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Preparation and spectroscopic characterization of a self-assembled monolayer of squarylium dye on gold

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Abstract

New squarylium dye-containing alkanethiol self-assembled monolayers (SAMs) on gold have been prepared. An unsymmetrical squarylium (SQ) dye for SAM has been synthesized from squaric acid. SQ dye monolayer was deposited on a gold surface by a stepwise method that includes covalent linkage of SQ dye to a cystamine monolayer-modified gold. The molecular structure of a SAM of SQ dye was investigated using visible absorption and Fourier-transform reflection absorption spectra (RAS). © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Self-assembled monolayer (SAM); Squarylium dye (SQ); Reflection absorption spectra (RAS); Alkanethiol

1. Introduction

Organic compounds containing sulfur adsorb strongly onto gold and other metals to form monolayers [1,2]. It has been established by a multitude of experimental methods that certain organosulfur compounds form stable, well-ordered self-assembled monolayers (SAMs). In a number of cases, well-packed quasi-crystalline monolayers were obtained. These SAMs offer multiple advantages as substrates for the study of organic surface chemistry. SAMs on metal surfaces have received considerable attention because of the importance of establishing how surface properties can be altered by light and how the behavior of SAMs is affected by structural rigidity [3]. These features, together with the SAM's stability, demonstrate the potential applicability of SAMs in catalysis, corrosion inhibition, lubrication, adhesion, optical imaging, and other applications [3].

Although squarylium dyes exhibit a sharp visible absorption in solvents, their absorption in the solid state is panchromatic and very intense [4]. This class of dyes has attracted much attention because of their potential application in xerographic organic photoreceptors [5,6], optical recording media [7] and organic solar cells [8], due to properties such as photoconductivity and their sharp and intense absorption in the visible or near infrared (NIR) region [9].

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We have previously reported the synthesis [10], electrochromic properties [11] and electroluminescence properties [12] of squarylium dyes (SQ) containing an indoline moiety. To our knowledge, there are no published studies on the synthesis and characteristics of sqyarylium dye-containing alkanethiol for SAM. Herein we report the preparation and characterization of a highly ordered, hydrogen-bonded, squarylium dye-containing alkanethiol monolayer, the latter achieved using of visible absorption and IR spectroscopy.

2. Experimental

Melting points were determined using an Electrothermal IA 900 appratus and are uncorrected. Elemental analyses were recorded on a Carlo Elba Model 1106 analyzer. The mass spectra were recorded on a Shimadzu QP-1000 spectrometer using an electron energy of 70 eV and the direct probe EI method.

2.1. Reagents

Squaric acid was reagent grade and was used without further purification. 2,3,3-Trimethylindolenine, 1,3,3-trimethyl-2-methyleneindoline, 2-bromoethanol, glutaric anhydride, cystamine and 1-ethyl-3-(3-(dimethylamino)propyl)-carbodiimide (EDC) (Aldrich Chemical Company) were used without further purification.

2.2. Synthesis of squarylium dye and intermediates

2.2.1. Monosubstituted squaric acid (**5**)

Compound **5** was prepared using previously described procedures [10,13]. Its structure was confirmed using data described in the literature and from the data shown below.

M.p. 297°C, EIMS, *m*/*z* (%) 269 (14.1), 241 (12.5), 158 (100). Elemental analysis: C; 71.47, H; 5.49, N; 5.21. $C_{16}H_{15}NO_3$, requires: C; 71.36, H; 5.61, N; 5.20%

2.2.2. Intermediates **8** and **9**

2.3.3-Trimethylindolenine (15.92 g, 0.1 mol) and bromoethanol (13.74 g, 0.11 mol) were refluxed for 8 h in $CHCl_3$ (100ml). The solvent was removed in vacuo and EtOAc (20 ml) was added to the reaction mixture. The precipitated solid was filtered, washed with $CHCl_3$ and dried, to give **8** as a red solid, 22.3% yield, m.p. 195–196°C. Compound **8** (6.33 g 22.3 mmol) was added to 10% aq. NaOH (300 ml) and the solution was extracted with $CHCl_3$ (200 ml). The extract was concentrated by rotary evaporation and the resulting oily product obtained was used without further purification. Yield 3.45 g (76.2%). Elemental analysis: C; 76.79, H; 8.89; N; 6.25. $C_{13}H_{17}NO$ requires: C; 76.84, H; 8.37, N; 6.89%.

2.2.3. Preparation of SQ dye **10**

SQ dye **10** was prepared from cyclobutanedione precursor **5** and compound **9** using a previously described procedure [13].

M.p. 219–221°C, yield: 1.2 g (71.4%), EIMS, *m*/*z* (%) 454 (2.1) [M^+], 438 (2.4), 158 (100). Elemental analysis: C; 76.29, H; 6.72, N; 6.28. $C_{29}H_{30}N_2O_3$ requires: C; 76.63, H; 6.65, N; 6.16%.

2.2.4. Preparation of SQ dye **12**

SQ dye **10** (0.5 g, 1.1 mmol) and glutaric anhydride (0.1 g., 1.5 mmol) were refluxed for 24 h in benzene (18 ml) and CH_3CN (2 ml). The reaction mixture was evaporated and subjected to column chromatography on silica gel with a $CHCl_3$:EtOAc:EtOH (5:4:1) mixture.

M.p. 192–193°C, yield: 0.14 g (22.4%). Analysis: C; 68.92, H; 8.21, N; 3.92. $C_{34}H_{36}N_2O_6$ requires: C; 68.69, H; 8.32, N; 4.18%.

2.3. Preparation of self-assembled monolayer film

A gold surface was prepared on a glass slide by electron-beam evaporation of 30 Å of nickel–chromium as an adhesion promotor, followed by 500 Å of Au. Stepwise chemical assembly of a squarylium dye monolayer was performed by covalent linkage of the carboxyl moiety of SQ dye **12** to a cystamine-monolayer-modified gold surface.

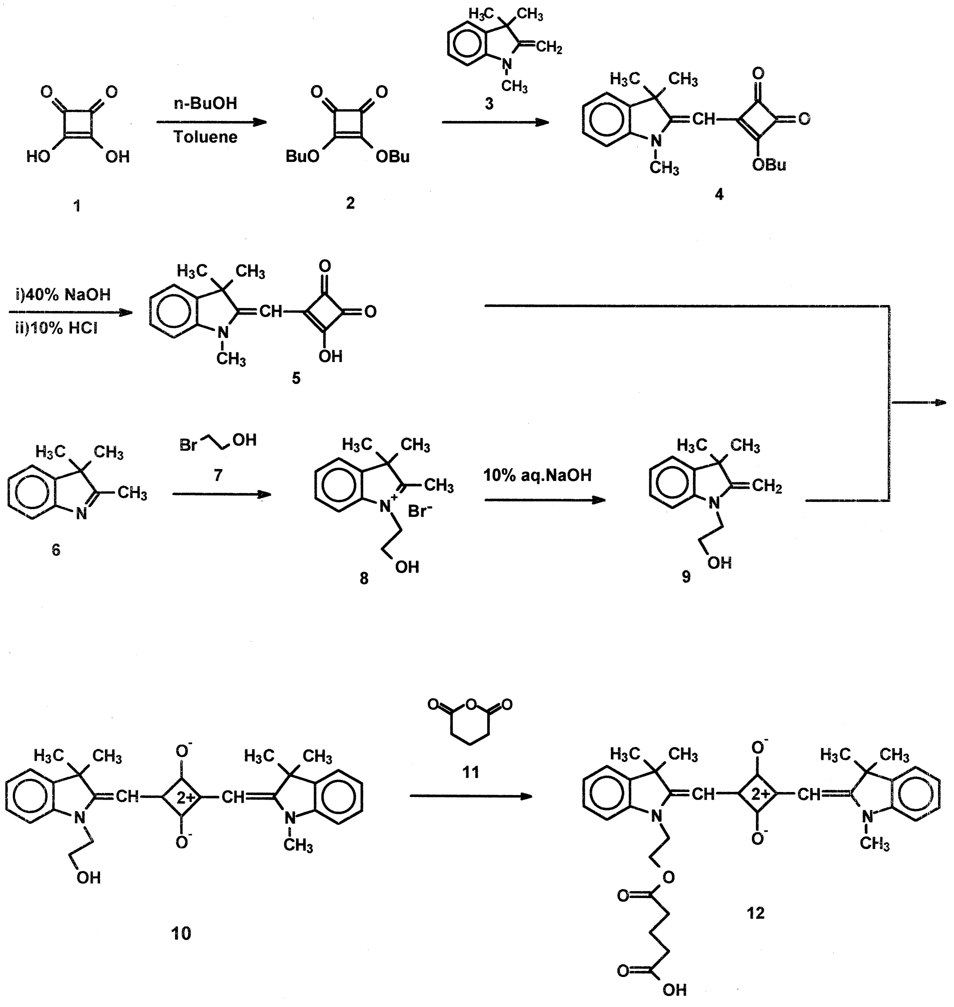
The Au deposited glass slide was immersed in a 1×10^{-2} M solution of cystamine · HCl in H_2O for 2 h followed by rinsing with deionized H_2O. After rinsing, the cystamine adsorbed gold layer was treated with an 1×10^{-2} M solution of EDC in EtOH and 5×10^{-4} M SQ dye **12** for 12 h. The resultant monolayer was rinsed several times with deionized H_2O and dried in N_2 gas [14].

2.4. Infrared measurements

FTIR-RAS (Fourier transform infrared reflection absorption spectroscopy) measurements were carried out using a Nicoler Magma-IRTM550 spectrometer. A narrow-band HgCdTe detector, cooled with liquid nitrogen, was used to detect the reflect light. For the IR-RAS measurement, GRASEBY SPACE grazing angle reflectance accessory equipped with a polarizer was used at 80°C. All spectra were collected with 2 cm^{-1} resolution. To minimize the signal-to-noise ratio, several hundred scans were made.

2.5. Visible absorption spectra

A multi-channel photodiode detector (MCPD, Otsuka Electronics, Co, Japan) was used to obtain visible absorption spectrum of SAM on Au surface. Light source, I_2 lamp, was projected and collected by Y-type optical fiber. UV-vis spectra were measured in solution using JASCO V-550 spectrophotometer.



Scheme 1.

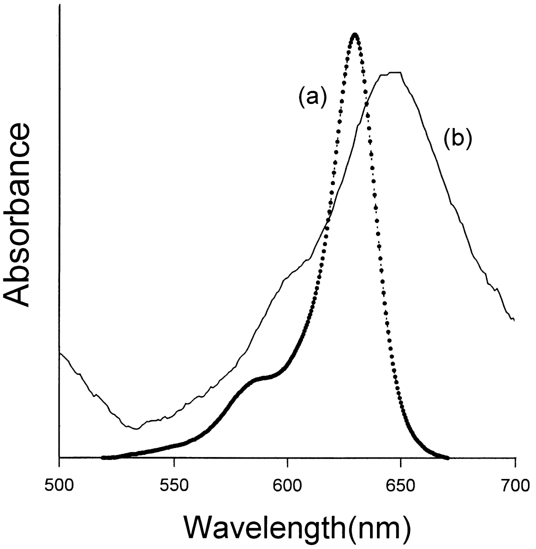
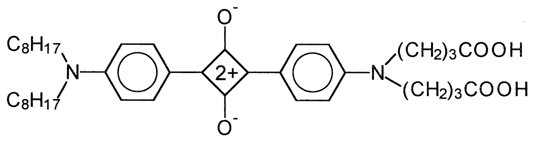


Fig. 1. Visible absorption spectra of SQ dye **12** in (a) EtOH and (b) SAM/Au.



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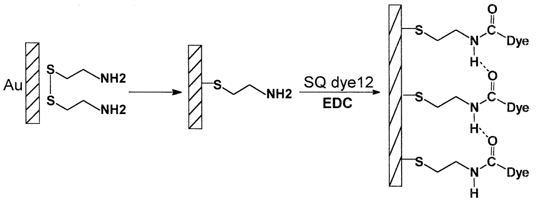
3. Results and discussion

The synthetic route to the SQ dye is outlined in Scheme 1. Fisher's base (**3**) was reacted with dibutyl squarate (**2**) to give the monosubstituted squaric ester **4**. Hydrolysis of this ester with 40% NaOH and subsequent acid work up afforded the monosubstituted squaric acid **5**. Condensation of **5** with **9** gave the unsymmetrical SQ dye **10**. The condensation were carried out in *n*-BuOH/PhMe using a Dean–Stark trap. The reaction of dye **10** with glutaric anhydride gave SQ dye **12** in a 22% yield.

A monolayer was assembled on Au as outlined in Scheme 2. A cystamine monolayer was first assembled on Au. SQ dye **12** was coupled to the base monolayer using a small amount of EDC, as



Scheme 2. Stepwise organization of SQ dye **12** monolayer on an Au layer.

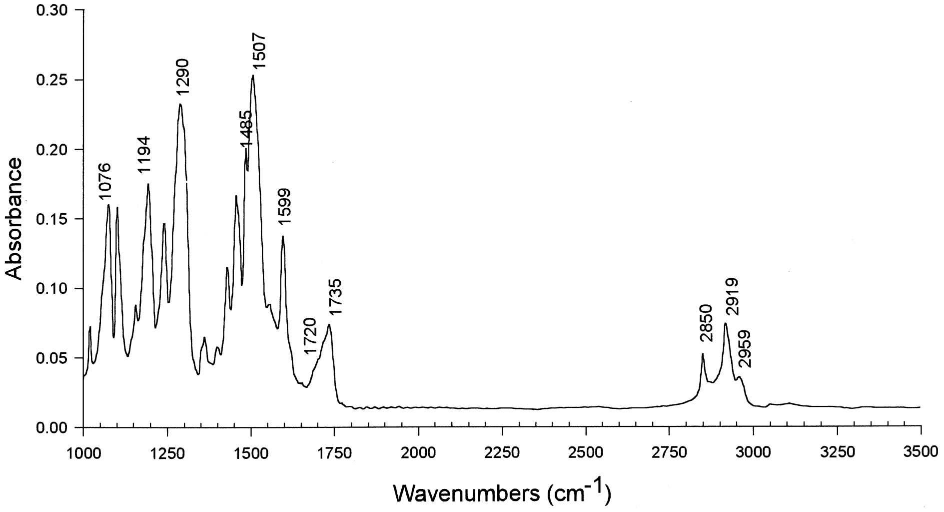


Fig. 2. Infrared transmission spectrum of SQ dye **10** in KBr.

recently described [15,16]. Over the years, EDC has emerged as the reagent of choice for amide coupling reactions [17].

The visible absorption spectra of SQ dye **10** in solution is shown in Fig. 1. There have been several attempts to study the aggregation behavior of the squarylium dyes as well as the driving forces involved in the aggregation process [18,19]. Chen has reported the formation of blue shifted aggregates of SQ dye **13** in DMSO–H_2O mixtures, using increasing amounts of H_2O in the mixture [18]. SQ dye **13** existed in aggregate (530 nm), dimeric (594 nm) and monomeric (650 nm) forms in this binary solvent system.

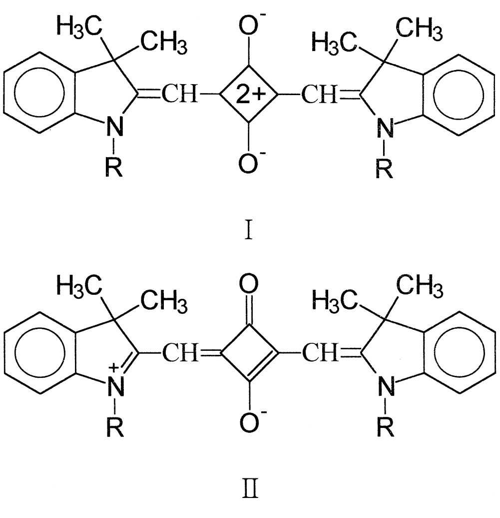


Fig. 3. Structure for a SQ dye. I (SQ dye **10**), II (SQ dye on SAM).

In Fig. 1, the absorption bands at 630 and 586nm correspond to the monomeric and dimeric forms of SQ dye **12**, respectively. The reflection absorption spectrum of the SAM of SQ dye **12** was quite different from that found in solution. The monolayer film of SQ dye **12** exhibited an absorption at 646 nm which corresponds to the monomeric band. From these results, it was noted that the dimer absorption for SQ dye **12** was not present in the monolayer state. The absorption of SQ dye **12** in monolayer film was red-shifted by ~15 nm versus the absorption in solution.

Kuramoto et al. reported the absorption spectra of the squarylium dye 2,4-bis[(3,3-dimethyl-1-octadecyl-2,3-dihydro-2-indolylidene)methyl]-1,3-cyclobutadienediylium-1,3-diolate in ethanol and in LB film, and found that the LB film state absorption spectrum was broad and red-shifted as compared to the solution spectrum [23]. Fig. 2 shows the bulk transmission (KBr pellet) IR spectrum of SQ dye **10**. The intense bands at 2919 and 2850 cm^{-1} correspond to CH_2 asymmetric and symmetric stretching of the hydrocarbon chain, and a weak band at 2959 cm^{-1} is assigned to CH_3 asymetric stretching. These frequencies are in agreement with those reported by other workers [20,21].

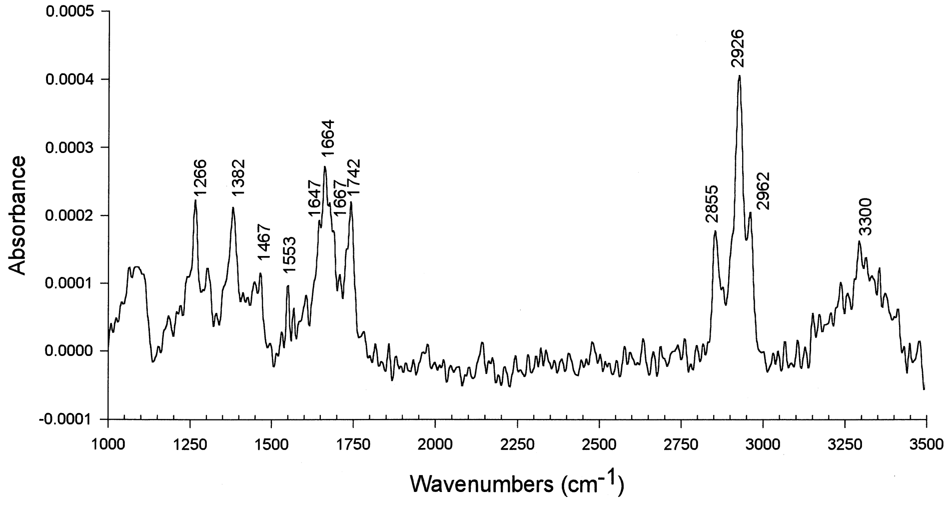


Fig. 4. FTIR-RA spectra for self-assembled SQ dye 12 on Au.

The two most characteristic features in the IR spectrum of a normal ester are the strong C=O, which appears at 1750 to 1735 cm^{-1}, and C–O stretching absorptions, which appear at 1300–1000 cm^{-1}. The bands at 1735 and 1720 cm^{-1} in Fig. 2 were assigned as the C=O groups of the ester and carboxylic acid, respectively.

A band at 1194 cm^{-1} may arise from ester C–O stretching, while the band at 1599 cm^{-1} is probably assignable to stretching of the central conjugated system, because the same intense bands were observed at 1590–1600 cm^{-1} in the IR spectra of other SQ dyes [10,22]. An intense band at 1507 cm^{-1} is due to stretching involving the central conjugated system and the indoline C–N group, which is in accord with previous results [23].

The results of IR spectroscopic analysis of SQ dye **10** indicated that the molecule has extensive bond delocalization, giving structure I in solid state (Fig. 3.). FTIR-RAS of a monolayer of SQ dye **12** is shown in Fig. 4.

To characterize the monolayer of SQ dye **12**, a cystamine modified gold slide was used as the base. IR bands arise from NH stretching (amide A) at 3300 cm^{-1}, C=O stretching (amide I) at 1647 cm^{-1}, and NH in-plane bending (amide II) at 1553 cm^{-1}. Clegg et al. prepared an amide-containing alkanethiol SAM on gold and obtained a well-ordered and mechanically stable monolayer through intermolecular hydrogen bonding between the neighboring amide moieties [24].

The most compelling evidence for intermolecular hydrogen bonding within the monolayer was obtained by using FTIR-RAS. A general broadening of the amide stretch appearing near 3300 cm^{-1} was judged to be indicative of the presence of intermolecular hydrogen bonding within SQ dye **12** containing SAM.

Bands at 2926 and 2855 cm^{-1} are due to CH_2 asymmetric and symmetric stretching of the hydrocarbon moiety. The band at 1725 and 1664 cm^{-1} may be due to the central four-membered ring C=O stretching and indoline $C{=}N^+$ stretching, respectively. These observations indicate that SAM of SQ dye **12** has structure II (Fig. 3).

Acknowledgements

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