

# Effect of cyclodextrin complexation on thermochromic Schiff bases

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## Abstract

The effects of complexation on thermochromic Schiff bases in  $\beta$ - and  $\gamma$ -cyclodextrin and their permethylated derivatives have been investigated in the solid state. The inclusion complexes formed have been found to be photochromic and fluorescent in the temperature range 298 K–77 K contrary to the photochromic Schiff bases which are fluorescent at low temperatures only.

**Keywords:** Inclusion complexes; Thermochromism; Photochromism

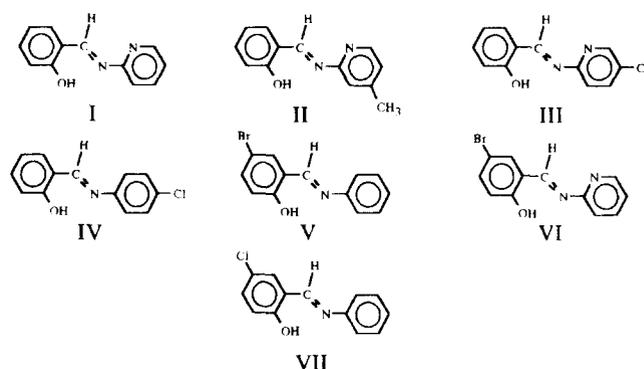
## 1. Introduction

The X-ray analyses of aromatic Schiff bases have shown that in the thermochromic crystal structure molecules are essentially planar and packed in stacks of parallel molecules with an interplanar distance of 3.3 Å; in the photochromic form, the aniline ring is twisted about the exocyclic N–C bond by 55° and molecular packing is consequently much more open [1]. Two results follow from these observations: (a) in the planar molecules the lone pair of the nitrogen does not overlap with the  $\pi$  electrons of the aniline ring whereas in the "twisted" structure such overlap is possible and consequently the basicity of the nitrogen and hence the strength of the H $\cdots$ N bond are higher in the planar, i.e. thermochromic form Qb (*cis*-quinoid form); (b) provided that the photochromic species is associated with Qc (*trans*-quinoid form), the required *cis*  $\rightarrow$  *trans* conversion is improbable in the plane-to-plane packing type of the thermochromic forms but possible in the "open structure" of the photochromic crystals (Fig. 1) [2,3]. If the hypothesis that photochromism in this class of compounds is attributed to geometrical isomerization is correct, then its formation and rate of coloration and decoloration must be sensitive to molecular environment.

In this work the effect of the environment of  $\beta$ - and  $\gamma$ -cyclodextrins ( $\beta$ -CD and  $\gamma$ -CD) and their permethylated derivatives ( $\beta$ -PMCD and  $\gamma$ -PMCD) on some thermochromic Schiff bases has been investigated for the purpose of continuing our efforts to find new ways to improve the photochromic systems and to study their structure, configu-

ration and properties [4,5]. The interest in photochromic materials arises from their many potential applications.

The inclusion complexes of the following thermochromic Schiff bases have been investigated in polycrystalline films: *N*-salicylidene-2-aminopyridine (**I**), *N*-salicylidene-2-amino-5-picoline (**II**), *N*-salicylidene-2-amino-4-chloropyridine (**III**), *N*-salicylidene-4-chloroaniline (**IV**), *N*-(5-bromosalicylidene)aniline (**V**), *N*-(5-bromosalicylidene)-2-aminopyridine (**VI**), and *N*-(5-chlorosalicylidene)aniline (**VII**).



## 2. Experimental details

### 2.1. Materials

*N,N*-dimethylformamide (DMF) (Merck) spectro grade was dried by stirring with molecular sieves (4 Å) and anhydrous BaO for 30 h and distilled three times under reduced

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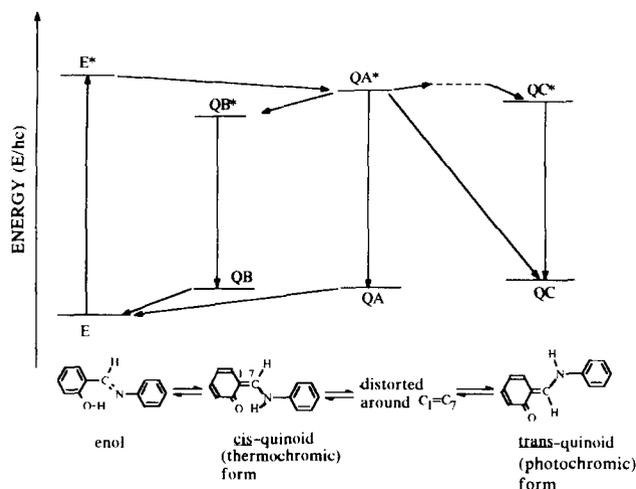


Fig. 1. Energy level scheme of the forward photoreaction of *N*-salicylideneaniline [3].

pressure. Methylcyclohexane (MCH) spectro grade, cyclohexane-*d*<sub>12</sub> (CH-*d*<sub>12</sub>) and DMF-*d*<sub>7</sub> (Aldrich) were used as received.  $\beta$ -CD (Fluka) and  $\gamma$ -CD (Wacker) of purity 99% (high performance liquid chromatography) were recrystallized twice from aqueous solutions at 80 °C after passage through a Millipore filter (type SM) of pore size 5.0  $\mu$ m. The crystalline material was dried under vacuum at 100 °C for 30 h.  $\beta$ -PMCD and  $\gamma$ -PMCD (Cyclolab) were used without further purification.

The Schiff bases were synthesized by direct condensation of the appropriate salicylaldehyde with the appropriate amine or aminopyridine in ethanol, followed by repeated recrystallizations from the same solvent. Elemental analysis, IR and melting points were utilized to establish the purity of the compounds.

The inclusion complexes of the Schiff bases in  $\beta$ -CD and  $\gamma$ -CD were obtained from concentrated solutions of the two components in DMF (molar ratio 1:1) which were left to evaporate slowly in a vacuum desiccator. The crystalline complexes were rinsed several times with absolute ethanol and chloroform. The complexes in  $\beta$ -PMCD and  $\gamma$ -PMCD were obtained from hot concentrated solutions of the Schiff base and the PMCD in MCH (molar ratio 5:1) and were left to reach room temperature. The crystalline material was rinsed with the same solvent. The molar ratio (Schiff base: CD) was calculated to be 1:1.

The polycrystalline films of the compounds were prepared from the melt between two optical quartz plates under pressure and those of the complexes by slow evaporation of a concentrated solution of the complex in DMF, placed in a Petri dish containing an optical quartz plate, in a vacuum desiccator. After completion of the evaporation, the plate was covered by another quartz plate. The quality of the films was examined under a polarizing microscope.

## 2.2. Instrumentation

The formation of the complexes was established by differential scanning calorimetry (DSC) thermograms obtained on

a Perkin–Elmer DSC-7 instrument and X-ray powder photographs taken with a Debye–Scherrer camera of radius 5.7 cm with Cu K $\alpha$  radiation at about 4 h exposure. The molecular ratios of the solid complexes were determined by dissolution in DMF-*d*<sub>7</sub> or CH-*d*<sub>12</sub> and integration of the proton signals in nuclear magnetic resonance (NMR) spectra. NMR measurements were performed on a Fourier transform NMR Bruker AC 250 instrument. The absorption and fluorescence spectra were obtained on a Perkin–Elmer Lambda 16 spectrophotometer and a Perkin–Elmer LS-5B spectrofluorimeter.

## 3. Results

The inclusion complexes of the aromatic Schiff bases I–VII in  $\gamma$ -CD,  $\beta$ -PMCD and  $\gamma$ -PMCD have been investigated

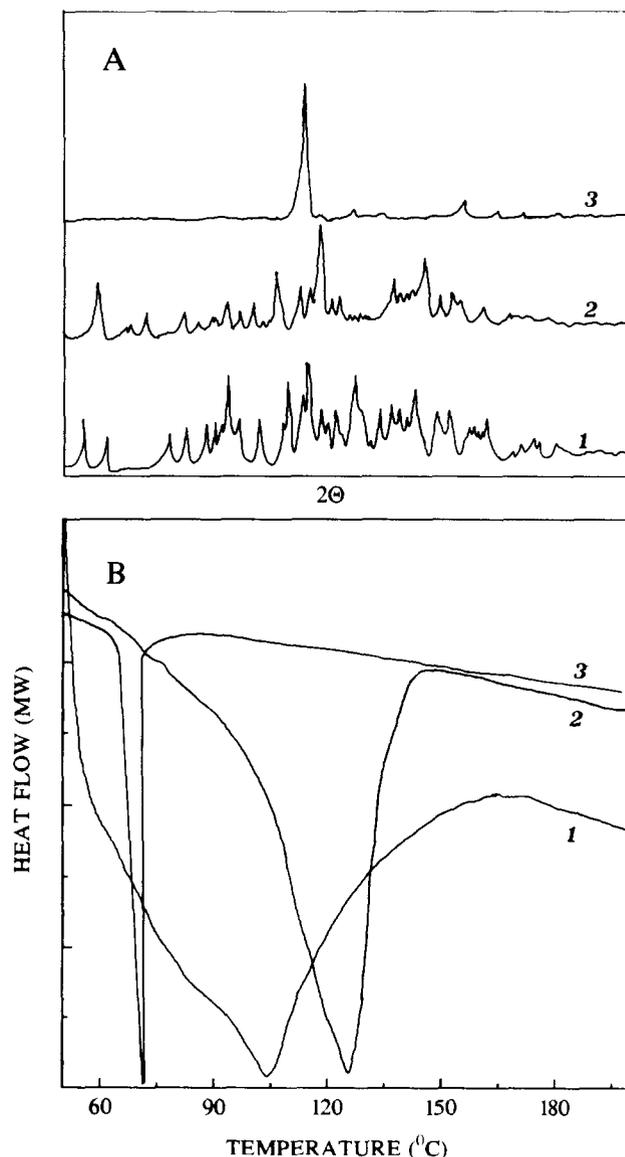


Fig. 2. (A) X-ray powder diffraction patterns and (B) DSC thermograms: curves 1, complex I in  $\gamma$ -CD; curves 2,  $\gamma$ -CD; curves 3, compound I.

but only the complexes of **I** and **II** in  $\beta$ -CD because of amorphous crystallization of the remainder.

### 3.1. Structural assignment

The formation of the complexes has been established by DSC thermograms and X-ray powder diffraction patterns (Fig. 2). From the study of the complexes in  $\beta$ -CD and  $\gamma$ -CD in DMF- $d_7$  by NMR spectroscopy it has been concluded that very weak complexation with the external rim of the CDs and no inclusion in the cavity take place. The supramolecular structure shown in Fig. 3(A) has been attributed to the complex of **I** in  $\gamma$ -CD according to the perturbation of the hydrogen atoms of the guest compound. Very weak complexation has been also observed in  $\beta$ -PMCD and  $\gamma$ -PMCD in CH- $d_{12}$  but in this case the guest molecules are partly held in the cavity between the methoxy groups and the hydrogen atoms at position 3 of the lower rim.

The structure in Fig. 3(B) is proposed for the inclusion complexes of compound **I** with the permethylated derivatives of the CDs since the largest shifts  $\Delta\delta$  are observed for the proton of the aminopyridine ring (Table 1). Compound **II** presents similar values to those of compound **I** but the protons of the salicylaldehyde ring are also affected in the case of  $\beta$ -

PMCD and  $\gamma$ -PMCD indicating the structures shown in Fig. 3(C).

### 3.2. Electronic absorption spectra

All the compounds studied in this work are thermochromic but lose this property and become photochromic in the environment of  $\beta$ -CD,  $\gamma$ -CD and their permethylated derivatives, with the exception of the complex **II** in  $\beta$ -CD which has not been found to be photochromic although the NMR spectra have shown that the molecule **II** takes the same position in both  $\beta$ -CD and  $\gamma$ -CD. The absorption spectra of polycrystalline films of compound **I**, free and complexed in  $\gamma$ -CD, at various temperatures, before and after irradiation, are presented in Fig. 4.

The photochemical reactions of aromatic Schiff bases are thermally activated [3,6] and the same holds good for their inclusion complexes studied. The complexes present the maximum intensity of photochromism in the range 180 K–170 K. However, the “usable temperature range”, i.e. the range between lower and upper temperature limits imposed by low yield and rapid fading respectively in which photo-coloration is observable, varies with the compound [6] and with the complex as well. The usable temperature ranges of

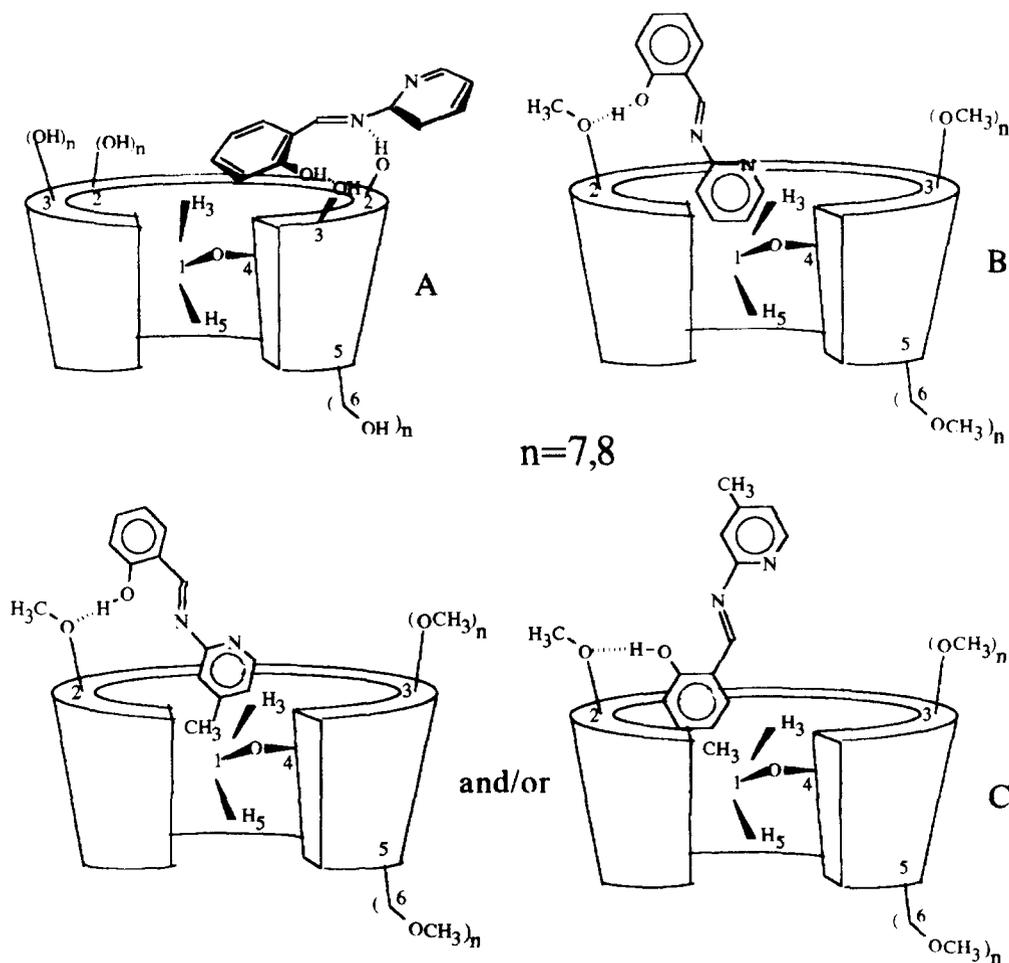


Fig. 3. Proposed structural configurations: (A) **I** in  $\beta$ -CD and  $\gamma$ -CD; (B) **I** in  $\beta$ -PMCD and  $\gamma$ -PMCD; (C) **II** in  $\beta$ -PMCD and  $\gamma$ -PMCD [6].

Table 1

Complexation induced chemical shift changes  $\Delta\delta = \delta_{\text{compl}} - \delta_{\text{free}}$  for the complexes of **I** with  $\gamma$ -CD in DMF- $d_7$  and with  $\beta$ -PMCD and  $\gamma$ -PMCD in CH- $d_{12}$ 

	Protons of <b>I</b>			CD protons		
	$\gamma$ -CD <sup>a</sup>	$\beta$ -PMCD	$\gamma$ -PMCD	$\gamma$ -CD <sup>a</sup>	$\beta$ -PMCD	$\gamma$ -PMCD
H7	-0.026	0.006	0.004	H1	-0.010	0.030
H6	-0.013	0.020	0.015	H2	0.0	0.006
H5	-0.003	0.007	0.005	H3	0.020	0.042
H4	-0.003	0.006	0.004	H4	0.0	0.045
H3	-0.005	0.004	0.003	H5	0.0	0.032
H6'	0.007	0.013	0.010	H6	0.0	0.006
H5'	-0.002	0.014	0.010	H6'	0.0	0.036
H4'	-0.004	0.017	0.012	Me3	-	-0.011
H3'	0.014	0.016	0.012	Me2	-	-0.035
OH	-0.007	0.017	0.014	Me6	-	-0.003

<sup>a</sup> Similar values were observed with  $\beta$ -CD.

the inclusion complexes of the compounds **I–VII** in  $\beta$ -CD,  $\gamma$ -CD,  $\beta$ -PMCD and  $\gamma$ -PMCD are presented in Table 2. The results show that the stability of the photochromic form decreases in the order  $\gamma$ -PMCD >  $\beta$ -CD,  $\gamma$ -CD >  $\beta$ -PMCD. Stronger temperature dependence is observed in the formation of the photocolouration of the complexes **III** in  $\beta$ -PMCD and **III** and **VI** in  $\gamma$ -PMCD.

### 3.3. Fluorescence spectra

Photochromic Schiff bases in the solid state are not fluorescent except at low temperatures while thermochemical compounds are fluorescent in the temperature range 298 K–77 K [1]. The photochromic inclusion complexes in  $\beta$ -CD,  $\gamma$ -CD and their permethylated derivatives investigated are fluorescent in the range 298 K–77 K. The emission spectra of the thermochemical compound **I** excited with 365 nm and 470 nm light and of the complex **I** in  $\gamma$ -CD excited with 365 nm light are shown in Fig. 5. Emission has not been detected from the complex **I** in  $\gamma$ -CD when excited with 470 nm light as the thermochemical form of the guest molecule only absorbs in this region; this form is lost by complexation. This experimental result proves the absence of the free compound in the polycrystalline material of the complex.

The fluorescence spectra of compound **I** are Stock shifted by 8200  $\text{cm}^{-1}$  and are composed of two parts (part A, 520 nm (QA\*  $\rightarrow$  QA); part B, 575 nm (QB\*  $\rightarrow$  QB)) at low temperatures; the A part (emission of the intermediate which is distorted around the C<sub>1</sub>=C<sub>7</sub> bond) exhibits vibrational

structure since the intramolecular hydrogen bond is interrupted because of the distortion around the C<sub>1</sub>=C<sub>7</sub> bond (Fig. 1). The broad structure of the B part (emission of the *cis*-quinoid form, i.e. thermochemical form) is a characteristic feature of hydrogen-bonded systems. The fluorescence spectra of the complex **I** in  $\gamma$ -CD at low temperatures are also composed of two parts, both without vibrational structure, since the distorted intermediate is hydrogen bonded to  $\gamma$ -CD in this case. The fluorescence spectra of the photochromic forms (*trans*-quinoid forms) of **I** in  $\gamma$ -CD and  $\gamma$ -PMCD excited with 480 nm light at 77 K (QC\*  $\rightarrow$  QC) are also included in Fig. 5; the photoproducts have been formed by irradiation with 365 nm light for 15 min at 173 K. The emission spectra of compounds **II–V** present the same characteristics as those of **I** (no fluorescence has been detected from compound **VI**) and the same holds good for the emission spectra of complexes **II–VI** in  $\gamma$ -CD compared with those of **I** in  $\gamma$ -CD. The fluorescence spectra of the complexes **I–VI** in  $\beta$ -PMCD and in  $\gamma$ -PMCD and of their photochromic forms have been also recorded.

## 4. Discussion

All the Schiff bases investigated are thermochemical but lose this property and become photochromic in the environment of  $\beta$ -CD,  $\gamma$ -CD and their permethylated derivatives, as is shown by the absorption spectra and the absence of reabsorption in the fluorescence spectra of the inclusion com-

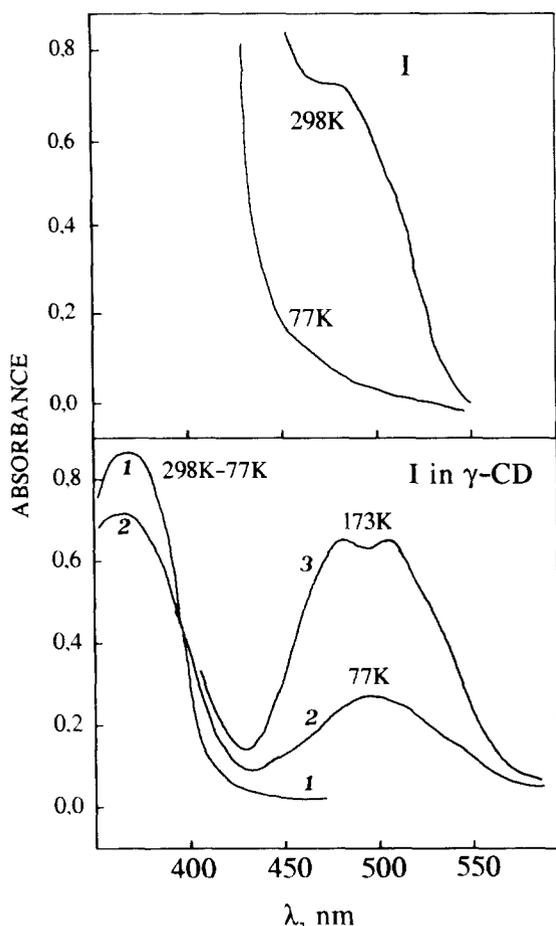


Fig. 4. Absorption spectra of polycrystalline films of the thermochromic compound **I** and the inclusion complex **I** in  $\gamma$ -CD at the indicated temperatures: before (spectrum 1) and after (spectra 2 and 3) irradiation with 365 nm light for 1 h (photochromic product).

Table 2  
Usable temperature range of the inclusion complexes of compounds **I–VII** in cyclodextrins

Inclusion complex	Usable temperature range
<b>I–VII</b> in $\beta$ -CD and <b>I–VII</b> in $\gamma$ -CD	220 K–77 K
<b>I, II, IV–VI</b> in $\beta$ -PMCD	200 K–77 K
<b>I, II, IV, V</b> in $\gamma$ -PMCD	230 K–77 K
<b>III</b> in $\beta$ -PMCD	200 K–125 K
<b>III</b> in $\gamma$ -PMCD	230 K–140 K
<b>VI</b> in $\gamma$ -PMCD	220 K–140 K

plexes formed. Photochromism has not been detected from the complex **II** in  $\beta$ -CD although the NMR spectra have shown that compound **II** occupies the same position in  $\beta$ -CD and in  $\gamma$ -CD.

These experimental results show that the intramolecular hydrogen bond O–H $\cdots$ N of the guest molecules is broken in the inclusion complexes. The interruption of the intramolecular bond is probably due to a deviation of the guest mol-

ecule from planarity and/or to the intermolecular bonds formed between the Schiff bases and the CDs. The existence of intermolecular bonds is also shown by the absence of vibrational structure on the A band of the fluorescence spectra of the inclusion complexes. Related to the intermolecular bonds may also be that the energy barrier situated in the transition  $QA^* \rightarrow QC^*$  is higher in the complexes of the derivatives of *N*-salicylidene-2-aminopyridine (**III**, **VI**) than of those of *N*-salicylideneaniline (**IV**, **V**) (Table 2).

The observed photochromism of the inclusion complexes is to be expected since the close contacts between the planes of the thermochemical molecules (ca. 3.3 Å) may cease to exist on complexation; thus, enough space is provided for the photoisomerization to take place. The dependence on the available space is also shown by the stabilization of the photochromic products in  $\gamma$ -PMCD which possess a wider cavity than  $\beta$ -PMCD (Table 2).

The photochromic inclusion complexes of the thermochemical Schiff bases in CDs are fluorescent in the solid state (transitions  $QA^* \rightarrow QA$  and  $QB^* \rightarrow QB$ ) in the temperature range 298 K–77 K while photochromic Schiff bases do not fluoresce except at low temperatures (lower than the usable temperature range) [6]. However, the inclusion complex of photochromic *N*-salicylideneaniline in  $\beta$ -CD is strongly fluorescent in the solid state [7]. The fluorescence of the *trans*-quinoid (photochromic) form of the complexes has been also recorded ( $QC^* \rightarrow QC$ ) while no fluorescence has been detected from the *trans*-quinoid form of *N*-salicylideneaniline except in stilbene and dibenzyl host crystals at very low

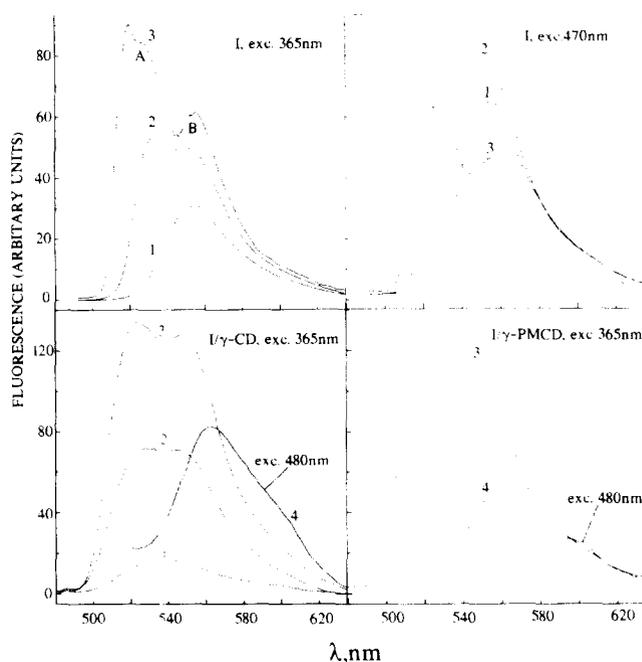


Fig. 5. Fluorescence spectra of polycrystalline films of the thermochemical compound **I** and the inclusion complexes **I** in  $\gamma$ -CD and **I** in  $\gamma$ -PMCD: spectra 1, at 298 K; spectra 2, at 143 K; spectra 3, at 77 K; spectra 4, at 77 K after irradiation with 365 nm light for 15 min (photochromic product).

temperatures (10 K) [3]. Fluorescence enhancement by complexation has been also observed in other cases [8]. These experimental results indicate the stabilizing effect of complexation on the electronically excited molecules. The energy level scheme of the forward photoreaction of *N*-sali-cyridenaniline shows that the common excited intermediate QA\* may deactivate by a number of radiationless transitions (Fig. 1); among them QA\* → QB\* does not seem to be affected by complexation as part B of the fluorescence spectrum of the guest molecules is higher than in the spectrum of the free compound (Fig. 5). Decreased transition probabilities of the remainder and of the radiationless transitions QB\* → QB and QC\* → QC may be expected.

In conclusion, a great number of new solid photochromic supramolecules may be prepared by means of CD complexation with thermochromic Schiff bases which are large in number [6].

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