

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

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Abstract

Interactions between excited state arenes and amines can lead to the formation of structures with distinct emission behavior. These excited state complexes or exciplexes can reduce the ability of the arene to participate in other reactions, such as CO₂ reduction, or increase the likelihood of degradation via Birch reduction. Exciplex geometries are necessary to understand photophysical behavior and probe degradation pathways but are challenging to calculate. We establish a detailed computational protocol for calculation, verification, and characterization of exciplexes. Using fluorescence spectroscopy, we first demonstrate the formation of exciplexes between excited state

oligo-(p-phenylene) (OPP), shown to successfully carry out CO₂ reduction, and triethylamine (TEA). Time-dependent density functional theory (TDDFT) is employed to optimize the geometries of these exciplexes, which are validated by comparing both emission energies and their solvatochromism with experiment. Excited state energy decomposition analysis confirms the predominant role played by charge transfer interactions in the red-shift of emissions relative to the isolated excited state OPP*. We find that although the exciplex emission frequency depends strongly on solvent dielectric, the extent of charge separation in an exciplex does not. Our results also suggest that the formation of solvent-separated ionic radical states upon complete electron transfer competes with exciplex formation in higher dielectric solvents, thereby leading to reduced exciplex emission intensities in fluorescence experiments.

Introduction

By accessing highly reactive radical states through photo-induced excitation and quenching, photoredox catalysts have immense potential as sustainable alternatives to otherwise energy-intensive, thermally activated reaction pathways.^{1,2} Organic catalysts present the added benefit over their inorganic counterparts of eliminating dependence on heavy metals, such as Ru and Ir, that constitute the most widely studied class of photoredox catalysts.³⁻⁵ Experimental studies demonstrate successful reduction of CO₂ with organic chromophores known as oligo-p-phenylenes (OPPs) to synthesize formate, amino acids, and hydrocarboxylated styrene.⁶⁻⁸ The proposed photoredox catalytic cycle for this transformation is shown in Figure 1. OPP is excited to singlet OPP* by UV-vis light. Triethylamine (Et₃N or TEA) quenches OPP* by transferring an electron. The quenched radical anion OPP^{•-} is highly reducing and capable of carrying out the otherwise thermally challenging one-electron reduction of CO₂.

Our previous study describes the electron transfer step from anion radical OPP^{•-} to CO₂ using quantum chemistry methods.⁹ In addition, we uncovered means by which cat-

alytic activity can be enhanced by increasing the electron-donating character of substituents (described by their Hammett parameters¹⁰), or R- groups in Figure 1. However, electron transfer rate coefficients do not exhibit an increase with electron-donating character beyond a certain value of substituent electrophilicity. Rate coefficients exhibit a quadratic dependence on electrophilicity, originating in plateauing free energy driving force as R becomes more electron-donating.

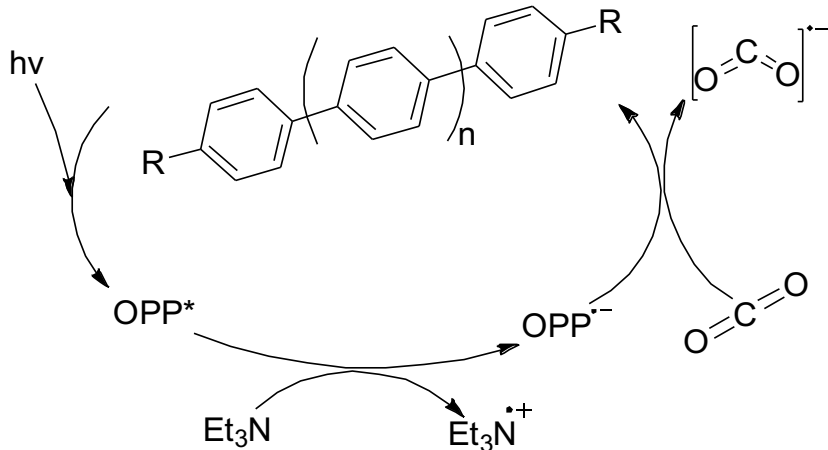


Figure 1: Proposed catalytic cycle of single electron reduction of CO₂ with oligoparaphenylene.^{9,11} This study focuses on OPP-3 and OPP-4 where $n=1$ and 2, respectively, and R = H. Reprinted (adapted) with permission from ref.⁹ Copyright 2020 American Chemical Society.

Understanding the CO₂ reduction step alone, however, is not enough to design a viable photoredox pathway. In addition to the inherent complexity associated with light-assisted pathways, experimental studies show that despite high activity towards CO₂ reduction, these chromophores exhibit very low turnover numbers.^{6,8} Prior studies attribute this to proton capture and subsequent Birch reduction of the chromophore in the case of OPP and carboxylation in the case of chromophores such as phenanthrene, anthracene, or pyrene.^{6,12} It is not yet known at which stage in the photoredox cycle (Figure 1) proton capture occurs or whether the chromophore is in its excited, radical anion, or any other state when capturing a proton.

One possible source of protons is the quenching amine (e.g. TEA) itself, as its α -CH bonds are typically easier to deprotonate compared to similar bonds in an aprotic solvent.¹³ While the proton generation from the amine and capture from solution by the arene radical anion can occur as separate steps, simultaneous deprotonation and proton capture may be favorable when the donor-acceptor species are in close proximity. Such encounter complexes between one species in its ground state and another in its excited state, known as excited-state complexes or *exciplexes*, have been reported to form between amines and arenes.^{14,15} Exciplexes are identified by their broad, red-shifted fluorescence emission peak relative to that of the isolated excited state chromophore. These emission peaks are distinctly visible in low dielectric solvents and peak intensities are concentration dependent due to the fact that exciplexes are encounter complexes.¹⁶ As exciplexes are proposed to form upon close contact of donor and acceptor species, the proton abstraction step of photo-Birch reduction could occur from exciplexes. In other words, the quenching process illustrated in Figure 1^{6,11} does not necessarily always lead to distinct radical anion/cation pairs.

To examine the possibility that degradation is initiated at the exciplex state, one must first calculate the geometry of the exciplex itself. Fluorescence spectroscopy carried out in this study confirms the formation of exciplexes between OPP* and TEA. Quantum chemistry methods are employed to both calculate and characterize the geometries of these exciplexes. We use time-dependent density functional theory (TDDFT) to calculate exciplex geometries formed by OPP-3* and OPP-4* with TEA in solution. The detailed procedure for excited state optimization is presented to serve as a guide for future computational studies. Exciplexes are verified via comparison with experimental fluorescence spectroscopy and solvatochromism and characterized by means of natural transition orbital calculations and excited-state energy decomposition analysis. The broad, red-shifted emission feature associated with an exciplex exhibits both solvatochromic shifts and diminishing intensity with increasing solvent dielectric in fluorescence experiments.^{17,18} In direct contradiction to conventional wisdom, excited-state Mulliken charge analysis reveals that solvent dielectric does

not affect donor-acceptor charge distribution in the exciplex, indicating that the ionic character of the exciplex does not vary with solvent dielectric. On the other hand, a comparison of dielectric dependence of exciplex ($[\text{OPP-TEA}]^*$) energies with those of contact radical ion pairs (CRIP, $\text{OPP}^{\cdot-}\text{-TEA}^{\cdot+}$) and solvent-separated radical ion pair (SSRIP, $\text{OPP}^{\cdot-} - - \text{TEA}^{\cdot+}$) reveals that SSRIPs are energetically more favorable in higher dielectric solvents. Direct formation of SSRIPs from OPP^* and TEA therefore competes with the formation of the exciplex in solvents of high dielectric. This work therefore demonstrates successful computational determination and verification of exciplexes and sheds light on solvent dependence of excited-state quenching processes in arene-amine systems.

Methods

Materials

Para-terphenyl, or the phenylene oligomer consisting of three phenyl groups coordinated in a para-fashion, is referred to as oligo(p-phenylene)-3 or OPP-3, and along similar lines para-quaterphenyl is referred to as OPP-4. OPP-3, OPP-4, triethylamine (TEA), and all solvents are purchased from Sigma Aldrich. All compounds are used without further purification.

Steady-state spectroscopy

Absorption spectra are obtained using a Cary 50 UV-VIS spectrophotometer. Emission spectra are collected on a Jobin-Yvon Fluoromax 5 fluorometer. OPP-3 and OPP-4 solutions of 1×10^{-5} M are used to obtain the steady state spectra in this paper. Measurements are made in a 1 cm fused quartz cuvette.

Computational methods

All simulations are carried out using the *ab initio* quantum chemistry software, Q-Chem version 5.2.1 and above.¹⁹ The conductor-like polarizable continuum model (C-PCM) for implicit solvation^{20–22} is employed for all simulations with the exception of excited state energy decomposition analysis. Time-dependent density functional theory (TDDFT)^{23,24} is widely used for studying excited state characteristics including exciplexes.^{25–29} However, practical difficulties associated with the accurate determination of exciplexes on largely shallow potential energy surfaces as well as their characterization, with some exceptions,^{25,28,30} are rarely addressed. Unlike ground states, physical intuition cannot guide the generation of a starting guess structure for exciplex calculation. In addition, an exciplex may not be completely represented by a single geometry or electronic structure as is indicated by the broad fluorescence peak in experiments.¹⁴ Using the OPP*-TEA system as a representative exciplex, this work aims to illustrate procedural aspects of the calculation as well as characterization of exciplexes using state-of-the-art quantum chemistry methods for excited states.

Optimization of excited states

Excited states are calculated for both isolated OPP-3 (OPP-3*) and OPP-4 (OPP-4*) as well as the corresponding exciplexes, each in the presence of a single TEA molecule. The starting guess is obtained via geometry optimization in the ground state. We describe the TDDFT/C-PCM excited state optimization³¹ protocol in depth as this may serve as a guide to address common operational challenges and high computing costs associated with quantum chemistry studies of excited states.

We do not recommend the use of the low-cost Tamm-Dancoff Approximation (TDA)³² for exciplex optimizations even though prior studies show that TDA can closely replicate TDDFT values of absorption and emission peaks for large conjugated molecules.³³ This is because a TDDFT calculation of the vertical excitation spectrum of OPP-TEA reveals two

states that possess non-negligible oscillator strengths. The higher energy state corresponds to emission out of the excited state of the isolated chromophore, which only weakly interacts with TEA. The second state that is lower in energy corresponds to exciplex emission. TDA fails to identify this critical second state. Therefore, full TDDFT is essential for capturing charge-transfer states in these arene-amine excited state complexes.

Geometry optimization calculations are first carried out at the B3LYP/6-311G** level of theory³⁴ with Grimme’s D3 dispersion corrections^{35–37} and dichloromethane as the representative solvent. Using the Q-Chem defaults for optimization stepsize (0.3 a.u.) can lead to a change in the order of states that possess nonzero oscillator strength. The state-following method in Q-Chem follows a user-defined input state number that does not change when the order of states changes in the course of optimization. To minimize the likelihood of the optimization method deviating away from the correct exciplex mode, the stepsize is reduced to 0.02 a.u. The gradient tolerance is also tightened (to 2×10^{-5} a.u.) from its default value (3×10^{-4} a.u.). These restrictions allow us to follow the correct exciplex state at every step and manually restart the optimization if the state-following algorithm begins to follow an incorrect state.

The converged geometries are subjected to a second optimization step at the desired level of theory. Our prior work studying electron transfer from the OPP-3^{•−} radical anion to CO₂ shows that B3LYP can lead to over-delocalization of electron density that directly affects charge transfer characteristics.³⁸ To overcome this issue, we utilize the ω B97X-D/def2-TZVP level of theory.^{39,40} However, we find no notable change in geometry upon re-optimization at the new level of theory. We therefore prescribe TDDFT optimization with a tractable level of theory (B3LYP/6-311G**) followed by a single point calculation at the desired level to determine the exciplex geometry with reasonable accuracy.

Characterization of Exciplexes

Upon successful convergence of TDDFT geometry optimization, additional steps are necessary to verify that the structure indeed corresponds to an excited state charge transfer complex. Owing to prohibitive computing and memory requirements, Hessian calculations (or vibrational analyses) are not performed to verify that the geometries are minima on the excited state potential energy surface. Instead, we employ both simple model variations as well as sophisticated computational characterization methods to verify and characterize the exciplex.

To determine components that contribute to OPP-TEA exciplex interactions, we utilize excited state energy decomposition analysis,³⁰ which we label ‘exEDA’ to distinguish from ground state EDA methods.^{41–44} This technique uses absolutely localized molecular orbitals^{45–48} to break down the shift in excitation energy occurring due to exciplex formation from an isolated molecule in its excited state into constituent frozen (Pauli repulsion and electrostatics), polarization, and charge transfer terms. Martin Head-Gordon’s group developed and employed exEDA to probe interfragment interactions where one fragment is in its excited state for various excited state dimers (noble gases, arenes), water-charge system, and exciplexes of formamide(halide)-water and pyridine(pyrimidine)-water using ground state and excited state minima, respectively.^{30,49} We apply exEDA to the TDDFT-optimized, solvated exciplex geometries to determine the type of underlying interactions that govern emission shifts in exciplexes. We note that exEDA is carried out in the gas phase as the excited state version of EDA that includes solvation is not yet available in Q-Chem.³⁸

To further confirm that the stability of the exciplex originates in charge transfer from the nitrogen lone pair in TEA to OPP*, we substitute N with CH in the optimized exciplex geometry. If the structure identified via TDDFT optimization is indeed an exciplex, the (lower energy) peak corresponding to exciplex emission is expected to vanish when N is replaced with CH. In other words, only the (higher energy) peak that is closer in energy to the emission of isolated OPP* is retained. We also generate visual representations of

exciplex interactions by means of natural transition orbital (NTO) calculations.^{50–52} NTOs are determined for isolated OPP-3*, the [OPP-3-TEA]* exciplex, and OPP-3* complexed with the CH modification of TEA.

To compare with experimental fluorescence spectra, emission energies are calculated using non-equilibrium PCM models.^{53–57} Non-equilibrium PCM enables a realistic representation of the condensed phase system for fast processes such as absorption and fluorescence. To determine vertical emission energies, the energy difference is calculated between the excited state with its equilibrium solvation shell and the corresponding ground state but without solvent relaxation. As illustrated in Table S1 of the Supporting Information (SI), equilibrium solvation models do not capture experimentally observed solvatochromic shifts in emission spectra for the systems examined here. Emission wavelengths are calculated using both B3LYP/6-311G** and ω B97X-D/def2-TZVP levels of theory. The following solvents are examined – chlorobenzene (PhCl, $\epsilon = 5.6$), bromobenzene (PhBr, $\epsilon = 5.2$), tetrahydrofuran (THF, $\epsilon = 7.6$), diethyl ether (Et₂O, $\epsilon = 4.3$), dibutyl ether (Bu₂O, $\epsilon = 3.1$), ethyl acetate (EtAc, $\epsilon = 6.0$), dichloromethane (DCM, $\epsilon = 8.9$), cyclohexane (cyHex, $\epsilon = 2.0$), and acetonitrile (AN, $\epsilon = 35.7$) – with their respective optical dielectric constants included in the calculation of dielectric response. Calculated emission spectra are contrasted with experiment for isolated OPP-3* and OPP-4* as well as their respective exciplexes, [OPP-3-TEA]* and [OPP-4-TEA]*.

Results and Discussion

Experimental demonstration of exciplex formation

Exciplex fluorescence is found for OPP-3 in cyHex for a range of concentrations of TEA as shown in Figure 2. The red-shifted peaks around 440 nm are broad and increase with increasing concentration of TEA, both of which indicate the formation of encounter complexes with the excited state OPP-3*. Fluorescence of isolated OPP-3* is centered around a

wavelength of 345 nm in cyHex. The spectra are consistent with prior studies across various donor-acceptor combinations, which assign the broad or diffuse red-shifted emission relative to the isolated excited state to an exciplex.^{14,58} The formation of exciplexes between OPP-3* and TEA across solvents of varying dielectric is shown in Figure 3. Solvatochromism is observed for the exciplex emission peaks with lower energy emissions for higher dielectric solvents.¹⁴ The spectra in both Figures 2 and 3 are normalized with respect to the maximum intensity so that their spectral features can be compared.

It is observed that exciplex emission decreases in intensity as the solvent dielectric constant increases, and that emission from the exciplex is no longer observed in solvents with dielectric constants above that of THF ($\epsilon=7.6$). Similar behavior has been observed for a variety of exciplexes in the literature.^{17,59-61} The most common explanation for this phenomenon is that the increased efficiency of charge separation in high dielectric solvents decreases the lifetime of the exciplex, and can even favor electron transfer which avoids the exciplex altogether.⁵⁹⁻⁶¹ This decrease in lifetime or population of the exciplex results in less emission. The emission is extinguished altogether in sufficiently high dielectric solvents. In a later section, we employ quantum chemistry calculations to show that relative energies of exciplexes and fully charge- and solvent-separated species support this hypothesis. Another possible explanation for decreasing emission intensity in high dielectric solvents is that in high dielectric solvents, the ionic character of the exciplex increases, which decreases the exciplex’s radiative rate constant.¹⁷ Computational results (described in a later section) however are in direct contradiction with this possibility as the extent of charge transfer remains about the same across all solvents.

Exciplex features: Geometry and charge transfer

This work outlines computational protocols and methods that can be employed to calculate and characterize the [OPP-TEA]* exciplex. Although there are prior studies that employ TDDFT to calculate excimers and exciplexes,²⁵⁻²⁹ we provide a detailed description of the

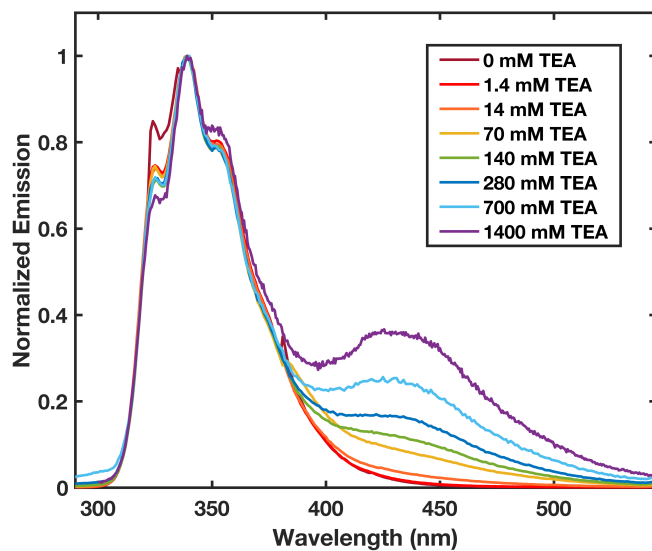


Figure 2: Fluorescence spectra of OPP-3 in cyclohexane in the presence of TEA for various concentrations of TEA.

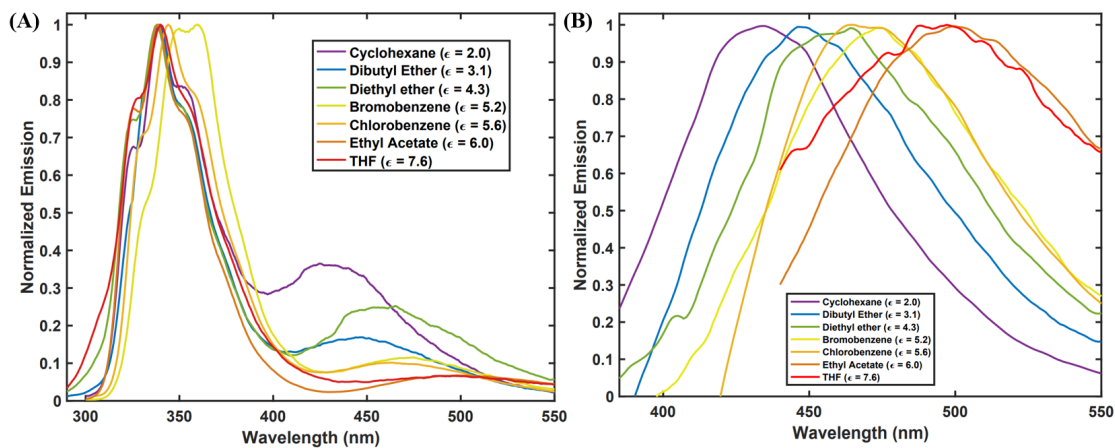


Figure 3: Fluorescence spectra of (A) OPP-3* in the presence of 1.4 M TEA for various solvents and (B) Exciplex emission, normalized for comparison of fluorescence wavelength.

procedure as the optimization is computationally intensive and requires significant user intervention to ensure that the mode-following algorithm follows the correct state on the excited state potential energy surface.

The TDDFT/C-PCM-optimized structures for isolated OPP-3* and the [OPP-3-TEA]* exciplex are shown in Figure 4. Isolated OPP-3* in the relaxed excited state (Figure 4, left) has an alternating tilted structure similar to that of the ground state reported in prior studies of oligophenylenes.^{9,62,63} Significant structural changes occur in OPP-3* upon interaction with TEA. OPP-3* loses the alternating configuration and curves slightly around TEA. As shown in Figure 5, this curvature is also observed in the exciplex formed by OPP-4*. Three of the four phenyl groups in this case create a geometry that closely resembles the [OPP-3-TEA]* exciplex. The fourth phenyl group has a torsional angle that is closer to that of the ground state OPP-4. A visual comparison of the exciplex geometries for the two oligomers suggests that OPP*-TEA interactions are local to the phenyl groups that are closest to TEA.

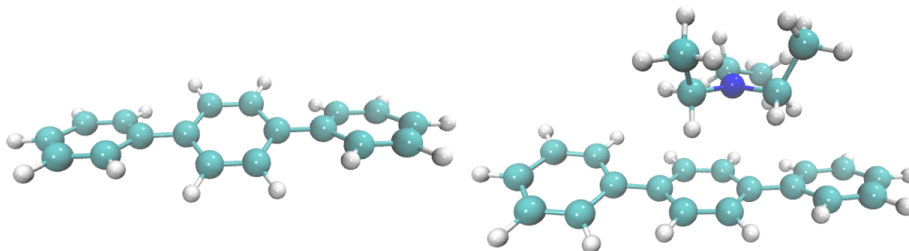


Figure 4: Optimized structure for isolated OPP-3* (left) and the optimized [OPP-3-TEA]* exciplex geometry (right). C: cyan; H: white; N: blue.

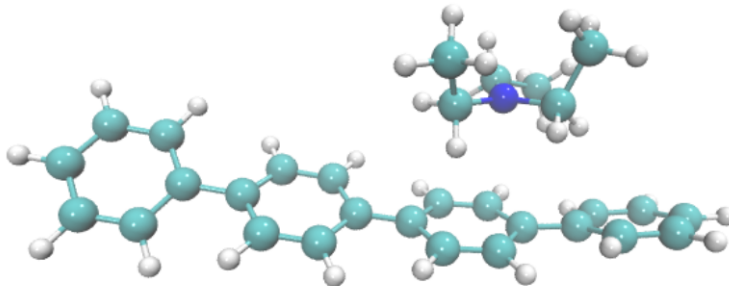


Figure 5: Optimized structure of the [OPP-4-TEA]* exciplex.

To determine whether ground state geometries serve as suitable guesses for exciplexes, we compare the geometries of the OPP-3-TEA complex in the ground state (obtained with DFT) with that of the [OPP-3-TEA]* exciplex (TDDFT). Illustrated in Table S2 of the SI, the exciplex state brings the two fragments closer to each other (from 4.08 Å to 3.84 Å between N of the TEA and nearest C–C bond of OPP-3*) and TEA is oriented closer to the middle ring of the phenylene relative to the ground state. In addition, relative phenyl ring orientations are markedly different in the ground and exciplex states. Although TDDFT yields a non-zero oscillator strength associated with exciplex emission from this ground state geometry, the emission energy is 0.6 eV higher than that obtained with the exciplex geometry and therefore farther away from experiment (Figure 7). Therefore, differences in both structural features and photophysical attributes strongly motivate the use of excited-state optimization methods over ground state approximations to study exciplexes.

A very simple control is employed to verify whether the TDDFT-optimized structure is indeed an exciplex. When the N in TEA is replaced with a CH group, the only state with a non-zero oscillator strength corresponds to that of emission from isolated OPP-3*. Disappearance of the red-shifted peak relative to isolated OPP* upon replacing the N in TEA with CH is a clear indicator that the peak corresponds to interaction of OPP* with the lone pair in the donor. Further confirmation that the exciplex is formed via charge transfer is obtained by contrasting the corresponding NTOs for isolated OPP*, OPP*-TEA, and the CH-modified system, shown in Table S3 of the SI. Each NTO pair is composed of a hole and a particle which reflects the occupied and virtual orbital. The NTO for the exciplex state depicts charge transfer occurring from the lone pair on TEA (‘hole’) to OPP* (‘particle’), serving as proof of formation of an exciplex. The absence of charge transfer to OPP* is evident in the CH-substituted system and the close resemblance of NTOs with isolated OPP*. NTOs thus serve as further confirmation that the geometry and electronic state identified with TDDFT represent an exciplex and that the emission spectra can be directly contrasted with fluorescence experiments reported in Figure 3.

Origins of exciplex stabilization: Energy decomposition analysis

Energy decomposition analysis of the excited state determines the contribution of frozen, polarization, and charge transfer interactions towards the change in emission energy of the exciplex relative to that of isolated OPP*. The gas phase exEDA results are depicted in Figure 6 for both [OPP-3-TEA]* and its CH-substituted analog. The y-axis represents the

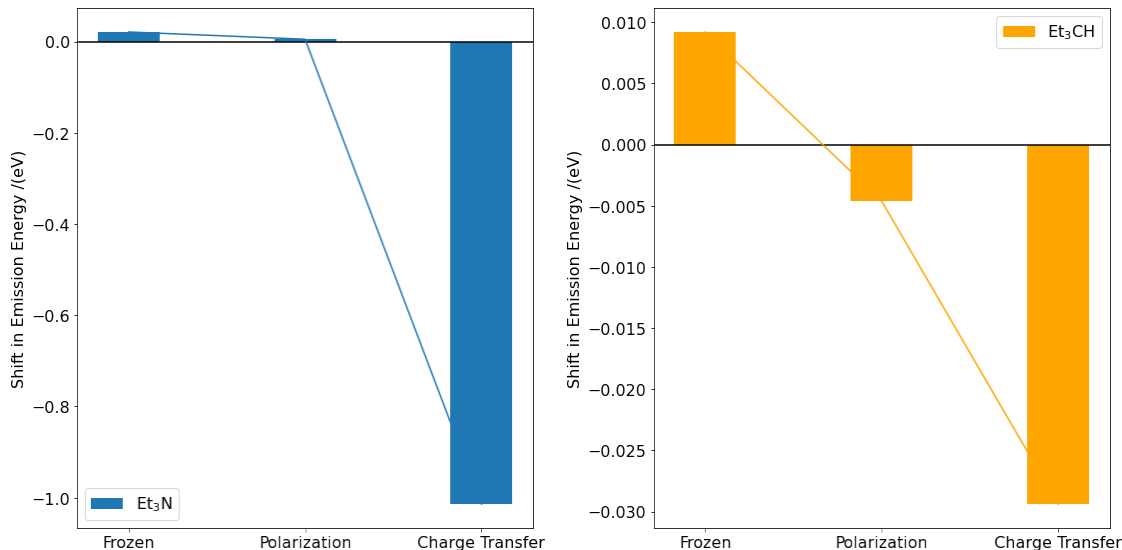


Figure 6: The shifts in emission energies /(eV) of the [OPP-3-TEA]* exciplex (left) and the analog where N in TEA is replaced with CH (right) with stepwise inclusion of frozen, polarization, and charge transfer interactions obtained with exEDA.

shift in emission energy of the exciplex referenced to isolated OPP-3*. The [OPP-3-TEA]* emission energy is increased by a very small amount compared to OPP-3* due to frozen interactions. Inclusion of polarization also leads to a negligible shift in emission energy. The biggest shift arises from charge transfer interactions, resulting in 1.01 eV reduction in emission energy. On the other hand, for the CH-substituted control (Figure 6, right), the magnitudes of the shifts in emission energy are all too small ($< 0.1\text{eV}$) to be deemed physically meaningful. In other words, the emission energy does not change for the complex where $\text{N} \rightarrow \text{CH}$, while the charge transfer-driven shift in emission for [OPP-3-TEA]* is consistent with the prevailing definition of an exciplex. This study does not extend the analysis to probe interactions spanning the entire range of interfragment separations as is often done

for excited-state dimers, also known as excimers. The difficulty of studying a range of interfragment separations stems from the asymmetry of the exciplex that makes it challenging to define a single, meaningful coordinate that can capture the range of possible emission energy shifts. The identification of a ‘charge transfer coordinate’ to examine the impact of interfragment separation on emission energy shifts is therefore a topic for future work.

Exciplex emission & solvatochromism

Experimental emission wavelengths across solvents are contrasted with TDDFT calculations using non-equilibrium solvation for the emission state of isolated OPP* and exciplex emission state of [OPP-TEA]* in Figure 7. The data is also available in Tables S4 and S5 of the SI. They show that solvatochromism, or the sensitivity of emission spectra to solvent, is more pronounced for the exciplexes than isolated OPP*. OPP-3* exhibits a very small red-shift in emission wavelength from 339 nm in cyHex ($\epsilon = 2.03$) to 341 nm in THF ($\epsilon = 7.58$), with anomalous red-shifts for aromatic solvents in the middle of this range, specifically PhBr (359 nm) and PhCl (344 nm). The emission maximum in PhBr appears to be associated with a different vibronic feature than in the other solvents, which partially accounts for the large red-shift observed in this solvent. Although we could find no prior evidence to explain this anomalous behavior, we believe that it may be the result of π -stacking interactions between OPP-3* and PhBr (PhCl) solvent molecules. We do not see similarly anomalous behavior for the exciplex in these solvents, possibly because the interaction between OPP-3* and TEA is more favorable than the reaction between OPP-3* and solvent molecules. Experimental emission wavelengths are longer for OPP-4* relative to OPP-3* by, on average, 17 nm. This is because the addition of a phenyl ring to OPP-3 lowers the optical gap of the system owing to extended π -delocalization in the excited state compared to OPP-3*.⁶³ Similar to OPP-3*, solvatochromic shifts for OPP-4* are small, with the exception of PhBr and PhCl, and emission wavelengths lie in the narrow range of 366-368 nm between cyclohexane and THF.

TDDFT underestimates emission wavelengths (or overestimates energies) for both OPP-

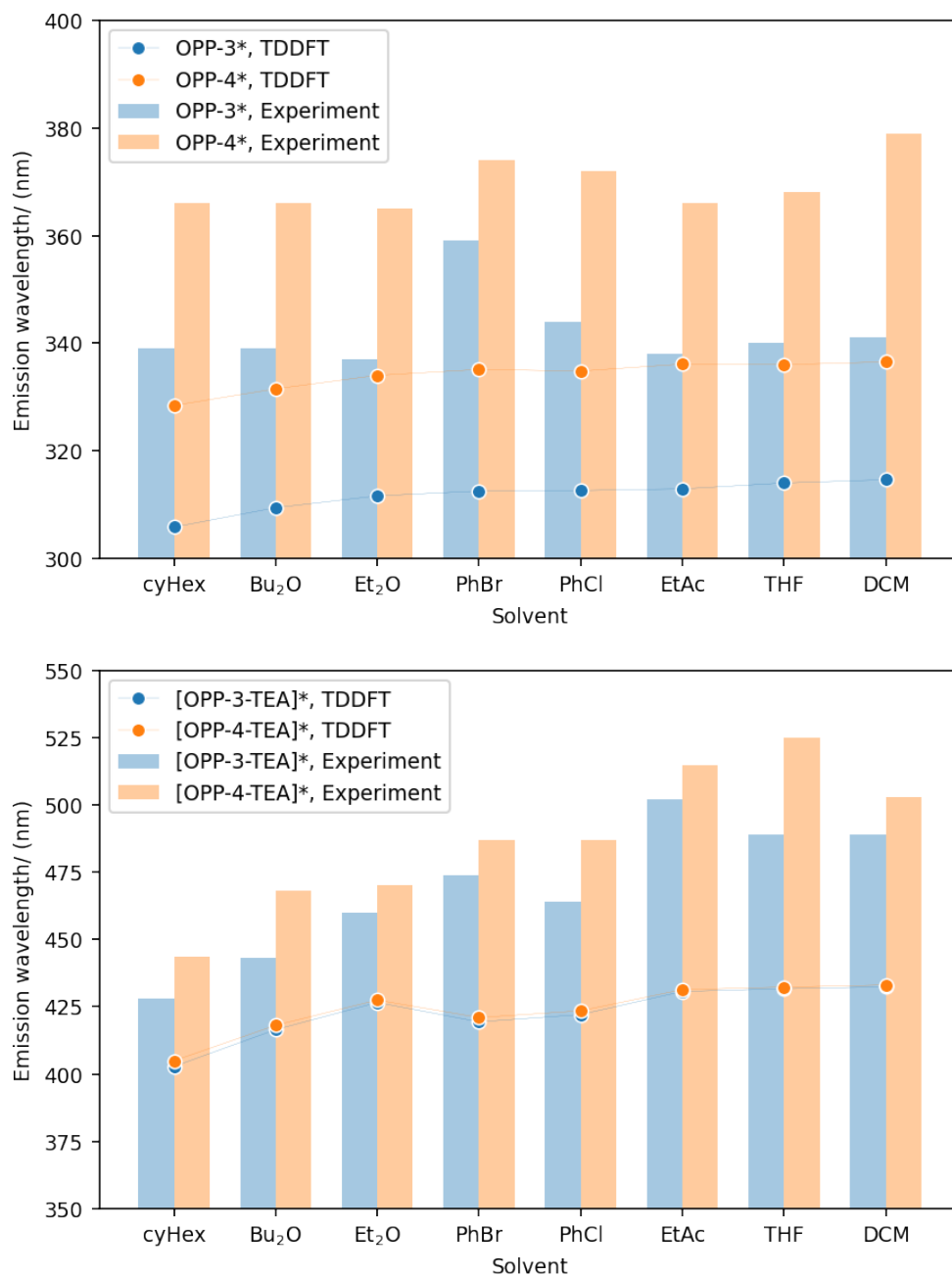


Figure 7: Emission wavelengths for OPP-3 and OPP-4 for both isolated catalysts (top) and their exciplex state (bottom) with TEA. All emission energies are calculated with ω B97X-D/def2-TZVP and non-equilibrium solvation.

3* and OPP-4* by 30 nm (0.35 eV) and 35 nm (0.36 eV) on average, respectively. These deviations from experiment are consistent with blue-shifted wavelengths obtained with hybrid and range-separated hybrid functionals.^{64–67} The emission spectrum for the control system where N in TEA is replaced with CH does not include the lower energy state corresponding to exciplex emission, thereby verifying that the spectra described in Figure 7 (bottom) indeed correspond to experimentally observed exciplexes. Computations do not capture the anomalous behavior of exciplexes in PhBr and PhCl as implicit solvation models do not capture specific solute-solvent interactions such as π -stacking. The emission wavelength shifts are small in magnitude but larger than experiment, ranging from 306 nm in cyclohexane to 315 nm in dichloromethane for OPP-3* and 328 nm to 338 nm for OPP-4*.

Experiments (Figures 3 and 7) show that exciplexes emit at longer wavelengths and exhibit more pronounced solvatochromic shifts than isolated OPP*. This difference is because the charge-transfer character of the exciplex results in a much higher dipole moment than that of the isolated OPP-3* molecule and therefore higher sensitivity to solvent environment. The exciplex in EtAc ($\epsilon = 6.02$) is red-shifted by 74 nm and 71 nm relative to cyHex for [OPP-3-TEA]* and [OPP-4-TEA]*, respectively. TDDFT results mirror both the shift relative to isolated OPP* as well as stronger solvatochromic shifts, although the deviations from experiment vary with solvent. Calculated solvatochromic shifts in particular lie in a narrower range when solvent is varied between cyHex and EtAc – 28 nm and 27 nm for [OPP-3-TEA]* and [OPP-4-TEA]*, respectively. Smaller solvatochromic shifts with TDDFT and long range-corrected hybrid functionals have been reported previously for organic heterocyclic dyes.⁶⁸ We also compute shifts for a higher dielectric solvent (Table S3 and S4 in SI) where emission from the exciplex is too weak to be observed experimentally, and find that the emission wavelength is 444.4 nm (444.0 nm) for [OPP-3-TEA]* ([OPP-4-TEA]*) in AN ($\epsilon = 35.7$). Notably, while the average experimental emission wavelengths are 17 nm higher for [OPP-4-TEA]*, the calculated difference is narrower, 1 nm. In summary, although the differences between calculated and observed emission energies for the exciplex state increase

with increasing solvent dielectric, overall trends in calculated and experimental emission spectra are in agreement for both oligomers.

The similarity in TDDFT exciplex emission energies for [OPP-3-TEA]* and [OPP-4-TEA]* mirrors the close resemblance between geometries shown in Figures 4 and 5. Even when the oligomer consists of four phenyl rings, only three interact closely with TEA. As the exciplex electronic state is the result of these localized charge transfer interactions between TEA and OPP*, emission energies are nearly identical across all solvents for the two oligomers. Since broad fluorescence peaks typically indicate that the exciplex is not a unique structure, we examine the range of possible emission energies for [OPP-4-TEA]* resulting from simple rotations of the terminal phenyl ring that is furthest from TEA. The emission energies resulting from out-of-plane (95.3°) and in-plane torsional rotation (24.4°) relative to the ‘equilibrium’ (or minimum energy) geometry are shown in Table S6 of the SI. Rotation of the fourth phenyl out-of-plane leads to on average 7 nm blue-shift in emission energies relative to the in-plane geometry, with the equilibrium emission in between the in-plane and out-of-plane values. Although in-plane rotations lead to [OPP-4-TEA]* emission wavelengths that are slightly higher than [OPP-3-TEA]* across all solvents, the differences are much smaller than experiment (Figure 7). Based on this analysis, we conclude that there are other possible exciplex geometries for [OPP-4-TEA]* that are yet to be identified.

Solvent dependence of exciplex formation

Figure 3 shows that exciplex peak intensities decrease as solvent dielectric increases. This implies that either SSRIPs are formed directly upon complete electron transfer from TEA to OPP* or the exciplex itself has distinct charge transfer characteristics, with greater charge separation favored in higher solvent dielectrics. Gould and coworkers’ landmark study addresses this question for exciplexes formed between alkyl-bound benzene donors and cyanoanthracene excited state acceptors using emission quantum yields to calculate efficiencies of exciplex formation in various solvents.¹⁷ They find that exciplexes are formed with unit effi-

ciency in most solvents although the SSRIP can be formed directly if the free energy driving force for complete charge separation and solvation is more favorable relative to exciplex formation.

We first examine the charge distribution in the fragments constituting the exciplex to quantify the extent of charge transfer from TEA to OPP* by varying solvent dielectric but using the exciplex geometry calculated in DCM. The sum of Mulliken atomic charges constituting the OPP-3* fragment in the exciplex electronic state are largely similar across solvents with an average of -0.689 e, ranging from -0.693 e for AN to -0.684 e for PhBr. Re-optimization of the exciplex geometry in a different solvent does not significantly alter the geometry or charge distribution when compared to the reference results with DCM. Within the constrained search space of exciplex geometries in this study and the approximate continuum treatment of solvent with no explicit involvement of solvent orbitals,¹⁷ we conclude that the extent of charge transfer in an an exciplex state is not sensitive to solvent screening.

We then explore the possibility that SSRIPs are more energetically favorable compared to exciplexes in higher dielectric solvents. Figure 8 depicts the energies of four key states – isolated OPP* and TEA ('OPP-3* - - - TEA'), exciplex state ([OPP-3-TEA]*), CRIP (OPP-3^{•-}-TEA^{•+}), and SSRIP (OPP-3^{•-} - - - TEA^{•+}) – relative to a reference isolated state calculated with cyHex. CRIP energies are calculated at the exciplex geometry using constrained density functional theory (CDFT)^{69,70} with the Becke partitioning scheme⁷¹ to isolate the single negative charge on the OPP fragment and positive charge on TEA. SSRIP energies are calculated using CDFT optimization for a system consisting of OPP-3^{•-} and TEA^{•+} that yields a geometry in which the fragments are separated by approximately 5.5 Å. Examination of the kinetics of direct charge transfer from TEA to OPP-3* at this separation to yield an SSRIP is a topic for future work.

Figure 8 shows that the formation of the exciplex from isolated OPP* and TEA is favorable by 1.1-1.2 eV in all solvents. In all cases, imposing complete charge separation on the exciplex geometry leads to a state that is higher in energy than the exciplex. The energy

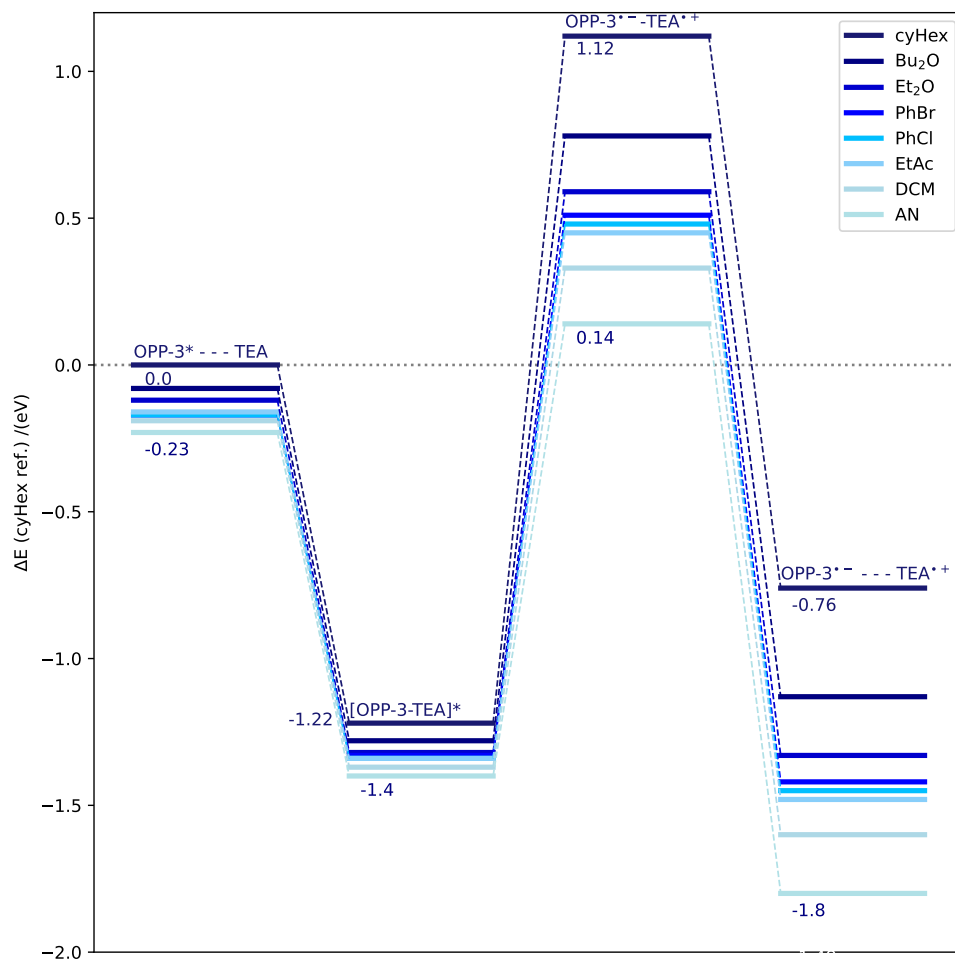


Figure 8: Potential energy surface representing four states (from left to right) – reference state with isolated OPP* and TEA, the exciplex, anionic OPP and cationic TEA radicals at the exciplex geometry (CRIP), and anionic OPP and cationic TEA radicals separated by about 5.5 Å (SSRIP). Dark → light blue indicates increase in solvent dielectric. Energies are reported relative to that of isolated OPP-3* and TEA in cyHex.

required to form the CRIP in place of the exciplex is highest for the solvent with the lowest dielectric. Higher CRIP energies also mean that charge separation from an exciplex to form SSRIP is associated with a high energetic barrier, and therefore it is more likely that an exciplex is quenched back to a neutral, ground state donor/acceptor pair than to an SSRIP.

Solvent stabilization of the radical ions, or the SSRIP state, lowers the energy relative to CRIP. SSRIPs for low dielectric solvents such as cyHex and Bu₂O are higher in energy compared to the exciplex, indicating that exciplex formation is energetically favored over SSRIP in these solvents. With increasing dielectric, SSRIP formation becomes increasingly favored, implying that this step competes with exciplex formation. Therefore, the decrease in emission intensity with increasing solvent dielectric in Figure 3 can be explained by the fact that excited state quenching to SSRIP becomes more favorable relative to the exciplex state. These observations for arene-amine exciplexes are in complete agreement with experiments for cyanoarene-benzene systems studied by Gould and coworkers.¹⁷ Solvent dielectric therefore does not influence the extent of charge separation in an exciplex state but strongly influences the relative energies of exciplexes and SSRIPs, thereby governing the outcomes of excited state quenching processes.

Conclusions

This work examines the quenching pathways for excited-state OPP* with TEA serving as the sacrificial electron donor by combining fluorescence spectroscopy with a suite of quantum chemistry methods. Experiments confirm the formation of exciplexes, identified by broad, red-shifted emission peaks that decrease in intensity with increasing solvent dielectric. We find that a ground-state donor-acceptor complex is a poor approximation to an exciplex, necessitating the use of excited-state mode-following and optimization methods. TDDFT optimization with tight tolerances and small step-sizes is essential to converge to the correct excited state minimum, an exciplex, in which both charge and excited state are shared by

the donor-acceptor complex. Although carrying out a Hessian calculation to verify TDDFT convergence to a minimum can be prohibitive for these systems, we outline techniques that serve to verify and characterize exciplexes. The formation of an exciplex is confirmed by calculating natural transition orbitals, contrasting emission wavelengths and solvatochromism with experiment, and by showing that the emission peak disappears if the N (containing a lone pair) in TEA is replaced with CH. Excited-state energy decomposition analysis shows that donor→acceptor charge transfer is the dominant contributor to the red-shift in emission energy associated with exciplexes. To understand why in experiments lower exciplex emission intensities are observed with increasing solvent dielectric, we determine solvent-dependence of the extent of charge transfer and contrast exciplex energies with those of solvent-separated ion-radical pairs. This analysis reveals that, with increasing solvent dielectric, the extent of charge transfer in an exciplex does not change but SSRIP energy becomes comparable to or lower than the exciplex. We therefore conclude that for these arene-amine systems, SSRIP formation competes with exciplex formation in solvents of higher dielectric, leading to a decrease in observed emission intensities.

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Supporting Information Available

Supporting information contains Cartesian XYZ coordinates for all initial and final states, as well as additional computational data and experimental references.

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Graphical TOC Entry

