"π-Hole−π" Interaction Promoted Photocatalytic Hydrodefluorination via Inner-Sphere Electron Transfer

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S *Supporting Information*

ABSTRACT: We describe a metal-free, photocatalytic hydrodefluorination (HDF) of polyfluoroarenes (FA) using pyrene-based photocatalysts (Py). The weak "π-hole−π" interaction between Py and FA promotes the electron transfer against unfavorable energetics (ΔG_{ET} up to 0.63 eV) and initiates the subsequent HDF. The steric hindrance of Py and FA largely dictates the HDF reaction rate, pointing to an inner-sphere electron transfer pathway. This work highlights the importance of the size and shape of the photocatalyst and the substrate in controlling the electron transfer mechanism and rates as well as the overall photocatalytic processes.

Electron transfer (ET) is a key step reaction in many organic transformations.[1] For example, photoredox catalysis typically involves light-induced, nonadiabatic outer-sphere ET within a loose encounter complex formed between the excited photocatalyst and the substrate,[2] during which a suitable overpotential, according to Marcus theory, is generally desirable to achieve fast ET kinetics.[3] If the ET step is energetically unfavorable, it is necessary to either noncovalently (e.g., via Lewis acid,[4] Brønsted acid,[5] or hydrogen bond[6]) or covalently (e.g., via organocatalysis[7]) modulate the substrate's redox potentials. Inner-sphere ET,[8] on the other hand, occurs adiabatically within an electron donor−acceptor (EDA) complex, for instance, where the strong electronic coupling circumvents the crossing of high potential energy surface, and thus proceeds significantly faster than that predicted by the outer-sphere model.[9] Moreover, since the charge-transfer (CT) transition of the EDA complex often appears in the visible region, the use of photocatalyst can be avoided.[10] In the past, EDA complexes formed between *two substrates* that constitute the ET partners have been utilized for synthesis.[11] Recent work by Melchiorre et al. on asymmetric photo(organo)catalysis further significantly expanded their application scope.[12]

Herein, we describe a new example in which the inner-sphere ET between *substrate* and *photocatalyst* plays a critical role to overcome the unfavorable ET energetics. Due to the "π-hole−π" interaction between polyfluoroarenes (FA) and pyrene-based photocatalysts (Py), photoinduced ET proceeds smoothly against a large underpotential (ΔG_{ET} up to 0.63 eV) and can be best described as an inner-sphere process, which is subsequently utilized to promote a hydrodefluorination (HDF) reaction to afford partially fluorinated arenes.[13]

Polyfluoroarene−arene (also known as "π-hole[14]−π") interaction is a directional and noncovalent intermolecular force. It

originates from the weak electrostatic interaction between arenes (negative surface potential) and polyfluoroarenes (positive surface potential due to the flipped quadruple moment)[15] and has found applications in crystal engineering,[16] controllable reactions,[17] and in some cases, regioselective catalysis.[18] Here, we chose three highly fluorescent pyrene derivatives Py1, Py2, and Py3, as the photocatalysts and three polyfluoroarenes, namely, HFB (hexafluorobenzene), PFB (pentafluorobenzene), and TFB (1,2,3,4-tetrafluorobenzene), as the substrates (Figure 1). The
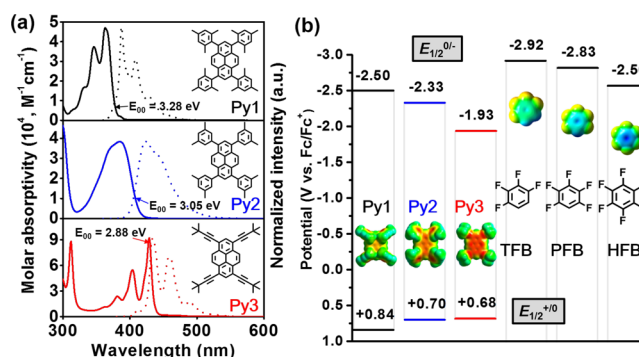

Figure 1. (a) UV−vis absorption and fluorescence emission spectra (λ_{ex} = 360 nm) of Py in DMA (dimethylacetamide). (b) Reduction potentials (all potentials mentioned hereafter are against Fc^+/Fc^0, Fc = ferrocene, see Figures S1−S2 for cyclic voltammograms) and density functional theory (DFT) computed electrostatic surface potential maps (inset) of Py and FA.

three Py photocatalysts provide a systematic variation of steric hindrance, a critical factor for inner-sphere ET.[19] Py2 and Py3 also appreciably absorb visible light ($\lambda > 390$ nm, Figure 1a). Importantly, the LUMO energies of Py are lower than those of FA (Figure 1b), suggesting not only it is more difficult to directly reduce FA (from an external electron donor) but also the ET from *Py to FA is unfavorable. Indeed, according to the outer-sphere model,[20] ΔG_{ET} was calculated ranging from 0.12 to 0.72 eV (based on the Weller equation; see Supporting Information Table S1 for details), which is also indicated by the negligible Stern−Volmer quenching constants ($K_{SV} < 0.1$ M^{-1}, Figure S8). We envisioned that, however, upon the formation of the "π-hole−π" Py:FA complexes, a good molecular orbital overlap could become possible to facilitate the inner-sphere ET to form FA$^{\bullet-}$. Followed by the expulsion of fluoride and hydrogen atom abstraction, an HDF process of FA should be developed.

We first use ^1H NMR titration to evaluate the intermolecular interaction of the nine Py-FA pairs in the ground state. The formation constant (K_c, based on a 1:1 stoichiometry) was obtained for Py3:HFB ($1.11 \ M^{-1}$), Py3:PFB ($0.64 \ M^{-1}$), Py2:HFB ($0.82 \ M^{-1}$), and Py2:PFB ($0.64 \ M^{-1}$) in $CDCl_3$ (Figure 2a; see Supporting Information section S-4 for details).[21]
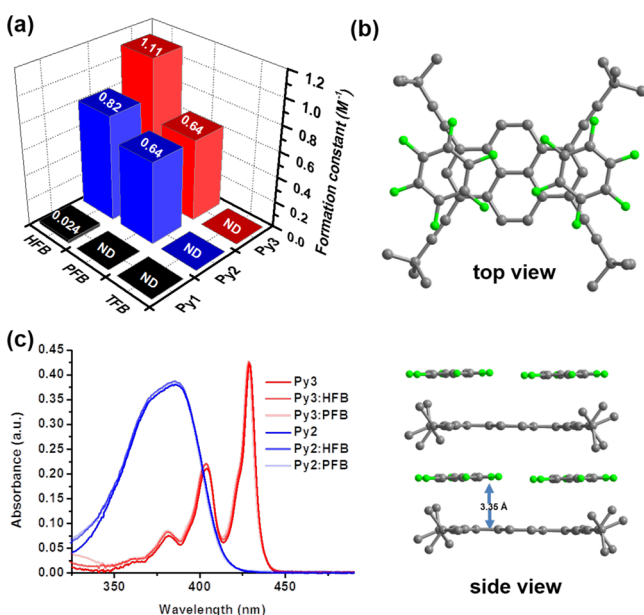

Figure 2. (a) Formation constants of nine Py:FA pairs. (b) Top and side view of single crystal structure of Py3:HFB. (c) UV−vis spectra of Py3, Py2, and their mixtures with HFB and PFB in DMA (at the Py:FA molar ratio <1:30 000).

The K_c of Py3:TFB and Py2:TFB were not reliably detectable, likely due to the relatively weak "π-hole" character of TFB. DFT-based structure optimization also confirmed that the binding energy decreases in the order of Py3:HFB > Py3:PFB > Py3:TFB (see Supporting Information S-14). As for three Py1:FA pairs, a small K_c ($0.024 \ M^{-1}$) was obtained for Py1:HFB, which however should not be considered as a real "π-hole$-\pi$" complex since the large steric hindrance of Py1 makes the good contact between the two π planes unlikely.

Single crystal structure analysis confirmed the expected "π-hole$-\pi$" interaction in three Py3:FA pairs, including the weak Py3:TFB complex. All three Py3:FA crystal structures reveal the 1:2 stoichiometry and the alternating parallel stacking with a small dihedral angle ($1.05°-2.37°$) (Figures 2b and S7).[22] Most importantly, the average interplane distances ($3.33-3.35$ Å) are all below the sum of the individual vdW radii of two aromatic molecules (~3.45 Å[23]), suggesting the stronger electrostatic interaction in Py3:FA than the typical $\pi-\pi$ stacking force. UV−vis spectra provide further support for the electrostatic nature of the "π-hole$-\pi$" interaction: no apparent bathochromic shift (an indication of CT transition) was observed (Figures 2c and S6).

We next chose the Py3:HFB pair ($K_c = 1.11 \ M^{-1}$, $\Delta G_{ET} = 0.36$ eV) to test the proposed HDF. To our delight, the reaction in the presence of a sacrificial electron donor and white light irradiation (26 W compact fluorescent lamp, CFL) at 45 °C in 12 h achieved the desired product PFB with a 51% yield (Figure 3a). Using the optimized conditions (solvent DMA and amine DIPEA: diisopropylethylamine) (see Supporting Information, Tables S6−S7), we further confirmed the essential role of the light irradiation, photocatalyst, and amine (Figure 3a). Extending the
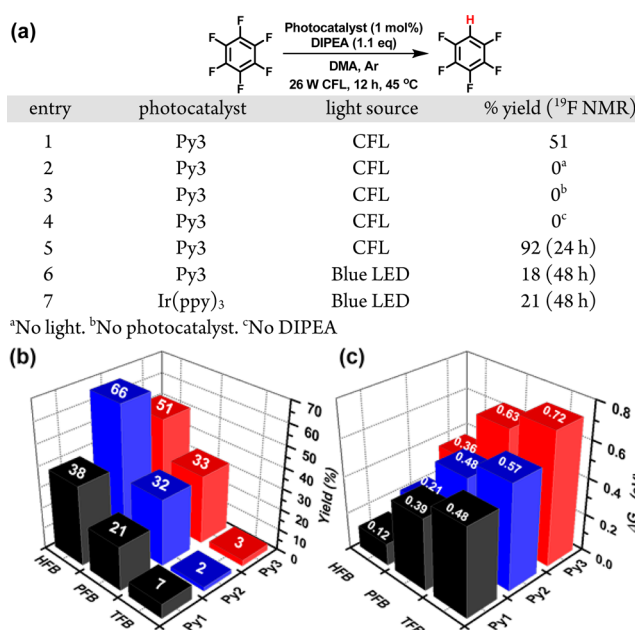

entry	photocatalyst	light source	% yield (^{19}F NMR)
1	Py3	CFL	51
2	Py3	CFL	0[a]
3	Py3	CFL	0[b]
4	Py3	CFL	0[c]
5	Py3	CFL	92 (24 h)
6	Py3	Blue LED	18 (48 h)
7	Ir(ppy)$_3$	Blue LED	21 (48 h)

[a]No light. [b]No photocatalyst. [c]No DIPEA

Figure 3. (a) HDF reaction for Py3:HFB. (b) HDF yields and (c) ΔG_{ET} for nine Py:FA pairs under the reaction conditions shown in Figure 3a.

reaction time to 24 h gave rise to an excellent yield (92%) (Figure 3a). The use of a blue LED (0.135 W, $\lambda_{max} = 465$ nm) resulted in a diminished yield (18%, 48 h), which however is attributed to the low power of the light source and the considerably smaller absorption coefficient (ε) of Py3 in this optical window (Figure S9). As a comparison, with the irradiation of the blue LED, strongly reductive Ir(ppy)$_3$ ($E_{1/2}^{III/II} = -2.77$ V, an overpotential of +0.21 V, Figure S1) afforded PFB with a similar yield (21%, Figure 3a).[24] Since the absorbance coefficients of Py3 and Ir(ppy)$_3$ are comparable around 465 nm (Figure S9), their similar photocatalytic efficiency suggests the "π-hole$-\pi$" interaction in the Py3:HFB complex is indeed important to overcome the endergonic ET energetics.

We next screened the HDF reaction for nine Py:FA pairs. Overall, the four Py:FA pairs with relatively large K_c gave the HDF product in good yields (12 h, 32−66%, unoptimized) (Figure 3b). In particular, the good reactivity of Py3:PFB ($K_c = 0.64 \ M^{-1}$, 33% yield) is highly remarkable considering the large ET underpotential ($\Delta G_{ET} = 0.63$ eV). In contrast, the HDF of Py3:TFB and Py2:TFB was drastically sluggish (3% and 2%, respectively), which is attributed to the significantly smaller K_c of the Py:TFB complexes (Figure 2a). As for the three weak Py1:FA pairs with large steric hindrance, a decrease of HDF yield from 38% (Py1:HFB) to 7% (Py1:TFB) was observed as expected on the basis of the increased ΔG_{ET} (Figure 3b and 3c).

Since the injection of an electron to FA is presumably the rate-limiting step of the overall HDF when the fragmentation of C−F is a sufficiently fast process,[25] a systematic comparison of the relative initial reactions rates should provide insights into the elemental ET kinetics. If the inner-sphere mechanism is operative, one would expect that a high concentration of substrate FA would result in a fast initial reaction rate due to the availability of a larger amount of the Py:FA complex. This is indeed the case for Py3:PFB and Py2:PFB, where the relative initial reaction rate (see Supporting Information section S-11 for details) nearly doubled when [PFB] increased from 0.075 to 0.30 M (Figure 4a). Surprisingly, such a substrate-concentration-dependent reaction rate was also observed for weak Py3:TFB and Py2:TFB pairs
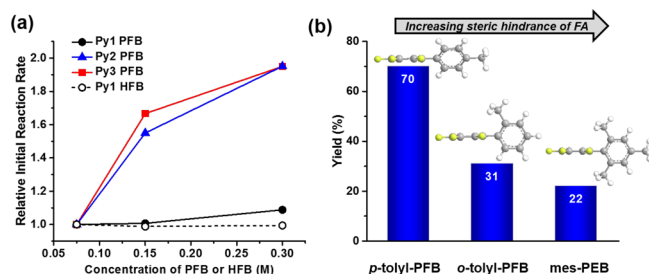
Figure 4. (a) Normalized relative initial reaction rate of Py:PFB and Py1:HFB at different substrate concentration. (b) HDF reaction yield of *p*-tolyl-PFB, *o*-tolyl-PFB, and mes-PFB with Py2 at reaction conditions outlined in Figure 3a.

albeit at much higher FA concentrations (e.g., 1.56 M) (Figure S11). In contrast, no significant increase of reaction rate was observed for three Py1:FA pairs including Py1:HFB with a measurable K_c (Figures 4a and S11),[26] suggesting the outer-sphere ET pathway being dominant in these cases. The importance of "π-hole$-\pi$" interaction is further supported via the systematic change of the steric hindrance of the substrate. For example, the reaction between Py2 and *p*-tolyl-PFB gives a significantly higher yield of the HDF product (70%) than sterically hindered *o*-tolyl-PFB (31%) and mes-PFB (22%) that have comparable $E_{1/2}$ (Figures 4b and S2).

Based on the HDF activities described above, a photocatalytic cycle is proposed (Scheme 1). Sterically less hindered Py2 and

**Scheme 1. Proposed Photocatalytic Cycle for HDF**
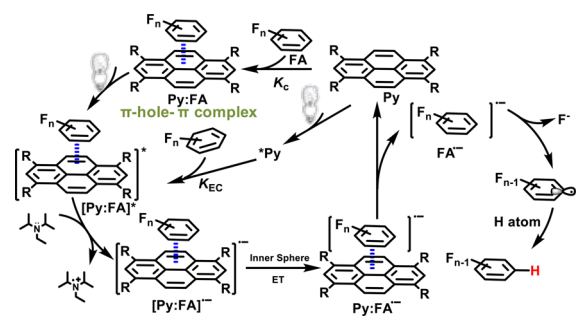
Py3 can, in principle, undergo the inner-sphere pathway as soon as the "π-hole$-\pi$" complex is formed and a good orbital overlap is achieved. Upon light irradiation, the "local" excitation of Py2/Py3 in the "π-hole$-\pi$" complex is first reductively quenched by a sacrificial electron donor (i.e., DIPEA; see Figure S8 for Stern–Volmer quenching experiments), forming an anionic radical complex intermediate [Py:FA]$^{\bullet-}$. Alternatively, it is also possible for *Py to form the excited encounter "π-hole$-\pi$" complex [Py:FA]* (with formation constant K_{EC}).[27] An inner-sphere ET within [Py:FA]$^{\bullet-}$ and subsequent complex dissociation regenerate Py and afford FA$^{\bullet-}$,[28] which undergoes the fast intramolecular dissociative ET to form the productive aryl radical by expulsion of the fluoride anion.[29] Following a hydrogen atom abstraction from the DIPEA radical cation, the HDF product is obtained.

We next turned our attention to exploit the utility of Py for the HDF of FA. Based on the proposed mechanism, polyfluoro-aromatics with small steric hindrance and appropriate binding capabilities with Py are expected to be suitable substrates. Indeed, Py2 works well with common polyfluoroaromatics including HFB (**1a**), PFB (**1b**), pentafluoropyridine (**1c**), and octafluoronaph-thalene (OFN, **1d**), and it is compatible with an array of functional

groups including aryl (**1e**), ester (**1f**), CF$_3$ (**1g**), and ether (**1h**) with the regioselectivity that can be rationalized based on the maximum spin density of the C$-$F bond in FA$^{\bullet-}$ (Table 1).[30]

Table 1. Scope of Photocatalytic HDF of FA[a]
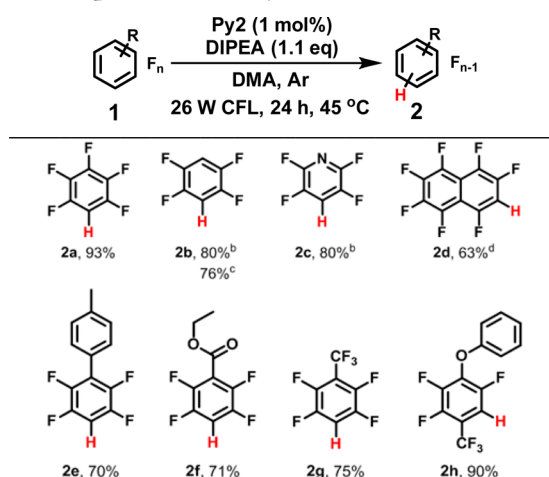
[a]^{19}F NMR yield. [b]3.0 equiv of DIPEA. [c]4.0 equiv of DIPEA, HFB as the substrate, [d]2.0 equiv of DIPEA.

Notably, under the optimized reaction conditions, HDF of PFB afforded the corresponding 1,2,4,5-TFB (**2b**) in good yield (80%). It is also possible to synthesize **2b** directly from HFB via one-pot di-HDF (4 equiv of DIPEA, 76% yield). Monitoring the reaction process via ^{19}F NMR revealed that the second HDF reaction did not start until most of HFB was converted to PFB (Figure S10), demonstrating a minimum effect of product inhibition. To the best our knowledge, this is the first example of metal-free catalytic HDF of PFB under mild conditions with high efficiency. Py2 is highly robust. A turnover number (TON) of 24 250 was obtained when 0.002 mol % of Py2 was used for the HDF of HFB (see Supporting Information section S-13 for details). Interestingly, Py2 can convert OFN (a strong π-hole) into the HDF product **2d** with a lower yield (63%) along with two di-HDF products (see Supporting Information section S-16), suggesting a possible product inhibition; that is, the mono-HDF product **2d** now effectively competes with OFN for the subsequent di-HDF reaction due to its large π-hole strength.

We further demonstrated the potential utility of Py in the metal-free C$-$F reductive alkylation (eq 1). Weaver et al. reported
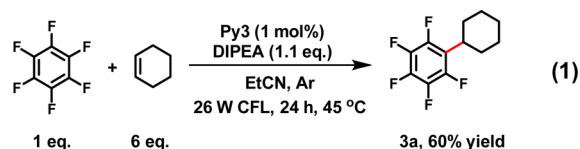
this reaction using Ir(ppy)$_3$ as the photocatalyst.[31] Here, Py3 was used as a metal-free photocatalyst to generate the perfluorophenyl radical that is intercepted by 6.0 equiv of cyclohexene to afford the C$-$C coupled product **3a** with a good yield (60%, determined by ^{19}F NMR).

In summary, we have described a new example showing the inner-sphere ET between photocatalyst and substrate plays an important role in the overall photocatalytic reaction. The appreciable formation constant and favorable steric hindrance within the "π-hole$-\pi$" Py-FA complexes facilitate an inner-sphere ET despite unfavorable ET energetics. This process is utilized in

the hydrodefluorination reaction to access partially fluorinated arenes. Our work points to the further development of the design paradigm for photoredox catalysis where the size[32] and shape of photocatalyst can be fine-tuned to enhance the overall catalytic activity. This work also constitutes a new example of the utility of weak, noncovalent interaction in small molecule catalysis.[33]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b08620.

> Materials, general procedures, synthesis, physical measurements, spectroscopic characterizations, CV diagrams, and NMR spectra (PDF)
> Crystallographic data (CIF, CIF, CIF)

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Notes
The authors declare no competing financial interest.

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