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PCCP

ELECTRONIC SUPPLEMENTARY INFORMATION

Excitons in poly(*para* phenylene vinylene): A quantum-chemical perspective based on high-level *ab initio* calculations†

Stefanie A. Mewes,[a] Jan-Michael Mewes,[a] Andreas Dreuw,[a] and Felix Plasser[a,b]

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Table of Contents

1 Evaluation of the accuracy of the approximate exciton size descriptor

Fig. 1: Benchmark of exciton size approximations: (a) Excitation energies of the first four singlet excited states of the oligomer series (PV)$_n$P with $n = 1,...,7$ calculated at the ADC(2)/SV level of theory using Q-Chem (solid lines) and at the RI-ADC(2)/SV level of theory using Turbomole (dashed lines); (b) Comparison of d_{exc} (solid lines), $\widetilde{d}_{exc}$ (dashed lines), both computed at the ADC(2)/SV level, and $\widetilde{d}_{exc}$ at the RI-ADC(2)/SV level (dotted lines); (c) errors of $\widetilde{d}_{exc}$ at the ADC(2)/SV (dashed lines) and RI-ADC(2) (dotted lines) levels with respect to d_{exc}.

2 *Electron-hole* correlation plots at the ADC(3) level of theory

Fig. 2: *Electron-hole* correlation plots of the first four electronically excited states of (PV)$_n$P oligomers with $n = 1,2,3$ calculated at the ADC(2)/SV(P) and ADC(3)/SV(P) levels of theory.

3 Triplet excitons in PPV oligomers of increasing size

Tab. 1: Excitation energies (ΔE, eV), singles amplitudes (t_1), charge-transfer measures (ω_{CT}) and exciton sizes (d_{exc}, Å) for the first four excited states of PPV oligomers (PV)$_n$P with $n = 1,...,7$ at the RI-ADC(2)/TZVP level of theory.

Fig. 3: (a) Vertical excitation energies (ΔE, eV), (b) approximate exciton sizes (d'_{exc}, Å), and (c) charge-transfer measure (ω_{CT}) of poly(*para* phenylene vinylene) oligomers of increasing chain length n computed at the RI-ADC(2)/TZVP (solid lines) and RI-ADC(2)/SV(P) (dotted lines) levels of theory.

Fig. 4: *Electron-hole* correlation plots of the first four triplet excited states of (PV)$_n$P computed at the RI-ADC(2)/TZVP level of theory.

1 Evaluation of the accuracy of the approximate exciton size descriptor

In the following we will address the question whether the simplified exciton size $\widetilde{d}_{exc}$ [Eq. 13] is a suitable approximation to the more rigorously defined d_{exc} measure [Eq. 9].

Simultaneously, the two ADC(2) implementations used are compared: the canonical implementation in Q-Chem,[1,2] which allows an efficient computation of density matrices and therefore d_{exc}, and the RI implementation of Turbomole,[3–5] which allows the treatment of larger systems.

First, the excitation energies computed at the ADC(2)/SV and RI-ADC(2)/SV levels of theory using the two implementations are compared. The results are presented in Fig. 1 (a), which reproduces the findings of Ref. 6: The lowest excited state is always the 1^1B_u state which is smoothly lowered in energy for increasing length of the π-conjugated system, from approximately 5 to 3 eV. For all systems except for the (PV)$_2$P oligomer, the second lowest state is 2^1A_g and similarly to the 1^1B_u state a convergence in excitation energy for larger chains is observed. The 2^1B_u energies fluctuate, being similar to the 2^1A_g ones first and higher for larger oligomers. The highest-energy state in this series is the 3^1A_g state for all oligomers. It starts at $\Delta E = 6.38$ eV for PVP, shows a significant drop until (PV)$_3$P and stays rather flat afterwards. In most cases the RI-ADC(2) excitation energies, shown as dashed lines in Fig. 1 (a) show only minor deviations when compared to the canonical implementation with differences on the order of 0.01 eV. However, these discrepancies are larger for the 3^1A_g energies, and in the cases of $n = 4,5,6$ there are deviations on the order of 0.05 eV indicating that the methods here converge on different states.

Having discussed the excitation energies, we turn to the main purpose of this section, an assessment of the accuracy of the simplified exciton size $\widetilde{d}_{exc}$, as defined in Eq. 13, by benchmarking against the more rigorously defined d_{exc} value. Owing to the differences present between the canonical and RI implementations,

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[a] *Interdisciplinary Center for Scientific Computing, Ruprecht-Karls University, Im Neuenheimer Feld 368, D-69120 Heidelberg, GERMANY.*

[b] *Institute for Theoretical Chemistry, University of Vienna, Währingerstr. 17, A-1090 Wien, AUSTRIA; E-mail: felix.plasser@univie.ac.at*

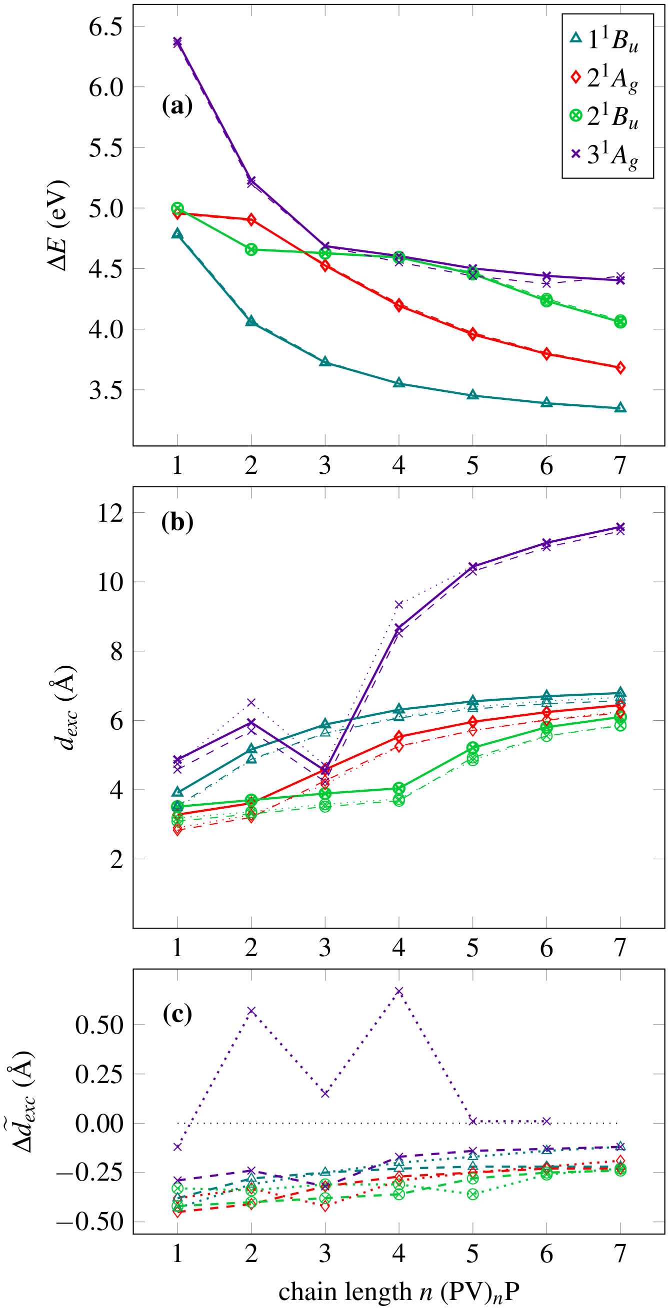

Fig. 1 Benchmark of exciton size approximations: (a) Excitation energies of the first four singlet excited states of the oligomer series (PV)$_n$P with $n = 1, \ldots, 7$ calculated at the ADC(2)/SV level of theory using Q-Chem (solid lines) and at the RI-ADC(2)/SV level of theory using Turbomole (dashed lines); (b) Comparison of d_{exc} (solid lines), $\tilde{d}_{exc}$ (dashed lines), both computed at the ADC(2)/SV level, and $\tilde{d}_{exc}$ at the RI-ADC(2)/SV level (dotted lines); (c) errors of $\tilde{d}_{exc}$ at the ADC(2)/SV (dashed lines) and RI-ADC(2) (dotted lines) levels with respect to d_{exc}.

we use three different protocols for the computation of the exciton size: (i) d_{exc} and (ii) $\tilde{d}_{exc}$ both from canonical ADC(2)/SV, as well as, (iii) $\tilde{d}_{exc}$ from RI-ADC(2)/SV. Going from (i) to (ii) amounts to a point-charge approximation, while the difference between (ii) and (iii) is of a more methodological nature: the different implementations and the use of approximate 1TDMs as explained in the Computational Details. The results are shown in Fig. 1 (b) using solid lines for (i), dashes for (ii) and dots for (iii). The deviations of the latter two methods against (i) are shown in Fig. 1 (c). At first sight the approximate exciton size values show a good agreement with the reference with the only difference that they are generally smaller. This can be explained by the fact that the former compresses the 1TDM into point charges while only the latter takes into account the size of the individual orbitals. This underestimation shows a value of about 0.45 Å for the smaller oligomers and steadily decreases with increasing oligomer size. A different trend is observed for the 3^1A_g states computed at the RI-ADC(2) level. These show larger fluctuations with also positive deviations as a consequence of describing different states.

Neither the systematic minor underestimation of the simplified exciton size (≈ 0.3 Å) nor the small differences between the ADC(2) and RI-ADC(2) excitation energies (< 0.05 eV) should affect the interpretative power of the computations performed. For these reasons, we choose the computationally most efficient protocol, RI-ADC(2), for the subsequent investigations. This method allows us to extend the basis set to the polarized triple-ζ level[7] as well as to compute a significantly enhanced number of excited states at an acceptable computational cost.

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2 Electron-hole correlation plots at the ADC(3) level of theory

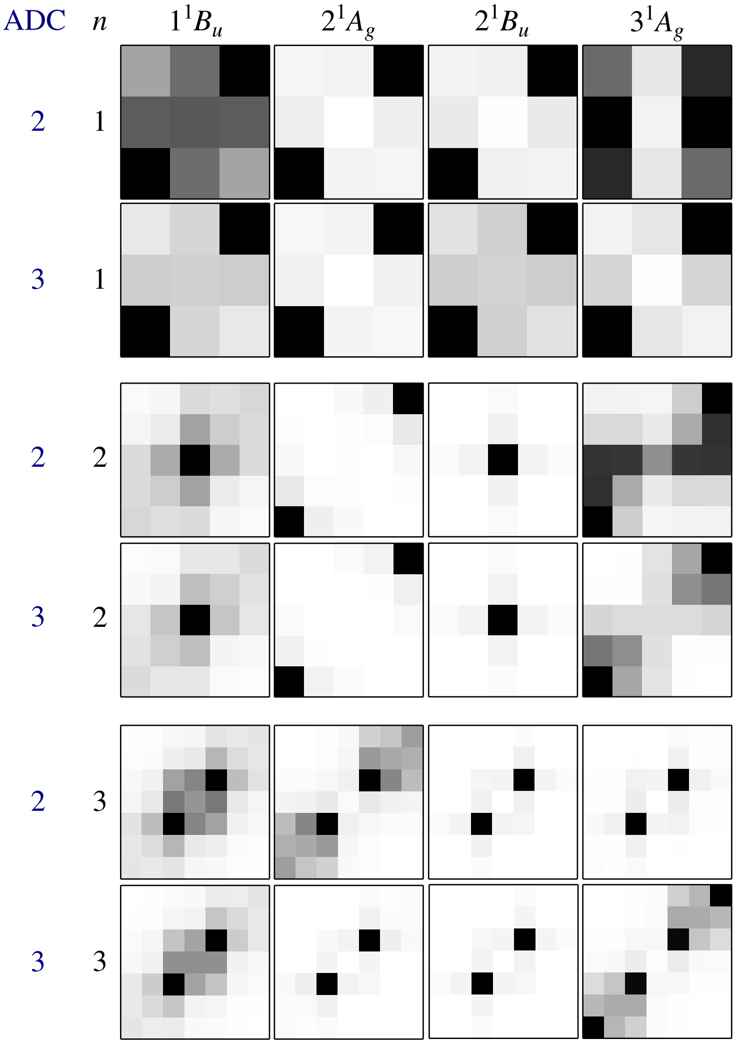

Fig. 2 *Electron-hole* correlation plots of the first four electronically excited states of (PV)$_n$P oligomers with $n = 1, 2, 3$ calculated at the ADC(2)/SV(P) and ADC(3)/SV(P) levels of theory. Only the plots corresponding to singly excited states are shown in the case of ADC(3) and the state nomenclature refers to the ADC(2) states.

3 Triplet excitons in PPV oligomers of increasing size

Table 1 Excitation energies (ΔE, eV), singles amplitudes (t_1), charge-transfer measures (ω_{CT}) and exciton sizes ($\widetilde{d}_{exc}$, Å) for the first four excited states of PPV oligomers (PV)$_n$P with $n = 1, \ldots, 7$ at the RI-ADC(2)/TZVP level of theory.

	state	$\Delta E\,$(eV)	t_1	ω_{CT}	$\widetilde{d}_{exc}$
$n=1$	1^3B_u	2.823	0.98	0.07	2.97
	1^3A_g	4.079	0.99	0.01	2.21
	2^3B_u	4.581	0.98	0.03	2.50
	2^3A_g	4.631	0.98	0.06	2.91
$n=2$	1^3B_u	2.439	0.98	0.14	3.79
	1^3A_g	3.082	0.98	0.07	2.95
	2^3B_u	3.982	0.99	0.02	2.52
	2^3A_g	4.463	0.99	0.01	2.04
$n=3$	1^3B_u	2.285	0.98	0.17	4.26
	1^3A_g	2.705	0.98	0.11	3.52
	2^3B_u	3.209	0.98	0.07	2.96
	2^3A_g	3.931	0.98	0.03	2.68
$n=4$	1^3B_u	2.212	0.98	0.19	4.52
	1^3A_g	2.500	0.98	0.14	3.91
	2^3B_u	2.878	0.98	0.10	3.40
	2^3A_g	3.284	0.98	0.07	2.96
$n=5$	1^3B_u	2.174	0.98	0.20	4.67
	1^3A_g	2.379	0.98	0.16	4.18
	2^3B_u	2.665	0.98	0.13	3.73
	2^3A_g	2.997	0.98	0.10	3.32
$n=6$	1^3B_u	2.151	0.98	0.20	4.76
	1^3A_g	2.304	0.98	0.18	4.37
	2^3B_u	2.526	0.98	0.15	3.97
	2^3A_g	2.792	0.98	0.12	3.60
$n=7$	1^3B_u	2.123	0.98	0.22	4.98
	1^3A_g	2.248	0.98	0.20	4.63
	2^3B_u	2.429	0.98	0.17	4.25
	2^3A_g	2.652	0.98	0.14	3.90

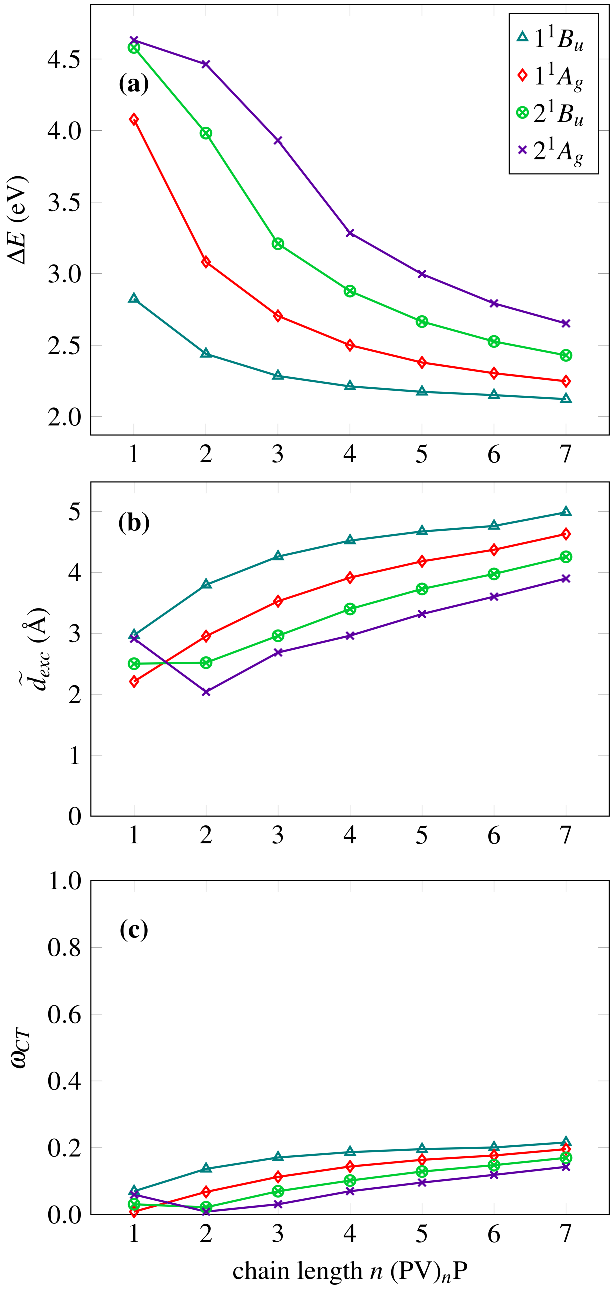

Fig. 3 (a) Vertical excitation energies (ΔE, eV), (b) approximate exciton sizes ($\widetilde{d}_{exc}$, Å), and (c) charge-transfer measure (ω_{CT}) of poly(*para* phenylene vinylene) oligomers of increasing chain length n computed at the RI-ADC(2)/TZVP (solid lines) and RI-ADC(2)/SV(P) (dotted lines) levels of theory.

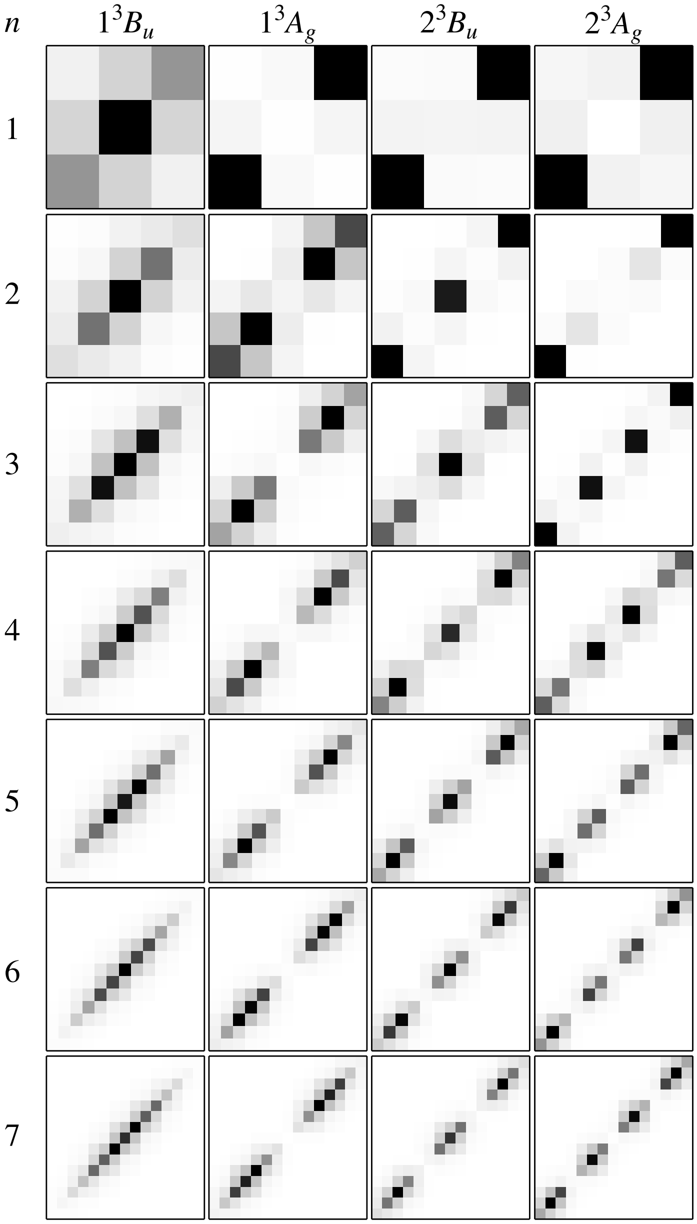

Fig. 4 *Electron-hole* correlation plots Ω_{AB} of the first four triplet excited states of $(\mathrm{PV})_n\mathrm{P}$ computed at the RI-ADC(2)/TZVP level of theory.