A three-level model for two-photon absorption
A combined VB and ELF approach?

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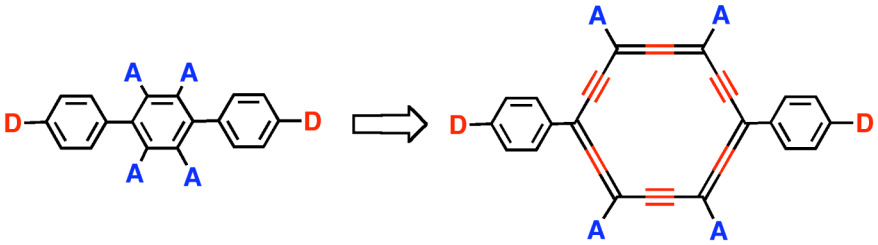
Toulouse - France

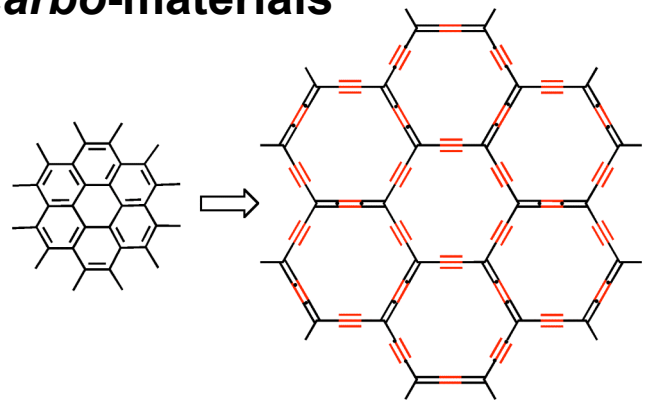
Paris 2012 Workshop on *ab initio* Valence Bond theory

Experimental targets

• *Carbo*-chromophores and *carbo*-materials



Donor = OR, NR_2,… **Acceptor** = F, CF_3, COOR,….



***Quadrupolar carbo*-benzenes**

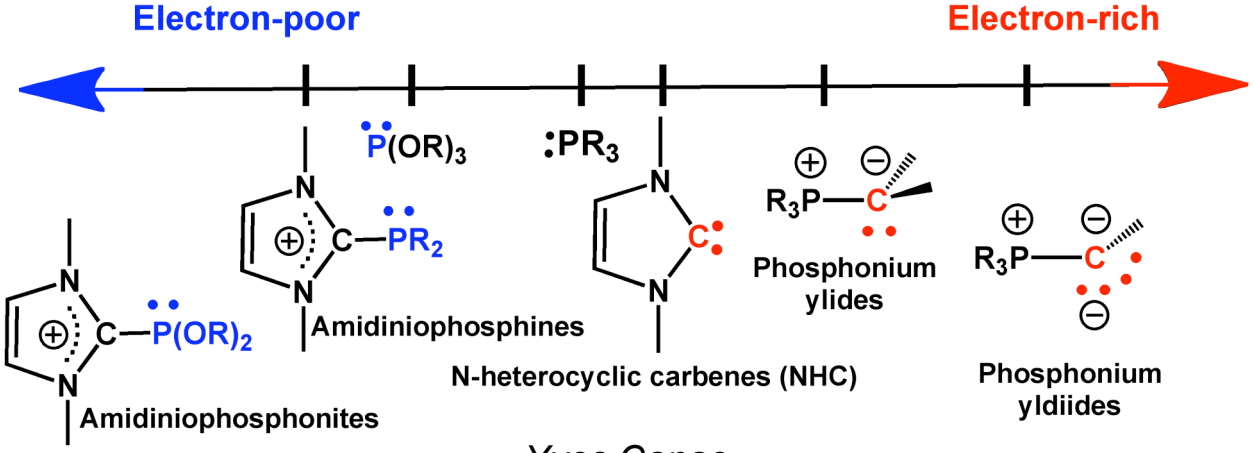
⇒ *Nonlinear optical properties*

***Carbo*-graphene**

⇒ *Optical, mechanical, conducting properties*

Valérie Maraval

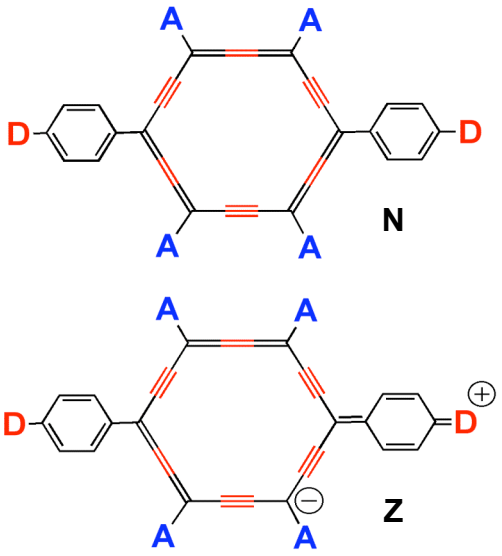
• Ligands for extending the scale of electron donation ⇒ *catalysis*



Yves Canac

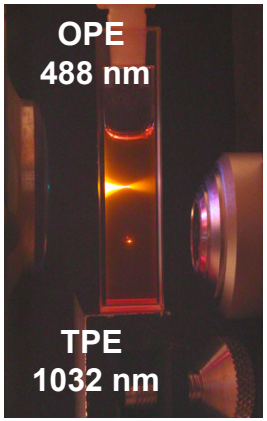
Two-photon absorption (TPA)

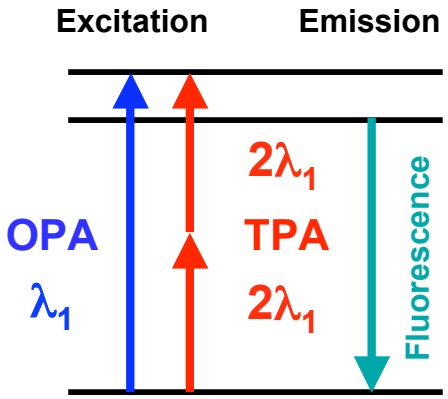
Carbo-chromophores



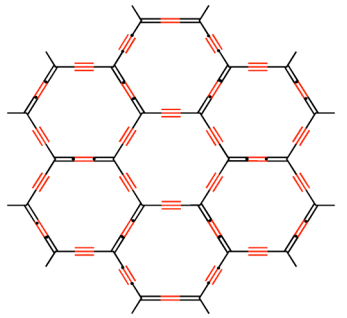
D – π – A – π – D

Confined excitation, NIR radiation
⇒ biomedical applications

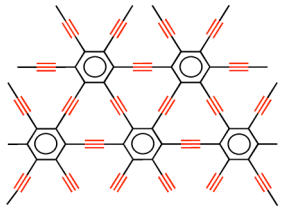




Carbo-graphene

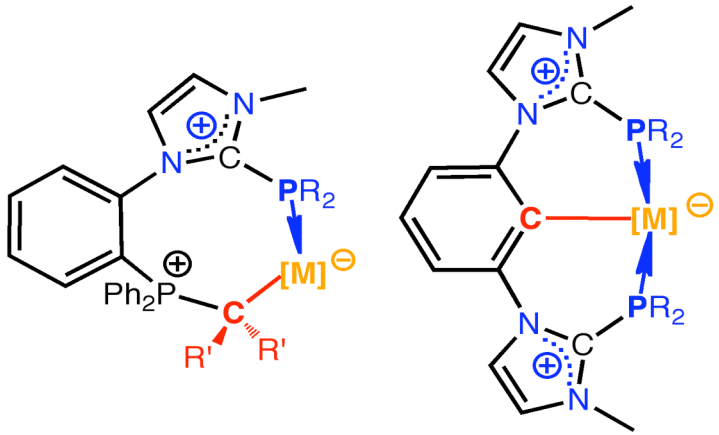


α-graphyne



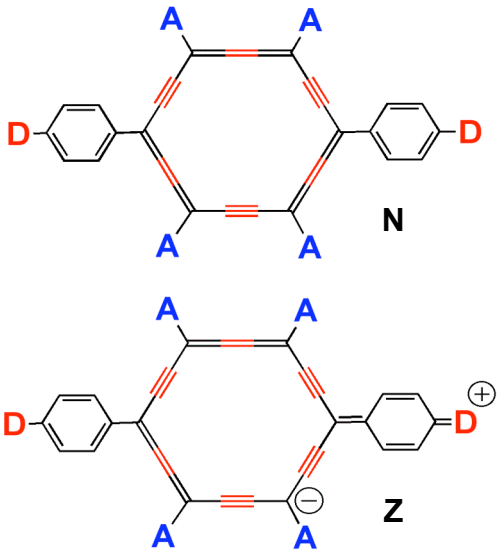
γ-graphyne

Hybrid « rich » - «poor » complexes



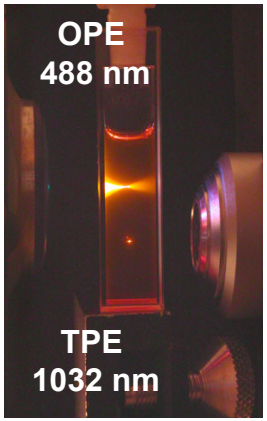
Two-photon absorption (TPA)

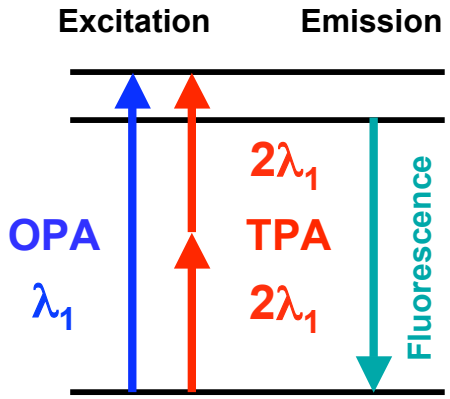
Carbo-chromophores



D – π – A – π – D

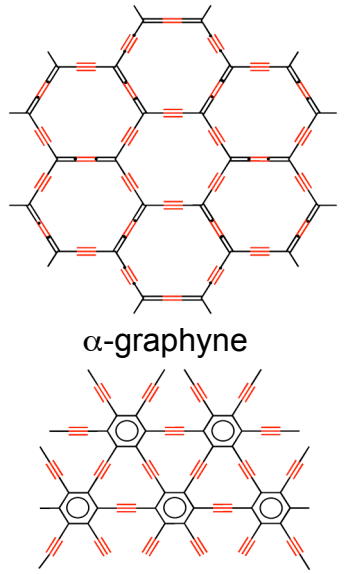
Confined excitation, NIR radiation
⇒ biomedical applications



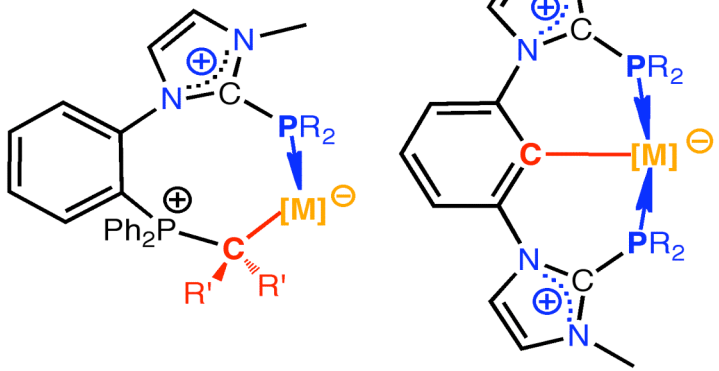


⇒ VB model : $\sigma_{TPA} \propto N, Z$

Carbo-graphene



Hybrid « rich » - «poor » complexes



Screening

Understanding

TPA cross-section calculation

$$\mu = \mu_0 + \alpha E + \beta E^2 + \gamma E^3 + \ldots$$

$\sigma_{TPA} \propto$ third-order nonlinear optical response γ

Sum-over-state approach

$$\delta_{TPA} = \sum_{\alpha\beta}[F \times S_{\alpha\alpha}S^*_{\beta\beta} + G \times S_{\alpha\beta}S^*_{\alpha\beta} + H \times S_{\alpha\beta}S^*_{\beta\alpha}] \qquad S_{\alpha\beta} = \sum_i [\frac{\langle 0|\mu^\alpha|i\rangle\langle i|\mu^\beta|f\rangle}{\omega_i - \omega_f/2} + \frac{\langle 0|\mu^\beta|i\rangle\langle i|\mu^\alpha|f\rangle}{\omega_i - \omega_f/2}]$$

$\Rightarrow$ **Excited states**

H. Agren *et al. J. Chem. Phys.* **2001**, *114*, 9813

TPA cross-section calculation

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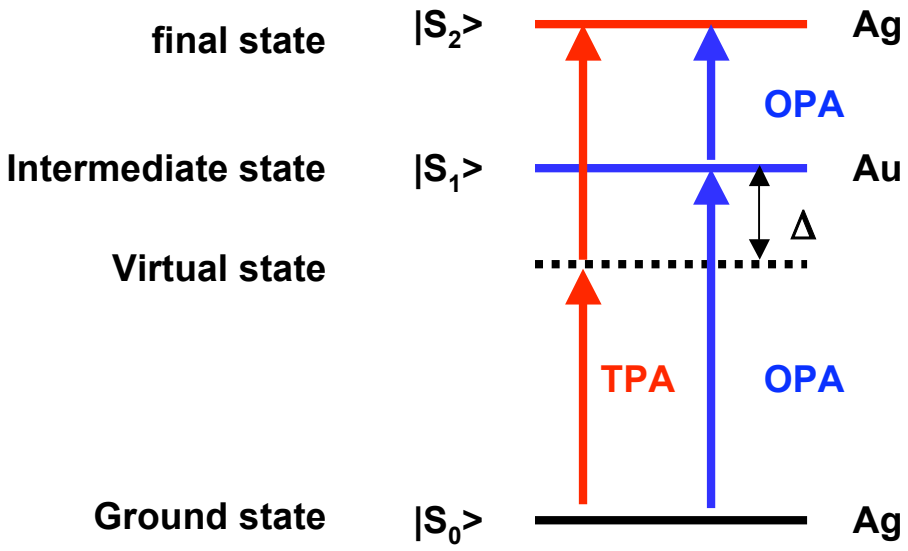
$\Rightarrow$ Excited states

Three-level model



Centrosymmetric chromophore

$$\sigma_{TPA} \propto \frac{\mu_{01}^2 \mu_{12}^2}{(2E_{01} - E_{02})^2 \Gamma}$$

$$\sigma_{TPA} \propto \frac{\mu_{01}^2 \mu_{12}^2}{\Delta^2}$$

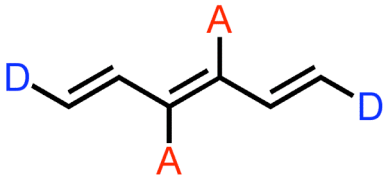
H. Agren *et al. J. Chem. Phys.* **2001**, *114*, 9813

Three-form three-state VB model

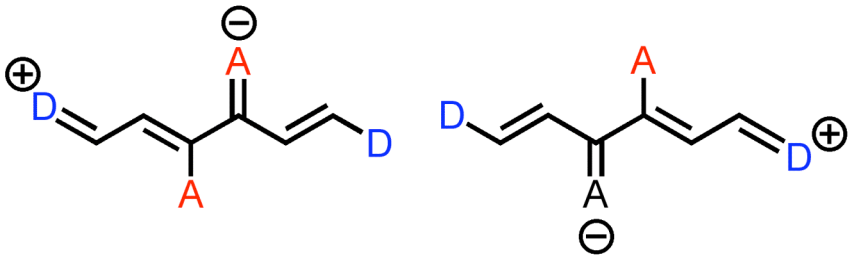
Centrosymmetric chromophore

VB structures

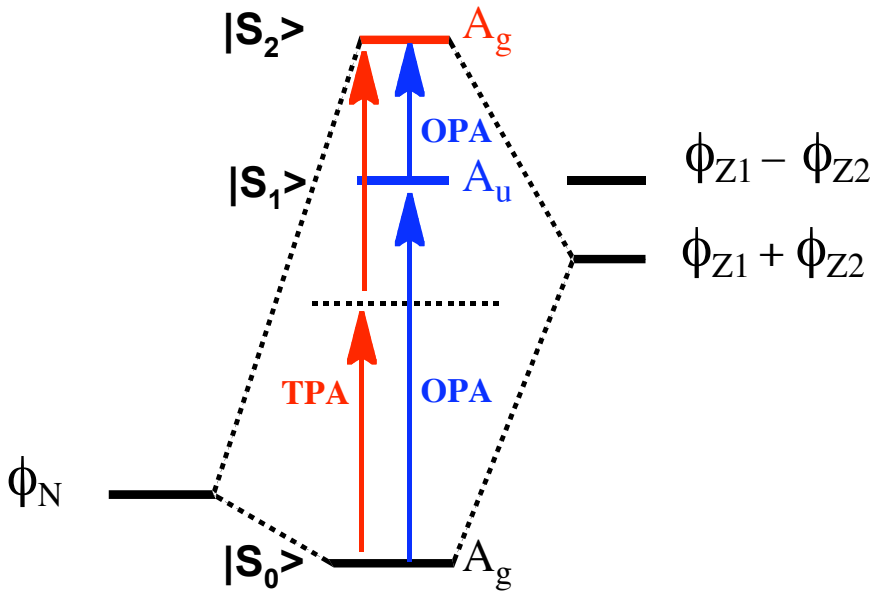
Covalent form (N)



Zwitterionic forms (Z_1, Z_2)



VB mixing diagram



M. Blanchard-Desce *et al*. *J. Chem. Phys*. **2000**, *113*, 3951.

Three-form three-state VB model

Centrosymmetric chromophore

VB structures

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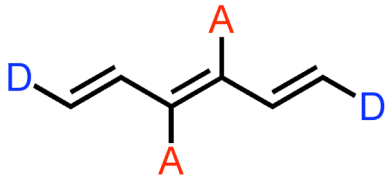

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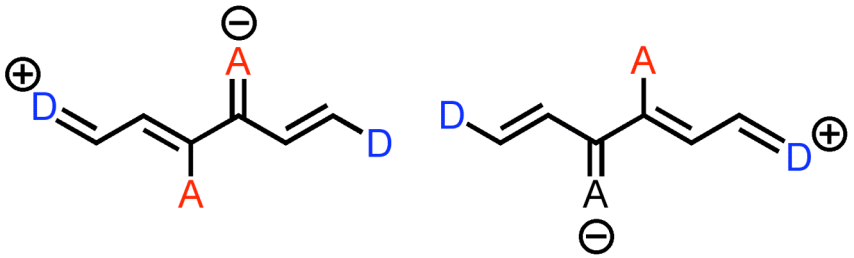
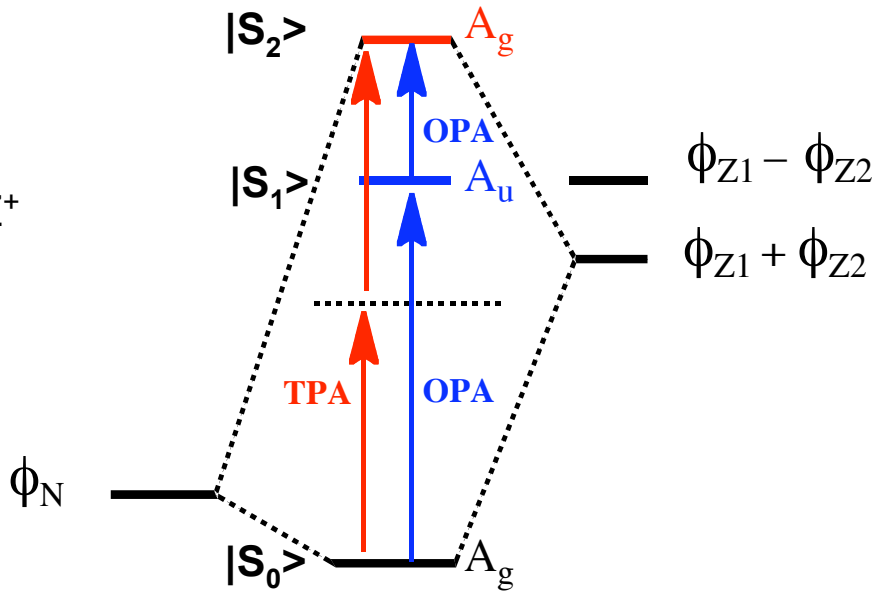


MIX = N - Z^+

VB mixing diagram



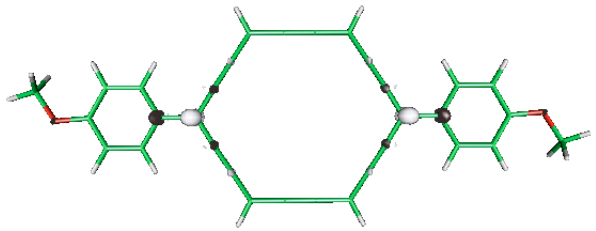
$$\sigma_{TPA} \propto \frac{3\mu_z^4}{4t^2\Gamma}\frac{(1-MIX^2)^2}{MIX^2}$$

Optimal TPA efficiency : MIX = 0

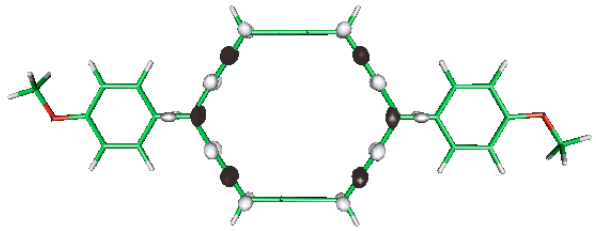
M. Blanchard-Desce *et al*. *J. Chem. Phys*. **2000**, *113*, 3951.

Essential states of *p*-dianisyl-*carbo*-benzene

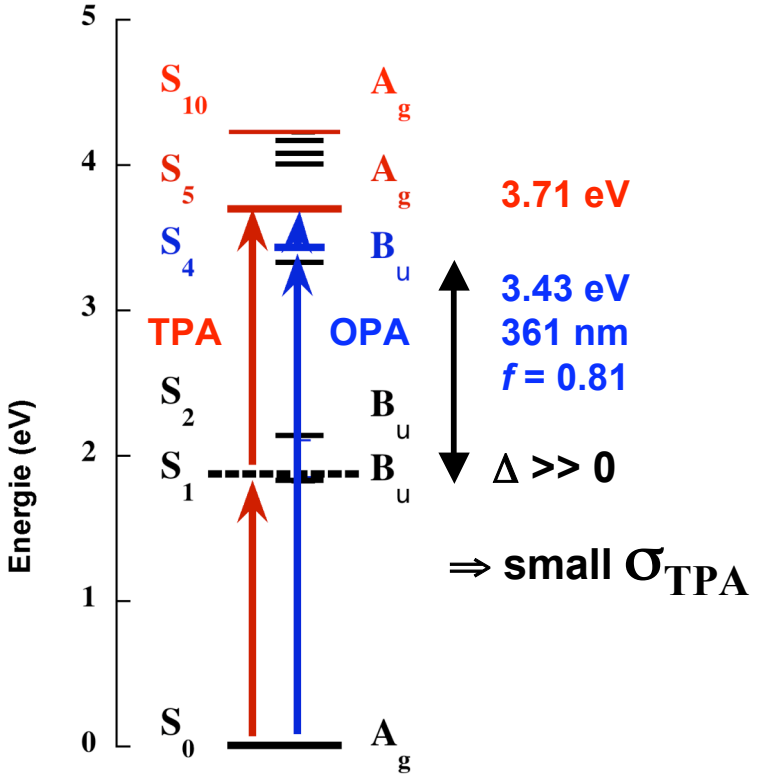
Excited states of same transition density

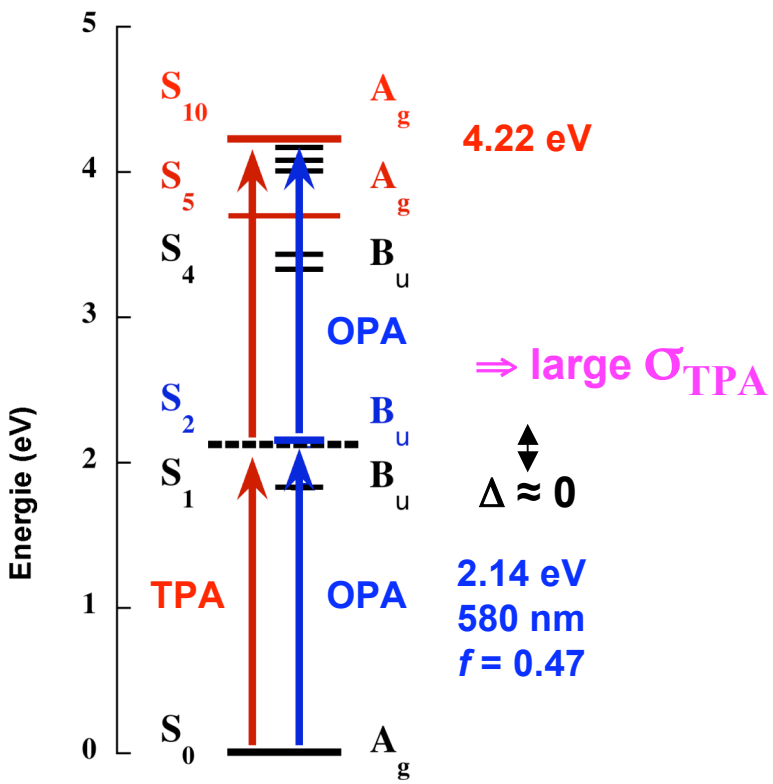


S_5 and S_4



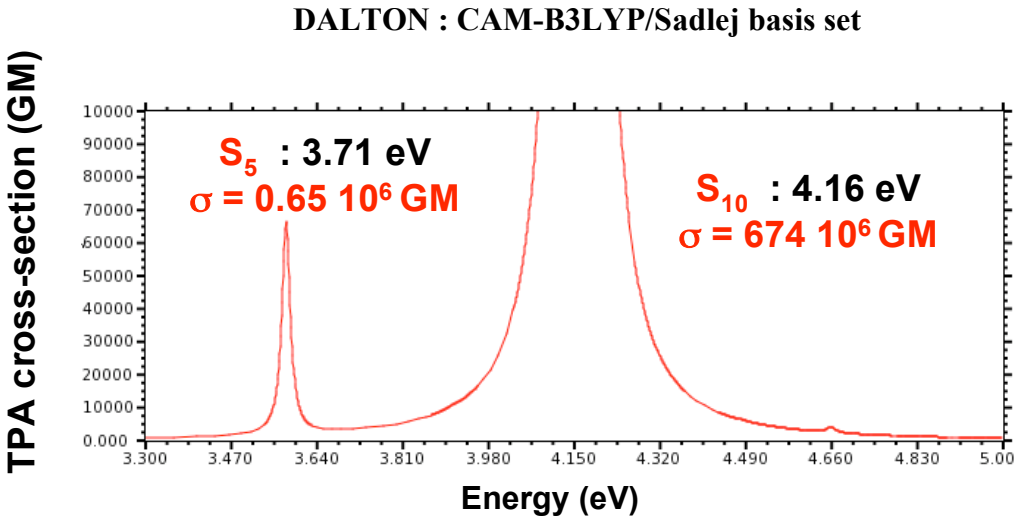
S_{10} and S_2

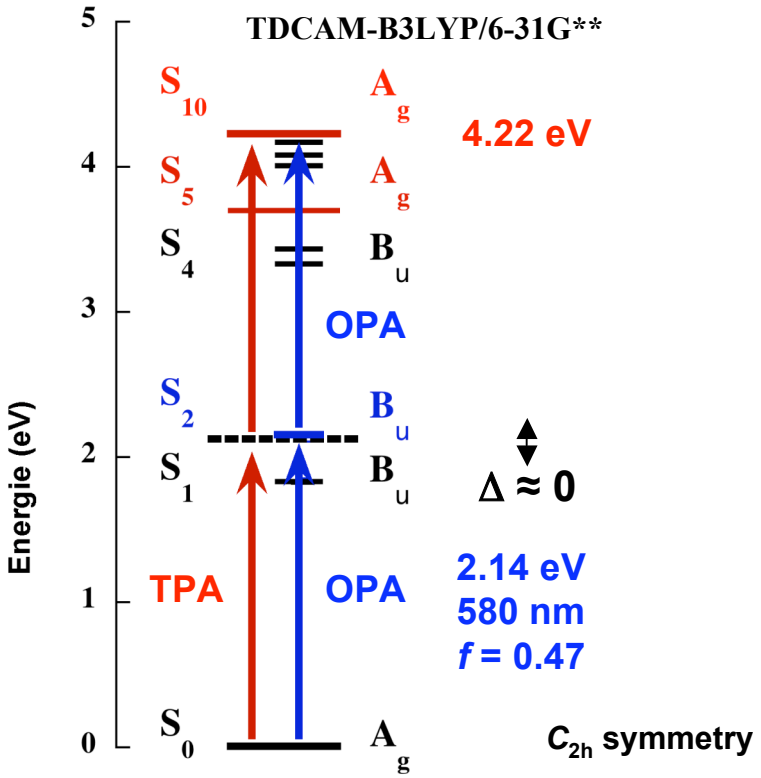




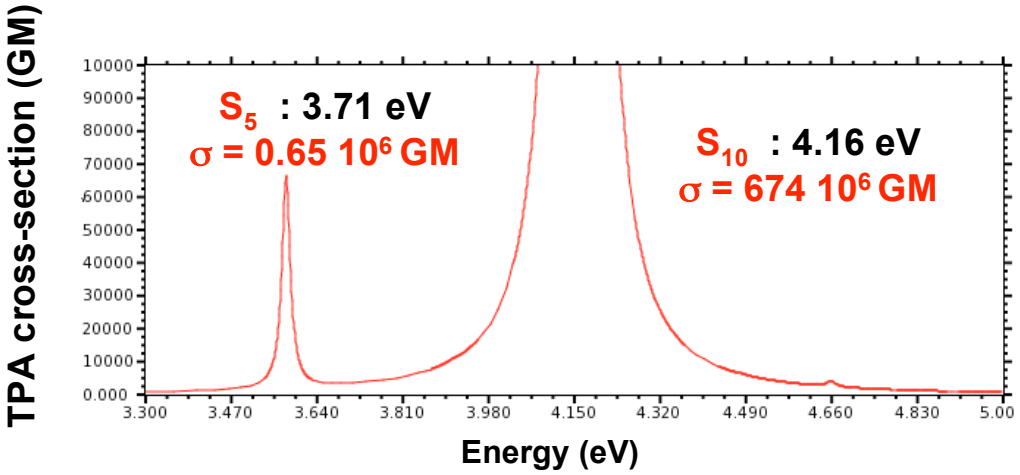
TDCAM-B3LYP/6-31G**

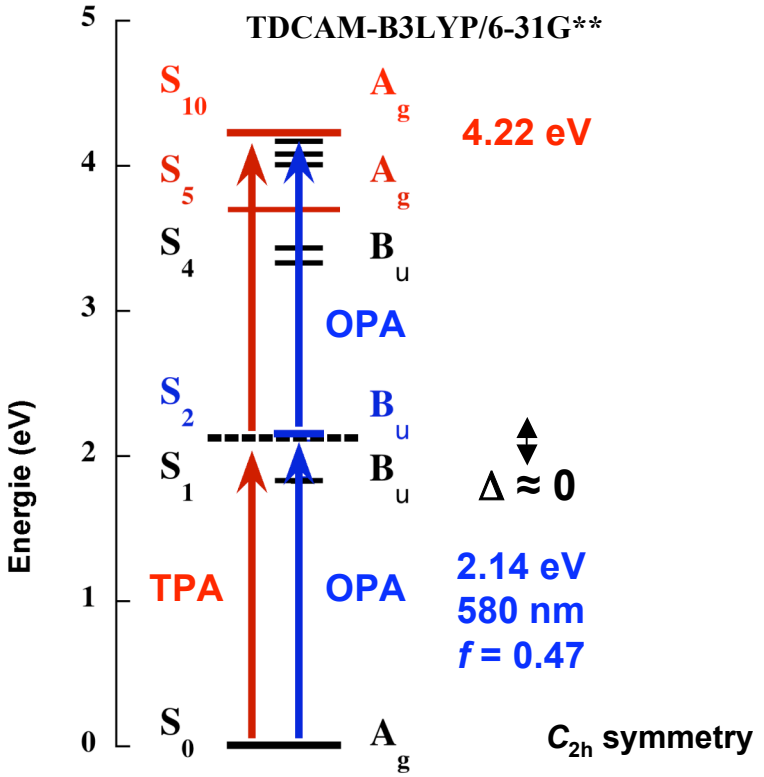
TPA efficiency of *p*-dianisyl-*carbo*-benzene



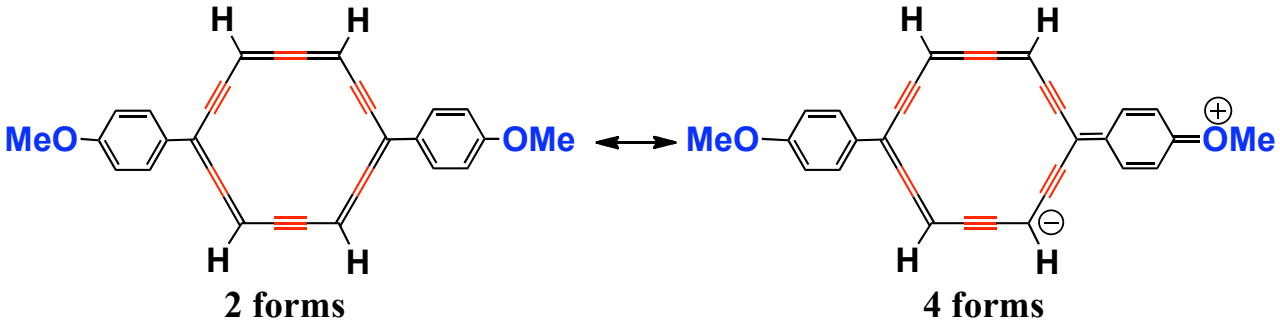


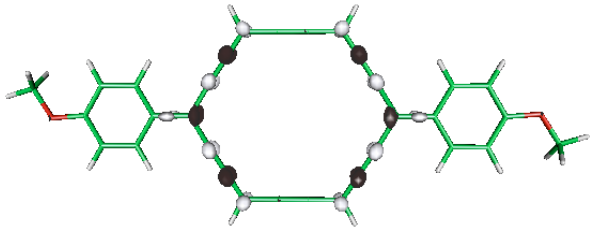
TPA efficiency of *p*-dianisyl-*carbo*-benzene





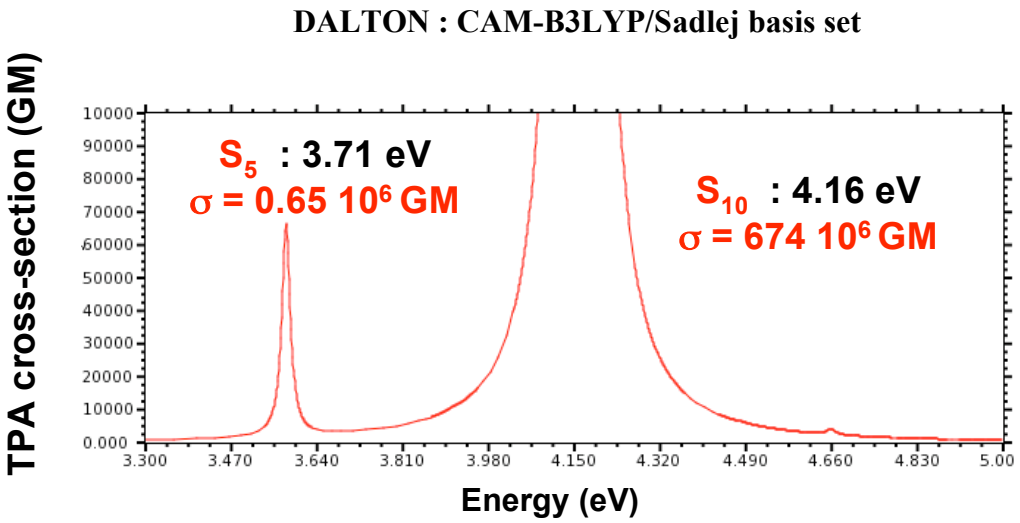
Intramolecular charge transfer

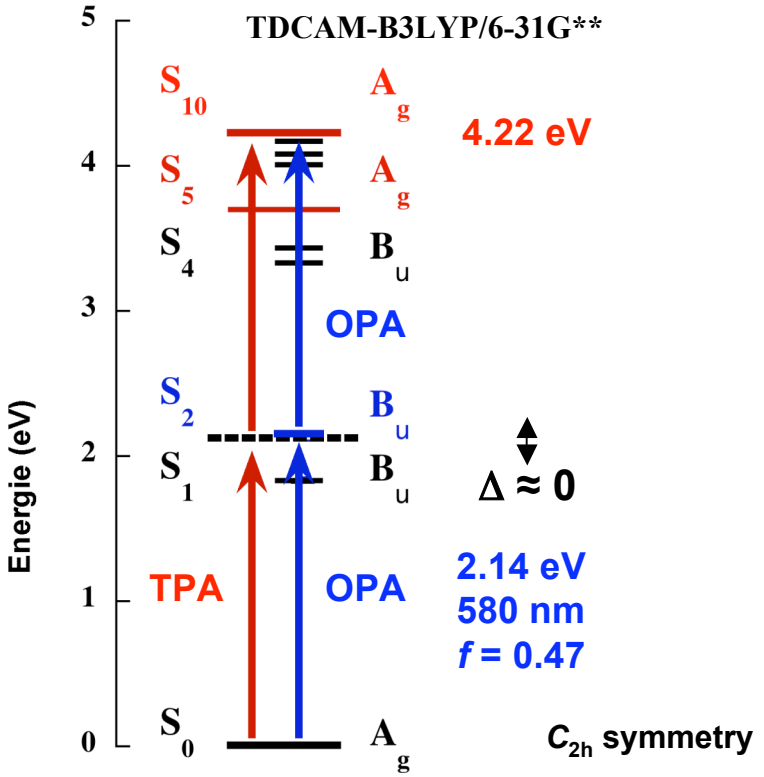




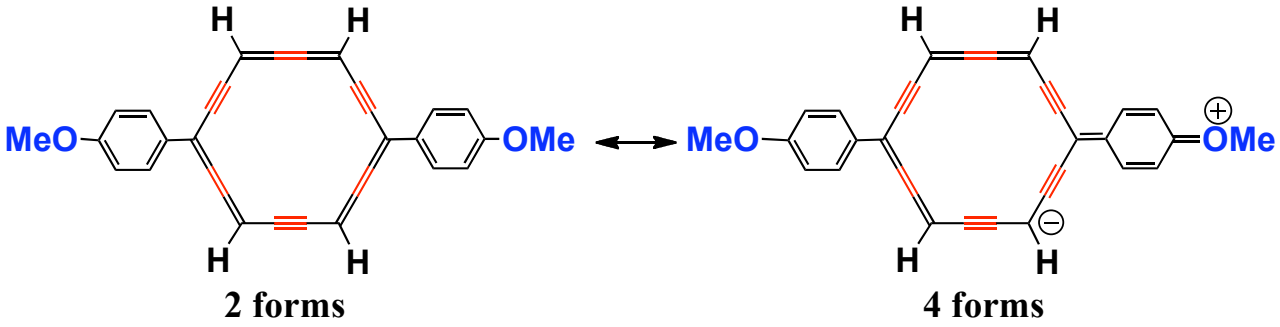
Transition density

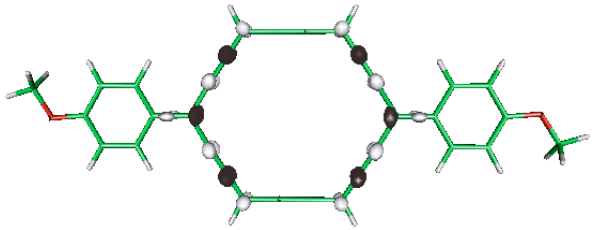
TPA efficiency of *p*-dianisyl-*carbo*-benzene





Intramolecular charge transfer

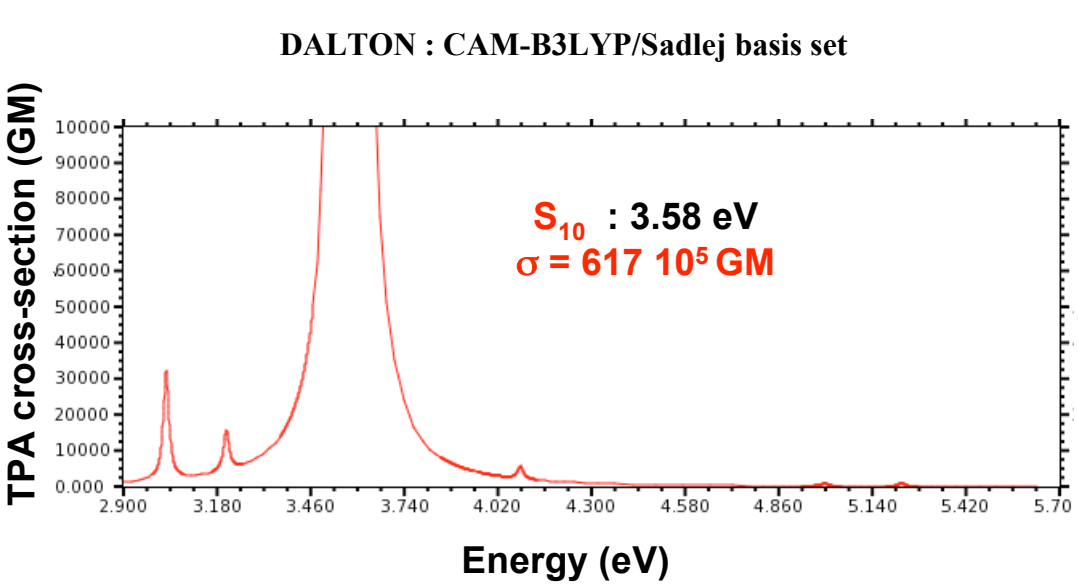


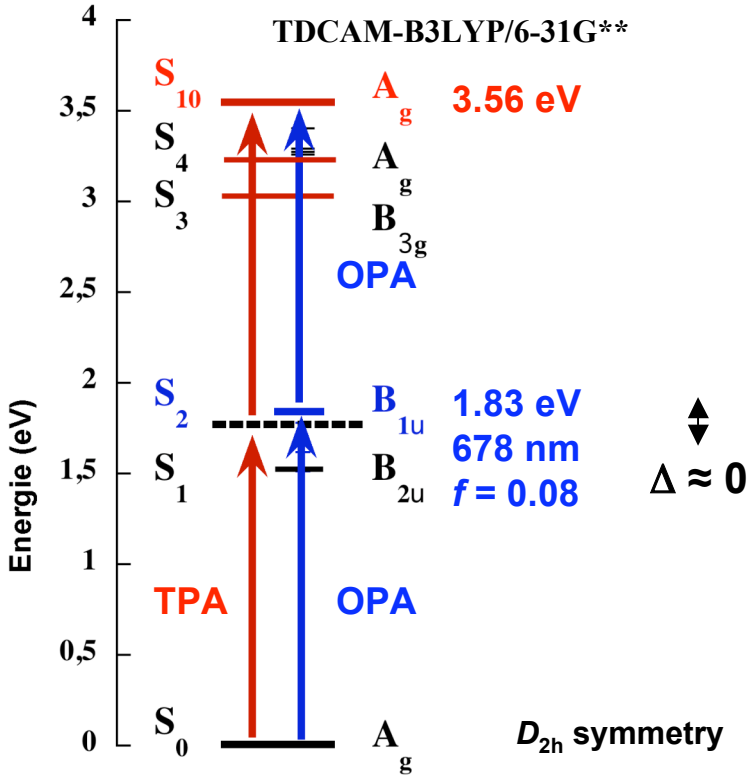


Transition density

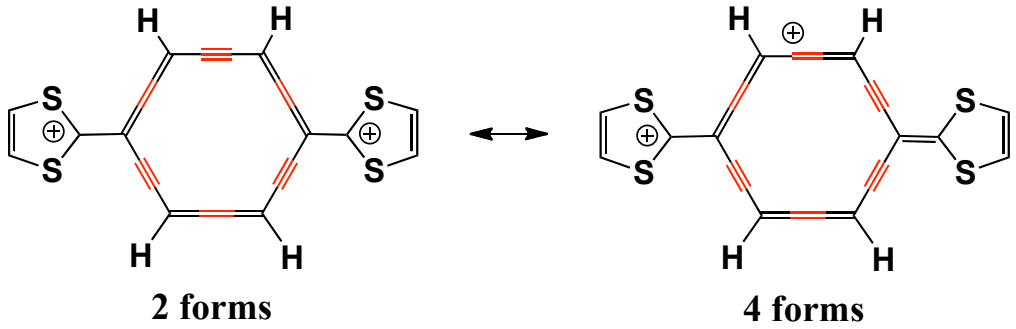
Larger TPA cross-sections : ⇒ Accepting side groups on the macrocycle

p-dithiafulvene-*carbo*-benzene *dication*

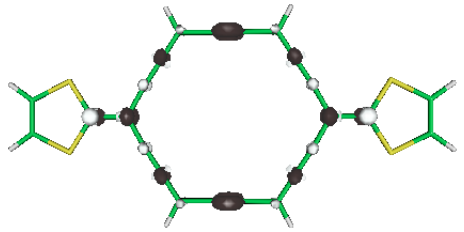




Intramolecular charge transfer



2 forms 4 forms



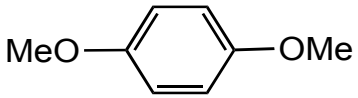
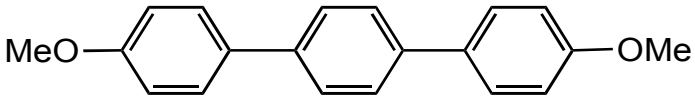
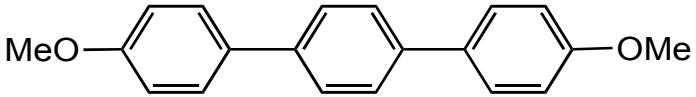
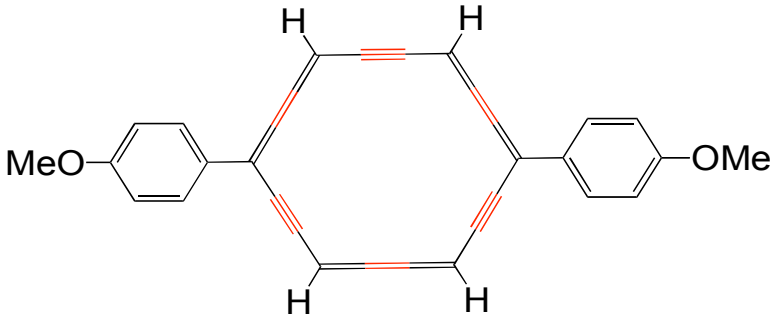
Transition density

Larger TPA cross-sections :

⇒ Donor substituents on the macrocycle

⇒ Accepting groups on dithiafulvenes

Carbo-mer effect on TPA efficiency

	Excited state symmetry	E (eV)	σ_{TPA}(GM)
 C_i	A_g	5.23	14.1
 C_i	A_g	4.99	20.8
	A_g	5.33	1940
	A_g	5.35	88.3
 C_{2h}	A_g	4.77	38.4
	A_g	5.11	3180
 C_{2h}	A_g	3.58	647 10^3
	A_g	4.16	674 10^6

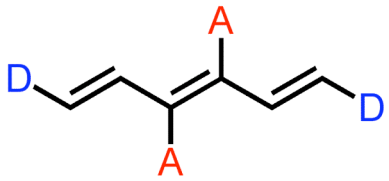
x 2 10^5

CAM-B3LYP/Sadlej basis set

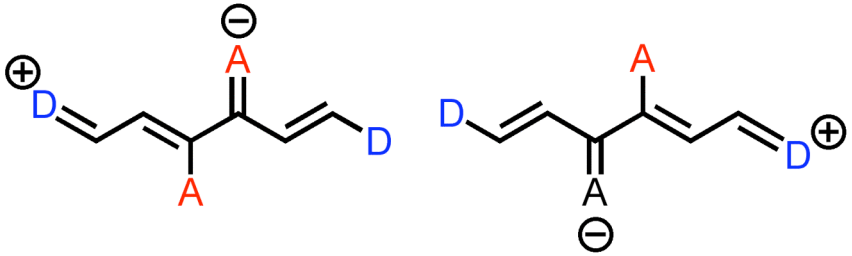
Three-form three-state VB model for TPA

Transition densities ⇒ VB structures

Covalent form (N)



Zwitterionic forms (Z_1, Z_2)



$$\sigma_{TPA} \propto \frac{3\mu_z^4}{4t^2\Gamma}\frac{(1-MIX^2)^2}{MIX^2}$$

MIX = N - Z^+

Most suitable weights ?

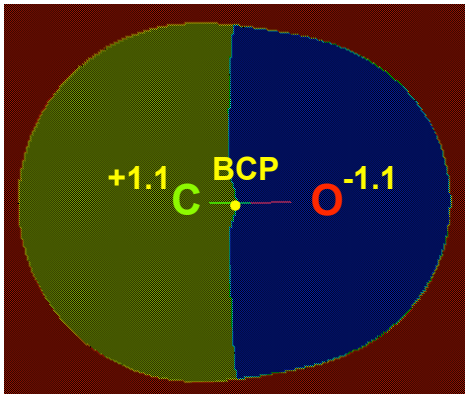
- VB weights ?
- Natural Resonance Theory ?
- ELF topological analysis ?
- *ELF + EDF ?*
- *.....*

⇒ Reliable
⇒ Large size systems
⇒ Systematic comparison
⇒ CO, C_2H_2, …

M. Blanchard-Desce *et al*. *J. Chem. Phys*. **2000**, *113*, 3951.

Topological analyses

AIM



AIM partition

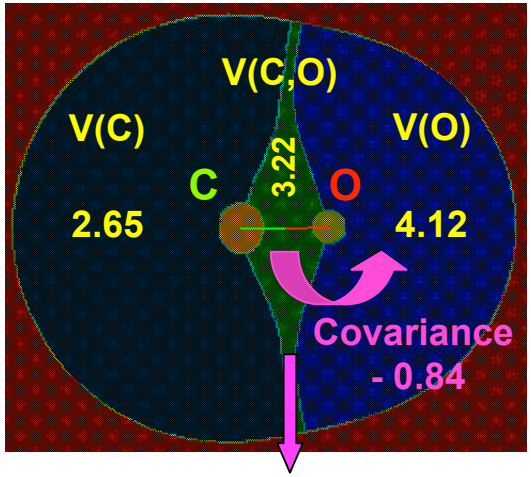
Atoms in Molecules

Topological analysis of the electron density ρ

- **Atomic basins and atomic charges**
- **Bond critical points and sign of $\nabla^2\rho$**

R. F. W. Bader *et al*. **1990**.

ELF



Variance (V(C,O)) = 1.41

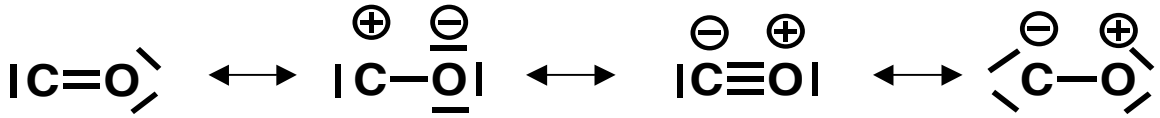
ELF partition

Electron localization function

$$\nabla^2 P^{\sigma\sigma}_{cond}(r,r')|_{r'=r}$$

- **Valence basins ⇔ bonds and lone pairs**
- **Populations and (co)variances of valence basins**

⇒ Weights of mesomeric forms



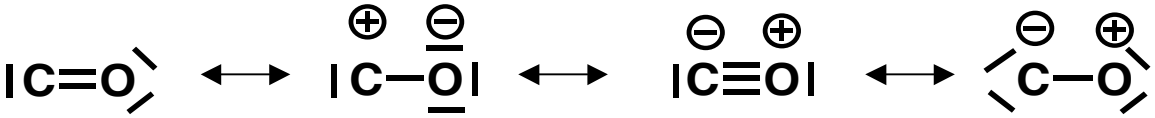
50% 12% 6% 32%

Electronic exchanges between ELF basins : electron delocalization

J. Phys. Chem. A **2003**, *107*, 4647.

B. Silvi, A. Savin, *Nature* **1994**, *371*, 683.

Most representative forms of carbon monoxide



Pauling	50 %	10 %	40 %	-
VB	>>	>		
NRT	-	-	100 %	-
ELF	50 %	12 %	6 %	32 %
ELF + EDF	28 %	20%	15 %	11 %

EDF : Electron number Distribution Functions

Collaboration B. Silvi and A. M. Pendas

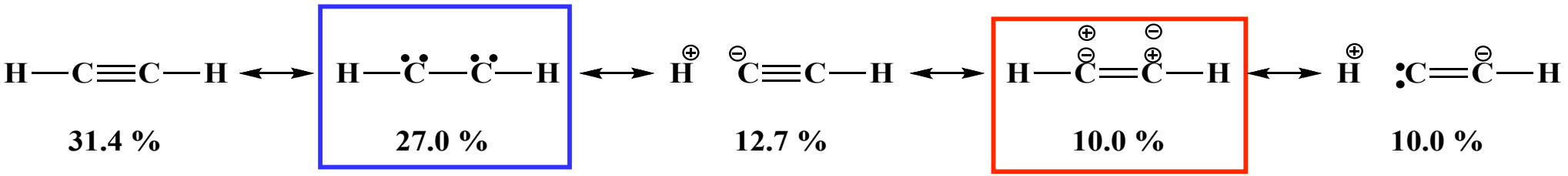
A. Martin Pendas *et al*. *J. Chem. Phys*. **2009**, *131*, 124125.

B3LYP/6-311+G*

J. Phys. Chem. A **2003**, *107*, 464.
Organometallics **2008**, *27*, 5263.

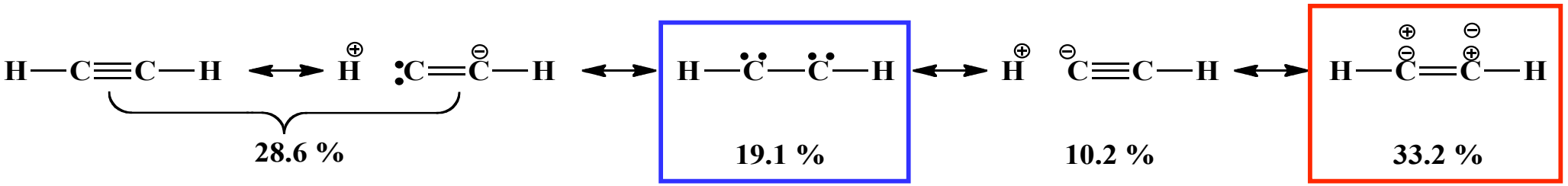
Most representative forms of acetylene

VB description



M. Raimondi and M. Simonetta *Mol. Phys.* **1977**, *34*, 745.

« ELF + EDF » description



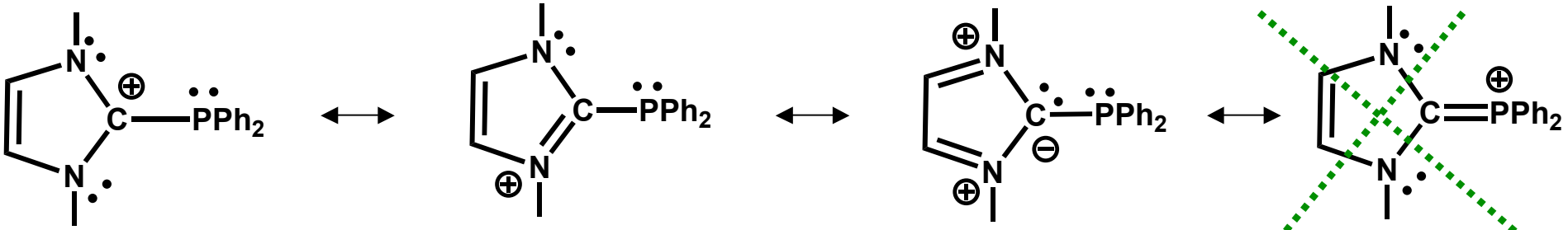
Collaboration B. Silvi and A. M. Pendas

B3PW91/6-311+G*

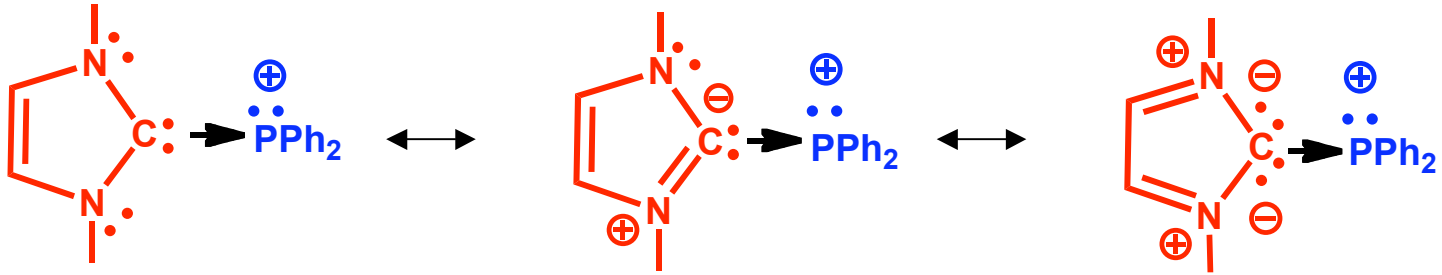
S. Shaik, D. Danovitch, B. Silvi, D. L. Lauvergnat, P. Hiberty *Chem. Eur. J.* **2005**, *11*, 6358.

Amidiniophosphines

ELF analysis



Dissociation energy analysis



NHC-phosphénium adduct

$\Delta G_{heterol} > \Delta G_{homol}$

Donor	Acceptor	$\Delta G_{homol} - \Delta G_{heterol}$
Ph^-	$^+PPh_2$	**-55.3**
NHC	$^+PPh_2$	8.4
H_3N	BH_3	106.4

$\Delta G_{heterol} < \Delta G_{homol}$

ΔG in kcal/mol (PCM-(U)B3PW91/6-31G) - acétonitrile**

C-P covalente ⇐ Triphenylphosphine Amidiniophosphine ⇒ Dative C-P

Chem. Eur. J. **2010**, *16*, 13095.

Conclusions

- ***Three-form three-state model for two-photon absorption***

  - Transition densities

  ⇒ Essential excited states and corresponding intramolecular charge transfer (ICT)

  ⇒ Validation of TDDFT calculations of excited states (N. Benamor, S. Hoyau - Toulouse)

  ⇒ Estimation σ_{TPA} from the weights of the mesomeric forms related to the ICT

- ***Comparison and significance of the weights obtained from various methods***

- ***Design of a weighting method suitable for large size chromophores***

Aknowledgments

Remi Chauvin

Dmytro Kandaskalov

Mie Vilhelmsen

Houria Hamdani

Mickael Gicquel

Collaborations

Pascal Lacroix : LCC -Toulouse

Jean-Louis Heully, Nadia Ben Amor,

Sophie Hoyau : LCPQ - Toulouse

Bernard Silvi : LCT - Paris VI

Angel Martin Pendas : Oviedo

CALMIP/ IDRIS / CINES

CNRS

ELF topological analysis

Electron Localization Function

$$ELF(r) = 1/[1+((D(r)/D_0(r))^2 \qquad D(r) = \nabla^2 P^{\sigma\sigma}_{cond}(r,r')|_{r'=r}$$

0 < ELF < 1

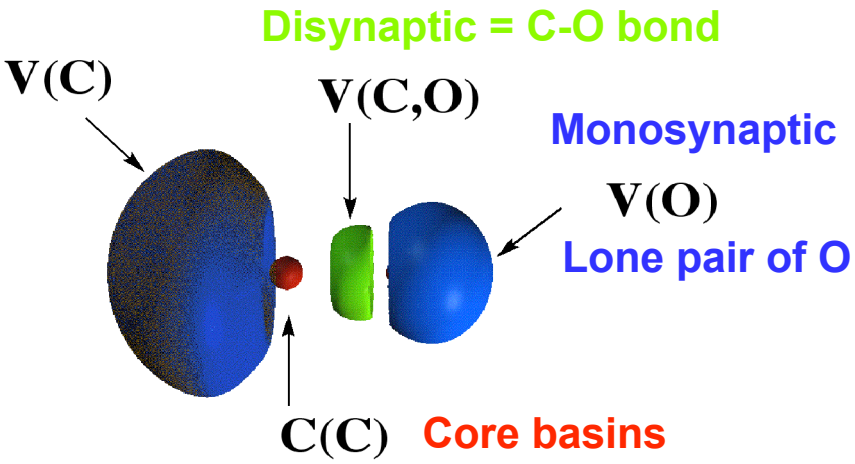
⇒Pauli repulsion probe,

⇒localization of pair domains

Topological analysis

Partition of the molecular space into core and valence basins

Carbon monoxide CO : ELF = 0.8



Valence basins

⇓⇑

Bonds and lone pairs of Lewis theory

⇒ Chemical bonding

A. D. Becke *et al. J. Chem. Phys.* **1990**, *92*, 5397.

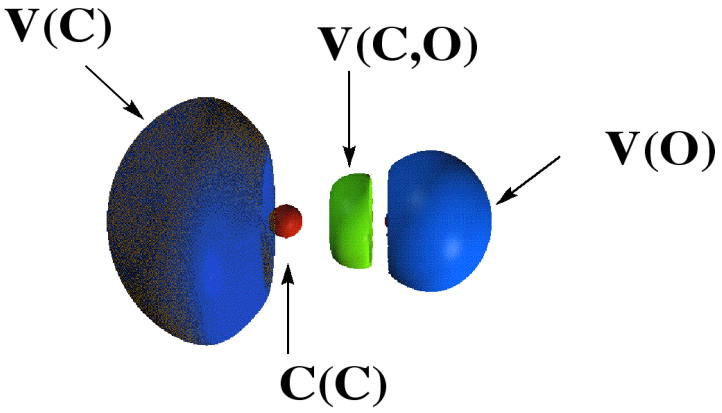
B. Silvi, A. Savin, *Nature* **1994**, *371*, 683.

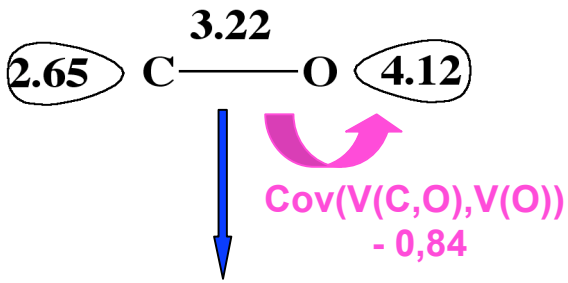
Méthode de pondération ELF des formes mésomères

Bassins ELF de valence

⇓⇑

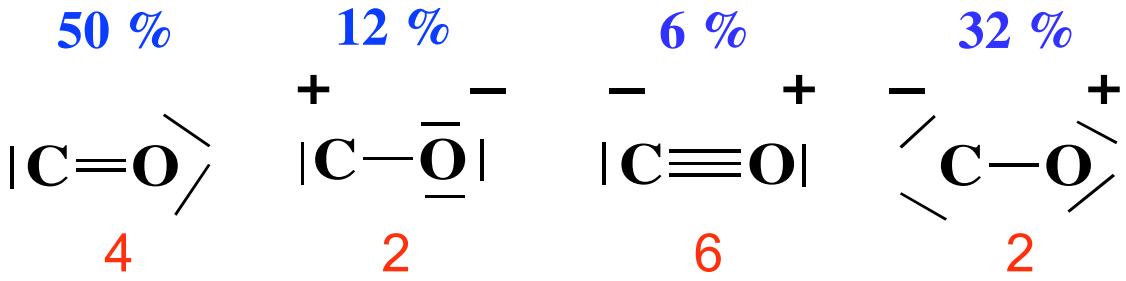
Liaisons et paires libres





Echanges électroniques
entre bassins ELF

Monoxyde de carbone CO



Populations Lewis liaison C-O

Système d'équations linéaires

Population V(C,O)

$4x + 2y + 2z + 6w = 3{,}22$

Variance V(C,O)

$4{*}4x + 2{*}2y + 2{*}2z + 6{*}6w = 1{,}41$

Covariance V(C,O), V(O)

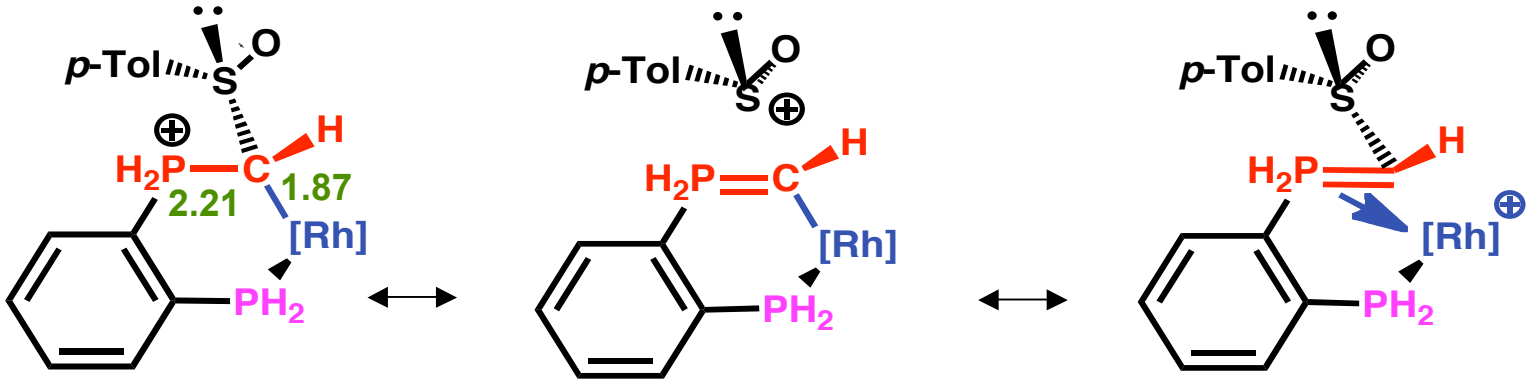
$4{*}4x + 2{*}4y + 2{*}2z + 6{*}2w = -0{,}84$

B3LYP/6-311+G*

J. Phys. Chem. A **2003**, *107*, 464.
Organometallics **2008**, *27*, 5263.

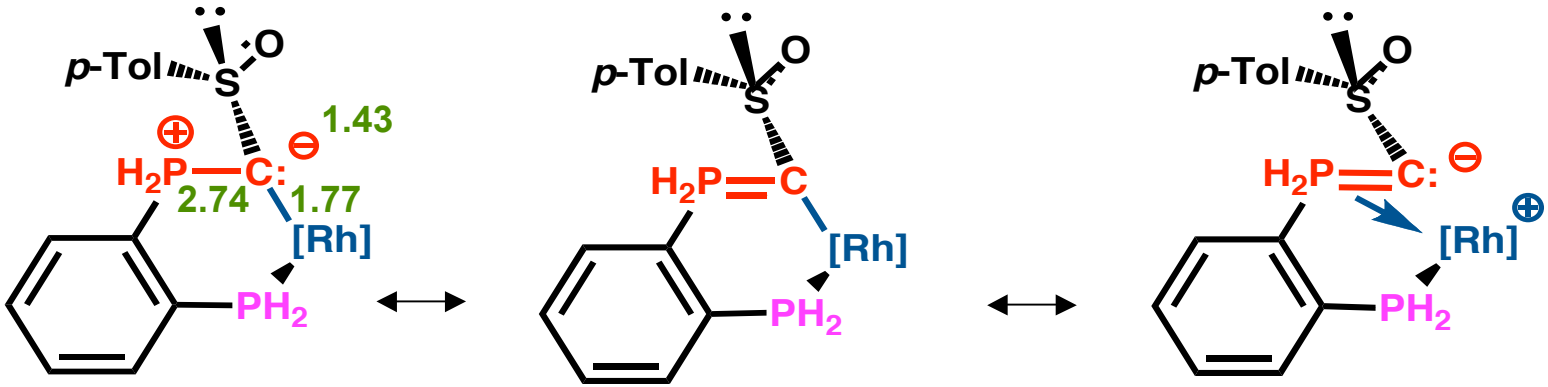
ELF analysis of the Rh-ylide and Rh-yldiide bond

Model complexes : $PPh_2 \rightarrow PH_2$, cod $\rightarrow CH_2{=}CH_2$



88 % 6 % 6 %

σ contribution **η2-P,C haptomeric form**



61 % 28 % 11 %

Selected ELF basins populations

B3PW91/6-31G/DGDZVP(Rh)// B3PW91/6-31G**/LANL2DZ(Rh)**

Inorg. Chem. **2009**, *48*, 2147.