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Unveiling Extreme Photoreduction Potentials of Donor−Acceptor Cyanoarenes to Access Aryl Radicals from Aryl Chlorides

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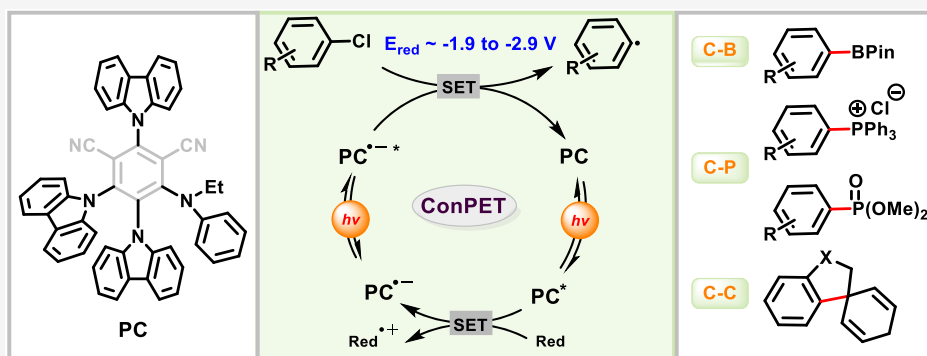
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ABSTRACT: Since the seminal work of Zhang in 2016, donor−acceptor cyanoarene-based fluorophores, such as 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN), have been widely applied in photoredox catalysis and used as excellent metal-free alternatives to noble metal Ir- and Ru-based photocatalysts. However, all the reported photoredox reactions involving this chromophore family are based on harnessing the energy from a single visible light photon, with a limited range of redox potentials from −1.92 to +1.79 V vs SCE. Here, we document the unprecedented discovery that this family of fluorophores can undergo consecutive photoinduced electron transfer (ConPET) to achieve very high reduction potentials. One of the newly synthesized catalysts, 2,4,5-tri(9H-carbazol-9-yl)-6-(ethyl(phenyl)amino)isophthalonitrile (3CzEPAIPN), possesses a long-lived (12.95 ns) excited radical anion form, 3CzEPAIPN$^{\bullet-}$*, which can be used to activate reductively recalcitrant aryl chlorides ($E_{red} \approx -1.9$ to -2.9 V vs SCE) under mild conditions. The resultant aryl radicals can be engaged in synthetically valuable aromatic C−B, C−P, and C−C bond formation to furnish arylboronates, arylphosphonium salts, arylphosphonates, and spirocyclic cyclohexadienes.

INTRODUCTION

Aryl chlorides are versatile building blocks in organic synthesis, being widely utilized as electrophilic partners in nucleophilic aromatic substitutions, in transition metal catalysis, and as precursors to organometallic complexes. Compared to the corresponding bromides or iodides, aryl chlorides are more abundant (Figure 1A), are frequently present in natural products and pharmaceutical molecules, and are often lower in cost and more stable, serving as excellent functional groups for late-stage derivatizations.[1,2]

Photoredox catalysis offers numerous opportunities for the convenient synthesis of active organic radical species through single electron transfer (SET), which is complementary to conventional two-electron processes.[3−6] However, compared to aryl bromides and iodides, aryl chlorides in photoredox catalysis have been largely underexplored due to the high energetic barrier for C(sp^2)−Cl bond activation (PhCl at ~97 kcal/mol).[7,8] Upon absorption of a photon, the excited photoredox catalyst promotes the single-electron reduction of aryl halides. Subsequent C−X bond cleavage delivers carbon-centered radicals, which can participate in a plethora of transformations. The reaction scope is therefore restricted by the energy of a photon. Visible light energy (e.g., a 440 nm blue photon possesses a maximum driving force of 2.8 eV) is typically diminished by 25%−50% through vibrational relaxation, internal conversion, and intersystem crossing, which is difficult to activate challenging nonactivated aryl chlorides,[9] that normally requires carcinogenic high-energy ultraviolet (UV) light.[10,11]

Several strategies have been developed during the past several years to address these challenges and enable the activation of aryl chlorides under visible light irradiation and

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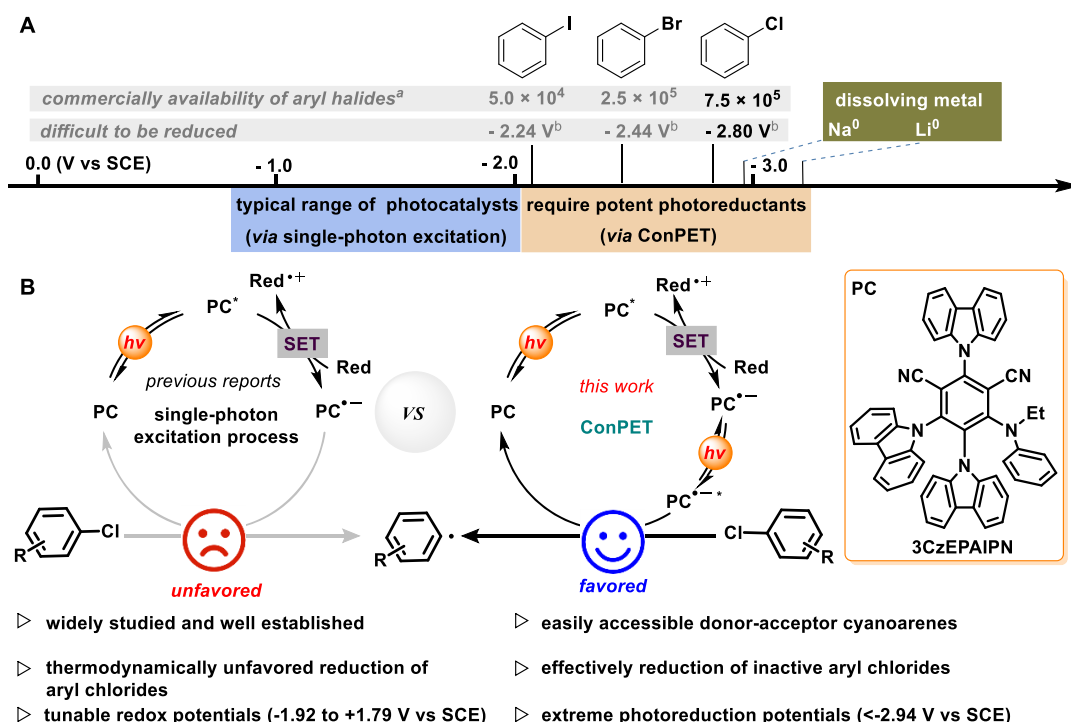
Figure 1. (A) Photocatalytic activation of aryl halides. (B) Disclosure of donor−acceptor cyanoarenes as efficient ConPET catalysts for aryl chloride activation. [a]Commercial availability of different arene sources: SciFinder, accessed April 2, 2021. [b]See details in Table S6, potentials vs SCE (saturated calomel electrode).

mild conditions, such as consecutive photoinduced electron transfer (ConPET), sensitization-initiated electron transfer (SenI-ET), electrophotocatalysis, and solvated electrons.[8,12,13] Among these strategies, ConPET represents the most operationally simple and green method[12,14] and does not require additives such as metal catalysts,[15] additional photo-sensitizers,[16] micelles,[17] electrolytes, or specialized electro-chemical equipment.[18,19] The ConPET strategy relies on a photocatalyst and a sacrificial electron donor that, upon visible light irradiation, results in a long-lived radical anion, which can be excited by a second photon to induce a much more powerful reducing species.[20] The König group pioneered this field by developing a perylene bisimide (PDI) photocatalyst whose photoreduced form can undergo consecutive absorption of a second photon to achieve a much stronger reducing species for aryl halide reduction.[21] Subsequently, several other organic dyes, including rhodamine 6G,[22] 9,10-dicyanoanthra-cene (DCA),[23] anthraquinone,[24] acridinium salts (Mes-Acr⁺),[25] and benzo[ghi]perylene (BPI),[26] were disclosed to be competent ConPET catalysts for aryl halide reduction,[21−25] Birch reduction,[26] and sulfonamide cleavage.[25] However, the majority of these ConPET catalysts are still effective only for electron-poor aryl chlorides,[21−24] and efficient catalytic systems for reductively recalcitrant aryl chlorides are rare[25,27] but highly desirable.[8]

Carbazoyl dicyanobenzenes were first reported as highly efficient thermally activated delayed fluorescence (TADF)[28] emitters by Adachi and co-workers.[29] Among these donor–acceptor fluorophores, 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicya-nobenzene (4CzIPN) has been widely applied as a versatile metal-free photoredox catalyst to replace Ru− and Ir−polypyridyl photocatalysts.[30,31] Its photophysical and electro-chemical properties can be fine-tuned by structural mod-ification of the electron donor or electron acceptor moieties of

the cyanobenzene scaffold to expand the redox window (−1.92 to +1.79 V vs SCE).[32] Upon absorption of a blue photon, the excited 4CzIPN can be quenched via single-electron reduction, resulting in the formation of the radical anion 4CzIPN•−. In the established 4CzIPN-based photoredox catalysis process, this radical anion species is typically oxidized to regenerate the parent catalyst to complete the catalytic cycle (Figure 1B, left cycle). We herein report an unprecedented discovery[27,33] that donor−acceptor cyanoarenes can effectively undergo a ConPET process to achieve a very strongly reducing photocatalytic system that can effectively reduce unactivated and electron-rich aryl chlorides (with reduction potentials, E_{red}, as low as −2.94 V vs SCE) for aromatic C−B, C−P, and C−C bond formation (Figure 1B, right cycle). This strategy features advantages such as not requiring transition metals, being operationally simple, proceeding under mild conditions, and functioning with a wide range of aryl halides including complex pharmaceutical molecules for late-stage derivatizations.

■ RESULTS AND DISCUSSION

Reaction Design and Optimization. Our study was first inspired by the observation that the radical anion of 4CzIPN (4CzIPN•−) generated from photoexcited 4CzIPN* and an electron donor N,N-diisopropylethylamine (DIPEA) is a long-lived radical anion species (stable for more than 3 h under argon in the dark, Figure S20). This species can be further excited by blue LED light to give a fluorescence band (λ_{max}^{em} = 448 nm) which is distinctly different from that of 4CzIPN* (λ_{max}^{em} = 545 nm, Figure S8G). The reductive potential of 4CzIPN $[E_{1/2}(PC/PC^{•−})] = -1.24$ V vs SCE] (Figure S13) is more negative than those of DCA (−0.82 V vs SCE),[18] PDI (−0.43 V vs SCE),[21] and Mes-Acr⁺ (−0.60 V vs SCE)[25] and is similar to that of BPI (−1.30 V vs SCE),[26] indicating that

Table 1. Optimization of Conditions for the Visible-Light-Induced Borylation of Aryl Chlorides

A) Selected conditions for reaction optimization
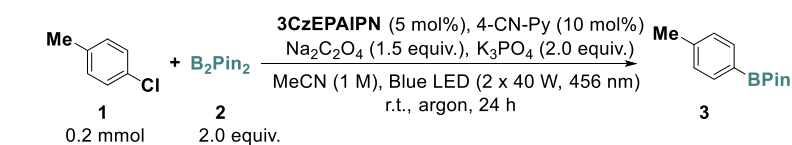
Entry	Variation to standard conditions	Yield of 3 [a]
1	none	96% (95%)[c]
2	**4CzIPN** instead of **3CzEPAIPN**	76%
3	**3CzMPAIPN** instead of **3CzEPAIPN**	85%
4	DIPEA (2.4 equiv.) instead of $Na_2C_2O_4$ and K_3PO_4	52%
5	L-AscNa$_2$ (1.5 equiv.) instead of $Na_2C_2O_4$	95%
6	no 4-CN-Py	26%
7	no K_3PO_4	33%
8	no $Na_2C_2O_4$	0
9	no light, or no **3CzEPAIPN**	0
10[b]	6 mmol of **1** instead of 0.2 mmol	79%[c] (1.03 g)

B) Synthesis and characterization of new donor-acceptor dicyanobenzenes

PC	$E_{1/2}$ (PC/PC$^{\cdot-}$) vs SCE	$E_{1/2}$ (PC*/PC$^{\cdot-}$) vs SCE	$E_{0,0}$	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	ε_{max} ($M^{-1}cm^{-1}$)	τ_f (ns)
4CzIPN	-1.24 V	+1.42 V	2.66 eV	430	545	6942	12.7
3CzMPAIPN (R = Me)	-1.40 V	+1.29 V	2.69 eV	426	597	8451	0.48
3CzEPAIPN (R = Et)	-1.42 V	+1.25 V	2.67 eV	427	597	7270	0.51

[a]Yields based on analysis of the ^{1}H NMR spectra of the crude product mixture by using CH_2Br_2 as an internal standard. [b]Blue LED (4 × 40 W, 456 nm); the reaction was performed for 36 h. [c]Isolated yields. 4-CN-Py = 4-cyanopyridine; L-AscNa$_2$ = L(+)-ascorbic acid disodium salt; $E_{0,0}$ = excited state energy; ε_{max} = molar extinction coefficient at the maximum absorption wavelength; τ_f = lifetime of the excited state; CzH = carbazole.

4CzIPN$^{\cdot-*}$ could be a powerful reducing species that can effectively reduce difficult aryl halides.

On the basis of the proposed ConPET process, we first attempted to develop a synthetically useful borylation reaction of chloroarenes, of which meaningful progresses have been made by Schelter,[10] Lambert−Lin,[18] Jiao,[34] Marder,[35] Larionov,[36] and König.[37] Our initial optimization revealed that when 4CzIPN was used as a photocatalyst, with a catalytic amount of 4-cyanopyridine, sodium oxalate as an electron donor, and K_3PO_4 as a base, borylation of p-chlorotoluene (**1**) afforded the corresponding boronic ester (**3**) in 76% yield under 2 × 40 W blue LED irradiation (Table 1A, entry 2). 4CzIPN was not stable[38,39] and easily decomposed to carbazoles under the reaction conditions (see details in Figures S29 and S31), which may cause a lower reaction efficiency. We thus synthesized a group of new donor−acceptor dicyano-benzenes through a straightforward two-step procedure (Table 1B)[30,40] by replacing one of the carbazole groups with amines to alleviate or avoid the decomposition of photocatalysts (Table S2). Among all the newly synthesized photocatalysts,

an improved yield was obtained when using tri(9H-carbazol-9-yl)-6-(methyl(phenyl)amino)isophthalonitrile (3CzMPAIPN) as the photocatalyst (entry 3), and further improvement to 95% isolated yield could be achieved by replacing the methyl substituent with an ethyl group (3CzEPAIPN, entry 1). The control experiments (Figure S30) illustrated that 3CzEPAIPN (in a radical anion form) could exist for a much longer time during the reaction process, although both 4CzIPN and 3CzEPAIPN decomposed after an extended reaction time (>24 h). When DIPEA was used as the electron donor instead of sodium oxalate, a moderate yield (52%) was achieved due to competing dechlorinated byproduct formation (Table 1A, entry 4). Using sodium ascorbate as the electron donor afforded the same efficiency as that with sodium oxalate (entry 5); thus, inexpensive sodium oxalate was employed in the scope study. Eliminating the catalytic 4-cyanopyridine led to a substantially reduced yield (entry 6), indicating its important role for the stable boryl radical formation.[41] The reaction became less efficient in the absence of K_3PO_4 (entry 7). Control experiments revealed the essential roles of both
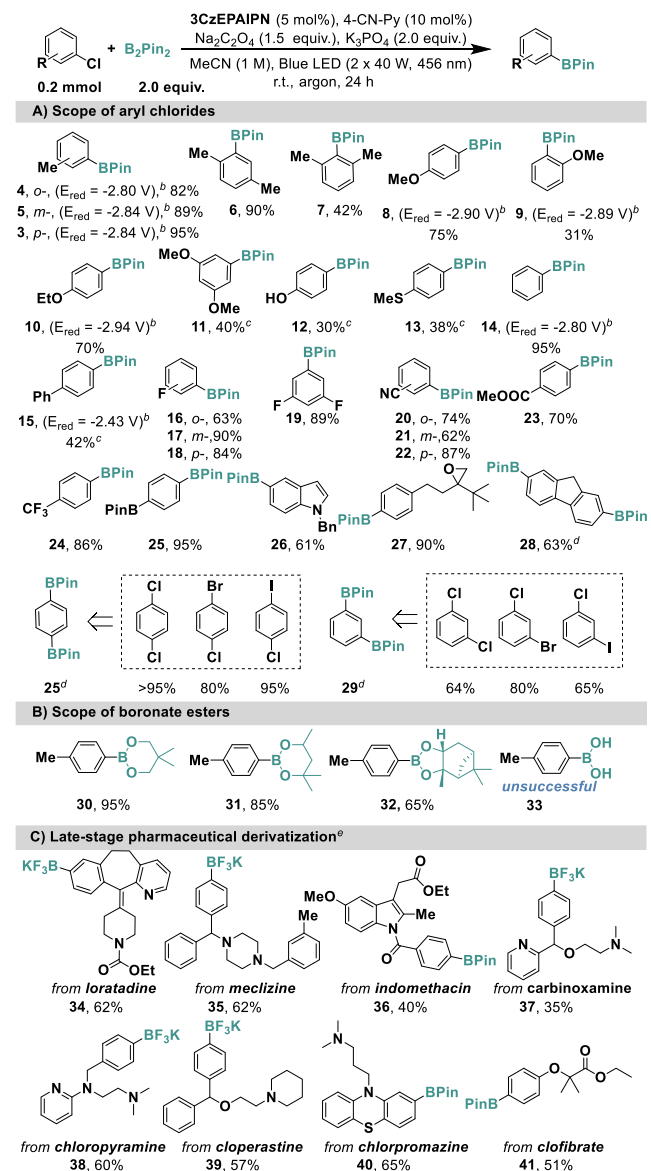
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sodium ascorbate and photoirradiation as no product was detected in the absence of either of them (entries 8 and 9). Gram-scale synthesis was easily achieved by employing more intensive light irradiation and a longer reaction time (entry 10), demonstrating the synthetic practicality of this method.

Scope of Borylation. With the optimized conditions in hand, we examined the scope of borylation of aryl chlorides through the ConPET process. We found that this protocol was effective with not only activated aryl chlorides (**15−25**) but also challenging nonactivated aryl chlorides (**14**) and electron-rich aryl chlorides (**3−13**) that possess very negative reduction potentials (up to −2.94 V, Table 2A). A number of functional groups were well tolerated, including ethers (**8−11**), phenols (**12**), sulfides (**13**), trifluoromethyl (**24**), and borates (**25**) as well as those potentially sensitive to strongly reducing conditions, such as aryl fluorides (**16−19**), nitriles (**20−22**), esters (**23**), indoles (**26**), and epoxides (**27**). Only moderate yields were obtained with some substrates (**9** and **11−13**), which were mainly due to the competing dechlorination side reaction and starting material recovery even with prolonged reaction time (36 h). No obvious correlation between the substrate reduction potential and reactivity was observed, indicating the radical anion fragmentation and borylation steps also played important roles to achieve an overall efficient transformation.[19] Diborylation products (**25**, **28**, and **29**), which have found wide application in materials science, were obtained in good to excellent yields when dihaloarenes were employed, probably because the generated monoborylated chloride intermediates were more reducible than dihaloarenes. Aryl borates other than pinacolborate could be smoothly generated by using the corresponding diboron esters (**30−32**, Table 2B). However, B$_2$(OH)$_4$ was not compatible with our method due to its insolubility in acetonitrile (**33**).

A wide range of pharmaceutical compounds performed well under a slightly modified borylation protocol by using DIPEA as the electron donor, which possesses multiple Lewis basic atoms and heterocyclic moieties that can potentially coordinate and be problematic in transition metal catalysis (Table 2C). Borylated derivatives of loratadine (**34**), meclizine (**35**), indomethacin (**36**), carbinoxamine (**37**), chloropyramine (**38**), cloperastine (**39**), chlorpromazine (**40**), and clofibrate (**41**) were generated in moderate to good yields. Some of the borylation products were isolated as organotrifluoroborate salts as a part of the work-up procedure to assist product isolation.

Transformations Other than Borylation. The scope of this carbazoyl dicyanobenzene-promoted ConPET strategy could be extended to the formation of C−P bonds by employing phosphines or phosphites as radical trapping agents. Arylphosphonium salts are widely used as organocatalysts, phase transfer reagents, ionic liquids, and so on. In addition, they can also be used as functional handles for further C−O, C−S, C−N, and C−C bond formation.[42−45] However, existing methods for the preparation of arylphosphonium salts from aryl halides or pseudohalides rely on transition metal catalysis and high-temperature processes.[46−48] We herein developed a metal-free synthesis of arylphosphonium salts under ambient conditions using 3CzEPAIPN as the photocatalyst and substoichiometric DIPEA as the electron donor (Figure 2A). Notably, this reactivity enabled engagement of both electron-rich and electron-poor aryl chlorides (**42−51**) as well as various arylphosphines (**52−54**), delivering the desired phosphonium salts in good to excellent yields. Moreover, exposure of aryl exclusively in chlorides with trimethyl

**Table 2. Scope of Visible-Light-Induced Borylation of Aryl Chlorides**[a]

Reaction scheme: R–(aryl)–Cl + B$_2$Pin$_2$ (2.0 equiv.) → R–(aryl)–BPin

Conditions: 3CzEPAIPN (5 mol%), 4-CN-Py (10 mol%), Na$_2$C$_2$O$_4$ (1.5 equiv.), K$_3$PO$_4$ (2.0 equiv.), MeCN (1 M), Blue LED (2 × 40 W, 456 nm), r.t., argon, 24 h. Aryl chloride 0.2 mmol.

A) Scope of aryl chlorides

- **4**, o-, (E$_{red}$ = −2.80 V),[b] 82%
- **5**, m-, (E$_{red}$ = −2.84 V),[b] 89%
- **3**, p-, (E$_{red}$ = −2.84 V),[b] 95%
- **6**, 90%
- **7**, 42%
- **8**, (E$_{red}$ = −2.90 V)[b] 75%
- **9**, (E$_{red}$ = −2.89 V)[b] 31%
- **10**, (E$_{red}$ = −2.94 V)[b] 70%
- **11**, 40%[c]
- **12**, 30%[c]
- **13**, 38%[c]
- **14**, (E$_{red}$ = −2.80 V)[b] 95%
- **15**, (E$_{red}$ = −2.43 V)[b] 42%[c]
- **16**, o-, 63%
- **17**, m-, 90%
- **18**, p-, 84%
- **19**, 89%
- **20**, o-, 74%
- **21**, m-, 62%
- **22**, p-, 87%
- **23**, 70%
- **24**, 86%
- **25**, 95%
- **26**, 61%
- **27**, 90%
- **28**, 63%[d]
- **25**[d] (from Cl/Cl, Br/Cl, I/Cl): >95%, 80%, 95%
- **29**[d] (from Cl/Cl, Cl/Cl, Cl/I): 64%, 80%, 65%

B) Scope of boronate esters

- **30**, 95%
- **31**, 85%
- **32**, 65%
- **33**, unsuccessful

C) Late-stage pharmaceutical derivatization[e]

- from loratadine **34**, 62%
- from meclizine **35**, 62%
- from indomethacin **36**, 40%
- from carbinoxamine **37**, 35%
- from chloropyramine **38**, 60%
- from cloperastine **39**, 57%
- from chlorpromazine **40**, 65%
- from clofibrate **41**, 51%

[a]Reaction conditions: aryl chloride (0.2 mmol), B$_2$Pin$_2$ (2.0 equiv), 4-CN-Py (10 mol %), Na$_2$C$_2$O$_4$ (1.5 equiv), K$_3$PO$_4$ (2.0 equiv), and 3CzEPAIPN (5 mol %) in MeCN (1 M) under irradiation with Kessil light (456 nm, 2 × 40 W) at rt for 24 h under argon. Isolated yields. [b]See references in Table S6; potentials vs SCE. [c]The reaction was performed for 36 h. [d]Only diborylation products were obtained. [e]Reaction conditions were slightly modified; see details in the Supporting Information.

phosphite to slightly modified conditions enabled a visible light promoted Arbuzov reaction for the generation of aryl phosphonates (**55−60**, Figure 2B).[49]

The synthetic utility of this ConPET protocol was further extended to dearomative hydroarylation of aryl chlorides to produce spirocyclic cyclohexadienes (**61−63**), probably through a reductive radical-polar crossover mechanism, as reported by Jui[50] (Figure 2C). The catalytic system could also be applied to reductive defluorination of trifluoromethylarenes to methylarenes (**64**, Figure 2D).[51] Moreover, the developed phosphorylation was amenable to scale-up with an operationally simple continuous-flow setup, which resulted in
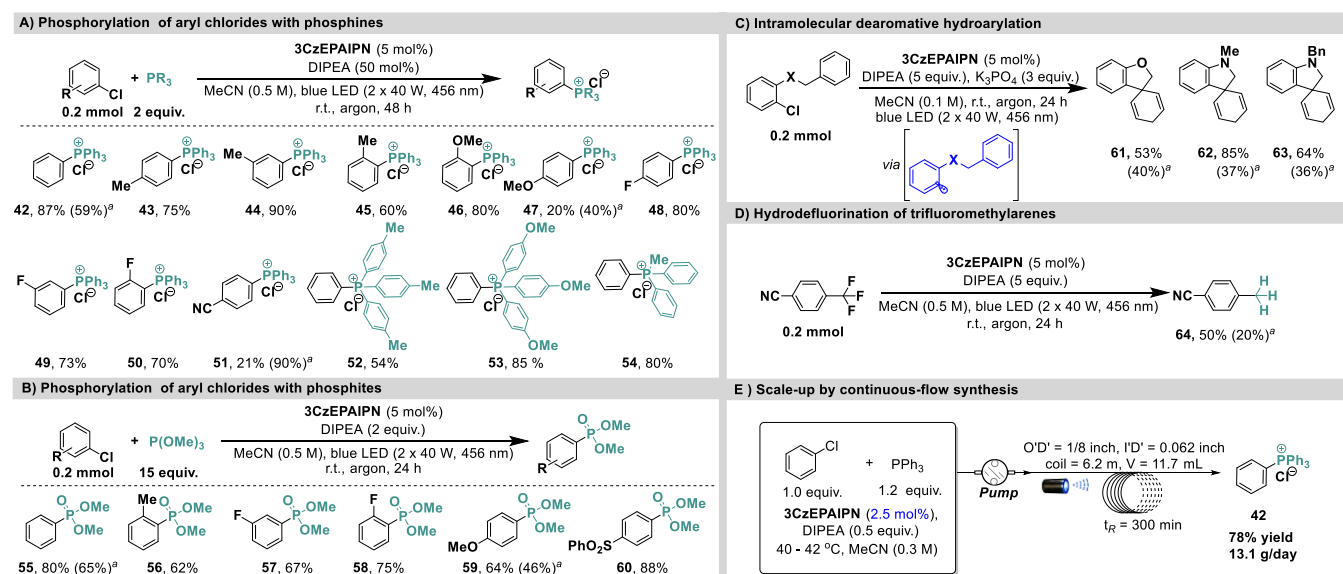
Figure 2. Various transformations promoted by the donor−acceptor cyanoarene-catalyzed reductive ConPET process. [a]Using 4CzIPN as the photocatalysts instead of 3CzEPAlPN.

phosphonium salts in good yield and gram-scale production with reduced amounts of Ph₃P (1.2 equiv) and photocatalyst (2.5 mol %), highlighting the excellent efficiency of micro-tubing flow reactors in photochemical synthesis (Figure 2E).

Mechanistic Investigations. To gain more insight into the proposed ConPET process, various spectroscopic studies and control experiments were performed (Figure 3). First, upon irradiation of a solution of 3CzEPAlPN and DIPEA with a blue LED light, a color change from yellow to light yellow was observed. UV−vis spectroscopy demonstrated a blue-shift of the maximum absorption peak (Figure 3A). The emission of these mixtures clearly underwent a hypsochromic shift (λ_{max}^{em} from 597 to 488 nm, Figure 3B; a very weak energy emission band was observed at λ_{max}^{em} = 546 nm when excited by ~525 nm green light, Figure S12) resulted from the formation of a new species, which is similar to the result observed for 4CzIPN. To verify that this new species was the long-lived radical anion 3CzEPAlPN•−, electron paramagnetic resonance (EPR) spectroscopy was conducted. The experimental EPR spectrum matches well with the simulated spectrum of 3CzEPAlPN•− (Figure 3C).[52] Near quadratic dependency of the conversion of aryl chlorides on the irradiation density further supported that the aryl radical formation mechanism involves an overall two-photon excitation (Figure 3D).[53]

Direct evidence of the ConPET process was obtained by ¹H NMR investigation (Figure 3E). The characteristic NMR signals of 3CzEPAlPN were detected with a mixture of the photocatalyst and DIPEA in CD₃CN (step 1). Upon direct exposure of the solutions within the NMR tube to blue light, line broadening and signal disappearance were observed, probably due to the generation of unpaired electron species (step 2), which have a strong influence on NMR resonance transverse relaxation rates of neighboring protons, indicating the generation of 3CzEPAlPN•−. This radical anion species was stable under argon for at least 3 h and could be quenched by air to convert back to the ground state catalyst (Figure S21). The addition of aryl chlorides showed no effect on the radical anion species in the absence of light (step 3). However, in the presence of light, they quenched the radical anion species back to 3CzEPAlPN, and the dehalogenation product

was detected by ¹⁹F NMR spectra (step 4), which is consistent with our proposal that photoexcited 3CzEPAlPN•−* is capable of reducing aryl chlorides to reactive aryl radicals.

The long lifetime of unexcited 3CzEPAlPN•− allows it to absorb a photon by using an LED light source to generate the excited state, whose properties were explored by time-correlated single photon counting (TCSPC) (Figure 3F).[26,54] Excitation of 3CzEPAlPN•− by irradiation at 375 nm resulted in a characteristic emission band of 3CzEPAlPN•−* (λ_{max}^{em} = 488 nm), whose average lifetime was measured to be 12.95 ns, much longer than the 6.33 ns of 4CzIPN•−*. The time-resolved emission quenching experiments revealed a linear photoluminescence lifetime quenching of 3CzEPAlPN•−* by aryl chlorides, which further supported the ConPET process (Figure 3G).

In light of all the experimental data, a plausible mechanistic pathway was proposed by using aryl borylation as a representative example (Figure 3H). Following light excitation, 3CzEPAlPN engages in single-electron transfer with an electron donor to generate a long-lived radical anion species, which is then excited by visible light irradiation again to afford excited 3CzEPAlPN•−*. 3CzEPAlPN•−* possesses strong reductive potential to undergo electron transfer with reductively recalcitrant aryl chloride, which generates a reactive aryl radical after fragmentation and re-forms 3CzEPAlPN in the ground state. The resulting aryl radical then couples with a Lewis base stabilized boryl radical,[41] yielding the desired arylboronate product (see the Supporting Information for the proposed mechanisms for C−P and C−C bond formations).

■ CONCLUSION

In conclusion, we have disclosed that donor−acceptor cyanoarene-based fluorophores can undergo ConPET to access catalysts with exceedingly high reducing power, which complements the well-established single-photon-promoted redox chemistry associated with this family of fluorophores. A new catalyst 3CzEPAlPN can be activated through this strategy to enable robust and efficient activation of aryl chlorides with very negative reduction potentials for C−B, C−P, and C−C bond formations to furnish a broad scope of
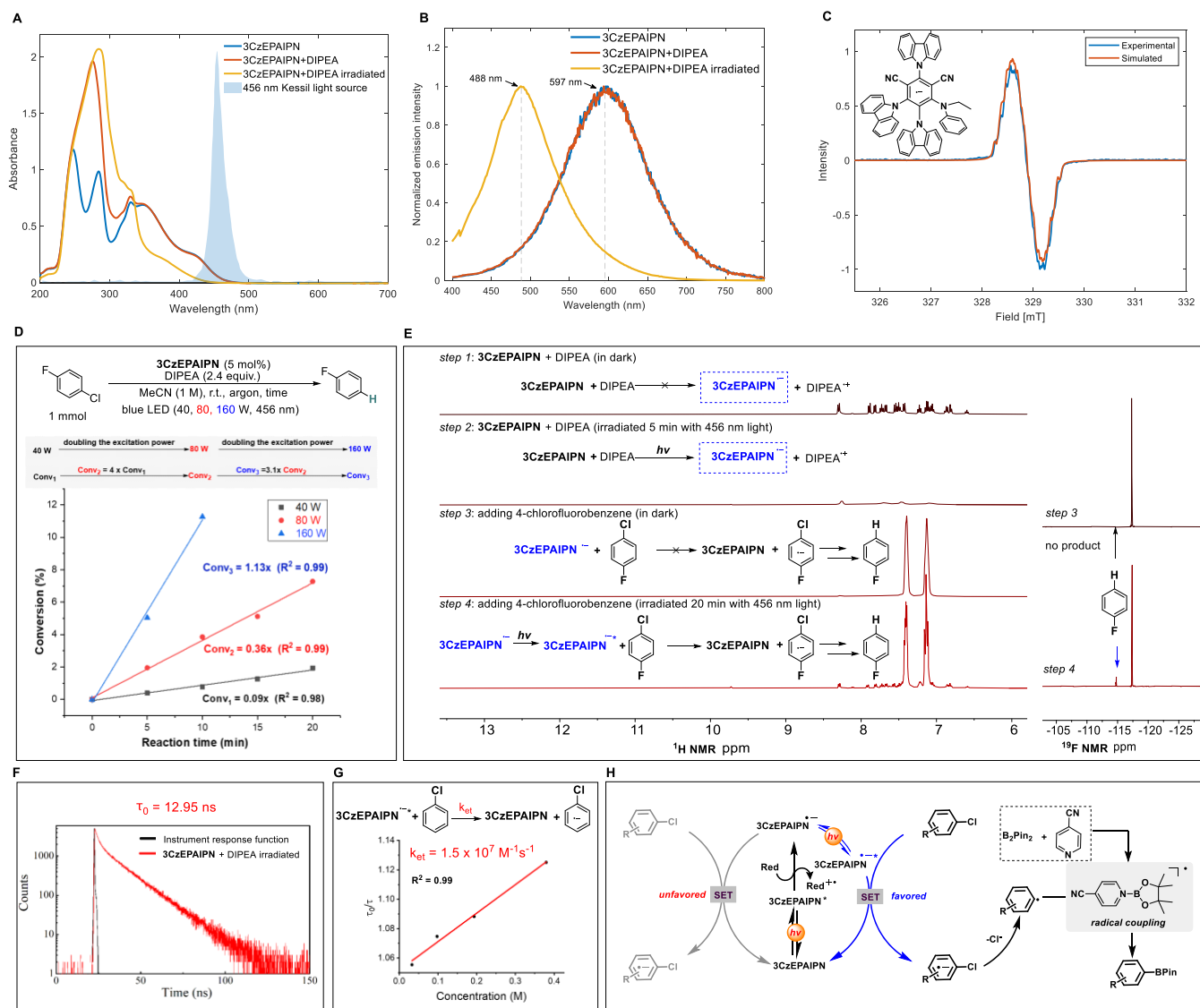
Figure 3. Proposed mechanism with supporting evidence. (A) Absorbance profiles for 3CzEPAIPN and 3CzEPAIPN$^{\bullet-}$ (3.3×10^{-5} M, 1.0 cm path length). (B) Emission profiles (excitation at 390 nm) for 3CzEPAIPN and 3CzEPAIPN$^{\bullet-}$ (3.3×10^{-5} M, 1.0 cm path length). (C) Experimental and simulated EPR spectra to support the presence of 3CzEPAIPN$^{\bullet-}$. (D) Near quadratic dependency of the conversion of aryl chlorides on the irradiation density to support the overall two-photon absorption process. R^2 is the coefficient of determination, known as the goodness of fit. (E) NMR spectroscopic evidence supporting the proposed ConPET process. (F) Determination of the average lifetime (τ_0) of the excited state of 3CzEPAIPN$^{\bullet-}$ by time-correlated single-photon counting measurements. (G) Measurement of the electron transfer rate constant (k_{et}) between various concentrations of chlorobenzene and 3CzEPAIPN$^{\bullet-}$* by time-resolved emission quenching experiments. τ is the lifetime of 3CzEPAIPN$^{\bullet-}$* in different concentrations of chlorobenzene. (H) Plausible mechanism of borylation of aryl chlorides through the ConPET process.

arylboronates, arylphosphonium salts, arylphosphonates, and spirocyclic cyclohexadienes. The ConPET process has been unambiguously supported by various spectroscopic investigations. The advantages associated with cyanoarene-based fluorophores, such as being inexpensive, metal-free, and modular, allow wide applications in the synthetic community and provide a platform to further explore and understand the design principles for more potent photocatalysts based on the ConPET process.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c05994.

General procedures, tables of reaction optimizations, analytical data, and NMR spectra (PDF)

Accession Codes

CCDC 2088426 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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