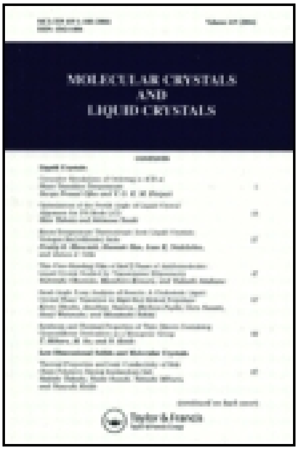

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Quantum Confinement of Translational Motion of Excitons in α-Perylene and Pyrene Microcrystals

Ken-Ichi Mizuno [a] & Atsuo Matsui [a]

[a] Department of Physics, Konan University, Okamoto, Kobe, JAPAN, 658

Version of record first published: 04 Oct 2006.

To cite this article: Ken-Ichi Mizuno & Atsuo Matsui (1992): Quantum Confinement of Translational Motion of Excitons in α-Perylene and Pyrene Microcrystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 218:1, 49-54

To link to this article: http://dx.doi.org/10.1080/10587259208047014

Mol. Cryst. Liq. Cryst. 1992, Vol. 218, pp. 49–54
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

QUANTUM CONFINEMENT OF TRANSLATIONAL MOTION OF EXCITONS IN α-PERYLENE AND PYRENE MICROCRYSTALS

Ken-ichi Mizuno and Atsuo Matsui
Department of Physics, Konan University, Okamoto,
Kobe, JAPAN 658

Abstract We observed that (1) the luminescence spectra of α-perylene shifted by 440 cm^{-1} as much as the change in the excitation photon energy, from 22100 cm^{-1} (452.5 nm) to 22540 cm^{-1} (443.7 nm), whereas the luminescence spectrum of pyrene shifted by 100 cm^{-1} according as the excitation photon energy in an energy region from 26940 cm^{-1} (371.2nm) to 26730cm^{-1}(374.1nm), (2) for pyrene microcrystals the luminescence decay under resonant excitation increased as the excitation energy increased, (3) in both materials intense free-exciton luminescence was observed but self-trapped exciton luminescence was not.

We concluded that in both materials (1) quantum confinement of translational motion of excitons occurs, and (2) excitons in microcrystals are not self-trapped.

INTRODUCTION

Exciton quantum confinement for organic systems is reported for two-dimensional quantum wells.[1-2] Quite recently quantum confinement of translational motion of excitons in anthracene microcrystals was found.[3] The result obtained for anthracene microcrystals implies that excitons in zero-dimensional, weak exciton-phonon coupled system are confined quantum mechanically. Does quantum confinement occur in strong exciton-phonon coupled system? From this motive we have studied luminescence spectra and luminescence decay of α-perylene and pyrene microcrystals. Those two materials were chosen because macrocrystals of those materials belong to the category of strong exciton-phonon coupled system and exciton dynamics in those macrocrystals have been known.[4-5]

QUANTUM CONFINEMENT IN α-PERYLENE MICROCRYSTALS

Microcrystals were grown on fibrous polyester filter papers with average pore size of 2 μm. At the top of the Figure 1, a 92-K luminescence spectrum of α-perylene microcrystals, which was excited with photons of 22990 cm^{-1} (435 nm), is shown. Bands A, B, C of microcrystal luminescence spectrum must be composed of luminescence bands of microcrystals with variety of crystal sizes.

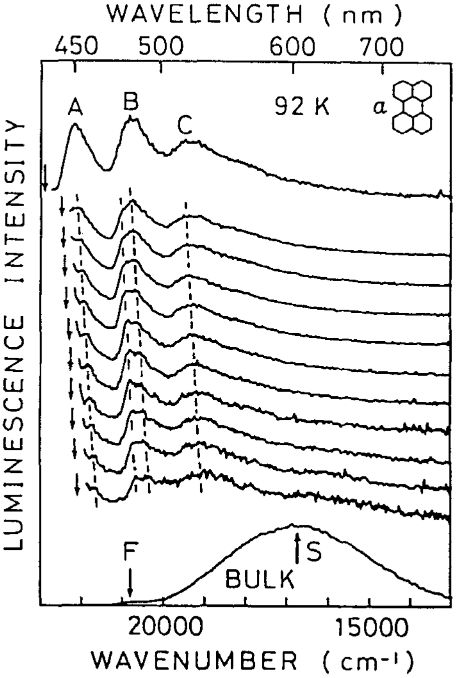

FIGURE 1 Luminescence spectra of α-perylene microcrystals under selective excitation.

We have applied a selective, resonant excitation method to obtain the luminescence spectrum of microcrystals with a narrower size distribution. The spectra thus obtained are illustrated in the middle portion of Fig. 1. The excitation photon energy is shown for each spectrum by a downward arrow. At the bottom a room-temperature spectrum of a large single crystal (a bulk crystal) is shown. The free-exciton luminescence band of a bulk crystal is indicated by letter F and the self-trapped exciton luminescence band by letter S. The 0-0 luminescence band (marked A) of microcrystals is located on the high energy side of band F.

The peak position of the luminescence bands under selective excitation are plotted in Fig. 2 as a function of the excitation photon energy. As is seen in Fig. 2 the spectrum shifts 440 cm^{-1} according as the change in the excitation photon energy (440 cm^{-1}). This shift is clear evidence that microcrystals were selectively excited depending on the size of the crystals: A smaller crystal has a higher excited electronic state than in larger crystals, which means that quantum confinement of exciton translational motion in perylene takes place.

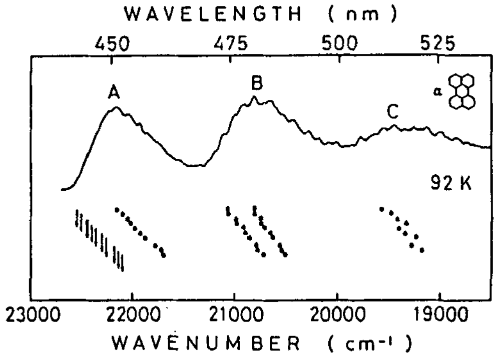

FIGURE 2 The peak positions of luminescence bands for selective excitation.

QUANTUM CONFINEMENT IN PYRENE MICROCRYSTALS

Microcrystals were grown on polycarbonate membranes with channel-pores of 150 A diameter. In Fig. 3 (top) luminescence spectra of pyrene microcrystals, size-selective luminescence spectra and (bottom) luminescence spectrum of a macrocrystal (bulk crystal) are shown. Under size-selective excitation, the luminescence spectrum shifted according as the excitation photon energy.

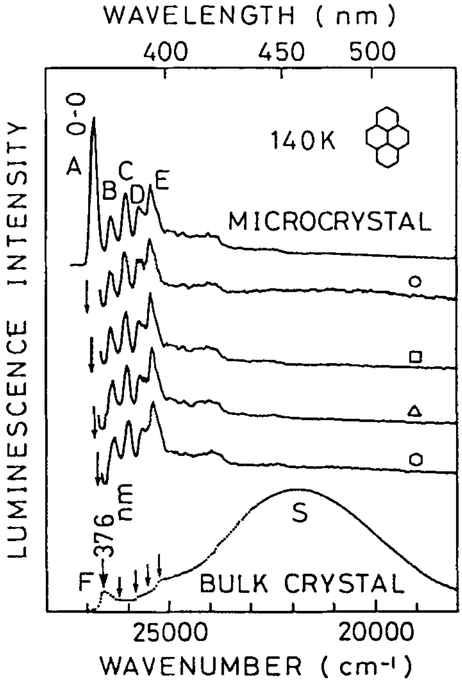

FIGURE 3 Luminescence spectra of pyrene microcrystals under selective excitation. Downward arrows indicate the excitation energies for corresponding spectra.

The spectral shift under size-selective excitation is illustrated in Fig. 4. As is seen in Fig. 4, the spectral shifts of 100 cm^{-1} for the luminescence bands B, C, D, E were not the same amount as the change of 210 cm^{-1} in the excitation photon energy, probably because absorption bands of microcrystals with various sizes are stacked together and in addition the spectral width of the excitation pulses we have used (70 cm^{-1}) was wide compared with the spectral width of the band A (180 cm^{-1}), leading to a smaller spectral shift.

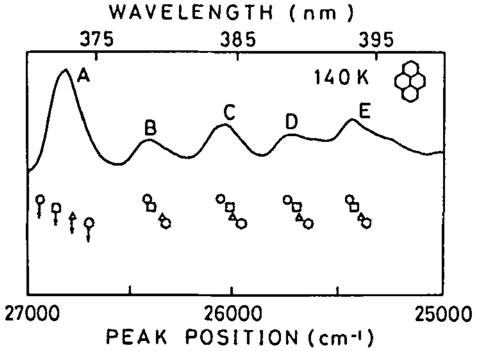

FIGURE 4 The peak positions of luminescence bands, B, C, D, E of pyrene microcrystals under selective excitation.

When quantum confinement of excitons occurs in microcrystals, luminescence decay time τ is inversely proportional to the third power of the diameter of a microcrystal for resonant excitation.[6] Therefore, τ increases as the diameter decreases. In Fig. 5 the decay time that was measured under selective excitation at 140 K with dye laser light is plotted as a function of the energy of the excitation photon energy. The decay was monitored at the photon energy by 2300 cm^{-1} below the excitation photon energy. A filled circle is for a bulk crystal. The decay time increased as the excitation photon energy increased for the energy

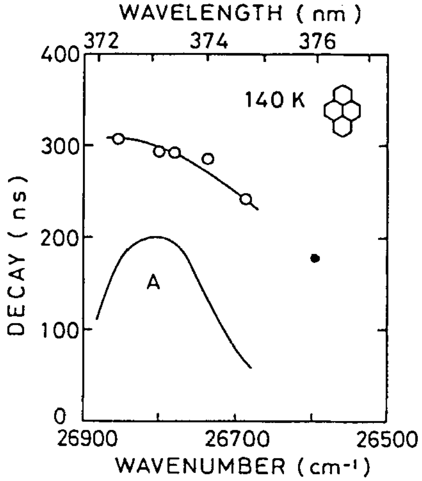

FIGURE 5 Luminescence decay time of the specimen under size-selective excitation.

range from 26690cm^{-1} (374.7nm) to 26850cm^{-1} (372.4nm). This result is consistent with the expected change in the decay time.

EXCITON-PHONON COUPLING

It is known that in bulk α-perylene and pyrene crystals the adiabatic potential energy curves are characterized by a double-well potential. Owing to the double-well potential, free and self-trapped exciton luminescence are observed simultaneously.[4] In Figs. 1 and 3, however, only vibronic luminescence bands which originate as free excitons are observed and any luminescence band which should be attributed to the self-trapped exciton luminescence band did not appear. This observation leads to suggest that excitons are not self-trapped in α-perylene and pyrene microcrystals.

This finding in microcrystals is strange in contrast with the observation for bulk crystals in which excitons are self-trapped as a result of strong exciton-phonon coupling. The problem to elucidate the size dependence of the exciton-phonon coupling strength is open for future study.

REFERENCES

1. F. F. So, S. R. Forrest, Y. Q. Shi and W. H. Steier, Appl. Phys. Lett. 56, 674 (1990).
2. F. F. So. and S. R. Forrest, Phys. Rev. Lett. 66, 2649 (1991).
3. K. Mizuno, A. Matsui and H. Nishimura, J. Phys. Soc. Jpn. (submitted).
4. A. Matsui and H. Nishimura, J. Phys. Soc Jpn. 49, 657 (1980).
5. H. Nishimura, A. Matsui and M. Iemura, J. Phys. Soc. Jpn. 51, 1341 (1982).
6. E. Hanamura, Phys. Rev. B37, 1273 (1988) and Phys. Rev. B38,1228 (1988).