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Quantum Chain Amplification in Nanocrystalline Dewar Benzenes by Intramolecular Sensitization

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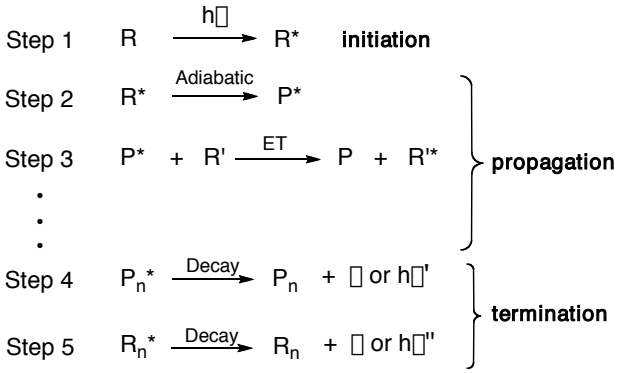
Quantum chain reactions are characterized by the formation of several photoproducts per photon absorbed ($\Phi_{QC} > 1$) and constitute a promising signal amplification mechanism. The triplet-sensitized isomerization of Dewar benzene is known to undergo quantum chain reactions characterized by an adiabatic valence-bond isomerization to the excited state of Hückel benzene, which is able to transfer its triplet energy to a new ground state Dewar benzene that reacts to continue the chain. Given that diffusion-mediated energy transfer is the chain-limiting event in solution, we demonstrate here that reactions in crystals are significantly more efficient by taking advantage of energy transfer by a presumed exciton delocalization mechanism. Using Dewar benzenes with covalently attached, high energy triplet sensitizers we have demonstrated the efficiency of the solid state by the amplification of a quantum yield of ca. $\Phi_{QC} \approx 76$ in acetonitrile solution to as much as ca. $\Phi_{QC} \approx 100–120$ in submicron size specimens prepared by the re-precipitation method, and up to ca. $\Phi_{QC} \approx 300$ with microcrystalline powders suspended in water.

Introduction

Most organic photochemical processes involve the excitation of a single molecule followed by return to the ground state by releasing heat, emitting a single photon, transferring its energy to another molecule, or undergoing a reaction to give a primary photoproduct.[1] Exceptions from this norm include nonlinear photochemical processes involving a non-identical number of photochemical events and photons absorbed. Such systems can be utilized for signal amplification devices, catalysis, and solar cells.[2-5] Examples include coherent and stepwise two photon absorption,[6,7] fusion of two or more low energy photons to generate one high-energy excited state by triplet-triplet annihilation, [8] and the fission of a single excitation generated with a high-energy photon that results in two excited states, each with half the energy of the original.[9,10] An equally interesting, but significantly less explored process, occurs when a single photon leads to many chemical events in a "quantum chain reaction".[11] Quantum chain reactions start by formation of an excited state (Step 1, Scheme 1) and are followed by a relatively uncommon propagation step involving an adiabatic photochemical reaction where the photoproduct is formed in the excited state (Step 2, Scheme 1).[12-15] This is followed by energy transfer to a new ground-state reactant that prolongs the chain (Step 3, Scheme 1). Chain termination occurs when either the excited-state product (P*) or reactant (R*) undergo thermal or radiative decay (Step 4 and/or Step 5, Scheme 1).

Scheme 1. Initiation, propagation and termination steps of a quantum chain reaction.



Despite the promise offered by chemical systems leading to multiple events per photon absorbed, quantum chain reactions are limited both by the small number of adiabatic reactions known at this time and the lack of convenient strategies to optimize the energy transfer step.[16-32] In this regard, singlet state quantum chains are severely limited by the short lifetimes of the excited photoproducts, which make energy transfer by diffusion-mediated mechanisms unfavourable. In fact, adiabatic reactions that take place in the singlet state are commonly established by detecting the fluorescence[33,34] or transient absorption of the excited photoproduct, rather than by observation of a quantum yield of product formation that is greater than one, which is the key signature of a quantum chain. We recently proposed that an effective way to circumvent this limitation is by carrying out quantum chain reactions in crystalline solids,[35,36] where energy transfer can occur by an ultrafast exciton delocalization mechanism.[37-41] We showed

[a] *Address here.*
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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

that the adiabatic decarbonylation of diphenylcyclopropenone to diphenyl acetylene could not enter a quantum chain process in solution despite having an adiabatic quantum yield $\Phi_{AR} = 1$ because there is no time for diffusion-mediated energy transfer within the ca. 8 ps lifetime of the excited photoproduct.[35,36,42] By contrast, quantum chain reactions with quantum yields up to $\Phi_{QC} = 3.3$ could be measured in aqueous nanocrystalline suspensions of diphenylcyclopropenone,[35,36] where energy transfer is mediated by a rapid exciton delocalization mechanism.[42] Efficient quantum chains ($\Phi_{QC} >> 1$) require adiabatic reactions with high quantum efficiencies ($\Phi_{AR} \approx 1$) and are limited by the number of energy transfer steps, n, as shown in Equations 1–3,[36]

$$\Phi_{QC} = (\Phi_{AR})^1 + (\Phi_{AR})^2 + (\Phi_{AR})^3 + ... \ (\Phi_{AR})^n \quad (1)$$

$$\Phi_{AR} = k_{AR} / [k_{AR} + k_{R\text{-}dec}] \quad (2)$$

$$n = k_{ET} / k_{P\text{-}dec} \quad (3)$$

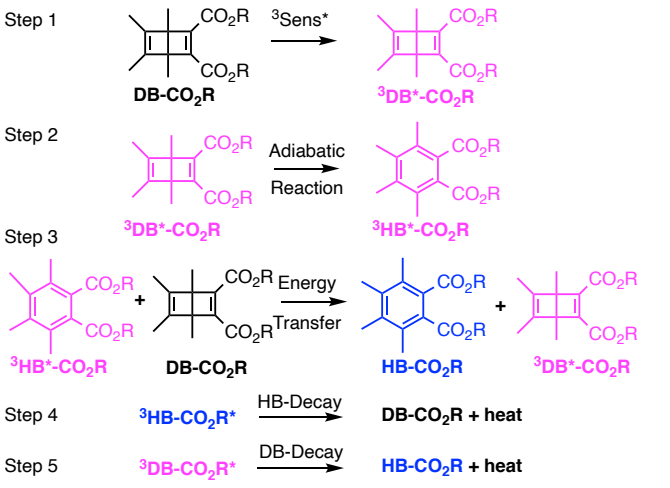
It should be noted that efficient adiabatic reactions ($\Phi_{AR} \approx 1$) require reaction rates that are much greater than that of the decay of the excited reactant by all other pathways ($k_{AR} >> k_{R\text{-}dec}$). The maximum value n in equation 1 is determined by the relative rates of energy transfer from the excited photoproduct (k_{ET}) in relation to its rate of decay ($k_{P\text{-}dec}$).[36]

Based on the above analysis, one may expect that triplet quantum chain reactions carried out in crystalline solids have the potential of reaching very high Φ_{QC} values by taking advantage of energy transfer by triplet exciton hopping, which is known to approach the picosecond time scale.[37-41,43] Assuming ideal adiabatic reactions with $\Phi_{AR} \approx 1$, the theoretical limit for a triplet quantum chain is given by the value of n in Eq. 1, as defined in Eq. 3. Based on a general approximation, one may expect $n = k_{ET}/k_{P\text{-}dec}$ to take values as large as 10^9 if triplet excitons were to have jumping rates of ca. $k_{ET} \approx 10^{12}$ s^{-1} and triplet lifetimes (τ_T) were to extend into the millisecond time scales ($\tau_T = 1/k_{dec} \approx 10^{-3}$ s).

As a first test of this hypothesis, we explore here the quantum chain reaction of crystalline Dewar benzene to Hückel benzene. Early studies by Turro[44] established a concentration-dependent quantum chain reaction that reaches a limiting experimental value of ca. $\Phi_{QC} = 0.5$ but extrapolates to $\Phi_{QC} \approx 10$ at infinite Dewar benzene concentration. It was shown that triplet energy sensitizers with $E_T > 63$ kcal/mol are required for efficient energy transfer, indicating an experimental upper limit for the triplet excitation energy of Dewar benzene.[44] More recently, using a Dewar benzene 3,4,5,6-tetramethyl-1,2-diester derivative (**DB-CO_2Me**, Scheme 2), Kiau et al. reported quantum yields as high as $\Phi_{QC} = 120$ in ethyl acetate,[45] and Ferrar et al. showed the feasibility of quantum chain reactions in polymer matrices upon the addition of external sensitizers and co-sensitizers.[46]

A key requirement to carry out a triplet state quantum chain reaction in the crystalline state is to have efficient access to the triplet excited state of the Dewar benzene reactant (**^{3}DB*-CO_2R**). A simple solution to this problem is to substitute the dicarboxymethyl groups in **DB-CO_2Me** for 4-hydroxy-benzophenones in **DB-CO_2BPh** so that triplet sensitization can occur intramolecularly. It is well known that electronic excitation of the benzophenone chromophore leads to intersystem crossing and efficient formation of the triplet n,π* excited state within a few picoseconds. Thus, the original excited state is localized on the benzophenone part of the bichromophoric compound (**DB-CO_2-^{3}BPh***, not shown in Scheme 2) and is followed by intramolecular energy transfer to the covalently attached Dewar benzene moiety **^{3}DB*-CO_2BPh**, which initiates the quantum chain (Step 1). An adiabatic triplet state reaction forms the triplet excited state of the Hückel benzene photoproduct, **^{3}HB*-CO_2BPh** Step 2, which acts as the quantum chain carrier. In Step 3, the triplet photoproduct **^{3}HB*-CO_2BPh** should be well suited in crystals to transfer energy to a neighboring ground-state Dewar benzene **DB-CO_2BPh** to propagate the chain. While chain termination is expected to occur via steps 4 or 5 when either excited state decays back to the ground state manifold, step 5 is accounted for in the quantum yield of the adiabatic reaction, so that the chain length given by the value of n depends on the relative rates of step 3 and 4. As described below, we were able to demonstrate a concentration-dependent quantum chain in solution with modest values ranging from ca. $\Phi_{QC} \approx 2.5$–76 for reactant concentrations ranging from 5–50 mM. By contrast, quantum chain reactions carried out with samples prepared by the re-precipitation method led to average quantum chain values of ca. $\Phi_{QC} \approx 100$, even though the samples were shown to be semi-crystalline. Notably, a qualitative comparison of the latter with microcrystalline powders suspended in water showed an increase in quantum chain values up to ca. $\Phi_{QC} \approx 300$. Evidence for a fast adiabatic reaction was obtained by nanosecond laser flash photolysis experiments showing that a long-lived transient generated from the starting Dewar benzene **DB-CO_2BPh** is identical to the one generated from the Hückel benzene isomer, which corresponds to the chain carrier **^{3}HB*-CO_2BPh**.

Scheme 2. Steps for the triplet sensitized quantum chain reaction of Dewar benzenes.



Experimental Section

Synthesis and Characterization of Dewar Benzenes. Samples of Dewar benzene derivatives used in this study were prepared by conventional synthetic procedures that are described in the Supplementary Information section.

Laser Flash Photolysis Detection of the Quantum Chain Carrier. Nanosecond laser flash photolysis experiments with **DB-CO_2BPh** and **HB-CO_2BPh** were carried out using a Brilliant B Quantel Nd:YAG laser operating at 355 nm with a pulse width of ca. 8 ns as the excitation source. Samples were introduced to a mounted 1 cm quartz flow cell through a continuous one-pass flow system to ensure that only unreacted material was continuously sampled. Samples were sparged with Argon for at least an hour prior to flowing into the flow cell and remained continuously sparged for the entire experiment. The characteristic triplet-triplet absorption of the benzophenone sensitizer was determined by measuring the triplet absorption and lifetime of 4-acetoxybenzopheone (**4-AcOBPh**).

Quantum Chain Reaction in Solution. The quantum yields of product formation from **DB-CO_2BPh** ($\Phi_{HB\text{-}OBPh}$) were determined using the photodecarbonylation of dicumyl ketone (**DCK**) as a chemical actinometer.[49] The selection of **DCK** was based on its known quantum yield in solution and in the solid state,[49] with the latter measured in nanocrystalline suspensions.[50] Thus, photochemical excitation of **DCK** in benzene solution at λ = 312 nm leads to the consumption of starting material with a quantum yield of $\Phi_{DCK\ (soln)}$ = 0.41 ± 0.04. Similarly, photochemical reactions in the crystalline state using optically dense nanocrystalline suspensions proceed with the exclusive formation of dicumene (**DC**) with a quantum yield of $\Phi_{DC\ (Cryst)}$ = 0.20 ± 0.02.[49]

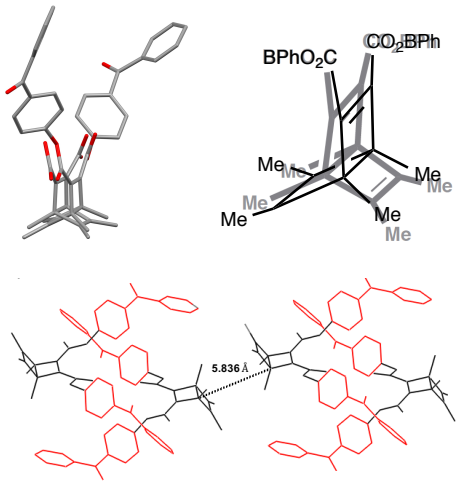


Fig. 1. (Upper left) Capped stick representation of the X-ray molecular structure of **DB-CO_2BPh** illustrating the disorder of the Dewar benzene group and, (upper right) line structure illustrating its two orientations. (Bottom) Packing view illustrating the interdigitated benzophenone arrangement between pairs of molecules, and the closest distance between neighbouring Dewar benzenes, which may be related to the distance for energy transfer.

Results and Discussion

Samples of **DB-CO_2BPh** proved to be crystalline after purification. Melting with concomitant reaction to the valence-bond isomerized product **HB-CO_2BPh** was shown to occur at ca. 109 °C. Diffraction data from cubic prisms obtained by slow evaporation from diethyl ether were solved in the space group $P2_1/n$ with 4 molecules per unit cell. Molecules of **DB-CO_2BPh** crystallize with the Dewar benzene fragments disordered over two positions, alternating their concave and convex faces with occupancies of 64% and 36%. The disorder extends to the carboxylate groups, which connect to the corresponding benzophenones in a manner that they themselves are not disordered, as illustrated in Figure 1.

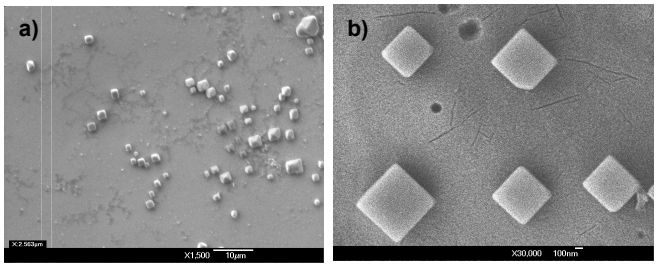


Fig. 2. SEM images of **DB-CO_2BPh** ca. 1 μm size crystals obtained from a dried suspension on a Si surface. Scale bars of a) 10 micron and b) 100 nm are shown.

Nanocrystalline Suspensions. Knowing that the determination of an efficient quantum chain must be established by measuring the quantum yield of reaction, which is given by the number of product molecules formed per photon absorbed, we had to verify that samples of **DB-CO_2BPh** are able to form nanocrystalline suspensions. It is well known that spectroscopic methods based on measurements of the transmission of light in bulk solids are extremely challenging due to the high optical density, scattering, birefringence, and dichroism that characterize single crystals and polycrystalline samples. These effects also make it difficult to measure the number of photons absorbed by the sample, which is essential for quantum yield measurements. We have previously shown that crystals with sizes that are equal or smaller than the wavelength of light are able to mitigate these optical challenges,[40,41,49,51] making it possible to measure transmission spectra, and to determine quantum yields with particle loadings that are high enough to trap every photon emitted from a calibrated light source. It is now well established that many compounds are able to form aqueous nanocrystalline suspensions of well-defined crystals with average dimensions on the order of 50–500 nm, depending on the specific sample and experimental parameters. In our case, concentrated MeCN solutions of **DB-CO_2BPh** were slowly added to a rapidly stirring solution of cetyl trimethyl ammonium bromide (CTAB) at concentrations that are 1/50th of the critical micelle concentration (CMC) in millipore water. Size determination by dynamic light scattering (DLS, SI page S14) and scanning electron microscopy revealed prismatic crystals in the range ca. 200 nm to ca. 1 μm in size (Figure 2).

Product Analysis in Solution and in Powder Samples. Dilute (ca. 0.1 M) degassed acetonitrile solutions of **DB-CO_2H** and **DB-CO_2BPh** exposed to UV light with $\lambda \geq 295$ nm resulted in full conversion to the corresponding Hückel benzenes **HB-CO_2H** and **HB-CO_2BPh** as the only product. Similar results were observed with dry powders placed between two glass slides, indicating that the reaction can proceed as a solid-to-solid transformation. Reactions of **DB-CO_2BPh** carried out in solution in the presence of oxygen lead to the formation of a new product consistent with the formation of an endoperoxide by reaction of the Dewar benzene with singlet oxygen. As expected, reactions carried out with **DB-CO_2BPh** powders and nanocrystalline suspensions were not affected by the presence of oxygen. Samples of **HB-CO_2BPh** could be crystallized and were shown to melt at 142 °C, higher than the melting point of the **DB-CO_2BPh** reactant (ca. 109 °C). This suggests the possibility of a solid-to-solid reaction. However, powder X-ray diffraction analysis of samples of **DB-CO_2BPh** before and after reaction revealed that the reaction proceeds by amorphization, rather than a potential single-crystal to single-crystal transformation, or a more common solid-to-solid reaction by a reconstructive phase transition. Unfortunately, we were not able to get diffraction-quality single crystals of the Hückel benzene photoproduct **HB-CO_2BPh**.

Spectroscopic Characterization. Included in Figure 3 is a comparison of the UV spectra of the sensitizer-linked Dewar benzene **DB-CO_2BPh** along with those of samples containing equimolar Dewar benzene methyl ester **DB-CO_2Me**, two equivalents of **4-AcOBPh** that was used as a model chromophore, and a 2:1 mixture of **4-AcOBPh** and **DB-CO_2Me**. A relatively weak interaction of the two proximal benzophenone esters and the Dewar benzene can be inferred by noting that the UV spectrum of **DB-CO_2BPh** is more intense and slightly broader than the spectrum obtained when the two independent chromophores are mixed in the same molar ratio (Figure 3). From this absorption spectra a ground-state energy value of ca. 59 kcal/mol can be calculated for **DB-CO_2BPh**. We determined the triplet energy of the benzophenone sensitizer by measuring the phosphorescence spectrum of Hückel benzene **HB-CO_2BPh** in dilute 2-methyltetrahydrofuran glass at 77 K (Figure 4). A characteristic emission with vibrational resolution and a relatively short (4.8 ms) lifetime typical of an n,π* excited state was obtained, along with a triplet energy of ca. 65 kcal/mol estimated from the onset of the 0-0 vibrational band.

As shown by the green dashed line in Figure 5, triplet **4-AcOBPh** has the characteristic triplet benzophenone absorption with a λ_{max} = 520 nm. Freeze-pump-thawed samples revealed a lifetime of 14.6 μs in dilute MeCN solution (SI, page S19). The spectrum obtained from solutions of **DB-CO_2BPh** was significantly different with broad absorption bands at ca. 480 and 520 nm. The spectrum of **DB-CO_2BPh** can be quenched with oxygen.

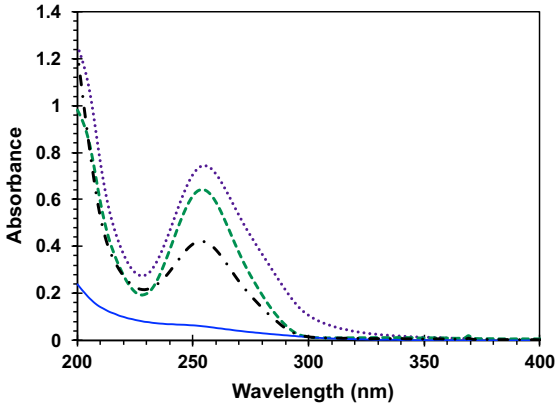


Fig. 3. UV Absorption spectra in MeCN of 2.08×10^{-5} M **DB-CO_2Me** (blue), 4.16×10^{-5} M **4-AcOBPh** (green), 1.65×10^{-5} M **DB-CO_2BPh** (purple), and a solution with 1:2 molar ratio of the **DB-CO_2Me** and **4-AcOBPh** (black).

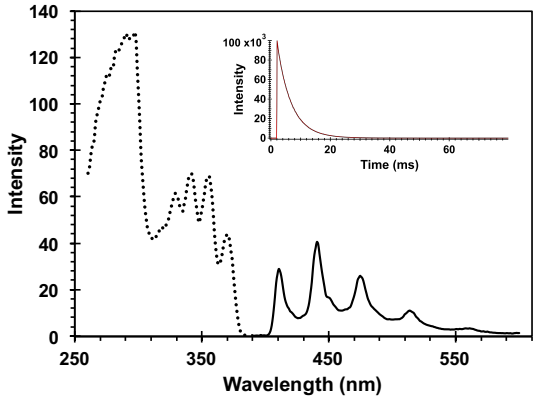


Fig. 4. Phosphorescence excitation (dashed line) and emission (solid line) spectra of **HB-CO_2BPh** in a 2-methyltetrahydrofuran glass at 77 K. The excitation spectrum was detected at 441 nm and the emission obtained by excitation at 343 nm. The phosphorescence decay shown in the inset occurs with a time constant of 4.8 ms.

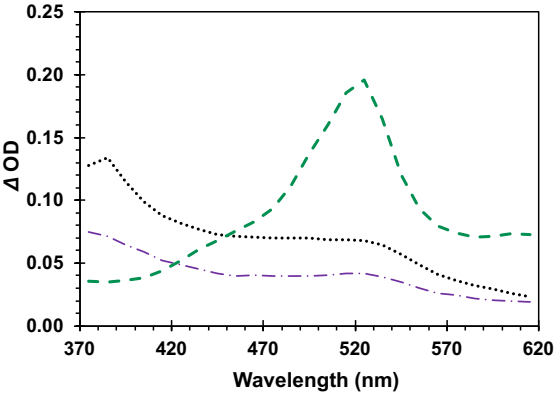


Fig. 5. Transient absorption spectra of 5 mM **4-AcOBPh** (green), 0.76 mM Dewar benzene **DB-CO_2BPh** (purple), and 1.5 mM Hückel benzene **HB-CO_2BPh** (black) acquired immediately after the laser pulse in Ar saturated MeCN.

Subsequent experiments carried out with Hückel benzene **HB-CO_2BPh** showed that the same transient is formed within the 8

ns pulse, suggesting the spectrum obtained upon irradiation of **DB-CO_2BPh** is indeed the triplet state **^{3}HB*-CO_2BPh** formed adiabatically from the originally sensitized **^{3}DB*-CO_2BPh**, in agreement with steps 1 and 2 in Scheme 2.

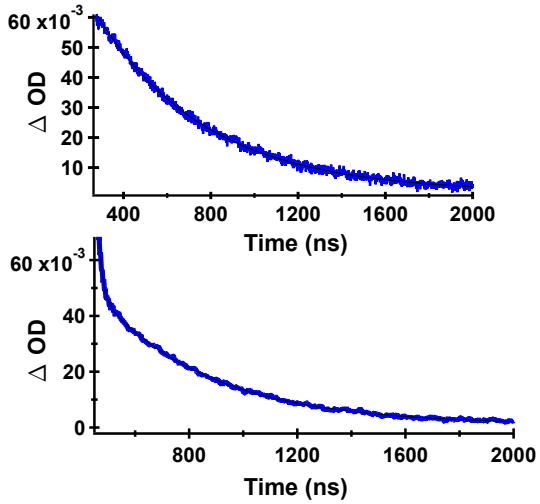


Fig. 6. Decay curves of **DB-CO_2BPh** in Ar-saturated MeCN detected at 385 nm (Top) and at 530 nm (Bottom). Data points are shown in blue and the corresponding fit with a black line. The decay data obtained from **HB-CO_2BPh** were essentially identical, indicating that they arise from the same species (Table 1).

Decays measured at 380–420 nm for **DB-CO_2BPh** showed clean monoexponential decay (top of Figure 6) with a lifetime of 503 ns (Table 1). Interestingly, absorption decays for the same sample measured at 530 nm revealed a double exponential with a short-lived component of ca. 16 ns that accounts for only 2% of the decay, and a majority (98%) long-lived component of 420 ns. As indicated in Table 1, the decay kinetics obtained from samples of **HB-CO_2BPh** were very similar. We tentatively assign the short-lived component at 530 nm as originating from a residual fraction of the originally excited benzophenone-localized triplet states, in the process of transferring their triplet energy to the corresponding Dewar or Hückel benzene chromophore, with the former undergoing a fast adiabatic reaction to form the observed triplet Hückel benzene. A monoexponential behavior at the shorter wavelength is consistent with having no significant absorption from the benzophenone chromophore at 385 nm, suggesting that it corresponds to the benzophenone-linked triplet benzene.

The importance of the intramolecular benzophenone sensitizer for the formation of the triplet state chain carrier was also demonstrated with samples of the Dewar benzene methyl ester **DB-CO_2Me**, which failed to produce an observable triplet transient on its own, as expected for a fast non-adiabatic singlet-

Table 1. Transient Lifetimes and Pre-exponential Factors of **DB-CO_2BPh** and **HB-CO_2BPh** in Ar-saturated MeCN.

Compound (λ_{det})[1]	A_1	τ_1 (%w$_1$)[2,3]	A_2	τ_2 (%w$_2$)[2,3]	χ^2 (10^4)
DB-CO_2BPh (530 nm)	0.024	16.2 (2%)	0.046	420 (98%)	5.7
DB-CO_2BPh (385 nm)	-	-	0.058	503	2.2
HB-CO_2BPh (530 nm)	0.022	14.5 (2%)	0.14	419 (98%)	11.5
HB-CO_2BPh (385 nm)	-	-	1	465	6.5

[1]Detection wavelength in parentheses. [2]Percentage weighted contribution of component "*i*" is given by $\%w_i = 100\ [(A_i\tau_i) / (A_1\tau_1 + A_2\tau_2)]$. [3]Lifetimes in nanoseconds

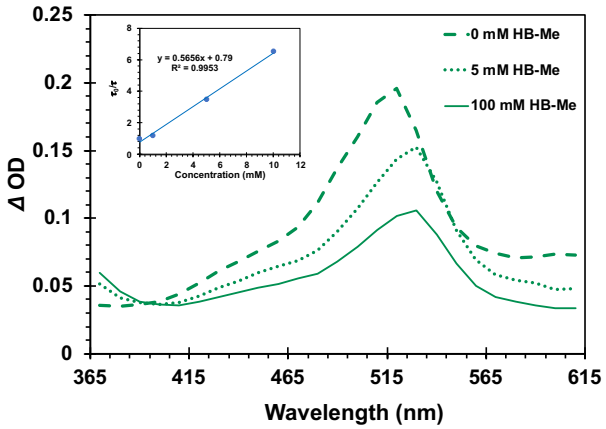
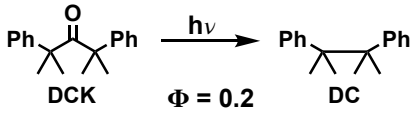


Fig. 7. Evolution of the transient absorption of **4-AcOBPh** as a function of added Hückel benzene **HB-CO_2Me**. Inset: Stern-Volmer plot built with the lifetime of triplet **4-AcOBPh** in the presence of increasing concentrations of **HB-CO_2Me**. A bimolecular rate constant $k_q = 6.3 \times 10^7\ M^{-1}s^{-1}$ can be estimated from this analysis.

state reaction and a low triplet yield that results from inefficient intersystem crossing. However, the spectroscopic signature of the suggested chain carrier was obtained using the ground-state Hückel benzene methyl ester **HB-CO_2Me** as a quencher of triplet **4-AcOBPh**. As shown in Figure 7, the spectrum of **^{3}4-AcOBPh*** (E_T ~ 60 kcal/mol) evolved into that of **^{3}HB*-CO_2Me** as the concentration of the ground-state Hückel benzene increased from 0 mM (Figure 7, dashed green line) to 100 mM (solid green line). The relatively intense signal of **^{3}4-AcOBPh*** with a maximum at ca. 520 nm was replaced by a red-shifted weaker signal with $\lambda_{max} \approx 530$ nm accompanied by an increase of the absorption intensity at 365 nm. Stern-Volmer analysis using changes in the decay rate as a function of increasing quencher concentration (Figure 7, inset) revealed a bimolecular quenching rate constant of $k_q = 6.3 \times 10^7\ M^{-1}s^{-1}$, which is about two orders of magnitude slower than diffusion control.[48]

Scheme 3. Photodecarbonylation of **DCK** in nanocrystalline suspension.



Quantum Chain Reaction in Solution. Knowing that the efficiency of a quantum chain reaction in solution depends on the efficiency of a concentration-dependent energy transfer step, one should expect the observed quantum yield to increase as a function of reactant concentration. With that in mind, we carried out quantum yield determinations with **DB-CO_2BPh** concentrations varying from ca. 3–50 mM in MeCN. Optically dense, deoxygenated samples of the Dewar benzene and the actinometer **DCK** (Scheme 3) were irradiated in parallel at 312 nm in 5 mL Pyrex tubes to assure that all photons entering each sample were absorbed and all samples were similarly exposed to the light source. The moles of product (N) formed from the sample and the actinometer were calculated with internal standards using ^{1}H NMR.

The following equation was utilized to calculate quantum yields,

$$\Phi_{QC} = \frac{A_{DB\text{-}CO2BPh}}{A_{DCK}} \cdot \frac{N_{HB\text{-}CO2BPh}}{N_{DCK}} \cdot \frac{\eta_{MeCN}}{\eta_{Benz}} \cdot \Phi_{DCK}$$

where $A_{DB\text{-}CO2BPh}$ refers to the absorbance of **DB-CO_2BPh**, A_{DCK} is the absorbance of **DCK**, $N_{HB\text{-}CO2BPh}$ are the number of moles of isomerized product **HB-CO_2BPh**, N_{DCK} is the number of moles of reacted **DCK**, and η_{MeCN} and $\eta_{Benzene}$ are the refractive indices of MeCN and benzene, respectively. Experiments were run up to five times over different reaction times with conversion values ranging from ca. 14% to 75%. Figure 8 displays the quantum yield of formation of **HB-CO_2BPh** photoproduct as a function of the initial concentration of **DB-CO_2BPh**, varying from 5 mM to 50 mM. An initial value of $\Phi_{HB\text{-}CO2BPh}$ = 2.5 ± 0.2 with 5 mM of Dewar benzene increased up to $\Phi_{HB\text{-}CO2BPh}$ = 76 ± 3.5 with a reactant concentration of 50 mM.

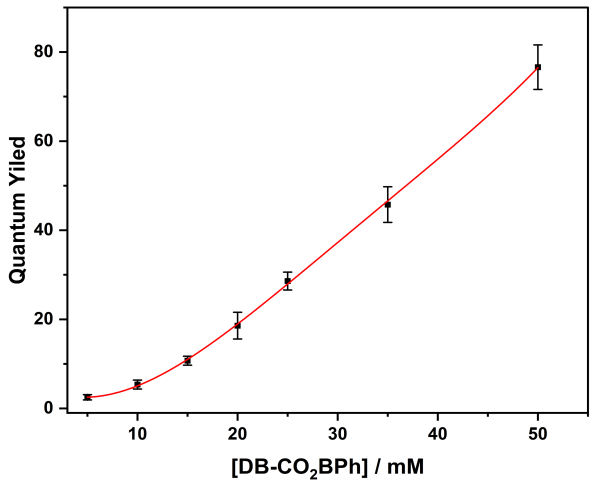


Fig. 8. Quantum yield values of **DB-CO_2BPh** at 5, 10, 15, 20, 25, 35, 50 mM in MeCN solution .

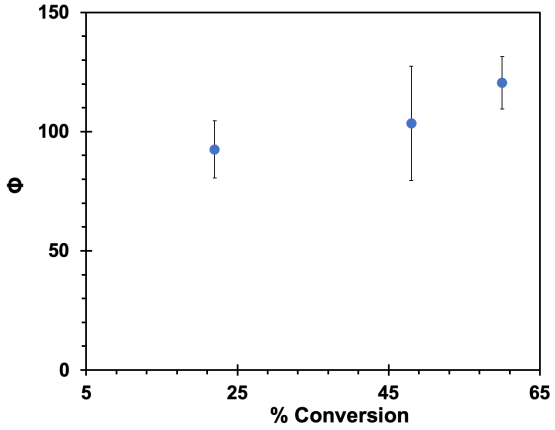


Fig. 9. Quantum yields of formation of **HB-CO_2BPh** in the solid state using suspensions prepared by the re-precipitation method.

Quantum Chain Reaction in Nanocrystalline Suspensions. Aqueous nanocrystalline suspensions of **DB-CO_2BPh** and **DCK** were generated by the re-precipitation method.[50] Sample loadings were adjusted to generate optically dense suspensions of **DB-CO_2BPh** and **DCK** that were optically matched, as indicated by a UV-Vis immersion probe. Suspensions were irradiated in 3 mL Pyrex tubes at 312 nm. Initial experiments revealed complete conversion of **DB-CO_2BPh** at the shortest irradiation time of 10 seconds. A modified setup required suspensions of **DB-CO_2BPh** and **DCK** to be irradiated with the former placed behind a 5 x 5 cm neutral density filter with a 1% transmission at 312 nm, so that the photon dose reaching the Dewar benzene was 100 times weaker (images of the setup can be found in page S25 of the Supporting Information). The results shown in Figure 9 reveal that quantum yields of product formation in the suspension sample have values that range from ca. $\Phi_{HB\text{-}CO2BPh}$ = 90–120, as the extent of reaction increases from 22% to 60% conversion. An increase in the observed quantum yield as a function of accumulated product suggests that the **HB-CO_2BPh** product may be a better absorber and potentially a more effective sensitizer. Alternatively, it is also possible that the efficiency of the solid-state adiabatic reaction is improved once the crystals of the reactant are perturbed by the presence of the photoproduct.

While the large reactivity and high quantum yields observed in Figure 9 support the expectation of an efficient quantum chain reaction, quantum yields on the order of 90–120 are far from the optimum if we assume a radiative triplet-state lifetime on the order of a few milliseconds (Figure 4, inset) with a fast adiabatic reaction, and exciton hopping in the picosecond time scale. If an adiabatic reaction in the nanosecond time scale were the limiting factor, one should expect chain lengths as high as 10^6, given by the number of reactions that can occur within a few milliseconds. Notably, all our attempts towards the optical detection of the proposed chain carrier **^{3}HB*-CO_2BPh** in the solid state led to no signal detection under conditions where nanocrystals of **4-AcOBPh**, used as a model compound, gave a strong signal with a relatively short 1.2 μs lifetime (SI, gage S18). The lack of an observable transient suggests that all 90 to 100

reactions in the chain take place within the ca. 8 ns laser pulse, indicating that a quenching event must be the chain-limiting factor. In fact, we have previously shown that crystalline benzophenones are susceptible of efficient self-quenching by a reductive charge transfer mechanism.[51] It was shown that nanocrystalline 4,4'-diamino-benzophenone, with strong electron donating aromatic rings ($\sigma+ = -1.3$), has a triplet lifetime of only ca. 6.2 ps at 298 K. On the other end, electron poor 4,4'-benzophenone dicarboxylic acid ($\sigma+ = 0.42$) has a triplet lifetime of ca. 97 μs, which is seven orders of magnitude greater. Self-quenching by the neighboring benzophenones in **HB-CO_2BPh** is also evident in solution by comparing the lifetimes of freeze-pump-thawed samples of the former with those of **4-AcOBPh.** A lifetime of 14.6 μs (SI, page S19) obtained for the isolated ketone at 298K in acetonitrile is reduced to 1.9 μs for the bichromophoric compound (SI, page S20). This suggests that self-quenching also accounts for the 1.2 μs lifetime of nanocrystalline **4-AcOBPh**, which has a $\sigma+ = -0.19$ and fits well in the previously published Hammet plot with a reaction constant $\rho = -2.85$.[51]

An alternative explanation based on the quality of the sample was explored by X-ray powder diffraction analysis of centrifuged and dried suspension samples of **DB-CO_2BPh**. The results revealed a largely amorphous powder, suggesting that the main sample population in suspension is not crystalline, even though one is able to find crystalline specimens by scanning electron microscopy (Figure 2). To determine whether the use of a higher quality, more crystalline sample can have a greater effect on the quantum chain, we carried out experiments to compare the extent of reaction between polycrystalline powders suspended in surfactant-containing water, and the nanocrystalline suspensions generated by the re-precipitation method. While aggregate sizes are different, and microcrystals are prone to multiple excitations and triple-triplet annihilation, we reasoned that a greater conversion in suspended polycrystalline powders would qualitatively confirm a greater efficiency for an exciton-mediated quantum chain amplification. Thus, suspended polycrystalline powder samples were prepared by dispensing about 10 mg of **DB-CO_2BPh** into 3 mL of a vortexing submiceller CTAB solution; nanocrystalline suspensions generated by the re-precipitation method could be obtained with loading values up to ca. 2 mg in 3 mL of submiceller CTAB. While stirring, the two sample types were irradiated using an immersion 302-nm pen lamp. Analyzing the total amount of product generated under such similar conditions revealed that ground crystals suspended in water have quantum yields of $\Phi_{QC} \approx 300$, indicating reactivity that is ca. 3–4 times greater than that of the mainly amorphous sample obtained by the re-precipitation method. This result qualitatively confirms that exciton-mediated energy transfer in the crystalline phase has the potential of increasing the quantum amplification in the triplet-sensitized reaction of Dewar benzenes.

Conclusions

Taking advantage of a crystalline tetramethyl Dewar benzene diester with 4-hydroxybenzophenone groups acting as intramolecular triplet sensitizers, we were able to show that triplet quantum chain reactions in the crystalline state display quantum yields of product formation in the range of $\Phi_{QC} = 100–300$, which are greater than those measured as a function of concentration in acetonitrile solution ($\Phi_{QC} = 5–76$), but significantly smaller than those expected based on assumed fast adiabatic reactions, efficient energy transfer, and long triplet lifetimes. The adiabatic and triplet state nature of the valence-bond isomerization reaction was confirmed in solution by taking advantage of laser flash photolysis, where the same transient was observed from both the Dewar and the Hückel benzene isomers. The lack of an observable transient in the solid state was interpreted in terms of a quantum chain that occurs within the ca. 8 ns laser pulse, suggesting a quenching mechanism as a limiting factor for the solid state quantum chain. Another contributing factor for the lower than expected quantum chain was unveiled when we showed that samples obtained by re-precipitation are formed as semicrystalline aggregates with coexisting amorphous and crystalline phases. With work in progress, we are addressing the roles of excited-state quenching and crystallinity to find conditions where exciton-mediated reactions can produce quantum chain reactions with values that extend into the thousands or millions of reactions per photon.

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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