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DEVELOPING COVALENT-ORGANIC FRAMEWORKS FOR PROTECTING AGAINST RADIATION

By

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Thesis Summary

This research focuses on the development of lightweight, thermostable dual-function materials for secondary radiation protection and sensing by the integration of hydrogen-rich aliphatic chains inside the porous matrix of covalent-organic frameworks (COFs). The main aims of this project are the synthesis of organic linkers for forming a robust porous COF, synthesizing the porous COF through a condensation reaction, the development of hydrogen-rich aliphatic chains, and integration of aliphatic chains into COFs through click chemistry. This manuscript outlines the methodology and development of a novel self-assembled crystalline, porous material engineered to combine the functions of a shield and sensitive dosimeter. The reported hydrogen-rich materials are the first examples of COFs displaying stability in a wide range of pH (1–12), low-density, and thermal stability for advancing the space suit technology.

Introduction

During extended space missions, astronauts are exposed to high levels of ionizing radiation, leading to increased risk of radiation-related health effects such as cancer, nervous system damage, or degenerative tissue diseases. According to the theory of “stochastic breakage”, the damage to human health caused by ionizing radiation is due to the breaking of one or both strands of the DNA double helix by reactive oxygen species and free radicals.¹ Cells that survive exposure to low doses accumulate damage that becomes evident in their progeny, expressing nonclonal chromosomal aberrations. Low doses of ionizing radiation have been shown to have carcinogenic effects both in exposed and subsequent generations.¹

In order to mitigate environmental health hazards of astronauts on long-term missions, improvements in space suit technology for protection against radiation is required. This research project focuses on developing materials for a dual sensing and protecting space suit by integrating thermally and chemically stable, crystalline, porous covalent-organic frameworks (COFs) in order to address current demands in lightweight, thermostable, hydrogen-rich materials for secondary radiation protection. These materials have the potential to significantly advance personal protection of astronauts on space missions through integration into a Sewable Attenuating Framework Equipped-Sensor (S.A.F.E.) space suit. The dual-function of hydrogen-decorated

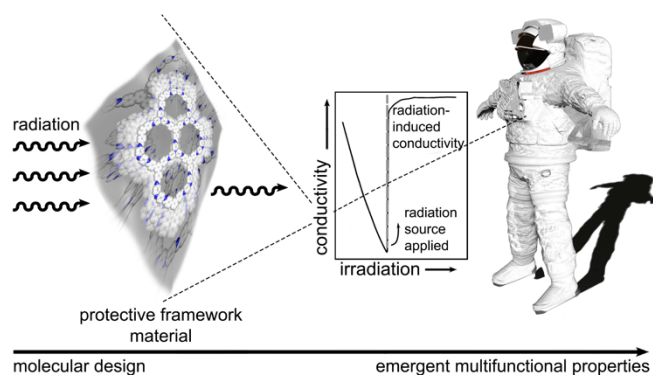


Figure 1. A schematic representation of a shielding material (left) for the adaptive space suit (right) consisting of a porous framework and performing as a shielding garment as well as sensitive dosimeter for astronauts working at the space station.

COFs contribute to the design of a S.A.F.E. space suit by offering both protection against radiation and acting as a sensitive dosimeter (Figure 1). Hydrogen-rich materials are ideal radiation shielding materials because hydrogen does not break down easily and it becomes a source for secondary radiation. Additionally, these hydrogen-rich materials are lightweight and thermostable.

By focusing on the synthesis of hydrogen-rich frameworks in which the hydrogen content can be modulated, efficient materials for radiation shielding can be developed. These purely organic materials are durable in the 1–14 pH range and thermally stable up to 773°

K, nearly four times higher than commercially available polyethylene, which is currently utilized for shielding against secondary ionization.² Other advantages of these purely organic frameworks include flexibility, low mass, and adaptability for direct garment integration through a mixed matrix membrane (MMM) approach.³ A recent report details how these frameworks can be grafted onto textile fibers by using a polymer as a binder.⁴ This strategy would be applied to engineer the adaptive sensing-integrated space suit. Furthermore, in contrast to traditional aliphatic systems, COFs operate at a wide temperature range and are more thermally stable due to scaffold rigidity. Ultimately, the main advantage of the reported approach is enhanced protection against ionizing radiation by using a MMM method for creation of a lightweight, porous, flexible framework that can be secured onto textile fibers to generate a protective and sensing suit.

Approach & Methodology

This project utilizes quantitative research methods to develop an effective COF to shield against secondary ionization, ultimately to be used to advance space suit technology.⁶ The initial building blocks for covalent organic frameworks, 1,3,5-tri-(4-aminophenyl)benzene, 2,5-dimethoxyterephthalaldehyde, and 2,5-bis(2-propynyloxy) terephthalaldehyde, were synthesized based on developed synthetic procedures (Figure 2). These building blocks were then combined in a stoichiometric fashion based on literature.⁵ A condensation reaction was performed to generate a robust, light, thermally stable, crystalline framework.

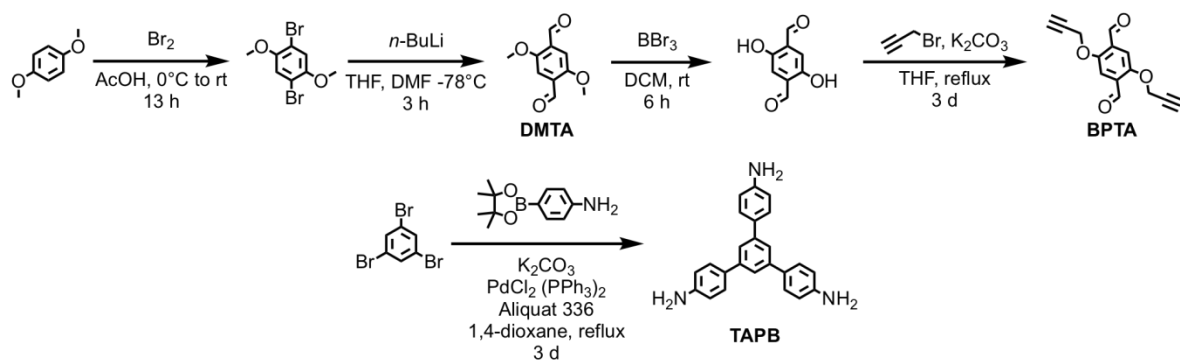


Figure 2. Synthesis of COF linkers.

The level of hydrogen content was varied through a post-synthetic modification approach by introducing aliphatic $-(CH_2)_n$ chains inside the porous matrix by click chemistry. Aliphatic chains of length varying from six to 12 carbons were synthesized in order to tune the hydrogen

content of the scaffolds over a wide range. The copper-catalyzed azide-alkyne cycloaddition of azides and terminal alkynes was utilized.⁶ The reported organic building blocks and copper-catalyzed azide-alkyne cycloaddition was employed based on the developed synthetic procedures.⁷

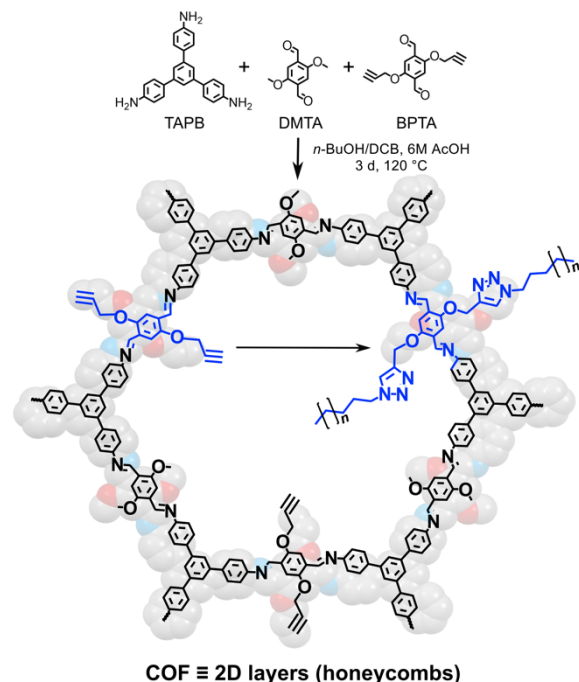


Figure 3. (top) A general scheme for COF synthesis. (middle) Enrichment of a COF with hydrogen content through post-synthetic modification through decoration of the framework walls.

resonances in the FTIR spectrum. In addition, we used PXRD to determine the crystallinity of the bulk material.

Formation of the hydrogen-rich azide molecules occurred by following a literature procedure. The products were analyzed through ^1H NMR spectroscopy and once they were pure, we pursued copper-catalyzed azide-alkyne cycloaddition reaction using a small organic building block, phenyl acetylene. We observed reaction progress using ^1H NMR spectroscopy, and once the reaction was complete, we were able to isolate and purify the product. We also utilized FTIR to observe the disappearance of the resonances at 2120 cm^{-1} ($\text{C}\equiv\text{C}$) and 3300 cm^{-1} ($\text{C}\equiv\text{C}-\text{H}$) in the spectrum that corroborated our conclusion that the reaction had gone to completion.

As a next step, we applied the developed reaction conditions (*N,N*-diisopropylethylamine/CuI/THF/ H_2O , $50\text{ }^\circ\text{C}$, 3 d) towards the reaction of the hydrogen-rich azide molecules and the insoluble COF. To monitor the reaction progress, solid-state techniques, such

Initial characterization of the organic building blocks was achieved through proton (^1H) nuclear magnetic resonance (NMR) spectroscopy. The ^1H NMR spectra of the three organic building blocks, e.g., 1,3,5-tri-(4-aminophenyl)benzene, 2,5-dimethoxyterephthalaldehyde, and 2,5-bis(2-propynyloxy) terephthalaldehyde, can be found in the Supporting Information (SI). Once the building blocks were determined to be pure by ^1H NMR spectroscopy, the condensation reaction could take place to form the extended framework (Figure 2). The framework was characterized using Fourier-transform infrared spectroscopy (FTIR) and powder X-ray diffraction (PXRD). In particular, we verified the presence of both the 2120 cm^{-1} ($\text{C}\equiv\text{C}$) and 3300 cm^{-1} ($\text{C}\equiv\text{C}-\text{H}$)

as FTIR, were employed. In particular, we observed the disappearance of 2120 cm^{-1} ($\text{C}\equiv\text{C}$) and 3300 cm^{-1} ($\text{C}\equiv\text{C}-\text{H}$) resonances in the FTIR spectrum, indicative of reaction completion. As a control experiment, we treated the COF under the same reaction conditions but without the presence of the azide-containing precursor. As expected, we observed preservation of both 2120 cm^{-1} ($\text{C}\equiv\text{C}$) and 3300 cm^{-1} ($\text{C}\equiv\text{C}-\text{H}$) resonances in the FTIR spectrum. Furthermore, utilizing PXRD, we confirmed the bulk crystallinity of the materials and verified that structural integrity was maintained after derivatization.

Thermogravimetric analysis was used to estimate framework thermostability and verified that the stability of the frameworks after incorporation of the hydrogen-rich molecules was maintained.

Conclusion

The outcome of this project is the full preparation of hydrogen-rich shielding materials with a function of mapping radiation exposure. The goal of the development of these hydrogen-rich COFs is to minimize the formation of secondary electrons and gamma rays by pair production and Bremsstrahlung, the deceleration of a charged particle produced when deflected by another charged particle. By decorating the walls of COFs with different-length alkyl chains, the hydrogen content in these scaffolds were able to be tuned over a wide range.

Another unique advantage of these purely organic materials is that they rely on simple, low-power electronics to measure conductivity changes upon exposure to radiation. Therefore, a framework-based sensor can turn “ON” in response to a change in conductivity corresponding to a predetermined radiation dose having been absorbed by the reported hydrogen-rich extended structures. These non-toxic, lightweight, and flexible shielding materials have the potential to protect astronauts from a residual dose of radiation while also serving as a real-time dosimeter, measuring the dose of ionizing radiation that is absorbed. Since these hydrogen-rich scaffolds exhibit a measurable, induced, transient conductivity under steady-state irradiation, they can function as a dosimeter. Consequently, these materials possess a dual function as both shielding attire and real-time dosimeters.

The proposed concept of a S.A.F.E space suit utilizing hydrogen-rich COFs will have a positive impact on improving personal protection, health, and survival of astronauts. Fundamental studies of radiation-induced conductivity in combination with the protective ability against

radiation will allow for the engineering of astronaut protective suits equipped with radiation sensors capable of reducing the risks of ionizing radiation. Radiation shielding both inside and outside a spacecraft is regulated by the NASA Radiation Health Program, which requires constant monitoring of the level of personal astronaut protection against radiation. This is one of the main factors determining the overall mission duration on the International Space Station. The proposed technology for the space suit advancement will allow for long-duration missions of Moon exploration or a two-year round-trip to Mars providing protection against much longer exposure of astronauts to damaging types of radiation, and therefore, keeping the astronauts below Permissible Exposure Limits.

Future Directions

Gas sorption studies will be employed to analyze material porosity and changes in the surface area upon material characterization. Electronic properties will be evaluated through two-probe and four-probe conductivity measurements.

After full material characterization, the desired materials will be deposited on a substrate, i.e., a fabrication of textile-integrated framework materials. The effect of substrate material (e.g., polyester, or nylon) on the morphology, orientation, and stability of framework coatings on their surface will be systematically examined. A MMM approach that has previously been developed and successfully applied for material integration will be employed.⁸ The electronic properties of the textile-integrated framework materials will then be explored.

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Supporting Information

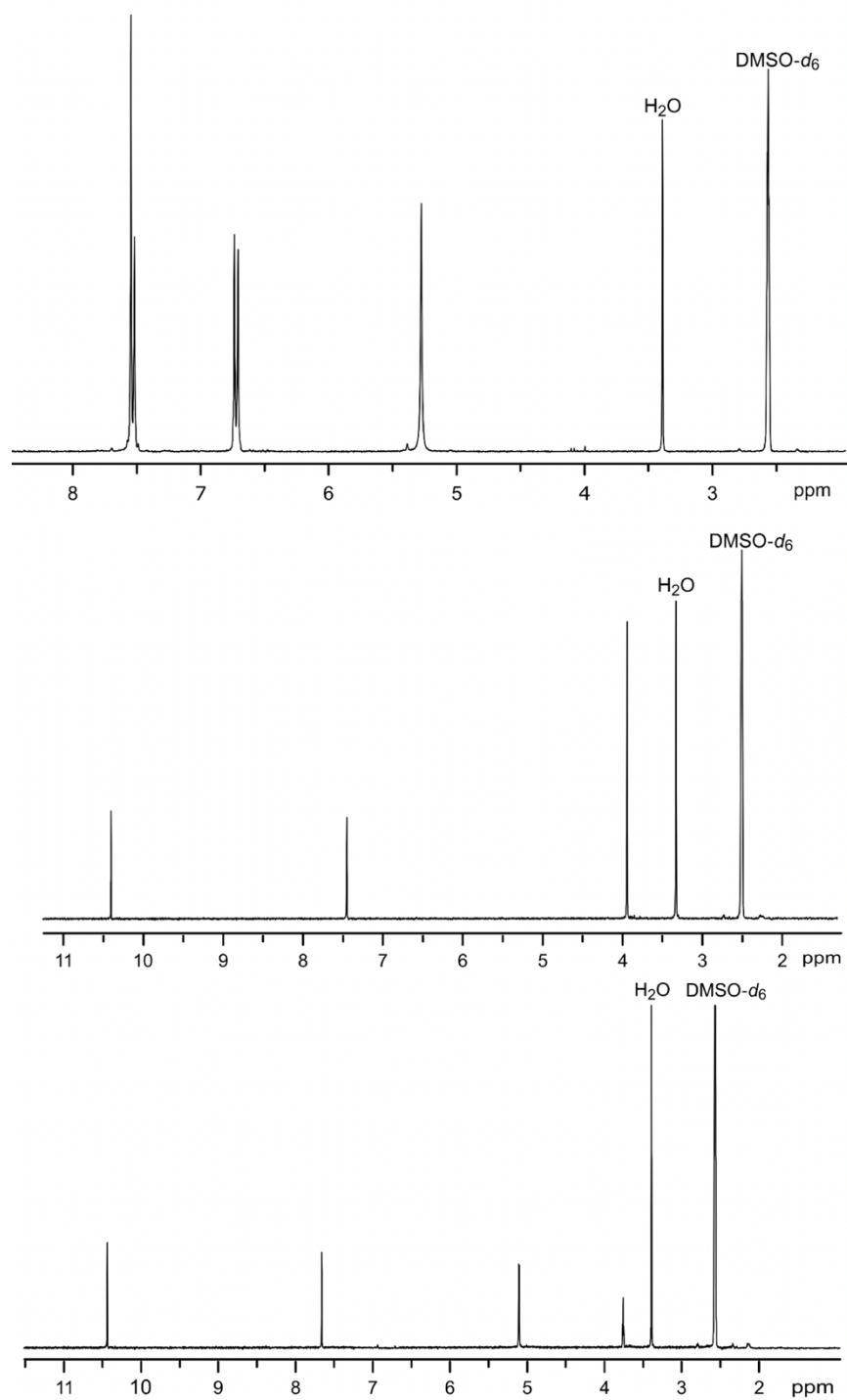


Figure 1. ^1H NMR spectra of (*bottom*) 2,5-bis(2-propynyloxy) terephthalaldehyde, (*middle*) 2,5-dimethoxyterephthalaldehyde, and (*top*) 1,3,5-tri-(4-aminophenyl)benzene.

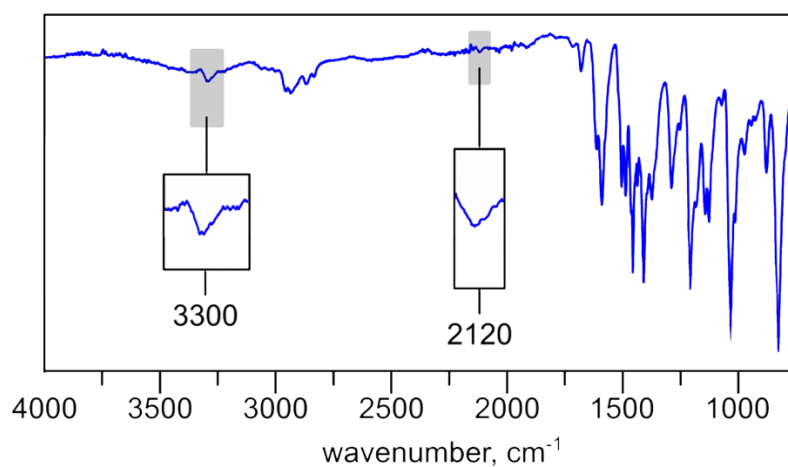


Figure 2. FTIR spectrum of COF, gray box highlights the $\text{C}\equiv\text{C}-\text{H}$ resonance at 3300 cm^{-1} .

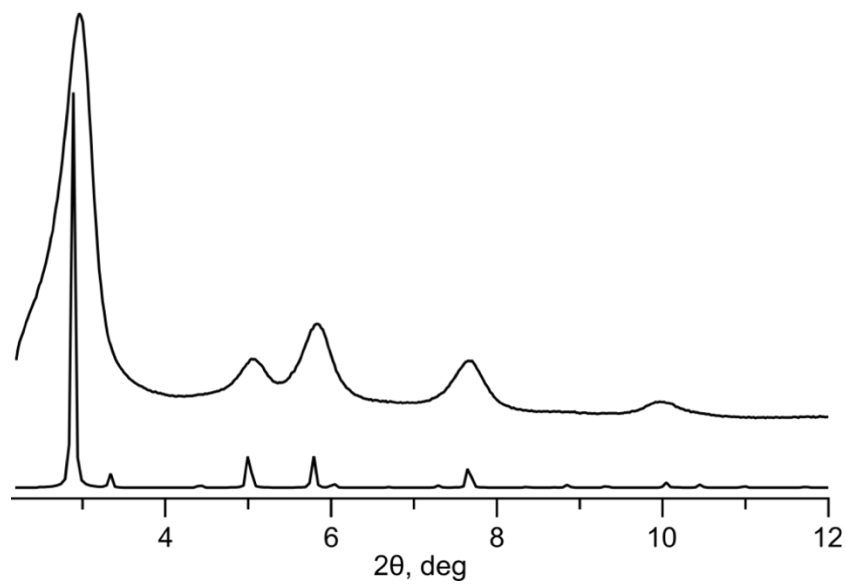


Figure 3. PXRD pattern of COF (*top*) and simulated (*bottom*).

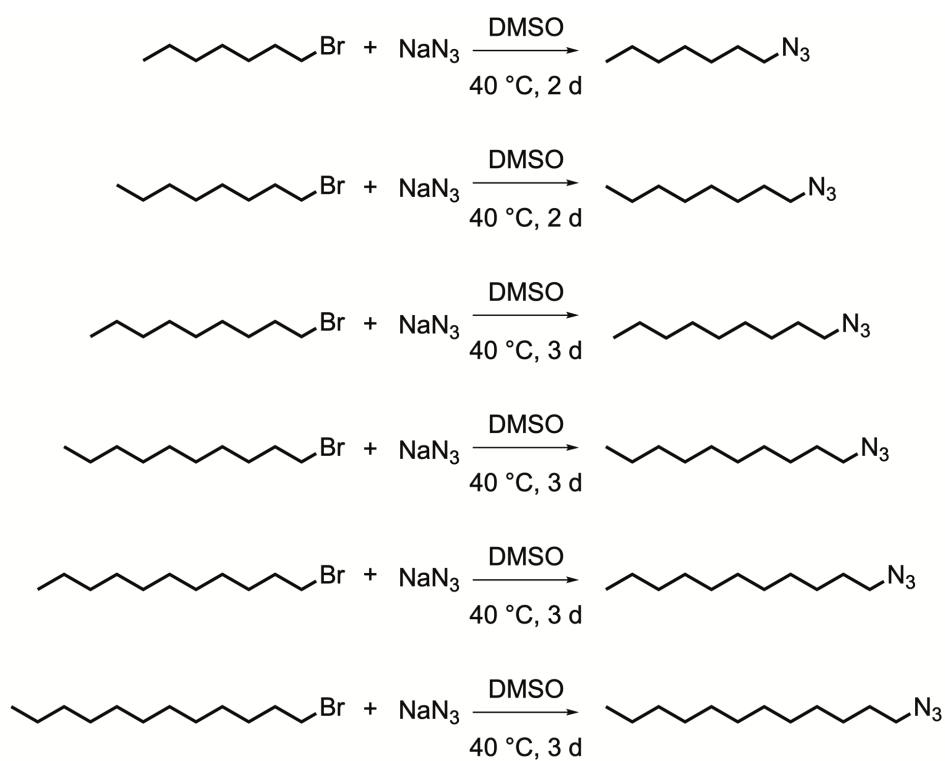


Figure 4. Synthetic route for preparing the azide-containing hydrogen rich molecules.

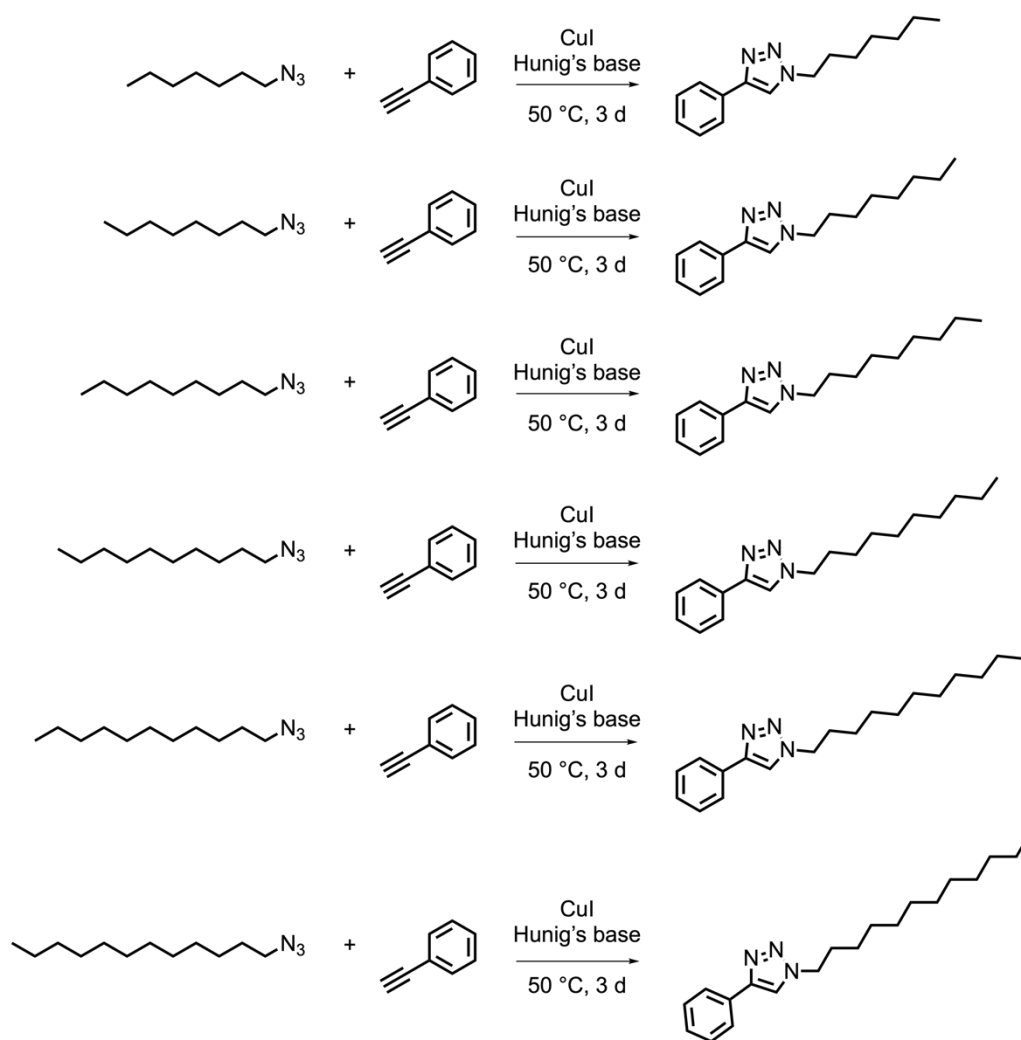


Figure 5. Copper-catalyzed azide-alkyne cycloaddition of the hydrogen-rich azide-based molecules and phenyl acetylene to perform a "molecular click".

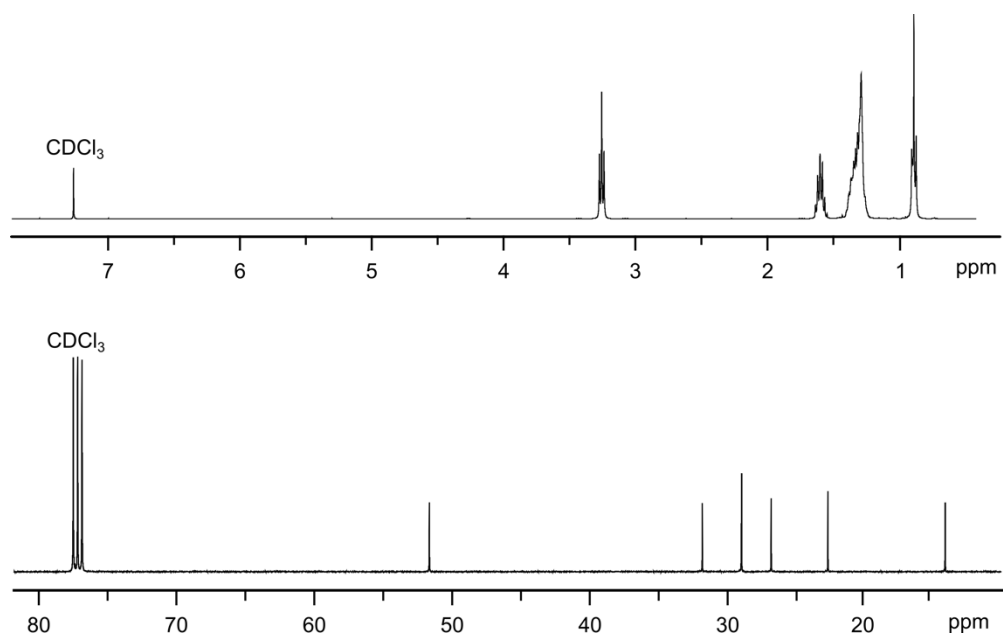


Figure 6. ^1H NMR (*top*) and ^{13}C NMR (*bottom*) spectra of 1-azidoheptane in CDCl_3 .

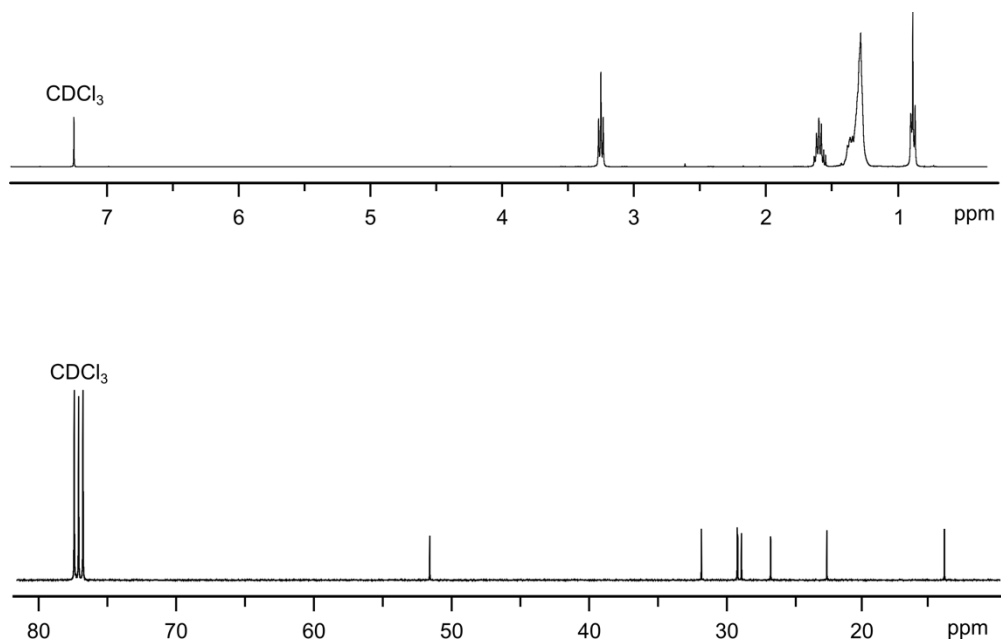


Figure 7. ^1H NMR (*top*) and ^{13}C NMR (*bottom*) spectra of 1-azidooctane in CDCl_3 .

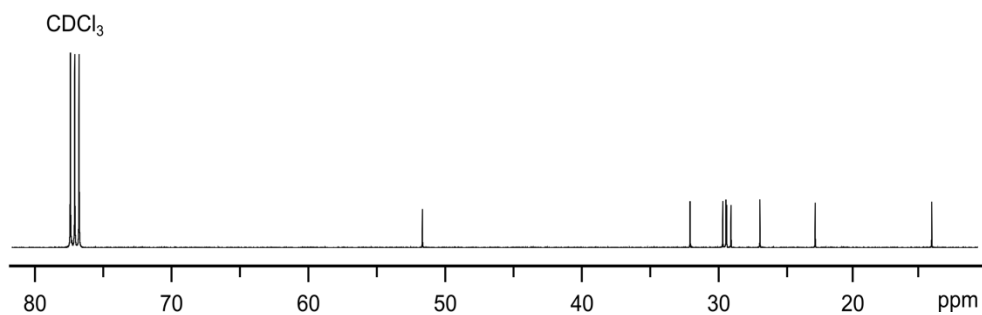
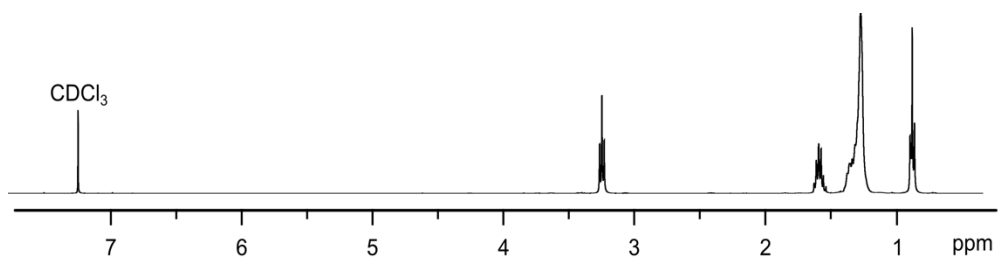


Figure 8. ^1H NMR (*top*) and ^{13}C NMR (*bottom*) spectra of 1-azidononane in CDCl_3 .

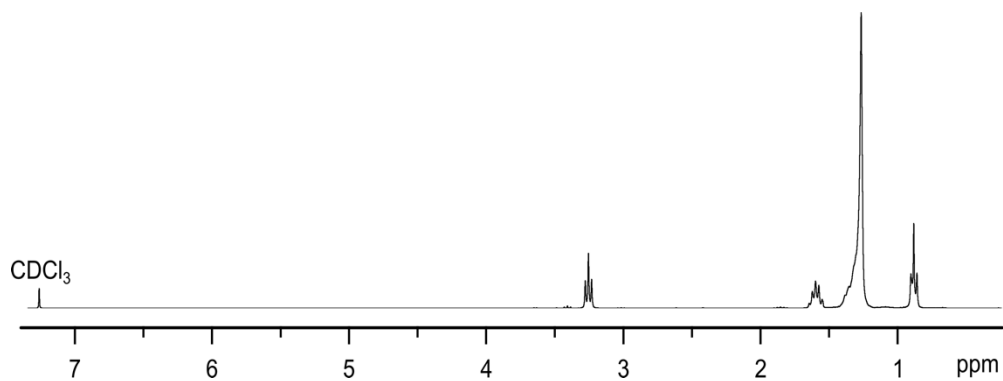


Figure 9. ^1H NMR (*top*) and ^{13}C NMR (*bottom*) spectra of 1-azidoundecane in CDCl_3 .

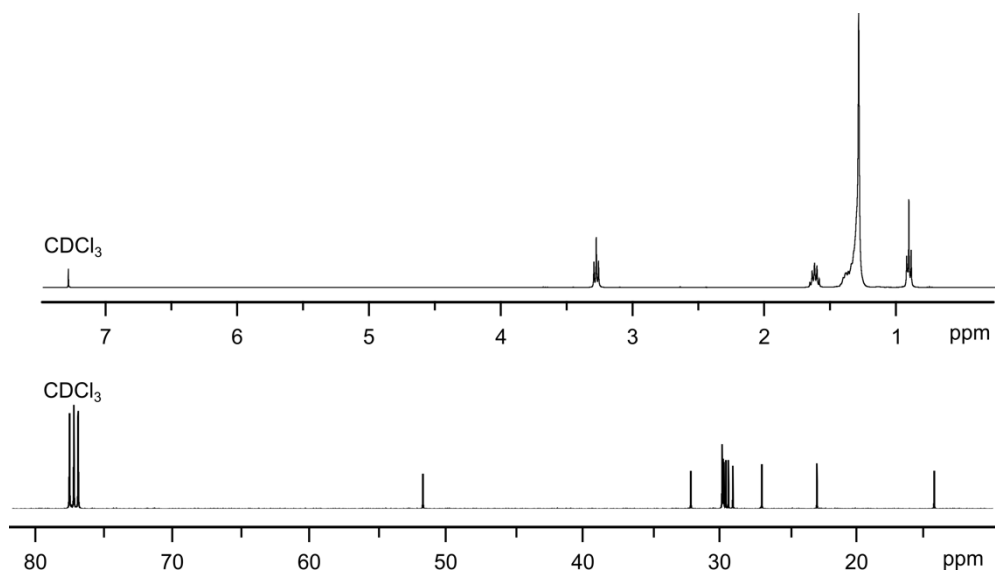


Figure 10. ^1H NMR (top) and ^{13}C NMR (bottom) spectra of 1-azidododecane in CDCl_3 .

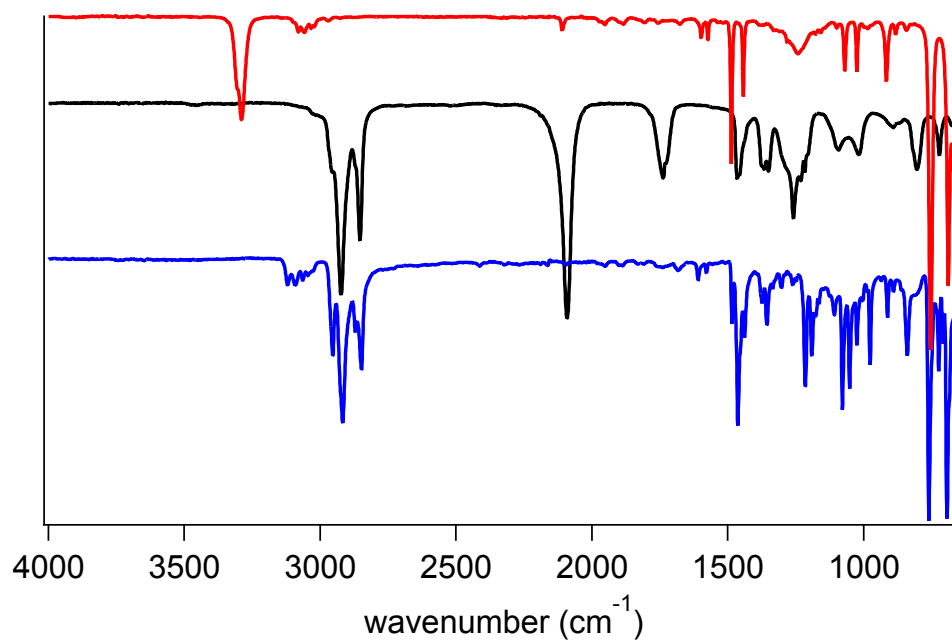


Figure 11. FTIR spectrum of (red) phenyl acetylene, (black) 1-azidododecane, and (blue) 1-dodecyl-4-phenyl-1H-1,2,3-triazole.

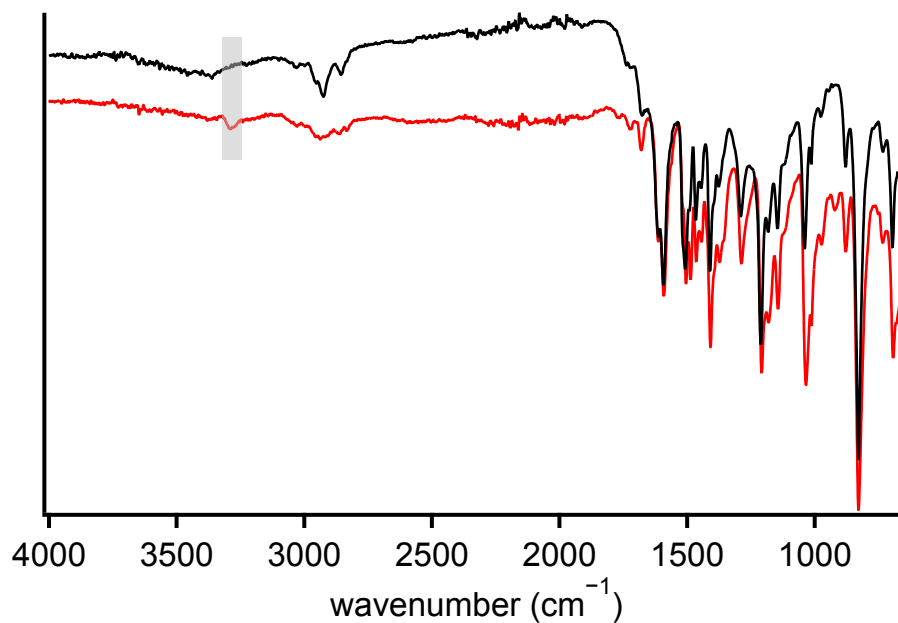


Figure 12. FTIR spectrum of (*red*) COF and (*black*) COF “clicked” with 1-azidododecane $-(\text{CH}_2)_n$, where $n = 12$. Gray box highlights the $\text{C}\equiv\text{C}-\text{H}$ resonance at 3300 cm^{-1} that is present in the red sample and is absent in the black sample.