A MOLECULE DETECTION SENSOR OF MODIFIED CYCLODEXTRIN BASED ON GUEST-RESPONSIVE INTRAMOLECULAR FLUORESCENCE QUENCHING

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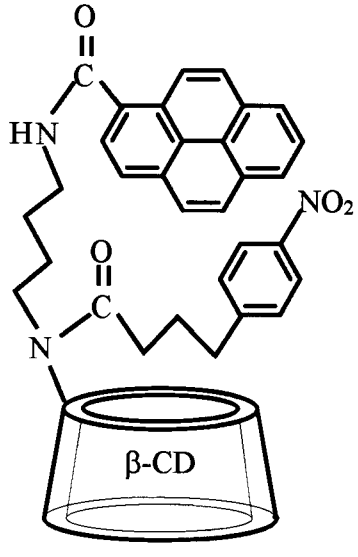
Abstract - A β-cyclodextrin derivative bearing both pyrene and *p*-nitrobenzene units exhibits remarkable guest-responsive fluorescence quenching and acts as a chemosensor for molecule detection.

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six (α-CD), seven (β-CD), and more D-glucose units. They have a cavity and include various organic compounds in aqueous solution.[1,2] CDs bearing an appending moiety form self-inclusion complexes and excludes the appending moiety from inside to outside of the CD cavity associated with guest accommodation.[3-7] On this basis, various types of molecule sensing systems have been constructed.[8] We report here a new type of sensory system (**1**), which has both fluorescent donor and acceptor and exhibits guest-responsive diminishment in fluorescence intensity based on the fluorescence quenching occurring upon guest accommodation.

A sensory system which employs metal-cation responsive fluorescence quenching was previously reported by Shinkai *et al.*[9] The system contains a calixarene bearing pyrene as a fluorophore and nitrobenzene as a quencher and works based on the distance change between pyrene and *p*-nitrobenzene caused by binding of alkali-metal cations. In this study we prepared a β-CD derivative (**1**) in which nitrobenzene is likely to be included in the cavity while pyrene always exists outside the cavity because of its large size to be included in the β-CD cavity. This system is expected to operate as a chemosensor for molecule detection because it excludes the nitrobenzene moiety from inside to outside the cavity upon guest accommodation so as to make the nitrobenzene moiety closer to the pyrene unit, thereby resulting in the effective quenching.



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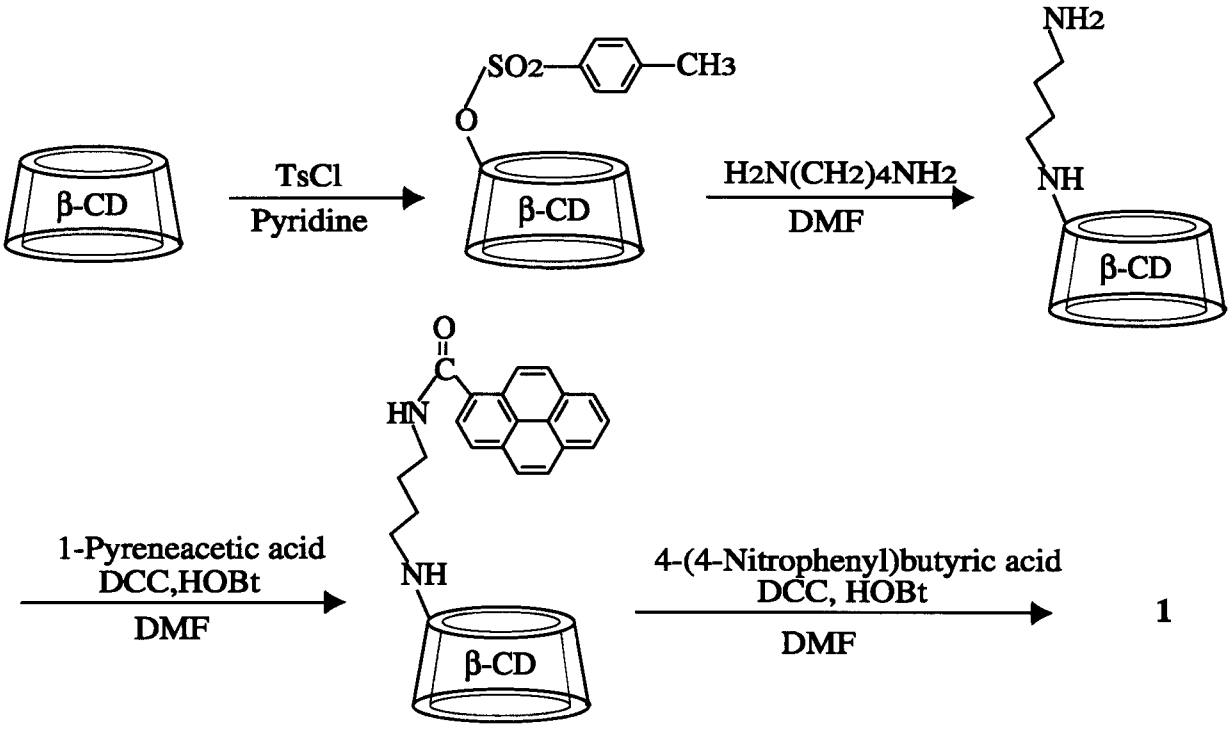

Scheme 1

Compound(**1**) was synthesized by the method shown in Scheme 1. The purity of **1** was identified by ^{1}H NMR, MS and elemental analysis. [10] The induced circular dichroism (ICD) spectrum of **1** has negative and positive bands at 222 and 270 nm simillarly to the ICD of β-CD complex with nitrobenzene.[11] This indicates that the appending nitrobenzene moiety of **1** is included in the β-CD cavity of **1**. ^{1}H NMR signals of *p*-nitrophenyl protons of **1** also suport the inclusion by showing 2 species in an equilibrium between included and not included states.[10]

Typical fluorescence spectra of **1** alone and in the presence of 1-adamantanol as a guest in aqueous solution are shown in Figure 1. The spectral intensity decreases with increasing concentration of 1-adamantanol. The guest-responsive decrease may be explained in terms of decreased distance or contact between the pyrene and nitrobenzene moieties, which is caused by exclusion of nitrobenzene from the CD cavity by guest accommodation. When the ratio of the decrease to the original

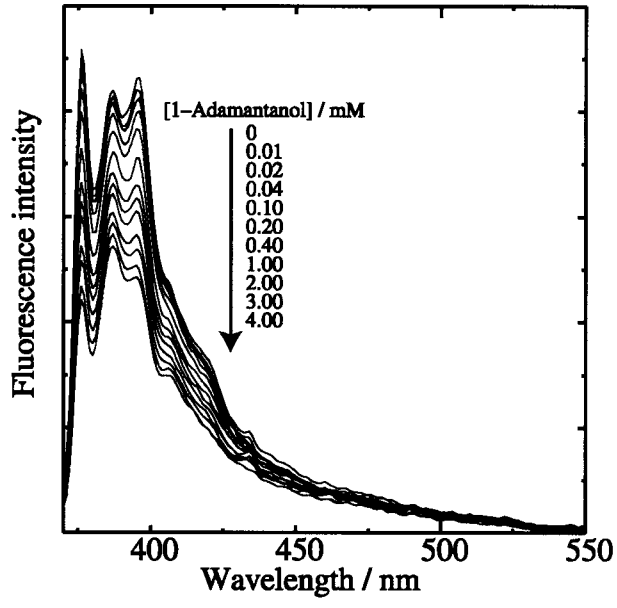

Figure 1 Fluorescence spectra of 1 (20 μM) in a 20% dimethyl sulfoxide solution containing various concentrations of 1-adamantanol at 25℃. The excitation wavelength is 354 nm.

intensity $\Delta I/I_0$ in the presence of 1 mM guest was measured at 398 nm (excitation wavelength was 354 nm), the $\Delta I/I_0$ values are 0.328, 0.235, 0.130, and 0.058 for 1-adamanatanecarboxylic acid, 1-adamantanol, (+)-borneol, cyclooctanol, respectively. The plots of $\Delta I/I_0$ against the guest concentration gave binding constants by curve-fitting analysis based on 1:1host:guest stochiometry (Figure 2).[12-14]

The values of binding constant (K) are 5060, 1370, 442, and 379 M^{-1} for 1-adamantanecarboxylic acid, 1-adamantanol, (+)-borneol, and cyclooctanol, respectively, and the order of 1-adamantanecarboxylic acid>1-adamantanol>(+)-borneol>cyclooctanol is parallel to the order of the $\Delta I/I_0$ values.

In conclusion, the results demonstrate that the induced-fit locational change of the appending nitrobenzene moiety of **1** affects the fluorescence quenching process (Figure 3) and the system works as a chemosensor for molecules.

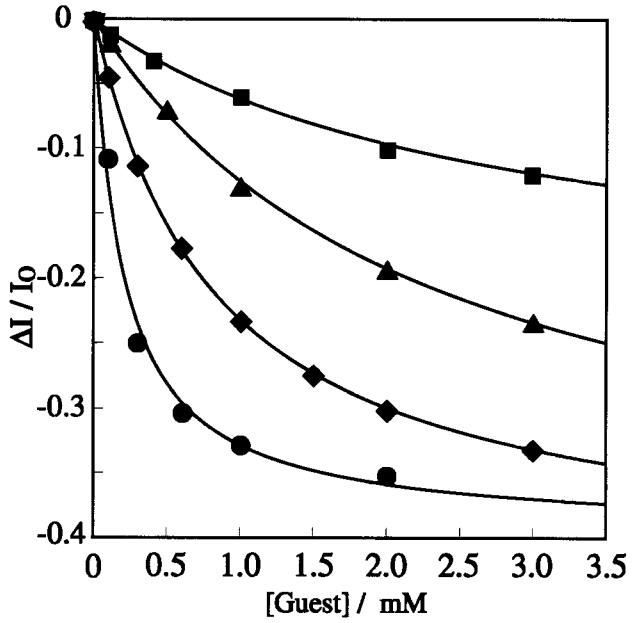

Figure 2 The curve fitting data for determing the biding constants based on 1:1 stoichiometry. The guests are 1-adamantanecarboxylic acid (●), 1-adamantanol (◆), (+)-borneol(▲), and cyclooctanol(■).

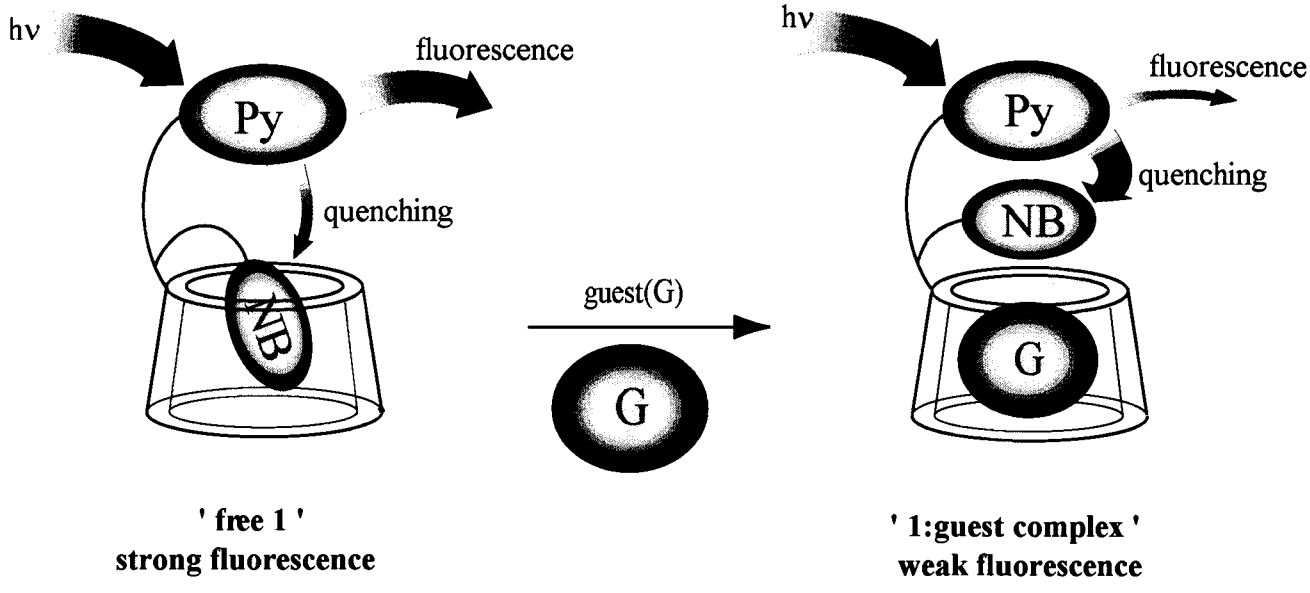

Figure 3 Schematic illustration for guest-responsive fluorescence quenching.

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10. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.70-4.90 (m, 7H, CH^1), 7.30 (d, J=8.5 Hz, 1H, nitrophenyl), 7.34 (d, J=8.5Hz,1H, nitrophenyl), 8.12 (d, J=8.5 Hz,1H, nitrophenyl), 8.18 (d, J=8.5 Hz,1H, nitrophenyl), 7.95-8.36 (m, 9H, pyrene); TOF-MS m/z 1640.9 ([M+H]$^+$) (calcd 1639.63); Anal. Calcd for $C_{74}H_{99}N_3O_{38}\cdot 4H_2O$: C, 51.96; H, 6.30; N, 2.46. Found: C, 52.10; H, 6.34; N, 2.43.
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