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SUPPORTING Information

Validating the “Greenness” of Chemicals via Life Cycle Assessment: The Case of Anisole as an Anti-solvent in Perovskite Solar Cells

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Synthesis of phenol from benzene (Industrial synthesis : 3 steps)¹

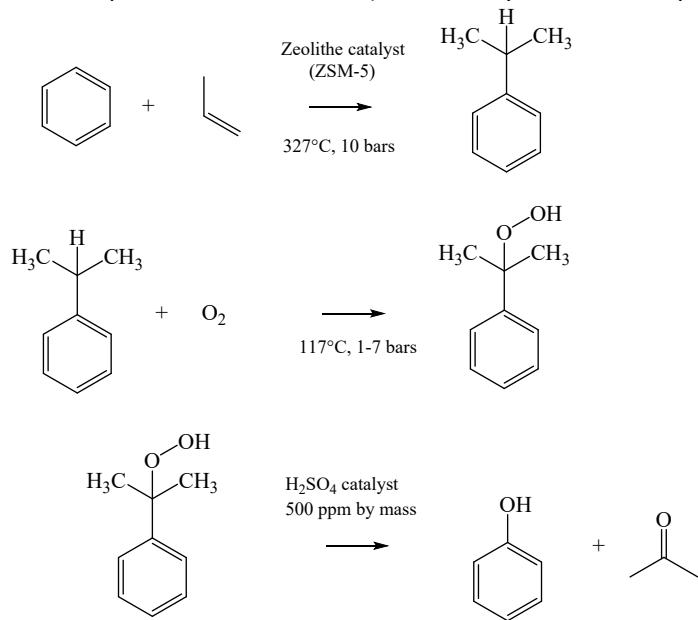


Table S1. Life cycle inventory for 1 kg of anisole produced in China represented by the rest-of-the-world region in the Ecoinvent database and transported to southern France for use in the laboratory synthesis of perovskite solar cells.²

Inputs	Quantity	Unit	Ecoinvent Dataset
Phenol	1.1750	kg	Phenol {RoW} market for phenol APOS, S
Sodium Hydroxide	0.5000	kg	Sodium hydroxide, without water, in 50% solution state {GLO} market for APOS, S
Water	5.0000	kg	Water, deionised {RoW} market for water, deionised APOS, S
Dimethyl Sulfate	0.7875	kg	Dimethyl sulfate {RoW} market for dimethyl sulfate APOS, S
Calcium Chloride	0.0125	kg	Calcium chloride {RoW} market for calcium chloride APOS, S
Benzene	0.0879	kg	Benzene {GLO} market for APOS, S
Transport	15.8704	tkm	Transport, freight, sea, container ship {GLO} market for transport, freight, sea, container ship APOS, S
Heating Energy	2.1665	MJ	Heat, district or industrial, natural gas {RoW} market for heat, district or industrial, natural gas APOS, S
Distillation Energy	0.3473	kWh	Electricity, medium voltage {CN} market group for APOS, S
Outputs	Quantity	Unit	Ecoinvent Dataset
Anisole	1	kg	N/A
Water	0.0050	m ³	Wastewater, average {RoW} market for wastewater, average APOS, S
Benzene	0.0879	kg	Benzene emission to water Unspecified
Phenol, treated	0.3023	kg	Process-specific burdens, hazardous waste incineration plant {RoW} market for process-specific burdens, hazardous waste incineration plant APOS, S
Phenol, waste	0.0024	kg	Phenol emission to water Unspecified
Sodium Hydroxide	0.1301	kg	Sodium Hydroxide emission to water Unspecified
Dimethyl Sulfate	0.2043	kg	Dimethyl Sulfate emission to water Unspecified
Sodium Sulfate	0.6584	kg	Sodium sulfate emission to water Unspecified
Water	0.1665	kg	Chemically Polluted Water emission to water Unspecified
Calcium chloride	0.0125	kg	Calcium chloride emission to water Unspecified
Anisole, end-of-life	1	kg	Methoxybenzene emission to air Unspecified

$$Q_{react} = \frac{Q_{heat} + Q_{loss}}{\eta_{heat}} = \frac{C_p \cdot m_{mix} \cdot (T_r - T_0) + A \cdot \frac{k_a}{s} \cdot (T_r - T_{out}) \cdot t}{\eta_{heat}} \quad (Equation S1)^3$$

Table S2. Characteristics of a 1000-liter reactor and parameters required to calculate heating energy during anisole synthesis according to equation S1.

Parameter	Symbol	Value	Unit
Surface area of the reactor	A	1.271	m^2
Insulation material glass fibre	κ_a	0.042	$W \cdot m^{-1} \cdot K^{-1}$
Insulation thickness	s	0.075	m
Efficiency of the heating device	η_{heat}	0.75	-
Final temperature	T_r	363	K
Room temperature	T_0	298	K
Time of the reaction	t	54000	s
Outside temperature	T_{out}	298	K

Table S3. Mass and specific heat capacities of precursor materials for anisole synthesis, the mass has been adjusted ensuring that the reactor is at 85% capacity.

Material	Mass (m) [kg]	Specific Heat Capacity (C _p) [J/kg*K]
<i>Anisole at 90 °C for 15 hours (133.89 kg is produced)</i>		
Phenol	157.32	2350.00
Sodium Hydroxide	66.94	59.52
Water	669.43	4184.00

$$R_{min} = \frac{1}{\alpha - 1} \left(\frac{X_{LD}}{X_{LF}} - \frac{\alpha(1 - X_{LD})}{1 - X_{LF}} \right) \quad (Equation S2)^3$$

$$Q_{dist} = \frac{Q_{heat} + Q_{vap} * (R + 1)}{\eta_{heat} - 0.1} = \frac{C_p m_{mix} (T_{boil} - T_0) + \Delta H_{vap} m_{dist} \cdot (1.2 R_{min} + 1)}{\eta_{heat} - 0.1} \quad (Equation S3)^3$$

Table S4. Parameters used for the calculation of the distillation energy consumed during anisole synthesis according to equation S2 and S3.

Parameter	Symbol	Value	Unit
Relative volatility of the solvents ⁴	α	1.94	-
Target purity of distillate (molar fraction)	X_{LD}	0.95	-
Molar fraction of target compound in feed	X_{LF}	0.62	-
Minimum reflux ratio	R_{min}	1.35	-
Enthalpy of vaporization	ΔH_{vap}	0.33	MJ/mol
Distillate mass	m_{dist}	1.09	kg
Heat of vaporization	Q_{vap}	0.36	MJ
Energy of distillation	Q_{dist}	1.36	MJ

Table S5. Life cycle inventory for 1 kg of monochlorobenzene produced in China represented by the rest-of-the-world region in the Ecoinvent database and transported to southern France for use in the laboratory synthesis of perovskite solar cells.

Inputs	Quantity	Unit	Ecoinvent Dataset
Monochlorobenzene	1.1750	kg	Monochlorobenzene {RoW} benzene chlorination APOS, S
Transport	0.5000	tkm	Transport, freight, sea, container ship {GLO} market for transport, freight, sea, container ship APOS, S
Outputs	Quantity	Unit	Ecoinvent Dataset
Monochlorobenzene, end-of-life	0.7875	kg	1,2-dichloro-benzene emission to air Unspecified

Materials characterization

X-ray diffraction (XRD) pattern of the perovskite films was acquired with a Bruker AXS diffractometer (D2 PHASER A26-X1-A2B0D3A) using a Cu anode ($\text{K}\alpha$ radiation). Surface characterization of powders and thin films was performed by X-ray photoelectron spectroscopy (XPS). A K-Alpha equipment (Thermo Fisher Scientific) with a monochromatized $\text{Al K}\alpha$ source ($h\nu = 1486.6$ eV) was used with an X-Ray spot size 200 μm in diameter. Perovskite thin films were stored and prepared in an N_2 glovebox on an XPS transfer modulus to avoid oxygen contamination. The full spectra (0–1100 eV) were recorded with a constant pass energy of 200 eV and high-resolution spectra were recorded with a constant pass energy of 40 eV.

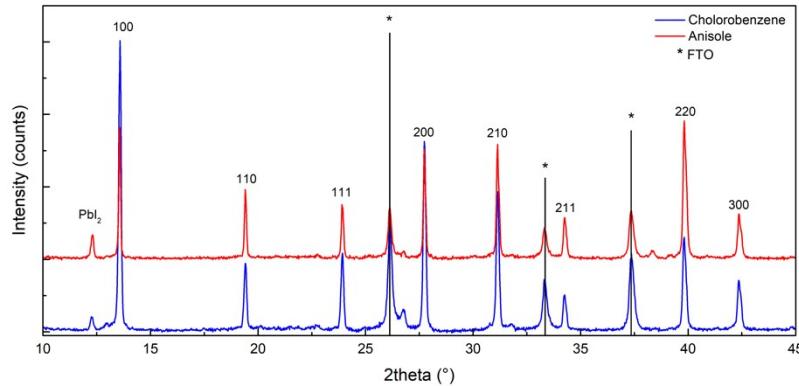


Figure S1. Comparison of the XRD pattern and intensities ratio of $\text{K}_{0.025}(\text{Cs}_{0.1}\text{FA}_{0.9})_{0.975}\text{PbI}_3$ film treated with chlorobenzene (blue line and dots) or anisole (red line and dots) antisolvents.

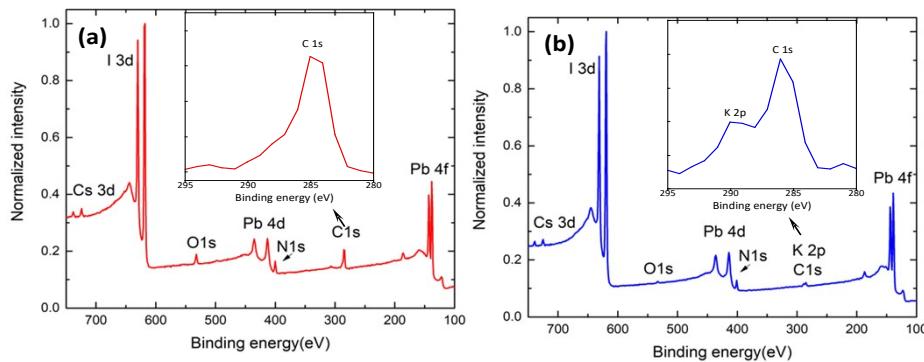


Figure S2. Comparison of the $\text{K}_{0.025}(\text{Cs}_{0.1}\text{FA}_{0.9})_{0.975}\text{PbI}_3$ surface XPS analysis of antisolvent treated films with (a) anisole, and (b) chlorobenzene.

Table S6. Atomic percentage detected on perovskite surface prepared using chlorobenzene and anisole as antisolvent.

Anti-solvents	Pb4f7	C1s	K2p	N1s	O1s	I3d5	Cs3d5
	Atomic percentage (%)						
Chloro-benzene	11.45	37.46	0.29	9.88	6.00	33.77	1.14
Anisole	6.99	54.17	0.00	7.03	11.2	20.15	0.48

Table S7. Photovoltaic parameters (forward scan of I-V curves) of $K_{0.025}(Cs_{0.1}FA_{0.9})_{0.975}PbI_3$ based solar cells using different amount of chlorobenzene and anisole as antisolvent.

Antisolvent	Amount of antisolvent, (μ L)	J_{sc} (mA cm $^{-2}$)	V_{oc} (V)	FF	Average PCE, (%)
Chlorobenzene	50	20.7 \pm 5.9	0.932 \pm 0.156	0.61 \pm 0.14	13.3 \pm 6.4
	100	20.6 \pm 7.9	0.832 \pm 0.339	0.56 \pm 0.21	12.2 \pm 8.6
	300	24.9 \pm 0.1	1.02 \pm 0.12	0.66 \pm 0.10	17.1 \pm 3.8
	500	24.9 \pm 0.46	1.06 \pm 0.01	0.71 \pm 0.02	18.8 \pm 0.6
Anisole	50	16.6 \pm 10.1	0.849 \pm 0.191	0.53 \pm 0.17	9.8 \pm 8.5
	100	25.9 \pm 0.1	1.06 \pm 0.01	0.73 \pm 0.01	20.0 \pm 0.3
	300	25.7 \pm 0.2	1.06 \pm 0.01	0.71 \pm 0.02	19.4 \pm 0.7
	500	25.6 \pm 0.2	1.06 \pm 0.01	0.74 \pm 0.02	20.1 \pm 0.5

Table S8. Life cycle impact assessment results of antisolvents: anisole (A) and chlorobenzene (C) compared on a 1-to-1 (1C), 1-to-2 (2C), 1-to-5 (5C) bases.

Impact Category	1A	1C	2C	5C	Unit
Human toxicity, cancer	1.85E-08	4.17E-08	8.34E-08	2.08E-07	CTUh
Human toxicity, non-cancer	1.15E-07	1.00E-07	2.00E-07	5.01E-07	CTUh
Ecotoxicity, freshwater	2.13E+02	3.74E+02	7.47E+02	1.87E+03	CTUe
Climate change	6.20E+00	2.83E+00	5.66E+00	1.41E+01	kg CO ₂ eq
Ionising radiation	3.16E-01	1.23E-01	2.46E-01	6.15E-01	kBq U-235 eq
Ozone depletion	6.93E-07	5.91E-07	1.18E-06	2.96E-06	kg CFC11 eq
Particulate matter	3.56E-07	1.83E-07	3.65E-07	9.13E-07	disease inc.
Photochemical ozone formation	2.78E-02	2.22E-02	4.43E-02	1.11E-01	kg NMVOC eq
Water use	4.27E+00	3.04E+00	6.08E+00	1.52E+01	m ³ depriv.
Acidification	4.13E-02	1.81E-02	3.63E-02	9.07E-02	mol H ⁺ eq
Eutrophication, marine	6.72E-03	3.52E-03	7.04E-03	1.76E-02	kg N eq
Eutrophication, freshwater	1.71E-03	7.00E-04	1.40E-03	3.50E-03	kg P eq
Eutrophication, terrestrial	7.09E-02	3.72E-02	7.45E-02	1.86E-01	mol N eq
Land use	1.47E+01	4.80E+00	9.61E+00	2.40E+01	Pt
Resource use, fossils	1.37E+02	6.84E+01	1.37E+02	3.42E+02	MJ
Resource use, minerals and metals	1.38E-04	1.25E-05	2.50E-05	6.24E-05	kg Sb eq

References:

- 1 <https://www.essentialchemicalindustry.org/chemicals/phenol.html>
- 2 G. S. Hiers and F. D. Hager, *Org. Syn.*, Coll. 1941, **1**, 58; 1929, **9**, 12.
- 3 F. Piccinno, R. Hischier, S. Seeger and C. Som, *J. Clean. Prod.*, 2016, **135**, 1085–1097.
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