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Photogeneration of Chlorine Radical from a Self-Assembled Fluorous 4CzIPN•Chloride Complex: Application in C–H Bond Functionalization

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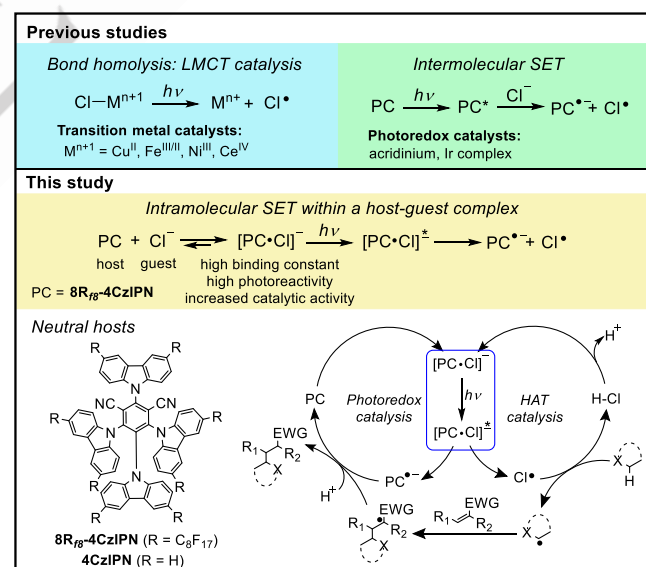
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Abstract: The chlorine radical is a strong HAT (Hydrogen Atom Transfer) agent that is very useful for the functionalization of C(sp³)–H bonds. Albeit highly attractive, its generation from the poorly oxidizable chloride ion mediated by an excited photoredox catalyst is a difficult task. We now report that **8R₁₈-4CzIPN**, an electron-deficient fluorous derivative of the benchmark **4CzIPN** photoredox catalyst belonging to the donor-acceptor carbazole-cyanoarene family, is not only a better photooxidant than **4CzIPN**, but also becomes an excellent host for the chloride ion. Combining these two properties ultimately makes the self-assembled **8R₁₈-4CzIPN**•Cl[−] dual catalyst highly reactive in redox-neutral Giese-type C(sp³)-H bond alkylation reactions promoted by the chlorine radical. Additionally, because of its fluorous character, the efficient separation/recovery of **8R₁₈-4CzIPN** could be envisioned.

In recent years, merging photoredox catalysis with HAT (Hydrogen Atom Transfer) catalysis has led to the development of mild and highly efficient reactions for the direct functionalization of C(sp³)–H bonds.^[1] Within this area, the use of the chlorine atom as a HAT reagent (BDE H–Cl = 105 kcal/mol, BDE = Bond Dissociation Energy) has received a particular interest due to its ability to cleave strong alkane C(sp³)–H bonds, including that of CH₄ (BDE C–H = 105 kcal/mol). In these reactions, the chlorine radical has most often been produced by photo-homolysis of transition metal–chloride bonds, implying irradiation into the LMCT (Ligand to Metal Charge Transfer) bands (Scheme 1).^[2] Much less explored are processes exploiting intermolecular SET (Single Electron Transfer). This requires a PC (Photoredox Catalyst) whose excited state is able to oxidize the chloride ion ($E_{\text{ox}} = +2.03$ V vs SCE).^[3] This was achieved using either the highly photooxidizing 9-mesityl-10-methylacridinium ion ($*E_{\text{red}} = +2.06$ V vs. SCE) in conjunction with HCl^[3a] or, the less oxidizing [Ir(dF(CF₃)ppy)₂(dtbbpy)]Cl complex ($*E_{\text{red}} = +1.21$ V vs. SCE).^[3b]

With the latter, running the reactions at 60–80 °C was mandatory due to the highly endergonic nature of the process. It was also proposed that the proximity of the chloride within the ionic complex might facilitate the necessary PC^{•+}/Cl[−] interaction.

Recent studies have highlighted the benefits of tuning the PC electronic properties in order to favor its binding with the substrate.^[4] This may allow access to higher energy



Scheme 1. Strategies of photogeneration of the chlorine radical from chloride ions exploited for the functionalization of C–H bonds by dual photoredox-HAT catalysis. The proposed dual catalytic cycle for the Giese-type reaction targeted in this study is shown, highlighting the chloride complexation with the PC that occurs in the ground-state.

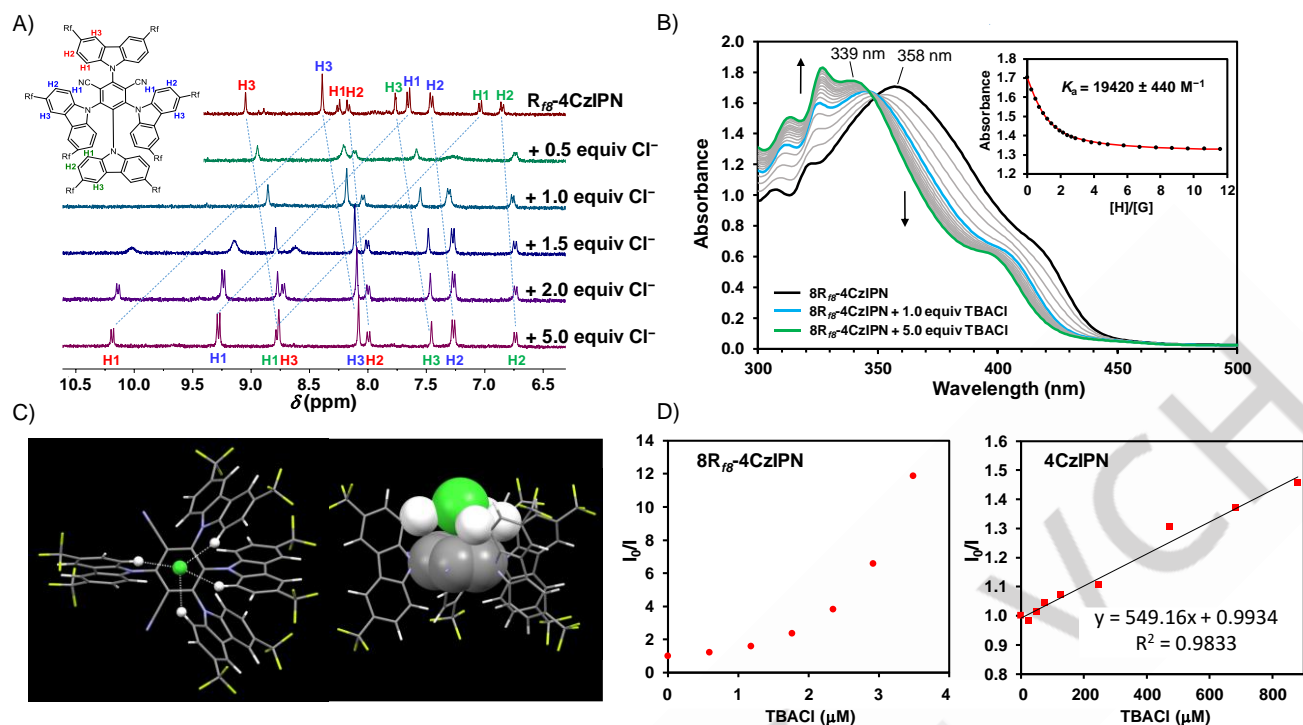


Figure 1. A) ^1H NMR spectra (aromatic region) upon titration of $8\text{R}_{18}\text{-4CzIPN}$ (2.01 mM, THF-d_6 , 293 K) with TBACl. B) UV-vis titration of $8\text{R}_{18}\text{-4CzIPN}$ (0.1 mM, TFT) with TBACl. The insert shows the fitting analysis to a 1:1 binding model at 358 nm. C) Top- and side-views of energy-minimized structures of the 1:1 $8\text{CF}_3\text{-4CzIPN}\cdot\text{Cl}^-$ complex highlighting the hydrogen bonds between Cl^- and H1 hydrogen atoms, and its close interaction with the π -aromatic system of the dicyanoarene. D) Stern-Volmer plots of $8\text{R}_{18}\text{-4CzIPN}$ (2.86 μM , TFT, 293 K) and 4CzIPN (28.6 μM , TFT, 293 K) quenching by Cl^- (Fluorescence spectra given in the SI). The linear fit is provided for 4CzIPN .

excited states, and/or to overcome diffusion-limited kinetics by moving from intermolecular to intramolecular processes. Interestingly, Meyer and co-workers showed that very efficient halide oxidations by Ru(II) complex excited-states, including chloride, was promoted by ground-state pre-organization of Ru complexes $\cdot\text{Cl}^-$ adducts.^[5]

In line with our ongoing interest in the development of photocatalytic methodologies for $\text{C}(\text{sp}^3)\text{-H}$ bond alkylations,^[6] we now report on the photogeneration of the chlorine radical occurring within a self-assembled organic PC \cdot HAT host-guest complex. We show that $8\text{R}_{18}\text{-4CzIPN}$ (Scheme 1), an electron-deficient fluorinated derivative of the benchmark 4CzIPN photoredox catalyst belonging to the donor-acceptor carbazole-cyanoarene family,^[7,8] is not only a better photooxidant than 4CzIPN ($^*E_{\text{red}} = +1.43$ V), but also becomes an excellent host for the chloride ion, two properties that ultimately render the self-assembled dual $8\text{R}_{18}\text{-4CzIPN}\cdot\text{Cl}^-$ catalyst highly reactive in $\text{C}(\text{sp}^3)\text{-H}$ bond alkylation reactions. Additionally, because of its fluorinated character,^[9] the separation/recovery of $8\text{R}_{18}\text{-4CzIPN}$ could be envisioned.^[10]

$8\text{R}_{18}\text{-4CzIPN}$ was prepared in a satisfactory overall yield (53%) by a four steps procedure (benzylation, Ullman coupling, debenylation, $\text{S}_{\text{N}}\text{Ar}$) (Scheme S1). The reaction sequence can be run on multi-gram scales from commercially-available 3,6-diiodo-9H-carbazole (see SI). Characterization of the optical, redox and photoredox properties of $8\text{R}_{18}\text{-4CzIPN}$ and 4CzIPN revealed that the HOMO-LUMO gap is significantly increased in $8\text{R}_{18}\text{-4CzIPN}$ ($E_{0,0} = 2.90$ eV, THF) compared to that of 4CzIPN

($E_{0,0} = 2.67$ eV, CH_3CN),^[8b] as anticipated with the introduction of strong electron withdrawing perfluorooctyl chains on the donor carbazole moieties (Table 1). The photooxidizing power of $8\text{R}_{18}\text{-4CzIPN}$ ($^*E_{\text{red}} = +1.73$ V) is also significantly improved compared to that of 4CzIPN ($^*E_{\text{red}} = +1.43$ V), but still lower than $8\text{CF}_3\text{-4CzIPN}$ ($^*E_{\text{red}} = +1.91$ V; CF_3 instead of C_8F_{17} groups), originally developed for application in blue organic light-emitting diodes,^[11a] and very recently exploited as photoredox catalyst for nucleophilic amination of benzylic C-H bonds.^[11b]

Table 1. Optical, redox and photoredox properties of 4CzIPN and $8\text{R}_{18}\text{-4CzIPN}$

	$\lambda_{\text{abs}}^{[a]}$ (nm)	$\lambda_{\text{fl}}^{[a]}$ (nm)	$\tau_{\text{p}}^{[b]}$ (ns)	$\tau_{\text{d}}^{[b]}$ (μs)	$E_{0,0}$ (eV)	E_{red} (V)	E_{ox} (V)	$^*E_{\text{red}}$ (V)	$^*E_{\text{ox}}$ (V)
4CzIPN	370	519	22	3.0	2.67 ^[c]	-1.24 ^[c]	+1.49 ^[c]	+1.43 ^[c]	-1.18 ^[c]
$8\text{R}_{18}\text{-4CzIPN}$	352	469	8.5	5.1	2.90 ^[d]	-1.17 ^[e]	+1.44 ^[e]	+1.73 ^[e]	-1.46 ^[e]

[a] In THF (spectra given in Figure S1); [b] Prompt and delayed fluorescence lifetimes in α,α,α -trifluorotoluene (Figure S2). [c] From ref. 8b. Recorded in CH_3CN , vs. SCE; [d] Estimated from the intersection of the absorption and emission spectra; [e] Recorded in THF (Figure S3), vs. SCE. Due to low reversibility, the potential values are taken at the peak.

In the course of our study we discovered that $8\text{R}_{18}\text{-4CzIPN}$ had a strong affinity for the chloride ion, the co-catalyst of the targeted catalytic process (Scheme 1). Addition of tetrabutylammonium chloride (TBACl) to a suspension of

8R_{fg}-4CzIPN in acetone enhanced its solubility, suggesting that complexation had occurred. The ¹H NMR spectra of **8R_{fg}-4CzIPN** upon titration with Cl⁻ confirmed that a strong host-guest complex forms in THF-d₈ as evidenced by the $\Delta\delta = 1.6$ -1.9 ppm downfield shift (Table S1) of the carbazole H1 proton resonances (Figure 1A; Figure S4 for assignments of H1, H2 and H3 protons). Such a large downfield shift indicates that Cl⁻ is H-bonded to the four aromatic C–H1 bonds that are pointing towards the center of the dicyanoarene ring.^[12] For all the other carbazole protons (H2, H3) a smaller upfield shift ($\Delta\delta = 0.1$ -0.3 ppm) was observed. The broadening of the resonances observed up to the addition of 1.5 equiv of Cl⁻ shows that a fast host/guest exchange occurs at the NMR time-scale. For **4CzIPN**, whose C–H1 bonds are less acidic, a weaker downfield shift ($\Delta\delta = 0.4$ -0.5 ppm) was observed for the H1 protons (Figure S5), consistent with weaker C–H...Cl⁻ H-bonds.

The binding constant and complex stoichiometry between **8R_{fg}-4CzIPN** and Cl⁻ were determined using UV-vis spectroscopy (Figure 1B). Upon addition of up to 5 equiv of Cl⁻ in TFT (α,α,α -trifluorotoluene), a hypsochromic shift (~20 nm) was observed for the low energy bands at 420 nm (shoulder) and 358 nm previously assigned for **4CzIPN** to transitions towards the S1 and S3 states, respectively.^[13] For the higher energy bands (~320 nm and 307 nm) that are most likely carbazole-centered electronic transitions (Figure S6), a bathochromic shift (~10 nm) associated to a significant increase of their intensity was noticed. Fitting of the spectra evolution at 358 nm to a 1:1 binding model provided an association constant $K_a = 19420 \pm 440 \text{ M}^{-1}$ ($\Delta G = -5.7 \pm 0.13 \text{ kcal.mol}^{-1}$, 293 K). A similar K_a ($24430 \pm 1220 \text{ M}^{-1}$, $\Delta G = -5.9 \pm 0.3 \text{ kcal.mol}^{-1}$) was determined in THF (Figure S7). For **4CzIPN**, only slight shifts (3 nm) of the low-energy bands were observed during titration with Cl⁻ (Figure S8). A $K_a = 610 \pm 23 \text{ M}^{-1}$ ($\Delta G = -3.7 \pm 0.14 \text{ kcal.mol}^{-1}$, 293 K) could be estimated from the ¹H NMR titration in THF-d₈ (Figure S5). Albeit being about 40 times lower, we note that **4CzIPN** exhibits a significant affinity for Cl⁻.

DFT calculations (B3LYP/6-31+G(d,p)) conducted on the **8CF₃-4CzIPN**·Cl⁻ complex (C₈F₁₇ groups replaced by CF₃ to lower the number of electrons while keeping similar electronic properties) afforded a stabilization energy (ΔG) of $-6.6 \text{ kcal.mol}^{-1}$, consistent with the value measured experimentally. In the energy-minimized structure Cl⁻ is H-bonded with the four C–H1 bonds of the carbazoles, as reflected by the H...Cl⁻ distances of 2.63 Å (average of the 4 bonds) (Figure 1C). However, the C–H...Cl⁻ interaction significantly deviates from linearity (average C–H...Cl⁻ angle = 156.3°), reflecting that the cavity delineated by the four H atoms does not perfectly accommodate Cl⁻. An average C...Cl⁻ distance of 3.62 Å is found between the C atoms of the dicyanoarene and Cl⁻ which is close to the sum of van der Waals radii of the C atom (1.70 Å) and chloride anion (1.81 Å). This suggests that an attractive interaction between an electron lone pair of Cl⁻ and the π^* orbital of the dicyanoarene exists.^[14] Such interaction would participate to the stabilization of the complex and would be responsible for the ~20 nm blue shift of the HOMO-LUMO internal charge transfer transitions observed during the complexation (Figure 1B). We note however that no CT band is appearing during the UV-vis titration (Figure 1B), which is not surprising with a dicyanoarene substituted by four electron-

donating carbazoles. Overall, this study reveals that **4CzIPN** and its derivatives should be considered as a new attractive class of neutral receptors for chloride ions.^[15]

Static fluorescence quenching studies of **8R_{fg}-4CzIPN** and **4CzIPN** by Cl⁻ were conducted in order to probe the reactivity of the PCs excited states.^[16] A strong positive deviation from linearity was observed for the Stern-Volmer plot of **8R_{fg}-4CzIPN**, which typically shows that both static and dynamic quenching is taking place (Figure 1D).^[16a] Also, dramatic quenching of the fluorescence occurred, i.e. a diminution as high as 86% upon addition of only 1 equiv of Cl⁻ to a 2.86 μM host solution (Figure S9). These results suggest that for **8R_{fg}-4CzIPN**, the combination of a high photooxidation potential with a high affinity for Cl⁻ leads to a highly efficient Cl⁻ to chlorine oxidation. In contrast, a linear plot was observed for **4CzIPN**, revealing a $K_{SV} = 549 \text{ M}^{-1}$ (in TFT) which is close to the measured K_a (610 M^{-1} , in THF). This suggests that for **4CzIPN** only static quenching results in the observed change (Figure 1D).

The photocatalytic activity of the **8R_{fg}-4CzIPN**·Cl⁻ complex was then evaluated. Under optimized reaction conditions (Table S2), the alkylation of cyclohexane by dimethyl maleate proceeded in TFT at room temperature using as low as 2 equiv of alkane, 2.5 mol% of **8R_{fg}-4CzIPN** (7.5 mM) and 5 mol% of TBACl (15 mM), to afford the hydroalkylated product **1** in 68% isolated yield in about 1 h (Figure 2). In these conditions the molar fraction of **8R_{fg}-4CzIPN**·Cl⁻ at t_0 is 98%. The reaction did not proceed without TBACl or light. Using **4CzIPN** only traces of product were formed, even with 10 equiv of cyclohexane. Such a dramatic reactivity increase in cyclohexane oxidation is consistent with a highly effective photo-oxidation of chloride into chlorine within the **8R_{fg}-4CzIPN**·Cl⁻ complex.

The donor scope was then evaluated using benzyldenemalononitrile as the acceptor (Scheme 2). Cyclohexane and cyclooctane were alkylated in 78% (**2**) and 86% (**3**) yields, respectively. The non-cyclic hydrocarbon 2,3-dimethylbutane afforded **4** in 66% yield with the main regioisomer resulting from the functionalization at the secondary carbon. The benzylic C–H bonds of toluene, ethylbenzene and 4-phenyltoluene reacted efficiently to produce the hydroalkylated adducts **5-7** in moderate to good yields. The methyl groups of N,N-dimethylbenzylamine and N,N-dimethylaniline were alkylated in 41% (**8**) and 97% (**9**) yields, respectively. The moderate yield for **8** is due to competitive alkylation at the benzylic CH₂ group. C(sp²)–H bonds of aromatic aldehydes could be functionalized, **10** and **11** being obtained in 61% and 66% yields, respectively. Both cyclic and acyclic ethers reacted very well to afford the α -alkylated ethers **12-15** in good to excellent yields. Finally, the Si–H bond of triethylsilane could be functionalized to give **16** in 48% yield.

Moderate to good yields of the hydro-alkylated products were obtained when reacting cyclohexane and/or THF with other acceptors such as dimethyl maleate (**1**, **17**), diisopropyl azodicarboxylate (**18**, **19**), N-phenylmaleimide (**20**) or benzyl methacrylate (**21**). Importantly, all the reactions tested using **4CzIPN** as photoredox catalyst led to traces (see **1**, **2**, **10**, **12**) or low yields (see **9**, **17**) of products.

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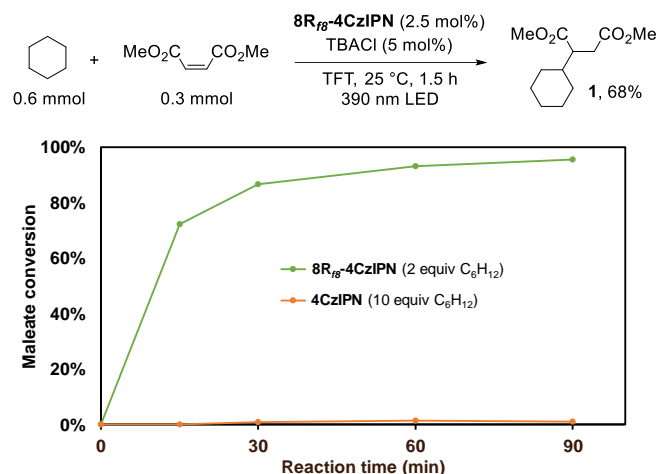
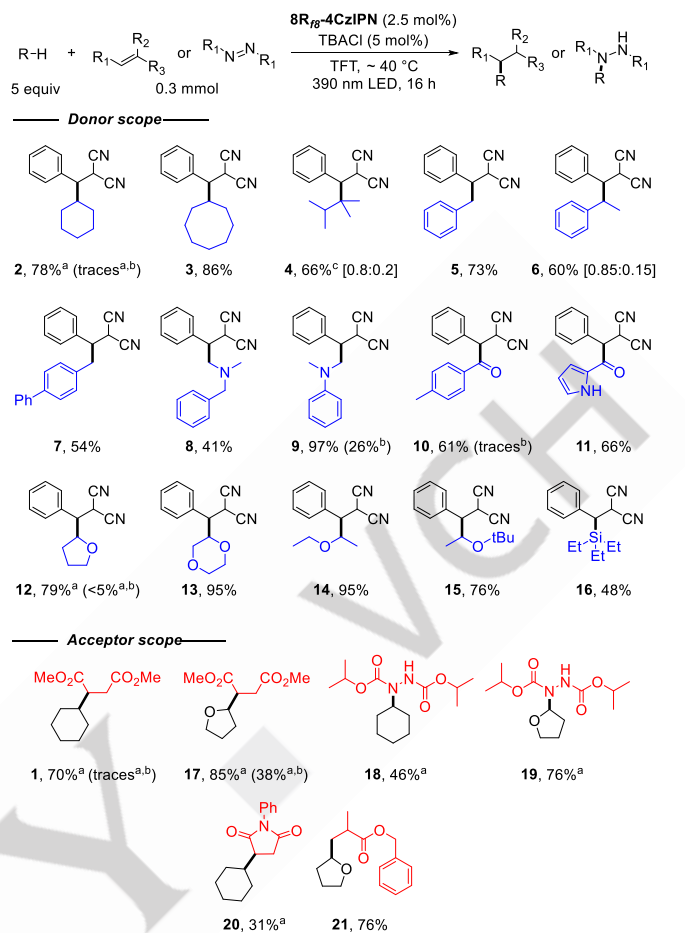


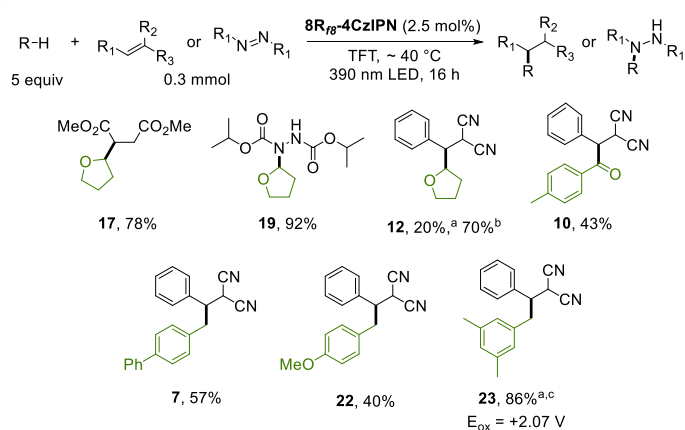
Figure 2. Cyclohexane photo-alkylation catalysed by **8R₁₈-4CzIPN**·Cl⁻, and comparison of reaction kinetics between **8R₁₈-4CzIPN** and **4CzIPN** (GC follow-up given in Figure S10). Two fans were used to keep the reaction temperature at 25 °C.

The high photooxidizing power of **8R₁₈-4CzIPN** (*E_{red} = +1.73 V vs. SCE) was then tested in reactions run in the absence of chloride, using donors whose oxidation potential would allow direct electron transfer to **8R₁₈-4CzIPN** photoexcited state. Deprotonation of the resulting cation radical would afford the carbon-centered radical that adds onto the alkene. Using THF the reactions proceeded well in the absence of TBACl, affording the products **17** and **19** in 78% and 92% yields, respectively (Scheme 3). Note that the reaction rate for the formation of **17** was circa 4 times faster in the presence of chloride (reaction completed in less than 15 min). The lower reactivity of the chloride-free process was reflected in the synthesis of **12**, which required THF as solvent to achieve a good yield compared to 2 equiv in the presence TBACl (Scheme 2). The benzylic C–H bonds of the electronically-enriched tolyl derivatives could be alkylated (**7**, **22**, **23**), including mesitylene whose oxidation potential is as high as +2.07 V vs. SCE.^[17]

Finally, because **8R₁₈-4CzIPN** is poorly soluble in most polar solvents including methanol (< 10 μM), a solid/liquid separation procedure was employed in order to evaluate its recyclability, but also to obtain preliminary information on its stability during catalysis. Indeed, previous work has highlighted that **4CzIPN** and its derivatives underwent efficient photosubstitution of a cyano group by alkyl/benzyl radicals.^[18] It was also shown that benzylated **4CzIPN** generated in the early stage of photocatalytic reactions, i.e. carboxylations^[18b] or benzylations,^[18c] were the catalytic species of the process. The recycling/stability issue was assessed on the reaction between cyclohexane and benzylidenemalononitrile, which requires the formation of a chlorine radical to proceed. After the first reaction (GC follow-up of the formation of **2** given in Figure S12), the solvent (TFT) was evaporated and methanol was added to the residue to extract the product. The catalyst, and/or modified catalyst, was separated by centrifugation, analyzed by ¹H NMR (Figure S13) and reused. By this procedure, 94% by weight of **8R₁₈-4CzIPN** initially employed was easily separated from **2** and recovered. In the first run, **2** was



Scheme 2. Substrate scope of dual photoredox/HAT-catalyzed Giese-type C–H alkylations. ^a 2 equiv of donor was used. ^b **4CzIPN** was used instead of **8R₁₈-4CzIPN**. ^c Yield of the mixture of regioisomers that could not be separated (Main regioisomer presented; Regioisomer ratio in bracket).



Scheme 3. Substrate scope of photoredox-catalyzed Giese-type C–H alkylations. ^a 10 equiv of donor was used. ^b Donor as solvent. ^c 60 h reaction time.

formed in 89% GC yield after 3 h of irradiation. We note that the reaction profile exhibits a significant upward curvature

(reproduced on three independent reactions) which could be the sign of a catalyst activation process (Figure S12). Nonetheless, the recovered "catalyst" was much less active in the second run, affording GC yields of 9% and 38% after 3 h and 24 h of irradiation, respectively. ^1H NMR revealed that the solid recovered after the first run exhibited none of the characteristic resonances of $8\text{R}_{\text{F}}-4\text{CzIPN}$ or $8\text{R}_{\text{F}}-4\text{CzIPN}\cdot\text{Cl}^-$ (Figure 1A), and that de-carbazolation occurred to some extent (Figure S13). Tetrabutylammonium was also present in the solid, as well as a few % of **2**. More extensive studies will be conducted to determine the extent of de-carbazolation, as well as possible photoalkylation reactions, and evaluate their impact on catalysis.

In summary, the introduction of electron-withdrawing perfluorooctyl groups into the carbazoles of **4CzIPN** not only makes this widely employed PC a strong photooxidant, but also transforms it into an excellent neutral host for chloride. Spectroscopic studies combined to DFT calculations revealed that the $8\text{R}_{\text{F}}-4\text{CzIPN}\cdot\text{Cl}^-$ complex harnesses H-bonds and an anion- π interaction. The self-assembled complex, which forms almost quantitatively under catalytic conditions, is highly photoreactive and becomes highly active for $\text{C}(\text{sp}^3)\text{-H}$ bond functionalization mediated by the chlorine radical. Overall, this work not only introduces the widely studied donor-acceptor carbazole-cyanoarene fluorophores as a new class of neutral host for chloride, but also highlights that when application of such compounds as photoredox catalyst is considered, the possible assembly with a co-catalyst, reagent or substrate should be envisioned to account for the observed reactivity or to develop more active catalytic systems.

Supporting Information

The authors have cited additional references within the Supporting Information.^[19-27]

Acknowledgements

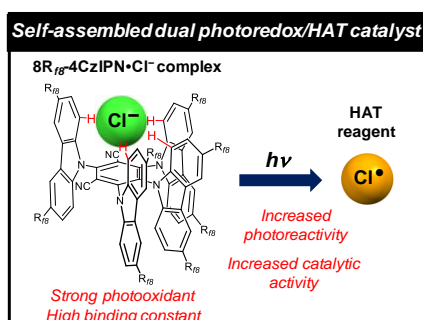
This study received financial support from the French government in the framework of the University of Bordeaux's France 2030 program / GPR "Post-Petroleum Materials". The University of Bordeaux and the CNRS are gratefully acknowledged for their financial support.

Keywords: Photoredox catalysis • C–H functionalization • Chloride oxidation • Chloride receptor • Donor-acceptor cyanoarenes

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The fluorous photoredox catalyst **8R_{f8}-4CzIPN** ($R_{f8} = C_8F_{17}$) forms a supramolecular complex with chloride ions with high affinity. Integrating fluorous chains on the parent dye greatly enhances both the ion-binding affinity, as well as the oxidizing ability of the catalyst. Efficient photooxidation of the chloride was observed, generating the chlorine HAT reagent, which was tested in the redox-neutral Giese-type C(sp³)-H bond alkylation reaction.