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Syntheses and nonlinear absorption of novel unsymmetrical cyanines

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Dedicated to the memory of Professor M. Matsuoka

Abstract

A new synthetic strategy for the generation of methine cyanine dyes with asymmetrical structures has been developed based on a modified Vilsmeier reaction and the condensation reaction of indoline derivatives with organic pyridinium iodide or 4-diphenylamino-benzaldehyde. The nonlinear absorption of some cyanines has been measured using the Z-scan technique.

Keywords: Unsymmetrical cyanine dyes; Indoline derivatives; Triphenylamine; Nonlinear absorption

1. Introduction

Methine cyanine dyes have attracted much attention because of their potential application in organic functional materials [1–5]. In recent years, they have been used extensively as optical recording materials [6–8]; cyanines with nonlinear optical properties have also been studied [9–12].

Cyanine dyes with short methine chains are readily soluble in common organic solvents such as ethanol and acetone. However, the convenient condensation of these short chains still needs to be developed. The majority of methine cyanines reported for use in optical recording materials belong to the class of symmetrical cyanine dyes, whereas unsymmetrical methine cyanines have superior optical properties and alcohol solubility [13]. During investigations into the syntheses of methine cyanines, we were intrigued at the possibility of accessing the methine chain system via the expeditious condensation reaction of (1,3,3-trimethyl-1,3-dihydro-indol-2-ylidene)-acetaldehyde with methylpyridinium iodide. This route, if realized, would allow access to methine cyanine dyes with asymmetrical structures. In addition, we found that organic pyridinium salts play an important role in the field of nonlinear, optical materials due to their high hyperpolarizability and particular chemical structure [14–17].

It was therefore considered worthwhile to try if, incorporated with organic pyridinium salts, the target cyanine compounds would have nonlinear

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optical properties. In this paper, we described the synthetic approaches and spectral properties of these novel unsymmetrical cyanine dyes with good optical properties.

2. Syntheses

The approaches that have been examined are outlined below and have relied on the condensation reaction of indoline derivatives with substitutional pyridinium iodide or 4-diphenylaminobenzaldehyde.

2.1. Trimethine cyanine dyes

The approach relied on a modified Vilsmeier reaction developed by Fritz [18]. Slight modification were introduced to make this procedure more efficient. For initial trial experiments, it appeared that in the basification procedure, saturated sodium hydroxide solution is required. Crude product **2a** precipitated from the solution after the solution was boiled and then cooled for 30 min. It is noteworthy that the use of diethyl ether for extraction is not necessary. With these modifications the trimethine cyanines **5a**–**5d** were obtained in 60–81% yield (Scheme 1).

Condensations of the indoline derivatives with substituted pyridinium iodides were achieved very effectively in methanol using piperidine as catalyst [19,20]. The dyes **5b** and **5d** are much more soluble in methanol than **5a** and **5c**, so they were treated with hot ethyl acetate to induce precipatation.

2.2. Dimethine cyanine dye

Another kind of methine cyanine **6** was obtained from condensation reaction of **3** with methylpyridinium iodide (Scheme 2). The intermediate compound **3** was prepared from 2-methyl-3 *H*-benzo[e]indole, which can be easily synthesized based on our patent [21]. Synthesis of 2-methyl-3 *H*-benzo[e]indole have been reported [22]. But the reaction reagents are expensive to gain and the requirements of those reaction conditions are strict. In the patent procedure we designed, the reaction reagents were cheap, non-hazardous to human and the condition of the reaction was easy to control.

2.3. Hemicyanine dyes

The direct conversation of triphenylamine to 4-diphenylamino-benzaldehyde has previously been descried [23]. Compound **1a** and **1b** reacted smoothly with **7** at reflux temperature without piperidine to afford **8a–8b** in high yield (Scheme 3).

3. Experimental

3.1. General methods and materials

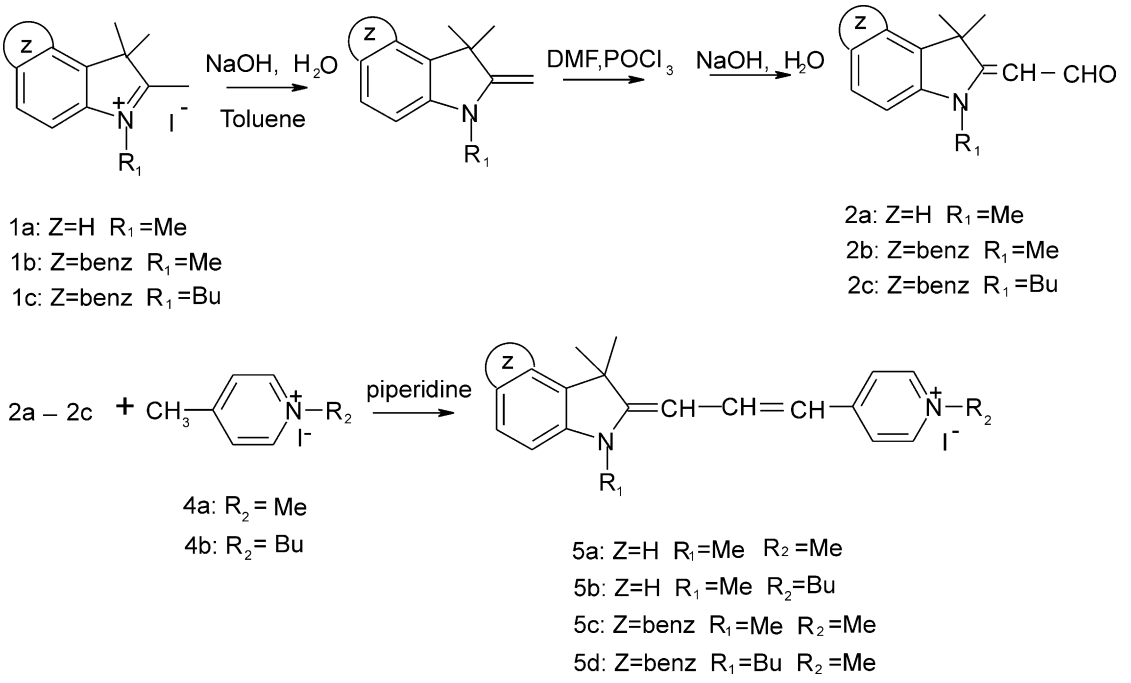
^{1}H NMR spectra were recorded on a Brücker DRX instrument at 300 and 500 MHz, and EI mass spectra (70 ev) were recorded using a Hitachi-80 spectrometer. UV/visible absorption spectra were recorded on a Shimadzu UV-260 instrument and an elementar vario EL III (made in Germany) analyzer was used for element analysis. All chemicals except triphenylamine were purchased from commercial suppliers and used without further purification. Triphenylamine was purchased from Acros Organics.

3.2. 1,2,3,3-Tetramethyl-3H-indolinium iodide (*1a*)

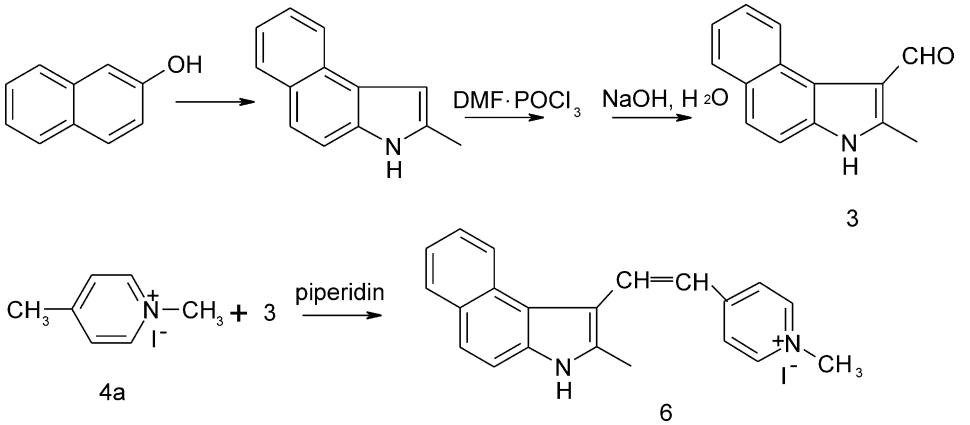
A mixture of 3.7 g (23.3 mmol) 2,3,3-trimethyl-3H-indole and 3.63 g (25.5 mmol) methyl iodide was refluxed in 15 ml acetonitrile for 2 h. Upon cooling to room temperature compound **1a** precipitated and was filtered off and washed with petroleum ether to give 5.1 g pink crystals (73%). mp 162 °C.

3.3. 1,1,2,3-Tetramethyl-1H-benzo[e]indolinium iodide (*1b*)

The preparation of **1b** employed the procedure described earlier for **1a**. After cooling to room temperature and filtering, the product was washed with cold ethanol, giving a white powder, (91%). mp 199 °C.



Scheme 1. Synthetic procedure of trimethine cyanine dyes.



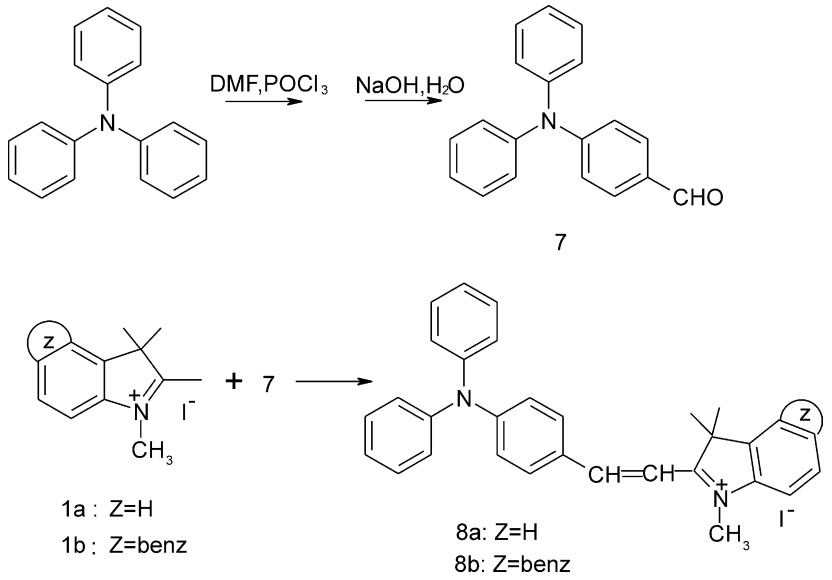
Scheme 2. Synthetic procedure of dimethine cyanine dyes.

*3.4. 3-Butyl-1,1,2-trimethyl-1H-benzo[e]indolinium iodide (**1c**)*

Five grams (24 mmol) 2,3,3-trimethyl-3 *H*-benzoindole and 4.4 g butyl iodide were refluxed in 20 ml *n*-butyl alcohol for 20 h. After cooling to room temperature the reaction mixture was poured into ethyl acetate and the precipitate was filtered to afford 5.4 g (57.3%) **1c** as pale yellow crystals, mp 159–161 °C.

*3.5. (1,3,3-Trimethyl-1,3-dihydro-indol-2-ylidene)-acetaldehyde (**2a**)*

2a was synthesized by a modification of a known procedure reported earlier [18]. $POCl_3$ (7.5 ml) was added dropwise to 24 ml cold DMF under stirring and isolated from water vapor, and the temperature was kept below 10 °C. After adding a mixture of 12.98 g (73.03 mmol) 1,3,3-trimethyl-2-



Scheme 3. Synthetic procedure of hemicyanine dyes.

methylen-indoline and 6 ml DMF to the reaction vessel at this temperature, the reaction solution was heated at 35 °C for 45 min. Then the reaction solution was poured into ice water and the mixture was basified to pH 10.0 by addition of saturated sodium hydroxide solution. The resulting solution was heated to boiling for a few minutes and cooled to room temperature. The product **2a** precipitated and was filtered off and washed with water, giving 9 g (60%) red crystals; mp 116 °C.

*3.6. (1,1,3-Trimethyl-1,3-dihydro-benzo[e]indol-2-ylidene)-acetaldehyde (**2b**)*

A mixture of 10 g (28.5 mmol) **1b** and 1.5 g (37.5 mmol) sodium hydroxide was stirred vigorously at room temperature in 75 ml water and then extracted with 50 ml toluene. The organic phase was dried ($MgSO_4$) and then concentrated under reduced pressure. The product was then isolated using the method described for **2a** and was recrystallized from ethyl acetate to give **2b** as white flakes (4.9 g; 66%); mp 159–160 °C. ^{1}H NMR($CDCl_3$): δ (ppm) 1.97 (s, 6H, CH_3), 3.43 (s, 3H, N–CH_3), 5.42 (d, 1H, CH, J = 8.89 Hz), 7.21 (d, 1H, J = 8.72 Hz), 7.38 (t, 1H), 7.55 (t, 1H), 7.86 (d, 2H, J = 8.72 Hz), 8.08 (d, 1H, J = 8.56 Hz), 10.13 (d, 1H, J = 8.84 Hz).

*3.7. (3-Butyl-1,1-dimethyl-1,3-dihydro-benzo[e]indol-2-ylidene)-acetaldehyde (**2c**)*

A mixture of 15.5 g (39.4 mmol) **1c** and 2.5 g (62.5 mmol) sodium hydroxide were stirred vigorously at room temperature in 60 ml water and then extracted with 18 ml toluene. Solvent removal and vacuum distillation of the oily product gave 9.4 g of a yellow green oil. This was purified using the route described for **2a** and recrystallized from ethyl acetate giving **2c** (8.9 g; 81%) as a sandy beige crystals; mp 114 °C. ^{1}H NMR($CDCl_3$): δ (ppm) 0.98 (t, 3H, CH_3), 1.47 (m, 2H, CH_2), 1.72 (m, 2H, CH_2), 1.97 (s, 6H, CH_3), 3.78 (t, 2H, N–CH_2), 5.46 (d, 1H, CH), 7.18 (d, 1H), 7.37 (t, 1H), 7.53 (t, 1H), 7.84 (d, 1H), 7.88 (d, 1H), 8.07 (d, 1H), 10.14 (d, 1H).

*3.8. 2-Methyl-3H-benzo[e]indole-1-carbaldehyde (**3**)*

2-Methyl-3*H*-benzo[e]indole was converted to (**3**) by a similar reaction sequenceto that used for preparing **2a.** Purification of the crude (**3**) by

chromatography on silica gel (ethyl acetate: petroleum ether = 1:1) afforded 1.5 g compound **3** as pale yellow flakes, mp 289 °C.

3.9. 1,4-Dimethyl-pyridinium iodide (*4a*)

Compound **4a** was prepared from a known method [20]. Equimolar amount of 4-methyl pyridine and methyl iodide were combined with methanol and refluxed for 2 h to produce a solution of **4a**. Excess methanol was removed under reduced pressure to give 95.7% yield light yellow crystals.

3.10. 1-Butyl-4-methyl-pyridinium iodide (*4b*)

In a similar fashion to the preparation of **4a**, **4b** was prepared as a brown oil from 4-methyl pyridine in 98.2% yield.

3.11. 1,3,3-Trimethyl-2-[3-(1-methyl-pyridin-4-yl)-allylidene]-2,3-dihydro-1H-indolinium iodide (*5a*)

A solution of 3 g (6.5mmol) **2a**, 1.52 g (6.5 mmol) **4a** and 0.7 ml piperidine in 7 ml methanol was refluxed for 3 h. The solution was cooled to room temperature and compound **5a** was isolated by filtration. Purification by recrystallization from methanol gave **5a** (2.1 g; 77.3%) as green purple crystals; mp > 300 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.62 (s, 6H, CH_3), 3.31 (s, 3H, N–CH_3), 4.07 (s, 3H, N–CH_3), 5.767 (d, 1H, CH, J = 12.43 Hz), 6.32 (d, 1H, CH, J = 14.39 Hz), 6.97 (t, 1H), 7.05 (d, 1H, J = 7.87 Hz), 7.25 (t, 1H), 7.42 (d, 1H, J = 6.83 Hz), 7.83 (d, 2H, J = 6.86 Hz), 7.99 (t, 1H, CH), 8.37 (d, 2H, J = 7.01 Hz). MS (EI, %): m/z 291(1), 277(6), 276(27), 261(33), 245(6), 169(15), 159(17), 158(28), 142(100), 127 (19). Element anal. calc. for $C_{20}H_{23}N_2I$ (417.9): C, 57.43; H, 5.50; N, 6.70. Found: C, 57.03; H, 5.52; N, 6.61%.

3.12. 2-[3-(1-Butyl-pyridin-4-yl)-allylidene]- 1,3,3-trimethyl-2,3-dihydro-1H-indolinium iodide (*5b*)

A mixture of 1 g (5 mmol) **2a**, 1.4 g (5 mmol) **4b** and 0.7 ml piperidine in 8 ml methanol was refluxed for 3 h. After removing the solvent under reduced pressure, 20 ml ethyl acetate was added and the mixture solution was refluxed for a few minutes. The dye **5b** precipitated from the hot solution and was isolated by filtration. Recrystallization from ethyl acetate/ethanol (8:1) gave 5b (2 g; 87% yield) as blue crystals; mp 164–167 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.97 (t, 3H, CH_3), 1.42 (m, 2H, CH_2), 1.68 (s, 6H, CH_3), 1.94 (m, 2H, CH_2), 3.32 (s, 3H, N–CH_3), 4.53 (t, 2H, N–CH_2), 5.68 (d, 1H, CH, J = 12.46 Hz), 6.17 (d, 1H, CH, J = 14.28 Hz), 6.84 (d, 1H, J = 8.11 Hz), 7.25 (t, 1H), 7.27 (t, 1H), 7.53 (d, 2H, J = 6.1 Hz), 7.97 (t, 1H), 8.58 (d, 2H, J = 6.23 Hz). MS (ESI, %): m/z 333(100), 269(7), 150(5). Element anal. calc. for $C_{23}H_{29}N_2I$ (459.9): C, 60.01; H, 6.30; N, 6.09. Found: C, 59.60; H, 6.25; N, 6.01%.

3.13. 1,1,3–Trimethyl-2-[3-(1-methyl-pyridin-4-yl)-allylidene]-2,3-dihydro-1H-benzo[e]indolinium iodide (*5c*)

Dye **5c** was obtained from the condensation reaction of **2b** and **4a** following the procedure described for **5a**. Recrystallization from methanol gave **5c** (75.6% yield) as golden green crystals; mp 178–181 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.99 (s, 6H, CH_3), 3.43 (s, 3H, N–CH_3), 4.32 (s, 3H, N–CH_3), 5.71 (d, 1H, CH, J = 12.57 Hz), 6.18 (d, 1H, CH, J = 14.17 Hz), 7.18 (d, 2H, J = 8.71 Hz), 7.38 (t, 1H), 7.5 (d, 2H, J = 6.7 Hz), 7.58 (t, 1H), 7.87 (m, 2H), 8.1 (m, 2H), 8.53 (d, 2H, J = 6.68 Hz). MS (EI, %): m/z 326(16), 311(19), 209(37), 194(11), 152(4), 142(100), 127(21). Element anal. calc. for $C_{24}H_{25}N_2I$ (467.9): C, 61.55; H, 5.34; N, 5.98. Found: C, 60.27; H, 5.85; N, 5.34%.

3.14. 3-Butyl-1,1-dimethyl-2-[3-(1-meyhyl-pyridin-4-yl)-allylidene]-2.3-dihydro-1H-benzo[e]indolinium iodide (*5d*)

Following the general procedure described for **5b**, dye **5d** was obtained from the condensation reaction of **2c** and **4a**. The product was purified by recrystallization from ethyl acetate/ethanol (8:1) to give **5d** (73% yield) as golden green crystals; mp 210–212 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.03 (t, 3H, CH_3), 1.48 (m, 2H, CH_2), 1.76 (m, 2H, CH_2), 1.98 (s, 6H, CH_3), 3.86 (t, 2H, CH_2), 4.30 (s, 3H, N–CH_3), 5.72 (d, 1H, CH, J = 12.61 Hz), 6.14 (d,

1H, CH, $J=14.10$ Hz), 7.16 (d, 1H, $J=8.77$ Hz), 7.39 (t, 1H), 7.47 (d, 2H, $J=6.31$ Hz), 7.57 (t, 1H), 7.85 (m, 2H), 8.1 (m, 2H), 8.47 (d, 2H, $J=6.52$ Hz). MS (EI, %): *m/z* 369(7), 368(23), 353(26), 264(8), 251(39), 250(8), 209(14), 208(41), 194(18), 152(8), 142(100), 127(27), 118(4). Element anal. calc. for $C_{27}H_{31}N_2I$ (509.9): C, 63.54; H, 6.07; N, 5.49. Found: C, 62.59; H, 5.97; N, 5.37%.

*3.15. (2-Methyl-1-[2-(1-methyl-pyridin-4-yl)-vinyl]-3H-benzo[e]indole (**6**)*

A mixture of 0.3 g (1.44 mmol) **3**, 0.34 g (1.44 mmol) **4a** and 0.3 ml piperidine was refluxed in 6 ml methanol for 10 h. The product **6** precipitated from solution after cooling to room temperature. This was filtered off and recrystallized from methanol to give 6 as brown crystals. The yield was 16.3%; mp > 300 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.69 (s, 3H, CH_3), 4.24 (s, 3H, N–CH_3), 6.89 (d, 1H, CH, $J=15.95$ Hz), 7.43 (t, 1H), 7.57 (m, 2H), 7.64 (d, 1H, $J=8.73$ Hz), 7.96 (d, 1H, $J=7.89$ Hz), 8.27 (d, 2H, $J=6.75$ Hz), 8.48 (d, 1H, $J=8.36$ Hz), 8.64 (d, 1H, $J=15.99$ Hz), 8.75 (d, 2H, $J=6.7$ Hz). MS (EI, %): *m/z* 226(3), 208(5), 182(15), 181(100), 180(91), 153(7), 152(14), 143(46), 116(9), 115(30).

*3.16. Diphenyl-{4-[2-(1,3,3-trimethyl-3H-indolinium-2-yl)-vinyl]-phenyl}-amine iodide (**8a**)*

A mixture of 1 g (3.66 mmol) **7** and 1.2 (4 mmol) **1a** was refluxed in 10 ml ethanol for 2 h. The resultant precipitate was collected by filtration to afford **8a** (1.8g; 88.7%) as a red solid. Recrystallization from methanol gave green leaflets; mp 176 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.81 (s, 6H, CH_3), 4.33 (s, 3H, N–CH_3), 7.01 (d, 1H, CH, $J=8.8$ Hz), 7.01 (d, 2H, $J=8.8$ Hz), 7.2 (d, 6H, $J=17.27$ Hz), 7.37 (t, 4H), 7.55 (m, 4H), 8.03 (m, 2H). MS (EI, %): *m/z* 173(27), 158(100), 128(35), 127(16), 115(6).

*3.17. Diphenyl-{4-[2-(1,3,3-trimethyl-1H-benzo[e]indolinum-2yl)-vinyl]-phenyl}-amine iodide (**8b**)*

Follow the same reaction route used for **8a**, **8b** was obtained from **7** and **1b**. The yield of crude product was 89%. Recrystallization from methanol gave **8b** as pink flakes; mp 198–201 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 2.05 (s, 6H, CH_3), 4.45 (s, 3H, CH_3), 7.03 (d, 1H, CH, $J=8.73$ Hz), 7.23 (m, 6H), 7.38 (t, 4H), 7.61 (m, 2H), 7.7 (m, 2H), 8.05 (m, 4H), 8.18 (m, 2H). MS (EI, %): *m/z* 479(3), 478(8), 465(26), 464(73), 463(25), 462(14), 448(10), 447(4), 282(3), 281(10), 271(15), 285(9), 209(40), 208(54), 194(15), 152(8), 142(100), 127(34). Element anal. calc. for $C_{35}H_{31}N_2I$ (606.52): C, 69.31; H, 5.15; N, 4.62. Found: C, 69.22; H, 5.08; N, 4.53%.

4. Result and discussion

4.1. Absorption and fluorescence properties

All of the dyes prepared except **6** and **8a** displayed good solubility (>4 mg/ml) in common organic solvents; dyes **5a–5d** had slight solubility in water. The absorption and fluorescence spectral data recorded on these cyanine dyes in absolute ethanol are listed in Table 1. Dyes **5a–5d** show intense and broad absorption (in the visible region) with high extinction coefficients in solution as shown in Fig. 1. In chloroform their absorption maxims and extinction coefficients depend on whether or not the indole ring is annelated. Dyes **5c** and **5d** absorbed at longer wavelength than **5a** and **5b**. These bathochromic effects could be attributed to the presence of phenyl groups on the indole rings.

Benzannelation of the indole ring increased the polarity of dye **8b**, and so this dye was much more

Table 1
Absorption and fluorescence spectra data of the dyes in absolute ethanol (**5a–5d**: 1.0×10^{-5} M; **6**, **8a**: 1.0×10^{-4} M)

Compound	Absorption		Fluorescence	
	λ_{max} (nm)	log ε	λ_{ex} (nm)	λ_{em} (nm)
5a	525.6	4.880	525.6	588.1
5b	529.8	5.052	529.8	617.0
5c	545.8	4.920	545.8	612.4
5d	548.8	4.872	548.8	614.3
6	463.6	2.778	463.6	545.5
8a	540.6	3.029	540.6	571.1
8b	548.0	3.663	548.0	579.2

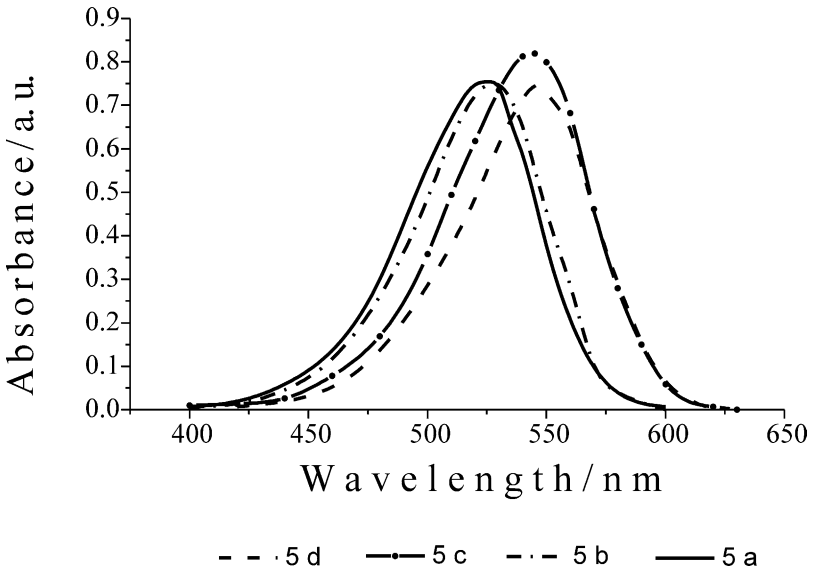


Fig. 1. Absorption spectra of dyes **5a**–**5d** in ethanol.

soluble than **8a** in ethanol. The absorption of **8b** is higher than **8a** and this can be seen clearly in Fig. 2.

4.2. Nonlinear absorptionproperties of dyes *5a–5d*

The Z-scan method is a simple and sensitive technique developed in recent years to measure the nonlinear refraction (closed aperture) and nonlinear absorption (open aperture) [24] of materials. In this work, we were mainly concerned with nonlinear absorption, and therefore used an open aperture Z-scan system (Fig. 3) to measure the optical nonlinear characteristics. By moving the sample along the Z axis through the focus ($z = 0$), we can obtain the intensity-dependent transmittance (D_2/D_1).

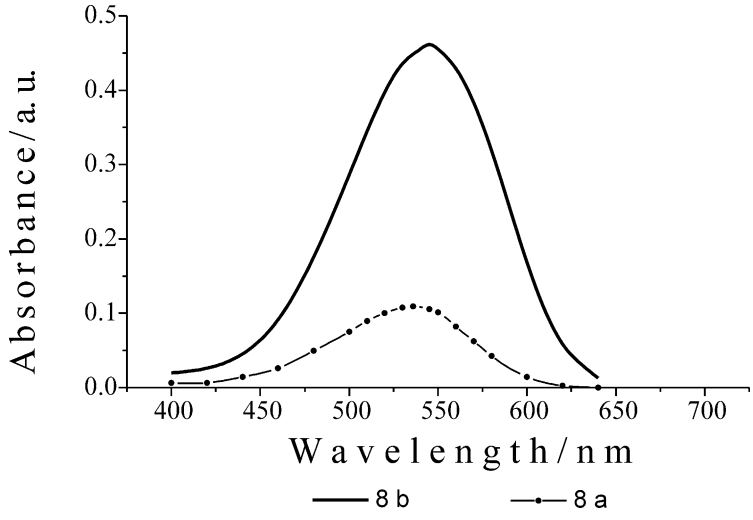


Fig. 2. Absorption spectra of dyes **8a, 8b** in ethanol.

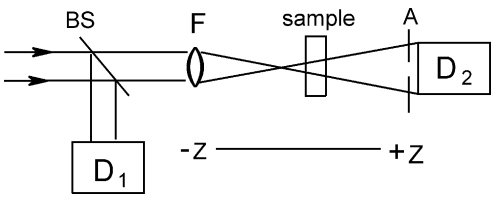


Fig. 3. Z-scan system for measuring nonlinear absorption, where D_1, D_2 are diodes, F is a lens and BS a beam splitter.

The expressions for the absorption coefficient of the material which has nonlinear absorption is

$$\alpha_T = \alpha + \beta I \quad (1)$$

where α is the linear absorption coefficient and β is the nonlinear absorption coefficient. When β is not large, it can be expressed as:

$$\beta = 2^{3/2}[1 - T(z=0)]/I_0 L_{\text{eff}} \quad (2)$$

where $T(z)$ is the Normalized transmittance, I_0 is the on-axis instantaneous intensity of the laser beam at the focus ($z=0$). $L_{\text{eff}}=[1-\exp(-\alpha L)]/\alpha$ is the effective thickness of the sample and L the sample thickness.

A Q-switched, injection-seeded Nd:YAG laser operating with a frequency of 10 Hz was used to perform the Z-scan. The frequency-doubled laser had an output wavelength of 532 nm and the pulse width was 10 ns. A positive lens ($f=21$ cm) was used to focus the laser. The samples were dissolved in methanol to make transparent solutions (2.0×10^{-5} mol/l). The normalized transmittances of dyes **5a**–**5d** are shown in Figs. 4–7 and the

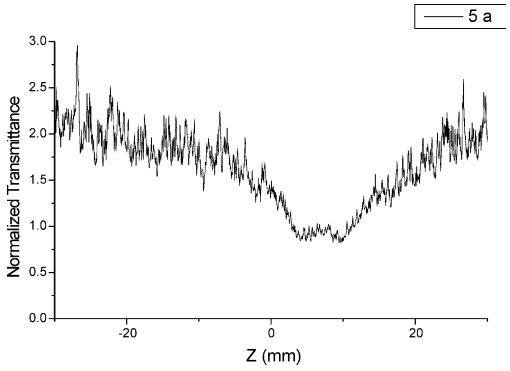


Fig. 4. Normalized transmittance of dye **5a**.

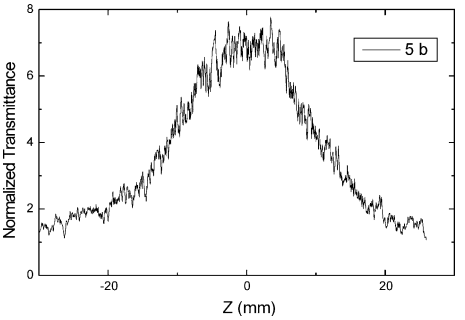


Fig. 5. Normalized transmittance of dye **5b**.

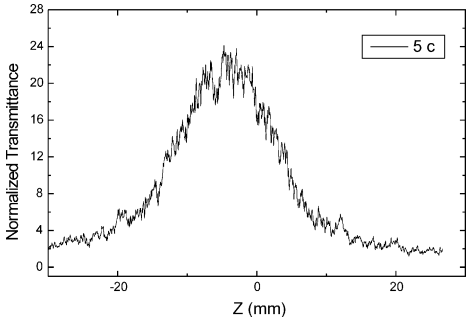


Fig. 6. Normalized transmittance of dye **5c**.

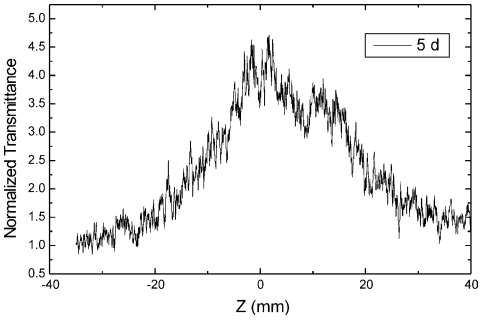


Fig. 7. Normalized transmittance of dye **5d**.

Table 2
Nonlinear absorption coefficient values of β

Compound	β (cm/mw)
5a	3.77×10^{-11}
5b	1.10×10^{-10}
5c	3.51×10^{-10}
5d	5.12×10^{-11}

absorption coefficient values of β which can be deduced from expressions (2) are listed in Table 2.

It can be seen in the figures that the normalized transmittance plotted as function of the sample position (z) measured with open aperture is symmetrical with respect to $z=0$. Dyes **5b** and **5c** have strong nonlinear saturation absorption, while dye **5a** has reverse saturated absorption. From the nonlinear absorption spectra with relation to their structures, it can be concluded that the system with highly π-conjugated structure, or the substitute attached to the system has high electron cloud density will have strong nonlinear absorption.

5. Conclusions

The synthesis of several novel methine cyanine dyes with unsymmetrical structures involving a new synthetic strategy has been described. Measurement of their nonlinear absorption spectra using the Z-scan technique showed that methine cyanines **5a–5d** which have highly π-conjugated structures have good nonlinear absorption properties. These unsymmetrical cyanine dyes are promising candidates for application in nonlinear optics and DVD-R optical recording disc.

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