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Heterogeneous Photoinduced Homolytic Aromatic Substitution of Electron-Rich Arenes with Perfluoroalkyl Groups in Water and Aqueous Media – A Radical-Ion Reaction

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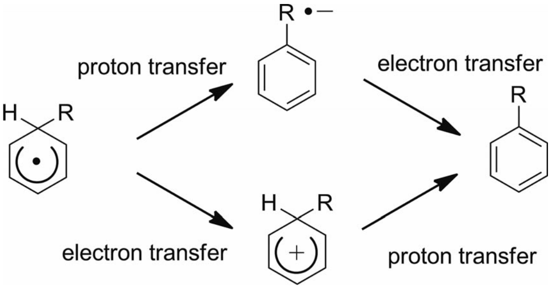
The photoinduced electron transfer (PET) substitution reaction of electron-rich aromatic nuclei with perfluoroalkyl R_f groups was carried out in water or aqueous mixtures to render substitution products resulting from replacement of aromatic H atoms with the R_f moiety in good yields (57–88 %). Some mechanistic aspects are discussed, supporting the notion of a PET reaction leading to a classical radical homolytic aromatic substitution (HAS) followed by an electron transfer (ET) and then a proton transfer (PT) sequence. A radical mechanism superimposed on a redox process is proposed to account for product formation. Evidence for the radical cation species (as an initiation event) generated from electron-rich arenes in the presence of perfluoroalkyl halides is provided by the UV/Vis transient spectra obtained by Nanosecond Laser Flash Photolysis techniques.

Introduction

Studer and Curran[1] have recently argued in favor of the homolytic aromatic substitution (HAS) pathway of many reported non-metal-mediated radical C–H activation or organocatalytic reactions leading to arylation of aromatic rings. It is well-accepted that the key step in these HAS reactions is the addition of an aryl radical to an arene, resulting in cyclohexadienyl-type radicals that promptly rearomatize. The possible mechanisms for rearomatization are well-known and long-established in the literature, i.e., disproportionation, reaction with an initiator by hydrogen transfer, and oxidation.[2] Examples of the former three rearomatization processes of the cyclohexadienyl-type radicals in water or aqueous mixtures are documented (see below).

Rearomatization of the intermediate cyclohexadienyl radical can occur by deprotonation to render the radical anion of the substitution product, followed by electron transfer (ET), or through ET to afford the cyclohexadienyl cation (Wheland intermediate), followed by proton transfer (PT), as shown in Scheme 1.[1]



Scheme 1. PT and ET of cyclohexadienyl-type radicals.

In contrast to radical perfluoroalkylation addition reactions of unsaturated compounds,[3,4a] fluoroalkyl radical substitution on the aromatic ring (HASs with perfluoroalkyl groups) has received little attention.[4b] Furthermore, aromatic radical perfluoroalkylation in aqueous mixtures is restricted to a few examples of sulfinatodehalogenation reactions.[4b,5]

Radical perfluoroalkylation reactions involving unsaturated compounds in aqueous media have also been reviewed.[6] In particular, activated aromatic nuclei, such as 1,3,5-trimethoxybenzene, were employed in perfluoroalkyl substitution radical reactions in aqueous media. When a mixture of 1,3,5-trimethoxybenzene and 1-bromo-1-chloro-2,2,2-trifluoroethane was treated under sulfinato-dehalogenation reaction conditions ($Na_2S_2O_4$/$NaHCO_3$ in MeCN/H_2O), a radical substitution reaction of H by R_f was achieved.[7] The authors[7] postulate a radical HAS mechanism such as that depicted in Scheme 2.

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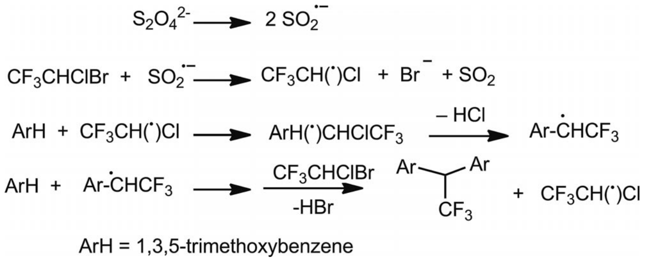


Scheme 2. Mechanism for the aromatic radical substitution reaction of H for R_f.[7]

In another report by the same leading author,[8] the aromatic substitution of trimethoxybenzenes, and pyrrols with $BrCF_2CF_2Br$ in aqueous media was attempted rendering the mono-R_f-substituted trimethoxybenzene and the 2-substituted pyrrols in 99 and 85% yields, respectively.

More recently, Lü and co-workers[9] have accomplished the polyfluoroalkylation of 2-aminothiazoles and derivatives. Reactions of 2-aminothiazole with n-C_4F_9I under sulfinatodehalogenation reaction conditions, afforded the substitution product in 80% yield with total selectivity at the 5-position of 2-aminothiazole. A number of N-substituted 2-aminothiazoles also react with R_fI and R_fBr in yields ranging from 58 to 90%.[9]

Chen and co-workers[10] achieved the radical perfluoroalkylation reaction of aromatic amines by substitution of aromatic H atoms for R_f groups in dimethyl sulfoxide (DMSO) as solvent, triggered through the decomposition of $Na_2S_2O_4$. They attained a series of 2-substituted 1,4-diaminobenzenes with R_f moieties that, upon further reaction, afforded intramolecular cyclization products.[11] In all these examples, the rearomatization of the cyclohexadienyl radical intermediate is achieved by hydrogen transfer.

More recently, Yamakawa and co-workers have accomplished the fluorination of aromatic compounds using the Fenton reagent in DMSO as solvent, in a metal-induced electron-transfer-like reaction.[12a,12b] They attempted a series of simple-substituted aromatic and heteroaromatic compounds with CF_3I and ethoxycarbonyl difluoromethyl bromide as fluorinating agents. In this case, the rearomatization of the cyclohexadienyl radical intermediate is achieved by metal-induced oxidation and then PT.

A photochemical method was successfully employed to effect perfluoroalkylation reactions of aromatic and heteroaromatic compounds to provide substitutions with the corresponding α-aryl-α,α-difluoroacetates and aryl-α,α-difluoromethylphosphonates in good to moderate yields in CH_2Cl_2 as solvent.[12c] Photonucleophilic aromatic substitution of 6-fluoroquinolones has also been successfully accomplished in water.[13a]

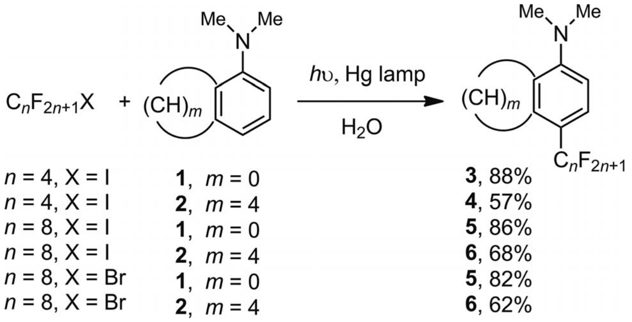
To the best of our knowledge, metal-free photoinduced electron transfer (PET) methodology has not been employed in water or aqueous mixtures to accomplish the perfluoroalkyl substitution reaction of aromatic nuclei efficiently.

In this account, we will demonstrate that for electron-rich nuclei such as N,N-dialkyl-substituted aromatic amines, N-substituted carbazoles, and methoxy-substituted aromatics, PET *does* take place in water or aqueous media in the presence of perfluoroalkyl iodides (and bromides), rendering this methodology appropriate for the synthesis of fluorinated aromatics in the heterogeneous water environment. Evidence for a radical-ion process and singlet excited state reactivity will be provided.

Results and Discussion

Aromatic Substitution Reactions of *N,N*-Dialkyl-Substituted Aromatic Amines, *N*-Substituted Carbazoles, and Methoxy-Substituted Aromatics with R_fX in Water and Aqueous Media

When an Ar-degassed heterogeneous mixture of N,N-dimethylaniline **1** or N,N-dimethyl-1-naphthylamine **2** (2–5 mmol) and n-C_4F_9I (1 mmol) in water (30 mL) was vigorously stirred in a photoinduced reaction [unfiltered medium-pressure Hg lamp (MPL),[13b] 4 h, 20 °C], the nonafluorobutyl *para* substitution product **3** and the 4-substitution product **4**, respectively, were obtained in yields ranging from 57 to 88%, based on n-C_4F_9I (Scheme 3 and Table 1, entries 1 and 2).



Scheme 3. Perfluoroalkyl group substitution of aromatic amines in water.

The product yields increased upon increasing the concentration of substrates, and the best product yields were obtained when the substrate/n-C_4F_9I ratio was ca. 5:1.

We also undertook the photoreaction of **2** and n-C_4F_9I in Ar-deoxygenated water with filtered (350 nm) fluorescent lamps (2× 40 W), and obtained a similar substitution yield of **4** (Table 1, entry 3), demonstrating that the lower emission wavelengths of the medium pressure Hg lamp (i.e., 313 nm) did not influence the product yield or distribution (see Exp. Sect. for lamp details).

To cast some light on the reactive excited state manifold of substrate **1** (or **2**), we carried out product studies of the PET reaction (at irradiation wavelength λ = 310 nm) of **1** (1 mmol), in the presence of n-C_4F_9I (1 mmol) and 4-methoxyacetophenone (MAP; 15 mmol), which is a well-known triplet energy sensitizer (E_T = 310 kJ mol^{-1}). Under these

Table 1. Reaction conditions tested in the HAS reaction of arenes with perfluoroalkyl halides in heterogeneous media under vigorous stirring.

Entry	Synthetic method	Substrates [mmol]	Solvent system [mL]	Product yield (%)[a]	$A_{\text{substrate}}$:A_{RfX}[b] $\text{pH}_{\text{initial}}$/$\text{pH}_{\text{final}}$[c]
1	MPL[d]	**1** (5), n-C_4F_9I (1)	H_2O (30)	**3** (88)	5.5:2.5[c]
2	MPL[d]	**2** (5), n-C_4F_9I (1)	H_2O (30)	**4** (57)	5.5:2.5[c]
3	λ = 350 nm[e]	**2** (5), n-C_4F_9I (1)	H_2O (30)	**4** (63)	5.5:2.5[c]
4	λ = 310 nm	**1** (1), n-C_4F_9I (1), MAP[f] (15)	H_2O (30)	**3** (–)	5.5:5.5[c]
5	λ = 310 nm	**2** (1), n-C_4F_9I (1), MAP[f] (15)	H_2O (30)	**4** (–)	5.5:5.5[c]
6	MPL[d]	**1** (5), n-$C_8F_{17}I$ (1)	H_2O (30)	**5** (86)	5.5:2.5[c]
7	MPL[d]	**1** (5), n-$C_8F_{17}Br$ (1)	H_2O (30)	**5** (82)	5.5:2.5[c]
8	MPL[d]	**2** (5), n-$C_8F_{17}I$ (1)	H_2O (30)	**6** (68)	5.5:2.5[c]
9	MPL[d]	**2** (5), n-$C_8F_{17}Br$ (1)	H_2O (30)	**6** (62)	5.5:2.5[c]
10	λ = 254 nm	**1** (0.1), n-C_4F_9I (10)	H_2O (4)	**3** (80)[g]	1:10[b]; 5.5:2.5[c]
11	λ = 254 nm	**2** (0.1), n-C_4F_9I (10)	H_2O (4)	**4** (65)[g]	1:10[b]; 5.5:2.5[c]
12	λ = 254 nm	**1** (2.5), n-C_4F_9I (0.5)	H_2O (4)	**3** (80)	100:1[b]; 5.5:2.5[c]
13	λ = 254 nm	**2** (2.5), n-C_4F_9I (0.5)	H_2O (4)	**4** (61)	100:1[b]; 5.5:2.5[c]
14	thermal (100 °c)	**1** (1), n-C_4F_9I (0.33)	H_2O (4)	**3** (–)	5.5:5.5[c]
15	thermal (100 °c)	**2** (1), n-C_4F_9I (0.33)	H_2O (4)	**4** (–)	5.5:5.5[c]
16	ultrasound (80 °c)	**1** (1), n-C_4F_9I (0.33)	H_2O (4)	**3** (–)	5.5:5.5[c]
17	ultrasound (80 °c)	**2** (1), n-C_4F_9I (0.33)	H_2O (4)	**4** (–)	5.5:5.5[c]
18	MPL[d]	**1** (5), n-C_4F_9I (1)	MeCN (30)	**3** (81)	
19	MPL[d]	**2** (5), n-C_4F_9I (1)	MeCN (30)	**4** (49)	
20	MPL[d]	**7** (1), n-C_4F_9I (0.25)	MeCN/H_2O[h] (30)	**8** (50)	5.5:2.5[c]
21	MPL[d]	**9** (5), n-C_4F_9I (1)	H_2O (30)	**11** (32)	5.5:2[c]
22	MPL[d]	**10** (5), n-C_4F_9I (1)	H_2O (30)	**12** (15)	5.5:2
23	MPL[d]	**13** (5), n-C_4F_9I (1)	H_2O (30)	–	5.5:2[c]
24	MPL[d]	**14** (5), n-C_4F_9I (1)	H_2O (30)	–	5.5:2[c]
25	λ = 254 nm	**15** (2.5), n-C_4F_9I (0.5)	H_2O (4)	**16** (85)[e]	5.5:2.5[c]

[a] Yield based on n-C_4F_9I or otherwise indicated. [b] Absorbance ratio of substrate and R_fX from a homogeneous solution at the irradiation wavelength. [c] pH of the solution before/after the reaction. [d] The medium pressure Hg lamp (MPL) has the most intense emission at 365–366 nm. This type of lamp has also very intense lines at wavelengths shorter than 365–366 nm and a quasi-continuum in the visible. [e] This commercial fluorescent lamp (coated-filtered Hg lamp) has an intense maximum emission at 350 nm, and the intensity of the emission at 313 nm can be disregarded (2 × 40 watts). The irradiation time was 4 h. See Exp. Sect. for lamp details. [f] MAP = 4-methoxyacetophenone. [g] Yield based on substrate **1** or **2**. [h] MeCN/H_2O = 1:1.

reaction conditions, no substitution product **3** (or **4** from substrate **2**) was observed [i.e., $E_T(\mathbf{2}) = 226\ \text{kJ mol}^{-1}$;[13c,13d] Table 1, entries 4 and 5]. This would seem to imply that the singlet excited state manifold is responsible for the formation of the aromatic substitution product in water, and that the sensitized population of the triplet state of the amine does not lead to an aromatic substitution reaction.

The n-$C_4F_9^{\cdot}$ radical shows a clear-cut electrophilic character in the aromatic substitution, as already reported for the addition to alkenes,[14,15] but the low regio- and chemoselectivities observed in organic solvents suggest that the polar effect is not the main factor in determining the high reactivity of perfluoroalkyl radicals toward aromatics (10^5–$10^6\ \text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$; 2–3 orders of magnitude more reactive than alkyl radicals).[15] The enthalpic factor, which is related to the bond energies involved, appears to be the predominant cause of the increased reactivity. The polar effect is considered to relate more to the polarizability than to the polarity of a radical (the σ-perfluoroalkyl radicals are considered less polarizable and hence less sensitive to polar effects than σ-carbon radicals).[16a]

We also subjected substrates **1** and **2** to the photoinduced (unfiltered medium pressure Hg lamp) substitution reaction with $C_8F_{17}X$ (X = I, Br) in water, obtaining substitution products **5** and **6**, respectively, in yields indicated in Table 1, entries 6–9, Scheme 3.

The photoreaction (unfiltered Hg lamp[13b]) of **2** (5 mmol) with n-$C_8F_{17}I$ (1 mmol) and of **2** (5 mmol) with n-$C_8F_{17}Br$ (1 mmol) in water (30 mL) was also monitored versus time in terms of product yields and pH; under these conditions, a steady increase of product yield was observed as the pH of the solution decreased and the reaction evolved, up to four hours of photoreaction, whereupon a plateau was reached (see the Supporting Information for a kinetics plot). We were unable to observe a difference between rates of formation of **6** when **2** reacted either with n-$C_8F_{17}I$ or with n-$C_8F_{17}Br$ (see the Supporting Information).

In a typical radical addition reaction of R_f radicals derived from $C_nF_{2n+1}X$ (n = 4, 6, 8, 10, X = I, Br) on alkenes under various radical initiation methodologies in water, the lower yields of addition products derived from R_fBr were interpreted as resulting from a higher BDE of R_f–Br compared to R_f–I in the radical addition mechanism.[3] The fact that aromatic substitution product yields with R_fI and R_fBr are comparable (see Table 1, entries 6 and 7 or 8 and 9), could again suggest or support the notion that either R_f–X bond homolysis is not rate limiting, or a different initiation event should be considered.

When substrates **1** or **2** (0.1 mmol) were allowed to react with n-C_4F_9I (10 mmol) in water (4 mL) under 254 nm light irradiation instead (40 W, quartz vessel, where $A_{\text{substrate}}/A_{\text{C4F9I}}$ = 1:10), products **3** and **4** were obtained in similar yields (based on substrate consumption; Table 1, entries 10 and 11). The UV/Vis spectra of substrates **1**, **2**, and reagent *n*-C_4F_9I are depicted in Figure 1.

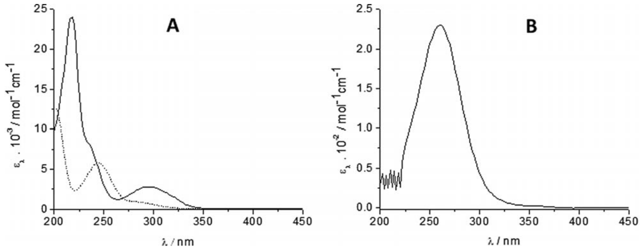


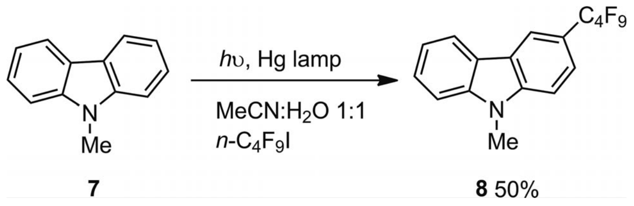
Figure 1. (A) UV/Vis spectra of substrates **1** (···) and **2** (—) in H_2O. λ_{max} [**1**; ε ($dm^3 mol^{-1} cm^{-1}$)] = 242 (5705), 287 (1145) nm; λ_{max} [**2**; ε ($dm^3 mol^{-1} cm^{-1}$)] = 218 (2.4×10^5), 294 (2741) nm. (B) UV/Vis spectrum of *n*-C_4F_9I in MeCN, λ_{max} = 262 (2300 $dm^3 mol^{-1} cm^{-1}$) nm.

Under these reaction conditions, and given the optical density at 254 nm of mixtures of **1** or **2** with *n*-C_4F_9I, appreciable homolysis of the C–I bond from *n*-C_4F_9–I is expected. The presence of substitution products under these reaction conditions (i.e., 254 nm irradiation; Table 1, entries 10 and 11) might indicate that a cyclohexadienyl-type substituted radical could be involved in the substitution mechanism. On the other hand, when reaction conditions were changed (UV-absorption at 254 nm) to increasing concentration of substrate **1** or **2** (2.5 mmol) to the detriment of *n*-C_4F_9I absorption (0.5 mmol, where $A_{substrate}/A_{C4F9I}$ = 100:1) in water (4 mL), products **3** or **4** were nonetheless obtained in fairly good yields (80 and 61% yields, respectively; Table 1, entries 12 and 13). This would seem to indicate that the reaction mechanism is initiated by a PET from substrate **1*** or **2*** to R_fI, and the substitution product is formed by either an ET–PT or PT–ET sequence (Scheme 1).

The thermally-induced (100 °C, 4 h, stirring) reaction of **1** or **2** with *n*-C_4F_9I in deoxygenated water did not yield any product (Table 1, entries 14 and 15, respectively). We also attempted to induce the above reactions by exposure to ultrasound at 80 °C for 4 h; however, we did not observe any product formation (Table 1, entries 16 and 17, respectively).

The photoreactions (unfiltered medium pressure Hg lamp, Pyrex) of **1** and **2** in the presence of *n*-C_4F_9I in a homogeneous MeCN solution, led to the formation of substitution products **3** and **4**, respectively, in fairly good yields (81 and 49%, respectively; Table 1, entries 18 and 19).

The photoreaction (unfiltered medium pressure Hg lamp) of *N*-methylcarbazole **7** with *n*-C_4F_9I in MeCN/water (1:1) (heterogeneous mixture) led to the formation of substitution product **8** in fairly good yields (Scheme 4 and Table 1, entry 20). As far as we know, the carbazole ring has only been trifluoromethylated before through Pd-catalysis with (triethylsilyl)trifluoromethane (STM) in organic solvents.[16b] Of note is the fact that we herein report the first perfluoroalkylation reaction (non-CF_3) of the carbazole ring. Interestingly, this substitution of the carbazole ring takes place solely at the 3-position, which is a position commonly activated in classical electrophilic aromatic substitution reactions.

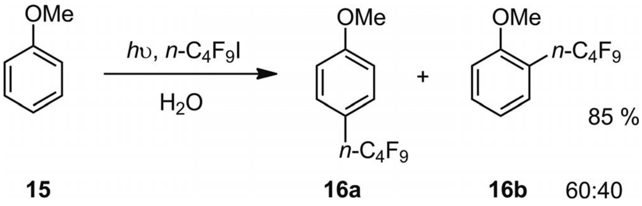


Scheme 4. Photoinduced perfluorobutylation reaction of carbazole rings in MeCN/H_2O.

When *N*-methylaniline (**9**) or *N*-methylnaphthylamine (**10**) was subjected to photoreaction (unfiltered medium pressure Hg lamp) with *n*-C_4F_9I in water under vigorous stirring, the R_f-substitution products **11** and **12** were obtained in lower yields (32 and 15% yields, respectively, based on *n*-C_4F_9I; Table 1, entries 21 and 22), although the global mass balance for the substrate was deficient (<50%). On the other hand, in the photoreactions of primary aromatic amines such as aniline **13** and 1-naphthylamine **14** with *n*-C_4F_9I in water (unfiltered medium pressure Hg lamp), no appreciable yields of substitution products were encountered (Table 1, entries 23 and 24, respectively).

We had previously tested (unpublished results) radical photosubstitution (254 nm) reactions in water of iodobenzenes with *n*-C_4F_9I, under reaction conditions in which only the latter absorbed the light, and obtained the *ipso* substitution product by a regular radical mechanism (leaving group iodine radical). In halobenzenes, the initial radical adduct formed loses a halogen radical to render the substitution product. Under these latter reactions conditions, ET to form the radical anion of the substrate or, later, the substitution product, is not feasible.

We also subjected methoxy-substituted aromatic compounds (with no conventional leaving groups), such as anisole **15**, in water, to the PET reaction with *n*-C_4F_9I, and obtained the aromatic substitution products **16a** and **16b** in 85% yield. The **16a**/**16b** isomer ratio obtained was 60:40 (Scheme 5, Table 1, entry 25).



Scheme 5. Perfluorobutyl group substitution of anisole in water.

This metal-free methodology for the perfluoroalkylation of aromatic amines or the carbazole ring does not require the presence of conventional leaving groups, organocatalysts, or thermal activation, and is conducted in environmentally friendly media in heterogeneous solutions.

Verification of the Reaction Mechanism – Intermolecular Interactions in the Ground and Excited States and the PET Mechanism

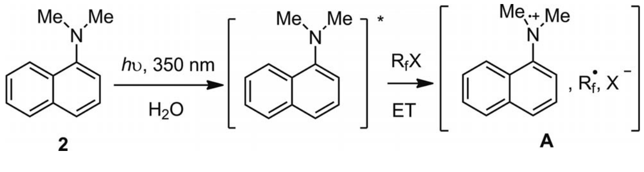
We could not find a charge transfer complex (CTC) in the UV/Vis spectra of **1** or **2** upon addition of n-C_4F_9I in MeCN as solvent. A series of fluorescence quenching experiments were performed with substrates **1**, **2**, and *N*-methylaniline (**9**) with n-C_4F_9I in MeCN, to obtain Stern–Volmer quenching rate constants, k_{sv}, in this solvent and hence the quenching rate constants of the fluorescence (k_q) of substrates **1**, **2**, and **9** with n-C_4F_9I (for fluorescence quenching spectra and Stern–Volmer graphs of substrates **1**, **2**, and substrate **9** with n-C_4F_9I, see the Supporting Information).

The quenching of fluorescence of **1** and **2** (and **9**) by n-C_4F_9I supports the PET mechanism. Furthermore, the quenching rate constants (Table 2, entry 4) show a good correlation between the oxidation peak potential of the amine (Table 2, entry 1) and the theoretical values of their HOMO energy calculated by using AM1 method (not shown). We could not find evidence for exciplex formation in the fluorescence spectra of **1** or **2** upon addition of n-C_4F_9I. This suggests a concerted ET and C–I bond breaking step[17,18] and that the reaction proceeds from the singlet excited state of **2** affording its radical cation ($\mathbf{2}^{+\cdot}$), n-$C_4F_9^{\cdot}$, and I^- (**A**; Scheme 6 for **2**).

Table 2. Rehm–Weller parameters for amines **1**, **2**, **9**, and n-C_4F_9I.

Entry		**1**	**2**	**9**	n-C_4F_9I
1	$E_{D/D+}$ [V]	+0.71[a]	+0.39	+0.73[b]	–
2	$E_{A/A-}$ [V]	–	–	–	–1.27
3	E^* [eV]	3.22 (3.87)[c]	3.39	3.12	
4	$\log k_q$ [$mol^{-1} dm^{-3} s^{-1}$]	11.05	10.88	11.4	
5	ΔG_{ET} [eV]	–1.29	–1.78	–1.17	
6	ΔG_{ET} [kcal/mol]	–29.7	–41.00	–26.9	
7	τ [ns]	2.24[d]	2.40[e]	1.22[d]	
8	$\phi_{fluorescence}$	0.042[d]	0.20[f]	0.032[d]	

[a] Ref.[22], E_{ox} (vs. SCE) = 0.83 V. [b] Ref.[23], measured in water, vs. NHE. [c] Ref.[24], τ = 2.78 ns. [d] Ref.[25], τ measured in water vs. NHE. [e] Ref.[26], measured in CH_2Cl_2. [f] Ref.[20], measured in $MeCN/H_2O$.



Scheme 6. PET between **2** and R_fX to generate radical ion pair **A**.

To gain further evidence for the ET mechanism (under irradiation with a MPL) in the perfluorobutylation substitution reaction of **1** and **2** in water, we employed the Rehm–Weller relationship – see Equation (1) – to assess whether the Gibbs energy change in the ET process (ΔG_{ET}) was spontaneous or not.

$$\Delta G_{ET} = E_{(D/D+)} - E_{(A/A-)} - E^* + \frac{Z_1 Z_2}{\varepsilon r_{12}} \tag{1}$$

In Equation (1), $E_{(D/D+)}$ is the redox potential of the donor, and $E_{(A/A-)}$ the redox potential of the acceptor, E* the singlet excited state energy of the aromatic amine, and the last term represents the coulombic energy necessary to form an ion pair with charges Z_1 and Z_2 in the medium of dielectric constant ε at a distance r12.

From an overlap of the UV/Vis and fluorescence plots of substrates **1**, **2**, and *N*-methylaniline **9**, the excited state (singlet) energies (E^*) were calculated for **1***, **2***, and **9*** (see the Supporting Information). The redox potential of the donor aromatic amines **1** and **2** were +0.71 V (vs. SCE, in MeCN)[19] and +0.39 V, respectively.[20] The coulombic term was taken as –0.05 eV, assuming a separation distance of 0.8 nm.[21] The redox potential of the acceptor n-C_4F_9I was taken to be –1.27 V, as an approximate measure given in *N*,*N*-dimethylformamide (DMF).[17]

Thus, ΔG_{ET} from **2** to n-C_4F_9I was calculated to be –1.78 eV (–41 kcal/mol), and that from **1** to n-C_4F_9I to be –1.29 V (–29.7 kcal/mol), which are clearly highly spontaneous processes. For comparison, the photoinduced ET addition of **2** to furanone[20] was determined by Hoffmann and co-workers to have a ΔG_{ET} of –0.37 eV (–8.5 kcal/mol) in a mixture of MeCN/water; the data are summarized in Table 2.[20] The remainder of the data for substrate **9** are also collected in Table 2.

Generally speaking, photochemical electron transfer reactions occur only when the charge transfer step is either exergonic or < 5 kcal/mol.[27]

In Table 2, measures of $\log k_q$ (logarithm of rate constant for fluorescence) quenching of amine substrates with n-C_4F_9I (see the Supporting Information for Stern–Volmer plots) of **1**, **2**, and **9** are given as a function of ΔG_{ET}, showing that the ET processes takes place at a diffusion rate in MeCN (in water the diffusion rate is taken as $8RT/3\eta$, where η is the viscosity of water taken as 8.90×10^{-3} dynes/cm^2 or 0.890 cP at about 25 °C). A plot (not shown) of $\log k_q$ of substrates **1**, **2**, and **9** (data from Table 2, entry 4) with n-C_4F_9I vs. ΔG_{ET} (Table 2, entry 5) demonstrates that the ET process has a slope nearing zero, indicating a diffusion-controlled process for these substrates in MeCN.[28–29]

We performed a series of Laser Flash Photolysis (LFP) experiments with *N*,*N*-dimethyl-1-naphthylamine **2** in the presence of n-C_4F_9I in MeCN as solvent. Figure 2 depicts the transient spectrum of the *N*,*N*-dimethyl-1-naphthylamine radical cation $\mathbf{2}^{\cdot+}$ (**B**) in the presence of n-C_4F_9I, and that of the triplet spectrum of **2** in the absence of n-C_4F_9I (**A**).

The wavelength maxima in spectrum **B** (Figure 2, right) at λ = 383, 440, and 675 nm, respectively, can be attributed to the radical cation species $\mathbf{2}^{\cdot+}$ generated after laser pulse excitation (355 nm) of **2** in the presence of n-C_4F_9I, which is in excellent agreement with the reported spectrum of $\mathbf{2}^{\cdot+}$ generated after laser pulse excitation of **2** in the presence of benzophenone (radical anion).[13a] On the other hand, in the absence of n-C_4F_9I (spectrum **A**, Figure 2, left), the wavelength maxima at 390 and 550 nm can be attributed to the triplet-triplet absorption spectrum of **2** ($^3\mathbf{2}^*$), also in agreement with reported data.[13a] It is observed from comparison of spectra **A** and **B** in Figure 2, that $\mathbf{2}^{\cdot+}$ is a more

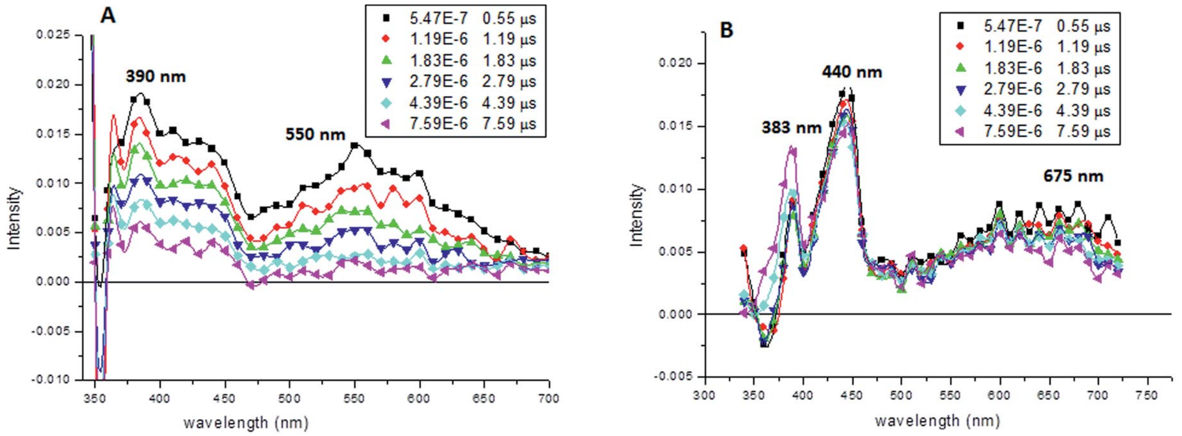


Figure 2. Transient UV/Vis spectra of *N*,*N*-dimethyl-1-naphthylamine **2** (0.8 mmol dm^{-3} in MeCN) after 0.55, 1.2, 1.8, 2.8, 4.4, and 7.6 µs of laser pulsing at 355 nm excitation wavelength: (**A**) in the absence of *n*-C_4F_9I; (**B**) in the presence of *n*-C_4F_9I (11.6 mmol dm^{-3}).

persistent transient (i.e., longer lived transient) than ^{3}**2***. This makes the former a better candidate as an intermediate (initiation event) in the photosubstitution reaction of amines with *n*-C_4F_9I.

Shizuka and co-workers[13a] showed that in MeCN, triplet energy transfer from triplet benzophenone (BP) to **2** produces triplet ^{3}**2*** and the corresponding triplet exciplex, whereas electron transfer took place during the deactivation of triplet BP to yield the benzophenone anion and **2**$^{\cdot+}$ cation radicals in MeCN/H_2O (4:1 v/v).[13c] The authors predicted schematically that added water may play an important role in altering the chemical interactions in the BP-**2**. Although we were unable to measure transient spectra in water or mixtures of water/MeCN of **2** and *n*-C_4F_9I, the claim of the participation of **2**$^{\cdot+}$ cation radicals in water is reasonable.[13c]

We were able to measure the quantum yield of **2**$^{\cdot+}$ cation radical production using ^{3}BP* in MeCN, and obtained a value of $\phi_{\mathbf{2}\cdot+} = 0.37$, which is, within error, close to the quantum yield of fluorescence of **2**, suggesting that **2**$^{\cdot+}$ is formed very efficiently under our reaction conditions.

Of note is the fact that these LFP transient experiments show that addition of *n*-C_4F_9I does not provoke enhancement of the spin-orbit coupling in **2** and that the triplet manifold is not a discrete intermediate in the photosubstitution reaction of **2** with *n*-C_4F_9I (cf. spectrum **A** and **B** in Figure 2).

An important mechanistic aspect was also revealed by the decrease in pH as a measure of the reaction progress (Table 1, column 6, and Table 3, column 6). The initial pH of the reaction mixture of **2** (5 mmol) and *n*-C_4F_9I (1 mmol) was 5.5. After two-hour photoreaction (MPL, pyrex), the pH of the solution decreased to 2.5. This would seem to imply that proton loss might be involved in the reaction mechanism, probably through rearomatization of a carbocation intermediate such as those postulated in classical aromatic electrophilic substitution reactions. The results of control pH experiments are shown in Table 3, entries 1 and 2.

For any given solvent or solvent mixture, the cage scape process is well-modeled as a unimolecular activated process that is characterized by an exponential decay, and the cage scape depends linearly on the solvent fluidity.[30] The time scale for cage scape is typically in the order of picoseconds. Thus, the higher the fluidity, the faster the cage scape process.[30] One likely mechanism would involve radical substitution within the solvent cage **A** (Scheme 6). The in-cage radical cation of the substrate adds the $R_f^{\cdot}$ radical within the cage, generating the cyclohexadienyl cation intermediate, which, upon proton loss, produces the substitution

Table 3. Experiments towards the mechanistic elucidation of the perfluoroalkylation reactions of arenes.

Entry	Synthetic method [λ_{max} irradiation (nm)]	Substrates [mmol]	Solvent system [mL]	Product (yield [%])[a]	$pH_{initial}/pH_{final}$[b]
1	254	**1** (0.1), *n*-C_4F_9I (–)	H_2O (4)	**3** (–)	5.5:5.5[c]
2	254	**2** (0.1), *n*-C_4F_9I (–)	H_2O (4)	**4** (–)	5.5:5.5[c]
3	MPL[c]	**1** (5), *n*-C_4F_9I (1), *p*-DNB (0.05)	H_2O (30)	**3** (80)	5.5:2.5[c]
4	MPL[c]	**2** (5), *n*-C_4F_9I (1), *p*-DNB (0.05)	H_2O (30)	**4** (45)	5.5:2.5[c]
5	254	**1** (2.5), *n*-C_4F_9I (0.5)	H_2O[d] (4)	**3** (70)	14:14[c]
6	254	**2** (2.5), *n*-C_4F_9I (0.5)	H_2O[d] (4)	**4** (41)	14:14[c]
7	254	**1** (2.5), *n*-C_4F_9I (0.5), *p*-DNB (0.05)	H_2O[d] (4)	**3** (71)	14:14[c]
8	254	**2** (2.5), *n*-C_4F_9I (0.5), *p*-DNB (0.05)	H_2O[d] (4)	**4** (41)	14:14[c]

[a] Yield based on *n*-C_4F_9I unless otherwise indicated. [b] pH of the solution before/after reaction. [c] The medium pressure Hg lamp has the most intense emission at 365–366 nm. This type of lamp has also very intense lines at wavelengths shorter than 365–366 nm and a quasi-continuum in the visible. [d] pH 14.

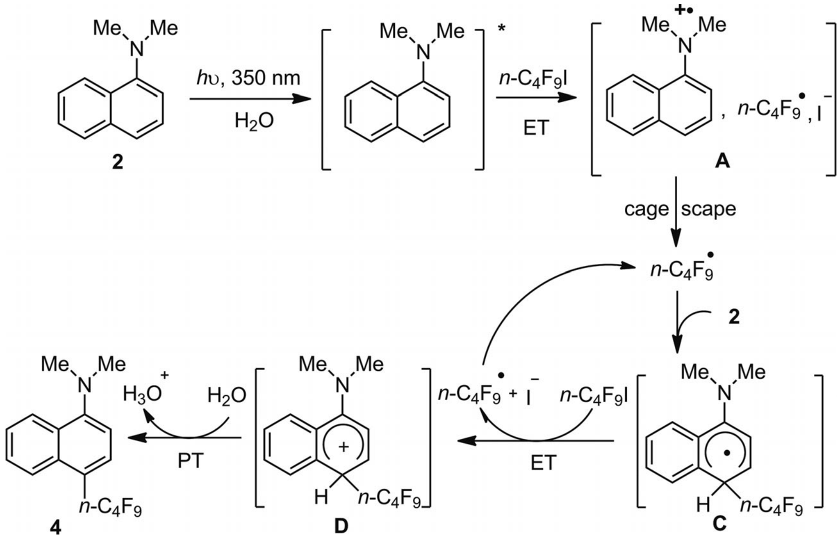
product. We argue against in-cage product formation as being a possible substitution route because the radical cation of the substrate is a long-lived intermediate, as depicted in Figure 2 (B), with sufficient time to escape the cage (1–10 µs time scale). We were able to measure quantum yields for substrate **2** consumption and products **4** and **6** formation upon reaction of **2** with n-C_4F_9I and n-$C_8F_{17}I$, respectively, by ferrioxalate actinometry, and obtained averaged values of $\phi_{-2} = 248 \pm 51$ for the disappearance of substrate **2** and $\phi_4 = 221 \pm 54$ and $\phi_6 = 199 \pm 65$ for the formation of products **4** and **6** from reaction of substrate **2** with n-C_4F_9I, and n-$C_8F_{17}I$, respectively (data displayed in the table in the Supporting Information). This would clearly indicate that these substitutions proceed by a chain mechanism and that, within error, consumption of **2** leading to **4** or **6** is the only photoprocess that takes place within the analyzed time range.

We thus postulate a photoinduced ET (PET) mechanism in which, upon light absorption by substrates **1** or **2**, the corresponding radical cation ($\mathbf{1}^{+\cdot}$ or $\mathbf{2}^{+\cdot}$) together with the n-$C_4F_9^{\cdot}$ and iodide anion are formed in the solvent cage by an ET (Scheme 7, for substrate **2**). This being the initiation step. Upon cage-scape of $\mathbf{2}^{+\cdot}$ (or $\mathbf{1}^{+\cdot}$) and n-$C_4F_9^{\cdot}$, the radical n-$C_4F_9^{\cdot}$ adds to the 4-position of **2** (and the *para* position of **1**) to render an aromatic substituted cyclohexadienyl radical intermediate **C** (in the case of **2**). Intermediate **C** donates an electron (ET) to n-C_4F_9I, to generate the oxidized cation intermediate **D** (a σ adduct that is stabilized by resonance effect from the N atom, i.e., a Wheland intermediate) and n-$C_4F_9^{\cdot}$ + I^-. This latter n-$C_4F_9^{\cdot}$ triggers a chain sequence. Upon proton loss (PT), adduct **D** generates the substitution product **4**. n-$C_4F_9^{\cdot}$ radicals enter the substitution cycle depicted in Scheme 7. It should be noted that this is a *chain* PET mechanism in which n-$C_4F_9^{\cdot}$ behaves as a radical chain carrier.

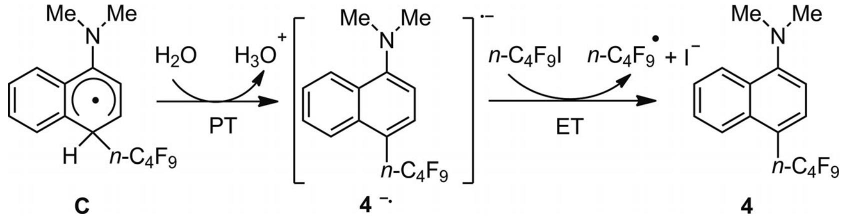
Another mechanistic possibility would involve the radical anion of the substitution product **4** (i.e., $\mathbf{4}^{\cdot-}$), generated by proton loss from intermediate **C** (see Scheme 8) through the action of a base (H_2O). Radical anion $\mathbf{4}^{\cdot-}$ would then transfer an electron to n-C_4F_9I to render thermoneutral **4** and n-$C_4F_9^{\cdot}$ radicals, which could add to **2** to render adduct **C**, continuing the propagation cycle as illustrated in Scheme 8. This constitutes a PT–ET sequence for the rearomatization of the cyclohexadienyl radical intermediate (see Scheme 1). A supporting piece of evidence for this mechanism would be the inhibition of the photoreaction in the presence of p-dinitrobenzene (p-DNB;[31] $E_{\text{red}} = -0.257$ V at pH 7;[32] E_{red} n-$C_4F_9I = -1.27$ V), a well-known radical anion scavenger or inhibitor. After addition of p-DNB (0.05 mmol) to the photoreaction (unfiltered medium pressure Hg lamp, Pyrex, 2 h) mixture of **1** or **2** (5 mmol) and n-C_4F_9I (1 mmol) in water (which represents approximately equal absorbances of substrate and p-DNB), we did not observe any change in the yield of product **3** or **4**, respectively (Table 3, entries 3 and 4) in comparison with experiments performed in the absence of p-DNB (Table 1, entries 1 and 2, respectively). We therefore conclude that the radical anion of **4** (i.e., $\mathbf{4}^{\cdot-}$) is not a discrete intermediate, as illustrated in Scheme 8.

We also conducted the photoreaction (254 nm irradiation) of n-C_4F_9I (0.5 mmol) and **1** or **2** (2.5 mmol) in water (4 mL, 2h) at pH 14 to explore the possibility of a PT–ET sequence in the rearomatization of the cyclohexadienyl-substituted intermediate **C** or its analogue induced by the strong basic medium. We did not obtain any appreciable change in the yield of substitution products **3** and **4** (Table 3, entries 5 and 6).[31] Furthermore, these latter reactions were not retarded in the presence of p-DNB, indicating the absence of radical anion intermediates ($\mathbf{4}^{\cdot-}$ and its analogue for substrate **1**) under these extremely basic conditions (Table 3, entries 7 and 8).

Probably, during direct photolysis (irradiation at 254 nm, conditions where $A_{\text{substrate}}/A_{\text{C4F9I}} \approx 100{:}1$, see Table 1, entry 12), the initiation entails a similar PET mechanism to that postulated to occur at 366 nm (i.e., Scheme 7; or medium pressure Hg lamp), and the chain is maintained through an



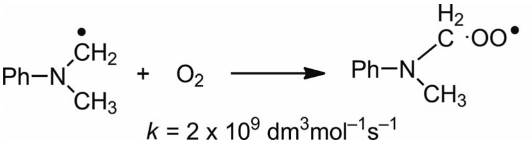
Scheme 7. Proposed reaction mechanism for the photoinduced ET (PET) perfluorobutylation substitution of aromatic amines in water.



Scheme 8. Possible reaction mechanism involving a radical anion species.

ET to n-C_4F_9I to generate n-$C_4F_9^{\cdot}$ radicals. Under different reaction conditions (irradiation at 254 nm for which $A_{substrate}/A_{C4F9I} \approx 1:10$, see Table 1, entry 10) the initiation entails homolysis of n-C_4F_9I, to render n-$C_4F_9^{\cdot}$ radicals which enter into the propagation cycle (Schemes 7 and 8). We argue in favor of a chain reaction triggered through ET from radical adduct **C** (Scheme 7) to R_fX, as evidenced by the lowering of pH (proton loss) in the reaction sequence (Table 1, column 6).

On the other hand, the radical cation $\mathbf{1}^{\cdot+}$ is known to undergo dissociation in the presence of nucleophiles (i.e., $H_2O \rightarrow H_3O^+$) to $\mathbf{1}^{\cdot}$ radicals, which could further react in the presence of oxygen, as shown in Equation (2), at the diffusion level.[33,34]



$$\mathrm{Ph{-}N(\dot{C}H_2)(CH_3)} + O_2 \longrightarrow \mathrm{Ph{-}N(CH_3)(CH_2OO^{\bullet})} \qquad k = 2 \times 10^9\ \mathrm{dm^3mol^{-1}s^{-1}} \tag{2}$$

Baciocchi and co-workers[35] have shown that α-amino carbon radicals such as N-methylanilinomethyl radicals shown in Equation (2), can be converted into the N-demethylated aniline (i.e., N-methylaniline **9**) by oxidation of N-methylanilinomethyl radicals to a carbinolamine, which, in turn, affords the N-methylaniline and CH_2O, which is detected as its dimedone adduct.[35] Although, in their case, the sequence of the oxidation reaction was triggered by the use of phthalimide N-oxyl radical (PINO), which generated the radical cation of the N,N-dialkylamine, one cannot rule out a side-reaction pathway like this to account for the large excess of substrate that we need in our substitution reactions; however, no N-methylaniline **9** was encountered in the reactions that were carried out by irradiation of the substrate N,N-dimethylaniline **1** in water under our reaction conditions.[36]

Hoffmann and co-workers[20] recently illustrated the photoinduced (350 nm) electron-transfer *addition* of N,N-dimethylnaphthylamines to electron-deficient alkenes in $MeCN/H_2O$, and postulated the generation of a PET intermediate (the radical cation of the amine) to rationalize the products obtained photochemically; this was supported by a deuterium isotope study.[20]

It is known that secondary amine radical cations decay immediately by deprotonation[34] (pK_a of N-methylaniline radical cation is 7.6[23a]). Therefore, as we postulate that the PET from **1**, or **2**, to n-C_4F_9I arises from population of the n,π^* singlet excited state of the amines (localization of spin distribution on N atom), these dimethyl-substituted and monomethyl-substituted aromatic amines, channel their reactivity into substitution reactions. Probably, the low mass balance obtained from N-methylaniline **9** could be attributed to a deprotonation process of the radical cation $\mathbf{9}^{\cdot+}$, as predicted by the studies of Brede and co-workers. It is likely that deprotonation of *primary* amine radical cations (pK_a of aniline radical cation is 6.4[23b,23c]) might be much more accelerated in water than deprotonation of *secondary* amine radical cations, diverting the aromatic-ring substitution pathways in the former.[37] Then, when the proton affinity of the solvent becomes comparable to or larger than that of the amine radical, this could assist in the deprotonation of the amine radical cation.

The electron-rich anisole substrate **15** also acts as a good electron donor to the n-C_4F_9I under photostimulation, as is the case for substrates **1**, **2**, and **9**. We surmise that, given the oxidation potential of **15** ($E_{(D/D+)}$ = 1.76 V[37d]), and its excited state (singlet) energy (E^* = 86 kcal/mol)[14] [see supplementary material for excited state (singlet) energy determination], the ΔG_{ET} ($\mathbf{15^*} \rightarrow R_fI$) equals –0.9 eV [or –25 kcal/mol, Equation (1)], an exergonic process. Unlike the charge transfer quenching of naphthols or phenols, which can occur either by electron or proton transfer,[38,39] compound **15** could only form a charge transfer complex by electron transfer to R_fI. However, the UV/Vis spectrum of **15**, upon addition of n-C_4F_9I, does not present an additional absorption maximum, and neither is an exciplex formed.

It has to be pointed out that PET from 2-naphthoxide ions to aliphatic halides proceeds with substitution on the 1-, 3-, and 6-positions of the naphthalene ring through a radical anion mechanism.[40a] Regarding substrate **15**, previously reported radical substitutions triggered by photodecomposition (185 nm) of azo compounds in benzene as solvent led to a different isomer distribution, i.e., *ortho*- (40%), *meta*- (23%), and *para*- (37%) substitution.[40b] Minisci and co-workers[16a] have demonstrated that in the radical perfluorobutylation reaction of various aromatic nuclei (including anisole) in tetrahydrofuran (THF) as solvent under various radical initiation methodologies, the electrophilic character of n-$C_4F_9^{\cdot}$ radical is, however, barely reflected in the orientation of the substitution, i.e., the *ortho*, *meta*, and *para* positions of aromatics are substituted with low selectivity.[16a,41–43] Our methodology involving water or aqueous mixtures leads to substitution at the 4- and 2-positions of the anisole ring, rendering a more regioselective radical substitution procedure than the previously reported approaches. The result of the substitution of carbazole **7** at the 3-position is also remarkable. It would appear that the orientation is related more to the stabilization of the substituted cation intermediate (electron availability of the ring) rather than the stability of the intermediate radical adducts, which are less sensitive to the substituent position (see Scheme 7).

Conclusions

We have shown that aromatic amines such as *N*,*N*-dimethylaniline, *N*,*N*-dimethyl-1-naphthylamine, *N*-substituted carbazoles, and methoxy-substituted aromatics react in water by PET with R$_f$X to render substitution products in fairly good yields. Of note is the fact that the proposed mechanism is a HAS mechanism in water or aqueous mixtures, followed by an ET and then proton transfer (PT) steps, accounting for the observed yields of substitution products, whereby the radical cations of the substrates are formed in the initiation step, and a radical mechanism seems to be superimposed on a redox process. Concerning some mechanistic details, the reaction is compared with radical and electrophilic aromatic substitutions.

Experimental Section

General Methods: The internal standard method was used for quantitative GC analysis using authentic samples when available; one of the following capillary columns was employed (1% phenyl-SiO phase): 5 m × 0.53 mm i.d. or 30m × 0.32 mm i.d. Oven program: 50 °C for 5 min then 5 °C/min to 250 °C. NMR spectra were recorded at 400 MHz (for ^{1}H) or 100.6 MHz (for ^{13}C) or at 376.17 MHz (for ^{19}F) in CDCl$_3$ as deuterated solvent and referenced to the residual solvent peak (δ = 7.26 ppm for ^{1}H, δ = 77.0 ppm for ^{13}C) and an external CF$_3$COOH reference for ^{19}F NMR spectra, respectively. The NMR spectrometers were commercial instruments: Varian Mercury 400. Hydrogen multiplicity (CH, CH$_2$, CH$_3$) information was obtained from carbon DEPT-135 experiments. Some NMR spectroscopic data connectivity (particularly that of **10a** and **10b**) were confirmed by ^{1}H-^{13}C HSQC and HMBC 2-D experiments. Mass spectra were acquired through direct insertion (EI-technique) in a probe heated at 180 °C, monitoring the ion current, by electron ionization technique (EI). FTIR spectra were obtained with 4 cm^{-1} resolution of sample-impregnated NaBr pellets with a commercial FTIR spectrometer Nicolet 5700 FT-IT/ATR. UV/Vis, fluorescence, and NLFP experiments were carried out with commercial instruments Varian Cary Eclipse. Reduced pressure distillation employed a bulb-to-bulb distillation apparatus with four glass bulbs. When necessary, compounds were isolated by flash chromatography performed on silica gel. High-resolution mass spectrometry measurements were performed with a resolution of 1–5 ppm on a ZAB-E instrument.

Water was obtained from a milli-pore system, and extraction and chromatographic solvents were HPLC-grade. Products from Table 1, and other sections were characterized by standard spectroscopic techniques and compared with spectroscopic data from the literature when available.

Materials: Perfluoroalkyl iodides and bromides were commercially available and used as received from the supplier. Aromatic substrates were also commercially available and were previously distilled and stored over molecular sieves (4 Å) prior to use.

Methods of Irradiation: An unfiltered medium pressure Hg lamp (λ_{max} = 365–366 nm) in water-cooled 20 or 30 mL Pyrex vessels was used for irradiation. The temperature was maintained at 20 °C by means of a circulating coolant liquid in the internal vessel. The assembly was maintained 20 cm from the lamp. The water-heterogeneous mixtures of substrates (5 mmol) and R$_f$X (1 mmol) were previously deoxygenated by means of a continuous stream of Ar for 15 min. prior to irradiation. The vessels contained a stirring bar and the mixtures were stirred continuously by means of a magnetic stirrer placed underneath the vessel during the whole irradiation (4 h). After photolysis, the heterogeneous mixtures were extracted into CH$_2$Cl$_2$ thrice and the organic layers gathered and dried through an anhydrous Na$_2$SO$_4$-packed column. The extracts were concentrated under reduced pressure, and either purified by column chromatography through silica-gel with CH$_2$Cl$_2$/heptane (50:50) or vacuum distilled. Irradiation at 254 nm (three 20 W lamps, λ = 254 nm) was conducted in 15 mL quartz cells under vigorous stirring. The vessels were placed 4 cm from the lamps. Irradiation with fluorescent 350 nm Hg lamps (2 × 40 W were conducted with two commercial Actinic BL 40 W lamps (BaSi$_2$O$_5$, Pb phosphor) in a 30-mL vessel in deoxygenated water with constant stirring during 4 h at 2 cm distance from the lamps.[43b]

Actinometry: The actinometry was carried out at 365 nm (unfiltered medium pressure Hg lamp). The conversion of the actinometer (potassium ferrioxalate) was monitored by measuring the absorbance of the complex Fe–(*o*-phenanthroline) at 510 nm. A radiant power of ca. 4×10^{-9} einsteins s^{-1} was achieved after 20 min irradiation. The conversion of **2** was followed by gas chromatographic techniques and kept as low as 5%. Product and substrate concentrations were determined relative to an internal standard (eicosane) and were corrected for relative FID response. The global mass balance exceeded 95%. All were run in duplicate parallel experiments and averaged over two determinations each (see Table S4 in the Supporting Information). The sample and the actinometer (duplicates) were placed equidistant from the lamp in a fixed arrangement. The preparation of the actinometer, potassium ferrioxalate, K$_3$Fe(C$_2$O$_4$)$_3$·3H$_2$O, was performed according to the protocol suggested by Hatchard and Parker.[43c]

Time-Resolved Absorption Spectroscopy: The Laser Flash Photolysis system was based on a pulsed Nd:YAG laser, using 355 nm radiation as excitation wavelength. The single pulses were of ca. 10 ns duration, and the energy was ca. 20 mJ/pulse.

Spectroscopic Characterization of Known Compounds: These compounds were purified by silica-gel column chromatography as mentioned above, and characterized by comparison of their ^{1}H, ^{13}C, and ^{19}F NMR spectroscopic data (when available) with those in the literature. Addenda data below are reported for the first time (references of compounds throughout the text).

***N*,*N*-Dimethyl-4-(1,1,2,2,3,3,4,4,4-nonafluorobutyl)benzeneamine (3):**[43] Yield 56 mg isolated (88% GC yield) [starting from **1** (1 mmol), *n*-C$_4$F$_9$I (0.2 mmol)]. ^{1}H NMR (300.01 MHz, CDCl$_3$): δ = 3.02 (s, 6 H, Me), 6.76 (d, J = 8.80 Hz, 2 H), 7.41 (d, J = 8.80 Hz, 2 H) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 40.4 (Me), 111.5 (CH), 128.3 (CH), 152.8 (C) ppm. ^{19}F NMR (376.17 MHz, CDCl$_3$): δ = –81.48 (CF$_3$), –109.84 (CF$_2$), –123.27 (CF$_2$), –126.04 (CF$_2$) ppm. GC/MS (EI): *m*/*z* (%) = 339 (50) [M$^{\cdot+}$], 320 (10), 170 (100). FTIR: $\tilde{\nu}$ = 1618 (s), 1350 (m), 1234 (broad s), 1201 (broad s), 868 (m), 810 (m), 741 (m) cm^{-1}.

***N*,*N*-Dimethyl-4-(1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctyl)benzeneamine (5):**[44] Yield 463 mg (86%). ^{1}H NMR (300.01,

$CDCl_3$): δ = 3.02 (s, 6 H, Me), 6.73 (d, J = 8.80 Hz, 2 H), 7.40 (d, J = 8.80 Hz, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 40.1 (Me), 111.3 (CH), 127.9 (CH), 152.3 (C) ppm. ^{19}F NMR (376.17 MHz, $CDCl_3$): δ = –81.29 (CF_3), –109.70 (CF_2), –120.56 (CF_2), –121.71 (CF_2), –122.12 (CF_2), –122.40 (CF_2), –123.18 (CF_2), –126.61 (CF_2) ppm. GC/MS (EI): m/z (%) = 539 (15) [$M^{\cdot+}$], 520 (5), 170 (100). FTIR: $\tilde{\nu}$ = 1618 (s), 1533 (m), 1368 (m), 1242 (br. s), 1151 (br. s), 815 (m), 655 (m) cm^{-1}.

1-Methoxy-4-(1,1,2,2,3,3,4,4,4-nonafluorobutyl)benzene (16a):[14,44a] Yield 11 mg isolated (85% GC yield); yellowish oil. ^{1}H NMR (300.01 MHz, $CDCl_3$): δ = 3.85 (s, 3 H, Me), 7.01 (d, J = 7.7 Hz, 2 H), 7.50 (d, J = 8.1 Hz, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 55.3, 120.3, 120.8, 133.6, 159.7 ppm. ^{19}F NMR (376.17 MHz, $CDCl_3$): δ = –81.09, –110.34, –122.38, –125.82 ppm. FTIR: $\tilde{\nu}$ = 2923 (s), 1583 (m), 1336 (m), 1203 (m), 992 (m) cm^{-1}.

1-Methoxy-2-(1,1,2,2,3,3,4,4,4-nonafluorobutyl)benzene (16b):[14,44a] Yield 9 mg isolated (85% GC yield); yellowish oil. ^{1}H NMR (300.01 MHz, $CDCl_3$): δ = 3.85 (s, 3 H, Me), 7.01 (m, 1 H), 7.12 (m, 1 H), 7.50 (m, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 55.8, 112.4, 117.6, 128.4, 128.5, 129.2, 158.5 ppm. ^{19}F NMR (376.17 MHz, $CDCl_3$): δ = –81.21, –110.75, –122.98, –125.96 ppm.

Spectroscopic Characterization of Unknown Compounds

***N*,*N*-Dimethyl-4-(1,1,2,2,3,3,4,4,4-nonafluorobutyl)naphthalene-1-amine (4):** Yield 86 mg isolated (57% GC yield); yellowish oil. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.95 (s, 6 H, Me), 7.05 (d, J = 8.1 Hz, 1 H), 7.41 (t, J = 8.06, 7.97 Hz, 1 H), 7.54 (m, 3 H), 7.70 (d, J = 8.25 Hz, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 45.2 (Me), 112.4 (C), 118.3 (CH), 123.3 (CH), 124.5 (CH), 125.6 (CH), 126.1 (CH), 129.2 (C), 132.2 (C), 155.6 (C) ppm. ^{19}F NMR (376.17 MHz, $CDCl_3$): δ = –81.32 (CF_3), –111.64 (CF_2), –123.3 (CF_2), –126.17 (CF_2) ppm. FTIR: $\tilde{\nu}$ = 2945 (m), 1581 (s), 1234 (br. s), 1098 (br. s), 806 (br. s) cm^{-1}. GC/MS (EI): m/z (%) = 389 (95) [$M^{\cdot+}$], 370 (18), 220 (100). HRMS (ESI): m/z calcd. for $C_{16}H_{12}F_9N$: 389.0826; found 389.0876. $C_{16}H_{12}F_9N$: calcd. C 49.37, H 3.11, F 43.93, N 3.60; found C 49.05, H 3.71, N 3.21.

***N*,*N*-Dimethyl-4-(1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctyl)naphthalene-1-amine (6):** Yellowish oil, 68% GC yield (25 mg isolated). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H = 2.96 (s, 6 H, Me), 7.08 (d, J = 8.06 Hz, 2 H), 7.54 (m, 2 H), 7.71 (m, J = 8.25 Hz, 1 H), 8.18 (d, J = 7.52 Hz, 1 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C = 45.1 (Me), 115.7 (C), 124.9 (CH), 125.6 (CH), 127.4 (CH), 128.3 (CH), 128.4 (CH), 131.7 (C) ppm. ^{19}F NMR (376.17 MHz, $CDCl_3$): δ_F = –81.16 (CF_3), –107.47 (CF_2), –120.53 (CF_2), –121.70 (CF_2), –122.12 (CF_2), –122.30 (CF_2), –123.09 (CF_2), –126.49 (CF_2) ppm. FTIR: $\tilde{\nu}$ = 2962 (m), 1582 (m), 1242 (br. s), 1210 (br. s), 802 (br. s) cm^{-1}. GC/MS (EI): m/z (%) = 589 (7), 220 (100). HRMS (ESI): m/z calcd. for $C_{20}H_{12}F_{17}N$ 589.0698, found 589.0658. $C_{20}H_{12}F_{17}N$ calcd. C 40.76, H 2.05, F 54.81, N 2.38; found C 40.05, H 2.61, N 2.41.

9-Methyl-1-perfluorobutyl-9*H*-carbazole (8): Yield 5 mg isolated (50% GC yield); white solid; m.p. 72–73 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.90 (s, 3 H, Me), 7.31 (m, J = 0.98, 7.21, 7.96 Hz, 1 H), 7.46 (d, J = 7.24 Hz, 1 H), 7.48 (d, J = 8.76 Hz, 1 H), 7.55 (m, J = 1.14, 7.15, 8.24 Hz, 1 H), 7.66 (dd, J = 0.80, 8.7 Hz, 1 H), 8.14 (m, J = 0.80, 1.14, 7.84 Hz, 1 H), 8.31 (d, J = 1.14 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.7 (CH_3), 108.9, 109.9, 119.5, 119.9, 120.0, 120.1, 120.6, 122.5, 123.9, 126.5, 141.8, 142.6 ppm. ^{19}F NMR (470.55 MHz, $CDCl_3$): δ = –181.71, –209.03, –223.12, –226.22 ppm. HRMS (EI): m/z calcd. for $C_{17}H_{10}F_9N$ 399.0670; found 399.0654.

***N*-Methyl-4-(1,1,2,2,3,3,4,4,4-nonafluorobutyl)benzeneamine (11):** Yield 45 mg (32%); yellowish oil. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.98 (s, 3 H, Me), 6.77 (d, J = 9 Hz, 2 H), 7.48 (m, 2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 30.7, 118.4, 125.6, 149.6 ppm. ^{19}F NMR (376.17 MHz, $CDCl_3$): δ = –80.32 (CF_3), –110.48 (CF_2), –123.45 (CF_2), –125.54 (CF_2) ppm. FTIR: $\tilde{\nu}$ = 3348 (w), 2964 (m), 1261 (s), 1093 (br. s), 1027 (br. s), 800 (s) cm^{-1}. GC/MS (EI): m/z (%) = 325 (1), 310 (17), 220 (100). HRMS (EI): m/z calcd. for $C_{11}H_8F_9N$ 325.0513; found 325.0514. $C_{16}H_{12}F_9N$, calcd. C 40.63, H 2.48, F 52.58, N 4.31; found C 40.05, H 2.71, N 4.21.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H, ^{19}F, and ^{13}C NMR spectra as well as FTIR spectra are provided for all key intermediates and final products; additional information as needed; LFP, UV, as well as fluorescence spectra.

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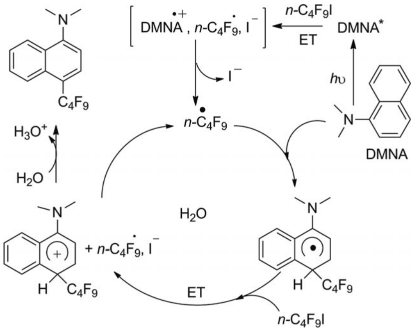
Aromatic Fluoroalkylation

Electron-rich aromatic compounds react in aqueous media by PET with R_fX to render substitution products in reasonable yields. The proposed mechanism is a homolytic aromatic substitution, followed by ET and (PT) steps, in the absence of base; radical cations of the substrates are formed in the initiation step. The reaction is compared with radical and electrophilic aromatic substitutions.



S. Barata-Vallejo, M. M. Flesia, B. Lantaño, J. E. Argüello, A. B. Peñéñory,* A. Postigo* 1–12

Heterogeneous Photoinduced Homolytic Aromatic Substitution of Electron-Rich Arenes with Perfluoroalkyl Groups in Water and Aqueous Media – A Radical-Ion Reaction

Keywords: Heterogeneous catalysis / Green chemistry / Radical reactions / Radical ions / Electron transfer / Alkylation