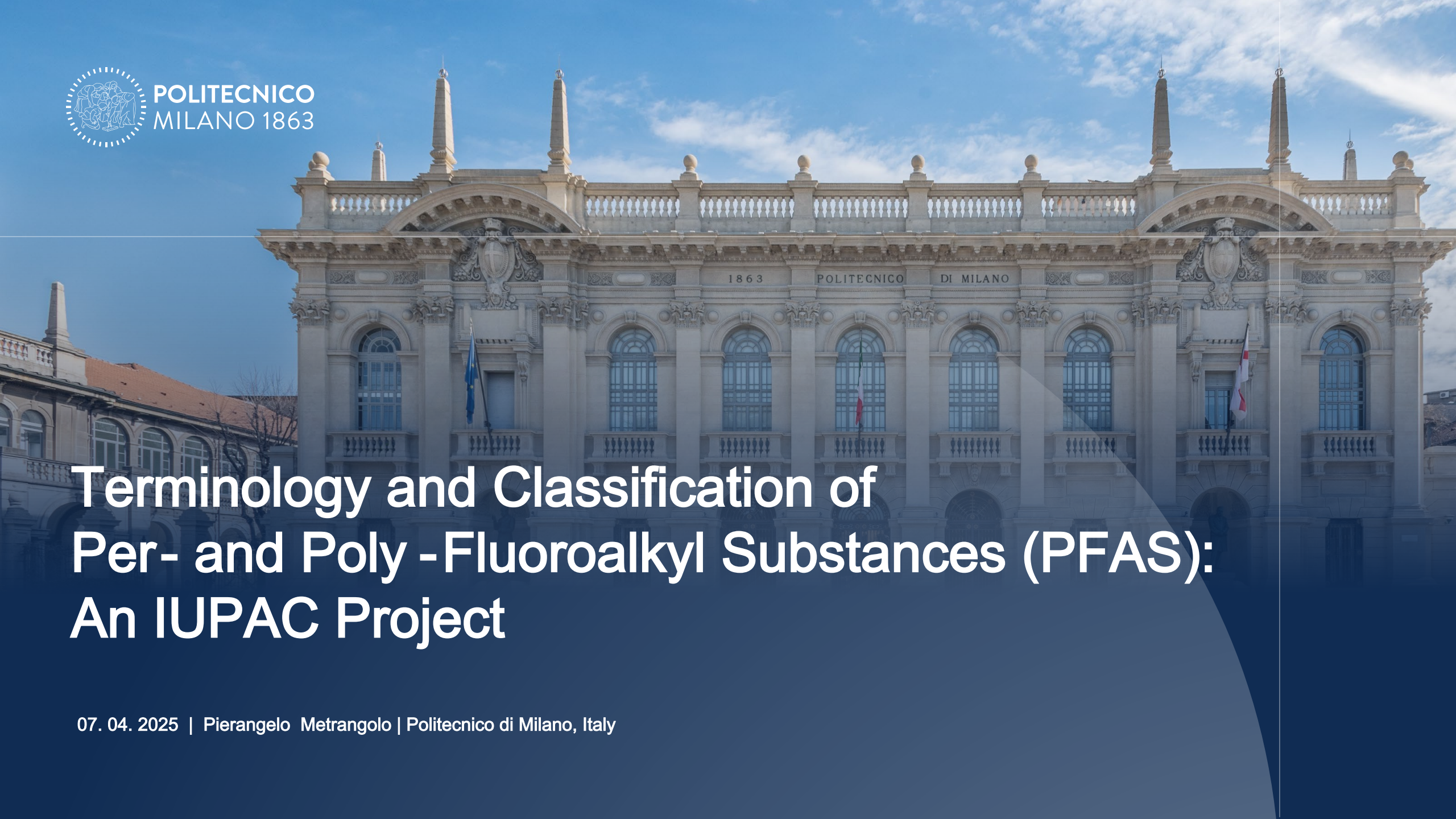


POLITECNICO
MILANO 1863

Terminology and Classification of Per- and Poly -Fluoroalkyl Substances (PFAS): An IUPAC Project

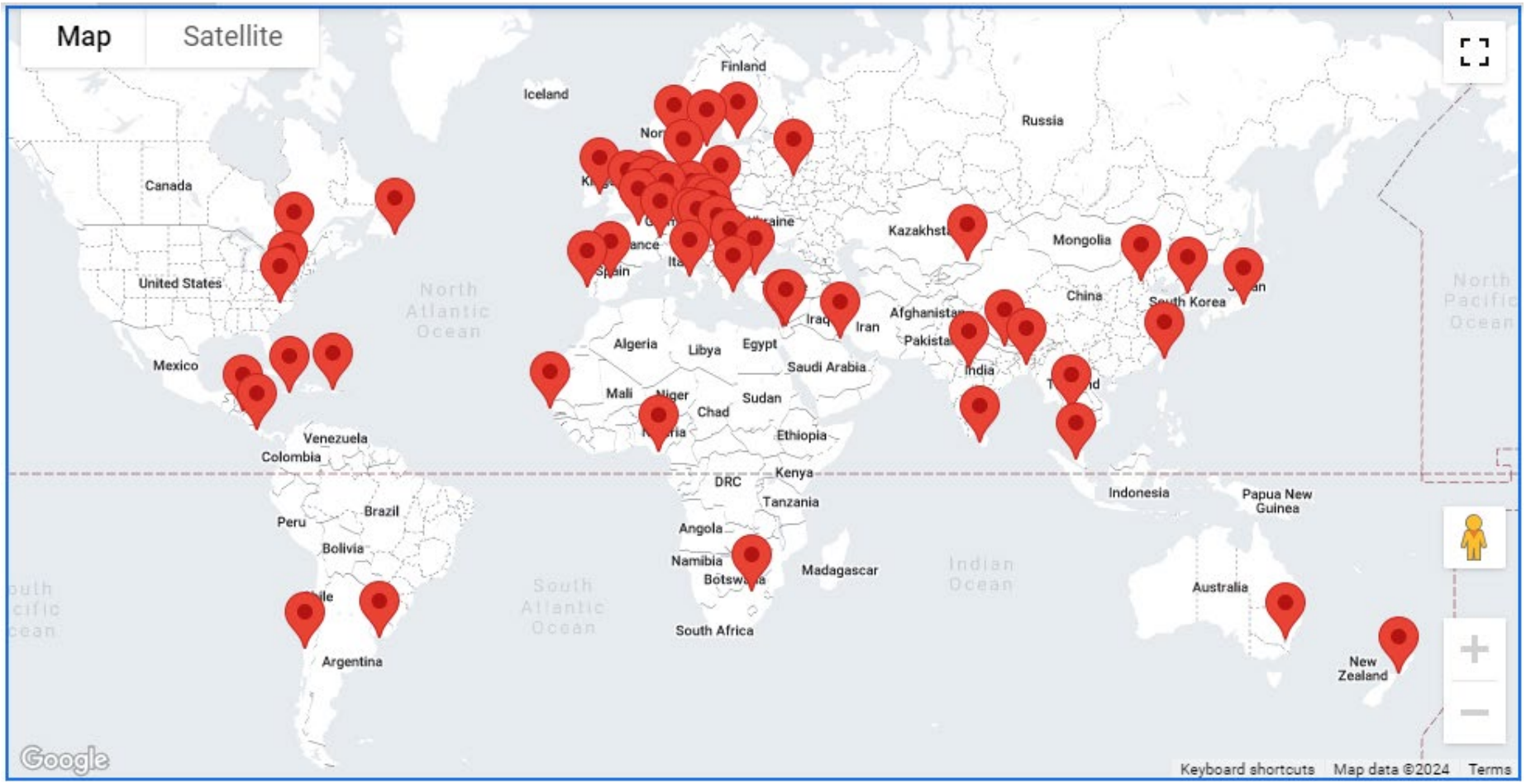
07. 04. 2025 | Pierangelo Metrangolo | Politecnico di Milano, Italy

The International Union of Pure and Applied Chemistry (IUPAC, https://iupac.org/)

- The International Union of Pure and Applied Chemistry (IUPAC) is the world authority on digital standards in chemistry; chemical nomenclature and terminology, including the naming of new elements in the periodic table; on standardized methods for measurement; and on atomic weights. Founded in 1919, IUPAC has been creating the common language of chemistry for more than a century.
- IUPAC is a leader in the provision of objective scientific expertise for the resolution of critical global issues that involve every aspect of chemistry, all of which have societal impact. Our scientific work is conducted largely through a formal project system, in which proposals from chemists around the world are peer-reviewed and, if meritorious, are approved and supported. In addition, IUPAC is involved in a wide range of diverse activities that ultimately impact both the chemical profession and society as a whole.
- IUPAC unites chemists worldwide and we fulfill our mission by fostering sustainable development, providing a common language for chemistry, and advocating the free exchange of scientific information.

***We are IUPAC** – International and Unique,*
advancing Pure and Applied Chemistry worldwide!

Nations Affiliated with IUPAC (https://iupac.org)



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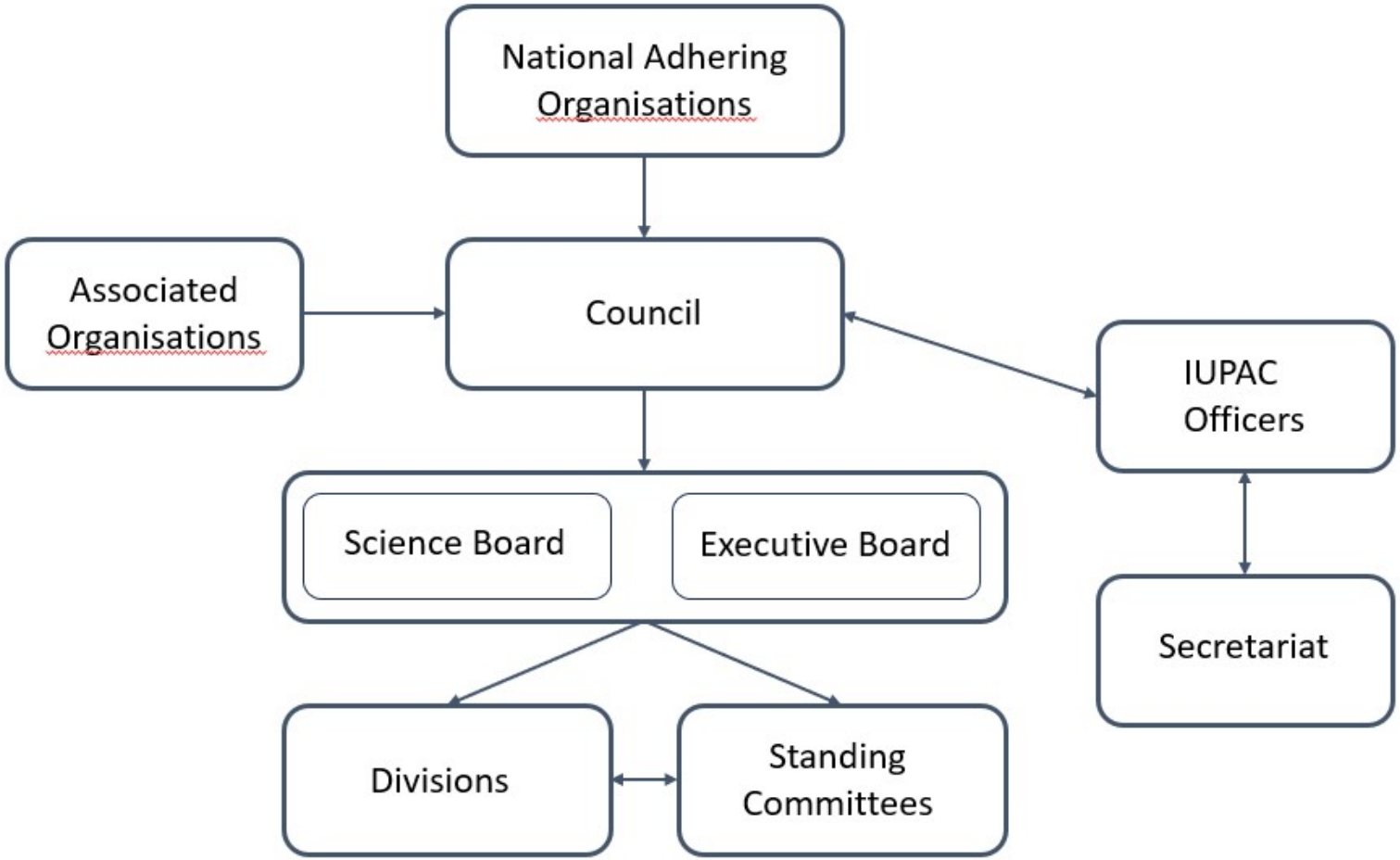
The IUPAC's Organization (https://iupac.org)



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IUPAC's Divisions and Standing Committees (https://iupac.org)

Physical and Biophysical Chemistry Division	I
Inorganic Chemistry Division	II
Organic and Biomolecular Chemistry Division	III
Polymer Division	IV
Analytical Chemistry Division	V
Chemistry and the Environment Division	VI
Chemistry and Human Health Division	VII
Chemical Nomenclature and Structure Representation Division	VIII

Project Committee	PC
Evaluation Committee	EvC
Committee on Chemical Research Applied to World Needs (CHEMRAWN)	CHEMR
Committee on Chemistry and Industry	COCI
Committee on Publications and Cheminformatics Data Standards	CPCDS
Finance Committee	FC
Interdivisional Committee on Terminology, Nomenclature and Symbols	ICTNS

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Committee on Chemistry Education	CCE
Committee on Ethics, Diversity, Equity and Inclusion	CEDEI
Centenary Endowment Board	CEB
International Younger Chemists' Network	IYCN

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IUPAC's Project System (https://iupac.org/projects)

THE CORE ACTIVITY OF IUPAC
is to provide critical evaluations of methods and data and to make recommendations for nomenclature, terminology, metrology, and measurement standards.

The scientific work of IUPAC is conducted largely through a formal Project system in which proposals from chemists around the world are peer-reviewed. The records of all current and completed projects are accessible through the database below. Various guidelines, FAQs, and project submission form are here easily accessible. [**more**]

2024-007-4-300	Human Wellness and Environmental Sustainability: How Chemistry can make the difference	1 Dec 2024
2024-012-2-500	Advanced methods for assessment of risks of false decisions in analytical chemistry (testing) laboratories – basic concepts and associated terms	7 Oct 2024
2024-011-1-024	IUPAC HELM Glycans Extension	30 Sep 2024
2024-010-2-021	Promoting Chemistry Applied to World Needs	16 Sep 2024

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The Mole Definition Project

A critical review of the proposed definitions of fundamental chemical quantities and their impact on chemical communities

Project No.:	2013-048-1-100
Start Date:	1 Dec 2013
End Date:	8 Jan 2018
Cite:	https://iupac.org/project/2013-048-1-100
Division:	Physical and Biophysical Chemistry Division

Chair
Jürgen Stohner

Members
Roberto Marquardt
Juris Meija
Zoltán Mester
Marcy H Towns
Ronald Weir

* Objective | Description | Progress | Partners

Objective

The objective of this task is to provide a Technical Report containing a critical review of the definitions for the quantity amount of substance and its unit, mole, as well as the related unit of the quantity mass.

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The Hydrogen Bonding Project

Categorizing hydrogen bonding and other intermolecular interactions

Project No.:	2004-026-2-100
Start Date:	1 Nov 2004
End Date:	8 Jul 2011
Cite:	https://iupac.org/project/2004-026-2-100
Division:	Physical and Biophysical Chemistry Division

✱ Objective | Description | Progress

Objective

To take a comprehensive look at intermolecular interactions and classify them and to give a modern definition of the hydrogen bond, taking in to account all current experimental and theoretical information, and including hydrogen bonded systems both in gaseous and condensed phases as well as in chemical and biological systems.

Chair

Elangannan Arunan
Steve Scheiner

Members

Ibon Alkorta
David C. Clary
Robert H. Crabtree
Joseph J. Dannenberg
Gautam R. Desiraju
Pavel Hobza
Henrik G. Kjaergaard
Roger A. Klein
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Benedetta Mennucci
David J. Nesbitt
Joanna Sadlej

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The Halogen Bonding Project

Categorizing Halogen Bonding and Other Noncovalent Interactions Involving Halogen Atoms

Project No.:	2009-032-1-100
Start Date:	1 Jan 2010
End Date:	1 Aug 2013
Cite:	https://iupac.org/project/2009-032-1-100
Division:	Physical and Biophysical Chemistry Division

Objective | Description | Progress

Objective

To take a comprehensive look at intermolecular interactions involving halogens as electrophilic species and classify them. To give a modern definition of halogen bonding, which takes into account all current experimental and theoretical pieces of information on both gaseous and condensed halogen-bonded systems in chemical and biological systems.

Chair

Pierangelo Metrangolo

Giuseppe Resnati

Members

Gautam R. Desiraju

P. Shing Ho

Lars Kloo

Anthony C. Legon

Roberto Marquardt

Peter A. Politzer

Kari Rissanen

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IUPAC Recommendations

	Documents	Citations	<2019	2019	2020	2021	2022	2023	Subtotal	>2023	Total
		Total	23454	5248	6012	6986	7108	4315	29669	2	53125
1	Physisorption of gases, with special reference to the evalua...	2015	1550	1244	1706	1968	2236	1525	8679		10229
2	Standards for photoluminescence quantum yield measurements i...	2011	681	178	192	156	194	116	836		1517
3	Definition of the halogen bond (IUPAC recommendations 2013)	2013	599	161	180	212	155	80	788		1387
4	Definition of the hydrogen bond (IUPAC Recommendations 2011)	2011	682	150	115	111	152	84	612		1294
5	Terminology of metal-organic frameworks and coordination pol...	2013	315	95	121	125	160	73	574		889
6	Defining the hydrogen bond: An account (IUPAC Technical Repo...	2011	497	74	76	77	57	25	309		806
7	Isotopic compositions of the elements 2009 (IUPAC technical ...	2011	469	56	64	43	47	18	228		697
8	Terminology for biorelated polymers and applications (IUPAC ...	2012	194	71	86	129	129	74	489		683
9	Polyaniline: The infrared spectroscopy of conducting polymer...	2011	248	50	55	55	45	18	223		471
10	Atomic weights of the elements 2013 (IUPAC Technical Report)	2016	117	71	81	84	76	39	351		468
11	Isotopic compositions of the elements 2013 (IUPAC Technical ...	2016	119	76	65	90	82	35	348		467
12	Terminology for reversible-deactivation radical polymerizati...	2010	309	40	39	37	16	10	142		451
13	Assessment of international reference materials for isotope-...	2014	153	54	62	67	64	34	281		434
14	Hydrated metal ions in aqueous solution: How regular are the...	2010	179	53	45	42	55	40	235		414

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PFAS. The Need for a unifying terminology

- Several definitions of PFAS are in use.
- The European Chemical Agency (ECHA) uses OECD one that defines PFAS as "substances containing at least one aliphatic CF_2 or CF_3 element".
- The U.S. Environmental Protection Agency defines PFAS as "per- and polyfluorinated substances that structurally contain the unit R–(CF_2)–C(F)(R_1)R_2. Both the CF_2 and CF moieties are saturated carbons and none of the R groups (R, R_1, or R_2) can be hydrogen."
- Trifluoroacetic acid (CF_3CO_2H) is a notable example, as it is considered a PFAS by ECHA but not by the U.S. EPA.

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PFAS: DEFINITIONS AND EXPANDING COMPLEXITY

1994 - 2007

- **Banks et al. (1994):** F-substances, highly fluorinated, perfluoro-
- **Kyoto Protocol (1997):** perfluorocarbons (PFCs)
- **OECD (2007):** Lists of PFOS, PFAS*, PFOA, PFCA, related compounds and chemicals that may degrade to PFCAs

**PFAS in OECD 2007 referred to perfluoroalkyl sulfonate*

2011

- **Buck et al. (2011):** "*The primary aim of this article is to recommend clear, specific, and descriptive terminology, names, and acronyms for PFASs, so as to promote a sound, unified understanding among all players in the PFAS industry…*"
- **Per-fluoroalkyl substances:** Aliphatic substances where all H atoms (attached to C) are replaced by F atoms
- **Poly-fluoroalkyl substances:** Aliphatic substances that contain the C_nF_{2n+1}- moiety

2018

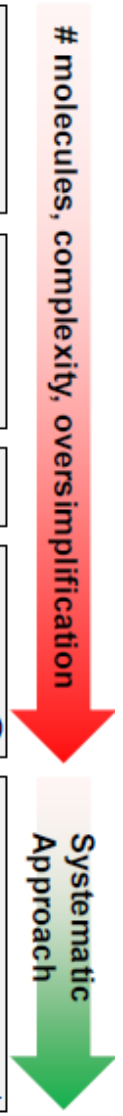
- **OECD (2018):** Published a list of **4730 PFAS** (commercial or R&D, $-C_nF_{2n}-$, n ≥ 3 and $-C_nF_{2n}OC_mF_{2m}-$, n and m ≥ 1)

2020-2021

- **Kwiatkowski et al. (2020):** Suggests scientific basis for **a class-based regulation** (-CF_3 or -CF_2-), i.e. any F-compound is or can lead to persistent, bioaccumulative, and/or toxic compounds
- **Balan et al. (2021):** CA DTSC commentary suggests **class-based regulation** (-CF_3 or -CF_2-)
- **EU CfE (2021):** 5 member states announce intention for a **class-based regulation** (any compound with a -CF_3 or -CF_2-)

2021-

- **Singh and Papanastasiou (2021) and Wallington et al. (2022):** Call for a **science-driven and methodological approach, and precise definitions** to properly guide future regulatory PFAS action
- **OECD (2021):** PFAS terminology report; **acknowledges the diversity among 1000s of F-substances and suggests clearly defining working scopes**
- **Anderson et al. (2022):** PFAS grouping strategy for risk assessment; **"all PFAS" should not be grouped together; persistence alone is not sufficient; inappropriate to assume equal toxicity or potency**
- **EPA (2021-)**: Strategic roadmap published; research papers on PFAS definitions, grouping & read-across strategies, etc.



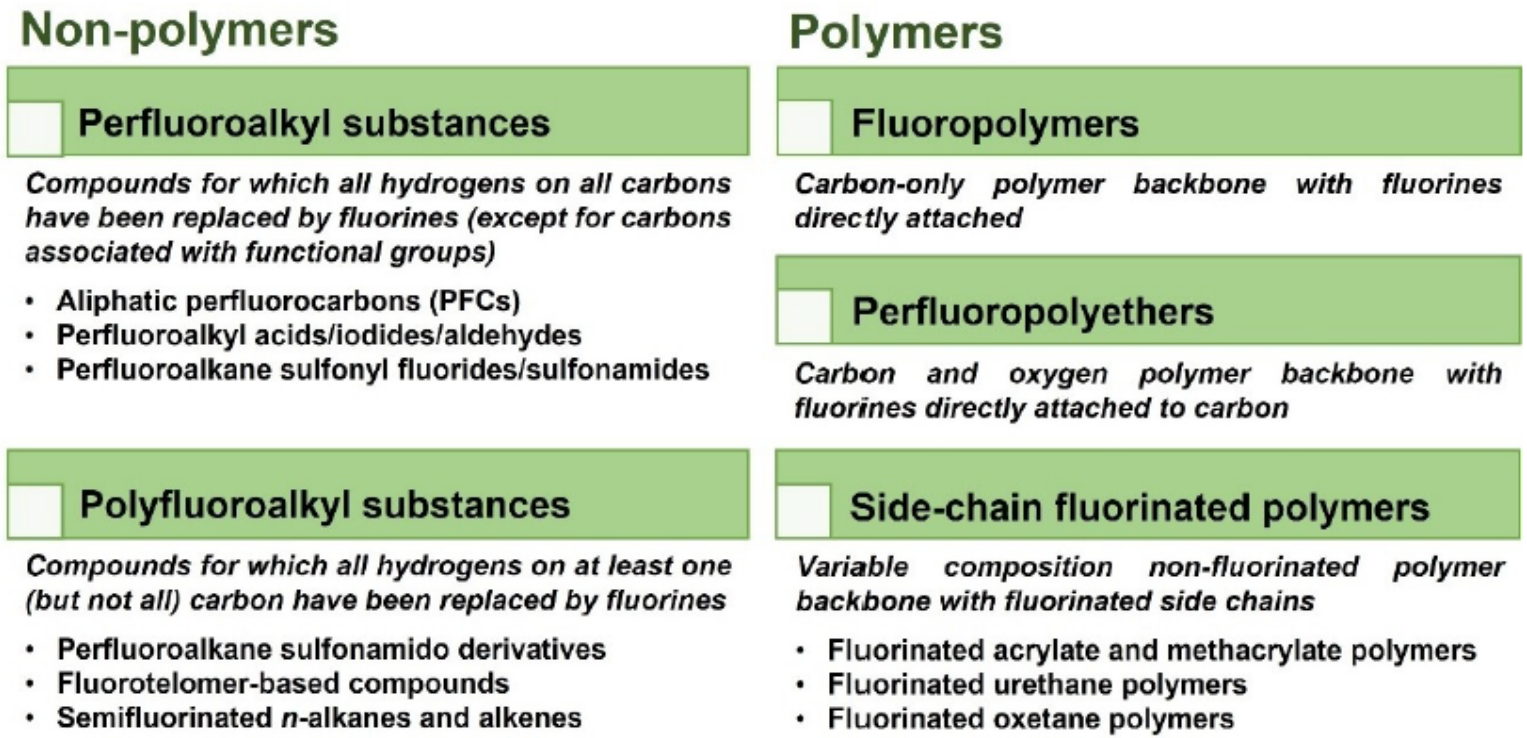


Figure 2. Classification hierarchy of PFAS proposed by Buck and coauthors in 2011 (Ref. [13]).

Chem. Asian J. 2025, e202500127.

$-CF_2-$

"highly fluorinated aliphatic substances that contain one or more carbon (C) atoms on which all the hydrogen (H) substituents (present in the nonfluorinated analogues from which they are notionally derived) have been replaced by fluorine (F) atoms, in such a manner that they contain the perfluoroalkyl moiety $C_nF_{2n+1}-$."

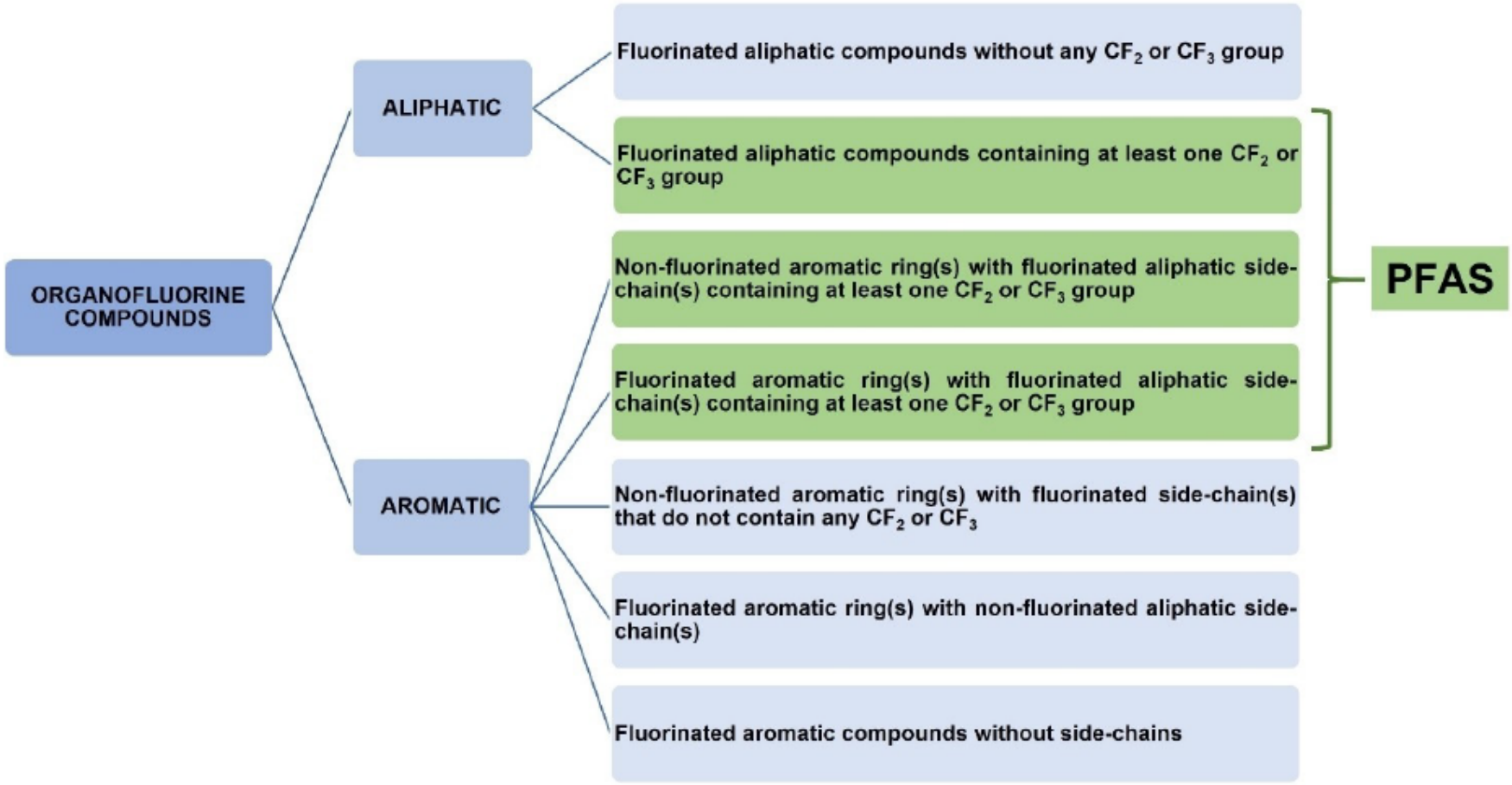
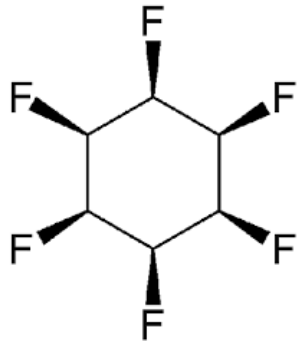


Figure 3. Schematic illustration of the different subclasses of organofluorine substances. Substances recognized as PFAS according to the OECD 2021 definition (Ref. [15a]) are highlighted by green boxes.

Chem. Asian J. 2025, e202500127.

CF_3-X



"fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group ($-CF_3$) or a perfluorinated methylene group ($-CF_2-$) is a PFAS."

IUPAC project no. 2024 -006 -3-100 (https://iupac.org)

Terminology and Classification of Per- and Poly-Fluoroalkyl Substances (PFAS)

Project No.:	2024-006-3-100
Start Date:	26 Jun 2024
End Date:	
Cite:	https://iupac.org/project/2024-006-3-100
Division:	Physical and Biophysical Chemistry Division

Chair
Pierangelo Metrangolo
Tim Wallington

Members
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Rai Kookana
Marie-Pierre Krafft
Sebastian Riedel
Justyna Walkowiak-Kulikowska

* Objective | Description | Progress | Partners

Objective

Per- and poly-fluoroalkyl substances (PFAS) have become an issue of global concern. This project aims to collect, and critically analyze existing information, providing a rigorous definition for PFAS, and standardizing terminology, classification, and nomenclature. The outcomes will benefit the global scientific, regulatory, and industrial communities, by means of a common terminology and a harmonized communication on PFAS. It will align with IUPAC's mission of providing a common language for chemistry and promoting free exchange of scientific information. These findings are expected to help national and global regulation and policy decisions, by filling information gaps and allowing targeted education campaigns.

IUPAC project no. 2019-029-1-600 (https://iupac.org)

Per and polyfluoroalkyl substances (PFAS) in the environment: Information for emerging economies on PFAS analyses in environmental media and their impacts on human health

Project No.:	2019-029-1-600
Start Date:	1 Dec 2019
End Date:	
Cite:	https://iupac.org/project/2019-029-1-600
Division:	Chemistry and the Environment Division

Chair

Mélanie Kah

Members

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Doo Soo Chung
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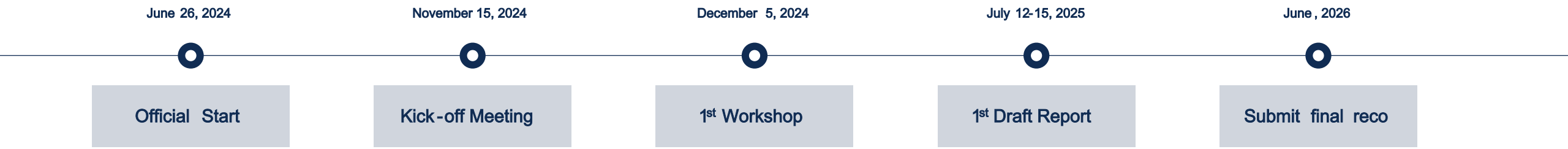
Rai Kookana
Joseph O. Lalah
Zoltán Mester
Bradley Miller
Divina Navarro
Gloria Obuzor
Willie J. G. M. Peijnenburg
Bipul Behari Saha
Weiping Wu
Guang-Guo Ying

Objective

The objective of this projects is to write a synthesis, based on critical evaluation of the current state of knowledge on per and polyfluroalkyl substances (PFAS), to distill learnings that can be beneficial to emerging economies.

Timeline of the PFAS Terminology Project

- 2-year duration.
- Bi-monthly meetings of the Task Group.
- The Task Group members consider themselves as spokespersons in charge of advancing the subject of PFAS definition and classification, for the benefit of the worldwide community of scientists, industries and regulatory agencies that are working in the field.
- The Task Group members will attend the major international meetings and conferences dedicated to PFAS, fluorinated chemicals, and fluoropolymers. These events will represent the most relevant opportunities for an effective and focused dissemination of results.



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Guiding principles for PFAS terminology:

(i) consistent with existing IUPAC definitions,
(ii) simple as possible,
(iii) based on chemical structure (and eventually physical properties, not biological effects),
(iv) consistent with generally accepted chemical nomenclature,
(v) self-consistent.

FLUORINATED SUBSTANCES

ELEMENT

F_2

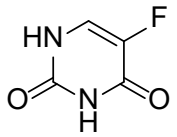
COMPOUNDS

FLUORINATED INORGANIC COMPOUNDS

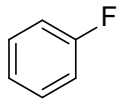
SF_6

FLUORINATED ORGANIC COMPOUNDS

Mono - fluorinated



5-fluorouracil



fluorobenzene

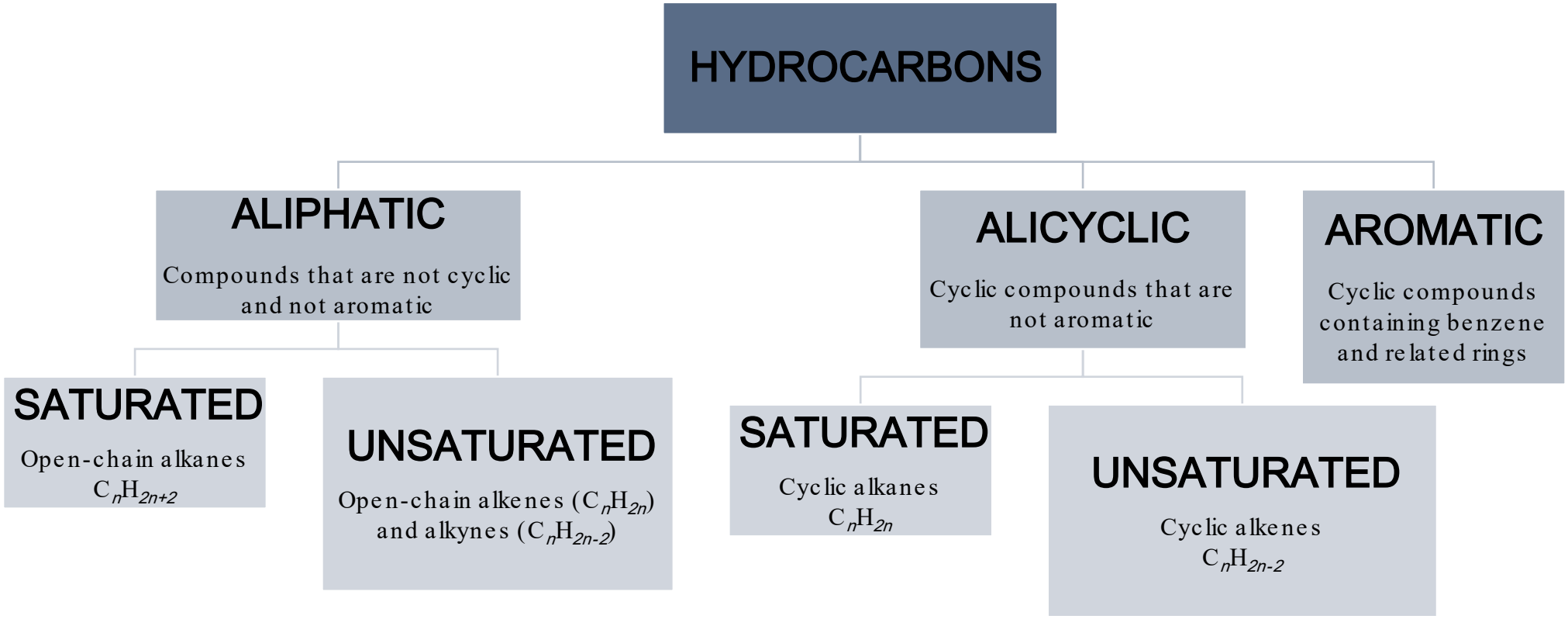
Poly - fluorinated

≥ 2 F
(di-, tri-, tetra-, …)

Per-fluorinated

All C-H replaced by C-F (except for functional groups)

What is a substance?
A substance is a chemical element and its compounds in the natural state or the result of a manufacturing process (ECHA).



Keeping the standard hydrocarbons' classification (see above) as a reference, we can establish an analogous classification for PERFLUORINATED ORGANIC COMPOUNDS:

Source: A. Burrows, J. Holman, A. Parsons, G. Pilling, G. Price, *Chemistry* ³, Oxford University Press, 2009.

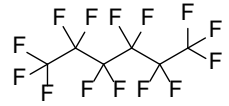
PERFLUOROCARBONS

ALIPHATIC

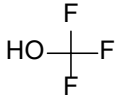
Compounds that are not cyclic and not aromatic

SATURATED

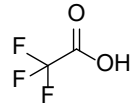
Open-chain perfluoroalkanes C_nF_{2n+2}



perfluorohexane



trifluoromethanol



trifluoroacetic acid

UNSATURATED

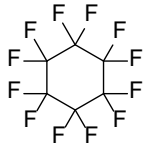
Open-chain perfluoroalkenes (C_nF_{2n}) and alkynes (C_nF_{2n-2})

ALICYCLIC

Cyclic compounds that are not aromatic

SATURATED

Cyclic perfluoroalkanes C_nF_{2n}



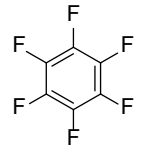
perfluoro-cyclohexane

UNSATURATED

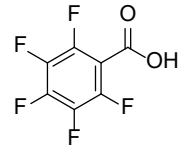
Cyclic perfluoroalkenes C_nF_{2n-2}

AROMATIC

Cyclic compounds containing benzene and related rings



hexafluorobenzene



pentafluorobenzoic acid

ALKYL GROUP = $-C_nH_{2n+1}$
ex. methyl group ($-CH_3$)

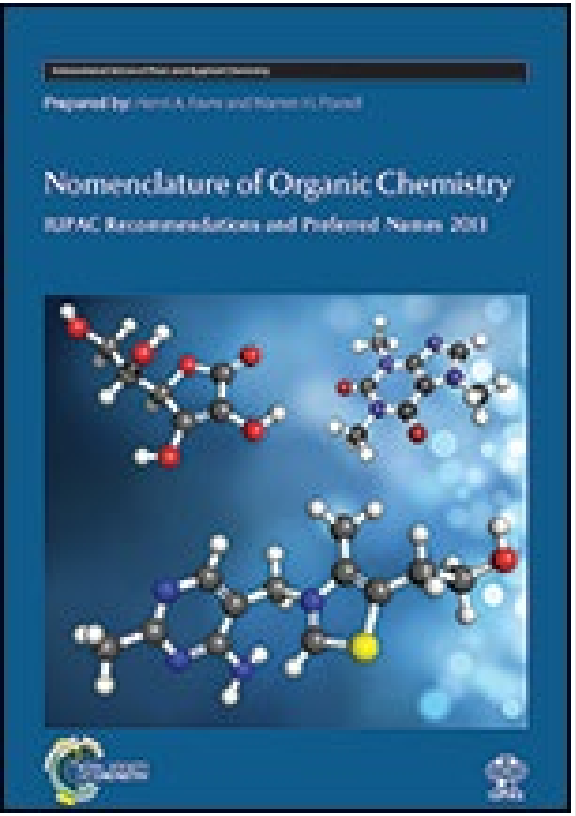
→ **PERFLUOROALKYL GROUP** = $-C_nF_{2n+1}$
ex. trifluoromethyl group ($-CF_3$)

ALKENYL GROUP
ex. vinyl group ($-CH=CH_2$)

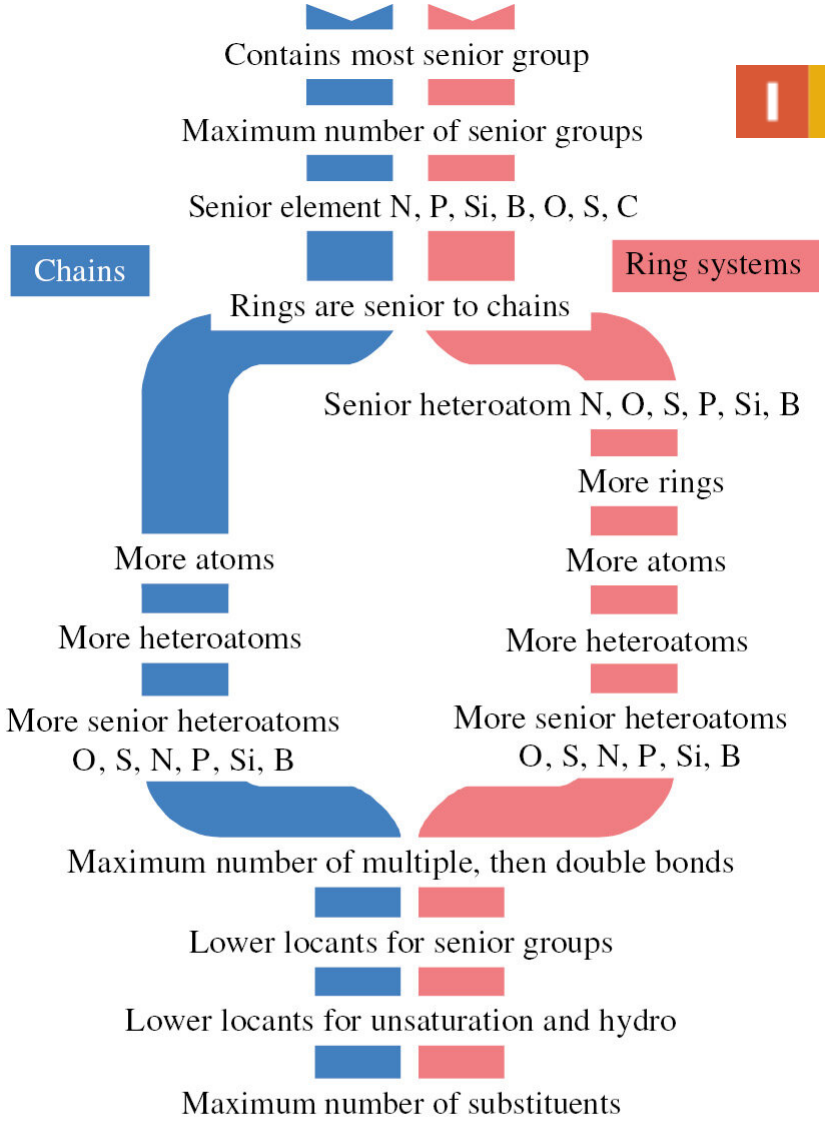
→ **PERFLUOROALKENYL GROUP**
ex. perfluorovinyl group ($-CF=CF_2$)

ALKYNYL GROUP
ex. ethynyl group ($-C\equiv CH$)

→ **PERFLUOROALKYNYL GROUP**
ex. fluoroethynyl group ($-C\equiv CF$)



1	Carboxylic Acid	carboxy-	-carboxylic acid -oic acid
2	Ester	(R)-oxycarbonyl	-oate
3	Acid Halide	halocarbonyl-	-oyl halide
4	Amide	carbonyl-	-carboxamide -amide
5	Nitrile	cyano-	-nitrile
6	Aldehyde	formyl-	-al -carbaldehde
7	Ketone	oxo-	-one
8	Alcohol	hydroxy-	-ol
9	Thiol	mercapto-	-thiol
10	Amine	amino-	-amine
11	Arene (cyclic arrays of C=C)	-	benzene
12	Alkene	alkenyl	-ene
13	Alkyne	alkynyl	-yne
14	Alkane	alkyl	-ane
15	Ether	alkoxy	-ane
16	Alkyl Halide	halo-	-ane
17	Nitro	nitro-	-ane



Blue Book
Nomenclature of Organic Chemistry: IUPAC Recommendations and Preferred Names 2013,
by Henri A Favre and Warren H Powell
RSC Publishing, 2014 [ISBN 978-0-85404-182-4];
https://doi.org/10.1039/9781849733069

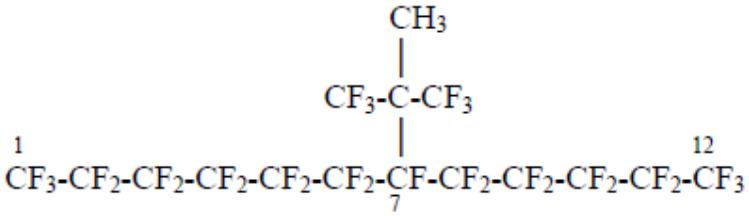
Preferred IUPAC Names 29
Chapter 1, September, 2004

P-14.3.3.3 All locants are omitted in compounds in which all substitutable positions are completely substituted or modified in the same way. The prefix 'per-' is no longer recommended. In case of partial substitution or modification, all numerical prefixes must be indicated.

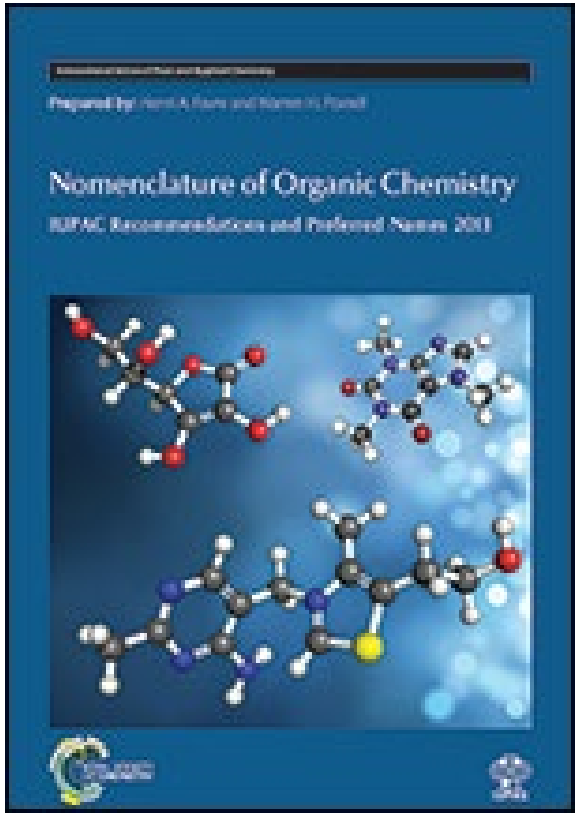
Examples:

heptafluorobutanoic acid (PIN) 2,2,3,3,3-pentafluoropropan-1-ol (PIN)

Preferred IUPAC Names 9
Chapter 6, Sect 60-64
September, 2004



7-(1,1,1,3,3,3-hexafluoro-2-methylpropan-2-yl)-1,1,1,2,2,3,3,4,4,5,5,6,6,7,8,8,9,9,-10,10,11,11,12,12,12-pentacosafluorododecane (PIN)
(preferred substituent prefix; see P-45.1)
7-[1-(trifluoromethyl)-1-methyl-2,2,2-trifluoroethyl]-1,1,1,2,2,3,3,4,4,5,5,6,6,7,8,8,9,9,-10,10,11,11,12,12,12-pentacosafluorododecane



Blue Book
Nomenclature of Organic Chemistry:
IUPAC Recommendations and Preferred Names 2013,
by Henri A Favre and Warren H Powell
RSC Publishing, 2014 [ISBN 978-0-85404-182-4];
https://doi.org/10.1039/9781849733069

My personal opinion:

MONOFLUOROALKYL SUBSTANCE: Any alkyl substance having in its structure only one F atom.

POLYFLUOROALKYL SUBSTANCE: Any alkyl substance having in its structure nF atoms with n ≥2.

PERFLUOROALKYL SUBSTANCE: Any organic substance having either a molecular formula C_nF_{2n+2}, *i.e.*, a perfluoroalkane, or containing at least one C_nF_{2n+1} or saturated C_nF_{2n} moiety (n ≥1), *i.e.*, at least one CF_3- or -CF_2- bound to functional groups.

(*i.e.*, PERFLUOROALKYL SUBSTANCES ARE A SUBSET OF POLYFLUOROALKYL SUBSTANCES)

Research Priorities in PFAS:

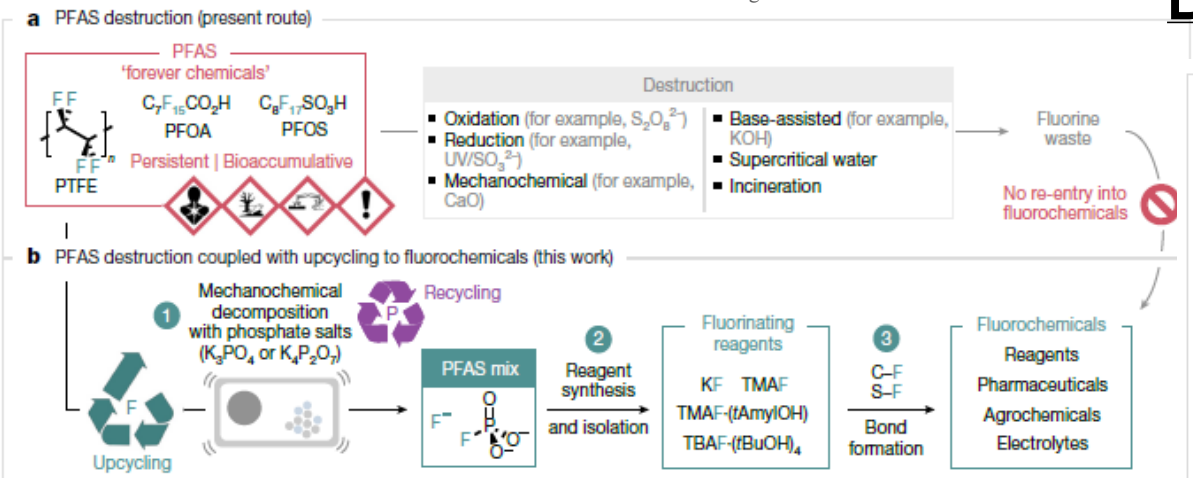
1) Ultrasensitive detection methods, needs for calibrated standards.

2) Efficient filtration materials for PFAS removal from soil, water, air.

3) Closed loop handling and recovery, also considering mineralization.

PFAS are NOT“forever chemicals ”.

DESTRUCTION



Phosphate-enabled mechanochemical PFAS destruction for fluoride reuse

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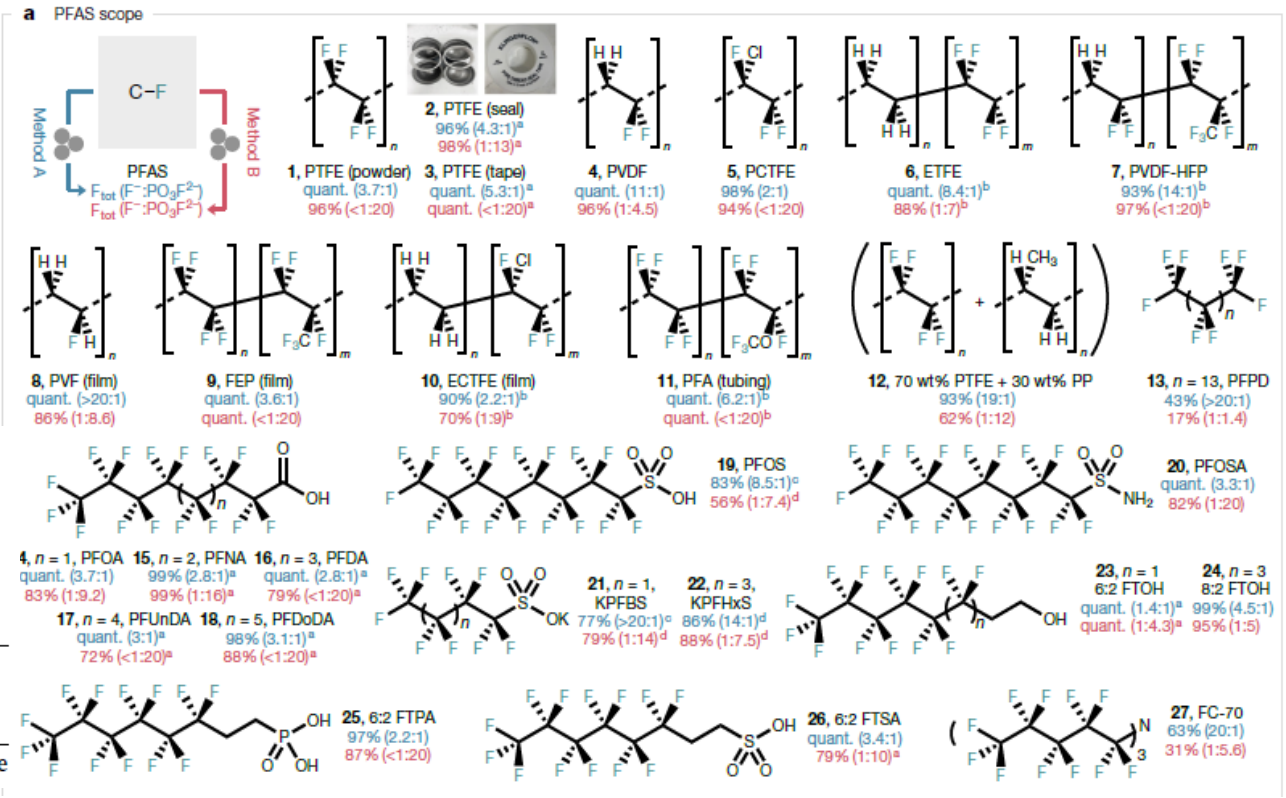
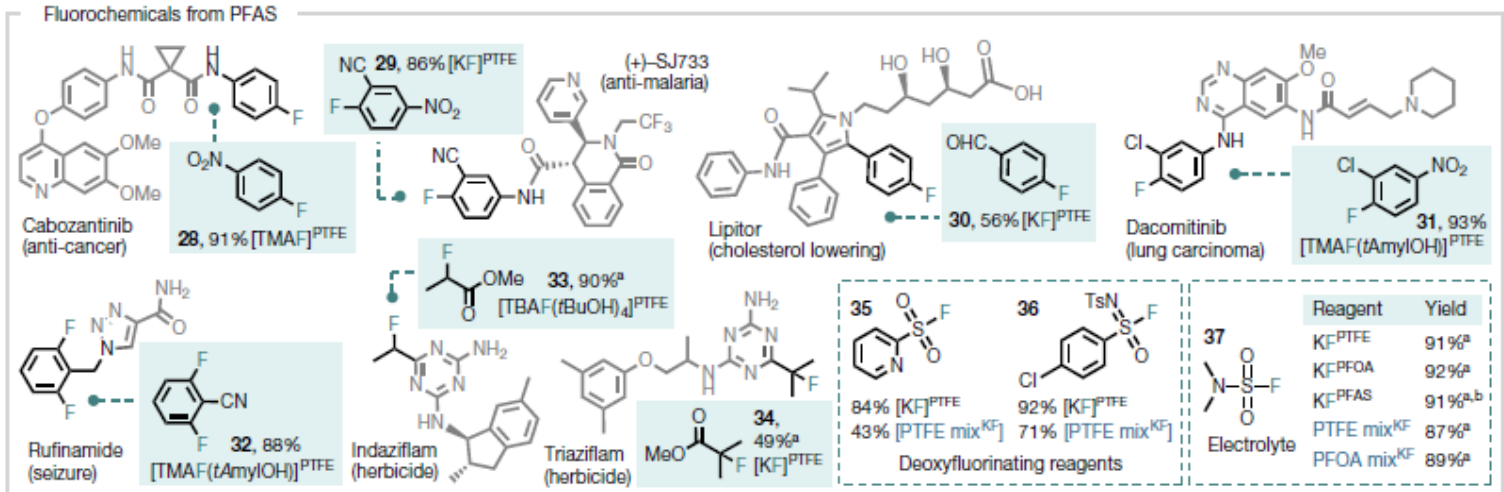
Long Yang[1,3], Zijun Chen[1,3], Christopher A. Goult[1], Thomas Schlatzer[1], Robert S. Paton[2]✉ & Véronique Gouverneur[1]✉

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are persistent, bioaccumulative





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The SupraBioNanoLab

The Project EU HORIZON-CL5-2023-D2-01- RENOVATE "A circular and chemistry-neutral approach for recycling and recovery of battery waste feeds" is gratefully acknowledged.

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Thanks for your attention

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