Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 78 (2008) 60–64

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

A new water-soluble near-infrared croconium dye

Xiangzhi Song*, James W. Foley

Rowland Institute at Harvard, Harvard University, 100 Edwin H. Land Boulevard, Cambridge, MA 02142, USA

Received 5 June 2007; received in revised form 4 October 2007; accepted 14 October 2007
Available online 22 October 2007

Abstract

A new water-soluble near-infrared (NIR) absorbing croconium dye, 2,5-bis[(4-carboxylic-piperidylamino)thiophenyl]-croconium, was synthesised by condensing croconic acid with 2-(4-carboxylic-piperidylamino)thiophene and characterised by ^{1}H NMR, high-resolution MS and UV–vis spectra. The dye showed a sharp and intense absorption band peaking near 800 nm and little absorption in visible region in several water-soluble polymers. It also exhibited excellent photostability in water, methanol and in the plastic films. Due to its good water solubility, a water-based coating process was developed to make NIR blocking plastic filters for use as attenuators of stray light in NIR laser systems.

Keywords: Near-infrared dye; Water-soluble; Croconium dye; Laser filters

1. Introduction

Infrared dyes have attracted much attention due to their important applications in laser optical storage systems, laser printing systems, laser filters, photography, biological and medicinal applications [1,2]. A significant challenge that is often associated with these uses centers on the incorporation of the dye into plastic matrixes by methods that minimize aggregate formation and the concomitant broadening of the absorption spectrum that usually accompanies this phenomenon, thus preserving the absorption band shape that characterises the monomeric species of a chromophore. A common method for achieving this goal involves the application of the dye to a substrate from a volatile organic compound (VOC). However, the growing awareness of the potential adverse effects to the environment, such as ozone depletion, acid rain and possibly a chemical imbalance of the earth's ecosphere, that are caused by the emission of some of these VOCs during the application and drying of solvent-based coatings, is leading to restrictions in the use of organic solvents for this purpose. In addition to these environmental concerns, the use of solvent-based coatings can constitute health and safety hazards and can result in increased costs of handling the VOCs. To these ends, water-based applications are being developed as a viable alternative to solvent-based coatings and, as a consequence, the discovery of new NIR dyes having good water solubility for use in these aqueous systems is of considerable and growing importance.

Croconium dyes are known to have narrow and intense absorption bands that peak in the 800 nm spectral region and in contrast to most cyanine dyes, to have good photostability [3–6]. Moreover, unlike many of the water-soluble NIR cyanine dyes that have been synthesised and widely applied [7–9], croconium dyes often have very little absorption in the visible region of the spectrum which makes them highly desirable for applications where even a small amount of color is detrimental, such as light-induced thermal welding of colourless plastic articles and NIR filter lens for goggles. These features make dyes of the croconium family attractive for many of the above mentioned applications, especially those based on the availability of cheap and powerful Ga–Al–As lasers which emit in the 780–830 nm wavelength range [10]. Although the literature contains many examples of organic solvent-soluble croconiums, to our best knowledge, none have been reported that are water-soluble; the potential utility of croconium dyes having this characteristic provided

---

* Corresponding author. Tel.: +1 617 497 4671; fax: +1 617 497 4627.
E-mail address: song@rowland.harvard.edu (X. Song).

0143-7208/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2007.10.006

the incentive for us to develop such a chromophore. Here we report the rational design, synthesis and spectral characterisation of a new water-soluble croconium dye **1** having the molecular structure shown in Fig. 1.

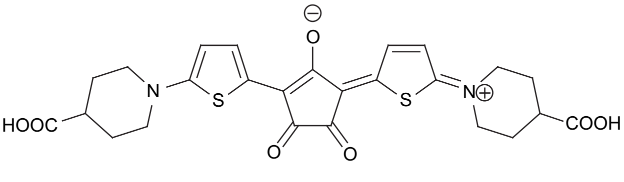


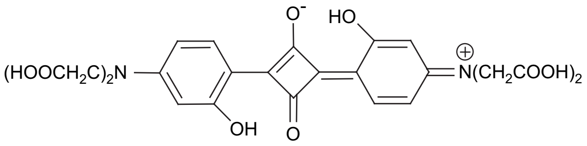
Fig. 1. Molecular structure of croconium dye **1**.

2. Results and discussion

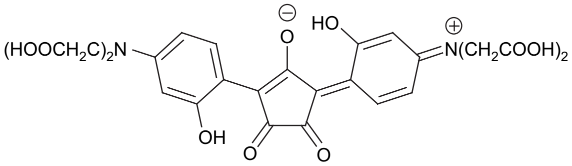
2.1. Design and synthesis of dye *1*

Several water-soluble squarylium dyes, such as dye **2** (Fig. 2), have previously been prepared by condensing squaric acid with 3-*N*,*N*-dialkylaminophenols bearing water-solublising groups such as carboxylic acid or sulfonic acid [11,12]. However, our initial exploratory studies designed to emulate this approach found that the corresponding croconium dyes had poor stability in aqueous or alcoholic solution. For example, when we attempted to prepare dye **3** in a solvent mixture consisting of toluene and *n*-butanol, we found that the intensity of the chromophore's peak absorption at 815 nm decreased during the late stages of the reaction (precipitation of the dye from solution was excluded as an explanation for this phenomenon); a small amount of dye that was removed from the reaction mixture was found to be bleached quickly when dissolved in hydroxylic solvents such as methanol or dilute $KHCO_3$ aqueous solution. Separately, we were surprised to find that the commercial dye **4**, while very stable in methylene chloride, also showed poor thermal stability in methanol. We attributed the decreased stability of these croconium dyes to a reaction between the hydroxyl group of the aminophenol rings and the adjacent carbonyl-like moieties of the central five-member bridge according to the mechanism first proposed by Tian et al. [13]. It follows that a croconium analogue devoid of the *meta*-hydroxyl group should be precluded from participating in this type of degradation reaction and, as a result, be thermally stable in hydroxylic solvents. Unfortunately, many of our attempts to prepare such dyes proved fruitless and are consistent with the reports of several other groups which also found that the anilino-hydroxyl group plays a key role in the preparation of this specific type of croconium dye and that unsubstituted *N*,*N*-dialkylanilines do not react with croconic acid to give the expected dye [14,15].

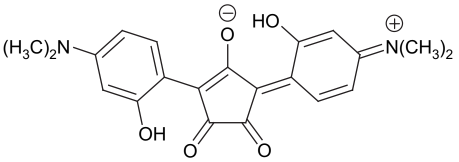
Recently, Keil et al. reported that 2-(dialkylamino)-substituted thiophenes reacted with croconic acid to give a new class of stable, hydroxyl-free croconium dyes [15–17]. Inspired by this report, we designed and synthesised the water-soluble thiophene croconium dye **1**, following the synthetic route shown in Scheme 1, and found that the potassium salt of this dye has both good water solubility and good photostability in solution and polymer films.



2



3

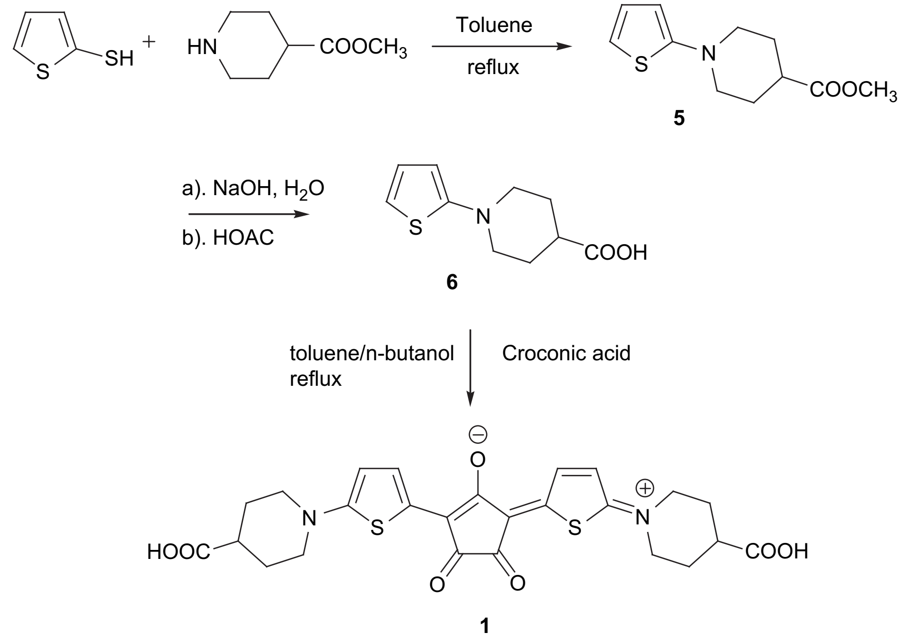


4

Fig. 2. Molecular structures of dyes **2**–**4**.

2.2. The absorption spectra of dye *1*

Solutions of the potassium salt of dye **1**, prepared by treating dye **1** with 2 equiv. of $KHCO_3$, were used for absorption spectra measurements in water, methanol and in dried films of water-soluble polymers including poly(anetholesulfonic acid, sodium salt) (PAS), poly(4-styrene-sulfonic acid, lithium salt) (PSS), poly(acrylic acid, sodium salt) (PAA) and polyvinyl alcohol (PVA). We note that because of the good water solubility of both the dye and all the polymers, most plastic films were made from aqueous mixtures of **1** and the respective polymer; however, to show feasibility, we also demonstrated that similar NIR filters could be prepared by imbibing colourless plastic sheets with aqueous solutions of the dye. The results are presented in Figs. 3 and 4 and show that **1** has a strong and sharp absorption band with peaks of maximum absorption (λ_{max}) at 783 and 787 nm in water and methanol, respectively; especially noteworthy is the observation that the visible spectral region is devoid of absorption bands of significant prominence other than in the far-red where the human eye has little sensitivity. A comparison of the line shapes of absorption spectra measured in solution shows that a slightly more pronounced distortion of the hypsochromic shoulder of the primary absorption band occurs in water relative to methanol suggesting that some aggregation of the dye takes place in the former solvent. When incorporated in the four polymers, PAA, PAS, PSS and PVA, the absorption spectra of **1** are similar to those recorded in the solvents having narrow and intense bands centered in the 803–808 nm range, depending on the polymer, thus making this dye nearly ideal for applications



Scheme 1. Synthetic route to dye **1**.

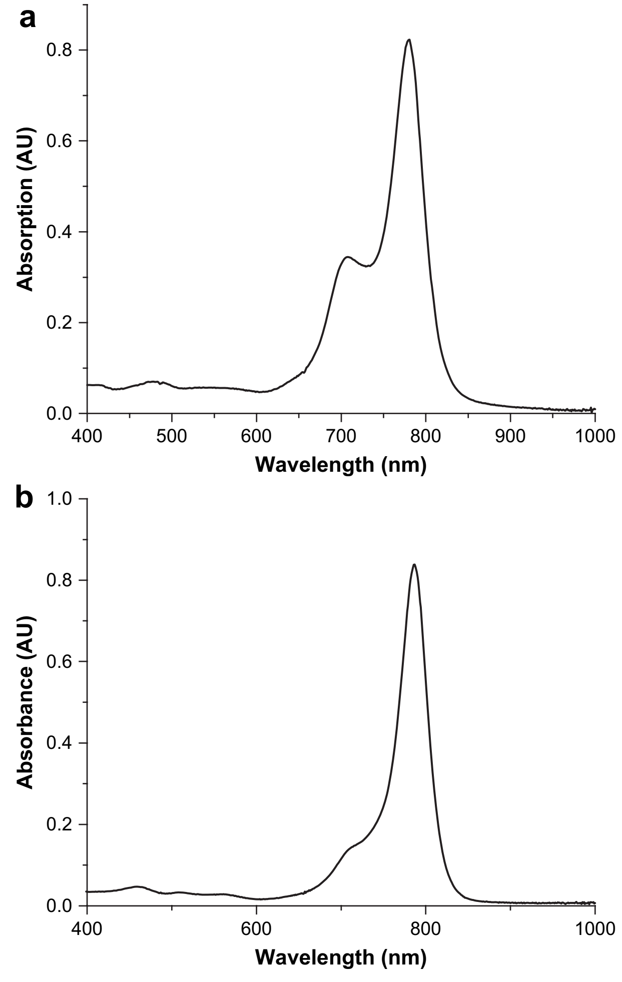


Fig. 3. (a) Absorption spectrum of **1** in water ($\lambda_{max} = 783$ nm, $\varepsilon_{max} = 2.0 \times 10^5$ $l\,mol^{-1}\,cm^{-1}$). (b) Absorption spectrum of **1** in methanol ($\lambda_{max} = 783$ nm, $\varepsilon_{max} = 2.1 \times 10^5$ $l\,mol^{-1}\,cm^{-1}$).

based on commercially available 808 nm laser systems. The 20 nm red shift in solid polymeric films as compared to λ_{max} values in solution indicates that this croconium dye possessed a strong polar character typical of a donor/acceptor dye [17]. Polymeric films of **1** having optical densities of ca. 1.0 appeared nearly colourless.

*2.3. Photostability of dye **1***

Good photostability is a critically important property that NIR dyes must have for consideration in some applications. The photostability of **1** was determined by measuring the absorption change of these samples exposed to the focused beam emanating from a slide projector. To date, most of the water-soluble near-infrared dyes having a λ_{max} in 808 nm spectroscopic region are cyanine dyes. IR 806 (Aldrich, structure shown in Fig. 5) was chosen as a benchmark for photostability study of dye **1** because its water solubility and spectral characteristics resemble those of dye **1**; it is commonly used as the active medium in NIR dye lasers and has also found use as a NIR absorbent heat generator [18]. The results indicated that only 6% and 4% of the dye **1** was bleached after 30 min irradiation in water and methanol, respectively. Under the same condition, IR 806 was completely bleached in water and 40% in methanol. When evaluated in a PVA film, **1** showed a remarkable stability, wherein the absorption intensity decreased only ca. 1% after 1 h irradiation.

3. Experimental

All chemicals were purchased from Aldrich Chemical Company. Silica gel (32–63 mm particle size) was purchased from Scientific Absorbents. Solvents were of reagent grade

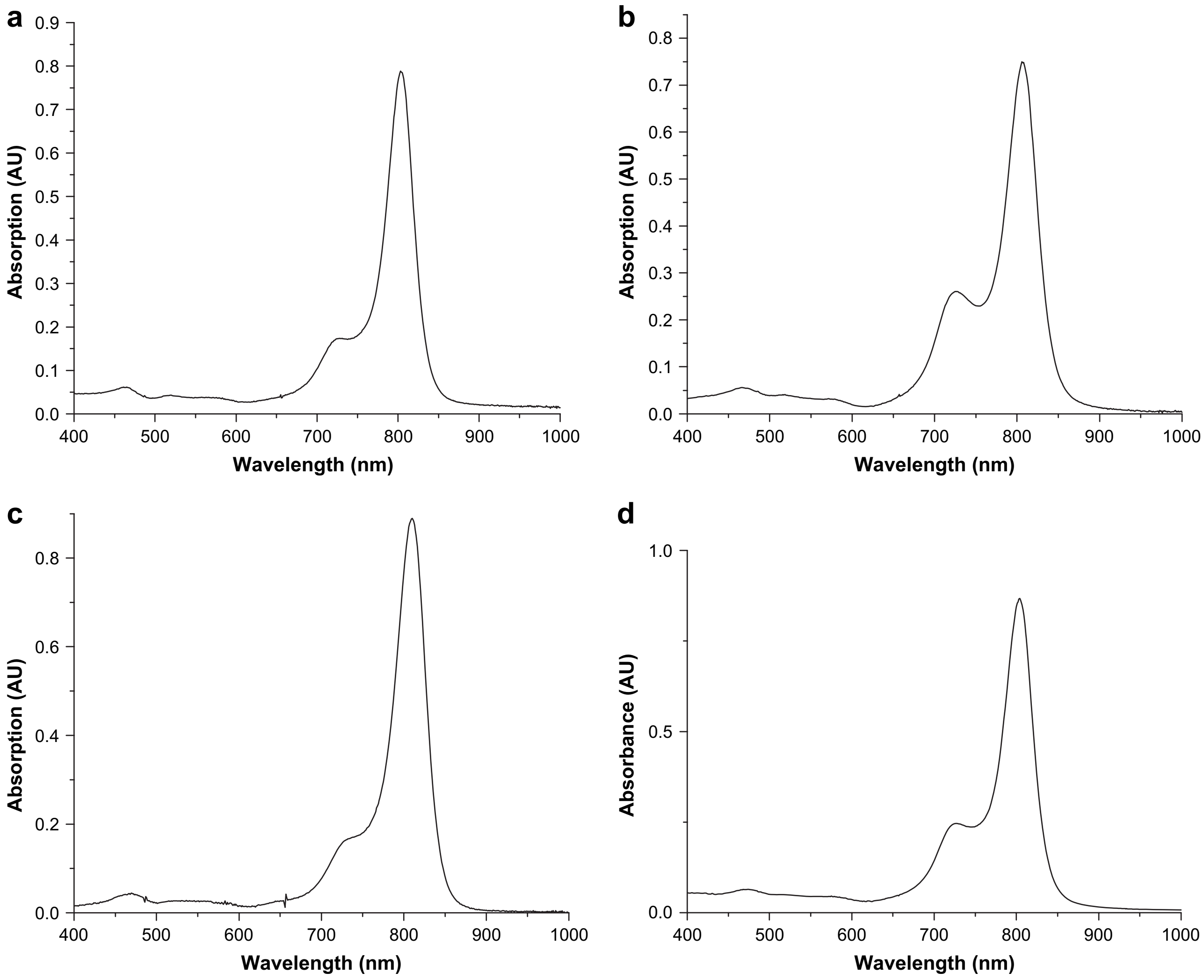


Fig. 4. Absorption spectra in (a) PAA ($\lambda_{max} = 803$ nm); (b) PAS ($\lambda_{max} = 806$ nm); (c) PSS ($\lambda_{max} = 808$ nm); (d) PVA ($\lambda_{max} = 808$ nm).

and used as received. Absorption spectra were recorded using an HP8453 spectrophotometer. ^{1}H NMR spectra were obtained using a Varian 400 MHz spectrometer using TMS as internal standard: chemical shifts are reported using standard terminology. High-resolution mass spectra (electrospray ionization (ESI)) were obtained from the Mass Spectroscopy Facility, Chemical and Chemical Biology Department, Harvard University.

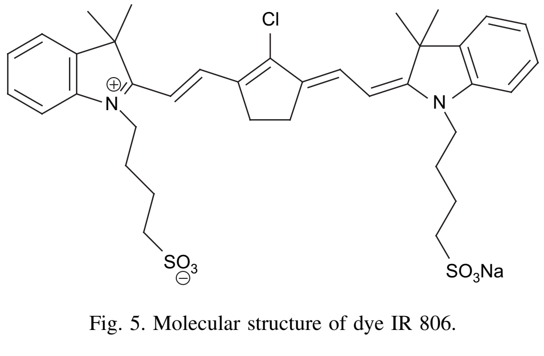


Fig. 5. Molecular structure of dye IR 806.

*3.1. Synthesis of [methyl 1-(thiophen-2-yl)piperidine-4-carboxylate] (**5**)*

A mixture of 2.32 g (20 mmol) of thiophene-2-thiol, 4.3 g (30 mmol) of methyl isonipecotate and 20 mL of toluene were placed in a 100 mL round-bottom flask equipped with a magnetic stirrer, an argon inlet tube and a water-cooled condenser. The resulting mixture was heated at reflux temperature for 2 h. After cooling to room temperature, the reaction mixture was filtered through a short silica gel column; the silica gel was washed with an additional 100 mL of ethyl acetate. The solvents from the combined filtrates were removed *in vacuo* to give a light yellow solid. The crude product was purified using medium pressure (50 psi) column chromatography with a silica gel solid phase and an eluent consisting of a 5:1 (v/v) mixture of hexane and ethyl acetate, respectively, to yield 3.5 g of pure **5** as a pale yellow solid (yield 78%). ^{1}H NMR (acetone-d_6): δ 6.74 (dd, 1 H); δ 6.65 (dd, 1H); δ 6.15 (dd, 1H); δ 3.66 (S, 3H); δ 3.49 (m, 2H); δ 2.84 (m, 2H); δ 2.06 (m, 1H); δ 1.99 (m, 2H); δ 1.80 (m, 2H).

*3.2. Synthesis of [1-(thiophen-2-yl)piperidine-4-carboxylic acid] (**6**)*

A 0.45 g (2 mmol) sample of **5** in 10 mL of 0.5 N sodium hydroxide solution was heated at reflux temperature for 1 h. After cooling to room temperature, the reaction mixture was acidified with 10% aqueous acetic acid which caused a precipitate to form. The product was isolated by filtration and, after drying under vacuum, gave 0.35 g of **6** as a white solid (yield 83%). ^{1}H NMR (CD_3OD): δ 6.72 (dd, 1 H); δ 6.64 (dd, 1H); δ 6.18 (dd, 1H); δ 3.50 (m, 2H); δ 2.77 (m, 2H); δ 2.38 (m, 1H); δ 2.00 (m, 2H); δ 1.85 (m, 2H).

*3.3. Synthesis of dye [2,5-bis[(4-carboxylic-piperidylamino)thiophenyl]-croconium] (**1**)*

Croconium dye **1** was prepared by refluxing 142 mg (1 mmol) of croconic acid and 422 mg (2 mmol) of **6** in 30 mL of 1:1 mixture of *n*-butanol and toluene for 1 h. After cooling to room temperature, the product was collected by filtration, washed with methanol and dried under vacuum to give 500 mg of pure dye **1** (yield 95%) as a black solid. *m*/*z* (ESI) $M^+ + 1$: calculated, 529.1103; found, 529.1108. ^{1}H NMR (DMSO-d_6): δ 8.50 (d, 2 H); δ 7.05 (d, 2H); δ 4.01 (m, 4H); δ 3.53 (m, 4H); δ 2.68 (m, 4H); δ 2.68 (m, 2H); δ 2.03 (m, 4H); δ 1.74 (m, 4H).

*3.4. Photostability of **1** and IR 806*

The optical density of each dye dissolved in air-saturated water or methanol was adjusted to an optical density of 1.7 in a standard 1 cm cuvette. The solution was placed six inched in front of the beam emanating from a Polaroid 610 slide projector and the optical density recorded as a function of time of irradiation. Results of these experiments are reported in Section 2. Dye **1** in a PVA matrix, optical density 2.5, coated on a glass substrate was mounted in a holder specially made to fit in the spectrophotometer in a manner that ensured that the same part of the film was analyzed each time the sample was reintroduced into the sample compartment. The mounted film was irradiated in the same manner described above for the solutions. About 1% and 2% decrease at the peak absorption wavelength was observed after one 2 h of irradiation, respectively. We were unable to prepare a comparable IR 806 film because the plastic matrix gradually became colourless during the drying phase of the sample preparation.

4. Conclusions

We successfully designed and synthesised a new water-soluble NIR absorbing croconium dye **1** which can be incorporated in a variety of anionic polymers to form plastic NIR attenuating filters. The dye exhibited a sharp absorption band peaking in the 780–808 nm spectral range, depending on its environment, has a high extinction coefficient and shows excellent photostability in a PVA matrix. While this new material may be useful for a variety of applications in its own right, it has the potential to serve as prototype upon which a new series of water-soluble, NIR chromophores might be based.

References

[1] Matsuoka M. Infrared absorbing dyes. Plenum; 1991.

[2] Fabian J, Nakazumi H, Matsuoka M. Near- infrared absorbing dyes. Chemical Reviews 1992;92(6):1197–226.

[3] Patel RC, Mott AW, Thien TV. Thermal-transfer printing material. EP56826; 1993.

[4] Kellogg RE, Ma SH. Donor element containing croconium compound for laser thermal-transfer recording. WO9301941; 1993.

[5] Yasui S, Matsuoka M, Kitao T. Syntheses and some properties of infrared-absorbing croconium and related dyes. Dyes and Pigments 1988;10(1):13–22.

[6] Sekar N. Squarilium and croconium dyes. Colourage 1999;46(4):47–50.

[7] Wang L, Peng X, Song F, Lu E, Cui J, Gao X, et al. New near-infrared indocyanines and their spectral properties in SiO_2 sol–gel. Dyes and Pigments 2004;61(2):103–7.

[8] Pham W, Medarova Z, Moore A. Synthesis and application of a water-soluble near-infrared dye for cancer detection using optical imaging. Bioconjugate Chemistry 2005;16(3):735–40.

[9] Yagi S, Hyodo Y, Matsumoto S, Takahashi N, Kono H, Nakazumi H. Synthesis of novel unsymmetrical squarylium dyes absorbing in near-infrared region. Journal of the Chemical Society, Perkin Transactions 1 2000;(4):599–603.

[10] Strekowski L, Mason CJ, Lee H, Gupta R, Sowell J, Patonay G. Synthesis of water-soluble near-infrared cyanine dyes functionalized with [(succinimido)oxy]carbonyl group. Journal of Heterocyclic Chemistry 2003;40(5):913–6.

[11] Li Y, Xie M. Synthesis of multidentate squaraines. Chinese Chemical Letters 2002;13(6):509–12.

[12] Theodoropulos S. Fluorescent squaraine dyes for labeling of biological substrates. US2002147354; 2002.

[13] Tian M, Tatsuura S, Furuki M, Sato Y, Iwasa I, Pu SL. Discovery of novel dyes with absorption maxima at 1.1 μm. Journal of the American Chemical Society 2003;125(2):348–9.

[14] Griffiths J. The functional dyes – definition, design and development. Chimia 1991;45(10):304–7.

[15] Keil D, Hartmann H, Reichardt C. Synthesis and spectroscopic characterization of new NIR absorbing (2-thienyl)- and (4-dialkylaminoaryl)-substituted croconic acid dyes. Liebigs Annalen der Chemie 1993;9:935–9.

[16] Keil D, Hartmann H, Moschny T. Synthesis and characterization of 1,3-bis(2-dialkylamino-5-thienyl)-substituted squaraines – a novel class of intensively coloured panchromatic dyes. Dyes and Pigments 1991;17(1):19–27.

[17] Hartmann H, Keil D, Moschny T. Preparation of thiophene ring-containing squaric acid dyes. DD294962; 1991.

[18] Skirtach AG, Antipov AA, Shchukin DG, Sukhorukov GB. Remote activation of capsules containing Ag nanoparticles and IR dye by laser light. Langmuir 2004;20(17):6988–92.