# New Fluorescent "Off-On" Behavior of 9-Anthryl Aromatic Amides through Controlling the Twisted Intramolecular Charge Transfer Relaxation Process by Complexation with Metal Ions

## Tatsuya Morozumi, Takahisa Anada, and Hiroshi Nakamura\*

Division of Material Science, Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan

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New fluorophores based on linear polyether N,N'-[oxybis(3-oxapentamethylenoxy)-2-phenyl]bis(9-anthracenecarbonamide) (3) and its analogues (2 and 4) have been synthesized, and their complexation properties with various alkali-metal and alkaline-earth-metal ions were investigated by fluorescence, UV, and <sup>1</sup>H NMR spectroscopies. In the absence of metal ion, 2-4 showed almost no fluorescence emission (fluorescence quantum yield  $\Phi = 0.0003$ , fluorescence "off" state) since twisted intramolecular charge transfer (TICT) occurred through the amide bond. However, 2-4 demonstrated a significant increase in fluorescence intensity around 430 nm upon complexation with alkaline-earth-metal ions. In the case of 4·Ca<sup>2+</sup>, a large enhancement effect on the fluorescence quantum yield ( $\Phi = 0.014$ ,  $[Ca^{2+}]/[4] = 5$ ,  $\Phi_{4:Ca^{2+}}/\Phi_{\text{free 4}} = 42$ , fluorescence "on" state) was observed. This "off-on" fluorescence characteristic was originated from the cooperative strong binding mode between the carbonyl group and the ethylenoxy moiety for alkaline-earth-metal ions, resulting in effective inhibition of photoinduced TICT relaxation. Fluorophores 2-4 formed a 1:1 complex (the order of the complex formation constants was  $Ca^{2+} > Sr^{2+} \approx Ba^{2+}$ ) and showed no considerable spectral changes upon complexation with alkali-metal ions and  $Mg^{2+}$ . The <sup>1</sup>H NMR study on 2–4 and their complexes indicated that free 2-4 formed a helical structure. After complexation, the conformational change of 2 from a helical structure to a semicircular structure was observed. The pseudocyclic form was supported as the complex structure of 3, whereas the large conformational change of 4 was not observed after the addition of metal ions.

#### Introduction

Over the last two decades, the search for new materials as chemical sensors<sup>1-5</sup> for metal ions, anions, and neutral small molecules has been an area of rapid development. Although these chemical sensors may consist of crown ethers,<sup>6-8</sup> cyclodextrins,  $^{9,10}$  and calix[n]arenes,  $^{11-13}$  significant attention has been on crown ethers since they have binding ability toward alkali-metal and alkaline-earth-metal ions that play various important roles in biochemistry and environmental science. In view of this trend, there is a real need to establish a simple and reliable analytical method to study these important ions. The well-known high sensitivity of various absorption and fluorescence spectroscopies led to the design and development of crown ethers functionalized by UV and fluorescence active groups for analytical use. In 1977, Takagi et al.14 developed the first example of these crown ethers, which are also called chromogenic crown ethers. These molecules contained both crown ether for the binding site with metal ions and the ionic chromophore moiety that transduced chemical information produced by the metal binding event into an optical signal. Since then, many kinds of chromogenic<sup>15-17</sup> and fluorimetric<sup>5,18,19</sup> crown ethers have been developed. Basically, chromogenic crown ethers consist of a crown ether moiety attached with proton-ionizable or proton-dissociable chromophore groups. In this state, chromogenic crown ethers exhibit a distinct color change upon complexation in the organic medium; this fact has been utilized photometrically in the determination of alkali-metal and alkaline-earth-metal ions.

It is also known that proton-dissociable and -ionizable groups often tend to make the analytical system complicated because free proton dissociation could also be occurring and cannot be neglected. To overcome this shortcoming, we focused on conformational changes of noncyclic crown ethers from linear to helical, such as glyme and poly(ethylene glycol) derivatives,<sup>20,21</sup> as an alternative method since it does not require the introduction of proton-ionizable or -dissociable chromophores. Noncyclic crown ethers and related compounds have also been known as complexing reagents<sup>22,23</sup> for alkali-metal and alkalineearth-metal ions and surfactants.<sup>24-26</sup> Most researchers, however, focus mainly on their ability as ion carriers $^{27-36}$  as in naturally occurring ionophores such as monensin.<sup>37,38</sup> The application of noncyclic crown ethers in oriented analytical utilization has been relatively limited. In this context, recently, we have been studying the complexation behavior of noncyclic crown ether derivatives bearing several symmetric and asymmetric fluorophores at their terminals.<sup>39-44</sup> This large conformational change upon complexation can transduce into a fluorometric signal. The binding event can be monitored via fluorescence emission changes from monomer to excimer and vice versa.

We have also studied the effect of varying the number of ethylenoxy units on the binding ability of metal ions in the presence of 9-anthracenecarbonamide.<sup>44</sup> Since Bazilevskaya et al.<sup>45,46</sup> reported anomalous photochemical behavior of 9-an-thracenecarboxylic acid (9-ACOOH), this subject has been the topic of discussion for many years.<sup>47–49</sup> Despite the interesting behavior shown by 9-ACOOH and its amide derivatives,<sup>50</sup> the

utilization as chemical sensors of 9-ACOOH derivatives is rather limited.<sup>51,52</sup> With this in mind, we examined the photophysical properties of the 9-ACOOH amide derivatives with the hope of widening this field of study. As a result, we recognized that fluorescence emission of 9-anthracene aromatic amide (9-AA) derivatives was almost quenched in solution whereas their crystal showed green-yellow-colored emission under UV irradiation. This observation suggested that 9-AA derivatives show a twisted intramolecular (internal) charge transfer (TICT) quenching relaxation in solution.

Recently, the TICT phenomenon has been a subject of interest to many photochemical researchers for years. The TICT model was first suggested by pioneering work of Rotkiewicz and Grabowski when they explained the photophysical property of p-(N,N-dimethylamino)benzonitrile, indicating the dual fluorescence and the large Stokes shifted emission in a polar solvent.53 Since then, explanation using the TICT model has been extended to other structurally related compounds showing anomalous dual fluorescence.54,55 These molecules have an aromatic ring with acceptor and donor groups at the para positions. The electron donor group is usually a dialkylamine, and the electron acceptor groups are several electron-withdrawing residues, such as cyano, formyl, carboxyl, ester, and sulfonamide groups. Aromatic groups which are able to bend along a single bond, for example, bianthryl,<sup>56,57</sup> p-(9-anthryl)-N,N-dimethylaniline,<sup>58,59</sup> 2-(4-(N,N-dimethylamino)phenyl)benzimidazole, benzothiazole,60 and 9-(N,N-dimethylamino)anthracene,<sup>61</sup> were also reported to function as either donor or acceptor groups. The molecular geometry of these parasubstituted N,N-dimethylanilines is flat in the ground state, whereas it changes to be completely twisted in its excited state before emitting. Next, we looked at another compound which involves anomalous dual fluorescence of benzanilide derivatives<sup>62,63</sup> and *p*-(*N*,*N*-dimethylamino)benzanilide<sup>64</sup> that functions as the TICT model. Most researchers, however, have focused mainly on the excited-state behavior of TICT molecules. If the degrees of electron transfer and molecular geometry can be controlled by using the methodology of molecular recognition chemistry, TICT molecules could be used as excellent tools for detecting ions and molecules, and examining microscopic molecular environments.

The photophysical behavior of 9-AA showed a different charge-transfer mode compared to N.N-dialkylaminoanthracene derivatives that display a photoinduced electron transfer (PET) mode as shown by de Silva et al.,<sup>65–68</sup> Czarnick et al.,<sup>69–71</sup> and Fabbrizzi et al.<sup>72–74</sup> This fact could be attributed to the absence of the nitrogen atom of the amide group, which would otherwise function as the electron-donating moiety. The behavior of 9-AA also prompted us to contemplate that a novel "on-off" signaling chemical sensor for metal ions could be developed on the basis of our knowledge as described below. Recently, we reported the complexation and fluorescence behavior of 2,2'-[oxybis(3oxapentamethyleneoxy)]bis[N-(1-pyrenylmethyl)benzamide] (4-PPAM)<sup>43</sup> with various metal ions. The ionophore 4-PPAM has two benzenes at both ends of the ethylenoxy chain, and 1-pyrenylmethylamine was introduced via an amide bond at the ortho position against the ethyleneoxy chain on the benzene ring. The free 4-PPAM gave mainly a defused emission at 490 nm due to excimer emission of pyrene, whereas the complexes 4-PPAM alkaline-earth-metal ions exhibited increasing monomer emission accompanied by a decrease of excimer emission. The detailed <sup>1</sup>H NMR studies indicated that this molecular design induced the stronger binding force as well as broken down  $\pi - \pi$  interactions of two pyrenes. These results also



**Figure 1.** Fluorescence spectra of 9-AA in various solvents at 25 °C: glycerol (dotted line), cyclohexane (dashed line), diethylene glycol (dashed-dotted line), acetonitrile or methanol (solid line). Excitation wavelength: 362 nm. [9-AA] =  $1 \times 10^{-5} \text{ mol/dm}^3$ .

suggest that the molecular design has good ability for free rotation of the anilide moiety of 9-AA to be inhibited upon complexation. It can be expected that the noncyclic ether connecting the ortho position of benzene in 9-AA via an ether linkage at both terminals will be exhibited dominantly through the TICT quench relaxation process in the absence of metal ions (no fluorescence, "off" state). Upon complex formation, photoinduced rotation of the 9-AA moiety will be interrupted by the strong cooperative binding ability between the carbonyl and ethylenoxy moieties for metal ions. Hence, the TICT relaxation pathway should be controlled, and fluorescence emission of 9-AA will be observed (fluorescence, "on" state). On the basis of this consideration, introduction of 9-AA at the end of a noncyclic crown ether is one of the favorable ways to fix the molecular geometry of 9-AA in the ground state upon complexation with metal ions.

In this paper, we report the results of the fluorescent "off on" behavior of a new noncyclic crown ether, N,N'-[oxybis(3-oxapentamethyleneoxy)-2-phenyl]bis(9-anthracenecarbonamide) (**3**) and its derivatives (**2** and **4**) using UV, fluorescence, and <sup>1</sup>H NMR spectroscopies in acetonitrile solution.

### **Results and Discussion**

Relaxation Process of N-Phenyl-9-anthracenecarbonamide from the Photoexcited State. Prior to a study on the complexation behavior of 2-4 for metal ions, photochemical examination using a model compound, 9-AA, was carried out. Figure 1 shows fluorescence spectra of 9-AA as a function of solvent. The model compound 9-AA showed only weak fluorescence emission in acetonitrile or methanol (solid line). On the other hand, in glycerol, 9-AA showed emission with a vibronic structure (dotted line), which is characteristic of a parent anthracene ring, and a strong fluorescence intensity. Diethylene glycol solution of 9-AA gave a vibronic fluorescence spectrum with a moderate intensity (dashed-dotted line). In cyclohexane (dashed line), a diffused fluorescence spectrum of 9-AA showing an emission maximum with longer wavelength was observed. The dependency of the fluorescence emission of 9-AA on various solvents could be summarized by saying that 9-AA showed no fluorescence emission in polar and low viscous solvent such as acetonitrile and methanol, whereas it indicated fluorescence emission in polar and viscous solvent (i.e., glycerol and diethylene glycol) and in nonpolar media (i.e., cyclohexane).

It is known that 9-ACOOH shows a strong concentration-



Figure 2. Schematic representation of a mechanism for the relaxation process of photoexcited 9-AA in various solvents.

dependent, broad, and structureless fluorescence emission band with an unusually large Stokes shift.<sup>45–49</sup> Werner et al.<sup>47</sup> pointed out that anomalous photochemical behavior of 9-ACOOH originated from a charge-transfer effect at the excited state. Their interpretation involved a rotation of the 9-carboxyl group in the excited state into a position approaching coplanarity with the anthracene ring. In this molecular configuration, a significant large resonance interaction between the carboxyl group and the aromatic ring was observed.

Besides it is known that benzanilide undergoes an anomalous fluorescence with a large Stokes shift which appeared at longer wavelength compared with that of its phosphorescence.<sup>75</sup> Azumaya and co-workers<sup>62</sup> reported the mechanism of dual fluorescence of benzanilide (BA) and *N*-methylbenzanilide (MBA) in methylcyclohexane. They concluded that the amide bond must be rotated for the emission of longer wavelength, and these emissions were originated from excited TICT species with a twisted amide bond.

On the basis of these two interpretations for the photochemical behavior of 9-ACOOH, BA, and MBA, the relaxation mechanism of 9-AA from the excited state can be considered as shown below. Figure 2 demonstrates a schematic representation of relaxation pathways of photoexcited 9-AA in various solutions. The molecular geometry of 9-AA in the ground state is perpendicular between the anilide moiety and the anthracene ring. If this configuration of 9-AA is maintained even at the excited state, the fluorescence spectrum will be similar to that of anthracene (excited state I). Glycerol and diethylene glycol have a large viscosity, which originates from strong hydrogenbonding ability. When 9-AA was included in the viscous media and/or the strong hydrogen bond network of glycerol, the structure of 9-AA in the ground state was almost fixed. Even the photo-driven rotation at the anilide moiety should be prevented, and the relaxation pathway from excited state I showed the anthracene-like emission. The fluorescence intensity of glycerol solution was larger than that of diethylene glycol. This shows that the more viscous media can effectively prevent photoinduced rotation of 9-AA. Although methanol has the ability of making a hydrogen-bonding network, it is clearly

weaker than that of glycerol and diethylene glycol. In methanol the structure of the anthracene and anilide moieties in 9-AA was not able to freeze out because of its loose hydrogen bond network (low viscosity); therefore, the TICT quenching occurred. On the other hand, in low viscous media such as cyclohexane and acetonitrile, the rotation of functional groups along the amide linkage axis is not prevented. When the anthracene moiety of 9-AA is photoexcited, the rotation of the anthracene-CO bond into a position approaching coplanarity occurs. In this molecular configuration, a significant large resonance interaction between benzene and anthracene will be generated through the amide bond (excited state II). It is wellknown that the nitrogen atom in the amide linkage has sp<sup>2</sup> orbital character, and the amide bond forms a coplanar structure. Thus, there is a possibility of conjugation interaction of both anthracene and benzene rings through the amide bond. The relaxation path from excited state II separates in two ways by the difference of solvent polarity. Through the coplanar molecular geometry at the excited state, the charge delocalization should have occurred over the whole molecular plane, hence generating an intramolecular exciplex of 9-AA. This relaxation path from excited state II showed a diffuse fluorescence spectrum at longer wavelength in cyclohexane. Due to low cyclohexane polarity, a stabilization effect for charge separation species is relatively small. Therefore, the complete charge separation species (radical-ion) will not be generated, and a fluorescent chemical species will be obtained in cyclohexane. In high polarity and low viscous solvent such as acetonitrile and methanol, the OC-N bond in the amide linkage rotates spontaneously from excited state II, and the OC-N bond must be in a bent conformation after the rotation. The highly polarized TICT structure of 9-AA (excited state III) will be generated successively, and should be effectively stabilized by the high polarity of acetonitrile and methanol. Since complete charge separation will occur, the resulting radical-ion pair species of 9-AA will show no fluorescence emission.

Fluorescence Spectra and Lifetime of 2-4 and Their Complexes with Alkaline-Earth-Metal Ions. Figure 3 shows the fluorescence spectra of 2-4 as a function of the concentration of Ca<sup>2+</sup> in acetonitrile at 25 °C. Fluorescence emissions of the anthracene moiety in 2-4 were quite weak in the absence of metal ions. On the other hand, in the case of 2 (Figure 3a) and 3 (Figure 3b) structureless broad spectra having a fluorescence emission maximum ( $\lambda_{max}$ ) around 440 nm were observed, and the fluorescence intensity increased with the addition of  $Ca^{2+}$ . These observations indicated that the TICT process of 2 and 3 was inhibited by coordination of metal ion at the ethylenoxy moieties and carbonyl group. The fluorescence emission bands and shapes also indicated that two anthracene fluorophores did not stack on each other. In the case of N,N'-(4,7,10-trioxatridecane-1,13-diyl)bis(9-anthracenecarbonamide), which showed a well-defined face to face conformation upon complexation with alkaline-earth-metal ion in the ground state, the excimer emission was observed at 490 nm.<sup>39,44</sup> This difference of the two  $\lambda_{max}$  values suggested that the emission of the complex originated from monomer-like chemical species. The  $\lambda_{max}$  of 2·Ca<sup>2+</sup> and 3·Ca<sup>2+</sup> shifted to relatively longer wavelength compared with that of a parent hydrocarbon. This is due to the fact that the structures of the excited state of 2.  $Ca^{2+}$  and **3**· $Ca^{2+}$  included charge transfer character. The shapes of the spectra of  $2 \cdot Ca^{2+}$  and  $3 \cdot Ca^{2+}$  are quite similar to that of a solution of 9-AA in cyclohexane. This strongly suggests that the structures of  $2 \cdot Ca^{2+}$  and  $3 \cdot Ca^{2+}$  have coplanar molecular geometry (see Figure 1) at the excited state. The same



**Figure 3.** Fluorescence spectra of **2** and its  $Ca^{2+}$  complex (a), **3** and its  $Ca^{2+}$  complex (b), and **4** and its  $Ca^{2+}$  complex (c) in acetonitrile at 25 °C. Excitation wavelength: 362 nm. [**2**]–[**4**] = 1 × 10<sup>-5</sup> mol/dm<sup>3</sup>.

observations were also obtained using 2 and 3 in the presence of  $Sr^{2+}$  and  $Ba^{2+}$ , respectively.

In the case of  $4 \cdot Ca^{2+}$  as shown in Figure 3c, structured fluorescence spectra with the strongest intensity were obtained. This showed that the structure of  $4 \cdot Ca^{2+}$  provided an effective prohibition mode for the TICT relaxation process, and the excited electrons were still localized on the anthracene ring compared with that of  $2 \cdot Ca^{2+}$  and  $3 \cdot Ca^{2+}$ . The considerable similarity of the fluorescence emission maximum and its shape between  $4 \cdot Ca^{2+}$  and  $9 \cdot AA$  in glycerol strongly suggests that the structure of  $4 \cdot Ca^{2+}$  at the excited state is similar to that of the ground state. The same results were also observed in the case of  $Sr^{2+}$  and  $Ba^{2+}$ . Compounds 2-4 did not respond for Na<sup>+</sup>, K<sup>+</sup>, or Mg<sup>2+</sup>. On the basis of our findings in Figure 3 and the model study (Figure 1), it can be inferred that the effect of complexation with metal ions involved an inhibition in the rotation of the 9-AA moiety in 2-4 at the excited state.

To determine the structures of fluorescent chemical species



Figure 4. UV spectra of 4 and its Ca<sup>2+</sup> complex in acetonitrile at 25 °C. [4] =  $1 \times 10^{-5}$  mol/dm<sup>3</sup>.

of the 9-AA moiety of 2-4, attempts of fluorescence lifetime measurement were carried out. Unfortunately, the fluorescence lifetime of  $4 \cdot Ca^{2+}$  was too short and could not be obtained by the present apparatus. The fluorescence lifetime of  $4 \cdot Ca^{2+}$  was shorter than nanosecond order.

UV Absorption Measurement. Figure 4 shows UV spectra of 4 and its  $Ca^{2+}$  complex as a typical result. UV spectral changes of all complexes on the anthracene moieties were not observed compared with that of free compounds. This observation suggests that two anthracene moieties did not interact with each other in the ground state significantly. Werner et al.47 pointed out that the carbonyl group was placed perpendicularly on anthracene ring. Compounds 2-4 also kept their molecular geometries perpendicular. Hence, even if 4 strongly bound Ca<sup>2+</sup> at carbonyl groups, the UV spectral change would be small or undetectable since the coordination effect on the anthracene ring gives relatively small electronic perturbation. The UV absorbance of 4·Ca<sup>2+</sup> around 275 nm, which originated from the benzene moiety, was decreased with the increase in Ca<sup>2+</sup> concentration. This may reflect that the microenvironment of the benzene moiety changed electronically and sterically upon complexation. The same results were also observed using 2 and **3** in the presence of  $Ca^{2+}$ ,  $Sr^{2+}$ , and  $Ba^{2+}$ .

Complex Formation Constants. The successive increase in monomer-like emission with the addition of metal ions will finally cause an inhibition of TICT quenching of the fluorophores. The degree of increase of monomer emission clearly depended on the concentrations of metal ions. The fluorescence intensity of 4 at 430 nm was plotted against the ratio [metal]: [ligand] (Figure 5). The obtained curve clearly indicates the formation of a 1:1 complex with Ca<sup>2+</sup>. The complex formation constant (K) was determined from the curve by means of a nonlinear least-squares curve-fitting method (Marquardt's method).<sup>76</sup> The other formation constants were evaluated in the same way and are summarized in Table 1. All ligands formed 1:1 complexes and preferred alkaline-earth-metal ions to alkalimetal ions. To quantify the effect on complexation for fluorescence intensity, fluorescence quantum yields ( $\Phi$ ) were also determined (Table 1).

The clear dependency of the chain length of ethylenoxy units and metal ions on complex formation constants was not observed. In all cases,  $Ca^{2+}$  complexes of **2**–**4** gave the largest complex formation constant (log *K*), whereas the value of log *K* for  $Sr^{2+}$  was almost equal to that of  $Ba^{2+}$ . This shows large affinity of the ethylenoxy moiety for  $Ca^{2+}$  compared with that of  $Sr^{2+}$  and  $Ba^{2+}$ . The order of log *K* was **4** > **3** > **2** for all



Figure 5. Dependence of the fluorescence intensity at 420 nm of 4 on the concentration of Ca<sup>2+</sup>. Excitation wavelength: 362 nm. [4] =  $1 \times 10^{-5} \text{ mol/dm}^3$ .

TABLE 1: Summary of Complex Formation Constants and Fluorescence Quantum Yields of Metal Complexes of 2-4 in Acetonitrile at 25 °C

ligand	guest ion	log K	fluorescence quantum yield ([ligand]:[metal ion]) <sup>a</sup>
2	none		0.00030
	$Ca^{2+}$	3.63	0.0039 (1:33.3)
	$Sr^{2+}$	3.44	0.0026 (1:33.3)
	$Ba^{2+}$	3.42	0.0019 (1:33.3)
3	none		0.00026
	$Ca^{2+}$	5.67	0.0042 (1:15)
	$Sr^{2+}$	4.35	0.0092 (1:25)
	Ba <sup>2+</sup>	4.53	0.0079 (1:20)
4	none		0.00033
	Ca <sup>2+</sup>	6.57	0.014 (1:5)
	$Sr^{2+}$	5.71	0.013 (1:7.5)
	$Ba^{2+}$	5.81	0.012 (1:7.5)

<sup>*a*</sup> The fluorescence quantum yields of all complexes were determined at these concentration ratios.

metal ions. It is obvious that the number of ethylenoxy units become larger the more stable the complexes formed.

It is also reasonable that the fluorescence quantum yield ( $\Phi$ ) of the complexes is related to the log *K* (except for  $3 \cdot Ca^{2+}$ ). In the absence of metal ions the values of  $\Phi$  for 2-4 were obtained as about 0.0003, which shows them to be nonfluorescent and difficult to detect. On the other hand, the value of  $\Phi$  for  $4 \cdot Ca^{2+}$  was 0.014, and this was 42.4-fold larger than that of 4 only. The enhancement effects on two  $\Phi$  values for  $4 \cdot Sr^{2+}$  and  $4 \cdot Ba^{2+}$  was 39.4- and 36.4-fold, respectively. In the case of 3, considerably large enhancement effects of both  $\Phi$  values (for  $3 \cdot Sr^{2+}$  35.4-fold and for  $3 \cdot Ba^{2+}$  30.4-fold) were obtained compared with that of free 3. The rate of increase in  $\Phi$  for 2 was also determined to be 13- for  $Ca^{2+}$ , 8.7- for  $Sr^{2+}$ , and 6.3-fold for  $Ba^{2+}$ , respectively. Despite small enhancement effects on  $\Phi$  of 2, all  $\Phi$  values were sufficiently large for detection by fluorescence spectroscopy.

Although  $3 \cdot Ca^{2+}$  gave the largest binding constant in this series, the value of  $\Phi$  for  $3 \cdot Ca^{2+}$  (0.0042) was about half of that of  $3 \cdot Sr^{2+}$  (0.0092) and  $3 \cdot Ba^{2+}$  (0.0079). This may reflect the difference of the structure of the complex between  $3 \cdot Ca^{2+}$  and  $3 \cdot Sr^{2+}$ ,  $Ba^{2+}$  in both the ground and excited states.

<sup>1</sup>H NMR Measurement of the Complexes. Fluorescence spectral data evidently showed structural and electronical change of 2-4 upon complexation with metal ions. To clarify these changes of the complexes in detail, a <sup>1</sup>H NMR study was carried out in the absence and presence of metal ions in acetonitrile- $d_3$  at 30 °C. The <sup>1</sup>H NMR spectra of **4** before and after addition



**Figure 6.** <sup>1</sup>H NMR spectra of **4** before (a) and after (b) the addition of various metal ions in acetonitrile- $d_3$  at 30 °C. **[4]** = 1 × 10<sup>-2</sup> mol/dm<sup>3</sup>. [metal·(ClO<sub>4</sub>)<sub>2</sub>] = 1 mol/dm<sup>3</sup>.

of  $Ca^{2+}$  are depicted in Figure 6 as a typical result. Peak assignments were made by  ${}^{1}H^{-1}H$  COSY and NOESY spectra. The chemical shift of 2-4 and their induced chemical shift changes on the formation of complexes with various metal ions are listed in Table 2.

Three significant characteristic results of Table 2 can be pointed out: (1) The centers of ethylene protons a-c of free 2-4 showed unexpected high-field chemical shifts (ca. 2.4–2.7 ppm). (2) Proton i in the benzene moiety exhibited an unusual lower chemical shift (8.48 ppm). This proton i induced a large higher magnetic chemical shift change upon complexation with all metal ions. (3) All protons of the anthracene ring indicated no significant chemical shift changes before and after complexation with all metal ions.

Unusually high field chemical shifts (ca. 2.4-2.7 ppm) for the centers of ethylene protons a-c of free 2-4 were obtained, whereas the usual peak position of these oxyethylene protons would be ca. 3.5 ppm. This diamagnetic shift should be due to the aromatic ring current. On the basis of the present NMR data, it is obvious that these fluorophores 2-4 mainly exist as helical conformers. In this conformation, these protons are covered with a shielding area of the anthracene moiety, resulting in unusually high field chemical shifts. This was also supported by the Corey-Pauling-Koltun (CPK) molecular model study.

To account for the NMR behavior of proton i, we carried out an NMR study using model compounds. Figure 7 shows <sup>1</sup>H NMR chemical shifts of 9-AA and N-(2-methoxyphenyl)-9-anthracenecarbonamide (2M9-AA) in acetonitrile- $d_3$  solution. The ortho proton of 2M9-AA against the amide nitrogen atom also indicated the unusually low magnetic field chemical shift (8.49 ppm). On the other hand, the ortho proton of 9-AA showed the usual value (7.78 ppm). This suggests that the unusually low magnetic field shift should be caused by steric repulsion between the methoxy group and carbonyl oxygen as shown in Figure 8a. On the basis of the model study, the characteristic NMR behavior of proton i in 2-4 can be explained as follows. The molecular geometry of the 9-AA molety in 2-4 is the same as that of 2M9-AA in the absence of metal ions. After the coordination of alkaline-earth-metal ions, the carbonyl group can stand opposite the ethylenoxy moiety via the metal ion through the aid of electrostatic interaction (Figure 8b). In this configuration change, proton i passes through the deshielding area of the carbonyl group, and the anomalous chemical shift is reversed to the normal value. This may reflect the decrease

TABLE 2: Chemical Shifts ( $\delta$ , ppm) of 2–4 and Their Changes upon Complexation with Various Cations<sup>*a*</sup>



	metal														
	ion	а	b	с	d	e	f	g	h	i	j	k	1	m	n
2	blank			2.41	3.06	3.74	6.94	7.14	7.14	8.46	8.63	8.00	7.48	8.07	8.53
	Ca <sup>2+</sup>			0.57	0.29	0.06	-0.15	0.04	-0.10	-0.82	0.54	-0.03	0.02	-0.03	0.07
	$Sr^{2+}$			0.59	0.30	0.10	-0.15	0.02	-0.11	-0.82	0.41	0.00	0.01	-0.04	0.06
	Ba <sup>2+</sup>			0.96	0.50	0.15	-0.25	-0.01	-0.09	-1.11	0.47	0.11	0.10	0.06	0.14
	Na <sup>+</sup>			0.47	0.14	-0.15	-0.40	-0.05	-0.16	-0.81	0.07	0.02	0.01	-0.03	0.05
3	blank		2.42	2.78	3.40	3.97	7.04	7.17	7.17	8.51	8.76	8.06	7.53	8.12	8.58
	Ca <sup>2+</sup>		0.64	0.50	0.48	0.50	0.07	-0.08	0.22	-1.35	0.83	0.14	0.17	0.08	0.21
	$Sr^{2+}$		0.50	0.49	0.37	0.32	0.07	0.06	-0.14	-1.19	0.33	-0.07	0.02	0.04	0.16
	Ba <sup>2+</sup>		0.56	0.53	0.35	0.28	0.11	-0.09	0.11	-1.06	0.21	-0.06	0.03	-0.04	0.06
4	blank	2.77	2.69	2.97	3.49	4.02	7.06	7.17	7.15	8.48	8.76	8.06	7.53	8.11	8.59
	Ca <sup>2+</sup>	-0.06	0.20	0.50	0.13	b	-0.31	0.05	-0.08	-0.86	0.56	-0.03	-0.01	-0.02	0.08
	$Sr^{2+}$	0.07	0.30	b	0.30	0.05	-0.19	0.07	-0.08	-0.87	0.37	0.02	0.01	-0.01	0.07
	Ba <sup>2+</sup>	-0.15	0.23	0.51	0.41	0.16	-0.24	0.02	-0.08	-1.01	0.29	0.03	0.04	0.01	0.08
	$Mg^{2+}$	-0.04	0.31	0.37	0.20	0.13	0.06	0.21	-0.03	-0.74	0.70	0.02	0.01	0.01	0.11
	Na <sup>+</sup>	-0.27	b	0.14	0.04	-0.06	-0.10	0.08	-0.08	-0.65	-0.04	-0.01	-0.04	-0.02	0.00

<sup>*a*</sup> Positive values show lower field shifts, and negative values show higher field shifts. The values in "blank" indicate the chemical shifts ( $\delta$ , ppm, from TMS) of the protons in acetonitrile- $d_3$  at 30 °C. <sup>*b*</sup> These values could not be assigned due to overlapping of the peak of water.



**Figure 7.** <sup>1</sup>H NMR chemical shift assignment of 9-AA and 2M9-AA in acetonitrile- $d_3$  at 30 °C.

of UV absorbance of 4·Ca<sup>2+</sup> around 275 nm (see Figure 4).

Chemical shift changes of the other benzene protons (f-h) exhibited complicated behavior. Relatively small higher (2 and 4) and lower (3) chemical shift changes were obtained. The <sup>1</sup>H NMR behavior of benzene protons f-h can be inferred in terms of a mixture of electronical perturbations and steric effects at the binding event. These may reflect the dependency on the difference of metal ions and chain length of the ethylenoxy unit.

The considerable chemical shift changes of protons on the anthracene ring (k-n) were not observed upon complexation with all metal ions. These results indicated that there are no interactions between the two anthracene rings. This interpretation was also suggested by UV spectra of all complexes in their ground state.

In the 4·Ca<sup>2+</sup> complex, oxyethylene proton peaks b-d shifted to low magnetic field ( $\Delta \delta = 0.20$ , 0.50, and 0.13 ppm, respectively) because of reduction of the electron density on



Figure 8. (a) Schematic representation of the stablest molecular configuration of 2M9-AA and (b) molecular configuration change of the 9-AA moiety in 2-4 before and after the addition of metal ions.

the oxygen atoms by the coordinated cations. On the other hand, protons a and e showed no significant chemical shift change. A relatively large low magnetic shift change of amide proton j was observed ( $\Delta \delta = 0.56$  ppm). These observations indicated that Ca<sup>2+</sup> was mainly bound by the carbonyl group and the two oxygen atoms attached to carbons b and c, and the two oxygen atoms attached to carbons a and e did not play an important role upon complexation. The later observation also reflects that a large conformational change of 4 was not induced during complexation with Ca<sup>2+</sup>. On the basis of the fluorescence and <sup>1</sup>H NMR study, an expected structural change of **4** before and after addition of Ca<sup>2+</sup> in the ground state is illustrated in Figure 9. When the anthracene moiety of  $4 \cdot Ca^{2+}$  was excited, photodriven rotations of OC-N and N-benzene bonds were interrupted through the strong cooperative coordination by  $Ca^{2+}$ . Furthermore, the existence of proton a can provide an obstacle to the excited rotation along the anthracene-CO bond. The same trends in <sup>1</sup>H NMR studies on 4·Sr<sup>2+</sup> and 4·Ba<sup>2+</sup> were also obtained.

The ethylene proton peaks b–d of **3** shifted to low magnetic field ( $\Delta \delta$  = ca. 0.64–0.35 ppm) in the presence of Ca<sup>2+</sup>, Sr<sup>2+</sup>,



Figure 9. Schematic representation of the proposed structural change of 4 after the addition of metal ions in the ground state.

and Ba<sup>2+</sup> in their <sup>1</sup>H NMR spectra. Proton e and amide proton j of 3·Ca<sup>2+</sup> exhibited considerably large low magnetic shift changes ( $\Delta \delta = 0.50$  ppm (e) and  $\Delta \delta = 0.83$  ppm (j)) compared with those of  $3 \cdot \text{Sr}^{2+}$  ( $\Delta \delta = 0.32$  ppm (e) and  $\Delta \delta = 0.33$  ppm (j)) and  $3 \cdot Ba^{2+}$  ( $\Delta \delta = 0.28$  ppm (e) and  $\Delta \delta = 0.21$  ppm (j)). The present <sup>1</sup>H NMR data showed that **3** bound Ca<sup>2+</sup> with the carbonyl oxygen and all of the oxygen in the oxyethylene moiety since four units of oxyethylene had the best fit for Ca<sup>2+</sup>. Because Ca<sup>2+</sup> penetrates so deeply into the oxyethylene moiety, structural crowdedness around the 9-AA moiety is relatively small (Figure 10a). On the other hand, the <sup>1</sup>H NMR spectra of  $3 \cdot Sr^{2+}$  and  $3 \cdot Ba^{2+}$  suggested that these metal ions cannot interact strongly with four units of the oxyethylene site since their ionic radii are too large. This binding mode of 3. Sr<sup>2+</sup> and 3. Ba<sup>2+</sup> should induce steric crowdedness between the two 9-AA residues (Figure 10b). This provides the relatively effective prohibition for the rotation of the anthracene-CO bond at the excited state. Through the difference of the complex structures, the 3·Ca<sup>2+</sup> showed a relatively small value of the fluorescence quantum yield.

In the <sup>1</sup>H NMR spectrum of free **2**, the center of oxyethylene proton c also gave an unusually high chemical shift (2.41 ppm). Upon complexation, proton c showed an induced large lower magnetic field shift ( $\Delta \delta = 0.64$  ppm for Ca<sup>2+</sup>) whereas proton e showed no induced chemical shift change. Amide proton j also showed a low magnetic field shift change ( $\Delta \delta = 0.54$  ppm for Ca<sup>2+</sup>). These NMR observations indicated that **2** mainly bound Ca<sup>2+</sup> with the carbonyl group and the oxygen atom attached between carbons c and d. The formation of **2**•alkaline-earth-metal ions induced the conformational change from helical to semicircular as illustrated in Figure 11.

The <sup>1</sup>H NMR data of  $2 \cdot Mg^{2+}$  indicated behavior different from that of other complexes. The peak assignment of complex  $2 \cdot Mg^{2+}$  was not possible since its peaks were too broad. The <sup>1</sup>H NMR observation of  $4 \cdot Mg^{2+}$  also gave a somewhat broad spectrum. This suggests that the Mg<sup>2+</sup> complex of 2 and 4 showed a slow molecular motion on the NMR time scale (~10 ms). In the case of  $4 \cdot Mg^{2+}$ , the values of chemical shift changes



**Figure 10.** Schematic representation of the proposed structural difference between (a)  $3 \cdot Ca^{2+}$  and (b)  $3 \cdot Sr^{2+}$  and  $3 \cdot Ba^{2+}$  in the ground state.



Figure 11. Schematic representation of the proposed structural change of 2 after the addition of metal ions in the ground state.

a-e (0.04–0.37 ppm) were much smaller than those of **4** with alkaline-earth-metal ions (0.06–0.5 ppm for Ca<sup>2+</sup>). Furthermore, the amide proton peak j shifted largely to lower magnetic field (0.70 ppm) compared with those of **4**·Ca<sup>2+</sup>(0.56 ppm), **4**·Sr<sup>2+</sup> (0.37 ppm), and **4**·Ba<sup>2+</sup>(0.29 ppm). From these results, Mg<sup>2+</sup> did not penetrate the oxyethylene moiety so deeply but did penetrate the carbonyl oxygen atoms. This limited coordination of **4**·Mg<sup>2+</sup> could not freeze the rotation of anthracene–CO, OC–NH, and N–benzene bonds at the excited and ground states.

Chemical shift changes of **2** and **4** in the presence of alkalimetal ion (Na<sup>+</sup>) are also listed in Table 2. Oxyethylene proton peaks c and d of  $2\cdot$ Na<sup>+</sup> were observed at low magnetic field ((c) 0.47 ppm and (d) 0.14 ppm). Proton i of  $2\cdot$ Na<sup>+</sup> and  $4\cdot$ Na<sup>+</sup> also exhibited higher magnetic shifts ( $\Delta \delta = 0.81$  ppm and  $\Delta \delta = 0.65$  ppm, respectively). However, amide proton peak j of both **2**·Na<sup>+</sup> and **4**·Na<sup>+</sup> did not shift to high and low magnetic fields. This shows that the Na<sup>+</sup> ion was bound mainly at the ethylenoxy site, and the coordination of Na<sup>+</sup> onto the carbonyl oxygen was weaker than that of alkaline-earth-metal ions. Although this binding mode of Na<sup>+</sup> may prevent the rotation of the N-benzene bond, the rotation around the anthracene-CO and OC-NH bonds of **2**-**4** is not controlled at the excited state.

#### Conclusion

The 9-AA moiety in 2-4 exhibited TICT quenching through the rotation around the anthracene-CO, OC-NH, and N-benzene bonds at the excited state in acetonitrile solution. Rotations of three bonds in 2-4 were controlled by the formation of complexes with Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup>. These metal ion complexes showed large enhancement effects on fluorescence intensity with the off-on fluorescence signal. The present fluorophores 2-4 will be available as a photodetecting system for analytical use with off-on fluorescent signaling character.

## **Experimental Section**

Materials. General Procedure of the Syntheses of 2-4. The synthetic pathway of compounds 2-4 is shown in Scheme 1. A solution of 9-anthracenecarboxylic acid (9-anthroic acid) (0.01 mol) in 30 mL of SOCl<sub>2</sub> was refluxed for 1.5 h. Excess SOCl<sub>2</sub> was distilled off in vacuo, and completely evaporated after addition of 10 mL of benzene four times. This acid chloride was dissolved in 80 mL of THF. To this solution was added 2-aminophenol (0.02 mol) dissolved in 20 mL of THF dropwise at room temperature. The mixture was stirred for 1 day, and N-(2-hydroxyphenyl)-9-anthrylamide (1) and a small amount of 2-aminophenol hydrochloride salt were precipitated. The solution was filtered, and the precipitate was washed with 30 mL of water, EtOH, and CHCl<sub>3</sub>, successively, and dried in vacuo. This compound 1 was used without further purification. A mixture of 1 (0.01 mol) and 0.01 mol of t-BuOK was dissolved in 50 mL of DMF, and 0.005 mol each of tri-, tetra-, and pentaethylene glycol p-ditosylate was added under N<sub>2</sub> conditions. The mixture was heated for 12 h at 75-80 °C. The solvent was evaporated under reduced pressure, and the residue was purified by recrystallization and/or silica gel column chromatography (Wakogel C-200). Compound 3 was purified by recrystallization from CH<sub>3</sub>COOH several times. Reagent 4 was purified by silica gel column chromatography (eluent CHCl<sub>3</sub>), and then recrystallized from EtOH. In the case of 5, the purification was carried out using column chromatography (eluent benzene/AcOEt). Their structures and purities were confirmed by <sup>1</sup>H NMR spectra and elemental analyses.

*N*,*N*<sup>'</sup>-[Ethylenedioxybis(ethyleneoxy)-2-phenyl]bis(9-anthracenecarbonamide) (**2**): yield 72.5%; mp 132–136 °C; <sup>1</sup>H NMR (acetonitrile-*d*<sub>3</sub>)  $\delta$  = 2.41 (C–CH<sub>2</sub>–O, s, 4H), 3.06 (–C– CH<sub>2</sub>–O, t, 4H), 3.74 (–C–CH<sub>2</sub>–O, t, 4H), 6.94 (aromatic, d, 2H), 7.17 (aromatic, t, 4H), 7.48–7.56 (aromatic, m, 8H), 8.06– 8.13 (aromatic, dd, 8H), 8.51 (aromatic, d, 2H), 8.58 (aromatic, s, 2H), 8.63 (NH, m, 2H). Anal. Found: C, 77.00; H, 5.59; N, 3.64. Calcd for C<sub>48</sub>H<sub>40</sub>O<sub>6</sub>N<sub>2</sub>•<sup>1</sup>/<sub>2</sub>H<sub>2</sub>O: C, 76.89; H, 5.51; N, 3.73.

*N*,*N*'-[Oxybis(3-oxapentamethyleneoxy)-2-phenyl]bis(9-anthracenecarbonamide) (**3**): yield 66.0%; mp 83–85 °C (as **3**· EtOH); <sup>1</sup>H NMR (acetonitrile- $d_3$ )  $\delta = 2.42$  (-C-CH<sub>2</sub>-O, t, 4H), 2.78 (-C-CH<sub>2</sub>-O, t, 4H), 3.40 (-C-CH<sub>2</sub>-O, t, 4H), 3.97 (-C-CH<sub>2</sub>-O, t, 4H), 7.04 (aromatic, d, 2H), 7.17 (aromatic, t, 4H), 7.50–7.56 (aromatic, m, 8H), 8.06–8.13 **SCHEME 1** 



(aromatic, dd, 8H), 8.51 (aromatic, d, 2H), 8.58 (aromatic, s, 2H), 8.76 (NH, m, 2H). Anal. Found: C, 75.81; H, 5.76; N, 3.54. Calcd for  $C_{50}H_{44}O_7N_2^{\bullet 1/2}H_2O$ : C, 75.65; H, 5.71; N, 3.53.

*N*,*N*<sup>'</sup>-[Ethylenedioxybis(3-oxaoctamethyleneoxy)-2-phenyl]bis(9-anthracenecarbonamide) (**4**): yield 58.3%; pale yellow solid; <sup>1</sup>H NMR (acetonitrile-*d*<sub>3</sub>)  $\delta$  = 2.77 (−C−CH<sub>2</sub>−O, s, 4H), 2.69 (−C−CH<sub>2</sub>−O, t, 4H), 2.97 (−C−CH<sub>2</sub>−O, t, 4H), 3.49 (−C−CH<sub>2</sub>−O, t, 4H), 4.02 (−C−CH<sub>2</sub>−O, t, 4H), 7.04 (aromatic, d, 2H), 7.17 (aromatic, t, 4H), 7.50−7.56 (aromatic, m, 8H), 8.06−8.13 (aromatic, dd, 8H), 8.51 (aromatic, d, 2H), 8.58 (aromatic, s, 2H), 8.76 (NH, m, 2H). Anal. Found: C, 73.71; H, 5.67; N, 3.26. Calcd for C<sub>52</sub>H<sub>48</sub>O<sub>8</sub>N<sub>2</sub>•H<sub>2</sub>O: C, 73.74; H, 5.95; N, 3.30.

**Measurement of Fluorescence and UV Spectra.** Fluorescence spectra were measured using a Shimadzu RF-5300PC at 25 °C. The concentrations of the fluorescent reagents were  $1 \times 10^{-5}$  mol/dm<sup>3</sup> in purified acetonitrile. Alkaline-earth-metal cations were added to the solution of fluorescent reagent as perchlorate salts. Temperature was maintained at 25 °C.

Fluorescence quantum yields were determined by the integration of corrected fluorescence spectra. Quinine sulfate in 0.5 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> was used for correction of fluorescence spectra as a fluorescent standard ( $\Phi = 0.54$ ).

Because the fluorescence lifetimes of free and metalcomplexed 2-4 were below 10 ns, the sample solutions were used without degassing.

UV spectra were recorded on a Shimadzu UV-2400 with an equipment temperature controller in spectral grade acetonitrile.

Measurement of Fluorescence Lifetime. Fluorescence lifetimes were measured using a Horiba NAES-500 at room temperature. The concentrations of the fluorescent reagents were  $1 \times 10^{-6}$  mol/dm<sup>3</sup>, and those of the metal cations were  $1 \times 10^{-3}$  mol/dm<sup>3</sup>. The excited wavelength was 362 nm, and the monitored wavelength was 430 nm. The sample solutions were degassed by the freeze, pump, and thaw method. All the experiments were carried out at room temperature.

**Measurement of** <sup>1</sup>**H NMR.** <sup>1</sup>**H** NMR spectra were measured using a JEOL JNM-EX400 at 30 °C. The concentrations of the reagents were  $1 \times 10^{-2}$  mol/dm<sup>3</sup> in acetonitrile- $d_3$ . In the case of the measurements of metal complexes, excess amounts of metal cations as perchlorate were added to these solutions.

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Supporting Information Available: <sup>1</sup>H NMR of 4 and its metal ion complexes and fluorescence spectra of 2-4 and their metal ion complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

#### **References and Notes**

(1) Lehn, J.-M. Supramolecular Chemistry; VCH: Weinheim, Germany, 1995.

- (2) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxely, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice T. E. *Chem. Rev.* **1997**,
- 97, 1515 and references therein.(3) Balzani, V.; Scandola, F. Supramolecular Photochemistry; Ellis-
- (5) Balzani, V.; Scandola, F. Supramolecular Photochemistry; Enis-Horwood: Chichester, U.K., 1991.
- (4) Scneider, H.-J.; Dürr, H. Frontiers in Supramoleculear Organic Chemistry and Photochemistry; VCH: Weinheim, Germany, 1991.
- (5) Czarnik, A. W. Fluorescent Chemosensors for Ion and Molecule Recognition; American Chemical Society: Washington, DC, 1992.
- (6) Gokel, G. W. Crown Ethers and Cryptands; Royal Society of Chemistry: London, 1991.
- (7) Hiraoka, M. Crown Ethers and Analogous Compounds; Elesevier: New York, 1992.
- (8) Takagi, M.; Ueno, K. Host Guest Complex Chemistry; Springer: Berlin, 1984.
- (9) Bender, M. L.; Komiyama, M. Cyclodextrin Chemistry; Springer-Verlag: New York, 1978.
  - (10) D'Souza, V. T.; Lipokwitz, K. B. Chem. Rev. 1998, 98, 1741.
- (11) Shinkai, S. *Tetrahedron* **1993**, 49, 8933.
- (12) Shinkai, S. Advances in Supramolecular Chemistry; JAI Press: Greenwich, CT, 1993; Vol. 3.
- (13) Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: London, 1989.
- (14) Takagi, M.; Nakamura, H.; Ueno, K. Anal. Lett. 1977, 10, 1115.
- (15) Dix, J. P.; Vögtle, F. Angew. Chem., Int. Ed. Engl. 1978, 17, 857.
- (16) Takagi, M.; Nakamura, H. J. Coord. Chem. 1986, 15, 53.
- (17) Hayashita, T.; Teramae, N.; Kuboyama, T.; Nakamura, S.; Yamamoto, H.; Nakamura, H. *J. Inclusion Phenom.* **1998**, *32*, 251 and references therein.
  - (18) Sousa, L. R.; Larson, J. M. J. Am. Chem. Soc. 1977, 99, 307.
  - (19) Larson, J. M.; Sousa, L. R. J. Am. Chem. Soc. 1978, 100, 1943.
  - (20) Vögtle, F.; Weber, E. Angew. Chem., Int. Ed. Engl. 1979, 18, 753.
  - (21) Tümmler, B.; Maass, G.; Weber, E.; Wehner, W.; Vögtle, F. J.
- Am. Chem. Soc. 1977, 99, 4683.
  (22) Down, J. L.; Lewis, J.; Moore, B.; Wilkinsons, G. W. Proc. Chem.
- Soc. 1957, 209.
- (23) Down, J. L.; Lewis, J.; Moore, B.; Wilkinsons, G. W. J. Chem. Soc. 1959, 3767.
  - (24) Ray, A.; Nemthy, G. J. Am. Chem. Soc. 1971, 93, 6787.
  - (25) Schott, H.; Kyuhan, S. J. Pharm. Sci. 1975, 64, 663.
- (26) Lundberg, R. D.; Bailey, F. E.; Callard, R. W. J. Polym. Sci., Part A-1 1966, 4, 1563.
- (27) Yamazaki, N.; Nakahama, S.; Hirao, A.; Negi, S. Tetrahedron Lett. 1978, 2494.
- (28) Kubokawa, H.; Yamaguchi, K.; Hirao, A.; Nakahama, S.; Yamazaki, N. Chem. Lett. 1982, 1937.
- (29) Yamazaki, N.; Hirao, A.; Nakahama, S. J. Macromol. Sci., Chem. 1979, A13, 321.
- (30) Kuboniwa, H.; Nagami, S.; Yamaguchi, K.; Hirao, A.; Nakahama, S.; Yamazaki, N. J. Chem. Soc., Chem. Commun. **1985**, 1468.

- (31) Kuboniwa, H.; Yamaguchi, K.; Hirao, A.; Nakahama, S.; Hori, K.; Ohashi, Y. Chem. Lett. **1988**, 923.
- (32) Kasuga, N.; Nakahama, S.; Yamaguchi, K.; Ohashi, Y.; Hori, K. Bull. Chem. Soc. Jpn. 1991, 64, 3584.
  - (33) Gardner, J. O.; Beard, C. C. J. Med. Chem. 1978, 21, 357.
  - (34) Hiratani, K.; Aiba, S.; Nakagawa, T. Chem. Lett. 1980, 477.
  - (35) Hiratani, K. Chem. Lett. 1981, 21.
- (36) Hiratani, K.; Sugihara, H.; Kasuga, K.; Fujiwara, K.; Hayashita, T.; Bartsch, R. A. J. Chem. Soc., Chem. Commun. **1994**, 319.
- (37) Choy, E. M.; Evans, D. F.; Cussler, E. L. J. Am. Chem. Soc. **1974**, 96, 7085.
- (38) Duax, W. L.; Smith, G. D.; Strong, P. D. J. Am. Chem. Soc. 1980, 102, 6725.
  - (39) Kakizawa, A.; Akita, T.; Nakamura, H. Chem. Lett. 1993, 1671.
  - (40) Tahara, R.; Hasebe, K.; Nakamura, H. Chem. Lett. 1995, 753.
- (41) Suzuki, Y.; Morozumi, T.; Kakizawa, Y.; Bartsch, R. A.; Hayashita, T.; Nakamura, H. *Chem. Lett.* **1996**, 617.
- (42) Tahara, R.; Morozumi, T.; Suzuki, Y.; Kakizawa, Y.; Akita, T.; Nakamura, H. J. Inclusion Phenom. **1998**, *32*, 283.
- (43) Suzuki, Y.; Morozumi, T.; Nakamura, H.; Shimomura, M.; Hayashita, T.; Bartsch, R. A. J. Phys. Chem. B **1998**, 102, 7910.
- (44) Anada, T.; Kitaoka, T.; Ota, H.; Kakizawa, Y.; Akita, Y.; Morozumi, T.; Nakamura, H. Bunseki Kagaku 1999, 48, 1107.
- (45) Bezilevskaya, N. S.; Cherkasov, A. S. Opt. Spectrosc. 1965, 18, 30.
- (46) Bezilevskaya, N. S.; Cherkasov, A. S. Zh. Prikl. Spectrosk. Akad. Nauk Belorussk. SSR 1965, 3, 548.
  - (47) Werner, T. C.; Hercules, D. M. J. Phys. Chem. 1969, 73, 2005.
- (48) Suzuki, S.; Fuji, T.; Yoshiike, N.; Komatsu, S.; Iida, T. Bull. Chem. Soc. Jpn. 1978, 51, 2460.
- (49) Agbaria, R. A.; Butterfield, M. T.; Warnar, I. M. J. Phys. Chem. 1996, 100, 17133.
  - (50) Werner, T. C.; Rodgers, J. J. Photochem. 1986, 32, 59.
  - (51) Chae, M. Y.; Czarnik, A. W. J. Fluoresc. 1992, 2, 225.
- (52) De Santis, G.; Fabrizzi, L.; Licchelli, M.; Mangano, C.; Sacchi, D. Inorg. Chem. **1995**, 34, 3581.
- (53) Rotkiewicz, K.; Grellmann, K. H.; Grabowski, Z. R. Chem. Phys. Lett. 1973, 19, 315.
- (54) Grabowski, Z. R.; Rotkiewicz, K.; Siemiarczuk, A.; Cowley, D. J.; Baumann, W. *Nouv. J. Chim.* **1979**, *3*, 443.
  - (55) Rettig, W. Top Curr. Chem. 1994, 169, 253.
- (56) Schneider, F.; Lippert, E. Ber. Bunsen-Ges. Phys. Chem. 1968, 72, 1155.
- (57) Schneider, F.; Lippert, E. Ber. Bunsen-Ges. Phys. Chem. 1970, 74, 624.
- (58) Okada, T.; Mataga, N.; Baumann, W.; Siemiarczuk, A. J. Phys. Chem. **1987**, *91*, 4490.
- (59) Wiessner, A.; Huttmann, G.; Kuhnle, W.; Staeek, H. J. Phys. Chem. 1995, 99, 14923.
  - (60) Dey, J.; Dogra, S. K. J. Chem. Phys. 1994, 98, 3638.
  - (61) Dey, J.; Warner, I. M. J. Phys. Chem. A 1997, 101, 4872.
- (62) Azumaya, I.; Kagechika, H.; Fujiwara, Y.; Itoh, M.; Yamaguchi, K.; Shudo, K. J. Am. Chem. Soc. **1991**, *113*, 2833.
- (63) Lewis, F. D.; Long, T. M. J. Phys. Chem. A 1998, 102, 5327.
- (64) Braun, D.; Rettig, W.; Delmond, S.; Letard, J.-F.; Lapouyade, R.
- J. Phys. Chem. A 1997, 101, 6836.
- (65) de Silva, A. P.; de Silva, S. A. J. Chem. Soc., Chem. Commun. 1987, 1709.
- (66) Bissell, R. A.; Calle, E.; de Silva, A. P.; de Silva, S. A.; Gunaratne, H. Q. N.; Habib-Jiwan, J.-L.; Peiris, A. S. L.; Rupasighe, R. A. D. D.;
- Samarasinghe, T. K. S.; Sandanayake, K. R. A. S.; Soumillion, J.-P. J. Chem. Soc., Perkin Trans. 2 1992, 1559.
- (67) de Silva, A. P.; Gunaratne, H. Q. N.; McCoy, C. P. Nature 1993, 364, 42.
- (68) de Silva, A. P.; Gunaratne, H. Q. N.; McCoy, C. P. J. Am. Chem. Soc. 1997, 119, 7891.
  - (69) Czarnik, A. W. Acc. Chem. Res. 1994, 27, 302.
- (70) Huston, M. E.; Haider, K. W.; Czarnik, A. W. J. Am. Chem. Soc. 1988, 110, 4460.
- (71) Huston, M. E.; Engleman, C.; Czarnik, A. W. J. Am. Chem. Soc. **1990**, *112*, 7054.
- (72) Fabbrizzi, L.; Licchelli, M.; Pallavicini, P.; Sacchi, D.; Taglietti, A. Analyst **1996**, 121, 1763.
- (73) Fabbrizzi, L.; Licchelli, M.; Pallavicini, P.; Perotti, A.; Taglietti, A.; Sacchi, D. *Chem. Eur. J.* **1996**, *2*, 75.
- (74) Santis, G. D.; Fabbrizzi, L.; Licchelli, M.; Poggi, A.; Taglietti, A. Angew. Chem., Int. Ed. Engl. 1996, 35, 202.
- (75) O'Connell, E. J., Jr.; Delmauro, M.; Irwin, J. Photochem. Photobiol. 1971, 14, 189.
  - (76) Marquardt, D. W. J. Soc. Ind. Appl. Math. 1963, 11, 431.