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A structural study of 1-phenyl-1,2,3,4-tetrahydroquinoline-based dyes for solid-state DSSC applications



PIGMENTS

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ABSTRACT

D- π -A architecture metal-free organic dyes, with a tetrahydroquinoline unit as electron donor, were designed and synthesized for solid-state dye-sensitized solar cells. The sensitizer series was designed to develop a structure–property relationship. These dyes are obtained from relatively cheap starting materials, without the use of expensive catalysts, rigorously anhydrous or oxygen-free conditions. The highest solid-state device conversion efficiency (η) 3.3% ($J_{SC} = -5.9$ mA cm⁻², $V_{OC} = 780$ mV) and fill factor *FF* = 0.72 under 100 mW cm⁻² (AM 1.5G) solar irradiation was achieved with dye **D4** employing a hydrazone fragment as the spacer between the donor 3-alkoxy-1-phenyl-1,2,3,4-tetrahydroquinoline and the rhodanine acceptor of the sensitizer.

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1. Introduction

Dye-sensitized solar cells (DSSCs) are regarded as the coming photovoltaics generation, and significant progress has been made since their inception in 1991 [1,2]. DSSCs are fabricated from cheap, easily processable materials, deriving their competitive performance from judicious molecular design and control of nanoarchitecture.

Ruthenium complexes as molecular sensitizers have shown impressive solar-to-electric power conversion efficiencies (PCE) in liquid electrolyte based devices, with the PCE reaching over 11% under standard AM1.5G full sunlight [3–7]. However, the disadvantages of liquid electrolyte based DSSCs, such as solvent evaporation and leakage, as well as corrosive and photochemical properties of iodine are strong driving forces in the search for alternatives. One of the possible solutions could be solid-state DSSCs (ssDSSCs) [8,9].

In ssDSSCs a solid hole-transporting material (HTM) is employed to replace the liquid redox electrolyte which is responsible for the dye regeneration and hole transfer to the counter electrode. Due to insufficient conductivity of solid organic HTMs, the ssDSSCs are currently restricted to using titania films $<3 \mu m$. Therefore, high molar extinction coefficient dyes are of great importance for this type of device in order to allow the use of thinner films.

In recent years, metal-free organic dyes have attracted increasing attention as they do not contain any toxic or costly metal and their properties are easily tuned by facile structural modification. In addition, they generally have much higher extinction coefficients when compared to Ru(II) polypyridyls, making them excellent for use in solid state DSSCs in combination with hole transporting materials such as P3HT [10] or spiro-MeOTAD [11].

A number of organic dye sensitizers have so far been developed, and the relationship between their chemical structures and photovoltaic performances of DSSC's based on the dyes has been examined. Generally, metal-free organic dyes possess the evident molecular structure on the donor and acceptor parts bridged by the conjugated fragment [12]. A large variety of donors has been investigated, including derivatives of indoline, coumarin, triarylamine, heteroanthracene, carbazole, phenothiazine, N,Ndialkylaniline, fluorine, and efficiencies of $\sim 10\%$ with liquid electrolytes [13–17] and up to 6% with solid HTM [18,19] have been reached.

Among other factors, the structure of the electron-donating group has a crucial influence on the conversion efficiency of the solar energy into electricity in DSSCs. To get a better understanding



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of the relationship between dye structure, photophysical and photoelectrochemical properties, and performance of the DSSCs, a series of different D- π -A organic dyes (Fig. 1) has been designed, synthesized, and investigated for the application in ssDSSCs. These dyes have been constructed based on the electron-donating moiety: 3-hydroxy-1-phenyl-1,2,3,4-tetrahydroquinoline. Tetrahydroquinoline donor is synthesized using simple and practical one-pot reaction route [20,21].

2. Experimental details

2.1. General

The purification of the reaction mixtures was performed by flash chromatography using a glass column with silica gel (0.035-0.070 nm, pore diameter ca. 6 nm). For thin layer chromatographic (TLC) analysis. Merck precoated TLC plates (silica gel 60 F254) were used. Melting points were determined on a Kleinfeld melting point apparatus (Capillary Melting point Apparatus) and are uncorrected. ¹H (300 MHz) and ¹³C NMR (75 MHz) NMR spectra were recorded at room temperature with a Varian Unity Inova spectrometer, ¹H (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded at room temperature with a Bruker Avance III 400 spectrometer. The chemical shifts, expressed in ppm, were relative to tetramethylsilane (TMS). Infrared spectra were recorded on a Bruker Tensor 27 spectrometer using KBr pellets. UV-Vis spectra were recorded on Perkin Elmer Lambda 35 UV/Vis spectrometer. Fluorescence spectra were recorded on a Perkin Elmer LS 55 spectrometer. Elemental analysis (C, H, and N) was done using Exeter Analytical CE-440 elemental analyzer, Model 440 C/H/N/.

2.2. Cyclic-voltammetry measurements

The electrochemical studies were carried out by a threeelectrode assembly cell from Bio-Logic and a Bio-Logic SP-150 potentiostat-galvanostat. The measurements were carried out with a glassy carbon electrode in dichloromethane solutions containing 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte, Ag/AgNO₃ as the reference electrode and a Pt wire counter electrode.

2.3. Ionization potential measurements

The ionization potential I_p of the layers of the synthesized compounds was measured by the electron photoemission in air method [22,23]. The samples for the ionization potential measurement were prepared by dissolving materials in CHCl₃ and

were coated on Al plates pre-coated with ~0.5 μ m thick methylmethacrylate and methacrylic acid copolymer adhesive layer. The thickness of the transporting material layer was 0.5–1 μ m. Usually the photoemission experiments are carried out in vacuum and high vacuum is one of the main requirements for these measurements. If vacuum is not high enough, the sample surface oxidation and gas adsorption are influencing the measurement results. In our case, however, the organic materials investigated are stable enough to oxygen and the measurements may be carried out in air.

The samples were illuminated with monochromatic light from a guartz monochromator with deuterium lamp. The power of the incident light beam was $(2-5) \cdot 10^{-8}$ W. A negative voltage of -300 V was supplied to the sample substrate. The counterelectrode with a $4.5 \times 15 \text{ mm}^2$ slit for illumination was placed at 8 mm distance from the sample surface. The counter-electrode was connected to the input of the BK2-16 type electrometer, working in the open input regime, for the photocurrent measurement. A 10^{-15} - 10^{-12} A strong photocurrent was flowing in the circuit under illumination. The photocurrent I is strongly dependent on the incident light photon energy hv. The $I^{0.5} = f(h\nu)$ dependence was plotted. Usually the dependence of the photocurrent on incident light quanta energy is well described by linear relationship between $I^{0.5}$ and $h\nu$ near the threshold. The linear part of this dependence was extrapolated to the $h\nu$ axis and the $I_{\rm p}$ value was determined as the photon energy at the interception point.

2.4. Computational details

All structures were optimized in the ground state at density functional theory level using the BP86 functional [24,25]. The resolution of the identity approximation and def2-SV(P) double-zeta basis sets with one set of polarization functions except on hydrogens were used in all calculations [26]. Vertical excitation energies and oscillator strengths were obtained without geometry reoptimization at the time-dependent density functional theory level using the B3LYP functional [27,28]. Due to the charge transfer character of the lowest excitation, excitation energies were also calculated using the algebraic diagrammatic construction method to approximate second order (ADC(2)) [29] in combination with the resolution of the identity-approach [30] and a reduced virtual space with a cutoff level of 50 eV (RVS-50) [31]. def2-TZVP-basis sets were used in the RVS-50 ADC(2) calculations. To obtain the electron affinities and ionization potentials, the ground state structures were reoptimized with charges +1 and -1. Single point calculations at BP86/def2-TZVP/COSMO level were done using the anion, cation



Fig. 1. Structures of 1-phenyl-1,2,3,4-tetrahydroquinoline-based dyes D1-D5.

and neutral structures, to obtain electron affinities and ionization potentials [32,33]. The TURBOMOLE program suite was used for all calculations [34].

2.5. Synthesis of dyes

Reagents and solvents were purchased from commercial suppliers and used without further purification. 3-Acetyl-1-phenyl-1,2,3,4-tetrahydroquinoline-6-carbaldehyde (**3**) was synthesized as previously reported [21].

2.5.1. 3-Hydroxy-1-phenyl-1,2,3,4-tetrahydroquinoline-6-carbaldehyde (**4**)

Aldehyde **3** (22.1 g, 75 mmol) was dissolved in 20 ml of methanol by heating, powdered 85% KOH (4.9 g, 75 mmol) was dissolved in 10 ml of H₂O and added to the mixture and it was refluxed for 35 min. At the end of the reaction half of the methanol was removed and the mixture was extracted with ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄, filtered and ethyl acetate was removed. The residue was dissolved in 40 ml of methanol and crystals formed upon standing at the -5 °C temperature. The crystalline product was filtered off, washed with 2propanol and recrystallized from methanol. Yield: 13.8 g (72.8%); m.p.: 198–200 °C (methanol).

¹H NMR (300 MHz, CDCl₃, δ , ppm): 9.61 (s, 1H, CHO), 7.55–7.52 (split s, 1H, H-5 of Het), 7.47–7.22 (m, 6H, Ar), 6.52 (d, *J* = 8.6 Hz, 1H, 8-H of Het), 4.43–4.33 (m, 1H, CH of Het), 3.79 (ddd, *J*₁ = 12.1 Hz, *J*₂ = 2.9 Hz, *J*₃ = 1.4 Hz, 1H, one H of NCH₂), 3.62 (ddd, *J*₁ = 12.1 Hz, *J*₂ = 5.5 Hz, *J*₃ = 1.7 Hz, 1H, other H of NCH₂), 3.16 (dd, *J*_{AB} = 16.2 Hz, *J*_{Ax} = 4.1 Hz, 1H, H_A of CH₂Ar), 2.93 (dd, *J*_{AB} = 16.2 Hz, *J*_{Bx} = 5.3 Hz, 1H, H_B of CH₂Ar), 2.87–2.78 (m, 1H, OH).

IR (KBr; v, cm⁻¹): 3600–3200 (broad): 3036, 2896, 2666, 1653, 1604, 1555, 1491, 1214, 943, 822, 791, 768, 702.

Anal. calcd. for C₁₆H₁₅NO₂: C, 75.87; H 5.97; N 5.53. Found: C, 75.78; H 5.65; N 5.64.

2.5.2. 1-Phenyl-3-propoxy-1,2,3,4-tetrahydroquinoline-6-carbaldehyde (**5a**)

Aldehyde **4** (5.0 g, 19.74 mmol) was dissolved in 50 mL of DMF and 1-brompropane (5.1 mL, 59.22 mmol) was added. Na₂SO₄ (1.12 g, 7.90 mmol) and freshly powdered 85% KOH (3.9 g, 59.22 mmol) were added to the reaction mixture in three portions in 1 h intervals. The reaction mixture was heated at 60–65 °C with intensive stirring. After starting the aldehyde was consumed (TLC control, eluent: acetone/n-hexane, 5/20, v/v) the reaction mixture was cooled to room temperature and extracted with ethyl acetate. The organic layer was dried over MgSO₄, filtered off and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: acetone/n-hexane, 1/24, v/v). Yield of **5a** was 60.0% (3.5 g).

¹H NMR (300 MHz, CDCl₃; δ , ppm): 9.70 (s, 1H, CHO), 7.60–7.23 (m, 7H, Ar), 6.55 (d, J_1 = 8.5 Hz, 1H, 8-H of Het), 4.01–3.92 (m, 1H, CH), 3.80 (ddd, J_1 = 12.0 Hz, J_2 = 3.4 Hz, J_3 = 1.7 Hz, 1H, H_A of NCH₂), 3.63 (ddd, J_1 = 12.0 Hz, J_2 = 6.8 Hz, J_3 = 1.2 Hz, 1H, H_B of NCH₂), 3.56–3.43 (m, 2H, OCH₂), 3.16 (dd, J_1 = 15.9 Hz, J_2 = 4.4 Hz, 1H, H_A of CH₂CH), 2.96 (dd, J_1 = 15.9 Hz, J_2 = 7.2 Hz, 1H, H_B of CH₂CH), 1.66–1.52 (m, 2H, CH₂), 0.90 (t, J_1 = 7.4 Hz, 3H, CH₃).

IR (KBr; v, cm⁻¹): 3062, 3038, 2962, 2935, 2875, 1680, 1607, 1589, 1561, 1507, 1493, 1103, 946, 914, 870, 769, 730, 700.

Anal. calcd. for C₁₉H₂₁NO₂: C, 77.26; H, 7.17; N, 4.74. Found, %: C, 77.42; H, 7.23; N, 4.65.

2.5.3. 3-Nonyloxy-1-phenyl-1,2,3,4-tetrahydroquinoline-6-carbaldehyde (**5b**)

Compound **5b** was prepared similarly to **5a**, except that 1-bromononane (11.3 mL, 59.22 mmol) was used in the reaction. Yield of **5b** was 58.7% (4.4 g).

¹H NMR (300 MHz, CDCl₃; δ , ppm): 9.68 (s, 1H, CHO), 7.62–7.22 (m, 7H, Ar), 6.54 (d, $J_1 = 8.5$ Hz, 1H, 8-H of Ht), 4.02–3.91 (m, 1H, CH), 3.81 (ddd, $J_1 = 12.0$ Hz, $J_2 = 3.4$ Hz, $J_3 = 1.7$ Hz, 1H, H_A of NCH₂), 3.62 (ddd, $J_1 = 12.0$ Hz, $J_2 = 6.8$ Hz, $J_3 = 1.2$ Hz, 1H, H_B of NCH₂), 3.55–3.42 (m, 2H, OCH₂), 3.16 (dd, $J_1 = 15.9$ Hz, $J_2 = 4.4$ Hz, 1H, H_A of CH₂CH), 2.96 (dd, $J_1 = 15.9$ Hz, $J_2 = 7.2$ Hz, 1H, H_B of CH₂CH), 1.60–1.42 (m, 2H, (OCH₂CH₂), 1.36–1.10 (m, 12H, ((CH₂)₆CH₃), 0.84 (t, $J_1 = 6.9$ Hz, 3H, CH₃).

Anal. calcd. for C₂₅H₃₃NO₂: C, 79.11; H, 8.76; N, 3.69. Found, %: C, 78.82; H, 8.43; N, 3.35.

2.5.4. 1-Phenyl-3-propoxy-1,2,3,4-tetrahydroquinoline-6carbaldehyde N-phenylhydrazone (**6a**)

5a (5.00 g, 19.74 mmol) was dissolved in 2-propanol (25 mL) and warmed to 85 °C, phenylhydrazine (2.1 mL, 21.31 mmol) was added and mixture stired for 3 h at 85 °C. After the end of the reaction (TLC control, *n*-hexane/diethyl ether, 3/2, v/v) the mixture was cooled down, obtained crystals were filtered off and washed with a mixture of n-hexane and 2-propanol (2/1, v/v) to give phenylhydrazone **6a** (6.2 g, 95.4%), which was used in the next reaction without further purification.

¹H NMR (400 MHz, CDCl₃; δ, ppm): 7.65 (s, 1H, CH=N), 7.42– 7.36 (m, 4H, Ar), 7.29–7.25 (m, 4H, Ar), 7.22 (dd, $J_1 = 8.6$ Hz, $J_2 = 1.8$ Hz, 1H, Ar), 7.15 (t, $J_1 = 7.3$ Hz, 1H, Ar), 7.02 (d, $J_1 = 7.7$ Hz, 2H, Ar), 6.85 (t, $J_1 = 7.3$ Hz, 1H, Ar), 6.75 (d, J = 8.5 Hz, 1H, 8-H of Het), 3.99–3.89 (m, 1H, CH), 3.82 (ddd, $J_1 = 11.5$, $J_2 = 3.5$ Hz, $J_3 = 1.4$ Hz, H_A of NCH₂), 3.59–3.44 (m, 3H, H_B of NCH₂, OCH₂), 3.18 (dd, $J_1 = 15.8$ Hz, $J_2 = 4.7$ Hz, 1H, H_A of CH₂CH), 2.92 (dd, $J_1 = 15.8$ Hz, $J_2 = 8.0$ Hz, 1H, H_B of CH₂CH), 1.68–1.54 (m, 2H, CH₂), 0.92 (t, $J_1 = 7.4$ Hz, 3H, CH₃).

¹³C NMR (100 MHz, CDCl₃; δ, ppm): 147.5, 145.6, 144.5, 138.3 (N=CH), 129.6, 129.3, 127.9, 125.9, 125.3, 124.8, 124.3, 122.3, 119.6, 115.2, 112.7, 71.4 (CH), 70.5 (OCH₂), 54.1 (N-CH₂), 34.4 (CH₂), 23.3 (CH₂), 10.72 (CH₃).

IR (KBr; ν, cm⁻¹): 3271, 3056, 3028, 2962, 2863, 1593, 1493, 1265, 1098, 1082, 746, 699, 693.

2.5.5. 3-Nonyloxy1-phenyl-1,2,3,4-tetrahydroquinoline-6-

carbaldehyde N-phenylhydrazone (**6b**)

Hydrazone **6b** was prepared similarly to **6a**, except that **5b** (3.8 g, 10 mmol) and an equivalent amount of phenylhydrazine (1.08 g, 10 mmol) were used in the reaction. After the end of the reaction (TLC control, *n*-hexane/diethyl ether, 3/2, v/v) the organic solvent was removed and the oil residue was used in the next reaction without further purification.

2.5.6. 1-Phenyl-3-propoxy-1,2,3,4-tetrahydroquinoline-6carbaldehyde N-(4-formyl)phenyl-N-phenylhydrazone (**7a**)

To the solution of compound **6a** (6.5 g, 16.86 mmol) in dry DMF (40 mL) *p*-fluorobenzaldehyde (3.15 g, 25 mmol) and K_2CO_3 (7.0 g, 50 mmol) were added and stirred at 90 °C under argon atmosphere for 3 h while all starting material was consumed (TLC control, acetone/*n*-hexane, 1/4, v/v). Then reaction mixture was quenched with water and extracted with ethylacetate. The organic layers were combined, washed with brine, dried over Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: acetone/ tetrahydrofuran/n-hexane, 0.5/0.5/24, v/v/v) to afford **7a**. The yield was 42.4% (3.5 g).

¹H NMR (300 MHz, CDCl₃; δ , ppm): 9.80 (s, 1H, CHO), 7.72 (d, J = 9.0 Hz, 2H, Ar), 7.62 (t, J = 7.4 Hz, 2H, Ar), 7.52 (t, J = 7.4 Hz, 1H, Ar), 7.41–7.31 (m, 3H, Ar), 7.28–7.09 (m, 9H, Ar), 6.68 (d, J = 8.6 Hz, 1H, 8-H of Het), 3.98–3.86 (m, 1H, CH), 3.83–3.73 (m, 1H, H_A of NCH₂), 3.61–3.39 (m, 3H, OCH₂, H_B of NCH₂), 3.15 (dd, $J_1 = 15.7$ Hz, $J_2 = 4.6$ Hz, 1H, H_A of CH₂CH), 2.89 (dd, $J_1 = 15.9$ Hz, $J_2 = 7.9$ Hz, 1H, H_B of CH₂CH), 1.65–1.50 (m, 2H, CH₂), 0.89 (t, J = 7.4 Hz, 3H, CH₃).

¹³C NMR (75 MHz, CDCl₃; δ , ppm): 190.9 (CHO), 152.4, 147.6, 145.2, 140.1, 138.8 (N=CH), 131.6, 131.2, 130.1, 129.7, 129.4, 128.8, 128.6, 125.9, 125.6, 125.1, 124.6, 122.2, 115.1, 114.1, 71.3 (CH), 70.6 (OCH₂), 54.2 (NCH₂), 34.4 (CH₂), 23.4 (CH₂), 10.8 (CH₃).

IR (KBr; v, cm⁻¹): 2958, 2926, 2870, 1688, 1600, 1588, 1504, 1494, 1384, 1302, 1221, 1157, 1100, 1061, 826, 699, 545.

Anal. calcd. for C₃₂H₃₁N₃O₂: C, 78.50; H, 6.38; N, 8.58; found: C, 78.41; H, 6.12; N, 8.32.

2.5.7. 3-Nonyloxy-1-phenyl-1,2,3,4-tetrahydroquinoline-6-carbaldehyde N-(4-formyl)phenyl-N-phenylhydrazone (**7b**)

7b was prepared similarly to that of **7a**, except that hydrazone **6b** (2.3 g, 4.9 mmol) was used in the reaction. Yield of **7b** was 57% (4.4 g).

¹H NMR (400 MHz, CDCl₃; δ, ppm): 9.80 (s, 1H, CHO), 7.73 (d, J = 9.0 Hz, 2H, Ar), 7.68–7.08 (m, 15H, Ar), 6.69 (d, J = 8.6 Hz, 1H, 8-H of Het), 3.98–3.86 (m, 1H, CH), 3.83–3.73 (m, 1H, H_A of NCH₂), 3.61–3.39 (m, 3H, OCH₂, H_B of NCH₂), 3.15 (dd, $J_1 = 15.7$ Hz, $J_2 = 4.6$ Hz, 1H, H_A of CH₂CH), 2.89 (dd, $J_1 = 15.9$ Hz, $J_2 = 7.9$ Hz, 1H, H_B of CH₂CH), 1.60–1.48 (m, 2H, OCH₂CH₂), 1.38–1.18 (m, 12H, (CH₂)₆CH₃), 0.87 (t, J = 6.9 Hz, 3H, CH₃).

¹³C NMR (75 MHz, CDCl₃; δ, ppm): 190.8 (CHO), 152.3, 147.3, 145.0, 139.8, 138.5 (N=CH), 131.4, 131.0, 130.0, 129.5, 129.2, 128.6, 128.3, 125.7, 125.4, 124.9, 124.4, 122.0, 114.9, 113.8, 71.1 (CH), 68.8 (OCH₂), 53.9 (N-CH₂), 34.1 (OCH₂CH₂), 31.9, 29.9, 29.5, 29.4, 29.2, 26.1, 22.6 (CH₂), 14.1 (CH₃).

IR (KBr; v, cm⁻¹): 2958, 2926, 2870, 1688, 1600, 1588, 1504, 1494, 1384, 1302, 1221, 1157, 1100, 1061, 826, 699, 545.

Anal. calcd. for C₃₂H₃₁N₃O₂: C, 78.50; H, 6.38; N, 8.58; found: C, 78.41; H, 6.12; N, 8.32.

2.5.8. 2-[5-(3-hydroxy-1-phenyl-1,2,3,4-tetrahydroquinolin-6methylene)-4-oxo-2-thioxothia-zolidin-3-yl]acetic acid (**D1**)

Aldehyde **4** (1.0 g, 3.95 mmol), rhodanine-3-acetic acid (0.9 g, 4.74 mmol) and ammonium acetate (0.1 g, 1.33 mmol) were stirred at 100 °C temperature in 2.5 mL of glacial acetic acid for 20 min. After the termination of the reaction, the obtained crystals were filtrated off, washed with water, followed by the mixture of hexane:propanol (1/1, v/v). The product was recrystallized from ethanol for three times. The yield was 59.5% (1.0 g). M.p.: 218–220 °C (methanol).

¹H NMR (300 MHz, DMSO- d_6 ; δ , ppm): 7.65 (s, 1H, CH=), 7.51– 7.45 (m, 2H, Ar, 5-H of Het), 7.33–7.27 (m, 4H, Ar), 7.20 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.1$ Hz, 1H, 7-H of Het), 6.49 (d, J = 8.8 Hz, 1H, 8-H of Het), 4.66 (s, 2H, CH₂COOH), 4.22–4.16 (m, 1H, CH), 3.75–3.70 (m, 1H, H_A of NCH₂), 3.49 (dd, $J_1 = 12.0$ Hz, $J_2 = 5.8$ Hz, 1H, H_B of NCH₂), 3.10–3.03 (m, 1H, H_A of CH₂CH), 2.79 (dd, $J_1 = 15.9$ Hz, $J_2 = 6.6$ Hz, 1H, H_B of CH₂CH).

¹³C NMR (75 MHz, DMSO- d_6 ; δ, ppm): 192.6 (CS), 167.4 (COOH), 166.4 (CO), 147.1, 145.5, 134.6, 133.7, 130.8, 129.9, 126.2, 121.8, 121.5, 114.3, 113.2, 61.3 (CH), 55.9 (CH₂NCH), 45.2 (CH₂COOH), 35.4 (CH₂CH).

IR (KBr; ν, cm⁻¹): 3462, 2918, 2612, 1710, 1576, 1551, 1512, 1319, 1201, 1243, 1214, 1116, 1067, 926, 698.

UV: λ_{max} , nm ($\epsilon^* 10^4$): 473 (3.59), 323(0.81), 206 (2.21).

Anal. calcd. for C₂₁H₁₈N₂O₄S₂: C, 59.14; H, 4.25; N, 6.57. Found, %: C, 59.17; H, 4.46; N, 6.52.

2.5.9. 2-[4-oxo-5-(1-phenyl-3-propoxy-1,2,3,4-tetrahydroquinolin-6-methylene)-2-thioxo-thiazolidin-3-yl]acetic acid (**D2**)

Aldehyde **5a** (1.0 g, 3.38 mmol), rhodanine-3-acetic acid (0.75 g, 3.93 mmol) and ammonium acetate (0.08 g, 1.04 mmol) were stirred at 100 °C temperature in 2.5 mL of glacial acetic acid for 20 min. After the termination of the reaction (TLC, *n*-hexane/toluene/methanol, 2/2/1, v/v/v) the reaction mixture was cooled to room temperature. Obtained crystals were filtered off, washed with water, then with the mixture of n-hexane/2-propanol (2/1, v/v). The product was recrystallized from ethanol for three times. The yield is 57.0% (0.9 g). M.p.: 191–193 °C (methanol).

¹H NMR (300 MHz, DMSO-*d*₆; δ, ppm): 13.42 (s, 1H, COOH), 7.66 (s, 1H, CH=), 7.51–7.46 (m, 2H, Ar, 5-H of Het), 7.32–7.27 (m, 4H, Ar), 7.20 (d, *J* = 8.8 Hz, 1H, 7-H of Het), 6.49 (d, *J* = 8.8 Hz, 1H, 8-H of Het), 4.70 (s, 2H, CH₂COOH), 3.97 (br.s., 1H, CH), 3.85–3.75 (m, 1H, H_A of NCH₂), 3.64 (dd, *J*₁ = 12.4 Hz, *J*₂ = 4.8 Hz, 1H, H_B of NCH₂), 3.43 (t, *J* = 6.6 Hz, 2H, OCH₂), 3.22–3.08 (m, 1H, H_A of CH₂CH), 2.90 (dd, *J*₁ = 16.2 Hz, *J*₂ = 4.9 Hz, 1H, H_B of CH₂CH), 1.56–1.39 (m, 2H, CH₂CH₃), 0.81 (t, *J* = 7.4 Hz, 3H, CH₃).

¹³C NMR (75 MHz, DMSO- d_6 ; δ, ppm): 192.6 (CS), 167.4 (COOH), 166.3 (CO), 147.2, 145.5, 134.8, 133.5, 131.0, 130.0, 126.1, 121.6, 121.5, 114.3, 113.4, 69.2 (CH), 69.0 (OCH₂), 53.5 (CH₂N), 44.8 (CH₂COOH), 32.7 (CH₂CH), 22.1 (CH₂CH₃), 11.7 (CH₃).

IR (KBr; v, cm⁻¹): 3400–2200, 2961, 2933, 2875, 1730, 1705,1578, 1551, 1512, 1492, 1426, 1396, 1368, 1324, 1305, 1277, 1251, 1229, 1197, 1111, 1056, 641, 698.

UV: λ_{max} , nm ($\epsilon^* 10^4$): 472 (5.06), 322 (1.31), 206 (3.63).

Anal. calcd. for C₂₄H₂₄N₂O₄S₂: C, 61.52; H, 5.16; N, 5.98. Found, %: C, 61.27; H, 5.46; N, 6.32.

2.5.10. 2-{4-oxo-5-[4-(1-phenyl-2-(1-phenyl-3-propoxy-1,2,3,4tetrahydroquinolin-6-methy-lene)hydrazinyl)benzylidene]-2thioxothiazolidin-3-yl}acetic acid (**D3**)

Aldehyde **7a** (1.0 g, 2.04 mmol), rhodanine-3-acetic acid (0.5 g, 2.62 mmol) and ammonium acetate (0.05 g, 0.65 mmol) were stirred at 100 °C temperature in 2 mL of glacial acetic acid for 2 h. After the termination of the reaction (TLC, acetone/*n*-hexane, 1/4, v/ v) the reaction mixture was extracted with ethyl acetate, the organic layer was dried over Na₂SO₄ and concentrated in vacuum. The product was purified by silica gel flash chromatography (eluent: toluene/methanol, 24/1, v/v). The yield of **D3** as dark red solid was 41.5% (0.5 g).

¹H NMR (300 MHz, CDCl₃; δ, ppm): 7.82–7.05 (m, 15H, Ar), 6.94 (dd, J_1 = 8.5 Hz, J_2 = 2.1 Hz, 1H, 7-H, Het), 6.76–6.68 (m, 1H, Ar), 6.41 (d, J = 8.9 Hz, 1H, 8-H, Het), 4.89 (s, 2H, CH₂COOH), 4.04–3.89 (m, 1H, CH), 3.89–3.41 (m, 4H, OCH₂, NCH₂), 3.27–2.84 (m, 2H, CH₂CH), 1.71–1.52 (m, 2H, CH₂CH₃), 1.03–0.83 (m, 3H, CH₃).

IR (KBr; v, cm⁻¹): 3421, 3032, 2930, 2869, 1706, 1576, 1505, 1420, 1380, 1295, 1196, 1176, 1103, 1053, 1002, 822, 751, 697, 640, 524.

UV: λ_{max} , nm ($\epsilon^* 10^4$): 469 (3.93), 373 (2.22), 324 (1.99), 206 (5.16).

Anal. calcd. for C₃₇H₃₄N₄O₄S₂: C, 67.05; H, 5.17; N, 8.45. Found: C, 67.17; H, 5.31; N, 8.58.

2.5.11. 2-{4-oxo-5-[4-(1-phenyl-2-(3-nonyloxy-1-phenyl-1,2,3,4-tetrahydroquinolin-6-methy-lene)hydrazinyl)benzylidene]-2-thioxothiazolidin-3-yl}acetic acid (**D4**)

D4 was prepared similarly to **D3**, except that aldehyde **7b** (1.5 g, 2.04 mmol) was used in the reaction. The product was isolated as dark red solid. The yield was 46.1% (0.9 g).

¹H NMR (400 MHz, CDCl₃; δ , ppm): 7.86–6.80 (m, 16H, Ar), 6.68–6.62 (m, 1H, Ar), 6.50 (d, J = 8.9 Hz, 1H, 8-H, Het), 4.65 (s, 2H, CH₂COOH), 3.95–2.65 (m, 7H, CH₂CH, OCH₂, NCH₂), 1.60–1.42 (m, 2H, OCH₂CH₂), 1.28–1.08 (m, 12H, (CH₂)₆CH₃), 0.92–0.81 (m, 3H, CH₃).



Scheme 1. Synthesis of the aldehyde 4.

IR (KBr; v, cm⁻¹): 3468, 3062, 3034, 2924, 2853, 1709, 1576, 1504, 1426, 1384, 1297, 1197, 1176, 1104, 1054, 1003, 823, 752, 698, 664, 526.

UV: λ_{max} , nm (ϵ *10⁴): 473 (3.83), 372 (2.30), 321 (2.06), 206 (5.15).

Anal. calcd. for C₄₃H₄₆N₄O₄S₂: C, 69.14; H,6.21; N, 7.50. Found: C, 68.87; H, 5.91; N, 7.18.

2.5.12. 2-Cyano-3-{4-[1-phenyl-2-(1-phenyl-3-propoxy-1,2,3,4-tetrahydroquinolin-6-methy-lene)hydrazinyl]phenyl}acrylic acid (**D5**)

Aldehyde **7a** (0.4 g, 0.8 mmol), cianoacetic acid (0.085 g, 1.0 mmol) and ammonium acetate (0.02 g, 0.25 mmol) were stirred at 100 °C temperature in 2 mL of glacial acetic acid for 6 h. After the termination of the reaction (TLC, acetone/n-hexane, v/v 1/4) the reaction mixture was extracted with ethyl acetate, the organic layer was dried over Na_2SO_4 and concentrated in vacuum. The product was purified by flash chromatography (eluent: toluene/methanol, 24/1, v/v). The yield was 66.7% (0.3 g).

¹H NMR (400 MHz, CDCl3; δ, ppm): 7.88–7.11 (m, 18H, Ar, N= CH), 6.80–6.67 (m, 1H, Ar), 3.98–3.69 (m, 2H, CH, H_A of NCH₂), 3.60–3.30 (m, 3H, OCH₂, H_B of NCH₂), 3.21–3.01 (m, 1H, H_A of CH₂CH), 2.99–2.37 (m, 1H, H_B of CH₂CH),1.66–1.45 (m, 2H, CH₂), 0.99–0.72 (m, 3H, CH₃).

IR (KBr; v, cm⁻¹): 3426, 3059, 3035, 2959, 2929, 2872, 2214, 1590, 1504, 1382, 1316, 1302, 1222, 1177, 1064, 830, 699, 515.

UV: λ_{max} , nm ($\epsilon^* 10^4$): 425 (3.95), 357 (1.83), 3.27 (1.60), 244 (1.36), 206 (4.23).

Anal. calcd. for C₃₅H₃₂N₄O₃: C, 75.52; H, 5.79; N, 10.06. Found: C, 75.22; H, 5.51; N, 9.78.

2.6. Fabrication and characterization of the solid-state dyesensitized solar-cells

A TiO₂ blocking layer was prepared on a fluorine-doped tin oxide (FTO)-covered glass substrate using spray pyrolysis [35]. A TiO₂ paste (Dyesol), diluted with terpineol, was applied by screen printing, resulting in a film thickness of 1.7 um. All films were then sintered for 45 min at 450 °C, followed by treatment in a 40 mM aqueous solution of TiCl₄ at 60 °C for 30 min, followed by another sintering step. The prepared samples with TiO₂ layers were pretreated with 5 mM solutions of 2-(p-butoxyphenyl)acetohydroxamic acid sodium salt or 2-(p-butoxyphenyl)acetohydroxamic acid tetrabutylammonium salt in ethanol. The electrodes were then dyed in 0.5 mM dye solution in CH₂Cl₂. Spiro-MeOTAD was applied by spin-coating from a solution in DCM (200 mg/mL) also containing 20 mM Li(CF₃SO₂)₂N. Fabrication of the device was completed by evaporation of 200 nm of silver as the counter electrode. The active area of the ssDSSC was defined by the size of these contacts (0.13 cm^2) , and the cells were masked by an aperture of the same area for measurements. The Current-voltage characteristics for all cells were measured with a Keithley 2400 under 1000 W/m^2 , AM 1.5G conditions (LOT ORIEL 450 W). The incident photon to current conversion efficiencies (IPCE) were obtained with an Acton *Research* Monochromator using additional white background light illumination.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic strategy (Scheme 1) displays the chemical reaction scheme that was used to synthesize the key compound 3hydroxy-1-phenyl-1,2,3,4-tetrahydroquinoline-6-carbal-dehyde (4). 3-Hydroxy-1-phenyl-1,2,3,4-tetrahydroquinoline (1) was obtained by a one-pot reaction of diphenylamine with epichlorohydrin [20,21]. In order to protect the hydroxyl group, 1 was converted to the acylated derivative 2. Vilsmeier-Haack formylation of 2, followed by the deprotection of the hydroxyl group in 3 yielded the desired aldehyde 4.

The synthesis procedure of the dyes **D1**, **D2** possessing a π -conjugated methine unit is depicted in Scheme 2. Condensation of the respective aldehyde **4** with rhodanine-3-acetic acid by the Knoevenagel reaction in the presence of ammonium acetate gave the desired dye **D1** in moderate yield. In order to improve its solubility in organic solvents and reduce the tendency to aggregate, propylation of the hydroxyl group of **4** was carried out. The resulting alkylated compound **5a** with substituted hydroxyl group was used in condensation reaction with rhodanine-3-acetic acid by the Knoevenagel reaction in the presence of ammonium acetate to yield **D2**.

Most of the organic sensitizers applied in DSSCs follow the characteristical pattern of donor and acceptor fragments being linked by a π -conjugation bridge, so called D- π -A structure. Recently it was shown that a bathochromic shift and broadening of the absorption range as well as enhanced absorptivities can be obtained by incorporating a hydrazone fragment as π -conjugation bridge [36]. In the current research we have decided to test a similar approach utilizing hydrazone moieties to form D-hydrazone-A configuration sensitizers. Synthesis of the dyes D3-D5 possessing a phenylhydrazone moiety and alkoxy groups of different chain length attached to the 1-phenyl-1,2,3,4tetrahydroguinoline donoric core is shown in Scheme 2. Condensation of the aldehydes 5a and 5b with phenylhydrazine afforded hydrazones 6a and 6b in quantitative yields. Subsequently, compounds 6a and 6b were used in arylation reaction with 4fluorobenzaldehyde to obtain hydrazones 7a, 7b. Finally, condensation of 7a and 7b with rhodanine-3-acetic acid or cyanoacetic acid by the Knoevenagel reaction in the presence of ammonium acetate yielded the dyes D3-D5.

3.2. Optical, electrochemical and photophysical properties

The absorption, emission, and electrochemical properties of the dye series are listed in Table 1. The UV–Vis spectra of the dyes **D1** and **D2** show absorption bands appearing at 250–360 nm, which are assigned as the π – π * transitions of the conjugated system (Fig. 2). When phenylhydrazone is used as π -conjugation bridge,



5a, 6a, 7a, D3 n=1; 5b, 6b, 7b, D4 n=7.

Scheme 2. Synthesis route to 1-phenyl-1,2,3,4-tetrahydroquinoline-based dyes D1-D5.

there are two absorption bands in this region, one at 322 nm and another one at 374 nm for the dyes **D3** and **D4**. In case of sensitizer **D5**, the second band is hypsochromically shifted by ~20 nm. All of the synthesized dyes, except for **D5**, have absorption maxima at

Table 1 Optical characteristics, HOMO, LUMO, I_n and band gap energies for **D1**-**D5**^a.

Compound	λ ^{abs} (nm) ^b	$(M^{-1} cm^{-1})$	λ ^{abs} (nm) (on TiO ₂)	FL _{max} (nm)	E _{HOMO} (V vs NHE)	E _{LUMO} (V vs NHE)	E ^{CV} (eV) ^c	Ip (eV) ^d
D1	473	35890	472	543	1.15	-1.26	2.41	5.54
D2	472	50590	450	540	1.16	-1.28	2.44	5.39
D3	469	39260	480	627	0.75	-1.32	2.07	5.15
D4	473	38290	485	630	0.74	-1.29	2.03	5.18
D5	425	39520	412	531	0.73	-1.82	2.55	5.11
spiro	387	69600	-	-	0.62	-2.33 ^e	2.95 ^f	5.00

^a CV measurements were carried out at a glassy carbon electrode in dichloromethane solutions containing 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte and Ag/AgNO₃ as the reference electrode. Each measurement was calibrated with ferrocene (Fc). Potentials measured vs Fc+/Fc were converted to normal hydrogen electrode (NHE) by addition of +0.63 V.

^b UV–Vis spectra measured in 10⁻⁴ M THF solution.

^c $E_g^{CV} = E_{HOMO} - E_{LUMO}$.

^d Ionization potential (I_p) was measured by the photoemission in air method from films.

^e $E_{\text{LUMO}} = E_{\text{HOMO}} - E_{\text{g}}^{\text{opt}}$.

^f Optical band gap E_{g}^{opt} estimated from the edge of electronic absorption spectra.

around 470 nm originating from intramolecular charge transfer (ICT) from the tetrahydroquinoline donor moiety to the rhodanine acceptor. Comparing structurally similar dyes **D3** and **D5** bearing different electron accepting units (rhodanine or cyanoacetic acid),

Table 2	
Quantum chemical calculation results	

Molecule	IP (eV) ^a	IP* (eV) ^b	EA (eV) ^c	S1 (nm) ^d	F1 ^e	S2 (nm) ^f	F2 ^g	S1 (nm) ^h	F1 ⁱ
D1	5.69	2.94	3.00	450	0.85	386	0.00	435	0.83
D2	5.63	2.86	2.71	447	0.85	388	0.00	436	0.17
D3	5.18	2.61	3.00	483	1.23	383	0.00	508	0.98
D4	5.18	2.61	3.00	484	1.24	384	0.00	508	0.99
D5	5.26	2.58	2.64	463	1.14	347	0.38	477	0.88

^a Ionization potential.

^b Excited state ionization potential (RVS-50 RI-ADC2/def2-TZVP).

^c Electron affinity.

^d First and second excited states with oscillator strengths (RVS-50 RI-ADC2/def2-TZVP).

^e First and second excited states with oscillator strengths (RVS-50 RI-ADC2/def2-TZVP).

 $^{\rm f}\,$ First and second excited states with oscillator strengths (RVS-50 RI-ADC2/def2-TZVP).

^g First and second excited states with oscillator strengths (RVS-50 RI-ADC2/def2-TZVP).

^h First excited state with oscillator strength (TDDFT/B3LYP/def2-SV(P)).

ⁱ First excited state with oscillator strength (TDDFT/B3LYP/def2-SV(P)).



Fig. 2. UV/Vis and fluorescence spectra of 1-phenyl-1,2,3,4-tetrahydroquinoline-based dyes D1–D5.

the introduction of the latter contributed to the hypsochromic shift of the absorption spectra by ~40 nm. Obviously, rhodanine-3acetic acid has stronger electron-withdrawing ability than cyanoacetic acid. It is also interesting to note that the introduction of the hydrazone moiety as a π -conjugation bridge between the tetrahydroquinoline-based donor and the rhodanine-based acceptor in sensitizers **D3**, **D4**, provided no significant shift in the ICT band compared with **D1**, **D2**, implying that this unit doesn't lead to better coplanarity than that achieved in the case of dyes **D1** and **D2**. However, ICT bands are broader and the onset of the absorption spectra of **D3** and **D4** reaches 542 nm which is red-shifted by about 16 nm relative to that of dyes **D1** and **D2**.

D1–D5 exhibit high extinction coefficients (Table 1), for example ε of **D2** ($5.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 472 nm) is more than four times and ε of **D3** ($3.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 469 nm) is more than three times higher than that of the standard Z907 ruthenium sensitizer ($\varepsilon = 1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 521 nm) [18]. This makes them especially suitable for solid-state devices, where the film thickness is crucial.

From the fluorescence spectra of the dyes it could be seen that the maximum emission wavelengths in THF solution were red-



Fig. 3. UV–Vis spectra of the dyes D1–D5 absorbed on TiO₂ surface.



Fig. 4. Photoemission in air spectra of the investigated dyes D1-D5.

shifted when the hydrazone unit was introduced as π -conjugated bridge into the structures of the sensitizers **D3**, **D4** (FL_{max} \approx 630 nm), compared with dyes **D1**, **D2** (FL_{max} \approx 540 nm). Change of the rhodanine-based acceptor with weaker cyanoacetic acid in **D5** also led to the noticeable blue shift of the emission maximum (FL_{max} \approx 530 nm). Dyes **D3**-**D5** exhibited relatively large Stokes shifts, which could be attributed to the geometrically relaxed structure of the donor center upon excitation [37].

The absorption spectra of **D1**, **D2** on a TiO₂ electrode are broader and absorption maxima are hypsochromically shifted, compared to results obtained in the THF solutions (Fig. 3), signifying that energy levels of the sensitizer molecules have somewhat changed due to the interaction with TiO₂. It could also indicate that these dye molecules form H-aggregates on the TiO₂ surface. Under similar conditions, the sensitizers **D3** and **D4** have a slight red shift of ~10 nm after being adsorbed on the TiO₂ electrode, indicating different type of packing of the hydrazone containing dyes compared with sensitizers without π -conjugated bridge **D1** and **D2**.

The E_{HOMO} and E_{LUMO} energies of D1–D5 were measured employing the cyclic voltammetry (CV) technique (Table 1). These values do not represent any absolute solid-state or gas-phase ionization energies, but can be used to compare different compounds relative to one another. The cyclic voltammograms of all synthesized compounds show quasi-reversible oxidation and reduction couples. The energy offset of the E_{LUMO} of the dye D1–D4 molecules is ca. -1.3 V vs normal hydrogen electrode (NHE), and for the **D5** it's -1.8 V vs NHE. These E_{LUMO} energy levels, with respect to the titania conduction band edge -0.5 vs NHE [38,39], provides the thermodynamic driving force for charge injection. The energy offset of the E_{HOMO} ca. 1.15 V for D1, D2 and ca. 0.75 V for D3–D5 relative to that of the spiro-MeOTAD (0.62 V, measured using CV) presents enough driving force for the dye regeneration process. The differences in the CV measurement results for the similar structures are quite small. Addition of the hydrazone fragment in the structures **D3–D5** lowers the E_{HOMO} by ca. 0.4 V. Substitution of the rhodanine acceptor with a weaker cyanoacetic acid in D5 lowers the E_{LUMO} by ca. 0.5 V. These variations in energy levels influence the size of the bandgap. E_g is larger in the structures without hydrazone π -bridge (**D1**, **D2**) or with weaker acceptor unit (**D5**).

When considering the use of an organic material for optoelectronic applications it is important to have an understanding of its solid state ionization potential (I_p). This understanding can help in identifying suitable organic transport and inorganic electrode

Table 3		

Photovoltaic	performance	of ssDSSCs	based on	the D1-	-D5 (dyes

Dye	$J_{\rm SC}$ [mA cm ⁻²]	V _{OC} [mV]	FF [%]	η [%]
D1	4.52	460	44	0.9
D2	4.75	720	71	2.4
D3	6.08	780	68	3.2
D4	5.87	780	72	3.3
D5	4.55	660	58	1.8

materials. The ionization potential was measured by the electron photoemission in air method (Fig. 4) and results are presented in Table 1.

As with the CV experiments, solid state I_p values for the dyes **D1**, **D2** without hydrazone bridge are noticeably higher compared with **D3–D5** that do possess it. The effect of aliphatic chains is much more pronounced in solid state than in solution for small molecules of **D1**, **D2** as they influence the way they pack and therefore have significant impact on energy levels. **D1** without any additional aliphatic fragments has the highest I_p among the investigated materials. Additional propyl chain in **D2** lowers the I_p by 0.15 eV. In case of larger and somewhat more complex dyes **D3–D5** these effects are far less pronounced, difference between propyl



Fig. 5. a) IPCE spectra of D1-D5 dye-sensitized devices and b) Current–voltage characteristics of ssDSSCs based on D1-D5 under 100 mW cm $^{-2}$, AM 1.5G illumination.

containing dye **D3** and nonyl one **D4** is just 0.03 eV. The smaller electron accepting unit in **D5** allows for a different, perhaps tighter, packing of the molecules. Results of these changes could be seen in I_p measurements, **D5** has the lowest ionization potential of all investigated materials. The ionization potential of spiro-MeOTAD was determined to be 5.0 eV, therefore, there is enough driving force for the dye regeneration process.

3.3. Quantum chemistry calculations

The distinct absorption peaks in the solution spectrum of **D1**– **D4** are described by the RVS RI-ADC(2)-calculations as a mixed pi– pi*/charge-transfer excitation. The second excited states of D1-D4 are dark, locally excited states in the near UV region. In **D5**, the absorption splits up into a charge-transfer absorption (first excited state) and a pi–pi*-absorption (second excited state). This is reflected also in the different spectral appearance of **D5**. Furthermore, this explains the systematic shifts from calculation results for absorption wavelengths of **D1–D4**, but the overestimation of the absorption wavelength for **D5**. Calculated ionization potentials reproduce the experimental values up to a systematic shift (see Table 2).

3.4. Photovoltaic performance

Owning to their high absorption extinction coefficient, tetrahydroquinoline-based dyes **D1–D5** were evaluated as sensitizers for the solid-state DSSCs using spiro-MeOTAD as HTM (photovoltaic performance is summarized in Table 3).

Fig. 5 shows the incident photon-to-current conversion efficiency (IPCE) spectra and the I-V characteristics under standard global AM 1.5 solar conditions of D1-D5 based ssDSSCs. Dyes D3 and D4 possessing hydrazone demonstrate respectable external quantum efficiencies of around 65%. Sensitizers without hydrazone π -conjugated bridge **D1**, **D2** demonstrate more modest results, 30% and 50% respectively. Interestingly, compound D5 with cyanoacetic acid acceptor exhibited very good external quantum efficiency, reaching 75% in the short wavelength region. Unfortunately, due to relatively weak electron accepting capabilities, compared with the rhodanine-based acceptor, absorbance of the dye D5 in the visible light region is very limited and overall device efficiency is only 1.8%. Presence of an unsubstituted hydroxy group in D1 also has pronounced negative effect on solar cell performance. Simple alkylation of the OH group in the sensitizer D2 increases efficiency more than twofold, from 0.9% to 2.4%. As expected, addition of the hydrazone π -conjugated bridge in **D3** and **D4** improves the ssDSSC performance, compared with **D2** it increases by approximately 35%.

Interestingly, the length of the aliphatic chain, attached to the donor end of the molecule, wasn't a major factor. Both sensitizers, **D3** with propyl and **D4** with nonyl chain, performed similarly. The best results were obtained using dye **D4**, showing overall conversion efficiencies (η) of 3.3% ($J_{SC} = 5.9$ mA cm⁻², $V_{OC} = 780$ mV, FF = 0.72).

4. Conclusions

In conclusion, we have demonstrated the design and synthesis pathway of D- π -A metal-free organic dye for ssDSSCs, employing a 1-phenyl-1,2,3,4-tetrahydro-quinoline fragment electron donating moiety. These dyes could be obtained using relatively cheap starting materials and simple synthetic procedures, without the use of expensive catalysts, rigorously anhydrous or oxygen-free conditions. Compared to the unalkylated dye **D1** and the structure without hydrazone π -bridge (**D2**), the more complex dyes possessing phenylhydrazone moiety and alkoxy group attached to 1-

phenyl-1,2,3,4-tetrahydroquinoline donoric core (**D3**, **D4**) exibit higher V_{OC} and I_{SC} , which results in the overall conversion efficiency over 3% under 100 mW cm⁻² solar irradiation. The proposed tetrahydroquinoline-based dyes pave the way for future structural design of new efficient and cheap metal-free sensitizers for use in thin film devices.

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References

- O'Regan B, Grätzel M. A low-cost, high-efficiency solar cell based on dyesensitized colloidal TiO₂ films. Nature 1991;353:737–40.
- 2] Grätzel M. Photoelectrochemical cells. Nature 2001;414:338-44.
- [3] Nazeeruddin MK, De Angelis F, Fantacci S, Selloni A, Viscardi G, Liska P, et al. Combined experimental and DFT-TDDFT computational study of photoelectrochemical cell ruthenium sensitizers. J Am Chem Soc 2005;127:16835–40.
 [4] Chiba Y, Islam A, Watanabe Y, Komiya R, Koide N, Han LY. Dye-sensitized solar
- (4) Chiba 1, Islan A, Watalabe 1, Kolmya K, Kole K, Hall 11. Dye-sentized solar cells with conversion efficiency of 11.1%. Jpn J Appl Phys 2006;45:L638–40. [5] Gao F. Wang Y. Shi D. Zhang I. Wang MK. Jing XY, et al. Enhance the optical
- [5] Gao F, Wang Y, Shi D, Zhang J, Wang MK, Jing XY, et al. Enhance the optical absorptivity of nanocrystalline TiO₂ film with high molar extinction coefficient ruthenium sensitizers for high performance dye-sensitized solar cells. J Am Chem Soc 2008;130:10720–8.
- [6] Cao YM, Bai Y, Yu QJ, Cheng YM, Liu S, Shi D, et al. Dye-sensitized solar cells with a high absorptivity ruthenium sensitizer featuring a 2-(Hexylthio)thiophene conjugated bipyridine. J Phys Chem C 2009;113:6290–7.
- [7] Chen CY, Wang M, Li JY, Pootrakulchote N, Alibabaei L, Ngoc-le CH, et al. Highly efficient light-harvesting ruthenium sensitizer for thin-film dyesensitized solar cells. ACS Nano 2009;3:3103–9.
- [8] Snaith HJ, Schmidt-Mende L. Advances in liquid-electrolyte and solid-state dye-sensitized solar cells. Adv Mater 2007;19:3187–200.
- [9] Yum JH, Chen P, Grätzel M, Nazeeruddin MK. Recent developments in solidstate dye-sensitized solar cells. ChemSusChem 2008;1:699–707.
- [10] Mor GK, Kim S, Paulose M, Varghese OK, Shankar K, Basham J, et al. Visible to near-infrared light harvesting in TiO₂ nanotube array–P3HT based heterojunction solar cells. Nano Lett 2009;9:4250–7.
- [11] Snaith HJ, Moule AJ, Klein C, Meerholz K, Friend RH, Grätzel M. Efficiency enhancements in solid-state hybrid solar cells via reduced charge recombination and increased light capture. Nano Lett 2007;7:3372–6.
- [12] Oayama Y, Harima Y. Molecular designs and syntheses of organic dyes for dye-sensitized cells. Eur J Org Chem 2009:2903–34.
- [13] Hara K, Sato T, Katoh R, Furube A, Ohga Y, Shinpo A, et al. Molecular design of coumarin dyes for efficient dye-sensitized solar cells. J Phys Chem B 2003;107:597–606.
- [14] Horiuchi T, Miura H, Sumioka K, Uchida S. High efficiency of dye-sensitized solar cells based on metal-free indoline dyes. J Am Chem Soc 2004;126: 12218–9.
- [15] Kim S, Lee JK, Kang SO, Ko J, Yum JH, Fantacci S, et al. Molecular engineering of organic sensitizers for solar cell applications. J Am Chem Soc 2006;128: 16701–7.
- [16] Hagberg DP, Edvinsson T, Marinado T, Boschloo G, Hagfeldt A, Sun LC. A novel organic chromophore for dye-sensitized nanostructured solar cells. Chem Commun 2006:2245–7.

- [17] Zeng W, Cao Y, Bai Y, Wang Y, Shi Y, Zhang M, et al. Efficient dye-sensitized solar cells with an organic photosensitizer featuring orderly conjugated ethylenedioxythiophene and dithienosilole blocks. Chem Mater 2010;22:1915– 25.
- [18] Cai N, Moon SJ, Cevey-Ha L, Moehl T, Humphry-Baker R, Wang P, et al. An organic d-π-a dye for record efficiency solid-state sensitized heterojunction solar cells. Nano Lett 2011;11:1452–6.
- [19] Liu X, Zhang W, Uchida S, Cai L, Liu B, Ramakrishna S. An efficient organic-dyesensitized solar cell with in situ polymerized poly(3,4ethylenedioxythiophene) as a hole-transporting material. Adv Mater 2010;22:E150–5.
- [20] Vorozhtsov NN, Kutkevichus SI. Study of products of interaction of epichlorohydrin with aromatic amines. Khim Geterotsikl 1965:374–8.
- [21] Getautis V, Stanisauskaite A, Malinauskas T, Stumbraite J, Gaidelis V, Jankauskas V. Hydrazones possessing a phenyl-1,2,3,4-tetrahydroquinoline moiety as hole transporting materials. Monatsh Chem 2006;137:1401–9.
- [22] Miyamoto E, Yamaguchi Y, Yokoyama M. Ionization potential of organic pigment film by atmospheric photoelectron emission analysis. Electrophotography 1989;28:364–70.
- [23] Daskeviciene M, Getautis V, Grazulevicius VJ, Stanisauskaite A, Antulis J, Gaidelis V, et al. Crosslinkable carbazolyl-containing molecular glasses for electrophotography. J Imaging Sci Technol 2002;46:467–72.
- [24] Becke AD. Density-functional exchange-energy approximation with correct asymptotic behavior. Phys Rev A 1988:33:3098–100.
- [25] Perdew JP. Density-functional approximation for the correlation energy of the inhomogeneous electron gas. Phys Rev B 1986;33:8822–4.
- [26] Weigend F, Ahlrichs R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: design and assessment of accuracy. Phys Chem Chem Phys 2005;7:3297–305.
- [27] Marques MAL, Ullrich CA, Noguiera F, Rubio A, Burke K, Gross EKU. Timedependent density functional theory: lecture notes in physics. Berlin: Springer; 2006.
- [28] Becke AD. Density-functional thermochemistry. III. The role of exact exchange. J Chem Phys 1993;98:5648–52.
- [29] Schirmer J. Beyond the random-phase approximation: a new approximation scheme for the polarization propagator. Phys Rev A 1982;26:2395–416.
- [30] Hättig C. Structure optimizations for excited states with correlated secondorder methods: CC2 and ADC(2). Adv Quant Chem 2005;50:37–60.
- [31] Send R, Kaila VRI, Sundholm D. Reduction of the virtual space for coupledcluster excitation energies of large molecules and embedded systems. J Chem Phys 2011;134:214114.
- [32] Eichkorn K, Weigend F, Treutler O, Ahlrichs R. Auxiliary basis sets for main row atoms and transition metals and their use to approximate coulomb potentials. Theor Chem Acc 1997;97:119–24.
- [33] Schaefer A, Klamt A, Sattel D, Lohrenz JCW, Eckert F. COSMO implementation in TURBOMOLE: extension of an efficient quantum chemical code towards liquid systems. Phys Chem Chem Phys 2000;2:2187–93.
- [34] TURBOMOLE 6.2. Karlsruhe, Germany: TURBOMOLE GmbH; 2010 [accessed July 2013], http://www.turbomole.com.
- [35] Peng B, Jungmann G, Jager C, Haarer D, Schmidt HW, Thelakkat M. Systematic investigation of the role of compact TiO₂ layer in solid state dye-sensitized TiO₂ solar cells. Coord Chem Rev 2004;248:1479–89.
- [36] Urnikaite S, Malinauskas T, Gaidelis V, Bruder I, Send R, Sens R, et al. Simple and inexpensive organic dyes with hydrazone moiety as π-conjugation bridge for solid-state dye-sensitized solar cells. Chem Asian J 2013;8:538–41.
- [37] Lai RY, Fabrizio EF, Lu L, Jenekhe SA, Bard AJ. Synthesis, cyclic voltammetric studies, and electrogenerated chemiluminescence of a new donor-acceptor Molecule: 3,7-[Bis[4-phenyl-2-quinolyl]]-10-methylphenothiazine. J Am Chem Soc 2001;123:9112–8.
- [38] Jiang X, Karlsson KM, Gabrielsson E, Johansson EMJ, Quintana M, Karlsson M, et al. Highly efficient solid-state dye-sensitized solar cells based on triphenylamine dyes. Adv Funct Mater 2011;21:2944–52.
- [39] Delcamp JH, Shi Y, Yum JH, Sajoto T, Dell'Orto E, Barlow S, et al. Chem Eur J 2013;19:1819-27.