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Influence of Self-Assembly and Solvent Polarity on Fluorescence Properties of Hydrophobic Organic Cations Based on Anthracene Skeleton

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Abstract: Fluorescence mode is influenced by the substituents, the polarity of the solvent, the steric factor and even the aggregation state of molecules in solvent under the testing environment. By comparing the fluorescent behavior of three anthracene derivatives, we observe that the hydrophobic interaction and steric effect in structures reduce fluorescence intensity, quantum yield and fluorescence lifetime. The emitting mode of two amphiphilic salts changes from aggregation emission in weak polar solvent to monomer emission in strong polar solvent and gives the similar variety in mixed solvent.

Key words: organic cations; fluorescence; self-assembly; solvent polarity; monomer emission; aggregation emission
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0 Introduction

Self-assembly of organic cations has been one of the most intensively studied areas in supramolecular chemistry. Supramolecules can exhibit a wide range of spectroscopic characteristics due to self-assembly. Aggregation induced emission (AIE) was found in the water-organic solvent and regarded as the result of molecular assembly [1,2]. However, we observed the AIE on hydrophobic organic cations in mixed solvents which usually was made of weak polar solvent and strong polar solvent with different proportion. Two hydrophobic organic cations based on anthracene skeleton with a characteristic of changing its conformations in different organic solvents were designed and prepared. Anthracene has high fluorescence quantum efficiency and its derivatives have been widely used as fluorescence sensors [3,4] or organic electroluminescent materials. A variety of anthracene derivatives were prepared via the two modified groups on 9 and 10 positions of anthracene skeleton [5, 6]. The light-emitting mechanism of the anthracene derivatives has been attracting more and more research attention [7-9]. In this article, we synthesized (1,1'-[9,10- Anthracenediylbis(methylene)]bis[3-octadecyl-1H-imidazolium]dichloride) (Labeled as **1**) and (1,1'-(anthracene-9,10-diylbis(methylene))bis(3-(3,4,5-tris(octadecyloxy)-benzyl)-1H-imidazolium) dichloride) (Labeled as **2**), which have the similar skeleton with 9,10-bis (imidazol-1-ylmethyl) anthracene (Labeled as BIMA). Com-

pound **1** was designed by introducing two octadecyl tails on both sides of the two imidazole rings of BIMA. Imidazole rings with positive charge and hydrophobic tails in structures are more favorable to obtain the better solubility in organic solvents. Compound **2** with symmetrical fan-shaped tails has more and lager hydrophobic moieties than **1**. Another purpose of introducing the alkoyl chains and bulky groups is to explore how the steric effects affects the conformation and causes the imidazole ring and the anthracene chromosphere as coplanar as possible or the existence of a smaller angle between the imidazole and anthracene.

The possible charge transfer between the positive charged imidazole groups and the electron-rich anthracene ring would relate with the conformation, which results in twisted internal charge transfer (TICT) emission [10-14]. TICT phenomenon quite widely exists in the process of the decay of the excited state of many fluorescent molecules and to a large extent becomes a key factor largely in controlling fluorescent quantum yield. However, there is a lack of detailed description and explanation about the relation between conformation changes of the excited state and fluorescence properties. In this paper, the fluorescent spectrums, fluorescent intensity, quantum yield and lifetime of three anthracene derivatives were compared in order to explicate the fluorescence emission mode. Fluorescence spectra of BIMA, **1** and **2** derivatives in different polar solvent were also recorded. It is expected to know whether the bulky fan-shaped tails of **2** would bring us a surprise on fluorescence mode. We also obtained the nanobelt morphology of **2** aggregates by transmission electron microscopy which would be described in another article.

1 Experimental

1.1 Materials and Instruments

All reagents and solvents were purchased from commercial sources and used as received unless specified. Tetrahydrofuran and toluene were purified and kept under an argon atmosphere prior to use. Synthetic procedures were carried out under an inert atmosphere. Elemental analyses were performed with an Elementar Vario EL. ^{1}H NMR data was obtained by a Bruker DMX-400 NMR spectrometer with $CDCl_3$ or DMSO-d_6 as solvent at room temperature. The chemical shifts were relative to tetramethylsilane at δ=0 for protons. All UV-visible absorption spectra were taken using a Shimadzu UV-2450. UV-vis spectrophotometer in a dual beam mode used a matched pair of 1 cm×1 cm quartz cells. Fluorescence emission and excitation spectra were measured in 1 cm×1 cm quartz cells by a Hitachi F-7000 spectrofluorometer with a xenon lamp as the excitation source. IR spectra (KBr) were measured with a Nicolet NEXUS 670 spectrometer. Fluorescence lifetime and fluorescence quantum yield study was performed using an Edinburgh FL-F7000 mode time-correlated single-photon counting (TCSPC) system equipped with a H_2 lamp as the excitation resource spectrophotometer. All measurements were carried out at room temperature.

1.2 Synthesis and Characterization of BIMA, 1 and 2

BIMA was synthesized according to Ref. [15]. Synthesis of **1**[16] was started from 9, 10-bis (chloromethyl) anthracene and 1-bromooctadecane instead of 1-butylimidazole. We could not obtain a single-crystal structure of **1** for the two long alkyloxy chains.

Compound **1**: light yellow powder, 500 mg, 78%, m. p. 223-225 ℃. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.88 (t, 6H), 1.00-1.47 (m, 62H), 1.55-1.79 (m, 6H), 4.07(s, 4H), 6.43-6.72 (d, 4H), 6.90-7.12 (m, 2H), 7.67-8.12 (d, 4H), 8.96 (s, 2H), 9.33 (s, 2H). Anal. Calcd(%) for $C_{58}H_{92}N_4Cl_2$: C 75.74, H 10.080, N 5.910; Found(%): C 76.03, H 10.12, N 6.11.

Compound **2**: white powder, 500 mg, 50%, m. p. 288-290 ℃ ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.88 (t, 18H), 1.28-1.47 (m, 160H), 1.65-1.79 (m, 32H), 3.78 (t, 8H), 3.85 (t, 4H), 5.07 (s, 4H), 6.32 (s, 4H), 6.58 (s, 4H), 6.90 (s, 2H), 7.32 (m, 4H), 7.92 (m, 4H), 8.72 (s, 2H), 9.55 (s, 2H). Anal. Calcd(%) for $C_{144}H_{248}N_4O_6C_{l2}$: C 78.53, H 11.35, N 2.54; Found(%): C 78.25, H 11.17, N 2.37.

2 Results and Discussion

2.1 Fluorescence Spectra

The fluorescence properties of compound **1** and **2** were compared with that of BIMA. BIMA had good solubility in chloroform or methanol with strongly blue emission (Fig. 1). Fine structures of the emission peaks emerge at 404, 424 and 449 nm.

In chloroform, freely rotating imidazole rings of BIMA are reverse to a certain optimal conformation of minimum energy where fluorescence intensity reaches the maximum. However, carbon-carbon single bond of methylene connected with anthracene works as the TICT mechanism and continues to twist with the help of solvation and hydrogen bonding interaction in chloroform or

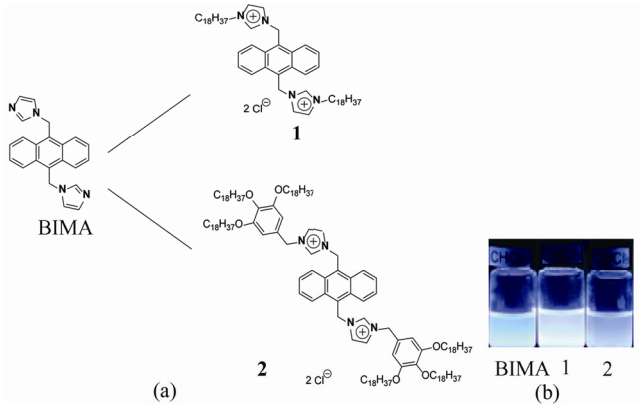

Fig. 1 Structures (a) and fluorescence photographs (b) of BIMA, 1, and 2 in chloroform at the concentration of 1.0×10^{-5} mol/L with λ_{ex} = 375 nm

methanol. Amphiphilic salts **1** and **2** have similar chromophore with BIMA. The loss of the planarity results in a decrease of the fluorescence intensity of **1** and **2** in organic solvent. Figures 2-4 show the fluorescence spectra of BIMA, **1** and **2** in different organic solvents. Compared with BIMA (Fig. 2), compound **1** has sufficient solubility in chloroform and methanol (Fig. 3(b) and 3(c)). In carbon tetrachloride (Fig. 3(a)), the emission intensity at 440 nm increases and all emission peaks show red-shift to longer wavelength. The results intimate that intermolecular hydrophobic interaction among long octadecyloxy chains causes the different emission mode for **1** in weak polar solvent. We speculate there is aggregates emission in carbon tetrachloride. Compound **1** has similar fluorescent spectra with BIMA in chloroform and methanol.

Compound **2** has more alkoxy chains than **1**. Considering that there may be more hydrophobic interaction, we add toluene as test solvent after carbon tetrachloride to learn more about emission behavior of **2** in weak polarity. In carbon tetrachloride (Fig. 4(a)), **2** gives yellow emission and the anthracene's fine peaks disappear. Emission peaks are observed at 532 nm even at low concentrations and the fluorescence intensity increases with the increasing of test concentration. Comparing Fig. 4(a) with 4(b) and 4(c), we find that the skeleton peaks of anthracene slightly red-shift that BIMA. However, peak intensity at 532 nm reduces from carbon tetrachloride to chloroform and then disappears.

As we have known, anthracene unit is often utilized as fluorophore in aggregation study [17]. In non-polar solvents, it is expected that the imidazole moiety will play a pivotal role for assemblies. In contrast, the hydrophobic moiety could be crucial for assemblies in polar solution. In both cases, anthracene moieties are supposed to be stacked. The emergence of broad emission peak of **2** at 532 nm in carbon tetrachloride can be considered as aggregation emission for the appearance of aggregation

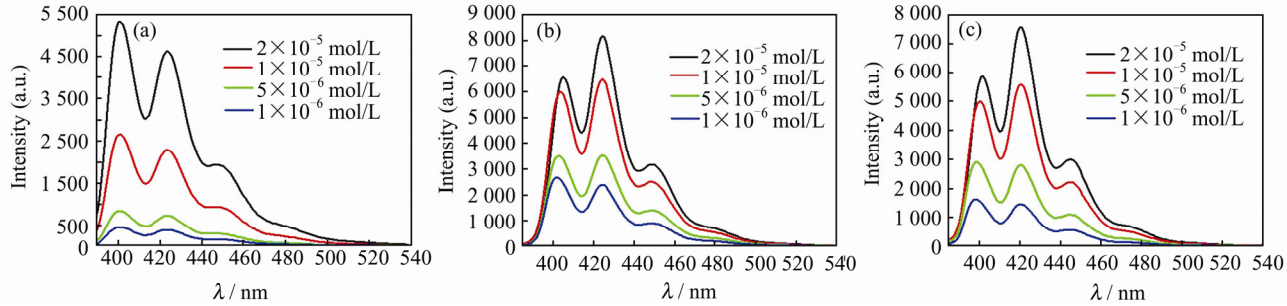

Fig. 2 Fluorescence spectra of BIMA with different concentration in organic solvents

(a) carbon tetrachloride; (b) chloroform; (c) methanol; λ_{ex}= 375 nm

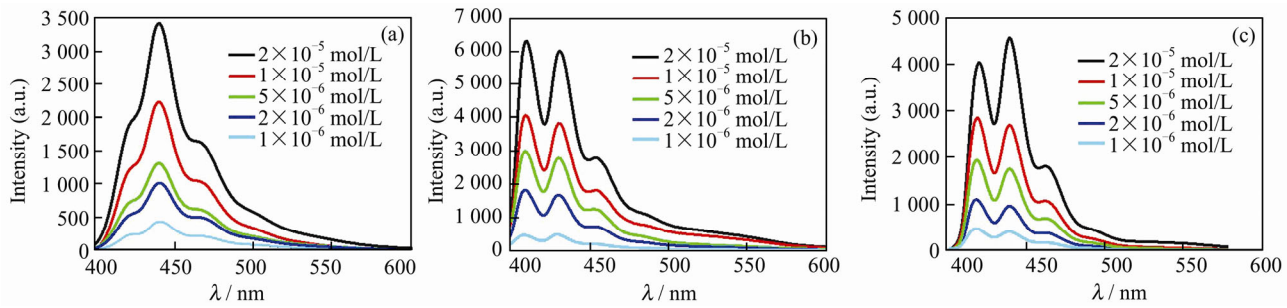

Fig. 3 Fluorescence spectra of compound 1 with different concentration in organic solvents

(a) carbon tetrachloride; (b) chloroform; (c) methanol; λ_{ex}= 365 nm for (a), and 375 nm for (b) and (c)

state in weak polar solvent. In strong polar solvents, such as chloroform or methanol, fluorescence spectra of **2** have similar emission peak positions and shape with parent skeleton of BIMA, which initiates that the monomer emission is main factor. In chloroform or methanol of **2** (Fig. 4), we observe multiple fine peaks of anthracene for the existing of monomer emission in strong polar solvents. In toluene, we obtain the monomer emission and aggregation emission simultaneously. Owing to the phase separation of **2**, it can be inferred that the interaction of bulky hydrophobic alkyl tails causes aggregation in non-polar solvent. By comparison, the blue emission of **2** in methanol results in the more monomer emission in methanol than in chloroform. The emission color of **1** in solvent changes from white in chloroform to blue in methanol appearing at the photograph in Fig. 1, which is the further proof of our speculation. We also observe the white emission phenomena in the fluorescence detection of **2** in chloroform solvent, which can be interpreted that in a certain ratio, the mixture of the monomer emission and aggregation emission is apt to generate pseudowhite emission[18].

The monomer and aggregation emission behaviors of **1** and **2** were studied in a mixture of weak/strong polar organic solvents with different fractions. Since the compounds are more easily to self-assembly for the long and bulky hydrophobic tails in weak polar solvents, increasing the strong solvent fraction in the mixed solvent could thus change their existing forms from aggregation state in pure carbon tetrachloride to mono state in pure methanol, which results in changes in the fluorescence spectra. Fluorescence spectra of BIMA, **1** and **2** were recorded in the mixed solvents of carbon tetrachloride/methanol with different varying ratios (Fig. 5).

On the addition of methanol in carbon tetrachloride of **1**, there is no change in the fluorescence spectra apart from a rational increase in fluorescence intensity, which illustrates that there is only single fluorescence mode in carbon tetrachloride or methanol. The different polar solvents just can bring the changes of the fluorescence intensity of BIMA instead of the fluorescence mode. An addition of small amount methanol to carbon tetrachloride of **1** results in a decrease and an increase of the intensities of the aggregation and the monomer emission, respectively. However, there was no obvious decrease in fluorescence intensity at 540 nm for the chloride anion and the salvation of the imidazole moieties to disturb ionic interaction among them, which acts as a binder for assembling. The color of the emission has changed from yellow in tetrachloride to be strongly blue in methanol. There are simultaneously of monomer and aggregation emission mode in **1**, which would generate white emis-

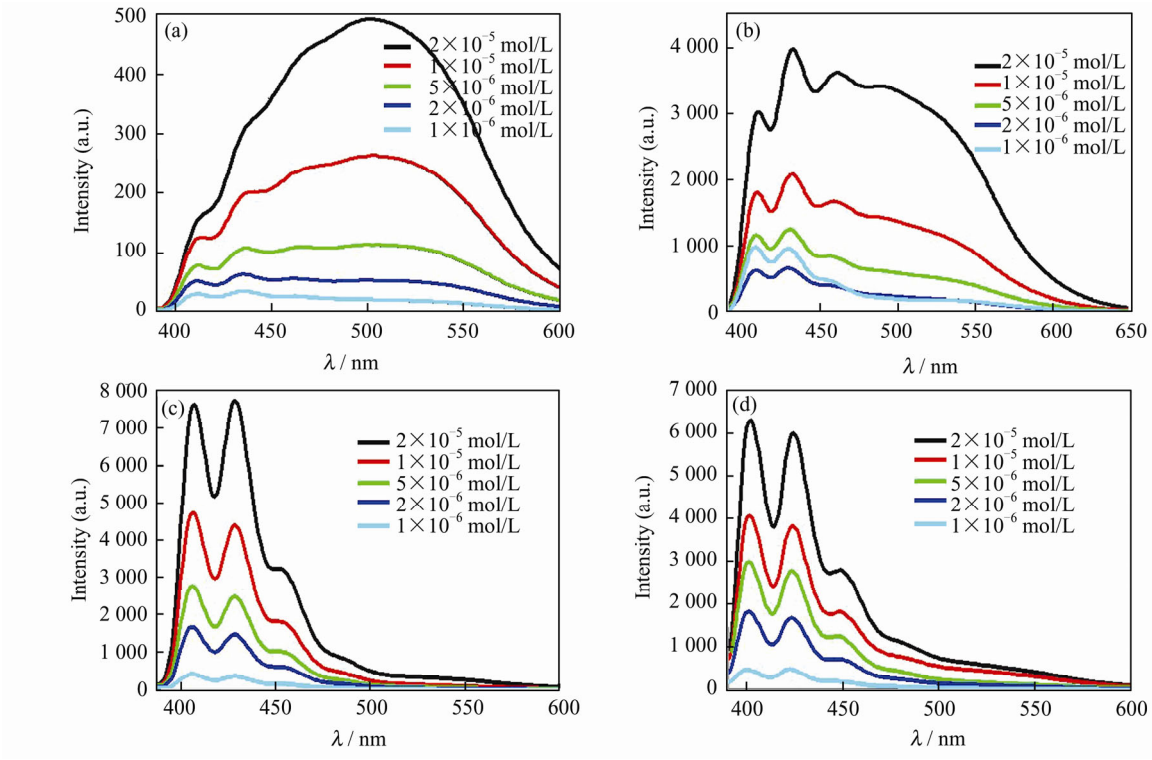

Fig. 4 Fluorescence spectra of compound 2 with different concentration in organic solvents

(a) carbon tetrachloride; (b) toluene; (c) chloroform; (d) methanol; λ_{ex}= 365 nm for (a) and 375 nm for (b)-(d)

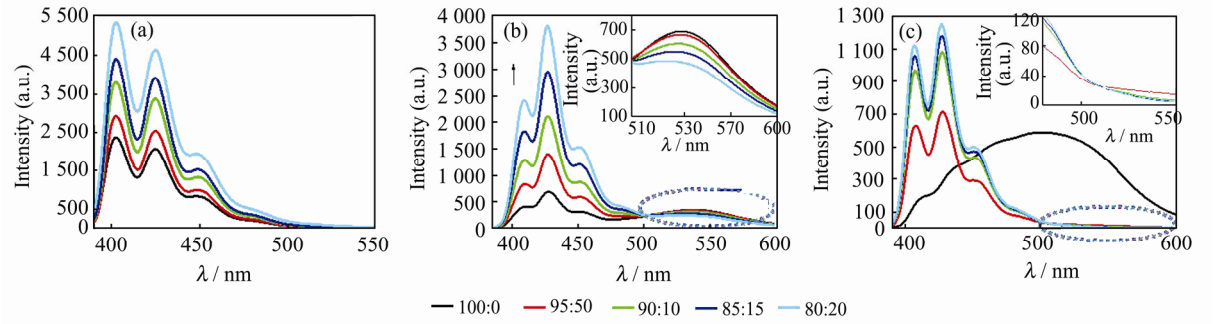

Fig. 5 Fluorescence changes of BIMA (a), 1 (b), and 2 (c) in different carbon tetrachloride/methanol (*V*/*V*) mixed solvents

λ_{ex} = 375 nm; Curves enclosed by dotted line are enlarged on upper right corner

sion when monomer emission and aggregation are mixed in a suitable proportion. In pure carbon tetrachloride, compound **2** shows broad and weak peak from 400 to 600 nm with the fine peaks of anthrance framework disappearing. However, strongly blue emission and sharp peaks with fine structure immediately appear when small amount methanol is first added into pure carbon tetrachloride of **2** and the peak intensity has no much change with the changes of methanol amount.

2.2 Fluorescence Yield and Lifetime

Fluorescence decay curve is generally used to measure the fluorescence lifetime (τ), the luminescence mechanism of the fluorophore and the change of the microenvironment of the luminescence group. Amphiphilic molecules especially with hydrophobic moieties are prone to aggregate in weak polar solvents but to be monomer state in strong solvents, which strongly affects the fluorescence yield and excites state lifetimes. Figure 6 illustrates the fluorescence decay curves of BIMA, **1** and **2.** There are three curves in the each figure, which are the actual measured intensity decay curve (IDC, black), the instrument response function (IRF, red) and the exponential fit (Blue).

The software on the instrument can give fitting indexes (χ^2) of attenuation curve of samples and other fluorescence parameter. According to the exponential fitting for experimental data, we obtained the fluorescence yield and fluorescence lifetime of BIMA, **1** and **2** in Table 1. The results show that BIMA would be a good blue emission organic optical functional material for its high fluorescence quantum yield (φ) labeled as 69% and fluorescence lifetime 8.01 ns.

Compound **1** had smaller fluorescence quantum yield 52% and a little longer fluorescence lifetime 8.66 ns for long alkoxy hydrophobic moieties hindering the rotation of the carbon-carbon single bond between the imidazole rings with anthracene ring, which has little influence on the luminous efficiency, and alkoxy hydrophobic moieties could achieve longer fluorescence lifetime from stable excited state. The conformation of BIMA and **1** resulting from intermolecular twisting is stabilized by the solvation effect, which leads to decay non-radioactively. In structure of **2**, the introduction of the bulky fan tail results in a new deactivation means (such as more vibration loss, etc.), which becomes the main factor of the significant decrease of fluorescence quantum yield[19]. For the excited state of **2**, fluorescence started to decay via three relaxation pathways with lifetimes of 0.41, 2.70 and 7.93 ns, respectively (Table 1). The result implies that **2** in a chloroform.

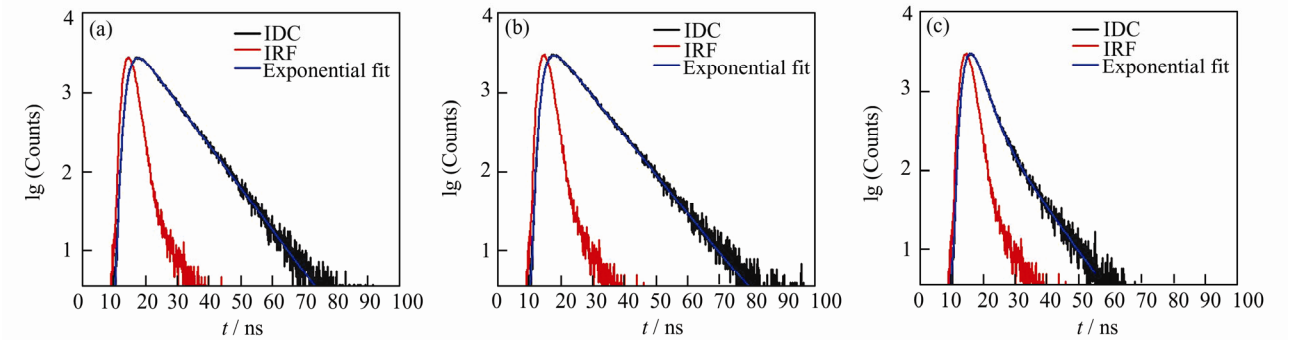

Fig. 6 Fluorescence decay curves of BIMA (a), 1 (b), and 2 (c) in chloroform at room temperature

The test concentration is 1.0×10^{-5} mol/L; λ_{ex} = 375 nm

Table 1 Parameters for the fluorescence quantum yield and lifetime measurements of BIMA, 1 and 2

Compound	Concentration/10^{-5} mol · L^{-1}	λ_{ex} /nm	φ/%	Lifetime / ns			χ^2
				τ_1	τ_2	τ_3	
BIMA	1.0	375	69	8.01	—	—	0.943
1	1.0	375	52	8.66	—	—	1.007
2	1.0	375	27	0.41	2.70	7.93	0.990

Measure was conducted at room temperature and the test solvent is chloroform

solution had a variety of different conformations, and therefore, the corresponding fluorescence attenuation performance for the form of a multi-exponential decay. The above results suggest that there is a best dihedral angle for luminescence between the imidazole and anthrance ring. Fluorescence quantum yield of the compound is strongly dependent on structure of the compound.

3 Conclusion

Two amphiphilic salts based on anthracene show solvent-polarity dependent fluorescence. Compared with anthracene, emission peaks of **1** or **2** red-shift and have lower fluorescence intensity. Research indicates that hydrophobic groups have an important effect on the fluorescence properties. Hydrophobic long chains of **1** and **2** increase solubility in weakly polar organic solvent and cause self-assembled aggregate emission. However, in polar organic solvent, monomer emission plays the major role for the solute solvation and has lower emission intensity. In mixed solvents with different polarities, **1** and **2** simultaneously exhibit multiple-modes of emissions. Colors of fluorescence can be obtained by adjusting the different proportions of the mixed solvent. In this paper, **1** and **2** show white fluorescence emission in a suitable proportion of the mixed solvent of carbon tetrachloride and methanol. **1** and **2** have lower fluorescence yield and lifetime than BIMA for the presence of hydrophobic groups. Results imply that hydrophobic groups change molecular conformation in excited state and reduce the degree of conjugation between anthracene and imidazole ring, which results in multiple exponential decay of fluorescence lifetime. For the intricate relationship between molecular structure and luminescence behavior caused by the complexity of the molecular fluorescence mechanism, it is difficult to specify a quantitative relationship in theory, but many empirical understandings could be acquired, which not only provide a useful reference for the design and synthesis of highly efficient light-emitting compounds but also provide important insights for future theoretical research.

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