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# Assessment of new *gem*-silanediols as suitable sensitizers for dye-sensitized solar cells

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### ABSTRACT

Four novel *gem*-silanediol-containing organic dyes featuring a highly conjugated backbone have been synthesized in order to investigate their potential as active materials for photovoltaics. After spectroscopic characterization, the compounds showing the best light harvesting and electrochemical properties were applied as sensitizers in dye-sensitized solar cells (DSSCs). Interestingly, photovoltaic cells built using the new silanediol dyes showed low power conversion efficiencies ( $\eta$ ), comparable to those obtained with silicon-based sensitizers having simple azobenzene moieties as the light-harvesting units. Such values are mostly due to unsatisfactory photocurrent densities; a computational study suggested that the latter can be justified considering the insufficient degree of charge transfer taking place during photoexcitation of the silicon-containing sensitizers, which is likely to make electron injection into the TiO<sub>2</sub> layer less efficient.

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### 1. Introduction

In recent years, dye-sensitized solar cells (DSSCs) have attracted much attention as efficient and potentially low-cost alternatives to traditional silicon-based photovoltaic cells [1]. Initially, sensitizers employed in such devices have been mostly metallorganic compounds, in particular complexes of ruthenium with bipyridine or terpyridine ligands [2,3]; DSSCs fabricated with such dyes have reached solar-to-electric power conversion efficiencies ( $\eta$ ) exceeding 11% [4]. More recently, a large number of metal-free organic dyes have also been introduced, and the corresponding solar cells have often displayed respectable power conversion efficiencies [5].

In a dye-sensitized solar cell, efficient attachment of the sensitizer to the semiconductor layer (most often constituted by TiO<sub>2</sub>) is required to achieve smooth electron transfer between these two elements. Most of the organic dyes reported so far possess

0022-328X/\$ – see front matter @ 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jorganchem.2012.10.012 cyanoacrylic acid or rhodanine-3-acetic acid fragments as anchoring groups [5,6]; a smaller number of dyes has been reported, which are attached to the semiconductor by other functionalities, such as carboxylate [2], phosphonate [7], sulfonate [8], catechol [9] and pyridine [10] groups.

Recently, a series of simple sensitizers having silicon-based anchoring groups was described by Unno, Hanaya and coworkers [11]. The choice of such anchoring functions was based on the fact that they form very strong bonds with a number of metal oxides, including titania [12], therefore potentially allowing the fabrication of highly stable photovoltaic cells. In those studies, the photovoltaic performances of DSSCs built with dyes **1a–c**, containing one or two azobenzene units, were compared with that of an analogous device fabricated using 4-carboxyazobenzene (**2**) as the sensitizer (Fig. 1).

It was found that the power conversion efficiencies of devices containing compounds **1a**–**c** were higher than that of the cell containing compound **2**, thus suggesting that dyes possessing a silicon anchoring function would yield more efficient solar cells than the corresponding carboxylic acids. However, the azobenzene unit is not an ideal chromophore for photovoltaic applications: first

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Fig. 1. Organic sensitizers 1 and 2, featuring azobenzene units [11].

of all, it has a short conjugation length, which results in absorption maxima just above 300 nm; secondly a large part of the solar energy absorbed by the dye can be lost due to *cis/trans* isomerization around the nitrogen-nitrogen double bond [13], thereby reducing the efficiency of the charge-transfer process toward the semiconductor. The efficiencies of DSSCs fabricated using sensitizers 1a-c and 2 were indeed very low; therefore, a meaningful assessment of the potential of silicon-containing groups as an anchoring moieties for DSSC sensitizers was difficult, since the low efficiency could be attributed to the use of an unsuitable chromophore.

Meanwhile, Grätzel et al. showed [14] that sensitizers containing a trialkoxysilane anchoring group indeed yielded less efficient DSSCs compared to the previously described dye **JK-2** having a cyanoacrylic anchoring function [15]. In particular, lower values of photocurrent were measured, which were attributed to a low density of absorbed siloxanes. This result is in contrast with the findings of Unno et al., who measured comparable absorption densities for compounds **1a–c** and **2** on TiO<sub>2</sub> based on the corresponding UV spectra [11]. Such discrepancy was surprising, given that both groups attribute the attachment of the silicon-bearing dyes on TiO<sub>2</sub> surface to the formation of Si–O–Ti bonds [11,14]. Finally, it should be mentioned that disilanylene polimers carrying silicon anchoring groups were also recently applied as DSSC sensitizers, giving moderate power conversion efficiencies [16].

Prompted by these findings, we decided to independently assess the viability of silanols as sensitizers for efficient and stable DSSCs. To this end, we synthesized a series of novel silanol-containing organic dyes whose structure was based on a previously reported sensitizer and measured the photovoltaic performances of the corresponding solar cells.

The structural model sensitizer was the well-known triphenylamino-thienyl derivative **D5** (Fig. 2) [17,18]. This substance was selected because it had already been shown to yield solar cells of good efficiency and has a rather simple structure which could easily be modified in order to accommodate a silanol anchoring group.

Herein, we describe the synthesis and characterization of compounds S1-4 (Fig. 2). In addition, we will report the results of photovoltaic measurements conducted on the corresponding dyesensitized solar cells, as well as the results of TD-DFT studies that provide a possible explanation of the observed performances.

### 2. Results and discussion

The synthesis of silicon-containing substances **S1** and **S2** was inspired by that of compound **D5**, with a suitable modification in the last step to allow the introduction of the silanediol moiety (Scheme 1).

Aldehyde **3** [19] was first subjected to a Wittig reaction with 2-thienylmethyltriphenylphosphonium chloride (**4**) [20] to afford alkene **5** as a mixture of E/Z diastereoisomers in good yield. A subsequent iodine-catalyzed equilibration yielded compound **5** as single *E* diastereoisomer, in 61% overall yield starting from aldehyde **3**.

Compound **5** was selectively metalated in position 2 of the thiophene ring employing *n*BuLi, and the resulting thienyllithium derivative was reacted with an excess of the appropriate aryl- or alkyltrichlorosilane, to give compounds **S1**–**2** after hydrolysis. Whereas the reaction with phenyltrichlorosilane proceeded smoothly to furnish silanol **S1** in good yield, problems were encountered in the purification of *tert*-butyl derivative **S2**, which was therefore isolated in lower yield.

At this stage, preparation of *gem*-silanediol **6** (Fig. 3) was attempted by reaction of compound **5** with *n*BuLi and tetra-chlorosilane. Unfortunately, such reaction proved unsuccessful.

Access to compound **6** would have been highly interesting due to the presence on its structure of two photoactive systems. The reaction attempted for its preparation was similar to those used for the synthesis of compounds **S1–2**, using tetrachlorosilane in place of an alkyl- or aryltrichlorosilane, but its stoichiometry proved hard to control and a mixture of products was consistently obtained, preventing isolation of compound **6** in pure form.

Compounds **S1**–**2** were found to have absorption maxima below 400 nm, which suggested an insufficient light-harvesting capacity in the visible region (*vide infra*). To overcome this problem, we reasoned that an increase in the conjugation length of the system could have a beneficial effect, causing a red shift in the light absorption of the resulting compounds. Thus, silanols **S3**–**4**, featuring an extra thiophene ring and a further double bond compared to **S1–2**, were prepared (Scheme 2).

Starting from common intermediate **5**, treatment with *n*BuLi in THF at -78 °C followed by quench with *N*,*N*-dimethylformamide and aqueous work-up afforded aldehyde **7** in good yield. The latter compound was once more subjected to a Wittig reaction with phosphonium salt **4** to give olefin **8** as a mixture of diastereoisomers, which were equilibrated to yield compound **8** as single (*E*,*E*) diastereoisomer. Unfortunately, in this case the Wittig reaction/ equilibration sequence proceeded in lower yield compared to preparation of compound **5**, possibly due to the lower reactivity of the highly conjugated aldehyde **7** compared to aldehyde **3** in the previous sequence of reactions.

Finally, compound (*E*,*E*)-**8** was reacted with *n*BuLi and the appropriate aryl- or alkyltrichlorosilane in a manner analogous to compound **5** (see above), to afford silanols **S3**–**4** in moderate yields after quenching with water.

Fig. 4 shows that compounds **S1–4** give rise to two structured absorption bands in the UV and visible regions of the spectrum.



Fig. 2. Structure of the organic dye D5 together with compounds S1-4 prepared in this study.



Scheme 1. Preparation of silicon-containing compounds S1 and S2.

More in detail, silanols **S1–2** have a first band around 302 nm and a second, stronger band below 400 nm, at 377 and 376 nm, respectively, with molar extinction coefficients of  $2.2-2.4 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>. This result indicates that the region where such compounds absorb light is not appreciably influenced by the organic substituent on the silicon atom (Ph vs. *t*Bu). The molar extinction coefficients of **S1–2** are comparable to those of several other organic sensitizers [5], suggesting that silanols with red-shifted absorption could be used for the construction of working DSSCs.

It is widely accepted that a photosensitizer to be employed in dye-sensitized solar cells should be able to absorb light efficiently in the visible and near-infrared region of the solar spectrum (where the photon flux is maximized) in order to give rise to well-performing photovoltaic devices [1]. Clearly, compounds **S1–2** displaying absorption maxima barely within visible wavelengths do not seem to fulfill such requirement. On the contrary, **S3–4** display a first absorption band at around 350 nm and absorption maxima at 425–427 nm, red-shifted of approximately 50 nm compared to **S1–2**, providing a beneficial effect for the efficiency of the resulting solar cells. Moreover, their molar extinction coefficients were much larger than those of the previous compounds, with values in the 3.6–3.7 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup> range.

As far as the emission spectra are concerned, silanols **S1–2** showed maxima at comparable wavelengths of 464–470 nm; once again, compounds **S3–4** displayed a notable red-shift of the corresponding emission, with maxima for both species at 528 nm (Fig. 5). Thus, compounds **S3–4** are characterized by smaller Stokes shifts (4480–4590 cm<sup>-1</sup>) compared to those shown by compounds **S1–2** (5044–5249 cm<sup>-1</sup>). The optical bandgaps of silanols **S1–4** (corresponding to the zero-zero transition energy,  $E_{0-0}$ ) were estimated from the intersection between their normalized absorption and emission spectra, and turned out to be in the 2.60–2.98 eV range.

The optical properties of compounds **S1–4** are summarized in Table 1.

Due to the results of the photochemical measurements, we decided to carry out the subsequent characterization only on those compounds that showed superior light-harvesting properties, namely **S3**–**4**. The ground-state oxidation potentials ( $E_{ox}$ ) of **S3**–**4** were evaluated by means of cyclic voltammetry in CH<sub>2</sub>Cl<sub>2</sub> solution (Fig. 6) [21]. The two compounds have very similar redox



Fig. 3. Compound 6 whose synthesis failed.

behavior. They undergo two close subsequent oxidation processes, the second of which is complicated by a further chemical reaction, as shown by the presence of a third peak in Fig. 6. The first oxidation process, observed at +0.70 V and +0.78 V vs. Ag/AgCl NaCl 3M (corresponding to +0.91 V and +0.99 V vs. NHE) for S3 and S4, respectively, can be assigned to the reversible removal of one electron from the triphenylamine portion of the compounds. This assignment was confirmed by the UV-Vis spectroelectrochemical characterization of S4 (vide infra). The second oxidation (observed at +0.86 V and +0.88 V vs. Ag/AgCl NaCl 3M for S3 and S4, respectively) is, on the contrary, assigned to removal of one electron from the bis-thiophene backbone. The values of the first oxidation potentials are more positive than the  $I^{-}/I_{3}^{-}$  redox potential (+0.4 V vs. NHE), thus assuring dye regeneration by the  $I^{-}/I_{3}^{-}$ redox couple in a DSSC. The electrochemical behavior of **S3–4** was not affected by the nature of the working electrode material (Glassy Carbon, ITO, Au). Considering the optical band gap (2.60–2.61 eV), we calculated the excited state oxidation potential  $(E^*_{ox})$  of the dyes to be -1.70 V and -1.61 V (vs. NHE) for S3 and S4, respectively (Table 1): such values are largely more negative than that of the conduction band of  $TiO_2$  (-0.5 V) and should guarantee smooth electron injection from the dye to the semiconductor. This is a consequence of the relatively large band gap observed for the silanediol-containing compounds, and it indicates that the latter have a higher-lying LUMO compared to most cyanoacrilic-based dyes [5,18]: such difference could help electron injection toward the semiconductor, but is also responsible for a blue-shift of their maximum absorption wavelength (vide supra).

The electrochemical characteristics of compounds **S3–4** are presented in Table 1.

To further characterize the spectroscopic features and the redox behavior of the new silanediol compounds we carried out spectroelectrochemical measurements by observing the UV–Vis spectral changes of compound **S4** upon oxidation in CH<sub>2</sub>Cl<sub>2</sub> solution (Fig. 7).

As previously noted, the UV–Vis spectrum of **S4** shows also in this solvent two structured bands, at 301 and 436 nm, respectively. The first one is probably due to the electronic  $\pi \rightarrow \pi^*$  transition between orbitals centered on the triphenylamine fragment, while the second one could be caused by intermolecular charge transfer between the triphenylamine and the thiophene moieties; such an absorption pattern has been previously described for organic DSSC sensitizers [22]. As shown in Fig. 7, removal of the first electron from S4 alters its UV-Vis spectrum and, predictably, both these bands decrease. At the same time, a couple of bands appear at lower energies (centered at 688 and 772 nm) and one isosbestic point is maintained at 490 nm, indicating the stability of the  $S4^+$  radical cation. The appearance of this group of bands, due to the HOMO/  $(HOMO-1) \rightarrow$  SOMO transitions in triarylamine radical cations, is a known phenomenon [23,24] and confirms our interpretation of the redox behavior.



Scheme 2. Preparation of silicon-containing compounds S3 and S4.

The spectroscopic and electrochemical data reported above suggest that silanediols **S3**–**4** are compounds suitable to be used as photosensitizers in dye-sensitized solar cells. Accordingly, we proceeded to build a few devices incorporating **S3** and **S4** as the photoactive components. The power conversion efficiency of the cells was measured under AM 1.5 G simulated solar irradiation at room temperature, using a  $I^-/I_3^-$  electrolyte (see Section 5 for details). The corresponding *J*–*V* curves are displayed in Fig. 8, while the relevant photovoltaic parameters are summarized in Table 2.

As can be seen from the table, both dyes **S3** and **S4** yielded working solar cells; compound **S3** showed superior photovoltaic properties compared to **S4**, which resulted in a higher power conversion efficiency. In both cases, however, efficiencies were low compared to those given by typical organic sensitizers having cyanoacrylic anchoring groups, mostly because of much smaller short-circuit currents (see for example **D5** in Table 2).

Interestingly, the trialkoxysilane dyes reported by Grätzel, which have a similar backbone, gave higher efficiencies than those obtained with dyes **S3–4** [14], the difference being mostly due to

better  $J_{sc}$  values; indeed, the values obtained in this study are much closer to those reported for azobenzene dyes 1a-c in the works published by Unno et al. [11].

The low photocurrent densities could be due to an insufficient absorption of the dyes on the TiO<sub>2</sub> surface. To verify this possibility, we measured the density of absorbed dye **S3** on titanium dioxide after a typical sensitization procedure (see Section 5 for details), and found a value of approx.  $5.0 \times 10^{-8}$  mol cm<sup>-2</sup>, which is indeed relatively low compared to values found for most organic dyes. On the other hand, such value is quite close to those reported by Grätzel for his trialkoxysilane dyes ( $6.2-7.3 \times 10^{-8}$  mol cm<sup>-2</sup>) [14], thereby suggesting that a low amount of absorbed dye is not responsible for the different performances of compounds **S3–4**.

### 3. Computational study

To help explaining the present results, we carried out density functional theory (DFT) calculations using the *Gaussian09* software package [25], in an attempt to gather some information on the electronic structure of the sensitizers.



Fig. 4. UV–Vis absorption spectra of compounds S1–4 in MeOH solution. Concentrations: S1–2, 1.12  $\times$  10<sup>-4</sup> M; S3–4, 5.6  $\times$  10<sup>-5</sup> M.



**Fig. 5.** Normalized emission spectra of compounds **S1–4** in MeOH solution (irradiation at maximum absorption wavelength).

Table	1
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Summary of the optical and electrochemical properties of compounds S1-4.

Compound	$\lambda_{max}(abs) (nm)^a$	$\varepsilon (\mathrm{M}^{-1} \mathrm{~cm}^{-1})^{\mathrm{a}}$	$\lambda_{max}(em) (nm)$	$E_{0-0} (eV)^{b}$	$E_{\rm ox}$ (V) <sup>c</sup>	$E^*_{ox}(V)^c$
S1	377	22,300	470	2.95		
S2	376	24,200	464	2.98		
S3	425	36,900	528	2.61	+0.91 (+0.70)	-1.70
S4	427	37,000	528	2.60	+0.99(+0.78)	-1.61

<sup>a</sup> UV–Vis spectra were recorded in MeOH at the following concentrations: **S1–2**,  $1.12 \times 10^{-4}$  M; **S3–4**,  $5.6 \times 10^{-5}$  M.

<sup>b</sup> Estimated from the intersection of the normalized absorption and emission spectra.

<sup>c</sup> Potentials vs. NHE (potentials vs. Ag/AgCl NaCl 3M are given in parentheses).

First of all, the ground-state geometries of compounds **S1** and **S3** were optimized *in vacuo* at the B3LYP/6-31G\* level. Subsequently, we performed calculations at the B3LYP and MPW1K/6-31G\* level on the same compounds, both in the gas phase and in acetonitrile solution, in order to determine the frontier orbital energies and the corresponding electronic distribution.

The results are reported in Table 3. It can be observed that the HOMO–LUMO energy gap computed for compound **S1** is larger than that relative to compound **S3** both in vacuum and in acetonitrile (3.25 eV vs. 2.69 eV and 3.16 eV vs. 2.63 eV, respectively); this result is in agreement with the relative magnitude of the optical band gap values derived from spectroscopic measurements (*vide supra*), and can be explained in terms of the more extended conjugation present on the molecular scaffold of **S3** compared to **S1**.

As far as the electronic distribution is concerned (Fig. 9), it appears that, in line with our expectations, the HOMO of both



**Fig. 6.** Semiderivative deconvoluted cyclic voltammograms recorded at a platinum electrode of a CH<sub>2</sub>Cl<sub>2</sub> solution of **S3** (a, 2.0 mM) and **S4** (b, 2.8 mM). [NBu<sub>4</sub>][PF<sub>6</sub>] (0.2 M) was used as the supporting electrolyte. Scan rates: 0.2 V s<sup>-1</sup> (solid line), 0.02 V s<sup>-1</sup> (dashed line).

compounds is mainly localized on the conjugated scaffold of the molecules, with a sizeable contribution coming from the terminal diphenylamino-donor groups. In the case of the LUMO, however, the electron density is also substantially found on the middle part of the two molecular structures; despite the fact that the coefficients seem to be slightly larger on the terminal thiophene rings, the contribution arising from the silanol oxygen atoms looks negligible.

TD-DFT computations conducted at the MPW1K/6-31G\* level both *in vacuo* and in acetonitrile solution, indicated that the excitation process for both dyes is mainly due to the HOMO  $\rightarrow$  LUMO transition, accounting for approx. 80% of the total, and that the oscillator strength for dye S3 is much larger than that of dye S1; this result is consistent with the molar extinction coefficients measured for both substances and reported in Table 1. The values obtained for the maximum absorption wavelengths were 364 (380) nm for S1 and 437 (457) nm for S3, in vacuo (in solution), in good agreement with the experimental values reported in Table 1, 377 and 425 nm for S1 and S3, respectively.

Based on these findings, the actual charge-transfer nature of the photoexcitation process appears questionable. As a consequence, efficient electronic communication between the dye molecules and the semiconductor surface could be hampered; the low efficiency of the electron injection process could therefore serve as an explanation of the poor power conversion efficiencies observed for the cells built using sensitizers **S3–4**.

### 4. Conclusions

Despite the remarkable results obtained so far with fully organic compounds as light-harvesting materials for dye-sensitized solar cells [5], the search for new and more efficient sensitizers is still a very active field of research. In particular, optimization of the anchoring moiety of the dyes could give access to more powerful and, above all, more stable photovoltaic devices. From this point of view, the silanediol function could represent a promising



Fig. 7. UV–Vis spectra recorded upon stepwise oxidation of S4 in an OTTLE cell in CH<sub>2</sub>Cl<sub>2</sub> solution; supporting electrolyte: [NBu<sub>4</sub>][PF<sub>6</sub>] (0.2 M).



**Fig. 8.** *J*–*V* characteristics of DSSCs sensitized with compounds **S3** ( $\blacklozenge$ ) and **S4** ( $\bigcirc$ ).

alternative to the usual cyanoacrylic acid functional group, due to the strong bonds it forms with metal oxides, and in particular with titania.

In this work, we synthesized a series of novel silanol-bearing compounds **S1–4**, inspired by the molecular structure of organic dye **D5**, and assessed their optical and photoelectrochemical properties, as well as their capacity to serve as photoactive materials for DSSCs.

Solar cells built with dyes **S3–4** had power conversion efficiencies in the 0.2–0.3% range, with **S3** being the most effective sensitizer. Such values are relatively close to those previously obtained with silicon-containing sensitizers having a simple azobenzene group as their light-harvesting unit [11]. Therefore, attachment of an extended organic chromophore, displaying a more intense and red-shifted absorption spectrum, to the *gem*-silanediol moiety does not seem to improve the photovoltaic properties of the resulting sensitizers.

Computational studies suggested that the photoexcitation process in compound **S3** happens with a smaller degree of charge transfer compared to a cyanoacrylic dye, which should reduce the efficiency of the electron injection process from the dye to the nanocrystalline semiconductor, thereby possibly explaining the low conversion efficiencies observed with the photosensitizers described in the present study.

As a consequence, we conclude that the *gem*-silanediol moiety does not appear to be a suitable replacement for the cyanoacrylic anchoring group in DSSC sensitizers. In this context, we would like to point out that the primary objective of the study was not to obtain cells of very high photovoltaic efficiency, but rather to verify the previous findings using rationally designed compounds. However, the promising results obtained with trialkoxysilane sensitizers and the possibility to form strong bonds with titanium dioxide should continue to foster research aimed at finding efficient silicon-containing photosensitizers.

#### Table 2

Summary of the photovoltaic parameters of the cells built using **S3–4** dyes compared with a standard organic dye (**D5**).

Compound <sup>a</sup>	$J_{\rm sc}~({\rm mA/cm^2})$	$V_{\rm oc}\left({\rm V}\right)$	ff	η (%)
S3	0.95	0.48	0.62	0.3
S4	0.66	0.43	0.58	0.2
D5	9.91	0.61	0.71	4.3

 $^a$  J–V curves measured under AM 1.5 G simulated solar irradiation (100 mW cm $^{-2}$ ) at room temperature; film thickness approx. 10  $\mu$ m; active area 0.2 cm<sup>2</sup>.

### Table 3

Energies of the lowest unoccupied and highest occupied Kohn–Sham orbitals of compounds **S1** and **S3** in vacuum and in CH<sub>3</sub>CN solution with the B3LYP functional. Energy in eV.

	S1		S3	
	Vac	AcN	Vac	AcN
L+2	-0.34	-0.36	-0.54	-0.44
L+1	-0.58	-0.50	-0.95	-1.05
L	-1.50	-1.67	-1.94	-2.09
Н	-4.75	-4.83	-4.63	-4.72
H – 1	-5.62	-5.76	-5.34	-5.34
H – 2	-6.58	-6.71	-6.12	-6.25

### 5. Materials and methods

### 5.1. General synthetic remarks

All air-sensitive reactions were performed using Schlenk techniques [26]. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl radical,  $CH_2Cl_2$  and *N*,*N*-dimethylformamide were stored under nitrogen over 4 Å molecular sieves. Petroleum ether was the 40–60 °C boiling fraction. Compound **D5** [17], aldehyde **3** [19] and 2-thienylmethyltriphenylphosphonium chloride (**4**) [20] were prepared according to literature methods, while all the other chemicals employed were commercially available and used as received. Thin layer chromatography was carried out on aluminum-supported Merck 60 F254 plates; flash column chromatography [27] was performed using Merck Kieselgel 60 (300–400 mesh) as the stationary phase.

<sup>1</sup>H-NMR spectra were recorded at 200, 300, or 400 MHz, and <sup>13</sup>C-NMR spectra were recorded at 50.3, 75.5, or 100.6 MHz, respectively, on *Varian* Gemini, *Varian* Mercury and *Bruker* Avance series instruments. Chemical shifts were referenced to the residual solvent peak (CHCl<sub>3</sub>,  $\delta$  7.26 ppm for <sup>1</sup>H-NMR and  $\delta$  77.0 ppm for <sup>13</sup>C-NMR). ESI-MS spectra were obtained by direct infusion using a *Thermo Scientific* LCQ-FLEET instrument and are reported in the form *m/z* (intensity relative to base = 100). IR spectra were recorded using a *Perkin–Elmer Spectrum BX* FT-IR spectrometer and are reported in cm<sup>-1</sup>. UV–Vis spectra were recorded with a *Varian Cary* 400 spectrometer, and fluorescence spectra were recorded with a *Varian Eclipse* instrument, irradiating the sample at the wavelength corresponding to maximum absorption in the UV spectrum.

### 5.2. (E)-2-[2-(4-diphenylaminophenyl)vinyl]thiophene (5)

In a round-bottom two-necked flask under an inert atmosphere of nitrogen was introduced phosphonium salt **4** (2.0 g, 5.1 mmol, 1.4 eq.), which was suspended in anhydrous THF (36 mL). The suspension was cooled down to -78 °C and potassium *tert*-butoxide (0.49 g, 4.4 mmol, 1.2 eq.) was then added; the resulting mixture was stirred at -78 °C for 1 h, after which aldehyde **3** (1.18 g, 4.3 mmol, 1.0 eq.) was added. The reaction mixture was warmed to rt and stirred overnight. After a TLC check (petroleum ether/EtOAc 50:1) had shown the disappearance of the starting material, the reaction was quenched with water. The two layers were separated, and the aqueous layer was washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered through a short pad of silica, eluting with CH<sub>2</sub>Cl<sub>2</sub>, affording 1.5 g (4.24 mmol) of crude olefin **5** as a mixture of *E* and *Z* diastereoisomers.

Crude compound **5** was dissolved in CHCl<sub>3</sub> (68 mL), and iodine (0.11 g, 0.43 mmol, 0.1 eq.) was added at rt. The resulting red-brown mixture was stirred overnight at rt. The organic layer was then washed with satd. aq. sodium metabisulphite (50 mL) and water (50 mL); the aqueous phase was then extracted with CHCl<sub>3</sub>.



Fig. 9. Wave function plots for compounds S1 and S3 in CH<sub>3</sub>CN solution.

The combined organic layers were dried over  $Na_2SO_4$  and filtered to give the crude product as a yellow oil. Purification by flash column chromatography (petroleum ether/EtOAc 50:1) afforded pure compound (*E*)-**5** as a yellow solid (0.92 g, 2.6 mmol, 61%).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 6.88 (d, J = 15.9 Hz, 1H), 6.98–7.01 (m, 6H), 7.10–7.13 (m, 4H), 7.16–7.18 (m, 2H;), 7.24–7.30 (m, 4H), 7.33–7.35 (m, 2H). <sup>13</sup>C-NMR (50.3 MHz, CDCl<sub>3</sub>): δ (ppm) 120.1, 123.0, 123.4, 123.8, 124.4, 125.5, 127.1, 127.5, 127.8, 129.2, 131.0, 143.2, 147.2, 147.5. ESI-MS: m/z 354 [M + H]<sup>+</sup>.

# 5.3. (E)-[2-[2-(4-diphenylaminophenyl)vinyl]thienyl](phenyl) silandiol (**S1**)

In a Schlenk tube under an inert atmosphere of nitrogen was placed nBuLi (sol. 1.6 M in hexane, 0.2 mL, 19 mg, 0.32 mmol, 1.6 eq.). Hexane was partially removed under vacuum and the concentrated solution was cooled down to -78 °C. Anhydrous THF (5 mL) was then added, followed by olefin 5 (70 mg, 0.20 mmol, 1.0 eq.), dissolved in anhydrous THF (5 mL). The resulting solution was stirred at -78 °C for 1 h and then at 0 °C for 0.5 h, during which it became dark. Phenyltrichlorosilane (0.064 mL, 0.40 mmol, 2.0 eq.) was subsequently added; the reaction mixture was warmed to rt and stirred overnight. The reaction was then checked by TLC (petroleum ether/EtOAc 3:1) and quenched with water (10 mL). The solution was diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and the layers were separated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL); the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and filtered to afford the crude product. The latter was purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane followed by washing with pentane to give silanol S1 as a brown amorphous solid (63 mg, 0.13 mmol, 64%). <sup>1</sup>H-NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  (ppm) 6.86–6.90 (m, 4H), 6.96–7.00 (m, 6H), 7.07-7.21 (m, 6H), 7.27-7.30 (m, 2H), 7.32-7.38 (m, 3H), 7.71–7.74 (m, 2H). <sup>13</sup>C-NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  (ppm) 121.0, 124.2, 124.3, 125.6, 127.8, 128.3, 128.7, 129.7, 130.4, 131.1, 132.4, 135.2, 135.6, 137.2, 138.0, 148.7, 148.8, 150.6. ESI-MS: *m*/*z* 492 [M + H]<sup>+</sup>.

# 5.4. (E)-[2-(2-(4-diphenylaminophenyl)vinyl)thienyl](tert-butyl) silandiol (**S2**)

The title compound was prepared according to a procedure analogous to that used for the synthesis of compound **S1** (see above), with *tert*-butyltrichlorosilane as the electrophile. The following compounds and quantities were used: *n*BuLi (sol. 1.6 M in hexane, 0.2 mL, 19 mg, 0.32 mmol, 1.6 eq.), olefin **5** (74 mg, 0.21 mmol,

1.0 eq.), *tert*-butyltrichlorosilane (80 mg, 0.42 mmol, 2.0 eq.), anhydrous THF (10 mL total). After work-up, drying and filtration, crude product **S2** was obtained. The latter was purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane followed by flash column chromatography (petroleum ether/EtOAc 3:1) to afford pure silanol **S2** as a brown amorphous solid (13 mg, 0.03 mmol, 13%). <sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>):  $\delta$  (ppm) 1.45 (s, 9H), 6.95 (d, *J* = 15.9 Hz, 1H), 7.01–7.07 (m, 4H), 7.09–7.14 (m, 4H), 7.15–7.29 (m, 7H), 7.31–7.35 (m, 2H). <sup>13</sup>C-NMR (50.3 MHz; CDCl<sub>3</sub>):  $\delta$  (ppm) 25.2, 29.5, 119.2, 122.9, 123.1, 124.4, 124.5, 124.7, 126.3, 127.0, 129.1, 130.5, 137.0, 147.1, 147.2, 149.3. ESI-MS: *m/z* 472 [M + H]<sup>+</sup>.

### 5.5. (E)-5-[2-(4-diphenylaminophenyl)vinyl]thiophen-2-al (7)

In a Schlenk tube under an inert atmosphere of nitrogen was placed nBuLi (sol. 1.6 M in hexane, 3.9 mL, 0.40 g, 6.26 mmol, 2.0 eq.). Hexane was partially removed under vacuum and the concentrated solution was cooled down to -78 °C. Anhydrous THF (20 mL) was then added, followed by compound 5 (1.14 g, 3.23 mmol, 1.0 eq.), dissolved in anhydrous THF (12 mL). The resulting solution was stirred at -78 °C for 1 h and then at 0 °C for 0.5 h, during which it became dark. N,N-dimethylformamide (1.18 g, 16.1 mmol, 5.0 eq.) was added, and the resulting mixture was warmed to rt and stirred overnight. The reaction was then checked by TLC (petroleum ether/EtOAc 30:1) and guenched with 10% aq. HCl (100 mL). The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>  $(3 \times 50 \text{ mL})$ . The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum to give the crude reaction product. The latter was purified by flash column chromatography (gradient: petroleum ether/EtOAc 30:1 to 3:1) to afford pure aldehyde 7 as a yellow solid (1.07 g, 2.81 mmol, 87%). <sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>): δ (ppm) 7.01–7.14 (m, 13H), 7.25–7.38 (m, 4H), 7.64 (d, *J* = 6.3 Hz, 1H), 9.83 (s, 1H).

The analytical data are in agreement with those reported in the literature [18].

# 5.6. (E,E)-2-[((5-(4-diphenylaminophenyl)vinyl)thien-2-yl)vinyl] thiophene (**8**)

The title compound was prepared according to a procedure analogous to that used for the synthesis of compound **5** (see above), employing aldehyde **7** instead of aldehyde **3**. The following compounds and quantities were used: aldehyde **7** (1.07 g, 2.81 mmol, 1.0 eq.), 2-thienylmethyltriphenylphosphonium chloride (**4**, 1.53 g, 3.88 mmol, 1.38 eq.), potassium *tert*-butoxide (0.41 g, 3.65 mmol, 1.3 eq.), anhydrous THF (total 140 mL). After work-up, drying and filtration, crude product **10** was obtained as a mixture of diastereoisomers (1.22 g, 2.65 mmol). The latter was treated with iodine (0.071 g, 0.028 mmol, 0.1 eq.) in CHCl<sub>3</sub> (40 mL) according to the same procedure reported previously for olefin **5** (see above). After work-up, the crude product was purified by flash column chromatography (petroleum ether/EtOAc 50:1), to give compound (*E*,*E*)-**8** as a yellow/brown solid (0.61 g, 1.32 mmol, 47%). <sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>):  $\delta$  (ppm) 6.84 (d, *J* = 15.6 Hz, 1H), 6.88–6.91 (m, 2H), 6.98–7.07 (m, 9H), 7.09–7.13 (m, 4H), 7.18 (d, *J* = 4.8 Hz, 1H), 7.23–7.29 (m, 4H), 7.32 (d, *J* = 8.8 Hz, 2H). <sup>13</sup>C-NMR (50.3 MHz; CDCl<sub>3</sub>):  $\delta$  (ppm) 120.1, 121.3, 121.5, 123.1, 123.3, 124.3, 124.5, 126.0, 126.5, 127.0, 127.1, 127.6, 128.1, 129.2, 130.9, 140.8, 142.2, 142.4, 147.40, 147.44. ESI-MS: *m/z* 462 [M + H]<sup>+</sup>.

# 5.7. (E,E)-[2-(((5-(4-diphenylaminophenyl)vinyl)thien-2-yl)vinyl) thien-2-yl](phenyl)silandiol (**S3**)

The title compound was prepared according to a procedure analogous to that used for the synthesis of compound S1 (see above), employing compound 8 as the starting material instead of 5. The following compounds and quantities were used: nBuLi (sol. 1.6 M in hexane, 0.06 mL, 6.1 mg, 0.10 mmol, 1.5 eq.), (E,E)-8 (30 mg, 0.065 mmol, 1.0 eq.), phenyltrichlorosilane (28 mg, 0.13 mmol, 2.0 eq.), anhydrous THF (total 4 mL). After work-up, drying and filtration, crude product **S3** was obtained. The latter was purified by precipitation from Et<sub>2</sub>O/pentane to afford pure silanol **S3** as a brown amorphous solid (14 mg, 0.024 mmol, 37%). <sup>1</sup>H-NMR (400 MHz;  $CDCl_3$ ):  $\delta$  (ppm) 3.35 (bs, 2H), 6.84–6.90 (m, 2H), 6.96–7.15 (m, 12H), 7.25–7.35 (m, 8H), 7.38–7.47 (m, 3H), 7.70–7.75 (m, 2H). <sup>13</sup>C-NMR (100 MHz; CDCl<sub>3</sub>): δ (ppm) 120.2, 120.8, 120.9, 123.0, 123.3, 123.5, 124.8, 126.6, 126.7, 127.2, 127.4, 127.8, 128.1, 128.5, 129.4, 129.6, 130.9, 131.1, 134.4, 137.9, 140.8, 142.9, 147.6, 149.7. IR (neat)  $\nu = 3406, 3068,$ 2924, 1650, 1589, 1508, 1492, 1428, 1328, 1280, 1124, 1073 cm<sup>-1</sup>. ESI-MS: m/z 598 [M – H]<sup>–</sup> (negative channel).

# 5.8. (E,E)-[2-(((5-(4-diphenylaminophenyl)vinyl)thien-2-yl)vinyl) thien-2-yl](tert-butyl)silandiol (**S4**)

The title compound was prepared according to a procedure analogous to that used for the synthesis of compound S1 (see above), employing compound 8 as the starting material instead of 5, and tert-butyltrichlorosilane as the electrophile instead of phenyltrichlorosilane. The following compounds and quantities were used: nBuLi (sol. 1.6 M in hexane, 0.09 mL, 9.3 mg, 0.14 mmol, 1.5 eq.), (*E*,*E*)-8 (43 mg, 0.093 mmol, 1.0 eq.), *tert*-butyltrichlorosilane (35 mg, 0.19 mmol, 2.0 eq.), anhydrous THF (total 5.5 mL). After work-up, drying and filtration, crude product S4 was obtained. The latter was purified by flash column chromatography (petroleum ether/ EtOAc 3:1) to afford pure silanol S4 as a brown amorphous solid (16 mg, 0.028 mmol, 30%). <sup>1</sup>H-NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  (ppm) 1.04 (s, 9H), 6.84 (d, I = 16.0 Hz, 1H), 6.88–6.91 (m, 2H), 7.02–7.07 (m, 7H), 7.10–7.12 (m, 5H), 7.24–7.28 (m, 6H), 7.32 (dd, J = 8.1 Hz, J = 3.4 Hz, 1H). <sup>13</sup>C-NMR (100 MHz; CDCl<sub>3</sub>):  $\delta$  (ppm) 25.7, 29.8, 120.2, 120.8, 122.9, 123.3, 123.5, 124.7, 126.7, 127.2, 127.4, 127.7, 128.5, 129.4, 131.0, 131.7, 137.5, 137.6, 140.8, 142.8, 147.6, 149.0. IR (neat)  $\nu = 3416$ , 3058, 2951, 2927, 2854, 1651, 1590, 1507, 1493, 1329, 1281, 1175, 1072 cm<sup>-1</sup>. ESI-MS: m/z 580 [M + H]<sup>+</sup>.

### 5.9. Electrochemical and spectroelectrochemical measurements

Electrochemical measurements were performed in a dichloromethane solution containing [NBu<sub>4</sub>][PF<sub>6</sub>] 0.2 M as the supporting electrolyte. Anhydrous 99.9% dichloromethane was obtained from Aldrich. Electrochemical grade [NBu<sub>4</sub>][PF<sub>6</sub>] was purchased from Fluka and used as received. Cyclic voltammetry was performed in a three-electrode cell containing a platinum working electrode, an Ag/AgCl NaCl (3M) and a platinum auxiliary electrode. All the potential values are referred to the Ag/AgCl electrode. Under the present experimental conditions, the one-electron oxidation of ferrocene occurs at  $E^{\circ\prime} = +0.42$  V. UV–Vis spectroelectrochemical measurements were carried out using a *Perkin–Elmer* Lambda 2 UV–Vis spectrophotometer and a Optically Transparent Thin Laver spectroelectrochemical (OTTLE) cell in guartz glass with an optical path-length of 1 mm, equipped with a Pt-minigrid working electrode, a Pt auxiliary electrode and an Ag/AgCl NaCl (3M) reference electrode. A nitrogen-saturated CH<sub>2</sub>Cl<sub>2</sub> solution of the compound under study was used with [NBu<sub>4</sub>][PF<sub>6</sub>] (0.2 M) as the supporting electrolyte. The in situ spectroelectrochemistry has been recorded by collecting spectra in the spectral window 250–1000 nm during the stepwise oxidation of the compound ( $E_i = +0.55 \text{ V}, \Delta E = 50 \text{ mV},$  $\Delta t = 1$  min). A BAS 100A electrochemical analyser was used as the polarising unit during all the experiments.

### 5.10. Solar cells fabrication and characterization

FTO glass (TEC-15/2.2 mm thickness, Solaronix) was used for transparent conducting electrodes. The substrate was first cleaned in an ultrasonic bath using a detergent solution, followed by acetone and ethanol (each step 15 min long). The FTO glass plates were immersed into a 40 mM aqueous TiCl<sub>4</sub> solution at 70 °C for 30 min and washed with water and ethanol. Dyesol 18NR-AO TiO<sub>2</sub> paste was spread on the FTO glass plates by doctor blading. The TiO<sub>2</sub> coated electrodes (thickness approx. 10  $\mu$ m, active area 0.2 cm<sup>2</sup>) were gradually heated under air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and 500 °C for 15 min. After the sintering process, the TiO<sub>2</sub> film was treated with 40 mM TiCl<sub>4</sub> solution, rinsed with water and ethanol. The electrodes were heated at 500 °C for 30 min and after cooling (80 °C) were immersed into sensitizing baths (anhydrous THF solutions of the S3/S4 dyes in 0.7 mM concentration). The sensitization process was conducted at room temperature for 4 h and then at 50 °C for further 18 h.

Counter electrodes were prepared by coating a pre-drilled FTO plate (TEC-15/2.2 mm thickness, Solaronix) with a drop of  $H_2PtCl_6$  solution (2 mg of Pt in 1 mL of ethanol) and heating at 400 °C for 15 min. The TiO<sub>2</sub> sensitized photoanode and Pt counter electrode were assembled into a sealed sandwich-type cell by a hot-melt ionomer film (Surlyn, 25  $\mu$ m thickness, Dyesol).

The cells were vacuum-filled with a few drops of lolitech ES-0004 HP electrolyte, containing 1-butyl-3-methylimidiazolium iodide, iodine, guanidinium thiocyanate and *tert*-butylpyridine in a mixture of valeronitrile and acetonitrile, with 0.1 M LiI added. Then, the hole drilled on the back of the counter electrode was sealed by using an additional Surlyn patch and a cover glass and finally a conductive Ag-based paint was deposed at the electrical contacts.

Photovoltaic measurements were recorded by means of an AM 1.5 solar simulator equipped with a Xenon lamp (*LOT-ORIEL* LS 0106). The power of incoming radiation, set at 100 mW/cm<sup>2</sup>, was checked by a piranometer. J-V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a *Keithley* model 2400 digital source-meter, under the control of dedicated LabTracer 2.0 software. A black shading mask was employed to avoid overestimation of the measured parameters.

### 5.11. Measurement of the density of absorbed dye on TiO<sub>2</sub>

A nanocrystalline  $TiO_2$  electrode (surface area 0.88 cm<sup>2</sup>) similar to those used for the photovoltaic measurements (see Section 5.10)

was immersed in a  $7.0 \times 10^{-4}$  M solution of dye **S3** in THF at 50 °C for 16 h. The stained dark yellow electrode was removed from the solution, dried under a stream of nitrogen and immersed in 6 mL of a 0.01 M KOH solution in MeOH/THF 2:1 at rt for 5 h; after this time full discoloration of the electrode was observed. The absorbance of the resulting yellow solution was measured by UV–Vis spectroscopy and compared to that of a standard  $5.0 \times 10^{-5}$  M solution of compound **S3** in the same solvent/base mixture. The amount of dye present in the unknown solution was calculated and divided by the electrode surface area, yielding a density value of approximately  $5.0 \times 10^{-8}$  mol cm<sup>-2</sup>.

### 5.12. Computational studies

Geometry optimizations of compounds **S1–S3** were performed in vacuo using the B3LYP functional, with a 6-31G\* basis set using the Gaussian09 (G09) program package.

TD-DFT calculations were performed using the Gaussian03 (G03) program package, in vacuo and in  $CH_3CN$  solution, with both the B3LYP and MPW1K functionals and 6-31G<sup>\*</sup> basis set.

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