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Perfluoroalkylation of Triarylamines by EDA complexes and Ulterior Sensitized [6π]-Electrocyclization to Perfluoroalkylated *endo*-Carbazoles. Mechanistic and Photophysical Studies

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Abstract. Blue LEDs-irradiation of a mixture of *N,N,N´,N´*-tetramethylethylenediamine (TMEDA) and perfluoroalkyl iodides (R_F-I) -Electron Donor Acceptor (EDA)-complex- in the presence of triphenylamines (TPAs) in an aqueous solvent mixture afforded mono-perfluoroalkylated triphenylamines (R_F-TPA) in good yields. These R_F-TPA were further subjected to acetone-sensitized [6π]-electrocyclization at 315 nm-irradiation affording exclusively perfluoroalkylated endo-carbazole derivatives (R_F-CBz) in quantitative yields. Mechanistic studies and photophysical properties of products are studied.

Introduction

Triphenylamine (TPA) possesses a distinctive structural characteristic centered around its nitrogen atom, which serves as the electroactive site, forming bonds with three phenyl groups arranged in a propeller-like geometry.[1] This unique arrangement facilitates reversible redox behavior and excellent film-forming properties,[2,3] making TPA-containing monomers[4,5] and polymers[3] highly desirable for synthesis and investigation of their properties.[5-8] Consequently, TPA finds extensive utility in materials chemistry, functioning as a redox-active platform,[9] with diverse applications ranging from dyes and semiconductors to serving as electrochemical redox mediators.[9-13]

Trifluoromethylated triphenylamines (CF_3-TPAs) have garnered attention for their incorporation into polyamide polymers, resulting in remarkable mechanical properties.[14] Recent studies have also highlighted the utilization of TPA units within coordination polymers-containing dyes, specifically for trifluoromethylation reactions.[15] However, the existing synthetic methods for CF_3-TPAs primarily rely on indirect protocols, commencing from pre-functionalized *p*-(trifluoromethyl)aniline, which is then coupled with other aromatic partners.[14] Unfortunately, the full potential and versatile applications of CF_3-TPAs, as well as other triphenylamines substituted with perfluoroalkyl groups (R_F-TPAs), have been hindered by the absence of a direct synthetic approach. As far as we are aware, there is currently no established late-stage protocol available for the synthesis of R_F-TPAs.

Within the realm of perfluoroalkylation reactions, our research group has made several contributions by developing radical visible-light photocatalytic methodologies. These innovative approaches facilitate the incorporation of perfluoroalkyl (R_F) groups into diverse organic frameworks, with a specific emphasis on utilizing perfluoroalkyl halides as effective precursors for generating perfluoroalkyl radicals.[17-20]] Harnessing the power of visible-light photocatalysis, these techniques present environmentally benign alternatives for the generation of the initial R_F radical species, utilizing various precursors such as perfluoroalkyl iodides (R_F-I).

In addition to their role as radical precursors in photocatalytic processes, R_F-I have found application in conjunction with Lewis bases (LB) through the utilization of halogen bonding (XB). Upon activation by visible light, this combination triggers an electron transfer (ET) process, where the electron pair from the LB is transferred to the σ* antibonding orbital of R_F-I, leading to the generation of the nascent R_F radical.[21-23] This efficient electron transfer event plays a crucial role in the production of the R_F radical, as illustrated in Scheme 1.

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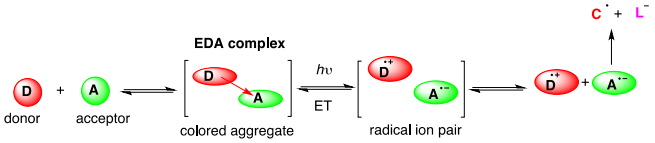


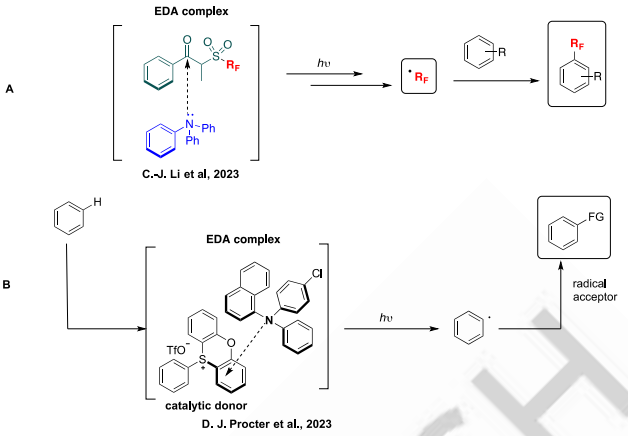
Scheme 1. EDA-complex-driven photoinitiation: A = acceptor, D = donor, C = radical (R_F), L = anion (I- from R_F-I)

The field of perfluoroalkylation reactions has witnessed the utilization of various Lewis bases (LB) as catalysts for this transformative process. LBs encompass a diverse range of compounds, including amines,[24] enamines,[25] carbonyl compounds,[26-28] phosphines,[29] chloride ions,[30] alcohols, water,[31,32] and more. This activation strategy, involving the interaction between the LB and perfluoroalkyl iodides (R_F-I), has emerged as a new paradigm in radical perfluoroalkylation reactions.[33] It has gained prominence, supplanting conventional methodologies such as photocatalysis, electrochemistry, thermal radical chemistry, metal-mediated processes, and direct homolysis of the R_F-I bond,[31] as an efficient means to generate the essential R_F radical species.[33]

Despite the widespread investigation of triphenylamines (TPAs) for their remarkable versatility and stability as electron donors, their potential as catalytic donors for radical generation remained largely unexplored until 2023.[34,35] However, a recent breakthrough by the research group led by C.-J. Li[34] has shed light on the catalytic capabilities of TPAs in the generation and functionalization of radicals in arenes, utilizing the concept of Electron Donor Acceptor (EDA) complexes for perfluoroalkylation reactions.[34] In this context, the EDA complex formed between α-perfluoroalkylsulfonylpropiophenone reagents and TPA acts as a catalyst, facilitating the perfluoroalkylation of C_{Ar}–H bonds in (hetero)arenes under visible light irradiation, all achieved under *p*H- and redox-neutral conditions (as depicted in Scheme 2A).[34]

In another recent report, the group of Procter and colleagues[35a] has shown the use of a triarylamine as a catalytic donor to a sulfonium salt (EDA complex), which upon illumination, generates an aryl radical precursor for the syntheses of alkyl-arenes and cyano-arenes (Scheme 2B). The one reason for choosing TPAs as catalytic donors over alkyl or aryl-alkylamines is connected to the known reactivity of the latter in ET reactions, where upon abstraction of one electron and fast deprotonation of the α-CH carbon, α-aminoalkyl radicals are promptly formed, acting in consequence as sacrificial donors instead of catalytic ones.

While the utilization of triphenylamines (TPAs) in EDA complexes with perfluoroalkylsulfones for the generation of R_F radicals has been investigated in recent studies[34] (Scheme 2A), the perfluoroalkylation of TPAs themselves through EDA complexes with R_F-I has not been previously proposed. Consequently, there exists a distinct need for a direct methodology that enabled the synthesis of perfluoroalkylated



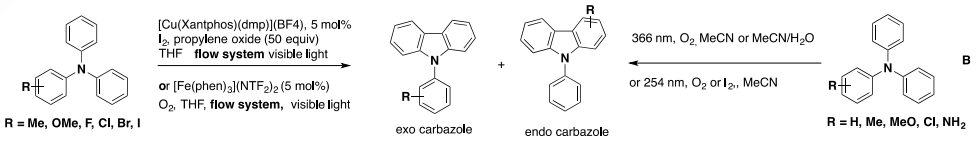
Scheme 2. Formation of an EDA complex with triarylamines

TPAs through visible light irradiation of an EDA complex, without the reliance on photocatalysts or additional additives.

On the other hand, *N*-phenylcarbazoles, which are the [6π]-electrocyclized products derived from TPAs, belong to the class of π-excessive nitrogen-containing aromatic heterocycles. These substances are particularly noteworthy due to their widespread presence in pharmaceuticals, diverse natural products, bioactive molecules, and materials science.[36]

The synthesis of 9-phenylcarbazole derivatives via direct cyclization of triphenylamines (TPAs) can be achieved through several different approaches. Photocatalytic methods (as shown in Scheme 3A, left)[37], direct UV-irradiation protocols (Scheme 3B, right)[38], and electrochemical techniques[39] are among the available strategies.[40] In the photocatalytic methods, complexes of copper (e.g., Cu(Xantphos)(dmp) and propylene oxide) or iron (e.g., $Fe(phen)_3(NTf_2)_2/O_2$) serve as photocatalysts under visible light irradiation.[37] These reactions often require extended reaction times, typically exceeding 20 hours, even when performed under flow conditions. If conducted under batch conditions, the conversion to products may take several weeks. Recent advancements in photocatalytic methods have also employed an iridium photocatalyst for the synthesis of carbazoles from diphenylamines.[41]

On the other hand, the direct irradiation of triphenylamines (TPAs) for the synthesis of 9-phenylcarbazoles under UV light (at wavelengths of 254 nm, 315 nm, or 366 nm, as depicted in Scheme 3B)[38] offers an alternative in terms of reaction times and product yields. However, the use of low-intensity light sources like 254 nm may raise environmental concerns, and the excited state behavior of TPA can deactivate through various channels other than photocyclization through the known triplet manifold.[38,40]



Scheme 3. Cyclization of TPAs. A: photocatalytic method under flow system. B: direct irradiation methods

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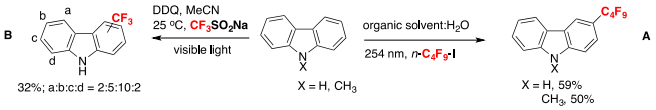


Scheme 4. A: Direct irradiation of *n*-C_4F_9-I for the perfluorobutylation of carbazole derivatives. B: Photocatalyzed (DDQ)-trifluoromethylation of carbazole with Langlois reagent

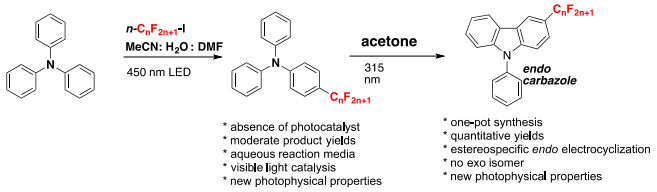
While perfluoroalkylated carbazoles have been synthesized through coupling reactions of carbazoles or carbazole precursors with perfluoroalkylated aryl rings,[42] direct perfluoroalkylation of the carbazole nucleus remains relatively unexplored. One approach for direct or late-stage perfluoroalkylation of carbazoles involves low-intensity UV irradiation in an aqueous medium, utilizing photolysis of C_4F_9-I (as illustrated in Scheme 4A, right).[43] However, this method necessitates a large excess of C_4F_9-I and employs potentially harmful low-intensity UV illumination. Another strategy utilizes a combination of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), visible light photocatalysis, and the Langlois reagent for the trifluoromethylation of carbazole. Although this approach is characterized by low yield and limited regioselectivity (Scheme 4B, left),[44] it represents an avenue for exploration in the field.

To our knowledge, there are no existing reports on the direct-, photocatalyzed-, or sensitizer-induced [6π]-electrocyclization of perfluoroalkylated triphenylamines (R_F-TPAs) for the synthesis of perfluoroalkyl-substituted carbazoles (R_F-Cbz).

The direct irradiation (at wavelengths of 254 nm or 366 nm) of TPAs towards [6π]-electrocyclization has only been successful with electron-rich and electron-neutral substituents. This is because strong electron-attracting groups on the phenyl rings promote the formation of charge transfer complexes (CTCs), which compete with the reactive triplet manifold responsible for cyclization in the direct irradiation events.[38a,45] The lack of photochemical reactivity observed in electron-poor-substituted TPAs towards [6π]-electrocyclization is attributed to the strong stabilization of these CTCs by polar solvents like methanol and acetonitrile. These CTCs are formed between the ArN− moiety and electron-withdrawing groups such as CHO, COMe, and NO_2.[38a,45] On the other hand, the visible light-photocatalyzed electrocyclization of substituted TPAs has only been achieved with electron-rich or electron-neutral substituents.[37,38a] This limitation arises from the stability of the radical cation intermediates proposed in visible light-photocatalyzed processes.[37,46]

Regarding electrocyclization through energy transfer processes (sensitized protocols) the electrocyclizations of diaryl amines towards carbazoles have recently been reported employing 4CzIPN[47] and $Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$ as catalysts.[48] These photocatalysts transfer their triplet energy to the amines ensuing photocyclization directly from the triplet manifold.

Our results will show the utilization of an EDA-complex methodology for the perfluoroalkylation of triphenylamines (TPAs), wherein TPAs function as acceptors of the resulting R_F radicals generated through blue LEDs-irradiation of R_F-I: TMEDA complex in an aqueous solvent mixture. These synthesized R_F-TPAs serve as valuable substrates for the acetone-sensitized [6π]-electrocyclization, enabling the synthesis of perfluoroalkyl-substituted *endo*-carbazoles (R_F-Cbz) under 315 nm-irradiation in excellent yields and chemoselectivity. The study also



Scheme 5. This work

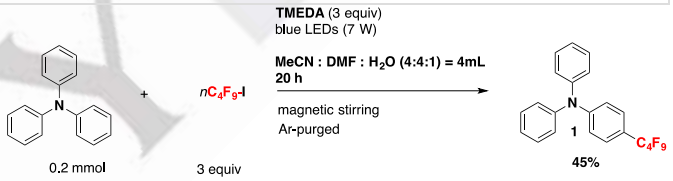
encompasses mechanistic investigations into the reactions and explores the photophysical properties of these newly synthesized R_F-TPAs and R_F-Cbz. The proposed methodology is illustrated in Scheme 5.

Results and Discussion

Synthetic Studies for R_F-TPA.

We undertook a study of optimization of the reaction conditions, according to Table 1, employing TPA and *n*-C_4F_9-I as source of perfluoroalkyl radicals.

Table 1. Screening of reactions conditions. Effects of photocatalysts, bases/additives, solvents on mono-substituted product formation



Entry	Change from standard reaction conditions	Yield 1 (%)[a]
1	No change in above reactions conditions	45
2	Without TMEDA	3
3	Without light	0
4	Eosin Y (3 mol%), Green LEDs	35
5	Eosin Y (3 mol%), Green LEDs, under O_2	30
6	Eosin Y (3 mol%), Green LEDs, under air	28
7	MeCN: DMF (1:1), Eosin Y (3 mol%), Green LEDs	21
8	MeCN, Eosin Y (3 mol%), Green LEDs	26
9	Rose Bengal (5 mol%), green LEDs	25
10	Eosin Y (3 mol%), Green LEDs, 36 h	61[b]
11	$[Ru(bpy)_3]^{2+}2Cl^-$ (5 mol%), blue LEDs	41
12	Cs_2CO_3 (3 equiv), Eosin Y (3 mol%), green LEDs	36

[a]Yields determined by HPLC analyses. [b] Total conversion was 92%. The ratio of TPA mono-C_4F_9-substituted: di- C_4F_9-substituted: tri- C_4F_9-substituted is 66:12:22.

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The reaction of TPA (0.2 mmol) in the presence of *n*-C_4F_9-I (3 equiv.) and *N,N,N`,N`*-tetramethylethylenediamine (TMEDA, 3 equiv.) under blue LEDs irradiation in a mixture of Ar-saturated MeCN: DMF: H_2O (4:4:1) for 20 h led to 45 % yield of *N,N*-diphenyl-4-(nonafluorobutyl)aniline **1** (Table 1, entry 1) and 50% of unreacted TPA. When the reaction is carried out in the absence of TMEDA, under blue LEDs irradiation, the yield of product **1** is very low (entry 2, Table 1). Employing Eosin Y as photocatalyst under green LEDs irradiation, the yield of product **1** drops to 35% (entry 3, Table 1). The presence of oxygen or air is deleterious to the reaction (entries 5 and 6, Table 1). When the reaction is carried out in the absence of water the yields of **1** are also lower (entries 7 and 8, Table 1).

Employing Rose Bengal as photocatalyst, under green LEDs irradiation, a 25% yield of **1** is obtained (entry 9, Table 1). The use of $Ru(bpy)_3^{2+}$ as photocatalyst under blue LEDs irradiation, provided a 41% yield of **1** (entry 11, Table 1). Under prolonged reaction times, full conversion of TPA is obtained (92%) under Eosin Y-photocatalysis, albeit with poor chemoselectivity, obtaining a mixture of mono-, di-, and trisubstituted TPAs in a 66 : 12 : 22 ratio which could not be fully separated (entry 10, Table 1). Replacing TMEDA for Cs_2CO_3, lower yields of product **1** are obtained, and di- and trisubstitution is observed even under shorter reaction times (entry 12, Table 1). As observed from Table 1, excluding water from the solvent mixture, prolonging the reaction times or the use of Cs_2CO_3 as additive (entries 7, 8, 10 and 12, respectively) have detrimental effects on the yields and chemoselectivity of the reaction. Also, the use of photocatalysts do not increase the yield of the monosubstitution **1** product substantially (entries 4, 9, and 11, Table 1), which confirms that the excitation of an EDA complex can induce formation of C_4F_9 radicals ensuing substitution very chemoselectively. Therefore, in order to obtain the best chemoselective conditions towards monosubstitution, reaction conditions as depicted in Table 1, entry 1 will be applied.

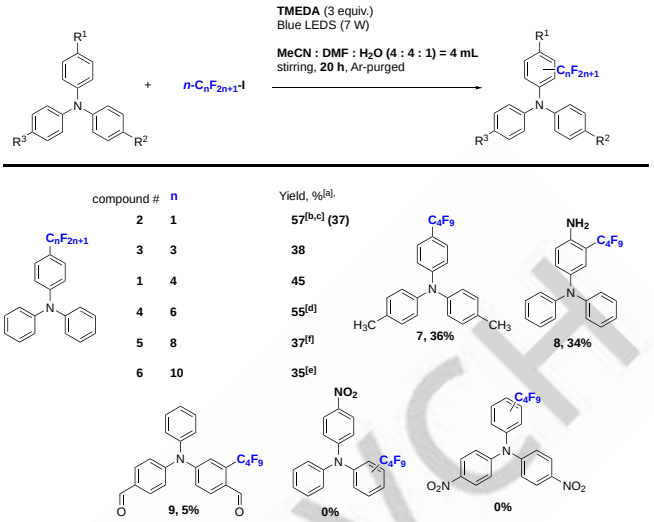
With the best reaction conditions in our hands, we set up to study the perfluoroalkylation of TPA and derivatives, according to Table 2.

The reaction of TPA (0.2 mmol) in the presence of I-C_nF_{2n+1} (3 equiv., n = 3, 4, 6, 8, 10) and TMEDA (3 equiv.) under blue LEDs irradiation in a mixture of MeCN: DMF: H_2O (4:4:1) led to products **1, 3 - 6** in 35-55 % yield range (Table 2). The trifluoromethylation of TPA was carried out with the Langlois reagent instead, due to the unavailability of CF_3-I reagent. A mixture of mono-, di-, and trisubstituted CF_3-TPA was obtained in 57 % global yield, with a ratio of mono : di : tri CF_3-substitued TPA being 66 : 16 : 16, respectively. We attempted to improve the chemoselectivity of the radical trifluoromethylation reaction of TPA towards the monosubstitution by varying the reaction conditions (reaction time and stoichiometry). However, the attempts were unsuccessful due to the high reactivity of the trifluoromethyl radical. The yield of monosubstituted compound **2** (*N,N*-diphenyl-4-(trifluoromethyl)aniline) was 37%.

The heptafluoropropylation of TPA rendered 38 % yield of product **3** (Table 2).

The perfluorobutylation of TPA rendered product **1** in 45 % yield whereas the perfluorohexylation afforded product **4** in 55% yield. The perfluorooctylation and perfluorodecylation of TPA gave products **5** and **6**, in 37 and 35% yields, respectively. The low product yields for **5** and **6** can be attributed to the poor solubility of reagents C_8F_{17}-I and $C_{10}F_{21}$-I in the reaction mixtures (Table 2).

Table 2. Scope of the photoinduced fluoroalkylation reaction of TPAs



[a]Yields determined by HPLC analysis. [b]Ratio of mono-, di- and tri-CF_3-substituted 68 : 16 : 16. [c]The reaction was realized by a different method: Blue LEDs (7 W), (0.2 mmol) TPA, (0.6 mmol) Langlois Reagent (CF_3SO_2Na) (3 equiv.), (Ir[dF(CF_3)ppy)]$_2$(dtbpy))PF_6 (1 mol%), $K_2S_2O_8$ (1 equiv.), MeCN:DMF (1:1), 20 h, under Ar atmosphere. [d] Reaction was realized with $C_6F_{13}I$ (7 eq.), TMEDA (7 eq.) and reaction time of 48 h. [e]The reaction was realized with *tetra-n*-butylammonium iodide (3 eq.) and the mixture was heated up to 35 °C.

The perfluorobutylation of 4-methyl-*N*-phenyl-*N*-(*p*-tolyl)aniline yielded product **7** in 36% yield. In 4-aminophenyl-diphenylamine, substitution took place in the more activated (electro-rich) ring, *ortho* to the amino group, rendering N^1,N^1-diphenyl-3-(perfluorobutyl)benzene-1,4-diamine **8** in 34% yield. This substitution pattern is observed in *p*-substituted aniline derivatives.[49] 4,4'-(Phenylazanediyl)dibenzaldehyde afforded perfluorobutylated product **9** in low yield, 5%. Product **9** has a peculiar substitution pattern, in which the perfluorobutyl moiety is attached *ortho* to the CHO group (see Figure S9, ESI for details). Mononitro- and dinitro-substituted TPA did not afford substitution products, consistent with the poor electron availability of the aryl rings and the high electrophilicity of the R_F radical.

The presence of the EDA complex TMEDA-C_4F_9-I has been investigated and informed before by Liu, Chen, Yu and colleagues.[50a,b] They found an association constant of $K_{TMEDA\text{-}C4F9\text{-}I\ binding}$ = 1.45 M^{-1} in $CDCl_3$ at 298 K. We conducted the titration experiment (Section 15, Table S3, Figures S11c, S12A, ESI) in CD_3CN, and found a $K`_{TMEDA\text{-}C4F9\text{-}I\ binding}$ = 8.00 M^{-1} at 298 K. Also, UV experiments confirmed the presence of an EDA complex between R_F-I and TMEDA in the mixture of solvents CH_3CN: DMF : H_2O = 4 : 4 : 1. This shows that the complex TMEDA-C_4F_9-I is a good candidate for generating C_4F_9 radicals upon blue LEDs-irradiation in our solvent system.

We also inspected the possibility for the formation of an EDA complex between TPA and R_F-I. Through Stern Volmer experiments, the fluorescence of TPA in MeCN is quenched upon addition of C_4F_9-I (Section 13, Figure S8a, ESI). A Stern Volmer rate constant of 68 M^{-1} is calculated. Through fluorescence quenching experiments (ESI) and by plotting log ((Io-I)/I)) *versus* log [C_4F_9-I] (*Hill* equation, being Io the fluorescence intensity of TPA without C_4F_9-I, and I the fluorescence of TPA in the presence of C_4F_9-I, Figure S10a Sections 14, ESI) a binding rate constant

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K_b =10 M^{-1} is obtained. Also UV-visible studies in CH_3CN: DMF : H_2O = 4 : 4 : 1 solvent system showed that there is an association complex between C_4F_9-I and TPA which seems to be of even higher absorbance than that of TMEDA-C_4F_9-I complex (section 16, Figures S12B,C, ESI); however, this complexation (i.e.: TPA-C_4F_9-I) is not as efficient in producing R_F radicals compared to that of TMEDA and R_F-I, as observed when blue LED-irradiation takes place in the absence of TMEDA (entry 2, Table 1). Also, through a ^{19}F NMR titration experiment of *n*-C_4F_9-I with TPA (Section 15, Figure S11a, ESI) no upfield shifts are observed in the I-**CF_2**-C_3F_7 ^{19}F resonance signals with increments of TPA concentration, purporting that no weakening of the C-I bond of *n*-C_4F_9-I is taking place through a halogen bonding interaction (*cf.* Figures S11a and S11c).

Photophysical Properties of R_F-TPA.

We next examined the photophysical properties of perfluoroalkylated TPAs (R_F-TPA), and the photophysical parameters measured in acetonitrile are illustrated in Table 3.

Table 3. Spectroscopic Data and Energies (ΔE) of Perfluoroalkylated Triphenylamines in Acetonitrile at 298 K[a]

Product	λ_{abs}^M (nm)	λ_f^M (nm)	$\Delta\upsilon^b$ (cm^{-1})	$\lambda^{(0,0)}$ (nm)	$\Delta E^{(0,0)}$ (eV)	λ_f^{ctc} (nm)	$\Delta\upsilon_{(CTC)}^c$ (cm^{-1})	$\Delta E_{(CTC)}^c$ (eV)	Φ_f^e
TPA	298	349	4904	330	3.76	-	-	-	0.050
2	296	-[d]	-	345	3.59	402	8908	3.08	0.186
3	297	-[d]	-	350	3.59	402	8794	3.08	0.024
1	297	-[d]	-	350	3.54	409	9220	3.03	0.035
4	297	-[d]	-	351	3.53	414	9515	2.99	0.051
5	297	-[d]	-	351	3.53	408	9160	3.04	0.058
6	298	-[d]	-	348	3.56	413	9457	3.00	0.048

[a]The concentration of the substrates was 5.0 × 10^{-5} mol dm^{-3}. [b]Calculated as follows: $\Delta v = 10^7[1/\lambda_{abs} - 1/\lambda_{fluo}]$ cm^{-1}. [c] CTC = charge transfer complex. [d]The emission of a Charge Transfer is observed instead, see column 7. [e]Actinometer: Triphenylamine (TPA).[45a] λ_{abs}^M: maximum wavelength of absorption; λ_f^M: maximum wavelength of fluorescence emission; $\Delta\upsilon$: Stokes shift; $\lambda^{(0,0)}$: wavelength of overlap absorption and emission; ΔE: energy of singlet excited state; λ_f^{CTC}: maximum wavelength of emission of Charge Transfer Complex; $\Delta\upsilon^{CTC}$: Stokes shift of Charge Transfer Complex; ΔE: energy of Charge Transfer Complex; [e] ϕ_f: quantum yield of fluorescence.

While the absorption maxima for all R_F-TPA are similar to that of TPA, for all R_F-substituted TPAs the emission maxima are quite red-shifted in MeCN as solvent with regards to TPA (spectra illustrated in ESI, Sections 3 - 5). These emission spectra correspond to the Charge Transfer Complexes (CTCs) instead of the emission of the amine fluorophores themselves, as revealed by the large Stoke shifts (column 8) compared to that of TPA (column 4, entry 1, Table 3). Figure 1 shows the UV-visible absorption spectra and the fluorescent emission spectra of perfluorobutylated triphenylamine **1** and unsubstituted TPA recorded in acetonitrile at 298 K where the emission spectrum of **1** was assigned to the corresponding CTCs in the excited state. This tendency (i.e.: formation of CTC) had already been noted in previous studies for TPAs substituted with electron-withdrawing groups such as NO_2, or CHO,[38a,45] where large Stokes shifts are observed, and the fluorescence emissions are assigned to the respective CTCs. These CTCs entities are formed in the excited state between the Ph_2N- moiety and the *p*-nitrophenyl or *p*-formylphenyl groups, respectively, which are strongly stabilized by the polar acetonitrile solvent.

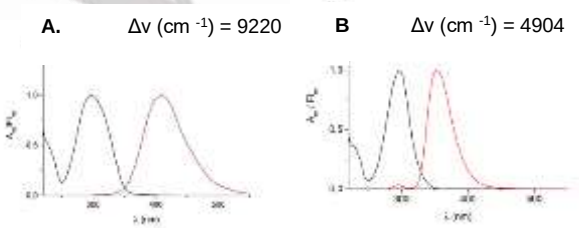

Figure 1. UV-visible absorption spectra (black line) and fluorescence emission spectra (red line) of: (**A**) perfluorobutyl triphenylamine **1** and (**B**) triphenylamine recorded in acetonitrile at 298 K under Ar atmosphere.

In the case of our R_F-TPAs, their fluorescence emissions are attributed to the respective CTCs which are formed by the electron-withdrawing inductive effect of the R_F substituents in the excited state that confer some charge separation. These CTC emissions are more prominent in polar solvents such as MeCN. We determined the spectroscopic data and energies (ΔE) of perfluoroalkylated triphenylamines, R_F-TPAs in other solvents as well, such as methanol, ethyl ether and cyclohexane (ESI, Table S1, Figures S2-S4). In non-polar cyclohexane, we did not find these CTCs, and the fluorescence spectra observed were attributed to the emissions of the excited amine themselves, whereas in ethyl ether, the contribution of the CTC to the fluorescence is becoming noticeable. In polar methanol, however, the emissions are ascribed to those of the CTCs.

Quantum yields of fluorescence ϕ were measured for all the series of R_F-TPAs in acetonitrile using triphenylamine as the actinometer,[45a] and are also collected in Table 3. All fluorescence quantum yields are similar to that of TPA, except for TPA substituted with CF_3 group, which shows a one-fold increment, with a value of ϕ = 0.186. Measurements of quantum yield of fluorescence were also carried out for all the compounds in ethyl ether, cyclohexane and methanol, respectively, and the data are collected in Table S1 (see SI, Section 6).

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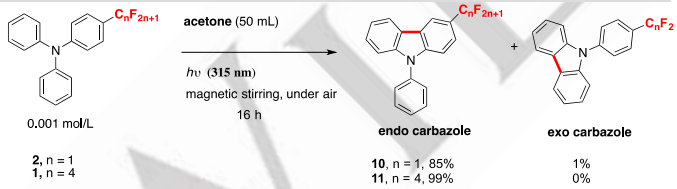
Synthetic Studies for R_F-CBz.

Perfluoroalkylated carbazoles have been synthesized in the past by indirect strategies (*vide supra*) and direct methodologies, such as illustrated in Scheme 4, with DDQ as photocatalyst and direct irradiation (254 nm) of an aqueous solution of C_4F_9-I and carbazole derivatives.[43,44] We attempted the perfluoroalkylation of 9-phenylcarbazole (9-phenylCBz) by the EDA complex TMEDA: C_4F_9-I under blue LEDs irradiation (see ESI, Sections 17). However, no perfluoroalkylated product was obtained and the substrate was recovered intact. We also attempted the Eosin Y-photocatalyzed reaction of 9-phenylCBz with *n*-C_4F_9-I (ESI, Section 18). However, after 20 h-reaction no perfluorobutylated carbazole product was obtained, and the carbazole was recovered unreacted.

Having failed in the perfluororalkylation reaction of 9-phenylCBz either with the EDA complex or with Eosin Y as photocatalyst, we proceeded to attempt the [6π]-electrocyclization of the perfluoroalkylated TPAs (i.e.: R_F-TPA) in order to obtain the perfluoroalkylated carbazole derivatives.[40] A series of optimization reactions were carried out by direct irradiation, such as those illustrated in Table 4.

The irradiation of an acetone solution of *N,N*-diphenyl-4-(perfluorobutyl)aniline **1** (10^{-3} mol·dm^{-3}) with light of 315 nm leads to 9-phenyl-3-(perfluorobutyl)-9*H*-carbazole **11** in quantitative yield (*endo* carbazole, entry 1, Table 4). No *exo* isomer (i.e.: 9-(4-(perfluorobutyl)phenyl)-9*H*-carbazole) was obtained. The reaction under 366 nm irradiation in acetone under prolonged reaction time led to 50% yield of **11** (*endo* isomer, entry 2, Table 4). The direct irradiation of **1** in methanol, either at 366, 315, or 254 nm (entries 3-5, Table 4) did not provide the expected *exo*/*endo* carbazole regioisomers while decomposition products were formed instead. The reaction of *N,N*-diphenyl-4-(trifluoromethyl)aniline **2** in acetone (7 h) at 315 nm provided product **10** in 85% yield (*endo* isomer), while the *exo* isomer could be detected in 1 % yield (entry 6, Table 4). *N,N*-diphenyl-4-(trifluoromethyl)aniline **2** was also irradiated at 366 nm in acetone (15 h), affording 58% of the *endo* isomer **10** and 5% of the *exo* carbazole (entry 7, Table 4). Direct irradiation of **2** in methanol (9 h), at 366 nm provided lower yields of carbazoles (entry 8, Table 4).

Table 4. Optimization of reaction conditions for the [6π]-electrocyclization of perfluoroalkyl-substituted TPA.



Entry	substrate	Change from standard reaction conditions	Yield (%)[a]	*endo* (%)[a]	*exo* (%)[a]
1	1	No change in above reaction conditions	99	99	0
2	1	366 nm, 54 h	50	50	0
3	1	MeOH, 366 nm, 24 h	-[b]	-	-
4	1	MeOH, 310 nm, 20 h	-[b]	-	-
5	1	MeOH, 254 nm, 5 h	-[b]	-	-
6	2	7 h	86	85	1
7	2	366 nm, 15 h	63	58	5
8	2	MeOH, 366 nm, 9 h	22	20	2

[a] Yield determined by HPLC analyses. [b] Decomposition products were obtained where the C_4F_9 chain was not intact. These products were not identified.

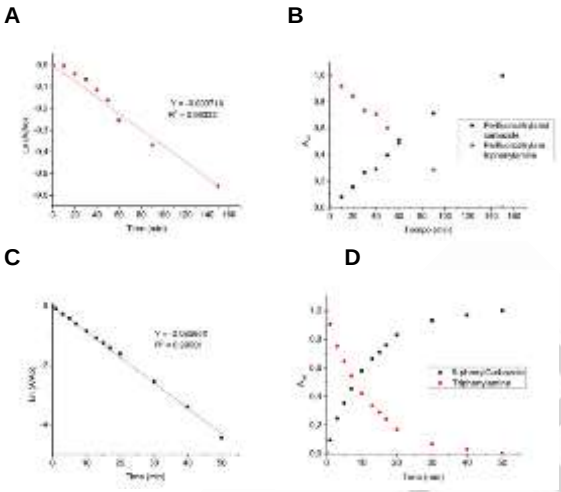


Figure 2. **A**. Calculation of the first-order rate constant (k_{obs} / min^{-1}) and **B** relative kinetic profile for the [6π]-electrocyclization in acetone of compound **1** (50 μM) under 310 nm irradiation to carbazole **11**. **C.** Calculation of the first-order rate constant (k_{obs} / min^{-1}) and **D** relative kinetic profile for the [6π]-electrocyclization in acetone of triphenylamine (50 μM) under 310 nm irradiation to 9-phenylcarbazole.

A kinetic profile of the [6π]-electrocyclization reaction of substrate **1** in acetone at 310 nm irradiation is compared with the [6π]-electrocyclization reaction of unsubstituted TPA in acetone and illustrated in Figure 2.

Compound **1** electrocyclizes to carbazole derivative **11** with a rate constant 0.22 s^{-1} compared to the cyclization of TPA to 9-phenylcarbazole, with a rate constant 5.1 s^{-1}, purporting that although the yields of both substituted and unsubstituted carbazoles are quantitative at 315 nm, there is a significant difference in cyclization rates.

We next decided to apply conditions reported in Table 4 (entry 1) to a series of monoperfluoroalkylated triphenylamines (**1** – **7**; for structures see Table 2) to obtain the respective carbazoles by the acetone-sensitized [6π]-electrocyclization reaction and the results thus obtained are collected in Table 5.

Triphenylamines **1 - 6** monosubstituted with perfluoroalkyl groups (C_nF_{2n+1}, n = 1, 3, 4, 6, 8, 10) electrocyclize in a most stereospecific fashion affording the respective *endo* carbazoles **10** - **15** in 85-99% yields. Particularly interesting is the case of TPA **7** (i.e.: 4-methyl-*N*-(*p*-tolyl)-*N*-(4-(trifluoromethyl)phenyl)aniline), which cyclizes to carbazole **16** exclusively. This is particularly noteworthy, since methyl-, chloro-, amino- and methoxy-substituted TPAs[38a,45] electrocyclize to the *exo* and *endo* carbazole derivatives respectively when direct irradiations are carried out in MeCN, MeOH, cyclohexane and ethyl ether, either at 254, 315, or 366 nm light. Furthermore, the reported *photocatalyzed* (by Cu, Fe complexes or other photocatalysts) -cyclization of substituted triphenylamines leads to a mixture of *endo* and *exo* carbazoles.[37] We are currently studying the preference of our perfluoroalkyl-substituted TPAs to electrocyclize to the *endo* regioisomer selectively through sensitization in acetone.

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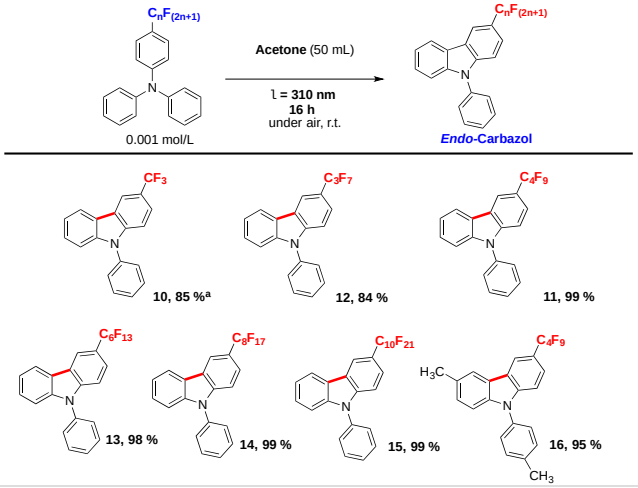
Table 5. Syntheses of perfluoroalkylated carbazoles upon direct irradiation (315 nm) of perfluoroalkylated triphenylamines under air atmosphere.



[a]The reaction time was 7 h.

Noteworthy, unlike TPAs bearing electron withdrawing groups such as NO_2 or CHO which were shown not to electrocyclize to carbazoles,[38a,45] our electron-withdrawing perfluoroalkyl-substituted TPAs **1 - 7**, show a very efficient photochemical [6π]-electrocyclization pathway. The inability of NO_2 or CHO -substituted TPAs to electrocyclize to carbazole derivatives was attributed to the formation of charge transfer complexes (CTCs), stabilized by resonance effects from the electron-withdrawing groups.[38a,45] These complexes show strong fluorescence emissions which depopulate the reactive triplet manifold responsible for [6π]-electrocyclization. Although our R_F-TPAs do also show CTC in polar solvents (MeCN, MeOH, and ethyl ether, see Table 3 and Table S1, Figures S4, ESI), no fluorescence emission is observed in acetone as a consequence of highly efficient triplet energy transfer from excited acetone to R_F-TPAs. Then, *endo* cyclization pathway proceeds efficiently from triplet excited state of R_F-TPAs (^3R_F-TPAs*) leading to the formation of the corresponding perfluoroalkyl-substituted carbazole (R_F-CBz).

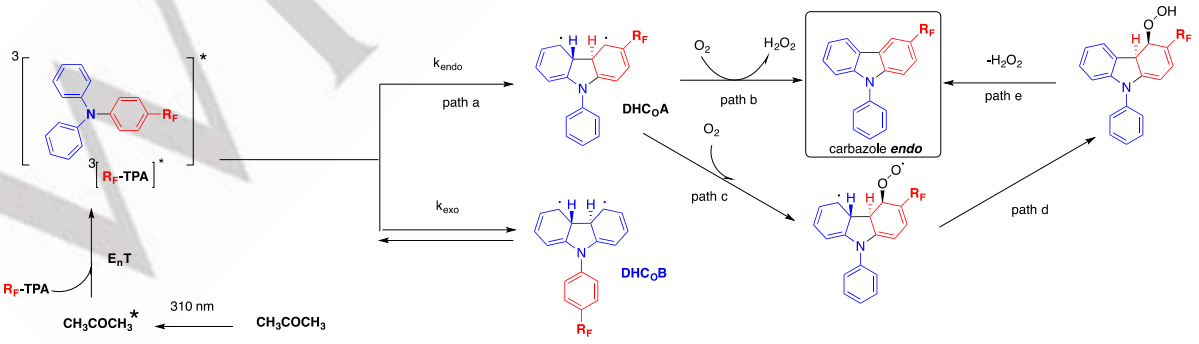
It is noteworthy the high chemoselectivity and efficiency by which this electrocyclization process can be carried out in acetone by irradiation at 315 nm, since, as pointed out before, only the *endo*-perfluoroalkyl-substituted carbazoles are formed.

A possible reaction pathway for the photosensitized [6π]-electrocyclization of R_F-TPAs by acetone is depicted in Scheme 6.

The presence of excited triplet ^3R_F-TPA* is irrevocably confirmed by the sensitization in acetone. In the proposed mechanism, excitation of acetone at 310 nm renders triplet acetone after fast and efficient intersystem crossing from the singlet excited state (E_T = 332 kJ·mol^{-1}, ϕ_{ISC} = 0.95, τ =47 μs[51]) which transfers its triplet energy efficiently to R_F-TPA assuming that the triplet energy of R_F-TPA is similar to that of TPA (295 kJ·mol^{-1} in MeOH)[38a] and giving a triplet energy gap (ΔE_T) of -37 kJ·mol^{-1} suggesting that the triplet energy transfer pathway is thermodynamically feasible. Triplet ^3R_F-TFA* electrocyclizes to diradical dihydrocarbazole intermediate DHCoA (*path a*, Scheme 6). DHCoA either reacts with dissolved oxygen by *path b* to render the *endo* R_F-CBz, or through *path c* to give the radical peroxyl intermediate, which rearranges to hydroperoxyl intermediate through *path d* that in turn, along *path e*, H_2O_2 loss renders the *endo* carbazole. The *exo* cyclization pathway would render intermediate DHCoB. Dihydro diradical intermediates (like DHCoA and DHCoB) have been proposed before and studied through Laser Flash Photolysis.[52] We surmised that DHCoB intermediate is disfavored, and back electrocyclization process from this intermediate is probably taking place furnishing the R_F-TPA in its ground state as a favorite deactivation pathway. We are currently studying the preference of the [6π]-electrocyclization pathway to proceed through one intermediate.

Photophysical Properties of R_F-CBz.

The photophysical properties of perfluoroalkyl carbazoles (R_F-CBz; **10** – **15**) were also examined and the photophysical parameters measured in acetonitrile at 298 K under inert atmosphere are collected in Table 6.



Scheme 6. Proposed reaction mechanism

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Table 6. Photophysical Properties of perfluoroalkylated Carbazoles Recorded in acetonitrile at 298 K.[a]

entry	Substrate	λ^{M}_{abs} (nm)	λ^{M}_{f} (nm)	$\Delta\upsilon$ (cm^{-1})[b]	$\lambda^{(0,0)}$ (nm)	$\Delta E^{(0,0)}$ (eV)	Φf[c]
1	**9-Phenylcarbazole**	339	341	147	340	3.64	0.104
2	**10**	338	353	1257	341	3.64	0.071
3	**12**	338	353	1257	341	3.64	0.071
4	**11**	338	353	1257	341	3.64	0.075
5	**13**	338	352	1177	341	3.64	0.067
6	**14**	338	353	1257	341	3.64	0.070
7	**15**	339	354	1250	341	3.64	0.081

[a]The concentration of the substrates was 5.0×10^{-5} mol dm^{-3}. [b]Calculated as follows: $\Delta v = 10^7[1/\lambda_{abs} - 1/\lambda_{fluo}]$ cm^{-1}. [c]Actinometer: 9-phenylcarbazole.[51b] λ_{abs}^{M}: maximum wavelength of absorption; λ_f^{M}: maximum wavelength of fluorescence emission; $\Delta\upsilon$: Stokes shift; $\lambda^{(0,0)}$: wavelength of overlap absorption and emission; $\Delta E^{(0,0)}$: energy of singlet excited state; ϕ_f: quantum yield of fluorescence.

As is apparent from Table 6, no perfluoroalkyl-substituent effect was observed on the lowest absorption bands of R_F-CBz **10** – **15** when compared to that of 9-phenylcarbazole (λ^{M}_{abs}), showing a $\Delta\lambda$ = -1 nm. This spectroscopic behavior was attributed to an electron-withdrawing inductive effect of the perfluoroalkyl groups (CF_3 and C_nF_{2n+1}) on the 9-phenylcarbazole moiety. However, the maximum fluorescence emission wavelength (λ^{M}_{F}) of R_F-CBz was found to depend on the nature of the perfluoroalkyl groups showing a $\Delta\lambda$ average value of +12 nm when compared to 9-phenylcarbazole.

The fluorescence emission spectra of perfluoroalkylated carbazoles are mirror images of the lowest absorption band (Figure 3) displaying Stokes shifts ($\Delta\nu$) between 1177 cm^{-1} and 1257 cm^{-1}. Furthermore, the $\lambda^{(0,0)}$ were also measured as the cross-point between the absorption and the fluorescence emission spectra and, from these data, the $\Delta E^{(0,0)}$ values were easily calculated and are also collected in Table 6. These data suggest that the π,π^* electronic transitions do not depend on the nature or the length of the C_nF_{2n+1} groups.

The fluorescence quantum yields (ϕ_f) of perfluoroalkylcarbazoles **10** – **15** were measured in acetonitrile under Ar atmosphere at 298 K using 9-phenylcarbazole as the actinometer[51b] and the data thus obtained are collected in Table 6. The ϕ_f values of compounds **10** – **15** are slightly lower than that of 9-phenylcarbazole concluding that the perfluoroalkyl groups do not quench efficiently the fluorescence emission of the carbazole moiety which is the fluorescent chromophore. Indeed, the ϕ_f values of the carbazoles **10** – **15** are *ca* 0.07 which are quite similar to that of 9-phenylcarbazole (ϕ_f: 0.10). Therefore, perfluoroalkyl carbazoles **10** – **15** are good and efficient fluorescent chromophores like 9-phenylcarbazole itself and that the nature as well as the length of the R_F chain do not affect the radiative deactivation of the singlet excited state.

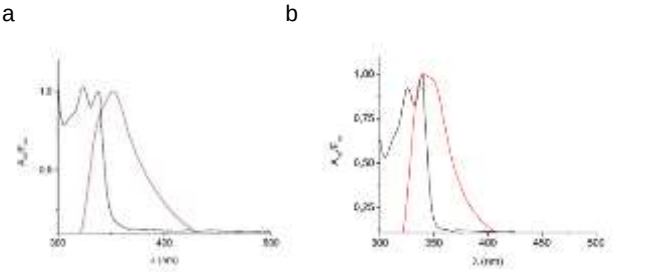

Figure 3. Normalized UV-visible absorption spectra (black line) and fluorescence emission spectra (red line) of: (**a**) perfluoroalkyl carbazole **12** and (**b**) 9-phenylcarbazole recorded in acetonitrile at 298 K under Ar atmosphere.

CONCLUSIONS

The chemoselective perfluoroalkylation of triphenylamines (TPAs) by visible light-irradiation of the EDA complexes formed between *N,N,N`,N`*-tetramethylethylenediamine (TMEDA) and perfluoroalkyl iodides (R_F-I) (i.e.: TMEDA: R_F-I) in an aqueous solvent mixture afforded highly regioselective perfluoroalkyl-mono-substituted TPAs, R_F-TPAs, in good to moderate yields. These R_F-TPAs were then subjected to acetone-sensitized [6π]-electrocyclization by irradiation at 310 nm affording the respective perfluoroalkyl-substituted *endo*-carbazoles, *endo*-R_F-CBZ, in excellent yields. It is to be noted that our EDA methodology for the syntheses of R_F-TPAs introduces new elements: i) a mild generation of the R_F radicals that effect monosubstitution of the TPA ring; ii) product yields that surpass those from photocatalytic techniques; iii) polysubstitution avoided (such as the case with Eosyn Y-photocatalyst, entry 10, Table 1); iv) and are carried out in an aqueous solvent mixture. Unlike the photocatalyzed (DDQ-photocatalyzed) perfluoroalkylation of carbazole which affords a low yielded-, poor-regioselective mixture of isomers,[44] the acetone-sensitized irradiation of R_F-TPAs surprisingly afforded very high/quantitative yields of the respective *endo*-carbazole derivatives R_F-CBz. This consequently becomes an optimum methodology to obtain *endo*-R_F-CBz derivatives. The high stereospecific cyclization reactions of R_F-TPAs towards the *endo* isomers is both intriguing and encouraging for establishing the acetone-sensitization methodology with other TPA substrates, such as those studied in previous reports.[38a,45]

Furthermore, we have thoroughly examined the formation of EDA complexes and binding constants utilizing methodologies such as nuclear magnetic resonance, ultraviolet spectroscopy, and fluorescence quenching. Photophysical properties of R_F-TPAs and R_F-CBz are studied. This comprehensive investigation offers valuable insights to aid readers in understanding the underlying mechanism.

Supporting Information

Supporting information is provided: Synthetic procedures and general experimental considerations. UV-visible and fluorescence spectra, kinetics plots, calculation of rate and association constants, and copies of ^{1}H, ^{19}F, and ^{13}C NMR spectra are provided. Additional references are given in this section.

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Keywords: EDA-complex • perfluoroalkylated triphenylamines • perfluoroalkylated carbazoles • [6π]-electrocyclization • spectroscopy data on carbazoles

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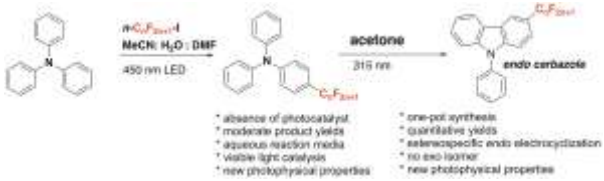

In this work, the chemoselective perfluoroalkylation of triarylamines (TAA) is accomplished by visible light activation of a halogen-bonding complex between TAA and perfluoroalkyl iodides R_F-I. The resulting perfluoroalkylated triarylamines, TAA-R_F, undergo stereospecific unprecedented 6-π-electrocyclization under photosensitized reaction in acetone to *endo*-carbazoles exclusively in quantitative yields.

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