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Photoluminescence changes of C_{70} nanotubes induced by laser irradiation*

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C_{70} nanotubes with a fcc lattice structure are polymerized through being irradiated by lasers with a wavelength of 514.5 nm at various power values. Raman spectra and photoluminescence (PL) spectra are employed to characterize the polymeric phases of the laser treated samples, showing that the disordered C_{70} oligomers are formed in the C_{70} nanotubes irradiated by such strong green lasers. Comparative studies further indicate that intermolecular bonds are formed between C_{70} molecules on the surface of nanotubes, which are similar to those formed under high pressure and high temperature (HPHT) conditions. And the content of intermolecular bonds increases obviously with the laser power increasing.

Keywords: fullerene, polymerization, photoluminescence, nanocrystals

PACS: 42.70.Gi, 68.35.Rh, 78.55.Hx, 78.30.Na **DOI:** 10.1088/1674-1056/ab9de2

1. Introduction

As a kind of unique semiconducting material, fullerene forms a new phase of carbon with distinctly different molecular structural and electronic properties.[1,2] In particular, a series of novel nanocrystals with individual fullerene molecule as building blocks has set off a renaissance in scientific research.[3–7] Such nanocrystals exhibit many excellent properties, which are expected to have a good potential applications in the fields, such as chemistry, physics, material science, and even biology.[3–8] Many efforts have been made to study C_{60}, in order to improve its properties to meet the needs in application.[9,10] As the second most abundant fullerene, C_{70} is expected to have properties superior to those of C_{60}, due to its elliptical molecular structure and relatively strong polarity. Nevertheless, less work has been done on the investigation of C_{70} nanocrystals. In our previous work, C_{70} nanocrystls with different shapes and good PL properties have been fabricated by introducing a series of alcohols as precipitant into a C_{70}/m-xylene solution.[11] However, the mechanisms for the PL emissions of C_{70} nanocrystals are still unclear. In the view of fundamental and practical point, it is therefore important to explore the PL mechanism of C_{70} and an efficient method to tune its PL properties.

As is well known, fullerene molecules in solid crystals can form covalent bonds with their molecular neighbors under extreme conditions.[12–16] The formation of inter-molecular covalent bonds usually induce polymeric structure to form, through which their physical and chemical properties can be tuned, such as PL properties.[13,14] As well discussed by previous researchers, fabricating polymeric fullerene materials by the HPHT method proved to be a productive way to obtain new functional materials. In our recent investigation, several types of polymeric phased fullerene nanocrystals were obtained through an HPHT method, and the PL properties of pristine fullerene crystals changed after such treatment.[15,16] On the other hand, when fullerene materials were exposed to strong irradiation, polymerized structure could also be obtained, particularly for thin films.[17–19] Compared with the HPHT method, the laser irradiation is a simple and low cost method to fabricate the fullerene materials. However, few work was reported on the photo-induced polymerization of fullerene nanocrystals, especially on C_{70} nanocrystals. It is therefore very important to explore a luminescence tuning method on C_{70} nanocrystals and to reveal the relationship between the luminescence properties and their polymeric phases.

In this work, C_{70} nanotubes are irradiated by a laser with a wavelength of 514.5 nm at different power values. Raman and PL spectra are employed to characterize the samples after the irradiating treatment. The center of the main PL band of C_{70} nanotubes is tuned from visible to near-infrared range through being irradiated by the strong laser. Raman results

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and the reference PL spectra of HPHT treated samples indicate that disordered C_{70} oligomers are formed when the laser power is higher than 2 mW. Furthermore, by analyzing in detail the laser power dependence of the fitted peaks of PL components, the mechanism for the luminescence of C_{70} nanotubes is revealed.

2. Experiment

C_{70} nanotubes were fabricated by introducing isopropyl alcohol into a saturated solution of C_{70} in m-xylene with a volume ratio of 10:1, followed by heat treatment on the as-grown samples at 150 °C in vacuum for 5 h, which was reported in our previous research.[20] The sample morphology was characterized by scanning electron microscopy (SEM, JEOL JSM-6700F). X-ray diffraction (XRD, Rigaku D/max-RA, Cu KR1 radiations $\lambda = 1.5406$ Å) showed that the pristine C_{70} nanotubes crystallize into the fcc structure. Raman spectroscopy (Renishaw inVia, UK) was first carried out using an 830-nm laser as excitation to avoid photo-polymerization. The ultraviolet-visible (UV) absorption spectra were measured with a UV spectrometer (Lambda 35 spectrophotometer).

To obtain the photo-polymerized structure in C_{70} nanotubes, lasers with a wavelength of 514.5 nm was employed to irradiate the surface of as-grown C_{70} nanotubes through a microscope (Leica, DMLM). And a 50× magnification microscopic objective was used in all the experiments. The numerical aperture of the objective was NA = 0.5 from the formula

$$D = 1.22\lambda/\mathrm{NA},$$

where D is the spot diameter.

The spot diameter on the sample front was calculated to be ~ 1.26 μm, and the spot area was ~ 1.4 μm^2. Laser with power of 0.2 mW, 1 mW, 2 mW, 10 mW, and 20 mW were separately focused on the surface of samples for 1 min. And then, micro-Raman and PL spectra were recorded at the same point of the sample, at room temperature, using Renishaw in Via Raman microscope, with 514.5-nm laser used as excitation. In both the Raman and PL experiments, the exposure times were all set to be 10 s.

Furthermore, the pristine samples were treated at a hydrostatic pressure of 2.0 GPa and the temperature of 700 K by using a piston-cylinder device for 1 h, in which silicone oil (Dow Corning DC200) was used as a pressure transmitting medium. Identical PL measurement was carried out on the HPHT treated samples.

3. Results and discussion

Figure 1(a) shows the SEM images of pristine C_{70} nanotubes. The image shows that the as-grown samples have tubular shapes, with outer diameters ranging from 300 nm to 500 nm. The insert in Fig. 1 shows the XRD pattern of pristine C_{70} nanotubes. Four diffraction peaks indexed as the (111), (220), (311), and (024) reflections of an fcc structure are shown in the XRD spectra, respectively. The lattice constant is $a = 1.492$ nm, which is similar to that of C_{70} bulk crystals measured at room temperature.[21]

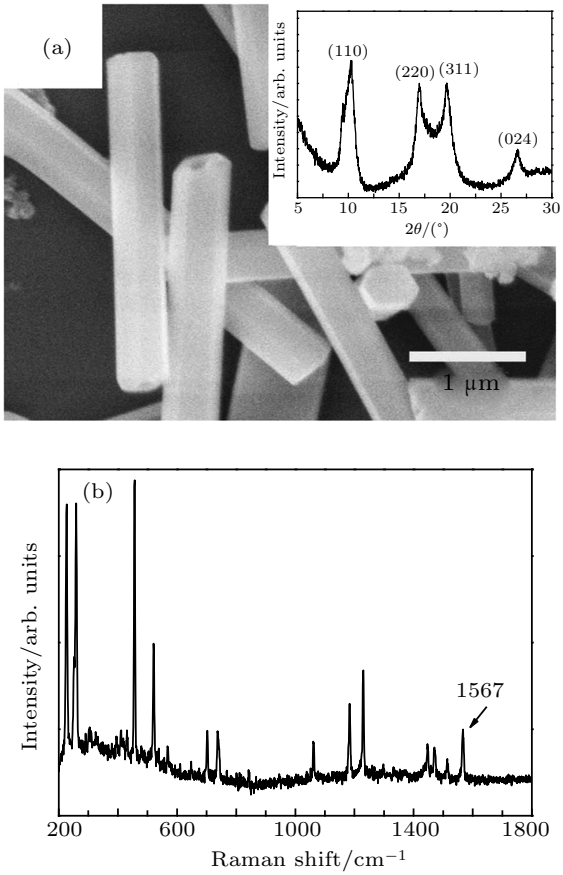


Fig. 1. (a) SEM image with insert showing XRD pattern of as-grown C_{70} nanotubes and (b) Raman spectrum with 830-nm laser used as excitation line of as-grown C_{70} nanotubes.

Raman spectroscopy is a powerful tool to characterize fullerene materials.As is well known, 53 Raman active modes for pure C_{70} molecules are predicted ($12A_1' + 22E_2' + 19E_1'$) from the D_{5h} point group according to group theory.[22,23] To obtain the initial vibration frequency of pristine sample, an infrared laser with a wavelength of 830 nm is first employed as an excitation in this work to avoid the polymerization induced by high energy laser. As shown in Fig. 1(b), Raman spectrum of as-grown C_{70} nanotubes is exhibited. At least fourteen strong Raman peaks are observed. All of these peaks are consistent with those of the C_{70} bulk crystals, which suggests that the as-grown sample is mainly composed of C_{70}. Notably, a peak corresponding to an E_2' mode of C_{70} is observed at 1567 cm^{-1}. This peak is known to be due to splitting or redshifting of the C_{70} in the polymeric phases.[16] Our result indicates that each of the as-grown samples consists of monomeric C_{70}.

To investigate the PL properties of pristine C_{70} nanotubes, we investigate the PL spectra of the as-grown C_{70} nanotubes

under ambient conditions. A 514.5-nm laser with a low power of 0.2 mW is employed as an excitation source, to avoid the polymerization induced by high power laser. The black curve in Fig. 1 shows the PL spectrum of pristine C_{70} nanotubes. It is obvious that the broad PL band of pristine C_{70} nanotubes has two peak centers, which suggests a complex band structure of our C_{70} nanotubes. To investigate the mechanism of these two PL emissions in detail, the PL peaks are well fitted to two peaks with a Gaussian fitting method. The two fitted peaks with the centers at 727 nm and 790 nm are named "peak A" and "peak B" in this paper, respectively. To study the natures of these two luminescence peaks, the UV-Vis absorption spectrum is measured by using an integrating sphere to study the band gaps of the pristine C_{70} nanotubes. The recorded UV-Vis spectra are shown in the insert of Fig. 2. The extrapolation of the linear section of the plot down to zero absorption gives a value of 700 for the absorption edge, which suggests a band gap of ~ 1.77 eV for the pristine samples. This result indicates that the energy value of peak A is ~ 0.7 eV smaller than that of the band gap. According to the discussion in previous work, peak A may originate from the recombination of excitons localized at defects consisting of adjacent C_{70} molecules.[24,25] However, the orientation of peak B has not been well discussed nor explained.

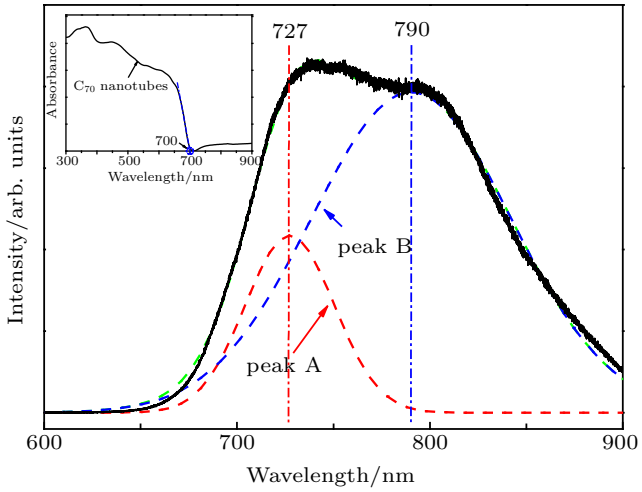


Fig. 2. PL spectrum of as-grown C_{70} nanotubes irradiated by 514.5-nm laser with power 0.2 mW, with insert showing UV-Vis absorption spectrum of as-grown C_{70} nanotubes, and red and blue dashed lines denoting two fitted peaks of the PL band of C_{70} nanotubes.

To investigate how the PL properties of C_{70} nanotubes can be tuned by laser irradiating treatment, the samples irradiated by 514.5-nm laser with the power of 0.2 mW, 1 mW, 2 mW, 10 mW, and 20 mW are characterized by PL spectroscopy, respectively. Their PL spectra are shown in Fig. 3. Obviously, both positions of peaks A and B shift toward longer wavelength. The redshifts of the PL spectra indicate that the band gap of C_{70} is reduced with increasing the laser power, which suggests that the interaction between the C_{70} molecules is enhanced by the effect of laser irradiation. Similar results are also found in our previous high pressure studies.[16]

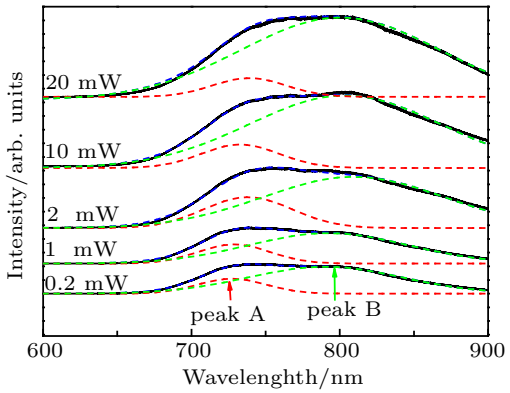


Fig. 3. PL spectra of pristine C_{70} nanotubes irradiated by 514.5-nm laser with 0.2 mW, 1 mW, 2 mW, 5 mW, and 10 mW, respectively.

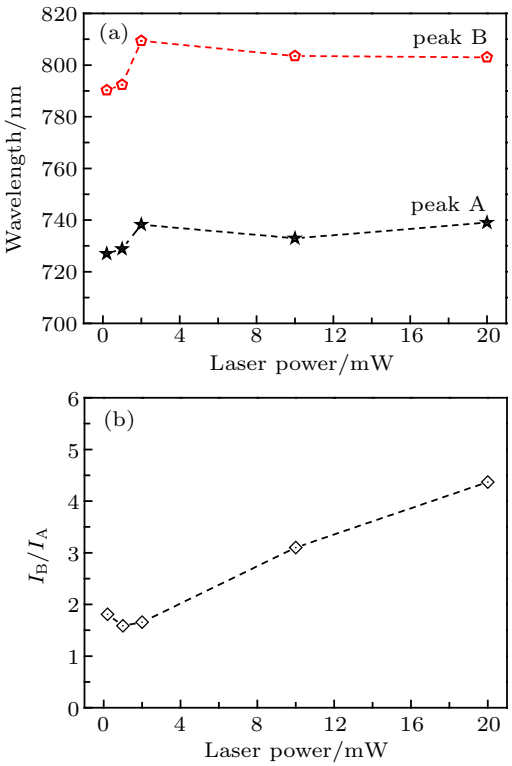


Fig. 4. (a) Laser power-dependent center positions of PL peak and (b) laser-power-dependent intensity ratio of peak B to peak A of C_{70} nanocrystals.

To determine the factors influencing the formation of intermolecular bonds in C_{70} nanotubes, the laser power-dependent center position of PL peak A and peak B are shown in Fig. 4(a). As shown in this figure, when the laser power is lower than 2 mW, these two peaks are red-shifted obviously with the increase of laser power. In contrast to the low energy range, the PL peak positions keep stable when the laser power is higher than 2 mW, which indicates that a stable phase forms when the power reaches 2 mW. Furthermore, the power-dependent intensity ratio of peak B to peak A is shown in Fig. 4(b). The intensity ratio keeps the value of ~ 1.6 below the laser power of 2 mW, but increases obviously with the laser power rising in the high power range. This result indicates that

peak A and peak B originate from different sources, and new phases are obtained in C_{70} nanotubes through being irradiated by laser. These phenomena indicate that the photo-increased new phase can only form when the laser power reaches 2 mW, and the content of the new phase increases with laser power rising.

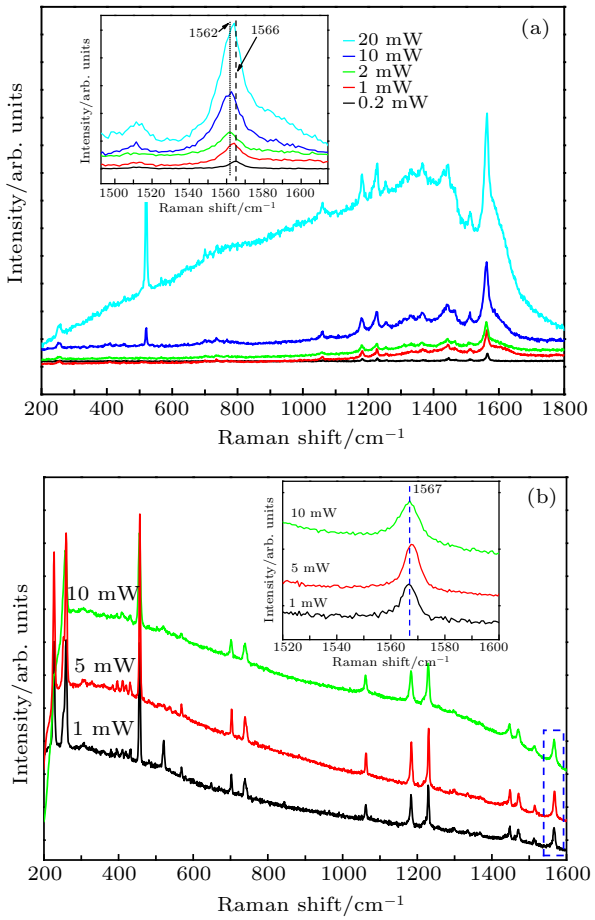


Fig. 5. Raman spectra of C_{70} nanotubes irradiated by (a) 514.5-nm laser and (b) 830-nm laser, respectively. Lasers with various powers are employed for comparison, and characterized E_2' Raman peak for samples irradiated with different values of laser power are shown in inserts.

To reveal the phase transition performance of C_{70} nanotubes under laser irradiation, Raman spectra of the samples irradiated by 514.5-nm laser with different power values are again examined. Raman spectra of the samples irradiated with the laser power of 0.2 mW, 1 mW, 2 mW, 10 mW, and 20 mW are shown in Fig. 5(a), respectively. By direct comparison on the characteristic E_2' peak shown in the insert, we can observe that the peak position of the sample irradiated by 0.2-mW laser appears at 1466 cm^{-1}, which indicates that no polymerization occurs under such conditions. The positions of the peak center shift toward the low frequency direction with the increase of laser power. Strikingly, the peak centers are kept at the position of 1462 cm^{-1} when the laser power is higher than 2 mW, which indicates the formation of a photo-polymerized phase. This spectrum is similar to that obtained in our previous HPHT studies on C_{70} nanotubes, which reveals the formation of disordered C_{70} oligomers.[16] Even the strongest 20-mW laser is employed to reach a more complete polymerization state, the peak position shows no obvious difference from that in the case of 2 mW, which gives no evidence of longer oligomers. This result is in good consistence with what is observed for the PL result. The results indicate that it is impossible to produce long oligomers (one-dimensional chain-like polymerized phases) with the 514.5-nm laser irradiating the C_{70} nanotubes. As is well known, to form the one-dimensional zigzag-type polymer chains, an ordered molecular orientation is needed. In this work, it is impossible to obtain linear polymer by using the laser irradiating C_{70} nanotubes, which is probably due to the initial disordered molecular orientation in the starting samples.

For comparisons, the pristine samples are also irradiated by using a 830-nm infrared laser at power of 1 mW, 5 mW, and 10 mW, respectively. As shown in Fig. 5(b), Raman spectra of the irradiated are recorded by using the 830-nm line as an excitation source. In each curve, more than ten Raman peaks are observed, and the positions of all these peaks are in good consistent. By the detailed comparison in the insert, peaks with the same positions at 1567 cm^{-1} are found for all the samples treated by such infrared lasers with different power values. This result suggests that it is impossible to achieve polymerized structures from C_{70} nanotubes by using the 830-nm laser. To obtain a photo-polymerization phase, it is necessary to use a light having photon energy higher than the band gap of C_{70} nanocrystal.

The natures of all the PL components of C_{70} nanotubes and their relationship with the photo polymerized structures are investigated. The results are shown in Fig. 6(a). The PL spectrum of C_{70} nanotubes irradiated by 10-mW laser is compared with that of C_{70} nanotube treated under an HPHT condition of 2.0 GPa and 700 K, which proves to have a disordered oligomers structure.[16] It is striking that the PL peak center of the HPHT-treated sample is located at 802 nm, which completely coincides with that of the fitted peak B. As described above, the position of peak B is kept stable in the irradiation induced phase, which is considered as a characterized PL peak for photo polymerized C_{70}. This comparison result further confirmed that peak B should be related to the polymerization of C_{70}.

As described in Fig. 4(b), the intensity ratio of peak B to peak A increases with the laser power rising, which indicates that the quantity of disordered C_{70} oligomers in the nanotubes increases with laser power rising. As shown in Fig. 6(b), the polymerized samples obtained by these two methods are almost the same. As shown in the insert, the center position of the characteristic E_2' mode of C_{70} is at 1562 cm^{-1} in the laser irradiated sample, and a weak shoulder is observed at 1567 cm^{-1}. In contrast, this peak is observed to be at 1564 cm^{-1} in that of the HPHT-treated samples, and a weak

shoulder at 1554 cm^{-1} is further observed. As investigated in our previous work,[16] this feature suggests the formation of disordered C_{70} oligomers. The slight difference between the two spectra indicates that the disordered oligomers induced by laser irradiation is weaker than that obtained by HPHT treatment.

According to the discussion in previous literature, peak A comes from the electronic transition in C_{70} monomers. However, the evidence of peak A is not observed in the PL spectrum of HPHT-treated C_{70} nanotubes in Fig. 6(a), which is different from that of laser irradiated sample. As the irradiating depth in the sample of laser is limited, the polymerization of C_{70} occurs mainly on the surface of C_{70} nanotubes, thereby suggesting that only part of C_{70} molecules are translated to disordered oligomers on the surface of the laser irradiated C_{70} nanotubes.

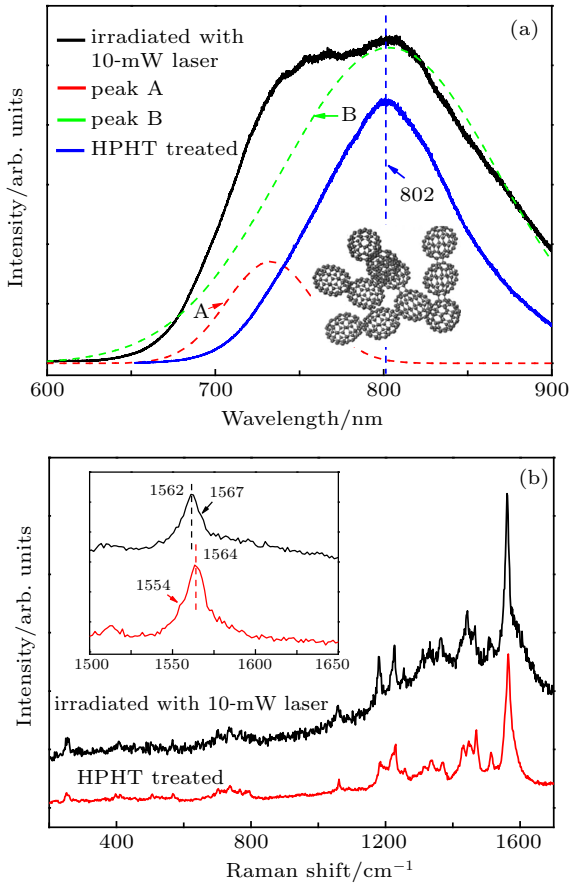


Fig. 6. (a) PL spectra of C_{70} nanotubes irradiated by 514.5-nm laser with power of 10 mW (black) and C_{70} nanotubes treated under 2.0 GPa, 700 K (red). PL spectrum of the laser irradiated sample is fitted to two peaks: Peak A (red dashed curve) and peak B (green dashed curve). (b) Raman spectra of C_{70} nanotubes irradiated by laser with 10-mW power and HPHT treated under 2.0 GPa, 700 K.

4. Conclusions

In this work, we tune the PL properties of C_{70} nanotubes by using the laser irradiation method. After irradiation treatment by using the 514.5-nm laser with the power of 0.2 mW, 1 mW, 2 mW, 10 mW, and 20 mW, respectively, the centers of the main PL band for C_{70} nanotubes shifts toward the longer wavelength, thereby suggesting the decrease of band gap and the formation of intermolecular polymerizations. The changes of the intensity ratio for these two PL components indicate that the intermolecular bonds increase with the increase of laser power employed. Raman spectra results further confirm the formation of disordered C_{70} oligomers in the sample irradiated by lasers with photon energy higher than its band gap. The laser-power-dependent intensity ratio for the PL components and the comparison of PL peak positions with the peak positions of HPHT-treated samples reveals the PL mechanism of C_{70} nanotubes. The PL band of C_{70} nanotubes originates from two kinds of common contributions, *i.e.*, the recombination of excitons localized at defects consisting of adjacent C_{70} molecules and the band structures related to the intermolecular polymerization of C_{70}.

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