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Introduction

Dye-sensitized solar cells (DSCs) have attracted growing interest as one of the alternatives to the conventional inorganic photovoltaic devices.1-3 Porphyrins are promising sensitizers due to the intense absorption from the visible region to the near-infrared (NIR) region.⁴ In order to extend the spectral adsorption to the NIR region, a strategy has been widely used in porphyrin molecular engineering, that is, elongation of the π -conjugation and loss of symmetry in porphyrins.⁵ Thus, the photovoltaic performance $(\sim 7\%)$ of porphyrin-sensitized solar cells has been improved intensively by the enhanced light adsorption.6 Recently, Diau et al. reported a series of zinc porphyrin dyes with donor- π -acceptor $(D-\pi-A)$ structures, which lead to efficiencies up to 10%.⁷⁻¹⁰ More recently, Yella et al. reported a further milestone in DSCs with an overall efficiency of 12.3%, by using a judiciously engineered porphyrin sensitizer (coded YD2-o-C8) associated with a pushpull co-sensitizer and cobalt(II/III)-based redox electrolyte.11 These efficient sensitizers show relatively weak light-harvesting ability in

D– π –A structured porphyrins for efficient dye-sensitized solar cells†

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In this study, new push-pull alkoxy-wrapped zinc porphyrin dyes with intramolecular donor- π -acceptor structures have been designed and synthesized for dye-sensitized solar cells (DSCs). The linkers based on thiophene or 2,3-dihydrothieno[3,4-b][1,4] dioxine with cyanoacetic acid can broaden the spectral response of porphyrins into the near-IR region (~850 nm), which is mainly attributed to the cyanoacetic acid group. However, porphyrins with cyanoacrylic acid as an anchoring group lead to a faster charge recombination rate at the dye-sensitized heterojunction interface, which lowers the device photovoltaic performance. By using porphyrins with a rigid π -linker feature structure that is 5-ethynylthiophene-2-carboxylic acid, highly efficient DSC devices with a power conversion efficiency of 9.5% can be obtained. Spectral, electrochemical, photovoltage transient decay and impedance measurements are performed to reveal the influence of π -conjugated linkers and anchoring groups upon the optoelectronic features of porphyrin dyes in DSCs.

the near-IR region, especially beyond 750 nm, which limits the photocurrent under full spectrum solar flux.¹²⁻¹⁴

As an electron spacer to connect the donor and acceptor, the π -linker determines not only the light-harvesting characteristics of the chromophore, but also the electron injection from the excited dyes to the TiO2 surface, accompanied by electron donor and acceptor moieties.15-23 To date, the design of sensitizers with good photovoltaic properties has focused primarily on engineering (i) the electronic nature of the D and A moieties and (ii) the conjugation of the π -linker. The former controls the D-A mixing with respect to a specific bridge, while the latter plays a key role in modulating D-A electronic coupling as well as the magnitude of the change in dipole moment.²⁴ For example, it was revealed that, in porphyrin dyes, the elongation of π -conjugation or loss of molecular structure symmetry can cause a splitting in π and π^* energy levels and a decrease in the energy gap between HOMO and LUMO, thus resulting in broadening and red shift of the absorption band together with an increasing intensity of the Q band relative to that of the Soret band.5 In order to broaden the absorption bands, various ancillary ligands and π -linker moieties have been investigated, including attachment of fused ring and bridged fused ring systems to the porphyrin core or combination of two porphyrin moieties by chemical bonds.²⁵⁻³³ Though the light-harvesting area can be successfully extended into the NIR, inefficient electron injection into the oxide has been found for these sensitizers. In this case, thiophene and its derivatives have been widely studied as π -linkers to boost light harvesting efficiency not only for organic dyes,34,35 but also for conductive polymers for the optoelectronics purpose.36

Herein, we report an experimental study of the synthesis and characterization of a series of zinc porphyrins based on the

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structure of LD14 with the same donor group, which is the 4ethynyl-N,N-dimethylaniline group at the meso-position, but using various hetero-aromatic bridges with 2-cyanoacrylic acid or 5-ethynylthiophene-2-carboxylic acid acting as the electron acceptor (see Scheme 1). 4-Ethynyl-N,N-dimethylaniline has been demonstrated as an effective donor group in construction of porphyrin dyes with D- π -A structures.^{9,24,37,38} The introduction of cyanoacrylic acid into organic dyes has an important role in the red-shift of adsorption spectra due to its strong electronpulling property.^{14,34,39,40} To assess the effect of the π -linker on the DSC photovoltaic performance, we systematically designed porphyrin dyes from a sensitizer with 4-ethynylbenzene (abbreviated as LW1) to ones with a 2-ethynylthiophene unit (LW2), or with 5-ethynyl-2,3-dihydrothieno[3,4-b][1,4] dioxine (LW3). We expected that the NIR light-harvesting ability of the porphyrins would be achieved by introduction of electron-rich units (thiophene or 2,3-dihydrothieno[3,4-b][1,4] dioxine (EDOT)) between the porphyrin ring and 2-cyanoacrylic acid, which would finally have an impact on the photovoltaic properties. In order to overcome the losses of charge collection and electron injection yields due to the floppy structure of 2-cyanoacrylic acid in LW1-3, we further designed and successfully synthesized the LW4 porphyrin with a rigid acceptor structure of 5-ethynylthiophene-2-carboxylic acid. Efficient DSC devices can be obtained with a power conversion efficiency (PCE) of 9.5% under full sunlight (AM 1.5G, 100 mW cm^{-2}) irradiation. This work presents a striking amelioration of the photo-induced charge separation in porphyrins by judiciously modifying their molecular and electronic structures.

Experimental section

A detailed synthesis procedure and characterization (including NMR, MS, UV-vis spectroscopy and electrochemical measurement) of LW series sensitizers are shown in the ESI.[†]

Device fabrication

The FTO glass plates (3 mm thickness, 7 Ω per square, Nippon Sheet Glass) were cleaned with detergent solution using an ultrasonic bath for 15 min and then rinsed with deionized water and ethanol for 15 min. The cleaned glass plates were immersed into 40 mM TiCl₄ (aq.) at 70 °C for 30 min, and then washed with water and ethanol. A 7.5 μ m thick transparent layer of



Scheme 1 Molecular structures of the LW1, LW2, LW3, LW4 and LD14 porphyrin sensitizers.

20 nm TiO₂ particles was first printed on the FTO conducting glass substrates and then coated with a 5 µm thick second layer of 400 nm light scattering anatase particles (WER2-O, Dyesol). The thickness of the film was measured using a Profile-system (DEKTAK, VECCO, Bruker). The details for the preparation of the TiO₂ films have been described elsewhere.³ The TiO₂ film was first sintered at 500 °C for 30 min and then cooled to about 80 °C in air. Then the TiO_2 film electrodes were dipped into a 200 µM dye solution in a mixture of toluene and ethanol (volume ratio, 1:1) at room temperature for 5 h. After washing with ethanol and dried by air flow, the sensitized titania electrodes were assembled with thermally platinized conductive glass electrodes. The working electrode and counter electrodes were separated by a 45 µm thick hot melt ring (Surlyn, DuPont) and sealed by heating. The internal space was filled with liquid electrolytes using a vacuum back filling system. In this study, a conventional triiodide/iodide electrolyte was used to investigate the influence of π -linker and acceptor on the light harvesting ability of the porphyrin dyes. The electrolyte (coded W08) for devices was 0.1 M LiI, 0.05 M I2, 0.6 M PMII, and 0.5 M 4-tertbutylpyridine in a mixture of valeronitrile and acetonitrile (volume ratio, 15:85).

DSC device characterization

A 450 W xenon light source solar simulator (Oriel, model 9119) with an AM 1.5G filter (Oriel, model 91192) was used to give an irradiance of 100 mW cm⁻² (1 sun light intensity) at the surface of solar cells. The current–voltage characteristics of the cell were obtained by applying external potential bias to the sample and measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, USA). A similar data acquisition system was used to control the incident photon-to-current conversion efficiency (IPCE) measurement. A white light bias (1% sunlight intensity) was applied onto the sample during the IPCE measurements with an ac model (10 Hz). The devices with the photoanode area of 0.16 cm² were tested using a metal mask with an aperture area of 0.072 cm².

Electrochemical impedance spectroscopy (EIS) and transient photovoltage decay measurements

Impedance measurements of DSCs were carried out with an Autolab Frequency Analyzer set-up, which consists of an Autolab PGSTAT 30 (Eco Chemie B.V., Utrecht, The Netherlands) producing a small-amplitude harmonic voltage, and a frequency response analyzer module. The determination of the interfacial recombination rate constant was carried out by performing transient photovoltage decay measurements and charge extraction experiments. Details can be found in our previous report.³

Time-resolved luminescence experiments

The time-resolved luminescence decays were recorded with Edinburgh instruments (FLSP920 spectrometers). The excitation light source was a picosecond pulsed light-emitting diode centered at 445 nm, operated at a frequency of 10 MHz. The TiO_2 nanoparticles were screen-printed on quartz substrates.

Similar treatment of TiO_2/FTO film was applied to the $TiO_2/$ quartz film. Quartz substrates coated with nanoparticles were immersed in 200 μ M dye solution, followed by rinsing with THF to remove the physically adsorbed dyes on the TiO_2 nanoparticles. The solution samples were prepared by dissolving the dyes in THF.

Results and discussion

In the present work, three D– π –A structured new porphyrin dyes with various linkers (the LW1 dye with 4-ethynylbenzene, the LW2 dye with 2-ethynylthiophene, and the LW3 dye with 5-ethynyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxine) were first designed and synthesized for understanding of the influence of substitution of the π -linker with various hetero-aromatic groups (see Scheme 1) on the light-harvesting ability of the sensitizers. The three porphyrin sensitizers (LW1, LW2, and LW3) have the same donor group as that of LD14 but with an extended π -bridge at the *meso*-position of the porphine ring and cyanoacrylic acid as an anchoring group. Thiophene and its derivatives as spacers and cyanoacrylic acid with strong electron-withdrawing property as an anchoring group are introduced as the bridge and acceptor into D– π –A structured porphyrins (LW1–3).

Scheme 1 outlines the molecular structures for the compounds LW1, LW2 and LW3. The preparation of Zn porphyrin dyes LW1-3 was achieved using a convergent synthesis strategy (Scheme S1[†]) on the basis of Pd-catalyzed Sonogashira coupling reactions.9,41 Bulky ortho-substituted alkoxyphenyl chains at meso-positions of the porphine core can retard dye aggregation and interfacial charge recombination.¹⁰ 4-Ethynylbenzaldehyde, 5-ethynylthiophene-2-carbaldehyde and 7-ethynyl-2,3-dihydrothieno[3,4-b][1,4] dioxine-5-carbaldehyde were synthesized for LW1, LW2, and LW3, according to the literature.42 The LD14 dye reported by Diau et al. was synthesized and used as a reference for comparison purpose.9,10 Details of the procedures are given in the ESI[†] (Scheme S1 and S2[†]). The sensitizers LW1, LW2, and LW3 and their precursor compounds are highly soluble in aromatic solvents (i.e., toluene and tetrahydrofuran) and other common organic solvents. The structure and purity of the newly synthesized compounds were fully confirmed by ¹HNMR, ¹³CNMR, and mass spectroscopy (see Fig. S1-S9[†]) which are found to be in good agreement with their structure.

The electronic absorption spectra of the LW1–LW3 and LD14 porphyrins in THF solution are presented in Fig. 1. The UV-vis data for each compound are summarized in Table 1. The molar extinction coefficients at the absorption maximum for the LW1–LW3 porphyrins were calculated to be 21.4×10^4 , 13.9×10^4 , and 15.2×10^4 mol⁻¹ cm⁻¹ in the range of 460–485 nm (S band) and 6.2×10^4 , 6.2×10^4 , and 6.3×10^4 mol⁻¹ cm⁻¹ in the range of 670–695 nm (Q band), corresponding to $S_0 \rightarrow S_2$ transition and the higher vibrational mode Q(1,0) and the lowest energy vibrational mode Q(0,0) of the $S_0 \rightarrow S_1$ transition, respectively.⁴³ It is clearly observed that the introduction of cyanoacrylic acid into the LW1 dye has led to a red-shift of the absorption spectrum by 8 nm compared with that of the LD14 dye.^{40,44,45} Switching of the phenyl unit ring to thiophene or EDOT



Fig. 1 Absorption spectra of the LW1, LW2, LW3, LW4, and LD14 porphyrin sensitizers in THF.

continuously shifts the Q band. The resulting porphyrin sensitizers of LW2 and LW3 are largely red-shifted by 18 and 17 nm compared to the LW1 dye. It was observed that the molar extinction coefficients (ε) of the LW1 to the LW3 dyes at the Q band gradually increased relative to the S band (Fig. 1 and Table 1). When these sensitizers were stained onto TiO₂ films, the spectra became significantly broadened relative to those in solution (see Fig. S12†). This result demonstrates that the hetero-aromatic units (acting as the π -linker) have a significant impact on the HOMO–LUMO energy levels of the D– π –A structured porphyrin dyes by loss of molecular structure symmetry as discussed below.⁵

The electrochemical behaviour of the prepared dyes in the THF solvent was investigated. The porphyrin samples exhibit reversible electrochemical reaction on the working electrode surface (see Fig. S10[†]). Two oxidation peaks were observed, which were assigned to one electron being abstracted from the electron-donating 4-dimethylaminophenyl group, and the other from the oxidation of the porphyrin ring, respectively.41 The potential for the first oxidation of porphyrins corresponds to the HOMO energy of the dye, which should be greater than that of the I^-/I_3^- couple (~0.5 V vs. NHE) for an efficient dye regeneration process.46,47 The first-oxidation potentials of the LW1-3 dyes were evaluated to be 0.69, 0.695, and 0.678 V (vs. NHE), respectively. Simultaneously, from the intersection of the normalized absorption and emission spectra, the zero-zero excitation energies (E_{0-0}) were calculated to be 1.808, 1.715, and 1.744 (see Table 1), respectively. Thus, the LUMO levels of the LW1-3 dyes were determined to be -1.118, -1.020, and -1.066V (vs. NHE), respectively, which are energetically favourable to the electron injection process in a DSC configuration.³ From these values, we can systematically record the contributions of different groups and attain a HOMO and LUMO schematic energy-level diagram by alternating the π -linker moiety independently (Fig. S11[†]). The introduction of a cyanoacrylic group into the acceptor moiety decreases the LUMO energy level compared to those dyes with carboxylic acid.

Table 1 Absorption wavelength, fluorescence maxima and first porphyrin-ring redox potentials of various porphyrins (LW1, LW2, LW3, and LW4) in THF^a

Dyes	Absorption λ_{\max}^{b}/nm ($\epsilon/10^3 M^{-1} cm^{-1}$)	Emission λ_{\max}^{c}/nm	Fluorescence lifetime/ns	Potentials and energy level		
				$E_{\rm ox}^{\ \ d}$ /V (vs. NHE)	E_{0-0}^{e}/V (vs. NHE)	$E_{\rm ox} - E_{0-0}/{\rm V}$
LW1	467(214.5); 674(61.6)	689, 756	1.62	0.69	1.808	-1.118
LW2	463(139.3); 692(61.7)	753	1.19	0.695	1.715	-1.020
LW3	481(152.4); 691(62.8)	745	1.15	0.678	1.744	-1.066
LW4	462(231.4); 671(56.4)	687, 752	1.54	0.713	1.826	-1.113
$LD14^{f}$	459(253.8); 667(64.1)	684, 744	1.69	0.716	1.840	-1.124

^{*a*} Electrochemical measurements were performed at 25 °C with each porphyrin (0.5 mM) in THF/0.1 M TBAP/N₂, GC working and Pt counter electrodes, Ag/AgCl reference electrode, scan rate = 50 mV s⁻¹. ^{*b*} Absorption and emission data were measured in THF at 25 °C. ^{*c*} Excitation wavelength/nm: LW1, 467; LW2, 463; LW3, 481; LW5, 462. ^{*d*} First porphyrin ring oxidation. ^{*e*} Estimated from the intersection wavelengths of the normalized UV-vis absorption and the fluorescence spectra. ^{*f*} LD14 was synthesized according to the literature.



Fig. 2 (a) *I–V* curves of LW1, LW2, LW3, LW4, and LD14 cells, LW1 (device A), LW2 (device B), LW3 (device C), LW4 (device D), and LD14 (device E) based DSCs measured under simulated AM 1.5 full-sunlight. (b) The photocurrent action spectra of LW1 (device A), LW2 (device B), LW3 (device C), LW4 (device D), and LD14 (device E) based DSCs.

The photocurrent-voltage curves of the DSC devices with the LW1-3 porphyrins in combination with volatile electrolytes are displayed in Fig. 2a. The photovoltaic parameters, power conversion efficiency (PCE), short-circuit photocurrent density $(J_{\rm sc})$, the open-circuit photo-voltage $(V_{\rm oc})$, and the fill factor (FF) under full sunlight (AM1.5G, 100 mW cm⁻²) of DSC devices, are summarized in Table 2. Device A (LW1 with 4-ethynylbenzene and cyanoacrylic acid) exhibits a $V_{\rm oc}$ of 0.648 V, a $J_{\rm sc}$ of 15.7 mA cm^{-2} , and a FF of 0.70, giving an overall PCE of 7.12%. As for device E using the reference porphyrin LD14, a 9.01% overall power conversion efficiency was obtained by a contribution from a high value of J_{sc} . In this study, a 7.5 µm thick TiO₂ (20 nm sized) transparent film was used, explaining the lower photocurrents and solar to electric power conversion efficiencies compared to the values reported by Diau *et al.* (PCE $\sim 10\%$),^{9,10} in which an optimized electrolyte composition and a photoanode structure were used. Compared to the reported DSC devices using ring-fused, unsymmetrical π -extended porphyrins, solar cells based on LW1 dye present an appreciated photovoltaic performance, which could be attributed to its intense light adsorption property and broadening of absorption spectra.31,48 Changing phenyl to thiophene or EDOT at the linker moiety in the porphyrin structure (LW2 and LW3) resulted in a similar $J_{\rm sc}$ but increased $V_{\rm oc}$, which are 0.685 V and 0.657 V, giving an overall PCE of 7.37% and 7.63% for devices B and C, respectively. Substitution of the thiophene unit (LW2) conjugated to porphyrin with EDOT (LW3) brings forth a slight decrease in open circuit voltage.

The photocurrent action spectra of DSCs with LW1–3 and LD14 as sensitizers are shown in Fig. 2b. The onset wavelengths of photocurrent responses were red-shifted stepwise from LW1 to LW3 from 800 nm to 850 nm, which were in good agreement with the electronic absorption of the titania films sensitized with dyes. Device B (with LW2) and device C (with LW3) possess relatively lower IPCE values with a summit of 45% at the absorption peaks of the films compared with the other two counterparts (50% at 690 nm for device A with LW1 and 61% at 675 nm for device E with LD14).

Time-resolved luminescence experiments were performed to examine the impact of electron injection from excited-state dye molecules to titania.11,45 Fig. 3 presents the emission decays of LW1-4 porphyrins or LD14 in THF solution and these dyesensitized nanocrystalline TiO₂ films filtered with the same volatile redox electrolyte, which were used in the photovoltaic experiments. The LW4 sensitizer will be discussed below. The fluorescence lifetimes for LW1-4 and LD14 in an organic solvent were evaluated to be 1.62, 1.19, 1.15, 1.54, and 1.69 ns, respectively, while the strong quenching of the emission for those sensitizers was observed when they were adsorbed onto the TiO₂ nanoparticle surface. By considering the re-convolution of the instrument response function of about 89 ps, the data fitting result indicates that the lifetime of the excited singlet state of the five porphyrins absorbed onto the TiO₂ is about 190 ps. This result confirms a rapid electron injection from the excited state of the dye into the conduction band of TiO₂.^{11,49} The slightly lower fluorescence lifetime found in the case of LW2 and LW3 compared to other sensitizers could be related to the free rotation feature caused by the double bond in the former, which might induce a tilted geometry for absorbing

Table 2 The photovoltaic parameters of porphyrin-sensitized solar cells, LW1 (device A), LW2 (device B), LW3 (device C), LW4 (device D), and LD14 (device E) AM 1.5G, 100 mW cm⁻²

	$J_{ m sc} [m mA \ cm^{-2}]$	$V_{\rm oc} \left[V \right]$	FF	PCE [%]
Device A	15.70	0.648	0.70	7.12
Device B	15.36	0.685	0.70	7.37
Device C	16.35	0.657	0.71	7.63
Device D	17.65	0.75	0.72	9.53
Device E	17.38	0.73	0.71	9.01



Fig. 3 Time-resolved PL decay traces of dye-grafted mesoporous titania films (red dotted lines) and dyes in THF solvent (black dotted lines). Excitation wavelength: 445 nm.

molecules on the TiO_2 film. This screening strategy can help us to optimize the TiO_2 -dye-hole transporting material system in terms of balance between photovoltage, driving forces and spectral response for future design of highly efficient porphyrin dyes by matching suitable donor-linker-acceptor moieties.

Electronic impedance measurements (EIS) under dark conditions were further performed to understand the differences in photovoltaic behavior of devices with various porphyrin sensitizers. The impedance spectra for each of the DSC devices (A, B, C, and E) studied reveal comparable characteristic information about the various kinetic processes. Using the transmission line model,⁵⁰ the important elements, including the electron transfer resistance in the TiO₂ film (R_t) and chemical capacitance (C_u), were derived by fitting the impedance data. As presented in Fig. 4a, the logarithm of the $R_{\rm f}$ shows parallel behavior for the three devices. The transport resistance R_t for electrons in the TiO₂ film with thickness d and the cross-section area A can be described by eqn (1), which depends on the density of electrons (n_c) in the conduction band and the mobility μ_e (related to the free electron diffusion coefficient according to the Einstein relation on diffusion of charged particles $D_{\rm e} = \mu_{\rm e} k_{\rm B} T/q$ where q is the elementary charge).

$$R_{\rm t} = \frac{d}{A} \frac{k_{\rm B}T}{q^2 D_{\rm e} N_{\rm cb}} \exp\left(-\frac{E_{\rm F,n} - E_{\rm c}}{k_{\rm B}T}\right)$$
$$= R_0 \exp\left(\frac{E_{\rm c} - E_{\rm F,redox}}{k_{\rm B}T}\right) \exp\left(-\frac{U}{k_{\rm B}T}\right) \tag{1}$$

where $R_0 (R_0 = (d/A)((k_BT)/(q^2D_eN_{cb})))$ is the film resistance at an applied bias ($U = E_{F,n} - E_{F,redox}$), where the electron Fermi level



Fig. 4 Derived equivalent circuit components obtained from impedance measurements under dark conditions for four different devices: device A (LW1), device B (LW2), device C (LW3), and device E (LD14). (a) Electron transport resistance (R_t) as a function of bias voltage, and (b) chemical capacitance as a function of bias obtained from impedance measurements in the dark.

 $(E_{\rm F,n})$ matches the conduction band edge $(E_{\rm c})$, and $E_{\rm F,redox}$ is the quasi-equilibrium potential for the redox couple. In this study, the electrolytes are identical for various devices, which permits direct comparison of Rt between the two sensitizers (LW1 and LD14) with different anchoring groups at a constant cell voltage. Presuming that electron mobility is the same among various devices, the TiO₂ conduction band edge energy level (E_c) relative to the quasi-equilibrium potential for the redox couple can be determined by linear extrapolation of the experimental points in Fig. 5a to their intersection with the abscissa. The R_t data from device A (with LW1 using cyanoacrylic acid as an anchoring group) were shifted upward (~20 mV) from those of device E (LD14 using carboxylic acid as an anchoring group). Since the conduction band edge of the photoanode (dye coated TiO_2 film) is independent of the redox potential of electrolytes, the shift of the potentials in devices A and E can be attributed to a displacement of the conduction band edge energy levels. It was found that the conduction band level of TiO2 can be modified with molecular dipoles.⁵¹ A further switching of the π -conjunction 4-ethynylbenzene in LW1 (device A) with the 2-ethynylthiophene unit in LW2 (device B), or with 5-ethynyl-2,3-dihydrothieno [3,4-b][1,4] dioxine in LW3 (device C) has very small influence on electron transporting resistance. The computed conduction band edge energy level of the TiO2 semiconductor in devices A-C with



Fig. 5 Effect of different sensitizers on the relationship between the photoinduced charge density and the recombination lifetime: device A (LW1), device B (LW2), device C (LW3), device D (LW4), and device E (LD14).

respect to that of the quasi-equilibrium potential of the electrolyte is in close agreement with the photovoltaic measurement results of the three devices. Fig. 4b illustrates the chemical capacitance of the TiO₂ film obtained from impedance measurements in the dark. Device A (with LW1) exhibits the smallest chemical capacitance of trapped states amongst the three devices at the same applied bias, as presented in Fig. 4b. The chemical capacitance is defined as the amount of electronic charge necessary for increasing the Fermi level of the nanocrystalline oxide film by 1 eV. As chemical capacitance is proportional to the density of states of TiO₂ at the Fermi level, the plots shown in Fig. 4b provide direct information on the distribution of traps, which is usually expressed by a dimensionless quantity α . The rise of chemical capacitance as a function of applied bias shows the expected exponential behavior, thus the parameter (α) in the mesoscopic TiO₂ films can be evaluated to be 0.32, 0.29, 0.3, and 0.25, respectively. Comparatively larger values of α correspond to a steeper drop of the DOS below the conduction band edge. A wide distribution of the trap state indicates a high possibility for interfacial charge recombination. A similar result has been reported by Diau et al., showing that introduction of cyanoacrylic acid as an anchoring group into the push-pull porphyrin sensitizers shifts the conduction band edge of TiO2 compared to those with carboxylic acids.45

Unravelling of the details of the electron recombination dynamics between the photo-injected electrons at TiO₂ and the oxidized electrolyte in various devices was undertaken by employing transient photovoltage measurements and charge extraction measurements.^{52,53} The electron lifetime as a function of charge for various solid-state devices is plotted in Fig. 5. The photovoltage decay measurement was performed under the conditions of open circuit. Thus, the voltage decay comes from the electron–hole recombination in DSC devices. Obviously, the recombination rate ($\sim \tau^{-1}$) between the electrons in the conduction band of TiO₂ and the oxidized state of redox species in the electrolyte at the TiO₂–dye–electrolyte interface in devices A–C is higher than in device E. In other words porphyrins with cyanoacrylic acid as an anchoring group lead to a faster charge recombination rate at the dye-sensitized heterojunction interface.

As discussed in the impedance study, these new porphyrins with various functional moieties have a less influence on the conduction band edge energy levels of TiO₂. Thus, a low photovoltage would be expected in these devices with porphyrins having cyanoacrylic acid as an anchoring group. This result agrees well with the photovoltaic data in Table 1, showing that the $V_{\rm oc}$ of devices A–C (LW1–3) was found to be lower than that of device E (the LD14). Similar phenomena have been reported by Bisquert⁴⁰ and Diau et al.,⁴⁵ ascribed to a faster interfacial charge recombination process in porphyrin-based DSCs when cyanoacrylic acid was introduced as an anchoring group. From the structural viewpoint, the adoption of cyanoacrylic acid as an anchoring group in LW1-3 sensitizers might not only enhance the pulling effect in the D- π -A porphyrin for the light-harvesting ability, but also provide free space for charge recombination because of the floppy structure. To bypass this dilemma, the LW4 porphyrin bearing 5-ethynylthiophene-2-carboxylic acid as an acceptor was further designed and synthesized based on the

above findings. 5-Ethynylthiophene-2-carboxylic acid was prepared for LW4 according to the reported procedures (see Scheme S1 and 2⁺).⁵⁴ Keeping in the mind a similar conjugation length of LD14 and LW4, it was found that the LW4 porphyrin with a thiophene π -linker has a smaller band gap value than that of LD14 (with the phenyl group acting as a π -linker). The LW4 sensitized cell (device D) presents a J_{sc} of 17.65 mA cm⁻², a $V_{\rm oc}$ of 0.75 V, and a FF of 0.72, yielding a remarkable overall power conversion efficiency of 9.53% (see Fig. 3 and Table 2). It is interesting to note that the PCE of device D is slightly higher than that of device E due to an increase in the J_{sc} and V_{oc} . This would mainly be ascribed to the more efficient inner charge transfer occurring from the porphyrin to the carboxylic acid through thiophene instead of phenyl.14,34,55 The increase of voltage in device D should be attributed to a retarded interfacial charge recombination process as illustrated in Fig. 5. Since the conduction band edge shift in device D compared to those of devices A–C could be small (~ 20 mV), the reduced interfacial charge recombination in devices D and E could be mainly attributed to their higher $V_{\rm oc}$ than those of devices A–C.

Conclusions

In summary, a series of promising novel near-IR porphyrin dyes are designed and synthesized. The DSC devices based on the new porphyrin LW2-3 dyes with a feature of using cyanoacrylic acid as an acceptor and thiophene or EDOT as a π -linker show an impressive near-infrared IPCE response over 850 nm. Though these push-pull structured porphyrin sensitizers work efficiently in DSC devices, a detailed examination with impedance and transient photovoltage decay measurements reveals that a fast recombination process takes place at the dye-sensitizer TiO₂-electrolyte interface due to the introduction of cyanoacrylic acid as an anchoring group. Based on these studies and findings, the LW4 porphyrin with a rigid π -linker feature structure (5-ethynylthiophene-2-carboxylic acid) was further designed and synthesized, which attains an improved power conversion efficiency of 9.53%. The present work illustrates that the photo-activity of push-pull porphyrin dyes in DSCs can be successfully improved by careful molecular engineering of the π -linker moiety of porphyrins.

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Notes and references

- 1 B. O'Regan and M. Grätzel, Nature, 1991, 353, 737-740.
- 2 M. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, T. Bessho and M. Grätzel, *J. Am. Chem. Soc.*, 2005, **127**, 16835–16847.
- 3 C. Chen, M. Wang, J. Li, N. Pootrakulchote, L. Alibabaei, C. Ngocle, J. Decoppet, J. Tsai, C. Grätzel, C. Wu, S. Zakeeruddin and M. Grätzel, ACS Nano, 2009, 3, 3103– 3109.
- 4 L. Li and E. W. G. Diau, Chem. Soc. Rev., 2013, 42, 291-304.
- 5 I. Hiroshi, T. Umeyama and S. Ito, *Acc. Chem. Res.*, 2009, **42**, 1809–1818.
- 6 W. Campbell, K. Jolley, P. Wagner, K. Wagner, P. Walsh, K. Gordon, L. Schmidt-Mende, M. Nazeeruddin, Q. Wang, M. Grätzel and D. Officer, *J. Phys. Chem. C*, 2007, 111, 11760–11762.
- 7 T. Bessho, S. Zakeeruddin, C. Yeh, E. Diau and M. Grätzel, *Angew. Chem., Int. Ed.*, 2010, **49**, 6646–6649.
- 8 S. Wu, H. Lu, H. Yu, S. Chuang, C. Chiu, C. Lee, E. Diau and C. Yeh, *Energy Environ. Sci.*, 2010, 3, 949–955.
- 9 Y. Chang, C. Wang, T. Pan, S. Hong, C. Lan, H. Kuo, C. Lo, H. Hsu, C. Lin and E. Diau, *Chem. Commun.*, 2011, 47, 8910-8912.
- 10 C. Wang, C. Lan, S. Hong, Y. Wang, T. Pan, C. Chang, H. Kuo, M. Kuo, E. Diau and C. Lin, *Energy Environ. Sci.*, 2012, 5, 6933–6940.
- A. Yella, H. Lee, H. Tsao, C. Yi, A. Chandiran, M. Nazeeruddin, E. Diau, C. Yeh, S. Zakeeruddin and M. Grätzel, *Science*, 2011, 334, 629–634.
- 12 J. Ball, N. Davis, J. Wilkinson, J. Kirkpatrick, J. Teuscher, R. Gunning, H. Anderson and H. Snaith, *RSC Adv.*, 2012, 2, 6846–6853.
- 13 M. Balanay, K. Kim, S. Lee and D. Kim, J. Photochem. Photobiol., A, 2012, 248, 63–72.
- 14 N. Santhanamoorthi, C. Lo and J. Jiang, *J. Phys. Chem. Lett.*, 2013, **4**, 524–530.
- 15 G. Li, K. Jiang, Y. Li, S. Li and L. Yang, J. Phys. Chem. C, 2008, 112, 11591–11599.
- 16 V. Nuay, D. Kim, S. Lee and J. Ko, *Bull. Korean Chem. Soc.*, 2009, **30**, 2871–2872.
- 17 H. Lu, C. Mai, C. Tsia, S. Hsu, C. Hsieh, C. Chiu, C. Yeh and
 E. Diau, *Phys. Chem. Chem. Phys.*, 2009, **11**, 10270–10274.
- 18 C. Chang, L. Luo, C. Chou, C. Lo, C. Lin, C. Hung, Y. Lee and
 E. Diau, *J. Phys. Chem. C*, 2009, **113**, 11524–11531.
- 19 C. Lin, Y. Wang, S. Hsu, C. Lo and E. Diau, *J. Phys. Chem. C*, 2010, **114**, 687–693.
- 20 M. Planells, L. Pelleja, J. N. Clifford, M. Pastore, F. De Angelis, N. Lopez, S. R. Marder and E. Palomares, *Energy Environ. Sci.*, 2011, 4, 1820–1829.
- 21 N. Cai, Y. Wang, M. Xu, Y. Fan, R. Li, M. Zhang and P. Wang, *Adv. Funct. Mater.*, 2013, **23**, 1846–1854.
- 22 B. Pelado, P. Cruz, V. González-Pedro, E. Barea and F. Langa, *Tetrahedron Lett.*, 2012, **53**, 6665–6669.
- 23 J. Zhang, Y. Kan, H. Li, Y. Geng, Y. Wu and Z. Su, *Dyes Pigm.*, 2012, **95**, 313–321.

- 24 S. LeCours, H. Guan, S. DiMagno, C. Wang and M. Therien, J. Am. Chem. Soc., 1996, **118**, 1497–1503.
- 25 S. Mathew, H. Iijima, Y. Toude, T. Umeyama, Y. Matano, S. Ito, N. Tkachenko, H. Lemmetyinen and H. Imahori, *J. Phys. Chem. C*, 2011, 115, 14415–14424.
- 26 J. Warnan, Y. Pellegrin, E. Blart and F. Odobel, *Chem. Commun.*, 2012, **48**, 675–677.
- 27 Y. Liu, N. Xiang, X. Feng, P. Shen, W. Zhou, C. Weng, B. Zhao and S. Tan, *Chem. Commun.*, 2009, 2499–2501.
- 28 L. Alibabaei, J. Kim, M. Wang, N. Pootrakulchote, J. Teuscher, D. Censo, R. Baker, J. E. Moser, Y. Yu, K. Kay, S. Zakeeruddin and M. Grätzel, *Energy Environ. Sci.*, 2010, 3, 1757–1764.
- 29 C. Mai, W. Huang, H. Lu, C. Lee, C. Chiu, Y. Liang, E. Diau and C. Yeh, *Chem. Commun.*, 2010, **46**, 809–811.
- 30 Y. Liu, H. Lin, J. Dy, K. Tamaki, J. Nakazaki, D. Nakayama,
 S. Uchida, T. Kubo and H. Segawa, *Chem. Commun.*, 2011, 47, 4010–4012.
- 31 C. Jiao, N. Zu, K. Huang, P. Wang and J. Wu, Org. Lett., 2011, 13, 3652–3655.
- 32 M. Griffith, K. Sunahara, P. Wagner, K. Wagner, G. Wallace, D. Officer, A. Furube, R. Katoh, S. Mori and A. Mozer, *Chem. Commun.*, 2012, 48, 4145–4162.
- 33 W. Julien, F. Ludovic, M. Frederic, S. Marjorie, B. Errol, P. Yann, J. Denis and O. Fabrice, *ChemSusChem*, 2012, 5, 1568–1577.
- 34 A. Mishra, M. Fischer and P. Bauerle, Angew. Chem., Int. Ed., 2009, 48, 2474–2499.
- 35 M. Jessing, M. Brandt, K. Jensen, J. Christensen and U. Boas, J. Org. Chem., 2006, 71, 6734–6741.
- 36 G. Barbarella, M. Melucci and G. Sotgiu, *Adv. Mater.*, 2005, 17, 1581–1593.
- 37 J. Lu, X. Xu, Z. Li, K. Cao, J. Cui, Y. Zhang, Y. Shen, Y. Li, J. Zhu, S. Dai, W. Chen, Y. Cheng and M. Wang, *Chem.-Asian J.*, 2013, 8, 956–962.
- 38 T. Zhang, Y. Zhao, K. Song, I. Asselberghs, A. Persoons, K. Clays and M. Therien, *Inorg. Chem.*, 2006, 45, 9703–9712.
- 39 Y. Wu and W. Zhu, Chem. Soc. Rev., 2013, 42, 2039-2058.
- 40 T. Ripolles-Sanchis, B. Guo, H. Wu, T. Pan, H. Lee, S. Raga,
 F. Fabregat-Santiago, J. Bisquert, C. Yeh and E. Diau, *Chem. Commun.*, 2012, 48, 4368–4370.
- 41 C. Lee, H. Lu, C. Lan, Y. Huang, Y. Liang, W. Yen, Y. Liu, Y. Lin, E. Diau and C. Yeh, *Chem.-Eur. J.*, 2009, **15**, 1403– 1412.
- 42 H. Zhan, S. Lamare, A. Ng, T. Kenny, H. Guernon, W. Chan,
 A. Djurisic, P. Harvey and W. Wong, *Macromolecules*, 2011,
 44, 5155–5167.
- 43 J. Rochford, D. Chu, A. Hagfeldt and E. Galoppini, *J. Am. Chem. Soc.*, 2007, **129**, 4655–4665.
- 44 M. Kang, S. Kang, S. Kim, I. Choi, J. Ryu, M. Ju, D. Cho, J. Lee and H. Kim, *Chem. Commun.*, 2012, **48**, 9349–9351.
- 45 Y. Chang, H. Wu, N. Reddy, H. Lee, H. Lu, C. Yeh and E. Diau, *Phys. Chem. Chem. Phys.*, 2013, **15**, 4651–4655.
- 46 E. Barea, R. Caballero, F. Fabregat-Santiago, P. Cruz, F. Langa and J. Bisquert, *ChemPhysChem*, 2010, **11**, 245–250.
- 47 A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595–6663.

- 48 M. Lee, K. Seo, H. Song, M. Kang, Y. Eom, H. Kang and H. Kim, *Tetrahedron Lett.*, 2011, **52**, 3879–3882.
- 49 S. Koops, B. O'Regan, P. Barnes and J. Durrant, *J. Am. Chem. Soc.*, 2009, **131**, 4808–4818.
- 50 M. Wang, P. Chen, R. Humphry-Baker, S. Zakeeruddin and M. Grätzel, *ChemPhysChem*, 2009, **10**, 290.
- 51 M. Wang, C. Grätzel, S. Moon, R. Humphry-Baker, N. Rossier-Iten, S. Zakeeruddin and M. Grätzel, *Adv. Funct. Mater.*, 2009, **19**, 2163–2172.
- 52 A. Zaban, M. Greenshtein and J. Bisquert, *ChemPhysChem*, 2003, 4, 859-864.
- 53 J. Bisquert, A. Zaban, M. Greenshtein and I. Mora-Sero, *J. Am. Chem. Soc.*, 2004, **126**, 13550–13559.
- 54 T. Suzuki, Y. Ota, Y. Kasuya, M. Mutsuga, Y. Kawamura, H. Tsumoto, H. Nakagawa, M. Finn and N. Miyata, *Angew. Chem., Int. Ed.*, 2010, **49**, 6817–6820.
- 55 J. Song, P. Amaladass, S. Wen, K. Pasunooti, A. Li, Y. L. Yu, X. Wang, W. Deng and X. Liu, *New J. Chem.*, 2011, **35**, 127–136.