## Letter

# 5-Alkyl-8-hydroxyquinolines: Synthesis and Application in Dye-Sensitized Solar Cells

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**Dye-Sensitized Solar Cell** 

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**Abstract** The use of co-adsorbents in dye-sensitized solar cells (DSCs) increases both the power-conversion efficiency and long-term stability of these devices. Co-adsorbents usually consist of a hydrophobic moiety attached on a carboxylic or phosphoric acid terminal anchoring group, which chemisorbs on the semiconductor surface. In this work, the synthesis of a new family of 8-quinolinol derivatives bearing alkyl chains of variable length at the 5-position is described and their comparative efficiency as effective bidentate co-adsorbents in DSCs is evaluated. The key step towards their straightforward modular synthesis is a Suzuki coupling between 5-chloro-8-methoxyquinoline and alkyltrifluoroborates. The new compounds showed better performance as co-adsorbents in terms of cell efficiency as compared to their alkylcarboxylic acid analogues, with the best results obtained from the derivative bearing the longer dodecyl alkyl chain.

Key words dye-sensitized solar cells, co-adsorbents, hydroxyquinoline, Suzuki coupling, organotrifluoroborates

Dye-sensitized solar cells (DSCs) emerged in early 1990s as promising alternatives to silicon-based photovoltaics, due to their low cost and ease of fabrication, panel flexibility, and high solar-energy conversion efficiency.<sup>1</sup> DCSs consist of a nanocrystalline metal-oxide semiconductor (usually TiO<sub>2</sub>) sensitized by a molecular dye (transition-metalbased or organic) acting as light-harvesting antenna, and a redox couple electrolyte as electron mediator. Although this kind of solar cells show quite impressive efficiencies for nonsilicon-based cells, of up to 13%,<sup>2</sup> charge recombination, dye aggregation, and gradual desorption have been identified as their main weak points. Research efforts have focused on overcoming these problems. One of these strategies focuses on the anchoring group, that is, the group responsible for binding the dye onto the semiconductor



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surface. The most commonly employed dye anchoring group is a carboxylic acid moiety, which chemisorbs the dye on the  $TiO_2$  surface.<sup>3</sup> Lately, though, its importance has been investigated and showed that it can affect both the

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DSC stability, due to unwanted dye desorption, as well as power conversion efficiency, through back-electron transfer suppression.<sup>4</sup> In this respect, alternative anchoring groups to carboxylates have been shown to exhibit superior results.<sup>5</sup> Among them, the 8-hydroxyquinoline has recently emerged as an alternative anchoring group in porphyrinbased DSCs, showing both improved long-term stability<sup>6</sup> as well as reduced charge recombination,<sup>7</sup> resulting in superior power conversion efficiency as compared to the carboxylic acid analogues.

The use of co-adsorbents has been used as another powerful tool to overcome the DSCs efficiency and stability drawbacks.<sup>8</sup> According to this approach, hydrophobic molecules are chemisorbed on the  $TiO_2$  surface together with the dye, resulting in suppressed dye-aggregation, charge recombination, and surface protonation. As in the case of dyes, the anchoring group is usually a carboxylic or phosphonic acid (Figure 1). Lately, the search for alternative, improved anchoring groups has led to the development of a number of novel co-adsorbents.<sup>8,9</sup>



Along these lines, we herein report the straightforward and modular synthesis of the new family of 5-alkylated 8quinolinol derivatives **1a-c** (Figure 2) bearing alkyl tails of variable length. The 8-quinolinol chemisorption mode mentioned above renders its 5-alkylated derivatives good potential candidates as co-adsorbent molecules in DSCs. In this regard, it is also worth mentioning that 8-quinolinol derivatives are very efficient bidentate ligands with numerous analytical, industrial, and biological applications.<sup>10</sup> Besides their synthesis, the performance of 5-alkylated 8quinolinol derivatives **1a-c** as co-adsorbents in DSCs devices is evaluated and compared with the respective alkyl-substituted carboxylic acids.

We initially opted for the synthesis of the desired 5-alkyl-substituted quinolinol derivatives starting from 4chloro-8-quinolinol, a cheap, commercially available compound, following a previously published procedure based on a lithium-halogen exchange reaction.<sup>11</sup> 5-Chloro-8quinolinol was thus protected using iodomethane towards



Figure 2 Targeted 5-alkylated 8-quinolinol compounds.

its methoxy derivative 2. Then, reaction of 2 with butyllithium should afford the 4-alkylated derivative 3a via an uncertain mechanism, allegedly involving a halogen-lithium exchange (Scheme 1). However, despite our repeated efforts, in our hands the desired product could not be isolated. Instead, we obtained the 2-butyl quinoline derivative 4 in 28% yield, as evidenced by its spectroscopic data.<sup>12</sup> Briefly, the <sup>1</sup>H NMR spectrum shows only four aromatic proton signals instead of five observed in **4** (and expected in **3a**). while the 'missing' proton seems to be the 2-quinolinyl most deshielded one in 2. Mass spectrometry verified the presence of the chlorine atom, showing the molecular ion of the proposed structure. In the same work of 1989,<sup>11</sup> the 5-octyl derivative **3b** was reportedly prepared from **2** and octyl bromide with the aid of phenyl lithium as auxiliary aryl-lithiation reagent. Again, in our hands, no alkylation occurred and only the 2-phenyl derivative 5 could be isolated in 57% yield.<sup>13</sup> Compounds 4 and 5 most probably stem from an oxidative nucleophilic aromatic substitution reaction, due to the ring electron deficiency imposed by the nitrogen heteroatom. The use of alkyl- or aryl-lithium compounds in such reactions is not seldom in quinoline chemistry<sup>14</sup> and, as shown in this work, is obviously competitive to lithium-halogen exchange in the employed conditions.

The above discouraging results prompted us to design a different route for the synthesis of 5-alkyl quinolinols **1a–c**. Cross-coupling seemed to be a good alternative, since it is modular and has been shown to result high yields of alkylation and, above all, the conditions required are not favorable for nucleophilic aromatic substitution reactions. Alkylation at the 5-position of 5-bromoquinoline derivatives has been achieved via palladium-catalyzed coupling reactions using alkylborates (Suzuki–Miyiaura coupling)<sup>15</sup> or alkylzinc (Negishi coupling)<sup>16</sup> derivatives as alkylating agents. Suzuki coupling using organotrifluoroborates as alkylating agents was chosen for our purposes, since they have been reported to be stable, easily accessible and excellent partners in the coupling reaction.<sup>17</sup> Also, they have been shown to react quite efficiently even when the generally less reac-

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**Scheme 1** Derivatization of **2** with lithium salts: (i) KOt-Bu, Mel, THF; (ii) *n*-BuLi, THF, -80 °C to r.t.; (iii) a) PhLi, Et<sub>2</sub>O, -80 °C, b)  $C_8H_{17}Br$ , -80 °C to r.t.

tive (but in our case easily accessible) aryl chlorides are their partners in coupling.<sup>18</sup> In this respect, potassium alkvltrifluoroborates **7a-c** were prepared from the reaction of the Grignard reagents of the corresponding alkyl bromides with trimethyl borate, followed by quenching with potassium hydrogen difluoride (Scheme 2). Then, Suzuki-Miyiaura coupling between 2 and the corresponding alkyltrifluoroborate using Pd(OAc)<sub>2</sub> as catalyst and RuPhos as ligand, afforded the 5-alkylated quinolines **3a-c** in excellent yields. It should be noted that the purity of **2** is of outmost importance for the outcome of this reaction, since the presence of even trace amounts of 5-chloro-8-quinolinol in the reaction mixture resulted in no reaction at all. As mentioned above. 8-quinolinols are themselves known as powerful transition-metal-chelating ligands due to the neighboring nitrogen heteroatom and hydroxyl group, thus probably behaving as a catalyst poison in this case. Finally, demethylation was performed in hydrobromic acid, yielding the desired quinolinols 1a-c.<sup>19</sup>



Et<sub>2</sub>O, (b) B(OMe)<sub>3</sub>, THF, -78 °C to r.t., (c) KHF<sub>2</sub>, 0 °C; (ii) **2**, Pd(OAc)<sub>2</sub>, RuPhos, Na<sub>2</sub>CO<sub>3</sub>, PhMe–H<sub>2</sub>O, 100 °C; (iii) 48% aq HBr, heat.

The ability of **1a–c** to act as co-adsorbents in DSCs was studied in solar cell devices using the benchmark MK-2 organic dye, in both iodine and cobalt based cells, and their performance was compared with that of the corresponding alkylcarboxylic acids, as well as in the absence of co-adsorbent. Figure 3 shows the characteristic *J–V* curves of the iodine electrolyte based solar cells obtained under illumination (1 sun) and under dark. The corresponding electrical

parameters (short-circuit current density,  $J_{sc}$ , open-circuit voltage,  $V_{oc}$ , fill factor, *FF* and power conversion efficiency,  $\eta$ ) are summarized in Table 1. There is an obvious trend in  $V_{oc}$  values, regarding the alkyl chain length of the co-adsorbent: the longer the chain, the higher the open circuit potential. This upward shift is supported by the parallel reduction of the dark current, indicating a higher recombination resistance. In fact, in the *J*–*Vs* curves registered in the dark, the onset of the cathodic currents is found beyond -500 mV vs. Pt, while the shift towards the negative potentials is more obvious for the best performing MK-2/1c cell, based on the hydroxyquinoline co-adsorbent with the longest alkyl chain.



**Figure 3** *J–V* curves under 1 sun illumination (solid lines) and dark conditions (dashed) of the iodine based cells sensitized with MK-2 (black), MK-2/**1a** (red), MK-2/**1b** (green), and MK-2/**1c** (blue) dye solutions, respectively.

**Table 1** Electrical Parameters (Jsc, Voc, FF, and  $\eta$ ) of the DSCs Incorporating the 8-Hydroxyquinoline Co-adsorbents **1a–c** in MK-2 Dye Solutions.

Dye/co-adsorbent	$J_{\rm sc}$ (mA cm <sup>-2</sup> )	V <sub>oc</sub> (mV)	FF	η (%)
ref. MK-2	12.30	750	0.65	6.03
MK-2/ <b>1a</b>	9.61	728	0.57	4.00
MK-2/ <b>1b</b>	13.09	752	0.63	6.16
MK-2/ <b>1c</b>	12.76	771	0.68	6.72

Thus, with regards to the cells using the iodide/triiodide redox couple, the best performing ones are those encompassing the longer-chain co-adsorbent **1c** in the dye solution. These devices reach a power conversion efficiency of 6.72%, an 11% improvement in comparison to the reference cells (only the MK-2 dye) showing an overall efficiency of 6.03%. On the other hand, the cells incorporating the short-chain co-adsorbent exhibited the lower electrical parameters and an overall conversion efficiency of only 4%, justi-

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fied by a positive shift of the cathodic dark current. Similar results were observed in the cobalt-based cells (see Supporting Information, Figure S1, Table S1).

In order to better understand the mechanism of the sensitization enhancement employing the newly synthesized molecules, solar cells with the analogous alkylcarboxylic acids (butanoic, octanoic, and dodecanoic acid) as co-adsorbents were developed and evaluated using both iodide/triiodide and cobalt-based electrolytes (see Supporting Information, Figure S2, Table S2). In this case, both the photocurrent densities and the open-circuit voltage values are drastically lower than those of the reference device (without co-adsorbent). Some positive effects are evident on increasing the alkyl chain length, but their poor overall performance as compared to the reference is not altered.

The above results can be rationalized if we consider the chemical structure of the new co-adsorbents. It is the combination of the strongly coordinating bidentate hydroxyquinoline group with the long alkyl chain that assures the chemisorption of a high amount of the MK-2 dye, concomitantly preventing electron recombination (back electron transfer from the semiconductor's conduction band to the oxidized form of the redox couple) thus leading to reduced dark current and higher  $V_{oc}$  values. The positive effect of the long alkyl chain could be furthermore attributed to the prevention of dye aggregation.

In conclusion, a new family of 5-alkyl-8-quinolinols with variable alkyl chain lengths has been synthesized and their performance as co-adsorbents in DSCs has been evaluated. Initial attempts to prepare the targeted compounds from the 5-chloro-8-methoxyquinoline through lithiumhalogen exchange failed, instead yielding the corresponding 2-alkyl or aryl 5-chloroquinoline derivatives. A high-yielding modular synthesis was accomplished via Suzuki coupling, using alkyltrifluoroborates as alkylating agents. When employed as co-adsorbents, these compounds afford DSC devices with improved performance, in comparison to the corresponding alkylcarboxylic acid derivatives. Additionally, it was found that the longer the alkyl chain of the co-adsorbent, the better the efficiency of the cell. Thus, the 5-dodecyl derivative increases the DSCs power-conversion efficiency by 11%, suggesting not only that 5-alkyl-8-quinolinols are promising co-adsorbents in DSCs, but also that the 8-quinolinol moiety can be of general use substituting the currently employed carboxylic anchoring strategy. The same family of quinolinol derivatives is currently being utilized as passivating agents in perovskite solar cells, as well as in polydiacetylene vesicles as metal-ion receptors.

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# **Supporting Information**

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Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588702.

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- (12) Spectroscopic Data for Compound 4
  - <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.43 (d, *J* = 8.7 Hz, 1 H), 7.45 (d, *J* = 8.4 Hz, 1 H), 7.44 (d, *J* = 8.7 Hz, 1 H), 6.94 (d, *J* = 8.4 Hz, 1 H), 4.06 (s, 3 H), 3.07–3.04 (m, 2 H), 1.83–1.77 (m, 2 H), 1.45 (sext, *J* = 7.4 Hz, 2 H), 0.96 (t, *J* = 7.4 Hz, 3 H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>): δ = 161.94, 153.50, 139.52, 132.21, 124.63, 124.62,

121.72, 121.36, 106.80, 55.40, 38.33, 31.47, 22.07, 13.35. ESI-HRMS: m/z calcd for C<sub>14</sub>H<sub>17</sub>ClNO: 250.0999; found: 250.0994 [M + H]<sup>+</sup>.

(13) Spectroscopic Data for Compound 5

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.59 (d, J = 8.8 Hz, 1 H), 8.20 (d, J = 7.3 Hz, 2 H), 8.02 (d, J = 8.8 Hz, 1 H), 7.57–7.41 (m, 4 H), 6.99 (d, J = 8.3 Hz, 1 H).

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- (19) Representative Synthetic Procedure for the Dodecyl Derivative 1c

## Potassium Dodecyltrifluoroborate (7c)

Dry and degassed  $Et_2O$  (20 mL) was added in flame-dried grinded magnesium turnings (300.0 mmol, 3.60 g, flame activated) under argon. Then, 1-bromododecane (50.0 mmol, 12.46 g) was added dropwise, resulting in a gentle refluxing mixture, and stirred for 1 h. The as-prepared Grignard reagent solution was added dropwise under Ar to a cooled (-78 °C), dry, and degassed THF (50 mL) solution of trimethyl borate (75 mmol, 7.79 g), and the mixture was stirred for 1 h at that temperature and at r.t. for another 1 h. After cooling to 0 °C, a 4.5 M aq KHF<sub>2</sub> solution (205 mmol, 45.5 mL) was added dropwise, and the resulting mixture was stirred for 30 min. The solvents were evaporated, the residue was extracted with hot acetone (3 × 50

mL), and the combined extracts were filtered. The filtrate was condensed to minimum volume solution, the product precipitated out after addition of Et<sub>2</sub>O (30 mL), filtered, and dried at 45 °C in vacuo (2 × 10<sup>-3</sup> mbar), furnishing pure **7c** as a white powder (7.00 g, 50%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 1.30–1.05 (m, 22 H), 0.88–0.82 (m, 3 H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 33.13, 31.24, 29.44, 29.21, 29.15, 29.06, 28.98, 28.66, 25.62, 22.02, 13.88.

## 5-Dodecyl-8-methoxyquinoline (3c)

A degassed mixture of 2 (3.07 mmol, 0.59 g), 7c (3.38 mmol, 934 mg), Na<sub>2</sub>CO<sub>3</sub> (9.21 mmol, 0.98 g), Pd(OAc)<sub>2</sub> (0.25 mmol, 0.06 g), and RuPhos (0.50 mmol, 0.23 g) in toluene-water (5:1, 15.3 mL) was stirred at 100 °C under argon for 24 h. After cooling to r.t., water (15 mL) was added, and the mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were dried (MgSO<sub>4</sub>) and the solvents evaporated. The residue was purified by column chromatography (EtOAc-PE = 1:1) yielding 3c as yellow oil (0.90 g, 90 %,  $R_f$  = 0.5). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.93 (dd, J = 4.2, 1.6 Hz, 1 H), 8.32 (dd, J = 8.6, 1.6 Hz, 1 H), 7.45 (dd, J = 8.6, 4.2 Hz, 1 H), 7.28 (d, J = 7.9 Hz, 1 H), 6.97 (d, J = 7.9 Hz, 1 H), 4.07 (s, 3 H), 2.99-2.92 (m, 2 H), 1.75-1.60 (m, 2 H), 1.45-1.25 (m, 20 H), 0.90-0.84 (m, 3 H). 13C NMR (50 MHz,  $CDCl_3$ ):  $\delta = 153.82, 148.69, 140.59, 132.48, 130.73, 127.86,$ 126.07, 121.27, 107.12, 55.95, 32.03, 31.15, 29.76, 29.74, 29.64, 29.46, 22.80, 14.25.

### 5-Dodecyl-8-quinolinol (1c)

A solution of methoxyquinoline 3c (2.75 mmol, 900 mg) in aq HBr (48%, 11.8 mL) was stirred at reflux for 22 h. After cooling to r.t., the mixture was washed with Et<sub>2</sub>O (30 mL), the organic washing was decanted, and the aqueous phase was basified with NaHCO<sub>3</sub> (pH 8) and extracted with  $Et_2O$  (3 × 30 mL). The combined organic phases were dried (MgSO<sub>4</sub>), the solvent was evaporated, and the residue was purified with column chromatography (EtOAc-PE = 1:9) affording 1c as pale yellow powder  $(373 \text{ mg}, 43 \%, R_f = 0.6)$ . <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 8.78$  (dd, J = 4.2, 1.4 Hz, 1 H), 8.35 (dd, J = 8.5, 1.4 Hz, 1 H), 8.30 (br s, 1 H), 7.46 (dd, J = 8.5, 4.2 Hz, 1 H), 7.28 (d, J = 7.8 Hz, 1 H), 7.10 (d, J = 7.8 Hz, 1 H), 2.99-2.91 (m, 2 H), 1.74-1.60 (m, 2 H), 1.42-1.26 (m, 18 H), 0.91–0.85 (m, 3 H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  = 150.56, 147.33, 138.78, 132.95, 129.50, 127.11, 127.11, 121.38, 109.47, 32.07, 31.94, 31.40, 29.81, 29.78, 29.68, 29.50, 22.84, 14.27. ESI-HRMS: *m*/*z* calcd for C<sub>17</sub>H<sub>24</sub>NO: 314.2484; found: 314.2478 [M + H]<sup>+</sup>.