Supplementary Information

Tailoring on Benzo[α]phenoxazine moiety for efficient photosensitizers in Dye Sensitized Solar Cell via DFT/TD-DFT method

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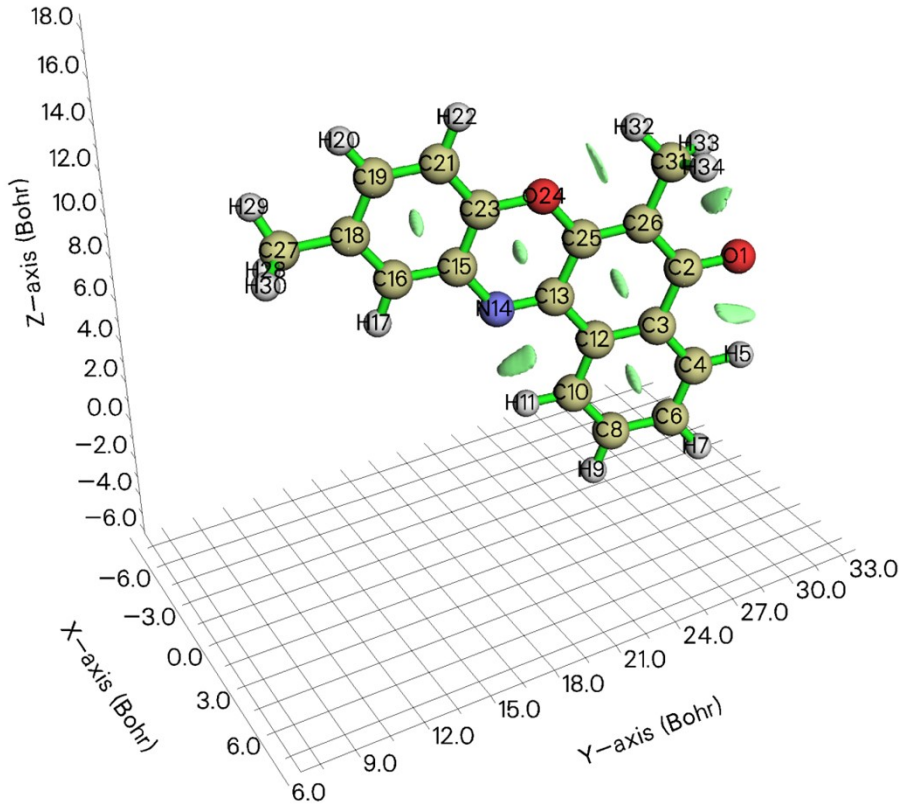
Figure Caption:

Table Captions:

M-0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Y−axis (Bohr)
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18.0
21.0
24.0
27.0
30.0
33.0
H22
H20
C21
C19
H32
H33
C31
H34
O24
C23
H29
C18
C25
C26
C27
C15
C2
O1
H28
H30
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C4
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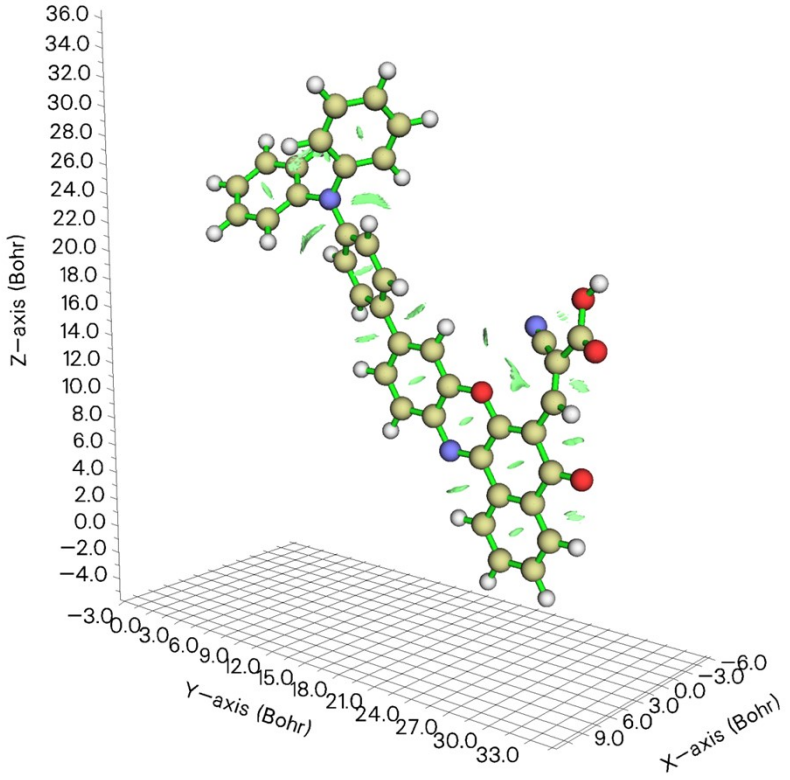
H7
H9

M-1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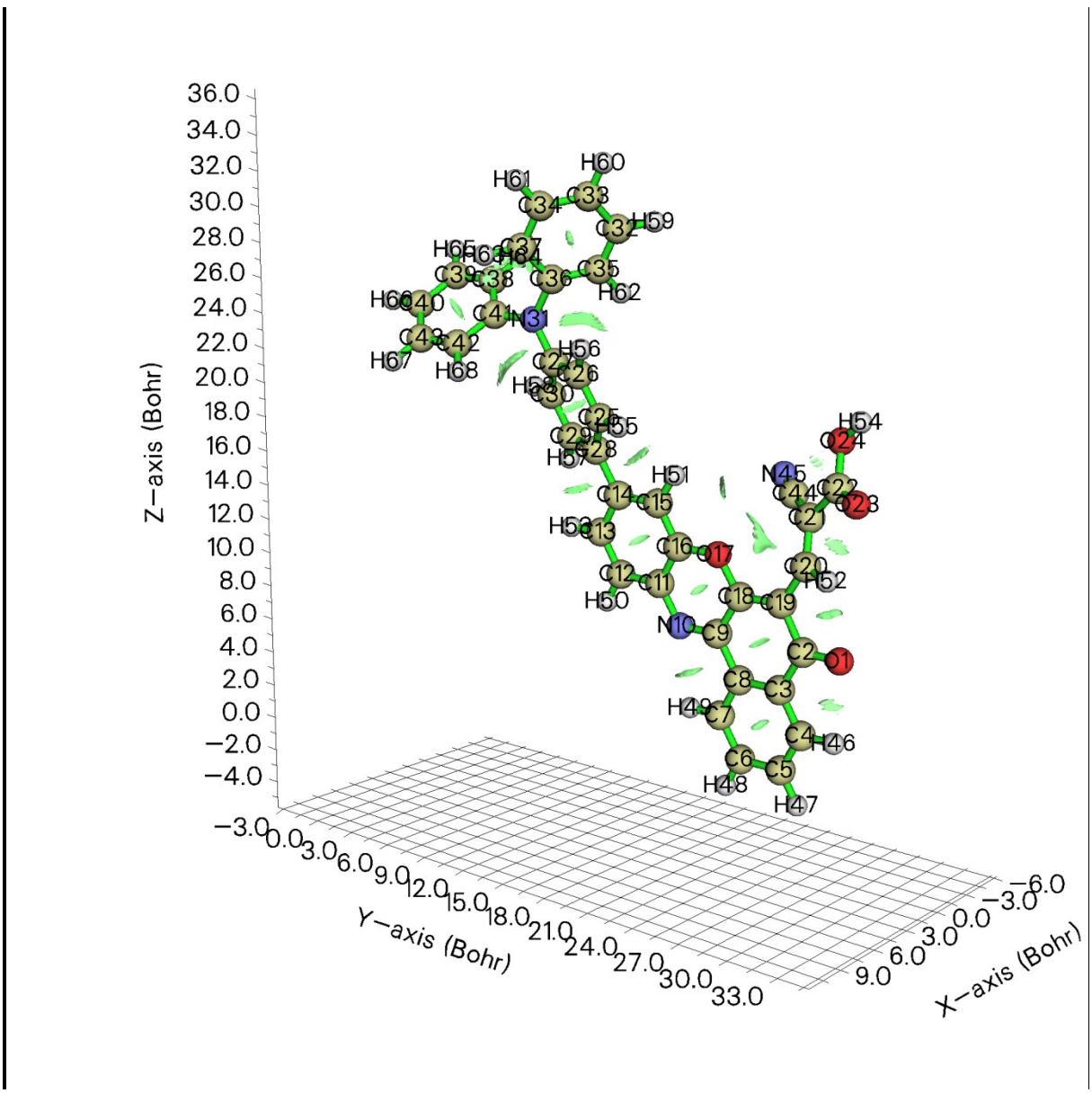
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C34
C33
C32
H59
C37
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H63
C39
C38
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C28
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H54
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C18
C19
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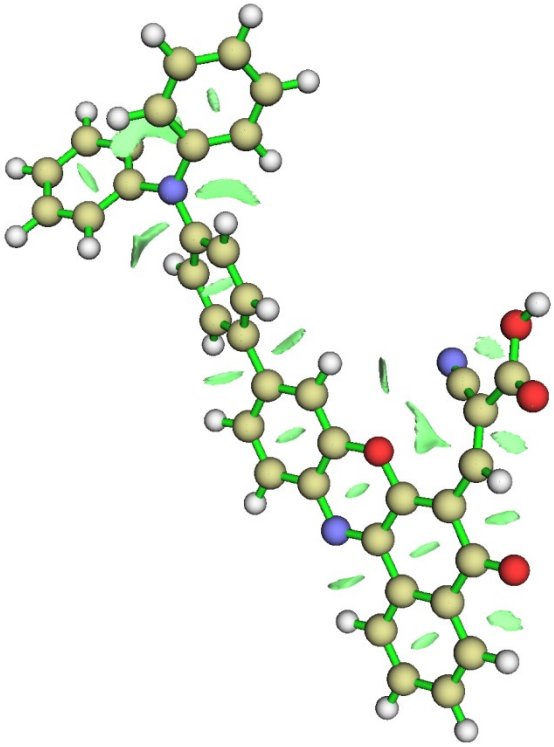

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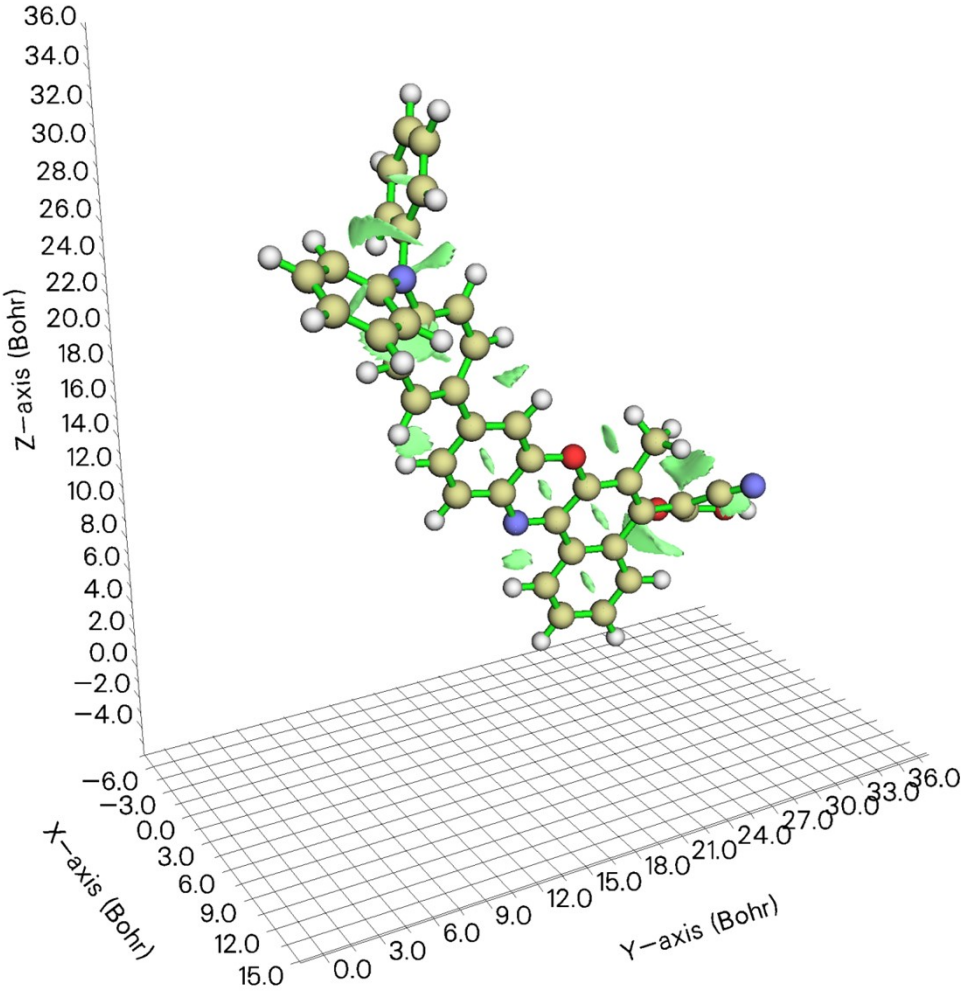
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28.0
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16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
−2.0
−4.0
X−axis (Bohr)
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−3.0
0.0
3.0
6.0
9.0
12.0
15.0
Y−axis (Bohr)
0.0
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9.0
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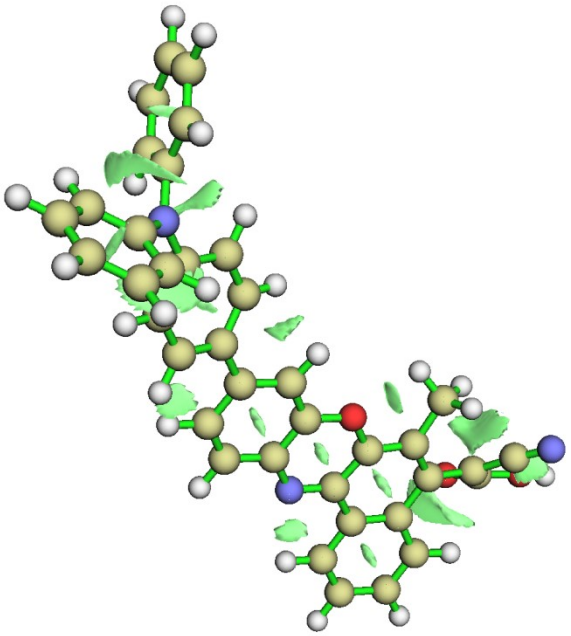

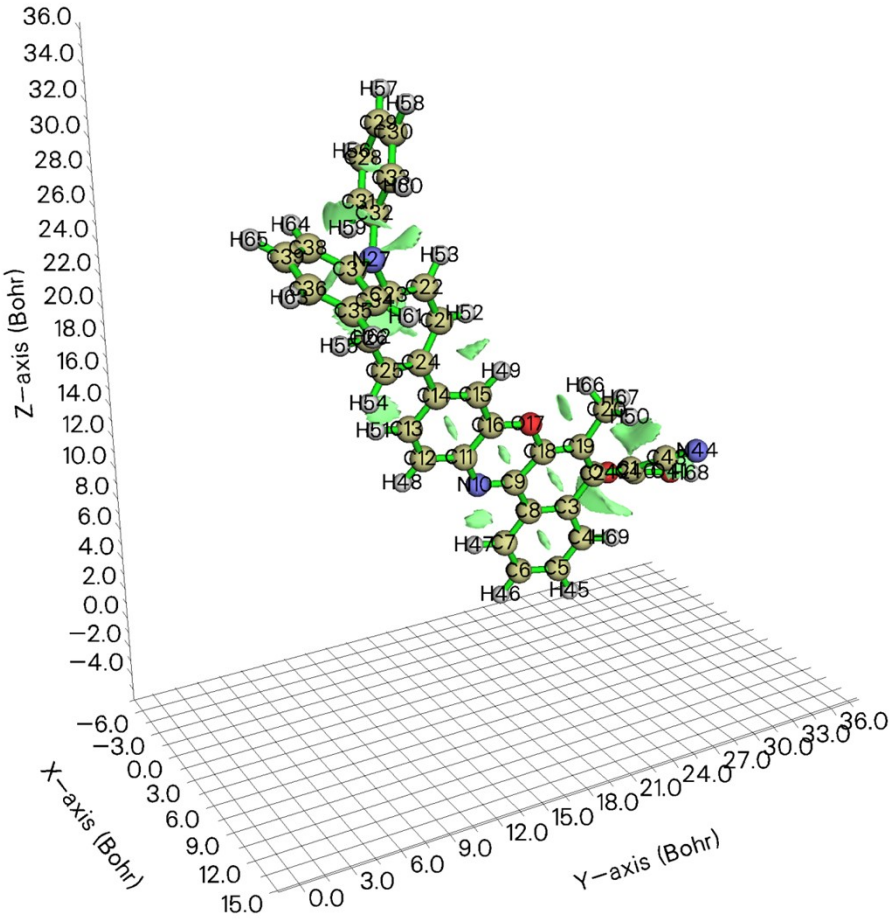
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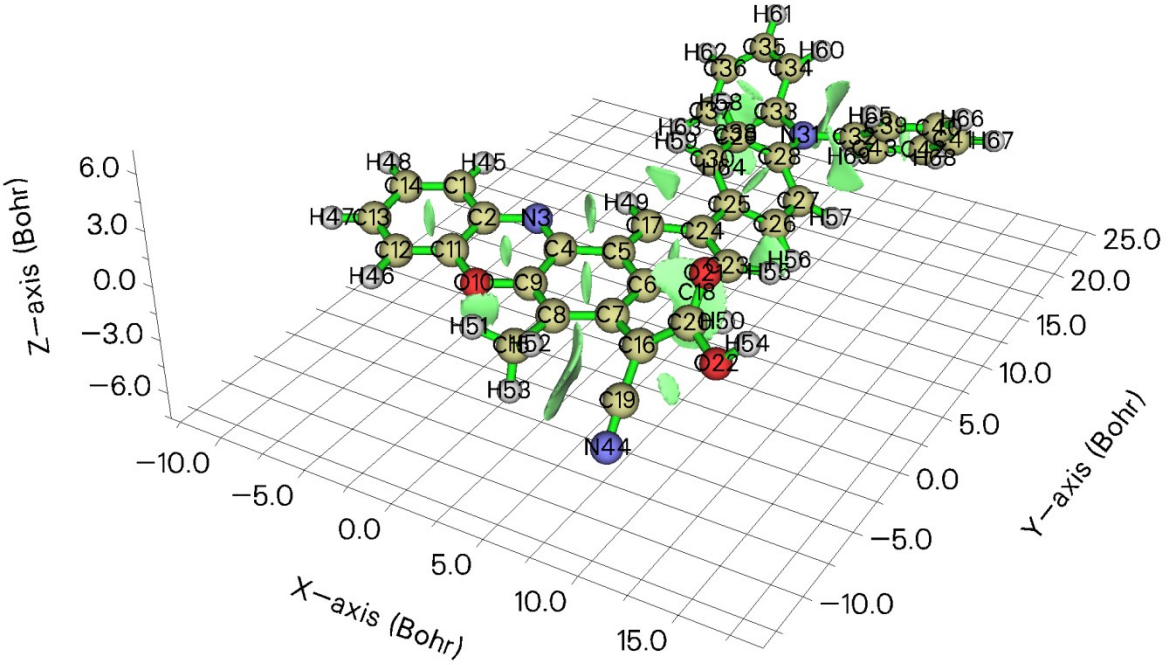
X−axis (Bohr)
Y−axis (Bohr)

M-3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Y−axis (Bohr)
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10.0
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−5.0
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H61
H62
C35
H60
C36
C34
C33
H65
H66
H67
H48
H45
C14
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N3
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C25
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C24
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H57
C12
C11
C4
C5
H56
H46
O10
C9
C6
C18
H55
C8
C7
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C16
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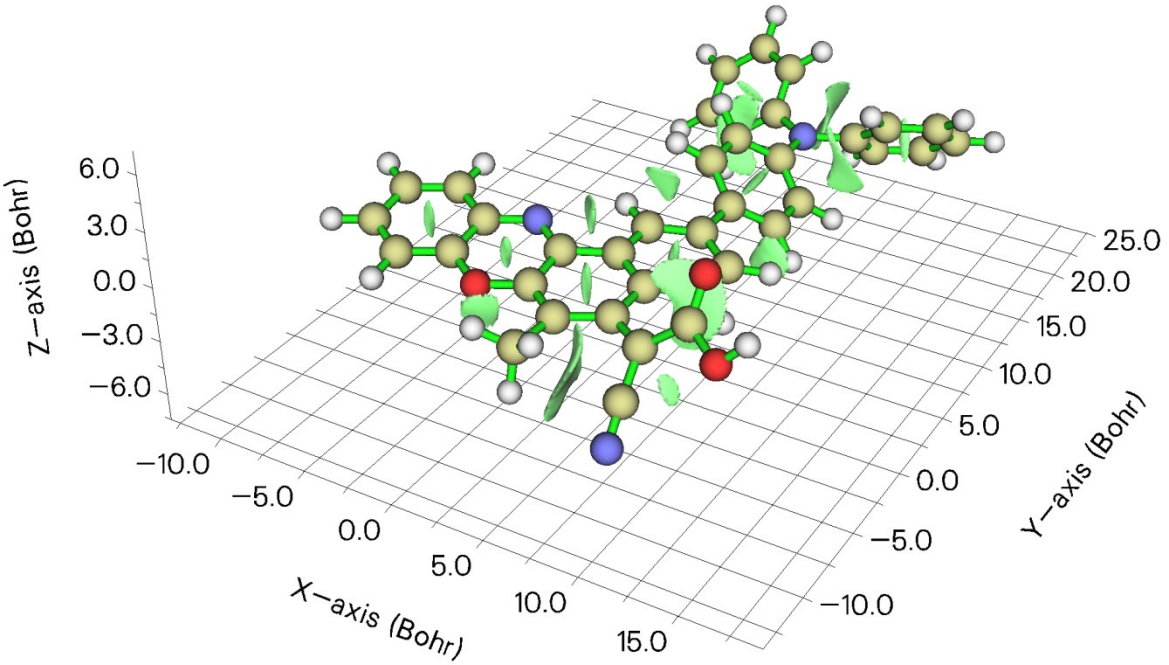
N44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Y−axis (Bohr)
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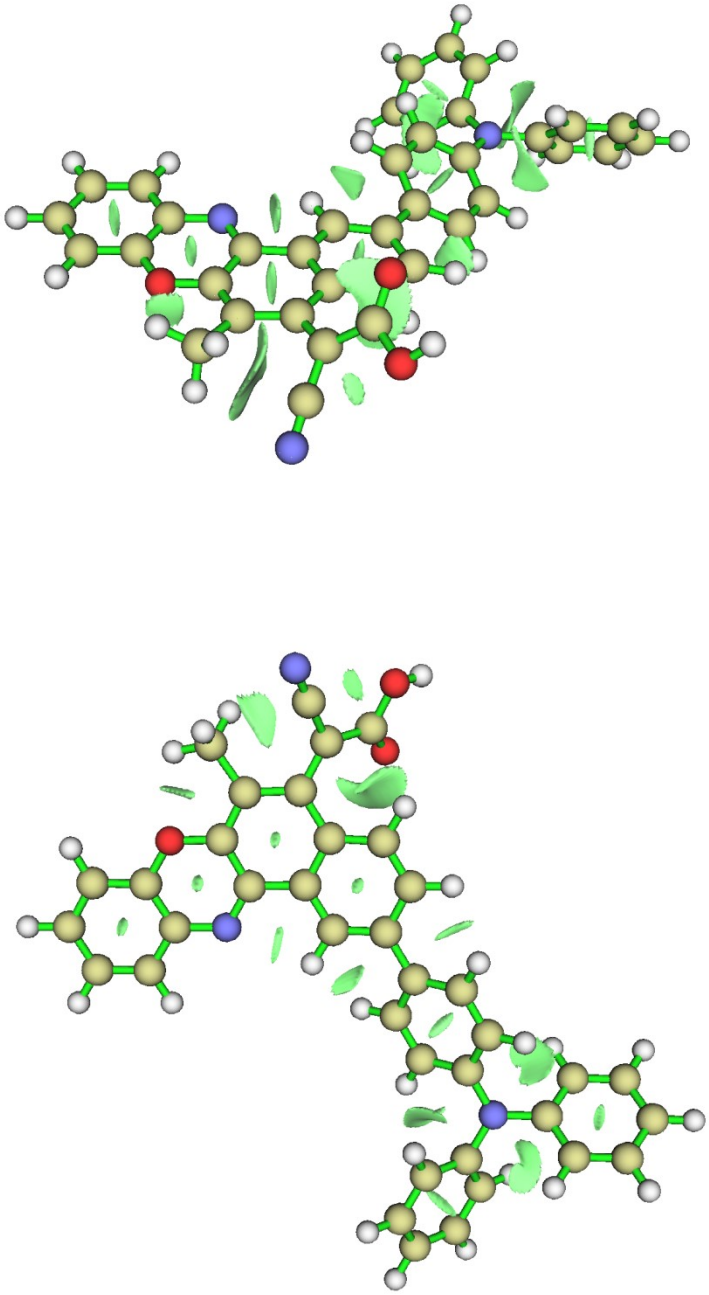
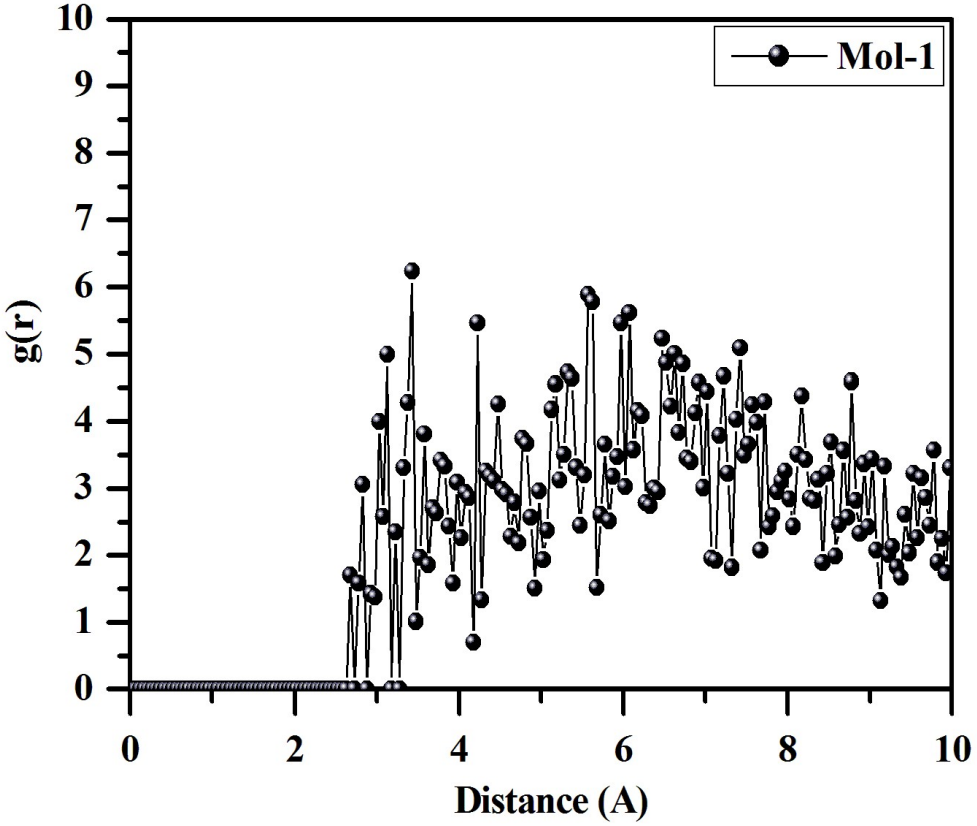
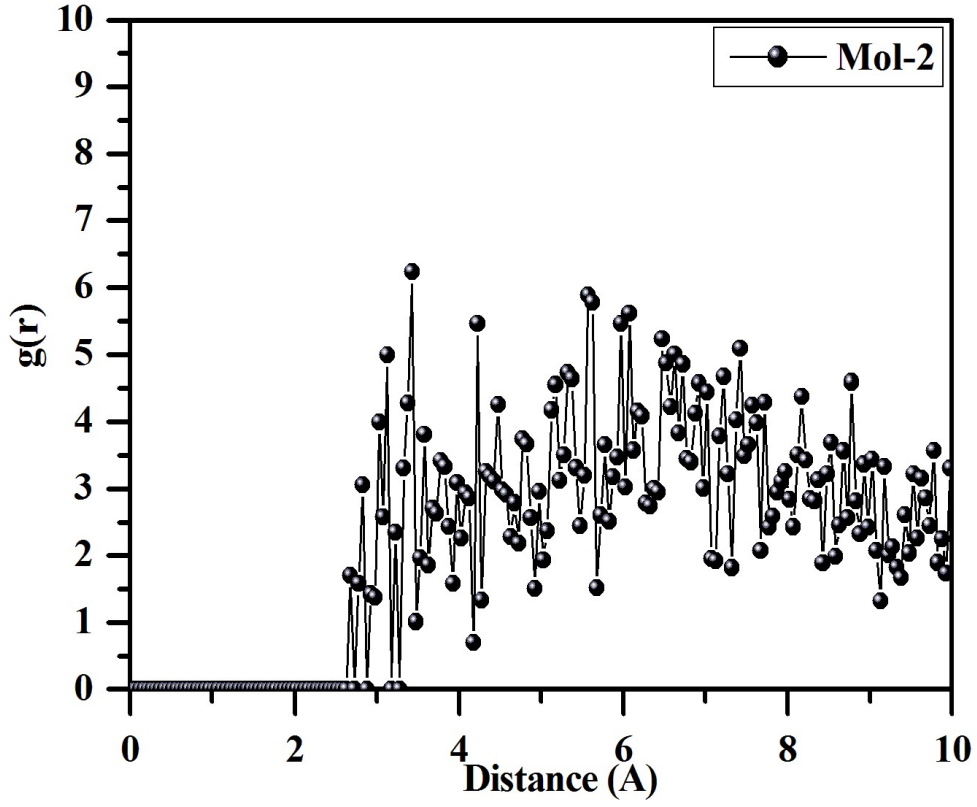


Figure S1 Non-Covalent interaction (NCI)-Reduced density gradient (RDG) plots of M-0, M-1, M-2 and M-3


Mol-1
g(r)
Distance (A)
0
1
2
3
4
5
6
7
8
9
10


Mol-2
g(r)
Distance (A)
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3
4
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6
7
8
9
10

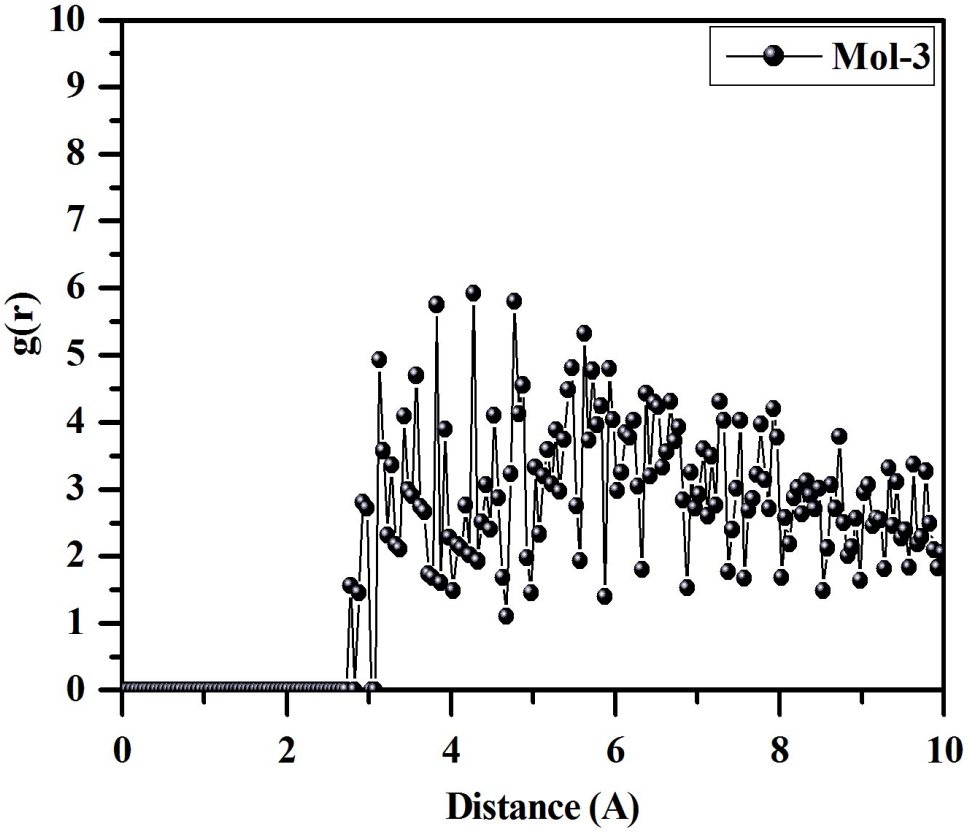

Figure S2 Radial Distribution plot

Table S1

Bond lengths (Å) and bond angles (°) of the optimized forms of M-3B, M-1, M-2 and M-3

Geometrical parameters	**M-3B**	**M-1**	**M-2**	**M-3**
Bond lengths (Å)				
C1-C2	1.407	1.425	1.428	1.411
C2-C3	1.391	1.383	1.380	1.388
C3-C4	1.410	1.415	1.417	1.413
C4-C5	1.409	1.412	1.418	1.413
C5-C6	1.398	1.387	1.387	1.395
C6-C1	1.396	1.409	1.408	1.394
C4-N7	1.383	1.364	1.357	1.372
N7-C8	1.301	1.311	1.319	1.309
C8-C9	1.467	1.454	1.442	1.451
C9-O10	1.367	1.346	1.356	1.356
O10-C5	1.369	1.370	1.363	1.364
C8-C11	1.471	1.467	1.456	1.462
C11-C12	1.413	1.414	1.423	1.421
C12-C13	1.490	1.486	1.471	1.468
C13-C14	1.463	1.479	1.427	1.436
C14-C9	1.368	1.391	1.394	1.388
C11-C15	1.407	1.408	1.410	1.402
C15-C16	1.393	1.392	1.388	1.403
C16-C17	1.404	1.405	1.406	1.416
C17-C18	1.393	1.392	1.388	1.386
C18-C12	1.405	1.406	1.416	1.414
C13-O19	1.241	1.237	–	–
C13- C19	–	–	1.443	1.435
C14-C20	1.503	1.442	1.510	1.510
C20-C21	–	1.371	–	–
C21-C22	–	1.429	–	–

C19-C22	—	—	1.414	1.418
C19-C21	—	—	1.467	1.467
C22-N23	—	1.158	1.166	1.164
C21-C24	—	1.493	—	—
C21-O24	—	—	1.223	1.224
C21-O25	—	—	1.367	1.360
C24-O25	—	1.216	—	—
C24-O26	—	1.345	—	—
C1-C27	—	1.475	—	—
C1-C26	—	—	1.474	—
C16-C26	—	—	—	1.480
C26-C27	—	—	1.413	1.411
C27-C28	—	1.413	1.389	1.392
C28-C29	—	1.389	1.413	1.410
C29-C30	—	1.413	1.412	1.410
C30-C31	—	1.412	1.390	1.391
C31-C32	—	1.390	—	—
C31-C26	—	—	1.413	1.412
C32-C27	—	1.413	—	—
C29-N32	—	—	1.403	1.409
C30-N33	—	1.404	—	—
N32-C33	—	—	1.429	1.427
N33-C34	—	1.429	—	—
C34-C35	—	1.406	1.406	1.406
C35-C36	—	1.397	1.397	1.397
C36-C37	—	1.400	1.400	1.400
C37-C38	—	1.400	1.398	1.397
C38-C39	—	1.398	—	—
C38-C33	—	—	1.405	1.406
C39-C34	—	1.405	—	—
N32-C39	—	—	1.429	1.427

N33-C40	–	1.429	–	–
C39-C40	–	–	1.405	1.406
C40-C41	–	1.405	1.398	1.397
C41-C42	–	1.398	1.400	1.400
C42-C43	–	1.400	1.400	1.400
C43-C44	–	1.400	1.397	1.337
C44-C39	–	–	1.406	1.406
C44-C45	–	1.397	–	–
C45-C40	–	1.406	–	–

Bond angles (°)

C1-C2-C3	120.09	121.75	121.80	120.29
C2-C3-C4	120.15	120.34	120.36	119.95
C3-C4-C5	118.60	117.49	117.45	120.69
C4-C5-C6	121.81	122.75	122.55	122.60
C5-C6-C1	118.55	119.59	119.72	118.24
C4-N7-C8	119.05	119.42	119.03	119.07
N7-C8-C9	122.39	121.64	122.00	122.29
C8-C9-O10	117.53	117.98	118.87	117.72
C9-C10-C5	120.41	121.11	120.80	120.81
O10-C5-C4	119.65	118.68	118.83	119.25
C5-C4-N7	120.97	121.11	121.25	120.83
C8-C11-C12	119.45	119.63	119.15	119.04
C11-C12-C13	120.89	121.19	120.68	121.08
C12-C13-C14	118.89	118.36	119.60	119.28
C13-C14-C9	118.96	118.66	118.25	118.27
C14-C9-C8	124.13	123.62	124.37	124.46
C9-C8 –C11	117.69	118.30	117.50	117.14
C11-C15 –C16	120.34	120.32	120.57	121.96
C15-C16-C17	120.19	120.30	119.62	116.90
C16-C17-C18	119.89	119.85	120.23	121.54
C17-C18-C12	120.51	120.50	121.52	121.95

C18-C12-C11	119.57	119.62	117.45	116.59
C12-C11-C15	119.49	119.41	120.40	120.88
C12-C13-O19	120.69	120.88	—	—
C12-C13-C19	—	—	119.99	120.10
C14-C13-O19	120.43	120.75	—	—
C14-C13-C19	—	—	120.39	120.61
C13-C14-C20	117.67	115.56	122.99	122.96
C9-C14-C20	123.37	125.55	118.51	118.41
C19-C20-C21	—	132.36	—	—
C13-C19-C22	—	—	120.55	120.89
C19-C22-N23	—	—	175.55	177.00
C13-C19-C21	—	—	122.81	123.12
C19-C21-O24	—	—	125.19	126.23
C19-C21-O25	—	—	117.62	112.56
C20-C21-C22	—	124.76	—	—
C21-C22-N23	—	176.41	—	—
C20-C21-C24	—	117.81	—	—
C21-C24-O25	—	124.56	—	—
C21-C24-O26	—	112.27	—	—
C26-C27-C28	—	—	121.93	121.79
C27-C28-C29	—	121.83	120.86	120.84
C28-C29-C30	—	120.86	117.80	117.86
C29-C30-C31	—	117.80	120.87	120.83
C30-C31-C32	—	120.87	—	—
C30-C31-C26	—	—	121.80	121.80
C31-C26-C27	—	—	116.84	116.86
C31-C32-C27	—	121.80	—	—
C33-C27-C28	—	116.84	—	—
C30-N33-C34	—	120.76	—	—
C30-N33-C40	—	120.76	—	—
C33-C34-C35	—	—	120.19	120.27

C34-C35-C36	—	120.19	120.43	120.48
C35-C36-C37	—	120.43	119.44	119.35
C36-C37-C38	—	119.44	120.43	120.43
C37-C38-C39	—	120.43	—	—
C37-C38-C33	—	—	120.19	120.28
C38-C39-C34	—	120.19	—	—
C34-C33-C40	—	118.48	—	—
C39-C40-C41	—	—	120.19	120.29
C40- C41-C42	—	120.19	120.43	120.48
C41-C42-C43	—	120.43	119.44	119.34
C42-C43-C44	—	119.44	120.43	120.48
C43-C44-C39	—	—	120.18	120.20
C44-C39-C40	—	—	119.32	119.12
C43-C44-C45	—	120.43	—	—
C44-C45-C40	—	120.18	—	—

Torsion angle (°)

C2-C3-C4-N7	-179.99	178.89	179.85	179.77
C3-C4-N7-C8	179.88	-179.74	-179.33	179.79
C4-N7-C8-C11	-179.99	178.28	178.36	178.07
N7-C8-C11-C15	-0.03	2.29	-3.80	-6.58
C1-C6-C5-O10	179.99	179.30	-178.80	-79.95
C5-O10-C9-C14	180.00	-179.73	-179.66	179.00
O10-C9-C14-C13	-179.89	-179.05	-178.53	174.54
C9-C14-C13-O19	179.86	—	—	—
C9-C14-C13-C19	—	-175.53	176.85	175.92
O10-C9-C14-C20	0.06	1.72	-4.36	4.84
C14-C13-C12-C18	-179.92	176.83	-168.20	-165.76
C12-C13-C14-C20	179.92	-179.63	-178.23	-179.00
C18-C12-C13-C19	—	—	10.64	13.15
C18-C12-C13-O19	0.09	-2.09	—	—
C12-C13-C19-C21	—	—	43.23	43.15

C12-C13-C19-C22	—	—	-137.78	-139.28
C13-C19-C22-N23	—	—	129.59	103.73
C13-C19-C21-O24	—	—	12.47	12.80
C13-C19-C21-O25	—	—	-171.15	-170.89
C19-C13-C14-C20	—	-0.71	—	—
C13-C14-C20-C21	—	151.79	—	—
C14-C20-C21-C24	—	178.11	—	—
C20-C21-C24-O26	—	-76.71	—	—
C20-C21-C22-O25	—	-3.45	—	—
C14-C20-C21-C22	—	-7.91	—	—
C20-C21-C22-N23	—	112.10	—	—
C24-C21-C22-N23	—	61.92	—	—
C14-C13-C19-C22	—	—	41.04	39.61
C13-C19-C22-N23	—	—	129.59	103.73
C15-C16-C26-C27	—	—	—	-152.92
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C2-C1-C27-C28	—	153.87	—	—
C2-C1-C27-C32	—	-26.15	—	—
C6-C1-C26-C31	—	—	-154.31	—
C6-C1-C31-C30	—	—	179.46	—
C6-C1-C27-C28	—	-25.85	—	—
C6-C1-C27-C32	—	154.13	—	—
C28-C29-N32-C33	—	—	30.95	-33.38
C29-N32-C33-C34	—	—	47.89	-46.32
C29-N32-C33-C38	—	—	-133.12	134.34
C28-C29-N32-C39	—	—	-149.10	145.78
C29 -N32-C39-C40	—	—	-133.19	135.40

C29 -N32-C39-C44	—	—	47.85	45.34
C29-C30-N33-C34	—	29.83	—	—
C30-N33-C34-C35	—	47.98	—	—
C30-N33-C34-C39	—	-132.90	—	—
C31-C30-C33-C40	—	29.30	—	—
C30-C33-C40-C41	—	-132.73	—	—
C30-C33-C40-C45	—	48.21	—	—

Table S2 NBO, HOMO and LUMO calculation data

Dyes Name	HOMO (Hartree)	LUMO (Hartree)	Energy gap	E_{total}
M-0	-0.2173	-0.1063	0.111	-897.993
Mol-1	-0.1668	-0.1315	0.961	-1924.954
Mol-2	-0.1672	-0.1372	0.817	-1850.856
Mol-3	-0.1633	-0.1369	0.719	-1850.964

Table S3 Adsorption energy Calculation

The obtained energies of Mol-1, Mol-2 and Mol-3 on TiO_2_anatase (1 0 1) surface determined from Monte Carlo simulation with simulation box size 43.54 × 30.20 × 54.03 Å, Fractional thickness: 4, Supercell: u= 8, v= 8 and one number of molecules in a 100kcal/mol energy window.

Systems	E_{total} (kJmol^{-1})	E_{ads} (kJmol^{-1})	E_{rigid} (kJmol^{-1})	E_{def} (kJ mol^{-1})	dE_{ads}/dN_i (kJ mol^{-1})
TiO_2_anatase (1 0 1) + Mol-1	-883.95	-1432.08	-1257.82	-174.25	-1432.08
TiO_2_anatase (1 0 1) + Mol-2	-637.26	-1324.73	-1082.93	-241.79	-1324.73
TiO_2_anatase (1 0 1) + Mol-3	-672.50	-900.12	-1147.12	246.99	-900.12

The energy obtained from the interactions of dye molecule and the accompanying species with the TiO_2_$anatase$ (1 0 1) surface is represented as $E_{interaction}$; and it is determined by the following expression

$$E_{interaction} = E_{total} - (E_{TiO2\_anatase\ (1\ 0\ 1)} + E_{molecule}) \quad (7)$$

Where E_{total} represents the total energy of the simulation system; $E_{TiO2\_anatase\ (1\ 0\ 1)}$ is the energy of the TiO_2 surface; and the energy of the molecule was designated as $E_{molecule}$