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Addition/Correction

Correction to "Light Directs Monomer Coordination in Catalyst-Free Grignard Photopolymerization"

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The original article stated that the excited-state lifetime of the polymer radical anion was 850 ± 6 ps (Figure S15). However, further analysis of our data (by the expanded research group listed as authors here) revealed that the excited-state lifetime reported is incorrect; it represents the lifetime of the neutral polymer, not a radical anion. Additionally, the *g*-value we observed for doped **P1** likely corresponds to trace metal-centered radical, not an organic radical anion.[1]

We have since found that our original conditions for polymer reduction with sodium napththalenide did not sufficiently reduce **P1**. Instead, excess Na metal does reduce **P1**, which we confirmed with UV−vis absorption and spectroelectrochemistry (Figures S24 and S25, respectively, in the revised Supporting Information presented here). The corrections include updated CW-EPR and femtosecond transient absorption spectroscopy (fsTA) data to reflect the reduced species. The corrected excited-state dynamics are calculated from global wavelength fitting in Matlab (revised Figure S15). Femtosecond transient absorption spectroscopy of $\mathbf{P1}^{\bullet -}$ displays biexponential decay with lifetimes of 0.56 and 4.68 ps. The shorter lifetime of 0.56 ps can be attributed to either vibrational relaxation or internal conversion from a higher-lying excited state.[2−4] The longer lifetime of 4.68 ps can be assigned as the excited-state lifetime of the **P1** radical anion. These data and experimental procedures have been included in the revised Supporting Information.

We have also re-collected the CW-EPR of reduced **P1** and the reaction mixture (updated Figure 2 below). Based on the instability of reduced **P1** in air, greater care was taken to exclude oxygen from the samples when they were transferred from the glovebox to the instrument, which allowed detection of the radical anion of interest. The *g*-value of the chemically reduced **P1** radical anion is 2.0035, and that of the reaction mixture is 2.0033, both of which are in agreement with the values for a dimer radical anion from a report by King and Zhukhovitskiy published after our original article.[1] The caption of Figure 2 has been corrected to reflect the revised procedure and data.

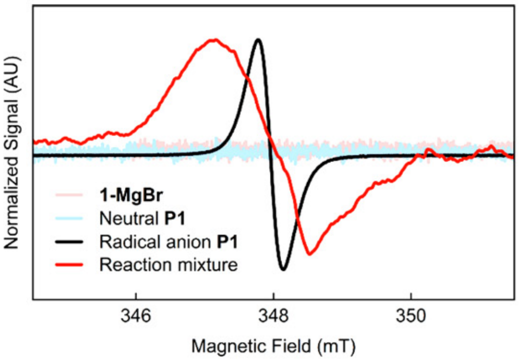
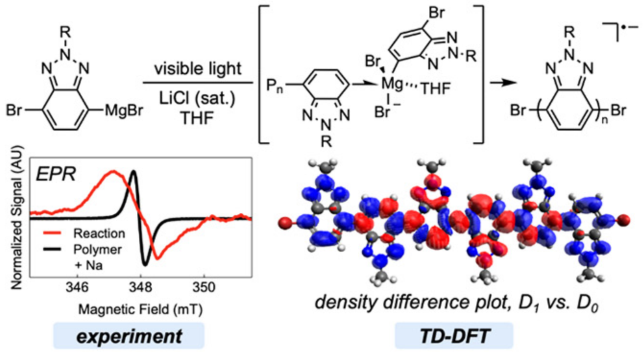


Figure 2. Continuous-wave electron paramagnetic resonance spectra of neutral **P1**, isolated and chemically reduced **P1**, **1-MgBr**, and polymerization reaction mixture (see SI for details).

The TOC graphic was also updated to include the updated CW-EPR data, as shown below:



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These revised data do not change our hypothesis or the conclusions in the original article.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c06271.

> Synthetic procedures; details of the computational methods; characterization data for new compounds; visualized HOMO and LUMOs of relevant structures; XYZ coordinates of calculated structures, with revised reduction procedure and corrected spectroelectrochemistry and transient absorption data (PDF)

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