

Rapid Recognition of Isomers of Monochlorobiphenyls at Trace Levels by Surface-Enhanced Raman Scattering Using Ag Nanorods as a Substrate

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ABSTRACT

Isomers and homologues of organic pollutants are hard to distinguish—especially in trace amounts—due to the similarities in their physical and chemical properties. We report here that by identifying the Raman characteristics of isomers of monochlorobiphenyls, these compounds can be recognized, even at trace levels, by using the surface-enhanced Raman scattering method with silver nanorods as a substrate. When dissolved in acetone, 2-, 3-, and 4-chlorobiphenyls were detected at a concentration of 10^{-8} mol/L, at which their characteristic Raman peaks were visible. This study may provide a fast, simple, and sensitive method for the detection and recognition of organic pollutants such as polychlorinated biphenyls.

KEYWORDS

Recognition, isomer, chlorobiphenyl, trace levels, SERS

1. Introduction

Persistent organic pollutants (POPs), e.g., dioxins, and polychlorinated biphenyls (PCBs), etc., are harmful and have polluted almost everywhere in the world [1]. The removal of these pollutants, which has aroused great research interest in recent years, requires techniques that are able to detect these compounds even at trace levels. This is because even in trace amounts in the environment, they can be accumulated at high dosage in human bodies through foods (vegetables, plants, animals, etc.) and cause severe health problems when they exceed the critical dose [1–3]. Currently, a combination of high-resolution gas chromatography and mass spectrometry is widely used as a powerful means for the detection of these

compounds; this method is, however, expensive and time-consuming, and is not always able to distinguish isomers [4–7].

Materials with dimensions on the nanometer scale exhibit many interesting properties and may find opportunities in the detection of trace amounts of organic pollutants [8–11]. For example, using nanostructures of noble metals (Cu, Ag, and Au) as the substrate, some organic species have been detected in trace amounts by surface-enhanced Raman scattering (SERS) [12–18]. The advantages of SERS are its high sensitivity, simplicity, fast detection speed, as well as its capability in the recognition of compounds. Therefore it is of interest to investigate the possibility of using SERS in detection/recognition of POPs such as PCBs. The difficulty of using SERS for PCBs is that they are

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insoluble in water, the solvent normally used in SERS measurements [19, 20]. Besides, little is known about the characteristics of their Raman spectra, which are essential for the recognition of isomers.

Here, we report an experimental and theoretical study of the Raman spectra of biphenyl and monochlorobiphenyl isomers, from which the characteristics of their Raman spectra were obtained, and then describe the detection and recognition of these compounds in trace amounts using aligned Ag nanorods as the substrate.

2. Experimental procedure

The Raman spectra of biphenyl, and 2-, 3-, and 4-chlorobiphenyls were measured with a Renishaw Raman 100 spectrometer using a 633 nm He–Ne laser as the excitation source at room temperature. Powders

of these compounds are commercially available from the AccuStandard Company. Simulation of the Raman spectra was performed by means of density functional theory using the Gaussian 03 program package in order to better understand the vibrational modes observed, and define the fingerprints of these compounds. For the SERS measurements, powders of chlorobiphenyls were dissolved in acetone to concentrations from 10^{-4} to 10^{-10} mol/L. The substrates were Ag nanorods prepared by electron beam deposition. The deposition of the Ag nanorods has been described elsewhere [21]. A small volume of each solution ($\sim 0.5 \mu\text{L}$) was dropped on the surface of Ag nanorods, and acetone was blown away using a nitrogen flow.

3. Results and discussion

Figures 1(a)–1(d) show the measured Raman spectra

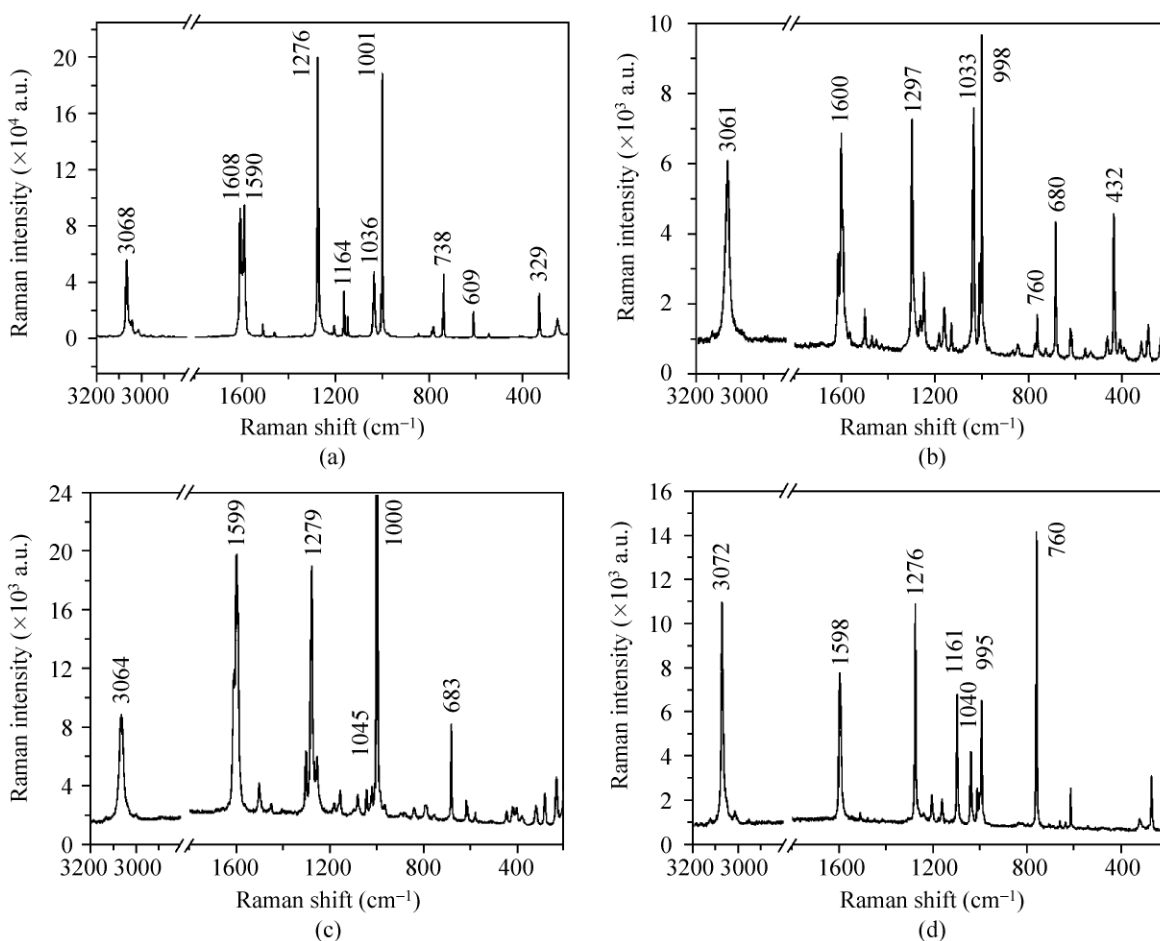


Figure 1 Raman spectra of (a) biphenyl; (b) 2-chlorobiphenyl; (c) 3-chlorobiphenyl; (d) 4-chlorobiphenyl, measured using powders commercially available from the AccuStandard Company

of biphenyl, and 2-, 3-, and 4-chlorobiphenyl, respectively. Each material has strong peaks at ~ 3065 , 1600, 1280, 1030, and 1000 cm^{-1} , demonstrating the common features of biphenyl and its derivatives. One may also notice differences between the Raman spectra of the four materials. For example: (1) biphenyl, 3- and 4-chlorobiphenyl all have a strong Raman peak around 1276 cm^{-1} , while the corresponding peak for 2-chlorobiphenyl is at $\sim 1297\text{ cm}^{-1}$; (2) biphenyl has a strong peak at 738 cm^{-1} , 2- and 4-chlorobiphenyl have strong peaks at $\sim 760\text{ cm}^{-1}$, but there are no significant peaks for 3-chlorobiphenyl in this region; (3) both 2- and 3-chlorobiphenyl have strong peaks around $\sim 680\text{ cm}^{-1}$, while biphenyl and 4-chlorobiphenyl have no visible peak nearby; (4) only 2-chlorobiphenyl has a strong peak at $\sim 432\text{ cm}^{-1}$. The above features might be used to detect and distinguish between biphenyl, and 2-, 3, and 4-chlorobiphenyl.

To gain a clear understanding of these features, we performed simulations using density functional theory with the Gaussian 03 program package. The simulations were carried out by Becke's three-parameter hybrid method using the Lee–Yang–Parr correlation functional (B3LYP), and the LANL2DZ basis set [22]. Gaussian View was used to input data visually. The π bond length of the benzene ring was set to be 1.409 \AA , the σ bond length between C and H atoms was set to be 1.088 \AA , and the σ bond length between C and Cl atoms was set to be 1.760 \AA .

Table 1 lists the major vibrational modes of the four materials obtained by the above simulations. The common features in their experimental Raman spectra at ~ 3065 , 1600, 1280, 1030, and 1000 cm^{-1} (see Fig. 1), can

be attributed to the C–H stretching mode ($\sim 3100\text{ cm}^{-1}$), the ring CCC stretching mode ($\sim 1650\text{ cm}^{-1}$), the C–C bridge bond stretching mode ($\sim 1280\text{ cm}^{-1}$), the C–H bending in-plane mode (1050 to 1100 cm^{-1}), and the CCC trigonal breathing mode ($\sim 1000\text{ cm}^{-1}$), respectively.

Replacement of the H by Cl atom results in different changes in the three CCC bending (ring deformation) in-plane modes (with calculated Raman shifts of 760 cm^{-1} , 680 cm^{-1} , and 460 cm^{-1}) for 2-, 3-, and 4-chlorobiphenyl. Figures 2(a)–2(c) show the most intense CCC bending in-plane mode for 2-, 3-, and 4-chlorobiphenyl, respectively. For 2-chlorobiphenyl, the 2–5 direction CCC bending at 460 cm^{-1} is the strongest, the 3–6 direction CCC bending at 680 cm^{-1} is slightly weaker, while the 1–4 direction bending at 760 cm^{-1} is weak. For 3-chlorobiphenyl, the 2–5 direction bending mode is negligible, the 3–6 direction bending mode is strong, while the 1–4 direction bending mode is weak. For 4-chlorobiphenyl, the 2–5 direction bending mode is negligible, the 3–6 direction bending mode is weak, while the 1–4 direction bending mode is strong. These results are in agreement with the experimental measurements (Fig. 1), and suggest that the intensities of the CCC bending in-plane modes can be used to distinguish between the three isomers.

The substrate used in the SERS measurements was Ag nanorods prepared by the electron beam deposition technique [21]. Figure 3 shows a typical scanning electron microscope (SEM) image of the Ag nanorods, taken with an FEI SEM (Quanta 200 FEG) working at 20 kV. Powders of 2-, 3-, and 4-chlorobiphenyl were dissolved in acetone and diluted to concentrations

Table 1 Major simulated vibrational modes for 2-, 3-, and 4-chlorobiphenyl

Vibrational mode	Raman shift (cm^{-1})	Raman intensity 2-chlorobiphenyl	Raman intensity 3-chlorobiphenyl	Raman intensity 4-chlorobiphenyl
C–H stretching	3100	511	359	351
CCC stretching	1650	31	34	38
C–C bridge bond stretching	1280	50	50	62
C–H bending in-plane	1050	46	22	15
Trigonal breathing	1000	34	44	27
CCC bending in-plane (1–4 direction)	760	3	4	23
CCC bending in-plane (3–6 direction)	680	11	8	7
CCC bending in-plane (2–5 direction)	460	13	0	0



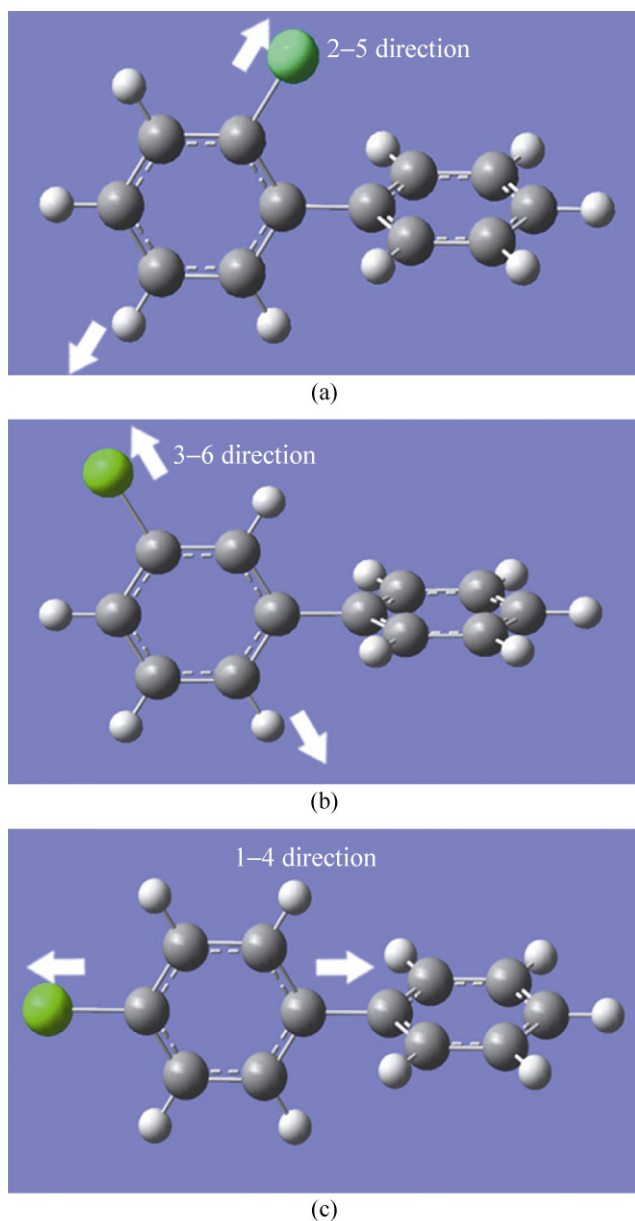


Figure 2 The most intense ring deformation in-plane modes for the three isomers of chlorobiphenyl: (a) 2-chlorobiphenyl; (b) 3-chlorobiphenyl; (c) 4-chlorobiphenyl

ranging from 10^{-4} to 10^{-10} mol/L. A small volume ($0.5 \mu\text{L}$) of these solutions was dropped on Ag nanorods and the acetone was blown away using a gentle nitrogen flow. Figures 4(a)–4(c) show the SERS spectra of the 2-, 3-, and 4-chlorobiphenyl, respectively, at various concentrations. The accumulation time of each spectrum was fixed at 30 s per 100 cm^{-1} , and we used only 10% laser power (0.47 mW) to avoid radiation damage. The characteristic Raman peaks are all clearly

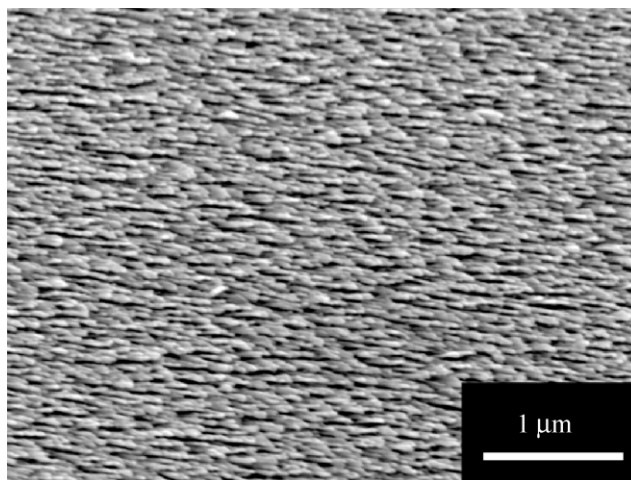


Figure 3 A typical SEM image showing the morphology of Ag nanorods used as the SERS substrate in this study

observed for each of the three isomers even at a concentration of 10^{-8} mol/L, suggesting that the SERS technique is able to detect chlorobiphenyls even at such a low concentration.

Figure 4(d) shows a comparison of the SERS spectra of the three isomers at a concentration of 10^{-6} mol/L. At this concentration the three spectra show the common features mentioned above around 1600, 1280, 1030, and 1000 cm^{-1} (the region around 3100 cm^{-1} was not scanned). The spectra also clearly show the individual characteristic Raman peaks for the three isomers, i.e., the difference in the CCC bending (ring deformation) in-plane modes caused by the Cl atom replacement. The spectra suggest that by using Ag nanorods as substrates, the SERS technique is capable of detecting chlorobiphenyls at trace levels and is capable of recognizing the isomers at low concentrations.

4. Concluding remarks

We have demonstrated a simple method to detect and recognize the isomers of chlorobiphenyls, even in trace amounts, by using the SERS technique with Ag nanorods as substrates, based on an understanding of Raman characteristics of these compounds. This method might be also applicable to the detection of PCBs, which is crucial for the effective removal of these hazardous substances.

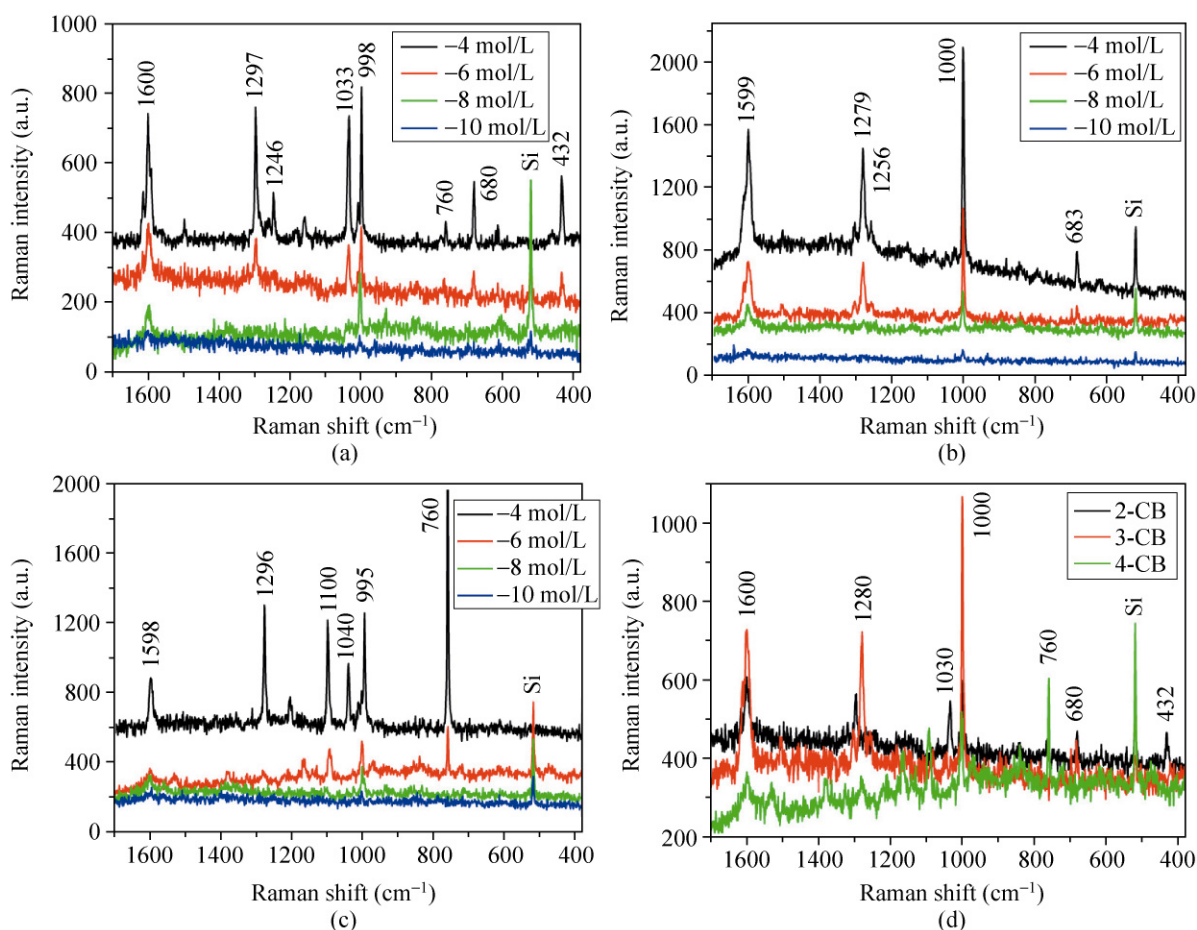


Figure 4 SERS spectra of (a) 2-chlorobiphenyl; (b) 3-chlorobiphenyl; (c) 4-chlorobiphenyl at concentrations from 10^{-4} to 10^{-10} mol/L in acetone. (d) A comparison of the SERS spectra of the three isomers at a concentration of 10^{-6} mol/L

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