

Monitoring Based on Narrow-Band Resonance Raman for “Phase-Shifting” π -Conjugated Polydiacetylene Vesicles upon Host–Guest Interaction and Thermal Stimuli

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The present study reports a quantified monitoring by means of in situ resonance Raman scattering that analyzes phase-shifting characteristics of π -systems upon interacting with target analytes. A chemo- and thermochromic polydiacetylene vesicular probe is evaluated with multiple-wavelength Raman scattering modes in resonance with its phases, respectively, and thus can trace the phase-shifts. This Raman scattering-based analytical quantification is also successful in monitoring host–guest recognition events by utilizing much narrower bands, compared to those in conventional absorption or photoluminescence (PL) methods. As one of the outcomes, the monitoring analysis overcomes the limitations based on widely used colorimetric response (%CR) or PL that failed in the case of interaction with a surfactant, CTAB.

Conjugated polymers have been widely investigated for a broad spectrum due to their important electronic and optical properties enabled by the extended π -electron delocalization along backbones.^[1,2] Accordingly, in response to external stimuli due to the transfer of the excitation energy along the whole backbone, the conjugated polymer-based sensors demonstrate an important advantage of amplification of fluorescence signals.^[1–4] Among them, polydiacetylene (PDA) represents one of the most explored conjugated polymers, and has been widely proposed as an ideal candidate for sensing materials upon their chromic and fluorescent transitions.^[5,6] Since the first synthesis by Wegner in 1969,^[7] PDA has been widely studied

and developed by several groups.^[8–10] It is known that when the aligned diacetylene monomers are irradiated by UV light, blue colored PDA is formed with its main absorption at ≈ 640 nm. Once it is stressed by external stimuli, blue-to-red color transition takes place and the main absorption shifts to ≈ 540 nm. Such colorimetric transition is interpreted as “phase-shifting” where the effective conjugation length of π -electrons of PDA gets substantially shortened.^[11,12] Based on these characteristics, Charych et al. first applied PDA bilayer assembly on colorimetric detection of a receptor–ligand interaction.^[13] Most of the later studies using PDA as sensing materials, the resulting signals were per-

formed as absorption or fluorescence with broad spectra.^[14,15] Hence, an analysis tool with narrow spectra will be a powerful supplement.

It is well known that resonance Raman spectroscopy (RRS) is a powerful tool used to characterize the vibrational and electronic properties of π -conjugated systems.^[16,17] The resonance effect can enhance Raman signal up to $\approx 10^7$ times that of normal Raman spectroscopy.^[18,19] A successful example is the use of RRS in exploring the properties of carbon-based nanomaterials with abundant sp^2 bonds such as graphene,^[20] carbon nanotube,^[21] and fullerene.^[22] In the field of π -conjugated polymers,^[23] the chemical nature of the backbone has been also well characterized by the RRS.^[24,25] RRS effect takes place when the incident laser photon energy matches with the absorption band of conjugated polymers. When the conjugated polymers undergo phase-shifts, the resonance effect will vary greatly due to mismatching with photon energy.^[26] As mentioned above, the PDA materials take place “phase-shifting” when they are exposed to external stimuli. Hence, characterizing the sensing performance using RRS may be an unprecedented approach. By selecting Raman laser wavelengths matching absorption band shifts, “phase-shifting” characteristics of PDA materials are able to be traced in terms of varying RRS signals, which further relates to its functions. Nevertheless, there has never been a report on evaluating quantitative colorimetric response of PDA-based sensor probes using resonance Raman signals.

In this study, we first demonstrate the resonance Raman-fluorescence effect on thermochromic phase-shifting PDA by in situ monitoring with multiple laser sources, which is followed by chemochromatic studies. We use resonance Raman response (rRR) to evaluate quantitative Raman scattering of the

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