Time of Proton Transfer and Electron Density in the Inner Cavity of Porphycenes

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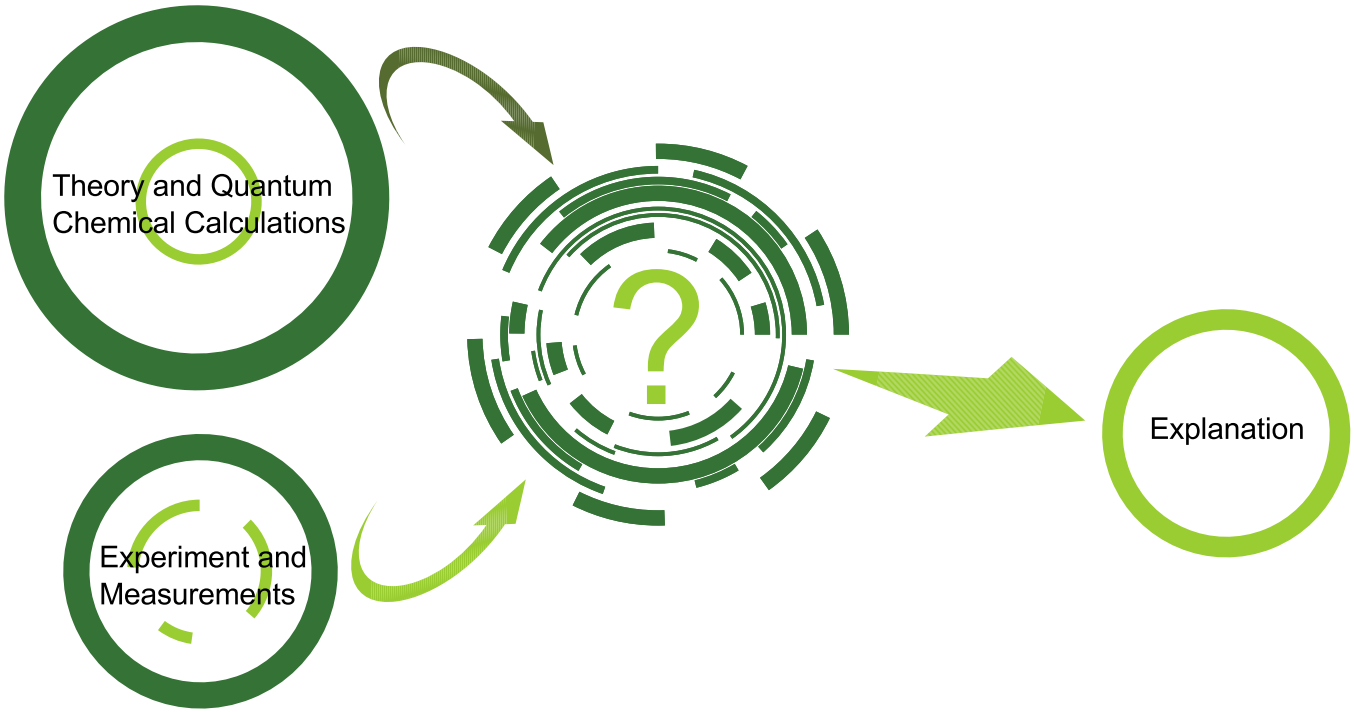
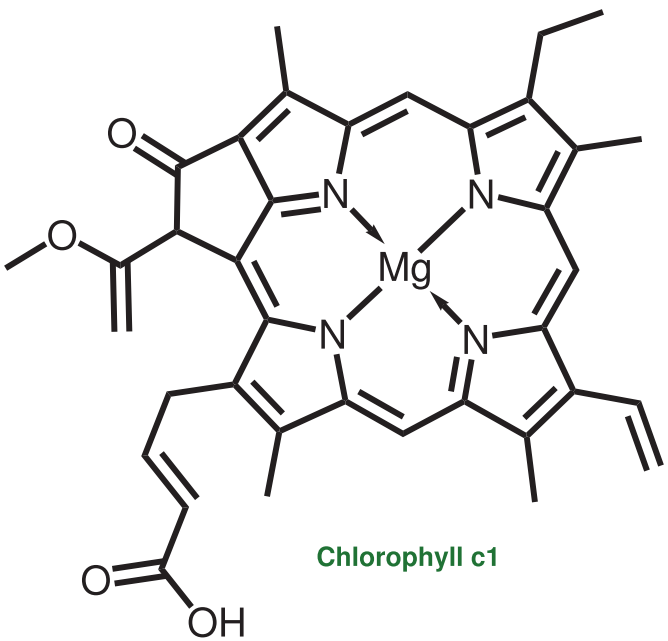
Possible subtitles of presentation

Can we connect the quantum theory calculations and data obtained by measurements to create useful explanation of some phenomenas?



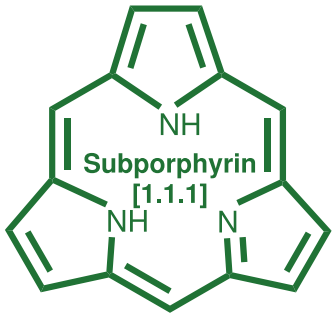
Porphycene is isomer of porphyrin

Occurring in nature

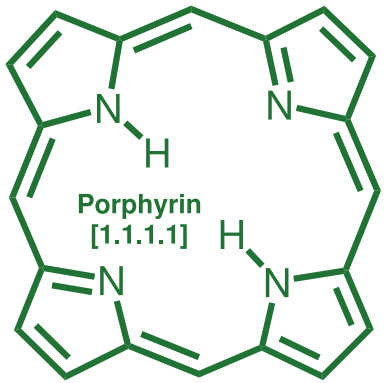


Chlorophyll c1

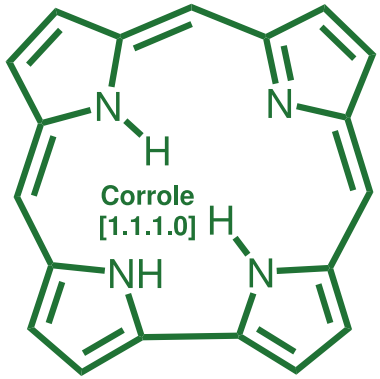
Synthetic



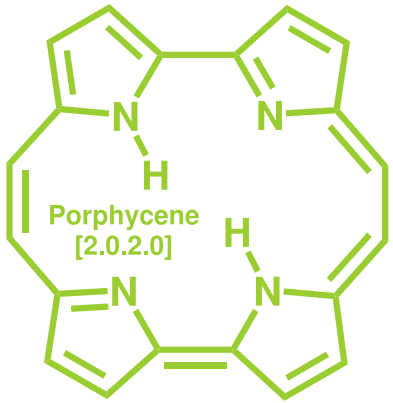
Subporphyrin
[1.1.1]



Porphyrin
[1.1.1.1]



Corrole
[1.1.1.0]



Porphycene
[2.0.2.0]

Motivation

Why are we interested in porphycenes?

- Model systems for experimental studying **hydrogen transfer** reactions and **H-bonds** properties.

  P. Fita, N. Urbańska, C. Radzewicz, J. Waluk, *Chem. Eur. J.* **15**, 4851 (2009);

- Inconsistence between **reaction rates** measured in crystals (nanosecond) and solutions (picoseconds).

  U.Langer, C. Hoelger, B. Wehrle, L. Latanowicz, E. Vogel, H.H. Limbach, J. Phys. Org. Chem. 13, 23 (2000);
  Z. Smedarchina, M. F. Shibl, O. Kuehn, A. Fernandez-Ramoz, Chem. Phys. Lett. 436, 314 (2007);

- Potential applications in **photodynamic therapy**.

  I. Czerski, A. Listkowski, J. Nawrocki, N. Urbańska, H. Piwoński, A. Sokołowski, O. Pietraszkiewicz, M.Pietraszkiewicz, J. Waluk, J. Porphyrins Phthalocyanines, 2012, 16, 589-602.

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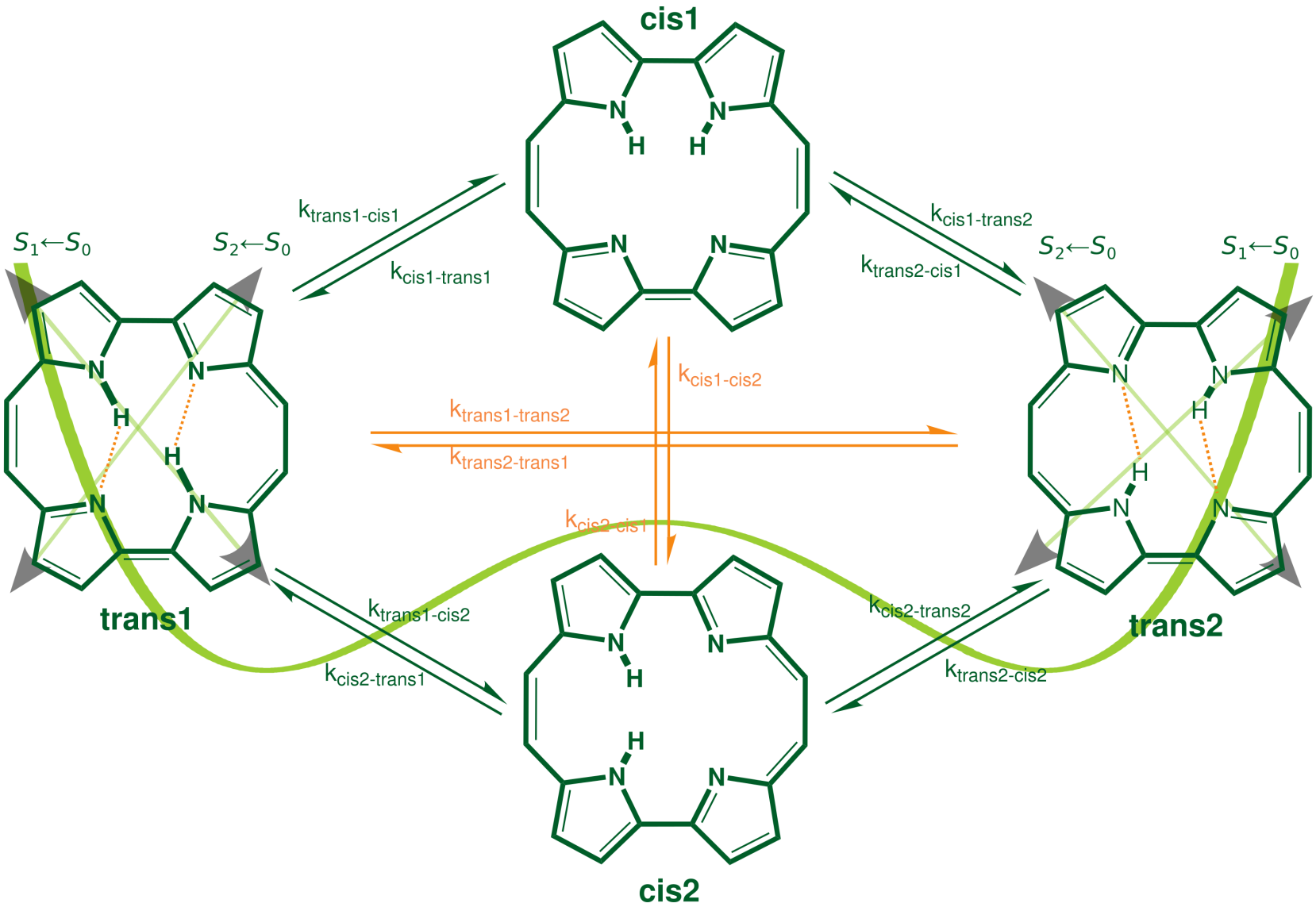
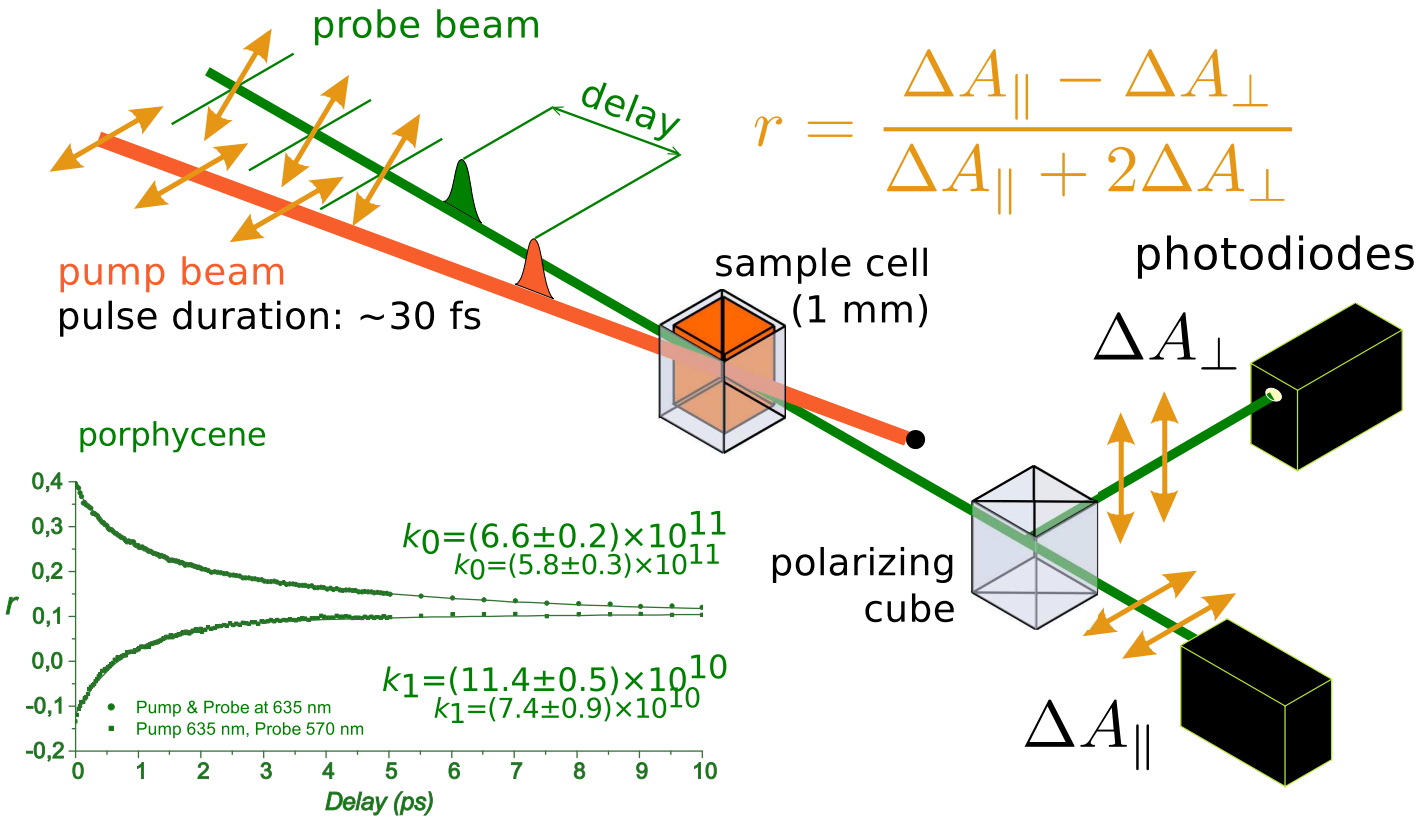
Ways of isomerization for porphycene (PC) molecule.



Transient absorption anisotropy measurements



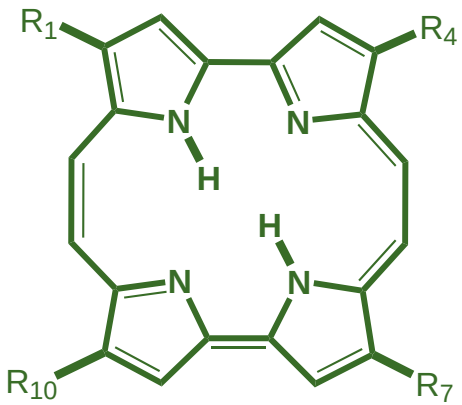
$$r = \frac{\Delta A_\parallel - \Delta A_\perp}{\Delta A_\parallel + 2\Delta A_\perp}$$

Data analysis

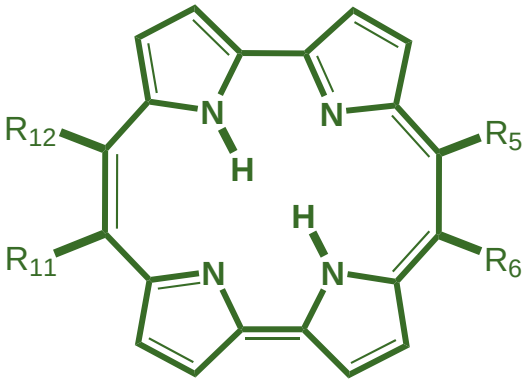
$$r(t) = \left[a\left(\left(r_0^0 - r_\infty^0\right)\mathrm{e}^{-t/\tau_r^0} + r_\infty^0\right) + (1-a)\left(\left(r_0^1 - r_\infty^1\right)\mathrm{e}^{-t/\tau_r^1} + r_\infty^1\right)\right] \times \mathrm{e}^{-t/\theta} \qquad \tau_r = \left(k_{1\to 2} + k_{2\to 1}\right)^{-1}$$

ground state — excited state — rotational diffusion

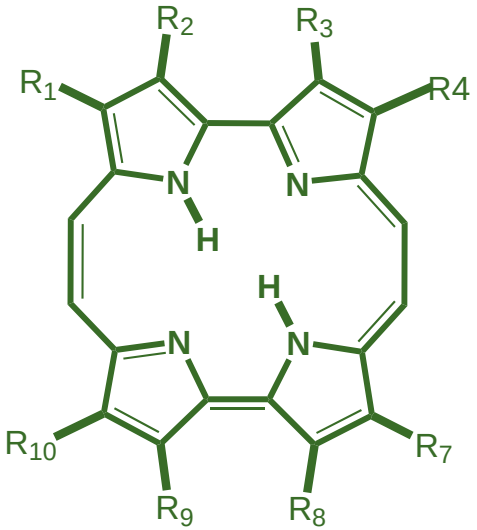
Measured porphycenes derivatives



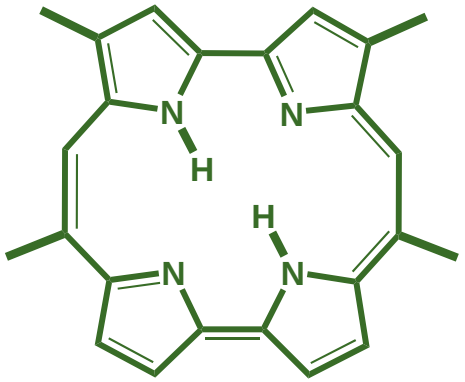
TTPO: R_1, R_4, R_7, R_{10} = -Ph
TTPC: R_1, R_4, R_7, R_{10} = -^{t}Bu



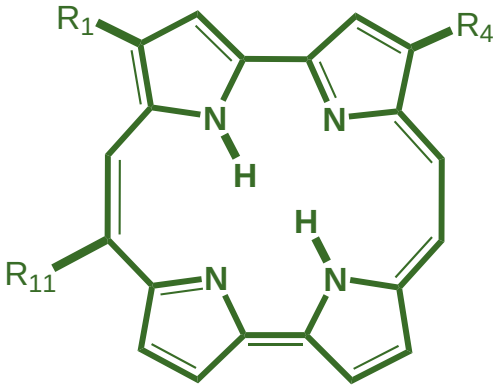
CMPC: R_5, R_6, R_{11}, R_{12} = -Me
PCRC: R_5, R_6, R_{11}, R_{12} = -^{n}Pr



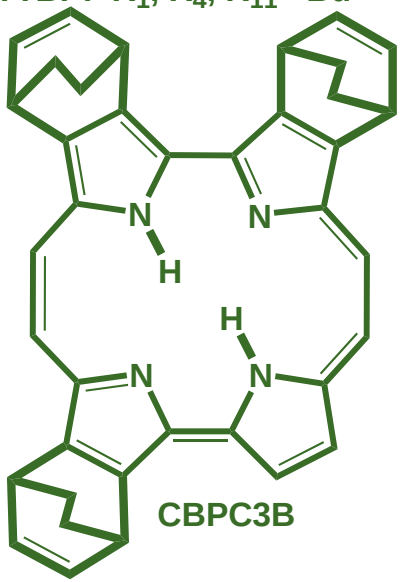
OEPC: R_1, R_2, R_3, R_4,R_7, R_8, R_9, R_{10} = -Et



2M2B: R_5, R_6, R_{11}, R_{12} = -Me
2MPC: R_5, R_6, R_{11}, R_{12} = -^{n}Pr

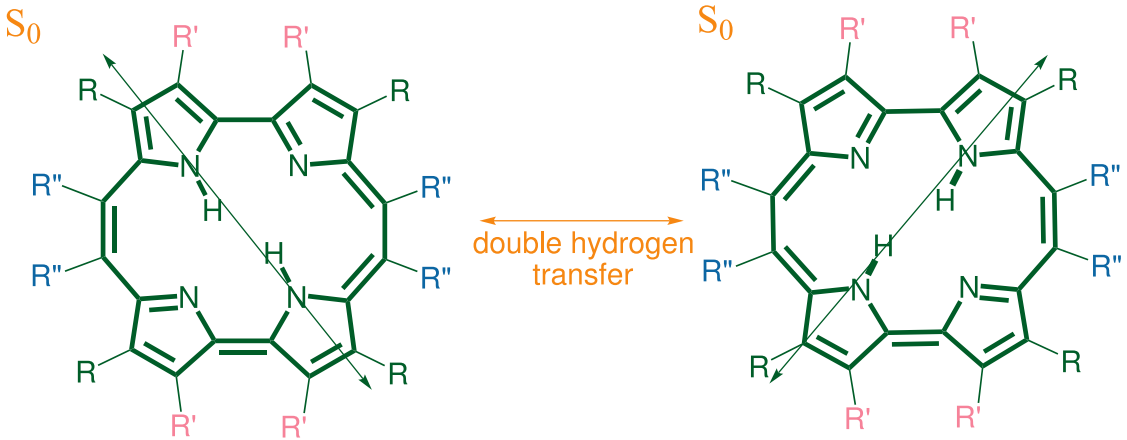


DTBP: R_1, R_4 = -^{t}Bu
MTBP: R_1, = -^{t}Bu
TTBP: R_1, R_4, R_{11} -^{t}Bu



CBPC3B

Measurements result

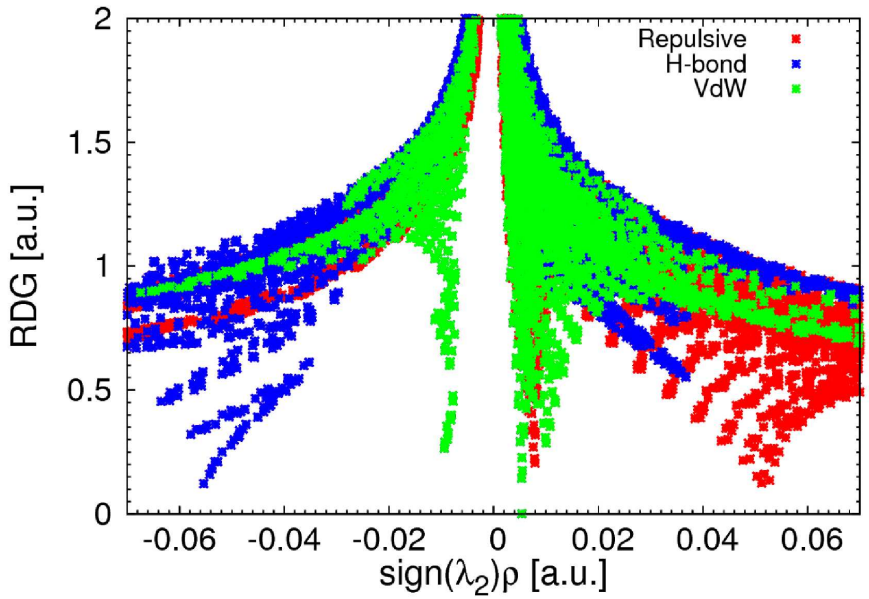


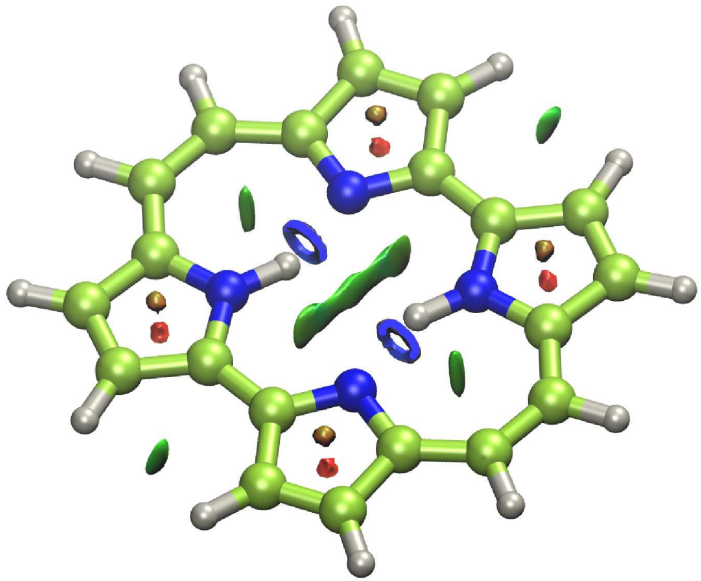
System	Measurement			B3LYP/6-311(d,p)		
-	$\tau_{PT} S(0)(ps)$	d^1_{N-N}	d^2_{N-N}	$sign(\lambda_2)\rho$	d^1_{N-N}	d^2_{N-N}
OEPC	100	2.80	2.73	-0.0405	2.275	2.756
PC	1.80(1)	2.63	2.83	-0.0555	2.576	2.903
DTBP	1.20(1)	-	-	-0.0550	3.669	2.823
TTBP	0.80(1)	-	-	-0.0556	2.674	2.823
TPPO	0.75(5)	-	-	-0.0556	2.668	2.846
TTPC	0.62(1)	2.63	2.8	-0.0560	2.669	2.871
2MPC	0.34(1)	-	-	-0.0568	2.637	2.809
2M2B	0.22(1)	-	-	-0.0604	2.639	2.880
CMPC	0.10(1)	2.53	2.90	-0.0704	2.586	2.902
PCRC	0.10(1)	2.53	2.90	-0.0720	2.576	2.903

Quantum Chemical Calculations

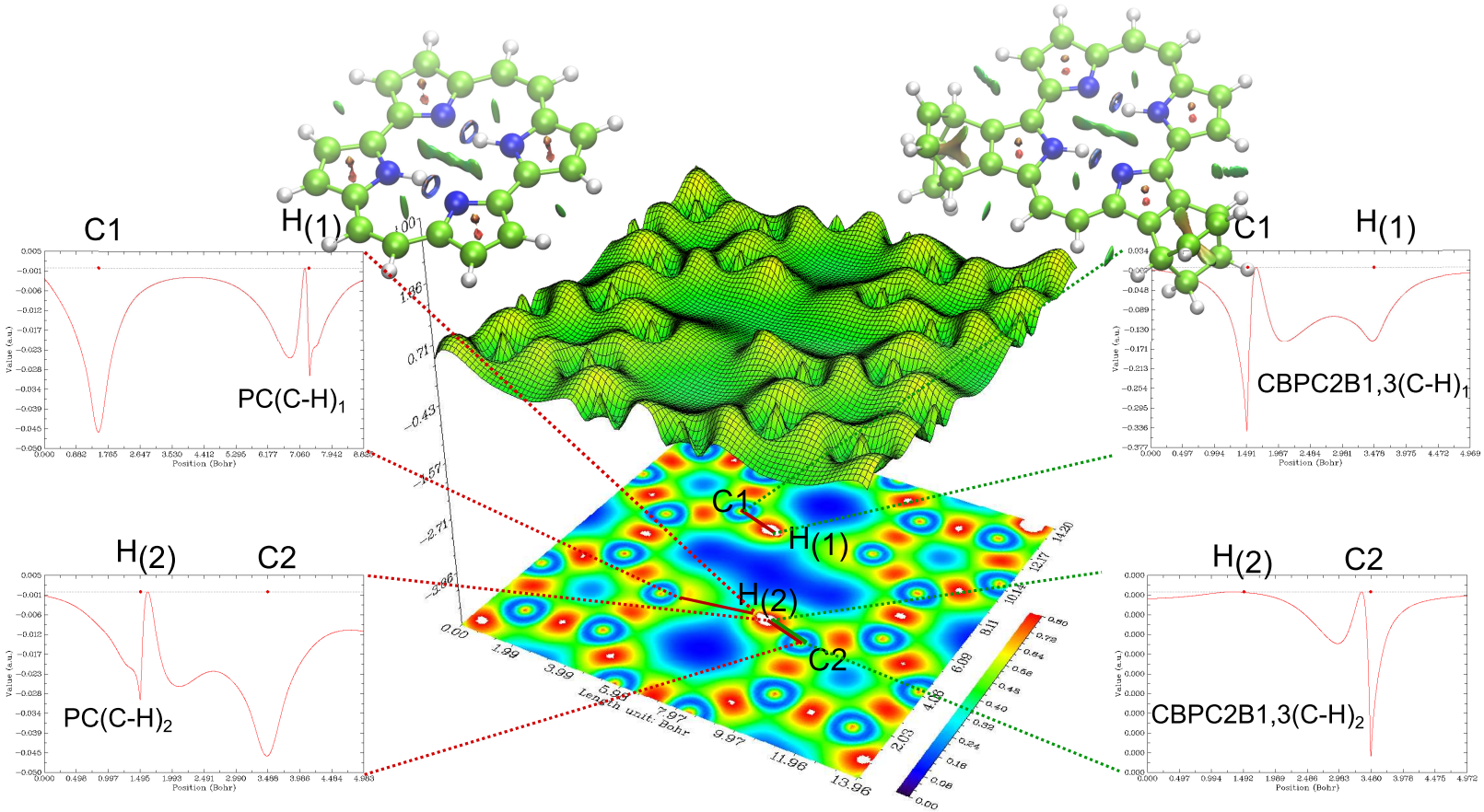
1. Computational Methods:
   - DFT/B3LYP - hybrid functional
2. Basis Sets:
   - 6-311(d,p)
   - 6-31G(d,p)
3. Computational Software:
   - Gaussian09 - geometry optimization
   - Cubegen - electrostatic potential and total density plot
   - NCIPlot - plots of the reduced density gradient (RDG)
4. Visualizations made in:
   - VMD - molecular graphics software
   - Multiwfn - multifunctional wavefunction analyzer
   - Molden - pre- and post processing program of molecular and electronic structure
   - TopMod - visualisation ELF (Electron Localisation Function) data
5. The nature of all stationary points has been verified by vibrational analysis;

NCI for porphycene

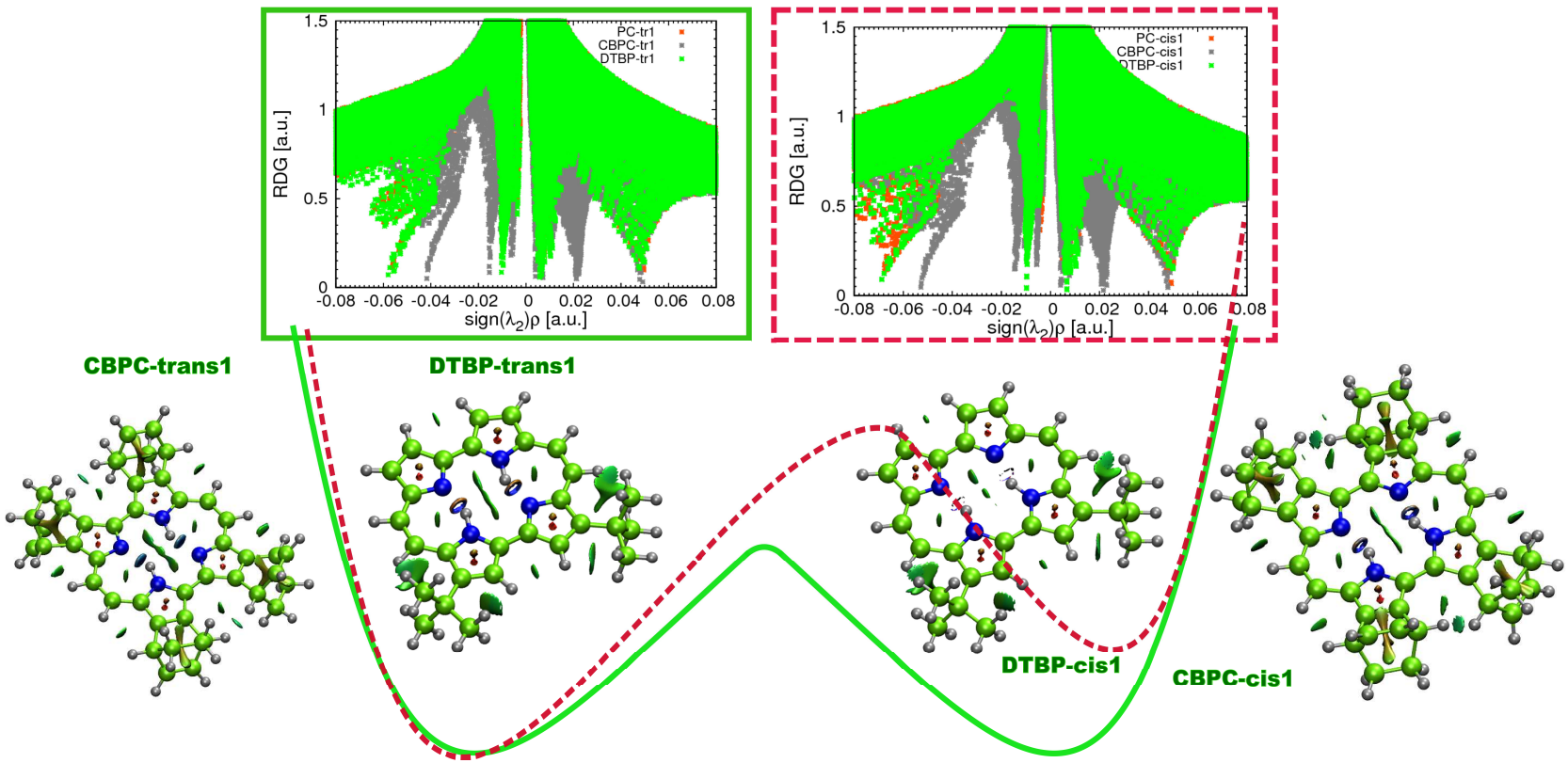




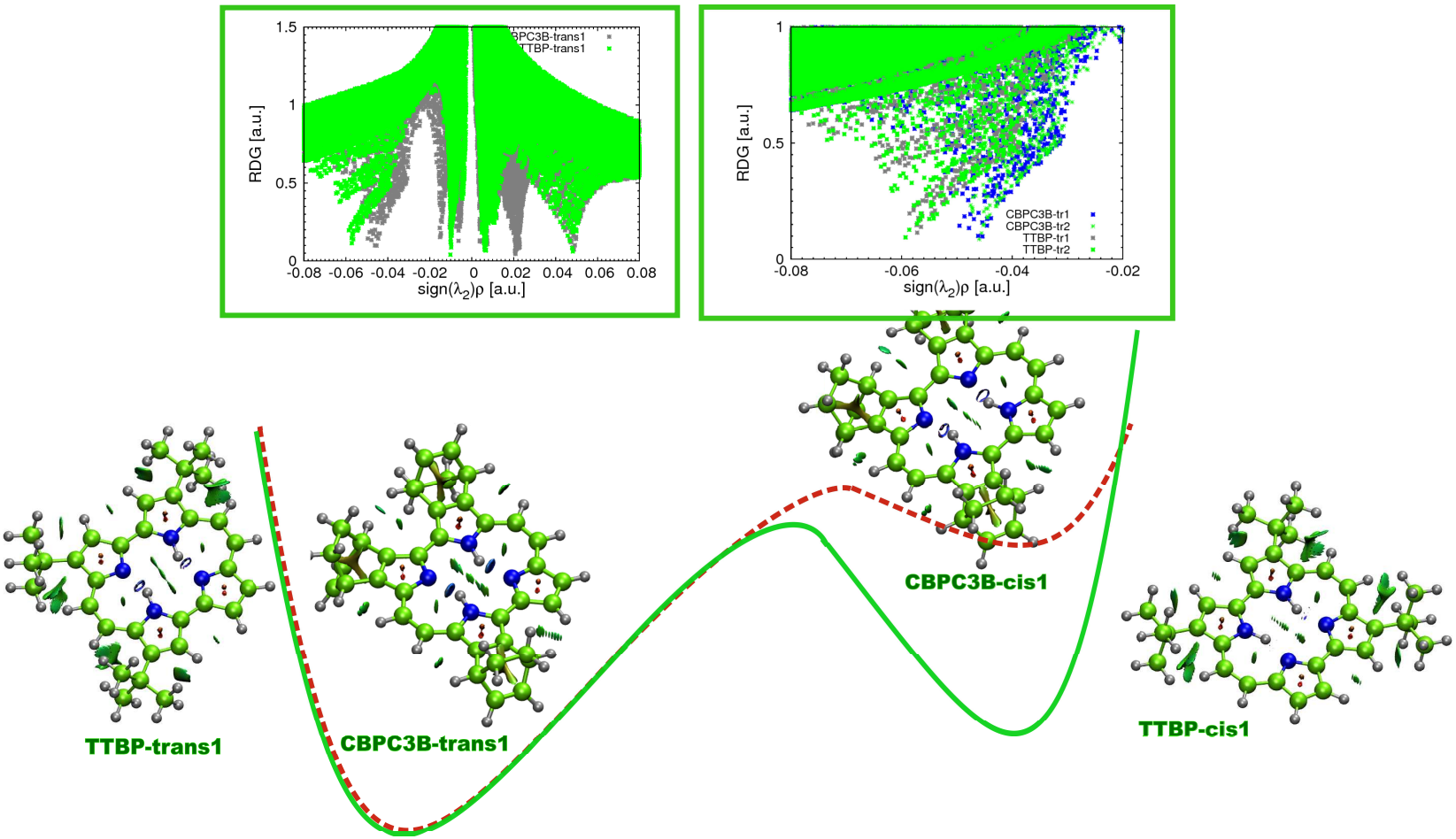
ELF analysis for porphycene



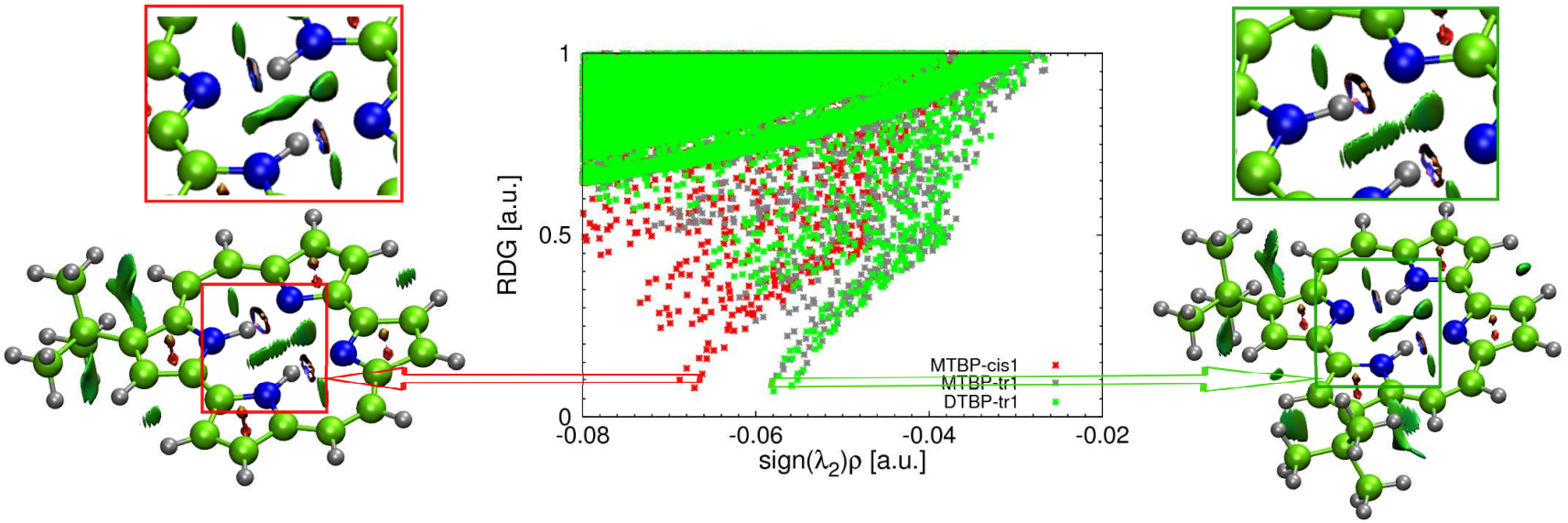
Isomerization - in case of symmetric substitution



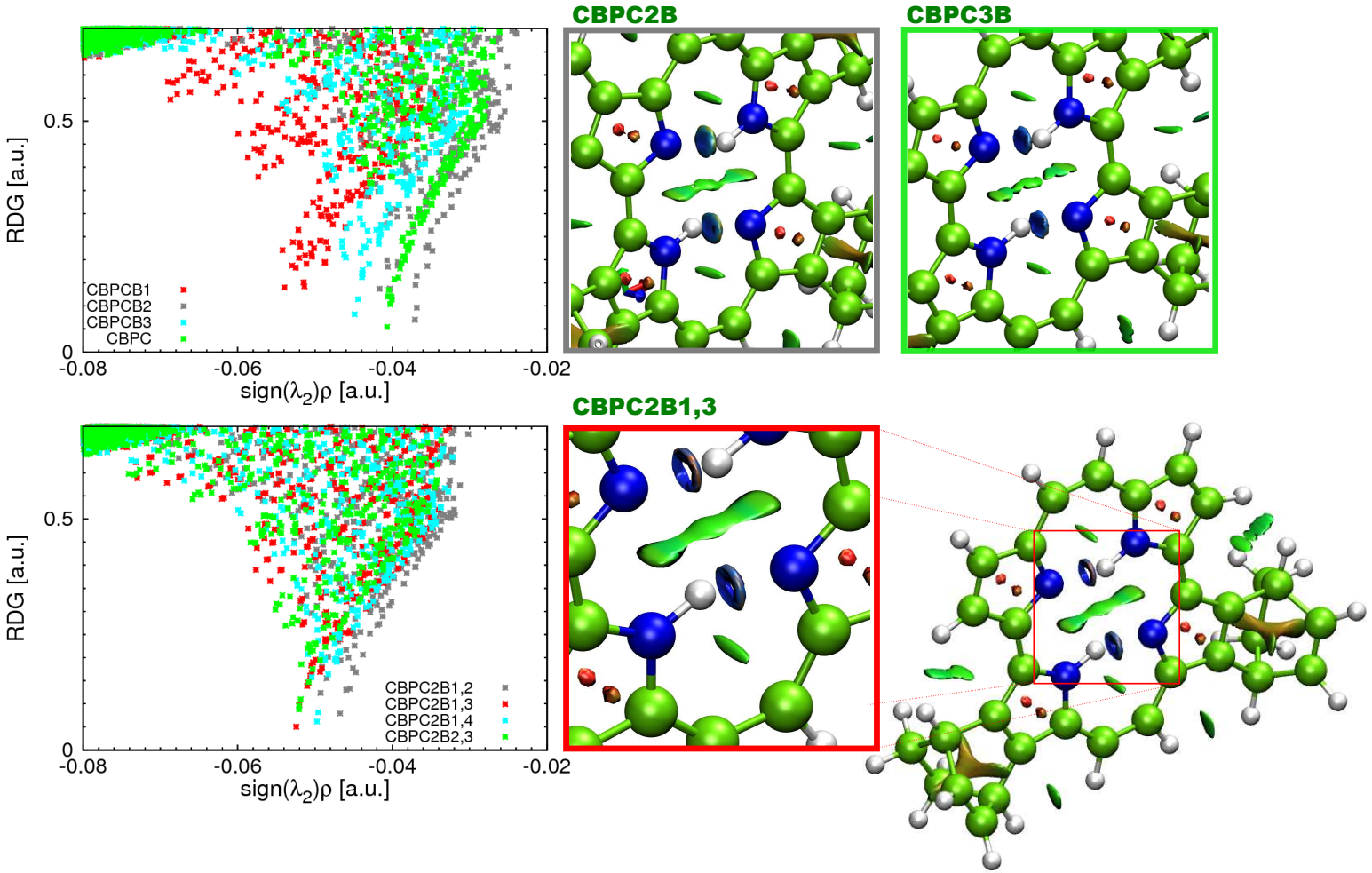
Isomerization - in case of lowered symmetry



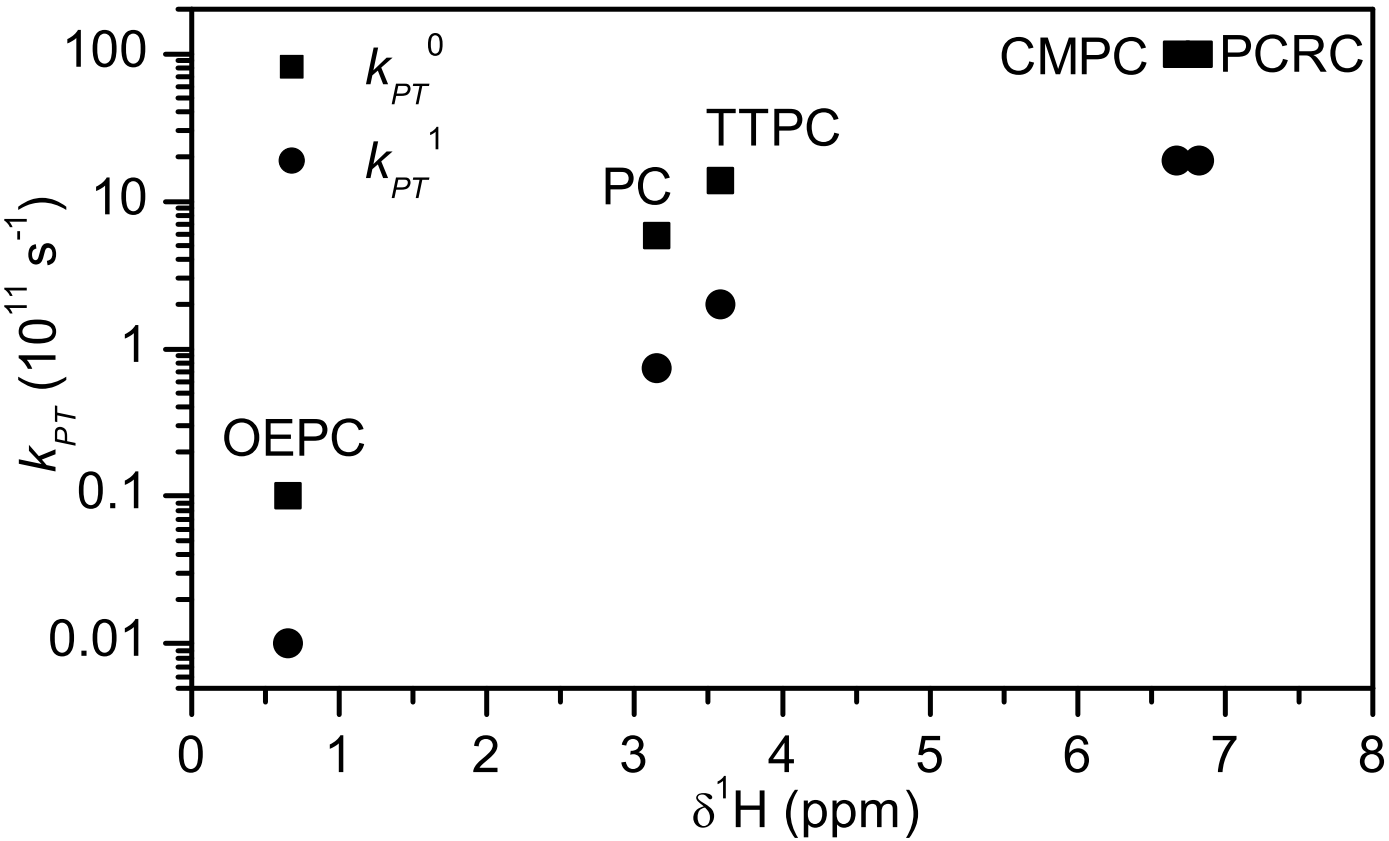
Effect of the substituent - number of substituents



Influence of bicyclo[2.2.2]octen substitution



Correlation with the chemical shift



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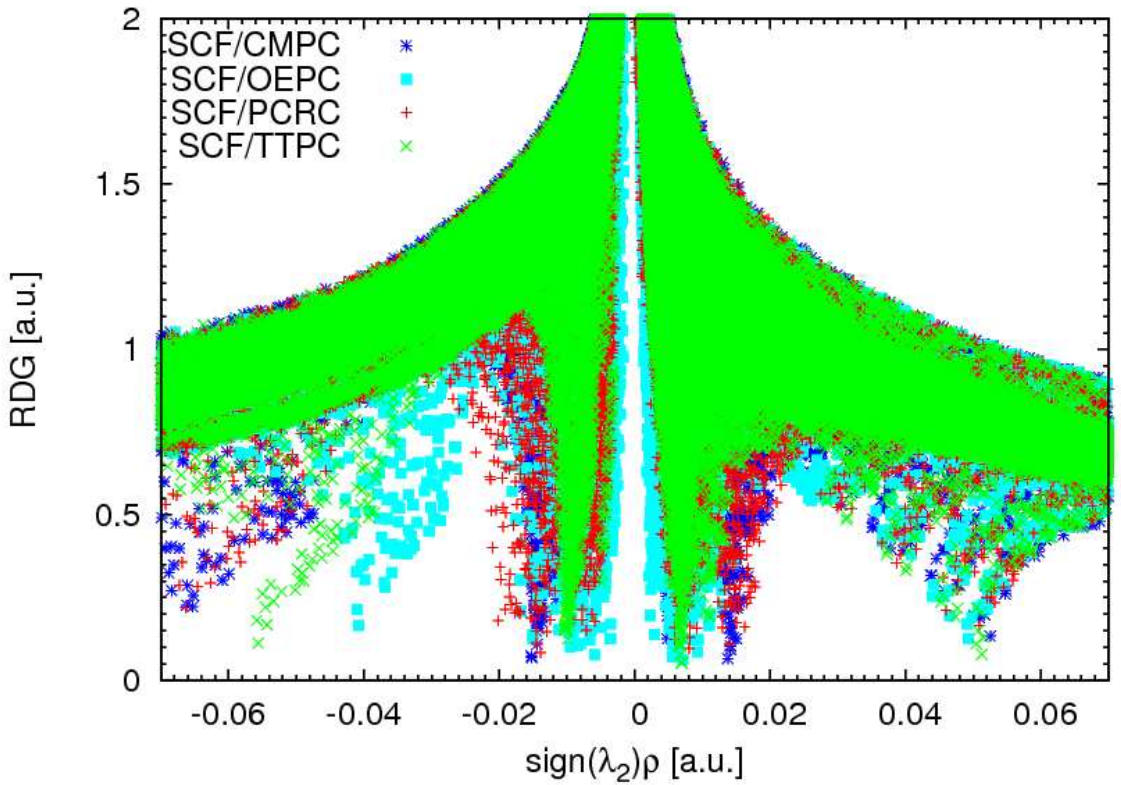
Correlation with the $sign(\lambda_2)\rho$ value



Correlation with the $sign(\lambda_2)\rho$ value

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OEPC	100	-0.0405
PC	1.80(1)	-0.0555
DTBP	1.20(1)	-0.0550
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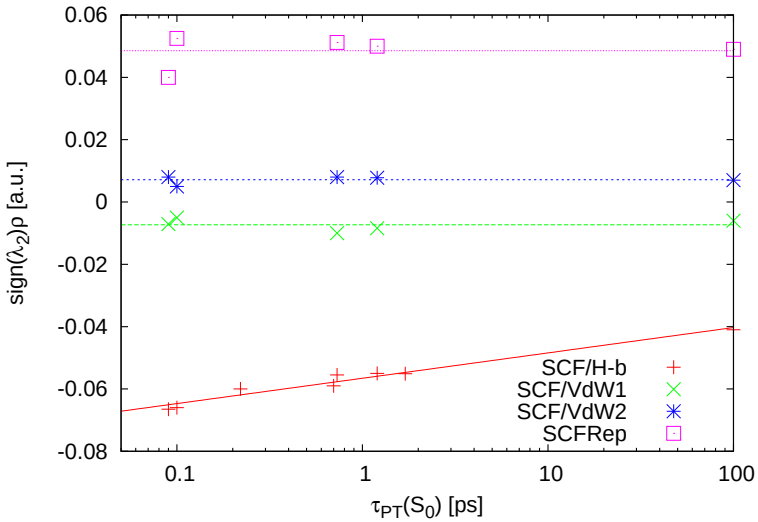
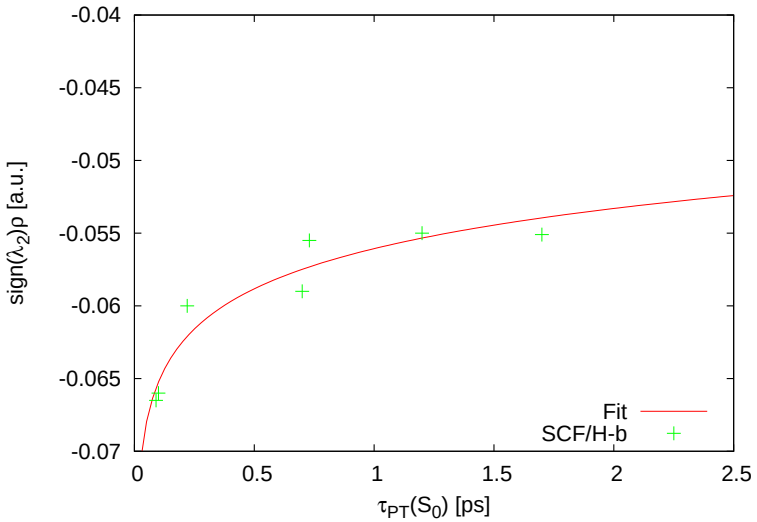
TTPC	0.62(1)	-0.0560
2MPC	0.34(1)	-0.0568
2M2B	0.22(1)	-0.0604
CMPC	0.10(1)	-0.0704
PCRC	0.10(1)	-0.0720

$sign(\lambda_2)\rho$ value as a function of proton transfer time





Conclusions

- Asymmetric distribution of electron density in the inner cavity of porphycenes is the result of asymmetric substitution;
- Hydrogen atoms transfer time depends on electron density located along the H-bonds;
- Thermodynamic parameters are not sufficient for predicting the proton transfer time;
- NCI analysis seems to be an ideal tool to search for the derivatives characterized by the time of proton transfer in the range of 10-100 ps;

Acknowledgements

This work was supported by the Foundation for Polish Science International PhD Projects Programme co-financed by the EU European Regional Development Fund and partially by the Ministry of Science and Higher Education of Poland (MNiSW)

- M. Sc. P. Ciąćka – for transient absorption anisotropy measurements
- Ph. D. Piotr Fita – for transient absorption anisotropy measurements and for useful conversations
- Prof. Czesław Radzewicz – for access to ultrafast phenomena lab