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Photophysical processes of some benzimidazole derivatives

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Abstract

The photophysical properties of *N*-(α-naphthyl)-benzimidazole (α-NABI), *N*-(β-naphthyl)-benzimidazole (β-NABI) and *N*-(α-pyridyl)-benzimidazole (α-PYBI) were studied and α-NYBI exhibit intramolecular charge transfer fluorescence in polar solvents. The fluorescence of benzimidazoles can be quenched by acetic acid and the existence of exciplexes was observed between the benzimidazole derivatives and acetic acid. Particularly, the maximum emission peak of solution of α-PYBI in mixed solvent, ether and acetic acid, presents obvious red-shift with the increase of concentration of acetic acid in the mixed solvent.

Keywords: Benzimidazole derivatives; Photophysical processes; Quenching; C_{60}; Acetic acid

1. Introduction

Benzimidazole groups exist extensively in biologically active substance and pharmaceutical molecule. The structures of cyanocobalamin (Vitamin B_{12}), as an example, contain a benzimidazole group [1]. Moreover, the derivatives of benzimidazole have been widely used in composition of optoelectronic functional materials, which due to their heteroatom-containing π-conjugated structure [2]. Rettig have found that the excited state of *N*-aryl-substituted derivatives of nitrogen-containing heterocycle, such as carbazole, indole, benzimidazole, etc., exhibit intramolecular charge transfer (ICT) with an increase in electron-accepting ability of the *N*-aryl-asmoiety [3,4].

In this paper, the photophysical processes of *N*-(α-naphthyl)-benzimidazole (α-NABI), *N*-(β-naphthyl)-benzimidazole (β-NABI) and *N*-(α-pyridyl)-benzimidazole (α-PYBI) were investigated using fluorescence quenching technique, etc., in which the formation conditions and mechanism of exciplex were especially investigated since the complexes of excited and ground states was often a middle state of photochemical, photophysical and photobiological primary processes [5].

2. Experimental

The reagents and chemicals for preparation these benzimidazole derivatives were used as received unless noted otherwise. Cyclohexane, ethyl acetate, chloroform, ethanol, benzene, diethyl ether, acetic acid and methanol were analytical grade reagents and treated according to standard method used before, which were applied to measurement of the light-emitting properties.

The compounds, α-NABI, β-NABI and α-PYBI were synthesized by reaction of carbon-nitrogen bond forming of benzimidazole with α-bromonaphthalene, β-bromonaphthalene and α-bromopyridine, respectively. The structures were characterized by IR, ^{1} HNMR and elementary analysis. The synthesis route was outlined in Scheme 1. [6]

The measurement of fluorescence was performed on a Perkin-Elmer LS-50B fluorometer with an excitation wavelength of 270 nm. Both excitation and emission bonds were set at 5 nm on these experimental conditions. All the experiments were carried out at 25 ± 1 °C.

3. Results and discussion

3.1. Absorption and fluorescence emission spectra

The UV–vis absorption spectra of α-NABI, β-NABI and α-PYBI in chloroform were shown in Fig. 1. It can be seen

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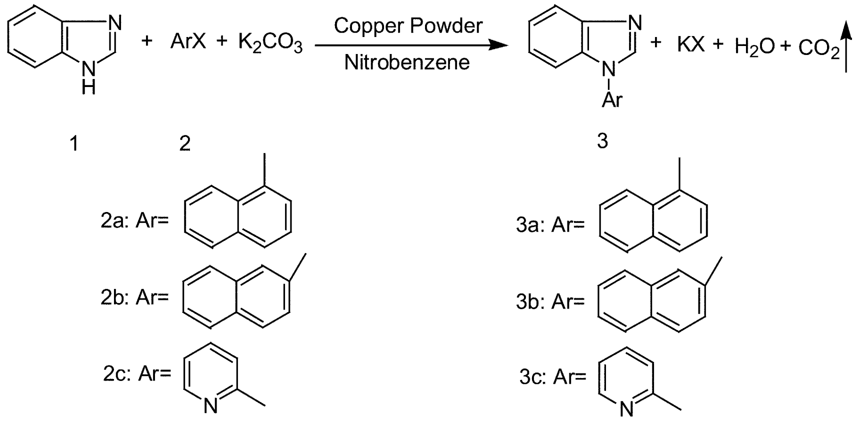

Scheme 1. The synthesis route of the compounds.

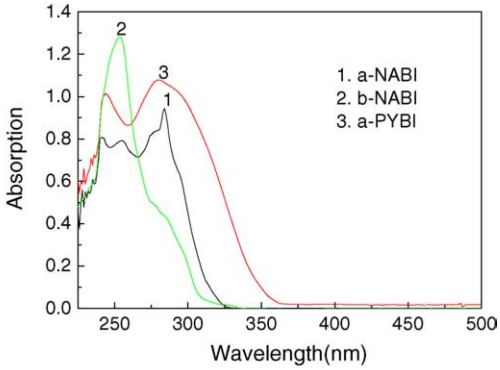

Fig. 1. Absorption spectra of α-NABI, β-NABI and α-PYBI in $CHCl_3$.

from Fig. 1 that the maximum absorptions of the α-NABI, β-NABI and α-PYBI are at 284, 278 and 253 nm, respectively. The fluorescence emission spectra of three compounds were shown in Fig. 2. The maximum emission peaks position of solution of α-NABI, β-NABI and α-PYBI in $CHCl_3$ are at 360, 375 and 388 nm, respectively. By comparison with α-NABI and β-NABI, the emission peak of α-PYBI exhibit an obvious red shift. Moreover, the fluorescence halfwidth $\Delta\nu$ of α-PYBI is larger compare with that of α-NABI and β-NABI [7].

3.2. Solvent effect on photoluminescence

N-aryl-substituted benzimidazole, α-NABI, β-NABI and α-PYBI, have good solubility in common organic solvents, such as cyclohexane, diethyl ether, ethyl acetate, chloroform, ethanol, benzene, etc. The emission spectra of α-NABI, β-NABI and α-PYBI were investigated in different solvents and the results showed the peak positions of emission spectra of α-NABI and β-NABI in different solvents are similar without an obvious change as a function of the solvent polarity. But the emission spectra of α-PYBI exhibit a charge in different solvents (Fig. 3). In contrast, a red shift, loss of the fine structure and broadened band in the emission spectra of α-PYBI are observed and the fluorescence halfwidth $\Delta\nu$ are increased with increasing of solvent polarity [8].

The spectral characteristics indicate the existence of a intramolecular charge transfer (ICT) in the excited α-PYBI [9].

Rettig and Zander predicted that the ICT emission will be observed if the molecular system satisfies

$$E(\mathrm{ICT}) - E(\mathrm{LE}) < 0$$

$$E(\mathrm{ICT}) = \mathrm{IP(D)} - \mathrm{EA(A)} + C + \Delta E_{\mathrm{solv}}$$

where E(ICT) and E(LE) are the energies of the lowest ICT state and the lowest locally excited state, respectively. IP(D) and EA(A) are the ionization potential and electron affinity of

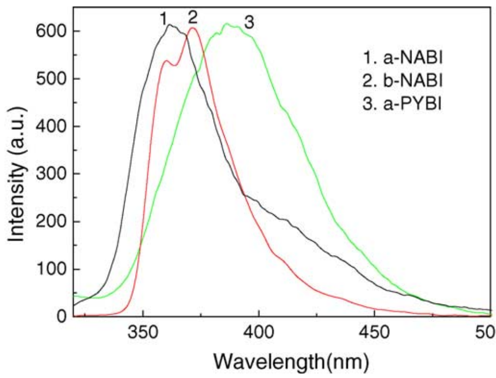

Fig. 2. Emission spectra of α-NABI, β-NABI and α-PYBI in $CHCl_3$.

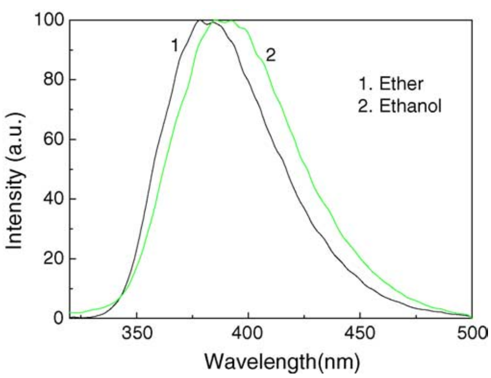

Fig. 3. Fluorescence spectra of α-PYBI in different solvents.

the donor and acceptor moieties of the molecule, respectively. C is the coulomb energy and ΔE_{solv} is the interaction between the charge-separated molecule and the polar solvent. On going from α-NABI or β-NABI to α-PYBI, the donor moiety is the some, but the electron-accepting ability of pyridyl is enhanced. Therefore ICT emission of α-PYBI can be seen in polar solvents [3,4].

3.3. *The quenching of fluorescence of α-NABI, β-NABI and α-PYBI by C_{60}*

The interactions between *N*-aryl-substituted benzimidazole derivatives and C_{60} were examined. The results of fluorescence quenching of α-PYBI, as a sample, were shown in Fig. 4. As we have seen in Fig. 4, on progressive increase in concentration of C_{60}, the emission intensity of fluorescence are decreased. The quenching process of fluorescence is conformed to Stern-Volmer equation, which demonstrated the strong interaction between α-PYBI and C_{60} happens in the excited.

The interactions of the benzimidazole with C_{60} are mainly coming from the photoinduced charge-transfer process of the π-electron system in α-NABI, β-NABI and α-PYBI with the electron acceptor (C_{60}).

3.4. *Interaction of α-NABI, β-NABI and α-PYBI with acetic acid*

The studies of interactions between *N*-aryl-substituted benzimidazole derivative and acetic acid were helpful to understand the photo-electronic properties and intramolecular charge transfer (ICT) processes of α-NABI, β-NABI and α-PYBI.

Figs. 5 and 6 give the fluorescence spectra of solutions of α-NABI and β-NABI in mixed solvent of ether and acetic acid, respectively. As we have seen in Figs. 5 and 6, on progressive increase in concentration of acetic acid, the simple molecule fluorescence of α-NABI and β-NABI are quenched efficiently. At the same time, the new emission bands appear at relatively longer wavelength. The emission intensity of the new band increase with increase in the concentration of acetic acid and the spectra all pass an isostilbic point, which indicate the exciplex are formed between α-NABI or β-NABI and acetic acid.

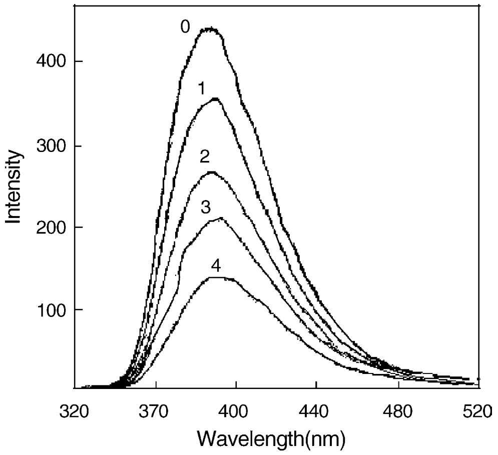

Fig. 4. The quenching of fluorescence of α-PYBI by C_{60} in $CHCl_3$. Concentration of α-PYBI is 8.63×10^{-7} mol/L; concentration of C_{60} (mol/L) (0) 0.00; (1) 2.38×10^{-7}; (2) 6.35×10^{-7}; (3) 1.43×10^{-6}; (4) 2.22×10^{-6}.

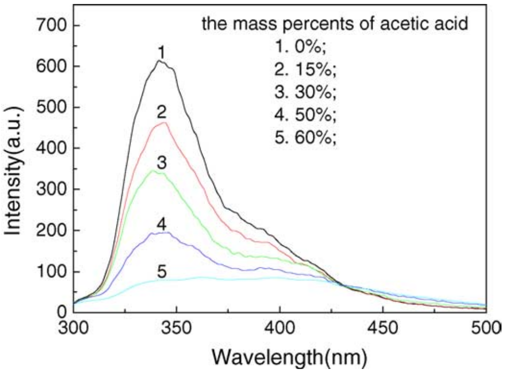

Fig. 5. Fluorescence spectra of solution of α-NABI in mixed solvents of ether and acetic acid.

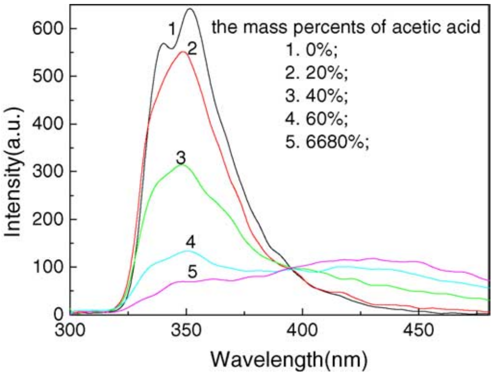

Fig. 6. Fluorescence spectra of solution of β-NABI in mixed solvents of ether and acetic acid.

Similarly, the fluorescence of α-PYBI are also quenched by acetic acid and the new emission band of exciplex appears in longer wavelength region (Fig. 7). However, it should be particularly indicated that the emission spectra of α-PYBI are

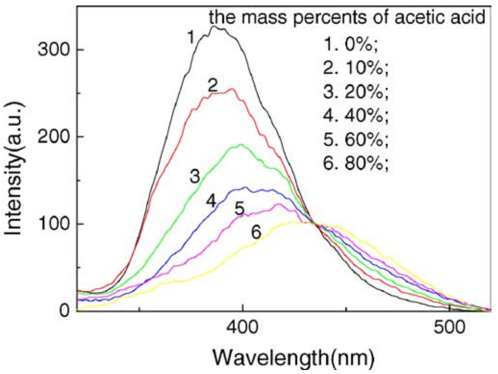

Fig. 7. Fluorescence spectra of solution of α-PYBI in mixed solvents of ether and acetic acid.

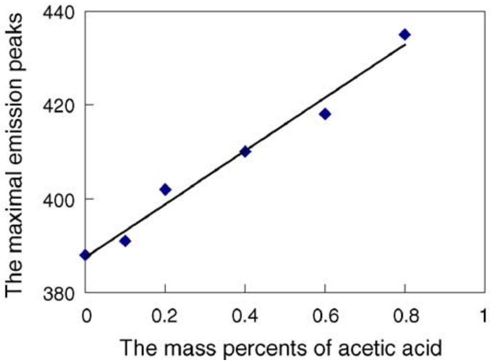

Fig. 8. The linear dependence of the maximal emission wavelength with mass percents of acetic acid.

obviously red shift with progressive increase in concentration of acetic acid in the mixed solvent of ether and acetic acid. The plots of maximal emission wavelength versus concentration of acetic acid in the mixed solvent show a linear dependence (Fig. 8). It have been well known that the excited molecule of α-PYBI has obvious intramolecular charge transfer, so the polarity of medium can efficiently affect molecular energy and existence state of α-PYBI. Acetic acid is not only a polar solvent but also an organic acid, so it can act on α-PYBI molecule, which bring about the red shift of emission peak with the increasing of acetic acid [9].

4. Conclusions

The photophysical properties of *N*-aryl-substituted benzimidazoles, α-NABI, β-NABI and α-PYBI, were investigated. α-PYBI exhibit intramolecular charge transfer fluorescence in polar solvent. The existence of exciplexes were observed between the benzimidazole derivatives and acetic acid. Particularly, the maximum emission peak of α-PYBI presents obvious red shift with the increase of concentration of acetic acid in mixed solvent of ether and acetic acid.

Acknowledgements

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