Mechanochemical Doping of Tetracence into Anthracene Crystals by Milling Technique

Kunihiro Ichimura* and Ken'ichi Aoki

Faculty of Science, Toho University, 2-2-1 Miyama, Funabashi 274-8510

Research Center for Materials with Integrated Properties, Toho University,
2-2-1 Miyama, Funabashi 274-8510

The wet bead milling of anthracence with tiny amounts of tetracene in water results in mechanochemical doping to exhibit solid-state singlet energy transfer. Changes of emission spectra are sensitive to milling conditions so that the couple can act as a fluorescent probe for milling. Perylene displays similar behavior, whereas pentacene and rubrene lead to insufficient fluorescence quenching due to their poor solubility in host crystals.

Aqueous dispersions of organic solid nanoparticles in the range of nanometer to submicrometer have been attracting current attention due to their "pseudo-solution" behavior.[1] In this context, organic nanocrystals dispersed in water have been studied recently to disclose their unique photophysical as well as photochemical properties featured by absorption and emission spectra,[2] solid-state photopolymerization,[3] and photooxidative catalytic activity.[4] Aqueous dispersions of nano-sized organic crystals have been prepared for these studies by the so-called reprecipitation technique,[2a,5] whereas the layer-by-layer vacuum deposition of water and aromatic molecules was also reported as an alternative way to give aqueous solid nanodispersions.[2b] Despite of the wide spread of mechanical milling to reduce particle sizes of organic solids including pigments[6] and pharmaceuticals,[7] scarce works have been done on revealing photofunctional peculiarities of milled nanoparticles from fundamental viewpoints. Recently, we have found that the sensitized solid-state photoacid generation through exciton diffusion in sensitizer crystals occurs when water-insoluble crystalline mixtures of a photoacid generator and a sensitizer were ground in water to give aqueous dispersions of nanoparticles.[8] This situation motivated us to examine solid-state energy transfer[9] among nano-sized crystals on account of its significance in organic light emitting diodes[10] and photovoltaic solar cells.[11] We show here that bead milling of crystalline mixtures of anthracene (AN) as a donor and polyaromatics as acceptors leads to mechanochemical doping exhibiting singlet energy transfer. We would like to suggest that the couples could act as a fluorescence probe for monitoring milling processes to achieve nano-downsizing of organic crystals.

A crystalline mixture of AN and 1.1×10^{-3} mol/mol of tetracene (TE) as a representative couple for energy transfer[9] was subjected to bead milling in water by using a planetary mill to give 5 wt% of aqueous dispersions of the solid. Poly(vinyl alcohol) of DP = 500 (5 wt%) was used to stabilize dispersions of hydrophobic particles. Figure 1a shows emission spectra ($\lambda^{exc} = 375$ nm) of dispersions prepared under various milling conditions, revealing that strengthening milling conditions enhances the energy-transfer efficiency. Levels of energy transfer can be expressed as I_{531}/I_{444}. I_{531} and I_{444} denote fluores-
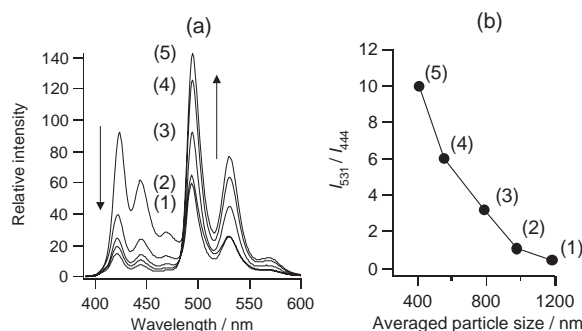

Figure 1. (a) Fluorescence spectra and (b) I_{531}/I_{444} as a function of particle size for 5 wt% aqueous dispersions of AN under 375-nm excitation in the presence of 1.1×10^{-3} mol/mol of TE at various milling conditions (diameter of zirconia beads, milling speed and time; (1) 3 mm, 400 rpm, 1 h, (2) 0.3 mm, 400 rpm, 1 h, (3) 0.3 mm, 500 rpm, 1 h, (4) 0.3 mm, 600 rpm, 1 h, (5) 0.3 mm, 650 rpm, 1 h.

cence intensity at 531 nm due to TE and at 444 nm due to AN, respectively. I_{444} at the second peak of AN was employed because of the internal filter effect of dispersions. I_{531}/I_{444} values were plotted against averaged particle sizes measured by dynamic light scattering (DLS). As shown in Figure 1b, solid-state fluorescence quenching efficiencies are leveled off at a particle size of 400 nm or less. Singlet exciton diffusion length (DL) in AN crystals has been estimated to be in a range of 46 to 130 nm.[2b,9,12] Whereas the values are scattered, it is evident that particle sizes of milled mixtures are too large when compared with the DL value. A reasonable explanation for this situation is made by assuming that particles detected by DLS are comprised of many sub-grains with diameters shorter than DL, just as in the case of solid-state electron transfer in aqueous dispersions.[8]

In order to reveal the dependence of TE concentrations on energy-transfer efficiency, guest concentrations ranging from 4×10^{-3} to 4×10^{-7} mol/mol were adjusted by adding AN crystals to an aqueous dispersion of AN and TE of known concentrations, followed by the milling. It was found that a decrease of I_{444} synchronizes with an increase of I_{531} as a function of the increment of guest concentrations (Figure 2S).[13] As shown in Figure 2, a double logarithmic representation of the I_{531}/I_{444} values versus TE concentrations displays a good linearity. The linear dependence of the guest to host fluorescence quantum yield ratios (Q_G/Q_H) on guest concentration in double logarithmic representation was reported for mixed crystals of TE/AN[14] whereas TE concentrations range from 10^{-1} to 10^{-7} mol/mol. Taking into consideration that I_{531}/I_{444} values are proportional
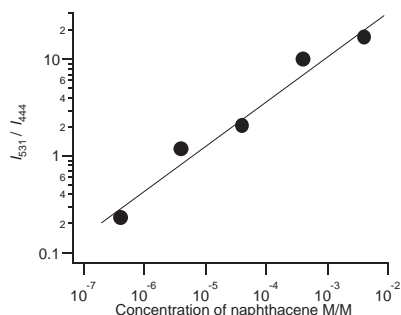
Figure 2. Double logarithmic representation of I_{531}/I_{444} vs. TE concentration.
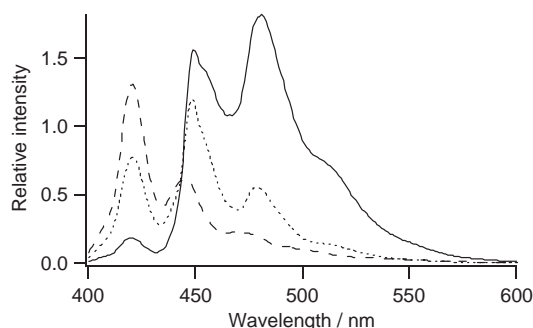

Figure 3. Fluorescence spectra of 5 wt % of aqueous dispersions of AN co-milled with (1) 2.89×10^{-3} mol/mol of PER (full line), (2) 1.66×10^{-3} mol/mol of PEN (dotted line), and (3) 1.23×10^{-3} mol/mol of RU (broken line) at 650 rpm for 2 h.

to Q_G/Q_H, the singlet energy transfer behavior in mixed crystals prepared by the melting method is quite similar to that of the present milled mixtures, indicating that the mechanical milling results in efficient mixing of crystals of the host and guest.

In order to determine the mechanochemical doping, the wet milling of AN in the presence of the other guest crystals was achieved under the same conditions (0.3 mm beads, 650 rpm, 1 h). Fluorescence spectra of aqueous dispersions thus prepared are shown in Figure 3 and classified into two guest groups. The first includes TE[14] and perylene (PER)[15] and displays sufficient fluorescence quenching accompanied by strong guest emission, supporting that the mechanochemical doping takes place effectively. The second group involving PEN[16] and rubrene (RU) quenches the host fluorescence insufficiently, implying that mechanochemical mixing of the host and the guests occurs hardly because of low solubility of the guests in host solid.[9] Whereas a level of fluorescence quenching by RU is not far from that of PEN, fluorescence intensity from the two are markedly different; no emission from RU was generated, while the fluorescence of PEN is observed though weaker when compared with TE and PER. This is because RU, which is weakly fluorescent in crystals, cannot be dissolved molecularly in host crystals.

In summary, aqueous dispersions of AN crystals of as a host in the presence of guest crystals were prepared by bead milling

to determine solid-state singlet energy transfer by fluorescence measurements. Fluorescence intensity ratios, I_{531}/I_{444}, exhibiting a level of energy transfer from AN to TE, are influenced sensitively by milling conditions, suggesting that the couple can be act as a fluorescence probe for milling processes. TE and PER as guests are doped in AN crystals during the wet milling to form mixed crystals as a result of mechanochemical effect.

References and Notes
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