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Synthesis and photophysical properties of two novel branched pyridinium inner salt dyes

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1. Introduction

Aminostyryl pyridinium dyes (hemicyanine dyes) are a type of important optoelectronic functional materials, which exhibit many outstanding properties such as organic nonlinear optical effect [1], frequency-upconverted lasing [2,3], optical power limiting [4], molecular electronics [5] and fluorescence probes [6]. Among them, two-photon absorption and related frequency-upconverted emission of these dyes attracted lots of attention. Prasad research group firstly reported high efficient two-photon excited fluorescence and lasing properties of a series of new aminostyryl substituted pyridinium dyes [7]. Very recently, Yu group reported the two-photon fluorescence imaging of DNA and RNA in living tissue with some vinylcarbazole substituted pyridinium dyes [8,9].

Generally, aminostyryl pyridinium dyes are easy to be prepared and crystallized and purified [10]. Comprehensive researches have been carried out to finely tune their chemical and physical

ABSTRACT

Two new branched pyridinium inner salt dyes, 2,6-di[2-(*N*-ethyl-carbazole-3-yl)vinyl]-*N*-(3-sulfonatepropyl)pyridinium, inner salt (**2**) and 2,4,6-tri[2-(*N*-ethyl-carbazole-3-yl)vinyl]-*N*-(3-sulfonatepropyl) pyridinium, inner salt (**3**), with *N*-ethyl-carbazolyl as electron donor group and pyridine cation as electron acceptor group have been synthesized. Their single- and two-photon related fluorescence properties in various solvents have also been examined. These dyes exhibit stronger fluorescence emission relative to the corresponding linear counterpart and common pyridinium dyes with discrete cation and anion components. Three-branched organic dye **3** has a high fluorescence quantum yield as 0.12 and exhibits strong orange two-photon excited fluorescence at 608 nm in THF with large twophoton absorption cross-section being 606 GM.

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properties by properly structurally modification, such as the donor/ acceptor strength, the rigidity of the π -bridge and introduction of branches. But most of common pyridinium dyes have discrete cation and anion components, there are a few papers reported pyridinium inner salts with the cation covalently linked to the anion, which show enhanced two-photon pumped lasing than cation/anion discrete analogues [11]. In addition, multi-branched structure is beneficial to the nonlinear optical properties of molecules because of some cooperative enhancement originating from inter-branch coupling [12–15].

As part of our ongoing efforts toward developing new twophoton absorption and fluorescence materials, the synthesis, single- and two-photon excited fluorescence properties of two new branched pyridinium inner salt dyes are presented in this work.

2. Experimental

2.1. Chemical and instruments

1,3-Propanesulfonate, 2,6-dimethylpyridine and 2,4,6trimethylpyridine were purchased from Aladdin Reagent Inc. Other reagents were purchased from Shanghai Reagents and were used as received directly without further purification. All of the solvents were freshly distilled before using. Nuclear magnetic



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resonance spectra were recorded on a Bruker Avance III 400 MHz spectrometer. Mass spectra were recorded on an Agilent Q-TOF6510 spectrometer. Infrared spectra were recorded on a Nicolet 380FT-IR spectrophotometer. Elemental analyses were carried out on a PE 2400 autoanalyzer.

2.2. Synthesis

The synthesis of linear dye **1** has been previously reported by our group [16]. The synthetic strategy for dyes **2** and **3** is outlined in Scheme 1. The dyes were synthesized via two steps. Firstly, 1,3-propanesulfonate reacted with one equivalent of 2,6-dimethylpyridine or 2,4,6-trimethylpyridine to afford **S-1** and **S-2**. Then dyes **2** and **3** were obtained by the reaction of **S-1** or **S-2** with *N*-ethylcarbazole-3-aldehyde. A pyridinium dye **1**' with discrete cation and anion components and similar structure with dye **1** was also synthesized.

2.2.1. 2,6-Di[2-(N-ethyl-carbazole-3-yl)vinyl]-N-(3-sulfonatepropyl)pyridinium, inner salt (2)

N-ethyl-carbazole-3-aldehyde (1.25 g (0.0056 mol)) and 80 mL isoamyl alcohol were added to a 250 mL one-necked flask with a stirrer and condenser, and then 0.32 g (0.0014 mol) S-1 and a few drops of piperidine were added in turn. The mixture was heated under reflux for 10 h. After cooling to room temperature, orange precipitate was filtered and re-crystallized by ethanol to give dye 2 as orange solid with a yield 56%. ¹H NMR (DMSO, 400 MHz), δ (ppm): 1.36(t, 6H, I = 7.0 Hz), 2.33(s, 2H), 2.92(t, 2H, I = 5.3 Hz), 4.51(q, 4H, I = 7.1 Hz), 5.17(t, 2H, I = 5.2 Hz), 7.28(t, 2H, I = 7.4 Hz),7.52 (t, 2H, *J* = 7.6 Hz), 7.67(d, 2H, *J* = 8.2 Hz), 7.71(d, 2H, *J* = 8.6 Hz), 7.87(d, 2H, J = 15.6 Hz), 8.04 (d, 2H, J = 15.6 Hz), 8.06(d, 2H, J = 7.9 Hz), 8.29–8.33(m, 5H), 8.92(s, 2H). ¹³C NMR (DMSO, 100 MHz), δ (ppm): 13.65, 37.14, 47.43, 78.54, 78.87, 79.20, 109.33, 109.46, 114.70, 119.45, 120.86, 121.67, 122.35, 122.75, 126.24, 127.37, 140.10, 140.88, 144.43, 152.93. MS for (M+H)⁺, Calcd exact mass: 640.2634, found 640.2619. IR (cm⁻¹): 3855, 3748, 3054, 2980, 1600,



Scheme 1. Synthetic strategy of dyes 2 and 3.

1566, 1483, 1331, 1226, 1193, 1030, 971, 811, 747, 518. Anal. Calcd. for $C_{40}H_{37}N_3O_3S$: C, 75.09; H, 5.83; N, 6.57. Found: C, 75.25; H, 5.85; N, 6.59.

2.2.2. 2,4,6-Tri[2-(N-ethyl-carbazole-3yl)vinyl]-N-(3-sulfonatepropyl)pyridinium, inner salt (**3**)

Dye **3** was prepared as a brownish-red powder with a yield 50% following a method similar to the preparation of dye **2**. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 1.21(t, 6H, *J* = 7.2 Hz), 1.31(t, 3H, *J* = 7.2 Hz), 2.16(s, 2H), 3.20(s, 2H), 4.03(q, 4H, *J* = 7.1 Hz), 4.15(q, 2H, *J* = 7.1 Hz), 4.55(s, 2H), 6.83(d, 1H, *J* = 16.0 Hz), 7.08(t, 2H, *J* = 7.3 Hz), 7.14–7.24(m, 10H), 7.32–7.47(m, 7H), 7.91(d, 3H, *J* = 8.2 Hz), 8.13(d, 3H, *J* = 7.5 Hz), 8.19 (s, 1H), 8.24 (s, 2H). ¹³C NMR (CDCl₃, 100 MHz), δ (ppm): 13.84, 25.48, 29.72, 37.62, 47.80, 76.71, 78.43, 108.62, 109.25, 114.33, 117.62, 119.78, 120.25, 120.88, 121.40, 121.97, 122.97, 123.20, 126.16, 126.64, 140.22, 141.22, 143.61. MS for (M + H)⁺, Calcd exact mass: 859.3682, found 859.3650. IR (cm⁻¹): 3867, 3741, 3053, 2980, 1578, 1532, 1485, 1327, 1238, 1157, 1128, 1029, 969, 795, 729, 513. Anal. Calcd. for C₅₆H₅₀N₄O₃S: C, 78.29; H, 5.87; N, 6.52. Found: C, 78.43; H, 5.89; N, 6.53.

2.2.3. 2-[2-(N-ethyl-carbazole-3-yl)vinyl]-N-methylpyridinium, iodide (1')

Dye **1**′ was synthesized by reaction of *N*-ethyl-carbazole-3-aldehyde and 4-methyl-*N*-methylpyridinium iodide according to Ref. [10]. ¹H NMR (DMSO, 400 MHz), δ (ppm): 1.35(t, 3H, *J* = 7.2 Hz), 4.41(s, 3H), 4.51(q, 2H, *J* = 7.2 Hz), 7.30 (t, 1H, *J* = 7.4 Hz), 7.53 (t, 1H, *J* = 7.6 Hz), 7.61 (d, 1H, *J* = 15.6 Hz), 7.69 (d, 1H, *J* = 8.4 Hz), 7.76 (d, 1H, *J* = 8.4 Hz), 7.83 (t, 1H, *J* = 7.2 Hz), 8.01 (d, 1H, *J* = 8.4 Hz), 8.19 (d, 1H, *J* = 15.6 Hz), 8.23 (d, 1H, *J* = 7.6 Hz), 8.46 (t, 1H, *J* = 7.8 Hz), 8.56 (d, 1H, *J* = 8.0 Hz), 8.73 (s, 1H), 8.86 (d, 1H, *J* = 6.0 Hz), ¹³C NMR (DMSO, 100 MHz), δ (ppm): 13.71, 37.23, 45.98, 109.68, 109.71, 113.71, 119.64, 120.52, 121.59, 122.13, 122.67, 123.98, 124.14, 125.94, 126.45, 126.89, 140.14, 141.09, 143.67, 144.60, 145.61, 152.92. Anal. Calcd. for C₂₂H₂₁IN₂: C, 60.01; H, 4.81; N, 6.36. Found: C, 60.12; H, 4.79; N, 6.35.

2.3. Measurements

UV/vis absorption spectra with $C = 5.0 \times 10^{-6} \text{ mol L}^{-1}$ were recorded on a Shimadzu UV2550 spectrophotometer. Steady-state fluorescence measurements were performed at room temperature with $C = 5.0 \times 10^{-6} \text{ mol L}^{-1}$ on an Edinburgh Instrument (FLS920) spectrometer. The fluorescence quantum yields Φ were measured by using a standard method [17] with coumarin 307 [18] as the standard. Two-photon excited fluorescence (TPEF) spectra of the dyes in THF with $C = 1.0 \times 10^{-4} \text{ mol L}^{-1}$ were performed with a femtosecond Ti:sapphire laser (80 MHz, 80 fs pulse width, Spectra-Physics Inc., Tsunami 3941-M1 BB) over the range 740– 880 nm as pump source.

3. Results and discussion

3.1. Linear absorption and single-photon excited fluorescence properties

The comprehensive photophysical properties of the compounds in various solvents with different polarity are listed in Table 1. Linear absorption and single-photon excited fluorescence (SPEF) spectra of dyes **2** and **3** are shown in Figs. 1 and 2, respectively.

As shown in Table 1 and Fig. 1, one can see that absorption properties of the dyes show some dependence on the polarity of the solvents. The dyes exhibit lower linear absorption in toluene than in other solvents. With increasing polarity of the solvents from THF to CH₃CN, the absorption peak position of dyes **2** and **3** exhibit slight blue shift, but the absorption peak position of dye **1** exhibits obvious blue shift. This characteristic indicates that the ground state of dye **1** has a certain polarity, but dyes **2** and **3** have a weak polarity.

Compared with absorption properties, SPEF properties of dyes **2** and **3** display obvious dependence on the solvent polarity. From Table 1 and Fig. 2, one can see that the dyes exhibit weak fluorescence emission in weak polarity solvent (toluene) and fluorescence intensity and quantum yields decrease from medium polarity solvent (THF) to strong polarity solvent (CH₃CN). The dyes exhibit the strongest fluorescence emission in THF. The weak fluorescence emission in toluene may be derived from the low absorption ability of the dyes. The dependence of fluorescence intensity on the polarity of the solvent may be explained by the twisted intramolecular charge transfer (TICT) model [19,20]. Upon increasing the solvent polarity, the fluorescence emission λ_{max} of dye **3** is slightly red-shifted.

Based on the discussion above, the dyes exhibit the strongest fluorescence emission in THF. Linear absorption and fluorescence properties of the three dyes in THF were compared and the spectra are shown in Fig. 3. As shown in Table 1 and Fig. 3(a), molar extinction coefficient values of dyes 2 and 3 are more than twice that of dye 1. From dye 2 to 3, molar extinction coefficient increase slightly. This may be because the two branches of dye 2 are almost parallel and the molecule can be regarded as a linear D $-\pi$ -A $-\pi$ -D type of molecule with lengthened conjugation length. According to molecular engineering design theory, molar extinction coefficient increases with the increase of conjugated bridge length. Dye 3 is can be regarded as a dye 2 molecule imported by a branch. According to the assumption reported by Blanchard-Desce et al. that for some multi-branched systems, each branch makes a similar contribution to the transition from the ground state to the excited state, which also can explain the change of molar extinction coefficient with the branches [21].

Linear absorption peaks of the dyes are 437 nm (1), 460 nm (2) and 464 nm (3), respectively. The linear absorption peaks of dyes 2 and 3 are red-shifted obviously relative to that of 1. The red shift of absorption peak may be derived from the longer molecular conjugation length.

As shown in Table 1 and Fig. 3(b), with the increase of branches, fluorescence quantum yield increases slightly, but the fluorescence

Table 1

Linear photophysical properties of dyes **1–3** in various solvents with $C = 5.0 \times 10^{-6} \text{ mol } \text{L}^{-1}$.

Solvents	1				2				3			
	λ ^{abs} [nm]	$\frac{\varepsilon_{\text{max}}}{[10^4 \text{cm}^{-1} \text{mol}^{-1} \text{L}]}$	λ ^{fluo} [nm]	Φ	λ ^{abs} [nm]	$\frac{\varepsilon_{\max}}{[10^4 \text{ cm}^{-1} \text{ mol}^{-1} \text{ L}]}$	λ ^{fluo} [nm]	Φ	λ ^{abs} [nm]	$e_{\rm max}$ [10 ⁴ cm ⁻¹ mol ⁻¹ L]	λ ^{fluo} [nm]	Φ
Toluene	424	2.06	590	0.06	453	3.51	598	0.08	466	5.08	599	0.09
THF	437	2.88	559	0.09	460	6.46	581	0.10	464	6.84	605	0.12
Acetone	425	2.86	565	0.03	458	6.58	578	0.03	462	7.48	610	0.05
CH ₃ CN	423	2.88	565	0.03	454	6.24	579	0.03	458	7.28	611	0.05



Fig. 1. Linear absorption spectra of dyes 2 (a) and 3 (b) in various solvents with $C\,{=}\,5.0\times10^{-6}\,mol\,L^{-1}.$

intensity of organic dyes show a substantial increase. The fluorescence intensity of two-branched dye **2** is about twice that of dye **1**, which may be derived from the enhanced absorbance. Although dye **3** exhibits similar molar extinction coefficient relative to **2**, its fluorescence intensity increases smartly, which indicates that dye **3** has stronger fluorescence emission ability. The fluorescence peak maximum of the dyes in THF are 559 nm (**1**), 581 nm (**2**) and 605 nm (**3**), respectively, which is red-shifted with the increase of branches. Larger molar extinction coefficient value and high fluorescence emission of branched molecules relative to the corresponding linear counterpart appears that there are intramolecular coupling effects between the branches.

A pyridinium dye 1' with discrete cation and anion components was also synthesized. Its absorption and fluorescence spectra in THF are shown in Fig. 3. Molar extinction coefficient and quantum yield ($\Phi = 0.03$) of 1 are almost one half times and three times, respectively, that of 1', which indicates that pyridinium inner salt structure is beneficial to fluorescence emission and exhibits strong fluorescence emission than common pyridinium dye with discrete cation and anion components.

3.2. Two-photon excited fluorescence properties

Two-photon excited fluorescence (TPEF) properties of the dyes in THF are also investigated. TPEF was collected at a direction



Fig. 2. Single-photon excited fluorescence (SPEF) spectra of dyes **2** (a) and **3** (b) in various solvents with $C = 5.0 \times 10^{-6} \text{ mol } \text{L}^{-1}$.

perpendicular to the pump beam. As shown in Fig. 4, the output fluorescence intensity of dye **3** is proportional to the square of the input power from 64 mW to 254 mW, which suggests the twophoton excitation mechanism. Two-photon excitation spectra of dyes 2 and 3 in THF with excitation wavelength from 730 nm to 860 nm are also shown in Fig. 4. Detailed experiments reveal that TPEF peak positions of the dyes are independent of the excitation wavelengths, but TPEF emission intensities are dependent over that range. From Fig. 4, we can see that the optimal excitation wavelength of both dyes 2 and 3 is 810 nm, which is smaller than twice that of the corresponding linear absorption maximum (460 nm (2), 464 nm (3)). TPEF spectra of the dyes 1–3 shown in Fig. 5 were taken at 810 nm. Dyes 2 and 3 exhibit strong yellow or orange TPEF emission in THF at 585 nm (2) and 608 nm (3), which are similar to that of the corresponding SPEF spectra. Based on this similarity and different linear absorption and two-photon excitation peak, we can think that the primary excited states obtained by single-photon absorption and two-photon absorption may be different because of the different parity selection rules, but they are likely to relax quickly to the same fluorescence emission states.

Both dyes **2** and **3** show much stronger frequency-upconverted fluorescence emission than that of **1**. Dye **3** exhibits the strongest TPEF and the intensity is almost four times that of **1**. Two-photon absorption (TPA) cross-sections of the dyes were measured using two-photon excited fluorescence method with coumarin 307 as



Fig. 3. Linear absorption (a) and single-photon excited fluorescence (b) spectra of dyes **1–3** in THF with $C = 5.0 \times 10^{-6}$ mol L⁻¹.



Fig. 4. Two-photon excitation (TPE) spectra of dyes **2** and **3** in THF with $C = 1.0 \times 10^{-4}$ mol L⁻¹. Inset: the output fluorescence intensity vs. the input power square for **3** with the excitation wavelength at 800 nm.



Fig. 5. Two-photon excited fluorescence (TPEF) spectra of dyes 1–3 in THF excited at 810 nm with $C = 1.0 \times 10^{-4}$ mol L⁻¹.

Ref. [22], which are 133 GM (1), 518 GM (2) and 606 GM (3) at 810 nm, respectively. All the data above indicate that there is some cooperative enhancement from the coupling effects among the branches connected by the pyridinium group. These two organic pyridinium dyes 2 and 3 show promising applications in nonlinear optical area.

4. Conclusion

Two new organic pyridinium inner salt dyes have been synthesized and the single- and two-photon excited fluorescence properties of the dyes are investigated. In summary, dye **3** has the strongest fluorescence emission ability and exhibits strong orange twophoton excited fluorescence at 608 nm in THF with two-photon absorption cross-section being 606 GM. These two organic pyridinium dyes show promising applications in nonlinear optical area.

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