



SYNTHESIS AND CHARACTERIZATION OF HEPTAMETHINE NIR ABSORBING CYANINE DYE COMPOUNDS**

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In this work, new heptamethine near infrared (NIR) absorbing cyanine dye compounds were designed and synthesized by the reaction of bis-aldehyde, (1-formyl-3-hydroxymethylene)cyclohexene with benzindole derivatives. These dyes contained different *N*-alkyl chain substituents and the resulting characteristics of dye compounds were studied. With considering the useful NIR absorbing properties, these dye compounds are greatly enjoyed the uses in optical recordings, optical storages, biological fluorescent stains and probe sensors. The prepared six types of new heptamethine NIR absorbing cyanine dye compounds were analyzed and the corresponding spectroscopic properties were determined.

INTRODUCTION

Cyanine dyes have been greatly attracted as photo-sensitizers for silver halide photography¹ and in correspondence with the developments of technology in the optical data storage and bio-probe sensor industry, the new potential interests toward cyanine dye compounds have been extensively increased.¹⁻⁵ Application areas of NIR absorbing cyanine dyes can be more broaden to optical recording, thermal writing display, laser printer, laser filter, infrared photography, and medical application. Among various chromophore systems, cyanine dye structures are allowed to provide the simplest way of obtaining NIR absorbing optical properties.⁵⁻⁷ To determine absorption wavelength, solubility of cyanine dye compounds in organic solvents is important and strongly affected by the nature of *N*-alkyl group substituents, hetero-aromatic rings and counter anions.

In this work, various *N*-alkyl substituents in benzindoline moiety were designed, namely methyl to octyl groups. The details of synthetic schemes and characterizations⁶⁻¹¹ were introduced and discussed.

EXPERIMENTAL

Preparation of bis-aldehyde intermediate

1. Preparation of 4-(4-nitrophenyl)cyclohexanone **3**
10.67 g (0.06 mole) of 4-phenylcyclohexanone was dissolved in a 98% sulfuric acid solution and cooled to 0-5°C temperature. 4.64 mL (0.06 mole) of 98% nitric acid was dropped to reaction mixture for 2h and stirring was continued at 0-5°C for 5h. The reaction mixture was dropped off with a mixture of iced water. The filtrate was filtered off and recrystallized few iso-propyl alcohol to give product (70%); mp: 108-110°C. Element anal. calc. for: C₁₂H₁₃NO₃: C, 65.74; H 5.98; N 6.39. Found: C, 66.05; H, 6.07; N, 6.47%. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 1.93(dd, 2H, *J*=2.58Hz), 2.23(d, 2H, *J*=3.15Hz), 2.51(m, 4H), 3.14(d, H, *J*=3.39Hz), 7.40(d, 2H, *J*=4.89Hz), 8.17(d, 2H, *J*=4.89Hz).

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2. Preparation of 4-(4-aminophenyl)cyclohexanone **4**

3.0 g (0.014 mole) of 4-(4-nitrophenyl)cyclohexanone, 120 mL of iso-propyl alcohol and 0.5 g of palladium 10% were added to hydrogen reactor and heated at 50°C. The reaction mixture was stirred for further 7h and the filtrate was concentrated under reduced pressure to give product (89%); mp: 108–110°C. Element anal. calc. for: C₁₂H₁₅NO: C, 76.16; H 7.99; N 7.40. Found: C, 76.15; H, 8.07; N, 7.46%. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 1.87(dd, 2H, *J*=7.11Hz), 2.15(d, 2H, *J*=6.21Hz), 2.46(m, 4H), 2.91(s, H), 3.58(broad, 2H), 6.63(d, 2H, *J*=2.7Hz), 7.01(d, 2H, *J*=4.65Hz).

3. Preparation of 4-(4-diethylaminophenyl)cyclohexanone **5**

0.49 g (2.6 mmole) of 4-amino-phenylcyclohexanone and 0.35 mL (2.6 mmole) of diethyl sulfate were dissolved in 20 mL of iso-propyl alcohol and refluxed for 2 h. After 2 h, 0.35 mL (2.6 mmole) of diethyl sulfate was added to the reaction mixture and refluxed for 2 h. After this reaction, 0.28 g (2.6 mmole) of sodium carbonate and 0.35 mL (2.6 mmole) of diethyl sulfate were added and refluxed for further 2h. The reaction mixture was cooled to room temperature and the filtrate was concentrated under reduced pressure to give product. The crude product was purified by column chromatography using chloroform to give the product (63%). Element anal. calc. for: C₁₆H₂₃NO: C, 78.32; H 9.45; N 5.71. Found: C, 78.15; H, 9.27; N, 5.36%. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 1.15(m, 6H), 1.89(dd, 2H, *J*=5.49Hz), 2.19(d, 2H, *J*=5.64Hz), 2.48(m, 4H), 2.93(s, H), 3.33(m, 4H), 6.65(d, 2H, *J*=8.09Hz), 7.09(d, 2H, *J*=8.71Hz).

4. Preparation of 1-formyl-2-chloro-3-hydroxymethylene-5-(4-diethylaminophenyl)cyclohexene **6**

A mixture of 4-(4-diethylaminophenyl)cyclohexanone 5.4 mL (30 mmole) was dissolved in a mixture of 12 mL of *N,N*-dimethylformamide and 12 mL of dichloromethane. The reaction was cooled to 0–5°C and dropped with a mixture of 12 mL of dichloromethane and 12 mL of phosphorus oxychloride for 2 h. The reaction was refluxed for 3 h and cooled to room temperature. The final intermediate compound was filtered off and washed with ether to give product (42%). Mass Spectrum (HRMS): found *M*= 319.1340 required for C₁₈H₂₂ClNO₂ *M*=319.1339, ¹H NMR (300 MHz, CDCl₃): δ (ppm) 1.12(s, 6H), 1.19(dd, 2H, *J*=5.67Hz), 2.27(quint, H, *J*=4.91Hz), 2.84(d, H, *J*=4.51Hz), 3.32(dd, 2H, *J*=6.7Hz), 3.86(q, 4H, *J*=5.10Hz), 6.64(d, 2H, *J*=7.83Hz), 7.09(d, 2H, *J*=8.11Hz), 10.23(s, H), 11.0(s, H).

Preparation of benzindoline intermediate

1. 1,1,2-trimethyl-3-methylbenzindoline iodide **8** (R₁ : methyl)

A mixture of 3.7 g (23.3 mmole) of 2,3,3-trimethyl-indole and 3.63 g (25.5 mmole) of methyl iodide was refluxed in 15 mL of acetonitrile for 2 h. The reaction was cooled to room temperature, filtered off and washed with ether to give 6.45 g of pink colored materials (92%); mp 260 °C. Element anal. calc. for C₁₂H₁₆I_N, C 47.86, H 5.35, N 4.65. Found: C 47.28, H 5.14, N 4.95%.

2. 1,1,2-trimethyl-3-ethylbenzindoline iodide **8** (R₁ : ethyl)

After obtaining 3.97 g (25.5 mmole) of ethyl iodide, the same experimental procedure as described above was followed to give 6.83 g of pink colored materials (93%); mp 224°C. Element anal. calc. for C₁₃H₁₈I_N, C 49.54, H 5.76, N 4.44. Found: C 49.23, H 5.35, N 4.65%.

3. 1,1,2-trimethyl-3-propylbenzindoline iodide **8** (R₁ : propyl)

After obtaining 4.33 g (25.5 mmole) of propyl iodide, the same experimental procedure as described above was followed to give 8.16 g of pink colored materials (94%); mp 159 °C. Element anal. calc. for C₁₄H₂₀I_N, C 51.08, H 6.12, N 4.25. Found: C 51.34, H 6.01, N 4.11%.

4. 1,1,2-trimethyl-3-butylbenzindoline iodide **8** (R₁ : butyl)

After obtaining 4.69 g (25.5 mmole) of butyl iodide, the same experimental procedure as described above was followed to give 8.33 g of pink colored materials (96%); mp 136 °C. Element anal. calc. for C₁₅H₂₂I_N, C 52.49, H 6.46, N 4.08. Found: C 52.32, H 6.74, N 4.48%.

5. 1,1,2-trimethyl-3-hexylbenzindoline iodide **8** (R₁ : hexyl)

After obtaining 5.41 g (25.5 mmole) of hexyl iodide, the same experimental procedure as described above was followed to give 8.21 g of pink colored liquid materials (95%). Element anal. calc. for C₁₇H₂₆I_N, C 54.99, H 7.06, N 3.77. Found: C 55.16, H 7.34, N 3.95%.

6. 1,1,2-trimethyl-3-octylbenzindoline iodide **8** (R₁ : octyl)

After obtaining 6.12 g (25.5 mmole) of octyl iodide, the same experimental procedure as described above was followed to give 8.56 g of pink colored liquid materials (92%). Element anal. calc. for C₁₉H₃₀I_N, C 57.14, H 7.57, N 3.51. Found: C 57.55, H 7.51, N 3.48%.

Preparation of heptamethinecyanine dyes

1. Synthesis of 2-[2-chloro-3-[2-(1,3-dihydro-1,3,3-trimethyl-2H-indolindine)ethyl-1-cyclohexyl]ethyl-5-(4-diethylamino)benzene-1,3,3-trimethylindoline iodide (cyanine dye **1**):

54.2 mg (1.7×10⁻⁴ mole) of bisaldehyde and 0.103 g (3.4×10⁻⁴ mole) of 1,1,2-trimethyl-3-methylbenzindoline iodide were dissolved in 5 mL of a mixture of 1-butanol and benzene (7:3) in a flask equipped with a Dean-Stark trap. The mixture was heated at reflux with stirring and the water formed was collected in the trap. After 4 h, the reaction was cooled to room temperature and the filtrate was concentrated under reduced pressure. The residue was washed with ether and filtered to give green colored cyanine dye **1** (46%). mp 186–187°C. Mass spectrum (FAB): found *M*=758 required for C₄₂H₄₉ClI_N₃ *M*=758. ¹H NMR (500 MHz, Acetone-d₆): δ (ppm) 1.17(m, 6H), 1.31(m, 10H), 1.61(dd, 2H, *J*=3.49Hz), 2.66(dd, 2H, *J*=7.16Hz), 3.02(m, 6H), 3.42(q, 4H, *J*=6.99Hz), 3.63(s, H), 3.84(d, 2H, *J*=6.89Hz), 6.61(d, 2H, *J*=7.84Hz), 6.71(d, 2H, *J*=7.31Hz), 7.07(d, 2H, *J*=6.49Hz), 7.22(d, 2H, *J*=8.65Hz), 7.31(d, 2H, *J*=6.34Hz), 7.40(d, 2H, *J*=7.62Hz), 7.44(dd, 2H, *J*=6.89Hz), 7.62(d, 2H, *J*=6.97Hz).

2. Synthesis of 2-[2-chloro-3-[2-(1,3-dihydro-1-ethyl-3,3-dimethyl-2H-indolindine)ethyl-1-cyclohexyl]ethyl-5-(4-diethylamino)benzene-1-ethyl-3,3-dimethylindoline iodide (cyanine dye **2**):

Using 0.107 g (3.4×10⁻⁴ mole) of 1,1,2-trimethyl-3-ethylbenzindoline iodide, the same experimental procedure as described above was followed to give green colored cyanine dye **2** (40%); mp 185–186°C. Mass spectrum (FAB): found *M*=786 required for C₄₄H₅₃ClI_N₃ *M*=786. ¹H NMR (500 MHz, Acetone-d₆): δ (ppm) 1.17(m, 6H), 1.28(m, 12H), 2.64(d, 2H, *J*=6.32Hz), 2.81(dd, 4H, *J*=6.38Hz), 3.06(dd, 2H, *J*=6.59Hz), 3.43(dd, 4H, *J*=6.97Hz), 3.59(d, 2H, *J*=7.02Hz), 3.65(s, H), 4.32(quad, 4H, *J*=5.76Hz), 6.49(d, 2H, *J*=7.09Hz), 6.75(d, 2H, *J*=8.62Hz), 7.10(d, 2H, *J*=7.25Hz), 7.30(d, 2H, *J*=7.76Hz), 7.44(quad, 4H, *J*=7.86Hz), 7.63(d, 2H, *J*=7.92Hz), 8.50(d, 2H, *J*=8.50Hz).

3. Synthesis of 2-[2-chloro-3-[2-(1,3-dihydro-1-propyl-3,3-dimethyl-2H-indolizine)ethyl-1-cyclohexyl]ethyl-5-(4-diethylamino)benzene-1-propyl-3,3-dimethylindoline iodide (cyanine dye 3):

Using 0.112 g (3.4×10^{-4} mole) of 1,1,2-trimethyl-3-propylbenzindoline iodide, the same experimental procedure as described above was followed to give green colored cyanine dye 3 (45%); mp 188-190°C. Mass spectrum (FAB): found $M=814$ required for $C_{46}H_{57}ClIN_3$ $M=814$. 1H NMR (500 MHz, Acetone- d_6): δ (ppm) 0.97(m,10H), 1.18(dd,4H, $J=3.5$ Hz), 1.32(m, 12H), 1.86(d, 2H, $J=5.0$ Hz), 1.99(d, 2H, $J=5.5$ Hz), 2.71(d, 2H, $J=4.9$ Hz), 3.1(d, 2H, $J=4.6$ Hz), 3.35(d, 2H, $J=5.4$ Hz), 3.55(s,H), 4.26(q, 4H, $J=4.0$ Hz), 6.53(d, 2H, $J=7.0$ Hz), 7.31(dd, 4H, $J=7.3$ Hz), 7.44(dd, 4H, $J=7.0$ Hz), 7.63(d, 2H, $J=7.5$ Hz), 8.39(d, 2H, $J=7.2$ Hz), 8.51(d, 2H, $J=7.5$ Hz).

4. Synthesis of 2-[2-chloro-3-[2-(1,3-dihydro-1-butyl-3,3-dimethyl-2H-indolizine)ethyl-1-cyclohexyl]ethyl-5-(4-diethylamino)benzene-1-butyl-3,3-dimethylindoline iodide (cyanine dye 4):

Using 0.117 g (3.4×10^{-4} mole) of 1,1,2-trimethyl-3-butylbenzindoline iodide, the same experimental procedure as described above was followed to give green colored cyanine dye 4 (52%); mp 186-187°C. Mass spectrum (FAB): found $M=842$ required for $C_{48}H_{61}ClIN_3$ $M=842$. 1H NMR (500 MHz, Acetone- d_6): δ (ppm) 0.89(m, 10H), 1.20(dd, 4H, $J=5.2$ Hz), 1.28(m, 16H), 1.8(m, 6H), 3.52(d, 2H, $J=5.4$ Hz), 3.55(d,2H, $J=5.56$ Hz), 3.78(s,H), 4.28(dd, 4H, $J=6.1$ Hz), 6.52(d, 2H, $J=7.0$ Hz), 7.32(dd, 4H, $J=7.2$ Hz), 7.44(dd, 4H, $J=7.2$ Hz), 7.63(dd, 4H, $J=7.5$ Hz), 8.51(d, 2H, $J=7.8$ Hz).

5. Synthesis of 2-[2-chloro-3-[2-(1,3-dihydro-1-hexyl-3,3-dimethyl-2H-indolizine)ethyl-1-cyclohexyl]ethyl-5-(4-diethylamino)benzene-1-hexyl-3,3-dimethylindoline iodide (cyanine dye 5):

Using 0.126 g (3.4×10^{-4} mole) of 1,1,2-trimethyl-3-hexylbenzindoline iodide, the same experimental procedure as described above was followed to give green colored cyanine dye 5 (47%); mp 188-189°C. Mass spectrum (FAB): found $M=898$ required for $C_{52}H_{69}ClIN_3$ $M=898$. 1H NMR (500 MHz,

Acetone- d_6): δ (ppm) 1.17(m, 8H), 1.28(m, 14H), 1.40(m, 8H), 1.84(m, 8H), 2.82(d, 2H, $J=3.5$ Hz), 3.04(d, 2H, $J=3.9$ Hz), 3.42(dd, 4H, $J=4.5$ Hz), 3.46(d, 2H, $J=4.8$ Hz), 3.87(s, H), 4.28(dd, 4H, $J=10.9$ Hz), 6.51(d, 2H, $J=7.34$ Hz), 6.74(d, 2H, $J=7.29$ Hz), 7.20(d, 2H, $J=7.27$ Hz), 7.31(dd, 2H, $J=7.37$ Hz), 7.45(dd, 4H, $J=7.87$ Hz), 7.63(d, 2H, $J=7.10$ Hz), 8.50(d, 2H, $J=7.81$ Hz).

6. Synthesis of 2-[2-chloro-3-[2-(1,3-dihydro-1-octyl-3,3-dimethyl-2H-indolizine)ethyl-1-cyclohexyl]ethyl-5-(4-diethylamino)benzene-1-octyl-3,3-dimethylindoline iodide (cyanine dye 6):

Using 0.135 g (3.4×10^{-4} mole) of 1,1,2-trimethyl-3-octylbenzindoline iodide, the same experimental procedure as described above was followed to give green colored cyanine dye 6 (47%); mp 182-183°C. Mass spectrum (FAB): found $M=954$ required for $C_{56}H_{77}ClIN_3$ $M=954$. 1H NMR (500 MHz, Acetone- d_6): δ (ppm) 0.84(m, 10H), 1.17(m, 10H), 1.24(m, 10H), 1.33(m, 8H), 1.41(m, 6H), 1.84(q, 4H, $J=3.75$ Hz), 2.64(d, 2H, $J=3.68$ Hz), 3.06(d, 2H, $J=4.24$ Hz), 3.42(dd, 4H, $J=6.9$ Hz), 3.79(s,H), 4.28(quart, 4H, $J=7.4$ Hz), 6.49(d, 2H, $J=7.0$ Hz), 6.73(d, 2H, $J=6.73$ Hz), 7.0(d, 2H, $J=7.55$ Hz), 7.20(d, 2H, $J=7.8$ Hz), 7.44(dd, 4H, $J=7.9$ Hz), 7.63(d, 2H, $J=7.87$ Hz), 8.49(d, 2H, $J=7.98$ Hz).

RESULTS AND DISCUSSION

Synthetic design methods

General synthetic route to prepare bis-aldehyde, (1-formyl-2-chloro-3-hydroxymethylene)cyclohexene 1 is shown in Fig. 1. For other intermediates 2 to 6, further reaction routes and synthesis procedures are shown in Fig. 2.

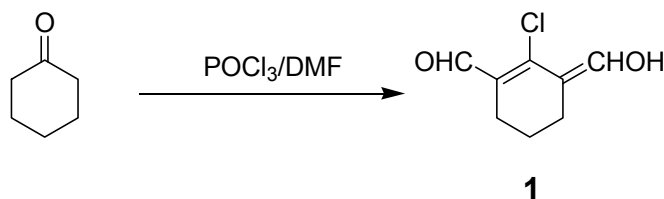


Fig. 1 – Synthesis of 2-chloro-1-formyl-3-hydroxymethylene-cyclohexene.

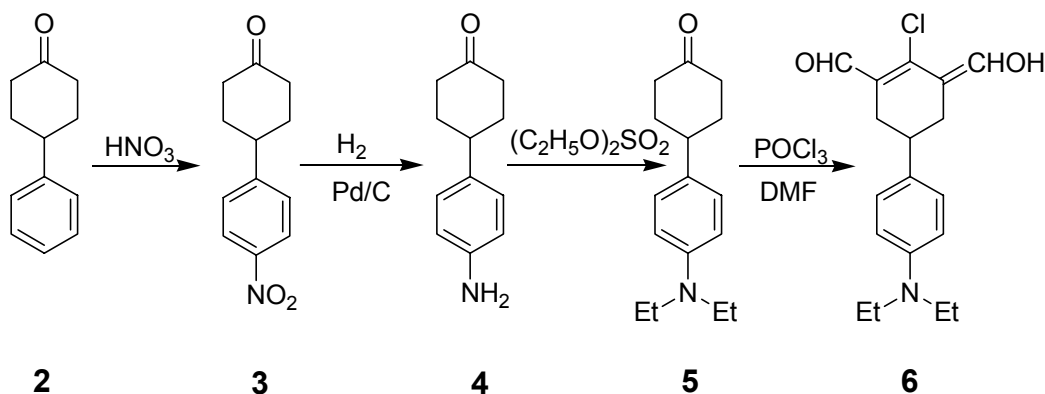


Fig. 2 – Synthesis of 2-chloro-1-formyl-3-hydroxymethylene-cyclohexene intermediate.

Reaction of benzindole **7** and alkyl iodide in boiling acetonitrile was proceeded to give the pink colored intermediate materials **8** with an excellent yield (Fig. 3). Obtained products were recrystallized using ethyl ether and impurities were readily and efficiently removed.

The cyanine dye compounds can be prepared by the condensation reaction between a heterocyclic base containing activated methyl group and an unsaturated bis-aldehyde or its equivalent. In this paper, we have reported synthesis and

characterization of new heptamethine cyanine dye compounds, showing NIR absorbing properties. The procedures for heptamethine cyanine dyes **9** are shown in Fig. 4. Reaction mixtures of quaternary salt of heterocyclic base containing an activated methyl group **8** (2 equiv) and bis-aldehyde, (1-formyl-2-chloro-3-hydroxymethylene-5-(4-diethyl-aminophenyl)cyclohexene moiety **6** were refluxed in a mixture solvent of 1-butanol and benzene (7:3) without any catalyst.¹²⁻¹⁷

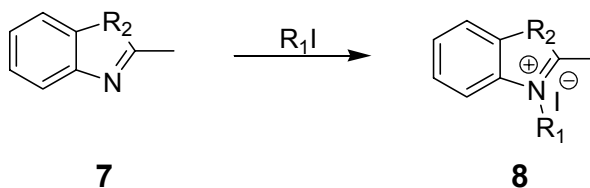


Fig. 3 – Synthetic procedure of the benzindoline.

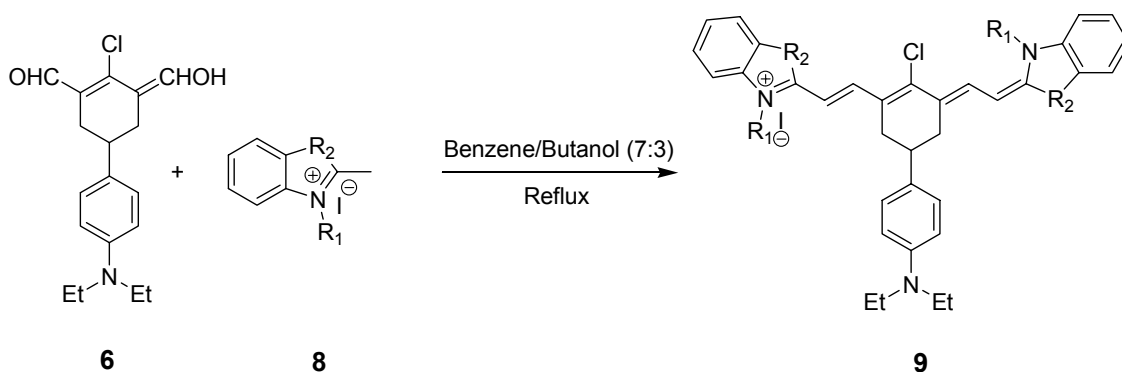


Fig. 4 – Synthetic procedure of the heptamethine cyanine dye compounds.

Formed water during the reaction was removed with an azeotrope by a Dean-Stark condenser. Dye compound products having pale green color were achieved from 5 h reaction. The mixtures were cooled to room temperature and the precipitates were filtered out, washed with diethyl ether and then dried in open air. The resulting cyanine dye compounds were collected after filtration step followed by twice complete washing with diethyl ether.

Characterization and absorption properties

The prepared heptamethine NIR absorbing cyanine dye compounds are listed in Table 1. The main feature of this synthesis can be proposed that the amino substituent in bis-aldehyde provides very important role for making the various heptamethine NIR absorbing cyanine dye compounds with functional groups. The corresponding spectroscopic and physical

properties of the heptamethine NIR absorbing cyanine dye compounds are displayed in Table 2. Hypsochromic shift (blue shift) was observed in polar solvent, methanol. The solvent dependent shift properties are due to the differences in relative solvating capabilities of solvents between the ground state of molecules and the excited state of the same molecules. In most molecules exhibiting $n \rightarrow \pi^*$ transitions, the ground state is more polar than the excited state. In particular, solvents being capable of hydrogen bonding may interact more strongly with unshared electron pairs of molecules in the ground state than they do in the excited state. As a result, the corresponding $n \rightarrow \pi^*$ transition may affect to shift its absorption maximum to shorter wavelength, as hydrogen bonding ability (polarity) of the solvent increases. In this context, these functionalized dye compounds have been designed to meet the potential interests such as solubility, absorption and the wavelength.

Table 1

Characterization data of cyanine dyes

Dyes	R ₁	R ₂	Yield(%)	Molecular Weight
1	methyl	C(CH ₃) ₂	46	758
2	ethyl	C(CH ₃) ₂	40	786
3	propyl	C(CH ₃) ₂	45	814
4	butyl	C(CH ₃) ₂	52	842
5	hexyl	C(CH ₃) ₂	47	898
6	octyl	C(CH ₃) ₂	47	954

Table 2

Properties of heptamethine cyanine dyes

Structure	ϵ_{\max}^a (Lmol ⁻¹ cm ⁻¹) in dichloromethane	Melting point (°C)	λ_{\max}^b (nm) in solvent		
			Dichloromethane	DMF	Methanol
1	312,000	186-187	784	786	774
2	300,280	185-186	783	787	776
3	332,400	188-190	788	789	779
4	322,670	186-187	787	789	780
5	366,610	188-189	787	790	781
6	358,410	182-183	790	791	781

a: Molecular extinction coefficients

b: Absorption maxima of wavelength

CONCLUSION

This work introduces new designed near infrared (NIR) absorbing dyes comprising of novel heptamethine cyanine chromophore with symmetrical structures. The cyanine dye compounds showed 780-790 nm of absorption wavelength ranges with a high molar extinction coefficient of 3.0-3.6×10⁵ ranges as well as a high solubility property. With this optical characteristic designed for NIR absorbing dye compounds, the prepared symmetrical heptamethine cyanine dye compounds can be potentially considered in optical data storages, shielding heat-light materials for film or glass, security sensors and bio-fluorophores.

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