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Fullerene sensors based on calix[5]arene

Takeharu Haino,[a] Hiromi Araki,[a] Yoshihisa Fujiwara,[b] Yoshifumi Tanimoto[b] and Yoshimasa Fukazawa*[a]

[a] *Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan. E-mail: fukazawa@sci.hiroshima-u.ac.jp*

[b] *Department of Mathematical and Life Sciences, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan*

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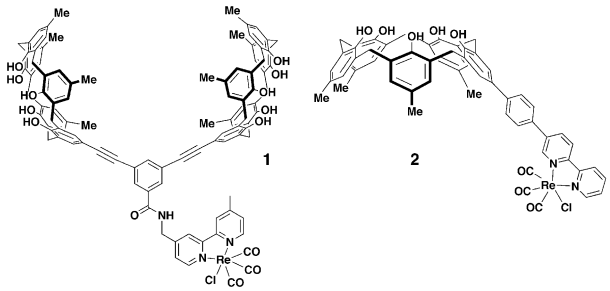
A new class of fullerene sensors based on calix[5]arenes has produced the highly sensitive detection of C_{60} and C_{70}.

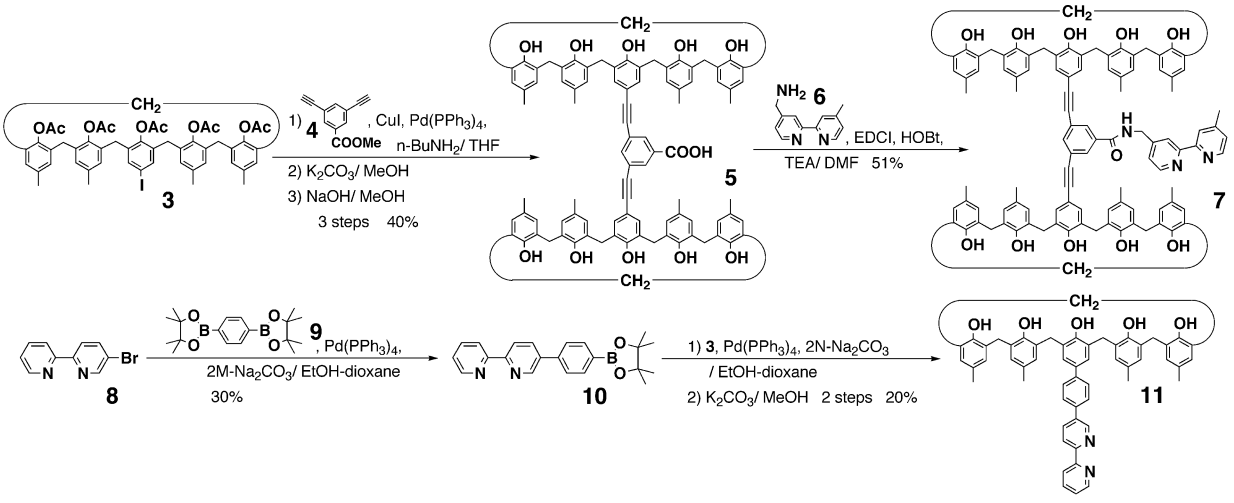
The development of chemical sensors has received broad attention in recent years. One of the most appealing approaches involves the combination of supramolecular concepts and luminescence techniques. A number of sensors[1] have been developed with a focus upon selective binding for metal ions, phosphates and neutral molecules coupled with luminescence signal modulation.

During our investigation on fullerene receptors, we have developed calix[5]arene-based fullerene receptors, which show high selective binding for C_{60} and/or C_{70}.[2] Among numerous studies on developing fullerene receptors reported so far,[3] the fullerene sensor is limited. We envisioned developing fullerene sensors. Our strategy for the fullerene sensor is based on the introduction of a covalently attached lumophore onto the fullerene binding site. Since it is well known that fullerene is a good acceptor in an energy transfer reaction, it might act as a good luminescence quencher. The luminescence of the sensor can be quenched when fullerene is situated in close proximity to the lumophore. This optical response should produce highly sensitive detection for fullerenes. Along this concept, sensors **1** and **2** have been designed.

The synthesis of sensors **1** and **2** was started according to Scheme 1. Coupling reaction of iodocalix[5]arene **3**[4] with methyl ester **4**[5] through palladium catalysis, followed by hydrolysis of ester groups produced double-calix[5]arene carboxylic acid **5**. Bipyridine **6**[6] was introduced to **5** to give double-calix[5]arene **7**. Reaction of **7** with $Re(CO)_5Cl$ in toluene at 100 °C produced sensor **1** in 60% yield. Bromobipyridine **8**[4] reacted with **9**[7] through Suzuki conditions to give **10**. Coupling reaction of **10** with **3**, followed by basic hydrolysis of acetyl groups furnished calix[5]arene derivative **11**, which reacted with $Re(CO)_5Cl$ in toluene at 100 °C, produced sensor **2** in 46% yield.



Sensors **1** and **2** are soluble in toluene. Strong orange luminescence showed up when the solution of **1** was exposed to 365 nm UV light (Fig. 1). Addition of C_{60} or C_{70} to the solution of **1** caused a dramatic change. The luminescence was immediately extinguished upon the addition of C_{60} or C_{70}. The steady-state phosphorescence spectral change of **1** in toluene (λ_{exc} = 400 nm) is shown in Fig. 2. The characteristic luminescence band appearing around 600 nm was assigned to the metal-to-ligand charge transfer (MLCT) band.[8] Upon the addition of C_{60} to the solution of **1** in toluene, the luminescence intensity gradually decreased (Fig. 2). In order to discuss the quenching quantitatively, Stern–Volmer analysis was carried out for **1**, **2** and $Re(bpy)(CO)_3Cl$ **12** with C_{60} or C_{70} in toluene. Steady-state luminescence quenching studies with C_{60} yielded two linear Stern–Volmer plots for **2** and **12**, as shown in Fig. 3. The results were interpreted in terms of diffusion-controlled intermolecular quenching between C_{60} and the lumophore. For **1** with C_{60} or C_{70}, the quenching is much more efficient than the others. The quenching of **1** with C_{60} or C_{70} produced curved Stern–Volmer plots (Fig. 3). There should be two luminescence quenching processes associated with the energy transfer from the lumophore to the fullerene: one is an intermolecular quenching process arising from the simple collision between the unbound fullerene and the lumophore, the other is an intra-



Scheme 1

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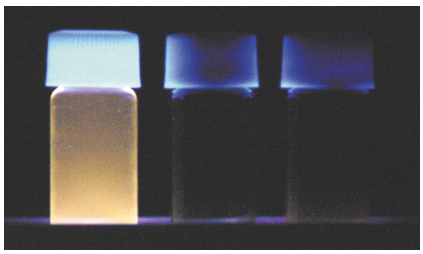

Fig. 1 Luminescence changes induced on sensor **1** (1.0×10^{-5} mol L^{-1}): (left) in the absence of fullerenes, (middle) with C_{60}, (right) with C_{70}.

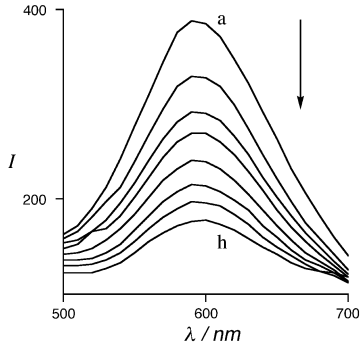

Fig. 2 Steady-state luminescence spectra (λ_{exc} = 400 nm) of **1** (5.6×10^{-6} mol L^{-1}) in toluene upon the addition of C_{60}: a; 0, b; 0.67, c; 1.3, d; 2.0, e; 3.3, f; 4.7, g; 6.0, h; 8.7 ($\times 10^{-5}$ mol L^{-1}).

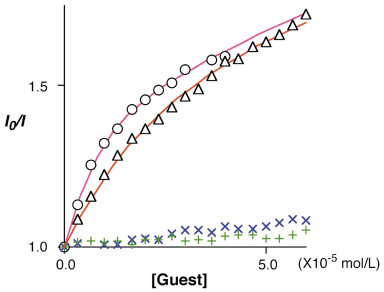

Fig. 3 Stern–Volmer plots of sensors **1**, **2** and **12** (5.6×10^{-6} mol L^{-1}) in the presence of fullerenes in toluene. The symbols represent the experimental data and the solid lines are given by curve-fitting analysis (○: C_{70} *vs.* **1**; △: *vs.* **1**; ×: C_{60} *vs.* **2**; +: C_{60} *vs.* **12**).

molecular quenching process between the bound fullerene and the lumophore of the complex. It is known that the receptor bearing two calix[5]arenes shows remarkably strong binding ability to the fullerenes in toluene.[2] Although these plots qualitatively account for the effect of the fullerene complexation, more detailed understanding is required to discuss the quenching properties. For this, luminescence lifetime measurements and the determination of the quenching rate constants were carried out.

The luminescence lifetimes (τ_0) of **1**, **2** and **12** in toluene were determined to be 41.4 ns (**1**), 39.3 ns (**2**), and 34.5 ns (**12**), respectively, by nanosecond laser spectroscopy. The quenching rate constants (k_q)[9] on **2** and **12** for C_{60} or C_{70} were determined on the basis of the Stern–Volmer plots and the luminescence lifetimes (**2**: $k_q(C_{60}) = 37.4 \times 10^9$ M^{-1} s^{-1}, **12**: $k_q(C_{60}) = 12.7 \times 10^9$ M^{-1} s^{-1} and $k_q(C_{70}) = 8.8 \times 10^9$ M^{-1} s^{-1}). On the other hand, the non-linear curve fitting analysis of the Stern-Volmer plots for sensor **1** with C_{60} or C_{70} yielded both the intermolecular (k_q) and the intramolecular quenching rate constants (k_q') in the bound state, and the binding constants (K_a) ($k_q(C_{60}) = 5.7 \times 10^9$ M^{-1} s^{-1}, $k_q'(C_{60}) = 0.0020 \times 10^9$ s^{-1}, K_a = 71000 M^{-1}; $k_q(C_{70}) = 12 \times 10^9$ M^{-1} s^{-1}, $k_q'(C_{70}) = 0.0012 \times 10^9$ s^{-1}, K_a = 360000 M^{-1}).

Slight enhancement of the quenching rate was observed between **2** and **12** for C_{60}. The relative quenching rate constant of **2** for C_{60} is only 3 times as large as that of **12**. This can be rationalized by the complexation of **2** to C_{60}.[10] It appears that the quenching is mainly due to the intermolecular collision; however, a small portion of the intramolecular quenching process should contribute to the quenching. A more obvious contribution of the intramolecular quenching process in the bound state is seen in the luminescence quenching of **1** with the fullerenes. The apparent quenching rate constants (k_q^{app}) are expressed as follows:

$$k_q^{app} = k_q[G]_0 \quad \text{for } \mathbf{2} \text{ and } \mathbf{12}$$
$$k_q^{app} = k_q[G] + k_q' \quad \text{for } \mathbf{1}$$

where $[G]_0$ and $[G]$ denote the concentration of total and unbound guests, respectively. The apparent quenching rate constants (k_q^{app}) were calculated using the K_a value and the total fullerene concentration of 5.6×10^{-6} mol L^{-1} (**12**: $k_q^{app}(C_{60}) = 7.1 \times 10^4$ s^{-1}, $k_q^{app}(C_{70}) = 4.9 \times 10^4$ s^{-1}; **2**: $k_q^{app}(C_{60}) = 21 \times 10^4$ s^{-1}; **1**: $k_q^{app}(C_{60}) = 200 \times 10^4$ s^{-1}, $k_q^{app}(C_{70}) = 120 \times 10^4$ s^{-1}). The apparent luminescence quenching rate constants of **1** for C_{60} and C_{70} are over 20 times higher than that of **12** at that concentration. This suggests that the apparent quenching rate constant is strongly associated with the concentration of the bound fullerene; thus, the high binding ability of **1** toward C_{60} and C_{70} brings about the extremely high sensitivity and selectivity[11] to them even at concentrations of less than 10^{-5} mol L^{-1}.

We have demonstrated the first example of the highly sensitive detection of fullerenes using calix[5]arene-based sensors produced by the combination of the supramolecular concept and the luminescence technique.

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9 The quenching rate conctants of **12** for C_{60} and C_{70} were determined by Stern–Volmer plots of the fullerene concentration *vs.* τ_0/τ.

10 **2**: $K_a(C_{60})$ = 1100 M^{-1}; **11**: $K_a(C_{60})$ = 1060 M^{-1}, $K_a(C_{70})$ = 170 M^{-1}.

11 A control experiment with anthracene as a small guest was carried out to test the selectivity of **1**. A Stern–Volmer plot of **1** produced k_q (2.1×10^9 $M^{-1}s^{-1}$) and k_q^{app} (11.9×10^4 s^{-1} at a total guest concentration of 5.6×10^{-6} mol L^{-1}) is 17 times as small as that of **1** with C_{60}. This indicates that sensor **1** shows selective detection of fullerenes even if a small aromatic guest is present.