
**ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)
FOR THE PCCP PAPER
NON-ADIABATIC MOLECULAR DYNAMICS INVESTIGATION OF THE
SIZE DEPENDENCE OF THE ELECTRONIC RELAXATION IN
POLYACENES**

**Evgeny Posenitskiy^{1*} Mathias Rapacioli² Bruno Lepetit¹ Didier Lemoine¹
Fernand Spiegelman²**

¹Laboratoire Collisions Agrégats et Réactivité (LCAR), IRSAMC UMR5589
Université de Toulouse (UPS) and CNRS
118 Route de Narbonne, F-31062 Toulouse, France

²Laboratoire de Chimie et Physique Quantiques (LCPQ), IRSAMC UMR5626
Université de Toulouse (UPS) and CNRS
118 Route de Narbonne, F-31062 Toulouse, France

*posenitskiy@irsamc.ups-tlse.fr

Table S1: Experimental [1, 2, 3] and theoretical [4, 5, 6] excitation energies for first and brightest excited singlet states of polyacenes ranging in size from naphthalene to octacene. Theoretical values computed at CASPT2, CC2, TD-DFT (this work) and TD-DFTB (this work) levels of theory.

Number of cycles	Lowest singlet excitation energy, eV					Brightest singlet excitation energy, eV			
	CASPT2 [4]	CC2 [5]	TD-DFT	TD-DFTB	Exp.	CASPT2 [6]	TD-DFT	TD-DFTB	Exp.
2	4.02	4.46	4.16	4.23	4.45	5.54	5.89	5.88	5.89
3	3.48	3.69	2.96	3.12	3.42	–	5.04	5.11	5.24
4	2.79	2.90	2.20	2.39	2.63	–	4.46	4.56	4.51
5	2.20	2.35	1.66	1.88	2.12	–	4.01	4.14	4.10
6	1.89	1.95	1.28	1.51	1.89	–	3.68	3.83	3.99
7	1.66	–	0.97	1.23	1.70	–	3.42	3.58	3.8
8	–	–	0.65	1.01	1.54	–	3.18	3.39	3.78

References

- [1] Habbo H. Heinze, Andreas Görling, and Notker Rösch. An efficient method for calculating molecular excitation energies by time-dependent density-functional theory. *The Journal of Chemical Physics*, 113(6):2088–2099, 2000.
- [2] Rajib Mondal, Christina Tönshoff, Dmitriy Khon, Douglas C. Neckers, and Holger F. Bettinger. Synthesis, stability, and photochemistry of pentacene, hexacene, and heptacene: A matrix isolation study. *Journal of the American Chemical Society*, 131(40):14281–14289, 2009.
- [3] Christina Tönshoff and Holger F. Bettinger. Photogeneration of octacene and nonacene. *Angewandte Chemie International Edition*, 49(24):4125–4128, 2010.
- [4] Fernanda Bettanin, Luiz F. A. Ferrão, Max Pinheiro, Adélia J. A. Aquino, Hans Lischka, Francisco B. C. Machado, and Dana Nachtigallova. Singlet Ia and Ib bands for n-acenes (n = 2–7): A casscf/caspt2 study. *Journal of Chemical Theory and Computation*, 13(9):4297–4306, 2017. PMID: 28719203.
- [5] Stefan Grimme and Maja Parac. Substantial errors from time-dependent density functional theory for the calculation of excited states of large π systems. *ChemPhysChem*, 4(3):292–295, 2003.
- [6] Mercedes Rubio, Manuela Merchán, Enrique Ortí, and Björn O. Roos. A theoretical study of the electronic spectrum of naphthalene. *Chemical Physics*, 179(3):395–409, 1994.

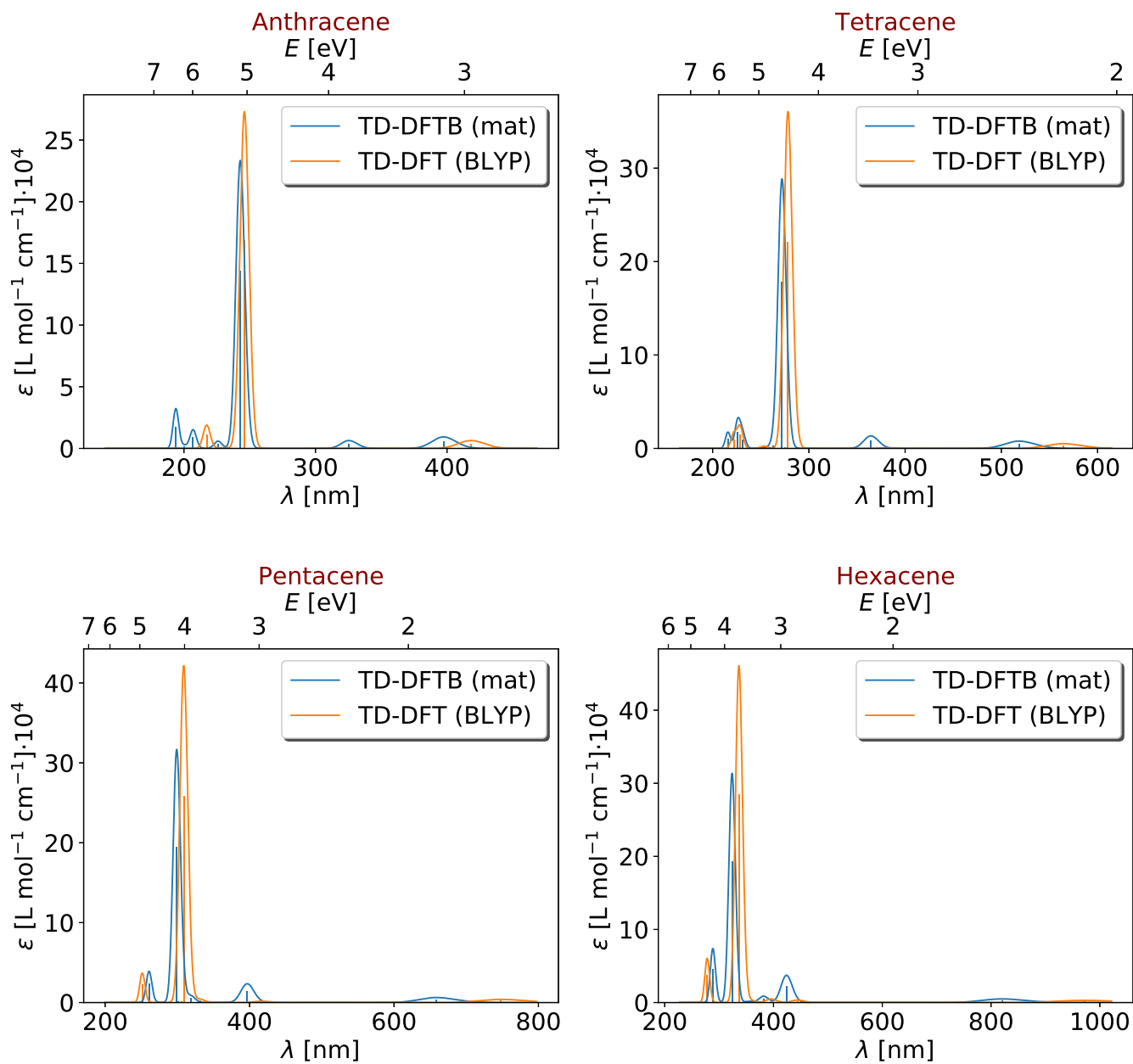


Figure S1: Absorption spectra (first 20 singlet excited states) of some polyacenes computed with TD-DFT BLYP functional using 6-31G(d,p) basis set (orange line) and TD-DFTB using matsci-0-3 set of parameters (blue line) at the equilibrium geometrical configuration. Absorbing bands (vertical sticks) were convoluted based on their oscillator strengths using Gaussian functions with standard deviation equal to 0.1 eV.

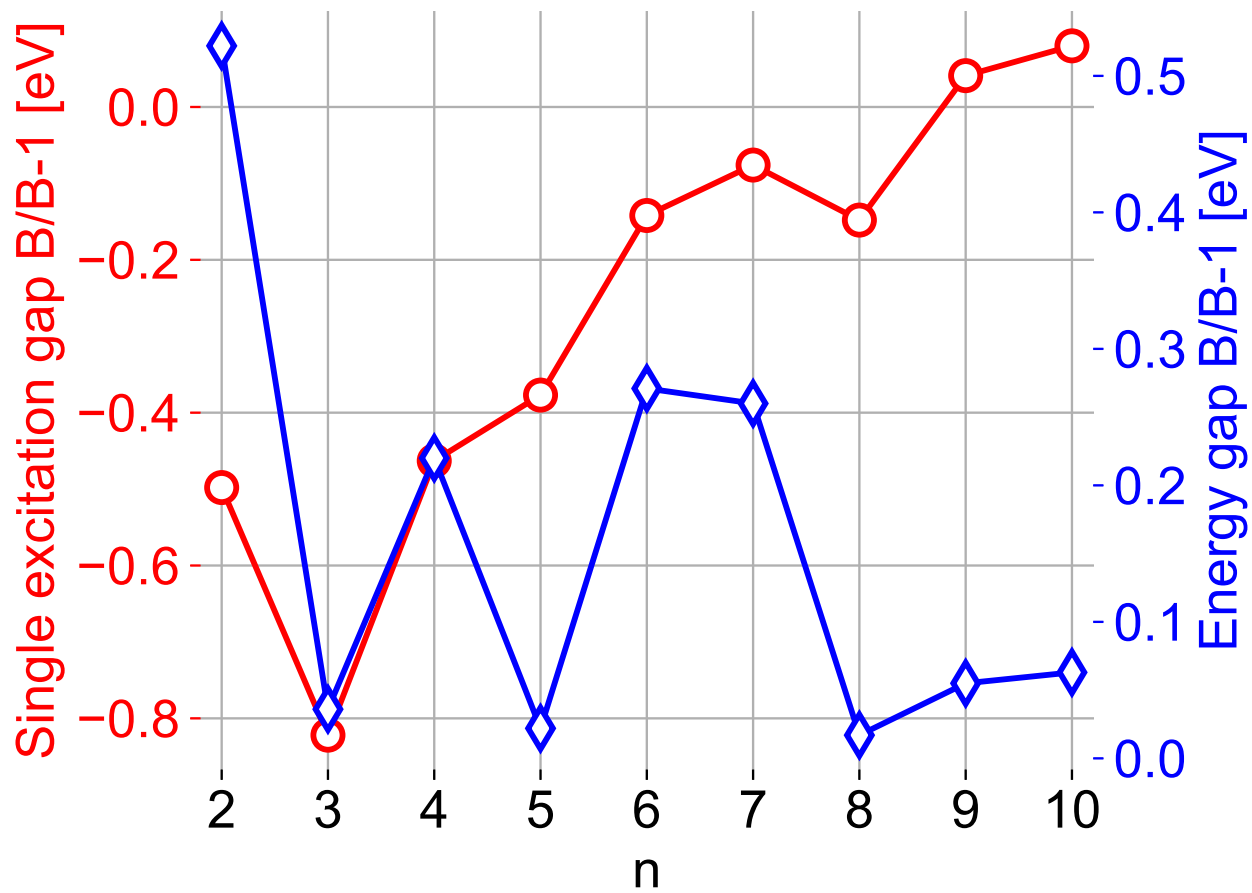


Figure S2: Energy gaps between the B and B-1 singlet excited states at the equilibrium geometry before (red circles) and after (blue diamonds) configuration interaction as a function of number of aromatic cycles in the polyacene.

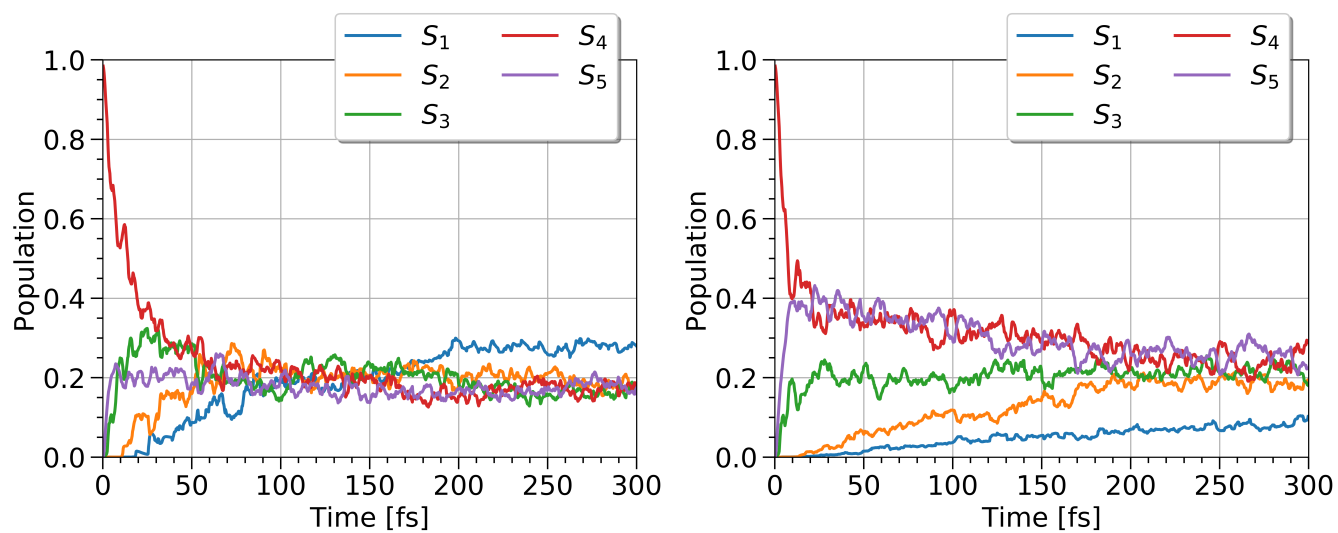


Figure S3: Population analysis of the first 5 singlet excited states in naphthalene for an ensemble of 63 trajectories with (left panel) and without (right panel) the decoherence correction. The initial (brightest) state is S_4 .