

Sustainability of Organic Dye-Sensitized Solar Cells: The Role of Chemical Synthesis

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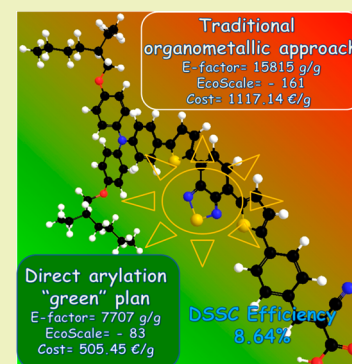
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Supporting Information

ABSTRACT: The synthesis of a novel and efficient π -extended D-A- π -A organic sensitizer (G3, $\eta = 8.64\%$) for dye-sensitized solar cells has been accomplished by applying the green chemistry pillars, aiming at overriding traditional routes involving organometallic intermediates with innovative synthetic strategies for reducing the waste burden and dye production costs. It has been demonstrated that the obtaining of a complex target sensitizer can be exclusively pursued via direct arylation reactions. Green metrics comparison with those of a traditional synthetic pathway clearly indicates that the new approach has a lower environmental impact in terms of chemical procedures and generated wastes, stressing the importance of the synergy between the molecular design and the synthetic plan in the framework of environmentally friendly routes to back up sustainable development of third-generation photovoltaics. Additionally, the stability of the G3-based photovoltaic devices was also investigated in aging tests on large area devices, evidencing the excellent potentialities of the proposed structure for all practical applications involving inorganic semiconductor/organic dye interfaces.

KEYWORDS: Green chemistry, dye-sensitized solar cell, direct arylation reactions, smart panels



INTRODUCTION

In the highly active search for potential alternatives to the available photovoltaic technologies, dye-sensitized solar cells (DSSCs) continue to attract worldwide attention due to several aspects such as their high light-to-energy conversion efficiencies, ease of fabrication and their unique peculiarity in terms of transparency and coloration, enabling the design of efficient colorful devices and smart panels also amenable to building integration.^{1,2} In its typical configuration, a classic DSSC is constituted by a photoanode (typically a suitably dye-sensitized semiconducting film of mesoporous titania), a counter-electrode and an electrolyte containing a redox couple.³ A great share of the research on DSSCs is focused on the dye, which has the role of harvesting photons and favoring the electron injection into the titania conduction band.⁴ However, the choice of the sensitizer heavily influences not only the device efficiency but also most of the environmental impact and costs related to the technology production.⁵ Therefore, with peculiar reference to the

sensitizer, although it is admissible that basic research on DSSCs should strive toward the achievement of higher and higher efficiencies, part of these efforts should also be directed toward the minimization of the environmental impact associated with the DSSCs production.

Fully organic sensitizers have demonstrated great potential in both design flexibility and amenability to optimization in terms of device performances.⁶ From the environmental viewpoint, the use organic dyes avoids the need to resort to rare heavy metals such as ruthenium or extremely toxic ones such as lead (a constituting element of perovskite-based solar cells currently in the "spotlight" for their high efficiency) for the prospected environmental aspects involving both production and postlife disposal.⁷ Among the several proposed molecular architectures, a very wide number of organic dyes has been synthesized

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according to the D- π -A concept, by putting in suitable conjugation an electron-donating group (D) and an electron-withdrawing group (A) capable of binding to the titania through an opportune π -spacer (π), the latter being the main focus of recent structural tailoring aimed at broadening the light-harvesting range.⁸ From the standpoint of synthetic chemistry, the drawback of the D- π -A concept is related to the asymmetric structure of the sensitizers, inevitably leading to a high number of synthetic steps required for the obtainment of the target molecule.

At the same time, it should be recognized that a key issue for the market breakthrough of DSSC will consist in bridging the gap between fundamental materials research and scalability. Standard laboratory practice, in fact, puts a bigger strain on the environment; moreover, it cannot always be transferred to an industrial scale. Environmental sustainability will have to be assured because the major challenges in environmental science are not only related to exploiting renewable energy sources but also to the evaluation, monitoring and minimization of the impact associated with materials chemistry behind a green technology.⁹ Thus, novel routes for organic synthesis of highly performing organic sensitizers maximizing sustainability (principally in terms of waste volumes) are highly desirable, being potentially amenable to scalability without severely impacting on the environment.

In this context, synthetic protocols based on the C-H bond activation for the construction of a π -conjugated scaffold can be considered the preferential tool to reduce the number of synthetic steps, because they permit to bypass the preparation of organometallic intermediates needed for the traditional cross-coupling methods.^{10–12} The paucity of examples employing C-H bond functionalization for the synthesis of organic sensitizers might be associated with the fact that some limitations of the available C-H activation protocols (such as the low selectivity in the presence of two or more active bonds) seem to constitute an insurmountable obstacle when applied to the assembly of the complex asymmetric structures of D- π -A organic sensitizers.^{13–16}

The idea at the basis of this work is to demonstrate that the roadmap toward highly performing dyes can be accompanied by a suitable plan of cleaner synthetic approaches, applying the green chemistry principles concerning the generation of less waste and the use of dangerous reactants. On these bases, proceeding with our studies on the role of a π -bridge extension in benzothiadiazole-based D-A- π -A sensitizers,^{17,18} a new dye (namely G3, Figure 1) was conceived utilizing the simplest available aromatic units (thiophene, benzothiadiazole, benzene) to warrant an optimal DSSC work cycle. Subsequently, a sustainable approach was substantially applied from the early

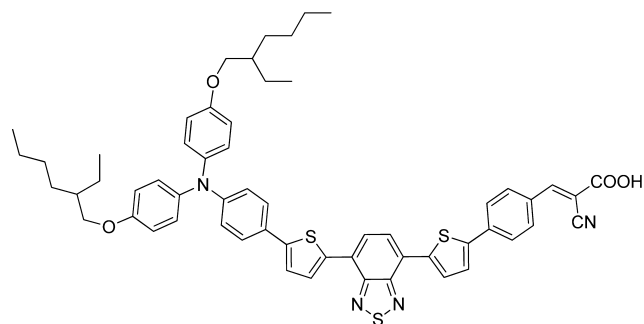


Figure 1. Chemical structure of the target sensitizer G3.

stage of the dye molecular design, because the adoption of more complex structures would have required additional synthetic steps, inevitably leading to higher waste production and costs.¹⁹ For the first time, two synthetic protocols have been compared: a traditional approach using organometallic intermediates (used for validating the hypothesis on effectiveness and potentialities of the dye) and a suitably optimized route exclusively based on direct arylation reactions. The green metrics (overall yields, E-factor,²⁰ EcoScale parameter)²¹ and the projected costs per gram of the two synthetic routes have been calculated providing guidelines that, if applied as good practice, will attenuate the environmental impact and costs related to the production of the “green” technologies employing organic materials.

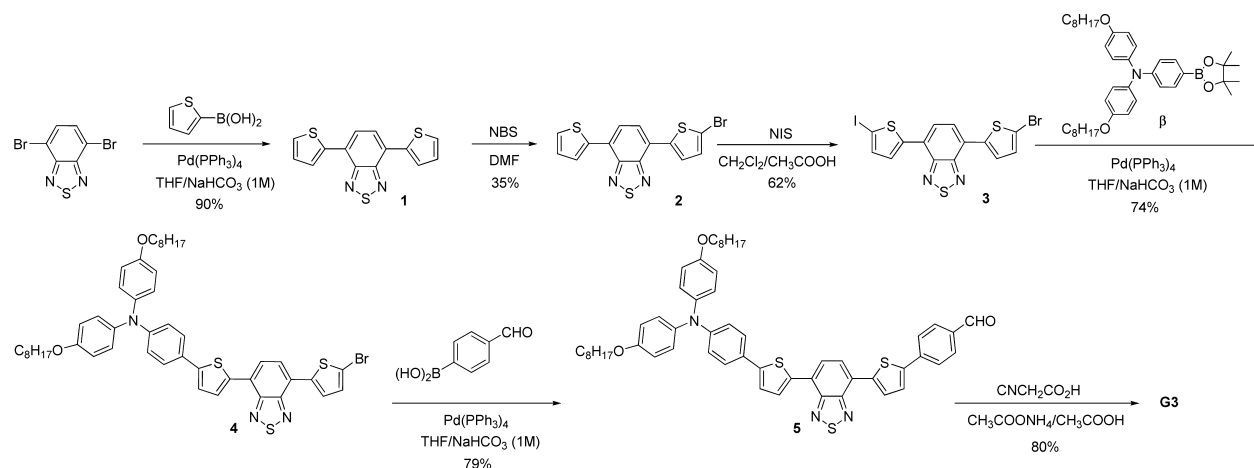
At the same time, while DSSCs continue to exhibit projected competitive prices with respect to those of the traditional silicon-based solar technologies, device stability is put at serious risk when organic sensitizers are used as light-harvesters, whereas the stability of ruthenium-based devices was estimated to be ~25 years under Southern European ambient conditions from accelerated aging tests.²² Therefore, once evaluated the environmental impact associated with its synthesis and costs, we deemed it worthwhile to also investigate the stability of the G3 sensitizer in an interesting DSSC application making use of transparent thin TiO₂ layers, which can find an evolution in aesthetically pleasant photovoltaic windows or smart panels.²³ In the case of G3-containing cells, the efficiency drop (15%) of large area devices after 1000 h of aging at 85 °C was found to be remarkably lower than that of ruthenium-based devices.

RESULTS AND DISCUSSION

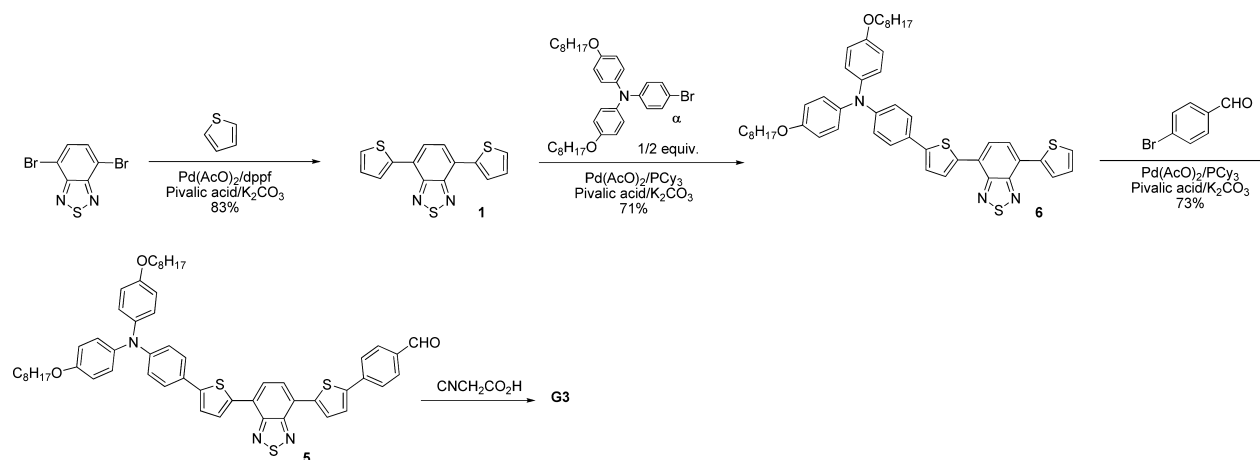
Synthesis and Environmental Aspects. The first approach for the synthesis of G3 was planned by employing traditional Pd-catalyzed Suzuki cross-coupling steps (Route A), as described in Scheme 1.²⁴ The achievement of the benzothiadiazole-containing chromophore started from the commercially available 4,7-dibromobenzothiadiazole, which was submitted to a Suzuki cross-coupling with thiophen-2-yl boronic acid yielding the corresponding dithienyl-derivative 1. Reaction of 1 with an equimolar amount of *N*-bromosuccinimide (NBS) afforded the corresponding bromo-derivative 2, which was then further halogenated by reaction with *N*-iodosuccinimide (NIS), yielding compound 3. To bind the electron-donor group to the chromophore, a Suzuki coupling between 3 and the opportune triarylamine boronic ester β (see the Supporting Information) was carried out, obtaining the intermediate 4, which, thanks to the halogen effect, is still endowed with the bromide leaving group. A subsequent Suzuki cross-coupling between 4 and 4-formylphenyl boronic acid allowed us to obtain the aldehyde-functionalized precursor 5, which was eventually converted into the target molecule G3 by a Knoevenagel reaction with cyano-acetic acid. The obtained sensitizer was then fully characterized by elemental analysis, NMR, UV-vis (Figure S1 of the Supporting Information) and electrospray ionization high resolution mass spectrometry (ESI-HRMS) that unequivocally confirmed its structure.

Next, we felt motivated in finding conditions for a synthetic scale-up of the material, and in deepening the environmental issues associated with its synthesis. Within this context, our investigation started by selecting overall yields, E-factor and EcoScale parameter associated with the G3 preparation to evaluate the sustainability of the first approach (Route A) from the chemical, waste generation and safety viewpoints,

Scheme 1. Synthetic Sequence for the Obtainment of G3 via a Traditional Approach (Route A)



Scheme 2. Synthetic Sequence Followed for the Obtainment of G3 via C–H Direct Arylations (Route B)



respectively. The details of the calculations have been reported in the Supporting Information. In particular, the high E-factor (15815.19 g/g) incompatible with a large-scale production of the dye substantiated the need for alternative and sustainable approaches.

The simplest (albeit not always sufficient) approach for reducing the environmental impact of a chemical synthesis is the diminution of the synthetic steps. To pursue this aim for the obtainment of **G3**, we deemed appropriate the setup of a synthetic sequence exclusively based on direct arylation reactions (Scheme 2) bypassing all metalation steps. On these bases, we embarked in the unprecedented synthesis of the chromophore **1**^{25–27} starting from 4,7-dibromobenzothiadiazole and activating the C–H bonds on the thiophene by using Pd(AcO)₂ as a palladium source and K₂CO₃ (1.5 equiv with respect to bromine atoms) as the base, pivalic acid (30% mol/mol with respect to bromine atoms) as a proton shuttle and tri(*t*-butyl)phosphane (2.0 equiv with respect to Pd) as the ligand. The initial screening of reaction conditions (Table 1) involved the solvent and the relative amount of thiophene. In the first attempts, to improve the reaction yields, the influence of thiophene excess (entries 1–3) was evaluated in toluene as the solvent. Unfortunately, under these conditions, the reaction was scarcely selective, probably because, after arylation of the first activated 2-position of the thiophene unit, the thiophene 5-position of the formed intermediate becomes more reactive

Table 1. Tuning of the Reaction Conditions for the Obtainment of **1** via Direct Arylation

entry	solvent	thiophene equiv ^a	ligand	yield (%) ^b
1	toluene	1.0	<i>t</i> -Bu ₃ P	traces
2	toluene	5.0	<i>t</i> -Bu ₃ P	8
3	toluene	10.0	<i>t</i> -Bu ₃ P	14
4	DMF	10.0	<i>t</i> -Bu ₃ P	traces
5	DMSO	10.0	<i>t</i> -Bu ₃ P	traces
6	thiophene	20.8	<i>t</i> -Bu ₃ P	35
7	thiophene	20.8	Cy ₃ P	38
8	thiophene	20.8	Ph ₃ P	47
9	thiophene	20.8	dppf	78
10	thiophene	20.8	dppf	83

^aPer bromine atom. ^bIsolated yields by chromatography or crystallization.

toward direct arylation, leading, as monitored by thin layer chromatography, to the formation of a significant amount of higher oligomers most likely with a thiophene-benzothiadiazole alternating structure. Increasing the polarity of the reaction medium (entries 4 and 5) did not lead to improvement of the reaction selectivity. It is reasonable to suppose that the acidity of the thiophene α -proton in the thiophene-benzothiadiazole segment (as well as in its higher homologues) is stronger than the acidity of the α -protons in isolated thiophene, due to the presence in the former of a strong electron-withdrawing unit²⁸

such as benzothiadiazole. Presumably, this aspect makes thiophene less prone toward the hydrogen abstraction step needed for the direct arylation and is responsible for the scarce selectivity of the reaction under these conditions.

By contrast, if the reaction is carried out in thiophene as the solvent (11.4 mL per gram of dibromobenzothiadiazole, 20.8 equiv per bromine atom, entry 6), the reaction yield increases to 35%. The strong thiophene excess quenched the side reactions by mass action, increasing the selectivity of the process, while the moderate yield seems to be associated with catalyst deactivation, which hampered a complete substrate conversion. Therefore, the subsequent efforts aimed at improving the reaction course were directed to the search for more robust catalytic systems by opportunely changing the phosphane ligand. From the ligand screening (entries 6–10), it was apparent that aryl phosphanes are more performing than aliphatic ones and that bidentate ligands (dppe and dppf) were the most appropriate for this reaction. The reaction carried out in the presence of dppf as the ligand allowed the obtainment of **1** in 83% isolated yield.

To reduce the waste burden deriving from the reaction, we focused particular attention on the workup procedure optimization: the excess solvent (thiophene) was removed by distillation. Moreover, the product was conveniently isolated by direct precipitation from a minimum amount of a water/ethanol mixture (due to the high solubility in this medium of K_2CO_3 , pivalic acid and of the byproduct KBr) followed by crystallization from ethanol. The ease of the purification step was substantially due to the absence of organic byproducts deriving from side reactions. Notably, the thiophene excess recovered by distillation was efficiently recycled for further preparation of **1** via C–H bond activation, obtaining the same results in terms of yields and purity of the target compound **G3**.

The E-factor calculation (see the Supporting Information) for this specific step of Route B (namely the obtainment of the building block **1**) returned a value of 83.53 g/g, which was approximately one-sixth of that obtained for Route A (478.57 g/g), representing a great improvement in terms of waste production for the obtainment of the same product. In this context, it is worth noting that the E-factor calculation for the obtainment of **1** in Route A is underestimated since it does not take into account that the use of previously dried and distilled solvents (such as toluene, DMF or DMSO) inevitably leads to further waste production. This consideration confers an added-value to the direct arylation protocol proposed in Route B.

Next, the behavior of **1** in direct arylation reactions was thoroughly investigated, in order to assess the environmental sustainability of an asymmetric structure assembly via subsequent C–H bond activations. As described in Scheme 2, it was decided to first bind the donor-containing triarylamine group onto the benzothiadiazole-based chromophore by reacting **1** with the bromo-derivative α using the standardized $Pd(AcO)_2/PCy_3$ catalytic system, in order to warrant the obtainment of a soluble reaction product. The screening was carried out (Table 2) by varying the **1**/ α molar ratio. Differently from the other substrates containing two identical C–H activated positions thus far explored in direct monoarylations (thiophene or bithiophene), in this case, it was found that the use of 2.0 equiv of **1** with respect to α is sufficient to ensure a satisfactory yield (71% with respect to the limiting reactant).

From an insight of the results reported in Table 2, it can be concluded that the reactivity of the active C–H bonds in **1** is

Table 2. Products Distribution of the Reaction between **1 and α via Direct Arylation Reactions**

entry	equiv ^a	recovered 1 (%)	monosub product (%) ^c	disub product (%) ^c
1	1.0	19	42	18
2	1.5	71 ^b	59	11
3	2.0	80 ^b	71	traces

^aEquiv of **1** with respect to α . ^bCalculated with respect to the used excess. ^cIsolated yields with respect to the limiting reactant (α).

comparable with that in **6**, because the use of 1.0 equiv of **1** with respect to α (entry 1) led to a nearly statistical products distribution. At the same time, the use of 2.0 equiv of **1** with respect to α constitutes the suitable compromise between yield maximization, minimization of waste production deriving from the reaction itself and the use of a reagent excess (with the relative waste burden connected with the synthesis of **1**). Under these conditions, in fact, the excess amount of the fine chemical **1** did not hamper the reaction purification procedures and, remarkably, most of the excess (80%) of **1** could be recovered and only traces of the disubstituted product were formed. Although the use of an excess of **1** led to an increase of the E-factor for this step, it is anyway proved the sustainability of the proposed Route B protocol not only for potential large scale applications, but also as a good practice for laboratory scale synthesis, applicable to a wide library of potentially similar structures to be synthesized.

The pathway toward the synthesis of **G3** exclusively via direct arylation reactions was further pursued by proving the reactivity of the asymmetric compound **6** in the presence of 4-bromobenzaldehyde to afford the aldehyde precursor **5**. It was found that the yield of the reaction using the $Pd(AcO)_2/PCy_3$ catalytic system was 73%.

Green metrics for **G3** were also calculated for the synthetic Route B and compared to those obtained for the conventional approach (Route A), and are summarized in Table 3. A first remark concerns the overall yield of Route B, which is noticeably higher with respect to Route A, reflecting the lower amount of synthetic steps. Regarding the environmental issues deriving from the comparison between two different synthetic approaches, a preliminary consideration has to be made: the comparison of E-factor values obtained for different approaches using different raw materials for the obtainment of the same product should be carried out very carefully. In fact, the proposed step-by-step assembly of the target molecule in Route A does not take into account that, although commercially available, thiophen-2-yl boronic acid and 4-formylphenyl boronic acid require further synthetic steps in order to be prepared, starting from the relevant raw materials (that instead are directly used as reactants in Route B), thus increasing the waste burden associated with Route A. At the same time, in the case of C–H activation reactions, a suitable combination of

Table 3. Green Metric and Cost Summary of the Two Processes for the Obtainment of the Final Sensitizer **G3**

entry	Route A (traditional approach)	Route B (C–H activation)
overall yield (%)	1.7	10.7
E-factor (g/g)	15815.19	7706.91
EcoScale parameter	−161.2	−82.7
cost (€/g)	1117.14	505.45

chemicals has to be used to generate the catalytic system, that differs from the simple $\text{Pd}(\text{PPh}_3)_4$ employed in Suzuki cross couplings. Any of the used commercial reactant has an environmental impact that cannot be evaluated by the E-factor calculation of individual reaction steps.

To tag this issue, it can be considered that the cost of a fine chemical can be useful for an approximated evaluation of the environmental impact associated with its employ, because the sale price of a fine chemical is composed also by a portion related to the waste disposal consequent to its production.²⁹ With this aim, although it should be possible to obtain lower published catalogue prices for all raw materials by negotiation, the cost of all intermediates was established on the only basis of the currently available raw materials prices. On these basis (see the Supporting Information), we evaluated the projected final cost per gram of G3 according to Route A (1117.14 €/g), which is extremely high for a fine chemical with a potential large scale application. On the other hand, the estimated cost per gram of G3 for Route B was 505.45 €/g, representing a great improvement (Table 3). Although not directly related to environmental impact, the synthetic choices leading to very significant cut-down in costs are necessary in the perspective of conferring competitiveness to the DSSC technology.³⁰ Great advantages were also obtained in terms of waste production, since the E-factor calculation for Route B (7706.91 g/g) is halved with respect to that obtained for Route A. Eventually, an additional important tool for environmental impact assessment of a process is the evaluation of the EcoScale parameter, the calculation of which includes issues such as toxicity and hazards related to the use of reagents and solvents, price, process setup and purification procedures. A higher EcoScale factor denotes a better process. The values obtained for Route A and B (reported in Table 3, albeit both very low (−161.2 and −82.7 for Route A and B, respectively)), due to the high number of synthetic steps, it is evident how Route B, based on the C–H activation pathway, is extremely favorable with respect to the conventional approach.

Photovoltaic Properties and Device Stability. The photovoltaic potentialities of G3 have been tested by constructing a series of liquid electrolyte DSSC devices; the best figures of merit are reported in Figure 2. The power conversion efficiency value ($\eta = 8.64\%$) exhibited by G3 can be

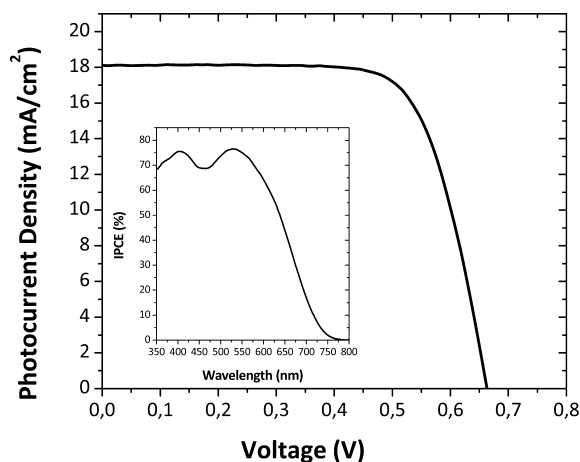


Figure 2. J – V curve of G3-based solar cell under 1.0 sun illumination ($J_{\text{SC}} = 18.11 \text{ mA/cm}^2$, $V_{\text{OC}} = 0.663 \text{ V}$, $\text{FF} = 0.72$). Inset: incident photon-to-current conversion efficiency (IPCE) of G3-based solar cell.

considered remarkably high, since it outperforms that of the ruthenium-based N719 dye⁴ (exhibiting an average efficiency of 8.3% in our laboratories) commonly used as a reference in DSSCs. Taking into consideration the very encouraging results in terms of efficiency, we felt motivated to investigate the stability of the G3-based solar cells. To this aim, the performances of large-area transparent DSSC prototypes (illustrated in Figure S2 and S3; details on device preparation are given in the Supporting Information) were evaluated before and after an aging test (1000 h at 85 °C in variable ambient humidity conditions) and, again, compared to those of the N719-based standard.

Before the aging procedure, open-circuit voltage (V_{OC}) and short-circuit current (J_{SC}) were found to be practically the same for both cells, independently of the employed dye (G3 or N719); the N719-based cells, however, showed a higher fill factor (FF) leading to slightly higher overall efficiencies (Figure 3A, Table S1 of the Supporting Information). After 1000 h of

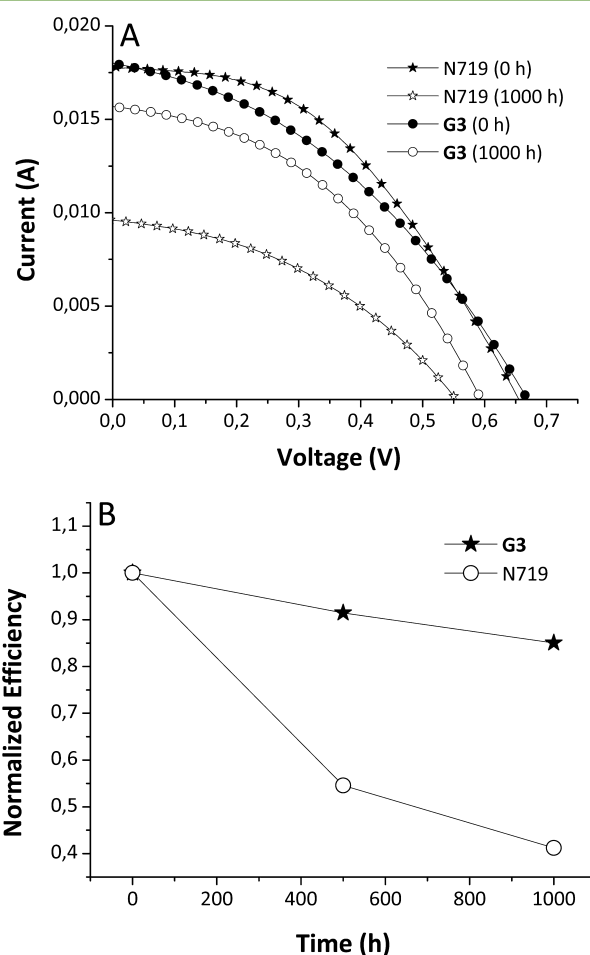


Figure 3. (A) I – V curves for the two dyes before and after 1000 h aging at 85 °C (potential scan direction from high to low voltages). (B) Efficiency decay vs time during the aging process.

aging, the N719-based cell showed a 59% efficiency drop, whereas the efficiency decrease of the G3-based device was only 15% (Figure 3B).

To interpret these data, it is necessary to consider that water diffusion is possible during prolonged aging in the absence of a humidity control system through the external seals at the constant aging temperature. This situation, giving more

information on long-term stability for a selected dye, suggests that G3-based devices are less sensitive to water contamination with respect to N719-based ones. The reason for this behavior can be explained by the trend of circuit resistance values shown in Table 4, obtained by electrochemical impedance spectroscopy.

Table 4. Data Fitting from EIS Plots^a

	G3		N719	
	0 h	1000 h	0 h	1000 h
time	0 h	1000 h	0 h	1000 h
Rct (ohm × cm ²)	9.53	9.60	8.77	14.06
Rrec (ohm)	0.71	0.59	1.72	1.34
Rd (ohm)	2.05	2.55	2.24	3.82

^aRct: charge transfer resistance at Pt layer. Rd: diffusion resistance of the redox couple in the electrolyte. Rrec: recombination resistance at the TiO₂/dye–electrolyte interface.

copy (EIS, see the Supporting Information for details, Figure 4). These values are strictly related to each other and their variation with time, is thought to be dependent on three main reasons: (i) lowering of Pt-based counter-electrode catalytic activity, (ii) dye detachment from the TiO₂ surface and (iii) electrolyte bleaching (decreasing I₃⁻ concentration in the electrolyte). Recombination resistance (Rrec) decrease suggests a recombination rate increase of the injected electrons onto the TiO₂ surface with the oxidized forms of the redox couple present in the electrolyte, due to a detachment of the dye from the photoanode.³¹ It can be reasonably supposed that this drawback is due to the hydrolysis of the titanium carboxylate bonds between the dye and the TiO₂ surface, promoted by water traces. In the case of N719, along with the Rrec decrease, a strong decrease of the value of the short circuit current (*I*_{SC}) is observed. This observation can be related to two effects, both caused by the interaction with water: dye detachment from the TiO₂ surface and dye modification (NCS → H₂O ligand exchange).^{32,33}

To further substantiate the water effect, we observed that the diffusion resistance (Rd) increases in both cases after the aging process, which can be due to electrolyte bleaching with time, as already reported in the literature.³⁴ Bleaching of the electrolyte

may be due to formation of iodate in the presence of water. To explain the larger Rd increase for N719-based devices, it can be taken into account the plausible ligands substitution (NCS → I₂ ligand exchange) in the N719 dye, determining a depletion of the I₂ species within the electrolyte. An increase of the charge transfer resistance (Rct) at the platinum electrode can be caused by the buildup of a partially blocking layer on the Pt surface. Stray dye molecules reaching the Pt catalytic surface can reduce its ability to promote the I₃⁻ → I⁻ conversion.^{35,36} The Rct increase is quite strong in the case of N719-based devices and almost negligible in the case of G3-based ones. This result further confirms that the molecular structure of G3 is less prone to be cleaved from the TiO₂ surface with respect to N719.

CONCLUSIONS

Green chemistry concepts have been applied for the first time to the synthesis of a complex system, i.e., a D-A-π-A organic sensitizer for DSSC applications, potentially amenable to synthetic scale-up due to its high efficiency in devices. It was observed that a conventional synthetic approach based on organometallic intermediates is poorly sustainable, especially in terms of waste generation. Considerable advantages in green metrics (overall yield, E-factor and EcoScale parameter) were obtained modifying the synthetic tools of the approach rather than optimizing the single steps of the conventional protocol. The “green” approach exclusively based on direct arylation reactions exhibited synthetic challenges connected with the obtainment of the dithienylbenzothiadiazole building block as well as with its reactivity necessary for obtaining the asymmetrically substituted dye structure. These issues were addressed by suitable tuning of the experimental conditions leading to the individuation of good practice rules, which kept the projected price-per-gram of the dye extremely competitive with respect to that estimated for the conventional approach. Additionally, the stability of the G3-based photovoltaic devices was also investigated in aging tests, evidencing the excellent potentialities of the proposed structure for all the practical applications involving inorganic semiconductor/organic dye interfaces. On the basis of these results, this work aims at stirring researchers to accompany the synthesis of high efficiency conjugated materials for organic photovoltaics to an evaluation of their environmental impact. In light of the new-wave applications of organic sensitizers to hydrogen production^{37,38} expecting to stir more interest in the years to come, this target can be reached by acting on both the molecular design and the synthetic approach, conveniently exploiting the full potentialities of direct arylation reactions.

ASSOCIATED CONTENT

Supporting Information

Detailed synthetic procedures, characterization of all intermediates, detailed calculations of green metrics and cost, details of devices construction, absorption spectrum of G3. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

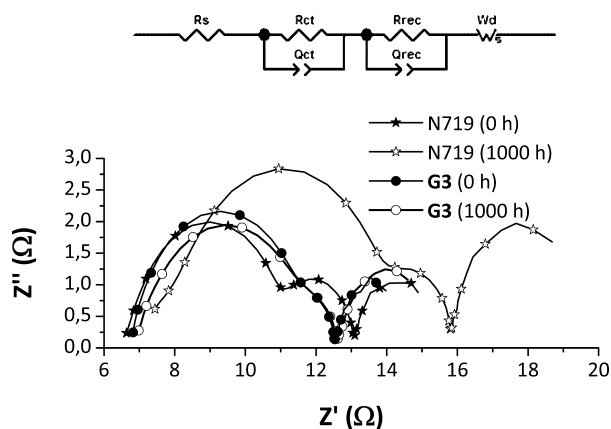


Figure 4. Nyquist plots for cells containing G3 and N719. (Top) equivalent circuit used for fitting the impedance data: Rs series resistance, Rct/Qct charge transfer and capacitance at the platinum surface (semicircle at high frequency); Rrec/Qrec recombination resistance and capacitance at the titania/dye–electrolyte interface (semicircle at intermediate frequency); Wd diffusion (semicircle at low frequency).

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REFERENCES

- (1) Zhang, S.; Yang, X.; Numata, Y.; Han, L. Highly efficient dye-sensitized solar cells: Progress and future challenges. *Energy Environ. Sci.* **2013**, *6*, 1443–1464.
- (2) Ooyama, Y.; Harima, Y. Photophysical and electrochemical properties, and molecular structures of organic dyes for dye-sensitized solar cells. *ChemPhysChem* **2012**, *13*, 4032–4080.
- (3) Mishra, A.; Fischer, M. K. R.; Bäuerle, P. Metal-Free organic dyes for dye-sensitized solar cells: From structure:property relationships to design rules. *Angew. Chem., Int. Ed.* **2009**, *48*, 2474–2499.
- (4) Yum, J.-H.; Baranoff, E.; Wenger, S.; Nazeeruddin, M. K.; Grätzel, M. Panchromatic engineering for dye-sensitized solar cells. *Energy Environ. Sci.* **2011**, *4*, 842–857.
- (5) Fakhruddin, A.; Jose, R.; Brown, T. M.; Fabregat-Santiago, F.; Bisquert, J. A perspective on the production of dye-sensitized solar modules. *Energy Environ. Sci.* **2014**, *7*, 3952–3981.
- (6) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Dye-sensitized solar cells. *Chem. Rev.* **2010**, *110*, 6595–6663.
- (7) Gao, P.; Grätzel, M.; Nazeeruddin, M. K. Organohalide lead perovskites for photovoltaic applications. *Energy Environ. Sci.* **2014**, *7*, 2448–2463.
- (8) Wu, Y.; Zhu, W. Organic sensitizers from D- π -A to D-A- π -A: Effect of the internal electron-withdrawing units on molecular absorption, energy levels and photovoltaic performances. *Chem. Soc. Rev.* **2013**, *42*, 2039–2058.
- (9) Burke, D. J.; Lipomi, D. J. Green chemistry for organic solar cells. *Energy Environ. Sci.* **2013**, *6*, 2053–2066.
- (10) He, C.-Y.; Wu, C.-Z.; Zhu, Y.-L.; Zhang, X. Selective thienylation of fluorinated benzothiadiazoles and benzotriazoles for organic photovoltaics. *Chem. Sci.* **2014**, *5*, 1317–1321.
- (11) Zhang, J.; Chen, W.; Rojas, A. J.; Jucov, E. V.; Timofeeva, T. V.; Parker, T. C.; Barlow, S.; Marder, S. R. Controllable direct arylation: Fast route to symmetrical and unsymmetrical 4,7-diaryl-5,6-difluoro-2,1,3-benzothiadiazole derivatives for organic optoelectronic materials. *J. Am. Chem. Soc.* **2013**, *135*, 16376–16379.
- (12) Schipper, D. J.; Fagnou, K. Direct arylation as a synthetic tool for the synthesis of thiophene-based organic electronic materials. *Chem. Mater.* **2011**, *23*, 1594–1600.
- (13) Kang, X.; Zhang, J.; O’Neil, D.; Rojas, A. J.; Chen, W.; Szymanski, P.; Marder, S. R.; El-Sayed, M. A. Effect of molecular structure perturbations on the performance of the D-A- π -A dye sensitized solar cells. *Chem. Mater.* **2014**, *26*, 4486–4493.
- (14) Kang, X.; Zhang, J.; Rojas, A. J.; O’Neil, D.; Szymanski, P.; Marder, S. R.; El-Sayed, M. A. Deposition of loosely bound organic D-A- π -A’ dyes on sensitized TiO₂ film: A possible strategy to suppress charge recombination and enhance power conversion efficiency in dye-sensitized solar cells. *J. Mater. Chem. A* **2014**, *2*, 11229–11234.
- (15) Jiang, S.; Fan, S.; Lu, X.; Zhou, G.; Wang, Z.-S. Double D- π -A branched organic dye isomers for dye-sensitized solar cells. *J. Mater. Chem. A* **2014**, *2*, 17153–17164.
- (16) Feng, Q.; Zhang, Q.; Lu, X.; Wang, H.; Zhou, G.; Wang, Z.-S. Facile and selective synthesis of oligothiophene-based sensitizer isomers: An approach toward efficient dye-sensitized solar cells. *ACS Appl. Mater. Interfaces* **2013**, *5*, 8982–8990.
- (17) Grisorio, R.; De Marco, L.; Agosta, R.; Iacobellis, R.; Giannuzzi, R.; Manca, M.; Mastrotrilli, P.; Gigli, G.; Suranna, G. P. Enhancing dye-sensitized solar cell performances by molecular engineering: Highly efficient π -extended organic sensitizers. *ChemSusChem* **2014**, *7*, 2659–2669.
- (18) Agosta, R.; Grisorio, R.; De Marco, L.; Romanazzi, G.; Suranna, G. P.; Gigli, G.; Manca, M. An engineered co-sensitization system for highly efficient dye solar cells. *Chem. Commun.* **2014**, *50*, 9451–9453.
- (19) Po, R.; Bernardi, A.; Calabrese, A.; Carbonera, C.; Corso, G.; Pellegrino, A. From lab to fab: How must the polymer solar cell materials design change? – An industrial perspective. *Energy Environ. Sci.* **2014**, *7*, 925–947.
- (20) Sheldon, R. A. The E factor: Fifteen years on. *Green Chem.* **2007**, *9*, 1273–1283.
- (21) Van Aken, K.; Strekowski, L.; Patiny, L. EcoScale, a semi-quantitative tool to select an organic preparation based on economical and ecological parameters. *Beilstein J. Org. Chem.* **2006**, *2*, DOI: 10.1186/1860-5397-2-3.
- (22) Harikisun, R.; Desilvestro, H. Long-term stability of dye solar cells. *Sol. Energy* **2011**, *85*, 1179–1188.
- (23) Cannavale, A.; Manca, M.; De Marco, L.; Grisorio, R.; Carallo, S.; Suranna, G. P.; Gigli, G. Photovoltachromic device with a micropatterned bifunctional counter electrode. *ACS Appl. Mater. Interfaces* **2014**, *6*, 2415–2422.
- (24) The proposed synthetic sequence has the lowest E-factor value and highest overall yield among the traditional synthetic strategies, investigated by us. Furthermore, it avoids the use of highly toxic tin-based derivatives.
- (25) During the preparation of this paper, two articles have been published on the synthesis of **1** using direct arylation reactions, which, however, do not deal with environmental aspects associated to the synthetic protocols.
- (26) Matsidik, R.; Martin, J.; Schmidt, S.; Obermayer, J.; Lombeck, F.; Nübling, F.; Komber, H.; Fazzi, D.; Sommer, M. C–H Arylation of unsubstituted furan and thiophene with acceptor bromides: Access to donor-acceptor-donor-type building blocks for organic electronics. *J. Org. Chem.* **2015**, *80*, 980–987.
- (27) Wang, X.; Wang, K.; Wang, M. Synthesis of conjugated polymers via an exclusive direct-arylation coupling reaction: A facile and straightforward way to synthesize thiophene-flanked benzothiadiazole derivatives and their copolymers. *Polym. Chem.* **2015**, *6*, 1846–1855.
- (28) He, C.-Y.; Wu, C.-Z.; Qing, F.-L.; Zhang, X. Direct (Het)arylation of fluorinated benzothiadiazoles and benzotriazole with (Het)aryl iodides. *J. Org. Chem.* **2014**, *79*, 1712–1718.
- (29) Anderson, N. G. *Practical Process Research and Development: A Guide for Organic Chemists*; Academic Press: Waltham, MA, 2012.
- (30) Osedach, T. P.; Andrew, T. L.; Bulović, V. Effect of synthetic accessibility on the commercial viability of organic photovoltaics. *Energy Environ. Sci.* **2013**, *6*, 711–718.
- (31) Heo, N.; Jun, Y.; Park, J. H. Dye molecules in electrolytes: New approach for suppression of dye-desorption in dye-sensitized solar cells. *Sci. Rep.* **2013**, *3*, 1712–1717.
- (32) Nguyen, P. T.; Andersen, A. R.; Skoud, E. M.; Lund, T. Dye stability and performances of dye-sensitized solar cells with different nitrogen additives at elevated temperatures—Can sterically hindered pyridines prevent dye degradation? *Sol. Energy Mater. Sol. Cells* **2010**, *94*, 1582–1590.
- (33) Nguyen, H. T.; Ta, H. M.; Lund, T. Thermal thiocyanate ligand substitution kinetics of the solar cell dye N719 by acetonitrile, 3-methoxypropionitrile, and 4-*tert*-butylpyridine. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 1934–1942.
- (34) Hauch, A.; Georg, A. Diffusion in the electrolyte and charge-transfer reaction at the platinum electrode in dye-sensitized solar cells. *Electrochim. Acta* **2001**, *46*, 3457–3466.
- (35) Mastroianni, S.; Asghar, I.; Miettunen, K.; Halme, J.; Lanuti, A.; Brown, T. M.; Lund, P. Effect of electrolyte bleaching on the stability and performance of dye solar cells. *Phys. Chem. Chem. Phys.* **2014**, *16*, 6092–6100.
- (36) Macht, B.; Turrión, M.; Barkschat, A.; Salvador, P.; Ellmer, K.; Tributsch, H. Patterns of efficiency and degradation in dye sensitization solar cells measured with imaging techniques. *Sol. Energy Mater. Sol. Cells* **2002**, *73*, 163–173.

(37) Rodriguez, C. A.; Modestino, M. A.; Psaltis, D.; Moser, C. Design and cost considerations for practical solar-hydrogen generators. *Energy Environ. Sci.* **2014**, *7*, 3828–3835.

(38) Li, X.; Cui, S.; Wang, D.; Zhou, Y.; Hu, Y.; Liu, J.; Long, Y.; Wu, W.; Hua, J.; Tian, H. New organic donor–acceptor– π –acceptor sensitizers for efficient dye-sensitized solar cells and photocatalytic hydrogen evolution under visible-light irradiation. *ChemSusChem* **2014**, *7*, 2879–2888.