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New near-infrared indocyanines and their spectral properties in SiO_2 sol-gel

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Abstract

Near-infrared dyes are becoming more and more important in modern technologies. To improve the stability and spectral properties, new heptamethine 3*H*-indocyanine dyes were synthesized and tested in solvents and SiO_2 sol-gel. The results show that the dyes containing cyclohexenylene bridge and *N*-(4-carboxy) benzyl groups have better photo-stability and longer absorption wavelength than those containing linear heptamethine bridge and/or *N*-(5-carboxy)-pentanyl groups. The absorption maxima are in reverse proportion to the polarity of the solvents. When dyes doped in SiO_2 sol-gel, the absorption maxima are between their relative ones in methanol and in DMF.

Keywords: Near-infrared dyes; Cyanine dyes; Fluorescent dyes; SiO_2 sol-gel

1. Introduction

Near-infrared fluorescent organic dyes are becoming more and more important in modern technologies: high-density optical recording media, thermal writing displays, laser printer and laser filter, medical applications and dye-sensitized solar cells [1,2]. Mostly, the dyes are used in a solid-state matrix, which is gotten from a well-known sol-gel technique. Since Avnir et al. [3] embedded rhodamine 6G into silica matrix via the sol-gel in 1984, many dyes including cyanines have been used in oxide matrices [4–7]. Levy et al. incorporated near-infrared fluorescent dye HITC (1,1′,3,3′-hexamethylindotricarbocyanine iodide **1a**) into sol-gel glasses [8,9], but the stability of the dye was a problem. Patonay [10] improved the stability with chlorocyclohexenylene, instead of linear "tricarbo-" bridge between two 3*H*-indo-moieties in dye molecules. In our recent research [11], we have discovered that the photo-stability can be further improved by introducing *N*-(*4*-carboxy)benzyl group (Scheme 1) in indocyanines. In this paper, we report the syntheses of some novel heptamethine 3*H*-indocyanine (Cy7) dyes (Scheme 2) with the *N*-(4-carboxy)benzyl group (**2a**) and the spectral properties of the dyes in solutions and in SiO_2 sol-gel material derived from tetraethylorthosilicate (TEOS).

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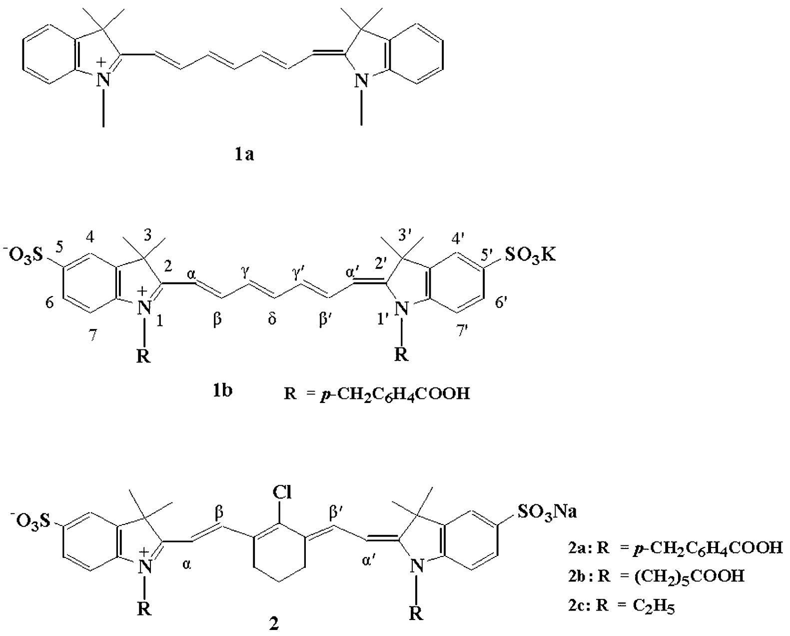
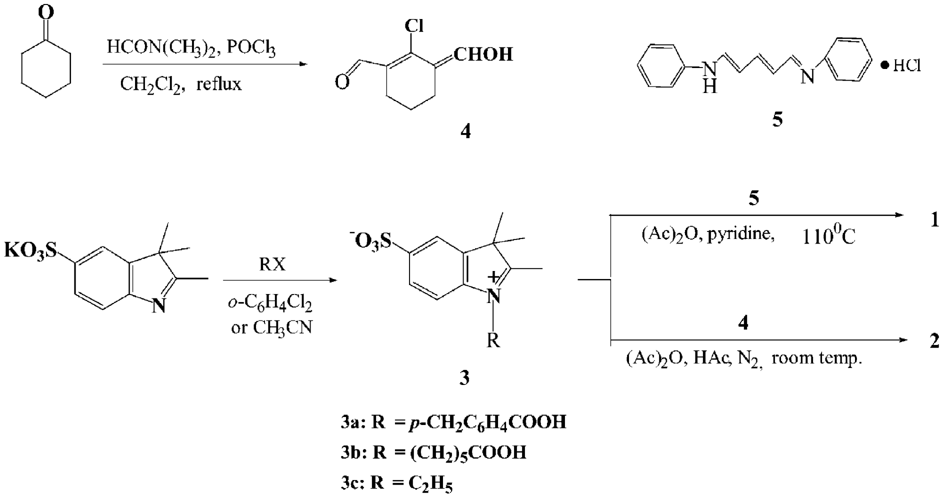


Scheme 1. Near infrared indocyanine dyes.



Scheme 2. The synthesis of near infrared indocyanines.

2. Experimental

Mass spectral determinations were made on HP1100 API-ES mass spectrometry. ^{1}H-NMR spectra were obtained in D_2O on a VARIAN 400 MHz NMR spectrometer. Fluorescence measurements were performed on a PTI-C-700 Felix and Time-Master system. The dyes were purified by conventional chromatography on C18-RP absorbent (Sinochrom C18, 40–75 μm, 100 Å, 280 m^2/g, Dalian Elite Company, China) eluting with water-methanol mixtures. Visible spectra were measured on a HP-8453 spectrophotometer. 6-Bromohexanoic acid and *N*-(5-anilino-2,4-pentadienylidene) aniline hydrochloride (**5**) were purchased from ACROS Chemical Co. (Belgium).

2.1. Synthesis of dyes ***3a–3c***

Compounds **3a–3c** were prepared by the quaternization of 2, 3, 3-trimethylindoleninium-5-sulfonate with *p*-(chloromethyl)benzoic acid, 6-bromohexanoic acid or ethyl iodide [11].

*2.2. Synthesis of 2-chloro-1-formyl-3-(hydroxymethylene)cyclohex-1-ene (**4**)*

Compound **4** was prepared from anhydrous *N*, *N*-dimethylformamide, phosphorus oxychloride and cyclohexanone in dry methylene chloride according to the procedure described in reference [12], yield: 85%; m.p. 130–131 °C; ESI-MS: $[M-H]^-$ ($m/z = 171.6$).

2.3. Synthesis of dye ***1b***

N-(5-Anilino-2, 4-pentadienylidene) aniline hydrochloride (**5**) (143 mg, 0.5 mmol) was dissolved in a mixture of acetic anhydride (4 ml) and pyridine (1 ml). **3a** (373 mg, 1.0 mmol) was added to the mixture and refluxed for 10 min, then cooled. A precipitate was obtained by the addition of diethyl ether to the cooled mixture, and then, the precipitate was dissolved in a minimum of methanol and re-precipitated with isopropanol. The product was purified by C18-RP column using methanol–water mixtures (1:1–4) to give the dye **1b** in 11% yield. ^{1}H NMR (D_2O) δ 7.91–7.83 (m, 6H, 4, 4′, Ar–H in *N*-*p*-carboxybenzyl group), 7.72–7.67 (m, 4H, β,β'-H and 6,6′-H), 7.37–7.30 (m, 1H, δ-H), 7.22–7.20 (d, 4H, Ar-H in *N*-*p*-carboxybenzyl group), 7.10–7.08 (d, 2H, $J = 8.0$ Hz 7,7′-H), 6.17–6.10 (t, 2H, γ,γ'-H), 6.07–6.04 (d, 2H, α,α'-H), 5.24 (s, 4H, CH_2 in *N*-*p*-carboxybenzyl group), 1.56 (s, 12H, $C(CH_3)_2$). ESI-MS: $[M-K]^-$ ($m/z = 806.5$), $[M-K-H]^{2-}$ ($m/z = 402.9$), $[M-K-2H+Na]^{2-}$ ($m/z = 413.9$), $[M-K-2H]^{3-}$ ($m/z = 268.3$), $[M-K-2H+2Na]^-$ ($m/z = 850.9$).

2.4. Synthesis of dye ***2***

A mixture of **3a** (3.0 mmol), **4** (347 mg, 2.0 mmol), anhydrous sodium acetate (470 mg, 5.0 mmol) and acetic anhydride (30 ml) was stirred for 6 h under the atmosphere of nitrogen at room temperature. After addition of ethyl acetate to the mixture, precipitate was obtained by filtration. The precipitate was dissolved in methanol and filtrated to remove insoluble impurities. The filtrate was concentrated in vacuum and purified by HPLC with C18-RP column using methanol–water mixtures (1:1–4) as eluting solvent to give product **2a** in yield 29%. ^{1}H NMR (D_2O): δ 8.01–7.97 (d, 2H, $J = 13.6$ Hz, β,β'-H), 7.85 (m, 6H, 4,4′-H, Ar–H in *N*-*p*-carboxybenzyl group), 7.75–7.73 (d, 2H, 6,6′-H), 7.26-7.23 (m, 6H, 7,7′-H, Ar–H in *N*-*p*-carboxybenzyl group), 6.03–5.99 (d, 2H, $J = 14.0$ Hz, α,α'-H), 5.31 (s, 4H, CH_2 in *N*-*p*-carboxybenzyl group), 2.09 (m, 4H, CH_2 in the cyclohexene), 1.51 (s, 12H, $C(CH_3)_2$), 1.38 (m, 2H, CH_2 in the cyclohexene). ESI-MS: $[M–Na]^-$ ($m/z = 881.8$), $[M-Na-H]^{2-}$ ($m/z = 440.3$), $[M-Na-2H]^{3-}$ ($m/z = 293.1$).

The synthesis of **2b** and **2c** was similar to the procedure described by Patoney [10].

2.5. Preparation of dye-doped SiO_2 gel

Tetraethylorthosilicate (TEOS), ethanol, distilled water (2:4:1 mol ratio) and hydrogen chloride were mixed at room temperature, hydrolyzing for 1 h to obtain solution A. The solution of an indocyanine dye in water was added into the solution A to form a transparent solution B. After adjusting the pH to 8 with diluted ammonia, the solution B was poured into a container and sealed for several weeks at room temperature, forming homogeneous transparent dye-doped SiO_2 gel slices. The detailed procedure was similar to that described in Ref. [13].

3. Results and discussion

Cyanine dyes are always synthesized by the condensation reaction between a heterocyclic base containing an activated methyl group and an unsaturated bisaldehyde or its equivalent, usually as schiff base in the presence of a catalyst such as sodium acetate. In the synthesis of heptamethine indocyanine dyes (or indotricarbocyanine dyes, Cy7), *N*-(5-anilino-2,4-pentadienylidene)aniline **5**, was traditionally used as the schiff base, forming near infrared dyes such as **1a**. Sulfo-groups are introduced to the dyes to increase the solubility in water, *N*-(5-carboxyl)pentanyl is used to link amino group in bio-molecules or hydroxyl group on nano-TiO_2. The disadvantage of this kind of Cy7 dyes is their poor photo- and chemical stability, but it can be improved by the substitution of linear bridge in **1a** with cyclohexenylene bridge (such as in **2b**) in the methine chain [10]. In contrast, **2a** has an *N*-(4-carboxyl)benzyl group instead of *N*-(5-carboxyl)pentanyl group (**2b**) on the *N* atom of 3,3-dimethyl-3H-indole ring. It is hoped to have better properties like trimethine (Cy3) dyes [11].

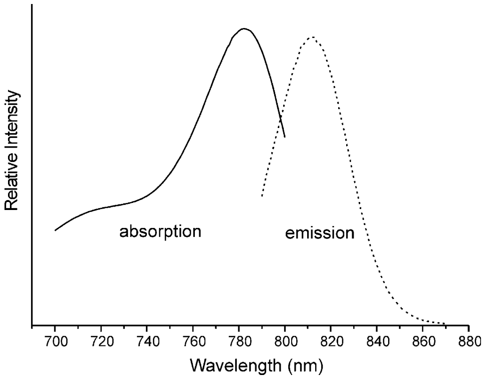


Fig. 1. The absorption and emission spectra of **2a**.

Table 1
Spectral data of Cy7 in solvents

Dye	Solvent	λ_{max}^{ab} (nm)	λ_{max}^{em} (nm)	Stock's shift $\Delta\lambda$ (nm)	ε (l $mol^{-1}\cdot cm^{-1}$)
1b	Water	749	787	38	170,020
	Methanol	755	790	35	
	DMF	767	803	36	
2a	Water	784	805	19	104,070
	Methanol	795	818	23	
	DMF	809	820	11	
2b	Water	783	812	29	170,810
	Methanol	791	825	34	
	DMF	804	821	17	
2c	Water	778	809	31	220,020
	Methanol	785	815	30	
	DMF	800	819	19	

3.1. Spectra of Cy7 dyes in solvents

Absorption and emission spectra of the dyes synthesized in this paper are similar and typically shown in Fig. 1. The maxima wavelength (see Table 1) of the absorption (λ_{max}^{ab}) and emission (λ_{max}^{em}) of the dyes, however, are different. Three dyes with cyclohexenylene group (**2a** 784, **2b** 783 and **2c** 779 nm in water) have a 30–35 nm red-shift compared with the linear tricarbocyanine (**1b**, 749 nm in water). The Stock's shifts are in the range of 11–38 nm.

The λ_{max} changed with the solvent polarity: the λ_{max} becomes shorter with the polarity of the solvent becomes more polar. For example, λ_{max}^{ab} of **2a** appeared at 784 in water, 795 in methanol and 809 nm in DMF. This suggests that the molecules have highly dipolar ground states and relatively low polar excited states.

3.2. Spectra of Cy7 dyes in sol-gel

Table 2 shows the λ_{max}^{ab} and λ_{max}^{em} of dye-SiO_2 sol-gel. There are red-shifts in λ_{max}^{ab} compared with that in water, but blue-shifts compared with in DMF. More intensive emissions are observed than in the solvents. It might be attributed to the quantum size confinement effect of nanometer microcapsule in SiO_2 gel networks. It seems that the polarity of the microenvironment of the dyes in SiO_2 gel material is between methanol and DMF, if the decisive factor of the shift of λ_{max}^{ab} is the polarity of environment.

Table 2
Spectral data of the indocyanine dyes in SiO_2 sol-gel

Dye	1b	2a	2b	2c
λ_{max}^{ab} (nm)	760	794	793	789
λ_{max}^{em} (nm)	788	821	811	808

3.3. Photostability

The photo-stability of **1b**, **2a**, **2b** in water was tested under the irradiation of a 40 W iodine-tungsten lamp. The sample was placed 125 cm away in a glass holder maintaining temperature at 25 °C with circulating water. After irradiation for 75 h, the absorption intensity of **1b** decreased 12%, **2a** 4% and **2b**, 7%, respectively. The dye **2a** was the most stable. Similar photo-stability order was observed in dye-doped SiO_2 gel slices. It is known that degradation is because of the photo-oxidation of the dyes by singlet oxygen, superoxides, peroxides or other active oxidative species. With the change of *N*-(5-carboxy)pentanyl group on the nitrogen atom in 3*H*-indo-ring in **2b** into *N*-(4-carboxy)benzyl in **2a**, the steric-hindrance in molecule must increase. This might help **2a** to prevent from the attack of the active oxidative species. The rigid cyclohexenylene in the molecule of **2a** and **2b** lets the dyes more photo-stable than linear poly-methine in **1b**.

4. Conclusion

The near infrared heptamethine indocyanine dyes containing cyclohexenylene bridge and *N*-*p*-carboxybenzyl group have better photo-stability and longer absorption wavelength than the dyes containing linear heptamethine bridge and/or *N*-(5-carboxy)pentanyl group. The absorption maxima are in reverse proportion to the polarity of the solvents. When doped in SiO_2 sol-gel, the absorption maxima are between their relative ones in methanol and in DMF.

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