Synthesis and Photophysical Properties of Fluorescent Anthracenophanes Incorporating Two Polyoxadioxoalkane Chains

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Anthraceno macrolides I_n (n = 1–4) display dual fluorescence ('monomer'/excimer) sensitive to the number of links of the chain n and temperature. The excimer fluorescence quantum yield is particularly high (0.24–0.39 in toluene) in comparison with those of related anthracenophanes or bichromophores. A thermodynamic study of the fluorescence emission has enabled us to evaluate the activation energy of excimer formation (25.1–27.2 kJ mol^{-1} for n = 1, 3, 4, and 15.0 kJ mol^{-1} for n = 2), its enthalpy of stabilization (−14.2 to −21.7 kJ mol^{-1}), and the repulsive potential in the ground state between two anthracenes after radiative deactivation of the intramolecular excited complex (38.5–53.1 kJ mol^{-1}). These values are discussed as a function of n and compared with literature data.

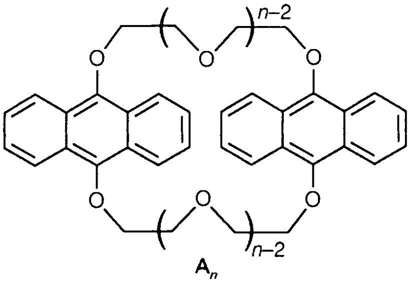
The spectroscopic properties of I_n were found to be weakly cation dependent except for I_4 and Sr^{2+} or Ba^{2+} where moderate effects were detected in UV absorption or fluorescence emission spectra. The failure to encapsulate the alkali and alkaline-earth cations is ascribable to the rigidity of the system which presumably hinders the formation of a stable co-ordinating sphere around the cation.

The fluorescence emission of the single crystals is described and correlated with the molecular packing mode. The excimer-type emitting crystals (n = 2 and 4) contain pairs or stacks of aromatic rings whereas 'monomer'-type emitting crystals do not show any important overlap between anthracenes.

Polycyclic aromatic hydrocarbons exhibit distinct advantages as luminophores. Their electronic absorption spectra are localized in a convenient wavelength range (visible or near UV region); and their highly efficient and most often dual ('monomer'/excimer) fluorescence emission, is indicative of the mutual orientation of the aromatic moieties, which can be modulated by structural factors.[1]

Some anthraceno crown ethers incorporating two anthracenes[2] have recently been designed in order to control light emission and photochemistry of the chromophores by selective cation complexation. Indeed, addition of $NaClO_4$ to fluid methanolic solutions of compound A_5 (n = 5) results in a marked enhancement and a net bathochromic shift of the excimer fluorescence emission at the expense of the locally excited 'monomer' state fluorescence (see Figure 1). A double sodium-cation-complexing loop forcing the two anthracenes to adopt a quasi-sandwich conformation[2,3] was shown to occur in the ground state preforming the red-shifted fluorescent excimer. This specific arrangement was, moreover, proved to generate the 9,9′-10,10′ photoproduct in contrast with the non-complexed material which gives the unsymmetrical 9,1′-10,4′ cyclomer. However, the fluorescence of compounds A_n, bearing polyoxa-alkane links, was found to show selectivity only towards alkali-metal cations. In order to enlarge the scope of anthraceno crown ethers to the optical detection of divalent cations of biological importance, we have designed new bis-anthracenes (I_n, n = 1–4) incorporating four ester groups within the polyoxa-alkane chains, to mimic natural or synthetic macrolides in which the carbonyl functions have been recognized[4] to play an important role in complexing divalent cations; compounds I_n could thus be considered as potential candidates for probing divalent cations by fluorescence techniques.

We report here the synthesis of the 'anthraceno-macrolides' I_n and a photophysical study of them in the absence or in the presence of several metal cations.



A_n

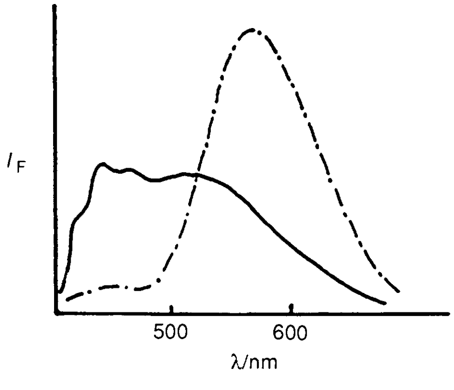
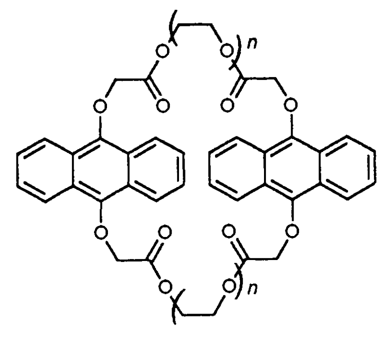


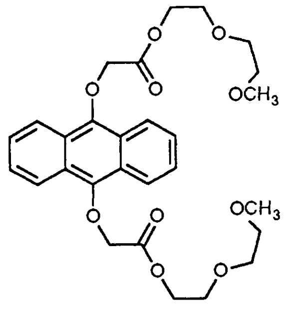
Figure 1. Emission fluorescence spectra of compound A_5 (n = 5) (conc. *ca.* 10^{-5} mol dm^{-3}, methanol): (——) without salt, (–•–•–) in the presence of $NaClO_4$ in excess (10^{-2} mol dm^{-3}).

Results and Discussion

Synthesis and Characterization of the Anthraceno Macrolides I_n.—Compounds I_n were prepared from anthracene-9,10-diyl diacetate[5] as outlined in Scheme 1.



I_n $n = 1 \rightarrow 4$



R

Table 1. Chemical yields and m.p.s. of the anthracenophanes I_n and the reference compound R; all the compounds form yellow crystals.

Compound	Yield (%)	M.p./°C
I_1	29	235–237
I_2	23	238–239
I_3	27	172–174
I_4	25	132–133
R	65	65–66

$$CH_3CO_2AOCOCH_3 \xrightarrow{i,ii} ClCOCH_2OAOCH_2COCl \xrightarrow{iii} HO(CH_2CH_2O)_nCOCH_2OAOCH_2(OCH_2CH_2)_nOH \xrightarrow{iv} I_n\ (n = 1\text{–}4)$$

Scheme 1. *Reagents:* i, $BrCH_2CO_2CH_3$–KOH–EtOH; ii, oxalyl chloride–benzene; iii, $HO(CH_2CH_2O)_nH$–pyridine–benzene; iv, $ClCOCH_2OAOCH_2COCl$–pyridine–benzene, high dilution technique. A = anthracene-9,10-diyl.

The anthraceno macrolides were purified by column chromatography (silica gel) and recrystallized. The purity of the compounds was checked by reversed-phase HPLC and were stored in the dark under an inert atmosphere (nitrogen). The yields (not optimized) of the last step of each synthesis are listed in Table 1 together with the melting point of the product. The molecular structures were established essentially by ^1H NMR, UV, and mass spectra, and the X-ray structure of the monocrystals[6] and was supported by elemental analyses (see the Experimental section).

The monochromophoric reference compound R was prepared according to the established procedure using anthracene-9,10-diyldioxydi(acetyl chloride) and diethylene glycol monomethyl ether (*i.e.* step iii of Scheme 1.)

Spectroscopic and Photophysical Study.—Electronic absorption spectra. U.V. absorption spectra are sensitive to molecular interactions in the ground state and the technique has been applied with success to bichromophoric systems.[7] The absorption spectra of compounds I_n in acetonitrile or toluene are similar in shape to that of the monoanthracene (reference) compound R. However, some modifications are to be noted in the relative intensities of the vibronic bands in both electronic transitions (for acetonitrile), *i.e.* $^1L_a \leftarrow A_1$ and $^1B_b \leftarrow A_1$ (Figure 2).

The $^1L_a \leftarrow A_1$ transition presents a marked hypsochromic effect compared with the reference compound R and the $^1B_b \leftarrow A_1$ transition is still more perturbed, the intensity of the less energetic component (*ca.* 257–259 nm) being decreased compared with the other (*ca.* 249–251 nm). Taking into account our recent results on cation-complexing anthracenophanes[2] these spectral changes can be attributed to intramolecular interactions between the rings of which the long axes experience some degree of parallelism. No significant solvent effect is detected with compounds I_n.

Addition of salts (perchlorates) (namely Li^+, Na^+, K^+, Rb^+, Cs^+ and Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) does not appreciably perturb the UV spectra of the anthraceno macrolides I_n except (but very moderately) Ba^{2+} and (to some extent) Sr^{2+} for I_4 [Figure 2 (*e*), (*f*)].

With Ba^{2+}, hypsochromism is noticeable for the two electronic transitions: *ca.* 125 and 370 cm^{-1} for $^1L_a \leftarrow A_1$ and $^1B_b \leftarrow A_1$ bands, respectively. Moreover, the relative intensities of the vibronic bands belonging to the high-energy transition are modified: the intensity of the less energetic component is decreased compared with the other and consequently the spectrum looks like that displayed by I_1 [Figure 2(*a*)] bearing the shortest chains. It can be assumed, as observed with Na^+ and A_5, that Ba^{2+} (ionic radius[8] r_i 1.43 Å) interacts with the links and enables the two aromatic moieties to experience a

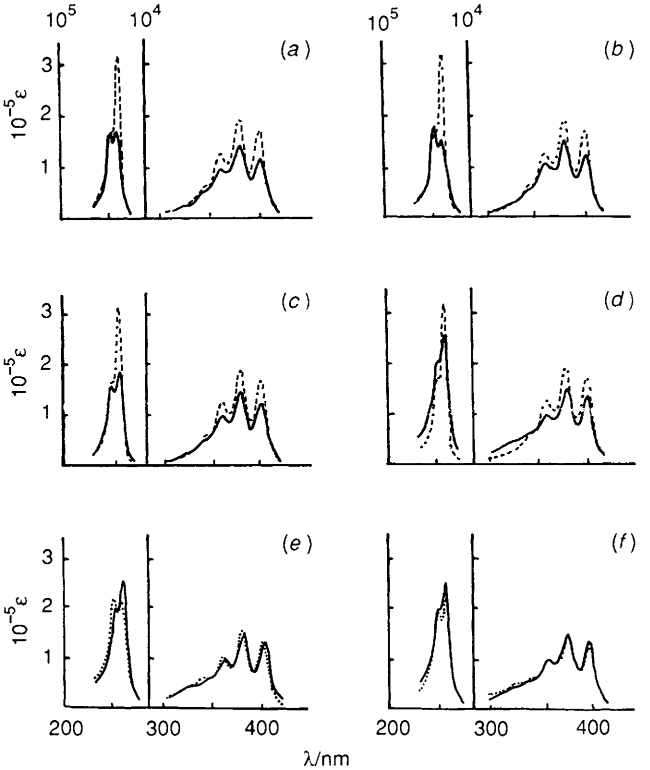


Figure 2. UV absorption spectra in acetonitrile at room temperature of compounds I_n (——) (conc. *ca.* 10^{-4} mol dm^{-3}) compared with that of reference compound R (– – – –) ($\varepsilon \times 2$).(*a*) I_1; (*b*) I_2; (*c*) I_3; (*d*) I_4; (*e*) spectrum of I_4 (——) without salt, and in the presence (••••••) of a large excess (*ca.* 1000 fold) of $Ba(ClO_4)_2$; (*f*) spectrum as for (*e*) but in the presence of $Sr(ClO_4)_2$

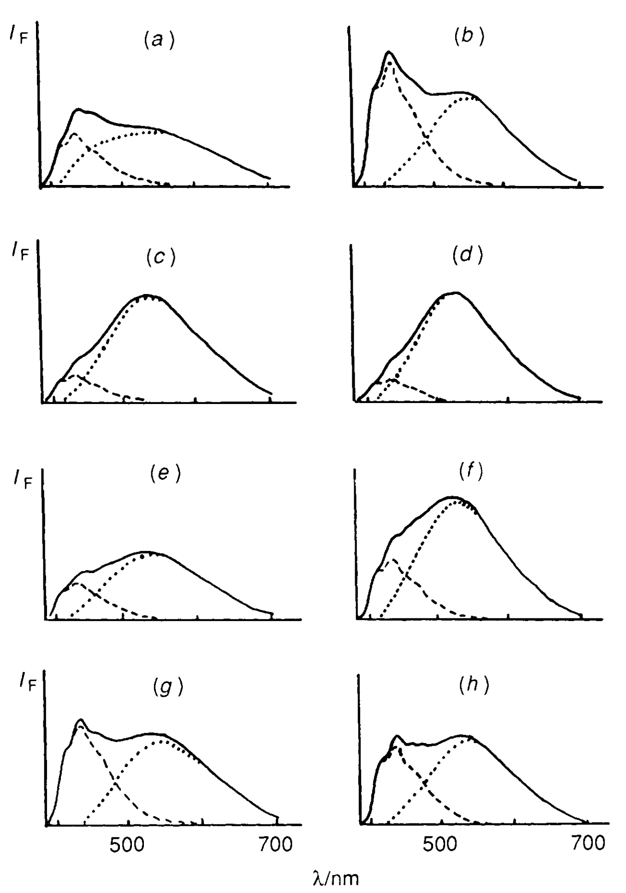


Figure 3. Corrected emission fluorescence spectra (normalized at the first vibronic band) in acetonitrile (Å) and toluene (T) of compounds I_n (——) and R (– – – –) at 20 °C, conc. $\leqslant 10^{-5}$ mol dm^{-3}, λ_{exc} = 380 nm. The excimer spectra (• • • • • •) were deduced by difference spectra of I_n and R. (*a*) I_1 (A); (*b*) I_1 (T); (*c*) I_2 (A); (*d*) I_2 (T); (*e*) I_3 (A); (*f*) I_3 (T); (*g*) I_4 (A); (*h*) I_4 (T).

Table 2. Fluorescence emission quantum yields (φ_F) of compounds R and I_n at 20 °C in toluene and acetonitrile ($c \geqslant 10^{-5}$ mol dm^{-3}).

	φ_F					
Solvent	R	I_1	I_2	I_3	I_4	
Toluene	0.75	0.20	0.04	0.09	0.11	monomer
	—	0.25	0.39	0.35	0.24	excimer
Acetonitrile	0.64	0.04	0.01	0.03	0.03_5	monomer
	—	0.09	0.09	0.12	0.08	excimer

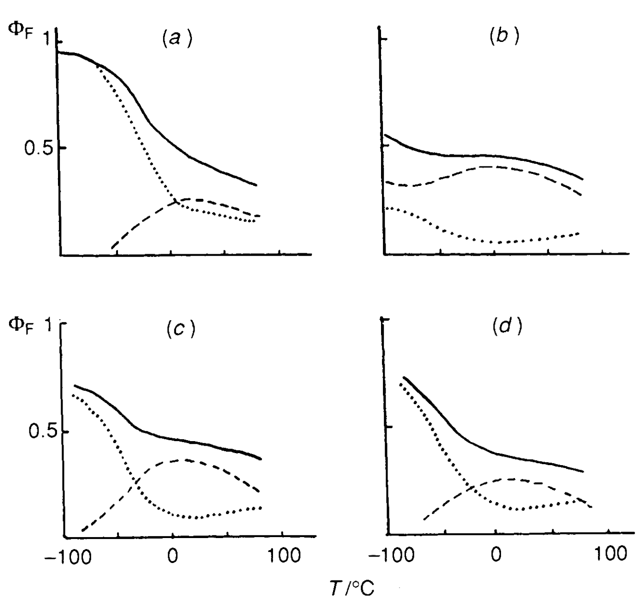


Figure 4. Temperature dependence of fluorescence quantum yields φ_F of compounds I_n in toluene: (——) total fluorescence: (• • • • • •) monomer φ_{FM}; (– – – –) excimer φ_{FE} parts. (*a*) I_1; (*b*) I_2; (*c*) I_3; (*d*) I_4.

better parallel mutual orientation. Smaller effects are detected with Sr^{2+} (r_i 1.27 Å) probably because of a weaker affinity between the cation and oxygen in relation to the respective size and polarizability (Sr^{2+}, 1.28 Å^3; Ba^{2+}, 2.50 Å^3)[8] of the ions, their hydration number (8), softness (σ *ca.* 0.17–0.18) and surface charge density (*ca.* 0.1 Å^{-2}) being similar.[8]

Fluorescence Emission and its Temperature Dependence.—Room temperature. The anthraceno macrolides I_n exhibit dual fluorescence: a structured part attributed to locally excited (monomer) species and a red-shifted, broad, structureless band ascribable[1,9] to an excimer. Indeed, the excitation spectra scanned on the monomer and excimer wavelengths were found to be similar, pointing to the common origin of the two emissions. The spectrum and the maximum of the excimer emission can be visualized from the difference between spectra displayed by I_n and R (Figure 3).

The contribution of excimer emission is marked for compounds I_n (Table 2) compared with A_n which instead exhibit[2,10] a strong 'monomer' emission. This disparity is assigned to the conformational characteristics of the chains linking the anthracenes; the four ester units could favour, in fluid apolar solutions, specific geometries similar to those experienced in the crystalline state.[6]

The fluorescence emission of I_n appears to be sensitive to the solvent; in acetonitrile, net quenching is observed although the ratio between the excimer and monomer emission intensity is weakly affected (except with I_1). Knowing the propensity of acetonitrile to form inclusion complexes with crown ethers,[11] a specific interaction, solvent–I_n, inducing a weakly fluorescent conformer could be assumed; however the polarity of the medium should not be neglected as inducing non-radiative deactivation through radical-ion pair formation[15] (*e.g.* between anthracenes and carbonyl groups).

Addition of cations to the solution (acetonitrile) does not modify the fluorescence properties of anthraceno macrolides I_n even with Ba^{2+} or Sr^{2+} which were found to influence the UV spectra. It indicates that the geometry of the intramolecular excimer is not sensitive to the presence of the cations under study. Attempts to grow monocrystals of barium or strontium complexes were unsuccessful.

Temperature dependence. The fluorescence emission spectra of I_n were recorded at various temperatures. The temperature dependence of the fluorescence quantum yields of 'monomer' and excimer parts is represented in Figure 4.

When the solution was cooled an increase of the total fluorescence emission was observed with a maximum intensity for excimer fluorescence slightly above 0 °C. Exciplex fluorescence spectra exhibited a temperature-dependent maximum as shown in Figure 5. When the temperature is raised from −50 to 80 °C, this maximum shifts to high energies probably in relation to the occurrence of a partially overlapping excimer.[12] Note that the excimer contribution is higher for compound I_2 Excitation spectra, not sensitive to temperature and wavelength, resemble the absorption spectra; this confirms the

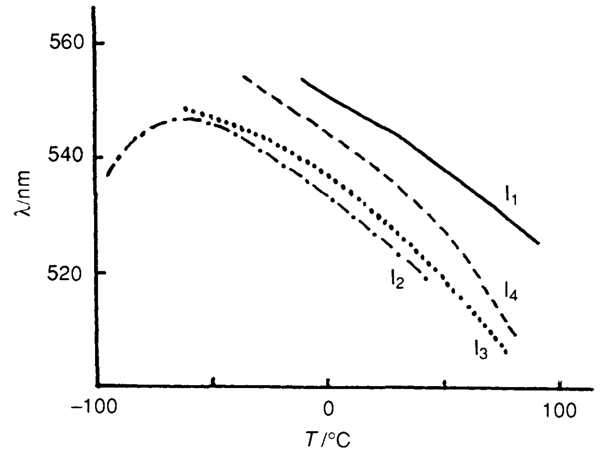


Figure 5. Wavelength-temperature dependence of excimer maximum emission for compounds I_n in toluene.

Table 3. Apparent activation energy (ΔE) and enthalpy of stabilization (ΔH) of intramolecular excimer for compounds I_n in toluene. E_r represents the repulsive potential in the ground state between two anthracenes after radiative deactivation of the excimers.

Compound	ΔE/kJ mol^{-1}	ΔH/kJ mol^{-1}	E_r/kJ mol^{-1}
I_1	27.2	−14.2	53.1
I_2	15.0	−18.0	41.0
I_3	27.6	−16.3	38.5
I_4	25.5	−21.7	42.2

common and non-temperature dependent origin of the emitting species.

Determination of the Thermodynamic Parameters.—Stevens showed[13] that, provided there is an interconversion between 'monomer' and excimer fluorescence, it is possibe to evaluate the activation energy (ΔE) for excimer formation and its enthalpy of stabilization (ΔH) from the tangents at high- and low-temperature regions at the curve $\ln(\varphi_E/\varphi_M)$ *versus* $1/T$ (Figure 6). However, these thermodynamic data (which are average values including different sets of conformers) have to be taken with caution owing to the approximations made (the radiative rate constants k_{FM} and k_{FE} for 'monomer' and excimer, respectively, being considered constant). These values and E_r, the repulsive potential in the ground state between two anthracenes after the radiative deactivation of the excimer, are listed in Table 3.

The activation energies ΔE are found to be close to 25–27 kJ mol^{-1} except for I_2 for which a lower value emerges (15.0 kJ mol^{-1}). This lower energy could explain why excimer is formed at low temperatures ($\varphi_E = 0.31$ at −90 °C in toluene). These activation energies ΔE compare well with the few data available for bisanthracenes holding a four- or a three-membered link (17–25 kJ mol^{-1}).[14]

The enthalpy of stabilization of the excimer was found to be higher for I_4 and lower for I_1 probably in connection with the dynamics of the links and the concomitant strains, I_4 seems to be less strained than I_1. These values −14.2 to −21.7 kJ mol^{-1}) are close to those observed for 9,10-dimethylanthracene (DMA) (−16.3 kJ mol^{-1} in chloroform), 9-methylanthracene (MA) (−19.2 kJ mol^{-1} in benzene)[15] and bis[(10-phenyl)-9-anthrylmethoxy]methane (DPAM) (−22.2 kJ mol^{-1} in methylcyclohexane).[16]

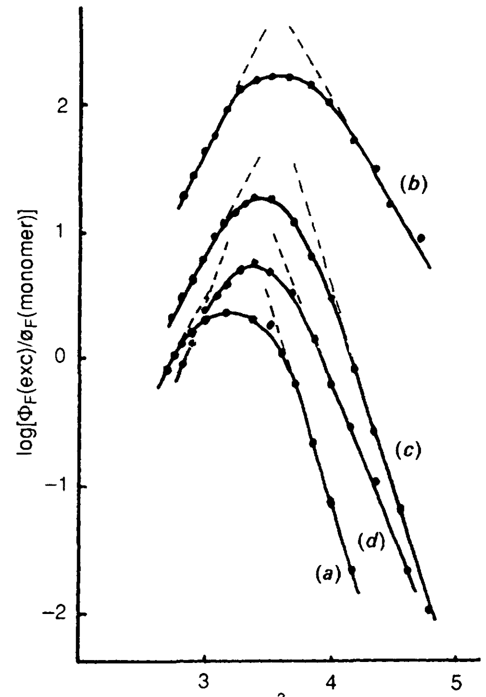
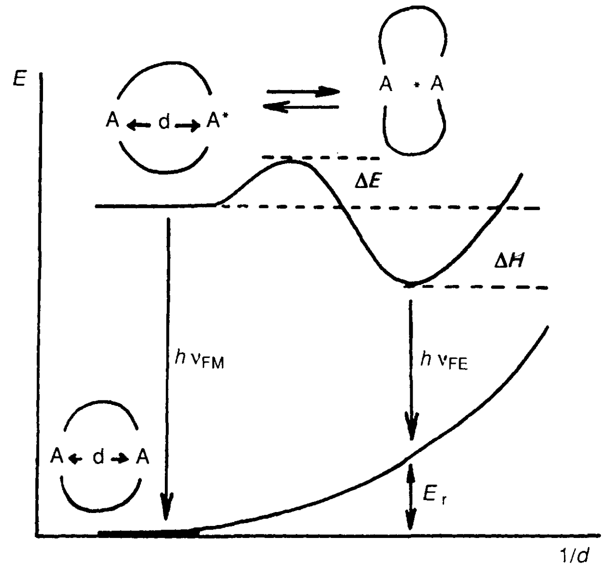


Figure 6. Plots of the logarithm of the ratio of fluorescence quantum yields in excimer and monomer parts *versus* $1/T$ in toluene (Stevens–Ban plots). (*a*) I_1; (*b*) I_3; (*c*) I_3; (*d*) I_4.



Scheme 2. Schematic potential-energy diagram of a pair of linked chromophores in the ground state (A A) and in the first singlet excited state (A A*), respectively, as a function of the intramolecular ring separation *d*. A*A denotes the intramolecular excimer. ΔE: activation energy for the excimer formation. ΔH: enthalpy of stabilization of the excimer. E_r: intramolecular repulsive potential in the ground state between two anthracenes after radiative deactivation of the excimer. $h\nu_{FM}$ and $h\nu_{FE}$ correspond to the fluorescence emission of the 'monomer' and excimer components, respectively.

The repulsive potential in the ground state E_r, between two anthracenes at the excimer inter-ring distance varies from 38.5 to 53.1 kJ mol^{-1}. The energy was found to be maximal for the shortest chain where the steric hindrance is expected to be more important. For DMA (chloroform) and MA (benzene) these energies[15] are 56.8 and 63.1 kJ mol^{-1}, respectively, whilst a

Table 4. Crystallographic constants of compounds I_n (n = 1, 3, and 4).

Compound	Space group	a	b	c	α	β	γ	Z
		Å			deg			
I_1 (flakes)	*Pbca*	10.632	18.042	16.989				4
I_3 (platelets)	$P2_1/c$	10.282	19.353	12.670		122.48		4
I_4 (needles)	$P\bar{1}$	8.408	8.689	16.178	88.26	85.70	81.23	2

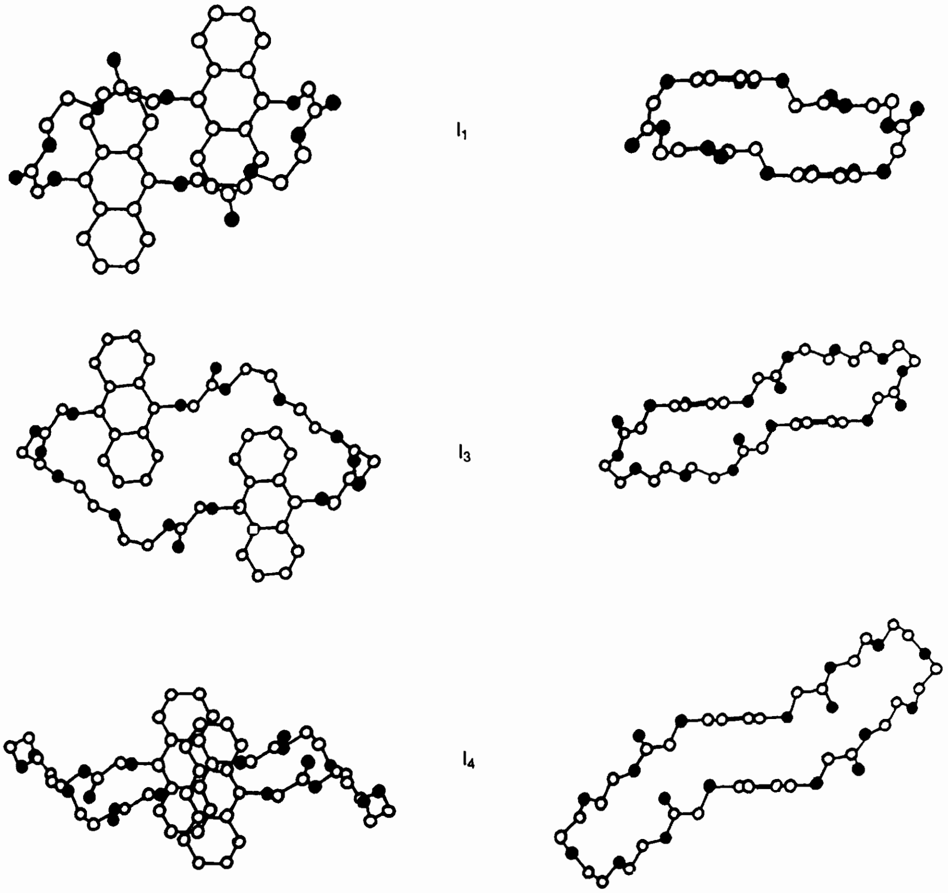


Figure 7. Projection of compounds I_n in the crystal perpendicular to aromatic planes (left) and along the main axis of the anthracene rings (right).

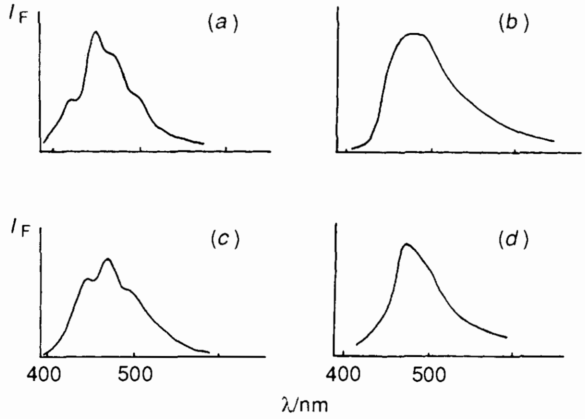


Figure 8. Emission fluorescence spectra of compounds I_n in the crystalline state, at 20 °C. λ_{exc} = 370 nm. (a) I_1; (b) I_2; (c) I_3; (d) I_4.

smaller repulsion, close to our compounds, has been published for DPAM in methylcyclohexane (35.9 kJ mol^{-1}).[16]

In the crystalline state. Monocrystals of X-ray analysis quality were grown from hot dimethyl sulphoxide solutions (n = 1,3) or from a 1:1 mixture of ligroin and acetone (n = 4); only polycrystalline material was obtained with I_2 despite a number of different attempts. Although a detailed description of the molecular and crystal structures is given in a recent paper,[6b] some salient features are depicted hereafter (see Table 4) together with the fluorescence emission properties of the solids.

In the crystal, compounds I_1, I_3, and I_4 are centrosymmetric, displaying intramolecular alignments of the aromatic planes (Figure 8). In this series, only I_4 exhibits significant intra- and inter-molecular overlap between the anthracenes, the intramolecular pairs of rings (3.48 Å apart) are stacked along the a axis with inter-ring separations of 3.50 Å.

The emission fluorescence spectra recorded on the samples used for X-ray structure determination (except for I_2) are represented in Figure 8. These spectra, which are different from those obtained for the fluid solution, where efficient molecular dynamics occur, can be classified into two categories: the monomer-like (structured band) and excimer-like (red-shifted non-structured band) emissions. Compounds I_1 and I_3 which belong to the first group adopt a packing mode where strong inter-ring π interactions are excluded. As a consequence, monomeric anthracene units are the sites of fluorescence emission as already observed and rationalized[17a] for A-type (or γ-type) anthracenic crystals.[17] I_2 and I_4 fall into the second category. The aromatic planes of I_4 display a β-type stacking (inter-ring distance <4 Å) which should induce an excimer-type fluorescence emission; the exciton traps being not regarded as monomeric units.[17] Although the packing mode of I_2 is not yet known, there is little doubt that the fluorescence behaviour of this material should originate in a β-type arrangement. Further comments on the role assigned to the link in the crystallization mode which controls the fluorescent properties of the materials is given in ref. 6(*b*).

Conclusions

Incorporation of carbonyl groups within the bridges of polyoxa[*x.x*](9,10)anthracenophanes confers a strong intramolecular excimer fluorescence to the materials which, however, present poor cation-binding abilities. Indeed, only moderate effects are detected with I_4 (displaying the largest cavity) and Ba^{2+} or Sr^{2+}. In this case, it is assumed that cations are complexed by the carbonyl groups and oxygens inside the cavities formed by the folding of the chains linking the anthracenes. The rigidity of the systems is presumably the cause of the weak complexing ability and of the very poor selectivity towards metal cations, in contrast with some natural ionophores.[18]

Evaluation of the thermodynamic parameters describing the fluorescence properties of I_n allows the determination of the activation energy for excimer formation and of the enthalpy of stabilization which compare well with those of other bisanthracenes; the similarity of the activation parameters suggests the weak influence of the chain on the energy barriers to the formation of intramolecular excimers. As already explained (*vide supra*), the thermodynamic data presented in this paper must be taken with caution; nevertheless they provide a good order of magnitude and are the first values for anthracenophanes.

The crystalline materials are highly fluorescent. The excimer-like emitting solids (I_2 and I_4) contain short contact ($\leqslant 4$ Å) pairs or stacks of parallel aromatic nuclei in contrast with monomer-like emitting samples which exhibit only weak interactions between anthracenes in the crystal.

Experimental

Physical Methods.—M.p.s were determined with a Kofler block and are uncorrected. A microbalance (Mettler ME 30, sensitivity 1 μg) was used to weight the samples for spectroscopic measurements. IR and UV spectra were recorded on a Perkin-Elmer model 412 instrument and on a Cary 219 spectrophotometer, respectively. ^{1}H NMR spectra were obtained using Perkin-Elmer R-12, R-24B (60 MHz) and Bruker AC 200 (200 MHz) instruments with Me$_4$Si as the standard. Mass spectra were recorded using a VG Micromass 70/70 instrument. The purity of all new compounds was checked by TLC (silica gel) and reversed-phase HPLC [S$_5$ octadecylsilane, SiC$_{18}$ Spherisorb (eluant methanol)]

The fluorescence spectra were recorded as described elsewhere[7a] with a Hitachi-Perkin-Elmer MPF 44 fluorimeter. The fluorescence quantum yields were determined by comparison with quinine sulphate in 1 mol dm^{-3} sulphuric acid.[19]

Solvents.—Acetonitrile (Solvents-Documentation Synthèses, Marseille; *pur*) was refluxed over K$_2$CO$_3$ and then distilled; toluene (Prolabo Paris, RP Normapur) was distilled over Na after reflux. No fluorescent impurities were detected under our experimental conditions.

Syntheses.—*Anthracene-*9,10-*diyldioxy*(*diacetic acid*). To a stirred and degassed solution of anthracene-9,-10-diyl diacetate[5] (34 g, 0.115 mol) in refluxing ethanol (1.2 dm^3), was added dropwise ethyl bromoacetate (40 g, 0.295 mol) then KOH (15 g, 0.28 mol) in ethanol (100 cm^3). The solution was then refluxed for 12 h after the addition of a further amount of KOH (15 g, 0.28 mol). The diacid, (33.7 g, 90%) m.p. 280 °C, precipitated when the cooled mixture was treated with a large volume (2 dm^3) of diluted hydrochloric acid. δ(CDCl$_3$) 4.63 (4 H, s), 7.17–8.50 (8 H, m), and 12.73 (2 H, s); ν_{max}(KBr) 3 250–2 800, 2 680, 2 570, 1 825, 1 730, 1 720, 1 680, 1 620, 1 590, 1 580, 1 435, 1 380, 1 335, 1 320, 1 305, 1 285, 1 255, 1 240, 1 210, 1 170, 1 095, 1 030, 1 010, 965, 930, 890, 875, 805, 770, 735. 695, 655, 620, and 605 cm^{-1}; *m/z* 326 ($M^{+\cdot}$). Satisfactory elemental analysis was obtained with the corresponding diethyl ester (m.p. 92 °C) readily obtained by refluxing the diacid in ethanol in the presence of a few drops of sulphuric acid, *m/z* 382 ($M^{+\cdot}$) (Found: C, 69.2; H, 5.8; O, 24.85. C$_{22}$H$_{22}$O$_6$ requires C, 69.11; H, 5.76; O, 25.14%).

9,10-*Anthracene-*9,10-*diyl-dioxydi*(*acetyl chloride*). To a stirred solution of anthracene-9,10-diyldioxy(diacetic acid) (5 g, 0.015 mol) in benzene (100 cm^3) was added oxalyl chloride (19 g, 0.15 mol). The mixture was gently refluxed and filtered. After removal of the solvent under reduced pressure the diacid chloride was obtained quantitatively as a yellow solid (m.p. 160 °C) and used without further purification. δ[(CD$_3$)$_2$SO] 4.63 (4 H, s) and 7.3–8.4 (8 H, m); ν_{max}(KBr) 2 930, 2 900, 1 800, 1 665, 1 620, 1 585, 1 435, 1 405, 1 380, 1 345, 1 330, 1 310, 1 300, 1 285, 1 205, 1 170, 1 090, 1 020, 985, 940, 810, 765, 730, 695, and 565 cm^{-1}.

9,10-*Bis*(1-*methoxy-*7-*oxo-*3,6-*dioxaoctyloxy*)*anthracene* (R). To a stirred solution of diethylene glycol monomethyl ether (8.8 g, 7.36 × 10^{-2} mol) in degassed and boiling benzene (200 cm^{-3}), was added dropwise anthracene-9,10-diyldioxy-(diacetyl chloride) (5.35 g, 1.47 × 10^{-2} mol) in degassed benzene solution (75 cm^3). When the addition was complete, the mixture was stirred for 12 h under reflux. The solution was then washed with water and dried over magnesium sulphate. A brown oil was obtained after removal of the solvent. Chromatography on silica column (ligroin–acetone 5:5) gave R as a yellow solid (5.05 g, 65%), m.p. 65 °C, δ(DCCl$_3$) 3.17 (6 H, s), 3.3–3.8 (12 H, m), 4.16–4.43 (4 H, m), 4.46 (4 H, s), and 7.20–8.33 (8 H, m); ν_{max}(KBr) 3 050, 2 910, 2 870, 2 810, 1 745, 1 660, 1 610, 1 590, 1 440, 1 430, 1 390, 1 350, 1 270, 1 240, 1 200, 1 165, 1 105, 1 090, 1 040, 995, 920, 910, 860, 845, 770, 730, 695, 665, 640, and 605 cm^{-1}; λ_{max}(CH$_3$CN) 400.1 (log ε 3.92), 378.5 (3.98), 359.6 (3.79), 343 (3.47), 258.2 (5.19), and 251.2 nm (4.92); *m/z* 530 ($M^{+\cdot}$) (Found: C, 63.3; H, 6.45; O, 30.25. C$_{28}$H$_{34}$O$_{10}$ requires C, 63.40; H, 6.41; O, 30.19%).

9,10-*Bis*(1-*hydroxy-*4-*oxo-*3-*oxapentyloxy*)*anthracene*. To a stirred solution of ethylene glycol (8.5 g, 13.7 × 10^{-2} mol) in degassed, boiling benzene (200 cm^3)–pyridine (2.2 g, 2.75 × 10^{-2} mol) solution was added dropwise 9,10-anthracene-9,10-diyldioxydi(acetyl chloride) (5 g, 1.37 × 10^{-2} mol in degassed benzene solution (70 cm^3). When the addition was complete, the mixture was stirred for 24 h under reflux. The usual work-up led to a brown solid which gave, after chromatography on a silica column (ligroin–acetone 3:7), 9,10-bis(1-hydroxy-3-oxo-4-oxapentyloxy)anthracene as a yellow waxy product (4.0 g, 70%), δ[(CD$_3$)$_2$SO] 3.23–4.10 (9 H, m), 4.48 (4 H, s), and 7.04–8.20 (8 H, m); ν_{max}(KBr) 3 500, 3 060, 2 990, 2 920, 2 870, 1 730, 1 670, 1 615, 1 515. 1 440, 1 405, 1 380, 1 365, 1 350, 1 260, 1 245, 1 230, 1 210, 1 170, 1 090, 1 030, 1 000, 955, 880, 845, 795, 765, 710, 670, and 605 cm^{-1}; *m*/*z* 414 ($M^{+\cdot}$).

The same procedure was applied for preparing the other diols.

9,10-*Bis*(1-*hydroxy*-7-*oxo*-3,6-*dioxaoctyloxy*)*anthracene*. From diethylene glycol (16 g, 15.1 × 10^{-2} mol) and anthracene-9-10-diyldioxydi(acetyl chloride) (5.5 g, 1.51 × 10^{-2} mol) was obtained 9,10-bis(1-hydroxy-7-oxo-3,6-dioxaoctyloxy)anthracene as a yellow waxy product (4.5 g, 59%), δ[(CD$_3$)$_2$SO] 3.10 (2 H, s), 3.26–3.83 (16 H, m), 4.13–4.31 (4 H, m), 4.46 (4 H, s), and 7.23–8.60 (8 H, m); ν_{max}(film) 3 660–3 120, 3 060, 2 940, 2 910, 2 870, 1 750, 1 620, 1 480, 1 460, 1 450, 1 435, 1 400, 1 375, 1 360, 1 350, 1 275, 1 210, 1 170, 1 130, 1 090, 1 065, 1 040, 1 020, 1 005, 950, 925, 885, 770, 735, 700, 670, and 610 cm^{-1}; *m*/*z* 502 ($M^{+\cdot}$).

9,10-*Bis*(1-*hydroxy*-10-*oxo*-3,6,9-*trioxaundecyloxy*)*anthracene*. From triethylene glycol (29 g, 19.3 × 10^{-2} mol) and 9,10-anthracene-9,10-diyldioxydi(acetyl chloride) (7 g, 1.93 × 10^{-2} mol) was obtained 9,10-bis(1-hydroxy-10-oxo-3,6,9-trioxaundecyloxy)anthracene as an orange waxy product (8.65 g, 76%), δ(CDCl$_3$) 2.90 (2 H, s), 3.40–3.65 (16 H, m), 3.55–3.85 (4 H, m), 4.27–4.50 (4 H, m), 4.77 (4 H, s), and 7.33–8.50 (8 H, m); ν_{max}(film) 3 660–3 120, 3 060, 2 920, 2 870, 1 750, 1 665, 1 635, 1 450, 1 435, 1 400, 1 370, 1 350, 1 300, 1 280, 1 260, 1 210, 1 170, 1 130, 1 090, 1 050, 965, 930, 885, 865, 800, 775, 730, 670, and 610 cm^{-1}; *m*/*z* 590 ($M^{+\cdot}$).

9,10-*Bis*(1-*hydroxy*-13-*oxo*-3,6,9,12-*tetraoxatetradecyloxy*)-*anthracene*. From tetraethylene glycol (26.7 g, 13.7 × 10^{-2} mol) and anthracene-9,10-diyldioxydi(acetyl chloride) (5 g, 1.37 × 10^{-2} mol) was obtained 9,10-bis(1-hydroxy-13-oxo-3,6,9,12-tetraoxatetradecycloxy)anthracene as an orange oil (8.5 g, 59%), δ(CDCl$_3$) 2.8 (2 H, s), 3.33–3.83 (28 H, m), 4.20–4.50 (4 H, m), 4.73 (4 H, s), and 7.30–8.46 (8 H, m); ν_{max}(film) 3 360–3 120, 3 060, 2 940, 2 920, 2 870, 1 750, 1 670, 1 620, 1 450, 1 435, 1 400, 1 350, 1 300, 1 285, 1 250, 1 205, 1 170, 1 130, 1 095, 1 050, 935, 885, 865, 775, 735, 700, and 610, cm^{-1}; *m*/*z* 678 ($M^{+\cdot}$).

3,8,27,32-*Tetraoxo*-1,4,7,10,25,28,31,34-[10.10](9,10)*anthracenophane* (I$_1$). To a stirred, boiling, degassed benzene (2.0 dm^3)–pyridine (0.8 g. 9.65 × 10^{-3} mol) solution was added simultaneously and dropwise, two degassed solutions in benzene (200 cm^3) of anthracene-9,10-diyldioxydi(acetyl chloride) (1.75 g, 4.83 × 10^{-3} mol) and 9.10-bis(1-hydroxy-4-oxo-3-oxapentyloxy)anthracene (2.0 g, 4.83 × 10^{-3} mol). When the addition was complete, the mixture was stirred for 24 h under reflux. The usual work-up, followed by chromatography on a silica column [ligroin–acetone (6:4)] gave I$_1$ as a yellow solid (1.04 g, 29%), m.p. 235 °C, δ(CDCl$_3$) 4.48 (8 H, s), 4.62 (8 H, s), and 7.08–8.40 (16 H, m); ν_{max}(KBr) 3 080, 3 060, 2 960, 2 920, 1 750, 1 730, 1 620, 1 435, 1 385, 1 350, 1 300, 1 275, 1 250, 1 220, 1 210, 1 190, 1 170, 1 125, 1 095, 1 040, 1 030, 1 000, 960, 930, 865, 845, 800, 775, 740, 730, 670, 645, and 605 cm^{-1}; λ_{max}(CH$_3$CN) 401 (log ε 4.08), 378.5 (4.16), 359 (3.99), 342 (3.70), 328.5 (3.57), 257.5 (5.23), and 250.5 nm (5.21); *m*/*z* 704 ($M^{+\cdot}$) (Found: C, 67.35; H, 4.75; O, 26.8. $C_{40}H_{32}O_{12}$ requires C, 68.18; H, 4.58; O, 27.24%). A satisfactory elemental analysis was not obtained, probably because of the difficulty of completely removing the solvent of the crystallization, the compound displaying some propensity to associate with it. I$_2$, I$_3$, and I$_4$ behave similarly. The other anthracenophanes were prepared according to the same procedure.

3,11,30,38-*Tetraoxo*-1,4,7,10,13,28,31,34,37,40-*decaoxa*-[13.13](9,10)-*anthracenophane* (I$_2$). From 9,10-bis(1-hydroxy-7-oxo-3,6-dioxaoctyloxy)anthracene (1.1 g, 2.2 × 10^{-3} mol) and 9,10-anthracene-9,10-diyldioxydi(acetyl chloride) (0.8 g, 2.20 × 10^{-3} mol) was obtained I$_2$ as a yellow solid (0.40 g, 23%), m.p. 238 °C, δ[(CD$_3$)$_2$SO] 3.3–4.6 (16 H, m), 4.73 (8 H, s), and 7.33–8.60 (16 H, m); ν_{max}(KBr) 3 060, 2 960, 2 920, 2 880, 1 760, 1 620, 1 480, 1 400, 1 370, 1 360, 1 290, 1 270, 1 250, 1 205, 1 165, 1 140, 1 090, 1 055, 1 045, 1 015, 940, 925, 900, 865, 815, 800, 765, 710, 680, 660, and 605 cm^{-1}; λ_{max}(CH$_3$CN) 401 (log ε 4.07), 379 (4.18), 360 (3.99), 342 (3.67), 257.5 (5.19), and 249 nm (5.25); *m*/*z* 792 ($M^{+\cdot}$) (Found: C, 66.4; H, 5.05; O, 27.5. $C_{44}H_{40}O_{14}$ requires C, 66.66; H, 5.08; O, 28.25%).

3,14,33,44-*Tetraoxo*-1,4,7,10,13,16,31,34,37,40,43,46-*dodecyloxa*[16.16](9,10)*anthracenophane* (I$_3$). From 9,10-(1-hydroxy-10-oxo-3,6,9-trioxaundecyloxy)anthracene (5.0 g, 8.46 × 10^{-3} mol) and 9,10-anthracene-9,10-diyldioxydi(acetyl chloride) (3.07 g, 8.46 × 10^{-3} mol) I$_3$ was obtained as a yellow solid (2.01 g, 27%) m.p. 172 °C, δ[(CD$_3$)$_2$SO] 3.29–3.76 (16 H, m), 4.09–4.42 (8 H, m), 4.47 (8 H, s), and 7.10–8.33 (8 H, m); ν_{max}(KBr) 3 060, 2 960, 2 880, 2 840, 1 750, 1 630, 1 480, 1 435, 1 425, 1 395, 1 380, 1 375, 1 350, 1 320, 1 275, 1 255, 1 205, 1 165, 1 125, 1 090, 1 035, 995, 960, 920, 870, 840, 790, 770, 730, 700, 670, and 605 cm^{-1}; λ_{max}(CH$_3$CN) 400 (log ε 4.11), 378.5 (4.18), 359 (4.00), 342.5 (3.70), 258 (5.29), and 249 nm (5.20); *m*/*z* 880 ($M^{+\cdot}$) (Found: C, 64.45; H, 5.5; O, 28.6. $C_{48}H_{48}O_{16}$ requires C, 65.45; H, 5.49; O, 29.06%).

3,17,36,50-*Tetraoxo*-1,4,7,10,13,16,19,34,37,40,43,46,49,52-*tetradecyloxa* [19.19](9,10)*anthracenophane* (I$_4$). From 9,10-(1-hydroxy-13-oxo-3,6,9,12-tetraoxatetradecyloxy)anthracene (5.0 g, 7.37 × 10^{-3} mol) and anthracene-9,10-diyldioxydi(acetyl chloride) (2.68 g, 7.37 × 10^{-3} mol) was isolated I$_4$ as a yellow solid (1.78 g, 25%) m.p. 132 °C,(from CH$_2$Cl$_2$), δ(CD$_2$Cl$_2$) 3.50–3.87 (24 H, m), 4.20–4.53 (8 H, m), 4.70 (8 H, s), and 7.17–8.17 (16 H, m); ν_{max}(KBr) 3 060, 2 960, 2 900, 2 860, 1 750, 1 615, 1 455, 1 430, 1 395, 1 370, 1 360, 1 345, 1 280, 1 270, 1 200, 1 160, 1 130, 1 090, 1 040, 1 025, 1 015, 1 000, 940, 920, 890, 860, 820, 800, 760, 720, 660, and 605 cm^{-1}; λ_{max}(CH$_3$CN) 400.5 (log ε 4.11), 379.5 (4.18), 360 (4.00), 343 (3.76), 327 (3.65), 259 (5.34), and 251 nm (5.23); *m*/*z* 968 ($M^{+\cdot}$) (Found: C, 58.2; H, 5.8; O, 25.05. $C_{52}H_{56}O_{18}\cdot 2CH_2Cl_2$ requires C, 57.94; H, 5.27; O, 25.28%).

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References

1 H. Bouas-Laurent, A. Castellan, and J.-P. Desvergne, *Pure Appl. Chem.*, 1980, **52**. 2633 and references therein.

2 H. Bouas-Laurent, A. Castellan, M. Daney, J.-P. Desvergne, G. Guinand, P. Marsau, and M.-H. Riffaud, *J. Am. Chem. Soc.*, 1986, **108**, 315.

3 G. Guinand, P. Marsau, H. Bouas-Laurent, A. Castellan, J.-P. Desvergne, and M. Lamotte, *Acta Crystallogr., Sect. C*, 1987, **43**, 857.

4 A. Shanzer, J. Libman, and F. Frolow, *Acc. Chem. Res.*, 1983, **16**, 60.

5 E. De Barry Barnett, N. F. Goodway, A. G. Higgins, and C. A. Lawrence, *J. Chem. Soc.*, 1934, 1224.

6 (*a*) J. Hinschberger, *Thesis*, Bordeaux, 1988; (*b*) J. Hinschberger, P. Marsau, J.-P. Desvergne, H. Bouas-Laurent, and A. Castellan, *Acta Crystallogr., Sect. C*, 1989, **45**, 1974.

7 (*a*) A. Castellan, J.-P. Desvergne, and H. Bouas-Laurent, *Nouv. J. Chim.*, 1979, **3**, 231; (*b*) D. T. Browne, J. Eisinger, and N. J. Leonard, *J. Am. Chem. Soc.*, 1968, **90**, 220; (*c*) M. Warshaw and I. Tinocco, Jr., *J. Mol. Biol.*, 1966, **20**, 29 and references therein; (*d*) J.-P. Desvergne, N. Bitit, A. Castellan, M. Webb, and H. Bouas-Laurent, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1885.

8 J. M. Lehn, *Struct. Bond.*, 1973, **16**, 1.

9 (*a*) F. C. De Schryver, N. Boens, and J. Put, *Adv. Photochem.*, 1977, **10**, 359; (*b*) M. A. Winnik, *Acc. Chem. Res.*, 1977, **10**, 173; (*c*) R. Todesco, J. Gelan, H. Martens, J. Put, and F. C. De Schryver, *J. Am. Chem. Soc.*, 1981, **103**, 7304.

10 A. Castellan, M. Daney, J.-P. Desvergne, M.-H. Riffaud, and H. Bouas-Laurent, *Tetrahedron Lett.*, 1983, **24**, 5215.

11 R. D. Rogers, L. K. Kurihara, and P. D. Richards, *J. Chem. Soc., Chem. Commun.*, 1987, 604.

12 (*a*) J. Ferguson, M. Morita, and M. Puza, *Chem. Phys. Lett.*, 1976,

42, 288; (*b*) J. Ferguson, A. Castellan, J.-P. Desvergne, and H. Bouas-Laurent, *Chem. Phys. Lett.*, 1981, **78**, 446.

13 B. Stevens and M. I. Ban, *Trans. Faraday Soc.*, 1964, **60**, 1515.

14 J.-P. Desvergne, N. Bitit, J. P. Pillot, and H. Bouas-Laurent, *J. Chem. Res.* (*S*), 1989, 146.

15 J. B. Birks, 'Photophysics of Aromatic Molecules,' Wiley-Interscience, London, 1970.

16 F. C. De Schryver, K. Demeyer, J. Huybrechts, H. Bouas-Laurent, and A. Castellan, *J. Photochem.*, 1982, **20**, 341.

17 (*a*) M. D. Cohen, Z. Ludmer, and V. Yakhot, *Phys. Stat. Sol.*, 1975, **67b**, 51; (*b*) P. Marsau, H. Bouas-Laurent, J.-P. Desvergne, F. Fages, M. Lamotte, and J. Hinschberger, *Mol. Cryst. Liq. Cryst.*, 1988, **156**, 383 and references therein.

18 (*a*) R. Hilgenfeld and W. Saenger, *Top. Curr. Chem.*, 1982, **101**, 1; (*b*) G. R. Painter and B. C. Pressman, *ibid.*, p. 83.

19 S. Hamai and F. Hirayama, *J. Phys. Chem.*, 1983, **87**, 83 and references therein.

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