

Stereoselective and quantitative [2 + 2] photodimerization of a symmetrical octafluoro stilbene in the solid state: Face-to-face stacking of the fluorinated rings in *trans*-1,2-bis(2,3,5,6-tetrafluorophenyl) ethylene

Michael A. Sinnwell^a, Benjamin J. Ingenthron^b, Ryan H. Groeneman^{b,*}, Leonard R. MacGillivray^{a,*}

^a Department of Chemistry, University of Iowa, Iowa City, IA 52242, USA

^b Department of Biological Sciences, Webster University, St. Louis, MO 63119, USA

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ABSTRACT

The symmetrical octafluoro stilbene *trans*-1,2-bis(2,3,5,6-tetrafluorophenyl)ethylene (**1**) undergoes a stereoselective and quantitative [2 + 2] photodimerization in the solid state. The olefin self-assembles via C-H...F and face-to-face interactions of the fluorinated phenyl rings into a geometry for a topochemical photodimerization. The crystal structure and stereochemistry of the photoproduct *rctt*-1,2,3,4-tetrakis(2,3,5,6-tetrafluorophenyl)cyclobutane (**2**) has been determined.

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1. Introduction

Understanding supramolecular interactions of organic fluorine continues to be important for advancing the design and syntheses of fluorinated materials [1]. Liquid crystals [2], pharmaceuticals [3], and fluorinated metal-organic frameworks [4] have demonstrated attractive physical properties [5] related to integrations of fluorine atoms. In this context, noncovalent interactions involving fluorine have been exploited to facilitate chemical reactivity in the solid state. Perfluorophenyl-phenyl (C₆F₆...C₆H₆) interactions (Scheme 1a) have, thus, been shown to support the syntheses of fluorine-containing cyclobutanes via the photoinduced [2 + 2] cycloaddition reaction, with reactions occurring in single- and multi-component solids [6]. Perfluorophenyl-perfluorophenyl (C₆F₆...C₆F₆) [7] (Scheme 1b) interactions, as well as analogous forces involving polyfluorophenyl rings [8], have been used to support the parallel stacking of carbon-carbon double bonds (C=C) required for [2 + 2] photodimerizations. In related work, fluorine-directed solid-state photoreactions of fluorocoumarins [9], fluorobenzylidenepiperitones [10], and diarylbutadienes [11] have been

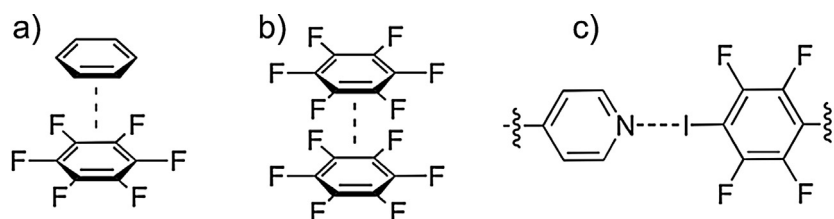
reported. Halogen bonds (Scheme 1c) have also been used to sustain photoreactivity in the solid state in more limited cases [12]. All of these examples illustrate how supramolecular interactions involving fluorine atoms can facilitate the syntheses of small molecules via [2 + 2] photodimerizations in solids.

Our interests lie in achieving chemical reactivity in the solid state using fluorine-functionalized olefins. Recently, we described the use of C₆F₅...C₆F₅ interactions, in combination with argentophilic forces, to direct a head-to-head intermolecular [2 + 2] photodimerization in the solid state (Scheme 2a) [13]. We more recently reported the ability of a rigid bipyridine to direct an intermolecular photodimerization via halogen bonds [14,15]. In particular, co-crystallization of *trans*-1,2-bis(4-iodotetrafluorophenyl)ethylene (2I-1) with 1,8-di(4-pyridyl)naphthalene afforded a four-component supramolecular assembly sustained by halogen bonds (Scheme 2b). UV-irradiation of the solid generated *rctt*-1,2,3,4-tetrakis(1-iodo-2,3,5,6-tetrafluorophenyl)cyclobutane (4I-2) stereoselectively and in quantitative yield [16]. The inherent photostability of 2I-1 as a pure solid required use of the bipyridine to achieve the solid-state photodimerization to form 4I-2.

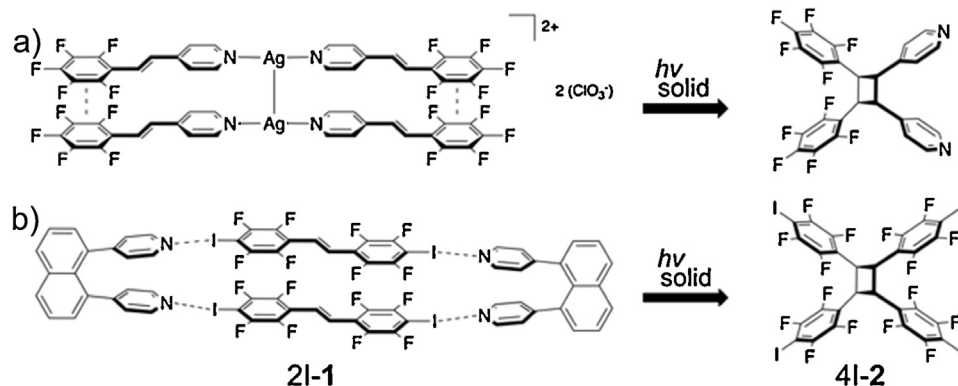
To this end, we endeavored to investigate how the removal of the terminal iodide atoms from 2I-1 in the form of *trans*-1,2-bis(2,3,5,6-tetrafluorophenyl)ethylene **1** would effectively influence the self-assembly of **1** in the solid state. Terminal C-H groups of polyfluoroarenes are useful synthons in organic synthesis

* Corresponding authors.

E-mail addresses: ryangroeneman19@webster.edu (R.H. Groeneman), len-macgillivray@uiowa.edu (L.R. MacGillivray).



Scheme 1. Integration of fluorine in supramolecular chemistry: (a) $C_6F_6 \cdots C_6H_6$ interactions, (b) $C_6F_6 \cdots C_6F_6$ interactions, and (c) halogen bonds.



Scheme 2. Photoactive assemblies: (a) $C_6F_5 \cdots C_6F_5$ interactions and argentophilic forces and (b) halogen bonding.

(e.g. arylations), which would also make a resulting cyclobutane an attractive synthetic target [17]. To our knowledge, the unsymmetrical alkene *trans*-1-(4-aminophenyl)-2-(2,3,5,6-tetrafluorophenyl)ethylene represents the only documented case of a solid-state photodimerization involving a polyfluoroarene that possesses a terminal C-H group [12].

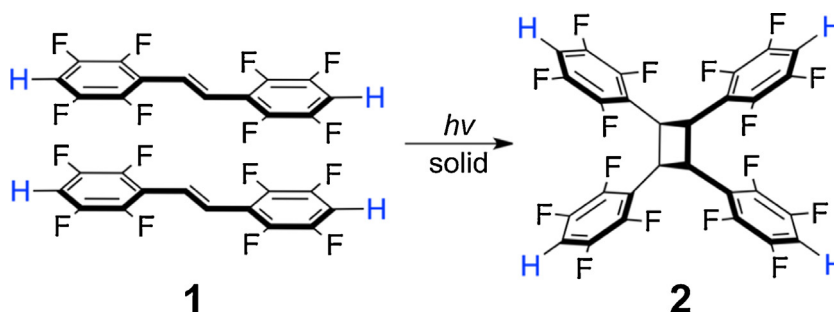
Here, we report the structure and photoreactivity of **1** in the solid state. We show **1** to undergo a [2+2] photodimerization stereoselectively to generate *rcctt*-1,2,3,4-tetrakis(2,3,5,6-tetrafluorophenyl)cyclobutane (**2**) in quantitative yield (Scheme 3). Face-to-face stacking involving the polyfluorophenyl rings, in combination with C-H \cdots F forces, dominate the assembly of **1** in the solid.

2. Results and discussion

The synthesis of **1** was accomplished using a Wittig reaction of triphenyl-(2,3,5,6-tetrafluorobenzyl)phosphonium bromide and 2,3,5,6-tetrafluorobenzaldehyde [18]. Single crystals of **1** suitable for X-ray diffraction studies in the form of colorless needles were obtained *via* slow evaporation from a toluene solution overnight (Table 1).

The alkene **1** crystallizes in the monoclinic space group $P 2_1/n$. The olefin sits around a crystallographic inversion center, with one-half of the molecule being present in the asymmetric unit (Fig. 1a). An analysis of the extended structure reveals **1** to self-assemble in the solid state *via* offset C-H \cdots F forces (H \cdots F (Å): 2.61, C \cdots F (Å): 3.330(2), C-H \cdots F ($^\circ$): 134.9, calc. 98% of sum of van der Waals radii) to form alternating 2D sheets within the crystallographic *bc*-plane (Fig. 1b) [19]. The sheets interact *via* offset face-to-face stacking of the polyfluoro rings, with metrics similar to analogous architectures [20]. The assembly of the sheets afford infinite stacks of **1** along the *a*-axis. As a consequence of the assembly process, the C=C bonds are parallel and separated by 3.81 Å, which conforms to the criteria of Schmidt for a [2+2] photodimerization in a solid (Fig. 1c) [21].

To determine the photoreactivity, a powder crystalline sample of **1** was placed between two glass plates and exposed to UV-radiation (broadband medium-pressure Hg lamp) for a period of approximately 30 h. A 1H NMR spectrum revealed a photodimerization to occur in the solid stereoselectively and in quantitative yield (Figs. S1–S4). Specifically, the formation of a cyclobutane ring was evidenced by the complete disappearance of



Scheme 3. Photodimerization of **1** to form **2** in the solid state.

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