

Synthesis and Investigation of New Solar Cell Photosensitizers Having a Fluorazone Backbone

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Abstract: A synthetic sequence for the preparation of fully conjugated, 2,7-disubstituted fluorazone (9H-pyrrolo[1,2-a]indol-9-one) derivatives was developed, comprising Elming-Clauson-Kaas type pyrrole formation, POCI3-mediated ring closure, selective halogenation and elongation of the conjugate backbone via crosscoupling reactions. As a proof of principle, such methodology was used to prepare for the first time two organic D-π-A dyes containing the fluorazone moiety. The new compounds displayed broad absorption of visible light when adsorbed on nanocrystalline TiO₂ and electrochemical properties compatible with their employment as photosensitizers in dye-sensitized solar cells. Small-scale photovoltaic devices fabricated with the fluorazone dyes yielded power conversion efficiencies in the 2.1-2.4% range, corresponding to approx. 70% of the efficiency obtained with reference organic dye DF15 under the same conditions.

Introduction

1-Aryl-1*H*-pyrrole-containing compounds serve as an important framework for the synthesis of various complex molecules, such as chiral ligands for enantioselective catalytic reactions,^{1,2} and exhibit a wide array of biological activities.³ From an electronic standpoint, the conjugation between their aromatic and heteroaromatic rings can be significantly increased if they are fixed in the same plane in a fused ring system, as it can be observed in the case of fluorazone (9*H*-pyrrolo[1,2-a]indol-9-one) and its analogues. As a consequence, fluorazone derivatives can show interesting photochemical properties, which prompted testing of this type of compounds as photosensitizing agents in

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redox reactions.⁴ Due to its multifaceted biological activity,⁵ the preparation and functionalization of the fluorazone core have been the subject of significant synthetic efforts; however, studies concerning the extension of its conjugate system⁶ and the enhancement of its photophysical properties have so far been missing. In particular, no report describing the preparation of nonsymmetrical, donor-acceptor-type structures incorporating the fluorazone core was reported in the literature. Despite that, we reasoned that fluorazone, thanks to its planar and fused structure, could be used as a linker in conjugated (hetero)aromatic systems with potential application in organic electronics. Therefore, we designed a novel synthetic route able to provide conjugated 2,7disubstituted fluorazone derivatives through the intermediacy of the corresponding 2,7-halogenated species. As a proof of concept we applied such sequence to the preparation of D- π -A type compounds HT157 and TA1314 (Figure 1), having the fluorazone core in the central part of the molecule, and featuring a π -bridge of different length (one thiophene ring for HT157 and two for TA1314), aiming to apply them as organic photosensitizers for testing in dye-sensitized solar cells (DSSC).7,8



Figure 1. Structure of new DSSC sensitizers HT157 and TA1314.

Both compounds have an alkoxy-substituted triphenylamine group as the donor part of the molecule and a typical cyanoacrylic acid anchoring group, which should make them suitable for the proposed application. Structures featuring the pyrrole ring connected to the donor group and the benzene ring attached to thiophene were preferred over their regioisomers (with an "inverted" central fluorazone core) based on the results of a TD-DFT computational analysis (see below). The synthesis, full spectroscopic and electrochemical characterization, and employment of the compounds in DSSC devices are described below.

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Scheme 1. Synthesis of fluorazones 5a and 5b.

Results and Discussion

Synthesis of Compounds HT157 and TA1314

A number of synthetic strategies have been developed for the preparation of (un)substituted-fluorazones and analogues,⁹⁻¹¹ among which the most appealing appear those featuring *ortho*-(1*H*-pyrrol-1-yl)aryl and heteroaryl carboxylic acids, in turn obtained by pyrrolation of *ortho*-aminoaryl (anthranilic) and *ortho*-aminoheteroaryl carboxylic acids, respectively.^{12–17} Our synthetic pathway was based on the preparation of two previously unreported key intermediates: 2,7-dihalo-9-oxo-9H-pyrrolo[1,2-a]indoles **5a-b**, from which the target compounds could be obtained by consecutive cross-coupling reactions in the presence of palladium catalysts, followed by the introduction of the cyanoacrylic acid moiety into the acceptor part of the molecules. Accordingly, an efficient synthesis of **5a** and **5b** was developed (Scheme 1).

The pyrrolidine amide derivatives of 5-halogeno-2-pyrrolobenzoic acid (3a or 3b) were prepared starting from the methyl ester of 5bromo- or 5-iodoanthranilic acid (1a or 1b), which was condensed with 2,5-dimethoxytetrahydrofuran (formation of 2a,b) according to the Elming-Clauson-Kaas-type pyrrole formation protocol,18 followed by reaction with pyrrolidine, which, however, proceeded only with moderate yield. Amides 3a-b were then treated with phosphorous oxychloride to yield fluorazones 4a and 4b in 81-78% yield. Regioselective monohalogenation of the β-position of the pyrrole ring was finally accomplished applying the mild conditions developed by our laboratory for the halogenation of 1phenyl-1H-pyrrole derivatives.¹⁹ It should be pointed out that 2,7dihalofluorazone derivatives such as 5a-b were never reported previously in the literature, and that in this case they could be accessed thanks to the selectivity of such monohalogenation protocol.

At this stage, the preparation of the donor and acceptor parts of dyes **HT157** and **TA1314** was carried out, with the intention of joining them to the central part of the molecule *via* efficient,



Figure 2. Structures of intermediates 6-8.

sequential cross-coupling reactions. We chose the Suzuki-Miyaura cross-coupling protocol due to its robustness and ease of application, and the fact that it had been previously applied by us to the preparation of organic DSSC sensitizers with good results.^{20,21} Thus, the mono- (**6**) and dithiophene (**7**) moieties of the acceptor parts were prepared according to slightly modified literature methods (Figure 2). Subsequently, boronic ester **8**, containing the donor portion, was assembled following a multistep literature procedure from 4-hexyloxybromobenzene, 4hexyloxyaniline and 4-iodobromobenzene *via* consecutive palladium-catalyzed *C-N* coupling reactions and Miyaura borylation (Figure 2, see SI for details on the preparation of compounds **6-8**).

For the preparation of compound **HT157**, we established that the best synthetic sequence was the one starting with the introduction of the acceptor unit: for this reason, in compound **6** the aldehyde function was protected as a cyclic acetal. Coupling of compound **5b** with boronic acid **6** under typical Suzuki-Miyaura conditions using Pd(PPh₃)₄ as catalyst proceeded selectively on the C-I bond to afford intermediate **9** in moderate yield. The latter was then subjected to reaction with boronic ester **8**: in this case, the catalyst species was generated by mixing palladium(II) acetate with 2.0 eq. of dppf, and the reaction proceeded in the presence of a sub-

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Scheme 2. Synthesis of fluorazone dyes HT157 and 13 (piperidine salt of TA1314).

stoichiometric amount of CuCl²² to provide, after acidic workup, 2,7-disubstituted fluorazone **10** in 40% yield. Direct treatment of aldehyde **10** with cyanoacetic acid and ammonium acetate in acetic acid/chloroform resulted in the desired product **HT157** as the free acid (Scheme 2).

In the case of compound **TA1314** the best yield was obtainedwhen the order of cross-coupling transformations was reversed. Thus, **5a** was reacted with boronic ester **8** in the presence of Pd(PPh₃)₄/potassium carbonate suspension in tetrahydrofuran, and product **11** was isolated from the organic solution with satisfactory yield (Scheme 2). Then, the bithiophene moiety (**7**) was connected to fluorazone **11** with a second Suzuki-Miyaura coupling, this time carried out in toluene, to obtain aldehyde **12**. It was found that condensation of the latter compound with cyanoacetic acid was best accomplished in the presence of piperidine in acetonitrile solution, leading to isolation of the desired product **TA1314** as its piperidine salt (**13**, Scheme 2). The free acid form of **TA1314** could then be released prior to

use by simple treatment of **13** with diluted aq. HCl followed by extraction in organic solvents.

Optical and electrochemical characterization

With compounds **HT157** and **TA1314** in hand, we carried out their optical and electrochemical characterization. The relevant results are reported in Table 1. Initially, we recorded their UV-Vis absorption spectra in dichloromethane solution (Figure 3a). Both dyes showed a relatively wide absorption band in the visible region covering the range between 300 and 550 nm: in each case the spectrum displayed two main absorption peaks, likely arising from different electronic transitions. While the first peak had almost the same position for both dyes (352 nm for **HT157** and 349 nm for **TA1314**), the second one was significantly red-shifted in the case of the latter compound (400 nm for **HT157** vs. 444 nm for **TA1314**), which could be obviously attributed to its longer conjugated structure (for a detailed computational analysis, see below). Both compounds absorbed light quite intensely, and their

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Figure 3. (a) UV-Vis absorption spectra of compounds HT157 (red squares) and TA1314 (blue circles) in CH_2Cl_2 solution; concentrations: HT157 - 2.38 × 10⁻⁵ M, TA1314 - 2.02 × 10⁻⁵ M. (b) Tauc plots for compounds HT157 and TA1314; intersection of the fitting straight line with the horizontal axis provides an estimation of the compounds optical band-gaps. (c) Normalized UV-Vis absorption spectra of compounds HT157 and TA1314 adsorbed on nanocrystalline TiO₂, obtained by difference from the spectrum of the bare semiconductor. (d) Cyclic voltammetries of compounds HT157 and TA1314 obtained in in CH_2Cl_2 solution.

Table 1. Optical and electrochemical characterization data for compoundsHT157 and TA1314.						
Comp.	λ _{max} (sol) [nm]ª	ε × 10 ⁴ [M ⁻¹ cm ⁻¹]	E ₀₋₀ [eV] ^b	λ _{max} (TiO ₂) [nm]	E _{ox} [V]	E* _{ox} [V] ^c
HT157	400	3.56	2.75	389	1.02 ^d	-1.73
TA1314	444	3.96	2.47	386	1.01 ^{<i>d</i>}	-1.46

[a] Measured in CH₂Cl₂ solution. [b] Estimated from the corresponding Tauc plot. [c] Determined from the equation: $E^*_{ox} = E_{ox} - E_{0.0}$. [d] Potentials vs. NHE. They were obtained by adding 0.2 V to potentials vs. the Ag/AgCl (sat. KCl) reference electrode used in the study.

molar extinction coefficients reached the respectable values of $3.5-4.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The optical band gap of the dyes could be estimated from their absorption spectra by calculating the corresponding Tauc plot Figure 3b),²³ and resulted of 2.47 eV for **TA1314** and 2.75 eV for **HT157**.

The optical properties of the new dyes were also measured after adsorption on a nanocrystalline TiO_2 film, similar to that employed in a typical DSSC device (see Experimental Section for details on film deposition). As can be seen from their spectra (Figure 3c), both dyes exhibited a significant blue-shift upon adsorption on the

semiconductor layer, which was much more pronounced in the case of compound **TA1314** (58 nm vs. only 11 nm for **HT157**). Such hypsochromic shift could be attributed to the formation of H-aggregates on TiO_{2} ,²⁴ which appears to be much more severe for compound **TA1314**, probably due to its longer and flatter structure around the acceptor region, resulting from the introduction of an extra thiophene ring. The absorption spectra of both compounds were remarkably wide, extending well above 600 nm, which proved positive in view of their potential use in DSSCs. **TA1314** displayed a slightly broader band compared to **HT157**, in agreement with the shape of the spectra recorded in solution.

Finally, characterization of the dyes was completed by measuring their oxidation potential at the ground state (E_{ox}) by means of cyclic voltammetry (Figure 3d). Such measurement was carried out to determine if the new compounds were able to participate to the electron injection and regeneration processes occurring in a DSSC (see below for a brief discussion).⁷ E_{ox} value was determined by averaging the anodic and cathodic peak potentials. As could be expected from their very similar structure and identical donor groups, the compounds presented very close E_{ox} values, in the range of 1.01-1.02 V vs. NHE. As a consequence, both sensitizers appeared to provide ample driving force (more than 0.6 V) for the ground state regeneration reaction, given the redox potential of the I^{-}/I_{3}^{-} couple typically used in the electrolyte (0.35 V vs. NHE).²⁵ The excited state oxidation potential (E^*_{ox}) of

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the dyes was estimated from the difference between their optical band-gap and their ground state oxidation potential ($E_{0-0} - E_{ox}$), and was found to be -1.73 V for **HT157** and -1.46 V for **TA1314**, respectively. Such values were largely sufficient to ensure effective electron injection from the excited dyes into the conduction band of TiO₂, thus making the new compounds suitable for employment in DSSC devices.

Computational analysis

To better understand the results of the dyes optical and electrochemical characterization, we subjected them to computational analysis, and compared the resulting data with those obtained for our previously reported organic dye DF15 (Figure S1, Supporting Information).²⁶ First, the structures of HT157 and TA1314 were optimized in vacuo by means of DFT calculations at the B3LYP/6-31G* level, using the Gaussian 09 program package.²⁷ From this analysis, it resulted that the compounds conjugated backbones were not perfectly planar, with dihedral angles of approx. 24-26° existing between the central fluorazone moiety and the flanking phenyl and thienyl groups (see Figure S2). The values of the frontier orbital energy gaps for the computed structures were then calculated and are reported in Figure 4, while the wave function plots of the corresponding orbitals are presented in Figure S2. While the HOMO orbitals were mostly localized on the donor moiety for both dyes, and had therefore a comparable energy (in agreement with the results of cyclic voltammetry experiments, see above), the HOMO-1 orbitals extended mostly on the central tricyclic portion of the molecules, with a smaller contribution from the donor (a bit more pronounced in the case of HT157), and had an energy difference of approx. 0.2 eV. The LUMO orbitals, instead, were clearly located on the acceptor parts of both compounds, with that of TA1314 being slightly stabilized relative to that of HT157 (probably due to the longer conjugation). As a consequence, the energy gap between frontier orbitals was smaller for TA1314 compared to HT157.

Subsequently, absorption maxima (λ^{a}_{max}), vertical excitation energies (E_{exc}) and oscillator strengths (f) in CH₂Cl₂ solution were calculated on the optimized structures via time-dependent DFT (TD-DFT) at the MPW1K/6-311+G(2d,p) level (Table 2). Solvent effects have been included by using the polarizable continuum model (PCM).²⁸ Interestingly, calculations showed that the main visible band in the spectrum of both dyes was generated by a mixed transition, whose foremost component was usually not the HOMO \rightarrow LUMO, but rather the HOMO–1 \rightarrow LUMO and HOMO \rightarrow LUMO+1 excitations. This was different from the situation for dye DF15, whose visible absorption was red-shifted compared to the new compounds, and was mostly attributed to a HOMO \rightarrow LUMO transition. In good agreement with the experimental spectra, the lowest-energy transition for HT157 was computed to take place at a shorter wavelength compared to TA1314, and calculated vertical excitation energies for the two dyes could reproduce the experimental values with relatively small differences (0.01-0.07 eV).

Finally, as briefly mentioned in the introduction, it should be noted that a TD-DFT computational analysis was carried out also on the regioisomeric form of dye **HT157**, featuring an "inverted" fluorazone core (*reg*-HT157, Figure S3). Similar to **HT157**, also

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Figure 4. Frontier orbital energies and energy gaps for dyes DF15,²⁶ HT157 and TA1314. The wave function plots of the orbitals are presented in Figure S2.

Table 2. Experimental (λ^{exp}_{max}) and computed (MPW1K/6-311+G(2d,p)) (λ^{a}_{max}) absorption maxima, oscillator strengths (*f*) and vertical excitation energies (E_{exc}) for dyes **HT157**, **TA1314** and **DF15** (taken as a reference) in CH₂Cl₂ solution.

Compd.	λ ^{exp} _{max} [nm]	λ ^a _{max} [nm]	<i>E_{exc}</i> [eV]	f	main transition	
HT157	400	392	3.16	0.8547	$H\!\!-\!\!1 \rightarrow L \ 63\%$	
TA1314	444	456	2.72	0.9758	$\begin{array}{l} H \rightarrow L\text{+1} \hspace{0.2cm} 41\% \\ H\text{-1} \rightarrow L \hspace{0.2cm} 33\% \end{array}$	
DF15	530 ^a	533	2.33	1.5344	$H \rightarrow L$ 89%	
[a] Value taken from ref. 26						

the regioisomeric compound showed a visible absorption band mostly due to a HOMO–1 \rightarrow LUMO transition. However, the band gap was larger than that of **HT157** (3.14 eV vs. 3.03 eV), and the HOMO–1 orbital was only located on the π -bridge and acceptor group, thus reducing the degree of charge transfer upon photoexcitation (Figure S3). Since no clear advantages against the original dyes could be appreciated from the computational analysis, the synthesis of the regioisomeric forms of compounds **HT157** and **TA1314** was not pursued further.

Photoelectrochemical Measurements

As mentioned above, we intended to test compounds **HT157** and **TA1314** as organic photosensitizers for dye-sensitized solar cells (DSSC).⁷ In such devices, a dye (organic or organometallic in nature) is used to sensitize a wide band-gap inorganic semiconductor (most commonly TiO_2) towards the absorption of

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Figure 5. Current-voltage curves for compounds HT157 (red squares), TA1314 (blue circles) and reference compound DF15 (black triangles), recorded in the absence (a) and presence (b) of CDCA as a disaggregating agent.

Table 3. Photovoltaic and electrochemical parameters for DSSCs built with dyes HT157, TA1314 and DF15.						
Compound	CDCA	J _{sc} [mA cm ⁻²]	V _{oc} [mV]	ff [%]	η [%]	R3 [Ω] ^b
117457	-	4.6±0.2	635±5	70±1	2.09±0.10	22.4
H1157	+*	4.5±0.3	639±7	74±2	2.13±0.08	23.4
TA4044	-	5.1±0.2	610±2	72±1	2.26±0.12	16.5
TA1314	+*	5.2±0.6	629±7	73±1	2.39±0.26	16.1
DE15	-	6.6±0.1	672±5	72±1	3.17±0.09	18.1
0513	+ª	7.1±0.2	672±4	70±1	3.40±0.10	18.9

[a] Obtained by staining the photoanode with a dye solution containing 2 mM CDCA. [b] Determined by electrochemical impedance spectroscopy (EIS) measurements (see text for discussion).

visible light: transfer of an electron from the photoexcited dye to the semiconductor (also called "electron injection") represents the key charge-separation step taking place within the cell. Regeneration of the dye from a suitable redox shuttle must take place in order to close the circuit, allowing production of an electric current. Both these steps require a precise alignment of energy levels among all cell components²⁹ which, in the present case, was ensured by the results of the electrochemical measurements described above.

The complete cell assembly procedure is reported in the Experimental Section. Briefly, photoanodes were prepared by deposing a TiO₂ blocking layer on a conductive glass (FTO) sheet by spin-coating of a TiCl₄ alcoholic solution, and then screen-printing a 6 µm thick nanocrystalline TiO₂ film using a commercial paste (Solaronix T/SP), which was then subjected to thermal sintering; the preparation procedure was completed by spin-coating a second time a TiCl₄ alcoholic solution and then sensitizing the electrode by immersion in a 0.2 mM solution of the relevant dye. Counter-electrodes were prepared by drilling a hole in the glass sheet for the subsequent electrolyte filling and

depositing a Pt-layer on the conductive side *via* sputtering, followed by thermal treatment. Cell assembly was then completed by sandwiching the photo-anode and the counter-electrode with a Surlyn[®] sealing gasket and vacuum cell filling (through the predrilled hole) with a commercial electrolyte containing the iodide / triiodide redox couple (Solaronix Z-100).

Photoanode sensitization was carried out either in the presence or in the absence of chenodeoxycholic acid (CDCA, 2 mM), which was used as a disaggregating agent. In addition, measurements were performed with our previously reported organic dye **DF15** as well, which was used as a reference. The corresponding J-V curves are reported in Figure 5, while the relevant photovoltaic parameters are provided in Table 3.

Considering first the results obtained without CDCA (Figure 5a), it can be observed that cells built with the two new dyes gave similar efficiencies, with **TA1314** yielding a slightly higher value, and were characterized by excellent fill factors. While **HT157** produced a higher photovoltage, **TA1314** gave a higher current density, which could be due either to its superior light-harvesting efficiency (Figure 3a,c) or to a more efficient electron injection into

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Figure 6. IPCE curves for compounds HT157 (red squares), TA1314 (blue circles) and reference compound DF15 (black triangles), recorded in the absence (a) and presence (b) of CDCA as a disaggregating agent.



Figure 7. (a) Equivalent circuit of DSSC used for EIS curve fitting. (b) Nyquist plot for EIS measurements of cells built in the absence of CDCA, together with fitting curves. (c) Nyquist plot for EIS measurements of cells built in the presence of CDCA, together with fitting curves. In both (b) and (c) plots: HT157, red squares; TA1314, blue circles; DF15, black triangles.

the semiconductor (see below the description of EIS measurements for a discussion). Addition of CDCA to the sensitizing bath (Figure 5b) had a very small effect on the efficiency of the **HT157**-containing cell, while a somewhat more pronounced influence could be observed for **TA1314**, resulting in the best η value of 2.39%: such performance improvement could be due to a better suppression of aggregation, which, in the case of **TA1314**, seemed more relevant than for **HT157**, as indicated by the large blue-shift of its absorption spectrum on TiO₂ relative to that in solution (see above). Finally, it should be observed that, under the conditions used in this study, dye **DF15** gave power conversion efficiencies of 3.17-3.40%, superior to those obtained with the new fluorazone sensitizers, with the best efficiency

measured for TA1314 reaching approx. 70% of that recorded with DF15.

Although the efficiencies obtained in this study were not very high when compared to the best results reported in the literature, it must be observed that some of the conditions employed here (i.e.: absence of a TiO₂ scattering layer, use of a relatively thin TiO₂ film and a commercial $1^{-}/I_{3}^{-}$ electrolyte) were far from those required to achieve record efficiencies, and were mainly selected to ensure a simple and reproducible cell fabrication procedure. Thus, the results obtained with sensitizers **HT157** and **TA1314** should be considered as a basis for potential future improvements, especially in view of a possible refinement of the dyes structure resulting from the data collected in this study.

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The IPCE curves recorded for the new dyes follow the same trends observed for the photocurrent produced by the cells, with **TA1314** giving rise to slightly higher values compared to **HT157** (Figure 6). It can be observed that all curves had a similar onset around 650 nm, but those relative to **TA1314** were broader and higher in the 500-600 nm range, consistent with the UV-Vis absorption spectra on TiO₂. Furthermore, the curves obtained in the presence of CDCA were very close to those recorded in the absence of the additive, in agreement with the similar current densities observed for the dyes in both cases.

Finally, DSSCs produced with the new dyes were subjected also to Electrochemical Impedance Spectroscopy (EIS) analysis³⁰ under illumination at V_{oc} , using Z-View software to fit the experimental curves with the equivalent circuit represented in Figure 7a. In such circuit, R1 represents the sum of all resistances due to the electrode layer materials and the external set-up of the circuit, while R2/CPE2 (constant-phase element) describe the properties of the counter-electrode and R3/CPE3 the properties of the TiO₂/dye/electrolyte interface. The corresponding Nyquist plots are also reported in Figure 7, both in the absence and in the presence of CDCA. Fitting the data, it is possible to obtain the value for the charge-transfer resistance at the dye-TiO₂ interface (R3 in the equivalent circuit), which is provided by the diameter of the mid-frequency semicircle in the plot. Under illumination, R3 should correlate with the photocurrent values (the lower the resistance, the higher the Jsc), provided that all other factors influencing the current are similar among different dyes. In the present case, R3 was consistently found to be lower for TA1314 than for HT157 (16.5 Ω vs. 22.4 Ω in the absence of CDCA; 16.1 Ω vs. 23.4 Ω in the presence of CDCA, Table 3): considering that dye regeneration should be almost equal for the two sensitizers since their Eox values were very close, we can thus suggest that the higher photocurrent produced by TA1314 is due to an enhanced electron injection rate caused by the smaller resistance at the TiO₂/dye interface, accompanied by a slightly superior light harvesting efficiency (as shown by its broader spectrum on TiO₂, see Figure 3c). On the other hand, the R3 values found for DF15 were intermediate between those for TA1314 and HT157 (18.1-18.9 Ω): the higher J_{sc} value of this dye should therefore mainly be attributed to a different factor, such as, for example, its stronger light absorption ability compared to the two new dyes (as highlighted by its red-shifted absorption both in solution and on TiO₂),²⁶ or a more efficient dye regeneration by the electrolyte.

Conclusions

In this paper, we reported a new methodology for the synthesis of fully conjugated molecules containing the fluorazone (9*H*-pyrrolo[1,2-*a*]indol-9-one) moiety. The synthetic sequence featured a Elming-Clauson-Kaas type pyrrole formation, a POCl₃-mediated ring closure and a selective halogenation, which allowed to access two previously unreported 2,7-dihalofluorazone derivatives. Extension of the conjugated system was then carried out by means of Suzuki-Miyaura cross-coupling reactions. The new procedure was applied to the synthesis of the first fluorazone containing D- π -A sensitizers for dye-sensitized solar cells, **HT157**

and **TA1314**. The compounds incorporated the tricyclic moiety in their middle conjugate section, where it was connected to one or two thiophene rings. The structure of the dyes was then completed by typical donor (4-alkoxy-substituted triphenylamine) and acceptor (cyanoacrylic acid) units.

Dyes **HT157** and **TA1314** both displayed intense absorption of visible light in dichloromethane solution, with the latter showing a significantly red-shifted maximum absorption peak. Moreover, their spectra on TiO_2 were much broader than those in solution, which was promising in view of the utilization of the dyes as DSSC sensitizers. In agreement with DFT computational analysis, cyclic voltammetry measurements, combined with the optical band-gap obtained from the UV-Vis spectroscopy experiments, suggested that the compounds had energy levels correctly aligned to be used in photovoltaic cells.

DSSCs built with the new dyes displayed moderate efficiencies in the 2.09-2.39% range, with **TA1314** giving the best result. The highest efficiency reached approx. 70% of that recorded with reference dye **DF15**. The successful development of an efficient synthetic route, as well as the spectroscopic and electrochemical data reported in the present study, will hopefully demonstrate useful for the design and synthesis of more optimized organic functional materials containing the fluorazone moiety.

Experimental Section

General Synthetic Remarks

All commercial starting materials were purchased from Sigma-Aldrich Kft. Hungary and Merck Kft. Hungary and were used without further purification The organometallic reactions were carried out in Schlenk-flasks under a dry nitrogen atmosphere. Solvents were typically freshly distilled or dried over molecular sieves. Tetrahydrofuran was obtained anhydrous by distillation from sodium wire after the characteristic blue colour of the in situ generated sodium diphenylketyl radical was found to persist. All reactions were monitored by thin-layer chromatography. TLC was carried out on Kieselgel 60 F254 (Merck) aluminium sheets (visualization of the product was made by exposing the plate to UV radiation or by staining it with the aqueous solution of (NH₄)₆Mo₇O₂₄, Ce(SO₄)₂ and sulfuric acid). Flash column chromatography was performed using a CombiFlash (Teledyne ISCO). Routine ¹H- and ¹³C-NMR spectra were obtained on a Bruker AV 300 or DRX 500 spectrometer. The chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (J) in Hz. Deuterated chloroform (CDCl₃) with tetramethylsilane (TMS), 1,4-dioxaned₈ and dimethylsulfoxide-d₆ (DMSO-d₆) were used as solvents, and signal positions were measured relative to the signals of TMS or solvents (δ_{TMS} = 0 ppm, $\delta_{chloroform}$ = 7.26 ppm, $\delta_{dioxane}$ = 3.53 ppm, δ_{DMSO} = 2.50 ppm for $^1H\text{-}$ NMR and δ_{TMS} = 0 ppm, $\delta_{chloroform}$ = 77.0 ppm, $\delta_{Dioxane}$ = 66.7 ppm, δ_{DMSO} = 39.4 ppm for ¹³C-NMR). Melting points were determined in capillary tubes, using a Gallenkamp melting point apparatus. High-resolution mass spectra (HRMS) were recorded on Waters LCT Premier XE spectrometer in electrospray ionization (ESI, 2.5 kV) mode, using water (0.035% trifluoroacetic acid)/acetonitrile (0.035% trifluoroacetic acid) as eluent in gradient elution (5%-95% acetonitrile); samples were prepared in acetonitrile.

Methyl5-bromo-2-(1*H*-pyrrole-1-yl)benzoate(2a).312,5-Dimethoxytetrahydrofuran (2.98 g, 22.6 mmol, 2.92 mL) was added into a
solution of methyl 2-amino-5-bromobenzoate (1a, 4.33 g, 18.8 mmol) in
glacial acetic acid (22 mL). The solution was stirred at boiling temperature
for 2 hours (TLC: hexane/ethyl acetate 3:1), then evaporated *in vacuo*. The

residue was dissolved in dichloromethane (40 mL) and washed with a 5% aqueous solution of sodium carbonate (3 x 20 mL). The organic phase was dried over sodium sulphate and concentrated *in vacuo*. The crude product (6.7 g) was purified by flash column chromatography (silica gel, hexane/ethyl acetate 3:1) to afford **2a** as a pale yellow oil. Yield: 81% (4.29 g); ¹H-NMR (500 MHz, CDCl₃): $\delta_{H} = 7.92$ (d, J = 2.4 Hz, 1H), 7.67 (dd, J = 8.5, 2.4 Hz, 1H), 7.25 (d, J = 8.5 Hz, 1H), 6.77 (t, J = 2.2 Hz, 2H), 6.31 (t, J = 2.2 Hz, 2H), 3.72 (s, 3H). Spectroscopic data are in agreement with those reported in the literature.³¹

Methyl 5-iodo-2-(1*H***-pyrrole-1-yl)benzoate (2b)**. It was prepared using the above described method starting from **1b** (5.21 g, 18.8 mmol). The product **2b** is a pale yellow oil. Yield 80% (4.92 g); ¹H-NMR (500 MHz, CDCl₃) $\delta_{H} = 8.10$ (d, J = 1.8 Hz, 1H), 7.85 (dd, J = 8.4, 1.8 Hz, 1H), 7.11 (d, J = 8.4 Hz, 1H), 6.76 (t, J = 1.9 Hz, 2H), 6.31 (t, J = 1.9 Hz, 2H), 3.71 (s, 3H). ¹³C-NMR (126 MHz, CDCl₃): $\delta_{C} = 165.9$, 141.1, 139.9, 139.1, 129.4, 128.2, 121.8, 110.1, 91.1, 52.6. HRMS (ESI): *m/z* calcd for C₁₂H₁₁INO₂ [M+H]⁺ 327.9835, found 327.9838.

(5-Bromo-2-(1H-pyrrole-1-yl)phenyl)(pyrrolidine-1-yl)methanone (3a). A solution of methylester 2a (3.0 g, 10.7 mmol) in pyrrolidine (3.0 g, 42.0 mmol, 3.5 mL) was stirred for 7 hours at 90 °C (TLC: hexane/ethyl acetate 4:1). After cooling down to room temperature, water (60 mL) and ethyl acetate (60 mL) were added. The phases were separated and the organic solution was washed with 0.1 M aqueous hydrochloric acid solution (45 mL), water (45 mL) and a 1% aqueous solution of sodium hydrogencarbonate (30 mL). The organic phase was dried over sodium sulphate and concentrated in vacuo to give **3a** as a light yellow solid, which was used in the next step without further purification. Yield: 47% (1.62 g); m.p. 92–93 °C; ¹H-NMR (300 MHz, CDCl₃): δ_H = 7.65–7.50 (m, 2H), 7.24 (d, J = 8.4 Hz, 1H), 6.93 (d, J = 2.1 Hz, 2H), 6.29 (d, J = 2.1 Hz, 2H), 3.46 (t, J = 6.8 Hz, 2H), 2.72 (br. s, 2H), 1.75 (quint, J = 6.6 Hz, 2H), 1.61 (quint, J = 6.6 Hz, 2H). ¹³C-NMR (75 MHz, CDCl₃): $\delta_{\rm C} = 165.8$, 136.3, 133.8, 133.3, 131.5, 125.7, 121.0 (2C), 120.1, 110.7 (2C), 47.1, 45.5, 25.6, 24.2. HRMS (ESI): m/z calcd for C15H16BrN2O [M+H]+ 319.0446, found 319.0453.

(5-lodo-2-(1*H***-pyrrole-1-yI)phenyI)(pyrrolidin-1-yI)methanone (3b)**. It was prepared starting from **2b** (8.37 g, 26.5 mmol), using the same method described for compound **3a**. Product **3b** was obtained as a light yellow solid, which was used in the next step without further purification. Yield: 56% (5.43 g); mp: 132–133 °C; ¹H-NMR (300 MHz, CDCI₃): $\delta_{H} = 7.89-7.62$ (m, 2H), 7.11 (d, J = 8.7 Hz, 1H), 6.93 (t, J = 2.1 Hz, 2H), 6.29 (t, J = 2.1 Hz, 2H), 3.46 (t, J = 6.7 Hz, 2H), 2.71 (br. s, 2H), 1.84–1.67 (m, 2H), 1.67–1.48 (m, 2H). ¹³C-NMR (75 MHz, CDCI₃): $\delta_{C} = 165.7$, 139.2, 137.3, 136.9, 133.9, 125.8, 120.9 (2C), 110.7 (2C), 90.9, 47.1, 45.5, 25.5, 24.2. HRMS (ESI): *m/z* calcd for C₁₅H₁₆IN₂O [M+H⁺] 367.0307, found 367.0305.

7-Bromo-9H-pyrrolo[1,2-a]indol-9-one (4a).17 A solution of 3a (2.31 g, 7.24 mmol) was stirred in phosphorous oxychloride (27.7 g, 181 mmol, 16.9 mL) for 8 h at 70 °C (TLC: hexane/ethyl acetate 3:1). The mixture was poured into ice before being extracted with toluene (100 mL). The undissolved tarry material was filtered off. The aqueous phase (500 mL) was treated at 0 °C with a concentrated solution of sodium hydroxide (50 g) in water (pH = 10), the sodium chloride precipitate was filtered of and washed with toluene. The aqueous phase was extracted with toluene (2 × 100 mL). The collected organic solutions were washed with distilled water (2 × 50 mL), dried over sodium sulphate and concentrated in vacuo to give 4a as a light brown solid. Yield: 81% (1.46 g). Further purification can be accomplished by recrystallization from toluene (15 mL) to afford a vellow solid; mp: 145–146 °C; ¹H-NMR (300 MHz, CDCl₃): δ_H = 7.66 (d, J = 1.7 Hz, 1H), 7.53 (dd, J = 8.2, 1.9 Hz, 1H), 7.06 (dd, J = 2.6, 0.6 Hz, 1H), 7.00 (d, J = 8.2 Hz, 1H), 6.80 (dd, J = 3.7, 0.6 Hz, 1H), 6.33 (dd, J = 3.7, 2.6 Hz, 1H). ¹³C-NMR (75 MHz, CDCl₃): δ_{C} = 177.9, 142.4, 136.4, 132.0, 131.9, 127.7, 119.9, 118.5, 116.5, 114.7, 111.7. HRMS (ESI): m/z calcd for C11H7BrNO [M+H]* 247.9706, found 247.9704.

7-Iodo-9*H***-pyrrolo[1,2-a]indol-9-one (4b).**¹² It was prepared from **3b** (2.65 g, 7.24 mmol), using the method described for compound **4a**. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate 4:1) to give **4b** as a light brown solid. Yield: 78% (1.67 g). Further purification can be accomplished by recrystallization from toluene (15 mL) to afford a yellow solid; mp: 182–183 °C; ¹H-NMR (500 MHz, DMSO-d₆): δ_{H} = 7.90 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.73 (d, *J* = 1.8 Hz, 1H), 7.66 (dd, *J* = 2.7, 0.6 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 6.85 (dd, *J* = 3.7, 0.6 Hz, 1H), 6.38 (dd, *J* = 3.7, 2.7 Hz, 1H). ¹³C-NMR (126 MHz, DMSO-d₆): δ_{C} = 177.0, 142.74, 142.71, 131.9, 131.3, 130.4, 122.4, 116.5, 114.5, 113.9, 89.4. HRMS (ESI): *m/z* calcd for C₁₁H₇INO [M+H]⁺ 295.9527, found 295.9545.

7-Bromo-2-iodo-9*H***-pyrrolo[1,2-a]indol-9-one (5a)**. *N*-iodosuccinimide (0.48 g, 2.12 mmol) was added into a solution of **4a** (0.50 g, 2.02 mmol) in anhydrous *N*,*N*-dimethylformamide (15 mL) and the mixture was stirred for 48 hours at 70 °C (TLC: hexane/ethyl acetate 3:1). The mixture was poured into distilled water (80 mL), the resulting precipitate was filtered off and washed with ice-cold distilled water. The residue was dissolved in ethyl acetate (20 mL) and washed with distilled water (2 × 15 mL). The organic phase was dried over sodium sulphate and concentrated *in vacuo* to give 0.68 g of crude product, which was recrystallized from isopropanol to give **5a** as orange coloured crystals. Yield 73% (0.55 g); mp: 176°C (decomp); ¹H-NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ = 7.70 (d, *J* = 1.5 Hz, 1H), 7.57 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.15 (s, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.89 (s, 1H). ¹³C-NMR (75 MHz, CDCl₃): $\delta_{\rm C}$ = 176.8, 142.0, 136.7, 132.5, 130.5, 128.1, 123.7, 122.4, 120.6, 119.1, 111.9. HRMS (ESI): *m/z* calcd for C₁₁H₄BrINO [M–H]⁻ 371.8526, found 371.8549.

2-Bromo-7-iodo-9*H*-pyrrolo[1,2-*a*]indol-9-one (5b).

bromosuccinimide (0.19 g, 1.08 mmol) was added to a solution of **4b** (0.30 g, 1.03 mmol) in anhydrous *N*,*N*-dimethylformamide (5 mL) at 0 °C and the mixture was stirred for 20 minutes at the same temperature (TLC: hexane/ethyl acetate 4:1). The mixture was poured into distilled water (60 mL), the resulting precipitate was filtered off and washed with ice-cold distilled water. The residue was dissolved in ethyl acetate (20 mL) and washed with distilled water (2 × 15 mL). The organic phase was dried over sodium sulphate and concentrated *in vacuo* to give the crude product, which was recrystallized from isopropanol to give **5b** as yellow coloured crystals. Yield: 84% (0.32 g); mp: 162–163 °C; ¹H-NMR (300 MHz, CDCl₃): $\delta_{\rm H} = 7.86$ (d, J = 1.3 Hz, 1H), 7.77 (dd, J = 8.1, 1.3 Hz, 1H), 7.09 (s, 1H), 6.88 (d, J = 8.1 Hz, 1H), 6.78 (s, 1H). ¹³C-NMR (75 MHz, CDCl₃): $\delta_{\rm C} = 177.3$, 142.9, 142.8, 133.7, 130.6, 130.4, 119.1, 115.7, 112.3, 103.7, 89.1. HRMS (ESI): *m/z* calcd for C₁₁H₄BrINO [M–H]⁻ 371.8526, found 371.8523.

2-Bromo-7-(5-(dioxolan-2-yl)thiophene-2-yl)-9H-pyrrolo[1,2-a]indol-

9-one (9). Under a nitrogen atmosphere, Pd(PPh₃)₄ (23 mg, 0.02 mmol) was added into a solution of fluorazone **5b** (0.37 g, 0,98 mmol) in degassed dry tetrahydrofuran (5 mL), followed by the addition of distilled and degassed water (2.5 mL) and dry sodium carbonate (0.21 g, 1.96 mmol). The suspension was stirred for 30 min at 40 °C before being treated with a solution of boronic acid **6** (0.29 g, 1.47 mmol) in degassed dry tetrahydrofuran (3 mL). After being stirred for 12 h at 70 °C (TLC: hexane/ethyl acetate 4:1) the mixture was quenched with distilled water (15 mL) and extracted with ethyl acetate (3 × 15 mL). The organic phase was dried over sodium sulphate and concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica gel, hexane \rightarrow hexane/ethyl acetate 5:1) to give product **9** as an orange solid. Yield: 43%, (0.17 g); mp: 169-170 °C; ¹H-NMR (500 MHz, 1,4-dioxane-d₈): $\delta_{\rm H}$ = 7.88 (d, *J* = 1.8 Hz, 1H), 7.69 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.40 (d, *J* = 0.7 Hz, 1H), 7.33 (d, *J* = 3.7 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.11 (d, *J* = 3.7 Hz,

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1H), 6.89 (d, J = 0.7 Hz, 1H), 6.03 (s, 1H), 4.09–4.01 (m, 2H), 3.98–3.90 (m, 2H). $^{13}\text{C-NMR}$ (75 MHz, 1,4-dioxane-d_8): δ_{C} = 178.6, 144.0, 143.5, 143.3, 133.3, 132.4, 131.7, 130.6, 127.9, 124.1, 122.3, 120.1, 115.2, 111.7, 103.2, 100.8, 65.8 (2C). HRMS (ESI): m/z calcd for $C_{18}\text{H}_{12}\text{BrNO}_{3}\text{S}$ [M+H]+ 401.9799, found 401.9807.

5-(2-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)-9-oxo-9H-pyrrolo[1,2a]indol-7-yl)thiophene-2-carbaldehyde (10). Under a nitrogen atmosphere, to a solution of bromide 9 (0.17 g, 0.42 mmol) in degassed dry N,N-dimethylformamide (5 mL) were added boronic ester 8 (0.48 g, 0.85 mmol), Pd(OAc)₂ (5 mg, 0.02 mmol), dppf ligand (23 mg, 0.04 mmol), copper(I) chloride (21 mg, 0.21 mmol) and dry cesium carbonate (0.55 g, 1.68 mmol). After being stirred for 16 h at 100 °C (TLC: hexane/ethyl acetate 4:1) the mixture was quenched with distilled water (10 mL) and extracted with ethyl acetate (3 x 10 mL). The organic phase was concentrated (to approximately 5 mL) and water 1 (mL) and acetic acid (100 μ L) were added to deprotect the aldehyde. After stirring for 4 h the phases were separated, the organic layer was washed with solution of 1% NaHCO₃/H₂O (5 mL), dried over sodium sulphate and concentrated in vacuo. The crude product was purified by flash column chromatography (silica gel, hexane \rightarrow hexane/ethyl acetate 5:1) to give aldehyde **10** as a red amorphous solid. Yield: 40% (0.12 g); ¹H-NMR (300 MHz, CDCl₃): δ_H = 9.87 (s, 1H), 7.90–7.61 (m, 4H), 7.44–7.21 (m, 3H), 7.14 (d, J = 8.0 Hz, 1H), 7.10–6.97 (m, 5H), 6.93 (d, J = 8.0 Hz, 2H), 6.82 (d, J = 8.1 Hz, 4H), 3.93 (t, 6.0 Hz, 4H), 1.78 (dt, J = 12.9 Hz, 6.2 Hz, 4H), 1.59–1.40 (m, 4H), 1.40–1.11 (m, 8H), 0.91 (t, J = 5.5 Hz, 6H). ¹³C-NMR (75 MHz, CDCl₃): δ_{C} = 182.6, 178.6, 155.6 (2C), 152.3, 148.2, 143.9, 142.6, 140.5 (2C), 137.4, 133.3, 132.6, 132.1, 131.0, 130.6, 126.6 (4C), 125.8 (2C), 124.9, 124.2, 122.0, 120.6 (2C), 115.4, 115.3 (4C), 111.6, 110.7, 68.3 (2C), 31.6 (2C), 29.3 (2C), 25.8 (2C), 22.6 (2C), 14.1 (2C). HRMS (ESI): m/z calcd for $C_{46}H_{47}N_2O_4S$ [M+H]⁺ 723.3257, found 723.3253.

3-(2-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)-9-oxo-9H-pyrrolo[1,2a]-indol-7-yl)thiophen-5-yl)-2-cyanoacrylate (HT157). Under a nitrogen atmosphere, to a suspension of the protected aldehyde precursor 10 (0.13 g, 0.17 mmol) in acetic acid (1.50 mL) were added cyanoacetic acid (19 mg, 0.22 mmol), ammonium acetate (3 mg, 0.04 mmol) and chloroform (3 mL). The solution was refluxed for 10 h at 100 °C (TLC: hexane/ethyl acetate 2:1). After cooling, the reaction mixture was extracted with chloroform. The organic layer was dried over anhydrous Na₂SO₄. The filtrate was concentrated under reduced pressure. Purification was performed by recrystallization in ethanol to yield HT157 as a dark red crystalline solid. Yield: 96% (0.125 g); mp: 202-203 °C; ¹H-NMR (300 MHz, DMSO-d₆): δ_{H} = 9.87 (1H, s), 8.42 (s, 1H), 8.04 (s, 1H), 7.94 (d, J = 4.5 Hz, 2H) 7.85–7.70 (m, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.41 (d, J = 8.1 Hz, 2H), 7.20 (s, 1H), 6.96 (d, J = 8.3 Hz, 4H), 6.86 (d, J = 8.3 Hz, 4H), 6.75 (d, J = 8.1 Hz, 2H), 3.90 (t, J = 6.0 Hz, 4H), 1.68 (dt, J = 13.2, 6.2 Hz, 4H), 1.45-1.35 (m, 4H), 1.35–1.22(m, 8H), 0.87 (t, J = 5.4 Hz, 6H). ¹³C-NMR (75 MHz, DMSO-d_6): δ_C = 177.8, 163.5, 157.0, 155.1 (2C), 147.2, 143.4, 140.8, 139.9 (2C), 132.5, 132.0, 131.6, 130.3, 129.8, 127.3, 126.5 (4C), 125.7, 125.7 (2C), 125.3, 125.0, 120.9, 119.7 (2C), 117.9, 116.7, 115.5, 115.4 (4C), 112.1, 111.3, 67.6 (2C), 31.0 (2C), 28.7 (2C), 25.2 (2C), 22.1 (2C), 13.9 (2C). HRMS (ESI): m/z calcd for C₄₉H₄₆N₃O₅S [M-H]⁻ 788.3164, found 788.3139.

2-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)-7-bromo-9H-pyrrolo[1,2a]indol-9-one (11). Under a nitrogen atmosphere, to a solution of fluorazone **5a** (175 mg, 0.47 mmol) in degassed dry tetrahydrofuran (3 mL) were added Pd(PPh₃)₄ (35 mg, 0.03 mmol), distilled and degassed water (1.5 mL) and dry potassium carbonate (195 mg, 1.41 mmol). The suspension was stirred for 30 min at 40 °C before being treated with a solution of boronic ester **8** (0.32 g, 0.56 mmol) in degassed dry tetrahydrofuran (3 mL). After being stirred for 24 h at 80 °C (TLC: hexane/ethyl acetate 3:1) the mixture was quenched with distilled water (15 mL) and extracted with ethyl acetate (2 × 15 mL). The organic phase was dried over sodium sulphate and concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica gel, hexane → hexane/ethyl acetate 5:1) to give bromide **11** as a red oil. Yield 56% (159 mg); ¹H-NMR (300 MHz, CDCl₃): δ_{H} = 7.85 (d, *J* = 0.9 Hz, 1H), 7.75–7.62 (m, 2H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.16 (s, 1H), 7.08 (d, *J* = 8.8 Hz, 4H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 4H), 3.94 (t, *J* = 6.5 Hz, 4H), 1.78 (dt, *J* = 14.3, 6.5 Hz, 4H), 1.46 (br. s, 4H), 1.40 – 1.28 (m, 8H), 0.91 (t, *J* = 6.1 Hz, 6H). ¹³C-NMR (75 MHz, CDCl₃): δ_{C} = 181.9, 155.7 (2C), 140.5 (2C), 137.2, 136.2, 133.2, 132.6, 130.9, 128.1, 127.0 (2C), 126.8 (4C), 125.1, 122.9, 120.4 (2C), 115.5, 115.3 (4C), 111.5, 111.3, 108.0, 68.3 (2C), 31.6 (2C), 29.7 (2C), 25.8 (2C), 22.6 (2C), 14.1 (2C). HRMS (ESI): *m*/*z* calcd for C₄₁H₄₄BrN₂O₃ [M+H]⁺ 691.2535, found 691.2543.

5'-(2-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)-9-oxo-9H-

pyrrolo[1,2-a]indol-7-yl)-2,2'-bithiophene-5 carbaldehyde (12). To a solution of bromide 11 (150 mg, 0.25 mmol) in degassed toluene (5 mL) was added boronic ester 9 (96 mg, 0.30 mmol) and the catalyst (Pd(PPh₃)₄ 17 mg, 0.015 mmol). The red coloured solution was stirred at room temperature for 20 min, then a solution of sodium carbonate (0.185 g, 1.75 mmol) in degassed distilled water was added. The mixture was stirred at 80 °C for 48 h (TLC: hexane/ethyl acetate 3:1), quenched with distilled water (15 mL) and extracted with ethyl acetate (2 x 15 mL). The organic phase was dried over sodium sulphate and concentrated in vacuo. The crude product was purified by flash column chromatography (silica gel, hexane \rightarrow hexane/ethyl acetate 5:1) to give aldehyde 12 as a crude product. According to the ¹H-NMR spectra the product contained just a small amount of starting material 11 and thus it was used without further purification in the next step. Yield 36% (0.071 g); ¹H-NMR (300 MHz, CDCl₃): $\delta_{H} = 9.87$ (s, 1H), 7.82 (dd, J = 11.1, 1.7 Hz, 1H), 7.69 (d, J = 4.0Hz, 2H), 7.67 (dd, J = 8.4, 1.8 Hz, 1H), 7.34 (d, J = 3.8 Hz, 1H), 7.31 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 7.4 Hz, 2H), 7.14 (d, J = 8.0 Hz, 1H), 7.06 (d, J = 8.9 Hz, 4H), 7.02 (d, J = 5.2 Hz, 1H), 6.95 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.9 Hz, 4H) 3.94 (t, J = 6.5 Hz, 4H), 1.78 (quint, J = 6.7 Hz, 4H), 1.47 (quint, J = 7.2 Hz, 4H), 1.40–1.28 (m, 8H), 0.91 (t, J = 6.9 Hz, 6H). ¹³C-NMR (126 MHz, CDCl₃) δ_{C} = 182.4, 178.9, 162.6, 155.5, 155.4, 148.0, 146.6, 144.3, 142.9, 141.7, 140.6, 140.5, 137.3, 132.9, 131.0, 126.6, 126.5 125.7, 124.3, 124.2, 120.6, 120.5, 115.3, 115.3, 111.3, 111.1, 110.6, 110.5 68.3, 31.6, 29.3, 25.8, 22.6, 14.1. HRMS (ESI): m/z calcd for $C_{50}H_{49}N_2O_4S_2$ [M+H]⁺ 805.3133, found 805.3126.

3-(5'-(2-(4-(Bis(4-(hexyloxy)phenyl)amino)phenyl)-9-oxo-9H-

pyrrolo[1,2-a]-indol-7-yl)-2,2'-bithiophen-5-yl)-2-cyanoacrylate (13, piperidine salt of TA1314). To a suspension of aldehyde 12 (70 mg, 0.087 mmol) in dry acetonitrile (2.5 mL) were added cyanoacetic acid (40 mg, 0.47 mmol), piperidine (39 mg, 0.46 mmol, 45 µL) and chloroform (2 mL). The resulting solution was refluxed for 3 h and stirred overnight at 50 °C (TLC: hexane/ethyl acetate 2:1). The solvent was evaporated in vacuo. The precipitated crystals were filtered off and washed with ice-cold acetonitrile. Product 13 was isolated as a dark red solid. Yield: 74% (0.061 g); mp: 160-161 °C; ¹H-NMR (500 MHz, CDCl₃): δ_H = 9.68 (br. s, 1H), 8.15 (s, 1H), 7.76 (dd, J = 9.0, 0.9 Hz, 1H), 7.62 (dd, J = 7.9, 1.3 Hz, 1H), 7.53 (d, J = 4.0 Hz, 1H), 7.28 (d, J = 8.8 Hz, 2H), 7.25 (s, 1H), 7.23 (d, J = 3.9 Hz, 1H), 7.17 (d, J = 3.9 Hz, 1H), 7.10 (d, J = 8.2 Hz, 1H), 7.05 (d, J = 8.9 Hz, 4H), 6.98 (s, 1H), 6.93 (d, J = 8.2 Hz, 2H), 6.82 (d, J = 8.9 Hz, 4H), 3.93 (t, J = 6.5 Hz, 4H), 3.30 (s, 1H), 3.21-3.14 (m, 4H), 2.01 (s, 1H), 1.93-1.83 (m, 4H), 1.78 (dt, J = 14.5, 6.6Hz, 4H), 1.68 (br. s, 2H), 1.47 (quint, J = 7.1 Hz, 4H), 1.39–1.32 (m, 8H), 0.91 (t, J = 6.8 Hz, 6H). ¹³C-NMR (75 MHz, CDCl_3): δ_{C} = 179.0, 168.1, 158.1, 155.5, 147.3 (2C), 143.5, 141.0, 140.6 (2C), 135.8, 132.9, 132.4, 130.9, 130.1, 129.6, 127.4, 126.6 (4C), 126.5, 125.8, 125.8 (2C), 125.4, 125.2, 124.1, 121.3, 120.7 (2C), 119.7, 118.5, 116.9, 116.3, 115.3 (4C), 112.9, 111.4, 68.3 (2C), 44.4 (2C), 31.6 (2C), 29.4 (2C), 27.4 (2C), 25.8 (2C), 22.7, 22.6 (2C), 14.1 (2C). HRMS

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(ESI): $m\!/z$ calcd for $C_{53}H_{50}N_3O_5S_2$ [M+H]+ 872.3186 (carboxylic acid), found 872.3173.

Spectroscopic and Electrochemical measurements

UV-Vis spectra were recorded with a Shimadzu UV-2600 spectrometer. UV-Vis spectra of the compounds on TiO₂ were recorded in transmission mode after sensitization of thin, transparent semiconductor films prepared with a procedure similar to that employed for the fabrication of the photovoltaic devices (*see below*). Cyclic voltammetry experiments were conducted in dichloromethane solution with a PARSTAT 2273 electrochemical workstation, employing a three-electrode cell having a glassy carbon working electrode, a platinum counter electrode, and the aqueous Ag/AgCl (sat. KCl) reference electrode. The supporting electrolyte used was electrochemical grade [N(Bu)₄]PF₆. Under these experimental conditions, the one-electron oxidation of ferrocene occurs at $E^{o} = 0.62$ V.

Solar Cells Fabrication

Transparent conducting glass, whose conductive layer was constituted by a nanometric layer of FTO (Fluorine-doped Tin Oxide, SnO₂:F), was cut in square sheets of 2.5 cm × 2.5 cm dimensions. The substrates were cleaned with both basic and acidic treatments to eliminate organic impurities. A "blocking layer" of TiO₂ was then deposed by spin-coating of a TiCl₄ alcoholic solution (0.05 M in EtOH) and subsequent thermal treatment at 450°C for 30'.³² At this stage, a nanocrystalline TiO₂ layer was screen-printed on the substrates employing a commercial paste (Solaronix T/SP) and was then sintered at 450°C in an oven. The final dimensions of the TiO₂ films were: thickness 6 µm measured by profilometer (Optical 3D Microscope, Bruker), area 0.25 cm². The screen-printed films were then treated once again by dip-coating process with a TiCl₄ alcoholic solution (0.04 M in EtOH) and subjected to thermal treatment to produce a protective layer on the nanocrystalline TiO₂ electrode.

For electrodes sensitization, two concentrated solutions of dyes **HT157** and **TA1314** in THF were prepared. Subsequently, these solutions were diluted with abs. EtOH so that their final concentration was 0.2 mM. For each dye, a 0.2 mM solution was also prepared, to which the disaggregating agent chenodeoxycholic acid (CDCA, Solaronix) was added, with a concentration of 2 mM. Sensitization of the electrodes was carried out by immersion in the above-mentioned dye solutions for 20 h in the dark. The dyed electrodes were then washed with abs. EtOH and dried in an oven. Counter-electrodes were prepared by drilling a hole in the glass sheets for the subsequent electrolyte filling, and then depositing a Pt-layer on the conductive side *via* sputtering and thermal treatment (500°C, 30 min).

Solar cells were assembled by sandwiching the photo-anode and the counter-electrode with a Meltonix[®] sealing gasket (25 μ m thickness), and thermally sealing the empty cell by heating at 90°C. The cells were filled (through the pre-drilled hole) by vacuum back-filling with lodolyte Z100 (Solaronix) commercial electrolyte (containing the iodide/triiodide redox couple). They were then closed with a small glass sheet and a small patch of sealing material, and some silver ink was finally applied on the edges of the electrodes of to create the electric contacts.

Photoelectrochemical measurements

Efficiency measurements were carried out by recording the characteristic *J*-*V* curves of the devices. To this end, the cells were illuminated with simulated solar light using an Abet Technologies SUN2000 AM 1.5G solar simulator, setting the power of incoming radiation to 100 mW/cm² (calibrated with a reference Si-cell); 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 used to avoid overestimation of the measured parameters. Incident-photon-to-electron conversion efficiency (IPCE) spectra were measured with a PVE300

apparatus (Bentham, UK). Electrochemical Impedance Spectroscopy (EIS) measurements were carried out under illumination at open circuit potential with an Autolab PGSTAT302N+FRA32 electrochemical workstation (Metrohm); spectra were recorded over a frequency range of 10^{-1} Hz to 10^{5} Hz with an amplitude of 10 mV. Data fitting was carried out using the Z-Lab software.

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Keywords: Organic dyes • Fluorazone derivatives • Elming-Clauson-Kaas pyrrole formation • Cross-coupling • Dyesensitized solar cells.

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synthetic А sequence for the preparation of two fully conjugated, 2,7-disubstituted fluorazone (9Hpyrrolo[1,2-a]indol-9-one) derivatives was developed. Thanks to their broad absorption of visible light and their favorable electrochemical properties, the new compounds could be successfully used as sensitizers for dye-sensitized solar cells.



Heterocyclic synthesis, Dyesensitized solar cells

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