Journal of Photoscience (2004), Vol. 11(1), pp. 7-9

A Smart Fluorescent Macrocycle with Recognition-Ability of the Neutral Molecules

Chang-Shik Choi[†*], Mi-Kyoung Kim[††], Ki-Seok Jeon[††], and Ki-Hwan Lee[††*]
[†]Research Institute for Basic Science, Kongju National University, Kongju 314-701, Korea
[††]Department of Chemistry, Kongju National University, Kongju 314-701, Korea

The synthesized macrocycle L was found to be a smart fluorescent receptor which distinguishable efficiently from various neutral molecules with the functional groups such as the electron donating (X = CH_3, $N(CH_3)_2$ and OCH_3) and electron withdrawing groups (X = F and Cl), respectively. In the case of guest molecules containing electron donating groups, the fluorescence of macrocycle L was enhanced in the presence of the guest molecules. On the contrary, in the case of guest molecules containing electron withdrawing groups, it was almost quenched in the presence of those.

key words: macrocycle L, fluorescent receptor, neutral molecules, recognition, electron donating group, electron withdrawing group

INTRODUCTION

In recent years, fluorescent receptors have gained much attention because those are useful to analyze and clarify the roles of biomolecules in living systems [1]. They have served as chemosensors for stoichiometric host-guest molecular recognition [2]. Accordingly, various fluorescent supramolecules including crown ethers have been designed and synthesized [3]. Although numerous fluorescent receptors have been prepared, a study on the recognition of neutral molecules by fluorescent receptor has been reported limitedly. This study is crucial to develop the biomimic systems for elucidating the roles of biomolecules in living systems. In addition, the convenient synthetic method for expanding number and function of fluorescent receptors has been demanded more and more. Therefore, we simply designed and synthesized the tetraaza macrocycle L as a host molecule as well as the aromatic imine conjugated systems containing various substituents as guest molecules, as shown in Figure 1.

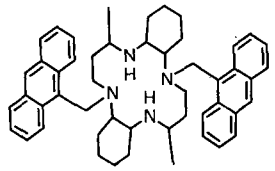

Figure 1. Syhthesized macrocycle L and guest molecules

MATERIALS AND METHODS

RESULTS AND DISCUSSION

3,14-Dimethyl-6,17-*N,N*-di(9-methylanthryl)-2,6,13,17-tetraazatricyclo [14, 4, $0^{1,18}$, $0^{7,12}$] docosane, the tetraaza macrocycle L which has two anthryl groups [4] was prepared in moderate yield by one-pot condensation reaction of 9-chloromethylanthracene with 3,14-dimethyl-2,6,13,17-tetraazatricyclo [14, 4, $0^{1,18}$, $0^{7,12}$] docosane [5] in methylene chloride. The guest molecules investigated in this study were also easily synthesized in high yield by one-pot imine condensation reaction between 1,4-phthalaldehyde and aniline derivatives in methylene chloride. Every synthesized molecules were well characterized by ^{1}H-NMR and mass spectroscopy along with elemental analysis [6].

All the spectroscopic measurements were carried out at the concentration of 1.00×10^{-6} mol dm^{-3} in acetonitrile at room temperature. The macrocycle L was found to have strong absorbance at 255 nm with weak intensity at 352 nm, 370 nm, and 389 nm [7]. In addition, the macrocycle L was strongly fluorescent with maximum emission peaks [8] at 396 nm, 418 nm, and 441 nm (fluorescence quantum yield (Φ_{rel}) = 0.02 in acetonitrile) [9] as shown in Figure 2.

To investigate the ability of recognition of guest molecules by the macrocycle L 1.00×10^{-6} mol dm^{-3}, the fluorescence intensity without (Fo) and with (F) the different concentration of guest molecules was plotted. Although the guest molecules were also fluorescent [10], the emission maxima were at

*To whom correspondence should be addressed.
E-mail : khlee@kongju.ac.kr
Received February 6, 2004; Accepted March 16, 2004

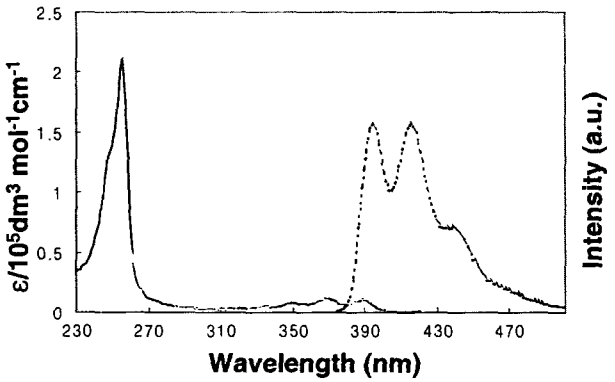

Figure 2. Absorption (—), excitation (···) and fluorescence (– – –) spectra of macrocycle L in acetonitrile at room temperature.

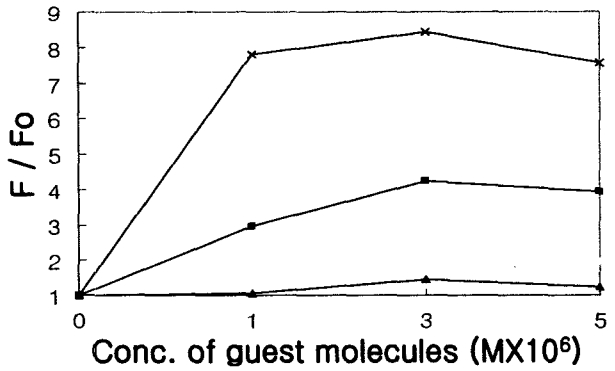

Figure 3. The change of fluorescence of macrocycle L as a function of the concentration of guest molecules in acetonitrile: **X** (**c**, X =OCH_3), ■ (**b**, X = $N(CH_3)_2$) and ▲ (**a**, X = CH_3).

around 300 nm which did not interfere with the fluorescence resulting from the macrocycle L.

As shown in Figure 3, in the case of guest molecules containing electron donating groups (X = CH_3, $N(CH_3)_2$ and OCH_3), the fluorescence of macrocycle L was enhanced in the presence of the guest molecules. In particular, in the case of guest molecules with the strong electron donating groups (X = $N(CH_3)_2$ and OCH_3), the fluorescence of macrocycle L was remarkably enhanced. Thus, we were able to observe six folds increase of the fluorescence intensity in the case of guest molecule **c** containing methoxy group compared to the guest molecule **a** containing methyl group. When the guest molecule **b** containing dimethyl amine group was presented, the fluorescence intensity of the macrocycle L increased three folds compared to the guest molecule **a**.

On the contrary, as shown in Figure 4, in the case of guest molecules containing electron withdrawing groups (**d**, X = F and **e**, X = Cl), the fluorescence of macrocycle L was almost quenched by the cumulative addition of those, respectively [11].

It is possible to draw some conclusions from the above results that the ability of recognition of guest molecules by fluorescence detection of macrocycle L shows very different

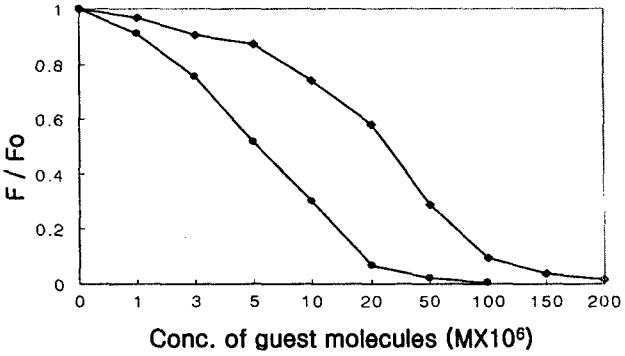

Figure 4. The change of fluorescence of macrocycle L as a function of the concentration of guest molecules in acetonitrile; ◆ (**d**, X = F) and ●(**e**, X = Cl)

tendency upon the kinds of guest molecules with other functional groups, although the parent group is same in that molecule. In addition, we could suppose that the functional groups of guest molecules have a major influence on the photoinduced electron transfer (PET) from the nitrogen of tetraaza macrocycle to anthryl group in macrocycle L, though reason for this different tendency of fluorescence is not clear yet.

In particular, we were known from above results that this macrocycle L is very smart fluorescent receptor distinguishable from various guest molecules with only different substituents, respectively.

Now, we are trying the experimental for elucidating the reason for this different tendency of fluorescence, and on the syntheses for the development of the receptors showing higher recognizable ability.

ACKNOWLEGMENT

This work was supported by Korea Research Foundation Grant (KRF-2002-075-C00013) and Kongju National University

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6. Characterization of macrocycle L**:** white powder (yield: 70 %). m.p.: >300°C . ^{1}H NMR (chloroform-d_3, 400 MHz) δ, ppm: 8.42 (s, 2H), 8.05-8.00 (8H), 7.50-7.46 (8H), 4.65-4.61 (4H), 3.61-3.57 (4H), 3.18-3.05 (4H), 2.91-2.75 (4H), 2.44-2.10 (10H), 1.88-1.77 (2H), 1.60 (broad, 8H), 1.38 (d, 6H, J = 4.8 Hz). Mass (FAB) *m/z*, 717 $[M]^+$. Anal. Found; C, 83.35; H, 8.92; 7.57% Calcd. for $C_{50}H_{60}N_4$: C, 83.75; H, 8.43; N, 7.81 %.

   Characterization of guest molecules**:** *N,N*-di(*p*-toluene) benzald-1,4-diimine (**a**): orange powder (yield: 87%). m.p.: 168°C. ^{1}H NMR (chloroform-d_3, 400 MHz) δ, ppm: 8.54 (s, 2H, C=N), 8.00 (d, 4H), 7.17-7.26 (m, 4H), 2.29 (s, 6H, CH_3). Anal. Found; C, 84.78; H, 6.52; N, 9.17% Calcd. for $C_{22}H_{16}N_2$: C, 84.58; H, 6.45; N, 8.97%. *N,N*-di(*p*-dimethylaniline)benzald-1,4-diimine (**b**): yellow powder (yield: 98%). m.p. (dec.): 320°C. ^{1}H NMR (chloroform-d_3, 400 MHz) δ, ppm: 8.56 (s, 2H, C=N), 7.95 (s, 4H), 7.26-7.32 (m, 4H), 6.76-6.78 (d, 4H), 3.00 (s, 12H, $N(CH_3)_2$). Anal. Found; C, 77.46; H, 7.10; N, 15.20% Calcd. for $C_{24}H_{26}N_4$: C, 77.80; H, 7.07; N, 15.12 %. *N,N*-di(*p*-anisole)benzald-1,4-diimine (**c**): yellow powder (yield: 94%). m.p.: 227°C. ^{1}H NMR (chloroform-d_3, 400 MHz) δ, ppm: 8.54 (s, 2H, C=N), 7.99 (s, 4H), 7.27-7.29 (m, 4H), 6.94-6.97 (d, 4H), 3.85 (s, 6H, OCH_3). Anal. Found; C, 77.20; H, 5.84; N, 8.28% Calcd. for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13%. *N,N*-di(*p*-fluorobenzene)benzald-1,4-diimine (**d**): ivory white powder (yield: 72%). m.p.: 150°C. ^{1}H NMR (chloroform-d_3, 400 MHz) δ, ppm: 8.45 (s, 2H, C=N), 8.01 (s, 4H), 7.37-7.39 (m, 4H), 7.18-7.20 (m, 4H). Anal. Found; C, 74.72; H, 4.42; N, 8.87% Calcd. for $C_{20}H_{14}N_2F_2$: C, 74.99; H, 4.40; N, 8.74%. *N,N*-di(*p*-chlorobenzene)benzald-1,4-diimine (**e**): yellow needle (yield: 87 %). m.p.: 180°C. ^{1}H NMR (chloroform-d_3, 400 MHz) δ, ppm: 8.51 (s, 2H, C=N), 8.00 (s, 4H), 7.23-7.27 (m, 4H), 7.08-7.13 (m, 4H). Anal. Found; C, 68.86; H, 4.12; N, 8.05% Calcd. for $C_{20}H_{14}N_2Cl_2$: C, 68.99; H, 3.99; N, 7.93%.
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9. Fluorescence quantum yield (Φ_{rel}) was calculated according to the following equation [12]; $\Phi_{unk} = \Phi_{std}\,(I_{unk}/A_{unk})\,(A_{std}/I_{std})\,(\eta_{unk}/\eta_{std})^2$, where Φ_{unk} is the fluorescence quantum yield of the sample, Φ_{std} is the quantum yield of the standard (Φ_F = 0.27, anthracene in ethanol) [13], I_{unk} and I_{std} are the integrated fluorescence intensities of the sample and the standard, respectively, A_{unk} and A_{std} are the absorbances of the sample and the standard at the excitation wavelength, respectively, and ς_{unk} and ς_{std} are the refractive indexes of the corresponding solutions.
10. The shorter absorption band by $\pi - \pi^*$ state and longer one by mostly n π^* state of guest molecules showed at 250 – 290 nm ($\varepsilon = 2 - 3 \times 10^4\,dm^3\,mol^{-1}\,cm^{-1}$) and 330 – 440 nm ($\varepsilon = 3.5 - 5.0 \times 10^4\,dm^3\,mol^{-1}\,cm^{-1}$, 370 – 530 nm in the case of guest molecule **b**), respectively in acetonitrile. The fluorescence of guest molecules **a**, **b** and **c** was very weak ($\Phi_{rel} = < 0.01$ in acetonitrile) [9] at the excitation of 260 nm, and there was no fluorescence in the case of guest molecules **d** and **e**.
11. It is considered that there is no a formation of charge transfer complex between the macrocycle L and the guest molecule with electron withdrawing group due to no observation of the new fluorescence more than 500 nm.
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