Microfluidic Fabrication-induced Luminescence of C_{60} Rods

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C_{60} rods were fabrication using a microfluidic liquid–liquid interfacial precipitation method at 17 °C. Using photoluminescence spectroscopy, it was found that the alcohol solvent molecules affect the excitation and emission properties of the C_{60} rods. This suggests that the microfluidic fabrication induces doping of alcohol solvents and a change in the optoelectronic properties of C_{60} crystals.

Solid fullerene C_{60} materials have recently attracted much attention owing to their unique physical and chemical properties.[1] Therefore, the discovery of new solid C_{60} structures with small-scale dimensions and an understanding of their optical properties are important for future devices. In particular, the photoluminescence (PL) of C_{60} has potential applications in optics and electronics.[2] Since the PL properties are determined by the microscopic crystalline structure, control of the synthesis conditions is critical.

Microfluidic synthesis is a high-throughput synthesis method for small-scale materials.[3] We previously reported that temperature is a significant factor for C_{60} crystallization inside a microfluidic device.[4] In this study, we report the significance of poor solvent molecules. The effect of a poor solvent reagent on the luminescence properties was investigated using PL spectroscopy.

C_{60} crystals were prepared using a microfluidic liquid–liquid interfacial precipitation method.[4,5] The raw material used was a commercial 99.5% C_{60} powder formed by electric-arc discharge technique (Honjo Chemical Co., Tokyo, Japan). Mixtures of a C_{60}–toluene solution and alcohols were used as the sample test solutions. The formation of C_{60}–alcohol solvates in microchannel reactors was expected.[5] In order to investigate the effect of alcohol molecules, two alcohols, 2-propanol (ipa) and ethanol (eth) were used. In all experiments, the concentration of C_{60} dissolved in toluene was kept constant at 0.58 mg/mL. Toluene and alcohol were introduced into a 100-µm wide, 40-µm deep, and 40-mm long Y-shaped glass microchannel (Institute of Microchemical Technology, Kawasaki, Japan). The room temperature and the water bath temperature was maintained at 17 °C using a thermocontroller.[4] C_{60}–toluene solution (good solvent) and alcohol (poor solvent) were independently introduced with a constant flow rate into the inlet channels using pressure-driven microsyringe pumps. The preparation conditions of the C_{60} crystals were described in Table 1.

Table 1. Six different conditions for the synthesis of C_{60} rods using the microfluidic device

Case	Good solvent (Org.)	Poor solvent (Alcohol)	Flow rate /$\mu L\,min^{-1}$	System
A	Toluene	2-Propanol	1.0	tol-ipa-1-1
B	Toluene	2-Propanol	10	tol-ipa-10-10
C	Toluene	2-Propanol	100	tol-ipa-100-100
D	Toluene	Ethanol	1.0	tol-eth-1-1
E	Toluene	Ethanol	10	tol-eth-10-10
F	Toluene	Ethanol	100	tol-eth-100-100

Figure 1 shows typical micrographs of the C_{60} rods inside the microchannel, fabricated using the toluene–2-propanol system (Figure 1a) and the toluene–ethanol system (Figure 1b). The morphology of the C_{60} rods was different for the two systems. The morphology of crystals is determined by i) crystal structure and ii) anisotropy of growth speed. In terms of the crystal structure, Raman spectra show that there was no peak shift of C_{60} between the two systems, indicating that each microscopic structure was almost the same (Figure 1c). In terms of crystal growth, the mixing time of the solvents was critical for supersaturation of C_{60}. Since the diffusion coefficient of 2-propanol to toluene is smaller than that of ethanol, the mixing time and supersaturation of C_{60} were different for the two systems.[6] Thus, the difference in the morphology resulted from not the crystal structure but the anisotropy of growth speed due to the difference in the supersaturation of C_{60}.

The intermolecular bonding in the C_{60} rods was investigated by PL spectroscopy. The PL spectra of the samples were measured with a spectrometer (Renishaw Ramascope, U.K.) using a

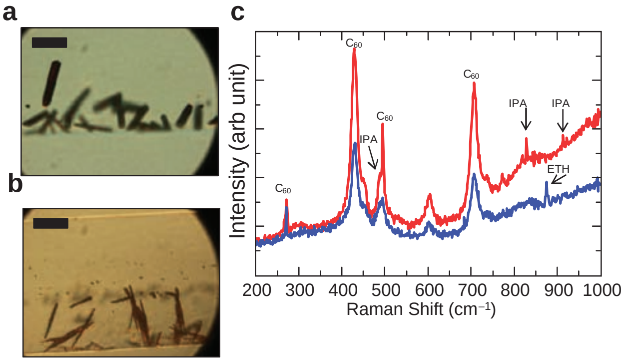

Figure 1. Optical micrographs of the C_{60} rods formed inside the microchannel using the (a) toluene–2-propanol system and (b) toluene–ethanol system. Scale bars in Figures 1a and 1b are 30 µm. (c) Raman spectra of the C_{60} rods synthesized with the toluene–2-propanol (top) and toluene–ethanol systems (bottom). The peaks at 490, 820, 946, (top) and 875 cm^{-1} (bottom) corresponded to 2-propanol and ethanol, respectively (marked with arrows).[7] Raman spectra of the samples were measured with a spectrometer (Renishaw Ramascope, U.K.) using a CCD detector. A He-Ne ion laser (632-nm excitation, irradiation power 0.3 mW) was used as the probing laser.

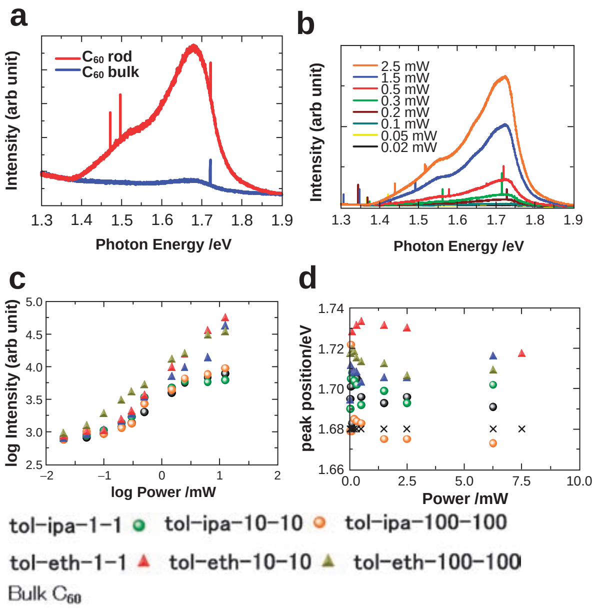

Figure 2. PL spectroscopy of the C_{60} rods. (a) PL spectra of the C_{60} rods and bulk crystal in toluene–2-propanol (1.0–1.0 µL/min, Case A). (b) PL spectra of the C_{60} rods in toluene–ethanol (10–10 µL/min, Case E) with different laser intensities. (c) Log–log scale plot of integrated PL intensities from 1.3 to 1.9 eV as a function of the excitation laser power. (d) Peak positions of the C_{60} rods around 1.70 eV as a function of the excitation laser power. Circles and triangles represent the toluene–2-propanol (Case A–C) and toluene–ethanol systems (Case D–F), respectively.

CCD detector. An Ar ion laser (514-nm excitation) was used as the probing laser, and the irradiation power for the PL measurements was varied from 0.02 to 12.5 mW. No changes were observed in the samples by illumination of the excitation-probing laser.[8] Figure 2a shows a comparison of the C_{60} rods with the bulk C_{60} crystals prepared using the toluene–2-propanol system at a flow rate of 1.0 µL/min (Case A). One emission band around 1.70 eV, known as the zero-phonon line (ZPL) corresponding to direct exciton–polaron recombination, was observed. The PL intensity of the rods was one order of magnitude higher than that of the bulk crystals. This may be attributed to a slight decrease in the symmetry of C_{60} molecules by doping with the guest solvent molecules.[8]

To investigate the doping effect, the PL spectra were measured as a function of the excitation laser power. Figure 2b shows a typical example of the C_{60} rods in tol-eth-10-10 (Case E). The increase in intensity of the 1.73-eV peak is in proportion to the laser intensity. The integrated PL intensity was plotted on a log–log scale as a function of the excitation laser power I_{EX} (Figure 2c). The integrated PL intensity I_{PL} was analyzed in terms of the equation $I_{PL} \propto I_{Ex}{}^{\alpha}$, where α is the power index, which provides a good measure for the characterization of the PL emission mechanism.[9] There was no significant difference in the PL intensity–power dependence for different flow rates. Conversely, an apparent difference between the toluene–2-propanol and toluene–ethanol systems was observed. For the toluene–2-propanol systems, α (gradient) was ≈(0.3–0.5). On the other hand, for the toluene–ethanol systems, α (gradient) was ≈(0.7–0.9). Since the Raman spectra show the guest alcohol molecules are trapped in the lattice structure of the C_{60} rods (Figure 1c), this difference suggests an effect on the excited electronic states. In general, toluene (good solvent), not alcohol solvent (poor solvent), molecules are trapped inside the lattice structure of the fullerene C_{60}.[10] Conversely, the data obtained here suggests that alcohol solvent molecules are significant for enhancement of the optoelectronic properties of C_{60} crystals formed in a microfluidic environment.

In addition, transition of the peak positions was noticed. Figure 2d shows the peak positions of the C_{60} rods around 1.70 eV (ZPL). The peak positions of the C_{60} rods fabricated in the microfluidic device were blue-shifted compared with those of the raw material C_{60}. In the toluene–ethanol systems, the peak positions were more blue-shifted compared to those in the toluene–2-propanol systems. HOMO–LUMO transitions are sensitive to the proximity of adjacent molecules. Therefore, the new peaks from the alcohol molecules (Figure 1c) suggest the blue shift may be the result of weak van der Waals interactions between C_{60} molecules and alcohol solvent molecules.

In summary, we have reported poor solvent molecule-dependent luminescence properties of C_{60} rods formed in a microfluid environment. While the morphology of the C_{60} rods was different for the toluene–2-propanol and toluene–ethanol systems, the solvent molecules did not change the original lattice structure of the C_{60} crystals. Thus, the PL properties were determined by not the morphology but by the C_{60}–solvent molecular interactions. The obtained rods C_{60} look promising as novel materials for micrometer-sized photodetectors or solvent molecule sensors. Unlike bulk-scale synthesis, this finding suggests the significance of poor solvent molecules on the optoelectronic properties in the microfluidic preparation of micro- and nanocrystals.

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