

Discovery of Novel Dyes with Absorption Maxima at 1.1 μm

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With the development of optical communications, third-order nonlinear optical (NLO) materials for ultrafast optical devices have been attracting much attention.^{1,2} In particular, a large variety of organic materials have been investigated for optical switching thus far.² Since dye J-aggregates exhibit an ultrafast NLO response near the maximum absorption wavelength (λ_{max}) of their red-shifted J band,³ we have studied such materials for application to optical switches.⁴ As a result, we have succeeded in fabricating J-aggregates of squaraine (SQ: substituted 3-oxo-1-cyclobutenolate) dye in spin-coated films and observed a sub-100-fs optical response. Moreover, on the basis of the concept of time-to-space conversion, we successfully realized single-shot demultiplexing at 1 T bit/s.⁵ However, such an ultrafast NLO response of SQ J-aggregates can be achieved only at ca. 770 nm. On the other hand, the wavelengths of optical pulses used in optical communications are 1.3 or 1.55 μm .

To overcome the problem in wavelength matching, the 2-photon excitation process has been considered;⁶ however, the optical switching efficiency of this process does not meet the requirements for practical use. Thus, we think it is necessary to develop new dyes that can exhibit the J band near 1.3 or 1.55 μm . One efficient way to realize the bathochromic shift of SQ molecules is the π -conjugation extension.⁷ Nevertheless, the formation of J-aggregates in thin films and the realization of high thermal stability are still great challenges for dyes with long π -conjugation. Therefore, we think it may be better to strengthen the electron-withdrawing ability of the acceptor in a dye molecule. The croconic acid moiety is considered to be a stronger electron acceptor than the squaric acid part, because croconaine (CR: substituted 3,4-dioxo-1-cyclopentenolate) dyes show absorption maxima that are red-shifted by ca. 100 nm as compared with those of the corresponding SQ.⁸ In particular, the λ_{max} of an anilino CR can reach 860 nm.⁹ Thus, we surmise that if such a CR dye could form J-aggregates, the λ_{max} would exceed 1.1 μm . On the other hand, we have verified that the four hydroxyls at the 2',6'-positions of the two phenyls can enhance the thermal stability and the sublimation ability of an anilino SQ dye more significantly than the two hydroxyls at the same 2'-positions.¹⁰ For these reasons, we attempted to synthesize 2,5-bis[4-(*N,N*-dialkylamino)-2,6-dihydroxyphenyl]-croconaines **2** to find some CR derivatives that can form J-aggregates. Such an effort led to the discovery of a novel class of dyes **1** that exhibit absorption maxima at 1.1 μm and potential for optical switching at 1.3 μm (Scheme 1).

The synthesis of **2** is relatively straightforward, involving the condensation reaction between croconic acid **3** and the corresponding aniline intermediate **4**.⁹⁻¹¹ Considering the solubility and the tendency to form J-aggregates of **2**,¹⁰ first we attempted the synthesis of the *N,N*-diisobutyl derivative. After the condensation of 5-(*N,N*-diisobutylamino)-1,3-benzenediol **4a** and **3** (2:1, molar

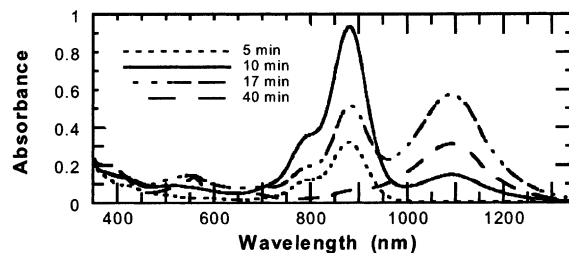
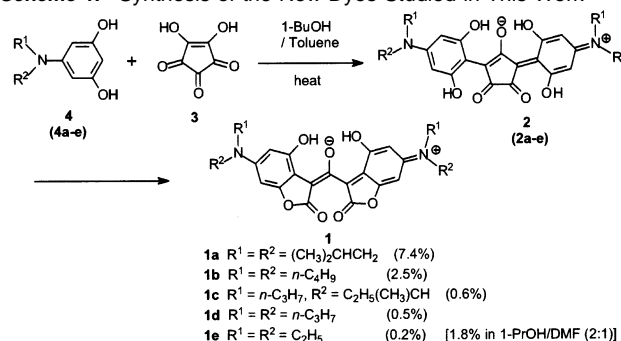


Figure 1. Absorption change of the reaction solution for the synthesis of **1a**. Samples were taken from the solution heated for 5 (69 °C), 10 (96 °C), 17, and 40 (reflux) min, and diluted with chloroform.

Scheme 1. Synthesis of the New Dyes Studied in This Work



ratio) in a mixture of toluene and 1-butanol (3:1) was carried out under azeotropic reflux in an atmosphere of dry nitrogen for 4 h, we measured the absorption spectra of the reaction solution. To our surprise, a strong and broad absorption band not at ca. 850 nm but at 1.1 μm was observed. Then, this reaction was carried out under different conditions, and the reproducibility of dye **1a** absorbing at ca. 1.1 μm was confirmed. Figure 1 shows a typical example of absorption change of the reaction solution. The absorption band at ca. 880 nm, which was assigned to **2a**, was observed before the absorption band at ca. 1.1 μm started to appear. The optimal yield of **1a** was achieved when the reaction mixture was refluxed for 10 to 15 min. After purification, **1a** was obtained as pure black–purple needle microcrystals in 7.4% yield.

The characterization data obtained by NMR, FD-MS, and IR spectroscopic methods, as well as by elemental analysis, indicate that **1a** has a di(benzofuranonyl)methanolate structure. This structure is completely different from those of CR dyes. To confirm this result, single crystals of **1a** were prepared for X-ray analysis. The results of X-ray crystallography confirmed the molecular structure of **1a**.¹² As shown in Figure 2, although the two furan rings of **1a** have a twisted conformation, the short bond length between the aromatic carbon atom and the nitrogen atom suggests the existence of a large intramolecular π -delocalization, which may be the reason for the extension to 1.1 μm of the λ_{max} of **1a**.

1a was formed probably via unexpected intramolecular tandem reactions. The double electrophilic attack by **3** on the electron-rich

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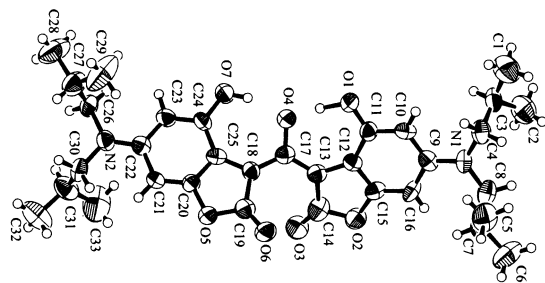


Figure 2. ORTEP diagram of **1a**.

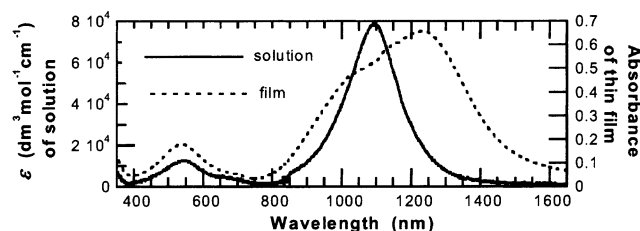


Figure 3. Absorption spectra of dye **1a** in 1,2-dichloroethane (solid line) and in a 63-nm-thick, spin-coated film (broken line).

aniline substrates gave the expected CR dye. Due to steric assistance, the OH groups ortho to the croconate ring might further attack the neighboring carbonyl groups to form the dibenzofuran intermediate, the unstable centric pinacol part of which might undergo a self-oxidation–reduction reaction with the opening of the croconate ring to afford **1a**. Since dye **2** is not sufficiently stable, we have not succeeded in its purification.

The aniline substrates with other *N*-alkyls were also used to react with **3**, and the corresponding dyes with absorption maxima at ca. 1.1 μm were formed without exception. However, their yields depended strongly on the *N*-alkyls. The aniline substrates with two branched *N*-alkyls tended to give a better yield of **1**. To improve the yields of **1**, other solvent systems such as 1-propanol/DMF (2:1) were also used and proved to be effective.

Compounds **1a–e** are soluble in halogenated solvents such as 1,2-dichloroethane (DCE) and chloroform. In particular, **1a** is also soluble in acetone and THF, and its initial decomposition temperature is 202.7 $^{\circ}\text{C}$. The solution spectra of these dyes are similar and, for example, in DCE, have a strong and broad absorption band at ca. 1.1 μm and a weak absorption band at ca. 550 nm (Figure 3). Moreover, thin films of **1a** on glass substrates could be fabricated by the spin-coating method from a 1 wt % DCE solution. The absorption spectrum of such a film is shown in Figure 3. The spin-coated film of **1a** exhibited a broad absorption band with the peak at 1228 nm. Compared to the absorption of its solution, the absorption of the spin-coated film is red-shifted by 135 nm. This indicates the formation of J-like aggregates in the spin-coated films. Such aggregates are very important for NLO applications.

The third-order NLO susceptibility $\chi^{(3)}$ at 1.3 μm of the spin-coated films of **1a** was investigated using the Z-scan technique.¹³ The **1a** film was moved along the traveling direction of the laser beam across the focal point, and a transmittance change was recorded as a function of film position *Z* (Figure 4). The result indicates a typical increase of transmittance in the vicinity of the beam focus due to bleached absorption. Normalized transmittance change reached as high as 26% under the irradiation intensity of 12 $\text{pJ}/\mu\text{m}^2$, and no obvious destruction of the sample was observed during the measurement. The imaginary part $\chi_1^{(3)}$ of **1a** film was calculated to be -0.83×10^{-7} esu. This value is larger than that of resonant $\chi^{(3)}$ of polyacetylene¹⁴ by more than 1 order of

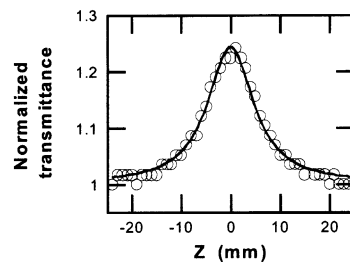


Figure 4. Z-scan signal of a 63-nm-thick, spin-coated film of **1a**. The source laser has a center wavelength of 1300 nm and pulse duration of 200 fs. Solid line is a fitted curve assuming low excitation regimes.

magnitude, which demonstrates the high capability of **1a** as an NLO material.

In summary, we have discovered a new class of dyes with absorption maxima at approximately 1.1 μm . These molecules have several unique characteristics such as a relatively short backbone structure, good solubility, and rather high thermal stability. Thin films of such dyes could be fabricated by spin-coating with the formation of J-like aggregates, and they are potential materials for optical switching at 1.3 μm . Further study on the NLO properties of these dyes and the application of such tandem reactions to the synthesis of other near-infrared-absorbing materials is in progress.

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Supporting Information Available: Details of synthesis, crystal growth, and characterization data for **1a** and crystallographic data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) X-ray data collected at 22.5 ± 2 $^{\circ}\text{C}$ for black–purple needle crystals of **1a**: tetragonal, $I4_1/a$, $a = b = 31.682(5)$ \AA , $c = 12.471(8)$ \AA , $\alpha = \beta = \gamma = 90^{\circ}$, $Z = 16$, $F(000) = 4960$, $R = 0.055$, $R_w = 0.162$, $\text{GOF} = 0.87$; Selected bond lengths (\AA) and torsion angles (deg): O(1)–C(11) 1.337(8), O(3)–C(14) 1.193(9), O(4)–C(17) 1.324(8), O(6)–C(19) 1.205(8), O(7)–C(24) 1.333(8), N(1)–C(9) 1.355(8), N(2)–C(22) 1.352(9); C(13)–C(17)–C(18)–C(19) 26(1), C(14)–C(13)–C(17)–C(18) 29(1).
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