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Solid-state Solvatochromic Behavior of Reichardt's Dye Crystals Hybridized with Silica Nanoparticles

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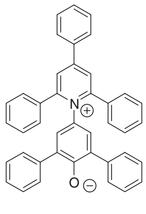
The dry bead milling of solvatochromic E_T30 with silica nanoparticles gave powdery nanohybrids, which exhibited color changes depending on environmental conditions.

The nano-downsizing of organic crystals with dimension in the range between 10 nm and a few 100 nm has been attracting interest because of the emergence of physiological and physicochemical properties due to the drastic enlargement of surface areas and the efficient suppression of light scattering.[1] Organic nanocrystals have been prepared by reprecipitation,[2] laser ablation,[3] and layer-by-layer vacuum deposition.[4] Whereas we carried out the wet milling of organic crystals in water to demonstrate the photoinduced electron transfer[5] and energy transfer[6] among fine crystals and the solid-state photoisomerization of azobenzene,[7] our recent efforts have been focused on the dry milling of organic pigments,[8,9] polyaromatics,[10] and azobenzene crystals[11] in the presence of silica powders to afford core–shell organic–inorganic nanohybrid powders. One of the characteristic features of the nanohybrids has been found in the melting point depression of molecular crystals owing to extraordinarily large surface areas.[10] This has motivated us to demonstrate other types of surface-specific behavior of organic crystals by core–shell nanostructuring. The solvatochromic Reichardt's dye (E_T30; Scheme 1) is attractive since absorption maximum (λ_{max}) is altered by microenvironmental polarity.[12] In this context, we achieved the dry bead milling of a mixture of E_T30 with silica nanoparticles to fabricate powdery hybrids to determine the effect of external polarity on λ_{max} in solid state. We have observed that the color of hybridized powders was changed from green into blue immediately under ambient conditions, whereas wetted powders were purple in color.

Silica nanoparticles were treated with a polysiloxane in advance to make silica surfaces hydrophobic.[8] The dry milling of a mixture of E_T30 and the surface-modified silica nanoparticles (m-SiO_2) was performed with the aid of a table-top planetary mill (Fritsch; P-7) according to our previous reports.[10,11] Weight ratios of E_T30 to m-SiO_2 were selected to range from 0.5:1 to 0.02:1 on the basis of the following consideration. In our previous work, the dry grinding of crystals of crystal violet lactone (CVL) and silica nanoparticles without the surface modification (u-SiO_2) resulted in the formation of monolayers of blue-colored triphenylmethane dye (CVL^+) due to the acid–base interactions of surface silanols with CVL.[13] The minimum amount of CVL required for the monolayer formation on 1.00 g of u-SiO_2 was about 60 mg. Specific surface areas of u-SiO_2 and m-SiO_2 determined by the BET (Brunauer–Emmett–Teller) method were 193.0 and 152.6 $m^2\,g^{-1}$,[8] respectively, whereas molecular areas of CVL^+ and E_T30 were estimated to be roughly 1.2 and 1.4 nm^2, respectively. Assuming that E_T30 molecules are adsorbed on surfaces of m-SiO_2 nanoparticles in a way similar to those of CVL^+ in a flat-laid manner, a minimum loading amount of E_T30 for monolayer adsorption was approximated to be about 40 mg for 1.00 g of m-SiO_2.



Scheme 1. E_T30.

A mixture of E_T30 and m-SiO_2 (2.00 g) was placed in a couple of zirconia vessels (25 mL) and milled with aid of nylon beads (9.5 mm ϕ) at a rotation speed of 400 rpm for 1 h to give voluminous, pale blue powders. Figure 1 shows TEM images of m-SiO_2 and a 0.1:1 (w/w) hybrid of E_T30 and m-SiO_2.[14] They are very close to each other, implying the core–shell nanohybridization of E_T30. The BET specific surface area of the 0.1:1 hybrid was 135.8 $m^2\,g^{-1}$ and somewhat smaller than m-SiO_2 probably because of the following reason. As we have already discussed,[8–11] primary particles of m-SiO_2 with an average diameter of 14.2 nm are densely aggregated, as seen in Figure 1a, so that organic solids may be filled in hollow spaces at joint sites of primary silica particles to result in the formation of locally thick shells to reduce surface areas.

When a 0.1:1 (w/w) powdery hybrid was placed on a hot plate and heated at ca. 140 °C, the bluish color turned into greenish (Figure 2a), and the original blue color was regenerated immediately upon exposure to ambient conditions (Figure 2b). Moreover, the change to purple was induced when the powder was wetted with water (Figure 2c). In order to record diffusive reflection spectra, the hybrid powder was placed in sealed polyethylene bags to prepare the following three types of samples. Granules of calcium chloride as a desiccant were placed in one of the bags to dry the powder, whereas no

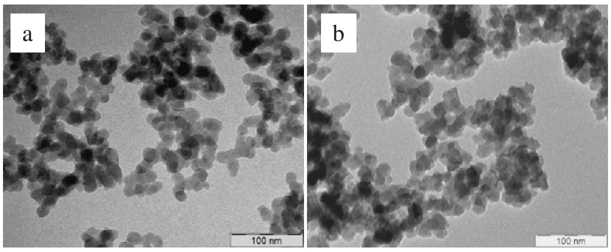


Figure 1. TEM images of (a) m-SiO_2 and (b) a 0.1:1 (w/w) hybrid of E_T30 and m-SiO_2.

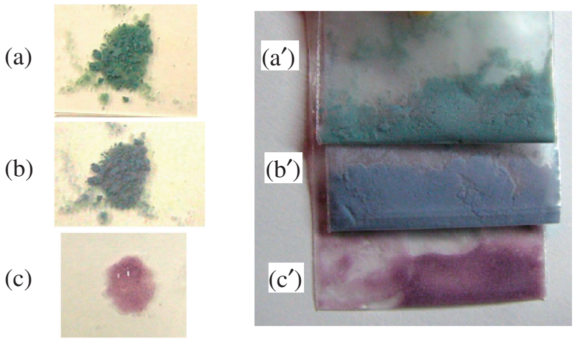


Figure 2. Photographs of a powdery 0.1:1 (w/w) hybrid of E_T30 and m-SiO_2 on a filter paper (a) at ca. 160 °C, (b) followed by standing at ambient conditions, and (c) after wetted with water. Photographs of the powder in sealed polyethylene bags (a′) in the presence of $CaCl_2$ as a desiccant, (b′) without a desiccant, and (c′) in the presence of water.

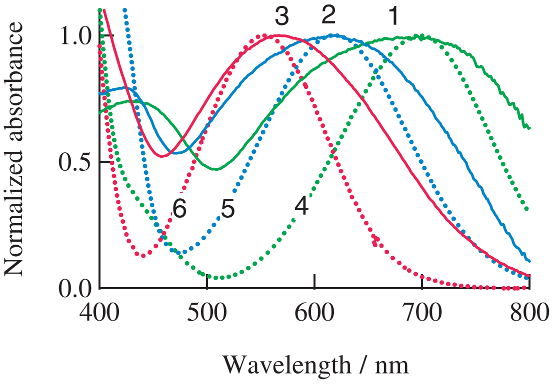


Figure 3. Diffusive reflection spectra of the E_T30 hybrid powder in sealed polyethylene bags in the presence of $CaCl_2$ as a desiccant (1; green solid line), without a desiccant (2; blue dotted line), and after wetted with water (3; red broken line) and absorption spectra of E_T30 in dichloromethane (4; green dotted line), acetonitrile (5; blue dotted line), and ethanol (6; red dotted line).

desiccant was present in the second bag to maintain ambient conditions. The powder filled in the third bag was wetted with water. As seen in Figures 2a′–2c′ the color of the powder in the bags is influenced markedly by external conditions. Note that the dark color of original E_T30 crystals is apparently unchanged under these conditions. The three types of bags were subjected directly to measurements of diffusive reflection spectra, and the results are shown in Figure 3 as solid lines after the transformation according to the Kubelka–Munk function. The powder exhibited λ_{max} at 695, 619, and 566 nm in dry, ambient, and wet conditions, respectively, and the λ_{max} values depended slightly on weight ratios of E_T30 to m-SiO_2. For comparison, absorption spectra of E_T30 dissolved in dichloromethane, acetonitrile, and ethanol are also displayed in Figure 3. This suggests that the microenvironmental polarity of nanohybridized E_T30 in dry, ambient, and wet conditions is approximated by the polarity of these solvents, whereas FWHM (full width at half maximum) values of the powder are far wider relative to those in the solutions.

It seems curious that the λ_{max} under dry conditions is far from that at 795 nm in dioxane as a less polar solvent and considerably blue-shifted even though molecules at the uppermost surface of the solvatochromic layers are exposed to the air. Reasonable interpretation is needed also for the results of the wetted hybrid, since the λ_{max} is noticeably red-shifted when compared with that at 435 nm in water.[12] Both of these results suggest strongly the involvement of the nearest neighboring E_T30 molecules in shell layers and/or hydrophobic silica surfaces. In the case of dried hybrid powders, the microenvironmental polarity of molecules at the uppermost surface is determined not only by the exposure to the air, but also by contact with the other betaine molecules. Consequently, the blue shift of λ_{max} of the dried powder occurs moderately. An analogous explanation can be made on the spectrum of the wetted powder. Whereas molecules at the topmost surface suffer from the influence of water molecules, they are also affected by nearest neighboring E_T30 molecules, the polarity of which is far lower than water. The polarity of hydrophobic silica surface plays also a certain role in the solvatochromic behavior. In this way, the color of the hybrid is governed by the polarity of both of external environment and the internal E_T30 molecules. It is worthy to suggest that the larger FWHM of powder spectra reflects the wide distribution of microenvironmental polarity ascribable to the contribution of both factors.

To summarize, core–shell hybridized nanoparticles of E_T30 and surface-modified silica nanopowder were fabricated by the dry beads milling to monitor the polarity of surfaces of E_T30 crystals. The color of the hybrid was dependent notably on external atmosphere and was greenish, bluish, and purple under dry, ambient, and wet conditions. The λ_{max} was determined by the polarity of both external environment and E_T30 molecules.

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