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A new family of light-emissive symmetric squarylium dyes in the solid state

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ABSTRACT

High-intensity light emission was observed from symmetric squarylium dyes bearing diaryl amine moieties in the solid state unlike typical squarylium analogues. The enhanced light emission in the solid state may be ascribed to the propeller-like dye architectures, which sterically hinder the intermolecular π−π interactions rather than the intramolecular charge transfer.

1. Introduction

Recently, the structure−property relationship investigations of luminescent π-conjugated functional dyes have resulted in high performance dyes that find application as optoelectronic devices and medical imaging tools for affected and targeted regions. Moreover, certain dyes have exhibited higher luminescence upon aggregation or in the solid state rather than the typical fluorescence quenching [1]. This unusual strong light emission of some organic dyes in the solid state has prompted extensive efforts in designing and synthesizing new photoluminescent compounds [2–16]. Certain dyes have also demonstrated enhanced fluorescence upon selective sensing of biomolecules. This aggregation-induced emission can be used to diagnose specific health conditions [1a,1b,17].

Squarine or squarylium dyes (SQDs) are an extensively studied family of functional dyes [18]. These dyes are expected to be used as organic electroactive and photoactive devices such as electroluminescent devices [19], bulk heterojunction organic photovoltaic cells [20], and dye-sensitized solar cells [21]. In the field of medical science, SQDs have been studied as a sensitizer for photodynamic therapy [22] and fluorophores for sensors [23]. Furthermore, investigations of their use as supramolecular modifiers have revealed their long-lived durability, which is sufficient for medical imaging [24]. Despite extensive synthetic work and photophysical studies, there have been few reports on the solid-state light emission of these dyes. However, studies have reported SQDs bearing an indolenium moiety showed red fluorescence with a weak quantum yield of only 0.02 [25a], whereas indolenine-derived semi-squaric acid showed a quantum yield of 0.2 [25b]. Recently, a new family of asymmetric-type squarylium dyes showing larger fluorescence quantum yield ~0.36 in the solid state was reported [25c].

In this study, we report the enhanced fluorescence of symmetric SQDs. Fluorescence quantum yields increased from <0.01 in DMF to 0.05–0.36 in the solid state. This solid-state fluorescence at such quantum yields is unprecedented in symmetric SQDs. These symmetric SQDs containing diaryl amine moieties can be synthesized from squaric acid and secondary arylamine in a one-step reaction with simple work up (Scheme 1) [26].

2. Experimental section

2.1. Materials and methods

N,*N*-dimethylformamide (DMF, Spectrosol®, DOJINDO Laboratories), (−)-Quinine sulphate dehydrate (98%) and conc. H_2SO_4

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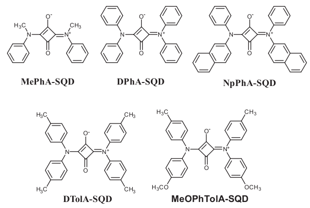

Scheme 1. Chemical structures of SQDs.

(Wako Pure Chemical Industries, Ltd., Japan) were used without further purification. Other solvents (Wako Pure Chemical Industries, Ltd., Japan) are used as received.

The SQDs containing diaryl moieties, i.e. **MePHA-SQD**, **DPhA-SQD**, **NpPhA-SQD**, **DTolA-SQD**, and **MeOPhTolA-SQD** were synthesized and obtained as described in our earlier report [26].

2.2. Measurements

Ultraviolet–visible electronic absorption spectra were obtained using a V-670 UV–vis spectrophotometer (JASCO Corporation) in a quartz glass cell with a 10 mm path length for ca. 1×10^{-6} M SQD solutions. Fluorescence spectra were obtained using an LS55 luminescence spectrometer (PerkinElmer Japan Co., Ltd.) in a quartz glass cell with a 10 mm path length for ca. 1×10^{-6} M SQD solutions. Fluorescence lifetimes in DMF and in the solid state were measured by a time-correlated single photon counting fluorescence spectroscopic method using a FluoroCube 1000U (HORIBA, Ltd.) equipped with a NonoLED-375L picosecond laser diode as an excitation light source (peak wavelength 378 nm, HORIBA, Ltd.). LUDOX® colloidal silica or glass plate were used as standards. Fluorescent lifetimes of SQDs were measured at their maximum fluorescence wavelengths (λ_{max}) in solution or in the solid state. Fluorescence lifetime measurements in DMF were performed after N_2 bubbling for 15 min. Lifetimes in the solid state were measured by placing SQD between sealed glass plates and fixing the plate edges with mending tape.

Crystal structures were visualized from CIF data using *Mercury* 3.5.1 (Cambridge Crystallographic Data Centre).

2.3. Estimation of fluorescence quantum yields

Fluorescence quantum yields (Φ_f) in the solid state were determined using a C9920-02 absolute fluorescence quantum yield measurement system (Hamamatsu Photonics K.K.). Fluorescence quantum yields in solution were obtained relative to an aqueous quinine sulphate solution. Quantum yields were calculated using the following equation with a Φ_s value of 0.55 for quinine sulphate in 0.5 M H_2SO_4 [27]:

$$\Phi_f = \Phi_s(I/I_s) \times (A_s/A) \times \left(n^2 / n_s^2\right),$$

where I is the integration of the fluorescent intensity, A is the absorbance at the excitation wavelength, n is the refractive index of solvent and the subscript s refers to the quinine standard.

3. Results and discussions

We already reported that a creation of symmetric SQDs containing diaryl amine moieties synthesized by only refluxing diaryl amine and squaric acid in a solution and the work up without chromatographic techniques yielded SQDs in good yield and purity (Scheme 1) [26]. These SQDs showed better electrochemical reversibility than required for optoelectronic device applications. Their crystal powders showed intense photoluminescence in the solid state upon UV light irradiation (Fig. 1). Typical SQDs show absorption in the visible light region in solution and emit in the red or near-IR regions if they are fluorescent; however, the diaryl amine-containing SQDs showed absorption near 400 nm in the blue-light region. Moreover, they showed fluorescence depending on their molecular structures in the solid state: light green for **MePhA-SQD**, orange for **DPhA-SQD** and **NpPhA-SQD** and green for **DTolA-SQD** and **MeOPhTolA-SQD**. Furthermore, the corresponding SQD solutions in DMF (10 μM) showed no photoluminescence to the naked eye (Fig. 1(c)).

To elucidate the photophysical properties of SQDs, their fluorescence was measured in DMF and in the solid state, together with the corresponding fluorescence quantum yields (Φ_f) (Fig. 2, Table 1). Except for **MePhA-SQD**, the SQDs in solution showed weak fluorescence at ca. 510 nm. However, in the solid state, they showed fluorescence at longer wavelengths than in solution, consistent with the stabilizing effects of π-conjugation in the solid (microcrystalline) state. Relative Φ_f

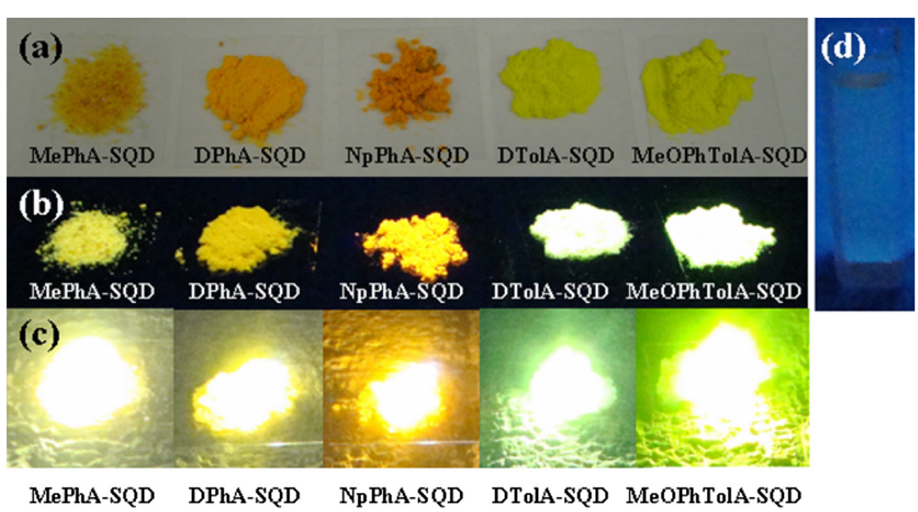

Fig. 1. Photographs of SQD powders; (a) SQDs under the ordinary fluorescent light, (b) SQDs under UV irradiation with black light (365 nm), (c) SQDs under UV irradiation a with laser pointer (405 nm), (d) 10 μM **MeOPhTolA-SQD** solution in DMF in a glass cell under UV irradiation (365 nm).