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Supramolecular control of photochromism in a β-cyclodextrin/Schiff base system

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ABSTRACT

The inclusion complex of a salicylaldehyde Schiff base (anil) in β-cyclodextrin (βCD) is reported for the first time. UV–vis spectroscopic and fluorescence studies show that *N*-(1-adamantyl)salicylaldimine (ASA), which is thermochromic as a free crystalline compound, becomes photochromic upon encapsulation into βCD. Characterisation of the complex has been performed by NMR spectroscopy in aqueous solution and by UV and fluorescence spectroscopy and powder X-ray diffraction in the crystalline state. The NMR studies indicate host:guest ratio of 1:1 and prove that only the adamantyl moiety of the guest is enclosed into the host cavity, whereas the hydroxyphenyl part is outside. Trials to grow single crystals of the complex produced a novel βCD lattice, which can be rationalized by applying the inclusion mode suggested by NMR spectroscopy. βCD in the crystal lattice seems to act as a medium allowing the *cis* to *trans* isomerisation of ASA, a volume-demanding process necessary for the expression of photochromism in this class of molecules. The study demonstrates that βCD nanocavities can lead to supramolecular control of the photochemical behaviour of appropriately designed anils, a property with many potential applications.

1. Introduction

The ability of cyclodextrins (CDs) to include in their cavities functional compounds, among which photochromic, thermochromic and fluorophoric molecules, has led to intensive study of such inclusion complexes [1–3]. The encapsulated guest molecules may display new molecular forms with novel photophysical properties, different than the ones of the free molecule, due to proton transfer [4] and restricted bond rotation [5] imposed by the host. The known [6] thermochromic and photochromic properties of Schiff bases of salicylaldehyde (anils) in the crystalline state arise from geometrical isomerisation: according to the generally accepted equilibria shown in Scheme 1, the thermo-product is the *cis*-keto form produced from the enol form by intramolecular hydrogen transfer in the ground state, whereas the photo-product is the *trans*-keto form, which results from the enol form in the excited state by H-transfer, subsequent rupture of the intramolecular H-bond and *cis-trans* isomerization [6,7].

The nature of the photo-product as the *trans*-keto form in the crystalline state has been proven experimentally [8]. The *cis* to *trans* transformation is a volume-demanding process, thus it has been proven [6] that anils with a crystal lattice exhibiting close π...π contacts ("open" lattice) are photochromic, whereas anils with a dense crystal packing are thermochromic. This communication presents for the first time the change of chromo-behaviour of an anil, due to its apparent encapsulation in β-cyclodextrin (βCD). Specifically, *N*-(1-adamantyl)salicylaldimine (ASA), which is thermochromic as a pure crystalline compound, exhibits photochromic behaviour in the inclusion complex βCD/ASA.

2. Experimental

2.1. Preparation of the βCD/N-(1-adamantyl)salicylaldimine complex

Synthesis of *N*-(1-adamantyl)salicylaldimine (ASA) was carried out by refluxing 1-adamantylamine and salicylaldehyde in dimethylformamide (DMF) according to a known method [9]. The product was a yellow crystalline solid, mp 92.5–94.5 °C, lit. [9] 82.5–84.5 °C. ^{1}H NMR (DMSO-d_6, 500 MHz) δ 14.401 (br s, 1H, OH), 8.549 (s, 1H, CH=N), 7.460 (d, J = 7 Hz, 1H, Ho), 7.294 (t, J = 8 Hz, 1H, Hp), 6.853 (t, J = 7, 1H, Hm), 6.824 (d, J = 8 Hz, 1H, Hm), 2.141 (bs s, 3H, H3), 1.806 (s, 6H, H4), 1.696 (two d, J = 12 Hz, 6H, H2). The βCD complex was prepared by dissolving equimolar quantities of ASA and βCD in hot DMF with stirring until a clear solution was obtained

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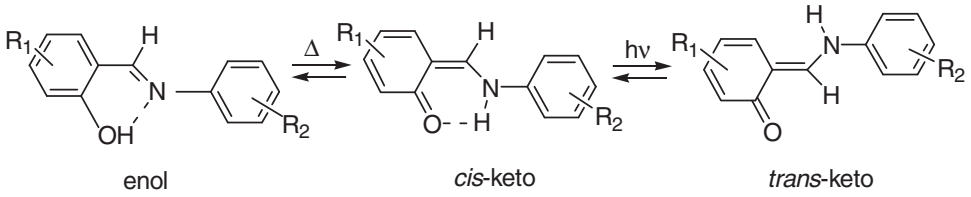


Scheme 1. Thermochromic and photochromic reversible processes in anils. The *cis* and *trans* labeling is based on the relative position of the N-bound H-atom with respect to the carbonyl O-atom.

and subsequent slow cooling to room temperature overnight. The product precipitated in the form of a yellow microcrystalline powder and collected by filtration.

2.2. Powder X-ray diffraction characterization

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku R-AXIS IV system using CuKa radiation (λ = 1.5418 Å) by the oscillation method. XRD patterns of (a) βCD, (b) ASA and (c) the prepared βCD/ASA inclusion complex were acquired

2.3. Structure determination by single crystal X-ray crystallography

Single crystals were obtained by mixing 100 mg of βCD with an equimolar quantity of ASA in absolute ethanol (∼6 mL) inside a hydrothermal cell at 80 °C. The alcoholic solution stayed in the hydrothermal cell for 3 days and then it was left to cool slowly. Crystals in the shape of pale yellow, diamond plates were obtained by slow evaporation of the solution. Data were collected by synchrotron radiation at 100 K at the EMBL-Hamburg outstation. The structure was solved by Molecular Replacement by the program DIRDIF [10], using the skeleton coordinates of a βCD molecule of the complex βCD/nonanoic acid [11]. The coordinates of the remaining non-H atoms and the solvent atoms were determined by consecutive difference Fourier maps. The refinement by full-matrix least-squares based on F^2 was carried out with the program SHELXL97 [12]. The occupation factors of the solvent atoms were first refined by keeping the temperature factors constant (U at 0.08 Å^2) and subsequently were kept constant, while the temperature factors were refined. The βCD non-hydrogen atoms and solvent atoms were treated isotropically up to R = 15% and then anisotropically. Hydrogen atoms were placed at idealized positions on the host carbon atoms and refined by the riding model ($U_H = 1.25U_C$). For the host's CH_2 groups bearing disordered hydroxyl groups (O63A, O21B), only the H-atoms of the major orientations were used. Details of crystal data and refinement are shown in Table 1. During the refinement and until its end, it was not possible to construct a model of the guest molecule (full or parts of it), thus the refinement was completed by considering the structure as a βCD-ethanol complex. However, based on some residual electron density and the electron density of two neighbouring ethanol molecules it was possible to fit the ASA model (by the program Coot [13]) in the crystal lattice with the adamantyl group residing inside a βCD cavity and the salicylidene group in an empty space of the lattice. Complete crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC 795380.

2.4. NMR spectroscopic studies

NMR spectra were obtained on a Bruker AVANCE 500 MHz spectrometer using an inverse broadband (BBI) probe and temperature regulation at 298 K. 2D ROESY NMR spectra were obtained using the built-in library sequence and a spin-lock time of 350 ms.

2.5. Spectroscopic and photochemical studies

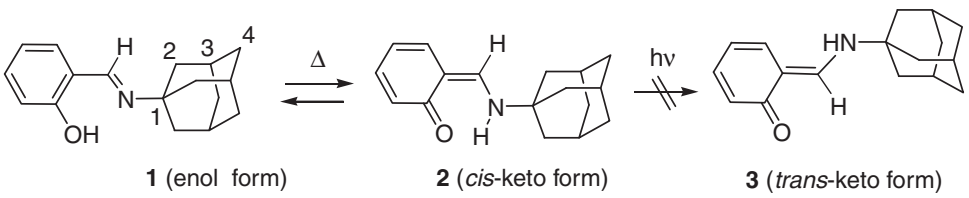
Absorption spectra were recorded on a Jasco V-5600 spectrophotometer and fluorescence spectra on a Jasco PTL-396S spectrofluorimeter. Steady state photochemical experiments employed a 200 W high-pressure Hg lamp using Corning glass filters. For studies at low temperature (liquid nitrogen) an Oxford cryostat with quartz windows was used. A thin polycrystalline film of ASA was prepared for screening for photochromic and/or thermochromic properties by placing the compound between optical quartz plates, heating it until melt (∼100 °C) under pressure and leaving overnight to cool. Its crystallinity was examined under a polarizing microscope. The same method was used to prepare thin polycrystalline films of the ASA/βCD inclusion complex. However, the films were not sufficiently transparent, possibly, because βCD and its complexes do not melt (actually they become dark and decompose above 180 °C), therefore, no absorption spectra could be recorded. The film's fluorescence and excitation spectra were taken at an angle of 45° with respect to the incident beam. Colour changes upon ultraviolet irradiation were followed visually.

3. Results and discussion

The guest molecule (ASA, **1**, Scheme 2) is a thermochromic anil, as are all anils of aliphatic amines [6,14], thus the absorption spectrum of a crystalline film of ASA does not exhibit the thermochromic band at 420 nm (Fig. 1) at liquid nitrogen temperature. Increase of temperature causes a tautomeric shift of the proton resulting in the thermo-product (**2**, Scheme 2) with an absorption band at 420 nm and a fluorescence band at *ca*. 500 nm, which is the mirror image of its absorption band at 420 nm, as is expected for the *cis*-keto forms [6,14]. The absence of photochromic behaviour was deduced from the lack of change of the absorption spectrum under UV irradia-

Table 1
Crystal data and structure refinement parameters.

Molecular formula	$2(C_{42}H_{70}O_{35})\cdot 5.46(C_2H_6O)\cdot 1.38(H_2O)$
Formula weight	2546.33
Temperature	100(2) K
Radiation/wavelength	0.8265 Å
Space group	$P2_1$
a, α	16.055(8), 90°
b, β	14.929(12) 103.19(2)
c, γ	30.029(14), 90
Volume/Z	7004(7) Å^3/2
Density (calculated)	1.207 Mg/m^3
2θ range for data collection	5.00–57.01°
Index ranges	$0 \le h \le 16$, $0 \le k \le 15$, $-31 \le l \le 31$
Reflections collected/observed $[F_o > 4\sigma(F_o)]$	7814/7318
Solution method	Molecular replacement
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7814/36/1694
Goodness-of-fit on F^2	1.642
Final R indices $[F_o > 4\sigma(F_o)]$	$R1 = 0.0942$, $wR2 = 0.2642$
R indices (all data)	$R1 = 0.1026$, $wR2 = 0.3086$
Largest diff. peak and hole	0.33 and −0.29



Scheme 2. Tautomeric proton transfer between enol form, **1**, and *cis*-keto form, **2**, of ASA. The crystal packing of pure crystalline ASA does not allow the *cis* to *trans* photo-isomerisation leading to **3**.

tion of the film at 365 nm, either at room temperature or at liquid nitrogen temperature (Fig. 1 and Supplementary Fig. S3).

The structure of crystalline ASA is the phenol-imine tautomer **1** [9]. The geometrical parameters indicate that a strong intramolecular O–H. . .N hydrogen bond is established between the O and N atoms, with N. . .H distance of 1.79 Å, N. . .O distance of 2.594 Å and O–H. . .N angle 155°. However, the crystal structure determination cannot exclude the presence of a small amount of the *cis*-keto form **2** in the crystal (Scheme 2) giving rise to the 420 nm thermochromic band at room temperature in Fig. 1, as in the thermochromic 5-Cl-salicylideneaniline [15], where the corresponding band is due to the presence of *ca*. 5% of the *cis*-keto form. ASA, in contrast to most thermochromic anils [6,14] is not a planar molecule, due to the adamantyl group, but the salicylaldimine moiety is "locked" in a planar geometry via the strong intramolecular H-bond. Although the packing lacks the short intermolecular π–π distances (~3.4 Å) of planar anils, the crystal packing cannot be characterized as "open" as in photochromic anils, either. The shortest distances between carbon atoms of the adamantyl and aromatic moieties are quite short, 3.716–3.913 Å [9] and the needed *cis* to *trans* isomerisation (Scheme 2) seems to be not feasible, because irradiation with 365 nm light does not affect the absorption spectrum (Fig. 1). This result indicates that older generalizations [6] characterising anils of aliphatic amines as both photochromic and thermochromic are not valid and that the decisive step for photochromism is the ability of the molecule to perform the volume-demanding *cis* to *trans* isomerisation.

Complexation of ASA with βCD resulted in a yellow crystalline product that was analyzed by X-ray powder diffraction. The sample showed poor crystallinity, which is common for CD inclusion complexes, usually due to disorder of the solvent and the guest molecules. However, compared to the X-ray powder patterns of pure βCD and ASA, (Fig. 2), some maxima in the powder diffraction are found at 2θ angles differing from these of the components (at 11.8°, 31.8°, 33.3°, *vide infra*).

Trials to grow single crystals of the inclusion complex from absolute ethanol gave single crystals, but the refinement of the structure

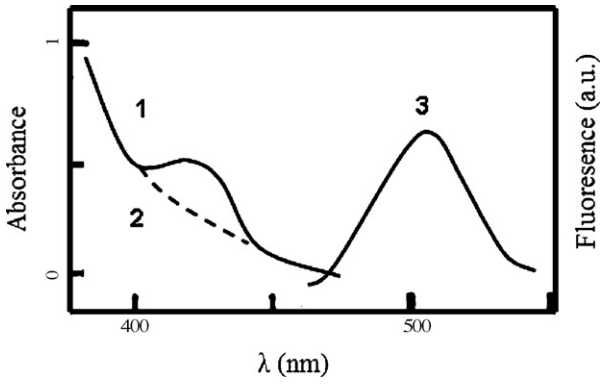


Fig. 1. Spectra of a thin polycrystalline film of ASA: (1) absorption spectrum at room temperature; (2) absorption spectrum at liquid nitrogen temperature; (3) fluorescence spectrum at room temperature (λ_{ex} = 365 nm).

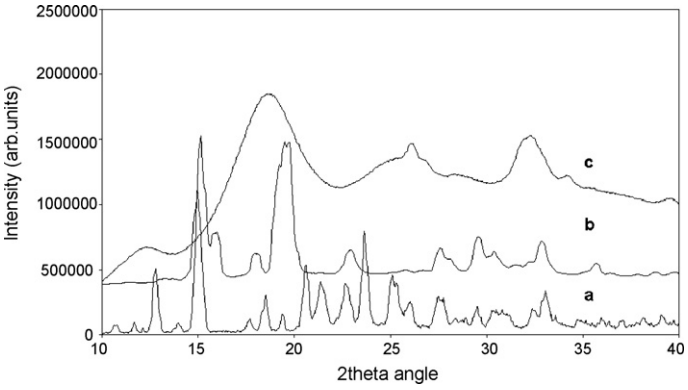


Fig. 2. Powder X-ray diffraction patterns of (a) βCD, (b) ASA, and (c) the complex βCD/ASA.

did not reveal a guest (or any parts of it), thus the structure has been refined as a βCD-ethanol complex. The structure however, differs from any of the three known forms, I–III of the βCD/ethanol inclusion complexes. Form I of the latter is a monomeric complex, isomorphous to the structure of the hydrated βCD itself [16]. Forms II and III are dimeric complexes [17]. In the present case however, the resulting crystals have a unique lattice (Table 1), with two βCD monomers (A and B) in the asymmetric unit having no resemblance to the lattice of βCD dimers [18]. The two βCD monomers associate by their primary hydroxyl groups through four H-bonds (Fig. 3).

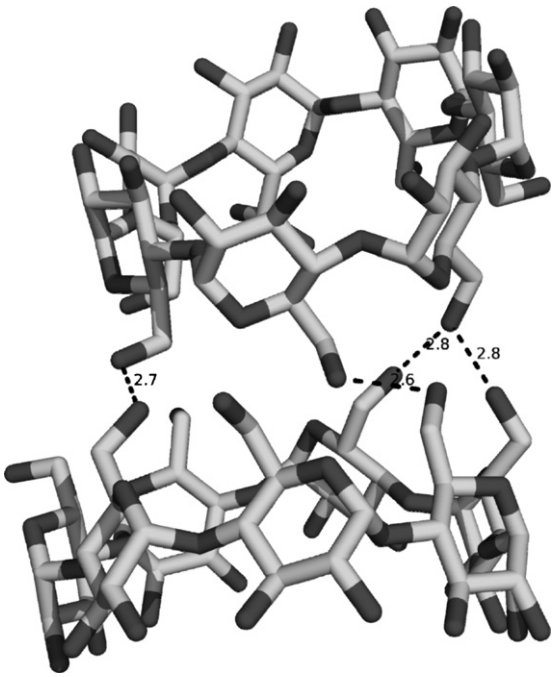


Fig. 3. The two βCD monomers, A (top) and B (bottom), of the asymmetric unit associating at their primary side via H-bonds [19].

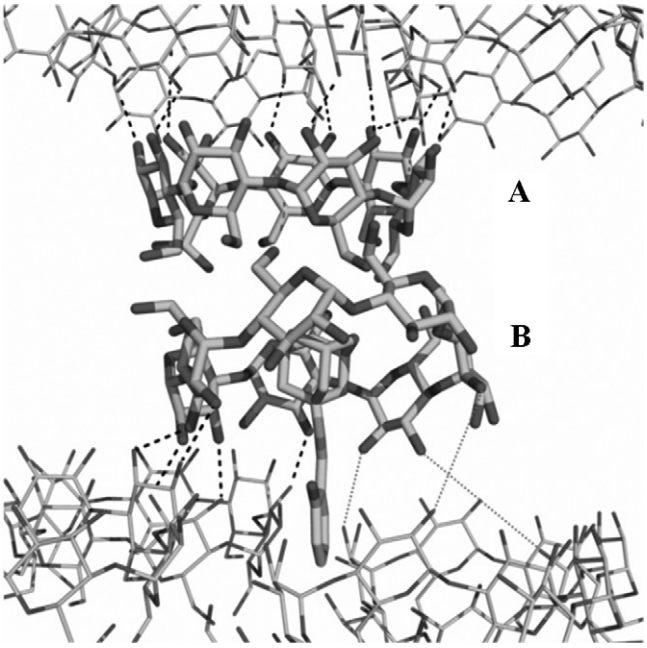


Fig. 4. The βCD A/B dimer in the middle interacts with dimers above and below: the secondary hydroxyls of molecule A form H-bonds with four βCD molecules above, whereas these of molecule B form H-bonds with two βCD molecules below (----), but are far from the remaining two βCD macrocycles (····) [19].

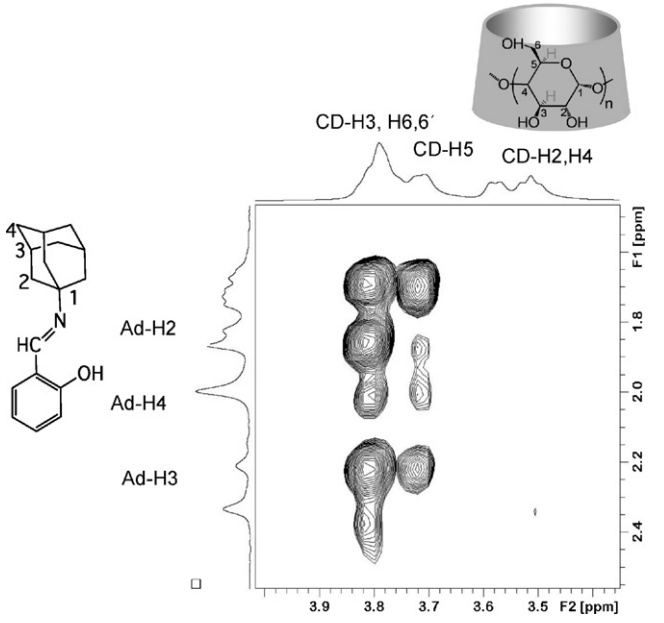


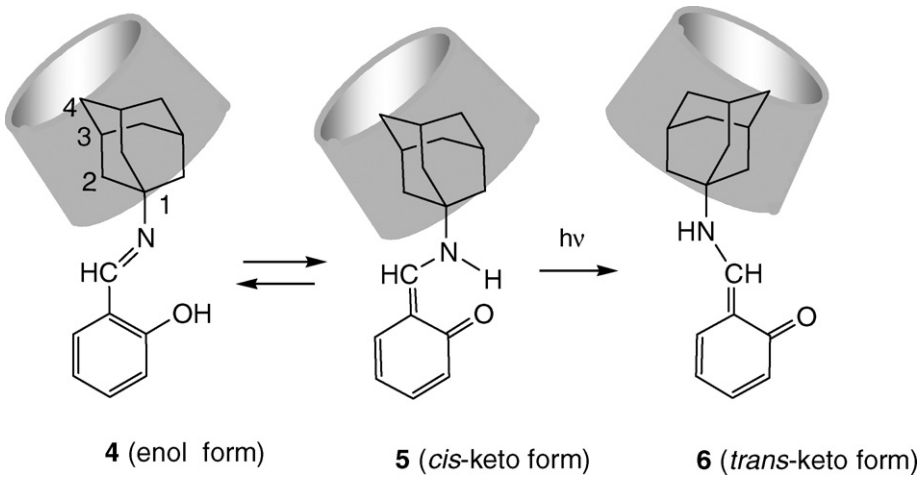
Fig. 5. Partial 2D ROESY NMR spectrum of the βCD/ASA complex in D_2O (protons on βCD: CD-H; on the adamantyl moiety: Ad-H).

The βCD macrocycles, in inclusion complexes with guest(s) that fit entirely into the monomer cavity, have the tendency to dimerise via the secondary hydroxyls forming seven strong H-bonds. The guest molecule promotes dimerisation, (e.g. when aromatic moieties interact inside the elongated cavity of the dimer via π…π interactions). In general, the guest plays crucial role in the formation of the crystal packing [18]. In the present case, ASA contains an adamantyl group, which is known for its high affinity for the βCD cavity. However the remaining salicylidene part is sufficiently hydrophilic and it probably extends outside the cavity of the βCD. If this hypothesis is valid, it is expected that in the crystals of the complex, βCD molecules will be located further apart than in complexes where the entire guest molecule is inside the cavity.

The crystal packing of the present structure supports the above hypothesis (Fig. 4). The secondary hydroxyls of molecule A of the A/B dimer are within H-bond distance with the secondary faces of four βCD molecules above, whereas the secondary face of molecule B in the one side is close to two βCD molecules below forming H-bonds, but it is far from the remaining two (shortest distance 5.91 Å), thus leaving some open space. It was possible to see that an ASA model could be accommodated by fitting it (using the program Coot [13]) in the crystal lattice with the adamantyl group residing inside a βCD cavity and the salicylidene group in the above mentioned open space without any short contacts with the neighboring macrocycles (Fig. 4). Moreover, comparison of the conformations of the two macrocycles showed that the one carrying the adamantyl group (B) is much more deformed than the other (Supplementary Table S1). Therefore, we propose that the βCD/ASA complex was formed and crystallised in absolute ethanol, but ASA was solvolysed during the prolonged heating process at 80 °C (by ethanol or water of crystallisation from βCD used) and the solvolysis products were dissolved in ethanol. However due to the low solubility of βCD in ethanol, the initial crystals were not destroyed, the lattice being preserved by substitution of the guest by several ethanol and four water molecules. The following are in support of the last statement: (a) the peaks not corresponding to the lattice of βCD in the powder diffraction pattern correspond to the lattice parameters of the present structure; (b) that the dimeric Forms II and III of the βCD/ethanol complexes were derived from trials to crystallise complexes of βCD with phenol and benzoic acid [17], which are dimeric, from aqueous solutions containing 50% ethanol, in which βCD is highly insoluble.

Characterization of the yellow crystalline product by NMR spectroscopy supports the above conclusion, i.e. inclusion complex formation. The ^{1}H NMR spectrum of the precipitate dissolved in DMSO revealed that: (i) the ratio βCD/ASA was 1:1, (ii) there was no evidence that ASA had been hydrolysed to its components and (iii) ~20% DMF was present in the precipitate (Supporting Fig. S1). Further, in order to verify inclusion of ASA in the cavity of βCD, the precipitate was placed in D_2O (partially soluble). The ^{1}H NMR spectrum showed clearly the CH=N signal at 8.346 ppm, without simultaneous presence of an aldehyde peak at ~9.0 ppm, indicating that the imine has not been hydrolysed (Supplementary Fig. S2). The adamantyl signals, showing numerous peaks in the region 1.856–1.656 ppm arising from protons at position 2 and at least two peaks owing to protons at position 3 were evidently much dispersed, compared with the signals of the free ASA in DMSO. A 2D ROESY spectrum immediately acquired (Supplementary Fig. S2), revealed strong and clear intermolecular NOE cross-peaks between host and guest signals (Fig. 5). The adamantyl group protons showed interaction with the βCD cavity protons H3 and H5, indicating that this part of ASA is located in the cavity. The aromatic and imino signals did not display any NOE interaction with the host.

Simultaneously, some hydrolysis signals (~20%) were detected due to the fact that ASA remained in the aqueous solution for the duration of the experiment (9 h). In order to ensure that the adamantyl group responsible for the observed interactions does not belong to the hydrolyzed component, 1-adamantylamine, but the anil itself, the same experiment was performed with a fresh sample and under low 2D resolution to conclude the experiment within 1.5 h in order to minimize hydrolysis. No signals corresponding to hydrolysis components were detected at the end in the ^{1}H NMR spectra (i.e. no aldehyde signal at ~9 ppm), whereas the previously observed host–guest cross-peaks were detected, as before. The above show beyond doubt formation of a βCD/ASA inclusion complex with the adamantyl group of ASA embedded in the cavity and the hydroxyphenyl part not included (form **4** in Scheme 3).



Scheme 3. Proposed tautomerization and photochromic transformation in the βCD/ASA complex.

Unlike ASA alone (Suplementary Fig. S3), examination of the βCD/ASA inclusion complex for thermochromic/photochromic properties showed only photochromic behaviour: upon changing temperature in the range 80 °C to liquid nitrogen, no change in colour was observed, whereas upon ultraviolet irradiation (365 nm light), the color turns to orange with simultaneous drop of fluorescence both at liquid nitrogen and room temperature (Suplementary Fig. S4). The latter is due to the isomerisation of the *cis*-keto form, **5**, to the *trans*-keto form, **6**, according to Scheme 3, of the βCD/ASA species, which is a direct proof that ASA is found in a different crystal lattice than its pure crystalline form. Fig. 6 shows the excitation and fluorescence spectra of the βCD/ASA complex at room temperature. The fluorescence spectrum is accompanied by the appearance of two maxima (489 and 506 nm) instead of one (500 nm) in pure crystalline ASA (Fig. 1). This "split" emission may result from two different *cis*-keto form species (**5**) in the excited state brought about by two different environments of the inclusion in the βCD lattice.

Since thermochromism and photochromism in this class of compounds arises from geometrical isomerisations, these properties are sensitive to the surrounding matrix. Thermochromism of the Schiff bases of salicilaldehyde is a property exhibited in the crystalline state. The lattice plays a crucial role in the stabilization of the *cis*-keto form and determines whether the *cis* to *trans* isomerisation (photo-product) can take place. In contrast, thermochromic anils have photochromic behaviour in solutions and in solid solutions (matrices) [14]. As discussed previously, the needed *cis* to *trans* isomerisation (Scheme 2) is not feasible in the crystal lattice of pure ASA, but in the ASA/βCD complex the intervening host forces ASA molecules to be apart from each other. Based on the model given by NMR (half of the ASA molecule outside the cavity) it is expected that the same happens in the crystalline state, given the adamantyl group's affinity for βCD cavity and based on other studies indicating similar structure in the crystalline state and in solution [20,21]. This is suggested also by the single crystal structure determined that shows a deformed macrocycle and an open space between the latter and neighboring macrocycles. Therefore, appearance of photochromism is attributed to the effect of the host lattice that allows for space available to ASA which now can perform the needed *cis* to *trans* isomerisation leading to the photo-product in the crystals, as in the liquid and solid solutions.

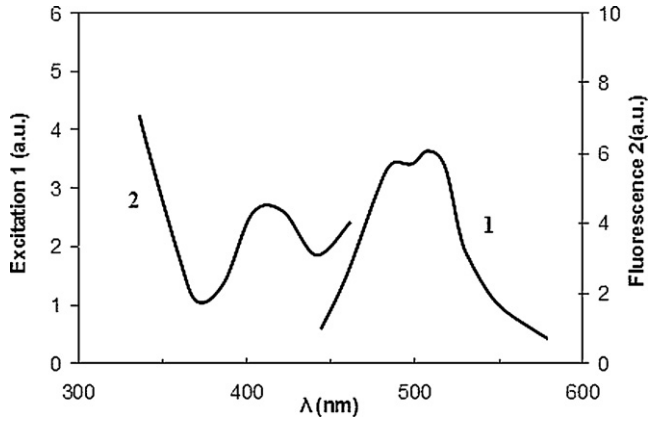


Fig. 6. (1) Fluorescence (λ_{ex} = 365 nm) and (2) excitation spectra (λ_{ex} = 506 nm) of the solid βCD/ASA complex at room temperature.

4. Summary

The communication reports for the first time the inclusion complex of the Schiff base *N*-(1-adamantyl)salicylaldimine (ASA) in β-cyclodextrin, which is followed by the change of its behaviour from thermochromic, as a free crystalline compound, to photochromic when encapsulated in βCD. The resulting complex is a crystalline yellow powder, whose X-ray diffraction pattern fits that of a complex, according to numerous literature examples. NMR spectroscopy is in accord with this result and indicates a host:guest ratio of 1:1. Proof of inclusion of ASA has been given also by 2D NMR spectroscopy experiments in aqueous solution, which show that only the adamantyl moiety of the ASA guest is enclosed into the host cavity, whereas the hydroxyphenyl part is outside. Although X-ray structure analysis of single crystals produced from trials to crystallize the inclusion complex from absolute ethanol did not reveal an enclosed guest, a model of ASA inclusion can be constructed based on the NMR results that justifies this completely novel and unusual lattice. The structural data support strongly the hypothesis that the crystals initially contained ASA, which was subsequently solvolysed during the prolonged crystallisation process at 80 °C and the solvolysis products were dissolved in ethanol, but the initial crystals were not destroyed, due to the low solubility of βCD in ethanol. The study demonstrates that the βCD lattice of the βCD/anil inclusion complex acts as a medium allowing a volume-demanding process like *cis* to *trans* isomerisation to take place and this property may be useful for generating space among molecules in order to control specific properties of appropriately designed systems.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2010.10.022.

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