

Title: Mechanochemical synthesis of an elusive fluorinated polyacetylene

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Abstract: Polymer mechanochemistry has traditionally been employed to study the effects of mechanical force on one or two chemical bonds within a polymer. It is underexploited for the scalable synthesis of wholly new materials by activating bonds along the entire polymer, especially products inaccessible by other means. Herein we utilize polymer mechanochemistry to synthesize a fluorinated polyacetylene, a long-sought-after air-stable polyacetylene that has eluded synthesis by conventional means. Construction of the monomer is achieved in four steps on gram scale and is highlighted by rapid incorporation of fluorine in an exotic photochemical cascade whose mechanism and exquisite diastereoselectivity were informed by computation. Site-selective polymerization and force activation via ultrasonication transforms an insulating plastic into a gold-colored, semiconducting fluoropolymer. This work demonstrates that polymer mechanochemistry is a valuable synthetic tool for accessing novel materials.

Main Text: In recent years, polymer mechanochemistry has emerged to harness mechanical force experienced by macromolecules into productive chemical reactions¹. Embedded force-responsive groups called mechanophores located in polymer chains experience a biased reaction pathway from an external force, and poised bonds can therefore be cleaved selectively². However, polymer mechanochemistry is still an underutilized method for the selective synthesis of novel targeted macromolecules. Most examples of force-responsive polymers feature the breakage of one or two bonds in mechanophores that are sparsely incorporated within a polymer³. While solid-phase small molecule ball-milling mechanochemistry has gained increasing importance in synthetic chemistry⁴, a necessary leap in the adoption of polymer mechanochemistry as a synthetic tool is to demonstrate its utility towards the synthesis of desired targets that are inaccessible by other means. Herein, we have achieved the first synthesis and characterization of a fluorinated polyacetylene by using polymer mechanochemistry to isomerize a large number of chemical bonds.

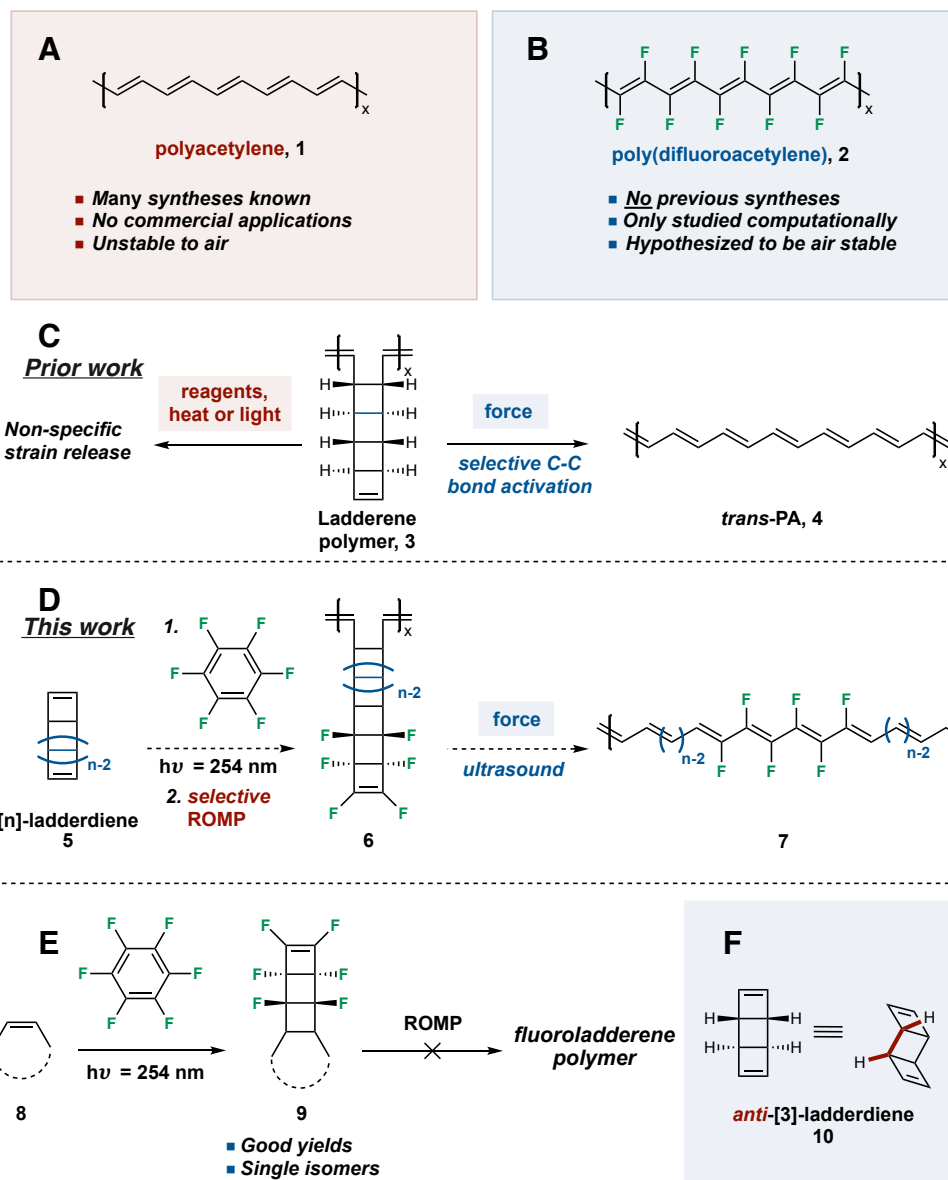


Fig. 1. Our approach to the synthesis of fluorinated polyacetylenes. (A) Polyacetylene (PA) **1** is a conjugated, semiconducting polymer with many reported syntheses. (B) Poly(difluoroacetylene) **2** is a novel conjugated fluoropolymer with no reported syntheses. (C) [n]-Ladderene polymer **3** is force-responsive and isomerizes to conjugated all *trans*-PA **4**. This isomerization is not possible with chemical reagents, heat, or light. (D) Our approach to a generic fluorinated polyacetylene **7** from fluoroladderene polymer **6** using solution ultrasonication. (E) A fluoroladderene extension reaction enables rapid access to non-polymerizable fluoroladderenes from unactivated alkenes in good yields and as single isomers. (F) Target *anti*-[3]-ladderdiene **10**.

Polyacetylene (PA, **1**, Fig. 1A) is a semiconducting organic polymer that contributed towards a revolution in organic electronic materials because of its conductivity in the metallic range upon doping^{5,6,7}. Although pioneering, difficulties in processing and low air-stability hampered the commercial success of PA⁸. In 1979, Fukui and Shirakawa appealed for the synthesis of poly(difluoroacetylene) (**2**, Fig. 1B) in part because it would be more air-stable than PA⁹. Their computational investigations on poly(difluoroacetylene) and poly(fluoroacetylene), as well as later reports by others¹⁰⁻¹², predicted that such fluorinated polyacetylene derivatives would have modified optical properties, improved solid-state packing, and be amenable to n-type doping for improved conductivity relative to undoped fluorinated polyacetylenes. Fukui and Shirakawa proposed a synthesis of poly(difluoroacetylene) **2** from the polymerization of pyrophoric and highly explosive mono- or difluoroacetylene gas¹³. Gould and coworkers later showed that the thermal polymerization of difluoroacetylene, upon warming from –196 to –95 °C, resulted in a material containing irregular CF, CF₂, and CF₃ incorporation¹⁴. We saw monomer instability and a lack of other synthetic efforts as impetus for development of a drastically different approach to preparing a fluorinated polyacetylene.

Some of us have studied a novel synthesis of PA via force-induced unzipping of natural product-inspired ladderene polymers (**3**, Fig. 1C) using solution ultrasonication¹⁵. This process occurs only with force, and it involves tandem retro-[2+2] ring openings within ladderene repeat units^{16,17} to produce long, all *trans*-PA segments, **4**. We envisioned that an analogous fluoroladderene polymer **6** (Fig. 1D) would grant access to a fluorinated polyacetylene **7** and circumvent the synthetic hurdle associated with polymerizing fluorinated acetylene. Polymer **7** contains segments of fluorinated polyenes and non-fluorinated polyenes, unlike poly(difluoroacetylene) or poly(fluoroacetylene). To realize a synthetic strategy, we anticipated

two major obstacles: 1) scalable preparation of an appropriate fluoroladderene monomer that can be efficiently polymerized, and 2) mechanochemical activation and characterization of an extended fluorinated polyene.

In designing a fluoroladderene monomer we sought to exploit a unique and underused photochemical cascade reaction between hexafluorobenzene and electronically unactivated alkenes (Fig. 1E)¹⁸⁻²¹. The power of this transformation lies in the fact that three fused cyclobutanes containing six fluorine atoms are added onto a variety of simple alkenes in a single operation (**8** to **9**, Fig. 1E). Efforts to directly polymerize fluoroladderenes into a fluorinated polymer by radical, anionic or ring-opening metathesis polymerization (ROMP) were unsuccessful (Supplementary Fig. 1). Taking advantage of the inertness of fluoroalkenes to metathesis reactions, we targeted an [n]-ladderdiene **5** (Fig. 1D) that could be engaged with one equivalent of hexafluorobenzene in a fluoroladderene extension, leaving the other cyclobutene terminus as a site for ROMP. Mechanochemical activation of fluoroladderene polymer **6** should then deliver **7** (Fig. 1D). With an eye towards simplicity, scalability, and maximizing fluorine content within the material, we selected the smallest thermally and photochemically stable ladderdiene: *anti*-[3]-ladderdiene **10** (Fig. 1F). The *anti* diastereomer was chosen rather than the *syn* diastereomer because of its superior thermal stability²² and faster ROMP kinetics¹⁷.

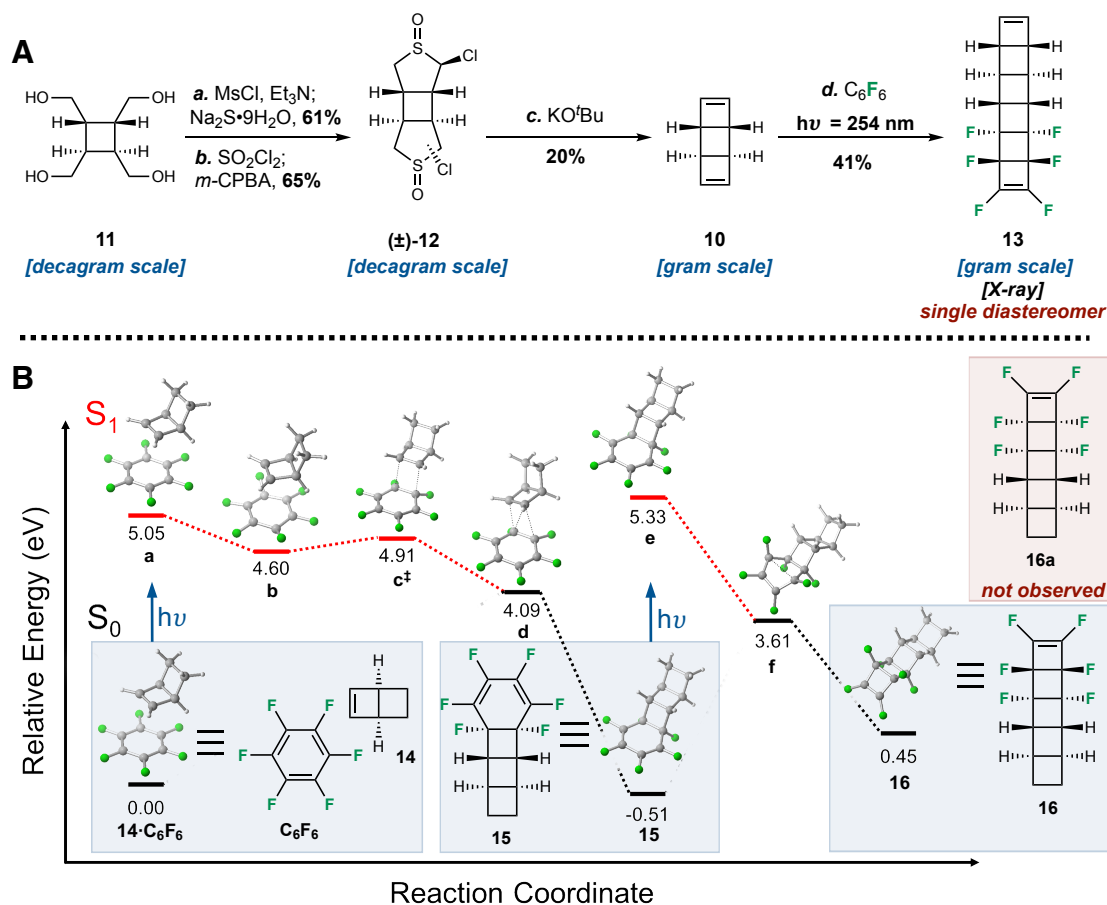


Fig. 2. Synthesis of fluoroladderene monomer and fluoroladderene extension mechanism on model system. (A) Gram-scale synthesis of **13**. (a) MsCl (6.0 equiv.), triethylamine (7.0 equiv.), DMF, $-30\text{ }^{\circ}\text{C}$ to room temperature, 3 hours, then sodium sulfide nonahydrate (2.4 equiv.), $80\text{ }^{\circ}\text{C}$, 20 hours, 61%. (b) sulfuryl chloride (2.0 equiv.), CH_2Cl_2 , $-20\text{ }^{\circ}\text{C}$, 2.5 hours, then *m*-CPBA (2.0 equiv.), CH_2Cl_2 , $-20\text{ }^{\circ}\text{C}$, 2.5 hours, 65%. (c) KO^tBu (12 equiv.), THF, $23\text{ }^{\circ}\text{C}$, 7 hours, 20%. (d) Hexafluorobenzene (1.0 equiv.), 254 nm light, pentane, $23\text{ }^{\circ}\text{C}$, 8 hours, 41%. MsCl, methanesulfonyl chloride; *m*-CPBA, *meta*-chloroperoxybenzoic acid. (B) Computed reaction coordinate diagram from **14** to **16** via ground (S_0 , black) and first singlet excited states (S_1 , red) using complete active-space self-consistent field (CASSCF) and complete active-space second-order perturbation (CASPT2) methods in vacuum [CASPT2(8,8)/6-311+G(d)//CAS-D3BJ(8,8)/6-31+G(d)]. Experimental conditions of the reaction of **14** with hexafluorobenzene (1.0 equiv.), 254 nm light, pentane, $23\text{ }^{\circ}\text{C}$, 36 hours, 57%.

Results and Discussion: Our target *anti*-[3]-ladderdiene **10** had previously been prepared by Nenitzescu and coworkers by the dimerization of dichlorocyclobutene²³. However, that synthesis yielded an inseparable mixture of ladderene diastereomers and hydrocarbon byproducts, used

chlorine gas, and required a 200-fold excess of lithium-mercury amalgam (Supplementary Fig. 2). Thus, we deemed it unsuitable for our purposes. Instead we developed a novel, inexpensive, and scalable route to **10** beginning from cyclobutane tetramethylalcohol **11** (Fig. 2A). Global mesylation of **11** and *in situ* displacement with sodium sulfide produced a bis(tetrahydrothiophene)cyclobutane, which, upon one-pot chlorination with sulfuryl chloride and oxidation with *meta*-chloroperoxybenzoic acid yielded bis(α -chlorosulfoxide)cyclobutane ($\pm$)-**12** in 40% yield over two steps as an inconsequential mixture of isomers. This sequence notably contains only one instance of chromatography and can be performed on decagram scale. Treatment of ($\pm$)-**12** with excess potassium *tert*-butoxide yielded *anti*-[3]-ladderdiene **10** in a double sulfoxide Ramberg–Bäcklund reaction previously developed by some of us for preparing strained terminal cyclobutenes²⁴. Fluoroladderene extension of **10** with one equivalent of hexafluorobenzene then gave a single all-*anti* diastereomer of [6]-hexafluoroladderdiene **13** on gram scale in 41% yield as a white crystalline solid, and the structure was confirmed by X-ray crystallography.

Delighted with the complete diastereoselectivity of the fluoroladderene extension, we sought to better understand its origin by investigating this unusual photochemical cascade by computing the reaction pathway of a related system. Bicyclohexene **14**^{15,24} reacted with hexafluorobenzene to give hexafluoroladderene **16** as a single diastereomer in 57% yield on gram scale (Fig. 2B). Experimental evidence strongly suggests this photochemical process proceeds via a singlet pathway²¹, and thus stationary points and conical intersections were optimized with CASSCF, the quintessential multiconfigurational method for computing photochemical excited states, on the ground singlet (S_0) and first singlet excited (S_1) states; perturbative energy corrections were applied to each of these structures with CASPT2. We calculated a pathway starting with **14** in a

dispersion-bound complex with hexafluorobenzene (**14**•C₆F₆). This complex is initially photoexcited to S₁ **a** (Fig. 2B), followed by relaxation to **b** and subsequent [2+2] cycloaddition²⁵ via transition state structure **c**[‡]. This pathway then proceeds through an S₁/S₀ conical intersection **d** to isolable cyclohexadiene intermediate **15**. This intermediate could then undergo two possible photochemical 4 π electrocyclizations to give diastereomers **16** or **16a**. Photoexcitation of **15** to S₁ **e** is followed by direct relaxation through S₁/S₀ conical intersection **f** to the observed product **16**. Examination of the S₁ potential energy surface (Supplementary Fig. 57) revealed that distortions of **15** on the pathway to diastereomer **16a** are energetically disfavored, while distortions on the pathway to **16** are universally downhill, leading to the observed diastereoselectivity²⁶. These computed potential energy surfaces will provide a theoretical basis for future cascade reactions with substrates other than hexafluorobenzene.

With a scalable synthesis of **13** completed, we then attempted a chemoselective polymerization. Gratifyingly, ROMP of **13** proceeded rapidly and selectively at room temperature using Grubbs III catalyst²⁷ to give fluorinated ladderene polymers **17a-17c** with complete conversion (Fig. 3A). Analysis of the ¹⁹F nuclear magnetic resonance (NMR) spectra of **17a** showed that the polymerization was selective for the non-fluorinated cyclobutene (Supplementary Fig. 4). Gel permeation chromatography (GPC) analysis (Fig. 3B) revealed a narrow molecular weight (MW) distribution with MW proportional to the monomer-to-catalyst ratio, and varying this ratio from 200 to 1000 produced polymers **17a-17c**. The polymerization was shown to proceed with first-order kinetics (Supplementary Fig. 5).

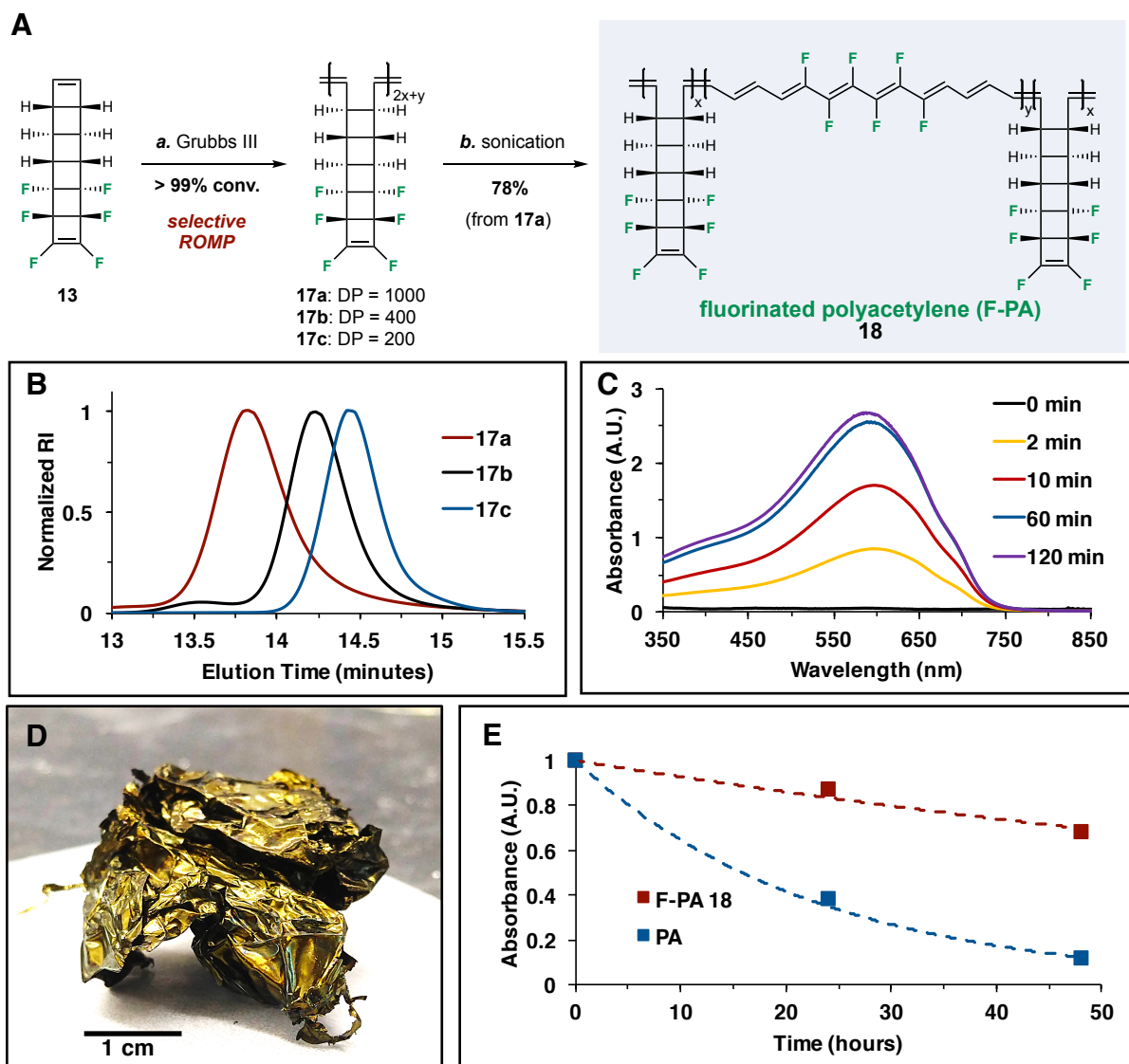


Figure 3. Synthesis and characterization of F-PA 18. (A) Synthesis of F-PA 18. (a) Grubbs III catalyst (17a: 0.10 mol %, 17b: 0.25 mol %, 17c: 0.50 mol %), CHCl₃, 25 °C, 18 minutes, ca. quantitative conversion. (b) Ultrasonication, tetrahydrofuran, 6-9 °C, 2 hours, 78% mass recovery. (B) Gel permeation chromatography of 17 at different molecular weights. (C) UV-vis absorption spectra in tetrahydrofuran of the visually clear supernatant during sonication of 17a at different sonication times. (D) Photograph of 85 mg of 18. (E) Decay of solutions of 18 and PA in tetrahydrofuran on the bench by measuring absorbance at the λ_{max} at various times.

Mechanochemical activation of fluorinated ladderene polymer 17a was achieved by standard solution ultrasonication to give partially fluorinated polyacetylene (F-PA) 18 (Fig. 3A).

Sonication of a solution of **17a** with a degree of polymerization (DP) of 1000 for one second resulted in a homogenous blue solution. A deeper blue and visibly homogenous solution was observed after twenty seconds of sonication and the presence of nanoscale aggregates was determined using dynamic light scattering (Supplementary Fig. 10). A UV-vis spectrum of this aliquot (Supplementary Fig. 6) showed the appearance of a broad absorbance peak with a maximum of 600 nm and an onset of 760 nm (Fig. 3C). Ultrasonication for 2 minutes and longer resulted in the appearance of a deep black color and precipitate (Supplementary Fig. 6). All UV-vis spectra of heterogeneous solutions were measured with visually clear supernatants. The UV-vis λ_{max} shifted hypsochromically to 591 nm with increasing intensity, while the optical onset wavelength of **18** is lower than PA¹⁵. Remarkably, **18** appeared as a golden iridescent solid (Fig. 3D) with 78% mass recovery upon removal of solvent. To provide evidence that the activation was mechanochemical and not thermal, we subjected different MW polymers to identical sonication conditions and observed that the rate of formation depended on the MW of the polymer, which is characteristic of polymer mechanochemistry (Supplementary Fig. 6). Further, simple thermolysis of **17a** did not produce **18**.

Various spectroscopic techniques were then utilized to characterize mechanochemically generated **18**. Cross-polarization magic-angle spinning ¹³C solid-state NMR spectroscopy (Supplementary Fig. 7) of **17a** and **18** showed the production of new sp²-carbon resonances and diminution of sp³-carbon resonances consistent with isomerization of fluoroladderene units into fluorinated polyenes. X-ray photoelectron spectroscopy (XPS) of **18** films was used: 1) to determine that the elemental composition of **18** retained the fluorine content after mechanochemical activation, and 2) to confirm that there was not disproportionation as observed by Gould¹⁴ (Supplementary Fig. 8). By comparing the integral of the F[1s] electron binding

energy region to the C[1s], we found the fluorine to carbon ratio to be 0.41 (predicted to be 0.43). The C[1s] region of **18** displayed two carbon environments that corresponded to CF and CH_x in a ratio of 0.74 (predicted to be 0.75). The absence of regions corresponding to CF₂ or CF₃ carbons like those observed during Gould's polymerization of difluoroacetylene allowed us to reason that **18** had not isomerized via migration of fluorine. Further evidence for F-PA production was provided by infrared (IR) spectroscopy (Supplementary Fig. 9).

Having activated and characterized F-PA **18**, we then set out to determine its electrochemical properties and air stability compared to PA prepared by mechanical activation¹⁵. Electrical conductivity was measured from a film of **18** prepared by evaporation without doping, annealing, or alignment (Supplementary Fig. 11). We measured a conductivity of 6.7×10^{-7} S/cm, which is lower than the reported value for Shirakawa's surface-grown aligned *trans*-PA (1.2×10^{-5} to 4.0×10^{-4} S/cm)⁶, but is similar to mechanochemically-generated PA (2.6×10^{-7} S/cm)¹⁵.

The stability of **18** was compared with mechanochemically produced PA in ambient conditions of air and light using UV-vis spectroscopy. Suspensions of **18** and PA prepared by two hours of sonication were diluted to an absorbance of 1 A.U. and then allowed to decay on the lab bench, and UV-vis spectra were taken over time (Fig. 3E). We observed a half-life for PA of 15.7 hours according to its observed exponential decay, and a half-life of **18** was extrapolated based on an exponential decay to be 86.6 hours. This increased lifetime in solution supports the longstanding hypothesis that fluorination increases the oxidative stability of PA⁹. As well, a suspension of **18** could be stored under an atmosphere of argon in the dark at 5 °C for weeks without a measurable change to the UV-vis spectra (Supplementary Fig. 12). Cyclic voltammetry was used to quantify the oxidation profile of **18** (Supplementary Fig. 13). A voltammogram of **18** suspended in tetrahydrofuran showed an irreversible oxidation with an anodic peak potential at +200 mV

relative to a ferrocene standard, which is 195 mV higher than for reported PA²⁸, consistent with a reduced reactivity of **18** with oxygen compared to PA.

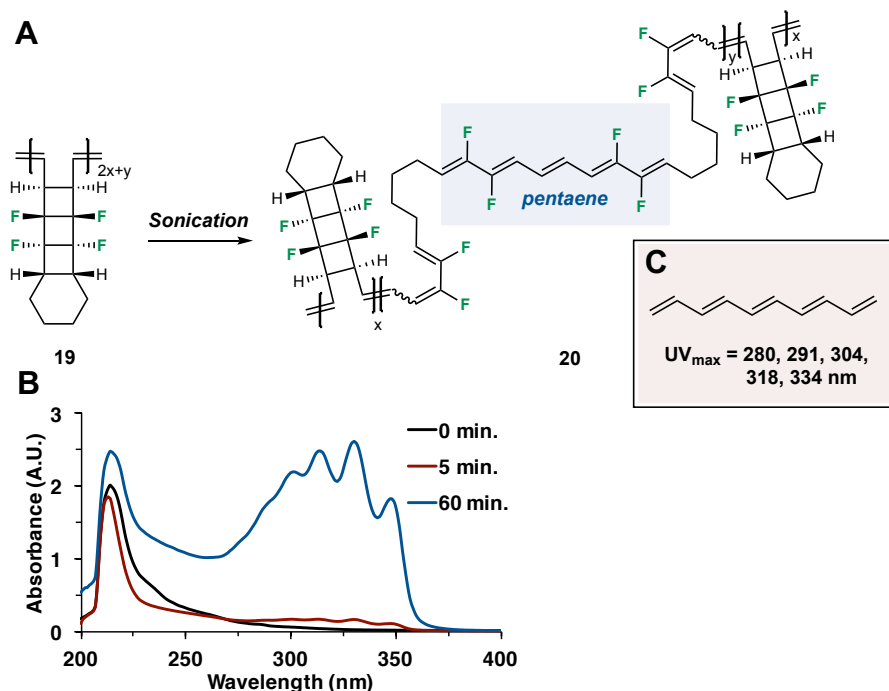


Fig. 4. Mechanochemical activation of **19 yields novel fluorinated polymer containing pentaenes.** (A) Mechanochemical activation of fluoroladderene polymer **19** to **20** in tetrahydrofuran contains repeating pentaenes. (B) UV-vis spectra of **20** after 0, 5 and 60 minutes of sonication. (C) The reported UV-vis λ_{max} absorption peaks of decapentaene for comparison.

The force-induced isomerization of fluoroladderene polymers is not restricted to producing fully conjugated polyenes, and discrete polyenes can also be prepared. Ultrasonication of fluoroladderene polymer **19** (Fig. 4A) was monitored by UV-vis spectroscopy, and produced five peaks between 289 and 347 nm that become more intense at longer sonication times (Fig. 4B). The relative absorbance and pattern of these peaks are in excellent agreement with a reported spectrum of comparable all *trans*-decapentaene²⁹. The quality of the UV-vis spectra of **20** showcases the remarkable selectivity of this force-mediated isomerization for producing

polyenes. Further, 2,3,8,9-tetrafluoropentaene has never been synthesized, thus highlighting the power of this approach to prepare other novel substituted polyenes.

This work demonstrates that force-mediated chemical transformations of precursor macromolecules can allow entry into new classes of exciting materials previously thought to be inaccessible. Here we have used it to access an air-stable, conductive, fluorinated polyacetylene by way of an efficient, gram-scale monomer synthesis and thus validate that such approaches can provide useful quantities of final materials. State-of-the-art multireference quantum mechanical calculations have reproduced experimental findings and are actively being leveraged to predict the outcomes of future cascade reactions.

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