

Raman spectroscopy is a convenient technique for the efficient evaluation of cyclodextrin inclusion molecular complexes of azo-dye colorants and largely polarisable guest molecules

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Abstract Raman spectroscopy has been successfully employed in order to investigate the formation of β -cyclodextrin host–guest inclusion molecular complexes with several different azo-dye structures. The Raman pattern of the carbohydrate framework results negligible when neared to the magnificent intensity of the highly polarisable guest systems and a complete and feasible comparison of the spectral features between the free and the complexed situation of the guest molecule is allowed. In general, with respect to the free guest state, it was found within the complex that a hampering of Raman intensity displays, accompanied by a levelling directed variation of the relative peak intensities, and peculiar Raman peak broadening with shifts occur, relatable to the host–guest settling of inclusive intermolecular interactions. Supportively to the other commonly established characterising methods, or in valid alternative, Raman technique has proved astoundingly useful under the perspective of the diagnostic evaluation of cyclodextrin host–guest molecular inclusion for azo-dyes

and, more generally, for a highly polarisable guest structure. It features sample non-destructivity, handiness, fastness and sensitive reproducibility, occasionally providing useful suggestions about the complexation topology.

Keywords β -Cyclodextrin · Azo-dyes · Host–guest inclusion phenomena · Raman spectroscopy

Introduction

Inclusion of molecules within large hosting cavities favours the expansion of the potential appliances for the included guest structures [1]. In particular, host–guest molecular complexation of hydrophobic molecules within the polar cyclodextrins [2] provides an outer hydrophilic surface that determines an evident solubility for such systems in polar solvents, such as water, becoming therefore essential in many technical and industrial processes, such as phase transfer catalysis [3], drug delivery [4], textile finishing [5].

However, the reliable assessment of the actual molecular inclusion within hosting cavities is of course ineludibly the eligible topic point in the aim of validating all these chemical routes. In general, confirmation of molecular complexation provided by cyclodextrin usually relies on both solution and solid-state spectroscopy and structural techniques. Primarily, both the solution and the solid state Cross-Polarization Magic Angle Spinning Nuclear Magnetic Resonance (NMR and CP MAS NMR) spectroscopy [6, 7], the Thermo Gravimetric Analysis and Differential Thermal Analysis (TGA-DTA) methods [8, 9], the X-ray Powder Diffraction (XRPD) [10] and a documented library of vibrational IR and Raman spectroscopy [11, 12] are successfully profited in complexing detection.

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In the vibrational context, the extreme electron polarisability of several potential guest apolar molecules that are easily included within the lipophilic cyclodextrin cavities can select these substrates as highly responsive targets for Raman spectroscopy. On the converse, the more modest polarisability of a carbohydrate frame is expected to provide a correspondingly more modest, or even comparably negligible, Raman activity [13].

In this paper, we report on an experimental study of assessment of complex molecular inclusion performed by β -cyclodextrin (β CD) of 12 different disperse azo-dyes (listed in Table 1) by mean of high-resolution solid state Raman spectroscopy. Spectroscopic results illustrated clearly variations of the vibrational features of structures as a consequence of the interactive modifications occurring after complex inclusion [14], with an extremely sensitive

responsiveness, that is comparable or even superior to the spectral responses available by the other commonly used techniques. In detail, the relative Raman transparency of cyclodextrinic host frame focused therefore Raman information exclusively on the highly active guest molecule, evidencing usefully the complete spectral comparison between the free and the complexed situation. In addition, the vibrational data provision by Raman method is featured by non-destructivity of the examined samples, combined with actual measurement fastness and handiness, and reproducible sensitiveness of observed responses.

Experimental section

Materials and methods

β -cyclodextrin (Cawamax W7 Pharma sample) was supplied by Wacker-Chemie Ltd (Burghausen, Germany). Azo-dyes ((1)–(12) labels of Table 1) were synthesised and characterised in accordance to established literature methods [15–30]. Detailed description of dye application with cyclodextrin are reported elsewhere [30–32]. β -cyclodextrin/dye molecular inclusion complexes (ICs) were formed experimentally by solid-state reaction of 2:1 cyclodextrin/guest molar mixtures, promoted mechanically by a multi-step ball-milling procedure (24 h total reaction time) [3, 33]. Crude products were used without further purification. With these experimental conditions, systematic TGA-DTA [3] supported by XRPD control measurements excluded the presence of the free dye after milling. Cyclodextrin excess extent is not excluded [30]. Ethanol was purchased by Fluka (Buchs, Switzerland). Dyes with different crystalline morphologies were obtained from the quiet or rapid (within Ar stream) evaporation of ethanol solution.

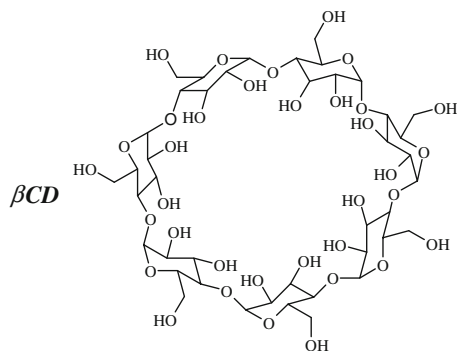
Instrumental measurements

High-Resolution Raman Spectra were collected on a Fourier-transformed Bruker RFS100 spectrophotometer, equipped with a Nd:YAG laser, emitting at 1.064 μm (NIR region), as the excitation source, and a liquid-nitrogen cooled Ge detector. Instrumental resolution was set at 1 cm^{-1} . Samples powders were systematically irradiated within Raman-inert common laboratory glass pipes. Low laser power was maintained constant at 50 mW throughout all measurements. 500 averaged scans were acquired for each spectrum. At such experimental setting, each single measurement lasted ca. 50 min. No final materials decomposition was observed when recovering each matter after Raman laser irradiation.

Table 1 Chemical description of the twelve ((1)–(12)) examined disperse colorant azo-dye guest molecules (*above*) included within the host cavity of β -cyclodextrin (*below*). Related azo-dye referencing is listed

Azo-Dye

Molecule	R ₁	R ₂	Reference
(1)	–NO ₂	–CN	[15–17]
(2)	–NO ₂	–OH	[16, 18–20]
(3)	–NO ₂	–H	[16, 20, 21]
(4)	–OMe	–CN	[16, 22]
(5)	–OMe	–OH	[22]
(6)	–OMe	–H	[22–24]
(7)	–CN	–CN	[16]
(8)	–CN	–OH	[25]
(9)	–CN	–H	[16, 24, 26]
(10)	–H	–CN	[16, 17, 22]
(11)	–H	–OH	[16, 20, 27]
(12)	–H	–H	[22–24, 28, 29]



X-ray Powder Diffraction (XRPD) diffractograms were acquired on a Thermo ARL 'Xtra instrumentation, equipped with a 1.540562 Å $K_{\alpha 1}$ Cu X-ray radiation source (operating at 45 kV voltage and 40 mA current), in the $2 < 2\theta < 100$ degree interval, at a 2.5 $2\theta/\text{min}$ scan rate.

Thermo Gravimetric Analysis (TGA) and Differential Temperature Analysis (DTA) simultaneous measurements were recorded on a TA Instruments TGA-DTA SDT 2960 device, within the 25–350 °C temperature range (N_2 atmosphere, 10 °C/min heating ramp).

Results and discussion

Results of the comparison between the 2:1 cyclodextrin\azo-dyes milled products containing the complexes and the respective free precursor molecules are reported for the several different examined species. Observed spectral trends were collected consistently for all the examined systems; an illustrative representative selection is presented hereafter.

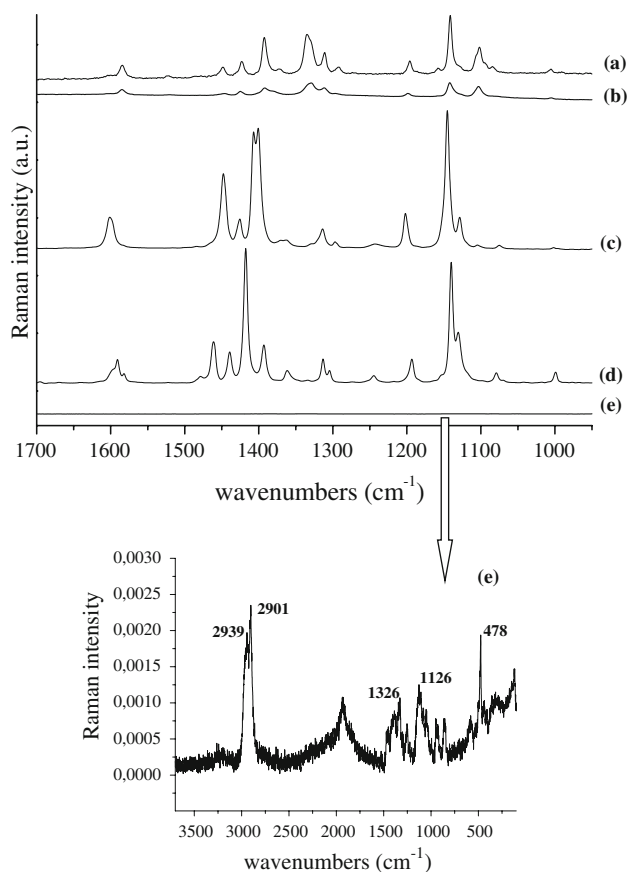


Fig. 1 Raman spectra of (1) (a), (2) (b), (4) (c) and (10) (d) azo-dyes guest molecules and β CD host (e), with the actual achieved experimental relative intensities at the operative conditions. The expansion below shows the magnification of β CD pattern (e) at the reported instrumental conditions

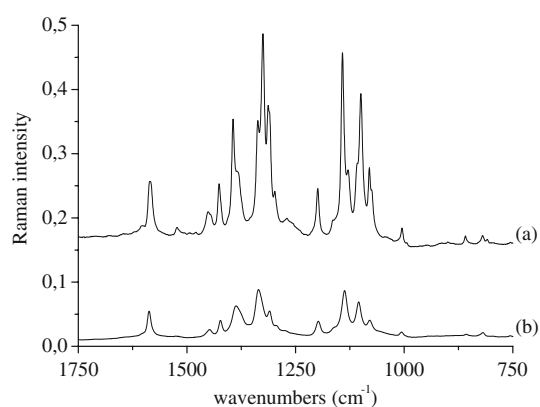


Fig. 2 Raman spectra of (3) (a) and β CD(3) inclusion complex (b). The actual achieved experimental relative intensities are reported

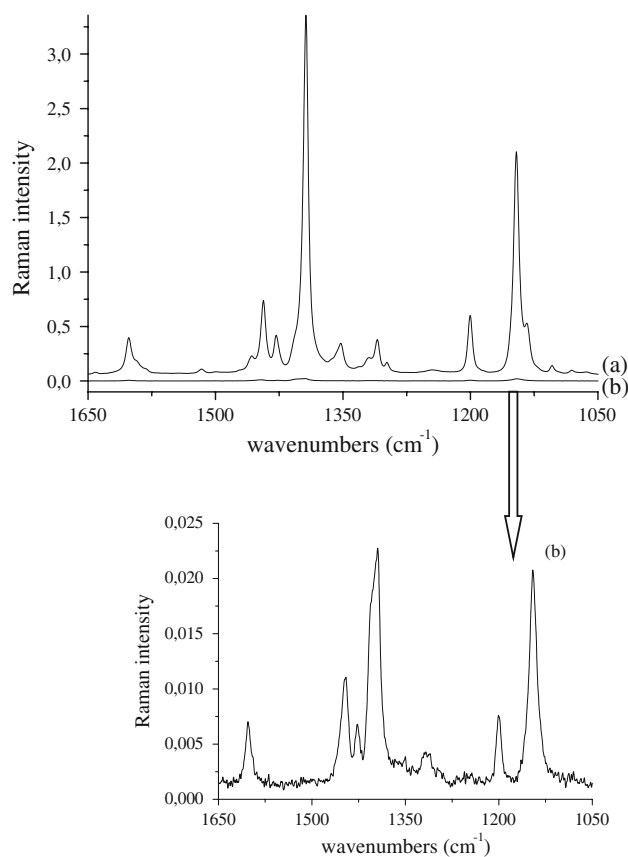


Fig. 3 Raman spectra of (5) (a) and β CD(5) inclusion complex (b). The actual achieved experimental relative intensities are reported. The expansion below shows the magnification of β CD(5) pattern (b)

Primarily, Raman spectrum intensity of the β CD within all the entire typical extension (i.e., 4000–100 cm^{-1}) is actually negligible when confronted with that of the free azo-dyes guest molecules. The markedly different electron α molecular polarisability, responsible of Raman activity, [34–36] discriminates the highly divergent strong and weak relative spectral intensities between the apolar unsaturated

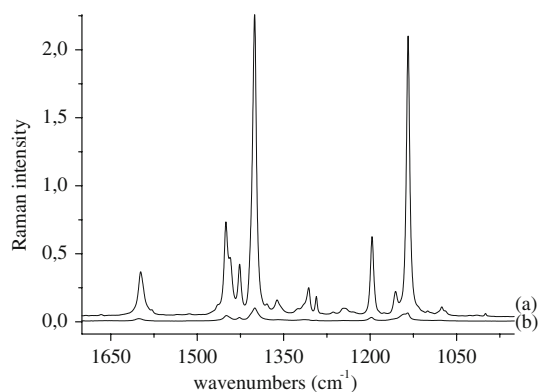


Fig. 4 Raman spectra of **(6)** (a) and β CD\(**6**) inclusion complex (b). The actual achieved experimental relative intensities are reported

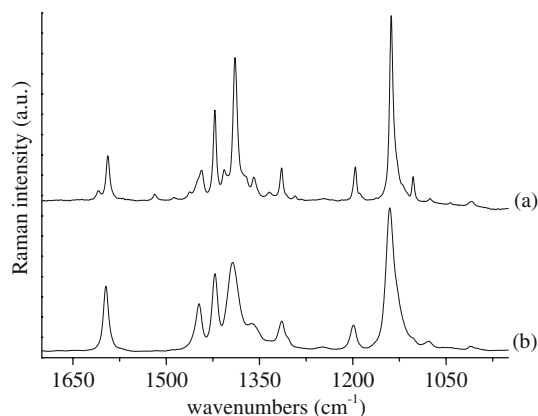


Fig. 5 Raman spectra of **(7)** (a) and β CD\(**7**) inclusion complex (b). Relative experimental spectral intensities have been scaled for comparison

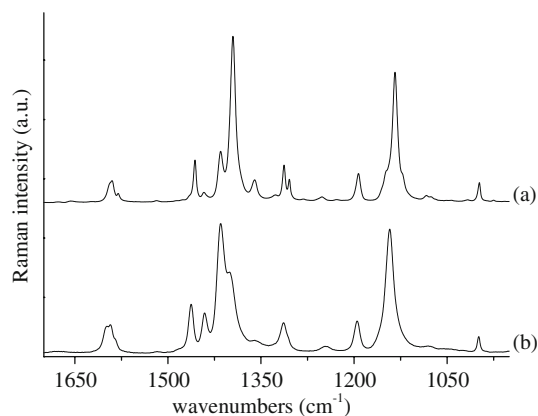


Fig. 6 Raman spectra of **(11)** (a) and β CD\(**11**) inclusion complex (b). Relative experimental spectral intensities have been scaled for comparison

conjugated organic guest and the polar oxidized saturated carbohydrate frames, respectively. In Fig. 1, exemplificative spectral comparisons between **(1)**, **(2)**, **(4)** and **(10)** free guests (Fig. 1a–d) and the β CD (Fig. 1e) profiles, reporting orderly the actual experimental achieved intensities, is

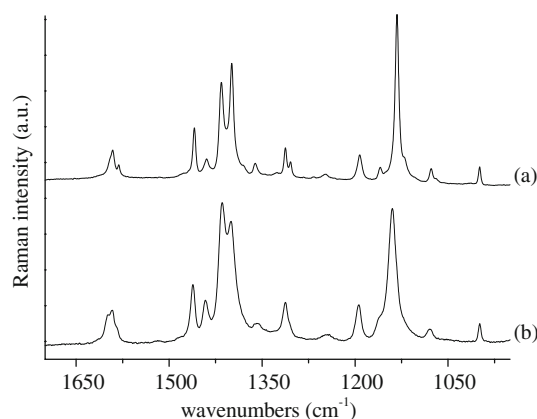


Fig. 7 Raman spectra of **(12)** and β CD\(**12**) inclusion complex. Relative experimental spectral intensities have been scaled for comparison

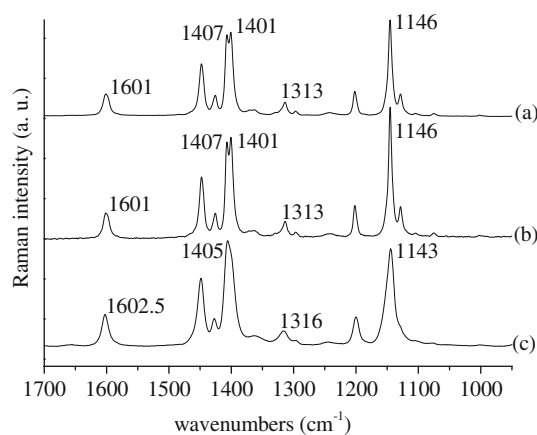


Fig. 8 Raman spectra of **(4)** (a), 2:1 β CD\(**4**) physical mixture (b) and β CD\(**4**) inclusion complex (c). Relative experimental spectral intensities have been scaled for comparison

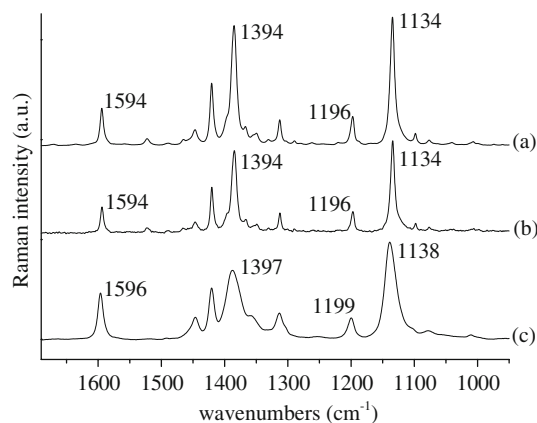


Fig. 9 Raman spectra of **(8)** (a), 2:1 β CD\(**8**) physical mixture (b) and β CD\(**8**) inclusion complex (c). Relative experimental spectral intensities have been scaled for comparison

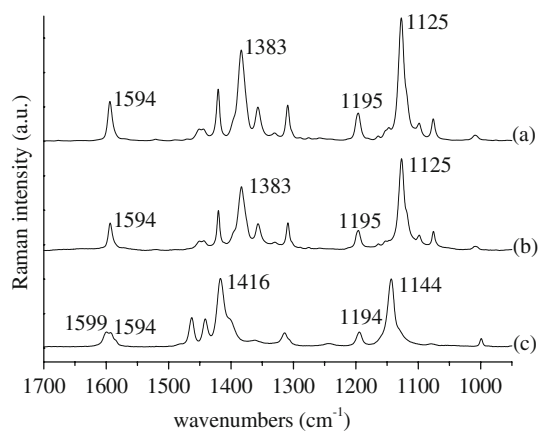


Fig. 10 Raman spectra of **(9)** (a), 2:1 β CD**(9)** physical mixture (b) and β CD**(9)** inclusion complex (c). Relative experimental spectral intensities have been scaled for comparison

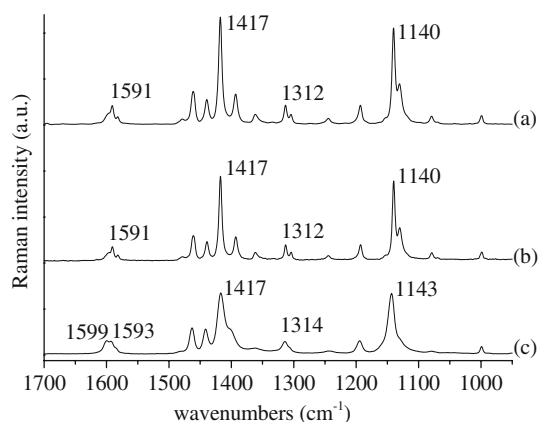


Fig. 11 Raman spectra of **(10)** (a), 2:1 β CD**(10)** physical mixture (b) and β CD**(10)** inclusion complex (c). Relative experimental spectral intensities have been scaled for comparison

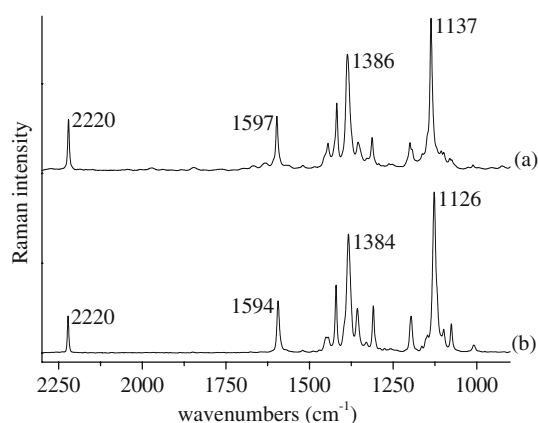


Fig. 12 Raman spectra of the separately ball-milled (a) and the untreated (b) **(9)** dye guest

illustrated for clarity. It appears well evident that this significant discrepancy of Raman intensity exalts the complete spectroscopic vibrational pattern of the included guest.

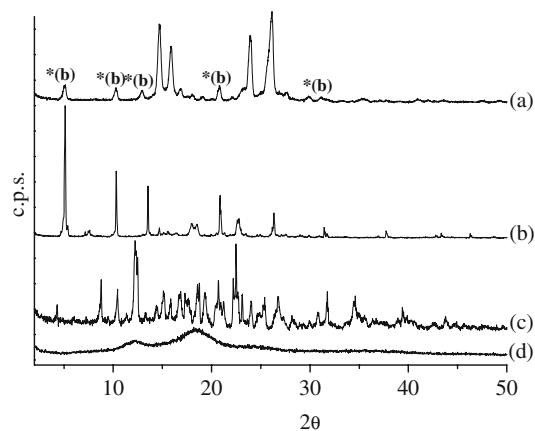


Fig. 13 XRPD spectra of the ball-milled azo-dye **(9)** (a), untreated azo-dye **(9)** (b), β -cyclodextrin (c) and β CD**(9)** inclusion complex (d). * Asterisked minor peaks in (a) correspond to the main crystal-phase reflections acquired in (b) pattern of **(9)**

Actually, there is not any relevant overlap of convoluting signals to the guest intense patterns provided by the relatively silent cyclodextrin guest. Hence, a convenient complete spectral comparison between the free and the included molecule is favoured. Of course, this situation represents a clear advantage, with reference to the analogous IR spectra [13, 30, 37], in which the vibrational activity of the polar cyclodextrin host is on the contrary pronouncedly evident, and diffuse merging overlap of the spectral patterns of the two host–guest counterparts prevents a clear complete confront with those of the uncomplexed free guest molecules.

At a further glance, a first experimental observed effect of each inclusion complex with respect to the free guest molecule situation is related to the hampering of the Raman activity for the included molecule. The event commonly overcomes the attended abatement provided by the 2:1 cyclodextrin molar mixture. Such generalised attenuation of signal intensity has to be directly connected to a fall down of electron molecular polarisability within the complex. The systematic decrease occurring at various entity appears reasonable, because of the quenching of the guest structural electron polarisability determined actually by interacting with the ‘frozen’ localised electron density of the polar carbohydrate host [38]. In Figs. 2, 3 and 4, a few examples on the purpose, displaying the actual experimental intensities, provided by **(3)**, **(5)** and **(6)** azo-dyes and their respective cyclodextrin complexes, are well representative. In particular, in the amphiphilic dye **(5)** case a drastic intensity hampering is observed on β CD complexation.

Furthermore, a general comparison of Raman patterns between the free and the included state of guest molecules provides mentionable distinctive features as a consequence of host–guest interactions.

Fig. 14 TGA patterns (N_2 , $10\text{ }^\circ\text{C}/\text{min}$ heating ramp) of **(9)** (a) and ball-milled **(9)** guest (b), with the respective simultaneously acquired DTA ($^\circ\text{C}$) profiles (a* and b*)

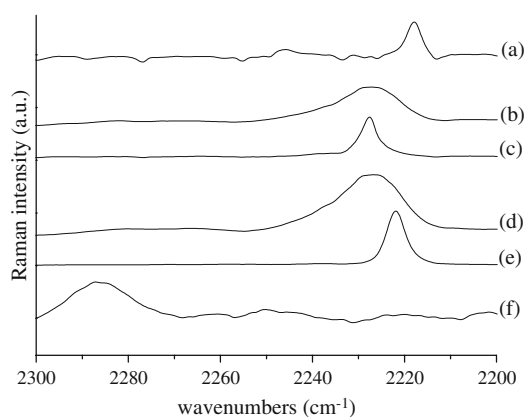
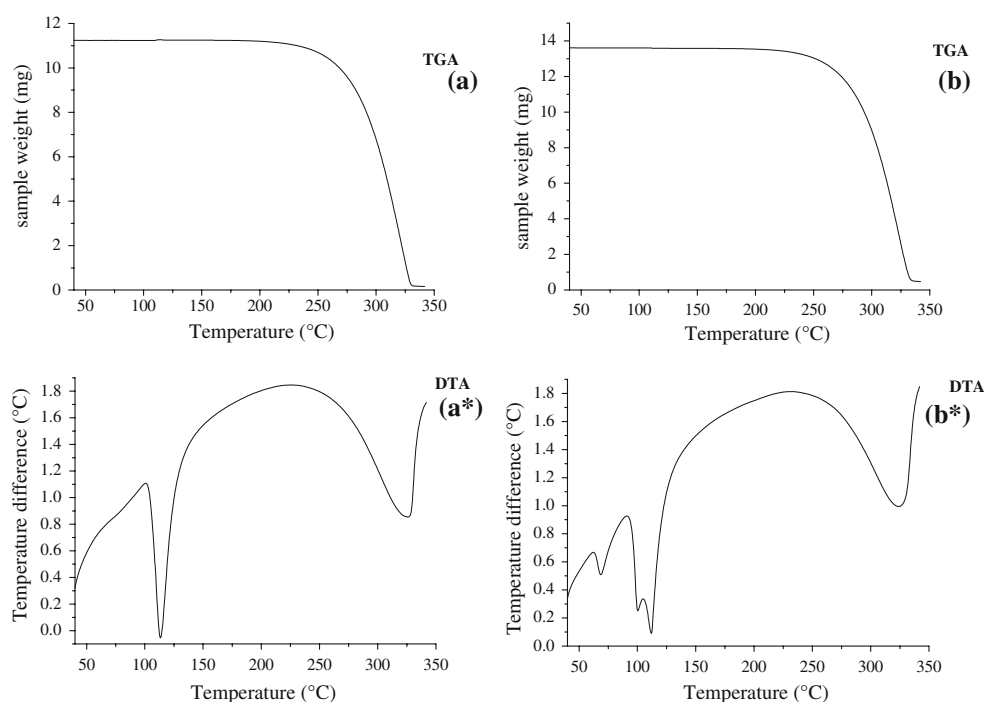


Fig. 15 Raman spectra of **(7)** (a), **(8)** (c) and **(9)** (e) azo-dye guest molecules and their respective β CD inclusion complexes (b), (d) and (f). Relative experimental spectral intensities have been scaled for comparison. The decreased broad spectral patterns of cyclodextrin complexes have been smoothed to better present Raman activity

In the relative intensity perspective, for complexed inclusion guests with comparison to the respective uncomplexed free molecules, observable relative pattern modifications occur. Clarifying examples on the topic are evidenced in Figs. 5, 6 and 7, in which the relative Raman intensities of **(7)**, **(11)** and **(12)** free guests and the respective β CD-inclusions have been scaled, for the purpose of comparison. It is noticed that hampered intensities in the complexes do not actually maintain a strict proportionality with those of separated guests [39], with rather a general signal-levelling tendency. A mediating modified electron situation of guest molecular polarisability

Table 2 Complete list of the observed experimental Raman frequencies (cm^{-1}) of the molecular skeletal aromatic stretching modes ($\nu_{\text{C}=\text{C}}$) [42] for the 12 examined guest compounds and the respective inclusion complexes within the β -cyclodextrin hosting cavity

Guest compound number (Ref. Table 1)	Free molecule (cm^{-1})	β CD Host-Guest IC (cm^{-1})	Frequency up-shifts ($\Delta\text{ cm}^{-1}$)
(1)	1,584	1587.5	3.5
(2)	1,584	1586	2
(3)	1,585	1587	2
(4)	1,601	1602.5	1.5
(5)	1,602	1602.5	– ^a
(6)	1,598	1601	3
(7)	1,593	1597	4
(8)	1,594	1596	2
(9)	1,594	1594, 1599	– ^a , 5 ^b
(10)	1,591	1593, 1599 ^b	2, 8 ^b
(11)	1,590	1593	3
(12)	1,591	1591.5	– ^a

Up-shift frequency differences are reported as $\Delta\text{ cm}^{-1}$

^a Frequency difference is lower than instrumental resolution

^b Indented scattering

established after inclusion within the isotropic cyclodextrin cavity necessarily accounts for the visible experimental variations in Raman activity [35].

Evidently, several merging pattern enlargements with additive peak shifts are first noticed in inclusion complexes when compared to the free state [17, 39, 40]. Four illustrative examples are reported in Figs. 8, 9, 10, 11, for the

(4), (8), (9) and (10) guest systems, again with a comparative spectral scale. At the same granted instrumental resolution, the spectral width amplifications for the included guest molecules are properly characteristically peculiar. Observable small peak shifts are on the whole either accompanied to or depend on the general broadening of signals [17, 39], after the partial overlapping of peaks not resolved. Both effects are pronouncedly more apparent for the smaller Raman signals, that may be also referred to more complex vibrational combination modes, or elongating second harmonic modes [41]. In particular, (9) dye within β CD exhibits a marked alteration of the spectral pattern with frequency upshift of the peculiar skeletal motifs, presumably due to a combined significant occurrence of both inclusive and hydrogen-bond structural interactions with the host system. However, also when spectrally isolated, a few peculiar profiles result systematically shifted, after cyclodextrin inclusion. E.g., within all the examined cases, the generally strong Raman signal set within the $1580 \div 1610 \text{ cm}^{-1}$ interval, which is basically consistent with the skeletal $\nu_{\text{C=C}}$ stretching modes of the aromatic ring motifs of the guest molecules [42], is up-shifted normally of about 3 cm^{-1} , on average, i.e., detectably above the operative 1 cm^{-1} instrumental resolution. These increments suggest a surrounding obstacle opposed to the Raman active vibrational mode. Worth to be noted, in this spectrum portion cyclodextrin Raman signals are absent, thus fully validating the actual spectral shift of the guest molecules. Table 2 reports free and host-included peak occurrences of these signals for all examined guests. Shifts (expressed as $\Delta \text{ cm}^{-1}$) are commonly positioned within the $2 \div 5 \text{ cm}^{-1}$ interval. For two systems, (5) and (12), a quantitative variation cannot be confidently expressed numerically, being nearly coincident with the 1 cm^{-1} instrumental experimental resolution. Comprehensively, the mostly evident observed alterations of Raman profiles are therefore expectably indicative of the flexibly homogeneous and constrained amphiphilic environment in which the included complexed molecule exerts its vibrational activity.

In order to exclude subtle vibrational spectral modifications attributable to possible solid state packing effects, Raman measurements were acquired from azo-dyes samples that were tested respectively in solid state phases of different crystallisation extents, as ascertained by experimental XRPD diffraction patterns. From each trial, no substantial significant difference between the more crystal and the more amorphous situations ever emerged, but a minimal negligible peak broadening. Therefore, the actual solid-state crystalline morphology of the examined matters reflects no practical influence on the main evidenced features of their vibrational spectra [43]. Similarly, the reported acquisition of Raman spectra from a simple mechanical mixture of β CD and an azo-dye (Figs. 8, 9, 10,

11) did not show any spectral pattern difference from the respective components examined separately, as expected [30]. Actually, detectable lesser Raman profile alterations of the pure azo-dye system, mostly visible in form of some peak shifts, only appear after a comprehensive 30 h ball-milling treatment, as a consequence of the deterioration of lattice crystallinity and of the partly mutated solid phase intermolecular environment, which are forced by protracted mechanical treatment, like observed for compound (9) commented in Fig. 12. XRPD measurements, aligned in Fig. 13, elucidate the situations, with the milled dye exhibiting a diversified crystal environment and diffuse amorphous condition displayed by the broadening of all diffraction pattern peaks. Similarly, the related TGA-DTA profiles, exposed in Fig. 14, are supportively concordant, with the DTA original dye peak that is accompanied in milled products by a second separate one, both preceded by a broad signal at ca. $80 \text{ }^\circ\text{C}$, compatible with an extent of amorphous phase. The observation relates the minor diversifications of Raman spectral property to a decidedly modified solid-state packing surrounding the molecular situation. However, Raman profile development after the cyclodextrin inclusion, sustained by XRPD and thermal test measurements, actually displays much more significant peculiarity, in terms of both evident characteristic large peak broadening and absorption position shifts, even after a shorter time of milling experimentally adopted for the achievement of inclusions. Therein, neither the usual solid state crystal effects nor a mechanical heterogeneous mixing of different phases can significantly alter the molecular vibrational profile. Evident spectral pattern variations are properly responsive of significant perturbing electron interactions at the molecular level [44], as indeed it occurs in inclusion phenomena.

Nevertheless, little can be in general reliably inferred from Raman measurements about the actual inclusion complex molar ratio, substantially because of the poorly structured weak broadened signals featured by the cyclodextrin host, which prevent any confident vibrational discrimination. However, it is assessed by different characterizing techniques that this topic class of aromatic functionalized guest molecules can be in general complexed by β CDs assuming particularly in the solid state various stoichiometry ratios, more commonly in the 1:1 or in the 2:1 host–guest proportion, depending on the actual physical and chemical guest molecular features.[2, 6, 10, 45] Interestingly, the Raman method focuses information exclusively on the guest target, indicating the operated cyclodextrin complexation deriving from a general reaction procedure regardless of the actual stoichiometry ratio. Eventually free CD exceeding fractions, on the other hand, do not import any significant spectral interference, because of their comparatively negligible spectral intensity.

However, in (7)–(9) molecular guests, a detailed examining of the visible Raman signal for the peculiar polarizable carbonitrile functional group linked to the aromatic ring, set in a spectral region that is free from competitive spectral interferences, states furthermore that every $-C\equiv N$ unit is evidently modified after β CD inclusion, with an hampered signal broadening and a frequency up-shift effect of 10 and 64 cm^{-1} for (7) and (9) cyanoguest molecules, respectively. A substantial frequency conservation is instead observed for (8) system. Collected results are illustrated in Fig. 15. Assuming that the increase of vibrational frequencies in inclusion complexes might be feasibly due to the settling of $-C\equiv N:\cdots H-O-$ hydrogen-bond interactions of the carbonitrile N: donor nitrogen with the outer cyclodextrin polar hydroxyl groups, the higher signal frequency up-shift corresponds to a stronger hydrogen-bond interaction of the mostly exposed aromatic carbonitrile group. Noteworthy, the *p*-cyano, hydroxy-ethyl (8) structure that is not spectrally shifted may presumably experience similar $-C\equiv N:\cdots H-O-$ intermolecular hydrogen bond interaction also in the free state, hence being the carbonitrile group not displaced after β CD complexation. Therefore, it can be tentatively deduced that inclusion in the hydrophobic cyclodextrin cavity occurs favourably from the more accessible lipophilic region of the guest structure, e.g., for (7) and (8) molecules, from the cyanophenyl portion of the system and, for (9) unit, from the diethyl ramified aromatic portion of the guest frame, as expected chemically.

Conclusion

The β -cyclodextrin host–guest molecular complexes of 12 different disperse azo-dyes structures have been investigated by mean of solid state Raman spectroscopy. Given the substantial Raman transparency of cyclodextrinic host frame sided to the inclusion target, because of its lesser electron polarisability, the characterisation availed information exclusively on the guest structures by a clean comparison, free of spectral interferences, between the free and the complexed situation. In general, Raman method resulted featured with a responsive sensitiveness to the slight environmental molecular variations, which occur after intermolecular interactions in the host–guest inclusion complex, primarily in terms of both absolute and relative Raman intensities and, also, of peak shifts. In occasionally suitable cases, hints at the actual structural complexation topology could be also tentatively performed. With respect to the other characterisation techniques which are classically employed for the assessment of molecular inclusion complexes, Raman method results distinct for a high reproducible reliability, combined with measurement

fastness, handiness and non-destructivity of the evaluated matters. Finally, the method appears to be validly reliable and extensible to a whole general class of large amphiphilic host and apolar polarisable guest structures, for the utile assessment of their molecular inclusion activity.

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References

1. Pluth, M.D., Raymond, K.N.: Reversible guest exchange mechanisms in supramolecular host–guest assemblies. *Chem. Soc. Rev.* **36**, 161–171 (2007). doi:10.1039/b603168b
2. Del Valle, E.M.M.: Cyclodextrines and their uses: a review. *Process Biochem* **39**, 1033–1046 (2004). doi:10.1016/S0032-9592(03)00258-9
3. Hedges, A.L.: Industrial applications of cyclodextrines. *Chem. Rev.* **98**, 2035–2044 (1998). doi:10.1021/cr970014w
4. Challa, R., Ahuja, A., Ali, J., Khar, R.K.: Cyclodextrines in drug delivery: An updated Review. *AAPS PharmSciTech* **6**, E329–E357 (2005)
5. Savarino, P., Viscardi, G., Quagliotto, P., Montoneri, E., Barni, E.: Reactivity and effects of cyclodextrins in textile dyeing. *Dyes Pigments* **42**, 143–147 (1999). doi:10.1016/S0143-7208(99)0004-2
6. Scheneider, H.J., Hacket, F., Rudiger, V., Ikeda, H.: NMR studies of cyclodextrins and cyclodextrin complexes. *Chem. Rev.* **98**, 1755–1785 (1998). doi:10.1021/cr970019t
7. Tatsuno, H., Ando, S.: Structure and dynamics of perfluoroalkane/beta-cyclodextrin inclusion compounds as studied by solid-state F-19 MAS and H-1 \rightarrow F-19 CP/MAS NMR spectroscopy. *J. Phys. Chem. B* **110**, 25751–25760 (2006). doi:10.1021/jp064579k
8. Cunha-Silva, L., Teixeira-Dias, J.J.C.: Solid-state inclusion compounds of small amphiphilic molecules (C_nE_m) in beta-cyclodextrin: A study at defined relative humidities. *New J. Chem.* **29**, 1335–1341 (2005). doi:10.1039/b507215h
9. Landau, R.N.: Expanding the role of reaction calorimetry. *Thermochim. Acta* **289**, 101–126 (1996). doi:10.1016/S0040-6031(96)03081-X
10. Braga, S.S., Goncalves, I.S., Herdtweck, E., Teixeira-Dias, J.J.C.: Solid state inclusion compound of *S*-ibuprofen in beta-cyclodextrin: Structure and characterisation. *N. J. Chem.* **27**, 597–601 (2003). doi:10.1039/b207272f
11. Lamcharfi, E., Kunesch, G., Meyer, C., Robert, B.: Investigation of cyclodextrin inclusion compounds using FT-IR and Raman spectroscopy. *Spectrochim. Acta Pt. A Mol. Biomol. Spectr.* **51**, 1861–1870 (1995). doi:10.1016/0584-8539(95)01428-W
12. Egyed, O.: Spectroscopic studies on beta-cyclodextrins. *Vib. Spectrosc.* **1**, 225–227 (1990). doi:10.1016/0924-2031(90)80041-2
13. Bertoluzza, A., Rossi, M., Taddei, P., Redenti, E., Zanol, M., Ventura, P.: FT-Raman and FT-IR studies of 1:2.5 piroxicam:beta-cyclodextrin inclusion compound. *J. Mol. Struct.* **481**, 535–539 (1999). doi:10.1016/S0022-2860(98)00734-0

14. Maeda, Y., Kitano, H.: Inclusion complexation by cyclodextrins at the surface of silver as evidenced by Surface-Enhanced Resonance Raman Spectroscopy. *J. Phys. Chem.* **99**, 487–488 (1995). doi:[10.1021/j100002a004](https://doi.org/10.1021/j100002a004)
15. Johri, S., Varshney, H.: Synthesis of some new disperse dyes. *J. Indian Chem. Soc.* **73**, 629–630 (1996)
16. Fedorov, L.A., Savarino, P., Dostovalova, V.I., Viscardi, G., Carpignano, R., Barni, E.: H-1-NMR spectra of a series of disperse azo-dyes. *Magn. Reson. Chem.* **29**, 747–748 (1991). doi:[10.1002/mrc.1260290721](https://doi.org/10.1002/mrc.1260290721)
17. Bridgeman, I., Peters, A.T.: Synthesis and electronic spectra of some 4-aminoazobenzenes. *J. Soc. Dyers Colour.* **86**, 519–521 (1970)
18. Matsui, M., Kawase, R., Funabiki, K., Muramatsu, H., Shibata, K.: Perfluoroalkylsulphonyl-substituted azobenzenes as second-order nonlinear optical chromophores. *Bull. Chem. Soc. Jpn.* **70**, 3153–3158 (1997). doi:[10.1246/bcsj.70.3153](https://doi.org/10.1246/bcsj.70.3153)
19. Komach, L.D., Zinchenkov, Y.Y., Rodionova, G.N., Karpov, V.V., Popov, E.V.: IR spectroscopy for dispersed-dye polymorphs. *J. Appl. Chem. U.S.S.R.* **63**, 1502–1504 (1990)
20. Bassignana, P., Cogrossi, E.: Absorption Ir du group –N=N– en colorant azoiques. *Tetrahedron* **20**, 2361–2363 (1964). doi:[10.1016/S0040-4020\(01\)90816-6](https://doi.org/10.1016/S0040-4020(01)90816-6)
21. Sigman, M.E., Leffler, J.E.: Supercritical carbon dioxide. The cis to trans relaxation and the π , π^* of the 4-(diethylamino)-4'-nitroazobenzene. *J. Org. Chem.* **52**, 3123–3126 (1987). doi:[10.1021/jo00390a030](https://doi.org/10.1021/jo00390a030)
22. Bortolus, P., Monti, S., Albini, A., Fasani, E., Pietra, S.: Physical quenching and chemical reaction of singlet molecular dioxygen with azo dyes. *J. Org. Chem.* **54**, 534–540 (1989). doi:[10.1021/jo00264a006](https://doi.org/10.1021/jo00264a006)
23. Albini, A., Fasani, E., Moroni, M., Pietra, S.: Photochemical decomposition of 4-aryloxy- and 4-aryloxy-*N,N*-dialkylanyliline *N*-oxides. *J. Chem. Soc. Perkin Trans. 2*, 1439–1444 (1986) doi:[10.1039/p29860001439](https://doi.org/10.1039/p29860001439)
24. Haessner, C., Mustrup, H.: Untersuchungen zum UV/VIS-spektralverhalten von Azofarbstoffen. XVIII. Substituenteneinflüsse auf die Absorptionmaxima der $n \rightarrow \pi$ und $\pi \rightarrow \pi^*$ -Banden von 4-*N,N*-Diethylaminoazobenzenen. *J. Prakt. Chem.* **329**, 493–498 (1987). doi:[10.1002/prac.19873290316](https://doi.org/10.1002/prac.19873290316)
25. Park, K.H., Twig, R.J., Ravikiran, R., Rhodes, L.F., Shick, R.A., Yankelevich, D., Knoesen, A.: Synthesis and nonlinear-optical properties of vinyl-addition poly(norbornene)s. *Macromolecules* **37**, 5163–5178 (2004). doi:[10.1021/ma040044i](https://doi.org/10.1021/ma040044i)
26. Lee, M.J., Piao, M.G., Yeong, M.Y., Lee, S.H., Kang, K.M., Yeo, S.J., Lim, T.G., Cho, B.R.: Novel azo octupoles with large first hyperpolarizabilities. *J. Mater. Chem.* **13**, 1030–1037 (2003). doi:[10.1039/b300777d](https://doi.org/10.1039/b300777d)
27. Ho, M.S., Natansohn, A., Barrett, C., Rochon, P.: Azo molecules for reversible optical storage. 8. The effect of polarity of the azobenzene groups. *Can. J. Chem.* **73**, 1773–1778 (1995). doi:[10.1139/v95-218](https://doi.org/10.1139/v95-218)
28. Zemskov, A.V., Rodionova, G.N., Tuchin, Y.G., Karpov, V.V.: IR spectra and structure of some azo dyes-*p*-benzene derivatives—in various aggregate states. *J. Appl. Spectrosc.* **49**, 1020–1024 (1988). doi:[10.1007/BF00657220](https://doi.org/10.1007/BF00657220)
29. Simova, S., Radeaglia, R., Fanghaenel, E.: 1, 2, 3-Triazabutadiene. XV. Einfluß der Substituenten auf die 15N- und 13C-chemischen Verschiebungen in Triazabutadienen und Azobenzenen. *J. Prakt. Chem.* **324**, 777–786 (1982). doi:[10.1002/prac.19823240511](https://doi.org/10.1002/prac.19823240511)
30. Parlatti, S., Barolo, C., Gobetto, R., Arrais, A., Buscaino, R., Medana, C., Savarino, P.: Preparation and application of a β -cyclodextrin-disperse/ reactive dye complex. *J. Incl. Phenom. Macrocycl. Chem.* **57**, 463–470 (2007). doi:[10.1007/s10847-006-9235-6](https://doi.org/10.1007/s10847-006-9235-6)
31. Savarino, P., Parlatti, S., Buscaino, R., Piccinini, P., Degani, I., Barni, E.: Effects of additives on the dyeing of polyamide fibres. Part I: β -cyclodextrin. *Dyes Pigments* **60**, 223–232 (2004). doi:[10.1016/S0143-7208\(03\)00142-6](https://doi.org/10.1016/S0143-7208(03)00142-6)
32. Savarino, P., Parlatti, S., Buscaino, R., Piccinini, P., Barolo, C., Montoneri, E.: Effects of additives on the dyeing of polyamide fibres. Part II: Methyl- β -cyclodextrin. *Dyes Pigments* **69**, 7–12 (2006). doi:[10.1016/j.dyepig.2005.02.003](https://doi.org/10.1016/j.dyepig.2005.02.003)
33. Torne, J.S., Vavia, P.R.: Inclusion complexation of anti-HIV drug with beta-cyclodextrin. *J. Incl. Phenom. Macrocycl. Chem.* **56**, 253–259 (2006). doi:[10.1007/s10847-006-9092-3](https://doi.org/10.1007/s10847-006-9092-3)
34. Polavarapu, P.L.: Ab initio vibrational Raman and Raman optical activity spectra. *J. Phys. Chem.* **94**, 8106–8112 (1990). doi:[10.1021/j100384a024](https://doi.org/10.1021/j100384a024)
35. Krishnakumar, V., Keresztury, G., Sundius, T., Ramasamy, R.: Simulation of IR and Raman spectra based on scaled DFT force fields: a case study of 2-(methylthio)benzotrile, with emphasis on band assignment. *J. Mol. Struct.* **702**, 9–21 (2004). doi:[10.1016/j.molstruc.2004.06.004](https://doi.org/10.1016/j.molstruc.2004.06.004)
36. Williams, S.D., Johnson, T.J., Gibbon, T.P., Kitchens, C.L.: Relative Raman intensities in C_6H_6 , C_6D_6 and C_6F_6 : A comparison of different computational methods. *Theor. Chem. Acc.* **117**, 283–290 (2007). doi:[10.1007/s00214-006-0135-z](https://doi.org/10.1007/s00214-006-0135-z)
37. Garcia-Zubiri, I.X., Gonzalez-Gaitano, G., Sanchez, M., Isasi, J.R.: Infrared study of solid dispersions of beta-cyclodextrin with naphthalene derivatives. *J. Incl. Phenom. Macrocycl. Chem.* **49**, 291–302 (2004). doi:[10.1023/B:JIPH.0000048317.30909.c5](https://doi.org/10.1023/B:JIPH.0000048317.30909.c5)
38. Wubbenhorst, M., van Turnhout, J., Klap, G., Jansen, J.C., Quintel, A., Hulliger, J.: Spontaneous polarization and orientational dynamics of polar rod-like molecules in host/guest materials. *IEEE Trans. Dielectr. Electr. Insul.* **7**, 523–530 (2000). doi:[10.1109/94.868072](https://doi.org/10.1109/94.868072)
39. Rossi, B., Verrocchio, P., Villani, G., Scarduelli, G., Mancini, I., Guella, G., Rossi, F.: Vibrational dynamics of inclusion complexes by Raman scattering: an experimental and numerical study. *Philos. Mag.* **87**, 557–567 (2007)
40. Da Silva, A.M.M., Amado, A.M., Ribeiroclaro, P.J.A., Empis, J., Teixeiraadias, J.J.C.: Beta-cyclodextrin complexes of benzaldehyde, vanillin and cinnamaldehyde—A Raman spectroscopic study. *J. Carbohydr. Chem.* **14**, 677–684 (1995). doi:[10.1080/07328309508005369](https://doi.org/10.1080/07328309508005369)
41. Efremov, E.V., Ariese, F., Mank, A.J.G., Gooijert, C.: Strong overtones and combination bands in ultraviolet resonance Raman spectroscopy. *Anal. Chem.* **78**, 3152–3157 (2006). doi:[10.1021/ac052253m](https://doi.org/10.1021/ac052253m)
42. Handbook of Raman Spectroscopy: from the Research Laboratory to the Process Line. Lewis, I.R., Edwards, H.G.M., Editors. Marcel Dekker, CRC Press, New York (NY). 1–1072 (2001)
43. Cong, H.P., Yu, S.H.: Recrystallization and shape control of crystals of the organic dye Acid Green 27 in a mixed solvent. *Chem. Eur. J.* **13**, 1533–1538 (2007). doi:[10.1002/chem.200600881](https://doi.org/10.1002/chem.200600881)
44. Arrais, A., Boccaleri, E., Croce, G., Milanesio, M., Orlando, R., Diana, E.: Synthesis, structural and spectroscopic study of the donor-acceptor complexes between fluorene and D_{2h} cyano molecular building blocks. *CrystEngComm* **5**, 388–394 (2003). doi:[10.1039/b308380b](https://doi.org/10.1039/b308380b)
45. Zhang, Y.M., Yu, S.B., Bao, F.: Crystal structure of cyclomaltoheptaose (beta-cyclodextrin) complexes with *p*-aminobenzoic acid and *o*-aminobenzoic acid. *Carbohydr. Res.* **343**, 2504–2508 (2008). doi:[10.1016/j.carres.2008.06.023](https://doi.org/10.1016/j.carres.2008.06.023)