**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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# Contents

# 1. Experimental section

## 1.1. Synthesis of the Rhodanine-based dyes

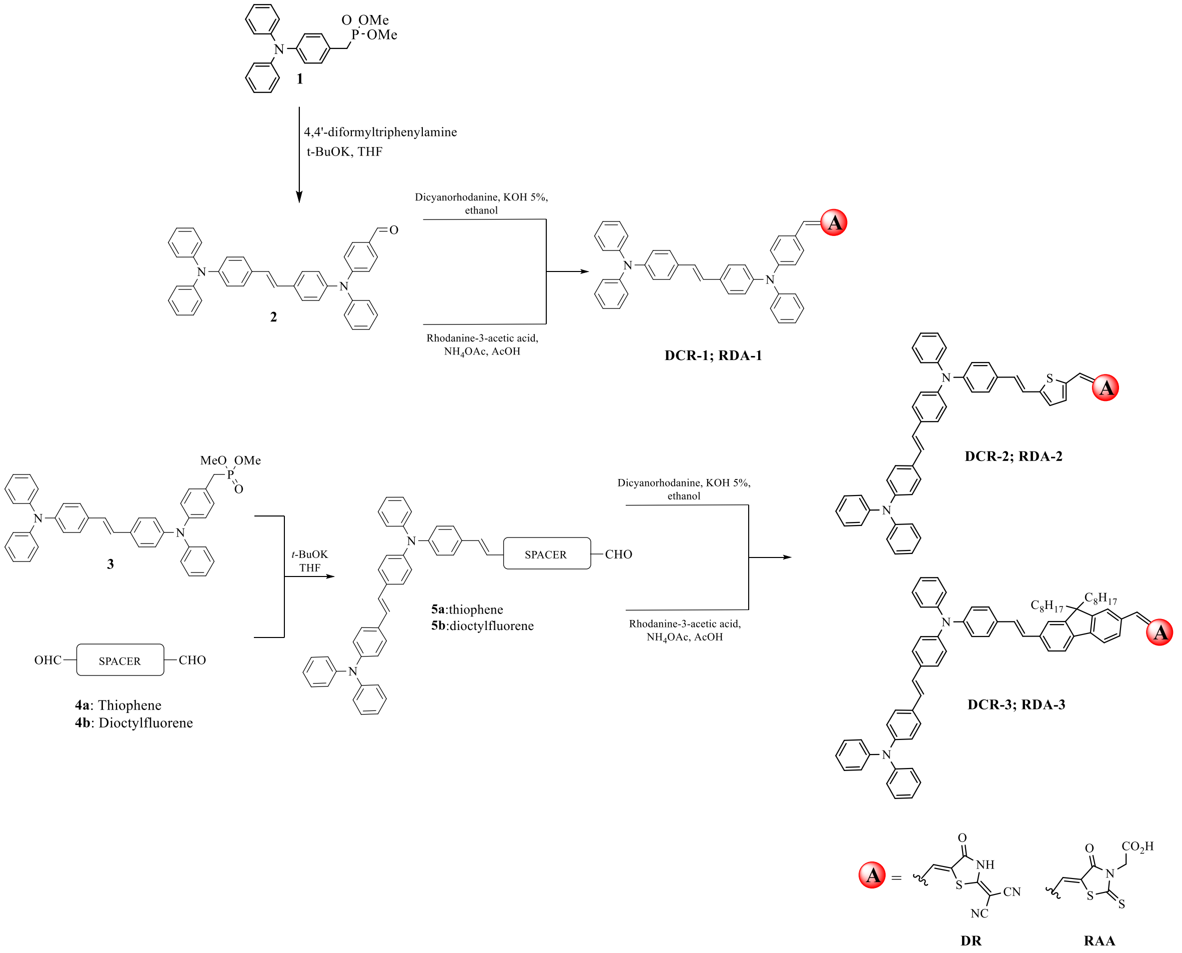

**Fig S1.** Synthesis of rhodanine-based dyes

**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 (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = 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 $CHCl_3$ 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 $Ag/AgNO_3$ electrode was used as a reference. Tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) (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-(1,1dicyanomethylene)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). $^1$H-NMR (DMSO-*d₆* , 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. $^{13}$C-NMR (DMSO-$d_6$, 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) υ: 3442, 2213, 1652, 1558, 825 $cm^{-1}$. M.p. > 350 ºC. Uv-vis $\lambda_{max}$ ($\varepsilon/M^{-1}cm^{-1}$, THF): 435(51000), 388(52000) nm. MS (MALDI): calcd. for $C_{45}H_{31}N_5OS$ 689.225; found 687.871 [$M^+$-1].

**DCR-2.** Black solid, (57%, 35 mg). $^1$H-NMR (DMSO-*d$_6$*, 400 MHz) δ: 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) δ: 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, 130.1, 128.4, 127.9, 127.2, 126.8, 125.2, 125.0, 124.5, 124.5, 123.7, 123.3, 122.3, 121.5, 120.4, 118.6, 117.0, 100.0, 48.0 ppm. FTIR (KBr) υ: 3443, 2213, 1647, 1583, 1325, 754 cm$^{-1}$. M.p. > 350 $^o$C. Uv-vis $\lambda_{max}$ (ε/M$^{-1}$cm$^{-1}$, THF): 495(38100), 396(56200) nm. MS (MALDI-TOF): calcd. for $C_{51}H_{35}N_5OS_2$ 797.228; found 797.230 [M$^+$].

**DCR-3.** Red solid, (66%, 38 mg). $^1$H-NMR (DMSO-*d$_6$* , 400 MHz) δ: 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) δ: 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, 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) υ: 3402, 2924, 2853, 2210, 1586, 1506, 1314, 751 cm$^{-1}$. M.p. > 350 $^o$C. Uv-vis $\lambda_{max}$ (ε/M$^{-1}$cm$^{-1}$, THF): 416(85600) nm. MS (MALDI-TOF): calcd. for $C_{76}H_{73}N_5OS$ 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) δ: 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, *4*H), 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) υ: 3432, 3024, 1707, 1577, 1498 cm$^{-1}$. M.p. > 350 $^{o}$C. Uv-vis $\lambda_{max}$ (ε/M$^{-1}$cm$^{-1}$, THF): 467(5600), 387(18500) nm. MS (MALDI-TOF): calcd. for $C_{44}H_{33}N_3O_3S_2$ 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) υ: 3432, 2952, 1707, 1576, 1178, 820 cm$^{-1}$. M.p. > 350 $^{o}$C. Uv-vis $\lambda_{max}$ (ε/M$^{-1}$cm$^{-1}$, THF): 514(25600), 396(36700) nm. MS (MALDI-TOF): calcd. for $C_{50}H_{37}N_3O_3S_3$ 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, 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) υ: 3375, 2924, 2853, 1587, 1488, 1273, 824 cm$^{-1}$. M.p. > 350 $^{o}$C. Uv-vis $\lambda_{max}$ (ε/M$^{-1}$cm$^{-1}$, THF): 404(84600) nm. MS (MALDI-TOF): calcd. for $C_{75}H_{75}N_3O_3S_2$ 1129.525; found 1129.531 [M$^+$].

## 1.2.Characterization of Rhodanine-based dyes

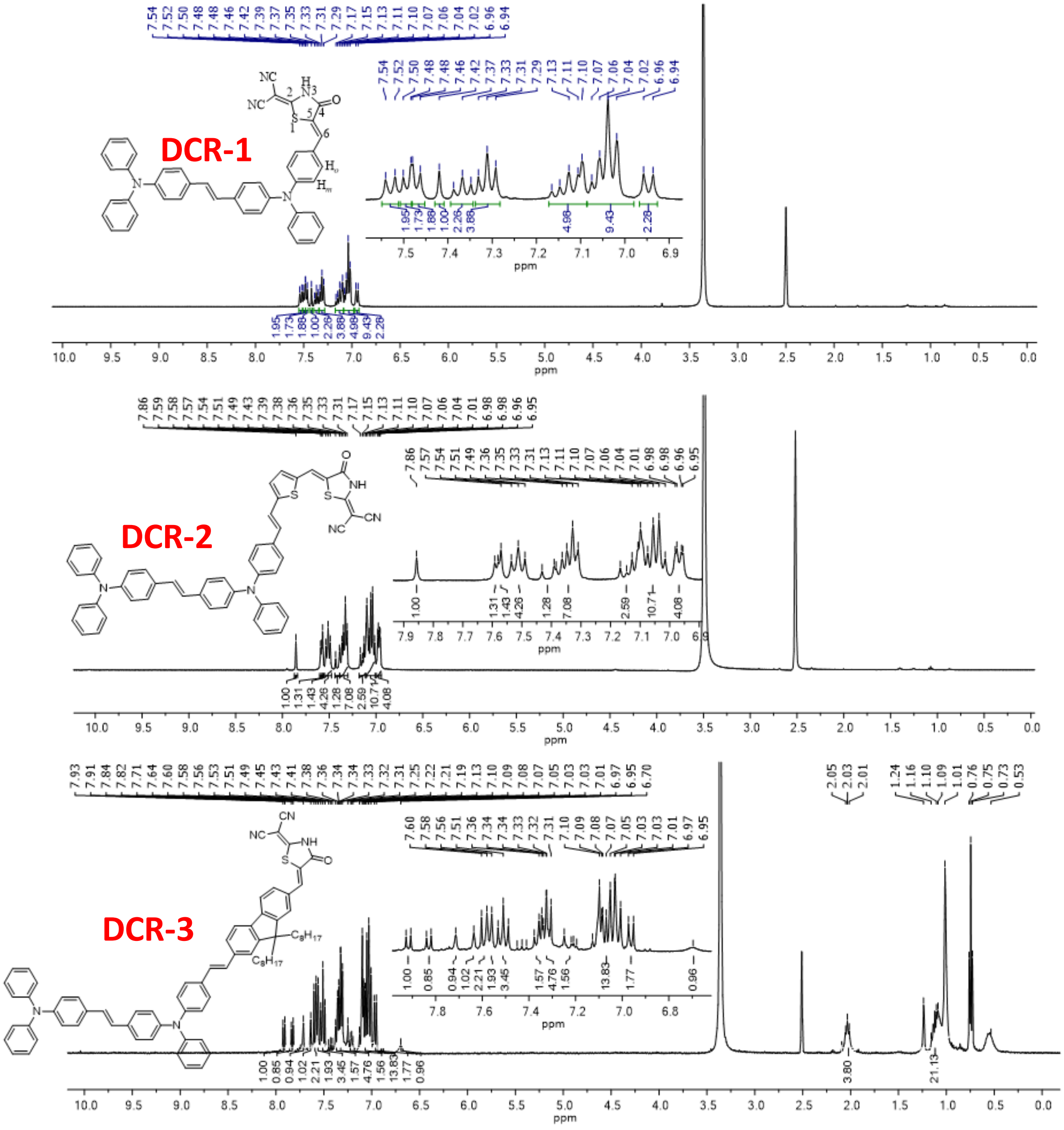

**Fig S1.** $^{1}$H NMR spectra (DMSO-$d_6$ - 400 MHz) for **DCR-(1-3).**

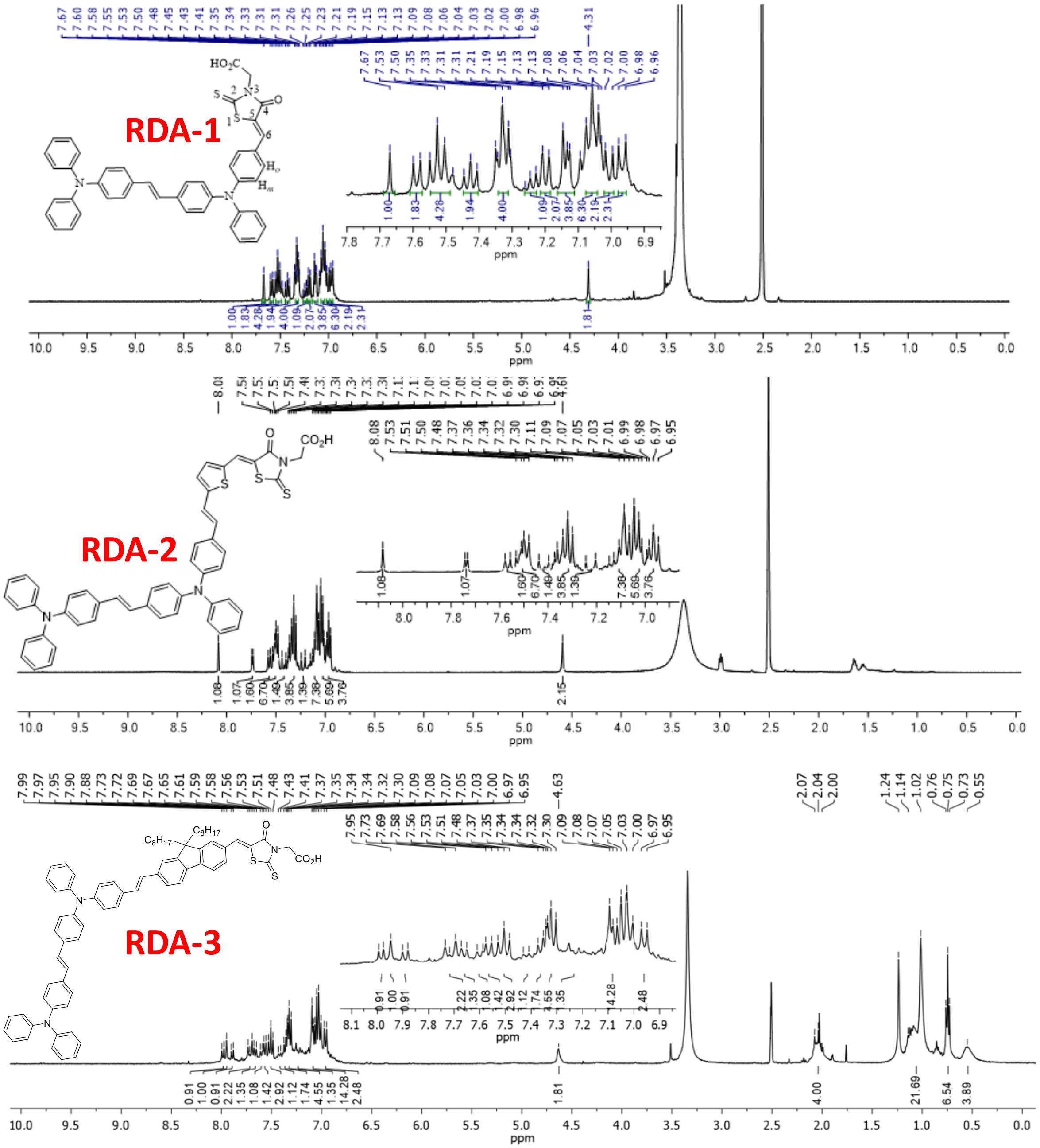

**Fig S2.** $^1$H NMR spectra (DMSO-$d_6$ - 400 MHz) for **RDA-(1-3).**

## 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 $CH_2Cl_2$ ($\phi_{std} = 0.87$)[1] as the standard. Where *F* and $F_{std}$ are the areas under the fluorescence curves of the compounds and the standard, respectively. $A$ and $A_{std}$ are the respective absorbance peaks of the sample and standard at the excitation wavelengths; $I$ and $I_{std}$ are the relative intensities of the exciting light, and $n^2$ and $n^2_{std}$ are the refractive indices of the solvents used for the sample and standard, respectively.[2]

$$\phi_F = \phi_F^{std} \frac{F A^{std} I n^2}{F^{std} A I^{std} n_{std}^2} \qquad (1)$$

| **Dye** | ***A*** | ***I*** | ***F*** | $\phi_f$ (x10$^{-3}$) |
|---|---|---|---|---|
| **DCR-1** | 0.05270 | 0.211495 | 21.2408 | 6.42 |
| **DCR-2** | 0.24393 | 0.6497 | 54.9527 | 4.26 |
| **DCR-3** | 0.60700 | 2.66783 | 255.348 | 7.03 |
| **RDA-1** | 0.05264 | 0.123919 | 11.3502 | 3.77 |
| **RDA-2** | 0,22831 | 0.108532 | 10.5205 | 0.76 |
| **RDA-3** | 0.30264 | 1.24258 | 112.806 | 6.57 |

### 1.4.Cell fabrication

**Photoanode.** FTO glass (TEC7) was cleaned and an under layer of $TiO_2$ was deposited by heating the substrates for 30 min at 70 ˚C in an aqueous solution of $TiCl_4$. Then an 8-µm layer of transparent $TiO_2$ was screen-printed. The paste used for this layer contained nanoparticles of 18 nm diameters. A scattering layer formed by 400 nm Ø nanoparticles (5 µm thick) was deposited on the transparent layer. The whole structure was calcined up to 500 ˚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 ˚C and cooled down to 80˚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˚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 – 25µm 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 $cm^2$.

### 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.[3] 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) δ: 7.97 (*s*, 1H), 7.79 (*d*, *J=8Hz*, 2H), 7.49 (*d*, *J=8Hz*, 2H), 7.40 (*d*, *J=8Hz*, 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 $C_{42}H_{31}N_3O_2$ 609.241; found 609.237 [$M^+$].

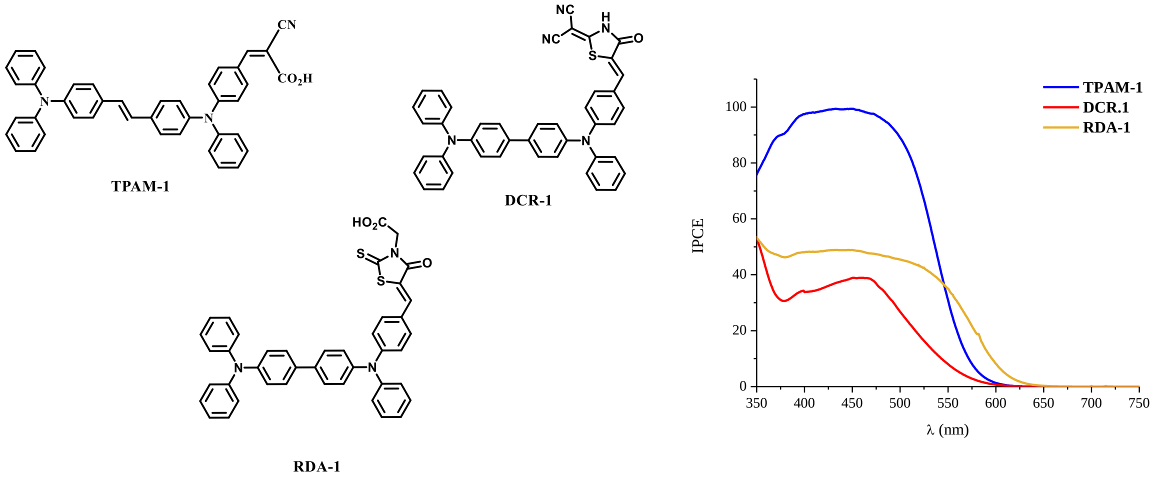

**Fig. S3.** Structures and IPCE spectra of dyes **TPAM-1**, **DCR-1** and **RDA-1**

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

| Dye | $J_{sc}$/mA $cm^{-2}$ | $V_{oc}$/V | FF | $\eta$ % (*) |
|---|---|---|---|---|
| **DCR-1** | 5.77 | 0.754 | 0.639 | 3.06 (2.87±0.27) |
| **DCR-2** | 5.46 | 0.567 | 0.586 | 1.80 (1.69±0.16) |
| **DCR-3** | 6.51 | 0.734 | 0.663 | 3.10 (2.98±0.14) |
| **RDA-1** | 6.72 | 0.726 | 0.643 | 3.15 (2.65±0.71) |
| **RDA-2** | 4.10 | 0.559 | 0.696 | 1.63 (1.31±0.36) |
| **RDA-3** | 6.64 | 0.721 | 0.660 | 3.17 (3.05±0.14) |
| **TPAM-1** | 8.14 | 1.080 | 0.698 | 6.13 (5.50±0.41) |
| **N719** | 15.04 | 0.804 | 0.534 | 6.31 (6.16±0.22) |

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

## 2. References

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2 A. T. R. Williams, S. A. Winfield and J. N. Miller, *Analyst*, 1983, **108**, 1067–1071.

3 C. A. Echeverry, R. Cotta, E. Castro, A. Ortiz, L. Echegoyen and B. Insuasty, *RSC Adv.*, 2015, **5**, 60823–60830.