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Absorption and emission spectra of molecular excitons in single perylene nanocrystals

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Nonlinear absorption spectra of single α-perylene nanocrystals of 150–300 nm in size were measured at low temperature by multichannel phase-sensitive pump-probe microspectroscopy. For nanocrystals, free exciton (FE) absorption blueshifts while self-trapped exciton (STE) emission redshifts and FE emission is intense, compared with bulk crystals. The mechanism of the redshift is suggested to be lattice softening from a redshift in space-resolved STE emission at the edge of bulk crystals. The FE absorption band of several single nanocrystals shows a double-peak structure, suggesting that the blueshift is due to B_u excitons, which are much stronger in oscillator strength than A_u excitons, yet difficult to observe in bulk crystals.

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Molecular crystals as an organic semiconductor are presently finding applications in wide areas in optoelectronic industry such as solar batteries and light-emitting diodes (LEDs). It is expected that organic nanocrystals will come into real application, as realized in inorganic nanocrystals, which is represented by semiconductor quantum dots. However, optical properties of organic nanocrystals are less understood than the latter. For example, perylene nanocrystals are reported to show an unusual "quantum size effect,"[1–3] that is, free Frenkel exciton (FE) absorption and self-trapped exciton (STE, or excimer) luminescence are both blueshifted compared with bulk crystals, despite their relatively large sizes (as large as hundreds of nanometers). These crystal sizes are more than ten times larger than those of inorganic nanocrystals, which show a similar size of their blueshift. The physical mechanisms of such unique features have not been well understood. One of the reasons is that, to the best of our knowledge, only the ensemble-averaged absorption spectra of organic nanocrystals have been measured so far, with the result that optical features of individual nanocrystals are hidden behind inhomogeneous broadening. Especially for organic nanocrystals, it is often the case that the lowest excited state is a STE. Thus, photoluminescence (PL) measurements provide information only about STEs. In order to study FE states in single organic nanocrystals, an absorption measurement is desired as an essential methodology to clarify the exciton properties of the system.

However, measurement of absorption spectra of single nanocrystals is a challenging task. This is because absorption of a single photon saturates the ground-state absorption in a nanocrystal and the photon shot noise of the probe light usually exceeds the absorption strength if the probe light intensity is as weak as it is below the saturation level. For organic nanocrystals, in addition, the FE band is broad (>10 meV),[4,5] caused by fast relaxation into the STEs of the order of a few picoseconds.[6,7] This is different from inorganic crystals, which have a very sharp homogeneous exciton bandwidth (<1 meV), for their absorption profiles to be probed by scanning a laser within a narrow spectral range.[8,9] In this Rapid Communication, we have combined confocal optical microscopy with the pump-probe method using multichannel double lock-in detection[10] and obtained absorption spectra of single organic nanocrystals with known sizes. We found that the size effect exists for single α-perylene nanocrystals but oppositely between the FE absorption and the STE emission.

Perylene α-crystal is monoclinic, having four molecules per unit cell, and crystals of perylene and its derivatives are widely studied.[4–7,11–15] Nanocrystals of α-perylene are known by their unusual quantum size effect but, to the best of our knowledge, their optical properties at low temperature have not been reported. The details of the sample preparation method are described in Ref. 16. Nanocrystals of α-perylene were made with the reprecipitation method[17] after purification by sublimation in 1-atm nitrogen gas. A polyvinyl alcohol (PVA) film dispersed with nanocrystals was made by spin coating on a cover glass and set in a cryostat. Bulk crystals were made directly on a cover glass by recrystallization from an acetone solution of purified perylene.

The experimental setup for the microscopic measurement of PL and nonlinear absorption (NA) spectra for bulk and single nanocrystals is described in Ref. 16. Briefly, PL spectra by excitation of a 408-nm (3.04-eV) laser were measured with a cooled CCD, and NA spectra were measured by a pump-probe setup with the same laser as a pump and a Xe lamp as a probe (unpolarized), using a confocal optical microscope combined with a 128-channel lock-in detection system. This system allowed us to detect the pump-induced probe transmission change in a wide wavelength range, from 400 to 550 nm at one time. The intensities of the pump and probe light were 90–130 and 30 W/cm^2, respectively, at the sample surface. The FE states created by the stationary pump laser are relaxed into STE states immediately. Under this condition, NA spectra were calculated from the measured difference spectrum of the probe between with and without the pump, corresponding to a difference spectrum between the STE and the ground state, respectively. In the NA spectra, ground-state absorbance

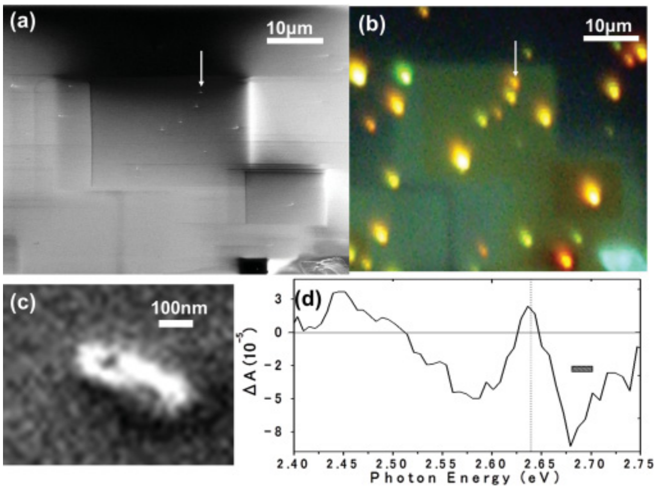

FIG. 1. (Color online) (a) The SEM image of perylene nanocrystals dispersed in a PVA film and (b) the PL image at 20 K of the same area by optical microscopy. Rectangular shapes in the images are due to beam-induced specimen contamination by SEM. (c) An expanded image of the single nanocrystal designated by the arrow and (d) its NA spectrum at 20 K. The dashed line and the hatched horizontal bar indicate the FE energy and the FWHM of the FE band, respectively, in bulk crystal at 20 K (Ref. 4). The energy resolution is 10 meV at 2.64 eV.

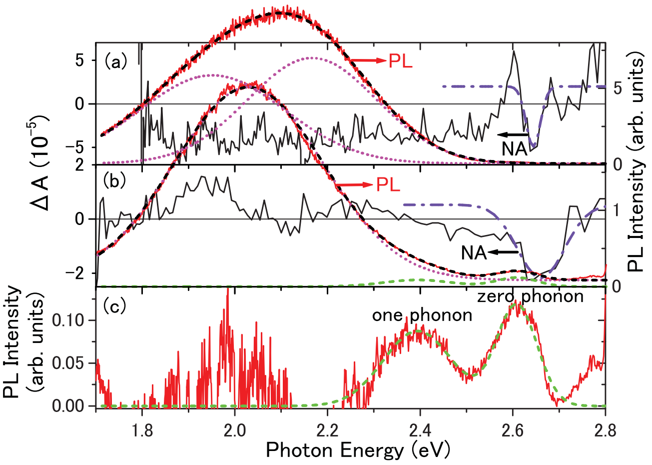

FIG. 2. (Color online) PL [dark gray (red)] and NA (black) spectra, respectively, of (a) a bulk perylene crystal and (b) a single perylene nanocrystal at 70 K excited by a 408-nm (3.04-eV) laser, measured through (a) a 1-μm-diam and (b) a 200-nm-diam window. The energy resolution in (a) and (b) is 10 and 24 meV, respectively, at 2.64 eV. (c) The FE luminescence spectrum [dark gray (red)] extracted from the PL spectrum in (b), by subtracting the fitted STE emission spectrum [dotted (magenta)] from the whole PL spectrum. (a)–(c) Dotted (magenta) and dotted-dashed (purple) curves are Gaussian functions fit to the STE emission and FE absorption bands, respectively. The dashed light gray (green) curves are Gaussian fits to the zero- and one-phonon bands of FE emission. The dashed black curves are the sum of the multiple Gaussians.

(GSA) appears as absorbance decreases due to ground-state depletion.

In order to locate by optical microscopy (OM) a specific nanocrystal whose crystal size is measured by scanning electron microscopy (SEM), we utilized beam-induced specimen contamination. In this phenomenon, hydrocarbons in a residual gas are adsorbed on the sample surface and interact with the electron beam to produce amorphous carbons.[18] Consequently, the magnified image by SEM is contrasted by nested rectangular shapes, each of which designates a scanned region, as shown in Fig. 1(a). The corresponding structure is clearly observed in the OM image of PL in Fig. 1(b). The crystal size and shape of a single nanocrystal marked by the arrow are clearly resolved in Fig. 1(c) and its NA spectrum at 20 K is shown in Fig. 1(d). The pump-induced absorption decrease in the FE band was observed, showing a blueshift in the FE energy compared with that in bulk crystal, 2.64 eV (21 290 cm^{-1}[4]). Note also that the linewidth (FWHM) of the FE band is broader (>40 meV) than that in the bulk, 20 meV.[4,16] This is in sharp contrast to the case of single semiconductor quantum dots, which show much narrower homogeneous bandwidths than 1 meV at low temperature.[8,9] This result suggests that the FE band of single perylene nanocrystals is inhomogeneously broadened: FEs are not fully delocalized coherently over the whole crystal, but are localized within a limited coherence volume and the components of the inhomogeneous groups have different partial occupations from each other. Even including the inhomogeneous broadening effect, however, it is not clear why it is as large as 40 meV.

Figure 2 shows typical PL and NA spectra of bulk and single perylene nanocrystals at 70 K. For bulk crystals, the FE energy was 2.64 eV and the STE energy was 2.05 eV at 70 K, as seen in the NA and PL spectra in Fig. 2(a), respectively, although there was a sample- or position-dependent variation in the STE peak energy. At 70 K, the FE luminescence intensity was negligibly small in bulk crystals. For single nanocrystals, as shown in Fig. 2(b), the FE band was blueshifted while the STE band was redshifted. In addition, slightly Stokes-shifted FE emission was observed even at 70 K. Its spectrum has a phonon sideband structure as shown in Fig. 2(c), which has a phonon energy close to ~170 meV observed in the FE absorption spectra of a bulk perylene crystal.[12,13] Since FE emission in nanocrystals was hardly observable at 20 K, thermal activation from the STE state is a likely mechanism for the FE emission at 70 K. However, it is hard to explain by thermal activation why FE emission is more prominent for nanocrystals than for bulk crystals, despite the fact that the STE state is redshifted and the FE state is blueshifted in nanocrystals compared with bulk crystals.

Figure 3(a) displays space-resolved PL spectra in a bulk crystal at 70 K. The crystal shape was a rectangular plate, which is typical of α-perylene, with the well-developed *a*-*b* plane and the *c* axis along the thin direction. The STE-emission band exhibited clear position dependence such that the emission from the crystal edge was redshifted compared with that in the center of the crystal (bottom curve I). In addition, the emission intensity was two or three times larger at the edge than in the center when it was compared in the same area size. FE emission was absent throughout the crystal. The mechanism for the redshift and the increased intensity at the edge is considered to be lattice softening.[1,19] That is, the number of molecules facing the surface is larger at the edge such that they and the neighboring molecules are more

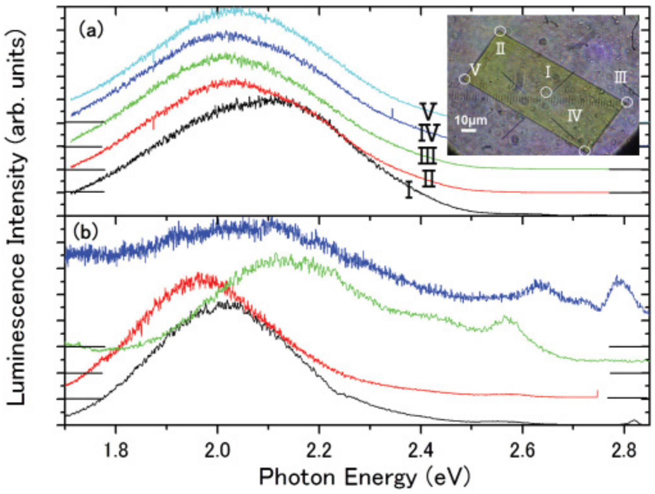

FIG. 3. (Color online) (a) Space-resolved PL spectra (normalized) of a bulk perylene crystal displayed in the inset, measured at selected spots marked by the circles through a 1-μm-diam window. The spectra at the edge were measured such that the vertex was positioned at the center of the window. (b) PL spectra of different single perylene nanocrystals at 70 K measured through a 200-nm-diam window.

loosely bound at the lattice positions in bulk crystal to be readily susceptible to lattice relaxation. Since the self-trapping process is the formation of a localized molecular dimer, the intradimer distance can be closer to gain more stabilization energy due to the dipole-dipole interaction. The increased emission intensity can be attributed to the symmetry-breaking effect in the optically forbidden STE-emission transition.[14]

Figure 3(b) displays the PL spectra of different single nanocrystals. The second lowest (red) spectrum is the most typical STE spectrum, which shows a redshift with respect to that in the bulk. Although it is not often the case, there exist nanocrystals which show blueshifted STE emission as shown by the second highest (green) curve. When the STE emission is blueshifted, FE emission is more prominent than in those crystals where STE emission is redshifted, as expected from thermal activation. Note also that there exist nanocrystals showing the emission from monomer molecules, as displayed by the topmost (blue) curve.[3]

Figure 4 shows NA spectra of single nanocrystals at 20 K, the size of which were evaluated by the SEM images. A typical NA spectrum is displayed in Fig. 4(a), exhibiting a single-peak FE band at 2.64 eV and its one-phonon sideband at ~2.84 eV. NA spectra from Figs. 4(b)–4(e), in contrast, exhibit a double-peak FE band. For example, in Fig. 4(c), which is the same as in Fig. 1(d), the higher-energy peak is blueshifted while the lower energy peak is redshifted from the FE energy in the bulk, 2.64 eV. Since the energy separation of the double peaks is 64–115 meV, this structure is not due to the phonon structure with a typical phonon energy of 170 meV (Refs. 12 and 13) but due to another origin. In Fig. 4(e), both peaks are redshifted from the bulk FE energy. This could be explained by the effect of Mie scattering, which induces an apparent redshift in large nanocrystals: Considering crystal sizes of an order of a few hundreds of nanometers, which is close to the probe light wavelengths, the effect of scattering on the NA spectra must be taken into account. We experimentally confirmed that crystals of more than ~100 nm in size exhibit a redshifted FE band in the extinction spectra measured by transmission geometry, with a small solid angle of observation.[20] Other weak structures, i.e., dips in Fig. 4(c) at 2.77 eV, in Fig. 4(d) at 2.74 eV, and in Fig. 4(e) at 2.72 eV, are possibly the one-phonon sideband.

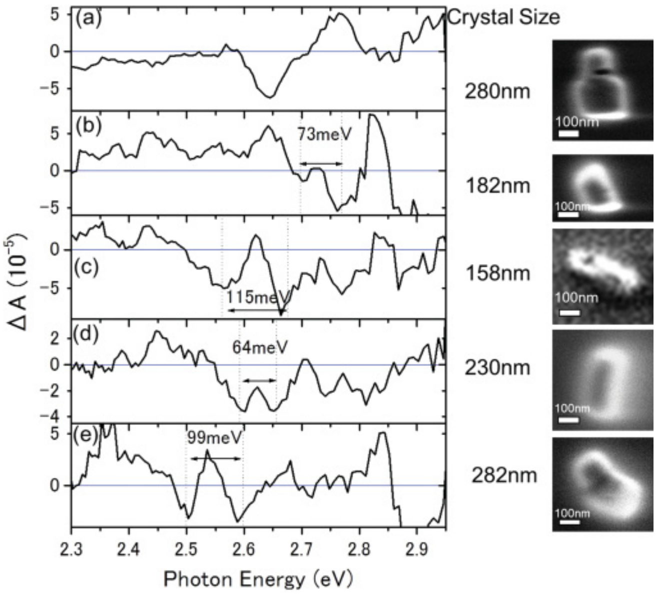

FIG. 4. (Color online) SEM images of single nanocrystals and their crystal sizes, and their corresponding NA spectra at 20 K. The crystal size of each nanocrystal was determined by the square root of the area of the nanocrystal image.

Figure 5 shows the crystal size dependence of the FE and STE energies at 20 K. Nanocrystals from 150 to 300 nm show redshifted STE emission than in the bulk crystals, but the STE energy fluctuates from one crystal to another, showing no

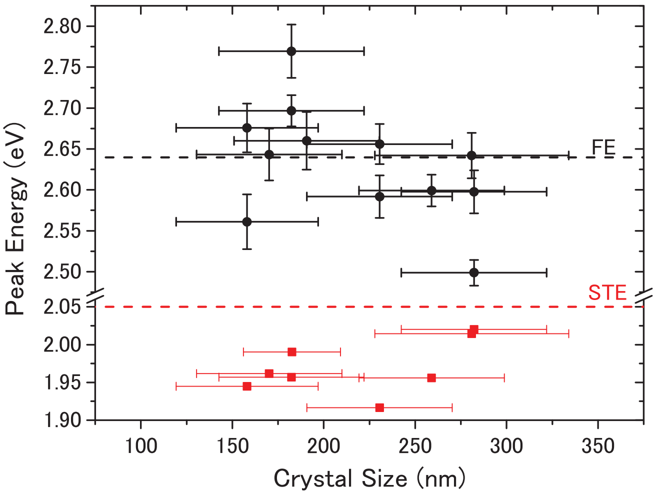

FIG. 5. (Color online) Crystal size dependence of the FE absorption (circles) and STE emission (squares) energies of single perylene nanocrystals at 20 K. The peak energies were determined by a Gaussian fit. The dashed lines correspond to the FE absorption (2.64 eV) and STE emission (2.05 eV) energies of bulk crystals at 20 and 70 K, respectively.

definite size dependence. This is not consistent with a previous report,[2] where STE emission is blueshifted with decreasing crystal size at room temperature. The FE energy of single perylene nanocrystals has a weak tendency to increase with decreasing size. Explicitly, nanocrystals smaller than 250 nm show blueshifted FE energy (for the higher-energy peak if there is a double-peak structure). This trend agrees with a previous study done for the ensemble average of perylene nanocrystals,[1] but the FE energy of individual nanocrystals rather fluctuates, similar to the STE energy. In addition, the FE band for several nanocrystals show double peaks, as seen for nanocrystals of 158, 182, 230, and 282 nm in Fig. 4. These observations suggest that not only crystal size but also its shape or orientation is relevant to the FE energy as described later.

The mechanism of the redshift in the STE energy can be understood from lattice softening, as supported by the position-dependent PL spectra of the bulk crystal in Fig. 3, although it is not clear if the redshift that is as large as 200 meV is explained by lattice softening alone. On the other hand, it is difficult to associate the blueshift in the FE energy that is as large as 100 meV with lattice modifications such as lattice softening. This is because the FE band is almost a zero-phonon line, as shown by the small Stokes shift (20 meV) in Fig. 2. Instead, the observation of the double peaks directs us to another possible mechanism as follows. The double peaks might be due to the zero-phonon lines of A_u and B_u excitons, which have mutually orthogonal polarization. Since the bulk α-perylene crystal has three distinguishable crystal axes, the exciton structure has a strong crystal orientation dependence in the absorption spectra,[4,5,11–13] which, to the best of our knowledge, was not previously studied on the ensemble average of randomly oriented nanocrystals. For a bulk crystal, *b*-polarized A_u excitons are usually probed but nearly *c*-polarized B_u excitons are not, with the light incident on the well-developed *a*-*b* plane. For nanocrystals, on the other hand, intense blueshifted B_u excitons are more accessible because other planes may have more of a chance to appear. The energy separation of the two excitons is 67 meV (540 cm^{-1}),[13] in partial agreement with the experimental observation of 70–120 meV. In order to verify this mechanism, polarization dependence of absorption should be measured in single nanocrystals.

In conclusion, by pump-probe absorption microspectroscopy with a multichannel lock-in amplifier using a white light from a discharge lamp as the probe, broadband nonlinear absorption spectra from 1.7 to 2.8 eV at low temperatures were measured for single α-perylene nanocrystals of sizes ranging from 150 to 300 nm. By probing molecular excitons in single nanocrystals by absorption as well as by luminescence at low temperature, the previously unknown properties of excitons in nanocrystals were revealed to shed light on the "size effect" on exciton energy.

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