz), 7.55 (d, 2H, J = 9.08 Hz), 7.27-7.37 (m, 3H), 7.19-7.24 (m, 3H), 7.09 (d, 2H, J = 7.44 Hz), 7.06 (d, 1H, J = 16.0 Hz), 6.95-6.98 (m, 3H). δ_C (100 MHz, THF-d₈) 163.1, 152.4, 148.2, 148.1, 145.4, 143.3, 138.9, 138.4, 135.5, 135.1, 134.7, 132.4, 131.2, 130.7, 128.9, 128.7, 128.2, 127.3, 127.2, 127.0, 126.9, 126.4, 126.2, 126.1, 125.9, 125.7, 123.9, 122.4, 122.0, 121.0, 120.2, 115.6, 98.6. MS (ESI, 70 eV): m/z (relative intensity) 599 (M^+ , 100); HRMS calcd for C₄₀H₂₇N₂O₂S: 599.1793, found 599.1789.

(E)-3-(5-((E)-4-((E)-4-(bis(4-(hexyloxy)phenyl)amino)styryl)-

styryl)thiophen-2-yl)-2-cyanoacrylic acid (YH-2). Compound YH-2 was synthesized according to the same procedure as that of YH-1. Dark red solid of YH-2 was obtained in 75% yield. $\delta_{\rm H}$ (400 MHz, CDCl₃) 8.31 (s, 1H), 7.70 (d, 1H, *J* = 4.12 Hz), 7.50 (s, 3H), 7.34 (d, 2H, *J* = 8.72 Hz), 7.28 (s, 3H), 7.23 (d, 2H, *J* = 1.2 Hz), 7.85 (d, 1H, *J* = 3.96 Hz), 7.07 (d, 4H, *J* = 8.88 Hz), 6.94 (d, 2H, *J* = 15.88 Hz), 6.91 (d, 1H, *J* = 8.56 Hz), 6.85 (d, 4H, *J* = 8.96 Hz), 3.95 (t, 4H, *J* = 6.52 Hz), 1.76-1.83 (m, 4H), 1.45-1.50 (m, 4H), 1.34-1.38 (m, 8H), 0.93 (t, 6H, *J* = 6.96 Hz). $\delta_{\rm C}$ (100 MHz, CDCl₃) 166.3, 155.6, 154.5, 148.7, 147.5, 140.3, 140.0, 138.9, 134.3, 134.1, 133.8, 129.4, 128.9, 127.4, 127.3, 126.9, 126.7, 126.6, 125.0, 120.0, 119.7, 115.8, 115.3, 68.2, 31.6, 29.3, 25.7, 22.6, 14.0. MS (ESI, 70 eV): m/z (relative intensity) 750 (M⁺, 100); HRMS calcd for C₄₈H₅₀N₂O₄S: 750.3491, found 750.3494.

(E)-2-cyano-3-(4-((E)-4-((E)-4-(naphthalen-1-yl(phenyl)-

amino)styryl)styryl)phenyl)acrylic acid (YH-3). Compound **YH-3** was synthesized according to the same procedure as that of **YH-1**. Dark red solid of **YH-3** was obtained in 78% yield. $\delta_{\rm H}$ (400 MHz, DMSO- d_6) 8.30 (s, 1H), 8.06 (d, 2H, J = 8.04 Hz), 8.02 (d, 1H, J = 8.16 Hz), 7.92 (d, 2H, J = 8.24 Hz), 7.85 (d, 1H, J = 8.32 Hz), 7.80 (d, 2H, J = 7.72 Hz), 7.63 (d, 2H, J = 7.92 Hz), 7.57-7.60 (m, 3H), 7.42-7.54 (m, 5H), 7.38 (d, 2H, J = 6.8 Hz), 7.31 (d, 1, J = 19.16 Hz), 7.25 (d, 2H, J = 8.04 Hz), 6.97-7.09 (m, 4H), 6.87 (d, 2H, J = 7.84 Hz). $\delta_{\rm C}$ (100 MHz, DMSO- d_6) 163.9, 153.9, 148.0, 147.8, 142.9, 142.5, 138.0, 135.8, 135.4, 132.0, 131.7, 131.0, 130.8, 130.6, 129.8, 129.0, 128.9, 128.1, 127.8, 127.7, 127.5, 127.3, 127.1, 127.0, 126.8, 126.3, 123.8, 122.8, 122.5, 121.0, 116.9, 103.0

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MS (ESI, 70 eV): m/z (relative intensity) 593 ((M-H)⁻, 100); HRMS calcd for $C_{42}H_{29}N_2O_2$: 593.2229, found 593.2227.

(E)-3-(4-((E)-4-((E)-4-(bis(4-(hexyloxy)phenyl)amino)styryl)-

styryl)phenyl)-2-cyanoacrylic acid (YH-4). Compound **YH-4** was synthesized according to the same procedure as that of **YH-1**. Black solid of **YH-4** was obtained in 78% yield. $\delta_{\rm H}$ (400 MHz, THF- $d_{\rm B}$) 8.24 (s, 1H), 8.08 (d, 2H, *J* = 7.88 Hz), 7.74 (d, 2H, *J* = 8.24 Hz), 7.60 (d, 2H, *J* = 8.32 Hz), 7.54 (d, 2H, *J* = 8.36 Hz), 7.36-7.43 (m, 3H), 7.29 (d, 1H, *J* = 16.28 Hz), 7.18 (d, 1H, *J* = 16.28 Hz), 7.01-7.06 (m, 5H), 6.85-6.89 (m, 6H), 3.97 (t, 4H, *J* = 6.44 Hz), 1.80-1.83 (m, 4H), 1.48-1.54 (m, 4H), 1.37-1.42 (m, 8H), 0.96 (t, 6H, *J* = 6.92 Hz). $\delta_{\rm C}$ (100 MHz, THF- $d_{\rm B}$) 155.9, 152.6, 148.6, 142.3, 140.4, 138.2, 135.5, 131.5, 131.2, 130.9, 129.4, 128.7, 127.1, 126.7, 126.5, 126.3, 125.0, 119.8, 115.0, 67.7, 31.6, 29.3, 25.7, 22.5, 13.4. MS (ESI, 70 eV): m/z (relative intensity) 744 (M^+ , 100); HRMS calcd for C₅₀H₅₂N₂O₄: 744.3927, found 744.3927.

(E)-2-cyano-3-(5-((4-((4-(naphthalen-1-yl(phenyl)amino)-

phenyl)ethynyl)phenyl)ethynyl)thiophen-2-yl)acrylic acid (YH-5). Compound YH-5 was synthesized according to the same procedure as that of YH-1. Black solid of YH-5 was obtained in 82% yield. $\delta_{\rm H}$ (400 MHz, DMSO- d_6) 8.50 (s, 1H), 8.03 (d, 1H, J = 8.12 Hz), 7.99 (d, 1H, J = 3.96 Hz), 7.95 (d, 1H, J = 8.2 Hz), 7.83 (d, 1H, J = 8.36 Hz), 7.52-7.62 (m, 7H), 7.41-7.48 (m, 4H), 7.30 (t, 2H, J = 8.04 Hz), 7.04-7.10 (m, 3H), 6.82-6.88 (m, 2H). $\delta_{\rm C}$ (100 MHz, DMSO- d_6) 168.9, 163.5, 149.0, 147.5, 147.2, 145.9, 142.5, 139.9, 137.3, 136.4, 135.4, 133.8, 133.2, 132.3, 131.9, 131.0, 130.5, 130.1, 130.0, 129.0, 127.9, 127.8, 127.6, 127.3, 127.2, 127.1, 126.8, 126.3, 123.8, 123.7, 123.5, 123.2, 119.8, 119.3, 116.9, 113.7, 98.7, 83.4. MS (FAB, 70 eV): m/z (relative intensity) 597 ((M+H)⁺, 100); HRMS calcd for C₄₀H₂₅N₂O₂S: 597.1631, found 597.1630.

(E)-3-(5-((4-((4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-

ethynyl)phenyl)ethynyl)thiophen-2-yl)-2-cyanoacrylic acid (YH-6). Compound YH-6 was synthesized according to the same procedure as that of YH-6. Dark red solid of YH-6 was obtained in 80% yield. $\delta_{\rm H}$ (400 MHz, THF- d_8) 8.39 (s, 1H), 7.84 (d, 1H, J = 3.64 Hz), 7.58 (d, 2H, J = 8.12 Hz), 7.52 (d, 2H, J = 7.96 Hz), 7.43 (d, 1H, J = 3.84 Hz), 7.30 (d, 2H, J = 8.44 Hz), 7.09 (d, 4H, J = 8.6 Hz), 6.90 (d, 4H, J = 8.6 Hz), 6.83 (d, 2H, J = 8.44 Hz), 3.98 (t, 4H, J = 6.32 Hz), 1.76-1.82 (m, 4H), 1.51-1.54 (m, 4H), 1.39-1.42 (m, 8H), 0.96 (t, 6H, J = 6.24 Hz). $\delta_{\rm C}$ (100 MHz, THF- d_8) 156.4, 149.4, 144.9, 139.7, 137.5, 132.6, 132.2, 131.4, 131.1, 127.2, 125.1, 120.9, 118.2, 115.4, 115.1, 112.9, 97.7, 92.9, 87.3, 83.2, 67.8, 31.6, 29.3, 25.7, 22.5, 13.4. MS (FAB, 70 eV): m/z (relative intensity) 746 (M⁺, 100); HRMS calcd for C₄₈H₄₆N₂O₄S: 746.3178, found 746.3176.

(E)-2-cyano-3-(4-((4-((4-(naphthalen-1-yl(phenyl)amino)phenyl)ethynyl)phenyl)ethynyl)phenyl)acrylic acid

phenyl)ethynyl)phenyl)ethynyl)phenyl)acrylic acid (YH-7). Compound YH-7 was synthesized according to the same procedure as that of YH-1. Red solid of YH-7 was obtained in 80% yield. $\delta_{\rm H}$ (400 MHz, DMSO- d_6) 8.29 (s, 1H), 8.05 (d, 2H, *J* = 8.32 Hz), 8.02 (d, 1H, *J* = 8.16 Hz), 7.93 (d, 1H, *J* = 8.44 Hz), 7.84 (d, 1H, *J* = 8.36 Hz), 7.72 (d, 2H, *J* = 8.2 Hz), 7.51-7.61 (m, 6H), 7.39-7.47 (m, 4H), 7.28 (t, 2H, *J* = 7.72 Hz), 7.07 (d, 2H, *J* = 7.92 Hz), 7.03 (t, 1H, *J* = 7.92 Hz), 6.82-6.86 (m, 3H). $\delta_{\rm C}$ (100 MHz, DMSO- d_6) 168.9, 163.4, 162.7, 152.4, 148.9, 147.4, 147.3, 142.5, 136.0, 135.4, 132.7, 132.2, 131.0, 129.9, 129.0, 127.9, 127.6, 127.3, 127.1, 126.8, 126.7, 126.2, 123.7, 123.4, 123.1, 120.5, 119.8, 116.9, 113.7, 93.3, 90.2. MS (ESI, 70 eV): m/z (relative

(E)-3-(4-((4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-

ethynyl)phenyl)ethynyl)phenyl)-2-cyanoacrylic acid (YH-8). Compound YH-8 was synthesized according to the same procedure as that of YH-1. Dark red solid of YH-8 was obtained in 82% yield. $\delta_{\rm H}$ (400 MHz, THF- d_8) 8.29 (s, 1H), 8.11 (d, 2H, *J* = 8.52 Hz), 7.70 (d, 2H, *J* = 8.48 Hz), 7.56 (d, 2H, *J* = 8.52 Hz), 7.51 (d, 2H, *J* = 8.32 Hz), 7.31 (d, 2H, *J* = 8.88 Hz), 7.08 (d, 4H, *J* = 8.84 Hz), 6.90 (d, 4H, *J* = 8.88 Hz), 6.84 (d, 2H, *J* = 8.84 Hz), 3.97 (t, 4H, *J* = 6.48 Hz), 1.76-1.83 (m, 4H), 1.50-1.54 (m, 4H), 1.37-1.42 (m, 8H), 0.96 (t, 6H, *J* = 7.12 Hz). $\delta_{\rm C}$ (100 MHz, THF- d_8) 162.6, 156.4, 152.4, 149.3, 139.7, 132.1, 131.8, 131.5, 131.1, 130.7, 127.4, 127.2, 124.7, 121.6, 118.3, 115.1, 113.0, 104.3, 92.6, 90.1, 87.3, 67.7, 31.6, 29.3, 25.7, 22.5, 13.3. MS (ESI, 70 eV): m/z (relative intensity) 740 (M⁺, 100); HRMS calcd for C₅₀H₄₈N₂O₄: 740.3614, found 740.3608.

2.2 Fabrication and Characterization of DSSCs.

Fluorine-doped tin oxide (FTO) conducting glass (FTO glass, Solaronix TCO22-7; sheet resistance = 7 Ω square⁻¹) and titania oxide pastes of Ti-Nanoxide T/SP and R/SP were purchased from Solaronix. A thin film of TiO₂ (10–12- μ m transparent layer + 5- μ m scattering layer) was coated onto a 0.28-cm² FTO glass substrate, which was then immersed in a THF solution containing 3×10^{-4} M dye sensitiser for 12 h, rinsed with anhydrous acetonitrile, and dried. Another piece of FTO glass with a 100-nm-thick layer of sputtered Pt was used as a counter electrode. The active area was controlled at a dimension of 0.28 cm² by adhering a 60- μ m-thick piece of polyester tape to the Pt electrode. The photocathode was placed on the top of the counter electrode and tightly clipped to form a cell, and an electrolyte was injected into the seam between the two electrodes. An acetonitrile solution containing LiI (0.5 M), I₂ (0.05 M), and 4-tert-butylpyridine (TBP; 0.5 M) was used as electrolyte. Devices composed of the commercial dye N719 under the same conditions (3 \times 10⁻⁴ M, Solaronix S.A., Switzerland) were used as references. The cell parameters were obtained under incident light with an intensity of 100 mW·cm⁻² (as measured using a thermopile probe; Oriel 71964) that was generated using a 300-W solar simulator (Oriel Sol3A Class AAA Solar Simulator 9043A, Newport) and passed through an AM 1.5 filter (Oriel 74110). The light intensity was further calibrated using an Oriel reference solar cell (Oriel 91150) and adjusted to 1.0 sun. The monochromatic quantum efficiency was recorded using a monochromator (Oriel 74100) under short-circuit conditions. The electrochemical impedance spectra of the DSSCs were recorded using an impedance/charge extraction method (CEM)/intensitymodulated photovoltage spectroscopy (IMVS) analyser (Zahner Ennium).

2.3 Quantum Chemistry Computations

The structures of dyes were optimized using the B3LYP/6-31G(d) hybrid functional. For the excited states, a time-dependent density functional theory (TDDFT) with the B3LYP functional was employed. All analyses were performed using the Q-Chem 3.0 software. The frontier orbital plots of the highest and lowest occupied molecular orbitals (hereafter referred to as the HOMO and LUMO, respectively) were drawn using GaussView 04.

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Scheme 1. Organic dye synthesis route. Reagents and conditions: (i) n-BuLi, DMF, THF, -78 °C; (ii) (a) NaH, CH₃PPh₃I, THF, 25–60 °C; (b) Pd(OAc)₂, P(*o*-tolyl)₃, 4-bromobenzaldehyde or 5-bromothiophene-2-carbaldehyde, triethylamine, 80 °C; (iv) piperidine, CNCH₂COOH, CH₂Cl₂, 70 °C; (v) Pd (PPh₃)₄, trimethylsilylacetylene, Cul, *i*-Pr₂NH, toluene, 80 °C; (vi) (a) K₂CO₃, THF/MeOH; (b) Pd (PPh₃)₄, 1-bromo-4-iodobenzene, Cul, *i*-Pr₂NH, toluene, 80 °C; (vii) Pd (PPh₃)₄, 1-bromo-4-iodobenzene, Cul, *i*-Pr₂NH, toluene, 80 °C; (vii) Pd (PPh₃)₄, 1-bromo-4-iodobenzene, Cul, *i*-Pr₂NH, toluene, 80 °C; (vii) Pd (PPh₃)₄, 1-bromo-4-iodobenzene, Cul, *i*-Pr₂NH, toluene, 80 °C; (vii) Pd (PPh₃)₄, 1-bromo-4-iodobenzene, Cul, *i*-Pr₂NH, toluene, 80 °C; (vii) Pd (PPh₃)₄, 1-bromo-4-iodobenzene, Cul, *i*-Pr₂NH, toluene, 80 °C; (vii) Pd (PPh₃)₄, Cul, *i*-Pr₂NH, toluene, 80 °C.

3 Results and discussion

3.1 Synthesis

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The structures of the dyes are illustrated in Fig. 1, and their synthesis procedures are presented in Scheme 1. The **YH**-series contained olefin or acetylene as the π -spacer linkage in the triarylene bridge between the arylamine donor and acceptor of cyanoacrylic acid in the sensitiser. The synthesis of the dyes began with 4-Bromodiarylaniline yielding the aldehyde group of compound **2** through formylation. An aldehyde group extended the π -bridge through Wittig and Heck reactions to yield compounds **4** and **5**. The π -spacer linkage of acetylene was constructed by repeating Sonogashira reactions to yield compounds **10** and **11**, and all aldehyde groups were verified using proton NMR (ESI). The compounds **4**, **5**, **10**, and **11** that contained aldehyde groups were used to yield final products through Knoevenagel condensation reactions. Eight final products were obtained with high yields of cyanoacrylic acid acceptor units that were easily purified. The structures of the eight compounds were characterised using spectroscopy.

3.2 Absorption spectra

The ultraviolet–visible absorption spectra of all sensitisers in CH_2Cl_2 solution are presented in Fig. 2, and the parameters of the sensitisers are listed in Table 1. The **YH**-series sensitisers exhibited

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two or three broad, high-intensity absorption peaks within the range of 344-504 nm. The short wavelength region (265-383 nm) was attributed to localised $\pi - \pi^*$ transitions, whereas the long wavelength region (405-490 nm) was attributed to intramolecular charge transfer (ICT) transitions. Compared with 1N-PPP and 1N-PPS, extending π -conjugation by insertion of π -spacer linkage, the absorption spectra of the dyes were red-shifted by approximately 30-64 nm with respect to those in the solution, except for YH-5, which had a slightly blue-shifted spectrum. The ICT absorption band was stronger when the olefin bonds were used π -spacer linkages than when triple bonds were used as π -spacer linkages, indicating that the full conjugation of the olefin linkage enhanced π -overlapping and led to increased red shift and an extensive absorption region. Hence, YH-1~YH-4 exhibited broader, high-intensity ICT transitions and approximately 25-87 nm red-shifted ICT transitions in CH₂Cl₂ solution. The acetylene moiety was more electronegative than the olefin bonds, and the electronegativity of the triple bonds weakened the electron-withdrawing ability of the electron acceptor because of the opposite dipole moment of the triple bond and electron acceptor. Thus, the absorption spectra of the dyes with triple bonds were blueshifted compared with those of dyes with double bonds.^{19,43} The absorption photocurrent (J_{sc}) and the intensity of absorption exhibited the same π -spacer linkage trend for dyes in solution.

Compared with the absorption spectra in methylene chloride, all dyes exhibited red-shift and spectral broadening on the TiO_2 film, because of intermolecular *J*-aggregation of sensitizer or strong interaction between the dye and semiconductor surface when it is anchored onto the TiO_2 surface.^{19, 43-44} And those absorption spectra of sensitizers with alkoxy long chain are broader than without, representing an advantageous spectral property for light harvesting.

3.3 Electrochemical Properties

The first oxidation potentials (E_{ox}) corresponding to the HOMO level of the photosensitisers were measured using cyclic voltammetry (Fig. S28). Two long hexyloxy chains in the arylamine donor moiety strongly affected the electron delocalisation and oxidation potential, increased the HOMO energy level to 0.29-0.32 eV, and reduced the HOMO-LUMO energy gap. The introduction of olefin and acetylene moieties as π -spacer linkages had nearly no effect on the HOMO energy level of the dyes but reduced the energy gap, indicating that the coplanarity and π -conjugation in the triarylene bridge was increased. Compared with the dye with acetylene as π -spacer linkage, the introduction of the olefin π -spacer linkage slightly increased the HOMO level. The lowest ionisation potentials of the dyes in CH₂Cl₂ solution decreased in the following order: YH-5 ≈ YH-7 > YH-1 ≈ YH-3 ≈ 1N-PPS ≈ 1N-PPP > YH-6 ≈ YH-8 > YH-2 \approx YH-4 (Fig. 4 and S31). Moreover, the LUMO levels of the dyes were estimated according to E_{ox} and the zero-zero band gaps at the onset of the absorption spectra (Table 1). The reduction of energy gap energies not only the hexyloxy chains in the arylamine donor group, but along with the thiophene unit in bridge. YH-1 and YH-2 had narrow HOMO-LUMO energy gaps, a trend consistent with the wider absorption ranges illustrated in Fig. 4. This trend was also confirmed using theoretical calculations, as discussed in the following section.



Fig. 2 Absorption spectra of dyes in CH₂Cl₂ solution.



Fig. 3 Absorption spectra of dyes absorbed on TiO₂.

3.4 Computational analysis

The effect of the use of dyes YH-1~8 on device performance was further explored through theoretical models. Complete geometrical optimisations were performed using TDDFT with the B3LYP functional in combination with the standard 6-31G(d) basis set within Q-Chem 3.0.⁴⁵ The use of olefin or acetylene as the π -spacer linkage in the triarylene bridge led to similar coplanarity, as demonstrated by the optimised structure determined using theoretical computation (Fig. S25). The frontier orbital electron distributions of the dyes are illustrated in Figs. 5 and S26. The electron densities in the HOMO and LUMO were mainly distributed around the triphenylamine donor moieties and the cyanoacrylic acid of the acceptor moieties, respectively. Previous relevant studies have reported that a disturbance to charge delivery, either through a distortion of the molecular geometry or intramolecular aggregation, may reduce the charge migration rate. As long as the chargeseparated state has a long lifetime, high device quantum efficiency can be achieved.^{39, 46} A delicate balance between charge separation and recombination must be maintained by modifying the molecular structures, bulky structures, and hydrophobic long chains that may reduce intermolecular aggregation and dark current.

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The difference in the Mulliken charge distributions of the ground state (S_0) and excited state (S_1) according to the estimate generated using TDDFT/B3LYP is presented in Fig. 6 and Table S2.⁺⁺ Dyes containing alkoxy chains exhibited optimal charge separation in the ICT state (bar chart, Fig. 6), because the chains enhance the electron-donating ability of arylamine donors.

Photoexcitation pumps an electron from the HOMO to the LUMO and thus shifts a considerable number of electrons from the donor to the acceptor. Consequently, the HOMO–LUMO energy gap of dyes YH-2, YH-4, YH-6, and YH-8 that contained alkoxy chains was lower than that of dyes YH-1, YH-3, YH-5, and YH-7 that did not contain alkoxy chains. Therefore, the ICT band in the even-numbered dyes exhibited a bathochromic shift compared with that in the oddnumbered dyes. A similar trend was identified for the dipole moment (YH-2: 11.6309 D > YH-1: 9.7556 D) and CT transition excitation in the YH-series sensitisers (Table S1).

The transition probability was estimated according to the excitations using TDDFT/B3LYP, and the calculated oscillator strength (*f*) is presented in Table S1.⁺⁺ The *f* values for the lowest energy ICT transitions (S₁ state) were all relatively high, ranging from 0.58 to 0.98. The results were consistent with the absorptivity of the dyes in solution.



Fig. 4 HOMO - LUMO energy levels of the YH-series sensitizer.



Fig. 5 The frontier HOMO and LUMO orbitals of YH-series dyes estimated by time-dependent DFT/B3LYP (6-31G* basis set).



Fig. 6 Difference of Mulliken charges between ground state (S_0) and excited state $(S_1 \text{ and } S_2)$, estimated by time dependent DFT/B3LYP model.

3.5 Photovoltaic performance of DSSCs

The DSSC devices composed of the designed photosensitisers were absorbed on the TiO₂ surface using a standard procedure. The electrolyte used to investigate the performance of the devices contained LiI (0.5 M), I₂ (0.05 M), and TBP (0.5 M) in MeCN. The experiments involving coabsorption were conducted using deoxycholic acid (DCA). The incident photocurrent conversion efficiency (IPCEs) and photocurrent–voltage (J-V) curve of all dyes were measured under AM 1.5 solar light (100 mW·cm⁻²). The short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and solar-to-electrical photocurrent density (η) are summarised in Table 1, wherein **N719** serves as a reference dye.

The *J*–*V* curve and IPCE of all devices are plotted in Fig. 7. An apparent improvement of 2–53 mV in V_{oc} was observed for dyes **YH-1**, **YH-3**, **YH-5**, and **YH-7** without long alkoxy chains, compared with V_{oc} obtained without DCA coabsorbent (Table 1). Favourable morphology and coverage of the dyes on the TiO₂ film reduced the Li⁺ or I₃⁻ ions in contact with the TiO₂ surface, enhancing V_{oc} because of an improved surface blocking effect and subsequently increasing the gap between the conduction bands of the TiO₂ and electrolyte.⁴⁷⁻⁴⁹ Dyes **YH-1**, **YH-3**, **YH-5**, and **YH-7** without long alkoxy chains had higher V_{oc} than the other dyes with alkoxy chains, indicating that they reduced dark current in the device by substantially reducing the charge recombination rate.

We modified the dyes' structures by using thiophene moieties as π -bridges near the anchoring group. Thiophene moieties can enhance light harvesting. However, the organic dyes with thiophene spacer exhibited lower V_{oc} than dyes with phenylene π -bridges. Dyes with more active sulphur sites had a higher tendency to form dye-iodine complexes because of the strong interactions between iodine and sulphur atoms.⁵⁰

Compared with devices using reference dyes without double or triple bond linkage units (such as **1N-PPP** or **1N-PPS**), we discovered that the devices using double-bond dyes had dramatically improved energy conversion efficiency η because of a large enhancement of J_{sc} (**YH-1** and **YH-3**). However, the introduction of triple bonds reduced η because of a low J_{sc} (**YH-5** and **YH-7**). This lower J_{sc} was because these dyes had narrower absorption spectra than the dyes with double bonds, and this result was consistent with the dye loading results for dyes on TiO₂ films (Table 1). After adding DCA (10 mM) as co-absorbent to all **YH**-series dyes improved the J_{sc} and quantum

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Table 1 Photo	chemical and electrochemical parameters of the dyes.							DOI: 10	View Article Online DOI: 10.1039/C7NJ00413C	
dye	λ_{\max}^{a} (nm)/ ϵ (10 ⁴ M ⁻¹ cm ⁻¹)	Е _{номо} ^ь (V)	E _g (eV)	Е _{LUMO} ^с (V)	J _{sc} (mA·cm ⁻²)	V _{oc} (mV)	FF	η ^{d ,e} (%)	Dyes Loading (10 ⁻⁷ mol/cm ⁻²)	
YH-1	476 (3.86)	-5.33	2.20	-3.13	14.80	635	0.65	6.14	15.82	
YH-2	490 (3.83)	-5.01	2.14	-2.87	11.80	582	0.60	4.16	9.63	
YH-3	439 (4.30)	-5.29	2.36	-2.93	13.80	695	0.67	6.47	11.27	
YH-4	450 (3.23)	-5.00	2.25	-2.75	10.10	693	0.66	4.63	9.05	
YH-5	406 (4.00)	-5.36	2.53	-2.83	7.62	644	0.69	3.37	4.79	
YH-6	403 (3.10)	-5.06	2.36	-2.70	9.13	602	0.62	3.43	7.75	
YH-7	405 (4.52)	-5.36	2.61	-2.75	8.48	704	0.68	4.07	5.96	
YH-8	420 (3.20)	-5.06	2.53	-2.53	8.84	693	0.68	4.17	6.88	
1N-PPP ^f	375 (3.74)	-5.33	2.78	-2.55	11.24	680	0.60	4.60		
1N-PPS ^f	422 (3.63)	-5.32	2.52	-2.80	14.20	660	0.60	5.68		
N719		-5.60 ^g	2.60 ^{<i>g</i>}	-3.00 ^g	14.86	744	0.66	7.29		

^{*a*} Absorption and Emission are in CH₂Cl₂. ^{*b*} Oxidation potential in CH₂Cl₂ (10^{-3} M) containing 0.1 M (n-C₄H₃)₄NPF₆ with a scan rate 50 mV·s⁻¹. ^{*c*} E_{LUMO} calculated by E_{HOMO} – E_g. ^{*d*} Performance of DSSCs measured in a 0.28 cm² working area on a FTO (7Ω /square) substrate. ^{*c*} Electrolyte : Lil (0.5 M), I₂ (0.05 M), and TBP (0.5 M) in MeCN. ^{*f*} see reference 25. ^{*g*} see reference 62.



Fig. 7 *J*-*V* plots and IPCE of DSSCs devices of **YH-1~8** without DCA co-absorbent. The plots were measured under the light intensity of 1.0 sun.

efficiency of the resultant DSSCs, the **YH-5** and **YH-7** still displayed lower J_{sc} than **YH-1** and **YH-3**. The result consisted with dye loading with DCA co-absorbent in Table 2. More confirmed the olefin π -spacer linkages of organic dyes showed better light harvesting effect than triple bonds π -spacer linkages of organic dyes.

Previous reports have revealed that long hydrophobic chains may prevent contact between I_3^- ions and the TiO₂ surface, and in this study, the compounds with long chains exhibited higher V_{oc} than those sensitisers without long chains.^{10, 51-52} However, the introduction of long hydrophobic chains may not always improve V_{oc} , because some reports have calculated higher V_{oc} when fewer or no long alkyl chains have been used.⁵³⁻⁵⁵ Our investigation revealed that sensitisers without long alkyl chains had higher V_{oc} (YH-1, YH-3, YH-5, and YH-7), indicating that the HOMO energy level of the sensitisers was near the I^-/I_3^- energy level, which may have reduced dye regeneration and increased the charge recombination rate.

The morphology of sensitisers on the TiO₂ surface is also a crucial factor for optimising the performance of DSSCs. The sensitiser must be placed sufficiently vertically on the TiO₂ film to prevent intermolecular aggregation that causes dark current. We also

investigated whether adding DCA as a coabsorbent prevented the horizontal alignment of the sensitiser on the TiO_2 surface. For dyes that cannot form high quality films, adding DCA can effectively improve dye alignment and consequently reduce the charge recombination rate.⁵⁶⁻⁵⁸

Adding DCA (10 mM) to all dyes improved the quantum efficiency of the resultant DSSCs by 1%-33% (Table 2). DSSCs containing YH-1 and YH-2 exhibited dramatic enhancements of 15.3% and 32.9%, respectively. It's observed enhancement in Fig. S30, dyes with thiophene moiety showed lower V_{oc} because of the strong interactions between iodine and sulphur atoms (YH-1, YH-2, YH-5, and YH-6). Addition of DCA can be suppressed to form dye-iodine complexes, and formed the good morphology on TiO₂ film. Adding DCA considerably increased $V_{\rm oc}$ and $J_{\rm sc}$, indicating an improvement in dye morphology. Thus, the addition of a DCA coabsorbent enabled the more vertical alignment of the dye on the TiO₂ surface. This effect was confirmed by the DSSCs' higher resistance determined using electrochemical impedance spectroscopy (EIS), as presented in the following section. The optimal photovoltaic efficiency was that of YH-1, with a J_{sc} of 16.23 $mA \cdot cm^{-2}$, a V_{oc} of 650 mV, and an FF of 0.67, corresponding to an overall conversion efficiency of 7.08%.



Fig. 8 J–V curves of DSSCs fabricated w/wo a DCA co-absorbent at a light intensity of 1.0 sun.

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Fig. 9. Impedance spectra of **YH**-series dyes in CH₂Cl₂ by using DCA as co-absorbent. **(a-b)** Nyquist plots (i.e., minus imaginary part of the impedance –Z" vs. the real part of the impedance Z' when sweeping the frequency). **(c-d)** Bode phase plots at -0.73 V bias in the dark. The electron diffusion lifetime $\tau_e = 1/2\pi f$.



Fig. 10. IMVS and CEM of **YH**-series dyes by using DCA as co-absorbent in CH_2Cl_2 . (a) Electron lifetime as a function of V_{oc} was measured by IMVS method. (b) Electron density as a function of V_{oc} was measured by CEM method.

3.6 Electrochemical impedance spectroscopy and electron lifetime by CEM / IMVS

EIS was performed to further illustrate the photovoltaic properties of the DSSCs. Nyquist and Bode plots were constructed under forward bias and dark conditions (Fig. 9). Semicircles were observed in the Nyquist plots for each sensitiser, which are associated with transport at the TiO₂/electrolyte/dye interfaces. A larger semicircle corresponds to larger charge recombination resistance at a low frequency, indicating a lower charge recombination rate and smaller dark current.⁵⁹ The radii of the semicircles increased in the orders YH-1 < YH-5 < YH-3 < YH-7 and YH-2 < YH-6 < YH-4 < YH-8, which was consistent with the V_{oc} of the dyes. The electron diffusion lifetime (τ_e) of the device was estimated by fitting the equation in a Bode plot, and a shift to a low frequency (f) corresponded to a longer electron lifetime. YH-3, YH-4, YH-7, and YH-8 displayed higher Voc than the dyes without coabsorbent DCA addition, indicating a lower charge recombination rate (Fig. 9b). Particularly, YH-7 (34.9 ms) and YH-8 (37.2 ms) had the highest V_{oc} , as verified by the Nyquist and Bode plots with the largest semicircles and longest electron lifetimes. respectively. DOI: 10.1039/C7NJ00413C

We further validated the correlation between $V_{\rm oc}$ and the electron lifetime of a device. The electron lifetime $(\boldsymbol{\tau}_r)$ was measured using IMVS, and the results are presented in Fig. 10. The electron lifetime reduced in the order YH-7 (40.59 ms) > YH-3 (35.80 ms) > YH-5 (31.33 ms) > YH-1 (27.39 ms) for devices under the same light intensity and with DCA addition, which was consistent with the data obtained from the Bode plot fits. V_{oc} is defined as the energy gap between the Fermi levels of $\rm TiO_2$ and the redox couple of the electrolyte. $^{\rm 60-61}$ A positive shift in the conduction band of TiO_2 may have reduced V_{oc} and the electron lifetime. YH-7 and YH-3, which did not contain more active sulphur sites of the thiophene moieties to form dye-iodine complexes, had reduced charge recombination and a higher electron lifetime than the other dyes. The CEM revealed that the conduction band edge of TiO_2 was more downshifted for YH-1 and YH-5 than for the other dyes, which again was consistent with the Nyquist plots. **YH-3** without DCA coabsorbent exhibited a favourable V_{oc} of 695 mV and an overall conversion efficiency of 6.47%.

Table 2 Photovoltaic parameters of DSSCs fabricated using YH-1~8 with and without DCA (10 mM)

	· · · ·					
dye	DCA^a	J _{sc}	Voc	FF	ηΰ	Dyes
	(mM)	(mA⋅cm ⁻²)	(mV)		(%)	Loading
YH-1	0	14.80	635	0.65	6.14	15.82
	10	16.23	650	0.67	7.08	19.80
YH-2	0	11.80	582	0.60	4.16	9.63
	10	13.24	651	0.64	5.53	10.98
YH-3	0	13.80	695	0.67	6.47	11.27
	10	14.07	703	0.66	6.58	14.65
YH-4	0	10.10	693	0.66	4.63	9.05
	10	10.84	705	0.63	4.81	9.88
YH-5	0	7.62	644	0.69	3.37	4.79
	10	8.21	652	0.70	3.74	5.32
YH-6	0	9.13	602	0.62	3.43	7.75
	10	9.46	653	0.65	4.05	8.05
YH-7	0	8.48	704	0.68	4.07	5.96
	10	8.60	713	0.67	4.11	6.23
YH-8	0	8.84	693	0.68	4.17	6.88
	10	8.98	714	0.68	4.34	7.08

^{*a*} Concentration of dye is 3×10^{-4} M in CH₂Cl₂. ^{*b*} Performance of DSSCs measured in a 0.28 cm² working area on an FTO (7Ω/square) substrate under AM 1.5 condition with electrolyte 1 (E1). ^{*c*}(10⁻⁷mol/cm⁻²)

We demonstrated that a simple D– π –A dipolar system and highperformance DSSC can be achieved using olefin or acetylene as the π spacer linkage in the triarylene bridge. Eight metal-free organic dyes **(YH-1–YH-8)** were synthesised. The olefin π -spacer linkages of **YH-1~YH-4** exhibited broader, high-intensity absorption than the acetylene-based linkages in CH₂Cl₂ solution and a higher IPCE and short-circuit photocurrent density. Organic dyes containing thiophene moieties with more active sulphur sites had a higher tendency to form dye–iodine complexes because of the strong interactions between iodine and sulphur atoms. Thus, organic dyes possessing thiophene spacers displayed lower V_{oc} than those with phenylene π -bridges. **YH-3** without DCA coabsorbent exhibited a favourable V_{oc} of 695 mV and an overall conversion efficiency of 6.47%.

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v	spacer linkage in the triarylene bridge. Eight metal-free
	1 VH 9) were supposed. The elefin π spacer links

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YH-1 contained thiophene spacers and displayed a low V_{oc} of 635 mV, but thiophene moieties may enhance light harvesting. **YH-1** had olefin as a repeat unit in the triarylene bridge and had broad absorption, leading to improved J_{sc} and film morphology with the DCA coabsorbent, resulting in favourable V_{oc} . A typical device fabricated using **YH-1** had a J_{sc} of 16.23 mA·cm⁻², a V_{oc} of 650 mV, and a FF of 0.67, corresponding to an overall conversion efficiency of 7.08%.

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