Comparison between Benzothiadizole–Thiophene- and Benzothiadizole–Furan-Based D–A–π–A Dyes Applied in Dye-Sensitized Solar Cells: Experimental and Theoretical Insights

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ABSTRACT: Three novel donor–acceptor–π–acceptor-type compounds (WSS, WS6, and WS7) were synthesized and investigated in dye-sensitized solar cells (DSSCs) exploring the effect of conjugated linkers on device performance. The new dyes showed strong light-harvesting ability in the visible region with relatively high molar absorption coefficients (>21 800 M⁻¹ cm⁻¹). This can be attributed to their intrinsic charge transfer (CT) from the arylamine to the acceptor group. Density functional theory (DFT) calculations revealed a favorable lowest unoccupied molecular orbital (LUMO) energy level, allowing efficient injection into the semiconductor conduction band after excitation. Upon application in DSSC devices, the WS dye containing 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole as conjugated linker mediated the highest device power conversion efficiency (PCE) amounting to 5.5%. This is higher than that of the WS6-containing dye based on the 4,7-di(thienophen-2-yl)benzo[c][1,2,5]thiadiazole linker (3.5%) and the WS7 dye based on the 4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole linker (4.3%) under AM 1.5 G illumination. The present results show furan-based dye linker systems to have a significant potential for improving DSSC efficiencies.

INTRODUCTION

Dye-sensitized solar cells (DSSCs) have attracted considerable attention due to their potential low cost and ease of fabrication.1 They are emulating the natural photosynthesis process, where light absorption and charge transport can be mediated through a photosensitizer and a semiconductor, respectively. To date, the performance of DSSCs has been strongly relying on the molecular structure of the photosensitizer. Photosensitizers based on porphyrins,2 ruthenium complexes,3 and metal-free molecular systems have been synthesized and used in DSSC devices.8–13 Although power conversion efficiencies above 11% have been reported employing ruthenium-based sensitizers,4,14,15 restricted access and ecological issues linked to ruthenium make it important to search for alternative dyes. Metal-free organic dyes represent one of the most widely considered alternative sensitizers for DSSCs due to their typically high extinction coefficients and low ecological impact.16 Nevertheless, the low efficiencies obtained so far in devices based on such dyes limit their practical application. Lately, much effort has been dedicated to overcome this bottleneck.17–20 In particular, thiophene or thiophene-based heterocycles have been employed as the π-connecting linker in organic dyes, for instance, carboxazol–oligothiophene,21 coumarin–thiophene,22 and benzothiadiazole–thiophene.12 Such organic dyes show good matching of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) mainly located on the thiophene moieties. In this perspective, furan, thiophene’s oxygen analogue, which normally displays a high oxidation potential, is expected to increase the performance when applied in organic dyes for DSSCs.23 The furan-based units are also expected to bring better stability to the organic dyes synthesized.

Generally, the most efficient organic dyes have at least one donor (D) unit and an acceptor (A) unit linked by a conjugated system to form a D–π–A structure that allows for intramolecular charge transfer (ICT).24 In comparison to D–π–A-type dyes, a D–A–π–A system can be simply made by adding an assisting acceptor unit between the D unit and the π bridge. This may result in more flexible photoelectric properties.25 Furthermore, this molecular arrangement (D–A–π–A) can work as a tool to fine-tune the energy-level positions to ensure facile electron transport from the D unit to the A groups.26 We have previously reported13 about metal-free, organic dyes based on a D–D–π–A configuration,
including arylamine as the electron donor, 2-cyanoacrylic acid as the electron acceptor, and a conjugated linker based on thiophene moieties. In contrast to benzene moieties, thiophene can lower the energy of charge transfer \(^{27,28}\) due to the lower resonance energy compared to benzene (thiophene, 29 kcal/mol; benzene, 36 kcal/mol).\(^{29}\) Therefore, it becomes interesting to incorporate also a furan ring with even lower resonance energy (16 kcal/mol) in the conjugated linker\(^{30}\) and investigate the performance in DSSC devices. It is notable that yields, which were 79, 78, and 87%, respectively. The 2

generate asymmetric and symmetric compounds in good yields, respectively. After the catalyzed C–C coupling reaction, the aldehyde group was introduced through the Vilsmeier–Haack reaction using POCl\(_3\) in DMF to get pure E, J, and K compounds in 84, 54, and 85% yields, respectively. The final step toward the target dyes was refluxing the aldehyde group precursor with 2-cyanoacetic acid in chloroform and adding drops of piperidine for 6 h through the Knoevenagel condensation reaction to get the violet WS7 dye in 64% yield. The WS5 and WS6 dyes were obtained in 65 and 69% yields, respectively.

### Theoretical Calculations
The optimized molecular structures along with the HOMO and LUMO distributions are illustrated in Figure 2. The three prepared dyes display a three-dimensional (3D) structure with the n-Bu groups pointing out from the core conjugated plane and affecting the coplanarity of the benzene rings attached to the central nitrogen atom. This 3D structure may potentially reduce the tendency of the dyes to aggregate on the surface of the semiconductor substrate.\(^{14}\) The dihedral angles around the central nitrogen atom is in the range of ~30 to ~45° for all of the dyes, due to the steric effects of the adjacent groups. The backbone of the dye is the part of the dye mainly affecting the interaction with the semiconductor substrate. For the WS7 dye, the dihedral angle between the benzene ring and the adjacent donor groups is ~29°, and on the other hand, coplanarity in the backbone of the dye is high with dihedral angles <2°. For the dye WS6, the dihedral angle with respect to the donor group is low, ~17°, and the remaining dye backbone is coplanar with dihedral angles <2°. For the dye WS5, the dihedral angles in the backbone are all highly coplanar with dihedral angles ≤2°. In this perspective, the WS5 dye structure may facilitate charge injection to the semiconductor carrier.

The spatial distribution of the frontier molecular orbitals, the HOMOs and LUMOs, is illustrated on the basis of the geometrically optimized structure at the same level of DFT calculation. For the three dyes under study, the spatial distribution of the HOMOs is extending over a large part of the dye, while the LUMOs are more localized close to the anchoring groups. This shows a good spatial separation between the HOMOs and LUMOs and indicates a good charge separation when excited. In addition, the LUMO localization on the anchoring groups provides expectations of efficient injection properties of the dyes.

### Photophysical Properties
The UV–vis absorption spectra of the WS5, WS6, and WS7 organic dyes dissolved in dichloromethane (10\(^{-5}\) M) are shown in Figure 3a, and the relevant spectral data are summarized in Table 1. The three organic dyes exhibit two typical absorption bands in the wavelength ranges of 330–420 and 450–530 nm, respectively. The band at shorter wavelengths can be ascribed to localized aromatic ring \(\pi–\pi^*\) transitions, whereas the band at longer wavelengths can be attributed to an intramolecular charge transfer (ICT) between the donor acceptor (triphenylamine) and electron acceptor (cyanoacrylic group) in the dyes. The ICT peaks of the WS5 and WS7 dyes correspond molar

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**RESULTS AND DISCUSSION**

**Synthesis of the Dyes.** Schemes 1 and 2 show the synthesis pathways of the WS5, WS6, and WS7 dyes. Compounds A, B, and C were synthesized via a palladium-catalyzed Suzuki coupling reaction\(^{32}\) through 4,7-dibromobenzothiadiazole and thiophen-2-ylboronic acid or furan-2-ylboronic acid (1:1 and 1:2 molar ratios, respectively) to generate asymmetric and symmetric compounds in good yields, which were 79, 78, and 87%, respectively. The 2',4'-dibutoxy-N-(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)-N-(4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-[1,1'-biphenyl]-4-amine (donor) compound was prepared according to literature.\(^{33}\) Compounds A, G, and H were made by condensation reaction to get the violet WS7 dye in 64% yield. The WS5 and WS6 dyes were obtained in 65 and 69% yields, respectively.

**Figure 1.** Molecular structures of the WS5, WS6, and WS7 organic dyes.
extinction coefficients ($\varepsilon$) of $1.67 \times 10^4 \text{M}^{-1} \text{cm}^{-1}$ at 497 nm and $1.89 \times 10^4 \text{M}^{-1} \text{cm}^{-1}$ at 499 nm, respectively. Moreover, the WS6 dye shows two separate ICT peaks at 532 nm ($\varepsilon = 2.18 \times 10^4 \text{M}^{-1} \text{cm}^{-1}$) and 419 nm ($\varepsilon = 2.95 \times 10^4 \text{M}^{-1} \text{cm}^{-1}$).

The molecular extinction coefficients of the WS5, WS6, and WS7 dyes are higher than those of the standard ruthenium dyes N3 and N719 (13 900 and 14 000 M$^{-1}$ cm$^{-1}$, respectively). These results indicate that the longer the conjugating system, the more red-shifted the absorption. Although WS6 shows a similar conjugation as the WS5 dye, the ICT peak of the WS5 dye displays a blue-shift by ca. 35 nm. This blue-shift can be attributed to the larger delocalization in the molecule when furan is employed instead of thiophene in the linker bridge. In addition, the electronegativity of the oxygen atom in the furan ring is higher than that of sulfur in the thiophene ring, and therefore the resonance energy is lower, 16 kcal/mol, as compared to 29 kcal/mol for furan and thiophene, respectively. For the WS7 dye, its absorption is blue-shifted due to the less coplanar molecular backbone.

The UV−vis absorption spectra of the dyes adsorbed onto TiO$_2$ films are shown in Figure 3b. The resulting ICT bands of WS5, WS6, and WS7 are determined to be 488, 525, and 480 nm, respectively. In comparison to their solution absorption spectra, the dyes show an ca. 7−20 nm blue-shift most likely owing to the deprotonation of the carboxylic acid groups upon adsorption to TiO$_2$.

**Electrochemical Properties.** Cyclic voltammetry (CV) was used to examine the electrochemical properties of the synthesized WS5, WS6, and WS7 dyes. The CV curves and the estimated energy-level diagrams are presented in Figure 4, and the associated data are listed in Table 1. The WS6 dye exhibits two strong and clear oxidation features (Figure 4a). We note that the oxidation potentials ($E_{\text{ox}}$) of the dyes WS5, WS6, and WS7 that correspond to the HOMO energy levels are located at 0.97, 0.97, and 0.99 V$_{\text{NHE}}$, respectively. The peak positions are calibrated with respect to the ferrocenium/ferrocene (Fc$^+/Fc$; see Figure S2) couple at 0.63 V$_{\text{Ag/AgCl}}$. Also, the first oxidation potentials of the three dyes correspond to the HOMO-1 energy levels. The energy-level diagrams (Figure 4b) show that the $E_{\text{ox}}$ values are considerably more positive than that of the iodide/triiodide ($I^-/I_3^-$) redox mediator (0.4 V$_{\text{NHE}}$), revealing suitable dye energy levels for efficient charge transfer upon dye regeneration. In addition, the $E_{\text{red}}$ energies of the WS5, WS6, and WS7 dyes, which are estimated from the intersections between absorption and emission spectra, are 2.07, 1.98, and 2.08 eV, respectively (Figure 5). Consequently, the WS dyes show more negative $E_{\text{red}}$ as compared to the conduction band (CB) of TiO$_2$. The energy gaps between the

**Scheme 1. Synthetic Pathway for the WS7 Dye**
reduction energy of the dyes and the CB of TiO₂ are calculated to be 0.64, 0.56, and 0.63 eV. These estimates are larger than the requirement typically considered necessary for efficient charge transfer (\( E_{\text{gap}} > 0.2 \text{ eV} \)). Consequentely, we expect all of the WS dyes to work well when applied in DSSCs. Nevertheless, the \( E_{\text{red}} \) value of WS6 compared to those of WS5 and WS7 shows that its driving force for electron injection is clearly lower.

**Photovoltaic Performance of the DSSC Devices.** The \( J-V \) characteristics of solar cells based on the WS5, WS6, and WS7 dyes and including an iodine-based mediator (I\(^-\)/I\(_3^-\)) investigated at 1 sun illumination under standard AM 1.5G conditions are presented in Figure 6, with the corresponding photovoltaic parameters summarized in Table 2. For the devices containing the dye WS5, including two furan rings, the results show a power conversion efficiency (PCE) of 5.5% with a short-circuit current density (\( J_{\text{SC}} \)) of 10.87 mA cm\(^{-2}\), an open-circuit voltage (\( V_{\text{OC}} \)) of 680 mV, and a fill factor (\( ff \)) of 75%. However, the devices based on the WS6 dye, instead of comprising two rings of thiophene, show a PCE of 3.5% with a low \( J_{\text{SC}} \) of 7.14 mA cm\(^{-2}\), a similar \( V_{\text{OC}} \) of 640 mV, and an equivalent \( ff \) of 77%. The lower PCE recorded for the WS6-based devices can mainly be assigned to the lower \( J_{\text{SC}} \). Although WS6 shows a red-shifted light absorption band and is characterized by a similar conjugated fragment as that in WS5, the WS6-based DSSCs display a lower \( V_{\text{OC}} \). A possible explanation can be associated with its low-lying \( E_{\text{LUMO}} \) (−1.06 V) and the small \( E_{\text{gap}} \) (0.56 eV) between \( E_{\text{LUMO}} \) and the CB of TiO₂. This could render the electron injection from excited WS6 dyes into the CB of TiO₂ considerably less efficient than for WS5 and WS7. For the solar cells based on the WS7 dye containing one ring of thiophene in the linker part, the DSSC results are intermediate with a PCE of 4.3%, a \( J_{\text{SC}} \) of 9.50 mA cm\(^{-2}\), a \( V_{\text{OC}} \) of 660 mV, and an \( ff \) of 68%. Also in this case it
can be noted that the $E_{\text{LUMO}}$ ($-1.13$ V) and $E_{\text{gap}}$ ($0.63$ eV) values of WS7 are lower than those of WS5.

The incident photon-to-current conversion efficiency (IPCE) spectra of the WS5, WS6, and WS7-based DSSC devices are depicted in Figure 6b. Both the WS5 and WS7 dyes demonstrate a broad absorption response in the visible region with the absorption extending to 650 nm. This explains the relatively good $J_{\text{SC}}$ recorded. In contrast, the WS6-based devices exhibit a quite weak absorption response with a maximum IPCE of 22%, resulting in a low $J_{\text{SC}}$. Also, the WS5- and WS7-based devices show higher and broader IPCE above 30% in the range of 500–630 nm. The integrated IPCE currents for the WS5, WS6, and WS7 dyes are 9.6, 6.8, and 9.4 mA cm$^{-2}$, respectively.

Moreover, the WS dye-based devices were examined using electrochemical impedance spectroscopy (EIS) to investigate the interfacial charge exchange. The Nyquist and Bode plots recorded under 1 sun illumination are shown in Figure 7. The larger the semicircle at lower frequencies (to the right) is interpreted as the charge-transfer resistance ($R_{\text{CT}}$), and the $R_{\text{CT}}$ was found to follow the order WS6 ($19$ $\Omega$) < WS7 ($24$ $\Omega$) < WS5 ($28$ $\Omega$). This suggests that the electron recombination rate should be in the order WS5 < WS7 < WS6, which is in agreement with the obtained $V_{\text{OC}}$ recorded for devices based on WS6 (640 mV) < WS7 (660 mV) < WS5 (680 mV).

![Figure 3](https://pubs.acs.org/doi/abs/10.1021/acs.omega.0c02060)  
**Figure 3.** Absorption spectra of the (a) WS5, WS6, and WS7 dyes in dichloromethane solution and (b) dyes adsorbed onto TiO$_2$ films.

![Figure 4](https://pubs.acs.org/doi/abs/10.1021/acs.omega.0c02060)  
**Figure 4.** (a) Cyclic voltammogram of the WS6 dye in dichloromethane solution using the Fc/Fc$^+$ couple as reference ($E^{\circ}(\text{Fc/Fc}^+) = 0.63$ V$_{\text{NHE}}$) and (b) energy-level diagrams of the WS5, WS6, and WS7 dyes.

| dye   | $\lambda_{\text{abs, max}}$ (nm) | $\lambda_{\text{em, max}}$ | HOMO$^d$ [V vs NHE] | $E_{\text{ox}}$ [V vs NHE] | $E_{\text{red}}$ [V vs NHE] | $E_{\text{gap}}$ [eV] |
|-------|---------------------------------|-----------------------------|----------------------|-----------------------------|-----------------------------|------------------------|
| WS5   | 497 (16 690) 474 (50 900)       | 710                         | 0.93                 | 2.07                        | 0.97                        | -1.14                  | 0.64                   |
| WS6   | 532 (21 800) 483 (29 530)       | 716                         | 0.92                 | 1.98                        | 0.97                        | -1.06                  | 0.56                   |
| WS7   | 499 (18 980) 354 (45 780)       | 710                         | 0.95                 | 2.08                        | 0.99                        | -1.13                  | 0.63                   |

$^a$Maximum absorption in CH$_2$Cl$_2$ solution (10$^{-5}$ M) at 25 °C. $^b$Maximum absorption on TiO$_2$ films. $^c$Maximum emission in CH$_2$Cl$_2$ solution (10$^{-5}$ M) at 25 °C. $E_{0-0}$ was calculated as the 1240/\(\lambda\) intersection. $E_{\text{red}}$ was calculated from $E_{\text{ox}} - E_{0-0}$. $E_{\text{gap}}$ is the energy gap between the $E_{\text{red}}$ of dye and the conductive band (CB) level of TiO$_2$. $^d$Estimated by subtraction of $E_{0-0}$ from the oxidation potential.
Moreover, the electron lifetime ($\tau$) of the injected photoelectrons can be evaluated from the peak frequency ($f$) at the intermediate frequency region in the Bode plots (Figure 7b) following the relation $\tau = 1/(2\pi f)$. The slower the charge recombination rate, the longer the electron lifetime affecting both $V_{OC}$ and $J_{SC}$. Figure 7b shows that $f$ increases in the order WS5 < WS7 < WS6. Therefore, $\tau$ increases in the order WS6 < WS7 < WS5. Consequently, the WS5-based devices are expected to show better performance than those based on WS6 and WS7.

**CONCLUSIONS**

The novel organic dyes WS5, WS6, and WS7 were designed and synthesized to study the effect of differences in the conjugated linker units between the arylamine donor and 2-cyanoacrylic acid acceptor and the subsequent performance of DSSCs using these dyes. Having a stronger electron-accepting unit, the WS6 dye was applied in DSSC and synthesized to study the electronic properties of the WS5, WS6, and WS7 dyes in dichloromethane solution.

Figure 5. UV−vis absorption and emission spectra of the WS5, WS6, and WS7 dyes in dichloromethane solution.

Table 2. Photovoltaic Parameters of DSSC Devices Based on the WS5, WS6, and WS7 Dyes with $I^-/I^{3-}$ as Redox Mediator and CDCA as a Co-adsorbent under 1 sun AM 1.5 G Illumination

| compounds | $J_{SC}$ (mA cm$^{-2}$) | $V_{OC}$ (mV) | ff (%) | $\eta$ (%) |
|-----------|-------------------------|--------------|--------|-----------|
| WS5       | 10.87 ± 0.11            | 680 ± 2      | 75.0 ± 3.0       | 5.54 ± 0.29 |
| WS6       | 7.14 ± 0.12             | 640 ± 0      | 77.0 ± 1.5       | 3.52 ± 0.13 |
| WS7       | 9.5 ± 0.30              | 660 ± 1      | 68.0 ± 2.0       | 4.26 ± 0.26 |

were purchased from Sigma-Aldrich. $^1$H- and $^{13}$C NMR spectra were recorded on Bruker 500 and 400 MHz instruments using the residual signals for CDCl$_3$ at $\delta = 7.26$ and 77.0 ppm, for dimethyl sulfoxide (DMSO)-$d_6$ at $\delta = 2.50$ ppm and 39.4 ppm, and for acetone-$d_6$ at $\delta = 2.05$, 29.84, and 206.26 ppm, as internal references for $^1$H and $^{13}$C NMR spectra, respectively.

**Dye Synthesis.** The details are provided in the Supporting Information.

The UV/vis absorption spectra were recorded on a PerkinElmer Lambda 750 UV/vis spectrophotometer. The emission spectra were obtained from a Varian Cary Eclipse fluorescence spectrophotometer.

All electrochemical measurements were carried out in a three-electrode system using an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie) with a carbon electrode ($\Phi$: 3 mm) as the working electrode, a platinum column as the counter electrode, and an Ag/AgNO$_3$ electrode as the reference electrode calibrated with ferrocene. All of the potentials in this work are reported with respect to normal hydrogen electrode (NHE). Cyclic voltammetry was carried out in a 0.05 M tetrabutylammonium hexafluorophosphate ([TBA]PF$_6$) dichloromethane solution with a 0.2 mM concentration of the desired dye.

The high-resolution mass spectra were recorded with a matrix-assisted laser desorption/ionization time-of-flight Shimadzu Maldi 7090 (MALDI-TOF) spectrometer.

All solvents, such as tetrahydrofuran, diethyl ether, toluene, acetonitrile, and dimethyl formamide, were dried before use. Fluorine-doped tin oxide (FTO) glass substrates were purchased from Pilkington (TEC15 and predrilled TEC8) and were used for the DSSC working and counter electrodes. Screen printing was used to generate a thin film based on a TiO$_2$ paste from Dyesol (DSL 18NR-T), as well as a layer of light-scattering particles (JGC C & C Ltd. PST-400 °C, from JGC Catalysts and Chemicals Ltd.).

Dye Bath. The rate of dye adsorption to the TiO$_2$ substrate may differ depending on the dye bath solvent and co-

Figure 6. (a) $J$−$V$ curves of the DSSC devices based on the WS5, WS6, and WS7 dyes in an iodine-based electrolyte and (b) the corresponding incident photon-to-current conversion efficiency (IPCE) spectra.

**EXPERIMENTAL SECTION**

Materials and Equipment. All starting materials were obtained from Acros Organics, Sigma-Aldrich, and Alfa Aesar and used without any purification. In particular, 4,7-dibromobenzo[b]thiophene, 2-ylboronic acid, furan-2-ylboronic acid, tris(dibenzylideneacetone)dipalladium, 2-cyanoacetic acid, tri-o-tolylphosphine, and phosphoursoxychloride...
adsorbents used. For electrolytes with redox mediators based on the I\(^{-}/I^3\) couple, this is less of a problem, and a co-adsorbent can be used to reduce aggregation. The respective dyes (0.2 mM) were dissolved in dichloromethane. Cheno-deoxycholic acid was added as the co-adsorbent in 2 mM into the dye solutions. The time duration of dying was 4 h. The electrodes were rinsed with ethanol and air-dried.

**Device Fabrication and Characterization.** The device fabrication was similar as described in previous reports.\(^3\) The \(J\text{--}V\) characteristics of DSSCs based on the new dyes (WS5, WS6, and WS7) were recorded under 100 mW cm\(^{-2}\) (AM 1.5) radiation using a Keithley model 2400 source meter. The light source was calibrated with a silicon reference cell before use. IPCE spectra were recorded by a computer-controlled setup comprising a xenon lamp (Spectral Products ASB-XE-175), a monochromator (Spectral Products CM110), and a Keithley multimeter (model 2700), calibrated by a certified reference solar cell. The electron lifetime data were recorded through EIS.

**Calculation Method.** The charge distribution and HOMO and LUMO energy levels were obtained using density functional theory (DFT)\(^3\) at a B3LYP/cc-pVDZ level of calculation using Gaussian 09\(^4\) and GaussView 5.0.\(^4\)

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02060.

Experimental details; cyclic voltammogram of WS5 and WS7 dyes in \(\text{CH}_2\text{Cl}_2\) solution electrolyte; and NMR spectroscopy and MADI-TOF spectra of WS5, WS6, and WS7 dyes (PDF)

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**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from the Swedish Research Council and the Swedish Energy Agency. They also would like to thank Prof. Licheng Sun for his support and allowing the synthetic work to be executed in his laboratory. The authors thank Dr. Yong Hua for recording the HR-MS spectra, as well as Dr. Martin Karlsson and Dr. Erik Gabrielson for their help in making D35 dye donor fragments.

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**Figure 7.** (a) Nyquist plot and (b) Bode plot of the fabricated DSSCs in an iodine-based electrolyte under 1 sun illumination.
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