

Research Article

Zn (II) and Cu (II) Halide Complexes of Poly(propylene amine) Dendrimer Analysed by Infrared and Raman Spectroscopies

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Two nondestructive and complementary spectral methods as infrared and Raman spectroscopies have been used for characterizations of poly(propylene amine) dendrimers comprising 1,8-naphthalimide units in the dendrimer periphery and their metal complexes with Cu^{2+} at Zn^{2+} ions.

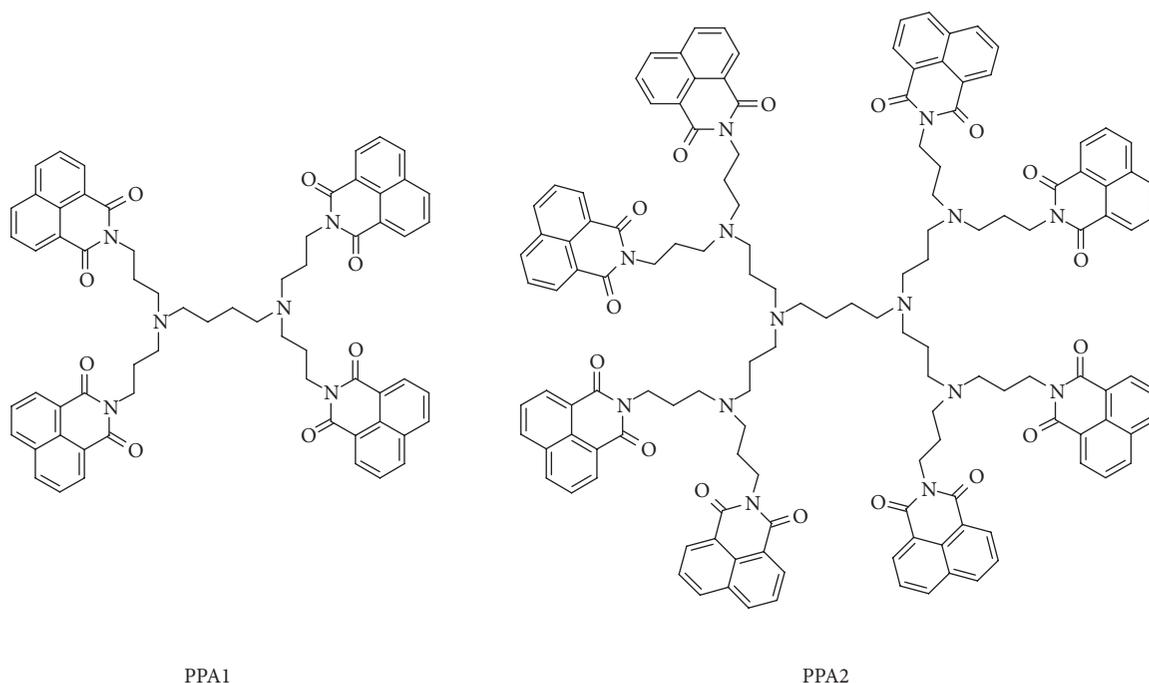
1. Introduction

Poly(propylene amine) (PPA) is a new class of commercial dendrimers possessing tertiary amino groups in the core and terminal primary amino groups in the dendrimer periphery [1]. Their luminescent characteristics can be customized by modifying the periphery with different fluorophores. We have extensively studied the dendrimer modifications with 1,8-naphthalimides in response to the needs of vanguard sensors for preventing environment pollution [2–7].

Different spectral methods and techniques as UV-vis and fluorescence, FTIR and Raman, NMR, AFM, and EPR are used for identification and characterization of dendrimers [8]. Some of these methods used for studying the vibrations of atoms in dendrimer molecules are infrared and Raman spectroscopies. The difference between both of spectral methods lies in the fact that while in infrared spectroscopy are important oscillations, changing dipole moment, in the Raman spectroscopy is characteristic the change of polarizability of molecules. The main advantage of Raman spectroscopy compared to Infrared spectroscopy is the small water absorption, which is offered especially for biological and medical investigations without further sample preparations. Surface-enhanced Raman spectroscopy (SERS)

takes the advantage of strongly increased Raman scattering signal generated by local field enhancement near metallic nanostructures [9]. An example exploits the local plasmon modes at the interface between two metal nanoparticles. A key requirement to achieve such detection is the placement of the analyte close to more than one plasmonic surface [10]. To date, isotropic and anisotropic metallic nanoparticles such as gold and silver have been promising SERS substrates because of their tunable optical properties, controllable particle size distribution, easy synthesis procedure, long-term stability, and high biocompatibility [11]. On the other hand, the infrared spectroscopy is more informative in the case of the investigations of polar functional groups in organic compounds. This means that these spectral methods are complementary and appropriate for researching the structure of organic molecules [12].

In this paper we present Raman and infrared spectral analyses on Zn (II) and Cu (II) halide complexes of poly(propylene amine) dendrimers of first and second generations, comprising 1,8-naphthalimide units in the dendrimer periphery. Their spectral characteristics have been investigated in solid state and in DMSO solution in the presence of Ag nanoparticles.



SCHEME 1: Chemical structure of dendrimers PPA1 and PPA2.

2. Experimental

2.1. Materials. First and second generations PPA dendrimers modified with 1,8-naphthalimide derivatives have the structures shown in Scheme 1. Their synthesis and metal complexes preparation have been published recently [6, 13].

2.2. Synthesis of Ag Nanoparticles. Before preparation of the colloids, the whole glassware was washed with aqua regia and rinsed with deionized water. Hydroxylamine reduced silver nanoparticles were prepared as reported by Leopold and Lendl [14]. Briefly, hydroxylamine hydrochloride (1.67×10^{-3} M) and NaOH (3.33×10^{-3} M) were dissolved in 90 mL deionized water. To the basic solution, 10 mL AgNO_3 (1×10^{-2} M) was added dropwise, stirred for 30 minutes, and stored in dark place. The concentration of the ultimate silver colloid solution was assumed as 1X. The study was carried out to find out the optimum concentration of silver colloid. 2.5 times concentrated solution gave the best signal enhancement for SERS measurements, and this concentration was used for all SERS measurements in the study.

2.3. Instrumentation. DeltaNu Examiner Raman Microscopy system with a 785 nm laser source, a motorized microscope stage sample holder, and a cooled charge-coupled device (CCD, at 0°C) detector were used. Instrument parameters were as follows: 20x objective, 30 μm laser spot size, 150 mW laser power, and 30 s acquisition time. Baseline correction was performed for all of the measurements. In solid sample measurement, sample was placed on a glass slide and Raman spectrum of the sample was obtained with micro-Raman system. In liquid sample measurement, sample was dissolved

in DMSO and then diluted with Milli-Q quality water ($18 \text{ M}\Omega\text{cm}$) up to 10^{-4} M concentration. After that 50 μL sample was mixed with 50 μL 10X Ag nanoparticles in Raman cuvette, and Raman spectrum of the mixture was obtained in the range of 200–2000 cm^{-1} at a resolution of 2 cm^{-1} with constant measurement parameters. Infrared analysis of both dendrimers and their complexes with metal ions was carried out using an infrared Fourier transform spectrometer (IRAffinity-1) with the diffuse-reflectance attachment (MIRacle Attenuated Total Reflectance Attachment) at a 2 cm^{-1} resolution.

3. Results and Discussion

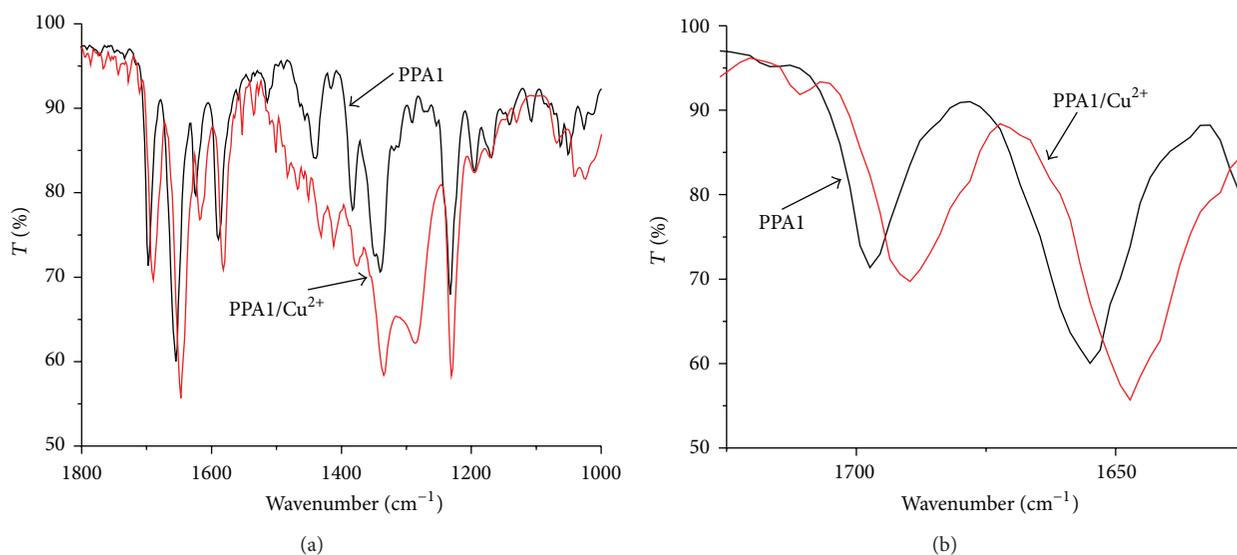
Stretching and deformation vibrations of the main functions in the infrared region of PPA dendrimers from first and second generations modified with 1,8-naphthalimides and their metal complexes are summarised in Table 1.

The carbonyl groups from the imide structure give rise to both of the frequency bands of C=O absorption [15]. The IR spectrum of the initial dendrimers PPA1 and PPA2 possesses very similar intensive bands at 1697 cm^{-1} , 1654 cm^{-1} , 1696 cm^{-1} , and 1655 cm^{-1} . The characteristic bands for the C–N bonds due to the tertiary amino group from aliphatic dendrimer structure and C–N–C imidic structure from the 1,8-naphthalimide are at 1354–1340 cm^{-1} , 1242–1232 cm^{-1} , and 1207–1174 cm^{-1} .

The aromatic naphthalene ring from the 1,8-naphthalimide units is responsible for the absorptions due to the C–H stretching vibrations at 3063–3072 cm^{-1} . The characteristic C–H out-of-plane deformation vibrations

TABLE 1: Experimental infrared wavenumbers of dendrimers in cm^{-1} .

	$\nu_{\text{C-H arom}}$	ν_{CH_2}	$\nu_{\text{C=O}}^{\text{AS}}$	$\nu_{\text{C=O}}^{\text{S}}$	$\nu_{\text{C=C arom}}$	ν_{CH_2}	$\nu_{\text{C-N}}$	$\delta_{\text{C-H arom}}$
PPA1	3068	2958 2874	1697	1655	1624 1589	1440	1340 1232 1194	845 777
PPA1/Cu ²⁺	3065	2966 2881	1690	1647	1617 1582 1455	1432	1335 1285 1230 1184	842 775
PPA1/Zn ²⁺	3072	2960 2793	1694	1648	1620 1586 1452	1434	1341 1232 1191	843 776
PPA2	3068	2958 2874	1696	1654	1624 1587	1437	1342 1232 1174	874 777
PPA2/Cu ²⁺	3068	2953 2870	1691	1646	1620 1583 1451	1432	1340 1228 1178	842 775
PPA2/Zn ²⁺	3063	2958 2832	1692	1647	1618 1584 1455	1432	1338 1230 1184	842 775

FIGURE 1: Infrared spectra of PPA1 dendrimer and PPA1/Cu²⁺ complex.

of the aromatic naphthalene rings are at $775\text{--}779\text{ cm}^{-1}$ and $843\text{--}874\text{ cm}^{-1}$.

PPA dendrimers under study comprise also aliphatic methylene ($-\text{CH}_2-$) groups in the dendrimer core. The absorption at $2832\text{--}2881\text{ cm}^{-1}$ for the asymmetric stretching vibrations and at $2953\text{--}2966\text{ cm}^{-1}$ for the symmetric stretching vibrations indicates the presence of hydrogen atom bonded to sp^3 hybridized carbon atoms (C-H).

Figure 1 shows the IR spectra of PPA1 and its metal complex PPA1/Cu²⁺ given as a comparison. It is seen that the absorption bands in the region $1500\text{--}1250\text{ cm}^{-1}$ are different (Figure 1(a)). A new intensive band at 1290 cm^{-1} was observed in the spectra of PPA1/Cu²⁺ complex which probably is due to the metal ions complex formation. The

characteristic C-H out-of-plane deformation vibrations of the aromatic naphthalene rings of PPA1 and PPA1/Cu²⁺ at the region $850\text{--}750\text{ cm}^{-1}$ are also very close. In the region where absorb C=O groups from the 1,8-naphthalimide structure ($1620\text{--}1720\text{ cm}^{-1}$) the difference is $6\text{--}8\text{ cm}^{-1}$ (Figure 1(b)) which can be explained by the possible metal ions coordination with C=O groups. The same results have been obtained in the case of PPA2 dendrimer and its metal complex. In Figure 2 the infrared spectra of PPA2 and PPA2/Zn²⁺ are plotted as an example. It is seen that in the region where absorb both carbonyl groups the difference is the same as that in the case of PPA1 dendrimer. The difference has been also observed and in the spectral region ($1200\text{--}1400\text{ cm}^{-1}$) where absorb tertiary amine and amide groups.

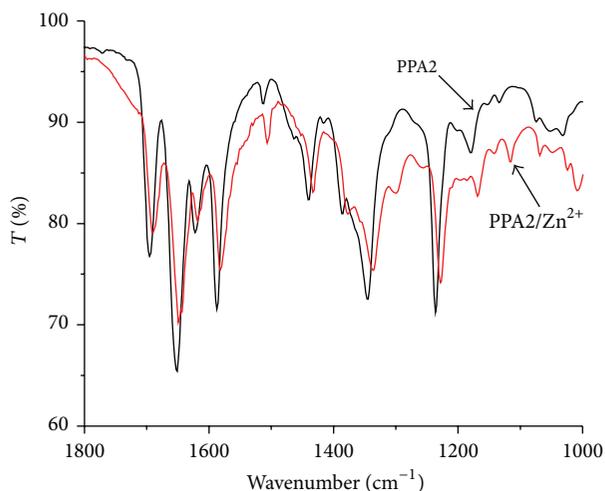


FIGURE 2: Infrared spectra of PPA2 dendrimer and PPA2/Zn²⁺ complex.

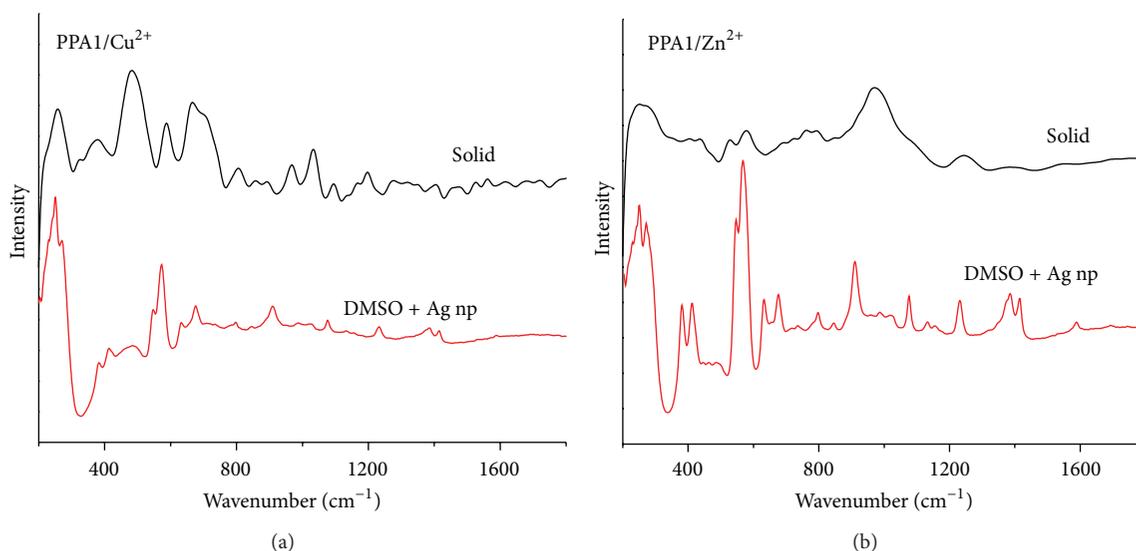


FIGURE 3: Raman spectra of PPA1 dendrimer complex in solid state and in DMSO solutions in the presence of silver nanoparticles.

When Raman active molecules are located near nanoparticles surface within the nanoparticles assembly, Raman signal intensities are substantially enhanced due to formation of hotspot. Metal nanoparticles have been used as the substrates for surface-enhanced Raman scattering (SERS) due to the enhancement mechanisms. The first mechanism has a chemical origin, which is due to the formation of a charge-transfer complex between the surface and the analyte molecules. The second mechanism can be attributed to the enhancement in electromagnetic field as a result of strong surface plasmon resonance of metal nanoparticle. The second mechanism amplifies the incident laser field and the scattered Raman field through their interaction with particle surface. The Raman scattering enhancement is attributed to plasmonic coupling between nanoparticles in close proximity, which results in local electromagnetic field enhancement on hotspots [16].

One of the major research topics is the development of nanoparticle assemblies which are capable of monitoring

SERS activity for application in environmental monitoring, diagnosis, and biodetection [17]. The analytical applications of Raman are limited due to low Raman cross-section of the analyte, which is often the case in inorganic metal species. However, SERS is a powerful spectroscopy technique for the monitoring spectral changes after interactions between metal cations and nanoparticles.

The metal ions complexes of dendrimers PPA1 and PPA2 have been analyzed by Raman spectroscopy in the region 200–2000 cm⁻¹ in solid state and in DMSO. Respective Raman spectra of the PPA/Cu²⁺ and PPA/Zn²⁺ are plotted in Figures 3, 4, and 5. In DMSO solution, silver nanoparticles have been used for better Raman signal enhancement, if compared to this investigated in solid state. The silver nanoparticles may aggregate in the presence of DMSO after the addition of metal complexes. This process may potentially affect the SERS signal. Therefore the experimental conditions

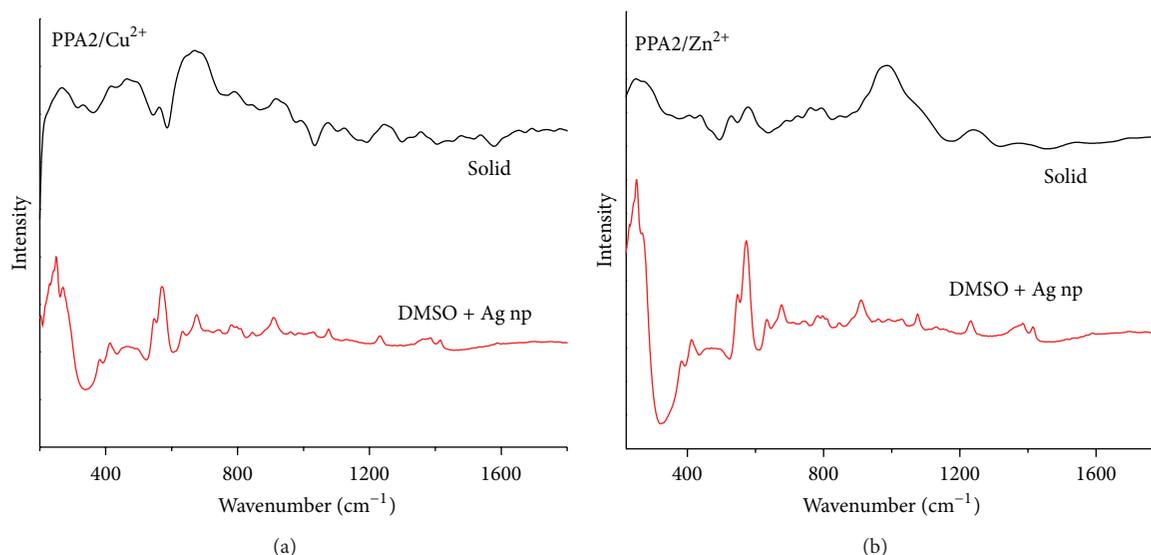


FIGURE 4: Raman spectra of PPA2 dendrimer complex in solid state and in DMSO solutions in the presence of silver nanoparticles.

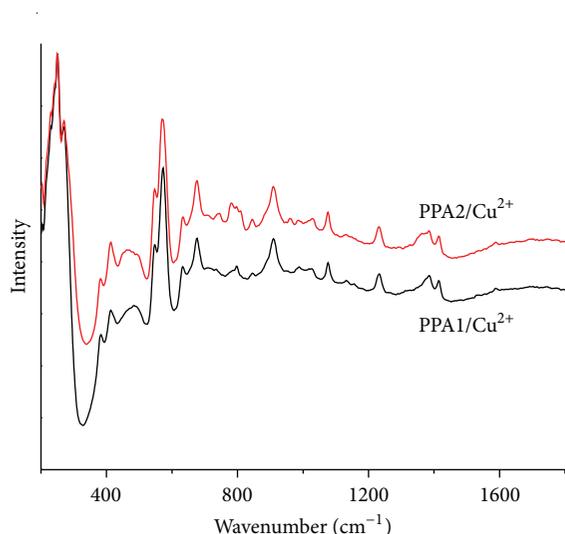


FIGURE 5: Raman spectra of PPA1/Cu²⁺ and PPA2/Cu²⁺ complex in DMSO solutions in the presence of silver nanoparticles.

such as the concentrations of silver nanoparticles and the type of solvent molecule are very important in order to get SERS signaling as much as possible. From the spectra in solutions and in solid state, it is seen that there are some changes in bands and lines intensity in the Raman spectra of both of the dendrimer complexes.

The strong bands of the Raman spectra of both of the dendrimer generations at 570–577 cm⁻¹ are characteristics for C–C–C in-plane aromatic vibration. The bands at 764–806 cm⁻¹ can be assigned for C–H out-of-plane bending while those at 1074–1096 cm⁻¹ are for C–H in-plane bending. The characteristic bands for the C–N bonds which are due to the tertiary amino group from aliphatic dendrimer structure are at 1230–1278 cm⁻¹. The C–N–C stretch from the imidic 1,8-naphthalimide structure is at 1355–1384 cm⁻¹.

The bands at 1538–1589 cm⁻¹ are assigned to the aromatic C–C stretching. The bending vibrations of CH₂ groups from the aliphatic dendrimer structure give rise to bands at 1413–1428 cm⁻¹. It should be stressed that in the Raman spectra vibrations of C=O groups do not demonstrate intensive bands as observed in the infrared spectra. The band attributed to C=O vibrations is detected with very small intensity near 1680 cm⁻¹.

Interest was demonstrated to investigate the type of dendrimer generation on the position of the signals in Raman spectra. In Figure 5 the Raman spectra of PPA1/Cu²⁺ and PPA2/Cu²⁺ complexes at 200–1800 cm⁻¹ range are presented as an example. It is seen that both spectra are almost identical which is due to the similar polarization of the dendrimer molecules. This is a proof that the generation of the dendrimers does not affect their polarization. The determining factor in this process is the type of the fluorophore comprised in the dendrimer.

In summary, it has been demonstrated that the infrared and Raman spectroscopies can be used as complementary methods for structural analysis, identification, and characterization of modified with 1,8-naphthalimide units poly(propylene amine) dendrimers from first and second generations and their Cu²⁺ and Zn²⁺ complexes.

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