Supporting information

Molecular environment effects that modulate the photophysical properties of novel 1,3-phosphinoamines based on 2,1,3-benzothiadiazole

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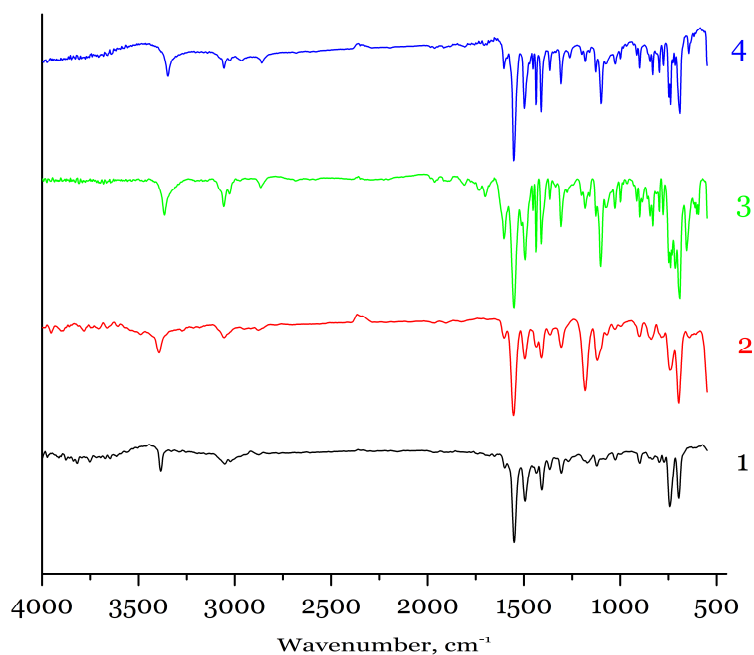
IR-spectra of the compounds

Figure S1. IR-spectra of compounds **1–4** recorded in KBr pellets.

Table S1. Crystal data and structure refinement for the compounds

| Identification code	1	2α	2β·thf	3	4
Empirical formula	$C_{25}H_{20}N_3PS$	$C_{25}H_{20}N_3OPS$	$C_{29}H_{28}N_3O_2PS$	$C_{25}H_{20}N_3PS_2$	$C_{25}H_{20}N_3PSSe$
Formula weight	425.47	441.47	513.57	457.53	504.43
Temperature/K	150(2)	240(2)	150(2)	150(2)	150(2)
Space group	$P{-}1$	$P2_1$	$Pbca$	$P2_1/n$	$P2_1/n$
a/Å	9.335(3)	5.8869(5)	10.9504(16)	9.2084(4)	9.1686(8)
b/Å	10.765(4)	19.2234(12)	17.815(3)	20.3488(10)	20.5591(17)
c/Å	12.793(5)	9.7889(10)	27.605(3)	12.6978(5)	12.7179(9)
α/°	65.636(11)	90	90	90	90
β/°	82.580(12)	104.521(4)	90	109.844(2)	109.002(2)
γ/°	65.493(12)	90	90	90	90
Volume/Å^3	1064.2(7)	1072.39(16)	5385.1(13)	2238.03(17)	2266.7(3)
Z	2	2	8	4	4
ρ_{calc}g/cm^3	1.328	1.367	1.267	1.358	1.478
μ/mm^{-1}	0.244	0.249	0.210	0.328	1.837
F(000)	444.0	460.0	2160.0	952.0	1024.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.492 to 48.846	4.238 to 53.024	2.95 to 48.898	4.004 to 54.246	4.816 to 52.764
Index ranges	$-10 \le h \le 10, -12 \le k \le 12, -13 \le l \le 14$	$-5 \le h \le 7, -24 \le k \le 17, -12 \le l \le 8$	$-12 \le h \le 12, -20 \le k \le 20, -32 \le l \le 32$	$-10 \le h \le 11, -26 \le k \le 26, -16 \le l \le 12$	$-11 \le h \le 11, -25 \le k \le 25, -15 \le l \le 15$
Reflections collected	7491	5271	39661	31244	25940
Independent reflections	3424 [R_{int} = 0.0824, R_{sigma} = 0.1288]	3627 [R_{int} = 0.0255, R_{sigma} = 0.0598]	4449 [R_{int} = 0.1484, R_{sigma} = 0.0888]	4923 [R_{int} = 0.0394, R_{sigma} = 0.0282]	4650 [R_{int} = 0.0598, R_{sigma} = 0.0413]
Data/restraints/parameters	3424/1/274	3627/2/283	4449/10/300	4923/1/283	4650/1/283
Goodness-of-fit on F^2	1.037	1.019	1.054	1.023	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0664, wR_2 = 0.1537	R_1 = 0.0406, wR_2 = 0.0759	R_1 = 0.0882, wR_2 = 0.2463	R_1 = 0.0437, wR_2 = 0.1066	R_1 = 0.0342, wR_2 = 0.0798
Final R indexes [all data]	R_1 = 0.0964, wR_2 = 0.1825	R_1 = 0.0542, wR_2 = 0.0821	R_1 = 0.1352, wR_2 = 0.2907	R_1 = 0.0533, wR_2 = 0.1131	R_1 = 0.0452, wR_2 = 0.0881
Largest diff. peak/hole / e Å^{-3}	0.66/-0.41	0.20/-0.24	1.00/-0.59	1.42/-0.41	0.57/-0.33
Flack parameter		0.04(7)			

Powder X-ray diffraction data
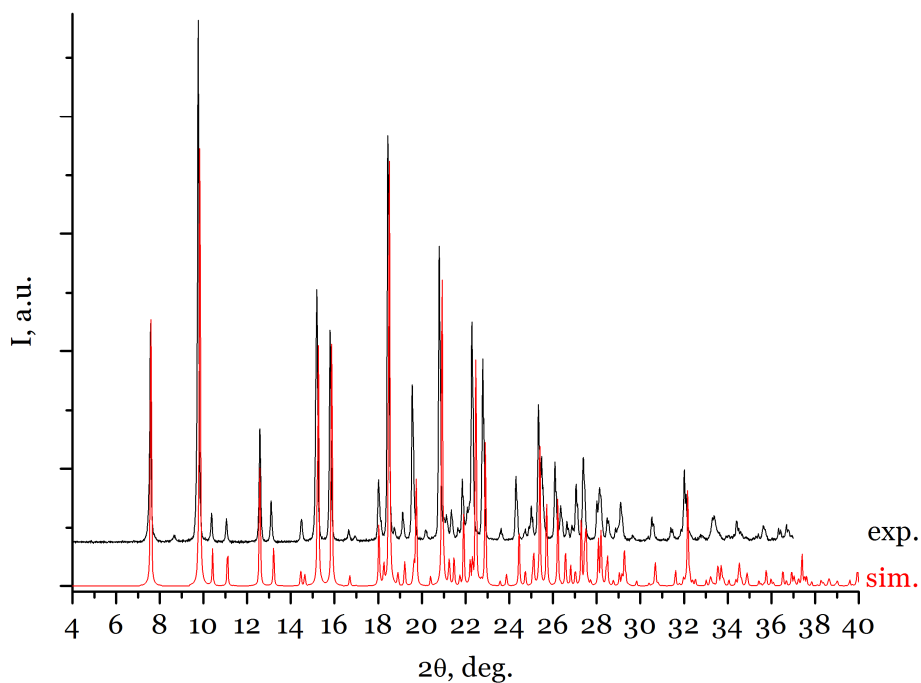
Figure S2. Simulated and experimental powder XRD patterns for compound **1** (Cu K$_\alpha$ radiation). Minor peak at 8.68° does not correspond to any of phase of oxidized species **2**.
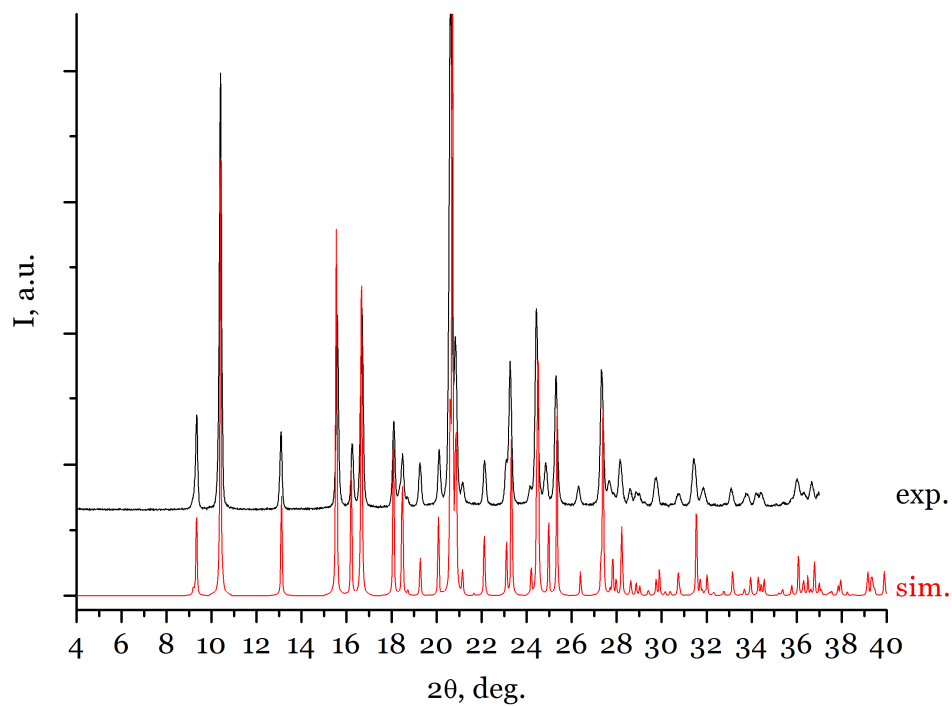

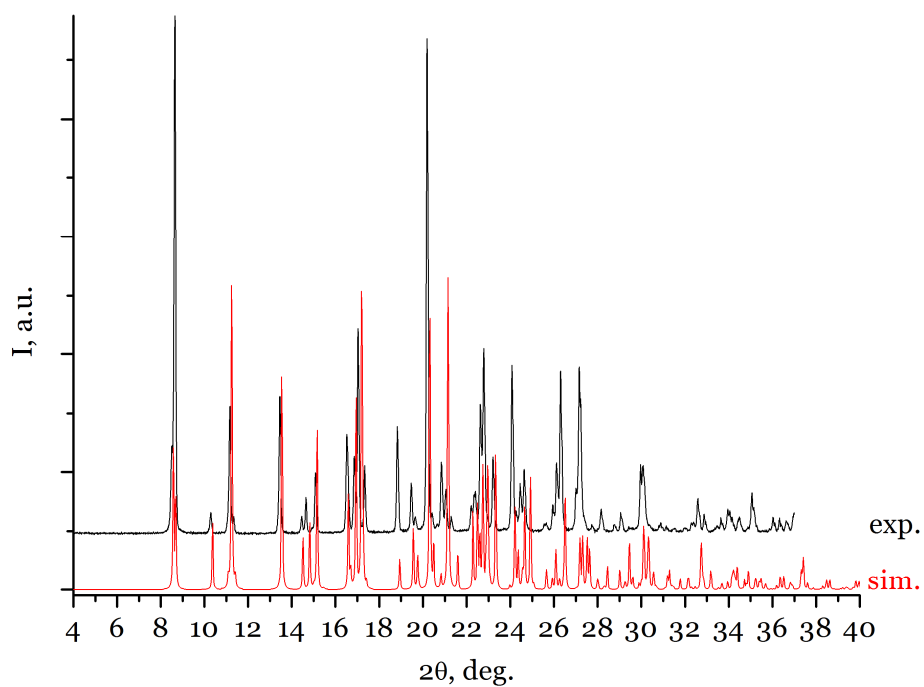Figure S3. Simulated and experimental powder XRD patterns for compound **2α** (Cu K$_\alpha$ radiation).

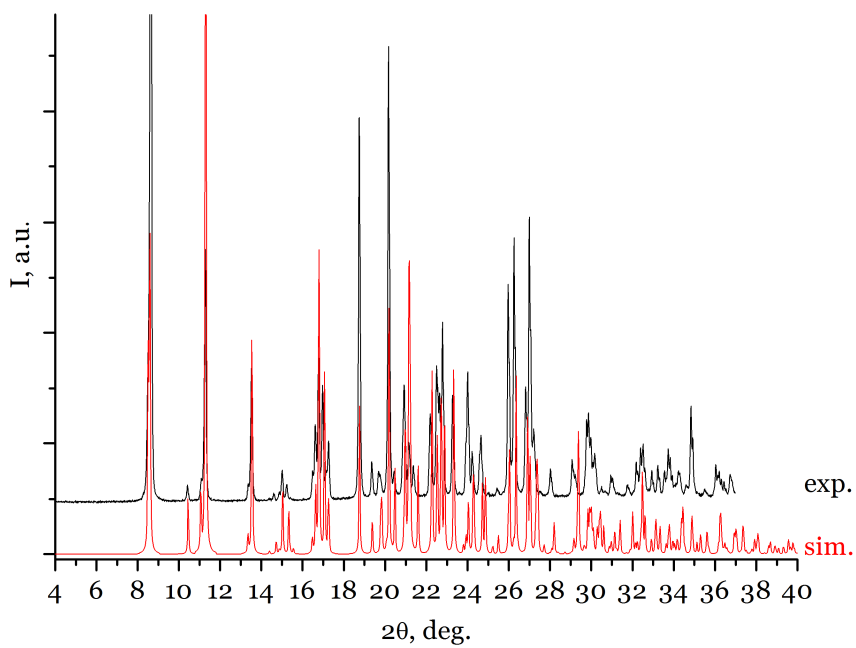Figure S4. Simulated and experimental powder XRD patterns for compound **3** (Cu Kα radiation).

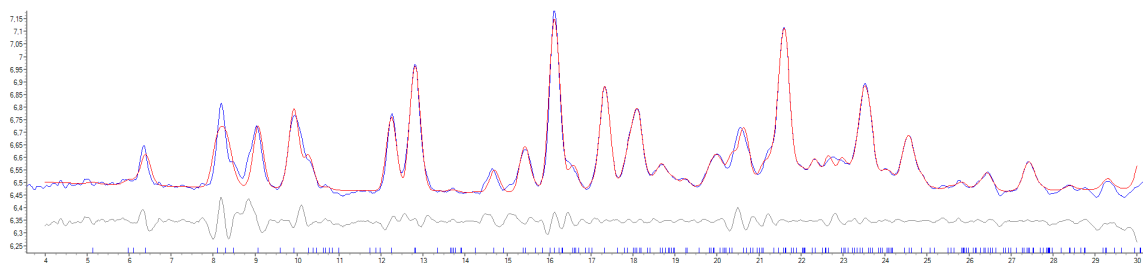Figure S5. Simulated and experimental powder XRD patterns for compound **4** (Cu Kα radiation).

Figure S6. Pawley refinement for the powder pattern for the solvate-free phase, **2β** (Cu K_α radiation, 150K). Refined unit cell parameters: monoclinic P, a = 17.21 Å, b = 10.41 Å, a = 27.64 Å, β = 91.43°, V = 4952.6 Å³. The fit at low angles is not good, probably because of the presence of a number of related phases.
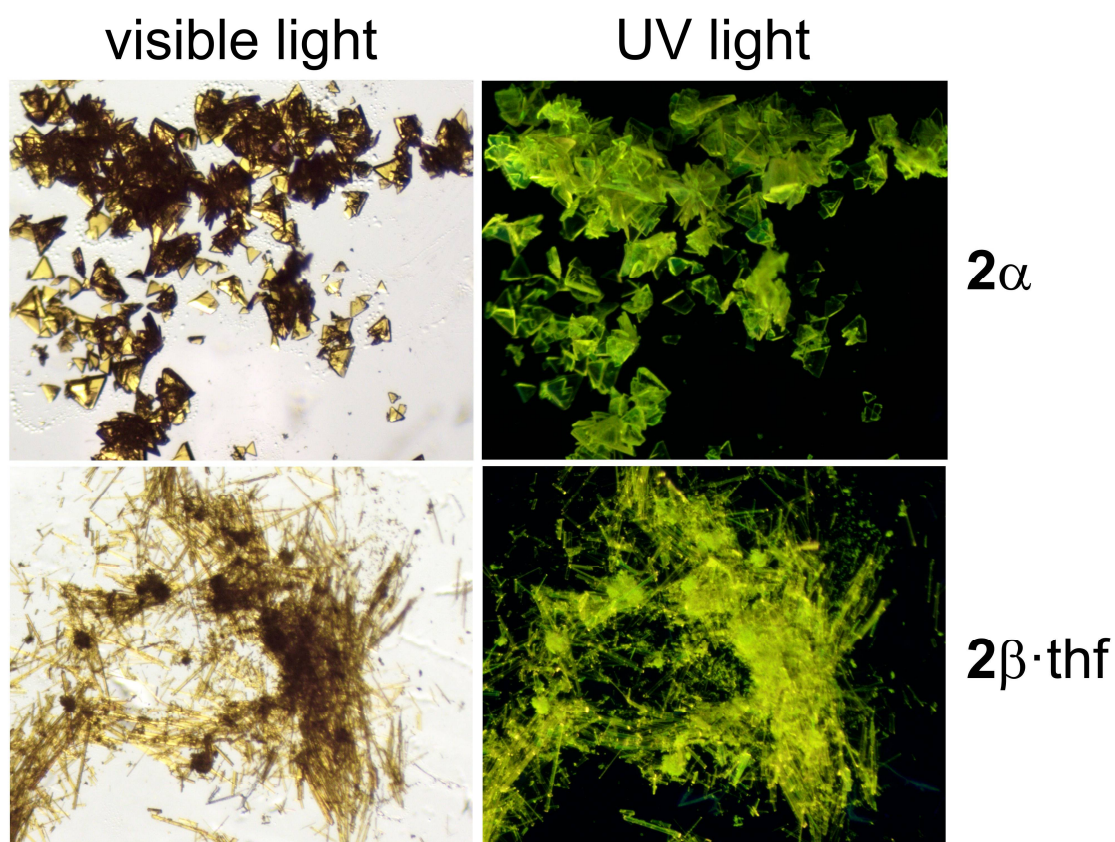

Figure S7. Photographs of crystals **2α** and **2β·**thf under visible and UV light.

Geometry and energy features of the molecules of the compounds

Table S2. Estimated contributions to the interaction energy (kJ/mol) between a couple of the molecules in **2α** and **2β**·THF, calculated in the CrystalExplorer v. 17.5 program. Level of theory B3LYP/6-31G(d,p).

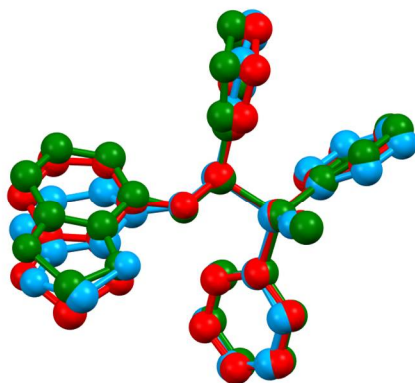|	electrostatic	polarization	dispersion	repulsion	total
2α	-22.4	-8.3	-68.8	46.3	-61.2
2β·THF	-51.3	-17.0	-83.4	87.3	-85.6

Figure S8. Overlay of the molecules of structures **2α** (red), **2β**·thf (blue), and **3** and **4** (green) on the example of the latter.

DFT calculation of Frank-Condon excitation processes

Table S3. TD-DFT calculated excitation transitions of **1** in the ground state (PBE0/def2-TZVP(-f)). H – HOMO, L – LUMO

State	Energy, cm⁻¹	Wavelength, nm	Oscilator strength	Transitions	Contributions
1	23603.2	423.7	0.088385263	H → L	0.983184
2	30858.3	324.1	0.000466761	H - 1 → L	0.992984
3	33796.6	295.9	0.035534635	H - 1 → L + 1 H → L + 1	0.013506 0.964632
4	34724.2	288.0	0.004914953	H → L + 2 H → L + 4	0.956257 0.012231
5	35163.6	284.4	0.008651734	H - 2 → L	0.973192
6	36289.2	275.6	0.010554810	H - 4 → L H → L + 3 H → L + 4	0.010929 0.928550 0.018669
7	36910.7	270.9	0.030703125	H - 5 → L H - 4 → L H - 3 → L H → L + 3 H → L + 4 H → L + 5 H → L + 6 H → L + 7	0.026211 0.374705 0.059173 0.038135 0.287557 0.021079 0.016580 0.116321
8	37515.1	266.6	0.001407458	H - 4 → L H - 3 → L H → L + 4	0.012650 0.901086 0.069235
9	37713.9	265.2	0.059277820	H - 4 → L H - 3 → L H - 1 → L + 1 H → L + 4 H → L + 5 H → L + 7	0.259063 0.025129 0.092984 0.478530 0.011550 0.077540
10	37918.9	263.7	0.056846632	H - 4 → L H - 1 → L + 1 H - 1 → L + 2 H → L + 1 H → L + 4 H → L + 5	0.016085 0.781297 0.011558 0.013295 0.036223 0.083727
11	38288.1	261.2	0.005869281	H - 1 → L + 1 H → L + 4 H → L + 5 H → L + 6	0.055339 0.062663 0.762327 0.092988
12	38355.0	260.7	0.001843530	H - 5 → L H - 4 → L	0.900025 0.071466

13	39113.8	255.7	0.025258606	H - 6 → L	0.024238
				H - 4 → L	0.014336
				H - 1 → L + 2	0.268146
				H - 1 → L + 3	0.054225
				H → L + 4	0.015528
				H → L + 5	0.028875
				H → L + 6	0.511625
14	39349.3	254.1	0.017835553	H - 10 → L	0.165630
				H - 6 → L	0.121298
				H - 5 → L + 1	0.010677
				H - 1 → L + 2	0.399077
				H - 1 → L + 3	0.040229
				H - 1 → L + 4	0.013603
				H → L + 5	0.027725
				H → L + 6	0.143151
15	39382.3	253.9	0.012700551	H - 10 → L	0.360734
				H - 7 → L	0.017900
				H - 6 → L	0.264096
				H - 1 → L + 2	0.101952
				H → L + 5	0.027357
				H → L + 6	0.183191
16	39881.5	250.7	0.001537155	H - 10 → L	0.333066
				H - 9 → L	0.010557
				H - 7 → L	0.077524
				H - 6 → L	0.546282
				H - 5 → L	0.010972
17	40449.2	247.2	0.000581606	H - 10 → L	0.093680
				H - 7 → L	0.885331
				H - 6 → L	0.012305
18	40994.4	243.9	0.109312117	H - 5 → L + 1	0.038261
				H - 5 → L + 2	0.021754
				H - 1 → L + 1	0.011175
				H - 1 → L + 2	0.138123
				H - 1 → L + 3	0.574798
				H - 1 → L + 4	0.084399
				H - 1 → L + 5	0.019592
				H - 1 → L + 6	0.020918
19	41755.9	239.5	0.021142081	H - 7 → L + 1	0.017262
				H - 7 → L + 3	0.016547
				H - 6 → L + 1	0.028102
				H - 5 → L + 2	0.027351
				H - 5 → L + 3	0.027088
				H - 3 → L + 1	0.016558
				H - 2 → L + 2	0.019060
				H - 1 → L + 3	0.160150
				H - 1 → L + 4	0.386272

				H - 1 → L + 5	0.032427
				H - 1 → L + 6	0.156600
				H → L + 6	0.020728
20	42607.8	234.7	0.006812253	H - 6 → L + 1	0.027828
				H - 6 → L + 2	0.010721
				H - 5 → L + 2	0.012360
				H - 3 → L + 2	0.034191
				H - 3 → L + 3	0.016479
				H - 3 → L + 4	0.056655
				H - 3 → L + 5	0.050855
				H - 2 → L + 1	0.020480
				H - 2 → L + 2	0.109913
				H - 2 → L + 4	0.063766
				H - 2 → L + 5	0.064120
				H - 2 → L + 6	0.075291
				H - 1 → L + 4	0.074597
				H - 1 → L + 5	0.260422
				H - 1 → L + 6	0.027229

Table S4. TD-DFT calculated excitation transitions of **2** in the ground state (PBE0/def2-TZVP(-f)). H – HOMO, L – LUMO

State	Energy, cm-1	Wavelength, nm	Oscilator strength	Transitions	Contributions
1	24452.0	409.0	0.093202804	H → L	0.982907
2	31060.0	322.0	0.006405624	H → L + 1	0.971445
				H → L + 2	0.017801
3	33346.9	299.9	0.007754882	H → L + 1	0.019074
				H → L + 2	0.956273
4	35724.0	279.9	0.007844019	H - 2 → L	0.028463
				H - 1 → L	0.099713
				H → L + 3	0.673194
				H → L + 5	0.171264
				H → L + 7	0.011693
5	36114.9	276.9	0.013274467	H - 1 → L	0.661009
				H → L + 3	0.191622
				H → L + 4	0.100547
				H → L + 5	0.019872
				H → L + 7	0.012689
6	36290.6	275.6	0.002032503	H - 1 → L	0.179554
				H → L + 4	0.597541
				H → L + 5	0.150762
				H → L + 6	0.051341
7	36969.6	270.5	0.009086558	H - 2 → L	0.160250
				H - 1 → L	0.036519
				H → L + 2	0.011967

				H → L + 3	0.084790
				H → L + 4	0.053615
				H → L + 5	0.224108
				H → L + 6	0.384419
				H → L + 7	0.029793
8	37694.1	265.3	0.033027295	H - 2 → L	0.289729
				H → L + 3	0.014242
				H → L + 4	0.104340
				H → L + 6	0.468185
				H → L + 7	0.091520
9	37774.5	264.7	0.068130443	H - 2 → L	0.264653
				H → L + 3	0.022543
				H → L + 4	0.135114
				H → L + 5	0.407429
				H → L + 6	0.077671
				H → L + 7	0.064229
10	39266.7	254.7	0.000059605	H - 11 → L	0.012242
				H - 3 → L	0.967068
11	39582.0	252.6	0.000040603	H - 11 → L	0.961607
				H - 3 → L	0.012033
12	40227.2	248.6	0.033392282	H - 2 → L + 1	0.017067
				H - 1 → L + 1	0.828545
				H - 1 → L + 2	0.097714
13	41843.3	239.0	0.006499257	H - 12 → L	0.017433
				H - 9 → L	0.016890
				H - 8 → L	0.050853
				H - 7 → L	0.052278
				H - 6 → L	0.014216
				H - 5 → L	0.406137
				H - 4 → L	0.405517
14	42224.0	236.8	0.051539131	H - 6 → L + 2	0.010922
				H - 5 → L	0.017765
				H - 5 → L + 1	0.033105
				H - 5 → L + 3	0.010007
				H - 5 → L + 4	0.017201
				H - 4 → L + 1	0.057468
				H - 4 → L + 2	0.028052
				H - 3 → L + 1	0.053709
				H - 3 → L + 4	0.012754
				H - 3 → L + 5	0.028906
				H - 2 → L + 2	0.013208
				H - 1 → L + 1	0.089189
				H - 1 → L + 2	0.441628
				H - 1 → L + 3	0.010315
				H - 1 → L + 6	0.050115

15	42401.5	235.8	0.001864814	H - 8 → L	0.031405
				H - 7 → L + 3	0.018270
				H - 6 → L	0.326099
				H - 6 → L + 1	0.038957
				H - 6 → L + 2	0.012509
				H - 5 → L	0.246126
				H - 5 → L + 1	0.011180
				H - 4 → L	0.228547
				H - 1 → L + 2	0.029961
16	42579.0	234.9	0.001808278	H - 6 → L	0.015125
				H - 6 → L + 1	0.011058
				H - 5 → L + 1	0.121507
				H - 5 → L + 3	0.021788
				H - 5 → L + 4	0.048464
				H - 4 → L + 1	0.061933
				H - 4 → L + 2	0.092235
				H - 4 → L + 3	0.023525
				H - 3 → L + 1	0.091093
				H - 3 → L + 5	0.095689
				H - 1 → L + 3	0.052809
				H - 1 → L + 4	0.117956
				H - 1 → L + 6	0.121427
17	42777.7	233.8	0.003880932	H - 8 → L	0.025998
				H - 7 → L	0.023336
				H - 7 → L + 3	0.036618
				H - 7 → L + 4	0.016922
				H - 6 → L	0.266538
				H - 6 → L + 1	0.102661
				H - 6 → L + 2	0.024710
				H - 5 → L	0.170073
				H - 4 → L	0.257313
				H - 1 → L + 2	0.013434
				H - 1 → L + 3	0.011986
18	43093.5	232.1	0.014453605	H - 7 → L	0.019873
				H - 7 → L + 3	0.032218
				H - 6 → L	0.212270
				H - 6 → L + 1	0.062859
				H - 6 → L + 2	0.027923
				H - 5 → L + 1	0.067911
				H - 4 → L	0.018446
				H - 4 → L + 1	0.032764
				H - 4 → L + 2	0.016972
				H - 3 → L + 1	0.056524
				H - 3 → L + 5	0.021038
				H - 1 → L + 1	0.010401
				H - 1 → L + 2	0.205101

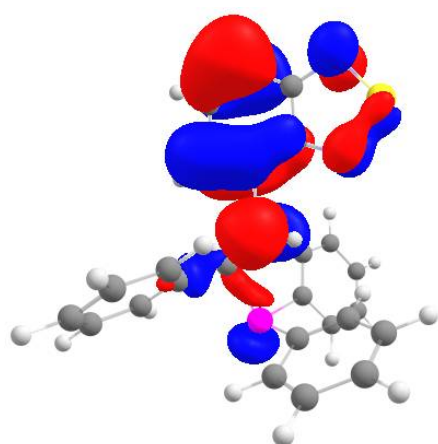| State	Energy, cm-1	Wavelength, nm	Oscilator strength	Transitions	Contributions
				H - 1 → L + 4	0.017128
				H - 1 → L + 6	0.064108
19	43204.2	231.5	0.028836467	H - 8 → L	0.145517
				H - 7 → L	0.591789
				H - 5 → L	0.044172
				H - 5 → L + 1	0.023821
				H - 4 → L	0.045320
				H - 4 → L + 2	0.012190
				H - 1 → L + 2	0.039296
				H - 1 → L + 6	0.013322
				H → L + 7	0.019673
20	43307.5	230.9	0.024382549	H - 8 → L	0.017834
				H - 7 → L	0.058846
				H - 7 → L + 2	0.013126
				H - 7 → L + 3	0.052431
				H - 7 → L + 4	0.032835
				H - 6 → L	0.148146
				H - 6 → L + 1	0.238928
				H - 6 → L + 2	0.030675
				H - 5 → L	0.011944
				H - 5 → L + 4	0.025775
				H - 4 → L + 2	0.040183
				H - 4 → L + 3	0.020897
				H - 3 → L + 1	0.031572
				H - 3 → L + 5	0.014107
				H - 1 → L + 2	0.086873
				H - 1 → L + 3	0.017083
				H - 1 → L + 6	0.057765

Table S5. TD-DFT calculated excitation transitions of **3** in the ground state (PBE0/def2-TZVP(-f)). H – HOMO, L – LUMO

State	Energy, cm-1	Wavelength, nm	Oscilator strength	Transitions	Contributions
1	24646.6	405.7	0.098596968	H → L	0.982543
2	31554.9	316.9	0.000122585	H - 1 → L	0.986023
3	32253.6	310.0	0.000546470	H - 2 → L	0.986274
4	32522.0	307.5	0.001654765	H - 1 → L + 2	0.011608
				H → L + 1	0.294326
				H → L + 2	0.672823
5	32900.2	303.9	0.000562491	H → L + 1	0.679752
				H → L + 2	0.293760
6	35354.6	282.8	0.009862619	H - 3 → L	0.010171
				H - 1 → L + 2	0.050954
				H → L + 3	0.395442

				H → L + 4	0.444448
				H → L + 5	0.070859
7	35644.4	280.5	0.018136818	H - 2 → L + 1	0.209668
				H - 1 → L + 1	0.663920
				H - 1 → L + 2	0.068698
				H → L + 4	0.024790
8	35992.4	277.8	0.028033330	H - 2 → L + 1	0.015232
				H - 1 → L + 1	0.081421
				H - 1 → L + 2	0.778714
				H → L + 2	0.015037
				H → L + 4	0.060330
				H → L + 5	0.013679
9	36186.6	276.3	0.014274214	H - 3 → L	0.035205
				H - 2 → L + 1	0.089773
				H - 2 → L + 2	0.014671
				H - 1 → L + 1	0.015313
				H - 1 → L + 2	0.036172
				H → L + 3	0.492297
				H → L + 4	0.213113
				H → L + 5	0.057185
				H → L + 6	0.012094
10	36373.6	274.9	0.011632147	H - 2 → L + 1	0.478027
				H - 2 → L + 2	0.207960
				H - 1 → L + 1	0.154769
				H - 1 → L + 2	0.013350
				H → L + 1	0.011827
				H → L + 3	0.073947
				H → L + 4	0.018826
11	36898.6	271.0	0.078599657	H - 4 → L	0.039938
				H - 3 → L	0.672184
				H → L + 4	0.101538
				H → L + 5	0.033186
				H → L + 6	0.019595
				H → L + 7	0.086655
12	37231.2	268.6	0.002774709	H - 2 → L + 1	0.174827
				H - 2 → L + 2	0.725451
				H - 1 → L + 1	0.046854
13	37494.7	266.7	0.006782619	H - 4 → L	0.075433
				H - 3 → L	0.156865
				H → L + 4	0.061434
				H → L + 5	0.557764
				H → L + 6	0.127539
14	37884.5	264.0	0.044685130	H - 5 → L	0.045070
				H - 4 → L	0.616992
				H - 3 → L	0.057207
				H → L + 5	0.118031

				H → L + 6	0.027568
				H → L + 7	0.102992
15	38736.1	258.2	0.000481069	H - 5 → L	0.895485
				H - 4 → L	0.091165
16	39238.5	254.9	0.001880633	H - 1 → L + 3	0.368365
				H → L + 4	0.034522
				H → L + 5	0.075280
				H → L + 6	0.479065
17	39288.6	254.5	0.005875222	H - 8 → L + 2	0.011845
				H - 2 → L + 3	0.028120
				H - 1 → L + 3	0.481911
				H - 1 → L + 4	0.058764
				H → L + 3	0.010570
				H → L + 4	0.024202
				H → L + 5	0.041425
				H → L + 6	0.307038
18	39424.2	253.7	0.000052775	H - 11 → L	0.974360
19	40302.9	248.1	0.000261880	H - 2 → L + 3	0.600364
				H - 2 → L + 4	0.039055
				H - 2 → L + 5	0.018596
				H - 1 → L + 4	0.286421
20	40753.2	245.4	0.011202698	H - 2 → L + 3	0.216165
				H - 2 → L + 4	0.046586
				H - 1 → L + 3	0.067204
				H - 1 → L + 4	0.561989
				H - 1 → L + 5	0.023421
				H → L + 6	0.011996

Table S6. TD-DFT calculated excitation transitions of **4** in the ground state (PBE0/def2-TZVP(-f)). H – HOMO, L – LUMO

State	Energy, cm-1	Wavelength, nm	Oscilator strength	Transitions	Contributions
1	24616.8	406.2	0.100692050	H → L	0.972388
2	28567.4	350.0	0.000526958	H - 1 → L	0.983238
				H → L	0.010709
3	29466.9	339.4	0.000416303	H - 2 → L	0.990800
4	31169.6	320.8	0.012446356	H - 2 → L + 1	0.020405
				H - 2 → L + 2	0.011318
				H - 1 → L + 1	0.173446
				H - 1 → L + 2	0.029861
				H → L + 1	0.601190
				H → L + 2	0.145299
5	31854.6	313.9	0.001087329	H - 1 → L + 1	0.043821
				H - 1 → L + 2	0.216688

				H → L + 1	0.136232
				H → L + 2	0.586290
6	32338.8	309.2	0.014399165	H - 2 → L + 1	0.335701
				H - 1 → L + 1	0.548007
				H → L + 1	0.090553
7	33188.7	301.3	0.016821731	H - 2 → L + 1	0.023915
				H - 2 → L + 2	0.070631
				H - 1 → L + 2	0.667460
				H → L + 2	0.204291
8	33464.9	298.8	0.006257015	H - 2 → L + 1	0.551306
				H - 2 → L + 2	0.087261
				H - 1 → L + 1	0.177631
				H → L + 1	0.154873
9	34466.2	290.1	0.003331934	H - 2 → L + 1	0.037685
				H - 2 → L + 2	0.791690
				H - 1 → L + 1	0.025540
				H - 1 → L + 2	0.050494
				H → L + 2	0.055131
				H → L + 3	0.013425
10	34892.3	286.6	0.014619474	H - 1 → L + 3	0.022564
				H → L + 3	0.467376
				H → L + 4	0.410051
				H → L + 5	0.052081
11	35650.5	280.5	0.008166630	H - 3 → L	0.011456
				H - 2 → L + 2	0.010067
				H - 1 → L + 3	0.124800
				H → L + 3	0.355467
				H → L + 4	0.396093
				H → L + 5	0.067647
				H → L + 6	0.010082
12	36532.4	273.7	0.004617130	H - 2 → L + 3	0.050978
				H - 1 → L + 3	0.743305
				H - 1 → L + 4	0.034330
				H → L + 3	0.114785
				H → L + 4	0.023751
13	36698.8	272.5	0.059385690	H - 4 → L	0.043926
				H - 3 → L	0.615651
				H - 1 → L + 3	0.011584
				H - 1 → L + 4	0.018208
				H → L + 4	0.060437
				H → L + 5	0.131002
				H → L + 6	0.015664
				H → L + 7	0.063258
14	37110.1	269.5	0.018791604	H - 4 → L	0.011776
				H - 3 → L	0.243732
				H - 2 → L + 3	0.019335

				H - 1 → L + 4	0.012286
				H → L + 4	0.034512
				H → L + 5	0.575168
				H → L + 6	0.065536
15	37472.6	266.9	0.005185902	H - 2 → L + 3	0.234712
				H - 1 → L + 4	0.650051
				H → L + 5	0.023363
				H → L + 6	0.041121
16	37774.6	264.7	0.045871278	H - 5 → L	0.012486
				H - 4 → L	0.678975
				H - 3 → L	0.067748
				H - 2 → L + 3	0.051018
				H → L + 5	0.028604
				H → L + 7	0.107901
17	38012.9	263.1	0.015403972	H - 4 → L	0.037673
				H - 2 → L + 3	0.527308
				H - 2 → L + 4	0.050422
				H - 1 → L + 3	0.055942
				H - 1 → L + 4	0.167187
				H - 1 → L + 5	0.021845
				H → L + 3	0.011205
				H → L + 5	0.024761
				H → L + 6	0.070120
18	38669.4	258.6	0.006293214	H - 2 → L + 3	0.024066
				H - 2 → L + 4	0.352542
				H - 1 → L + 4	0.020576
				H - 1 → L + 5	0.275696
				H → L + 6	0.290604
19	38747.7	258.1	0.000449211	H - 5 → L	0.957471
				H - 4 → L	0.027537
20	38917.9	257.0	0.011894574	H - 2 → L + 3	0.012426
				H - 2 → L + 4	0.532882
				H - 1 → L + 5	0.106275
				H - 1 → L + 6	0.029428
				H → L + 4	0.023167
				H → L + 5	0.035634
				H → L + 6	0.228919

Frontier orbitals

HOMO
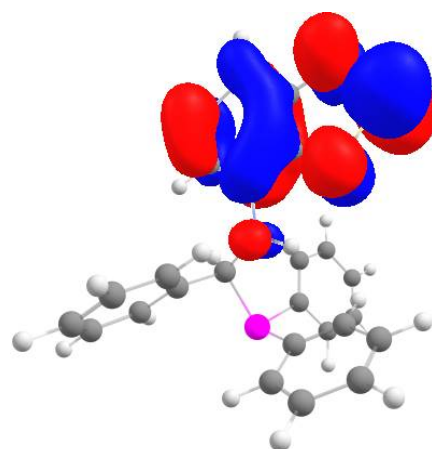
LUMO
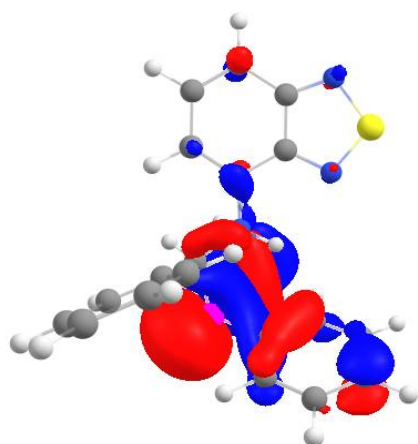
HOMO-1
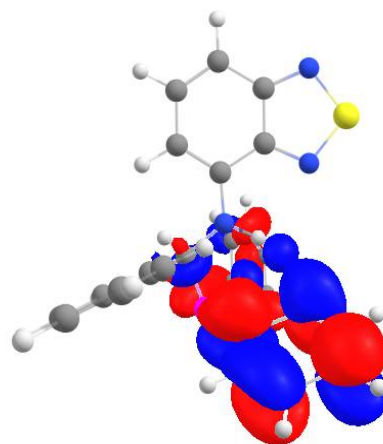
LUMO+1
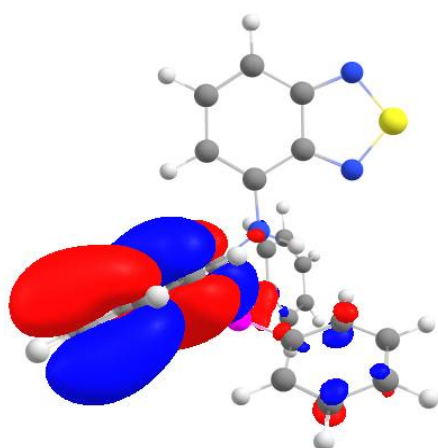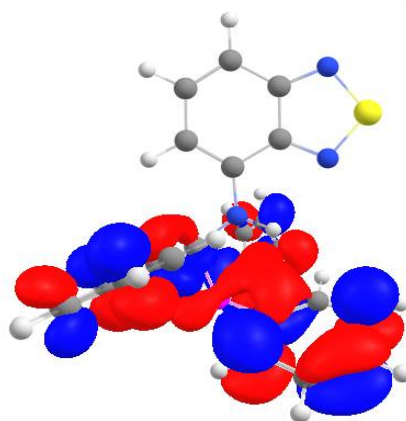
HOMO-2

LUMO+2

Figure S8. Frontier orbitals of **1** in the ground state geometry (PBE0/def2-TZVP(-f), isosurface = 0.03)
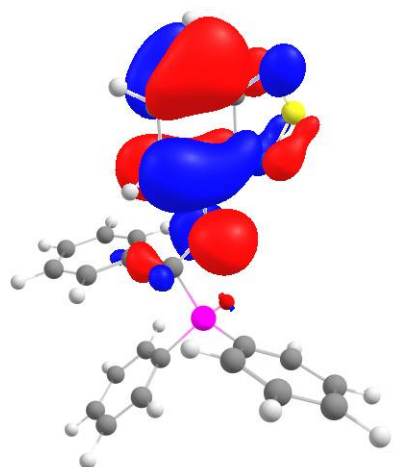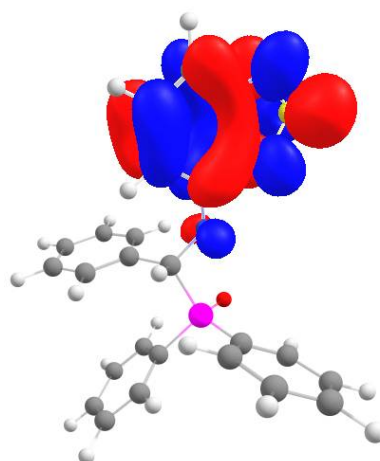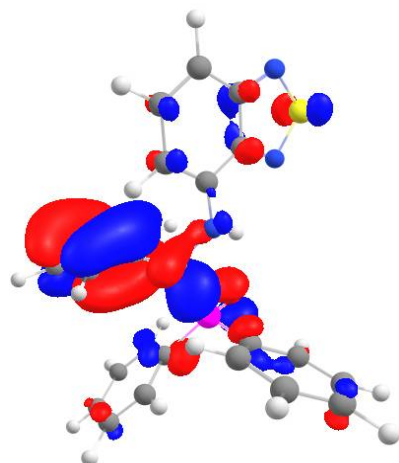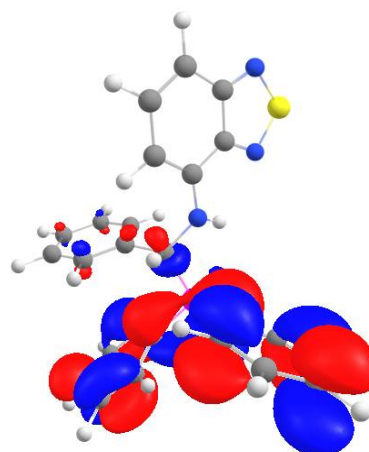
HOMO
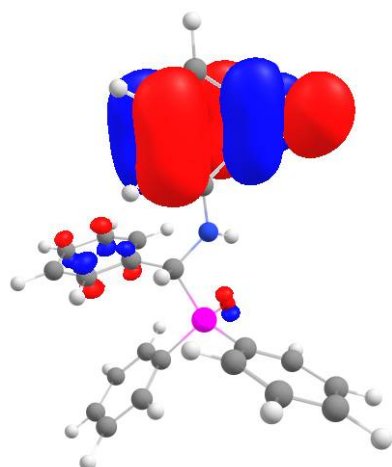
LUMO
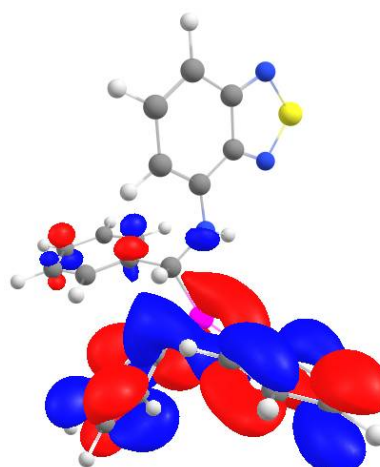
HOMO-1

LUMO+1

HOMO-2

LUMO+2

Figure S9. Frontier orbitals of **2** in ground state geometry (PBE0/def2-TZVP(-f), isosurface = 0.03)
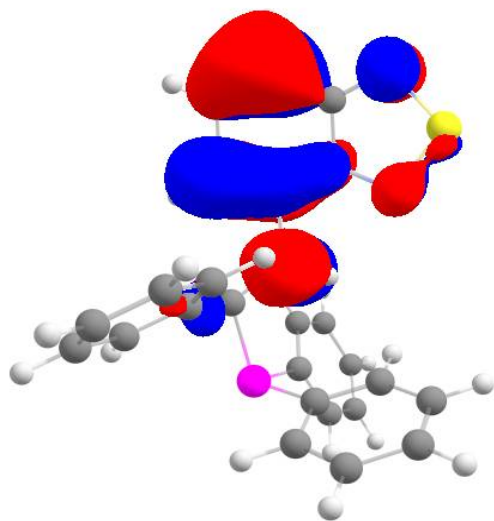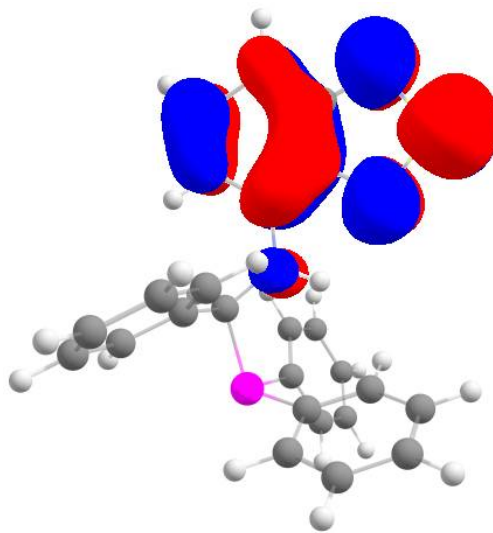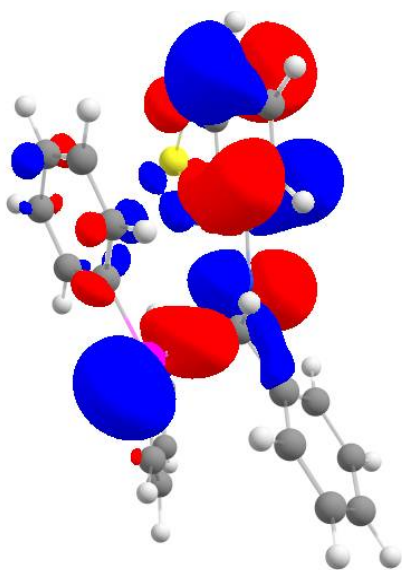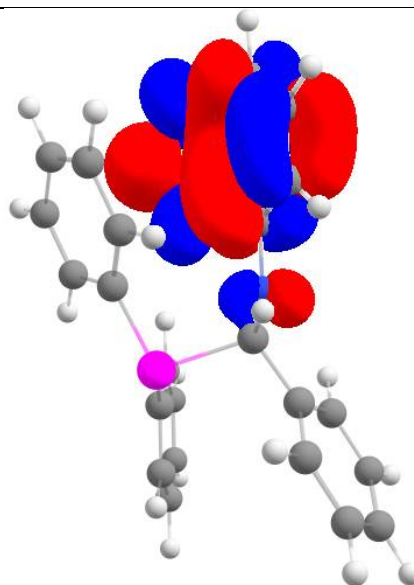
HOMO

LUMO

HOMO-1
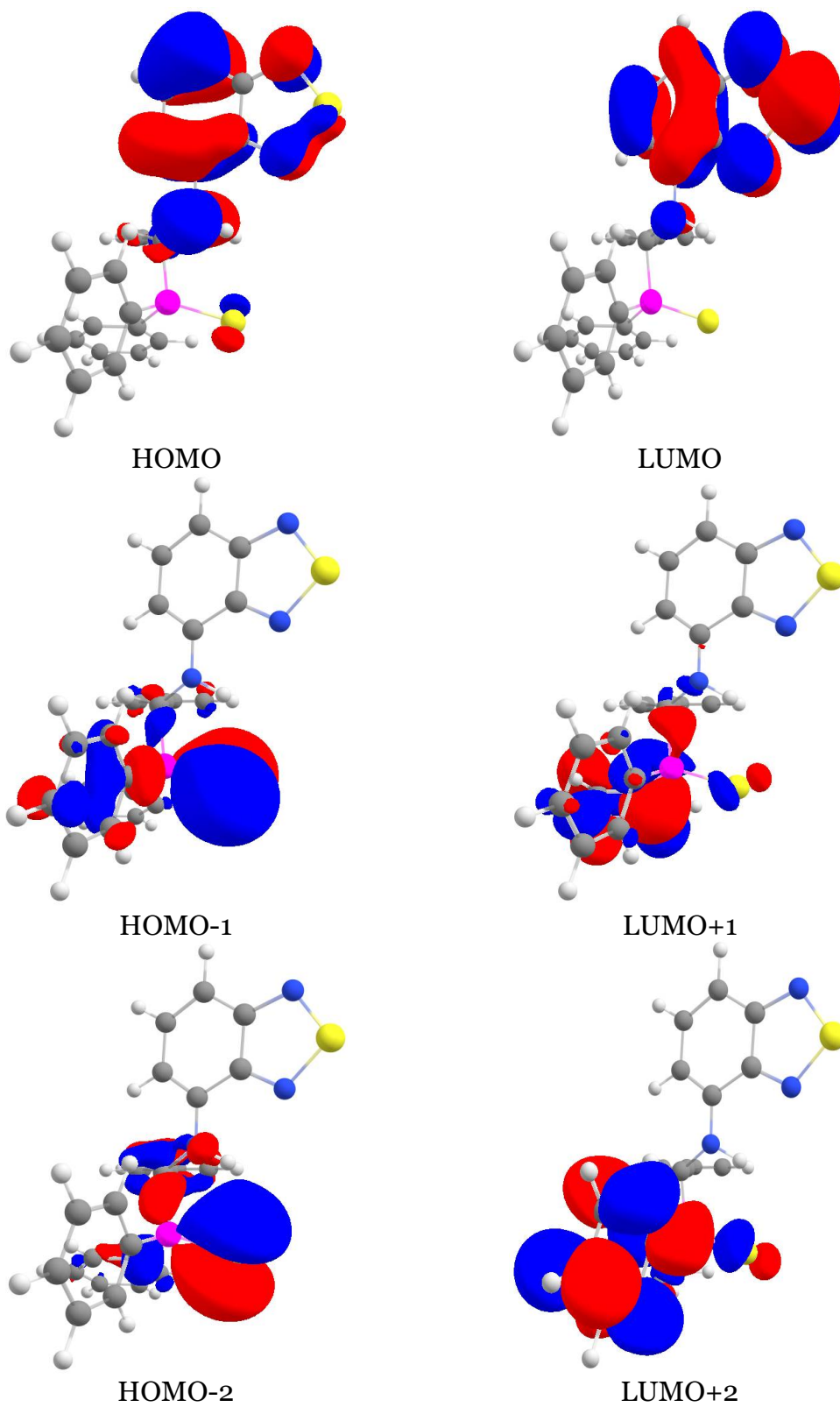
LUMO+1

HOMO-2

LUMO+2

Figure S10. Frontier orbitals of **3** in ground state geometry (PBEO/def2-TZVP(-f), isosurface = 0.03)
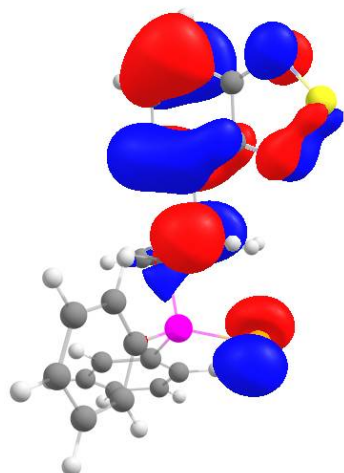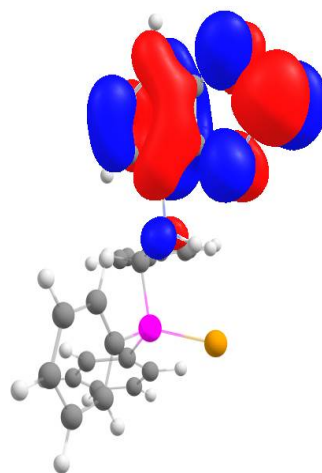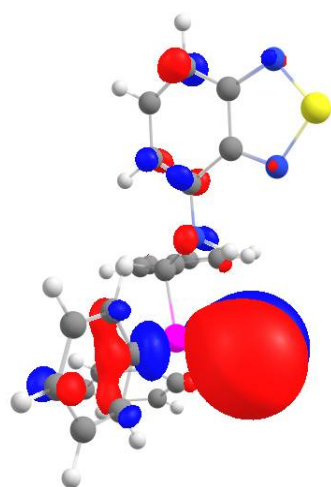
HOMO

LUMO

HOMO-1
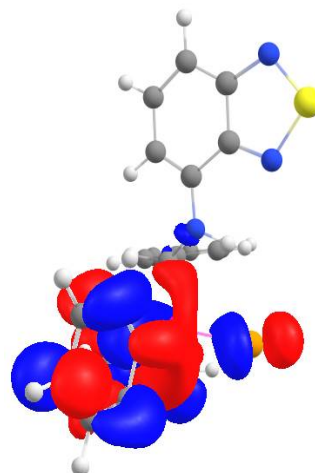
LUMO+1
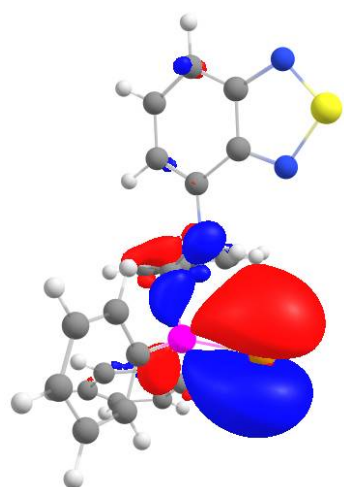
HOMO-2
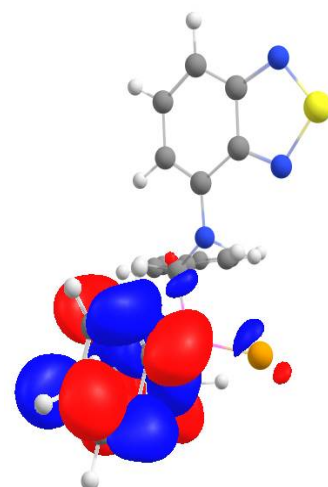
LUMO+2

Figure S11. Frontier orbitals of **4** in ground state geometry (PBE0/def2-TZVP(-f), isosurface = 0.03)

HOMO   LUMO

S₁

HOMO   LUMO

T₁

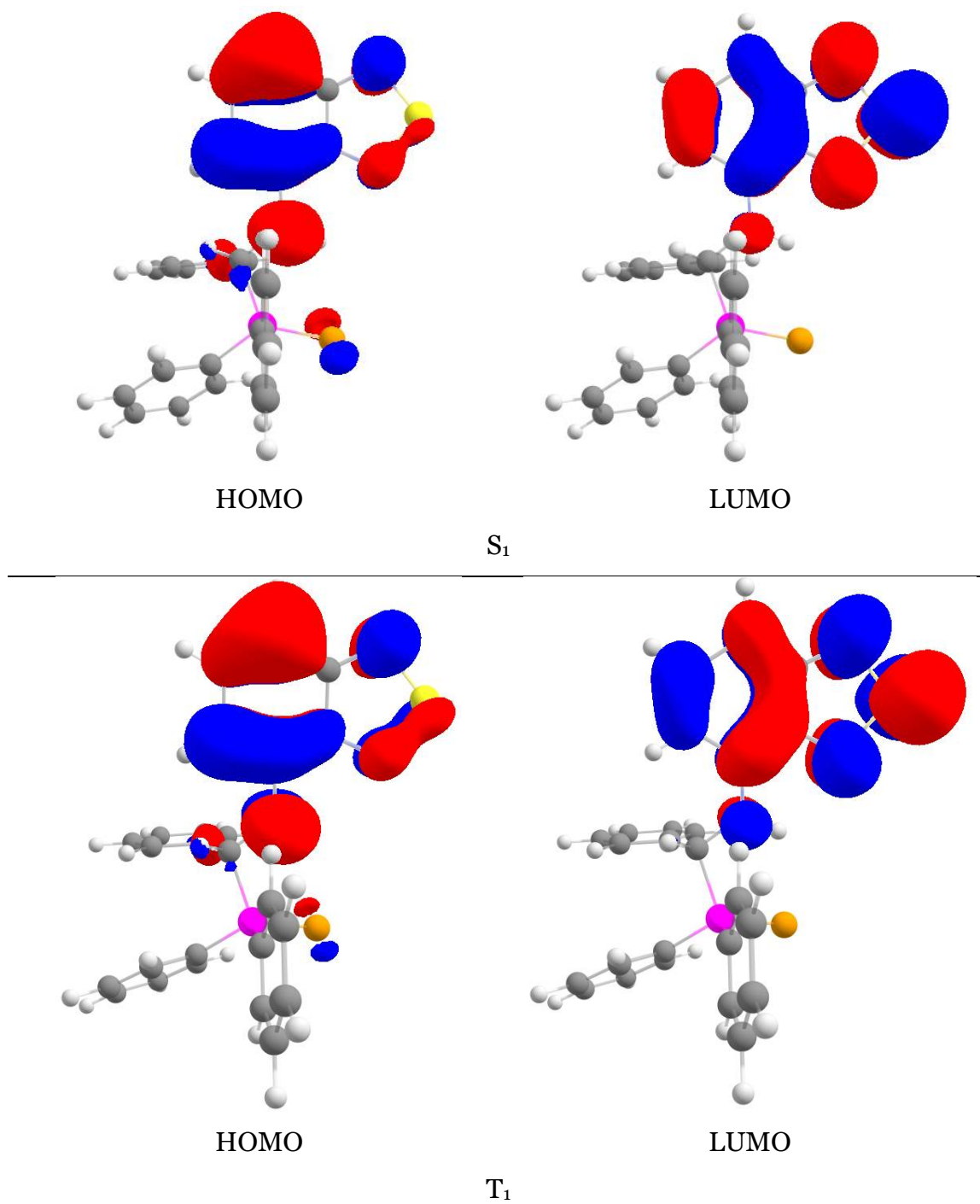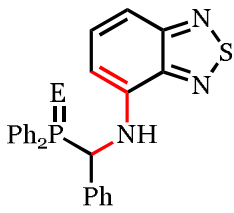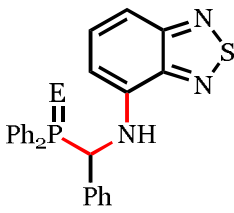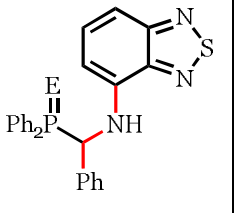Figure S12. Frontier orbitals of **1** in equilibrium geometries of S1 and T₁ states (isosurface = 0.03 a.u.)

HOMO   LUMO

S₁

HOMO   LUMO

T₁
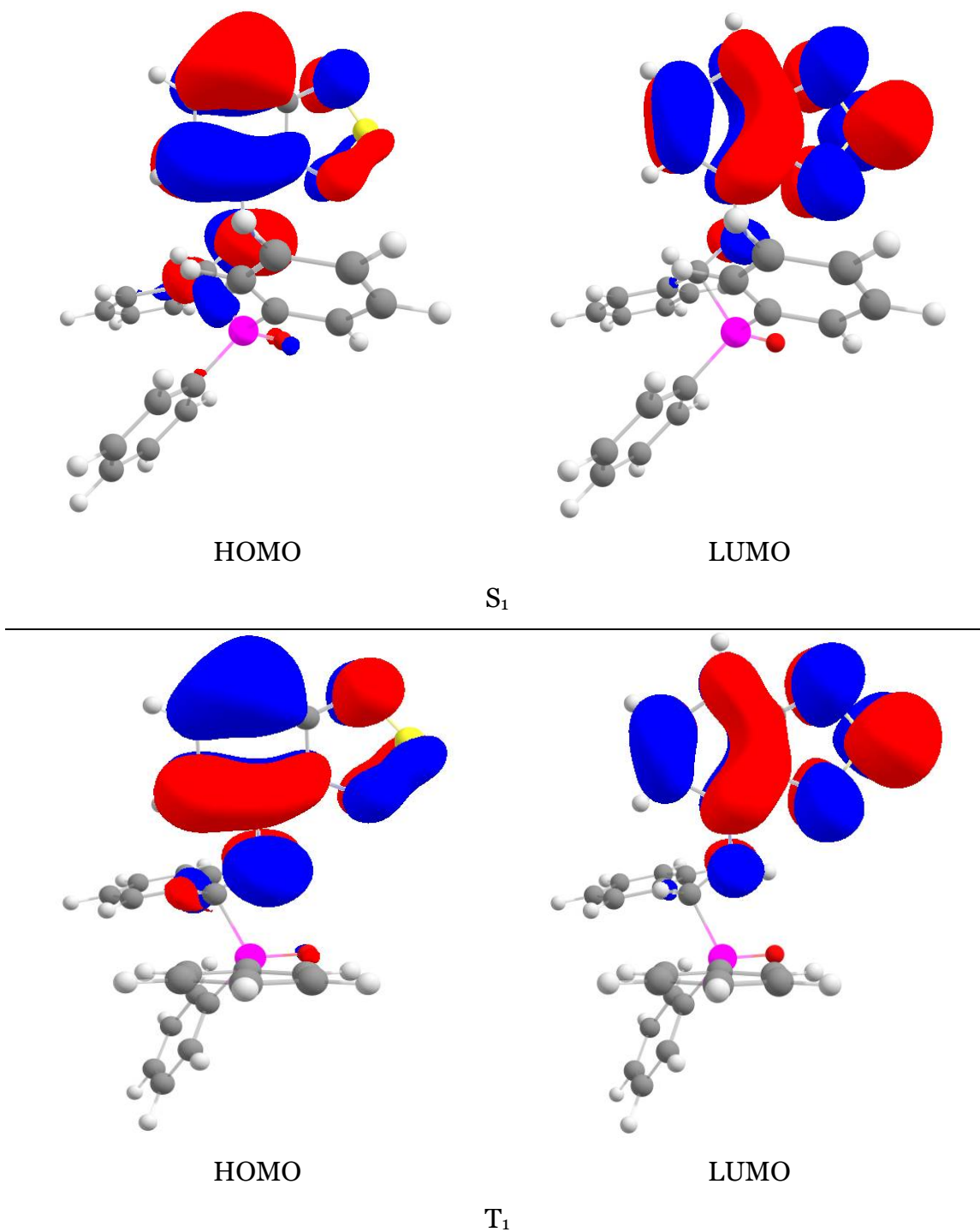
Figure S13. Frontier orbitals of **2** in equilibrium geometries of S1 and T₁ states
(isosurface = 0.03 a.u.)

HOMO LUMO

S$_1$
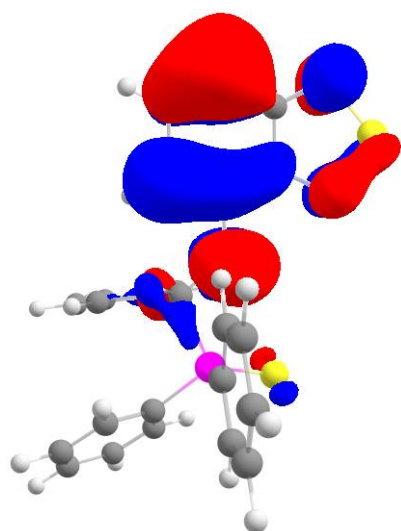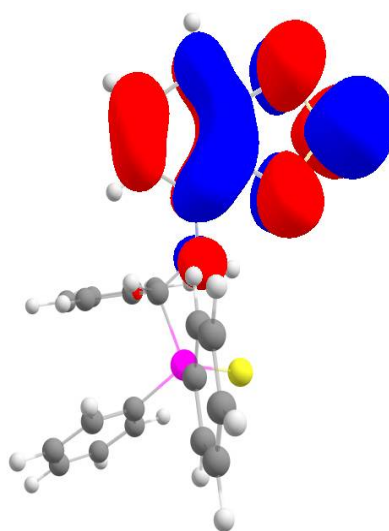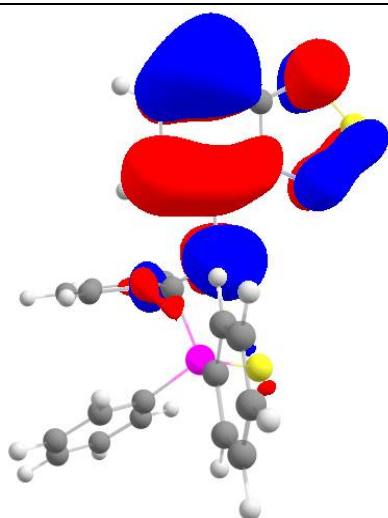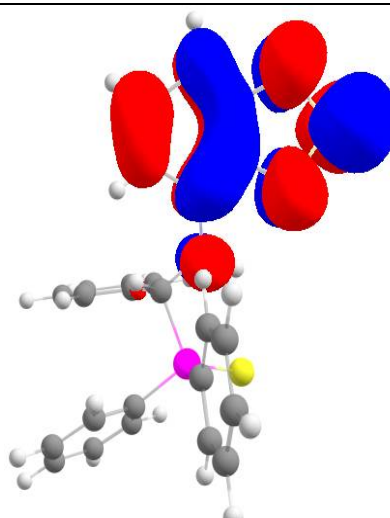
HOMO LUMO

T$_1$

Figure S14. Frontier orbitals of **3** in equilibrium geometries of S1 and T$_1$ states (isosurface = 0.03 a.u.)

HOMO   LUMO
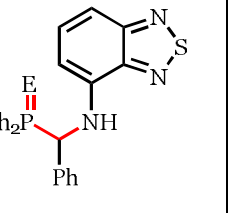
S₁

HOMO   LUMO

T₁

Figure S15. Frontier orbitals of **4** in equilibrium geometries of S1 and T₁ states (isosurface = 0.03 a.u.)

DFT calculation of relaxation processes

Table S7. 0-0 transition wavelengths and energies, calculated by PBE0/def2-TZVP(-f) over equilibrium excited state geometries.

Compound	S_1	T_1
1	528.2 nm (2.347 eV)	904.3 (1.371 eV)
2	519.0 nm (2.389 eV)	821.2 (1.510 eV)
3	509.6 nm (2.433 eV)	821.4 nm (1.510 eV)
4	508.1 nm (2.440 eV)	819.8 nm (1.512 eV)

Table S8. Selected geometric parameters of the molecules calculated in S1 and T1 excited states

	CCNC, deg	CNCP, deg	CNCC, deg	NCPE, deg
1				
S1	8.79	166.51	71.36	-
T1	38.38	94.21	143.36	-
2				
S1	8.60	140.94	98.04	51.81
T1	3.43	155.84	77.29	34.11
3				
S1	1.99	160.32	77.49	44.85
T1	0.19	164.08	73.52	45.84
4				
S1	2.39	159.90	77.40	44.59
T1	0.48	163.65	73.60	44.64

Photoluminescence spectra
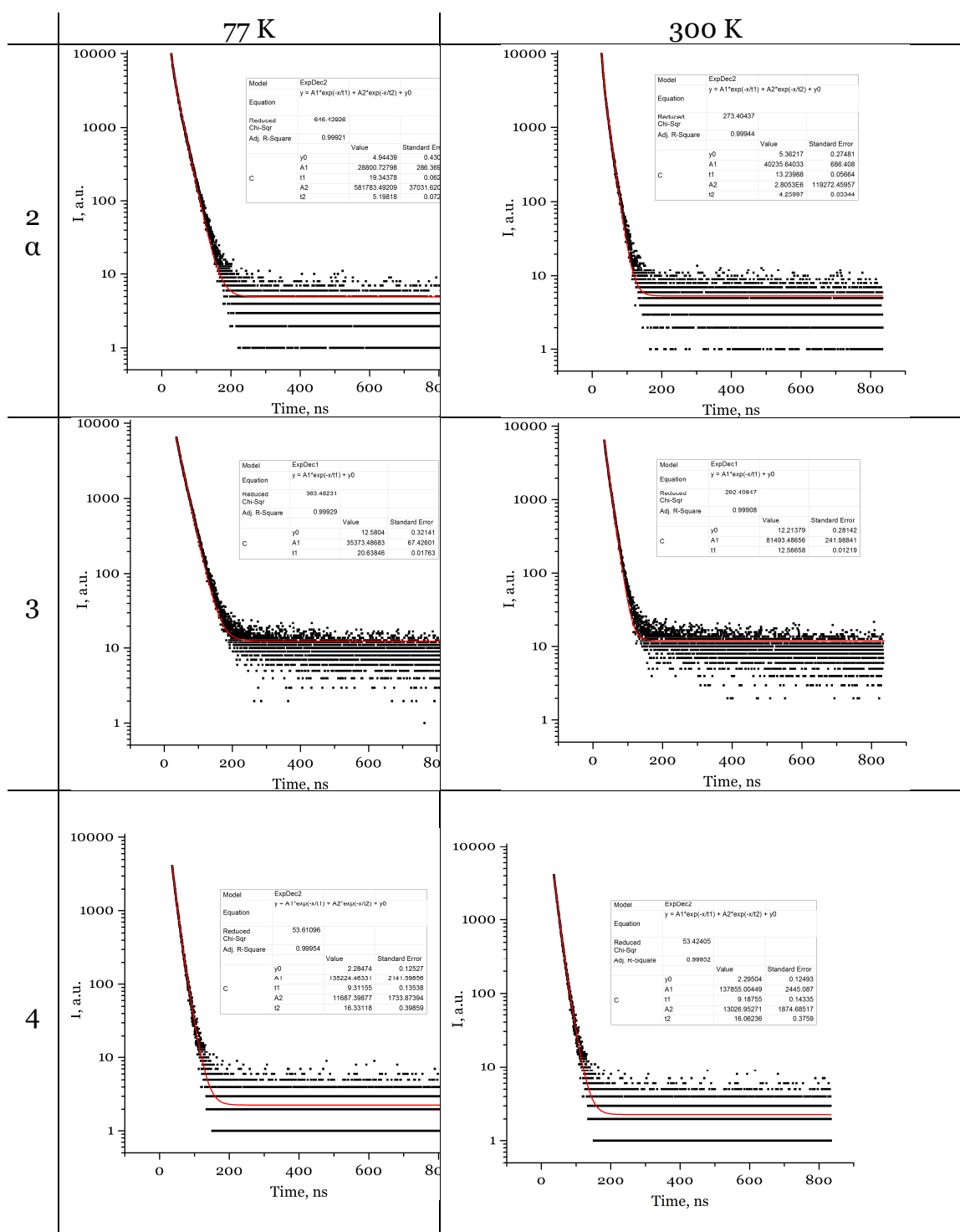
Figure S16. Emission decay kinetics of the compounds at 77 and 300 K. The fit is shown as red line.
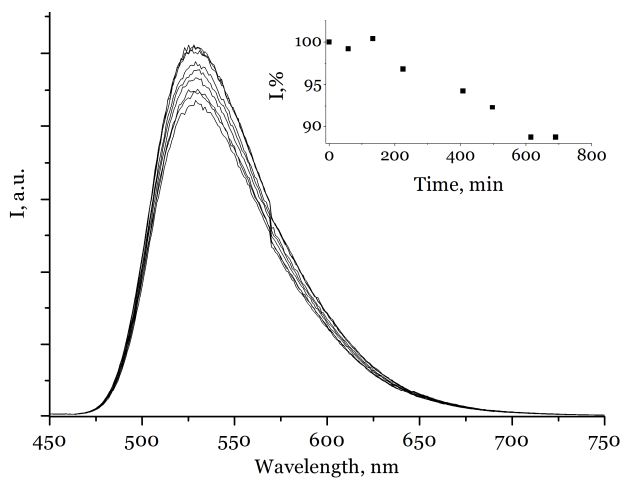
Figure S17. PL spectra of compound **3** upon continuous irradiation with a visible light on air. Inset: the emission intensity at 530 nm normalized on 100% vs irradiation time.
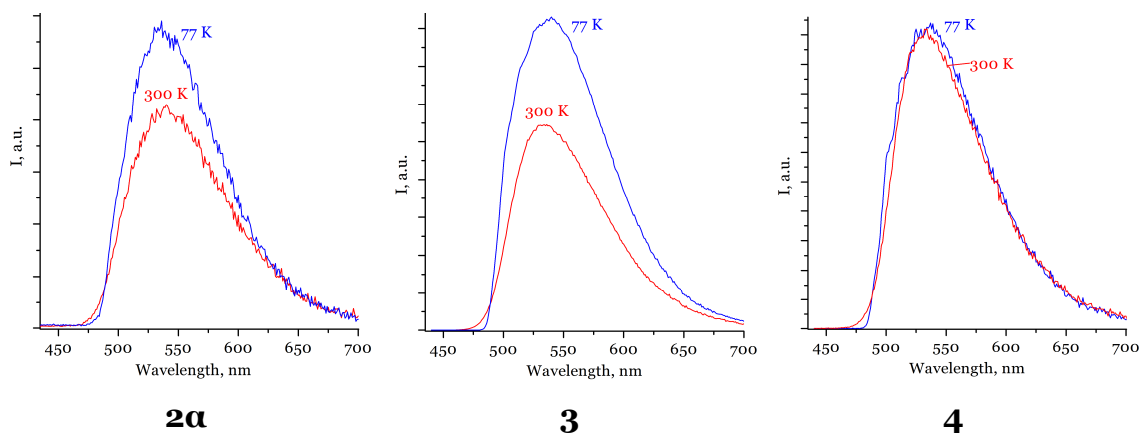

2α   **3**   **4**

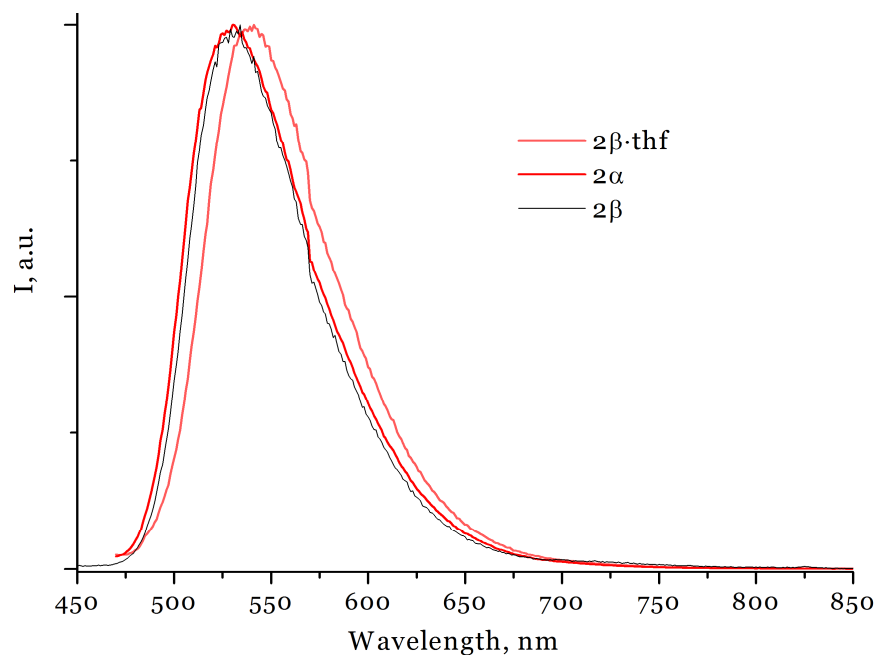Figure S18. Comparison of the PL spectra for the compounds at 77 and 300K.

Figure S19. Comparison of the normalized PL spectra for compounds **2α**, as-synthesized **2β**·thf, and unsolvated **2β**.
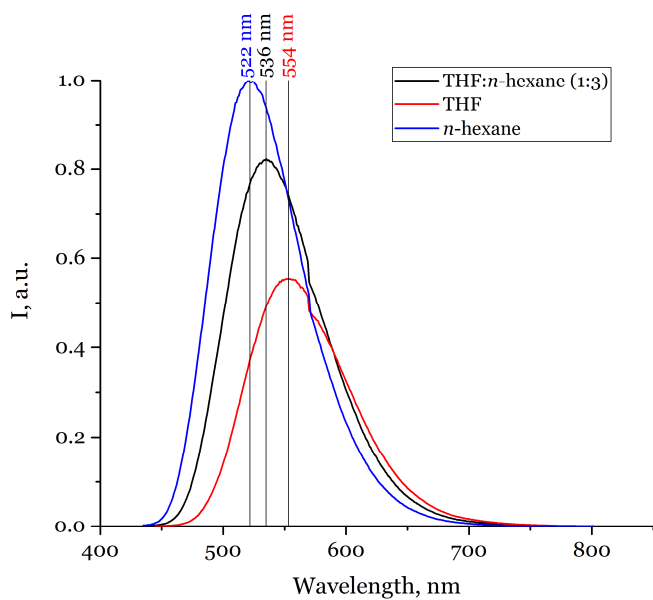

Figure S20. PL spectra of **1** in THF, *n*-hexane and mixture (THF:*n*-hexane = 1 : 3), intensities normalized to relative to spectrum of *n*-hexane solution
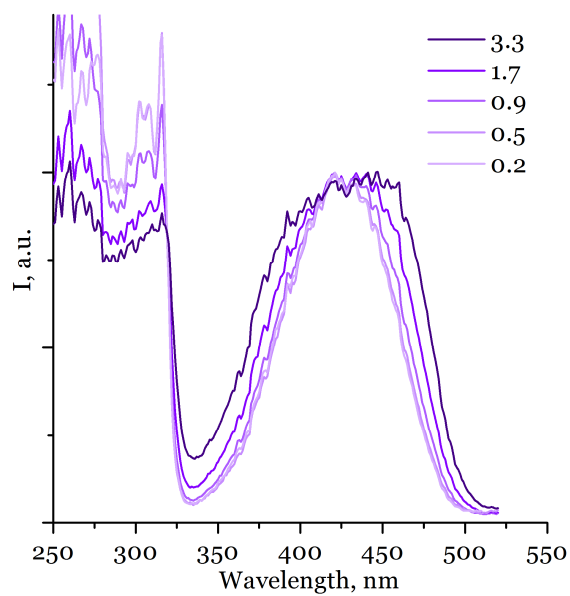
Figure S21. Excitation spectra at 520 nm of polystyrene films containing **2** with a mass fraction from 0.2 to 3.3%, normalized on the long wavelength band.