Synthesis and fluorescence behavior of calix[4]resorcinarenes possessing pyrenyl group(s)

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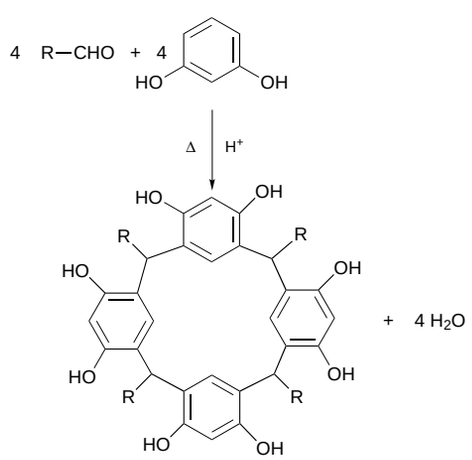
A mixture of octa-*o*-acetylated calix[4]resorcinarenes (CRAs) with varying numbers of 2-(pyren-1-yl)ethyl residues is synthesized by acid-catalyzed condensation of resorcinol with 3-(pyren-1-yl) propanal, followed by acetylation. The product is separated using reversed phase silica gel column HPLC. NMR spectra of the isolated octa-*o*-acetylated CRAs substituted with different numbers of pyrenyl groups revealed that all the cyclic tetramers are of the crown conformation. The product distribution is almost in accordance with theoretical values, assuming that the reaction rates of the two aldehydes are the same. ^{1}H NMR chemical shifts of the pyrenyl groups are shifted to an upper field with increasing number of pyrenyl groups because of the ring current effect. Measurements of steady state spectra and decay time of pyrene fluorescence of the CRAs revealed that they form two types of excimer and that strain in the excimer does not depend on the number of pyrenylethyl groups.

Introduction

Calix[4]resorcinarenes (CRAs), which are synthesized from an aldehyde and a molar equivalent of resorcinol as shown in Scheme 1, have been attracting current interest with a view to



Scheme 1 Synthetic pathway to CRAs

achieving the molecular design of molecular receptors for the recognition of guest molecules.[1–3] Studies on conformational analysis and formation thermodynamics of CRAs and their derivatives revealed that the crown conformer is the most thermodynamically stable isomer.[4,5] In the crown conformer, all of the four substituents at the methylene bridges linking the resorcinol moieties are tethered from the upper rim of the cylindrical structure in the same direction so that it is reasonable to regard the molecules as a fragmented model of two-dimensionally self-assembled monolayers formed on solid surfaces. We have recently found that CRAs and their derivatives are adsorbed readily onto polar surfaces of amorphous solids from less polar solutions to form densely packed monolayers as a result of multi-point adsorptivity[6] and that the surface adsorption of a CRA having four azobenzene residues on colloidal silica particles results in the photocontrol of dispersibility in organic solvents.[7] These facts have led us to prepare CRAs substituted with pyrenyl groups to embark upon elucidating microenvironmental conditions of self-assembled monolayers of CRAs by monitoring the emission behavior of pyrene as a fluorescent probe. Whereas some reports described the stepwise synthesis of calixarene derivatives possessing pyrenyl groups derived from monophenols,[8–10] there has been no report dealing with the synthesis of CRAs substituted with pyrene derived from resorcinol. We report here the synthesis and emissive properties of crown conformers of CRA derivatives having different numbers of pyrene residues which have a potential value as fluorescent probes of self-assembled monolayers.

Experimental

Materials

Pyrene-1-carbaldehyde and ethyl diethylphosphonoacetate were used as received commercially. A toluene solution of diisobutylaluminum hydride was obtained from Aldrich.

Ethyl 3-(pyren-1-yl)prop-2-enoate. Ethyl diethylphosphonoacetate (15.2 g, 67.8 mmol) was added dropwise to a benzene suspension (30 ml) of sodium hydride (2.71 g, 113 mmol). After stirring for 1 h at room temperature, a benzene solution of pyrene-1-carbaldehyde (12.4 g, 53.7 mmol) was added dropwise and stirred for a few hours at 15–20 °C, followed by removal of the solvent under reduced pressure. The yellow solid residue was purified by recrystallization from benzene to give yellow needles (84%), mp 111–112 °C (Calc. for $C_{21}H_{16}O_2$; C, 83.98; H, 5.37%. Found: C, 83.52; H, 5.29%).

Ethyl 3-(pyren-1-yl)propenoate. Ethyl 3-(pyren-1-yl)prop-2-enoate (13.0 g, 43.3 mmol) was dissolved in a mixture of ethanol and ethyl acetate (100 ml each). The solution was stirred under hydrogen in the presence of palladium on charcoal at room temperature overnight. The catalyst was removed by filtration, the solvent was evaporated and the residue was

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recrystallized from benzene–methanol to give white crystals (58%), mp 65–67 °C (Calc. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00%. Found: C, 82.47; H, 6.75%).

3-(Pyren-1-yl)propanal. To a dichloromethane solution of ethyl 3-(pyren-1-yl)propanoate (1.00 g, 3.3 mmol) was added dropwise a 1.0 M toluene solution of diisobutylaluminum hydride (3.4 ml, 3.4 mmol), and the mixture was stirred for 20 min at dry ice–methanol temperature. After the addition of 0.5 ml of methanol, the mixture was stirred for 30 min, and then the precipitate was removed by filtration, followed by evaporation of the solvent. The solid residue was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane (1 : 3) as eluent, followed by recrystallization from ethanol to give white crystals (64%), mp 74–75 °C (Calc. for $C_{19}H_{14}O$: C, 88.34; H, 5.46%. Found: C, 87.78; H, 5.38%).

Octa-*o*-acetylated tetrapropylcalix[4]resorcinarene (1). The preparation of tetrapropylcalix[4]resorcinarene is reported elsewhere.[6] Tetrapropylcalix[4]resorcinarene was dissolved in a mixture of acetic anhydride and pyridine and then 3-dimethylaminopyridine was added. The solution was stirred for 13 h at 80 °C. After water was added to the solution, the product was extracted with ethyl acetate and then subjected to purification with a mixture of acetone and hexane to give white crystals (65%), mp >300 °C (Calc. for $C_{56}H_{64}O_{16}$: C, 67.73; H, 6.50%. Found: C, 67.64; H, 6.49%).

Octa-*o*-acetylated tetrabis[2-(pyren-1-yl)ethyl]calix[4]resorcinarene (2). 3-(Pyren-1-yl)propanal (24.2 mg, 0.0937 mol) and 10.4 g of resorcinol (0.0945 mol) were dissolved in 50 ml of 2-methoxyethanol, and the solution was stirred at 80 °C for 12 h and subsequently at 120 °C for 5 h. The solution was cooled, water was added to it, and then the precipitate was separated by filtration and washed with water until the washings had a pH of *ca*. 7 to give the crude CRA. The crude CRA was dissolved in acetic anhydride (30 ml) and pyridine (10 ml) and 3-dimethylaminopyridine (10 mg) was added to it and the resulting solution was stirred at 80 °C for 20 min and subsequently at room temperature overnight. After work-up with water, the product was extracted with diethyl ether and purified by column chromatography on silica gel using a 1 : 5 (v/v) mixture of ethyl acetate and chloroform as eluent to give the octa-*o*-acetylated pyrene CRA (28%), mp 173–176 °C (Calc. for $C_{116}H_{88}O_{16}$: C, 80.17; H, 5.10%. Found: C, 79.46; H, 5.15%).

Octa-*o*-acetylated CRAs substituted with different numbers of pyrenes [CRA-Py(*n*)]. CRA-Py(*n*)s were prepared twice with slight modification of reaction conditions. In the first run, an ethanol (30 ml) solution containing 0.70 g of 3-(pyren-1-yl)propanal (2.7 mmol), 0.58 g of butanal (8.1 mmol) and 1.19 g of resorcinol (10.8 mmol) was refluxed for 8 h. The product was extracted with ethyl acetate after work-up with water. After evaporating the solvent, the residual solid was dissolved in 20 ml of pyridine, and 10 ml of acetic anhydride and 2 mg of 3-dimethylaminopyridine were added, and the solution was stirred at 50 °C for 5 h. The reaction was worked up with water, extracted with diethyl ether and purified by column chromatography on silica gel using a 1 : 5 (v/v) solvent of ethyl acetate and chloroform to give the product (23% by weight).

In the second run, 0.66 g of 3-(pyren-1-yl)propanal (2.6 mmol), 0.19 g of butanal (2.6 mmol) and 0.57 g of resorcinol (5.2 mmol) were heated in 2-methoxyethanol (30 ml) at 120 °C for 15 h. Subsequent procedures were the same as for the first run to give the product (48% by weight). The products of both runs were subjected to preparative HPLC to isolate octa-*o*-acetylated CRAs with different numbers of pyrenes using the conditions stated below.

Analytical methods

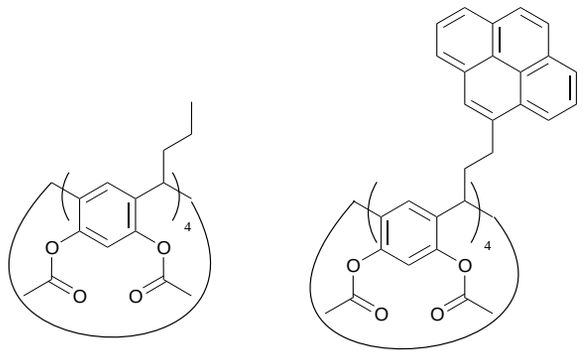
Reversed phase silica gel columns, Jasco Crestpak C18S and Merck LiChrispher 100 RP-18, were used as an analytical HPLC column and a preparative HPLC column, respectively. The ratio of methanol–water used as eluent was 90 : 10 for first 5 min, graduated to 100% of methanol during the following 25 min and finally 100% of methanol. The flow rate was 1 or 4 ml min^{-1} for analytical or preparative HPLC, respectively. Detection was made at a wavelength of 274 nm. NMR spectra were taken on a JEOL EX500 spectrometer at room temperature. Absorption and fluorescence spectra were obtained with a Hitachi UV320 spectrometer and a F4000 fluorospectrometer, respectively. The excitation wavelength used for the fluorescence spectra was 345 nm. Fluorescence decay times were determined using a PRA time-correlated single photon counting system equipped with a multichannel analyzer (Norland IT-5300). As an excitation source, a deuterium-filled (0.5 atm) flash lamp (PRA model 510) was used, operating at 30 kHz. The half-width of the pulse was *ca.* 2 ns. The wavelength of the excitation light passed through the monochromator was 345 nm. The concentration of sample solutions was adjusted so that the absorbance at 345 nm was 0.2. The fluorescence from monomer and excimer was passed through glass filters which cut off light of wavelengths <350 nm and >420 nm (Toshiba UV-37 and UV-D33S) and a glass filter which cuts off light of wavelengths <450 nm (Toshiba Y-47), respectively. The decay curves were deconvoluted using an interactive nonlinear least-squares method.

Results and discussion

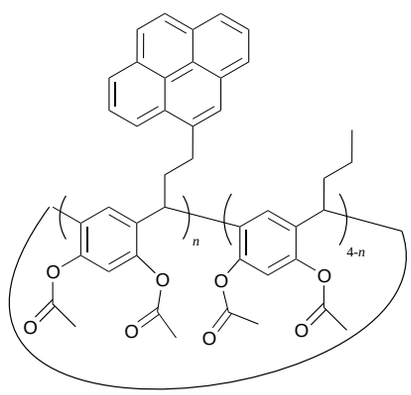
Synthesis of octa-*o*-acetylated CRAs possessing pyrenyl group(s) [CRA-Py(*n*)]

CRAs have been prepared by the condensation of the corresponding aldehyde with resorcinol in the presence of hydrochloric acid. In order to obtain CRAs substituted with different numbers of pyrenyl residues, resorcinol was reacted with an equimolar amount of a mixture of 3-(pyren-1-yl)propanal and butanal. Two experiments were performed with different ratios of the two aldehydes in ethanol and 2-methoxyethanol, respectively. Since the purification of CRAs by column chromatography is very hard due to the strong adsorptivity of phenolic OH groups on chromatographic carriers, the OH groups of the products were acetylated so that they could be subjected to reversed phase HPLC separation. As shown in Fig. 1, five definite peaks were observed for both runs performed with different ratios of the aldehydes. The elution times of the first peak and the fifth peak were in line with that of authentic samples of CRA-Py(0) (**1**) and CRA-Py(4) (**2**). For the first run, small peaks were observed just after the definite peaks as shoulders whereas only sharp peaks were observed for the second run. There is a possibility that these shoulder peaks were due to a conformational isomer of each peak product. Hogberg[4] and Abis *et al.*[5] have showed that CRAs are formed as a mixture of different conformers at an early stage of the acidolytic condensation, and after a prolonged reaction period, the predominant transformation to the most thermodynamically stable crown conformer takes place. According to these references and our experimental result that when the acid-catalyzed condensation that was stopped after 4 hours and then acetylated larger minor peaks were observed in the HPLC, the minor peaks in the HPLC were assigned to conformational isomers of CRA. Since the second run was for 15 hours at 120 °C and the first run for 8 hours at 80 °C, the second run should favor the formation of crown conformers with different numbers of pyrene residues. In other words, the products in the first run contain mixtures of CRA conformers other than crown conformers.

Using a preparative HPLC column, the second, third and fourth fractions of the second run were collected to isolate octa-*o*-acetylated CRA derivatives. The structural elucidation of each fraction was performed by NMR spectroscopy. An NMR spectrum of the third fraction is shown in Fig. 2 as a representative example. The presence of a sharp singlet at 6.97 ppm assignable to H*a* of the benzene rings confirms the crown



1 Authentic samples **2**



CRA-Py(*n*), *n* = 2, 3, 4

conformation.[5] H*b* of the benzene rings of octa-*o*-acetylated CRA derivatives appears as a broad signal, as described in a literature.[5] The crown conformation was also confirmed for the second and the fourth fractions in a similar way. Judging from the integration data from the NMR spectra, the second fraction was identified as the octa-*o*-acetylated CRA possessing one pyrenylethyl and three propyl groups [CRA-Py(1)] while the third and fourth ones were identified as the acetylated CRA with two pyrenylethyl and two propyl groups [CRA-Py(2)] and that with three pyrenylethyl groups and a propyl group [CRA-Py(3)], respectively. Although two structural isomers of CRA-Py(2) should exist with the two pyrenylethyl groups at either adjacent positions or opposite positions, the separation of these isomers was unsuccessful under the present HPLC conditions. The UV absorption of CRA-Py(*n*) at this wavelength is due to both the resorcinol moiety and the pyrene chromophore. The molar absorption coefficients at 274 nm, at which HPLC peaks were detected by UV absorption, of CRA-Py(0), CRA-Py(1), CRA-Py(2), CRA-Py(3) and CRA-Py(4) were measured in methanol to be 4.4×10^3, 4.7×10^4, 9.0×10^4, 1.3×10^5 and 1.8×10^5, l mol^{-1} cm^{-1}, respectively. Using these absorption coefficients and the area ratio of HPLC peaks of each fraction, the product distributions of both runs were calculated. The ratio of CRA-Py(*n*) ($n = 0$ to 4) produced was considered to be the same as the ratio of the CRA-Py(*n*) purified by column chromatography after acid-catalyzed condensation and acetylation, which was analyzed by HPLC, since the column chromatography retention times for five fractions of CRA-Py(*n*) ($n = 0$ to 4) were the same under the conditions used. The ratio of the fractions was equal to the ratio of the concentrations of CRA-Py(*n*) ($n = 0$ to 4) in the solution used for the HPLC analysis. Each concentration was calculated by dividing the HPLC peak's area at 274 nm by the absorption coefficient (ε) at 274 nm of the appropriate CRA-Py(*n*) ($n = 0$ to 4).

For the first run, the HPLC areas of the small signals were added up to the corresponding main signals. As shown in Table 1, the experimental values are in good agreement with the calculated ones with the assumption that the condensation reactions of the two aldehydes proceed at the same rate.

Table 1 The ratio of CRA-Py(*n*) ($n = 0$–4) in the octa-*o*-acetylated products

		n				
Run		0	1	2	3	4
1	Observed[a]	0.39	0.37	0.18	0.05	0.01
	Estimated[b]	0.32	0.42	0.21	0.05	0.003
2	Observed[a]	0.09	0.24	0.34	0.25	0.08
	Estimated[b]	0.06	0.25	0.38	0.25	0.06

[a] Calculated from the HPLC area of the absorption monitored at 274 nm. [b] Calculated with the assumption that the reaction rates of the two aldehydes are the same.

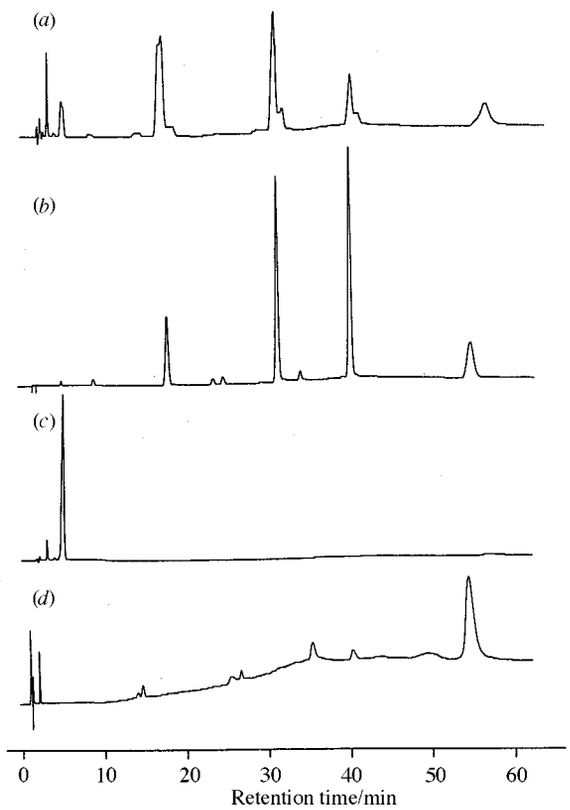


Fig. 1 HPLC charts of CRA-Py(*n*) obtained (*a*) in the first run and (*b*) in the second run and of authentic samples **1** (*c*) and **2** (*d*)

Intramolecular interaction between pyrenyl groups

The absorption maximum at 345 nm due to the pyrene moiety in chloroform is not influenced by the number of the pyrene residues. The molar absorption coefficients of the four CRAs with different numbers of pyrenes at 345 nm are summarized in Table 2. The fact that the absorption maximum and the absorption coefficient per pyrenyl unit are not dependent on the number of pyrene substituent(s) implies that there is essentially no intramolecular interaction in the electronic ground state between pyrenyl groups. On the other hand, the NMR signals due to pyrenyl group(s) in the higher field region are quite different for the four CRA derivatives, as shown in Fig. 3. All the signals due to the pyrenyl group shift to a higher field when the number of pyrenyl groups increases. This result is interpreted in terms of the crowded conformation of the pyrenyl substituents which causes the ring current effect of the aromatic ring system to bring about an upper field shift. The full assignment of the ^{1}H signals of the pyrene ring of CRA-Py(1) and

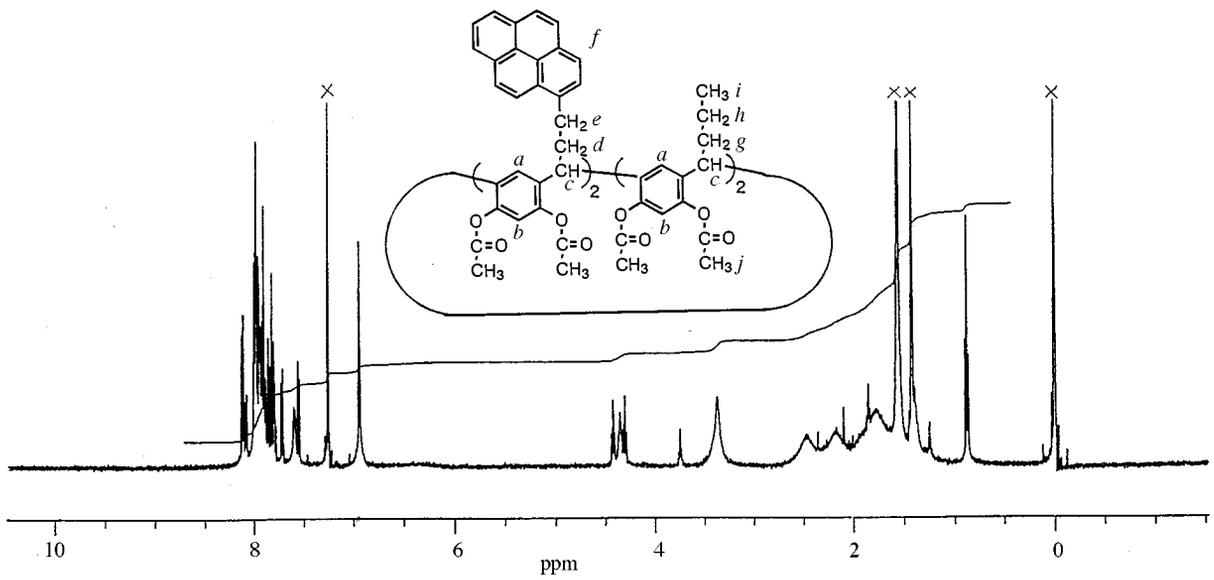


Fig. 2 NMR spectrum of the third fraction separated by HPLC of the second run: H*i*, 0.87; H*j*, 1.5–2.0; H*d*, H*g* and H*h*, 2.0–2.6; H*e*, 3.37; H*c*, 4.2–4.5; H*b*, 6–7 (not observed clearly, see text); H*a*, 6.97; H*f*, 7.5–8.2 ppm; × refers to solvent and TMS signals

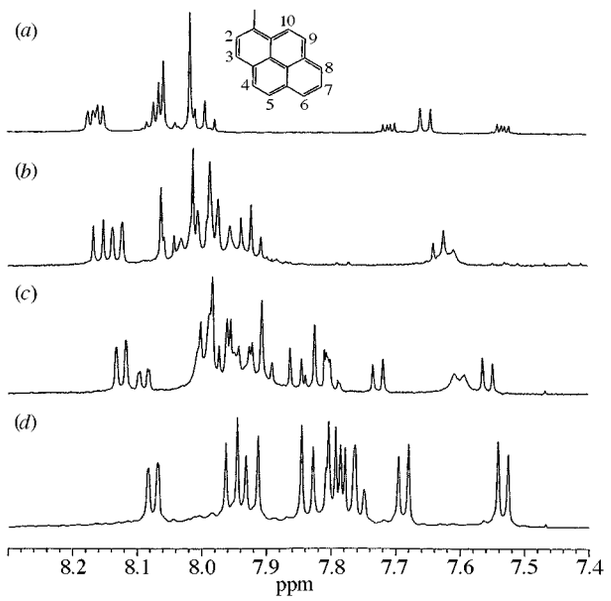


Fig. 3 NMR spectra of separated fractions of the second run in the pyrenyl proton region; CRA-Py(1) (*a*), CRA-Py(2) (*b*), CRA-Py(3) (*c*) and CRA-Py(4) (*d*)

Table 2 Molar absorption coefficients of CRA-Py(*n*) (*n* = 1–4) in chloroform

n	ε_{342}/l mol^{-1} cm^{-1}	ε_{342} per pyrenyl unit/l mol^{-1} cm^{-1}
1	3.3×10^4	3.3×10^4
2	6.8×10^4	3.4×10^4
3	9.8×10^4	3.2×10^4
4	1.23×10^5	3.3×10^4

CRA-Py(4) was performed by comparison with all the ^{1}H NMR signals of α,ω-di(pyren-1-yl)alkanes assigned in reference 11 as summarized in Table 3, however the NMR spectra of CRA-Py(2) and CRA-Py(3) were too complicated for all of the peaks to be assigned. The peaks assigned to H(2) and H(6) of CRA-Py(3) are each separated into two doublets. It is noteworthy that the integration ratio of (upper field doublet) : (down field doublet) is 1 : 2 for each set of two doublets (Fig. 3). This shows that the ring current effect on a pyrenyl group that has pyrenyl groups on each side is different from that of a pyrenyl group which has no neighboring pyrenyl group and that the ratio of the population of neighboring and opposite isomers of CRA-Py(2) was 2 : 1. The extent of the ring current effect was evaluated by the difference ($\Delta\delta$) between the chemical shifts of each proton of CRA-Py(1) and CRA-Py(4). As shown in Table 3, H(3), H(8) and H(9) display larger $\Delta\delta$ values for all pyrene protons because of the stronger ring current effect indicating that these three protons are closer to the center of another pyrenyl group compared with the other protons. This situation was proved by a space filling molecular model. This result forms a striking contrast to the report by Zachariasse and coworkers.[11] They studied the relationship between NMR spectra and fluorescence properties of bichromophoric systems in which two pyrenyl residues are linked through polymethylene spacers with varying chain lengths.[11] They showed that *J* values of the neighboring protons of the two pyrenyl groups do not influence each other at all, and the proton chemical shifts are essentially identical for all of the dipyrenyl compounds. The marked ring current effect in the multi-chromophoric system in the present work is obviously due to the restricted mobility of the cyclic skeleton. In other words, the orientation of functional groups tethered to the lower rim of the cyclic CRA is restricted.

Steady state fluorescence in solution

The intramolecular interaction of the pyrene residues of CRA derivatives was more clearly grasped by measuring fluorescence spectra of CRA-Py(*n*) in solution. As expected, the emission intensity ratio of excimer to monomer (I_e/I_m) increased as the number of pyrenyl groups increased, as presented in Fig. 4. Note here that the difference of I_e/I_m between CRA-Py(2) and CRA-Py(3) is larger than that between CRA-Py(3) and CRA-Py(4). This indicates that the excimer formation is more favored by the additional attachment of a pyrenyl group to CRA-Py(2) than to CRA-Py(3). The effect of attaching an additional pyrene group to both neighboring and opposite isomers of CRA-Py(2) for excimer formation were greater than to CRA-Py(3), whose pyrenyl groups are already packed close enough for excimer formation. The emission maximum of the excimer is not affected by the number of pyrenyl groups. When compared with intermolecular excimer emission observed in a 4.6 mM solution of a monomeric ethyl 3-(pyren-1-yl)propanate (Fig. 5), the excimer of CRA-Py(*n*) formed intramolecularly appears at a shorter wavelength region. This may result again from the restricted mobility of the cyclic molecular framework which leads to the formation of the intramolecular excimer with a relatively higher electronic energy in the lowest singlet

Table 3 Assignment of ^{1}H NMR peaks of CRA-Py(*n*)*

	CRA-Py(1)		CRA-Py(2)		CRA-Py(3)				CRA-Py(4)		Δδ between CRA-Py(1) and CRA-Py(4)
	δ	*J*/Hz	δ	*J*/Hz	δ		*J*/Hz		δ	*J*/Hz	
H(2)	7.651		7.632		7.556	7.600[c]			7.534		0.117
H(3)	8.064		*a*		7.726	*b*			7.688		0.376
$J_{2,3}$		7.69		7.69			8.06	7.33		7.69	
H(4)	8.016		*a*			*b*			7.954		0.062
H(5)	8.016		*a*			*b*			7.837		0.179
$J_{4,5}$		—								8.79	
H(6)	8.166		8.158		8.089	8.124[c]			8.075		0.091
H(7)	7.992		*a*			*b*			7.793		0.199
H(8)	8.158		8.128			*b*			7.756		0.402
$J_{6,7}$, $J_{7,8}$		7.33		7.69			6.56	7.32		7.33	
H(9)	8.047		*a*			*b*			7.795		0.252
H(10)	8.073		*a*			*b*			7.922		0.151
$J_{9,10}$		9.16								9.16	

* δ: ±0.0007 ppm; *J*: ±0.37 Hz. [a] 7.906–8.060. [b] 7.788–8.001. [c] Integral ratio 1 : 2.

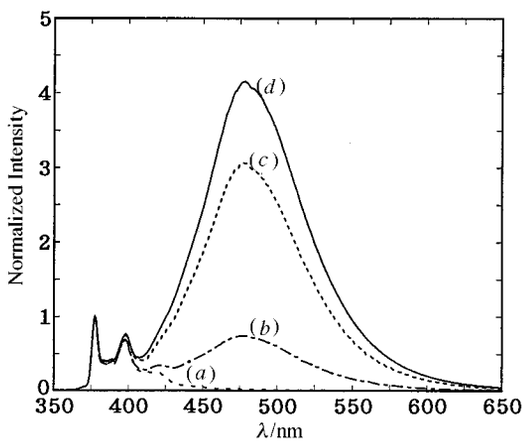


Fig. 4 Fluorescence spectra normalized at 377.5 nm of CRA-Py(*n*) in THF; CRA-Py(1) (*a*), CRA-Py(2) (*b*), CRA-Py(3) (*c*) and CRA-Py(4) (*d*)

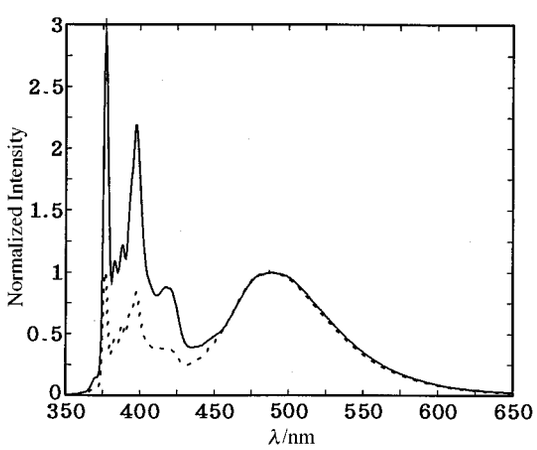


Fig. 5 Fluorescence spectra normalized at λ_{max} of the excimer of ethyl 3-(pyren-1-yl)propanate in THF (——) and in cyclohexane (---); both concentrations are 4.6 mM

state. The intramolecular excimer emission of CRA-Pr(*n*) ($n > 2$) exhibits a slight (2 nm) blue-shift in cyclohexane irrespective of the number of pyrenes when compared with that in THF as shown in Fig. 6 whereas no solvent effect was observed for the intermolecular excimer emission from the monomer at all as shown in Fig. 5. This means that solvation of the intramolecular excimer of CRA-Py(*n*) molecules depends more or less on the nature of the solvent. The structure of the intermolecular excimer of a pyrene derivative is the most stable 'face-to-face' one in any solvent whose fluorescence does not

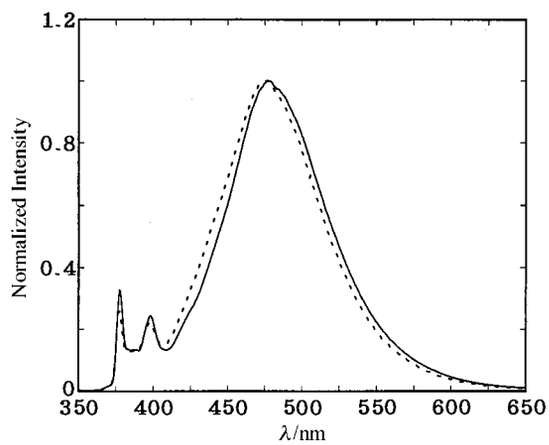


Fig. 6 Fluorescence spectra normalized at λ_{max} of the excimer of CRA-Py(3) in THF (——) and in cyclohexane (---)

depend on the solvent nature. In contrast, the intramolecular pyrene groups linking the CRA cannot form the most stable 'face-to-face' excimer but instead form the solvated excimer and the stronger solvation in polar THF red-shifts the fluorescence more than non-polar cyclohexane.

It has been reported that the λ_{max} of intramolecular emission of α,ω-di(pyren-1-yl)alkanes in methylcyclohexane solution is influenced by the number of methylene groups (*m*) linking two pyrenyl residues;[12] as *m* increases, λ_{max} is blue-shifted from 20×10^3 cm^{-1} (500 nm) ($m = 3$) to 22×10^3 cm^{-1} (455 nm) ($m = 5,6$) and then red-shifted to 20.5×10^3 cm^{-1} (488 nm) ($m = 13$) and not shifted when *m* is larger than 13 as a result of the strained conformation of the intramolecular excimer. λ_{max} of the excimer of CRA-Py(*n*) (473 nm in cyclohexane) is almost the same as those of 1,4-di(pyren-1-yl)butane (471 nm) and 1,9-di(pyren-1-yl)nonane (474 nm) in methylcyclohexane. These facts suggest that the conformational strain in excimers of the CRA-Py(*n*) series is not affected by *n* despite the increase in the molecular crowding with increases in *n* and that the extent of the strain of CRA-Py(*n*) is in a range similar to that of the dipyrenyl compounds with tetra- and nona-methylene spacers.

Fluorescence decay time in solutions

Emission decay times of CRA-Py(*n*) in THF or cyclohexane were measured using a single photon counting system. All the deconvoluted data were fitted well with triple exponentials as expressed in eqns. (1) and (2), where A_1, A_2, $A_3 > 0$ and $-B_1 = B_2 + B_3 > 0$.

$$I_m(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3) \quad (1)$$

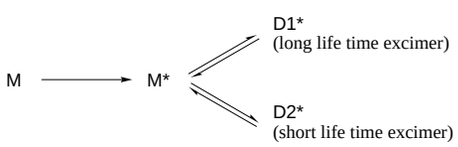
Table 4 Fluorescence decay time constants and preexponential factors

Sample	Solvent	Temp.	Monomer emission			Excimer emission		
			τ_1/ns (A_1	τ_2/ns A_2	τ_3/ns A_3)[a]	τ_1/ns (B_1	τ_2/ns B_2	τ_3/ns B_3)[b]
CRA-Py(1)	Tetrahydrofuran	Room temp.			217			
CRA-Py(2)			4.2	32	121	8.8	58	116
			(0.30	0.26	0.44)	(−0.91	0.44	0.56)
CRA-Py(3)			11	33	112	11	39	106
			(0.65	0.22	0.13)	(−0.96	0.63	0.37)
CRA-Py(4)			5.8	22	101	7.6	38	96
			(0.63	0.26	0.11)	(−0.90	0.56	0.44)
CRA-Py(1)	Cyclohexane	Room temp.			185			
CRA-Py(2)			3.5	27	124	9.9	35	112
			(0.18	0.25	0.57)	(−0.85	0.59	0.41)
CRA-Py(3)			15	40	130	12	45	120
			(0.55	0.35	0.09)	(−0.85	0.81	0.19)
CRA-Py(4)			5.8	28	111	6.7	42	94
			(0.62	0.29	0.09)	(−0.77	0.71	0.29)
1,3-Di(pyren-1-yl)propane[c]	Methylcyclohexane	40 °C	5.1	54.6	149.9	5.1	56.5	145.2
			(0.96	0.036	0.0072)	(−0.98	0.67	0.33)
1,3-Di(pyren-2-yl)propane[c]			5.2	—	139.6	5.1	—	149.7
			(0.98	—	0.015)	(−0.99	—	1.00)
1,3-Di(pyren-1-yl)propane[d]	Toluene	20 °C	not described			8.1	57.9	129.8
						(−1.00	0.71	0.29)
1,13-Di(pyren-1-yl)tridecane[d]			not described			15.7	52.1	—
						(−1.00	1.00	—)

[a] A_ns were calculated to make $A_1 + A_2 + A_3 = 1$. [b] B_ns were calculated to make $B_2 + B_3 = 1$. [c,d] Data from ref. 14, 10, respectively.

$$I_e(t) = B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) + B_3 \exp(-t/\tau_3) \quad (2)$$

The decay data are summarized in Table 4. τ_1, τ_2 and τ_3 are very close to the decay time constants of 1,3-di(pyren-1-yl)propane reported previously.[13–15] According to the literature,[13,14] the above-mentioned equations were fitted within a kinetic scheme consisting of three excited species; one excited monomer and two excimers (Scheme 2), whereas the decay processes



Scheme 2 The kinetic scheme for excimer formation of 1,3-dipyren-1-yl)propane proposed by Zachariasse *et al.*[15]

of 1,13-di(pyren-1-yl)tridecane and 1,3-di(pyren-2-yl)propane were analyzed as a double exponential.[11,13,14] As shown in Table 4 which also contains the data for the dipyrenyl compounds, one type of excimer specifically made from 1,3-di(pyren-2-yl)-propane has a long time decay constant while another type of excimer originating from 1,13-di(pyren-1-yl)tridecane has a short time decay constant. Both types of excimers are produced from 1,3-di(pyren-1-yl)propane and CRA-Py(*n*). The pre-exponential factors, B_2 and B_3, indicate the ratio of the two types. Though the ratio of these two excimers are different in CRA-Py(*n*), the fluorescence wavelength and broadness are almost same, which means the energy levels are almost the same. Both excimers are fully overlapped excimers since the energy level of a partially overlapped excimer is different and the fluorescence wavelength shifts. The two excimers must have different structures. The structure of the former type of excimer, whose life time is almost same as the excimer of 1,3-di(pyren-2-yl)propane, must be face-to-face symmetric because 1,3-di(pyren-2-yl)propane has a symmetric structure itself. The other type of excimer is seen in 1,13-di(pyren-1-yl)tridecane whose decay time constant is shorter and has a different structure, asymmetric rather than symmetric one. It is reasonable that the ratio of the symmetric type excimer to the asymmetric one is larger in THF than that in cyclohexane, since cyclohexane is a poor solvent for CRA-Py(*n*). The ratio decreases markedly as *n* changes from 2 to 3, but increases as *n* changes from 3 to 4. When $n = 2$, the pyrenyl groups are not so crowded, and the symmetric type of excimer, whose decay time constant is long, is made more easily than for CRA-Py(3) or CRA-Py(4) whose pyrenyl groups are crowded. The fact that a symmetric type excimer is made more easily in CRA-Py(4) than in CRA-Py(3) can be explained by two hypotheses (i) that closer pyrenyl groups form a symmetric type excimer more easily than further groups do and (ii) that excimers are made between closer pyrenyl groups more easily in CRA-Py(4) whose pyrenyl groups are too crowded to make excimers between the further pyrenyl groups compared with CRA-Py(3).

Conclusion

A mixture of five species of calix[4]resorcinarene possessing varying numbers of pyrenylethyl group was synthesized by the reaction of resorcinol with a mixture of pyrenylpropanal and butanal, followed by acetylation to enable HPLC separation. The analysis of the production distribution indicated that the reaction rates of the two aldehydes are almost the same. The intramolecular interactions between pyrenyl groups of the crown conformer of CRAs were too weak to influence their electronic absorption spectra, but strong enough to shift NMR chemical shifts of proton peaks of the pyrenyl groups markedly. The CRAs possessing pyrenylethyl groups form intramolecular excimers, and the strain of the excimers is almost the same as that of α,ω-dipyrenyl compounds with tetra- and nona-methylene spacers. The decay time data showed that CRAs substituted with pyrenyl groups form two types of intramolecular excimer just as in the case of 1,3-di(pyren-1-yl)propane.

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