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The mechanism of TNT detection with amino acid-capped quantum dots: A density functional theory study

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Table S1 Net (NPA) charge (in e) of selected atoms and groups for TNT, Cys, **S1**, **S2**, **S3** and **S4** calculated with M06-2X/6-311++G(d,p).

Atom	TNT	**S1**	**S2**	**S3**	**S4**
C1	0.047	0.096	-0.120	0.047	-0.117
C2	0.094	-0.010	0.029	0.097	0.036
C3	-0.141	-0.087	-0.102	-0.152	-0.125
C4	0.078	-0.048	-0.023	0.081	-0.041
C5	-0.141	-0.089	-0.140	-0.144	-0.124
C6	0.094	-0.014	0.069	0.079	0.036
C7	-0.610	-0.611	-0.377	-0.610	-0.397
Nitro group					
C2–NO2	-0.239	-0.390	-0.437	-0.240	-0.391
C4–NO2	-0.250	-0.384	-0.500	-0.238	-0.458
C6–NO2	-0.239	-0.380	-0.325	-0.234	-0.392

Table S2 HOMO and LUMO energy levels and their gaps (in eV) calculated with M06-2X/6-311++G(d,p).

	HOMO	LUMO	Gaps
TNT	-9.986	-2.456	7.530
Cys	-8.317	-0.132	8.185
S1	-7.640	-2.558	5.082
S2	-6.833	-2.214	4.619
S3	-8.310	-2.522	5.788
S4	-6.579	-1.995	4.584

Table S3 Compositions of HOMO to LUMO transitions.

	α		β		γ	
TNT	310 nm	f = 0.017	237 nm	f = 0.249	221 nm	f = 0.304
HOMO:58	49 → 59	-0.15411	49 → 60	-0.10582	49 → 60	-0.25833
LUMO:59	49 → 61	0.30817	57 → 60	0.11202	50 → 61	-0.12914
	50 → 60	0.25041	58 → 59	0.66644	52 → 61	0.10750
	50 → 63	0.12634			57 → 60	0.48742
	52 → 60	-0.29507			58 → 59	-0.12450
	52 → 63	-0.14166			58 → 61	-0.33008
	54 → 60	0.10668				
	57 → 59	-0.16338				
	57 → 61	0.28882				
	58 → 60	-0.15913				
Cys	203 nm	f = 0.041	178 nm	f = 0.016	173 nm	f = 0.0119
HOMO:32	32 → 33	-0.32759	32 → 33	-0.17759	31 → 33	-0.12840
LUMO:33	32 → 34	-0.32094	32 → 34	0.12425	31 → 34	0.10627
	32 → 36	-0.19948	32 → 35	0.40334	31 → 36	-0.10278
	32 → 37	0.39176	32 → 36	0.31238	31 → 38	-0.17095
	32 → 40	0.13029	32 → 37	0.15080	32 → 33	0.19133
	32 → 41	-0.13523	32 → 38	-0.30921	32 → 35	-0.21619
	32 → 48	0.11340	32 → 41	-0.13688	32 → 36	0.32164
					32 → 37	0.32121
					32 → 40	-0.19539
					32 → 41	0.12511
					32 → 42	0.17220
S1	451 nm	f = 0.219	340 nm	f = 0.388	307.9 nm	f = 0.010
HOMO:90	90 → 91	0.69941	90 → 92	0.69244	78 → 92	0.16771
LUMO:91					80 → 91	0.11531
					81 → 92	0.21276
					81 → 93	0.11527
					82 → 92	-0.12552
					84 → 91	0.47315
					85 → 91	0.10148
					88 → 91	-0.15892
S2	508 nm	f = 0.155	408 nm	f = 0.366	320 nm	f = 0.134
HOMO:90	90 → 91	0.63586	90 → 91	0.28995	79 → 91	-0.11571
LUMO:91	90 → 92	-0.29358	90 → 92	0.62756	83 → 91	0.11968
			90 → 93	0.10956	85 → 91	0.15711
					86 → 91	0.29459
					86 → 93	0.13520
					88 → 91	0.15195
					90 → 93	0.48538
S3	311 nm	f = 0.010	277 nm	f = 0.014	259 nm	f = 0.012

HOMO:90	77 → 92	-0.11780	75 → 91	0.11294	87 → 91	-0.22782
LUMO:91	77 → 93	-0.10132	77 → 91	-0.11204	87 → 92	0.12624
	78 → 91	-0.15578	78 → 91	-0.10923	88 → 91	0.16589
	78 → 92	-0.18049	79 → 91	0.10060	88 → 92	0.25441
	78 → 93	-0.18306	82 → 91	-0.10265	89 → 92	0.40320
	78 → 94	0.10730	89 → 91	0.54424	90 → 92	0.32816
	81 → 91	0.16270	89 → 93	-0.19756	90 → 93	0.10144
	81 → 92	0.16207	90 → 91	-0.19724		
	81 → 93	0.15370				
	82 → 91	0.11803				
	82 → 92	0.15242				
	82 → 93	0.15262				
	87 → 91	-0.17425				
	87 → 92	-0.17653				
	87 → 93	-0.17668				
S4	523 nm	f = 0.157	404 nm	f = 0.348	323 nm	f = 0.235
HOMO:58	58 → 59	0.70210	58 → 60	0.69205	51 → 61	-0.10298
LUMO:59			58 → 61	0.11384	52 → 59	-0.12590
					54 → 59	-0.19512
					56 → 60	0.12549
					58 → 60	-0.11245
					58 → 61	0.60941

α, β, γ stand for the first three adsorption peak with oscillator strength larger than 0.01.

Table S4 Selected vibration frequencies and intensities of **S1** and **S2**

	S1		**S2**	
	Freq.	IR Inten.	Freq.	IR Inten.
1	1315.0	2937.0	1341.0	3554.3
2	1242.8	2021.5	1176.9	3237.3
3	1248.8	1246.4	1094.4	2446.2
4	1036.8	947.9	3445.2	1123.2
5	1610.8	712.7	1559.5	848.3
6	1080.1	680.4	1707.6	642.6
7	1204.0	597.3	1222.4	525.6
8	1694.2	594.8	1853.9	505.0
9	1578.4	492.2	1039.1	499.9
10	1322.0	476.0	1230.8	403.0
11	1857.8	454.6	1622.5	389.6
12	1332.2	361.3	1495.4	353.6
13	1092.4	334.8	3351.8	350.8
14	1183.1	315.6	1455.8	340.7
15	1624.5	267.0	1330.8	330.7
16	1523.2	247.2	3456.8	303.1
17	3769.6	221.9	1083.9	286.7
18	3428.5	216.8	1228.6	270.9
19	1495.2	209.6	1603.7	247.6
20	948.9	198.4	1380.4	219.3
21	3354.3	192.2	3515.1	203.3
22	1553.6	181.2	822.2	201.0
23	1303.9	158.6	1271.6	193.1
24	736.9	134.5	1446.1	193.0
25	1394.4	133.3	1638.9	185.1
26	987.0	123.0	1523.7	179.2
27	1478.3	121.8	1170.6	165.3
28	654.4	103.7	801.7	157.4
29	685.1	84.8	765.1	152.7
30	1433.1	84.6	1425.8	137.5

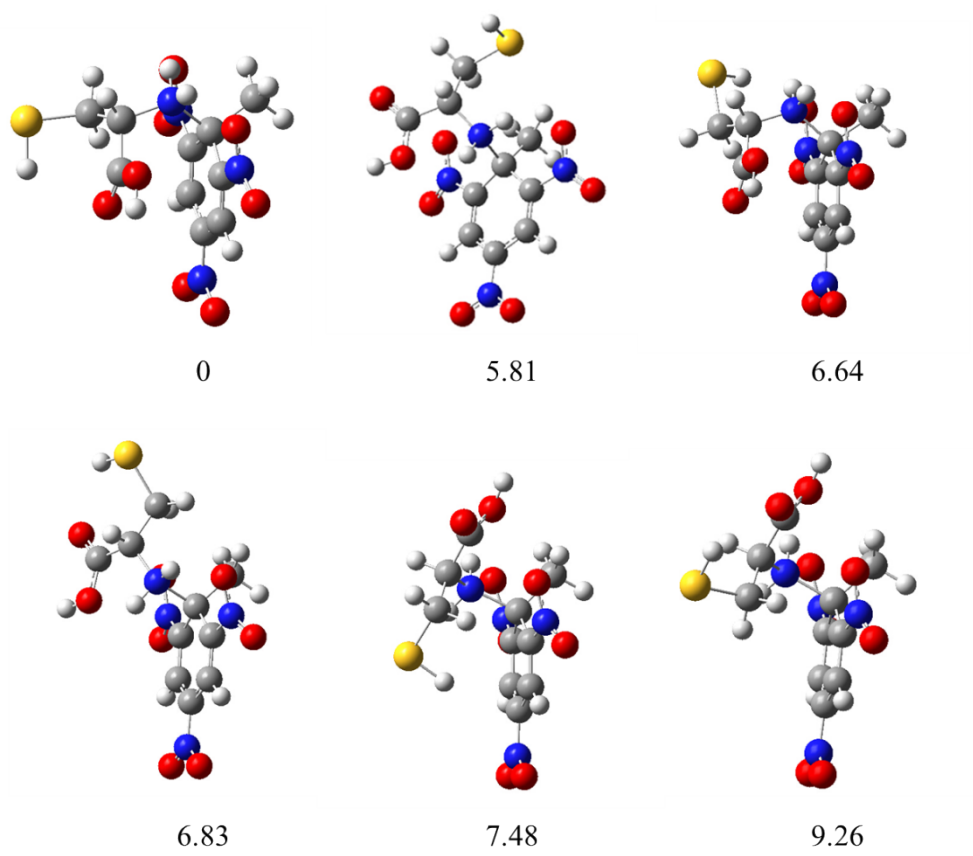

Fig. S1 Structures and relative energy (in kcal/mol) of the low-lying **S1** isomers in water calculated with M06-2X functional.

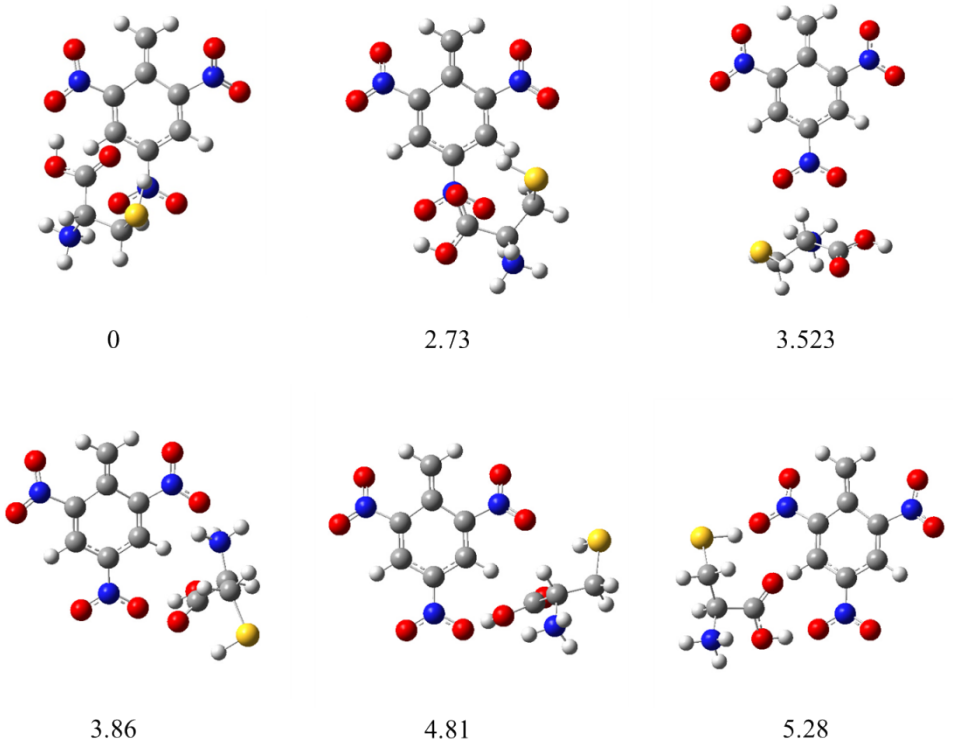

Fig. S2 Structures and relative energy (in kcal/mol) of the low-lying **S2** isomers in water calculated with M06-2X functional.

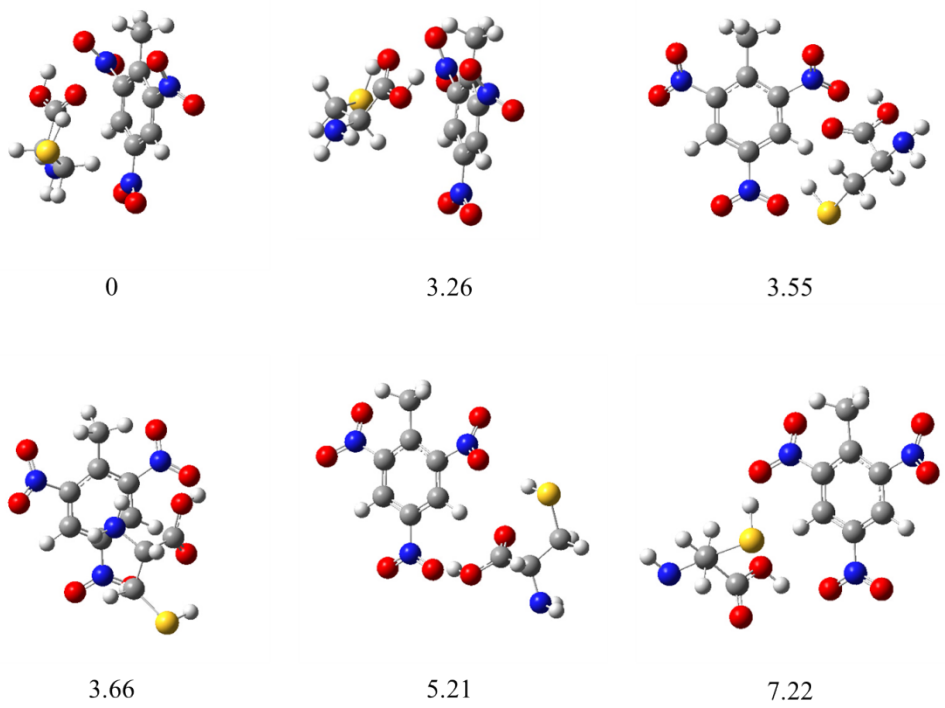

Fig. S3 Structures and relative energy (in kcal/mol) of the low-lying **S3** isomers in water calculated with M06-2X functional.

Cartesian coordinates of S1 in water:

S1			
C	2.628692	-0.484687	-0.433238
H	3.284424	-0.534066	0.435302
H	1.956072	-1.339356	-0.424357
S	3.722736	-0.618758	-1.884096
H	2.768759	-0.964855	-2.760878
C	1.878589	0.842725	-0.441412
H	2.591727	1.648758	-0.623442
C	0.842540	0.897358	-1.568828
N	1.254111	1.194819	0.891117
H	1.098404	2.212219	0.927764
O	0.478752	2.152193	-1.824485
H	-0.160383	2.163184	-2.554922
O	0.454599	-0.066714	-2.165587
O	-0.551911	3.238390	0.841111
O	-2.415553	2.942602	-0.178843
O	-3.734797	-1.338645	-1.643971
O	-2.698618	-3.109366	-0.993929
O	0.902744	-2.846425	2.057363
O	1.851347	-0.964373	2.468860
N	-1.423089	2.503900	0.370049
N	-2.850325	-1.894965	-1.006691
N	0.944493	-1.633627	1.967934
C	-0.102877	0.574259	1.342144
C	-1.218682	1.084391	0.448713
C	-2.089293	0.299005	-0.247441
H	-2.879447	0.767180	-0.819675
C	-1.955225	-1.090014	-0.240734
C	-0.938854	-1.692513	0.503882
H	-0.839188	-2.769954	0.516849
C	-0.060660	-0.934795	1.220232
C	-0.309453	1.026302	2.802909
H	-1.268524	0.626262	3.131230
H	-0.336745	2.111099	2.881410
H	0.472516	0.642797	3.454115
H	1.931110	0.952495	1.623774

Cartesian coordinates of S2 in water:

S2			
C	3.727212	-1.091585	-0.306225
H	4.661668	-1.423493	0.148057
H	2.903773	-1.599508	0.196211
S	3.833427	-1.624569	-2.041407
H	2.540129	-1.432742	-2.340072
C	3.607177	0.419532	-0.158292
H	4.333321	0.928275	-0.796423
C	2.222087	0.953804	-0.521552
N	3.916527	0.828017	1.253142
H	4.894379	0.641522	1.488248
H	3.741565	1.828962	1.387113
O	2.059171	2.194787	-0.085568
H	1.152224	2.526633	-0.280745
O	1.409897	0.324951	-1.142260
H	3.306692	0.310470	1.903510
O	-2.605827	3.272586	-0.598866
O	-0.518063	3.212645	-0.114796
O	1.499601	-0.264543	1.984825
O	0.733861	-2.279077	1.859599
O	-3.724409	-2.999958	0.150404
O	-4.243936	-1.683654	-1.459091
N	-1.635107	2.666845	-0.182126
N	0.594340	-1.073224	1.698223
N	-3.627908	-1.939074	-0.441640
C	-4.186207	0.982150	-0.434560
H	-5.000648	0.306561	-0.646935
H	-4.377613	2.038433	-0.497888
C	-2.972110	0.503652	-0.100260
C	-1.768472	1.303245	0.215593
C	-0.687635	0.787922	0.879902
H	0.116094	1.436960	1.188924
C	-0.595929	-0.572500	1.154894
C	-1.606367	-1.453804	0.698317
H	-1.490259	-2.523072	0.809555
C	-2.695336	-0.940038	0.081480