Supporting Information for

Computational Modelling of Exciton Localization in Self-Assembled Perylenes Helices: Effects of Thermal Motion and Aggregates size

Alekos Segalina,[a] *Xavier Assfeld,*[a] *Antonio Monari,*[a] *and Mariachiara Pastore*[a]

[a]Université de Lorraine & CNRS, Laboratoire de Phisique et Chimie Théoriques (LPCT),

Boulevard des Aiguillettes, BP 70239 54506 Vandoeuvre-lès-Nancy Cedex, France

FUNCTIONAL	*E 0-0 ACN (EV)*	*E 0-0 WAT (EV)*	*E MAXWAT (EV)*
B3LYP	2.21	2.21	2.38
PBE0	2.28	2.29	2.45
MPW1K	2.49	2.49	2.64
CAM-B3LYP	2.52	2.52	2.69
EXP (ACN)	2.36		2.38

Table 1S. Calculated E0-0 and vertical excitation energies in eV for the PDI molecule in acetonitrile (ACN) and water (water)

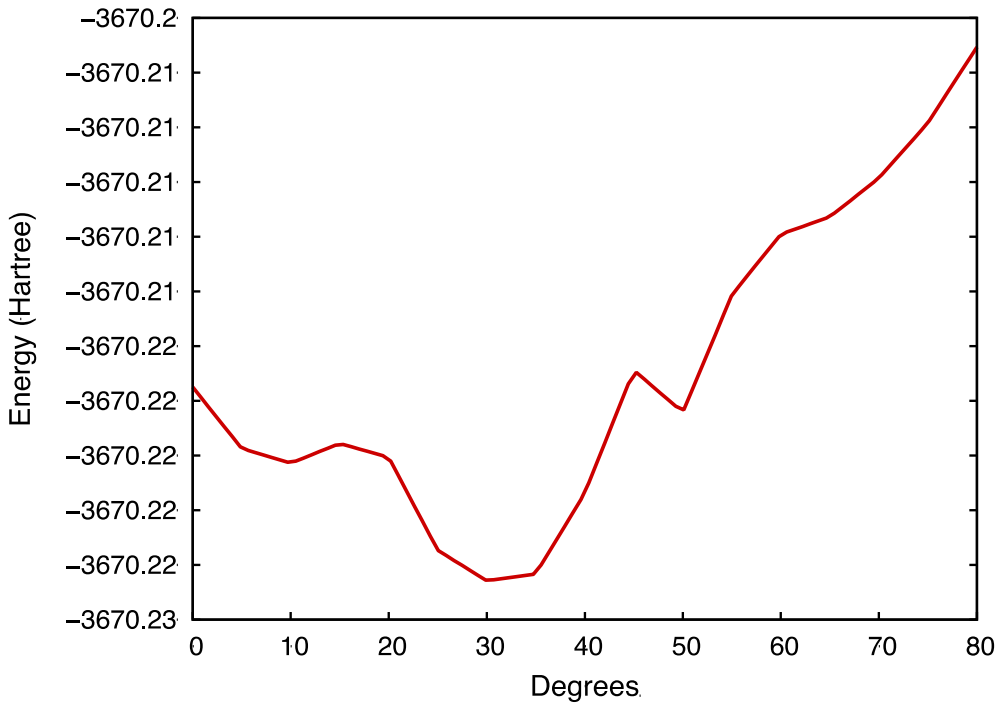

Figure S1. Relaxed dihedral angle scan of the PDI dimer at M062X/6-31G* level of theory in water (C-PCM)

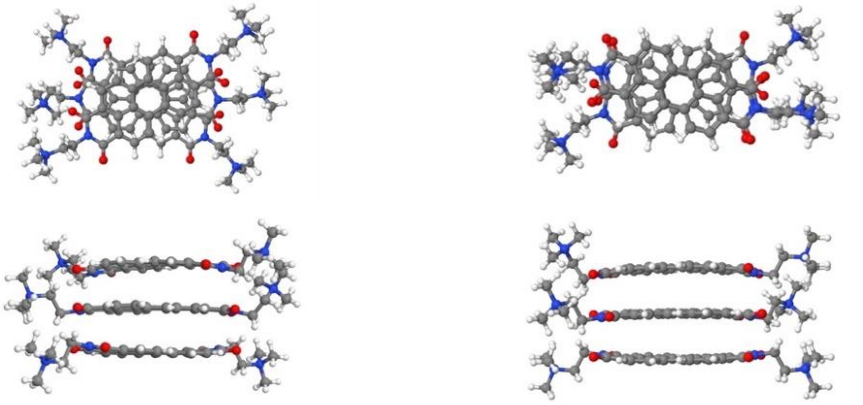

Figure S2. PDI trimer in “helix like” geometry (left) and in “alternated type” geometry (right)

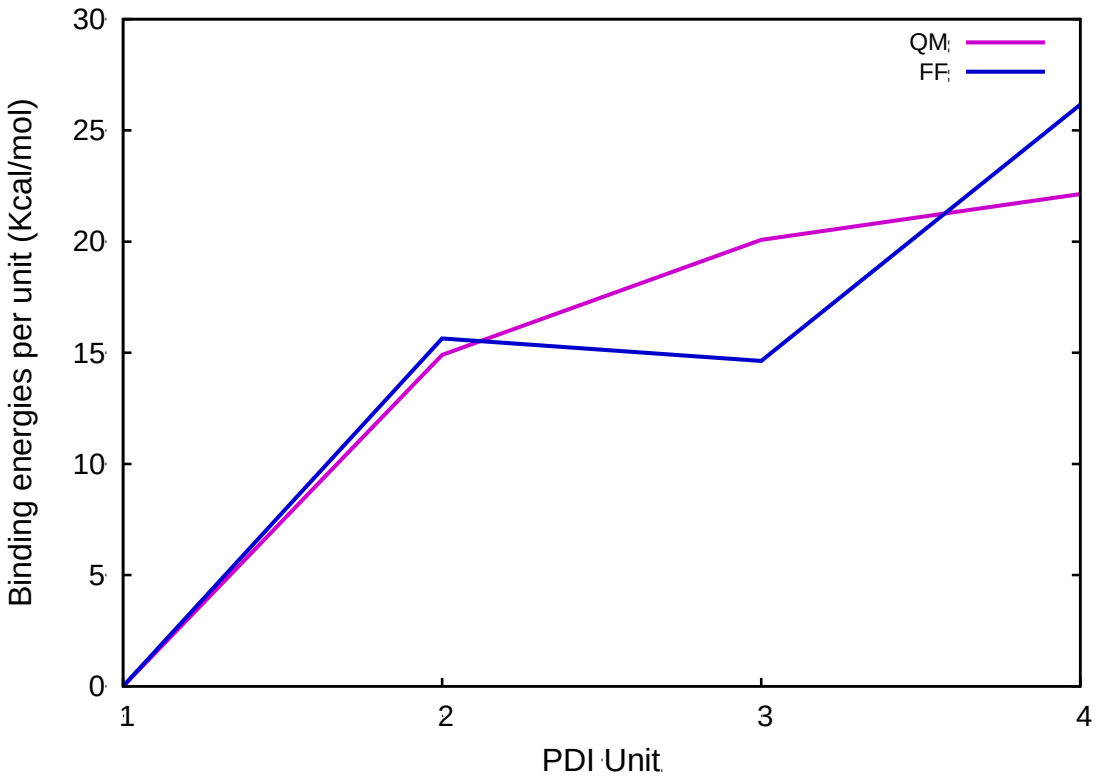

Figure S3. Binding energies per unit for the aggregates system obtained at the M062X/6-31G* level of theory in water (CPCM) considering the DFT optimized geometries (QM) and the F.F. geometries (FF)

	B3LYP				CAM-B3LYP			
PDI system	**monomer**	**dimer**	**trimer**	**tetramer**	**monomer**	**dimer**	**trimer**	**tetramer**
TDDFT	2.38 e.V f = 0.902	2.47 e.V f = 1.339	2.50 e.V f= 1.096	2.54 e.V f= 1.235	2.69 e.V f = 1.061	2.77 e.V f = 1.148	2.90 e.V f = 1.00	2.89 e.V f = 1.343
TDA	2.57 e.V f = 1.272	2.70 e.V f= 1.945	2.75 e.V f = 2.129	2.78 e.V f = 2.322	2.87 e.V f = 1.368	3.01 e.V f = 2.108	3.06 e.V f = 1.387	3.12 e.V f= 1.608
TDA F.F.	2.41 e.V f = 1.354	2.49 e.V f = 1.924	2.54 e.V f= 2.604	2.56 e.V f = 2.239	2.60 e.V f= 1.391	2.71 e.V f = 1.903	2.74 e.V f = 2.811	2.80 e.V f = 2.312
TDA F.F. COSMO	2.37 e.V f = 1.377	2.45 e.V f = 2.006	2.49 e.V f = 2.746	2.52 e.V f = 2.380	2.56 e.V f = 1.408	2.67 e.V f = 1.898	2.70 e.V f = 2.907	2.76 e.V f = 2.339
TDA F.F. COSMO (no chains)	2.39 e.V f = 1.263	2.48 e.V f = 1.802	2.51 e.V f = 2.448	2.54 e.V f = 2.118	2.59e.V. f = 1.299	2.70 e.V f = 1.743	2.72 e.V f = 2.607	2.78 e.V. f = 2.073

Table 2S. B3LYP and CAM-B3LYP TDA and TD-DFT excitation energies obtained on the optimized M06-2X geometries of the PDI and its aggregates in water (CPCM) considering different approximations

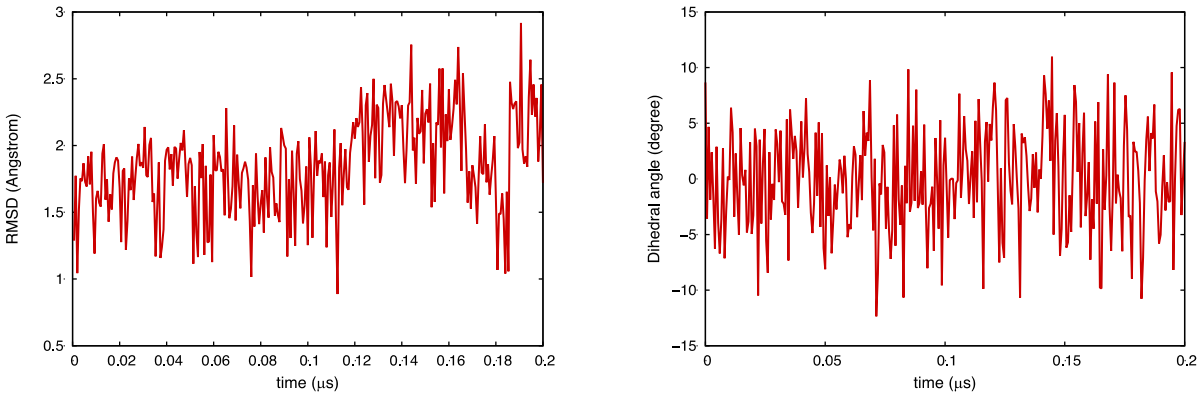

Figure S4. RMSD (Å) (left) considering the F.F. minimized structure as reference. The average RMSD is 1.85 Å. Out of plane distortion of PDI monomer along the MD simulation (right). The average value of the computed dihedral angle is 3.73 degrees. These graphs were obtained from 300 snapshots randomly extracted from the MD production run

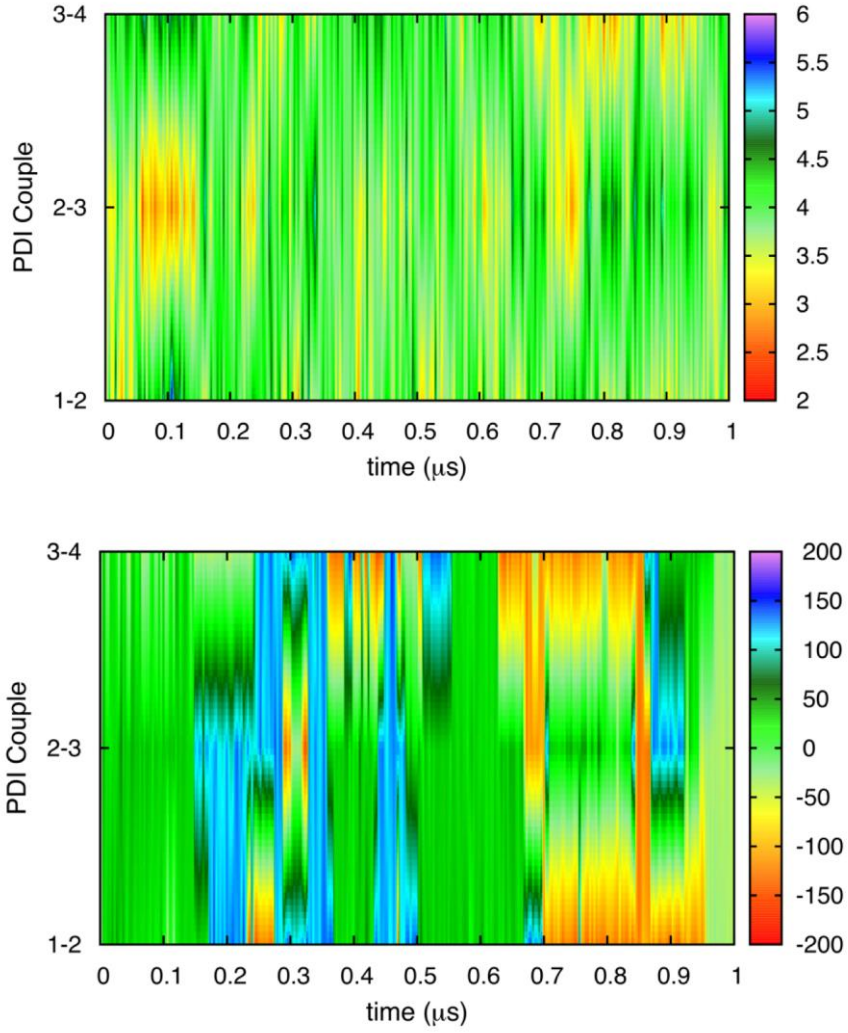

Figure S5. Temporal evolution of the center of mass distance (top panel) and dihedral angle (bottom panel) between each couple of PDI (1-2, 2-3, 3-4) along the MD run of the tetramer. The plotted data refer to 300 snapshots randomly extracted from the MD production run

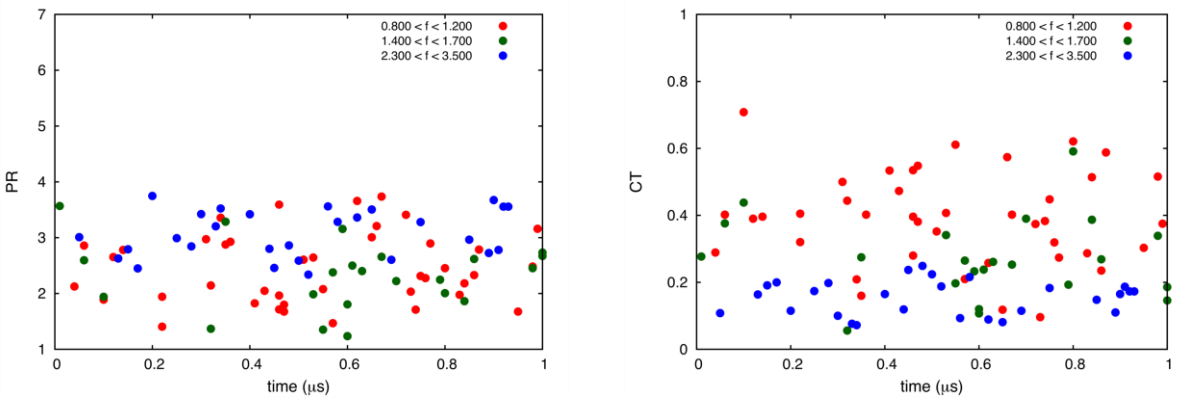

Figure S6. Temporal evolution of the CT numbers and the PR computed from the TDA calculations obtained from 100 snapshots randomly extracted from the PDI tetramer MD production run

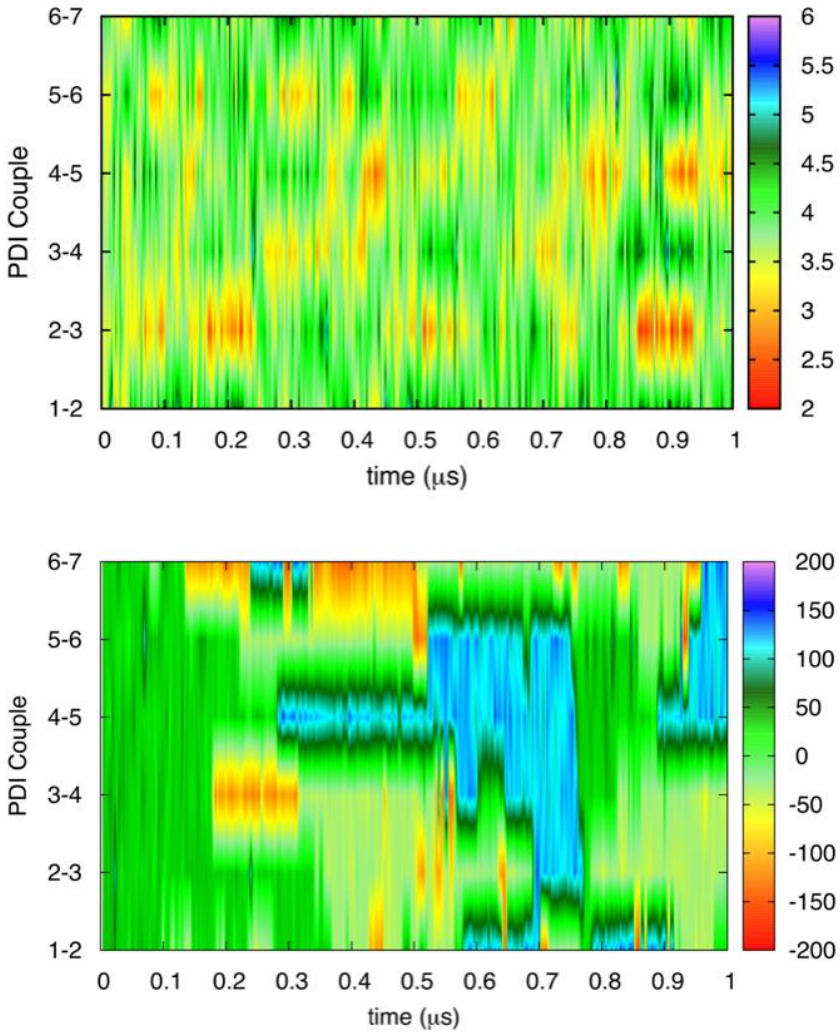

Figure S7. Temporal evolution of the center of mass distance (top panel) and dihedral angle (bottom panel) between each couple of PDI (1-2, 2-3, 3-4, 4-5, 5-6, 6-7) along the MD run of the heptamer. The plotted data refer to 300 snapshots randomly extracted from the MD production run

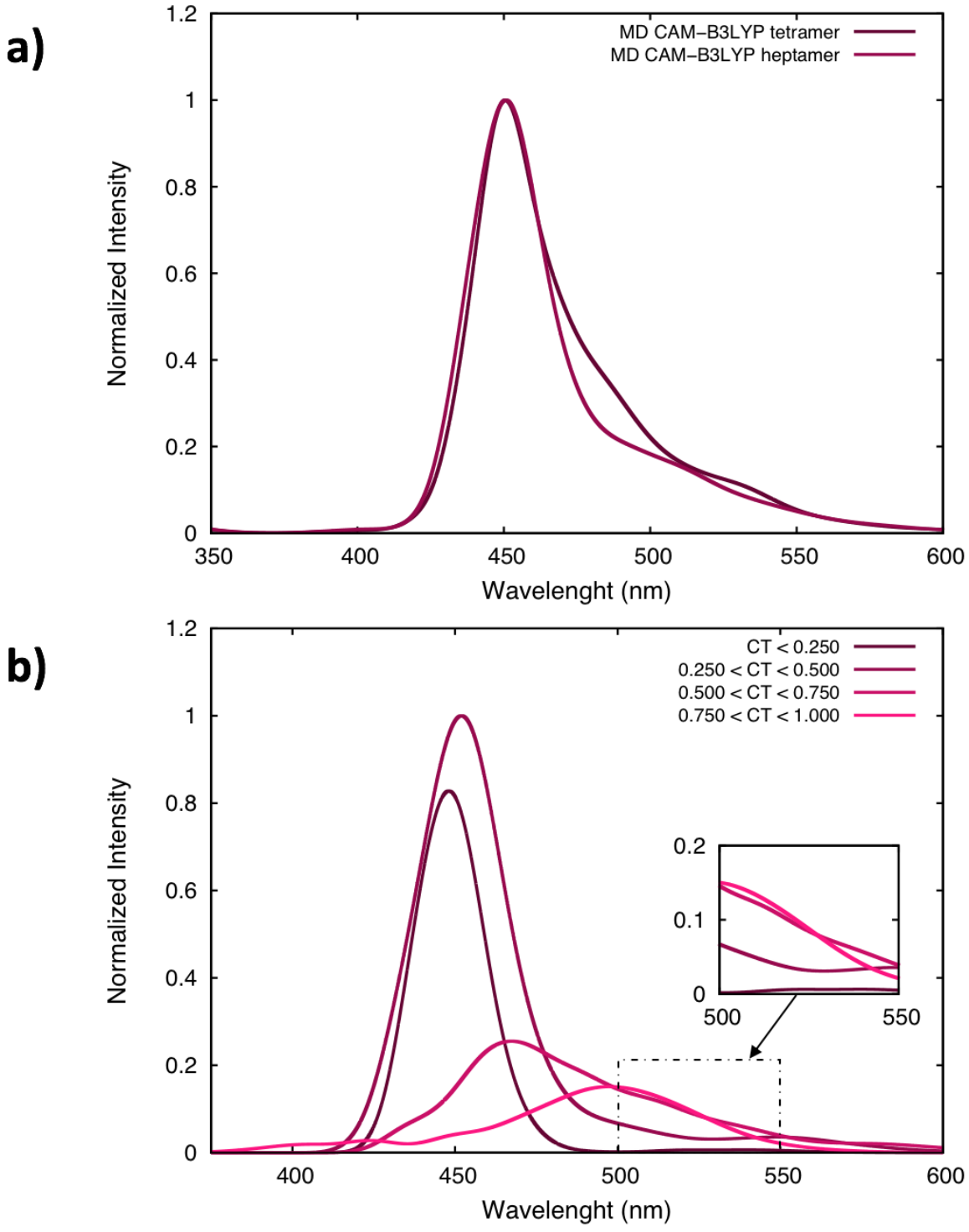

Figure S8. a) Theoretical spectra of the PDI tetramer and PDI heptamer at the TDA-DFT CAM-B3LYP/6-31G* level of theory in water (COSMO) obtained from the convolution of 100 TDA-DFT calculations from as many snapshots randomly extracted from the PDI MD production runs. b)

Decomposition of the calculated spectra taking into accounts only states having specific charge-transfer character (CT index).

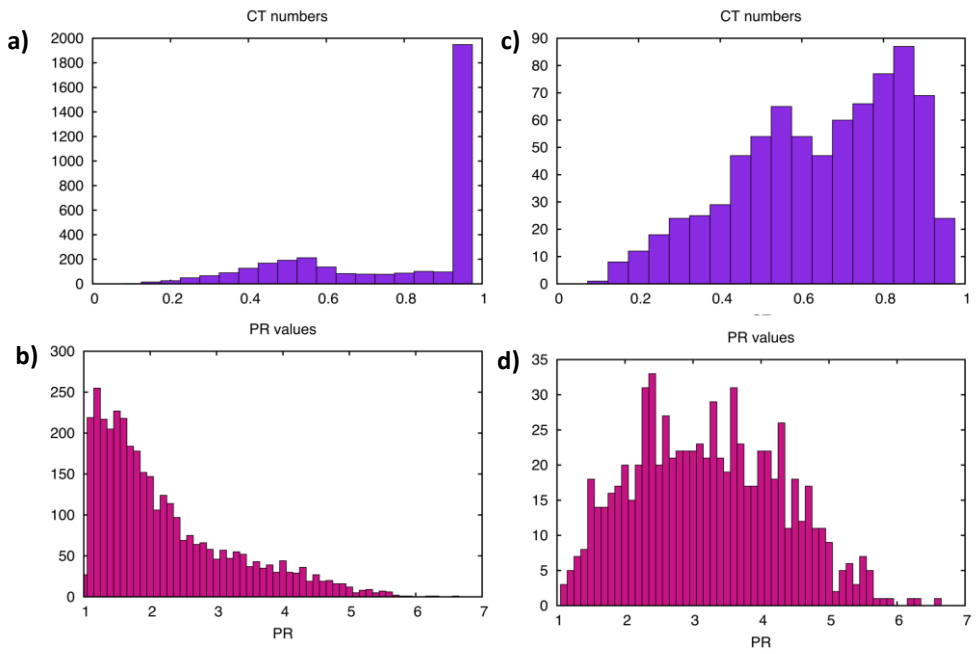

Figure S9. Distribution of the CT numbers and PR values computed from the TDA calculations obtained from MD frames of the PDI heptamer considering only the states localized on the central PDI units (i.e. for which the position operator, POS, is comprised between 3 and 5). In the left column are reported the analyses for all the calculated states, in the right column for the brightest state and all the states below