

Surface interaction and self-assembly of cyclodextrins with organic dyes

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Abstract The interaction of seven novel substituted merocyanine dyes, i.e. 1-methyl-4-[2-(3-methoxy-4-hydroxyphenyl)ethenyl]pyridinium iodide, 1-methyl-4-[2-(3,5-dimethoxy-4-hydroxyphenyl)ethenyl]pyridinium iodide, 1-methyl-4-[2-(4-dimethylaminophenyl)ethenyl]pyridinium iodide, their quinoid forms as well as 1-methyl-4-[2-(3-methoxy-4-oxocyclohexadienylidene)ethylidene]-1,4-dihydropyridine, 1-methyl-4-[2-(3,5-dimethoxy-4-oxocyclohexadienylidene)ethylidene]-1,4-dihydropyridine, with α -CD, γ -CD as well as functionalized γ -cyclodextrin phosphate sodium salt is studied by the methods such as UV–Vis and fluorescence spectroscopy, linear-polarized infrared (IR-LD) spectroscopy of oriented colloids in nematic host, ^1H - and ^{13}C -NMR spectroscopy, HPLC ESI tandem mass spectrometry, scanning electron and tunneling microscopy, powder X-ray diffraction as well as thermal methods. A formation of the 1D and 2D “supramolecular polymers” with nanosizes is found. The dyes are adsorbed on the CDs surface and form a hexagonal microcrystalline sub-structures. Remarkable fluorescence properties depending of the type of the substituent in the dyes, in solid-state are observed.

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Introduction

The optical and nonlinear optical properties (NLO) of organic and polymer materials are currently under intensive study as a result of their importance and variety application for fundamental science, material research, nanotechnology and industry [1–10]. Major research efforts are towards the searching for new molecules possessing large NLO polarizability, as well as controlling molecular orientation to influence bulk properties. Organic molecules, such as quinoid forms of the merocyanine dyes, having conjugated electron systems or low-lying charge transfer (CT) excited states often possess extremely large second-order NLO polarizability [11–16]. However, the enormous potential of these molecules often cannot be utilized because of unfavourable alignment in the crystalline phase. In the case of second harmonic generation (SHG), second-order susceptibility vanishes for centrosymmetric crystals. Many different approaches have been taken to counter this problem. The strategy for using of the chiral molecule ensures formation of a noncentrosymmetric crystal and physically guarantees a non-vanishing of the second-order susceptibility, but not necessarily a large one [11–16]. Another strategy for the tuning of the NLO properties in the bulk is using the host–guest systems with macromolecular matrices, such as cyclodextrins (CDs) [17]. The p-nitroaniline- β -CD inclusion complex generates second harmonic radiation when exposed the 106 μm output of a Nd-YAG laser. The conversion efficiency is 2–4 times higher, that this of an urea, usually used as standard. However, the formation of the inclusion complexes depends on the cavity size of the CDs as well as the reaction conditions. The application of

the stibazolium salts as guest molecules in host–guest systems with cyclodextrins has been used as strategy in crystal engineering for obtaining photodimeric products [17]. The interaction of 4-[(1-methyl-4(1*H*)-pyridinylidene)-ethylidene]-2,5-cyclohexadien-1-one with modified β -CD has led to the formation of the inclusion complex at molar ratio 1:1. The wide application of cyclodextrins and their derivatives in optical and nanotechnologies have already been discussed, thus giving a wide area for future investigations in this respect [18].

Therefore, we have studied in detail the interaction of the seven substituted derivatives of merocyanine dyes with α -, γ -cyclodextrin (α -CD (**1**), γ -CD (**2**)) and the functionalized derivative, γ -cyclodextrin phosphate sodium salt (**2a**) (Scheme S1, supplementary materials s.m.). The synthesized eighteen novel systems are elucidated both in solution and in solid-state by means of methods such as UV–VIS and fluorescence spectroscopy, IR-LD spectroscopy of oriented colloids in nematic host, ^1H - and ^{13}C -NMR spectroscopy, HPLC ESI tandem mass spectrometry, scanning electron microscopy (SEM), scanning tunneling microscopy (STM), powder X-ray diffraction (XRD) as well as thermal methods.

Experimental

Materials and methods

Conventional and polarized IR-spectra were measured on a Thermo Nicolet FTIR-spectrometer (4000–400 cm^{-1} , 2 cm^{-1} resolution, 200 scans) equipped with a Specac wire-grid polarizer. Non-polarized solid-state IR spectra were recorded using the KBr disk technique. The oriented samples were obtained as a colloid suspension in a nematic liquid crystal ZLI 1695. The theoretical approach, as well as the experimental technique for preparing the samples and the procedures for polarized IR-spectra interpretation and the validation of this new linear-dichroic infrared (IR-LD) orientation solid-state method for accuracy and precision has been presented previously [11–16]. The influence of the liquid crystal medium on peak positions and integral

absorbances of the guest molecule bands, the rheological model, the nature and the balance of the forces in the nematic liquid crystal suspension system, as well as the morphology of the suspended particles have also been discussed [11–16].

HPLC–ESI–MS/MS analysis. The analyses of the samples were performed with a Thermo Finnigan surveyor LC-Pump. Compounds were separated on a Luna C18 column (150 \times 2 mm, 4 μm particle size) from Phenomenex (Torrance, CA, USA). The mobile phase consisted of water + 0.1% HCOOH (A) and acetonitrile + 0.1% HCOOH (B) using a gradient program presented in Table 1. The compound was detected via UV and a TSQ 7000 (Thermo Electron Corporation, Dreieich, Germany) mass spectrometer. The spectra were obtained using the TSQ 7000 equipped with an ESI ion source and operated with the following conditions: capillary temperature 180 $^{\circ}\text{C}$; sheath gas 60 psi and spray voltage 4.5 kV. 1 mg/ml of the sample was dissolved in acetonitrile and injected into the ion source by an auto sampler (Finnigan Surveyor). The data were processed by using the Excalibur 1.4 software.

^1H - and ^{13}C -NMR measurements, referenced to sodium 3-(trimethylsilyl)-tetradeuteriopropionate, were made at 298 K with a Bruker DRX-400 spectrometer using 5 mm tubes and D_2O as solvent.

Electronic (UV–Vis) and fluorescence spectra were recorded on a Tecan Safire Absorbance/Fluorescence XFluor 4 V 4.40 and Evolution 300 spectrophotometers, operating between 190 and 900 nm, both in the solid state and in solution at a concentration of 2.5×10^{-5} M, using 0.0921 cm quartz cells.

The *thermal analyses* were performed in the range of 300–500 K on a Differential Scanning Calorimeter Perkin-Elmer DSC-7, and a Differential Thermal Analyzer DTA/TG (Seiko Instrument, model TG/DTA 300). The experiments were carried out at a scanning rate of 10 K/min under an argon atmosphere.

The *elemental analysis* was carried out according to the standard procedures for C and H (as CO_2 , and H_2O) and N (by the Dumas method).

SEM experiments were performed on A HITACHI S-3500 N instrument.

Table 1 UV–VIS spectra of the systems studied in solution

CDs/dyes	λ (nm), (ϵ_v [$\text{L mol}^{-1} \text{cm}^{-1}$])						
	Dye-1a	Dye-1b	Dye-1c	Dye-1d	Dye-1e	Dye-2	
α -CD	384 (10345) 466 (982)	269 (11231) 321 (1021)	391 (12561)	481 (1132)	380 (1456)	421 (1672)	413 (2351)
γ -CD	270 (14567) 282 (2318)	288 (11341) 311 (789)	290 (13461)	315 (1267)	286 (11345) 320 (1321)	288 (16781) 350 (1345)	382 (1871)
Funcionalized γ -CD	361 (1011)	345 (1356)	277 (992)	318 (1172)	360 (1892)		425 (2341)

Scanning tunneling microscopy (STM) experiments were performed by using an Easyscan STM System with a Pt-Ir tip fabricated by Nanosurf AG of Switzerland and carried out with a sample bias voltage of +400 mV.

X-ray powder diffraction (XRD) patterns were obtained using a Rigaku MiniFlex powder diffraction system, equipped with a horizontal goniometer in the $\theta/2 - \theta$ mode (Tokyo, Japan). The X-ray source was nickel-filtered K- α emission of copper (1.54056 Å). Samples were packed into an aluminum holder using a back-fill procedure and were scanned over the range of $50-6^\circ 2 - \theta$, at a scan rate of $0.5^\circ 2 - \theta/\text{min}$. Using a data acquisition rate of 1 point per second, the scanning parameters equate to a step size of $0.0084^\circ 2 - \theta$. Calibration of each powder pattern was effected using the characteristic scattering peaks of aluminum at 44.738 and $38.472^\circ 2 - \theta$.

Theoretical calculations

Quantum chemical calculations were performed with the GAUSSIAN 98 and Dalton 2.0 program packages [19, 20]. The output files are visualized by means of the ChemCraft program [21]. The geometries were optimized at the second-order Moller-Pleset perturbation theory (MP2) level, using the 6-31++G** basis set. The molecular geometries of the studied species were fully optimized by the force gradient method using Bernys' algorithm. For each structure, the stationary points found on the molecule potential energy hypersurfaces were characterized using standard analytical harmonic vibrational analysis. The absence of imaginary frequencies (i.e., negative eigenvalues of the second-derivative matrix) confirmed that the stationary points correspond to minima on the potential energy hypersurfaces. The calculated vibrational frequencies and infrared intensities were checked to establish which kind of performed calculations agreed best with the experimental data. The MP2/6-31++G** data are presented in the result and discussion part of the manuscript, where a modification of the results using the empirical scaling factor 0.8929 is made to achieve better correspondence between the experimental and the theoretical values. The UV spectra of the compound in the gas phase and in aqueous solution are obtained by CIS/6-311++G** and TDDFT calculations.

Synthesis

The **Dye-1a-e** was obtained by the synthetic scheme shown in [11–16]. The 1-butyl-4-[2-(4-dimethylaminophenyl)ethenyl]pyridinium chloride (**Dye-2**) was synthesized by mixing of the 2.35 g (10.0 mmol) 1-butyl-4-methylpyridinium chloride and 1.22 g (10.0 mmol) 4-dimethylaminobenzaldehyde in 50 ml toluol. In addition 0.77 g (10.0 mmol) of ammonium acetate was also added under

continuous stirring and heating at 40 °C for 24 h. After leaving to stand, red crystals were obtained from the resulting red solution and were filtered off and dried under air. (Found: C, 72.08; H, 7.80; N, 8.92; $[\text{C}_{19}\text{H}_{25}\text{N}_2\text{Cl}]$ calcd.: C, 72.02; H, 7.95; N, 8.84%). The HPLC ESI MS–MS data show a formation of one reaction product with peak at abundance time of 11.2 min. The most intensive signal in the positive mass spectrum is that of the peak at m/z 281.77, corresponding to the singly charged cation $[\text{C}_{19}\text{H}_{25}\text{N}_2]^+$ with a molecular weight of 281.47. The TGV and DSC data in the temperature range of 300–500 K showed an absence of the included solvent molecules. $^1\text{H-NMR}$ data: $\delta = 3.44, 2.21, 2.20, 1.59$ ppm (t, 2H, m, 4H, t, 3H, N- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), AA'BB' signals $\delta_{\text{AA}'}, 6.44, 2\text{H}, \text{H-2}', \text{H-6}'$, $\delta_{\text{BB}'}, 7.18, 2\text{H}, \text{H-3}', \text{H-5}'$; AB-signals 6.55 1H, H-8, 7.41 1H, H-7, $^3J_{\text{AB}} = 17.0$ Hz, AA'BB' signals $\delta_{\text{AA}'}, 7.55, 2\text{H}, \text{H-2}, \text{H-6}, \delta_{\text{BB}'}, 8.11$ ppm, 2H, H-3, H-5. $^{13}\text{C-NMR}$ data: $\delta = 46.33, 35.1, 30.22, 31.2$ (N- $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 115.11 (d, C-7), 120.88 (d, C-3', C-5'), 122.55 (s, C-1'), 122.69 (d, C-3, C-5), 132.33 (d, C-2', C-6'), 143.99 (d, C-2, C-6), 145.18 (d, C8) and 155.81 ppm (s, C-4).

The “supramolecular polymers” of the CDs with the dyes were obtained after mixing of the equimolar amounts of each of the components in 20 mL aqueous solutions under continuous stirring and heating at 40 °C for 20 min. The obtained solutions rest at normal conditions for 2 weeks. The corresponding polymers, thus obtained (Fig. 1) were filtered off and dried on air at room temperature. In these conditions the interaction of the dyes with β -CD leads to a faster crystallization of the β -CD, which known structure was confirmed by single crystal X-ray diffraction.

Results and discussion

The electronic spectra of the α -CD and γ -CD displays “transparency” in the whole range within 200–800 nm, whereas the corresponding γ -cyclodextrin phosphate sodium salt is characterized with a band (262 nm, $\epsilon = 1189$ L mol $^{-1}$ cm $^{-1}$) originated of $n \rightarrow \pi^*$ transition of the P=O group (Fig. 2a and b). The corresponding UV–VIS spectra of the starting dyes are characterized with the CT bands within 390–500 nm with the ϵ_v values of 2000–5700 L mol $^{-1}$ cm $^{-1}$ (Fig. 2c). The observed sub-component bands is a result of the presence of monomeric dye and dimeric H-type aggregates [17, 22, 23]. The UV–VIS spectra both in solution and in solid-state show a disappearance of the CT bands, typical for the monomeric species (Fig. 2a).

The molecular status of the systems α -CD-dye is examined using solid-state fluorescence measurements (Fig. 3). The corresponding measurements in solution are also performed. Both in both condense phases the systems are characterized with same properties. Charge transfer emission of solids was

Fig. 1 Microscopic photographs of α -CD/(Dyes-1a–Dyes-1c) systems under UV-irradiation as well as of γ -CD/Dye-2 and functionalized γ -CD/Dye-2 (Dye-2a)

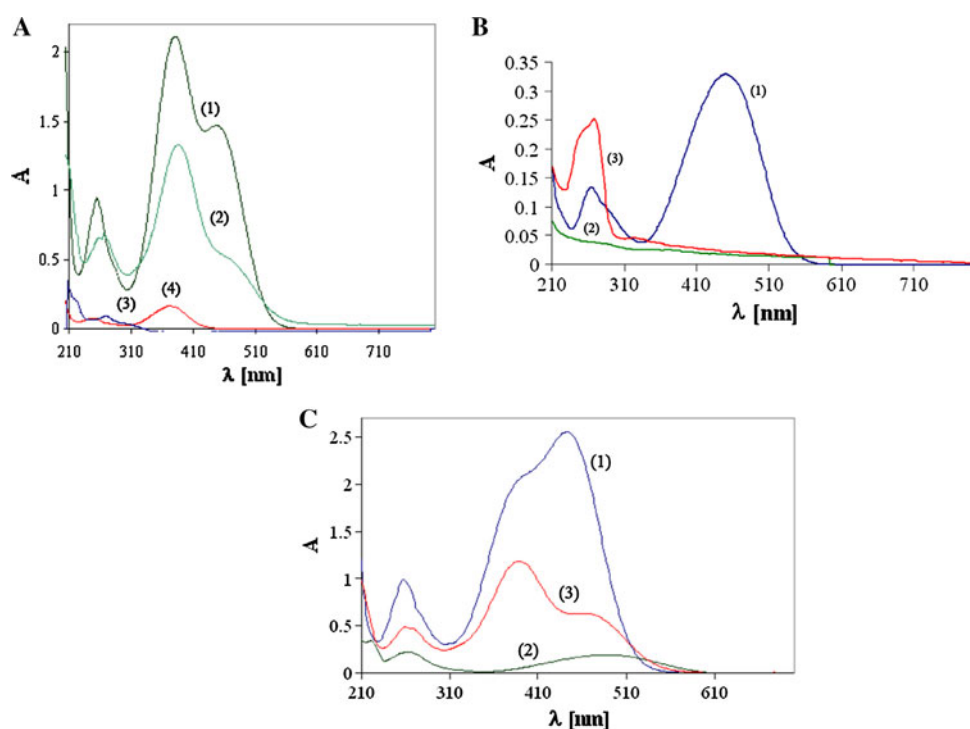
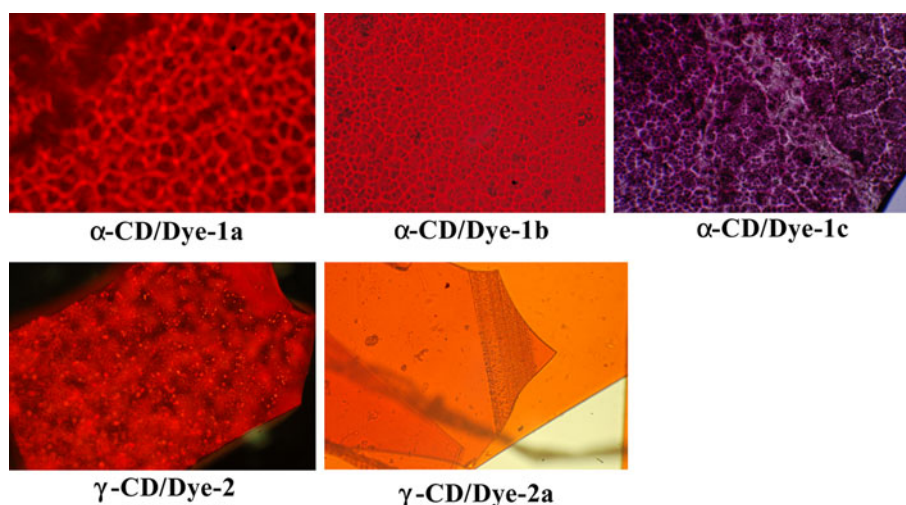


Fig. 2 a UV–Vis spectra of systems α -CD/Dye-1a (1), α -CD/Dye-1b (2), α -CD/Dye-1c (3) in solution, Solid-state UV–Vis pectrum of α -CD/Dye-1a (4); b of the 1-butyl-4-[2-(4-dimethylaminophenyl)ethenyl]pyridinium chloride (Dye-2) (1), γ -CD/Dye-2 (2) and functionalized γ -cyclodextrin phosphate sodium salt/Dye-2 (3); c UV–Vis spectra of the pure Dyes-1a–Dyes-1c, i.e. 1-methyl-4-[2-(3-methoxy-

4-oxocyclohexadienylidene)ethylidene]-1,4-dihydropyridine (1); 1-methyl-4-[2-(3,5-dimethoxy-4-oxocyclohexadienylidene)ethylidene]-1,4-dihydropyridine (3) and 1-methyl-4-[2-(4-dimethylaminophenyl)ethenyl]pyridinium iodide (3) in aqueous solution at $2.5 \cdot 10^{-5}$ mol/L concentration and 1-cm quartz cell

shown at 525, 543 and 580 nm, respectively. These results suggest that the observed shift in the fluorescence peak could be due to the specific properties of the systems. The compounds possess solid-state fluorescence properties, untypically for each of the starting materials [24].

The performed quantitative determination of the components in the α -CD-dye systems, using the standard linear plot method, show that in all cases the molar ratio 1:1 (Fig. S1,

s.m.). According to previous investigations the dye-cyclodextrin interaction often leads to a formation of the inclusion complexes with the same molar ratio [5–8, 25–28]. However our mass spectrometric data show only the peaks at m/z of the pure CDs (Fig. S2, s.m.), thus indicating only the weak Van der Waals interactions between the CDs and the dyes, which is in contrast to cases, where the inclusion complexes are obtained.

Fig. 3 Fluorescence spectra of α -CD/**Dyes-1a** (red line (1)), α -CD/**Dyes-1b** (blue line (2)) and α -CD/**Dyes-1c** (green line (3)) systems in solid-state; Photographs of the systems without and under UV-irradiation, show the effect of the UV-light on their fluorescence properties

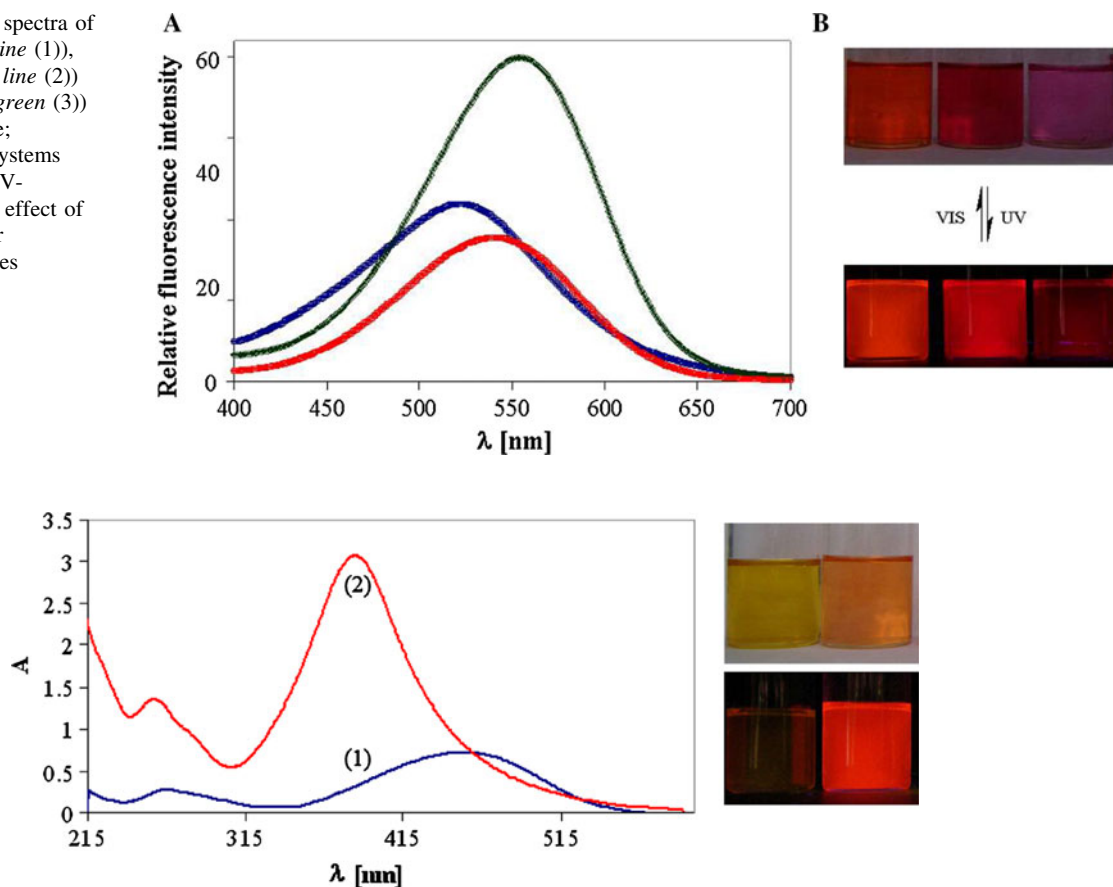


Fig. 4 UV-Vis spectra of the systems γ -CDs 1-butyl-4-[2-(4-dimethylaminophenyl)ethenyl]pyridinium chloride with γ -cyclodextrin (**Dye-2**) (1) and its functionalized derivative (**Dye-2a**) (2) in aqueous

solutions with concentration 2.5×10^{-4} mol/L and quartz cell with thickness of 1 cm; Photographs of the systems **Dye-2** and **Dye-2a** without and under UV-irradiation

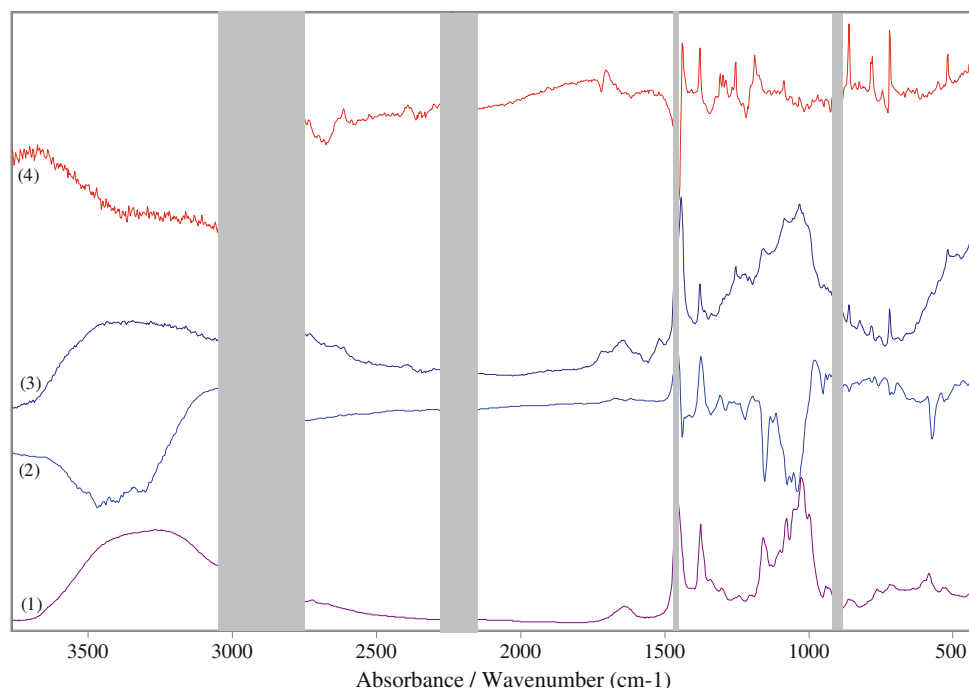
The **Dye-2** is characterized with absorption bands 266, 287 and 451 nm belonging to K- and B- bands of the aromatic (pyridyl- and phenyl-) fragments as well as the CT band (Fig. 4). The corresponding ϵ values are 12 341, 2455 and 7351 L mol⁻¹ cm⁻¹, respectively. The data are in good agreement also with the theoretical electronic spectrum of the dye in aqueous solution, obtained by means of calculations at TD-DFT level of theory, giving bands at 260, 285 and 450 nm, respectively.

The UV-Vis spectra of the complexes of the **Dye-2** with the two γ -CDs studied show that their interaction leads to a bathochromic shift of 32 nm of the CT band in the first case, accompanied with the hypochromic effect of 800 L mol⁻¹ cm⁻¹ in the **Dye-2** system. On the contrary, the system-modified γ -CD/**Dye-2** (**Dye-2a**) is characterized with the hypsochromic effect of 64 nm for the CT band. On the other side only the system **Dye-2** is characterized with the fluorescence properties in the solid state giving a band at 493 nm [24]. We performed for the purpose a quantitative determination of the organic dye in the two complexes using the standard linear plot method. Independently from the fact that the synthesis of the complexes is obtained at molar ratio

cyclodextrin:dye 1:1, the quantitative analysis shows that the ratio of the γ -CD:dye in the system **Dye-2** is 1:1.33, whereas in the second system (**Dye-2a**) the ratio of 1:1 is obtained. This means that part of the γ -CD rests non-reacted with the system during the interaction of the γ -CD with the dye. This result raised the questions about identifying the form with the excess of the organic dye in the complex with γ -CD, as well as whether and to what extent the obtained fluorescence properties are affected? Additional experimental data are required in order to answer these questions. The electronic spectra of the systems studied are summarized in Table 1.

The self-assembly of the CDs in the presence of the dyes is studied by the IR-LD spectroscopy of oriented colloids (s.m.). The comparison between the data of the pure CDs and those of corresponding systems CDs-dyes is performed. In addition the theoretical quantum chemical calculations of the vibrational properties of -butyl-4-[2-(4-dimethylaminophenyl)ethenyl]pyridinium cation are performed (s.m.). The obtained data show that in the pure CDs, a reasonable degree of macro orientation of suspended CDs is observed, as a result of the layers of herringbone-like motifs, typical for crystalline compounds

Fig. 5 Non-polarized IR-spectra of γ -CD (1), γ -cyclodextrin phosphate sodium salt (3); Difference IR-LD spectra of γ -CD (2) and γ -cyclodextrin phosphate sodium salt (4)



(Fig. 5). In contrast, the difference IR-LD spectra of the CDs-dyes systems are characterized with series of positive and negative IR-bands, belonging to the included molecule of the dyes, whereas the IR-bands of the CDs are eliminated. These data show that the herringbone-like structure of the CDs is distorted.

In order to compare the thermal stabilities of the systems CDs-dyes the thermal analysis is performed. The “complexes” started to lose weight at 388 °C (α -CD/Dye-1a), 344 °C (α -CD/Dye-1b) and 413 °C (α -CD/Dye-1c), and at about 500 °C they lost within 32–66%, of their original weights. DTA experiments are performed and they indicated that the systems display exothermic peaks within 265–344 °C. The “complexes” γ -CD/Dye-2 and modified γ -CD/Dye-2, started to lose weight at 300 and 321 °C, respectively. About 500 °C they lost 44 and 72%, respectively, of their original weight. DTA experiments were performed and they indicated that the γ -CD/Dye-2 system displays an exothermic peak at 312 °C and a weak exothermic peak at 213 °C. A clear-cut exothermic peak at 431 °C was obtained for the system Dye-2a.

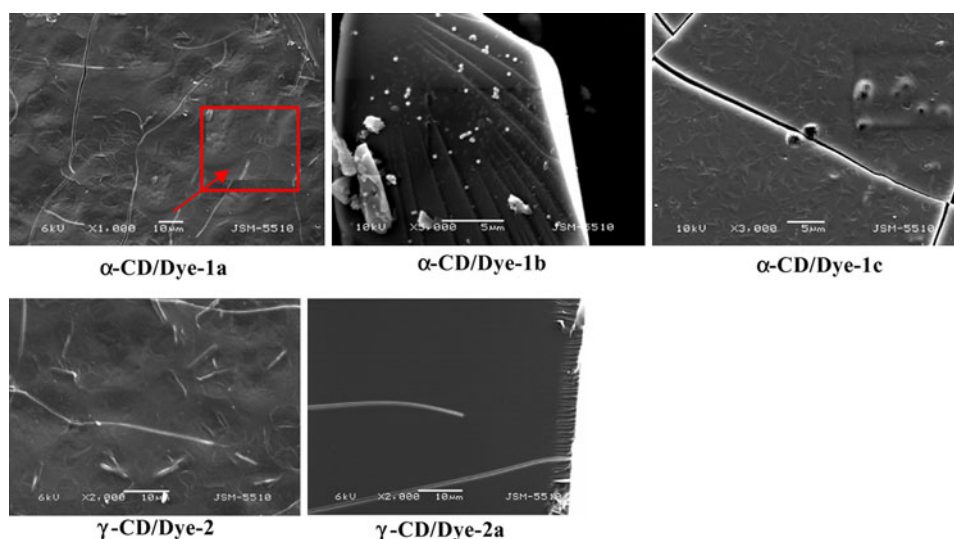
In order to compare the surface morphologies of the systems studied, as well as for the starting materials, the SEM experiments are performed. The SEM images in Fig. 6 gave the hexagonal “printing” macrostructures information as well as underlined sheet structures of all of the systems studied [24].

Obviously, difference in surface morphologies of the α -CD and the systems α -CD-dye indicated that the presence of the macrostructures or the self-assembly of the host. Moreover, regular hexagons are observed in the SEM

image in Fig. 6, which could be interpreted in support of the presence of microcrystallines of the dye. These data corroborate with the spectroscopic findings (vide supra), indicating the presence of excess of the dye in the system. Comparing the data for corresponding pure γ -CDs and treated with the dyes systems, the surfaces of the systems Dye-2 and Dye-2a are different (Fig. 6). Such difference in surface morphologies indicated that the presence of the 1-butyl-4-[2-(4-dimethylaminophenyl)ethenyl]pyridinium chloride changed the macrostructures or the self-assembly of the CDs studied.

In order to elucidate this phenomenon we are preformed the powder X-ray diffraction experiment. The obtained reflections in the XRD patterns (Fig. S7, s.m.) are similar to those of corresponding dyes. They indicate that some differences are observed in the presence of α -CD but the small amount of the excess of the dye is characterized with the ordered microcrystalline structure. The formation of the 2D supramolecular structure of the α -CD is accompanied with the parallel crystallization of the dye on the surface.

The obtained reflections appearing at 2θ 20.1° (3.21 Å), 22.6° (3.10 Å) and 31.1° (2.13 Å) in the XRD pattern in Fig. S7 (s.m.) are similar to those of the 1-butyl-4-[2-(4-dimethylaminophenyl)ethenyl]pyridinium chloride at 2θ 20.3° (3.66 Å), 22.2° (3.00 Å) and 36.2° (2.48 Å). They indicate that some differences are observed in the presence of γ -CDs but the small amount of the excess of the dye is characterized with the ordered microcrystalline structure. This result is in accord with the proposed statement that the excess of the dye in the system Dye-2 is microcrystallines. The formation of the changed macrostructure of the CD in

Fig. 6 SEM images of systems studied

the system **Dye-2** is accompanied with the parallel crystallization of the dye on the surface of the γ -CD complex.

STM is a convenient and widely employed method for the elucidation of the certain microstructures of the supramolecular aggregates. Visualization of the STM experiments of the complexes was also performed. A nanometer-sized molecular wire with the size of ca. 10–15 nm is seen. The STM images provide direct evidence for the formation of the 2D supramolecular pseudo polymer structure in all of the systems. A nanometer-sized molecular wire with the size of ca. 5–10 nm is seen for the systems γ -CD/**Dye-2** and functionalized γ -CD/**Dye-2a** systems (Fig. S8, s.m.).

Conclusions

In conclusion, we could draw that the interaction of substituted 4-[(1-methyl-4(1*H*)-pyridinylidene)-ethylidene]-2,5-cyclohexadien-1-one and 1-butyl-4-[2-(4-dimethylaminophenyl)ethenyl]pyridinium chloride with α -CD, γ -CD as well as functionalized γ -cyclodextrin phosphate sodium salt, leads to the following results: (i) The interaction of substituted 4-[(1-methyl-4(1*H*)-pyridinylidene)-ethylidene]-2,5-cyclohexadien-1-one with smaller α -cyclodextrin from leads to formation of 2D nanosize “supramolecular polymers”. The dyes are adsorbed on the CD surface and form a hexagonal microcrystalline sub structures. Molar ratio α -CD:dye is 1:1. Nanometer-sized molecular wires in the 2D structure are with approximately 10–15 nm lengths. Fluorescence properties in solid-state are observed at 525, 543 and 580 nm, respectively, depending of the type of the substituent in the dyes. (ii) The interaction of γ -CD and its phosphate sodium salt with 1-butyl-4-[2-(4-dimethylaminophenyl)ethenyl]pyridinium chloride leads to the formation of “supramolecular polymers” of both γ -CDs with the molar

ratio of the cyclodextrin:organic dye 1:1.33 and 1:1, respectively. Nanometer-sized molecular wire with approximately 5–10 nm length was obtained for both systems studied. The excess of the dye in the first case form hexagonal microcrystalline structures on the “supramolecular polymers”. Remarkable fluorescence properties at 412 nm in the system γ -cyclodextrins/dye are detected, which are not present in the corresponding pure γ -CD and in 1-butyl-4-[2-(4-dimethylaminophenyl)ethenyl]pyridinium chloride, both in solution and in the solid-state.

Supporting information

Supporting information includes the linear dependency data for standard solutions, mass spectrometric data, linear polarized spectroscopic data; theoretical quantum chemical calculations, powder X-ray diffraction data and STM, respectively.

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