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The effect of additional electron donating group on the photophysics and photovoltaic performance of two new metal free D- π -A sensitizers.

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Abstract

The synthesis, photophysical, electrochemical and photovoltaic properties of two D- π -A organic sensitizers, having triphenylamine as electron donor (and hexyloxy as additional electron donating group), carboxylic acid as electron acceptor and benzimidazole group as π -bridge, are described in detail. The photophysical measurements were carried out for the dyes in solutions and on TiO₂ and Al₂O₃ nanostructured films using time resolved spectroscopy in the fs-ps and ns timescale. The electron injection dynamics on a series of TiO₂ nanostructured films sensitized with the two dyes, have shown a faster electron injection for the dye with additional electron donating group. The photovoltaic characterization has shown a maximum overall conversion efficiency of 3.4% for dye sensitized solar cells with a quasi-solid state electrolyte. The performance of the solar cells is explained in terms of the photophysical properties, electron injection dynamics and local resistance to charge transfer across the TiO₂-electrolyte interface measured with electrochemical impedance spectroscopy.

Keywords: Donor/ π -bridge/acceptor structure, dye sensitized solar cells, photophysics, electron injection dynamics, impedance spectroscopy.

1. Introduction

Third generation dye sensitized solar cells (DSSCs) have been proposed within the last two decades, as low-cost alternatives to conventional amorphous silicon photovoltaics owing to the simplicity of their fabrication procedure, practically under ambient conditions with mild chemical processes [1,2]. The unique design of DSSCs offers choices for systematically changing the materials of the different parts that constitute the DSSCs in order to optimize and improve their performance. One of the main components of the DSSCs is the photosensitizer which is responsible for the visible and near-infra-red utilization of the solar light since metal oxide semiconductors which are also employed in the cells, absorb only in the ultraviolet spectral region. At present, ruthenium complexes and metal porphyrins photosensitizers have an overall solar to energy conversion efficiency higher than 12% for small size devices [3,4]. However, metal free organic dyes can also be considered as an alternative choice for the conversion of solar energy to electricity in DSSCs [5-11]. Pure organic dyes can be prepared according to cheap synthetic routes or finally obtained from nature as component of flowers and fruits. The reason for choosing pure organic dyes is that they have certain advantages over metal based photosensitizers; they are easily modified with common synthetic procedures, while they exhibit high molar extinction coefficients compared to metal complexes. Organic dyes with high molar extinction coefficients can be used advantageously in thin TiO₂ film based solar cells which are mainly required in solid state devices where the mass transport and pore filling are limited affecting the performance of the cells.

In recent years, most of the published work on the synthesis of new pure organic dyes for DSSCs has been focused on the Donor- π -Acceptor (D- π -A) system owing to its effective photo-induced intramolecular charge transfer characteristics [12-17]. Compounds commonly used as electron donors are derivatives of triphenylamine [18-20], coumarin [21, 22], carbazole [23, 24] or indoline [25, 26], with the triphenylamine being the most popular. Thiophene [27], benzene [28] or fluorene [29] fragments act, among others, as the π -conjugated linker between the electron donor and acceptor. The electron acceptor, usually a carboxyl group or cyanoacrylic acid fragment, also plays the role of an anchoring group responsible for binding on the TiO₂ mesoporous film surface. Although a reasonable number of pure organic sensitizers have been reported to date, a quest for dyes exhibiting high molecular extinction coefficients and additional optimized properties to meet the criteria needed for efficient DSSCs devices is still ongoing. This is obvious by the large number of recently published articles in the field [30-36]. In several cases adding auxiliary electron donating groups coupled to the triphenylamine moiety, has been shown to improve the properties of the sensitizer by enhancing their intramolecular charge transfer characteristics and by inducing a bathochromic shift of the absorption spectrum [37-39]. In addition, introducing auxiliary electron donating groups can lead to a decreased possibility of π - π aggregation. On the other hand, the addition of bulky donors can also have detrimental effects by reducing the amount of adsorbed dye molecules. In a very recent work, we have reported on the effect of additional methoxy groups coupled to the triphenylamine where an enhanced spectral response was observed for the methoxy-substituted dye [40]. However, an undesired faster electron-cation recombination was also observed in these dyes.

In this respect, we present here the synthesis and detailed photophysical and solar cell characterization of two new organic dyes with D-π-A structure (MZ-341 and MZ-235, Scheme 1), where the donor is a triphenylamine group which, in the case of MZ-235, is coupled to additional electron donating hexyloxy groups. The effect of this additional electron donating groups on the photophysical and solar cell properties of these dyes is reported. The π -conjugated bridge between donor and acceptor is benzimidazole derivative. It is the first time that a weak acceptor such as benzimidazole group is used between donor (triphenylamine group) and acceptor (carboxylic acid) to achieve lower reduction potential and to facilitate charge transfer. The photophysical properties of the dyes are studied in dye solution with different solvent polarity by means of steady state absorption and fluorescence spectroscopy as well as with time resolved fluorescence spectroscopy in the fs-ps and ns time scale. The injection dynamics are studied for the dyes adsorbed on the surface of TiO₂ films. Finally, electrochemical impedance spectroscopy (EIS) measurements and electrical characterization of DSSCs employing the new dyes were performed for thin TiO2 nanocrystalline films (~2 µm) and quasi-solid state electrolyte while the results are discussed in terms of the photophysical properties of the dyes and electrochemical impedance measurements.

2. Experimental Section

2.1 Dyes and synthetic route

The chemical structures of the newly synthesized sensitizers are presented in Scheme 1. The electron donor in MZ-341 is a triphenylamine group which in the case of MZ-235 is coupled to additional electron donating hexyloxy groups. The electron

acceptor is a carboxylic acid while benzimidazole group is used a π -conjugated linker. The synthesis of the sensitizers is described below and briefly the procedure is presented in Scheme 2:

Synthesis of 1-(hexyloxy)- 4-iodophenol (1). A mixture of 4-iodophenol (8.8g, 40mmol), potassium carbonate (5.6g, 40mmol), 18-Crown-6 (1g, 4mmol), acetone (100mL) and1-bromohexane (6.6g, 40mmol) were added in a round bottomed flask and refluxed with stirring overnight. The reaction was controlled and ended with thin-layer chromatography (TLC), cooled down to room temperature, filtered and the reaction mixture was extracted with diethylether (2 x 20mL) and water (2 x 20mL). The organic phase was separated, dried over sodium sulphate and the solvent was evaporated by rotary evaporator. The crude product was purified by column chromatography (dichloromethane/hexane: 1/1, V/V) to obtain a colorless oil (91%, yield). ¹H NMR (400 MHz CDCl₃): δ 7.50 (d, 2H), 6.63 (d, 2H), 3.87 (t, 2H), 1.76-1.70 (m, 2H), 1.44-1.39 (m, 2H), 1.34-1.29 (m, 4H), 0.89 (t, 3H). ¹³C NMR (400 MHz CDCl₃): δ 138.37, 117.18, 68.35, 31.84, 29.41, 25.96, 22.87, 14.30.

Synthesis of (4-bromopheny)bis[4-(hexyloxy)phenyl]amine (2). In a round bottomed flask, a mixture of CuI (0.2g, 1mmol) and phenanthroline (0.18g, 1mmol) were added and dissolved in toluene (10mL). Dean-Stark aparatus and reflux condenser were set and the reaction mixture was stirred for half an hour. 1-(hexyloxy)-iodobenzene (5g, 16mmol), 4-bromoaniline (1.65g, 9,6mmol), potassium hydroxate (4.8g, 77mmol) and toluene (20mL) were added and the mixture was refluxed with stirring overnight. The reaction was controlled and ended with TLC, cooled to the room temperature, filtered over celite and washed with dichloromethane. The reaction mixture was extracted with

dichloromethane (3x20mL) and water (3x20mL). The organic phase was separated, dried over sodium sulphate and the solvent was evaporated by rotary evaporator. The crude product was purified by column chromatography (dichloromethane/hexane: 1/4, V/V) on silica gel to yield yellow oil (66% yield). ¹H NMR (400 MHz CDCl₃): δ 7.21 (d, 2H), 7.00 (d, 2H), 6.8 (d, 6H), 3.91 (t, 4H), 1.78-1.72 (m, 4H), 1.46-1.42 (m, 4H), 1.36-1.32 (m, 8H), 0.90 (t, 6H). ¹³C NMR (400 MHz CDCl₃): δ 168.37, 134.67, 131.33, 130.50, 128.98, 127.89, 127.24, 125.16, 110.48, 40.43, 40.23, 40.02, 39.81, 39.60.

Synthesis of (4-[bis]4-(hexyloxy)phenyl]amino]phenyl)boronic acid (3). A round bottomed flask was vacuumed and given argon which provides isolated atmosphere. (4bromophenyl)bis[4-(hexyloxy)phenyl]amine (3.8g, 7.3mmol) was dissolved with dry THF (10mL) and added to the flask. The temperature was set to -80°C with acetone and dry ice. N-butyl lithium (3.75mL, 7.25mmol) was added dropwise into the flask carefully and stirred for half an hour. Trimethylborate (8.4mL, 72.6mmol) was added dropwise to the mixture and stirred overnight. The reaction was controlled and ended with TLC. The residue was extracted with diethylether (3x30mL) and 1M hydrochloric acid aqueous solution (3x30mL). The organic phase was separated, dried over sodium sulphate and the solvent was evaporated by rotary evaporator. The crude product was purified by column chromatography (ethylacetate/hexane: 3/1, V/V) on silica gel to obtain white solid (74% yield). ¹H NMR (400 MHz d_6 -DMSO): δ 7.68 (s, 2H), 7.57 (d, 2H), 6.97 (d, 4H), 6.85 (d, 4H), 6.66 (d, 2H), 3.89 (t, 4H), 1.70-1.63 (m, 4H), 1.42-1.36 (m,4H), 1.30-1.26 (m, 8H), 0.85 (t, 6H). ¹³C NMR (400 MHz CDCl₃): δ 156.03, 150.073, 140.37, 135.87, 127.65, 118.08, 116.07, 68.30, 31.66, 29.37, 25.87, 14.53.

Synthesis 6-(4-{bis[4-(hexyloxy)phenyl]amino}phenyl)-1H,3Hof benzo[de]isochromene-1,3-dione (4). In a round bottomed flask a mixture of 6-bromo-1,3-benzoisochromene-1,3-dione (103mg, 0.4mmol), (4-{bis[4-(hexyloxy) phenyl] amino} phenyl) boronic acid (150mg, 0.3mmol) was added and dissolved in 1,2dimethoxyethane (15mL). After that, [1,1'-Bis (diphenylphosphino) ferrocene] dichloropalladium (II) (20mg, 0.022mmol) and potassium carbonate aqueous solution (1M, 2mL) were added. The system was isolated under argon atmosphere, heated up to boiling temperature and stirred overnight. The reaction was controlled and ended with TLC, extracted with, dichloromethane (3x20mL) and water (3x20mL). The organic phase was separated, dried over sodium sulphate and the solvent was evaporated. The crude product was purified by column chromatography (dichloromethane/hexane: 1/2, V/V) on silica gel to obtain red solid. ¹H NMR (400 MHz CDCl₃): δ 8.62 (m, 2H), 8.54 (dd, 1H), 7.74 (dd, 2H), 7.31(d, 2H), 7.16 (d, 4H), 7.05 (d, 2H), 6.89 (d, 4H), 3.96 (t, 4H), 1.79 (m, 4H), 1.47 (m, 4H), 1.35 (m, 8H), 0.91 (t, 6H). ¹³C NMR (400 MHz CDCl₃): δ 156.56, 139.89, 134.90, 133.25, 130.65, 129.00, 128.07, 127.73, 127.34, 119.14, 115.91, 68.69, 31.61, 29.32, 26.00, 23.02, 14.23. The ¹H-NMR and ¹³C-NMR spectra of the molecule appear in supporting information as Fig. S1.

Synthesis of 4-(4-{bis[4-(hexyloxy)phenyl]amino}phenyl)-7-oxo-7Hbenzimidazo[2,1-a]benzo[de]isoquinoline-11-carboxylic acid (5). In a round bottomed flask a mixture of 6-(4-{bis[4-(hexyloxy)phenyl]amino}phenyl)-1H,3Hbenzo[de]isochromene-1,3-dione (70mg, 0.1mmol), 3,4-diaminobenzoic acid (33mg, 0.2mmol), zinc acetate (20mg, 0.1mmol) was added and dissolved in pyridine (15mL). The mixture was refluxed with stirring overnight. The reaction was controlled and ended with TLC. The reaction mixture was neutrealized by addition of 1M hydrochloric acid aqueous solution and was extracted with dichloromethane (3x20mL) and water (3x20mL). The organic phase was separated, dried over sodium sulphate and the solvent was evaporated by rotary evaporator. The crude product was purified by column chromatorgraphy (dichloromethane/hexane: 9.5/0.5, V/V) on silica gel to obtain red solid. ¹H NMR (400 MHz CDCl₃): δ 8.86 - 8.75 (d, 1H), 8.60 (t, 1H), 8.18 (m, 1H), 8.01 (m, 1H), 7.90 (m, 1H), 7.72 (m, 2H), 7.47 (m, 2H), 7.34 (m, 2H), 7.14 (m, 4H), 7.07 (m, 2H), 6.89 (m, 4H), 3.96 (t, 4H), 1.35 (m, 16H), 0.91 (m, 6H). ¹³C NMR (400 MHz CDCl₃): δ 164.14, 156.28, 149.68, 140.53, 130.65, 129.64, 127.41, 119.45, 115.70, 68.67, 31.82, 29.90, 29.55, 25.98, 22.69, 14.55. The ¹H-NMR and ¹³C-NMR spectra of the molecule appear in the supporting information as Fig. S2.

Synthesis of methyl 4-bromo-7-oxo-7H-benzimidazo[2,1-a]benzo[de]isoquinoline-11-carboxylate(6). A mixture of 6-bromo-1H,3H-benzo[de]isochromene-1,3-dione (28mg, 0.1mmol), methyl 3,4-diaminobenzoate (33mg, 0.2mmol), zinc acetate (20mg, 0.1mmol) were added in a round bottomed flask and dissolved in pyridine (15mL). The reaction was refluxed overnight and was controlled with TLC. The reaction mixture was neutrealized by 1M hydrochloric acid aqueous solution and extracted with dichloromethane (3x20mL) and water (3x20mL). The organic phase was dried with sodium sulphate and the solvent was evaporated by rotary evaporator. The crude product was purified by column chromatorgraphy (dichloromethane/hexane: 9.5/0.5, V/V) on silica gel to obtain a yellow solid. ¹H NMR (400 MHz d_6 -DMSO): δ 8.88 (m, 1H), 8.71 (t, 1H), 8.56 - 8.46 - 8.45 (m, 1H), 8.20 (m, 1H), 8.09 (m, 1H), 8.08 (m, 1H), 7.98 - 7.91 (m, 1H), 7.89 - 7.85 (m, 1H), 4.00 (s, 3H). ¹³C NMR (400 MHz CDCl₃): δ 163.51,148.41, 147.31, 133.32,131.96, 131.68, 131.43, 130.34, 129.49, 128.46, 127.62, 127.10, 125.48, 124.12, 122.50, 116.28, 51.75. The ¹H-NMR and ¹³C-NMR spectra of the molecule appear in the supporting information as Fig. 3S.

Synthesis of methyl 4-[4-(diphenylamino)phenyl]-7-oxo-7H-benzimidazo[2,1albenzo[de]isoquinoline-11-carboxylate (7). A mixture of methyl 4-bromo-7-oxo-7Hbenzimidazo[2,1-a]benzo[de]isoquinoline-11-carboxylate (123mg, 0.3mmol), 4-(diphenylamino)phenylboronic acid (90mg, 0.3mmol) were added in a schlenk flask and dissolved in 1,2-dimethoxyethane (10mL). Then [1,1'-bis (diphenylphosphino) ferrocene] dichloropalladium (II) (12mg, 0,02mmol) and potassium carbonate aqueous solution (1M, 2mL) were added to the mixture. The system was isolated under argon atmosphere, heated up to boiling temperature and stirred overnight. The reaction was controlled and ended with TLC while the extraction was made with dichloromethane (3x20mL) and water (3x20mL). The organic phase was dried with sodium sulphate and the solvent was purified by column chromatography evaporated. The crude product was (dichloromethane/hexane: 1/2, V/V) on silica gel to obtain orange solid. ¹H NMR (400 MHz CDCl₃): δ 8.90 - 8.84 (m, 2H), 8.65 - 8.64 - 8.57 (m, 1H), 8.48 (d, 1H), 8.19 (t, 1H), 7.97-7.86 (d, 1H), 7.81-7.72 (m, 1H), 7.42 - 7.37 - 7.34 (m, 6H), 7.27 - 7.21(m, 6H), 7.11 (t,2H), 6.93 (t, 2H), 4.00 (s, 3H). ¹³C NMR (400 MHz CDCl₃): δ 164.31, 163.60, 148.33, 147.26, 134.54, 133.64, 133.48, 131.99, 131.82, 131.57, 131.00, 130.79, 129.58, 128.31, 127.94, 127.77, 127.17, 126.79, 125.04, 123.71, 122.68, 122.57, 122.38, 122.27, 120.95, 120.62, 116.09, 51.66. The ¹H-NMR and ¹³C-NMR spectra of the molecule appear in the supporting information as Fig. 4S.

Synthesis 4-[4-(diphenylamino)phenyl]-7-oxo-7H-benzimidazo[2,1of a]benzo[de]isoquinoline-11-carboxylic acid (8). Methyl 4-[4-(diphenylamino)phenyl]-7oxo-7H-benzimidazo[2,1-a]benzo[de]isoquinoline-11-carboxylate was added in a round bottomed flask and dissolved in THF:ethanol (1:1) mixture. 1 M KOH solution was added in the reaction flask and refluxed overnight. The reaction was controlled and ended with TLC while the organic solvent was evaporated and the mixture was acidified with 1M HCl. The precipitate was filtered and washed with pure water. The crude product was purified by column chromatorgraphy (dichloromethane/methanol: 9.5/0.5, V/V) on silica gel to obtain red solid. ¹H NMR (400 MHz CDCl₃): δ 8.96 - 8.89 (m, 1H), 8.67 - 8.56 (m, 1H), 8.26 (t, 1H), 7.82 (m, 2H), 7.71 (m, 1H), 7.54 (m, 1H), 7.42 - 7.41 (m, 2H), 7.34 (m, 4H), 7.23 (m, 8H), 7.11 (t, 2H).¹³C NMR (400 MHz CDCl₃): δ 166.39, 163.96, 163.77, 153.38, 148.43, 147.46, 147.26, 133.49, 131.99, 131.82, 131.58, 130.98, 130.80, 129.49, 128.30, 127.76, 126.76, 125.09, 123.71, 122.52, 122.38, 120.95, 116.09. The ¹H-NMR and ¹³C-NMR spectra of the molecule appear in the supporting information as Fig. 5S.

2.2 Materials

All solvents and reagents, unless otherwise stated, were of puriss quality and used as received. Copper (I) iodide and 1-bromohexane were purchased from Fluka; Acetone, dichloromethane, toluene, 18-crown-6, phenanthroline, n-butyllithium, 1,2dimetoxyetane, tetrahydrofuran (THF), trimethylborate, [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II), 4 bromo naphthalene and 3,4 diaminobenzoic acid were purchased from Sigma-Aldrich. 4-iodophenol and 4bromoaniline were purchased from Alfa Aesar. Potassium carbonate and zinc acetate were purchased from Riedel de Haen.

For fabrication of solar cells, TiO2 and Al2O3 films: Lithium iodide, iodine, 1methyl-3-propylimidazolium hexachloroplatinate(IV) iodide. hydrogen hydrate $(H_2PtCl_6),$ poly(propylene glycol)bis(2-aminopropyl) 3ether. isocyanatopropyltriethoxysilane, guanidine thiocyanate and all solvents were purchased from Sigma-Aldrich. SnO₂:F transparent conductive electrodes (FTO, TECTM A8), 8 Ohm/square, were purchased from Pilkington NSG Group. Commercial ultra pure titanium isopropoxide (TTIP, 97%, Aldrich), aluminum tributoxide (AlBuO, 95%, Aldrich), Triton X-100 (polyoxyethylene-10- isooctylphenyl ether) surfactant (99.8%, Aldrich) and glacial acetic acid (AcOH, Aldrich) were used to make the precursors for TiO₂ and Al₂O₃ sols. The preparation of TiO₂ and Al₂O₃ films was described in previous publications [41, 42].

2.3 Preparation of solar cells

In the construction of the solar cells a quasi-solid state electrolyte was used. This was chosen as it combines the high ionic conductivity of liquids while it reduces the risk of leaks minimizing sealing problems in the cells. For the gel electrolyte applied to the DSSCs, we used a hybrid organic-inorganic material, ICS-PPG230, which was prepared according to a procedure described in previous publications [43, 44]. Briefly, 0.7 grams of the functionalized alkoxide precursor ICS-PPG230 were dissolved in 1.6 grams of sulfolane and 0.8 grams of 3-methoxypropionitrile under vigorous stirring. Then, 0.368 g AcOH were added followed by 0.3 M 1-methyl-3-propylimidazolium iodide, 0.1 M LiI

and 0.05 M I₂ in a final molar ratio of AcOH:LiI:MPImI:I₂ = 2.5:0.1:0.3:0.05. Finally 0.204 g of *tert*-butyl pyridine and 0.036 g of guanidine thiocyanate was added to the above mixture. After few hours of stirring, one drop of the obtained sol was placed on the top of the titania electrode with adsorbed dye molecules and a slightly platinized FTO counter electrode was pushed by hand on the top. The platinized FTO glass was made by exposing it to a H₂PtCl₆ solution (5mg/1ml of *i*-PrOH) followed by heating at 450 °C for 10 minutes. The two electrodes tightly stuck together by -Si-O-Si bonds developed by the presence of ICS-PPG230. The cell active area for the electrical measurements was 0.28 cm² determined by a black mask.

2.4 Methods

Electrochemical measurements for MZ-341 and MZ-235 dyes were carried out with CH 440B Instruments potentiometer. FT-IR spectra were recorded on a Thermo Scientific Nicolet iS5 FT-IR Spectrometer using an ATR system (4000–650 cm⁻¹). ¹H and ¹³C NMR (Varian-400 MHz) data were recorded at 25°C using CHCl₃-d and d₆-DMSO as solvents and TMS as an internal standard. The steady state absorption and fluorescence spectra were taken using a Hitachi U-2900 UV-Vis spectrophotometer and a Hitachi F-2500 fluorescence spectrophotometer, respectively. The accuracy of the fluorescence measurements was checked by detecting the emission band of Europium Eu³⁺ (⁵D₀→⁷F₂ transition) at 613 nm as a reference. The fluorescence spectra of the solid samples were collected using a specific holder which had an inclination angle of 10° assuring the exact same geometry in all measurements and avoiding increased reflections towards the detector. Unsensitized TiO₂ and Al₂O₃ films were used as reference samples

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for obtaining the spectra of the sensitized ones. The thickness of the oxide films was about $2 \mu m$ according to cross section scanning electron microscopy images.

The fluorescence dynamics were studied by using a femtosecond time resolved upconversion system that has been described in details elsewhere [41,42,45,46]. The excitation beam was the second harmonic of a Ti:Sapphire femtosecond laser, at 400 nm (80 fs pulse duration) and the average excitation power was less than 3 mW. The Instrument's Response Function (IRF) was 140 fs, while the samples were dilute solutions of the two dyes in toluene and THF (10^{-5} M concentration), or TiO₂ and Al₂O₃ films sensitized with the dyes. All dynamics were detected under magic angle conditions. For obtaining the long-lifetime (nanosecond) dynamics, a Time Correlated Single Photon Counting (TCSPC) method has been used. This is based on a Fluotime 200 spectrometer (Picoquant), where two pulsed diode lasers, at 403 and 470nm, were used for the excitation and a Microchannel-Plate Photomultiplier (MCP-PMT) was used for the detection. The IRF of the TCSPC spectrometer was ~80 ps.

For solar cells' characterization and for obtaining the *J-V* curves, the samples were illuminated with Xe light using a Solar Light Co. solar simulator (model 16S-300) equipped with AM 0 and AM 1.5 direct Air Mass filters to simulate solar radiation at the surface of the earth. The light intensity was kept constant at 1000 W/m² measured with a Newport power meter (843-R). Finally, the *J-V* curves were recorded by connecting the cells to a Keithley Source Meter (model 2601A) which was controlled by Keithley computer software (LabTracer). We made three cells for each dye which were tested under the same conditions in order to avoid any misleading estimation of their efficiency. Cell performance parameters, including short-circuit current density (*J_{SC}*), open circuit voltage (V_{OC}), maximum power (P_{max}), fill factor (*FF*) and overall cell conversion efficiency *n*, were determined from each *J*-*V* characteristic curve.

EIS characterization was carried out under illumination using the same Xe light source that was used for the *J-V* curves. EIS measurements were performed without the use of a mask with Metrohm Autolab 3.v potentiostat galvanostat (Model PGSTAT 128N) through a frequency range of 100 kHz-0.01 Hz using a perturbation of ± 10 mV over the open circuit potential. Experimental data are presented by scattering symbols while lines represent the fitted plots obtained using Nova 1.10 software.

3. Results and discussion

3.1 Electrochemical properties

The electrochemical properties of the MZ dyes were examined by the cyclic voltammetric method in a 0.1M solution of Bu_4NPF_6 in acetonitrile with a scan rate of 100mVs⁻¹. A glassy-carbon was used as the working electrode, platinum as the counter electrode and Ag/AgCl as the reference electrode. The oxidation potentials were found at 0.89 V and 0.78 V (vs. Fe+/Fc) for MZ-341 and MZ-235, respectively. They are assigned to the oxidation of the triphenylamine donor moiety. The reduction potentials were found at -1.13 and -1.67 V for MZ-341 and at -1.16 and -1.56 V for MZ-235 respectively. They are assigned to the reduction of the benzimidazole and carboxylic acid acceptor that can be anchored to the TiO₂ surface. It is worth noting that the presence of electron-donating groups coupled to the triphenylamine backbone reduces the oxidation potentials while LUMO levels for both dyes were calculated from the oxidation potentials. HOMO levels are located at

5.18 and 5.30 eV while LUMO levels at 3.24 and 3.27 eV for MZ-235 and MZ-341 respectively. Cyclic voltammograms for both dyes are presented in Fig.1.

3.2 FT-IR measurements of the MZ dyes

The IR spectra obtained for both dyes are presented in Fig.2. The O–H bonds of the dyes resonate at around 3400 cm^{-1} and they are believed to arise from COOH. The peak at around 1700 cm⁻¹ is based on the C=O stretch of the carboxylic acid group. Aromatic and aliphatic CH groups exhibited characteristic absorption bands around 2900 and 2800 cm⁻¹. These three important peaks proved that carboxyl groups are successfully integrated on MZ dyes.

3.3 Photophysical properties in solutions and films

Figures 3a and 3b present the absorption and fluorescence spectra of dyes MZ-341 and MZ-235 in toluene and THF dilute solutions, respectively. The photophysical parameters are summarized in Table 1. The dyes exhibit almost identical absorption spectra, regardless of the solvent used, with peaks at 441-443 nm for MZ-341 and at 459 nm for MZ-235, denoting a relatively polarity-independent nature of the ground state. A red-shift (~17-19 nm) of the absorption's peak for MZ-235 compared to MZ-341 in both solvents is observed. This originates from the hexyloxy substituents on the para position of the two benzenes of the triphenylamine donor [39, 40]. The addition of these extra electron donating groups (hexyloxy groups) on the triphenylamine donor reduces the oxidation potential by giving triphenylamine an enhanced nucleophilic character, resulting in an increased HOMO level of the dye. This is reflected by a red shift of the

absorption maximum for MZ-235 relative to MZ-341 where these substitution groups are absent.

On the other hand, the fluorescence spectra in toluene and THF display several differences in both dyes, with those in toluene being narrower and hypsochromically shifted compared to those in THF. Specifically, the fluorescence spectra in toluene show peaks at 547 and 576 nm for MZ-341 and MZ-235, respectively. The corresponding values in THF are 595 and 613 nm. The bathochromic shift as well as the broader spectrum in THF compared to toluene, is an indication that the excited state presents an intense charge transfer character. This is consistent with the non normalized fluorescence spectra (they are not presented), where MZ-341 and MZ-235 exhibit approximately 10-fold and 80-fold decreased fluorescence intensity in THF relative to toluene. Finally, a bathochromic shift (18-29 nm) of the fluorescence peak accompanied by a broader spectrum in both solvents is evident for MZ-235 with the extra electron donating groups, indicating that this dye adopts a more relaxed excited state than its analogue MZ-341 without the additional donor group.

The absorption and fluorescence spectra of MZ-341 and MZ-235 on Al_2O_3 and TiO_2 substrates are shown in Figures 4a and 4b. In Table 1, the related photophysical results are summarized. Regarding the absorption spectra, the two dyes exhibit broad peaks at 430-450 nm for MZ-341 and at 460-470 nm for MZ-235. As in the solutions, MZ-235 exhibits a bathochromic shift of the absorption spectrum compared to MZ-341 due to the hexyloxy groups. In general, the absorption spectra of the dyes on TiO₂ and Al_2O_3 films are influenced by possible formation of H- or J- aggregates and by the deprotonation of the carboxyl group. The formation of H-aggregates as well as the

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deprotonation of the carboxyl group would lead to a hypsochromic shift while Jaggregates would lead to a bathochromic one. In our case, the absorption peaks in films do not show significant differences compared to the corresponding values in solutions. This means that the influence of the above mentioned effects may be canceled. However, in films, the absorption spectra display a long tail towards the red-edge indicative of the inhomogeneity and the formation of aggregates.

Interestingly, the fluorescence spectra of MZ-341 and MZ-235 on Al_2O_3 and TiO_2 exhibit peaks at almost similar wavelengths namely 580-590 nm (Table 2). These peaks are red-shifted compared to the peaks in toluene but they are blue-shifted compared to the values in THF. The latter indicates that the emitting state in films has a less intense charge transfer character than in THF which possibly indicates deprotonation of the carboxylate group where the carboxylate anion has a decreased electron accepting capability relative to its neutral form (higher LUMO level).

The fluorescence dynamics of MZ-341 and MZ-235 have been studied by means of fs time resolved spectroscopy in toluene and THF solutions and on TiO_2 and Al_2O_3 substrates on a temporal range from -0.5 up to 500 ps and in specific occasions up to 1000 ps. Besides, for lifetime measurements in the ns timescale, a Time Correlated single Photon Counting (TCSPC) technique has been used. Figures 5a and 5b show the dynamics of the two dyes in toluene and THF obtained by the fs spectroscopy, while figure 5c shows the dynamics obtained by TCSPC technique. The fluorescence transients by means of fs spectroscopy have been detected at various emission wavelengths within the whole emission spectrum of the dyes. In Figures 5a and 5b, the dynamics are shown at the peaks of emission spectra of the two compounds in each solvent while figures S6 and S7 show the dynamics at all wavelengths.

The dynamics of the two dyes exhibit substantial differences. However, both dyes in THF decay reasonably faster relative to toluene, confirming the lowering of the LUMO level towards a stronger coupling in the excited state and therefore an enhanced charge transfer character. In order to analyze the dynamics, a global fitting method has been employed using a multi-exponential function convoluted with the IRF. Thus, common decay times have been given at all wavelengths while the pre-exponential factors have been determined as a function of wavelength. The results are summarized in Table 2 for the dynamics at the peaks of the emission spectra and in Tables S1 - S4 for all the detected wavelengths.

Regarding MZ-341 in toluene, two short time constants equal to 1.7 and 5.5 ps were found. Both time constants exhibit positive pre-exponential factors at short wavelengths which become negative at long ones, thus leading to a transient relaxation of the emission spectrum (Table S1). In THF, time constants of 0.63 and 1.0 ps were found which also refer to a relaxation of the emission towards low-energies as their pre-exponential factors become negative at long wavelengths (Table S2). The above mentionned behavior of the short-time dynamics is common in charge trasfer dyes and is due to ICT formation and solvation of the polar excited state [15,47]. MZ-341 in THF also exhibits a decay component of 5 ps with positive amplitudes at all wavelengths which possibly indicates the existence of a non-radiative mechanism depleting the excited state. On a longer timescale, MZ-341 in both solvents exhibits a slow decay component of ~4.2-4.4 ns (Fig. 5c and Table 3) which was found the same upon both 403

and 470 nm excitation and is considered as the lifetime of the emitting state. This decay lifetime was determined by means of TCSPC technique. The similarity of the lifetimes in both solvents indicates that the emitting state of MZ-341 is the same in both solvents. Apart from the 4.2-4.4 ns lifetimes a shorter decay time of 0.85 ns has also been found for MZ-341 in toluene. This time is too slow to be considered as a relaxation time and could be tentatively ascribed to the emission from an intermediate unrelaxed state.

The dynamics of MZ-235, having the additional electron donating groups, also show fast decay at short wavelengths while as the detection is shifted to longer ones the decay is slower and rise components are also observed (Figure S7). The spectral relaxation for MZ-235 in toluene occurs with components of 1.1 and 4.0 ps respectively while in THF a single relaxation component of 0.4 ps is observed (Tables S3 and S4). MZ-235 in toluene exhibits a fast non-radiative decay of 26 ps while at long timescales a slow decay component of 3.2 ns is observed which is however accompanied by a shorter one of 0.5 ns. Both ns decay components were found by TCSPC (Table 3). As in the case of MZ-341, they can be associated to the lifetime of the relaxed excited state and possibly to an unrelaxed state.

It is noted that the fluorescence intensity of MZ-235 in THF totally vanishes within the first 500 ps showing a lifetime of 70 ps as obtained by the global fitting analysis. This fast decay in THF was also accompagied by a significant drop of the fluorescence intensity in this solvent relative to toluene. Such an abrupt decrease of the lifetime as the solvent polarity increases has been also observed in the past for other dipolar dyes and has been attributed to the formation of a Twisted Intramolecular Chrge Transfer state (TICT) [48-50]. In general, apart from a fast decay of the excited state, the presence of a TICT state shifts the emission spectrum to longer wavelengths (or cause the appearance of an intense shoulder at long wavelengths) and decreases the emission efficiency because of the conical intersection of the TICT state and the ground state surfaces which allows the population to transfer to the ground state non-radiatively. In order to test whether a TICT is formed when MZ-235 is disolved in THF, we prepared solutions of MZ-235 in THF after adding polystyrene (PS). This polymer was chosen because it disolves easily in THF and it is non-polar [51]. Various solutions were prepared by adding PS until they became highly viscous (concentration of polystyrene up to 40 mg/ml). By increasing the viscosity of the solutions, the rotational freedom of MZ-235 is restricted and thus the formation of a TICT should be hindered. Therefore, if the decrease of the lifetime in THF is due to the formation of a TICT, the fluorescence dynamics should become slower in the viscous solutions. In Figure 5b, the fluorescence decay of MZ-235 in THF with 40 mg/ml polystyrene is shown. It is obvious that the decay is identical to that without PS. In addition, the steady state fluorescence spectrum of MZ-235 in THF/PS solution has been detected and is shown in Figure 3b. Similar to the dynamics, the spectrum of MZ-235 in THF/PS is found identical to the neat THF solutions. Therefore, it is highly unlikely that a TICT is formed and the decrease of the lifetime in THF can be ascribed to the fast, mostly non-radiative, decay of the ICT state due to the polar solvent molecules.

Figure 6 presents the fluorescence transients of dyes MZ-341 and MZ-235 on Al_2O_3 and TiO_2 nanocrystalline films. The dynamics on TiO_2 are significantly faster than on Al_2O_3 indicating efficient electron injection from the dye's LUMO to the TiO_2 conduction band [52-54]. After fitting the results with a three exponential function, the

time constants for MZ-341 were found 1 (0.37), 5.8 (0.42) and 44 ps (0.21) on TiO₂ and 3.1 (0.44), 17.6 (0.36) and 156 ps (0.20) on Al₂O₃. The corresponding time constants for MZ-235 were found 0.6 (0.53), 4.7 (0.34) and 48 ps (0.13) on TiO₂ and 2 (0.46), 23.3 (0.32) and 387 ps (0.22) on Al₂O₃. Table 4 summarizes the results. The observed faster decay of MZ-235 on TiO₂ compared to MZ-341 is ascribed to the presence of the hexyloxy group onto the triphenylamine moiety, which enhances its electron donating strength. The same dye on Al₂O₃ exhibits a faster component within the first few picoseconds compared to MZ-341, which is also ascribed to its enhanced electron donating efficiency and can be possibly due to electron injection towards trap states in Al₂O₃. However, at longer timescales a slower decay is evident for MZ-235 on Al₂O₃ (τ_3 =387 ps for MZ-235 vs. 156 for MZ-341). This difference in the long lifetimes is ascribed to the reduced aggregation leads to a decreased possibility for quenching and thus to an increased lifetime of MZ-235 on Al₂O₃.

3.4 Solar cells performance

The current-voltage (*J-V*) characteristic curves of the quasi-solid state DSSCs under one sun illumination using MZ-341 and MZ-235 newly synthesized dyes as sensitizers, are presented in Figure 7a. For each sensitizer, we prepared three cells which were tested under the same conditions. The electrical characteristics are presented in Table 5 and concern the average values obtained from the cells. In all cases, the active area of the cells was 0.28 cm². The quasi-solid state DSSCs constructed with MZ-341 showed an overall efficiency of 3.4 % slightly better than that obtained for MZ-235 (3.0 %). The open circuit voltage for both dyes was measured around 660 mV while the short circuit current density was 6.83 and 6.45 mA/cm² for MZ-341 and MZ-235 respectively. Since the short circuit current value is rather low, we believe that this is ascribed to two factors: The low extinction coefficient value and the ineffective visible light exploitation. Besides, the relatively lower values for electrical characterisitcs obtained for MZ-235 can be explained in terms of lower absoprtion of the sensitized TiO₂ photoelectrode compared to that measured for MZ-341 as it can be seen in the inset of Fig. 7a. However, the devices showed good stability when subjected to 1 sun light irradiance from a Xe lamp after 300 h of continuous visible light soaking. The cells were all unsealed and were used without any further treatment after the electrolyte was gelled. The cells with the two dyes were also examined as efficient photoelectrodes in DSSCs measuring the dark current suppression. Figure 7b shows that the dark current density in the cells does not have substantial differences however, the electron leakage, in the cells made with the dye MZ-235 is higher compared to the cells made with MZ-341. This corroborates with the slightly reduced overall performance of the MZ-235 DSSCs under light exposure.

Figure 8 shows the Nyquist plots obtained from the cells with the two dyes. The first semicircle corresponds to the Pt/electrolyte interface, R_{pt} . The charge transfer resistance at the counter electrode (R_{pt}) is represented as a semicircle in the impedance spectra and as a peak in the Bode phase angle plot. The resistance element related to the response in the intermediate frequency represents the charge transport at the TiO₂/dye/electrolyte interface (R_{tr}) and shows diode like behavior. The semicircle at the low frequency, which is attributed to the diffusion in the electrolyte (R_{dif}), was small and not well formed indicating a fast diffusion. Finally, the intercept of the horizontal axis

stands for the resistance of the sheet resistance of the FTO substrate and the contact resistance of the FTO/TiO_2 (R_h) [55,56].

The total series resistance of the cell can be calculated using equation (1)

$$R_s = R_h + R_{pt} + R_{dif} \tag{1}$$

The semicircles at the Nyquist plots are obtained from a frequency scan through a wide range of high, intermediate and low frequency. Thus, the Bode phase plots, shown in Fig. 9, also feature three characteristic frequency peaks corresponding to each of the Nyquist characteristic peaks. The equivalent circuit which we used to fit the experimental data is presented as an inset in Figure 8. For electrodes having a rough surface, the capacitance element in the equivalent circuit is replaced by a constant phase element (CPE, Q) which depends on the parameters Y_0 and N. It is possible to convert a CPE element, which is in parallel with a resistance, to a pseudo capacitance using equation (2)

$$C_{pseudo} = Y_{o}^{1/N} \cdot R^{\left(\frac{1}{N}-1\right)}$$
(2)

The parameters obtained by fitting the data in Fig. 8, are presented in Table 6. The cells with MZ-341 and MZ-235 dyes exhibit a quite similar behavior of the charge transport resistance at the $TiO_2/dye/electrolyte$ interface. However, an increased value for the total series resistance for the cells employing MZ-235 dye is obtained, which agrees with the slightly smaller energy conversion efficiency of these cells.

Bode plots obtained from cells with both dyes are presented in Figure 9. From these plots in the medium-frequency range, the characteristic frequency is associated with the electron transport in the mesoscopic TiO_2 film and the back reaction at the TiO_2 /electrolyte interface. The electron lifetime in TiO_2 electrodes for both cells

employing MZ-235 and MZ-341 was calculated using equation (3), where f is the characteristic frequency of the peak from the Bode phase plots [57].

$$\tau_n = \frac{1}{2 \cdot \pi \cdot f} \tag{3}$$

The electron lifetime for the cells with MZ-235 was calculated to be 2.8 ms which was slightly lower than the one obtained for MZ-341 (3.5 ms). This is also an additional evidence for the better performance of cells employing MZ-341 as photosensitizer. Moreover, the low and high frequency peak observed in the Bode plots correspond to triiodide diffusion in the electrolyte and charge transfer at the counter electrode, respectively. There are no significant changes at least at high frequency peaks implying that no unexpected reaction had occurred within the electrolyte and counter electrode for the two dyes.

Overall, by comparing the photodynamics and solar cell performance of the two sensitizers, it is concluded that MZ-235, with the additional electron donating groups, exhibits enhanced intramolecular charge transfer properties and faster electron injection. Taking into account the fact that this dye exhibits a better spectral response than MZ-341, it was expected to show a higher solar cell efficiency than MZ-341, without the additional electron donor. However, the opposite is observed. The smaller solar cell efficiency of the DSSCs prepared with MZ-235 is in agreement with the EIS results such as higher total series resistance and smaller electron lifetime in TiO₂ electrodes compared to the cells made with MZ-235. Another tentative explanation of the smaller performance in the hexyloxy substituted sensitizer is a faster recombination of injected electrons with the dye cations since the hexyloxy groups are expected to increase the positive charge on the triphenylamine moiety of the dye [40].

3. Conclusions

In conclusion, two new triphenylamine based organic dyes with or without additional electron donating hexyloxy groups, having benzimidazole moiety as π -bridge are synthesized and examined photophysically and as sensitizers in thin TiO₂ film based DSSCs. The dye with the hexyloxy groups, MZ-235, attached to the triphenylamine has shown a bathochromic shift of its absorption spectrum thus exhibiting a better coverage of the visible spectrum. In addition, it has shown faster intramolecular charge transfer state formation and faster electron injection toward TiO₂ as it was found through time resolved fluorescence spectroscopy in the fs-ps and in the ns timescale. However, the dye without additional groups attached to triphenylamine, MZ-341, proved to be more efficient in solar cell performance while a maximum overall performance of 3.4% was obtained for a quasi-solid state DSSC. The better performance of MZ-341 was explained in terms of higher absorbance on TiO₂ photoelectrode compared to the MZ-235 dye and also examined through electrochemical impedance spectroscopy measurements.

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References

- [1] Hagfeldt A, Boschloo G, Sun L, Kloo L, Pettersson H. Dye-sensitized solar cells. Chem Rev 2010;110:6595-663.
- [2] Gong J, Liang J, Sumathy K. Review on dye-sensitized solar cells (DSSCs): Fundamental concepts and novel materials. Renew Sustain En Rev 2012;16:5848-60.
- [3] Yella A, Lee HW, Tsao HN, Yi C, Chandiran AK, Nazeeruddin MK et al. Porphyrin-Sensitized Solar Cells with Cobalt (II/III)–Based Redox Electrolyte Exceed 12 Percent Efficiency. Science 2011;334:629-34.
- [4] Gao F, Wang Y, Zhang J, Shi D, Wang M, Humphry-Baker R, et al. A new heteroleptic ruthenium sensitizer enhances the absorptivity of mesoporous titania film for high efficiency dye-sensitized solar cell. Chem Commun 2008;:2635-7.
- [5] Kumaresan D, Thummel RP, Bura T, Ulrich G, Ziessel R. Color Tuning in New Metal-Free Organic Sensitizers (Bodipys) for Dye-Sensitized Solar Cells. Chem Eur J 2009;15:6335-9.
- [6] Guo K, Yan K, Lu X, Qiu Y, Liu Z, Sun J, et al. Dithiafulvenyl Unit as a New Donor for High-Efficiency Dye-Sensitized Solar Cells: Synthesis and Demonstration of a Family of Metal-Free Organic Sensitizers. Org Lett 2012;14:2214-7.
- [7] Duan T, Fan K, Zhong C, Chen X, Peng T, Qin J. A new class of organic dyes containing b-substituted 2, 20-bithiophenene unit as a p-linker for dye-sensitized solar

cells: Structural modification for understanding relationship of structure and photovoltaic performances. J of Power Sources 2013;234:23-30.

- [8] Matano Y, Hayashi Y, Nakano H, Imahori H. N,S,P-. Hybrid Donor–π–Acceptor Organic Dyes for Dye-Sensitized Solar Cell: Synthesis, Optical Properties, and Photovoltaic Performances. Heteroatom Chem 2014;25:533-47.
- [9] Hagberg DP, Marinado T, Karlsson KM, Nonomura K, Qin P, Boschloo G, et al. Tuning the HOMO and LUMO energy levels of organic chromophores for dye sensitized solar cells. J Org Chem 2007;72:9550-6.
- [10] Mishra A, Fischer MKR, Bauerle P. Metal-Free Organic Dyes for Dye-Sensitized Solar Cells: From Structure: Property Relationships to Design Rules. Angew Chem Int Ed 2009;48:2474-99.
- [11] Yen YS, Chou HH, Chen YC, Hsu CY, Lin JT. Recent developments in moleculebased organic materials for dye-sensitized solar cells. J Mater Chem 2012;22:8734-47.
- [12] Gao F, Wang Y, Shi D, Zhang J, Wang M, Jing X, et al. Enhance the Optical Absorptivity of Nanocrystalline TiO₂ Film with High Molar Extinction Coefficient Ruthenium Sensitizers for High Performance Dye-Sensitized Solar Cells. J Am Chem Soc 2008;130:10720-8.
- [13] Babu DD, Gachumale SR, Anandan S, Adhikari AV. New D-π-A type indole based chromogens for DSSC: Design, synthesis and performance studies. Dyes Pigments 2005;112:183-91.
- [14] Jiang S, Fan S, Lu X, Zhou G, Wang ZS. Double D–π–A branched organic dye isomers for dye-sensitized solar cells. J Mater Chem A 2014;2:17153-64.

- [15] Bairu SG, Mghanga E, Hasan J, Kola S, Rao VJ, Bhanuprakash K, et al. Ultrafast Interfacial Charge-Transfer Dynamics in a Donor-π-Acceptor Chromophore Sensitized TiO₂ Nanocomposite. J Phys Chem C 2013;117:4824-35.
- [16] Dryza V, Nguyen JL, Kwon TH, Wong WWH, Holmes AB, Bieske EJ. Photophysics and aggregation effects of a triphenylamine-based dye sensitizer on metal-oxide nanoparticles suspended in an ion trap. Phys Chem Chem Phys 2013; 15:20326-32.
- [17] Sobuś J, Burdziński G, Karolczak J, Idígoras J, Anta JA, Ziółek M. Comparison of TiO₂ and ZnO solar cells sensitized with an indoline dye: Time resolved laser spectroscopy studies of partial charge separation processes. Langmuir 2014;30: 2505-12.
- [18] Yu X, Ci Z, Liu T, Feng X, Wang C, Ma T, et al. Influence of different electron acceptors in organic sensitizers on the performance of dye-sensitized solar cells. Dyes Pigments 2014;102:126-32.
- [19] Shen P, Liu YJ, Huang XW, Zhao B, Xiang N, Fei JJ, et al. Efficient triphenylamine dyes for solar cells: Effects of alkyl-substituents and π-conjugated thiophene unit. Dyes Pigments 2009;83:187-97.
- [20] Wan Z, Jia C, Duan Y, Zhou L, Lin Y, Shi Y. Phenothiazine–triphenylamine based organic dyes containing various conjugated linkers for efficient dye-sensitized solar cells. J Mater Chem 2012;22:25140-7.
- [21] Hara K, Wang ZS, Sato T, Furube A, Katoh R, Sugihara H, et al. Oligothiophene containing coumarin dyes for efficient dye-sensitized solar cells. J Phys Chem B 2005;109:15476-82.

- [22] Wang J, Li M, Qi D, Shen W, He R, Lin SH. Exploring photophysical properties of metal-free coumarin sensitizers: An efficient strategy to improve the performance of dye-sensitized solar cells. RSC Advances 2014;4:53927-38.
- [23] Ooyama Y, Shimada Y, Ishii A, Ito G, Kagawa Y, Imae I, et al. Photovoltaic performance of dye-sensitized solar cells based on a series of new-type donor-acceptor p-conjugated sensitizer, benzofuro[2,3-c]oxazolo[4,5-a] carbazole fluorescent dyes. J Photochem Photobiol A Chem 2009;203:177-85.
- [24] Hara K, Wang ZS, Cui Y, Furube A, Koumura N. Long-term stability of organic dye-sensitized solar cells based on an alkyl-functionalized carbazole dye. Energy Environ Sci 2009;2:1109-14.
- [25] Sobuś J, Karolczak J, Komar D, Anta JA, Ziółek M. Transient states and the role of excited state self-quenching of indoline dyes in complete dye-sensitized solar cells. Dyes Pigments 2015;113:692-701
- [26] Rohwer E, Richter C, Heming N, Strauch K, Litwinski C, Nyokong T, et al. Ultrafast photodynamics of the indoline dye D149 adsorbed to porous ZnO in dyesensitized solar cells. ChemPhysChem 2013;14:132-9.
- [27] Liu WH, Wu IC, Lai CH, Lai CH, Chou PT, Li YT, et al. Simple organic molecules bearing a 3,4-ethylenedioxythiophene linker for efficient dye-sensitized solar cells. Chem Comm 2008; 5152-4.
- [28] Chen KF, Hsu YC, Wu QY, Yeh MCP, Sun SS. Structurally simple dipolar organic dyes featuring 1,3-cyclohexadiene conjugated unit for dye-sensitized solar cells. Org Lett 2009;11:377-80.

- [29] Chen CH, Hsu YC, Chou HH, Thomas KRJ, Lin JT, Hsu CP. Dipolar Compounds Containing Fluorene and a Heteroaromatic Ring as the Conjugating Bridge for High-Performance Dye-Sensitized Solar Cells. Chem Eur J 2010;16:3184-93.
- [30] Wang L, Liang M, Zhang Y, Cheng F, Wang X, Sun Z, et al. Influence of donor and bridge structure in D-A-p-A indoline dyes on the photovoltaic properties of dyesensitized solar cells employing iodine/cobalt electrolyte. Dyes Pigments 2014;101:270-9.
- [31] El-Sherbiny D, Cheema H, El-Essawy F, Abdel-Megied A, El-Shafei A. Synthesis and characterization of novel carbazole-based terpyridyl photosensitizers for dyesensitized solar cells (DSSCs). Dyes Pigments 2015;115:81-7.
- [32] Baheti, A, Thomas KRJ, Lee CP, Li CT, Ho KC. Organic dyes containing fluoren-9ylidene chromophores for efficient dye-sensitized solar cells. J of Mat Chem A 2014;2:5766-79.
- [33] Lee J, Im H, Kim S, Kim C. Carbazole-functionalized organic photosensitizer for dye-sensitized solar cells. J Nanosci Nanotech 2015;15:1434-42.
- [34] Qian X, Gao HH, Zhu YZ, Lu L, Zheng JY. Biindole-based double D-π-A branched organic dyes for efficient dye-sensitized solar cells. RSC Advances 2015;5:4368-75.
- [35] Zhong C, Gao J, Cui Y, Li T, Han L. Coumarin-bearing triarylamine sensitizers with high molar extinction coefficient for dye-sensitized solar cells. J of Power Sources 2015;273:831-8.
- [36] Ju ZM, Jia HL, Ju XH, Zhou XF, Shi ZQ, Zheng HG, et al. Improvement of dyesensitized solar cells performance through introducing different heterocyclic groups to triarylamine dyes. RSC Advances 2015;5:3720-7.

- [37] Tan LL, Chen HY, Hao LF, Shen Y, Xiao LM, Liu JM, et al. Starburst triarylamine based dyes bearing a 3,4-ethylenedioxythiophene linker for efficient dye-sensitized solar cells. Phys Chem Chem Phys 2013;15:11909-17.
- [38] Bonnier C, Machin DD, Abdi OK, Robson KCD, Koivisto BD. The effect of donor-modification in organic light-harvesting motifs: triphenylamine donors appended with polymerisable thienyl subunits. Org Biomol Chem 2013;11:7011-5.
- [39] Hagberg DP, Yum JH, Lee H, De Angelis F, Marinado T, Karlsson KM, et al. Molecular Engineering of Organic Sensitizers for Dye-Sensitized Solar Cell Applications. J Am Chem Soc 2008;130:6259-66.
- [40] Fakis M, Hrobárik P, Yushchenko O, Sigmundová I, Koch M, Rosspeintner A, et al. Excited State and Injection Dynamics of Triphenylamine Sensitizers Containing a Benzothiazole Electron-Accepting Group on TiO₂ and Al₂O₃ Thin Films. J Phys Chem C 2014;118:28509-19.
- [41] Dori M, Seintis K, Stathatos E, Tsigaridas G, Lin TY, Lin JT, et al. Electron injection studies in TiO₂ nanocrystalline films sensitized with fluorene dyes and photovoltaic characterization. The effect of co-adsorption of a bile acid derivative. Chem Phys Let 2013;563:63-9.
- [42] Fakis M, Stathatos E, Tsigaridas G, Giannetas V, Persephonis P. Femtosecond decay and electron transfer dynamics of the organic sensitizer D149 and photovoltaic performance in quasi-solid-state dye-sensitized solar cells. J of Phys Chem C 2011;115:13429-37.

- [43] Stathatos E, Lianos P, Stangar UL, Orel B, Judeinstein P. Structural Study of Hybrid Organic/Inorganic Polymer Gels Using Time-Resolved Fluorescence Probing. Langmuir 2000;16:8672-6.
- [44] Stathatos E. Organic-inorganic nanocomposite materials prepared by the sol-gel route as new ionic conductors in quasi solid state electrolytes. Ionics 2005;11:140- 5.
- [45] Giannouli M, Fakis M. Interfacial electron transfer dynamics and photovoltaic performance of TiO₂ and ZnO solar cells sensitized with Coumarin 343. J of Photochem and Photobiol A Chem 2011;226:42-50.
- [46] Fakis M, Dori M, Stathatos E, Chou HH, Yen YS, Lin JT, et al. Electron injection in TiO₂ films and quasi-solid state solar cells sensitized with a dipolar fluorene organic. J of Photochem and Photobiol A Chem 2013;251:18-24.
- [47] Ziolek M, Yang X, Sun L, Douhal A. Interrogating the ultrafast dynamics of an efficient dye for sunlight conversion. Phys Chem Chem Phys 2010;12:8098-8107.
- [48] Ramakrishna G, Ghosh HN. Efficient Electron Injection from Twisted Intramolecular Charge Transfer (TICT) State of 7-Diethyl amino coumarin 3carboxylic Acid (D-1421) Dye to TiO₂ Nanoparticle. J Phys Chem A 2002;106:2545-2553.
- [49] Verma S, Ghosh HN. Tuning Interfacial Charge Separation by Molecular Twist: A New Insight into Coumarin-Sensitized TiO2 Films. J Phys Chem C 2014;118:10661-10669.
- [50] Debnath T, Maity P, Lobo H, Singh B, Shankarling GS, Ghosh HN. Extensive Reduction in Back Electron Transfer in Twisted Intramolecular Charge-Transfer

(TICT) Coumarin-Dye-Sensitized TiO₂ Nanoparticles/Film: A Femtosecond Transient Absorption Stydy. Chem Eur J 2014;20:3510-3519.

- [51] El-Zohry A, Orthaber A, Zietz B. Isomerization and Aggregation of the Solar Cell Dye D149. J Phys Chem C 2012;116:26144-26153.
- [52] Zhang J, Yao Z, Cai Y, Yang L, Xu M, Li R, et al. Conjugated linker correlated energetics and kinetics in dithienopyrrole dye-sensitized solar cells. Energy Environ Sci 2013;6:1604-14.
- [53] Chang YC, Wu HP, Reddy NM, Lee HW, Lu HP, Yeh CY, et al. The influence of electron injection and charge recombination kinetics on the performance of porphyrinsensitized solar cells: effects of the 4-tert-butylpyridine additive. Phys Chem Chem Phys 2013;15:4651-5.
- [54] Ziólek M, Cohen B, Yang X, Sun L, Paulose M, Varghese OK, Grimes GA, Douhal A. Femtosecond to millisecond studies of electron transfer processes in a donor-(π -specer)-acceptor series of organic dyes for solar cells interacting with titania nanoparticles and ordered nanotube array films. Phys Chem Chem Phys 2012;14:2816-31.
- [55] Santiago FF, Belmonte GG, Seró IM, Bisquert J. Characterization of nanostructured hybrid and organic solar cells by impedance spectroscopy. Phys Chem Chem Phys 2011;13:9083-118.
- [56] Wang Q, Moser JE, Grätzel M. Electrochemical Impedance Spectroscopic Analysis of Dye-Sensitized Solar Cells. J Phys Chem B 2005;109:14945-53.

[57] Adachi M, Sakamoto M, Jiu J, Ogata Y, Isoda S. Determination of Parameters of Electron Transport in Dye-Sensitized Solar Cells Using Electrochemical Impedance Spectroscopy. J Phys Chem B 2006;110:13872-80.

Schemes:

Scheme 1. Chemical structures of MZ-341 and MZ-235 dyes. Scheme 2. Synthetic procedures of the MZ-235 and MZ-341

Tables:

Table 1: Photophysical parameters of MZ-341 and MZ-235 dyes.

Table 2: Decay parameters of MZ-341 and MZ-235 in toluene and THF obtained by fs upconversion spectroscopy upon excitation at 400 nm. The results were obtained after a global analysis method on five different detection wavelengths and are shown here for the wavelength corresponding to the peak of the fluorescence spectra.

Table 3: Decay parameters of MZ-341 in toluene and THF and MZ-235 in toluene obtained by TCSPC spectroscopy upon excitation at 403 nm.

Table 4: Decay parameters of MZ-341 and MZ-235 on TiO_2 and Al_2O_3 substrates upon excitation at 400 nm.

Table 5: Solar cells parameters for DSSCs with TiO₂ photoelectrodes sensitized with MZ-235 and MZ-341.

Table 6: Fitted parameters derived from electrochemical impedance spectroscopy.

Figure captions:

Figure 1. IR spectra of MZ-235 and MZ-341 dyes.

Figure 2. Cyclic voltammograms of the MZ-235 (a) and MZ-341 (b) dyes

Figure 3. Absorption and fluorescence spectra of (a) MZ-341 and (b) MZ-235 in toluene and THF solutions. Additionally, the fluorescence spectrum of MZ-235 in THF/PS solution is presented in (b).

Figure 4. Absorption and fluorescence spectra of (a) MZ-341 and (b) MZ-235 on TiO_2 and Al_2O_3 substrates.

Figure 5. (a) Fluorescence dynamics of MZ-341 in toluene and THF solutions at 550 nm and 600 nm, respectively and (b) Fluorescence dynamics of MZ-235 in toluene and THF solutions at 575 nm and 610 nm and in THF/PS at 610 nm respectively. The dynamics in (a) and (b) were obtained by fs upconversion fluorescence spectroscopy. (c) Fluorescence dynamics of MZ-341 in toluene and THF solutions at 550 nm and 600 nm, respectively and of MZ-235 in toluene at 575 nm obtained by TCSPC spectroscopy. The fitting curves have been derived by multiexponential functions and they are represented by solid lines.

Figure 6. Fluorescence dynamics of MZ-341 and MZ-235 on TiO_2 and Al_2O_3 substrates at 590nm. The fitting curves have been derived by three exponential decay functions and they are represented by solid lines.

Figure 7. (a) *J-V* curves of quasi-solid state solar cells employing MZ-341 and MZ-235 dyes under illumination (1.5 A.M, $1000W/m^2$) and (b) in dark.

Figure 8. Impedance spectra: Nyquist plots of MZ-235 and MZ-341 sensitized DSSCs performed under illumination $(1.5 \text{ A.M}, 1000 \text{W/m}^2)$.

Figure 9. Bode phase plots of MZ-235 and MZ-341 sensitized DSSCs performed under illumination (1.5 A.M, $1000W/m^2$).

Supporting Information:

Figure S1. (a) ¹H-NMR of $6-(4-\{bis[4-(hexyloxy)phenyl]amino\}phenyl)-1H,3H-benzo[de]isochromene-1,3-dione (b) ¹³C-NMR of <math>6-(4-\{bis[4-(hexyloxy)phenyl]amino\}phenyl)-1H,3H-benzo[de]isochromene-1,3-dione$

Figure S2. (a) ¹H-NMR of 4-(4-{bis[4-(hexyloxy)phenyl]amino}phenyl)-7-oxo-7Hbenzimidazo[2,1-a]benzo[de]isoquinoline-11-carboxylic acid (b) ¹³C-NMR of 4-(4-{bis[4-(hexyloxy)phenyl]amino}phenyl)-7-oxo-7H-benzimidazo[2,1-

a]benzo[de]isoquinoline-11-carboxylic acid

Figure S3. (a) ¹H-NMR of methyl 4-bromo-7-oxo-7*H*-benzimidazo[2,1-a]benzo[de]isoquinoline-11-carboxylate (b) ¹³C-NMR of methyl 4-bromo-7-oxo-7*H*-benzimidazo[2,1-a]benzo[de]isoquinoline-11-carboxylate

Figure S4. (a) ¹H-NMR of methyl 4-[4-(diphenylamino)phenyl]-7-oxo-7*H* benzimidazo[2,1-a]benzo[de]isoquinoline-11-carboxylate (b) ¹³C-NMR of methyl 4-[4-(diphenylamino)phenyl]-7-oxo-7*H*-benzimidazo[2,1-a]benzo[de]isoquinoline-11-carboxylate

Figure S5. (a) ¹H-NMR of 4-[4-(diphenylamino)phenyl]-7-oxo-7*H*-benzimidazo[2,1-*a*]benzo[*de*]isoquinoline-11-carboxylic acid (b) 13 C-NMR of 4-[4-(diphenylamino)phenyl]-7-oxo-7*H*-benzimidazo[2,1-*a*]benzo[*de*]isoquinoline-11-carboxylic acid

Figure S6. Fluorescence dynamics of MZ-341 in (a) toluene at 500 nm, 550 nm and 600 nm and in (b) THF at 530 nm, 600 nm and 670 nm, respectively.

Figure S7. Fluorescence dynamics of MZ-235 in (a) toluene at 525 nm, 575 nm and 625 nm and in (b) THF at 540 nm, 610 nm and 660 nm, respectively.

Table S1. Decay parameters of MZ-341 in toluene obtained by fs upconversion spectroscopy upon excitation at 400 nm. The results were obtained after a global analysis method on five different detection wavelengths.

Table S2. Decay parameters of MZ-341 in THF obtained by fs upconversion spectroscopy upon excitation at 400 nm. The results were obtained after a global analysis method on five different detection wavelengths.

Table S3. Decay parameters of MZ-235 in toluene obtained by fs upconversion spectroscopy upon excitation at 400 nm. The results were obtained after a global analysis method on five different detection wavelengths.

Table S4. Decay parameters of MZ-235 in THF obtained by fs upconversion spectroscopy upon excitation at 400 nm. The results were obtained after a global analysis method on four different detection wavelengths.



Scheme 1. Chemical structures for (a) MZ-341 and (b) MZ-235 dyes.



Scheme 2. Synthetic procedures of the MZ-235 and MZ-341

	$\lambda_{abs} (nm)$	λ_{fluor} (nm)	$\lambda_{abs} (nm)$	λ_{fluor} (nm)	
	MZ-	341	MZ-235		
Toluene	443 (3240)*	547	460 (5840)*	576	
THF	441 (9050)	595	460 (4870)	613	
TiO ₂ film	440	591	472	585	
Al ₂ O ₃ film	438	582	472	583	

Table 1: Photophysical parameters of MZ-341 and MZ-235 dyes.

^{*} The molar extinction coefficients in M^{-1} cm⁻¹ are shown in parentheses.

Table 2: Decay parameters of MZ-341 and MZ-235 in toluene and THF obtained by fs upconversion spectroscopy upon excitation at 400 nm. The results were obtained after a global analysis method on five different detection wavelengths and are shown here for the wavelength corresponding to the peak of the fluorescence spectra.

Solvent	λ _{det} (nm)	A ₁	<mark>τ1 (ps)</mark>	A ₂	<mark>τ₂ (ps)</mark>	A ₃	<mark>τ₃ (ps)</mark>	$\mathbf{A_4}$	<mark>τ₄ (ps)</mark>		
<u>MZ-341</u>											
Toluene	<mark>550</mark>	<mark>-0.36</mark>	<mark>1.7</mark>	<mark>0.22</mark>	<mark>5.5</mark>	<mark>0.78</mark>	ns com	nponent			
THF	<mark>600</mark>	<mark>-0.42</mark>	<mark>0.63</mark>	<mark>0.18</mark>	<mark>1.0</mark>	0.51	<mark>5.0</mark>	<mark>0.31</mark>	ns component		
				M	<mark>IZ-235</mark>						
Toluene	<mark>575</mark>	<mark>-0.06</mark>	<mark>1.1</mark>	<mark>0.60</mark>	<mark>4.0</mark>	<mark>0.14</mark>	<mark>26</mark>	0.25	ns component		
THF	<mark>610</mark>	-	-	<mark>0.17</mark>	<mark>0.40</mark>	<mark>0.76</mark>	<mark>1.2</mark>	<mark>0.07</mark>	<mark>70</mark>		

Table 3: Decay parameters of MZ-341 in toluene and THF and MZ-235 in toluene obtained by TCSPC spectroscopy upon excitation at 403 nm.

Solvent	Wavelength (nm)	A ₁	τ_1 (ns)	A_2	τ_2 (ns)					
MZ-341										
Toluene	550	0.10	0.85	0.9	4.4					
THF	600	-	-	1.0	4.2					
	M	Z-235								
Toluene	575	0.43	0.50	0.57	3.2					
THF*	610	-	-	-	-					

* No data for MZ-235 in THF were recorded, as it presents only picoseconds decay components.

Substrate	A ₁	<mark>τ1 (ps)</mark>	A ₂	τ₂ (ps)	A ₃	<mark>τ₃ (ps)</mark>	-					
<u> </u>												
TiO ₂	<mark>0.37</mark>	1.0	<mark>0.42</mark>	<mark>5.8</mark>	<mark>0.21</mark>	<mark>44</mark>						
Al_2O_3	<mark>0.44</mark>	<mark>3.1</mark>	<mark>0.36</mark>	<mark>17.6</mark>	<mark>0.20</mark>	<mark>156</mark>						
MZ-235												
TiO ₂	<mark>0.53</mark>	<mark>0.6</mark>	<mark>0.34</mark>	<mark>4.7</mark>	<mark>0.13</mark>	<mark>48</mark>						
Al ₂ O ₃	<mark>0.46</mark>	<mark>2.0</mark>	<mark>0.32</mark>	<mark>23.3</mark>	<mark>0.22</mark>	<mark>387</mark>						
							-					

Table 4: Decay parameters of MZ-341 and MZ-235 on TiO_2 and Al_2O_3 substrates upon excitation at 400 nm.

Table 5: Solar cells parameters for DSSCs with TiO_2 photoelectrodes sensitized with MZ-341 and MZ-235

Dye	$V_{oc} (mV)$	J_{sc} (mA/cm ²)	FF	n (%)
MZ-341	<mark>663±2</mark>	6.83±0.02	0.74	3.4
MZ-235	<mark>662±2</mark>	<mark>6.45±0.02</mark>	0.69	3.0

Table 6: Fitted parameters derived from electrochemical impedance spectroscopy.

Dye	$\mathbf{R}_{\mathbf{h}}\left(\Omega ight)$	$\mathbf{R}_{\mathrm{pt}}\left(\Omega ight)$	C _{pt} (µF)	$\mathbf{R}_{\mathrm{tr}}(\Omega)$	$C_{tr}(\mu F)$	$\mathbf{R}_{\mathrm{dif}}\left(\Omega\right)$	C _{dif} (mF)
MZ-341	<mark>6.09±0.03</mark>	<mark>1.13±0.03</mark>	> 35	<mark>3.38±0.18</mark>	125	<<0.81	-
MZ-235	7.22±0.03	<mark>0.669±0.03</mark>	53.1	<mark>3.85±0.18</mark>	799	<mark>0.810±0.18</mark>	188



Figure 1. Cyclic voltammograms of (α) the MZ-341 and (b) MZ-235 dyes



Figure 2 : IR spectra of (α) MZ-341 and (β) MZ-235 dyes.



Figure 3. Absorption and fluorescence spectra of (a) MZ-341 and (b) MZ-235 in toluene and THF solutions. Additionally, the fluorescence spectrum of MZ-235 in THF/PS solution is presented in (b).



Figure 4. Absorption and fluorescence spectra of (a) MZ-341 and (b) MZ-235 on TiO_2 and Al_2O_3 substrates.

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Figure 5. (a) Fluorescence dynamics of MZ-341 in toluene and THF solutions at 550 nm and 600 nm, respectively and (b) Fluorescence dynamics of MZ-235 in toluene and THF solutions at 575 nm and 610 nm and in THF/PS at 610 nm respectively. The dynamics in (a) and (b) were obtained by fs upconversion fluorescence spectroscopy. (c) Fluorescence dynamics of MZ-341 in toluene and THF solutions at 550 nm and 600 nm, respectively and of MZ-235 in toluene at 575 nm obtained by TCSPC spectroscopy. The fitting curves have been derived by multiexponential functions and they are represented by solid lines.



Figure 6. Fluorescence dynamics of MZ-341 and MZ-235 on TiO_2 and Al_2O_3 substrates at 590nm. The fitting curves have been derived by three exponential decay functions and they are represented by solid lines.



Figure 7. (a) *J-V* curves of quasi-solid state solar cells employing MZ-341 and MZ-235 dyes under illumination (1.5 A.M, $1000W/m^2$) and (b) in dark. Inset of Fig.7a: the absolute absorbance of sensitized TiO₂ films with both dyes.



Figure 8. Impedance spectra: Nyquist plots of MZ-341 and MZ-235 sensitized DSSCs performed under illumination of 1sun.



Figure 9. Bode phase plots of MZ-341 and MZ-235 sensitized DSSCs performed under illumination of 1sun.

Supporting Information

for

The effect of additional electron donating group on the photophysics and photovoltaic performance of two new metal free D- π -A sensitizers.

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Figure S1. (a) ¹H-NMR of $6-(4-\{bis[4-(hexyloxy)phenyl]amino\}phenyl)-1H,3H-benzo[de]isochromene-1,3-dione (b) ¹³C-NMR of <math>6-(4-\{bis[4-(hexyloxy)phenyl]amino\}phenyl)-1H,3H-benzo[de]isochromene-1,3-dione$



Figure S2. (a) ¹H-NMR of 4-(4-{bis[4-(hexyloxy)phenyl]amino}phenyl)-7-oxo-7Hbenzimidazo[2,1-a]benzo[de]isoquinoline-11-carboxylic acid (b) ¹³C-NMR of 4-(4-{bis[4-(hexyloxy)phenyl]amino}phenyl)-7-oxo-7H-benzimidazo[2,1a]benzo[de]isoquinoline-11-carboxylic acid



Figure S3. (a) ¹H-NMR of methyl 4-bromo-7-oxo-7*H*-benzimidazo[2,1-a]benzo[de]isoquinoline-11-carboxylate (b) ¹³C-NMR of methyl 4-bromo-7-oxo-7*H*-benzimidazo[2,1-a]benzo[de]isoquinoline-11-carboxylate



Figure S4. (a) ¹H-NMR of methyl 4-[4-(diphenylamino)phenyl]-7-oxo-7*H* benzimidazo[2,1-a]benzo[de]isoquinoline-11-carboxylate (b) ¹³C-NMR of methyl 4-[4-(diphenylamino)phenyl]-7-oxo-7*H*-benzimidazo[2,1-a]benzo[de]isoquinoline-11-carboxylate

Figure S5. (a) ¹H-NMR of 4-[4-(diphenylamino)phenyl]-7-oxo-7*H*-benzimidazo[2,1-a]benzo[de]isoquinoline-11-carboxylic acid (b) . ¹³C-NMR of 4-[4-(diphenylamino) phenyl]-7-oxo-7*H*-benzimidazo[2,1-a]benzo[de]isoquinoline-11- carboxylic acid

Figure S6. Fluorescence dynamics of MZ-341 in (a) toluene at 500 nm, 550 nm and 600 nm and in (b) THF at 530 nm, 600 nm and 670 nm, respectively.

Figure S7. Fluorescence dynamics of MZ-235 in (a) toluene at 525 nm, 575 nm and 625 nm and in (b) THF at 540 nm, 610 nm and 660 nm, respectively.

Table S1	. Decay	parameters	of	MZ	-341	in	toluene	obtained	by	fs	upcon	nversion
spectrosco	py upon	excitation at	400) nm.	The	resu	ilts were	obtained	after	ag	global	analysis
method on	five diff	erent detection	on v	vavel	engtl	hs.						

	A ₁	τ ₁ (ps)	A ₂	τ ₂ (ps)	A ₃	<mark>τ₃(ps)</mark>
<mark>500</mark>	<mark>0.17</mark>		<mark>0.51</mark>		<mark>0.32</mark>	
<mark>525</mark>	<mark>-0.12</mark>		<mark>0.57</mark>		<mark>0.43</mark>	<mark>ns</mark>
<mark>550</mark>	<mark>-0.36</mark>	<mark>1.7</mark>	<mark>0.22</mark>	<mark>5.5</mark>	<mark>0.78</mark>	component
<mark>575</mark>	<mark>-0.08</mark>		<mark>-0.26</mark>		1	
<mark>600</mark>	<mark>-0.18</mark>		<mark>-0.19</mark>		1	

Table S2. Decay parameters of MZ-341 in THF obtained by fs upconversion spectroscopy upon excitation at 400 nm. The results were obtained after a global analysis method on five different detection wavelengths.

	A ₁	<mark>τ₁(ps)</mark>	A ₂	<mark>τ₂(ps)</mark>	A ₃	τ ₃ (ps)	A ₄	<mark>τ₄(ps)</mark>
<mark>530</mark>	<mark>0.95</mark>		<mark>0.04</mark>		<mark>0.01</mark>		<mark>0</mark>	
<mark>565</mark>	<mark>-0.16</mark>		<mark>0.73</mark>		<mark>0.22</mark>		<mark>0.05</mark>	<mark>ns</mark>
<mark>600</mark>	<mark>-0.42</mark>	<mark>0.63</mark>	<mark>0.18</mark>	<mark>1.0</mark>	<mark>0.51</mark>	<mark>5.0</mark>	<mark>0.31</mark>	component
<mark>635</mark>	<mark>-0.71</mark>		<mark>0.03</mark>		<mark>0.42</mark>		<mark>0.55</mark>	
<mark>670</mark>	<mark>-0.64</mark>		<mark>-0.12</mark>	,	<mark>0.20</mark>		<mark>0.80</mark>	

Table S3. Decay parameters of MZ-235 in toluene obtained by fs upconversion spectroscopy upon excitation at 400 nm. The results were obtained after a global analysis method on five different detection wavelengths.

	A ₁	<mark>τ₁(ps)</mark>	A ₂	<mark>τ₂(ps)</mark>	A ₃	<mark>τ₃(ps)</mark>	A4	<mark>τ₄(ps)</mark>
<mark>525</mark>	<mark>0.60</mark>		<mark>0.29</mark>		<mark>0.07</mark>		<mark>0.04</mark>	
<mark>550</mark>	<mark>0.29</mark>		<mark>0.60</mark>		<mark>0.09</mark>		<mark>0.11</mark>	<mark>ns</mark>
<mark>575</mark>	<mark>-0.10</mark>	<mark>1.1</mark>	<mark>0.60</mark>	<mark>4.0</mark>	<mark>0.15</mark>	<mark>26</mark>	<mark>0.25</mark>	component
<mark>600</mark>	<mark>-0.20</mark>		<mark>0.20</mark>		<mark>0.38</mark>		<mark>0.42</mark>	
<mark>625</mark>	<mark>-0.13</mark>		<mark>-0.10</mark>		<mark>0.26</mark>		<mark>0.74</mark>	

Table S4. Decay parameters of MZ-235 in THF obtained by fs upconversion spectroscopy upon excitation at 400 nm. The results were obtained after a global analysis method on four different detection wavelengths.

	A ₁	<mark>τ₁(ps)</mark>	A ₂	τ ₂ (ps)	A ₃	<mark>τ₃(ps)</mark>
<mark>540</mark>	<mark>0.96</mark>		<mark>0.03</mark>		<mark>0.01</mark>	
<mark>575</mark>	<mark>0.66</mark>	<mark>0.4</mark>	<mark>0.33</mark>	<mark>1.2</mark>	<mark>0.01</mark>	<mark>70</mark>
<mark>610</mark>	<mark>0.17</mark>		<mark>0.76</mark>		<mark>0.07</mark>	
<mark>660</mark>	<mark>-0.119</mark>		<mark>0.75</mark>		<mark>0.25</mark>	

Highlights

- 1. Synthesis of D- π -A organic sensitizers with benzimidazole group as π -bridge.
- 2. Solar cell conversion efficiency of 3.4% with the D- π -A sensitizers.
- 3. Electron injection dynamics on TiO₂ and Al₂O₃ films sensitized with the two dyes.