MEMOIRE

Présenté devant
l'Université de Rennes 1

HABILITATION À DIRIGER DES RECHERCHES

Présentée le 8 juin 2017

par

Pierre-Antoine Bouit

Chargé de Recherche CNRS

Jury:
Dr D. Bourissou (CNRS, Univ. Toulouse III, France), rapporteur
Pr. G. Fernandez (Univ. Münster, Allemagne), rapporteur
Pr. L. De Cola (Univ. Strasbourg, France), rapportrice
Dr H. Bock (CNRS, Univ. Bordeaux, France), examinateur
Pr. M. Hissler (Univ. Rennes 1, France), examinatrice
Dr O. Siri (CNRS, Aix-Marseille Univ., France), Président

Institut des Sciences Chimiques de Rennes
UMR 6226

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Part 1

Curriculum vitae

Pierre-Antoine BOUIT

Adress : 4 rue Beaugeard Lancelot
35700 Rennes
FRANCE
Tel: +33(0)223234536 (laboratoire)
+33(0)622052123 (mobile)
E-Mail : pierre-antoine.bouit@univ-rennes1.fr

Birth date: 02/06/1982
Nationality: French

CNRS Researcher

Education and qualification

2005-2008 **PhD in Chemistry,** ENS-Lyon (Lyon).

2004-2005 **Master of Molecular Chemistry,** Ecole Polytechnique (Palaiseau).

2002-2005 École Nationale Supérieure de Chimie de Paris (**Chimie-ParisTech**), a graduate school of chemical sciences and engineering.

Professional Experience

since déc. 2010 **CNRS Researcher**
Phosphorus and Molecular Materials (Pr. M. Hissler), UMR 6226 Institut des Sciences Chimiques de Rennes, Université de Rennes 1 (France).

2008-2010 **Post-doctoral formation**
IMDEA Nanoscience - Universidad Complutense de Madrid (Spain) (Supervisor: Pr. N. Martín).

2005-2008 **PhD student**
Laboratoire de Chimie, UMR 5182, Ecole Normale Supérieure de Lyon (France) (Supervisors : Dr O. Maury and Dr C. Andraud).

2004-2005 **Master Internship**: Laboratoire de Chimie et Biochimie des Complexes Moléculaires, UMR 7576, ENSCP, Paris (France) (Supervisor: Pr. G. Jaouen).

Avr-Sept 2004 **R&D internship**: Physicians Formula (Los Angeles, USA).

Juillet 2003 **Technician Internship** : Chloralp (Pont de Claix, France).

Scientific production

33 articles (11 related to my work as CNRS researcher). H-factor jan. 2017: 16.
2 patents (1 related to my work as CNRS researcher).
16 oral communications in national/international congresses (2 invited lectures).
5 invited seminars in french/international academic laboratories.

Funding

- 2016: ANR JCJC "Heterographen". 175 000 € (2017-2021). **Scientific coordinator**.
- 2015: Maturation project "HLED". 12 months post-doctoral contract granted by "SATT Sud-Est". Scientific partner.
- 2013: PHC Balaton with the Budapest University of Technology and Economics. Scientific partner.
- 2013: 12 months postdoctoral contract granted by Solvay. Scientific partner.
- 2012-2016: LIA MOF Rennes (France)- Zhenghzou (China). Scientific partner.
- 2012: SAD "PGraphen". 75 000 € (01-12 2012) 12 months postdoctoral contract granted by the Région Bretagne. **Scientific coordinator**.
- 2011: Allocation d'Installation Scientifique (AIS). 20 000 € granted by Rennes Metropole

Award

2014 : Prix « Claude DUFOUR 2014 de Chimie Organique Prospective » given by the association Chimie Paristech Alumni.

Publications

[33] "Coordination complexes of P-containing polycyclic aromatic hydrocarbons: optical properties and solid-state supramolecular assembly" F. Riobé, R. Szűcs, C. Lescop, R. Réau, L. Nyulászi,* P.-A. Bouit,* M. Hissler,* *Organometallics* **2017**, om-2016-00715e.R2.

[32] "Strategies toward phosphorus-containing PAHs and the effect of P-substitution on the electronic properties" R. Szűcs, F. Riobé, A. Escande, D. Joly, P.-A. Bouit, L. Nyulászi, *M. Hissler,* *Pure Appl. Chem.* **2017**, PAC-CON-16-09-09.

[31] "π-Conjugated Phospholes and their Incorporation into Devices: A Component with a Great Deal of Potential" M. Duffy, W. Delaunay, P.-A. Bouit, M. Hissler,* *Chem. Soc. Rev.* **2016**, 45, 5296-5310.

[30] "Organophosphorus derivatives for electronic devices" D. Joly, P.-A. Bouit, M. Hissler,* *J. Mater. Chem. C*. **2016**, 4, 3686-3698.

[29] “Synthesis and electronic properties of Polycyclic Aromatic Hydrocarbons doped with Phosphorus and Sulfur” W. Delaunay, R. Szűcs, S. Pascal, A. Mocanu, P.-A. Bouit, L. Nyulászi,* M Hissler,* *Dalton Trans.* **2016**, 45, 1896-1903.

[28] “Edge Modification of PAHs” R. Szűcs, P.-A. Bouit, M Hissler,* L. Nyulászi,* *Struct. Chem.* **2015**, 26, 1351-1357.

[27] “Synthesis, electronic properties and WOLED devices of planar phosphorus-containing polycyclic aromatic hydrocarbons” F. Riobé, R. Szűcs, P.-A. Bouit, D. Tondelier, B. Geffroy, F. Aparicio, J. Buendía, L. Sánchez, R. Réau, L. Nyulászi,* M. Hissler* *Chem. Eur. J.* **2015**, 21, 6547-6556.

[26] “Phosphorus-based chromophores: Emitters for OLEDs” M. Duffy, P.-A. Bouit, B. Geffroy, D. Tondelier, M. Hissler* *Phosphorus, Sulfur, and Silicon and the Related Elements* **2014**, DOI: 10.1080/10426507.2014.980414

[25] “Concise multigram-scale synthesis of push-pull tricyanofuran-based hemicyanines with giant second-order nonlinearity: an alternative for electro-optic materials” W. Bentoumi, J.-C. Mulatier, P.-A. Bouit, O. Maury, A. Barsella, J.-P. Vola, E. Chastaing, L. Divay, F. Soyer, P. Le Barny, Y. Bretonnière, C Andraud,* *Chem. Eur. J.* **2014**, 20, 8909-8913.

[24] “1,2-dihydrophosphete: A platform for the molecular engineering of electroluminescent phosphorus materials for light-emitting devices” H. Chen, S. Pascal, Z. Wang, P.-A. Bouit, Z. Wang, Y. Zhang, D. Tondelier, B. Geffroy, R. Réau,* F. Mathey,* Z. Duan,* M. Hissler,* *Chem. Eur. J.* **2014**, 20, 9784-9793.

[23] “Efficient light harvesters based on the 10-(1,3-dithiol-2-ylidene) anthracene core” P.-A. Bouit, L. Infantes, J. Calbo, R. Viruela, E. Ortí, J. L. Delgado, N. Martín,* *Org. Letters* **2013**, 15, 4166-4169.

[22] S. Pascal, P.-A. Bouit, B. Le Guennic, S. Parola, O. Maury, C. Andraud* *Proc. SPIE 8622 Organic Photonic Materials and Devices XV*, **2013**, 86220F doi:10.1117/12.2008220.

[21] “Benzofuran fused phosphole: synthesis, electronic and electroluminescence properties” H. Chen, W. Delaunay, J. Li, Z. Wang, P.-A. Bouit, D. Tondelier, B. Geffroy, F. Mathey, Z. Duan,* R. Réau,* M. Hissler* *Org. Letters* **2013**, 15, 330-333.

[20] “Tuning the electronic properties of non-planar exTTF-based push-pull chromophores by aryl-substitution” R. García, Mª Á. Herranz, Mª R. Torres, P.-A. Bouit, J. L. Delgado, J. Calbo, P. M. Viruela, E. Ortí, N. Martín* *J. Org. Chem* **2012**, 77, 10707-10717.

[19] “Excited state absorption: a key phenomenon for the improvement of biphotonic based optical limiting at telecommunication wavelengths” Q. Bellier, N. S. Makarov, P.-A. Bouit, S. Rigaut, K. Kamada, P. Feneyrou, G. Berginc, O. Maury, Joseph W. Perry,* C. Andraud* *Phys. Chem. Chem. Phys.* ***2012***, 14, 15299-15307.

[18] “Donor-π-acceptors containing the 10-(1,3-Dithiol-2-ylidene)anthracene unit for dye-sensitized solar cells” P.-A. Bouit, M. Marszalek, R. Humphry-Baker, R. Viruela, E. Ortí, S. M. Zakeeruddin,* M. Grätzel,* J. L. Delgado,* N. Martín,* *Chem. Eur. J.* **2012**, 18, 11621-11629.

[17] "Dibenzophosphapentaphenes: Exploiting P-chemistry for gap fine-tuning and coordination-driven assembly of planar polycyclic aromatics hydrocarbons" P.-A. Bouit, A. Escande, R. Szűcs, D. Szieberth, C. Lescop, L. Nyulaszi,* M. Hissler,* R. Réau,* *J. Am. Chem. Soc.* **2012**, 134, 6524-6527.

[16] "Powering reductive charge shift reactions-linking fullerenes of different electron acceptor strength to secure an energy gradient" C. Villegas, J. L. Delgado, P.-A Bouit, B. Grimm, W. Seitz, N Martín,* D. M. Guldi,* *Chem. Sci.* **2011**, **2**, 1677-1681.

[15] "Efficient light harvesting anionic heptamethine cyanine–[60] and [70]fullerene hybrids" C. Villegas, E. Krokos, P.-A. Bouit, J. L. Delgado, D. M. Guldi,* N. Martín,* *Energy Environ. Sci.* **2011**, 4, 679-684.

[14] "ExTTF-based dyes absorbing from the visible to the NIR spectral range" P.-A. Bouit, C. Villegas, J. L. Delgado, P. M. Viruela, R. Pou-Amérigo, E. Ortí,* N. Martín,* *Org. Letters* **2011**, 13, 604-607.

[13] "Efficient utilization of higher lying excited states to trigger charge transfer events" P.-A. Bouit, F. Spänig, G. Kuzmanich, E. Krokos, C. Oelsner, M. A. Garcia-Garibay, J. L. Delgado, N. Martín,* D. M. Guldi,* *Chem. Eur. J.* **2010**, 16, 9638-9645.

[12] "Organic Photovoltaics: A Chemical Perspective" J.L Delgado, P.A Bouit, S. Fillipone, M. A. Herranz, N. Martín,* *Chem. Commun.* 2010, 46, 4853-4865.

[11] "Efficient electron transfer and sensitizer regeneration in stable π-extended tetrathiafulvalene-sensitized solar cells" S. Wenger, P.-A Bouit, Q. Chen, J. Teuscher, D. Di Censo, R. Humphry-Baker, J.-E. Moser, J.L. Delgado, N. Martín,* S. M. Zakeeruddin,* M. Grätzel,* *J. Am. Chem. Soc.* **2010**, 132, 5164–5169.

[10] "Continuous symmetry breaking induced by ion pairing effect in heptamethine cyanine dyes: beyond the cyanine limit '' P.-A. Bouit, C. Aronica, L. Toupet, B. Le Guennic, C. Andraud, O. Maury* *J. Am. Chem. Soc.* **2010**, 132 , 4328-4335.

[9] "A cyanine-cyanine" salt exhibiting photovoltaic properties" P.-A. Bouit, D. Rauh, S. Neugebauer, J. L. Delgado, E. Di Piazza, S. Rigaut, O. Maury, C. Andraud, V. Dyakonov,* N. Martín,* *Org. Lett.* **2009**, 11, 21, 4806-4809.

[8] "Competitive retro-cycloaddition reaction in fullerene dimers connected through pyrrolidino-pyrazolino rings" J.L. Delgado, S. Osuna, P.-A. Bouit, R. Martínez-Alvarez, E. Espíldora, M. Solà, N. Martín,* *J. Org. Chem.* **2009**, 74, 21, 8174-8180.

[7] "Two-photon absorption around telecommunication wavelength" P.-A. Bouit, O. Maury, C. Andraud,* *Nonlinear Optics, Quantum Optics* **2009**, 38, 3-4, 245-258.

[6] "Diastereoselective supramolecular ion-pairing between TRISPHAT anion and *pro*-chiral heptamethine cyanine dye" P.-A. Bouit, C. Aronica, L. Guy, A. Martinez, C. Andraud, O. Maury,* *Org. Biomol.* **2009**, 7, 3086-3090.

[5] "Dendron-decorated cyanine dyes for optical limiting applications in the range of telecommunication wavelengths '' P.-A. Bouit, R. Westlund, P. Feneyrou, O. Maury, M. Malkoch, E. Malmström, C. Andraud,* *New J. Chem.* **2009**, 33, 964–968.

[4] "Two-photon absorption related properties of functionalized BODIPY dyes in the infrared range up to telecommunication wavelengths" P.-A. Bouit, G. Berginc, L. Toupet, P. Feneyrou, K. Kamada, O. Maury, C. Andraud,* *Adv. Mater*. **2009**, 21, 1151-1154.

[3] "Stable NIR anionic polymethine dyes: structure, photophysical and redox properties" P.-A. Bouit, E. Di Piazza, S. Rigaut, L. Toupet, C. Aronica, B. Le Guennic, C. Andraud,* O.Maury,* *Org. Lett*. **2008**, 10, 19, 4159-4162.

[2] "Near IR nonlinear absorbing chromophores with optical limiting properties at telecommunication wavelengths" P.-A. Bouit, G. Wetzel, G. Berginc, B. Loiseaux, L. Toupet, P. Feneyrou, Y. Bretonnière, K. Kamada, O. Maury, C. Andraud,* *Chem. Mater*. **2007**, 19, 22, 5325-5335.

[1] "Synthesis of the 11β-hydroxymethyl-androst-4-en-3,17-dione" E. Stéphan,* M. Brossat, V. Lecomte, P.-A. Bouit, *Tetrahedron* **2006**, 62, 13, 3052-3055.

Patents

«Luminescent hybrid nanomaterials with aggregation induced emission», (CNRS/UR1/AMU), N: FR2014005147020140224, EP2014017300120140618; WO2015EP53859 20150224 (2015), inventors : J. Ackermann, P.-A. Bouit, M. Hissler, O. Margeat.

"Passive Optical Limiter Having Nonlinear Material", (Thales/CNRS/ENS), N°: FR20090000834 20090224 , US20100706930 20100217, inventors : G. Berginc, P. Feneyrou, P.-A. Bouit, O. Maury, C. Andraud.

COMMUNICATIONS

Oral communications in international congresses

42nd International Conference on Coordination Chemistry (ICCC), Brest (France), "P-containing Polycyclic Aromatic Hydrocarbons: coordination chemistry and opto-electronic applications", July 3-6th, 2016.

International Workshop on Nano and Bio-photonics (IWNBP), Cabourg (France), "P-containing Polycyclic Aromatics Hydrocarbons" (invited lecture), December 6-11th, 2015.

Workshop on Optically-Active Molecules (OptMol 2015), Rennes (France), "Structure-property relationships in P-containing polyaromatics", November 19-20th, 2015.

16th International Symposium on Novel Aromatic Compounds (ISNA), Madrid (Spain) "Phosphorus-containing Polycyclic Aromatic Hydrocarbons: synthesis, electronic properties and device incorporation", July 5th-10th, 2015.

Korea-France joint workshop on active polymers for pattern integration, "P-containing Polycyclic Aromatic Hydrocarbons", Paris (France), June 23th - 25th, 2015.

20th International Conference on Phosphorus Chemistry (ICPC), Dublin (Ireland), "Using organophosphorus chemistry to tune the properties of Polycyclic Aromatic Hydrocarbons (PAHs)", June 28th - July 2nd, 2014.

KOPO 2013, Retzbach-Zellingen (Germany), "Exploiting P chemistry for gap fine-tuning and coordination-driven assembly of polycyclic aromatic hydrocarbons", Sept. 15-18th, 2013.

11th International Symposium on Functional π-electron systems (Fπ), Arcachon (France), "Exploiting P chemistry for gap fine-tuning and coordination-driven assembly of polycyclic aromatic hydrocarbons", June 2-7th, 2013.

5th French-Japanese joint workshop on frontier materials, Rennes (France), "Pi-conjugated organophosphorus derivatives: from phosphole oligomers to P-containing planar aromatic polycycles" Dec. 2-6th, 2012.

3rd International Workshop on Advanced Nano- and Biomaterials and Their Device Applications (NABM), Timisoara (Roumania), *"*Exploiting P chemistry for gap fine-tuning and coordination-driven assembly of polycyclic aromatic hydrocarbons" (invited lecture), Sept. 19-23th, 2012.

4th EuCheMS Chemistry Congress, Prague (Czech Republic) *"*Exploiting P chemistry for gap fine-tuning and coordination-driven assembly of polycyclic aromatic hydrocarbons", Aug. 26-30th, 2012.

Symposium on Organometallics for Optics, Rennes (France) *"P-containing PAHs"*, June 28th, 2012.

Simposio Consolider en nanociencia molecular, Miraflores de la Sierra (Spain), *"fullerene-cyanine dyads, toward new colored fullerenes"*, June 7-9th, 2009.

Oral communications in national congresses

Science et Technologie des Systèmes pi-Conjugués (**SPIC**), Angers (France), "Polycycles aromatiques contenant un atome de P", Oct. 12th-16th, 2015.

Congrés de la Société Chimique de France, section Bretagne – Pays de Loire, Nantes (France), "Polycycles aromatiques organophosphorés", May 18th - 20th, 2015.

French chemical society meeting (SCF), Rhône-Alpes section. "Synthesis of organic chromophores for nonlinear optics in the infrared*"*, Grenoble (France), June 5, 2008.

Invited seminars in universities/institutes

IMDEA Nanociencia, "Phosphorus containing π-conjugated systems: from heteropolyaromatics to emissive ligands for hybrid nanomaterials", Madrid (Spain), July 28th, 2015.

ChimieParistech, "Electronique plastique: des molecules organiques dans ma télé?" Paris (France), Nov. 4th, 2014.

Budapest University of Technology and Economics, "P-containing Polycyclic Aromatic Hydrocarbons", Budapest (Hungary), Dec. 8th, 2013

Zhengzhou University, "Exploiting P-chemistry for gap-tuning and coordination driven assembly of Polycyclic Aromatic Hydrocarbons", Zhengzhou (China), July 23th, 2013

NIMBE, CEA, "Polycycles aromatiques étendus contenant un atome de phosphore", Saclay (France), dec. 7th, 2012

Poster communications in congresses

42nd International Conference on Coordination Chemistry (ICCC), Brest (France), 2016**,** "Phosphole-based Iridium cyclometalated complexes »**,** O. A. Mocanu, H. Belaidi, W. Delaunay, L. E. E. Broeckx, E. Abou Nakad, P.-A. Bouit, C. Müller, A. Boucekkine, J.-F. Halet, M. Hissler.

Science et Technologie des Systèmes pi-Conjugués (**SPIC**), Angers, 2015**,** "Fluorescence induite par agrégation : Fluorophores organiques et hybrides" T. Dombray, P.-A. Bouit, O. Margeat, J. Ackermann, M. Hissler.

Journées de Chimie de Coordination (JCC), Rennes (France), 2014, **"**Phosphole-based Iridium cyclometalated complexes" W. Delaunay, L. E. E. Broeckx, C. Latouche, P.-A. Bouit, C. Müller, A. Boucekkine, J.-F. Halet, M. Hissler.

International Workshop on Molecular Materials, Sanxenxo (Spain), 2010, "Molecular engineering of π-extended tetrathiafulvalene (exTTF) for dye sensitized solar cells" P.-A. Bouit, S. Wenger, Q. Chen, J. Teuscher, D. Di Censo, R. Humphry-Baker, J.-E. Moser, J. L. Delgado, S. M. Zakeeruddin, M. Grätzel, Nazario Martín.

European Materials Research Society (EMRS Spring meeting): "Synthesis of NIR dyes for two-photon absorption at telecommunication wavelengths", Strasbourg (France), 2008, P.-A. Bouit, K. Kamada, P. Feneyrou, Y. Bretonnière, O. Maury, C. Andraud.

Société Française de Chimie, section Rhône-Alpes, "Synthèse et propriétés optiques de chromophores absorbant dans le proche IR", Villeurbanne (France), 2006, P.-A. Bouit, O. Maury, C. Andraud.

3rd International Conference on Photoresponsive Organics and Polymers (3rd ICPOP) "Synthesis of near infrared dyes", Val Thorens (France), 2006, P.-A. Bouit, O. Maury, C. Andraud.

Short term stay in laboratories

LPICM (Ecole Polytechnique, UMR 7647): three stays of one week from 2011 to 2014 for OLED preparation and characterization.

Moltech Anjou (UMR 6200): stay of three days in Sept. 2013 for solid-state self-assembly studies.

International Phosphorus Lab, Zhengzhou University (China): stay of one week in July 2013 in the frame of the IAL.

Budapest University of Technology and Economics (Hungary): stay of one week in Dec. 2013 in the frame of the PHC « Balaton » (Theoretical chemistry formation).

Supervision of students/researchers

Post-doctorate fellows:

Dr François Riobé (contract SAD-Région Bretagne, Jan. - Dec. 2012). "Synthesis of P-containing polycyclic aromatic hydrocarbons". (3 publications) Now CR CNRS at ENS Lyon (France).

Dr Matthew Duffy (CNRS - Solvay, Jan. - Dec. 213). co-supervision with M. Hissler. "Synthesis of π-conjugated phospholes for photovoltaics". (2 publications). Now Post-doc at ISCR (Rennes, France).

Dr Thomas Dombray (contrat : maturation SATT Sud-Est, June 2015 - May 2016). Co-supervision with M. Hissler: "Synthesis of fluorescent hybrids nanoparticles". Now Post-doc at ISCR (Rennes, France).

PhD students

Wylliam Delaunay (co-supervision ; PhD director : Prof M. Hissler, 2011-2013). "Synthèse et caractérisation de nouveaux matériaux organophosphorus pour des applications en optoélectronique" (3 publications in common; 1 oral communications in international symposium on our common work).

Anabella Mocanu (co-supervision with M. Hissler, since oct. 2014, defence planned in autumn 2017). "Synthesis of π-conjugated organophosphorus derivatives for optoelectronic applications". (1 publication; 2 oral communications in international symposia).

Rózsa Szűcs (co-supervision ; PhD directors : Prof M. Hissler and Prof L. Nyulászi, since Feb. 2014, co-tutelle Budapest University of Technology and Economics - Université de Rennes 1, defence planned spring 2017). "Investigation of heteroatom-modified aromatic systems". (6 publications in common; 2 oral communications in international conferences/symposia).

Reka Mokrai (co-supervision ; PhD directors : Prof M. Hissler and Dr Z. Benko, since Jan. 2017, co-tutelle Budapest University of Technology and Economics - Université de Rennes 1, defence planned in 2020).

Master students:

Simon Pascal (International master in molecular catalysis and green chemistry, Université de Rennes 1, Feb. - July 2011). 2 publications. Now CNRS at CINaM (France).

Elie Abou Nakad (International master in molecular catalysis and green chemistry, Université de Rennes 1, Sept 2012 - July 2013). Now PhD in Univ. Strasbourg (France).

Matthieu Denis (Master de chimie moléculaire, Université de Rennes 1, Feb-Aug. 2014). Now PhD in Univ. Southampton (UK).

Yohan Chéret (Master de chimie moléculaire, Université de Rennes 1, Feb-July 2015).

Jad Rabah (International Master in Molecular Catalysis and Green Chemistry, Université de Rennes 1, Sept 2016 - July 2017).

Undergraduated students:

Marianne Ernoult (L3 Université de Rennes 1, May - June 2011).

Matthieu Bourand (L3 Université de Rennes 1, May - June 2012).

Anabella Mocanu (M1 University of Cluj-Napoca (Roumania), July- Sept. 2013).

Antoine Escola (L3 Université de Rennes 1, May - June 2016).

Visiting Students

Michal Maciejczyk, PhD Student**,** Institute of Physical Chemistry, Warsaw (Poland), May-July 2011.

Chen Hui, PhD student, Zhengzhou University (China), IAL exchange, Nov. 2013.

Reka Mokrai, Master student, Budapest University of Technology and Economics (Hungary), Erasmus exchange, June 2014.

Peter Wonneberger, PhD student, Leipzig University (Germany), COST STSM, Dec. 2015.

Ines Bennour, PhD student, Institut de Ciencia de Materials de Barcelona (Spain), COST STSM, Apr. 2016.

Teaching activities

« Introduction to NMR spectra interpretation », International Master in Molecular Catalysis and Green Chemistry, Université de Rennes 1, 2016-2017, (8 h of teaching).

Jury member of L3 students internships, Université de Rennes 1 (June 2013 and 2016), 8 h.

Practical classes of organic chemistry: L3 chimie, ENS Lyon (2007-2008), 48 h.

Elaboration and correction of an exam subject of chemistry for students preparing the nationwide exam of « Agregagtion de Physique » (option : physics), ENS Lyon (2006, 2007), 32 h.

Responsibilities in the institute

Member of the "communication" unit of the Institute of Chemical Sciences of Rennes.

Responsible for internal seminar of the PMM group (2012-2016).

Responsible for internal seminars in the OMC team (since 2016).

Conference organization

Organizing committee for:

- "**Groupement d'Etude en Chimie Organique**" (GECO 58), Dinard (France), Aug. 27th - Sept. 1st, 2017.

- "**16th International Conference on Chiroptical Spectroscopy**" (CD2017), Rennes (France), June 11-15th, 2017.

- "**Journées de Chimie de Coordination"** (JCC), Rennes (France), Jan. 30-31th, 2014.

- "**3rd PhoSciNet Training School"** « New Frontiers in Phosphorus Chemistry », Rennes (France), March 19-21th, 2012.

- "**European Workshop on Phosphorus Chemistry"** (EWPC-9), Rennes (France), March 22-23th, 2012.

Other:

Logistic help during the "**42nd International Conference on Coordination Chemistry**" (ICCC), Brest (France), july 3-6th, 2016.

Research evaluation

Occasional referee for peer-reviewed journals: RSC (*Chem. Commun.*, *Soft Matter*, *Polym. Chem.*), ACS (*Inorg. Chem.*), Elsevier (*Dyes and Pigments*).

Participation to the PhD jury of Simon Pascal (ENS Lyon, France, 27/06/2104) as invited member.

Participation to the PhD jury of Maria Gallego (Universidad Complutense de Madrid, Spain, 27/07/2015).

Science popularization

"Immersion Sciences" 2014 and 2015 (CNRS – Académie de Rennes). A seminar followed by a roundtable discussion is given with college student in order to make them discover the job of researcher.

Presentation of my research activities in colleges around Lyon and Rennes (Brindas (69), Cesson-Sévigné (35), Bruz (35)…).

“Portes ouvertes de l’UMR 6226 “ / “Village des sciences”. The objective of these interventions is to present to a general audience the Institut des Sciences Chimiques de Rennes.

« Observation internships » of secondary school students.

Part 2: PhD thesis

Synthesis of near-infrared absorbing dyes for nonlinear optics

Synthesis of near-infrared absorbing dyes for nonlinear optics

Key-words : Chromophore - Cyanines - Bodipy - Delocalization - Spectroscopy – Two-photon absorption - Optical limiting

I did my PhD at the Laboratoire de Chimie (UMR 5182, ENS Lyon, France) under the supervision of Dr. C. Andraud and Dr. O. Maury with a grant from the DGA (Délégation Générale de l'Armement). The subject dealt with the synthesis of near-infrared absorbing dyes for nonlinear optical (NLO) applications and in particular optical limiting at telecommunications wavelengths. Thales R&T, an industrial partner, was involved for the nonlinear optical characterizations.

Materials displaying multiphotonic absorption properties have been extensively studied for applications in the field of materials science (optical storage, optical limitation, microfabrication) or in biology (imaging, photodynamic therapy) in the visible range.[1] The rapid development of frequency-tuneable pulsed laser in the telecommunications wavelengths (TW, 1400-1600 nm) prompted the scientific community to design new materials for nonlinear absorption in the near infrared region (NIR). In particular, optical limiters are crucial devices to afford efficient protection against these new lasers sources. A good optical limiting (OL) aims at protecting optical sensors (eyes, camera…) against damages caused by high-energy laser illumination.[2] It has to be transparent in the spectral range of the detector as long as the light intensity remains below a safety threshold and instantaneously attenuate the laser when it exceeds this limit. Two-photon absorption (2PA) is an efficient way to promote the OL phenomenon. When this project started, only one example of 2PA with an organic chromophore was described.[3a]

Given the additional specifications of OL (gram scale quantities, thermal stability, high solubility…) we decided to study the 2PA of heptamethine cyanines dyes (Fig. 1). These chromophores are cationic (**1**), anionic (**2**) or neutral (**3**) polyenic systems featuring an odd number of C-sp^2 delocalized between two heterocycles. This structure confers them specific photophysical properties: intense sharp linear absorption / emission bands both located in the NIR. In addition, these compounds display numerous chemical functionalization sites (Cl, N…) which is a clear advantage to reach chemical diversity.

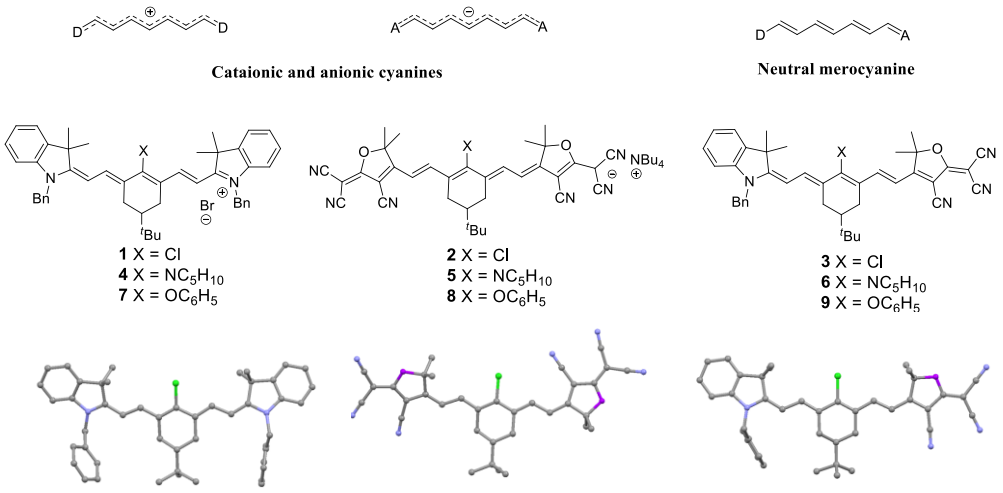


Fig. 1 : Molecular structures of the synthesized heptamethine cyanines and crystallographic structures of **1**, **2** and **3** (counterions have been omitted for clarity).

A first family of chloro-heptamethines (**1**-**3**) has been synthesized. They all absorb in the 700-900 nm region (Fig. 2). The substitution of the central Cl atom by an amine allows a blue-shift the absorption/emission, while substitution by a phenolate allow the introduction of functional groups without affecting the optical properties. A family of 9 NIR absorbing heptamethines has thus been synthesized and fully characterized. A combined study of reactivity, structure analysis and optical properties clearly evidenced that the 3 chloro-heptamethine cyanines **1**-**3** belong to the same family of compounds even if they display different charges.

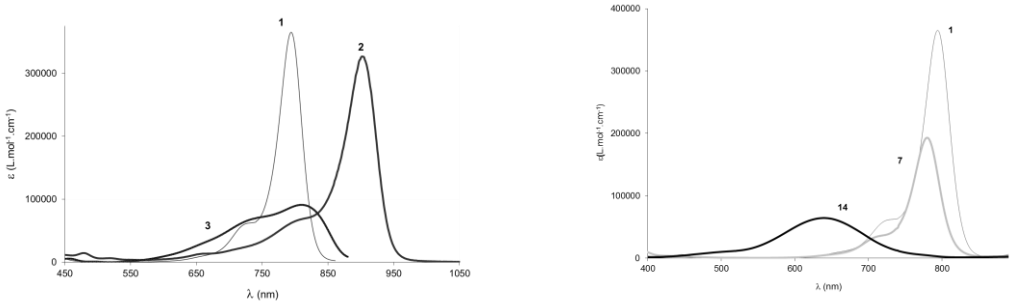


Fig. 2 : UV-vis-NIR absorption of **1**- **3** in DCM (left) and effect of the subsitution on the absorption of **1**, **4** , **7**.

2PA properties in the fs regime have been measured. Chloro-and phenoxy-heptamethine possess relatively high 2PA cross sections ($\sigma_{2PA} \simeq$ 800 GM, Fig. 3) at TW while amino-heptamethine display very low NLO properties. The good 2PA properties have then been exploited to study the OL properties in the ns regime. As an example, **1** presents a 50% attenuation of the incident signal at 3 J.cm^{-2} with λ_{ex} = 1520 nm (Fig. 3). At that time, this represented the first example of 2PA-based OL at TW reported in the literature.[4] However, a careful comparison of the data in the ns/fs regime showed that the mechanism of the OL is a formal 3PA (2PA followed by excited state absorption ESA, see Fig. 3. In another study comparing organic dyes (featuring strong 2PA properties) to organometallic derivatives (displaying long excited state lifetime but low 2PA), we showed the importance of maximizing both 2PA and ESA at the same wavelength to obtain efficient OL.[5]

Finally, the 2nd order NLO properties of all these derivatives were also studied. This study showed that the dipolar compound **3** present competitive μβ values compared to benchmark derivatives.[6] Given the straightforward synthesis of **3**, this opened new perspective for 2nd order NLO materials.

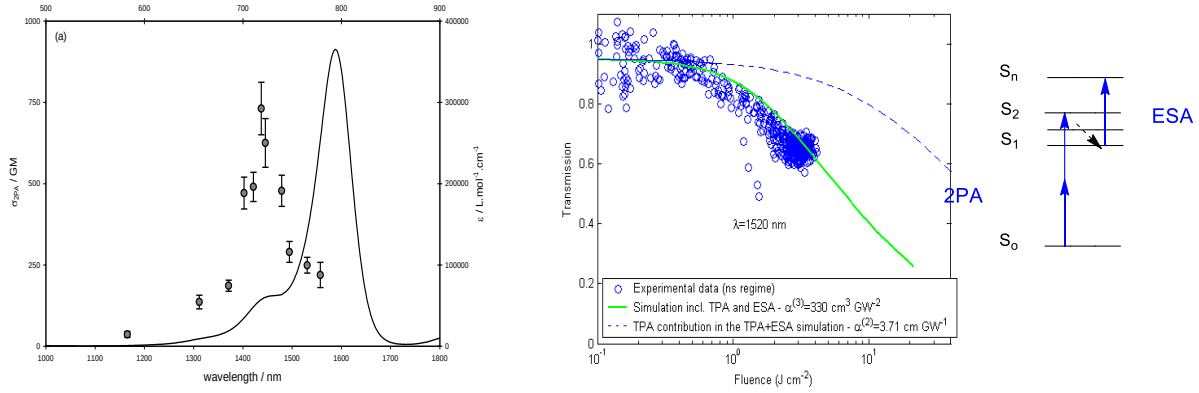


Fig. 3 : 2PA vs spectrum of **1** (left), OL curve of **1** (middle), mechanism of 3PA based OL phenomenon (right).

In addition to the study of its NLO properties, heptamethine cyanine appears as a fascinating scaffold to study the electronic delocalization of a charge along an odd numbered C-sp^2 backbone and its effect on the optical properties. As an example, we showed that the choice of the counterion of cationic heptamethine dyes dramatically impacts its optical properties in the solid-state or in solution.[7] While the properties of cyanines with "soft and bulky" anions (TRISPHAT) remain unchanged by changing the solvent, the properties of cyanines with "hard and small" anions are drastically modified. This phenomenon was interpreted by a combined spectroscopic and crystallographic study. We showed that it is possible to switch between an "ideal polymethine state" (responsible of the sharp NIR absorption) and a "dipolar state" by stabilizing/destabilizing the perfectly delocalized structure. This was achieved by associating/dissociating the counterion depending on the nature of the solvent. Since then, the crucial role of the counterion on the electronic properties of cationic cyanines dyes has been exploited in various solid-state application such as thin film 2PA and organic photovoltaics.[8]

Another family of NIR absorbing dyes has been tested for OL: the π-extended aza-boron dipyrromethene (**10**-**11**, abbreviated aza-Bodipy, Fig. 4) that can also be viewed as a rigidified monomethine. These compounds showed strong 2PA at TW as well as 2PA based OL at these wavelengths.[9]

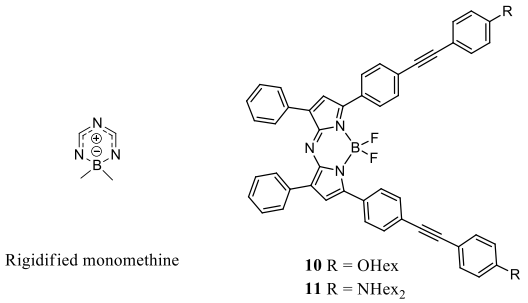


Fig. 4 : general scheme and molecular structure of Aza-Bodipy **10**-**11**.

In conclusion, we synthesized and studied the linear and nonlinear optical properties of different families of NIR absorbing dyes, with a particular interest for the heptamethine cyanines. We developed the two first examples of organic dyes displaying 2PA-based OL at TW.

This PhD project was highly multidisciplinary. In addition to the skills in organic synthesis, this work developed my competences in spectroscopies (UV-vis absorption, emission, nonlinear spectroscopy). During these 3 years I had the opportunity to actively collaborate with several teams in France (Thales R&T, PPSM Cachan) or abroad (KTH Fiber & Polymer Technology, Stockholm, Sweden), academic or industrial.

More generally, this work developed my interest for structure-optical property relationships of organic compounds and for projects at the interface between chemistry, physics and material science.

Part 3: Post-doc

Synthesis of organic sensitizers for photovoltaic applications

Synthesis of organic sensitizers for photovoltaic applications

Key-words : Organic sensitizers - TTF - Fullerenes - Dye-sensitized solar cells - Organic solar cells - Electron transfer

After my PhD, I spend two years at IMDEA Nanoscience (Madrid, Spain) as post-doctorate fellow in the group of Pr. N. Martin to develop organic sensitizers for photovoltaic applications.

One of the strongest challenges of the XXIth century is to drastically diminish our dependence toward fossil fuel energy sources. To do this, our society needs to operate an energetic transition toward a more sustainable model. In this context, harvesting solar energy appears as a seducing and credible alternative.

Since the end of the 90's, the preparation of photovoltaic (PV) cells from organic (organic solar cells (OSCs) or hybrid (dye-sensitized solar cells (DSSCs) materials passed from an emerging academic research field to an industrial stake.[10a-c] My two main research projects at IMDEA Nanoscience were linked with these two applications.

DSSCs can efficiently convert solar energy into electricity by a light-harvesting sensitizer attached to a mesoporous inorganic semiconductor (TiO_2). Efficiencies up to 14% were recorded with Ru complexes and metalated porphyrins.[10b] However, the low availability of such metals remains a drawback for large-scale energy production by DSSCs. On the other hand, organic sensitizers can be synthesized rather inexpensively, and their absorption properties can be easily tuned by suitable molecular engineering. Efficiencies up to 10% have been recorded with "metal free" organic sensitizers.[11]

In this project we investigated the PV potential of extended-tetrathiafulvalene (exTTF, Fig. 5) based sensitizers. TTF is a well-known electron donor which electron transfer ability toward carbon nanostructure is well documented.[12] However no PV properties were reported for such derivatives.

A series of three exTTF sensitizers (**12**-**14**, Fig. 5) was designed and synthesized. All three sensitizers have in common the donor part (exTTF) and acceptor/anchoring site (cyanoacrylic acid). They only differ by the length and nature of the conjugated bridge. They all present moderate absorption coefficients ($\varepsilon < 30\ 000$ L.mol^{-1}.cm^{-1}) in the visible range. Hence, even if the exTTF has a very low oxidation potential (-0.25 V vs Fc^+/Fc), its highly distorted structure (Fig. 5) strongly diminishes the conjugation along the π-conjugated bridge. Furthermore, the oxidation potential of the three compounds ($\simeq -0.1$ V vs Fc^+/Fc) predicted a very low driving force for the dye regeneration by the redox mediator (< 150 mV) in the device. Interestingly, despite this theoretical detrimental parameter, DSSCs with standard configuration displaying efficiency between 3% and 4% were obtained. Even if these efficiencies remain far from the records, these results opened new perspectives for molecular engineering of sensitizers with low driving forces. Hence, large driving force, which was supposed to be mandatory for dye regeneration, also imply a loss in photovoltage.[13]

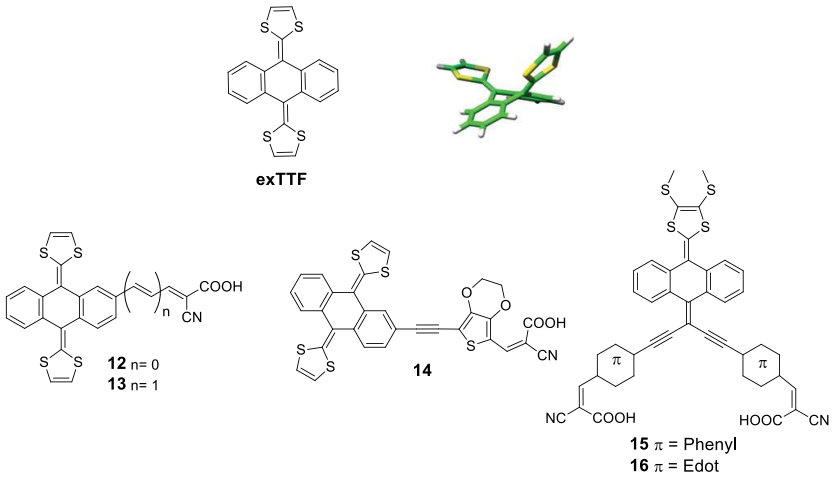


Fig. 5 : Structure of exTTF (up) and molecular structure of sensitizers **12**-**16** (down).

In this context, we extended the family of exTTF dyes for DSSC by synthesizing **15** and **16** (Fig. 5). These derivatives only possess one dithiol ring and are conjugated through the anthracene moiety. They display better π-conjugation and thus higher extinction coefficient and more red-shifted absorption. However, they also display higher oxidation potentials (+0.25 V vs Fc^+/Fc) and do not belong anymore to the "low driving force" category. Their PV performances were also measured and they display moderate performances in classical DSSCs (Power Conversion Efficiency PCE: 3.5% - 4%). This study confirmed that TTF based dyes may be used for PV applications.

In addition to the DSSCs, OSCs also appeared as appealing PV devices. In these systems both the p-semiconductor ("donor") and the n-semi-conductor ("acceptor") are organic (in n-DSSCs, the acceptor is an inorganic metal oxide). The most widely used acceptors are by far fullerene derivatives.[10a, 10c] It is thus highly important to fully understand the electron transfer (ET) processes in which C_{60} derivatives are involved. This aspect was studied in the frame of two additional projects.

In the first one, the ET between cyanine dyes and pyrolidinofullerene was studied. Hence, harvesting light in the NIR part of the spectrum remains a challenge for high efficiency solar cells. Furthermore, these NIR dyes have very low HOMO-LUMO gap and electron transfer toward an acceptor might thus be difficult. A family of four dyads where a cyanine (**1** or **2**, Fig. 1) is covalently attached to a fullerene derivative (either C_{60} or C_{70}) were prepared (see for example 17-18, Fig. 6). These compounds were fully characterized and their optical and electrochemical properties were studied. It appeared that both entities keep their characteristic electronic features in the dyad. As expected, transient absorption spectroscopy proved that ET from the cyanine to the fullerene is occurring. The lifetime of the charge separated state is low (30 ps): this can be explained by the spatial proximity between the two entities that favors a fast recombination. However, it has been shown that the ET occurs from both the S1 and S2 states of the cyanine, which is rather unusual for short excited state lifetime organic dyes.[14] The same phenomenon has been observed for the anionic cyanine that displays similar first reduction potential than the pyrolidinofullerene.[15]

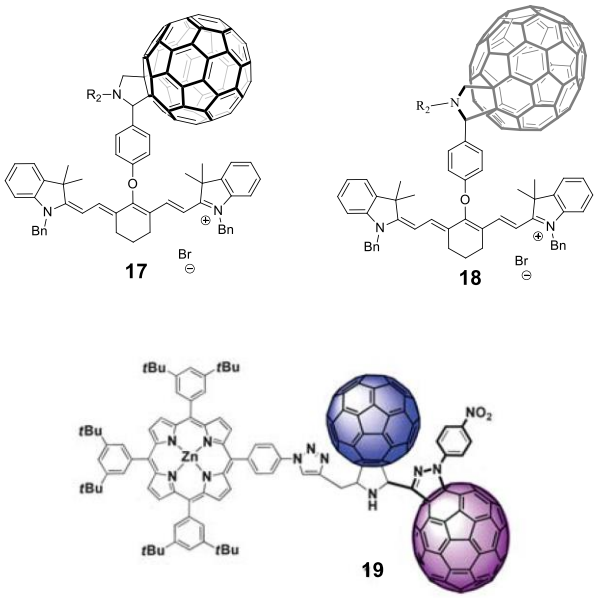


Fig. 6 : Molecular structures of the fullerene-based dyads and triads **17-19**.

ET processes in fullerene-based systems has also been studied for triad **19** which is the first triad containing two different fullerenes (pyrolydinofullerene and pyrazolinofullerene). As the functionalization affects the redox potentials, the challenge was to find a molecular design to obtain a redox gradient between the donor (Zn-porphyrin), the intermediate acceptor (pyrolidinofullerene (in blue Fig. 6)) and the final acceptor (in purple Fig. 6). A synthetic method was developed and the transient absorption proved the occurrence of an ET from the porphyrin to the pyrazolinofullerene (lifetime: 100 ns).[16]

Finally, those projects clearly confirmed the potential of organic sensitizers for PV applications (organic/hybrid). These two technologies, even if they keep improving their record, appeared to be at a crossroad in their history. Hence, even if industrial applications are still credible, many actors of the "plastic electronic" community quickly shifted these last years toward the perovskite technology.[17]

However, all the concepts developed during these projects are also important in the context of the perovskite solar cells and are also the base of many photocatalytic devices.[18]

This post-doctoral stay confirmed my interest for structure - electronic properties relationships, and in particular the redox aspects, which was not envisaged during my PhD. It also allowed me to gain experience in the field of PV devices. More generally, I spent two years in a laboratory where the other scientific interests were the chemistry of carbon nanostructures (fullerenes, carbon nanotubes, graphene) and the supramolecular chemistry, which allowed me to extend a lot the scope of my scientific "culture".

Part 4: CNRS Researcher

Phosphorus-containing π-conjugated systems for optoelectronic applications

Phosphorus-containing π-conjugated systems for optoelectronic applications: Polyaromatic derivatives and hybrid fluorophores

Group: Phosphorus and Molecular Materials
Team: Organometallic Materials and Catalysis
Institute of Chemical Sciences of Rennes

Key-words : Organophosphorus - Polycyclic Aromatic Hydrocarbons - Optical/electronic properties - Aromaticity - Solid-state emission - OLEDs - Hybrid materials

After my two years of post-doc in Madrid I was hired as CNRS researcher in December 2010 at the Institute of Chemical Sciences of Rennes, in the group "Phosphorus and Molecular Materials" (PMM) of Pr. R. Réau/Prof. M. Hissler. The scientific project that I proposed was the use of P-chemistry to tune the properties of molecular graphene. Our idea was to use the background of the PMM group in organophosphorus chemistry and to combine it with my skills in organic synthesis in the context of carbon nanoforms.

The field of opto-electronic devices has been growing extremely fast during the last 20 years because of its applications in photovoltaics, photonics, and consumer electronics. In this context, the organic semiconductors ("small" molecules, oligomers or polymers) are the building blocks of flexible, lightweight, and low-cost electronic devices of the future (Organic Solar Cells (OSCs), Organic Light-Emitting Diodes (OLEDs), Organic Field-Effect Transistors (OFETs)).

In this international competition involving both academic and industrial researchers, synthetic chemists have a crucial role to play. Early works in this field have been mainly devoted to linear π-conjugated systems (from small molecules to polymers), such as poly(phenylenevinylene)s. Shirakawa, McDiarmid and Heeger received in 2000 the Nobel Prize in chemistry for their pioneering work in this area. Then, chemists introduced more complex (macro)-molecules featuring heteroatoms (N, B, S, Si, P…), fused systems or donor-acceptor moieties. However, in order to develop new products with enhanced performances (efficiency, stability…), new organic semiconductors are still required. And thus, novel synthetic strategies for the preparation of these compounds are also needed.

In all the different projects in which I have been involved, our objective has been to prepare new organic/organometallic/hybrid materials based on organophosphorus π-conjugated systems. Once prepared, the compounds are fully characterized at the molecular level and their optical and electrochemical properties were systematically studied. In the frame of collaborations, these data were always compared to DFT calculations in order to rationalize them. Based on these data, the incorporation of these compounds into opto-electronic devices was envisaged.

In this manuscript I will detail in three chapters the main projects I developed:

- P-containing polyaromatics: from synthesis to device incorporation.
- Preparation of fluorescent hybrid nanoparticles based on "Aggregation-Induced Emission" ligands
- And finally, the last chapter will gather some smaller projects that I have been involved in.

P-containing polyaromatics:

The discovery of graphene in 2004 by Geim and Novoselov (Nobel Prize in physics in 2010) opened new perspectives in the field of molecular materials. Its two-dimensional monolayer of *sp*2 carbon atoms confers to graphene exceptional electronic, thermal and mechanical properties that make it one of the most promising classes of carbon-based materials for various applications ranging from optoelectronics to energy storage.[19]

Given its expected applications, the synthesis of graphene-based materials is a growing research field. Since the first isolation of graphene in 2004 by the Nobel Prize winners Geim and Novoselov, numerous research groups tried to find more reproducible and efficient synthetic methods.[19-20] In this context, two main synthetic strategies emerged.[21] The first one, based on graphite exfoliation or oxidation, also referred as the "top-down" approach, implies the use of mechanical/chemical input to separate graphene sheets from bulk graphite. The advantage of this method is that scaling up the quantities is possible. However, the rather harsh reaction conditions make difficult the control of the defects location and nature. These defects, which can be located either within the planar π-conjugated system or on the edge, are crucial for the electronic properties of the compounds as they determine their bandgap. An appealing strategy to tune the properties of the graphene-based material has consisted in introducing heteroatoms in the structure. Due to their different electronegativity compared to C, these heteroatoms can be viewed as localized defects that will perturb the conjugated C-backbone. Graphene or graphene oxide doped with N, B, S or P have thus been synthesized. These materials showed promising activity for oxygen reduction, fuel cells or Li-ion battery applications.[22] Even if these results are exciting, a precise structure-properties understanding is not provided as the exact nature of the heteroatoms (oxidation degree…) as well as their quantity and localization are hardly controlled. This is where the synthetic chemist can play a crucial role. The second approach takes advantage of performing molecular engineering of polycyclic aromatic hydrocarbon (PAHs) using the power of organic synthesis to overcome these problems. This "total synthesis" of molecular graphene fragments is also referred as the "bottom-up approach". Indeed PAHs (such as hexaperibenzocoronene **20**, Fig. 7) or nanographenes (NG) are prepared through the connection of small aromatic synthons using simple organic reactions (C-C cross-coupling, oxidations…). This method cannot be used to prepare micrometric graphene fragments, but it allows the preparation of well-defined molecules up to 10 nm (NG or Graphene NanoRibbons (GNRs). This is a first step toward graphene materials. In this field, pioneering work was performed by the group of K. Müllen during the 90's. They showed that with suitable polyaromatic precursors, the Scholl reaction (also called cyclodehydrogenation) can be used to "graphenize" large polyaromatic framework.[23] Using the latest developments in C-C cross-coupling for the precursors synthesis and mild Scholl conditions (Lewis acid), they synthesized well-defined and soluble molecular graphene fragments from the prototype hexaperibenzocoronene HBC (**20**, Fig. 7) to the preparation of defects-free GNRs up to 52 000 $g.mol^{-1}$ (**21**, Fig. 7), which represents 20 repeated units.[24] A precise structure-property study on the effect of cycles number, shape (disc shape vs ribbons), edge structure (zig-zag, bay, cove, fjord…), can be properly performed as the compounds are monodisperse. Organic solar cells and field-effect transistors have been successfully prepared using these compounds as active layer.[23a] The efficient hole transport properties of these compounds make them particularly appealing for these applications.

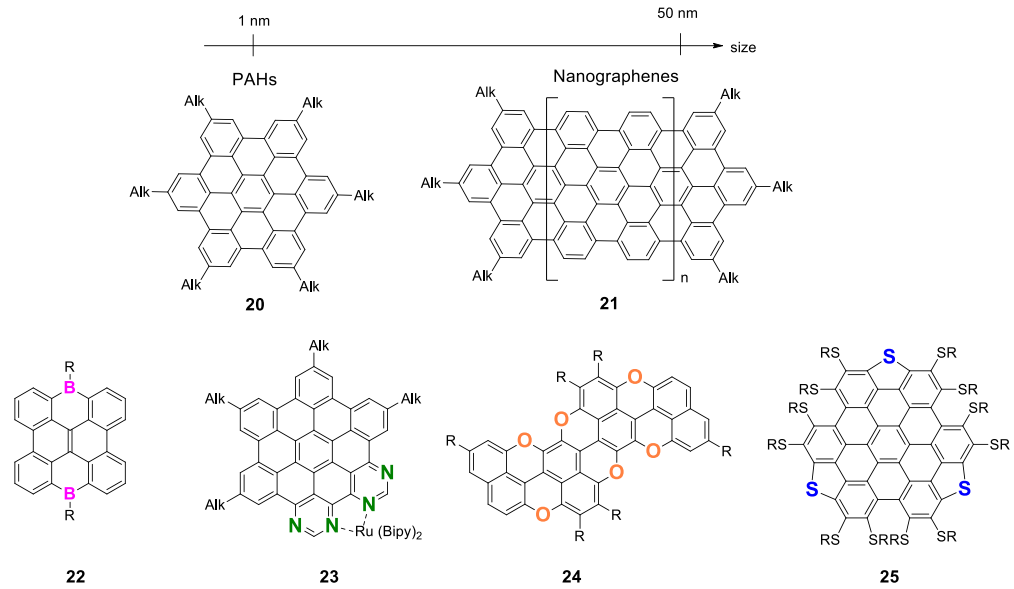


Fig. 7: Exemples of reported PAHs (upper part) and heteroatom-containing PAHs (lower part)

Over the last ten years, another strategy was followed for the gap tuning of PAHs: heteroatoms have been introduced into the polycyclic backbone.[25] Even if polycyclic heteroaromatic molecules such as flavanthrone are known since the beginning of the 20th century, I consider that the pioneering work in this area has been achieved by Draper *et al.* Hence, their N-doped benzocoronene (**23**, Fig. 7, also referred as **N**-heterosuperbenzene) clearly comes from the strategy of inserting **N** atoms inside a hexaperibenzocoronene scaffold.[26] The authors used the basicity and the coordination ability of the pyrimidine moiety to tune the optical properties of the molecular graphene. Other N-containing PAHs including extended porphyrins have also been prepared.[27] Following this work, S-doped molecular graphenes were also synthesized (**25**).[28] Such compounds were recently used as active layer in organic or hybrid solar cells, taking advantage of the charge transport properties of both the PAH backbone and the thienyl ring.[17, 29] O-doped PAH (namely O-doped benzorylenes, **24**) were also recently prepared by Bonifazi *et al.*[30] Recently, a new step was passed with the insertion of highly reactive B atom into these fragments. B-doped PAHs (molecule 22, Fig. 7) were reported by the groups of S. Yamaguchi[31] or M. Wagner[32]. These electron-deficient molecular graphenes can react with anions and display tuneable properties, demonstrating the power of the heteroatomic approach.

Finally, polyheteroatoms-containing PAH such as NS,[33] BN,[34] BO[35] have also been prepared. The case of BN - PAH is particularly interesting as the B-N bond is isoelectronic of a C-C bond and boron nitride itself is a promising 2D-material for opto-electronic applications.[36]

A crucial point in this field in the need to adapt the synthetic approaches developed for the "classical" PAHs to the specific reactivity of the hetero-atoms. When the stability of the compound is sufficient, the cyclodeshydrogenation is the preferred method. However, photocyclization is also an alternative. More generally, preparing such compounds always represent a synthetic challenge.

All those examples showed the pertinence of modifying a planar sp^2 scaffold with heteroatoms. This prompted us to evaluate the impact of a P atom into such a fragment. It was previously shown by the PMM group in Rennes that chemical modifications and coordination to transition metals of the σ^3,λ^3-P center allowed the development of new functional molecules. Their HOMO and LUMOs are thus precisely tuneable and they are stable enough to be inserted as active layer of coloured and white OLEDs.[37]

Regarding the insertion of P-atom into an extended π-conjugated systems, there were no example when this project started (2011).[38] The main challenge was thus to find a synthetic strategy to insert a reactive **P**-atom inside the PAH structure.

As previously discussed, PAHs synthesis usually occurs through the Scholl reaction from polyaromatic synthons. Previous results of the laboratory showed that this method does not work for pentaphenylphosphole (PPP) derivatives (**B**, Fig. 8): the oxophosphole ring does not stand these conditions. Photocyclization was also envisaged. Even if it did not allowed to obtain full cyclization, this method appeared as a more promising alternative.

We decided to use a new key intermediate (**C**, Fig. 8) and we thus prepared a phosphole with phenyl rings at the 3,4 position that are already connected to each other. To this purpose, the classical Fagan-Nugent or Urabe-Sato synthetic procedures were used.[39] Photocyclization of oxophosphole **26a^{O}** (Fig. 8) was then performed. A complicated mixture was formed with the unsymmetrical **27a^{O}** as major product. Increasing reaction time or introducing an acid scavenger (propylene oxide PPO)[40] did not improved the reaction. Thus, we changed **26a^{O}** to **26a^{S}**, which is less sensitive to the acidic medium. Indeed, the photocyclization in optimized conditions (hν, stoichiometric I_2, propylene oxide) led to a mixture of two main compounds that could be separated through chromatography. They were unambiguously characterized as the partially fused **27a^{S}** (50%) and fully fused **28a^{S}** (20%) (Fig. 8).[41] Both compounds were also characterized by X-ray diffraction (see Fig. 9 for **28a^{S}**). The reaction was also successfully applied to **26b^{S}**, a highly soluble version of **26a^{S}**. In the case of the thiophene containing phospholes **29-30**, the photochemical method only led to the formation of the dissymmetric derivatives **31-32** (Fig. 8).[42]

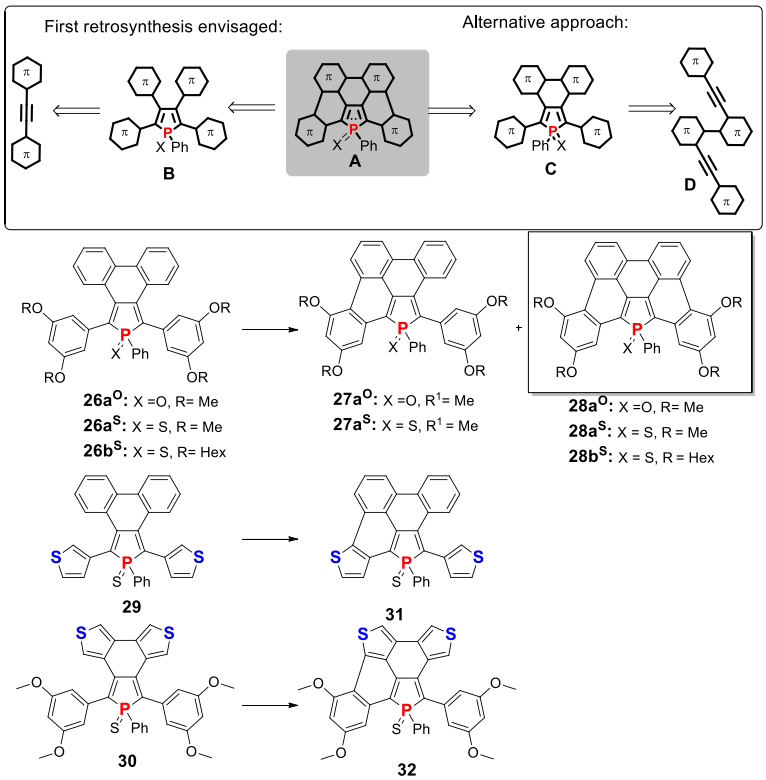


Fig. 8 : Retrosynthetic approaches of targeted PAH **A** and synthesis of phospholes **26-32**

As expected, X-ray diffraction revealed that the sp^2-C backbone of **28a^{S}** is planar. The C-C bond lengths are comprised between 1.35 Å and 1.49 Å, as classically observed in HBC. This

crystallographic structure evidenced that **28a^S** possesses all the structural features of both phospholes and PAHs. The packing consists in head-to-tail dimers with classical intermolecular distances for graphitic materials (3.45 Å).

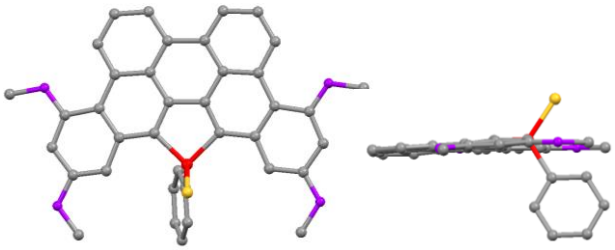


Fig. 9 : Crystallographic structure of **33a^S**

To the best of our knowledge, **28a^S-b^S** are the first examples of planar π-conjugated framework incorporating a P atom. However, this was only a first step in our strategy. In order to validate our approach, it is indispensable to find a synthetic procedure to deprotect **28a^S** it into its reactive analogue **34** (Fig. 10). This was achieved through a two-step alkylation-reduction method. This step was crucial because it allowed us obtaining our key PAH **34** featuring the reactive P atom. Interestingly, despite the presence of the 2D π-extended framework, this compound really displays a « phosphine-like » reactivity as it can be easily oxidized (**28a^O**), alkylated (**35**) or coordinated to transition metals (Au(I), Pd(II), Cu(I), Re(I)…). Apparently, the lone is not involved in the delocalization (*vide infra* for theoretical details about the delocalization)

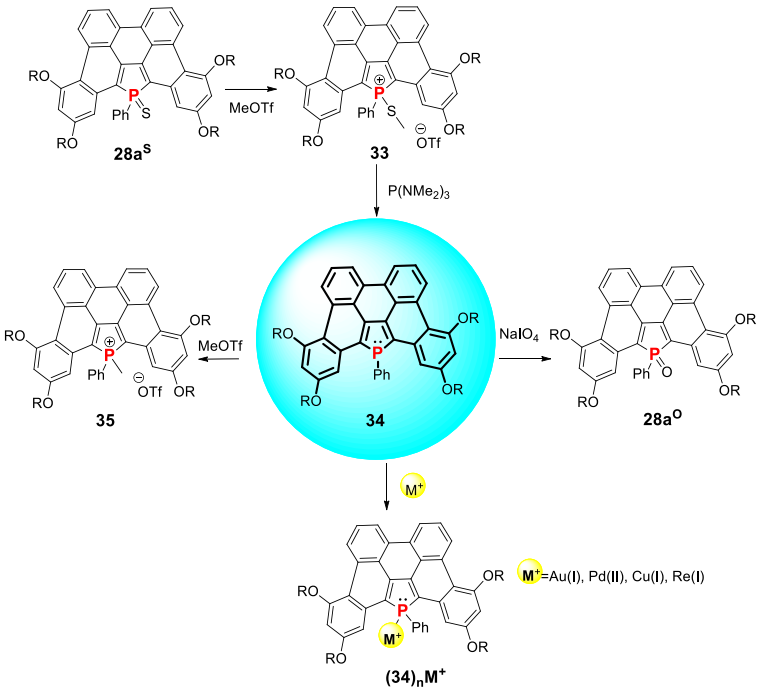


Fig. 10 : Synthesis and chemical derivatization of σ^3,λ^3-P-containing PAH **34**

In the crystallographic structures of coordination complexes **34**, the PAH ligand conserves its structural characteristics (planarity, angles, bond lengths…). The coordination spheres of all

the complexes are classical for phosphine coordinated to transitions metals. The most interesting aspect comes from the study of the solid-state packing (Fig. 11). In most of the cases (Au(**34**), Au(**34**)$_2$, Re(**34**), Cu(**34**)$_2$), infinite π-columns are observed in the solid state due to the π-stacking ability of the ligand. In the case where two ligands are in the coordination sphere, the π-stacking can be intermolecular (Au(**34**)$_2$, as the linear geometry around Au(I) prevents intramolecular stacking) or both inter- and intramolecular (Cu(**34**)$_2$). This property is promising considering the potential optoelectronic applications of these derivatives. Hence, using the same PAH based ligand, which does not π-stack in the solid-state, a large diversity of supramolecular structures is obtained only by varying the metallic cation. As an example, a great diversity of chare transport in these materials is anticipated. This unique property validates the strategy of inserting a coordinating P-atom inside the PAH backbone.

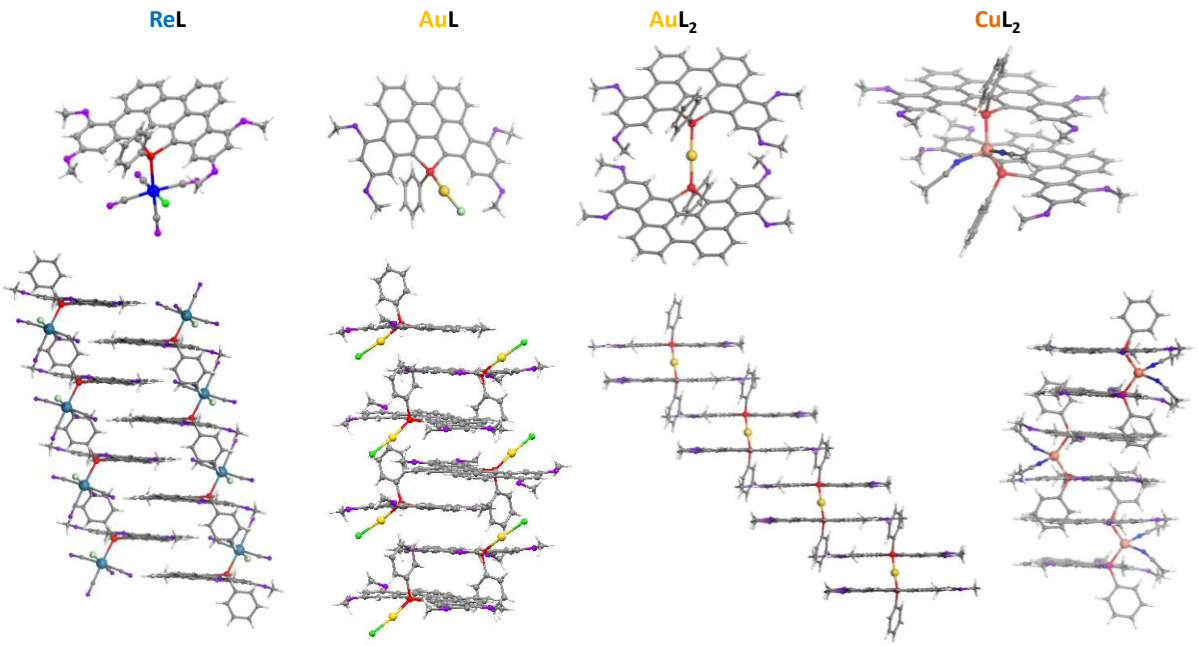


Fig. 11 : Infinite π-columns observed in the packing of coordination complexes of **34**.

All the general reactions known with simple phosphine could be reproduced with the P-containing PAH. This shows that despite its 2D π-extended framework, the P-atom retain its characteristic reactivity. However, the solid-state packing of coordination complexes of **34** shows the added value of the extended 2D framework compared to "standard phosphines". In addition, the intense colour changes (Fig. 16) observed during the reactions qualitatively informed us about the impact of P-environment entire π-framework. The electronic properties of these compounds will be studied both experimentally and theoretically.

In addition, the presence of the (thio)oxo-phosphole ring inside the PAH system confer it another unusual reactivity. Hence, this antiaromatic fragment can act as diene in [4+2] Diels-Alder reactions. As the bay position of perylenes is also known to react in [4+2] cycloadditions,[43] the reactivity of both sites during this reactions were compared. As anticipated, the thermal reaction between **33a**^{S} and the activated alkyne DMAD afforded the PAH **35** resulting in the cycloaddition on the phosphole ring followed by a retro-cycloaddition. **35** is a highly distorted PAH due to the repulsion between the ester groups and the CH bonds, as evidenced by the crystallographic structure (Fig. 12).

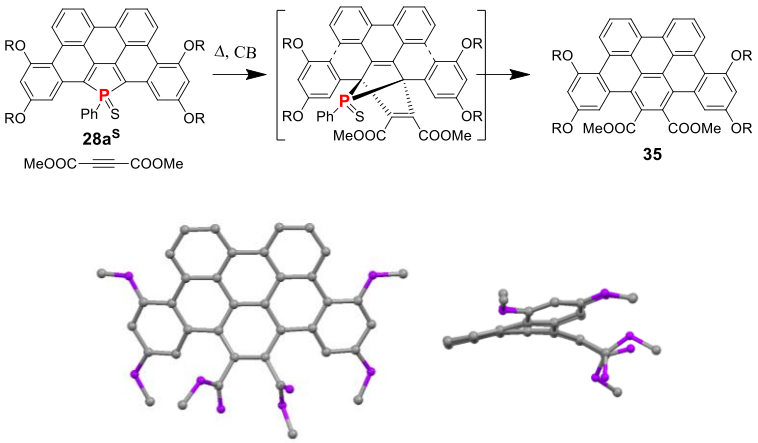


Fig. 12 : Reaction scheme and cristallographic structure (top and side view) of **35**.

In this first part devoted to synthesis and reactivity of P-containing PAHs, we developed the synthetic access to the first planar π-conjugated framework incorporating a P atom. We showed that despite its π-extended nature, the versatile reactivity of its phosphine fragment is preserved.

In a second part, the respective role of both the P-atom and the PAH backbone in the electronic properties of this family of compounds will be investigated in detail by a combined experimental (spectroscopic and electrochemical) and theoretical study.

The optical properties of all the derivatives were investigated (Fig. 13) by UV-vis/ fluorescence spectroscopy. The absorption spectrum of phospholes **26a^{O,S}** has the typical shape of π-conjugated phospholes with a broad π-π* transition in the visible range. A gradual red-shift accompanied by a hyperchromic shift appears from **37a^{O,S}** to the P-containing PAHs **28a^{O,S}**. These latter show the typical hyperfine structure of PAHs. Unlike precursors **26-27a^{O,S}**, the polycyclic **28a ^{O,S}** are highly fluorescent in solution (λ_{em} ≃550 nm, ϕ > 20%). Interestingly, the picture is rather different in the solid state as **28a^{S}** is fluorescent in powder / thin film contrary to **26a^{S}**. Actually, this was explained on the basis of the aggregation-induced emission (AIE)/aggregation caused quenching (ACQ) phenomenon. The emission properties of **26-28a^{S}** were studied in acetone/water mixtures. As these compounds are poorly water-soluble, this technique allows to form micro- / nanoaggregates. As expected for PAHs derivatives, the emission of **28a^{S}** is quenched upon increasing the water ratio (Fig. 13). On the contrary, the emission of **26a^{S}** was enhanced by 10 once the water ratio was superior to 70%. This AIE is due to the restriction of intermolecular rotations, that restaures the luminescence in the aggregated state.[44] This phenomenon has already been observed on phenyl-substituted siloles and phospholes.

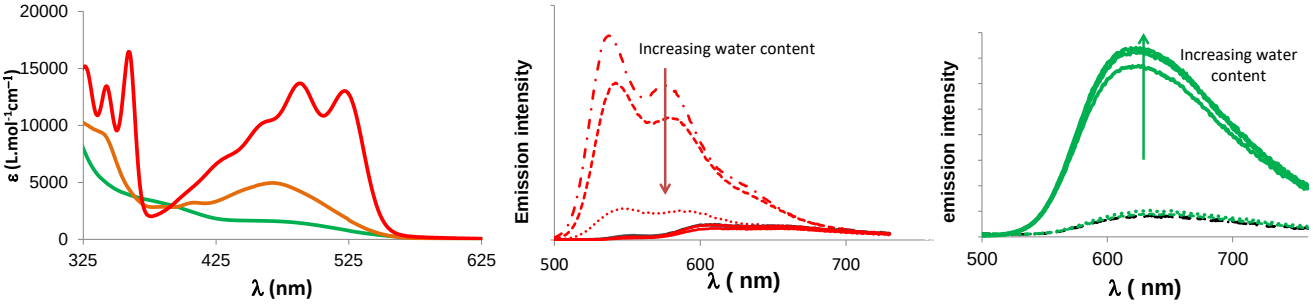


Fig. 13: UV-Vis absorption of **26a^{S}** (green), **27a^{S}** (orange), **28a^{S}** (red) in DCM, (left), Evolution of emission intensity of **28a^{S}** (middle) and **26a^{s}** (right) in acetone/water mixtures with increasing water content

The redox properties were studied by Cyclic Voltammetry (CV). **26a^{S}** displays an irreversible oxidation and a quasi-reversible reduction (E_{ox} = 0.7 V vs Fc^{+}/Fc; E_{red}= -1.7 V vs Fc^{+}/Fc). The effect of two consecutives intramolecular bond formations from **27a^{S}** to **28a^{S}** is a gradual increase of both oxidation and reduction potentials. As the effect is more intense on E_{ox}, a decrease of the electrochemical gap is observed. This was in agreement with the decrease of the optical gap and was also corroborated by DFT calculations.

After looking at the effect of the polycyclic backbone, the effect of P-substitution on the optical properties was also studied. To facilitate the reading in all this section as well as in the theoretical part, compound **28a^{S}**, **28a^{O}**,**34**, **33** and **35** will be nominated **P^{S}**, **P^{O}**, **P**, **P^{SMe+}**, **P^{Me+}** respectively.
Compound **P** displays a large and structured band in the visible (λ_{abs} = 472 nm). A marked bathochromic shift is observed with (thio)oxidation (**P^{S}**, **P^{O}**) and formation of the cationic phospholium **P^{Me+}** and **P^{SMe+}**. The striking effect of the P-heterocycle on the optical properties can also be seen by comparing with a reported compound where the phosphole is replaced by a benzene (λ_{abs} = 376 nm, λ_{em} = 415 nm).[45] P-containing PAHs are emissive in diluted solution with the same gradual red-shift than observed for the absorption in the series **P**, **P^{S}**, **P^{O}**, **P^{Me+}**, **P^{SMe+}** (Fig. 14). Excepted for **P^{SMe+}**, which emits in the red part of the spectrum (λ_{em} = 669 nm), the emissions are structured and the quantum yields are over 20%.
In addition, these data show that the molecular engineering of both polycyclic backbone and P-environment allows for the absorption to cover almost the entire visible spectrum (Fig. 14). This nicely illustrates the strong impact of a localized chemical transformation on the P-atom for the tuning of the optical properties. P-containing PAHs are emissive in diluted solution with the same gradual red-shift than observed for the absorption in the series **P**, **P^{S}**, **P^{O}**, **P^{Me+}**, **P^{SMe+}** (Fig. 14). Excepted for **P^{SMe+}**, which emits in the red part of the spectrum (λ_{em} = 669 nm), the emissions are structured and the quantum yields are over 20%.

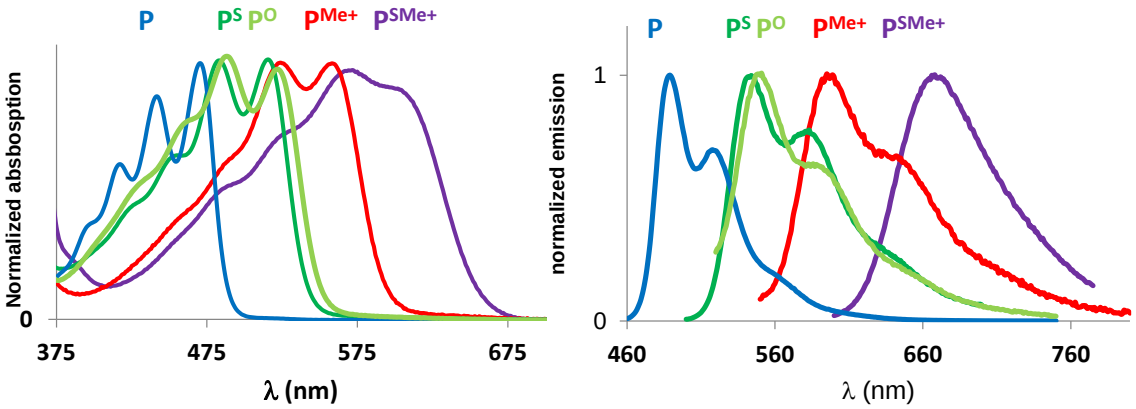


Fig. 14: Normalized UV-vis absorption and emission spectra of **P**, **P^{S}**, **P^{O}**, **P^{Me+}**, **P^{SMe+}** in DCM

Regarding the redox properties, σ^3,λ^3 **P** displays an irreversible oxidation wave while no reduction wave was observable in these experimental conditions. P-modifications in the series **P**, **P^{S}**, **P^{O}**, **P^{Me+}**, **P^{SMe+}** lead to a gradual increase of both oxidation and reduction potentials, as observed for the phosphole oligomers (except for **P**, all reduction waves are quasi-reversible). The variation is stronger for the reduction potentials, which leads to a decrease of the gap in this series, according to the optical measurements and the DFT calculations.

To go deeper in the understanding of the effect of P-modifications on the optical and redox properties, **P**, **P^{S}**, **P^{O}**, **P^{Me+}**, **P^{SMe+}** were investigated computationally (B3LYP/6-

31+G*). All P-modified PAHs show the characteristic phosphole-type HOMO and LUMO orbitals: the orbitals of the parent molecule displayed in Fig. 15 are clearly recognizable in the series. However the electronic density is spread all over the polycyclic backbone. In a very simple picture, this explains why the modifications on the P atom have such an impact on the optical properties. From **P**, $\mathbf{P}^{S}$, $\mathbf{P}^{O}$, $\mathbf{P}^{Me+}$, $\mathbf{P}^{SMe+}$ the rising of the HOMO energy level is accompanied by a stronger stabilization of the LUMO (Fig. 15) resulting in the reduction of the HOMO-LUMO gap. This effect on the LUMOs is due to a hyperconjugative interaction between the exocyclic σ^*_{PC} MO and the π-MOs of sp^2-C skeleton. This is in full agreement with the experimental data. TD-DFT calculations (B3LYP/6-31+G*) also showed that the long-wavelength UV-Vis absorption mainly results from HOMO-LUMO transitions.

To investigate in depth the aromaticity inside the polycyclic structure, Nucleus Independent Chemical Shift (NICS (1))[46] values were calculated for **P**, $\mathbf{P}^{S}$, $\mathbf{P}^{O}$, $\mathbf{P}^{Me+}$, $\mathbf{P}^{SMe+}$ and are schematically represented in Fig. 15. The local aromaticity values in the P-heterocycles are in good accordance with the aromaticities of the parent phospholes. In all the cases, the cationic σ^3,λ^3 P-heterocycles exhibit the biggest antiaromaticity (orange/red colour in Fig. 15). Interestingly, the increasing antiaromaticity of the P-ring is accompanied by an increase of the antiaromaticity of its endocyclic 6-membered ring as well.[47] This is another proof that the modifications performed at the P-atom impact the entire π-system. To the best of our knowledge, this gradual switch between aromaticity/antiaromaticity upon chemical modification performed on a single atom of a PAH does not have any equivalent in the literature.
It should be noted that the increase in the antiaromatic character is in good accordance with the decrease of the HOMO-LUMO gap.

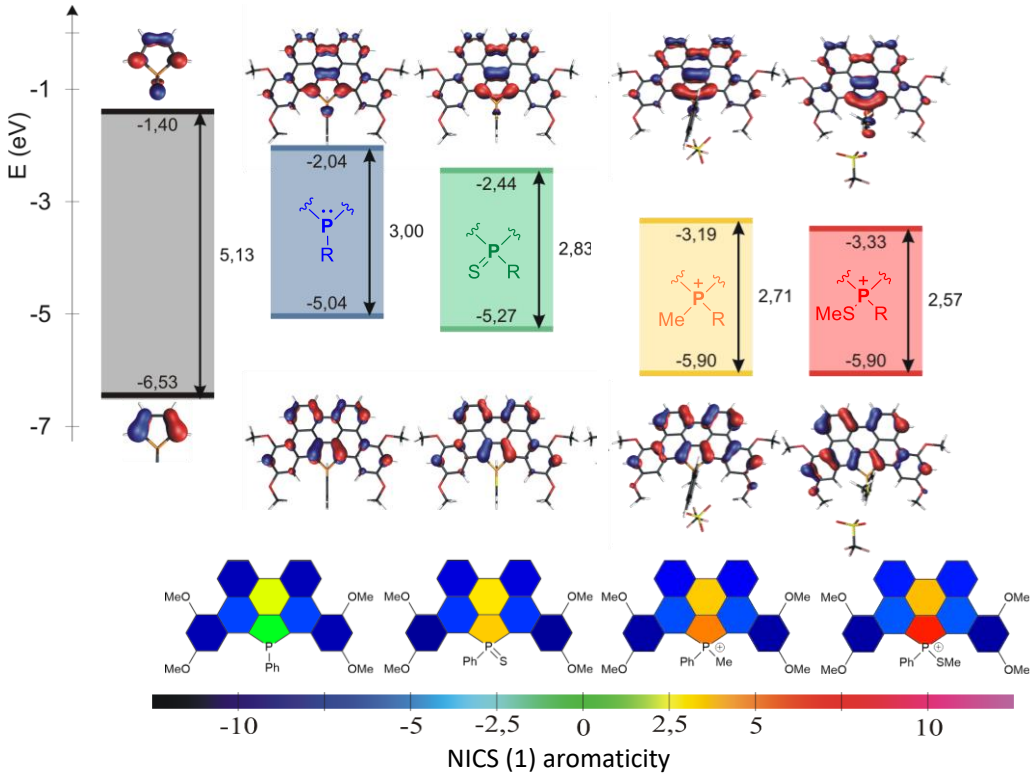


Fig. 15: Frontier MOs for the parent phosphole, **P**, $\mathbf{P}^{S}$, $\mathbf{P}^{Me+}$, $\mathbf{P}^{SMe+}$, (up) and schematic representation of the NICS(1) aromaticities (down).

As an example of device application for these new family of PAH, we decided to insert them as emitting layer (EML) in OLEDs. As $\mathbf{P^S}$ / $\mathbf{P^O}$ are orange-emissive in diluted solution or matrix, we decided to use them to dope a blue emitting α-NPB (N,N'-diphenyl-N,N'-bis (1-naphthylphenyl)-1,1'-biphenyl-4,4'-diamine) matrix to obtain white light in a multi-layered OLED device. Electroluminescence spectrum observed with $\mathbf{P^S}$ in α-NPB displays both blue emission characteristic of α-NPB and orange emission of the P-containing PAH (λ_{em} = 548 nm, similar in shape as the solution photoluminescence at λ_{em} = 544 nm). Careful modification of the doping rate allowed to tune the emission from the orange (CIE coordinates: x = 0.45; y = 0.44, doping rate of 5.5%) to the white area (x = 0.32; y = 0.37, doping rate of 1.1%). For this latter device, turn-on voltage is rather low (5.5 V) with external quantum efficiency (EQE) of 1.7%, brightness of 1122 $cd.m^{-2}$ and power efficiency of 0.96 $lm.W^{-1}$ at 30 mA/cm^2. Device stability was satisfaying. Slightly better performances could be obtained with $\mathbf{P^O}$. Even if the device performances remain moderate, these data demonstrate that P-containing PAH can be used in opto-electronic devices such as OLEDs.[48] However, given their planar structure, applications in OFET are also envisaged, even though all preliminary tests were unsuccessful. Preparing an OFET using organophosphorus derivative as the semi-conductor remains a scientific challenge, as only one example using the unusual diphosphacyclobutane-2,4-diyls scaffold is reported.[49]

In conclusion for this project, we developed an unprecedented method of molecular engineering of PAHs using P-reactivity. This approach allowed us to fine-tune the optical/redox properties of the compounds (as visually evidenced by the pictures of Fig. 16) as well as their coordination driven assembly. As proof of concept of utilization in opto-electronic devices, we prepared a white-emitting OLED.

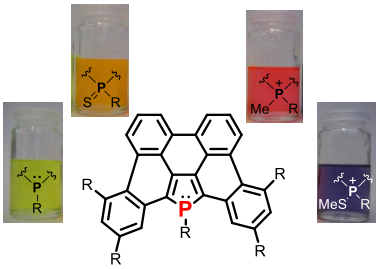


Fig. 16 : Pictures of the colour changes observed upon P-modifications- metre la nouvelle appellation

Preparation of fluorescent hybrid nanoparticles based on "Aggregation-Induced Emission" ligands

Fluorescence of organic compounds in the solid state (or aggregated state) is widely used in material science (OLEDs) or in biology (fluorescent probes). Even if numerous examples are found in the literature, it still remains difficult to answer to these two questions:

- will the organic compound be fluorescent in the solid state?
- how the emission wavelength will evolve from the diluted solution to the solid state?

In this context, the concept of "aggregation-induced emission" developed by Tang became very popular in the last 5 years.[44] This concept was based on observations of hexaphenylsiloles HPS derivatives (Fig. 17). These compounds present very low emission in diluted solution but strong luminescence in the aggregated state (suspension in water/acetone mixture) or in the solid state (crystals, powder, thin films…). The phenomenon has been attributed to the restriction of intramolecular rotations (RIR) in the aggregated /solid state. This behaviour is opposite to the aggregation-caused quenching (ACQ) of perylene/PAH derivatives. Since this observation, many compounds presenting this phenomenon have been described in the literature. However, despite its pedagogic character for the HPS derivatives and their analogues, this concept remains ambiguous in many cases and sometime misunderstood.

Given the structural similarity between HPS and pentaphenylphospholes PPP derivatives, we started to investigate the behaviour of these compounds. For example, we showed that the planar phosphole derivative **28a^S** and the PPP oxide **35^O** display the typical ACQ vs AIE phenomenon, and the RIR mechanism gives a satisfying explanation for this behaviour (Fig. 17).[50]

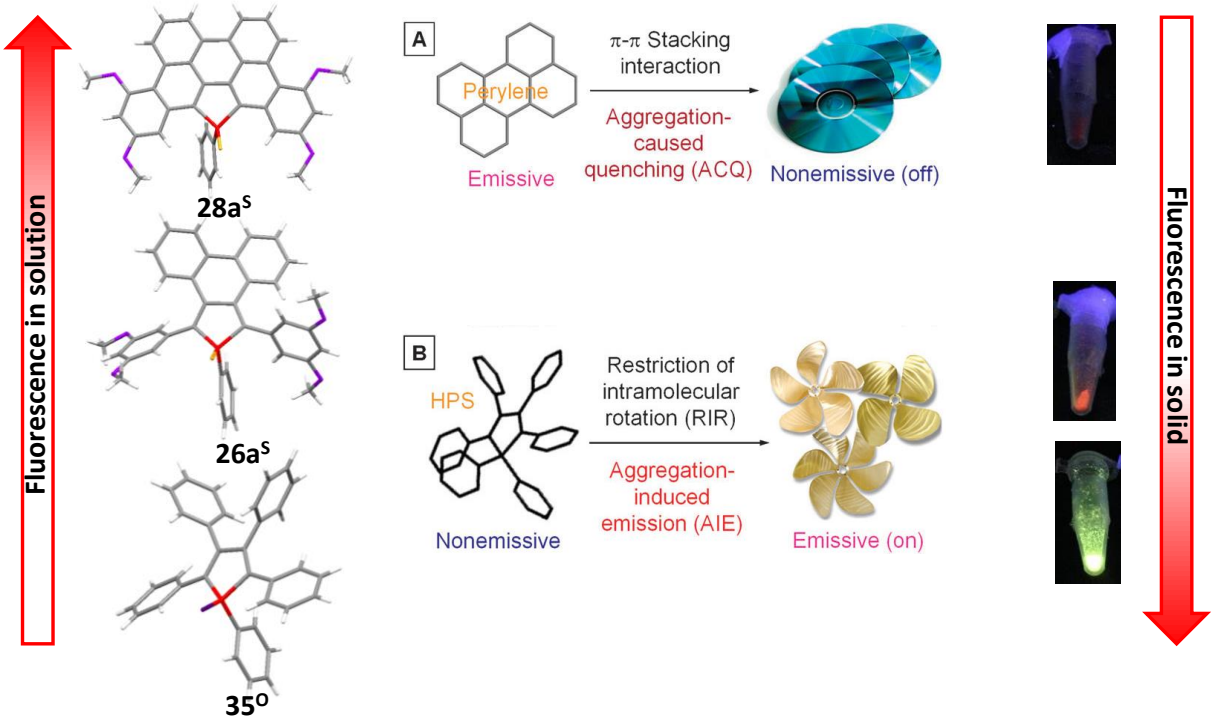


Fig. 17: AIE/ACQ phenomenon and its illustration using the polyaromatic phosphole family. (Figure adapted from Tang *et al. Chem. Soc. Rev.* **2011**, *40*, 5361)

Our objective was to use the ease of modifications on the P-atom to develop solid-state emitters with chemical functions that would allow combining them with various substrates to obtain novel multifunctional materials. As an example, the coordination of the lone pair to

metallic ions can give access to fluorescent complexes **40**; simple methylation leads to cationic derivatives **36** that can be easily combined with anionic substrate. Cleavage of the exocyclic P-C bond followed by oxidation allows to easily prepare derivatives with a phosphinic acid such as **38**. Anionic compounds can be easily obtained from deprotonation of the latter compound. The anion **38** can thus be combined with various cations. If wisely selected, the substrate can bring a new property to the structure, in addition to the solid-state emission of the P-fluorophore.

In the following part, I will detail the properties of hybrid nanomaterials composed of ZnO NP and phosphoric acid **37** will be described. This work is done in collaboration with J. Ackermann and O. Margeat (CINaM, Marseille, France)

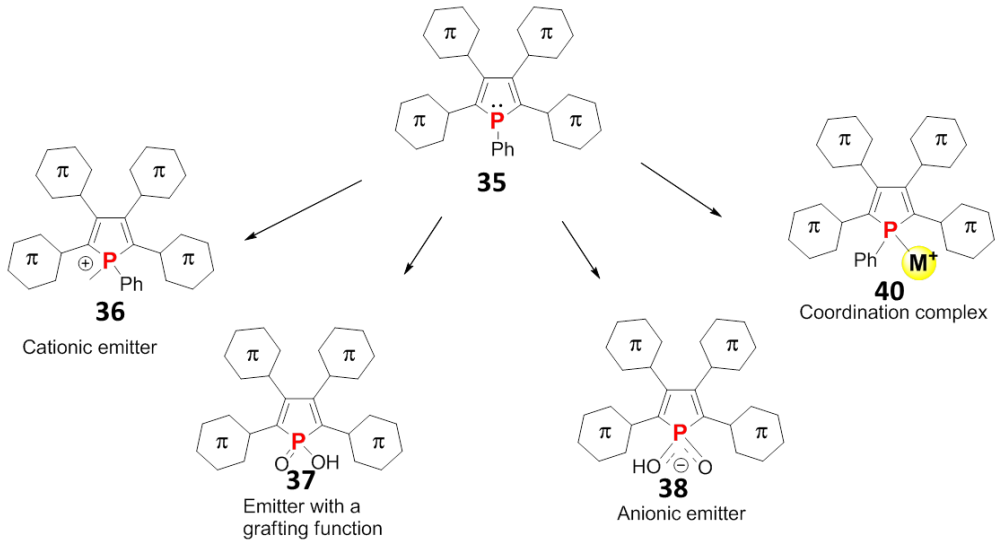


Fig. 18: Strategies to obtain various solid-state emitters based on the RIR mechanism

Grafting of chromophores on metal oxides such as TiO_2, ZnO, NiO is a basic principle of many hybrid devices such as p- or n-DSSC.[10b, 51] In these devices, a sensitizer substituted by a carboxylic acid or phosphinic acid is covalently attached to the inorganic substrate. One example of π-extended hydroxy-oxophosphole grafted to mesoporous TiO_2 displaying moderate photovoltaic performances in n-DSSC devices has previously been reported.[52]

As a preliminary study, we were thus interested in studying the grafting of the tetraphenyl hydroxy-oxophosphole **40** to ZnO NP of average diameter of 5 nm (collaboration J. Ackermann / O. Margeat, CINaM, Marseille). Upon mixing a suspension of ZnO NP in $CHCl_3$ with a diluted solution of **40** in $CHCl_3$, a small red-shift in the UV-vis absorption is observed together with an increase in the baseline. When measuring the fluorescence, we were surprised to observe a strong increase of the luminescence of the solution (Fig. 19) by a factor of 400 during the first 15 mn after the mixing then leading to a stable fluorescent solution. This high photoluminescence, typical of the emission of the organic fluorophore, was conserved in thin films and in evaporated powders (Fig. 19).[53] The hybrid material formed was further characterized by microscopy (TEM) and spectroscopy (FTIR, XPS…). In particular, FTIR showed the disappearance of P-OH vibration and the appearance of a new band at 1110 cm^{-1}, compatible with a bidentate grafting (similar to the carboxylate grafting) of the fluorophore to the NP. This bidentate grafting was also supported by DFT calculations.

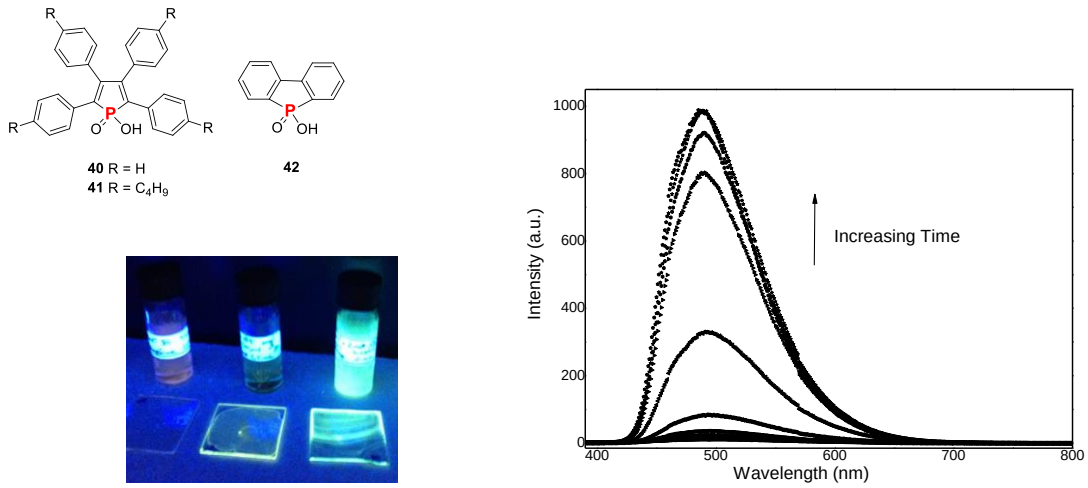


Fig. 19: Increase in photoluminescence upon addition of ZnO to **40** in $CHCl_3$ and photo of the solution and drop-casted films of ZnO solution, **40**, and **40**-ZnO (from left to right).

The strong fluorescence enhancement (FE) may be induced by different factors:

- chemical modification of **40** by the grafting on the ZnO NP and corresponding modification of its optical and electronic structures.
- RIR of the fluorophore at the surface of individual NP.
- Formation of **40**:ZnO clusters due to the grafting that will further induced the RIR.

To verify these hypotheses, the same experiment was carried out with hydroxy-oxo-dibenzophospholes **42** (Fig. 19) in which no bond rotation could be restricted due to molecular design. In this case, the fluorescence of the organic fluorophore was quenched upon grafting. This confirmed that the RIR mechanism plays a crucial role in the FE. However, the fact that this phenomenon is linked to the grafting or to interparticles clustering still remained to be proved.

Time resolved absorption / fluorescence emission spectroscopy was used to study this phenomenon. To avoid reproducibility problems, studies were performed on the same sample for both absorption and fluorescence. Thus when the segments in the absorption are zero in Fig. 20, the fluorescence is being analysed and vice versa. Fig. 20 (left) shows the absorbance at 600 nm of **40**:ZnO. As the hybrid do not absorb at this wavelength, the light scattering due to cluster formation is the only contribution. After injection of ZnO into a diluted solution of **40**, the scattering signal is constant. In parallel, the fluorescence of **40** increases by a factor of 5-10 (Fig. 20, middle). These spectroscopic modifications are attributed to the grafting of the ligand on ZnO. After the first 15 min of experiment, the scattering signal at 600 nm starts to increase strongly and saturates in intensity at 45 min indicating the formation of **40**:ZnO clusters. Corresponding fluorescence intensity increases simultaneously very fast with the cluster formation. The increase in fluorescence emission goes perfectly in line with the formation of nanohybrids clusters so that both cluster size and emission saturate at the same time (45 minutes). The formation of **40**:ZnO clusters was confirmed by TEM (Fig. 20) and DLS.

This experiment was also carried out with **41**, an analogue of **40** bearing solubilizing aliphatic chains (Fig. 19). Interestingly, it only showed a small FE (x 5-10) and no cluster formation. However, powder sample or spin-coated films of **41** on glass remained highly luminescent (Fig. 25).

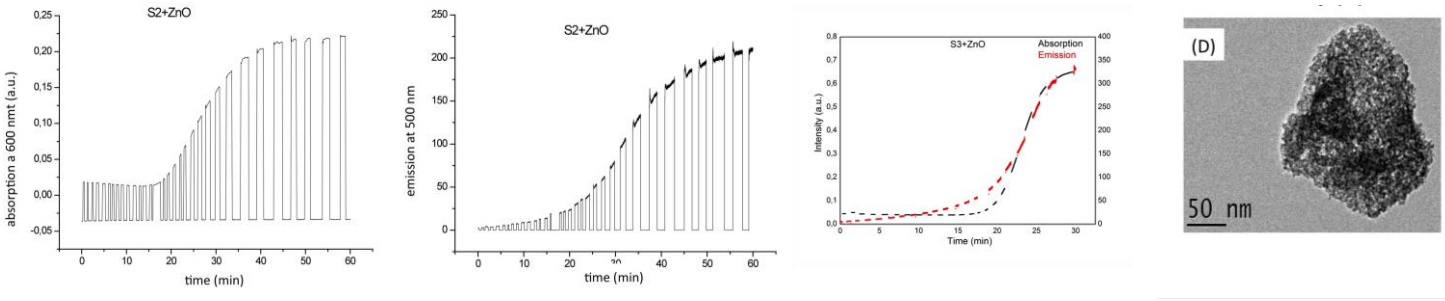


Fig. 20: Time resolved UV-vis and fluorescence of ZnO:**40** and TEM image of ZnO:**40** cluster.

From these experiments, we could thus interpret FE process observed for **40-41**. The grafting of **40** (respectively **41**) lead to a small increase of the fluorescence intensity (x 5-10), probably due to the suppression of the O-H vibrator in the molecule. Then two pathways are possible (Fig. 21):

- if the hybrid particle has a low solubility (case of **40**:ZnO), interparticles clustering occurs leading to RIR of the fluorophore and thus to a strong FE.
- if the particles are soluble (case of **41**:ZnO), the solution keeps the moderate luminescence of the grafted fluorophore but the RIR mechanism can be induced by solid-state deposition.

The RIR induced FE effect was further confirmed by simple deprotonation experiments performed by 1 eq. of NEt_3 on diluted solution of **40** / **41** in DCM that showed similar behaviour: precipitation and strong FE (x 120) for **40** and small FE (x 5) without precipitation for **41**.

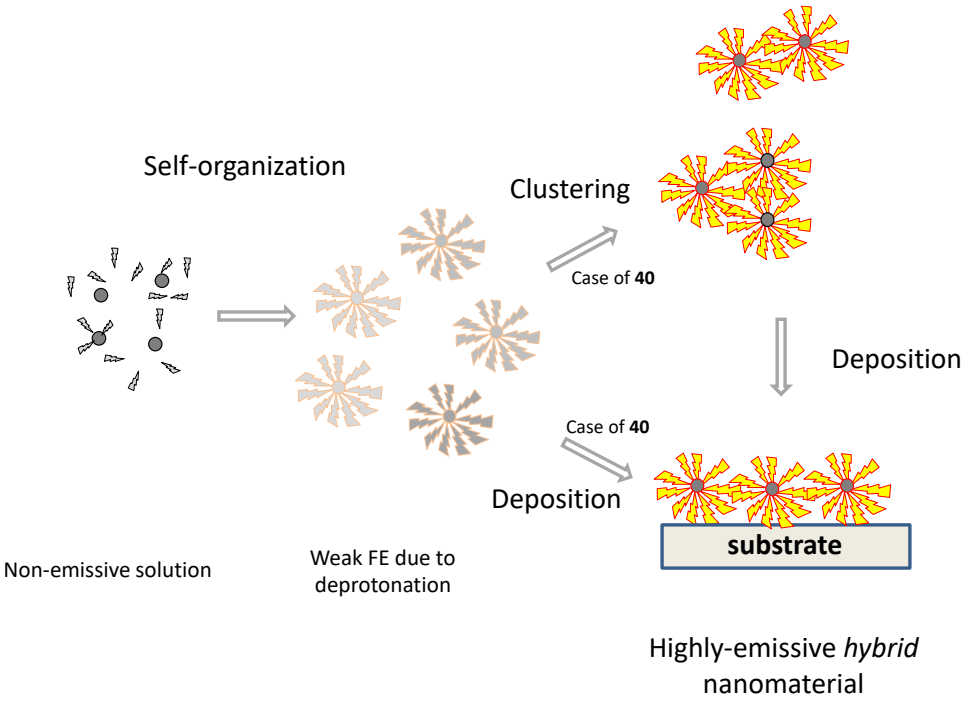


Fig. 21: Schematic interpretation of the FE of the hybrid nanomaterials

This first study on hybrid materials based on simple phosphinic acid-containing fluorophores was highly promising in the context of new emissive materials. Furthermore, it is a rare example of AIE due to RIR at the surface of an hybrid material.[54]

We thus decided to prepare a family of hydroxy-oxophospholes derivatives and study the PL properties of the hybrid solids. Our objective was to find a systematic and reproducible synthetic method to prepare fluorophores covering the whole visible spectrum.

First, a family of tetra-aryl substituted hydoxy-oxophospholes was prepared using the classical Fagan-Nugent heterole synthesis (Fig. 22). Various π-conjugated systems (phenyls, fluorenyls…) have thus been inserted on the hydroxy-oxophosphole platform. This allowed tuning the emission of the compounds between 500 nm and 600 nm. As expected, the extension of the π-conjugated system leads to a red shift of absorption/emission (Fig. 24). This method is efficient for π-systems of moderate size without functionalities but it is difficult to envisage preparing red-emitting fluorophores using this approach.

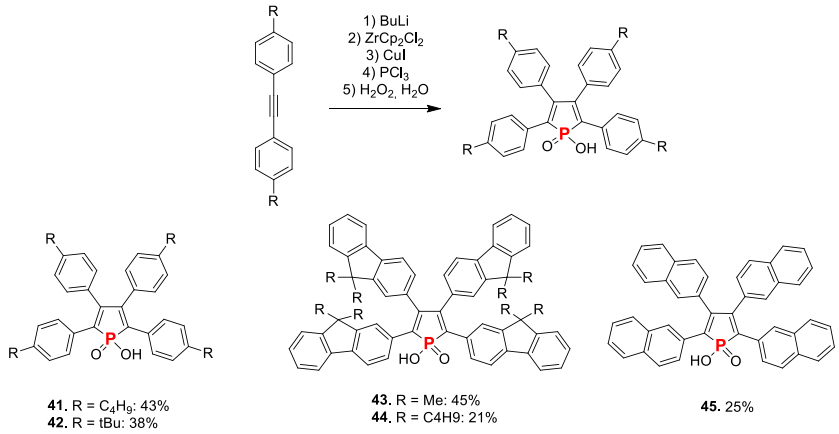


Fig. 22: Synthesis of tetra-arylated hydroxyoxophospholes **41**-**45**

In order to extend the spectral windows of the family toward the blue, π-extended hydroxy-oxophosphindoles were prepared. These compounds display smaller conjugation and thus absorb/emit at lower wavelengths compared to their tetra-aryl analogues. Phosphindole oxides are also described to be efficient solid-state emitters.[55] We adapted a recently published radicalar method in order to prepare the corresponding derivatives.[56] The same alkynes could be used and a new family of phosphindoles emitting from 400 nm to 500 nm was prepared. As anticipated, the absorption/emission is lower compared to their tetra-substituted phospholes analogues (Fig. 24) and the same gradual red-shift is observed upon increasing the π-conjugated system.

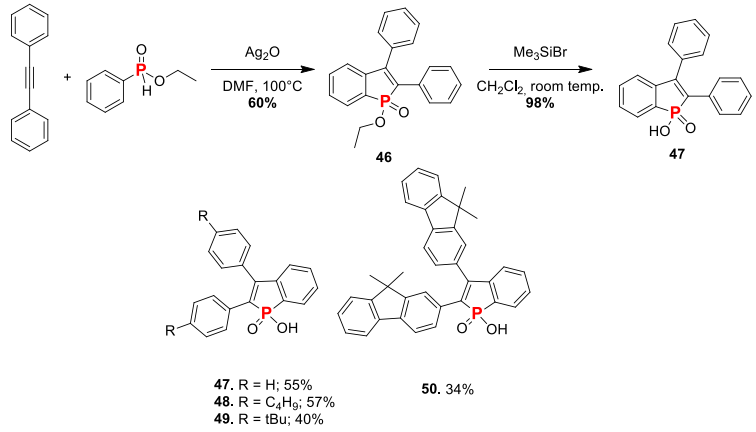


Fig. 23: Synthesis of phosphindoles **47**-**50**

Importantly, all the hydroxy-oxophospholes/phosphindoles synthesized display weak or moderate emission in solution (ϕ < 0.1% for the phenyl derivatives). This low values are expected as the compounds are designed to be desactivated by internal rotations in diluted solutions. However, the fact that the fluorenyl derivatives luminescence is moderate (($\phi \simeq$ 5%) showed that the steric hindrance of the fluorenes already activate the RIR even in solution.

As expected by the molecular design, all compounds display more intense emission in the solid-state (Table 2).However, the presence of the O-H vibrator is suspected to be a cause of desexcitation in these systems and explain that these values are not as high as the values of their oxophospholes analogues.

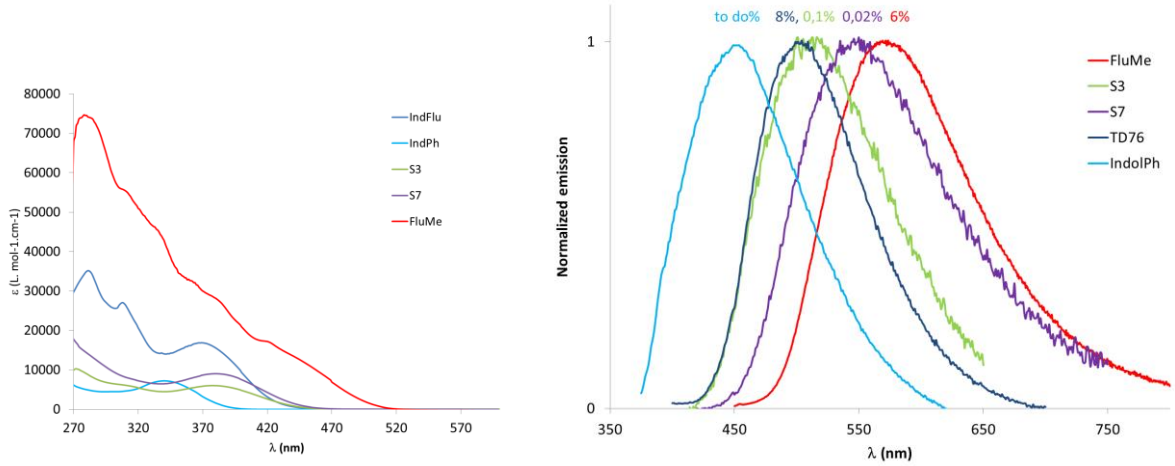


Fig. 24: UV-vis absorption (left) and emission spectra of the ligands with the PL QY (right) in diluted DCM

All the ligands were grafted on the ZnO NP at CINaM and the effect of the grafting on the optical properties was studied. In all the cases, the grafting was successful and luminescent hybrid materials have been obtained.

As observed in our preliminary results, the emission of the hybrids are blue-shifted compared to the ligands and the PL QY in the solid state are higher than the ligands with values higher than 20% (Fig. 20 and table).

This strategy thus allowed us to prepared luminescent hybrid materials where the shape of the hybrid is determined by the inorganic core (spheric NP in our case, but preliminary tests with ZnO nanorods show similar results) and the emission is only determined by the nature of the organic shell. In this sense, these nano-objects display opposite behaviour compared to quantum dots whose emission is dependant of the size of the inorganic core.

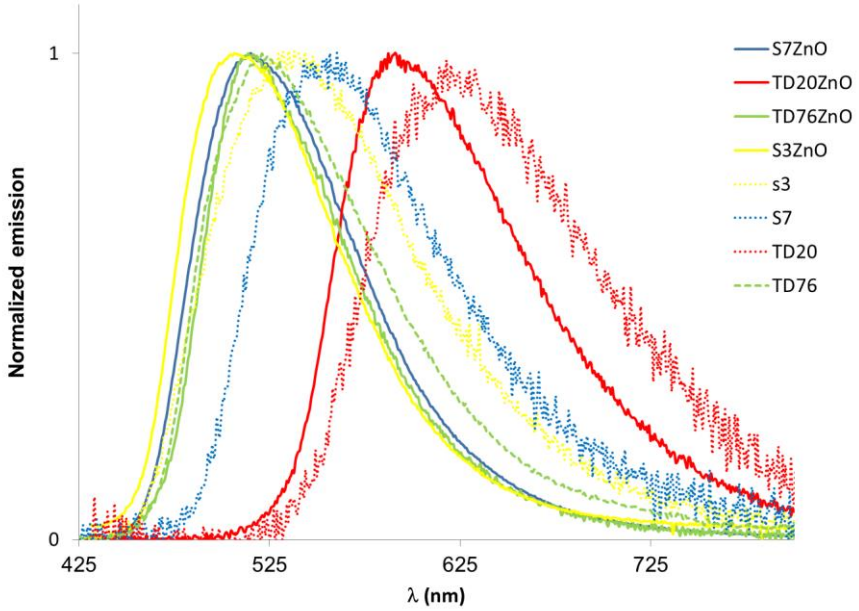


Fig. 25: Solid-state fluorescence of ligands (dashed) vs hybrids (solid)

Table 2: Photophysical data

Ligand **L**	$\lambda_{em\ liq}$ [a] [nm]	Φ_F [b]	$\lambda_{em\ powder}$ [c] [nm]	Φ_F [d]	**L.ZnO** $\lambda_{em\ powder}$ [c] [nm]	**L.ZnO** Φ_F [d]
40 (S3)	513	0,001	534	0.14	505	0.38
41 (S7)	545	0,002	542	0.15	515	0.72
43FlMe	570	0.06	612	0.07	587	0.24
47		x	453	0.8	x	x
50	500	0.08	520	x	513	0.38

In this project, we developed a new family of luminescent hybrid materials based on the self-assembly of organic fluorophores at the surface of ZnO NP. Our objective now is to test these novel materials in luminescent devices. Our idea is to take advantage of the charge transport of the inorganic substrate and the luminescence of the organic fluorophore to prepare hybrid LEDs.

Synthesis, coordination chemistry and opto-electronic applications of novel heterocyclic π-conjugated systems

In this last chapter about my scientific results, the first topic that I will develop will be the development of a new coordination mode for phosphole derivatives and its impact on its electronic properties.

Cyclometalated complexes are a particular class of organometallic derivatives featuring a σ carbon-metal bond.[57] In the case of Ir(III) complexes, and depending on the coordination sphere, they can display MLCT-based luminescence that has been widely used in the field of phosphorescent OLEDs.[58] In the context of catalysis, they also found promising applications for example water oxidation.[59]

Concerning the cycle containing the $\sigma_{C\text{-}M}$ bond, most of the examples use phenylpyridine - based fragments (Fig. 26). Recently, the first P-containing heterocycle cyclometalated complex were described using phosphinines ligands.[60] Phosphinines are weak σ-donors because of their low lying MO involving the lone pair (Fig. 26). Replacing this ring by a phosphole ring, whose σ-donor character is stronger, will modify the reactivity and the properties of the complexes. We thus started to investigate the cyclometalation of phosphole-based ligands.

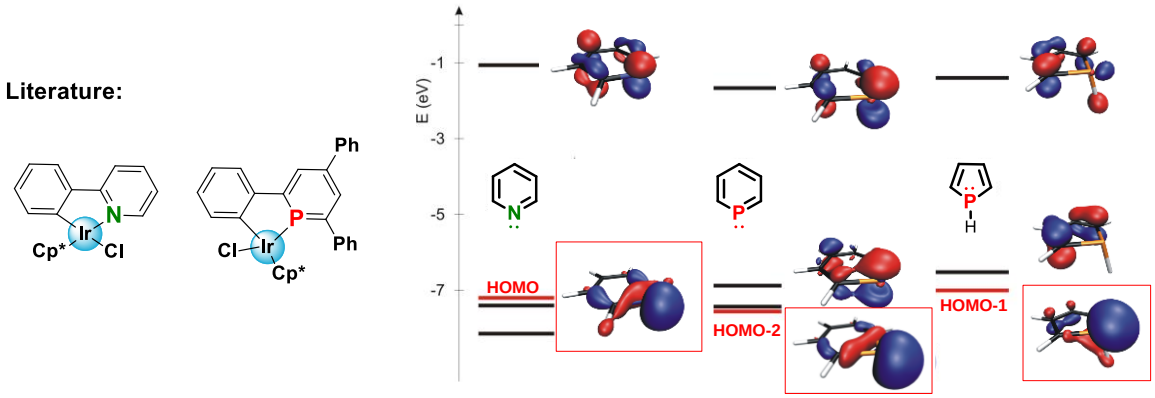


Fig. 26: exemple of Ir-based cyclometalated complexes (left), and views of the FMOs and the MO involving the lone pair of pyridine, phosphinine and phosphole (B3LYP/6-31+G*).

After unsuccessful attempts using various Ir(III) precursors ($IrCl_3$, $(IrCl_2Cp^*)_2$), we developed a stepwise strategy to prepare cyclometallated Ir-phosphole complexes.
Ligand **50** was complexed with half an equivalent of $[Cp^*IrCl_2]$, to reach the monovalent Ir(III) complex **51 (**Fig. 27**).** When heated in presence of sodium acetate, **51** converted into a mixture of two products (^{31}P NMR: + 34.9 ppm; + 36.2 ppm). X-ray crystallography allowed assigning them to the two diastereoisomers of cyclometallated complex **52Cl** (Fig. 27**)**. Hence, compared to their pyridine or phosphinine analogues, the presence of the stereogenic P-atom in addition to the Ir center, makes that **52X** can exist as 4 diastereoisomers. However, when **51** was reacted with $AgBF_4$ in presence of acetone and 3 equivalents of potassium pivalate, the reaction led to the formation of a single diastereoisomer (^{31}P NMR: +38.0 ppm). This product was fully characterized and its structure unambiguously attributed to the cyclometallated complex **52Piv** (Fig. 27). This compound was then reacted with AgOTf in

presence of acetonitrile to reach the cationic cyclometallated complex **53**. Its structure was also confirmed by X-ray diffraction.

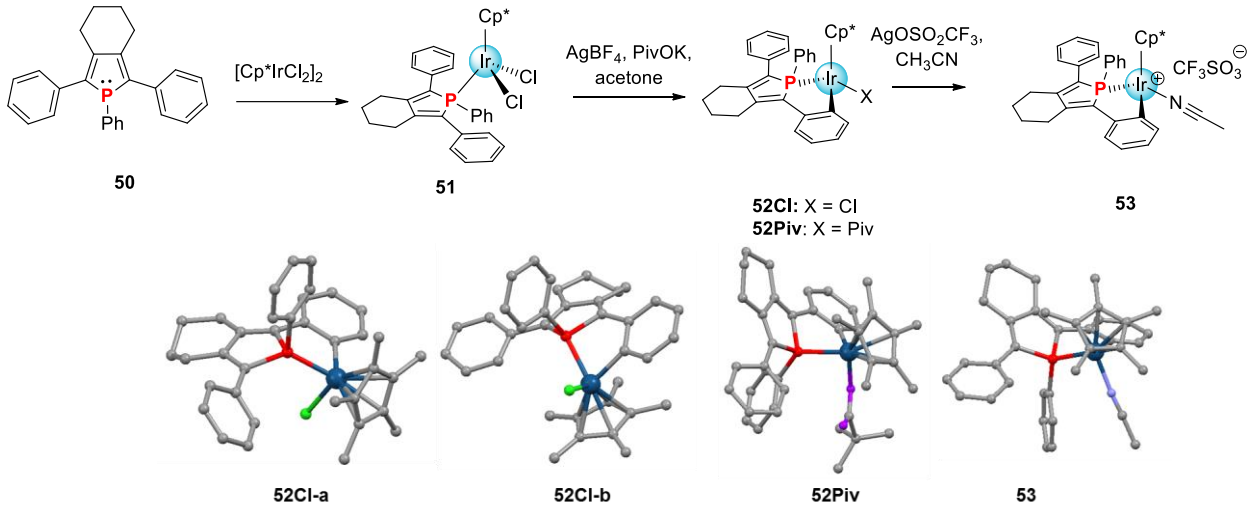


Fig. 27: Synthesis and X-ray structures of cyclometallated complexes **52-53**

This method was then applied to different ligands: a new family of cyclometallated complexes **54-56** could be synthesized and characterized, thus showing the versatility of the approach.

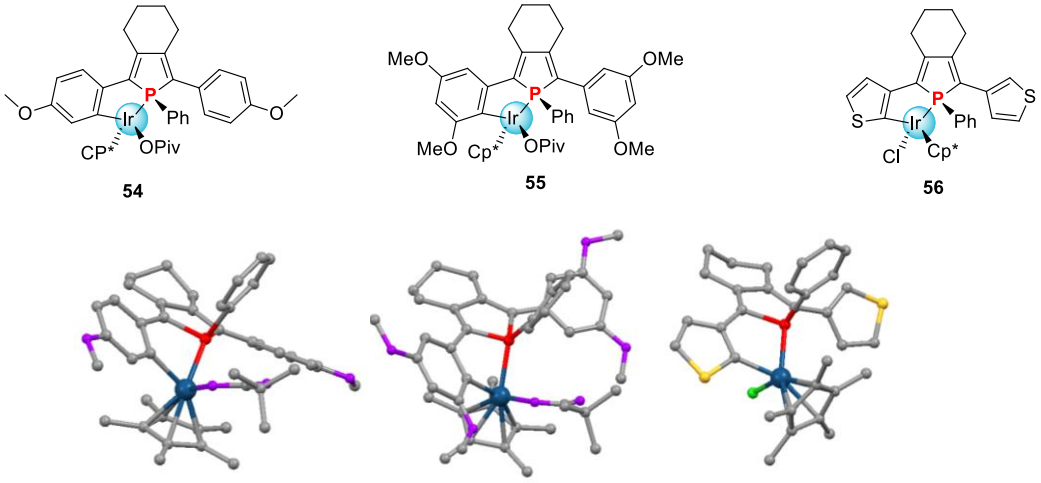


Fig. 28: Molecular and crystallographic structures of cyclometallated complexes

The effect of cyclometallation on the optical properties was studied by mean of UV-vis absorption (Fig. 29). The UV-vis absorption spectrum of **50** consists in a large band in the visible attributed to a π-π* transition. As expected, this transition is slightly red-shifted following the complexation of the Ir fragment in the case of **51**. This was attributed to a combined ILCT/LLCT transition by TD-DFT calculations (B3LYP/LANL2DZP, collaboration with A. Boucekkine/J. F. Halet, ISCR). The UV-vis absorption of the cyclometallated complexes **52-53** is more complicated. It consists in two main bands (for **52Piv**: λ = 325 nm, λ = 395 nm). The most red-shifted band possesses a strong MLCT character, according to TD-DFT (Fig. 29). As a general trend, cyclometallation leads to a red-shift of the UV-vis absorption of the complexes.

As usually observed for IrCp*X based organometallic complexes, no emission is observed.
In terms of electrochemical properties, cyclic voltammetry showed that the cyclometallation lead to a strong decrease of oxidation potential (E_{ox} (**52Piv**) = 0.24 V vs Fc^+/Fc, while E_{ox} (**51**)= 0.72 V vs Fe). In the case of the cyclometalated complex, the oxidation occurs on the metallic ion and not on the π-system anymore.

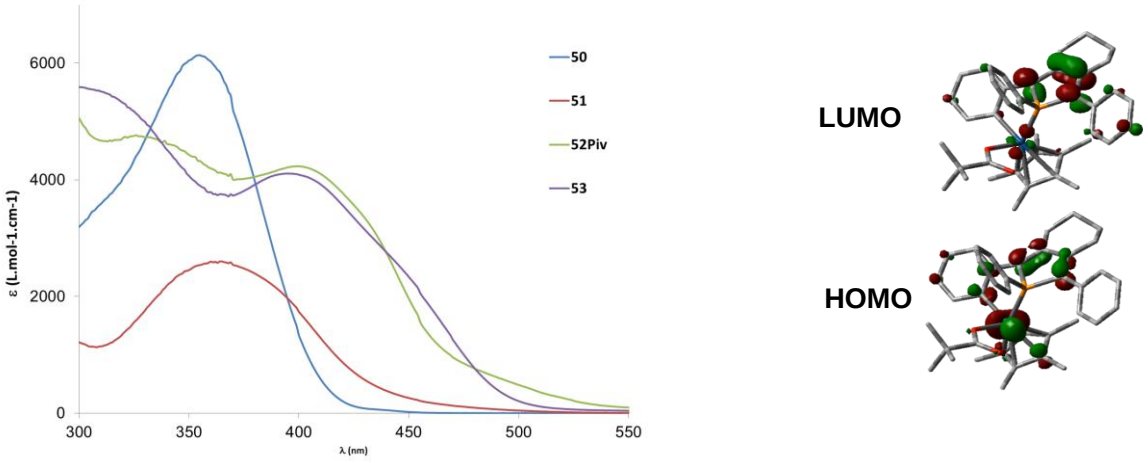


Fig. 29: UV vis absorption of **50-53** in DCM and views of the frontiers MOs of **52Piv**

In addition to these projects, where the synthesis is exclusively made at the ISCR, our team is involved in the International Associated Laboratory "Functional Organophosphorus Materials" (IAL-FOM) with the group of Pr. D. Zhengh/Pr. F. Mathey at the University of Zhenghzou (China). The scientific objectives of this IAL are the synthesis of new organophosphorus building blocks for the development of functional materials (mainly done at Zhengzhou University), the physical studies of these new functional materials and the development of devices for plastic electronics (mainly done in Rennes).

A first family of P-containing organophosphorus compounds has thus been studied: the 1,2-dihydrophosphetes(Fig. 30). Dihydrophosphetes are a particular class of phosphine in which the P-atom is locked into a 4-membered unsaturated ring. As phosphines, intermolecular aggregation is prevented in the solid state by the pyramidal P-atom, which is a key factor to obtain solid-state emission. Various extended π-systems were introduced on the 4-membered ring through chemical engineering (**57-60,** Fig. 30), as well as different substituents on the P-atom. We showed by a combined spectroscopic and electrochemical study that the substituent on the P-atom as low influence on the electronic properties of the phosphete, while tailoring the π-system allows adapting the absorption/emission wavelength and the redox potentials. OLEDs with the following structure ITO/CuPc/α-NPB/EML/DPVBi/ BCP/Alq_3/LiF were prepared. All devices emit in the blue region of the spectrum with low efficiencies when the P-derivative is used as single emitter (EQE_{max} = 0.9 % for **58**). Doping into a matrix (CPB /DPVBi) allowed improving their properties (EQE_{max} = 2.5 % for **58**). Better charge transport in the layer was believed to be the reason this improvment. In the series, the best performing compound was **58** (diluted in DPVBi). Furthermore it exhibited current independent CIE coordinates. This first study performed on dihydrophosphetes clearly showed the potential of this scafold for opto-electronic applications.[61]

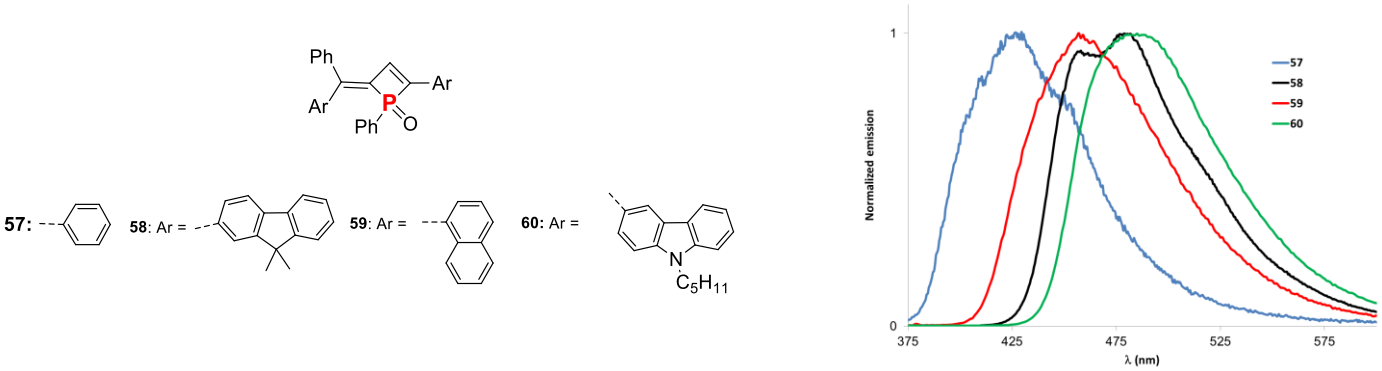


Fig. 30: structure of the synthesized phosphete and emission spectra in diluted DCM solution.

Another class of studied compounds are the furane-heterole ladders. A synthetic strategy to access novel benzofuran fused-phosphole or -siloles derivatives has been developed and their electronic properties were studied. These mixed P,O / P,Si containing heterocycles showed solution and solid-state emission in the blue-green (Fig. 31) area as well as reversible electrochemical processes. Incorporation of these compounds as emitter in OLEDs device having classical multilayer structure (EQE = 2.3% for **61a** and **2.5%** for **62b** respectively) shows that these compounds might be used for future opto-electronic applications.[62]

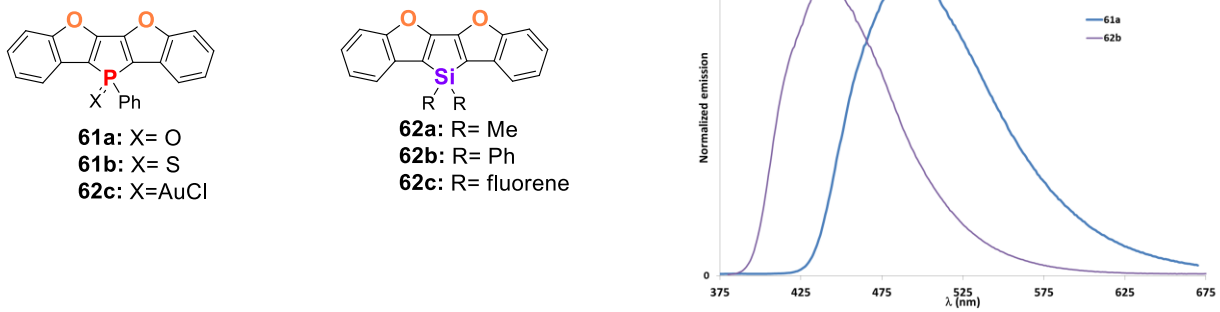


Fig. 31: Structures and emission spectra in diluted DCM of mixed P,Si-O ladder compounds **61-62**

The objectives of this joint-project are to develop new heteroatomic π-conjugated systems for opto-electronic applications. New derivatives are currently under investigation in our laboratory. The complementarity between the skills of our chinese collaborators (fundamental heterochemistry) and our knowledge about the physico-chemical properties of such derivatives is one of the key of the success of this IAL.

During these six years, I have been involved in the field of organophosphorus π-conjugated systems. The main project that I developed has been the P-containing polyaromatics. In 2012, we developed the first example of P-containing PAH. The impact of the P-atom on the molecular properties was unprecedented and we could insert them into white-emitting OLEDs. Since then, no other P-containing polyaromatics have been reported, showing the synthetic difficulty to prepare such derivatives. The project section will propose strategies to tackle this obstacle.

In the meantime, we prepared highly luminescent hybrid nanoparticles based on P-fluorophores and ZnO nanotemplates. We showed that the RIR mechanism was responsible of the solid-state emission. We also synthesized different fluorophores to tune the emission wavelengths of the nanohybrids and we are currently trying to prepare an LED to demonstrate the potential of these novel materials.

Finally, I have been involved in other projects linked with heterocyclic and organometallic chemistry.

Before my recruitment, my main skills were the organic synthesis and the study of optical/electronic properties of organic derivatives. Since 2011, I developed a lot my background in heterocyclic/organometallic chemistry. I also had the opportunity to collaborate actively with partners in different fields (Opto-electronic devices, Theoretical chemistry…) and I spent several weeks in their laboratories in the frame of these collaborations. Furthermore, I also gain a lot of interest in the field of organometallic/coordination chemistry and catalysis (in particular C-H bond activation) that are well developed at the institute of Chemical sciences in Rennes.

All these different aspects clearly influenced me a lot for the development of the projects I want to develop after my habilitation.

Part 5: Research projects

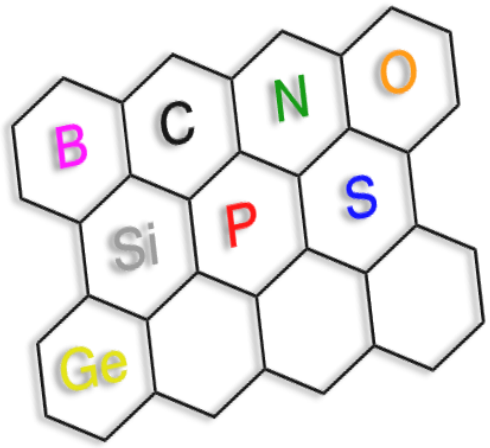
The two main research projects that I want to develop in this manuscript ("P-containing polyaromatics" and "fluorescent hybrids") are clearly the base of the scientific projects I want to carry on during the years following my habilitation.

As already mentioned, since our first report on the P-containing polyaromatics in 2012, no other planar P-analogs have been published by other groups. Heteroatom containing PAHs being a growing field, it is not a lack of interest, but clearly the difficulty of synthesis that explain this.

A first objective will thus to develop alternative synthetic methods to access new families of P-containing polyaromatics, and in particular more efficient synthetic approach, as almost gram scale quantities are needed for device optimization. Furthermore the method has to be compatible with bigger structures as well as with the incorporation of other heteroatoms (group 14 in this case). Another project will be to exploit the diversity of bonding modes in organophosphorus derivatives to prepare low-valent P-containing PAHs.

Finally, even if some representative examples of N-containing PAHs are known since 2002, the rich coordination chemistry of (poly)pyridine has not been exploited in the context of PAHs.

To summarize, my project is to develop novel synthetic methods to prepare more efficiently large heteroatom-containing PAHs (σ^3,λ^3-P, σ^3,λ^2-P, Si, Ge, N) in order to fully exploit the reactivity and in particular the coordination chemistry (P, N), to compare on a given PAH family the effect of different heteroatoms (P, Si, Ge) and to be able to prepare large quantities suitable for device incorporation and optimization (OFETs, OSCs,…).



New synthetic approach toward P, Si and Ge containing PAHs
(ANR JCJC 2017-2021)

Our preliminary results on the synthesis of P-containing PAHs clearly constituted a proof of concept. However, to perform systematic molecular engineering of PAHs using heterochemistry or for the synthesis of heteroatom-containing PAHs of larger size, a more efficient synthetic strategy has to be defined.

Hence, our published synthetic strategy is a low-yielded multi-step procedure that implies a photochemical reaction as graphenization step. Only low yields (ca. 30%) were obtained for this crucial reaction. Furthermore, the classical Fagan-Nugent/Sato [39] route to heteroles also afforded moderate yields in the case of the **26a-b** (Fig. 8). The new strategy has to avoid these two limiting steps that clearly restrict the preparation of large quantities of the compounds. In

order to prepare new heteroatom-containing PAHs, we plan to develop a new strategy that will use as key synthons, planar PAHs such as **12** (Fig. 32). These building blocks will then be engaged in C-**X** bond formation either (i) catalyzed by transition metals (Pd-catalyzed C-**P** [63] and Rh-catalyzed C-**Si** [64] and C-**Ge** [65]) or (ii) by intramolecular cyclization (**P**-Friedel [66], **Si**-Friedel [67]) or radicalar reactions [68]) as depicted Fig. 32. This strategy is based on the latest developments in heterole synthesis. Noteworthy, this new approach will allow using the widely studied cyclodehydrogenation (Scholl reaction) as the final graphenization step, as Müllen *et al.* successfully did by for the preparation of GNRs.[23]

The validity of these methods will be evaluated with model PAHs. To this end, 4-bromophenanthrene will be a model molecule of choice[69] since it is the smallest PAH featuring a 2-bromobiphenyl fragment. A first criterion of success for the project will be the development of an efficient synthetic method on these model molecules. The possibility of using different synthetic strategies based on the same precursors (catalytic cyclization, hetero-Friedel, radicalar cyclization) as well as the general knowledge of the ISCR on homogeneous catalysis make us think this step will be quite straightforward.

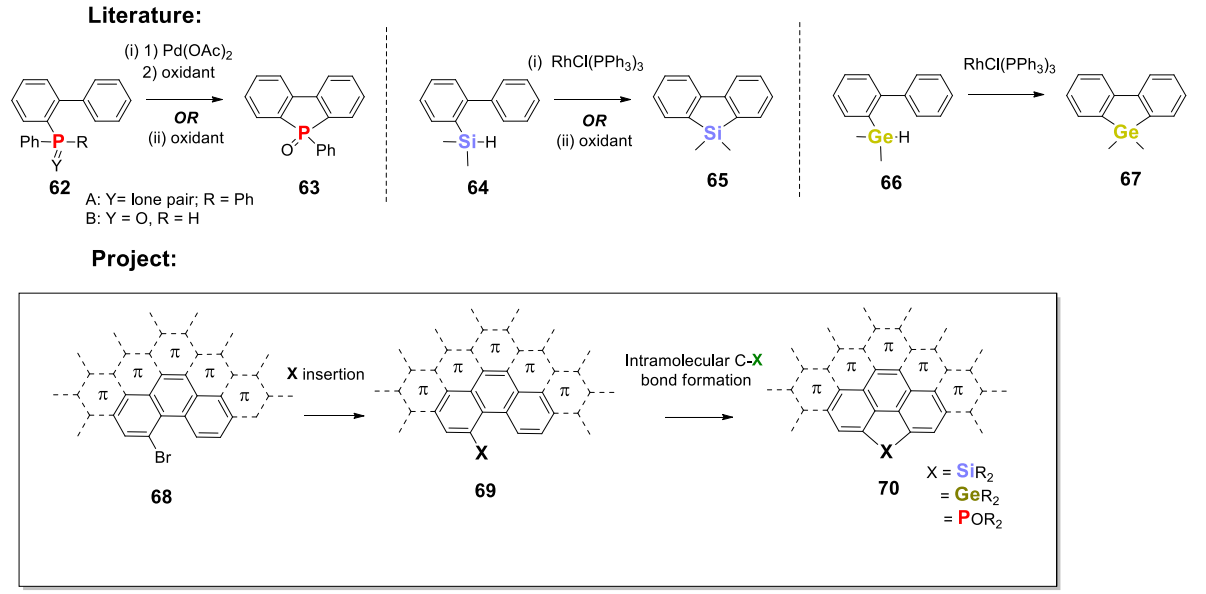


Fig. 32: *Recent examples of C-**X** bond formation for heterole synthesis and synthetic strategy toward new heteroatom-containing PAHs **70***

Once optimized on the model compound, this strategy can be applied to pyrene analogs (**71**, Fig. 33), naphthalene diimides NDI (**72**, Fig. 33) or perylene diimides PDI (**73-74**, Fig. 33).[70] Theses small polycyclic compounds are fluorescent dyes with high electron affinity that are widely used in the field of molecular electronics from sensors to electron acceptors. The combination of their properties with the original properties of heteroles has never been reported and will be studied.

For example, **P**-containing pyrene derivatives **71** (Fig. 33) will be synthesized in few steps starting from the commercially available pyrene-1-boronic acid and (2-bromophenyl)diphenylphosphine. The C-**P** bond formation will then be applied to this derivative to provide the targeted compound.

Following a similar strategy, the perylene/naphthalene diimide fused PAH derivatives (**72** - **74**, Fig. 33) can be obtained starting from the corresponding bromoperylenediimide [71] or bromonaphtalenediimide.[72]

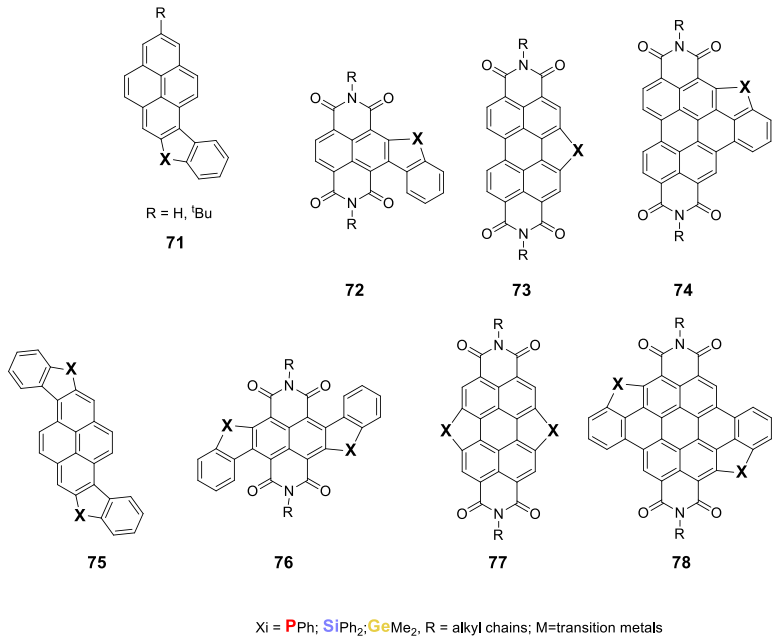


Fig. 33*: Synthesis of heteroatom-containing pyrene, NDI and PDI.*

These methods also open the possibility to prepare poly-heteroatomic PAHs scaffold. These compounds can be for example multi-**P** containing PAHs (if X_1=X_2 = **P**Ph in Fig. 33) or mixed **P**/**Si** (or mixed **P**/**Ge** or **Ge** /**Si**) PAHs ($X_1 \neq X_2$ in Fig. 33). Again, after being tested on small molecules such as dibenzodiphospholes or triphenylenes analogs, the strategy will be extended to larger structures such as pyrene **75**, NDI **76** or PDI **77**-**78** (Fig. 33) using their corresponding dibromo precursors.[71-72]

The strategy will be then extended to larger π-systems. A key molecule will be the **P**/**Si**/**Ge**-hexaperibenzocoronene (**79**, Fig. 34), as this compound represents the prototype for molecular graphene (HBC **20**, Fig. 7).[23] The first step toward this molecule will be the preparation of the HBC precursor with halogen atoms (I or Br) situated in the correct position (molecule **81**, Fig. 34). Numerous synthetic strategies are described (Diels-Alder or C-C cross coupling reaction) to access this type of compounds.[23] The cyclodeshydrogenation, which is tolerant to the presence of arylbromide will be used to graphenize the synthons into HBC **81**. The heteroatom will be inserted through classical substitutions between phosphine/silane precursors and the lithio- or organomagnesio-analog of molecule **80**. Then, the final step will be the C-**P**/C-**Si**/C-**Ge** coupling to produce heteroatom-containing HBC **79** (for example **82** in the case of **Si**-containing HBC, Fig. 34). Another approach will involve the bromination of classical HBC (that only possess bay positions).

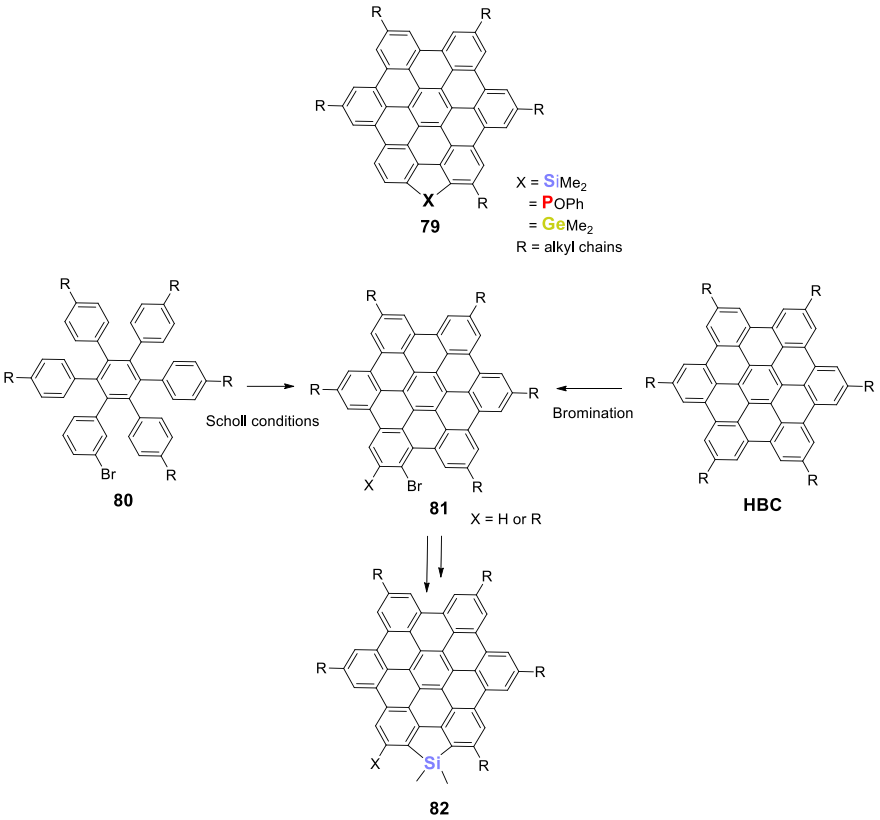


Fig. 34*: General structure of hetero-HBC **79** and synthesis of Si-containing HBC **82***

This molecule will represent a striking example of the validity of our strategy as HBC are the most widely used PAHs in optoelectronic applications. Based on this example, others PAHs of various size and shape can be designed and synthesized.

More generally, the wide amount of literature on the synthesis of PAHs will be used and adapted for the preparation of this new family of heteroaromatic derivatives.

It is highly important to note that the synthetic strategy allows the incorporation of several lateral side chains (R groups attached to the phenyls or directly linked to the heteroatom. These groups are crucial for several reasons. First of all, they will provide solubility to the compounds that will allow their full characterizations. Secondly, they play an important role on the supramolecular organization of the compounds in the solid state. The role of their nature (alkyl chains, polyethers, …) on the solid-state organization and the optical properties will also be studied in details.

Thus this strategy will allow preparing heteroatom-containing PAHs incorporating **P**, **Si** or **Ge** atoms. This approach is highly innovative from the point of view of the synthetic methods, as it uses the latest developments of C-**P,** C-**Si** and C-**Ge** bond formation. Above all, it is highly innovative regarding the structures that will be obtained. The supramolecular assembly and the (opto)-electronic properties of these unprecedented molecules will be studied.
All these examples use small PAHs/functional PAHs in which the starting materials are described in the literature. However, it is applicable to any PAH displaying an halogen in a bay environment and can thus be used to prepare to prepare PAHs of bigger sizes. This is a long term perspective for this project.

Photophysical (UV-vis absorption, fluorescence) and electrochemical (cyclic voltammetry) characterizations will be performed. These data will be subject to detailed investigation. These properties will be compared with theoretical models at the DFT level (B3LYP, 6-31G*)

for HOMO-LUMO gap and aromaticities and TD-DFT for optical transitions. This comparison will allow us to rationalize the electronic properties of the compounds and guide us for the synthesis of optimized structures. This study will be performed by the group of L. Nyulaszi (Budapest University of Technology and Economics).
A key parameter will be the determination of the HOMO-LUMO gap of these compounds based on optical, electrochemical and theoretical data. This will give information on the electron delocalization within the structures and also for the band offset with the electrodes or the different interlayers of a device (vide infra).

This study will allow us to determine if these compounds can be further used in optoelectronic devices. Even though some other devices can be envisaged, two particular classes of devices will be targeted: the OSCs and the OFETs.

- Considering the low-lying LUMOs of heteroles, [73] their use as acceptor will be considered (Fig. 35). In particular, the perylenes recently appeared as promising fullerene substitutes in OSCs.[70, 74] Their accepting character will be reinforced by the presence of the heterole and for example, the perylene analogs appeared as excellent candidates for this purpose. An important parameter will thus be to compare the LUMO of the synthesized compounds with the one of PCBM (evaluated at -4.2 eV).[10a] More generally, the presence of the heterole usually decreases the bandgap[73] which favors light absorption until the NIR part of the visible, which is also an important feature for light harvester in an OSC. To date, only one example of efficient (PCE > 1%) P-derivative (used as donor) for OSC has been reported.[75]

- To design a semi-conductor for OFETs applications, the compound needs a preferential organization to favor the charge transport between the source and the drain. The presence of a large π-system and lateral aliphatic chains is usually necessary. In this context, most of the compounds described might be used for OFETs applications (Fig. 35). In terms of reduction potentials, semi-conductor for air-stable n-type OFET usually displays reduction potential superior to 0.66 V vs SCE.[76] Using the expected good electron-accepting properties of the compounds together with the π-stacking ability of PAHs, n-type transistors will be tested. To our knowledge, no P-containing π-conjugated systems have been used in OFETs.[75] Successful incorporation of our derivatives into OFETs would represent a real proof of concept and open new perspectives for opto-electronic applications of heteroatom containing PAHs.

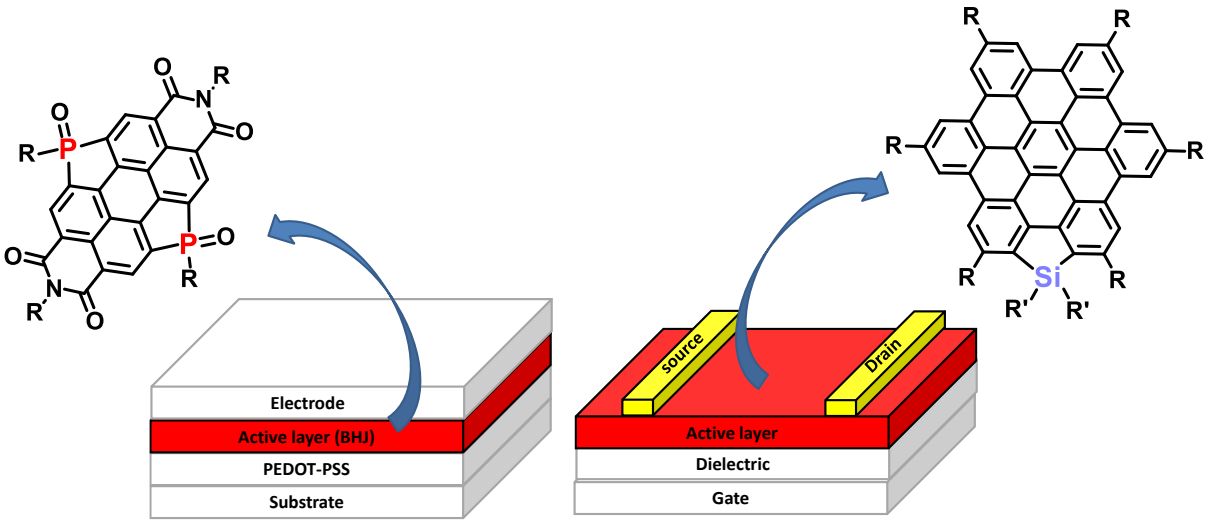


Fig. 35: Simplified representation of BHJ OSC (left) and OFET (right) and example of targeted molecule for the application.

The goal of this project is to develop a new synthetic method to afford heteroatom-containing PAHs (**X**-doped PAHs) of various size and shape. This method will be based on the use of C-**X** bond formation (**X** = **P**, **Si**, **Ge**). This will allow generalizing the molecular engineering using heterochemistry to obtain new PAHs with appealing structures. The supramolecular organization of the compounds will be studied. The electronic properties of the compounds will be studied in solution and in the solid state. The impact of the heteroatom (P vs Si vs Ge), of the heteroatom environment and of the supramolecular organization on the electronic properties will be studied. These parameters will allow us to determine the suitability of these derivatives for further incorporation into optoelectronic devices (OLEDs, OSC).

However, other application might b envisaged for example in the field of batteries or supercapacitor where there is a high demand of carbon based materials.[77]

Polyaromatic phosphinines

The bonding modes of P-derivatives are various. For example, we prepared σ^3,λ^3-P- and σ^4,λ^5-P- containing PAHs. But other coordination states exist in particular the low valent σ^2,λ^3-P (phosphalkenes) or σ^1,λ^3-P (phosphalkynes).
As already mentioned, phosphinines (also referred as phosphabenzene) and phospholes have marked electronic properties (Fig. 26). Phosphinines are strong π-acceptors and very weak σ-donor due to the low-lying MO involving the lone pair. Until recently, they were mainly used as ligands for catalysis. It is only since the last years that their use as building blocks for π-conjugated systems has been envisaged.[78] Even if their stability remains a problem for any application, their use in this context is gaining interest.
It is thus of interest to find a synthetic approach to insert this low-valent P-heterocycle in a 2D π-conjugated system and study its impact on the electronic properties as well on the chemical stability. For example, we can imagine that the conjugation in such PAH would dedcrease the reactivity of the P=C bond, which is a usual way of degradation of phosphinines.
As a first approach, two strategies are envisaged to prepare what would be the first example of polyaromatic derivative including a phosphinine ring **83** (Fig. 36): first, a cyclo-addition strategy between our previously reported P-containing PAH **28** and a phosphalkyne (Fig. 36) to yield **84**.[79] A second approach involves the substitution of pyrilium derivatives with

tris(trimethylsylil)phosphine (Fig. 36).[79] For this approach, the reactivity will be tested with the pyrilium **87**, which synthesis has been reported previously.[80]
Here again, after validating the strategy with small PAHs such as **84** or **86**, the long term objective will be to prepare bigger PAHs. In particular, all the phosphole-based PAH described in the first part of this project section will be suitable starting materials for the preparation of the π-extended phosphinines using the first approach.

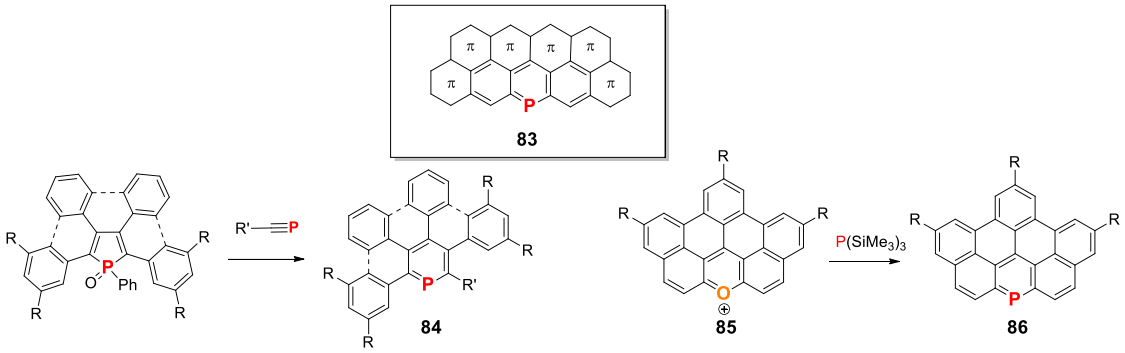


Fig. 36: synthetic approach toward π-extended phosphinines

The success of this project would represent a big achievement in the "phosphorus community", because, even if their discovery is concomitant to the one of the phospholes,[81] the phosphinines are really less developed due to the lack of synthetic procedure and their high reactivity.

N-containing PAHs

As discussed in the results section (Fig. 7), N-containing PAHs are already described since 2002[26a] and macromolecules up to GNR have been prepared using this fragment.[82]

However, due difficulty of synthesis (this aspect is clearly a natural challenge regarding this field), the rich chemistry of pyridines ligands has not been fully exploited with PAH-based ligands. In particular, no examples of cyclometallated complexes such as **88** (Fig. 37) using large polyaromatic ligands have been described. Their exceptional optical properties (mainly MLCT based emission for Pt(II), Ir (III))[58, 83] as well as their self-assembling properties (d-d interactions of Pt(II))[83] could be combined with the intrinsic properties of PAH to obtain unprecedented molecular materials.

Furthermore, the presence of two pyridine on a PAH ligand will also open the way toward PAH based coordination polymers such as **90** (Fig. 37). The supramolecular association of such polymer, as well as their optical properties will be drastically modified by the presence of the metal and the large polyaromatic system.

Another reactivity of polypyridines that has not been studied with PAHs is their alkylation to obtain polypyridinium or π-extended viologens ananlogs **89** (Fig. 37). Methyl viologen is a widely used electron-acceptor and supramolecular synthons.[84] Again, the incorporation of such backbone to a PAH core could lead to novel derivatives with stronger π-stacking ability and optical transitions shifted to the red because of the extended conjugation.

In both context, the diazaperylene fragment **91**, reported by He *et al.* appear as a perfect buiding block to test this approach.[33] After being validated on this fragment, the concept will be extended to bigger structures.[25a]

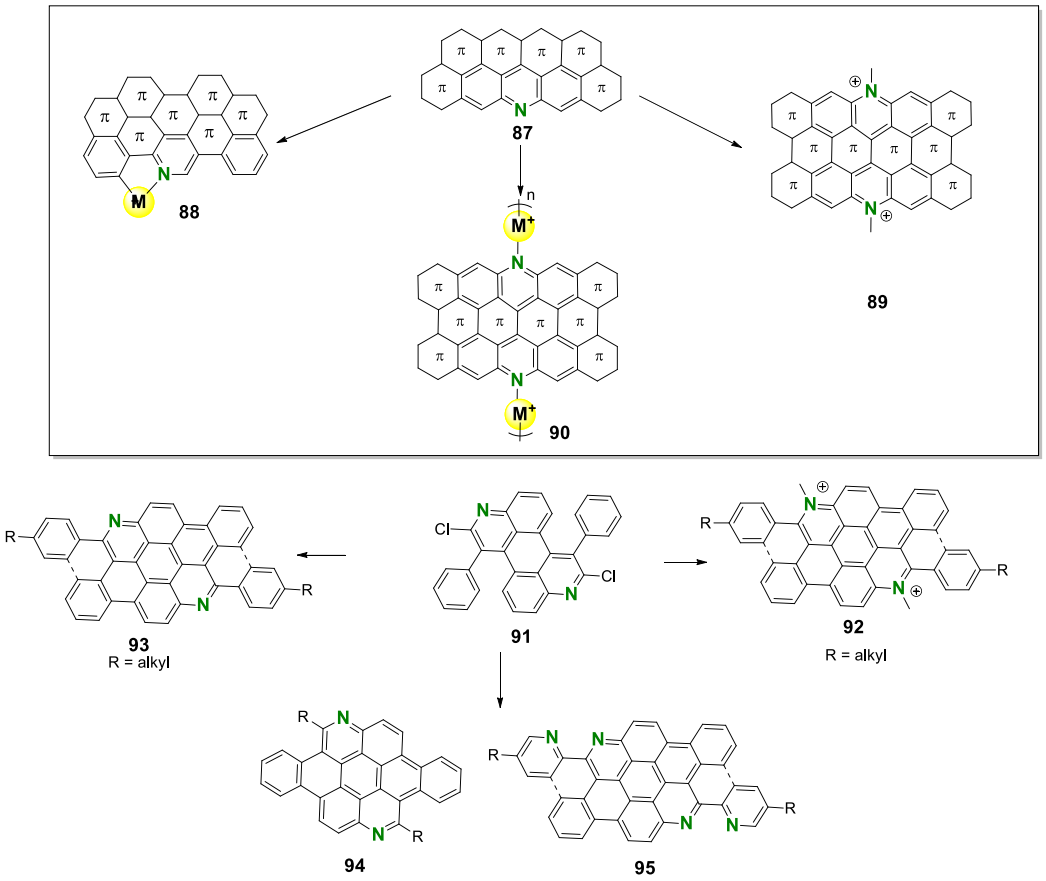


Fig. 37: Schematic representation of the strategy of utilization of novel N-containing PAHs and example of model molecule (**92**-**95**)

As a conclusion, these projects aim at developing new heteroatomic-containing PAHs to fully exploit their reactivity and in particular the coordination chemistry. Furthermore, the synthetic strategies have to be efficient enough to provide sufficient quantities for optimization of devices (OSCs, OFETs, batteries…).

As long term perspective, the development of new synthetic approach should permit to prepare heteroatom-containing-GNR with defined structure to study the effect of one single heteroatom "defect" on GNR.

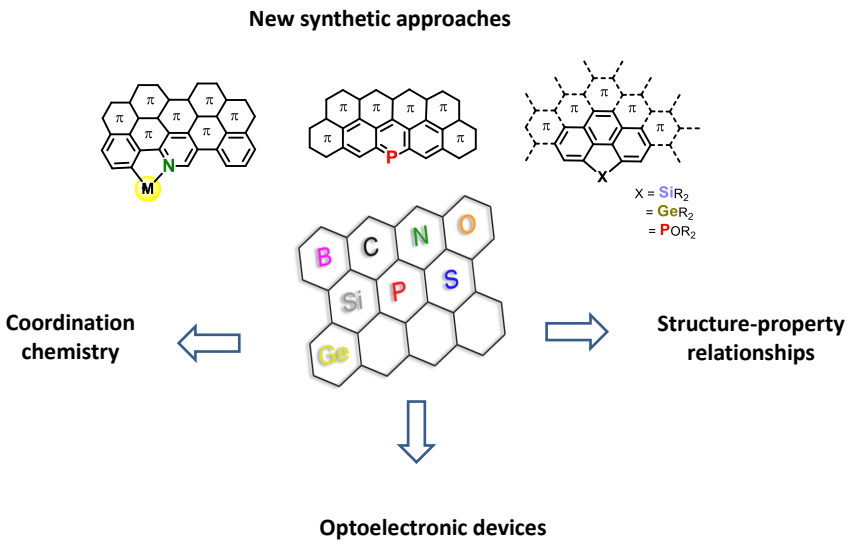


Fig. 38: Schematic representation of the research projects on polyaromatics

As mentioned Fig. 18, the reactivity of the P-atom can be used to design novel solid-state emitters possessing chemical functions that would allow combining them with various substrates to obtain novel multifunctional materials.
Alkylation allows preparing cationic derivatives such **36** that can be easily combined with anionic substrate. For example, assembly of **36** with anionic polyoxometallates POM can be envisaged. This will permit to obtain systems combining the fluorescence of the P-fluorophores with the redox or photochromic properties of the POM.
Anionic compounds can also be easily obtained from deprotonation of the corresponding phosphoric acid. This anion can thus be combined with various functional cations. For example, ion pairing with a family of organogelifiant or liquid-crystalline imidazolium can be envisaged. Preliminary results of ion pairing with the deprotonated phosphoric acid **40** allowed us to obtain highly luminescent organogels in hexane (compound **97**, Fig. 39, collaboration F. Camerel, Institut des Sciences Chimiques de Rennes). Such compound offers the possibility to easily prepare luminescent soft materials and for example study the impact of the supramolecular structure on the properties of a light-emitting electrochemical cell LEEC.

In all these examples, the specific reactivity of the P-atom will be used to adapt the fluorophore to the corresponding substrate, while the colour tuning can be achieved by π-system modifications. If wisely selected, the substrate can bring a new property to the structure, in addition to the solid-state emission of the P-fluorophore.

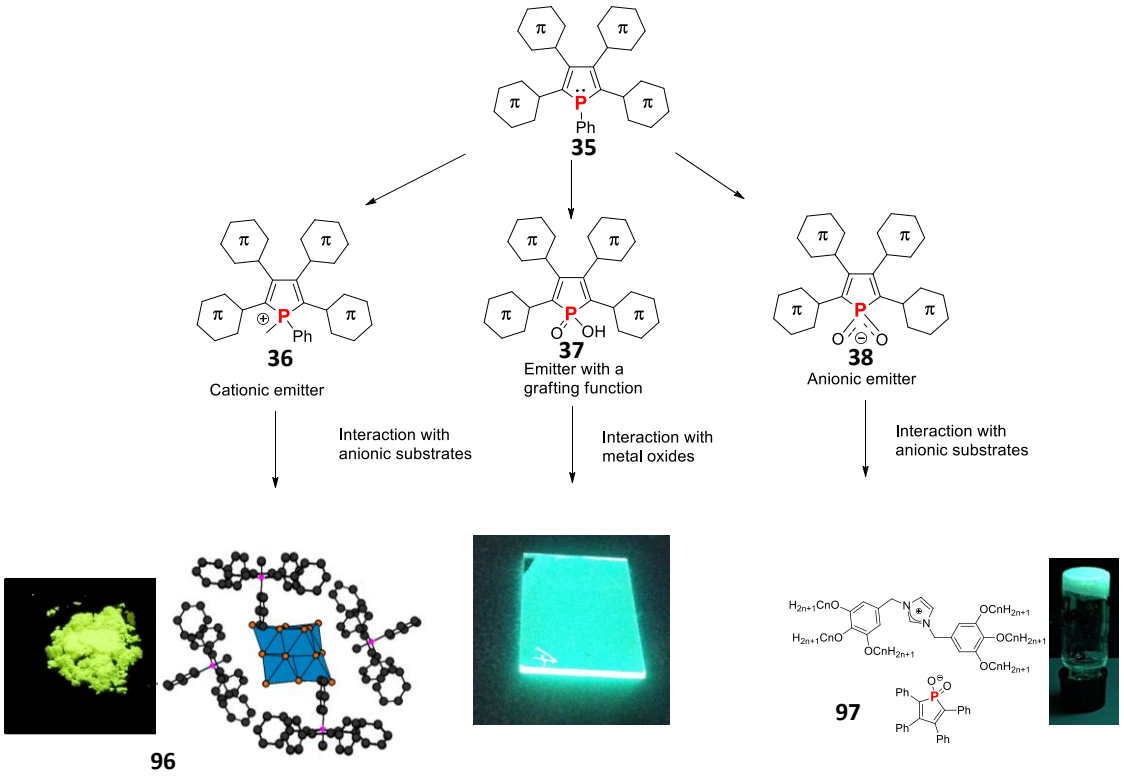


Fig. 39: Multifunctional solid state P-emitters

The most promising project regarding this approach is linked to the fluorescent nanohybrids. We made a proof of concept for a novel family of emitters in the blue-green-orange area. For this project, the main directions we want to follow are: the generalization of the concept and

the use of these new materials for optoelectronic applications. These two aspects will be developed in the following section.

The fist idea is to generalize the concept to different AIE emitters and different nanotemplates.
In the field of molecular engineering, we want to extend the scope of emitters with two objectives in mind. We can extend our phosphole family by using different grafting unit such as thiophosphinic PSSH bond **100** or a carboxylic acid grafted on an aryl substituent **101** (Fig. 40). An important aspect will be to test other families of AIE emitters (tetraphenylethenes **98**, siloles **99**, Fig. 40) and in particular to develop red-emitters. This will imply using others family of fluorophores that the hydroxy-oxophospholes as we saw that the extension of the conjugation was not straightforward using our previous approaches. The use of carboxylic acid grafting unit on solid-state red emitters previously reported in the literature such as push-pull dyes (**102** Fig. 40) is a good alternative.[85] In case of electro-active metal oxide such as ZnO, the possibility of electron transfer clearly exists and will be studied carefully. In this case, the design of the ligands (HOMO-LUMO level, localization of the grafting unit…) will be crucial.

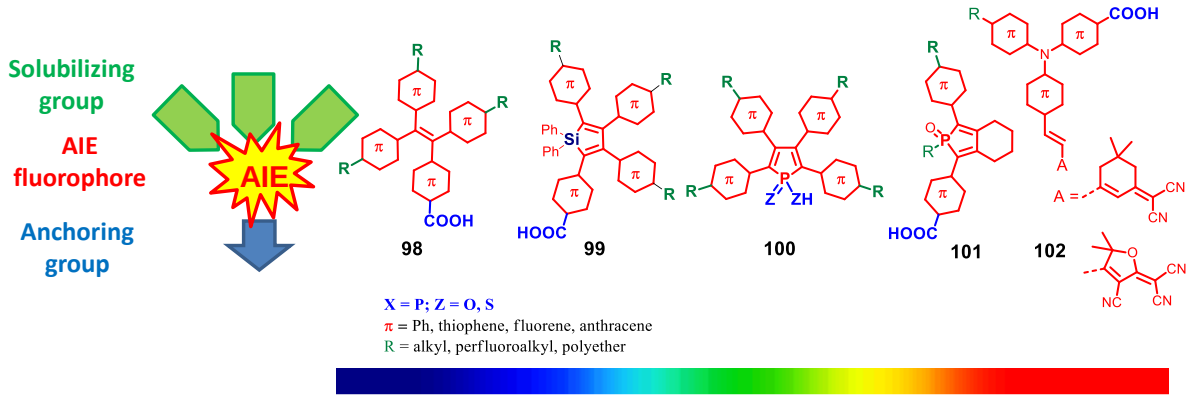


Fig. 40: Molecular engineering of functionalizable AIE emitters

We also want to use different emitters (on the same particle or two particles grafted with different emitters) to achieve white light-emission through energy transfer. Another interesting study can be to combine AIE and ACQ fluorophores (such as perylene bisimides) to see if it is possible to turn on the solid-state emission of the ACQ dye by preventing its self-assembly.

Regarding the inorganic core, the generalization of the concept will imply studying the impact of the nanoparticle shape (spheres, rods, pyramids…) and nature (for example comparing with insulating SiO_2 or ZrO_2) on the properties of the hybrid. As the hybrid layer plays the role of nanotemplates, it is envisaged that all these materials will keep their fluorescence (collaboration O. Margeat/J. Ackerman (CINaM, Marseille).

Regarding potential application, the objective is to prepare a prototype device of hybrid-LED by wet process. One idea is to take advantage of both the charge transport properties of the metal oxide (when the template is semi-conductor) and the emission of the organic shell (collaboration B. Geffroy/D. Tondelier, LPICM, Palaiseau). This aspect is highly challenging as we need to develop a new LED structure compatible with the nanohybrid in terms of processing and electronic.

The obtention of a prototype of LED device using these fluorophore is thus the main objective of this project in term of application .
However, regarding other potential applications, it will be of interest to study these nano-objects by nonlinear optical techniques. In particular, highly luminescent compounds are attractive for two-photon induced fluorescent imaging techniques.

As a long term perspective, preparing bioprobes (studied either by linear or nonlinear optical techniques) may be envisaged. The idea would be to use the nanotemplate to concentrate AIE responsive emitter having a certain affinity with a biological target. This would imply preparing an hydrosoluble version of our emitter. Given our background regarding bio-applications, this is obviously a long term project. However, this application seems credible for a biocompatible version of our nanohybrids.

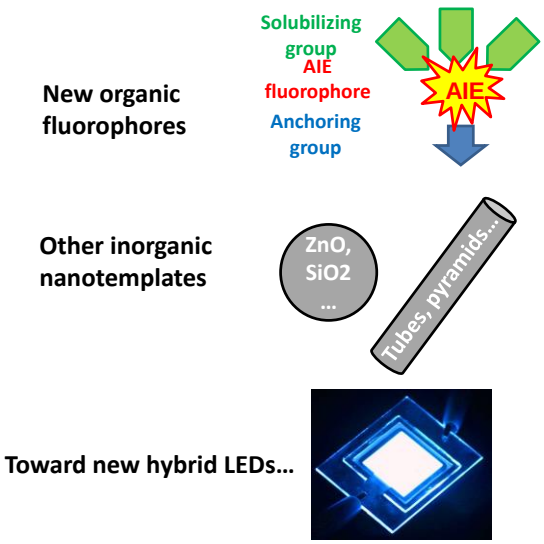


Fig. 41: strategy for new nanohybrids toward LED applications

This project is highly multidisciplinary and thus will imply the strong collaboration with different actors.
Regarding our contribution in this project, our main task will be to prepare solid-state emitting fluorophores. In addition to the synthetic work, the study of their optical properties in the solid-state will be a project of interest in itself. Hence, even if numerous solid-state emitters are described, the structural factors that govern the absorption and emission ($\lambda_{abs}/\lambda_{em}$, ϕ…) in the solid-state are not that well understood. For example, many cases of mechanochromism, thermochromism are reported and such properties are hardly understood. Such comprehension will imply a careful study of the intermolecular interactions that take place in an organic solid.

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