Supporting information

Content

Powder X-Ray diffraction data

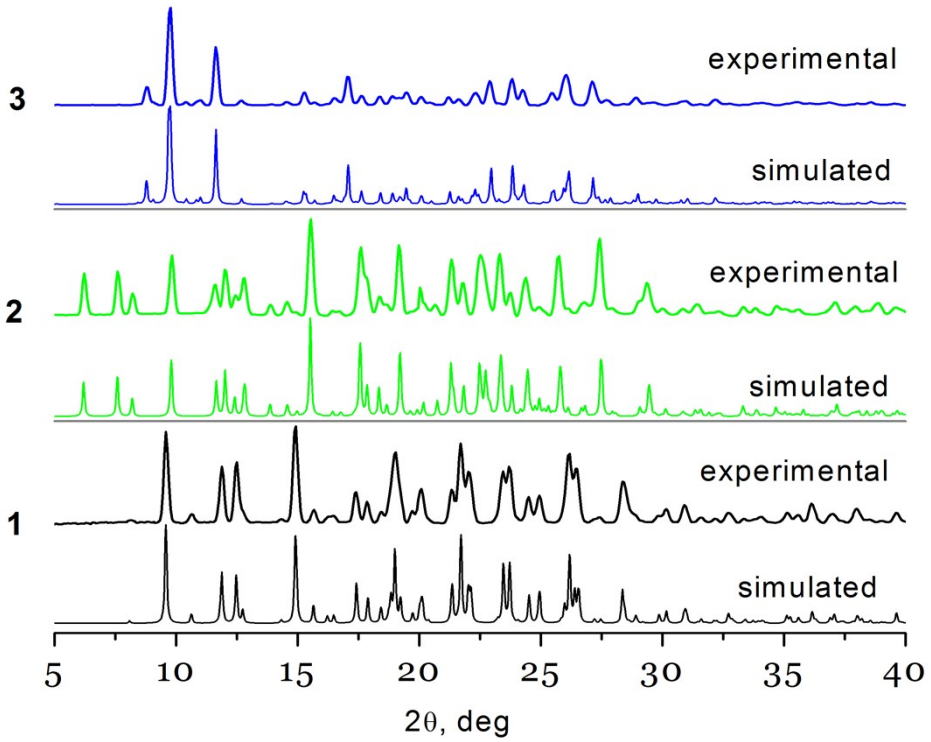


Figure S1 – Experimental (top) and simulated (bottom) PXRD patterns for **1** (black), **2** (green) and **3** (blue).

Geometry parameters

Table S1 – Experimental hydrogen bond characteristics for compounds **1**–**3**. *D* is a donor atom, *A* is an acceptor atom.

	D	H	*A*	*D*–H, Å	H···*A*, Å	*D*···*A*, Å	*D*–H···*A*, deg
1	N2	H2	N1	0.850(13)	2.009(15)	2.7167(16)	140.2(15)
2	N12	H12	N11	0.871(9)	1.950(13)	2.6944(17)	142.6(16)
	N22	H22	N21	0.871(9)	2.025(13)	2.7513(17)	140.1(16)
3	N12	H12	N11	0.873(9)	1.941(15)	2.669(2)	139.9(18)
	N22	H22	N21	0.875(9)	1.956(15)	2.694(2)	141.2(18)

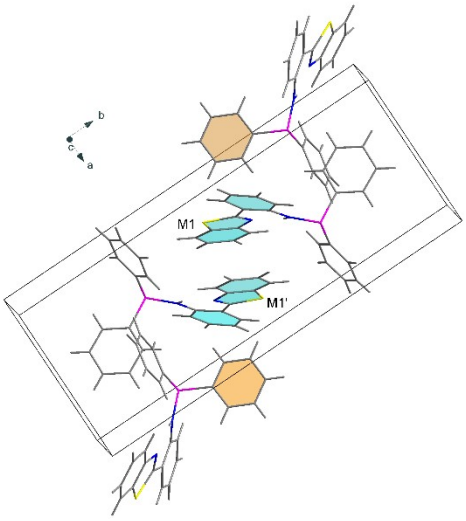


Fig. S2 – A fragment of crystal packing for compound **1** showing parallel arrangement of *pbt* moielties highlighted turquoise. Phenyl groups capping the pair of parallel *pbt*s are highlighted orange. *pbt* moiety is denoted as M1, crystallographically related one is denoted with an apostrophe.

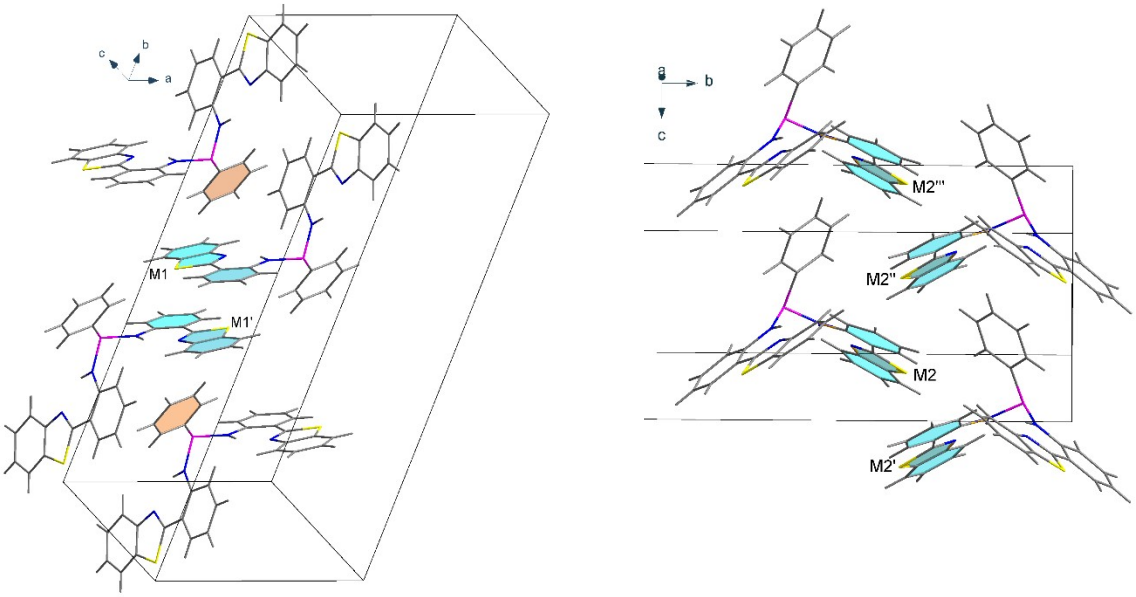


Fig. S3 – A fragment of crystal packing for compound **2** showing parallel (left) and inclined (right) arrangement of *pbt* moielties highlighted turquoise. Phenyl groups capping the pair of parallel *pbt*s via T-shaped C–H···π contacts are highlighted orange. Crystallographically independent *pbt* moieties are denoted as M1–M2; crystallographically related ones are denoted with an apostrophe.

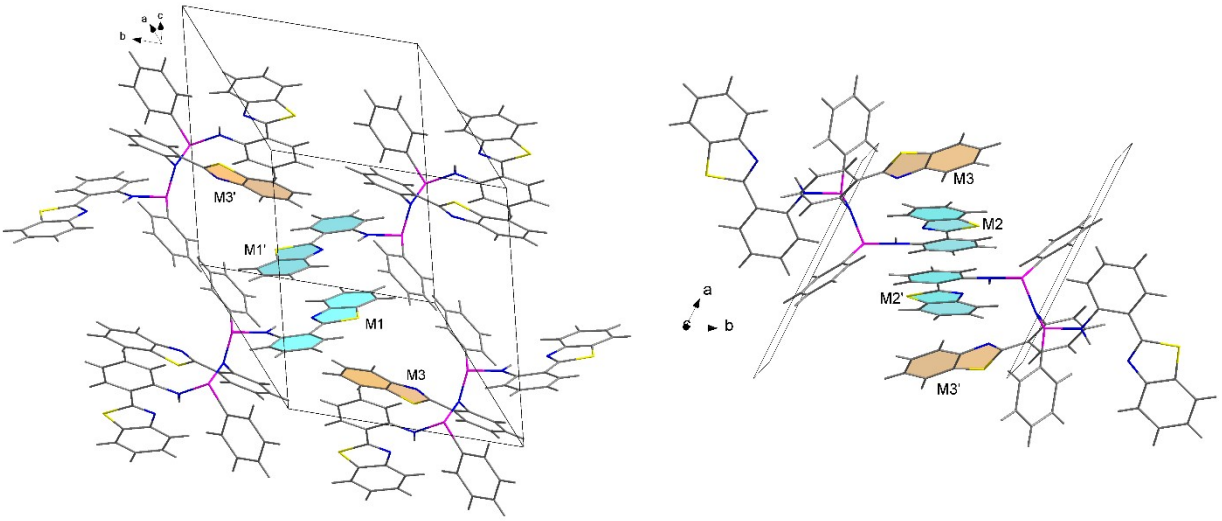
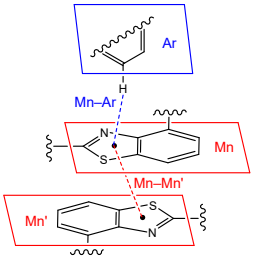


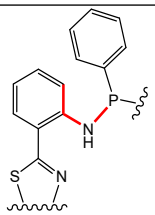
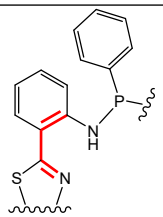
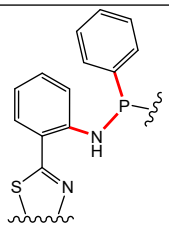
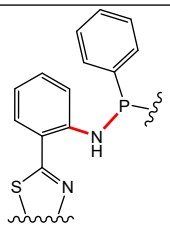
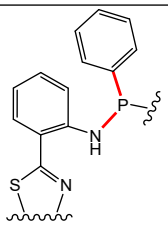
Fig. S4 – A fragment of crystal packing for compound **3** showing parallel arrangement of different *pbt* moielties highlighted turquoise. Moieties capping the pair of parallel *pbt*s via T-shaped C–H···π contacts are highlighted orange. Crystallographically independent *pbt* moieties are denoted as M1–M3; crystallographically related ones are denoted with an apostrophe.

Table S2 – Experimental characteristics of π-π contacts for **1**–**3**: intercentroid distance between heterocycles (M*n*–M*n*'), shortest C–H···heterocyclic center distance (M*n*–Ar), dihedral angle between heterocyclic planes (M*n*–M*n*'), dihedral angle between heterocyclic and aryl planes (M*n*–Ar); *n* is *pbt* unit number.



	1		**2**		**3**	
	M1–M1'	M1–Ar	M*n*–M*n*'	M*n*–Ar	M*n*–M*n*'	M*n*–Ar
distance, Å	3.87	3.07	3.69, 4.63	3.33, 3.32	3.74, 3.44, 6.29	3.02, 4.32, 3.79
angle, deg	0	89.1	0, 60.7	45.9, 60.7	0, 0, 45.6	43.6, 19.7, 37.8

Table S3 – Selected geometry parameters for experimental and optimized structures in the ground state

						
	CCNP, deg	NCCC, deg	CNPC, deg	CNP,deg	NPC, deg	NH, Å
			1			
DFT in gas phase	13.05	1.32	99.82, 157.13	126.43	96.14, 103.19	1.022
Periodic DFT	4.48	16.55	98.17, 158.77	123.46	99.63, 101.17	1.101
Experimental	7.73	13.76	101.35, 154.65	124.87	100.15, 103.03	0.849
			2			
DFT in gas phase	15.69, 28.51	0.31, 15.48	58.47, 165.98	123.57, 131.83	97.60, 102.34	1.020, 1.021
Periodic DFT	0.04, 0.76	1.53, 2.19	45.64, 152.26	128.67, 130.84	95.81, 98.16	1.098, 1.103
Experimental	2.02, 3.03	3.40, 4.12	51.64, 144.26	127.62, 131.92	97.23, 100.96	0.870, 0.872
			3			
DFT in gas phase	21.62, 32.08, 79.86, 77.09	10.77, 23.44, 174.14	40.08, 40.93, 150.39, 171.49	124.95, 122.00, 121.61, 123.05	96.00, 98.39, 101.79, 102.46	1.018, 1.023
Periodic DFT	18.49, 23.55, 74.19, 80.12	2.35, 2.96, 13.00	33.95, 41.59, 148.16, 158.22	122.74, 123.76, 124.02, 124.12	96.95, 97.95, 100.43, 102.28	1.112
Experimental	7.53, 12.58, 79.52, 84.64	0.97, 1.45, 161.45	33.60, 42.33, 149.49, 157.94	126.40, 121.50, 122.72, 125.76	95.69, 98.82, 103.32, 101.51,	0.880

RDG analysis

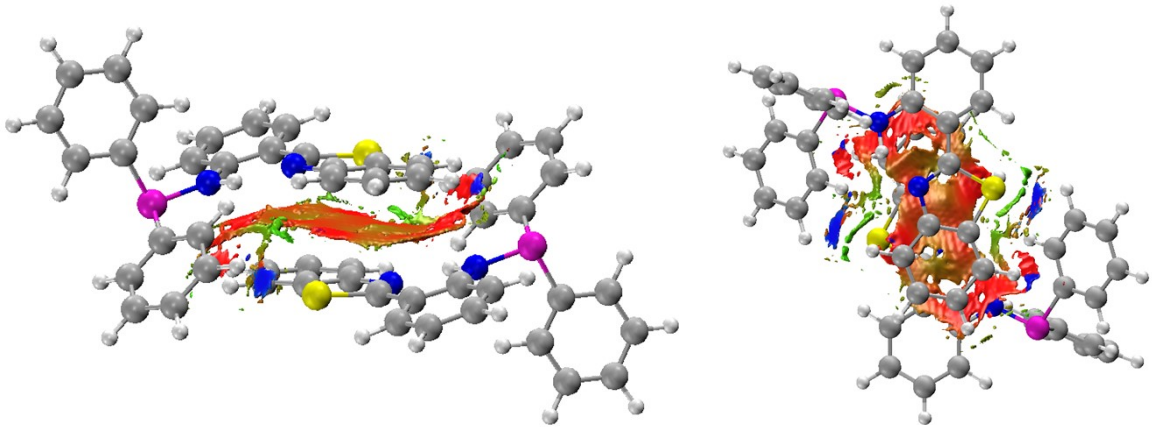


Figure S5 – Two projections of plot of sign(λ_2)·ρ mapped over the RDG for **1** (isovalue s = 0.5, -0.01 a.u.< sign(λ_2)·ρ <0.01 a.u., isosurfaces colored via red-green-blue scale, where red – attractive, blue – repulsive).

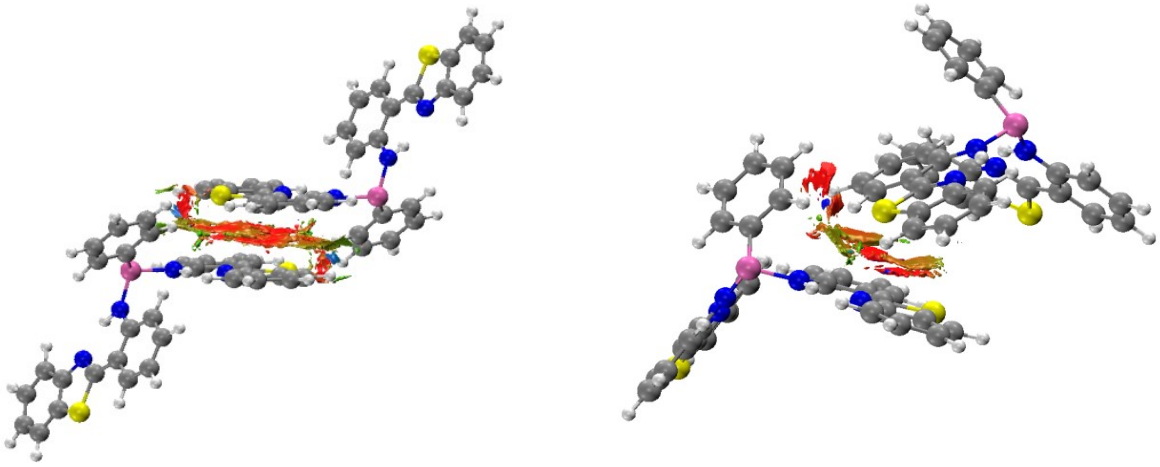


Figure S6 – Plot of sign(λ_2)·ρ mapped over the RDG for two fragments of **2** (isovalue s = 0.5, -0.01 a.u.< sign(λ_2)·ρ <0.01 a.u., isosurfaces colored via red-green-blue scale, where red – attractive, blue – repulsive).

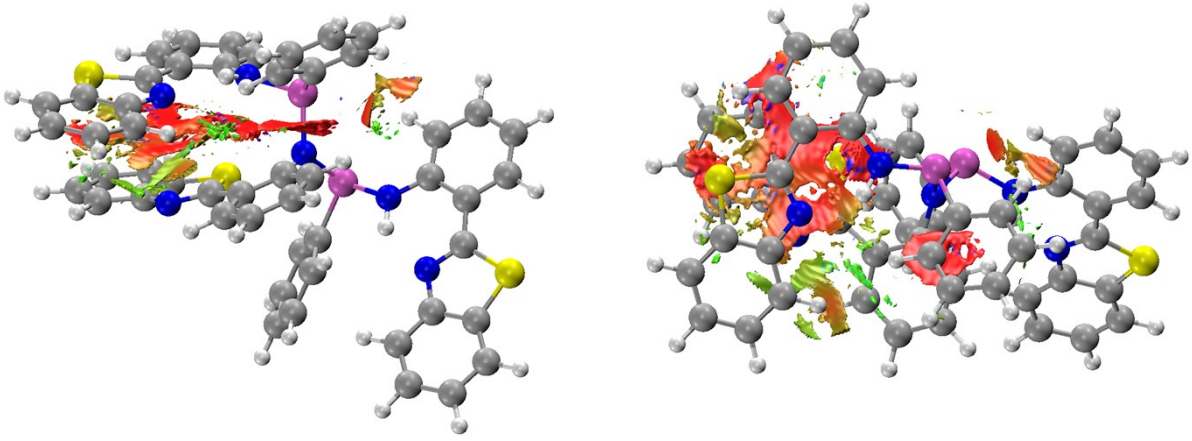


Figure S7 – Two projections of plot of sign(λ_2)·ρ mapped over the RDG for **3** (isovalue s = 0.5, -0.01 a.u.< sign(λ_2)·ρ <0.01 a.u., isosurfaces colored via red-green-blue scale, , where red – attractive, blue – repulsive).

Single point calculations with periodic boundary conditions

Table S4 – HOCO-LUCO energies (PBE0-D3/DZVP-MOLOPT-SR-GTH) and onset optical gaps

Compound	HOCO-LUCO, eV	Optical gap, eV
1	3.59	2.92
2	3.30	2.91
3	3.21	2.88

DFT calculation of Frank-Condon excitation processes

Table S5 – Main excitation transitions of **1** in the ground state (TD-B2PLYP for singlets and TDA-B2PLYP for triplets). H – HOMO, L – LUMO

State	Wavelength, nm	Energy, eV	Oscillator strength	Transition	Contribution
S_1	369.6	3.355	0.2190	H → L	0.9769
S_2	301	4.119	0.0335	H-2 → L H-1 → L H-1 → L+1 H → L+1	0.0159 0.3199 0.0186 0.6189
S_3	299.9	4.134	0.1514	H-3 → L H-2 → L H-1 → L H → L+1	0.0134 0.0132 0.6064 0.3251
S_4	289.8	4.278	0.0423	H-3 → L H-2 → L H → L+2 H → L+3 H → L+6	0.0729 0.4401 0.3613 0.0389 0.0253
S_5	286.6	4.326	0.0333	H-3 → L H-2 → L H-1 → L+2 H → L+2 H → L+3	0.1453 0.1895 0.0153 0.5661 0.0376
S_6	278.7	4.449	0.1025	H-3 → L H-2 → L H-2 → L+3 H-1 → L H-1 → L+3 H → L+2 H → L+3 H → L+4 H → L+6	0.5143 0.1905 0.0155 0.0302 0.0179 0.0242 0.0744 0.0642 0.0380
S_7	269.9	4.593	0.1060	H-3 → L H-2 → L H-1 → L+4 H → L+4 H → L+5	0.0174 0.0490 0.0194 0.8372 0.0108
S_8	264	4.696	0.0020	H-3 → L H-2 → L H-1 → L+1 H → L+3 H → L+5 H → L+6	0.1181 0.0178 0.0119 0.7404 0.0488 0.0223
S_9	260.9	4.752	0.0012	H-1 → L+5 H → L+3 H → L+5	0.0358 0.0481 0.8518

S_{10}	253	4.900	0.1188	H-4 → L+2 H-2 → L+1 H-1 → L+1 H → L+1 H → L+3 H → L+4	0.0105 0.0841 0.8296 0.0182 0.0124 0.0111
T_1	451.5	2.746	-	H-1 → L H → L H → L+7	0.0982 0.8505 0.0111
T_2	368.8	3.361	-	H-8 → L+7 H-3 → L H-3 → L+3 H-2 → L H-2 → L+6 H-1 → L H → L H → L+6 H → L+7	0.0170 0.0827 0.0136 0.4944 0.0126 0.2325 0.0562 0.0119 0.0152
T_3	339.1	3.656	-	H-6 → L+5 H-5 → L+2 H-5 → L+5 H-4 → L+4 H-2 → L+1 H-1 → L+1 H-1 → L+2 H-1 → L+4 H → L+1 H → L+2 H → L+4	0.0125 0.0479 0.0102 0.0364 0.0197 0.1910 0.0118 0.0118 0.5257 0.0288 0.0161
T_4	334.1	3.711	-	H-10 → L+3 H-8 → L H-3 → L H-3 → L+3 H-3 → L+7 H-2 → L H-2 → L+6 H → L+2 H → L+6	0.0133 0.0176 0.5935 0.0663 0.0309 0.1244 0.0190 0.0110 0.0425
T_5	324.3	3.823	-	H-6 → L+2 H-6 → L+4 H-5 → L+1 H-5 → L+5 H-4 → L+1 H-4 → L+5 H-3 → L H-2 → L H-2 → L+6 H-1 → L H-1 → L+2 H-1 → L+3 H-1 → L+4 H → L+1 H → L+2 H → L+4 H → L+6	0.0245 0.0163 0.0534 0.0182 0.0496 0.0117 0.0529 0.0103 0.0222 0.0311 0.0863 0.0104 0.0153 0.0432 0.3006 0.0850 0.0558
T_6	317.7	3.902	-	H-8 → L H-6 → L+2 H-6 → L+4 H-5 → L+1	0.0133 0.0189 0.0131 0.0340

				H-5 → L+5 H-4 → L+1 H-3 → L H-2 → L+2 H-2 → L+4 H-2 → L+6 H-1 → L H-1 → L+2 H-1 → L+4 H → L+2 H → L+3 H → L+6 H → L+7	0.0114 0.0365 0.0680 0.0209 0.0144 0.0518 0.0956 0.0541 0.0204 0.0150 0.1014 0.2872 0.0111
T_7	310.6	3.992	-	H-7 → L H-3 → L H-3 → L+3 H-2 → L H-1 → L H-1 → L+7 H → L H → L+3 H → L+6 H → L+7	0.0246 0.0175 0.0110 0.2540 0.4728 0.0109 0.0534 0.0143 0.0451 0.0136
T_8	298.4	4.155	-	H-10 → L H-10 → L+3 H-8 → L H-8 → L+3 H-3 → L H-3 → L+3 H-3 → L+6 H-2 → L H-2 → L+3 H-2 → L+7 H-1 → L+3 H-1 → L+7 H → L+2 H → L+3 H → L+6 H → L+7	0.0165 0.0158 0.0434 0.0234 0.0570 0.2745 0.0148 0.0117 0.0916 0.0326 0.0463 0.0305 0.0191 0.0730 0.1072 0.0309
T_9	294.4	4.212	-	H-9 → L+1 H-7 → L+1 H-6 → L+2 H-6 → L+4 H-6 → L+5 H-5 → L+1 H-5 → L+2 H-5 → L+5 H-4 → L+1 H-4 → L+4 H-2 → L+1 H-2 → L+3 H-1 → L+1 H → L+1 H → L+2 H → L+6	0.0236 0.0345 0.0488 0.0196 0.0956 0.0126 0.1085 0.0141 0.0554 0.0868 0.0168 0.0160 0.0259 0.2259 0.0688 0.0270
T_{10}	291.5	4.253	-	H-8 → L H-7 → L+4 H-6 → L+5 H-5 → L+2	0.0239 0.0156 0.0242 0.0182

				H-4 → L+1 H-4 → L+4 H-4 → L+5 H-2 → L+3 H-1 → L+2 H-1 → L+4 H → L+1 H → L+2 H → L+3 H → L+4 H → L+5	0.0321 0.0466 0.0359 0.0178 0.0117 0.0832 0.0339 0.2320 0.0686 0.1916 0.0119

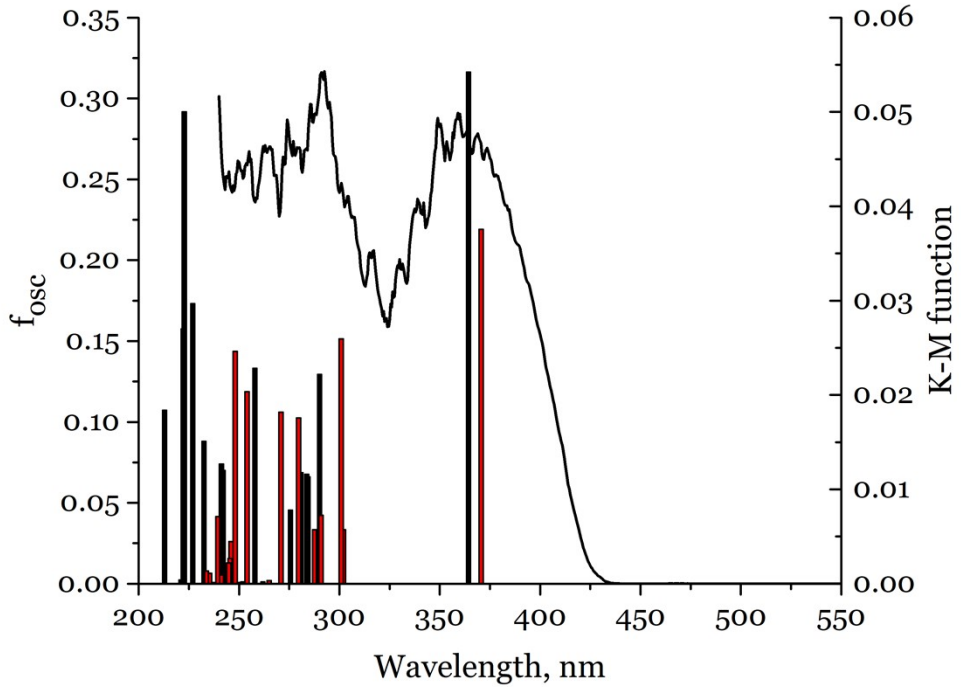


Figure S8 –Overlaid solid-state UV-Vis spectrum and calculated TD-DFT transitions for **1**, red bars – TD-PBE0, black bars – TD-B2PLYP levels

Table S6 – Main excitation transitions of **2** in the ground state (TD-B2PLYP for singlets and TDA-B2PLYP for triplets). H – HOMO, L – LUMO.

State	Wavelength, nm	Energy, eV	Oscillator strength	Transition	Contribution
S_1	350.8	3.534	0.5581	H-1 → L H-1 → L+1 H → L H → L+1	0.1162 0.1937 0.5680 0.0494
S_2	345.8	3.586	0.1478	H-1 → L H-1 → L+1 H → L H → L+1	0.1845 0.1868 0.0717 0.4893
S_3	295.4	4.197	0.0237	H-5 → L H-4 → L+1 H-3 → L H-2 → L H-2 → L+1 H-1 → L H-1 → L+2 H-1 → L+6 H → L+1 H → L+7	0.0128 0.1182 0.3343 0.0808 0.1682 0.0639 0.0216 0.0142 0.0289 0.0112

S_4	293.5	4.224	0.1877	H-5 → L H-4 → L H-4 → L+1 H-3 → L H-3 → L+1 H-2 → L H-2 → L+1 H-1 → L+1 H-1 → L+7 H → L+1 H → L+2 H → L+6	0.0208 0.0396 0.1202 0.1354 0.1397 0.1473 0.0924 0.0552 0.0125 0.0294 0.0477 0.0231
S_5	299.9	4.135	0.0354	H-6 → L H-6 → L+1 H-6 → L+8 H-5 → L H-4 → L+3 H-3 → L+1 H-2 → L+1 H-2 → L+3 H-1 → L H-1 → L+1 H-1 → L+3 H → L H → L+1 H → L+2 H → L+3	0.0144 0.2150 0.0154 0.0262 0.0120 0.0321 0.0153 0.0150 0.0261 0.2725 0.0302 0.0794 0.1301 0.0256 0.0149
S_6	292.5	4.238	0.0521	H-6 → L H-6 → L+1 H-5 → L H-5 → L+1 H-5 → L+9 H-4 → L H-3 → L+4 H-2 → L H-2 → L+4 H-1 → L H-1 → L+3 H-1 → L+4 H → L H → L+1 H → L+4	0.0109 0.0863 0.2954 0.0311 0.0166 0.0102 0.0181 0.0261 0.0162 0.1972 0.0121 0.0287 0.0663 0.0334 0.0340
S_7	292.6	4.237	0.0040	H-6 → L+1 H-5 → L H-5 → L+1 H-5 → L+9 H-4 → L H-3 → L H-3 → L+4 H-1 → L H-1 → L+1 H-1 → L+4 H-1 → L+7 H → L H → L+2 H → L+4 H → L+6 H → L+7	0.0491 0.2747 0.0145 0.0136 0.0100 0.0641 0.0192 0.1816 0.0213 0.0139 0.0102 0.1118 0.0363 0.0126 0.0149 0.0273
S_8	293.3	4.227	0.0125	H-6 → L	0.0182

				H-6 → L+1 H-6 → L+8 H-4 → L+1 H-4 → L+3 H-3 → L H-3 → L+1 H-2 → L+1 H-2 → L+3 H-1 → L H-1 → L+1 H-1 → L+3 H-1 → L+6 H → L+1 H → L+3 H → L+6	0.2395 0.0133 0.0181 0.0145 0.0135 0.0591 0.0258 0.0106 0.0937 0.1466 0.0215 0.0165 0.1940 0.0134 0.0180
S_9	275.1	4.507	0.1048	H-3 → L H-3 → L+1 H-2 → L H-2 → L+1 H-2 → L+2 H-2 → L+3 H-1 → L H-1 → L+1 H-1 → L+7 H → L H → L+2 H → L+6 H → L+7	0.0109 0.0341 0.0401 0.0719 0.0852 0.0121 0.0300 0.0222 0.0186 0.0446 0.4422 0.0281 0.0141
S_{10}	280.4	4.421	0.0139	H-12 → L+1 H-11 → L+1 H-10 → L+1 H-9 → L+1 H-6 → L+1 H-4 → L H-4 → L+1 H-2 → L+1 H-2 → L+2 H → L+2	0.0796 0.0129 0.0166 0.0606 0.0169 0.0144 0.2884 0.3034 0.0175 0.0465
T_1	415.8	2.982	-	H-8 → L+9 H-5 → L H-5 → L+4 H-3 → L H-2 → L H-1 → L H-1 → L+1 H → L H → L+1 H → L+7	0.0184 0.0217 0.0164 0.0273 0.0521 0.2861 0.0250 0.3779 0.0316 0.0104
T_2	408.6	3.034	-	H-10 → L+8 H-6 → L+1 H-6 → L+3 H-4 → L+1 H-3 → L+1 H-2 → L+1 H-1 → L H-1 → L+1 H → L H → L+1	0.0125 0.0213 0.0165 0.0264 0.0124 0.0728 0.0347 0.3696 0.0226 0.2588
T_3	342.9	3.616	-	H-6 → L+1	0.0411

				H-6 → L+3 H-4 → L H-4 → L+1 H-4 → L+6 H-3 → L+1 H-2 → L+1 H-1 → L+1 H-1 → L+8 H → L+1 H → L+6 H → L+8	0.0297 0.0151 0.2366 0.0108 0.0974 0.1039 0.0342 0.0273 0.1574 0.0115 0.0253
T_4	340	3.646	-	H-8 → L+9 H-5 → L H-5 → L+4 H-4 → L H-3 → L H-3 → L+1 H-3 → L+4 H-2 → L H-1 → L H-1 → L+9 H → L H → L+9	0.0128 0.0570 0.0490 0.0424 0.3422 0.0296 0.0108 0.0951 0.0199 0.0278 0.1225 0.0387
T_5	331.1	3.745	-	H-10 → L+2 H-9 → L+2 H-9 → L+3 H-9 → L+6 H-7 → L+5 H-6 → L+1 H-6 → L+3 H-4 → L+2 H-4 → L+3 H-4 → L+6 H-3 → L+2 H-2 → L+2 H-2 → L+3 H-2 → L+6 H → L+2	0.0131 0.0407 0.0114 0.0131 0.2247 0.0112 0.0162 0.0924 0.0205 0.0448 0.0122 0.2102 0.0354 0.0163 0.0527
T_6	327.7	3.784	-	H-14 → L+3 H-10 → L+1 H-9 → L+1 H-8 → L+1 H-7 → L+5 H-6 → L H-6 → L+1 H-6 → L+2 H-6 → L+3 H-6 → L+8 H-4 → L+2 H-4 → L+6 H-4 → L+8 H-4 → L+11 H-3 → L+6 H-2 → L+6 H-2 → L+8 H-1 → L+2 H-1 → L+6 H-1 → L+8 H → L+2	0.0162 0.0443 0.0271 0.0244 0.0292 0.0132 0.1078 0.0210 0.1131 0.0196 0.0539 0.0301 0.0104 0.0134 0.0225 0.0241 0.0160 0.0146 0.0257 0.0461 0.0152

				H → L+6 H → L+8 H → L+11	0.0482 0.0238 0.0113
T_7	325.6	3.808	-	H-13 → L+4 H-10 → L H-8 → L H-5 → L H-5 → L+1 H-5 → L+4 H-5 → L+9 H-3 → L H-3 → L+2 H-3 → L+7 H-3 → L+9 H-2 → L H-2 → L+9 H-1 → L+2 H-1 → L+7 H-1 → L+9 H → L+4 H → L+7 H → L+9	0.0208 0.0318 0.0725 0.1189 0.0112 0.1475 0.0201 0.0505 0.0141 0.0612 0.0402 0.0123 0.0207 0.0108 0.0309 0.0127 0.0115 0.0597 0.0102
T_8	299.5	4.140	-	H-6 → L H-6 → L+1 H-6 → L+3 H-6 → L+8 H-5 → L H-4 → L H-4 → L+1 H-4 → L+2 H-4 → L+6 H-3 → L+1 H-3 → L+7 H-2 → L H-2 → L+1 H-1 → L+1 H-1 → L+2 H-1 → L+6 H-1 → L+7 H-1 → L+8 H-1 → L+11 H → L+2 H → L+6 H → L+8	0.0151 0.1551 0.0657 0.0255 0.0385 0.0112 0.0730 0.0119 0.0214 0.0557 0.0115 0.0201 0.0328 0.0162 0.0170 0.0362 0.0193 0.0113 0.0186 0.0725 0.0834 0.0130
T_9	298.4	4.154	-	H-6 → L+1 H-6 → L+3 H-5 → L H-5 → L+1 H-5 → L+4 H-5 → L+9 H-4 → L+1 H-3 → L H-3 → L+2 H-3 → L+6 H-3 → L+7 H-2 → L H-2 → L+1 H-1 → L H-1 → L+2	0.0264 0.0106 0.1940 0.0227 0.0379 0.0205 0.0133 0.1015 0.0130 0.0139 0.0509 0.0223 0.0182 0.0115 0.0412

				H-1 → L+4 H-1 → L+6 H-1 → L+7 H → L+4 H → L+7 H → L+11	0.0165 0.0277 0.0386 0.0275 0.1072 0.0171
T_{10}	288.8	4.293	-	H-13 → L H-8 → L H-8 → L+4 H-6 → L+1 H-5 → L H-5 → L+1 H-5 → L+4 H-5 → L+7 H-3 → L+4 H-3 → L+9 H-2 → L+4 H-1 → L+4 H-1 → L+7 H-1 → L+9 H → L+4 H → L+6 H → L+7	0.0256 0.0101 0.0218 0.0173 0.2295 0.0170 0.1627 0.0128 0.0731 0.0148 0.0266 0.0275 0.0265 0.0113 0.0216 0.0106 0.0451

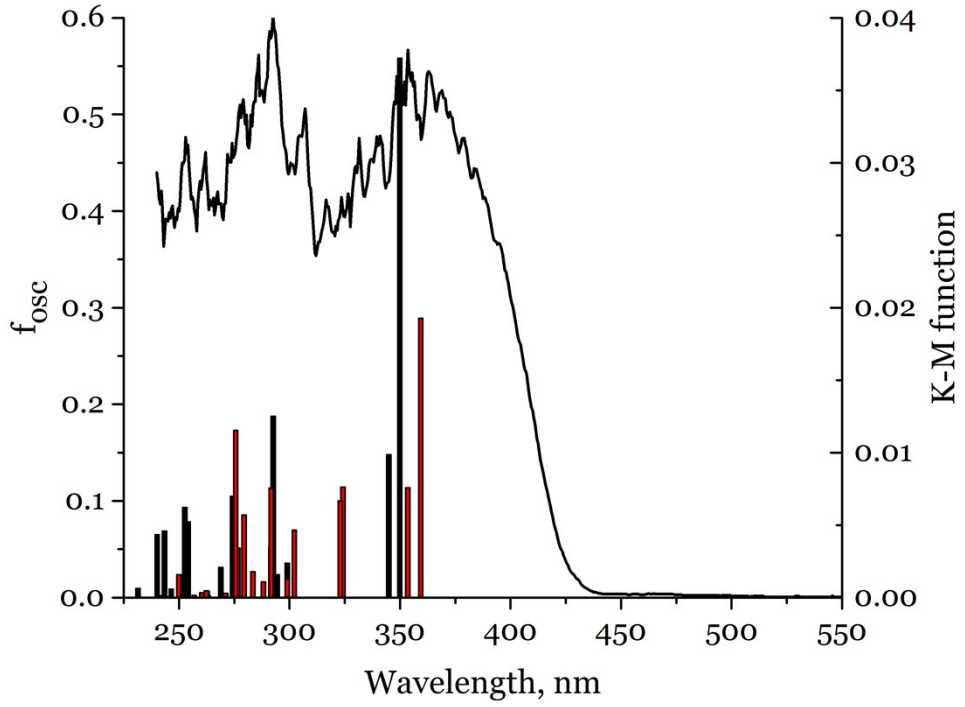


Figure S9 – Overlaid solid-state UV-Vis spectrum and calculated TD-DFT transitions for **2**, red bars – TD-PBE0, black bars – TD-B2PLYP levels.

Table S7 – Main excitation transitions of **3** in the ground state (TD-PBE0 for singlets and TDA-PBE0 for triplets). H – HOMO, L – LUMO.

State	Wavelength, nm	Energy, eV	Oscillator strength	Transition	Contribution
S_1	362.1	3.424	0.1135	H-2 → L H-1 → L	0.0960 0.2208

				H → L H → L+1	0.6086 0.0429
S_2	353.5	3.507	0.1585	H-1 → L H-1 → L+1 H → L H → L+1 H → L+2	0.0213 0.0304 0.0239 0.8476 0.0285
S_3	343.5	3.609	0.0273	H → L+1 H → L+2	0.0450 0.9173
S_4	331.8	3.737	0.0295	H-2 → L H-1 → L H → L	0.0798 0.5457 0.3469
S_5	325	3.815	0.0407	H-4 → L H-2 → L H-2 → L+1 H-1 → L H-1 → L+1	0.0157 0.2879 0.2405 0.0502 0.3445
S_6	322.8	3.841	0.0468	H-4 → L H-3 → L H-2 → L H-2 → L+1 H-2 → L+2 H-1 → L H-1 → L+1	0.0350 0.0113 0.4602 0.1198 0.0112 0.0970 0.2293
S_7	315.3	3.933	0.0685	H-2 → L+1 H-2 → L+2 H-1 → L+1 H-1 → L+2 H → L+1	0.2534 0.0101 0.1868 0.5053 0.0132
S_8	313.5	3.955	0.1290	H-3 → L+1 H-3 → L+2 H-2 → L+1 H-2 → L+2 H-1 → L+1 H-1 → L+2	0.1329 0.0242 0.1780 0.4044 0.0667 0.1523
S_9	306.2	4.049	0.0219	H-3 → L H-3 → L+1 H-3 → L+2 H-2 → L+2	0.0151 0.7079 0.0260 0.1885
S_{10}	302.9	4.093	0.0030	H-9 → L H-7 → L H-6 → L H-5 → L H-4 → L H-3 → L H-2 → L H-1 → L	0.0119 0.0135 0.0422 0.0231 0.5415 0.2405 0.0469 0.0360
T_1	433.2	2.862	-	H-5 → L+1 H-2 → L+1 H-1 → L+1 H-1 → L+2 H → L+1 H → L+2	0.0154 0.0148 0.0785 0.0596 0.5032 0.2326
T_2	430.1	2.882	-	H-7 → L H-2 → L H-1 → L H → L	0.0506 0.2705 0.3381 0.2558
T_3	418	2.966	-	H-6 → L+1 H-6 → L+2	0.0113 0.0134

				H-3 → L+1 H-3 → L+2 H-2 → L+1 H-2 → L+2 H-1 → L+1 H-1 → L+2 H → L+1 H → L+2	0.0281 0.0248 0.1853 0.2336 0.1515 0.1396 0.0258 0.0718
T_4	367.6	3.372	-	H-9 → L H-8 → L+4 H-7 → L H-4 → L H-2 → L H-1 → L H → L	0.1024 0.0125 0.5089 0.0356 0.0133 0.0457 0.0833
T_5	366.5	3.383	-	H-6 → L+1 H-6 → L+2 H-5 → L+1 H-5 → L+2 H-4 → L+1 H-4 → L+2 H-3 → L+1 H-1 → L+2 H → L+1 H → L+13	0.0122 0.0132 0.2846 0.1308 0.1607 0.0491 0.0317 0.0138 0.0982 0.0182
T_6	355.5	3.488	-	H-5 → L+1 H-4 → L+2 H-3 → L+1 H-3 → L+2 H-2 → L+1 H-2 → L+2 H → L+2	0.0438 0.0286 0.3225 0.3577 0.0342 0.0345 0.0225
T_7	348.3	3.559	-	H-5 → L+2 H-4 → L+2 H-3 → L+1 H-3 → L+2 H-1 → L+1 H-1 → L+2 H → L+1 H → L+2 H → L+3	0.0147 0.0187 0.0455 0.0208 0.0192 0.0310 0.2144 0.5165 0.0103
T_8	342.9	3.616	-	H-6 → L+1 H-6 → L+2 H-6 → L+15 H-5 → L+1 H-5 → L+2 H-4 → L+1 H-4 → L+2 H-3 → L+1 H-2 → L+1 H-2 → L+2 H-1 → L+1 H-1 → L+2 H → L+2	0.2373 0.1258 0.0102 0.0699 0.0230 0.0669 0.0319 0.0189 0.0870 0.0531 0.0599 0.0445 0.0101
T_9	337.2	3.677	-	H-19 → L H-9 → L H-9 → L+4 H-8 → L H-2 → L	0.0168 0.0382 0.0115 0.1841 0.0545

				H-2 → L+4 H-2 → L+6 H-1 → L H-1 → L+1 H-1 → L+4 H-1 → L+6 H → L H → L+3 H → L+4 H → L+6	0.0142 0.0150 0.0424 0.0332 0.0374 0.0206 0.2189 0.0341 0.0183 0.0220
T_{10}	335.2	3.698	-	H-10 → L H-9 → L H-8 → L H-4 → L H-1 → L H-1 → L+4 H-1 → L+6 H → L	0.0160 0.0470 0.0771 0.0108 0.2438 0.0140 0.0112 0.3946

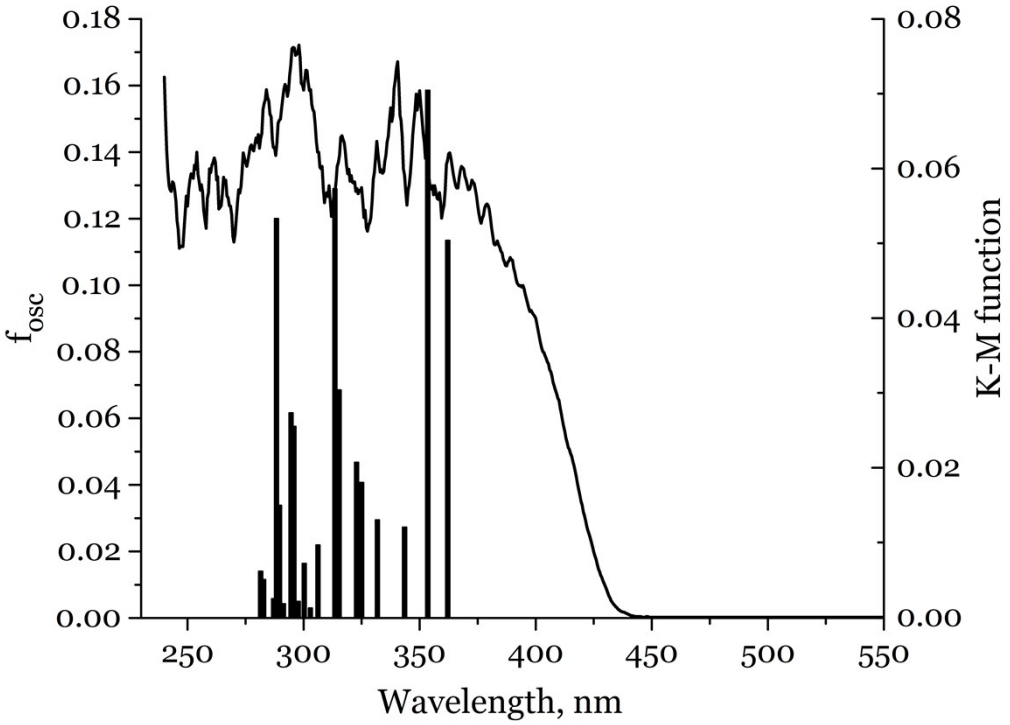


Figure S10 – Overlaid solid-state UV-Vis spectrum and calculated TD-DFT transitions for **3** (TD-PBE0 level).

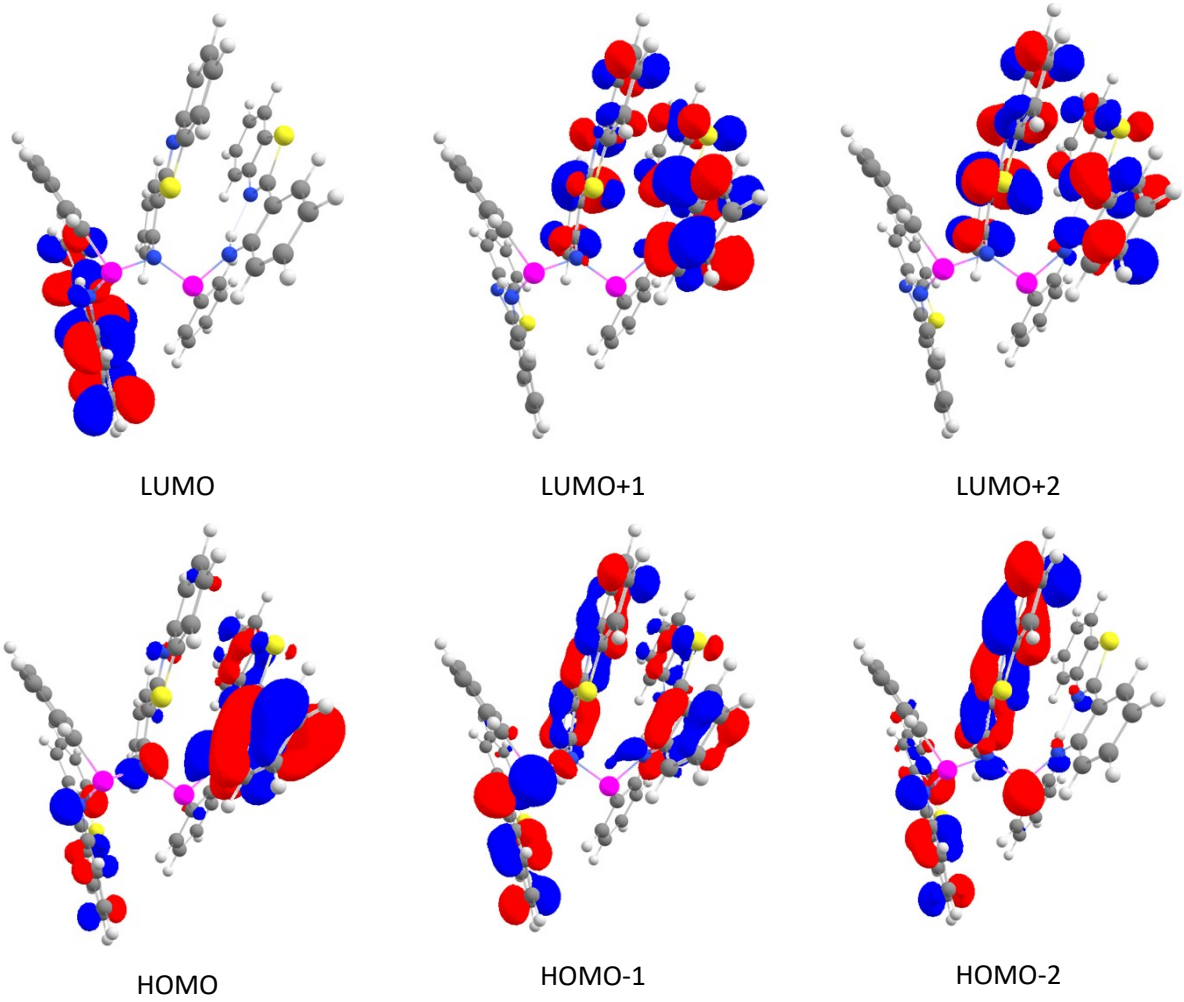


Figure S11 – Frontier orbitals of **3** (PBE0/def2-TZVP(-f), isovalue = 0.03)

Experimental photophysical properties

Table S8. CIE x,y chromacity coordinates of compounds **1–3** depending on the excitation wavelength λ_{Ex}, nm.

1			**2**			**3**		
λ_{Ex}	x	y	λ_{Ex}	x	y	λ_{Ex}	x	y
300	0.34	0.43	300	0.18	0.19	340	0.37	0.46
340	0.39	0.49	375	0.2	0.17	375	0.31	0.37
380	0.29	0.32	400	0.19	0.16	400	0.21	0.23
400	0.23	0.22	420	0.21	0.21	420	0.20	0.25
420	0.24	0.27						

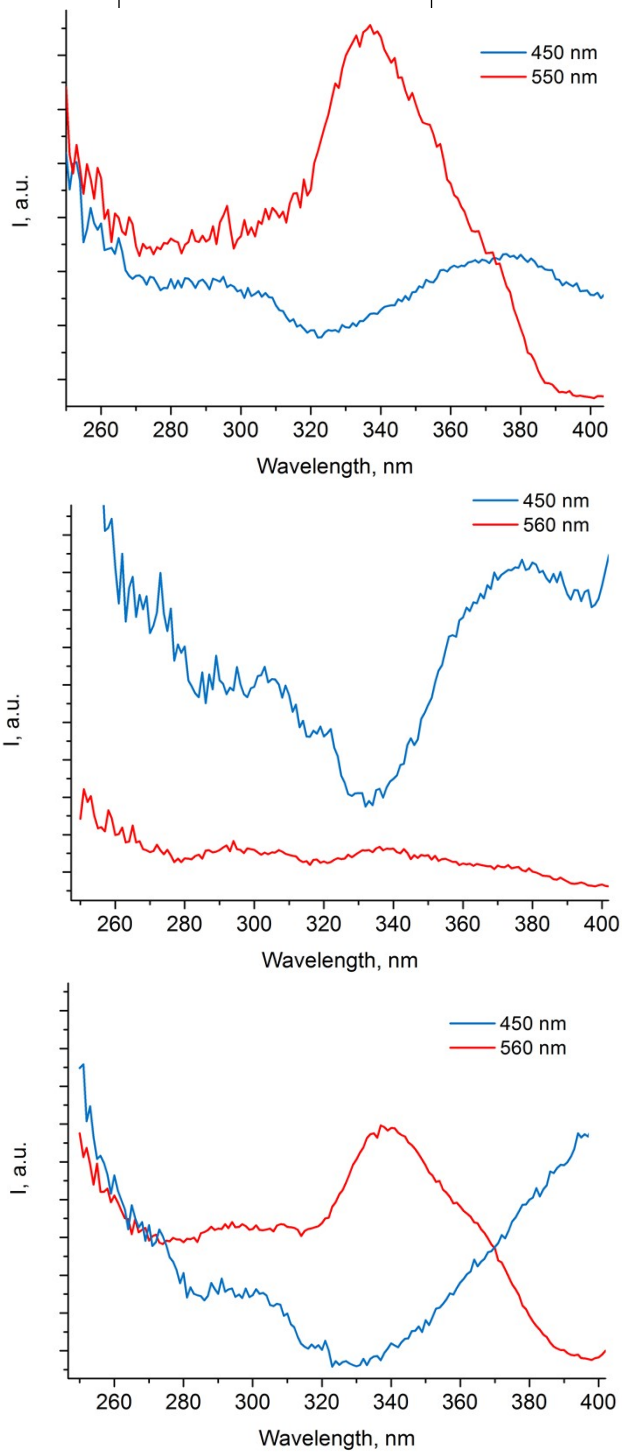


Figure S12. Excitation spectra of solid compounds **1**–**3** for the emission at 450 and 550 nm

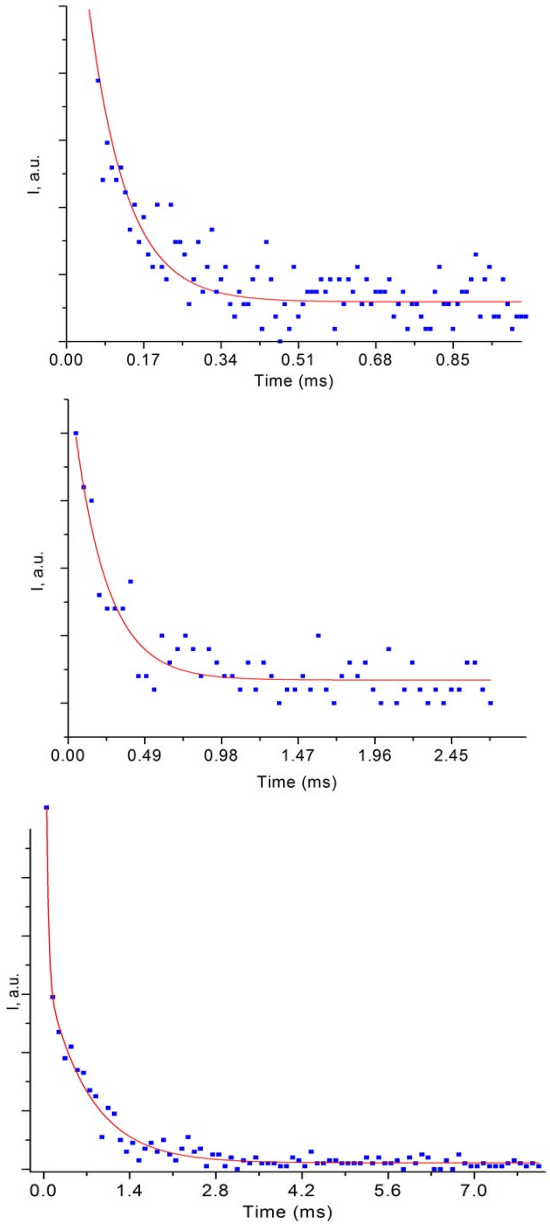


Figure S13. Decay kinetics data for solid compounds **1**–**3** at λ_{Em} of 550 nm. Blue dots – experiment, red line – fitting.

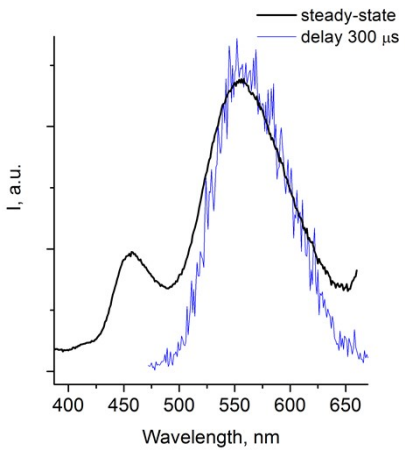


Figure S14. Steady-state (black line) and delayed (300 μs delay, blue line) emission spectra for solid compound **3**.

DFT calculation of relaxation processes

Table S9 - Selected geometry parameters for optimized excited states of **1**. LE – locally excited state, TICT – "twisted" intramolecular charge transfer state.

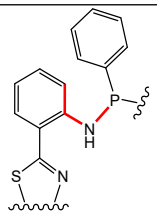
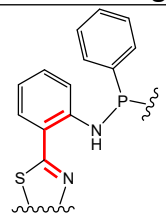
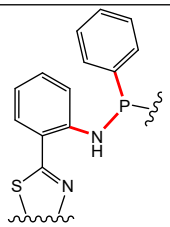
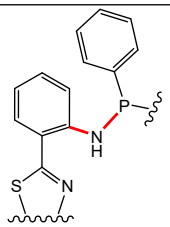
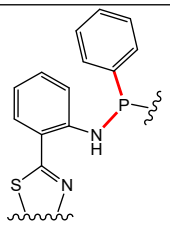
					
	CCNP, deg	NCCC, deg	CNPC, deg	CNP, deg	NPC, deg
^{1}LE	2.53	10.61	76.62, 179.12	129.16	97.08, 102.76
^{1}TICT	66.60	8.98	88.78, 149.32	117.19	109.62, 111.85
^{3}LE (T_1)	11.74	1.35	86.02, 170.25	127.59	95.29, 102.70
^{3}TICT (T_1)	56.86	3.66	42.80, 157.19	121.60	102.14, 111.11
^{3}LE (T_2)	2.93	0.78	92.77, 164.53	128.33	96.35, 102.06
^{3}TICT (T_2)	50.85	6.54	62.50, 169.74	120.00	98.68, 107.24

Table S10 - Selected geometry parameters for optimized excited states of **2**. LE – locally excited state, TICT – "twisted" intramolecular charge transfer state.

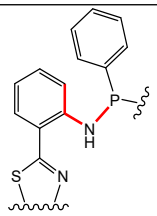
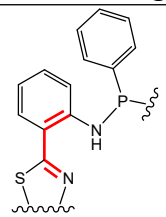
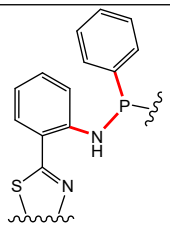
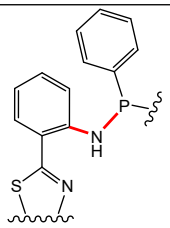
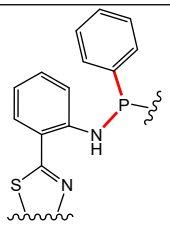
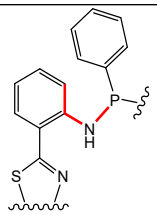
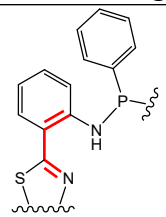
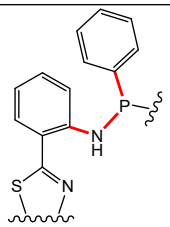
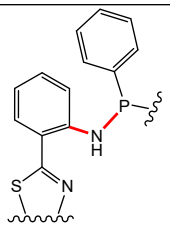
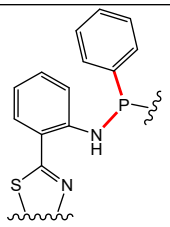
					
	CCNP, deg	NCCC, deg	CNPC, deg	CNP, deg	NPC, deg
^{1}LE	1.13, 21.75	0.65, 1.01	72.93, 163.97	126.04, 132.36	98.50, 101.83
^{1}TICT	46.22, 57.09	2.14, 6.81	102.17, 160.76	119.75, 120.12	104.85, 110.36
^{3}LE (T_1)	27.76, 28.74	0.81, 18.86	68.95, 178.32	125.99, 130.00	95.93, 106.16
^{3}TICT (T_1)	35.26, 56.86	5.79, 10.89	79.17, 163.19	120.16, 123.68	96.55, 103.53

Table S11 - Selected geometry parameters for optimized excited states of **3**. LE – locally excited state, TICT – "twisted" intramolecular charge transfer state.

					
	CCNP, deg	NCCC, deg	CNPC, deg	CNP, deg	NPC, deg
^{1}LE	0.65,	4.58,	39.77, 49.68,	120.85,	97.94, 98.74,

	4.63, 74.70, 86.81	2.64, 161.30	139.07, 142.25	123.18, 126.25, 126.45	102.82, 103.23
[1]TICT	17.44, 62.58, 78.07, 81.86	3.71, 7.48, 172.78	28.97, 44.60, 155.73, 163.65	118.34, 123.70, 125.57, 126.01	98.81, 99.26, 105.12, 108.22,
^{3}LE (T_1)	2.38, 3.45, 81.60, 82.67,	4.16, 18.57, 179.91	33.90, 62.09, 125.31, 133.31	119.05, 124.49, 126.48, 126.78	95.78, 100.04, 101.36, 105.18
^{3}TICT (T_1)	22.83, 32.52, 75.70, 83.31	12.34, 23.99, 176.13,	39.47, 42.93, 146.95, 171.03	120.85, 122.75, 123.09, 125.13	96.26, 98.50, 101.90, 102.05

Table S12 – 0-0 transition wavelengths and energies, calculated by B2PLYP for **1** and **2** and by PBE0 for **3** over equilibrium excited state geometries.

State character	S_1		T_1		T_2	
Compound **1**						
LE	431.5 nm	2.874 eV	531.2 nm (546.9)[1]	2.334 eV (2.267)[1]	425.5 nm	2.914 eV
TICT	701.9 nm	1.767 eV	497.3 nm	2.493 eV	401.0 nm	3.092 eV
Compound **2**						
LE	393.0 nm	3.155 eV	547.8 nm	2.263 eV	–[2]	–[2]
TICT	697.1 nm	1.779 eV	547.4 nm	2.265 eV	–[2]	–[2]
Compound **3**						
LE	408.7 nm	3.034 eV	557.7 nm	2.223 eV	–[2]	–[2]
TICT	700.8 nm	1.769 eV	609.7[1] nm	2.034[1] eV	–[2]	–[2]

[1]Geometry optimized by UPBE0/def2-TZVP(-f)

[2]No data

Spin-orbital coupling matrix coefficients

Table S13 - Selected SOCME values for **1** (TDA-PBE0, RI-SOMF(1x))

Transition	SOC, cm^{-1}	Transition	SOC, cm^{-1}	Transition	SOC, cm^{-1}
$S_0 \rightarrow T_1$	2.62	$S_7 \rightarrow T_4$	2.05	$S_8 \rightarrow T_7$	4.18
$S_2 \rightarrow T_1$	2.90	$S_0 \rightarrow T_5$	11.80	$S_9 \rightarrow T_7$	4.04
$S_3 \rightarrow T_1$	5.31	$S_1 \rightarrow T_5$	1.42	$S_{10} \rightarrow T_7$	2.38
$S_6 \rightarrow T_1$	1.25	$S_2 \rightarrow T_5$	4.07	$S_0 \rightarrow T_8$	3.36
$S_7 \rightarrow T_1$	1.71	$S_3 \rightarrow T_5$	3.39	$S_1 \rightarrow T_8$	1.59
$S_8 \rightarrow T_1$	1.41	$S_4 \rightarrow T_5$	2.69	$S_2 \rightarrow T_8$	2.56
$S_9 \rightarrow T_1$	1.37	$S_5 \rightarrow T_5$	1.47	$S_3 \rightarrow T_8$	1.72
$S_0 \rightarrow T_2$	2.04	$S_9 \rightarrow T_5$	1.34	$S_7 \rightarrow T_8$	1.01
$S_1 \rightarrow T_2$	1.16	$S_{10} \rightarrow T_5$	1.69	$S_8 \rightarrow T_8$	2.58
$S_3 \rightarrow T_2$	1.28	$S_0 \rightarrow T_6$	8.34	$S_0 \rightarrow T_9$	12.22
$S_0 \rightarrow T_3$	32.59	$S_1 \rightarrow T_6$	2.16	$S_1 \rightarrow T_9$	1.17
$S_1 \rightarrow T_3$	2.32	$S_2 \rightarrow T_6$	2.62	$S_2 \rightarrow T_9$	2.05
$S_2 \rightarrow T_3$	2.36	$S_3 \rightarrow T_6$	2.77	$S_4 \rightarrow T_9$	2.90
$S_4 \rightarrow T_3$	3.44	$S_4 \rightarrow T_6$	1.51	$S_6 \rightarrow T_9$	1.01
$S_6 \rightarrow T_3$	1.35	$S_5 \rightarrow T_6$	3.47	$S_8 \rightarrow T_9$	3.12
$S_7 \rightarrow T_3$	1.56	$S_8 \rightarrow T_6$	1.62	$S_9 \rightarrow T_9$	1.26
$S_8 \rightarrow T_3$	4.51	$S_9 \rightarrow T_6$	1.20	$S_{10} \rightarrow T_9$	3.86
$S_9 \rightarrow T_3$	1.58	$S_0 \rightarrow T_7$	18.67	$S_0 \rightarrow T_{10}$	15.95
$S_{10} \rightarrow T_3$	3.05	$S_1 \rightarrow T_7$	7.29	$S_1 \rightarrow T_{10}$	1.29
$S_0 \rightarrow T_4$	3.51	$S_3 \rightarrow T_7$	5.07	$S_2 \rightarrow T_{10}$	3.17
$S_1 \rightarrow T_4$	2.24	$S_4 \rightarrow T_7$	4.25	$S_4 \rightarrow T_{10}$	1.54
$S_2 \rightarrow T_4$	4.19	$S_5 \rightarrow T_7$	10.24	$S_6 \rightarrow T_{10}$	1.30
$S_3 \rightarrow T_4$	8.37	$S_6 \rightarrow T_7$	2.91	$S_8 \rightarrow T_{10}$	1.12
$S_6 \rightarrow T_4$	1.95				

Table S14 - Selected SOCME values for **2** (TDA-PBE0, RI-SOMF(1x))

Transition	SOC, cm^{-1}	Transition	SOC, cm^{-1}	Transition	SOC, cm^{-1}
$S_0 \rightarrow T_1$	1.56	$S_6 \rightarrow T_4$	3.09	$S_8 \rightarrow T_7$	1.61
$S_1 \rightarrow T_1$	1.12	$S_0 \rightarrow T_5$	11.95	$S_9 \rightarrow T_7$	1.00
$S_2 \rightarrow T_1$	2.17	$S_1 \rightarrow T_5$	1.91	$S_{10} \rightarrow T_7$	1.07
$S_4 \rightarrow T_1$	3.85	$S_2 \rightarrow T_5$	1.42	$S_0 \rightarrow T_8$	11.98
$S_5 \rightarrow T_1$	1.42	$S_3 \rightarrow T_5$	1.09	$S_1 \rightarrow T_8$	2.20
$S_6 \rightarrow T_1$	2.44	$S_4 \rightarrow T_5$	3.63	$S_4 \rightarrow T_8$	1.29
$S_0 \rightarrow T_2$	1.47	$S_5 \rightarrow T_5$	5.40	$S_5 \rightarrow T_8$	4.09
$S_1 \rightarrow T_2$	1.23	$S_6 \rightarrow T_5$	3.11	$S_6 \rightarrow T_8$	1.91
$S_3 \rightarrow T_2$	3.50	$S_7 \rightarrow T_5$	1.17	$S_8 \rightarrow T_8$	3.17
$S_5 \rightarrow T_2$	8.03	$S_0 \rightarrow T_6$	6.33	$S_0 \rightarrow T_9$	10.12
$S_6 \rightarrow T_2$	3.52	$S_2 \rightarrow T_6$	1.79	$S_1 \rightarrow T_9$	1.20
$S_7 \rightarrow T_2$	1.27	$S_3 \rightarrow T_6$	1.05	$S_2 \rightarrow T_9$	2.51
$S_8 \rightarrow T_2$	2.89	$S_4 \rightarrow T_6$	2.52	$S_4 \rightarrow T_9$	1.17
$S_{10} \rightarrow T_2$	2.00	$S_5 \rightarrow T_6$	5.20	$S_5 \rightarrow T_9$	1.06

$S_0 \rightarrow T_3$	3.56	$S_6 \rightarrow T_6$	1.14	$S_6 \rightarrow T_9$	3.38
$S_2 \rightarrow T_3$	1.18	$S_8 \rightarrow T_6$	1.54	$S_8 \rightarrow T_9$	1.47
$S_3 \rightarrow T_3$	2.20	$S_0 \rightarrow T_7$	10.84	$S_9 \rightarrow T_9$	2.21
$S_5 \rightarrow T_3$	1.61	$S_1 \rightarrow T_7$	4.45	$S_0 \rightarrow T_{10}$	6.51
$S_8 \rightarrow T_3$	1.15	$S_3 \rightarrow T_7$	1.91	$S_2 \rightarrow T_{10}$	2.79
$S_9 \rightarrow T_3$	2.37	$S_4 \rightarrow T_7$	1.07	$S_5 \rightarrow T_{10}$	3.86
$S_0 \rightarrow T_4$	3.04	$S_5 \rightarrow T_7$	5.65	$S_7 \rightarrow T_{10}$	1.21
$S_4 \rightarrow T_4$	1.68	$S_6 \rightarrow T_7$	6.99	$S_8 \rightarrow T_{10}$	1.34
$S_5 \rightarrow T_4$	1.40	$S_7 \rightarrow T_7$	2.51	$S_9 \rightarrow T_{10}$	1.37

Table S15 - Selected SOCME values for **3** (TDA-PBE0, RI-SOMF(1x))

Transition	SOC, cm^{-1}	Transition	SOC, cm^{-1}	Transition	SOC, cm^{-1}
$S_5 \rightarrow T_1$	1.46	$S_6 \rightarrow T_4$	1.69	$S_5 \rightarrow T_8$	2.07
$S_6 \rightarrow T_1$	1.35	$S_{10} \rightarrow T_4$	1.74	$S_6 \rightarrow T_8$	2.04
$S_7 \rightarrow T_1$	1.80	$S_0 \rightarrow T_5$	1.56	$S_7 \rightarrow T_8$	1.79
$S_8 \rightarrow T_1$	1.53	$S_8 \rightarrow T_5$	1.37	$S_8 \rightarrow T_8$	1.41
$S_9 \rightarrow T_1$	4.06	$S_9 \rightarrow T_5$	1.07	$S_9 \rightarrow T_8$	3.79
$S_1 \rightarrow T_2$	1.19	$S_0 \rightarrow T_6$	1.73	$S_0 \rightarrow T_9$	2.26
$S_4 \rightarrow T_2$	3.08	$S_1 \rightarrow T_6$	1.19	$S_1 \rightarrow T_9$	1.70
$S_5 \rightarrow T_2$	3.38	$S_2 \rightarrow T_6$	4.25	$S_4 \rightarrow T_9$	1.41
$S_6 \rightarrow T_2$	2.94	$S_3 \rightarrow T_6$	3.35	$S_5 \rightarrow T_9$	2.78
$S_{10} \rightarrow T_2$	6.77	$S_6 \rightarrow T_6$	0.93	$S_6 \rightarrow T_9$	2.66
$S_0 \rightarrow T_3$	0.94	$S_7 \rightarrow T_6$	3.71	$S_{10} \rightarrow T_9$	5.63
$S_7 \rightarrow T_3$	2.13	$S_0 \rightarrow T_7$	3.13	$S_0 \rightarrow T_{10}$	4.01
$S_9 \rightarrow T_3$	1.16	$S_3 \rightarrow T_7$	1.04	$S_1 \rightarrow T_{10}$	3.97
$S_0 \rightarrow T_4$	4.31	$S_7 \rightarrow T_7$	2.88	$S_4 \rightarrow T_{10}$	1.29
$S_1 \rightarrow T_4$	2.08	$S_8 \rightarrow T_7$	4.84	$S_5 \rightarrow T_{10}$	2.23
$S_4 \rightarrow T_4$	0.93	$S_9 \rightarrow T_7$	2.16	$S_6 \rightarrow T_{10}$	1.54
$S_5 \rightarrow T_4$	2.01	$S_0 \rightarrow T_8$	1.17	$S_{10} \rightarrow T_{10}$	2.53

Single-crystal X-Ray diffraction data

Table S16. Crystal data and structure refinement for compounds **1**–**3**.

Identification code	**1**	**2**	**3**
Empirical formula	$C_{25}H_{19}N_2PS$	$C_{32}H_{23}N_4PS_2$	$C_{51}H_{36}N_6P_2S_3$
Formula weight	410.45	558.63	890.98
Temperature/K	150(2)	150(2)	150(2)
Space group	$P2_1/n$	$P2_1/c$	P–1
a/Å	9.1649(2)	11.8294(3)	11.3435(2)
b/Å	21.8384(4)	28.4993(8)	11.9478(2)
c/Å	10.3694(2)	7.9989(2)	17.8044(4)
α/°	90	90	77.3170(10)
β/°	101.1510(10)	100.2360(10)	88.6900(10)
γ/°	90	90	64.310(2)
Volume/Å^3	2036.22(7)	2653.75(12)	2114.26(8)
Z	4	4	2
ρ_{calc}g/cm^3	1.339	1.398	1.400
μ/mm^{-1}	0.252	0.292	0.297
F(000)	856.0	1160.0	924.0
Crystal size/mm^3	0.13 × 0.1 × 0.07	0.15 × 0.13 × 0.08	0.16 × 0.13 × 0.1
Crystal colour	pale yellow	colourless	pale yellow
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.73 to 57.428	4.518 to 55.788	4.178 to 52.764
Index ranges	-12 ≤ h ≤ 12, -29 ≤ k ≤ 29, -14 ≤ l ≤ 14	-15 ≤ h ≤ 15, -37 ≤ k ≤ 37, -10 ≤ l ≤ 10	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -22 ≤ l ≤ 22
Reflections collected	24167	33626	25570
Independent reflections	5269 [R_{int} = 0.0326, R_{sigma} = 0.0287]	6348 [R_{int} = 0.0379, R_{sigma} = 0.0288]	8605 [R_{int} = 0.0330, R_{sigma} = 0.0401]
Data/restraints/parameters	5269/1/265	6348/2/358	8605/178/647
Goodness-of-fit on F^2	1.033	1.039	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0367, wR_2 = 0.0923	R_1 = 0.0343, wR_2 = 0.0843	R_1 = 0.0387, wR_2 = 0.0889
Final R indexes [all data]	R_1 = 0.0460, wR_2 = 0.0985	R_1 = 0.0421, wR_2 = 0.0898	R_1 = 0.0497, wR_2 = 0.0966
Largest diff. peak/hole / e Å^{-3}	0.32/-0.28	0.32/-0.29	0.33/-0.33