UNCONVENTIONAL APPROACHES FOR THE DIRECT READOUT OF CHIRAL INFORMATION

Alexander Kuhn

Institut des Sciences Moléculaires, UMR 5255

Ecole Nationale Supérieure de Chimie, Biologie et Physique Bordeaux

University of Bordeaux, CNRS, Bordeaux INP

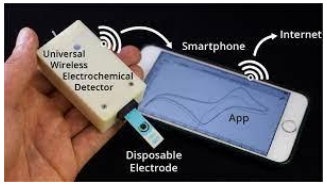
Examples of readout strategies

HPLC

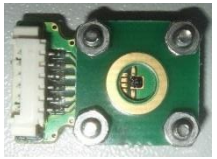
CD

CPL

EC



Actuators



Swimmers

Classic

Unconventional

Electrochemistry

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EDITORIAL

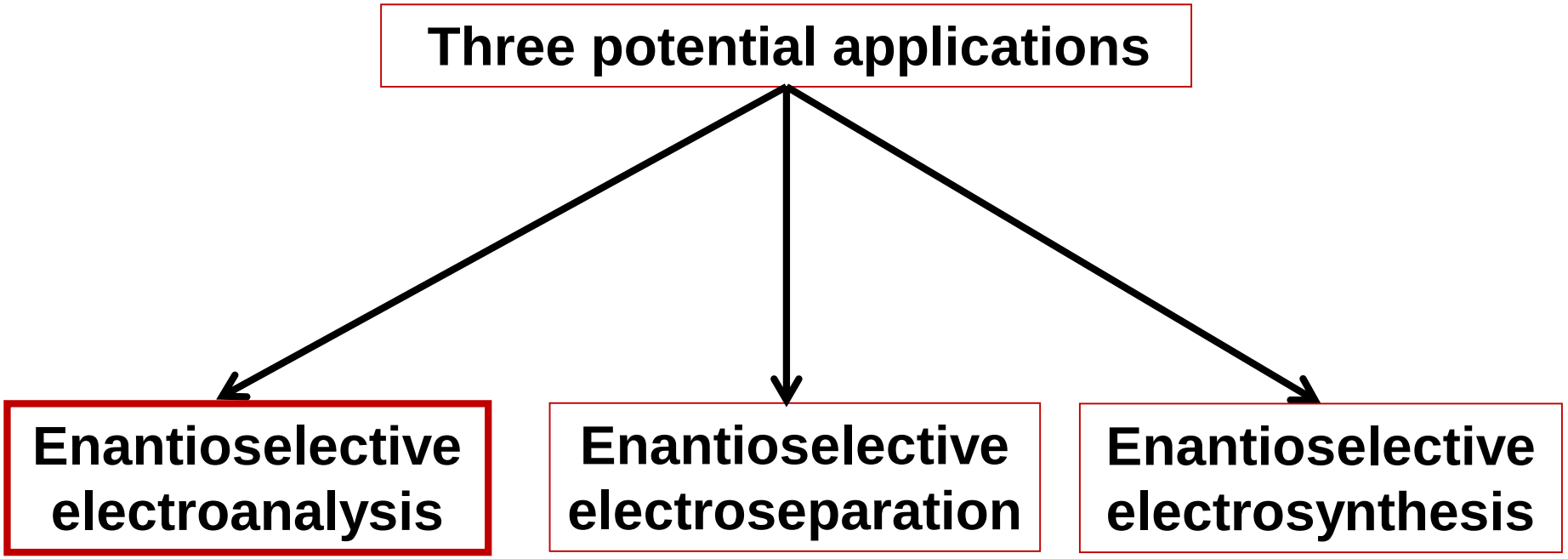
The Rising and Receding Fortunes of Electrochemists

This is the golden age of electrochemistry. Never before has this discipline found itself at the nexus of so many developing technologies: batteries, capacitors, fuel cells; solar-to-electrical energy conversion at liquid junctions; nanocrystalline solar cells; and organic solar cells. New electrochemical energy-harvesting technologies are also being explored for thermal energy harvesting,[1] and these are just the electrochemistry-related technologies pertaining to energy. Capacitive water deionization and electrochemical sensors and actuators are being widely explored, and the use of electrochemical methods in electronic manufacturing, coatings, and the synthesis of materials (including aluminum) remains as important as ever.

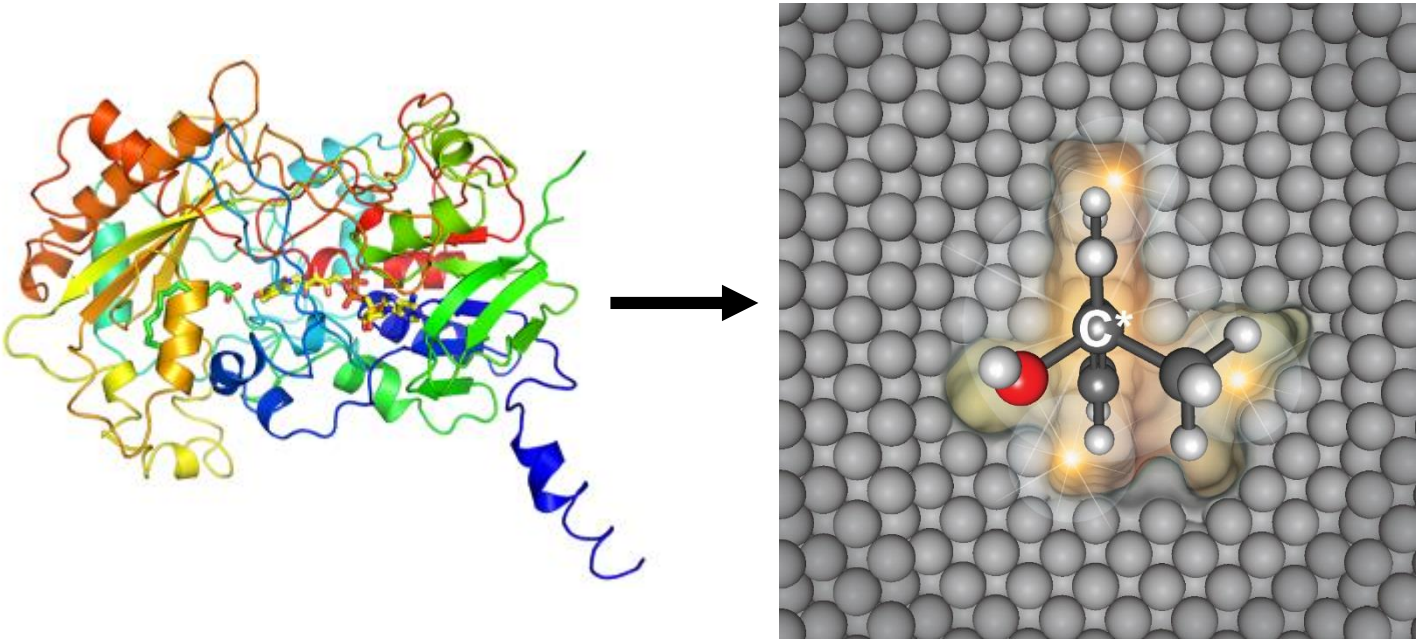
Energy is an international priority and an abundance of research funding has been made available for applied electrochemistry. Prominent programs just the United States include The Energy Innovation Hubs, grants from the ARPA-E, many of the Energy Frontier Research Centers (EFRCs), and others. Research (ONR), Department of Energy (DOE), and the National Science Foundation (NSF) filled this niche, but these programs disappeared in the 1990s, well in advance of the recent excitement and investment in applications. While some fundamental science is being carried out at the various EFRCs as well as through NSF-funded programs, there do not appear to be any programs, at any U.S. agencies, focused on fundamental electrochemistry science issues. Historically, these programs not only provided financial support but also knitted the community together, fostering interactions between electrochemists working on fundamental science issues. The Basic Energy Sciences Division of DOE and Chemistry Division of NSF would be obvious sources of support in the United States, and we hope that those and other funding agencies around the world have the will to support fundamental electrochemical science.

Key issues that are ripe for investigation include the following: the kinetics of coupled electron transfer and ion insertion/

Chirality and electrochemistry



Artificial biomimetic electrodes

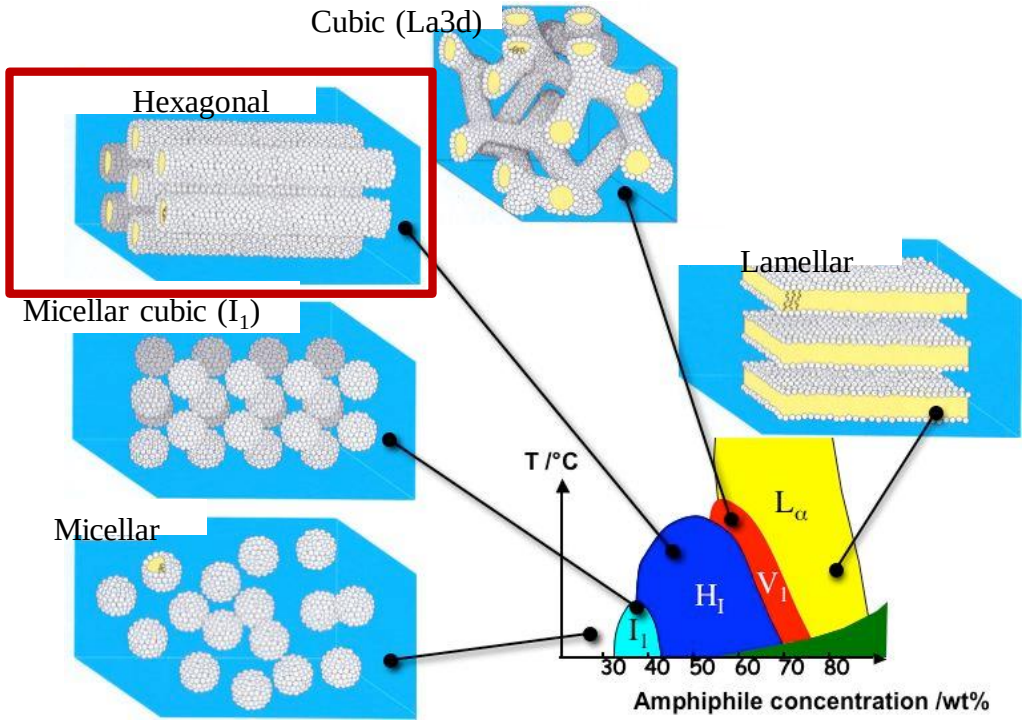


Chiral imprinting of porous metals

Mesoporous electrodes

Soft template: lyotropic liquid crystals

Lyotropic liquid crystalline phases (LLC)



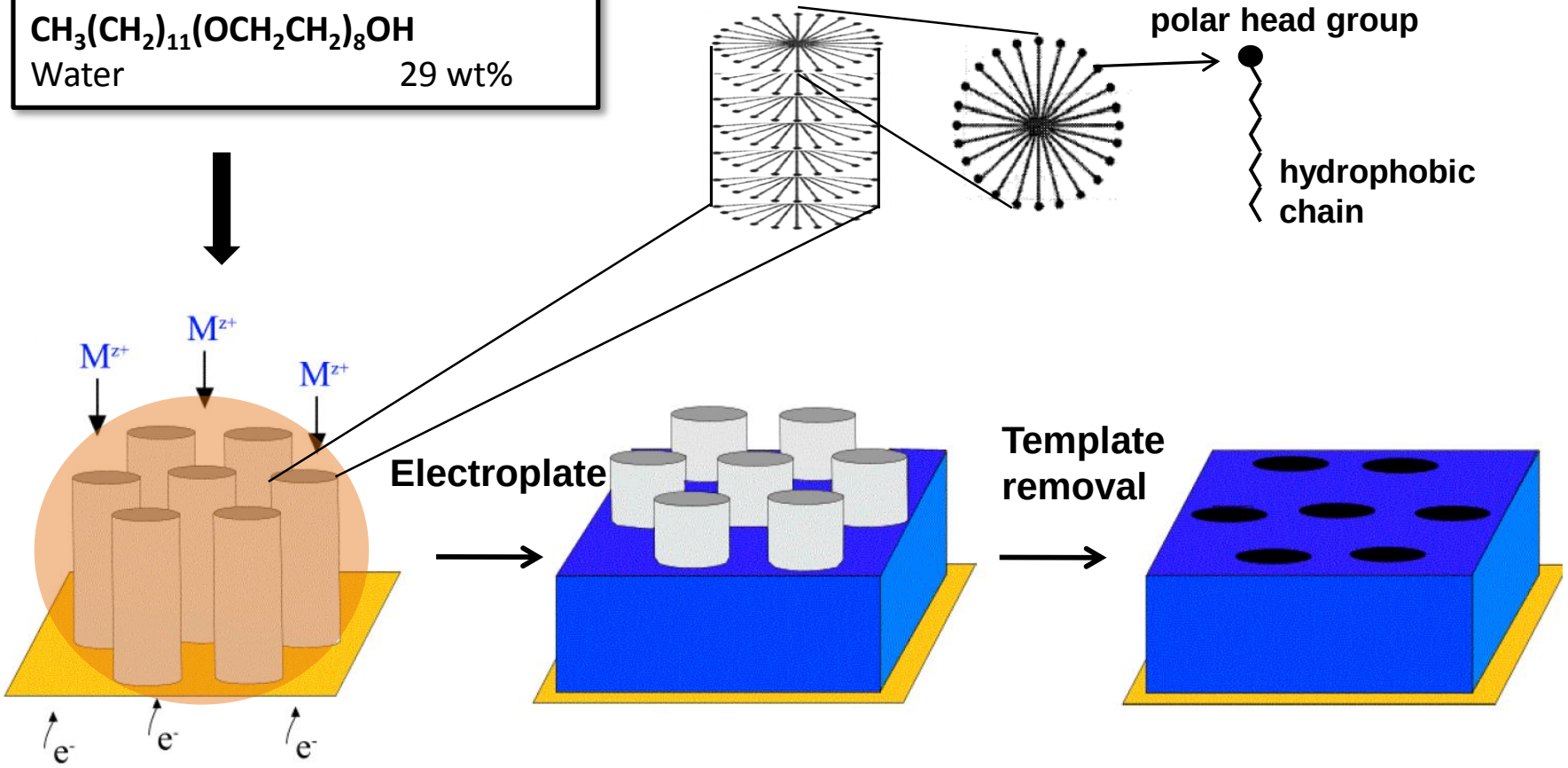
http://en.wikipedia.org/wiki Lyotropic_liquid_crystal

Chiral imprinting of porous metals

Mesoporous electrodes

Lyotropic liquid crystal templating:

Platinum salt	29 wt%
H_2PtCl_6	
Surfactant	42 wt%
$CH_3(CH_2)_{11}(OCH_2CH_2)_8OH$	
Water	29 wt%



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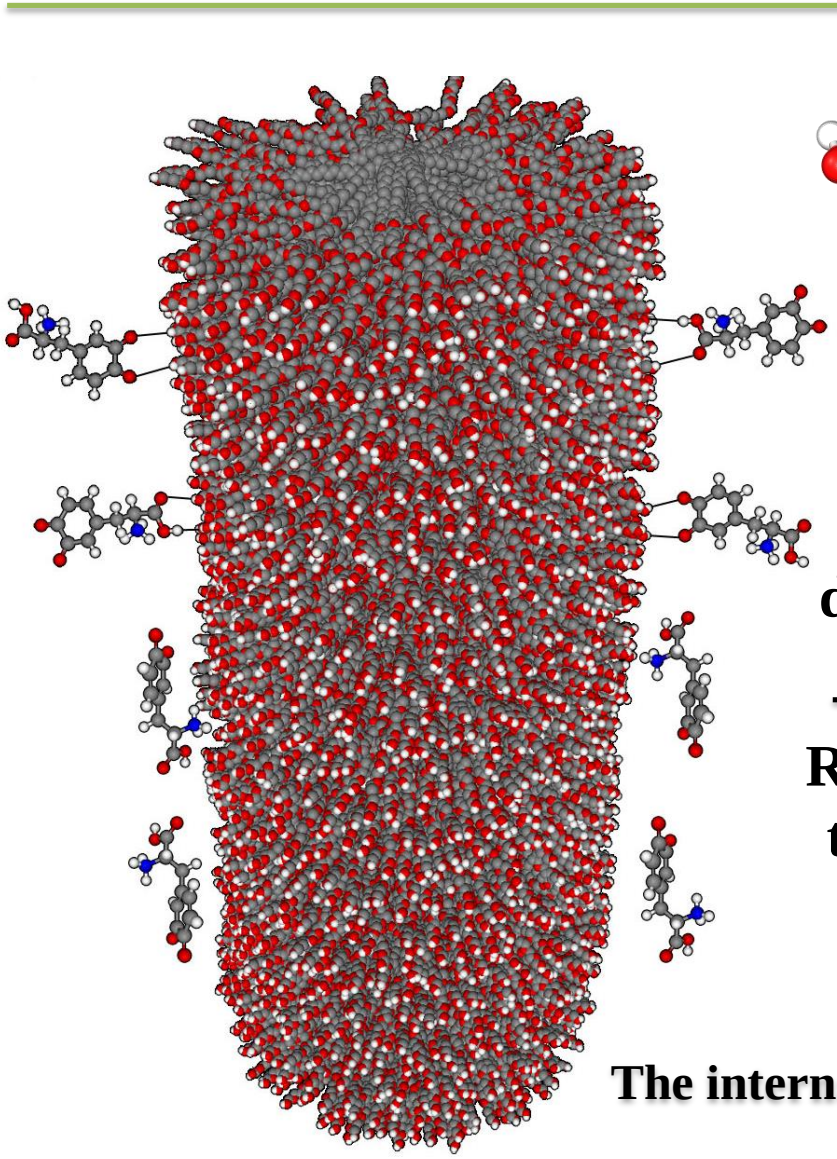
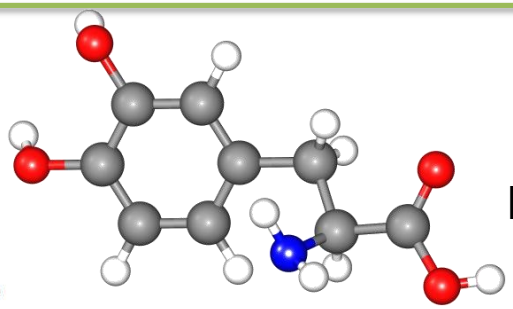
Preparation of mesoporous chiral metal



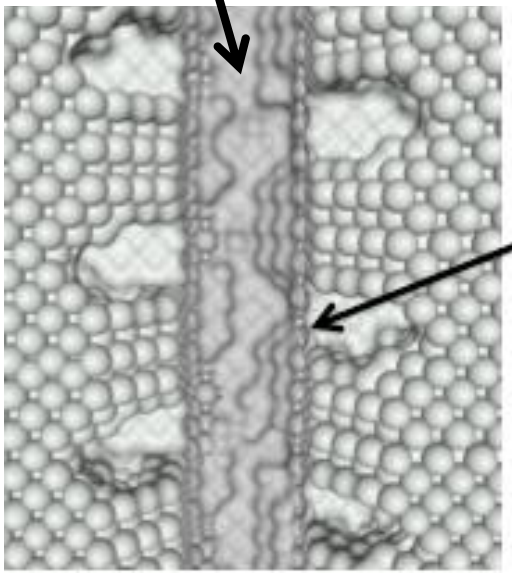


DOPA

Mesopore

Pt deposition

Removal of templates



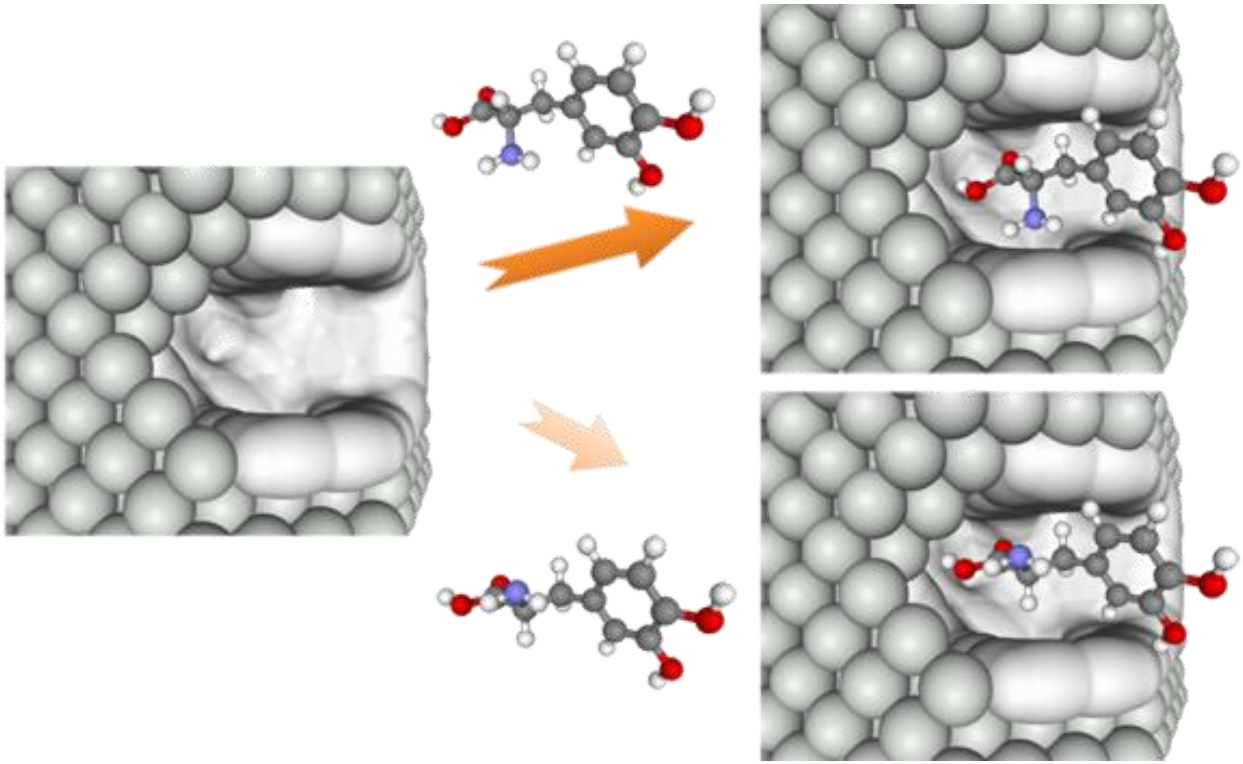
Chiral cavities

The internal surface of the mesopores is chirally imprinted.

Wattanakit C., Bon Saint Côme Y., Lapeyre V., Bopp P., Heim M., Yadnum S., Nokbin S., Warakulwit C., Limtrakul J., Kuhn A., **Nature Comm. 2014**, 5, 3325

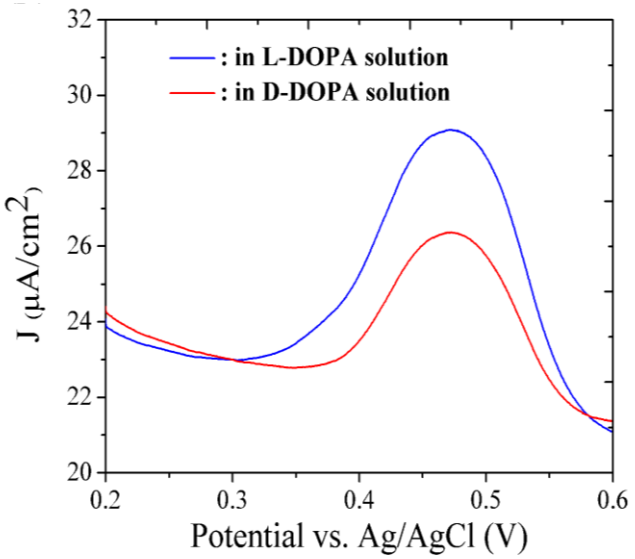
Selectivity

Enantioselective recognition of 3,4-dihydroxy-phenylalanine (DOPA) enantiomers on chiral imprinted mesoporous platinum electrodes by **differential pulse voltammetry**

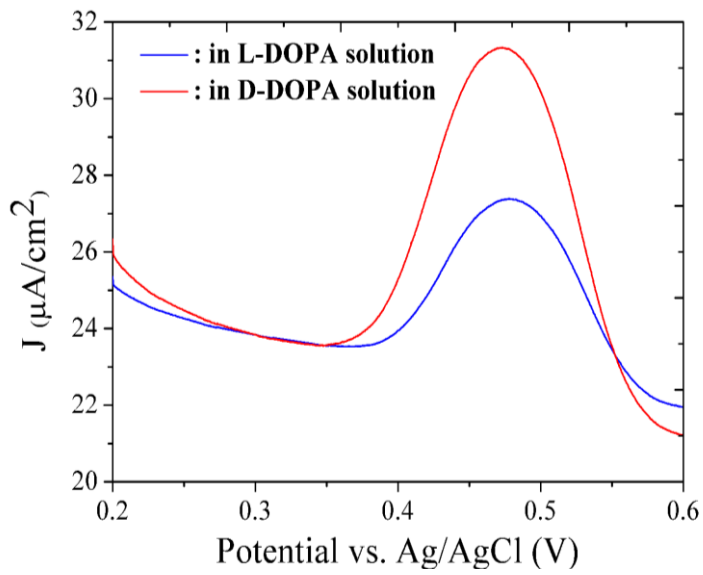


Enantioselective recognition

Electrooxidation of DOPA on chiral imprinted mesoporous Pt



Imprinted with L-DOPA
(L-DOPA/$PtCl_6^{2-}$ = 0.04)



Imprinted with D-DOPA
(D-DOPA/$PtCl_6^{2-}$ = 0.04)

C. Wattanakit, Y. Bon Saint Côme, V. Lapeyre, P. Bopp, M. Heim, S. Yadnum, S. Nokbin, C. Warakulwit, J. Limtrakul, A. Kuhn, **Nat. Comm. 2014**, 5, 3325

T. Yutthalekha, C. Wattanakit, V. Lapeyre, S. Nokbin, C. Warakulwit, J. Limtrakul, A. Kuhn, **Nat. Comm. 2016**, 7, 12678

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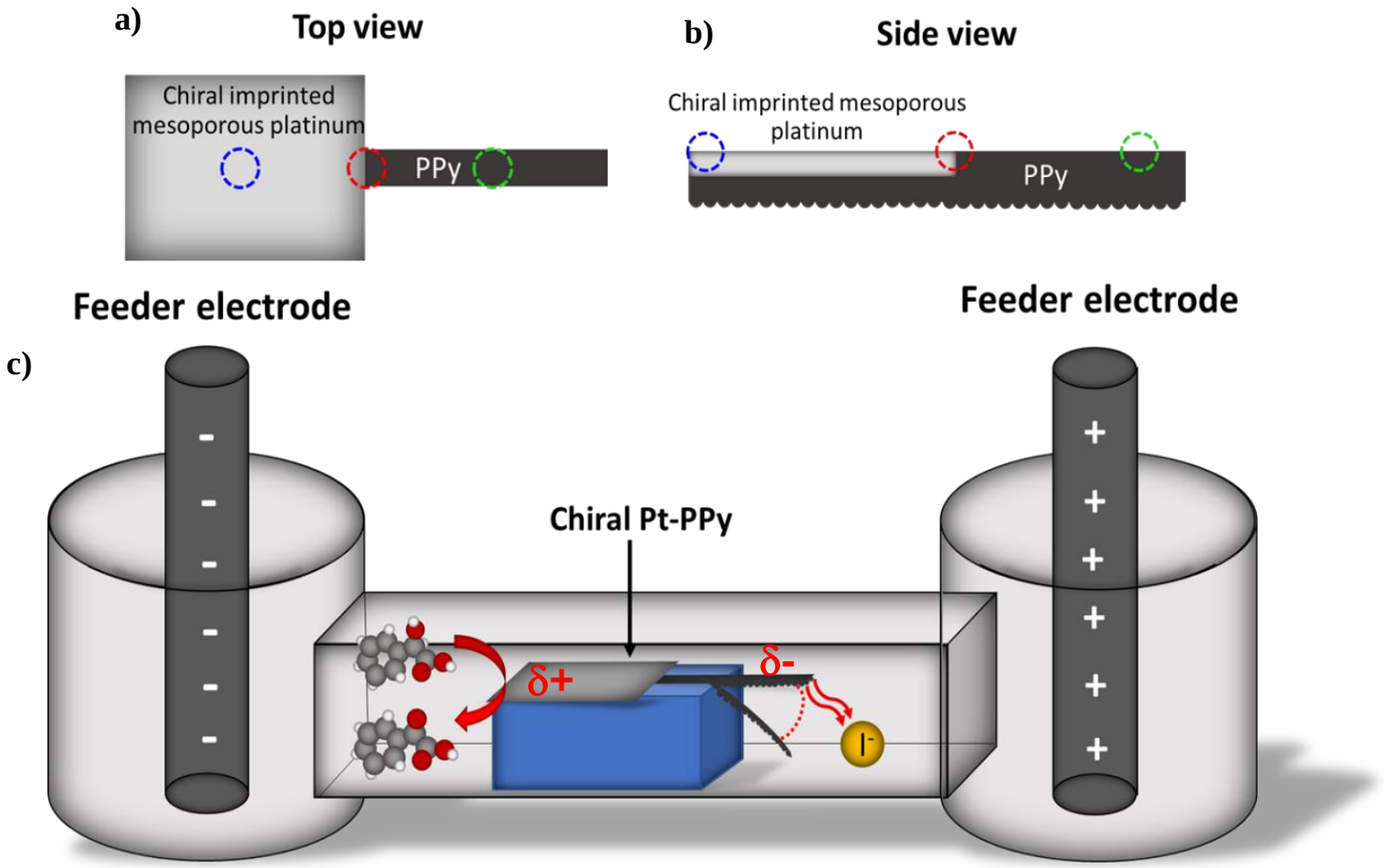
S. Assavapanumat, M. Ketkaew, A. Kuhn, C.Wattanakit, **J. Am.Chem.Soc**. 141 (**2019**) 18870

S. Butcha, S. Assavapanumat, S. Ittisanronnachai, V. Lapeyre, C. Wattanakit, A. Kuhn, **Nat. Comm**.12 (**2021**) 12, 1314

Enantioselective actuation with bipolar electrochemistry



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B. Gupta, B. Goudeau, P. Garrigue, A. Kuhn, **Adv.Funct. Mater.** (2018) 1705825
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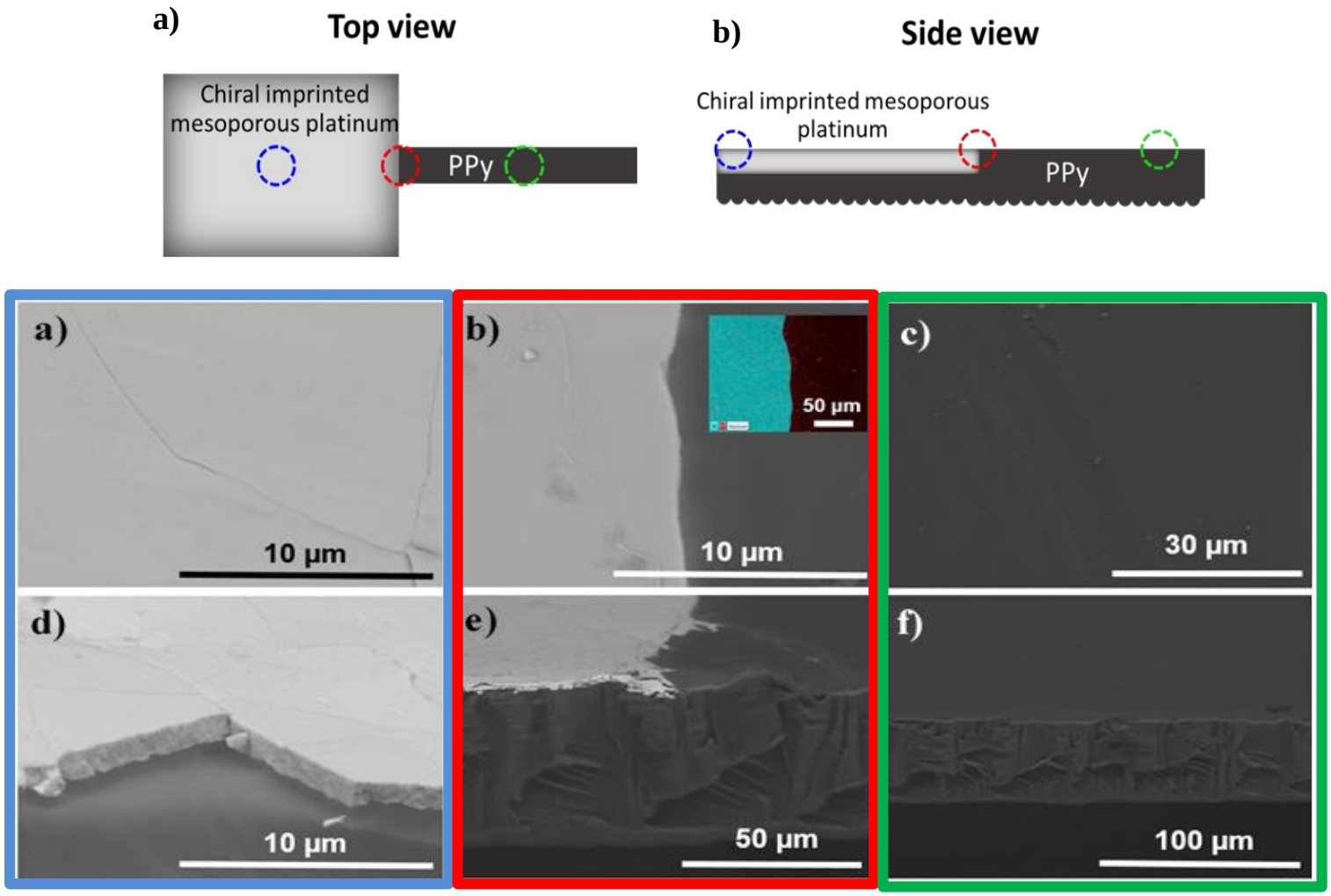
B. Gupta, L. Zhang, A. Melvin, B. Goudeau, L. Bouffier, A. Kuhn, **Chem.Sci. 12** (2021) 2071
S. Assavapanumat, B. Gupta, G. Salinas, B. Goudeau, C. Wattanakit, A. Kuhn, **Chem.Comm. 55** (2019) 10956

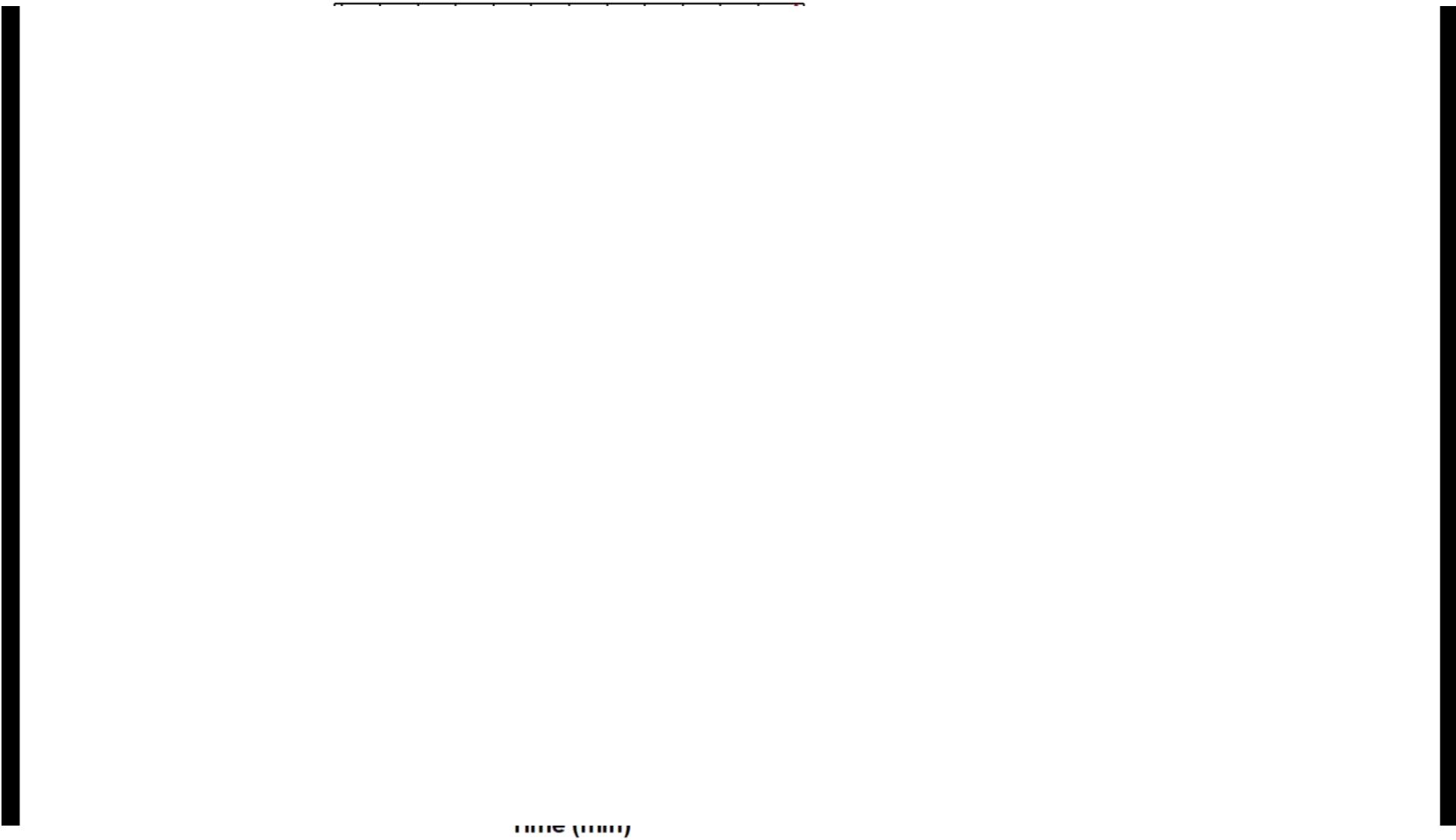
Enantioselective actuation with bipolar electrochemistry



B. Gupta, B. Goudeau, A. Kuhn, **Angew.Chem.Int.Ed. 56** (2017) 14183
B. Gupta, B. Goudeau, P. Garrigue, A. Kuhn, **Adv.Funct. Mater.** (2018) 1705825
L. Zhang, B. Gupta, B. Goudeau, N. Mano, A. Kuhn , **J.Am.Chem.Soc. 140** (2018) 15501
B. Gupta, L. Zhang, A. Melvin, B. Goudeau, L. Bouffier, A. Kuhn, **Chem.Sci. 12** (2021) 2071
S. Assavapanumat, B. Gupta, G. Salinas, B. Goudeau, C. Wattanakit, A. Kuhn, **Chem.Comm. 55** (2019) 10956

Enantioselective actuation with bipolar electrochemistry

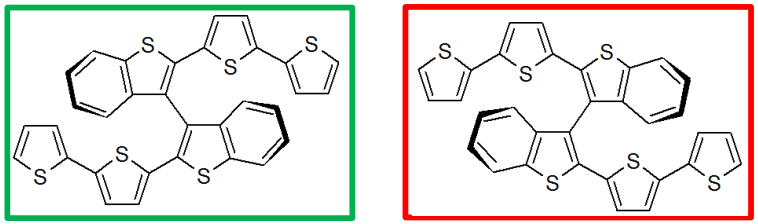
Recognition of mandelic acid on chiral metal/polypyrrole actuators



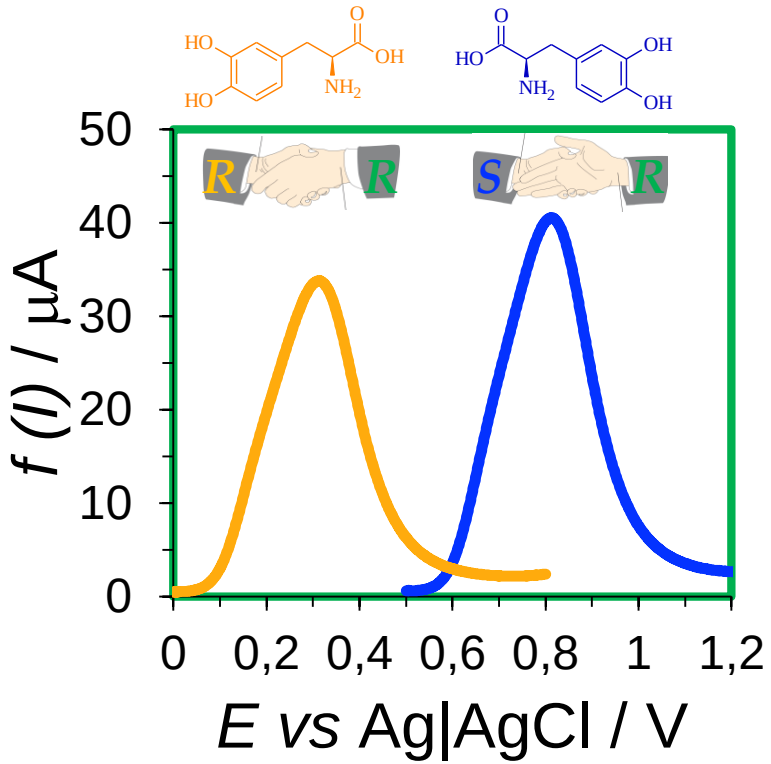
S. Assavapanumat, B. Gupta, G. Salinas, B. Goudeau, C. Wattanakit, A. Kuhn, **Chem.Comm. 55** (2019) 10956

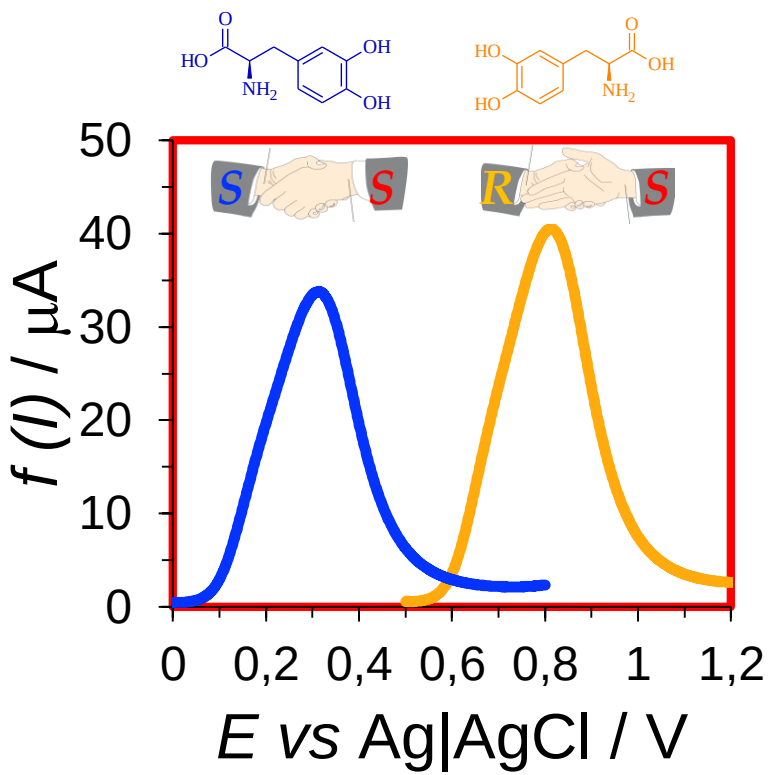
Enantioselective actuation with bipolar electrochemistry

Replacing the chiral metal by inherently chiral oligomers



Electropolymerisation of the inherently chiral enantiopure monomers on polypyrrole





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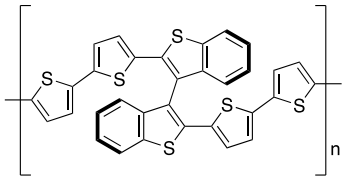
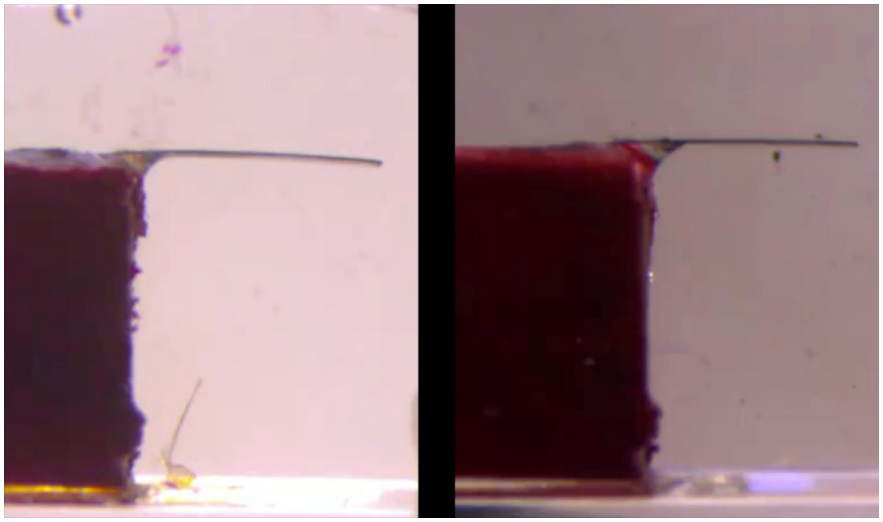
S. Arnaboldi, B. Gupta, T. Benincori, G. Bonetti, R. Cirilli, A. Kuhn, **Anal. Chem. 92** (2020) 14, 10042

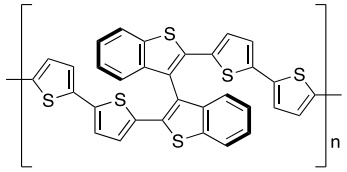
Enantioselective actuation with bipolar electrochemistry

Absolute enantioselective determination with inherently chiral oligomers

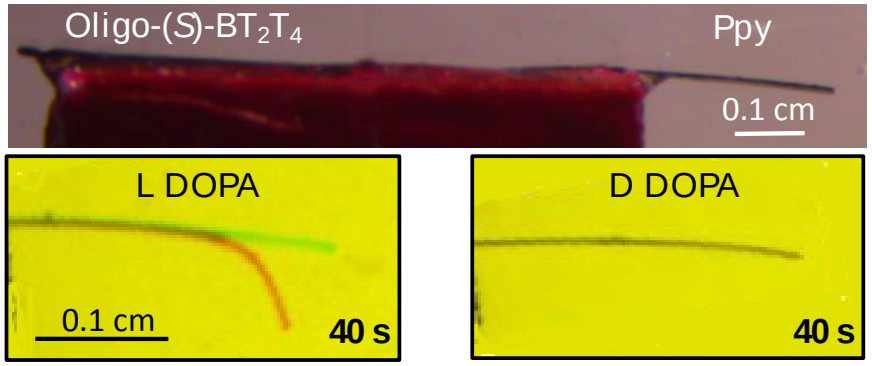


Oligo-(*R*)





Oligo-(*S*)



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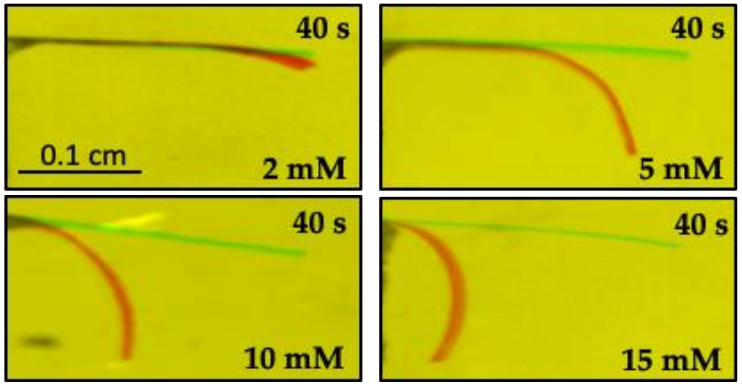
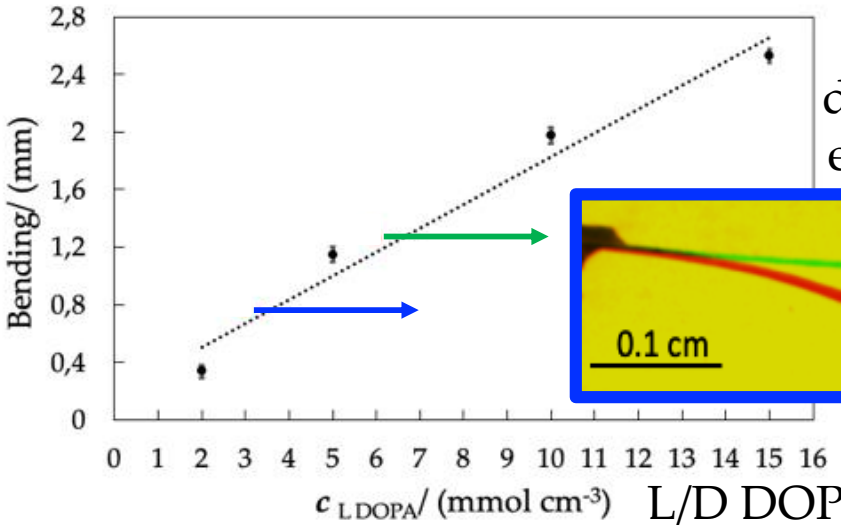
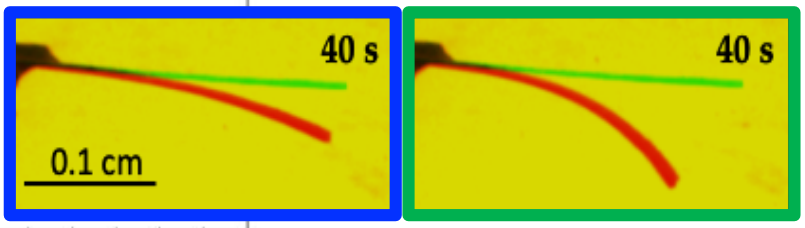
Enantioselective actuation with bipolar electrochemistry

Concentration dependent enantioselective actuation





Indirect determination of the enantiomeric excess



L/D DOPA 3mM/ 6mM

L/D DOPA 6mM/ 3mM

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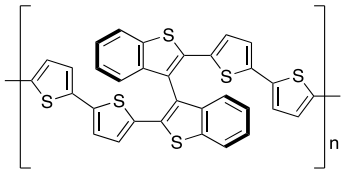
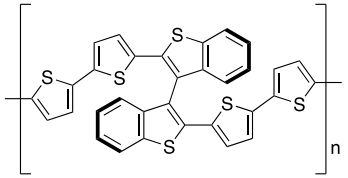
Enantioselective actuation with bipolar electrochemistry

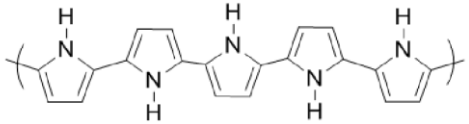
Direct readout of enantiomeric excess



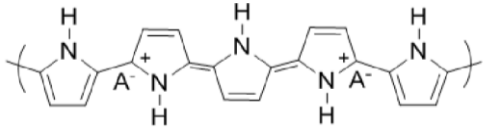
(*S*)-oligo



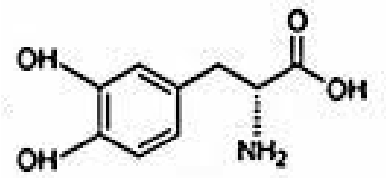
(*R*)-oligo



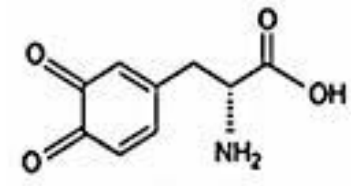
Ppy_{red}



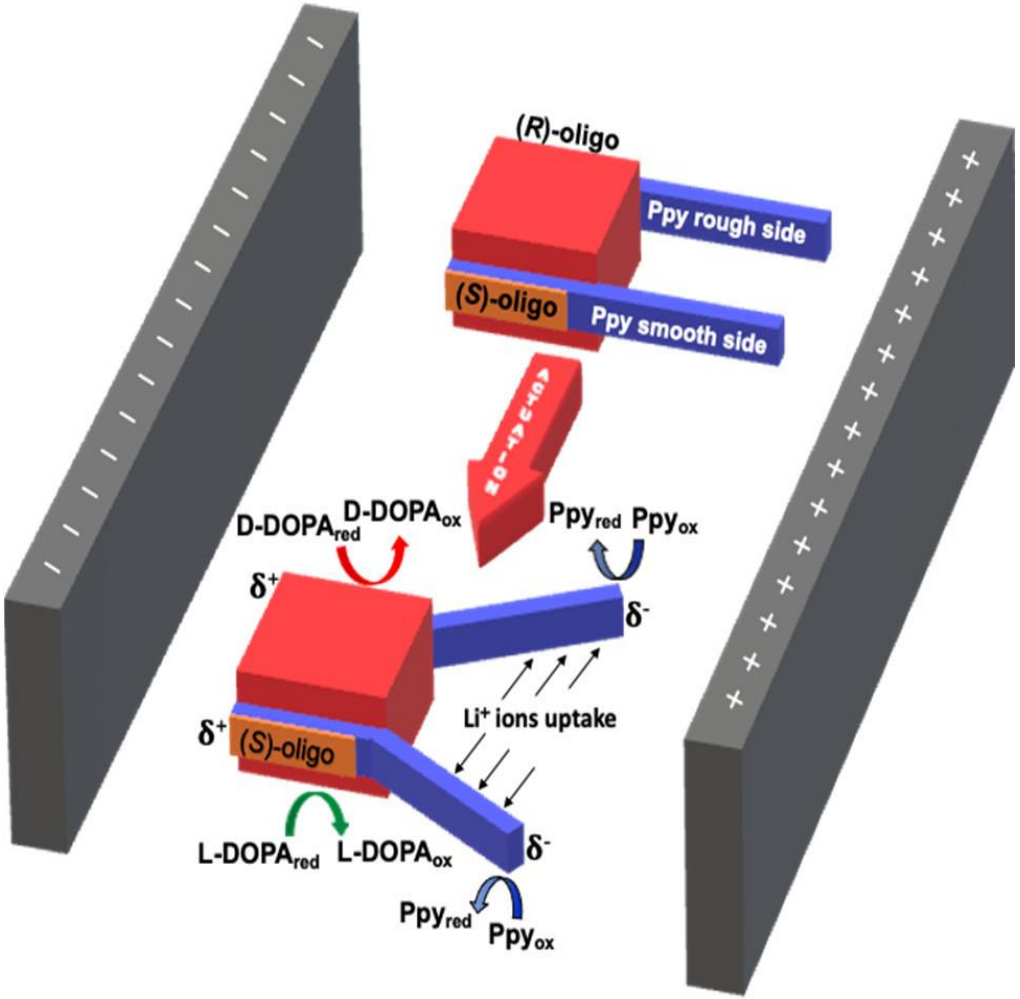
Ppy_{ox}



$DOPA_{red}$



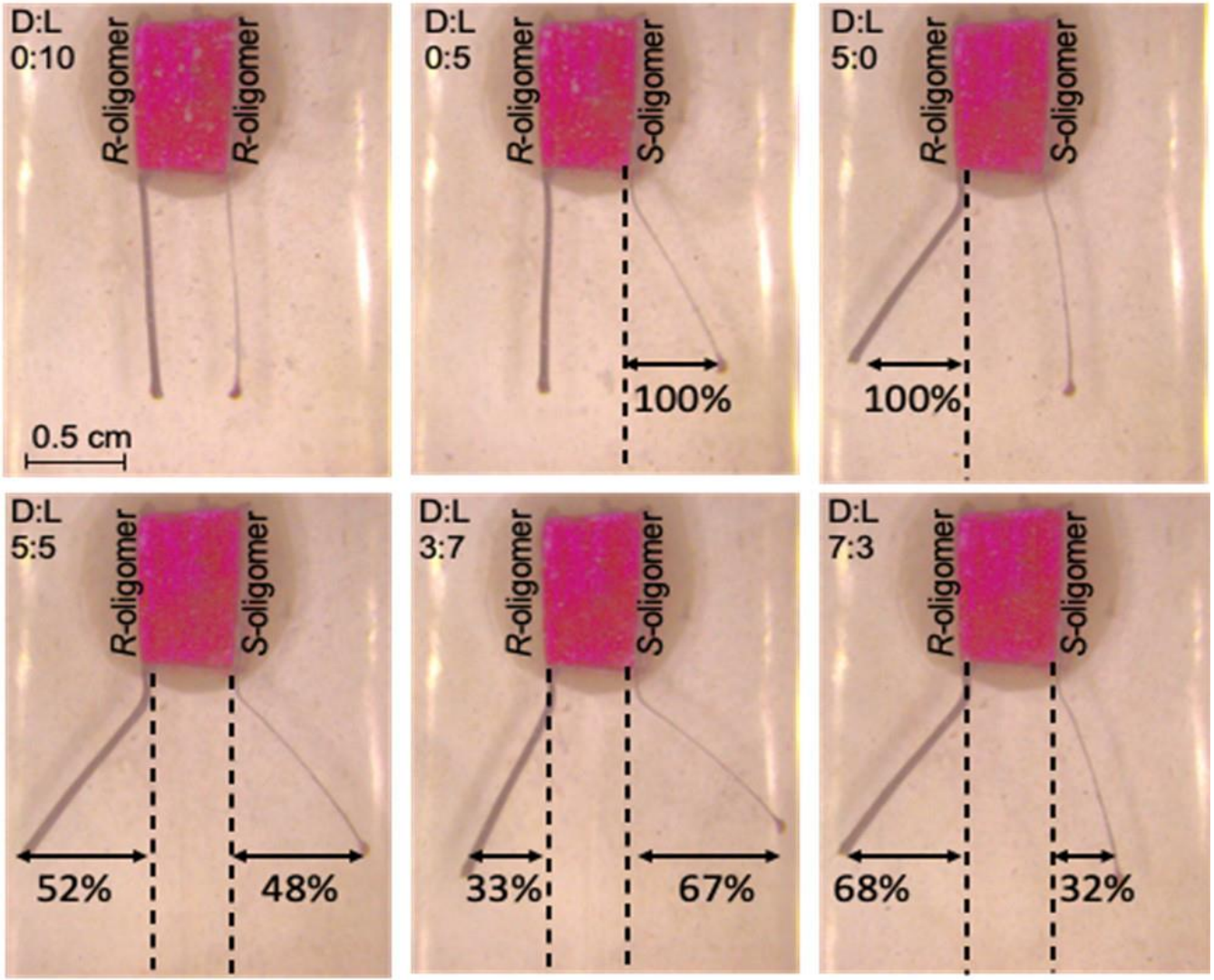
$DOPA_{ox}$



S. Arnaboldi, G. Salinas, G. Bonetti, R. Cirilli, T. Benincori, a. Kuhn, **ACS Meas. Au.** (2021) 10.1021/acsmeasuresciau.1c00011

Enantioselective actuation with bipolar electrochemistry

Direct readout of enantiomeric excess

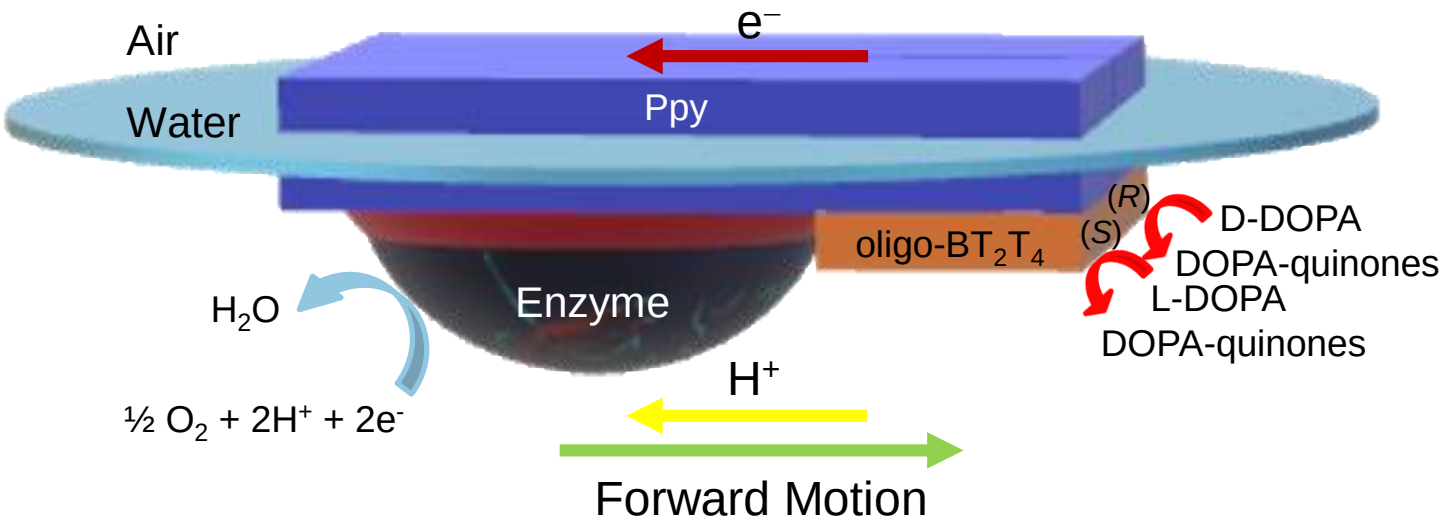


L-DOPA+D-DOPA = 10 mM
$LiClO_4$ 0.2 M + H_20
Electric field 0.6 V cm^{-1}

S. Arnaboldi, G. Salinas, G. Bonetti, R. Cirilli, T. Benincori, a. Kuhn, **ACS Meas. Au.** (2021) 10.1021/acsmeasuresciau.1c00011

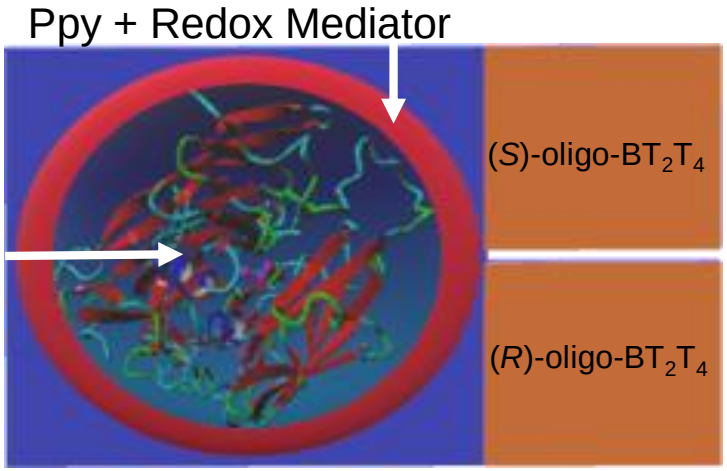
Enantioselective autonomous motion

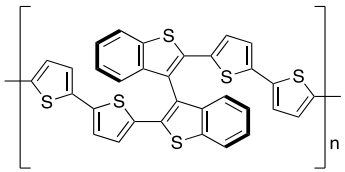
Intrinsic bipolar swimmer

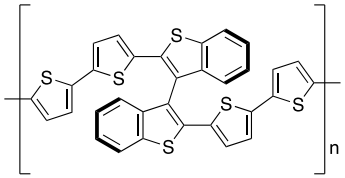


Top view of the swimmer

Ppy + Redox Mediator + Enzyme



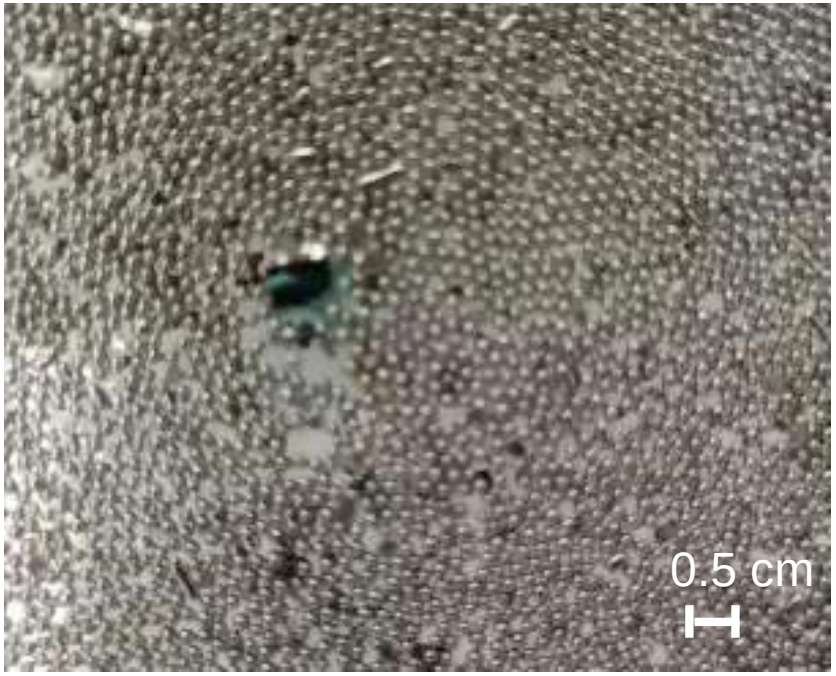


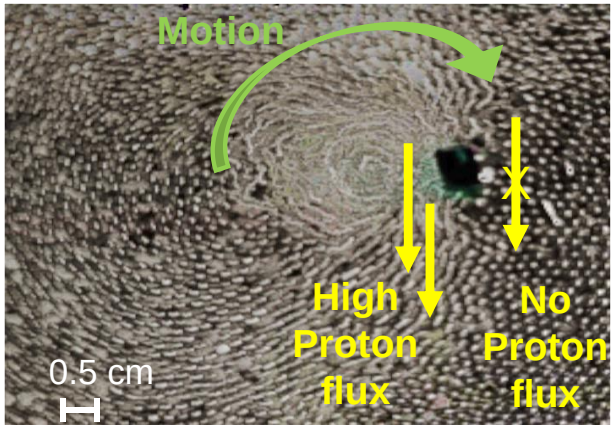


S. Arnaboldi, G. Salinas, A. Karajic, P. Garrigue, G. Bonetti, R. Cirilli, T. Benincori, S. Bichon, S. Gounel, N. Mano, A. Kuhn, **Nat.Chem. 13** (2021) 1241–1247

Enantioselective autonomous motion

Self-electrophoresis mechanism





The swimmer is placed in a 5 mM D-DOPA 0.3 M citrate/phosphate buffer (pH 5).

$DOPA \rightarrow DOPA_{quinone} + 2\ e^- + 2\ H^+$ (anode)

$\frac{1}{2}\ O_2 + 2\ H^+ + 2e^- \xrightarrow{BOD} H_2O$ (cathode)

$Med_{ox} + e^- \leftrightarrows Med_{red}$ (cathode)

The swimmer is on purpose immobilized at a fixed position.

Only the liquid can move and the hydrodynamic flow can be tracked by adding carbon beads (1 μm) to the solution.

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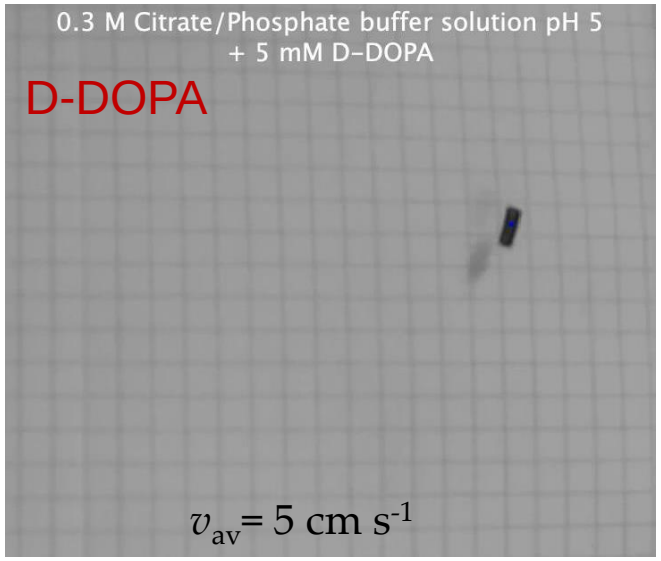
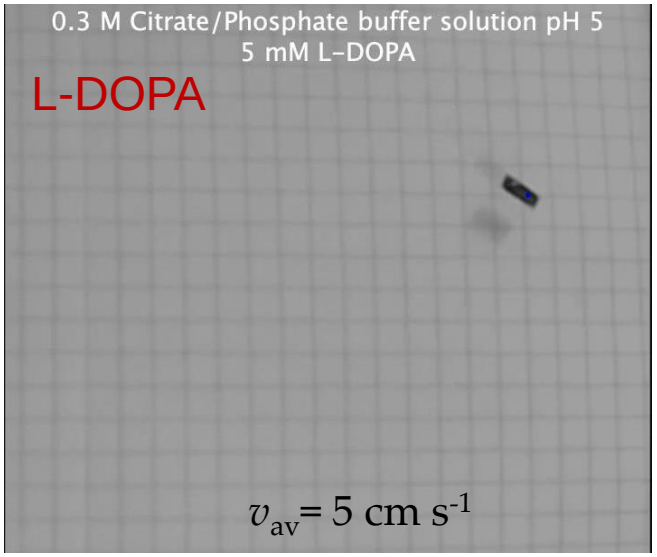
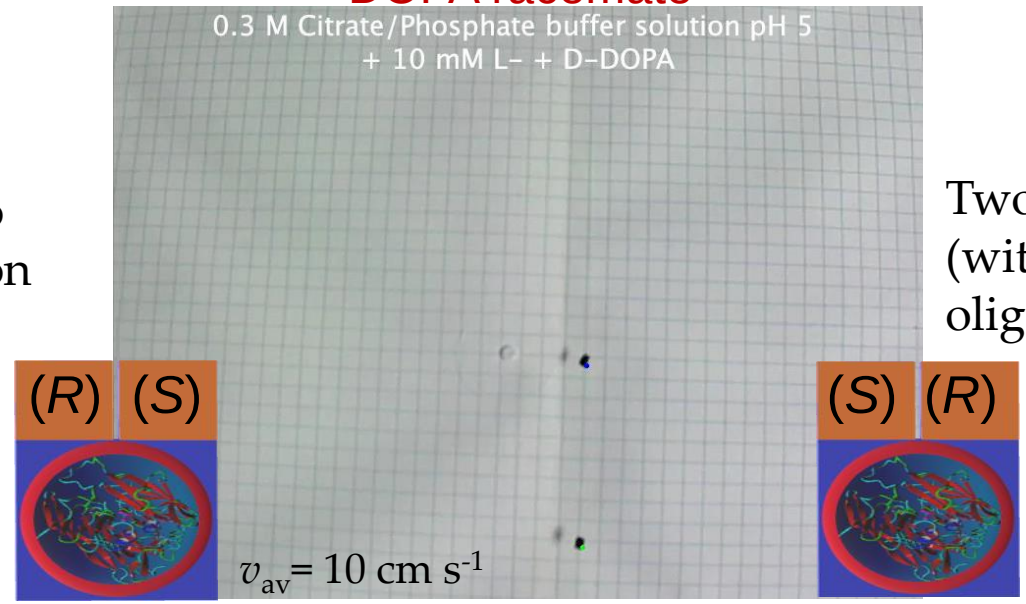
Enantioselective autonomous motion





DOPA racemate

Conversion of molecular information into macroscopic action



Two swimmers (with opposite oligomer configuration)

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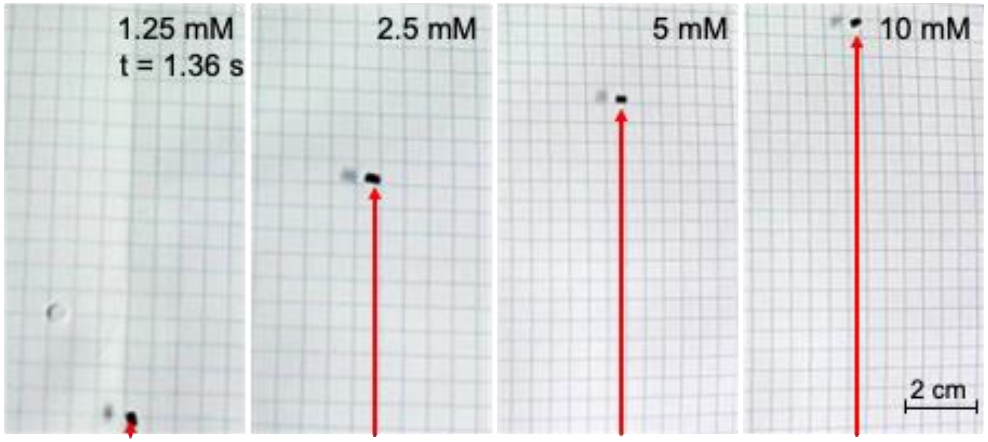
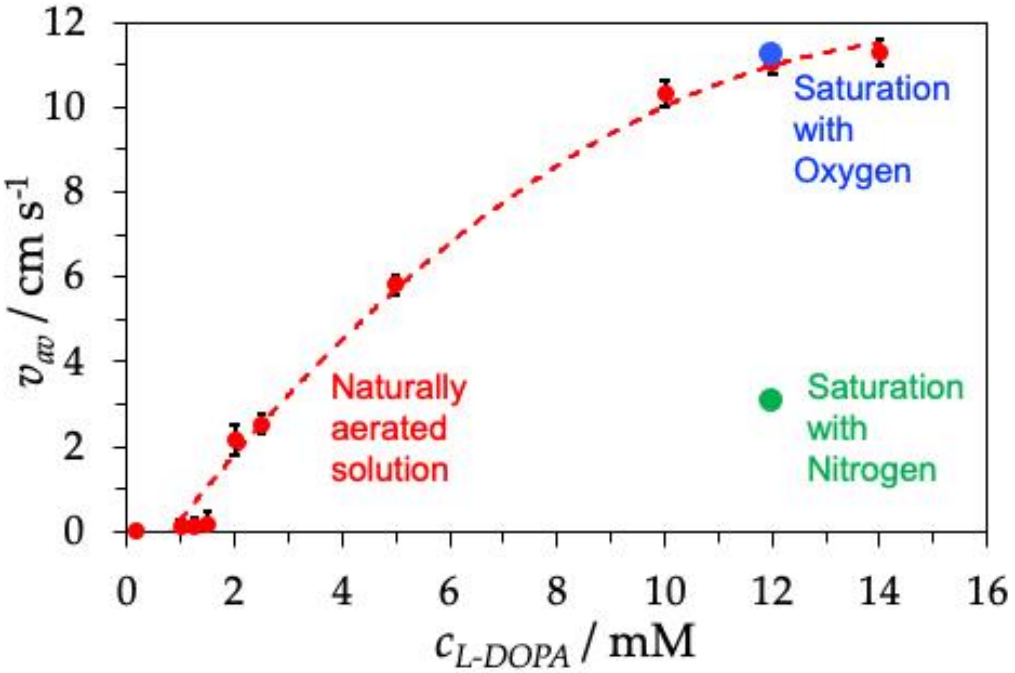
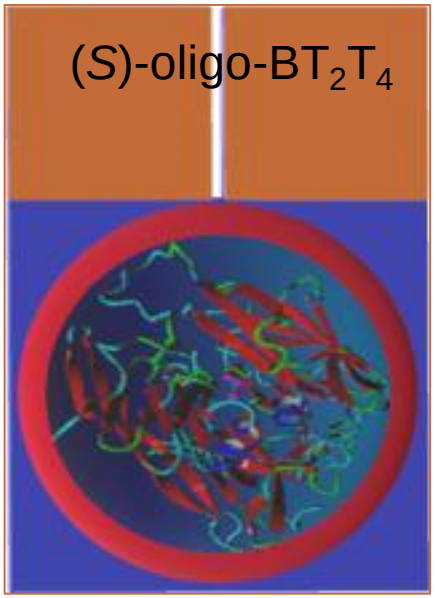
Enantioselective autonomous motion

Concentration dependent speed





Only (*S*)-BT_2T_4 oligomer is deposited on the entire extremity of the swimmer to generate linear motion.



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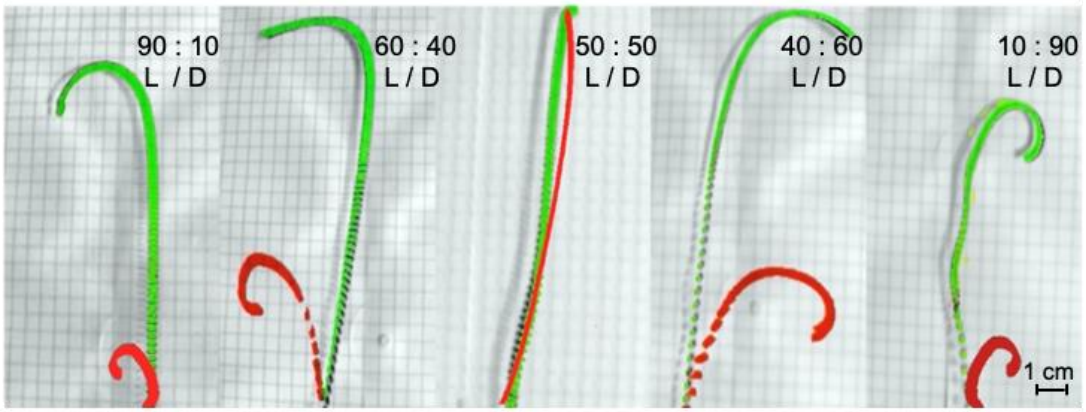
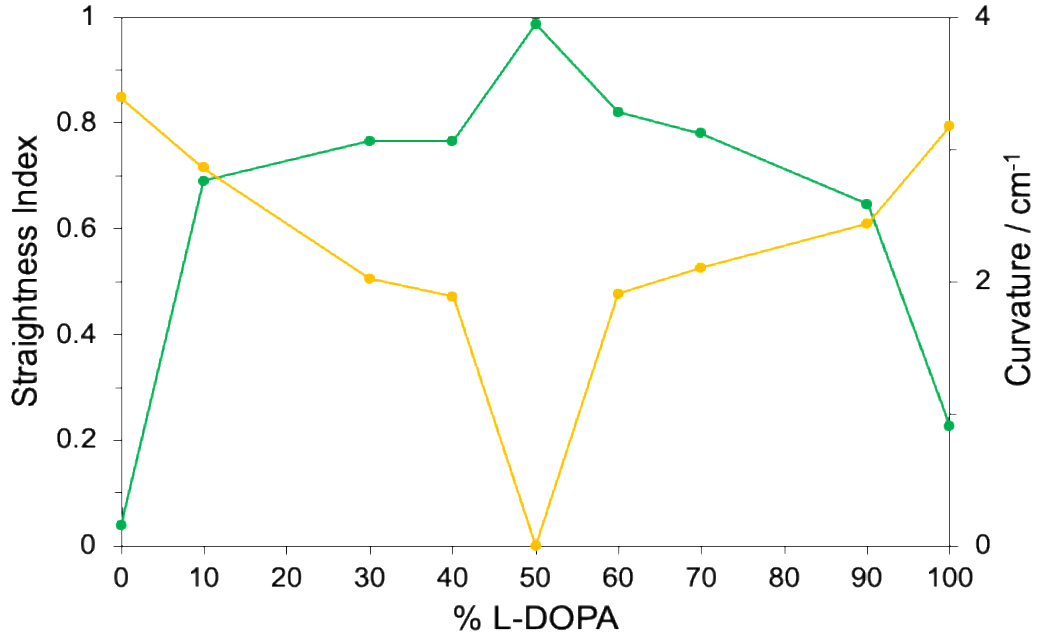
Enantioselective autonomous motion

Direct readout of enantiomeric excess



Green trajectories
L- + D-DOPA 5 mM
Red trajectories
L- + D-DOPA 2.5 mM.



0.3 M citrate/phosphate buffer solutions at pH 5

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CONCLUSION

Biomimetic recognition of chiral molecules

at unconventional chiral surfaces

with a straightforward readout

in an unconventional way

Applications in analysis

electroseparation

and synthesis

Thanks

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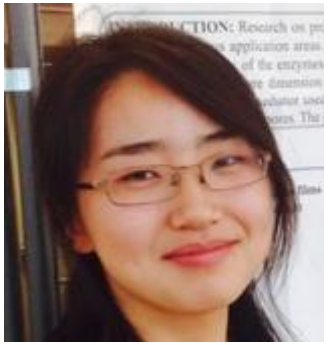

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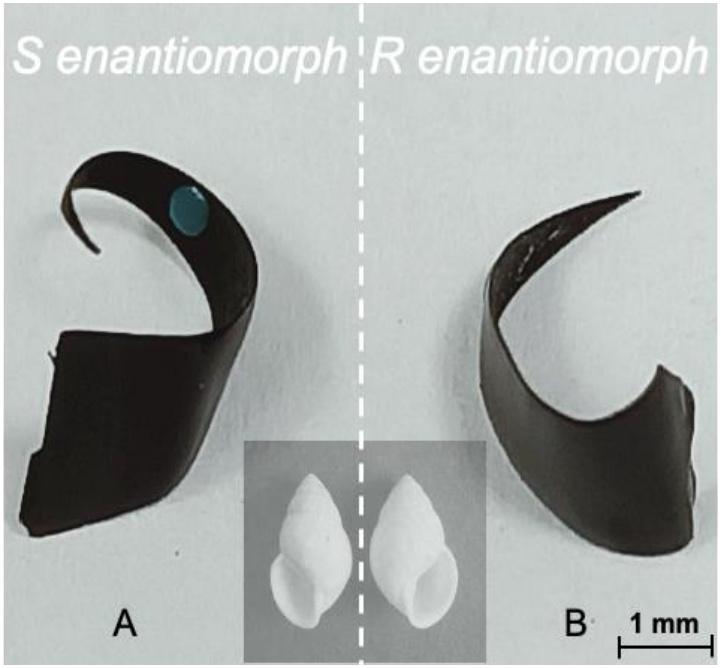
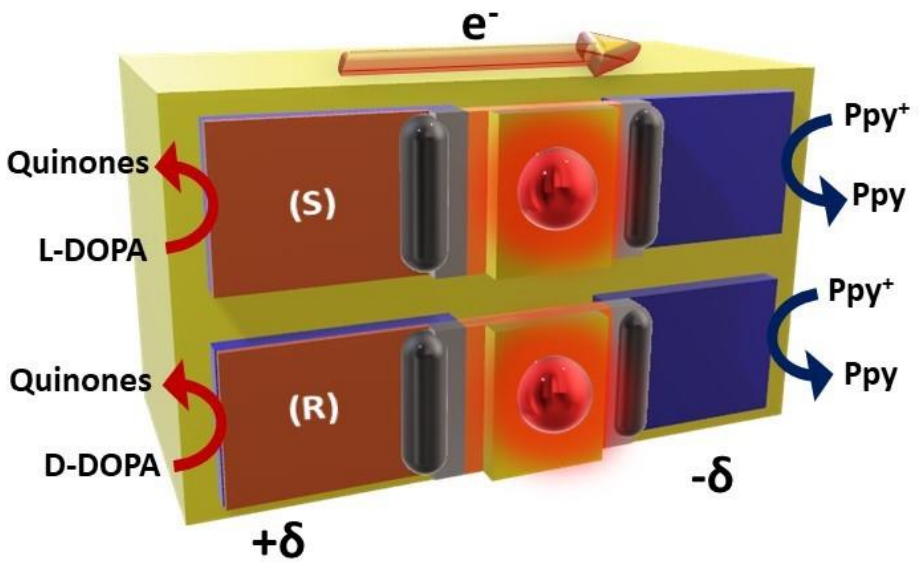
Thank YOU for your attention





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