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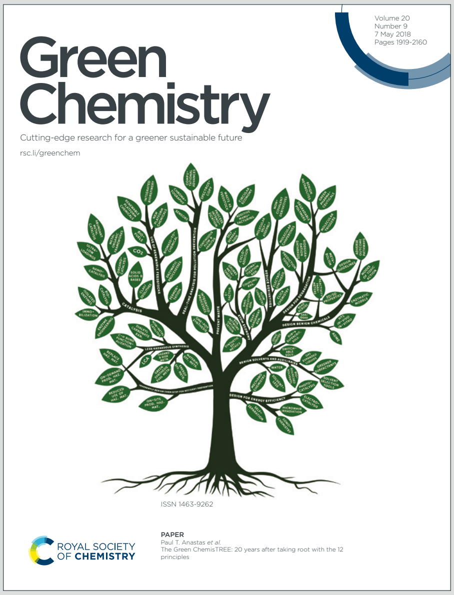

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Green foundation

1. Metal-organic frameworks (MOFs) could revolutionize supercapacitors and accelerate the renewable energy transition. To guide sustainable material development, this work provides the first life cycle assessment (LCA) of a conductive layered MOF, $Cu_3(HHTP)_2$.
2. This work finds that $Cu_3(HHTP)_2$ exhibits environmental impacts three to four orders of magnitude higher than a benchmark activated carbon electrode. We highlight promising future synthesis directions that incorporate green chemistry strategies such as prevention (reducing solvent waste via recycling or different washing procedures), safer solvents (replacing fluorinated and chlorinated solvents with greener alternatives), and atom economy (increasing yield in the HTTP linker synthesis).
3. Although the proposed synthesis modifications are expected to reduce environmental impacts, their practicality and effect on supercapacitor performance remain to be experimentally validated. Future research should also explore additional MOF families and novel synthetic methods, integrated alongside LCAs that incorporate supercapacitor performance.

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Life Cycle Assessment of a Layered Metal-Organic Framework for Supercapacitor Applications

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Abstract

Conductive layered metal-organic frameworks (MOFs) offer potential applications both as model research materials to study the electrode behaviour of fast-charging energy storage devices, and as an alternative electrode material in commercial supercapacitors. MOFs such as copper(II) 2,3,6,7,10,11-hexahydroxytriphenylene, $Cu_3(HHTP)_2$, have recently demonstrated competitive capacitive performance in supercapacitors, but their environmental implications are currently unknown. In this work, we perform a preliminary cradle-to-gate life cycle assessment to estimate the environmental impacts of lab-scale $Cu_3(HHTP)_2$ production and compare it to a benchmark activated carbon system. The environmental impacts of $Cu_3(HHTP)_2$ are found to be three to four orders of magnitude higher than activated carbon across all indicators. Hotspot and sensitivity analysis identifies solvent washing and linker production as key drivers and shows that modifying these steps could enable up to a two order of magnitude reduction in environmental impacts. These results suggest that finding new solvent-free methods for greener synthesis of conductive layered MOFs and significant improvements in capacitive performance relative to benchmark systems will be needed to enable sustainable application of these materials in commercial supercapacitor devices.

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1. Introduction

Supercapacitors are high-power energy storage devices that could support the transition to a renewable energy supply and electric transportation.[1,2] State-of-the-art supercapacitors utilise electrodes made from activated carbon, which are low-cost materials typically prepared from waste organic materials such as coconut shells.[3–7] However, the relatively low energy densities of supercapacitors compared to rechargeable batteries inhibit their wider uptake, and the highly disordered structures of activated carbon hinders an understanding of structure-property relationships which could otherwise aid their systematic optimisation (Figure S1a).[8] Hence, there is a developing interest in new electrode materials for supercapacitors with well-defined structures. One such promising family of materials is conductive layered metal-organic frameworks (MOFs), such as copper(II) 2,3,6,7,10,11-hexahydroxytriphenylene, $Cu_3(HHTP)_2$.[9–12] In addition to their ordered crystalline framework, which provides an ideal model for study of structure-performance relationships in electrochemical applications (Figure S1b), some systems have reported gravimetric capacitance comparable to conventional activated carbon electrodes and potential for commercial scale-up.[9–12] However, considerable research is still needed to optimise these materials to meet other electrochemical benchmarks critical for commercial applications, such as extended operating voltage windows, rate capabilities, and electrochemical cycling stability.[13] Whilst the capacitance values of MOFs at slow charging rates may be competitive in a laboratory setting (Figure S1), the potential of their scalability to higher voltage devices with competitive capacitance at high charging rates remains unclear.

Despite the proposed application of MOFs in electrochemical devices for a green energy transition, there has not yet been any work to assess the environmental impacts of these materials through life cycle assessment (LCA). Conducting LCA early in the research process makes it easier to improve energy technologies before they are deployed, reducing potential unintended consequences upon scaling.[14,15] However, in both the supercapacitor and MOF research fields, LCAs are notably lacking, with less than 0.001% of papers in these fields to-date publishing an LCA (Table S1). Existing LCAs have focused on the most commonly synthesised MOFs at laboratory scale, evaluated from cradle-to-gate (*i.e.*, from raw material extraction to synthesis, not including the eventual use and disposal of the produced MOFs).[16–23] Although no conductive MOFs have been analysed via LCA, there are some relevant findings for MOF syntheses in general. Namely, organic solvents have been found to dominate the environmental impacts of non-conductive MOFs, accounting for up to 90% of evaluated indicators.[16,18–20,22] Moreover, the solvents used in washing stages and MOF purification often account for a higher impact than the solvent used for synthesis itself.[20,22] The consumption of finite resources is also a key concern in MOF LCAs, particularly metal depletion due to the

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use of metal precursors, as well as fossil depletion from organic solvent use.[24] As such, solvent recycling has been shown to be essential in reducing impact of their synthesis.[25] On the other hand, room temperature and energy efficient synthetic routes have tended to be ineffective at reducing associated impacts, as the energy requirements of synthesis are typically overshadowed by those of solvent production.[21,22] The importance of solvent impacts therefore further motivates the need for an LCA study on the conductive layered MOF family, which is currently synthesised almost exclusively through solvothermal methods.[12,26,27]

Within the supercapacitor literature, many different supercapacitor compositions with varying electrodes and electrolytes have been reported, but few feature accompanying LCAs, even for the most common carbon-based electrode materials.[6,7] The contribution of the electrode to the overall impacts of commercial supercapacitor assembly varies dramatically depending on the selected material, in some cases accounting for the majority of a supercapacitor cell's impact.[6,7,28] For example, activated carbon from coconut shells has relatively low environmental impacts compared to reduced graphene oxide electrodes or biochar aerogel electrode sources, but offers minimal benefits relative to fossil-derived activated carbon.[6] Conventional beliefs about the lower environmental impact of aqueous electrolytes have also been challenged in recent LCA studies, which showed that an ionic liquid electrolyte supercapacitor system could achieve the same performance as an aqueous electrolyte supercapacitor with 60-80% lower carbon emissions and energy demands[29] Thus, there is clearly potential to reduce the impacts of supercapacitor systems through co-optimisation of electrode material preparation and supercapacitor performance.

In this work, a cradle-to-gate LCA for the layered MOF $Cu_3(HHTP)_2$ is conducted and compared to a benchmark supercapacitor electrode material, activated carbon. The analysis follows the hypothetical and optimistic assumptions that conductive layered MOFs are (i) electrochemically optimised and (ii) available at sufficient quantity and cost to effectively act as a direct replacement for carbon electrodes, on a gram for gram scale. A hotspot analysis is used to identify the most important contributions to the MOF's inflated impacts relative to the benchmark material across all environmental indicators. Potential opportunities to reduce these impacts are then assessed through sensitivity analysis, primarily exploring modifications in precursor synthesis and solvent use. These insights are key to understanding the potential impacts of MOFs at scale in commercial supercapacitor devices, as well as how the associated challenges might be addressed through synthetic modification.

2. Methods

The cradle-to-gate LCA compares the active electrode material for our supercapacitor system of interest, $Cu_3(HHTP)_2$ MOF (**Figure 1a**), against a benchmark activated carbon from the

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ecoinvent version 3.8 database (**Figure 1b**, see Tables S2-S4 for life cycle inventories and derivation details). The study focuses on comparing the impacts associated with the respective supercapacitor active electrode materials, as the electrode film formation process, cell construction, and components were considered to be identical across the MOF and activated carbon systems, as has been demonstrated in the literature.[7,12]

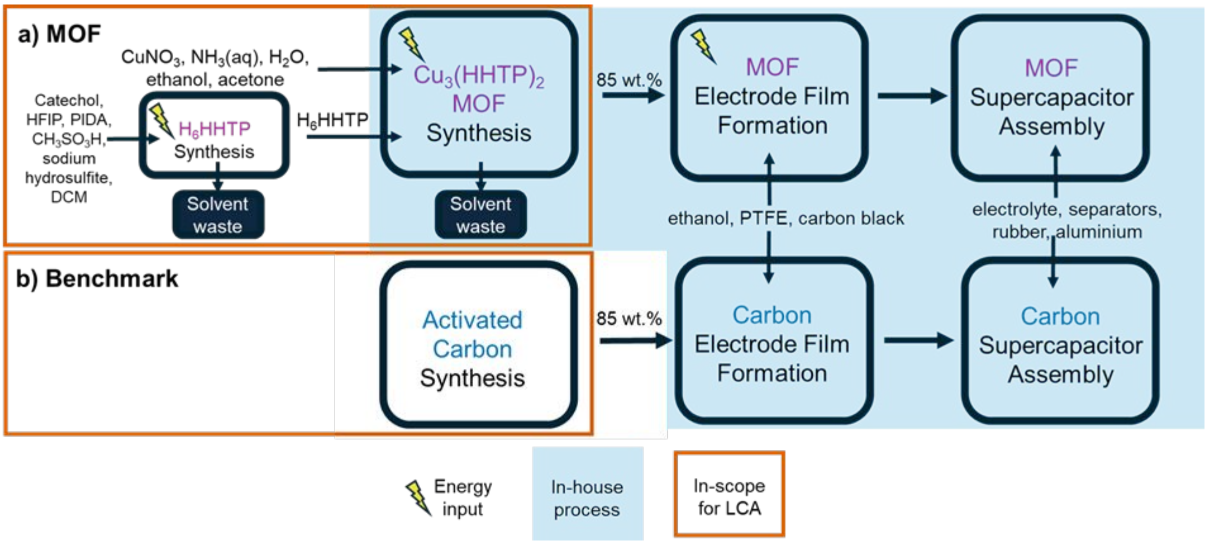

Figure 1: Flow diagram of supercapacitor assembly for the **a)** $Cu_3(HHTP)_2$ MOF system, synthesised in-house according to the reported literature and **b)** benchmark activated carbon system, from ecoinvent database, starting from their respective active electrode materials.[12] An additional LCA was necessary to account for the impact of the MOF linker's starting material, 2,3,6,7,10,11-hexahydroxytriphenylene (H_6HHTP), with this analysis based on the available literature.[30] As film formation and supercapacitor assembly is identical for both materials, these steps were excluded from the life-cycle assessment. The lightning bolt indicates energy consumption for the relevant steps.

A functional unit of a 5 F commercial supercapacitor was chosen, consistent with a previously reported LCA of an activated carbon supercapacitor.[7] As such, the life cycle inventories for the active electrode materials (Tables S1-S3) were developed based on the available literature and ecoinvent version 3.8. The mass of active electrode material required for a 5 F commercial supercapacitor was based on the previously reported activated carbon system, assuming an equivalent gravimetric capacitance for $Cu_3(HHTP)_2$ and activated carbon based on comparative studies of their performance at low current densities.[7] For $Cu_3(HHTP)_2$, the inventory was based on a scale-up of our in-house synthesis as previously reported.[12] The synthesis proceeds by moderately heating an aqueous solution of copper salt mixed with the hydrated linker starting material, 2,3,6,7,10,11-hexahydroxytriphenylene hydrate ($H_6HHTP.xH_2O$), in the presence of an ammonia solution that acts as a base to deprotonate the linker to HHTP and a modulator for MOF formation (**Figure 1a**).[31] Subsequently, the MOF is purified and separated by centrifuge solvent washing and vacuum filtration. The uncertainty of the inventory was approximated using the standard deviation of our in-house experimental yield (±6%) and used as a basis for Monte Carlo uncertainty analysis with 1,000 iterations.

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The production of the H_6HHTP starting material required the development of a separate life cycle inventory, which was based on a metal-free one-step synthesis under mild conditions, as reported in the literature (**Figure 1a**).[30] Proxies were used for several organic starting materials due to a lack of data availability in the ecoinvent database. Importantly, hexafluoroethane, as the only fluorinated small organic molecule available in ecoinvent, was used as proxy for hexafluoroisopropanol. However, it should be noted that this compound lacks the alcohol functionality of hexafluoroisopropanol and is a gas, rather than liquid, at room temperature and pressure, giving it significantly different properties. Phenyl acetic acid, a different oxygen-functionalised aromatic species, served as a proxy for (diacetoxyiodo)benzene. Both solid compounds are formed by single-step reactions from benzene derivatives but differ in functionality and reactivity as only (diacetoxyiodo)benzene is used as an oxidizing agent (full list of proxies in the Electronic Supplementary Information, ESI). In both cases, the proxies were selected for similarities in their production methods for the purpose of the LCA, rather than their viability in the reaction. Data for the benchmark activated carbon was directly extracted from the ecoinvent database.

Impact assessment was conducted using the ReCiPe 2016 hierarchist approach, with both endpoint and midpoint impacts considered. Endpoint indicators are broad areas of protection including (i) human health (in disability-adjusted loss of life years), (ii) the natural environment (in time-integrated species loss resulting in damage to ecosystem quality), and (iii) finite resource depletion (in surplus cost due to damage to resource availability), whereas midpoint indicators are individual environmental problems such as global warming potential or land use that contribute to those areas of protection.

3. Results and Discussion

An initial LCA of a complete 5 F commercial supercapacitor was performed and confirmed that the MOF electrode is expected to drive the environmental impacts of an assembled commercial supercapacitor (see Tables S5-S9 for life-cycle inventories), contributing ≥99.7% to all environmental impacts, of which the MOF material alone is responsible for at least 96% (Tables S10-S13). When comparing the electrode materials alone, LCA results across the three endpoint indicators show that the $Cu_3(HHTP)_2$ MOF system significantly exceeds the benchmark activated carbon system, by three orders of magnitude (**Figure 2a**). The top five midpoint impact contributions to these endpoint areas of protection include global warming potential (contributing significantly to impacts on human health and the natural environment); fine particulate matter formation (impacting human health); land use and terrestrial acidification (contributing to impacts on the natural environment); and fossil resource scarcity, (dominating the impact on finite resource depletion) (**Figure 2a**).

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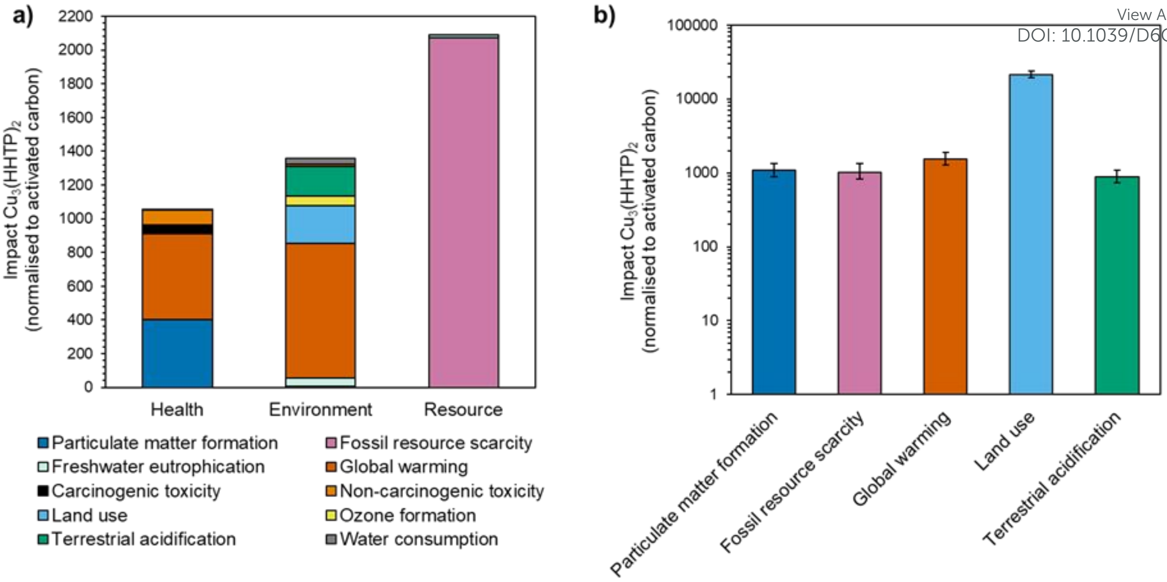

Figure 2: Life cycle impact assessment results for $Cu_3(HHTP)_2$, normalised relative to a benchmark carbon system **a)** Overall results from ReCiPe Endpoint (H), showing individual contributions of midpoint impacts to human health deterioration, environmental degradation, and finite resource depletion, respectively, relative to the endpoint impacts of activated carbon, which would be equal to one on this plot. The legend shows only midpoint impact contributions that account for >1% of the endpoint impact. **b)** Results from ReCiPe Midpoint (H) for the five most significant midpoint impacts, with error bars representing a 95% confidence interval determined from a Monte-Carlo uncertainty analysis with 1,000 iterations. A logarithmic scale is used to represent the scale of the impact, which is between 1,000 times and 100,000 times that of the relative midpoint impacts for the activated carbon benchmark. Note the different scales between figures arises from the different calculations for endpoint and midpoint impacts.

When assessing these five midpoint impact categories relative to the benchmark carbon system, every criterion is found to be three to four orders of magnitude larger for $Cu_3(HHTP)_2$ (**Figure 2b**). This trend is consistent across all 18 impact categories (Figure S2). We note that the activated carbon LCA comes from an industrially scaled process, compared to an in-house MOF synthesis, and so the benchmark would be expected to be significantly more energy efficient. However, given that energy efficiency has been previously found to be a minor factor in LCA compared to chemical inputs for MOF synthesis, we assume that this difference does not play a significant role, which is later verified (see **Figure 3**).[21,22] Moreover, the ecoinvent data for the activated carbon benchmark is coal-derived, whilst coconut-shell and other bio-derived carbons are commonly used for supercapacitor applications.[3–7] Thus, the impacts of the benchmark may vary compared to conventional supercapacitor electrodes. However, it has previously been reported that the variation between coal-derived and coconut-derived carbon is within an order of magnitude for all five highlighted impact categories except land use, for which the impact of coconut-derived carbon is significantly greater.[6] Given the multiple orders of magnitude difference between $Cu_3(HHTP)_2$ and the benchmark system, the potential variation across different sources of activated carbon is therefore expected to be insignificant relative to our findings.[6] Further, Monte Carlo uncertainty analysis with 1,000 iterations

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suggests that the results are expected to be statistically significant (**Figure 2b**, Figure S2).[32] The calculated environmental impacts of $Cu_3(HHTP)_2$, normalised by mass, are within the range of values reported by LCAs of other MOFs, albeit consistently at the higher end of the literature range.[22] These higher impacts likely result from the lower technology-readiness level of the layered MOFs studied here compared to the MOFs studied in previous LCAs, which are produced closer to a commercial scale and for which the synthesis has been more thoroughly optimised.

Although this analysis assumes a similar capacitive performance for the MOF as the benchmark based on previously reported gravimetric capacitances at low current densities, we note that (i) capacitance at low current density is not a true reflection of commercial supercapacitor operation (where high current densities are mostly commonly employed) and (ii) $Cu_3(HHTP)_2$ MOF shows lower capacitances than activated carbons at high current densities.[13,31] Consequently, our approximation overestimates the performance of the MOF electrode.[13] Additionally, MOFs have an inferior cycling stability in supercapacitors compared to activated carbons, and thus a future cradle-to-grave LCA that considers performance over the lifetime of the supercapacitor would likely exhibit even higher environmental impacts.[13] As such, this is a prospective LCA where the emerging MOF technology is modelled at a future, developed stage which is more technologically relevant.[33] Nevertheless, even under these optimistic conditions, the LCA results collectively demonstrate the significantly higher impacts of $Cu_3(HHTP)_2$ in comparison to a benchmark activated carbon material and thus motivate further consideration and improvement of the MOF electrode material's environmental performance.

To determine which components of the MOF synthesis contribute most to each environmental impact metric, hotspot analysis was conducted (**Figure 3a**).[34] Across the five key midpoint indicators identified above, the hotspot analysis shows that the top contributions originate from the (i) synthesis of the HHTP linker starting material (upstream impact), which accounts for 4-56% of each metric; (ii) production of solvents used for washing the MOF post-synthesis (upstream impact), including ethanol (1-94%) and acetone (1-51%); and (iii) incineration of hazardous spent solvent waste (downstream impact), which contributes 1-52%.[30] Acetone dominates fossil resource scarcity due to its reliance on fossil-derived propylene. The treatment of spent solvent dominates global warming as its incineration produces ~2 kg CO_2e per kg of waste combusted. Ethanol production dominates land use as it is derived from fermentation of a bio-based sugar feedstock. Meanwhile, the production of the HHTP linker starting material dominates both particulate matter formation and terrestrial acidification, the causes of which are explored in more detail later.

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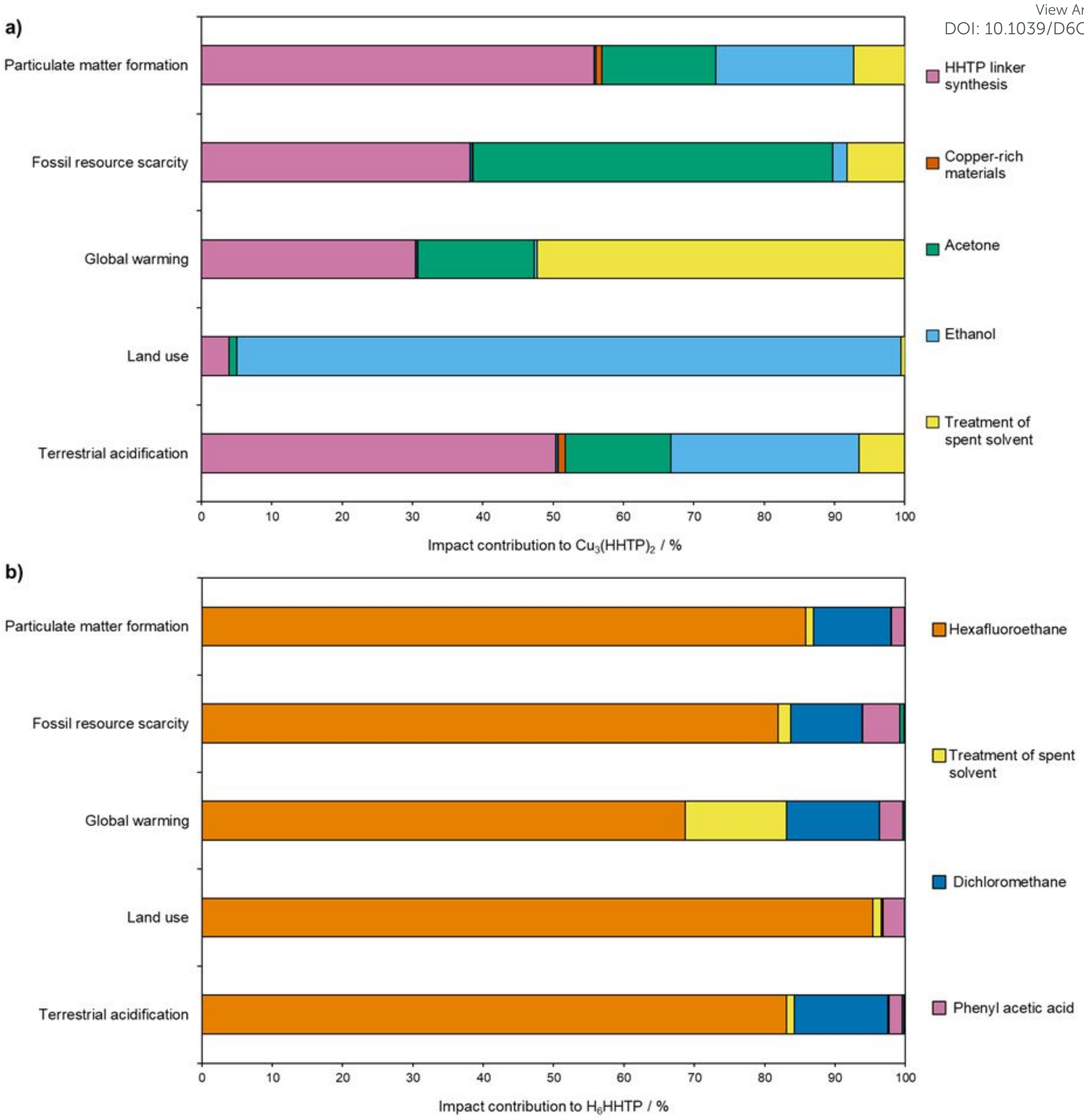

Figure 3: a) Hotspot analysis of select midpoint environmental impacts of the in-house $Cu_3(HHTP)_2$ MOF synthesis, and **b)** corresponding breakdown of impact contributions for H_6HHTP, the HHTP linker starting material LCA based on a literature synthesis.[30] For each, the legend lists impact contributions that are >1% of the total measured midpoint impact. See Figure S3 for full hotspot analysis.

The consumption of ethanol and acetone, at 1.1 kg and 1.7 kg per supercapacitor functional unit (containing 1.7 g of MOF), and the production of solvent waste, at 5.1 kg per functional unit, are inherently connected and controlled by the in-house MOF synthesis, with the majority arising from repeated centrifuge washing of the MOF.[31] The relatively high impact of this organic solvent washing is consistent with previous LCAs of MOF syntheses.[20,22] Previous work has reported >1000 L of solvent being used to scale-up a lab-scale MOF synthesis to

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1 kg, in line with the quantities reported here.[20] Even for more efficient commercial scale MOF syntheses, several hundred litres of solvent may be used to produce 1 kg of MOF.[22]

H_6HHTP, the HHTP linker starting material, is commercially purchased (though made at a relatively low commercial scale). Given its dominating impact (**Figure 3a**), detailed hotspot analysis of its production based on a synthesis from the literature was conducted to provide more insight (**Figure 3b**).[30] Across all five environmental categories, the measured impacts are dominated (69-95%) by the production of hexafluoroethane (the proxy for hexafluoroisopropanol), which is used as a solvent in the linker synthesis. Significant contributions are also associated with dichloromethane (the solvent used in washing the product, at 0-13%), phenyl acetic acid (the proxy for (diacetoxyiodo)benzene, a starting reagent, at 2-5%), and further treatment of the spent solvent waste (1-14%, **Figure 3b**).

Despite the clear conclusions which can be drawn from the overall hotspot analysis, namely that organic solvent use and waste are sizeable impact contributors, there are limitations within this assessment (**Figure 3**). The impact of the waste is attributed to output data from “spent solvent waste” treatment in the ecoinvent database. However, this generic waste stream contains several components that are not representative of the solvent waste from the in-house synthesis, which features only a limited number of constituents. Some of the impacts associated with this hazardous waste are therefore expected to be overestimated relative to the waste generated in-house. This overestimation likely only significantly impacts the global warming potential, as the contribution of waste treatment to other impact categories is minor. However, there is no suitable alternative in the database to assess the potential variation in impact of this hazardous liquid waste. This result may be considered an upper bound to waste solvent impacts in the absence of solvent recycling, which is explored later. Moreover, the LCA for the HHTP linker starting material is based on a reported literature synthesis with a relatively low yield (45%), which may not accurately reflect optimised commercial production.[30] Several chemicals identified in the hotspot analysis of this material, namely hexafluoroethane and phenyl acetic acid, are also proxies for the actual reagents, hexafluoroisopropanol and (diacetoxyiodo)benzene (see Table S4), due to limited data availability. Whilst the functionalities of the proxies differ slightly to those of the reagents, they are similar in their starting material precursors and compound size, so can be considered reasonable first approximations to their associated environmental impacts.[35] Furthermore, the quantity of dichloromethane used has been approximated, as the literature contained insufficient detail on volume. Additionally, as dichloromethane is used in washing, it can often be replaced with a greener solvent alternative.[36] Although the assumptions around these key contributors may have under- or over-estimated their true impacts, the hotspot analysis nevertheless offers some clear directions on where the MOF synthesis might be improved.

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Sensitivity analysis was performed to assess the potential to improve the in-house MOF synthesis as well as the linker precursor synthesis (**Figure 4**).[34] The hotspot analysis above clearly highlighted the key areas to improve MOF synthesis in-house were through minimisation of organic solvent consumption and solvent waste generation. Therefore, the following changes were considered in sensitivity analysis: (i) reducing and, in the extreme, eliminating centrifuge washing with organic solvent, and (ii) recycling ethanol and acetone from the solvent waste at a rate of up to 90% (**Figure 4a**).[37] The electricity required for solvent recovery was estimated by the embodied energy of the solvents to approximate the enthalpy for distillation.[38] Whilst this is likely a significant underestimation, it does not negate the key finding that electricity consumption remains an insignificant contribution to the impacts of synthesis relative to other factors.[39] As such, both strategies achieve reductions of between 34-95% and 37-86% respectively across all impact categories relative to the baseline LCA, as they simultaneously address the impacts of solvent consumption and organic waste production (**Figure 4a**). Additionally, there is potential to combine both reduced washing and solvent recovery in parallel, leading to an additional decrease of up to 17% in impact (see **Figure 5a**). However, eliminating the solvent washing of the MOF would likely compromise material quality and thus supercapacitor device performance. In particular, in-pore ion accessibility, which has been shown to correlate with gravimetric capacitance, may be inhibited by incomplete removal of impurities.[40] These trade-offs between performance and environmental impact require further investigation to test their practical feasibility. This would necessitate an experimentally-verified performance functional unit which accounts for differences in performance resulting from the proposed modified MOF synthesis route(s).

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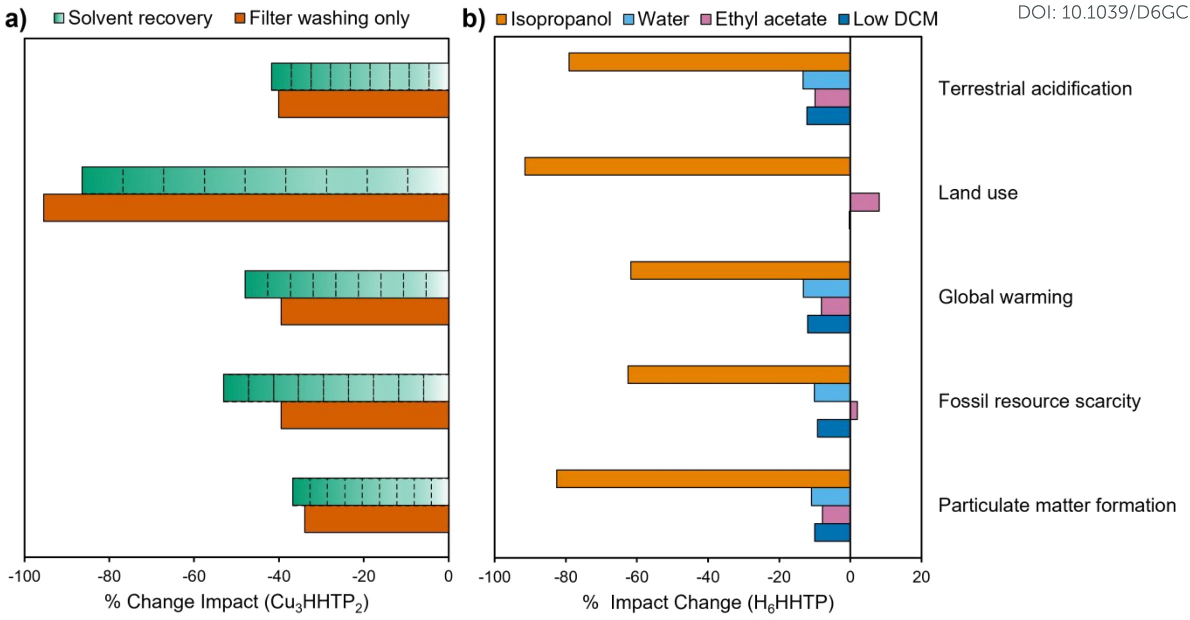

Figure 4: a) Tornado plot showing sensitivity analysis as a % change relative to the baseline LCA (Figure 2b) due to changing the way ethanol is used in the in-house $Cu_3(HHTP)_2$ synthesis, including (i) eliminating centrifuge washing entirely and only washing on a filter or solvent recycling of ethanol and acetone (optimistic case, 90% recovery rate in increments of 10% from lighter to darker green).[37] **b)** Tornado plot showing sensitivity analysis as a % change in midpoint impacts for H_6HHTP, the HHTP linker starting material, considering (i) replacing hexafluoroisopropanol with isopropanol, (ii) replacing dichloromethane (DCM) with water, (iii) replacing dichloromethane with ethyl acetate, or (iv) reducing the amount of dichloromethane by 90%. See Figures S4 and S5 for full results.

The second sensitivity analysis focussed on reducing the impact of the commercially synthesised HHTP linker starting material, H_6HHTP (**Figure 4b**), based on its hotspot analysis (**Figure 3b**). These hypothetical modifications employed greener alternatives to the most impactful organic solvents, including (i) using the un-fluorinated analogue of hexafluoroisopropanol, isopropanol; replacing dichloromethane with (ii) water, based on an alternative reported washing procedure, or (iii) ethyl acetate, a typical greener solvent alternative recommended by solvent selection guides due to its tower toxicity and environmental impact; or finally (iv) reducing the amount of dichloromethane used by up to 90%, given that its quantity was unreported in the literature (**Figure 4b**).[30,36,41] Substitution of hexafluoroisopropanol for isopropanol led to significant reductions of 60-90% across all impact categories, making it an effective strategy to reduce the overall impact of the linker starting material synthesis (**Figure 4b**, Figure S5). However, the fluorine functionality of hexafluoroisopropanol is related to its effectiveness as a solvent, making the feasibility of this change unlikely.[42] Replacing dichloromethane with water also had consistently beneficial effects, though more moderate in magnitude (~10% reduction, **Figure 4b**), aside from land

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use where it had no net effect. These impacts are similar in magnitude to the potential reduction of dichloromethane consumption to an approximated lower bound (**Figure 4b**).

Finally, replacement of dichloromethane with ethyl acetate successfully diminishes three of the key impacts by 8-10%, but gives rise to small increases of up to 8% across other metrics including land use and fossil resource scarcity (**Figure 4b**).[41] This is because ethyl acetate is synthesised from ethanol and acetic acid precursors. The ethanol is produced from fermentation of sugars contributing to increased land use, and acetic acid from methanol carbonylation contributing to fossil resource scarcity. The positive reductions from substitution of hexafluoroisopropanol and reduction or substitution of dichloromethane may also occur simultaneously, with additive effects (**Figure 4b**). Thus, there is potential that the overall impact of H_6HHTP synthesis may be reduced dramatically. It is also possible that this lower impact may in fact reflect the true linker production, depending on the current commercially used synthesis route.

From our sensitivity analysis above, routes to reduce the impacts of synthesising $Cu_3(HHTP)_2$ were identified. To test their combined potential effect on the overall MOF impact, we considered the LCA of a hypothetical improved synthesis route compared to the baseline LCA, both normalised relative to benchmark activated carbon (**Figure 5**). This optimistic improved synthesis combines (i) reduced organic solvent washing with (ii) an ambitious in-house ethanol and acetone recovery (90%), (iii) a MOF yield improvement from 77% to 83%, based on an upper observed in-house experimental yield, and (iv) an optimised H_6HHTP synthesis that uses isopropanol and water in place of hexafluoroisopropanol and dichloromethane and improves the yield from 45% to 65%, based on the maximum yield in the literature (**Figure 5a**).[30] Combining these changes enables environmental impact reductions of up to two orders of magnitude across all key midpoint metrics (**Figure 5a**). However, experimental validation is still needed to verify that this improved scenario can successfully produce the linker starting material and high-quality MOFs. As such, introducing only moderate, short-term improvements to the MOF and linker synthesis reduces the associated endpoint impacts by around half (**Figure 5b, second bars**). Whilst even the most optimistic scenario, which implements all considered changes, still leaves the overall MOF endpoint impacts two orders of magnitude higher than incumbent activated carbon (**Figure 5b, third bars**).

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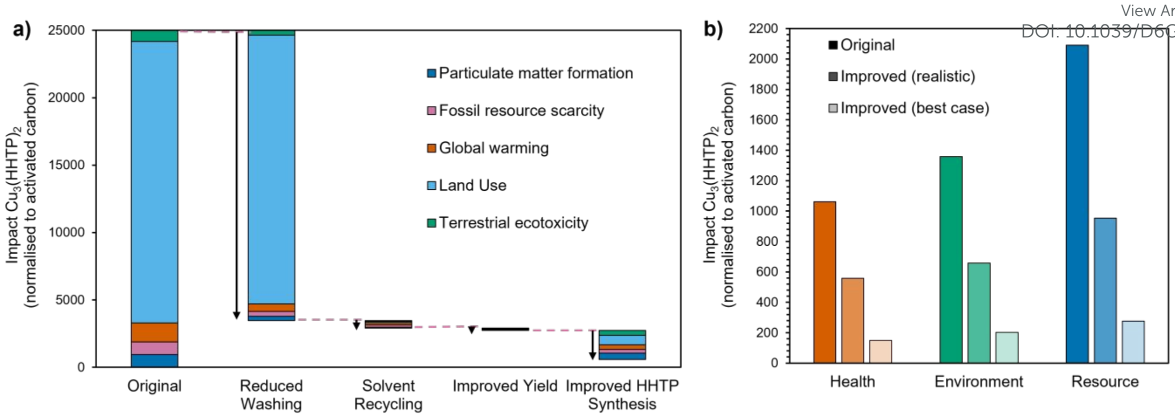

Figure 5: a) Stacked waterfall chart showing the effect of incremental synthesis improvements on the summed midpoint LCA impacts of $Cu_3(HHTP)_2$, normalised relative to benchmark activated carbon system. Improvements include (i) reduced washing with organic solvents, (ii) enhanced solvent recovery, (iii) an optimistic experimental yield, and (iv) improved HHTP linker starting material synthesis. For each consecutive modification, the top of the bar indicates the impact before that modification, and the bottom of the bar indicates the impact after the modification, with the length of the bar and size of the arrow indicating the magnitude of impact reduction. Modifications are cumulative. The breakdown of the bar shows the change in each midpoint factor, all normalised to the benchmark system. **b)** Results from ReCiPe Endpoint (H) LCA for human health deterioration, environmental degradation, and finite resource depletion relative to activated carbon for, from dark to light;the original (solid colour), moderately improved (realistic) and best-case improved (faded colour) $Cu_3(HHTP)_2$ synthesis (see Figure S6 for full results). The moderately improved scenario encompasses 50% reduced washing, 50% solvent recovery rate, improved yields based on experimental results for the MOF and HHTP linker starting material syntheses, and replacement of the dichloromethane in washing the linker material with water.

In summary, whilst modifications of the linker and MOF syntheses could lead to significant reductions in the impacts of $Cu_3(HHTP)_2$, additional changes will be necessary to synthesise layered MOFs that are environmentally competitive with the benchmark carbon system. Such alterations may include exploring entirely new MOF families, as well as new synthetic strategies where there is less need for purification. For example, for the MOF Zeolitic Imidazolate Framework-67, an extrusion synthesis was found to reduce impacts by 3-5 orders of magnitude relative to traditional synthesis methods when its LCA was considered at an industrial scale.[23] However, even solvent-free synthesis methods for MOFs, such as mechanosynthesis, often use organic solvents during purification.[43,44] Alternative MOF purification methods to centrifugation and filtration, such as calcination, solvent exchange, supercritical CO_2, freeze drying, microwave heating, ultrasound, UV/Vis (radical and photothermal processes), induction heating, and acid treatment are also either solvent intensive or unlikely to be feasible with $Cu_3(HHTP)_2$, which is relatively thermally unstable.[12,43,44] Further, whilst previous studies recommend commercially supplied linkers for reduced impact, the HHTP linker starting material is currently produced industrially at such small scale that its synthesis may be less efficient than other potential linkers.[45]

As these experimental variations are implemented, future LCAs should verify the resulting MOFs' environmental performance while also incorporating a number of additional

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considerations. First, the system boundary could be expanded to cradle-to-grave or cradle-to-cradle, thereby accounting for the impact of MOF disposal and potential recycling routes. Second, an experimentally-verified commercial supercapacitor performance-based functional unit should be considered. Given that layered MOFs have not been scaled to commercial supercapacitors and currently exhibit inferior lifetimes and performance compared to conventional carbon-based supercapacitors at high current densities, a revised performance functional unit would likely further amplify the relative impact of MOF electrodes.[13] Alternative functional units could also be evaluated, as conductive MOFs could be limited by (or benefit from) other performance characteristics such as stability in air, compatibility with aqueous electrolytes, or production cost. Looking forward, dramatic changes in synthetic methods, such as linkers which are produced at a larger commercial scale for new MOF families and solvent-free synthesis methods, as well as performance enhancements guided by LCA and other analysis techniques, will be required to transition MOFs toward becoming a scalable and viable alternative in supercapacitor applications.[16,23,45]

3. Conclusions

This is the first reported LCA of MOF supercapacitor electrode materials and as such provides insights into the potential opportunities and limitations for their scale-up from model electrode materials to commercial devices. The cradle-to-gate environmental impacts of $Cu_3(HHTP)_2$ were found to consistently be orders of magnitude higher than those approximated for an activated carbon incumbent, even when optimistically assuming identical performance between the devices. In line with LCAs of other MOFs, hotspot analysis identified that the largest contributions come from solvent use in washing the MOFs, solvent waste treatment, and production of the organic linker starting material.[16,18–20,22] Consequently, sensitivity analysis was used to assess hypothetical improvements related to changing solvent use and linker synthesis procedures. Despite up to 100-fold reductions, the environmental impacts of the MOF remained two orders of magnitude higher than activated carbon. Moreover, the experimental feasibility of these changes and their impact on MOF quality must still be assessed for trade-offs with electrochemical performance. The performance of new materials for supercapacitors should be considered alongside their full LCA from the outset of exploratory research to streamline their optimisation. At present, LCA suggests that MOF supercapacitors are not environmentally competitive with conventional activated carbon electrodes, although key innovations around synthetic procedures, guided by our LCA, such as solvent-free methods and new MOF families with linkers produced on a larger commercial scale could change these outcomes in the future. Nevertheless, MOFs remain a useful model supercapacitor electrode material to study the fundamentals of charge storage and inform the optimisation of other electrode materials toward a greener energy future.

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Author Contributions

C.J.B: Conceptualization, formal analysis, investigation, methodology, writing – original draft, writing – review & editing; A.C.F: Supervision, methodology, writing – review & editing ; T.U: Supervision, methodology, writing – review & editing.

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Supporting Information

Additional methodological details, supporting tables (Tables S1-S13), and supporting figures (Figures S1-S6).

Data availability

The data supporting this article have been included as part of the Electronic Supplementary Information.

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