APPLIED PHYSICS LETTERS **99**, 053304 (2011)

Effect of light scattering on the transmission spectra of organic nanocrystals

Heisuke Ishino,[1] Selvakumar V. Nair,[2] Kazuya Nakagawa,[1] Takayoshi Kobayashi,[3] and Eiji Tokunaga[1,4,a)]

[1]*Department of Physics, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan*
[2]*Centre for Advanced Nanotechnology, University of Toronto, 170 College Street, Toronto M5S3E3, Canada*
[3]*Department of Applied Physics and Chemistry and Institute for Laser Science, University of Electro-Communications, 1-5-1 Chofugaoka, Chofu, Tokyo 182-8585 Japan*
[4]*Research Center for Green and Safety Sciences, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan*

(Received 11 March 2011; accepted 16 July 2011; published online 3 August 2011)

The effect of light scattering on the extinction spectra of organic nanocrystals was investigated by absorption and extinction measurement and by theoretical calculation for typical organic nanocrystals of α-perylene. In the extinction spectra, the exciton band shows a size-dependent redshift and tail toward longer wavelengths due to scattering as the crystal size is increased beyond ∼50 nm. In the absorption spectra, the exciton band blueshifts from that in the bulk crystal for crystal sizes less than ∼200 nm due to the anisotropic exciton structure in perylene. The calculation qualitatively supports these results. The effect of scattering always makes the extinction band redshift from the absorption band. © *2011 American Institute of Physics*. [doi:10.1063/1.3623434]

Recently, organic nanocrystals have been studied extensively because of their potential application as functional nanomaterials.[1,2] Their optical and electronic properties, however, are less understood compared to those of their inorganic counterparts, i.e., semiconductor quantum dots. Organic nanocrystals show unique optical features different from either bulk crystals or monomers. For example, perylene nanocrystals of a few hundreds of nanometers in diameter show an unusual "quantum size effect" with a blue-shifted exciton absorption compared to the bulk crystal.[3–8] These crystal sizes are more than ten times larger than those of semiconductor quantum dots which show the same amount of blueshift. Similar size-dependent blueshifts are observed also for polymer nanocrystals such as poly-diacetylene nanocrystals for the sizes of the order of 100 nm,[9] which is also of great interest.

Organic nanocrystals are readily fabricated by a reprecipitation method.[10] At present, the control of nanocrystal shape and size is not perfect since the formation of nanocrystal is due to a self-assembly mechanism. Thus individual nanocrystals have their own, respective optical properties, requiring absorption measurement of single organic nanocrystals for their proper characterization. There have been several reports on absorption measurement of single semiconductor quantum dots as small as several tens of nanometers.[11,12] Very recently we have realized broadband absorption microspectroscopy of single organic nanocrystals.[13,14] Because the typical sizes of organic nanocrystals formed by the reprecipitation method are in the range from 50 nm to 100 nm or more, which is a significant fraction of the light wavelength in the material, the effect of light scattering on the absorption spectra must be taken into account. Although the effect of scattering on the optical response of metal nanoparticles has been studied fairly well,[15] there has been little work on the scattering effect on the absorption spectra of organic and semiconductor nanocrystals.[16] While the formal difference between extinction and absorption is very clear, almost all optical measurements of organic nanocrystals implicitly assume that the difference is small. Since the measurement of extinction spectra of single organic nanocrystals has been realized, a careful analysis of the effect of scattering on the spectra is necessary.

In this letter, we show that experimental extinction spectra includes the effect of scattering so that absorption spectra of organic nanocrystals need to be carefully interpreted using theoretical modelling. We investigate nanocrystals of α-perylene.[3–8] Perylene is a representative polycyclic aromatic hydrocarbon and is a candidate for blue organic light-emitting diodes or is used for optical tagging in biological studies. Nanocrystalline form may have advantages over bulk crystal or monomers for these applications,[2] whereas several aspects of optical properties such as the unusual blueshift are not understood. Our calculation includes an accurate model for the dielectric constant of perylene reflecting the crystal and molecular anisotropy as well as electromagnetic propagation effects. Our results show that there is a "spurious" red-shift in extinction and therefore an analysis taking scattering into account is necessary for understanding size and shape-dependent blue-shift in perylene nanocrystals.

Perylene nanocrystals were made by the reprecipitation method.[10] Briefly, perylene/acetone solution was mixed with distilled water to crystallize the nanocrystals. Aqueous suspensions of nanocrystals were obtained after vaporizing acetone. Controlling the concentration of perylene and the solution/water ratio, nanocrystals of average size from 100 to 200 nm can be fabricated. For larger crystals, nanocrystals grown in water are used as nuclei for further crystal growth by mixing perylene/acetone solution with the aqueous suspension of nanocrystals. For smaller crystals, a hot perylene/dimethylsulfoxide solution with a high perylene concentration was mixed with cool distilled water. The scanning electron microscope (SEM) images of nanocrystals are shown in Fig. 1.

[a)]Electronic mail: eiji@rs.kagu.tus.ac.jp.

0003-6951/2011/99(5)/053304/3/$30.00

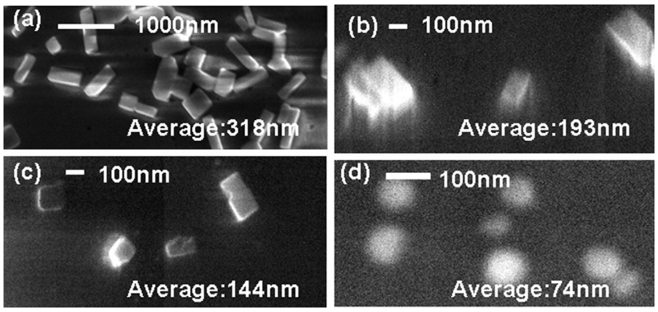

FIG. 1. SEM images of nanocrystals. The samples were prepared starting from an aqueous suspension of nanocrystals that was cast and dried on a slideglass.

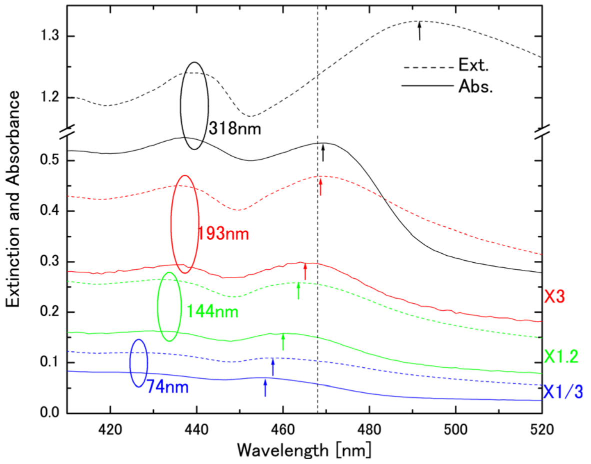

FIG. 2. (Color online) Extinction and absorption spectra for water suspensions of perylene nanocrystals of 74 nm, 144 nm, 193 nm, and 318 nm in average diameter.[17] The peak positions are designated by the arrows. The dashed line at 468 nm is the free exciton energy of bulk crystal at 312 K.

The absorption spectra of perylene nanocrystals suspended in water for average sizes of 74 nm, 144 nm, 193 nm, and 318 nm in diameter were measured with a spectrophotometer with an integrating sphere (JASCO, V-7200) as shown by the solid curves in Fig. 2. The exciton band shows a blueshift with respect to that in bulk as the crystal size is reduced. This large "quantum size effect" is an intriguing property of perylene nanocrystals.

By comparison, the dashed curves in Fig. 2 show the extinction spectra of the same samples, measured with a spectrophotometer in transmission geometry with a small solid angle of collection (Shimadzu, UV-3150). The spectra show a redshift of the exciton band as the crystal size is increased with respect to that in the absorption spectra and a strong tail extending toward longer wavelengths. These features are caused by scattering, as demonstrated by the theoretical calculation below. Both the experiment and theory show that scattering has the effect of producing an apparent redshift in large nanocrystals. This could be wrongly interpreted as a size-dependent blueshift as the nanocrystal size is reduced.

Scattering by spherical particles of isotropic materials can be rigorously calculated by the Mie scattering theory.[18] However, even if we assume a spherical shape, perylene is an optically anisotropic crystal (C_{2h} monoclinic), so a numerical approach is necessary. We used the Purcell-Pennypacker method[19] (also known as the discrete dipole approximation or DDA), which involves dividing a crystallite of dielectric constant ϵ into a discrete cubic array of cells $j = 1,2,\ldots,n$.

The calculation requires knowledge of the frequency-dependent dielectric constant ϵ of perylene. As there is little reliable data on the dielectric constant in the visible region of interest, we developed a model for ϵ starting from the molecular polarizability α and dipole-dipole interaction between the molecules. The local field at each molecule in a unitcell is calculated self-consistently in terms of the sum of the dipole fields due to all other molecules. We then obtain the susceptibility as the ratio of the dipole moment per unit volume and the macroscopic field. Details will be published elsewhere. Non-zero components of ϵ are

$$\begin{aligned}\epsilon_{bb} &= \left[1 + 4\left(\frac{v_c}{4\pi}\alpha^{-1} - \mathcal{L}_+\right)^{-1}\right]_{bb}\\ \epsilon_{ij} &= \left[1 + 4\left(\frac{v_c}{4\pi}\alpha^{-1} - \mathcal{L}_-\right)^{-1}\right]_{ij} \quad \text{for } i,j \neq b,\end{aligned} \tag{1}$$

where the indices run over the crystal axes a, b and c' and v_c is the volume of the unit cell and $\mathcal{L}_\pm$ are the dipole sum tensors[20] for the crystal lattice of perylene as tabulated in Table I. The components of α along the molecular axes were modelled as sums of Lorentzians. We included the lowest 7 molecular transitions that cover energies up to 6 eV with oscillator strengths and transition frequencies taken from Ref. 3.

Fig. 3 shows the calculated extinction and absorption spectra of spherical nanocrystals 20 nm, 100 nm, and 300 nm in diameter. Although the shape is assumed to be spherical, full anisotropy of the dielectric constant is included and all results are orientationally averaged. For 20 nm nanocrystal, scattering is negligible and absorption and extinction are almost indistinguishable. As the size increases to 100 nm, scattering is not negligible but the spectral features and especially the lowest energy peak position are nearly the same as seen in extinction and absorption. In contrast, for nanocrystals as large as 300 nm, the extinction spectrum deviates considerably from the absorption spectrum. The latter develops a broad tail below the onset of absorption and exhibit an apparent redshift in the lowest energy peak. The long-wavelength tail is due to the well-known Rayleigh scattering while the broad peak in the extinction spectrum is due to size-dependent resonances in scattering interfering with absorption.

Considering that there are no adjustable parameters in the model for ϵ, the good agreement between theory and experiment is striking. The calculation clearly shows that the apparent redshift observed in the transmission measurement is due to scattering. More importantly, the blue-shift in the excitonic absorption peak in small nanocrystals (<200 nm) is well reproduced in the calculation. The origin of this

TABLE I. The dipole sum tensors for perylene crystal in the molecular coordinates. $\mathcal{L}_+$ and $\mathcal{L}_-$ appearing in Eq. (1) correspond to symmetries A_u and B_u, respectively.

Symmetry	$\mathcal{L}_{LL}$	$\mathcal{L}_{MM}$	$\mathcal{L}_{NN}$	$\mathcal{L}_{LM}$	$\mathcal{L}_{LN}$	$\mathcal{L}_{MN}$
A_u	0.0421	−0.1816	1.9865	0.2579	−0.9128	2.9448
B_u	−1.4463	−0.2377	3.8216	0.5458	−1.3339	0.3706

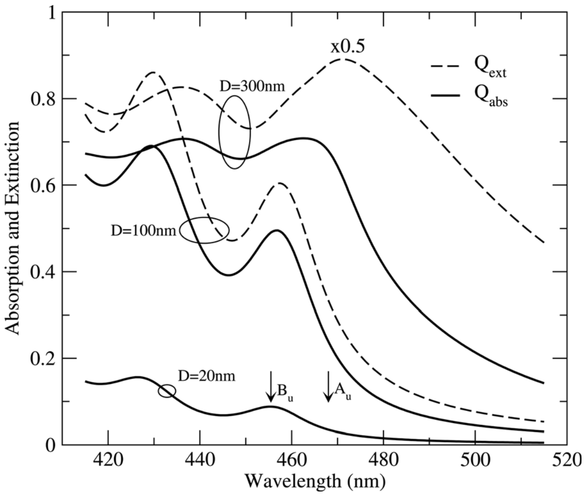

FIG. 3. Calculated absorption efficiency (Q_{abs}) and extinction efficiency (Q_{ext}) of randomly oriented spherical nanocrystals of diameter $D = 20$, 100, and 300 nm. The absorption and extinction are virtually identical for $D = 20$ nm.

blue-shift may be understood from the nature of the lowest energy exciton state in perylene. It arises from a transition polarized along the long axis of the molecule that splits into two excitonic states with A_u and B_u symmetry in the crystal. The energies of these excitons in our calculated epsilon are indicated by arrows in Fig. 3. The A_u exciton defines the band-edge and is polarized along the b-axis of the crystal. It is very weak because the b-axis nearly orthogonal to the long-axis of the molecule. The B_u exciton is polarized in the $a - c$ plane with a much stronger dipole moment as the c axis is nearly parallel to the long-axis of the molecule. Thus, in a collection of randomly oriented nanocrystals, the absorption is dominated by the B_u exciton which is blue-shifted from the A_u exciton by Davydov splitting. In general, peaks in absorption are determined by the resonances in ϵ as well as the electromagnetic field profile inside the nanocrystal. As the nanocrystal size increases, the field profile is significantly modified by scattering effects and this accounts the slight redshift and change in line shape of absorption for the larger, 300 nm, nanocrystal.

In conclusion, the effect of scattering on the absorption spectra of an ensemble of perylene nanocrystals was evaluated experimentally and theoretically. Experimental data shows that scattering cannot be neglected for sizes more than about 50 nm since it makes the extinction spectra exhibit an apparent redshift for larger sizes. The calculated extinction spectra are in qualitative agreement with this observation. Further, the blue-shift in the onset of absorption is attributed to the strong absorption by the B_u exciton. More importantly, the easy access to the strong B_u excitonic absorption in perylene nanocrystals as opposed to bulk crystals may help making more efficient optoelectronic devices based on perylene. Our result indicates that the scattering could mask the true shape and position of absorption bands, a result applicable to all nanocrystals that are comparable in size to the wavelength.

The authors thank Hitoshi Kasai for valuable suggestions about the fabrication method for smaller nanocrystals.

[1] *Single Organic Nanoparticles*, edited by H. Masuhara, H. Nakanishi and K. Sasaki (Springer, Berlin, 2003).
[2] S. Masuo, A. Masuhara, T. Akashi, M. Muranushi, S. Machida, H. Kasai, H. Nakanishi, H. Oikawa, and A. Itaya, Jpn. J. Appl. Phys. **46**, L268 (2007).
[3] J. Tanaka, Bull. Chem. Soc. Jpn. **36**, 1237 (1963).
[4] R. M. Hochstrasser, J. Chem. Phys. **40**, 2559 (1964).
[5] J. Tanaka, T. Kishi, and M. Tanaka, Bull. Chem. Soc. Jpn. **47**, 2376 (1974).
[6] K. Fuke, K. Kaya, T. Kajiwara, and S. Nagakura, J. Mol. Spectrosc. **63**, 98 (1976).
[7] A. Matsui, K. Mizuno, and M. Iemura, J. Phys. Soc. Jpn. **51**, 1871 (1982).
[8] H. Kasai, H. Kamatani, S. Okada, H. Oikawa, H. Matsuda, and H. Nakanishi, Jpn. J. Appl. Phys. **35**, L221 (1996).
[9] J.-A. He, K. Yang, J. Kumar, S. K. Tripathy, L. A. Samuelson, T. Oshikiri, H. Katagi, H. Kasai, S. Okada, H. Oikawa, and H. Nakanashi, J. Phys. Chem. B **103**, 11050 (1999).
[10] H. Kasai, H. Oikawa, S. Okada, and H. Nakanishi, Bull. Chem. Soc. Jpn. **71**, 2597 (1998).
[11] E. T. Batteh, J. Cheng, G. Chen, D. G. Steel, D. Gammon, D. S. Katzer, and D. Park, Phys. Rev. B **71**, 15532 (2005).
[12] A. N. Vamivakas, M. Atatüre, J. Dreiser, S. T. Yilmaz, A. Badolato, A. K. Swan, B. B. Goldberg, A. Imamoglu, and M. S. Ünlü, Nano Lett. **7**, 2892 (2007).
[13] H. Ishino, S. Iwai, S. Iwamoto, T. Okumura, T. Kobayashi, and E. Tokunaga, Opt. Rev. **17**, 337 (2010).
[14] H. Ishino, S. Iwai, S. Iwamoto, T. Okumura, T. Nishimoto, S. V. Nair, T. Kobayashi, and E. Tokunaga, Phys. Rev. B **84**, 041303(R) (2011).
[15] F. J. García de Abajo, Rev. Mod. Phys. **79**, 1267 (2007).
[16] A. Petukhova, A. S. Paton, Z. Wei, I. Gourevich, S. V. Nair, H. E. Ruda, A. Shik, and E. Kumacheva, Adv. Funct. Mater. **18**, 1961 (2008).
[17] As the nanocrystals are not spherical, the average diameter is calculated as that of an equal volume sphere.
[18] H. C. van de Hulst, *Light Scattering by Small Particles* (Dover, New York, 1981).
[19] E. M. Purcell and C. Pennypacker, Astrophys. J. **186**, 705 (1973).
[20] C. J. F. Böttcher, *Theory of Electric Polarization* (Elsevier, Amsterdam, 1978), Vol. **2**, p. 433.