

Correction to “Modeling and characterization of exciplexes in photoredox CO₂ reduction: Insights from quantum chemistry and fluorescence spectroscopy”

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This is a correction to the article titled, “Modeling and Characterization of Exciplexes in Photoredox CO₂ Reduction: Insights from Quantum Chemistry and Fluorescence Spectroscopy,” Kareesa J. Kron, Jonathan Ryan Hunt, Jahan M. Dawlaty, and Shaama Mallikarjun Sharada The Journal of Physical Chemistry A 2022 126 (15), 2319-2329.
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The structure of OPP-3* reported in pg. 2323 (Figure 4(a)) of the article is incorrect because the TDDFT optimization routine followed a mode other than the first excited state. Following the correct mode using the ω B97X-D/def2-TZVP level of theory leads to the structure reported in Figure 1(a), a correction to Figure 4 in the article. We are grateful

to George Baffour Pipim and Prof. Anna Krylov (USC) for pointing out and correcting the error.

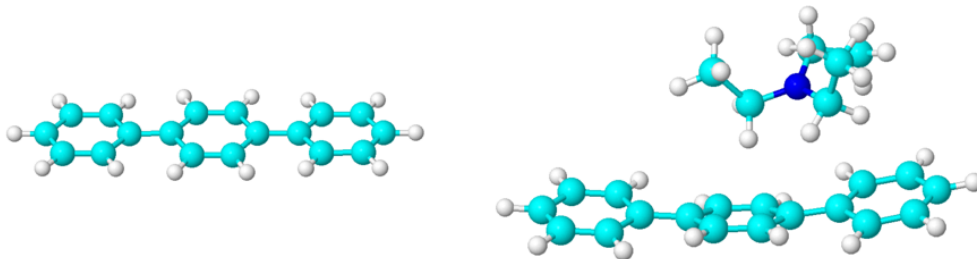


Figure 1: Correction to Figure 4 in the article – Optimized structures of (a) isolated OPP-3*, and (b) [OPP-3-TEA]* exciplex geometry. C: cyan; H: white; N: blue.

The choice of B3LYP-D3 for optimization of OPP-3* and OPP-4* instead of ω B97X-D was justified in the article (pg. 2321) based on ground state dipole moments and solvatochromic shifts arising from the incorrect geometry. In this correction, we report excited state dipole moments (obtained using excited state analysis) for the correct structures, optimized using both B3LYP-D3/6-311G** and ω B97X-D/def2-TZVP level of theory in Table 1. Consistent with experimental observations of higher solvatochromism for the exciplex, the excited-state dipole moment for the exciplex is higher than that of isolated OPP-3*. Therefore, the statement in the article recommending B3LYP optimization for OPP* (pg. 2321) is not entirely justified. Figure 2(a) is a correction to Figure 7(a) of the article, obtained by following the correct mode and re-optimizing all OPP* geometries with ω B97X-D. Figure 2(b) is identical to Figure 7(b) of the article.

Table 1: Calculated excited state dipole moments (Debye) for OPP-3* and [OPP-3 TEA]*.

System	ω B97X-D/def2-TZVP	B3LYP-D3/6-311G**
OPP-3*	0.00043	0.00051
[OPP-3-TEA]*	11.98982	15.33275

For the correct, planar OPP* geometries, calculated emission energies are red-shifted relative to experiment. Emission wavelengths range from 354 nm in cyclohexane to 372 nm in dichloromethane for OPP-3* and 382 nm to 400 nm for OPP-4*. This observation runs

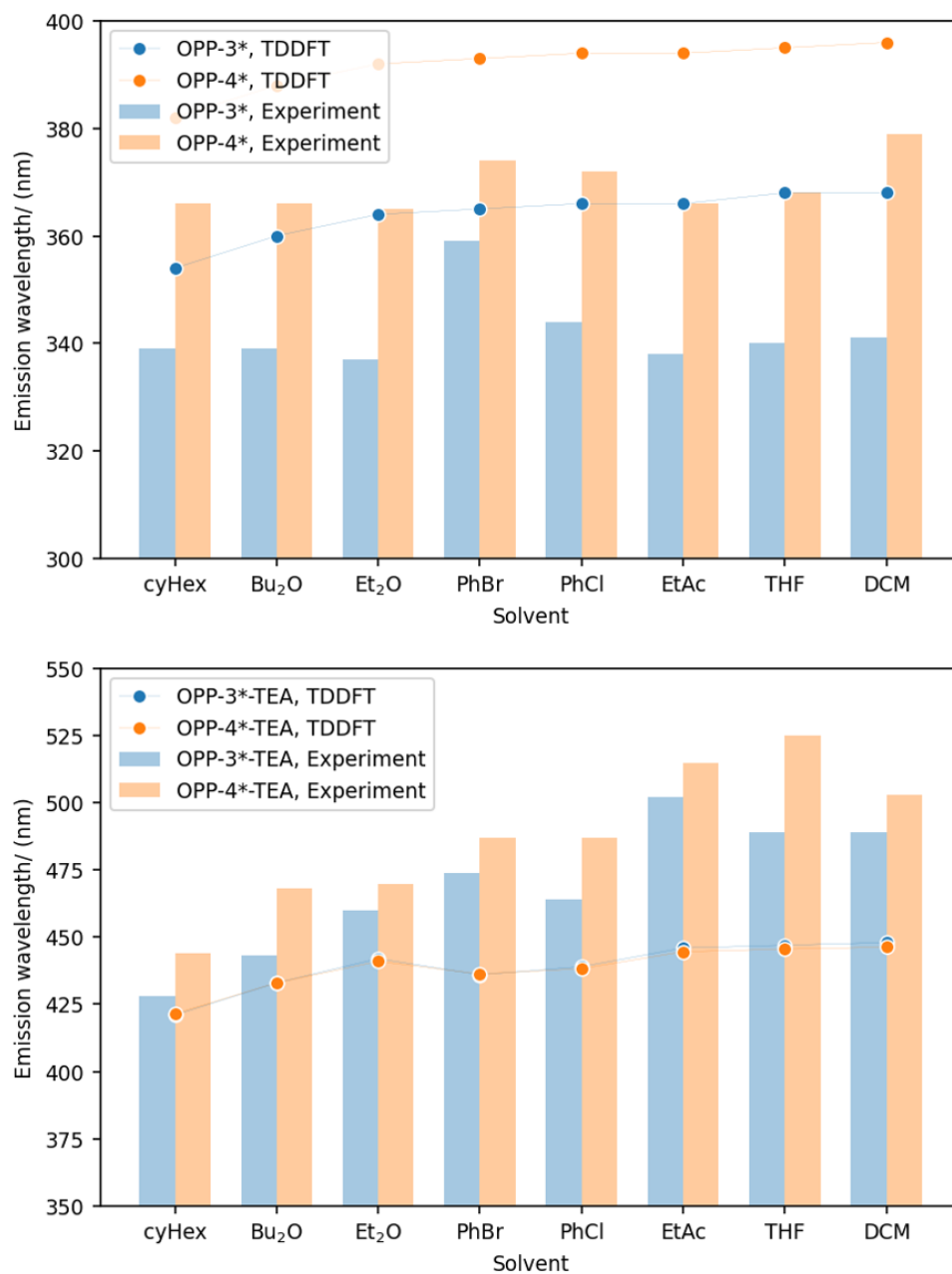


Figure 2: Emission wavelengths for OPP-3 and OPP-4 for (a) isolated catalysts (geometry optimized at ω B97X-D/def2-TZVP level of theory), and (b) their exciplex state with TEA (geometry optimized at ω B97X-D/def2-TZVP level of theory). All emission energies are calculated at the ω B97X-D/def2-TZVP level of theory using non-equilibrium solvation.

counter to prior TDDFT studies cited in the article (pg. 2325) that report blue-shifts of emission wavelengths obtained using hybrid and range-separated hybrid functionals. One possible reason for this that is grounds for future studies is that experimental and calculated vertical emission wavelengths cannot be directly compared without explicitly considering vibronic transitions, determined using Franck-Condon overlap integrals.

Supporting Information Available

Supporting information contains the emission wavelengths of the exciplex state calculated with non-equilibrium and equilibrium solvation for several solvents as well as experimental emission energies. Natural transition orbitals are also shown for isolated OPP-3, [OPP-3-TEA]* and the CH-modified system. Cartesian XYZ coordinates for all geometries constituting the potential energy surface are included. Additional analysis of geometric features of both OPP-3 and OPP-4 interacting with TEA is also presented.