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Engineering diketopyrrolopyrrole sensitizers for highly efficient dye-sensitized solar cells: enhanced light harvesting and intramolecular charge transfer†

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Two asymmetric DPP dyes with a D–π–A structure are reported, where DPP is used as a bridge to connect the triphenylamine donor and cyanoacetic acid acceptor. The compact dyes exhibit high light absorption ability covering the whole visible spectral region. The most efficient cell exhibited a short-circuit current density of 17.72 mA cm^{-2}, an open-circuit voltage of 725 mV, and a fill factor of 74%, yielding a power conversion efficiency of 9.51% under standard test conditions (irradiation of 1000 W m^{-2}, air mass = 1.5 G), which is the highest value reported for DPP-based DSCs employing an I$^-$/I$_3^-$ redox couple. Furthermore, the DPP dyes show remarkable stability under long-term irradiation over 1000 h. Considering the facile synthesis and excellent stability, the DPP sensitizer would be a promising option for highly efficient DSCs. The results show that judicious molecular engineering is crucial for constructing highly efficient charge transfer sensitizers in DSCs.

Introduction

As one of the key components in dye-sensitized solar cells (DSCs), the sensitizer exerts a significant influence on the device power conversion and stability.[1] With ruthenium complexes[2a–d] and zinc porphyrin dyes,[2e–g] high power conversion efficiencies of up to 8–12% have been reported. On the other hand, metal-free organic dyes, usually with an electron donor–π bridge–electron acceptor (D–π–A) configuration, have been actively pursued due to their molecular tailoring flexibility and raw material abundance, and comparable efficiencies have been achieved.[3] In the D–π–A organic dyes, triarylamine and cyanoacrylic acid were widely used as donor and acceptor, respectively, and various π-conjugated linkers were employed to bridge the donor and acceptor units to create a large number of D–π–A dyes for DSCs. It is well known that a linker is of paramount importance in tuning the molecular energy gap, and the electronic and steric structures, strongly affecting device performances.[4]

Diketopyrrolopyrrole (DPP) chromophore has a uniquely planar conjugated bicyclic structure with electron-withdrawing property, and its derivatives are extensively used as high-performance pigments due to its exceptional photochemical, mechanical and thermal stability.[5] Following its successful investigations in a series of optical electronic devices,[6] it was also employed as a linker in development of sensitizers for DSCs in recent years.[7] Following the first report in 2010,[7a] Han's group introduced a strong electron donor indoline in a DPP dye, giving efficiency of 7.4%.[7d] Recently, asymmetric DPP sensitizer **DPP07** with intense absorption in the red/near-IR region were prepared with efficiencies of ~8.6% using a I$^-$/I$_3^-$ based electrolyte.[8] In our previous report, a compact DPP dye **ICD-1**, was designed, where diphenylamine unit was directly connected to phenyl–DPP unit with D–π–A structure, giving a power conversion efficiency of 8.61%. The result demonstrated that the electron communication in **ICD-1** is more favourable as compare with that in the similar structured sensitizer **ICD-2** with a triphenylamine donor.[9] Encouraged by the result, we focused on the further structural optimization of DPP-based dyes for improving light harvesting ability. Here, two compact asymmetric DPP dyes (**ICD-8** and **ICD-9**), were designed, and an efficiency up to 9.51% was achieved in a DSC with an I$^-$/I$_3^-$ based electrolyte under standard AM 1.5 conditions. The chemical structures of the dyes are shown in Fig. 1.

Results and discussion

The synthetic route of **ICD-8** and **ICD-9** is described in Fig. 2. Their UV-Vis absorption spectra examined in dichloromethane solutions were displayed in Fig. 3, and the relevant parameters

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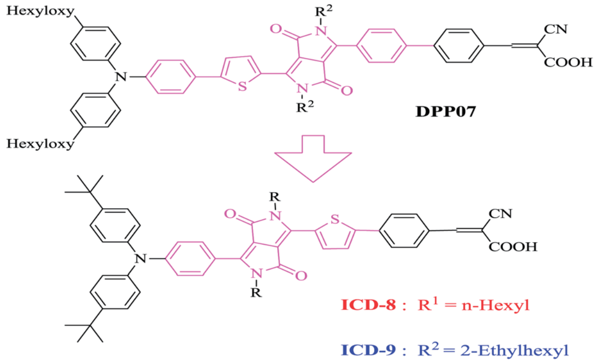

Fig. 1 Molecular structures of DPP07, ICD-8 and ICD-9.

are collected in Table 1. Both the dyes show broader absorption spectra with two absorption bands covering a wide range in the visible region. The maximum absorption peak of **ICD-9** is at 581 nm, which is 21 nm red shift compared to that (560 nm) of the similar dye **DPP07** where an additional phenyl unit is included.[8a] More importantly, the absorption spectrum of **ICD-9** covers the whole visible range, while the latter lacks absorption between 360–450 nm.[8a] The result indicates that **ICD-9** dye is compact in structure, and possesses highly potential light harvesting ability as sensitizer in DSCs. In the case of **ICD-8**, the maximum absorption peak (λ_{max}, 620 nm) was significantly red shifted by 39 nm as compared with that in **ICD-9**. The large difference can be explained by the increased dihedral twist at the Ph–DPP–Th bonds in the presence of two large ethylhexyl units in **ICD-9**. The bulky units can attenuate the tendency of dye aggregation on TiO_2 surface, and improve the device performance.

In order to gain insight into the geometrical configuration and electron distribution of the frontier orbitals of the two dyes, density functional theory (DFT) calculations were made on a B3LYP/6-31G level as shown in Fig. 4. As shown in Fig. 4, the frontier HOMOs of both the dyes are homogeneously delocalized over the whole triphenylamine and DPP units, while their LUMOs are on the cyanoacrylic acid group and part of the DPP macrocycle. Thus electron communication may be favourable between the donor and the acceptor in both the dyes, allowing an efficient electron transfer from dye to TiO_2 electrode under light irradiation. The larger twist angels are expected to localize the triphenylamine radical cation away from the acceptor, and might be beneficial for retarding the back electron transfer from TiO_2 to the oxidized dye and improving the device open-circuit voltage.[8a]

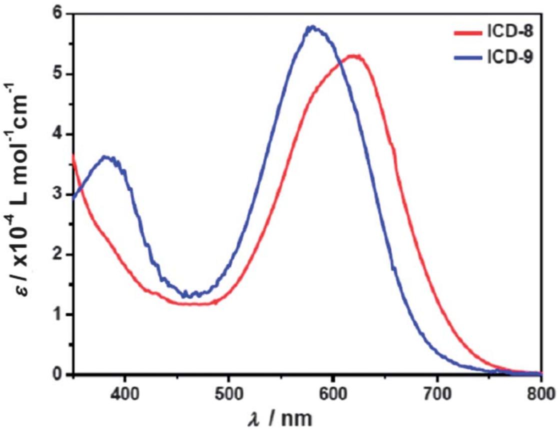

Fig. 3 Absorption spectra of ICD-8 and ICD-9 measured in dichloromethane solution.

To further investigate the molecular energy levels, cyclic voltammetry measurements were performed in a 0.1 M dichloromethane solution of tetrabutylammoniumhexafluorophosphate with ferrocene as internal standard at 0.63 V *vs.* NHE. The first oxidation potentials ($E_{s+/0}$) of **ICD-8** and **ICD-9** were observed to be 0.92 and 0.93 V *vs.* NHE, respectively, which are assigned to the oxidation of triphenylamine units. Both the potential values are substantially more positive than the iodide/tri-iodide couple redox (0.4 V *vs.* NHE), indicating that the

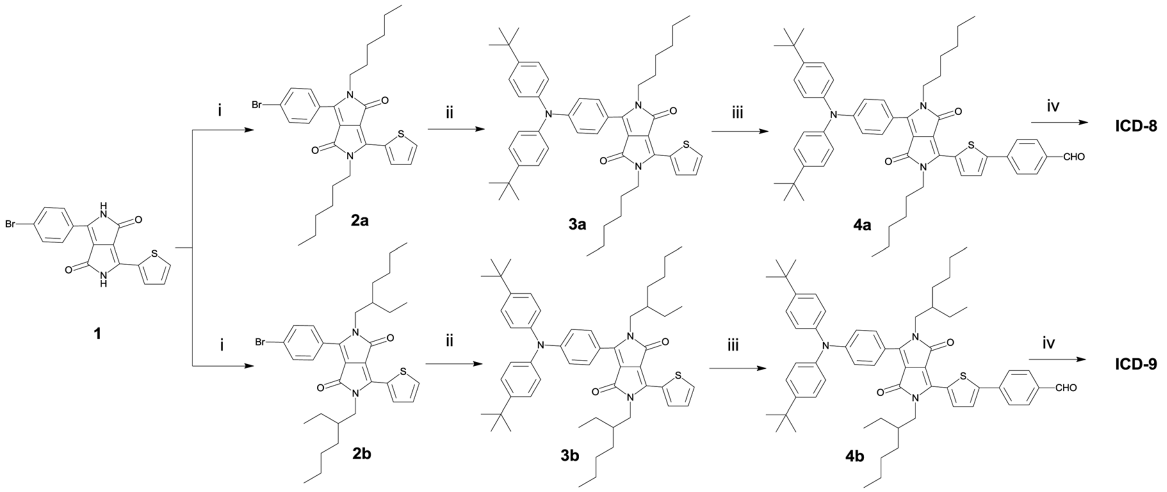

Fig. 2 Synthetic routes of dye ICD-8 and ICD-9. (i) KOBu^t, NMP; (ii) Pd(OAc)$_2$, P(Bu^t)$_3$, *t*-BuONa, PhMe, Ar, 90 °C; (iii) *n*-BuLi, (*n*-Bu)$_3$SnCl, −78 °C; PdCl$_2$(PPh$_3$)$_2$, Ar, 65 °C; (iv) cyanoacetic acid, piperidine, THF, Ar, reflux.

ground-state sensitizer regeneration is energetically favorable in DSC.[10]

The optical transition energies (E_{0-0}) were 1.81 eV for **ICD-8** and 1.89 eV for **ICD-9**, estimated from the intersection of their absorption and emission spectra. excited-state redox potential, $E_{s+/*}$, determined by subtracting E_{0-0} from $E_{s+/0}$, were −0.89 V for **ICD-8** and −0.96 eV for **ICD-9**. Both the values are negative enough to allow their excited state electron transfer into the TiO_2 conduction band (−0.5 V *vs.* NHE).[11]

For preparation of the DSCs, a double TiO_2 electrode containing an 11 μm transparent layer and a 6 μm scattering layer was employed. The electrodes were prepared by screen printing method, and sintered at 500 °C in air for 30 min, followed with treatment by 0.05 M titanium tetrachloride solution and subsequent heat treatment at 500 °C for 30 min.[12] The prepared TiO_2 electrodes were stained in the dye solution of 0.2 mM **ICD-8** or **ICD-9** in a mixture of acetonitrile, *tert*-butylalcohol and tetrahydrofuran (1 : 1 : 0.2, v/v/v). In the solution, 20 mM 3α,7α-dihydroxy-5β-cholic acid (chenodeoxycholic acid) was added as co-adsorbent to prevent dye aggregation on TiO_2 surface. The final device was prepared in a sandwich-type, where the dyed TiO_2 electrode and a Pt-counter electrode was sealed with a hot-melt film, and filled with an I^-/I_3^- electrolyte between them. The electrolyte contains 0.68 M dimethyl imidiazolium iodide, 0.05 M iodine, 0.10 M LiI, 0.05 M guanidinium thiocyanate, and 0.40 M *tert*-butylpyridine in the mixture of acetonitrile and valeronitrile (85 : 15, v/v).

Fig. 5a shows action spectra in the form of monochromatic incident photon-to-current conversion efficiencies (IPCEs). Both the dye-based DSCs exhibited a strong and broad response in the entire visible spectral region with the highest value of 85% and 83% at 593 nm for **ICD-9** and **ICD-8**, respectively. In the spectra, **ICD-8** showed slightly higher response in the long wavelengths 660–800 nm but much lower IPCE values at the other spectral regions, compared to **ICD-9**, which is in good agreement with absorption spectra. Both the dyes are rare examples having panchromatic spectral response, because most organic dyes show narrow absorption bands, could not absorb efficiently over the entire visible in DSCs with a single sensitizer.[13] The compact **ICD-9** exhibits a broader spectral response, as compared to the dye **DPP07** mentioned above, where the device lacks efficient response between 400 and 500 nm.[8a]

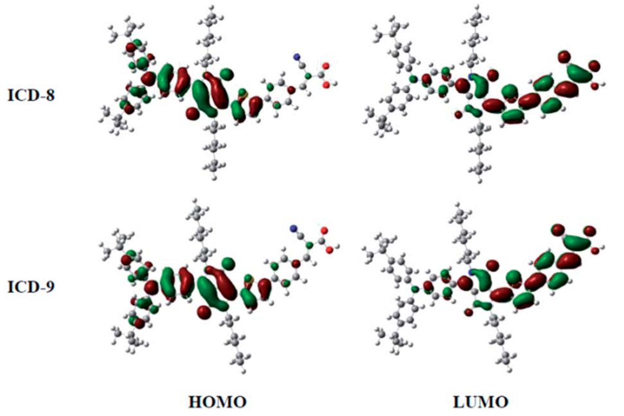

Fig. 4 Frontier molecular orbitals of the HOMO and LUMO for **ICD-8** and **ICD-9**, calculated with DFT on a B3LYP/6-31+G(d) level (isodensity = 0.03 au).

Fig. 5b shows the photocurrent density–voltage characteristics for DSCs with **ICD-8** and **ICD-9** measured under AM 1.5 G simulated solar light at a light intensity of 100 mW cm^{-2}. **ICD-9** based-device gave a short circuit photocurrent density (J_{sc}) of 17.72 ± 0.20 mA cm^{-2}, an open circuit voltage (V_{oc}) of 725 ± 10 mV, and a fill factor (FF) of 0.74 ± 0.02, corresponding to an overall conversion efficiency (η), derived from the equation $\eta = J_{sc} \times V_{oc} \times$ FF/light intensity, of 9.51%, while **ICD-8** based device gave J_{sc} of 16.76 ± 0.20 mA cm^{-2}, V_{oc} of 683 ± 10 mV, FF of 0.66 ± 0.02, and η of 7.56% under the same conditions. The large differences in the efficiencies come mainly from the differences in the V_{oc} and FF between them. In the given systems with different dyes, generally, the V_{oc} is strongly affected by the charge recombination at the dyed TiO_2 interface due to the dye aggregation. Considering their structural difference, the higher V_{oc} can be assigned to the effective aggregation suppression from branched 2-ethyl-hexyl chains in **ICD-9**.[14]

For further elucidating the large difference in V_{oc}s for **ICD-8** and **ICD-9**, electrochemical impedance spectroscopy (EIS) was performed to investigate the FTO/TiO_2/dye interfaces. The

Table 1 Photoelectrochemical properties of ICD-8 and ICD-9, and their solar cell performance

Dye	$\lambda_{max}{}^a$ [nm]	ε [L mol^{-1} cm^{-1}]	$E_{0-0}{}^b$ [eV]	$E_{s+/0}{}^c$ [V]	$E_{s+/*}{}^d$ [V]	J_{sc} [mA cm^{-2}]	V_{oc} [mV]	FF	η^e [%]
ICD-8	620	53 000	1.81	0.92	−0.89	16.76 ± 0.20	683 ± 10	0.66 ± 0.02	7.56
	339	39 800							
ICD-9	581	57 800	1.89	0.93	−0.96	17.72 ± 0.20	725 ± 10	0.74 ± 0.02	9.51
	393	35 400							

[a] Absorption in CH_2Cl_2 solutions (1×10^{-5} M) at rt. [b] E_{0-0} values were estimated from the intersection of the absorption and emission spectra. [c] The oxidation potentials of the dyes were measured in CH_2Cl_2 solutions with tetrabutylammoniumhexafluorophosphate ($TBAPF_6$, 0.1 M) as electrolyte, Pt wires as working and counter electrode, Ag/Ag^+ as reference electrode; calibrated with ferrocene/ferrocenium (Fc/Fc^+) as an internal reference and converted to NHE by addition of 630 mV. [d] The estimation was determined by subtracting E_{0-0} from $E_{s+/0}$. [e] The data were recorded under AM 1.5 G simulated solar light at a light intensity of 100 mW cm^{-2}, and represents the average of three devices, where TiO_2 films with 11 μm thick nanocrystalline layer and 6 μm thick scattering layer were used with an electrolyte containing 0.68 M dimethyl imidiazolium iodide, 0.05 M iodine, 0.10 M LiI, 0.05 M guanidinium thiocyanate, and 0.40 M *tert*-butylpyridine in a mixture of acetonitrile and valeronitrile (85/15, v/v), and each data was averaged by three parallel samples.

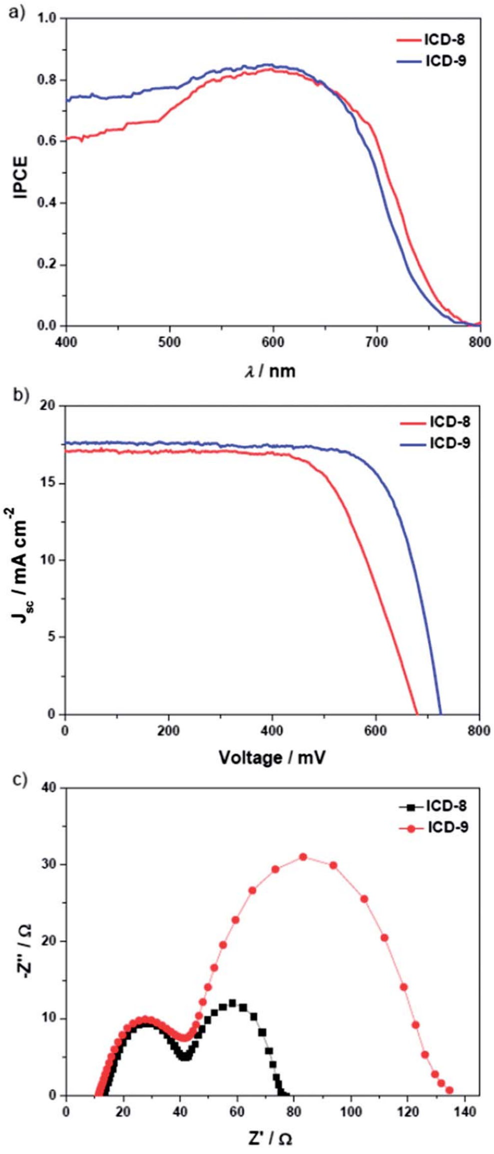

Fig. 5 a) Incident photon-to-electron conversion efficiency (IPCE) action; (b) I–V characteristics measured under AM 1.5 conditions; (c) electrochemical impedance spectra measured in the dark at a forward bias of 0.6 V for the DSCs employing **ICD-8** and **ICD-9**.

Nyquist plots of DSCs were recorded in the dark with a forward bias of 0.6 V, as shown in Fig. 5c. Two semicircles from left to right in the Nyquist plot were assigned to the resistances of charge transfer (R_{Pt}) on the Pt counter electrode and charge recombination (R_r) at the interface of the TiO_2/electrolyte.[15] Clearly, the semicircle for R_r is larger in **ICD-9** than that in **ICD-8**, indicating the effective suppression of charge recombination at the interface of the TiO_2/electrolyte in **ICD-9** based device, which is consistent with the observed high V_{oc} value.

For testing long-term stability, photovoltaic performance of **ICD-9** based devices was recorded discontinuously over the entire 1000 h testing period at room temperature under one-sun light soaking. As shown in Fig. 6, the photovoltaic parameters J_{sc}, V_{oc} and FF of the **ICD-9** based cell changed slightly with the time, and the final conversion efficiency retained 92% of its initial value. The high stability may come from strong adsorption ability of the compact dye on TiO_2 surface, and will be favourable for the practical application.

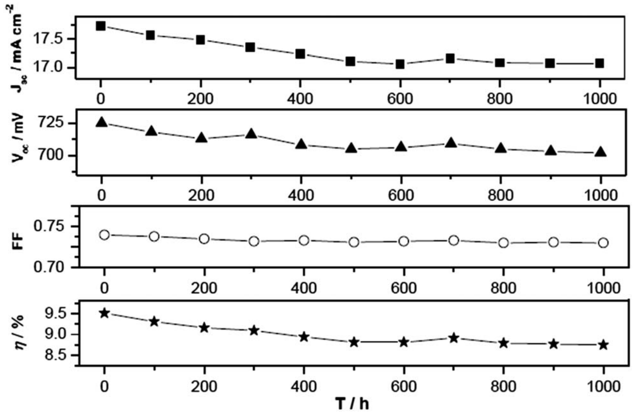

Fig. 6 Variations of the photovoltaic parameters (J_{sc}, V_{oc}, FF, and η) with aging time for the DSSC device based on RD-II under one-sun light soaking.

Conclusions

In conclusion, two new asymmetric DPP dyes with a D–π–A structure were designed with high light absorption ability covering the whole visible spectral region. The panchromatic dye **ICD-9** exhibits high power conversion efficiency of 9.51% under standard AM 1.5 conditions, which is the highest values reported for DPP dye-based DSCs employing a I^-/I_3^- redox couple. Furthermore, the DPP dyes show remarkable stability under long-term irradiation over 1000 h. Considering the facile synthesis and excellent stability, the DPP sensitizer would be a promising option for high efficient DSCs. Further improvement of the performance could be expected for DPP sensitizers through further extending spectral response for high short circuit photocurrent, and employing Co^{2+}/Co^{3+} redox couple for high open circuit voltage.[16] More importantly, judicious molecular engineering is crucial for constructing highly efficient charge transfer sensitizers in DSCs. The results would provide valuable, basic guidelines for rational designs of D–π–A molecules for high-performance DSCs and other optoelectronic devices.

Experimental

General information

Unless otherwise noted, all solvents were treated by standard methods before use. All reagents were commercially available and used without further purification unless indicated otherwise. Thin lay all chemicals were analytical grade and used as received. NMR spectra were recorded on a BRUKER AVANCE 400 MHz instruments. The residual solvent protons (^1H) were used as internal standards. ^1H-NMR data are presented as follows: chemical shift in ppm (δ) downfield from tetramethylsilane (multiplicity, coupling constant (Hz), integration).

The following abbreviations are used in reporting NMR data: s, singlet; br.s, broad singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; m, multiplet. Mass spectra were taken on a Bruker Daltonics Inc. APEXII FT-ICR spectrometer. The material 3-(4-bromophenyl)-6-(thiophen-2-yl)-2,5-dihydro-pyrrolo[3,4-*c*]-pyrrole-1,4-dione (DPP) were prepared according to the literature procedures.[17]

Synthesis of 2a

In an oven-dried 250 mL three-necked flask, 8 g (18 mmol) **DPP** (**1**) and 4.03 g (36 mmol) potassium *tert*-butoxide were dissolved in 150 mL of dry NMP, the solution was vigorously stirred at 60 °C for 30 min, after which time 20.8 g (108 mmol) of 1-bromohexane was dropwised over a period of 90 min. The reaction was maintained for another 20 hours. After cooling to room temperature, toluene was added and the organic phase was filtered through a silica-gel pad. The filtrate was washed with water (3 × 50 mL) and brine (3 × 50 mL). The combined organic phases were evaporated under reduced pressure and the residue purified by silica-gel column chromatography to give the desired product. 2.5 g (22%) of bright orange needles were obtained.

Synthesis of 3a

An oven-dried 100 mL three-necked flask was charged with compound **2a** (0.6 g, 1.0 mmol), $Pd(OAc)_2$ (22 mg, 0.1 mmol), P^tBu_3 (20 mg, 0.1 mmol), bis(*tert*-butylphenyl)amine (0.48 g, 1.30 mmol), ^tBuONa (0.48 g, 5.0 mmol). The flask was evacuated and backfilled with nitrogen, with the operation being repeated twice. Then 20 mL toluene was added and the mixture was heated at 90 °C for 16 h. After cooling to room temperature, dichloromethane were added and the organic phase was filtered through a silica-gel pad. The filtrate was with water (3 × 20 mL) and brine (3 × 20 mL). The combined organic phases was dried on $MgSO_4$, filtered and evaporated under reduced pressure and the residue purified by silica-gel column chromatography to give a purple solid (0.61 g, 62%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.80–0.86 (m, 6H), 1.26–1.31 (m, 25H), 1.54 (s, 5H), 1.71 (s, 4H), 3.83 (t, J = 8.0 Hz, 2H), 4.00 (t, J = 8.0 Hz, 2H), 7.03 (d, J = 4.8 Hz, 3H), 7.12 (d, J = 8.8 Hz, 4H), 7.33 (d, J = 8.4 Hz, 4H), 7.60 (d, J = 5.2 Hz, 1H), 7.75 (d, J = 8.8 Hz, 2H), 8.84 (d, J = 3.2 Hz, 1H).

Synthesis of 4a

In an oven-dried 250 mL three-necked flask, compound (**3a**) (0.8 g, 1 mmol) and dried THF (50 mL) were added under N_2 atmosphere. *n*-Butyl lithium (0.42 mL, 2.4 M in hexane, 1 mmol), was added dropwise at −78 °C stirred for 1 h with the temperature maintained −78 °C. then the mixture was warmed up to −40 °C for 3 h and cooled to −78 °C again, tributyltin chloride (0.27 mL, 1 mmol) was added one portion. The mixture was warmed to room temperature slowly and stirred for another 24 h. Then 4-bromobenzaldehyde (0.28 g, 1.5 mmol) and $PdCl_2(PPh_3)_2$ (120 mg, 0.171 mmol) were added, the solution was stirred at 65 °C for another 15 h, cooled and concentrated on the rotary evaporator. The residue was subjected to column chromatography to afford an dark solid (812 mg, 90%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.86–0.90 (m, 6H), 1.27–1.31 (m, 30H), 1.75 (4H), 3.86 (d, J = 7.6 Hz, 2H), 4.04 (t, J = 7.6 Hz, 2H), 7.03 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 6.8 Hz, 4H), 7.34 (d, J = 8.8 Hz, 4H), 7.59 (d, J = 4.0 Hz, 1H), 7.77 (d, J = 8.8 Hz, 2H), 7.83 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H), 8.86 (d, J = 4.4 Hz, 1H), 10.02 (s, 1H).

Synthesis of ICD-8

An oven-dried 100 mL one-necked flask was charged with compound **4** (4.2×10^{-4} mol), cyanoacetic acid (8×10^{-3} mol), 10 mL of dry THF and 0.5 mL piperidine. The solution was heated to reflux for 15 h and the colour turned to deep red. After cooling to room temperature, dichloromethane and a diluted solution of hydrochloric acid were added and the organic phase was washed with water (3 × 20 mL) and brine (3 × 20 mL). The combined organic phase was dried on $MgSO_4$, filtered and evaporated under reduced pressure and the residue purified by silica-gel column chromatography to give a dark-purple solid (78%). ^{1}H-NMR (DMSO, 400 MHz) δ (ppm): 0.79–0.85 (m, 6H), 1.19–1.34 (m, 30H), 1.54–1.60 (m, 4H), 3.78 (2H), 3.93 (2H), 6.83 (d, J = 8.0 Hz, 4H), 7.10 (d, J = 8.0 Hz, 4H), 7.42 (d, J = 8.0 Hz, 4H), 7.76 (d, J = 4.4 Hz, 2H), 7.76–7.98 (m, 8H), 8.83 (d, J = 4 Hz, 1H); MS (MALDI-TOF): *m*/*z* found: 912.7 (M+).

Synthesis of 2b

In an oven-dried 250 mL three-necked flask, 8 g (18 mmol) DPP (**1**) and 4.03 g (36 mmol) potassium *tert*-butoxide were dissolved in 150 mL of dry NMP, the solution was vigorously stirred at 60 °C for 30 min, after which time 20.8 g (108 mmol) of 1-bromo-2-ethylhexane was dropwised over a period of 90 min. The reaction was maintained for another 20 hours. After cooling to room temperature, toluene was added and the organic phase was filtered through a silica-gel pad. The filtrate was washed with water (3 × 50 mL) and brine (3 × 50 mL). The combined organic phases were evaporated under reduced pressure and the residue purified by silica-gel column chromatography to give the desired product. 2.5 g (22%) of bright orange needles were obtained.

Synthesis of 3b

An oven-dried 100 mL three-necked flask was charged with compound **2b** (0.6 g, 1.0 mmol), $Pd(OAc)_2$ (22 mg, 0.1 mmol), P^tBu_3 (20 mg, 0.1 mmol), bis(*tert*-butyl phenyl)amine (0.48 g, 1.30 mmol), ^tBuONa (0.48 g, 5.0 mmol). The flask was evacuated and backfilled with nitrogen, with the operation being repeated twice. Then 20 mL toluene was added and the mixture was heated at 90 °C for 16 h. After cooling to room temperature, dichloromethane were added and the organic phase was filtered through a silica-gel pad. The filtrate was with water (3 × 20 mL) and brine (3 × 20 mL). The combined organic phases was dried on $MgSO_4$, filtered and evaporated under reduced pressure and the residue purified by silica-gel column chromatography to give a purple solid (0.61 g, 62%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.80–0.94 (m, 12H), 1.28–1.38 (m, 28H), 1.61–1.68 (m, 6H), 1.68 (s, 2H), 3.83 (t, J = 7.6 Hz, 2H), 3.99 (t, J = 7.6 Hz, 2H), 7.03 (d, $J = 4.8$ Hz, 3H), 7.12 (d, $J = 8.8$ Hz, 4H), 7.33 (d, $J = 8.4$ Hz, 4H), 7.60 (d, $J = 5.2$ Hz, 1H), 7.75 (d, $J = 8.8$ Hz, 2H), 8.84 (d, $J = 3.2$ Hz, 1H).

Synthesis of 4b

In an oven-dried 250 mL three-necked flask, compound (**3b**) (0.8 g, 1 mmol) and dried THF (50 mL) were added under N_2 atmosphere. *n*-Butyl lithium (0.42 mL, 2.4 M in hexane, 1 mmol), was added dropwise at −78 °C stirred for 1 h with the temperature maintained −78 °C. then the mixture was warmed up to −40 °C for 3 h and cooled to −78 °C again, tributyltin chloride (0.27 mL, 1 mmol) was added one portion. The mixture was warmed to room temperature slowly and stirred for another 24 h. then 4-bromobenzaldehyde (0.28 g, 1.5 mmol) and $PdCl_2(PPh_3)_2$ (120 mg, 0.171 mmol) were added, the solution was stirred at 65 °C for another 15 h, cooled and concentrated on the rotary evaporator. The residue was subjected to column chromatography to afford an dark solid (812 mg, 90%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 0.76–0.94 (m, 12H), 1.27–1.38 (m, 29H), 1.60–1.66 (m, 6H), 1.68 (s, 1H), 3.86 (d, $J = 7.6$ Hz, 2H), 4.0 (d, $J = 7.6$ Hz, 2H), 7.03 (d, $J = 8.8$ Hz, 2H), 7.11 (d, $J = 8.8$ Hz, 4H), 7.32 (d, $J = 8.4$ Hz, 4H), 7.58 (d, $J = 4$ Hz, 1H), 7.72 (d, $J = 8.8$ Hz, 2H), 7.82 (d, $J = 8.4$ Hz, 2H), 7.93 (d, $J = 8$ Hz, 2H), 8.85 (d, $J = 4$ Hz, 1H), 10.03 (s, 1H).

Synthesis of ICD-9

An oven-dried 100 mL one-necked flask was charged with compound **4b** (4.2×10^{-4} mol), cyanoacetic acid (8×10^{-3} mol), 10 mL of dry THF and 0.5 mL piperidine. The solution was heated to reflux for 15 h and the colour turned to deep red. After cooling to room temperature, dichloromethane and a diluted solution of hydrochloric acid were added and the organic phase was washed with water (3 × 20 mL) and brine (3 × 20 mL). The combined organic phase was dried on $MgSO_4$, filtered and evaporated under reduced pressure and the residue purified by silica-gel column chromatography to give a dark-purple solid (78%). ^{1}H-NMR (DMSO, 400 MHz) δ (ppm): 0.78–0.88 (m, 12H), 1.16–1.38 (m, 29H), 1.55–1.62 (m, 6H), 1.74 (s, 1H), 3.80 (s, 2H), 3.87 (d, $J = 6.8$ Hz, 2H), 6.84 (d, $J = 8.4$ Hz, 4H), 7.10 (d, $J = 8.4$ Hz, 4H), 7.41 (d, $J = 8.4$ Hz, 4H), 7.76 (d, $J = 4.4$ Hz, 2H), 7.86–7.99 (m, 6H), 8.80 (d, $J = 4$ Hz, 1H); MS (MALDI-TOF): *m*/*z* found: 968.5 (M+).

DSC fabrication

The nanocrystalline TiO_2 pastes (particle size, 20 nm) were prepared using a previously reported procedure.[18] Fluorine doped thin oxide (FTO, 4 mm thickness, 10 ohms per sq, Nippon Sheet Glass, Japan) conducting electrodes were washed with soap and water, followed by sonication for 10 min in acetone and isopropanol, respectively. Following a drying period, the electrodes were then submerged in a 40 mM aqueous solution of $TiCl_4$ for 30 min at 75 °C, and then washed by water and ethanol. On the electrodes, an 11 μm thick nanocrystalline TiO_2 layer and 6 μm thick TiO_2 light scattering layer (particle size, 400 nm, PST-400C) were prepared by screen-printing method. The TiO_2 electrodes were heated at 500 °C for 30 min, followed by treating with a 40 mM aqueous solution of $TiCl_4$ for 30 min at 75 °C and subsequent sintering at 500 °C for 30 min. The thickness of TiO_2 films was measured by a profiler, Sloan, Dektak3. The electrodes were immersed in a dye bath containing 0.2 mM **ICD-8** or **ICD-9** and 20 mM 3α,7α-dihydroxy-5β-cholic acid (chenodeoxycholic acid) in 4-*tert*-butanol–acetonitrile mixture–tetrahydrofuran (1 : 1 : 0.2, v/v) and kept for 24 h at room temperature. The dyed electrodes were then rinsed with the mixed solvent to remove excess dye. A platinum-coated counter electrode was prepared according to the reporter,[19] and two holes were drilled on its opposite sides. The two electrodes were sealed together with a 25 μm thick thermoplastic Surlyn frame. An electrolyte solution was then introduced through one of the two holes in the counter electrode, and the holes were sealed with the thermoplastic Surlyn. The electrolyte contains 0.68 M dimethyl imidiazolium iodide, 0.05 M iodine, 0.10 M LiI, 0.05 M guanidinium thiocyanate, and 0.40 M *tert*-butylpyridine in the mixture of acetonitrile and valeronitrile (85 : 15, v/v). All the devices were prepared with a photoactive area of about 0.3 cm^2, and a metal mask of 0.165 cm^2 was covered on the device for photovoltaic property measurements.

Characterization

The photocurrent–voltage (*I*–*V*) characteristics were recorded at room temperature using a computer-controlled Keithley 2400 source meter under air mass (AM) 1.5 simulated illumination (100 mW cm^{-2}, Oriel, 67005), and each data was averaged by three parallel samples. The action spectra of monochromatic incident photo-to-current conversion efficiency (IPCE) for solar cells were performed using a commercial setup (PV-25 DYE, JASCO). A 300 W xenon lamp was employed as light source for generation of a monochromatic beam. Calibrations were performed with a standard silicon photodiode. IPCE is defined by $\text{IPCE}(\lambda) = hcJ_{sc}/e\varphi\lambda$, where h is Planck's constant, c is the speed of light in a vacuum, e is the electronic charge, λ is the wavelength in meters (m), J_{sc} is the short-circuit photocurrent density (A m^{-2}), and φ is the incident radiation flux (W m^{-2}).

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Notes and references

1 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737.
2 (*a*) M. K. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, B. Takeru and M. Grätzel, *J. Am. Chem. Soc.*, 2005, **127**, 16835; (*b*) Y. Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide and L. Han, *Jpn. J. Appl. Phys.*, 2006, **45**, L638; (*c*) F. Gao, Y. Wang, D. Shi, J. Zhang, M. Wang, X. Jing, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin and M. Grätzel, *J. Am. Chem. Soc.*, 2008,

130, 10720; (*d*) K.-J. Jiang, N. Masaki, J. Xia, S. Noda and S. Yanagida, *Chem. Commun.*, 2006, 2460; (*e*) A. Yella, H. W. Lee, H. N. Tsao, C. Y. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W. G. Diau, C. Y. Yeh, S. M. Zakeeruddin and M. Grätzel, *Science*, 2011, **334**, 629; (*f*) Y.-C. Chang, C.-L. Wang, T.-Y. Pan, S.-H. Hong, C.-M. Lan, H.-H. Kuo, C.-F. Lo, H.-Y. Hsu, C.-Y. Lin and E. W.-G. Diau, *Chem. Commun.*, 2011, **47**, 8910; (*g*) A. Yella, C.-L. Mai, S. M. Zakeeruddin, S.-N. Chang, C.-H. Hsieh, C.-Y. Yeh and M. Grätzel, *Angew. Chem., Int. Ed.*, 2014, **53**, 1.

3 (*a*) K. Hara, K. Sayama, Y. Ohga, A. Shinpo, S. u Suga and H. Arakawa, *Chem. Commun.*, 2001, 569; (*b*) S. Kim, J. K. Lee, S. O. Kang, J. Ko, J. H. Yum, A. Fantacci, F. D. Angelis, D. Di Censo, M. K. Nazeeruddin and M. Grätzel, *J. Am. Chem. Soc.*, 2006, **128**, 16701; (*c*) Y. Bai, J. Zhang, D. Zhou, Y. Wang, M. Zhang and P. Wang, *J. Am. Chem. Soc.*, 2011, **133**, 11442; (*d*) S. Li, K.-J. Jiang, K. Shao and L. Yang, *Chem. Commun.*, 2006, 2792; (*e*) T. Horiuchi, H. Miura, K. Sumioka and S. Uchida, *J. Am. Chem. Soc.*, 2004, **126**, 12218; (*f*) D. P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt and L. Sun, *Chem. Commun.*, 2006, 2245; (*g*) S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka, P. Liska, P. Comte, P. Pechy and M. Gratzel, *Chem. Commun.*, 2008, 5194; (*h*) T. Bessho, S. M. Zakeeruddin, C.-Y. Yeh, E. W.-G. Diau and M. Graetzel, *Angew. Chem., Int. Ed.*, 2010, **49**, 6646; (*i*) W. Zeng, Y. Cao, Y. Bai, Y. Wang, Y. Shi, M. Zhang, F. Wang, C. Pan and P. Wang, *Chem. Mater.*, 2010, **22**, 1915; (*j*) N. Koumura, Z.-S. Wang, S. Mori, M. Miyashita, E. Suzuki and K. Hara, *J. Am. Chem. Soc.*, 2006, **128**, 14256.

4 (*a*) G. L. Zhang, Y. Bai, R. Z. Li, D. Shi, S. Wenger, S. M. Zakeeruddin, M. Grätzel and P. Wang, *Energy Environ. Sci.*, 2009, **2**, 92; (*b*) G. L. Zhang, H. Bala, Y. M. Cheng, D. Shi, X. J. Lv, Q. J. Yu and P. Wang, *Chem. Commun.*, 2009, 2198; (*c*) J. Y. Liu, D. F. Zhou, M. F. Xu, X. Y. Jing and P. Wang, *Energy Environ. Sci.*, 2011, **4**, 3545; (*d*) S. Haid, M. Marszalek, A. Mishra, M. Wielopolski, J. Teuscher, J.-E. Moser, R. Humphry-Baker, S. M. Zakeeruddin, M. Grätzel and P. Bäuerle, *Adv. Funct. Mater.*, 2012, **22**, 1291; (*e*) M. F. Xu, M. Zhang, M. Pastore, R. Z. Li, F. D. Angelis and P. Wang, *Chem. Sci.*, 2012, **3**, 976; (*f*) N. Cai, R. Z. Li, Y. L. Wang, M. Zhang and P. Wang, *Energy Environ. Sci.*, 2013, **6**, 139; (*g*) M. Zhang, Y. L. Wang, M. F. Xu, W. T. Ma, R. Z. Li and P. Wang, *Energy Environ. Sci.*, 2013, **6**, 2944.

5 S. Y. Qu and H. Tian, *Chem. Commun.*, 2012, **48**, 3039.

6 (*a*) M. Fukuda, K. Kodama, H. Yamamoto and K. Mito, *Dyes Pigm.*, 2004, **63**, 115; (*b*) Z. Qiao, Y. Xu, S. Lin, J. Peng and D. Cao, *Synth. Met.*, 2010, **160**, 1544; (*c*) M. Tantiwiwat, A. Tamayo, N. Luu, X.-D. Dang and T.-Q. Nguyen, *J. Phys. Chem. C*, 2008, **112**, 17402; (*d*) H. Bronstein, Z. Chen, R. S. Ashraf, W. Zhang, J. Du, J. R. Durrant, P. S. Tuladhar, K. Song, S. E. Watkins, Y. Geerts, M. M. Wienk, R. A. J. Janssen, P. S. T. Anthopoulos, H. Sirringhaus, M. Heeney and I. McCulloch, *J. Am. Chem. Soc.*, 2011, **133**, 3272; (*e*) J. C. Bijleveld, A. P. Zoombelt, S. G. J. Mathijssen, M. M. Wienk, M. Turbiez, D. M. Leeuw and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2009, **131**, 16616.

7 (*a*) S. Y. Qu, W. J. Wu, J. L. Hua, C. Kong, Y. T. Long and H. Tian, *J. Phys. Chem. C*, 2010, **114**, 1343; (*b*) C. Kanimozhi, P. Balraju, G. D. Sharma and S. Patil, *J. Phys. Chem. C*, 2010, **114**, 3287; (*c*) J. Warnan, L. Favereau, Y. Pellegrin, E. Blart, D. Jacquemin and F. Odobel, *J. Photochem. Photobiol., A*, 2011, **226**, 9; (*d*) S. Y. Qu, C. J. Qin, A. Islam, Y. Z. Wu, W. H. Zhu, J. L. Hua, H. Tian and L. Y. Han, *Chem. Commun.*, 2012, **48**, 6972; (*e*) S. Y. Qu, B. Wang, F. L. Guo, J. Li, W. J. Wu, C. Kong, Y. T. Long and J. L. Hua, *Dyes Pigm.*, 2012, **92**, 1384; (*f*) T. W. Holcombe, J.-H. Yum, J. Yoon, P. Gao, M. Marszalek, D. Di Censo, K. Rakstys, M. K. Nazeeruddin and M. Grätzel, *Chem. Commun.*, 2012, **48**, 10724.

8 (*a*) J.-H. Yum, W. H. Thomas, Y. Kim, J. Yoon, K. Raksty, M. K. Nazeeruddina and M. Grätzel, *Chem. Commun.*, 2012, **48**, 10727; (*b*) J.-H. Yum, T. W. Holcombe, Y. Kim, K. Rakstys, T. Moehl, J. Teuscher, J. H. Delcamp, M. K. Nazeeruddin and M. Grätzel, *Sci. Rep.*, 2013, **3**, 2446.

9 F. Zhang, K.-J. Jiang, J.-H. Huang, C.-C. Yu, S.-G. Li, M.-G. Chen, L.-M. Yang and Y.-L. Song, *J. Mater. Chem. A*, 2013, **1**, 4858.

10 M. Grätzel, *Nature*, 2001, **414**, 338.

11 A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595.

12 S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Péchy and M. Grätzel, *Prog. Photovoltaics*, 2007, **15**, 603.

13 (*a*) J.-H. Yum, E. Baranoff, S. Wenger, M. K. Nazeeruddin and M. Gratzel, *Energy Environ. Sci.*, 2011, **4**, 842; (*b*) C.-M. Lan, H.-P. Wu, T.-Y. Pan, C.-W. Chang, W.-S. Chao, C.-T. Chen, C.-L. Wang, C.-Y. Lin and E. W.-G. Diau, *Energy Environ. Sci.*, 2012, **5**, 6460; (*c*) M. Cheng, X. Yang, F. Zhang, J. Zhao and L. Sun, *J. Phys. Chem. C*, 2013, **117**, 9076; (*d*) L. Yu, K. Fan, T. Duan, X. Chen, R. Li and T. Peng, *ACS Sustainable Chem. Eng.*, 2014, DOI: 10.1021/sc400532g; (*e*) C.-L. Wang, J.-Y. Hu, C.-H. Wu, H.-H. Kuo, Y.-C. Chang, Z.-J. Lan, H.-P. Wu, E. W.-G. Diau and C.-Y. Lin, *Energy Environ. Sci.*, 2014, **7**, 1392.

14 (*a*) C. Kim, J. Liu, J. Lin, A. B. Tamayo, B. Walker, G. Wu and T.-Q. Nguyen, *Chem. Mater.*, 2012, **24**, 1699; (*b*) L. Dou, J. Gao, E. Richard, J. You, C.-C. Chen, K. C. Cha, Y. He, G. Li and Y. J. Yang, *J. Am. Chem. Soc.*, 2012, **134**, 10071.

15 F. Fabregat-Santiago, J. Bisquert, G. Garcia-Belmonte, G. Boschloo and A. Hagfeldt, *Sol. Energy Mater. Sol. Cells*, 2005, **87**, 117.

16 J. Luo, M. Xu, R. Li, K.-W. Huang, C. Jiang, Q. Qi, W. Zeng, J. Zhang, C. Chi, P. Wang and J. Wu, *J. Am. Chem. Soc.*, 2013, **136**, 265.

17 Y. b. Xu, Y. Jin, W. h. Lin, J. b. Peng, H. f. Jiang and D. Cao, *Synth. Met.*, 2010, **160**, 2135.

18 P. Wang, S. M. Zakeeruddin, P. Comte, R. Charvet, R. Humphry-Baker and M. Grätzel, *J. Phys. Chem. B*, 2003, **107**, 14336.

19 S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin and M. Grätzel, *Thin Solid Films*, 2008, **516**, 4613.