

# CURRICULUM VITAE



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Laboratory of Electrochemistry and Physical Chemistry of the Solid State.  
Institute of chemistry – UMR 7177  
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## Skills

Expert with the electrochemical techniques : coulometry, polarography, cyclic and stationary voltammetry, Ring-Disk voltammetry, electrocatalysis.  
Teaching undergraduate courses in electrochemistry and general chemistry

## Research: Molecular Electrochemistry

### Structure-redox activity correlations.

The understanding of the redox behaviour of **Conjugated Donor – Acceptor** carried out the last five years, allowed us to get insights in more complex non-planar A-D structures that may be of interest for optoelectronics. Indeed, non-planar conjugated D-A have some interesting properties compared to planar structures. Non-planar systems show less aggregation, a better solubility and quite often it is easier to sublime. All these characteristics as well as their electrochemical characteristics make this derivatives as good candidates for optoelectronics. During the next years new D-A compounds will be synthesised by the François Diederich group (ETH Zurich, Switzerland) and investigated to be able to improve the structure-activity correlation and find the adequate structure for possible applications in optoelectronics.

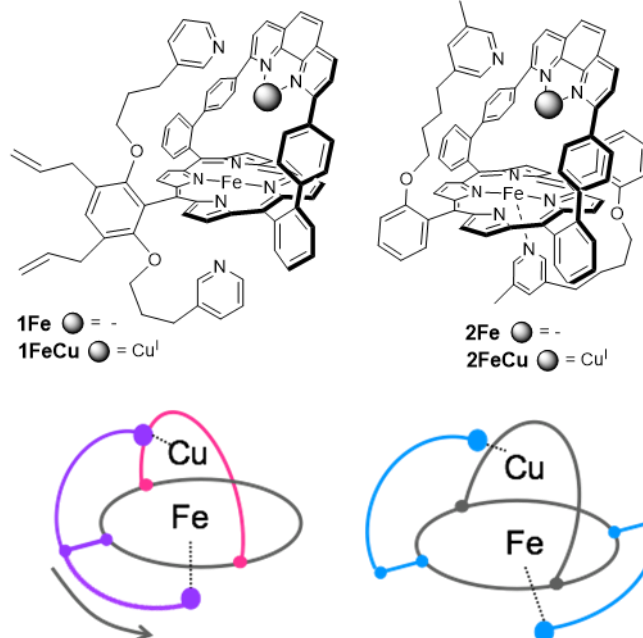
### Cofacial architectures

Cofacial bis-porphyrin architectures have been the subject of intense research as models of photosynthetic events and have progressively taken a new turn toward potential applications in recognition and activation of small molecules, sensing or information storage. In particular, scaffolds in which two tetrapyrrolic macrocycles are maintained in face-to-face arrangement by a calixarene platform acting as a hinge were investigated and a chewing motion induced by electrochemistry has been observed (Pognon, G.; Boudon, C.; Schenk, K.J.; Bonin, M.; Bach, B.; Weiss, J.; *J. Am. Chem. Soc.* 2006, *121*, 3488-3489).

### Models of Cytochrome c Oxidase

To investigate how structural changes affect the binding of oxygen and carbon monoxide and the electrocatalytic reduction of oxygen, the Weiss group (CLAC-UMR7177) has designed several cytochrome c oxidase models based on a phenanthroline-strapped porphyrin.

Refinement of the binding behavior of these models led to the ditopic ligand **1**, which was used in the preparation of the Fe<sub>a3</sub>-Cu<sub>B</sub> active site of CcO. This model appears to be a highly realistic mimic of intermediate A, which is the first oxygenated intermediate in the catalytic cycle of CcO. However, the four electron reduction of oxygen is more efficient in the iron complex **1Fe** than in the iron-copper complex [**1FeCu**].



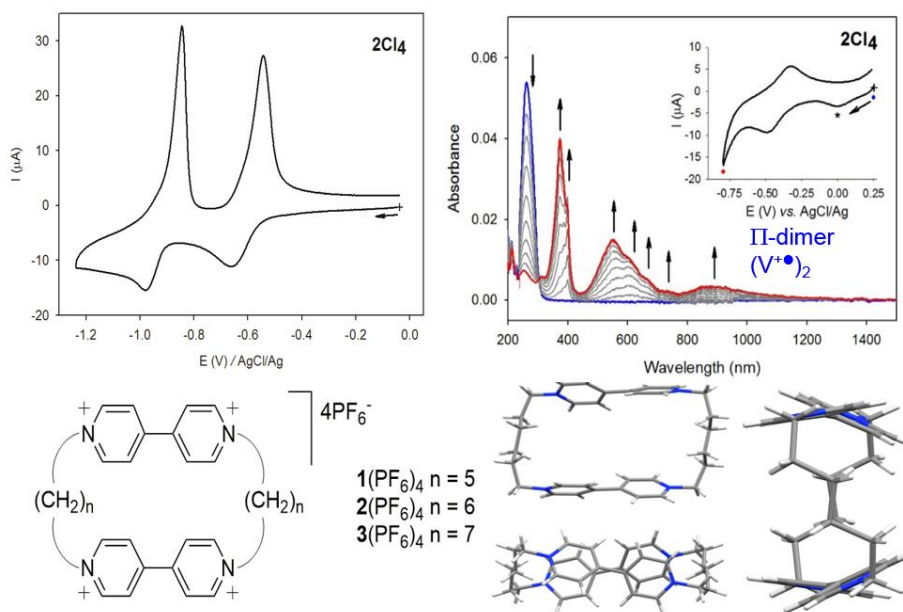
Cytochrome c oxidase models constructed around a phenanthroline-strapped porphyrin and cartoon representations of the models. The phenanthroline pocket provides the distal binding site, whereas the open face of the porphyrin is the proximal site.

#### *Electrocatalytic RRDE studies*

For models [**1Fe<sup>II</sup>**]<sup>2+</sup> and [**1Fe<sup>II</sup>-Cu<sup>I</sup>**]<sup>+</sup>, it was previously reported that the presence of copper(I) in the latter facilitated the reduction of oxygen and that four-electron reduction predominated, with only 4% of two-electron reduction. In addition, hydrogen peroxide production was lower in the presence of copper than in the model containing just iron(II). However, for models [**2Fe<sup>II</sup>**]<sup>2+</sup> and [**2Fe<sup>II</sup>-Cu<sup>I</sup>**]<sup>+</sup>, the rotating ring-disk electrode (RRDE) studies showed that both models were less efficient than [**1Fe<sup>III</sup>**]<sup>3+</sup> and [**1Fe<sup>III</sup>-Cu<sup>I</sup>**]<sup>2+</sup> in the electrocatalytic reduction of O<sub>2</sub>.

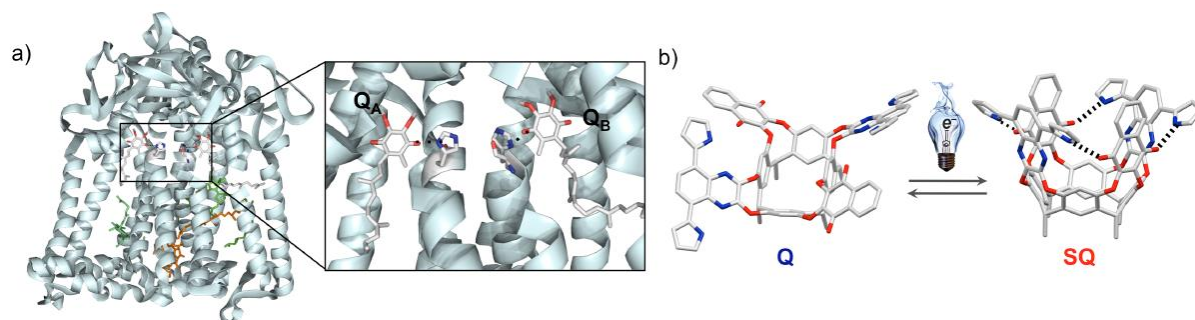
#### **Flexible Viologen Cyclophanes.**

Comparative electro- and spectro-electrochemical studies of flexible cyclophane with different linkers show that the development of intramolecular interactions in aqueous solution depends on the length of the bridges. This dependence is confirmed by EPR and DFT studies of the magnetic coupling in the diradical dication species. (Berville M., Choua S., Gourlaouen C., Boudon C., Ruhlmann L., Bailly C., Cobo S., Saint Aman E., Wytko J.A., Weiss J, *Chem.Phys.Chem.* **18**, issue 7(2017) 796-803).



### Photoredox-Switchable Resorcin[4]arene CavitanDs: Radical Control of Molecular Gripping Machinery via Hydrogen Bonding

Molecular grippers feature a binary conformational switch in response to external stimuli that results in reversible encapsulation of smaller molecules. This behavior makes them potentially applicable as delivery systems, sensors, receptors, or elements in nanorobotics. However, the control of molecular machinery by physical stimuli, such as electrical charge or light, is a prerequisite to their application. We therefore developed in collaboration with Prof. F. Diederich and Dr. Jovana Milić (ETH Zurich) photoredox-switchable molecular grippers based on resorcin[4]arene cavitand platforms equipped with alternating quinone (Q) and quinoxaline walls carrying hydrogen bond donating groups, which were inspired by the role of semiquinones (SQ) in natural photosynthesis (Figure 15). The SQ state was generated electrochemically *via* cyclic voltammetry and photochemically by using  $[\text{Ru}(\text{bpy})_3]^{2+}$  as a photocatalyst. The properties were studied by UV-Vis spectroelectrochemistry, EPR, ENDOR, and transient absorption spectroscopy, in conjunction with DFT calculations. It was shown that these systems adopt an open conformation in the oxidized Q state until redox interconversion to the paramagnetic SQ radical anion provides the stabilization of the closed form through hydrogen bonding. The tunable magnetic properties and enhanced binding affinities of the grippers, along with high reversibility and responsiveness to electrical and electromagnetic stimuli, set the stage for a new generation of artificial molecular machines and devices based on this switching concept in the future.



Schematic representation of the (a) photosynthetic reaction center of *Rb. sphaeroides* (PDB 1DV3) that inspired the design of (b) the switching concept of the photoredox-switchable molecular grippers.

#### Main important point in research activities

- Structure–redox activity correlations: *Collaboration* : Prof. F. DIEDERICH (ETH, Zurich – Suisse )
- Models of Cytochrome c Oxidase
- .*Collaborations* : Prof. P.HELLWIG, J.WEISS ( UMR 7177), B.BOITREL ( Rennes)

- Chewing motion induced by electrochemistry in Cofacial bis-porphyrin architectures  
*Collaboration : J. WEISS (UMR 7177 )*
- Redox properties, comparative spectro-electrochemical studies of flexible cyclophane structures – Bipyridium tetraester, stability of the corresponding reduced species.  
*Collaboration : J. WEISS- J. WYTKO (UMR 7177)*

### **Scientific Production :**

130 international publications, national and international communications.

### **Collaborations :**

- Pr. F. Diederich ( ETH Zürich, Suisse ) depuis 1993
- Dr. R. Faust ( Heidelberg, Allemagne ) depuis 1997
- Dr. J.F. Nierengarten ( IPCMS Strasbourg ) ( ECODEV/ADEME 2000 – 2003 )
- Drs J. Weiss et J. Wytko ( UMR 7177 CNRS – Strasbourg )
- Pr. P. Hellwig ( UMR 7177 CNRS – Strasbourg )
- Dr. B. Boitrel ( Université de Rennes )
- Pr. R.R.Tykwinski – Friederich-Alexander-Universität-Erlangen, Allemagne
- Pr. I. Biaggio – Department of Physics-Bethlehem – USA
- Pr.M. Stöhr – University of Groningen – Groningen – The Netherlands
- Pr.M. Irie – Kyushu University – Fukuoka – Japon
- Pr G. Gescheidt – Institut für Physikalische und Theoretische Chemie-TU Graz-Autriche

Co-worker in PRCI French-German DEFCEMSKALL (2016-2019) (Dr E. Gimenez-Arnau-UMR 7177\_ICS-Strasbourg)(187257 Euros) - ANR Blanc PRIMO (2012-2015)( Dr J. Weiss-UMR 7177-ICS-Strasbourg and Dr. C.Bucher-UMR 5250-DCM-Grenoble)

### **EDUCATIONAL BACKGROUND**

**2004- present : Full Professor**, University of Strasbourg, Laboratory of Electrochemistry and of Physical Chemistry of the Solid State, Institute of Chemistry (UMR 7177)

**1988- 2004: Associate Professor**, University of Strasbourg, Laboratory of Electrochemistry and of Physical Chemistry of the Solid State, Institute of Chemistry (UMR 7177)

#### **1987: Ph'D in Physical Chemistry (HDR)**

Supervisors: Professor Maurice Gross and Dr Jean-Paul Gisselbrecht

President: Professor Jean-Marie Lehn

University Louis Pasteur, Strasbourg, France. 30 mars 1987

#### **1979 : Ph'D in Electrochemistry,**

Supervisors: Professor Maurice Gross and Dr François Peter

President: Professor Jean-Marie Lehn

University Louis Pasteur, Strasbourg, France. 17 novembre 1979

## Publications since 2009

**P.78 Frank, B. B.; Camafort Blanco, B.; Jakob, S.; Ferroni, F.; Pieraccini, S.; Ferrarini, A.; Boudon, C.; Gisselbrecht, J. P.; Seiler, P.; Spada, G. P.; Diederich, F.**

N-Arylated 3,5-Dihydro-4H-dinaphtho[2,1-c:1',2'-e]azepines: Axially Chiral Donors with High Helical Twisting Powers for Nonplanar Push-Pull Chromophores  
*Chem.-Eur.J.* 2009, 15, N° 36, 9005-9016.

**P.79 Jarowski, P. D.; Wu, Y. L.; Boudon, C.; Gisselbrecht, J. P.; Gross, M.; Schweizer, W. B.; Diederich, F.**

New donor-acceptor chromophores by formal [2+2] cycloaddition of donor-substituted alkynes to dicyanovinyl derivatives  
*Org.Biomol.Chem.* 2009, 7, N° 7, 1312-1322.

**P.80 Kato, S. I.; Kivala, M.; Schweizer, W. B.; Boudon, C.; Gisselbrecht, J. P.; Diederich, F.**

Origin of Intense Intramolecular Charge-Transfer Interactions in Nonplanar Push-Pull Chromophores  
*Chem.-Eur.J.* 2009, 15, N° 35, 8687-8691.

**P.81 Kivala, M.; Boudon, C.; Gisselbrecht, J. P.; Enko, B.; Seiler, P.; Mueller, I. B.; Langer, N.; Jarowski, P. D.; Gescheidt, G.; Diederich, F.**

Organic Super-Acceptors with Efficient Intramolecular Charge-Transfer Interactions by [2+2] Cycloadditions of TCNE, TCNQ, and F4-TCNQ to Donor-Substituted Cyanoalkynes  
*Chem. Eur. J.* 2009, 15, N° 16, 4111-4123, S4111-1.

**P.82 Lo, M.; Mahajan, D.; Wytko, J. A.; Boudon, C.; Weiss, J.**

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*Org.Lett.* 2009, 11, N° 12, 2487-2490.

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Chiral and Achiral Charge-Transfer Chromophores with a Dendralene-Type Backbone by Electronically Controlled Cycloaddition/Cycloreversion Cascades  
*Eur.J.Org.Chem.* 2010, N° 13, 2487-2503.

**P.84 Kato, S. i.; Beels, M. T. R.; La Porta, P.; Schweizer, W. B.; Boudon, C.; Gisselbrecht, J. P.; Biaggio, I.; Diederich, F.**

Homoconjugated Push-Pull and Spiro Systems: intramolecular Charge-Transfer Interactions and Third-Order Optical Nonlinearities  
*Angew.Chem., Int.Ed.* 2010, 49, N° 35, 6207-6211, S6207-1.

**P.85 Wu, Y. L.; Bures, F.; Jarowski, P. D.; Schweizer, W. B.; Boudon, C.; Gisselbrecht, J. P.; Diederich, F.**

Proaromaticity: organic Charge-Transfer Chromophores with Small HOMO-LUMO Gaps  
*Chem.-Eur.J.* 2010, 16, N° 31, 9592-9605, S9592-1.

**P.86 Frank B.B., Laporta P.R., Breiten B., Kuzyk M.C., Jarowski P.D., Schweizer W.B., Seiler P., Biaggio I., Boudon C., Gisselbrecht J.P. and Diederich F.**

Comparison of CC Triple and Double Bonds as Spacers in Push-Pull Chromophores.  
*Eur. J. Org. Chem.* (2011) 4307-4317

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Donor-substituted octacyano[4]dendralenes: a new class of cyano-rich non-planar organic acceptors.  
*Chem. Sci.*, 2, (2011) 88-93.

**P.88 Jordan M., Kivala M., Boudon C., Gisselbrecht J. P., Schweizer W. B., Seiler P., Diederich F.**

Switching the regioselectivity in cycloaddition-retro-electrocyclizations between donor-activated alkynes and the electron-accepting olefins TCNE and TCNQ.  
*Chem. Asian J.*, 6 (2011) 396-401

- P.89 Jayamurugan G., Gisselbrecht J.P., Boudon C., Schoenebeck F., Schweizer W.B., Berneta B., and Diederich F.**  
Expanding the chemical space for push-pull chromophores by non-concerted [2+2] and [4+2] cycloadditions: access to a highly functionalised 6,6-dicyanopentafulvene with an intense, low-energy charge-transfer band  
*Chem. Commun.*, **47** (2011) 4520–4522
- P.90 Fesser P., Iacovita C., Wäckerlin C., Vijayaraghavan S., Ballav N., Howes K., Gisselbrecht J.P., Crobu M., Boudon C., Stöhr M., Jung T.A., and Diederich F.**  
Visualizing the Product of a Formal Cycloaddition of 7,7,8,8-Tetracyano-p-Quinodimethane (TCNQ) to an Acetylene-Appended Porphyrin by Scanning Tunneling Microscopy on Au(111)  
*Chem. Eur. J.* **17** (2011) 5246 – 5220
- P.91 Silvestri F., Jordan M., Howes K., Kivala M., Rivera-Fuentes P., Boudon C., Gisselbrecht J.P., Schweizer W.B., Seiler P., Chiu M., and Diederich F.**  
Regular Acyclic and Macrocyclic [AB] Oligomers by Formation of Push–Pull Chromophores in the Chain-Growth Step  
*Chem. Eur. J.* **17** (2011) 6088 – 6097
- P.92 Pochorowski I., Boudon C., Gisselbrecht J.P., Ebert M.O., Schweizer W.B., and Diederich F.**  
Quinone-Based, Redox-Active Resorcin[4]Arene Cavitands  
*Angew. Chem. Int. Ed.*, **51** (2012) 262-266
- P.93 Chiu M., Jaun B., Beels M.T.R., Biaggio I., Gisselbrecht J.P., Boudon, C., Schweizer W.B., Kivala M. and Diederich F.**  
N,N'-Dicyanoquinone Diimide-Derived Donor-Acceptor Chromophores: Conformational Analysis and Optoelectronic Properties.  
*Organic Letters*, **14** (1) (2012) 54-57
- P.94 Melin F., Trivella A., Lo M., Ruzié C., Hijazi I., Wytko J.A., Boitrel B., Boudon C., Hellwig P. and Weiss J.**  
Comparative Studies in Series of Cytochrome C Oxidase Models.  
*J. Org. Biochemistry* **108** (2012) 196-202
- P.95 Rivera-Fuentes P., Von Wantoch-Rebowski M., Schweizer W. B., Gisselbrecht J.P., Boudon C. and Diederich F.**  
Cascade Carbopalladation Reaction between Alkynes and gem-Dibromoolefins: Facile Access to Monoannulated Pentalenes.  
*Organic Letters* **14** (16) (2012) 4066-4069
- P.96 Tancini F., Wu Y-L., Schweizer W. B., Gisselbrecht J.P., Boudon C., Jarowski P.D., Beels M.T.R., Biaggio I. and Diederich F.**  
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*Eur.J.Org. Chem.* (2012) 2756-2765
- P.97 Wu Y-L., Tancini F., Schweizer W. B., Paunescu D., Boudon C., Gisselbrecht J.P., Jarowski P.D., Dalcanale E. and Diederich F.**  
Proacetylenic Reactivity of a Push-Pull Buta-1,2,3-Triene: New Chromophores and Supramolecular Systems.  
*Chem. Asian.J.* **7** (2012) 1185-1190
- P.98 Pochorowski I., Ebert M.O., Gisselbrecht J.P., Boudon C., Schweizer W. B., and Diederich F.**  
Redox-Switchable Resorcin [4]Arene Cavitands: olecular Grippers.  
*J.Am.Chem.Soc.* **134** (2012) 14702-14705
- P.99 Finke A.D., Dumele O., Zalibera M., Confortin D., Cias P., Jayamurugan G., Gisselbrecht J.P., Boudon C., Schweizer W. B., Gescheidt G. and Diederich F.**  
6,6-Dicyanopentafulvenes: Electronic Structure and Regioselectivity in [2+2] Cycloaddition-Retroelectrocyclisation Reactions.  
*J.Am.Chem.Soc.* **134** (2012) 18139-18146

**P. 100 Wu Y.L., Stuparu M.C., Boudon C., Gisselbrecht J.P., Schweizer W. B., Baldrige K.K., Siegel J.S. and Diederich F.**

Structural, Optical and Electrochemical Properties of Three Dimensional Push-Pull Coroannulenes.  
*J. Org.Chem* **77** (2012) 11014-11026

**P.101 Breiten B., Jordan M., Taura D., Zalibera M., Griesser M., Confortin D., Boudon C., Gisselbrecht J.P., Schweitzer W.B., Gescheidt G., Diederich F.**

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*The Journal of Organic Chemistry*, **78** (2013) 1760-1767

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Post-Cycloaddition-Retroelectrocyclization Transformations of Polycyanobutadienes.  
*European Journal of Organic Chemistry*, (2013) 869-879.

**P.103 Jayamuragan G., Dumele O., Gisselbrecht J.P., Boudon C., Schweizer W.B., Bernet B., Diederich F.** Expanding the Chemical Structure Space of Opto-Electronic Molecular Materials: Unprecedented Push-Pull Chromophores by Reaction of a Donor-Substituted Tetracyanofulvene with Electron-Rich Alkynes  
*J. Am. Chem. Soc.* **135** (2013) 3599-3606.

**P. 104 Martin Stefko M. Tzirakis M.D., Breiten B., Ebert M.-O., Dumele O., Schweizer W.B., Gisselbrecht J.-P. Boudon C., Beels M.T., Biaggio I., Diederich F.**

Donor-Acceptor (D-A)-Substituted Polyene Chromophores: Modulation of Their Optoelectronic Properties by Varying the Length of the Acetylene Spacer  
*Chemistry – A European Journal* **19** (2013) 12693-12704.

**P.105 Yamada M., Tancini F., Sekita M., Guldi D.M., Boudon C., Gisselbrecht J.P., Alberti M.N., Schweizer W.B., Diederich F.**

Ground and Excited State Electronic Interactions in Push-Pull Chromophore [60]Fullerene Conjugates.  
*Fullerenes, Nanotubes, and Carbon Nanostructures*, **22** (2014) 99-127

**P.106 Gawel P., Dengiz C., Finke A.D., Trapp N., Boudon C., Gisselbrecht J.P., Diederich F.**

Synthesis of Cyano-Substituted Diaryltetracenes from Tetraaryl[3]cumulenes  
*Angew. Chem. Int. Ed.*, **53** (2014) 4341-4345.

**P.107 Tancini F., Monti F., Howes K., Belbakra A., Listorti A., Schweizer W.B., Retenauer P., Alonso-Gomez J.L., Chiorboli C., Urner L.M., Gisselbrecht J.P., Boudon C., Armroli N., Diederich F.**

Cyanobuta-1,3-dienes as Novel Electron Acceptors for Photoactive Multicomponent Systems.  
*Chemistry – A European Journal* , **20** (2014) 202-216.

**P.108 Jayamuragan G., Finke A.D., Gisselbrecht J.P., Boudon C., Schweizer W.B., Diederich F.**

One-Pot Access to Push-Pull oligoenes by Sequential [2+2] Cycloaddition-Retroelectrocyclization Reactions.  
*J. Org. Chem.*, **79** (2014) 426-431.

**P .109 Denzig C., Dumele O., Kato S.-I., Zalibera M., Cias P., Schweizer W.B., Boudon C., Gisselbrecht J.P., Gescheidt G. and Diederich F.**

From Homoconjugated Push-Pull Chromophores to Donor-Acceptor-Substituted Spiro Systems by Thermal rearrangement  
*Chemistry – A European Journal* , **20** (2014) 1279-1286

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alkynes and gem dibromoolefins.  
*Chemical Sciences*, **5** (2014) 965-972

**P.111 Tzirakis D.T., Gisselbrecht J.P., Boudon C., Trapp N., Diederich F.**

Alleno-acetylenic scaffolding for the construction of axially chiral C60 dimers  
*Tetrahedron*, **70** (2014) 6193-6202

**P. 112 Urner L.M., Sekita M., Trapp N., Schweizer W.B., Würle M., Gisselbrecht J.-P., Boudon C., Guldi D.M., and Diederich F.**

Systematic Variation of Cyanobuta-1,3-dienes and Expanded Tetracyanoquinodimethane. Analogues as Electron Acceptors in Photoactive, Rigid Porphyrin Dyads  
*Eur. J. Org. Chem.* (2015), 91–108

**P.113 Dengiz C., Breiten B., Gisselbrecht J.-P., Boudon C., Trapp N., Schweizer W.B., and Diederich F.**  
Synthesis and Optoelectronic Properties of Janus-Dendrimer-Type Multivalent Donor–Acceptor Systems  
*J. Org. Chem.* **80** (2015) 882–896

**P. 114 Gawel P., Wu Y.L., Finke A.D., Trapp N., Zalibera M., Boudon C., Gisselbrecht J.-P., Schweizer W.B., Gescheidt G. and Diederich F.**  
Push-Pull Buta-1,2,3-Trienes: Exceptionally Low Rotational Barriers of Cumulene C=C Bonds and their Proacetylenic Reactivity.  
*Chem.Eur.J.* **21** (2015) 6215-6225

**P. 115 Finke A.D., Jahn B.O., Saithalavi A., Dahlstrand C., Nauroozi D., Haberland S., , Gisselbrecht J.P., Boudon C., Mijangos E., Schweizer W.B., Ott S., Ottoson H. and Diederich F.**  
The 6,6-Dicyanofulvene Core : A Template for the Design of Electron Acceptor Compounds.  
*Chem.Eur.J.* **21** (2015) 8168-8176

**P.116 Cao J., Londdon G., Dumele O., von Wantoch Rebowksi M., Trapp N., Ruhlmann L., Boudon C., Monstanger A. and Diederich F.**  
The Impact of Antiaromatic Subunits in  $[4n + 2]$   $\pi$  Systems : Bispentalenes with  $[4n + 2]$ - Electron Perimeter but Antiaromatic Character.  
*J.A.C.S.*, **137** (22) (2015) 7178-7188

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*Eur. J. Org. Chem.* **33**, (2015), 7264-7275

**P.119 Dengiz C., Prange C., Gawel P., Trapp N., Ruhlmann L., Boudon C. and Diederich F.**  
Push-Pull Chromophores by Reaction of 2,3,5,6- Tetrahalo-1,4-Benzoquinones with 4-(N,N'-Dialkylanilo) Acetylenes.  
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Design and Synthesis of Aviram-Ratner Dyads and Rectification Study in Langmuir Blodgett (LB) Films  
*Chem. Europ. J.*, **22**, issue 30 (2016) 10539-10547

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Resorcin [4] arene – Based Molecular Grippers with Semiquinone Walls : Paramagnetic Intermediates of six-State Redox Switches.  
*J. Phys. Chem. Lett.* **7** (2016) 2470-2477

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Synthesis of Cyano-Substituted Benzo- [c] Fluorenes From Tetraaryl [3] Cumulenes.  
*Eur. J. Org. Chem. Com.* **17** (2016) 2919-2924

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N-Heterocyclic Carbene based Tri-Organyl-Zn-Alkyl Cations : Synthesis, structures and use in CO<sub>2</sub> Functionalization.  
*Chem.Eur.J.* **23**, issue 23 (2017)5509-5519
- P.125 Reekie T., Sekita M., Urner L., Bauroth S., Ruhlmann L., Gisselbrecht J.P., Boudon C., Trapp N., Clark T. and Diederich F.**  
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