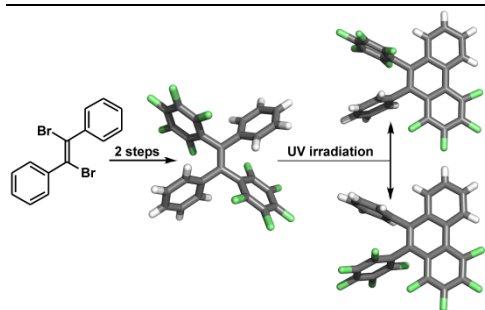# Synthesis and Photocyclization of Fluorinated Tetraphenylethylenes

Zhenglin Zhang, Thien Lieu, Xiqu Wang, Olafs Daugulis* and Ognjen Š. Miljanić*

Department of Chemistry, University of Houston, 3585 Cullen Boulevard #112, Houston, TX 77204-5003, USA.

Supporting Information Placeholder

ABSTRACT: Five extensively fluorinated tetraphenylethylene (TPE) derivatives have been synthesized using combinations of Cu-catalyzed C–H functionalization reactions and Stille couplings. Surprisingly, in contrast to the parent TPE, these compounds show little to no aggregation-induced emission (AIE). Instead, photocyclization into fluorinated phenanthrene products occurs. Effects of solvent and oxygen on the yield and selectivity of this photocyclization have been examined.

Tetraphenylethylene (**1**, TPE) is a classic example of a molecule exhibiting aggregation-induced emission (AIE)[1] and has been widely used to develop responsive fluorescent materials in physical, chemical, and biological settings.[2] Fluorination of functional organic molecules and materials has often been used to modulate their physical and chemical characteristics.[3] Partial fluorination of the TPE structural motif was reported to increase the fluorescence quantum yields in crystals[4a,b] in addition to simplifying the separation of isomers on account of strong dipole-dipole intermolecular interactions.[4c] Our work on fluorinated aromatic pyrazoles[5] suggested that the intra- and intermolecular interactions of fluorinated aromatic rings influence the molecules' AIE activity[6] and allow emission color switching in aggregates and the solid state.[7] The fluorinated TPEs studied thus far have been ornamented with one, two, or three fluorine atoms on their aromatic rings, and they maintained AIE behavior. In this Letter, we report the synthesis and extensive characterization of four new, more extensively fluorinated tetraphenylethylene derivatives **2**, **3a**, **3b**, and **3c** (Scheme 1), as well as a triarylated ethylene **4**. We also report on the investigation of their crystal structures and optical properties, as well as their photochemical cyclization.

Syntheses of **2**–**4** commenced with the known dibrominated precursors **A**–**D**.[8] The introduction of the first pentafluorophenyl group was achieved by the direct C–H functionalization of pentafluorobenzene under Cu-catalyzed conditions (Scheme 1). Re-

placement of the second bromine atom required the use of Stille coupling with either PhSnBu$_3$ in the case of **2**, or C$_6$F$_5$SnBu$_3$ in the case of **3a**–**c** and **4**. The two-step sequences provided compound **2** with a single fluorinated ring, and compound **3a**–**3c** with two fluorinated rings in three isomeric arrangements. Our attempts to produce the perfluorinated derivative of **1** failed, as one of the bromine atoms in **D** got reductively replaced with hydrogen—leading instead to the extensively fluorinated triarylated alkene **4**. Compounds **2**–**4** were obtained in moderate overall yields ranging from 23 to 49%,[9] and were characterized by ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy, FT-IR spectroscopy, mass spectrometry, and elementary analysis (details provided in the SI).

Diffraction-quality single crystals of compounds **3b**, **3c**, and **4** were obtained by slow evaporation of their solutions (1 mg mL^{-1}) in MeOH; a preliminary crystal structure of **3a** was also obtained, but the data was of insufficient quality to allow full refinement. Crystal structures of **3a**–**c** and **4** are shown in Figure 1. Noticeable is the significant twisting of aromatic rings in all four systems. This deplanarization effectively prevents face-to-face [π···π] stacking despite the presence of electronically complementary fluorinated and non-fluorinated aromatic motifs.

The prepared crystals of fluorinated compounds show solid-state fluorescence (Figure S40), with emission maxima at 450 (for compound **2**), 449 (**3a**), 428 (**3b**), 521 (**3c**), and 416 (**4**) nm. The blue shift of the emission maximum from **1** (452 nm) to **3b** (428 nm) to

4 (416 nm) can be rationalized by the increasing HOMO–LUMO gaps, which were calculated to be 95.6 kcal mol^{-1} for **1**,[10] 103.4 kcal mol^{-1} for **3b**, and 113.3 kcal mol^{-1} for **4**. The calculated HOMO–LUMO gap of **3a** (104.8 kcal mol^{-1}) is higher than in **3b**, but **3a** has a solid-state emission peak at a longer wavelength (449 nm) than **3b** (428 nm), implying intermolecular conjugation in the crystal of **3a**. This viewpoint is tentatively supported by **3a**'s preliminary crystal structure, which shows intermolecular slipped [π··· π] stacking (Figure S38). The HOMO–LUMO energy gap of **3c** (108.2 kcal mol^{-1}) is higher than those of **3a** and **3b** but shows a batochromically shifted solid-state emission maximum at 521 nm, which is also due to slipped intermolecular [π··· π] stacking (Figure S39).

Scheme 1. Syntheses of fluorinated TPE derivatives **2** and **3a**–**c**, and compound **4**.
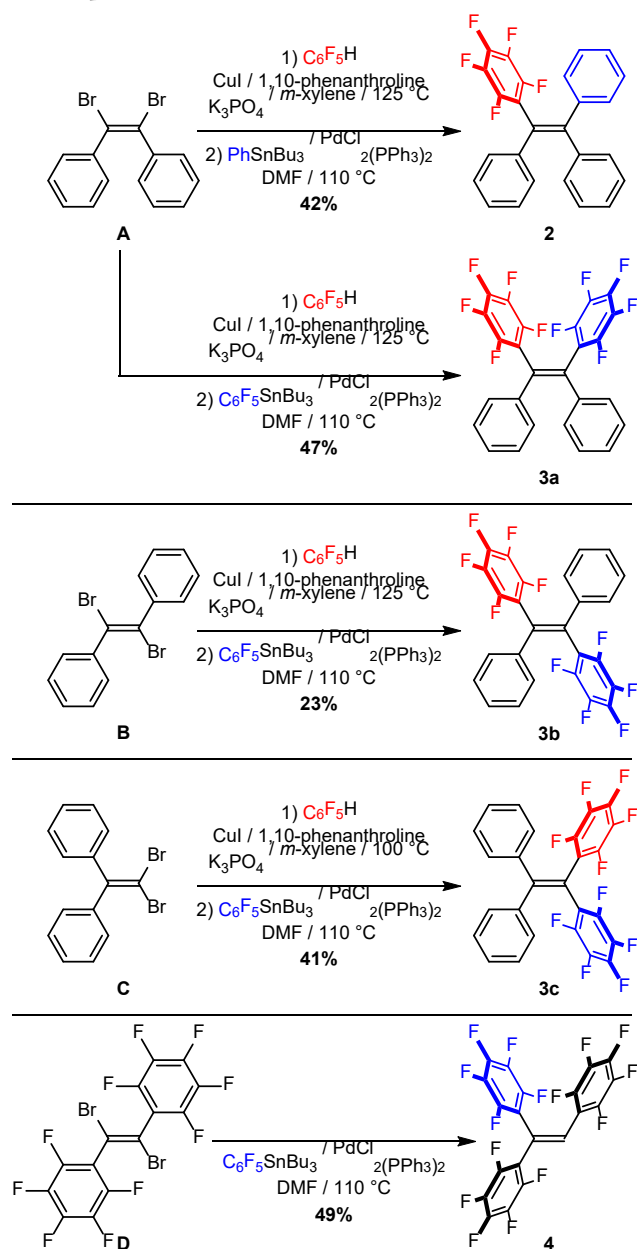
The solid-state fluorescence of crystals of **2**, **3a**–**c** and **4**, as well as their chemical similarity to **1** led us to expect that these new fluorinated TPEs should be AIE active. However, the intensity of their emission decreases under solvent conditions promoting aggregation (H$_2$O:THF=99.3:0.7, volume ratio) to only 20% (**2**), 43% (**3b**), and 31% (**4**) of the original emission intensity in pure THF solutions, respectively (Figure S41). Under the same aggregation-inducing solvent conditions, the emission intensity of **3c** increases by about 65% compared to that in pure THF solution. In contrast, the aggregation of **1** under the same conditions increases its emission 13.5 times. Further research on **3a** and **3b** indicates that UV irradiation increased and decreased emission intensity for samples in solution and aggregation, respectively (see Figure 2 and S45, and Table S8 and S9).
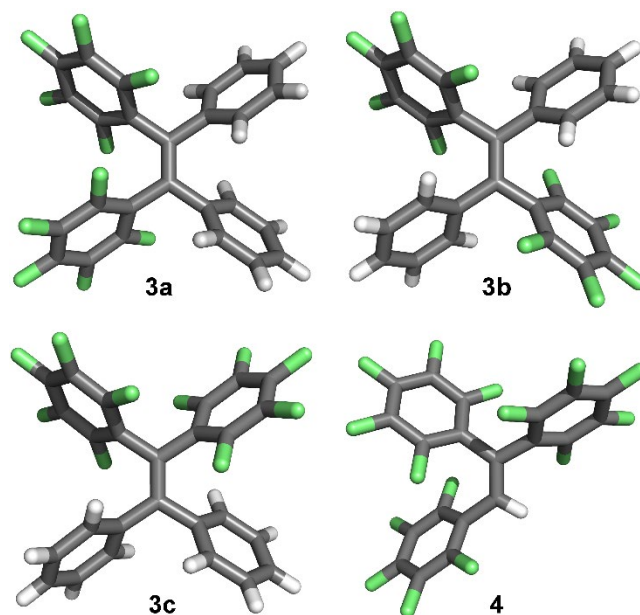

Figure 1. Crystal structures of **3a**–**c** and **4**. Element colors: C— gray, H—white, F—lime. Crystal structure of **3a** is preliminary and shown only to illustrate connectivity; only one of the eight and one of two asymmetric molecules in their unit cells are shown for **3a** and **4**, respectively.

Research on AIE mechanisms suggests that the aggregation of TPE derivatives can restrict the intramolecular rotations,[11a,b] vibrations,[11c] and Z/E isomerization along the central C=C bond,[4e,11d–f] which control the molecules' excited state decay via fluorescence. In our case, the mixed H$_2$O:THF (99.3:0.7) solvent indeed caused aggregation in all studied compounds, as indicated by the dynamic light scattering profiles which suggested aggregates of average sizes in the 135–165 nm range (Figure S42). Therefore, a nonradiative decay of the excited states of fluorinated TPE derivatives occurred, which cannot be prevented by aggregation.

During our UV/Vis absorption studies, we noticed that fluorinated TPEs are photosensitive in solution (Figure S43): the THF solutions of **2** and **3a** changed color from colorless to yellow upon UV irradiation. Further absorption spectroscopy revealed a new conjugation system with peaks between 302 and 306 nm forming upon irradiation of **2** and **3a**–**c** (illustrated for **3a** and **3b** in Figure 2; full details in Figure S44). NMR spectroscopy and crystallography

(vide infra and SI) conclusively demonstrated that the UV irradiation at 302 nm of THF solutions of **2** and **3a–c** generated phenanthrenes **5** and **6a–c** (Scheme 2) through either oxidative or redoxneutral photocyclizations. No photocyclization was observed in the case of **4**. Despite extensive experimentation, we were unable to obtain **5** in its pure form. Compounds **1–4** can be seen as derivatives of *cis*-stilbene, which is well-known to photocyclize into *trans*-4a,4b-dihydrophenanthrene under UV irradiation; rapid oxidation of this unstable intermediate produces phenanthrene.[12] The derivatives of *cis*-stilbene with leaving groups (X) such as F,[13a,b] Cl,[13c] Br,[13d] I,[13e] and OCH₃,[13f] photocyclize into phenanthrenes without an oxidant through the elimination of HX. A few papers also reported that 9,10-diphenylphenanthrenes were detected after the oxidative photocyclization of **1** and its derivatives.[14a–d]
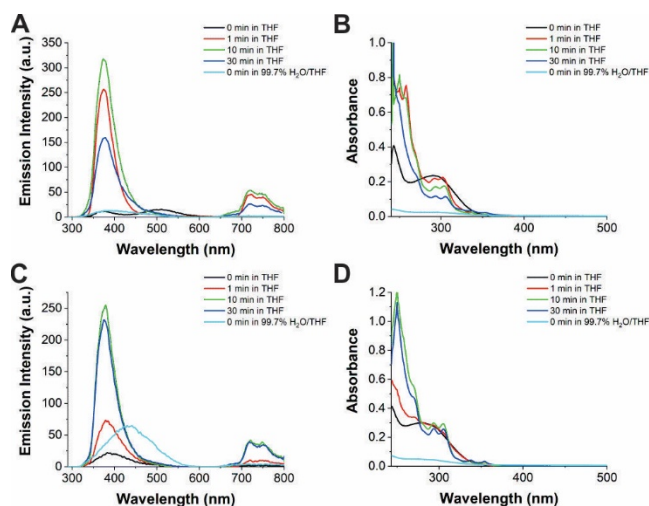

Figure 1. Emission spectra for **3a** (**A**, λ_{exc} = 290 nm) and **3b** (**C**, λ_{exc} = 280 nm) and absorption spectra for **3a** (**B**) and **3b** (**D**) in 20 μM THF solution. The samples were irradiated with UV (302 nm) light for 0, 1, 10, and 30 min. Spectra of **3a** and **3b** in the aggregated state (H₂O:THF, 99.3:0.7) included for comparison.

Both the *Z*-configured **3a** and its *E*-isomer **3b** generated a mixture of phenanthrenes **6a** and **6b**, suggesting that the rates of *Z/E* photoisomerization and photocyclization are comparable. Since the formation of **6a** requires an oxidant and that of **6b** does not, we tested the effects of oxygen exclusion on the ratio of **6a** and **6b**. The photoreactions of **3a** and **3b** were carried out under either O₂ and N₂ atmosphere, in CH₂Cl₂ and THF (Table 1). Although all solvents were degassed by the freeze-pump-thaw method, the reactions performed under N₂ atmosphere still generated significant yields of oxidized **6a**. Previous reports suggested that trace amount of O₂ could result in oxidative photocyclization.[12,14b] Reactions run in CH₂Cl₂ as the solvent gave higher **6a:6b** ratios than their counterparts performed in THF; in the case of **3a** as the starting material, **6a** was obtained as essentially the only product. We tentatively attributed this solvent-dependent selectivity to the lower solubility of HF in CH₂Cl₂ than in THF,[15] which was reported to trap the acid side product in the photocyclization of *cis*-stilbene.[13a,16] Photocyclizations of **2** into **5** and **3c** into **6c** could—and did—only generate one product.

Scheme 2. Photocyclization of compounds **2** and **3a–c** into phenanthrenes **5** and **6a–c**. See also Table 1.
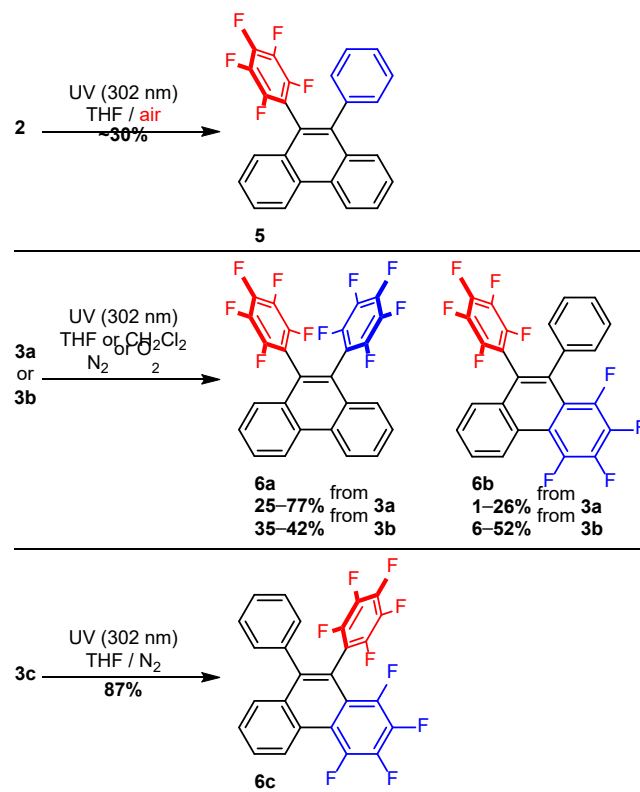

Table 1. Photocyclizations of **3a** and **3b** under different conditions.[a]

Reaction	Starting compound	Solvent	Atmosphere	Yield of **6a**	Yield of **6c**
1	**3a**	THF	O₂	42%	13%
2	**3a**	THF	N₂	25%	26%
3	**3a**	CH₂Cl₂	O₂	73%	1%
4	**3a**	CH₂Cl₂	N₂	77%	2%
5	**3b**	THF	O₂	39%	52%
6	**3b**	THF	N₂	36%	34%
7	**3b**	CH₂Cl₂	O₂	35%	10%
8	**3b**	CH₂Cl₂	N₂	42%	6%

[a] General reaction conditions: the starting material **3a** or **3b** were dissolved in THF or CH₂Cl₂ (~2 mg/mL). Then, the solution was degassed by freeze-pump-thaw method and either O₂ or N₂ were bubbled through it. All reactions were carried out at room temperature with UV (302 nm) irradiation for 15 h. Each reaction was repeated three times; the reported yields are averages, determined by ¹H or ¹⁹F NMR with 1,2,4,5-tetrafluorobenzene as the internal standard.

Recent theoretical investigations and ultrafast time-resolved spectroscopy suggested that the cyclization of **1** into 9,10-diphenyl-4a,4b-dihydrophenanthrene proceeds through a conical intersection, which may be responsible for nonradiative decay.[17] Calculations suggest that **1** cyclizes faster[17a,17c,18] and with less structural reorganization[17a] compared to the rotation along C=C bond during the *Z/E* isomerization. Since the photocyclization of **3a–3c** does not require significant conformational adjustment, their aggregation cannot stop it.[17a] It had been suggested that there is no energy

barrier between the Franck-Condon structure and cyclized structure in the excited state.[17c]

X-ray diffraction quality single crystals of photocyclized **6a** and **6b** were grown from CDCl₃, while those of **6c** were obtained from CH₂Cl₂. These crystal structures (Figure 3) reveal remarkably similar [π⋯π] stacking motifs which organize molecules of **6a**–**c** into dimers with [C⋯C] interactions of 3.35 Å for **6a**, 3.26~3.37 Å for **6b**, and 3.30 and 3.37 Å for **6c**. Curiously, only the dimer of **6c** organizes its partially fluorinated phenanthrenes in the self-complementary head-to-tail fashion; in **6b**, they stack in an apparently unfavorable head-to-head style. The UV/Vis spectra of **6a**–**c** are dominated by the absorptions of the phenanthrene moiety at ~300 nm (see Figure S46). These compounds show aggregation-caused quenching (ACQ) because their planarized aromatic structures facilitate [π⋯π] stacking, offering a nonradiative decay pathway (see Table S10 and S11).[1a]
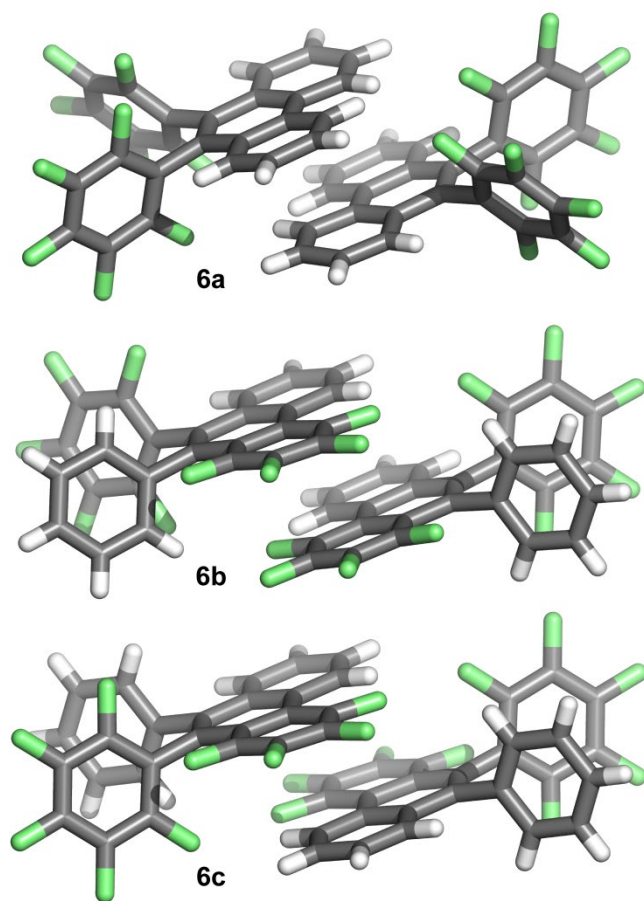

Figure 3. Crystal structures of **6a**–**c**; two molecules are shown to highlight [π⋯π] stacking. Element colors: C—gray, H—white, F—lime.

In conclusion, five TPE derivatives functionalized with pentafluorophenyl groups were synthesized using Pd- and Cu-catalyzed C–C coupling reactions. While fluorescent in the solid state, they do not exhibit aggregation-induced emission, in contrast to the TPE parent system. Instead, their UV irradiation leads to rapid photocyclizations into phenanthrenes. The planarity of these phenanthrenes intensifies their intermolecular interactions, further quenching fluorescence after aggregation. Our results show that the photocyclization in extensively fluorinated TPEs presents an effec-

tive nonradiative decay pathway for their excited states—both in dilute solutions and in the aggregated state.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at pubs.acs.org. Crystallographic Information Files for **3b**, **3c**, **4**, and **6a**–**c** have been deposited with the Cambridge Crystallographic Data Centre under deposition codes 2082832–2082837.

AUTHOR INFORMATION

Corresponding Author

Olafs Daugulis, email: olafs@uh.edu
Ognjen Š. Miljanić, email: miljanic@uh.edu

Author Contributions

Compounds **2**–**4** were synthesized by T. L.; Z.Z. prepared compounds **5** and **6**, produced single crystals of **3**–**4** and **6**, analyzed their optical properties, and performed theoretical calculations. X.W. performed single crystal X-ray diffraction and solution refinement. The manuscript was written by Z.Z. and O.Š.M. incorporating input from all authors.

The authors declare no competing financial interest.

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