

Photochemical dynamics of organic photocatalysts showing reverse intersystem crossing and thermally activated delayed fluorescence

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Introduction

Photocatalysts are molecules that are activated by absorption of UV or visible light, and which then use the energy gained from the light to accelerate chemical reactions. Because the light source can be energy-efficient LEDs or sunlight, photocatalysis offers a sustainable alternative to the more traditional heating of reaction mixtures. This energy-efficient approach becomes even more sustainable when small organic molecules are used as photocatalysts, instead of conventional expensive and toxic heavy metal-containing alternatives. Attractive applications include lower-energy routes to the synthesis of pharmaceuticals, agrochemicals, polymers, and advanced materials.

Many designs of organic photocatalysts have been proposed and tested in synthetic chemistry and polymerization reactions.¹ At their core, these compounds typically contain a conjugated organic chromophore to promote strong absorption of visible or near-UV light. The properties of their electronically excited states can be tailored by structural modifications to other organic groups attached to the central core, such as by introduction of electron donating or withdrawing moieties. Using the LIFETIME facility at the Rutherford Appleton Laboratory, we have previously explored the photochemistry of various dihydrophenazine, phenoxazine and phenothiazine derivatives proposed for use in photoredox catalytic cycles, for example in organocatalyzed atom-transfer radical polymerization (O-ATRP).²⁻⁴

Recently, Kwon and coworkers have explored the use of another class of organic chromophores for photoredox catalyzed O-ATRP.⁵ These chromophores are based on the so-called “luminous butterfly” designs developed by Adachi and coworkers as thermally activated delayed fluorescence (TADF) emitters in thin films, with numerous applications in lighting and display technologies.⁶ The TADF emission arises because the first excited singlet (S_1) and triplet (T_1) states of these molecules lie close in energy, allowing efficient intersystem crossing (ISC) from S_1 to T_1 , and reverse intersystem crossing (RISC) from T_1 to S_1 with a small activation barrier that can be overcome by thermal energy.⁷ One characteristic signature of these compounds is the emission of fluorescence over prompt and extended timescales. The prompt emission comes from the initially photoexcited S_1 -state population, and the delayed fluorescence results from ISC to T_1 followed by RISC to the emissive S_1 state. Using samples of these prospective organic photocatalysts synthesized by Kwon and coworkers at Seoul National University (SNU), we have conducted transient absorption (TA) and time-resolved infra-red (TRIR) spectroscopy measurements to characterize the ISC and RISC

pathways for several example compounds. Comparison with fluorescence lifetime measurements made by time-correlated single photon counting (TCSPC) at SNU reveals that some of the studied organic compounds only behave as TADF emitters when aggregated in solution. Connections are also established between the excited state relaxation pathways and the performance of the different organic compounds as photocatalysts for O-ATRP.

Methods

TRIR measurements were made for solutions of four organic photocatalysts (typically 1.0 – 2.5 mM) in dichloromethane (DCM) and N,N-dimethyl formamide (DMF). Using the LIFETIME facility, TRIR time delays from 1 picosecond to several microseconds were readily accessible. The OPCs were photoexcited in their longest wavelength absorption bands (either at 360 nm or 425 nm), and the photochemical dynamics were probed with a pair of broadband mid-IR pulses spanning 1400 – 1800 cm^{-1} . Results were compared with TCSPC measurements for 10 μM solutions of the OPCs.

Results and Discussion

The organic photocatalysts chosen for investigation are shown in Figure 1, together with their abbreviated names.

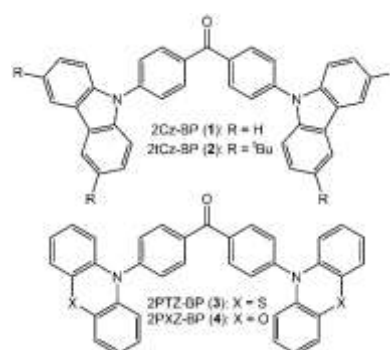


Figure 1: Structures of the studied organic photocatalysts.

These OPCs all have donor-acceptor-donor (D-A-D) structures with donor carbazole, phenoxazine or phenothiazine groups attached to a central acceptor benzophenone core. Figure 2 shows example TRIR spectra and kinetics for S_1 , T_1 and S_0 populations extracted from fitting to excited-state absorption and ground-state bleach feature intensities. The kinetics of S_1 decay and S_0 recovery show two time components (here, 8.3 ± 0.2 and 2430 ± 250 ns for 2tCz-BP in DCM) indicating RISC behaviour. These results are consistent with TCSPC measurements which reveal

time constants for fluorescence decay of 8.7 ± 0.01 and 12600 ± 3600 ns, attributed to TADF emission. The discrepancy between the longer time components in TRIR and TCSPC measurements is likely to result from poorer exclusion of dissolved oxygen in the circulating samples used for TRIR, with the dissolved O_2 quenching the T_1 state of the organic photocatalyst.

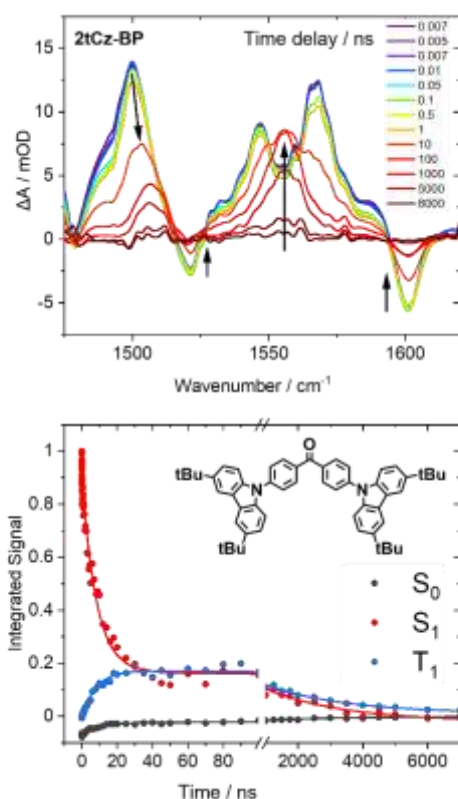


Figure 2: Example TRIR spectra (top) and extracted decay kinetics (bottom) for S_1 and T_1 populations of a photoexcited 2tCz-BP solution in DCM.

Similar agreement is found between LIFETIME TRIR measurements and TCSPC data for solutions of 2Cz-BP, confirming that it also behaves as a TADF emitter in dilute solutions. However, for the 2PTZ-BP and 2PXZ-BP compounds containing phenothiazine and phenoxazine donor groups, significant discrepancies are seen between TRIR and TCSPC measurements. For example, while the TCSPC data are well-fitted to biexponential decays consistent with TADF emission (with illustrative time constants of 1.07 ± 0.04 ns and 300 ± 20 ns for 2PXZ-BP in DMF) the corresponding decays observed by TRIR spectroscopy are mono-exponential and faster (with a time constant of 0.046 ± 0.001 ns for 2PXZ-BP in DMF) and there is no evidence for RISC. These discrepancies are proposed to arise from aggregation-induced emission, making 2PXZ-BP and 2PTZ-BP AIEgens (aggregation-induced emission luminogens). In the monomeric state in solution, these compounds have rapid, non-radiative $S_1 \rightarrow S_0$ relaxation pathways accessible through structural changes to the molecule in the S_1 state. These non-radiative decay pathways quench fluorescence emission. If the monomers are in excess in solution, TRIR measurements will preferentially report on the photochemical dynamics of these species. In contrast, in dimers or higher aggregates, the molecular motions in the S_1 state that access non-radiative decay pathways (such as out-of-plane twisting of the donor groups) are inhibited, and the aggregated species instead relax from their excited states by fluorescence emission. The TCSPC measurements are blind to the non-emissive monomers, but are sensitive to the small fraction of fluorescent aggregates present in solution. TCSPC therefore reports on the kinetics of radiative decay of the

aggregates, and the biexponential decays observed indicate TADF behaviour. The comparison of TRIR and TCSPC measurements therefore distinguishes photochemical pathways for the monomers and aggregates in solution.

The four organic photocatalysts shown in figure 1 have been tested for their performance in polymer synthesis using photoredox catalyzed O-ATRP. 2Cz-BP and 2tCz-BP showed significantly superior monomer conversion and polymer growth performance than 2PTZ-BP and 2PXZ-BP. These outcomes can be understood in terms of the low quantum yields for T_1 -state population in 2PTZ-BP and 2PXZ-BP, which instead show rapid S_1 population decay back to the ground electronic state. In contrast, the high T_1 quantum yields and RISC behaviour for 2Cz-BP and 2tCz-BP promote excited-state electron transfer reactions with the polymerization initiators which create the reactive radical species needed for polymerization to occur.

Conclusions

Four organic molecules with D-A-D structures (Figure 1) have been tested for TADF behaviour in DCM and DMF solutions using a combination of TRIR, TA and TCSPC measurements, the former made at the LIFETIME Facility at the Rutherford Appleton Laboratory. Comparison of transient absorption and time-resolved fluorescence spectroscopy data reveals TADF emission for two carbazole derivatives of benzophenone (2Cz-BP and 2tCz-BP), whereas benzophenone chromophores with appended phenoxazine or phenothiazine groups (2PXZ-BP and 2PTZ-BP) have fast $S_1 \rightarrow S_0$ non-radiative relaxation pathways that outcompete intersystem crossing and fluorescence emission. However, discrepancies between relaxation time constants measured by TRIR and TCSPC reveal that 2PXZ-BP and 2PTZ-BP are AIEgens (they emit fluorescence only when aggregated). In their aggregated forms, these two compounds exhibit TADF emission. These insights into the photochemical pathways for the four organic compounds studied reveal why 2Cz-BP and 2tCz-BP are effective photoredox catalysts for polymer synthesis by O-ATRP, whereas 2PXZ-BP and 2PTZ-BP perform poorly.

Acknowledgements

We thank the Science and Technology Facilities Council for access to the LIFETIME Facility at the STFC Rutherford Appleton Laboratory. Synthesis of the organic photocatalysts and TCSPC measurements at Seoul National University were supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. 2021R1A5A1030054).

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