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Microwave assisted synthesis of a series of charge-transfer photosensitizers having Quinoxaline-2(1H)-one as anchoring group onto TiO₂ surface

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Keywords: Quinoxaline, electron-transfer, anchor group, Knoevenagel reaction.

HIGHLIGHTS

- Efficient preparation of push-pull dyes having quinoxaline-2(1H)-one as anchoring group by microwave irradiation method.
- Ferrocene group acts as a quencher inhibiting photoinduced electron injection onto TiO₂.
- The quinoxaline-2(1H)-one was linked to several electro-donor fragments through Knoevenagel reaction.
- Calculated electronic properties were consistent with the experimental data, confirming the feasibility of photoinduced electrons in TiO₂.
- The efficiency of push-pull compounds depend on the molecular structure and the nature of the donor-groups

GRAFICAL ABSTRACT

Microwave assisted synthesis of a series of charge-transfer photosensitizers having Quinoxaline-2(1H)-one as anchoring group onto TiO₂ surface

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ABSTRACT:

In this work, we present the synthesis of novel donor-acceptor compounds based on 3methylquinoxaline-2(1H)one which follow an easy synthetic route, involving Knoevenagel reaction with electron-donor groups such as N,N-dimethylaminobenzene, ferrocene, triphenylamine (TPA) and ((*E*)-4,4'-(ethene-1,2-diyl)bis(N,N-diphenylaniline). Additionally, the optical properties were measured by means of the absorption and emission spectroscopy suggesting a push-pull behavior which was further confirmed by electrochemical experiments. Finally, the quinoxaline-2(1H)one fragment not only bestow wide absorption, but also can chelate to titanium ions on the TiO₂ surface, allowing a strong electron coupling between the excited-state energy level of the dyes and the conduction band of TiO₂.

Keywords: Triphenylamine, TiO₂, anchor group, qinaxoline, push-pull, microwave irradiation.

1. INTRODUCTION

Organic molecular systems can be assembled (anchored) onto a metal oxide substrate in different ways: covalent attachment, electrostatic interaction, hydrogen bonding, hydrophobic interaction, van der Waals forces, or physical entrapment [1]. However, finding new anchoring groups for the preparation of contact structures, that provide both stability and high contact transparency, is a critical issue in molecular materials and molecular electronics [2-4].

Actually, the development of a wide variety of materials for areas such as electrical conducting materials, non-linear optics (NLO), molecular rectification, dyes, solvatochromism, and photovoltaics (PV) [5], employ interactions between organic molecules and semiconductor oxides. For example, dye-sensitized solar cells (DSSCs), firstly reported by Grätzel in 1991[6], absorbed dye molecules on the surface of titanium dioxide (TiO₂).

The DSSCs have the potential to improve the present conventional solar cells based on silicon [7-8]. The immobilization of the light harvesting molecules onto the surface of semiconductor metal oxide nanoparticles, which collectively act as the working electrode in a DSSCs, is crucial for initiating a charge separation process via the injection of electrons from the excited organic molecule (dye) into the conduction band of the metal oxide; thus mimicking the natural

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photosynthesis[9]. The most featured and commonly used anchoring groups for DSSCs are carboxylic acid and cyanoacrylic acid group[10-12].

On the other hand, new anchoring groups have emerged which not only improve the understanding of the fundamental processes involved in DSSCs but also increase the number of new sensitizing materials. For example, recently a novel electron acceptor 2-(1,1-dicyanomethylene)rhodanine, exhibiting high light harvesting and conversion efficiency [13-14] was reported.

Microwave irradiation (MWI) is a technique that has been widely employed in synthetic chemistry owing several advantages compared to traditional methods, especially those related to selective heating, which minimizes or avoids side reactions. Microwave assisted organic synthesis (MAOS) has also emerged as a powerful tool for high-throughput procedures. Accordingly, this technique can improve the yield and purity of the final compounds while shortening the reaction times by means of a precise control of parameters, such as, irradiation power, pressure and temperature [15-19].

In this work, we report the microwave assisted synthesis of a novel series of photosensitizers based on triphenylamine (TPA), N,N-dimethylaminobenzene, ((*E*)-4,4'-(ethene-1,2-diyl)bis(N,N-diphenylaniline) and Ferrocene as electron-donor groups and quinoxaline-2(1H)-one as anchoring group. A detailed study was conducted to understand the relevance of electronic structure on the photoinjection properties, as well as on the electrochemical properties and impedance spectroscopy of devices containing the new dyes.

2. EXPERIMENTAL

2.1 Materials and equipments.

Reagents were used as purchased without further purification unless stated otherwise. Solvents used in photochemical measurements were spectroscopic grade. All air-sensitive reactions were conducted under argon atmosphere using dried solvents prepared according to recommended standard procedures. FTIR spectra were recorded using a Shimadzu FT-IR 8400 spectrophotometer. Absorption spectra were registered in a Jasco V-730 spectrophotometer

using fused quartz glass cuvettes with 10.0 mm optical path. Fluorescence measurements were performed in a Jasco spectrofluorometer (FP-8500). NMR spectra were recorded on a BRUKER 400 MHz UltraShield Advance II NMR (¹H: 400 MHz, ¹³C: 100 MHz) spectrometer at 298 K using deuterated solvents with TMS as internal standard. Coupling constants (*J*) are reported in Hz and chemical shifts (δ) in ppm. Nuclear spin coupling multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet-doublet. Mass spectra were recorded on a Shimadzu MS-QP 2010 spectrometer operating at 70 eV. Analytical thin layer chromatography (TLC) was performed using aluminum coated Sorbent Technologies 60 UV254 plates. Microwave experiments were carried out on a focused microwave reactor (300W CEM Discover).

2.2. Electrochemical measurements.

Electrochemical measurements were performed in a METR Ω N Autolab PGSTAT 300N potentiostat/galvanostat, using a three-electrode configuration system. The measurements were carried out using a 0.1 M tetrabutylammoniun hexafluorophosphate (TBAPF₆) solution in electrochemical grade CH₃CN as electrolyte. A glassy-carbon electrode (3 mm diameter) was used as the working electrode, and a platinum wire and an Ag electrode were employed as the counter and the pseudo-reference electrodes respectively. The ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as the internal reference to measure the potentials. Both the counter and the reference electrodes were directly immersed in the electrolyte solution. The surface of the working electrode was carefully polished to mirror like finish with 0.3 and 0.5 alumina slurries prior use. Solutions were deaerated by bubbling argon for few minutes prior each voltammetric scan at 100 mV/s, unless otherwise specified.

2.3. DSSCs Fabrication

The **MQ1-MQ5** dyes described below were applied in DSSCs according to an adapted literature procedure [20]. Colloidal TiO₂ nanoparticles (25 nm large) paste were made by dispersing the nanoparticles in terpineol, ethylcellulose and ethanol mixture as described previously [21]. Mesoporous TiO₂ nanoparticles electrodes were prepared spreading the colloidal paste on pieces of conducting FTO (resistance ~15 Ω sq⁻¹) that were subsequently dried in air, heated to 120 °C for an hour and sintered for 30 min at 450 °C.

After cooling down to room temperature, the electrodes were dipped into $1.0 \ge 10^{-4} \mod L^{-1}$ solution of MQ1-MQ5 dyes in acetonitrile. The dye-sensitized electrodes were hot-pressed (110 °C) together with a platinum doped FTO counter electrode and a 40 mm thick Surlyn spacer intercalated in between. Finally, a hole was drilled and the electrolyte solution (0.5 M tert-butylpyridine, 0.6 M tetrabutylamonium iodide, 0.1 M LiI, 0.1 M I₂ in methoxypropionitrile) introduced in after making vacuum inside. Then I $\ge 1 \ge 1 \le 10^{-1}$ M and electrochemical impedance spectroscopy (EIS) measurements were registered using a AutoLab PGSTAT30 potentiostat/galvanostat while irradiating the devices with an ABB class AM 1.5 Oriel solar simulator (ASTM, JIS, IEC) calibrated with a standardized Si light meter (VISI standards, oriel P/N 91150V). Electrochemical impedance spectra were registered from 0.01 to 100,000 Hz at cell open circuit potential (V_{OC}) modulating the frequency of the superimposed sinusoidal potential wave (amplitude = 30 mV). IPCE spectra were registered using an Oriel Spectral Luminator as light irradiation source.

2.4. Synthesis and Characterization

The starting materials 4-formyltriphenylamine **3** and 4,4'-diformyltriphenylamine **4**, were prepared following literature procedures [22]. The compound **5** was prepared by Michaelis-Arbuzov reaction [23] and the starting material **6** was obtained by Horner-Emmons reaction [24]. The preparation of the target molecules (**MQ1-MQ5**) was performed using a Knoevenagel condensation with compound **1** under basic conditions and using microwave irradiation, as shown in Scheme 1.

2.4.1. Synthesis of MQ1

A mixture of formyltriphenylamine **3** (80 mg, 0.29 mmol), 3-methylquinoxalin-2(1H)-one **1** (39 mg, 0.24 mmol) and piperidine (3 drops), were subjected to microwave irradiation, at 120 °C for 2 min and a maximum power of 300 W. Then, the reaction mixture was purified by column chromatography using a mixture of $CH_2Cl_2/ethyl$ acetate (15:1) as eluent, to get pure **MQ1** as orange solid, 78% yield.

¹H NMR (DMSO-d₆, 400 MHz) δ : 12.45 (s, 1H), 8.02 (d, *J* = 16.0 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 6.8 Hz, 2H), 7.45-7.52 (m, 2H), 7.37 (t, *J* = 8.0 Hz, 4H), 7.28-7.31 (m, 2H), 7.10-7.16 (m, 6H), 6.95 (d, *J* = 12.0 Hz, 2H) ppm; ¹³C NMR (DMSO-d₆, 100 MHz) δ :

155.3, 153.7, 149.0, 147.0, 137.2, 133.0, 132.0, 130.2, 129.9, 129.8, 129.5, 128.6, 125.5, 124.5, 123.9, 121.9, 120.0, 115.7 ppm; FTIR v= 3415, 1662 cm⁻¹, MS (IE): m/z 415 [M⁺].

2.4.2. Synthesis of MQ2

A mixture of formylferrocene **7** (100 mg, 0.47 mmol), 3-methylquinoxalin-2(1H)-one **1** (63 mg, 0.39 mmol) and piperidine (3 drops), were subjected to microwave irradiation, at 120 °C for 3 min and a maximum power of 300 W. Then, the reaction mixture was purified by column chromatography using CH₂Cl₂ as eluent, to get pure **MQ2** as dark purple solid, 62% yield. ¹H NMR (DMSO-d₆, 400 MHz) δ : 12.38 (s, 1H), 7.96 (d, *J* = 16.0 Hz, 1H), 7.76 (d, *J* = 16.0

Hz, 1H), 7.18-7.47 (m, 4H), 4.73-4.81 (m, 4H), 4.16-4.31 (m, 5H) ppm; ¹³C NMR (DMSO-d₆, 100 MHz) δ : 164.2, 163.4, 155.3, 149.5, 139.0, 136.4, 133.8, 132.7, 125.2, 123.7, 71.0, 70.4, 69.9, 69.8, 68.7, 68.5 ppm; FTIR v = 3395, 1661 cm⁻¹; MS (IE): m/z 356 [M⁺].

2.4.3 Synthesis of MQ3

A mixture of (E)-4-((4-(4-(diphenylamino)styryl)phenyl)(phenyl)amino)benzaldehyde **6** (100 mg, 0.18 mmol), 3-methylquinoxalin-2(1H)-one **1** (25 mg, 0.16 mmol) and piperidine (3 drops), were subjected to microwave irradiation, at 130 °C for 2.2 min and a maximum power of 300 W. Then, the reaction mixture was purified by column chromatography using a mixture of CH₂Cl₂/ethyl acetate (15:1) as eluent, to get pure **MQ3** as orange solid, 58% yield.

¹H NMR (CDCl₃, 400 MHz) δ = 12.03 (s, 1H), 8.18 (d, *J* = 16.8 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 16.0 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.28-7.51 (m, 12H), 7.21 (d, *J* = 6.8 Hz, 2H), 7.14-7.17 (m, 7H), 6.96-7.12 (m, 10H); ¹³C NMR (CDCl₃, 100 MHz) δ : 156.7, 153.3, 148.8, 147.6, 147.2, 147.0, 146.3, 138.0, 133.7, 133.0, 131.8, 130.7, 130.3, 129.5, 129.5, 129.3, 129.2, 128.2, 127.3, 127.3, 127.3, 126.4, 125.4, 125.2, 125.1, 124.9, 124.7, 124.5, 124.2, 124.0, 123.7, 123.03, 122.6, 122.3, 119.4, 115.5 ppm; FTIR v = 3320, 1660 cm⁻¹; MS (IE): m/z 684 [M⁺].

2.4.4. Synthesis of MQ4

A mixture of 4,4'-diformyltriphenylamine **4** (100 mg, 0.33 mmol), 3-methylquinoxalin-2(1H)one **1** (80 mg, 0.50 mmol) and piperidine (3 drops), were subjected to microwave irradiation, at 150 °C for 5 min and a maximum power of 300 W. Then, the reaction mixture was purified by column chromatography using a mixture of CH_2Cl_2 /ethyl acetate (15:1) as eluent, to get pure **MQ4** as orange solid, 52% yield.

¹H NMR (DMSO-d₆, 400 MHz) δ : 12.48 (s, 1H), 12.31 (s, 1H), 8.05 (d, J = 16.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 3H), 7.57 (d, J = 8.0 Hz, 1H), 7.39-7.52 (m, 4H), 7.26-7.32 (m, 4H), 7.12-7.23 (m, 4H), 7.07 (d, J = 8.0 Hz, 3H) ppm; ¹³C NMR (DMSO-d₆, 100 MHz) δ : 159.7, 158.1, 155.3, 153.6, 137.01, 136.4, 130.4, 129.8, 129.6, 129.6, 128.7, 128.4, 126.3, 125.3, 124.0, 123.6, 123.5, 120.1, 120.7, 115.7 ppm; FTIR v = 3455, 1660 cm⁻¹; MS (IE): m/z 585 [M⁺].

2.4.5. Synthesis of MQ5

A mixture of 4-(dimethylamino)benzaldehyde 8 (120 mg, 0.81 mmol), 3-methylquinoxalin-2(1H)-one 1 (107 mg, 0.67 mmol) and piperidine (3 drops), were subjected to microwave irradiation, at 150 °C for 2 min and a maximum power of 300 W. Then, the reaction mixture was purified by column chromatography using CH_2Cl_2 as eluent, to get pure MQ5 as a red solid, 65% yield.

¹H NMR (CDCl₃, 400MHz) δ = 12.26 (s, 1H), 8.16 (d, *J* = 16.0 Hz, 1H), 7.84 (t, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 16.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H, 7.45 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 2H), 3.06 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ : 166.1, 165.6, 165.3, 165.1, 165.0, 164.9, 161.2, 160.8, 160.6, 159.26, 153.0, 152.3, 152.1, 152.0, 148.7, 148.5, 57.3 ppm; FTIR *v* = 3325, 1668 cm⁻¹; MS (IE): m/z 291 [M⁺].

3. RESULTS AND DISCUSSION

3.1. Synthesis

We reported the syntheses of new dye molecules having quinoxaline-2(1H)one as surface anchoring moiety and triphenylamine as electron-donor units, based on a simple synthetic method (scheme 1). The 3-methylquinoxaline-2(1H)one starting material was obtained by a procedure described in literature [25]. The formyl derivatives **3** and **4** were obtained by a Vilsmeier-Haack reaction. Subsequently, the derivative **6** was synthesized starting from dialdehyde **4** and diethyl (4-(diphenylamino)benzyl)phosphonate **5** at reflux in dry THF under argon. Finally, in order to diminish the amount of solvent and save time, Knoevenagel reactions were carried out between the 3-methylquinoxaline-2(1H)one 1 and the starting materials 3, 4, 6, 7 and 8 to obtain the target molecules MQ1-MQ5 in good yields (52-79%).

The structures of the new compounds were confirmed using analytical and spectroscopic techniques such as ¹H and ¹³C nuclear magnetic resonance (NMR), fourier infrared (FTIR) and mass spectrometry. FT-IR spectra of the target molecules showed the band corresponding to v(C=O) stretching mode around 1660 cm⁻¹.



Scheme 1. Reaction conditions: *i*) POCl₃, DMF, reflux; *ii*) piperidine, MW, 2-5 min, 120-150 °C, 300 W; *iii*) **4**, THF (dry), *t*-BuOK, argon, reflux.

Moreover, the ¹H NMR spectra of these compounds not only showed the aromatic protons, but a singlet around 12.45 ppm corresponding to the N-H proton of the quinoxaline ring, Furthermore, compounds **MQ1-MQ5** showed two doublets corresponding to the vinyl protons around 7.96-818 and 7.64-7.70 ppm with a coupling constant about 16.0 Hz. The mass spectrometry experiments showed that the m/z molecular ion peak in agreement with the molecular weight of the expected dye molecules.

3.2. Absorption and emission spectroscopy

The absorption and emission spectra of compounds **MQ1-MQ5** measured in acetonitrile are shown in figure 1. The absorption spectra of **MQ1**, **MQ3** and **MQ4** and **MQ5** solution exhibit the typical features of TPA based compounds: an absorption band around 250 nm assigned to a π - π * electronic transition and a second band around 320 nm attributed to a n- π * transition. Additionally, the band at 385-451 nm can be attributed to intramolecular charge transfer (ICT) from the TPA donor to the quinoxaline-2(1H)one acceptor [14].



Figure 1. a) Absorption spectra of MQ1-MQ5 measured in acetonirile. b) Absorption spectra o MQ1 in different solvents.

The obtained compounds exhibit the same acceptor and π spacer segments, therefore the changes in their absorption behaviors will be affected by the strength of the donor parts

under investigation. For instance, the absorption maxima of **MQ1** and **MQ2** appear at 434 and 386 nm, respectively. Their structures differ in their electron-donor fragments: the former sensitizer has a relatively strong donor TPA group, whereas the latter has a relatively weaker donor ferrocene group. In this manner, replacing the strong electron donor TPA for a weaker donor resulted in a blue-shifted absorption maxima by 48 nm.

The normalized absorption ICT band of **MQ1** (figure 1b) is dependent on the solvent, exhibiting a bathochromic shift as a function of the solvent polarity (donor number or basicity), as expected for charge-transfer transitions. In this case, the positive and negatively charged moieties are stabilized more efficiently by polar solvents thus decreasing the energy of the excited state species. Similar behavior was observed for **MQ5**, which exhibits a typical absorption spectrum pattern of a TPA derivative.

Fluorescence spectra measured upon excitation at λ_{max} in air-equilibrated acetonitrile solution, at 298 K, are shown in figure 2. The emission spectra of **MQ1-MQ5** compounds, exhibit a band at 565-570 nm, which is slightly red-shifted as compared to the respective ICT absorption band. This is consistent with a lowest energy charge-transfer excited state which favors electron-donor capability of the triarylamine and the other fragments, and eventually favoring the electron injection in TiO₂ thus leading to convertion of light into electricity. On the other hand, the weak solvatochromism for **MQ1**, and the separated charges in the ICT excited state seems to be more or less delocalized (figure 2b), indicating that this is the lowest excited state species. The absorption and emission wavelengths are summarized in Table 1.



Figure 2. a) Normalized emission spectra of MQ1-MQ5 measured in acetonirile. b) Normalized emission spectra of MQ1 in different solvents.

Compound	λ^{ICT}_{max}/nm $(\epsilon/M^{-1} \text{ cm}^{-1})^{a}$	λ_{Em}^{b}/nm	
MQ1	434 (26490)	569	
MQ2	386 (12064)	599	
MQ3	385 (19164)	570	
MQ4	451 (16746)	565	
MQ5	442 (47875)	570	

Table 1. Absorption and emission data of MQ1-MQ5 measured in acetonitrile

a) The ϵ was measured for the ICT band for the compounds at concentrations of 1×10^{-5} M, b) The λ_{Em} was measuring according to λ_{max} for each compound at concentrations of 1×10^{-5} M.

3.3. DSSC Performance and electrocemical analysis

Accordingly with the above observations, we decided to prepare DSSCs, which were assembled using mesoporous TiO_2 electrodes and sensitized with the **MQ1-MQ5** dyes, their electron photoinjection and recombination properties were also evaluated.

The curves of short-circuit current density as a function of potential are showed in figure 3. The **MQ3** and **MQ4** dyes showed higher power efficiency as expected for their higher values of Jsc and Voc (table 2). Coincidentally, these dyes are those with larger structures. This suggests that these structures decrease the recombination processes by preventing the approach of triiodide ions to semiconductor surface, thus decreasing the electron transfer from TiO₂ conduction band to triiodide ions electrolyte. On the other hand, the higher efficiency of the **MQ3** and **MQ4** can also be attributed due to the greater contribution of triphenylamine units and the presence of more anchoring amide groups which improve the electron injection into semiconductor conduction band and therefore improving the photovoltaic performance. It is to be noted that the lower efficiency of the **MQ2** dye, indicate that the ferrocene group is acting as an electron recombination site and/or preventing the vectorial transfer of electrons to TiO₂ due to its electron acceptor characteristics.



Figure 3. a) The short-circuit current density vs potential curve and b) the power vs potential curve of DSSCs built with non-sensitized a mesoporous TiO₂ electrode and electrodes sensitized with MQ1-MQ5.

Compounds	V _{oc} (V)	J_{sc} (mA/cm ²)	P _{max} (mW)	FF (%)	η (%)
MQ1 1	0.410	0.306	0.012	59.5	0.07
MQ1 2	0.418	0.295	0.012	59.8	0.07
MQ1 3	0.425	0.296	0.012	61.3	0.08
MQ2 1	0.120	0.013	6.73E-05	26.6	4.20E-04
MQ2 2	0.086	0.007	2.46E-05	24.5	1.54E-04
MQ2 3	0.025	0.003	2.65E-06	24.3	1.65E-05
MQ3 1	0.457	0.924	0.044	65.3	0.28
MQ3 2	0.459	0.921	0.044	65.5	0.28
MQ3 3	0.474	0.985	0.049	65.9	0.31
MQ4 1	0.479	1.094	0.055	66.0	0.35
MQ4 2	0.486	1.221	0.064	67.5	0.40
MQ4 3	0.465	1.088	0.050	61.4	0.31
MQ5 1	0.399	0.378	0.015	60.1	0.09
MQ5 2	0.403	0.357	0.014	60.8	0.09
MQ5 3	0.411	0.299	0.012	61.5	0.08
TiO₂ 1	0.418	0.206	0.008	56.4	0.05
TiO₂ 2	0.404	0.179	0.005	46.7	0.03
TiO₂ 3	0.418	0.199	0.008	60.1	0.05

Table 2. Short circuit current density (Jsc), open circuit voltage (Voc), Fill factor (FF), maximum power (Pmax) and efficiency parameters obtained through curves I vs. V.

A study of the electrical properties of the solar cells interfaces/junctions was carried out by electrochemical impedance spectroscopy (EIS) (figure 4). Nyquist impedance spectra provide information about charge transfer resistance of interface/junction based on the size of the respective arc in spectrum [26]. On the other hand, the time scales of the charge transfer processes are best seen in the Bode phase plot. By simulation of EIS spectrum using an equivalent circuit based on the transmission line model, parameters such as the electron recombination resistance (R_r), electron diffusion resistance (R_t), chemical capacitance (C_{μ}) , electron diffusion coefficient (D_n) , electron lifetime (t_n) and electron diffusion length (L_n) in TiO₂ conduction band can be determined. Thus, the EIS technique can be used to characterize the electrical properties of all interfaces/junctions presented in running DSSCs [27-28]. The electron transfer resistance in the counter electrode/electrolyte interface is assigned to the first arc at high frequencies in the Nyquist spectrum (figure 5a). The electron recombination resistance (\mathbf{R}_r) and the electron diffusion resistance (\mathbf{R}_t) in the TiO₂ mesoporous film can be determined by analyzing the second arc at intermediate frequencies. Finally, the resistance for ion diffusion in the electrolyte is associated with the last arc at low frequency region.



Figure 4. Nyquist and Bode phase spectra of running DSSCs prepared with the **MQ1-MQ5** dyes and non-sensitized TiO₂ electrode for comparison.

The diameter of the arc at intermediate frequency of **MQ1-MQ5** exhibit variations that can be attributed to R_r values change (figure 4a and table 3). All photosensitizers showed lower

recombination resistance than the device prepared with non-sensitized mesoporous TiO_2 electrode which exhibited much larger electron recombination rates. In Bode phase spectrum (figure 4b), the band assigned to electron recombination process (10^0-10^2 Hz) in DSSCs incorporating **MQ1-MQ5** showed lower frequency that can be associated with shorter electron lifetimes as confirmed in table 3. Despite the impedance technique is a powerful tool to analyze the electron recombination and diffusion process in TiO₂ conduction band, it was not possible to find a clear tendency correlating the DSSCs performance with those impedance parameters. This fact can be attributed to other more relevant processes determining the overall device efficiency. Accordingly, the primordial electron photoinjection process by the excited photosensitizers was studied based on their photoaction spectra.

Table 3. Diffusion resistance (R_t), recombination resistance (R_r) and lifetime (t_n) of electrons in TiO₂ conduction band determined by simulation of EIS using an equivalent circuit based on the transmission line model.

Compound	R _t (Ω)	R _r (Ω)	T _n (ms)
MQ1	43.1	28.1	11.4
MQ2	34.7	6.5	5.0
MQ3	56.6	12.7	9.4
MQ4	57.7	11.2	3.5
MQ5	43.1	5.6	1.9
TiO ₂	26.9	52.1	28.7

The incident photo-to-current efficiency (%IPCE) of DSSCs sensitized with the new photosensitizers are shown in figure 5. The MQ1, MQ3, MQ4 and MQ5 exhibited bands around 480 nm associated with the ICT transition. The MQ3 and MQ4 dyes presented the highest photoaction efficiencies indicating more efficient electron injection to TiO_2 conduction band from photosensitizers excited charge-transfer state species. The photoaction efficiency of MQ2 was virtually zero, confirming the hypothesis that the ferrocene group probably is acting as a quencher which inhibits the electron injection from the photosensitizer to TiO_2 conduction band. As expected, the DSSCs overall efficiency (figure 3) tended to increase as a function of the phoaction efficiencies (figure 5), showing a clear dependence of devices performance with dyes electron photoinjection properties.



Figure 5. Photo-action spectra of DSSCs sensitized with **MQ1-MQ5** dyes. A device prepared with non-sensitized mesoporous TiO₂ was included for comparison.

The **MQ1-MQ5** dyes were electrochemically characterized in solution by cyclic voltammetry to evaluate the energy levels and explain the photo-injection properties described above.

The cyclic voltammetry experiments of compounds **MQ1-MQ5** was measured acetonitrile containing 0.1 M of TBAPF₆ (Figure S3 of Supporting Information). The first oxidation potential peak ($E_{ox} vs$. NHE) can be associated to the energy of the highest occupied molecular orbital (HOMO) and the first reduction potential peak ($E_{red} vs$. NHE) can be associated to the lowest unoccupied molecular orbital (LUMO). The LUMO energy can be calculated from experimental values of E_{ox} (HOMO) and E_{0-0} (zero-zero excitation energy) using the equation $E_{red} = E_{ox} - E_{0-0}$. Table 4 summarizes the redox potentials for **MQ1-MQ5**.

Table 4. Electrochemical data of compounds **MQ1-MQ5** measured by cyclic voltammetry experiments in acetonitrile solution at 100 mV scan rate with Fc/Fc^+ as reference system.

Compound	λ_{int}/nm	E_{0-0}^{a} / eV	Eox vs NHE/V	Ered vs NHE/V	$E_{\rm gap}^{\rm b}/{ m V}$
MQ1	503	2.47	1.35	-1.12	0.62
MQ2	646	1.92	0.81	-1.11	0.61
MQ3	510	2.43	1.20	-1.23	0.73
MQ4	512	2.42	1.28	-1.14	0.64
MO5	524	2.37	1.42	-0.95	0.45

a) $\overline{E_{0-0}}$ values were calculated from the intersection of the normalized absorption and the emission spectra (λ_{int}): $E_{0-0} = 1240/\lambda_{int}$. b) E_{gap} is the energy gap between the E_{red} of the compound and the conduction band level of TiO₂ (-0.5 V vs NHE).

The oxidation potential *vs.* NHE for the novel dyes were found at 0.81-1.35 V range. **MQ1**-**MQ4** photosensitizers showed a favorable redox potential relative to the Γ/I_3^- couple (~ 0.4 V vs. NHE), providing enough driving force for efficiently regenerating the oxidized dye after photo-induced electron injection, thus minimizing charge recombination. **MQ5** exhibited a higher oxidation potential peak at 1.42 V. On the other hand, the reduction potential *vs.* NHE and relative LUMO's of those molecules were found to be significantly higher in energy than the energy of TiO₂ conduction band (-0.5 V vs. NHE).

The negative shift of these potentials with respect to the lower edge of TiO_2 conduction band indicates that the excited dyes can inject electrons in TiO_2 conduction band, as confirmed by the photo-action spectra (figure 6).

In summary, we present the synthesis and characterization of novel dyes MQ1-MQ5 possessing quinoxaline-2(1H) one as surface anchoring group. EIS investigation and the photovoltaic performance confirm that the anchoring group promotes photo-induced electron transfer into TiO_2 conduction band.



Figure 6. Energy level diagram of MQ1-MQ5 dyes. The redox potential of the iodine couple and the lower edge of TiO_2 conduction band (CB) are included for comparison purpose.

4. CONCLUSION

A series of soluble compounds consisting on quinoxaline-2(1H)one anchoring group and TPA derivatives, ferrocene and 4-(dimethylamino)benzaldehyde as electron-donor sites were synthetized and characterized. All compounds were prepared by means of a convenient and efficient microwave irradiation method and tested as photosensitizers in Grätzel type solar cells. Unfortunately, the poor electron-acceptor character of the quinoxaline-2(1H)one anchoring group seems to decrease the vectorial energy transfer processes from the TPA donor to semiconductor conduction band thus decreasing the photoinjection efficiencies. Also, this fundamental process was shown to be limiting the overall energy conversion efficiencies that can eventually be improved by introducing an electron-withdrawing substituent is bond in 5-, 6-, 7- and 8-position of the quinoxaline ring.

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Supporting Information

Microwave assisted synthesis of several electroactive molecules based in Quinoxaline-2(1H)-one like efficient anchor group on TiO₂ surface.

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Figure S1. Compounds (dyes) solutions in acetonitrile. The DSSCs electrodes were prepared by immersing the TiO_2 films to solutions of dyes in acetonitrile (figure S1). The concentration of the **MQ1-MQ5** solutions is $1.0x10^{-4}$ M.





Figure S2. a) TiO₂ films with MQ1-MQ5 absorbed, b) DSSCs prepared with I_3 /I and FTO.



Figure S3. Cyclic voltammogram *vs.* (Fc/Fc⁺) of **MQ1-MQ5** dyes in acetonitrile solution at 100 mV scan rate.