Microwave-assisted Solvent-free Synthesis of Some Dimethine Cyanine Dyes, Spectral Properties and TD-DFT/PCM Calculations

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A series of dimethine cyanine dyes were synthesized in a fast, efficient and high yield by the condensation of quaternary salts with 1H-indole-3-carbaldehyde in the presence of piperidine under solvent-free microwave irradiation. The products were identified by ^{1}H NMR, IR, UV-Vis spectra and elemental analysis. The absorption and fluorescence properties of these dyes were investigated both experimentally and theoretically. Calculations performed at a combination of time-dependent density functional theory (TD-DFT) and the polarizable continuum model (PCM) reproduced the π-π^* type absorption bands of the dyes. Regression analysis was used for studying theoretical results of the absorption maxima in different solvents. Compared with experimental counterparts, estimated overall uncertainties in the absorption maxima were about ±2%.

Key Words : Dimethine cyanine dye, Microwave irradiation, UV-Vis spectrum, TD-DFT/PCM

Introduction

Methine cyanine dyes are among the most important organic functional dyes. They are widely used as photographic sensitizers,[1] as optical recording materials in laser disks[2] and, as sensitizers in solar cell.[3] With the development of relative technology, methine cyanine dyes have been studied as photodynamic therapy tools,[4] fluorescent labels and probes for cells, micelles and organelles.[5-7] The dimethine cyanine or hemicyanine dyes are usually prepared by refluxing the mixture of aromatic aldehyde, a quaternary salt with reactive methyl group and catalyst in organic medium.[8] This preparation has substantial drawbacks, such as relatively strenuous reaction conditions namely refluxing reactants for several hours in organic solvents, a lot of organic solvents to be not friendly to environment and complexity of isolation of the products.

Microwave irradiation presents a powerful tool toward organic reactions. Solvent-free microwave irradiation is well known as environmentally benign method, which offers several advantages including shorter reaction times, cleaner reaction profiles and simple experimental/product isolation procedures.[9] In this paper a microwave-assisted preparation of a series of dimethine cyanine dyes *via* condensation of quaternary salts having reactive methyl and 1H-indole-3-carbaldehyde without solvent was described in high yield (Scheme 1). The approach provided an attractive and environmentally friendly pathway to several synthetically useful dimethine cyanine dyes.

A further objective of this study is to establish the structure-color relationships of prepared dimethine cyanine dyes. Among a variety of quantum chemistry techniques, TD-DFT[10,11] has been rapidly emerging for the transition energy predictions in the UV-Vis region of electronic spectra. TD-DFT calculations of excited states of large organic molecules[12,13] and the chromophoric properties of organic dyes[14] have been made accessible for practical applications.

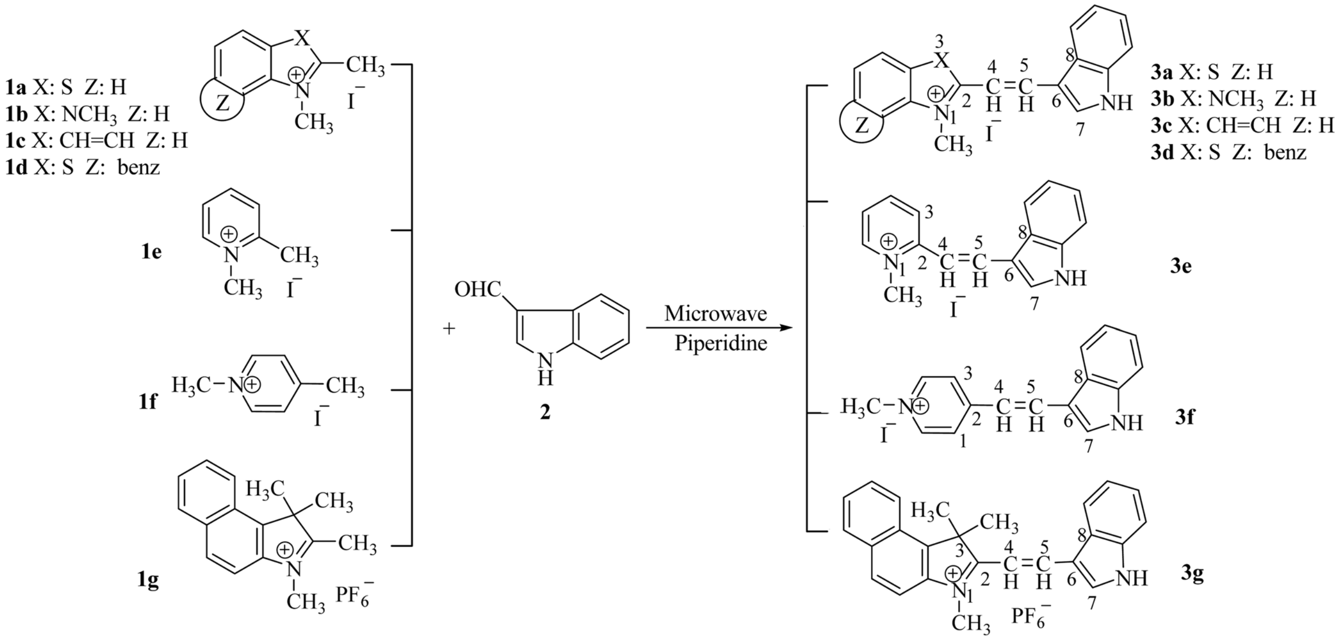
This paper is organized as follows. In the next section, the synthesis and the experimental characterizations of some dimethine cyanine dyes are described. Next, the computational procedure is outlined, followed by geometric structures and fluorescence. In particular, we focused on the investigation of the different calculation method of the $\lambda_{\max}$ of the target compounds and regression analysis used for studying theoretical results of the $\lambda_{\max}$ in different solvents. We also analyzed computationally the UV-Vis spectral characteristics of these dimethine cyanine dyes by means of TD-DFT/PCM calculations. The final section summarizes this article.

Experimental

Measurements. Melting points were taken on a XT-4 micromelting apparatus and uncorrected. Elemental analyses were performed with Vario EL-III instrument. IR spectra in cm^{-1} were recorded on a Bruker Equiox-55 spectrometer. ^{1}H NMR spectra were recorded at 400 MHz on a Varian Inova-400 spectrometer and chemical shifts were reported relative to internal Me_4Si. The absorption spectra were recorded on a Shimadzu UV-1700 UV-Vis spectrometer. Fluorescence measurements were carried out on an Hitachi F-4500 spectrofluorimeter.

Preparation of the quaternary salts 1a-1g having reactive methyl group. 1,2-Dimethyl benzothiazolium iodide, 1,2-dimethyl quinolium iodide, 1,2-dimethyl-β-naphthothiazolium iodide, 1,2,3-trimethyl benzimidazolium iodide, 1-methyl-2-picolinium iodide, 1-methyl-4-picolinium iodide and 1,2,3,3-tetramethyl benzindolium hexfluorin phosphate were prepared according to the literatures.[15-19]

Preparation of the dimethine cyanine dyes 3a-3g. The condensation of seven quaternary salts having reactive methyl with 1H-indole-3-carbaldehyde was carried out in a



Scheme 1

Galanz microwave oven. 1 mmol quaternary salts, 1mmol 1H-indole-3-carbaldehyde and a few drops of piperidine were mixed together at ambient temperature in a glass conical flask (100 mL). The mixture was subjected to microwave irradiation at optimized power and time under solvent-free conditions. After cooling, the reaction mixture was recrystallized form EtOH-H_2O to afford pure dyes **3a**-**3g**. The details of reaction conditions and yields are provided in Table 1.

3-[2-(1-Methyl-benzothiazolium-2-yl)-vinyl]-1H-indole iodide (**3a**): orange crystals. mp 272-273 °C. ^{1}H NMR (400 MHz, CH_3COCH_3-d_6) δ 4.32 (s, 3H, N^+CH_3), 7.36-7.40 (m, 2H, ArH, CH=CH), 7.69 (t, 1H, J = 8.0 Hz, ArH), 7.76 (t, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 2H, ArH), 7.88 (t, 1H, J = 8.0 Hz, ArH), 8.19 (d, 1H, J = 8.4 Hz, ArH), 8.24 (d, 1H, J = 8.0 Hz, ArH), 8.30 (d, 1H, J = 8.0 Hz, ArH), 8.43 (s, 1H, pyrrole-H), 8.60 (d, 1H, J = 15.6 Hz, CH=CH). IR (KBr) υ: 3445, 3140, 1594, 1568, 1427, 1396, 939, 750 cm^{-1}. Anal. Calcd. for $C_{18}H_{15}N_2SI$ = 418.30: C, 51.69; H, 3.61; N, 6.70; Found: C, 51.80; H, 3.52; N, 6.78.

3-[2-(1,3-Dimethyl-benzimidazolium-2-yl)-vinyl]-1H-indole iodide (**3b**): yellow crystals. mp >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.15 (s, 6H, NCH_3), 7.15 (d, J = 16.4 Hz, 1H, CH=CH), 7.26-7.32 (m, 2H, ArH, CH=CH), 7.54-7.56 (m, 1H, ArH), 7.64-7.67 (m, 2H, ArH), 7.99-8.04 (m, 2H, ArH), 8.08 (s, 1H, pyrrole-H), 8.18-8.20 (m, 2H, ArH), 12.08 (s, 1H, NH). IR (KBr) υ: 3445, 3135, 1617, 1510, 1476, 1425, 983, 732 cm^{-1}. Anal. Calcd. for $C_{19}H_{18}N_3I$ = 415.28: C, 54.95; H, 4.37; N, 10.12; Found: C, 54.66; H, 4.18; N, 9.98.

Table 1. The reaction conditions and yields for the dyes

Dye	Power (W)	Time (min)	Yield (%)
3a	252	3	69
3b	700	2	72
3c	173	2	95
3d	252	2	65
3e	173	9	92
3f	173	10	95
3g	567	8	88

3-[2-(1-Methyl-quinolium-2-yl)-vinyl]-1H-indole iodide (**3c**): brown crystals. mp 264-265 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.48 (s, 3H, N^+CH_3), 7.31-7.33 (m, 2H, ArH, CH=CH), 7.56-7.60 (m, 2H, ArH), 7.85 (t, 1H, J = 8.0 Hz, ArH), 8.09 (t, 1H, J = 8.0 Hz, ArH), 8.21-8.27 (m, 2H, ArH), 8.40 (s, 1H, pyrrole-H), 8.46 (d, J = 9.2 Hz, 1H, ArH), 8.60-8.68 (m, 2H, ArH, CH=CH), 8.84 (d, J = 9.2Hz, 1H, ArH), 12.34 (s, 1H, NH). IR (KBr) υ: 3447, 3133, 1592, 1568, 1508, 1463, 1427, 958, 747 cm^{-1}. Anal. Calcd. for $C_{20}H_{17}N_2I$ = 412.27: C, 58.27; H, 4.16; N, 6.79; Found: C, 58.09; H, 4.11; N, 6.63.

3-[2-(1-Methyl-β-naphthothiazolium-2-yl)-vinyl]-1H-indole iodide (**3d**): orange crystals. mp 226-227 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.72 (s, 3H, N^+CH_3), 7.33-7.35 (m, 2H, ArH, CH=CH), 7.57 (s, 1H, ArH), 7.65 (d, 1H, J = 16.0 Hz, CH=CH), 7.82-7.91 (m, 2H, ArH), 8.24-8.30 (m, 3H, ArH), 8.35 (d, 1H, J = 8.4 Hz, ArH), 8.44 (d, 1H, J = 16.0 Hz, CH=CH), 8.47 (s, 1H, pyrrole-H), 8.94 (d, 1H, J = 8.4 Hz, ArH), 12.45 (s, 1H, NH). IR (KBr) υ: 3446, 3067, 1595, 1567, 1469, 1428, 1397, 995, 917, 797, 727 cm^{-1}. Anal. Calcd. for $C_{22}H_{17}N_2SI$ = 468.35: C, 56.42; H, 3.66; N, 5.98; Found: C, 56.25; H, 3.47; N, 5.87.

3-[2-(1-Methyl-pyridium-2-yl)-vinyl]-1H-indole iodide (**3e**): yellow crystals. mp 274 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.34 (s, 3H, NCH_3), 7.23-7.30 (m, 3H, one CH=CH, two ArH), 7.53 (d, 1H, J = 6.8 Hz, ArH), 7.70 (t, 1H, J = 8.0 Hz, ArH), 8.12-8.15 (m, 2H, pyrrole-H, pyridinio-H), 8.36 (t, 1H, J = 8.0 Hz, pyridinio-H), 8.29 (d, 1H, J = 15.6 Hz, CH=CH), 8.52 (d, 1H, J = 8.4 Hz, pyridinio-H), 8.77 (d, 1H, J = 6.8 Hz, pyridinio-H), 12.06 (s, 1H, NH). IR (KBr) υ: 3466, 3162, 3033, 1610, 1563, 1499, 1455, 1428, 951, 741 cm^{-1}. Anal. Calcd. for $C_{16}H_{15}N_2I$ = 362.21: C, 53.06; H, 4.17; N, 7.73; Found: C, 52.90; H, 3.98; N, 7.58.

3-[2-(1-Methyl-pyridium-4-yl)-vinyl]-1H-indole iodide (**3f**): orange crystals. mp 277-278 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.18 (s, 3H, N^+CH_3), 7.22-7.33 (m, 3H, one CH=CH, two ArH), 7.52 (d, 1H, J = 7.6 Hz, ArH), 7.99 (s, 1H, pyrrole-H), 8.13 (d, 2H, J = 6.0 Hz, pyridinio-H), 8.17 (d, 1H, J = 8 Hz, ArH), 8.25 (d, 1H, J = 15.6 Hz, CH=CH), 8.69 (d, 2H, J = 6.0 Hz, pyridinio-H), 11.96 (s, 1H, NH). IR (KBr) υ: 3419, 3178, 3028, 1606, 1561, 1501, 1457, 1420, 953, 763, 736 cm^{-1}. Anal. Calcd. for $C_{16}H_{15}N_2I$ = 362.21: C, 53.06; H, 4.17; N, 7.73; Found: C, 52.85; H, 3.87; N, 7.54.

3-[2-(1,3,3-Trimethyl-4,5-benzindolium-4-yl)-vinyl]-1H-indole iodide (**3g**): red crystals. mp 253-254 °C. ^{1}H NMR (400 MHz, CH_3COCH_3-d_6) δ 2.19 (s, 6H, $C(CH_3)_2$), 4.33 (s, 3H, N^+CH_3), 7.43-7.45 (m, 2H, ArH), 7.50 (d, 1H, J = 15.6 Hz, CH=CH), 7.67-7.72 (m, 2H, ArH), 7.79 (t, 1H, J_1 = 8.8 Hz, J_2 = 6.8 Hz, ArH), 8.03 (d, 1H, J = 8.8 Hz, ArH), 8.19 (d, 1H, J = 7.6 Hz, ArH), 8.26-8.31 (m, 2H, ArH), 8.45 (d, 1H, J = 8.8 Hz, ArH), 8.63 (s, 1H, pyrrole-H), 9.00 (d, 1H, J = 15.6 Hz, CH=CH). IR (KBr) υ: 3397, 3087, 3030, 2995, 2913, 1593, 1573, 1487, 1433, 1404, 968, 943, 833 cm^{-1}. Anal. Calcd. for $C_{25}H_{23}N_2PF_6$ = 496.44: C, 60.48; H, 4.64; N, 5.65; Found: C, 60.31; H 4.39; N, 5.63.

Determination of absorption and fluorescence properties. The absorption spectra of the prepared dimethine cyanine dyes were examined at room temperature in methanol and recorded using 1 cm quartz cells on a Shimadzu UV-1700 UV-Vis spectrometer. Fluorescence measurements were carried out at room temperature on an Hitachi F-4500 spectrofluorimeter in methanol in 1 cm quartz cells. Excitation maximum was fixed by 3D-fluorescence spectra. A stock solution (10^{-3} mol/L) of the dyes diluted to a suitable volume in order to obtain the required concentrations. The absorption and fluorescence spectral data are listed in Table 2.

Table 2. Absorption and fluorescence spectra data of the dyes in methanol

Dye	Absorption		Fluorescence	
	λ_{max} (nm)	$\varepsilon \times 10^{-4}$ ($L \cdot mol^{-1}cm^{-1}$)	λ_{ex} (nm)	λ_{em} (nm)
3a	465.0	5.6	465.0	521.6
3b	376.0	1.8	376.0	–
3c	474.0	5.0	474.0	548.6
3d	470.0	4.9	469.0	540.6
3e	422.0	3.1	424.0	512.6
3f	436.0	3.8	436.0	540.6
3g	484.0	5.7	487.0	537.6

Results and Discussion

Synthesis. In all cases investigated, we found that the dimethine cyanine dyes formation reactions proceeded efficiently with high to excellent in short reaction time (Table 1) and reactions proceeded well even when both the starting reactants were solids and the reaction temperature was maintained below the melting points of both components using the microwave-assisted strategy. A series of dimethine cyanine dyes were successfully synthesized with high yields 65-95% within 2-10 min when a mixture of 1 mmol quaternary salts, 1 mmol 1H-indole-3-carbaldehyde and a few drops of piperidine was subjected to microwave irradiation at 173-700 watts under solvent-free conditions. The products could be easily purified by recrystallization from EtOH-H_2O. Besides, the waste disposal of solvents and excess chemicals in classical synthesis of dimethine cyanine dyes was avoided or minimized.

In order to get optimized experiment conditions, we examined the effect of microwave power and irradiation time on yield. The results are listed in Table 1. It could be found that the sequence of the reaction activity for 1H-indole-3-carbaldehyde and various heterocyclic quaternary salts was **1c** ≈ **1e** ≈ **1f** > **1d** ≈ **1a** > **1g** > **1b**. The reason was suggested that the electron-withdrawing ability of the group attached to carbon of $C=N^+$ was –C=C– > –S– > $-C(CH_3)_2-$ > $-N(CH_3)-$, leading to the order of the hydrogen' activity and the carbon' nucleophilicity of reactive methyl in investigated heterocyclic quaternary salts was **1c** ≈ **1e** ≈ **1f** > **1d** ≈ **1a** > **1g** > **1b**. The stronger the carbon' nucleophilicity of reactive methyl is, the easier the condensation of quaternary salts with 1H-indole-3-carbaldehyde is.

Structural confirmations. The structure of the prepared dimethine cyanine dyes was confirmed by elemental analysis, UV-Vis absorption spectra, IR and ^{1}H NMR. IR spectra of dyes **3a-3g** shows typical aromatic absorption ($\upsilon_{=C\text{-}H}$, 3178-3028 cm^{-1}, $\upsilon_{C=C}$, 1617-1568 (s) cm^{-1}, $\delta_{=CH}$, 995-727 cm^{-1}), resonance conjugated unsaturated stretching modes in the chromophore (C=C, C=N, 1510-1396 cm^{-1}) and the absorption of indole ring (υ_{NH} 3466-3397 cm^{-1}). The ^{1}H NMR chemical shift data and the UV-Vis absorption spectra (Table 2) are in accordance with the structures of dyes **3a-3g**.

The IR spectrum of dye **3a** shows absorption bands at 3445 cm^{-1} (υ_{NH}), 3140 cm^{-1} ($\upsilon_{=C\text{-}H}$), 1594 cm^{-1}, 1568 cm^{-1}, 1427 cm^{-1} and 1396 cm^{-1} ($\upsilon_{C=C}$, $\upsilon_{C=N}$, resonance conjugated unsaturated stretching mode), 939 cm^{-1}, 750 cm^{-1} ($\delta_{=CH}$). ^{1}H NMR (400 MHz, CH_3COCH_3-d_6) of dye **3a** shows signals at 4.32 ppm (s, 3H, N^+CH_3), 7.36-7.40 ppm (m, 2H, ArH, CH=CH), 7.69 ppm (t, 1H, J = 8.0 Hz, ArH), 7.76 ppm (t, 2H, J_1 = 4.0 Hz, J_2 = 8.0 Hz, ArH), 7.88 ppm (t, 1H, J = 8.0 Hz, ArH), 8.19 ppm (d, 1H, J = 8.4 Hz, ArH), 8.24 ppm (d, 1H, J = 8.0 Hz, ArH), 8.30 ppm (d, 1H, J = 8.0 Hz, ArH), 8.43 ppm (s, 1H, pyrrole-H), 8.60 ppm (d, 1H, J = 15.6 Hz, CH=CH).

Absorption and fluorescence properties. The absorption and fluorescence spectral data recorded on these dimethine cyanine dyes in methanol are listed in Table 2. Dyes **3a-3g**

absorb in the region 376.0-484.0 nm and have molar absorptivity values of 18000-57000 L·mol^{-1}cm^{-1}. They show intense and broad absorption with high extinction coefficients in methanol. The dimethine cyanine dyes also exhibit fluorescence properties in methanol at room temperature except **3b**. Their fluorescence maxima are located at 512.6-548.6 nm. Compared with the position of the excitation maximum for the dyes, the emission spectra are shifted to the red in the range of 50-90 nm. From Table 2, it can also been found that the sequence of the $\lambda_{\max}$ is **3g** > **3c** > **3d** > **3a** > **3f** > **3e** > **3b**. The order of the basicity of heterocyclic nuclei used in experiment is benzindole < quinoline < thiazole < 2-picoline < 4-picoline < benzimidazole. Therefore increasing $\lambda_{\max}$ is considered to indicate decreasing basicity of heterocyclic nucleus. Benzimidazole appears to be the most strongly basic nucleus and the benzindole nucleus the least in the heterocyclic nuclei used in our experiment. Consequently, the minimum $\lambda_{\max}$ is 376.0 nm for benzimidazole dye **3b** and the $\lambda_{\max}$ reaches a maximum value of 484.0 nm for benzindole dye **3g** in methanol solvent.

Computational

In this work, the ground-state geometries, the lowest energy transitions and the absorption spectra were calculated with adiabatic approximation of the TD-DFT using two hybrid exchange-correlation functionals, B3LYP[20] and PBE1PBE,[21] including 20% and 25% of Hartree-Fock (HF) exchange, respectively. The geometries were fully optimized at the DFT level using 6-31G* basis set. We also took into account the solvent polarity effects and adopted the PCM model at the B3LYP/6-31G* and PBE1PBE/6-31G* level respectively. In this model, the dye molecule is embedded in a cavity surrounded by an infinite dielectric with the value of the desired solvent ($\varepsilon = 4.90$, $\varepsilon = 24.55$, $\varepsilon = 32.63$, $\varepsilon = 46.70$ and $\varepsilon = 78.39$ for chloroform, ethanol, methanol, DMSO and water respectively). In our calculation, the anion was neglected as the experiment proved that the anion would not affect the spectra of the cationic dyes in the solvent. Calculations of the vertical excitation energies and oscillator strengths in low-lying singlet excited states were carried out using TD-DFT/PCM method. Analytic frequency calculations were done to confirm the optimized structures to be an energy minimum. All calculations reported in this work were carried out with the Gaussian 03 program.[22]

Geometric structures and fluorescence. The geometries of seven dimethine cyanine dyes were fully optimized with the PBE1PBE/PCM method in methanol. From our calculation, it can be found that the carbon-carbon bond lengths on seven dyes molecular skeleton are intermediate between typical C–C single (0.154 nm) and C=C double (0.134 nm) bonds, and carbon-nitrogen bond lengths are also intermediate between typical C–N single (0.147 nm) and C=N double (0.127 nm) bonds. All C–C–C bond angles are close to 120°. It indicates that the π electrons in seven dyes molecule are delocalized. Table 3 lists some selected dihedral angles of seven dyes molecule. From Table 3, we can see that: (1) the molecular frameworks of dyes **3f** and **3g** are planar, and their fluorescence intensity is strong; (2) the molecular frameworks of dyes **3e**, **3a** and **3d** are slightly distorted, and their fluorescence intensity is lower than that of dyes **3f** and **3g**; (3) dyes **3b** and **3c** are of bad planar structure, their fluorescence intensity is weak, and **3b** has almost no fluorescence. The reason is that the compound can emit fluorescence is closely related to the molecular structure, the better planar structural rigidity and the larger π conjugated system of the molecular, the stronger fluorescence it appeared.[23]

Table 3. The dihedral angles (°) and relative fluorescence intensity of the dimethine cyanine dyes

Dyes	D(1,2,4,5)[a]	D(3,2,4,5)[a]	D(4,5,6,7)[a]	D(4,5,6,8)[a]	Intensity[b]
3a	−174.7	6.3	2.0	−178.1	13.29
3b	−147.5	33.1	6.6	−174.2	–
3c	32.86	−147.25	6.5	−174.5	4.39
3d	167.7	−13.0	−3.4	177.1	11.75
3e	164.9	−16.1	−4.5	176.0	14.13
3f	−180	0	0	180	53.99
3g	−180	0	0	−180	76.29

[a]The atom labels are marked in Scheme 1. [b]c = 10^{-5}mol/L (methanol).

UV-Vis absorption spectra. To obtain the reliable spectrum data, several DFT methods (B3LYP, PBE1PBE, B3LYP/PCM and PBE1PBE/PCM) were used for investigating the absorption spectra of seven dimethine cyanine dyes, and regression analysis was used for studying theoretical results of the absorption maxima in different solvents.

Methodological study: Plot of experimental and theoretical $\lambda_{\max}$ of seven dimethine cyanine dyes is shown in Figure 1. It can be seen that the $\lambda_{\max}$ obtained by pure B3LYP method deviates significantly from the experimental data. PBE1PBE overestimates $\lambda_{\max}$ 0.5 nm for dye **3g**, 0.6 nm for dye **3c**, 8.9 nm for dye **3f**, 12.9 nm for dye **3e** and 21.5 nm for dye **3b**, and underestimated $\lambda_{\max}$ 13.7 nm for dye **3d**, 26.9 nm for dye **3a**, relative to experimental data. Comparison of absolute deviation for each dye molecule reveals that PBE1PBE method is more suitable than B3LYP method for studying the absorption spectra of the dimethine cyanine dyes. The introduction of a solvent reaction field and the combination of PCM and PBE1PBE method (route 1 and 2) leads to the results that are much closer with the experimental values. Route 1 is on the basis of gas-phase optimized geometries for spectrum calculations in methanol, and route 2 uses the solvated geometries for TD-DFT/PCM calculations, which reduces the absolute deviation to 0.4 nm for dye **3e**, 3.3 nm for dye **3f**, 8.0 nm for dye **3c**, about 10 nm for **3b**, **3d** and **3g**, and 26.7 nm for **3a**. It indicates that the accuracy is increased remarkably when taken into account the solvent effects.

Regression analysis: In view of different experimental conditions, more variables need to be considered in order to find a reliable equation, which can realize the optimized $\lambda_{\max}$ to validate and predict the experimental values. We apply TD-DFT/PCM approach to these dye molecules in order to explore the effects of solvent on absorption spectra and to

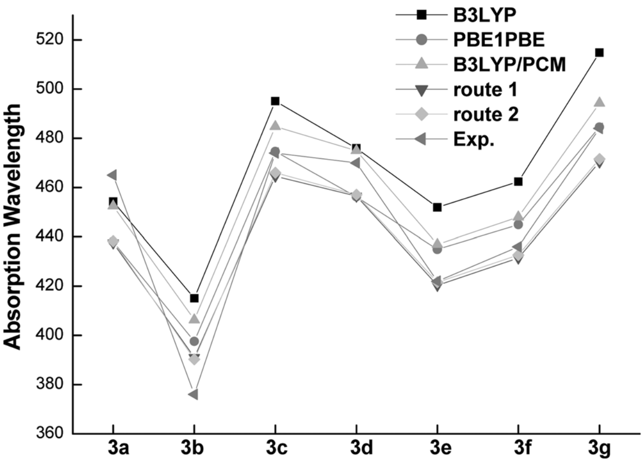


Figure 1. Plot of experimental and theoretical λ_{max} of seven dimethine cyanine dyes. Route 1: PBE1PBE/TD-DFT(PCM)/6-31G*; Route 2: PBE1PBE(PCM)/TD-DFT(PCM)/6-31G*.

test the theoretical approach against the available experimental results. Here five solvents: chloroform, ethanol, methanol, DMSO and water (their dielectric constant amounts to 4.90, 24.55, 32.63, 46.70 and 78.39, respectively) are considered.

We apply multiple linear regression to investigate the relationship between calculated and experimental results. The variables considered are presented in Table 4. The relationship between the response variable (λ_{max}) and the predictor variables (calculated λ_{max} by route 1 and route 2, and solvent dielectric constant) is formulated as a linear model:

$$\begin{aligned}\text{Opt.}\ (\lambda_{max}) = &-112.24 + 3.00\lambda_{max}\,(\text{route 1})\\ &- 1.70\lambda_{max}\,(\text{route 2}) - 0.34\,\varepsilon\end{aligned}$$

where ε is the solvent dielectric constant. This equation provides an adjusted R^2 of 0.9903. The *t*-test for the individual regression coefficients (excluding the constant) is in the 99.99% confidence interval (*p*-value for *t*-test is at the significance level of 0.0001), and the *F*-value for testing all the regression coefficients is at level 0.0001.

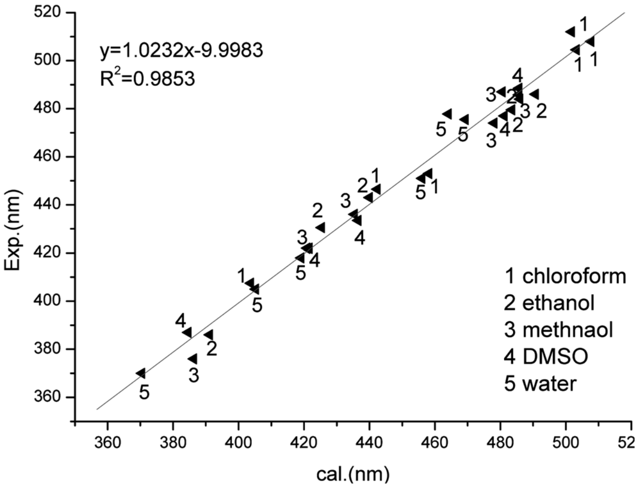


Figure 2. Comparison of experimental and optimized theoretical λ_{max} for dimethine cyanine dyes.

By using this model, the maximal deviation between optimized and experimental λ_{max} falls to about 0.2-10 nm for the dimethine cyanine dyes. Then, test calculations of the λ_{max} for 3-[2-(3,3-dimethyl-1-n-butyl-4,5-benzindolium-4-yl)-vinyl]-1H-indole iodide are performed in different solvents (Table 4). The scatter plots of all results are reproduced in Figure 2 with the fitted lines. Estimated overall uncertainties (relative deviation) in the absorption maxima are about ±2% in different solvents. This definitively confirms the validity of the equation for a quantitative evaluation of the λ_{max} of dimethine cyanine dyes.

Table 4. Absorption maximum (λ_{max}) obtained by the TD-PBE1PBE/PCM/6-31G* method

Dyes	Route 1	Route 2	Opt.	Exp.
chloroform				
3b	397.4	396.8	403.7	407.5
3c	476.4	477.7	503.2	504.5
3e	429.5	430.7	442.4	446.5
3f	442.0	443.5	458.1	453.0
3g	479.6	480.6	507.7	508.0
ethanol				
3b	392.1	391.0	391.2	386.0
3c	466.5	467.9	483.5	479.5
3e	421.7	423.0	425.4	430.5
3f	433.0	434.4	440.0	443.0
3g	471.9	473.2	490.7	486.0
methanol				
3b	391.0	390.3	386.3	376.0
3c	464.6	466.0	478.1	474.0
3e	420.3	421.6	420.9	422.0
3f	431.4	432.7	435.4	436.0
3g	470.3	471.5	486.0	484.0
dimethyl sulphoxide				
3b	394.0	393.7	384.6	387.0
3c	470.3	471.5	481.2	477.0
3e	423.9	424.8	421.6	422.0
3f	435.9	437.0	436.5	433.5
3g	474.1	475.5	485.7	488.5
water				
3b	390.6	389.6	370.5	370.0
3c	464.0	468.8	456.1	451.0
3e	419.7	420.5	405.2	405.0
3f	430.7	431.9	419.1	418.0
3g	469.4	470.5	469.3	475.5
3-[2-(3,3-dimethyl-1-*n*-butyl-4,5-benzindolium-4-yl)-vinyl]-1H-indole iodide				
chloroform	474.5	475.3	501.7	512.0[a]
ethanol	467.6	468.7	485.6	485.8[a]
methanol	466.0	467.2	480.6	487.0[a]
DMSO	470.0	470.8	481.5	510.0[a]
water	465.2	466.2	464.1	477.8[a]

[a]Ref.[24].

Assignment of the calculated transition. Table 5 lists the

Table 5. Main orbital compositions and excitation energies of dyes

Dyes	State	Transition feature	PBE1PBE/PCM[a]		
			Transition character[b]	ΔE (eV)	f
3a	^{1}A	$\pi \rightarrow \pi^*$	H → L (79.0%)	2.83	1.0965
3b	^{1}A	$\pi \rightarrow \pi^*$	H → L (83.6%)	3.18	1.0142
3c	^{1}A	$\pi \rightarrow \pi^*$	H → L (83.3%)	2.66	0.9377
3d	^{1}A	$\pi \rightarrow \pi^*$	H → L (80.6%)	2.71	1.2109
3e	^{1}A	$\pi \rightarrow \pi^*$	H → L (81.4%)	2.94	0.8041
3f	^{1}A	$\pi \rightarrow \pi^*$	H → L (79.1%)	2.87	0.9660
3g	^{1}A	$\pi \rightarrow \pi^*$	H → L (80.4%)	2.63	0.8841

[a] Solvent is methanol. [b] H and L stand for HOMO and LUMO respectively, and the proportion of the main transition are given in parenthesis.

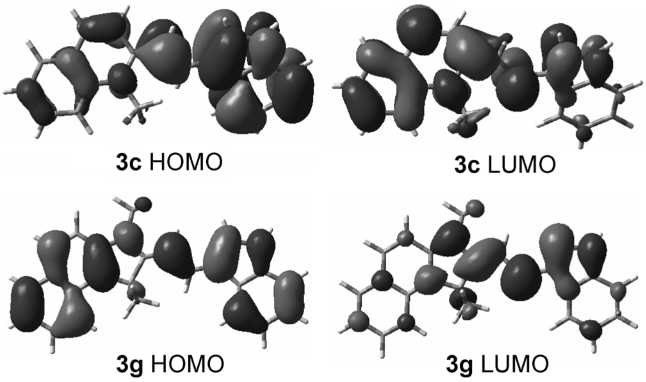


Figure 3. Sketch of the main molecular orbitals involved in the domainant dipole-allowed transition for the **3c** and **3g**, obtained at the PBE1PBE(PCM)/6-31G*level of approximation.

main orbital compositions of the computed lower-lying singlet excited states and transition feature of the dye molecules obtained at the PBE1PBE(PCM)/6-31G* level. From Table 5, we can see that the lowest energy absorption in dyes is due to the first dipole-allowed $\pi \rightarrow \pi^*$ transition in which the dominant configurations involve the HOMO with LUMO. From our calculation, it can also be found that the frontier orbitals of dye **3b**, **3c**, **3e** and **3f** are very similar to that of dye **3a** and, **3d** is similar to **3g**. Figure 3 lists the sketches of these molecular orbitals for one representative molecule of each series, the **3c** and **3g** molecules. It can be seen that the HOMO of dye **3c** and **3g** is mainly localized on the whole molecular skeleton, the LUMO of dye **3c** is mainly distributed at quinoline nucleus and vinyl fragment, and the LUMO of dye **3g** is mainly distributed at five element heteronucleus and vinyl fragment. The HOMO → LUMO transition of dye **3c** goes from the indole group to the quinoline moiety, and for molecule **3g**, the HOMO → LUMO absorption transition involves the electron displacement from the two external phenyl rings to the central moiety with a large dipole moment.

Conclusion

We describe a rapid and highly efficient method for the synthesis of dimethine cyanine dyes under solvent-free microwave irradiation by the condensation of quaternary salts with 1H-indole-3-carbaldehyde in the presence of piperidine. Prepared dyes absorb in the region 376.0-484.0 nm and their fluorescence maxima are located at 512.6-548.6 nm. In addition, PBE1PBE/PCM method gives a reliable description of the molecular absorption characters in different solvent and reproduces the π-π^* type absorption bands of the dyes. Multiple linear regression is also applied to examine the interrelationships between calculated and experimental $\lambda_{\max}$ in five solvents, and estimated overall uncertainties in the absorption maxima are about ±2%.

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