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Maj. Gen (Ret) Dr. / Mostafa H. Azab  
Col. Dr./ M. Gobara

Cairo Univ.  
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<b>CEEA-1</b>	<b>Photocatalytic decomposition of dimethoate using some selected metal oxides powder</b> M. I. Awaad, M. S. Fayed, M. K. Abd El-Magid and A. Baraka
<b>CEEA-2</b>	<b>Effect of Hydrogen Peroxide Addition on the Photochemical and Sonochemical Destruction of Pyridine in Wastewater</b> M. A. Elsayed
<b>CEEA-3</b>	<b>Photochemical Studies and Dye Sensitized Solar Cell Based on 8-Hydroxyquinoline</b> K. A. Ali and M.S.A. Abdel-Mottaleb

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### CEEA-3

## Photochemical Studies and Dye Sensitized Solar Cell Based On 8-Hydroxyquinoline

K.A. Ali\* and M.S.A. Abdel-Mottaleb<sup>†</sup>

### Abstract:

8-Hydroxyquinoline(HQ) is a monoprotic bidentate chelating agent, which forms a fluorescent complex with  $AlCl_3$  in the ground and the excited states. The formation constants are determined from the least squares fitting of Benesi-Hildebrand and Hill plots.

8-hydroxyquinoline and 8-hydroxyquinoline aluminum salt ( $AlHQ_3$ ) show photostability in the presence of suspended  $TiO_2$  (Degussa P25). The photostability of the surface complexes ( $8-HQ-TiO_2$ ) and ( $AlHQ_3-TiO_2$ ) has been examined in the presence of ( $I/I_2$ ) electrolyte solution showing a significant changes in the absorption and the fluorescence spectra of  $AlHQ_3$  and the rate of the reaction is determined.

The photostability results of 8-Hydroxyquinoline favor its exploitation as a sensitizer in dye-sensitized solar cell (DSSC). Light into electricity conversion efficiency is calculated from the current -voltage (I-V) curve for 8-HQ sensitized solar cell. Although 8-HQ reveals an appreciated photostability, it is not an efficient dye for light to electricity conversion due to its limited light absorption range (290-340nm).

### Keywords:

Photostability, Dye-sensitized solar cell, 8-HQ, 8-Hydroxyquinoline aluminum salt

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## 1-Introduction

8-Hydroxyquinoline is well known to react as a chelating agent with several metal ions because of the presence of basic nitrogen, and a phenolic group in its structure, (Fig.1). 8-HQ is non-fluorescent and sometimes it displays very weak fluorescence due to the intramolecular

proton transfer process (from oxygen to nitrogen) in its excited state, which provides a route for non-radiative relaxation [1,2]. Once this proton is lost, 8-HQ becomes highly fluorescent [1,3]. Consequently, this unique 8-HQ property can provide an on-off sensing response to metal ion binding.

Application of TiO<sub>2</sub> in photocatalyst processes is based on its remarkable activity, chemical stability and also on its non-toxic-properties. However, only light of wavelengths below 400nm can be absorbed by TiO<sub>2</sub> particles to generate e<sup>-</sup>/h<sup>+</sup> pairs [19]. It is known that less than about 5% of the solar energy reaching the surface of the earth is ultraviolet light [4]. TiO<sub>2</sub> (Degussa P25) is one of the most photochemically active commercial forms of TiO<sub>2</sub>, which consists of about 70% anatase and 30% rutile [5].

The dye-sensitized solar cell (DSSC) is a device for the conversion of visible light into electricity based on the sensitization of wide band gap of semiconductors [6, 7, 8].

The performance of the cell mainly depends on the dye used as sensitizer. The absorption spectrum of the dye and the anchorage of the dye to the surface of TiO<sub>2</sub> are important parameters determining the efficiency of the cell [6, 9].

Research on organometallic complexes has attracted scientific and commercial attention due to their promising applications in organic devices such as organic light emitting diode (OLED) and organic solar cells. AlHQ<sub>3</sub> is the most common organometallic complex that has been widely studied as organic semiconductor many years ago. This is because AlHQ<sub>3</sub> possesses a very good luminescent efficiency, which emits in the green spectral region with a broad emission peak at about 525 nm, high electron mobility and thermal stability. Due to this fact, AlHQ<sub>3</sub> has been so far one of the best electron transport material and emission material that is used in multilayer OLED [18].

The paper is focusing on the formation of the complex AlHQ<sub>3</sub> in the ground state and the excited state and the calculation of the formation constants using Benesi-Hildebrand and Hill plots. The photostability of the surface complexes (8-HQ-TiO<sub>2</sub>) and (AlHQ<sub>3</sub>-TiO<sub>2</sub>) is examined in the presence of redox couple (I<sub>3</sub><sup>-</sup>/I<sup>-</sup>) for possible use as sensitizers for nanocrystalline solar cell. A dye-sensitized solar cell based of 8-HQ is fabricated and its conversion efficiency will be evaluated.

## 2-Experimental

### 2.1 Chemicals

8-Hydroxyquinoline was obtained from Sigma. Aluminium chloride and iodine were obtained from Merck company. Ethanol absolute (Riedel) for HPLC measurements. Potassium iodide was obtained from Fluka Company. The TiO<sub>2</sub> fine powder (Degussa P25), which is a 70:30 mixture of anatase : rutile from Degussa- Hüls Company. Titanium (IV) isopropoxide was obtained from Aldrich. Stannous chloride AR was obtained from S.D. FIN-CHEM

LTD. Antimony trioxide was obtained from B.D.H. England. Ethylene glycol was obtained from B.H.E. England. All the chemicals were used as received.

## 2.2 Instrumentation

The absorption spectra were recorded using Helios & Unicamspectrophotometer. Fluorescence measurements were recorded using RF 5301 PC Shimadzu spectrofluorometer. The photostability setup consisted of an irradiation source of 150W Xenon arc lamp with a wavelength range (190-900nm) from Photon technology international company. The power of the lamp was adjusted at 70W during the photostability tests. The light intensity was measured using radiometer (IL1700 International Light). The photochemical reactor was a cylindrical

Double-walled quartz cell with inlet and outlet for cooling by water to maintain the temperature constant at (22±0.2°C).

## 2.3 Fabrication of dye-sensitized solar cell (DSSC)

A thin film of conducting SnO<sub>2</sub> doped with antimony trioxide on a commercially glass plate was used for the starting material for the electrodes, [12]. The surface resistivity was measured using an avometer (model Keithley 2635, USA) with current-voltage ranges (20fA-1.5A) and (1μV-202V). The glass plates, coated with a thin film of nanocrystalline TiO<sub>2</sub> were soaked in an ethanolic solution of 8-HQ forming a surface complex capable of electron injection.

Applying a thin carbon film on another piece of conductive glass plate made the counter electrode. The two opposing glass plates were offset so that the counter electrode covered all of the TiO<sub>2</sub>. One or two drops of (KI/I<sub>2</sub>) electrolyte solution were placed at the edges of the plates. Light should enter the glass sandwich through the TiO<sub>2</sub> coated glass plate. Current-voltage [I-V] curve for the cell was plotted from which the conversion efficiency of sunlight to electrical energy is calculated.

## 2.4 Data analysis

The formation constant is estimated from the changes in both absorbance and fluorescence intensities from a Benesi-Hildebrand plot, equation (1), [10,11].

$$\frac{1}{A_{\text{obs}} - A_o} = \frac{1}{A_C - A_o} + \frac{1}{K_{\text{formation}} (A_C - A_o) [Al^{3+}]} \quad (1)$$

Where  $A_{\text{obs}}$  is the absorbance of 8-HQ solution containing of different concentrations of  $Al^{3+}$  ions.  $A_o$  and  $A_c$  are the absorbances of 8-HQ and the complex  $Alq_3$  respectively. Therefore, a

plot of  $\frac{1}{A_{\text{obs}} - A_o}$  versus  $\frac{1}{[Al^{3+}]}$  should yield a linear relationship with a slope equal

to  $\frac{1}{K_{\text{formation}} (A_C - A_o)}$  and the intercept equals  $\frac{1}{A_C - A_o}$ . From the slope and the intercept, we obtain  $k_{\text{formation}}$

The apparent association constant ( $K_{\text{app}}$ ) in the formation of the surface complex (8HQ-TiO<sub>2</sub>) is determined from the plot  $\frac{1}{A_{\text{obs}} - A_o}$  versus  $\frac{1}{[TiO_2]}$ , equation (2).

$$\frac{1}{A_{\text{obs}} - A_o} = \frac{1}{A_C - A_o} + \frac{1}{K_{\text{app}} (A_C - A_o) [TiO_2]} \quad (2)$$

For the fluorescence data,  $K_{\text{formation}}$  of AlHQ<sub>3</sub> complex can be estimated from equation (3)

$$\frac{1}{I_{\text{obs}} - I_o} = \frac{1}{A_C - A_o} + \frac{1}{K_{\text{formation}} (I_C - I_o) [Al^{3+}]} \quad (3)$$

The plot of  $\frac{1}{I_{\text{obs}} - I_o}$  versus  $\frac{1}{[Al^{3+}]}$  should yield a linear relationship with a slope equal to  $\frac{1}{K_{\text{formation}} (I_C - I_o)}$  and the intercept equals  $\frac{1}{I_C - I_o}$ . From the slope and the intercept, we obtain  $K_{\text{formation}}$ .

The rate constant of the photostability test for the surface complex (AlHQ<sub>3</sub>-TiO<sub>2</sub>) in presence of ( $\bar{I}/I_2$ ) electrolyte solution in both the ground state and the excited state are defined by equations, (4 and 5).

$$\ln \frac{A_o}{A_t} = kT \quad (4)$$

$$\ln \frac{I_o}{I_t} = kT \quad (5)$$

Where  $A_o/I_o$  is the (absorbance / fluorescence) intensity before irradiation and ( $A_t/I_t$ ) is the (absorbance / fluorescence) intensity at different time intervals. A plot of left term against time gives a straight line, the slope of which is the rate constant of the reaction [12]. When there is an increase in both absorbance and fluorescence intensities on continued exposure of the sample to radiation, the rate constant is determined from equations (6 and 7).

$$\ln \frac{A_f}{A_f - A_s} = kT \quad (6 \text{ and } 7)$$

$$\ln \frac{I_f}{I_f - I_s} = kT$$

The plot of the left term versus time gives a straight line, the slope of which is the rate constant of the reaction.

The conversion efficiency of sunlight to electrical energy is calculated from the equation (8)

$$\% \text{ efficiency} = \frac{\text{maximum output power}}{\text{input power}} = \frac{I_m V_m}{\text{incident light intensity} \times \text{area of the active layer}} \quad (8)$$

$I_m$ : Maximum current output

$V_m$ : Maximum voltage output

### 3-Results and Discussion

#### 3.1 Spectroscopic properties of 8-HQ

8-HQ is a conjugated system and at the same time a bifunctional hydrogen bonding molecule, which in protic solvents simultaneously acts as an H donor via its acidic O-H group and as a protic acceptor at the basic N atom.

The absorption spectrum of 8-HQ in ethanol shows an absorption peak at 312nm. This result can provide relevant information about a specific solute–solvent association such as hydrogen bonding or an electron donor-acceptor interactions [14]. The lack of the fluorescence intensity of 8-HQ in ethanol is attributed to an intramolecular proton transfer process in the excited state, which provides a route for non-radiative relaxation [1,2].

### 3.2 Complex formation between 8-HQ and AlCl<sub>3</sub>

#### In the ground state

Different portions of a stock solution of AlCl<sub>3</sub>, 10<sup>-3</sup>M, are transferred into a number of 10-ml volumetric flasks each containing 1.0 ml of 8-HQ solution, 10<sup>-3</sup>M, and diluted with ethanol. The absorption band of 8-HQ of wavelength 312nm undergoes a noticeable disappearance and at the same time a new absorption peak is shown at longer wavelength (365nm) as the concentration of Al<sup>3+</sup> ions increases and an isosbestic point appears at 340 nm. These results suggest the formation of a chelating complex between 8-HQ and of Al<sup>3+</sup> ions (AlHQ<sub>3</sub>), (Fig.3).

#### In the excited state

The fluorescence spectrum due to the reaction between 8-HQ and AlCl<sub>3</sub> is obtained by exciting into the formed complex absorption peak at 340nm. The fluorescence intensity increases as the concentration of Al<sup>3+</sup> ions increases. It is a fluorescent complex because the non-bonded electrons in 8-HQ bind to Al<sup>3+</sup> ions forming a ring which increases the rigidity of the molecule, (Fig. 4), [15].

In AlHQ<sub>3</sub>, the Al<sup>3+</sup> ions stabilize the MOs of oxygen that carries most of the negative charge of the ligand. The nitrogen–aluminum interaction is relatively weak, (Fig.2), [16].

The formation constant values of the formed complex (AlHQ<sub>3</sub>) in the ground state and the excited state are estimated from a Benesi-Hildebrand and Hill plots.

### 3.3 Effect of irradiation on the surface complexes in the ground state and the excited state

#### In absence of (KI/I<sub>2</sub>) solution

100 ml of ethanolic solutions of 8-HQ/AlHQ<sub>3</sub> are illuminated with Xe arc lamp in a water cooled reactor with continuous stirring for 1 hr in the presence of suspended TiO<sub>2</sub> (Degussa P25) and absorbance / fluorescence measurements are recorded at different time intervals. Both surface complexes (8-HQ-TiO<sub>2</sub>) and (AlHQ<sub>3</sub>-TiO<sub>2</sub>) show a photostability upon 1hr of illumination.

#### In the presence of (KI/I<sub>2</sub>) solution

When the surface complexes are illuminated in the presence of (I<sup>-</sup>/I<sub>2</sub>) electrolyte solution for 1hr, no significant changes in the absorption spectrum neither the fluorescence spectrum of the surface complex (8-HQ-TiO<sub>2</sub>) are observed indicating a high photostability of 8-HQ which implies no interaction between 8-HQ and (I<sup>-</sup>/I<sub>2</sub>) electrolyte solution, but a steady decrease in the absorption spectrum of (AlHQ<sub>3</sub>-TiO<sub>2</sub>) and an increase is observed in the fluorescence intensity of (AlHQ<sub>3</sub>-TiO<sub>2</sub>), due to the interaction between AlHQ<sub>3</sub> and iodide ions that may form a complex with Al<sup>3+</sup> ions or a mixed complex with AlHQ<sub>3</sub> [17]. The results are treated and the rate constants of the reactions are calculated, (Fig. 5).

### 3.4 Fabrication of dye-sensitized solar cell based on 8-HQ

#### Effect of colloidal solution of TiO<sub>2</sub> on the absorption spectrum of 8-HQ

The effect of increasing TiO<sub>2</sub> concentration on the absorption spectrum of 8-HQ, (Fig. 6) shows an increase in the absorbance and slight amount of red shift in the absorption spectrum of 8-HQ. It reveals an interaction between the nanoparticles of TiO<sub>2</sub> and 8-HQ due to a chemisorption between 8-HQ and TiO<sub>2</sub> through a phenolic group (OH) and TiO<sub>2</sub>. The association constant is estimated from the changes in absorbance intensity from a Benesi-Hildebrand plot at different TiO<sub>2</sub> concentrations.

#### I-V characterization of dye sensitized solar cell

I-V plot for DSSC of active area 0.5cm<sup>2</sup> is shown in the figure. The maximum product of current and voltage (obtained near the "knee" of the curve) is divided by the incoming light power to obtain the conversion efficiency of light energy, (Fig. 7), which is around 0.015% for 8-HQ sensitized solar cell.

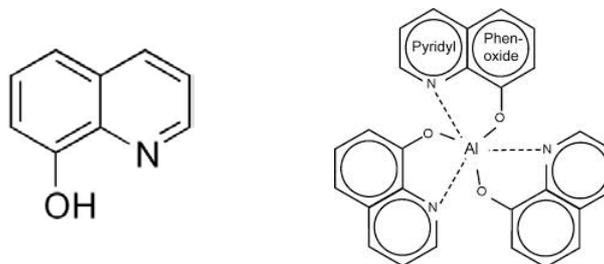
### 4-Conclusion

8-Hydroxyquinoline forms a fluorescent complex AlHQ<sub>3</sub> in ethanol and the photostability studies favors 8-HQ exploitation as a sensitizer in DSSC. The fabricated DSSC showed low conversion efficiency (0.015%) due to its limited absorption range.

### 5-References

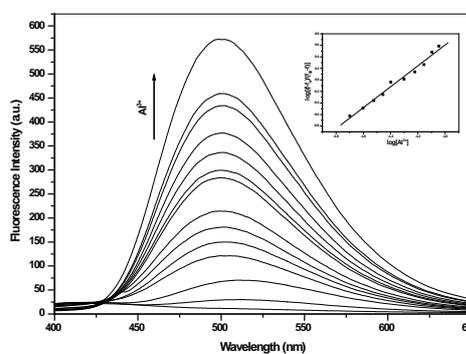
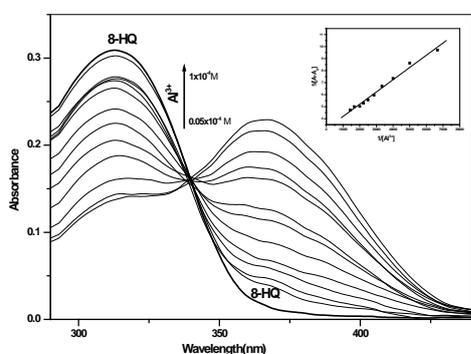
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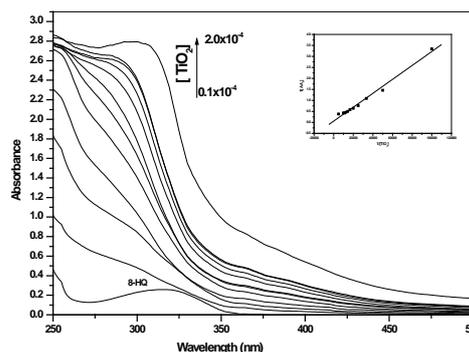
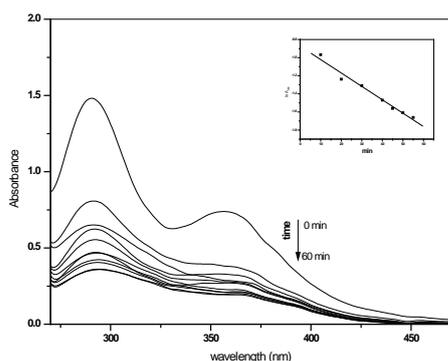


**Fig.1. The molecular structure of 8-Hydroxyquinoline**

**Fig. 2. The molecular structure of 8-hydroxyquinoline aluminium salt**



**Figures 3 and 4. The effect of Al<sup>3+</sup> ions on the absorption and fluorescence spectra of 8-HQ. The insertions for the determination of the formation constants of the complex**



**Fig.5. The effect of irradiation on the absorption spectrum of the surface complex in the presence of (I<sup>-</sup>/I<sub>2</sub>) electrolyte solution. The insertion is the rate constant of the reaction (k= 0.015 min<sup>-1</sup>)**

**Fig.6. The effect of colloidal TiO<sub>2</sub> on the absorption spectrum 8-HQ. The insertion is the apparent association constant (K= 1x10<sup>5</sup>M)**

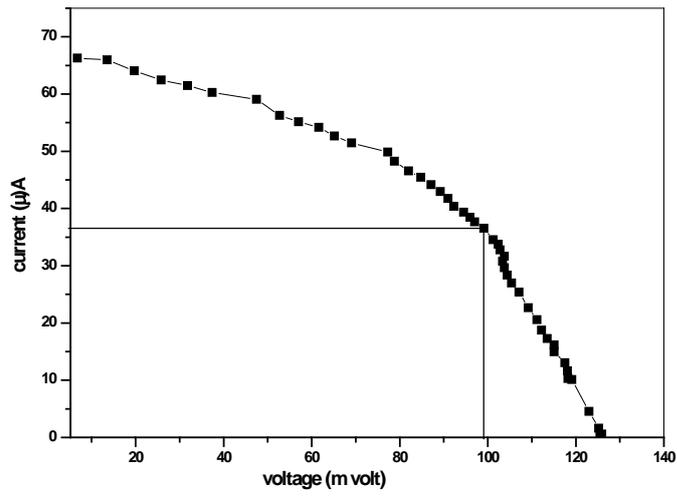


Fig.7. Current-voltage curve for illuminated 8-HQ solar cell