

## Simultaneous Raman and Fluorescence Spectroscopy of Single Conjugated Polymer Chains

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Simultaneous surface enhanced Raman scattering (SERS) and fluorescence is demonstrated from single conjugated polymer chains. As resonance enhancement of SERS depends on the spectral overlap of the polymer's absorption and the incident laser, resonance Raman and fluorescence effectively probe the absorbing and emitting part of the polymer, respectively. The optical phonon energies change along the polymer chain, providing a window to spatially track excited state relaxation. Whereas a mean spatial redistribution of the excitation is witnessed by a change in vibronic fingerprint following interchromophoric energy transfer, intrachromophoric exciton self-trapping leaves the vibrations unchanged.

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A particularly appealing aspect of the science of organic semiconductors lies in the ability to dissect the bulk material into its individual molecular constituents. Whereas many parallels exist between molecular and conventional electronics on the bulk level, the richness of synthetic organic chemistry avails ubiquitous opportunities for molecular scale engineering of electronic properties. Consequently, molecular level characterization techniques are in high demand. While ensemble methods such as ultrafast or site-selective spectroscopy offer insight into elementary photophysical processes and excited state dynamics relevant to devices, it is often hard to distinguish between homogeneous intrinsic and inhomogeneous extrinsic, i.e., disorder induced, effects. Single molecule spectroscopy readily overcomes disorder but can make reliable fingerprinting of a particular molecular system hard due to the plethora of dynamic characteristics [1,2]. A conjugated polymer chain consists of many covalently bound repeat units (monomers) which share  $\pi$  electrons. Scissions in the delocalized  $\pi$  system due to structural or chemical defects lead to the formation of individual chromophoric units on the polymer chain. Plasmonic field enhancement on rough silver films [3] allows us to perform surface enhanced (resonance) Raman scattering [SE(R)RS] [4–9] on individual chromophores on the single polymer chain and uncover unambiguous structural fingerprinting. As the resonance enhancement of SERRS depends on the spectral overlap between the polymer's absorption and the laser line, the SERRS intensity provides a measure of absorption strength. Vibrational modes determined by SERRS are characteristic of the absorbing part of the polymer molecule, whereas the vibronic progression in the luminescence relates to the emitting unit.

The technique allows us to discriminate between two processes which contribute to excited state relaxation in multichromophoric macromolecular complexes: phonon-assisted exciton self-trapping within the chromophore and

energy transfer between chromophores. Simultaneous photoluminescence (PL) and SERRS provide direct insight into spatial dynamics of the exciton through vibronic fingerprinting. While intramolecular energy transfer coincides with a difference in vibronic fingerprints of absorbing and emitting chromophores, surprisingly, the fingerprint is retained following the collapse of the exciton wave function due to self-trapping [10,11]. This observation implies that exciton localization occurs randomly throughout the extension of the chromophore so as to probe the same vibrations relevant to absorption. In addition, the unprecedented accuracy in determining vibrational modes of the chromophore is important in developing a microscopic understanding of polaron formation [12], and phonon-assisted hopping or resonant tunneling. On the other hand, highly polarizable conjugated polymers with distinct collective vibrational modes and narrow electronic transitions at low temperatures [2] themselves provide versatile systems to study the underlying physics of SERRS as the polymer molecule shifts in and out of resonance with the light source [7,8,13].

Since its discovery, SERS has received much attention in physics and materials science [4,7–9,13,14], not least due to its single molecule sensitivity [5,6,15–19]. While the theory of SERS is well advanced [7], it is not always straightforward to find reproducible experimental implementations [17]. In particular, as the analyte density approaches the single molecule level vibronic signatures of contaminants, which are equally amplified, become a severe problem [17]. Rather than restricting ourselves to the strong C=C mode around  $1600\text{ cm}^{-1}$  characteristic of many organic compounds but also prevalent among contaminants [17], we chose a system containing alkyne units (C≡C) vibrating at  $\sim 2200\text{ cm}^{-1}$ .

We prepared SERS substrates following the Tollens silver mirror reaction [19,20]. Single polymer chain samples were produced by spin coating highly dilute con-

jugated polymer solutions ( $\sim 10^{-10}$  mol/l in toluene) directly onto the metal. The samples were mounted in a He cold-finger cryostat and excited in the polymer's absorption band using an  $\text{Ar}^+$  laser at  $21.84 \times 10^3 \text{ cm}^{-1}$  ( $\sim 200 \text{ W cm}^{-2}$ ) in an epifluorescence microscope setup [2]. Turning to low temperatures (all measurements were performed at 5 K) minimizes molecular motion around the plasmonic hot spot and yields narrow electronic resonances on the molecule [2]. Figure 1 shows the structure of the poly(phenylene-ethynylene-butadiynylene) polymer ( $M_w = 70 \text{ kD}$ ;  $D = 3.2$ ) along with typical PL and SERRS spectra of two single chains. The PL spectrum was superimposed from 12 successive measurements of the same single chain of 2 s integration time each, whereas the SERRS spectrum consists of 250 recordings of 2 s duration. Direct comparison of the vibronic frequencies in PL and Raman requires shifting of the PL spectrum along the abscissa by the zero-phonon (PL peak) energy. The Raman normal modes  $\omega_{\text{RS}}$  are virtually identical to the vibronic PL modes  $\omega_{\text{PL}}$  and agree with the ensemble values reported for diphenyldiacetylenes. This direct agreement between PL and SERRS is particularly remarkable in view of the fact that Raman and ensemble PL have previously been found to be only indirectly related in the inherently disordered ensemble of model  $\pi$  systems [21]. Evidence for the presence of single polymer chains comes from the spectral dynamics, intensity fluctuations, and the scatter of PL and Raman peak energies (see below). This scatter is expected from the dispersion of chromophore and phonon energies witnessed in site-selective fluorescence and resonant Raman scattering (RRS) [22,23] of the inhomogeneously broadened ensemble. Nonresonant SERS was also observed at  $19.44 \times 10^3 \text{ cm}^{-1}$  excitation and  $\sim 50$ -fold power density and in principle agreed with the observations in resonance.

The frequency of observed events on our SERS substrates agrees with expectations: from Ref. [19] we arrive at about 20 hot spots per area of  $(7.5 \mu\text{m})^2$ . A rough estimate for the probability  $P$  of an isolated chain to

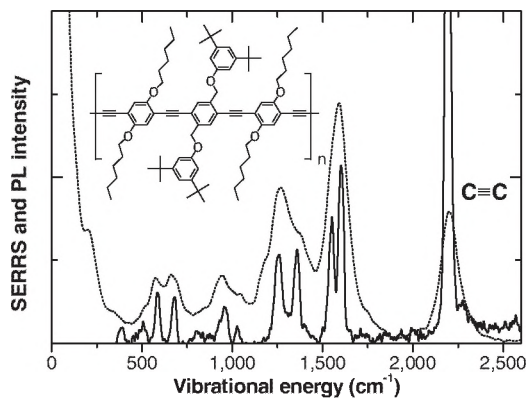


FIG. 1. PL (dotted line) and SERRS spectra of single poly(phenylene-ethynylene-butadiynylene) chains at 5 K under excitation at  $21.84 \times 10^3 \text{ cm}^{-1}$ . The energy of the PL maximum is shifted to  $0 \text{ cm}^{-1}$ .

interact with a hot spot comes from the number of hot spots expected per average area occupied by a polymer molecule. To a first approximation, this area is the polymer's average length ( $L \approx 150 \text{ nm}$ ) squared, leading to  $P \approx (150 \text{ nm})^2 / (7.5 \mu\text{m})^2 \times 20 \approx 1\%$ . On average, we observe SERRS from  $\sim 2$  single chains in a field of view of  $(50 \mu\text{m})^2$ . Depending on how much of the roughly  $20 \mu\text{l}$  polymer solution spin-coated remains on the substrate of size  $(15 \text{ mm})^2$ , we expect between  $10^3$  and  $10^4$  single chains to be deposited in the field of view. The observed likelihood  $P < 2/10^3 \approx 0.2\%$  of a single chain experiencing field enhancement is remarkably close to the rough estimate expected from the density of hot spots and the length of the polymer, considering  $L^2$  is clearly an overestimate of the interaction area.

We studied a total of 696 single polymer chains at different spatial positions on different Tollens substrates. Roughly 75% displayed PL only, 15% Raman only and 10% combined Raman and PL. The latter case is the most interesting as it allows us to study both the resonance condition in SERRS as well as excited state relaxation. Rather than tuning the laser across resonance with the material as in conventional ensemble RRS [22,23], we exploit the fact that the resonance condition is controlled by the spectral dynamics of the single chromophore. Figure 2 summarizes evidence for the simultaneous occurrence of PL and SERRS from a single chromophore within an individual chain. We observed a total of 16 such clear-cut events. Panel (a) plots light intensity against time (2 s resolution). We chose a logarithmic color coding of intensity [given in panel (d)] which clearly reveals two features: spectrally narrow bands, which only fluctuate in intensity but not in spectral position; and broader bands which fluctuate both in intensity and spectral position. The former correspond to the Raman bands, whereas the latter originate from PL exhibiting spectral diffusion, a feature characteristic of single polymer chains. Two example spectra recorded at the times marked by arrows in panel (a) are displayed in panel (b). While RRS and PL occur simultaneously from the polymer chain studied, the Raman shift axis shown on the right is only physically meaningful for the Raman and not for the PL bands (in contrast to the two separate measurements in Fig. 1)—the relative spectral positions of PL and RRS bands do not carry any information. The spectra suggest that the relative amplitudes of RRS and PL are linked to the spectral positions of the PL bands. Figure 2(c) shows a systematic analysis of this observation by plotting the RRS intensity of the  $\text{C}\equiv\text{C}$  mode  $I_{\text{C}\equiv\text{C}}^{\text{RRS}}$  as a function of the photon energy of the  $\text{C}\equiv\text{C}$  mode in PL  $E_{\text{C}\equiv\text{C}}^{\text{PL}}$ . As the PL shifts to the red, i.e., the zero-phonon line moves out of resonance with the laser, the Raman intensity decreases. Simultaneously, the PL intensity decreases as the absorption strength is reduced so that  $I_{\text{C}\equiv\text{C}}^{\text{RRS}}$  also correlates with  $I_{\text{C}\equiv\text{C}}^{\text{PL}}$  [panel (d)]. Note that for this measurement the Raman filter with a cutoff at  $21.46 \times 10^3 \text{ cm}^{-1}$  truncated part of the zero-phonon line.

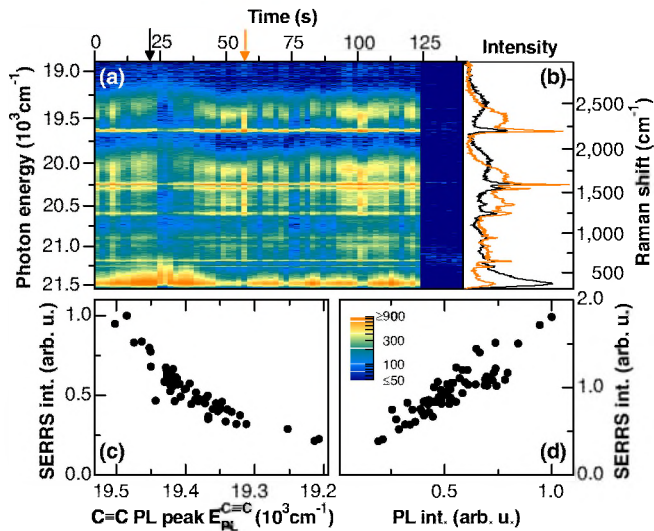


FIG. 2 (color online). Influence of spectral diffusion on simultaneous SERRS and PL from a single chromophore on a single polymer chain. (a) Intensity time trace showing PL and RRS [logarithmic color coding of intensity given in panel (d)]. (b) Two example spectra taken at times marked by arrows in (a). (c) Correlation between SERRS intensity and PL photon energy of the C $\equiv$ C mode. (d) Correlation between SERRS and PL intensity of the C $\equiv$ C mode.

Dynamics in SERS intensity are often attributed to thermal effects and a change in coupling between single molecule and plasmonic hot spot [17,24]. In the present low temperature measurement, the dynamics clearly arise from intrinsic spectral diffusion of the electronic transition of the polymer chromophore, leading to a change in electronic coupling and SERRS intensity as recently predicted theoretically [13]. At  $t = 124$  s the PL vanishes but a very weak Raman signal remains. We attribute this to residual (nonresonance) SERS from the chromophore once the  $S_0 \rightarrow S_1$  transition has photobleached.

The correlation between PL photon energy ( $E_{\text{C}\equiv\text{C}}^{\text{PL}}$ ) and SERRS intensity ( $I_{\text{C}\equiv\text{C}}^{\text{RRS}}$ ) shown in Fig. 2 provides a clear indication that RRS and PL occur from the same chromophore on the chain. Figure 3, on the other hand, illustrates an example where no such correlation is observed (total of 40 events). In this case the emission is substantially redshifted to  $\sim 20.96 \times 10^3 \text{ cm}^{-1}$ . At  $t = 492$  s the PL intensity suddenly drops and returns blueshifted to  $\sim 21.46 \times 10^3 \text{ cm}^{-1}$  at  $t = 610$  s. Panel (b) plots  $I_{\text{C}\equiv\text{C}}^{\text{RRS}}$  against  $E_{\text{C}\equiv\text{C}}^{\text{PL}}$  and displays no correlation. In the region  $t = 610$ – $674$  s of blueshifted emission (marked by a box), however, a correlation in the spectral diffusion of the chromophore is observed [panel (c)]. We propose that the correlation of spectral diffusion with Raman intensity is not observed because of intramolecular interchromophoric energy transfer: RRS and PL occur from two different chromophores. Once the lower energy emitting chromophore has photobleached, energy transfer is impeded and absorption, emission and RRS occur from the same chromophore as summarized in the sketch.

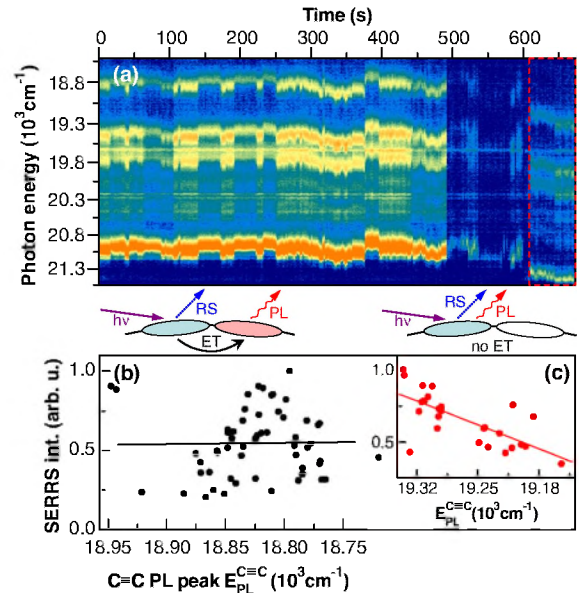


FIG. 3 (color online). PL and SERRS occurring from different chromophores of a single polymer chain. (a) PL and SERRS (logarithmic scale) as a function of time. (b) Absence of a correlation between SERRS intensity and PL photon energy of the C $\equiv$ C mode. (c) A correlation is observed following the spectral jump to the blue at  $t = 610$  s (box), suggesting SERRS and PL now arise from the same chromophore (sketch).

We detected narrow ( $< 80 \text{ cm}^{-1}$  width) zero-phonon lines at down to  $20.41 \times 10^3 \text{ cm}^{-1}$ . As the PL intensity was comparable for all single chains studied we conclude that it is generally the zero-phonon transition which absorbs rather than a vibronic sideband. This large shift between absorption and emission of over  $1370 \text{ cm}^{-1}$ , which is much greater than the  $S_1$  relaxation energy, is accounted for by intramolecular energy transfer. This is further supported by the efficient depolarization of the PL of single chains: multiple chromophores with different orientations on a single chain absorb, but excitation energy is subsequently funneled to only a few which emit so that the polarization anisotropy is greater in emission than in excitation (not shown).

The phonon energy differs between polymer chains due to, e.g., local variations in strain [25], but can potentially also change along the chain. SERRS and PL provide separate routes to determining the phonon energies of the absorbing and emitting units within one single multichromophoric polymer chain. Generally, we would not expect these to agree: both excited state relaxation mechanisms, intrachromophoric self-trapping and interchromophoric energy transfer, imply that emission occurs from a different part of the polymer molecule than absorption as sketched in Fig. 4. Figure 4 shows a plot of  $\omega_{\text{RS}}^{\text{C}\equiv\text{C}}$  vs  $\omega_{\text{PL}}^{\text{C}\equiv\text{C}}$  for 56 single chains recorded at different spatial positions on different substrates. A steep Raman filter ( $21.65 \times 10^3 \text{ cm}^{-1}$  cutoff) allows complete detection of the PL zero-phonon line required for accurate determination of  $\omega_{\text{PL}}^{\text{C}\equiv\text{C}}$ , the frequency shift of the C $\equiv$ C band with respect

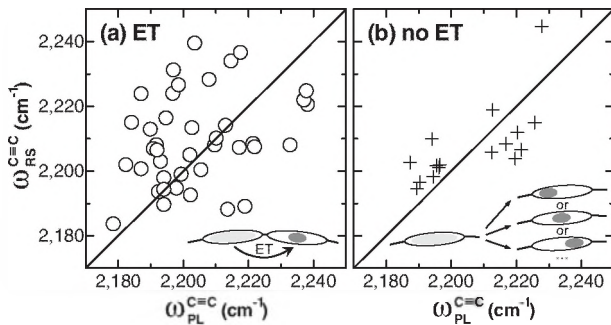


FIG. 4. Scatter plot of phonon energies  $\omega^{\text{C}\equiv\text{C}}$  about the ideal line, derived from 56 different single chains displaying simultaneous PL and SERRS. We distinguish situations for which energy transfer (ET) is (a) probable and (b) improbable. (a) The absorbing chromophore has a different phonon energy ( $\omega_{\text{RS}}^{\text{C}\equiv\text{C}}$ ) to the emitting one ( $\omega_{\text{PL}}^{\text{C}\equiv\text{C}}$ ). (b) Absorbing and emitting chromophores are identical. PL and SERRS display the same phonon energies, indicating that exciton self-trapping occurs randomly throughout the chromophore. This is illustrated in the cartoon by the transition from light to dark gray.

to the main PL line (error  $\delta\omega_{\text{PL}}^{\text{C}\equiv\text{C}} \approx 10\text{--}20\text{ cm}^{-1}$ , depending on PL intensity). Panel (a) summarizes polymer chains for which energy transfer is suspected as the emission is statistically redshifted (emission range  $20.53\text{--}21.37 \times 10^3\text{ cm}^{-1}$ ) and no  $E_{\text{C}\equiv\text{C}}^{\text{PL}} - I_{\text{C}\equiv\text{C}}^{\text{RRS}}$  correlation is observed (i.e., the situation in Fig. 3). Here, the phonon energies derived from PL and SERRS are clearly not the same. In contrast, if an  $E_{\text{C}\equiv\text{C}}^{\text{PL}} - I_{\text{C}\equiv\text{C}}^{\text{RRS}}$  correlation is observed (the situation in Fig. 2) and the PL energy is statistically closer to the excitation energy (emission range  $21.37\text{--}21.65 \times 10^3\text{ cm}^{-1}$ ), energy transfer is considered improbable. Consequently, the two phonon energies relevant in absorption and emission coincide within experimental error ( $\delta\omega_{\text{RS}}^{\text{C}\equiv\text{C}} < 5\text{ cm}^{-1}$ ) as only one chromophore is involved in both processes [panel (b)].

This coincidence provides important information on the nature of phonon-assisted self-trapping in organic semiconductors, which is often thought of as a collapse of the exciton wave function to the center of the conjugated segment following structural relaxation [10]. The distribution in phonon energies (Fig. 4) between 2180 and 2240  $\text{cm}^{-1}$  in part arises due to local inhomogeneities which influence equilibrium interatomic distances [25]. As the  $\text{C}\equiv\text{C}$  optical phonon is highly localized, the only way for the self-trapped exciton observed in PL ( $\omega_{\text{PL}}^{\text{C}\equiv\text{C}}$ ) to report the same phonon energy as the delocalized exciton observed in SERRS ( $\omega_{\text{RS}}^{\text{C}\equiv\text{C}}$ ) within a chromophore is for the self-trapping events to occur randomly on all available sites within the chromophore during repeated excitation in the measurement process. While the trapped exciton may be static (structural relaxation energy  $\gg kT$ ), the collapse of the exciton may occur on any site within the chromophore. The measurement then samples the temporal average, so that on average the same sites (i.e., the same  $\text{C}\equiv\text{C}$  units) are probed in absorption and emission.

Our results illustrate how PL and SERRS provide equally significant insight into the vibrational characteristics of single polymer chains and how a combination of both illuminates excited state relaxation mechanisms in these complex multichromophoric macromolecules. This vibronic fingerprinting reveals that while energy transfer leads to a mean spatial redistribution of the exciton wave function, surprisingly, mere exciton self-trapping does not. An interesting avenue to pursue in the future will be a direct control of the electronic transition of a chromophore on a single chain using the Stark effect in conjugated polymers. This will enable us to fine tune the light-matter interaction in RRS directly rather than resorting to random spectral diffusion. In addition, time-gated single chain detection [2] will allow a separation of quasi-instantaneous Raman scattering from spontaneous emission. We also anticipate microscopic structural insight into much more complex phases of conjugated polymers such as those found in polyfluorenes.

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