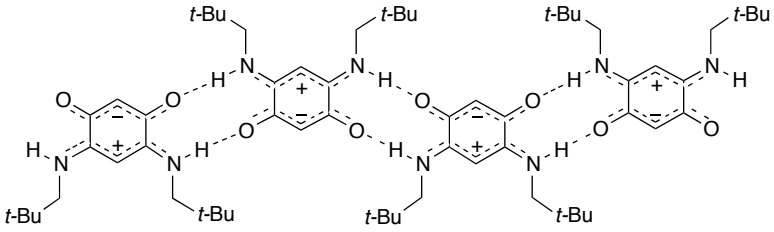
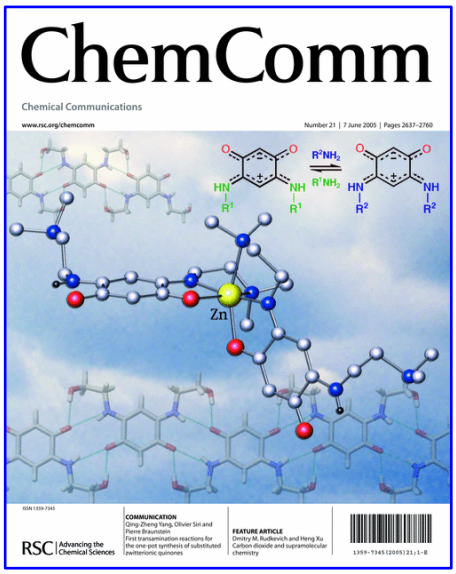
4) *Quinonoid Zwitterions, Synthesis, Coordination Chemistry, Deposition on Surfaces and Molecular Electronics*

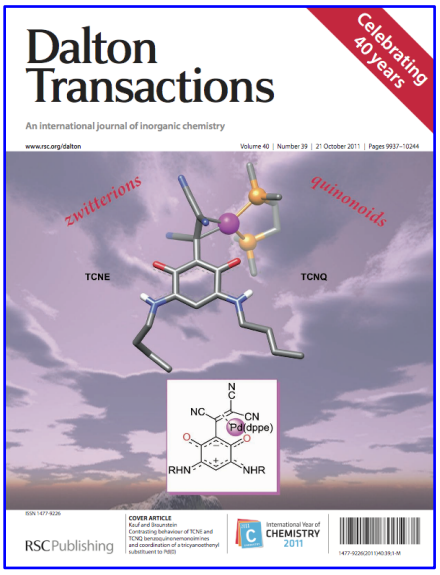
In a yet different area, our group has developed a new family of potentially antiaromatic 12π electron zwitterionic organic quinonoid dyes with unprecedented electronic structure and properties (*Chem. Commun.* 2002, 208; *J. Am. Chem. Soc*. 2003, *125*, 12246, see C&E News 11/02/2002, p. 26). Theoreticians worldwide have immediately been excited by the remarkable properties of this zwitterion that is more stable than its canonical forms.



This work was coined "an unprecedented synthetic accomplishment" (Haas and Zilberg, *JACS* 2004, *126*, 8991). These molecules are most efficient bridging ligands for electronic communication in di- or polynuclear complexes. An unprecedented transamination reaction in quinonoid chemistry was discovered, which allows easy functionalization of these molecules (even in water) (*Chem. Commun*. 2005, 2660-2662). Endowed with a large dipole of 10 D, they can be selectively functionalized by TCNE or TCNQ and can also confer totally novel electronic properties to dielectric surfaces with applications to spintronics.

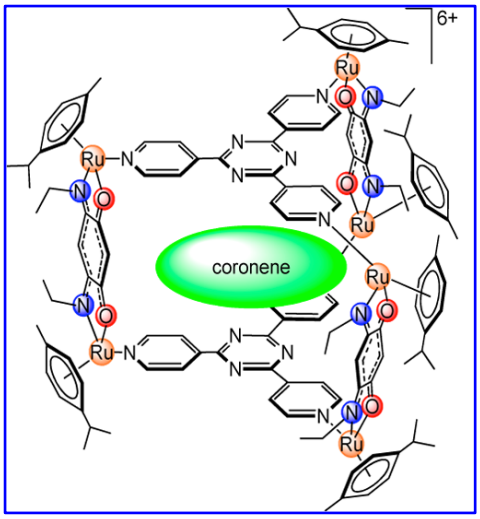


Q.-Z. Yang, O. Siri, P. Braunstein. First Transamination Reactions for the One-Pot Synthesis of Substituted Zwitterionic Quinones. *Chem. Commun*. **2005**, 2660-2662.



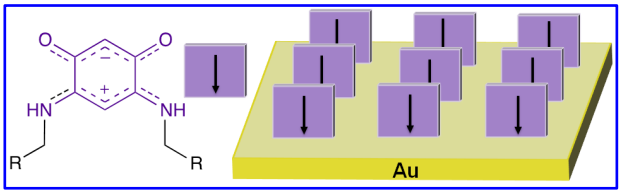
T. Kauf, P. Braunstein. Contrasting Behaviour of TCNE and TCNQ Zwitterionic benzoquinonemonoimine derivatives and coordination of tricyanoethenyl substituent to Pd(0). *Dalton Trans*. **2011**, *40*, 9967-9970.

The coordination chemistry of these unique ligands has led to numerous developments and recently, an international collaborative effort has led to the design of metalla-cages for host-guest chemistry and therapeutic purposes.

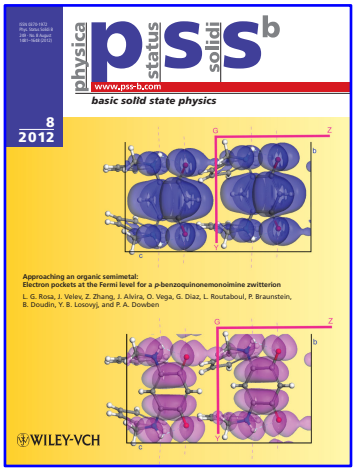


M. Yuan, F. Weisser, B. Sarkar, A. Garci, P. Braunstein, L. Routaboul, B. Therrien. Synthesis and Electrochemical Behavior of a Zwitterion-Bridged Metalla-Cage
Organometallics, **2014**, *33*, 5043-5045.

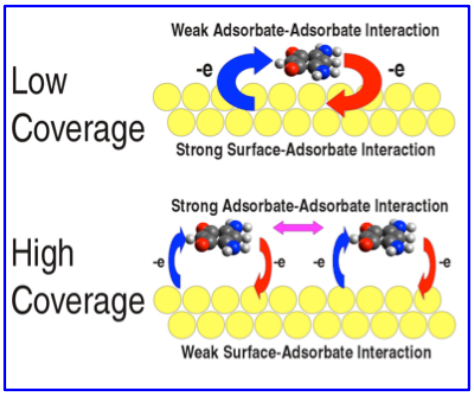
The self-assembly on these zwitterions on various metal surfaces has been studied in collaboration with physicists (*J. Phys. Chem. C*, 2013, *117*, 16406-16415; *J. Chem. Phys*. 2015, *142*, 101921/1-9). Remarkable arrangements are observed that show clear differences between Cu(111), Ag(111) and Au(111) surfaces. Such zwitterionic, highly dipolar molecules may be used for altering the interface dipole screening at the metal electrode interface in organic electronics.



L. Routaboul, P. Braunstein, J. Xiao, Z. Zhang, P. A. Dowben, G. Delmas, V. Dacosta, O. Felix, G. Decher, L. G. Rosa, B. Doudin. Altering the Static Dipole on Surfaces Through Chemistry: Molecular Films of *p*-benzoquinonemonoimine Zwitterions.
J. Am. Chem. Soc. **2012**, *134*, 8494-8506



L. G. Rosa, J. Velev, Z. Zhang, J. Alvira, O. Vega, G. Diaz, L. Routaboul, P. Braunstein, B. Doudin, Y. B. Losovyj, P. A. Dowben Approaching an Organic Semi-metal: Electron Pockets at the Fermi Level for *p*-benzoquinonemonoimine Zwitterion
Phys. Status Solidi B, **2012**, *249*, 1571-1576.



S. Simpson, D. A. Kunkel, J. Hooper, J. Nitz, P. A. Dowben, L. Routaboul, P. Braunstein, B. Doudin, A. Enders, E. Zurek.
J. Phys. Chem. C **2013**, *117*, 16406−16415

Using these zwitterionic quinonoid ligands, the stepwise synthesis of homodinuclear Pt(II) and heterodinuclear Pd(II-Pt(II) complexes was achieved; the latter being the first heterodinuclear complex bridged by a quinonoid ligand. They exhibit very colourful solutions depending on the electronic properties of the metal–quinonoid moieties.

P. Kar, M. Yoshida, A. Kobayashi, L. Routaboul, P. Braunstein, M. Kato*. Colour tuning by the stepwise synthesis of mononuclear and homo- and hetero-dinuclear Pt(II) complexes using a zwitterionic quinonoid ligand.
Dalton Trans. **2016**, *45*, 14080-14088.