Photochemical reaction mechanisms and kinetics with molecular nanocrystals: surface quenching of triplet benzophenone nanocrystals

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Organic molecular nanocrystals suspended in water are useful when studying reactions that occur in the solid state because they retain not only the reactive and supramolecular properties of bulk crystals, but are also amenable to transmission spectroscopy. Having previously studied the triplet state of benzophenone nanocrystals by laser flash photolysis transmission spectroscopy, we now report nanosecond experiments in the presence of several possible quenchers: anionic and cationic surfactants, dissolved oxygen, and as a function of solvent deuteration (H_2O and D_2O). After finding these to have no effect, several anionic quenchers (I^-, Br^-, and N_3^-) were tested by Stern–Volmer analysis. Significant correlation between the quenching rates in solution and in nanocrystals suggests that the electronic excitation is accessible to quenchers at the surface. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: nanocrystalline; surface quenching; benzophenone; solid-state reaction kinetics; nanosecond flash photolysis; particle size

INTRODUCTION

Photochemical reactions in crystalline solids have been the subject of numerous studies since the 1830s when phenomenological descriptions of the mechanical and optical changes of single crystals exposed to sunlight were first documented in the literature.[1–3] At a later time, it became possible to carry out a detailed structural characterization of the reaction products, which, with the development of single crystal X-ray diffraction, led to the formulation[4] and subsequent confirmation[5] of the topochemical postulate. Based on least-motion and packing-induced pre-organization arguments, the topochemical postulate states that reactions in crystals occur with a minimum amount of atomic and molecular motion. Mechanistic studies in the second half of the 20th century[6] focused on structure–reactivity correlations based on single crystal X-ray diffraction and product analysis. These investigations led to valuable insights into the distances and orientations required between prospective reactive centers in the $[2\pi + 2\pi]$ dimerization of alkenes,[5] the γ-hydrogen abstraction of excited carbonyls,[7] the selectivity for cyclization *versus* cleavage of 1,4-biradicals,[8] and conformational specificity of 1,2-shifts in arylalkyl carbene reactions,[9–11] to mention just a few. Mechanistic information in reactions that occur by kinetically stabilized radical pairs could be obtained in a few cases by taking advantage of *in situ* EPR analysis of suitable single crystalline precursors.[12] However, detailed mechanistic studies based on the direct observation of excited states and short-lived transient species have been a serious challenge due to complications associated with the high optical density and anisotropic optics of crystalline solids.[13,14] In optically dense crystals, not only is the penetration of light restricted to just a few microns, but also their orientation-dependent refractive index

(birefringence) and extinction coefficient (dichroism) convolute data analysis.[13] This is combined with the scattering caused by defects, roughness, or small particle sizes, to make the quantitative analysis of absorbed or transmitted light extremely difficult. While some of these limitations can be circumvented with the use of diffuse-reflectance methods with powdered samples,[15,16] complications arise from undesirable biphotonic processes, such as triplet–triplet annihilation, that occur as a result of the high laser power needed in those experiments. Notably, these complications are further exacerbated in the case of long-lived excited states that are capable of delocalizing through the crystal by exciton delocalization mechanisms.[17] Until recently, the simplest way to determine the absolute rates of excited state reactions in the solid state was by taking advantage of changes in emission yields and lifetimes caused by competing chemical decay pathways, which we developed and implemented for the study of hydrogen atom transfer by quantum mechanical tunneling.[18–21]

Knowing that transmission UV–Vis spectroscopy of molecular nanocrystals suspended in water provides a simple means to

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assess aggregation states in terms of simple spectral shifts,[22–26] we assumed that they may also be ideal for the study of reaction kinetics in the solid state. With this in mind, we set out to investigate the triplet state of benzophenone as a test system.[27] We have previously shown that nanocrystalline suspensions of organic solids allow for multi-gram photochemical reactions,[28,29] and that optically dense suspensions can be used to determine the absolute quantum yield of reactions by chemical actinometry. In the case of benzophenone, nanocrystalline suspensions can be readily obtained by the reprecipitation method. These benzophenone nanoparticles are ca. 200–700 nm in size, as detected by dynamic light scattering (DLS) and atomic force microscopy (AFM). *In situ* circular dichroism (CD) and *ex situ* X-ray powder diffraction (XPD) of centrifuged crystals showed that the benzophenone nanoparticles have the same morphology as the bulk crystals grown from solution.

From a photophysical perspective, one of the simplest and most important indications that the nanocrystalline benzophenone retains most of the properties of its macroscopic counterpart came from the room temperature detection of its phosphorescence and its insensitivity to added oxygen. Pump–probe detection of the well-characterized triplet–triplet absorption (T_1–T_n) at $\lambda = 510$ nm using 100 fs pulses at $\lambda_{exc} = 270$ nm revealed that the rate of intersystem crossing from the excited singlet to the triplet state is shorter (2×10^{11} s^{-1}) in the nanocrystals than in the homogeneous solution (0.8–1.25×10^{11} s^{-1})[30] or in large single crystals (3.6×10^{10} s^{-1}).[31,32] Similarly, nanosecond transient kinetics determined with a Nd:YAG laser ($\lambda = 355$ nm, <10 ns) were insensitive to O_2 and decayed mono-exponentially with a rather short triplet lifetime of $\tau_{dec(NC)} = 2.0$ μs. Given that the triplet lifetime of benzophenone in dilute glasses at 77 K is ca. 8 ms,[33] and that the triplet lifetime in bulk crystals and powders is best described as a complex multiexponential with components that last up to several milliseconds,[34] a lifetime of only 2 μs was both surprising and unexpected. Indeed, a lifetime that is over three orders of magnitude shorter in the nanocrystals, relative to dilute glasses, coupled with a lowered quantum yield of phosphorescence of ca. $\Phi \approx 0.001$ strongly suggests an efficient quenching mechanism.[27]

In this paper, we report a series of nanosecond pump–probe experiments aimed at determining the importance of quenching effects at the surfaces of nanocrystalline benzophenone. Triplet lifetime measurements were carried out with cationic and anionic surfactants, without surfactants, as a function of solvent deuteration (H_2O and D_2O), and as a function of added oxygen. After finding no effects under any of the above conditions, we decided to test the effects of anionic quenchers (I^-, Br^-, and N_3^-) in the form of Stern–Volmer experiments with surfactant-free nanocrystalline suspensions. Due to the significant correlation between quenching rates in solution and in nanocrystals, it was concluded that the triplet excitation is accessible to quenchers at the surface. Our results also suggest that the concentration of oxygen near the surface of the nanocrystals is much lower than the concentration in the bulk solvent.

EXPERIMENTAL

Nanocrystalline suspensions

Samples for laser flash photolysis experiments and DLS studies were prepared by injecting 5 μl of a benzophenone (0.4 M) solution in acetone into 3 ml of vortexing water (Millipore). The resulting suspension (7.0×10^{-4} M) was sonicated three times at room temperature for 4 min, allowing for 2 min rest between runs. Suspensions produced in this manner have a suitable absorbance of ca. 0.5 at 355 nm, with an average particle size of 400 nm, as determined by DLS and confirmed by scanning electron microscopy (SEM). The optical density of the resulting suspensions can be adjusted using serial dilutions with Millipore water in a similar manner as that used with solution samples. Suspensions made in the presence of surfactant, either CTAB (cetyl trimethylammonium bromide) or SDS (sodium dodecyl sulfate), were prepared at 1/20th of the critical micelle concentration (cmc) level to avoid the formation of micelles.[35,36] Suspensions were generally purged for 15 min with argon, air, or oxygen, as required by the specific experiment.

Time resolved absorption

These measurements were performed by using a transmission nanosecond laser flash photolysis setup described previously.[37] Briefly, measurements were obtained by excitation of oxygen-, air-, or argon purged solutions at 355 nm using a frequency tripled Quanta Ray DCR-2 Nd:YAG laser (3–20 mJ/pulse). Transient absorption decay was monitored using a probe beam from a Hanovia 100-W xenon lamp passed through a Jarrell-Ash 82-410 monochromator (250 μm slits) and detected using a Hamamatsu R928 photomultiplier tube (PMT). Data output from the PMT was collected using a LeCroy 9350 oscilloscope coupled to a Macintosh G4 computer using Labview software. Kinetic curves were averaged over 30–70 laser pulses. Decay traces were curve fitted using Igor Pro 3.1 software.

Quenching experiments

Nanosecond laser flash photolysis at 355 nm of benzophenone suspensions (3 ml) was conducted in argon-saturated suspensions. To minimize changes in ground-state absorption, a small volume (1 μl) of the inorganic salt (KI, NaI, NaBr, NaN$_3$) in Millipore water (typically 0.1–1 M) was added to the suspension, which was then mixed thoroughly. The $T_1 \rightarrow T_n$ Stern–Volmer quenching data were recorded at 515 nm for an average of 120 laser shots for all suspensions. The resulting Stern–Volmer quenching plots were determined in triplicate.

Dynamic light scattering (DLS)

The DLS measurements were conducted using a Beckman-Coulter N4 Plus particle analyzer with a 10 mW helium–neon laser at 632.8 nm. The particle size was determined using a detector angle of 90° and it was calculated using the size distribution processor (SDP) analysis package provided by the manufacturer. A reasonable match was obtained by SEM.

Scanning electron microscopy (SEM)

Benzophenone nanocrystals obtained by the reprecipitation protocol were analyzed by SEM to verify their size, shape, and formation of crystal faces. SEM studies were performed with a JEOL JSM-6700F field-emission scanning electron microscope. To prepare the SEM sample, a dilute benzophenone suspension (4×10^{-4} M) was drop-cast onto a freshly cleaned silicon wafer and allowed to dry in a desiccator. Both isolated crystals and aggregates consisting of 2–10 crystals were observed. Figure 1
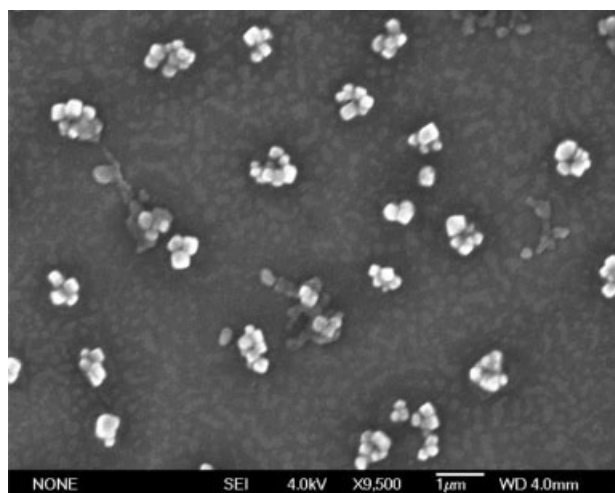
Figure 1. Scanning electron microscopy (SEM) image of benzophenone nanocrystals prepared by the reprecipitation method and deposited onto a silicon substrate. The faceted and highly symmetric crystalline particles are ca. 200–500 nm in size

shows benzophenone nanocrystals with sizes ranging between ca. 200 and 500 nm, in general agreement with the DLS results from the fluid suspension. The particles are clearly faceted and crystalline.

RESULTS AND DISCUSSION

The triplet–triplet absorption spectrum of benzophenone nanocrystals in the presence of CTAB at sub-micellar concentrations was essentially identical to that reported previously by Khin *et al.* with a band that extends from ca. 400–600 nm and a λ_{max} at ca. 520 nm (Fig. 2).[27]

The triplet decay occurs with a single exponential rate constant of $k_{dec} = 5 \times 10^5 \, s^{-1}$, which corresponds to the reported triplet lifetime $\tau_T = 1/k_{dec} = 2.0 \, \mu s$. A representative kinetic trace is illustrated in Fig. 3. We established that signal intensities are approximately linear with benzophenone nanocrystal loading values that range from 1.0×10^{-4} to
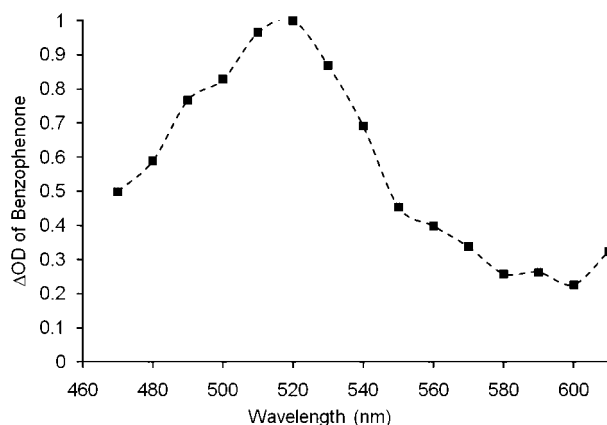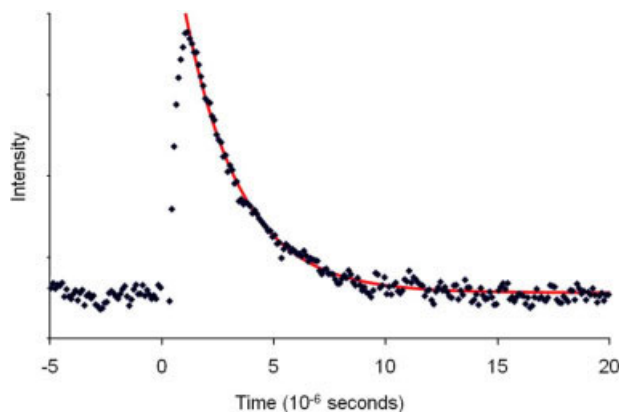

Figure 3. Kinetic trace of the T_1–T_n absorption signal of nanocrystalline benzophenone obtained by excitation with 10 ns pulses of an Nd:YAG laser at $\lambda = 355$ nm and detected at 510 nm. The line represents a single exponential fit with a lifetime of 2 μs.

8.0×10^{-4} M, and that the triplet lifetime is concentration independent within this range. As indicated in Fig. 4, these loading values correspond to ground state absorbances at 355 nm that vary from 0.075 to 0.4. Lower loading values produced signals that are too weak for analysis and higher loadings resulted in suspensions that were too turbid for transmission measurements. Based on these results, most of the experiments were carried out with samples prepared with a benzophenone loading of ca. 4.0×10^{-4} M, and ground state absorbance at 355 nm of ca. 0.3 (Fig. 4).

As a starting point to explore potential quenching effects at the surface of the nanocrystals, a series of measurements varying oxygen concentration, surfactant, and solvent were conducted, as indicated in Table 1. Considering that the short lifetime of nanocrystalline benzophenone could be explained by bromide ion quenching in experiments carried out in the presence of submicellar CTAB, we first explored the effects of other surfactants. As shown in Table 2, nanocrystals prepared in the presence of anionic sodium dodecyl sulfate showed no
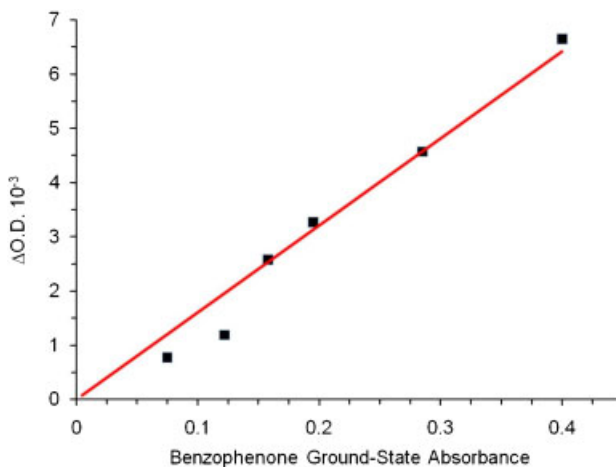

Figure 2. T_1–T_n absorption spectrum of nanocrystalline benzophenone obtained by excitation with 10 ns pulses of an Nd:YAG laser at $\lambda = 355$ nm

Figure 4. Intensity of the T_1–T_n absorption signal obtained as a function of benzophenone loading with absorbance values varying between 0.075 and 0.4.

Table 1. Triplet–triplet lifetime of benzophenone nanocrystals measured under different experimental conditions

Conditions		Lifetimes ($\pm$0.1) (μs)
Surfactant	CTAB	1.9
	SDS	2.0
	None	2.0
Oxygen content	O_2 Purge	1.9
	Air Purge	2.0
	Argon Purge	2.0
Solvent	H_2O	2.0
	D_2O	2.0

significant effect on the triplet lifetime as compared to those prepared in CTAB. We also discovered that we could make stable nanocrystalline suspensions with no surfactant at all. After showing that the triplet lifetime remains unaltered with the surfactant-free samples, all other experiments were performed with nanocrystals without surfactant. In a subsequent set of experiments, and in agreement with our previous study,[27] the triplet lifetime is not affected by equilibration with air or oxygen. However, the signals of dissolved benzophenone obtained in benzene solutions submitted to analogous treatment were completely quenched. Measurements carried out with argon-saturated samples did not extend the lifetime and measurements carried out with air-equilibrated suspensions showed no changes when prepared in H_2O or D_2O.

Having shown that the triplet lifetime is insensitive to the nature of the surfactant, dissolved oxygen content, or solvent deuteration, we investigated the possible role of multiphotonic quenching mechanisms. It is well known that long-lived triplets are susceptible to intensity-dependent triplet–triplet annihilation that occurs when two delocalized excitations, diffusing by energy transfer, converge into neighboring molecules and interact to form one molecule in the ground state and the other one in the singlet excited state.[38] Experiments carried out with laser power values ranging between 0.2 and 5.9 mJ confirmed a linear dependence on laser power, suggesting that only single excitations occur within this intensity range.[27]

Table 2. Rate constants for bimolecular quenching (k_q) of benzophenone by selected anions in acetonitrile–water solutions and in benzophenone nanocrystals suspended in water

Quencher	H_2O–MeCN	Nanocrystals–H_2O
KI	3.5×10^9	7.4×10^9
NaN$_3$	1.3×10^9	7.0×10^9
NaBr	5.0×10^7	4.8×10^7
H-OH	4.9×10^6	n.a.[a]

[a] The extent of quenching by hydroxide anion in neutral water with $[OH^-] = 10^{-7}$ M should be unimportant.

Quenching with anions

Triplet benzophenone is quenched by triplet oxygen in solution, according to spin statistics, at about a third of the bimolecular diffusion rate, i.e., $k_q \approx 3 \times 10^9\,M^{-1}\,s^{-1}$.[39] Since the concentration of O_2 in oxygen-saturated water at 25°C is $[O_2] = 1.27 \times 10^{-2}$ M[40] and the lifetime of benzophenone in solution is ca. 5 μs,[41] the Stern–Volmer equation

$$I_o/I = \tau_o/\tau = 1 + k_q\,\tau[O_2]$$

predicts a decrease of the original triplet intensity and lifetime of ca. 200-fold, which explains why there is no observable signal when measurements are carried out in oxygen-saturated solutions. We suggest that the lack of quenching by dissolved oxygen in the nanocrystalline specimens may be the result of a low concentration of oxygen at the surface of the nanocrystals. Interfacial quenching experiments reported in the literature have shown that water and surface geometry can inhibit oxygen quenching of excited state benzophenone.[42–44] As we also became interested in exploring the loci of excitation in the nanocrystals, we decided to explore the use of a few well-known, water soluble, anionic quenchers, which could be used in much higher concentrations than oxygen itself. Systematic quenching experiments might shed light on the location of the triplet excitation: whether trapped within the interior of the nanocrystals, or available to interact with quenchers at the surface.

Based on literature studies in aqueous acetonitrile,[45] the effects of added iodide, bromide, and azide anions were analyzed. The anions are known to quench benzophenone by an electron transfer mechanism with rates that vary by a factor of 70, from near diffusion-controlled $k_q = 3.5 \times 10^9\,M^{-1}\,s^{-1}$, in the case of I^-, to $5.0 \times 10^7\,M^{-1}\,s^{-1}$, in the case of Br^- (Table 2).[46] A representative Stern–Volmer plot constructed with the results of quenching experiments carried out with suspended nanocrystals by the addition of the 2–15 μM iodide is illustrated in Fig. 5. Analogous results with N_3^- and Br^- required somewhat greater concentrations, as expected from their smaller bimolecular quenching rate constants.

As illustrated in Fig. 5, changes in the ratio of the rate constants with and without quencher (k_q/k_0) are linear, clearly indicating a
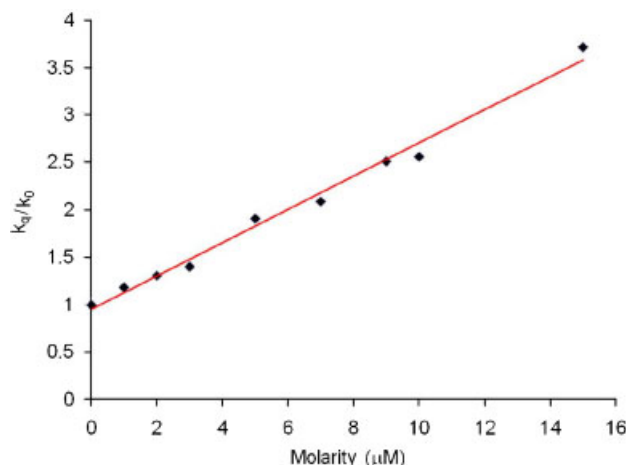
Figure 5. Stern–Volmer plot of the $T_1–T_n$ absorption signal intensity as a function of KI.

dynamic quenching mechanism mediated by diffusion of the quencher to the nanocrystalline surface, and not a static interaction between the quencher and the benzophenone surface. From the slope of the Stern–Volmer plots and the value of the triplet lifetime in the absence of quencher (2 μs), we can determine the quenching constant. In the case of iodide, k_q $(I^-) = 7.4 \times 10^9\,M^{-1}\,s^{-1}$, a value that is slightly greater than that previously reported in solution.[45] Quenching by azide anion produced very similar results, with a rate constant for nanocrystals of $k_q(N_3^-) = 7.0 \times 10^9\,M^{-1}\,s^{-1}$ that is also greater than the value reported in aqueous acetonitrile (Table 2). Also listed in Table 2, the results with bromide gave a rate constant $k_q(Br^-) = 4.8 \times 10^7\,M^{-1}\,s^{-1}$ that is essentially the same as that reported in solution. The cationic counterion had no effect on the quenching rate as indicated by KI and NaI having identical quenching constants. This would further support an anionic quenching mechanism similar to the solution counterpart. It is worth noting that the rate constant for benzophenone quenching by hydroxide ion has also been measured, $k_q(HO^-) = 4.9 \times 10^6\,M^{-1}\,s^{-1}$, an order of magnitude smaller than that of Br^-. This value suggests that triplet quenching by hydroxide should be unimportant at neutral pH, with the hydroxide concentration being $[OH^-] = 10^{-7}\,M$.

CONCLUSIONS

The results summarized in Table 2 clearly show that electronic excitation in the nanocrystals is available to surface quenchers. Our results are consistent with classic literature reports on the extent of triplet delocalization in crystalline benzophenone,[47] which indicate that as many as ca. 10^7 molecules may become excited by energy hoping within the lifetime of the excited state triplet. Assuming a cubic crystal of ca. 300 nm per side, a molecular volume of 0.177 nm³ for benzophenone,[48] and a packing density of 0.7 for the crystal,[49] one can estimate that there are ca. 10^8 molecules per nanocrystal, suggesting that the excitation may be delocalized through the entire nanocrystalline specimen, which may act as a large supramolecular entity. The discrepancy between the triplet lifetimes of benzophenone as a bulk solid and as nanocrystals remains unaccountable. Having eliminated the surfactants as quenchers and knowing that water should not play a significant role in shortening the triplet lifetime, we tentatively conclude that nanocrystals may be susceptible to self-quenching interactions between neighboring molecules in the lattice. Given that Wolf *et al.*[50] and Schuster *et al.*[51] have studied the self-quenching of several aryl substituted benzophenones in solution, experiments are now in progress in our group with several crystalline 4,4′-disubstituted benzophenones with electron-donating and electron-withdrawing substituents to test our hypothesis.

Acknowledgements

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