Structure-Dependent Electron Transfer Rates for Dihydrophenazine, Phenoxazine and Phenothiazine Photoredox Catalysts Employed in Atom Transfer Radical Polymerization

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ABSTRACT

Organic photocatalysts (PCs) are gaining popularity in applications of photoredox catalysis but few studies have explored their modus operandi. We report a detailed mechanistic investigation of the electron transfer activation step of organocatalyzed atom transfer radical polymerization (O-ATRP) involving electronically excited organic PCs and a radical initiator, methyl 2-bromopropionate (MBP). This study compares nine N-aryl modified PCs possessing dihydrophenazine, phenoxazine, or phenothiazine core chromophores. Transient electronic and vibrational absorption spectroscopies over sub-picosecond to nanosecond and microsecond time intervals, respectively, track spectroscopic signatures of both the reactants and products of photoinduced electron transfer in N,N-dimethylformamide, dichloromethane, and toluene solutions. The rate coefficients for electron transfer exhibit a range of values up to \( \sim 10^{10} \text{ M}^{-1} \text{ s}^{-1} \) influenced systematically by the PC structures. These rate coefficients are an order of magnitude smaller for catalysts with charge transfer character in their first excited singlet (S\(_1\)) or triplet (T\(_1\)) states than for photocatalysts
with locally excited character. The latter species show nearly diffusion-limited rate coefficients for the electron transfer to MBP. The derived kinetic parameters are used to model the contributions to electron transfer from the S$_1$ state of each PC for different concentrations of MBP. Comparisons of singlet and triplet reactivity for one of the phenoxazine PCs reveal that the rate coefficient $k_{ET}(T_1) = (2.7 \pm 0.3) \times 10^7 \text{M}^{-1}\text{s}^{-1}$ for electron transfer from the T$_1$ state is two orders of magnitude lower than that from the S$_1$ state, $k_{ET}(S_1) = (2.6 \pm 0.4) \times 10^9 \text{M}^{-1}\text{s}^{-1}$. The trends in bimolecular electron transfer rate coefficients are accounted for using a modified Marcus theory for dissociative electron transfer.

1. INTRODUCTION

Atom transfer radical polymerization (ATRP) is a controlled polymerization method which exploits electron transfer (ET) processes leading to activation and deactivation of growing polymer chains.\textsuperscript{1-4} In ATRP, an organic radical is formed by a dissociative electron transfer reaction involving a catalyst and an initiator, often an organohalide. This radical reacts with alkene monomers to grow polymers. Deactivation involves the regeneration of the catalyst by a reverse electron transfer process which terminates further radical addition steps. These sequential processes are shown schematically in Figure 1(a). While ATRP has been a popular method for polymer synthesis since its inception in 1995,\textsuperscript{2,3} a surge in applications of photoredox catalysis in synthetic organic chemistry\textsuperscript{5-7} has steered research developments in ATRP in new directions. The first development exploited the benefit that, in photoredox catalysis, photoinduced ET provides an activation mechanism. The excited states of traditional transition-metal based catalysts were used to drive ET rather than their ground states, thereby exploiting the greater excited-state oxidizing/reducing potentials. Fors and Hawker first demonstrated this strategy by using $fac$-[Ir(ppy)$_3$] as a photocatalyst (PC) for polymerization of methacrylates.\textsuperscript{8}

However, the problems of toxicity and scarcity associated with transition-metal based catalysts have refocussed development towards organic dyes as alternative photocatalysts for organocatalyzed ATRP (O-
ATRP). The use of organic dyes as photocatalysts has simultaneously gained popularity in multiple fields of synthetic organic chemistry benefiting from photoredox catalysis strategies. Seminal work by Fukuzumi, Nicewicz and others has shown application of organic PCs in accelerating a range of reactions of synthetic utility. Hawker and Matyjaszewski separately demonstrated the use of N-aryl phenothiazines as PCs for O-ATRP. In recent years, Miyake and co-workers have extended the list of O-ATRP catalysts by introducing a plethora of new N,N-diaryl dihydrophenazine, N-aryl phenoxazine and N-aryl phenothiazine catalysts, with varying degrees of control over polymer molecular weights and dispersity. Kwon and co-workers have also introduced several new organic photocatalysts for O-ATRP, as well as for other controlled polymerization methods.

Continuing progress with the design of organic PCs raises the question of what makes an organic dye molecule a good candidate to be an O-ATRP catalyst. For an oxidative quenching cycle, as is the case for most photoredox based ATRP cycles, key requirements are to have a highly reducing PC* (S_1/T_1) excited state which can reduce an alkyl halide radical initiator, and a high oxidizing potential for the PC•+ radical cation, such that the growing polymer is efficiently deactivated. Currently, many of these catalysts are designed using principles deriving from transition-metal based photocatalysts, with metal-to-ligand charge transfer (MLCT) character in the excited state, and ultrafast intersystem crossing (ISC) populating long-lived, reducing or oxidizing T_1 states, leading to efficient ET. The organic PC equivalent of this MLCT character is an excited state involving charge transfer from the chromophore moiety to pendant groups such as aryl rings. Miyake and co-workers have reported that O-ATRP catalysts with excited electronic states of CT-character are generally better at controlling polymer dispersity and molecular weights, compared to the PCs which have locally excited (LE) character in which the electron density remains localized on the chromophore moiety orbitals. They suggested that the CT character in these catalysts promotes ISC and therefore more efficient bimolecular electron transfer.

Subsequent photophysical studies by Damrauer and co-workers using transient absorption spectroscopy measurements showed that indeed many of these catalysts with CT character in their S_1 states undergo
They invoked spin-orbit charge-transfer ISC to account for this behaviour: PCs with CT-character $S_1$ states and orthogonally oriented donor and acceptor moieties can undergo efficient ISC because a significant change in orbital angular momentum promotes a change in spin angular momentum.\textsuperscript{26-28, 33-34} However, previous reports from our laboratory question the generality and benefits of these photophysical properties on two fronts. First, we found that at least two of the N,N-diaryl dihydrophenazine catalysts previously reported to have CT character in their $S_1$ states (PC-N3 and PC-N5, shown in Figure 1(b)), and which exert good ATRP control, do not undergo significant ISC.\textsuperscript{35-36} The inefficient ISC might be because of short-lived excited singlet states, particularly in solvents such as N,N-dimethylformamide (DMF) which is one of the preferred solvents for O-ATRP.\textsuperscript{35-36} Second, transient vibrational and electronic absorption spectroscopy (TVAS and TEAS) measurements show that some of the LE-character catalysts can also undergo efficient ISC, although they are reported to be poor at controlling polymerization.\textsuperscript{37}

Although they display a range of photophysical attributes, catalysts with excited-state CT-character as a class seem to outperform their LE counterparts in controlling polymer dispersity.\textsuperscript{23, 38} To resolve why that is the case, both activation and deactivation ET steps must be examined. However, mechanistic investigations of these steps have been fewer in number compared to the photophysical studies. One of the first mechanistic investigations involving organic PCs in ATRP was by Matyjaszewski and co-workers; using a combination of computational studies, laser flash photolysis and cyclic voltammetry measurements, they examined both activation and deactivation mechanisms in some N-aryl phenothiazines and other organic PCs.\textsuperscript{20} Koyama \textit{et al.} studied both the photophysics and the ET activation step for 5,10-bis(4-fluorophenyl)-5,10-dihydrophenazine (PC-N3, previously called PCF, and shown in Figure 1(b)) and 5,10-bisphenyl-5,10-dihydrophenazine (PC-N2, previously called PCH) using TVAS and TEAS.\textsuperscript{36} These investigations, in combination with our recently published study on another N,N-diaryl dihydrophenazine catalyst (PC-N5, previously called PCBN),\textsuperscript{35} showed that for PC-N3 and PC-N5, both of which have CT excited-state character and are reported to be good ATRP photocatalysts, negligible ISC was observed in DMF solution. These studies therefore suggest that the ET happens from these PCs in their highly reducing
S$_1$ states. Moreover, comparison of the electron transfer steps for the three PCs shows that the rates are not dominated by their CT or LE character. The trends in the rates can instead be accounted for by Marcus-Savéant theory, and depend on the Gibbs energies of the PC$^*(S_1)$ and PC$^+*(D_0)$ species.

Previous mechanistic studies have largely focussed on investigating structural modifications within a single class of catalysts. Here, we report a systematic study of nine PCs chosen from the various N, N-diaryl dihydrophenazine, N-aryl phenoxazine, and N-aryl phenothiazine PCs, with the structures shown in Figure 1(b). Our measurements of the rates of electron transfer reactions use the complementary techniques of TEAS and TVAS. The chosen compounds have been reported as O-ATRP catalysts exerting varying degrees of control over polymer dispersity and molecular weights. Some show LE characteristics (PC-N1, PC-N2, and PC-O1), while others display CT characteristics in their excited states. Although most of the chemical modifications are to the N-aryl groups, PC-O3 is chosen as an example of a core-modified PC. TEAS and TVAS data for three of these catalysts (PC-N2, PC-N3, and PC-N5) were reported in previous publications from our group, but the results are incorporated and extended here to provide a consolidated picture of the structural dependence of PC performance.

Using the LIFETIME laser facility at the Rutherford Appleton Laboratory, we obtained TVAS measurements over time delays extending from 1 ps to tens of microseconds. This broad range of time delays with ultrafast (1 ps) resolution allowed us to observe the complete photochemistry of these molecules in a single continuous measurement, from the initial population of the relatively short-lived S$_1$ states to ISC into longer-lived triplet states and subsequent steps in the photoredox cycle. Our investigation of these multiple steps in the O-ATRP cycle involving PC-N5, and our findings on the solvent-dependent photodynamics of these PCs in the absence of electron-accepting polymerization initiators, are reported elsewhere. In the current work, we focus on the activation step of the O-ATRP process, i.e., we look at ET from the excited states (PC*) of these PCs to an alkyl halide radical initiator, methyl 2-bromopropionate (MBP).

\[
P C^* (S_1/T_1) + M B P \rightarrow P C^{++} (D_0) + M P^* (D_0) + B r^- (1)
\]
We investigate the reactivity of these PCs from their S\textsubscript{1} and/or T\textsubscript{1} states in three solvents, toluene (toluene-d\textsubscript{8} for TVAS), dichloromethane (DCM) and DMF, and derive values for the second order rate coefficients for bimolecular electron transfer reactions. To explain the difference between their reactivities, we employ the “sticky” model of dissociative electron transfer.\textsuperscript{20} We find that irrespective of their chemical class, the LE catalysts undergo faster ET than their CT counterparts. For PCs with significant T\textsubscript{1} populations, ET is efficient from both S\textsubscript{1} and T\textsubscript{1} states at synthetically relevant concentrations of the PC and MBP. However, efficient ISC is not required for a PC to be an effective O-ATRP catalyst.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{A photoredox cycle and the photocatalysts for atom transfer radical polymerization (ATRP) studied in this work. (a) Photoredox cycle operative in the ATRP process. The dissociative photoinduced electron transfer (DPET) activation step which is the focus of the present study is highlighted in black; (b) Structures of the organic PCs studied in this work, and the naming scheme used throughout. Abbreviations in parentheses are the labels used in prior publications from our group.}
\end{figure}

2. METHODS

Transient absorption spectroscopy measurements were made using ultrafast laser systems at the University of Bristol (UoB) and the LIFETIME facility at the STFC Rutherford Appleton Laboratory. Both set-ups
have been described elsewhere,\textsuperscript{45-49} and only brief accounts of key experimental procedures are provided here. Further summaries of the laser systems and their use are provided in the SI section S2. As is discussed further in the SI, the experimental conditions used for the laser-based studies reported here allow measurement of kinetic parameters that can be directly applied to the interpretation of O-ATRP studies using light-emitting diodes for sample photoexcitation.

All photocatalysts were synthesized at UoB using either previously reported or modified syntheses,\textsuperscript{23-24, 37} and the synthetic methods are reported in previous publications.\textsuperscript{37, 39} Sample solutions of photocatalysts at concentrations in the range 1.0 - 7.5 mM were prepared in dichloromethane (Sigma Aldrich anhydrous, 99.8%), toluene (Spectroscopic grade, 99.8%, Sigma Aldrich), and N,N-dimethyl formamide (Sigma Aldrich anhydrous, 99.8%) in sealed amber Duran flasks. Toluene-d\textsubscript{8} (Sigma Aldrich, 99.6 atom% D) was used for TVAS experiments to avoid interfering solvent absorption bands in the probed region. DMF was used in lieu of N,N-dimethylacetamide (DMA), the solvent of choice in polymerization experiments for these photocatalysts, because DMF is less absorbing in the probed IR region. However, DMF and DMA have similar physical properties; for example, the dielectric constants for DMF and DMA are 36.7 and 37.8 respectively. Nitrogen was bubbled for 30-40 minutes through the sample solutions immediately prior to use to displace dissolved O\textsubscript{2}. The radical initiator methyl 2-bromopropionate (Sigma Aldrich, 98%) was added to each solution in increasing concentrations from 0.05 - 2.0 M. Higher concentrations of MBP (typically \( \geq 100 \text{ eq.} \)) compared to the synthetic studies (10 eq.) were required to observe the MP radical signals in the TVAS measurements.

Using a peristaltic pump, the sample solutions flowed through a Harrick cell comprised of two CaF\textsubscript{2} windows separated by a PTFE spacer, 100-380 \( \mu \text{m} \) thick. A customized sealed flow system was used for the experiments, the details of which are described elsewhere.\textsuperscript{35} In all TVAS measurements, concentrations of the photocatalysts were adjusted to give optical densities (OD) < 0.5 at the pump wavelength for the selected pathlength through the sample. All N,N-diaryl dihydrophenazine catalysts (PC-N1 to PC-N5) were
excited with a UV wavelength of $\lambda_{\text{exc}} = 370$ nm, but PC-O1, PC-O2, and PC-S were instead excited at $\lambda_{\text{exc}} = 318$ nm. The N-aryl phenoxazine PC-O3 was excited at $\lambda_{\text{exc}} = 389$ nm because the extended conjugation to the biphenyl side groups shifts the absorption maximum to longer wavelengths. Laser pulse durations were $\sim 50$ fs for TEAS measurements, (UoB laboratory), and $< 260$ fs for TVAS experiments at the LIFETIME facility.

For both TEAS and TVAS experiments, pump and probe beams were polarized at the magic angle ($54.7^\circ$) to remove any effects of rotational anisotropy on the measured time-evolving signals. The collected spectra, which were extensively averaged to improve signal-to-noise ratios, were analysed by spectral decomposition using the Koala software package. A combination of Gaussian and other basis functions was used to extract the time evolutions of the TEAS and TVAS spectral features. More specific details of these analyses are provided in the Results and Discussion section.

3. RESULTS AND DISCUSSION

3.1. Steady State Characterization. The choice of UV or visible photoexcitation wavelength of the PCs requires knowledge of their electronic absorption spectra, and interpretation of TVAS measurements benefits from identification of ground-state IR bands of the PCs. Steady state characterization of solutions of the photocatalysts (by UV-Vis, FTIR and fluorescence spectroscopy) in the three chosen solvents was therefore undertaken and the outcomes are reported in another publication. As the focus of the work reported here was on studying the electron transfer reaction between the excited state PCs and MBP, it was important to characterize the resulting intermediates from reaction (1). While the short-lived MP$^\cdot$ radicals are hard to characterize by steady state methods, PC$^{\cdot+}$ can be prepared in solution by the oxidation of the PCs in their ground state using a concentrated FeCl$_3$ solution. The resulting FTIR and UV spectra are shown in the Supporting Information figures S1 and S2. The UV-Vis spectra of all the oxidized PC solutions show a band shifted to longer wavelengths than the first PC(S$_0$) absorption band (300-400 nm) and appearing in the region between 400 and 600 nm, which we assign to the PC radical cation, $^2$PC$^{\cdot+}$(D$_0$).
3.2. Tracking Reactive Intermediates. The electron transfer reactions between excited states of the photocatalysts and the radical initiator MBP were tracked using the complementary methods of transient vibrational and electronic absorption spectroscopies.

3.2.1. TVAS Measurements. The TVAS data shown in this study were collected at the LIFtime facility at the RAL. This laser system allowed us to follow these reactions over time delays after photoexcitation ranging from 1 ps to beyond 10 µs. In TVAS data, the mid-IR region between 1450 and 1700 cm\(^{-1}\) was used as a probe because it covered IR bands associated with both the ring modes of the catalysts and the CO stretching region, allowing us to track PC*, PC, MP\(^{•}\) and PC\(^{•+}\) vibrational signatures simultaneously. Prior to studying the electron transfer step, the TVA spectra of all the PCs shown in Figure 1(b) were measured in DCM, DMF and toluene-d\(_8\) to characterize the PC excited state dynamics in the absence of an electron acceptor. A detailed account of this work is reported elsewhere,\(^4\) but for illustrative purposes an example set of TVA spectra for PC-S in DCM (with no added MBP) is shown in Figure 2(a). The spectra show a strong ground state bleach (GSB) centred at 1465 cm\(^{-1}\) and corresponding to depletion of PC-S (S\(_0\)) by photoexcitation, as well as two excited state absorption (ESA) bands of PC-S\(^*\) (S\(_1\)) centred at 1495 cm\(^{-1}\) and 1530 cm\(^{-1}\) and two weaker GSB features at 1573 and 1591 cm\(^{-1}\). The kinetic traces obtained by fitting Gaussian functions to the GSB and ESA features at 1465 and 1495 cm\(^{-1}\) respectively, are shown in Figure 2(b). The kinetics identify a biexponential recovery for the GSB with time constants of 3.9 ± 0.3 ns and 50.4 ± 3.2 ns (with one standard error uncertainties derived from the exponential fits). The first time constant, which can be globally fitted to the ESA decay as well, is assigned to the decay of population of the S\(_1\) state of PC-S, either by relaxation to the ground state through radiative and non-radiative processes, or by populating triplet states through intersystem crossing. The second time constant is assigned to the lifetime of the T\(_1\) state. We find that the triplet lifetimes of these catalysts, which were previously reported to be several µs by Sartor et al.,\(^{27-28}\) are sensitive to the presence of dissolved oxygen, and 50 ns is a lower limit to the T\(_1\) lifetime of PC-S because of residual oxygen in our samples. The TVA spectra of the other PCs (Figure 1(b)) show similar features to PC-S with varying degrees of ISC quantum efficiency, and
different excited state lifetimes which also depend to a great extent on the solvent. Table 1 summarizes the
PC*(S$_1$) lifetimes and triplet quantum yields for all the PCs, the derivations of which have been reported
elsewhere.$^{44}$

To follow the ET reaction, we added MBP in increasing concentrations to a PC solution in DCM. As can
be seen in Figure 2(c), with the addition of MBP the TVA spectra change in four distinct ways: (1) a band
centred at 1660 cm$^{-1}$ arises which we assign to $^3$MP'(D$_0$) based on previous work;$^{36}$ (2) the decay of the PC-
S* (S$_1$) ESA bands becomes faster; (3) A peak corresponding to PC-S radical cation (PC-S$^{+}$) appears at
1536 cm$^{-1}$ (See Figure S1 for support of this assignment from steady state oxidation experiments with
FeCl$_3$), shifted to higher wavenumber than the PC*(S$_1$) ESA feature; (4) all the GSB features (centred at
1465 cm$^{-1}$, 1573 cm$^{-1}$ and 1591 cm$^{-1}$) show incomplete recovery on the timescales reported here. In the case
of solutions in DMF, the strong solvent absorption allowed only a narrow window of observation in the
mid-IR probe region, thus showing only the decay of the PC* ESA and the growth of the PC$^{+}$ absorption
band, as can be seen in Supplementary Figure S10.

The changes in intensity of the bands assigned to the $^3$MP'(D$_0$) radical, PC-S* (S$_1$) ESA, PC-S$^{+}$ (D$_0$), and
PC-S(S$_0$) GSB at 1465 cm$^{-1}$ can be globally fitted to obtain a single exponential time constant as shown in
Figure 2(d). For this dataset, the time constant is 1.08 ± 0.04 ns. As this time constant is shorter than the
S$_1$ state lifetime in the absence of MBP, it is evident that at the concentration of MBP used (~100 equivalents
of [PC]) most of the electron-transfer reactions between PC* and MBP happen from the PC*(S$_1$) state for
PC-S. Note that we do not see a distinctive band for a PC$^+$/MBP$^-$. complex, in accord with the work of
Koyama et al.,$^{36}$ showing that within our experimental time resolution the C-Br bond promptly dissociates
to make the MP$^-$ radical, a Br$^-$ ion and the PC$^{+}$ cation. Indeed, dissociative electron transfer to alkyl halides
is a widely observed phenomenon and is well characterized.$^{51}$

The features evident in the spectra in the region 1400-1700 cm$^{-1}$ again do not change markedly between the
various N,N-diaryl dihydrophenazine, N-aryl phenoxazine and N-aryl phenothiazine catalysts reported in
this study. Full sets of TVA spectra for each of the PCs with MBP in DCM, DMF and toluene-d$_8$ are shown in the Supporting Information (Figures S3 to S11). An exceptional case arises for PC-N4, where we do not see any reaction between photoexcited PC-N4* and MBP in any of the solvents, even at the higher concentrations of MBP (up to 2 M). Interestingly, PC-N4 which has CT character in both its S$_1$ and T$_1$ state, is reported to be a good O-ATRP catalyst for control over polymer dispersity. It is not surprising that we see no reactivity in our timescales (up to 10 µs) from the PC-N4*(S$_1$) state in DCM and DMF because the S$_1$ lifetimes are short in these solvents (500 ps in DCM, and 135 ps in DMF) and there is no evidence for ISC to populate the T$_1$ state.$^{44}$ However, in toluene-d$_8$, the PC behaves very differently, with an S$_1$ state lifetime of 5.7 ns and significant population of a long lived T$_1$ state ($\Phi_{ISC} = 0.57$). Hence, reaction between PC-N4* and MBP in toluene-d$_8$ might be expected. Interestingly, with the addition of MBP at concentrations as low as 0.2 M (and at a 5 mM PC-N4 concentration) we see a precipitate forming in the solution upon photoexcitation, which may originate from the formation of a PC-N4$^+$Br$^-$ salt.

Experiments conducted with PC-N1 or PC-O1 in DCM without MBP show incomplete recovery of the GSB features as well as the growth of PC$^\bullet+$ peaks. We attribute these observations to the reaction between photoexcited PC*(S$_1$) and DCM, consistent with prior reports of reaction of certain excited organic chromophores with halogenated solvents.$^{37, 52}$ Nevertheless, in the presence of MBP, electron transfer to this acceptor is faster than to the solvent, even at low MBP concentrations.
Figure 2. TVAS measurement of PC-S in DCM without and with the electron acceptor MBP. (a) TVA spectra of 7.5 mM PC-S in DCM shown in the wavenumber range of 1450-1680 cm\(^{-1}\); (b) Kinetic traces of PC-S*(S\(_1\)) and PC-S(S\(_0\)) band intensities in the absence of MBP (circles) and their single and biexponential fits (solid lines). The first time constant (3.9 ± 0.3 ns) is assigned to the S\(_1\) state lifetime, and the second time constant (50.4 ± 3.2 ns) is assigned to quenching of T\(_1\) state population by dissolved O\(_2\) (with one standard error uncertainties derived from the exponential fits); (c) TVA spectra of PC-S with 0.8 M MBP; (d) Normalized kinetic traces of \(^2\)MP*(D\(_0\)), \(^1\)PC-S*(S\(_1\)), \(^2\)PC-S***(D\(_0\)) and \(^1\)PC-S(S\(_0\)) band intensities, which were obtained by fitting Gaussian functions to the labelled bands in the TVA spectra in panel (c). Solid lines show a global fit of the data to single exponential functions, giving a common time constant of 1.08 ± 0.04 ns. Arrows in panels (a) and (c) are colour coded to their labels and show the directions of change for the associated peaks.

At the sub-molar concentrations of MBP used in the current study, the ET occurs primarily from the PC*(S\(_1\)) states, but this behaviour does not rule out the possibility of reaction from the longer-lived PC*(T\(_1\)) states at lower concentrations of MBP where diffusive encounters are less frequent. However, the absence of
observable triplet bands in our probe spectral range for most PCs makes it difficult to observe triplet state reactivity. For example, computational data previously reported by our laboratory for PC-O1 showed that the triplet bands were either weak or shifted from our IR probe window of 1400-1700 cm\(^{-1}\). The decay of intensity of such bands caused by electron transfer to MBP would provide a direct measure of the rate of electron transfer from the T\(_1\) state. For PC-O2 we see a triplet band at 1485 cm\(^{-1}\) and analysis of the ET observed using this band is discussed in section 3.4.

Table 1. Lifetimes (ns) of the S\(_1\) States of the Studied PCs in DMF, DCM, and Toluene-d\(_8\) Solutions and Intersystem Crossing Quantum Yields (\(\Phi_{ISC}\)).\(^{(a,b)}\)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Lifetime (ns) and ISC quantum yield</th>
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<tbody>
<tr>
<td></td>
<td>DMF</td>
</tr>
<tr>
<td>PC-N1</td>
<td>38.5 ± 1.3</td>
</tr>
<tr>
<td>PC-N2(^{(c)})</td>
<td>16.8 ± 2.0</td>
</tr>
<tr>
<td></td>
<td>(\Phi_{ISC} = 0.71)</td>
</tr>
<tr>
<td>PC-N3(^{(c)})</td>
<td>0.635 ± 0.022</td>
</tr>
<tr>
<td></td>
<td>(\Phi_{ISC} = 0.19)</td>
</tr>
<tr>
<td>PC-N4</td>
<td>0.135 ± 0.003</td>
</tr>
<tr>
<td></td>
<td>(\Phi_{ISC} = 0.19)</td>
</tr>
<tr>
<td>PC-N5(^{(c)})</td>
<td>5.2 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>(\Phi_{ISC} = 0.14)</td>
</tr>
<tr>
<td>PC-O1(^{(c)})</td>
<td>2.1 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>(\Phi_{ISC} = 0.84)</td>
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<tr>
<td>PC-O2</td>
<td>8.6 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>(\Phi_{ISC} = 0.74)</td>
</tr>
<tr>
<td>PC-O3</td>
<td>3.3 ± 0.4</td>
</tr>
<tr>
<td>PC-S</td>
<td>5.9 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>(\Phi_{ISC} = 0.37)</td>
</tr>
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</table>

(a) The ISC quantum yield is given for PCs with non-zero ISC efficiencies.
(b) More detailed descriptions of the photodynamics of these PCs are reported elsewhere.\(^{44}\)
(c) S\(_1\) lifetime values previously reported by Koyama \textit{et al.}\(^{36}\), Sneha \textit{et al.}\(^{37}\) and Lewis-Borrell \textit{et al.}\(^{35}\)
3.2.2. TEAS Measurements. As with the TVAS measurements, TEAS spectra were first collected for the PC in solution without an added electron acceptor. These spectra and their analysis are reported elsewhere, and Table 1 summarizes the relevant excited state lifetime data.\textsuperscript{44} The reactions between MBP and the photoexcited PC* were then followed by observing the changes in the transient spectra upon addition of MBP. Figure 3 shows examples of such TEA spectra for PC-N1 with 2.0 M MBP in DCM and DMF solutions. As is evident from the figure, in both solvents the broad double-peaked spectra seen at early times decay, giving rise to a narrower, slightly structured absorption feature centred at 470 nm. We assign the early time spectra to a combination of PC*(S\textsubscript{n}) and PC*(S\textsubscript{1}) ESAs, and the late time spectra to the PC-N1\textsuperscript{•+} cation on the basis of the steady-state UV-Vis spectra obtained by oxidation of the PCs using FeCl\textsubscript{3} (see Supporting Information Figure S2). The PC-N1\textsuperscript{•+} band changes only slightly between DCM and DMF solutions. However, while the structure of the PC-N1\textsuperscript{•+} absorption band measured by TEAS in DMF closely resembles the steady state absorption spectrum of PC-N1\textsuperscript{•+} (Figure S2), the band structures in DCM differ. One explanation could be that in DCM, some of the PC-N1\textsuperscript{•+} forms a complex with Br\textsuperscript{-}, giving a slightly shifted absorption to that of the free form. Panels 3(b) and (d) show the kinetic traces obtained by decomposing the TEAS data into contributions from an early time basis function (taken from TEA spectrum of PC-N1 in DCM without MBP at 50 ps and attributed to PC*(S\textsubscript{1}) ESA) and a PC\textsuperscript{•+} spectral basis function corresponding to the late time spectrum recorded at 1200 ps for each solvent.

The time evolutions of the fits of TEA spectra to these basis functions are shown in Figures S31-S32 of the Supporting Information. The kinetic traces for decay of PC*(S\textsubscript{1}) ESA and growth of PC\textsuperscript{•+} absorption can be globally fitted to biexponential functions. As no triplet state population was observed for PC-N1 in DCM or DMF, and the internal conversion from PC*(S\textsubscript{n}) to PC*(S\textsubscript{1}) takes only ~4 ps, the electron transfer to MBP is inferred to occur from the PC-N1*(S\textsubscript{1}) state. Moreover, in DMF the PC-N1*(S\textsubscript{1}) state has a lifetime of ~40 ns, whereas the ET happens with a time constant of ~112 ps for a 2.0 M MBP concentration, showing that ET outcompetes relaxation back to the ground state. We investigate this fast electron transfer further in section 3.3.
The TEAS measurements for the other studied PCs with MBP are shown in the Supporting Information (Figures S3-S11). In contrast to the TVAS data, the TEA spectra do show significant changes in observed bands for different PCs; however, for most cases and at the concentrations of MBP used as discussed in section 3.3, we only see reactivity from the PC*(S₁) state. This apparent specificity could be for two reasons: (1) with the exception of PC-O1, we do not see clear signatures for ESA from a PC*(T₁) state in our TEAS data. Even for PC-O1, we see the formation of PC⁺ almost concurrently with the rise of the PC*(T₁) absorption band, which indicates that PC-O1⁺ originates from reaction in the S₁ state. (2) Our TEAS measurements are limited to reaction times up to ~1.3 ns, which makes it difficult to observe reactivity from the T₁ state.

Figure 3. TEAS measurement of reaction of 2.5 mM PC-N1 with 2.0 M MBP. The excitation wavelength was 370 nm and the WLC probe spanned a wavelength range from 340-700 nm. (a) TEA spectra in DCM; (b) kinetic traces for PC-N1*(S₁) and PC-N1** in DCM obtained using spectral decomposition methods described in the main text; (c) TEA spectra in DMF; (d) kinetic traces of PC-N1*(S₁) and PC-N1** in DMF. Arrows in (a) and (c) show the directions of change of the electronic bands. For each solvent, the kinetic traces were globally fitted to biexponential functions (solid lines) to account for both static and dynamic reactive quenching of the PC-N1*(S₁) state at this concentration of MBP (see text).
3.3. Rates of Electron Transfer.

The rates of electron transfer between the various PC*(S\textsubscript{1}/T\textsubscript{1}) and MBP can be determined either by following the growth of the product MP\textsuperscript{*} radical and PC\textsuperscript{+} absorption bands, or the PC\textsuperscript{*} ESA-band decays in both TEAS and TVAS data (note that the MP\textsuperscript{*} radical is not observed in TEAS). The latter method is equivalent to a Stern-Volmer analysis. We discuss each of these approaches below, and how depending on the concentration of MBP, the bimolecular rate coefficients for ET can be determined by either a pseudo-first order kinetic model or fitting to a diffusional kinetic model based on Smoluchowski theory.

3.3.1. Dynamic vs Static Quenching. At low concentrations of MBP (≤0.4 M), the intermolecular electron transfer reactions between an electron donor (PC\textsuperscript{*}) and electron acceptor (MBP) can be treated as requiring diffusional encounters, with single-exponential kinetics in the pseudo-first order regime of [MBP] >> [PC\textsuperscript{*}]. However, at higher sub-molar concentrations of the MBP radical initiator, a significant fraction of the PC may exist in close proximity to an MBP co-solute, trapped within a solvent cage. This fraction can potentially undergo prompt electron transfer upon photoexcitation without the need for diffusive encounters, which is referred to as static quenching. Under these conditions, electron transfer processes will deviate from single exponential kinetics, and to a first approximation can be treated as biexponential with the larger rate coefficient assigned to the static quenching and the smaller rate coefficient associated with diffusional quenching. The TEAS measurements shown in Figure 3 illustrate these biexponential ET kinetics of PC-N1*(S\textsubscript{1}) with MBP; fitting gives two time constants for the ET reaction, 8.3 ± 0.6 ps for static quenching and 112 ± 6 ps for the diffusional quenching component in DMF. When our data show significant deviations from mono-exponential behaviour, we fit to biexponential kinetics and use the second time constant to extract the dynamic/diffusional rate coefficients for electron transfer, as reported in Table 2. In the following sections, we develop a pseudo first order kinetic model for the diffusive electron transfer process through analysis of PC*(S\textsubscript{1}) decay or MP\textsuperscript{*} growth.
Vauthey and co-workers instead described application of a Smoluchowski model of diffusive reactions which takes into consideration the time-dependent rate coefficient as the rate switches from the static limit to the dynamic limit. Kinetic modelling of our data using Smoluchowski theory is reported in the Supporting Information, where in Table S1 we also compare the rate coefficients obtained with those from single or biexponential kinetic fitting. The two analysis methods are found to be in satisfactory agreement, with the exception of PC-N1 solutions in DCM and toluene, for which we report Smoluchowski model rate coefficients in Table 2.

3.3.2. PC* Quenching. Following photoexcitation from the PC(S0) state to a higher lying singlet state, the PC*(S1) state rapidly internally converts and relaxes to the PC*(S1) state. The population in the PC*(S1) state can undergo unimolecular decay either by radiative and non-radiative relaxation to the ground state or through ISC to the triplet manifold of states, with decay rate coefficients $k_R$ and $k_{ISC}$ respectively, as shown in equations 2 and 333. Rapid internal conversion is assumed to occur within the triplet manifold to populate T1. However, upon adding MBP, dissociative electron transfer to MBP, generating an MP• radical, serves as an additional bimolecular decay pathway for PC*(S1), with a rate coefficient denoted here as $k_{ET}$, as shown in equation 4. Additionally, MBP can react with PC*(T1) to generate PC•++ + MP• as shown in equation 5. The rate of decay of PC*(S1) is expressed by equation 6, which includes the above-mentioned pathways. This analysis relates the observed rate coefficient, $k_{obs}$ for the decay of the PC*(S1) band intensities in either TEA or TVA spectra to the rate coefficient for electron transfer and the lifetime ($= 1/k_0$) of PC*(S1), as shown in equation 7. The corresponding analysis for reactivity from the PC*(T1) state is reported in the Supporting Information.

\[ PC^*(S_1) \xrightarrow{k_R} PC(S_0) \]  
\[ PC^*(S_1) \xrightarrow{k_{ISC}} PC^*(T_n) \rightarrow PC^*(T_1) \]  
\[ PC^*(S_1) + MBP \xrightarrow{k_{ET}} MP^* + PC^{**} + Br^- \]  

PC*(S0)
\[
PC^*(T_1) + MBP \xrightarrow{k_{ET}^T} MP^* + PC^* + Br^- \tag{5}
\]
\[
\frac{d[PC^*(S_1)]}{dt} = -k_D[PC^*(S_1)] - k_{ET}[PC^*(S_1)][MBP] \tag{6}
\]
where \(k_D = k_R + k_{ISC}\), and is the reciprocal of the lifetime of the PC*(S_1) state in the absence of MBP.

\[
k_{obs} = k_D + k_{ET}[MBP] \tag{7}
\]

Figure 4(a) shows the dependence of the rate coefficient \(k_{obs}\) for decay of the PC-N1*(S_1) ESA band intensity on changing [MBP] concentration in DMF solution, measured using TVAS. The gradient of the inset plot of \(k_{obs}\) vs [MBP] gives a value of \(k_{ET} = (1.0 \pm 0.1) \times 10^{10} M^{-1}s^{-1}\) for reaction of PC-N1*(S_1) with MBP in DMF. As is shown in Table 1, PC-N1 is a photocatalyst with a negligible triplet quantum yield in DMF solution. The data shown in Figure 4(a) were obtained for a 4.2 mM PC-N1 solution, with MBP concentrations in the range 0.045 - 0.36 M. The lowest concentration of 0.045 M MBP corresponds to 10 equivalents of the PC, in line with typical polymerization conditions. For experiments where higher MBP concentrations were used, the linearities of this and other pseudo-first-order kinetic plots indicate no adverse effects on the ET kinetics, and that our derived rate coefficients for electron transfer can be applied under the synthetic conditions used for polymer growth.

Complementary information can be obtained from analysis of TEAS data, and the global fitting of the kinetics of decay of the PC-N1 ESA band and growth of the PC-N1•+ band derived from TEAS measurements for different [MBP] concentrations gives a rate coefficient for ET of \(k_{ET} = (1.3 \pm 0.1) \times 10^{10} M^{-1}s^{-1}\). This value matches the rate coefficient value derived from the independent TVAS data within two standard errors. This Stern-Volmer type quenching analysis is particularly useful for analysis of decaying ESA bands in TEAS data, or of TVA spectra in DMF solutions for which the MP• product band is masked by strong solvent absorptions.

### 3.3.3. Growth of MP' Band

In toluene-d_8 and DCM solutions, analysing the growth of the MP' radical absorption band observed at 1660 cm\(^{-1}\) in the TVAS data provides an alternative way to obtain \(k_{ET}\) values.
A kinetic analysis based on this spectroscopic feature must also take account of decay pathways for the MP radical, as shown in equations 8 and 9. Under our experimental conditions, MP can primarily decay via two pathways: either by radical-radical self-quenching or by reaction with residual dissolved oxygen. A third pathway of back electron transfer to PC is discounted on the timescales of our measurements (up to 10 µs) because we do not see decay of the PC absorption bands.

\[ MP^* + MP^* \xrightarrow{k_{t1}} (MP)_2 \]  
\[ MP^* + O_2 \xrightarrow{k_{t2}} MPOO^* \]  

As can be seen in Figure S30, the time constant for decay of the MP band can vary from 300 ns to ~5 µs (depending on the extent to which dissolved oxygen has been purged out of the flow system), which is \(10^2-10^3\) times slower than its rise (less than 2 ns at concentrations used here) by an electron transfer reaction. Additionally, at the concentrations of MBP used for most of these studies, the rate of electron transfer is much faster than the rate of ISC, even for the catalysts with otherwise high \(\Phi_{ISC}\) values reported in Table 1. The fact that kinetic traces of PC(S), MP, and PC(S) can be fit with a global time constant as seen in Figure 2(d) further argues that ISC is not significant in our measurements. Hence, under these conditions, we obtain a pseudo first order kinetic equation for the growth of MP radical concentration within the first ~10-20 ns as shown by equation 10.

\[ \frac{d[MP^*]}{dt} = k_{ET}[PC^*(S_1)] \]  

where \(k_{ET} = k_{ET}[MBP]\). Substituting the value for \([PC^*(S_1)]\) from integration of equation 6, we get the overall rate coefficient for the growth of MP which is related to the rate coefficient for ET as:

\[ k_{MP} = k_D + k_{ET}[MBP] \]  

Figure 4(b) shows the kinetic traces obtained for the growth of the MP band intensity with increasing concentrations of MBP (from 0.18 to 1.4 M) for a 7.5 mM solution of PC-S in DCM. The inset shows a plot of \(k_{MP}\) vs [MBP]; the gradient of the linear fit gives the rate coefficient for electron transfer from
PC*(S₁) to MBP, \( k_{ET} = (1.4 \pm 0.1) \times 10^9 \, \text{M}^{-1} \text{s}^{-1} \). This rate of electron transfer is slower by an order of magnitude than the expected diffusion-controlled rate coefficient in DCM \((1.5 \times 10^{10} \, \text{M}^{-1} \text{s}^{-1})\) at 20 °C.\(^{54}\) The rate coefficient for ET in toluene-d₈ obtained from such an analysis also gives \( k_{ET} = (1.4 \pm 0.1) \times 10^9 \, \text{M}^{-1} \text{s}^{-1} \).

While the kinetic analysis of the MP’ band intensities from TVAS measurements does provide an additional measure for determining the ET rate coefficient, it is not always possible to perform. Firstly, the MP’ band is completely masked by strong solvent absorption in DMF solutions. Secondly, for some photocatalysts, the MP’ band intensities observed in toluene are much weaker than in DCM. What causes this discrepancy is unclear. The above kinetic analysis is also valid for growth of the intensity of the PC⁺ product band, as revealed both in TVAS and TEAS data.

Depending on the solvent, and the intensity of the MP’ absorption band, both PC*(S₁) quenching and MP’ band growth kinetics can be used to determine the rate coefficients for electron transfer between PC*(S₁) and MBP for all the organic PCs studied here (Figure 1(b)). Concentration plots akin to Figure 4 are shown in Supporting Information for all the PCs, and the values of \( k_{ET} \) obtained are summarized in Table 2. Note that most of the \( k_{ET} \) values reported in Table 2 are derived from the analysis of TVAS data. PC* band decays in the TEAS data were instead used to extract the rate coefficients for those PCs for which the signal-to-noise ratios in TVAS data were poor and resulted in noisy kinetics. Where possible, ET rate coefficients obtained from these two different spectroscopic techniques are reported for better comparison. For example, for PC-O2 in DCM, the rate coefficient for ET from the PC*(S₁) state obtained from TVAS data is \((8.5 \pm 1.5) \times 10^9 \, \text{M}^{-1} \text{s}^{-1}\) which is in reasonable agreement with the \( k_{ET} \) value of \((1.0 \pm 0.1) \times 10^9 \, \text{M}^{-1} \text{s}^{-1}\) obtained using TEAS data analysis. The kinetic fits for PC-O2 are shown in the Supporting Information.
Figure 4. Kinetics of electron transfer reactions of PC-N1*(S1) and PC-S*(S1) with MBP from TVAS measurements. Rates of (a) decay of PC-N1*(S1) in DMF and (b) production of 2MP*(D0) radical in DCM by electron transfer from PC-S*(S1) to MBP. Insets show pseudo-first order kinetic plots. The rate coefficient for electron transfer from PC-N1*(S1) to MBP is obtained from the linear fit as $k_{ET} = (1.0 \pm 0.1) \times 10^{10} M^{-1}s^{-1}$ in DMF and from PC-S*(S1) to MBP is $k_{ET} = (1.4 \pm 0.1) \times 10^9 M^{-1}s^{-1}$ in DCM.

For each of the studied PCs, the magnitudes of their ET rate coefficients show some variation, but not marked change, between toluene(-d8), DCM and DMF solutions. This observation is particularly relevant for the N,N-diaryl dihydrophenazines as most of these PCs show highly solvent dependent photodynamics. However, comparing the $k_{ET}$ values between different PCs reveals one important distinction: PC-N1, PC-N2 and PC-O1, all of which have LE character for their $S_1$ states, have nearly diffusion-controlled rate coefficients for excited-state ET to MBP. In contrast, PC-N3, PC-N5, PC-O3 and PC-S, with $S_1$ CT-character, undergo slower ET with rate coefficients 5-10 times lower than the predicted diffusion-limited rate coefficients in the respective solvents. These diffusional rate coefficients are estimated to be $1.5 \times 10^{10} M^{-1}s^{-1}$ in DCM, $1.1 \times 10^{10} M^{-1}s^{-1}$ in Toluene, and $7.6 \times 10^9 M^{-1}s^{-1}$ in DMF at 20 °C. The causes of these differences are discussed in section 3.6.

In synthetic O-ATRP experiments, monomers are used in high concentrations to increase polymerization yields. Because these monomers are typically low-polarity molecules, the polarity of the reaction mixture will be lower than that of the solvent. To investigate this effect, we also measured the rate constant for ET for a solution of 3.2 mM PC-O2 with 0.3 M MBP in 20 mL dichloromethane, to which the monomer
isoprene was added in increasing aliquots up to a final concentration of 2 M. At the higher isoprene concentrations, the measured $k_{\text{ET}}$ value is larger than for PC-O2 and MBP in DCM alone. Instead, at a 2-M concentration of isoprene, $k_{\text{ET}} = 2.6 \times 10^9 \, M^{-1} \, s^{-1}$ is closer to the value obtained in toluene-d$_8$ (see Table 2), most likely because the dielectric constant for isoprene is similar to that of toluene. As most of the monomers used in ATRP studies are low-polarity molecules, our $k_{\text{ET}}$ values in dichloromethane and toluene should serve as good approximations for the solvent mixtures used in O-ATRP.

**Table 2.** Rate Coefficients for Bimolecular ET between PC*(S$_1$) and MBP in Toluene-d$_8$, DCM, and DMF.\(^{(a)}\)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$k_{\text{ET}}$(S$_1$)/($10^9 , M^{-1} , s^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Toluene</td>
</tr>
<tr>
<td>PC-N1</td>
<td>38 ± 6(^{\dagger})</td>
</tr>
<tr>
<td>PC-N2(^{(b)})</td>
<td>13 ± 0.2</td>
</tr>
<tr>
<td>PC-N3 (^{(b)})</td>
<td>2.90 ± 0.04(^{#})</td>
</tr>
<tr>
<td>PC-N4 (^{(c)})</td>
<td>-</td>
</tr>
<tr>
<td>PC-N5 (^{(d)})</td>
<td>3.1 ± 0.1</td>
</tr>
<tr>
<td>PC-O1</td>
<td>17 ± 1(^{#}) (33 ± 2)</td>
</tr>
<tr>
<td>PC-O2</td>
<td>2.3 ± 0.1</td>
</tr>
<tr>
<td>PC-O3</td>
<td>3.4 ± 0.1</td>
</tr>
<tr>
<td>PC-S</td>
<td>1.4 ± 0.1</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Most of the $k_{\text{ET}}$ values reported are from the analysis of TVAS data; TEAS values are instead reported where TVAS data have poorer signal to noise ratios. $k_{\text{ET}}$ values obtained from both methods are shown for PCs where possible, with values with the larger standard fitting errors shown in parentheses. \(^{(b)}\) The rate coefficient in DCM was reported previously by Koyama et al.\(^{36}\) \(^{(c)}\) No electron transfer was observed for PC-N4. \(^{(d)}\) Values reported previously by Lewis-Borrell et al.\(^{35}\) \(^{\#}\) value obtained from TEAS data. \(^{\dagger}\) Rate coefficient obtained by Smoluchowski kinetic analysis.

### 3.4. Reaction from $^3$PC*(T$_1$) States.

Electron transfer from $^3$PC*(T$_1$) is deemed to be desirable in photoredox catalysed synthetic procedures because of the relatively longer lifetimes of triplet states and the lower likelihood of reaction quenching by back electron transfer.\(^{9}\) Therefore, a preference for PCs with high ISC yields and long-lived triplet states has motivated the design of new PCs for O-ATRP applications. Thus far, we have only looked at the electron transfer dynamics from the S$_1$ states of PCs. In part, this is because at the concentrations of MBP used in these studies, the electron transfer is dominated by the S$_1$ state in all cases. Evidence for a negligible role of the triplet states in most of the studied PCs (Figure 1(b))
comes from the $^1\text{PC}^*(S_1)$, $^3\text{PC}^*$(D$_0$) and MP$^*$ radical kinetic traces all being fitted to the same time constants. Moreover, for several of the PCs, ISC efficiencies are low (Table 1),$^{34}$ hence ET is favoured from singlet excited states. However, this is not the case for PC-N2, PC-O1, PC-O2 and PC-S, which show high ISC yields irrespective of the solvent used. While the absence of triplet state signatures in the TVAS data for PC-N2, PC-O1 and PC-S makes it difficult to investigate the reactivity of the triplet state exclusively, TVAS data for PC-O2 in toluene-d$_8$ show a triplet band at 1482 cm$^{-1}$ (also seen in DCM), as shown in Figure 5(a). With increasing MBP concentrations from 0.02 - 0.15 M (6 to 50 equivalents) in a 3.2 mM PC-O2 solution in toluene-d$_8$, we observe that this band decays faster, as can be seen from the kinetic traces in Figure 5(b). Moreover, by observing the recovery of the GSB band at 1489 cm$^{-1}$ (Figure 5(c)), as well as the decay of the PC$^*$(S$_1$) band and growth of the $^3\text{PC}^*$(T$_1$) band, we find that the reaction is competitive between S$_1$ and T$_1$ states, because with increasing MBP concentrations, the S$_1$ state population also decays faster. Figure 5(d) shows the pseudo first-order rate coefficients for ET from the S$_1$ and T$_1$ states (fitted using equation (6) for the S$_1$ state, and methods discussed in Supporting Information for the T$_1$ state). Linear fits gives bimolecular rate coefficients of $k_{ET}(S_1) = (2.6 \pm 0.4) \times 10^9 \text{M}^{-1}\text{s}^{-1}$ for reaction from the S$_1$ state and $k_{ET}(T_1) = (2.1 \pm 0.5) \times 10^7 \text{M}^{-1}\text{s}^{-1}$ for reaction from the T$_1$ state (which could include a component of T$_1$ quenching to S$_0$ by the MBP). At MBP concentrations of 0.4 M or higher, we do not see the T$_1$ band for PC-O2, which shows that at these concentrations, most of the PC$^*$(S$_1$) state reacts with MBP before ISC can occur. However, it is important to note that under synthetic conditions, the PC:MBP concentrations used are in a 1:10 ratio, similar to that for data plotted in Figure 5, which shows that for PCs with high ISC yields, ET can happen from both S$_1$ and T$_1$ states under synthetically relevant concentrations.

The comparative magnitudes of the ET rate coefficients for the PC$^*$(T$_1$) and PC$^*$(S$_1$) states will depend markedly on the energetics of the excited states, as well as their reduction potentials for reaction with the radical initiator. Jockusch and Yagci$^{55}$ reported studies on singlet and triplet reactivities of N-phenyl phenothiazine using fluorescence lifetime measurements (for ET from S$_1$) and laser flash photolysis (for...
ET from T1). They found that when using methyl α-bromoisobutyrate (MBI) as a radical initiator in N,N-
dimethylacetamide, the rate coefficients for singlet and triplet state reactivity differed by two orders of
magnitude (10⁹ vs 10⁷ M⁻¹ s⁻¹ respectively). In contrast, using ethyl α-bromophenylacetate (EBPA) as
an electron acceptor / initiator, the rate coefficients of ET from PC*(S1) and PC*(T1) were comparable
(~10⁹ M⁻¹ s⁻¹). They reasoned that the difference in reactivity arises from the less favourable reduction
potential for MBI (-0.52 V vs. SCE) compared to EBPA (~0.22 V vs. SCE) as well as the lower reduction
potential of the PC*(T1) than the PC*(S1) state for N-phenyl phenothiazine. Given that MBP is reported to
have a reduction potential (-0.56 V vs SCE) with a value similar to MBI, and that the reduction potential
for the PC-O2*(S1) state (-2.06 V) is higher than that of T1 (-1.90 V), our observations of 100-fold faster
ET from the S1 than the T1 state of PC-O2 are in accord with those of Jockusch and Yagci.

3.5. Photochemical Quenching Quantum Yields from PC*(S1/T1) States.

An important metric for synthetic chemists is the quantum yield for quenching of PC* excited states by
alkyl halides. Values for the PCs studied here can be calculated for both the singlet and triplet excited states
using measured singlet and triplet lifetimes, the rate constants for electron transfer from each state, and the
concentration of MBP used. The required formulas are given in the SI section S7, and Table S2 reports
example values of quenching quantum yields for the S1 states of all nine PCs at two different concentrations
of the MBP quencher. Quenching of triplet state PCs by dissolved oxygen in our solutions prevents us from
determining the unquenched triplet state lifetimes; nevertheless, we can make a reasonable estimate of T1-
state quenching yields if these lifetimes are much longer than the lifetimes in the presence of the MBP
quencher. At the concentrations of MBP used in this study, we find that for the nine PCs examined, the S1
state is in large part quenched by MBP. For example, at a concentration of 0.4 M, the greatest extent of S1
quenching is observed for PC-N1 (99%), and lowest extent is observed for PC-N3 (42%). Consequently,
even for PCs with high ISC efficiencies, at these MBP concentrations most of the PC(S1) will undergo
bimolecular ET in preference to crossing to the triplet state manifold. The lower quenching quantum yield
for PC-N3 derives from its short $S_1$ lifetime and relatively smaller rate constant for ET to MBP, not from ISC.

Of particular interest are ET yields at the experimental concentrations of MBP (10 - 50 mM MBP) typically used in polymerization experiments. For LE catalysts with relatively long lived $S_1$ states (see Table 1) such as PC-N1 and PC-N2, even at concentrations as low as 10 mM, the quantum yield for $S_1$-state quenching by MBP is calculated to be 0.80. The corresponding quantum yields are significantly smaller for CT catalysts (e.g., 0.09 for PC-N5 and 0.02 for PC-N3), but this does not imply that quenching occurs by ET from the triplet state because the quantum yields for this process are also very small. Instead, the $S_1$ state is mostly relaxing by radiative and internal conversion pathways.

The above analysis identifies an important distinction between the CT and LE catalysts studied here: for LE catalysts with long $S_1$ lifetimes, even at low concentrations of MBP most of the ET reactivity will come from the $S_1$ state irrespective of their ISC efficiencies. In contrast, for CT catalysts with high ISC efficiencies, ET from triplet states will become important at the concentrations of MBP used in O-ATRP. For example, for PC-O2 at 10 mM MBP concentration in toluene, only 5% of the $S_1$ state is quenched by ET, whereas up to 70% of the ET happens from the $T_1$ state. While quenching by O$_2$ makes it difficult for us to determine the exact lifetime of the $T_1$ state, and hence its quenching quantum yield, an upper limit of this $T_1$-state reactivity will be given by the $T_1$ quantum yield. Interestingly, even at such low reactivity from their $S_1$ states, both PC-N3 and PC-N5, which show no ISC, are reported to exert good control over polymerization, giving low polymer dispersity and high monomer conversion.$^{23}$ These combined observations suggest that for O-ATRP, only very low concentrations of the radical are necessary to obtain good polymerization control.
3.6. Modified Marcus Theory for Kinetic Evaluation of the ET Mechanism. As discussed in section 3.3, there is a clear trend of larger rate-coefficients for ET to MBP from the PC*(S₁) states with LE character compared to PC*(S₁) states with CT character. To understand this trend, we invoke the “sticky” model of dissociative electron transfer which is a modification to Marcus-Savéant theory. Electron transfers to alkyl halides are known to be concerted dissociative processes in which C–X bonds dissociate promptly
upon RX accepting an electron from the photoexcited PC*. The Gibbs energy of activation for this
dissociative ET is determined by the Marcus-Savéant model to be:

$$\Delta G^\ddagger = \frac{E_{BD} + \lambda_0}{4} \left(1 + \frac{\Delta G_{ET}}{E_{BD} + \lambda_0}\right)^2$$

(12)

where $E_{BD}$ is the dissociation energy of the C–X bond, $\lambda_0$ is the solvent reorganization energy, and $\Delta G_{ET}$ is the Gibbs energy for electron transfer, given by equation (1).

$$\Delta G_{ET} = F\{E^0(PC^*/PC) - E^0(RX/R^-X^-)\} - E(PC^*(S_1)) - \frac{N_Ae^2}{4\pi\varepsilon_0\varepsilon_r}$$

(13)

In this equation, $E^0$ are reduction potentials and $E(PC^*(S_1))$ is the energy of the S₁ state of the PC in a given solvent, which is estimated here using the wavelength of the onset of emission of the PC in that solvent.²⁰ The last term in equation (13) corresponds to the Coulombic interaction between the ionic products of the ET reaction. We restrict this analysis to DMF, as the oxidation and reduction potentials of PC and RX used to determine $\Delta G_{ET}$ were measured in either acetonitrile or DMF. As acetonitrile and DMF have similar dielectric constants, we approximate that the acetonitrile values of redox potentials can be used for studies in DMF (see SI section S11 for details).

Isse et al. showed that the kinetics of activation of copper-catalysed ATRP were better described by modifying the Marcus-Savéant model to account for the X⁻ ion from dissociative electron attachment interacting with the R⁺ radical, forming an ion-radical pair. This modification involved adding a further interaction energy $D_p$ to equation (1).²¹ The resulting model is known as the “sticky” model of dissociative electron transfer and was later shown by Matyjaszewski and co-workers to apply to electron transfer from organic phenothiazine based catalysts to RX.²⁰ According to this model, the Gibbs energy of activation becomes:

$$\Delta G^\ddagger = \frac{\lambda_0 + \sqrt{E_{BD} - D_p}}{4} \left(1 + \frac{\Delta G_{ET} - D_p}{\lambda_0 + \sqrt{E_{BD} - D_p}}\right)^2$$

(14)

This activation energy can then be used to calculate the rate coefficient for the ET process using
\[ k_{\text{ET}} = Z e^{-\frac{\Delta G^\ddagger}{RT}} \]  

(15)

where \( Z \) is the collision frequency and \( R \) is the gas constant. Details of the calculation of \( Z \), and other parameters in equations (14-15) can be found in the Supporting Information.

Table 3 shows the important parameters for each PC in DMF, and it compares the calculated and experimentally measured values of the rate coefficients for ET. The comparisons made in Table 3 show that for most PCs in DMF, the calculated and measured \( k_{\text{ET}} \) values are in reasonable agreement, suggesting that the sticky model of dissociative ET is applicable to the PC\(^*\) + MBP systems studied in this work. Not including the sticky correction to the Marcus-Savéant model yields \( k_{\text{ET}} \) values that do not agree as well with the experimental results. The predicted values are reasonable for the PCs with CT \( S_1 \) character, while the model overestimates the \( k_{\text{ET}} \) values for locally excited PCs because these ET reactions are diffusion-limited, and thus experimentally \( k_{\text{ET}} \) is not determined by the electron transfer step. In addition, the activation energy \( \Delta G^\ddagger \) values in Table 3 account for trends in PC\(^*\) electron transfer rates observed experimentally in DMF. As discussed earlier, for PC-N1, PC-N2, and PC-O1, which have LE character in their \( S_1 \) state, we see near diffusion-controlled \( k_{\text{ET}} \) values, whereas for the other PCs with CT character, ET from the \( S_1 \) state is slower. PC-N1, PC-N2, and PC-O1 have lower activation energies for electron transfer compared to the other PCs, which is why these PCs have faster ET rates.

Using the data shown in Table 3 and SI Table S4, we can plot the experimental \( k_{\text{ET}} \) against \( \Delta G_{\text{ET}} \) for DMF, commonly referred to as a Rehm-Weller plot, and our data are shown in Figure 6. The upward trend in the value of \( k_{\text{ET}} \) with increasingly negative \( \Delta G_{\text{ET}} \) values can be seen for the PCs. The calculated values of \( k_{\text{ET}} \) for each PC are plotted for comparison, with any values predicted to be above the diffusion limit capped at the estimated diffusion-limited rate coefficient in DMF at 20°C for better comparison.
Table 3. Calculated Values of Activation Energies, Rate Coefficients and Relevant Thermodynamic Parameters Required for the Sticky Model of Dissociative Electron Transfer.(a)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Excited state character ((S_i \text{ and } T_i))</th>
<th>Measured (k_{ET}/(10^9 \text{ M}^{-1}\text{s}^{-1}))</th>
<th>(\Delta G_{ET}/(\text{kJ/mol}^{-1}))</th>
<th>(\Delta G^\ddagger/(\text{kJ/mol}^{-1}))</th>
<th>(Z/(10^{11} \text{ s}^{-1}))</th>
<th>Calculated (k_{ET}/(10^9 \text{ M}^{-1}\text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-N1</td>
<td>LE</td>
<td>10 ± 1</td>
<td>-206.4</td>
<td>1.93</td>
<td>2.96</td>
<td>134(e)</td>
</tr>
<tr>
<td>PC-N2</td>
<td>LE</td>
<td>22 ± 1</td>
<td>-211.5</td>
<td>1.56</td>
<td>2.52</td>
<td>133(e)</td>
</tr>
<tr>
<td>PC-N3</td>
<td>CT</td>
<td>2.8 ± 0.4</td>
<td>-152.7</td>
<td>9.53</td>
<td>2.67</td>
<td>5.3(d)</td>
</tr>
<tr>
<td>PC-N4</td>
<td>CT</td>
<td>(\lambda(\text{b}))</td>
<td>-</td>
<td>-</td>
<td>2.81</td>
<td>-</td>
</tr>
<tr>
<td>PC-N5</td>
<td>CT</td>
<td>1.8 ± 0.1(\text{c})</td>
<td>-155.1</td>
<td>9.07</td>
<td>2.67</td>
<td>6.5(d)</td>
</tr>
<tr>
<td>PC-O1</td>
<td>LE</td>
<td>10 ± 1</td>
<td>-224.2</td>
<td>0.75</td>
<td>2.58</td>
<td>190(e)</td>
</tr>
<tr>
<td>PC-O2</td>
<td>CT</td>
<td>2.0 ± 0.3</td>
<td>-147.1</td>
<td>10.7</td>
<td>2.72</td>
<td>3.4</td>
</tr>
<tr>
<td>PC-O3</td>
<td>CT</td>
<td>3.6 ± 0.2</td>
<td>-156.0</td>
<td>11.4</td>
<td>4.08</td>
<td>3.8</td>
</tr>
<tr>
<td>PC-S</td>
<td>CT</td>
<td>1.9 ± 0.1</td>
<td>-131.2</td>
<td>14.3</td>
<td>2.47</td>
<td>0.7</td>
</tr>
</tbody>
</table>

(a) For all the PCs studied, parameters correspond to electron transfer to MBP in DMF solution at a temperature of 293 K. (b) No ET observed. (c) Value reported previously. (d) The higher calculated \(k_{ET}\) value could result from errors in \(\Delta G_{ET}\) because of the difficulty in determining the onset emission wavelengths for these PCs in DMF, and/or because the \(E^0(\text{PC}/\text{PC})\) values used were measured in acetonitrile for the PC-N species. (\text{e}) Values will be limited by diffusion.

Comparing the values of \(k_{ET}\) in Table 3, and also in Figure 6, shows that in DMF solutions, the values of \(\Delta G_{ET}\) are more negative for the PCs with LE electronic states compared to the CT character PCs. It is the more exothermic \(\Delta G_{ET}\) values that result in small (1-2 kJ/mol) activation energies for ET from the LE catalysts, which in turn lead to the values of \(k_{ET}\) being close to the estimated diffusional rate coefficients for DMF at 20 °C. Therefore, \(\Delta G_{ET}\) can be classified as one of the most important factors in the design of such PCs for ATRP, an argument which was also developed in our prior publications.\(^{35-36, 44}\) A recent study by Damrauer and co-workers of four phenoxazine based PCs adopts a similar argument.\(^{56}\)
Figure 6. A Rehm-Weller plot for the rate coefficients for electron transfer from the photoexcited PCs shown in Figure 1(b) to MBP in DMF. The symbols representing each PC are specified in the inset legend. PCs with locally excited $S_1$/$T_1$ character are represented by hollow symbols and PCs with charge transfer $S_1$/$T_1$ character are shown as filled symbols. Calculated $k_{ET}$ values are shown for comparison as grey circles and the curved line is added to guide the eye. Calculated values for $k_{ET}$ that exceed the diffusion limit are capped at the predicted diffusion-limited rate coefficient in DMF at 20 °C for better comparison with experiment.

4. CONCLUSIONS

The kinetics of the O-ATRP activation step involving electron transfer from the excited state of a photocatalyst to a radical initiator have been studied using the complementary techniques of transient vibrational and electronic absorption spectroscopies. Rate coefficients are reported for ET reactions of nine different organic PCs, selected from the classes of N,N-diaryl dihydrophenazines, N-aryl phenoxazines and N-aryl phenothiazines, with the electron acceptor methyl 2-bromopropionate. These rate coefficients were determined by concentration dependent studies using TEAS and TVAS to measure the loss of photoexcited
PC* (S\textsubscript{1}/T\textsubscript{1}), and TVAS to monitor the growth of the radical product of a dissociative electron transfer to MBP. These PCs all possess highly reducing S\textsubscript{1} and T\textsubscript{1} states, so are attractive candidates for photoredox catalysis, but are known to have varying degrees of control over polymerization from prior synthetic studies. Irrespective of whether they have a long-lived T\textsubscript{1} state, the catalysts with S\textsubscript{1} states of locally excited character were previously shown to be inferior to their counterparts with charge-transfer excited-state character in their control over polymer dispersity.

This behaviour can in part be explained by the current studies. The rate coefficients for ET from the PC(S\textsubscript{1}) state to MBP reveal an important distinction: ET-reactions of the LE catalysts have nearly diffusion-controlled rate coefficients, whereas those for CT catalysts are 5-10 times smaller. The origins of this difference are explained by a modified Marcus-Savéant model, the “sticky” model of dissociative electron transfer. Using this model, we predict that the LE-character catalysts have small Gibbs energies of activation ($\Delta G^\ddagger = 1-2$ kJ/mol) for electron transfer to MBP compared to the CT-character catalysts ($\Delta G^\ddagger = 9-14$ kJ/mol) in DMF. These differences arise from the Gibbs energy changes for the electron transfer. We propose that the faster rates of ET from the LE-character catalysts may be detrimental for their performance as O-ATRP catalysts because they lead to poorer control of MP\textbullet radical concentrations, resulting in polymers with higher dispersity. While it could be argued that a low (e.g., ppm) loading of the PC and/or the MBP initiator might therefore improve the control of the polymerizations, the photoredox cycle deactivation step may also play a major role in determining what makes a PC a good candidate for controlled ATRP.

The concentrations of MBP used in most of these studies are between 50 and 1000 equivalents of the PC concentration. At these high concentrations, we find the ET is predominantly from the PC*(S\textsubscript{1}) state, even for PCs with high triplet quantum yields. At these high MBP concentrations, ET serves as the primary channel for PC*(S\textsubscript{1}) quenching, and it outcompetes the radiative or non-radiative decay back to the ground state and ISC to the triplet manifold. Our analysis of the MBP-dependent decay of the T\textsubscript{1}-state population seen in TVAS data for PC-O2 shows that at synthetically relevant concentrations of radical initiator (10
equivalents of [PC]), the ET reaction can happen from both $S_1$ and $T_1$ states for PCs which have sufficiently high ISC quantum yields. The absence of triplet state signatures in the TVA spectra for other PCs prevented further such studies.

The solvent and photocatalyst dependent kinetic parameters of excited state lifetimes, ISC timescales, and electron transfer rate coefficients derived from our measurements can be used to make quantitative estimations of the quantum yields for excited-state quenching by the electron acceptor MBP, and their variation with MBP concentration. Interesting insights emerge from this analysis about the balance between the efficiencies of electron-transfer from the $S_1$ and $T_1$ states. When compared with synthetic data, this analysis shows that for O-ATRP, a high ISC efficiency is not necessarily required for a PC to be effective at controlling polymerization. For example, PC-N3 and PC-N5 have short $S_1$ lifetimes and low triplet quantum yields, with the consequence that at MBP concentrations relevant to polymer synthesis, less than 5% of the PC* $S_1$ states are quenched by MBP. Yet these PCs have been shown to exert good control over polymerization, with high monomer conversions and low polymer dispersity. In contrast, LE catalysts such as PC-N1 and PC-N2, show much higher quenching quantum yields from their $S_1$ states, but are poorer at polymerization control. For PCs with high ISC efficiencies, reaction from the triplet state will be the major contributor at synthetic MBP concentrations, but the polymer growth will depend on the $k_{ET}$ and hence the PC*$\text{(T}_1\text{)}$ reduction potential. While an outcome that may not hold true for all PCs and radical initiators, for PC-O2 the rate coefficient for electron transfer to MBP from the $T_1$ state, with a reported reduction potential of -1.90 V, is two orders of magnitude smaller than that for the $S_1$ state, which has a reduction potential of -2.06 V in toluene-$d_8$.

The extensive study of the nine catalysts based on three different core structural motifs reported here brings important insights to PC design for O-ATRP. We find that while long-lived triplet states for PCs may be a desirable property in many photoredox catalysed synthetic chemistry processes, for ATRP this is not a defining factor in designing a good photocatalyst for polymer dispersity control. Instead, the design of
these catalysts can be based on quantifiable thermodynamic parameters such as Gibbs energies of electron transfer which control the activation and deactivation steps.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at [to be completed when the manuscript is accepted for publication].

FTIR and UV-Vis Spectra for each organic photocatalysts in DCM and for their oxidized forms; fluorescence spectra for the organic photocatalysts in DMF; TVAS and TEAS spectra for PC with MBP solutions for the PCs and solvents used; kinetic modelling; kinetic analysis of experimental data for the PCs in Toluene, DCM and DMF; comparison of rate coefficients obtained by biexponential and Smoluchowski theory data analysis methods; spectral decomposition of TEA data; calculations of thermodynamic and kinetic factors for PCs using the sticky model of dissociative electron transfer.
Data Availability

Data are available at the University of Bristol data repository, data.bris, at https://doi.org/10.5523/bris.jud6zf0aehpn2pjwv1klmba58.

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