Sulfur Heterocycles

Electron-Poor Thiophene 1,1-Dioxides: Synthesis, Characterization, and Application as Electron Relays in Photocatalytic Hydrogen Generation

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Abstract: The synthesis and characterization of electronpoor thiophene 1,1-dioxides bearing cyanated phenyl groups are reported. The electron-accepting nature of these compounds was evaluated by cyclic voltammetry, and highly reversible and facile reductions were observed for several derivatives. Moreover, some of the reduced thiophene dioxides form colorful anions, which were investigated spectroelectrochemically. Photoluminescence spectra of the electrondeficient sulfones were measured in CH₂Cl₂, and they emit in the blue-green region with significant variation in the quantum yield depending on the aryl substituents. By expanding the degree of substitution on the phenyl rings, quantum yields up to 34% were obtained. X-ray diffraction data are reported for two of the thiophene 1,1-dioxides, and the electronic structure was probed for all synthesized derivatives through DFT calculations. The dioxides were also examined as electron relays in a photocatalytic water reduction reaction, and they showed potential to boost the efficiency.

Introduction

Stable and efficient electron-transport materials are far less abundant than hole-transporting substances, but they are in high demand for both small-molecule and polymer technology.^[1] They are particularly valuable for energy-related applications such as homogenous, photocatalytic water reduction^[2] and electrochromic devices.^[3]

Photocatalytic water reduction in homogenous systems generally relies on a photosensitizer to absorb light and donate the excited electron to a reduction catalyst.^[4] Electron acceptors with highly reversible electrochemistry can be used in this process to shuttle electrons efficiently from the photosensitizer to the catalyst. Electrochromic devices also require versatile acceptors. These compounds must undergo significant color changes upon reduction and must be reproducibly switched from the neutral to anionic state.^[3]

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Among available electron acceptors, methyl viologen (MV^{2+} , Figure 1) is a popular material that has been successfully used in both water reduction^[5] and electrochromics.^[3] Reduction of MV^{2+} causes a dramatic color change from yellow to the deep blue of the MV^{++} radical cation. This radical is fairly stable and reduction occurs readily and reversibly. Despite these desirable qualities, expansion from viologens towards neutral acceptors would be advantageous, because neutral species may be soluble in a wider variety of solvents to allow exploration of new device environments and fabrication techniques. Additionally, the mechanism of solid-state and solution-based charge transport may be different for neutral structures as compared to the ionic viologen.



Figure 1. Methyl viologen (MV^{2+}) and 2,5-diphenylthiophene 1,1-dioxide (DPTD).

Thiophene 1,1-dioxide attracted our attention as a scaffold for uncharged acceptors (Figure 1).^[6] These heterocycles are accessible from well-known thiophene precursors^[7] and have significantly higher electron affinity than their unoxidized counterparts.^[6] Oligothiophenes bearing the dioxide moiety have already been explored as acceptors in organic photovoltaics to replace commonly used fullerenes.^[6,8] Thiophene dioxide materials are also highly emissive, and various derivatives have

Chem. Eur. J. 2015, 21, 11517 - 11524

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been explored in organic light-emitting diodes $^{\rm [9]}$ and cell-imaging applications. $^{\rm [10]}$

Appending strongly electron-withdrawing groups (EWGs) to the π system of organic materials is often used as a strategy to enhance electron affinity.^[1a-c,11] We recently observed significantly more facile reduction of the thiophene dioxide when *p*-C₆H₄NO₂ or *p*-C₆H₄CN groups are attached at the 2- and 5-positions.^[12] Herein, the effect of π -accepting cyano functionality was explored in 2,5-diphenylthiophene dioxides (DPTDs) by installing cyano groups on various positions of the phenyl ring. Redox potentials of the new cyanated compounds follow a clear trend, and some derivatives produce highly colored anions upon reduction. Both the stability and color of the reduced compounds led us to explore these spectroelectrochemically and as electron relays in photocatalytic water reduction.

Results and Discussion

Using our previously reported Stille cross-coupling methodology,^[12] a series of compounds was prepared to explore the impact of both the position and number of cyano groups on the **DPTD** structure (Scheme 1). Analogues to the previously reported **4-CNDPTD**^[12] were prepared with the cyano group in the *ortho* and *meta* positions (**2-CNDPTD** and **3-CNDPTD**) from 2-bromo and 3-bromobenzonitrile.



Scheme 1. Preparation of functionalized DPTDs.

Derivatives with multiple cyano groups (2,4-CNDPTD and 2,4,5-CNDPTD) were prepared from 4-bromoisophthalonitrile and 5-bromobenzene-1,2,4-tricarbonitrile, both of which were derived from their respective carboxylic acids (see Supporting Information). The coupling of these multiply cyanated arene rings to the dioxide heterocycle proceeded in moderate yields (67% for 2,4-CNDPTD and 42% for 2,4,5-CNDPTD). All newly synthesized DPTDs were characterized by NMR spectroscopy (¹H and ¹³C) and mass spectrometry.

Crystallography

Crystals suitable for X-ray diffraction were grown for **2,4-CNDPTD** by slow evaporation of a chloroform solution (Figure 2), whereas **2,4,5-CNDPTD** crystallized from dichloromethane (Figure 3). In both compounds, the SO₂ moiety is perpendicular to the heterocyclic ring; the S=O bond lengths for



Figure 2. Solid-state molecular structure of **2,4-CNDPTD**. Thermal ellipsoids at 50%. Selected bond lengths [Å] and angles [°]: S1=O1 1.4357(9), S1=O2 1.4332(10), S1-C1 1.7819(12), S1-C4 1.7856(11), C1-C2 1.3405(17), C2-C3 1.4606(18), C3-C4 1.3400(16), S2=O3 1.4314(10), S2=O4 1.4383(9), S2-C21 1.7835(11), S2-C24 1.7795(14), C21-C22 1.3386(19), C22-C23 1.4679(19), C23-C24 1.3441(17); C1-S1-C4 93.93(6), C21-S2-C24 94.21(6).



Figure 3. Solid-state molecular structure of **2,4,5-CNDPTD**. Thermal ellipsoids at 50%. Selected bond lengths [Å] and angles [°]: S1=O1 1.4204(16), S1=O2 1.4248(16), S1-C1 1.7843(16), S1-C4 1.7793(15), C1-C2 1.319(2), C2-C3 1.471(2), C3-C4 1.322(2); C1-S1-C4 92.54(7).

both **2,4-CNDPTD** and **2,4,5-CNDPTD** (1.42–1.44 Å) are comparable to those of the previously reported **DPTD** (S=O 1.418(5) and 1.427(5) Å).^[13]

The C–C bond lengths of the thiophene dioxide illustrate the lack of aromaticity for this ring system with strong differentiation of single and double bonds within the five-membered structure (e.g., C1–C2 1.3405(17), C2–C3 1.4606(18), C3–C4 1.3400(16) Å for **2,4-CNDPTD**). This is in sharp contrast to 2,5-diphenylthiophene, in which all C–C bond lengths of the thiophene ring are within 0.03 Å (1.36–1.39 Å).^[13] The loss of aromaticity due to sulfur oxidation is also indicated by the longer S–C bond lengths in the thiophene dioxides (1.7819(12) and 1.7856(11) Å for **2,4-CNDPTD**) as compared to 2,5-diphenylthiophene (1.718(6) and 1.726(6) Å).^[13]

The crystallization behavior of these two compounds is quite interesting. For **2,4-CNDPTD** (Figure 2), two different orientations are observed in the unit cell. In one case, the dihedral angles between the 2,4-CN aryl rings and the central heterocycle are 24.9 and 30.1° . In the other case, the outer rings are twisted in different directions, with dihedral angles of 33.1 and -27.0° .

In **2,4,5-CNDPTD** (Figure 3), the 2,4,5-tricyano aryl rings are significantly more twisted from the central thiophene dioxide with dihedral angles of 62.7 and -59.5° . Interestingly, the electron-deficient nature of the arene ring results in short distan-

Chem. E	Eur. J.	2015,	21,	11517 –	11524
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ces to adjacent oxygen atoms in the crystal lattice. The lone pair- π interaction observed for the oxygen atom of the sulfone to an adjacent tricyanobenzene has a distance of only 3.329 Å.

DFT calculations and photophysics

DFT calculations were performed to evaluate the frontier orbitals of the dioxides. Calculated HOMOs for all new derivatives extend over the thiophene dioxide heterocycle and its phenyl substituents, as in previously reported DPTDs (Figure 4).^[12] The LUMOs also mirror those of earlier analogues, residing mainly on the heterocycle with heavy contributions from its π antibonding orbitals.



Figure 4. Frontier orbitals calculated for the parent DPTD and representative cyano derivative 2,4,5-CNDPTD.

Absorbances of the electron-deficient thiophene dioxides just reach into the visible region (Supporting Information). For all derivatives, λ_{max} spans a small range of 16 nm (370–386 nm) and shows no clear trend related to the substitution pattern (Table 1). The absorption was assigned as a π – π * transition by means of time-dependent (TD) DFT calculations (Supporting Information). All of the compounds luminesce in dichloromethane with a maximum near 480 nm.

Interestingly, significant variation in the luminescence quantum yield was observed in the series. **DPTD** and **3-CNDPTD** emit fairly weakly (1.8 and 3.5%, respectively) compared to **2-CNDPTD** and **4-CNDPTD** (8.0 and 10.6%, respectively), each of which has a cyano group in conjugation with the thiophene dioxide. Addition of a second cyano group in conjugation with the heterocycle had a profound impact on photoluminescence: a quantum yield of 34.1% was recorded for 2,4-CNDPTD. However, adding a third cyano group at the 5-position (2,4,5-CNDPTD), which is not in resonance with the heterocycle, does not improve the quantum yield. Clearly, cyano substituents that participate in the singlet excited state with the thiophene dioxide affect the vibrational modes or relative energies of states in such a way as to slow vibrational decay and other deactivation pathways. The basic calculations presented here do not provide further insight into the effect of the cyano groups, since the frontier orbitals for all derivatives vary only in the amount of participation of the cyano groups, and TDDFT calculations predict the same major types of transitions for all compounds. Past literature does, however, describe similar drastic changes in quantum yield on adding cyano groups to terthiophenes.^[14]

Electrochemistry

Redox behavior was probed experimentally by cyclic voltammetry in acetonitrile under an inert atmosphere. Oxidation is observed within the solvent window for the parent **DPTD** but not for the cyano derivatives in which EWGs stabilize the HOMO. At least two reductions are seen for all the DPTDs, and these processes shift anodically, becoming easier as the quantity of cyano groups increases (Table 1). With three cyano groups per phenyl ring, **2,4,5-CNDPTD** boasts a reduction shifted by +0.93 V relative to **DPTD** (Figure 5). This impressive shift brings the only third reduction of the series into view and makes the first two reductions of **2,4,5-CNDPTD** easier than that of the well-known acceptor fullerene (E_{red} of C_{60} : -0.44 V vs. SCE).^[15]

Beyond the large influence of the number of cyano groups, their positioning has some effect on potential, as evidenced by comparison of **2-CNDPTD**, **3-CNDPTD**, and **4-CNDPTD** (Figure 6). In this series, reduction is facilitated by placing the cyano group on the phenyl substituent in the *ortho* (**2-CNDPTD**, $E_{red} = -0.83$ V) or *para* position (**4-CNDPTD**, $E_{red} = -0.77$ V) rather than the *meta* position (**3-CNDPTD**, $E_{red} = -0.90$ V). The electrochemical effect of the cyano group in **3-CNDPTD** is diminished due to the inability of the aryl *meta* position to provide resonance stabilization of the thiophene diox-

Table 1. Photophysical and electrochemical properties of thiophene 1,1-dioxides.											
Entry	λ _{max,abs} ^[a] [nm]	ε [cm ⁻¹ м ⁻¹]	$\lambda_{max,em}^{[a]}$ [nm]	$arPsi^{[a]}$ [%]	HOMO ^[b] [eV]	LUMO ^[b] [eV]	E _{ox} ^[c] [V vs. SCE]	E _{red1} [c] [V vs. SCE]	$\Delta E_{\rm red1}$ [mV]	E _{red2} ^[c] [V vs. SCE]	$\Delta E_{\rm red2}$ [mV]
DPTD	383	16200	493	1.8	-5.942	-2.477	1.85 ^[d]	-1.16 ^[e]	66.7	-1.73 ^[f]	-
2-CNDPTD	370	14700	474	8.0	-6.545	-3.097	-	-0.83	86.2	-1.23	109.7
3-CNDPTD	374	15700	478	3.5	-6.686	-3.134	-	-0.90 ^[e]	66.7	_[g]	-
4-CNDPTD	386	18500	489	10.6	-6.670	-3.365	-	-0.77 ^[e]	60.3	-1.16 ^[e]	82.4
2,4-CNDPTD	377	18200	479	34.1	-7.189	-3.906	-	-0.48	77.1	-0.71	74.4
2,4,5-CNDPTD ^[h]	377	18700	477	33.9	-7.707	-4.436	-	-0.23	61.8	-0.37	59.6

[a] Absorption and emission spectra were recorded in CH_2CI_2 and quantum yields were measured versus quinine sulfate. [b] Frontier orbital energies were obtained from DFT calculations with the B3LYP functional and 6-31G(d,p) basis set (Supporting Information). [c] Potentials were measured with a three-electrode system in degassed MeCN solutions containing $0.1 \text{ M} \text{ Nn}Bu_4\text{PF}_6$ and 1.9 mM analyte. An internal ferrocene reference was employed (Fc/Fc⁺ 0.40 V vs. SCE). [d] Irreversible. [e] Quasireversible. [f] The process is irreversible and is much lower in intensity than the first reduction. [g] Process is not well defined. [h] 2,4,5-CNDPTD exhibits a third reversible reduction at -1.81 V with $\Delta E_{red} = 90.1 \text{ mV}$.

Chem. Eur. J. 2015, 21, 11517 - 11524



Figure 5. Cyclic voltammograms of **2,4-CNDPTD** (solid) and **2,4,5-CNDPTD** (dashed) showing the modulation of reduction with increasing cyano content. Voltammograms were recorded at 0.1 Vs⁻¹ in degassed acetonitrile with 0.1 \times NnBu₄PF₆ supporting electrolyte and 1.9 mm analyte.



Figure 6. Cyclic voltammograms of **2-CNDPTD** (black), **3-CNDPTD** (black dashed), and **4-CNDPTD** (gray dashed). All voltammograms were recorded at 0.1 Vs⁻¹ in degassed acetonitrile with NnBu₄PF₆ supporting electrolyte and 1.9 mM analyte.

ide, where reduction is expected to occur. This lack of resonance is illustrated by the absence of cyano participation with the heterocycle in the calculated LUMO of **3-CNDPTD** (Figure 7). However, the calculated LUMO energies for **2-CNDPTD**, **3-CNDPTD**, and **4-CNDPTD** do not accurately reflect the relationship between experimental potentials.

Cyano positioning also controls the reversibility of reduction (Figure 6). With *m*-CN, a first, quasireversible reduction is followed by a poorly defined process. Two quasireversible reductions are observed for **4-CNDPTD**, whereas completely reversible reductions are achieved for all derivatives having cyano groups in the *ortho* position (**2-CNDPTD**, **2,4-CNDPTD**, and **2,4,5-CNDPTD**).

Simple electronic features of the *ortho* position cannot explain its role in reversibility, since the *ortho*- and *para*-substituted compounds have similar LUMOs (Figure 7). A model compound was synthesized to probe how the sterics of an *ortho*-substituted phenyl ring may influence reduction reversibility. An $o-C_6H_4Me$ group was installed at the 2- and 5-positions of the thiophene dioxide (**2-MeDPTD**; see Supporting Informa-



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Figure 7. LUMOs for **2-CNDPTD**, **3-CNDPTD**, and **4-CNDPTD**, calculated by using the B3LYP/6-31G(d,p) basis set. These images identify the site of reduction while exploring the effect of cyano positioning.

tion) for comparison with the o-C₆H₄CN substituent. Interestingly, the 2-MeDPTD showed only quasireversible reductions, that is, steric effects alone are not responsible for the electrochemical differences observed in the different DPTD derivatives. The reversibility for 2-CNDPTD persists even in a nonpolar solvent (CH₂Cl₂), and this eliminates the possibility that reversibility results from increased solvent stabilization of the reduced state of o-CN derivatives. Therefore, the impact of an o-CN group is likely a combination of sterics, electronics, and other factors such as intramolecular forces. Hammett parameters could not be used to help explain the change in reduction behavior from ortho to para, since constants for ortho substituents are not available.^[16] Previous work on triaryl amines suggests that steric effects of ortho substituents can affect redox potential, though a change in the reversibility of the triaryl amine oxidation was not observed.^[17]

Regardless of the exact link between reversibility and cyano positioning, all derivatives without *o*-CN clearly undergo significant degradation in the reduced form. The nature of this process was examined by using **3-CNDPTD** as a representative example. Generation of degradation products in **3-CNDPTD** is substantiated by the appearance of multiple, low-intensity oxidative processes following the initial cathodic sweep of the first reduction. The degradation products limit the reversibility of the first reduction irrespective of whether the second reduction is scanned. Meanwhile, concentration studies revealed that cathodic peak potential and reversibility (i_{pa}/i_{pc}) of the first reduction show initial dependence on analyte concentration before leveling off at higher concentrations (Figure 8).

Although C–S bond cleavage and dimerization are common causes of irreversibility in organic sulfones,^[18] monomolecular processes including C–S cleavage can be ruled out here.^[18a,19] Reductive dimerization or multistep coupling could still be envisioned, but further experimentation such as EPR spectroscopy would be needed to substantiate this. As expected, no correlation with concentration is seen for the reversible reductions of **2-CNDPTD**.

Along with complexity, the electrochemistry reveals possible applicability. Compounds having multiple cyano groups per phenyl ring (**2,4-CNDPTD** and **2,4,5-CNDPTD**) rival the impressive reductions of viologens (methyl viologen dichloride: $E_{red} = -0.687, -1.121$ V vs. SCE).^[20] This indicates a strong possibility for charge-transport or electron-relay functionality.

The first reduction of derivatives having *o*-CN functionality also causes an intense visible color change from yellow to blue

Chem. E	Eur. J.	2015,	21,	11517 -	11524
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Figure 8. Concentration dependence of the reversibility (i_{pa}/i_{pc}) of the first reduction. The dashed line represents the behavior of an ideal reversible reduction, filled squares correspond to **2-CNDPTD**, and empty squares correspond to **3-CNDPTD**. Reductions were measured by cyclic voltammetry in degassed acetonitrile with NnBu₄PF₆ supporting electrolyte.

at the electrode surface. To investigate this for possible electrochromic applications, absorbance spectra were recorded during cyclic voltammetry. Spectral features representing the color change of the first reduction generally appear as the potential of that process is traversed, but in the case of **2-CNDPTD**, the changes are low in intensity, and their detection lags behind the reduction (Supporting Information). The spectral changes are similar in all *o*-CN derivatives and include partial loss of the absorbance of the neutral species near 350 nm and the appearance of two new signals for the reduced anion: a major peak below 750 nm and a smaller, low-energy feature (Figure 9). The new signals are redshifted as the π system is extended, and the major absorbance ranges from 621 nm for **2-CNDPTD** to 647 nm for **2,4-CNDPTD** and 709 nm for **2,4,5-CNDPTD** (Figure 10).

Despite the many similarities of the o-CN derivatives, the spectral behavior on passing the second reduction and reversing the voltammogram differentiates 2,4-CNDPTD and 2,4,5-CNDPTD from 2-CNDPTD. In the last-named, progression of the voltammogram ultimately leads to increased absorbance near 458 nm that remains prominent while the signal of the singly reduced species ($\lambda_{max} = 621 \text{ nm}$) fades. Such dynamic spectroelectrochemistry suggests slight degradation over time, which is not detected by electrochemistry but has been encountered previously for *p*-nitrophenyl methyl sulfone.^[18c] However, for 2,4-CNDPTD and 2,4,5-CNDPTD, the second reduction does not cause a spectral change, and instead the intense absorbances of the first reduction persist throughout the voltammogram and for several seconds after its completion. Radical anions formed from 2,4-CNDPTD and 2,4,5-CNDPTD thus appear to be stable on a timescale longer than that of cyclic voltammetry. Such charge stability in these derivatives combined with the intensity and low turn-on voltage of their color change make them interesting candidates for electrochromic devices.



Figure 9. Spectroelectrochemistry of **2,4-CNDPTD**. Bottom: absorbance spectrum and difference spectra showing the change in absorbance both during and after cyclic voltammetry. Top: corresponding cyclic voltammogram with bars identifying the range of potentials traversed during collection of each difference spectrum.

The blue color that appears in the *o*-CN derivatives is also visible during the first reduction of **3-CNDPTD** and **4-CNDPTD** but is too fleeting for detection. A more unique color change occurs in the previously reported parent **DPTD**, reduction of which creates a red appearance corresponding to emergence of an absorbance near 547 nm (Figure 10). The blueshift in this absorbance is due to the simpler π system of **DPTD**. Ultimately, the red color of **DPTD**, like the blue color of **3-CNDPTD** and **4-CNDPTD**, is short-lived due to redox instability.



Figure 10. Absorbance spectra representing the height of the redox-induced color change for all compounds investigated by spectroelectrochemistry. The spectra were taken past the second reduction wave and show a mixture of absorbances from the original species (\approx 350–400 nm) as well as from the reduced species (\approx 450–725 nm).

Chem. Eur. J. 2015, 21, 11517 – 11524



Photocatalytic dihydrogen generation

Given their rich electrochemical properties, the **DPTD**s were investigated as electron relays (ERs) for photocatalytic water reduction. Setups for photogeneration of H_2 from H_2O can include three components (Scheme 2A): a photosensitizer, a sacri-



Scheme 2. A) Three-component setup for dihydrogen generation with an iridium photosensitizer, triethylamine, and a platinum catalyst. B) Four-component setup including a DPTD electron relay. C) Thermodynamics of an electron-transfer cascade observed after reductive quenching of the photosensitizer in a four-component setup. Displayed energy levels are based on the experimental first reduction potentials of the components. The rate of electron transfer (ET) between the partners greatly influences the hydrogen-evolution kinetics of the system.

ficial donor, and a proton reduction catalyst. Hydrogen generation can also involve an electron relay as a fourth component, which shuttles electrons from the photosensitizer (PS) to the catalyst (Scheme 2B). To date, a variety of iridium catalysts have proven to be efficient photosensitizers in hydrogen generation (up to 2400 photosensitizer turnover numbers in THF),^[21] and recently, an iridium catalyst with aryl silyl substituents exhibited exceptional performance for water reduction.^[22]

We explored a popular three-component system that uses $[Ir(ppy)_2(dtbbpy)]PF_6$ (ppy=2-phenylpyridine, dtbbpy=4,4'-ditert-butyl-2,2'-bipyridine) as the photosensitizer, triethylamine (TEA) as the sacrificial donor, and K₂PtCl₄ as a precursor to the colloidal platinum catalyst.^[21] In THF, this system produces approximately 570 μ mol of H₂ in 70 h. However, as evidenced in Figure 11 (no-relay trace), the rate of H₂ production is signifi-



Figure 11. Comparison of the amount of H₂ generated by using DPTD derivatives as ERs. **2-CNDPTD** was found to be the most efficient ER, generating over 1600 µmol H₂ even after an illumination period of 70 h. Reactions conditions: 0.1 mm photosensitizer, 0.2 mm ER, and 30 µm K₂PtCl₄ in THF/water/TEA (8/1/1) solution.

cantly diminished after only 5 h. The addition of DPTDs to act as ERs decreased the rate of H_2 formation initially, but afforded a significantly more robust water reduction system with larger amounts of H_2 generated over time (Figure 11).

The thiophene dioxide clearly facilitates the electron-transfer process from the photosensitizer to the proton reduction catalyst, and control experiments in the absence of photosensitizer did not produce any H₂, which confirms that the DPTDs do not act as the light absorbers. All the compounds bearing cyano groups generated more H₂ as compared to the unsubstituted **DPTD**, indicating that the former act as more resilient ERs. Moreover, the cyanated compounds seem to impart robustness to the overall system since some of the reactions continued to produce H₂ even after 70 h of illumination. CN binding to the colloidal platinum could result in efficient electron transfer to the reduction catalyst and facilitate the overall relay process.^[23]

Like the electrochemical behavior, the yield of H₂ was dramatically influenced by the structure of the DPTD chosen as the ER. In THF, **2-CNDPTD** underwent 1605 ER TON and produced the largest amount of H₂ for all experiments. Meanwhile, electronically similar **3-CNDPTD** and **4-CNDPTD** produced only 1067 and 717 TON, respectively. The derivatives lacking *o*-CN groups exhibit only quasireversible reductions in cyclic voltammetry, which is likely to lead to degradation during ER redox activity. Interestingly, **2,4-CNDPTD** and **2,4,5-CNDPTD**, which have completely reversible reductions, still do not perform as well as **2-CNDPTD**. Two factors likely contribute to the excellent behavior observed for **2-CNDPTD**. First, the smaller size of **2-CNDPTD** compared to derivatives with multiple cyano groups may allow faster diffusion from the photo-



sensitizer to the catalyst. Also, the LUMO of **2-CNDPTD** may be best positioned between the LUMOs of the photosensitizer and catalyst to streamline electron transfer.

The effect of coordinating solvents like MeCN on photosensitizer stability and overall catalytic performance has been well documented.^[24] Unlike traditional systems, the current fourcomponent system yielded substantial TONs for some of the DPTDs in MeCN, which confirmed their viability as ERs. The trends in H₂ yield are similar in both solvents (Figure 12),



Figure 12. Comparison of H₂ generation, PS TON, and ER TON in THF (back) and MeCN (front). All reactions involved 0.1 mm photosensitizer, 0.2 mm ER, and 30 μ mol K₂PtCl₄ in solvent/water/TEA (8/1/1) solution.

except for **2,4-CNDPTD**, which maintains essentially the same performance (1062 TON in THF and 1073 TON in MeCN). Experiments are ongoing to evaluate why **2,4-CNDPTD** maintains the same efficiency while all the other derivatives exhibit a drop in relay performance in MeCN.

Dynamic quenching studies were carried out in MeCN with the Ir^{III} photosensitizer (Supporting Information) to obtain a better mechanistic understanding of H₂ generation. Stern-Volmer plots were generated for all derivatives and revealed that cyano-bearing compounds quench the photosensitizer emission better than the parent DPTD. Given the electronpoor nature of the dioxides, oxidative quenching would be expected to take place in this instance. As suspected, the electron-accepting ability was found to increase with increasing cyano content, with 2,4,5-CNDPTD having the largest quenching constant of $k_q = 7.4 \times 10^9 \,\mathrm{m}^{-1} \,\mathrm{s}^{-1}$ (Supporting Information). Moreover, the k_q values follow the trend of the first reduction potentials E_{red1} and the calculated SOMO energy levels of the anion (Supporting Information). These results strongly suggest that lowering of the LUMO level as a consequence of cyano substitution facilitates electron transfer from the excited state of the Ir photosensitizer. From these trends, one would expect 2,4,5-CNDPTD to be the best ER for photocatalysis. However, as observed from the H₂-evolution results (Figure 12), 2-CNDPTD was the most active ER in THF, and 2,4-CNDPTD performed slightly better in MeCN.

The observed quenching trend does not match the trend found for ER performance due to the complexity of water reduction (four components). The photocatalytic system involves two additional participants, that is, the sacrificial agent (TEA) and the water reduction catalyst (K_2 PtCl₄/colloidal Pt). TEA is

known to reductively quench the Ir^{III} excited state (k_{α} on the order of $10^7 - 10^8 \,\text{m}^{-1} \text{s}^{-1})^{[25]}$ and is present at a comparatively higher concentration (0.7 M) than the ER (0.2 MM), which likely makes reductive guenching the dominant process. Since the ER acts as an electron shuttle between the photochemically reduced photosensitizer and platinum, the position of its LUMO energy level is critical for efficient electron transfer. Although a low-lying energy level favorably assists electron injection from the HSOMO of the photosensitizer, it could also give rise to competitive quenching pathways (with TEA), energy-level mismatch with the catalyst, or even the possibility of energy transfer rather than the desired electron transfer, which would lead to an overall decrease in efficiency. In this regard, the LUMO energy level of 2-CNDPTD in THF seems to be optimally positioned such that both transfer from the photosensitizer and to the catalyst have sufficient driving force without too great of an energy change (Scheme 2C). In MeCN, 2-CNDPTD still performs well (971 TON), but 2,4-CNDPTD produces more H₂ (1073 TON), which suggests that more factors are at play in a highly coordinating and polar solvent.

Conclusion

The synthesis and characterization of a series of electron-poor thiophene 1,1-dioxides have been reported. The phenyl substituents appended to the dioxide structure have a marked influence on the electrochemical and photophysical behavior of the compound. In particular, phenyl substituents with ortho cyano groups exhibit significantly more stable electrochemical behavior than their meta and para congeners. Increasing the cyano content of the phenyl rings facilitates electrochemical reduction while increasing radical-anion stability. Many of the diphenyl thiophene 1,1-dioxides produce colored radical anions, which were analyzed by spectroelectrochemistry. The 2,4-CNDPTD and 2,4,5-CNDPTD derivatives exihibit stability beyond the timescale of electrochemical cycling. The electrochemical properties of the synthesized dioxides led to their exploration in photocatalytic hydrogen generation. The DPTDs function well as ERs and can significantly enhance the amount of H₂ generated with an iridium photosensitizer, triethylamine, and a platinum proton reduction catalyst. Compound 2-CNDPTD outperformed all other derivatives in THF, while 2,4-CNDPTD was the best ER in MeCN. Studies on the enhanced stability with an electron-withdrawing substituent in the ortho position are currently underway.

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