Supporting information: A method to capture the large relativistic and solvent effects on UV-vis spectra of photo-activated metal complexes

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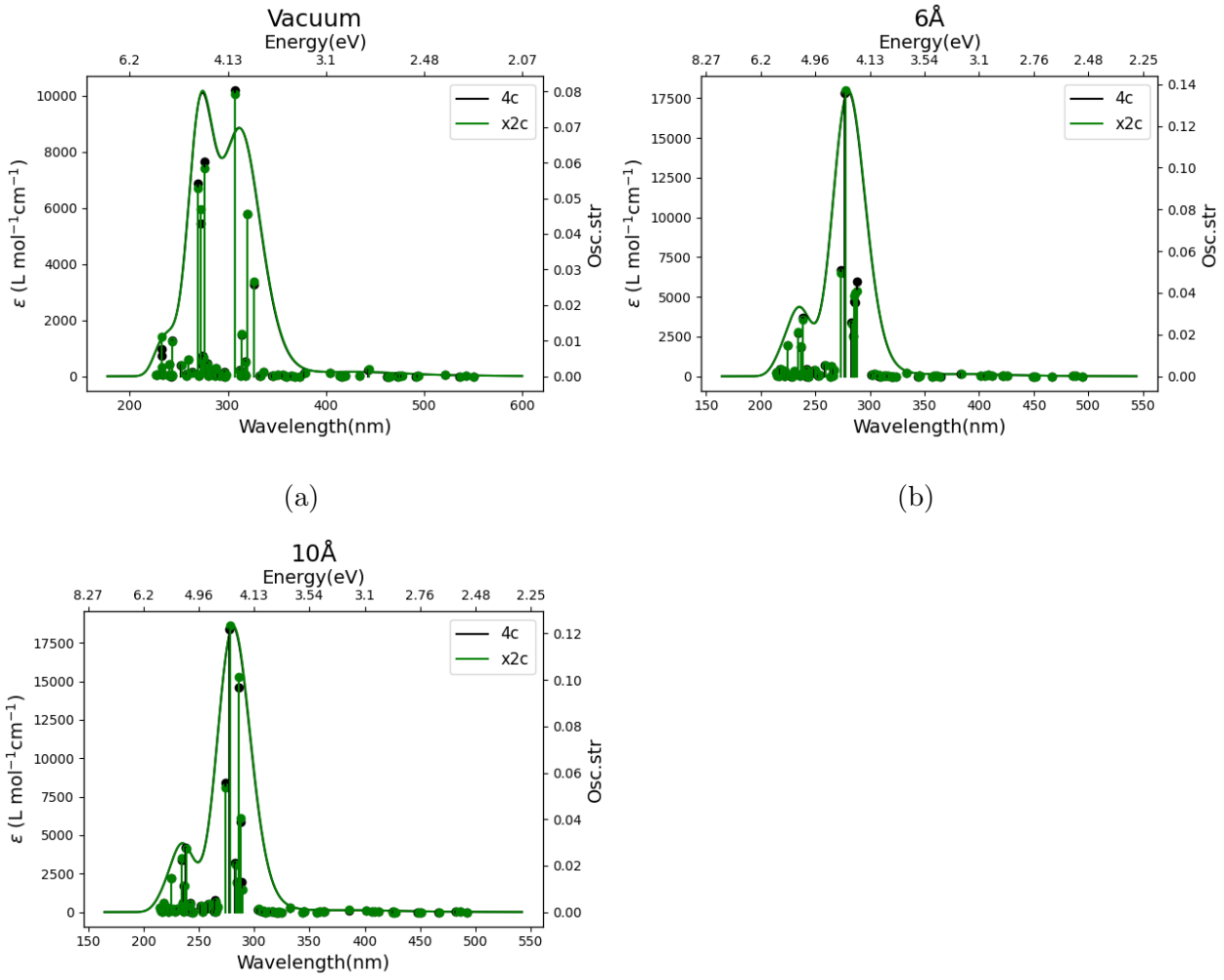


Figure S1: UV-vis spectra calculated using TDDFT with the CAM-B3LYP functional comparing X2C with 4C for (a) Complex in vacuum taken from structure optimized with BP86 (b) Complex solvated in a 6 Å sphere of water molecules (optimized with BP86) (c) Complex solvated in a 10 Å sphere of water molecules (optimized with BP86).

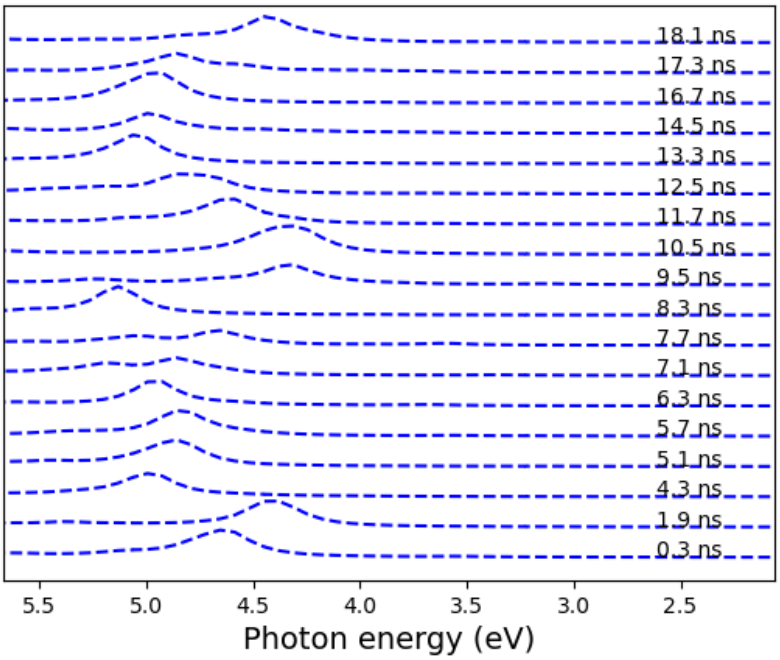
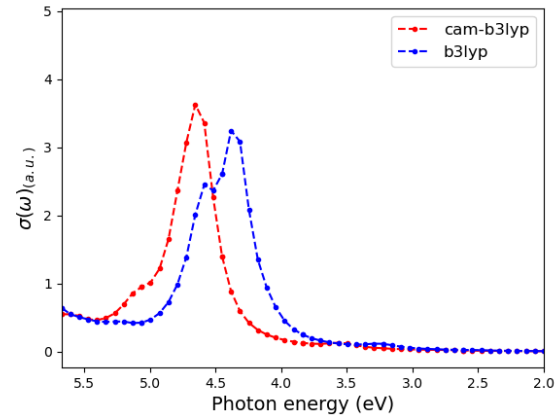


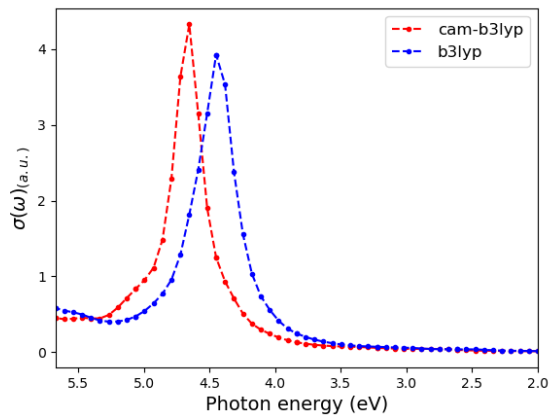
Figure S2: Spectra calculated for various snapshots from md simulation. Peak positions are reported in Table S1

Snapshot	Peak energy (eV)	$\sigma(\omega)$ [a.u]
0.3 ns	4.653	2.586
1.3 ns	4.517	3.256
1.7 ns	4.517	2.363
1.9 ns	4.381	2.458
2.9 ns	4.857	2.425
3.9 ns	4.313	2.099
4.3 ns	4.993	2.21
4.5 ns	4.993	2.911
4.9 ns	4.585	1.347
5.1 ns	4.857	2.531
5.3 ns	4.789	1.537
5.7 ns	4.857	2.437
5.9 ns	4.653	3.079
6.1 ns	4.993	2.571
6.3 ns	4.925	2.319
6.5 ns	4.789	1.857
6.7 ns	4.993	2.527
7.1 ns	4.857	1.689
7.3 ns	4.993	1.357
7.5 ns	4.789	2.182
7.7 ns	4.653	1.414
7.9 ns	4.653	1.732
8.1 ns	4.517	2.533
8.3 ns	5.129	2.716
8.7 ns	5.061	2.84
9.5 ns	4.313	1.908
10.3 ns	4.993	2.412
10.5 ns	4.313	2.704
10.9 ns	5.129	3.029
11.3 ns	4.653	1.403
11.7 ns	4.585	2.383
11.9 ns	5.129	2.839
12.1 ns	4.857	2.786
12.5 ns	4.857	1.894
12.9 ns	5.061	1.287
13.1 ns	5.061	2.64
13.3 ns	5.061	2.725
13.5 ns	4.789	2.131
14.5 ns	4.993	1.903
15.1 ns	4.857	2.215
16.1 ns	4.653	2.879
16.7 ns	4.925	2.874
16.9 ns	4.789	2.952
17.1 ns	4.381	2.6
17.3 ns	4.857	1.846
17.7 ns	4.789	2.775
17.9 ns	4.857	2.902
18.1 ns	4.449	2.458
18.3 ns	5.061	1.615

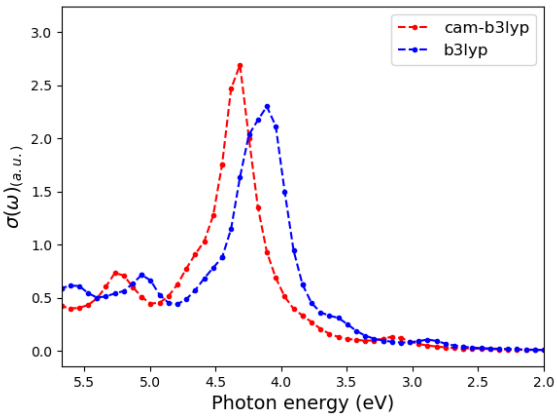
Table S1: Data for the peaks of all md snapshots



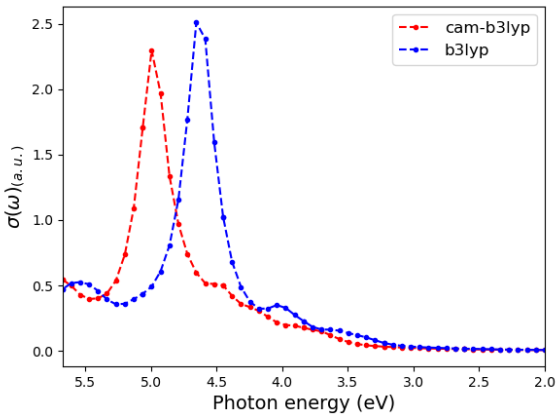
(a)



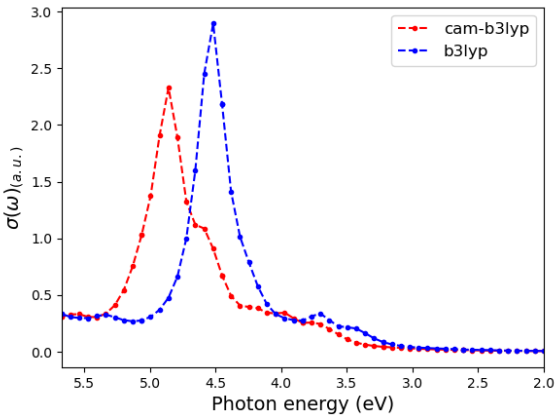
(b)



(c)

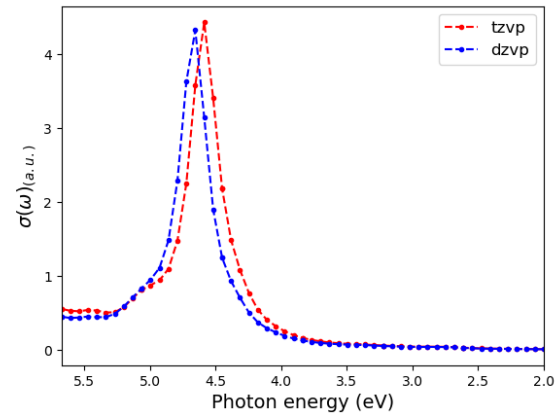


(d)

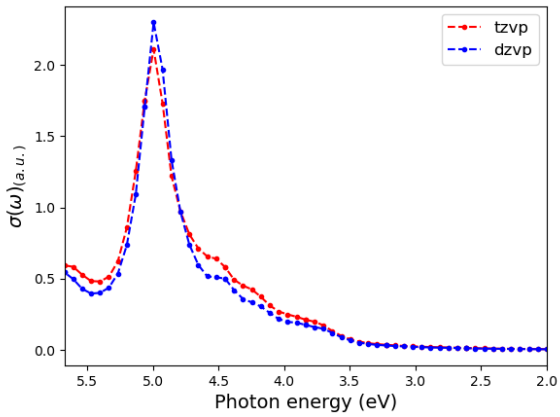


(e)

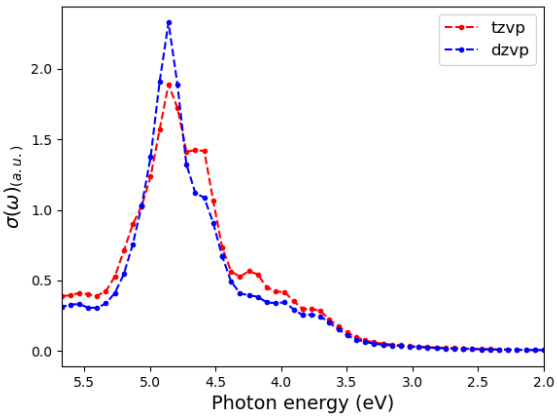
Figure S4 Comparison of B3LYP and CAM-B3LYP for 5 structures



(a)

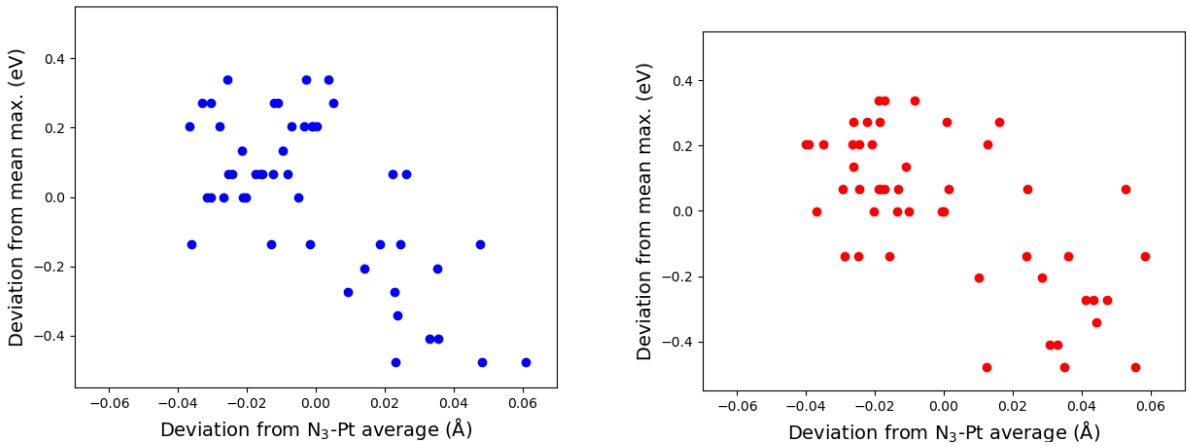


(b)



(c)

Figure S5 Comparison of spectra obtained with DZVP (def2-sv(p) for ligands and dyall.v2z for Pt) and TZVP (def2-tzvp for the ligands and dyall.v3z for Pt) using CAM-B3LYP for 3 structures.



(a) (b)

Figure S6 The figures show the deviation from the average peak displayed against the deviation from the average bond length with respect to the two N_3-Pt bond distances.

Snapshots	Peak (eV)	$\sigma(\omega)$ $[a.u.]$	Snapshots	Peak (eV)	$\sigma(\omega)$ $[a.u.]$
1–10	4.67 ±0.23	2.42 ±0.48	1–10	4.67 ±0.23	2.42 ±0.48
11–20	4.87 ±0.11	2.15 ±0.54	1–20	4.76 ±0.21	2.29 ±0.52
21–30	4.76 ±0.27	2.22 ±0.47	1–30	4.76 ±0.23	2.27 ±0.51
31–40	4.87 ±0.26	2.37 ±0.59	1–40	4.79 ±0.24	2.30 ±0.53
41–49	4.78 ±0.17	2.46 ±0.42	1–49	4.79 ±0.23	2.33 ±0.52

TABLE S2: Averages and deviations for excitation energies and absorption cross sections (either blocks of 10 snapshots or cumulative).