## **Supplementary Information**

## A quinoxaline-fused tetrathiafulvalene-based sensitizer for efficient dyesensitized solar cells

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## **Experimental Section:**

**General:** All solvents and reagents were of commercial quality and used without further purification. All reactions, unless mentioned, were carried out under Ar. Column chromatography was performed using silica gel from Fluka, pore size 60 Å, 230-400 mesh particle size or neutral or basic aluminium oxide from CAMAG. In some cases column chromatography was performed on a Biotage Isolera 4. The UV-vis absorption spectrum was recorded on a Perkin-Elmer Lambda 900. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were obtained on a 300 MHz and 75 MHz (Bruker AVANCE 300) instrument respectively. Due to aggregation, <sup>13</sup>C-NMR spectrum of **1** was performed on a Bruker AVANCE II 400 at 50°C. Spectra were calibrated using the solvent residual peak as reference. High resolution Mass spectra were measured on a Thermo Scientific LTQ Orbitrap XL with a Nanospray Ionsource in positive or negative mode. 1,6-Bis(triisopropylsilyl)-hexa-1,5-diyne-3,4-dione<sup>1</sup> and 5,6-diamino-1,3-benzodithiol-2-thione<sup>2</sup> were synthesized as published.



Scheme 1 A synthetic route to the target dye 1: (a) ethanol, at reflux, 68%; (b) mercuric acetate,  $CH_2Cl_2$ , 98%; (c) 4,5-bis(hexylsulfanyl)-1,3-dithiol-2-thione (2 equiv.), triethylphosphite/toluene, 130 °C, 71%; (d) tetrabutylammonium fluoride, THF, -88 °C, 93%; (e) 4-iodobenzoic acid (5 equiv.), Pd(PPh\_3)\_2Cl\_2, diisopropylamine, 80 °C, 12%.

**6,7-Bis((triisopropylsilyl)ethynyl)-[1,3]dithiolo[4,5-g]quinoxalin-2-thione (5):** A mixture of 1,6-bis(triisopropylsilyl)-hexa-l,5-diyne-3,4-dione (204.0 mg, 0.4872 mmol) and 5,6-diamino-1,3-benzodithiol-2-thione (104.4 mg, 0.4871 mmol) was added to ethanol (4 mL) and heated to reflux for 30 minutes. The crude product was purified by flash column chromatography with hexane:CH<sub>2</sub>Cl<sub>2</sub> (3:1) to afford **5** as a pale orange solid. Yield: 198 mg (68%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 8.08$  (s, 2H), 1.18-1.19 (m, 42H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 211.6, 144.6, 140.8, 139.1, 120.4, 103.4, 101.0, 18.9, 11.6; HRMS (ESI): *m/z* Calcd. for C<sub>31</sub>H<sub>45</sub>N<sub>2</sub>S<sub>3</sub>Si<sub>2</sub>: 597.2278; found 597.2265.

**6,7-Bis((triisopropylsilyl)ethynyl)-[1,3]dithiolo[4,5-g]quinoxalin-2-one** (4): A suspension of compund **5** (2.12 g, 3.55 mmol) and mercuric acetate (3.45 g, 10.8 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (24 mL) was stirred for 25 minutes in air. Gradient flash column chromatography in hexane and CH<sub>2</sub>Cl<sub>2</sub> yielded **4** as an off-white powder: Yield: 2.01 g (98%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 8.14$  (s, 2H), 1.18-1.19 (m, 42H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 188.5$ , 140.5, 139.1, 136.9, 122.3, 103.4, 101.0, 18.9, 11.6; HRMS (ESI): *m/z* Calcd. for C<sub>31</sub>H<sub>45</sub>ON<sub>2</sub>S<sub>2</sub>Si<sub>2</sub>: 581.2506; found 581.2486.

**2-[4,5-Bis(hexylsulfanyl)-1,3-dithiol-2-ylidene]-6,7-bis((triisopropylsilyl)ethynyl)-[1,3]dithiolo[4,5-g]quinoxaline (3):** A mixture of compound **4** (1.05 g, 1.81 mmol) and 4,5-bis(hexylsulfanyl)-1,3-dithiol-2-thione (1.33 g, 3.63 mmol) in toluene (8 mL) and triethylphosphite (15 mL) was bubbled with Ar, and heated to 130°C in an oil bath for 30 minutes. After cooling to room temperature, methanol (100 mL) was added to the solution which was then kept in the freezer. After filtration, the precipitate was collected and rinsed copiously with methanol. Gradient flash column chromatography with CH<sub>2</sub>Cl<sub>2</sub> and hexane gave **3** as a red powder. Yield: 1.16 g (71%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.76 (s, 2H), 2.80 (t, 4H, *J* = 7.30 Hz), 1.61 (m, 4H), 1.43-1.23 (m, 12H), 1.16 (m, 42H), 0.86 (t, 6H, *J* = 6.71 Hz);<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 142.8, 139.6, 127.9, 119.5, 115.4, 108.2, 103.6, 99.4, 36.6, 31.5, 29.9, 28.4, 22.7, 18.9, 14.2, 11.6; HRMS (ESI): *m/z* Calcd. for C<sub>46</sub>H<sub>70</sub>N<sub>2</sub>S<sub>6</sub>Si<sub>2</sub>: 898.3396; found: 898.3377.

**2-[4,5-Bis(hexylsulfanyl)-1,3-dithiol-2-ylidene]-6,7-diethynyl-[1,3]dithiolo[4,5-g] quinoxaline (2):** Compound **3** (340 mg, 0.38 mmol) was dissolved in THF (5 mL), After cooling to -88°C with an acetone/liquid N<sub>2</sub> bath, tetrabutylammonium fluoride (1 M in THF, 0.83 mL) was added and stirred for 10 minutes. A saturated ammonium chloride in water (6 mL) was added. The product was filtered and rinsed with methanol to remove an orange impurity. The dark red product was analytically pure with no further purification necessary. Yield: 0.20 g (93%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.79 (s, 2H), 3.57 (s, 2H), 2.83 (t, 4H, *J* = 7.33 Hz), 1.64 (m, 4H), 1.46-1.28 (m, 12H), 0.89 (t, 6H, *J* = 6.82 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 144.17, 139.73, 139.35, 127.97, 119.44, 116.23, 107.46, 83.83, 80.13, 36.57, 31.45, 29.88, 28.35, 22.68, 14.15. HRMS (ESI): *m/z* Calcd. for C<sub>28</sub>H<sub>30</sub>N<sub>2</sub>S<sub>6</sub>: 586.0728; found: 586.0737.

**2-[4,5-Bis(hexylsulfanyl)-1,3-dithiol-2-ylidene]-6,7-bis(4-ethynylbenzoic** acid)-**[1,3] dithiolo[4,5-g]quinoxaline (1):** To a microwave vial (Biotage, 2-5 ml) with stir bar was added compound **2** (356.6 mg, 0.6074 mmol), 4-iodobenzoic acid (754.5 mg, 3.042 mmol, 5 eq.), and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (42.6 mg, 0.0607 mmol, 10%). The vial was purged with Ar, then degassed diisopropylamine (3 mL) was added. The vial was then immersed in an oil bath at 80°C for two hours. After cooling to room temperature, deionized water (50 ml, pH 4.4) was added and then the mixture was filtered and rinsed with hexane and methanol. The crude product was purified using column chromatography with gradient elution of THF, then THF:methanol 20:1, then THF:methanol:acetic acid 20:2:1. Solvent was evaporated < 40°C to yield **1** as a dark blue powder. Yield: 57.2 mg (12%). <sup>1</sup>H NMR (300 MHz,  $d_8$ -THF):  $\delta$  = 8.08 (d, 4H, J = 8.23 Hz), 7.98 (s, 2H), 7.77 (d, 4H, J = 8.20 Hz), 2.88 (t, 4H, J = 7.23 Hz), 1.72-1.60 (m, 4H), 1.48-1.28 (m, 12H), 0.90 (t, 6H, J = 6.85 Hz); <sup>13</sup>C NMR ( $d_8$ -THF, 50 °C):  $\delta$  = 166.73, 143.98, 141.06, 140.74, 132.96, 132.81, 130.71, 129.02, 126.72, 120.70, 95.17, 89.79, 37.05, 32.21, 30.70, 29.02, 23.35, 14.22. HRMS (ESI): *m/z* Calcd. for C<sub>42</sub>H<sub>38</sub>N<sub>2</sub>O<sub>4</sub>S<sub>6</sub>: 826.1150; found: 826.1186.

# Electrochemistry

Cyclic voltammetric experiments were conducted in THF solution containing supporting electrolyte of 0.1 M TBAPF<sub>6</sub> with Pt half bead polycrystal electrode as the working electrode. The Pt wires serve as the counter and reference electrodes. The potential of Pt reference electrode was calibrated by the Fc/Fc<sup>+</sup> redox couple. Before each experiment, the Pt working electrode was annealed in a butane flame for 1 min for obtaining a clean and smooth surface. The hot electrode was then quickly transferred into a tube flowing with a mixture of Ar/H<sub>2</sub> (V<sub>Ar</sub>/V<sub>H2</sub> = 4:1), and allowed to cooled down to room temperature. The Pt electrode was then quickly transferred into the glass cell and brought in contact with the electrolyte in a hanging meniscus configuration at E = 0.60 V vs. Fc/Fc<sup>+</sup>. All CV measurements were carried out under Ar atmosphere.

# **Computational methods**

Optical transitions were computed using with the Gaussian 09 software package<sup>3</sup> using Dunning's correlation consistent basis set (cc-pVTZ).<sup>4,5</sup> The relaxed structure of of the molecule in its electronic ground state was obtained using density functional theory (DFT)<sup>6,7</sup> with the PBE0<sup>8,9</sup> exchange-correlation functional, applying no symmetry constraints. The ten lowest lying electronic excitations were calculated by time-dependent DFT (TDDFT).<sup>10</sup>



Fig. S1. The optimized geometry of dyad 1.

Atoms	Angle [deg]
C1-S3-C3	94.88
S3-C3-S4	112.58
C3-S4-C2	94.87
S4-C2-C1	116.43
C2-C1-S3	116.42
S3-C3-C4	123.64
S4-C3-C4	123.72
C3-C4-S6	122.74
C3-C4-S7	122.76
C4-S6-C5	95.60
S6-C5-C6	115.93
C5-C6-S7	115.92
C6-S7-C4	95.61

**Table S1.** Bond angles of the TTF moiety of dyad **1** optimized at the PBE0/ccpVTZ level. **Table S2.** Selected backbone bond distances of dyad **1** optimized at the PBE0/ccpVTZ level.

Atoms	<b>d</b> [Å]
S1-C1	1.744
C1-S3	1.763
S3-C4	1.754
C4-S4	1.754
S4-C2	1.763
C2-S2	1.744
C1-C2	1.348
C3-C4	1.343
C4-S5	1.754
S5-C5	1.747
C5-C6	1.422
C6-S6	1.747
C4-S6	1.754
C5-C7	1.368
C7-H1	1.082
C7-C9	1.409
C9-C10	1.423
C10-C8	1.409
C8-H2	1.082
C6-C8	1.368
C9-N1	1.345
N1-C11	1.316
C11-C12	1.439
C12-N2	1.316
N2-C10	1.345
C11-C13	1.418
C13-C15	1.207
C12-C14	1.418
C14-C16	1.207

**Table S3.** TD-DFT input coordinates of dyad **1** optimized at the PBE0/cc-pVTZ level.

Element	X [Å]	Y [Å]	Z [Å]
Ο	0.504089	6.145347	0.710270
С	0.632516	-4.857593	0.343130
Ο	10.704385	-4.352099	0.130985
С	8.334031	-4.154472	0.233856
С	8.347855	-2.813767	-0.142365
С	7.166480	-2.111712	-0.258247
С	5.943429	-2.743661	0.001760
С	5.935627	-4.092677	0.375187
С	7.121726	-4.789886	0.491184
С	4.726185	-2.028974	-0.113763
С	3.684880	-1.426168	-0.212276
С	2.463908	-0.717945	-0.349776
Ν	1.349577	-1.409623	-0.460611
С	0.204307	-0.720669	-0.614466
С	-1.010427	-1.424893	-0.733068
С	-2.178186	-0.732294	-0.900080
S	-3.729685	-1.505403	-1.118599
С	-4.671426	-0.027945	-1.027166
С	-6.006602	-0.025344	-0.881637
S	-6.980252	1.432855	-0.856421
С	-8.376622	0.667439	-0.099849
S	-9.716568	1.684937	0.358230
С	-8.942741	2.806292	1.574120
С	-9.990134	3.793230	2.048475
С	-8.374170	-0.680371	-0.060336
S	-9.711820	-1.673375	0.454400
С	-8.932255	-2.737571	1.716997

С	-9.979290	-3.697316	2.245061
S	-6.974511	-1.483411	-0.769865
S	-3.733443	1.443154	-1.211733
С	-2.179733	0.689355	-0.946139
С	-1.013413	1.393836	-0.824355
С	0.202665	0.701412	-0.658944
Ν	1.344790	1.401632	-0.534360
С	2.460053	0.720804	-0.376428
С	3.672621	1.439703	-0.219865
С	4.704521	2.047864	-0.069273
С	5.913971	2.763353	0.108090
С	7.022633	2.145806	0.701721
С	8.198394	2.846178	0.871057
С	8.293121	4.170892	0.452176
С	9.580807	4.872268	0.657697
0	10.555544	4.378621	1.163346
0	9.564112	6.143188	0.217281
С	7.194349	4.791926	-0.136573
С	6.013557	4.096581	-0.306340
Н	10.400257	-6.501971	0.749553
Н	9.301365	-2.341444	-0.341277
Н	7.171397	-1.071699	-0.558332
Н	4.989726	-4.579940	0.572555
Н	7.114800	-5.831701	0.781506
Н	-0.982929	-2.506085	-0.689707
Н	-8.563291	2.202213	2.398603
Н	-8.103932	3.317812	1.102238
Н	-9.555220	4.472125	2.784168
Н	-10.373200	4.392451	1.220723
Н	-10.833415	3.283146	2.517384

Н	-8.098435	-3.274137	1.264517
Н	-8.545125	-2.096258	2.509137
Н	-9.541088	-4.342159	3.008887
Н	-10.817517	-3.162699	2.695313
Н	-10.370209	-4.333670	1.449318
Н	-0.988638	2.475706	-0.847870
Н	6.941925	1.118217	1.032209
Н	9.063430	2.384871	1.330104
Н	10.442705	6.499575	0.398590
Н	7.270812	5.821385	-0.459221
Н	5.155540	4.573098	-0.762242



Fig. S2. Frontier molecular orbitals of dyad 1.

State	Wavelength [nm]	Oscillator strength $f_{calc}$	Major contributions	s [%]	μ [Debye]	Character
$S_0$					3.997	
$\mathbf{S}_1$	565.93	0.4673	$HOMO \rightarrow LUMO$	100	12.7034	$\pi \to \ \pi^* \ \mathrm{CT}$
$S_2$	494.40	0.0440	HOMO $\rightarrow$ LUMO+1	100	4.7139	$\pi \to \ \pi^* \ \mathrm{CT}$
$S_3$	415.12	0.0015	HOMO $\rightarrow$ LUMO+3	100	4.0179	$\pi \to \ \pi^* \ \mathrm{CT}$
$S_4$	381.35	0.4303	HOMO-4→ LUMO HOMO-2 → LUMO+1 HOMO-1 → LUMO	3 7 90	9.3987	$\begin{array}{l} \pi \rightarrow \ \pi^{*} \ \mathrm{CT} \\ \pi \rightarrow \ \pi^{*} \ \mathrm{CT} \\ \pi \rightarrow \ \pi^{*} \ \mathrm{CT} \end{array}$
S <sub>5</sub>	365.56	0.0720	HOMO-3 → LUMO HOMO-2 → LUMO HOMO-1 → LUMO+1	6 84 10	4.8637	$\begin{array}{l} \pi \rightarrow \pi^{*} \\ (CT) \\ \pi \rightarrow \pi^{*} \\ (CT) \\ \pi \rightarrow \pi^{*} \\ (CT) \end{array}$
$S_6$	361.05	0.0035	$\rm HOMO \rightarrow \rm LUMO+2$	100	4.0386	$\pi \rightarrow \pi^*$ (CT)
$S_7$	355.72	0.0009	HOMO-6 → LUMO HOMO-6 → LUMO+2 HOMO-5 → LUMO	59 3 38	4.0081	$\begin{array}{l} \sigma \rightarrow \ \pi^{*} \\ \sigma \rightarrow \ \pi^{*} \\ \sigma \rightarrow \ \pi^{*} \end{array}$
$S_8$	354.31	0.0006	HOMO-1 $\rightarrow$ LUMO+1 HOMO $\rightarrow$ LUMO+4 HOMO $\rightarrow$ LUMO+5	9 52 39	4.0036	$\begin{array}{l} \pi \rightarrow \pi^{*} \\ (CT) \\ \pi \rightarrow \pi^{*} \\ (CT) \\ \pi \rightarrow \pi^{*} \end{array}$
S9	349.16	0.2741	HOMO-4 $\rightarrow$ LUMO+1 HOMO-2 $\rightarrow$ LUMO HOMO-1 $\rightarrow$ LUMO+1 HOMO $\rightarrow$ LUMO+3 HOMO $\rightarrow$ LUMO+4	8 10 72 3 7	7.1482	$\begin{array}{l} \pi \rightarrow \ \pi^{*} \ \mathrm{CT} \\ \pi \rightarrow \ \pi^{*} \\ \pi \rightarrow \ \pi^{*} \\ (\mathrm{CT}) \\ \pi \rightarrow \ \pi^{*} \\ (\mathrm{CT}) \\ \pi \rightarrow \ \pi^{*} \end{array}$
S <sub>10</sub>	329.15	0.9424	$\begin{array}{l} \text{HOMO-4} \rightarrow \text{LUMO} \\ \text{HOMO-3} \rightarrow \text{LUMO+1} \\ \text{HOMO-2} \rightarrow \text{LUMO+1} \\ \text{HOMO-1} \rightarrow \text{LUMO} \end{array}$	37 4 48 11	14.209	$\begin{array}{l} \pi \rightarrow \ \pi^{*} \ \mathrm{CT} \\ \pi \rightarrow \ \pi^{*} \ \mathrm{CT} \\ \pi \rightarrow \ \pi^{*} \ \mathrm{CT} \\ \pi \rightarrow \ \pi^{*} \ \mathrm{CT} \end{array}$

**Table S4.** Wavelength, oscillator strength, major orbital contributions, total electric dipole moments and nature of the transitions for the first ten excited states of dyad **1**.

#### Preparation of the Dye-Sensitized Solar Cell Based on Dye 1:

Electrodes with 8  $\mu$ m transparent layer and 4  $\mu$ m scattering layer of TiO<sub>2</sub> were screenprinted on fluorine-doped tin oxide (FTO) as reported in the literature.<sup>11</sup> After sintering at 500 °C for 0.5 h and cooling to room temperature, the electrodes were treated with 33 mM TiCl<sub>4</sub> solution at 70 °C for 0.5 h. The films were sintered at 500 °C for 0.5 h and cooled to 80 °C before dipping into dye solution (0.1 mM dye in THF with or without 5 mM chenodeoxycholic acid) for 3 h. After the sensitization, the electrodes were rinsed with acetonitrile and dried in air. The cells were sealed with a Surlyn film and a platinized FTO counter electrode. The composition of electrolyte of this study was 1.0 M 1,3-dimethylimidazolium iodide, 0.05 M LiI, 0.03 M  $I_2$ , 0.1 M guanidinium thiocyanate, and 0.5 M 4-*tert*-butylpyridine in acetonitrile:valeronitrile (85:15, v/v).

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