Dehydrogenative homocoupling of tetrafluorobenzene on Pd(111) via para-selective C–H activation†

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Aryl homocoupling reactions via meta- and ortho-selective C–H activation have been achieved on surfaces, but the highly important para-selective C–H activation has not been reported yet. Combined with scanning tunneling microscopy, time-of-flight secondary ion mass spectrometry and density functional theory, here we describe dehydrogenative homocoupling of tetrafluorobenzene on Pd(111) via para-selective C–H activation to form perfluorinated oligo-(p-phenylene).

C–H bond activation and functionalization is an extremely attractive synthetic method because this atom-economic pathway produces H₂ as the only by-product. Functionalization of the C–H bond instead of a prefunctionalization approach reduces the number of synthetic steps, providing an attractive alternative to classical coupling reactions. Over the past few decades, the development of C–H bond functionalization reactions in organic solution has experienced an explosion of creative advances in substrate and catalyst design to meet the challenges of selectivity and reactivity. Despite these advances, the selectivity for the aromatic C–H activation is still one of the most challenging topics in organic synthesis, due to the high bond dissociation energy of the C–H bond and the existence of multiple reaction sites. Nevertheless, direct C–H functionalization of polyfluorobenzenes has been achieved in solution in various cross-coupling reactions catalyzed by transition metals, affording versatile perfluorine-containing compounds useful as pharmaceuticals, agrochemicals and organic functional materials.

After the pioneering work by Grill et al. in 2007, on-surface reactions, which take place on solid surfaces under ultra-high vacuum (UHV), have attracted tremendous attention owing to their significant potential for fabrication of nanostructures and nanomaterials. In such processes, reactants, intermediates, and products of the organic reactions are all adsorbed on surfaces and the reactions proceed within a two-dimensional space. The synergy between the surface morphology and catalytic reactivity provides a unique approach for some inefficient reactions in solution to proceed efficiently on a surface.

Some coupling reactions have been investigated at atomic resolution on surfaces using scanning tunneling microscopy (STM), including Ullmann coupling of aryl halides, Glaser coupling of alkynes, homocoupling of terminal alkynyl bromides, dimerization of alkenes, decarboxylative polymerization, and cross coupling of porphyrin bromide with aryl bromide. Ullmann reactions of aryl halides and other aryl couplings have been used to generate diverse macro-molecular systems, including polymeric chains, hyperbranched oligomers, graphene ribbons, porous molecular networks, super honeycomb frameworks, and other structures.

Coupling of aryl compounds via C–H activation is preferable to Ullmann coupling of aryl halides because it produces H₂ as the only by-product, thereby avoiding halide contamination on the surface. Aryl coupling via C–H activation of benzene has been achieved on various surfaces with meta- and ortho-selectivity. However, the highly important para-selective C–H activation of benzene which can afford poly(para-phenylene) (PPP) has not been reported.

Conjugated polymer PPPs, consisting of phenylene rings sequentially connected at the 1- and 4-positions, have received considerable attention from both the academic and industrial communities due to their numerous applications in low-cost organic electronic devices such as light-emitting diodes, field-effect transistors, photodetectors, nonvolatile memory devices, batteries, supercapacitors, solar cells and thermoelectric generators. Perfluorinated PPPs have excellent electron-transport abilities and therefore work as efficient n-type semiconductors, which have been applied extensively in organic light-emitting diodes and field-effect transistors. Here we report for the first time the on-surface aryl homocoupling via para-selective C–H activation, using 1,2,4,5-tetrafluorobenzene...
monomers and a crystalline surface of Pd(111) to generate perfluorinated oligo(p-phenylene)s with good control over product length. The para-selectivity of the C–H activation originates from the different chemical properties of the C–H bond and C–F bond. This is a rare example of using the surface of Pd on-surface synthesis, although Pd is the most frequently used coupling catalyst in solution.

In a commercial UHV system (base pressure, \( \sim 3 \times 10^{-10} \) mbar) equipped with a variable-temperature STM (SPECs, Aarhus 150), 1,2,4,5-tetrafluorobenzene \( 1 \) was deposited (deposition condition: \( 1 \times 10^{-10} \) mbar) onto clean Pd(111) held at room temperature, and then annealed to 200 °C (Fig. 1). The STM analysis of the sample showed only the surface of Pd(111) and no coupling products were detected (scanning temperature: 110 K), indicating that the monomer desorbed from the surface. This result is coincident with the DFT calculation of the low adsorption energy (0.96 eV) for \( 1 \). Then we tried to deposit 1,2,4,5-tetrafluorobenzene \( 1 \) onto clean Pd(111) held at 160 °C for 15 min, followed by annealing to 200 °C for 15 min. STM images showed that short sticks formed on the Pd(111) surface (Fig. 2a), although the coverage of the product was rather low. Most sticks were 18.0 ± 0.2 Å long, consistent with the 18.0 Å predicted by density functional theory (DFT) calculations for perfluorinated quaterphenyl \( 2 \). These results suggest that four 1,2,4,5-tetrafluorobenzene molecules were coupled via C–H activation with para-selectivity to afford product \( 2 \) whose amount was over 90% on the surface. It is noteworthy that the sticks adsorbed along the [\( 1\overline{2}1 \)] or equivalent directions of the substrate were brighter than those adsorbed along the [\( 0\overline{1}1 \)] or equivalent directions, and the difference in the height between two kinds of sticks is about 0.5 Å (Fig. 2b). The reason for the impact of the adsorption direction on the STM appearances of the molecule is not clear at this stage. Some bent-chain by-products were observed, likely caused by radical migration. No organometallic intermediate containing a C–Pd–C moiety was observed.

To confirm the identity of product \( 2 \), ex situ time-of-flight secondary ion mass spectrometry (ToF-SIMS) was performed. The mass spectrum of negative ions with an \( m/z \) range from 240 to 660 amu is shown in Fig. 3. The peak at \( m/z = 592.95 \) amu corresponds to the quasi-molecular ion peak of \( 2 \) ([PhF4]2H2 [+M – H+], calculated value is 592.98). It is noteworthy that the peaks at \( m/z = 574.96 \) and 554.95 amu correspond to \([M – F]^- \) of 2 ([C24H2F15]–, [M – F]–, calculated value is 574.99) and \([M – HF – F]^- \) of 2 ([C24H2F14], [M – HF – F]–, calculated value is 554.99). The peaks at \( m/z = 444.96 \) and 296.98 amu correspond to the \([M – H]\) of terphenyl product ([PhF4]H2) (calculated \( m/z \) for \( C18H12F4 \): 444.99) and biphenyl product ([PhF4]H3) (calculated \( m/z \) for \( C12H8F8 \): 296.99), respectively.

These perfluorinated terphenyl and biphenyl products may have been generated as fragments via cleavage of \( 2 \) in the gas phase during mass spectrometry. Alternatively, they may have been produced from the coupling of 1,2,4,5-tetrafluorobenzene via C–H activation, but their high mobility made them invisible in STM. Due to these results, the C–F cleavage can be excluded because the quasi-molecular ion peaks of such products do not exist.

In order to obtain longer chains of perfluorinated poly(p-phenylene), 1,2,4,5-tetrafluorobenzene \( 1 \) was deposited (deposition condition: \( 5 \times 10^{-9} \) mbar) onto Pd(111), and the sample was annealed to 500 °C in 20 min and then cooled down (Fig. 4). Note that the chamber pressure was kept at \( 5 \times 10^{-9} \) mbar by dosing molecule \( 1 \) continuously throughout the annealing process and then dosing was shut off after the annealing. This ensured sufficient molecules of \( 1 \) on the surface despite the remarkable desorption from the hot surface.
STM showed that this procedure generated longer chains of 1 with 5–9 units through coupling via similar C–H activation with para-selectivity (Fig. 5). Chains with 7–8 units are predominant (60–70%) in all products. Chains grew primarily along the [011], [112], [101] and equivalent directions of the surface. The dim, stripe-like features in the centre of the image rather seem related to contamination due to the strong adsorption property of the surface of Pd(111). Once again, no organometallic intermediate containing C–Pd–C was observed.

To elucidate the mechanism of the homocoupling of 1,2,4,5-tetrafluorobenzene via para-selective C–H activation, we performed DFT calculations. The dehydrogenation reaction and the coupling of the resulting intermediate were analyzed using the climbing image nudged elastic band (CI-NEB) combined with the dimer method, as implemented in the plane wave-based Vienna ab initio simulation package (VASP).

The calculated reaction barrier ($E_{\text{barrier}}$) and reaction energy ($E_{\text{react}}$) for the dehydrogenation of 1,2,4,5-tetrafluorobenzene on Pd(111) were 1.51 eV and 1.06 eV (Fig. 6), which were comparable to the dehydrogenation of benzene on Cu(110).

The DFT-calculation of dehydrogenation of the dimer of 1,2,4,5-tetrafluorobenzene on Pd(111) gave an $E_{\text{barrier}}$ of 1.41 eV and $E_{\text{react}}$ of 0.88 eV (see the ESI, Fig. S2), although the calculation of the dehydrogenation of longer chains was not carried out due to the resource limitation. The results demonstrated that the growth of the dimer would also be smooth. The adsorption energy of the dimer was 1.03 eV and the similar calculated adsorption energies may indicate some reduced interaction of the dimer with the surface, presumably due to an interphenylene rotation ($34^\circ$).

In summary, we report a dehydrogenative coupling of 1,2,4,5-tetrafluorobenzene on Pd(111) to form perfluorinated oligo($p$-phenylene) chains as the first example of aryl homocoupling via para-selective C–H activation. Chain length can be varied by modifying reaction conditions. The reaction was studied at single-molecule resolution using UHV-STM as well.
as ToF-SIMS analysis. DFT calculations suggest that the reaction proceeds via dehydrogenation of 1,2,4,5-tetrafluorobenzene followed by coupling of the resulting intermediates. This reaction generates para-perfluorinated phenylenes which might be used as efficient n-type semiconductors, illustrating its potential usefulness for preparing electron-transporting organic materials in a two-dimensional space.

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Notes and references