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Graphical Abstract



Molecular Engineering of Largely π-Extended Metal-Free Sensitizers Containing Benzothiadiazole Units: Approaching 10% Efficiency Dye-Sensitized Solar Cells Using Iodine-Based Electrolytes

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Abstract

Based on the structural motif of a robust organic dye, new largely π -extended organic sensitizers for dye-sensitized solar cells (DSSCs) have been designed to optimize the interactions between the dye/TiO₂ layer and the redox electrolyte. The molecular tailoring was performed by *i*) positioning an alkyl chain onto the π -spacer and *ii*) increasing the bulkiness of the electron-donor. A deep theoretical investigation reveals that the main electronic transitions of the three dyes own only a weak charge-transfer character. Notwithstanding these unusual photo-excitation dynamics experimentally supported by solvatochromism, impressive photovoltaic performances are obtained

for the three sensitizers, reaching, power conversion efficiencies up to 9.8% under 1.0 sun illumination, that were remarkably higher than those shown by N719 standard. This result represents one of the highest performances exhibited by fully organic sensitizers employing the Γ /I₃⁻ redox shuttle.

Keywords D–A– π –A sensitizer, dye-sensitized solar cell, density functional theory, iodine-based electrolyte.

Introduction

The prospected low manufacturing cost and potential building integration of dye-sensitized solar cells (DSSCs) continue to fuel a vivid research effort mainly devoted to the dye optimization [1]. The state-of-the-art of DSSC efficiencies has until recently been a prerogative of ruthenium-based complexes (~11%) [2] and zinc-porphyrin sensitizers (~13%) [3]. Although the vast majority of highly performing fully-organic sensitizers currently exhibits lower performances (~10%) [4], a conspicuous share of the DSSC scientific community remains intrigued by the molecular engineering potential of metal-free dyes, also considering that the use of a low-abundance metal such as ruthenium as well as the many low-yielding steps needed to obtain suitably functionalized porphyrins might jeopardize the perspective of full-scale DSSC mass production. The great efforts aimed at unravelling the potential of fully organic sensitizers has been recently realised in the obtainment of devices with outstanding efficiencies (up to 12.5%) [5], sustaining the research for more and better performing organic dyes.

For years, the molecular design of efficient sensitizers has been dominated by the rule of putting into conjugation an electron-donating and electron-accepting unit (the latter suitably

designed to act as the anchoring group for the inorganic semiconductor) via an electron-rich π -segment (namely the D- π -A architecture) [6]. The consequent "push-pull" configuration determines the photo-induced shift of the electron density towards the anchoring region bound on the inorganic semiconductor, thereby promoting the electron transfer step [7]. The molecular engineering of the π -bridge has been mainly devoted to the amplification of the light-harvesting properties of the corresponding sensitizers; however, a mere conjugation extension of the chromophoric core was proven as detrimental for device performance [8]. Recently, the incorporation of a further electron-withdrawing unit within the π -bridge (leading to a D-A- π -A architecture) has opened new routes for improving the lightharvesting and stability of the corresponding organic sensitizers [9]. However, placing an electron-deficient aromatic unit within the π -bridge leads to structure-property relationships that cannot be trivially anticipated. By gathering electron density at the excited state of the corresponding D–A– π –A sensitizer, the introduction of a further electron-withdrawing system within the π -spacer could indeed prevent an efficient electron transfer onto the TiO₂ surface [10]. Consequently, the position of the electron-accepting aromatic unit with respect to the anchoring moiety as well as the introduction of functional groups causing distortion of the chromophore backbone have to be accurately pondered when drawing the "molecular blueprint" of a D–A– π –A sensitizer. Our role in perfectioning the D–A– π –A sensitizers has mainly been focused on the π -bridge extension as well as on the judicious selection of lowenvironmental impact structures and synthetic strategies [11], in the awareness that even minor structural modification can exert a significant influence on the performance of a selected class of organic dyes.

In this contribution, the properties and the photovoltaic performances of new D–A– π –A fully organic sensitizers (G4 and G5, Figure 1) have been investigated. These dyes have been assembled on the basis of the structural motif characterizing a robust organic dye (G3), that achieved high power conversion efficiency (8.6%) and exhibited an excellent stability

during device operation [11a]. The new sensitizers were conceived to gain a control at the interface between the dye/TiO₂ layer and the redox electrolyte, aiming at enhancing the corresponding device photocurrent and photovoltage. The molecular tailoring of the G3 scaffold was consequently carried out by suitable positioning an alkyl chain onto the π -spacer (G4 *vs* G3) and by increasing the bulkiness of the electron-donating unit (G5 *vs* G4) extending its conjugation. Remarkable power conversion efficiencies (PCE) up to 9.8% were achieved by G5 (the best of the series) using iodine-based electrolytes; the obtained PCE were found to be higher than those shown by traditional N719 standard dye formulations [12].



Figure 1. Chemical structures of G3, G4 and G5.

Results and discussion

Synthesis and characterization

Differently from the previously reported synthesis of G3, which could be accomplished by C-H activation reactions [11a], the syntheses of G4 and G5 posed additional complications due to the unsymmetrical placement of the n-hexyl functionality with respect to the benzothiadiazole core (Scheme 1). Concerning the electron-donating building block, 4-

(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*,*N*- bis((2-ethylhexyloxy)phen-4-yl)aniline it was obtained following a literature procedure [11a]. Conversely, the preparation of the electron-donating unit of G5 started with the reaction of bromo-triphenylamine with two equivalents of N-iodo-succinimide (NIS) to afford the diiodo-derivative 1. A Suzuki crosscoupling reaction between 1 and two equivalents of 2-((2-ethylhexyloxy)phen-4-yl)-4,4,5,5tetramethyl-1,3,2-dioxaborolane gave the bromo-derivative 2 prone to be functionalized with bis(pinacolato)diboron affording the relevant boronic ester **3**. Concerning the synthesis of the chromophoric π -bridge, the benzothiadiazole-containing derivative 4 was reacted in a Suzuki coupling with an equimolar amount of thienyl-boronic acid yielding the unsymmetrically substituted compound 5. A selective bromination on the activated thiophene ring with N-bromo-succinimide (NBS) afforded the corresponding bromoderivative 6. A Suzuki reaction between 6 and 4-formylphenyl boronic acid placed the aldehyde functional group for the subsequent conversion into the anchoring moiety. A further NBS bromination of the so obtained intermediate 7 yielded the bromo-derivative 8. The synthetic procedures were completed by carrying out a Suzuki cross-coupling between 8 and the relevant boronic-esters of the electron donating groups, concluded by a Knovenagel condensation of the obtained aldehydes 9 and 10 with cyanoacetic acid affording G4 and G5, respectively.



Scheme 1. Synthetic approach followed for the preparation of **G4** and **G5**. Reaction conditions: *i*) NIS, DMF; *ii*) 2-((2-ethylhexyloxy)phen-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, Pd(PPh₃)₄,

1M NaHCO₃, THF; *iii*) bis(pinacolato)diboron, PdCl₂(dppf), potassium acetate, dioxane; *iv*) thiophen-2-yl boronic acid, Pd(PPh₃)₄, 1M NaHCO₃, THF; *v*) NBS, DMF; *vi*) 4-formylphenyl boronic acid, Pd(PPh₃)₄, 1M NaHCO₃, THF; *vii*) 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*,*N*-bis((2-ethylhexyloxy)phen-4-yl)aniline, Pd(PPh₃)₄, 1M NaHCO₃, THF; *viii*) **3**, Pd(PPh₃)₄, 1M NaHCO₃, THF; *ix*) cyanoacetic acid, piperidine, CHCl₃.

The UV–Vis absorption of G3-5 in THF are depicted in Figure 2A highlighting that all sensitizers exhibit two major absorption bands at 350–400 nm and 500–550 nm, often simplistically ascribed to localized aromatic π – π * transitions or to intramolecular charge-transfer (ICT) transitions. However, a deeper insight into the nature of these two absorption bands has been provided by theoretical calculations (*vide infra*). Concerning the absorption wavelengths, the dye structural tailoring seems to have a non-negligible effect on the absorption profiles of the triad. The absorption peaks falling in the UV region are located at 378 (G3), 370 (G4) and 354 (G5) nm, with molar extinction coefficients of 41600, 33600

and 48600 $M^{-1}cm^{-1}$ respectively, whereas the lower energy bands peaked at 535 (G3), 527 (G4) and 524 (G5) nm, with corresponding molar extinction coefficients of 38300, 27900 and 30100 $M^{-1}cm^{-1}$. Their absorption onsets in THF solution followed the trend observed for the maxima (641, 635 and 624 nm for G3, G4 and G5, respectively), confirming potentially significant light-harvesting properties for all dyes. Nevertheless, it is apparent how the introduction of the alkyl chain onto the π -bridge induces a blue-shift of the absorption maxima in G4 and G5 with respect to G3 with a corresponding lowering of the relevant molar extinction coefficients.

Suitable investigation of the solvatochromic behavior of an organic dye can be useful to predict the influence on the absorption profile consequent to the sensitizer immobilization on TiO₂ surface. The formation of titanium carboxylate upon dye adsorption process might indeed cause a detrimental blue-shift of its absorption profile [13]. The absorption properties of the dyes in their deprotonated form can be evaluated in solution using a large excess of triethylamine (TEA) thus bypassing the complications due to scattering and aggregation that can occur carrying out the investigation on titania [14]. As shown in Figure 2A, the G3-5 absorption profiles recorded in the presence of excess of TEA are very similar to the corresponding ones recorded in THF (the blue-shift of the absorption bands being contained within 5 nm) substantiating the assumption that the original light-harvesting properties of these molecules are preserved from the deprotonation-induced blue-shift. It can also be anticipated that the peculiar structural motifs of these D–A– π –A dyes lead to electronic transitions with a low ICT character, suggesting us to carefully deepen their nature and the relevant photo-excitation dynamics typical of the DSSC work cycle. This behaviour was confirmed by recording the absorption spectra of the three sensitizers adsorbed onto a TiO_2 substrate (Figure S1) that were nearly superimposable to those measured in THF solution.



Figure 2. (A) Absorption profiles of G3-5 in THF and THF/triethylamine (3/1 v/v) solutions.
Anodic (B) and cathodic (C) cyclic voltammograms of G3, G4 and G5 as thin films with ferrocene as the reference. (D) Calculated and experimental ionization potential, calculated and experimental electron affinity, HOMO and LUMO energy levels of G3, G4 and G5.

Electrochemistry provides crucial insights into the thermodynamics of the electron injection as well as of the dye regeneration by the redox shuttle. The electrochemical properties of the three sensitizers were investigated by cyclic voltammetry (CV) aiming at determining the energy levels of their frontier orbitals. The anodic and cathodic scans for the three sensitizers are illustrated in Figure 2B and Figure 2C, respectively. The observed oxidation potentials correspond to highest occupied molecular orbitals (HOMO) energy levels located at -5.04, -5.02 and -5.24 eV for G3, G4 and G5, respectively, implying a thermodynamically feasible regeneration of the dyes by the I^-/I_3^- redox shuttle during the DSSC work cycle. To confirm the reversibility of the redox events in the case of G4 and G5,

their electrochemical behavior was also studied in CH₂Cl₂ solution (see Figure S2). It is evident that G5 shows a downshifted HOMO energy value (~0.2 eV) compared to G3 and G4, suggesting an important role of the electron-donating unit in determining the ionization potential of the relevant sensitizer, as confirmed (vide infra) by theoretical calculations. It is reasonable to suppose that the introduction of a further phenyl spacer (biphenyl vs phenyl) reduces the mesomeric contribution to the electron-donating properties of the relevant triarylamine, to which an important contribution is also provided by the alkoxy groups. This effect produces the HOMO stabilization observed in G5 despite the increased number of aromatic units involved in the electronic delocalization. By contrast, the effect of the n-hexyl chain functionalization was mainly observed on the lowest unoccupied molecular orbital (LUMO) energy levels of the three sensitizers, that were found to be -3.24, -3.15 and -3.17eV for G3, G4 and G5, respectively. The slight upshift of the LUMO energy values of G4 and G5 with respect to that of G3 can be reasonably ascribed to the distortion of the π bridge backbone (vide infra) induced by the introduction of the alkyl chain. The LUMO energy values lie above the conduction band edge of TiO₂, ensuring sufficient driving force for the electron injection from the excited dyes into the conduction band of the inorganic semiconductor. On these grounds, all three sensitizers are qualified for potential application in DSSCs.

Theoretical calculations

To gain insight into the photophysical and electronic properties of the three sensitizers, a theoretical investigation was performed applying density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations on the geometrically optimized suitable molecular models, at the B3LYP/6-31G(d,p) level of the theory using the Gaussian 09 program packages [15]. Since the calculations were carried out including solvent effects (THF) using non-equilibrium implementation of the conductor-like polarizable continuum model (C-

PCM), in order to reduce the computational load, the 2-ethyl-hexyl chains were replaced by methyl groups, in consideration of their minor influence on the molecules conformation. The analysis of the optimized geometry (Figure S3) of the three sensitizers revealed a near planar conformation of the π -bridge with low dihedral angles between benzothiadiazole and thiophene units, while higher dihedral angles were observed at the linkage between thiophene and benzene units. The introduction of the *n*-hexyl chain onto the thiophene unit induced a pronounced distortion of the corresponding thiophene/benzene dihedral angle (~37°) in **G4** and **G5** without, however, any apparent influence on the electronic distribution of the frontier orbitals. The calculated electron density distributions of the main energy levels are shown in Figure S4. The HOMOs are principally distributed on the electron-rich triarylamine group as well as on part of the chromophoric π -bridge, confirming the experimental observation previously reported that the electron binding energy for the HOMOs is not sensitive to the structural modifications involving the π -spacer extension, but only those inherent the electron-donating unit. Conversely, the LUMOs of the three sensitizers are partially localized on the π -bridge and in the proximity of the anchoring group.

The ionization potentials (the absolute value of the HOMO energy level) of G3, G4 and G5 were calculated as the difference between the total energies of the (N-1)-electron and (N)-electron states [16]. All energies were calculated starting from the geometrically optimized structures of the sensitizer neutral states. The calculations returned ionization potentials following the same trend observed by CV measurements (see Figure 2D). With the same approach, the electron affinities (the absolute value of the LUMO energy level) of G3-5 were obtained calculating the difference between the total energies of the (N)-electron and (N+1)-electron states (Figure 2D).

The optical behavior of the three sensitizers was deepened by investigating the vertical $S_0 \rightarrow S_n$ excitation energies at the TD-DFT level of theory using the CAM-B3LYP functional

[17] including solvent effects (THF) with the C-PCM simulation. It was found that the calculated optical data in terms of both excitation energies and oscillator strength are in good agreement with the experimental measurements (Figure S5–S7). The same considerations can be made for the calculation of the absorption spectra of the deprotonated form of the three sensitizers, substantiating the accurateness of the theoretical calculations and the corresponding interpretation on the basis of the solvatochromic measurements. According to the calculation (Table 1), the $S_0 \rightarrow S_1$ excitations of G3-5 sensitizers are predominantly described as HOMO \rightarrow LUMO transitions with additional and significant HOMO \rightarrow LUMO+1 contributions. On the other hand, the $S_0 \rightarrow S_2$ excitations can principally be described as HOMO \rightarrow LUMO+1 and HOMO \rightarrow 2 \rightarrow LUMO character.

Dye	Transition	λ(nm)	f	configuration	
G3	$S_0 \rightarrow S_1$	531.3	1.75	H→L (56%); H−1→L (33%); H→L+1 (9%)	
	$S_0 \rightarrow S_2$	396.8	0.51	H–1→L (43%); H→L+1 (26%); H–2→L (24%); H→L (8%)	
G4	$S_0 \rightarrow S_1$	519.3	1.59	H→L (56%); H–1→L (32%); H→L+1 (9%)	
	$S_0 \rightarrow S_2$	388.2	0.52	H–1→L (45%); H→L+1 (25%); H–2→L (23%); H→L (7%)	
G5	$S_0 \rightarrow S_1$	511.0	1.66	H→L (49%); H–1→L (39%); H→L+1 (7%)	
	$S_0 \rightarrow S_2$	384.5	0.51	H–1→L (35%); H→L+1 (24%); H–2→L (23%); H–1→L+1 (10%); H→L (8%)	

Table 1. Excitation energies (1), oscillator strength (f) and configuration of the main calculated

transitions $(S_0 \rightarrow S_1 \text{ and } S_0 \rightarrow S_2)$ of **G3**, **G4** and **G5**.

Therefore, the TD-DFT calculations describe the fundamental absorption peak as an electronic transition composed of different contributions, complicating an interpretation straightforwardly based on the electron density shift upon photo-excitation of the dye. In cases such as this, it is more opportune to analyze the individual excited states using natural transition orbitals (NTOs), consisting of a simple orbital picture of the TD-DFT calculations obtained by representing the electronic transition (exciton) in terms of two molecular

orbitals (describing electron and hole respectively) thus allowing to straightforwardly monitor the electron density shift from the ground state (hole) to the excited state (electron). The calculated NTOs of the three sensitizers (Figure 3) visually describe the photo-dynamics of the main excitation $(S_0 \rightarrow S_1)$ implying a partial shift of the electron density towards the acceptor unit of the dyes, allowing in principle the electron transfer from the excited dye to the semiconductor conduction band at the dye/titania interface. However, contrary to what was observed in the case of G3, the π -backbone distortion in G4 and G5 seems to impair the photo-induced shift of the electronic density towards the anchoring group, thereby resulting to be mostly localized around the electron-withdrawing benzothiadiazole unit upon photoexcitation. Since the hole/electron NTOs of the $S_0 \rightarrow S_1$ excitation are mainly localized on the chromophoric π -bridge of the three sensitizers, the low ICT character of these electronic transitions emerging from the solvatochromic behavior previously described finds a deeper rationale. Also the higher energy $S_0 \rightarrow S_2$ excitation (the relevant NTOs are shown in Figure S8) only promoting a densification of the electron density in proximity of the anchoring group during the photo-excitation can be classified as a low ICT character transition, thereby also partially contributing to photon-to-current conversion in DSSC under ambient solar illumination. On these bases, however, it is reasonable to suppose that the electron transfer process at the dye/TiO₂ interface is not only dependent on the involved electronic transition $(S_0 \rightarrow S_1 \text{ or } S_0 \rightarrow S_2 \text{ excitation})$ but also relatively slower with respect to the very wide range of organic sensitizers endowed with strong ICT absorption bands.



Figure 3. Calculated natural transition orbitals (NTOs) describing the photo-excitation dynamics of the $S_0 \rightarrow S_1$ transition in G3, G4 and G5.

Photovoltaic properties

In view of their favourable optical and electrochemical properties, the photovoltaic performances of G3-5 were evaluated using the Γ/I_3^- couple as the redox shuttle and comparing them with those of the ruthenium-based sensitizer N719 as the reference dye. In order to avoid the undesirable dye aggregation on the TiO₂ surface and to suppress detrimental recombination processes leading to dark current [18], several tests using different amounts of chenodeoxycholic acid (CDCA) were carried out for the dyeing of the TiO₂ electrodes, as summarized in Table 2 along with the relevant device figures of merit. The appropriate amount of CDCA significantly enhanced the dye performances: their power conversion efficiency (PCE) was, in fact, increased from 4.1% to 8.6% in the case of G3 (using 30 mM CDCA), from 5.1% to 9.5% in the case of G4 (using 10 mM CDCA) and from 5.5% to 9.8% in the case of G5 (using 10 mM CDCA). These results markedly

outperform those obtained using the very well-known ruthenium-based N719 reference dye which reached a PCE of 8.7% in DSSC fabricated with the same architecture. Furthermore, the performances of **G3-5** sensitizers were also recorded under intensities simulating diffuse sunlight (0.66 and 0.33 sun) observing that the efficiencies were even increased, reaching, in the case of the most performing dye **G5**, a PCE of 10.3% under 0.33 sun (Figure 4A). These results can be interpreted considering that, at reduced sun intensity, mass-transport limitations of the redox mediators are remarkably alleviated.

It is apparent how **G4** and **G5** exhibited the better performances using lower CDCA amounts compared to those employed in the case of **G3**. Reasonably, the presence of the *n*-hexyl chain in **G4** and **G5** effectively contributes to space the sensitizer molecules onto the TiO_2 surface preventing the analogous effect exerted by the CDCA molecules at the expense of the photoanode active area, as supported by dye loading measurements (Table S1).

A significant aspect emerges from the analysis of the spectra of monochromatic incident photon-to-current conversion efficiencies (IPCEs) recorded for the DSSCs. Notwithstanding the presence of large TiO₂ scattering nanoparticles in the photoanode broadening the shape of the IPCE spectra, these (Figure 4B) seem to be in agreement with the light-harvesting range of sensitizers, although not following the UV–Vis absorption profiles previously discussed. It is rational to ascribe this behavior to the different electron injection efficiency of the two electronic transitions characterizing the "camel-back" absorption profiles of G3-5 sensitizers, which was suggested by our theoretical calculations. Notwithstanding the broadest light-harvesting response exhibited by G3-based devices, their IPCE spectrum showed the highest values (~75%) at wavelengths below 550 nm. By contrast, G4 and G5 maintained a much higher (~85%) IPCE value across the visible wavelengths ranging from 450 to 600 nm. Although G4 showed a slightly broader IPCE profile with respect to that of G5, better conversion efficiencies below 500 nm were observed for G5, plausibly deriving from its higher molar extinction coefficients (*vide supra*) with respect to G4 in this region.



Figure 4. (A) J–V curves of DSSCs based on the three sensitizers **G3**, **G4** and **G5** under 1.0, 0.66 and 0.33 sun illumination. (B) Incident photon-to-current conversion efficiency (IPCE) behaviour

of the same cells.

To deepen the relationship between dye molecular structure and photovoltaic performance, impedance spectroscopy (IS) measurements were performed on the CDCA-optimized DSSCs at different bias potentials under 1.0 sun irradiation. In the framework of our investigation, the IS measurements principally aim at associating the differences in devices performance with the shift of the TiO₂ conduction band (EC) or with the recombination rate, both aspects having a strong influence on the net charge-transfer at the TiO₂/dye interface during the DSSC work cycle [19]. IS spectra were analyzed through the well-known equivalent circuit proposed by Bisquert [20]. Figure 5A and Figure 5B show the capacitance (C_{μ}) and recombination resistance (R_{ct}) plotted versus voltage drop (V_{corr}) at the sensitized electrode. The V_{corr} in the sensitized electrode is obtained after correcting the applied potential (V_{app}) for the drop of total series resistance V_{series} (contacts, counter electrode, electrolyte diffusion) collected from impedance spectroscopy data as $V_{corr} = V_{app} - V_{series}$ [21]. The chemical capacitance (C_{μ}) represented in Figure 4A provides information about the position of the conduction band [22]. From the analysis of C_{u} , we could

straightforwardly identify the upward shift of the conduction band edge of titania in the case of the DSSC fabricated with the G3 dye with respect to G4 and G5. On the other hand, a lower ECB for G4- and G5-based devices should decrease the energy difference from the Γ /I₃⁻ redox potential, which would result in a lower open-circuit voltage (V_{OC}) with respect to G3. On the contrary, G5-based cells show the highest V_{OC}, due to their higher chargetransfer resistance (R_{ct}, Figure 5B).



Figure 5. EIS of CDCA-optimized DSSCs at different bias potentials under 1.0 sun irradiation.
Capacitance (A) and recombination resistance (B) with respect to the Fermi level voltage (removing the effect of series resistance, V_{corr}). Capacitance (C) and recombination resistance (D) replotted with respect to the equivalent common conduction band voltage (V_{ecb}) using G5 as reference dye, so that distance between Fermi level and conduction band is the same in all cases.

To gain more insight into the recombination resistance behavior, the R_{ct} was determined on the basis of a similar number of injected electrons, *i.e.* at the same energy gap between the electron Fermi level and TiO₂ conduction band. To this purpose, the voltage scale in Figure 5C has been shifted, so that chemical capacitances coincide. In this graph, the voltage is obtained as $V_{ecb} = V_{corr} - \Delta E_C$, where "ecb" stands for "common equivalent conduction band" and $\Delta E_{\rm C}$ is the shift of the conduction band with respect to G5 taken as reference sample [22b]. In Figure 5D, the recombination resistance is plotted using the same scale. This procedure equalizes the conduction band of titania for all the cells and allows a better comparison of the charge-transfer rate. Under the same equivalent conduction band level, the R_{ct} values of G4 and G5 are clearly confirmed as higher than those of G3 (Figure 5D), indicating that the parasitic charge recombination between injected electrons into TiO₂ from the excited sensitizer and the oxidized form of the redox shuttle occurs in a higher extent in G3 with respect to G4 and G5. This results can be ascribed to the insulating effect of the nhexyl chain on the π -bridge of G4 and G5 dyes which suppresses the dark current. Moreover, the steric hindrance of the G5 triarylamine-based donor group further hinders charge recombination, explaining the higher V_{OC} and the higher short-circuit current density (J_{SC}) observed for the G5-based photovoltaic cell.

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Dye	CDCA	PCE (%)	FF	V _{OC} (mV)	J_{SC} (mA/cm ²)	Sun				
N719	0 mM	8.67	0.66	751	17.51	1.0				
G3	0 mM	4.14	0.69	666	9.00	1.0				
G3	20 mM	7.44	0.74	661	15.21	1.0				
<i>G3</i>	30 mM	8.64	0.72	663	18.11	1.0				
G3	30 mM	8.94	0.73	660	12.25	0.66				
G3	30 mM	9.20	0.74	661	6.21	0.33				
G3	40 mM	7.85	0.71	663	16.67	1.0				
G4	0 mM	5.11	0.66	693	11.16	1.0				
G4	5 mM	6.84	0.68	702	14.24	1.0				
<i>G4</i>	10 mM	9.49	0.68	704	19.76	1.0				
G4	10 mM	9.57	0.70	702	12.85	0.66				
G4	10 mM	9.83	0.73	701	6.34	0.33				
G4	15 mM	9.52	0.70	708	19.23	1.0				
G5	0 mM	5.49	0.67	714	11.54	1.0				
G5	5 mM	7.68	0.68	722	15.53	1.0				
<i>G5</i>	10 mM	9.77	0.68	721	19.80	1.0				
G5	10 mM	9.90	0.69	720	13.15	0.66				
G5	10 mM	10.26	0.72	715	6.58	0.33				
G5	15 mM	9.45	0.70	735	18.40	1.0				

Table 2. Photovoltaic performance of DSSCs based on G3, G4 and G5 using the Γ/I_3^- redox

shuttle.

Conclusions

Taking into consideration that even the slightest structural modification conceived for an organic sensitizer can exert a strong influence on the relevant DSSC performances, based on the structural motif of a robust D–A– π –A organic dye (G3), new largely π -extended organic sensitizers (G4 and G5) have been designed with the main aim of favourably modulating the interactions between the dye/TiO₂ layer and the employed redox shuttle. Complying with the guidelines traditionally followed to retard disadvantageous charge recombination and to inhibit detrimental interactions between dye molecules onto the titania surface, the molecular tailoring of the G3 scaffold was performed by suitably positioning an alkyl chain onto the π -spacer (G4 vs G3) and increasing the dimension of the electron-donating unit (G5

vs G4). A detailed TD-DFT study has revealed that the main $S_0 \rightarrow S_1$ electronic transitions of the three sensitizers is endowed with only a weak charge-transfer character, being the hole/electron densities mainly localized on the largely π -extended bridge, and implying, upon photo-excitation, a limited shift of the electron density towards the anchoring group. Notwithstanding these unusual photo-excitation dynamics, the photovoltaic performances of G3, G4 and G5 can be regarded as impressive, reaching, in the case of G5, power conversion efficiencies up to 9.8%, ranking among the highest reported for metal-free organic sensitizers employing iodine-based electrolytes.

Experimental Section

General remarks on dye synthesis and characterization: All reactants and raw materials were purchased from standard commercial sources and used without any further purification. All solvents used were carefully dried and freshly distilled according to standard laboratory practice. All manipulations were carried out under inert dinitrogen atmosphere. The synthesis of 4-bromo-7-(4-hexylthiophen-2-yl)benzo[2,1,3]thiadiazole (4) [8b], 2-((2ethylhexyloxy)phen-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [11a] and 4-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)-N,N-bis((2-ethylhexyloxy)phen-4-yl)aniline [23] have been carried out adapting literature procedures. Column chromatography were carried out on a Biotage Isolera One instrument using K-Sil cartridges. The NMR spectra were recorded on a Bruker Avance 700 MHz instrument. Elemental analyses were obtained on a EuroVector CHNS EA3000 elemental analyser on the basis of three replicates. UV-Vis spectra were recorded on a Jasco V-670 instrument. FT-IR measurements were carried out on a JASCO FT/IR 4200 spectrophotometer. The cyclic voltammetry experiments were carried out using a Metrohm Autolab PGSTAT 302-N potentiostat. In a typical experiment, the samples were drop cast on a platinum working electrode from THF solutions of 1 mg/mL concentration. Measurements have been performed at a 50 mV/s scan rate in acetonitrile solution

containing tetrabutylammonium tetrafluoroborate (0.1 M) as supporting electrolyte at 25 °C. Potentials were measured versus Ag/Ag^+ as quasi-reference electrode. The potential of the Ag/Ag^+ electrode was calibrated against Fc/Fc^+ after each experiment. After calibration against Fc/Fc^+ , the HOMO and LUMO energy levels were calculated according to the following equations:

$$E_{HOMO} (eV) = - [E_{ox}^{onset} - E_{1/2}(Fc/Fc^{+}) + 4.8]$$
$$E_{LUMO} (eV) = - [E_{red}^{onset} - E_{1/2}(Fc/Fc^{+}) + 4.8]$$

where $E_{1/2}(Fc/Fc^+)$ is the half-wave potential of the Fc/Fc⁺ couple, while E_{ox}^{onset} and E_{red}^{onset} represent the onset potentials of the first oxidation and reduction event, respectively. The analyses of the ground-state structures were carried out by density functional theory (DFT) calculations. The B3LYP function was used in conjunction with the 6-31G(d,p) basis set. Time-dependent DFT (TD-DFT) was applied for the assessment of excited-state transition energies. All theoretical calculations have been carried out using the Gaussian09 program package on isolated molecules.

DSSC fabrication and photovoltaic measurement: Fluorine-doped tin oxide (FTO, 15 Ω /sq, provided by Solaronix S.A.) glass plates were first cleaned in a detergent solution using an ultrasonic bath for 15 min, and then rinsed with water and ethanol. Double-layer electrodes (overall thickness 19 µm) were prepared as follows: a layer of commercial colloidal titania paste (Dyesol 18NR-T) was deposited onto the FTO glass and gradually heated in an oven in air to obtain a ~14 µm transparent nano-crystalline film; the temperature gradient was programmed as follows: 170°C (40 min), 350°C (15 min) and 430°C (30 min). This procedure was repeated for the scattering layer (5 µm) constituted by Solaronix D/SP colloidal paste. The double-layer electrode was eventually sintered at 450°C

for 30 min. The thickness and the active area (0.16 cm^2) of the sintered photo-anodes was measured using a profilometer (Veeco Dektak 150 Surface Profiler). The dye loading was performed by keeping the electrodes for 14 h and under dark in 0.2 mM THF solutions of G3, G4 or G5 dyes containing a known amount of chenodeoxycholic acid (CDCA). The reference photo-anodes were prepared analogously by dyeing the electrodes with 0.2 mM solutions bis(tetrabutylammonium)-cis-di(thiocyanato)-N,N'-bis(4-carboxylato-4'of carboxylic acid-2,2'-bipyridine) ruthenium(II) (N719, purchased by Solaronix S.A.) in a mixture of acetonitrile and tert-butyl alcohol (1:1 v/v). The counter-electrodes were prepared by sputtering a 50 nm Pt layer on a hole-drilled cleaned FTO plate. In a typical device construction procedure, the photo-anode and the counter-electrode were faced and assembled using a suitably cut 50 µm thick Surlyn® hot-melt gasket for sealing. The iodine redox electrolyte (0.1 M LiI, 0.05 M I₂, 0.6 M 1-methyl-3-propylimidazolium iodide, and 0.5 M tert-butylpyridine in dry acetonitrile) was vacuum-injected into the space between the electrodes through pre-drilled holes on the back of the counter electrode. The holes were eventually sealed using Surlyn[®] hot melt film and a cover glass. Photocurrent-voltage measurements were performed using a Keithley unit (Model 2400 Source Meter). A Newport AM 1.5 Solar Simulator (Model 91160A equipped with a 1000 W Xenon arc lamp) serving as a light source. The light intensity was calibrated to 100 mW/cm² using as reference a Si solar cell. The incident photon-to-current conversion efficiency (IPCE) was measured by the DC method using a computer-controlled xenon arc lamp (Newport, 140 W, 67005) coupled with a monochromator (Newport Cornerstore 260 Oriel 74125). The light intensity was measured by a calibrated silicon UV-photodetector (Oriel 71675) and the short circuit currents of the DSSCs were measured by using a dual channel optical power/energy meter (Newport 2936-C). Single layer transparent photoelectrodes (5 µm thick) sensitized for 4 h in the best performing dye bath solutions were used for absorption spectra measurement of the dyes on TiO₂ surface. Electrochemical impedance spectroscopy (EIS)

was performed by an AUTOLAB PGSTAT 302N (Eco Chemie B.V.) in a frequency range between 100 kHz and 10 mHz. The impedance measurements were carried out at different voltage biases under 1.0 sun illumination. The resulting impedance spectra were fitted by using ZView (Scribner Associates) software.

Synthetic procedures: 4-Bromo-*N*,*N*-bis(4-iodophenyl)aniline (1). *N*-iodo-succinimide (2.25 g, 10.00 mmol) was added portionwise to a solution of 4-bromo-*N*,*N*-diphenylaniline (1.62 g, 5.00 mmol) in DMF (50 mL) kept at 0 °C. After the addition, the obtained reaction mixture was warmed to room temperature and allowed to react overnight before quenching with water (50 mL). The compound was extracted with diethyl ether (3×50 mL) and the combined organic phases were washed with water (50 mL) and dried over Na₂SO₄. After solvent removal, the crude product was purified by column chromatography (SiO₂, petroleum ether 40-60 °C/CH₂Cl₂ = 10/1 v/v) to afford **1** (2.05 g, 71%) as a off-white solid. ¹H NMR (700 MHz, CDCl₃): δ 7.56 (d, J = 8.8 Hz, 4H); 7.39 (d, J = 8.9 Hz, 2H); 6.96 (d, J = 8.9 Hz, 2H); 6.84 (d, J = 8.8 Hz, 4H) ppm. ¹³C{¹H} NMR (176 MHz, CDCl₃): δ 146.7, 145.9, 138.5, 132.6, 126.0, 125.9, 116.2, 86.5 ppm. Elem. Anal. calcd for C₁₈H₁₂BrI₂N: C 37.53, H 2.10, N 2.43; found: C 37.57, H 2.06, N 2.46.

4-Bromo-*N*,*N*-bis(4'-(2-ethylhexyloxy)-1,1'-biphenyl-4-yl)aniline (**2**). Compound **1** (1.15 g, 2.00 mmol), 2-((2-ethylhexyloxy)phen-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.46 g, 4.40 mmol) and Pd(PPh₃)₄ (0.12 g, 0.10 mmol) were put into a three-necked 50 mL round bottom flask. Degassed THF (15 mL) and 1M NaHCO₃ aqueous solution (10 mL) were added to the flask and the obtained mixture was refluxed for 24 h. After cooling down the reaction to room temperature, methylene chloride (50 mL) was added to the mixture and the resulting organic phase was separated, washed with water (50 mL) and dried over Na₂SO₄. After solvent removal, the crude product was purified by column chromatography (SiO₂,

petroleum ether 40-60 °C/CH₂Cl₂ = 10/1 v/v) to obtain **2** (1.04 g, 71%) as a white solid. ¹H NMR (700 MHz, CDCl₃): δ 7.51 (d, J = 8.5 Hz, 4H); 7.47 (d, J = 8.5 Hz, 4H); 7.37 (d, J = 8.7 Hz, 2H); 7.16 (d, J = 8.5 Hz, 4H); 7.04 (d, J = 8.7 Hz, 2H); 6.98 (d, J = 8.5 Hz, 4H); 3.92-3.87 (m, 4H); 1.79-1.73 (m, 2H); 1.56-1.32 (m, 16H); 0.98-0.91 (m, 12H) ppm. ¹³C{¹H} NMR (176 MHz, CDCl₃): δ 158.8, 146.9, 145.9, 135.9, 132.8, 132.2, 128.8, 127.7, 127.5, 125.2, 124.6, 114.9, 70.7, 39.4, 30.6, 29.1, 23.9, 23.1, 14.1, 11.1 ppm. Elem. Anal. calcd for C₄₆H₅₄BrNO₂: C 75.39, H 7.43, N 1.91; found: C 75.47, H 7.36, N 1.96.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*,*N*-bis-(4'-(2-ethylhexyloxy)-1,1'-biphen-4-yl)aniline (3). Compound 2 (1.00 g, 1.36 mmol), bis(pinacolato)diboron (1.04 g, 4.08 mmol), PdCl₂(dppf) (0.05 g, 0.07 mmol) and potassium acetate (0.20 g, 2.04 mmol) were put into a three-necked 50 mL round bottom flask. Degassed dioxane (25 mL) was added to the flask and the obtained mixture was stirred at 80 °C for 24 h. After cooling down the reaction to room temperature, methylene chloride (50 mL) was added to the mixture and the resulting organic phase was separated, washed with water (50 mL) and dried over Na₂SO₄. After solvent removal, the crude product was purified by column chromatography (SiO₂, petroleum ether 40-60 °C/CH₂Cl₂ = 2/1 v/v) to obtain **3** (0.80 g, 74%) as a white solid. ¹H NMR (700 MHz, CDCl₃): δ 7.74 (d, J = 8.2 Hz, 2H); 7.54 (d, J = 8.9 Hz, 4H); 7.50 (d, J = 8.9 Hz, 4H); 7.21 (d, J = 8.9 Hz, 4H); 7.16 (d, J = 8.2 Hz, 2H); 7.00 (d, J = 8.9 Hz, 4H); 3.95-3.89 (m, 4H); 1.81-1.76 (m, 2H); 1.60-1.41 (m, 16H); 1.38 (s, 12H); 1.00-0.93 (m, 12H) ppm. ¹³C{¹H} NMR (176 MHz, CDCl₃): δ 158.8, 150.4, 146.0, 136.0, 135.9, 132.9, 127.8, 127.5, 125.1, 122.0, 114.8, 83.6, 70.6, 39.4, 30.6, 29.1, 25.0, 23.9, 23.2, 14.1, 11.1 ppm. Anal. calcd for C₅₂H₆₆BNO₄: C 80.08, H 8.53, N 1.80; found: C 79.99, H 8.56, N 1.78. 4-(4-Hexyl-thiophen-2-yl)-7-(thiophen-2-yl)benzo[2,1,3]thiadiazole (5). Compound 4 (5.15 g, 13.50 mmol), thiophen-2-yl boronic acid (1.90 g, 14.85 mmol) and Pd(PPh₃)₄ (0.31 g, 0.27 mmol) were put into a three-necked 250 mL round bottom flask. Degassed THF (50

mL) and 1M NaHCO₃ aqueous solution (40 mL) were added to the flask and the obtained mixture was refluxed overnight. After the reaction was allowed to reach room temperature, the compound was extracted with diethyl ether (50 mL) and the resulting organic phase was washed with water (50 mL) and dried over Na₂SO₄. After solvent removal, the crude product was purified by column chromatography (SiO₂, petroleum ether 40-60 °C/CH₂Cl₂ = 5/1 v/v) yielding **5** (4.05 g, 78%) as a red solid. ¹H NMR (700 MHz, CDCl₃): δ 8.12 (dd, J = 3.6, 1.1 Hz, 1H); 8.00 (d, J = 1.4 Hz, 1H); 7.87 (d, J = 7.5 Hz, 1H); 7.85 (d, J = 7.5 Hz, 1H); 7.46 (d, J = 5.0 Hz, 1H); 7.22 (dd, J = 5.0, 3.6 Hz, 1H); 7.06 (d, J = 1.4 Hz, 1H); 2.71 (t, J = 7.7 Hz, 2H); 1.75-1.70 (m, 2H); 1.45-1.39 (m, 2H); 1.37-1.33 (m, 4H); 0.92 (t, J = 7.0 Hz, 3H) ppm. ¹³C{¹H} NMR (176 MHz, CDCl₃): δ 152.7, 152.6, 144.4, 139.4, 138.9, 129.1, 128.0, 127.5, 126.8, 126.3, 125.8, 125.5, 121.6, 31.7, 30.7, 30.5, 29.1, 22.6, 14.1 ppm. Anal. calcd for C₂₀H₂₀N₂S₃: C 62.46, H 5.24, N 7.28; found: C 62.49, H 5.26, N 7.24.

4-(5-Bromo-4-hexylthiophen-2-yl)-7-(thiophen-2-yl)benzo[2,1,3]thiadiazole (**6**). A solution of *N*-bromo-succinimide (1.78 g, 10.00 mmol) in DMF (60 mL) was added dropwise to a solution of compound **5** (3.85 g, 10.00 mmol) in DMF (90 mL) kept at 0 °C. After the addition, the obtained reaction mixture was warmed to room temperature and allowed to react for further 2 h before quenching with water (100 mL). The compound was extracted with diethyl ether (3×100 mL) and the combined organic phases were washed with water (50 mL) and dried over Na₂SO₄. After solvent removal, the crude product was purified by column chromatography (SiO₂, petroleum ether 40-60 °C/CH₂Cl₂ = 5/1 v/v) to afford **6** (3.48 g, 75%) as a red solid. ¹H NMR (700 MHz, CDCl₃): δ 8.13 (dd, J = 3.6, 1.1 Hz, 1H); 7.23 (dd, J = 5.0, 3.6 Hz, 1H); 7.78 (d, J = 7.7 Hz, 2H); 1.74-1.70 (m, 2H); 1.46-1.39 (m, 2H); 1.38-1.32 (m, 4H); 0.93 (t, J = 7.0 Hz, 3H) ppm. ¹³C{¹H} NMR (176 MHz, CDCl₃): δ 152.6, 152.3, 143.0, 139.3, 138.6, 128.1, 128.0, 127.6, 126.9, 126.1, 125.7, 125.3,

125.0, 111.5, 31.6, 29.7, 29.6, 29.0, 22.6, 14.1 ppm. Anal. calcd for C₂₀H₁₉BrN₂S₃: C 51.83, H 4.13, N 6.04; found: C 51.79, H 4.16, N 6.04.

4-(3-Hexyl-5-(7-(thiophen-2-yl)benzo[2,1,3]thiadiazol-4-yl)thiophen-2-yl)benzaldehyde (7). Compound 6 (3.20 g, 6.90 mmol), 4-formylphenyl boronic acid (1.14 g, 7.59 mmol) and Pd(PPh₃)₄ (0.16 g, 0.14 mmol) were put into a three-necked 100 mL round bottom flask. Degassed THF (30 mL) and 1M NaHCO₃ aqueous solution (20 mL) were added to the flask and the resulting mixture was refluxed for 24 h. After cooling down the reaction to room temperature, methylene chloride (50 mL) was added to the mixture and the resulting organic phase was separated, washed with water (50 mL) and dried over Na₂SO₄. After solvent removal, the crude product was purified by column chromatography (SiO₂, petroleum ether 40-60 °C/CH₂Cl₂ = 3/1 v/v) to obtain 7 (2.53 g, 75%) as a red solid. ¹H NMR (700 MHz, CDCl₃): δ 10.08 (s, 1H); 8.15 (dd, 3.6, 1.1 Hz, 1H); 8.04 (s, 1H); 7.97 (d, J = 8.3 Hz, 2H); 7.89 (s, 2H); 7.72 (d, J = 8.3 Hz, 2H); 7.48 (dd, J = 5.0, 1.1 Hz, 1H); 7.23 (dd, J = 5.0, 3.6 Hz, 1H); 2.80 (t, J = 7.7 Hz, 2H); 1.74-1.69 (m, 2H); 1.45-1.38 (m, 2H); 1.38-1.32 (m, 4H); 0.93 (t, J = 7.0 Hz, 3H) ppm. ${}^{13}C{}^{1}H$ NMR (176 MHz, CDCl₃): δ 191.6, 152.7, 152.6, 141.3, 140.8, 139.3, 138.7, 135.1, 130.5, 130.0, 129.5, 128.0, 127.6, 126.9, 125.7, 125.6, 125.5, 31.6, 30.9, 29.2, 29.1, 22.6, 14.0 ppm. Anal. calcd for C₂₇H₂₄N₂OS₃: C 66.36, H 4.95, N 5.73; found: C 66.29, H 4.96, N 5.74.

4-(5-(7-(5-Bromothiophen-2-yl)benzo[2,1,3]thiadiazol-4-yl)-3-hexylthiophen-2-

yl)benzaldehyde (8). A solution of *N*-bromo-succinimide (0.91 g, 5.12 mmol) in DMF (30 mL) was added dropwise to a solution of compound 7 (2.50 g, 5.12 mmol) in DMF (45 mL) kept at 0 °C. After the addition, the obtained reaction mixture was warmed to room temperature and allowed to react for further 2 h before quenching with water (50 mL). The compound was extracted with diethyl ether (3×50 mL) and the combined organic phases were washed with water (50 mL) and dried over Na₂SO₄. After solvent removal, the crude product was purified by column chromatography (SiO₂, petroleum ether 40-60 °C/CH₂Cl₂ =

3/1 v/v) to afford **8** (2.35 g, 81%) as a red solid. ¹H NMR (700 MHz, CDCl₃): δ 10.08 (s, 1H); 8.05 (s, 1H); 7.97 (d, J = 7.9 Hz, 2H); 7.88 (d, J = 7.4 Hz, 1H); 7.83-7.80 (m, 2H); 7.72 (d, J = 7.9 Hz, 2H); 7.17 (d, J = 4.0 Hz, 1H); 2.79 (t, J = 7.7 Hz, 2H); 1.77-1.71 (m, 2H); 1.43-1.36 (m, 2H); 1.34-1.28 (m, 4H); 0.93 (t, J = 7.0 Hz, 3H) ppm. ¹³C{¹H} NMR (176 MHz, CDCl₃): δ 191.6, 152.4, 152.4, 141.4, 140.7, 140.6, 138.5, 138.1, 135.1, 130.7, 130.6, 130.1, 129.5, 127.3, 125.9, 125.4, 125.2, 125.1, 114.7, 31.6, 30.9, 29.7, 29.2, 22.6, 14.0 ppm. Anal. calcd for C₂₇H₂₃BrN₂OS₃: C 57.14, H 4.08, N 4.94; found: C 57.19, H 4.06, N 5.00.

4-(5-(7-(5-(4-(N,N-Bis-(4-(2-ethylhexyloxy)-phenyl)-amino-phenyl)-thiophen-2-

yl)benzo[2,1,3]thiadiazol-4-yl)-3-hexylthiophen-2-yl)benzaldehyde (9). 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-N,N-bis((2-ethylhexyloxy)phen-4-yl)aniline (0.61 g, 0.97 mmol), compound 8 (0.50 g, 0.88 mmol) and Pd(PPh₃)₄ (0.05 g, 0.04 mmol) were put into a three-necked 50 mL round bottom flask. Degassed THF (15 mL) and 1M NaHCO₃ aqueous solution (10 mL) were added to the flask and the resulting mixture was refluxed for 24 h. After cooling down the reaction to room temperature, methylene chloride (50 mL) was added to the mixture and the resulting organic phase was separated, washed with water (50 mL) and dried over Na₂SO₄. After solvent removal, the crude product was purified by column chromatography (SiO₂, CH₂Cl₂) to obtain 9 (0.74 g, 85%) as a purple solid. ¹H NMR (700 MHz, CDCl₃): δ 10.10 (s, 1H); 8.16 (d, J = 3.8 Hz, 1H); 8.05 (s, 1H); 7.99 (d, J = 8.5 Hz, 2H); 7.93-7.88 (m, 2H); 7.74 (d, J = 8.5 Hz, 2H); 7.52 (d, J = 8.5 Hz, 2H); 7.31 (d, J = 3.8 Hz, 1H); 7.11 (d, J = 8.7 Hz, 4H); 6.97 (d, J = 8.5 Hz, 2H); 6.88 (d, J = 8.7 Hz, 4H); 3.87-3.84 (m, 4H); 2.79 (t, J = 7.7 Hz, 2H); 1.79-1.72 (m, 4H); 1.57-1.30 (m, 24H); 0.99-0.89 (m, 15H) ppm. ¹³C{¹H} NMR (176 MHz, CDCl₃): δ 191.9, 156.0, 152.6, 152.5, 148.7, 146.3, 141.3, 140.9, 140.2, 138.9, 137.7, 137.0, 135.0, 130.3, 130.1, 129.5, 129.1, 126.9, 126.5, 126.4, 125.8, 125.7, 124.9, 122.7, 120.1, 115.3, 70.7, 39.4, 31.6, 30.9, 30.6, 29.7,

29.3 29.2, 29.1, 23.9, 23.2, 22.6, 14.2, 14.1, 11.1 ppm. Anal. calcd for C₆₁H₆₉N₃O₃S₃: C 74.12, H 7.04, N 4.25; found: C 74.19, H 7.06, N 4.28.

4-(5-(7-(5-(4-(N,N-Bis-(4'-(2-ethylhexyloxy)-1,1'-biphen-4-yl)-amino-phenyl)-thiophen-2yl)benzo[2,1,3]thiadiazol-4-yl)-3-hexylthiophen-2-yl)benzaldehyde (10). Compound 3 (0.76 g, 0.97 mmol), compound 8 (0.50 g, 0.88 mmol) and Pd(PPh₃)₄ (0.05 g, 0.04 mmol) were put into a three-necked 50 mL round bottom flask. Degassed THF (15 mL) and 1M NaHCO₃ aqueous solution (10 mL) were added to the flask and the resulting mixture was refluxed for 24 h. After cooling down the reaction to room temperature, methylene chloride (50 mL) was added to the mixture and the resulting organic phase was separated, washed with water (50 mL) and dried over Na₂SO₄. After solvent removal, the crude product was purified by column chromatography (SiO₂, CH₂Cl₂) yielding **10** (0.87 g, 87%) as a purple solid. ¹H NMR (700 MHz, CDCl₃): δ 10.10 (s, 1H); 8.18 (d, J = 3.8 Hz, 1H); 8.07 (s, 1H); 7.99 (d, J = 8.2 Hz, 2H); 7.93-7.91 (m, 2H); 7.74 (d, J = 8.2 Hz, 2H); 7.64 (d, J = 8.4 Hz, 2H); 7.55 (d, J = 8.3 Hz, 4H); 7.52 (d, J = 8.3 Hz, 4H); 7.39 (d, J = 3.5 Hz, 1H); 7.25 (d, J = 8.3 Hz, 4H); 7.21 (d, J = 8.4 Hz, 2H); 7.00 (d, J = 8.3 Hz, 4H); 3.94-3.88 (m, 4H); 2.82 (t, J = 7.7 Hz, 2H); 1.81-1.73 (m, 4H); 1.57-1.30 (m, 24H); 0.99-0.89 (m, 15H) ppm. ¹³C{¹H} NMR (176 MHz, CDCl₃): δ 191.8, 158.8, 152.6, 147.5, 145.9, 141.4, 140.8, 138.9, 137.8, 137.7, 135.8, 135.0, 132.8, 130.4, 130.1, 129.6, 129.5, 129.0, 128.1, 128.0, 127.7, 127.5, 126.7, 126.2, 125.7, 125.1, 125.0, 124.8, 123.6, 123.3, 114.8, 70.6, 39.4, 31.7, 30.9, 30.5, 29.3, 29.2, 29.1, 23.8, 23.2, 22.6, 14.2, 14.1, 11.1 ppm. Anal. calcd for C₇₃H₇₇N₃O₃S₃: C 76.87, H 6.80, N 3.68; found: C 76.79, H 8.76, N 3.65.

3-(4-(5-(7-(5-(4-(N,N-Bis-(4-(2-ethylhexyloxy)-phenyl)-amino-phenyl)-thiophen-2-

yl)benzo[2,1,3]thiadiazol-4-yl)-3-hexylthiophen-2-yl)phenyl)-2-cyanoacrylic acid (**G4**). Compound **9** (0.49 g, 0.50 mmol), cyanoacetic acid (0.09 g, 1.00 mmol) and piperidine (0.04 g, 0.50 mmol) were put into a three-necked 100 mL round bottom flask. Degassed chloroform (50 mL) was introduced into the flask and the resulting mixture was refluxed for

4 h. After cooling down the reaction to room temperature, the solvent was evaporated and the residue was purified by column chromatography (SiO₂, CH₂Cl₂/MeOH = 20/1 v/v) yielding **G4** (0.25 g, 47%) as a purple solid. ¹H NMR (700 MHz, DMSO-d₆): δ 8.29 (s, 1H), 8.18-8.08 (m, 6H), 7.73 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 3.7 Hz, 1H), 7.05 (d, J = 8.6 Hz, 4H), 6.94 (d, J = 8.6 Hz, 4H), 6.81 (d, J = 8.1 Hz, 2H), 3.84 (d, J = 5.8 Hz, 4H); 2.74 (t, J = 6.8 Hz, 2H); 1.71-1.65 (m, 4H); 1.49-1.22 (m, 24H); 0.93-0.82 (m, 15H) ppm. Anal. calcd for C₆₄H₇₀N₄O₄S₃: C 72.83, H 6.68, N 5.31; found: C 72.77, H 6.65, N 5.28. IR (KBr): v_{max} 3445, 3041, 2954, 2924, 2854, 2223, 1697, 1588, 1504, 1236, 829 cm⁻¹.

3-(4-(5-(7-(5-(4-(*N*,*N*-Bis-(4'-(2-ethylhexyloxy)-1,1'-biphen-4-yl)-amino-phenyl)-thiophen-2-yl)benzo[2,1,3]thiadiazol-4-yl)-3-hexylthiophen-2-yl)phenyl)-2-cyanoacrylic acid (**G5**). Compound **10** (0.57 g, 0.50 mmol), cyanoacetic acid (0.09 g, 1.00 mmol) and piperidine (0.04 g, 0.50 mmol) were put into a three-necked 100 mL round bottom flask. Degassed chloroform (50 mL) was introduced into the flask and the resulting mixture was refluxed for 4 h. After cooling down the reaction to room temperature, the solvent was evaporated and the residue was purified by column chromatography (SiO₂, CH₂Cl₂/MeOH = 20/1 v/v) to obtain **G5** (0.27 g, 45%) as a purple solid. ¹H NMR (700 MHz, DMSO-d₆): δ 8.22-8.12 (m, 5H), 8.10-8.03 (m, 3H), 7.75-7.67 (m, 5H), 7.64-7.57 (m, 7H), 7.16 (d, J = 7.8 Hz, 4H), 7.12 (d, J = 8.1 Hz, 2H), 7.01 (d, J = 7.8 Hz, 4H), 3.89 (d, J = 5.9 Hz, 4H); 2.77 (t, J = 6.9 Hz, 2H); 1.73-1.66 (m, 4H); 1.48-1.23 (m, 24H); 0.92-0.81 (m, 15H) ppm. Anal. calcd for C₇₆H₇₈N₄O₄S₃: C 75.59, H 6.51, N 4.64; found: C 75.59, H 6.56, N 4.65. IR (KBr): v_{max} 3435, 3032, 2955, 2923, 2854, 2217, 1597, 1491, 1244, 820 cm⁻¹.

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Highlights

New D-A- π -A organic sensitizers were structurally tailored to enhance DSSC performances. TD-DFT calculations were performed for providing insights into the excitation dynamics. Photophysical and electrochemical properties are in good agreement with the theoretical results. DSSC performances up to 9.8% in terms of PCE were obtained.

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