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Electronic Supplementary Information for:

Surface hopping dynamics reveal ultrafast triplet generation promoted by S_1-T_2-T_1 spin-vibronic coupling in 2-mercaptobenzothiazole

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Table SM1: Symmetry and harmonic frequency (ω) of the vibrational modes of MBT at MP2/aug-cc-PVTZ level of theory.

No.(Sym.)	Freq (in cm^{-1})
$\nu_1(a'')$	92.0720
$\nu_2(a'')$	184.6766
$\nu_3(a')$	209.5027
$\nu_4(a'')$	277.2714
$\nu_5(a')$	378.3835
$\nu_6(a')$	401.1337
$\nu_7(a'')$	414.3494
$\nu_8(a')$	497.3884
$\nu_9(a'')$	508.1080
$\nu_{10}(a'')$	546.1555
$\nu_{11}(a'')$	582.1962
$\nu_{12}(a')$	613.2564
$\nu_{13}(a'')$	656.6858
$\nu_{14}(a')$	665.0128
$\nu_{15}(a')$	714.0417
$\nu_{16}(a'')$	750.5626
$\nu_{17}(a'')$	845.1070
$\nu_{18}(a')$	877.5735
$\nu_{19}(a'')$	925.1144
$\nu_{20}(a'')$	946.1409
$\nu_{21}(a')$	1036.3980
$\nu_{22}(a')$	1064.9191
$\nu_{23}(a')$	1107.9035
$\nu_{24}(a')$	1149.6771
$\nu_{25}(a')$	1175.6754
$\nu_{26}(a')$	1247.2210
$\nu_{27}(a')$	1282.0751
$\nu_{28}(a')$	1311.8605
$\nu_{29}(a')$	1437.2533
$\nu_{30}(a')$	1475.2271
$\nu_{31}(a')$	1494.0887
$\nu_{32}(a')$	1513.2085
$\nu_{33}(a')$	1614.7176
$\nu_{34}(a')$	1637.7736
$\nu_{35}(a')$	3205.6328
$\nu_{36}(a')$	3213.7655
$\nu_{37}(a')$	3223.7123
$\nu_{38}(a')$	3233.8427
$\nu_{39}(a')$	3598.8645

Table SM2: Ground-state (S_0) equilibrium geometry of MBT optimized at MP2/aug-cc-PVTZ level of theory.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	-1.021778	0.016214	0.000000
C	0.000000	0.978049	0.000000
C	-0.295498	2.340441	0.000000
C	-1.633384	2.720539	0.000000
C	-2.655222	1.762593	0.000000
C	-2.361090	0.402139	0.000000
C	1.309653	-0.972813	0.000000
H	0.495846	3.079010	0.000000
H	-1.885967	3.772198	0.000000
H	-3.688188	2.083286	0.000000
H	-3.149675	-0.338300	0.000000
N	1.249704	0.391373	0.000000
H	2.118421	0.908785	0.000000
S	2.670804	-1.893212	0.000000
S	-0.339207	-1.589760	0.000000

Table SM3: S_1^{min} geometry of MBT obtained at ADC(2)/def2-TZVP level of theory using external ORCA optimizer.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	-0.967041	-0.011402	0.059871
C	0.025077	0.982640	0.184640
C	-0.312543	2.328736	0.033518
C	-1.632233	2.653266	-0.266640
C	-2.614162	1.665176	-0.397283
C	-2.286923	0.321474	-0.234835
C	1.344037	-0.929644	0.531285
H	0.442364	3.101010	0.134640
H	-1.901449	3.695016	-0.398546
H	-3.635115	1.944626	-0.628446
H	-3.040499	-0.451836	-0.332700
N	1.267814	0.465931	0.480656
H	2.110331	0.993489	0.291437
S	2.294908	-1.921945	-0.588084
S	-0.297807	-1.590376	0.391955

Table SM4: S_2^{min} geometry of MBT obtained at ADC(2)/def2-TZVP level of theory using external ORCA optimizer.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	-1.016676	0.006003	0.149097
C	0.017833	0.973695	0.112697
C	-0.282991	2.336267	-0.022035
C	-1.614075	2.706838	-0.116633
C	-2.642322	1.747968	-0.086340
C	-2.355155	0.396562	0.038842
C	1.287089	-0.977193	0.449953
H	0.509937	3.075769	-0.044930
H	-1.867388	3.756338	-0.211943
H	-3.674437	2.070003	-0.159955
H	-3.146076	-0.344442	0.057672
N	1.247991	0.397741	0.196690
H	2.125645	0.893052	0.081952
S	2.515610	-1.835425	-0.597434
S	-0.357438	-1.589532	0.240302

Table SM5: T_1^{min} geometry of MBT obtained at ADC(2)/def2-TZVP level of theory using external ORCA optimizer.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	-0.943762	-0.001937	-0.068013
C	0.061136	0.965612	0.177008
C	-0.245971	2.331492	0.088730
C	-1.536808	2.697596	-0.259608
C	-2.528541	1.736961	-0.516668
C	-2.237158	0.382500	-0.429043
C	1.307894	-1.010188	0.560496
H	0.515237	3.080028	0.279757
H	-1.785106	3.750265	-0.333417
H	-3.529128	2.054904	-0.783511
H	-2.997132	-0.366014	-0.622878
N	1.261771	0.404143	0.466577
H	2.106354	0.942869	0.605188
S	2.469659	-1.934165	-0.368764
S	-0.313487	-1.599979	0.144069

Table SM6: T_2^{min} geometry of MBT obtained at ADC(2)/def2-TZVP level of theory using external ORCA optimizer.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	-0.980150	0.003028	0.042842
C	0.025642	0.964935	-0.143049
C	-0.291493	2.322187	-0.141396
C	-1.618928	2.697805	0.055913
C	-2.615932	1.739800	0.249156
C	-2.303591	0.379904	0.239444
C	1.281483	-0.997497	-0.439579
H	0.482461	3.068784	-0.285819
H	-1.875933	3.750766	0.061544
H	-3.642138	2.051872	0.403293
H	-3.075083	-0.368900	0.379178
N	1.280095	0.405344	-0.292701
H	2.027057	0.936070	-0.723950
S	2.671437	-1.869537	0.242604
S	-0.333954	-1.623363	-0.048728

Table SM7: S_2/S_1 MECP geometry of MBT obtained at ADC(2)/def2-TZVP level of theory using external ORCA optimizer.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	-1.001741	0.004285	0.040904
C	0.054003	0.950215	0.105863
C	-0.205635	2.323970	-0.014606
C	-1.516875	2.726823	-0.192109
C	-2.566552	1.790511	-0.261978
C	-2.320902	0.431033	-0.157582
C	1.253158	-1.038115	0.473778
H	0.603576	3.044022	0.038776
H	-1.741651	3.783924	-0.273888
H	-3.583072	2.140150	-0.399487
H	-3.127686	-0.290376	-0.218209
N	1.259699	0.341527	0.254019
H	2.159759	0.807613	0.195425
S	2.514937	-1.859102	-0.585098
S	-0.377040	-1.601557	0.105407

Table SM8: S_1/T_2 MECP geometry of MBT obtained at ADC(2)/def2-TZVP level of theory using external ORCA optimizer.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	-0.973760	0.001465	-0.088202
C	0.040126	0.941276	0.182170
C	-0.220613	2.307058	0.061755
C	-1.487422	2.708434	-0.353666
C	-2.490819	1.774144	-0.628065
C	-2.240068	0.409584	-0.496584
C	1.221263	-1.047344	0.602618
H	0.552874	3.036763	0.276274
H	-1.696606	3.766464	-0.462376
H	-3.470121	2.110865	-0.946730
H	-3.013256	-0.321073	-0.705731
N	1.220661	0.352129	0.577305
H	2.100256	0.849299	0.531271
S	2.415494	-2.010092	-0.291816
S	-0.412121	-1.625349	0.224023

Table SM9: T_2/T_1 MECP geometry of MBT obtained at ADC(2)/def2-TZVP level of theory using external ORCA optimizer.

	Coordinates (Angstroms)		
Atom	X	Y	Z
C	-0.975589	0.014356	-0.038617
C	0.013597	1.006264	-0.030116
C	-0.342304	2.351012	-0.016524
C	-1.696901	2.686931	-0.003831
C	-2.679038	1.697774	-0.002933
C	-2.323762	0.346941	-0.026931
C	1.357341	-0.907681	-0.181507
H	0.421252	3.121892	-0.006712
H	-1.983463	3.732109	0.012408
H	-3.726733	1.974098	0.012295
H	-3.083715	-0.426229	-0.039914
N	1.307258	0.491899	-0.016583
H	2.049324	1.038490	-0.438450
S	2.638623	-1.768817	0.706753
S	-0.276234	-1.596730	-0.142667

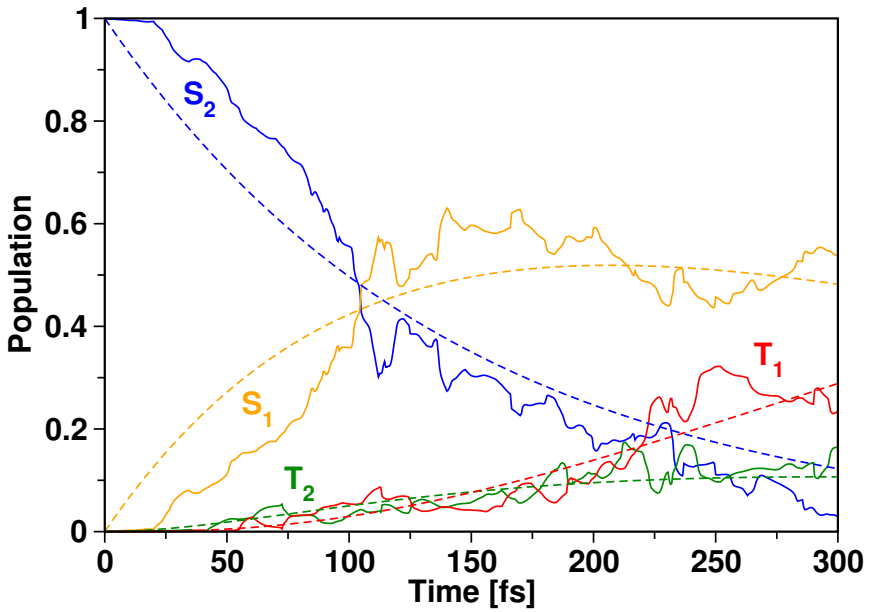

Figure SM1: Time-evolution of the low-lying singlets (S_1 and S_2) and triplets (T_1 and T_2) generated upon photoexcitation to "bright" S_2 of MBT and the corresponding population fit (shown by solid and dashed lines, respectively) as obtained through SHARC.