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Synthesis and electrochemical properties of symmetric squarylium dyes containing diarylamine

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ABSTRACT

We studied the synthesis and electrochemical properties of symmetric squarylium dyes (SQDs) containing diarylamine with various structures. It was shown that several of our synthesized SQDs had improved electrochemical properties and might be a promising and an easy modifiable π-conjugate core block of active materials for electroactive and photoactive devices.

1. Introduction

Squaraine dyes or squarylium dyes (SQDs) are a well-known family of functional dyes to be used as colouring materials [1], photoconductive materials in photocopiers [2] and the active layer in optical memory such as digital versatile discs [3]. In this decade, SQDs have been studied as a core block of active materials for new types of organic electroactive and photoactive devices such as electroluminescent devices [4], bulk heterojunction organic photovoltaic cells [5], and dye-sensitized solar cells [6]. In the field of medicinal science, SQDs with near-infrared absorption properties have been studied as a fluorophore for sensing materials [7] and a sensitizer for photodynamic therapy [8]. Moreover, SQDs have attracted attention as unique colourants of π-conjugate units for supramolecular ion sensing [9], foldarmer formation [10], extended π-conjugate compounds [11] such as low bandgap polymers for organic conductors [12], π-extended systems such as bis-squarylium compounds [13], and squarylium oligomers [14]. Thus, SQDs are considered unique units of π-conjugate dyes for the various applications mentioned above, and their unique reactivity [15] and capacity for supramolecular modification in high durability applications in the field of medicine [16] have been explored. Although the previously discussed SQDs have been extensively studied, they absorb primarily in the visible to near-infrared regions. New SQDs that absorb in the blue laser region (~405 nm) are needed for new applications in which blue lasers are used, such as active materials for optical memory or sensitizers for photochemical reactions.

Recently, for their usefulness in well-defined molecular structure designs, π-conjugate compounds have garnered much attention as candidates for active materials of organic electroactive and photoactive devices. Better electrochemical properties of the π-conjugate compounds, such as electrochemical reversibility, might be needed in the active materials for rechargeable batteries [17]. On the other hand, better electrochemical reversibility of π-conjugate compounds, both transporting materials and emitting materials, in electroluminescent devices might be considered essential for designing high-performance π-conjugate compounds [18]. The electrochemical reversibility may become necessary as better design criteria emerges for electroactive and photoactive materials.

To develop SQDs as potential blue-laser absorption dyes and as promising candidates for the core block of functional dyes, we have studied the synthesis and electrochemical properties of symmetric SQDs containing diarylamine with blue light absorption (Scheme 1). These compounds can be synthesized in a one-step reaction with

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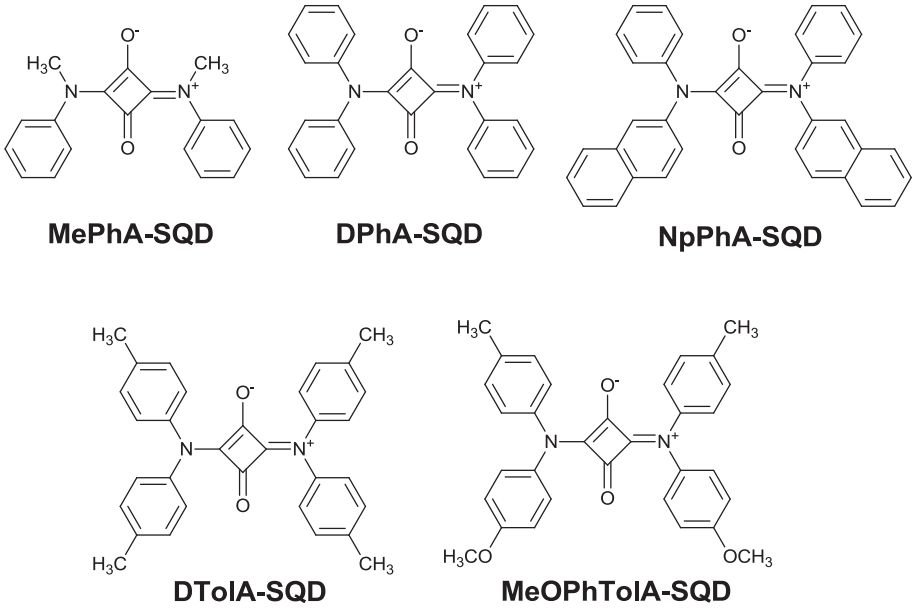

Scheme 1. Chemical structures of symmetric SQDs.

easy workup from squaric acid and secondary arylamine. It was shown that several of our extended SQDs have and better electrochemical reversibility than primitive SQDs and might be a promising π-conjugate core block of an active material for electroactive and photoactive devices using blue laser or other lasers for applications mentioned above. Further modification of arylamine as a raw reagent will offer the versatility for creating new symmetric SQDs with high performance based on this study.

Related to this paper, the synthesis [19] and electrochemical properties [20] of primitive SQDs containing diarylamine (MePhA-SQ and DPhA-SQD) were reported. The previous studies have primarily focused on analysis of the chemical structure of primitive SQDs, including dialkylamine and diarylamine. The electrochemical properties such as reversibility of other extended symmetric-type SQDs are reported here for the first time.

2. Experimental section

2.1. General

Dichloromethane (super dehydrated), *N*,*N*-dimethylformamide (Spectrosol®, DOJINDO Laboratories) and squaric acid were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. All other reagents and solvents were purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. Water was deionised with an Elix UV 3 Milli-Q integral water purification system (Nihon Millipore K.K).

^{1}H NMR and ^{13}C NMR were recorded on an AVANCE 500 (500 MHz, Bruker BioSpin K.K.) spectrometer. MALDI–TOF MS was performed with an autoflex III (Bruker Daltonics Inc.) using sinapinic acid as a matrix. Elemental analysis was performed with a Yanaco CHN corder MT-5 (Yanaco New Science Inc.). Single-crystal X-ray diffraction data were recorded on a SMART APEX II Ultra X-ray diffractometer (Bruker AXS K.K.) with CuKα at −50 °C. Crystal structures were visualised from CIF data using Mercury (Cambridge Crystallographic Data Centre). Electrochemical measurements were carried out with an electrochemical analyzer model 708c (CH Instruments, Inc.). Electronic absorption spectra within the ultraviolet–visible region were measured with a V-670 UV–vis spectrophotometer (JASCO Corporation) by using a 10 mm path length of a quartz glass cell (concentration of a measured SQD solution: $\sim 1 \times 10^{-6}$ M).

2.2. Synthesis of SQDs

2.2.1. MePhA-SQD

Under N_2 atmosphere, *n*-butanol/toluene [1:1 (v/v), 5 mL], *N*-methylaniline (3.00 g, 27.4 mmol), and squaric acid (1.28 g, 11.2 mmol) were combined and stirred at 110 °C for 21 h, then cooled to room temperature. The obtained precipitate was filtered, washed with methanol and dried in vacuo to yield an orange powder (2.95 g, yield 90.8%). ^{1}H NMR (500 MHz, DMSO-*d*6, TMS, δ, ppm): 7.22 (m, 8H, Ar–H), 7.29 (m, 2H, Ar–H at the para position), 3.84 (s, 6H, N–CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, TMS, δ, ppm): 177.47, 168.52, (141.24, 141.09), 129.24, 127.27, 123.00, (39.19, 38.73). MALDI–TOF MS: calcd for $C_{18}H_{16}N_2O_2$ (MW = 292.12): m/z = 292.61 [M^+]. Elemental anal. calcd for $C_{18}H_{16}N_2O_2$: C, 73.95%; H, 5.52%; N, 9.58%. Found: C, 73.93%; H, 5.59%; N, 9.66%. It is worth noting that in ^{13}C NMR spectrum of MePhA-SQD might show peaks based on conformers as shown in the literature describing squalyrium dyes [21].

2.2.2. DPhA-SQD

Under N_2 atmosphere, *n*-butanol/toluene [1:1 (v/v), 5 mL], diphenylamine (3.00 g, 17.6 mmol), and squaric acid (809 mg, 7.09 mmol) were combined and stirred at 110 °C for 21 h, then cooled to room temperature. The obtained precipitate was filtered, washed with methanol and dried in vacuo to yield an orange powder (1.73 g, yield 58.5%). ^{1}H NMR (500 MHz, DMSO-*d*6, TMS, δ, ppm): 7.44 (t, 8H, J = 7.7 Hz, Ar–H), 7.35 (t, 4H, J = 7.3 Hz, Ar–H at the para position), 7.25 (d, 8H, J = 7.6 Hz, Ar–H). ^{13}C NMR (125 MHz, $CDCl_3$, TMS, δ, ppm): 178.82, 168.09, 140.44, 128.94, 127.67, 125.43. MALDI–TOF MS: calcd for $C_{28}H_{20}N_2O_2$ (MW = 416.15): m/z = 416.82 [M^+]. Elemental anal. calcd for $C_{28}H_{20}N_2O_2$: C, 80.75%; H, 4.84%; N, 6.73%. Found: C, 80.62%; H, 4.79%; N, 6.78%.

2.2.3. NpPhA-SQD

Under N_2 atmosphere, *n*-butanol/toluene [1:1 (v/v), 5 mL], *N*-methylaniline (4.81 g, 21.3 mmol), and squaric acid (1.00 g, 8.77 mmol) were combined and stirred at 110 °C for 25 h, then cooled to room temperature. The obtained precipitate was filtered,