Supplementary Materials

Conformation-driven (de)localization of exciton in 2-Phenylpyridine oligomers: Non-adiabatic surface hopping dynamics

Palak Mandal and Aditya N. Panda*

Department of Chemistry, Indian Institute of Technology Guwahati, 781039, India

E-mail: anp@iitg.ac.in

List of Tables

List of Figures

Computational details

The TD-DFTB and LC-TD-DFTB calculations are carried out using the ob2 Slater-Koster file[1] utilizing the DFTB+[2] software. The RI-ADC(2) calculations are performed using the def2-SV(P) basis set in conjunction with the resolution of identity (RI) approximation.[3] Turbomole V7.2[4] software is used for the RI-ADC(2) calculations. For the excited-state dynamics simulation, initially, we have generated 500 sets of initial conditions (ICs) using the harmonic-oscillator Wigner distribution.[5] From these initial 500 sets, sets of ICs were selected starting from the bright states by applying a narrow energy window shown in Figures S1. The following bright excited states are considered for the two conformers while selecting the ICs: S_1, S_3 in **(PhPy)**$_2$-**A**, S_1, S_3, and S_7 in **(PhPy)**$_2$-**B**, S_1, S_4, and S_6 in **(PhPy)**$_5$-**A**, and S_3, and S_6 states in **(PhPy)**$_5$-**B**. In these figures the bar plots are for the optimized geometries and the sticks are for the 500 ICs. In **(PhPy)**$_2$-**A**, the 4.40±0.20 eV energy window produces 89 ICs in the S_3 state and the 4.25±0.20 eV energy window produces 47 ICs in the S_1 state. In **(PhPy)**$_2$-**B**, the energy window 4.96±0.20 eV produces 39 ICs in the S_7 state, 4.55±0.20 eV produces 65 ICs in the S_3 state, and 4.30±0.20 eV produces 27 ICs. In the case of dimers, we only discuss the dynamics results starting from the S_3 states. Similarly, in the case of pentamers, the dynamics results, which started from the S_4 (**(PhPy)**$_5$-**A**) and S_3(**(PhPy)**$_5$-**B**) states, are discussed. The trajectory surface hopping (TSH) dynamics were carried out utilizing Newton-X[6] software.

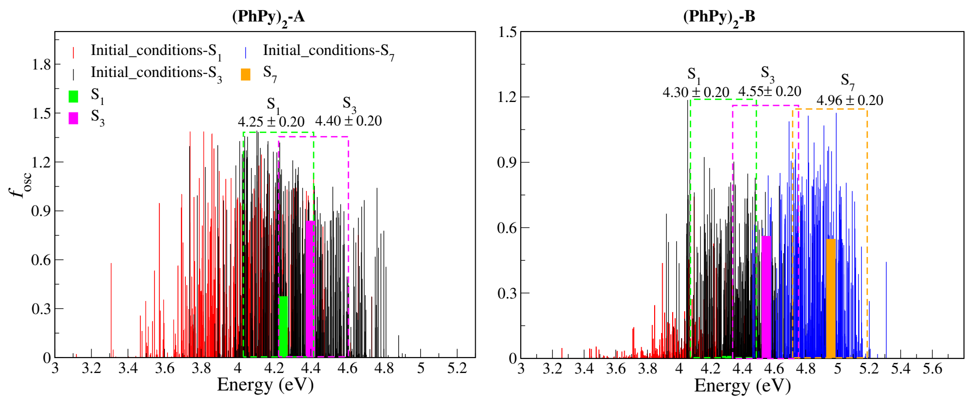

Figure S1: Energy window for the initial condition sampling of $\mathbf{(PhPy)}_2$.

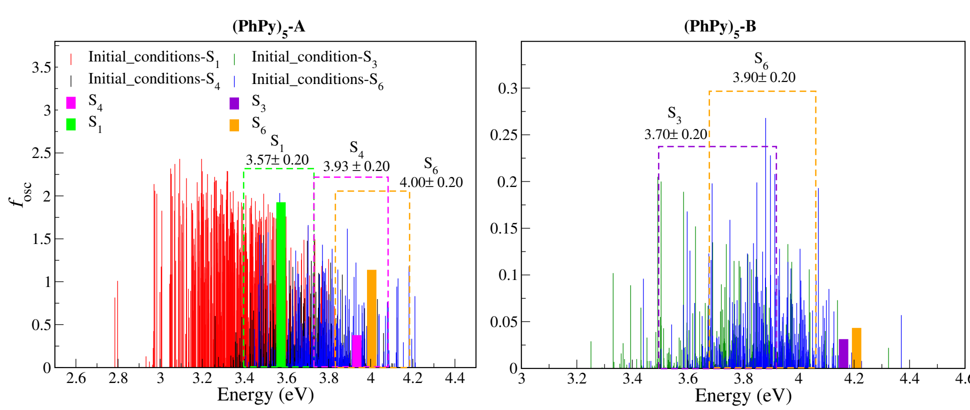

Figure S2: Energy window for the initial condition sampling of $\mathbf{(PhPy)}_2$.

CT analysis

In CT analysis, at first, the CT numbers, denoted as Ω_{AB} between the fragments A and B, are computed from the one-electron transition density matrix (1TDM).[7,8] Once the full Ω matrix consisting of all Ω_{AB} is constructed, descriptors such as CT parameter (ω_{CT}),[7,9] and the participation ratio of natural transition orbitals (NTOs) ($\mathrm{PR_{NTO}}$)[7,10] are computed to analyze the excited states. The values of ω_{CT} range from 0 to 1; 0 is for a locally excited (LE) state and 1 is for a pure CT state. The value of $\mathrm{PR_{NTO}}$ indicates the number of pairs of NTOs involved in a particular electronic transition. For the computation of the Ω matrix containing all Ω_{AB} values, each monomeric unit (**PhPy** unit) is considered as a one fragment; therefore, **(PhPy)**$_2$ and **(PhPy)**$_5$ have two and five fragments, respectively. The plotting of Ω gives 2x2 and 5x5 matrices for **(PhPy)**$_2$ and **(PhPy)**$_5$, respectively, and these plots are known as the *e*-*h* correlation plots. For the dimer, the *e*-*h* correlation plots shown in Figure S3 display the *h* and *e* positions along the horizontal and vertical axes, respectively. The diagonal of the *e*-*h* correlation plots (from lower left to upper right) shows the extent of local exciton, and the off-diagonal contributions show the amount of CT between the fragments. . The CT analysis is carried out using the TheoDORE 3.0 software package[11]

Table S1: Excitation energy (E_{g}) and the corresponding oscillator strengths (f_{osc}) values for the first ten excited states of $\mathbf{(PhPy)_2}$ and $\mathbf{(PhPy)_5}$

			A			
		$\mathbf{(PhPy)_2}$			$\mathbf{(PhPy)_5}$	
State	TD-DFTB	LC-TD-DFTB	RI-ADC(2)	TD-DFTB	LC-TD-DFTB	RI-ADC(2)
S_1	4.25 / 0.374	4.23 / 0.046	4.51 / 1.539	3.57 / 1.922	4.11 / 2.065	4.04 / 5.185
S_2	4.36 / 0.102	4.40 / 0.000	4.63 / 0.268	3.71 / 0.037	4.17 / 0.019	4.34 / 0.066
S_3	4.40 / 0.838	4.66 / 1.555	4.77 / 0.003	3.90 / 0.022	4.19 / 0.036	4.53 / 0.084
S_4	4.79 / 0.003	4.98 / 0.000	4.85 / 0.055	3.93 / 0.374	4.22 / 0.650	4.54 / 0.001
S_5	5.08 / 0.027	5.05 / 0.000	4.90 / 0.046	3.99 / 0.001	4.26 / 2.083	4.54 / 0.011
S_6	5.16 / 0.001	5.41 / 0.003	5.06 / 0.010	4.01 / 1.135	4.40 / 0.000	4.60 / 0.004
S_7	5.27 / 0.006	5.55 / 0.001	5.11 / 0.003	4.03 / 0.051	4.51 / 0.060	4.67 / 0.320
S_8	5.32 / 0.024	5.65 / 0.011	5.17 / 0.033	4.04 / 0.077	4.83 / 0.352	4.74 / 0.024
S_9	5.41 / 0.006	5.73 / 0.004	5.21 / 0.014	4.08 / 0.003	4.98 / 0.000	4.75 / 0.006
S_{10}	5.43 / 0.007	5.77 / 0.000	5.53 / 0.002	4.11 / 0.006	4.98 / 0.000	4.79 / 0.059
			B			
S_1	4.30 / 0.010	4.34 / 0.004	4.57 / 0.822	4.06 / 0.002	4.27 / 0.001	4.34 / 0.167
S_2	4.43 / 0.002	4.39 / 0.001	4.68 / 0.015	4.13 / 0.004	4.28 / 0.000	4.47 / 1.465
S_3	4.55 / 0.560	4.46 / 0.001	4.75 / 0.073	4.16 / 0.031	4.29 / 0.001	4.51 / 0.538
S_4	4.75 / 0.009	4.84 / 1.133	4.81 / 0.189	4.18 / 0.001	4.32 / 0.004	4.56 / 0.066
S_5	4.83 / 0.090	5.04 / 0.000	4.83 / 0.008	4.19 / 0.001	4.33 / 0.004	4.59 / 0.073
S_6	4.89 / 0.013	5.32 / 0.199	4.94 / 0.227	4.21 / 0.043	4.35 / 0.000	4.61 / 0.013
S_7	4.96 / 0.547	5.48 / 0.254	5.10 / 0.035	4.22 / 0.014	4.36 / 0.002	4.61 / 0.089
S_8	5.28 / 0.001	5.51 / 0.003	5.17 / 0.016	4.23 / 0.007	4.38 / 0.003	4.63 / 0.140
S_9	5.40 / 0.003	5.78 / 0.000	5.22 / 0.030	4.24 / 0.006	4.44 / 0.000	4.66 / 0.018
S_{10}	5.47 / 0.005	5.79 / 0.003	5.42 / 0.599	4.25 / 0.005	4.64 / 0.173	4.69 / 0.105

Table S2: Excitation energy (E_g), oscillator strengths (f_{osc}), and ω_{CT} values for the first ten excited states at different times of single representative trajectories for $(PhPy)_2$-A and B

TD-DFTB								
	$(PhPy)_2$-A				**$(PhPy)_2$-B**			
	0 fs (S_3)		138 fs (S_1)		0 fs (S_3)		141 fs (S_1)	
State	E_g/ f_{osc}	ω_{CT}	E_g/ f_{osc}	ω_{CT}	E_g/ f_{osc}	ω_{CT}	E_g/ f_{osc}	ω_{CT}
S_1	4.04 / 0.585	0.58	2.27 / 0.018	0.47	4.25 / 0.013	0.77	2.99 / 0.037	0.30
S_2	4.08 / 0.002	0.37	3.19 / 0.070	0.54	4.45 / 0.015	0.23	3.36 / 0.145	0.69
S_3	4.34 / 0.643	0.63	3.30 / 0.000	0.53	4.71 / 0.566	0.57	3.48 / 0.010	0.97
S_4	4.60 / 0.001	0.82	3.48 / 1.572	0.55	4.90 / 0.261	0.65	3.67 / 0.621	0.61
S_5	4.90 / 0.007	0.60	3.63 / 0.004	0.04	4.96 / 0.009	0.71	3.79 / 0.077	0.48
S_6	4.94 / 0.024	0.39	3.89 / 0.002	0.78	5.11 / 0.012	0.24	3.93 / 0.208	0.65
S_7	5.04 / 0.007	0.68	4.02 / 0.002	0.90	5.16 / 0.015	0.45	4.02 / 0.007	0.43
S_8	5.10 / 0.006	0.51	4.24 / 0.000	0.90	5.22 / 0.018	0.49	4.10 / 0.111	0.55
S_9	5.13 / 0.006	0.47	4.24 / 0.001	0.56	5.26 / 0.033	0.74	4.30 / 0.048	0.59
S_{10}	5.21 / 0.005	0.54	4.26 / 0.024	0.53	5.29 / 0.012	0.71	4.47 / 0.002	0.25
RI-ADC(2)								
S_1	4.26 / 0.729	0.29	2.87 / 0.006	0.07	4.51 / 0.232	0.32	3.44 / 0.080	0.08
S_2	4.46 / 0.209	0.11	3.63 / 0.665	0.32	4.59 / 0.004	0.05	3.77 / 0.567	0.37
S_3	4.54 / 0.633	0.16	3.76 / 1.488	0.36	4.77 / 0.101	0.10	3.89 / 0.320	0.32
S_4	4.64 / 0.175	0.21	3.92 / 0.004	0.23	4.84 / 0.351	0.14	4.09 / 0.401	0.22
S_5	4.71 / 0.012	0.19	4.12 / 0.002	0.01	4.90 / 0.260	0.26	4.21 / 0.046	0.26
S_6	4.90 / 0.003	0.11	4.36 / 0.002	0.09	5.01 / 0.067	0.16	4.35 / 0.032	0.22
S_7	4.94 / 0.026	0.11	4.57 / 0.005	0.24	5.09 / 0.182	0.19	4.55 / 0.027	0.14
S_8	4.99 / 0.003	0.03	4.70 / 0.007	0.29	5.23 / 0.112	0.16	4.57 / 0.015	0.06
S_9	5.04 / 0.052	0.17	4.74 / 0.001	0.38	5.36 / 0.035	0.14	4.75 / 0.142	0.16
S_{10}	5.38 / 0.017	0.14	4.78 / 0.005	0.25	5.86 / 0.306	0.22	4.83 / 0.357	0.17

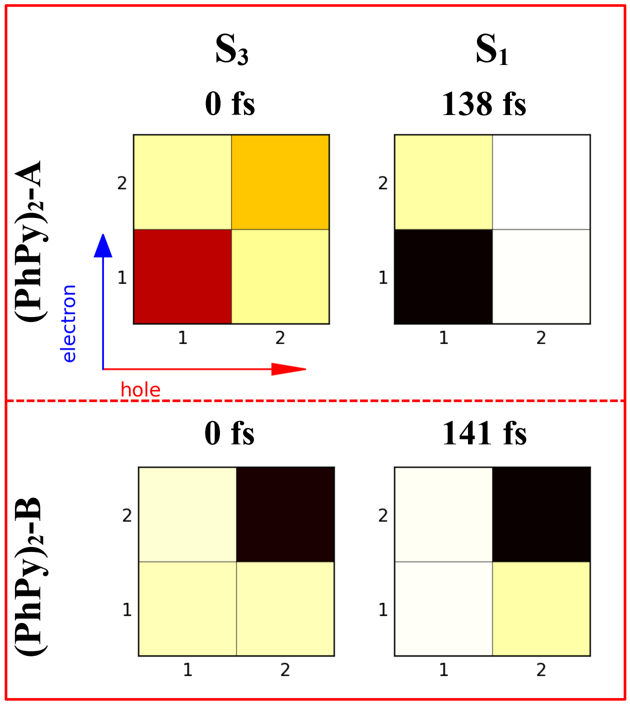

Figure S3: Electron-hole correlation plots involved in the current states of a selected trajectory at different times for **(PhPy)**$_2$**-A** and **B** obtained at the RI-ADC(2) level.

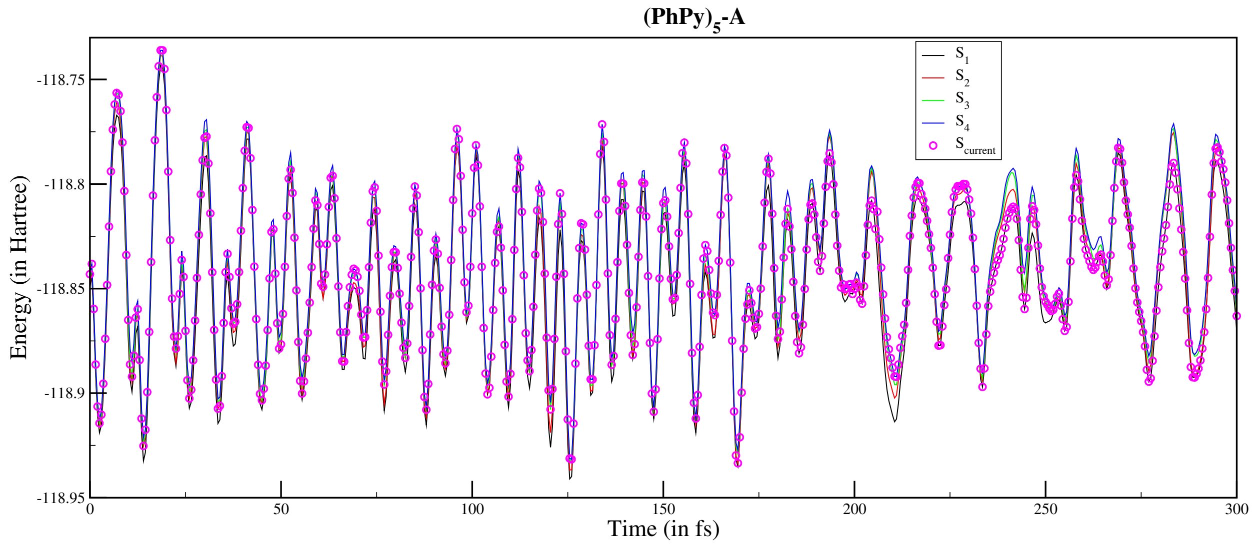

Figure S4: Energies of the first four excited states S_1-S_4 of a single representative trajectory as a function of time of $\mathbf{(PhPy)_5}$-**A**. Magenta circles indicate the current state of the system.

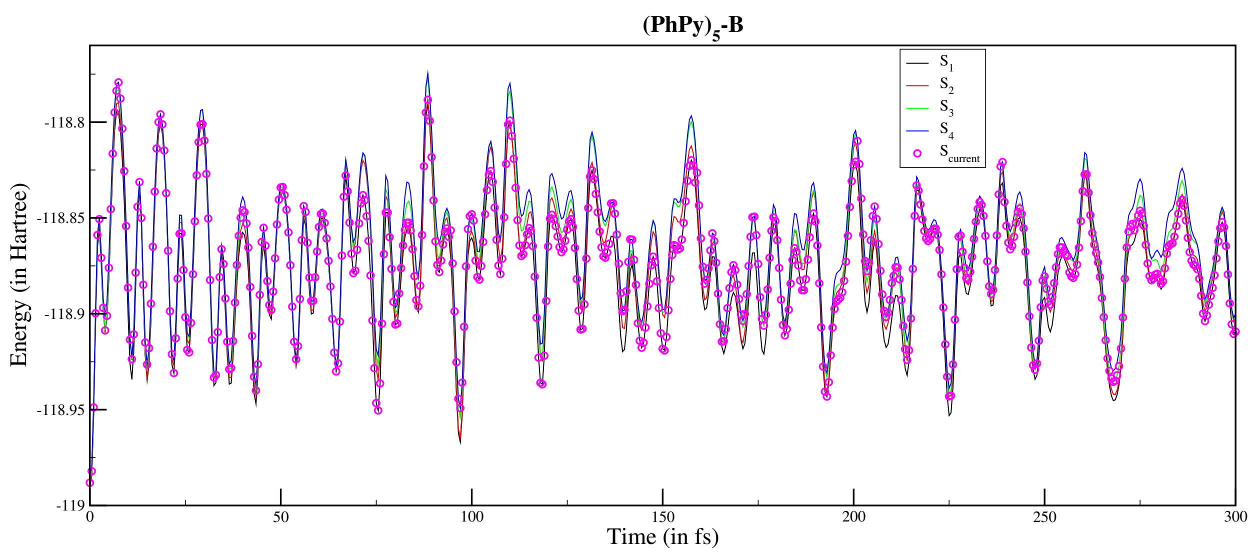

Figure S5: Energies of the first four excited states S_1-S_4 of a single representative trajectory as a function of time of $\mathbf{(PhPy)_5}$-**B**. Magenta circles indicate the current state of the system.

Table S3: Excitation energy (E_{g}), oscillator strengths (f_{osc}), and ω_{CT} values for the first ten excited states at different times of single representative trajectories for $(\mathrm{PhPy})_5$-A

	TD-DFTB							
	0 fs (S_4)		2 fs (S_3)		13 fs (S_2)		101.5 fs (S_1)	
State	$E_{\mathrm{g}}/f_{\mathrm{osc}}$	ω_{CT}	$E_{\mathrm{g}}/f_{\mathrm{osc}}$	ω_{CT}	$E_{\mathrm{g}}/f_{\mathrm{osc}}$	ω_{CT}	$E_{\mathrm{g}}/f_{\mathrm{osc}}$	ω_{CT}
S_1	3.69 / 1.049	0.87	3.46 / 1.669	0.83	2.79 / 0.729	0.93	2.64 / 1.393	0.78
S_2	3.75 / 0.001	0.93	3.56 / 0.010	0.94	3.00 / 1.365	0.87	2.72 / 0.420	0.64
S_3	3.88 / 0.079	0.86	3.65 / 0.155	0.93	3.06 / 0.153	0.90	2.79 / 0.029	0.97
S_4	3.89 / 0.142	0.87	3.70 / 0.363	0.89	3.19 / 0.156	0.76	2.81 / 0.182	0.92
S_5	3.96 / 0.027	0.85	3.76 / 0.015	0.87	3.30 / 0.462	0.86	3.03 / 0.096	0.92
S_6	3.96 / 0.725	0.85	3.77 / 0.003	0.95	3.39 / 0.075	0.89	3.07 / 0.113	0.86
S_7	3.97 / 0.157	0.91	3.84 / 0.001	0.71	3.41 / 0.771	0.76	3.13 / 0.094	0.93
S_8	4.02 / 0.037	0.87	3.88 / 0.293	0.87	3.53 / 0.066	0.68	3.16 / 0.011	0.98
S_9	4.07 / 0.002	0.53	3.91 / 0.074	0.67	3.55 / 0.085	0.73	3.17 / 0.013	0.75
S_{10}	4.08 / 0.012	0.91	3.94 / 0.280	0.84	3.56 / 0.042	0.75	3.25 / 1.225	0.83
	RI-ADC(2)							
S_1	4.17 / 4.471	0.44	3.92 / 4.381	0.46	3.49 / 4.415	0.44	3.30 / 4.133	0.51
S_2	4.28 / 0.061	0.13	4.27 / 0.025	0.37	3.61 / 0.341	0.29	3.44 / 0.029	0.50
S_3	4.33 / 0.006	0.15	4.32 / 0.248	0.48	3.85 / 0.197	0.44	3.69 / 0.225	0.49
S_4	4.35 / 0.022	0.51	4.34 / 0.024	0.26	4.11 / 0.023	0.35	3.73 / 0.082	0.38
S_5	4.46 / 0.094	0.42	4.36 / 0.022	0.43	4.17 / 0.040	0.30	3.97 / 0.104	0.37
S_6	4.50 / 0.072	0.47	4.37 / 0.003	0.09	4.24 / 0.378	0.45	4.07 / 0.013	0.13
S_7	4.59 / 0.190	0.39	4.40 / 0.022	0.41	4.31 / 0.006	0.11	4.11 / 0.638	0.50
S_8	4.63 / 0.419	0.43	4.45 / 0.094	0.50	4.36 / 0.020	0.38	4.19 / 0.005	0.15
S_9	4.68 / 0.012	0.45	4.48 / 0.007	0.47	4.39 / 0.060	0.51	4.22 / 0.016	0.66
S_{10}	4.71 / 0.017	0.43	4.55 / 0.515	0.43	4.46 / 0.014	0.45	4.23 / 0.022	0.50

Table S4: Excitation energy (E_g), oscillator strengths (f_{osc}), and ω_{CT} values for the first ten excited states at different times of single representative trajectories for $(PhPy)_5$-B

			TD-DFTB			
	0 fs (S_3)		3 fs (S_2)		22 fs (S_1)	
State	E_g/f_{osc}	ω_{CT}	E_g/f_{osc}	ω_{CT}	E_g/f_{osc}	ω_{CT}
S_1	3.54 / 0.000	1.00	3.43 / 0.021	0.48	3.46 / 0.002	0.99
S_2	3.62 / 0.007	0.99	3.51 / 0.000	1.00	3.60 / 0.012	0.97
S_3	3.67 / 0.067	0.57	3.53 / 0.000	1.00	3.69 / 0.153	0.80
S_4	3.68 / 0.001	0.65	3.58 / 0.000	1.00	3.70 / 0.006	0.91
S_5	3.80 / 0.030	0.95	3.65 / 0.005	0.97	3.72 / 0.002	0.75
S_6	3.83 / 0.005	0.99	3.66 / 0.013	0.89	3.75 / 0.005	0.97
S_7	3.92 / 0.001	0.96	3.70 / 0.000	1.00	3.76 / 0.026	0.86
S_8	3.92 / 0.008	0.98	3.75 / 0.009	0.95	3.84 / 0.003	0.93
S_9	3.93 / 0.021	0.96	3.79 / 0.004	0.72	3.85 / 0.004	0.82
S_{10}	3.99 / 0.010	0.61	3.79 / 0.018	0.92	3.88 / 0.072	0.87
			RI-ADC(2)			
S_1	4.05 / 0.511	0.31	3.98 / 0.290	0.38	4.02 / 0.209	0.46
S_2	4.16 / 0.301	0.35	4.08 / 0.016	0.33	4.12 / 1.556	0.44
S_3	4.29 / 0.001	0.17	4.14 / 0.812	0.42	4.16 / 0.083	0.49
S_4	4.32 / 0.019	0.27	4.17 / 0.022	0.23	4.24 / 0.102	0.44
S_5	4.43 / 0.622	0.47	4.25 / 0.115	0.37	4.30 / 0.285	0.55
S_6	4.44 / 0.469	0.49	4.27 / 0.071	0.43	4.43 / 0.000	0.49
S_7	4.48 / 0.022	0.45	4.28 / 0.492	0.49	4.47 / 0.164	0.47
S_8	4.51 / 0.222	0.64	4.36 / 0.501	0.39	4.47 / 0.129	0.45
S_9	4.54 / 0.188	0.60	4.41 / 0.114	0.49	4.52 / 0.067	0.43
S_{10}	4.55 / 0.432	0.54	4.42 / 0.148	0.33	4.55 / 0.958	0.48

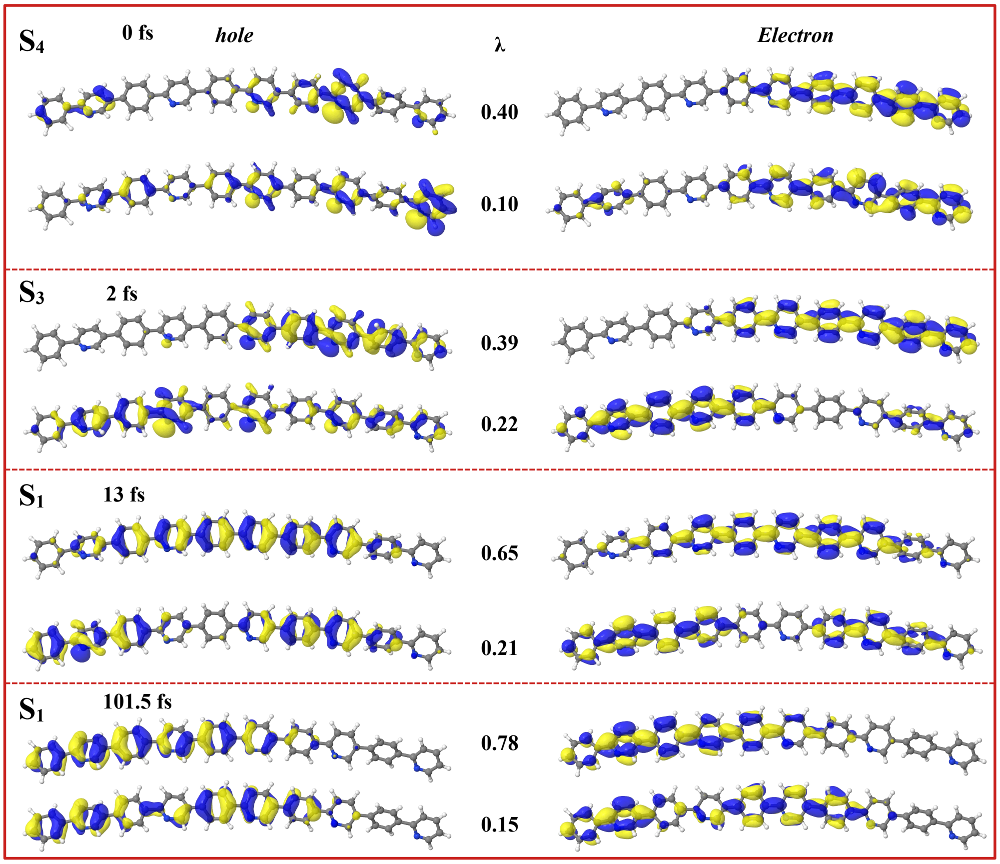

Figure S6: NTOs involved in the current state of a selected trajectory at different times for **(PhPy)**$_5$-**A** obtained at the RI-ADC(2) level.

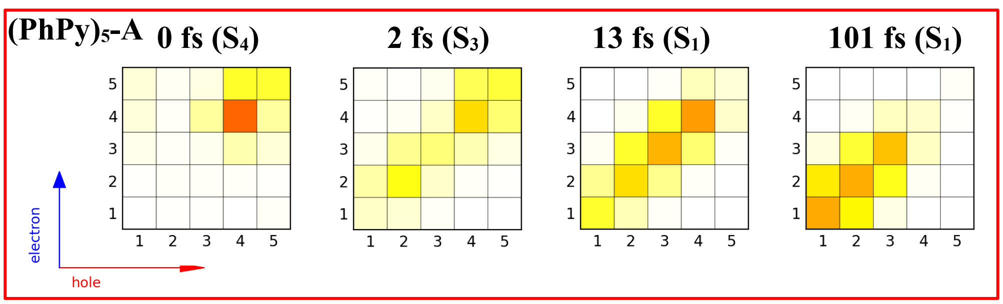

Figure S7: Electron-hole correlation plots involved in the current state of a selected trajectory at different times for **(PhPy)**$_5$-**A** obtained at the RI-ADC(2) level.

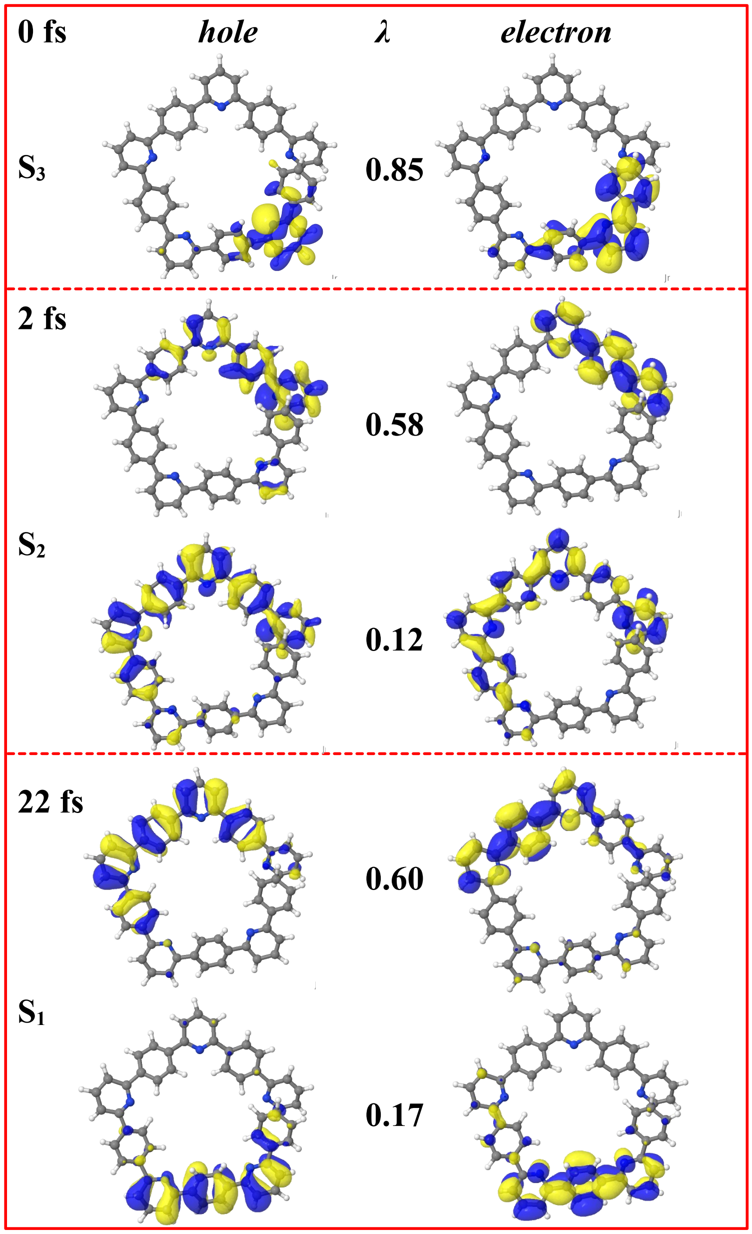

Figure S8: NTOs involved in the current state of a selected trajectory at different times for **(PhPy)**$_5$-**B** obtained at the RI-ADC(2) level.

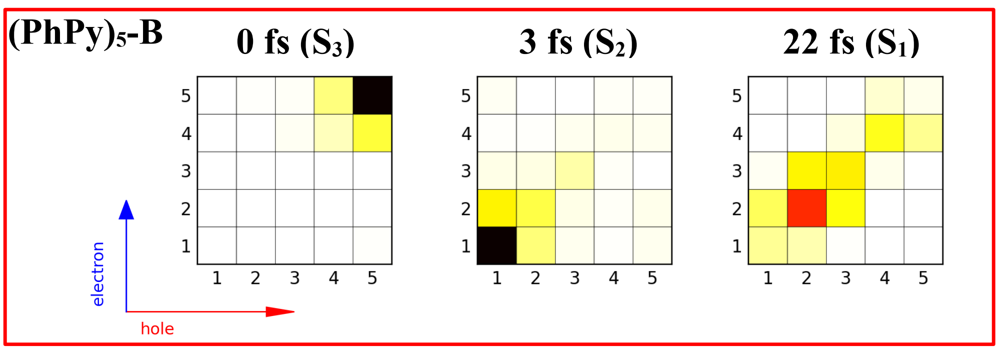

Figure S9: Electron-hole correlation plots involved in the current state of a selected trajectory at different times for **(PhPy)**$_5$**-B** obtained at the RI-ADC(2) level.

References

(1) Vuong, V. Q.; Akkarapattiakal Kuriappan, J.; Kubillus, M.; Kranz, J. J.; Mast, T.; Niehaus, T. A.; Irle, S.; Elstner, M. Parametrization and Benchmark of Long-Range Corrected DFTB2 for Organic Molecules. *J. Chem. Theory Comput.* **2018**, *14*, 115–125.

(2) Hourahine, B.; Aradi, B.; Blum, V.; Bonafe, F.; Buccheri, A.; Camacho, C.; Cevallos, C.; Deshaye, M.; Dumitrică, T.; Dominguez, A. et al. DFTB+, a software package for efficient approximate density functional theory based atomistic simulations. *J. Chem. Phys.* **2020**, *152*, 124101.

(3) Hättig, C.; Weigend, F. CC2 excitation energy calculations on large molecules using the resolution of the identity approximation. *J. Chem. Phys.* **2000**, *113*, 5154–5161.

(4) TURBOMOLE V7.2 2016, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from `https://www.turbomole.org`.

(5) Wigner, E. On the Quantum Correction For Thermodynamic Equilibrium. *Phys. Rev.* **1932**, *40*, 749–759.

(6) Barbatti, M.; Bondanza, M.; Crespo-Otero, R.; Demoulin, B.; Dral, P. O.; Granucci, G.; Kossoski, F.; Lischka, H.; Mennucci, B.; Mukherjee, S. et al. Newton-X Platform: New Software Developments for Surface Hopping and Nuclear Ensembles. *J. Chem. Theory Comput.* **2022**, *18*, 6851–6865.

(7) Plasser, F.; Lischka, H. Analysis of excitonic and charge transfer interactions from quantum chemical calculations. *J. Chem. Theory Comput.* **2012**, *8*, 2777–2789.

(8) Plasser, F.; Wormit, M.; Dreuw, A. New tools for the systematic analysis and visualization of electronic excitations. I. Formalism. *J. Chem. Phys.* **2014**, *141*.

(9) Le Bahers, T.; Adamo, C.; Ciofini, I. A qualitative index of spatial extent in charge-transfer excitations. *J. Chem. Theory Comput.* **2011**, *7*, 2498–2506.

(10) Czader, A.; Bittner, E. R. Calculations of the exciton coupling elements between the DNA bases using the transition density cube method. *J. Chem. Phys.* **2008**, *128*, 01B613.

(11) Plasser, F. TheoDORE: A toolbox for a detailed and automated analysis of electronic excited state computations. *J. Chem. Phys.* **2020**, *152*, 084108.