Pump–probe spectroscopy and circular dichroism of nanocrystalline benzophenone—towards absolute kinetic measurements in solid state photochemical reactions†

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Nanocrystals suspended in water can be used to record steady state and pump–probe absorption spectra, which should be useful for the study of excited states and reactive intermediates in the solid state.

A simple method for the analysis of excited states and reactive intermediates in crystalline solids would have a strong impact on solid state photochemistry.[1] Despite progress in the design of solid state photochemical reactions,[2] mechanistic studies are generally restricted to product analysis[3] and computational modeling.[4] Structure–reactivity correlations based on X-ray diffraction have led to valuable structural insights to predict whether reactions in crystals may or may not be allowed.[5,6] However, the observation of excited states and short-lived transients by transmission pump–probe methods represents a serious challenge due to complications associated with the anisotropic optical properties of crystalline solids.[7] Whether used as single crystals or fine powders, their high optical densities limit the penetration of light to a few microns. Additionally the orientation-dependent refraction index and extinction coefficient (birefringence and dichroism)[7] combined with the light scattering caused by defects and roughness complicate the quantitative analysis of transmitted light. Furthermore, rapid excited state delocalization (excitons) leads to biphotonic processes when high laser power and long-lived species are involved.[8]

Given these challenges, the detection of short-lived intermediates by time-resolved spectroscopy is difficult and limited to thin crystals or to diffuse-reflectance methods using powders.[9] However, it has been recently shown that size-dependent effects on absorption and emission frequencies[10] and emission intensities[11] can be easily assessed for samples in the nanoscale regime by simple UV-Vis absorption and emission studies. Inspired by that, we decided to explore the use of benzophenone (BPh) as a model system to evaluate the use of nanocrystals to analyze excited states and reactive intermediates. In addition to possessing a well characterized and easily detectable triplet,[9,12] BPh forms chiral crystals by adopting a helical homochiral conformation.[13] Knowing that chiral crystals of non-chiral molecules have a tendency to form one of the two enantiomorphous phases by self-seeding,[14] we reasoned that the integrity of the crystal could be assessed by circular dichroism (CD).

Nanocrystalline suspensions were prepared‡ as reported by Kasai *et al.*,[15] by adding a saturated acetone solution of BPh into a rapidly stirring aqueous solution of cetyl trimethyl ammonium bromide (CTAB) 20–100 times below the critical micelle concentration of 8×10^{-4} M.[16] Sample appearance ranged from clear to cloudy as BPh loadings varied from *ca.* 0.01 to 2.0 mg ml^{-1} (Fig. 1). Notably, the UV-Vis absorption spectrum obtained by conventional steady state transmission methods matched the spectrum obtained by diffuse reflectance of bulk powders relatively well.[17] The n,π* transition has an onset at *ca.* 380 nm and a λ_{max} at 345 nm and the π,π* band of the nanocrystals is red shifted with respect to the bulk from 245 nm to 260 nm.

While phosphorescence cannot be observed in homogeneous solution at ambient temperature, oxygen-saturated samples of nanocrystalline BPh later shown to have an average particle size of *ca.* 200 nm, displayed the bright blue glow shown in Fig. 1 and a T_1–S_0 spectrum identical to that of bulk solids (Fig. 2). The phosphorescence decay (Fig. 2, inset) fits a mono-exponential with a lifetime $\tau_P = 2.0$ μs, which was shown to be independent of O_2 concentration. These observations indicate that phosphorescence is indeed due to nanocrystalline benzophenone and not to benzophenone in solution, which is known to be quenched by oxygen near diffusion-controlled rates. The T_1–T_n absorption spectrum acquired by excitation at $\lambda = 355$ nm using a Nd–Yag laser (pulse width <10 ns) was a good match to those in previous reports (Fig. 3).[9,12] The kinetics of triplet decay detected at $\lambda = 510$ nm

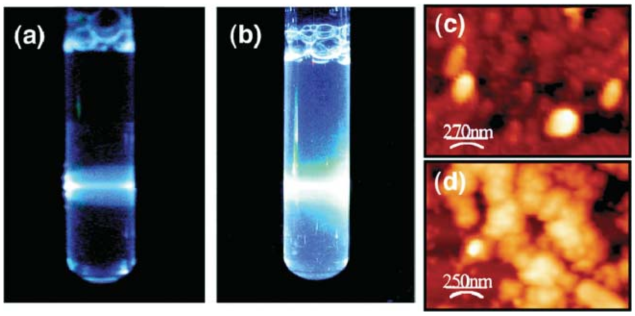

Fig. 1 Nanocrystalline suspensions of benzophenone (BPh) with loadings of (a) 0.015 and (b) 1.8 mg ml^{-1} with a 355 nm Nd–YAG laser beam passing through to highlight their phosphorescence, transmittance, and scattering. AFM images of the 0.015 mg ml^{-1} sample drop cast on a glass surface showing (c) isolated and (d) surface-conglomerated nanocrystals.

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† Electronic supplementary information (ESI) available: nanocrystal preparation, and photophysical and particle size measurements. See DOI: 10.1039/b709166d

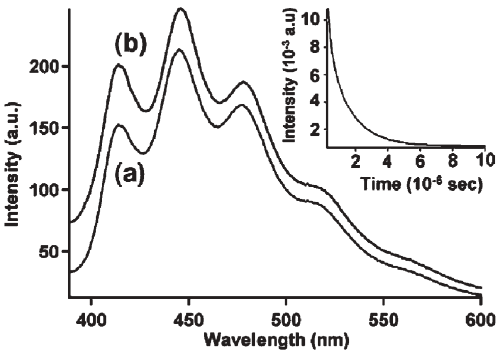

Fig. 2 Phosphorescence spectra of (a) an air-saturated suspension of nanocrystalline BPh acquired by excitation and emission at right angles, and (b) a polycrystalline sample acquired by front-face excitation and detection. The inset illustrates the emission decay from the suspension sample.

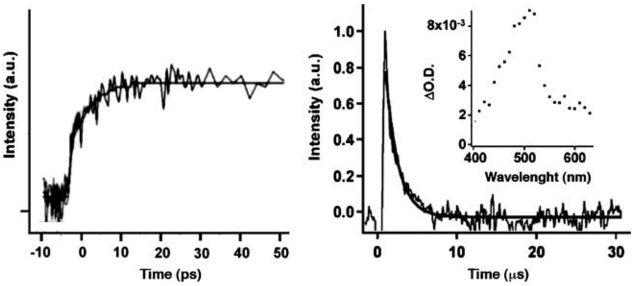

Fig. 3 Transient kinetics of excited benzophenone as a nanocrystalline suspension, with a loading of 1.8 mg ml^{-1} in H_2O and CTAB. (Left) Growth of the triple state (τ_{ISC} = 5 ps) by excitation with 100 fs pulses at λ = 270 nm and, (b) decay of the triplet state (τ_{ISC} = 2 μs) measured by 10 ns excitation pulses at 355 nm. Both were detected at 510 nm. The inset on the right frame illustrates the T_1–T_n absorption spectrum showing a λ_{max} at 510 nm.

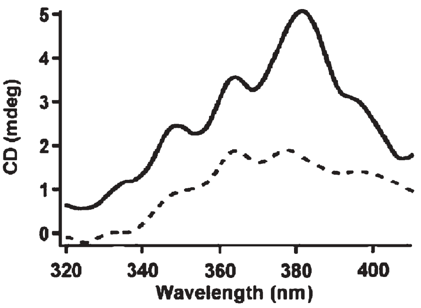

Fig. 4 (Solid line) Circular dichroism (CD) spectrum of BPh crystals in a Nujol mull showing contributions due to linear birefringence and/or circular intensity differential scattering by 380 nm, and (dotted line) CD spectrum of nanocrystals suspended CTAB–H_2O.

were insensitive to O_2, and their initial intensity was a linear function of particle loading between 0.01 and 2.0 mg ml^{-1}. In agreement with the phosphorescence data, the T_1–T_n decay fit a mono-exponential with τ_T = 2.0 μs.[18] To demonstrate that pump probe measurements with suspended nanocrystals are only limited by the resolution of the instrument, experiments were also carried out with 100 fs pulses at 270 nm to analyze the rate of intersystem crossing (S_1–T_n). A time constant of 5.0 ps turned out to be significantly shorter than those in CTAB micelles (7.1 ps), in homogeneous solution (8–12 ps),[19] and in single crystals (28 ps).[18,20] Notably, suspended nanocrystals share kinetic features with solution and bulk solids: the short mono-exponential is similar to that observed in oxygen-free solvents and the insensitivity to O_2 is reminiscent of the solid state.[21]

A comparison of the FTIR spectrum of nanocrystals obtained by filtration with that from X-ray characterized specimens suggested identical morphologies. Further evidence was obtained from CD measurements, which confirmed the enantiomorphous nature of the nanocrystals.[22] For a positive control we determined the CD spectrum of a sample prepared from a single crystal in a Nujol mull. It is known that homochiral crystals prepared in this manner (or in KBr pellets) give rise to CD spectra that are comparable to those obtained in solution.[23] The two CD spectra in Fig. 4 are very similar to the one previously reported by Szyrszyng *et al.*[24] in a KBr matrix. The reason for the small differences observed by 380 nm is not known but it might be due to contributions from residual linear birefringence[7] and/or circular intensity differential scattering.[25] The CD spectrum shows a positive Cotton effect on the n,π* transition, which corresponds to the P,P designation[26] for the molecular helicity of the corresponding BPh enantiomorph.[27]

The size of the nanocrystals used in our experiments was analyzed by a combination of dynamic light scattering (DLS), and atomic force microscopy (AFM). DLS carried at out 298 K with a detector at 90 degrees revealed average particle sizes of *ca.* 200 ± 30 nm. Microscopic analysis by AFM on a glass substrate showed isolated specimens and crystal aggregates, with most specimens having those dimensions (Fig. 1). The observation of a CD spectrum is also an indication of crystals that are smaller than the wavelength of light.

In conclusion, we have shown that molecular nanocrystals of BPh are ammenable to transmission pump–probe methods for the detection of transients spanning lifetimes from picoseconds to microseconds. The crystalline nature of the samples used in this study was established by taking advantage of the supramolecular chirality of crystalline benzophenone, which was shown to have a tendency for self-seeding in either enantiomorphous phase. The significance of these observations is that the detailed kinetic and spectroscopic characterization of many photophysical and photochemical processes taking place in crystalline media should be readily accessible by this relatively simple method.

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Notes and references

‡ Nanocrystalline suspensions were prepared by adding 5–25 μL of an 80 mM solution of BPh in acetone to a rapidly vortexing 0.04 mM solution of CTAB in water. The suspensions were purged with air while stirring for 30 min at 298 K to eliminate residual acetone. UV-Vis, phosphorescence, triplet–triplet absorption, and CD spectra were recorded by transmission methods with conventional equipment. CD spectra of samples dispersed in Nujol as a thin film over a quartz plate were nearly identical to those obtained with suspended nanocrystals at loadings of *ca.* 0.01 mg ml^{-1}. Crystal sizes were analyzed by polarized optical microscopy, dynamic light scattering (DLS), and atomic force microscopy (AFM) in tapping mode. A

detailed description of sample preparation and additional spectra can be found in the supplementary information section†.

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