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Fluorescence properties of dyad compounds containing 1,8-naphthalimide and 1,3,4-oxadiazole

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Abstract

Absorption and fluorescence spectra of several dyad compounds consisting of 1,8-naphthalimide and 1,3,4-oxadiazole moieties have been investigated in different solvents. The intramolecular energy transfer from oxadiazole to naphthalimide was observed. The fluorescence decay lifetimes of these dyad systems were measured by nanosecond time-resolved laser photolysis. © 1997 Published by Elsevier Science S.A.

Keywords: Dyad compounds; Time-resolved laser photolysis; Electroluminescence; Intramolecular energy transfer

1. Introduction

Organic electroluminescent (EL) devices have a wealth of applications, such as back-light for thin flat television screens, computer displays and wristwatch faces, but there is a question of lifetime. It is well known that to achieve good performance in EL devices, the injection of electron and hole should be in balance. The electron-withdrawing oxadiazole unit is thought to have high electron affinity and to facilitate electron injection [1]. On the other hand, various types of EL devices with multilayer or single-layer structures have been reported, and various emitting colors and even white light have been obtained [2,3]. Considering the complication of doping in the emitter layer and intermolecular excited energy transfer in EL devices, we therefore focused on developing dyad and triad compounds, in which both electron and hole transporting units were connected directly with the emitting unit via covalent bonds. Thus, the possibility of developing organic EL devices without layer–layer exciton quenching is quite high. In our previous study, new dyad compounds containing 1,3,4-oxadiazole and 1,8-naphthalimides were synthesized, and we have investigated the use of a new dyad dye for the fabrication of organic EL devices. Greenish-yellow EL peaked at 532 nm with a maximum luminance of 225 cd m^{-2} was observed [4]. The improved performance is believed to result from the high electron affinity of the oxadiazole unit in the dyad molecules. Intramolecular energy transfer (Intra-ET) from oxadiazole to naphthalimide in these dyad compounds consisting of 1,8-naphthalimide and 1,3,4-oxadiazole moieties has been observed.

Intra-ET in fluid solution is of great interesting in both mechanistic and synthetic organic photochemistry. For molecules containing donor and acceptor groups separated by one, two or three methylene groups, different excited singlet energy transfer efficiency was attained in each case [5,6], which indicated that the methylene bridge plays an important role in intramolecular singlet energy transfer. The lengthening the ''bridge'' from one to three methylene groups does not significantly alter the distance between the chromophores because of the flexibility of the methylene chain.

This paper describes a preliminary study of Intra-ET in these dyad dyes by comparing the fluorescence lifetime of the dyes, measured by nanosecond time-resolved fluorescence spectrometry. 1,3,4-Oxadiazole has a high absorption coefficient at the wavelength of the UV radiation, and therefore the absorption of the compounds in this study in the UV region is quite strong. At the same time the blue fluorescence of the oxadiazole groups is quenched, which indicates that the intramolecular singlet–singlet energy transfer (Intra-SSET) from oxadiazole to naphthalimides is effective. Fig. 1 shows the chemical structures of the dyad compounds synthesized by us.

2. Experimental

The synthesis and the structural data of these dyad compounds were published in [4]. Absorption and fluorescence

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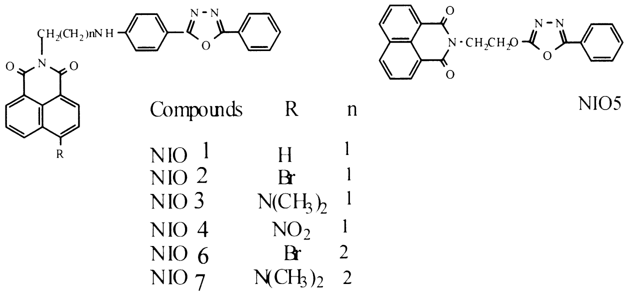

Compounds	R	n
NIO 1	H	1
NIO 2	Br	1
NIO 3	$N(CH_3)_2$	1
NIO 4	NO_2	1
NIO 6	Br	2
NIO 7	$N(CH_3)_2$	2

Fig. 1. The structures of the dyad compounds in this study.

spectra were recorded using a Shimadzu UV-260 spectrometer and a Hitachi-850 fluorospectrometer, respectively. The nanosecond time-resolved fluorescence decay kinetics was measured by a fast-response diode (DET2-Si, Thorlabs Inc.), which connects with a digital storage oscilloscope (Tektronix TDS 420). The excitation light is from a nitrogen gas laser, 337 nm with a 6–7 ns pulse width (Radiant Dyes Laser Acce.). In front of the photodiode there is a color optical filter (Type FAL, transmittivity 0.7, half-width 66 nm, CZG, Germany), whose wavelengths are centered on 408, 450, 480, 538 and 601 nm, respectively. All measurements were performed in air at room temperature.

3. Results and discussion

The absorption and fluorescence spectral data of these dyad compounds and comparison systems are listed in Table 1. The fluorescence maximum wavelength of NIO3 is 517 nm regardless of the different excitation wavelengths (333 and 413 nm). NIO7 shows a similar result as listed in Table 1. Comparing the spectra in Fig. 2, the absorption of the dyad compound is the exact sum of that of the constituent chromophores. Other compounds show similar results. This indicates that there is little or no interaction between the chromophores in the ground state, so that their individual characteristics should be maintained in the dyad compounds. The absorption and emission spectra of *N*-ethyl-4-bromo-1,8-naphthalimide (NBP, $\lambda_{\max}^{ab} = 340$ nm, $\lambda_{\max}^{fl} = 390$ nm in THF) are almost identical with those of 2-phenyl-5-[4-(2-amino)ethylamino]phenyl-1,3,4-oxadiazole (OXZ), so only one absorption peak and one emission peak were observed in the experiments for NIO2 and NIO6, probably due to the similar contribution of NBP and OXZ. It cannot be determined whether or not the emission of the oxadiazole moiety in NIO2 and NIO6 was quenched. Therefore, it could not be concluded that there is an intramolecular energy transfer between the two chromophors only based on the results of emission spectra. However, because the absorption and emission maxima of *N*-ethyl-4-dimethylamino-1,8-naphthalimide (NP, $\lambda_{\max}^{ab} = 407$ nm, $\lambda_{\max}^{fl} = 508$ nm in THF) are located at longer wavelengths than those of OXZ, their individual absorption characteristics are maintained in NIO3 and NIO7, so that two absorption peaks due to the different contributions of NP and OXZ, respectively, could be observed. However, in NIO3 and NIO7 the emission of oxadiazole was quenched, which means there exists an effective intramolecular singlet–singlet energy transfer due to the larger overlap between the absorption of the NP moiety and emission of the OXZ moiety in NIO3 and NIO7.

Table 1
Absorption ($\lambda_{\max}^{ab}$) and fluorescence ($\lambda_{\max}^{fl}$) maximum wavelengths of the compounds studied [a,b]

	NIO2	NIO3	NIO6	NIO7	NP + OXZ [c]	NP	OXZ
$\lambda_{\max}^{ab}$/nm	340	333; 413	340	332; 411	340; 407	407	338
$\lambda_{\max}^{fl}$/nm	406	517	409	515	423 [d]; 509 [e]	508	419

[a] The fluorescence data of the compounds were obtained by excitation at their absorption maximum wavelengths.

[b] The concentration of each compound in tetrahydrofuran (THF) is 2.5×10^{-5} M.

[c] NP is *N*-ethyl-4-dimethylamino-1,8-naphthalimide; OXZ is 2-phenyl-5-[4-(2-amino)ethylamino]phenyl-1,3,4-oxadiazole. In the NP + OXZ mixture the molar ratio between NP and OXZ is 1:1.

[d] Excitation at 340 nm.

[e] Excitation at 407 nm.

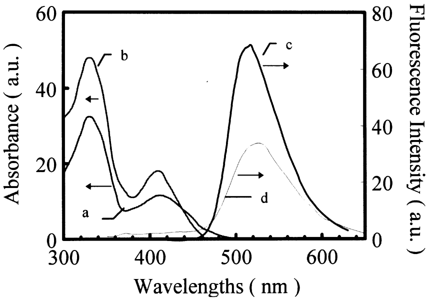

Fig. 2. The absorption spectrum in THF (a) and fluorescence spectra in different solvents of the dyad compound NIO3. The concentration of all samples is 2×10^{-5} M. The fluorescence spectra were obtained by excited at 333 and 338 nm for the solutions of THF (c) and EtOH (d), respectively. Curve b is the absorption of the mixture NP + OXZ (1:1 mol/mol) in THF (2.5×10^{-5} M).

As seen as in Fig. 2 in [4], there is only the characteristic emission of the 1,8-naphthalimide moiety in the EL spectrum. Comparing the absorption spectrum of NIO7 in solution, which was shown in Table 1, the absorption maximum wavelengths of NIO7 in thin solid state shifts to the red by about 8–18 nm. Because oxadiazole unit has a high electron affinity, it is possible that the electron is injected into the LUMO of oxadiazole in the case of an EL device. On the other hand, oxadiazole was linked through the imide. Electron transfer from oxadiazole to 1,8-naphthalimide is very difficult since the imide nitrogen contains a negative charge [7]. When a voltage is applied to the EL device, both holes and electrons are injected from the corresponding electrodes and the π and π^* orbitals of the oxadiazole moiety, and recombine there. Then the energy of the excited oxadiazole moiety (donor) transfers to the 1,8-naphthalimide moiety (acceptor) and the EL originates from it.

Figs. 2 and 3 show the solvent effect on the emission of dyad compounds NIO7 and NIO3 in different solvents. The

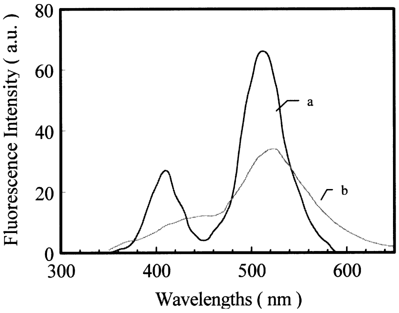

Fig. 3. Fluorescence spectra of dyad compound NIO7 (2×10^{-5} M) in (a) THF and (b) EtOH: the excitation wavelengths are 332 and 338 nm, respectively.

Table 2
The fluorescence decay lifetimes of the compounds in THF solution (detected at different optical filter wavelengths λ_{fl} and excited at 337 nm)

	NP	NP + OXZ	OXZ	NIO3	NIO7	NIO1	NIO5
$\tau\pm0.2$/ns	4.8	6.2 [a]	4.6	4.5	4.8; 2.5	4.3	4.0
λ_{fl}/nm	538	538	450	538	538; 450	408	408

[a] No signal detected at 408 and 450 nm.

absorption maximum wavelengths of these dyad compounds in absolute ethanol were red shifted compared with those in THF. Corresponding to this, the emission maximum wavelengths of the dyes in different solvents are also shifted. This indicates that the electron-donor ability of the oxadiazole unit in the dyad compounds is stronger in ethanol solvent. Meanwhile, the relative quantum efficiency of the dyes in ethanol decreases, clearly due to electron transfer from oxadiazole to naphthalimide. For NIO3, the relative quantum efficiency in ethanol is 2%, whereas in THF it is 17.6%; For NIO7, the relative quantum efficiency in ethanol is 2.3%, whereas in THF it is 23.8%.

The fluorescence decay lifetimes of the different compounds and systems are listed in Table 2, in which the decay lifetimes were obtained according to first-order decay kinetics. The NP + OXZ mixture system has a fluorescence decay lifetime of 6.2 ns at 538 nm. However, the corresponding dyad compounds (NIO3 and NIO7) synthesized in this study have lifetimes of 4.5–4.8 ns detected at 538 nm, which are shorter than that of the mixture. When detected at 450 nm for NIO7, the fluorescence decay lifetime is very short (2.5 ± 0.4 ns). This result means that the 1,8-naphthalimide moiety affects the fluorescence decay of 1,3,4-oxadiazole via a polymethano-connecting chain. This additional process has a rate constant k_{add} which could be obtained by the equation as follows [8]: $k_{add}=1/\tau-1/\tau_0$. For NIO7 at the emission of the 1,3,4-oxadiazole moiety (450 nm), $\tau=2.5$ ns, $\tau_0=4.6$ ns, so $k_{add}=1.83\times10^8$ s^{-1}. The quenching of the emission of the 1,3,4-oxadiazole moiety in these dyad compounds is very obvious. Compared with the mixture NP + OXZ, the additional process total rate constant in the dyad compounds, $k'_{add}=6.09\times10^7$ s^{-1} for NIO3 at 538 nm ($\tau=4.5$ ns, $\tau_0=6.2$ ns), $k'_{add}=4.7\times10^7$ s^{-1} for NIO7 at 538 nm ($\tau=4.8$ ns, $\tau_0=6.2$ ns).

Acknowledgements

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