Electronic Supplementary Information (ESI)

Benzothiadiazole-Containing Donor-Acceptor-Acceptor Type Organic Sensitizers for Solar Cells with ZnO Photoanodes

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Experimental section

Materials and instrumentation.

All solvents used were purified by standard procedures, or purged with nitrogen before use. ¹H NMR spectra were recorded on a Bruker 400 MHz spectrometer. Absorption spectra were recorded on a Dynamica DB-20UV-Vis spectrophotometer. All chromatographic separations were carried out on silica gel (60 M, 230–400 mesh). Mass spectra (FAB) were recorded on a VG70-250S mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

ZnO nanoparticles synthesis.

ZnO used for the electron transparent layer was manufactured as described below: ZnO powder (4.23 g, Degussa VP AdNano[®]ZnO20) with an approximate particle size of 20 nm was thoroughly mixed with 20 mL of EtOH and DI-water (v/v = 70/30) mixture. This colloidal solution was stirred for 3 days to form a well mixed 20 wt% ZnO. The film thickness was measured to be ~15 μ m by a profilometer (Dektak3, Veeco/Sloan Instruments Inc., USA).

Synthesis of hierarchical ZnO nanostructures.

ZnO nanoparticles with brush-like hierarchical nanostructures were synthesized in a one-pot process. In a typical reaction process, $Zn(NO_3)_2 \cdot 6 H_2O(3.2 \text{ g})$ was dissolved in 15 mL of deionized water and stirred for 10 min. After addition of polyvinilpyrrolidone (PVP) (0.030 g, Aldrich, Mw = 200,000), the solution was slowly added 10 mL of NaOH (4 M in H₂O) under constant stirring for 30 min. The solution was then heated at 50 °C for 5 h. The white precipitate formed was washed thoroughly with deionized water for several times, and dried at 60 °C under vacuum for 12 h.

Cell fabrication and characterization of DSSCs.

The ZnO electrode with a 0.16 cm² geometric area was immersed in a mixture of acetonitrile and *tert*–butyl alcohol or THF (volume ratio of 1:1) containing 3×10^{-4} M of an organic sensitizer or 5-[[4-[4-(2,2-diphenylethenyl)phenyl]-1,2,3-3*a*,4,8*b*-hexahydrocyclopent[*b*]indol-7-yl]methylene]-2-(3-ethyl-4-oxo-2-thioxo-5-thiazolidi-nylidene)-4-oxo-3-thiazolidineacetic acid (D149) at room temperature for overnight. A platinized FTO was used as a counter electrode and was controlled to have an active area of 0.16 cm² by adhered polyester tape with thickness of 60 µm. After rinsing with

ACN or THF, the photoanode was placed on top of the counter electrode and clipped together tightly to form a cell. Electrolyte was injected into the space and then sealing the cell with the Torr Seal cement (Varian, MA, USA). The electrolyte was composed of lithium iodide (0.1 M), iodine (0.005 M), 1,2-dimethyl-3-propylimidazolium iodide (0.6 M) and guanidine thiocyanate (0.1 M) dissolved in the mixture of acetonitrile and 3-methoxypropionitrile. The photoelectrochemical characterizations of the solar cells were carried out by using an Oriel Class A solar simulator (Oriel 91195A, Newport Corp.). Photocurrent current-voltage characteristics of the DSSCs were recorded with a potentiostat/galvanostat (CHI650B, CH Instruments, Inc., USA) at a light intensity of 1.0 sun calibrated by an Oriel reference solar cell (Oriel 91150, Newport Corp.). Incident photon-to-current conversion efficiency (IPCE) curves were obtained at short-circuit condition. The light source was a class A quality solar simulator (PEC-L11, AM1.5G, Peccell Technologies, Inc.); light was focused through a monochromator (Oriel Instrument, model 74100) onto the photovoltaic cell and the measured with an optical detector (Oriel Instrument, model 71580) and power meter (Oriel Instrument, model 70310). The photovoltage transients of the assembled devices were recorded with a digital oscilloscope (model LT322, LeCroy, USA). Pulsed laser excitation was applied by a frequency-doubled Q-switched Nd:YAG laser (model Quanta-Ray GCR-3-10, Spectra-Physics laser) with a 2 Hz repetition rate at 532 nm,

and a 7 ns pulse width at half-height. The average electron life-time could approximately be estimated by fitting a decay of the open-circuit voltage transient with $\exp(-t\tau_e^{-1})$, where *t* is the time and τ_e is an average time constant before recombination.¹

Quantum chemistry computation.

The structures of the molecules were optimized using B3LYP/6-31G*. For each molecule, a number of possible conformations were examined and the one with the lowest energy was used. For the excited state, we employed the time-dependent density functional theory (TDDFT) with the B3LYP functional. All of them were performed with Q-Chem 4.0 software.² There exist a number of previous works that employed TDDFT to characterize excited states with charge-transfer character.³ In some cases underestimation of the excitation energies was seen.^{3,4} Therefore, in the present work, we use TDDFT to characterize the extent of the charge-shift and avoid drawing conclusions from the excitation energy.

Synthesis of the materials.

Scheme 1 describes the synthetic pathways to the desired dyes. Palladium catalyzed Stille coupling reaction⁵ of 7-bromobenzo[c][1,2,5]thiadiazole-4-carbaldehyde⁶ with appropriate stannyl derivatives of arylamine provided formyl intermediates, subsequent Knoevenagel condensation with cyanoacetic acid afforded the desired

products.

7-(4-(Diphenylamino)phenyl)benzo[c][1,2,5]thiadiazole-4-carbaldehyde (RL1-a). Under nitrogen atmosphere, 7-bromo-benzo[1,2,5]thiadiazole-4-carbaldehyde (0.50 g, 2.01 mmol),⁶ N,N-diphenyl-4-(tributylstannyl)aniline (1.64 g, 3.02 mmol) and Pd(dba)₂ (0.31g, 2 mol%) were dissolved in 30 mL of toluene. The reaction mixture was heated at 100 °C and refluxed for 24 h. After cooling, the mixture was quenched by Potassium fluoride (KF). Ether was added, the aqueous layer was extracted with ether. The combined organic layers were dried over MgSO₄ and after filtration the filtrate was evaporated to dryness. The solid was purified by chromatography on silica gel (ethyl acetate/hexanes: 1:5). **RL1-a** was obtained in 76% yield (0.64 g).¹H NMR (400 MHz, acetone- d_6): δ 10.80 (s, 1H), 8.33 (d, J = 7.6 Hz, 1H), 8.10 (d, J = 6.8 Hz, 2H), 8.06 (d, *J* = 7.6 Hz, 1H), 7.37–7.41 (m, 4H), 7.13–7.21 (m, 8H).

2-Cyano-3-(7-(4-(diphenylamino)phenyl)benzo[1,2,5]thiadiazol-4-yl)acrylic acid (RL1).

A mixture of 7-(4-(diphenylamino)phenyl)benzo[1,2,5]thiadiazole-4-carbaldehyde (0.32 g , 0.80 mmol), cyanoaceticacid (0.13 g, 1.6 mmol) and three drops of piperidine were dissolved in 20 mL of acetonitrile. Under nitrogen atmosphere, the reaction mixture was heated to 100 °C and refluxed for 24 h. The solid was filtered and washed with methanol. The desired compound was obtained as a dark red solid in

50% yield (0.20 g).¹H NMR (400 MHz, THF- d_8): δ 9.31 (s, 1H), 9.02 (d, J = 7.6 Hz, 1H), 8.26 (d, J = 8.4 Hz, 2H), 8.19 (d, J = 7.6 Hz, 1H), 7.46–7.50 (m, 4H), 7.33–7.35 (m, 6H), 7.24–7.27 (m, 2H). ¹³C NMR (THF- d_8): δ 156.43, 154.11, 150.12, 148.50, 145.56, 137.94, 131.49, 130.94, 130.64, 130.43, 127.50, 126.24, 125.81, 124.72, 123.05. HRMS (FAB) (m/z [M+H]⁺): calcd for C₂₈H₁₈N₄O₂S 475.1228; found, 475.1235. Anal. calcd: C₂₈H₁₈N₄O₂S: C, 70.87; H, 3.82; N, 11.81. Found: C, 70.75; H, 4.27; N, 12.05.

7-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)benzo[c][1,2,5]thiadiazole-4-

carbaldehyde (RL2-a).

Under nitrogen atmosphere, 7-bromo-benzo[1,2,5]thiadiazole-4-carbaldehyde (0.30 g, 1.23 mmol), 4-(hexyloxy)-*N*-(4-(hexyloxy)phenyl)-*N*-(4-(tributylstannyl)phenyl)aniline (1.36 g, 1.85 mmol) and Pd(PPh₃)₄ (0.029 g, 2 mole%) were dissolved in 20 mL of toluene. The reaction mixture was heated to 100 °C and refluxed for 24 h. After cooling, the mixture was quenched by aqueous potassium fluoride (KF). Ethyl acetate was added, and the aqueous layer was extracted with ether. The combined organic layers were dried over MgSO₄ and after filtration the filtrate was evaporated to dryness. The solid was purified by chromatography on silica gel (ethyl acetate/hexanes = 1:3 by vol.). The **RL2-a** was obtained in 30% yield (0.22 g).¹H NMR (400 MHz, CDCl₃): δ 10.71 (s, 1H), 8.23 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 4H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 4H), 3.92–3.95 (m, 4H), 1.73–1.79 (m, 5H), 1.43–1.47 (m, 10H), 0.90–0.91 (m, 7H).

3-(7-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)benzo[*c*][1,2,5]thiadiazol-4-yl)-2-c yanoacrylic acid (RL2).

A mixture of 7-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)benzo[c][1,2,5]thiadiazole-4-carbaldehyde (0.22 g, 0.36 mmol), cyanoaceticacid (0.031 g, 0.36 mmol) and three drops of piperidine were dissolved in 20 mL of acetonitrile. Under nitrogen atmosphere, the reaction mixture was heated to 100 °C and refluxed for 24 h. The resulting compound was purified by chromatography on silica gel (DCM/acetic acid = 10:0.15 by vol.). The compound was isolated as a purple solid in 30% yield (0.080 g). ¹H NMR (400 MHz, THF- d_4): δ 9.19 (s, 1H), 8.87 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 8.4Hz, 2H), 7.98 (d, J = 7.6 Hz, 1H), 7.12 (d, J = 8.4 Hz, 4H), 6.98 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.4 Hz, 4H), 3.95–3.98 (m, 4H), 1.29–1.37 (m, 14H), 0.93 (m, 8H). ¹³C NMR (THF-*d*₈): δ 157.23, 141.13, 132.32, 127.86, 127.34, 126.39, 124.88, 123.92, 120.66, 116.14, 68.84, 32.65, 30.37, 26.80, 23.59. HRMS (FAB) $(m/z [M+H]^+)$: calcd for C₄₀H₄₂N₄O₄S 675.3004; found, 675.3014. Anal. calcd: C₄₀H₄₂N₄O₄S: C, 71.19; H, 6.27; N, 8.30. Found: C, 71.36; H, 6.72; N, 7.97.

7-(5-(4-Bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)benzo[c][1,2,5]thiadi

azole-4-carbaldehyde (RL3-a).

Under nitrogen atmosphere, 7-bromo-benzo[1,2,5]thiadiazole-4-carbaldehyde (0.20 g, 0.823 4-(hexyloxy)-N-(4-(hexyloxy)phenyl)-N-(4-(5-(tributylstannyl)thiommol), phen-2-yl)phenyl)aniline (0.87 g, 1.07 mmol) and Pd(PPh₃)₄ (0.030 g, 3 mole%) were dissolved in 15 mL of toluene. The reaction mixture was heated to 100 °C and refluxed for 24 h. After cooling, the mixture was quenched by aqueous potassium fluoride (KF). Ethyl acetate was added, and the aqueous layer was extracted with ether. The combined organic layers were dried over MgSO₄ and after filtration the filtrate was evaporated to dryness. The solid was purified by chromatography on silica gel (DCM/hexanes = 1:1 by vol.). The **RL3-a** was obtained in 54% yield (0.23 g).¹H NMR (400 MHz, acetone- d_6): δ 10.00 (s, 1H), 7.64 (d, J = 4.0 Hz, 1H), 7.54 (d, J =8.8 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 6.87 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 4.0 Hz, 1H), 6.36 (d, J = 8.8 Hz, 4H), 6. 6.21 (d, J = 7.6 Hz, 4H), 6.12 (d, J = 8.8 Hz, 2H), 3.23-3.27 (m, 4H), 1.29-1.30 (m, 5H), 1.00-1.06 (m, 5H), 0.70-0.76 (m, 10H), 0.60–0.62 (m, 2H).

(E)-3-(7-(5-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)benzo[c][1,2,
5]thiadiazol-4-yl)-2-cyanoacrylic acid (RL3).

A mixture of 7-(5-(4-bis(4-(hexyloxy)phenyl)amino)phenyl)thiophen-2-yl)benzo[c] [1,2,5]thiadiazole-4-carbaldehyde (0.12 g, 0.174 mmol), cyanoaceticacid (0.050 g, 0.51 mmol) and three drops of piperidine were dissolved in 20 mL of acetonitrile. Under nitrogen atmosphere, the reaction mixture was heated to 100 °C and refluxed for 24 h. The solid was purified by chromatography on silica gel (EA/acetic acid: 10:0.1). The desired compound was obtained as a purple solid in 38% yield (0.050 g).¹H NMR (400 MHz, THF- d_8): δ 9.16 (s, 1H), 8.86 (d, J = 7.6 Hz, 1H), 8.37 (d, J =4.0 Hz, 1H), 8.18 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 4.0 Hz, 1H), 7.06 (d, J = 8.8 Hz, 4H), 6.91 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 4H), 3.93–3.97 (m, 4H) 1.73–1.77 (m, 2H), 1.50 (m, 4H), 1.36–1.37 (m, 8H), 1.36–1.50 (m, 8H), 1.29 (m, 2H), 0.91–0.93 (m, 6H). ¹³C NMR (THF-*d*₈): δ 157.49, 157.10, 156.41, 153.90, 151.20, 147.19, 141.38, 140.82, 138.90, 131.30, 131.15, 130.65, 128.29, 127.89, 126.60, 123.30, 119.49, 116.19, 116.10, 68.83, 32.64, 30.69, 30.35, 26.80, 23.59, 14.44. HRMS (FAB) $(m/z [M+H]^+)$: calcd for C₃₉H₃₀N₄O₂S 757.2881; found, 757.2898. Anal. calcd: C₄₄H₄₄N₄O₄S₂: C, 69.81; H, 5.86; N, 7.40. Found: C, 69.67; H, 6.43; N, 7.46.

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(i) Pd(PPh₃)₄, toluene (ii) cyanoacetic acid, piperidine, acetonitrile

Scheme S1. Synthetic pathways of the RL dyes.



Fig. S1. Absorption spectra of RL dyes on ZnO thin film.



Fig. S2. Cyclic voltammograms of RL dyes recorded in THF.



Fig. S3. (a) Electrochemical impedance spectra (Nyquist plots) of DSSCs based on the dyes measured in the dark. (b) Electrochemical impedance spectra (Nyquist plots) of DSSCs based on the dyes measured under (AM 1.5) illumination.

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Fig. S4. Schematic division and dihedral angles of molecules.





Fig. S5. Selected frontier orbitals of the dyes.



Fig. S6. Schematic representation of the calculated electronic structures of the complexes in the gas-phase.



Fig. S7. Plot of the difference in the Mulliken charges between the ground-state and the excited state.



Fig. S8. (a) SEM images of bare ZnO. SEM images of ZnO after dye soaking for 24 h: **RL1** (b), **RL2** (c), N3 (d), **RL3** (e) and D149 (f).



Fig. S9. (a)~(c) SEM images of the secondary ZnO nanostructures at different magnifications (d) XRD pattern of brush-like hierarchical ZnO nanostructures.



Fig. S10. (a) *J-V* curves of DSSCs based on the **RL** dye. The photoanode consists of TL and SL. (b) IPCE spectra of DSSCs based on the **RL** dye.

	$\lambda_{abs} \left(\varepsilon \times 10^{-4} \text{ M}^{-1} \text{cm}^{-1} ight)^{a}$	$\lambda_{em}{}^{a)}$	$E_{1/2} (\mathrm{ox})^{\mathrm{b}}$	HOMO/LUMO	$E_{0-0}^{\ \ c)}$	$E_{0-0}^{*d)}$
Dye						
	nm	nm	mV	eV	eV	eV
RL1	324 (2.37), 486 (1.53)	626	546	5.65/3.42	2.23	-0.98
RL2	347 (1.65), 513 (1.36)	635	330	5.43/3.31	2.12	-1.09
RL3	362 (2.12), 540 (1.72)	658	266	5.37/3.31	2.06	-1.09

Table S1. Electrooptical Parameters of the Dyes.

^{a)}Recorded in THF solutions at 298K.^{b)}Recorded in THF solutions. $E_{ox} = 1/2(E_{pa} + E_{pc})$, $\Delta E_p = E_{pa} - E_{pc}$ where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively. Oxidation potential reported is adjusted to the potential of ferrocene which was used as an internal reference. The values in parentheses are the peak separation of cathodic and anodic waves. Scan rate: 100 mVs⁻¹.^{c)}The band gap, E_{0-0} , was derived from the intersection of the absorption and emission spectra. ^{d)} E_{0-0} *: The excited state oxidation potential vs NHE.

	1	-	5							
	dipole moment (Debye)									
_	Х	У	Z	total						
RL1	-6.1043	-0.2584	-1.3173	6.2501						
RL2	-6.4749	-4.4247	0.2756	7.8472						
RL3	-11.3085	-1.8608	0.3608	11.4663						
S1	-4.9521	-2.1394	-1.0691	5.4994						

Table S2. Ground-state dipole moments of the dyes.

Table S3. Calculated lower-lying transitions of the dyes.^{*a*}

dye	State	excitation ^b	$\lambda_{\rm cal,}$	ſ ^b	Δ (Mulliken	$f \times \Delta q$	dye	State	excitation ^b	$\lambda_{\mathrm{cal},}$	f^{\flat}	Δ (Mulliken	$f \times \Delta q$
			eV		charge), ^{d} e					eV		charge), $^{d} \mathbf{e} $	
RL1	\mathbf{S}_1	$\mathrm{H} \rightarrow \mathrm{L} \ (100\%)$	1.94	0.47	Am: 0.59	-0.09	RL2	S_1	$\mathrm{H} \rightarrow \mathrm{L} \ (100\%)$	1.80	0.55	Am': 0.63	-0.10
					Ph: 0.21							Ph: 0.17	
					Btz: -0.61							Btz: -0.61	
					Ac: -0.19							Ac: -0.19	
	S_2	H1 \rightarrow L (41%)	2.92	0.00	Am: 0.38	0.00		S_2	$\mathrm{H1} \rightarrow \mathrm{L}(27\%)$	2.76	0.00	Am': 0.48	0.00
		$H \rightarrow L1 (57\%)$			Ph: 0.19				$H \rightarrow L1 (71\%)$			Ph: 0.21	
					Btz: -0.39							Btz: -0.44	
					Ac: -0.18							Ac: -0.25	
	S_3	H1 \rightarrow L (56%)	3.09	0.53	Am: 0.35	-0.09		S_3	H1 \rightarrow L (70%)	2.94	0.49	Am': 0.37	-0.07
		$H \rightarrow L1 (42\%)$			Ph: 0.15				$\mathrm{H} \rightarrow \mathrm{L1}\;(27\%)$			Ph: 0.15	

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					Btz: -0.33							Btz: -0.38	
					Ac: -0.17							Ac: -0.15	
RL3	\mathbf{S}_1	$\mathrm{H} \rightarrow \mathrm{L} \ (100\%)$	1.62	0.67	Am': 0.55	-0.11	S1	\mathbf{S}_1	$\mathrm{H} \rightarrow \mathrm{L} \ (99\%)$	1.87	0.53	Am: 0.55	-0.07
					Ph: 0.22							Ph: 0.23	
					T: -0.02							Btz: -0.52	
					Btz: -0.57							T: -0.12	
					Ac: -0.17							Ac: -0.14	
	S_2	H1 \rightarrow L (94%)	2.42	0.36	Am': 0.25	-0.02		S_2	$\mathrm{H1} \rightarrow \mathrm{L} \ (19\%)$	2.51	0.00	Am: 0.43	0.00
					Ph: 0.05				$\mathrm{H} \rightarrow \mathrm{L1}\;(79\%)$			Ph: 0.23	
					T: 0.18							Btz: -0.32	
					Btz: -0.43							T: -0.11	
					Ac: -0.06							Ac: -0.23	
	S_3	$H \rightarrow L1 (93\%)$	2.76	0.37	Am': 0.44	-0.12		S_3	$\mathrm{H1} \rightarrow \mathrm{L} \ (77\%)$	2.71	0.52	Am: 0.25	-0.02
					Ph: 0.23				$\mathrm{H} \rightarrow \mathrm{L1} \ (19\%)$			Ph: 0.06	
					T: 0.13							Btz: -0.36	
					Btz: -0.49							T: 0.09	
					Ac: -0.32							Ac: -0.04	
S2	\mathbf{S}_1	$\mathrm{H} \rightarrow \mathrm{L} \ (99\%)$	2.42	0.70	Am: 0.57	-0.29							
					Ph: 0.14								
					T: -0.29								
					Ac: -0.41								
	S_2	$H1 \rightarrow L (90\%)$	3.44	0.56	Am: 0.20	-0.10							
		$H \rightarrow L1 (8\%)$			Ph: -0.02								
					T: 0.00								
					Ac: -0.18								
	S_3	$H3 \rightarrow L (10\%)$	3.83	0.01	Am: 0.14	0.00							
		$H \rightarrow L1 (15\%)$			Ph: -0.12								
		$\mathrm{H} \rightarrow \mathrm{L2}~(66\%)$			T: 0.00								
					Ac: -0.02								

^{*a*}Results are based on gas-phase TD-DFT calculation. ^{*b*}H = HOMO, L = LUMO, H1 = The next highest occupied molecular orbital, or HOMO – 1, H2 = HOMO – 2, L1 = LUMO + 1, L2 = LUMO + 2. In parentheses is the population of a pair of MO excitations. ^{*c*}Oscillator strength. ^{*d*}The difference of the Mulliken charge between the ground state and excited state.

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