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Efficient One-Pot Three-Component Synthesis of Monomethine Cyanine Dyes with Quinoline Nucleus and Their Spectral Properties

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An improved method for the preparation of monomethine cyanine dyes with quinoline nucleus by one-pot three-component using 1-methyl-2-quinolinethione, quaternized 2- or 4-methylheterocyclic compounds and methyl *p*-toluenesulfonate as starting materials was described. Compared with the traditional methods, the new synthetic method reduced the reaction steps, shortened the reaction time, avoided the separation and purification of the intermediate and reduced cost. The dyes absorbed in the region 478.0-563.0 nm and had molar extinction coefficients of 1.3×10^4 - 9.4×10^4 L mol^{-1} cm^{-1}. Their fluorescence maxima and Stokes shifts were in the range of 525.2-594.4 nm and 16.2-80.6 nm in different solvents, respectively. From the spectral properties of the dyes in different solvents, it could be found that the λ_{max} of the dyes were shorter in protonic solvents, and showed hypsochromic shifts with the increase of polarity of the solvents.

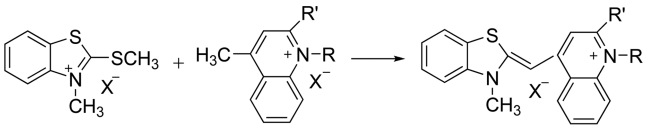
Key Words : Synthesis, Monomethine cyanine dyes, Quinoline nucleus, UV-Vis, Fluorescence

Introduction

Monomethine cyanine dyes have been known for a long time and are used in a variety of applications,[1] such as photosensitizers for silver halide emulsion,[2] bactericidal agents,[3] markers for flow cytometry[4] and phototherapeutic agents.[5,6] In recent years there has been extensive growth in the synthesis of cyanine dyes suitable as non-covalent labels for nucleic acid detection.[7-11] The synthesis of these cyanine dyes has therefore received considerable attention.

Most of the preparations of monomethine cyanine dyes are based on the method in which quaternary salts of heterocyclic 2- or 4-alkylthio compounds are reacted by heating in the presence of a basic reagent with a quaternary salt having a reactive methyl group.[12-16] Brooker and his coworkers reported the synthesis of some monomethine cyanine dyes by the reaction of 2-methylthiobenzothiazolium salts with 1-alkyl-4-methylquinolinium salts[17-19] (Scheme 1).

Moreover, Todor G. Deligeorgiev *et al.*[20] used 2-imino-3-methylbenzo thiazoline and 1-alkyl-4-methylquinolinium salts as starting materials for the preparation of the asymmetric monomethine cyanine dyes. Further, they prepared some monomethine cyanine dyes by heating together a sulfobetaine from an *N*-alkylheterocyclic compound and the quaternary salt of a heterocyclic 2- or 4-methyl compound (Scheme 2).[21]

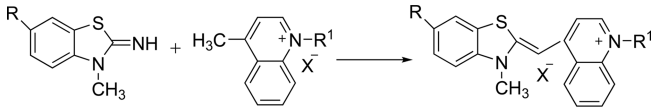


R = CH_3, C_2H_4I, C_6H_5, R' = H, Cl, $N(C_2H_5)_2$, OCH_3, X^- is acid radical ions

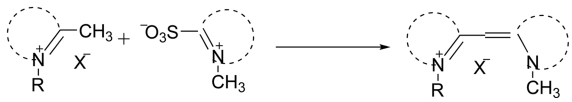
Scheme 1. Synthesis of some monomethine cyanine dyes by Brooker and co-workers.

Larive H. *et al.* synthesized some monomethine cyanine dyes by the condensation of quaternized 2-chloro-heterocycles with quaternized 2- or 4-methylheterocyclic compounds in the presence of a basic agent (Scheme 3).[22]

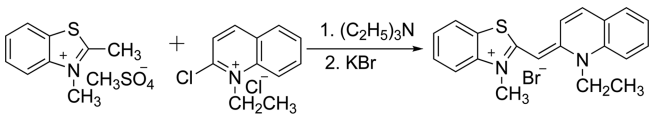
For the synthesis of monomethine dyes, Tariq Mahmood and his co-workers chose 10-methyl acridone as starting material and reacted with thionyl chloride afforded the corresponding 9-chloro-10-methylacridinium chloride, which was subsequently reacted with 1,3,3-trimethyl-2-methyleneindoline to produce the monomethine cyanine dye (Scheme 4).[23]



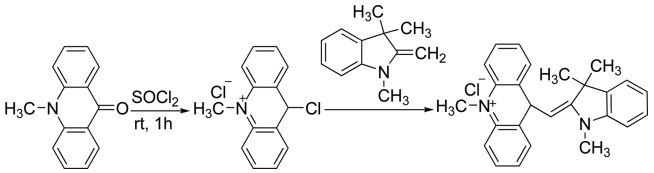
R = H, Cl, NO_2, CH_3O, CH_3CONH, HOC_2H_4O; R^1 = CH_3, C_2H_5 ,C_2H_4OH;
X = CH_3SO_4, ClO_4, Br, I



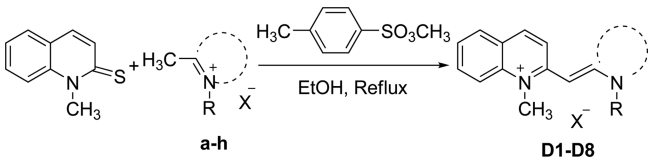
Scheme 2. Synthesis of some monomethine cyanine dyes by Todor G. Deligeorgiev and co-workers.



Scheme 3. Synthesis of some monomethine cyanine dyes by Larive H. and co-workers.



Scheme 4. Synthesis of some monomethine cyanine dyes by Tariq Mahmood and co-workers.



Scheme 5. Synthesis of some monomethine cyanine dyes **D1**-**D8** by the new methods.

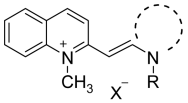
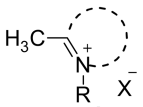
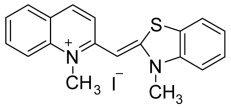
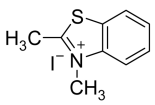
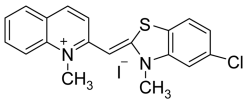
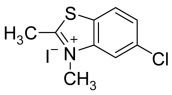
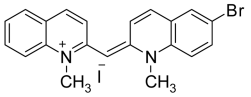
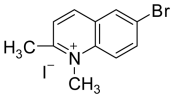
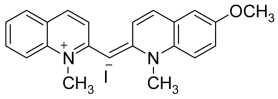
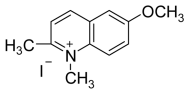
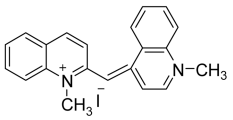
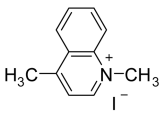
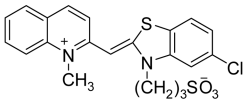
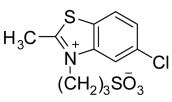
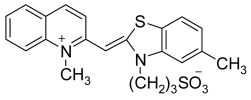
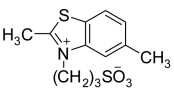
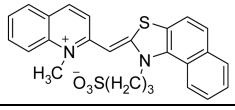
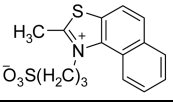
The continued interest in the development of the novel synthetic methods and the improvement of known synthetic procedures has attracted our attention. Herein, we report an efficient, simple and practical method for synthesis of some monomethine cyanine dyes, that is, using 1-methyl-2-quinolinethione, quaternized 2- or 4-methylheterocyclic compounds and methyl *p*-toluenesulfonate as starting materials by one-pot three-component method synthesizes some monomethine cyanine dyes with quinoline nucleus (Scheme 5, Table 1).

Experimental

General. Melting points were taken on a XT-4 micro-melting apparatus and uncorrected. IR spectra in cm^{-1} were recorded on a Brucker Equiox-55 spectrometer. ^1H NMR spectra were recorded at 400 MHz on a Varian Inova-400 spectrometer and chemical shifts were reported relative to internal Me_4Si. HRMS was recorded on a Brucker micr-OTOF-QMS spectrometer. The UV-Vis absorption spectra were recorded on a General TU-1201 UV-Vis spectrometer. Fluorescence measurements were taken on Hitachi F-4500 spectro- fluorometer.

Synthesis. Equimolar ratios (0.03 mol) of 1-methyl-2-quinolinethione, a quaternary heterocyclic salt (**a**~**h**) and methyl *p*-toluenesulfonate were dissolved in ethanol (50

Table 1. The molecular structures, reaction times, melting points, yields and appearance of dyes **D1-D8**

Dye	 D1-D8	 a-h	Time (h)	mp/°C	Yield (%)	Appearance
D1			6	285-286	30.7%	red crystal
D2			6	268-269	27.9%	orange crystal
D3			7	254-255	46.7 %	dark red crystal
D4			6	208-210	26.1%	red crystal
D5			7	282-283	34.7%	green crystal
D6			10	< 295	18.7%	dark red crystal
D7			10	< 295	21.1%	orange crystal
D8			11	< 295	20.9%	reddish-brown crystal

mL) and then a few drops of triethylamine were added. The reaction mixture was refluxed for reasonable time, and was filtered while hot. Then the mother liquor was concentrated to half its volume, and cooled to room temperature. The precipitate was filtered off and dried. The dyes **D1-D5** purified by recrystallization from methanol/ethanol, and dyes **D6-D8** were purified by soxhlet extraction using methanol/ethanol as solvent. The results were given in Table 1.

Spectral Behavior Studies. The dye stock solutions (2.5×10^{-3} mol L^{-1} in DMSO) were diluted with different solvents and resulted in working solutions of dyes (1.0×10^{-5} mol L^{-1}). The absorption spectra were examined at room temperature in different solvents and recorded using 1 cm quartz cells on a General TU-1900 UV-Vis spectrometer. Fluorescence measurements were carried out at room temperature on a Hitachi F-4500 spectrofluorimeter in 1 cm quartz cells. Fluorescence emission was excited at the maximum of the absorption. The absorption and fluorescence spectral data were listed in Table 4.

Structural Confirmations.

D1: UV-Vis (MeOH) λ_{max}: 481 nm. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.95 (s, 3H, N-CH_3), 4.13 (s, 3H, N^+CH_3), 6.17 (s, 1H, -CH=), 7.43 (t, J = 7.6 Hz, 1H, ArH), 7.62 (b, 2H, ArH), 7.79 (d, J = 8.4 Hz, 1H, ArH), 7.92 (t, J = 7.6 Hz, 1H, ArH), 8.04 (d, J = 7.6 Hz, 2H, ArH), 8.09 (d, J = 9.2 Hz, 1H, ArH), 8.15 (d, J = 8.8 Hz, 1H, ArH), 8.46 (d, J = 9.2 Hz, 1H, ArH). IR (KBr) ν: 3005 (w, $\nu_{=C-H}$) 1617, 1564 (s, $\nu_{C=C}$, $\nu_{C=N}$), 1473, 1439, 1393, 1274, 1232 (s, ν_{C-N}, δ_{C-H}), 735 (s, $\delta_{=C-H}$). HRMS (TOF MS ES-) calculated for $C_{19}H_{17}N_2S^+$: 305.1107; found: 305.1119.

D2: UV-Vis (MeOH) λ_{max}: 482 nm. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.91 (s, 3H, N-CH_3), 4.17 (s, 3H, N^+CH_3), 6.19 (s, 1H, -CH=), 7.47 (d, J = 8.8 Hz, 1H, ArH), 7.65-7.68 (m, 1H, ArH), 7.95 (b, 2H, ArH), 8.02 (d, J = 8.0 Hz, 1H, ArH), 8.07-8.11 (m, 2H, ArH), 8.20 (d, J = 8.8 Hz, 1H, ArH), 8.53 (d, J = 9.2 Hz, 1H, ArH). IR (KBr) ν: 3015 (w, $\nu_{=C-H}$), 1614, 1522 (s, $\nu_{C=C}$, $\nu_{C=N}$), 1469, 1440, 1386, 1271, 1231 (s, ν_{C-N}, δ_{C-H}), 876, 808, 738 (s, $\delta_{=C-H}$). HRMS (TOF MS ES-) calculated for $C_{19}H_{16}ClN_2S^+$: 339.0717; found: 339.0719.

D3: UV-Vis (MeOH) λ_{max}: 526 nm. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.93 (s, 3H, -N-CH_3), 4.06 (s, 3H, -N^+-CH_3), 5.84 (s, 1H, -CH=), 7.57-7.60 (m, 1H, ArH), 7.76-7.82 (m, 2H, ArH), 7.87-7.91 (m, 3H, ArH), 7.99 (d, J = 8.8 Hz, 2H, ArH), 8.06 (d, J = 8.0 Hz, 1H, ArH), 8.17 (s, 1H, ArH), 8.23 (d, J = 8.8 Hz, 1H, ArH). IR (KBr) ν: 3009 (w, $\nu_{=C-H}$), 2840 (w, ν_{C-H}), 1607, 1558, 1509 (s, $\nu_{C=C}$, $\nu_{C=N}$), 1474, 1439, 1351, 1288, 1249 (s, ν_{C-N}, δ_{C-H}), 863, 815, 737 (s, $\delta_{=C-H}$). HRMS (TOF MS ES-) calculated for $C_{21}H_{18}BrN_2^+$: 377.0648; found: 377.0638.

D4: UV-Vis (MeOH) λ_{max}: 531 nm. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.91 (b, 6H, N-CH_3, -OCH_3), 4.05 (s, 3H, N^+CH_3), 5.75 (s, 1H, -CH=), 7.48 (t, J = 8.0 Hz, 2H, ArH), 7.53 (s, 1H, ArH), 7.67 (d, J = 8.8 Hz, 1H, ArH), 7.77-7.91 (m, 4H, ArH), 7.98-8.02 (t, J = 8.8 Hz, 2H, ArH), 8.17 (d, J = 8.8 Hz, 1H, ArH). IR (KBr) ν: 3006 (w, $\nu_{=C-H}$), 1599, 1562, 1505 (s, $\nu_{C=C}$, $\nu_{C=N}$), 1451, 1332, 1281, 1224 (s, ν_{C-N}, δ_{C-H}), 903, 823, 736 (s, $\delta_{=C-H}$). HRMS (TOF MS ES-) calculated for $C_{22}H_{21}N_2O^+$: 329.1648; found: 329.1650.

D5: UV-Vis (MeOH) λ_{max}: 556 nm. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 4.03 (s, 3H, -NCH_3), 4.09 (s, 3H, -N^+CH_3), 6.51 (s, 1H, -CH=), 7.42 (d, J = 7.6 Hz, 1H, ArH), 7.53 (d, J = 6.8 Hz, 1H, ArH), 7.69 (b, 1H, ArH), 7.79-7.83 (m, 1H, ArH), 7.90-8.09 (m, 5H, ArH), 8.10 (d, J = 8.8 Hz, 1H, ArH), 8.25 (d, J = 6.8 Hz, 1H, ArH), 8.58 (d, J = 8.4 Hz, 1H, ArH). IR (KBr) ν: 3005 (w, $\nu_{=C-H}$), 1607, 1552, 1525, 1504 (s, $\nu_{C=C}$, $\nu_{C=N}$), 1474, 1434, 1351, 1279, 1252 (s, ν_{C-N}, δ_{C-H}), 819, 738 (s, $\delta_{=C-H}$). HRMS (TOF MS ES-) calculated for $C_{21}H_{19}N_2^+$: 299.1543; found: 299.1556.

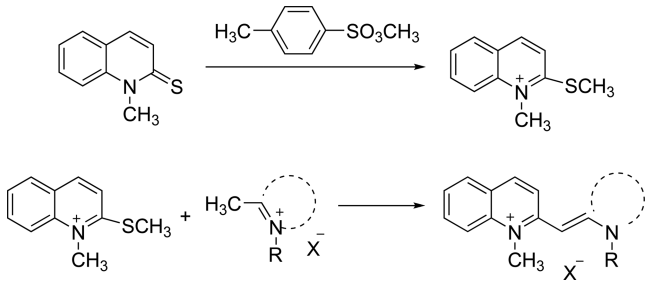
D6: UV-Vis (MeOH) λ_{max}: 483 nm. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.13 (b, 2H, -N-α-CH_2), 2.69 (b, 2H, -N-β-CH_3), 4.17 (s, 3H, -N^+CH_3), 4.80 (b, 2H, -N-δ-CH_2), 7.18 (s, 1H, -CH=), 7.36-7.42 (m, 2H, ArH), 7.60 (b, 1H, ArH), 7.72 (b, 1H, ArH), 7.86 (d, J = 8.0 Hz, 1H, ArH), 8.02 (b, 2H, ArH), 8.61 (d, J = 8.0 Hz, 1H, ArH), 9.11 (d, J = 8.4 Hz, 1H, ArH). IR (KBr) ν: 3022 (w, $\nu_{=C-H}$), 1608, 1564, 1510 (s, $\nu_{C=C}$, $\nu_{C=N}$), 1435, 1353, 1304, 1173 (s, ν_{C-N}, δ_{C-H}), 884, 800, 744 (s, $\delta_{=C-H}$). HRMS (TOF MS ES-) calculated for $C_{21}H_{19}ClNa\ N_2O_3S_2^+$: 469.0418; found: 469.0419.

D7: UV-Vis (MeOH) λ_{max}: 486 nm. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.12 (b, 3H, Ar-CH_3), 2.66 (b, 4H, -NCH_2CH_2), 4.18 (s, 3H, -N^+CH_3) 4.74 (b, 2H, -N-δ-CH_2) 6.54 (s, 1H, -CH=), 7.28 (s, 1H, ArH), 7.54-7.71 (m, 3H, ArH), 7.91 (b, 1H, ArH), 8.04 (b, 1H, ArH), 8.18 (b, 2H, ArH), 8.45 (s, 1H, ArH). IR (KBr) ν: 3025 (w, $\nu_{=C-H}$), 2946, 2921 (w, ν_{C-H}), 1619, 1516 (s, $\nu_{C=C}$, $\nu_{C=N}$), 1441, 1362, 1226 (s, ν_{C-N}, δ_{C-H}), 857, 803, 769 (s, $\delta_{=C-H}$). HRMS(TOF MS ES-) calculated for $C_{22}H_{23}N_2O_3S_2^+$: 427.1145; found: 427.1138.

D8: UV-Vis (MeOH) λ_{max}: 502 nm. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.90 (b, 4H, -NCH_2CH_2), 4.19 (s, 3H, -N^+CH_3) 5.15 (b, 2H, -N-δ-CH_2) 6.62 (s, 1H, -CH=), 7.60 (b, 1H, ArH), 7.71 (d, J = 7.2 Hz, 1H, ArH), 7.81 (b, 1H, ArH), 7.89 (b, 1H, ArH), 8.02 (t, J = 8.0 Hz, 2H, ArH), 8.09 (b, 1H, ArH), 8.15-8.23 (m, 3H, ArH), 8.41 (d, J = 9.2 Hz, 1H, ArH), 8.64 (d, J = 9.2 Hz, 1H, ArH). IR (KBr) ν: 3073 (w, $\nu_{=C-H}$), 1615, 1561, 1513 (s, $\nu_{C=C}$, $\nu_{C=N}$), 1404, 1365, 1290, 1253 (s, ν_{C-N}, δ_{C-H}), 837, 736 (s, $\delta_{=C-H}$). HRMS (TOF MS ES-) calculated for $C_{25}H_{23}N_2O_3S_2^+$: 463.1145, found: 463.1140.

Results and Discussion

Synthesis of Dyes. The traditional methods of the preparations of 2-quinoline monomethine cyanine dyes were as follows: The quaternary salts of 2-alkylthio quinoline heterocyclic compounds, which were prepared by the methyl *p*-toluenesulfonate or iodomethane and 1-methyl-2-quinolinethione, were reacted with quaternized 2- or 4-methyl-heterocyclic compounds to produce the monomethine cyanine dyes (Scheme 6). We found that the preparation of monomethine cyanine dyes with quinoline nucleus could be carried out by one-pot three-component method using 1-methyl-2-quinolinethione, the quaternary salt of a heterocyclic 2- or 4-methyl compound and methyl *p*-toluenesulfonate as starting materials in ethanol and with the presence of triethylamine. It can be seen that the traditional



Scheme 6. The traditional methods of the preparations of 2-quinoline monomethine cyanine dyes.

methods of the preparation of 2-quinoline monomethine cyanine dyes need two steps and our new method only need one step. And the new methods will reduce the synthetic steps, shorten the reaction time and avoid the separation and purification of the intermediate.

In order to get optimized experiment conditions, the effect of reaction time in ethanol on yields was examined. Table 2 listed the effect of reaction time on the yields of dye **D1**. The reaction yield was lower at first, and then the yield of the dye was increased with the increasing of reaction time. Until the reaction time reached to 7 h, the yield of the dye began to decrease. Therefore the optimized reaction time was 6 h. In addition, supplementary experiments were carried out to find the optimal catalysts. The piperidine or triethylamine was used as catalyst in the synthesis and the effect of the two kinds of catalysts on the yields of dyes **D1-D8** was shown in Table 3. From the table, the effect of triethylamine was better than that of piperidine. That was because the alkaline of piperidine was stronger than that of triethylamine, and in the presence of piperidine the reactive methyl groups in quaternary salts rapidly transformed to methylene form, at this time the alkylthio was not yet formed, leading to unexpected products.

Table 2. The effect of reaction time on the yields of dye **D1**

Time (h)	Yield (%)
1	12.4
2	13.5
3	16.0
4	22.3
5	28.6
6	30.7
7	30.5

Table 3. The effect of catalysts on the yields of dyes **D1-D8**

Dye	Time (h)	Piperidine Yield (%)	triethylamine Yield (%)
D1	6	11.2%	30.7%
D2	6	11.6%	27.9%
D3	6	11.7%	46.7%
D4	7	23.2%	26.1%
D5	7	11.7%	34.7%
D6	10	4.3%	18.7%
D7	10	8.8%	21.1%
D8	11	9.0%	20.9%

Spectral Properties of Dyes. The absorbance and fluorescence properties of dyes **D1-D8** in different solvents were summarized in Table 4. It could be found that the maximum absorption (λ_{max}) of **D1-D8** was located at 478.0-563.0 nm in different solvents and a blue shift of the λ_{max} occurred in the protonic solvents compared with aprotic solvents (*e.g.*

Table 4. Spectral characteristics of dyes **D1-D8** in different solvents

Dye	Solvent	λ_{max} (nm)	ε ($\times 10^4$ L mol^{-1}cm^{-1})	$\lambda_{ex}/\lambda_{em}$ (nm)	Stocks shifts (nm)
D1	H_2O	478.0	5.23	478.0/539.6	61.6
	EtOH	484.0	5.50	484.0/534.4	50.4
	MeOH	481.0	6.01	481.0/531.6	50.6
	DMSO	489.0	6.26	489.0/552.2	63.2
	$CHCl_3$	496.0	4.73	496.0/553.6	57.6
D2	H_2O	481.0	3.67	481.0/561.6	80.6
	EtOH	484.0	5.05	484.0/525.2	41.2
	MeOH	482.0	5.50	482.0/560.6	78.6
	DMSO	488.0	5.22	488.0/554.2	66.2
	$CHCl_3$	496.0	4.91	496.0/555.8	59.8
D3	H_2O	526.0	5.66	526.0/561.6	35.6
	EtOH	528.0	6.53	528.0/567.6	39.6
	MeOH	526.0	6.71	526.0/567.2	41.2
	DMSO	534.0	5.85	534.0/566.2	32.2
	$CHCl_3$	538.0	5.93	538.0/575.0	37.0
D4	H_2O	530.0	5.85	530.0/567.6	37.6
	EtOH	533.0	6.93	533.0/575.0	42.0
	MeOH	531.0	7.48	531.0/571.8	40.8
	DMSO	539.0	6.57	539.0/571.2	32.2
	$CHCl_3$	542.0	6.59	542.0/576.2	34.2
D5	H_2O	554.0	5.12	554.0/594.4	40.4
	EtOH	558.0	8.79	558.0/574.2	16.2
	MeOH	556.0	9.41	556.0/581.6	25.6
	DMSO	563.0	7.96	563.0/589.8	26.8
	$CHCl_3$	563.0	8.49	563.0/587.2	24.2
D6	H_2O	481.0	1.59	481.0/–	–
	EtOH	485.0	1.39	485.0/–	–
	MeOH	483.0	1.35	483.0/–	–
	DMSO	488.0	1.33	488.0/527.6	39.6
	$CHCl_3$	495.0	1.43	495.0/555.8	60.8
D7	H_2O	481.0	3.18	481.0/–	–
	EtOH	488.0	4.43	488.0/543.6	55.6
	MeOH	486.0	4.48	486.0/–	–
	DMSO	490.0	4.37	490.0/543.2	53.2
	$CHCl_3$	498.0	4.44	498.0/554.0	56.0
D8	H_2O	502.0	1.75	502.0/–	–
	EtOH	504.0	3.97	504.0/565.8	61.8
	MeOH	502.0	4.01	502.0/–	–
	DMSO	507.0	3.93	507.0/553.2	46.2
	$CHCl_3$	516.0	3.78	516.0/566.0	50.0

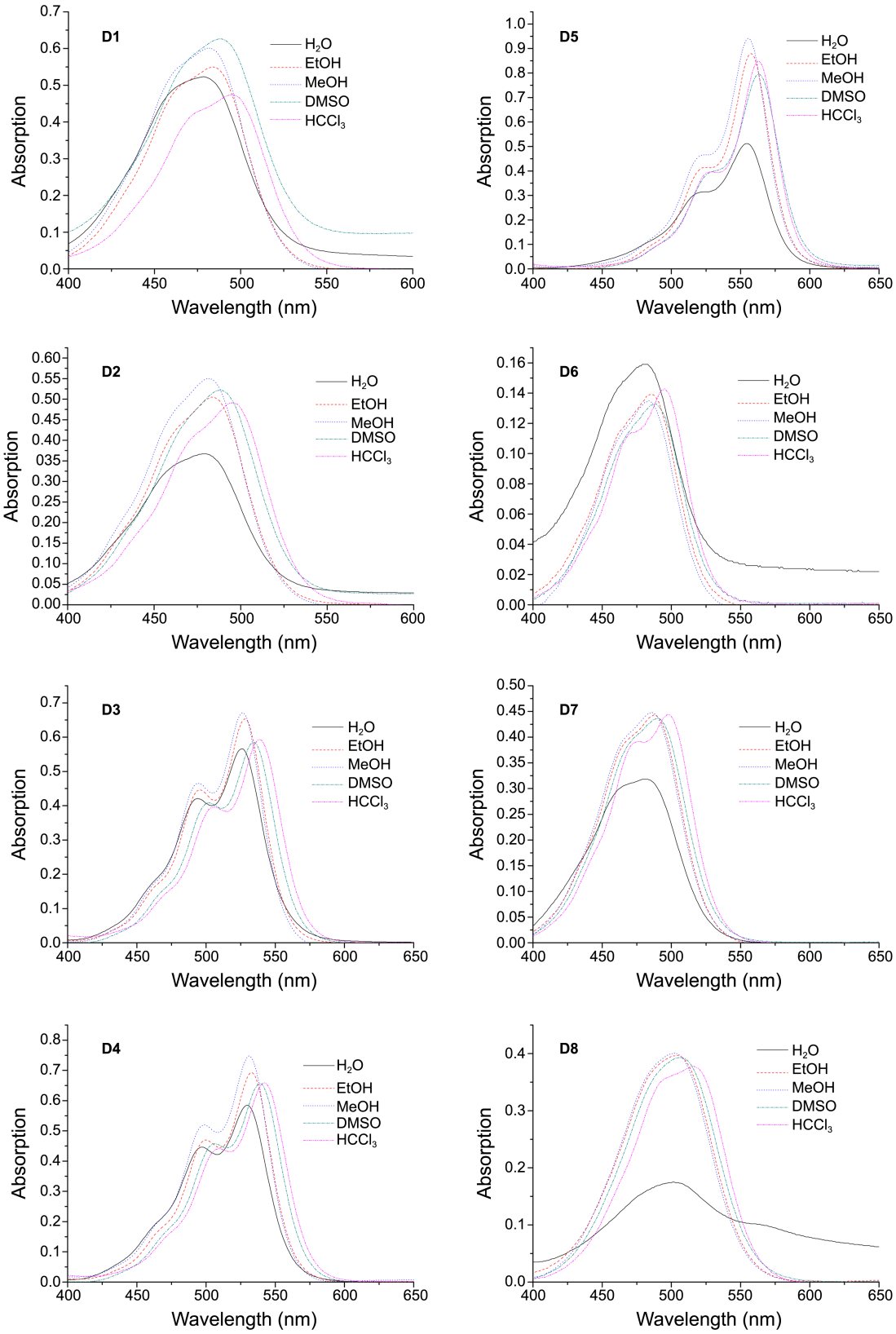


Figure 1. Absorption spectra of dyes **D1-D8** in different solvents.

D1: λ_{max} in H_2O, MeOH, EtOH was 478.0 nm, 481.0 nm and 484.0 nm, respectively; λ_{max} in DMSO and chloroform was 489.0 nm and 496.0 nm). These properties might be due to hydrogen-bonding interaction between the protonic solvents and the dye molecules, which made the transition energy difference between the ground state and the first excited

state increase, leading to a blue shift in the absorption spectra.[24] From the Table 4, it could also be found, almost all the dyes (except **D3** and **D8**), displayed a blue shift in the absorption spectra with increasing the polarity of the solvent in the protonic solvents. These hypsochromic shifts were most likely explained as follows: since these dyes were ionic dyes, which exhibited a polar character in the ground state, hence the solvent molecules were oriented in such a way as required by the polar character of the dye molecule. During the transition, the excited dye molecules were within a solvent cage which was suitable for the electronic distribution in the ground state molecule and no longer adopted to the electronic requirements of the excited molecules. Thus, a polar solvent created a stabilizing solvent cage around this ionic dye molecule in the ground state, but a destabilizing solvent cage for the excited state. The transition energy was increased with increasing solvent polarity and an increase in solvent polarity resulted in a blue shift in the absorption spectra.[25] In the aprotic solvents, it was the same case.

The absorption spectra of dyes **D1-D8** in the different solvent were shown in Figure 1. It could be found that the λ_{max} of dyes had minor differences in different solvents, but the absorption band shapes of dyes were almost the same. The result showed that the distribution of energy level at the first electronic excited state was not changed by the different solvents for the dyes. It could also be seen that different dyes had different existence forms in solvents and these existence forms were not changed by the change of solvents. Take **D1** and **D3** for example, the existence form of **D1** in different solvents was mainly under both the monomeric form (M) and the aggregate form (H), and the existence form of **D3** in different solvents was mainly under its monomeric form and the aggregate form was relative smaller.

During our experiment, it was found that the fluorescence of dyes **D1-D8** in different solvent was much weak, even in some solvents, the fluorescence of dyes **D6-D8** could not be observed. To be specific, the fluorescence of dyes **D1-D5** could be observed in five different solvents; the fluorescence of dyes **D7-D8** could be observed only in ethanol, DMSO, chloroform and the fluorescence of dyes **D6** could be observed only in DMSO, chloroform. From Table 4, it could be found that the maximum emission of **D1-D5** was located at 525.2-594.4 nm and compared with the position of the maximum absorption for the dyes, the emission spectra were shifted to the red in the range of 16.2-80.6 nm (namely Stokes shift). The different heterocycle which was the composition of dyes effected the Stokes shifts of the dyes. For example, the Stokes shifts of **D1** and **D2** were 61.6 and 80.6 nm in the water, respectively, but the Stokes shifts of **D3** and **D4** were only 35.6 and 37.6 nm in the water, respectively. In the other solvents, the same condition also could be observed.

Conclusion

Eight monomethine cyanine dyes were synthesized by one-pot three-component method and characterized by ^{1}H NMR, IR, UV-Vis and HRMS spectroscopy. Compared with the traditional methods, the new synthetic method reduced the reaction steps, shortened the reaction time, avoided the separation and purification of the intermediate and reduced costs. The investigations of UV-Vis showed a solvent dependent absorption. The λ_{max} of dyes was shorter in protic solvents, and showed blue-shifted with the increasing polarity of the solvents.

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