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# WP 5 Chemical Deuteration

ESS: H.Wacklin, Anna Leung

# DEUNET Platform

- Benefit from **methods/expertise/manpower** at all facilities
- **Cost effective platform** to share materials
- **Include University, international and industrial partners**

## Goals:

1. **User access** to existing products and services of the labs
2. **Development** of new methods and products
3. **Innovative materials** synthesized in collaboration between labs
4. **Coordinated access** for all European neutron users by 2019

- **ISIS:** Chemical deuteration by catalytic H-D exchange and synthesis of surfactants
- **ILL:** Extraction and purification of molecules from deuterated cell cultures
- **FZJ:** Polymer synthesis
- **ESS:** Synthesis of complex deuterated molecules

Network coordination

*Survey of European deuteration needs*

*Business plan to secure further funding by 2019*

# Updates & Discussion

- **Welcome to Rachel Morrison at ILL and Anna Leung at ESS!  
Soon welcome to Kun Ma at STFC!**
- **Recruitments completed**
- **WP5 kick-off at ISIS 27 Nov 2015 (STFC Deuteration facility workshop)**
- **User survey on deuteration needs and platform organisation (2016-2017)**
- **Web-resource and chemicals data base for users**
- **Chemical and Biological Deuteration Workshop in Lund May-June 2017**
- **Several short and long visits planned for collaborations**

# WP5 Deliverables

D	Name	Lead	Type	Diss	Month
5.1	Webpage and user portal	ESS	DEC	PU	9
5.2	Synthesis of deuterated precursors	STFC	R	CO	12
5.3	Novel route for isoprene synthesis	FZJ	R	PU	15
5.4	Synthesis of L- and D-lactic acid	ESS	DEM,R	PU	18
5.5	Synthesis of deuterated polythiophenes	FZJ	R	PU	20
5.6	<b>Report on DEUNET requirements (workshop)</b>	ESS	R	PU	24
5.7	Synthesis of surfactants for non-UK users	STFC	R, DEM	PU	28
5.8	Synthesis of deuterated polylactic acid	FZJ	R, DEM	PU	30
5.9	Optimisation of purification methods	ILL	R	PU	36
5.10	Physico-chemical characterisation	ILL	R	PU	42
5.11	Synthesis of deuterated lipids/surfactants	ESS	R	PU	42
5.12	Platform management, operation and access	ESS	R	PU	48



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## Chemical Deuteration

Coordinator: [Hanna Wacklin](#) (ESS)

Partners: ESS, ILL, STFC, FZJ

### Overview

With the recent advances in neutron sources and instrumentation, and the start-up of ESS, there is an urgent need for deutrating complex molecular architectures for studying a range of advanced materials with neutron scattering.

DEUNET will address the issue by developing:

- A cost-effective platform to provide access to a broad range of materials and expertise
- New synthetic methods and products
- Synthesis of innovative materials in collaboration with partners
- Coordinated service for European neutron users

### Tasks and Partners

#### Task 1. Chemical deuteration by catalytic H-D exchange and synthesis of surfactants

Task leader: ISIS

A range of compounds will be synthesized on request. There are already a number of priorities for new

✓ D5.1, M9  
thank you Ines!



Members of WP5 in Copenhagen, 2015

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▶ Meetings

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#### ▶ SAMPLE ENVIRONMENT

#### ▶ E-TOOLS

#### ▶ DETECTORS

#### ▶ DATA TREATMENT

#### Social Media





## ISIS Deuteration Facility



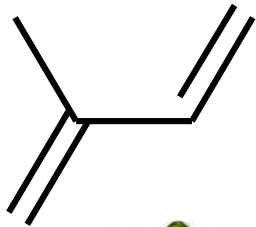
- New equipment
- Dr. Kun Ma recruited
- Medium condition deuterium exchange for e.g. rac-glycerol
- Expanding deuterated chemicals synthesis
- New catalyst synthesis
- Microwave assisted synthesis

# ISIS Deuteration Facility

- ✓ Synthesis of precursors & access for non-UK users:
  - Perdeuterated ligand for the nanomagnetism materials synthesis (Italy).
  - Routine deuterated surfactants (CTAB etc.) Sweden
  - Non-routine molecules: Deuterated Triolein, Sweden, Deuterated resorcinol, urea, choline chloride (ICMM-CSIC, Spain).

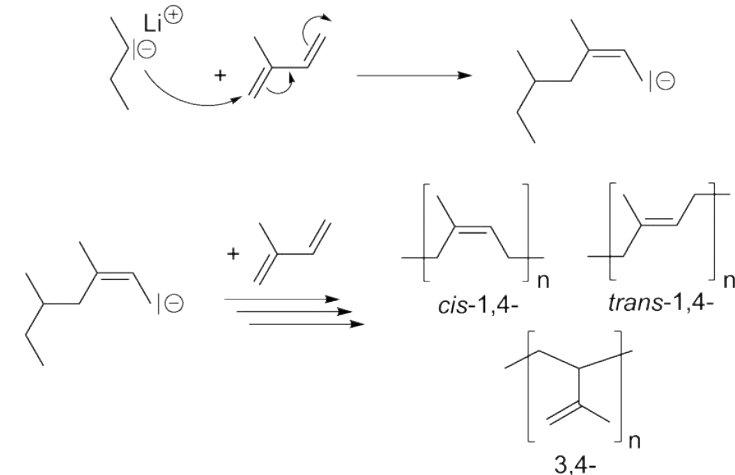


# Isoprene and polyisoprene rubbers (Andreas Raba)



2-methyl-1,3-butadiene  
(*mp* -146°C, *bp* 34°C)

- **600 mio. t** of isoprene p.a. are produced by plants
- Ca. **800.000 t** of isoprene p.a. produced the chemical industry
- Main use: production of synthetic rubbers
- **2/3 of rubber is synthetic**
- Most common hydrocarbon in the atmosphere after methane
- Structural feature of many natural molecules; e.g. steroids, terpenes...

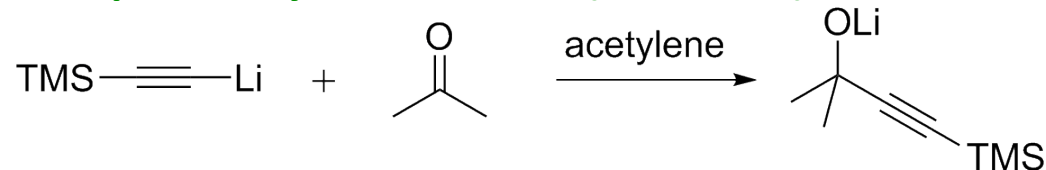


Microstructure depends on:

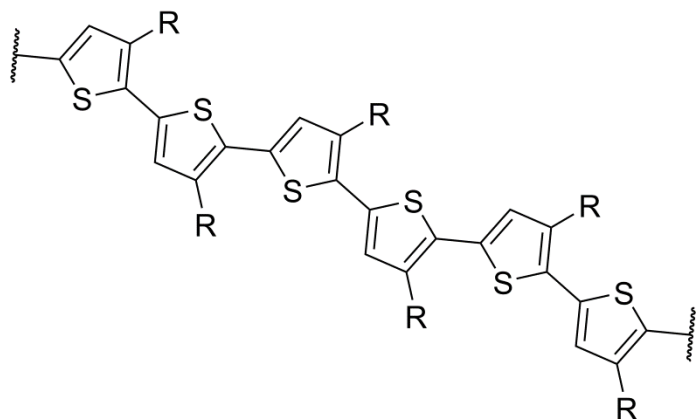
- Counter ion
- Monomer concentration
- Chain-end concentration
- Solvent
- Temperature

→ **Need pure starting material**

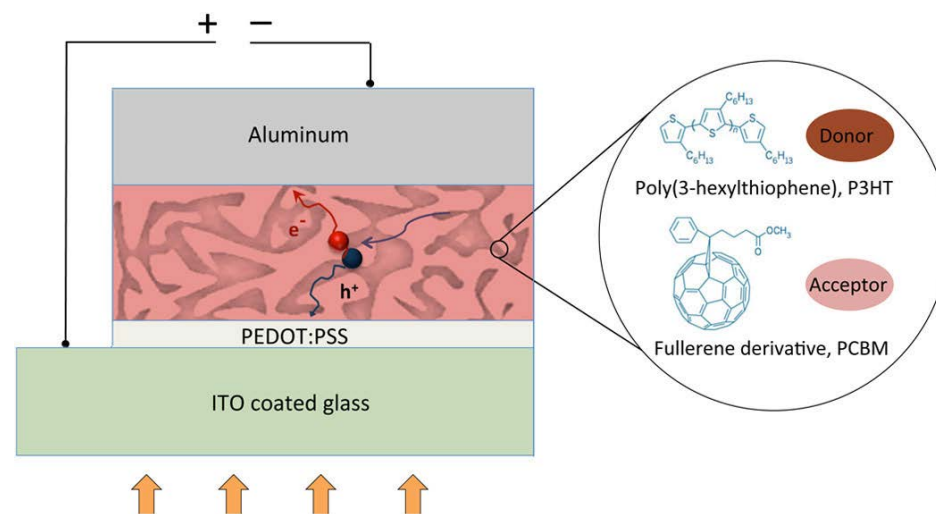
## ✓ Improved Synthesis at FZJ (D5.3 M15)



# Poly(3-hexylthiophene) - P3HT

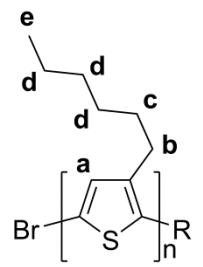
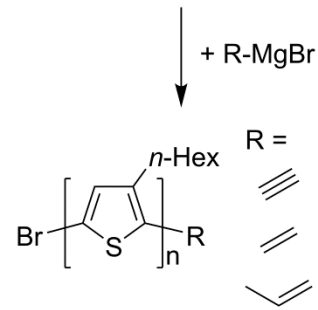
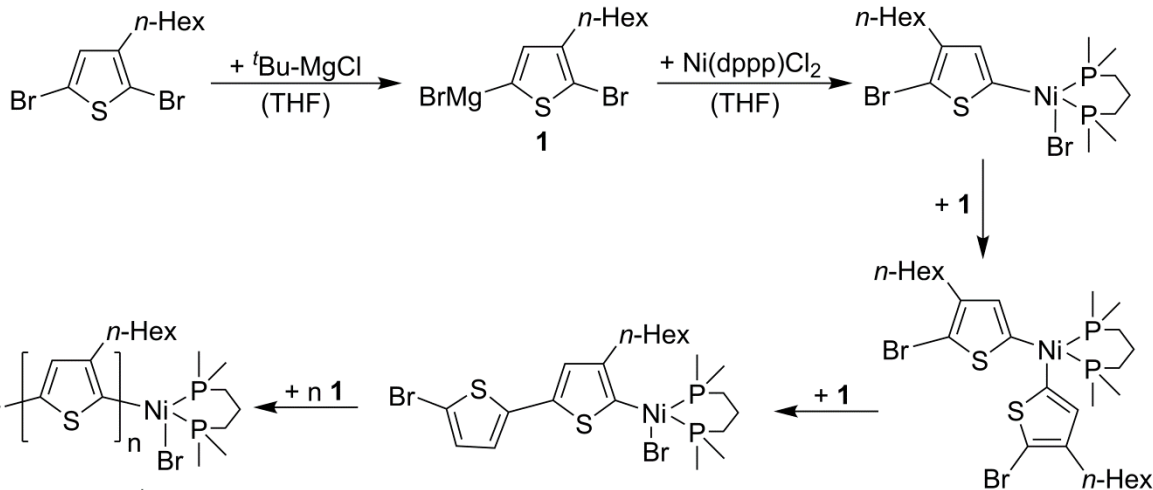


Organic solar cells, OLEDs, OFETs...

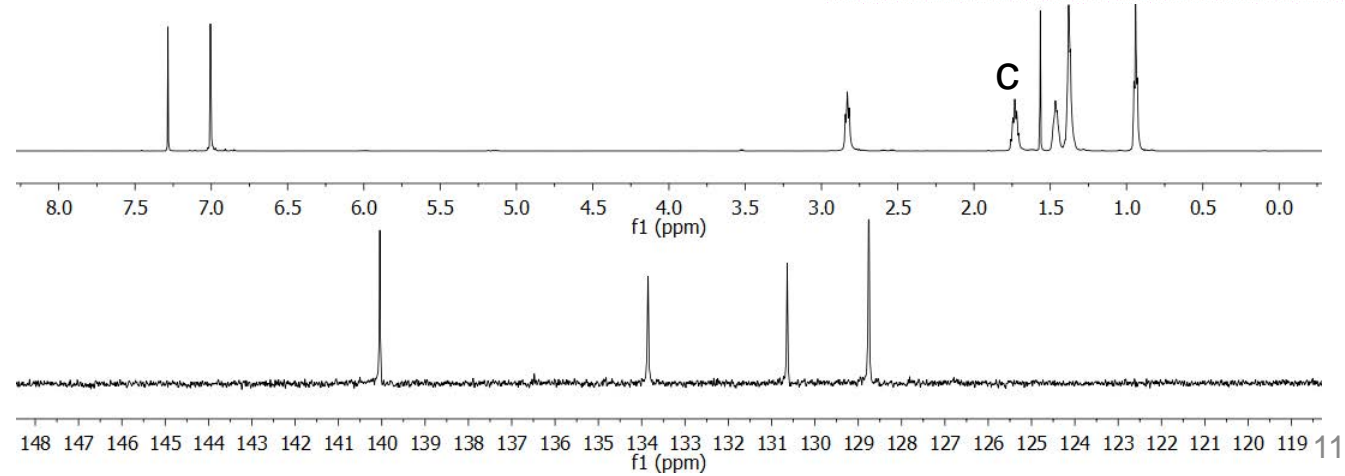
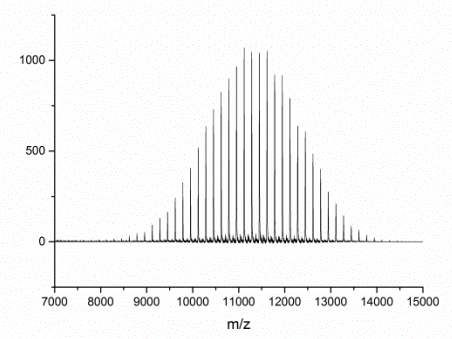
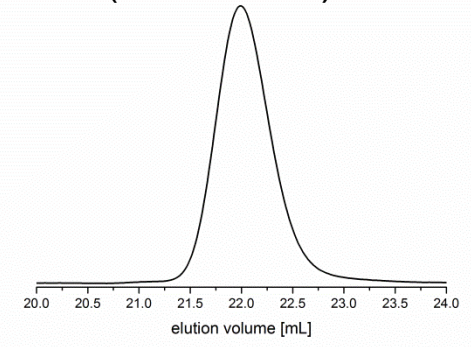


M. C. Stefan et al., *Polym. Chem.* **2012**, 3, 1693; A. Kiriy et al. *Macromol. Rapid Commun.* **2011**, 32, 1503; D. McCullough *Acc. Chem. Res.* **2008**, 41, 1202.

# ✓ P3HT-Synthesis (D5.5 M18)



GPC (PDI = 1.03)



# Establishment of Chemical Deuteration Laboratory at ESS ERIC

Complements existing biological deuteration at ESS

- Organic synthesis, purification and characterisation
  - Automated flash chromatography, GC
  - NMR spectroscopy, mass spectrometry (through Lund university/ Medicon Village)

Anna Leung



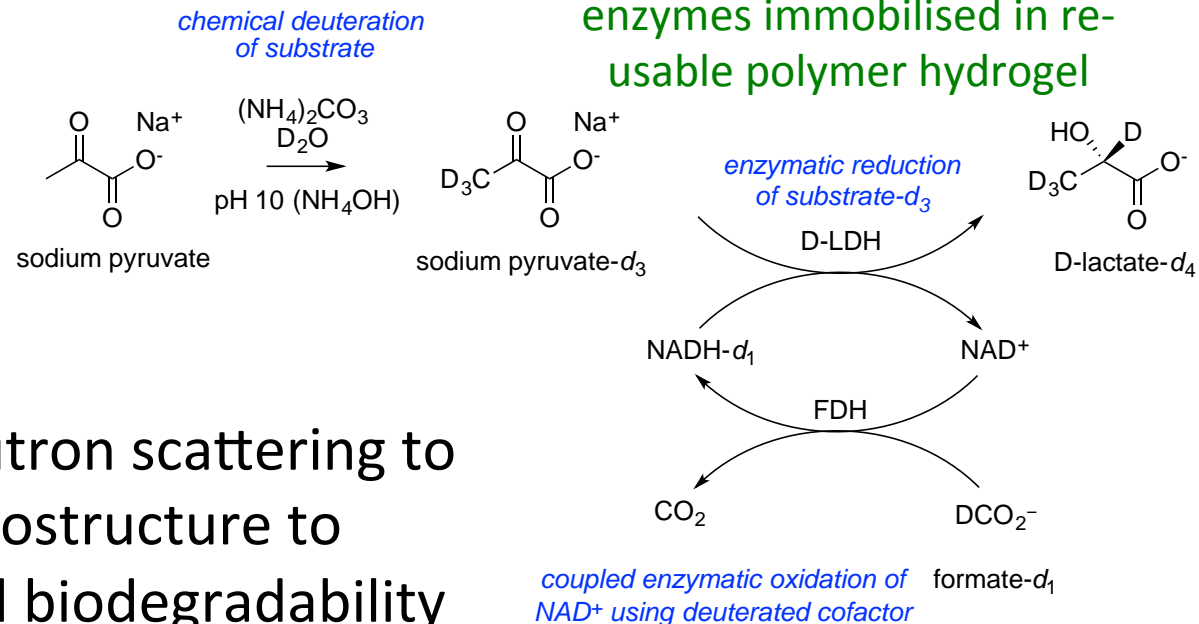
- First collaborative project with FZJ, in progress; collaborative project with ILL on-going - further collaborations welcomed



# Biodegradable polymers from lactic acid

## Poly(lactic acid) PLA - Renewable, biodegradable polymers (D5.4, M18)

- ESS, Sweden: enzymatic synthesis of D- and L-lactic acid- $d_4$
- FZJ, Germany: polymerisation of D- and L-lactic acid- $d_4$  in varying ratios of D-/L- and H/D



no side reactions or  
bi-products = clean

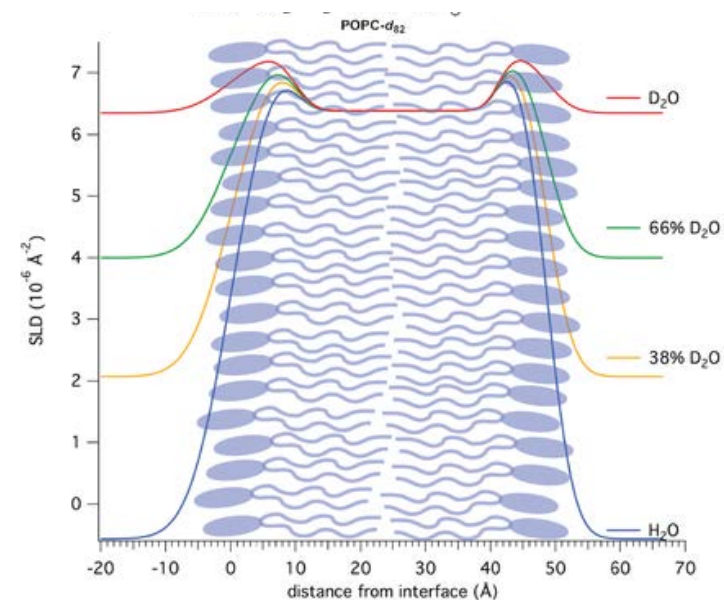
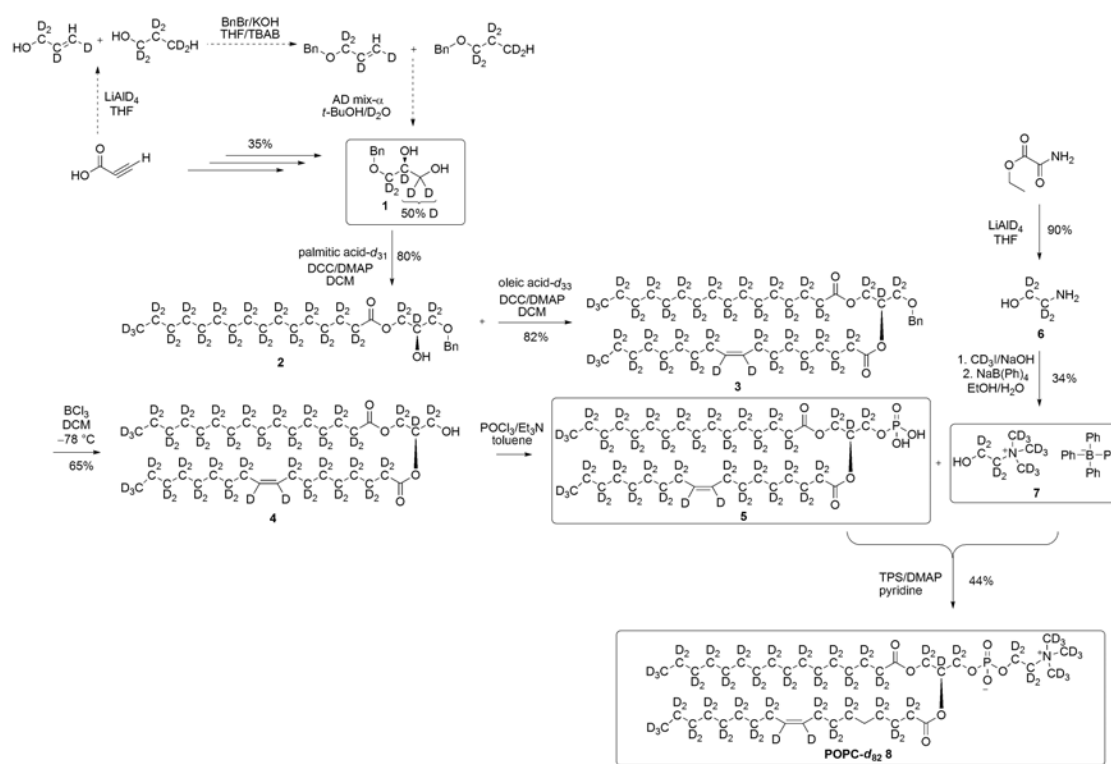
- Aachen University: neutron scattering to correlate polymer microstructure to physical properties and biodegradability
- Further applications: e.g. amino acids, other chiral biomolecules

# Collaboration with ANSTO NDF (Observer)

Wacklin, H. P. et al, *ChemPlusChem* **2016**, *81*, 315-321.

## Synthesis of well-defined perdeuterated unsaturated lipids

### POPC, PLPC





# SINE2020 Project at ILL - Rachel Morrison

Extraction and purification of lipids from deuterated cell cultures

- Selection of suitable organisms for growth in the D-lab
- Optimisation of extraction protocols for lipids **(D5.9, M36)**
- Developing methods for lipid separation
- Developing protocols for characterisation of the prepared **lipids (D5.10, M42)**
- Aiming for the “mass production” for the user community.

**Recent work by Robin Delhom (ESS-ILL joint PhD):**

- The effects of  $^2\text{H}$  and growth media on lipid production
- Metabolic effects in drug resistance (collaboration with ESS & LP3 at Lund University)

**Planned work:**

- Adaption of *Gluconacetobacter* to D-growth media for the production of perdeuterated PC lipids
- Extraction and separation procedures of lipids
- **GC-FID analysis in collaboration with ESS**

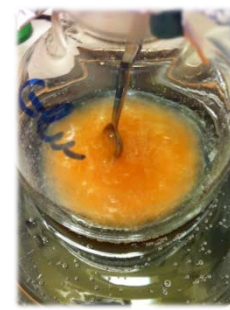
# Update on recent work- Robin Delhom



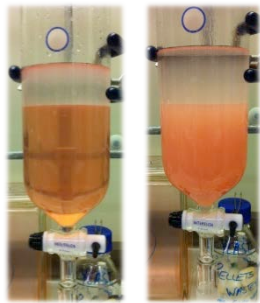
Freeze-dry  
& grinding



Denaturation  
of lipases



Folch  
Extract



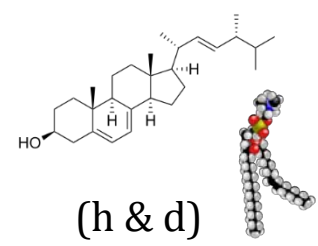
Drying  
  
*Total lipid  
extract*



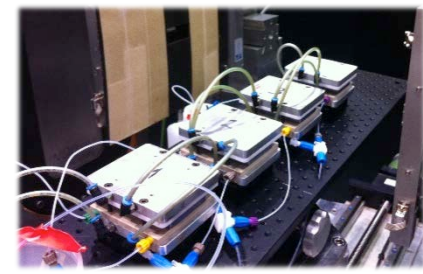
LC



Separation  
of lipids



Analysis & reconstruction  
of biomembranes





**Thank you for your attention**

# Task 5.1 (ISIS)

- **Chemical deuteration by catalytic H-D exchange and synthesis of surfactants:**
- ***Provision of starting materials*** for currently unavailable compounds, e.g. polymers/selectively labelled lipids (D5.1, 5.5) **M12 = Oct 2016, M20**
- **Recruitment:** Kun Ma
- ***Expanding access to European (non UK) researchers*** (D5.7) **M28, M42**
- Improved syntheses for deuterated ***unsaturated fatty acids*** (D5.7, D5.11)
- ***Development of routes to novel bio-surfactants*** in collaboration with ILL and ESS (D5.11). **M42**

## Task 5.2 (ILL)

- **Extraction and purification of small molecules from deuterated cell cultures:**
- *Lipid components of biomembranes, gangliosides, polysaccharides* (D5.9) [M36](#)
- *Characterisation using EPN facilities: PSCM, ESRF, ILL* (D5.10) [M28](#)
- Improved syntheses for deuterated *unsaturated fatty acids* (D5.7, D5.11) [M28, M42](#)
- *Development of routes to novel bio-surfactants* in collaboration with ILL and ESS (D5.11). [M42](#)

## Task 5.3 (ESS)

- **Synthesis of complex deuterated molecules:**
- *Enzyme-catalysed synthesis* of chiral deuterated compounds e.g. lactic acid (D5.4) [M18 = March 2017](#)
- *Synthesis of polylactic acid polymers* (biodegradable plastics) in collaboration with FZJ (D5.8). [M30](#)
- *Development of methods* for chemical reactions using deuterated materials, and synthesis of labelled compounds in collaboration with ISIS, ILL and FZJ (D5.11) [M42](#)

## Task 5.4 (FZJ)

- **Polymer synthesis:**
- ***New synthesis procedures*** for deuterated monomers and polymers, e.g. isoprenes for synthetic rubbers (D.5.3) **M15 = Dec 2016** and polythiophenes for photovoltaics (D5.5) **M20**
- ***Synthesis of polylactic acid polymers*** (biodegradable plastics) in collaboration with ESS (D5.8). **M30**
- ***Polymer modification of deuterated lipids*** (PEGylated d-lipids) in collaboration with ESS (D5.11) **M42**

## Task 5.5 (ESS)

- **Network coordination and platform activities :**
- Networking events, *annual meetings* and dissemination of results
- *User workshop* to define scope and strategy for DEUNET (D5.6) M24 = Sep 2016
- Set up *collaboration network with universities, user organisations, industry*
- Coordinate *platform management, operation and access* (D5.12) M48
- ✓ In collaboration with WP2 (Dissemination), set up a *webpage and user portal (D5.1)*  
*M9 = June 2016*
- In collaboration with WP3 (e-learning), provision of *e-learning material about deuterium labelling*
- In collaboration with WP4 (Industry), develop *industry-specific outreach material*