Chinese Chemical Letters Vol. 14, No. 2, pp 159 – 162, 2003
http://www.imm.ac.cn/journal/ccl.html

The Electron Transfer Reaction between *p*-Nitrobenzoates and *β*-N, N-Dimethylaminonaphthalene

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Abstract: A few of *p*-nitrobenzoates were synthesized, and the electron transfer of them with *β*-N, N-dimethylaminonaphthalene (DMAN) in methanol solution was studied. Steady-state fluorescence results showed the cyclodextrin moiety in *p*-nitrobenzoyl-*β*-cyclodextrin would block the electron transfer pathway from DMAN compared with other electron acceptors, thus, reduced the electron transfer efficiency.

Keywords: Electron transfer, *β*-cyclodextrin, naphthalene derivatives, fluorescence.

Photoinduced electron-transfer (PET) reactions are fundamentally important in biology and technology[1,2]. Because of the complexity of PET in biological systems, many simple compounds were synthesized to look into its detailed mechanism[3]. In previous papers, we reported the electron transfer reaction in the supramolecular systems assembled by mono-6-*p*-nitrobenzoyl-*β*-cyclodextrin **6** and naphthalene derivatives in aqueous solution[4]. In the present paper the intermolecular electron transfer from *β*-N, N-dimethylaminonaphthalene (DMAN) to a series of *p*-nitrobenzoates **1~6** (**Figure 1**) in methanol solution and the effect of substitutes on the electron transfer efficiency are reported.

Experimental

p-Nitrobenzoyl chloride was obtained from Sigma and used without further purification. α-Naphthoic acid (NA) was purified by sublimation at reduced pressure. **1~5** were prepared from *p*-nitrobenzoyl chloride and relevant alcohols and purified by recrystallized in water-methanol. **6** was prepared in known procedures[4]. Deionized water was used throughout the experiments.

Fluorescence emission spectra were measured with a Hitachi MP850 spectrometer in degassed solution at room temperature.

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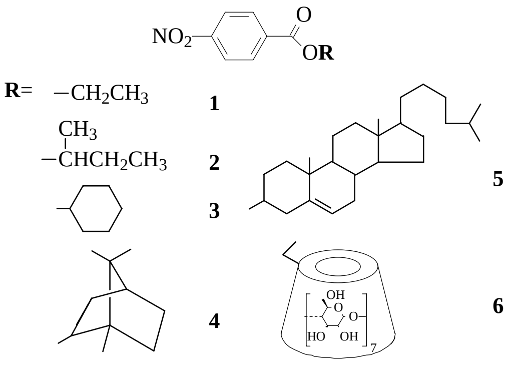
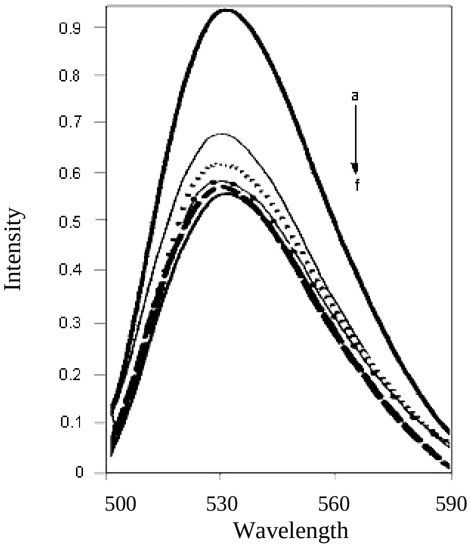
Figure 1 The structure of electron acceptors



Results and Discussion

The fluorescence of DMAN could be strongly quenched by **1**~**6** in methanol solutions and **Figure 2** shows the representative fluorescence spectra.

Figure 2 The fluorescence spectra of DMAN in the presence of different concentration of **1** in methanol



[DMAN]: 2×10^{-6} mol/L; [**1**]: 0, 20, 30, 40, 50, and 60 μmol/L (from a to f)

These quenching were attributed to electron transfer from DMAN to *p*-nitrobenzoate **1**~**6**[4]. In water-methanol binary solvents, the fluorescence quenching constant for **1**-DMAN increased, compared to **6**-DMAN in which the fluorescence quenching constant decreased, when the methanol was increased from 0 to 100% in binary solvents[4]. This showed that the routes of electron transfer were different for **1**-

DMAN and **6**-DMAN systems in water. **6** and DMAN form host-guest complex in aqueous solution[4], which will be destroyed in pure methanol solution because of its smaller polarity. It was supported by the fluorescence measurements. α-Naphthoic acid (NA)-**6** system was probed in water and methanol solution, respectively. **Figure 3** shows fluorescence intensity of NA increased when the concentration of **6** increased in water. It is concluded that NA was included into the cavity of **6** in water[5]. According to the comparison experiment, NA was not included by **6** in methanol because of the no change fluorescence intensity. It is reasonable to predict DMAN not to be included into the cavity of **6**, and the electron transfer can only occur between **6** and free DMAN just like **1**~**5**-DMAN systems in methanol solution.

Figure 3 Fluorescence intensity change of NA-**6** system in water and methanol

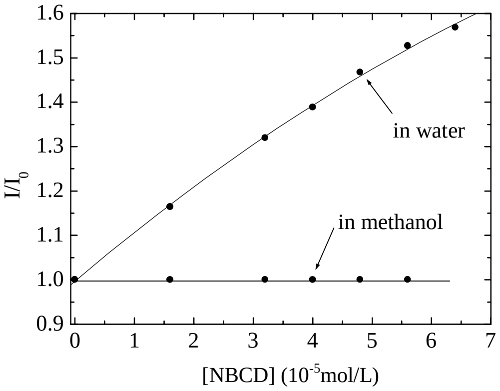
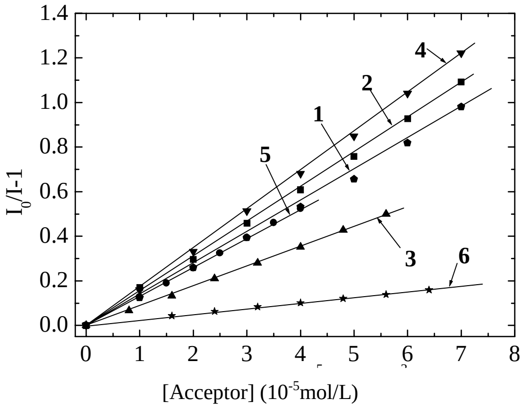


Figure 4 Stern-Volmer plots for the fluorescence quenching of DMAN with **1**~**6** in methanol at 25°C.



I_0 is the fluorescence intensity in the absence of acceptor, I is the fluorescence intensity in the presence of acceptor, respectively.

The experimental results obtained in methanol were well fitted with dynamic Stern-Volmer equation and the Stern-Volmer plots of DMAN with compounds **1**~**6** were showed in **Figure 4**.

The Stern-Volmer constants (K_{SV}) and the fluorescence quenching constants (k_q) were showed in **Table 1**.

Table 1 Constants of Stern-Volmer and fluorescence quenching for DMAN with **1**~**6**

Acceptor	**1**	**2**	**3**	**4**	**5**	**6**
K_{SV} (M^{-1})	14014	15608	11000	17467	12133	2483
k_q (10^{11} $M^{-1}s^{-1}$)^a	5.628	6.268	4.418	7.015	5.274	0.997

^{a} $k_q = K_{SV} / \tau_0$, and τ_0=24.9ns[4].

The results showed that the fluorescence quenching constants for compounds **1**~**5** were much larger than that of the cyclodextrin derivative **6**. This indicated that the electron transfer in **6**-DMAN system was less efficient than in the systems of **1**~**5**-DMAN. In our previous work[6], it has been demonstrated that the *p*-nitrobenzoyl group covered the rim of the cavity of *β*-cyclodextrin in **6**. Thus, the interaction between the electron donor and acceptor center would be influenced by big volume of the *β*-CD moiety. In compounds **1**~**5**, the *p*-nitrobenzoyl group is easy to approach to the electron donor DMAN, therefore, the electron transfer reactions occurred with high efficiency.

In summary, **1**~**6** caused the decrease of the fluorescence intensity of DMAN and the quenching data can be fitted with dynamic Stern-Volmer equation in methanol solution. The dynamic quenching process should be attributed to the electron transfer from DMAN to *p*-nitrobenzoyl group of **1**~**6**. The rim-covering conformation of **6** would block the pathway of the electron transfer and decrease the electron transfer efficiency in **6**-DMAN species.

Acknowledgment

This work was financially supported by the National Natural Science Foundation of China (No.29972038).

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Received 3 April, 2002