

## Cation-controlled Emission of Crowned Acetophenone

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Effects of alkali- and alkaline-earth-metal cations on the emission properties of 4'-acetylbenzo-15-crown-5 (**1a**), 4'-acetylbenzo-18-crown-6 (**1b**), 4'-acetylbenzo-21-crown-7 (**1c**), and 3,4-dimethoxyacetophenone (**2**) have been studied in degassed EtOH–MeOH (4:1 v/v) glasses at 77 K. The fluorescence quantum yields ( $\phi_f$ ) for (**1a–c**) were negligibly small (0.009–0.014). The phosphorescence quantum yields ( $\phi_p$ ) for (**1a**), (**1b**), (**1c**), and (**2**) were 0.26, 0.47, 0.51, and 0.52, respectively, being dependent on the ring size of the crown ether moiety. Binding of alkaline-earth-metal cations decreased the phosphorescence peak at 470 nm concomitant with an appearance of the fluorescence peak at 365 nm. The  $\phi_f/\phi_p$  values increased with an increase in the binding ability of alkaline-earth-metal cations to (**1a–c**). Although  $\phi_p$  values of (**1a–c**) slightly decreased on addition of alkali-metal cations, the exception being a slight enhancement of  $\phi_p$  for (**1a**)–Cs<sup>+</sup>, (**1b**)–Cs<sup>+</sup>, and (**1b**)–Rb<sup>+</sup> systems, no fluorescence peak appeared.

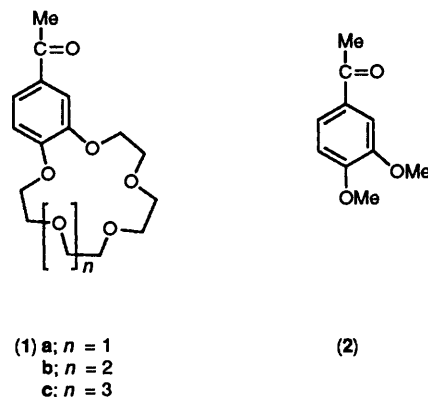
The binding of alkali- and alkaline-earth-metal cations to crown ethers is a well-known phenomenon.<sup>1</sup> The cation binding ability of crown ethers is primarily governed by the relationship between cation diameter and crown-ether hole size. Crown ethers, mono-aza-crown ethers, and cryptands which have fluorescent moieties such as naphthalene,<sup>2,3</sup> anthracene,<sup>4,5</sup> or benzoxazinone<sup>6</sup> have been synthesized and the effect of the binding of alkali- and alkaline-earth-metal cations on the fluorescence and/or phosphorescence properties of the ionophores studied. It has also been reported that a drastic change in the fluorescence of acyclic polyethers with quinoline or naphthalene moieties<sup>7</sup> is observed by the binding of Li<sup>+</sup>. The fluorescence enhancement of dibenzo-18-crown-6 by the binding of alkali-metal cations has been studied.<sup>8</sup>

Crown ethers can be used for the spectrophotometric detection of alkali- and alkaline-earth-metal cations by means of the ion-pair extraction of complexes between a crown ether and a cation with a counter-anion such as picrate<sup>9</sup> and by means of the chromogenic crown ether reagents.<sup>10,11</sup> The absorption spectrum of the chromogenic reagents, which are molecules bearing chromophoric units and crown-ether units, changes remarkably in response to alkali- and alkaline-earth-metal cations. Since fluorimetry can, in principle, be more sensitive than absorption photometry, it is of importance for chemical trace analyses.

In a recent communication<sup>12</sup> we have reported that the phosphorescence intensity of acetophenone derivatives with a crown ether moiety changes markedly on addition of alkaline-earth-metal cations. In the current paper the effects of alkali- and alkaline-earth-metal cations on the quantum yields of phosphorescence and cation-induced fluorescence of acetobenzocrown ethers of different ring size are reported. It is of interest in relation to the field of photochemistry and photophysics to study the effect of cation binding on the emission properties of functionalized crown ethers.

### Experimental

**Materials.**—1,17-Dichloro-3,6,9,12,15-pentaoxaheptadecane (b.p. 180 °C/10<sup>−3</sup> mmHg) was obtained in 70% yield from SOCl<sub>2</sub> and hexaethylene glycol, which was synthesized in 26% yield from diethylene glycol, bis-(2-chloroethyl) ether, and sodium.<sup>13</sup>

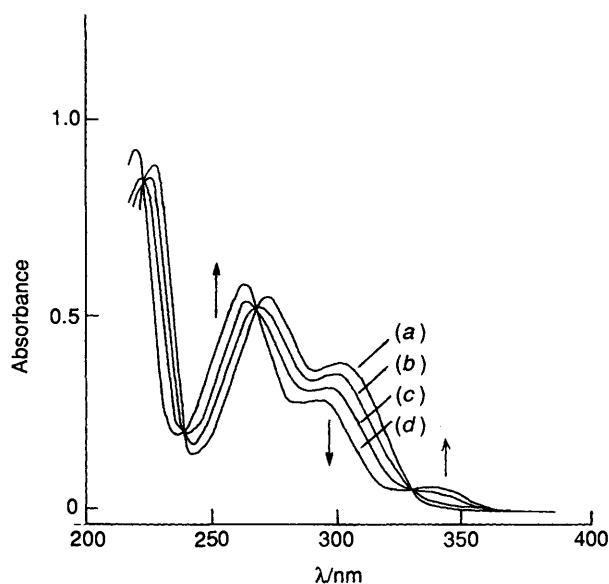


**4'-Acetylbenzo-21-crown-7 (1c).** A solution of 3,4-dihydroxyacetophenone (15 g, 0.099 mol) in butanol (285 cm<sup>3</sup>) was purged with nitrogen and charged with KOH (11 g, 0.2 mol) in water (11 cm<sup>3</sup>). To the refluxing mixture was added dropwise 1,17-dichloro-3,6,9,12,15-pentaoxaheptadecane (32 g, 0.1 mol) and refluxing was continued overnight. After being cooled to room temperature, the reaction mixture was acidified with 18% HCl and filtered. The filtrate was concentrated under reduced pressure. The oily residue was continuously extracted with hot heptane, whereupon cooling yielded slightly yellow crystals (13.8 g, 35%): m.p. 58–59 °C (from heptane);  $\delta_H$ (60 MHz; solvent CDCl<sub>3</sub>; standard SiMe<sub>4</sub>) 2.6 (3 H, s, Me), 4.4–3.5 (20 H, m, CH<sub>2</sub>), and 7.0–7.8 (3 H, m, Ph);  $\nu_{max}$ (KBr) 1 680 (aromatic ketone), 1 600 (CH=CH), and 1 180 cm<sup>−1</sup> (C–O–C).

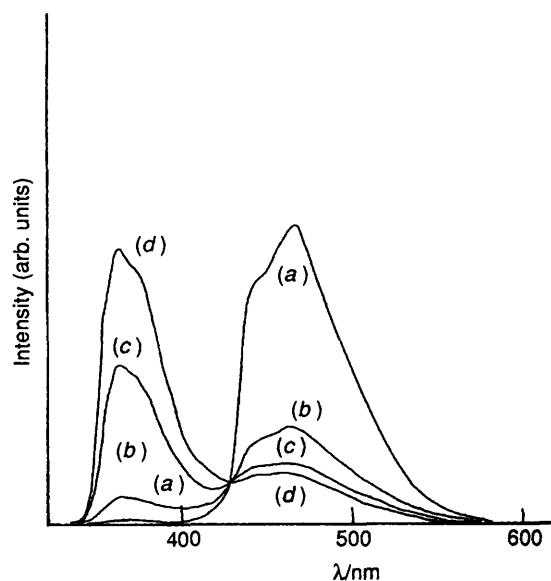
**4'-Acetylbenzo-15-crown-5 (1a)** and **4'-acetylbenzo-18-crown-6 (1b)**. These were prepared according to the method described by Smid and co-workers.<sup>14</sup>

3,4-Dimethoxyacetophenone (**2**) from Aldrich was used after purification. MeOH, EtOH, and alkali- and alkaline-earth-metal chlorides were of reagent grade and used without purification.

**Method.**—The phosphorescence and fluorescence spectra were measured in uncracked EtOH–MeOH (4:1 v/v) glasses at 77 K *in vacuo* using a Shimadzu RF-500 spectrofluorophotometer. The slit widths of excitation and emission were 3 and 10 nm, respectively. The wavelength of the excitation light was 330



**Figure 1.** Absorption spectra of (1b) ( $1.0 \times 10^{-4}$  mol dm $^{-3}$ ) in the presence of BaCl $_2$  at room temperature in an EtOH–MeOH (4:1 v/v) mixture. Concentrations of BaCl $_2$  in mol dm $^{-3}$ : (a) 0; (b)  $1.0 \times 10^{-5}$ ; (c)  $2.5 \times 10^{-5}$ ; (d)  $1.0 \times 10^{-4}$ .



**Figure 2.** Emission spectra of (1b) ( $1.0 \times 10^{-4}$  mol dm $^{-3}$ ) in the presence of SrCl $_2$  in degassed EtOH–MeOH (4:1 v/v) glasses at 77 K. Concentrations of SrCl $_2$  in mol dm $^{-3}$ : (a) 0; (b)  $1.0 \times 10^{-4}$ ; (c)  $5.0 \times 10^{-4}$ ; (d)  $2.0 \times 10^{-3}$ .

nm. The absorbances of samples at 330 nm were kept below 0.1. The quantum yields of phosphorescence ( $\phi_p$ ) and fluorescence ( $\phi_f$ ) were determined by comparison of the intensities of the phosphorescence and fluorescence spectra of (1a–c) and (2) with the phosphorescence of *p*-methoxyacetophenone ( $\phi_p = 0.68$ )<sup>15</sup> having the same absorbance at the excitation wavelength. Absorption spectra were taken with a Shimadzu UV-265 spectrophotometer. The formation constants for 1:1 complexes of (1b, c) with K $^+$  and Ba $^{2+}$  in MeOH were determined at 28 °C by conductimetry.<sup>16</sup> The conductance measurements were carried out by means of TOA conductivity apparatus, model CM-2A, in a silicone oil bath thermostatted at 28 °C. A cell of cell constant 0.101 cm $^{-1}$  was used. Because of a small shift of the absorption peaks of (1b, c) on addition of K $^+$ , accurate

formation constants for the complexes were not obtained by the spectrophotometric method.

## Results and Discussion

Figure 1 shows the changes in the absorption spectra of (1b) on addition of Ba $^{2+}$  in EtOH–MeOH (4:1 v/v) at room temperature. On addition of Ba $^{2+}$  the absorption peaks at 270 ( $\epsilon = 1.05 \times 10^4$  dm $^3$  mol $^{-1}$  cm $^{-1}$ ) and 305 nm ( $\epsilon = 7.20 \times 10^3$  dm $^3$  mol $^{-1}$  cm $^{-1}$ ) shifted to shorter wavelengths and a new absorption band appeared at 345 nm ( $\epsilon = 8.00 \times 10^2$  dm $^3$  mol $^{-1}$  cm $^{-1}$ ) at [Ba $^{2+}$ ]/[crown] = 30. Isosbestic points were observed at 238, 268, and 330 nm. A similar spectral change was observed on addition of Sr $^{2+}$  and Ca $^{2+}$ , although the magnitude of the shift of the absorption peak decreased in the order Ba $^{2+} \approx$  Sr $^{2+} >$  Ca $^{2+}$ . The magnitude of the peak shifts of (1a) and (1c) decreased in the order Ba $^{2+} >$  Sr $^{2+} >$  Ca $^{2+}$ . For Ba $^{2+}$ , Sr $^{2+}$ , and Ca $^{2+}$  the magnitude of the peak shift decreased in the order (1b) > (1c) > (1a). For the systems of alkali-metal cations and (1a–c), similar spectral changes were observed, except that the new absorption peak at 345 nm did not appear. No absorption spectral changes of (2) were observed on addition of alkali- and alkaline-earth-metal cations. Thus, the absorption spectral change of (1a–c) on addition of cations is due to the cation binding of (1a–c), as has been observed for many crown ether–cation systems.<sup>17</sup> The continuous variation method using the absorbance changes at 305 nm showed that (1a–c) can bind alkali- and alkaline-earth-metal cations in a 1:1 fashion. The binding constants for the systems of K $^+$ –(1b), K $^+$ –(1c), Ba $^{2+}$ –(1b), and Ba $^{2+}$ –(1c) were found to be  $9.55 \times 10^3$ ,  $1.20 \times 10^4$ ,  $1.17 \times 10^4$ , and  $1.12 \times 10^4$  dm $^3$  mol $^{-1}$  in MeOH at 28 °C, respectively. These values were smaller than the binding constants of K $^+$  and Ba $^{2+}$  by benzo-18-crown-6 and 21-crown-7 by about one order of magnitude.<sup>18</sup> The electron-withdrawing acetyl group on the benzene ring lowers the cation-binding ability. The finding that the new absorption band at 345 nm of (1b) was not observed on addition of K $^+$  is not explained by the difference in the binding constants of K $^+$ –(1b) and of Ba $^{2+}$ –(1b). The appearance of the absorption peak of the crowned acetophenones at 345 nm is essential for the binding of divalent cations.

On excitation with 330 nm light (1a–c) and (2) showed phosphorescence at 467–470 nm. The phosphorescence lifetimes were 1.1–1.2 s in EtOH–MeOH (4:1 v/v) at 77 K, being eventually independent on the structure of the compounds. The quantum yields ( $\phi_p$ ) of the phosphorescence of (1a), (1b), (1c), and (2) were 0.26, 0.47, 0.51, and 0.52, respectively, being dependent on the ring size of the crown-ether moiety. Figure 2 shows the emission spectral changes of (1b) on addition of SrCl $_2$ . Although the emission peak at 365 nm of (1b) was negligibly small, on addition of Sr $^{2+}$  this peak enhanced along with a decrease of the phosphorescence peak at 470 nm. An isosbestic point was observed at 430 nm. A similar emission property was observed when Ba $^{2+}$  and Ca $^{2+}$  were added. The lifetime of the emission at 365 nm was shorter than 3 ns, suggesting that it is fluorescence. The emission at 365 nm is not a delayed fluorescence because the lifetime is much shorter than that of phosphorescence. (The lifetime of delayed fluorescence has been known to be nearly equal to the lifetime of phosphorescence.<sup>19</sup>) Any changes in the emission spectrum of (2) were not observed on addition of Ba $^{2+}$ , Sr $^{2+}$ , and Ca $^{2+}$ . This suggests that the change of emission spectrum is due to the cation binding of the crown-ether moiety of (1b). On addition of alkali-metal chlorides the phosphorescence intensity at 470 nm was slightly changed; however, no fluorescence peak at 365 nm was observed.

Table 1 shows the fluorescence quantum yield ( $\phi_f$ ) and  $\phi_p$

**Table 1.** Fluorescence ( $\phi_f$ ) and phosphorescence ( $\phi_p$ ) quantum yields of (1a-c) and (2) in degassed EtOH-MeOH (4:1 v/v) glasses at 77 K.<sup>a</sup>

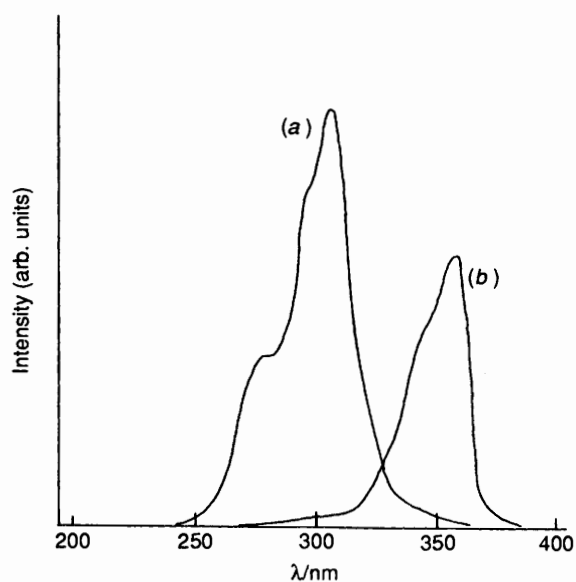
Salt added/ 10 <sup>-4</sup> mol dm <sup>-3</sup>	(1a)		(1b)		(1c)		(2)	
	$\phi_f$	$\phi_p$	$\phi_f$	$\phi_p$	$\phi_f$	$\phi_p$	$\phi_f$	$\phi_p$
None	0.009	0.26	0.013	0.47	0.014	0.51	0.52	
CaCl <sub>2</sub>	1	0.009	0.21	0.016	0.19	0.026	0.48	0.52
	5	0.011	0.19	0.11	0.15	0.046	0.45	0.52
	20	0.009	0.10	0.14	0.21	0.032	0.34	—
SrCl <sub>2</sub>	1	0.019	0.21	0.053	0.19	0.031	0.27	0.53
	5	0.020	0.12	0.28	0.085	0.047	0.23	0.52
	20	0.036	0.13	0.31	0.073	0.12	0.27	—
BaCl <sub>2</sub>	0.2	—	—	0.012	0.14	0.039	0.32	—
	1	0.028	0.15	0.17	0.10	0.16	0.063	0.52
	5	0.037	0.14	—	—	—	—	—
	10	0.051	0.16	0.17	0.057	0.14	0.072	0.48
	20	0.044	0.22	—	—	—	—	—

<sup>a</sup> Concentration of crowned acetophenones  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>; wavelength of excitation lights 330 nm.

**Table 2.** Phosphorescence quantum yields ( $\phi_p$ ) of (1a-c) and (2) in degassed EtOH-MeOH (4:1 v/v) glasses at 77 K.<sup>a</sup>

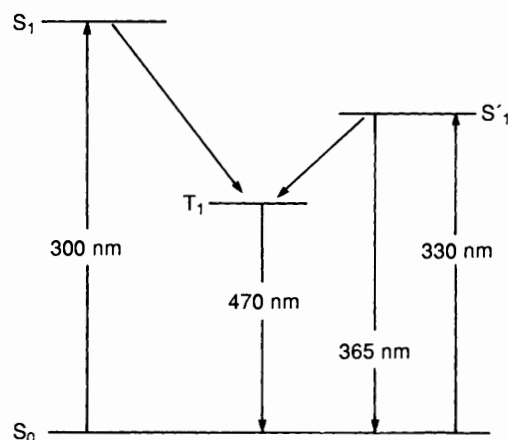
Salt added	$\phi_p$			
	(1a)	(1b)	(1c)	(2)
None	0.26	0.47	0.51	0.52
NaCl	0.077	0.45	0.40 <sup>b</sup>	0.46
KCl	0.21	0.44	0.50 <sup>b</sup>	0.43
RbCl	0.19	0.55	0.46 <sup>b</sup>	0.42
CsCl	0.38	0.73	0.51 <sup>b</sup>	0.44

<sup>a</sup> Concentrations of crowned acetophenones and salts added  $1.0 \times 10^{-4}$  and  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup>, respectively; wavelength of excitation light 330 nm. <sup>b</sup> Concentration of salts added  $5.0 \times 10^{-4}$  mol dm<sup>-3</sup>.



**Figure 3.** Excitation spectra of (1b) ( $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>)-BaCl<sub>2</sub> ( $1.0 \times 10^{-4}$  mol dm<sup>-3</sup>) system in degassed EtOH-MeOH (4:1 v/v) glasses at 77 K. The emission was monitored at (a) 470 nm and (b) 400 nm.

values of (1a-c) and (2) on addition of alkaline-earth-metal cations;  $\phi_f$  values for (1a-c) were negligibly small (0.009-0.014).



Scheme 1.

It has been shown that no fluorescence is observed for acetophenone and its derivatives because the quantum yield of singlet-triplet intersystem crossing is almost unity.<sup>19</sup> When alkaline-earth-metal cations were added to (1a-c)  $\phi_p$  decreased and  $\phi_f$  increased, with the total emission quantum yields ( $\phi_f + \phi_p$ ) always decreasing. No significant change in  $\phi_p$  of (2) was observed on addition of cations. Thus, the changes in  $\phi_p$  values were caused by the cation binding of (1a-c) and the  $\phi_p$  values were not affected by the ionic strength of the solid solutions. The  $\phi_f/\phi_p$  values at [cation]:[crown] ratio of unity can be taken as a measure of the cation sensitivity of the crowned acetophenones. The highest  $\phi_f/\phi_p$  value at [cation]:[crown] ratio of unity was observed to 2.54 for the Ba<sup>2+</sup>-(1c) system, where the  $\phi_f/\phi_p$  value increased by a factor of 94 compared with the value in the absence of cations. The  $\phi_f/\phi_p$  values at [cation]:[crown] ratio of unity for (1a-c) decreased in the order Ba<sup>2+</sup> > Sr<sup>2+</sup> > Ca<sup>2+</sup>. This order is consistent with that of cation-binding ability of crown ethers of corresponding ring size.<sup>18</sup> For each alkaline-earth-metal cation examined, the highest  $\phi_f/\phi_p$  values at [cation]:[crown] ratio of unity were observed for the following systems: Ca<sup>2+</sup>-(1b), Sr<sup>2+</sup>-(1b), and Ba<sup>2+</sup>-(1c).

Table 2 shows the  $\phi_p$  values for (1a-c) and (2) on addition of alkali-metal chlorides. A slight decrease in  $\phi_p$  was observed on addition of alkali metal cations, except for slight increases in  $\phi_p$  for (1a)-Cs<sup>+</sup>, (1b)-Rb<sup>+</sup>, and (1b)-Cs<sup>+</sup>. The increase in  $\phi_p$  for these systems may be due to a heavy-atom effect operating for Cs<sup>+</sup> and perhaps Rb<sup>+</sup>, which increases  $\phi_p$  by increasing both the rate of intersystem crossing from the excited singlet state to the excited triplet state and the rate of phosphorescence, as observed for the system comprising 2,3-naphtho-20-crown-6 and alkali-metal cations.<sup>2</sup>

Figure 3 shows the excitation spectra of (1b) in the presence of Ba<sup>2+</sup> in degassed EtOH-MeOH (4:1 v/v) glasses at 77 K. When the emission at 470 nm was monitored, the peak of the excitation spectrum was observed at 310 nm; when the emission at 400 nm was monitored, the peak was at 360 nm. It is evident that a new photoexcited state of (1a-c) is formed by the binding of the divalent cations. Scheme 1 shows an energy state diagram for the relaxation processes of the complexes of crowned acetophenone and alkaline-earth-metal cations, where S<sub>0</sub>, S<sub>1</sub>, and T<sub>1</sub> are the ground, singlet excited, and triplet excited states, respectively, and S'<sub>1</sub> is a new excited state induced by the binding of divalent cations in the crown-ether cavity. When the (1b)-Ba<sup>2+</sup> system was excited with 300 nm light, the emission at 470 nm was observed but not that at 365 nm. This means that no energy migration from S<sub>1</sub> to S'<sub>1</sub> occurs because of the rapid S<sub>1</sub>-T<sub>1</sub> intersystem crossing process. As shown in Table 1, the  $\phi_p$  values for (1b) in the presence of Ba<sup>2+</sup>

were lower than that in the absence of  $\text{Ba}^{2+}$ . Thus, the efficiency of  $S_1-T_1$  intersystem crossing is lower than that of  $S_1-T_1$ . Since the quantum yield of total emission ( $\phi_f + \phi_p$ ) of the  $(\mathbf{1b})-\text{Ba}^{2+}$  system is lower than that of  $(\mathbf{1b})$ , the non-radiative deactivation process of the  $S_1$  state tends to occur.

### References

- 1 F. Vogtle, 'Host-Guest Complex Chemistry I,' Springer Verlag, Berlin, 1981.
- 2 L. R. Sousa and J. M. Larson, *J. Am. Chem. Soc.*, 1977, **99**, 307.
- 3 J. M. Larson and L. R. Sousa, *J. Am. Chem. Soc.*, 1978, **100**, 1943.
- 4 J. P. Konopelski, F. K. Hibert, J. M. Lehn, J. P. Desvergne, F. Fages, A. Castellan, and H. B. Laurent, *J. Chem. Soc., Chem. Commun.*, 1985, 433.
- 5 A. P. Silva and S. A. Silva, *J. Chem. Soc., Chem. Commun.*, 1986, 1709.
- 6 S. F. Fogues, M. T. Bris, J. P. Guette, and B. Valeur, *J. Chem. Soc., Chem. Commun.*, 1988, 384.
- 7 K. Hiratani, *J. Chem. Soc., Chem. Commun.*, 1987, 960.
- 8 H. Shizuka, K. Takada, and T. Morita, *J. Phys. Chem.*, 1980, **84**, 994.
- 9 F. Vogtle and E. Weber, 'Host-Guest Complex Chemistry III,' Springer Verlag, Berlin, 1984.
- 10 K. Nakasima, S. Nakatsuji, S. Akiyama, I. Tanigawa, T. Kaneda, and S. Misumi, *Talanta*, 1984, **31**, 749.
- 11 H. G. Lohr and F. Vogtle, *Acc. Chem. Res.*, 1985, **18**, 65.
- 12 M. Shirai and M. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1988, 381.
- 13 M. Newcomb, S. S. Moore, and D. J. Cram, *J. Am. Chem. Soc.*, 1977, **99**, 6405.
- 14 S. Kopolow, T. E. Hogen-Esch, and J. Smid, *Macromolecules*, 1973, **6**, 133.
- 15 N. C. Yang, D. S. McCluve, S. L. Murov, J. J. Houser, and R. Dusenbery, *J. Am. Chem. Soc.*, 1967, **89**, 5466.
- 16 Y. Takeda, H. Yano, M. Ishibasi, and H. Isozumi, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 72.
- 17 C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017.
- 18 R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, and J. J. Christensen, *Chem. Rev.*, 1985, **85**, 271.
- 19 N. J. Turro, 'Modern Molecular Photochemistry,' Benjamin/Cummings Publishing, California, 1978.

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