Hole-mediated PhotoRedox Catalysis: Tris(\textit{p}-substituted)biarylaminium Radical Cations as Tunable, Precomplexing and Potent Photooxidants.

Shangze Wu,† Jonas Žurauskas,†‡ Michał Domański,†‡ Patrick S. Hitzfeld,†‡ Valeria Butera,⊥ Daniel J. Scott,† Julia Rehbein,† Ajeet Kumar,§ Erling Thyraug,§ Jürgen Hauer,§ and Joshua P. Barham*†

*Corresponding Author. E-mail: Joshua-Philip.Barham@chemie.uni-regensburg.de

†Universität Regensburg, Fakultät für Chemie und Pharmazie, 93040 Regensburg, Germany
‡Central European Institute of Technology, CEITEC, Brno, 61200 Czech Republic
⊥Technische Universität München, Fakultät für Chemie, 85748 Munich, Germany

Abstract: Electrochemically-mediated Photoredox Catalysis emerged as a powerful synthetic technique in recent years, overcoming fundamental limitations of electrochemistry and photoredox catalysis in the single electron transfer activation of small organic molecules. However, the mechanism of how photoexcited radical ion species with ultrashort (picosecond-order) lifetimes could ever undergo productive photochemistry has eluded synthetic chemists. We report tri(\textit{para}-substituted)biarylamines as a tunable class of electroactivated photocatalysts that become superoxidants in their photoexcited states, even able to oxidize molecules (such as dichlorobenzene and trifluorotoluene) beyond the solvent window limits of cyclic voltammetry. Furthermore, we demonstrate that precomplexation not only permits the excited state photochemistry of tris(\textit{para}-substituted)biarylaminium cations, but enables and rationalizes the surprising photochemistry of their \textit{higher-order} doublet (D\textsubscript{n}) excited states.
**Introduction** Synthetic Organic Electrochemistry (SOE) (1-5) and visible light PhotoRedox Catalysis (PRC), (6-12) which offer entries to single electron transfer (SET) chemistry and radical intermediates under mild conditions, have risen to the fore of contemporary organic synthesis. A key factor underpinning the success of PRC is the host of available photocatalyst structures with well-characterized photophysical and redox data, allowing chemists to match a given excited state to a desired process. Although PRC exhibits a selectivity benefit in transferring the energy of visible light photons to a colored transition metal-based or organic dye photocatalyst, its scope of applications are redox potential-limited by the energy of single photons (*ca.* 1.8-3.1 eV). Multiple-photon-accumulating strategies such as consecutive photoelectron transfer (conPET) (13-17) and triplet-triplet annihilation upconversion (TTA-UC), (18-20) have represented an elegant means to achieve powerful SET reductions, but their use in oxidations has so far been elusive. However, these techniques place limiting requirements on reactions, such as the requirement in conPET for both ground and radical ion states to be visible-light active. Furthermore, net-oxidative/reductive PRC processes employ excess of a sacrificial oxidant/reductant which is necessary for photocatalyst turnover, but which may (or whose by-products may) i) interfere with the desired downstream chemistry and ii) may require separation from the desired products. The conPET strategy likewise suffers from this requirement. In comparison to PRC processes, SOE can employ uncapped potentials to chemical redox reactions at the turn of a dial. However, electrode surfaces typically (21-22) cannot discriminate between organic molecules aside from their innate order of thermodynamic redox potentials. Moreover, low electrical conductivity in organic solvents typically require applied potentials to be higher than the redox potential of the target substrate. (23) This encourages deleterious higher order or solvent redox processes especially if target SET processes lie near the solvent electroactive window (+3 to -3 V for typical electrolyte-containing solvents). (23-25) In addition, mechanistic characterization of the heterogeneous “electrocatalysis” step (referring to heterogeneous SET at the electrode surface) (26) has remained a key challenge in SOE. Screening of electrode materials is often inevitable, despite best efforts to characterize materials by overpotential, electrical resistivity, surface area, stability and cost. (27-28) As a result of these limitations, in recent years synthetic photoelectrochemistry is emerging as a state-of-the-art in SET-mediated chemistry. (29-33) Different categories for the merger of photochemistry and electrochemistry have been reported, including interfacial photoelectrochemistry (iPEC) involving photoelectrodes (34-37) and
decoupled photoelectrochemistry (dPEC) where photo- and electrochemical steps serve separate roles in the reaction mechanism. (38-39)

Figure 1: A. Electroactivated Photoredox Catalysts employed in net-oxidative synthetic processes. B. Triarylamines as e-PRC catalysts. C. This work.

A third category involves an intimate and synergistic relationship of photo- and electrochemical steps within the same catalytic cycle. (40-51) A variety of nomenclature has been coined in the literature for this sub-category of PEC, such as: “electrophotocatalysis” (45-47,51) “photoelectrocatalysis” (46,50) and “electron-primed photoredox catalysis” (51). We coined the general nomenclature “electrochemically-mediated PhotoRedox Catalysis (e-PRC)” as a blanket term to cover both net-oxidative and net-reductive variants (29) and to avoid misunderstanding with iPEC. e-PRC leverages the unique benefits of both parent technologies PRC and SOE in order to i) compile potential and photon energies to achieve photocatalyst excited-state potentials beyond those normally accessible via visible light photons alone (44-46,51) and to ii) obviate the need for sacrificial oxidants/reductants. (48,50) Pioneering reports on e-PRC realized these benefits in a number of net-reductive/net-oxidative transformations. (44-51) In the net-oxidative direction, previous
examples of electroactivated PhotoRedox Catalysts (e-PRCats) include i) 9-mesityl-10-methylacridinium dye, (44) ii) phenothiazine (40) and iii) an exotic trisaminocyclopropenium cation, (45) which have accomplished SET oxidations from alkyl-substituted arenes up to challenging chloroarenes. Elsewhere, tri(p-substituted)arylamines, discovered by Walter and co-workers (52) are renowned for their photophysical properties as hole-transport materials in OLEDs and in photovoltaics, (53-54) as oxidative mediators in SOE (55-59) and as oxidants in radical chain reactions. (60-61) They exhibit fully reversible 1e⁻ oxidations by cyclic voltammetry. Generally colorless in their neutral state, their oxidized tris(para-substituted)aminium radical cation forms are intensely colored. While the commercial tris(4-bromophenyl)aminium radical cation presents issues and non-innocence as an oxidant in synthesis, (62-64) better behaved radical cations could derive from tri(para-substituted)biarylamines (TPAs) that are in turn easily be prepared in a single/few steps from Pd-catalyzed cross-coupling reactions of tri-p-bromophenylamine with appropriate partners or after appropriate activation. Barham et al. reported the use of tris(para-substituted)arylaminium radical cations bearing p-Me or p-Ph substituents that exhibited good stability in solution and excellent stability as isolated solids, that mediated highly selective N-CH₃ oxidative functionalization reactions. (65) Given their favorable properties and facile synthetic accessibility, we foresaw TPAs as a suitable class of customizable e-PRC catalyst that would open new avenues to customize redox and photophysical parameters of e-PRCats; an important concept which has not yet been disclosed. Although moderate oxidants in their tris(para-substituted)biarylaminium (TPA⁺) state, subsequent photooxidation would provide formidable oxidation potentials. Moreover, the excellent stability of isolated TPA⁺s could be leveraged in i) probing the reaction mechanisms of their e-PRC reactions and ii) their photophysical characterization. Herein, we disclose TPAs as powerful and effective e-PRCats that engage unactivated or electron-poor aromatic systems ($E^{\text{p}_{\text{ox}}}_{\text{p}} = +2.1 \text{ V to }>3.0 \text{ V}$) in SET oxidation. Of key importance is the discovery of precomplexation in the ground state, which i) circumvents ultrashort lifetimes of excited states, ii) allows engagement of higher order excited states and iii) enables contra-thermodynamic redox selectivity. Photoexcited triarylaminium radical cations are demonstrated as novel superoxidants in organic synthesis (Figure 1).
**Synthetic Results** We began by screening different TPA e-PRCats (Generation 1, **Figure 2**) with different half-wave oxidation potentials in the Nicewicz model reaction; (66) the oxidative C-H amination of mesitylene ($E_{\text{ox}}^{\text{p}} = +2.1 \text{ V vs. SCE}$) (66) with pyrazole (**Table 1**). A carbon foam anodic working electrode (WE) and Pt cathodic counter electrode (CE) were employed in a H-cell divided by a porous frit, whose anodic compartment was placed atop a water-cooled block atop a 400 nm LED. Acetic acid was employed as a proton source for the cathodic half-reaction. TPA catalysts were typically poorly soluble in MeCN containing 0.1 M $^+$Bu$_4$PF$_6$. After setting an anodic constant potential of $U_{\text{cell}} = +1.4 \text{ V}$ (**Figure 3**), solid particles gradually disappeared and color developed in the anodic compartments for each TPA e-PRCat, consistent with the expected formation of their TPA$^+$s. Gratifyingly, irradiation under the specified conditions afforded C-H activation product 3aa. No product was observed in the absence of light and only traces in the absence of potential (4%) or TPA e-PRCat (2%), confirming the operation of e-PRC. Generally, the yield of 3aa increased with increasing oxidation half-wave potentials ($E_{1/2}$) of the TPA (**Figure 2 and Table 1**, entries 1-3), suggesting that the TPA$^+$'s excited state potential is more relevant to success than the steady-state concentration of electrogenerated radical cation.

![Figure 2](image_url)

**Figure 2.** Generation 1 TPA e-PRCats (top). Cyclic voltammograms of Gen. 1 e-PRCats (bottom).
Table 1. Optimization of e-PRC C-H heteroamination using first generation TPAs.

| Entry | R<sup>1</sup> | R<sup>2</sup> | Anode/Cathode | Yield 3aa/r.s.m.<sup>a</sup> | Solvent |
|-------|--------------|-------------|---------------|--------------------------|---------|
| 1     | Ac           | OMe         | C<sub>foam</sub>/Pt | 21/-                      | MeCN    |
| 2     | Ac           | Me          | C<sub>foam</sub>/Pt | 23/14                    | MeCN    |
| 3     | Ac           | Br          | C<sub>foam</sub>/Pt | 35/-                      | MeCN    |
| 4     | Ac           | Ph          | C<sub>foam</sub>/Pt | 69/15                    | MeCN    |
| 5<sup>b</sup> | Ac         | Ph          | C<sub>foam</sub>/Pt | 18/-                      | MeCN    |
| 6     | Me           | Ph          | C<sub>foam</sub>/Pt | 72/-                      | MeCN    |
| 7     | Me           | Ph          | C<sub>fei</sub>/Pt | 53/-                      | MeCN    |
| 8     | Me           | Ph          | C<sub>foam</sub>/Fe | 70/-                      | MeCN    |
| 9     | Me           | Ph          | C<sub>foam</sub>/Cu | 88<sup>c</sup>/-         | MeCN    |
| 10    | Me           | Ph<sup>d</sup> | C<sub>foam</sub>/Cu | 75/-                      | MeCN    |
| 11    | Me           | Ph          | C<sub>foam</sub>/Cu | 60/-                      | MeCN<sup>e</sup> |
| 12    | Me           | Ph          | C<sub>foam</sub>/Cu | -/-                      | DMF     |
| 13    | Me           | Ph          | C<sub>foam</sub>/Cu | 82/-                      | DCM     |

r.s.m., returned starting material. <sup>a</sup>Yields determined by <sup>1</sup>H NMR using dibromomethane as an internal standard. <sup>b</sup>0.35 W 400 nm LED. <sup>c</sup>Average of two replicates. <sup>d</sup>5 mol% TPA was used. <sup>e</sup>LiClO<sub>4</sub> used as electrolyte.

Interestingly, tri(1,1'-biphenyl)-4-yl)amine (TpBPA) afforded a notably higher yield of 3aa than the commercial tris(4-bromophenyl)amine (entry 4) despite having an appreciably lower <i>E<sub>1/2</sub></i>. Comparisons of the UV-visible spectra of TPA<sup>+</sup> revealed a plausible explanation; that TpBPA benefitted from the strongest absorption at 400 nm. Decreasing LED input power by ca. 10x decreased the yield (entry 5). Screening of other protic sources revealed MeOH to be most effective (entry 6). Carbon foam was a superior anodic WE to carbon felt, likely due to its higher surface area (entries 6-7). Gratifyingly, screening of other CE materials revealed copper to be the optimal cathodic CE (entries 8-9). A decreased TpBPA loading (5%) gave an inferior (but still high) yield (entry 10) and LiClO<sub>4</sub> as an electrolyte was inferior (entry 11). While DMF as solvent gave no reaction, we were surprised the reaction performed well in DCM as solvent, despite its lower
conductivity (entries 12-13). The yield of 3aa tracked well with increasing applied constant potential (Figure 3). For full optimization studies, see the Supplementary Information.

![Graph showing current and yield as a function of potential](image)

**Figure 3.** Yield as a function of increasing applied $U_{\text{cell}}$(top). Development of color with increasing applied $U_{\text{cell}}$(bottom).

With optimal conditions in hand, the amination of arenes with a variety of pharmaceutically-relevant $N$-heterocycles was explored (Table 2). Halide-bearing and carbonyl (aldehyde, ketone and ester)-bearing pyrazoles, triazole, benzotriazole, and a functionalized derivative of benzimidazole afforded generally good to excellent (50-89%) yields of aminated mesitylenes 3aa-3aj. We note that benzimidazole derivatives have not been reported as nucleophiles in previous photoelectrochemical arene amination or conPET photocatalytic methods. (37,45,67) 6-Chloro-2-fluoropurine afforded a modest yield of 3ak (32%), presumably due to its steric hinderance as a nucleophile. Xylenes and toluene were tolerated to afford aminated arenes 3bb-3fb in moderate to excellent (30-88%) yields.
Table 2. e-PRC C-H heteroaminations using TpBPA.

Unless otherwise stated, all reactions used 3.5 eq. arene; isolated yields. Yields in parenthesis determined by $^1$H NMR. *A Pt CE was used and AcOH.

Interestingly, the product yields of xylenes followed the order meta- > ortho- > para-xylene, despite the $E_{\text{ox}}$ following the opposite trend. (68) Toluene has an even higher $E_{\text{ox}}$ than xylenes but reacted to give 81% of 3eb. (68) Bromobenzene afforded a 30% yield of 3fb with notable r.s.m., while iodobenzene gave no reaction at all (60% r.s.m.). Benzene and PhCl were unsuccessful, presumably due to their notably higher $E_{\text{ox}}$ (only a 10% yield of 3gb’s combined C1/C2 isomers was obtained, even when using a large excess of PhCl and after 72 h). Substitution of Cu for Pt wire cathode increased the yield to 15%; substitution of MeOH for AcOH increased the yield to 35% (Table 3). Despite exhaustive efforts, we could not improve the conversion/yield beyond this threshold.
Leveraging the facile synthetic customization of TPAs, we synthesized derivatives of TpBPA (Figure 4) with electron-withdrawing groups to bolster their respective TPA$^+$ excited state potentials (entries 1-4). Of these, we were delighted to find that tris(4’-cyano-[1,1’-biphenyl]-4-yl)amine (TCBPA) increased the yield of 3gb to 46% (Table 3). In contrast to TpBPA, the optimal TCBPA catalyst loading was 5 mol% (entries 4-8), increasing the yield of 3gb to 69% with no detected starting material (entry 6). Notably, the reaction was still quite efficient with only 1.5 mol% of TCBPA (entry 8). With these optimal conditions in hand, reactions of PhCl, benzene and even fluorobenzene were enabled, affording 3gb-3ib in modest to good (30-65%) yields (Table 4).
Table 3. Optimization of e-PRC C-H heteroamination using Generation 2 TPAs.

| Entry | R¹ | R² | Yield 3gb/r.s.m. | Catalyst loading 'x' |
|-------|----|----|------------------|----------------------|
| 1     | H  | H  | 35/33            | 10                   |
| 2     | iBu| H  | 38/22            | 10                   |
| 3     | F  | F  | 36/18            | 10                   |
| 4     | CN | H  | 46b/25           | 10                   |
| 5     | CN | H  | 40/18            | 20                   |
| 6     | CN | H  | 69/-             | 5                    |
| 7     | CN | H  | 52/-             | 3                    |
| 8     | CN | H  | 45/25            | 1.5                  |

r.s.m., returned starting material. aYields determined by 1H NMR using dibromomethane as an internal standard. bAverage of two replicates. cThe reaction was conducted with 1g (1 mL), 2b (0.4 mmol), TCPBA (0.006 mmol), AcOH (4 mmol), Bu₄NPF₆ ((1.2+1.2) mmol), MeCN (3.5+3.5 mL).

Interestingly, under the same applied constant potential Ucell as in Table 2 and in contrast to the use of TpBPA, here toluene underwent benzylic oxidation instead of amination, while a pyrazole-4-carboxaldehyde (either before or after benzene C-H amination) underwent oxidation to its carboxylic acid (Table 4, bottom). Bromobenzene gave a lower yield of 3fb than that in Table 2. The above observations indicate a less oxidizing TPA⁺ excited state (such as that from TpBPA⁺) is beneficial for certain substrates and demonstrates the value of tunability presented by this class of e-PRCats. We further probed the limits of arene SET oxidations with TCBPA⁺, by targeting 1,2-dichlorobenzene and trifluorotoluene, and were encouraged to detect products, albeit in low yields, from each when using TCBPA (17% of 3jb and 7%, respectively). Yields did not increase with extended reaction time (96 h) or higher applied potential (U_cell = +1.8 V), which suggested that we had reached the oxidizing limit of this photoexcited TPA⁺.
Table 4. e-PRC C-H heteroamination using TCBPA.

Gratifyingly, further e-PRC tuning in the form of the even more electron-deficient tris(2’,4’-dicyano-[1,1’-biphenyl]-4-yl)amine (TdCBPA) increased the yield of 3jb to a much more satisfactory 31% (Table 5). Although polyfluorinated arenes were activated to afford 3ob and 3hb in only modest yields (~20%), it should be emphasized that oxidative S_NAr-type activation of such challenging substrates with pyrazoles has not to our knowledge been previously accomplished. In competition with C-H activation, C-F substitution occurred to give 3ob. (46,69) Interestingly, C_6H_5-bearing compound 3hb was isolated from the reaction of trifluorotoluene, indicating a SNAr of a CF_3 group. While the role of CF_3 groups in promoting SNAr reactions is well-known, to our knowledge no prior examples of a formal C(sp^3)-CF_3 to C(sp^3)-N(Het-Ar) substitution exist. The oxidation potentials of trifluorotoluene and 1,2,4-trifluorobenzene cannot be measured by cyclic voltammetry; they exceed the solvent windows of MeCN and DMF (>3.0 V vs. SCE). This reflects the remarkable oxidizing power of TdCBPA’s excited state.
Table 5. e-PRC C-H heteroamination using TdCBPA.

Isolated yields. Yields in parenthesis determined by $^1$H NMR.

An intriguing theme running through the TPA-mediated e-PRC substrate scope is the apparent influence of steric effects on reactivity. In contrast to a previous report (45) and in line with the trends observed in Table 2, product yields increased as a function of the substitution pattern on dichloroarenes (1,4- $< 1,3- \leq 1,2$-dichlorobenzene). This was surprising, given the corresponding increasing order of $E^{\text{ox}}$ (1,4- $< 1,2- \leq 1,3$-dichlorobenzene).

**Mechanistic studies** Spectroelectrochemical analysis of TpBPA (Figure 5) TCBPA and TdCBPA (see Supplementary Information) revealed the formation of their respective TPA$^+$s by the disappearance of the TPA band ($\lambda_{\text{max}} = \text{ca.} 345 \text{ nm}$) and appearance of two broad absorption bands between 360-430 nm ($\lambda_{\text{max}} = \text{ca.} 420 \text{ nm}$) and between 600-900 nm ($\lambda_{\text{max}} = \text{ca.} 719, 856 \text{ nm}$), when the potential was increased from 0 to +1.3 V. Excellent reversibility was observed upon returning the potential to +0.0 V, indicating high stability of the TPA$^+$s as e-PRCats. While TpBPA is a white solid that does not absorb 400 nm light, it possesses a strong absorption at $\lambda_{\text{max}} = 365 \text{ nm}$, where TpBPA$^+$ absorbs poorly. Performing our optimized synthetic procedure for 3aa with 365 nm LEDs afforded only 11%, suggesting photoexcitation of neutral TpBPA is not a dominant factor in the mechanism. The aforementioned control reaction without applied potential afforded only 4% of 3aa. In contrast...
to TpBPA, TCBPA is a pale yellow solid that does absorb appreciably at 400 nm. Nevertheless, in the absence of an applied potential for the optimized synthesis of 3gb, only a 12% yield of 3gb was observed. The detection of small amounts of product in the aforementioned control reactions corroborates a conPET-type mechanism (13-17) where photoexcitation of TpBPA or TCBPA leads to SET reduction of protons or trace O₂ (reactions were bubbled by N₂ for 5 min during preparation and sealed; no further strict precautions were taken) to generate the corresponding TPA⁺. In any case however, the very substantial yield differences when applied potential is present or absent confirm the pivotal role of the TPA⁺s and that e-PRC is the main product-forming pathway in both reactions.

Figure 5. Spectroelectrochemistry of TpBPA, 0 to +1.3 V vs. Ag/AgCl (left) and +1.3 to 0 V (right).

Inspecting the UV-visible absorption spectra of TpBPA⁺ and TCBPA⁺, we reasoned that the longest wavelength bands (λ_{max} at ca. 719 and 856 nm, respectively) must contain their D₀→D₁ transitions. Based on the chemist’s interpretation of Kasha’s rule that prohibits photochemistry from higher order excited states, we therefore irradiated the reactions forming 3aa and 3gb with commercially-available LEDs at 740 nm and 850 nm and were mystified to observe no reaction in either case (Figure 6). That successful reaction was only observed at 400 nm implicated anti-Kasha behavior; a higher-order excited state participated in SET photooxidation. Such behavior is as surprising as it is intriguing, since i) not only are examples of photochemistry violating (the photochemical interpretation of) Kasha’s rule rarely reported in organic synthesis (15,17,70-71) but ii) the reported lifetimes of photoexcited radical ion species are already ultrashort. (72-73) In fact, despite a number of conPET/e-PRC reports invoking their photochemistry in
super-oxidations/reductions, the question of how photoexcited radical ion species could ever participate in photochemical processes has remained elusive, given the ultrashort lifetimes of these species which lie beneath the timescales of diffusion/bimolecular quenching. (15,17)

Greatly aiding our mechanistic study of this phenomenon was the fact that TPA⁺s can be preparatively isolated as their bench stable PF₆ salts. (65) Their XRD crystal structures revealed a common propeller-type structure, also observed for parent TPAs (Figure 7). However, attempts to investigate quenching of photoexcited TPA⁺s were thwarted by the fact that they do not exhibit steady-state fluorescence (see Supplementary Information). Consistent with this observation, the reported lifetimes of related excited N radical cation species (74-76) lie within the femto- to picosecond timeframe. As a result, transient absorption spectroscopy (TAS) was employed to determine the lifetimes of excited TpBPA⁺ and TCBPA⁺. Pumping with a broadband visible light source (490-900 nm) revealed a ground state bleach in the 600-850 nm bands (Figure 8) and an excited state absorption between 490-570 nm, indicative of absorption by the D₁ (or D₂) excited states. The lifetimes of the D₁ excited states of TpBPA⁺ and TCBPA⁺ were 4.6 ps and 8.6 ps, respectively, clearly ruling out photochemistry by diffusion-control and bimolecular quenching. It is reasonable to assume that higher order excited states possess even shorter lifetimes, and that precomplexation can therefore be the only rationalization for productive, unimolecular SET and the aforementioned anti-Kasha behaviour.
Presuming that precomplexes may possess different UV-vis absorption than their parent TPA⁺s, we investigated quenching of the absorption of TPA⁺s in the presence of representative concentrations of arenes (Figure 9). In the presence of mesitylene, the spectrum of TpBPA⁺ was unchanged. Gratifyingly, irradiation with 400 nm light effected gradual conversion of TpBPA⁺ to TpBPA, corroborating the expected SET from mesitylene to the photoexcited TPA⁺. Interestingly and in contrast, the spectrum of TCBPA⁺ was altered by addition of PhCl; a small bathochromic perturbation of the peak at 384 nm to 395 nm occurred, indicating complexation between TCBPA⁺ and PhCl. Irradiation with 400 nm led to complete conversion of TCBPA⁺ to TCBPA after 5 min. Given the paramagnetic nature of these species, we reasoned that a change in the EPR spectra of TPA⁺s in the presence of arene substrates (350 eq., mirroring the reaction conditions) would be more conclusive in corroborating precomplexation.
Figure 8. Transient absorption and decay-associated spectra of TpBPA\(^+\) and TCBPA\(^+\). Data were treated with a smoothing function for visualization, see Supplementary Information for raw data.

Figure 9. UV-vis spectroscopy of TpBPA\(^+\) (left) and TCBPA\(^+\) (right) in the presence of mesitylene and PhCl, respectively and after irradiation at 400 nm.
The EPR signal of $\text{TpBPA}^+$ showed a triplet ($\alpha_n = 8.9$ G). Addition of mesitylene to $\text{TpBPA}^+$ caused its EPR signal to shift ($\Delta B = 4.5$ G) to lower G values (Figure 10), but the signal shape was largely unchanged. This indicates that the spin density of the $\text{TpBPA}^+$ is largely unaffected when it undergoes precomplexation with mesitylene. A less pronounced shift in G value occurred in the presence of iodobenzene ($\Delta B = 2.0$ G) but flattening of the triplet shoulders was observed (see Supplementary Information for detailed discussion). Based on these spectroscopic differences, we hypothesize that a different type of precomplex must occur in this case that is unreactive, to rationalize the inability to engage this substrate under the reaction conditions despite its more accessible redox potential ($E^\text{pox}_{\text{ox}} = +2.07$ vs. SCE) than toluene ($E^\text{pox}_{\text{ox}} = +2.28$ V vs. SCE). (77) In contrast to $\text{TpBPA}^+$, simulated fitting of the EPR signal from $\text{TCBPA}^+$ revealed two radical species, one triplet and one superimposed singlet appearing as a large broad central feature. We presume that this particular $\text{TPA}^+$ exists as a mixture of rotamers in solution, one propeller-type as observed in the solid state, and one in which a biphenyl unit falls into conjugation with the N radical cation, consistent with reported behaviour for similar compounds. (78-80) Addition of PhCl caused a notable change in the signal shape, giving exclusively the triplet signal (Figure 11), consistent with the change in UV-vis (Figure 9) and indicating that the spin density of $\text{TCBPA}^+$ is notably affected by precomplexation with PhCl. A similar change was detected upon addition of 1,2-dichlorobenzene, but not for its 1,4-congenor (17% yield of $\text{3jb}$ vs. 6% yield of $\text{3lb}$ under $\text{TCPBA}^-$ e-PRC) and not for PhBr (22% of $\text{3fb}$ from $\text{TCPBA}^-$ e-PRC) which instead all gave spectra clearly favoring the unreactive complex (singlet signal).

Figure 10. EPR spectra of $\text{TpBPA}^+$ with reactive mesitylene (left, 350 eq.) and unreactive iodobenzene (right, 350 eq.).
To shed further light on the spectroscopic observations, Density Functional Theory (DFT) calculations were employed to model precomplexation of various TPA$^+$/arene combinations (Table 6). For unsymmetrical (halo)arene substrates, orientations of the complex with halogen facing both ‘in’ to the N radical cation and ‘out’ were explored (see Supplementary Information for full investigations). We assumed that π-stacking interactions ($\delta$1-82) at the TPA$^+$’s biphenyl unit could be responsible for precomplexation. Attempts to position PhCl or mesitylene substrates in a sandwich or parallel-displaced π-π stacking interaction (“π-π” complex) around the inner N-bearing ring of their respective TPA$^+$s led predominantly to dissociation, whereas positioning of the substrates around the terminal aromatic ring identified a local minima for the complexes resembling a T-type stacking interaction (“T-π” complex). For this complex, minimal change in the spin density was detected for TpBPA$^+$ + mesitylene (Figure 12), whereas a large shift in spin density occurred for TCBPA$^+$ + PhCl where the Cl atom was facing inwards (Figure 13). This is consistent with the changes in EPR and UV-vis spectra, and so we assigned this “T-π” complex as the one responsible for the triplet EPR signal and successful reactivity, since the oxidizing power of the N radical cation remains localized on its N atom. On the other hand, for less successful substrate PhBr and unsuccessful PhI (no product, 60% 2b recovered), a “π-π” complex was presumed to be responsible for the broad singlet EPR signal. Delocalization of the N radical cation over the biphenyl aromatic system would lead to stabilization, presumably decreasing $E_{p,ox}$ of the photoexcited TPA$^+$. 

**Figure 11.** EPR spectra of the TCBPA$^+$ with reactive (left) vs. unreactive (right) substrates (350 eq.).
### Table 6. Free energies and intermolecular distances for T-π or π-π precomplexes.

| Complexa          | Complexation ΔG (kcal mol⁻¹) | Intermolecular distance (Å) |
|-------------------|------------------------------|-----------------------------|
|                   | T-π  | π-π  | T-π  | π-π  |
| TpBPA⁺ +1,3,5-TMB  | +7.2b | +4.9c,f | 3.3-5.5b | 3.6-4.2c,f |
|                   | +28.4b,d | +28.3b,d | 4.7-6.5b,d | 5.2-5.3b,d |
|                   | +28.1b,e | +26.1b,e | 3.8-6.2b,e | 6.2-6.8b,e |
|                   | +4.5b,d | 4.5-6.8b,d |             |             |
| TpBPA⁺ +PhI       | +3.5c,d | +2.9c,e,f | 3.2-5.3c,d | 3.7-4.3c,e,f |
|                   | +5.1b,e | 4.8-7.4b,e |             |             |
| TCBPA⁺ +PhCl      | +30.8b,d | 29.7b,d | 3.4-6.2b,d | 4.9-5.4b,d |
|                   | +31.4b,e | N.D.b,e | 3.7-6.9b,e | N.D.b,e |
| TCBPA⁺ +1,2PhClCl | +4.5b,d | +6.6b,d | 4.2-6.4b,d | 5.3-5.7b,d |
|                   | +4.7b,e | N.D.b,e | 4.6-6.9b,e | N.D.b,e |
| TCBPA⁺ +1,3PhClCl | +4.9b,d | N.D.b,d,g | N.D.b,d | N.D.b,d,g |
|                   | +5.2b,e | N.D.b,e,g | 4.9-7.4b,e | N.D.b,e,g |
| TCBPA⁺ +1,4PhClCl | N.D.b,g | +4.2b,d | N.D.b,g | 5.5-5.8b,d |

N.D. not determined; these complexes could not be converged or dissociated. In all cases, a solvent of MeCN was modelled implicitly. Pseudopotentials were applied to I and Br atoms (see Supplementary Information for details). Intermolecular distances quoted are not centroid-to-centroid of the arene rings and are defined in the Supplementary Information. aHypothesized orientation of the precomplex that matches with UV-vis/EPR data and reactivity patterns. bB3LYP/6-31+g(d,p). cωB97XD/6-31+g(d,p). dHalogen atom(s) facing “out”. eHalogen atom(s) facing “in”. fRearranged from the T-π complex. gDissociated.

Free energies of precomplexation were all found to be endergonic at the level of theory employed, (83-84) intermolecular distances for T-π stacking and π-π stacking were close to previously-reported distances for simpler complexes/dimers. (83-89) Mesitylene, chlorobenzene, 1,2-dichlorobenzene and their respective TPA⁺s; for which the ‘reactive’ T-π complex was predicted by EPR studies; all had accessible ΔG values (+3.5-7.2 kcal mol⁻¹). An accessible ΔG value was also found for 1,3-dichlorobenzene (+4.9-5.2 kcal mol⁻¹) consistent with its reactivity (20% 3kb under the TCBPA e-PRC of Table 4). Iodo- and bromobenzene as substrates gave very high ΔG values for T-π complexes and their π-π complexes were more accessible albeit still highly endergonic. Attempts to obtain a T-π complex for TCBPA⁺ with 1,4-dichlorobenzene led to dissociation, while its π-π complex was found to be accessible.
Figure 12. DFT spin densities of $\text{TpBPA}^+$ without (left) vs. with (right) mesitylene, T-$\pi$ complex.

Figure 13. DFT spin densities of $\text{TCBPA}^+$ without (left) vs. with (right) PhCl, T-$\pi$ complex, Cl atom facing “in”.

Time-dependent density functional theory (TD-DFT) calculations were then used to investigate the energies higher order excited D$n$ states for $\text{TpBPA}^+$, $\text{TCBPA}^+$ and $\text{TdCBPA}^+$, using both CAM-B3LYP/6-31G(d,p) and wB97XD/6-31+G(d,p) (a solvent of MeCN or DCM was modelled implicitly, counterions were omitted). The calculated UV-visible spectra of the radical cations of $\text{TpBPA}^+$ and $\text{TCBPA}^+$ in MeCN were in reasonable agreement with their experimental spectra (Figure 14). Since the broad visible band (ca. 580-850 nm) is known to result from symmetry breaking of the first excited state D$_E$ in solution and in the excited state to give the D$_1$ and D$_2$ states (two overlapping bands), and TD-DFT calculations assumed only the propeller-type structure that converged, predictions of the 580-850 nm region were less accurate than for higher order excitations. (79)
Figure 14. Computed (CAM-B3LYP/6-31G(d,p), CPCM = MeCN, blue lines) vs. experimental UV-vis spectra of TpBPA\(^+\) and TCBPA\(^+\) in MeCN containing 0.1 M \(n\)Bu4NPF6. Negligible TD-DFT excitations (coefficient \(f<0.0010\)) in grey. Assignments are based on the optical transitions.

Canonical molecular orbital (MO) calculations \((74,91)\) revealed that excited states involved HOMO\(^-\)\(-\)n’ to SOMO transitions, typical of hole-particle excitations (Figure 15A). \((45,74)\) As was the case herein, canonical MOs for higher order excited states and for hole-particle excitations often present a substantial list of orbital transitions with similar coefficients without a single dominant component. Here, Natural Transition Orbitals (NTOs) are a helpful tool to visualize the changes in ‘hole density’ during transitions. \((92)\) A common theme for all TPA\(^+\)s studied was that the first (and second) excited states \((D_0\rightarrow D_E\rightarrow D_{1,2})\) involved \(\pi\rightarrow\pi^*\) transitions around the core aromatic rings, while the higher order excited states \((D_0\rightarrow D_n)\) associated with the excitation wavelength of interest \((395 \text{ nm})\) involved \(\pi\rightarrow\pi^*\) transitions around the peripheral aromatic rings (Figure 15B). It seems noteworthy that the concentration of ‘hole density’ at the peripheral aromatic rings is exactly where it would be in closest proximity to the arenes in reactive T-\(\pi\) precomplexes.

Ruling out participation of the first two excited states and states accessed at wavelengths <380 nm, we predict ‘effective maximum’ excited state potentials of TpBPA\(^+\) at +4.02 V, TCBPA\(^+\) at +4.19 V and TdCBPA\(^+\) at +4.41 V vs. SCE from the Rehm-Weller equation. Although, naturally, a proportion of the excited state TPA\(^+\)’s energy will be dissipated by vibrational relaxation and solvent reorganization (observed by TAS, see Supplementary Information).
A mechanism is proposed consistent with spectroscopic and computational studies herein (Figure 16). Anodic SET oxidation generates the TPA\(^+\) from its TPA. Photoexcitation of the TPA\(^+\) to its D\textsubscript{1}/D\textsubscript{2} or higher D\textsubscript{n} states followed by bimolecular SET reductive quenching is prohibited by the TPA\(^+\)'s picosecond lifetime. Instead, preassociation occurs to give a reactive T-\(\pi\) or an unreactive \(\pi-\pi\) precomplex, depending on the sterics of the arene substrate. In the latter case, conjugative stabilization of the N radical cation decreases \(E_{\text{pox}}\) of the *TPA\(^+\) below the threshold for productive unimolecular SET such that photoexcitation leads simply to non-radiative photophysical relaxation processes (such as internal conversion). In the former case, photoexcitation yields unimolecular SET reductive quenching of the *TPA\(^+\), regenerating the TPA and generating the arene radical cation to be intercepted by the N-heterocyclic nucleophile 2b followed by loss of protons and further SET (anodic or by the TPA\(^+\)) to yield product 3. The prerequisite for precomplexation rationalizes the typical requirement for an excess of arene (3.5 eq. up to 1 mL, ~40 eq. herein) to drive precomplexation equilibrium in arene amination reactions mediated by radical cations (45-46).
**Conclusion** In conclusion, we report tri(p-substituted)biarylaminium radical cations (TPAs\(^{+}\)) as a novel class of tunable, electroactivated photoredox catalyst. Photoexcited tris(p-substituted)biarylaminium radical cations (TPAs\(^{+}\)) have been demonstrated as highly potent and tunable SET oxidants despite their ultrashort excited state lifetimes. As demonstrated herein, straightforward customization of neutral TPAs lends itself to the tuning of UV-vis absorptions, redox potentials and handles for Preassociative Photoredox Catalysis (‘Pre-PRC’) within the TPAs\(^{+}\). Wavelength-dependent control reactions and excited state potentials, as estimated by cyclic voltammetry and TD-DFT calculations, corroborate the participation of higher order (than D\(_1/D_2\)) excited states in the photochemistry. Precomplexation of TPAs\(^{+}\) and arene substrates was evidenced by EPR spectroscopy, UV-vis spectroscopy and supported by DFT calculations. To our knowledge, this study constitutes an unprecedented example of dispersion interactions (\(\pi\)-stacking) as a control element in photochemistry. In this way, Pre-PRC enabled remarkable photochemical phenomena: i) circumvention of the ultrashort lifetimes of excited radical ion states for their use in photocatalysis, ii) anti-Kasha fashion engagement of higher order excited states in photocatalysis, iii) overturning of thermodynamic selectivity dictated by redox potentials by virtue of steric/electronic factors involved in the precomplex. Phenomena (iii) is particularly an advantage over direct electrolysis, where electrodes typically discriminate between molecules based on redox potentials. In context of the findings herein, we foresee ‘Pre-PRC’ as an important next evolution of photoredox catalysis, that presents tremendous opportunities in novel
reactivity and selectivity to the synthetic chemist.

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Author Contributions
‡J.Ž., M.D. and P.H. contributed equally to this work.
S.W. performed the optimization study, conducted all photoelectrochemical reactions, synthesized TPA⁺s and measured spectroelectrochemistry and UV-vis spectra of compounds. S.W., J.B. and J.Ž. designed TPAs while J.Ž. synthesized second generation TPAs (with support from M.D.) and performed XRD on TCBPA. While M.D. synthesized some starting materials. Under the guidance of J.R., P.H. measured and analyzed all EPR spectra of TPA⁺s and precomplexes. V.B. and J.B. shared the DFT calculations of precomplexes, spin densities and TD-DFT calculations. D.J.S. performed XRD studies on TPA⁺s. A.K. measured TAS of TPA⁺s. E.T. measured fluorescence, EEM spectra and TCSPC of TPA⁺s. J.H. and E.T. analyzed and interpreted TAS and luminescence data. J.B. and S.W. together wrote the manuscript and analyzed all other spectroscopic data. J.B. conceived and guided the study, designed photoelectrochemical cells, conducted all CV measurements, guided the overall project, facilitated collaborations. All authors checked the manuscript.
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