

## SUPPLEMENTARY INFORMATION

# Pump-Probe Spectroscopy and Circular Dichroism of Nanocrystalline Benzophenone – Towards Absolute Kinetic Measurements in Solid State Photochemical Reactions

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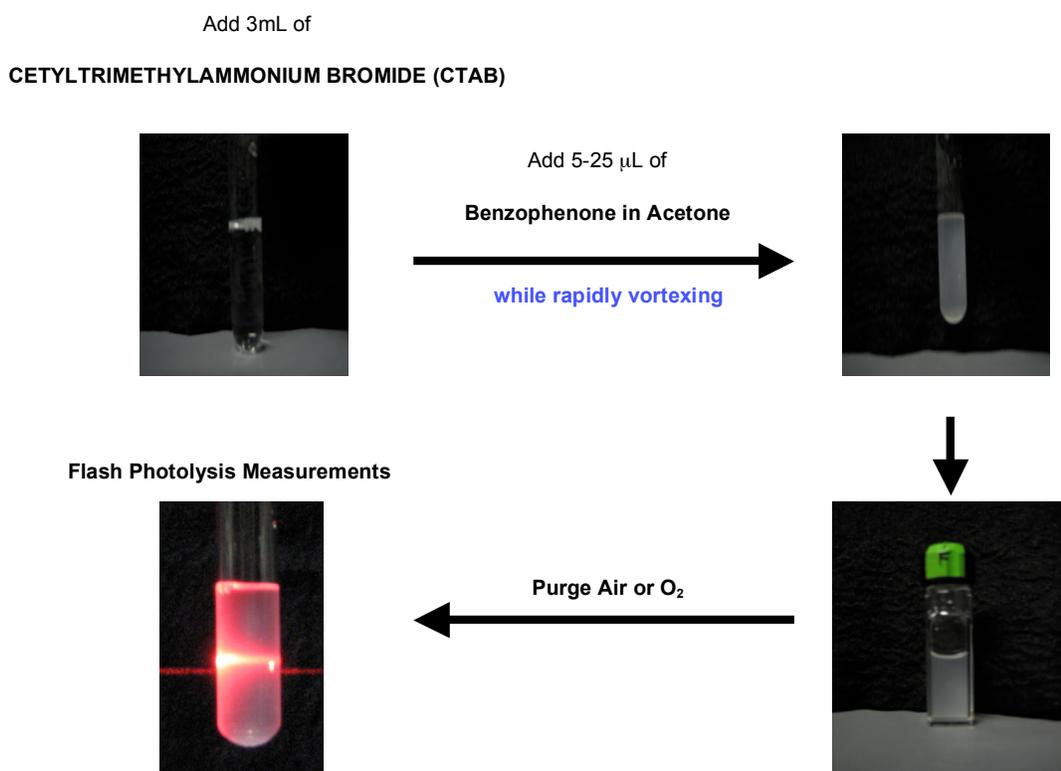
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### Experimental Section

**Materials.** Benzophenone (purity 99%) and cetyltrimethylammonium bromide (CTAB) were purchased from Aldrich Chemical Company. Acetone (spectrophotometric grade) and Methanol (Omnisolv spectrophotometric grade) were obtained from EMI. Doubly distilled water was obtained using a Super-Q Millipore water system. All chemicals were used as received except for benzophenone, which was recrystallized from acetone and from methanol prior to use.

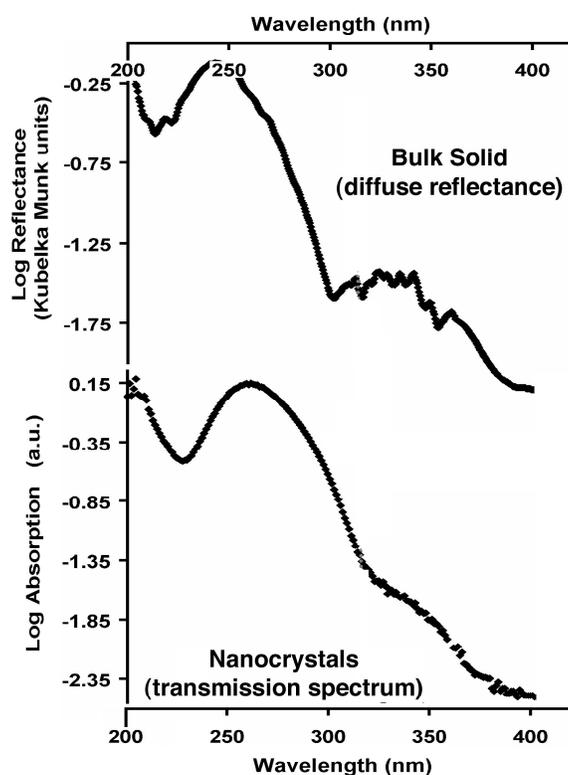
**Preparation of Benzophenone Suspensions.** 5-25  $\mu\text{L}$  of an 80 mM solution of benzophenone in acetone was added to a rapidly vortexing 0.04 mM solution of CTAB in water. The suspension was purged with air or oxygen for 30 minutes at room temperature in order to eliminate any residual acetone and to quench any triplet states in solution (Scheme S1).

### Scheme S1



**Measurements.** Measurements were taken using four sided transparent quartz cuvettes. There was negligible change in the solution after purging and was verified by noting no change in absorption spectrum.

*UV-Vis Absorption Spectra* were obtained using Hewlett-Packard 8453 and Beckman DU-650 spectrophotometers. The  $n,\pi^*$  transition of nanocrystalline benzophenone measured by transmission matches well the spectrum of bulk samples obtained by diffuse reflectance with an onset at ca. 380 nm and a  $\lambda_{\text{max}}$  of 345 nm (Figure S1). The  $\pi,\pi^*$  transition nanocrystalline benzophenone is red shifted with respect to that in the bulk by ca. 15 nm from 245 nm to 260 nm.



**Figure S1.** UV Absorption spectra of benzophenone in the bulk solid (top) and in a nanocrystalline suspension (bottom). [NOTE. Features in the  $n,\pi^*$  region of the diffuse reflectance spectrum are not reproducible and we consider them an artifact].

### *Phosphorescence Spectra*

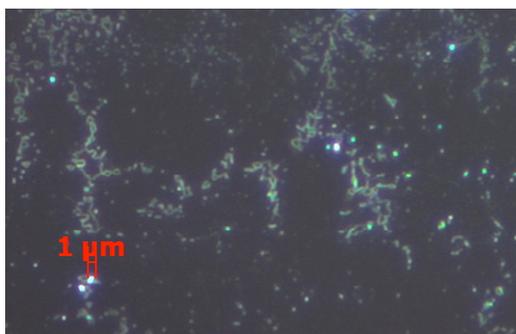
*Triplet Lifetime Measurements* were collected using a frequency tripled (355 nm) Nd:YAG laser, pulse width < 10 ns as the excitation source, illuminating the sample in a front face arrangement. The emission was collected using a Princeton instruments PI-MAX ICCD coupled to a 0.3 m monochromator fitted with a 300 grooves/mm grating. The excitation pulse and the ICCD were synchronized using a BNC model 500 pulse generator. Integrating the area under each spectrum and plotting vs. time generated the decay curves.

*Time Resolved Absorption* measurements were performed by using a transmission nanosecond laser flash photolysis setup described previously.<sup>1</sup> Briefly, measurements were obtained by excitation of oxygen or air 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  $\mu\text{m}$  slits) and detected using a Hamamatsu R928 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.

The femtosecond transient absorption apparatus consists of a kilohertz pulsed laser source and a pump-probe optical setup. The laser pulse train was provided by a Ti:Sapphire regenerative amplifier (Clark-MXR, Model CPA-1000) pumped by a diode-pumped CW solid-state laser (Spectra Physics, Model Millennia V). The typical laser pulse was 100 fs at 790 nm, with a pulse energy of 0.9 mJ at a repetition rate of 1 kHz. Most of the laser energy (80%) was used to pump an optical parametric amplifier (IR-OPA, Clark-MXR). The excitation pulse was sent through a computer-controlled optical delay line. The remaining laser output (20%) was focused into a 1.2 cm rotating quartz plate to generate a white light continuum. The continuum beam was further split into two identical parts and used as the probe and reference beams, respectively. The probe and reference signals were focused onto two separated optical fiber bundles coupled to a spectrograph (Acton Research, Model SP275). The spectra were acquired on a dual diode array detector (Princeton Instruments, Model DPDA-1024). The kinetics of So-T<sub>n</sub> intersystem crossing were measured in acetonitrile solution, in CTAB micelles and in nanocrystalline suspensions. The transient spectrum obtained by detection at different wavelengths had an excellent match with the T<sub>1</sub>-T<sub>n</sub> transient spectrum detected in the microsecond regime.

Femtosecond measurements were carried out in Arizona State University with the help and advise of Prof. Ana Moore.

*Polarized optical microscopy* revealed that the largest crystallites are about 1-2  $\mu\text{m}$  in size with most of the sample being in the submicron range (Figure S2..



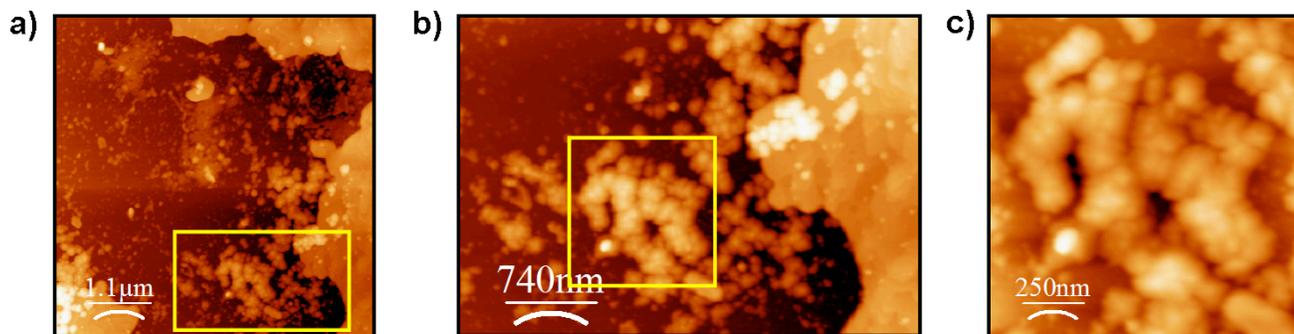
**Figure S2.** Optical microscope image obtained under cross polarizers of a sample of nanocrystalline benzophenone drop cast on a glass surface.

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(1) Arbogast, J. W.; Foote, C. S. *J. Am. Chem. Soc.* **1991**, *113*, 8886-8889.

*Dynamic light scattering (DLS)* was conducted using a Beckman-Coulter N4 Plus particle analyzer with a 10 mW helium-neon laser at 632.8nm. The particle size was determined using a detector angle of 90 degrees and was calculated using the SDP analysis package provided by the manufacturer. An average particle size of 200 nm with a standard deviation of  $\pm 30$  nm was obtained in five independent measurements at room temperature.

*Atomic force microscopy (AFM)* studies were performed in tapping mode with a Multi-Mode Nanoscope IIIa Veeco Instruments using rotated monolithic silicon probes with a tip radius reported as less than 10 nm (BS-Tap 300, Budget Sensors, Sophia, Bulgaria). Images acquired over several magnifications revealed nanocrystals of the approximate same size indicated by DLS either isolated or aggregated (Figure S3).



**Figure S3.** Atomic Force Microscopy images of a benzophenone nanocrystalline suspension deposited on a clean glass substrate by drop casting and slow evaporation of water showing different magnification scales: a) 1100 nm b) 740 nm c) 250 nm. The nanocrystalline suspensions showed a large tendency for the nanocrystals to agglomerate into larger aggregates upon evaporation of water on the glass substrate. Highlighted regions demonstrate crystals sizes consistent with dynamic light scattering experiments, *ca.* 200±30 nm.

**Time resolved control experiments.** Time resolved transient absorption experiments were conducted on samples with no benzophenone to show that the transient species observed is due solely to benzophenone and not to constituents of the crystalline suspension system. Laser excitation (355 nm) of air saturated solutions of CTAB-H<sub>2</sub>O and CTAB-H<sub>2</sub>O containing acetone showed no transient.

**Decay traces under air and under oxygen.** The transient absorption of crystalline suspensions of benzophenone were measured in both air saturated and oxygen saturated conditions to demonstrate that the triplet-triplet absorption originates within the nanocrystals and not in solubilized benzophenone. Studies conducted under identical experimental conditions with benzophenone dissolved in benzene showed nearly complete transient quenching under air saturated conditions and no detectable transient absorption in oxygen saturated conditions.

In another control experiment, the triplet-triplet absorption of an oxygen-saturated suspension was quenched by dissolving the nanocrystals with a small amount of methanol. This experiment was carried out by detection at 620 nm where there is no significant absorption by the benzophenone ketyl radical that forms by hydrogen abstraction from the solvent. This experiment further demonstrates that the triplet-triplet absorption observed by flash photolysis studies originates from the suspended nanocrystalline particles.

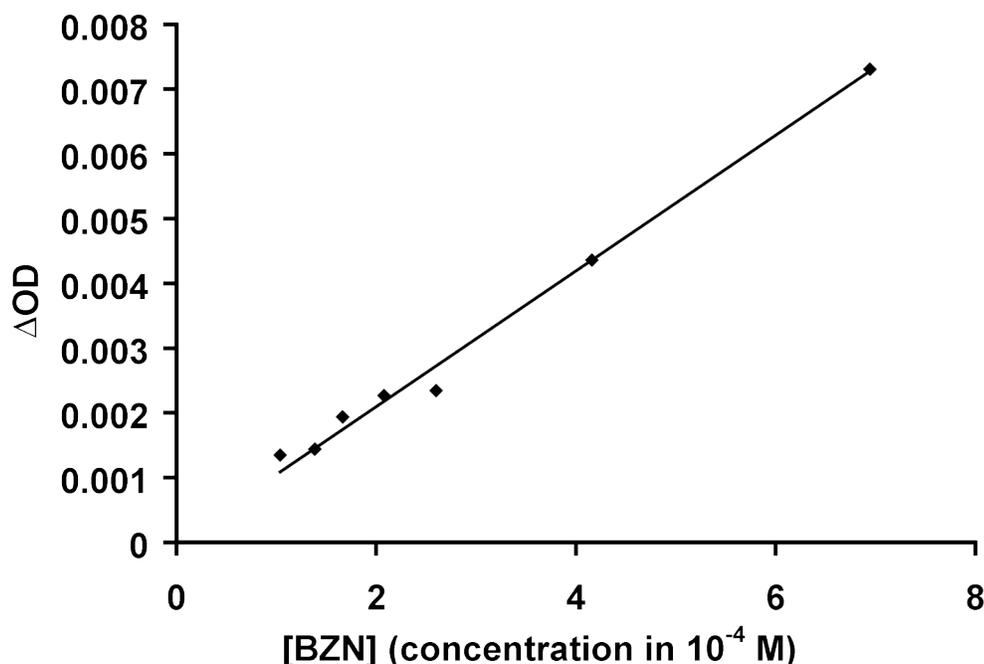
**Triplet-Triplet absorption spectrum of a nanocrystalline benzophenone suspension.** The triplet-triplet absorption spectrum recorded under air saturated conditions shows similar spectral features as the triplet-triplet absorption spectrum of a benzophenone single crystal reported by Willsher, *et al.*<sup>2</sup> and benzophenone adsorbed on a MCM-41 surface reported by Kazani, *et al.*<sup>3</sup> using

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<sup>2</sup> Willsher, C.J.; Wilkinson, *Chem. Phys. Lett.* **1984**, *104*, 272-276

diffuse reflectance laser flash photolysis. A large absorption maximum is centered at 520 nm and smaller absorption maxima are found at 320 nm and 650 nm. The decay traces measured at each observed wavelength (300 nm-700 nm) show similar kinetics and lifetimes.

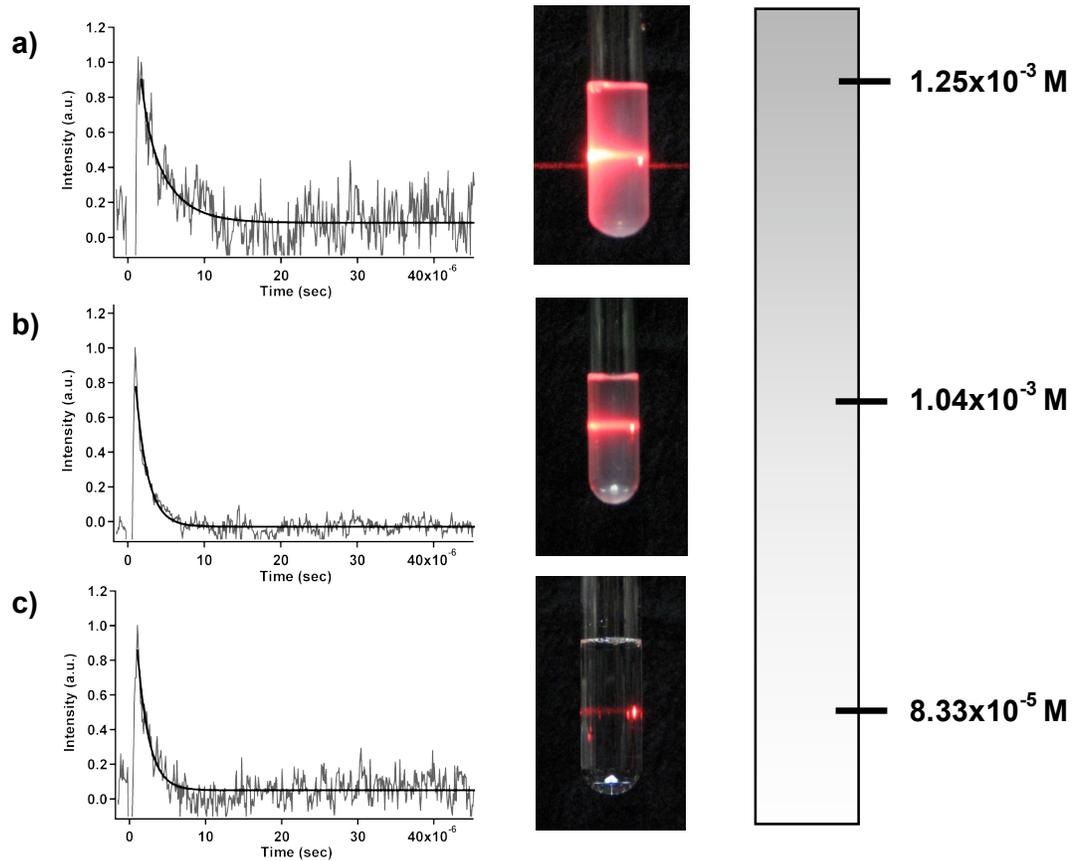
**Concentration effects of benzophenone in a nanocrystalline suspension.** The initial intensity of the transient absorption was measured with different loadings of benzophenone (Figure S4) prepared by serial dilution. At very low loadings, the intensity of the transient absorption is low due to the small amount of benzophenone. At increasing amounts of benzophenone there is steady increase in transient absorption. Samples with benzophenone loadings much higher than  $10^{-5}$  M became opaque and gave a diminished signal. This is reflected in the signal-to-noise ratio (Figure S5).



**Figure S4.** Initial intensity of transient absorption at different loading amounts of benzophenone in a nanocrystalline suspension.

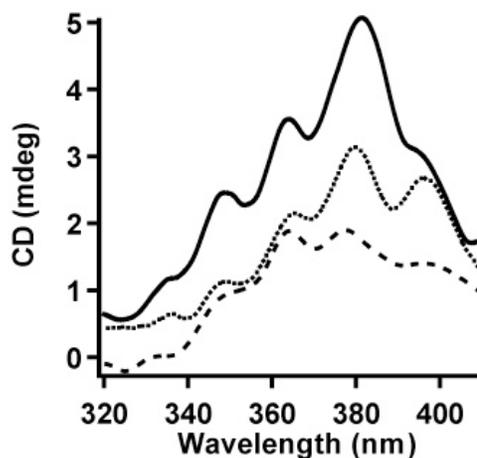
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<sup>3</sup> Kazanis, S.; Azarabi, A.; Johnston, L. J. *J. Phys. Chem.* **1991**, *95*, 4430-4435.



**Figure S5.** Initial intensity of transient absorption at different loading amounts of benzophenone in a crystalline suspension. a) high loading of benzophenone resulting a translucent suspension of crystalline benzophenone. b) medium loading of benzophenone. c) low loading of benzophenone.

**Circular Dichroism spectra of benzophenone nanocrystals in suspension and in nujol mull.** The circular dichroism (CD) spectrum of a benzophenone was obtained by taking 10-15 mg of a single crystal and grinding it to a fine powder with a pestle and mortar, followed by addition of nujol to make a fine paste over a quartz plate. The solid-state CD spectrum of benzophenone (Figure S6) prepared from a randomly selected single crystal from a commercial source (Aldrich) showed a positive CD, indicating that benzophenone in that crystal existed in its P,P configuration. Similar results were observed from Nujol mulls prepared with benzophenone nanocrystals filtered from the suspensions and from analogous measurements using suspended nanocrystals.



**Figure S6.** Circular dichroism spectra of benzophenone as a nujol mull of a single crystal (solid line), nujol mull of suspension crystals (dotted line), and in CTAB-H<sub>2</sub>O suspension (dashed line).