Supplementary Information (SI) for RSC Sustainability.

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]

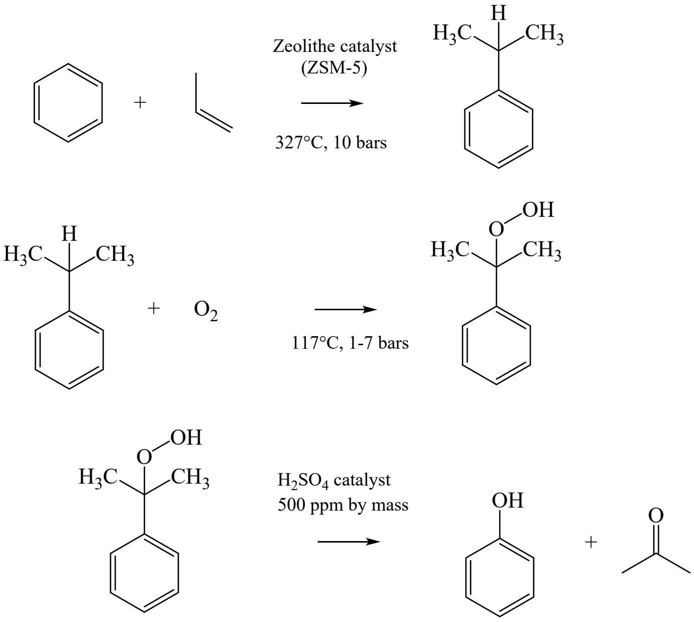

Table S1. Life cycle inventory for 1 kg of anisole produced in China represented by the rest-of-the-world region in the Ecoinvent database and transported to southern France for use in the laboratory synthesis of perovskite solar cells.[2]

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	0.0879	kg	Process-specific burdens, hazardous waste incineration plant {RoW}| market for process-specific burdens, hazardous waste incineration plant | APOS, S
Phenol, waste	0.3023	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

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

(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	k_a	0.042	$W \cdot m^{-1} \cdot K^{-1}$
Insulation thickness	s	0.075	m^2
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]**
Anisole at 90 °C for 15 hours (133.89 kg is produced)		
Phenol	157.32	2350.00
Sodium Hydroxide	66.94	59.52
Water	669.43	4184.00

$$R_{min} = \frac{1}{\alpha - 1}\left(\frac{X_{LD}}{X_{LF}} - \frac{\alpha(1 - X_{LD})}{1 - X_{LF}}\right)$$

(Equation S2)[3]

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

(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 (Kα 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 Al Kα source (hν = 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.

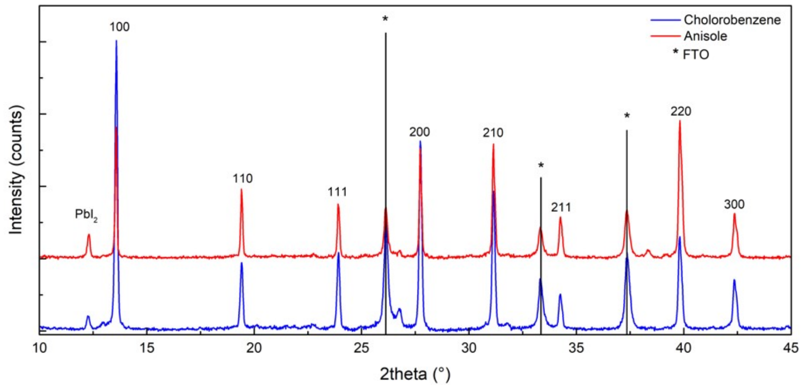

Figure S1. Comparison of the XRD pattern and intensities ratio of $K_{0.025}(Cs_{0.1}FA_{0.9})_{0.975}PbI_3$ film treated with chlorobenzene (blue line and dots) or anisole (red line and dots) antisolvents.

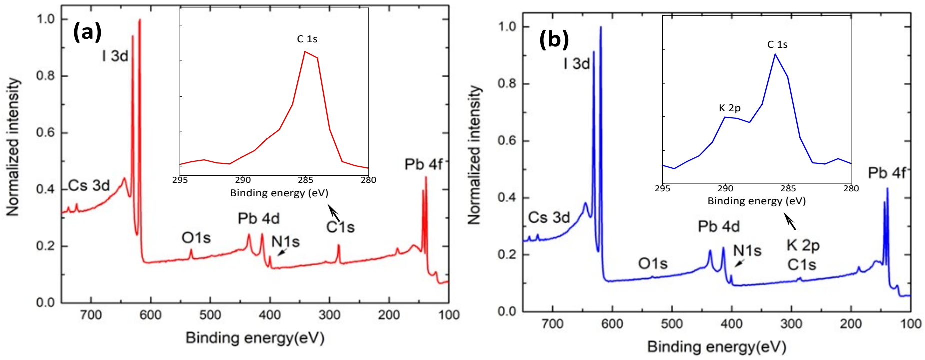

Figure S2. Comparison of the $K_{0.025}(Cs_{0.1}FA_{0.9})_{0.975}PbI_3$ surface XPS analysis of antisolvent treated films with (a) anisole, and (b) chlorobenzene.

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

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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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