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ASYMMETRIC, WATER-SOLUBLE CYANINE DYES: SYNTHESIS AND FLUORESCENT PROBE FOR THE Fe^{3+} ION

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ABSTRACT. Two known symmetric and four novel asymmetric water-soluble pentamethyl cyanine dyes were synthesized and fully characterized by IR, MS and NMR. These dyes exhibited good water solubility and possessed good stability at different pH environment. On the basis of investigation toward the change of U-vis absorption spectra under heat or illumination, these results indicated that the asymmetric cyanine dyes have better photo-thermal stability than that of symmetric dyes under the state of solution, which was also proved by the results of thermogravimetric analysis (TGA). Meanwhile, the researches on the fluorescent probes for metal ions detection demonstrated that the dyes can be considered as a fluorescent probe for detection of Fe^{3+} ion, and the anti-interference experiments displayed that the dye exhibits excellent selectivity towards Fe^{3+} ion over other common metal cations (Cr^{3+}, Zn^{2+}, Ni^{2+}, Al^{3+}, Mg^{2+}, Cu^{2+}).

Keywords: *chemical sensor, ferric ion, fluorescent probe, cyanine dyes, near-infrared dyes.*

INTRODUCTION

Owing to the unique optical properties and the easy chemical modification of their molecular structures of cyanine dyes, it has been attracting the researcher's development interest [1-5], which leads to its diversity of molecular structure, and the new application fields have been developing besides for traditional application. Especially in recent years, a lot of breakthroughs are

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reported in the field of medicine [6-10] and fluorescent probes [11, 12], which puts forward specific requirements for the structure and performance of cyanine dyes under the consideration of application, because the solubility and stability is especially critical, so it becomes a research hot point for the preparation of water-soluble cyanine dyes, and their photo-thermal stability is also improved on the basis of the structural modification [13, 14]. In order to apply as fluorescent probe for detection of metal ions in aqueous media, in the paper, four novel asymmetric cyanine dyes with the better water solubility and stability are designed and synthesized, the hydrophilic character of dyes are enhanced through introducing sulfonate groups, while the photo-thermal stability of the dye can be improved due to the design of asymmetric structure. As known, the component containing the nitrogen hetero-cycle has more influence toward its properties in the molecular structure of cyanine dyes, and the cyanine dye with indole cycle is the most stability [15, 16], therefore, in this study, 2,3,3-trimethylindolenine was selected as a raw material. Firstly, the hydrophilic sulfonate group is introduced through the reaction with sulfophactone, and then the intermediate was further reacted with different modified indolium salts under the presence of malonaldehyde dianilide hydrochloride, two known symmetric and four novel asymmetric water soluble cyanine dyes were successfully synthesized (as illustrated in Scheme 1).

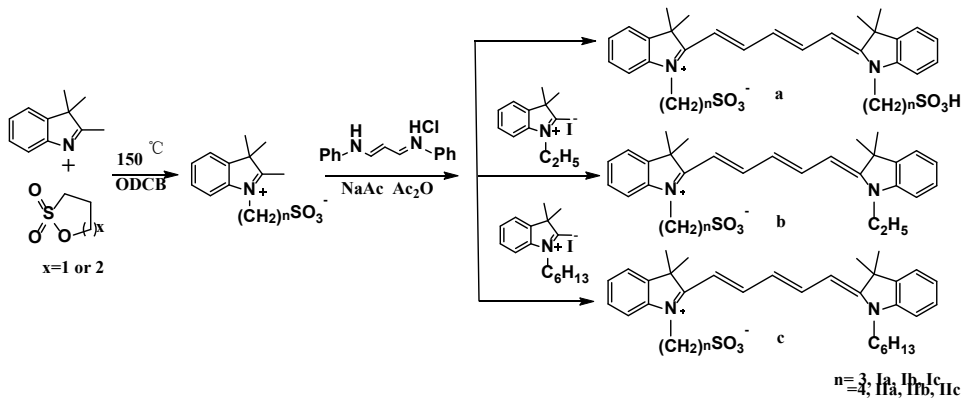
Many researches have proved that it is an effective method to detect the cations and anions utilizing fluorescent probes technique [17, 18], and a variety of NIR dyes have been utilized as a sensor for the detection of the Fe^{3+} ion[19-21]. However, because of poor selectivity and solubility in aqueous media for present chemical sensor, their application scope is restricted. Herein, a novel cyanine dyes were investigated as the fluorescent probe for the detection of Fe^{3+} ion, and it exhibited the notable characters of highly sensitive, selective sensing under the aqueous environment.

RESULTS AND DISCUSSION

The Synthesis of Cyanine Dyes

As shown in Scheme 1, through the reaction of the two sultones (1,3-propanesultone or 1,4-butanesultone) with 2,3,3-trimethylindolenine, the two intermediates of indolium quaternary salts were conveniently prepared under the condition of 1,2-dichlorobenzene solvent and high temperature(150℃), after purification, further condensation with hemi-molar quantity of malonaldehyde dianilide hydrochloride in the presence of sodium acetate and acetic anhydride,

two known symmetric, water soluble cyanine dyes (**Ia** and **IIa**) were synthesized [22, 23], and while three components of malonaldehyde dianilide hydrochloride, *N*-alkylindolium and sulfonated indolium[24] was mixed at equimolar quantity, four novel asymmetric, water soluble cyanine dyes with different chain lengths were obtained (seeing supplementary information in detail), their maximum absorption wavelength was observed at about 650 nm (in DMF), and their spectroscopic data are summarized in Table 1.



Scheme 1. The synthesis route of cyanine dyes

Table 1. Spectroscopic data of six prepared dyes in methanol

Dye	**Ia**	**Ib**	**Ic**	**IIa**	**IIb**	**IIc**
λ_{ab} (nm)	642	642	642	642	642	642
λ_{em} (nm)	721	722	726	718	721	718
Stokes shift (nm)	79	80	76	74	79	74

The measurement results show that the all six dyes exhibit almost same maximum absorption and emission wavelength, which indicates that the structural differences do not affect the spectral performance, meanwhile, the highest value of Stokes shift was also summarized in Table 1. And the larger the Stokes shift, the more favorable the reducing interference of background fluorescence, it indicates that these cyanine dyes have great potential applications in fluorescence labeling and multi-color imaging.

As a functional material, the stability is the important parameter under the consideration for its application, meanwhile, in order to assess the effect of molecular structure on the stability, the photo-thermal stability of six cyanine dyes were investigated at the state of solution and solid by analyzing the

UV-Vis-NIR spectroscopy and thermogravimetric analysis (TGA). Firstly, through measuring the changes of absorption spectra under the condition of illumination or heat, on the basis of relationship between absorbance intensity (A) and time (T), a linear fitting relationship is hypothesized between A and T, when the dye completely disappears, the A is zero, and the time referred as decomposition time is calculated through the linear equation hypothesized. Here, the summary of these results are displayed in Table 2 (seeing supplementary information in detail).

According to analytical results (Table 2), we can find that the decomposition time of the asymmetric dyes are longer than that of corresponding to symmetric dyes regardless illumination or heat at solution, meanwhile, the analytical results also indicate the longer alkyl chain is advantageous for increasing the decomposition time, and the same conclusion is also confirmed by the results of TGA. The excellent material among the six compounds prepared is the **IIc** with long alkyl chain (butyl sulfonate group and hexyl group), it displays the highest decomposition temperature. But on the consideration of hydrophilic character, the suitable alkyl length must be chosen[25], and the present research results clarify the structure-effect relationship about the stability of cyanine dyes designed.

Table 2. The decomposition time of six dyes in solution[a] and TGA

Compound	Illumination[b](h) (Increase ratio)	Heat[c](h) (Increase multiple)	Thermal decomposition temperature[d](℃)
Ia	12.2	9.8	220
Ib	16.6(36.1%)	37.8(2.9)	315
Ic	24.9(104.1%)	43.6(3.4)	320
IIa	13.6(11.5%)	12.9(0.3)	240
IIb	15.7(15.4%)	21.0(0.6)	340
IIc	17.7(30.1%)	31.6(1.4)	360

[a] Estimated by linear relationship between absorption (A) and the time (t), when A=0 (the dye is completely decomposed), the time is calculated.The value in bracket represents the rate or multiple of change.
[b] Illuminated wavelength between 400 nm and 750 nm.
[c] At 70 ℃ without light.
[d] Decomposition 5% (lost weight).

Application as Fluorescent Probe

1. The pH Dependence

Because the stability of free probe is an important reference index under different pH conditions[26], and in order to decide where the prepared dyes are suitable for fluorescent probe, the effect of pH toward the stability

was investigated, and two cyanine dyes (**Ia** and **IIb**) were selected to analyze the changes of UV spectrum under different pH value, the results are shown in Figure 1.

The results (Figure 1) displayed that no significant change in either the absorption intensity or wavelength of **Ia** and **IIb** was observed in different pH environment, which indicates that these dyes are stable between pH 0.95 and 13.53. We guess that the reason is attributed to the special structure of dyes containing alkyl sulfony ammonium inner salt, which is stable under acid or base condition owing to its intramolecular acid-base equilibrium. And the good stability at different pH value can expand its application field.

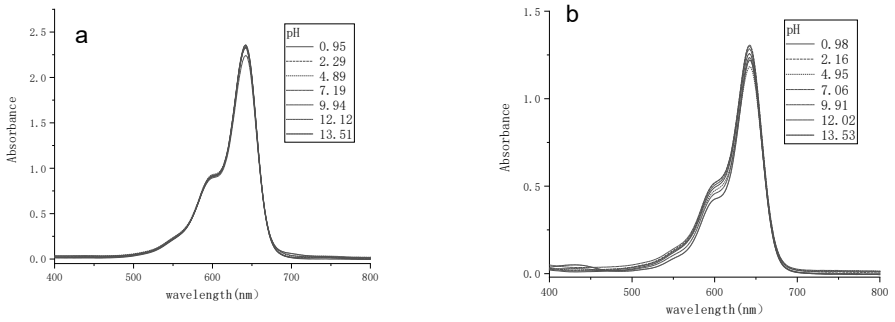


Figure 1. The UV-Vis spectra of dye **Ia** (a) and **IIb** (b) in aqueous solution of different pH

2. Sensitivity and Selectivity Study of Probe

Further, on the basis of investigation of fluorescent spectra of dyes, the researches on the fluorescent probes for metal ions in aqueous solution were implemented. Many metal ions (Cr^{3+}, Zn^{2+}, Ni^{2+}, Al^{3+}, Mg^{2+}, Cu^{2+} and Fe^{3+}) were chosen as targets, through utilizing the fluorescence spectrum and analyzing the change of spectra after adding metal ions, the detectability of dyes toward metal ions was determined. The dye **IIb** was used as a example of probe (other results can be found in the supplementary materials), the analytical results are displayed in Figure 2.

According to the results shown in Figure 2, the fluorescence quenching phenomenon was observed while adding Fe^{3+} ion to the aqueous of dye **IIb**, and adding other metal ions (Cr^{3+}, Zn^{2+}, Ni^{2+}, Al^{3+}, Mg^{2+}, Cu^{2+}) only slightly reduce the fluorescence intensity, which indicates that the series of dyes prepared can be used as a fluorescent probe to recognize and capture the

Fe^{3+} ion. But the complexity of real sample maybe present a great challenge to detection of probe for metal ion in detection selectivity, in order to effectively apply in practical environment detection conditions of co-existence of Fe^{3+} with other metal ions, it's necessary to investigate the specific and selective detection of probe when other interfering metal ions also exist, thus, the selectivity studies were carried out to evaluate the performance of probe, the anti-interference experiments were implemented under the conditions of co-existence of Fe^{3+} with other metal ions, the results are shown in Figure 3.

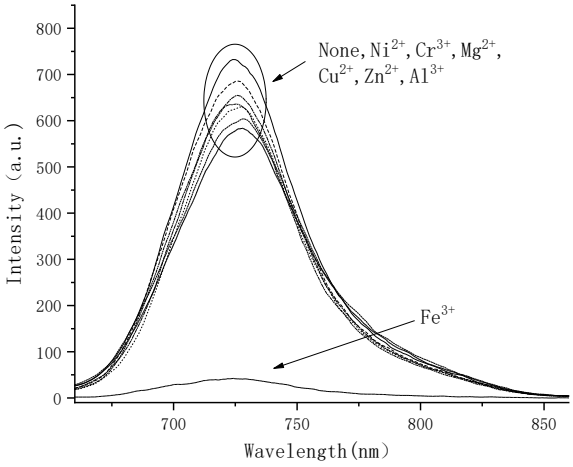


Figure 2. Fluorescence spectra change of **IIb** (2.0×10^{-4} mol/L) after adding different metal ions in aqueous solution (5.0×10^{-4} mol/L)

The blank box in Figure 3 depicts the fluorescence intensity of probe **IIb** in the presence of the different metal ions, it displays that the used metal ions hardly change the fluorescence intensity of **IIb** (seeing the Figure 2). Subsequently, the Fe^{3+} ion (5.0×10^{-4} mol/L) was added to the above solutions to form a co-existence mixture of two metal ions, then its fluorescence spectra were measured again, and the fluctuation of the fluorescence intensity was recorded as a stripe box in Figure 3.

The fluorescence quenching phenomenon induced by adding Fe^{3+} ion was almost observed in the presence of various competitive metal ions. The results show that dye **IIb** has anti-interference ability for other metal ions (Cr^{3+}, Zn^{2+}, Ni^{2+}, Al^{3+}, Mg^{2+}, Cu^{2+}) while detecting Fe^{3+} ions, which demonstrates that probe **IIb** is quite selective in detecting Fe^{3+} ion even if the conditions of co-existence of other metal ions.

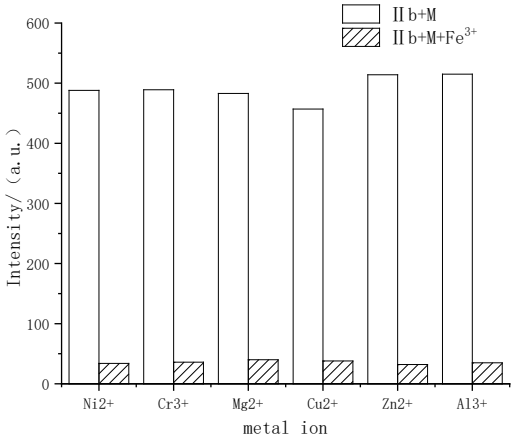


Figure 3. Effect of other metal ions on the recognition of Fe^{3+} (5.0×10^{-4} mol/L) by probe **IIb** (2.0×10^{-4} mol/L)

In brief, investigation results illustrated in Figure 2 and Figure 3 indicate that dye **IIb** possesses strong anti-interference capability and superior selectivity for Fe^{3+} over other coexisting metal ions.

3. Limit of Detection

In order to further investigate the recognition ability for Fe^{3+} by probe **IIb**, the limit of detection (LOD) was calculated through fluorescence titration. The titration results are shown in Figure 4, on the basis of the titrations of the probe **IIb** with different concentration of Fe^{3+}, the Job's plot was obtained [27].

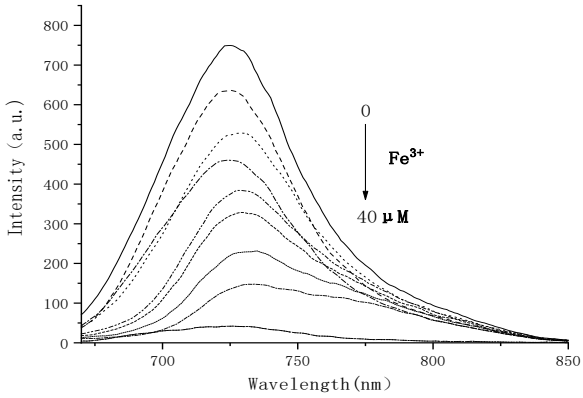


Figure 4. Fluorescence response of **IIb** to various concentration of Fe^{3+} in aqueous solution

As shown in Figure 5, the quenching efficiency (I_0/I) disclosed a good linear relationship (R^2=0.9691) versus the concentration of Fe^{3+}. The LOD is then calculated through the equation: limit of detection =3δ/k [28], where δ is the standard deviation of blank measurements; k is the slope between intensity versus sample concentration. The limit of detection was measured to be 6.8μM, which indicates that probe **IIb** can be applied as an efficient fluorescent probe for Fe^{3+} detection. The structure of the probe **IIb** and Fe^{3+} coordination compound was determined by using the Job's plot. A distinct inflection point at the Job's plot was observed when the ratio of [Fe^{3+}]/([Fe^{3+}]+[**IIb**]) was 0.494, indicating a 1:1 binding stoichiometry between dye **IIb** and Fe^{3+} (Figure 6).

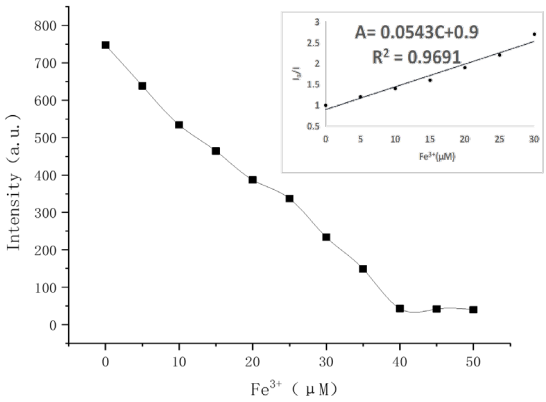


Figure 5. Plot of relative fluorescence intensity of **IIb** and concentration of Fe^{3+}, inset: linear relationship between A (I_0/I) and C (concentration of Fe^{3+})

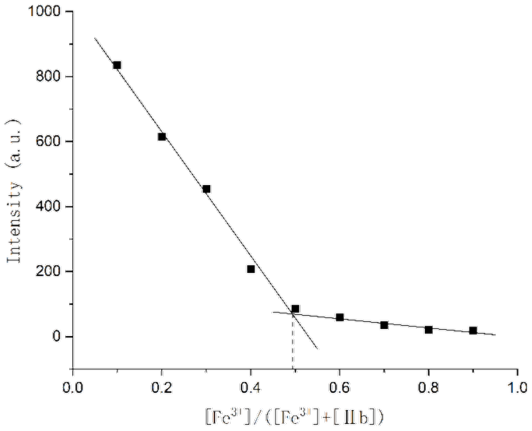


Figure 6. Job plot for the determination of the dye IIb and Fe^{3+} in the complex, the excitation wavelength was set at 721 nm

CONCLUSION

In summary, four novel asymmetric and two known symmetric water-soluble pentamethyl cyanine dyes were synthesized and fully characterized by IR, MS and NMR, and their spectroscopic properties were analysed. On the basis of investigation on Uv-vis spectra and TGA, photo-thermal stability of six cyanine dyes were compared, and the effect factors toward the stability of dyes prepared was also analyzed, which simply give the structure- effect relationship about the stability of cyanine dye. A lot of investigations about fluorescence spectra indicate that these dyes can be considered as a fluorescent probe for detection of Fe^{3+} ion, and exhibits excellent selectivity and anti-interference capability towards Fe^{3+} over other common metal cations，and **IIb** possesses a limit of detection of 6.8μM for the detection of Fe^{3+} ion, meanwhile, Job's plot analysis reflects the 1:1 complexation of dye **IIb** and Fe^{3+} complexes. Notably, this probe can be applied in aqueous media, which expands their application scope.

EXPERIMENTAL SECTION

Chemical Reagents

2,3,3-trimethylindole, 1,3-propanesultone, 1,4-butane sultone, malonaldehyde dianilide hydrochloride, methanol, dichloromethane, sodium acetate, acetic anhydride were commercially purchased and used directly without treatment. The two N-alkyl indolium salts (1-ethyl-2,3,3-trimethyl-3H-indol-1-ium iodide and 1-hexyl-2,3,3-trimethyl-3H-indol-1-ium iodide) were prepared by our lab. The stock solutions of metal ions were prepared from $Cr(NO_3)_3 \cdot 9H_2O$, $FeCl_3 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ with distilled water.

Instrumentation

The NMR of the dyes were measured with a AC-400 Nuclear magnetic resonance apparatus. The Ms of the dyes were measured with a Waters UPLC-Quattro Micro LC-MS. The functional groups of the dyes were measured with a NICOLET 380 Fourier infrared spectrometer. UV-vis absorption spectra were measured with a Optizen 2120 spectrophotometer. Emission spectra were taken on a VARIAN fluorescence spectrophotometer.

The Synthesis of Six Cyanine Dyes

1. Intermediate of Indoline

Under nitrogen atmosphere, 1,3-propanesultone (9.22g, 0.76mol), 2,3,3-trimethyl-indole (10.22g, 0.64mol) and 5ml 1,2-dichlorobenzene (ODCB) was added into a two-necked bottle, the reaction mixture was heated for 4 h at 150℃, after cooling to r.t., pouring the upper liquid, then washing with acetone for 3 times, the resulting residue was recrystallized with methanol, the intermediate of 3-(2,3,3-trimethyl-3H-indol-1-ium-1-yl)propane-1-sulfonate (12.27g) was obtained, which was purple solid with a yield of 68%. IR(KBr) (cm^{-1}) 3044-3019 (Ar-H), 2995~2920(-CH_3, -CH_2), 1659 (C=N), 1480 (C=C), 1199 (S-O); ESI-MS: $[M+H]^+$: m/z= 282.06 (observ.), 282.10 (calc.).

The same procedure, the intermediate of 4-(2,3,3-trimethyl-3H-indol-1-ium-1-yl)butane-1-sulfonate was also prepared.

2. The symmetric Cyanine dye (Ia)

In a two-necked bottle, 3-(2,3,3-trimethyl-3H-indol-1-ium-1-yl)propane-1-sulfonate (0.97g, 3.45mmol), malonaldehyde dianilide hydrochloride (0.30g, 1.15mmol), sodium acetate (0.11g, 1.29mmol) and 10ml acetic anhydride was added, then heated for 2h at 120℃ under N_2 atmosphere, after cooling to r.t., the solvent was removed at reduce pressure, the residue was isolated by silica gel column eluted with mixed solvent of dichloromethane / methanol (v/v =4/1), the product with a metallic luster (0.43g) was obtained, yield is about 62%. IR(KBr) (cm^{-1}) 3065-3019 (Ar-H), 2995-2925 (-CH_3, -CH_2), 1659 (C=N), 1465 (C=C), 1189 (S-O); UV-Vis: λ_{ab}= 642nm, FI: λ_{em}=721nm (CH_3OH); ESI-HRMS: $[M+H]^+$: m/z= 599.2240 (observ.), 599.2205 (calc.);
^{1}H-NMR (400 MHz, CD_3OD) δ 8.29(t, J = 12.0 Hz, 2H), 7.48(d, J = 7.5 Hz, 2H), 7.40(d, J = 4.2 Hz, 4H), 7.25(dt, J = 8.0, 4.2 Hz, 2H), 6.68(s, 2H), 6.40(d, J=13.7 Hz, 2H), 4.33(t, J=7.9 Hz, 4H), 3.01(t, J = 7.0 Hz, 4H), 2.26(t, J = 7.8 Hz, 4H), 1.72(s, 12H).
^{13}C-NMR(101 MHz, CD_3OD) δ 174.7, 155.7, 143.5, 142.6, 129.8, 127.4, 126.2, 123.4, 112.1, 104.6, 51.7, 50.6, 43.9, 28.5, 28.0, 24.1.

3. The asymmetric Cyanine dye (Ib)

In a two-necked bottle, 3-(2,3,3-trimethyl-3H-indol-1-ium-1-yl)propane-1-sulfonate (0.26g, 1.27mmol), malonaldehyde dianilide hydrochloride (0.30g, 1.15mmol), sodium acetate (0.11g, 1.29mmol) and 5ml acetic anhydride was added, then heated for 2h at 120℃ under N_2 atmosphere, after cooling to r.t., 1-ethyl-2,3,3-trimethyl-3H-indol-1-ium iodide (0.38, 1.22mmol) was added into the reaction mixture, and then afer further reacting for 30 min at 120℃, the solvent was removed at reduce pressure, the residue was isolated by

silica gel column eluted with mixed solvent of dichloromethane / methanol (v/v =8/1), the product with a metallic luster (0.21g) was obtained, yield is about 36%. IR(KBr) (cm^{-1}) 3053-3015 (Ar-H), 2965-2905 (-CH_3, -CH_2), 1660 (C=N), 1485 (C=C), 1209 (S-O); UV-Vis: λ_{ab}= 642nm, FI: λ_{em}= 722nm (CH_3OH); ESI-MS: $[M+H]^+$: m/z=505.41 (observ.), 505.42 (calc.);
^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 2H), 7.31 – 7.28 (m, 2H), 7.21 (d, J = 7.3 Hz, 2H), 7.13 (t, J = 7.5 Hz, 2H), 7.05 (d, J = 8.3 Hz, 2H), 7.01 (d, J = 7.6 Hz, 1H), 6.68 (d, J = 12.7 Hz, 1H), 6.10 (d, J = 13.5 Hz, 1H), 4.47 (s, 2H), 4.05 (d, J = 7.6 Hz, 2H), 3.22 (d, J = 7.1 Hz, 2H), 2.32 (s, 2H), 1.60 (s, 6H), 1.54 (s, 6H), 1.36 – 1.32 (m, 3H).
^{13}C-NMR (101 MHz, $CDCl_3$) δ 173.9, 172.7, 142.5, 141.8, 128.9, 128.6, 127.7, 126.4, 125.1, 125.1, 122.4, 122.2, 121.5, 111.3, 110.3, 105.0, 102.9, 49.5, 48.1, 39.4, 28.0, 23.4, 12.6.

4. The asymmetric Cyanine dye (Ic)

The same as procedure of **Ib** preparation except for replacing the 1-ethyl-2,3,3-trimethyl-3H-indol-1-ium iodide using 1-hexyl-2,3,3-trimethyl-3H-indol-1-ium iodide, the Ic also was obtained at the yield of 32%. IR(KBr) (cm^{-1}) 3044-3019 (Ar-H), 2965-2925 (-CH_3, -CH_2), 1659 (C=N), 1480 (C=C), 1195 (S-O); UV-Vis: λ_{ab}= 642nm, FI: λ_{em}= 726nm (CH_3OH); HRMS: $[M+H]^+$: m/z= 561.3144 (observ.), 561.3106 (calc.);
^{1}H- NMR (400 MHz, $CDCl_3$) δ 8.21 (t, J = 13.1 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 2.4 Hz, 1H), 7.36 (d, J = 1.9 Hz, 2H), 7.34 (d, J = 1.5 Hz, 2H), 7.23 (d, J = 3.3 Hz, 1H), 7.21 (d, J = 3.3 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 7.02 (d, J = 8.1 Hz, 1H), 6.25 (d, J = 13.6 Hz, 1H), 6.03 (d, J = 13.6 Hz, 1H), 4.54 (s, 2H), 3.91 (t, J = 7.7 Hz, 2H), 3.11 (d, J = 6.4 Hz, 2H), 2.34 (d, J = 8.7 Hz, 2H), 2.10 (s, 2H), 1.78 (s, 12H), 1.34 (q, J = 4.8 Hz, 6H), 0.90 – 0.87 (m, 3H).
^{13}C- NMR (101 MHz, $CDCl_3$) δ 174.0, 173.2, 142.2, 141.6, 128.9, 128.9, 128.6, 128.5, 126.7, 125.1, 123.8, 122.6, 122.5, 122.4, 120.0, 110.6, 110.2, 103.7, 103.0, 49.6, 49.5, 47.7, 44.3, 31.5, 28.3, 28.0, 27.8, 27.5, 27.4, 26.8, 24.8, 22.6, 21.2, 14.1.

5. The Cyanine dye (II)

According to the preparation procedure of I, three cyanines (**II**) were also synthesized, the analytical data were displayed as following:

IIa: Yield was 46%. IR(KBr) (cm^{-1}) 3064-3025 (Ar-H), 2956-2887 (-CH_3, -CH_2), 1659 (C=N), 1485 (C=C), 1158 (S-O); UV-Vis: λ_{ab}= 642nm, FI: λ_{em}= 718nm (CH_3OH); ESI-MS: $[M+H]^+$: m/z=626.21 (observ.), 626.25 (calc.);
^{1}H- NMR (600 MHz, DMSO-D6) δ 8.33 (t, J = 13.1 Hz, 2H), 7.61 (d, J = 7.4 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 7.3 Hz,

2H), 6.60 (t, J = 12.4 Hz, 1H), 6.36 (d, J = 13.8 Hz, 2H), 4.10 (t, J = 7.5 Hz, 4H), 2.48 (d, J = 7.4 Hz, 4H), 1.77 (d, J = 15.0, 7.1 Hz, 4H), 1.70 (s, 6H), 1.69 (s, 2H), 1.68 (s, 6H), 1.24 (d, J = 11.7 Hz, 2H).
^{13}C- NMR (101 MHz, DMSO-D6) δ 176.51, 172.50, 154.03, 142.06, 141.11, 128.42, 125.74, 124.60, 122.37, 111.17, 103.31, 50.68, 48.85, 27.19, 26.02, 24.20, 22.42.

IIb: Yield was 29%. IR(KBr) (cm^{-1}) 3062-3017 (Ar-H), 2965-2915 (CH_2-H, C-H), 1660 (C=N), 1482 (C=C), 1197 (S-O); UV-Vis: λ_{ab}= 642nm, FI: λ_{em}= 721nm (In CH_3OH); ESI-MS: $[M+H]^+$: m/z=626.21 (observ.), 626.25 (calc.);
^{1}H- NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 14.9 Hz, 1H), 7.92 (t, J = 13.0 Hz, 2H), 7.62 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.22 (d, J = 7.1 Hz, 2H), 7.13 (t, J = 7.5 Hz, 1H), 7.04 (d, J = 7.7 Hz, 2H), 6.75 (t, J = 12.4 Hz, 1H), 6.40 (d, J = 13.6 Hz, 1H), 6.19 (d, J = 13.4 Hz, 1H), 4.13 (s, 2H), 4.04 (d, J = 7.1 Hz, 2H), 3.07 (d, J = 7.6 Hz, 2H), 1.91 (s, 2H), 1.62 (s, 6H), 1.59 (s, 6H), 1.31 (t, J = 7.0 Hz, 5H).
^{13}C- NMR (101 MHz, $CDCl_3$) δ 173.0, 171.8, 142.1, 141.8, 141.3, 141.2, 129.2, 128.9, 128.7, 126.9, 125.2, 123.9, 122.7, 120.1, 112.0, 110.4, 103.1, 50.4, 49.4, 49.3, 28.5, 28.2, 12.6.

IIc: Yield was 36%. IR(KBr) (cm^{-1}) 3044-3025 (Ar-H), 2956-2887 (-CH_3, -CH_2), 1659 (C=N), 1485 (C=C), 1158 (S-O); UV-Vis: λ_{ab}= 642nm, FI: λ_{em}= 718nm (CH_3OH);
^{1}H- NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 2H), 7.40 (d, J = 7.7 Hz, 1H), 7.37 (d, J = 1.5 Hz, 1H), 7.36 – 7.33 (m, 2H), 7.22 (d, J = 6.0 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 7.14 (d, J = 8.0 Hz, 1H), 7.02 (d, J = 8.1 Hz, 1H), 6.74 (t, J = 12.5 Hz, 2H), 6.09 (d, J = 13.5 Hz, 1H), 4.21 (t, J = 8.1 Hz, 2H), 3.93 (t, J = 7.7 Hz, 2H), 3.06 (t, J = 6.2 Hz, 2H), 2.19 – 2.12 (m, 2H), 1.78 (t, J = 7.7 Hz, 2H), 1.72 (s, 6H), 1.64 (s, 6H), 1.44 (d, J = 7.8 Hz, 2H), 1.34 (q, J = 3.8 Hz, 4H), 1.25 (s, 2H), 0.91 – 0.87 (m, 3H).
^{13}C- NMR (101 MHz, $CDCl_3$) δ 173.8, 154.0, 142.4, 141.1, 129.0, 128.7, 126.9, 125.5, 124.9, 122.4, 122.3, 111.1, 110.2, 102.9, 49.5, 44.4, 31.6, 28.3, 28.1, 27.4, 26.8, 22.9, 22.6, 14.1.

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