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Molecular Design to Improve the Performance of Donor–π Acceptor Near-IR Organic Dye-Sensitized Solar Cells

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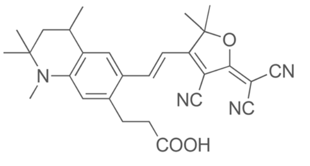
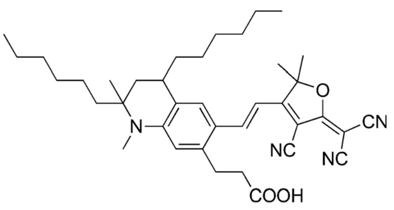
Since Grätzel and O'Brian first reported dye-sensitized solar cells (DSCs) in 1991, much effort has been devoted towards improving their energy conversion efficiency.[1–3] Recently, the design and synthesis of infrared/near-infrared (IR/near-IR)-dyes has become an important topic in the area of solar cells since it has been recognized that the solar spectrum has a large photon flux in the region of 500–1000 nm. Improving the absorption of solar light in this region is one of the main directions in aiming for DSC efficiencies beyond 15 %. Near-IR sensitizers are also of interest because of their potential applications in transparent solar cells for windows and tandem cells.

When used in DSCs, near-IR dyes reported in the literature, such as squaraines,[4–6] zinc phthalocyanines[7–10] and perylene dyes,[11–13] normally show low incident-photon-to-current conversion efficiency (IPCE) values and poor stability compared to donor–π spacer–acceptor (D–π-A) organic dyes. Recently, Ko[5] and Marder[6] independently reported several panchromatic squaraine sensitizers, which yielded relatively high power conversion efficiencies (PCEs) (6.29 % and 6.74 %) under AM 1.5 G irradiation. However, both displayed low IPCE values (< 70 %) from in the wavelength range 400–770 nm. Also, although a promising PCE of 4.6 % was achieved in a DSC based on a structurally related zinc phthalocyanine by Taya and co-workers,[9] the highest IPCE value was only 80 % at 680 nm.

Recently, novel D–π-A organic dyes with two features were reported: new chromophores for sensitization in the near-IR region and new design of the anchoring group.[14] Compared to conventional D–π-A dyes (that use cyanoacrylic acid as acceptor and anchoring group), the anchoring group in these dyes was separated from the acceptor units. This change allowed tuning of the highest occupied–lowest unoccupied molecular orbital (HOMO–LUMO) levels (absorption spectra) in an easier way, through modifying the structure of the acceptor units. By adopting this strategy, we succeeded for the first time in extending the absorption spectra of D–π-A sensitizers for DSCs to the near-IR region. In particular, the dye HY103 gave a maximum IPCE of 86 % at 660 nm and an overall solar-energy-to-electricity conversion efficiency (η) of 3.7 %. The low open-circuit voltage (464 mV) limited its photovoltaic performance.



HY103



HY113

To improve this system, we report a novel D–π-A organic dye with a lateral anchoring group: HY113. In HY113, a flexible, long carbon chain replaces the methyl group of the donor part of HY103. The aim of the present work is to make use of this carbon chain to prevent the formation of molecular aggregates on the semiconductor nanoparticles, thereby blocking charge recombination at relatively high open-circuit voltages and short-circuit photocurrent densities. HY113 performed impressively, with a maximum IPCE of 93 % at 660 nm and an overall solar-energy-to-electricity conversion efficiency of 5.1 %; the highest IPCE value in the near-IR region and the highest PCE value of a D–π-A organic dye in the near-IR region reported so far for DSCs.

The synthesis of HY113 was conducted in eight steps in moderate yields, in a manner similar to HY103. Related synthetic procedures of these dyes and their DSCs fabrication process are described in Scheme 1 and the Supporting Information.

Figure 1 shows optical absorption spectra of HY113 in CH_2Cl_2 solution and on TiO_2 film. The peak of HY113 in CH_2Cl_2 at 615 nm ($\varepsilon = 88867\,\text{M}^{-1}\,\text{cm}^{-1}$) is due to the π–π* transition of the conjugated molecule. The absorption spectrum of HY113/TiO_2 shows a peak at 650 nm, that is, red-shifted by 35 nm compared to the dye in solution. This red-shift might be due to interactions between the TiO_2 surface and the acceptor moiety of the dye molecule. Usually, deprotonation of the carboxyl group of a dye anchored on the surface of TiO_2 causes a blue-shift.[15] J-aggregation may also be involved. This observed red-shift warrants further investigation.

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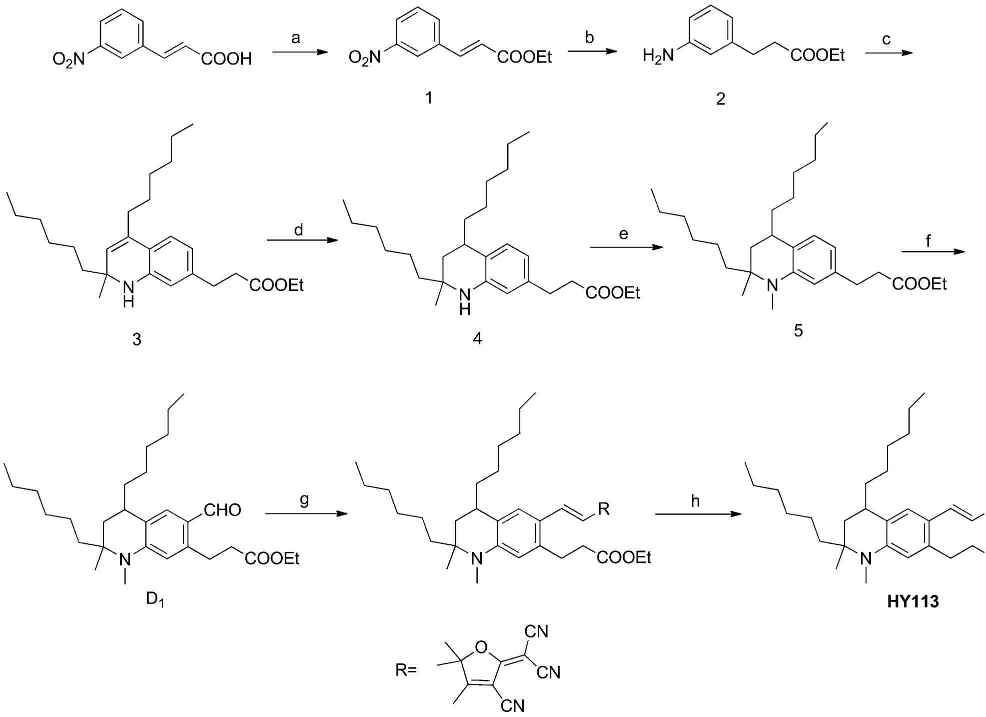

Scheme 1. Synthetic route towards HY113. Reagents and conditions: a) EtOH, concentrated H_2SO_4, reflux (overnight), 74 %; b) EtOH, Pd/C (5 %), 4 h, 81 %; c) 2-octanone, *p*-TsOH, cyclohexane, 80–90 °C, 8–10 h, 49 %; d) Raney-Ni, H_2 (1 MPa), 130 °C, 99 %; e) $(CH_3)_2SO_4$, benzene, reflux 2 h, 79 %; f) DMF/$POCl_3$, 55 °C, 6 h, 55 %; g) 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran/2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile/2,2′-(1H-indene-1,3(2 H)-diylidene)dimalononitrile, pyridine, acetic acid, room temperature (overnight); h) 2.0 M aqueous LiOH, EtOH, 50 °C, 5 h, quantitative.

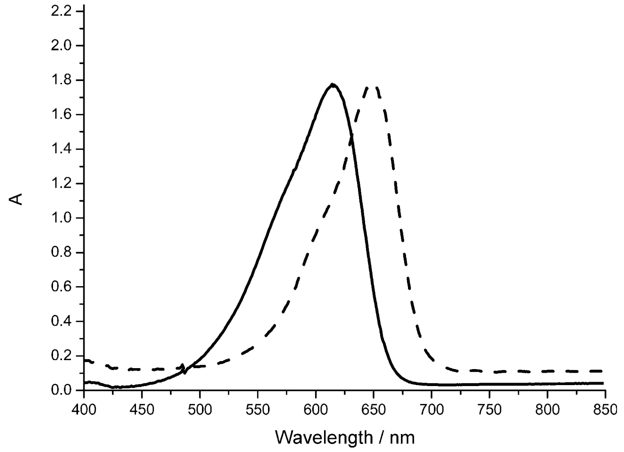

Figure 1. UV/Vis spectra of HY113 in CH_2Cl_2 solution (2×10^{-5} M; solid line) and on TiO_2 film (dashed line).

Table 1. Absorption and electrochemical properties of HY113.

Dye	Absorption[a] λ_{max} [nm]	ε [$M^{-1}cm^{-1}$]	λ_{max} on TiO_2[b] [nm]	E_{0-0}[c] [V]	E_{ox}[d] [V]	$E_{ox}-E_{0-0}$ [V]
HY113	615	88 867	650	1.922	1.098	−0.820

[a] Absorption, emission spectra were measured in CH_2Cl_2 solution (2×10^{-5} M) at room temperature. [b] Absorption spectra on TiO_2 were obtained by measuring the dye adsorbed on TiO_2 film in CH_2Cl_2. [c] E_{0-0} was estimated from onset point of absorption spectra. [d] The oxidation potential of the dyes were measured in CH_3CN with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as electrolyte (working electrode: glassy carbon; reference electrode: Ag/Ag^+; calibrated with ferrocene/ferrocenium (Fc/Fc^+) as an internal reference and converted to NHE by addition of 630 mV,[17] counter electrode: Pt).

The oxidation potential (E_{ox}) of HY113, corresponding to its HOMO level, was measured by cyclic voltammetry (CV) in CH_3CN solution (Table 1) at 1.098 V vs. NHE, sufficiently more positive than the iodine/triiodide redox potential value (0.4 V vs. NHE). This indicates that thermodynamically, the oxidized dye formed after electron injection into the CB of TiO_2 could accept electrons from I^-. In addition, the LUMO level of HY113 was −0.820 V, more negative than E_{cb} of TiO_2 (−0.5 V vs. NHE),[16] indicating that HY113 has enough driving force for electron injection from its excited state. Because the HOMO level of the dye is much more positive than the redox potential of iodine, it is possible to optimize the molecule structure of the dye to extend its absorption spectrum further into infrared region.

The IPCE of a cell based on HY113 is shown in Figure 2. A device based on HY113 gave high IPCE values between 480 nm and 800 nm, with a highest value of 93 % at 660 nm; the highest IPCE value for near-IR dyes in DSCs reported so far. The relatively high IPCE values in the 600–800 nm range are particularly intriguing because of their potential applications in solid-state solar cells and possible tandem systems.

The DSC was fabricated in CH_2Cl_2 (2×10^{-4} M) with chenodeoxycholic acid (2×10^{-4} M) as co-adsorbent. It shows an im-

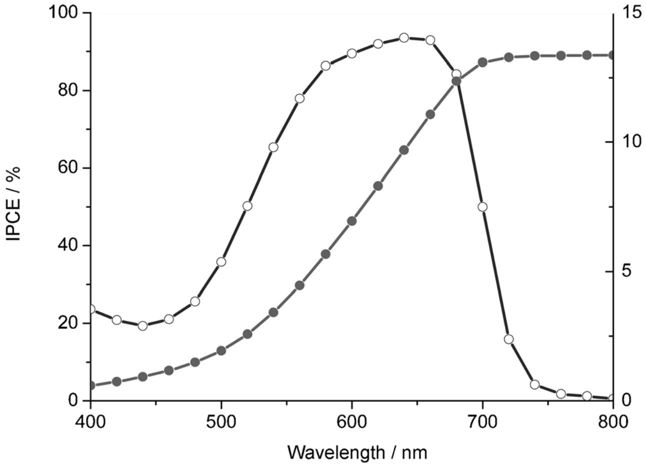

Figure 2. Spectral response of the photocurrent of DSC based on HY113 dye. The left ordinate shows the IPCE as a function of the wavelength of monochromatic light (○). The right ordinate shows the integral of the IPCE with AM 1.5 G solar emission (ASTM G173-03 Reference Spectra Derived from SMARTS v. 2.9.2) against wavelength (●).

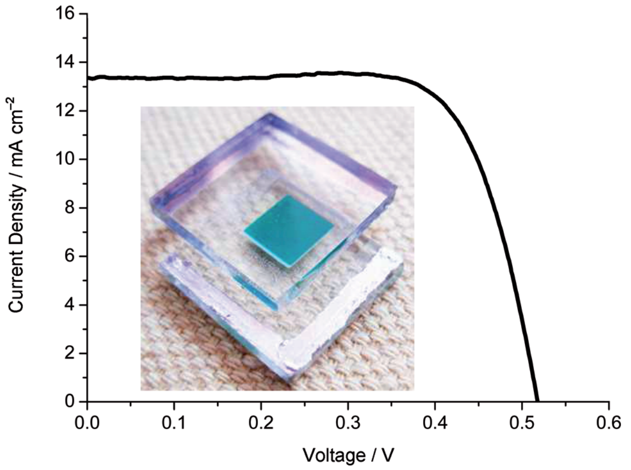

Figure 3. Photovoltaic performance of a DSC based on HY113.

pressive performance, with 5.1 % efficiency under simulated solar irradiation (Figure 3 and Table 2) with a short-circuit current J_{sc} of 13.35 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 519 mV, and a fill factor (*FF*) of 0.73. To the best of our knowledge, this is the highest efficiency ever reported for organic near-IR dye-sensitized TiO_2 solar cells. Compared to the cell based on the dye HY103 reported earlier, the J_{sc} of the device based on HY113 was increased by 1.5 mA cm^{-2} and the V_{oc} was also increased by 55 mV. As a result, the solar-energy-to-electricity conversion efficiency of the DSC based on HY113 was considerably increased, from 3.7 % to 5.1 % (i.e., by about 35 %). This result corroborates our initial design of the dye structure. The long flexible carbon chain in HY113 may function as barrier to block the charge recombination between electrons in the conduction band of TiO_2 and the oxidized dye. The IPCE at maximum absorption reached 93 %, and integration of the curve over the spectrum gave a short-circuit current J_{sc} of 13.35 mA cm^{-2}, in agreement with the measured value.

Table 2. Photovoltaic performance of DSCs based on HY103 and HY113 dyes.[a]

Dye	J_{sc} [mA cm^{-2}]	V_{oc} [mV]	Fill factor	η [%]
HY103	11.76	464	0.67	3.7
HY113	13.35	519	0.73	5.1

[a] Irradiated light: AM 1.5 G (100 mW cm^{-2}); working area: 0.159 cm^2; electrolyte: 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide (DMPII), 0.5 M LiI, 0.02 M I_2, 0.1 M tetrabutyl ammonium iodide (TBAI) in acetonitrile/valeronitrile = 85:15.

Figure 4 shows electrochemical impedance spectra (EIS)[18–21] for devices based on HY103 and HY113 under forward bias (−0.6 V) in the dark. The larger semicircles in the Nyquist plots are attributed to the charge-transfer processes occurring at the TiO_2/dye/electrolyte interface. Evidently, the charge-transfer resistance at the interface of the device based on HY113 was decreased in comparison to the device based on HY103. The addition of the long carbon chain (HY113) shifts the mid-frequency peak to lower frequencies, as seen in Figure 4 b. The calcu-

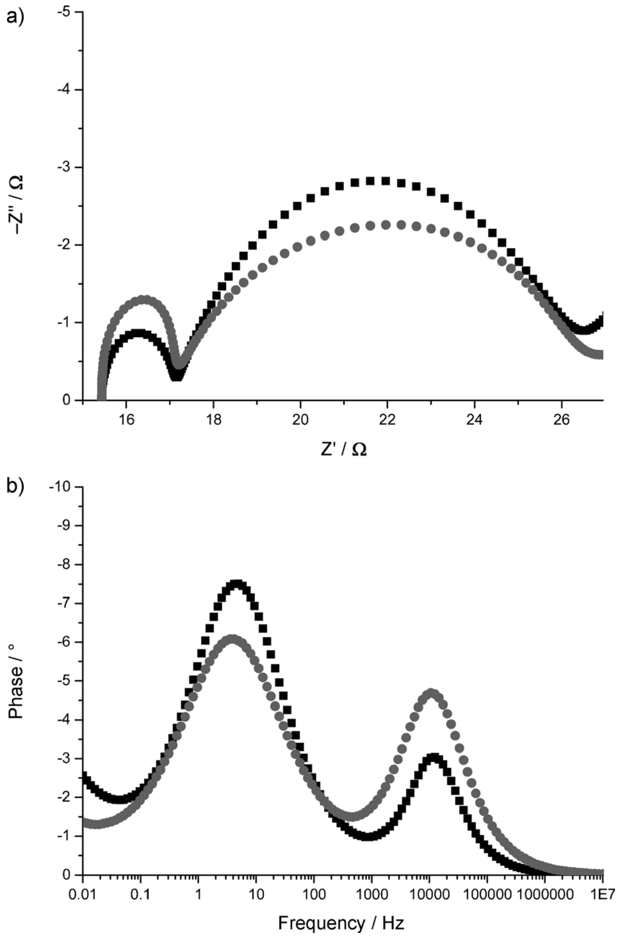

Figure 4. Electrochemical impedance spectra, scanned from 10^{-2} to 10^7 Hz at room temperature, for devices based on HY103 and HY113. a) Nyquist plots, and b) Bode phase plots. The cells were measured at −0.6 V in the dark. The alternate current (AC) amplitude was set at 10 mV.

lated EIS with variation of the electron lifetime shows qualitatively the same behavior. The electron lifetime (τ) in TiO_2 film for DSC sensitized by the dye HY113 is 42 ms, which is longer than that for the DSC sensitized by the dye HY103 (32 ms). It can be concluded that the charge recombination is suppressed for the device based on the HY113, increasing both the electron lifetime in TiO_2 and the photovoltage. This result is in accordance with the increased V_{oc} and J_{sc} of cells based on HY113.

Figure 5 shows the amounts of HY103 and HY113 dye adsorbed on TiO_2 films sensitized in CH_2Cl_2 solvent.[22] The absorbed amounts of dye are 9.02×10^{-5} mM cm^{-2} and 3.645×10^{-5} mM cm^{-2} for devices sensitized by HY103 and HY113, respectively. That is, a higher amount of dye HY103 absorbed, but the device had a lower J_{sc} than the one with HY113. This result reveals that HY103 has stronger tendency to aggregate on TiO_2. The flexible long carbon chains in the dye HY113 minimize molecular aggregation, on the semiconductor nanoparticles, leading to the higher J_{sc} and V_{oc} values.

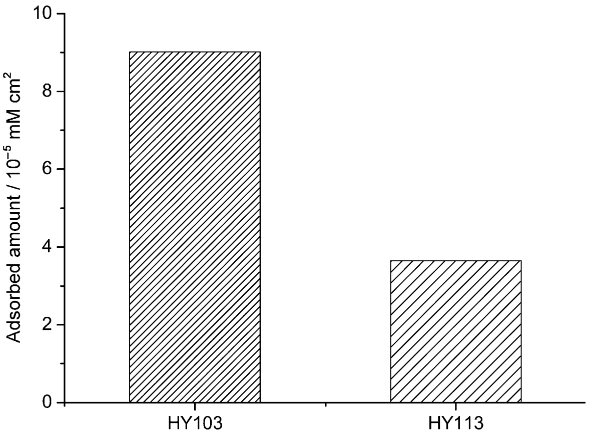

Figure 5. Adsorbed amount of dyes HY103 and HY113 on TiO_2 films sensitized in CH_2Cl_2 solvent.

In conclusion, we demonstrate that D–π-A near-IR organic dyes with lateral anchoring groups are efficient sensitizers. The dye HY113 gives maximum IPCE value of 93 % at 660 nm and an overall solar-energy-to-electricity conversion efficiency of 5.1 %. These are the highest IPCE value of a near-IR organic dye and the highest PCE value of a D–π-A near-IR organic dye reported in DSCs. The stability of the dyes in photovoltaic devices is good, with increased PCE in a month under the usual sunlight at room temperature. Further structural optimization of dyes to reduce the aggregation on TiO_2 and to direct the charge distribution in the excited states of the dyes is likely to yield more efficient DSCs. Also, further accurate stability analysis is in progress.

Experimental Section

Ethyl 3-(2,4-dihexyl-2-methyl-1,2-dihydroquinolin-7-yl)propanoate (**3**): To a solution of ethyl 3-(3-aminophenyl)propanoate **2** (38.6 g, 0.2 mol) and toluenesulfonic acid (1.9 g) in cyclohexane (20 mL), 2-octanone (89 mL, 0.57 mol) was added at 80~90 °C for 8~10 h. The resulting water was removed by co-boiling with cyclohexane. Sodium carbonate (0.55 g) in water (20 mL) was poured into the reaction mixture. The reaction mixture was stirred overnight at RT for 1 h. The organic layer was washed with water and dried over magnesium sulfate. The solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel, acetic ester/hexane = 1:20) to give **3** as colorless oil. (20.72 g, 25 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): $\delta = 6.97$ (d, $J = 7.7$ Hz, 1 H), 6.42 (d, $J = 7.6$ Hz, 1 H), 6.26 (s, 1 H), 5.15 (s, 1 H), 4.13 (q, $J = 7.1$ Hz, 2 H), 3.54 (s, 1 H), 2.79 (t, $J = 7.8$ Hz, 2 H), 2.57 (t, $J = 8.0$ Hz, 2 H), 2.31 (m, 2 H), 1.51 (m, 5 H), 1.29 (m, 19 H), 0.88 ppm (dd, $J = 15.7$, 6.7 Hz, 6 H). HRMS-EI (m/z): $[M]^+$ calcd. for $C_{27}H_{43}NO_2$, 413.3294; found, 413.3284.

Ethyl 3-(2,4-dihexyl-2-methyl-1,2,3,4-tetrahydroquinolin-7-yl)propanoate (**4**): To a solution of **3** (12.05 g) in absolute ethanol was added a 50 % (w/w) slurry of Raney nickel in ethanol (1 g). The reaction was hydrogenated over H_2 gas (1 MPa) at 130 °C. The resulting solution was filtered carefully over celite and washed with ethanol. The solvent was removed in vacuo and the residue **4** (12 g, ~99 %) was used for the next reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.09$ (d, $J = 7.8$ Hz, 1 H), 6.52 (d, $J = 7.7$ Hz, 1 H), 6.35 (s, 1 H), 4.14 (q, $J = 7.1$ Hz, 2 H), 2.80 (m, 3 H), 2.57 (t, $J = 8.0$ Hz, 2 H), 1.74 (dd, $J = 14.3$, 11.1 Hz, 2 H), 1.61 (m, 5 H), 1.27 (m, 21 H), 0.88 ppm(dd, $J=11.0$, 6.3 Hz, 6 H). HRMS-EI (m/z): $[M]^+$ calcd. for $C_{27}H_{45}NO_2$, 415.3450; found, 415.3460.

Ethyl 3-(2,4-dihexyl-1,2-dimethyl-1,2,3,4-tetrahydroquinolin-7-yl)propanoate (**5**): **4** (4.15 g, 10 mmol) and $(CH_3)_2SO_4$ (0.76 g, 6 mmol) were dissolved in benzene. The mixture was refluxed overnight. 10 % NH_4OH (10 mL) was added at 70 °C and stirred for 1 h. The organic layer was dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by chromatography (silica gel, dichloromethane/hexane = 1:2) to provide **5** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.04$ (d, $J = 7.6$ Hz, 1 H), 6.48 (d, $J = 7.5$ Hz, 1 H), 6.41 (s, 1 H), 4.14 (q, $J = 7.1$ Hz, 2 H), 2.88 (t, $J = 7.8$ Hz, 2 H), 2.76 (s, 3 H), 2.61 (m, 3 H), 1.65 (dd, $J = 14.5$, 11.0 Hz, 2 H), 1.49 (m, 5 H), 1.27 (m, 21 H), 0.88 ppm(dd, $J=11.2$, 6.4 Hz, 6 H). HRMS-EI (m/z): $[M]^+$ calcd. for $C_{28}H_{47}NO_2$, 429.3607; found, 429.3613.

Ethyl 3-(6-formyl-2,4-dihexyl-1,2-dimethyl-1,2,3,4-tetrahydroquinolin-7-yl)propanoate (**D1**): $POCl_3$ (0.49 mL, 5.4 mmol) was added dropwise with stirring to a solution of **5** (2.27 g, 5.3 mmol) in fresh distilled DMF (1.3 mL, 16.7 mmol) at 15~20 °C under N_2. The mixture was held at 55 °C for 6 h and then cooled, ice (100 g) was added, and then 5 N NaOH to pH 6. The mixture was extracted further with dichloromethane (3×20 mL) and water. The combined organic layers were dried over $MgSO_4$. The solvent was removed by rotary evaporation and the residue was purified by column chromatography (silica gel, dichloromethane) to provide **D1**: light yellow oil (yield 89 %). HRMS-EI (m/z): $[M]^+$ calcd. for $C_{29}H_{47}NO_3$, 457.3556; found, 457.3567.

(*E*)-3-(6-(2-(4-cyano-5-(dicyanomethylene)-2,2-dimethyl-2,5-dihydrofuran-3-yl)vinyl)-2,4-dihexyl-1,2-dimethyl-1,2,3,4-tetrahydroquinolin-7-yl)propanoic acid (**HY113**): A mixture of **D1** (1.12 g, 2.45 mmol), 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (0.48 g, 2.40 mmol), pyridine (20 mL), and several drops of acetic acid was stirred at room temperature overnight. Pyridine was distilled out under vacuum. The resulting coarse product was used in the next step without further purification. The residue ester was hydrolyzed in 2 M LiOH in equal volume of ethanol and water by heating at 50 °C for 5 h. The reaction mixture was diluted by water and the solution pH was adjusted to 6 by adding 1 M HCl at room temperature. The mixture was diluted with 100 mL of 1 M citric acid and washed with ethyl acetate (3×75 mL). The combined organic layers were washed with ice-cold H_2O (3×100 mL), dried ($MgSO_4$), and concentrated under reduced pressure. After chromatography purification (silica gel, CH_2Cl_2/MeOH = 50:1 as eluent), the target compound was obtained as dark solids (yield 90%). ^{1}H NMR (400 MHz, [D_6]acetone): $\delta = 8.36$ (d, $J = 15.50$ Hz, 1H), 7.78 (s, 1H), 6.90 (d, $J = 15.5$ Hz, 1H), 6.71 (s, 1H), 3.11 (t, $J = 7.8$ Hz, 2H), 3.04 (s, 3H), 2.80 (m, 1H), 2.65 (t, $J = 7.6$ Hz, 2H), 1.89 (dd, $J = 14.3$, 11.1 Hz, 2H), 1.82 (s, 6H), 1.62 (m, 7H), 1.35 (m, 16H), 0.88 ppm (dd, $J = 13.7$, 6.8 Hz, 6H).

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