Supporting Information

A combined experimental and theoretical investigation on the excited-state dynamics of 2,4,6-trinitrotoluene (TNT) in DMSO solvent

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Table S1. Excitation energies (eV), Oscillator strengths *f*, and molecular orbital contributions to the excited state transitions, calculated at SMD/M06-2X/def2-TZVP level of theory at the optimized ground state geometry. (HOMO and LUMO are molecular orbitals of 58 and 59, respectively)

	Singlet					Triplet			
state	transition	contrib.	E(eV)	*f*	state	transition	contrib.	E(eV)	*f*
1	57→60	20.4%	4.043	0.0031	1	54→60	37.7%	2.856	0.0
	49→60	19.2%				56→60	37.6%		
	52→61	15.0%				56→62	11.4%		
	50→61	9.8%			2	55→59	39.3%	2.858	0.0
2	49→61	19.8%	4.046	0.0186		55→61	36.1%		
	52→60	17.4%				56→62	11.0%		
	57→61	15.2%			3	55→59	65.8%	2.868	0.0
	50→60	12.0%				55→61	22.5%		
3	53→59	43.0%	4.072	0.0000		55→63	15.3%		
	51→59	22.0%			4	57→60	33.0%	3.466	0.0
	53→61	13.0%				52→61	13.4%		
4	51→61	22.3%	4.523	0.0008		58→59	12.7%		
	48→60	16.6%			5	49→61	19.4%	3.570	0.0
	53→61	11.4%				52→60	16.9%		
	50→60	10.2%				57→60	16.4%		
5	51→60	22.3%	4.531	0.0003		50→60	11.6%		
	48→61	21.0%			6	53→59	41.6%	3.628	0.0
	53→60	12.2%				51→59	21.6%		
6	48→59	28.4%	4.550	0.0001		53→61	13.3%		
	50→59	19.7%			7	58→59	62.4%	3.941	0.0
	52→59	14.7%							
7	57→59	46.5%	4.910	0.0009					
	58→60	44.3%							
8	58→59	90.4%	5.224	0.2779					
9	58→61	41.6%	5.628	0.3057					

	57→59	36.2%							
10	57→60	41.7%	5.768	0.3157					
	58→61	28.5%							
	49→60	13.4%							
11	58→61	62.3%	6.006	0.0207					
	57→60	31.3%							
12	57→61	71.8%	6.147	0.0452					

Table S2. Excitation energies (eV), Oscillator strengths *f*, and molecular orbital contributions to the excited state transitions, calculated at SMD/M06-2X/def2-TZVP level of theory at the geometry of the optimized first singlet excited state S_1.

	Singlet					Triplet			
state	transition	contrib.	E(eV)	*f*	state	transition	contrib.	E(eV)	*f*
1	58→59	71.2%	2.019	0.0001	1	56→59	57.8%	0.881	0.0
	55→59	16.1%				55→59	44.7%		
						56←59	-16.0%		
						58→59	15.9%		
						55←59	-15.5%		
					2	58←59	61.2%	1.608	0.0
						55→59	27.0%		
					3	58→59	81.6%	2.787	0.0

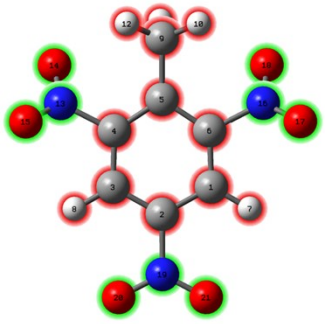
Figure S1. Charge transfer analysis based on the hole and electron difference on the methylphenyl group (red) and nitro group (green).

S_0-S_9

Fragment 1: Hole 84.5% Electron 31.12% Diff 53.38%
Fragment 2: Hole 15.5% Electron 68.88%

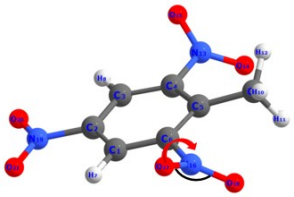
S_0-S_{10}

Fragment 1: Hole 87.11% Electron 19.51% Diff 67.60%
Fragment 2: Hole 12.89% Electron 80.49%

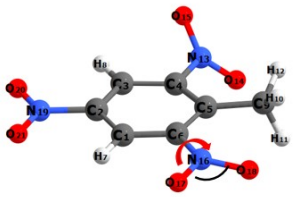


Fragment 1: methylphenyl group; (red region)
Fragment 2: Nitro groups (green region)

Figure S2. Optimized structures for the S_0 state and S_1 state for the DMSO solvated TNT molecule at SMD/M06-2X/def2-TZVP level.



Optimized S_0 state geometry



Optimized S_1 state geometry

Table S3. Structural information for the optimized S_0 and S_1 state geometry.

	S_0 state geometry	S_1 state geometry
D(C_1-C_6-N_{16}-O_{17})	-40.94	-2.27
A(O_{17}-N_{16}-O_{18})	125.02	104.40
B(C_6-N_{16})	1.478	1.368
B(N_{16}-O_{17})	1.211	1.282

Table S4. Vertical excitations of DMSO solvated TNT at S_0 minimum calculated using M06-2X and STEOM-CCSD with def2-TZVP basis set.

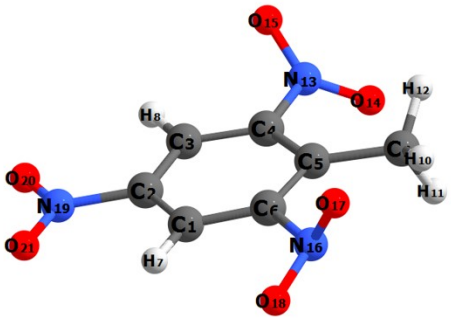
Singlet state	M06-2X/def2-TZVP		STEOM-CCSD/def2-TZVP	
	E(eV)	*f*	E(eV)	*f*
S_1	4.043	0.0031	3.923	0.0002
S_2	4.046	0.0186	3.985	0.0134
S_3	4.072	0.0000	3.990	0.0071
S_4	4.522	0.0008	4.360	0.0000
S_5	4.522	0.0008	5.362	0.3156
Triplet state	M06-2X/def2-TZVP		STEOM-CCSD/def2-TZVP	
	E(eV)	*f*	E(eV)	*f*
T_1	2.856	0.0	3.245	0.0
T_2	2.858	0.0	3.450	0.0
T_3	2.869	0.0	3.489	0.0
T_4	3.466	0.0	3.491	0.0
T_5	3.570	0.0	3.767	0.0

Table S5. Vertical excitations of DMSO solvated TNT at S_1 minimum calculated using M06-2X and STEOM-CCSD with def2-TZVP basis set.

Singlet state	M06-2X		STEOM-CCSD	
	E(eV)	*f*	E(eV)	*f*
S_1	2.019	0.0001	1.933	0.0002
S_2	4.013	0.0094	3.916	0.0025
S_3	4.024	0.0000	3.947	0.0150
S_4	4.452	0.0499	4.340	0.0880
S_5	4.520	0.0088	5.300	0.2738
Triplet state	M06-2X		STEOM-CCSD	
	E(eV)	*f*	E(eV)	*f*
T_1	0.881	0.0	1.583	0.0
T_2	1.601	0.0	2.070	0.0
T_3	2.789	0.0	3.023	0.0
T_4	3.315	0.0	3.517	0.0
T_5	3.557	0.0	3.524	0.0

The geometry optimization for the S_0-S_1 PES conical intersection is performed based on the spin-flip TDDFT method with B3LYP functional and def2-TZVP basis set. The optimization is converged with the E_{CI} energy difference less than 0.0001 Hatree. Single point energy calculation than carried out at M06-2X/def2-TZVP level to compare with the $S_{1\text{-min}}$ energy. All calculations employ CPCM/SMD solvent model to evaluate the solvent effect.

Figure S3. Optimized structure of the S_0-S_1 conical intersection.



Optimized S_0-S_1 conical intersection structure

Table S6. Structural information for the optimized S_0 and S_1 conical intersection geometry.

	CI geometry
D(C_1-C_6-N_{16}-O_{17})	-105.81
A(O_{17}-N_{16}-O_{18})	91.59
B(C_6-N_{16})	1.428
B(N_{16}-O_{17})	1.320

Figure S4. Schematic view for the DMSO solvated TNT excited state dynamics from S_1 to S_0

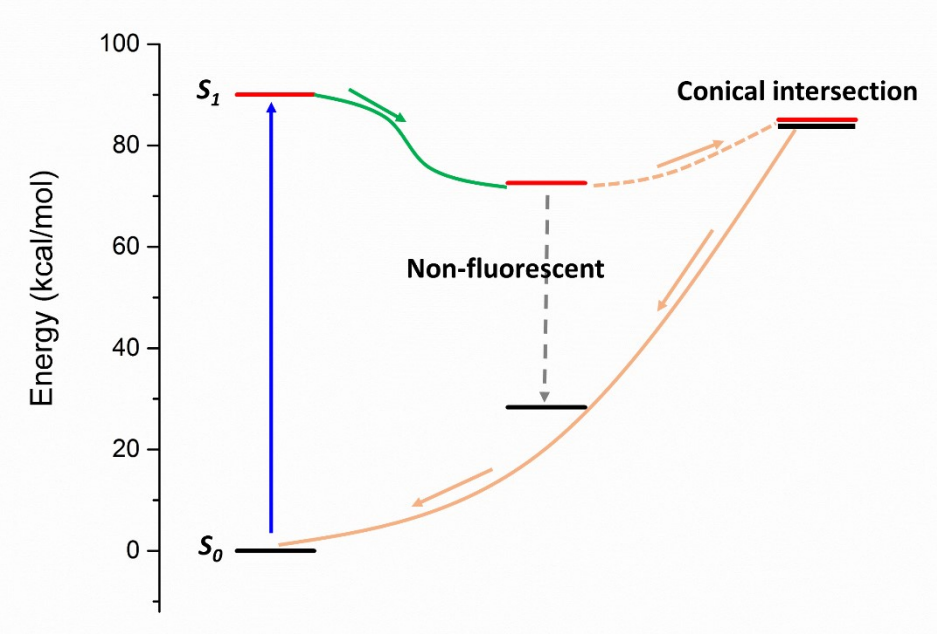
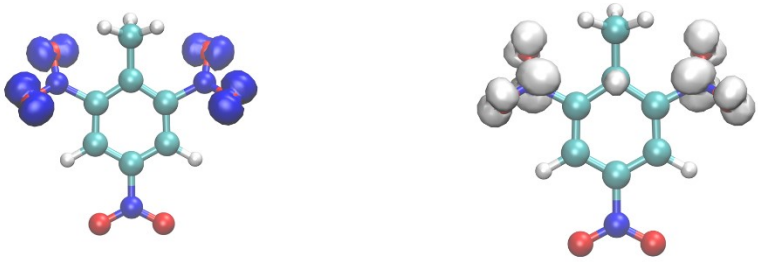


Figure S5. *Hole-electron* orbitals for TNT S_0-S_1 transition. Blue: *hole*; white: *electron*.

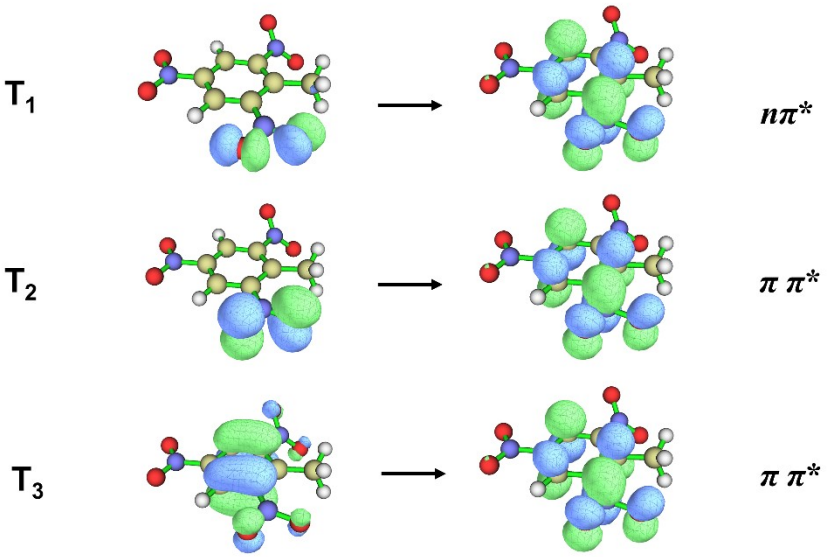


D (Å)	S_r	Ec (eV)	HDI	EDI
0.09	0.53	4.655	13.97	10.85

Table S6. The STEOM-CCSD/def2-TZVP calculated triplet states were shown

	E (Hatree)	MOs		Contrib.
T_1	1.583	55 -> 59		70.5 %
T_2	2.070	56 -> 59		70.4 %
T_3	3.023	57 -> 59		45.0%

Figure S6.



Cartesian coordinates for the key structures in the current theoretical study.

Optimized ground state geometry of TNT:

C	-0.88147300	-1.20676100	-0.01385400
C	-1.54834400	0.00004000	-0.04075500
C	-0.88141200	1.20681000	-0.01385300
C	0.49745500	1.16846100	0.02594400
C	1.26167900	-0.00003400	0.06711200
C	0.49739400	-1.16848100	0.02594800
H	-1.41330100	-2.14826500	-0.03208300
H	-1.41319700	2.14834100	-0.03208400
C	2.75238500	-0.00010800	0.22837100
H	3.07592500	-0.88218800	0.77563500
H	3.24078300	-0.00014000	-0.74662500
H	3.07603600	0.88192400	0.77563900
N	1.17080400	2.48367900	0.01297900
O	2.15099500	2.60471200	-0.68827700
O	0.68167500	3.36703100	0.68299000
N	1.17068400	-2.48372700	0.01300300
O	0.68133200	-3.36713800	0.68277400
O	2.15103100	-2.60472300	-0.68804200
N	-3.02118300	0.00007800	-0.09515900
O	-3.58214000	1.07384200	-0.11529600
O	-3.58220200	-1.07365400	-0.11536400

Optimized S_1 state geometry of TNT molecule

C	-0.85151400	-1.21378200	-0.00962200
C	-1.54731700	-0.02980600	-0.01372400
C	-0.91483000	1.19831800	0.00234200
C	0.46919700	1.19945300	0.01374300
C	1.26782900	0.06214700	0.06188300
C	0.54698400	-1.15892600	0.02778200
H	-1.37082100	-2.16277900	-0.03881900
H	-1.47509300	2.12301700	-0.01057000
C	2.75352200	0.10320900	0.19196000
H	3.10113100	-0.67983100	0.86688500
H	3.23431400	-0.04745400	-0.77913500
H	3.09615500	1.05687400	0.58796100
N	1.09329300	2.53202000	-0.03116000
O	2.01542200	2.69522700	-0.80361200
O	0.62341400	3.39103000	0.68672500
N	1.18606800	-2.36810800	0.04507900
O	0.61463600	-3.51538900	0.07131100
O	2.43102500	-2.63548900	-0.08173900
N	-3.01539700	-0.07137400	-0.04987400
O	-3.60728700	0.98911800	-0.06844800
O	-3.54929200	-1.16215700	-0.05684000

Optimized S_0-S_1 conical intersection geometry

C	-0.802423	-1.213554	-0.140431
C	-1.525679	-0.033951	-0.138378
C	-0.908861	1.195689	-0.005490
C	0.473960	1.227581	0.085510
C	1.282687	0.086812	0.077607
C	0.577045	-1.127089	-0.015161
H	-1.293659	-2.172649	-0.204924
H	-1.485154	2.108224	0.013751
C	2.781027	0.113157	0.153557
H	3.177866	-0.833070	0.510229
H	3.191370	0.303470	-0.840850
H	3.130662	0.905569	0.812117
N	1.075708	2.574339	0.166183
O	2.083366	2.786488	-0.487503
O	0.510517	3.398863	0.866378
N	1.330861	-2.339374	-0.046245
O	1.872965	-2.872749	1.032754
O	0.738888	-3.491639	-0.363794
N	-2.993004	-0.089169	-0.257267
O	-3.599481	0.969450	-0.307832
O	-3.517225	-1.191078	-0.298086