Supplementary Information (SI) for Green Chemistry.

Supplementary Information

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

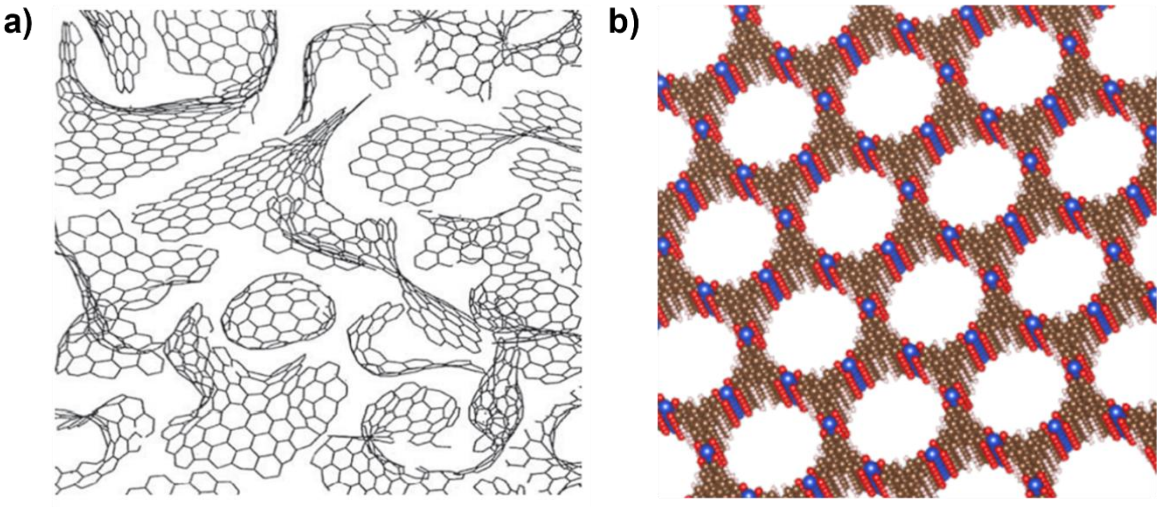
Chloe J. Balhatchet[1], Alexander C. Forse[1], Taylor Uekert[1*]

[1] Yusuf Hamied Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK.

* Contact: tmu22@cam.ac.uk

Table of Contents

Introduction to MOFs



Activated Carbon

- Commercial supercapacitor application
- Industrially produced
- Capacitance: 80-140 F g^{-1} at 0.05 A g^{-1}

Layered MOF $Cu_3(HHTP)_2$

- Lab-scale supercapacitor application
- mg-scale production
- Capacitance: 110 F g^{-1} at 0.05 A g^{-1}

This Work: Life-Cycle Assessment Comparison

- Benchmark material (ecoinvent database)
- Material under investigation

Figure S1: a) Schematic of activated carbon, conventionally used in commercial supercapacitors, which has a disordered amorphous structure. Figure from Harris.[1] Capacitance range for activated carbon from a number of sources, taken from Sheberla *et al.*[2] **b)** Layered MOFs have an ordered crystalline structure, with a well-defined pore size, example shown is $Cu_3(HHTP)_2$, HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene. Computer structure shared by Matthias Goulomb. Capacitance taken from Gittins *et al.*[3]

Topic	Number of Papers	% of total
"**Supercap**" + "Life Cycle Assessment"	>98,000 62	- 0.0006
"**MOF**" + "Life Cycle Assessment"	>136,000 37	- 0.0003
"**Supercap**" + "**MOF**" + "Life Cycle Assessment"	>3,400 0	- 0

Table S1: Number of mentions of "Life Cycle Assessment" in supercapacitor and MOF papers compared to total papers. From *webofknowledge database*. Accessed 30/01/2025.

Introduction to LCA Methods

ReCiPe 2016 is a state-of-the-art life cycle assessment (LCA) method which calculates 18 midpoint impact categories, such as global warming potential.[4] In this methodology, midpoint impacts can be combined into three endpoint impact categories: (i) the natural environment via time-integrated species loss resulting in damage to ecosystem quality; (ii) resource scarcity through surplus cost due to damage to resource availability; and (iii) human health through disability-adjusted loss of life years.

Using ReCiPe 2016, impacts can be considered with three different perspectives: 20-year (Individualist), 100-year (Hierarchist) or 1000-year-infinite (Egalitarian) timescales. Additional assumptions are associated with each of these methodologies.[5] The Individualist perspective (ReCiPe 2016 I) is based on short-term interests, including only undisputed impacts, and has an optimistic perspective with respect to human technological adaptation to impacts. The Hierarchist perspective (ReCiPe 2016 H) is based on scientific consensus, in terms of both impact timeframe and potential impact mechanisms. Finally, the Egalitarian perspective (ReCiPe 2016 E) is the most precautionary approach which considers all possible impact pathways and the longest possible time frame. This work follows the best scientific consensus using the Hierarchist approach, ReCiPe 2016 H.

Due to the approximations involved with data in the life cycle inventory, there is inherent uncertainty in the LCA results. Monte Carlo analysis is a commonly used method to quantitatively assess this by running repeated assessments using random input values within a specified probable range.[6] From the variation in output data, the effect of uncertainty in the input data on the output results can be measured, and a quantifiable uncertainty in the impact measurements produced.

Life Cycle Inventories

Background Data

All LCAs were conducted in OpenLCA using the ecoinvent database version 3.8.

Benchmark Life Cycle Inventory of Activated Carbon

Data were normalised relative to the LCA impacts of 1.7 g of activated carbon in the database using ReCiPe Midpoint (H) and ReCiPe Endpoint (H) as the impact assessment methods (**Table S2**).[4] Whilst the scale of the LCA considers one 1 x 5 F commercial supercapacitor, 10 wt.% of both carbon and MOF electrodes is made up of carbon black, and 5 wt.% PTFE so both of these contributions can be excluded here.[7] Hence, 1.7 g total is considered for all our active materials. As the ecoinvent database only has one type of activated carbon, this is assumed to be representative for supercapacitor electrode application. However, it has been shown that activated carbon from different sources can be associated with impacts of varying magnitude, with the ecoinvent coal-derived activated carbon compared to coconut-derived activated carbon by Glogic *et al.*; differences on average tend to average out when comparing between different impact categories.[7]

Designation	Item	Amount	Unit
consumable	activated carbon, granular	1.7	g

Table S2: LCA inventory for 1.7 g of activated carbon, the output of which was used for normalisation of other impacts relative to carbon.

Life Cycle Inventory for $Cu_3(HHTP)_2$

The life cycle inventory for the laboratory-scale synthesis of 1.7 g of copper(II) 2,3,6,7,10,11-hexahydroxytriphenylene, $Cu_3(HHTP)_2$, is given in **Table S3**, based on a literature synthesis from Gittins *et al.*[8] The data were used to produce the LCA with ReCiPe Midpoint (H) and ReCiPe Endpoint (H) as the impact assessment methods.[4] Further, a Monte Carlo analysis of 1000 iterations was used to conduct the uncertainty analysis. For this, the standard deviation of the experimental yield recorded in-house was used (±6%). Electricity calculations were based on the energy consumption ratings of lab equipment. In scaling the MOF synthesis reagents from the mg scale to achieve the required 1.7 g of active electrode material, the energy inputs were not scaled, as the same size of equipment was assumed to be applicable. The life cycle inventory for starting material 2,3,6,7,10,11-hexahydroxytriphenylene hydrate ($H_6HHTP.xH_2O$), with one-step linker synthesis from Morimoto *et al.*, is also given in **Table S4**, where the literature synthesis was already of a suitable scale.[9] Other approximations based on data availability are given below.

Designation	Item	Amount	Unit
consumable	acetone	1.7	kg
consumable	ammonia, anhydrous, liquid (approx. for 35% NH_3 solution)	11	g
consumable	copper-rich materials (approx. for $CuNO_3$)	1.9	g
utility	electricity, medium voltage	350	kWh
consumable	ethanol, without water, in 99.7% solution state, from fermentation	1.1	kg
consumable	H_6HHTP linker*	1.6	g
consumable	water, deionised	1.5	kg
waste output	spent solvent mixture	5.1	kg
output	$Cu_3(HHTP)_2$	1.7	g

Table S3: LCA inventory for 1.7 g of $Cu_3(HHTP)_2$ based Gittins *et al.*[10] *The H_6HHTP linker LCA inventory is in table **Table S4**. Substitutions are given in parentheses. Amounts are given to two significant figures.

Approximations due to lacking data entry:

- 35% ammonia solution approximated as ammonia
- Copper nitrate approximated by copper-rich materials

Designation	Item	Amount	Unit
consumable	hexafluoroethane (approx. for hexafluoroisopropanol)	420	g
consumable	phenyl acetic acid (approx. for (diacetoxyiodo)benzene)	33	g
consumable	o-aminophenol (approx. for catechol)	3.6	g
consumable	methane sulfonic acid	3.1	g
consumable	dichloromethane	210	g
consumable	sodium hydrogen sulfite	0.5	g
utility	electricity, medium voltage	2.1	kWh
waste output	spent solvent mixture	423	g
output	H_6HHTP	1.6	g

Table S4: LCA inventory for 1.6 g of the H_6HHTP linker, based on the synthesis from Morimoto *et al.*[9] Amounts are given to two significant figures.

Approximations due to lacking data entry:

- Hexafluoroisopropane approximated as hexafluoroethane
- (diacetoxyiodo)benzene approximated as phenyl acetic acid
- Catechol approximated as o-aminophenol

Approximations due to unknown quantities:

- Sodium hydrosulfite quantity approximated as 0.1 g per synthesis
- Solvent evaporation assumed to be on a rotary evaporator for six minutes
- Dichloromethane washing volume estimated as 100 mL per gram of product

Life Cycle Inventory for Assembled Commercial Supercapacitor

To validate the methodology of comparing the active electrode material of MOF and carbon electrodes, a full LCA of a commercial supercapacitor (based on those used by Cossutta *et al.*) employing MOF electrodes was compared to that with standard activated carbon electrodes.[11] Their respective life cycle inventories are given in **Table S5** and **Table S6**. **Table S7** and **Table S8** are the life cycle inventories for their constituent electrodes, following the procedure for composite MOF films published by Gittins *et al.*[10] **Table S9** gives the life cycle inventory for the organic electrolyte.

Designation	Item	Amount	Unit
consumable	MOF electrode*	2.0	g
consumable	synthetic rubber	0.57	g
consumable	metal working, average for aluminium product manufacturing	2.9	g
consumable	organic electrolyte**	1.6	g
consumable	battery separator	0.28	g
utility	electricity, medium voltage	0.41	MJ

Table S5: LCA inventory for a two-electrode commercial supercapacitor based on the inventory used by Cossutta *et al.*, with $Cu_3(HHTP)_2$-composite film electrodes of 1.0 g each.[11] *LCA inventory for MOF film is in **Table S8**. **LCA inventory for organic electrolyte is in **Table S9**. Amounts are given to two significant figures.

Designation	Item	Amount	Unit
consumable	Carbon electrode*	2.0	g
consumable	synthetic rubber	0.57	g
consumable	metal working, average for aluminium product manufacturing	2.9	g
consumable	organic electrolyte**	1.6	g
consumable	battery separator	0.28	g
utility	electricity, medium voltage	0.41	MJ

Table S6: LCA inventory for a two-electrode commercial supercapacitor based on the inventory used by Cossutta *et al.*, with activated carbon (ecoinvent) film electrodes of 1.0 g each.[11] *LCA inventory for carbon film is in **Table S8**. **LCA inventory for organic electrolyte is in **Table S9**. Amounts are given to two significant figures.

Designation	Item	Amount	Unit
consumable	$Cu_3(HHTP)_2$*	1.7	g
consumable	polyvinylfluoride, dispersion (approx. for PTFE binder)	0.1	g
consumable	carbon black	0.2	g
consumable	ethanol, without water, in 99.7% solution state, from fermentation	47	g
utility	electricity, medium voltage	240	kWh
output	MOF electrode	2.0	g

Table S7: LCA inventory for 85 wt.% $Cu_3(HHTP)_2$-composite film of total 2.0 g. *LCA inventory for $Cu_3(HHTP)_2$ is in **Table S3**. Substitutions are given in parentheses. Amounts are given to two significant figures where possible.

Designation	Item	Amount	Unit
consumable	activated carbon, granular	1.7	g
consumable	polyvinylfluoride, dispersion (approx. for PTFE binder)	0.1	g
consumable	carbon black	0.2	g
consumable	ethanol, without water, in 99.7% solution state, from fermentation	47	g
utility	electricity, medium voltage	240	kWh
output	Carbon electrode	2.0	g

Table S8: LCA inventory for 85 wt.% activated carbon-composite film of total 2.0 g. Substitutions are given in parentheses. Amounts are given to two significant figures where possible.

Designation	Item	Amount	Unit
consumable	sodium tetrafluoroborate (approx. for tetraethylammonium tetrafluoroborate)	0.39	g
consumable	acetonitrile	1.2	g
output	Organic electrolyte	1.6	g

Table S9: LCA inventory for 1.6 g of organic electrolyte, 1M tetraethylammonium tetrafluoroborate (NEt_4BF_4) in acetonitrile. Substitutions are given in parentheses. Amounts are given to two significant figures.

Life Cycle Assessment Results

		Activated Carbon Benchmark Supercapacitor Production		
	Unit	Impact	Electrode / %	Other / %
Fine particulate matter formation	kg PM2.5 eq	0.000246	89.1	10.9
Fossil resource scarcity	kg oil eq	0.0122	65.7	34.3
Freshwater ecotoxicity	kg 1,4-DCB	0.00266	33.7	66.3
Freshwater eutrophication	kg P eq	0.0000175	73.0	27.0
Global warming	kg CO2 eq	0.0347	56.8	43.2
Human carcinogenic toxicity	kg 1,4-DCB	0.00333	44.9	55.1
Human non-carcinogenic toxicity	kg 1,4-DCB	0.0627	70.9	29.1
Ionizing radiation	kBq Co-60 eq	0.00184	60.4	39.6
Land use	m2a crop eq	0.0652	99.7	0.3
Marine ecotoxicity	kg 1,4-DCB	0.00344	35.9	64.1
Marine eutrophication	kg N eq	0.000111	99.3	0.7
Mineral resource scarcity	kg Cu eq	0.000194	44.0	56.0
Ozone formation, Human health	kg NOx eq	0.000243	86.0	14.0
Ozone formation, Terrestrial ecosystems	kg NOx eq	0.000260	86.6	13.4
Stratospheric ozone depletion	kg CFC11 eq	0.000000419	98.9	1.1
Terrestrial acidification	kg SO2 eq	0.000795	92.8	7.2
Terrestrial ecotoxicity	kg 1,4-DCB	0.148	72.5	27.5
Water consumption	m3	0.00113	89.6	10.4

Table S10: Midpoint impact contributions of activated carbon electrode benchmark to supercapacitor.

	Unit	$Cu_3(HHTP)_2$ MOF Supercapacitor Production Impact	Electrode / %	Other / %
Fine particulate matter formation	kg PM2.5 eq	0.0228	99.9	0.1
Fossil resource scarcity	kg oil eq	3.67	99.9	0.1
Freshwater ecotoxicity	kg 1,4-DCB	0.597	99.7	0.3
Freshwater eutrophication	kg P eq	0.00445	99.9	0.1
Global warming	kg CO2 eq	19.1	99.9	0.1
Human carcinogenic toxicity	kg 1,4-DCB	0.543	99.7	0.3
Human non-carcinogenic toxicity	kg 1,4-DCB	12.8	99.9	0.1
Ionizing radiation	kBq Co-60 eq	0.645	99.9	0.1
Land use	m2a crop eq	1.65	100	0.0
Marine ecotoxicity	kg 1,4-DCB	0.784	99.7	0.3
Marine eutrophication	kg N eq	0.00356	100	0.0
Mineral resource scarcity	kg Cu eq	0.0430	99.7	0.3
Ozone formation, Human health	kg NOx eq	0.0297	99.9	0.1
Ozone formation, Terrestrial ecosystems	kg NOx eq	0.0317	99.9	0.1
Stratospheric ozone depletion	kg CFC11 eq	0.0000294	100	0.0
Terrestrial acidification	kg SO2 eq	0.0574	99.9	0.1
Terrestrial ecotoxicity	kg 1,4-DCB	58.8	99.9	0.1
Water consumption	m3	0.179	99.9	0.1

Table S11: Midpoint impact contributions of $Cu_3(HHTP)_2$ MOF electrode to MOF supercapacitor.

		Activated Carbon Benchmark Electrode Production	
	Unit	Carbon / %	Other / %
Fine particulate matter formation	kg PM2.5 eq	10.8	89.2
Fossil resource scarcity	kg oil eq	49.6	50.4
Freshwater ecotoxicity	kg 1,4-DCB	34.7	65.3
Freshwater eutrophication	kg P eq	61.9	38.1
Global warming	kg CO2 eq	68.1	31.9
Human carcinogenic toxicity	kg 1,4-DCB	40.3	59.7
Human non-carcinogenic toxicity	kg 1,4-DCB	37.4	62.6
Ionizing radiation	kBq Co-60 eq	66.4	33.6
Land use	m2a crop eq	0.1	99.9
Marine ecotoxicity	kg 1,4-DCB	34.8	65.2
Marine eutrophication	kg N eq	0.5	99.5
Mineral resource scarcity	kg Cu eq	6.5	93.5
Ozone formation, Human health	kg NOx eq	16.3	83.7
Ozone formation, Terrestrial ecosystems	kg NOx eq	15.2	84.8
Stratospheric ozone depletion	kg CFC11 eq	0.7	99.3
Terrestrial acidification	kg SO2 eq	9.6	90.4
Terrestrial ecotoxicity	kg 1,4-DCB	7.8	92.2
Water consumption	m3	3.3	96.7

Table S12: Midpoint impact contributions of activated carbon to benchmark electrode.

		$Cu_3(HHTP)_2$ MOF Electrode Production	
	Unit	MOF / %	Other / %
Fine particulate matter formation	kg PM2.5 eq	99.1	0.9
Fossil resource scarcity	kg oil eq	99.9	0.1
Freshwater ecotoxicity	kg 1,4-DCB	99.9	0.1
Freshwater eutrophication	kg P eq	99.9	0.1
Global warming	kg CO2 eq	100	0
Human carcinogenic toxicity	kg 1,4-DCB	99.8	0.2
Human non-carcinogenic toxicity	kg 1,4-DCB	99.8	0.2
Ionizing radiation	kBq Co-60 eq	99.9	0.1
Land use	m2a crop eq	96.1	3.9
Marine ecotoxicity	kg 1,4-DCB	99.9	0.1
Marine eutrophication	kg N eq	96.9	3.1
Mineral resource scarcity	kg Cu eq	99.8	0.2
Ozone formation, Human health	kg NOx eq	99.4	0.6
Ozone formation, Terrestrial ecosystems	kg NOx eq	99.4	0.6
Stratospheric ozone depletion	kg CFC11 eq	98.6	1.4
Terrestrial acidification	kg SO2 eq	98.8	1.2
Terrestrial ecotoxicity	kg 1,4-DCB	99.8	0.2
Water consumption	m3	99.5	0.5

Table S13: Midpoint impact contributions of $Cu_3(HHTP)_2$ MOF to MOF electrode.

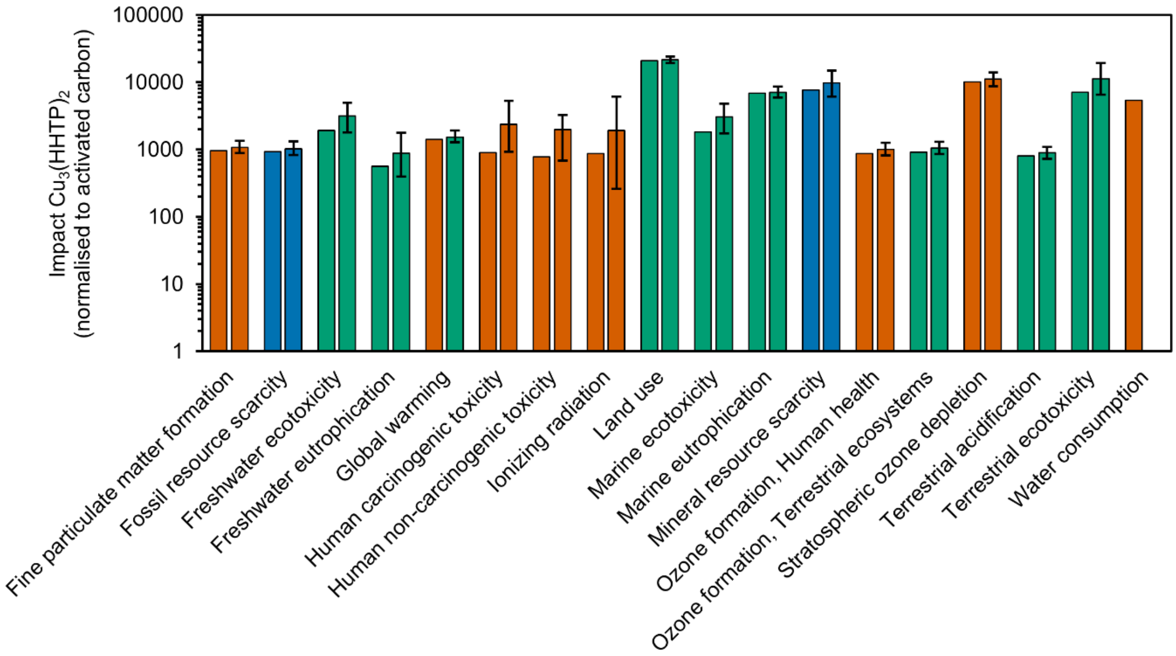


Figure S2: Life cycle assessment impacts of $Cu_3(HHTP)_2$, normalised relative to benchmark carbon system. A logarithmic scale is used to represent the scale of the impact, which is between 1000 times and 100,000 times that of carbon. The first bar for each impact category was determined by ReCiPe Midpoint (H) LCA, whilst the second bar is the average determined from a Monte-Carlo uncertainty analysis with error bars representing a 95% confidence interval (the methodology for water depletion gave an erroneous negative value through Monte-Carlo analysis due to systematic error in the software so is omitted).[4] Blue is indicative of resource impacts, green of environmental impacts and red health impacts.

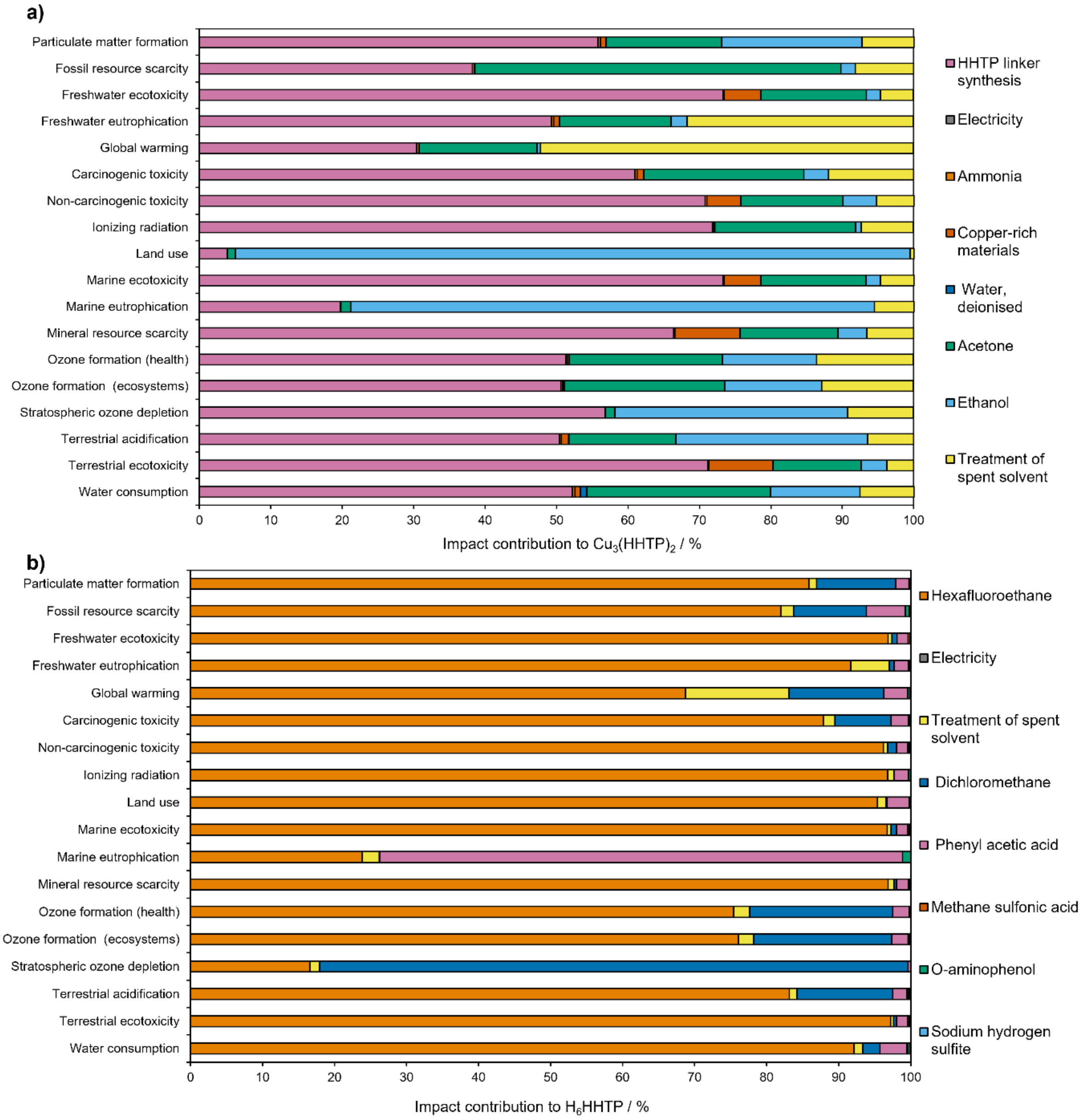


Figure S3: a) Hotspot analysis of midpoint impact contributions of the in-house $Cu_3(HHTP)_2$ MOF synthesis, and **b)** corresponding breakdown of impact contributions for the HHTP linker starting material LCA based on a literature synthesis.[12]

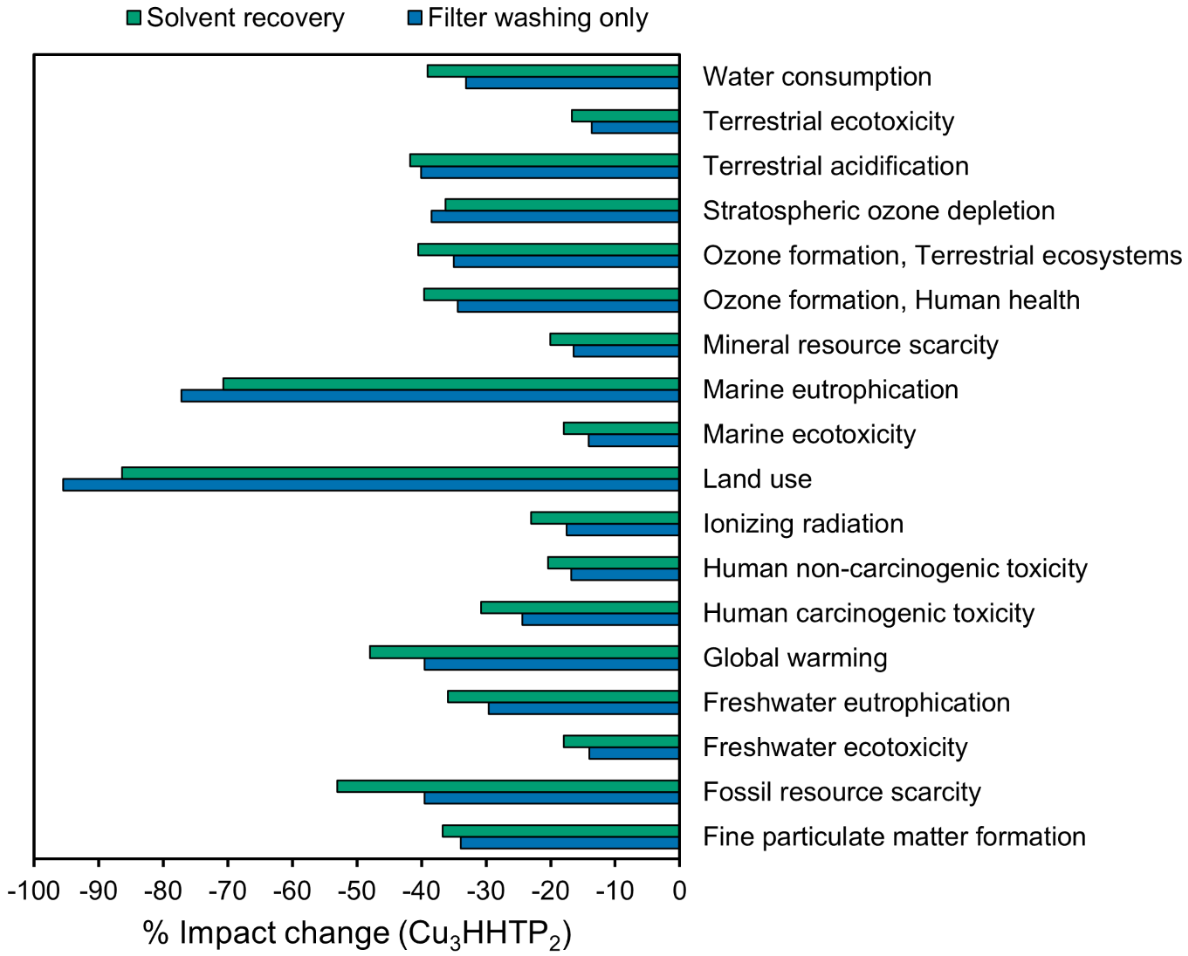


Figure S4: Tornado plot showing sensitivity analysis as a % change in midpoint impacts from changing the way ethanol is used in the in-house $Cu_3(HHTP)_2$ synthesis, considering (i) eliminating centrifuge washing entirely and only washing on the filter and (ii) solvent recycling of ethanol and acetone (optimistic case, 90% recovery rate).[13]

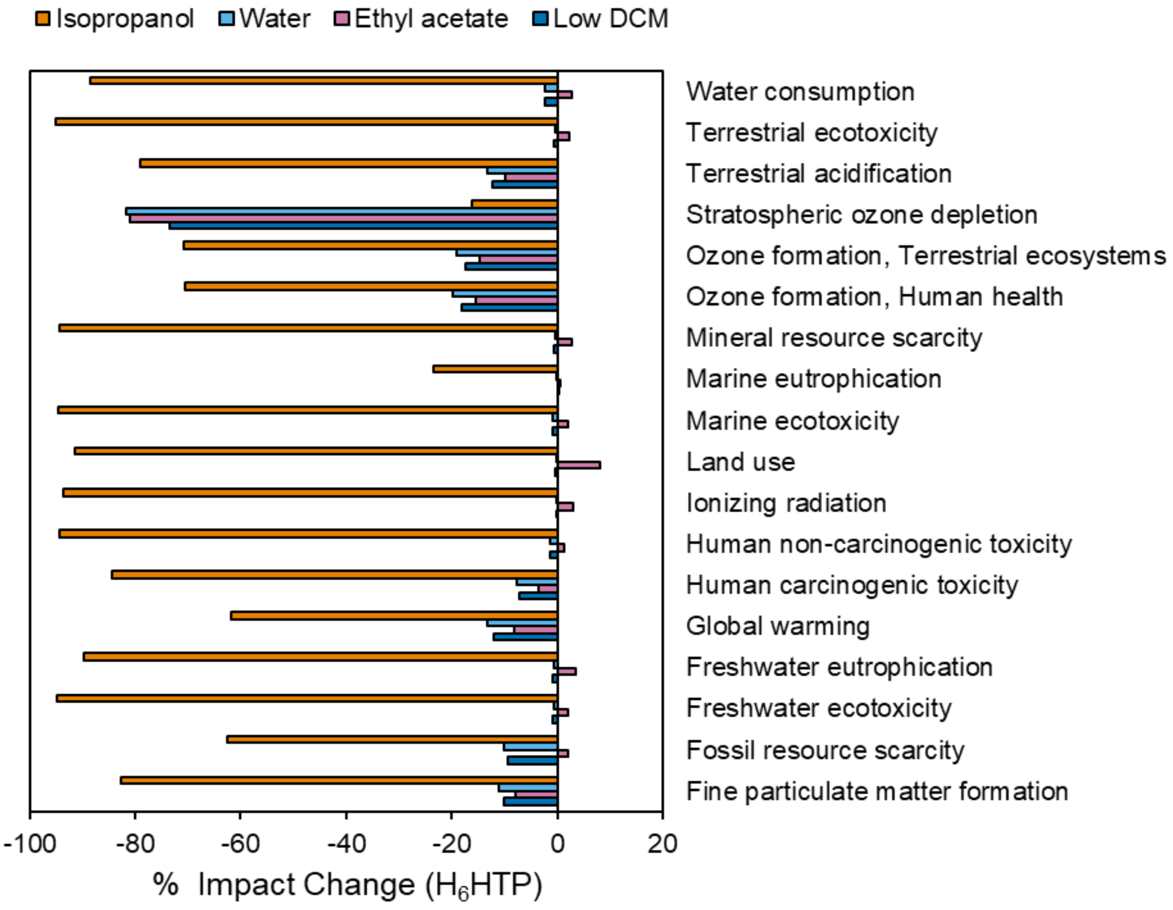


Figure S5: Tornado plot showing sensitivity analysis as a % change in midpoint impacts for the HHTP linker starting material, H_6HHTP, considering employing alternative solvents in its synthesis, water or ethyl acetate in place of dichloromethane (DCM), and isopropanol in place of hexafluoroisopropanol, or a 90% reduction in the quantity of dichloromethane.

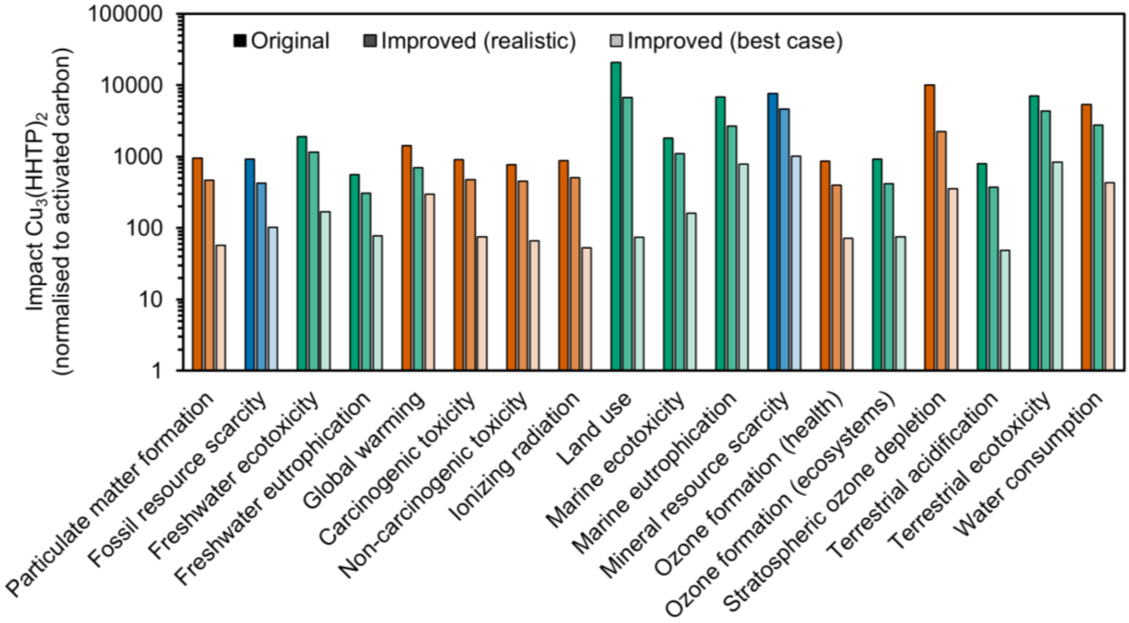


Figure S6: Life cycle assessment impacts of Cu_3(HHTP)$_2$ determined by ReCiPe Midpoint (H) LCA normalised relative to benchmark carbon system. A logarithmic scale is used to represent the scale of the impact, which is between 1000 times and 100,000 times that of carbon. The first bar is the original synthesis, with the results consistent with Figure S2. The second and third bars represent hypothetical moderately improved (realistic) and optimistic (best case) scenarios combining reduced washing, solvent recovery, higher yields and greener solvent used for the linker synthesis. Blue is indicative of finite resource depletion impacts, green of environmental degradation impacts and orange human health deterioration impacts, where global warming and water consumption contribute to two endpoint categories.

References

(1) Harris, P. J. F. Fullerene-like Models for Microporous Carbon. *J. Mater. Sci.* **2013**, *48* (2), 565–577. https://doi.org/10.1007/s10853-012-6788-1.

(2) Sheberla, D.; Bachman, J. C.; Elias, J. S.; Sun, C.-J.; Shao-Horn, Y.; Dincă, M. Conductive MOF Electrodes for Stable Supercapacitors with High Areal Capacitance. *Nat. Mater.* **2017**, *16* (2), 220–224. https://doi.org/10.1038/nmat4766.

(3) Gittins, J. W.; Balhatchet, C. J.; Chen, Y.; Liu, C.; Madden, D. G.; Britto, S.; Golomb, M. J.; Walsh, A.; Fairen-Jimenez, D.; Dutton, S. E.; Forse, A. C. Insights into the Electric Double-Layer Capacitance of Two-Dimensional Electrically Conductive Metal–Organic Frameworks. *J. Mater. Chem. A* **2021**, *9* (29), 16006–16015. https://doi.org/10.1039/D1TA04026J.

(4) Huijbregts, M. A. J.; Steinmann, Z. J. N.; Elshout, P. M. F.; Stam, G.; Verones, F.; Vieira, M.; Zijp, M.; Hollander, A.; Van Zelm, R. ReCiPe2016: A Harmonised Life Cycle Impact Assessment Method at Midpoint and Endpoint Level. *Int. J. Life Cycle Assess.* **2017**, *22* (2), 138–147. https://doi.org/10.1007/s11367-016-1246-y.

(5) Huijbregts, M. A. J.; Steinmann, Z. J. N.; Elshout, P. M. F.; Stam, G.; Verones, F.; Vieria, M. D. M.; Hollander, A.; Zijp, M.; Zelm, R. van. *ReCiPe 2016 A Harmonized Life Cycle Impact Assessment Method at Midpoint and Endpoint Level*; RIVM; I; National Institute for Public Health and the Environment: P.O. Box 1, 3720 BA, Bilthoven, The Netherlands, 2016. https://www.rivm.nl/bibliotheek/rapporten/2016-0104.pdf (accessed 2025-03-04).

(6) Raynolds, M.; Checkel, M. D.; Fraser, R. A. Application of Monte Carlo Analysis to Life Cycle Assessment. *J. Mater. Manuf.* **1999**, *108*, 1–9.

(7) Glogic, E.; Kamali, A. K.; Keppetipola, N. M.; Alonge, B.; Kumara, G. R. A.; Sonnemann, G.; Toupance, T.; Cojocaru, L. Life Cycle Assessment of Supercapacitor Electrodes Based on Activated Carbon from Coconut Shells. *ACS Sustain. Chem. Eng.* **2022**, *10* (46), 15025–15034. https://doi.org/10.1021/acssuschemeng.2c03239.

(8) Gittins, J. W.; Ge, K.; Balhatchet, C. J.; Taberna, P.-L.; Simon, P.; Forse, A. C. Understanding Electrolyte Ion Size Effects on the Performance of Conducting Metal–Organic Framework Supercapacitors. *J. Am. Chem. Soc.* **2024**, *146* (18), 12473–12484. https://doi.org/10.1021/jacs.4c00508.

(9) Morimoto, K.; Dohi, T.; Kita, Y. Oxidative Trimerization of Catechol to Hexahydroxytriphenylene. *Eur. J. Org. Chem.* **2013**, *2013* (9), 1659–1662. https://doi.org/10.1002/ejoc.201201515.

(10) Gittins, J. W.; Balhatchet, C. J.; Chen, Y.; Liu, C.; Madden, D. G.; Britto, S.; Golomb, M. J.; Walsh, A.; Fairen-Jimenez, D.; Dutton, S. E.; Forse, A. C. Insights into the Electric Double-Layer Capacitance of Two-Dimensional Electrically Conductive Metal–Organic Frameworks. *J. Mater. Chem. A* **2021**, *9* (29), 16006–16015. https://doi.org/10.1039/D1TA04026J.

(11) Cossutta, M.; Vretenar, V.; Centeno, T. A.; Kotrusz, P.; McKechnie, J.; Pickering, S. J. A Comparative Life Cycle Assessment of Graphene and Activated Carbon in a Supercapacitor Application. *J. Clean. Prod.* **2020**, *242*, 118468. https://doi.org/10.1016/j.jclepro.2019.118468.

(12) Morimoto, K.; Dohi, T.; Kita, Y. Oxidative Trimerization of Catechol to Hexahydroxytriphenylene. *Eur. J. Org. Chem.* **2013**, *2013* (9), 1659–1662. https://doi.org/10.1002/ejoc.201201515.

(13) Aboagye, E. A.; Chea, J. D.; Yenkie, K. M. Systems Level Roadmap for Solvent Recovery and Reuse in Industries. *iScience* **2021**, *24* (10), 103114. https://doi.org/10.1016/j.isci.2021.103114.