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Electro-oxidation of indole-based squaraine dye: A combined in-situ spectroelectrochemical and theoretical study

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ABSTRACT

Indole-based squaraine (ISQ) is a promising group of electroactive dyes that have been widely used as organic photoelectric materials. However, their chemical structure is stable and will cause environmental pollution after being released into nature. Herein, the electrochemical redox chemistry of ISQ and its degradation mechanism on a Pt polycrystalline electrode was investigated. Many results are obtained from voltammograms, electrochemical in-situ UV–Vis and FTIR spectra and quantum chemical calculations: 1) while the potentials were below 1.2 V, ISQ was first oxidized to the radical anion with C═O bond formation whereas oxidation shows fully electrochemical irreversibility. 2) an unexpected IR band of CO_2 was collected at increasing potentials whereas a new absorption of 420 nm appeared in UV–Vis spectra, suggesting that cleavage of the C═C double bond had occurred in the molecular structure of ISQ. 3) The oxidation products of ISQ were 1-methyl-3,3-dimethylndolenium-2-one and 3-oxo-cyclobut-1-enol anion. These findings provide useful information for better understanding the reaction mechanism and designing a suitable treatment strategy for dye pollutants.

1. Introduction

Squaraine dyes (SQDs) are a family of functional dyes that possess a typical donor-acceptor-donor (D-A-D) molecular architecture [1]. They are considered to be the most promising candidates for sensitizers due to their high photo-stability and exhibiting intense absorption and fluorescence in the visible and near-IR regions [2,3]. These properties make SQDs extensively studied for a broad range of application, such as sensing [1,3–5], imaging [6], photodynamic therapy [7], electroluminescent devices [8,9] and dye-sensitized solar cells [10].

Despite the wide application of SQDs, little attention has been paid to their potential to cause ecological damage. The structural features of π-conjugated systems give organic dyes a high thermal and chemical stability, for example, azo [11], thiazin [11,12], SQDs [13,14] and fluorescein based dyes [14], making them degradation-resistant. Moreover, the artificial synthesis and release of these dyes in water would significantly change water chromaticity and decrease the dissolved oxygen level, which could further cause serious environmental pollution [15,16]. For the treatment of these textile dyes, physical, chemical and biological methods are being used [17,18]. However, many previously published results mainly focused on investigating the removal performance while the reaction mechanisms were seldom deeply explored. Thus, designing a suitable treatment strategy to respond to specific toxic groups in these molecular structures could be a promising method for relevant pollution control.

Former studies examining the degradation pathway of SQDs only investigated TiO_2 photocatalysis under visible light [13,14]. Cleavage of the C═C double bond in SQDs was proposed to dominate over the whole photo-degradation process regardless of the solvent used [13,14]. However, little has been reported about the electro-oxidation mechanism of SQDs. A better understanding of the electrochemical properties of π-conjugate compounds may become necessary as better design criteria emerge for novel organic dyes. This, in particular, is crucial for environmental degradation.

The investigation reported in this work included both an experimental study and a theoretical part looking at FTIR spectroscopy of SQDs and its electro-oxidation derivatives. The squaraine conjugates comprising a central squaraine unit and peripheral indole groups

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Table 1
The IR signals of ISQ and products, experimental data and theoretical assignments [25,27,28].

Compounds	Theoretical data	Experimental	Experimental	Reference	IR
	(In this work)	Data in KBr	Data in DMF	Data in KBr	Assignments
	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	~
ISQ	1592	1590	1590	~	$\nu_{(C=O)}$
	1575	1571	1571	~	$\nu_{(C=C)}$
	1508	1506	1503	~	$\nu_{(C=C)}$
	1465	1465	1460_{upward}	~	$\nu_{(C=C)}$
	1429	1427	1429_{upward}	~	$\delta_{(C-H)}$ scissor
	1294	1292	~	~	ω(indole ring)
	1234	1234	~	~	ω(indole ring)
DMF	~	1674	1674	~	$\nu_{(C=O)}$
TBAP	~	1475	1475	1473.87	$\delta_{(CH2)}$
	~	1390	1390	1384.01	$\delta^{s}_{(CH3)}$
ISQ$_1$/ ISQ$_2$	1730	~	$1735_{downward}$	~	$\nu_{(C=O)}$
	1643	~	$1635_{downward}$	~	$\nu_{(C=O)}$
	1499	~	$1503_{downward}$	~	$\nu_{(C=C)ring}$
I$_1$	1733	~	$1735_{downward}$	~	$\nu_{(C=O)}$
	1621	~	$1635_{downward}$	~	$\nu_{(C=C)ring}$
	1484	~	$1490_{downward}$	~	$\sigma_{(C=C)}$
Q$_2$	1729	~	$1735_{downward}$	~	$\nu_{(C=O)}$
	1634	~	$1635_{downward}$	~	$\nu_{(C=C)ring}$
CO$_2$	~	~	2325	2390–2285	$\nu_{as(C-O-C)}$

(namely ISQ) were chosen since both components are widely used in electro-optical materials [6,19]. Voltammetry, electrochemical in-situ UV–Vis spectroscopy (in-situ UV–Vis) and GC-Mass spectroscopy were employed to evaluate the potential-dependent oxidation process. Since more vibrational information of particular species can be collected during the electrochemical reaction by using electrochemical in-situ FTIR spectroscopy (in-situ FTIR) [20–22], it is thus employed to obtain important intermediates and further details on the degradation pathway. To identify the vibrational modes responsible for the functional group of the IR signal, we presented a theoretical calculation and analysis based on density functional theory (DFT). The electro-oxidation mechanism of ISQ could be elucidated in detail with this approach.

2. Experimental procedures

2.1. Synthesis and characterization

ISQ was synthesized and purified according to previously work reported by Dirk et al… [23] and Borrelli et al [24]. The details of synthesis process were shown in Supporting Information. The molecular structure of ISQ was characterized by nuclear magnetic resonance spectroscopy (Bruker AVANCE 400, Perkin Elmer, America) and Raman spectroscopy (inVia confocal Raman microscope, Renishaw, England) (Figs. S1 and S2). Tetrabutyl ammonium perchlorate (TBAP, Sigma Aldrich), *N*, *N*-Dimethylformamide (DMF, Sinopharm Chemical Reagent Co., Ltd) and other chemicals were of analytical grade.

2.2. Electrochemical section

A Pt polycrystalline disk electrode with an inner diameter of 3 mm was used as the working electrode. An Ag wire was taken as reference electrode and subsequently calibrated with respect to a Ag/AgCl (3 M KCl) electrode in all electrochemical tests. To avoid the interference of the applied negative potentials on the electrolysis process, the counter electrode of Pt wire was set in a home-made glass tube (3 mm in diameter) that was filled with porous ceramics at the bottom (Fig. S3). 0.1 M TBAP dissolved in DMF solution (TBAP-DMF) was transferred into the glass tube to reduce the liquid potential. The working electrode was polished in 1, 0.3 and 0.05 μm Al_2O_3 powders and was then rinsed with double distilled water several times before experiments. It was swept by cyclic voltammetry (CV) in 0.5 M H_2SO_4 solution to activate its surface. The electrochemical behaviour of ISQ on the clean Pt electrode surface was studied in 0.1 M TBAP-DMF solution by employing CVs, differential pulse voltammetry (DPV), and controlled potential electrolysis (CHI440, China). Bubbling nitrogen and maintained this atmosphere during the whole experiment. All experiments were carried out at room temperature.

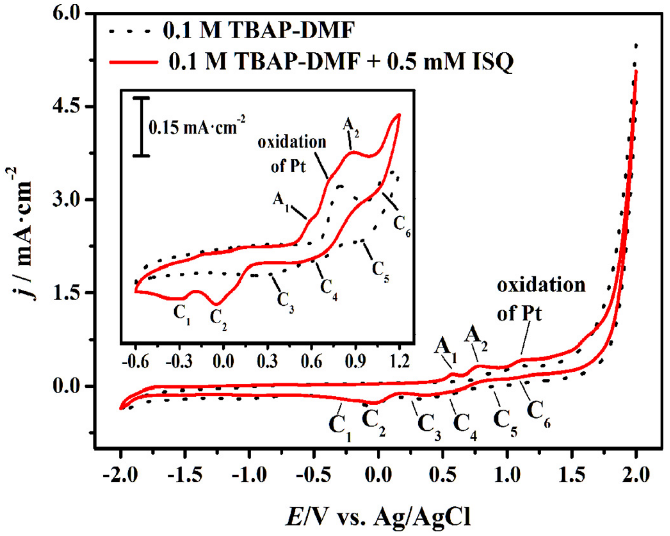

Fig. 1. CVs of a bare Pt polycrystalline electrode in 0.1 M TBAP-DMF solution without (dot line) and with (solid line) 0.5 mM ISQ, sweep rates: 50 mV s^{-1}; The inset is the CVs with a limited scanning potential range from −0.6 to 1.2 V.

2.3. In-situ UV–vis spectroscopic measurements

In-situ UV–Vis spectroscopic examinations were conducted in a quartz cell (1 cm in length) with a Lambda 800 UV/VIS spectrometer (PerkinElmer, America). UV–Vis spectroscopy was collected in the spectral region of 800–250 nm with sample width of 1 nm. The three-electrode system was similar as the system described above. To reduce the volatilization of organic solvent, all the electrodes were set in the closed system (Fig. S3).