Electronic supplementary information

Rhodanine-based light-harvesting sensitizers: Rational comparison between 2-(1,1-dicyanomethylene)rhodanine and Rhodanine-3-acetic acid

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1. Experimental section

1.1. Synthesis of the Rhodanine-based dyes

![Chemical structures](image)

**Fig S1.** Synthesis of rhodanine-based dyes

**General:** All reagents and solvents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh or Scharlau 60, 230-240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminum coated Merck Kieselgel60 F254 plates. Melting points were determined on a Sanyo Gallenkamp apparatus. NMR spectra were recorded on a Bruker Avance 400 (\(^1\)H: 400 MHz; \(^{13}\)C: 100 MHz) spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (\(\delta\)) in ppm. Multiplicities are denoted as follows: \(s = \text{singlet}, d = \text{doublet}, t = \text{triplet}, m = \text{multiplet}, br = \text{broad}\). FT-IR spectra were recorded on a Bruker Tensor...
27 (ATR device) spectrometer. UV-Vis spectra were recorded on a Varian Cary 50 spectrophotometer using CHCl₃ as solvent. Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) experiments (MALDI-TOF) were recorded on a HP1100MSD spectrometer and a Bruker REFLEX spectrometer respectively. Cyclic voltammetry was performed using an AutolabPGStat 30. A glassy carbon working electrode (Metrohm 6.0804.010) was used after being polished with alumina (0.3 μm) for 1 min, and platinum wire was used as counter electrode. A Ag/AgNO₃ electrode was used as a reference. Tetra-n-butylammonium hexafluorophosphate (TBAPF₆) (0.1 M) was used as supporting electrolyte and dry tetrahydrofuran as solvent. The samples were purged with argon prior to measurement. The scan rate was 100 mV/s.

**Synthetic procedure for DCR-(1-3) dyes**

As shown in Scheme S1, the corresponding aldehyde (2, 5a-b) (50 mg), 2-(1,1-dicyanomethylene)rhodanine (1.5 eq.) and five drops of a 5% ethanolic solution of KOH were stirred and refluxed in ethanol for 12 h. The ethanol was evaporated, the solid was washed with a solution of HCl 0.1M and filtered. The solid obtained was purified further by recrystallization from ethanol and column chromatography (DCR-3).

**DCR-1.** Red solid, (55%, 35 mg). ¹H-NMR (DMSO-δ₆, 400 MHz) δ: 7.53 (d, J = 8.0 Hz, 2H), 7.50-7.46 (m, 4H), 7.42 (s, 1H), 7.39-7.35 (m, 2H), 7.33-7.29 (m, 4H), 7.17-7.10 (m, 5H), 7.07-7.02 (m, 10H), 6.95 (d, J = 8.0 Hz, 2H) ppm. ¹³C-NMR (DMSO-δ₆, 100 MHz) δ: 181.4, 179.8, 148.4, 147.5, 147.1, 146.7, 145.9, 113.5, 132.1, 131.4, 130.3, 130.1, 128.1, 128.1, 128.0, 127.6, 127.3, 126.7, 125.7, 125.2, 124.8, 124.6, 123.7, 123.6, 122.3, 118.5, 117.2, 100.0, 47.6 ppm. FTIR (KBr) ν: 3442, 2213, 1652, 1558, 825 cm⁻¹. M.p. > 350 ºC. Uv-vis λₘₐₓ (ε/M⁻¹cm⁻¹, THF): 435(51000), 388(52000) nm. MS (MALDI): calcd. for C₄₅H₃₁N₅O₅ 689.225; found 687.871 [M⁺].
DCR-2. Black solid, (57%, 35 mg). $^1$H-NMR (DMSO-$d_6$, 400 MHz) $\delta$: 7.86 (s, 1H), 7.59 (d, $J = 4.0$ Hz, 1H), 7.57 (br, 2H), 7.51 (m, 4H), 7.41 (d, $J = 16.0$ Hz, 1H), 7.38-7.31 (m, 7H), 7.17-7.11 (m, 3H), 7.10-7.01 (m, 11H), 6.97 (dd, $J_1 = 8.0$ Hz, $J_2 = 4.0$ Hz, 4H) ppm. $^{13}$C-NMR (DMSO-$d_6$, 100 MHz) $\delta$: 180.7, 178.8, 147.5, 147.1, 147.0, 146.4, 146.0, 138.3, 136.4, 134.1, 132.8, 132.1, 130.2, 128.4, 127.9, 127.2, 126.8, 125.2, 125.0, 124.5, 124.5, 123.7, 123.3, 122.3, 121.5, 118.6, 117.0, 100.0, 48.0 ppm. FTIR (KBr) $\nu$: 3443, 2213, 1647, 1583, 1325, 754 cm$^{-1}$. M.p. > 350 °C. Uv-vis $\lambda_{\text{max}}$ ($\varepsilon$/M$^{-1}$cm$^{-1}$, THF): 495(38100), 396(56200) nm. MS (MALDI-TOF): calcd. for C$_{51}$H$_{35}$N$_5$O$_7$ 797.228; found 797.230 [M$^+$].

DCR-3. Red solid, (66%, 38 mg). $^1$H-NMR (DMSO-$d_6$, 400 MHz) $\delta$: 7.92 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.71 (s, 1H), 7.64 (s, 1H), 7.59 (d, $J = 8.0$ Hz, 2H), 7.57 (d, $J = 8.0$ Hz, 2H), 7.53-7.49 (m, 3H), 7.45-7.41 (m, 1H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.34-7.31 (m, 5H), 7.25-7.19 (m, 2H), 7.13-7.01 (m, 14H), 6.96 (d, $J = 8.0$ Hz, 2H), 6.70 (br, 1H), 2.05-2.01 (m, 4H), 1.24-1.01 (m, 21H), 0.75 (t, $J = 8.0$ Hz, 6H), 0.53 (br, 4H) ppm. $^{13}$C-NMR (DMSO-$d_6$, 100 MHz) $\delta$: 179.9, 173.5, 152.2, 152.0, 147.6, 147.3, 147.1, 146.7, 143.5, 139.3, 137.8, 132.4, 131.8, 131.7, 129.4, 129.3, 128.2, 127.5, 127.2, 126.9, 126.5, 124.8, 124.5, 124.2, 123.8, 123.7, 123.4, 123.0, 100.0, 55.2, 31.8, 30.0, 29.3, 29.2, 24.0, 22.7, 22.6, 14.1 ppm. FTIR (KBr) $\nu$: 3402, 2924, 2853, 2210, 1586, 1506, 1314, 751 cm$^{-1}$. M.p. > 350 °C. Uv-vis $\lambda_{\text{max}}$ ($\varepsilon$/M$^{-1}$cm$^{-1}$, THF): 416(85600) nm. MS (MALDI-TOF): calcd. for C$_{76}$H$_{73}$N$_5$O$_{11}$ 1103.554; found 1103.552 [M$^+$].

**Synthetic procedure for RDA-(1-3) dyes**

As shown in Scheme S1, the corresponding aldehyde (2, 5a-b) (50 mg), Rhodanine-3-acetic acid (4 eq.), ammonium acetate (100 mg) and glacial acetic acid (15 mL) were stirred and heated at 120 °C for 10 h. The acetic acid was evaporated and the solid was washed with water and filtered. The solid obtained was purified further by recrystallization from ethanol and column chromatography (RDA-3).

RDA-1. Black solid, (62%, 41 mg). $^1$H-NMR (DMSO-$d_6$, 400 MHz) $\delta$: 7.67 (s, 1H), 7.58 (d, $J = 8.0$ Hz, 2H), 7.54-7.47 (m, 4H), 7.45-7.41 (m, 2H), 7.32 (m, 4H), 7.25-
7.18 (m, 3H), 7.14-7.12 (m, 4H), 7.09-7.03 (m, 6H), 7.00 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.0 Hz, 2H), 4.31 (s, 2H) ppm. $^{13}$C-NMR (DMSO-d$_6$, 100 MHz) δ: 195.8, 193.0, 146.5, 143.5, 129.8, 128.2, 128.0, 127.4, 127.1, 126.9, 126.5, 126.2, 126.3, 99.3, 62.6 ppm. FTIR (KBr) ν: 3432, 3024, 1707, 1577, 1498 cm$^{-1}$. M.p. > 350 °C. Uv-vis $\lambda_{max}$ ($\varepsilon$/M$^{-1}$cm$^{-1}$, THF): 467(5600), 387(18500) nm. MS (MALDI-TOF): calcd. for C$_{44}$H$_{33}$N$_3$O$_3$S$_2$ 715.196; found 714.723 [M$^+$].

**RDA-2.** Black solid, (52%, 33 mg). $^1$H-NMR (DMSO-d$_6$, 400 MHz) δ: 8.08 (s, 1H), 7.74 (d, J = 4.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.53-7.48 (m, 7H), 7.42 (d, J = 16.0 Hz, 1H) 7.37-7.30 (m, 4H), 7.22 (d, J = 16.0 Hz, 1H), 7.11-7.07 (m, 7H), 7.05-7.01 (m, 6H), 6.98-6.95 (m, 4H), 4.60 (s, 2H) ppm. $^{13}$C-NMR (DMSO-d$_6$, 100 MHz) δ: 192.3, 167.8, 166.5, 152.7, 147.9, 147.5, 147.0, 146.2, 135.8, 133.0, 132.0, 131.8, 130.5, 130.2, 130.0, 128.7, 128.5, 127.9, 127.3, 126.7, 125.3, 124.7, 124.5, 123.7, 122.9, 119.8, 118.8, 45.3 ppm. FTIR (KBr) ν: 3432, 2952, 1707, 1576, 1178, 820 cm$^{-1}$. M.p. > 350 °C. Uv-vis $\lambda_{max}$ ($\varepsilon$/M$^{-1}$cm$^{-1}$, THF): 514(25600), 396(36700) nm. MS (MALDI-TOF): calcd. for C$_{50}$H$_{37}$N$_3$O$_3$S$_3$ 823.199; found 821.858 [M$^+$-1].

**RDA-3.** Red solid, (54%, 32 mg). $^1$H-NMR (DMSO-d$_6$, 400 MHz) δ: 7.98 (d, J = 8.0 Hz, 1H), 7.95 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.73-7.69 (m, 2H), 7.66 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.51 (m, 3H), 7.42 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.34-7.30 (m, 5H), 7.23 (d, J = 16.0 Hz, 1H), 7.16-7.00 (m, 14H), 6.96 (d, J = 8.0 Hz, 2H), 4.63 (s, 2H), 2.07-2.00 (m, 4H), 1.24-1.02 (m, 21H), 0.75 (t, J = 8.0 Hz, 6H), 0.55 (br, 4H) ppm. $^{13}$C-NMR (DMSO-d$_6$, 100 MHz) δ: 193.5, 174.9, 171.8, 167.7, 167.0, 152.4, 151.9, 147.5, 147.2, 147.0, 146.5, 142.2, 139.1, 138.4, 134.6, 132.6, 132.1, 132.1, 130.4, 130.1, 130.0, 128.1, 127.9, 127.1, 126.8, 124.9, 124.5, 124.3, 123.6, 121.7, 121.3, 79.6, 55.2, 31.6, 29.6, 29.5, 28.9, 23.8, 22.5, 21.1, 14.3 ppm. FTIR (KBr) ν: 3375, 2924, 2853, 1587, 1488, 1273, 824 cm$^{-1}$. M.p. > 350 °C. Uv-vis $\lambda_{max}$ ($\varepsilon$/M$^{-1}$cm$^{-1}$, THF): 404(84600) nm. MS (MALDI-TOF): calcd. for C$_{75}$H$_{75}$N$_3$O$_3$S$_2$ 1129.525; found 1129.531 [M$^+$].
1.2. Characterization of Rhodanine-based dyes

Fig S1. $^1$H NMR spectra (DMSO-$d_6$ - 400 MHz) for DCR-(1-3).
Fig S2. $^1$H NMR spectra (DMSO-$d_6$ - 400 MHz) for RDA-(1-3).

1.3. Fluorescence quantum yield

The relative fluorescence quantum yields ($\phi_f$) were calculated from Eq. (1) using $N,N$-dimethyl-6-propionyl-2-naphthylamine (PRODAN) in CH$_2$Cl$_2$ ($\phi_{std} = 0.87$) as the standard. Where $F$ and $F_{std}$ are the areas under the fluorescence curves of the compounds and the
standard, respectively. \( A \) and \( A_{\text{std}} \) are the respective absorbance peaks of the sample and standard at the excitation wavelengths; \( I \) and \( I_{\text{std}} \) are the relative intensities of the exciting light, and \( n^2 \) and \( n^2_{\text{std}} \) are the refractive indices of the solvents used for the sample and standard, respectively.\(^2\)

\[
\phi_F = \frac{\phi_{F_{\text{std}}} F A^{\text{std}} I n^2}{F_{\text{std}} A I_{\text{std}} n^2_{\text{std}}}
\]  

(1)

<table>
<thead>
<tr>
<th>Dye</th>
<th>( A )</th>
<th>( I )</th>
<th>( F )</th>
<th>( \phi_f \times 10^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCR-1</td>
<td>0.05270</td>
<td>0.211495</td>
<td>21.2408</td>
<td>6.42</td>
</tr>
<tr>
<td>DCR-2</td>
<td>0.24393</td>
<td>0.6497</td>
<td>54.9527</td>
<td>4.26</td>
</tr>
<tr>
<td>DCR-3</td>
<td>0.60700</td>
<td>2.66783</td>
<td>255.348</td>
<td>7.03</td>
</tr>
<tr>
<td>RDA-1</td>
<td>0.05264</td>
<td>0.123919</td>
<td>11.3502</td>
<td>3.77</td>
</tr>
<tr>
<td>RDA-2</td>
<td>0.22831</td>
<td>0.108532</td>
<td>10.5205</td>
<td>0.76</td>
</tr>
<tr>
<td>RDA-3</td>
<td>0.30264</td>
<td>1.24258</td>
<td>112.806</td>
<td>6.57</td>
</tr>
</tbody>
</table>

**1.4. Cell fabrication**

**Photoanode.** FTO glass (TEC7) was cleaned and an under layer of \( \text{TiO}_2 \) was deposited by heating the substrates for 30 min at 70 \(^\circ\)C in an aqueous solution of \( \text{TiCl}_4 \). Then an 8-\( \mu \)m layer of transparent \( \text{TiO}_2 \) was screen-printed. The paste used for this layer contained nanoparticles of 18 nm diameters. A scattering layer formed by 400 nm \( \Phi \) nanoparticles (5 \( \mu \)m thick) was deposited on the transparent layer. The whole structure was calcined up to 500 \(^\circ\)C.

**Sensitization.** Solutions containing 0.3 mM of each dye in THF/EtOH (1:4) mixture were prepared. Prior the immersion in the solutions, the photoanodes were heated to 450 \(^\circ\)C and cooled down to 80\(^\circ\)C. The sensitization process lasted 15 hours.

**Cell assembly.** Twice platinized (drop casting of a solution of 8 mM hexachloroplatinic acid in \( n \)-propanol followed by heating to 410\(^\circ\)C for 15 min) FTO glass pieces with a pre-drilled holes served as counter electrodes. They were sealed with dried sensitized photoanodes by hot-melt polymer rings (Surlyn, Dupont – 25\( \mu \)m thickness). Electrolyte (1 M dimethylimidazolium iodide, 0.03 M \( I_2 \), 0.1 M guanidinium thiocyanate, 0.5 M \( t \)-butylpyridine, 0.05 M lithium iodide in MeCN/\( s \)-BuCN 85:15 v/v) was driven into the device.
via a pre-drilled hole using a vacuum pump. The hole was sealed with a polymer and a covering glass.

**Measurement:** A 450 W xenon light source (Oriel, USA) was used to characterize the solar cells. The spectral output of the lamp was matched in the region of 350–750 nm with the aid of a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) so as to reduce the mismatch between the simulated and true solar spectra to less than 2%. The current–voltage characteristics of the cell under these conditions were obtained by applying external potential bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, USA). A similar data acquisition system was used to control the incident photon-to-current conversion efficiency (IPCE) measurement. Under computer control, light from a 300 W xenon lamp (ILC Technology, USA) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd., UK) onto the photovoltaic cell under test. The devices were masked to attain an illuminated active area of 0.159 cm².

### 1.5. Optimization of PV devices

To compare the effect of the anchoring unit, we synthesized dye **TPAM-1** as reference using cyanoacrylic acid as acceptor unit as previously described. For optimization of PV measures, we built for each dyes different devices, reporting uncertainty for the measures (Table S1).

**TPAM-1.** $^1$H-NMR (DMSO-$d_6$, 400 MHz) $\delta$: 7.97 (s, 1H), 7.79 (d, $J=8$Hz, 2H), 7.49 (d, $J=8$Hz, 2H), 7.40 (d, $J=8$Hz, 2H), 7.34-7.31 (m, 2H), 7.23-7.20 (m, 4H), 7.15-7.09 (m, 3H), 7.03 (br, 4H), 6.98-6.93 (m, 6H), 6.85 (br, 4H) ppm; MS (MALDI-TOF): calcd. for C$_{42}$H$_{31}$N$_3$O$_2$ 609.241; found 609.237 [M$^+$].
Fig. S3. Structures and IPCE spectra of dyes TPAM-1, DCR-1 and RDA-1

Table S1. PV performance of the best cells based on rhodanine

<table>
<thead>
<tr>
<th>Dye</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt;/mA cm&lt;sup&gt;2&lt;/sup&gt;</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt;/V</th>
<th>FF</th>
<th>η % (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCR-1</td>
<td>5.77</td>
<td>0.754</td>
<td>0.639</td>
<td>3.06 (2.87±0.27)</td>
</tr>
<tr>
<td>DCR-2</td>
<td>5.46</td>
<td>0.567</td>
<td>0.586</td>
<td>1.80 (1.69±0.16)</td>
</tr>
<tr>
<td>DCR-3</td>
<td>6.51</td>
<td>0.734</td>
<td>0.663</td>
<td>3.10 (2.98±0.14)</td>
</tr>
<tr>
<td>RDA-1</td>
<td>6.72</td>
<td>0.726</td>
<td>0.643</td>
<td>3.15 (2.65±0.71)</td>
</tr>
<tr>
<td>RDA-2</td>
<td>4.10</td>
<td>0.559</td>
<td>0.696</td>
<td>1.63 (1.31±0.36)</td>
</tr>
<tr>
<td>RDA-3</td>
<td>6.64</td>
<td>0.721</td>
<td>0.660</td>
<td>3.17 (3.05±0.14)</td>
</tr>
<tr>
<td>TPAM-1</td>
<td>8.14</td>
<td>1.080</td>
<td>0.698</td>
<td>6.13 (5.50±0.41)</td>
</tr>
<tr>
<td>N719</td>
<td>15.04</td>
<td>0.804</td>
<td>0.534</td>
<td>6.31 (6.16±0.22)</td>
</tr>
</tbody>
</table>

(*) These efficiencies correspond to the parameter obtained from two or three devices

2. References

