Mapping photochemical cycles over femtosecond to millisecond timescales using transient absorption spectroscopy

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Introduction

Photochemical reactions are initiated by the absorption of ultraviolet (UV) or visible light, and they have many important applications in chemical and materials sciences. Topical examples include the use of photoredox catalysis in both organic synthesis and the controlled growth of polymers.[1,2] The light-induced chemistry often follows a complicated sequence of reaction steps, each involving short-lived reactive intermediates such as free radicals or electronically excited molecules. The chemistry spans many timescales, from the ultrafast (femtosecond to picosecond) excited-state dynamics of the molecular chromophores responsible for the light absorption to the nanosecond and microsecond diffusive reactions of the reactive intermediates. Using the LIFEtime facility, we have been able to map the multi-step reaction sequences of a range of photochemical reactions in solution by time-resolved infra-red (TRIR) spectroscopy,[3-5] identifying the transient intermediates through their IR spectral signatures, and quantifying the kinetics of each reaction step. The outcomes allow direct observation of the mechanisms of complex reaction cycles and provide unprecedented insights.

Our recent work with LIFEtime has focused on two classes of reactions. One is organic radical chemistry controlled by photoredox catalysis,[6,7] and the other is radical reaction cycles initiated by homolytic photochemical cleavage of C-I bonds.[8] Progress with unravelling the complex chemistry of these two reaction types is summarized here. The mechanistic understanding that has emerged should lead to improved designs of photoredox catalysts, and better harnessing of light-activated radical reactions in organic synthesis of polymers, pharmaceuticals, and other fine chemicals.

Section 1: Photoredox catalytic cycles

Figure 1 shows a generalized photoredox catalysed reaction cycle in which a photoredox catalyst (PC) is excited by absorption of UV light and initiates a sequence of radical reactions by dissociative electron transfer to an organobromide. The initial photon absorption is to a singlet excited state $PC^*(S_n)$ connected to the ground state $PC(S_0)$ by an electric-dipole allowed transition (typically a strong $\pi^* \leftarrow \pi$ excitation). Ultrafast internal conversion populates the lowest excited singlet state (S_1) on timescales shorter than a few picoseconds. Relaxation pathways of the $PC^*(S_1)$ population include fluorescence, intersystem crossing (ISC) to the manifold of triplet spin states (leading to T_1 following further relaxation), non-radiative pathways back to the ground state via conical intersections, and intermolecular electron transfer with an electron acceptor (RX in Figure 1). The rates of these pathways, and hence the branching between them, depend on both the structure of the PC and its interactions with the surrounding solvent.

The S_1 and T_1 states of the photocatalyst may have locally excited (LE) or charge-transfer (CT) electronic orbital character,

depending on the choice of chromophore and the structural modifications to attached groups. The LE or CT character has consequences for the energies of the excited S_1 and T_1 states, the sensitivity of these energies to solvent polarity, and the rates of bimolecular electron transfer. Hence design of the PCs for optimum performance requires a detailed understanding of the effects of the PC structure and electronic properties on the kinetics and mechanisms of each step in the photoredox catalytic cycle. We have therefore examined a variety of PC designs, as shown in Figure 2, and conducted experiments in solvents of different polarity (N,N-dimethylformamide, dichloromethane, and toluene).
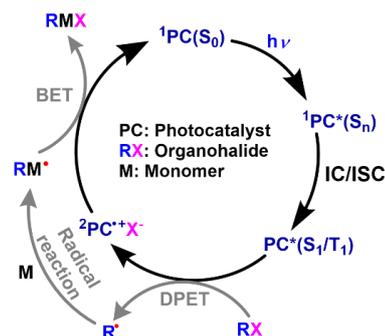

Figure 1: Schematic representation of a photoredox catalyzed reaction cycle. PC is an organic photocatalyst, which undergoes dissociative photoinduced electron transfer (DPET) from its S_1 or T_1 electronically excited states, making a radical cation $PC^{\cdot+}$. The electron acceptor is an organohalide RX, which dissociates upon electron attachment to make a radical $R\cdot$. This radical initiates further reactions before back electron transfer (BET) to $PC^{\cdot+}$ recovers the ground state PC.
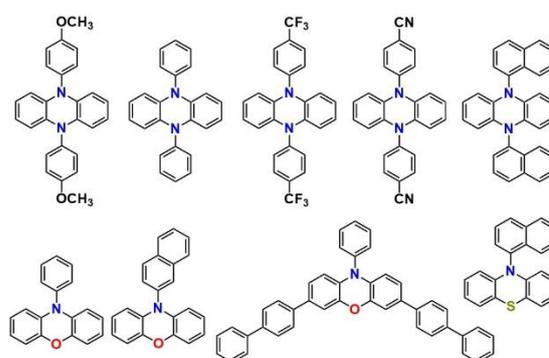

Figure 2: Structures of the nine organic photocatalysts studied, with architectures based on dihydrophenazine, phenoxazine or phenothiazine core chromophores. The appended aryl groups, with electron withdrawing or donating substituents, influence the CT or LE character of the photoexcited states.

An example of a set of transient IR spectra is shown in Figure 3 for 318-nm photoexcitation of a phenoxazine-based photocatalyst in solution in dichloromethane. Features corresponding to growth and decay of population in the S_1 and T_1 states (the latter via quenching by dissolved O_2) are clearly resolved, as are the kinetics of ground-state recovery.
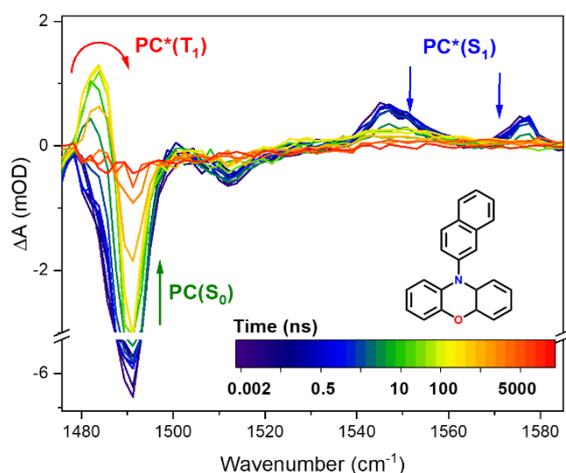

Figure 3: Time-resolved IR spectra of a phenoxazine-based photocatalyst (shown inset) in dichloromethane solution following 318-nm excitation. The coloured spectra correspond to different time delays after photoexcitation as shown by the key.

From the structure-dependent studies of PC response to UV excitation, we have determined S_1-state lifetimes, quantum yields for ISC to the T_1 state, and electron transfer rate coefficients from S_1 (and, in some cases, T_1) states, as well as their dependence on solvent properties.[5-7] By comparing to published reports of the use of these PCs in chemical synthesis, the consolidated results from our time-resolved spectroscopy studies provide an understanding of how LE or CT excited state characters, and ISC propensities influence PC performance. They therefore point to principles for future design of improved PCs tailored for specific chemical applications.

Section 2: Carbon-carbon bond formation using boronate complexes and radical chemistry

Boronate complexes offer a powerful strategy for C-C bond forming chemistry in organic synthesis. A proposed mechanism for an example reaction is illustrated in Figure 4, with photolysis of ethyl iodoacetate (B) initiating a radical chain cycle by reaction with boronate A to generate product F. This reaction proved amenable to detailed mechanistic study by TRIR with LIFEtime using shifts in the wavenumber of the IR band for the ester carbonyl group as markers for radical intermediates D and E, and the product F.
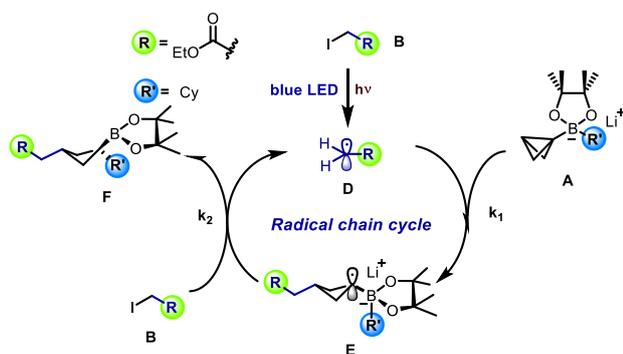

Figure 4: C-C bond-forming chemistry using a boronate complex A and a free radical D produced by photolysis of the organoiodide species B. In LIFEtime experiments, B was chosen to be ethyl iodoacetate.

The key outcomes from this study are summarized here. By following the time-resolved evolution of the radical D carbonyl band intensity, we were able to watch its initial photolytic production and its partial loss by fast geminate recombination and slower reaction with the boronate complex A. Later time growth of the radical band is attributed to its regeneration through reaction of intermediate E with further ethyl iodoacetate, as shown in the cycle in Figure 4. This time-resolved spectroscopic observation reveals the radical concentration entering steady state behaviour before its long-time decay by termination reactions. Moreover, we observe an intermediate product of this reaction (not shown in the figure) which controls the rate of build-up of product F. The TRIR capabilities of LIFEtime over timescales from sub-ps to 100 μs permit a complete mapping of the complex radical reaction cycle, and kinetic fitting yields rate coefficients for each step. The methodology is now being applied to further examples of this type of chemistry where controversy persists about the reaction mechanisms inferred from studies unable to observe the reactive intermediates directly.

Conclusions

The extended timescales for TRIR spectroscopy and the extraordinary sensitivity of the LIFEtime instrument allow us to undertake unprecedented studies of the pathways of multi-step photochemical reactions in solution. The ability to watch the growth and decay of a sequence of reactive intermediates offers new ways to determine the mechanisms and rates of every step in these complex reactions. With this greater mechanistic understanding, better design of photochemical and photoredox catalyzed reaction schemes should follow.

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