Two-dimensional correlation spectroscopic studies of hydrogen-bonded supramolecular assemblies between azaaromatic molecule with dicarboxylic acid

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Abstract

Infrared (IR) spectra have been measured for a supramolecular assembly based on intermolecular hydrogen bonding between sebacic acid (SEA) molecule as a proton donor and azopyridine (AZP) molecules as a proton acceptor ([SEA·AZP]) over a temperature range from 29 to 155 °C in order to explore the involved hydrogen-bonding species and heat-induced structural variations. The temperature-dependent IR spectra have shown that the intermolecular hydrogen bondings are formed and stable enough in the supramolecular assembly but they become slightly decoupled when temperature is higher than the clearing point of supramolecular assembly. Two-dimensional (2D) correlation spectra in 1780–1660 cm^{-1} region have provided information about the structural variations of intermolecular hydrogen bonding concerning with C=O group. While, 2D correlation spectra in 880–820 cm^{-1} region have revealed hydrogen bonding changes concerning with proton in the adjacent position of pyridyl ring. Three different hydrogen-bonded species in the supramolecular assembly have been clarified by the 2D correlation analysis. The specific order of the temperature-induced structural changes in the involved intermolecular hydrogen-bonded species in supramolecular assembly has also been elucidated in the present study.
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Keywords: Two-dimensional correlation spectroscopy; Infrared spectroscopy; Intermolecular hydrogen bonding; Supramolecular assembly

1. Introduction

Hydrogen bonding is one of the principal intermolecular forces that often play key roles in the molecular recognition and self-assembly [1,2]. By choosing an appropriate proton acceptor and a proton donor, stable intermolecular hydrogen bonding can be formed, often thereby providing a novel system with new properties [3,4]. The formation of these supramolecular assemblies was promoted by site-specific hydrogen bonding between the complementary hydrogen bonding groups connected to a functional derivative. The process of hydrogen bonding directed molecular recognition leading to the generation of the functional assemblies [5–12]. Recently, a series of supramolecular assemblies based on hydrogen bonding between azaaromatic molecular with dicarboxylic acids (Scheme 1) have been designed and synthesized [13]. The formation of thes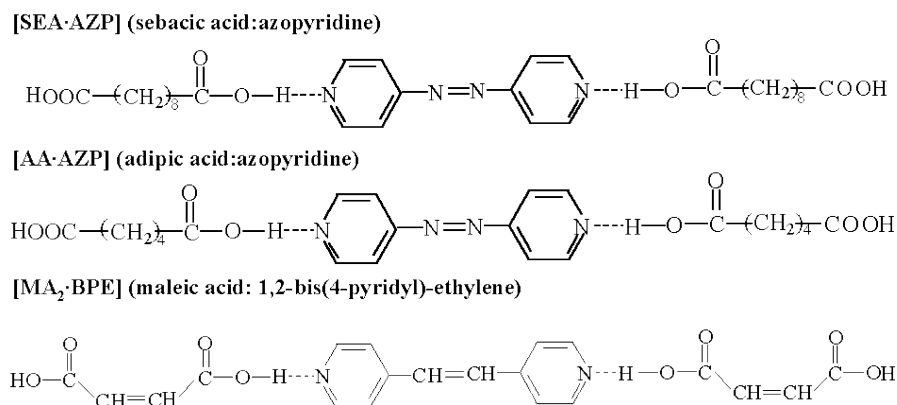e supramolecular assemblies was promoted by site-specific hydrogen bonding between the complementary hydrogen-bonding functional groups connected to the azaaromatic molecules [13]. In the present study, we employ temperature-dependent infrared (IR) spectroscopy to investigate the thermal behavior of different hydrogen-bonded species involved in the supramolecular systems and the heat-induced structural changes. The obtained IR spectra are rather complicated because they contain many overlapping bands involved in the different species of hydrogen bonding. Thus, generalized two-dimensional (2D) correlation spectroscopy analysis [14,15] is employed.

2D correlation spectroscopy has recently been a subject of much attention from the points of both basic science and practical applications [14,15]. Besides the ability of resolution enhancement, 2D correlation spectroscopy has two more notable advantages that other techniques do not have. It enables one to correlate many bands in the region concerning with the hydrogen bonding, making the band assignments more feasible. By using the 2D spectroscopy, it is also possible to probe the specific order of the hydrogen bonding intensity changes upon perturbation. Thus, in the present study, we use 2D correlation spectroscopy to unravel the

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[SEA·AZP] (sebacic acid:azopyridine)

[AA·AZP] (adipic acid:azopyridine)

[MA₂·BPE] (maleic acid: 1,2-bis(4-pyridyl)-ethylene)

Scheme 1. Chemical structure of the hydrogen-bonded supramolecular assemblies: (a) sebacic acid–azopyridine ([SEA·AZP]); (b) adipic acid–azopyridine ([AA·AZP]); (c) maleic acid–1,2-bis(4-pyridyl)-ethylene ([MA2·BPE]).

complex spectra and to clarify different hydrogen-bonded species in the supramolecular assembly of sebacic acid and azopyridine [SEA·AZP].

2. Experimental

2.1. Materials

1,2-Bis(4-pyridyl)-ethylene (BPE) and AZP were synthesized following the procedures described in the literature [16,17]. Other reagents and solvents were received from commercial suppliers and used without further purification. All complexes were prepared by the reaction of BPE or AZP with the appropriate dicarboxylic acid in a 1:1 molar ratio, which were mixed in a solution of 8:3 (v/v) acetone and ethanol and heated until they were dissolved completely and allowed to stand at room temperature for several days. After most of the solvent evaporated, co-crystals, [SEA·AZP], [AA·AZP] and [MA2·BPE] (SEA = sebacic acid, AA = adipic acid, MA = maleic acid), were obtained.

2.2. Infrared spectra

FT-IR spectra were obtained with a spectral resolution of $4 \, cm^{-1}$ by using a Bruker IFS-66V FT-IR spectrometer equipped with a DTGS detector. Temperature was adjusted and controlled within $\pm 0.2 \, °C$ by a home-made hot stage. In order to obtain a thin smooth film for the IR study, the sample was placed in a cell consisting of two KBr windows without any surface treatment. The sample was heated to $10 \, °C$ higher than its clear point, then cooled down to room temperature. Temperature-dependent IR spectra were measured after the sample had been kept at each temperature point for 15 min.

2.3. Differential scanning calorimeter (DSC)

The thermal properties of the complex were investigated with a NETZSCH DSC 204/1/G instrument. The rate of

heating and cooling was at $10 \, °C/min$; the weight of the sample was 8.2 mg.

2.4. 2D correlation analysis

Powerful, yet easily executable, software named KG2D for constructing generalized 2D correlation spectra has been composed by Y. Wang (Kwansei Gakuin University) with the Array Basic programming language (The Galactic Industries Corp.) [22]. This 2D software was programmed on the basis of the newly developed algorithm of generalized 2D correlation spectroscopy [21].

3. Results and discussion

3.1. Specification of the hydrogen bonding in the complex of [SEA·AZP]

The chemical structure of [SEA·AZP] is shown in Scheme 1. IR spectra of AZP, SEA and [SEA·AZP] at 20 °C are shown in Fig. 1a–c, respectively. The spectrum of SEA (Fig. 1b) shows a C=O stretching band at 1697 cm^{-1}. This band along with a very broad band centered at 3000 cm^{-1} proves the formation of carboxylic acid (–COOH) dimmer in SEA by means of intermolecular hydrogen bonding [18].

In the IR spectrum of complex [SEA·AZP] in Fig. 1c, C=O stretching mode of the carboxylic acid group in SEA is changed to 1700 cm^{-1}. Notably, two new bands centered at 2517 and 1908 cm^{-1} are observed in Fig. 1c. The formation of the complexes between SEA and AZP was usually tested by two bands centered around 2500 and 1900 cm^{-1} resulting from self-association of carboxylic acid and pyridine through intermolecular hydrogen bonding [19,20]. Therefore, two bands in Fig. 1c should be the evidences for an intermolecular hydrogen bonding interaction between the pyridyl ring and the carboxylic acid groups. In addition, the bending mode of C–H in the adjacent position of pyridyl ring at 837 cm^{-1} splits into two bands at 845 and 835 cm^{-1} (see the enlarged spectrum in Fig. 1). Theses results demonstrate
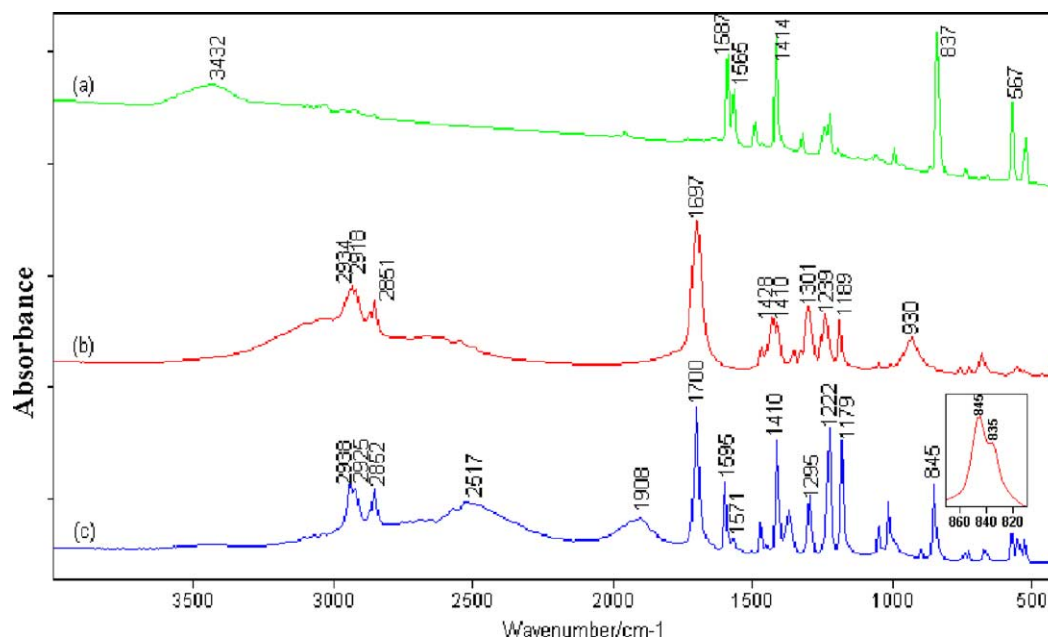
Fig. 1. FT-IR spectra of azopyridine (AZP) (a), sebacic acid (SEA) (b), and the supramolecular assembly of [SEA·AZP] (c) in KBr pellet at 20 °C.

that the hydrogen bonding is formed between the proton in adjacent position of the pyridyl ring and the carboxylic acid group of SEA. Moreover, the splitting of the band at 837 cm^{-1} into 845 and 835 cm^{-1} indicates that there are two kinds of hydrogen bondings concern with the proton in the adjacent position of the pyridyl ring. These results elucidate that there may exist at least three kinds of hydrogen bondings in the complex of [SEA·AZP].

3.2. Thermal dynamic of the complex of [SEA·AZP] revealed by DSC and temperature-dependent IR spectra

Fig. 2 shows IR spectra of [SEA·AZP] in the KBr windows measured at 29, 138, 141 and 148 °C, respectively. Close inspection of IR spectra in Fig. 2 shows gradual and continuous decreases in the bands centered at 2517 and 1908 cm^{-1} with temperature. Such a temperature effect on the hydrogen bonding was previously reported for other pyridyl–carboxylic acid systems [19,20]. It is noted that the two bands at 2517 and 1908 cm^{-1} still exist even at 148 °C. These results show that the intermolecular hydrogen bonding is weakened as the temperature is increased, while it is stable enough to persist to some extent even close to its clear point at 151 °C as revealed by differential scanning calorimeter.

The temperature-dependent IR spectral variations elucidate that the significant structural changes occur in the investigated hydrogen-bonded assembly. The plot of frequency of the carbonyl stretching band of [SEA·AZP] versus temperature is reported in Fig. 3. Great change in the plots is observed between 150 and 155 °C, which is consistent with the DSC result in Fig. 4. DSC analysis is used to study the thermal property of the complex of [SEA·AZP]. Its phase

transition property is demonstrated in Fig. 4. Notably, only one endothermic peak at 151 °C is observed in the process of heating, which corresponds to the phase transition from crystal to isotropic phase. Significant changes observed in Fig. 3 illustrate that great structural variation of hydrogen bonding occurs in this temperature region.

However, the thermal dynamics and the detailed structural variations of [SEA·AZP], such as the changes in the involved hydrogen bonding are still not very clear up to now. Powerful spectral analysis techniques need to be employed to explore such temperature-dependent structural variations. We have used 2D correlation analyses in the several spectral regions between 3500 and 500 cm^{-1} to probe the thermal-induced structural variations of a new
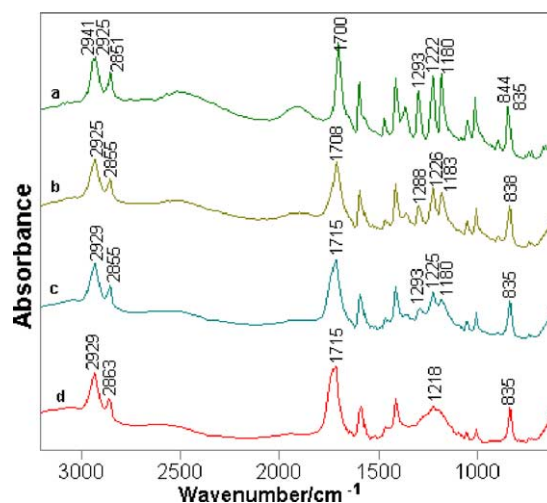

Fig. 2. FT-IR spectra of the supramolecular assembly of [SEA·AZP] measured at: (a) 29 °C; (b) 138 °C; (c) 141 °C; (d) 148 °C.
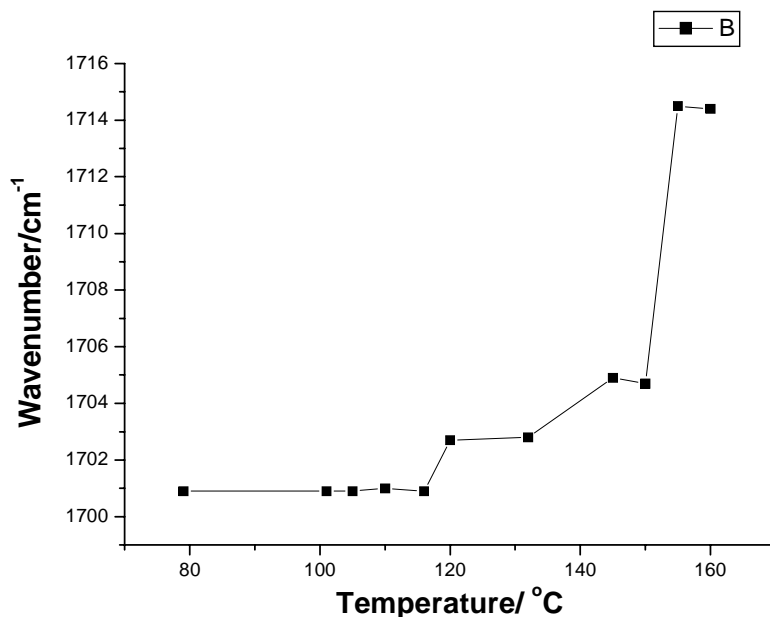
Fig. 3. DSC thermogram of supramolecular assembly of [SEA·AZP] in second heating process.

azobenzene derivative supramolecular system based on hydrogen-bonding [5] and another hydrogen-bonded supramolecular liquid-crystal material, DBS–BD–DBS [6], in the previous studies.

3.3. Temperature-induced structural variations in the complex revealed by 2D IR correlation spectroscopy

3.3.1. 2D IR correlation spectra in 1780–1660 cm^{-1} region

In order to explore temperature-induced structural variations of the –COOH groups in the complex of [SEA·AZP],

2D correlation analysis is applied to the temperature-dependent IR spectra in the spectral region of 1780–1660 cm^{-1}. Fig. 5 shows synchronous (a) and asynchronous (b) 2D correlation spectra in the 1780–1660 cm^{-1} region constructed from the IR spectra in the temperature range from 29 to 132 °C. Throughout this paper, solid and dashed lines in the 2D contour maps denote positive and negative correlation peaks, respectively. The synchronous spectrum in Fig. 5a is dominated by three autopeaks at 1743, 1731 and 1700 cm^{-1}, respectively. The 2D asynchronous map in Fig. 5b indicates striking band intensity changes in the C=O stretching bands of free (1743 cm^{-1}), weakly
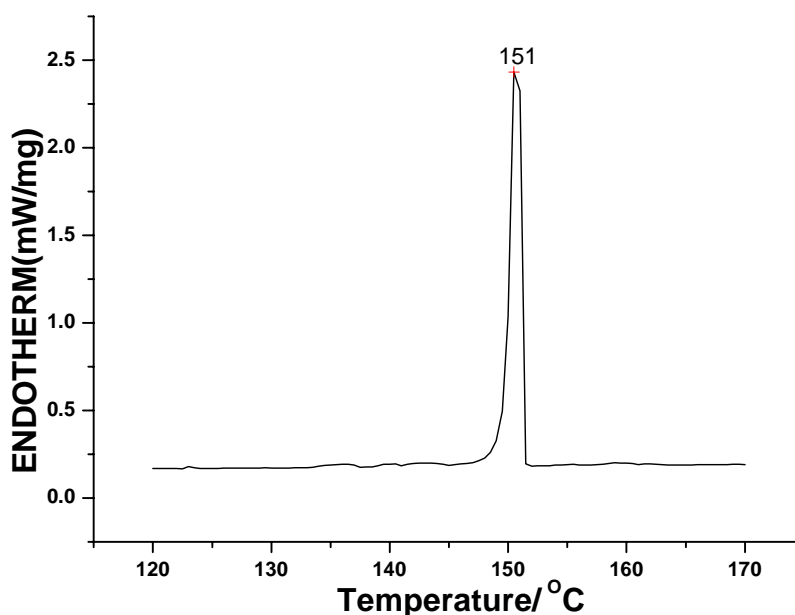

Fig. 4. Plot of temperature-induced frequency shift of C=O stretching mode in the supramolecular assembly of [SEA·AZP].
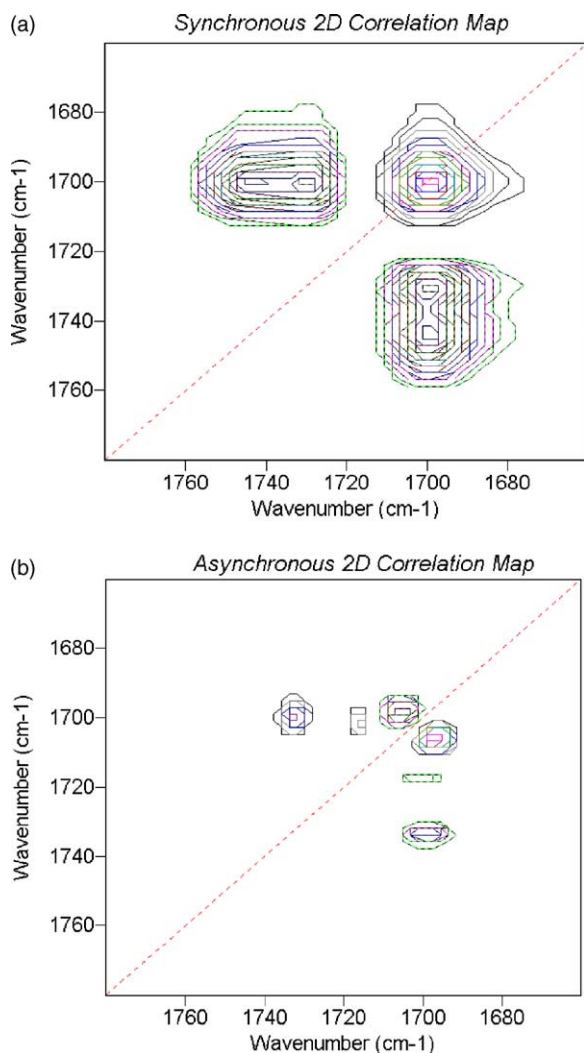
Fig. 5. Synchronous (a) and asynchronous (b) spectra in the 1780–1660 cm^{-1} region constructed from the temperature-dependent IR spectra between 29 and 132 °C of [SEA·AZP].
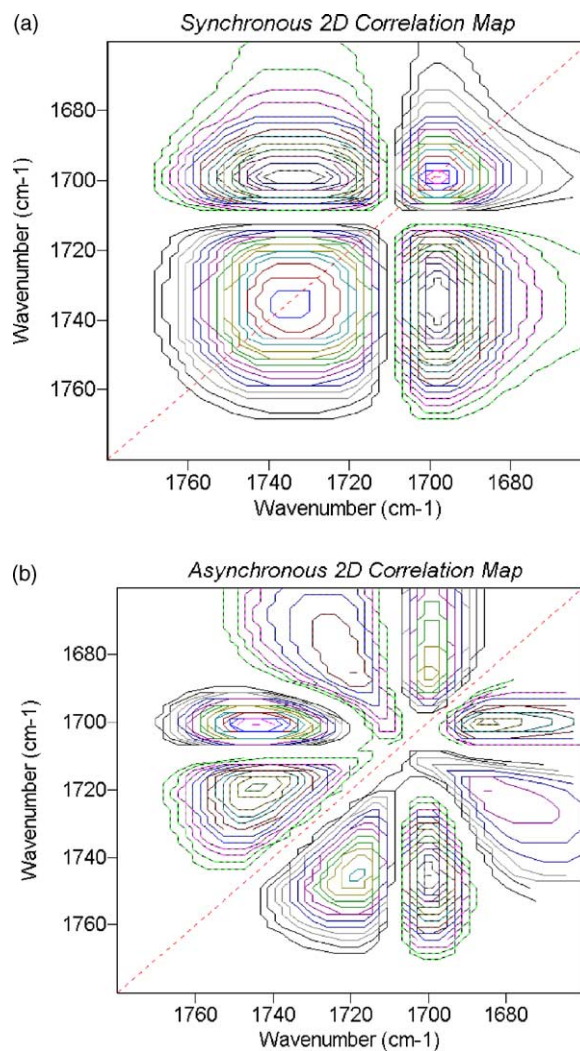

Fig. 6. Synchronous (a) and asynchronous (b) spectra in the 1780–1660 cm^{-1} region constructed from the temperature-dependent IR spectra between 132 and 155 °C of [SEA·AZP].

hydrogen-bonded (1731 cm^{-1}), and strongly hydrogen-bonded (1697 cm^{-1}) –COOH species with the temperature increase. The negative cross-peaks at (1731, 1697) and (1743, 1697) cm^{-1} reveal that the direction of the band intensity change at 1743 and 1731 cm^{-1} are opposite to that of the intensity changes at 1697 cm^{-1}, that is, the number of free (1741 cm^{-1}) and weakly hydrogen-bonded COOH groups increases while the number of the strongly hydrogen-bonded –COOH groups (1697 cm^{-1}) decrease with temperature. The asynchronous spectrum in Fig. 5b provides more useful information than the synchronous spectrum in Fig. 5a. Two new bands are observed at 1716 and 1706 cm^{-1} in Fig. 5b, which are attributed to the new species of hydrogen bondings appear in the heating process. These results demonstrate that the asynchronous spectrum is more powerful in the bands deconvolution of hydrogen bonding in comparison with synchronous spectrum.

Synchronous and asynchronous 2D correlation spectra in the 1760–1660 cm^{-1} region constructed from the IR

spectra in the temperature range from 132 to 155 °C are shown in Fig. 6a and b. Two strong autopeaks are observed at 1735 and 1698 cm^{-1} in the synchronous spectrum in Fig. 6a. Negative cross-peaks between them indicates the direction of the band intensity change at 1735 and 1698 cm^{-1} are opposite to each other with temperature increase. The corresponding asynchronous spectrum in Fig. 6b provides three deconvoluted bands at 1744, 1718 and 1698 cm^{-1}. Based on the general rules proposed by Noda [21], the sign of the positive cross-peak at (1718, 1744) cm^{-1} reveals that the intensity of the band at 1744 cm^{-1} changes at higher temperature than that of band at the 1718 cm^{-1}.

3.3.2. 2D IR correlation spectra in 880–820 cm^{-1} region

In order to clarify the structural changes of the intermolecular hydrogen bonding in the complex of [SEA·AZP] more efficiently, 2D correlation analysis is applied to the
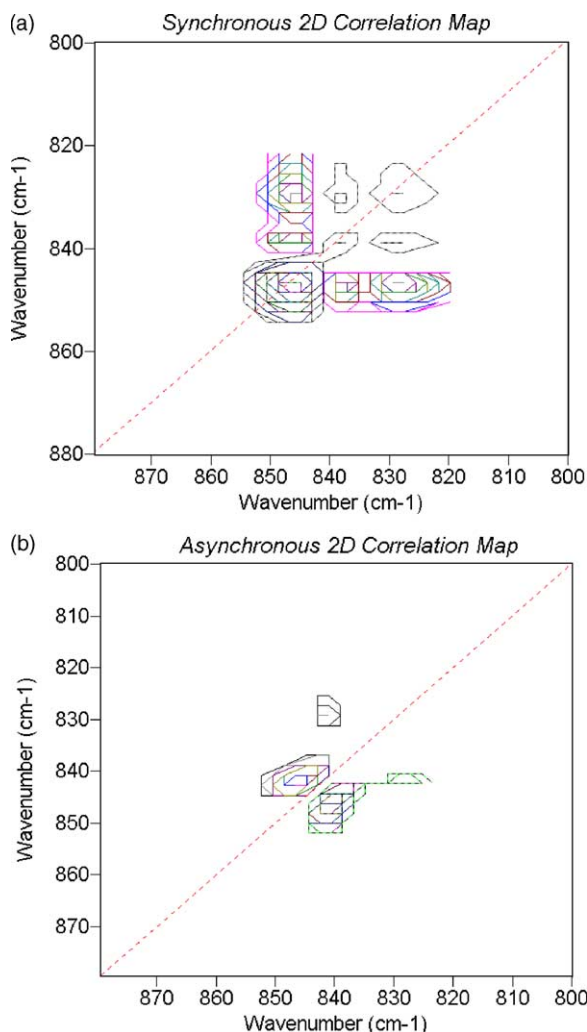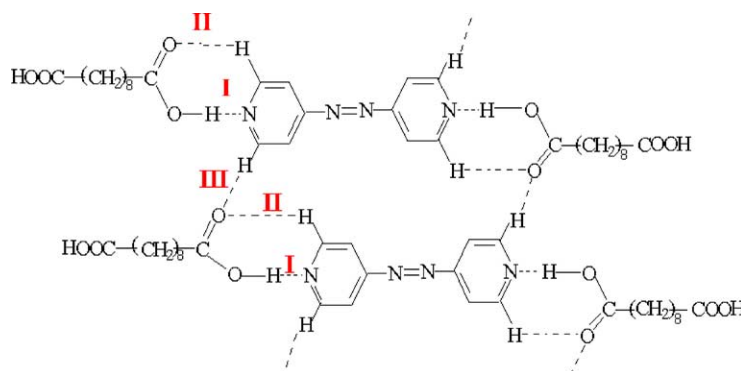
Fig. 7. Synchronous (a) and asynchronous (b) spectra in the 880–820 cm^{-1} region constructed from the temperature-dependent IR spectra between 29 and 132 °C of [SEA·AZP].

the 880–820 cm^{-1} region constructed from the IR spectra in the temperature range from 29 to 132 °C. The synchronous spectrum is dominated by three autopeaks along the diagonal line at 846, 838 and 829 cm^{-1}, respectively, which are assigned to the bending mode of C–H in the adjacent position of pyridyl ring with strong hydrogen bonding (846 cm^{-1}) and weak hydrogen bonding (838 cm^{-1}). The autopeak at 829 cm^{-1} probably generates from the baseline shift in this region. The negative cross-peak at (846, 838) cm^{-1} indicates the direction of the band intensity change of 846 cm^{-1} is opposite to that of 838 cm^{-1} with temperature increase. One pair of cross-peaks at (846, 838) cm^{-1} is observed in the asynchronous map in Fig. 7b. The positive sign of the cross-peaks in the asynchronous spectrum provides the additional information about the sequence order of the intensity changes in different bands. The intensity of the band at 846 cm^{-1} varies at low temperature than that of the bands at 838 cm^{-1}. That is, the strength of hydrogen bonding corresponding to the band at 838 cm^{-1} is stronger than that corresponding to the band at 846 cm^{-1}. X-ray diffraction study [13] of the crystal of the complex of [SEA·AZP] revealed that two kinds of hydrogen bondings are formed between the protons of pyridyl ring and carbonyl oxygen of SEA. The distance and angles of these two hydrogen bondings are 2.40 Å and 153.5° for C(13)–H(13)⋯O(1) (corresponded hydrogen bonding II in Scheme 2), and 2.72 Å and 126.9° for C(14)–H(14)⋯O(2) (corresponded hydrogen bonding III in Scheme 2), respectively. Therefore, based on the result of X-ray diffraction [13], the deconvoluted bands at 838 and 846 cm^{-1} should be assigned to the hydrogen-bonding species of II and III in Scheme 2, respectively.

Generalized 2D correlation spectrum has two advantages for analyzing the structural changes with external perturbation in supramolecular assembly based on hydrogen bonding. The overlapped bands can be deconvoluted by the synchronous spectrum, and the sequential order of various bands can also be revealed by the asynchronous spectrum. Combination of 2D correlation analysis with the results of X-ray diffraction, three kinds of hydrogen bondings are clarified in the complex, as show in Scheme 2. Moreover,

temperature-dependent IR spectra in the spectral region of 880–820 cm^{-1} which involved bending mode of C–H in the adjacent position of pyridyl ring. Fig. 7a and b show synchronous and asynchronous 2D correlation spectra in

Scheme 2. Proposed hydrogen-bonding species in the supramolecular assembly of [SEA·AZP] based on the 2D correlation IR spectra.

we concluded that the strength of the hydrogen bonding can be described as follows: I > II > III.

4. Conclusion

The present study has demonstrated the usefulness of 2D correlation spectroscopy in the study of the supramolecular assemblies based on hydrogen bonding. 2D correlation analysis has provided the information about the sequence in the change of the hydrogen bonding in the supramolecular assemblies. Following conclusions can be achieved in the present study. (1) As illustrated in Scheme 2, there are three different hydrogen-bonding species exist in the supramolecular assembly of [SEA·AZP]. (2) 2D correlation spectra constructed from the 1780–1660 cm^{-1} region reveal that the hydrogen bonding between the group of carboxyl and the atom of nitrogen in the pyridyl ring is stable than the two others, that is, the strength of them is: I > II and III. (3) 2D correlation spectra constructed from the 880–820 cm^{-1} region let us conclude that the stability of hydrogen bonding formed between the carboxyl and the proton in the adjacent position of pyridyl ring is: II > III. In conclusion, the sequential strength of three kinds of hydrogen bondings in the complex is: I > II > III.

Acknowledgements

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