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Naphthalene-based fluorophores: Synthesis characterization, and photophysical properties

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ABSTRACT

U-type, 1,8-diarylnaphthalenes and 1,8-diarylethynylnaphthalenes were synthesized and their structures were characterized by spectroscopic methods. Emission performance of these compounds with donor and acceptor was largely depended upon the solvent polarity and environmental acidity, which implied that they might be used as solvent polarity sensors or pH sensors as well. Moreover, some 1,8-diarylnaphthalenes exhibited aggregation-induced emission enhancement (AIEE) based on their photophysical investigation and might be used as light emitting materials for optoelectronic applications.

1. Introduction

Over the past decades, organic fluorescent compounds had received considerable attention for their various applications in many fields, such as biochemistry, supermolecular chemistry, analytical chemistry and organic optoelectronics [1–3]. For example, fluorescent pH sensors [4], metal ion sensors [5,6] and anion sensors [7–10] were widely used in biological and environmental evaluation due to their high selectivity and high sensitivity [11,12]. In the field of optoelectronics, more and more research had not only been focused on optimizing device structure for better performance, but also on searching new fluorescent compounds for practical application [13]. In order to efficiently create new fluorophores with high quantum yields, some fluorescent structure–property relationships were thereby established based on photoluminescent observation and theoretical calculation [14]. For this purpose, numbers of compounds with unique structure were developed for this investigation, such as, linear donor (D)–π–acceptor (A) system [15,16], D and A modified tetrahedral spirofluorene [17,18], D and A modified cruciform tetrakis(arylethynyl)benzene [19–21] and so on. As an extension of our research on fluorescent structure–property relationships [22–24], we herein report the synthesis and the structural characterization of naphthalene-based, U-type fluorophores, and their photoluminescent properties as well.

2. Results and discussion

2.1. Synthesis

Scheme 1 illustrated the synthetic routes to the target compounds **1a–h** and **2a–g**. Symmetrical 1,8-diarylnaphthalenes **1a–d** and **1h** were prepared by palladium catalyzed Suzuki coupling between 1,8-dibromonaphthalene and corresponding aryl boronic acid in a single step. Unsymmetrical 1,8-diarylnaphthalenes **1e–g** were synthesized by Suzuki coupling step by step. Similarly, 1,8-diarylethynylnaphthalenes **2a–g** were constructed *via* the Sonogashira coupling reaction. Reactions proceeded smoothly and products were obtained in moderate to good yields. All compounds were fully characterized by ^{1}H and ^{13}C NMR (Fig. S1), and high-resolution mass spectroscopy (HRMS).

2.2. Absorption and emission measurement

All synthesized compounds were soluble in common organic solvents, such as cyclohexane, dichloromethane, tetrahydrofuran, chloroform, methanol, dimethyl formamide, acetonitrile and so on. Absorption and emission spectra of these compounds were measured in these solvents and in a concentration of 1×10^{-5} M for comparison. Maximum absorption wavelengths were used as excitation wavelengths to record their emission spectra, accordingly. Table 1 summarized photophysical properties of all compounds in cyclohexane solutions.

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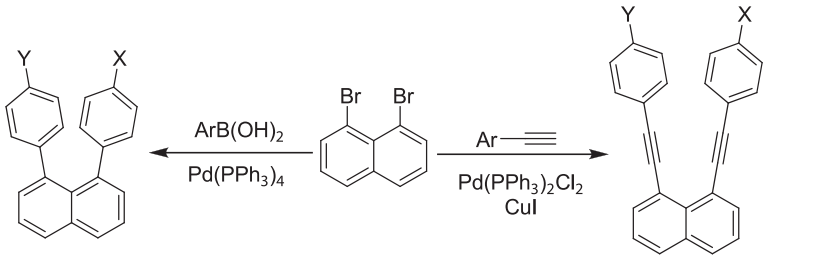

1a X=Y=H
1b X=Y=F
1c X=Y=CN
1d X=Y=OMe
1e X=F, Y=OMe
1f X=CN, Y=OMe
1g X=CN, Y=$N(Me)_2$
1h X=Y=$C(Me)_3$

2a X=Y=H
2b X=Y=F
2c X=Y=CN
2d X=Y=OMe
2e X=F, Y=OMe
2f X=CN, Y=OMe
2g X=CN, Y=$N(Me)_2$

Scheme 1. Synthesis of naphthalene-based, U-type fluorophores.

Table 1
Absorption and emission of **1a–h** and **2a–g** in cyclohexane.

Compounds	Abs.(nm)	Em. (nm)	Stokes' shift (nm)	HOMO[a] (eV)	LUMO[a] (eV)	Gap[a,b] (eV)	Φ[c]
1a	300	371	71	−8.73	−0.50	8.23	0.032
1b	297	373	76	−8.93	−0.71	8.22	0.0085
1c	275	379	104	−9.12	−0.98	8.14	0.059
1d	300	382	82	−8.68	−0.47	8.21	0.021
1e	300	380	80	−8.78	−0.59	8.19	0.018
1f	296	398	102	−8.88	−0.73	8.15	0.092
1g	303	388,459	85	−8.63	−0.68	7.95	0.054
1h	303	376	73	−8.69	−0.46	8.23	0.037
2a	341	369,389	28	−8.47	−0.91	7.56	0.46
2b	340	369,389	29	−8.64	−1.06	7.58	0.37
2c	348	378,398	30	−8.84	−1.30	7.54	0.57
2d	348	377,398	29	−8.36	−0.87	7.49	0.15
2e	341	379,398	38	−8.50	−1.00	7.50	0.32
2f	343	395,415	52	−8.74	−1.20	7.54	0.54
2g	339	382,478	43	−8.49	−1.17	7.32	0.23

[a] Energy levels of HOMO and LUMO were calculated by PM3 level of theory.
[b] Energy gap related to the energy difference between LUMO and HOMO.
[c] Quantum yields were calculated on the basis of 9,10-diphenylanthracene as standard (Φ=0.95 in hexane).

2.3. Absorption and emission vs. molecular structure

Maximum absorption wavelengths of 1,8-diarylnaphthalenes **1a–h** in cyclohexane were observed at about 300 nm except for the case of **1c** with a slightly blue-shift to 275 nm (Fig. 1A). Extension of the aryl group with the triple bond from **1** to **2**, better conjugation between the aryl group and naphthalene was approached. In cases of 1,8-diarylethynylnaphthalenes **2a–g**, absorption spectra in cyclohexane were all bathochromic-shifted in comparison with those of **1a–g**, accordingly (Fig. 1C). The absorption difference between two series was significant and could be predicted and understood by the energy gaps between levels of HOMO and LUMO, which were calculated by PM3 method (Table 1).

Besides **1g** and **2g**, no UV absorption was detected above 350 nm. Absorption spectra could be simply accounted for a combination of naphthalene and phenyl/phenylethynyl chromophores. There was no obvious spectroscopic evidence to support for a significant charge-transfer interaction between the parallel aryl groups of these compounds in cyclohexanes, even for compounds with a D–A system (**1e**, **1f**, **2e** and **2f**). These compounds exhibited similar absorption spectra with those of **1a** and **2a**. It could be explained in terms of the electron cloudy distribution in ground states, which was concentrated on methoxyphenyls for **1e**, **1f**, **2e** and **2f** (Table 2). Long tail absorption was detected for **1g** and **2g** in cyclohexane, which could be referred to the intramolecular charge transfer (ICT). This phenomenon could also be illustrated by the electron cloudy distribution of ground states of **1g** and **2g**. The calculated results presented a concentrated electron cloudy distribution on naphthalenes and clearly pointed out that there was the existence of ICT from dimethylamino to naphthalene.

Emission wavelengths at local excited band (LE) for **1a–h** in cyclohexane varied from 371 to 398 nm, while those of **2a–f** were observed from 369 to 395 nm with vibrational structures, respectively. ICT emission spectra were detected for the cases of **1g** and **2g** in cyclohexane (Fig. 1B and D), which were in a good accordance with their absorptions. For compound **2g**, the emission from LE band was hardly expressed. Relative larger Stokes' shifts were observed for the series of **1a–h** in comparison with those of **2a–g**, respectively.

2.4. Absorption and emission vs. solvent polarity

Based on the polarity of organic solvent varied, the solvatochromism of all compounds was examined. The absorption spectra of all compounds were nearly independent of solvent polarity, which focused around 300 nm for 1,8-diarylnaphthalenes **1a–h**, and around 345 nm for 1,8-diarylethynyl -naphthalenes **2a–g**. Compounds **1g** and **2g**, with strong electron–donating group (dimethylamino) and electron-withdrawing group (cyano), presented almost identical absorption spectra in different solvents (Fig. 2A).

In sharp contrast, emission spectra showed quite different behaviors. They were unchanged for **1a**, **1b**, **1h**, **2a** and **2b** as lacking of either electron-donating or strong electron-withdrawing groups. Emission spectra of **1c**, **1d**, **2c**, and **2d** were slightly red-shifted as the solvent polarity increased. Unlike compounds above, emission spectra of **1e**, **1f**, **1g**, **2e**, **2f**, and **2g** showed strong solvent polarity dependence, which implied that these compounds might be used for solvent polarity sensors (Fig. 2B and C).

A standard dipolar model for solvent stabilization (Scheme 2) could be employed to explore this solvatochromic character [25]. When a fluorophore was excited, an electron transition occurred from S_0 to S_1, the dipole moment of S_1 state was much larger than that possessed by S_0 state. In cases of **1c**, **1d**, **2c** and **2d**, the energy levels of S_1 were lowered due to the degree of reorientation of polar solvent around S_1. This effect became larger as the solvent polarity increased, resulting in the emission at a longer wavelength (Scheme 2A). With charge-transfer process existing in **1g**