Electronic Supplementary Information

for

Mechanisms of Fluorescence Quenching in Prototypical Aggregation-Induced Emission Systems: Excited State Dynamics with TD-DFTB

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1. Vertical excitation energies

Table S1: Vertical excitation energies of TPE, DPDBF and DMTPS computed with different methods for geometries optimized at ω B97XD/Def2-SVP. All energies are in eV, while oscillator strengths are indicated in parentheses.

TPE	S ₁	S ₂	S₃
TD-PBE/Def2-SVP	3.32(0.2732)	3.76(0.0027)	3.85(0.0901)
TD-B3LYP/Def2-SVP	3.70(0.3401)	4.31(0.0030)	4.42(0.1394)
TD-PBE0/Def2-SVP	3.80(0.3567)	4.47(0.0025)	4.58(0.1540)
TD-CAM-B3LYP/Def2-SVP	4.15(0.4208)	4.88(0.0012)	5.05(0.1549)
TD-LC-ωPBE/Def2-SVP	4.50(0.4774)	5.18(0.0001)	5.33(0.0000)
TD-DFTB	3.57(0.4671)	4.16(0.0063)	4.17(0.0042)
TD-DFTB (30b)	3.56(0.3297)	4.16(0.0049)	4.16(0.0022)
LC1-TD-DFTB	4.82(0.6724)	5.10(0.0000)	5.12(0.0047)
LC2-TD-DFTB	3.77(0.5053)	4.42(0.0003)	4.43(0.1911)
ADC(2)/Def2-TZVPD	4.12(0.4517)	4.55(0.0008)	4.79(0.0814)
DPDBF			
TD-PBE/Def2-SVP	2.86(0.0018)	3.17(0.3325)	3.63(0.0047)
TD-B3LYP/Def2-SVP	3.29(0.0034)	3.50(0.4118)	4.15(0.0012)
TD-PBE0/Def2-SVP	3.40(0.0040)	3.59(0.4308)	4.28(0.0012)
TD-CAM-B3LYP/Def2-SVP	3.83(0.0080)	3.89(0.4996)	4.66(0.0174)
TD-LC-ωPBE/Def2-SVP	4.18(0.5537)	4.24(0.0145)	4.93(0.0390)
TD-DFTB	3.02(0.0169)	3.29(0.5882)	3.74(0.0105)
LC1-TD-DFTB	4.20(0.0419)	4.28(0.5908)	4.76(0.0004)
LC2-TD-DFTB	3.39(0.0379)	3.41(0.5695)	4.12(0.0001)
ADC(2)/Def2-TZVPD	3.53(0.0032)	3.81(0.5072)	4.41(0.0041)
DMTPS			
TD-PBE/Def2-SVP	2.93(0.1743)	3.27(0.0466)	3.53(0.0050)
TD-B3LYP/Def2-SVP	3.27(0.2166)	3.86(0.0977)	4.13(0.0072)
TD-PBE0/Def2-SVP	3.36(0.2221)	4.00(0.1129)	4.25(0.0127)
TD-CAM-B3LYP/Def2-SVP	3.64(0.2421)	4.56(0.1994)	4.81(0.0842)
TD-LC-ωPBE/Def2-SVP	3.93(0.2486)	4.97(0.1615)	5.22(0.1733)
TD-DFTB	3.02(0.2742)	3.32(0.0401)	3.53(0.0717)
LC1-TD-DFTB	3.94(0.2632)	4.51(0.0313)	4.92(0.3030)
LC2-TD-DFTB	3.15(0.2227)	3.15(0.0032)	3.38(0.0135)
ADC(2)/Def2-TZVPD	3.63(0.2593)	4.31(0.1208)	4.53(0.0691)

2. Character of excited states

LUMO

	S1	S2	S3	
TPE	$H \rightarrow L (0.9153)$	H-1 → L (0.5328)	H-2 → L (0.5219)	
	H-1 → L+3 (0.1881)	H → L+2 (0.3319)	H → L+1 (0.4837)	
DBDPF	H-1 → L (0.8879)	H → L (0.9398)	H-1 → L (0.5827)	
	H-1 → L+1 (0.2265)	$H-2 \rightarrow L+5 (0.1372)$	H → L+1 (0.5431)	
DMTPS	$H \to L (0.9045)$	H-1 → L (0.8421)	H-2 → L (0.9024)	
	$H-11 \rightarrow L (0.2280)$	$H-10 \rightarrow L (0.3052)$	$H-4 \rightarrow L (0.2359)$	

Table S2: Main character for the three lowest singlet excited states for TPE, DBDPF and DMTPS with the coefficient in parenthesis, computed with LC2-TD-DFTB.



Fig. S1: Kohn-Sham orbitals (LC2-TD-DFTB) involved in the three lowest singlet transition of TPE (isovalue=0.03).

LUMO+1

LUMO+2

LUMO+3



Fig. S2: Kohn-Sham orbitals (LC2-TD-DFTB) involved in the three lowest singlet transition of DPDBF (isovalue=0.03).



LUMO

Fig. S3: Kohn-Sham orbitals (LC2-TD-DFTB) involved in the three lowest singlet transition of DMTPS (isovalue=0.03).

3. Details of molecular dynamics

Table S3: Summary of parameters used for dynamics simulations of the 3 investigated molecules. For systems where S_1/S_2 interstate gap is larger than 0.5 eV (Table S1) we assume that nonadiabatic effects involving excited states higher than S_1 will not be important and run only S_1 adiabatic dynamics (in case of TPE both adiabatic and nonadiabatic are compared). In case of adiabatic dynamics, nuclei can be propagated with a larger time step without significant loss of accuracy. For LC1 simulations we used a slightly wider S_1/S_0 energy threshold gap to terminate the dynamics, due to the inherent instability of the electronic structure method.

Parameters of dynamics		Gas phase		Hexane solvent			
		Time step [fs]	Gap threshold [eV]	Number of trajectories	Time step [fs]	Gap threshold [eV]	Number of trajectories
TPE	no LC	0.48 ^a	0.1	100	-	-	-
	no LC (<i>3ob)</i>	0.48 ^a	0.1	100	-	-	-
	LC1	0.1 ^b / 0.5 ^a	0.3	100	0.5ª	0.3	100
	LC2	0.1 ^b / 0.5 ^a	0.1	100	0.5ª	0.1	100
DPDBF	LC1	0.1 ^b	0.3	100	0.1 ^b	0.3	30
	LC2	0.1 ^b	0.1	100	0.1 ^b	0.1	30
DMTPS	LC1	0.5ª	0.3	100	0.5ª	0.3	100
	LC2	0.1 ^b	0.1	100	0.1 ^b	0.1	30

^a Adiabatic molecular dynamic (AMD)

^b Nonadiabatic molecular dynamic (NAMD)

Table S4: Summary of dynamics simulations of the 3 investigated molecules. Different deactivation mechanisms were identified. The computed excited state lifetimes are obtained from a single exponential decay. Note that in case of nonadiabatic dynamics, cumulative decay of all 3 excited states is computed ($S_1+S_2+S_3$).

Results		Gas phase			Hexane solvent		
		Total time [ps]	Mechanism	Computed lifetime [ps]	Total time [ps]	Mechanism	Computed lifetime [ps]
TPE	No LC AMD	1.5	43ª 55 ^b 2*	0.67	-	-	-
	No LC (<i>3ob</i>) AMD	1.5	11ª 89 ^b	0.57	-	-	-
	LC1 NAMD	1.5	98ª 2 ^b	0.15	-	-	-
	LC1 AMD	1.5	100ª	0.12	1.5	100ª	0.13
	LC2 NAMD	1.5	64ª 35 ^b 1°	0.31	-	-	-
	LC2 AMD	1.5	74 ^a 26 ^b	0.25	10	73ª 27 ^b	0.83
DPDBF	LC1 NAMD	20	10ª 84 ^b 3 ^c 3*	4.72	12	11 ^a 9 ^b 5 ^c 5*	9.89
	LC2 NAMD	3.5	100 ^b	0.76	12	1ª 21 ^b 3 ^c 5*	8.15
DMTPS	LC1 AMD	5	30 ^d 70 ^e	1.31	60	22 ^d 78 ^e	9.62
	LC2 NAMD	5	100 ^e	1.80	7.2	25 ^e 5*	5.97

^a Photocyclization

^b Ethylenic twist

^c Benzene-type photo deactivation

^d Bond length alternation of the ring for DMTPS
^e Bond length alternation of the ring and out-of-plane silicon for DMTPS
* S₀/S₁ crossing point not reached within simulation time

4. Excited state dynamics of TPE

4.1.1. Population decay in gas phase



Fig. S4: Population of the different electronic states with respect to time in (a) TD-DFT (data taken from ref. 33 from the main text), (b) TD-DFTB, (c) LC1-TD-DFTB and (d) LC2-TD-DFTB. All simulations are done with nonadiabatic dynamics except for TD-DFTB simulation done within the adiabatic dynamic approximation. The exponential fitting for the decay of the excited state is shown by the black dotted curve for the dynamics at LC-TD-DFTB.



4.1.2. TD-DFTB level with 3ob parameter (adiabatic; gas phase)

Fig. S5: (a) Evolution of the distance d (minimum length among the 8 possible C-C involved in cyclization) and CC=CC dihedral angle θ of TPE 100 trajectories (adiabatic dynamics; gas phase; TD-DFTB with *3ob* parametrization). The green dots represent the geometries of the initial conditions for the different trajectories. The black dots represent the geometries corresponding to the S₁/S₀ crossing for the different trajectories. (b) Time evolution of the assumed electronic states population.



4.1.3. LC1-TD-DFTB level (adiabatic; gas phase)

Fig. S6: (a) Evolution of the distance d (minimum length among the 8 possible C-C involved in cyclization) and CC=CC dihedral angle θ of 100 TPE trajectories (adiabatic dynamics; gas phase; LC1-TD-DFTB level). The green dots represent the geometries of the initial conditions for the different trajectories. The black dots represent the geometries corresponding to the S₁/S₀ crossing for the different trajectories. (b) Time evolution of the assumed electronic states population with a fitted exponential (black) for the decay of S₁ and the corresponding lifetime.

4.1.4. LC2-TD-DFTB level (adiabatic; gas phase)



Fig. S7: (a) Evolution of the distance d (minimum length among the 8 possible C-C involved in cyclization) and CC=CC dihedral angle θ of 100 TPE trajectories (adiabatic dynamics; gas phase; LC2-TD-DFTB level). The green dots represent the geometries of the initial conditions for the different trajectories. The black dots represent the geometries corresponding to the S₁/S₀ crossing for the different trajectories. (b) Time evolution of the assumed electronic states population with a fitted exponential (black) for the decay of S₁ and the corresponding lifetime.

4.2.1. LC1-TD-DFTB level (adiabatic; QM/MM)



Fig. S8: (a) Evolution of the distance d (minimum length among the 8 possible C-C involved in cyclization) and CC=CC dihedral angle θ of 100 TPE trajectories (adiabatic dynamics; hexane solvent; LC1-TD-DFTB level). The green dots represent the geometries of the initial conditions for the different trajectories. The black dots represent the geometries corresponding to the S₁/S₀ crossing for the different trajectories. (b) Time evolution of the assumed electronic states population with a fitted exponential (black) for the decay of excited state S₁ and the corresponding lifetime.

4.2.2. LC2-TD-DFTB level (adiabatic; QM/MM)



Fig. S9: (a) Evolution of the distance d (minimum length among the 8 possible C-C involved in cyclization) and CC=CC dihedral angle θ of 100 TPE trajectories (adiabatic dynamics; hexane solvent; LC2-TD-DFTB level). The green dots represent the geometries of the initial conditions for the different trajectories. The black dots represent the geometries corresponding to the S₁/S₀ crossing for the different trajectories. (b) Time evolution of the assumed electronic states population with a fitted exponential (black) for the decay of excited state S₁ and the corresponding lifetime



Fig. S10: Time evolution of assumed electronic states population (adiabatic dynamics; hexane solvent; LC2-TD-DFTB level) of all 100 TPE trajectories separated into (a) 73 trajectories leading to cyclization and (b) 27 trajectories leading to an ethylenic twist and their respective lifetime computed with a single exponential fitting (black curve).

5. Excited state dynamics of DPDBF





Fig. S11: (a) Time evolution of the CC=CC dihedral angle Θ of DPDBF for 100 trajectories (nonadiabatic dynamics; gas phase; LC1-TD-DFTB level). The black dots represent the geometries corresponding to the S₁/S₀ crossings, while the green dots represent the initial conditions. (b) Time evolution of the different electronic states population in nonadiabatic dynamics with a fitted exponential (black) for the cumulative decay of excited states (S₁+S₂+S₃) and the corresponding lifetime.



5.2.1. LC1-TD-DFTB level (nonadiabatic; QM/MM)

Fig. S12: (a) Time evolution of the CC=CC dihedral angle Θ of DPDBF for 30 trajectories (nonadabiatic dynamics; hexane solvent; LC1-TD-DFTB level). The black dots represent the geometries corresponding to the S₁/S₀ crossings, while the green dots represent the initial conditions. (b) Time evolution of the different electronic states population in nonadiabatic dynamics with a fitted exponential (black) for the cumulative decay of excited states (S₁+S₂+S₃) and the corresponding lifetime.

5.2.2. LC2-TD-DFTB level (nonadiabatic; QM/MM)



Fig. S13: (a) Time evolution of the CC=CC dihedral angle Θ of DPDBF for 30 trajectories (nonadiabatic dynamics; hexane solvent; LC2-TD-DFTB level). The black dots represent the geometries corresponding to the S₁/S₀ crossings, while the green dots represent the initial conditions. (b) Time evolution of the different electronic states population in nonadiabatic dynamics with a fitted exponential (black) for the cumulative decay of excited states (S₁+S₂+S₃) and the corresponding lifetime.

6. Excited state dynamics of DMTPS

6.1. LC1-TD-DFTB level (adiabatic; gas phase)



Fig. S14: (a) Evolution of the bond length d_1 (C=C double bond in silole ring) and the average bond length d_2 (C-C single bond in silole ring) for 100 DMTPS trajectories (adiabatic dynamics; gas phase; LC1-TD-DFTB level). The black dots represent the geometry corresponding to the S_1/S_0 crossing for the different trajectories. The green dots represent the geometries of the initial condition for the different trajectories. (b) Time evolution of the assumed electronic states population with a fitted exponential (black) for the decay of excited state S_1 and the corresponding lifetime.

6.2.1. LC1-TD-DFTB level (adiabatic; QM/MM)



Fig. S15: (a) Evolution of the bond length d_1 (C=C double bond in silole ring) and the average bond length d_2 (C-C single bond in silole ring) for 100 DMTPS trajectories (adiabatic dynamics; hexane solvent; LC1-TD-DFTB level). The black dots represent the geometry corresponding to the S_1/S_0 crossing for the different trajectories. The green dots represent the geometries of the initial condition for the different trajectories. (b) Time evolution of the assumed electronic states population with a fitted exponential (black) for the decay of excited state S_1 and the corresponding lifetime.





Fig. S16: (a) Evolution of the bond length d_1 (C=C double bond in silole ring) and the average bond length d_2 (C-C single bond in silole ring) for 30 DMTPS trajectories (nonadiabatic dynamics; hexane solvent; LC2-TD-DFTB level). The black dots represent the geometry corresponding to the S_1/S_0 crossing for the different trajectories. The green dots represent the geometries of the initial condition for the different trajectories. (b) Time evolution of the different electronic states population in nonadiabatic dynamics with a fitted exponential (black) for the cumulative decay of excited states ($S_1+S_2+S_3$) and the corresponding lifetime.