Synthesis and Photovoltaic Applications of a 4,4′-Spirobi[cyclopenta[2,1-b;3,4-b′]dithiophene]-Bridged Donor/Acceptor Dye

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ABSTRACT
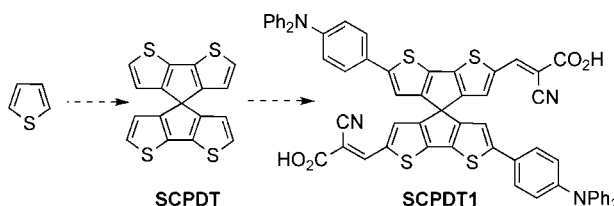
A new donor/acceptor (D−A) spiro dye (SCPDT1) featuring two bithiophene units, connected through an sp³-hybridized carbon atom, was prepared by a multistep synthetic sequence involving the convenient assembly of the spiro system under mild catalytic conditions. The photocurrent spectrum of dye-sensitized solar cells incorporating SCPDT1 covers the spectral region ranging from 350 to 700 nm and reaches a wide maximum of ∼80% in the 420−560 nm range. Power conversion efficiencies of up to 6.02% were obtained.

Spiro compounds in which two identical or different π-conjugated systems are connected by a common sp³-hybridized atom are actively investigated as organic molecular materials for optoelectronics.[1] Indeed, their peculiar cross-shaped rigid structure with two perpendicularly oriented molecular halves results in favorable properties, such as improved morphological stability in the solid state and reduced tendency to form aggregates thanks to the inhibition of intermolecular interactions. Spiro compounds also hold higher solubility with respect to the corresponding nonspiro-linked parent compounds. In addition, electronic interactions between the two halves of spiro compounds are greatly reduced due to their orthogonal arrangement, and the two π-systems are usually

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considered to be independent despite the existence of specific spiro interactions in the excited states.[1a,2] Molecules possessing a spiro-configured central unit and tailor-made optical and redox properties have thus found applications in electrochemiluminescence studies,[3] organic light-emitting devices,[4] electrochromic devices,[5] field-effect transistors,[1a] lasers,[6] and organic- or dye-sensitized solar cells (DSSC).[7] In this context, 2,2′7,7′-tetrakis (*N*,*N*-di-*p*-methoxyphenylamine)-9,9′-spirobifluorene (spiro-MeOTAD) and related compounds have received great attention as hole transporters in solid-state DSSC since 1998.[7a,8] The potential of the spiro arrangement in the design of organic photosensitizers for DSSC, with particular regard to the suppression of aggregation-induced self-quenching processes and to the introduction of multiple anchoring groups on the same molecule, has been demonstrated more recently.[7e,9]

Most spiro compounds for optoelectronics developed so far, including those used in solar cells, are based on the easily accessible 9,9′-spirobifluorene core. In order to further expand this field of research, the availability of alternative spiro cores with different electronic characteristics would be highly beneficial. As also suggested by computational studies,[10] the replacement of the 9,9′-spirobifluorene core with 4,4′-spirobi[cyclopenta[2,1-*b*;3,4-*b*′]dithiophene] (**SCPDT**, Figure 1) is particularly attractive.[11] However, the synthesis of spiro compounds based on **SCPDT** still remains a challenge. Thus, the few reported examples of spirocyclopenta-derivatives of 2,2′-bithiophene concern either heteroatom-bridged spiro-bithiophenes,[12] or mixed spiro compounds where only one-half of the central core consists of a bithiophene unit.[7e,13] In an outstanding paper,[11a] Salbeck and co-workers actually described the preparation of a tetraphenyl-substituted derivative of **SCPDT** by Suzuki coupling of phenylboronic acid and 2,2′,6,6′-tetrabromo-4,4′-spirobi[cyclopenta[2,1-*b*;3,4-*b*′]dithiophene] (**4Br-SCPDT**, Figure 1), but the synthetic pathway leading to this valuable starting material was not disclosed there.

We here report the preparation of **SCPDT** from simple 2,2′-bithiophene derivatives and its further elaboration to give the dipolar dye **SCPDT1** (Figure 1) featuring two perpendicularly aligned donor/acceptor chromophore couples attached to the **SCPDT** core. The new spiro-configured dye has been investigated as a component of DSSC, showing that the replacement of the spirobifluorene core with **SCPDT** has positive effects on the photovoltaic performance of the device. The new dye extends the sensitization effect to the red zone of the solar spectrum, without enlarging the size of the conjugated bridge.
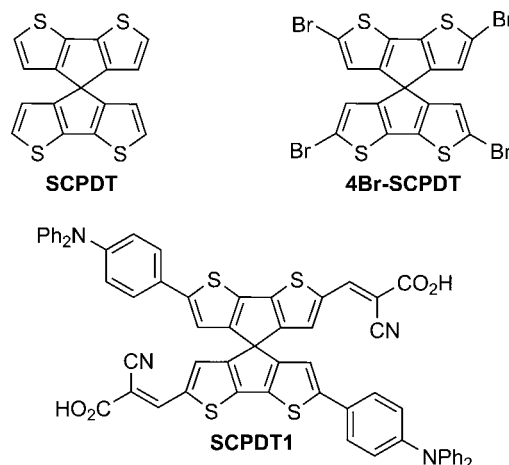
Figure 1. 4,4′-Spirobi[cyclopenta[2,1-*b*;3,4-*b*′]dithiophene] derivatives.

Inspired by previous literature reports,[13] we first tried to generate **SCPDT** by acid-mediated intramolecular Friedel–Crafts cyclization of a tertiary carbinol obtained in turn by the reaction of cyclopenta[2,1-*b*;3,4-*b*′]dithiophen-4-one and 3-lithio-2,2′-bithiophene formed *in situ* by a selective lithium-bromo exchange reaction of 3-bromo-2,2-bithiophene with *n*-BuLi (see Supporting Information, SI). Among the various cyclization conditions tested, only the use of H_2SO_4 in *n*-octane provided traces of **SCPDT**, hardly separable from tars. Other Lewis and Brønsted acids completely failed to give the desired product, in line with earlier findings of Wynberg and co-workers who did not succeed in preparing spiranes using cyclopenta[2,1-*b*;3,4-*b*′]dithiophen-4-one as starting material since the intermediate carbinols containing two α-thienyl units decomposed prior to ring closure.[14] In order to overcome this limitation and to avoid the occurrence of intermolecular side reactions,[13a] we decided to protect the electron-rich α-positions of the thiophene units by bromination prior to the cyclization step, as outlined in Scheme 1.

The synthetic sequence leading to **SCPDT** started with the selective lithiation of 3,5,5′-tribromo-2,2′-dithiophene **1** (conveniently obtained in two steps from commercially available thiophene precursors, see SI) followed by quenching with chlorotrimethylsilane (TMSCl) to give the TMS-capped bithiophene **2**. Further treatment of

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this intermediate with n-BuLi and subsequent addition of 2,6-dibromo-cyclopenta[2,1-b;3,4-b']dithiophen-4-one **3** (see SI) afforded the tertiary carbinol **4** that was desilylated/brominated with NBS yielding the corresponding tetrabromo-derivative **5**. After a careful survey of reaction conditions, we found that the intramolecular Friedel−Crafts cyclization of **5** to give **4Br-SCPDT** can be achieved under mild reaction conditions, using a catalytic amount of inexpensive, easy to handle, and environmentally friendly FeCl$_3$. As previously exemplified,[11] this spiro-compound might be used as such as a starting material for a variety of symmetrically tetrasubstituted **SCPDT** derivatives. In the present case it was debrominated by treatment with an excess of n-BuLi and electrophilic quenching with water to give **SCPDT**.

**Scheme 1.** Synthesis of **SCPDT**
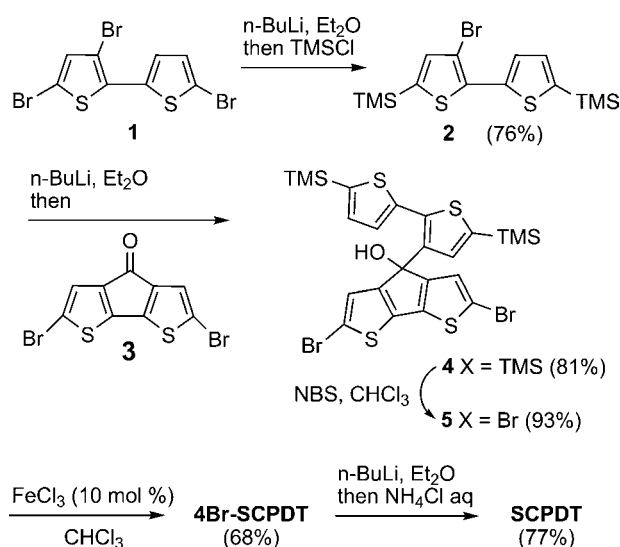
The selective introduction of two formyl groups in the 2,2′ positions of **SCPDT** by the Vilsmeier reaction to give **6** (Scheme 2) is another key step in the synthetic route toward **SCPDT1**. This was made possible by the well-documented loss of reactivity toward electrophiles experienced by electronically connected thiophene rings upon introduction of an electron-withdrawing substituent in one of them.[15,16] Bromination of the remaining free 6,6′-positions of **6** with NBS, followed by a Pd(0)-catalyzed coupling reaction of the obtained intermediate **7** with 4-(diphenylamino)phenylboronic acid pinacol ester, gave dialdehyde **8**. Knoevenagel condensation of the latter with cyanoacetic acid in the presence of piperidine afforded the target dye **SCPDT1**.

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(16) The correct insertion of formyl groups was confirmed by derivatization of **6** with an enantiomerically pure amine to give the corresponding imino-derivative as a diastereoisomeric couple (Supporting Information).

Scheme 2. Selective Functionalization of **SCPDT**
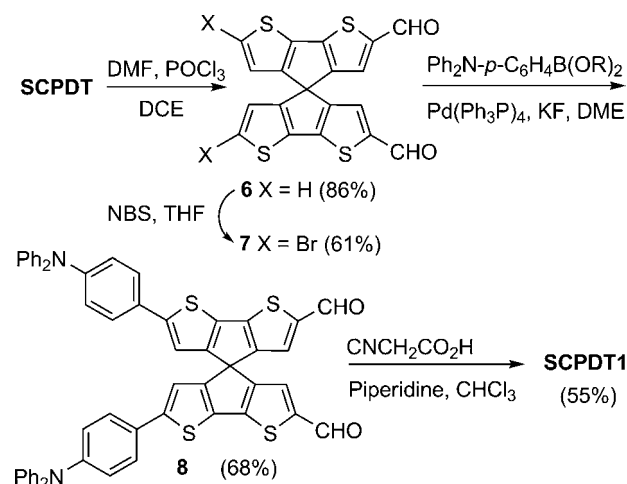
The main optical parameters of **SCPDT1** are summarized in Table 1 (see Figure S2 in SI for the absorption spectra in solution and adsorbed onto TiO$_2$ film). Three distinct absorption bands were observed: two in the UV region (λ_{max} = 285 and 361 nm), corresponding to the $\pi-\pi^*$ electronic transition of the bithiophene core, and the other in the visible region (λ_{max} = 462 nm) corresponding to a donor−acceptor intramolecular charge transfer band.[10,12,17] The higher absorption intensity of the latter with respect to those related to $\pi-\pi^*$ transitions indicate that coplanarity of each bithiophene moiety of **SCPDT1** is retained, thus maximizing the photostimulated charge transfer process.[17] On the other hand, AM1 semiempirical calculations show that the highest occupied molecular orbital (HOMO) of **SCPDT1** is located mainly on the triphenylamine groups, while its lowest unoccupied molecular orbital (LUMO) is centered on the cyanoacrylic acid units (Figure S4 in SI). Thus, photoinduced transitions are likely to produce directional charge transfer states, with electron population around the anchoring groups, which can efficiently interact with the conduction band of TiO$_2$.

Table 1. Optical and Electrochemical Properties of **SCPDT1**

λ_{max}^{a} (nm)	λ_{max}^{b} (nm)	E_{ox}^{c} (V)	HOMO^{d} (eV)	LUMO^{e} (eV)
462^{f}	480	0.44	−5.54	−3.56

^{a} Absorption maxima in solution of acetonitrile. ^{b} Absorption maxima adsorbed on TiO$_2$ film. ^{c} Oxidation potentials with reference to ferrocene (Fc) used as internal standard. ^{d} Absolute energy scale calculated with $E_{HOMO} = -(E_{ox}$ vs Fc/Fc$^+ + 5.1)$. ^{e} $E_{LUMO} = E_{HOMO} + E_{gap}$ ($E_{gap} = 1240/\lambda_{onset}$. = 1.98 eV). ^{f} Molar extinction coefficient = 4.2×10^4 M^{-1} cm^{-1} measured in acetonitrile−toluene (1:1) solution.

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SCPDT1 was self-adsorbed on TiO_2 nanostructured film by an electrode soaking in an absolute ethanol solution of the dye. **SCPDT1** remained on the electrode after several solvent rinses due to the anchoring capability of the two carboxylic acid groups, which are able to form bidentate binding states with TiO_2.[7e,9,18] The absorption spectrum of **SCPDT1** adsorbed onto TiO_2 nanostructured films displays broader and red-shifted bands compared to those in solution, revealing the interaction between the dye and the nanostructured semiconductor oxide. Actually, this effect has been previously observed for related D−A dyes based on the 2,2′-bithiophene unit, and it has been ascribed to the intimate contact between the carboxylate group and the Ti^{4+} ions.[17a]

Differential pulse voltammetry (see SI) was employed to analyze the redox properties of **SCPDT1** and to calculate the energy level of the frontier molecular orbitals (Table 1). Differential pulse voltammograms recorded at the Pt electrode are characterized by two reversible redox waves at a value of $E_{1/2}$ of 0.44 and 0.71 V vs the Ferrocene couple used as the internal standard.[11a,17] Taking into account the optical band gap (1.98 eV) of **SCPDT1**, we calculated the LUMO energy level to be −3.56 eV (absolute scale). A comparison of the energy levels of TiO_2 (−4.0 eV), **SCPDT1**, and the I^-/I_3^- redox couple (−4.85 eV), revealed that both the photoinduced electron transfer from **SCPDT1** to TiO_2 and the reduction of the oxidized dye by the redox couple are energetically favorable processes, an essential prerequisite for the realization of DSSCs.

Figure 2a presents the short circuit photocurrent action spectrum of **SCPDT1**-based DSSCs (constructed as described in SI) in terms of the Incident monochromatic Photon to Current Conversion Efficiency (IPCE%). The IPCE photocurrent response of the photoactive layer closely matched the absorption spectrum of **SCPDT1**. The IPCE spectrum of the devices covered the spectral region ranging from 350 to 700 nm and reached a wide maximum of ∼80% in the 420−560 nm range. Thus, the use of **SCPDT1** dye, holding the 4,4′-spirobi[cyclopenta-[2,1-*b*;3,4-*b*′]dithiophene] core, allowed the construction of DSSCs with a near-panchromatic response, keeping all the spiro conformation advantages.[1,9] Those characteristics allowed solar cells with suitable energy conversion efficiencies to be obtained. Figure 2b shows the current−voltage (*J*−*V*) curve under standard global AM 1.5G solar irradiation. For solar cells based on **SCPDT1**, a short-circuit photocurrent density (J_{SC}) of 12.83 mA/cm^2, an open-circuit voltage (V_{OC}) of 0.69 V, and a fill factor (ff) of 0.68 were obtained, yielding an overall conversion efficiency (η) of 6.02%. These data compare favorably with those obtained using a dye with a similar conjugated

bridge extension, but a 9,9′-spirobifluorene core (J_{SC} = 8.9 mA/cm^2, V_{OC} = 0.63 V, ff = 0.67, η = 3.75%).[9a]
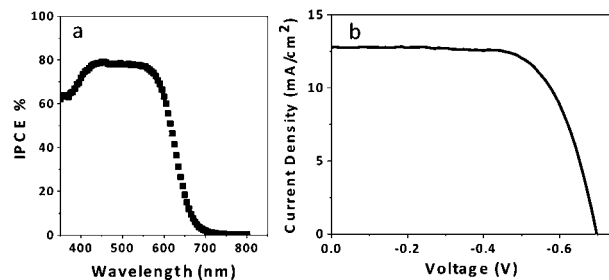
Figure 2. (a) Photocurrent action spectra of **SCPDT1**-based DSSCs. (b) Photocurrent density vs voltage for **SCPDT1**-based DSSCs under AM 1.5 G simulated solar light (100 mW cm^{-2}).

DSSCs assembled with the new spiro D−A dye exhibited very good performance due to the favorable optical and electrochemical characteristics of the photosensitizer. In addition, the cross-shaped rigid structure of **SCPDT1** can possibly help to isolate the photogenerated positive charges (centered on the remote triphenylamine moieties) from the TiO_2 surface, thus reducing the incidence of undesired back electron transfer phenomena.[9a] Another expected positive consequence of the peculiar 3D structure of **SCPDT1** is that both staggered carboxylate groups might act as anchoring units, thereby ensuring the effective interaction of the dye with the TiO_2 coordination sites.[9a]

In summary, we have designed and investigated an unprecedented panchromatic spiro-configured D−A sensitizer, **SCPDT1**, which proved to be a promising candidate for the realization of efficient solar energy conversion DSSCs devices. The synthetic approach disclosed here offers a general and convenient access to 4,4′-spirobi-[cyclopenta[2,1-*b*;3,4-*b*′]dithiophene] derivatives, an almost unexplored class of compounds with great potential in optoelectronics.

Supporting Information Available. Synthesis, characterization, copies of ^{1}H and ^{13}C NMR spectra, spectroscopic and electrochemical analysis, device fabrication, and optimization of solar cells. This material is available free of charge via the Internet at http://pubs.acs.org.

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