

D-A₃ TADF Emitters: The role of the density of states for achieving faster triplet harvesting rates: Supporting Information

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S1 Cartesian Coordinates of the Critical Points on the Potential Energy Surface

	x	y	z		x	y	z		x	y	z
C	0.0608	0.1228	1.3893	C	-0.3644	3.5661	-3.4911	O	1.0341	2.9709	-7.9076
C	0.0000	-1.1723	0.8218	C	0.0340	3.8914	-4.7860	O	2.3462	4.9589	-7.0666
C	0.0000	1.2982	0.6046	C	1.2093	3.3383	-5.2649	H	0.1889	-1.3269	5.2708
C	0.0027	1.1420	-0.8015	C	2.0076	2.4839	-4.4991	H	-0.4813	-4.1206	1.1885
C	0.0008	-1.2652	-0.5895	C	1.6160	2.1807	-3.1999	H	-0.1020	-3.7831	5.4443
C	-0.0642	-0.1256	-1.4247	C	-0.3216	-4.8156	-1.3373	H	-0.4764	-5.1491	3.4047
N	0.1067	0.0000	2.7755	C	0.1301	-6.0901	-1.0014	H	-0.4208	3.0835	2.9884
C	0.0203	-1.3525	3.1097	C	1.3440	-6.1994	-0.3450	H	-0.4628	5.5180	2.7719
C	-0.0914	-2.1149	1.9267	C	2.1282	-5.0890	-0.0197	H	-0.1928	6.6051	0.5557
C	-0.1047	2.7258	0.8703	C	1.6822	-3.8214	-0.3767	H	0.0378	5.2308	-1.4938
N	0.0045	2.4035	-1.3924	S	2.1414	4.0819	6.5758	H	-0.6427	1.0432	-4.1332
C	-0.0554	3.3694	-0.3857	C	3.5335	4.2587	5.4705	H	-0.0818	-3.9044	-3.7877
C	-0.2302	-0.6096	-2.7873	C	3.4193	3.4029	4.3714	H	-0.4503	-2.8180	-5.9847
N	-0.0176	-2.4072	-1.3874	S	1.8993	3.5769	-6.8955	H	-0.7691	-0.3597	-6.1317
C	-0.1530	-2.0180	-2.7221	C	3.2821	2.5067	-6.5277	H	-1.1727	0.7267	4.9564
C	0.0491	-1.9303	4.3782	C	3.2011	2.0056	-5.2255	H	-0.3895	2.3965	6.6524
C	-0.3057	-3.4959	2.0557	S	2.1082	-7.7149	0.2120	H	2.3509	1.3982	2.5988
C	-0.1140	-3.3061	4.4669	C	3.5035	-6.8276	0.8898	H	-1.3008	3.9437	-3.0888
C	-0.3146	-4.0773	3.3163	C	3.3702	-5.4503	0.6929	H	-0.5722	4.5453	-5.4082
C	-0.2882	3.5253	2.0088	C	4.5975	5.1272	5.6402	H	2.2051	1.5204	-2.5689
C	-0.3251	4.9075	1.8824	C	5.5916	5.1360	4.6614	H	-1.2880	-4.6797	-1.8154
C	-0.1837	5.5201	0.6322	C	5.4980	4.2919	3.5540	H	-0.4640	-6.9712	-1.2307
C	-0.0547	4.7571	-0.5204	C	4.4178	3.4236	3.4005	H	2.2581	-2.9298	-0.1436
C	-0.4891	-0.0243	-4.0358	C	4.3134	2.1871	-7.3936	H	4.6530	5.7805	6.5075
C	-0.1982	-2.8265	-3.8567	C	5.3078	1.3254	-6.9295	H	6.4419	5.8062	4.7620
C	-0.4036	-2.2104	-5.0838	C	5.2467	0.8111	-5.6335	H	6.2783	4.3121	2.7965
C	-0.5730	-0.8237	-5.1678	C	4.1990	1.1443	-4.7759	H	4.3573	2.7754	2.5291
C	0.4509	-3.6902	-1.0255	C	4.5863	-7.3926	1.5409	H	4.3437	2.5945	-8.4011
C	0.5554	0.9691	3.7008	C	5.5790	-6.5345	2.0152	H	6.1327	1.0520	-7.5830
C	0.4217	2.7140	-2.7063	C	5.4659	-5.1556	1.8325	H	6.0270	0.1375	-5.2866
C	-0.2214	1.2377	4.8336	C	4.3670	-4.6050	1.1742	H	4.1631	0.7305	-3.7707
C	0.2080	2.1736	5.7719	O	1.3153	-8.3214	1.2815	H	4.6570	-8.4688	1.6781
C	1.4057	2.8274	5.5378	O	2.5195	-8.5319	-0.9292	H	6.4437	-6.9437	2.5321
C	2.1949	2.5777	4.4114	O	1.3218	5.2935	6.5672	H	6.2455	-4.4986	2.2115
C	1.7705	1.6272	3.4888	O	2.5634	3.5084	7.8532	H	4.2903	-3.5278	1.0449

Table S1: The cartesian coordinates of the ground state geometry.

	x	y	z		x	y	z		x	y	z
C	0.0487	0.1232	1.4024	C	-0.2474	3.4711	-3.5878	O	1.2749	2.5384	-7.8816
C	0.0000	-1.1789	0.8294	C	0.1917	3.7280	-4.8863	O	2.5015	4.6500	-7.2268
C	0.0000	1.3105	0.6045	C	1.3870	3.1614	-5.2947	H	0.2666	-1.2117	5.2537
C	0.0078	1.1353	-0.8318	C	2.1770	2.3737	-4.4536	H	-0.3863	-4.1582	1.2592
C	0.0136	-1.2733	-0.5729	C	1.7413	2.1319	-3.1557	H	0.0380	-3.6965	5.5036
C	-0.0701	-0.1168	-1.4316	C	-0.2882	-4.7929	-1.2602	H	-0.3094	-5.1140	3.5010
N	0.1530	0.0000	2.7617	C	0.1457	-6.0703	-0.9080	H	-0.3291	3.1100	2.9639
C	0.1007	-1.3335	3.1038	C	1.3744	-6.1914	-0.2821	H	-0.1472	5.5300	2.7508
C	-0.0299	-2.1210	1.9357	C	2.1943	-5.0953	-0.0014	H	0.1462	6.5823	0.5098
C	-0.0551	2.7187	0.8425	C	1.7643	-3.8248	-0.3696	H	0.2399	5.1932	-1.5459
N	0.0526	2.3849	-1.4305	S	1.1272	4.7741	6.0597	H	-0.5865	1.0146	-4.1678
C	0.0342	3.3550	-0.4292	C	2.8342	4.6331	5.6037	H	0.1298	-3.9098	-3.7488
C	-0.1715	-0.6156	-2.7971	C	3.0606	3.4975	4.7845	H	-0.2016	-2.8543	-5.9736
N	0.0812	-2.3901	-1.3673	S	2.1052	3.2757	-6.9293	H	-0.5839	-0.4100	-6.1586
C	-0.0349	-2.0147	-2.7174	C	3.5173	2.2948	-6.4382	H	-1.6523	0.9612	4.5071
C	0.1471	-1.8662	4.3955	C	3.4088	1.8883	-5.1055	H	-1.2996	2.9848	5.9555
C	-0.2067	-3.5009	2.1010	S	2.1218	-7.7158	0.2844	H	2.4425	1.2186	3.1313
C	0.0132	-3.2382	4.5181	C	3.5579	-6.8477	0.8980	H	-1.1987	3.8620	-3.2357
C	-0.1780	-4.0408	3.3820	C	3.4504	-5.4717	0.6771	H	-0.3991	4.3402	-5.5633
C	-0.1714	3.5410	1.9881	C	3.8377	5.5331	5.9322	H	2.3219	1.5221	-2.4683
C	-0.0986	4.9144	1.8555	C	5.1195	5.3158	5.4364	H	-1.2596	-4.6451	-1.7253
C	0.0686	5.5006	0.5922	C	5.3686	4.2018	4.6143	H	-0.4706	-6.9435	-1.1071
C	0.1233	4.7293	-0.5708	C	4.3656	3.3038	4.2895	H	2.3672	-2.9423	-0.1723
C	-0.4025	-0.0466	-4.0551	C	4.5935	1.9544	-7.2399	H	3.6194	6.3878	6.5693
C	-0.0198	-2.8375	-3.8358	C	5.6026	1.1733	-6.6753	H	5.9252	6.0019	5.6848
C	-0.2057	-2.2370	-5.0785	C	5.5149	0.7574	-5.3461	H	6.3742	4.0373	4.2308
C	-0.4152	-0.8602	-5.1835	C	4.4228	1.1094	-4.5543	H	4.5892	2.4416	3.6629
C	0.5187	-3.6851	-0.9843	C	4.6501	-7.4232	1.5241	H	4.6491	2.2879	-8.2733
C	0.3921	1.0345	3.7231	C	5.6776	-6.5779	1.9445	H	6.4631	0.8893	-7.2763
C	0.5189	2.6638	-2.7409	C	5.5904	-5.2008	1.7355	H	6.3108	0.1510	-4.9200
C	-0.6933	1.4671	4.5481	C	4.4818	-4.6391	1.1036	H	4.3710	0.7796	-3.5191
C	-0.4870	2.5871	5.3500	O	1.3442	-8.2739	1.3895	H	4.7024	-8.4975	1.6826
C	0.7476	3.2163	5.3473	O	2.4721	-8.5612	-0.8551	H	6.5500	-6.9963	2.4402
C	1.8785	2.7089	4.5996	O	0.4796	5.8635	5.2935	H	6.3974	-4.5544	2.0726
C	1.6518	1.6047	3.7732	O	0.9313	4.8135	7.5177	H	4.4273	-3.5632	0.9533

Table S2: The cartesian coordinates of the S₁ optimised geometry.

	x	y	z		x	y	z		x	y	z
C	-0.0921	0.1246	1.3871	C	-0.3265	3.5078	-3.5248	O	1.0747	2.7694	-7.9155
C	0.0000	-1.1712	0.8227	C	0.0710	3.8011	-4.8286	O	2.3591	4.8090	-7.1578
C	0.0000	1.2973	0.6035	C	1.2489	3.2404	-5.2919	H	-0.6695	-1.3171	5.2219
C	-0.0053	1.1385	-0.8052	C	2.0533	2.4146	-4.5020	H	-0.2520	-4.1516	1.1348
C	0.1223	-1.2580	-0.5839	C	1.6612	2.1419	-3.1965	H	-0.7939	-3.7913	5.3688
C	-0.0249	-0.1312	-1.4241	C	0.1617	-4.8397	-1.3678	H	-0.5920	-5.1811	3.3226
N	-0.2506	0.0000	2.7632	C	0.6453	-6.0705	-0.9323	H	0.3523	3.0781	2.9980
C	-0.3039	-1.3572	3.0873	C	1.7755	-6.0964	-0.1408	H	0.5728	5.5031	2.7660
C	-0.1605	-2.1225	1.9083	C	2.4875	-4.8754	0.2466	H	0.5573	6.5767	0.5289
C	0.1230	2.7222	0.8688	C	1.9650	-3.6323	-0.2027	H	0.3292	5.1969	-1.5227
N	0.0465	2.3955	-1.3968	S	-2.0709	4.1280	6.6244	H	-0.6621	0.9731	-4.1413
C	0.1394	3.3602	-0.3904	C	-0.6341	3.6877	7.5928	H	0.4309	-3.8873	-3.7817
C	-0.1191	-0.6335	-2.7874	C	0.0973	2.6685	6.9768	H	-0.0222	-2.8471	-5.9840
N	0.2554	-2.3963	-1.3755	S	1.9347	3.4280	-6.9320	H	-0.6009	-0.4385	-6.1423
C	0.1032	-2.0265	-2.7157	C	3.3338	2.3917	-6.5272	H	-2.4609	1.4298	2.4449
C	-0.5354	-1.9311	4.3356	C	3.2531	1.9284	-5.2111	H	-3.3142	3.1910	4.0057
C	-0.2891	-3.5170	2.0108	S	2.5397	-7.5320	0.5510	H	0.9075	0.7257	5.0122
C	-0.6182	-3.3157	4.4065	C	3.8368	-6.5531	1.2549	H	-1.2608	3.8976	-3.1288
C	-0.5043	-4.0994	3.2528	C	3.6329	-5.1430	1.0088	H	-0.5370	4.4369	-5.4675
C	0.3020	3.5188	2.0098	C	-0.2580	4.2590	8.7963	H	2.2570	1.5068	-2.5461
C	0.4466	4.8928	1.8748	C	0.9030	3.7835	9.4067	H	-0.7604	-4.7717	-1.9368
C	0.4379	5.4989	0.6129	C	1.6480	2.7652	8.8105	H	0.1321	-6.9919	-1.1982
C	0.2988	4.7364	-0.5388	C	1.2536	2.2019	7.5975	H	2.4405	-2.6969	0.0799
C	-0.4073	-0.0756	-4.0401	C	4.3739	2.0577	-7.3776	H	-0.8500	5.0510	9.2484
C	0.1820	-2.8321	-3.8505	C	5.3755	1.2221	-6.8822	H	1.2277	4.2094	10.3531
C	-0.0666	-2.2401	-5.0827	C	5.3138	0.7461	-5.5718	H	2.5504	2.4041	9.2987
C	-0.3836	-0.8804	-5.1727	C	4.2580	1.0931	-4.7300	H	1.8450	1.4082	7.1462
C	0.8351	-3.6143	-0.9800	C	4.9138	-7.0325	1.9715	H	4.4060	2.4345	-8.3970
C	-0.7360	0.9895	3.6504	C	5.8359	-6.1156	2.4802	H	6.2072	0.9395	-7.5230
C	0.4619	2.6779	-2.7210	C	5.6598	-4.7191	2.2626	H	6.1004	0.0931	-5.2005
C	-1.9250	1.6659	3.3602	C	4.5939	-4.2328	1.5500	H	4.2227	0.7112	-3.7122
C	-2.3995	2.6471	4.2276	O	1.6921	-8.1161	1.5967	H	5.0385	-8.1004	2.1360
C	-1.6763	2.9069	5.3793	O	3.0464	-8.4213	-0.4989	H	6.6926	-6.4671	3.0489
C	-0.5001	2.2238	5.7016	O	-1.9249	5.4756	6.0747	H	6.3915	-4.0271	2.6737
C	-0.0219	1.2572	4.8223	O	-3.2994	3.7677	7.3308	H	4.4746	-3.1634	1.3929

Table S3: The cartesian coordinates of the T₁ optimised geometry.

	x	y	z		x	y	z		x	y	z
C	0.0426	0.1432	1.4055	C	-0.7428	3.3907	-3.4393	O	0.1687	2.6570	-7.9348
C	0.0000	-1.1817	0.8114	C	-0.5688	3.7015	-4.7868	O	1.1433	4.9423	-7.4592
C	0.0000	1.3107	0.6146	C	0.6135	3.3144	-5.3943	H	0.1220	-1.2620	5.2308
C	-0.0107	1.1403	-0.8021	C	1.6434	2.6596	-4.7123	H	-0.4452	-4.1401	1.1741
C	0.0383	-1.2753	-0.5948	C	1.4679	2.3576	-3.3649	H	-0.1522	-3.7429	5.4319
C	-0.0703	-0.1372	-1.4345	C	-0.1898	-4.8281	-1.2930	H	-0.4586	-5.1384	3.4065
N	0.1140	0.0000	2.7578	C	0.2737	-6.0879	-0.9165	H	-0.1947	3.1767	2.9795
C	0.0299	-1.3446	3.0808	C	1.4801	-6.1635	-0.2425	H	-0.0215	5.5818	2.7193
C	-0.0764	-2.1190	1.9003	C	2.2531	-5.0383	0.0562	H	0.2007	6.6202	0.4592
C	-0.0006	2.7465	0.8651	C	1.7985	-3.7862	-0.3437	H	0.2431	5.1821	-1.5743
N	0.0564	2.3828	-1.3845	S	0.9101	4.7124	6.1903	H	-0.7097	0.9849	-4.1541
C	0.0683	3.3657	-0.4016	C	2.6459	4.5407	5.8793	H	0.1422	-3.9218	-3.7688
C	-0.2058	-0.6304	-2.7877	C	2.9177	3.4116	5.0643	H	-0.2552	-2.8641	-5.9765
N	0.0869	-2.4142	-1.3864	S	1.0226	3.5255	-7.1246	H	-0.7170	-0.4280	-6.1397
C	-0.0514	-2.0370	-2.7156	C	2.6284	2.7809	-6.8921	H	-1.8077	0.9878	4.3510
C	0.0234	-1.8967	4.3556	C	2.8090	2.3649	-5.5698	H	-1.5357	2.9798	5.8572
C	-0.2810	-3.5059	2.0364	S	2.2483	-7.6560	0.3767	H	2.3902	1.1726	3.3246
C	-0.1371	-3.2746	4.4504	C	3.6292	-6.7356	1.0391	H	-1.6619	3.6501	-2.9203
C	-0.3043	-4.0672	3.3031	C	3.4900	-5.3667	0.7927	H	-1.3440	4.2193	-5.3463
C	-0.0716	3.5782	1.9869	C	3.6356	5.4147	6.3051	H	2.2329	1.8438	-2.7886
C	0.0039	4.9608	1.8263	C	4.9503	5.1771	5.9163	H	-1.1521	-4.7160	-1.7859
C	0.1293	5.5398	0.5565	C	5.2455	4.0698	5.1001	H	-0.3071	-6.9822	-1.1286
C	0.1547	4.7471	-0.5826	C	4.2559	3.1980	4.6776	H	2.3677	-2.8840	-0.1354
C	-0.4856	-0.0677	-4.0472	C	3.5905	2.6101	-7.8721	H	3.3811	6.2647	6.9349
C	-0.0340	-2.8532	-3.8479	C	4.7874	1.9940	-7.5057	H	5.7456	5.8425	6.2425
C	-0.2563	-2.2535	-5.0768	C	4.9902	1.5700	-6.1917	H	6.2765	3.8895	4.8001
C	-0.5071	-0.8750	-5.1709	C	4.0086	1.7510	-5.2178	H	4.5141	2.3407	4.0578
C	0.5696	-3.6906	-1.0003	C	4.7088	-7.2682	1.7225	H	3.4178	2.9470	-8.8913
C	0.2964	1.0211	3.7454	C	5.6897	-6.3856	2.1761	H	5.5666	1.8453	-8.2492
C	0.2621	2.7033	-2.7540	C	5.5701	-5.0148	1.9429	H	5.9289	1.0928	-5.9206
C	-0.8435	1.4670	4.4851	C	4.4749	-4.4967	1.2531	H	4.1845	1.4182	-4.1973
C	-0.6830	2.5700	5.3187	O	1.4404	-8.2230	1.4554	H	4.7863	-8.3379	1.9000
C	0.5623	3.1684	5.4342	O	2.6733	-8.5064	-0.7333	H	6.5508	-6.7698	2.7174
C	1.7402	2.6489	4.7723	O	0.3512	5.8204	5.3820	H	6.3405	-4.3391	2.3069
C	1.5589	1.5625	3.9102	O	0.5913	4.7456	7.6269	H	4.3945	-3.4252	1.0846

Table S4: The cartesian coordinates of the optimised S_1 - S_2 conical intersection geometry.

S2 Excited State Energies at the Minimum of the T₁ state

State	Nature	<i>f</i>	Δ E / eV
S ₀		-	0.36
T ₁	³ LE(A)	-	2.81
T ₂	³ CT/ ³ LE(A)	-	3.43
T ₃	³ CT/ ³ LE(A)	-	3.53
S ₁	¹ CT	0.07	3.56
T ₄	³ CT/ ³ LE(A)	-	3.57
T ₅	³ CT/ ³ LE(A)	-	3.59
T ₆	³ CT	-	3.67
S ₂	¹ CT	0.026	3.72
T ₇	³ LE(D)/ ³ CT	-	3.77
T ₈	³ LE(D)/ ³ CT	-	3.84

Table S5: Energy, nature and oscillator strength (*f*) of the lowest electronic triplet and singlet states at the geometry of minimum of T₁ state. CT denotes a charge transfer from the donor (D) to the acceptor (A) and LE(A), LE(D) are local excitons on the acceptor and donor, respectively. All Energies are relative to the energy of the ground state at the Franck-Condon Geometry.

S3 Spin Orbit Coupling Matrix Elements

SOC	T ₁	T ₂	T ₃	T ₄	T ₅	T ₆	T ₇	T ₈	T ₉	T ₁₀
S1	0.874	0.726	0.745	0.667	0.179	0.206	0.640	0.347	0.212	0.191
S2	0.330	0.616	0.625	0.844	0.553	0.344	0.395	0.143	0.140	0.334
S3	0.369	0.621	0.614	0.827	0.339	0.575	0.394	0.158	0.334	0.158
S4	1.041	0.458	0.390	0.121	0.087	0.118	0.981	0.076	0.156	0.200
T1	-	0.252	0.269	0.240	0.553	0.542	0.355	0.715	1.317	1.380
T2	-	-	0.130	0.246	0.477	0.691	0.823	1.155	1.894	1.507
T3	-	-	-	0.251	0.630	0.468	0.853	2.039	0.941	1.428
T4	-	-	-	-	0.678	0.660	0.297	0.893	1.184	1.181
T5	-	-	-	-	-	2.168	0.204	0.637	0.365	0.654
T6	-	-	-	-	-	-	0.130	0.725	0.575	0.193
T7	-	-	-	-	-	-	-	0.546	0.622	0.605
T8	-	-	-	-	-	-	-	-	0.112	0.153
T9	-	-	-	-	-	-	-	-	-	0.231

Table S6: Spin-orbit coupling matrix elements between the low lying singlet and triplet excited states at the optimised ground state geometry. All values reported in cm⁻¹.

SOC	T ₁	T ₂	T ₃	T ₄	T ₅	T ₆	T ₇
S ₁	0.647	0.610	0.311	0.215	0.221	1.072	0.641
S ₂	0.669	0.854	0.597	0.185	0.174	0.182	0.244
T ₁	-	1.122	1.169	0.193	0.266	0.846	0.572
T ₂	-	-	0.517	0.201	0.483	1.141	0.591
T ₃	-	-	-	0.266	0.464	0.766	0.593
T ₄	-	-	-	-	0.069	0.198	0.782
T ₅	-	-	-	-	-	0.302	0.419
T ₆	-	-	-	-	-	-	0.309

Table S7: Spin-orbit coupling matrix elements between the low lying singlet and triplet excited states at the optimised S₁ excited state geometry. All values reported in cm⁻¹.

SOC	T ₁	T ₂	T ₃	T ₄	T ₅	T ₆	T ₇	T ₈
S ₁	1.315	0.606	0.559	0.187	0.323	0.695	0.319	0.359
S ₂	0.296	0.735	0.590	0.056	0.194	0.117	0.236	0.204
T ₁	-	1.765	2.263	0.095	0.684	0.720	1.019	0.383
T ₂	-	-	0.631	0.348	0.363	0.545	0.374	0.280
T ₃	-	-	-	0.389	0.529	0.881	0.488	0.275
T ₄	-	-	-	-	0.276	0.436	1.018	0.314
T ₅	-	-	-	-	-	0.341	0.234	1.052
T ₆	-	-	-	-	-	-	0.799	0.391
T ₇	-	-	-	-	-	-	-	1.901

Table S8: Spin-orbit coupling matrix elements between the low lying singlet and triplet excited states at the optimised T₁ excited state geometry. All values reported in cm⁻¹.

SOC	T ₁	T ₂	T ₃	T ₄	T ₅	T ₆	T ₇
S ₁	0.880	0.702	0.946	0.466	0.197	0.275	0.415
S ₂	0.277	0.759	0.305	0.855	0.275	0.287	0.355
S ₃	0.038	0.298	0.272	0.341	0.486	0.748	0.307
S ₄	0.026	0.341	0.372	0.167	0.762	0.603	0.574
T ₁	-	0.831	0.422	1.485	0.071	0.315	0.244
T ₂	-	-	1.009	1.224	0.485	0.620	0.774
T ₃	-	-	-	0.822	0.330	0.313	0.580
T ₄	-	-	-	-	0.150	0.285	0.279
T ₅	-	-	-	-	-	0.192	0.737
T ₆	-	-	-	-	-	-	0.525

Table S9: Spin-orbit coupling matrix elements between the low lying singlet and triplet excited states at the optimised S₁-S₂ conical intersection geometry. All values reported in cm⁻¹.

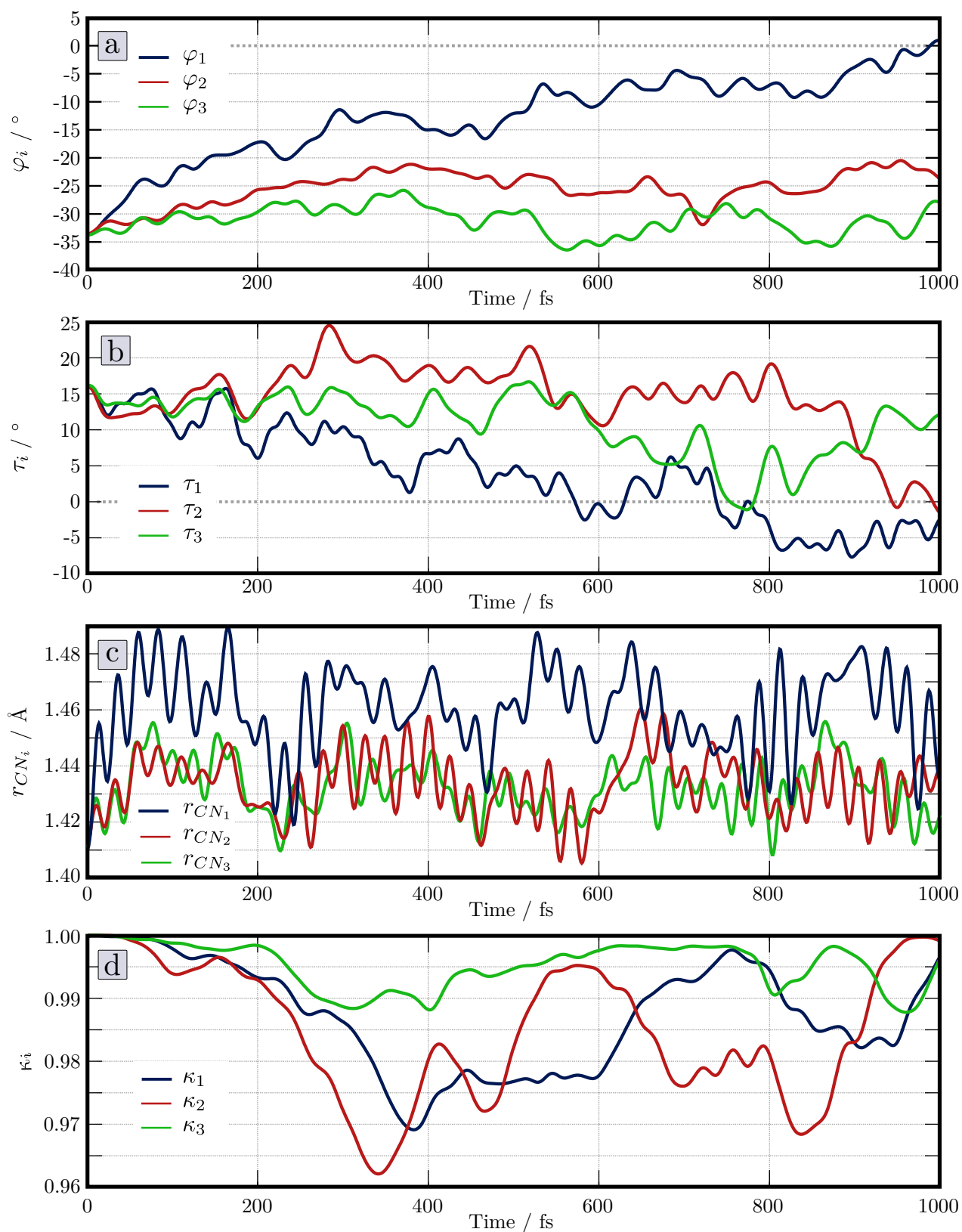


Figure S1: Evolution of the a) φ_i , b) τ_i angles, c) r_{CN_i} bond lengths and d) κ_i donor orientations along the trajectory starting from the Frank-Condon geometry in S_1 . This first trajectory has been computed at 0K to ensure that it reaches a geometry close to S_1 minimum.

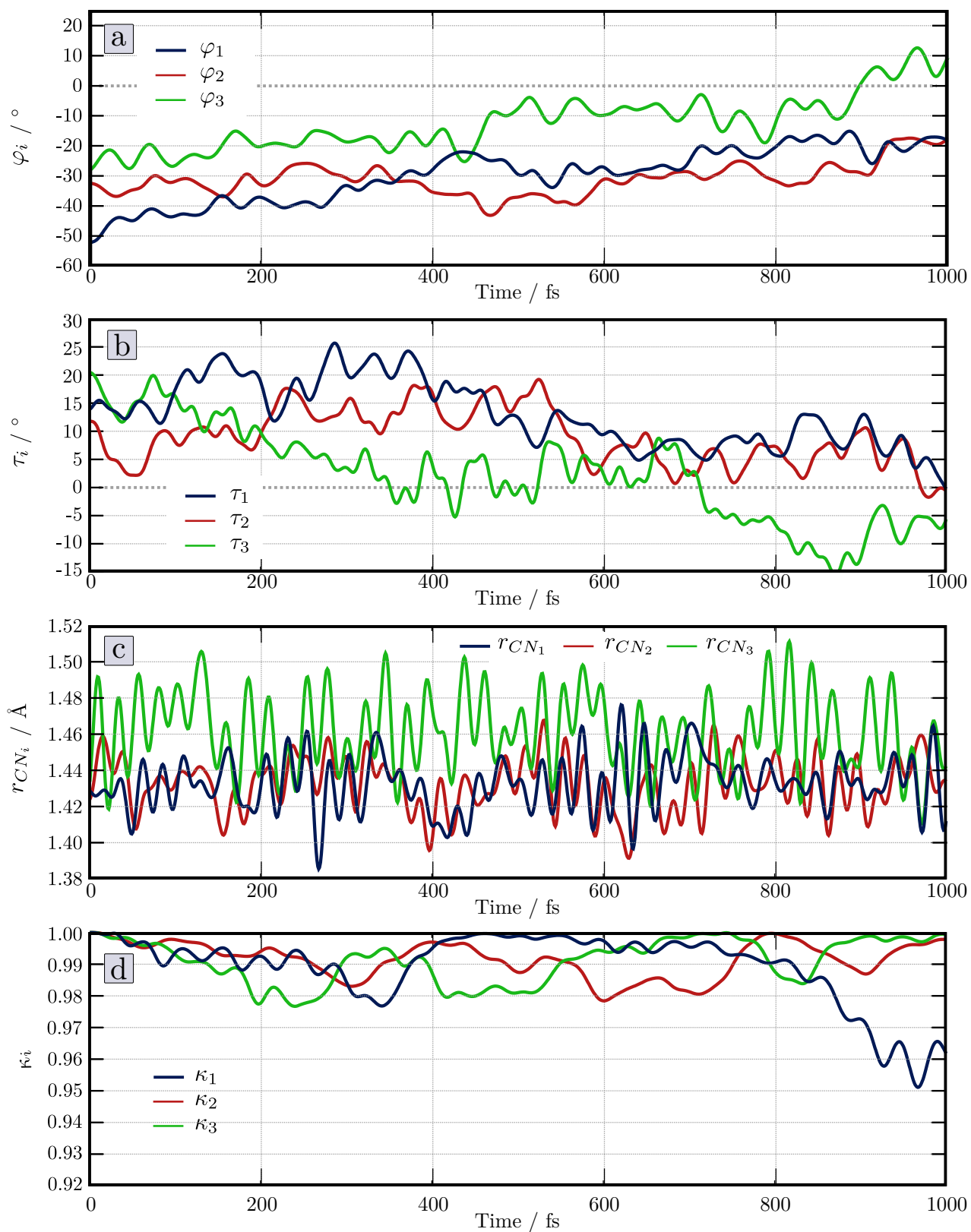


Figure S2: Evolution of the a) φ_i , b) τ_i angles, c) r_{CN_i} bond lengths and d) κ_i donor orientations along the trajectory starting from the Frank-Condon geometry in S_1 . This second trajectory has been computed at 0K to ensure that it reaches a geometry close to S_1 minimum.

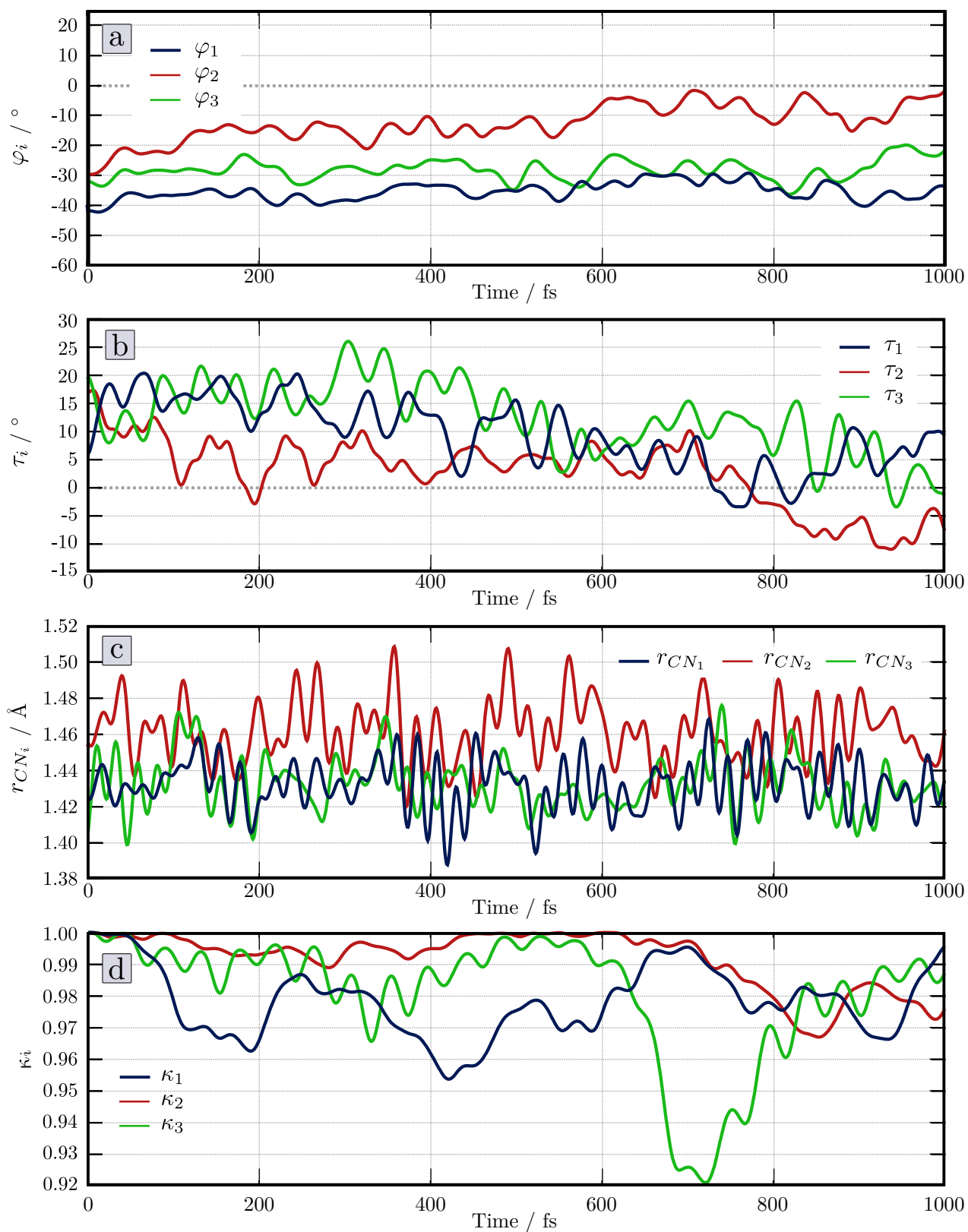


Figure S3: Evolution of the a) φ_i , b) τ_i angles, c) r_{CN_i} bond lengths and d) κ_i donor orientations along the trajectory starting from the Frank-Condon geometry in S_1 . This third trajectory has been computed at 0K to ensure that it reaches a geometry close to S_1 minimum.

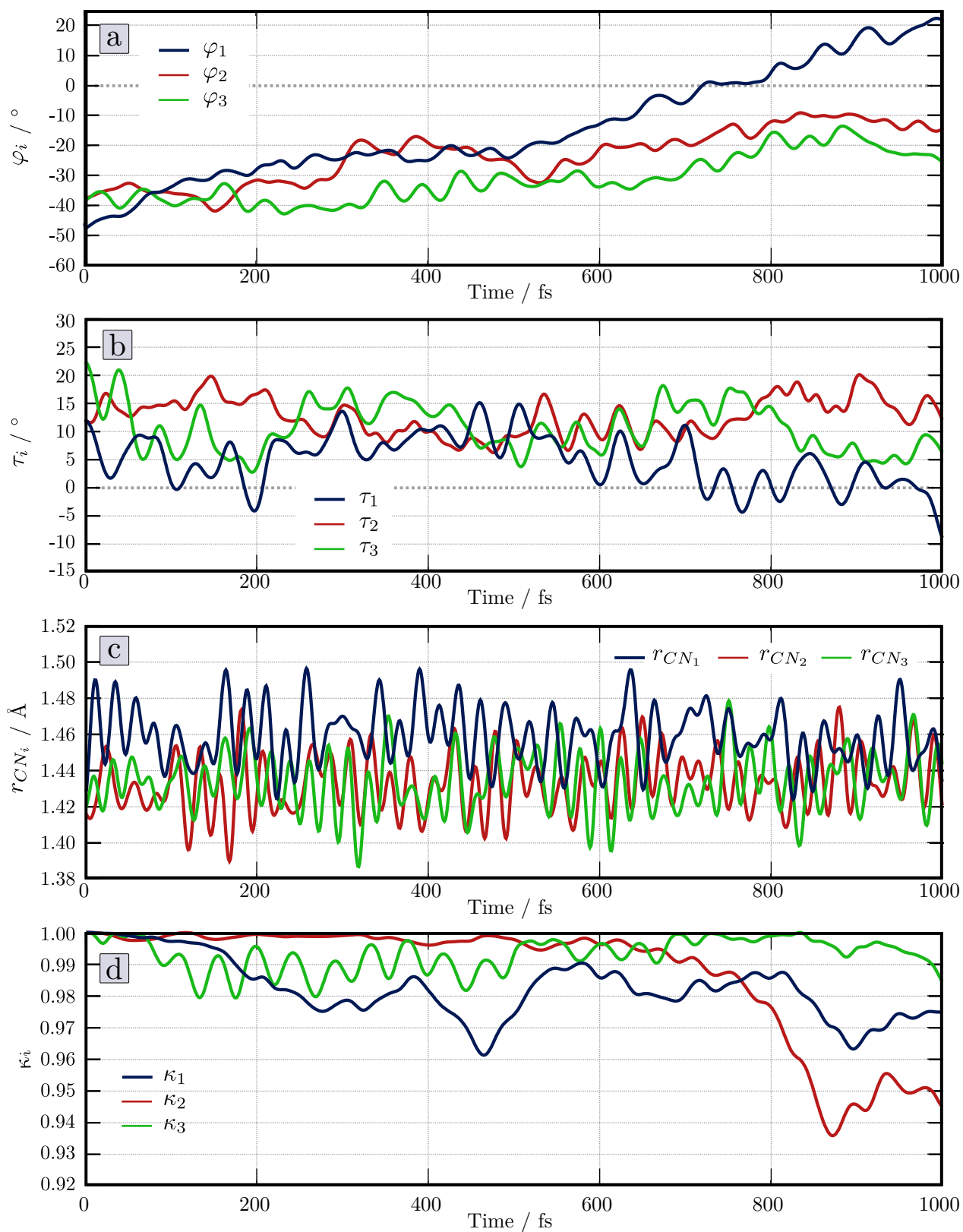


Figure S4: Evolution of the a) φ_i , b) τ_i angles, c) r_{CN_i} bond lengths and d) κ_i donor orientations along the trajectory starting from the Frank-Condon geometry in S_1 . This fourth trajectory has been computed at 0K to ensure that it reaches a geometry close to S_1 minimum.

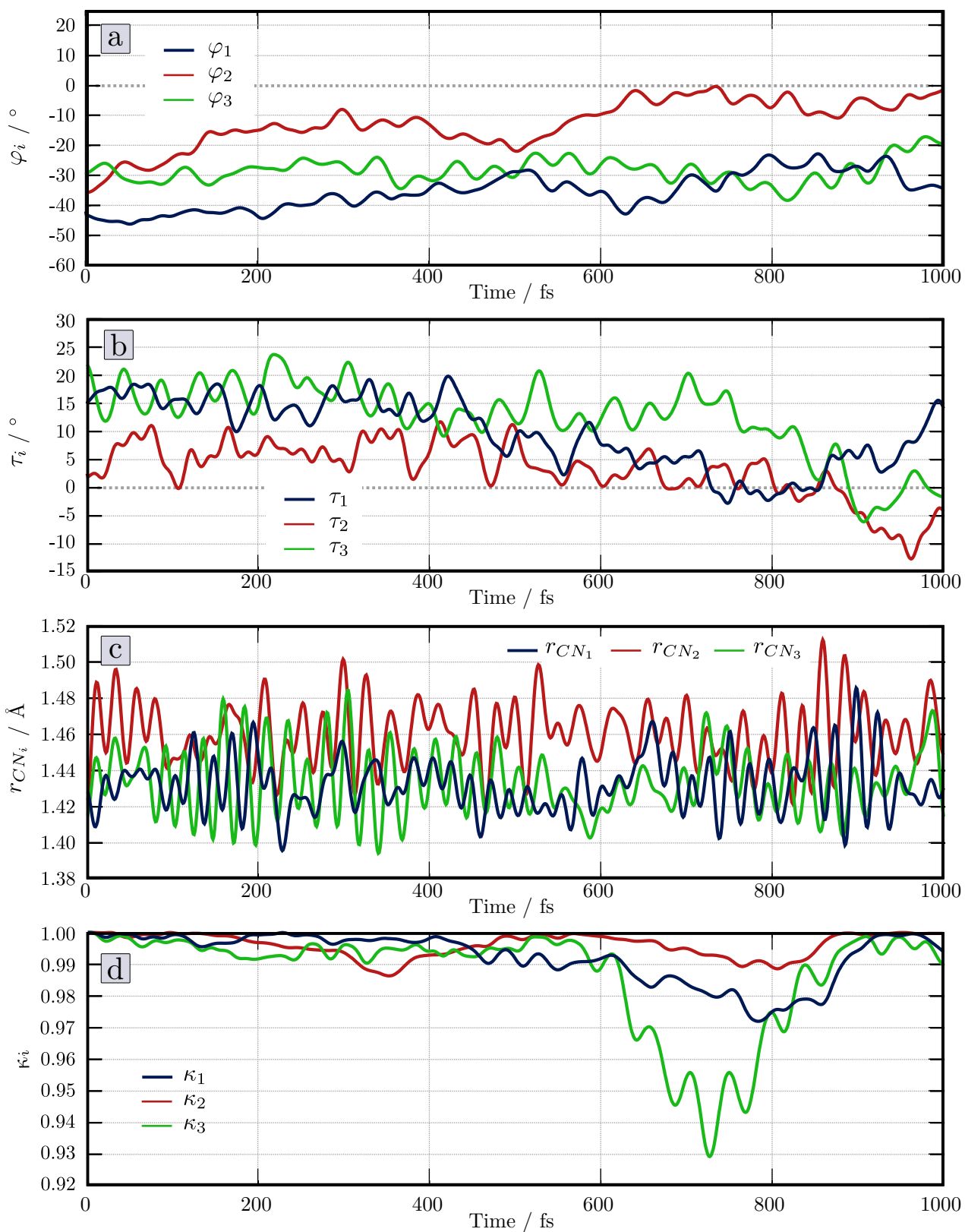


Figure S5: Evolution of the a) φ_i , b) τ_i angles, c) r_{CN_i} bond lengths and d) κ_i donor orientations along the trajectory starting from the Frank-Condon geometry in S_1 . This fifth trajectory has been computed at 0K to ensure that it reaches a geometry close to S_1 minimum.

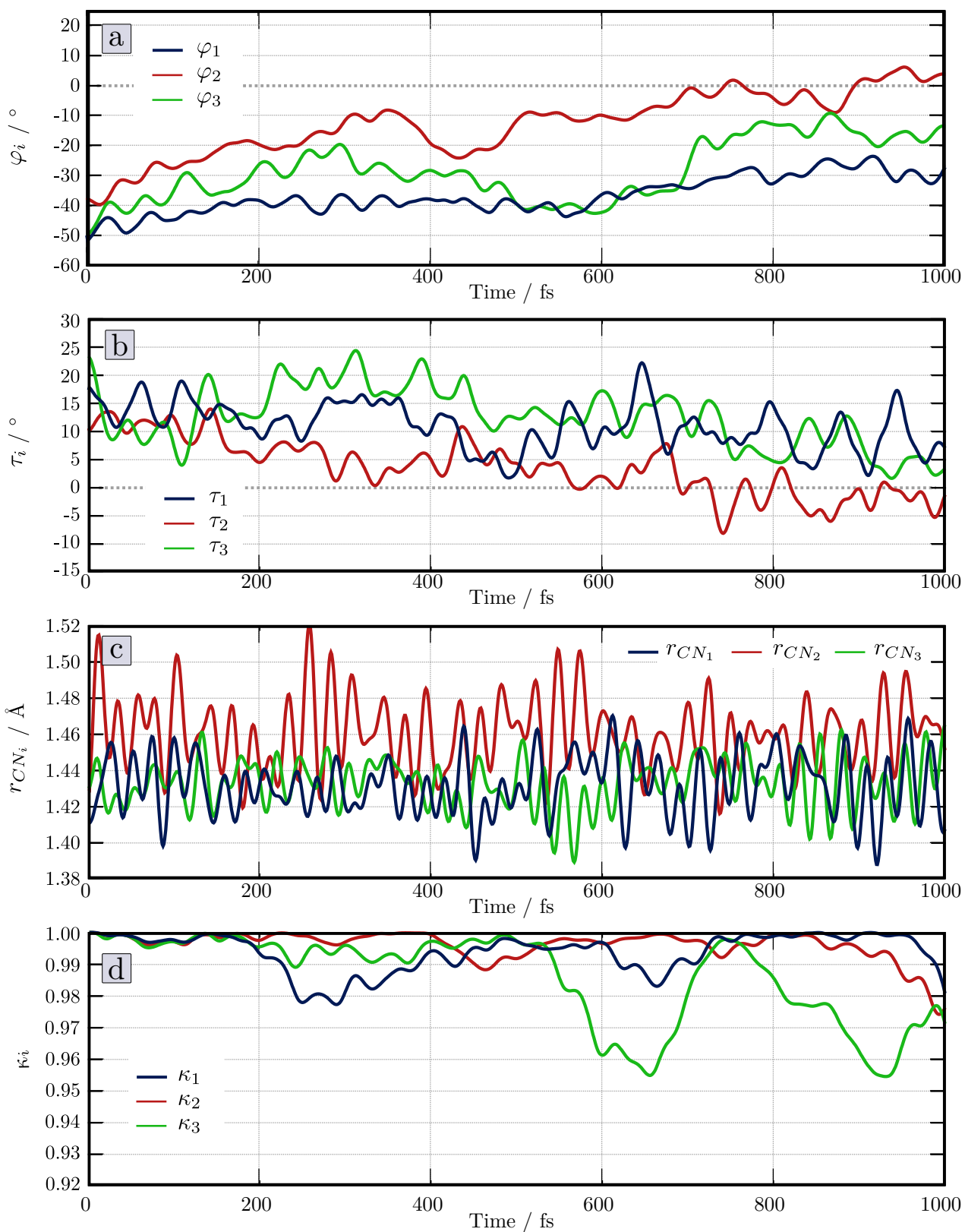


Figure S6: Evolution of the a) φ_i , b) τ_i angles, c) r_{CN_i} bond lengths and d) κ_i donor orientations along the trajectory starting from the Frank-Condon geometry in S_1 . This sixth trajectory has been computed at 0K to ensure that it reaches a geometry close to S_1 minimum.