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# Molecular Design of Efficient Organic D-A- $\pi$ -A Dye Featuring Triphenylamine as Donor Fragment for Application in Dye-Sensitized Solar Cells

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Abstract: We designed, synthesized and characterized a novel metal-free organic sensitizer, suitable for the application in dyesensitized solar cells (DSSCs), both experimentally and theoretically. The structure of the novel donor-acceptor-π-bridge-acceptor (D-A-π-A) dye has triphenylamine (TPA) segment and 4-(Benzo[c][1,2,5] thiadiazol-4-ylethynyl) benzoic acid (BTEBA). The triphenylamine unit is widely used as electron donor for the photosensitizers due to its outstanding characteristics, i.e. the non-planar molecular configuration and excellent electron donating capability while 4-(Benzo[c][1,2,5] thiadiazol-4-ylethynyl) benzoic acid is used as electron acceptor unit. We investigated the influence of iodide/triiodide, Cobalt(bpy)32+/3+ and Copper(tmby)<sub>2</sub><sup>2+/+</sup>complexes as redox electrolytes on the DSSC device performance. The maximal monochromatic incident photon to current conversion efficiency (IPCE) reached up to 81%. The solar light to electrical energy conversion efficiency of the devices with Cu(tmby)22+/+ reached up to 7.15%. The devices with Co(bpy)<sub>3</sub> and Iodide/triiodide electrolytes showed 5.22% and 6.14% efficiency, respectively. The lowest device performance of Co(bpy)<sub>3</sub><sup>3+/2+</sup> based electrolyte is attributed to the increased charge recombination process.

#### Introduction

Dye-sensitized solar cells (DSSCs), pioneered by Grätzel and coworkers, have attracted sustained attention due to their

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potential in low-cost solar-to-electricity conversion, outstanding performance under indoor condition with low intensity light, greater flexibility and relatively less environmental issues.<sup>[1–8]</sup> In DSSC, the sensitizer is a critical component in light harvesting and electron injection and thereby influencing the performance of solar cell as well as the stability of the cells.<sup>[9],[10]</sup> Initial forms of this technology employed ruthenium based dyes which showed over 12.0% power conversion efficiency (PCE).<sup>[11–13]</sup> However, the disadvantages of Ru-complexes such as rare sources, difficult purification steps, high costs, unfriendly environmental issues, and relatively lower molar extinction coefficients limit their application.<sup>[14],[15]</sup>

As a result, many efforts have been turned to organic donoracceptor (D–A) dyes with various structures because of their flexible design of molecular structures, multiple synthetic pathways, high molar extinction coefficients as well as low cost and environmental friendliness compared to organometallic dyes.<sup>[16–18]</sup>

Generally, the organic dyes are composed of donor and acceptor moieties bridged by the conjugated chain (D- $\pi$ -A). Photovoltaic properties can be changed significantly by applying small variations in each section of the mentioned common configuration of organic dyes.<sup>[19,20]</sup> Up to now, many research efforts have been dedicated to construct diverse organic dyes, an overwhelming majority of which employed the conventional cyanoacrylic acid (CA) as the electron acceptor.<sup>[21–27]</sup>

Recently, 4-(Benzo[c][1,2,5] thiadiazol-4-ylethynyl)benzoic acid (BTEBA) as a promising electron acceptor was coupled with strong electron-donating segments for dyes C281, WEF1 and WEF2 (Fig. S1, Supporting info), accompanied by a high power conversion efficiency.<sup>[27,28]</sup> Because of its strong electron withdrawing character, BTEBA could lower the energy level of the lowest unoccupied molecular orbital (LUMO) and further reduce the energy gap of dye molecules. So, BTEBA may also be suitable to combine with some well-known donors with simple structure and easier synthetic method to improve the DSSC performance.<sup>[27]</sup>

Keeping in mind the above findings in designing the new D-A- $\pi$ -A dye, we have slightly tailored the simple donor part based on triphenylamine (TPA) segment (Figure 1), which is often used as an electron donor for the photosensitizers because of its nonplanar molecular configuration, aggregation resistance as well as excellent electron donating capability.<sup>[6]</sup> Since it is well known that some detrimental processes such as dye aggregation and charge recombination can be successfully reduced by introducing alkyl chains on the donor part, we designed TPA which is end-capped with hexyloxy to mainly mitigate dye aggregation at TiO<sub>2</sub> surface and charge recombination at the TiO<sub>2</sub>/electrolyte interface.<sup>[29]</sup> Also, the presence of hexyloxy chain increases the basicity of donor

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and which creates a directionality in the molecule. Optical spectra, electrochemical and photovoltaic properties of the new sensitizer, which is coded as **ND**, with different redox electrolytes solutions are reported here.



Figure 1. Structure of the dye ND

#### **Results and Discussion**

#### Synthesis and characterization

Scheme 1 presents the synthetic routes applied for organic D-A- $\pi$ -A dye ND. The dye **ND** was conveniently obtained by the Suzuki-Miyaura coupling reaction of compound **1** and methyl 4-((7-bromobenzo[c][1,2,5] thiadiazol-4-yl)ethynyl)benzoate and then hydrolysis of compound **2**. New compounds were characterized using various spectroscopic tools (Fig. S2-10, Supporting info).

#### **Optical properties**

Fig. 2(a) shows the UV-visible spectra of **ND** in DCM solution (2×  $10^{-5}$  M). Absorption data are summarized in Table 1. The dye reveals two absorption bands at around 323 and 489 nm. The higher energy band can be ascribed to the  $\pi - \pi^*$  transitions, whereas the lower energy band is attributed to charge transfer (CT) transitions. Further, the dye shows relatively high molar extinction coefficient indicating good light harvesting capability. Upon adsorption onto a 3.2  $\mu$ m transparent nanocrystalline TiO<sub>2</sub> film, the absorption spectra of the **ND** dye (Fig. 2(b)) was blue shifted compared to that in solution due to the intermolecular interaction and deprotonation of the carboxylic acid.

Table 1. Optical and electrochemical properties of dye ND							
Samples	Quantity	Value and unit					
	a a	489 (nm)					
	$\lambda_{max}$	323 (nm)					
	$\varepsilon^{a}$	31600 [M <sup>-1</sup> cm <sup>-1</sup> ]					
ND in solution		56200 [M <sup>-1</sup> cm <sup>-1</sup> ]					
	HOMO <sup>b</sup>	0.87 [V] (vs. SHE)					
	E <sub>0-0</sub> °	2.09 [V]					
	LUMO <sup>c</sup>	-1.22 [V] ( <i>vs.</i> SHE)					
	$\lambda_{max}^{d}$	483 (nm)					
ND on TiO <sub>2</sub>	HOMO <sup>e</sup>	1.05 [V] ( <i>vs.</i> SHE)					
	LUMO <sup>e</sup>	-1.04 [V] (vs. SHE)					

[a] Absorption peaks ( $\lambda_{max}$ ) and molar extinction coefficients ( $\varepsilon$ ) in DCM. [b] The highest occupied molecular orbital (HOMO) was measured in DCM by cyclic voltammetry (CV), based on a three electrode system, using glassy carbon or Pt as the working electrode, Pt wire as the counter electrode, and Ag/AgCl/saturated LiCl (ethanol) as the reference electrode, calibrated with ferrocene as an external reference and converted to standard hydrogen electrode (SHE) by the addition of 0.624 V.<sup>[30]</sup>). [c] E<sub>0-0</sub> value was determined from the absorption thresholds of dye adsorbed on 3.2  $\mu$ m TiO<sub>2</sub> film, the lowest unoccupied molecular orbital (LUMO) was calculated according to LUMO = HOMO - E<sub>0-0</sub>. [d] Absorption peaks on 3.2  $\mu$ m TiO<sub>2</sub> films. [e] voltammogram measurement of ND in adsorbed state on TiO<sub>2</sub>.



Figure 2. Absorption spectra of dye ND (a) in DCM solution (2× 10<sup>-5</sup> M) and (b) anchored on a 3.2  $\mu$ m TiO<sub>2</sub> film.

#### **Electrochemical properties**

For an efficient operation of the dye in DSSC, suitable LUMO and HOMO energy levels of sensitizer are needed to match the conduction band of  $TiO_2$  electrode and the redox energy level of

the electrolyte, respectively. The excited state must be at more negative electrochemical potential (higher energy level) than the  $TiO_2$  conduction band edge for the efficient injection of electrons into the conduction band of  $TiO_2$ . Furthermore, the oxidation potential of dye must be more positive (lower energy level) than

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the redox electrolyte energy applied for regeneration of the dye cation after photo induced electron injection on to  $TiO_2$  film.<sup>[31]</sup>

To evaluate the feasibility of electron injection from the excited dye into the conduction band of  $TiO_2$  and to explore the ability of dye regeneration by the redox mediator, cyclic voltammetry (CV) was performed to measure the oxidation potential of the dye in DCM with tetra-n-butylammonium hexafluorophosphate (0.1 M, Fig. 3(a)). The corresponding data are collected in Table 1.

As shown in Fig. 3(b), the redox potential of the ND sensitizer in DCM solution (0.87 V vs. SHE) is more positive than the iodide/triiodide (0.35 V vs. SHE) and Co(bpy)<sub>3</sub><sup>3+/2+</sup> (0.56 V vs. SHE). The observed redox potential of ND in solution is *comparable* to that of  $Cu(tmby)_2^{2+/+}$ . The latter was reported to be 0.87 V (vs. SHE) in acetonitrile medium<sup>[32]</sup>, which, provided the data measured in solution corresponds to the energy levels in a complete solar cell device, would lead to the intriguing finding of 'zero' driving force for dye-regeneration. Since device data (see below) for Cu(tmby)<sup>2+/+</sup> shows that the dye regeneration is highly efficient, this is very unexpected. To address this explicit paradox. we first measured the redox potential of Cu(tmby)<sup>2+/+</sup> redox mediator in the same medium as our dve (in dichloromethane. cf. Fig. 3(a)) to assess possible solvent/electrolyte effects. (As the ND dve is insoluble in acetonitrile, we have chosen dichloromethane because it dissolves both ND and Cu(tmby)<sub>2</sub> easily). Our measured redox potential of Cu(tmby)<sup>2+/+</sup> is 0.94 V vs. SHE, which is positive of the literature value measured in acetonitrile solution of LiTFSI (0.87 V vs. SHE)<sup>[32]</sup> confirming that the effects of solvent (acetonitrile/dichloromethane) and electrolyte (LiTFSI/TBAPF<sub>6</sub>) are not negligible in this particular case. The fact, that the redox potentials of ND and  $Cu(tmby)_2^{2+/+}$ (measured in the same medium) are so close to each other is further documented on the voltammogram of their mixture (Fig. 3(a), curve labeled 'mix'). We do not trace any double-wave shape for the mix, solely broadening of waves. Nevertheless, the CVs in dichloromethane even boost the paradox about incompatible redox potentials for dye regeneration. More specifically, the difference of redox potentials of ND and Cu(tmby)22+/+ is now negative (-70 mV). This would indicate a "negative driving force" of dye regeneration, which is not realistic.

The problem of virtually 'negative' driving force is elucidated, if we measure the voltammogram of **ND** adsorbed on  $TiO_2$  (black curve in Fig. 3(a)) in acetonitrile solvent. This study is based on the

effect of cross surface ambipolar charge percolation between dye molecules.<sup>[33]</sup> The oxidation of **ND** is accompanied by pronounced color changes, which are demonstrated in Fig. S11 (Supporting Info). The corresponding voltammogram of **ND**@TiO<sub>2</sub> has very small peak-to-peak splitting (smaller than that of ideally reversible solution redox couple, i.e. 59 mV), which is to be expected for adsorbed species. More importantly, the found the redox potential of **ND**@TiO<sub>2</sub> is now 1.05 V vs. SHE, i.e. 0.18 V more positive than in solution (providing now a realistic positive driving force for dye regeneration of 0.18 V).

For comparison, we made a reference study using the standard Y123 dye. The results are shown in Fig. S12 (Supporting Info). The found redox potentials (in V vs. SHE) of Y123 are 0.89 (in solution) and 1.07 (in adsorbed state; the latter entry matches the literature value).<sup>[32]</sup> Interestingly, both dyes, **ND** and Y123 show identical positive shift of 0.18 V in the adsorbed state referenced to solution, but this might be coincidental. We should note that the found redox potential of **ND**@TiO<sub>2</sub> (1.05 V vs. SHE) is the lowest one compared to values of other popular dyes for Cu-mediated DSSCs, i.e. D35 and LEG4.<sup>[34]</sup> The redox potential of **ND** dye is lower than D35 and LEG4 is due to the lower donacity of donor moiety present in these dyes compared to **ND** dye.

Our detailed electrochemical analysis leads to two fundamental findings: (i) The significant potential positive shift (0.18 V) of adsorbed dye must be taken into account in accurate determination of energy levels in DSSCs. Though this effect was mentioned already in the early pioneering work<sup>[33]</sup>, solution data are sometimes used for determination of the dye energy levels. (ii) The redox potential (1.05 V vs. SHE) of our ND dye is the smallest one compared to various other previously tested dyes (such as D35, LEG4 and Y123), hence the driving force for dye regeneration is also the smallest one in this particular case.<sup>[32,34]</sup> This proved that the oxidized dye, formed upon electron injection to TiO<sub>2</sub>, can accept electrons from the electrolyte redox mediator. The excited state energy level was determined from (oxidation potential)  $- E_{0-0}$ ,<sup>[4,35]</sup> and is ultimately based on the absolute value for the standard hydrogen electrode (SHE). The optical band gap E<sub>0-0</sub> was determined from the wavelength at 10% maximum absorption intensity as shown in Table 1. The value of the excited state of the dye ND in adsorbed state (-1.04 V vs. SHE) guarantees the ample electron injection from the excited dye into the TiO<sub>2</sub> conduction band (-0.50 V vs. SHE).



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Figure 3. (a) Cyclic voltammograms on Pt-electrode, scan rate 10 mV/s; from top to bottom: 2 mM Cu(tmby)<sub>2</sub>+TFSI in 0.1 M TBAPF<sub>6</sub>/DCM (red), *ditto* upon addition of ferrocene (red dashed), 2 mM **ND** dye in 0.1 M TBAPF<sub>6</sub>/DCM (blue), *ditto* upon addition of ferrocene (blue dashed), mixture of 1 mM **ND** + 1 mM Cu(tmby)<sub>2</sub>+TFSI with added ferrocene (magenta). The last voltammogram (black) is for **ND** dye adsorbed on TiO<sub>2</sub>/FTO electrode in 0.1 M LiTFSI/acetonitrile, scan rate 5 mV/s. Curves are offset for clarity, but the current density scale is identical for all voltammograms. (b) Schematic diagram of the energy levels of TiO<sub>2</sub> conduction band, dye **ND**, Is<sup>1</sup>/r, Co(bpt)<sub>3</sub><sup>3+/2+</sup> and Cu(tmby)<sub>2</sub><sup>2+/+</sup>redox couples.

#### **Theoretical approach**

Ground state geometry optimizations were performed with density functional theory (DFT) on a B3LYP/6-311G(d,p) level using selfconsistent reaction field in a polarizable continuum model (PCM) corresponding to DCM. The dyes were embedded in dichloromethane (DCM) solvent with solvent radii taken from the united atom topological model as implemented in Gaussian09. Time-dependent DFT were performed to assess the optical transitions and their oscillator strengths showing that the transition furthest into the visible is dominated (99%) by a transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The next band approaching the UV-region is a combined transition from HOMO→LUMO +1 (64%) and HOMO-1→LUMO (34%), and a deeper band with many transitions in the 300-350 nm region with a strongest contributions from HOMO-1  $\rightarrow$  LUMO+1 but also HOMO-4 $\rightarrow$ LUMO, HOMO $\rightarrow$ LUMO+2 and HOMO $\rightarrow$ LUMO+3 among others (Table S1, supporting info). The three main transitions are shown in Figure 4 together with the relative orbital energies. One should note that the static description of the difference between the orbital energies is not the same as the energy of the optical transition which is lower in energy due to polarization change upon moving an electron and the linear combination of the orbitals as described by the TDDFT. The HOMO-LUMO gap is typically slightly higher than the optical gap and electrochemical band gap.<sup>[36]</sup> In the TDDFT calculations, the main optical transition in the visible occurs at 677 nm using a DCM model and at 648 nm upon protonation (Table S1, S2, supporting info), redshifted in comparison to the experimental spectrum in DCM. In our case, the theoretical static HOMO-LUMO gap (2.18 eV) in solution corresponds quite well to the experimentally determined HOMO-LUMO gap in solution (2.09, Table 1). As the HOMO in the experiments is approximated by the redox energy, we performed a geometry optimization of the ND dye cation (ND+) in the PCM solution model showing a reorganization energy of 0.164 eV. The theoretical estimation of the  $E_{\text{redox}}\text{-}\text{LUMO}$  gap in DCM solution is 2.02 eV, very close to the experimental value.

The frontier orbitals of the ND dye show a relatively even distribution of the electron density (ED) of the HOMO on the backbone of the dye, whereas an electron redistribution away from the tri-arylamine is seen for the LUMO, localized largely on the sulphur-nitrogen moiety and on the □-system. The deeper transitions ending at LUMO+1 show a more pronounced charge transfer character over the backbone of the ND dye (Figure 4).



Figure 4. Theoretical energy levels from ground state optimization of ND dyes on a B3LYP/6-311G(d,p) level in DCM solvent and the dominating optical transitions determined from TDDFT. The electron densities of the optically active orbitals are also depicted.

#### Photovoltaic device performance

The photocurrent–voltage (I–V) curves of the DSSCs based on the synthesized dye, ND, were measured under an irradiance of simulated AM1.5G sunlight (100 mW.cm<sup>-2</sup>) using iodide/triiodide,  $Co(bpy)_3^{3+/2+}$  and  $Cu(tmby)_2^{2+/+}redox$  mediators (Fig. 5(a)). Detailed photovoltaic parameters including short-circuit photocurrent density (J<sub>SC</sub>), open-circuit voltage (V<sub>OC</sub>), fill factor (FF) and power conversion efficiency (PCE) are summarized in Table 2. For the dyeing of the TiO<sub>2</sub> electrode different amounts of chenodeoxycholic acid (CDCA) as an anti-aggregating agent<sup>[35]</sup> and solvents with different ratio were tested (details are reported in Table S3 and S4, supporting info). The best performance was achieved using 0.2 mM CDCA for dye ND with THF: EtOH (2:8 v/v) as solvents.

Among the three redox couples, ND-based DSSC with  $Cu(tmby)_2^{2+/+}$ complexes as redox electrolyte achieved the best performance, 7.15%, and a remarkably high open circuit voltage value of more than 1.0 V with a short-circuit current of 9.26 mA.cm<sup>-2</sup> and a fill factor of 0.75. The devices with  $Co(bpy)_3^{3+/2+}$  and iodide/triiodide based redox electrolytes showed 5.22% and 6.14% efficiency, respectively. Unexpectedly, V<sub>OC</sub> values of 760 mV was obtained with  $Co(bpy)_3^{3+/2+}$  electrolyte, which is lower than that of iodide/triiodide electrolyte (860 mV). The lower device performance of  $Co(bpy)_3^{3+/2+}$  based electrolyte will be discussed in terms of electron lifetime measurements, below. The IPCE spectra for the DSSC devices employing the three different redox couples are given in Fig. 5(b). For iodide/triiodide based electrolyte, the maximum IPCE is found to be 81% at 520 nm. For

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 $Co(bpy)_3^{3+/2+}$  and  $Cu(tmby)_2^{2+/+}$  complexes, the maxima are 77 and 75%, respectively, around 520 nm. The integrated value for iodide/triiodide,  $Co(bpy)_3^{3+/2+}$  and  $Cu(tmby)_2^{2+/+}$  complexes were equal to 10.45, 10.17 and 9.47, respectively.



Figure 5. (a) The J-V curves of ND sensitized solar cells with three electrolytes under full AM 1.5 solar intensity. (b) Incident photon-to-electric current conversion efficiencies of ND sensitized DSSC devices employing three electrolytes

Table 2. Photovoltaic parameters of DSSCs based on dyes ND							
Redox couple	J <sub>sc</sub> (mA.cm <sup>-2</sup> )	v <sub>oc</sub> (V)	FF	PCE (%)			
Iodide/triiodide	10.45	0.806	0.711	6.14			
Co(bpy) <sub>3</sub> <sup>3+/2+</sup>	9.34	0.760	0.720	5.22			
Cu(tmby) <sub>2</sub> <sup>2+/+</sup>	9.26	1.02	0.750	7.15			

#### Charge extraction and electron lifetime measurement

To analyze the photovoltaic data above and in particular to get further understanding of the observed differences in the open circuit photovoltages, V<sub>OC</sub>, we performed tool-box experiments; charge extraction and electron lifetime.<sup>[37]</sup> The V<sub>OC</sub> is obtained as the difference between the Fermi level, E<sub>F</sub>, of electrons in the TiO<sub>2</sub> and the redox potential of the electrolyte. The redox potentials of I<sup>/</sup>I<sub>3</sub>, Co(bpy)<sub>3</sub><sup>3+/2+</sup> and Cu(tmpy)<sub>2</sub><sup>2+/+</sup> are, vs NHE, 0.35V, 0.56V and 0.87V, and the V<sub>OC</sub> are 0.806V, 0.760V and 1.02V, respectively.

It is clear that the difference in redox potential alone cannot explain the obtained  $V_{OC}$ . The Fermi level of TiO<sub>2</sub> depends on the position of the conduction band and the electron concentration. Relative differences in the former can be measured by charge extraction and the latter is obtained by electron lifetime

measurements. The amount of charge,  $Q_{OC}$ , for the devices with the different redox couples were measured at different voltages of the devices. These voltages were corrected for the different redox potentials to get a comparable Fermi level, and  $Q_{OC}$  vs  $E_F$  are plotted in Fig. 6a. We note that the lines for  $1^{-}/l_3^{-}$  and  $Co(bpy)_3^{2+/3+}$  are parallel and thus we can conclude that the conduction band positions of TiO<sub>2</sub> is the same when using these redox couples. For Cu(tmpy)\_2<sup>2+/+</sup> the line is shifted positively of about 0.1V, which then explains part of the smaller difference in V<sub>OC</sub> between this redox couple and  $1/l_3^{-}$  (if  $E_F$  would be the same, V<sub>OC</sub> should differ by 0.52V instead of the observed 0.16V).

To explain the unusual difference in V<sub>oc</sub> between  $1/I_3^-$  and Co(bpy)<sub>3</sub><sup>3+/2+</sup> (the Co-complex normally gives significantly higher V<sub>oc</sub> due to the more positive redox potential) we performed electron lifetime measurements, Fig. 6b. We observe a substantially longer electron lifetime for  $1/I_3^-$  plotted vs  $E_F$  compared to both the Co and Cu-complexes. This long lifetime can also explain the high V<sub>oc</sub> of 0.806V for  $1/I_3^-$ . The drastically shorter electron lifetimes of Co and Cu-complexes result in the lower V<sub>oc</sub> for these redox couples compared to  $1/I_3^-$  as would have been expected from the redox potentials. The plotted line for Cu(tmby)<sub>2</sub><sup>2+/+</sup> is shifted 0.1V positively due to the shift in conduction band positions. When this is done we note that the lifetimes of Co and Cu-complexes are similar and the main part of the difference in V<sub>oc</sub> of 0.31V.

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Figure 6. (a) Charge extraction and (b) electron lifetime measurements with respect to quasi-Fermi level of electrons in the TiO<sub>2</sub> electrode (represented by the corresponding electrochemical potentials). ND sensitized solar cells employed the iodide/triiodide, Co(bpy)<sub>3</sub><sup>3+/2+</sup> and Cu(tmby)<sub>2</sub><sup>2+/+</sup> redox mediators (E<sub>F</sub>=E<sub>redox</sub>-V<sub>oc</sub>).

#### Conclusions

In summary, a new organic sensitizer with D-A- $\pi$ -A configuration was designed, synthesized and characterized for application in DSSCs. The influence of iodide/triiodide, Co(bpy)33+/2+ and Cu(tmby)<sub>2</sub><sup>2+/+</sup>complexes as redox mediators on the DSSC device performance were studied. Their photophysical and electrochemical characterization were investigated. Under standard global AM 1.5 solar condition, the overall light-toelectricity conversion efficiency of ND-based DSSC with  $Cu(tmby)_2^{2+/+}$  complexes electrolyte was 7.15%, which was the highest efficiency among the other two redox couples. Electrochemical studies highlight the significant difference in redox potentials of dyes if they are measured in solution or in adsorbed state on TiO<sub>2</sub>, the latter being shifted positively by 0.18 V both for Y123 and ND dyes. Ignoring this difference would lead to wrong prediction about driving force for dye regeneration by the electrolyte redox mediator.

Using  $Cu(tmby)_2^{2+/+}$  complexes as redox electrolyte showed lower recombination rate for electrons in the TiO<sub>2</sub> with Cu(II) species in ND-based devices. Our newly developed dye ND exhibits the lowest redox potential (1.05 V vs. SHE in adsorbed state) as compared to the redox potentials of other dyes used in Cumediated DSSCs (Y123, D35, LEG4). Our study confirms the fundamentally interesting fact that even very small driving force (down to 0.18V) for dye regeneration is still efficiently operating in Cu-mediated DSSCs. Interestingly, the largest internal potential drop in the Cu-complex device is now related to the injection of electrons from the excited state of the dye to the conduction band of TiO2. Thus, a future interesting research direction will be to minimize the energy offset at the oxide/dye interface.

#### **Experimental Section**

Material

The synthetic route of ND dye is detailed in Scheme 1. 4-Bromo-N,Nbis[4(hexyloxy)phenyl]aniline, bis(pinacolato)diboron, Pd(PPh<sub>3</sub>)<sub>4</sub>, Potassium NaOH, Lithium Potassium acetate. carbonate. bis(trifluoromethanesulfonyl)imide (LiTFSI), 4-tert-butylpyridine (TBP) and Ferrocene (Fc) were purchased from Sigma-Aldrich, Merck, and TCI Chemicals. Y123 dye, Co(bpy)<sub>3</sub> (TFSI)<sub>2</sub> and Co(bpy)<sub>3</sub>(TFSI)<sub>3</sub> were purchased from Dyenamo AB. Cu(tmby)<sub>2</sub>(TFSI) and Cu(tmby)<sub>2</sub>(TFSI)<sub>2</sub> available from our previous work.[32] were Methyl 4-((7bromobenzo[c][1,2,5] thiadiazol-4-yl)ethynyl)benzoate was prepared according to the literature method.<sup>[38]</sup> All solvents and other chemicals are reagent grade and were obtained from commercial sources and used without further purification. Analytical TLC was carried out on Merck 60 F254 silica gel plate and for chromatographic purification, we used Silica Gel 60 (230-400 mesh, Merck, Germany).

#### Synthesis

4-(hexyloxy)-N-(4-(hexyloxy)phenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2 yl)phenyl)aniline (1): To a solution of 4-Bromo-N,Nbis[4(hexyloxy)phenyl]aniline (402 mg, 0.77 mmol) in 10 mL dioxane was added Bis(pinacolato)diboron (140 mg, 0.6 mmol) and potassium acetate (112 mg, 1.2 mmol). Then, the solution was degassed for 20 min under nitrogen and then Pd<sub>2</sub>dba<sub>3</sub> (9 mg) and X-Phos (15 mg) were added simultaneously. The solution was allowed to warm to 80 °C for 12h. The reaction was then cooled to RT and extracted with dichloromethane (DCM) and then dried over MgSO4. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography with a mixture of DCM / Hexane (1/1, v/v) as eluent on silica gel to afford 1 as a colorless oil. (210 mg, 48%). <sup>1</sup>H NMR (400 MHz, CDCl3) 5: 7.61 (d, J = 7.56 Hz, 2H), 7.03-7.09 (d, J = 6.48 Hz, 4H), 6.87-6.89 (d, J=7.28 Hz, 2H), 6.83-6.85 (d, J=8.28 Hz, 4H), 3.95 (t, 4H), 1.76-1.83 (m, J = 7.12, 4H), 1.46-1.50 (m, J = 6.34, 4H), 1.35-1.38 (m, 8H), 1.34 (s, 12H), 0.94 (t, J = 5.88 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl3)  $\delta$ : 155.80, 140.20, 135.73, 127.13, 118.54, 115.26, 83.38, 77.34, 77.23, 77.02, 76.70, 68.24, 31.62, 29.34, 25.77, 24.84, 22.62, 14.057.

#### Methyl

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

yl)ethynyl)benzoate (2): Compound 1 (200 mg, 0.35 mmol), Methyl 4-((7bromobenzo[c][1,2,5] thiadiazol-4-yl)ethynyl)benzoate (112 mg, 0.30 mmol), Pd(PPh3)4 (46 mg, 0.04 mmol), and  $K_2CO_3$  (2 M, 15 mL) were dissolved in THF (40 mL), and the mixture was heated at 80°C for 7 h

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under argon. After cooling to room temperature, the mixture was extracted with water and DCM. The combined organic layers were washed with brine and dried over anhydrous sodium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography with Hexane/DCM (1/3, v/v) as eluent on silica gel to afford 2 as a red solid (170 mg, 65%). <sup>1</sup>H NMR (400 MHz, CDCl3)  $\delta$ : 8.09 (d, *J* = 7.72 Hz, 2H), 7.89-7.91 (d, *J* =7.24 Hz, 1H), 7.85-7.87 (d, *J* =8.04 Hz, 2H), 7.75-7.77 (d, *J* =7.72 Hz, 2H), 7.67-7.69 (d, *J* = 7.28 Hz, 1H), 7.15-7.17 (d, *J* = 8.0 Hz, 4H), 7.06–7.08 (d, *J* = 8.0 Hz, 2H), 6.88–6.90 (d, *J* = 7.92 Hz, 4H), 3.97 (t, 4H), 3.99 (s, 3H), 1.79-1.83 (m, 4H), 1.49 (m, 4H), 1.38 (m, 8H), 0.94 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl3)  $\delta$ : 166.55,155.97, 155.40, 153.22, 149.54, 140.08, 135.06, 133.63, 131.83, 129.89, 129.56, 127.89, 127.61, 127.22, 126.05, 119.29, 115.38, 113.86, 94.54, 88.55, 52.29, 31.62, 29.72, 29.33, 25.78, 22.63, 14.06.

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

4-yl)ethynyl)benzoic acid (ND): Compound 2 (90 mg, 0.12 mmol) was dissolved in THF (30 mL), methanol (20 mL), and a solution of NaOH (20% wt/wt) (8 mL) was added. The mixture was heated at 40°C for 2 h under argon. The reaction mixture was then cooled and THF solvent was removed by rotary evaporation. DCM was added and the organic layers were separated. The organic layer was extracted with 1M HCl for 2 times and then washed with water, dried over anhydrous sodium sulfate and filtered. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography with DCM/EtOH (11:1) to give ND as red powder (66 mg, 75%). <sup>1</sup>H NMR (400 MHz, Aceton- $d_6$ )  $\delta$ : 8.16 (d, J = 7.72 Hz, 2H), 8.03-8.05 (d, J = 7.40 Hz, 1H), 7.99-8.01 (d, J =8.16 Hz, 2H), 7.88-7.90 (d, J =7.40 Hz, 1H), 7.81-7.83 (d, J = 7.80 Hz, 2H), 7.17-7.19 (d, J = 7.92 Hz, 4H), 6.98–7.00 (d, J = 7.96 Hz, 6H), 4.04 (t, J = 6.16 Hz, 4H), 1.79-1.82 (m, 4H), 1.51 (m, 4H), 1.39 (m, 8H), 0.94 (s, 6H). <sup>13</sup>C NMR (100 MHz, Aceton-d<sub>6</sub>) δ: 203.96, 156.31, 155.35, 153.08, 149.67, 139.98, 134.80, 133.79, 131.63, 130.07, 129.88, 127.74, 127.42, 127.37, 126.02, 118.58, 115.44, 94.05, 88.53, 67.92, 31.46, 29.52, 28.75, 25.61, 22.40, 13.42. HR-MS (MALDI-TOF) m/z calculaed. for (C45H45N3O4S): 723.3131. Found: 723.3128.

#### Characterization

 $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 400 MHz spectrometer in CDCl<sub>3</sub> and aceton-d6 with tetramethylsilane as inner reference. Mass spectra were obtained with Bruker Daltonics, FT-ICR/APEX II, spectrometer operating in ESI mode. MALDI-TOF mass spectra were recorded using Micromass TOF Spec 2E instrument. The absorption spectra of the new dye were measured in DCM solution (2  $\times$  10<sup>-5</sup> M) at room temperature by JASCO V630 UV-visible Spectrophotometer.

#### **Electrochemical characterization**

Electrochemical characterization was carried out by cyclic voltammetry (CV) using an Autolab potentiostat (Metrohm). Three-electrode cell was assembled with a glassy carbon or platinum disk-working electrodes, a Ptwire auxiliary electrode, and an Ag/AgCl (sat. LiCl in ethanol) reference electrode. The reference electrode was interfaced to a fritted bridge containing the same supporting electrolyte solution as the tested system. For some experiments, the FTO-supported, sensitized TiO<sub>2</sub> film was also used. This electrode is essentially identical to that used in actual DSSCs (see below), except for the TiCl<sub>4</sub> treatment that was omitted in this case. Cyclic voltammograms were acquired in 2 mM dye solutions prepared in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in DCM. The redox potential was calibrated with ferrocene as the internal reference. Alternatively, voltammetric tests of ND@TiO<sub>2</sub> were also carried out in 0.1 M LiTFSI in acetonitrile.

#### **Device fabrication**

To prepare the working electrode, F-doped SnO<sub>2</sub> (FTO) glasses (NSG-10, Nippon Sheet Glass) were first cleaned with a detergent solution (Deconex) in ultrasonic bath for 45 minutes and then rinsed with water and ethanol. After the treatment with a UV-O3 (Model no.256-220, Jelight, Inc.) for 15 min, FTO glasses were immersed into a 40 mM TiCl<sub>4</sub> solution at 70 °C in an oven for 30 min to allow the formation of blocking layer and rinsed with water and ethanol. This step was repeated 2 times. An active TiO<sub>2</sub> layer (0.28 cm<sup>2</sup>) was formed on the FTO glass via screen-printing using a paste consisting of 30 nm in diameter sized TiO<sub>2</sub> particles (Dyesol). Then, the second layer with 400 nm sized particles (scattering layer) was additionally deposited and calcined. The substrates were sintered on a hot plate with a ramped temperature profile, keeping the temperature at 125, 250, 370, 450, and 500 °C for 5, 5, 5, 5, and 30 min, respectively, with 5 min ramp duration between each temperature. The resulting TiO2 film thickness was 8  $\mu$ m (4  $\mu$ m + 4  $\mu$ m). Finally, TiO<sub>2</sub> films were treated with 20 mM TiCl<sub>4</sub> solutions to increase the surface area of the TiO<sub>2</sub> particles and followed by another sintering process at 500 °C for 60 min. Before dipping the TiO<sub>2</sub> electrodes into dye solutions, they were annealed with a heat gun for 30 min at 500 °C. The working electrodes were prepared by immersing the TiO<sub>2</sub> films into a 0.2 mM solution of dye with 0.2 mM of 3a,7a-dihydroxy-5b-cholic acid (Chenodeoxycholic acid, CDCA) for 16h.

To prepare the PEDOT counter electrode which was used for Cu(tmby)<sup>2+/+</sup> redox electrolyte, FTO glasses (TEC 6, Pilkington) were cleaned with Hellmanex III (2% wt in water), ethanol, and acetone with 30 min duration for each and coated with PEDOT via electrochemical deposition from EDOT. Also, Pt catalyst was deposited on cleaned FTO glasses by coating with a drop of H<sub>2</sub>PtCl<sub>6</sub> solution (10 mM in 2-propanol solution) with heat treatment at 400 °C for 15 min to prepare Pt counter electrode to use in devices based on iodide/triiodide and Co(bpy)<sub>3</sub><sup>3+/2+</sup> redox electrolytes.

The working electrodes and counter electrodes were assembled in a sandwich-type cell in a drybox with 35 µm of Surlyn (Du Pont) as a sealant and spacer between electrodes. The electrolyte was injected into the device through a predrilled hole in the counter electrode under vacuum. Three types of electrolyte redox mediators were used, viz. iodide/triiodide<sup>[39]</sup>, Co(bpy)<sub>3</sub><sup>3+/2+</sup> <sup>[40]</sup> and Cu(tmby)<sub>2</sub><sup>2+/+</sup>. <sup>[32]</sup> lodide/triiodide electrolyte coded Z960, contained 1.0 M 1,3-dimethylimidazolium iodide, 0.05 M Lil, 0.03 M l<sub>2</sub>, 0.5 M TBP, and 0.1 M guanidinium thiocyanate (GNCS) in the mixed solvent of acetonitrile and valeronitrile (v/v, 85/15). The other two electrolyte solutions consisted of 0.25 M Co(II) + 0.06 M Co(III) or alternatively 0.2 M Cu(I) + 0.06 M Cu(II) complexes with 0.1 M LiTFSI and 0.6 M TBP in acetonitrile. Then, the sheet edges of FTO were coated by ultrasonic soldering (Cerasolzer alloy 246, MBR Electronics GmbH) to improve electrical contacts.

#### **Characterization of DSSCs**

Current–voltage (I–V) characteristics were measured using a Keithley 2400 source meter and a 450 W xenon light source (Oriel, U.S.A). A black mask (0.16 cm<sup>2</sup>) was used during IV measurements.

Incident photon to current conversion efficiency (IPCE) spectra were measured from 350 to 800 nm by 300 W xenon light source (ILC Technology, USA), monochromator (JobinYvon Ltd., UK) and a Keithley 2700 multi-meter. A white light bias was used to have similar light intensity conditions as during normal operation.

To measure electron lifetimes a white LED light source (Seoul Semiconductors), a 16-bit resolution digital acquisition board (National Instruments), and a current amplifier (Thorlabs PDA200C). In charge

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extraction experiment, firstly, the DSSC device was kept at open-circuit conditions and subsequently the LED light was turned on. After a certain time (1 s), the light source was turned off and the device was switched to short-circuit condition. The total extracted charge was integrated over time and the measurement was repeated at different light intensities in order to obtain a complete charge-potential curve. For electron lifetime measurements, the light source was controlled by a modulated current on top of a bias current. The open-circuit voltage responses were measured and the lifetimes were extracted from fitting parameters of the open-circuit voltage response curves.

#### **Computational methods**



and PCM.

Scheme 1. Synthetic route to ND. Reagents and conditions: (i) bis(pinacolato)diboron, Pd<sub>2</sub>dba<sub>3</sub>, X.Phos, potassium acetate, dioxane, 80°C, 12 h; (ii) Methyl 4-((7-bromobenzo[c][1,2,5] thiadiazol-4-yl)ethynyl)benzoate, Pd(PPh<sub>3</sub>)<sub>4</sub>, 2M K<sub>2</sub>CO<sub>3</sub>, THF, 80°C, 7 h; (iii) NaOH (20% wt/wt), THF, MeOH, 40°C, 2 h.

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Density functional theory (DFT) and time-dependent density functional

theory (TDDFT) calculations were conducted using the Gaussian 09

software package.[41] The solvent effects were modelled by using self-

consistent reaction field (SCRF) with a polarizable continuum model

(PCM) of packed solvent cavities surrounding the dye. The solvent radii

were taken from the united atom topological model as implemented in

Gaussian 09. The hybrid B3LYP functional and the 6-311G(d,p) basis set

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A novel metal-free organic sensitizer, suitable for the DSSCs, was synthesized and characterized both experimentally and theoretically. The structure of the novel D-A-π-A dye has triphenylamine (TPA) segment and 4-(Benzo[c][1,2,5] thiadiazol-4-ylethynyl) benzoic acid (BTEBA) as electron donor and acceptor part, respectively. The influence of iodide/triiodide, Cobalt(bpy)32+/3+ and Copper(tmby)<sub>2</sub><sup>2+/+</sup>complexes as redox electrolytes on the DSSC device performance was investigated. The solar light to electrical energy conversion efficiency of the devices with Cu(tmby)22+/+ reached up to 7.15%.



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Molecular design of Efficient Organic D-A- $\pi$ -A Dye Featuring Triphenylamine as Dc. o. Fragment for Application in Dy e-Sensitized Solar Cells