Electronic Supplementary Information

Excitation wavelength dependent emission of silver(I) complexes with a pyrimidine ligand

Nikita A. Shekhovtsov,*[a,b] Katerina A. Vinogradova,*[a,b] Alexei S. Berezin,[a] Taisiya S. Sukhikh,[a] Viktor P. Krivopalov,[c] Elena B. Nikolaenkova[c] and Mark B. Bushuev*[a,b]

[a] Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 3, Acad. Lavrentiev Ave., Novosibirsk, 630090, Russia, E-mail addresses: shna1998@mail.ru (N. A. Shekhovtsov), kiossarin@mail.ru (K. A. Vinogradova), bushuev@niic.nsc.ru (M. B. Bushuev); Fax: +7 383 330 94 89; Tel: +7 383 316 51 43.

[b] Novosibirsk State University, 2, Pirogova str., Novosibirsk, 630090, Russia.

[c] N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences, 9, Acad. Lavrentiev Ave., Novosibirsk, 630090, Russia.

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Synthesis

General

The ligand 2-amino-4-phenyl-6-methylpyrimidine (L) was synthesized using reported procedure,[1] all other reagents and solvents were commercially available. Ethanol was distilled prior to use. Elemental analysis (C, H, and N) was performed on a Carlo–Erba analyzer using a standard technique. The XPRD analysis of samples was performed on a Shimadzu XRD-7000 diffractometer (Cu-Kα radiation).

Synthesis of $[Ag_3L_2(H_2O)_{0.55}(NO_3)_3]_n$ (1)

A warm solution of $AgNO_3$ (0.450 mmol, 76.7 mg) in 3 ml of EtOH/MeCN (2:1) was added to a warm solution of L (0.300 mmol, 55.5 mg) in 3 ml of MeCN/$CHCl_3$ (2:1). The resulting mixture was transparent; nothing precipitated. This mixture was heated and concentrated to 0.5 ml. After that it was cooled at room temperature. Suddenly, a white powder appeared. The precipitate was filtered off, washed with 2 ml of MeCN/EtOH (1:1) and dried in ambient air. Yield: 87.9 mg (66 %). Anal. calc. for $Ag_3C_{22}N_9H_{23.1}O_{9.55}$, %: C, 29.7; H, 2.6; N, 14.2. Found, %: C, 30.0; H, 2.8; N, 14.3.
Colorless transparent single crystals of **1** were obtained by slow crystallization of a solution containing $AgNO_3$ (0.0810 mmol, 13.8 mg) and L (0.0540 mmol, 10.0 mg) in 3 ml of EtOH/MeCN /$CHCl_3$ (1:1:1) at room temperature for three months.

Synthesis of $[Ag_2L_2(PPh_3)_2(NO_3)_2]$ (2)

A solution of L (0.270 mmol, 50.0 mg) and PPh_3 (0.270 mmol, 70.9 mg) in 2.5 ml of $CHCl_3$ was slowly added to a solution of $AgNO_3$ (0.270 mmol, 45.9 mg) in 1 ml of MeCN. The resulting mixture was transparent; nothing precipitated. This mixture was concentrated to 0.5 ml. After a week of crystallization, large colorless crystals appeared in this solution. The crystals were filtered off, washed with 2 ml of MeCN and dried in ambient air. Yield: 44.4 mg (27 %). Anal. calc. for $AgC_{29}N_4H_{26}PO_3$, %: C, 56.4; H, 4.2; N, 9.1. Found, %: C, 56.4; H, 4.2; N, 9.1.

X-Ray diffraction

Single-crystal XRD data for the compound **1** were collected a Bruker Apex DUO diffractometer equipped with a 4K CCD area detector using the graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 298 K. The ϕ- and ω-scan techniques were employed to measure intensities. Absorption correction was applied with the use of the SADABS program.[2] The crystal structure was solved using the SHELXT[3] and was refined using SHELXL[4] programs with OLEX2 GUI.[5] Atomic displacement parameters for non-hydrogen atoms were refined anisotropically. One nitrate was disordered over two positions as bridging/terminate ligand with the corresponding refined occupancies of 45/55%. DFIX, DANG, SIMU and ISOR restraints were used. Fourier difference map revealed the presence of a partially occupied H_2O ligand, which equalizes coordination numbers of Ag atoms with disordered bridging and terminal nitrates. Thus, the occupancy of O atom of the aqua ligand was refined together with that of the terminal nitrate. Hydrogens of the aqua ligand were not located but included in the final formula of the compound.

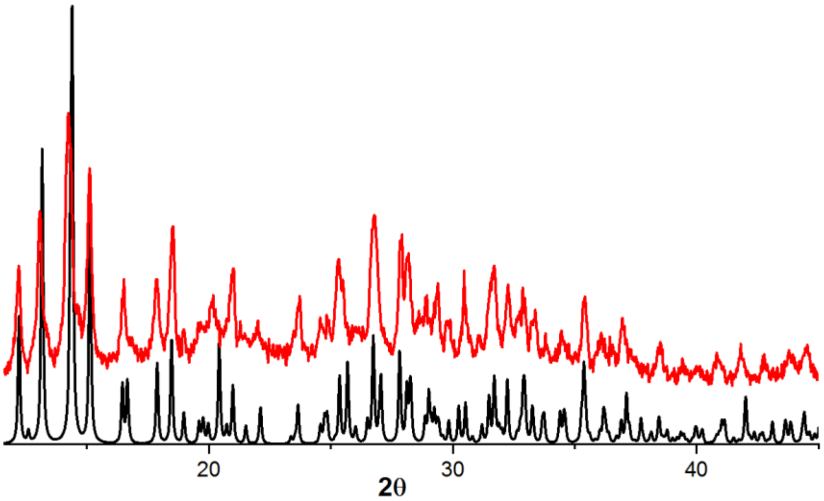


Fig. S1. PXRD pattern for the complex **1**. Red curve is an experimental powder diffractogram (293 K), black one is a theoretical diffractogram calculated from single X-ray data (298 K).

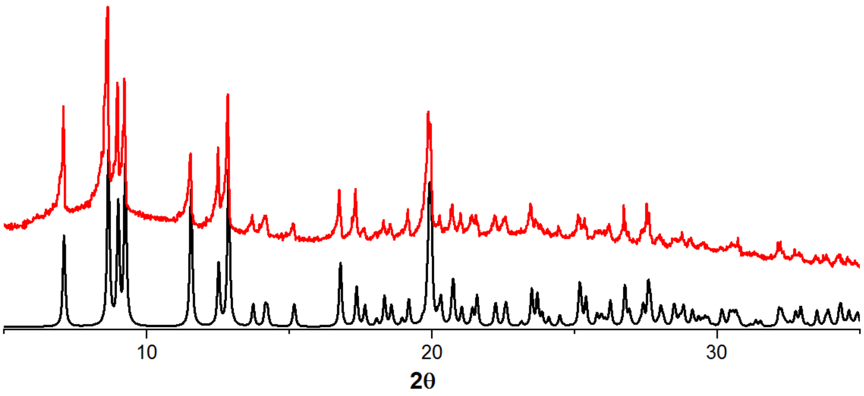


Fig. S2. PXRD pattern for the complex **2**. Red curve is an experimental powder diffractogram (293 K), black one is a theoretical diffractogram calculated from single X-ray data (298 K).

Table S1. Crystallographic data of the compounds.

Compound	**1**	**2**
Empirical formula	$C_{22}H_{23.1}Ag_3N_9O_{9.55}$	$C_{29}H_{26}AgN_4O_3P$
Formula weight	889.82	617.38
Space group	*Pc*	*P*-1
a/Å	10.0066(8)	9.8657(3)
b/Å	10.6023(8)	11.0186(3)
c/Å	14.1784(11)	13.7663(4)
α/°	90	67.9270(10)
β/°	98.056(3)	75.6170(10)
γ/°	90	83.3680(10)
Volume/Å^3	1489.4(2)	1342.92(7)
Z	2	2
ρ_{calc}g/cm^3	1.984	1.527
μ/mm^{-1}	2.019	0.848
F(000)	871.0	628.0
2Θ range for data collection/°	3.842 to 51.5	4.764 to 54.25
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 12$, $-11 \le l \le 17$	$-12 \le h \le 11$, $-13 \le k \le 14$, $-17 \le l \le 17$
Reflections collected	12392	11320
Independent reflections	4578 [R_{int} = 0.0232, R_σ = 0.0321]	5790 [R_{int} = 0.0330, R_{sigma} = 0.0372]
Restraints/parameters	158/436	0/344
Goodness-of-fit on F^2	1.064	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0474, wR_2 = 0.1223	R_1 = 0.0244, wR_2 = 0.0642
Final R indexes [all data]	R_1 = 0.0582, wR_2 = 0.1295	R_1 = 0.0274, wR_2 = 0.0665
Largest diff. peak/hole / e Å^{-3}	0.80/-1.01	0.30/-0.51
Flack parameter	0.040(14)	

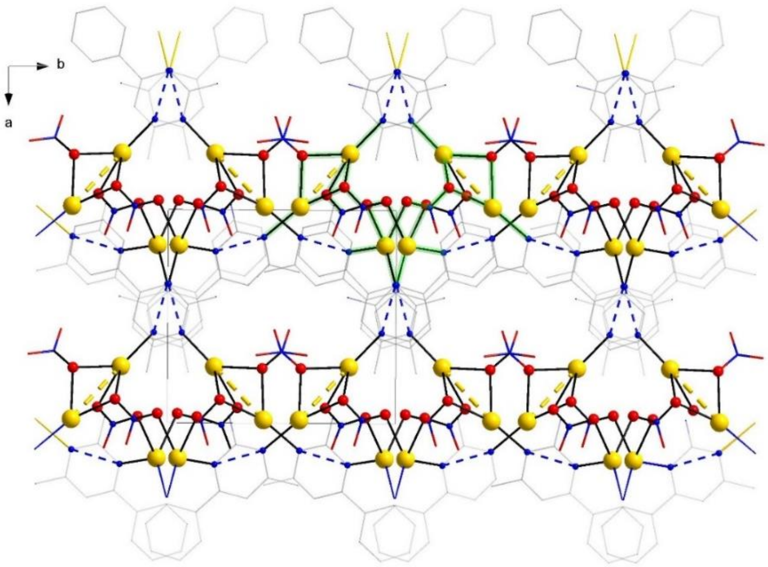


Fig. S3. Crystal packing of the compound **1** along *c* direction. One of the chains formed only by Ag–NO_3 bonds is highlighted green. {$Ag_2(NO_3)_3$} units are highlighted by yellow dashed lines between Ag atoms. Dashed blue lines indicate bridging L ligands. Atoms not directly bonded to Ag atoms are simplified. Only one position of disordered nitrate is shown. Hydrogen atoms are not shown.

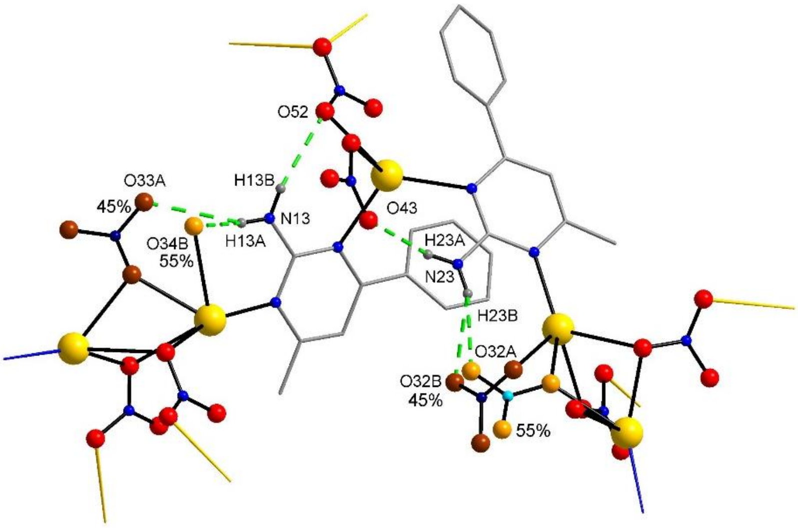


Fig. S4. Fragment of the structure **1** showing intramolecular hydrogen bonds between H atoms of the amino groups and O atoms of the nitrate or aqua ligands. Atoms of the nitrate and water in alternative positions with occupancy of 55 and 45% are differently colored. Hydrogen atoms not involved in hydrogen bonding are omitted. Donor···acceptor distances (Å) are: N13···O33A 3.41; N13···O34B 2.91; N13···O52 3.43; N23···O32A 3.18; N23···O32B 3.17; N23···O43 2.97.

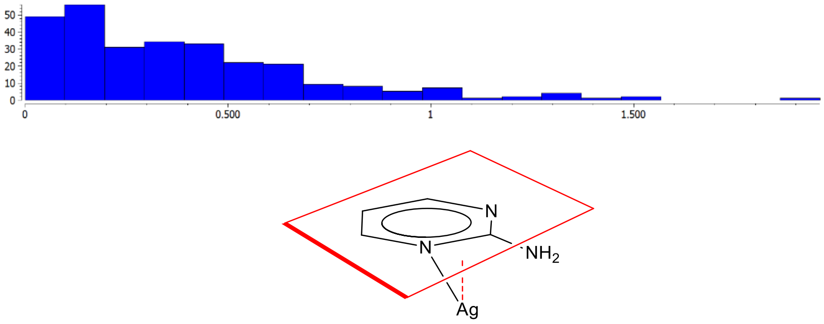


Fig. S5. Histogram of separation between Ag and pyrimidine plane (Å) in the structures of Ag complexes with aminopyrimidines found in CSD.

Quantum chemical calculations and photophysics

DFT and TD-DFT calculations

To analyze the electronic structures of **L**, **L$_2$**, **1** and **2**, quantum chemical calculations were performed using a density functional theory (DFT) approach with the three-parameter hybrid functional of Becke based on the correlation functional of Lee, Yang, and Parr (B3LYP)[6,7] for geometry optimizations and time dependent DFT calculations (TD-DFT). The DGDZVP basis set[8,9] was applied for the calculations of L and L$_2$, the def2-SVP basis set[10,11] was applied for the calculations of **1** and **2**. Gaussian 09 code[12] was used in all calculations. Experimental X-ray geometries were used for ground state geometry (S_0) optimizations of **1**, **2**, **L** and **L$_2$**. The ground state molecular geometries of **1**, **2**, **L** and **L$_2$** are found to be in a good agreement with the geometry obtained from the X-ray single crystal diffraction analysis. Resulting ground state optimized geometries were used as initial guesses for the excited state geometry optimizations of **2**, **L** and **L$_2$**. All frequencies in harmonic approximation for the calculated minimum energy geometries are positive and atomic coordinates are given in the Tables S2–S6.

Photophysics

The electronic spectra of L and 1 in MeCN solution were recorded on an SF 2000 spectrophotometer. The electronic diffuse reflectance spectra were recorded on a UV-3101 PC Shimadzu spectrophotometer. $BaSO_4$ was used for the baseline. Spectra are reported as the Kubelka–Munk function, $F(R) = (1 - R)^2/2R$, where R is the diffuse reflectance of the sample as compared to $BaSO_4$. Corrected photoluminescence spectra were recorded on a Fluorolog 3 spectrometer (Horiba Jobin Yvon) with a cooled PC177CE-010 photon detection module equipped with an R2658 photomultiplier. The absolute values of quantum yields were recorded using a Fluorolog 3 Quanta-phi device. Temperature dependences of luminescence were carried out using Optistat DN optical cryostats (Oxford Instruments). Luminescence decay kinetics was recorded by a Time-Correlated Single Photon Counting (TCSPC) technique using a NanoLED pulsed light source and a NanoLED-C2 controller.

Table S2. Calculated (B3LYP/DGDZVP) gas phase geometries of L in cartesian (XYZ) coordinates.

Ground state (S_0)				Lowest singlet state (S_1)			
N	2.697448	2.442885	-0.163047	N	2.701949	2.505275	0.062776
H	2.117438	3.191266	-0.519260	H	2.120225	3.277296	-0.238566
H	3.669353	2.448633	-0.443976	H	3.664746	2.535945	-0.249843
N	2.928379	0.141612	-0.022388	N	2.889538	0.160563	-0.005293
N	0.758055	1.178229	-0.111309	N	0.824934	1.093696	0.004807
C	-2.033627	1.112710	0.319174	C	-2.026271	1.156460	0.006335
H	-1.480044	2.014671	0.559209	H	-1.472080	2.090786	0.013619
C	-3.429454	1.108297	0.334367	C	-3.414214	1.182379	0.009339
H	-3.969046	2.015816	0.594948	H	-3.928242	2.141535	0.016441
C	-4.135126	-0.058210	0.015792	C	-4.160683	-0.009476	0.002696
H	-5.222512	-0.060735	0.024317	H	-5.246782	0.016172	0.005743
C	-3.431411	-1.220327	-0.319234	C	-3.471830	-1.237010	-0.008272
H	-3.970483	-2.127693	-0.580880	H	-4.031969	-2.169852	-0.014171
C	-2.034355	-1.218104	-0.326781	C	-2.084663	-1.282376	-0.011276
H	-1.507950	-2.124883	-0.611027	H	-1.595556	-2.252004	-0.023150
C	-1.315350	-0.052860	-0.004047	C	-1.307193	-0.081120	-0.002920
C	0.173261	-0.026182	-0.001281	C	0.117679	-0.096908	-0.003162
C	0.947232	-1.192573	0.121762	C	0.967489	-1.261337	-0.003796
H	0.493530	-2.168343	0.250878	H	0.539669	-2.256840	0.001405
C	2.102545	1.201054	-0.107242	C	2.123528	1.263497	0.005679
C	2.339597	-1.057787	0.099716	C	2.333175	-1.088457	-0.000278
C	3.259581	-2.246992	0.213807	C	3.310884	-2.235061	0.008748
H	3.917043	-2.296434	-0.660278	H	3.966105	-2.185446	-0.868052
H	2.705573	-3.185742	0.293501	H	2.790562	-3.194720	0.005374
H	3.902566	-2.139788	1.093570	H	3.950979	-2.183163	0.896614

Table S3. Calculated (B3LYP/DGDZVP) gas phase geometries of L_2–amino in cartesian (XYZ) coordinates.

Ground state (S_0)				Lowest singlet state (S_1)			
N	1.329456	-1.377053	-0.100005	N	1.297529	-1.388679	0.018530
H	0.325841	-1.206738	0.016792	H	0.277883	-1.240407	0.010239
H	1.701985	-2.292625	0.108554	H	1.686215	-2.322924	0.011460
N	1.709878	0.909563	-0.163330	N	1.642262	0.891093	0.011901
N	3.524478	-0.668492	-0.033722	N	3.481448	-0.686634	0.006778
C	6.249835	-1.333946	-0.345137	C	6.206517	-1.378129	0.004781
H	5.489660	-2.049075	-0.642194	H	5.437356	-2.142547	0.009675
C	7.596502	-1.699256	-0.307763	C	7.551870	-1.731561	0.002593
H	7.889488	-2.709145	-0.585138	H	7.829053	-2.783726	0.006424
C	8.568735	-0.771446	0.084951	C	8.553504	-0.746234	-0.004124
H	9.617578	-1.056723	0.117206	H	9.603926	-1.025821	-0.006612
C	8.180970	0.525006	0.440898	C	8.177024	0.606985	-0.007711
H	8.927075	1.248867	0.759839	H	8.939948	1.382410	-0.012479
C	6.833911	0.892982	0.395528	C	6.833263	0.969745	-0.005220
H	6.552770	1.898095	0.696749	H	6.586249	2.027229	-0.006730
C	5.849395	-0.029999	-0.001343	C	5.807054	-0.013857	0.000609
C	4.407486	0.338402	-0.061704	C	4.390546	0.329103	0.001592
C	3.977754	1.674900	-0.158015	C	3.910006	1.672067	-0.002262
H	4.677469	2.499699	-0.221769	H	4.592669	2.513460	-0.011107
C	2.214772	-0.345070	-0.092567	C	2.185925	-0.349483	0.011719
C	2.602209	1.911991	-0.201479	C	2.541307	1.913230	0.003790
C	2.040817	3.309193	-0.296379	C	1.971962	3.307755	0.002378
H	1.390595	3.513505	0.561147	H	1.345080	3.467718	0.888102
H	1.432711	3.411788	-1.201603	H	1.340131	3.464595	-0.880423
H	2.831755	4.062774	-0.320659	H	2.759515	4.065064	-0.001237
N	-1.329664	1.377429	0.100421	N	-1.269675	1.322516	-0.016745
H	-0.325934	1.207128	-0.015476	H	-0.242915	1.157543	-0.007280
H	-1.702164	2.292727	-0.109395	H	-1.642377	2.264845	-0.011060
N	-1.709864	-0.909176	0.165847	N	-1.652663	-0.944182	-0.012281
N	-3.524557	0.668538	0.033505	N	-3.467376	0.670593	-0.007704
C	-6.250134	1.334296	0.341574	C	-6.180457	1.409956	0.004774
H	-5.490183	2.049975	0.637866	H	-5.400212	2.163047	0.006176
C	-7.596795	1.699468	0.302726	C	-7.520039	1.783707	0.007631
H	-7.890008	2.709819	0.578171	H	-7.781495	2.839627	0.011010
C	-8.568737	0.770933	-0.088996	C	-8.535532	0.813008	0.006119
H	-9.617574	1.056101	-0.122398	H	-9.581444	1.108562	0.008929
C	-8.180680	-0.526109	-0.442460	C	-8.181062	-0.545600	0.000963
H	-8.926545	-1.250567	-0.760605	H	-8.955839	-1.308850	-0.000946
C	-6.833629	-0.893928	-0.395625	C	-6.843059	-0.928663	-0.002140
H	-6.552280	-1.899550	-0.694936	H	-6.612660	-1.989798	-0.008174
C	-5.849399	0.029783	0.000261	C	-5.803868	0.040079	0.000079
C	-4.407492	-0.338412	0.062080	C	-4.392451	-0.324944	-0.002226
C	-3.977665	-1.674743	0.160199	C	-3.933462	-1.676694	0.000298
H	-4.677296	-2.499569	0.224466	H	-4.631692	-2.504988	0.008132
C	-2.214859	0.345337	0.093527	C	-2.176021	0.305025	-0.011688
C	-2.602116	-1.911641	0.204640	C	-2.565164	-1.946911	-0.005896
C	-2.040639	-3.308692	0.301291	C	-2.023330	-3.351291	-0.005943
H	-1.390456	-3.514054	-0.556019	H	-1.398457	-3.519483	-0.890819
H	-1.432477	-3.410105	1.206606	H	-1.394150	-3.518413	0.876123
H	-2.831530	-4.062291	0.326534	H	-2.824657	-4.093843	-0.003463

Table S4. Calculated (B3LYP/DGDZVP) gas phase geometries of L_2–imino in cartesian (XYZ) coordinates

Ground state (S_0)				Lowest singlet state (S_1)			
N	1.288829	-1.418898	-0.018095	N	1.173506	-1.316458	-0.000684
H	-0.724902	-1.036842	0.012446	H	-0.674633	-1.091677	-0.001233
H	1.726810	-2.339559	-0.023393	H	1.594628	-2.247912	-0.000812
N	1.745726	0.854607	-0.006757	N	1.694084	0.926027	-0.000454
N	3.557195	-0.704825	-0.011175	N	3.458601	-0.677987	-0.000310
C	6.247655	-1.382200	0.029253	C	6.151728	-1.387340	-0.001154
H	5.470882	-2.130931	0.050136	H	5.362978	-2.123128	-0.002468
C	7.594217	-1.737721	0.029069	C	7.488864	-1.769987	-0.000842
H	7.872957	-2.782936	0.051539	H	7.742600	-2.822249	-0.001932
C	8.584640	-0.750256	0.000048	C	8.506194	-0.807825	0.000900
H	9.630680	-1.026856	-0.000220	H	9.545195	-1.108598	0.001067
C	8.214699	0.595989	-0.029213	C	8.163607	0.551515	0.002430
H	8.973134	1.367124	-0.053293	H	8.940752	1.304703	0.003928
C	6.865406	0.953575	-0.028478	C	6.829431	0.942949	0.002146
H	6.608471	2.002550	-0.055130	H	6.603772	2.000240	0.003736
C	5.860611	-0.029663	0.001299	C	5.787637	-0.017525	0.000243
C	4.413164	0.314037	0.001880	C	4.375948	0.347831	-0.000255
C	3.961004	1.670914	0.016634	C	3.923354	1.696502	-0.000974
H	4.645482	2.500377	0.034897	H	4.621517	2.516625	-0.001799
C	2.183706	-0.475355	-0.012091	C	2.136955	-0.381718	-0.000497
C	2.608063	1.910705	0.010345	C	2.569370	1.982551	-0.000913
C	1.996788	3.281539	0.021504	C	1.985215	3.361331	-0.001216
H	1.357372	3.412950	0.896634	H	1.356906	3.524054	0.878551
H	1.370704	3.433188	-0.860037	H	1.356567	3.523661	-0.880817
H	2.768056	4.048322	0.035856	H	2.772400	4.112364	-0.001535
N	-1.288842	1.418934	0.015021	N	-1.152703	1.277740	-0.001206
H	0.724868	1.036949	-0.014015	H	0.665097	1.055010	-0.000615
H	-1.726783	2.339616	0.019710	H	-1.566447	2.211772	-0.001129
N	-1.745710	-0.854512	0.005794	N	-1.703567	-0.962712	-0.000789
N	-3.557219	0.704868	0.009799	N	-3.445884	0.665079	-0.000327
C	-6.247720	1.382122	-0.030367	C	-6.129592	1.407895	0.001582
H	-5.470983	2.130847	-0.052751	H	-5.330997	2.133027	0.002491
C	-7.594292	1.737607	-0.029741	C	-7.461773	1.807412	0.001688
H	-7.873077	2.782784	-0.053418	H	-7.702033	2.862995	0.002672
C	-8.584667	0.750155	0.001271	C	-8.491828	0.858525	0.000506
H	-9.630714	1.026726	0.001884	H	-9.527053	1.172406	0.000679
C	-8.214669	-0.596040	0.032083	C	-8.165743	-0.504818	-0.000893
H	-8.973066	-1.367162	0.057726	H	-8.952270	-1.248433	-0.001942
C	-6.865367	-0.953592	0.030902	C	-6.836377	-0.913054	-0.001029
H	-6.608380	-2.002521	0.058851	H	-6.623771	-1.973036	-0.002471
C	-5.860621	0.029634	-0.000883	C	-5.781708	0.033624	0.000290
C	-4.413168	-0.314027	-0.001964	C	-4.374608	-0.349557	0.000343
C	-3.960977	-1.670904	-0.015833	C	-3.941413	-1.706472	0.001154
H	-4.645444	-2.500396	-0.033166	H	-4.650828	-2.517021	0.002561
C	-2.183730	0.475415	0.010225	C	-2.125784	0.355301	-0.000768
C	-2.608027	-1.910653	-0.010046	C	-2.593730	-2.009517	0.000462
C	-1.996718	-3.281476	-0.020480	C	-2.027801	-3.396350	0.000888
H	-1.357786	-3.413539	-0.895866	H	-1.402975	-3.569497	-0.879714
H	-1.370135	-3.432429	0.860825	H	-1.401742	-3.568579	0.880794
H	-2.767970	-4.048292	-0.033815	H	-2.825597	-4.136193	0.001828

Table S5. Calculated (B3LYP/def2-SVP) gas phase geometry of the fragment of **1** in cartesian (XYZ) coordinates

Ground state (S_0)			
N	2.189768	-0.178168	-0.832421
N	3.065532	-2.277115	-0.428883
N	-1.103391	0.811816	1.221704
N	-1.077222	3.104194	1.801329
N	4.542811	-0.504752	-0.581013
C	3.269174	-0.956166	-0.610915
C	2.378380	1.126595	-1.077956
C	-3.039807	2.157564	1.002548
H	-4.101582	2.220432	0.753586
C	1.161475	1.934622	-1.363332
C	-0.500282	1.877516	1.722449
C	4.734570	0.791232	-0.802245
C	-3.127935	-0.264374	0.422055
C	-4.143588	-0.177374	-0.546349
H	-4.424861	0.796211	-0.953208
C	0.084252	1.371166	-2.065436
H	0.125196	0.322416	-2.366401
C	-2.386778	3.241476	1.422324
C	3.668570	1.668252	-1.077866
H	3.845279	2.719909	-1.300989
C	1.065322	3.278411	-1.023294
H	1.886071	3.744504	-0.470443
C	-3.373382	-2.685650	0.405425
H	-3.047292	-3.663780	0.762533
C	-4.356742	-2.587768	-0.581925
H	-4.797546	-3.492749	-1.004270
C	-2.420993	0.953497	0.899177
C	-4.748989	-1.330356	-1.047136
H	-5.506166	-1.247598	-1.830325
C	-0.067653	4.014598	-1.295161
H	-0.167154	5.056569	-0.992025
C	-1.020355	2.099156	-2.352771
H	-1.835356	1.603393	-2.887548
C	-1.112583	3.338738	-2.003657
H	-2.015505	3.915493	-2.234695
C	-2.759174	-1.536263	0.902723
H	-1.977506	-1.632466	1.657818
C	6.154839	1.296855	-0.744836
O	0.704500	-2.643956	1.945856
O	-1.496847	-3.877217	-2.370578
O	-1.403162	-1.730086	-2.164115
O	-0.056957	-2.926075	-1.043256
N	-0.935449	-2.829293	-1.870437
Ag	0.134957	-0.799269	0.132288
O	2.197356	-2.813408	3.499744
O	1.919660	-0.952144	2.490576
N	1.600643	-2.111742	2.660303
C	-2.977136	4.621455	1.483312
N	0.763254	1.734810	2.177708
H	2.114489	-2.631158	-0.323755
H	6.845814	0.449337	-0.643786
H	6.292520	1.969624	0.119182
H	6.410658	1.872406	-1.650202
H	-2.431397	5.229167	2.223652

H	-4.052965	4.591742	1.737580
H	-2.879128	5.117455	0.495928
H	1.229957	2.541040	2.568174
H	3.836222	-2.818443	-0.059681
H	1.182139	0.797907	2.274681

Table S6. Calculated (B3LYP/def2-SVP) gas phase geometries of **2** in cartesian (XYZ) coordinates

Ground state (S_0)				Lowest triplet state (T_1)			
Ag	1.820679	-0.852990	-0.023427	Ag	-1.880336	0.516228	-0.222037
P	2.060143	-3.316224	-0.036847	P	-2.383066	2.939713	-0.094537
N	5.633945	1.367528	-1.020327	N	-5.696250	-1.610881	-1.121295
O	0.076933	0.184112	-1.384828	O	0.043113	-0.215160	-1.442891
N	3.607676	0.708275	0.065375	N	-3.570191	-1.093435	-0.080613
N	0.180014	0.631856	-2.581282	N	-0.057775	-0.687546	-2.631803
O	-0.771874	1.238442	-3.078107	O	0.943313	-1.140594	-3.186321
C	2.559897	-4.042408	-1.660312	C	-2.708465	3.760650	-1.711342
C	3.291849	-3.974857	1.170404	C	-3.831813	3.342833	0.969876
O	1.232181	0.435751	-3.207494	O	-1.166569	-0.668102	-3.191806
N	3.913887	0.435199	-2.227238	N	-3.867786	-1.016594	-2.380755
C	0.498465	-4.196885	0.398067	C	-0.992020	3.891734	0.649532
C	6.140993	1.787050	0.141117	C	-6.258214	-1.889541	0.097106
C	7.528571	2.329880	0.117700	C	-7.632187	-2.187966	0.186592
C	8.170392	2.536826	-1.117457	C	-8.466055	-2.170521	-1.011848
H	7.626018	2.286764	-2.028532	H	-7.981260	-1.914288	-1.952960
C	4.371055	-4.791047	0.796834	C	-4.970186	4.016993	0.501348
H	4.498486	-5.091036	-0.245020	H	-5.015908	4.367403	-0.531088
C	3.347201	-3.261082	-2.523938	C	-3.119484	2.970035	-2.797171
H	3.625196	-2.240957	-2.244556	H	-3.224571	1.888579	-2.678039
C	8.229584	2.642055	1.297025	C	-8.302011	-2.530431	1.439519
H	7.769869	2.477555	2.272911	H	-7.736475	-2.560313	2.370591
C	9.466768	3.047975	-1.171777	C	-9.805983	-2.466026	-0.951379
H	9.947310	3.205478	-2.140931	H	-10.405736	-2.442442	-1.865500
C	4.393207	0.856684	-1.032795	C	-4.443099	-1.259982	-1.183306
C	3.152545	-3.591180	2.518369	C	-3.799870	2.883674	2.301184
H	2.325747	-2.943194	2.822335	H	-2.920069	2.352196	2.675935
C	4.091336	1.166481	1.236334	C	-4.051395	-1.466381	1.122840
C	5.371053	1.721577	1.316175	C	-5.378098	-1.866141	1.265220
H	5.739509	2.089927	2.271383	H	-5.743241	-2.140968	2.252091
C	9.528433	3.150358	1.242379	C	-9.649215	-2.822693	1.467950
H	10.057946	3.382700	2.169840	H	-10.122013	-3.077192	2.420436
C	5.142656	-4.853377	3.094680	C	-6.014948	3.795377	2.678711
H	5.862641	-5.195207	3.842923	H	-6.864407	3.972875	3.342836
C	5.292420	-5.225039	1.756592	C	-6.056656	4.238909	1.354651
H	6.129864	-5.858811	1.452850	H	-6.939294	4.762494	0.979112
C	2.184057	-5.335467	-2.063684	C	-2.552232	5.146576	-1.891441
H	1.559539	-5.952699	-1.414667	H	-2.218683	5.771315	-1.059839
C	3.765559	-3.771664	-3.756226	C	-3.382739	3.557932	-4.038787
H	4.375541	-3.151676	-4.418081	H	-3.697784	2.932178	-4.877051
C	10.151555	3.357660	0.007980	C	-10.434055	-2.800520	0.286179
H	11.168396	3.756674	-0.033698	H	-11.499186	-3.034992	0.322837
C	3.392013	-5.060339	-4.147011	C	-3.230244	4.936290	-4.208366
H	3.711478	-5.454976	-5.115120	H	-3.429306	5.394005	-5.180562
C	4.069648	-4.037904	3.471985	C	-4.883658	3.119186	3.149472
H	3.947203	-3.738985	4.516278	H	-4.844266	2.767591	4.183332
C	2.597692	-5.839274	-3.299766	C	-2.813352	5.729400	-3.133347

H	2.294256	-6.844803	-3.602937	H	-2.686935	6.806997	-3.264031
C	-0.718542	-3.592923	0.038538	C	0.315051	3.511386	0.300483
H	-0.712089	-2.611797	-0.443390	H	0.475854	2.678239	-0.389267
C	3.204462	1.094378	2.446103	C	-3.111014	-1.441530	2.295096
H	2.462633	1.910998	2.412306	H	-2.366037	-2.249545	2.198522
H	3.784078	1.206245	3.372795	H	-3.649006	-1.592863	3.241096
H	2.637139	0.153146	2.487223	H	-2.548758	-0.497454	2.357455
C	0.478678	-5.437100	1.057987	C	-1.176009	4.940019	1.566133
H	1.414953	-5.909295	1.364044	H	-2.182882	5.237649	1.864826
C	-1.931811	-4.227770	0.316710	C	1.415300	4.165196	0.858732
H	-2.870943	-3.744837	0.037984	H	2.421994	3.829002	0.601371
C	-0.737227	-6.067517	1.338034	C	-0.071623	5.599271	2.114528
H	-0.741190	-7.030685	1.855117	H	-0.227564	6.411854	2.828386
C	-1.943184	-5.466610	0.965052	C	1.224863	5.212721	1.765000
H	-2.893210	-5.958113	1.190267	H	2.086076	5.718618	2.208125
H	4.488857	0.671707	-3.027357	H	-4.432905	-1.194110	-3.200739
H	2.903679	0.355833	-2.403106	H	-2.858106	-0.886559	-2.501245
Ag	-1.820716	0.853006	0.023384	Ag	1.906619	-0.628302	0.184073
P	-2.060147	3.316238	0.036825	P	2.412285	-3.053710	0.049497
N	-5.633887	-1.367515	1.020427	N	5.665778	1.656478	1.124020
O	-0.076973	-0.184102	1.384811	O	-0.011746	0.155084	1.398407
N	-3.607684	-0.708233	-0.065368	N	3.617889	1.011441	0.071434
N	-0.180037	-0.631853	2.581263	N	0.094011	0.629718	2.586966
O	0.771867	-1.238419	3.078083	O	-0.905223	1.091667	3.140593
C	-2.559855	4.042458	1.660283	C	2.788137	-3.872780	1.657803
C	-3.291888	3.974844	-1.170408	C	3.830299	-3.477798	-1.051086
O	-1.232198	-0.435781	3.207497	O	1.200535	0.604248	3.147444
N	-3.913736	-0.435133	2.227229	N	3.948785	0.742166	2.354520
C	-0.498476	4.196863	-0.398164	C	1.002482	-4.008012	-0.657676
C	-6.140981	-1.787033	-0.141002	C	6.154351	2.079989	-0.044634
C	-7.528548	-2.329892	-0.117555	C	7.546442	2.612574	-0.041644
C	-8.170260	-2.537110	1.117614	C	8.244167	2.715398	1.176447
H	-7.625822	-2.287217	2.028696	H	7.737361	2.395420	2.086795
C	-4.371127	4.790979	-0.796812	C	4.937734	-4.231455	-0.632128
H	-4.498554	5.090950	0.245047	H	4.982836	-4.623364	0.385437
C	-3.347180	3.261164	2.523919	C	3.420948	-3.113366	2.657325
H	-3.625204	2.241042	2.244549	H	3.657326	-2.060429	2.479126
C	-8.229646	-2.641847	-1.296886	C	8.197070	3.020252	-1.220758
H	-7.770011	-2.477118	-2.272773	H	7.693670	2.945508	-2.185472
C	-9.466616	-3.048311	1.171934	C	9.545917	3.213638	1.214892
H	-9.947073	-3.206032	2.141094	H	10.070614	3.286146	2.170794
C	-4.393149	-0.856662	1.032836	C	4.422714	1.154351	1.155383
C	-3.152583	3.591194	-2.518381	C	3.797629	-2.970372	-2.364293
H	-2.325759	2.943250	-2.822368	H	2.939157	-2.382852	-2.702931
C	-4.091375	-1.166447	-1.236309	C	4.082312	1.474512	-1.105413
C	-5.371090	-1.721556	-1.316095	C	5.362188	2.024021	-1.206274
H	-5.739583	-2.089938	-2.271277	H	5.713315	2.393196	-2.167050
C	-9.528476	-3.150198	-1.242239	C	9.500376	3.518580	-1.182101
H	-10.058061	-3.382359	-2.169705	H	9.988259	3.828591	-2.109273
C	-5.142759	4.853308	-3.094648	C	5.951818	-3.985621	-2.821434
H	-5.862770	5.195116	-3.842876	H	6.777057	-4.184764	-3.509655
C	-5.292524	5.224942	-1.756551	C	5.993999	-4.480307	-1.515475
H	-6.129992	5.858673	-1.452790	H	6.852611	-5.066393	-1.178248
C	-2.183969	5.335507	2.063640	C	2.464104	-5.214987	1.919488
H	-1.559433	5.952712	1.414615	H	1.962581	-5.814597	1.157083
C	-3.765517	3.771771	3.756203	C	3.738717	-3.692956	3.889188
H	-4.375518	3.151812	4.418068	H	4.229057	-3.092030	4.658773

C	-10.151490	-3.357774	-0.007832	C	10.179854	3.618954	0.035662
H	-11.168315	-3.756828	0.033847	H	11.199573	4.010790	0.064956
C	-3.391926	5.060438	4.146974	C	3.415461	-5.029277	4.141158
H	-3.711375	5.455095	5.115081	H	3.654929	-5.478420	5.108201
C	-4.069718	4.037891	-3.471978	C	4.850359	-3.232606	-3.243514
H	-3.947271	3.738994	-4.516277	H	4.809681	-2.842302	-4.263360
C	-2.597580	5.839338	3.299721	C	2.775433	-5.787671	3.155561
H	-2.294108	6.844859	3.602882	H	2.514667	-6.831028	3.349843
C	0.718529	3.592905	-0.038622	C	-0.297864	-3.611981	-0.300369
H	0.712072	2.611818	0.443386	H	-0.440588	-2.765110	0.376915
C	-3.204530	-1.094345	-2.446101	C	3.165947	1.412837	-2.292428
H	-2.462701	-1.910965	-2.412322	H	2.401754	2.205279	-2.210565
H	-3.784170	-1.206194	-3.372779	H	3.712745	1.573064	-3.231814
H	-2.637196	-0.153118	-2.487224	H	2.622177	0.458494	-2.352651
C	-0.478682	5.437057	-1.058125	C	1.167390	-5.075021	-1.556397
H	-1.414956	5.909254	-1.364183	H	2.168751	-5.386030	-1.860167
C	1.931803	4.227741	-0.316802	C	-1.409713	-4.270482	-0.829952
H	2.870935	3.744830	-0.038028	H	-2.412709	-3.929202	-0.564050
C	0.737227	6.067453	-1.338202	C	0.051935	-5.735999	-2.079625
H	0.741195	7.030602	-1.855319	H	0.193215	-6.562307	-2.780683
C	1.943182	5.466554	-0.965195	C	-1.237496	-5.335128	-1.719889
H	2.893209	5.958050	-1.190421	H	-2.107746	-5.844009	-2.141367
H	-4.488637	-0.671625	3.027400	H	4.527073	0.959683	3.155319
H	-2.903512	-0.355744	2.403004	H	2.941118	0.632897	2.510717

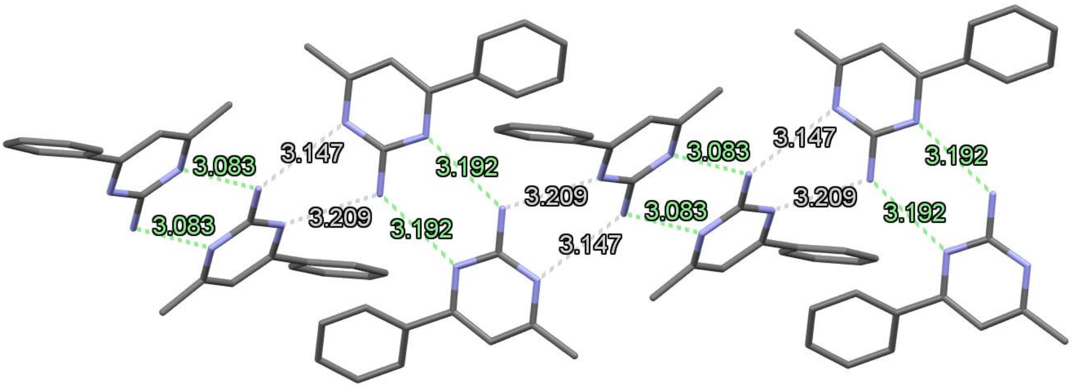


Fig. S6. Crystal packing of **L**: an infinite network of hydrogen bonded molecules. C and N atoms are shown in "stick model", hydrogen atoms are omitted for clarity.

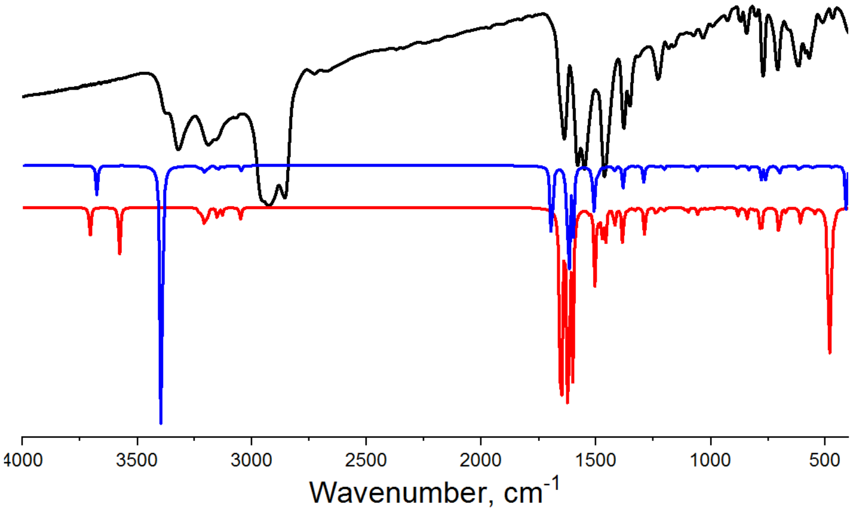


Fig. S7. Experimental IR spectrum of **L** (black); calculated IR spectrum of the monomer **L** (red); calculated IR spectrum of the dimer $\mathbf{L_2}$ (blue).

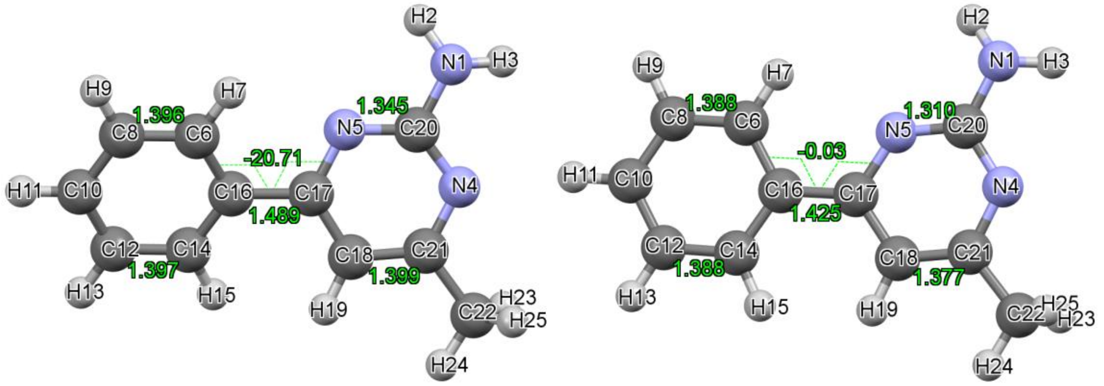


Fig. S8. Ground state S_0 (left) and first singlet state S_1 (right) geometry optimized structures of **L**

Table S7. Selected bond lengths in optimized S_0 and S_1 geometries of **L**

Bond	Length in S_0 optimised geometry, Å	Length in S_1 optimised geometry, Å
C18-C21	1.399	1.377
N5-C20	1.345	1.310
C16-C17	1.489	1.425
C8-C6	1.396	1.388
C12-C14	1.397	1.388

Table S8. Merz-Singh-Kollman charges on optimized S_0 and S_1 geometries of **L**

Atom / Group	Charge on optimized S_0 geometry	Charge on optimized S_1 geometry
N1	-0.874441	-0.870037
H2	0.369248	0.357001
H3	0.374085	0.367270
N4	-0.820358	-0.856007
N5	-0.792959	-0.776317
C6	-0.142482	-0.043080
H7	0.155955	0.098554
C8	-0.136858	-0.168524
H9	0.132988	0.134412
C10	-0.125321	-0.095006
H11	0.132723	0.125877
C12	-0.123989	-0.140491
H13	0.132162	0.125812
C14	-0.178785	-0.130973
H15	0.137576	0.125627
C16	-0.018366	-0.039239
C17	0.688487	0.581283
C18	-0.870010	-0.752640
H19	0.251082	0.208418
C20	0.975019	1.013980
C21	0.866276	0.912826
C22	-0.618066	-0.757185
H23	0.159989	0.188893
H24	0.149309	0.181884
H25	0.176736	0.207661
Ph[a]	-0.034397	-0.007031

a – Phenyl substituent of the pyrimidine ring in L

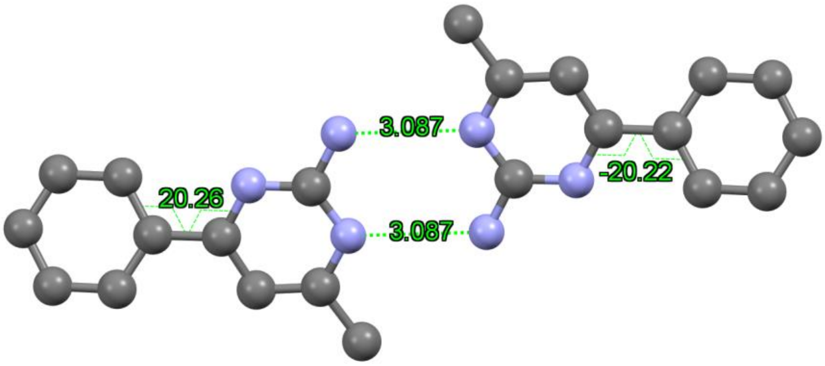


Fig. S9. Ground state (S_0) geometry optimized structure of **L_2**. Hydrogen atoms are omitted for clarity.

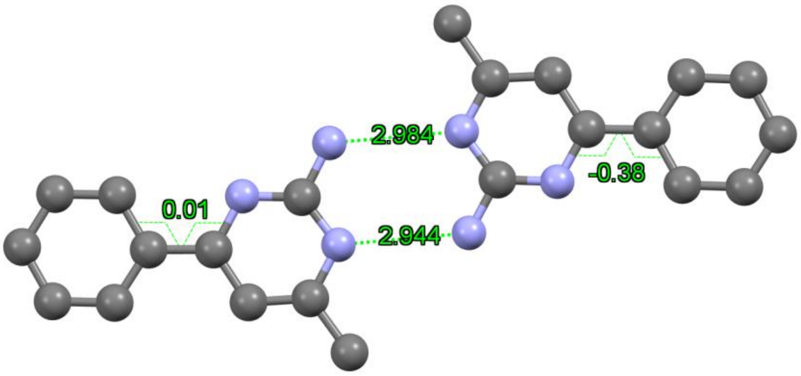
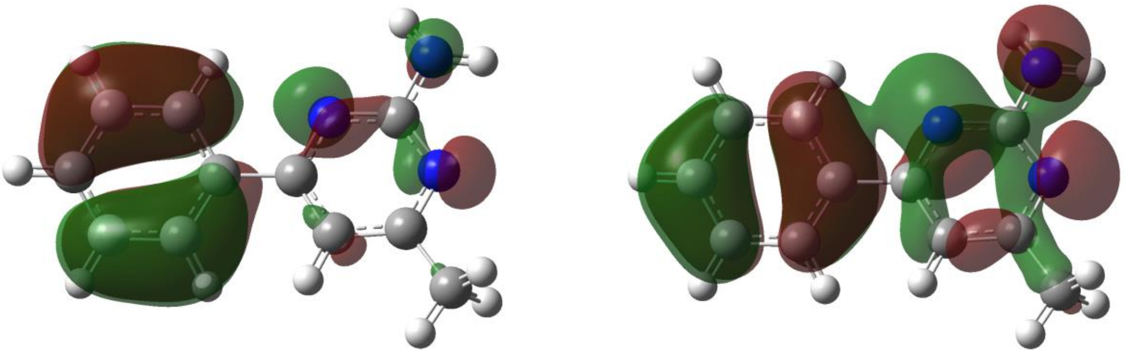
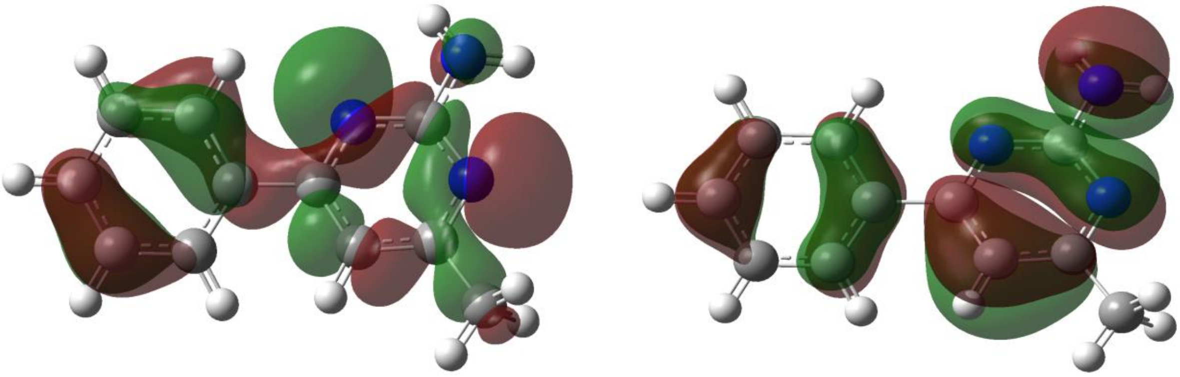


Fig. S10. First singlet state (S_1) geometry optimized structure of **L_2**. Hydrogen atoms are omitted for clarity.

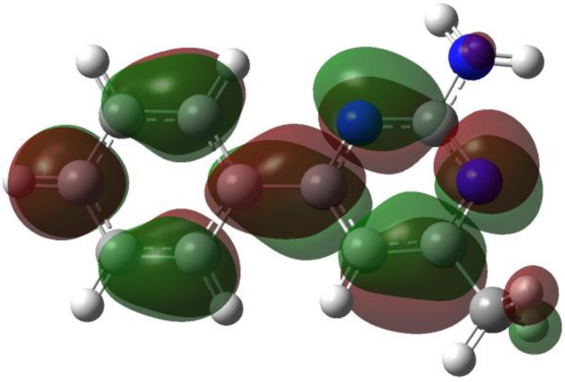
Table S9. Iso-surface contour plots (iso-value = 0.02) of the molecular orbitals of **L** as calculated at the B3LYP/DGDZVP theory level in the ground state (S_0) geometry.



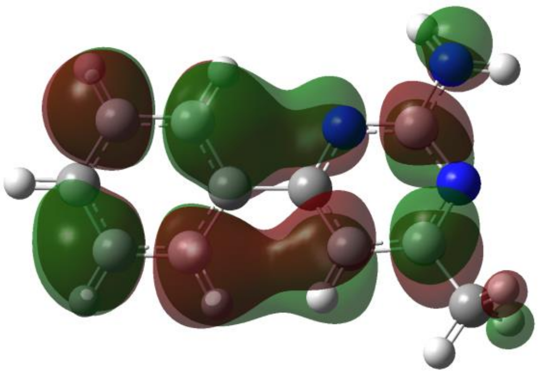
HOMO-3 **HOMO-2**



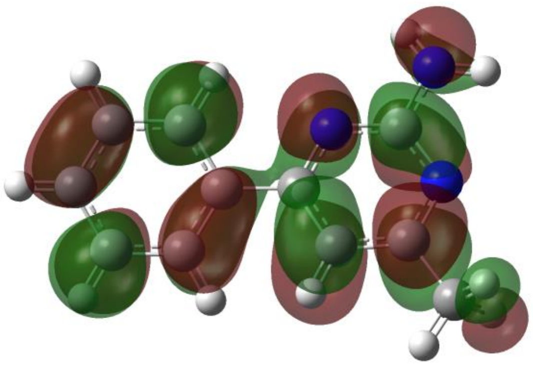
HOMO-1 **HOMO**



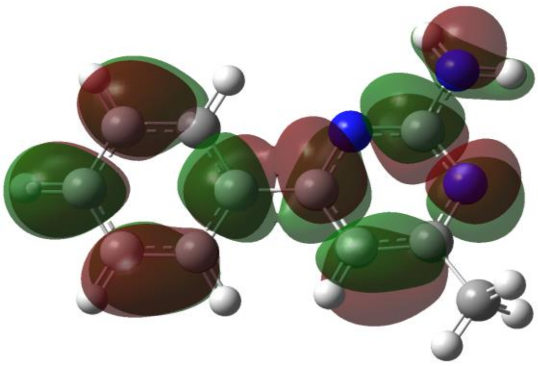
LUMO



LUMO+1



LUMO+2



LUMO+3

Table S10. Excited state properties of **L** obtained from TD-DFT calculations for the gas phase relaxed geometry of the ground state (S_0).

State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	4.12	301	HOMO – LUMO (24%), HOMO-1 – LUMO (66%)	0.0354	π–π*, n–π*
S2	4.13	300	HOMO – LUMO (70%), HOMO-1 – LUMO (17%), HOMO-2 – LUMO (9%)	0.1148	π–π*, n–π*
S3	4.71	263	HOMO – LUMO+1 (11%), HOMO-2 – LUMO (13%), HOMO-3 – LUMO (57%)	0.0332	π–π*, n–π*
S4	4.89	254	HOMO-2 – LUMO (67%), HOMO-3 – LUMO (18%)	0.2918	π–π*, n–π*
S5	5.19	239	HOMO-1 – LUMO+2 (25%), HOMO-1 – LUMO+1 (50%)	0.0065	π–π*, n–π*

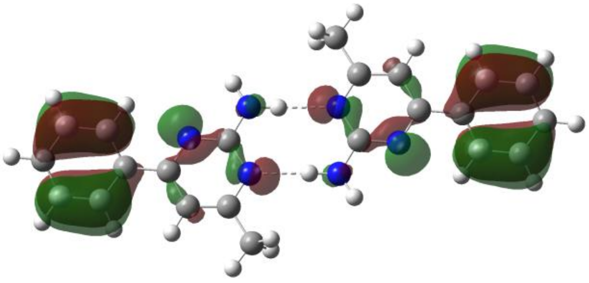
Table S11. Orbital energies and characters resulting from Mulliken population analysis calculated for **L** at the ground state (S_0) optimized geometry.

Orbital	Energy (eV)	Contributions (%)			
		Pym[a]	NH_2[b]	CH_3[c]	Ph[d]
HOMO-3	-7.12	6	1	0	92
HOMO-2	-6.93	32	9	1	58
HOMO-1	-6.85	78	1	2	19
HOMO	-6.28	59	27	1	13
LUMO	-1.61	56	0	2	42

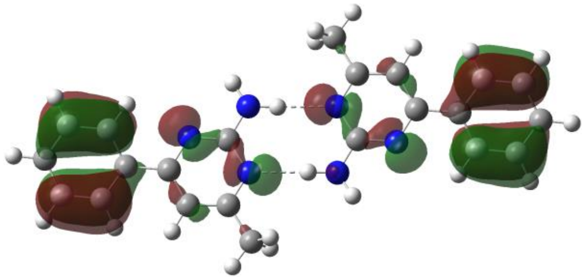
LUMO+1	-0.57	28	2	1	69
LUMO+2	-0.18	53	3	2	42
LUMO+3	0.49	44	4	1	50

a – Pyrimidine ring in **L**, b – NH_2 substituent of the pyrimidine ring in **L**,
c – CH_3 substituent of the pyrimidine ring in **L**, d – Phenyl substituent of the pyrimidine ring in **L**

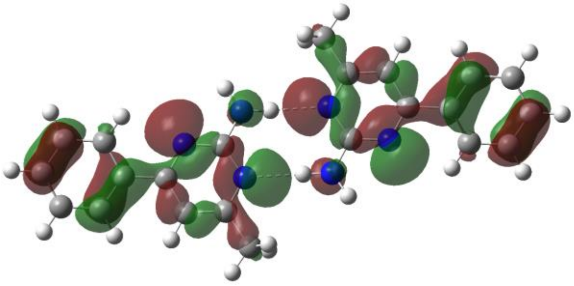
Table S12. Iso-surface contour plots (iso-value = 0.02) of the molecular orbitals of **L_2–amino** as calculated at the B3LYP/DGDZVP theory level in the ground state (S_0) geometry.



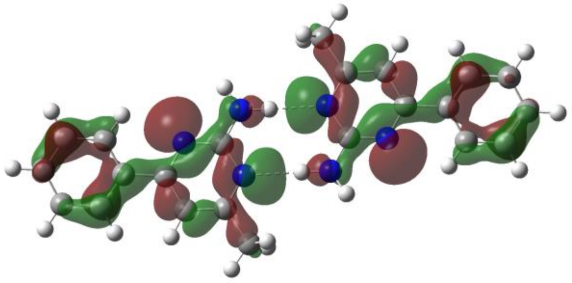
HOMO-7



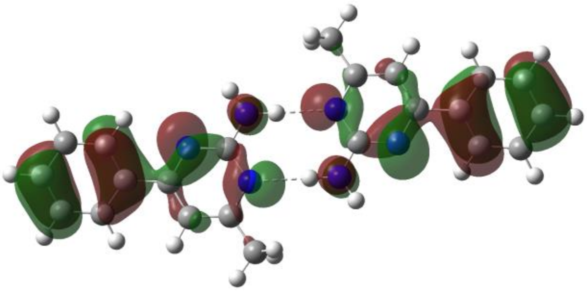
HOMO-6



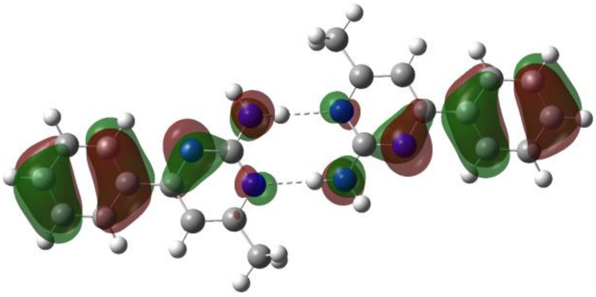
HOMO-5



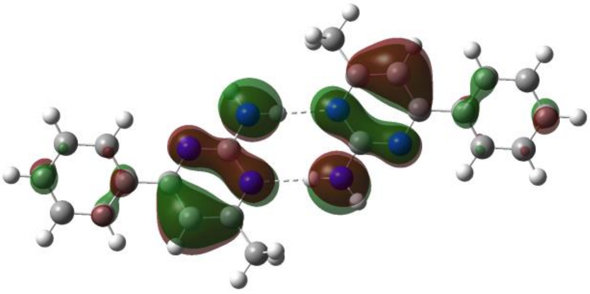
HOMO-4



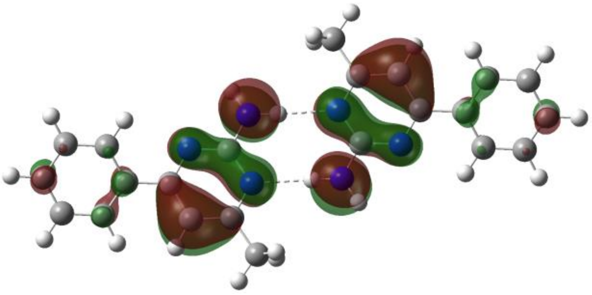
HOMO-3



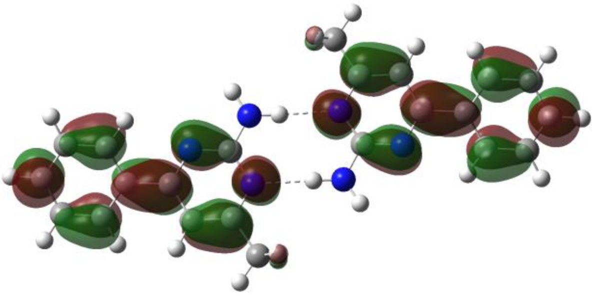
HOMO-2



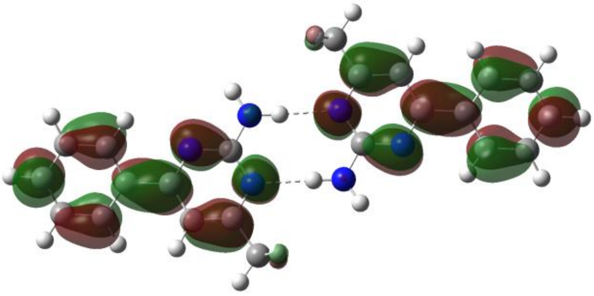
HOMO-1



HOMO



LUMO



LUMO+1

Table S13. Excited state properties of **L_2–amino** obtained from TD-DFT calculations for the gas phase relaxed geometry of the ground state (S_0).

State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	3.94	315	HOMO – LUMO+1 (71%), HOMO-1 – LUMO (25%)	0.2426	n–π*
S2	4.09	303	HOMO – LUMO+1 (24%), HOMO-1 – LUMO (70%)	0.0093	n–π*
S3	4.19	296	HOMO-5 – LUMO (30%), HOMO-4 – LUMO+1 (36%), HOMO-3 – LUMO (11%)	0.0005	π–π*, n–π*
S4	4.19	296	HOMO-5 – LUMO+1 (27%), HOMO-4 – LUMO (41%), HOMO-3 – LUMO+1 (10%)	0.0093	π–π*, n–π*
S5	4.69	264	HOMO-7 – LUMO (27%), HOMO-6 – LUMO+1 (25%), HOMO-3 – LUMO+1 (9%), HOMO-2 – LUMO (16%)	0.1285	π–π*, n–π*

Table S14. Orbital energies and characters resulting from Mulliken population analysis calculated for **L_2–amino** at the ground state (S_0) optimized geometry.

Orbital	Energy (eV)	Contributions (%)							
		(1)Pym[a]	(1)NH_2[b]	(1)CH_3[c]	(1)Ph[d]	(2)Pym[a]	(2)NH_2[b]	(2)CH_3[c]	(2)Ph[d]
HOMO-7	-7.12	6	0	0	43	6	0	0	44
HOMO-6	-7.11	6	0	0	44	6	0	0	43
HOMO-5	-6.97	34	2	1	13	34	2	1	13
HOMO-4	-6.93	40	1	1	9	40	1	1	9
HOMO-3	-6.84	15	2	0	31	15	3	0	34
HOMO-2	-6.84	11	4	0	37	10	3	0	35
HOMO-1	-6.17	30	16	0	3	30	16	0	3
HOMO	-6.07	30	17	0	3	30	17	0	3
LUMO	-1.64	29	0	1	20	28	0	1	20
LUMO+1	-1.60	28	0	1	21	28	0	1	21

a – Pyrimidine ring in L, b – NH_2 substituent of the pyrimidine ring in L,

c – CH_3 substituent of the pyrimidine ring in L, d – Phenyl substituent of the pyrimidine ring in L

(1) – First molecule of L in L_2–amino, (2) – Second molecule of L in L_2–amino

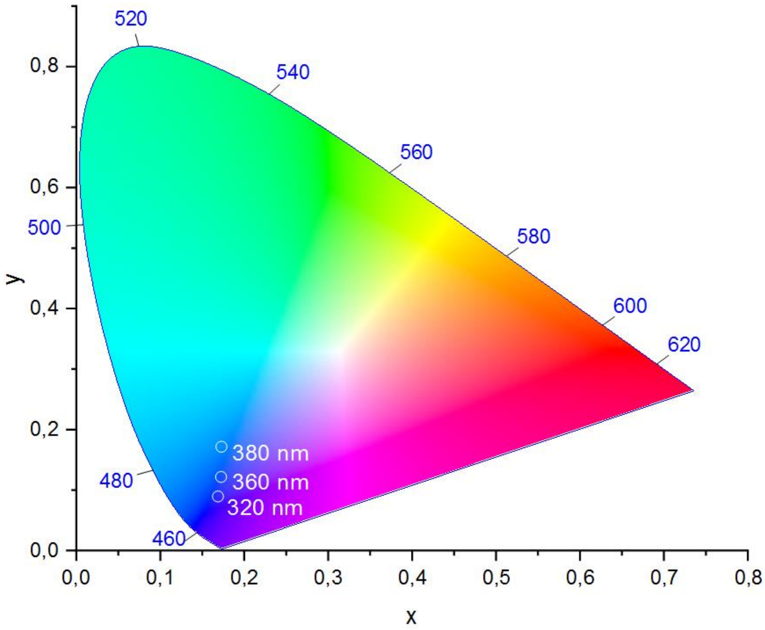


Fig. S11. CIE 1931 chromaticity diagram showing the chromaticity of the emission of **L** recorded at 300 K at λ_{ex} = 320, 360 and 380 nm.

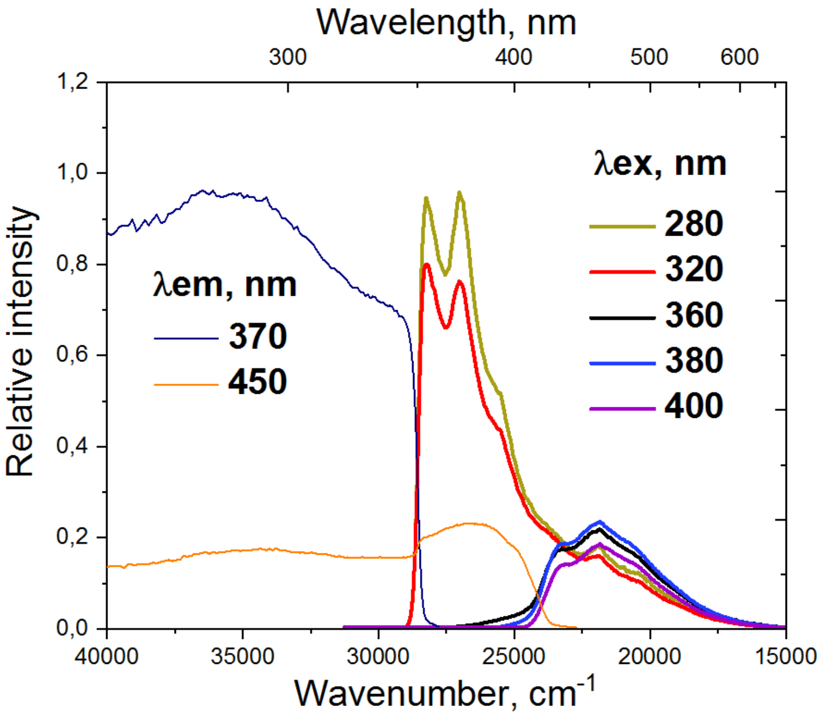
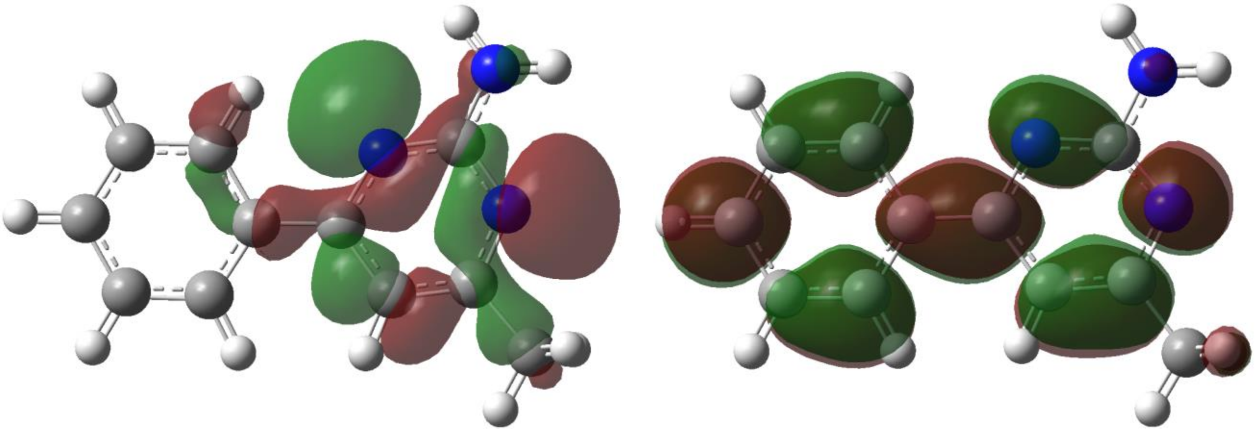


Fig. S12. Normalized emission (λ_{ex} = 280, 320, 360, 380 and 400 nm) and excitation (λ_{em} = 370 and 450 nm) spectra of **L** in the solid state at 77 K.

Table S15. Iso-surface contour plots (iso-value = 0.02) of the molecular orbitals of **L** as calculated at the B3LYP/DGDZVP theory level in the first singlet excited state (S_1) geometry.



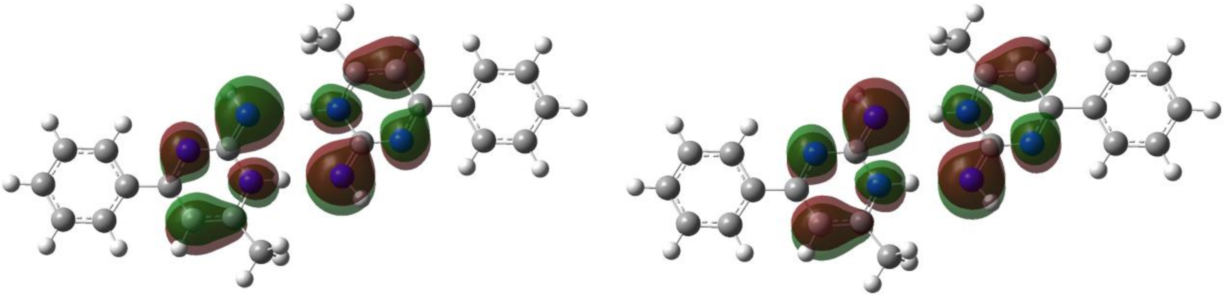
HOMO **LUMO**

Table S16. Orbital energies and characters resulting from Mulliken population analysis calculated for **L** at the first excited singlet state (S_1) optimized geometry.

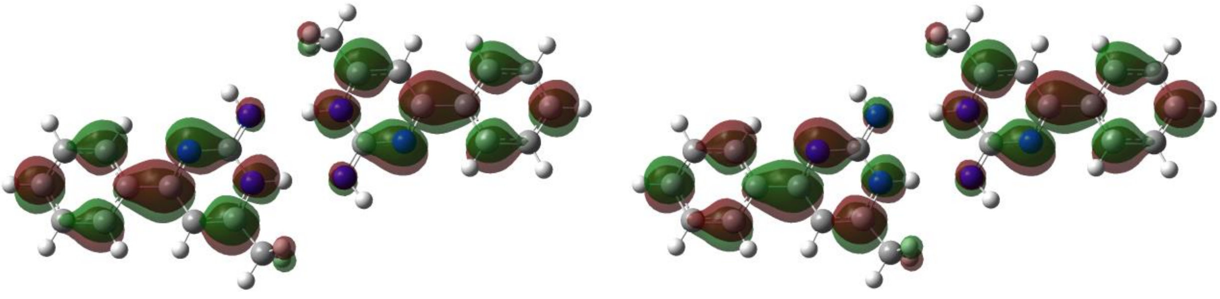
Orbital	Energy (eV)	Contributions (%)			
		Pym[a]	NH_2[b]	CH_3[c]	Ph[d]
HOMO	-6.08	96	0	2	2
LUMO	-1.98	52	0	1	47

a – Pyrimidine ring in **L**, b – NH_2 substituent of the pyrimidine ring in **L**,
c – CH_3 substituent of the pyrimidine ring in **L**, d – Phenyl substituent of the pyrimidine ring in **L**

Table S17. Iso-surface contour plots (iso-value = 0.02) of the molecular orbitals of **L_2-imino** as calculated at the B3LYP/DGDZVP theory level in the first singlet excited state (S_1) geometry.



HOMO-1 **HOMO**



LUMO **LUMO+1**

Table S18. Orbital energies and characters resulting from Mulliken population analysis calculated for **L_2-imino** at the first excited singlet state (S_1) optimized geometry.

Orbital	Energy (eV)	Contributions (%)							
		(1)Pym[a]	(1)NH_2[b]	(1)CH_3[c]	(1)Ph[d]	(2)Pym[a]	(2)NH_2[b]	(2)CH_3[c]	(2)Ph[d]
HOMO-1	-5.50	25	24	0	1	25	25	0	1
HOMO	-5.37	25	25	0	0	25	25	0	0
LUMO	-2.07	31	1	1	17	30	1	1	17
LUMO+1	-2.00	31	1	1	17	30	1	1	17

a – Pyrimidine ring in **L**, b – NH_2 substituent of the pyrimidine ring in **L**,
c – CH_3 substituent of the pyrimidine ring in **L**, d – Phenyl substituent of the pyrimidine ring in **L**,
(1) – First molecule of **L** in L_2, (2) – Second molecule of **L** in L_2

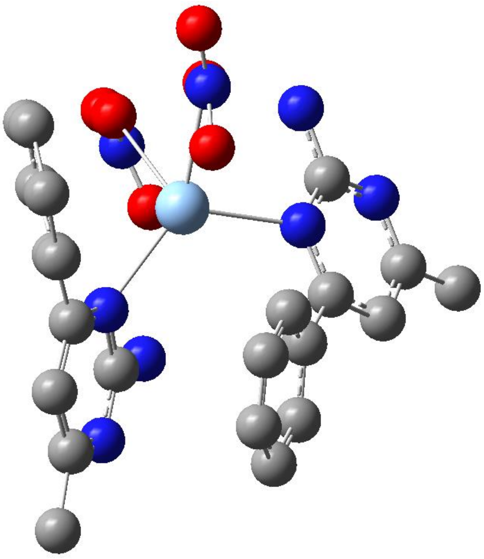
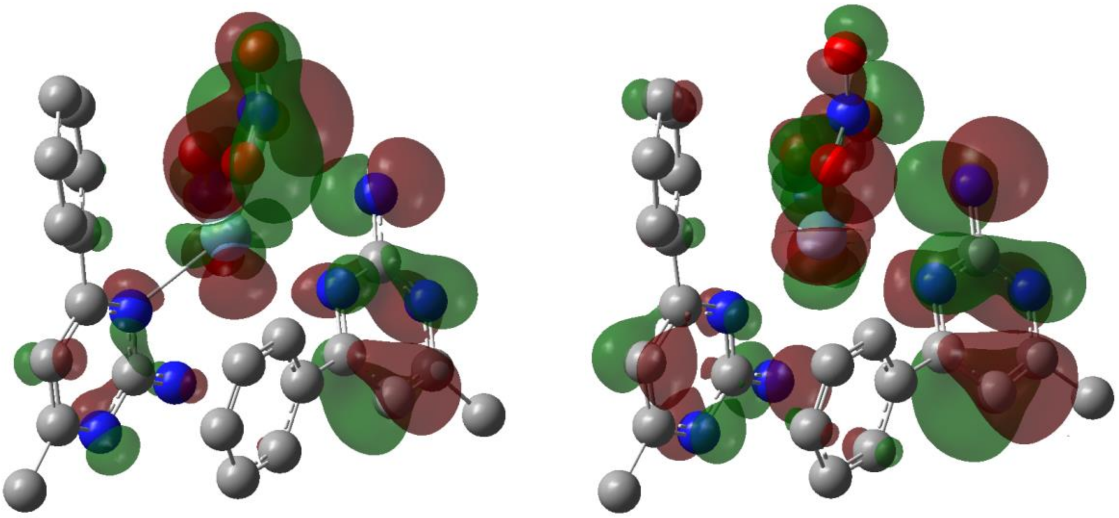
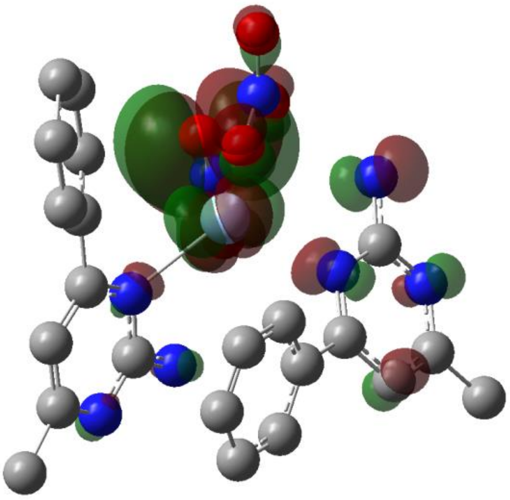


Fig. S13. Fragment of **1** taken for the ground state geometry optimization.

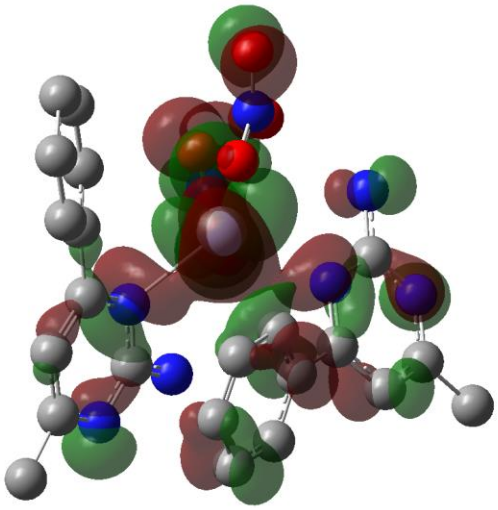
Table S19. Iso-surface contour plots (iso-value = 0.02) of the molecular orbitals of the fragment of **1** as calculated at the B3LYP/def2-SVP theory level in the ground state (S_0) geometry.



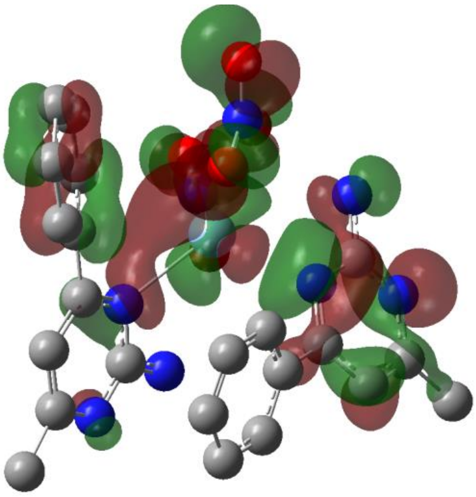
HOMO-7 **HOMO-6**



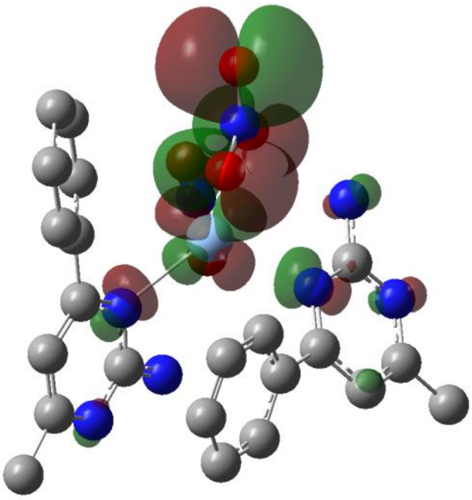
HOMO-5



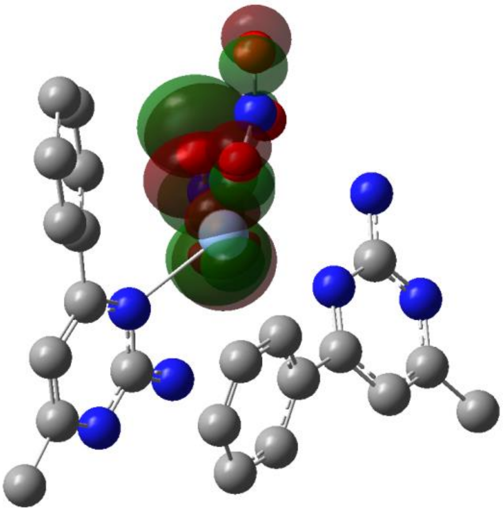
HOMO-4



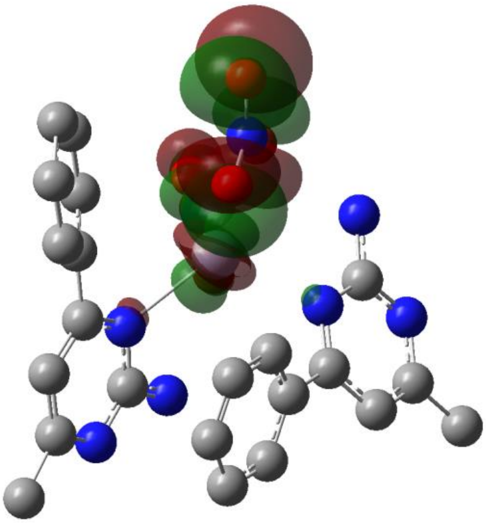
HOMO-3



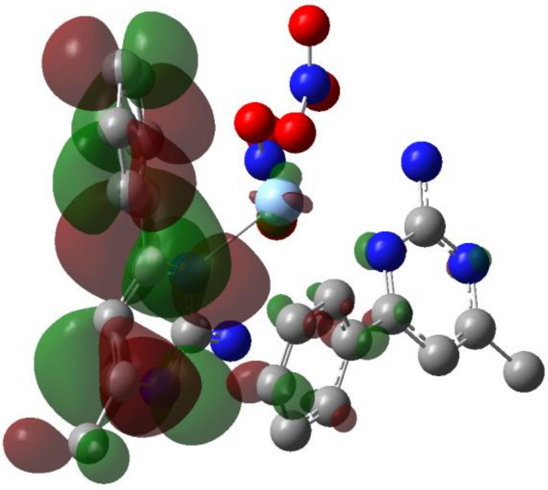
HOMO-2



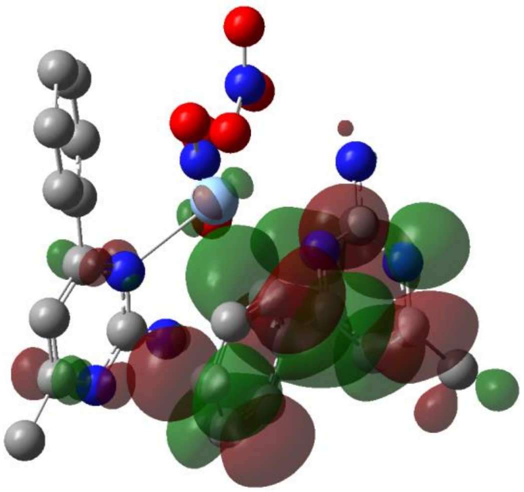
HOMO-1



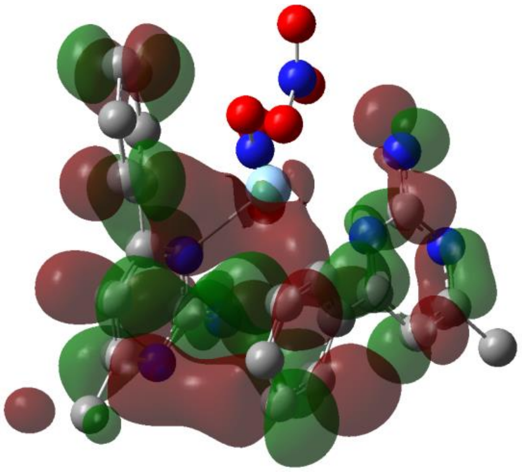
HOMO



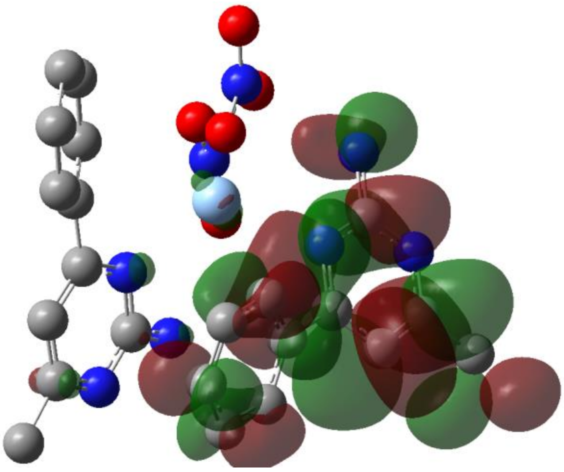
LUMO



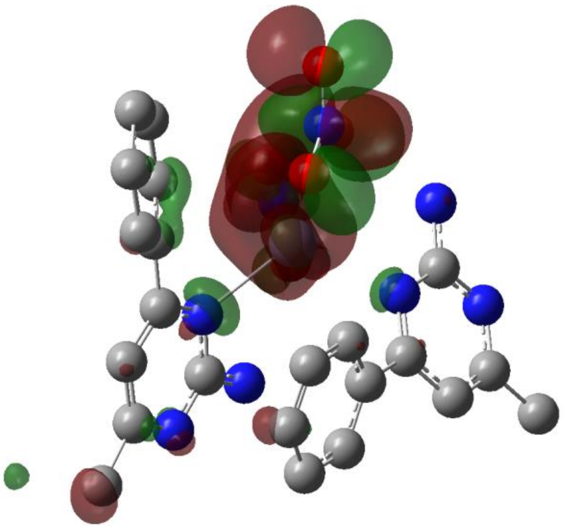
LUMO+1



LUMO+2



LUMO+3



LUMO+10

Table S20. Excited state properties of the fragment of **1** obtained from TD-DFT calculations for the gas phase relaxed geometry of the ground state (S_0).

State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	2.21	560	HOMO – LUMO (99.1%)	0.0006	(M+X)LCT[a]

S2	2.46	504	HOMO – LUMO+1 (99.2%)	0.0009	(M+X)LCT
S3	2.55	487	HOMO-1 – LUMO (99.5%)	0.0001	(M+X)LCT
S4	2.73	454	HOMO-1 – LUMO+1 (99.6%)	0.0003	(M+X)LCT
S5	3.25	382	HOMO-3 – LUMO (39.1%), HOMO-2 – LUMO+1 (48.6%)	0.0049	(M+X)LCT + LC[b]
S6	3.35	370	HOMO-1 – LUMO+2 (88.4%)	0.0001	(M+X)LCT
S7	3.37	368	HOMO-4 – LUMO (14.9%), HOMO-3 – LUMO (25.3%), HOMO-3 – LUMO+1 (31.4%), HOMO-2 – LUMO+1 (10.9%)	0.0089	(M+X)LCT + LC
S8	3.41	363	HOMO-3 – LUMO (32.5%), HOMO-3 – LUMO+1 (31.5%), HOMO-2 – LUMO (22.5%)	0.0203	(M+X)LCT + LC
S9	3.49	356	HOMO-4 – LUMO (59.0%), HOMO-2 – LUMO (14.9%), HOMO – LUMO+3 (10.5%)	0.0008	(M+X)LCT + LC
S10	3.50	355	HOMO – LUMO+3 (87.6%)	0.0003	(M+X)LCT
T1	2.21	560	HOMO – LUMO (98.4%)	0.0000	(M+X)LCT
T2	2.45	507	HOMO – LUMO+1 (99.2%)	0.0000	(M+X)LCT
T3	2.54	488	HOMO-1 – LUMO (99.5%)	0.0000	(M+X)LCT
T4	2.72	456	HOMO-1 – LUMO+1 (99.6%)	0.0000	(M+X)LCT
T5	2.98	417	HOMO-7 – LUMO (21.5%), HOMO-3 – LUMO (40.8%)	0.0000	(M+X)LCT+ LC
T6	3.13	396	HOMO-7 – LUMO (12.6%), HOMO-4 – LUMO (14.2%), HOMO-2 – LUMO (35.6%)	0.0000	(M+X)LCT+ LC
T7	3.18	390	HOMO-6 – LUMO+1 (26.9%), HOMO-4 – LUMO+1 (14.2%), HOMO-2 – LUMO+1 (11.4%)	0.0000	(M+X)LCT + LC
T8	3.19	388	HOMO-4 – LUMO (10.1%), HOMO-4 – LUMO+1 (15.5%), HOMO-3 – LUMO+1 (42.2%)	0.0000	(M+X)LCT + LC
T9	3.31	375	HOMO – LUMO+2 (76.5%), HOMO – LUMO+10 (10.8%)	0.0000	(M+X)LCT
T10	3.31	374	HOMO-7 – LUMO (21.5%), HOMO-4 – LUMO (19.4%), HOMO-3 – LUMO (20.2%)	0.0000	(M+X)LCT + LC

a – Metal + nitrate anion to ligand charge transfer, b – Ligand centered charge transfer

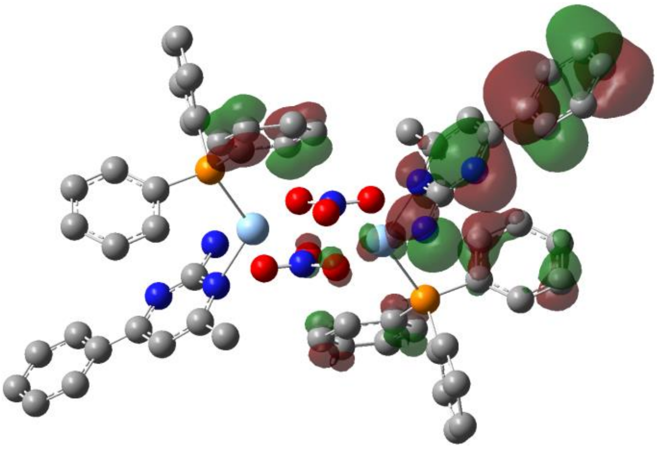
Table S21. Orbital energies and characters resulting from Mulliken population analysis calculated for the fragment of **1** at the ground state (S_0) optimized geometry.

Orbital	Energy (eV)	Contributions (%)			
		Ag	NO_3-	(1)L[a]	(2)L[b]
HOMO-7	-3.92	7	25	66	3
HOMO-6	-3.77	13	24	10	53
HOMO-5	-3.62	8	82	4	6
HOMO-4	-3.57	43	28	12	17
HOMO-3	-3.36	40	29	13	18
HOMO-2	-3.27	11	80	4	5
HOMO-1	-2.41	4	95	0	0
HOMO	-2.14	5	94	1	0
LUMO	0.66	1	0	90	9
LUMO+1	0.86	1	0	8	91
LUMO+2	1.78	3	0	38	59

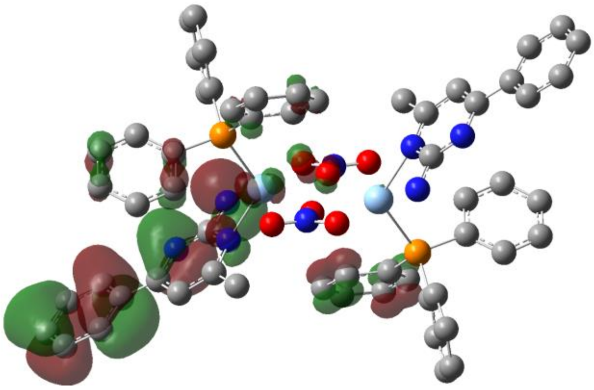
LUMO+3	1.87	2	0	2	97
LUMO+10	3.55	15	80	3	3

a – The first ligand **L** in the fragment of **1**, b – The second ligand **L** in the fragment of **1**

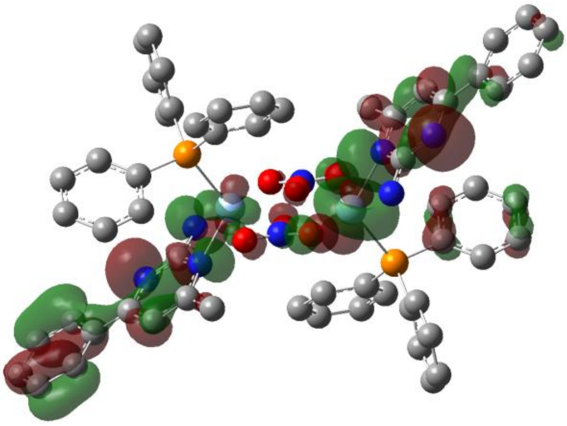
Table S22. Iso-surface contour plots (iso-value = 0.02) of the molecular orbitals of **2** as calculated at the B3LYP/def2-SVP theory level in the ground state (S_0) geometry.



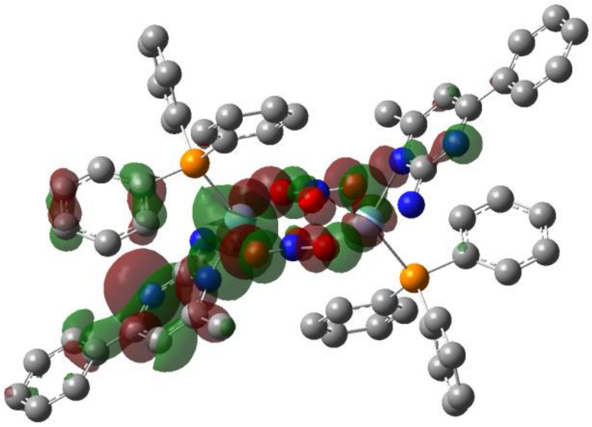
HOMO-9



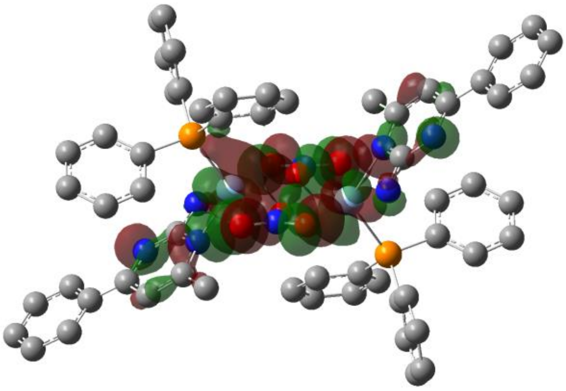
HOMO-8



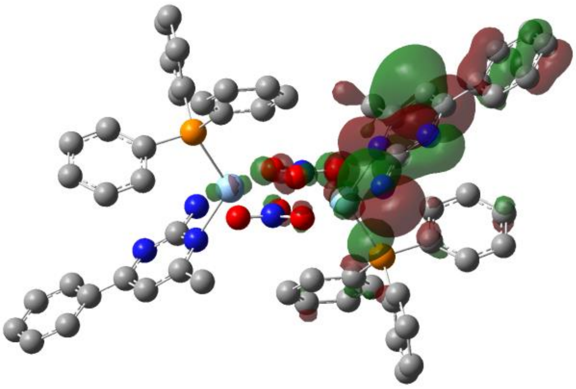
HOMO-7



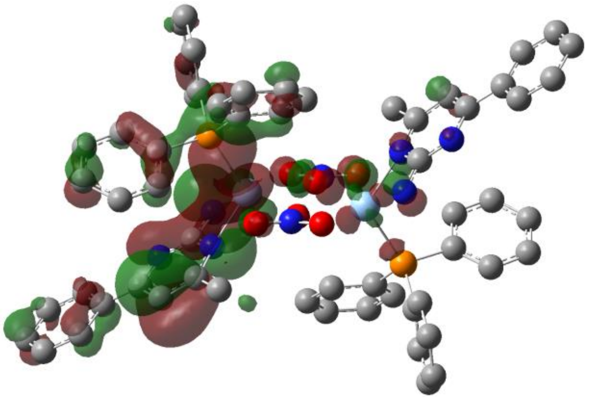
HOMO-6



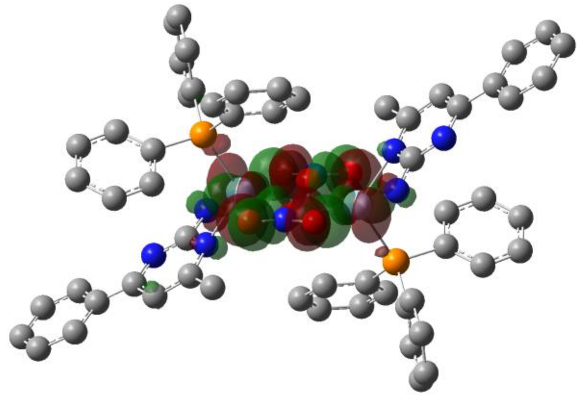
HOMO-5



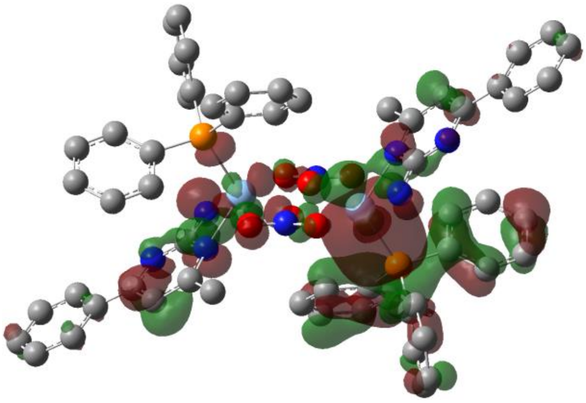
HOMO-4



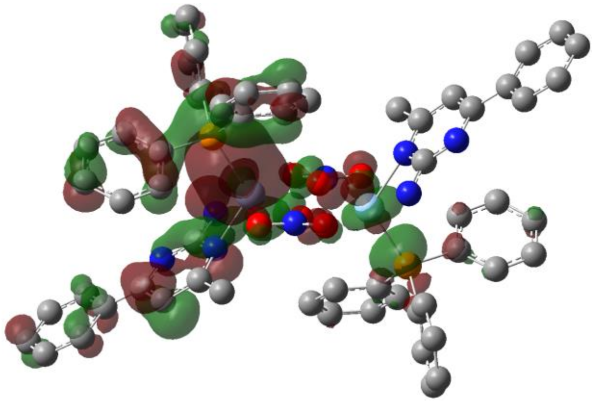
HOMO-3



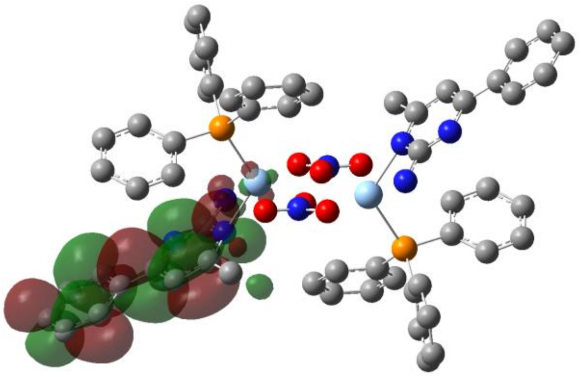
HOMO-2



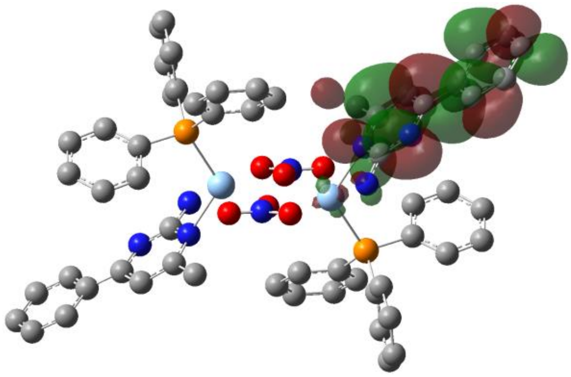
HOMO-1



HOMO



LUMO



LUMO+1

Table S23. Excited state properties of **2** obtained from TD-DFT calculations for the gas phase relaxed geometry of the ground state (S_0).

State	Energy (eV)	Energy (nm)	Contributions (%)	Oscillator strength	Character
S1	3.14	394	HOMO – LUMO (95.4%)	0.1680	(M+X)LCT[a] + LLCT[b]
S2	3.34	371	HOMO-2 – LUMO (89.7%)	0.0108	(M+X)LCT
S3	3.38	367	HOMO-1 – LUMO (82.3%)	0.0282	(M+X)LCT + LLCT
S4	3.46	358	HOMO-3 – LUMO (72.1%), HOMO-5 – LUMO (10.1%)	0.0357	LC[c]
S5	3.54	350	HOMO-5 – LUMO (44.6%), HOMO-6 – LUMO (23.5%), HOMO-3 – LUMO (15.0%)	0.0013	LC + (M+X)LCT
S6	3.61	344	HOMO – LUMO+1 (58.4%), HOMO-1 – LUMO+1 (38.7%)	0.0842	(M+X)LCT + LLCT
S7	3.73	333	HOMO – LUMO+1 (39.9%),	0.0359	(M+X)LCT + LLCT

			HOMO-1– LUMO+1 (48.9%)		
S8	3.76	330	HOMO-2– LUMO+1 (94.8%)	0.0053	(M+X)LCT
T1	2.31	536	HOMO-3– LUMO (33.6%), HOMO – LUMO (38.3%), HOMO-1– LUMO (15.0%), HOMO-8– LUMO (6.8 %)	0.0000	(M+X)LCT + LLCT + LC
T2	3.02	411	HOMO-4– LUMO+1 (51.7%), HOMO-1– LUMO+1 (17.1%), HOMO-9– LUMO+1 (10.8%)	0.0000	(M+X)LCT + LLCT + LC
T3	3.07	404	HOMO-8– LUMO (50.5%), HOMO-3– LUMO (25.4%)	0.0000	LC + (M+X)LCT
T4	3.15	393	HOMO-8– LUMO (13.5%), HOMO-6–LUMO (12.5%), HOMO-3– LUMO (13.5%), HOMO – LUMO (38.6%)	0.0000	(M+X)LCT + LLCT + LC
T5	3.31	375	HOMO-6– LUMO (16.7%), HOMO-5– LUMO (19.3%), HOMO-1– LUMO (21.9%), HOMO – LUMO (15.7%)	0.0000	(M+X)LCT + LLCT + LC
T6	3.36	369	HOMO-2– LUMO (81.3%)	0.0000	(M+X)LCT
T7	3.42	363	HOMO-9– LUMO+1 (43.5%), HOMO-4– LUMO+1 (24.9%)	0.0000	(M+X)LCT + LC
T8	3.45	360	HOMO-3– LUMO (16.8%), HOMO-1– LUMO (56.8%)	0.0000	(M+X)LCT + LLCT + LC

a – Metal + nitrate anion to **L** charge transfer, b – Ligand triphenylphosphine (PPh$_3$) to ligand **L** charge transfer, c – Ligand **L** centered charge transfer

Table S24. Orbital energies and characters resulting from Mulliken population analysis calculated for **2** at the ground state (S$_0$) optimized geometry.

Orbital	Energy (eV)	Contributions (%)			
		Ag	NO$_3$-	L[a]	PPh$_3$[b]
HOMO-9	-6.96	1	1	89	9
HOMO-8	-6.86	5	24	89	2
HOMO-7	-6.84	20	6	68	6
HOMO-6	-6.83	17	27	48	8
HOMO-5	-6.72	1	1	94	4
HOMO-4	-6.48	15	63	19	4
HOMO-3	-6.34	2	5	86	7
HOMO-2	-6.14	17	68	8	7
HOMO-1	-6.10	25	12	8	55
HOMO	-5.96	25	11	8	56
LUMO	-3.38	1	0	98	1
LUMO+1	-1.80	1	0	98	1

a – The ligands **L** in **2**, b – The triphenylphosphine (PPh$_3$) ligands in **2**

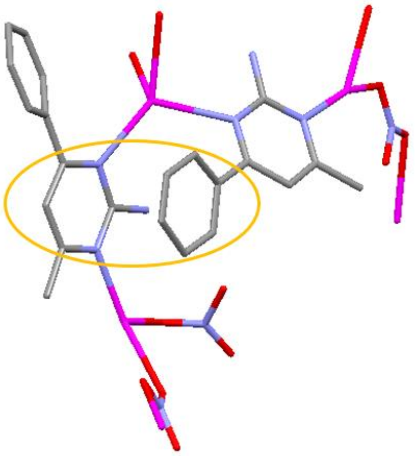


Fig. S14. Excimer generated by the aggregation through π–π intermolecular interactions between the pyrimidine and phenyl rings of the ligands **L** in the complex **1**.

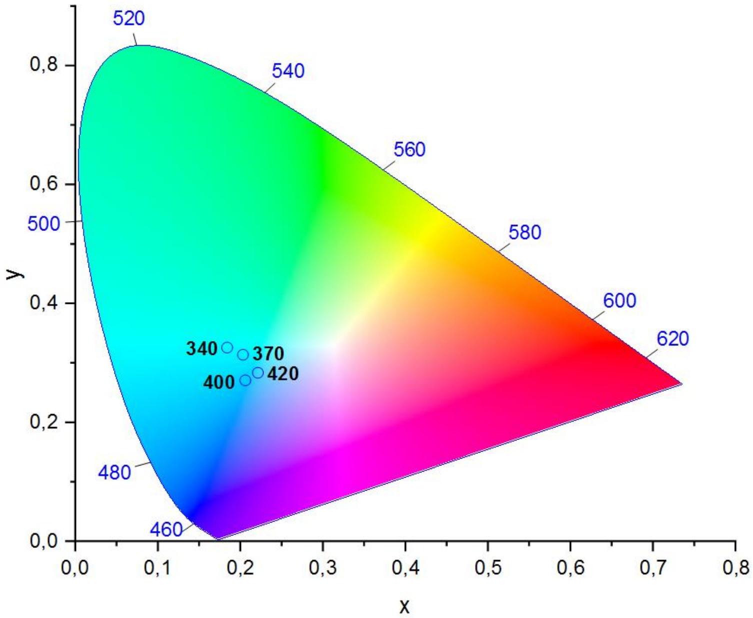


Fig. S15. CIE 1931 chromaticity diagram showing chromaticity of emission of **1** recorded at λ_{ex} = 340, 370, 400 and 420 nm (T = 77 K).

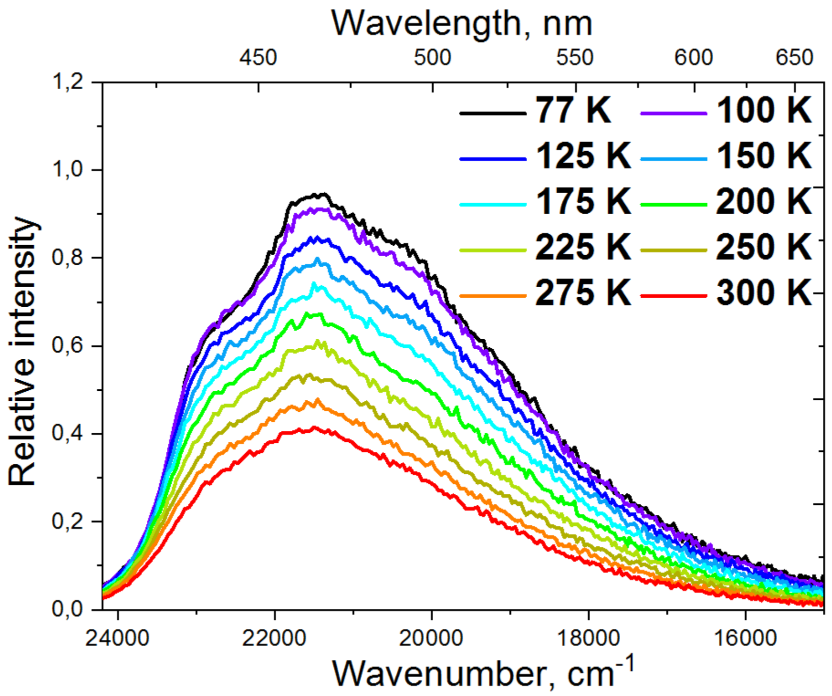


Fig. S16. Temperature dependence of the emission of **1** at λ_{ex}=340 nm.

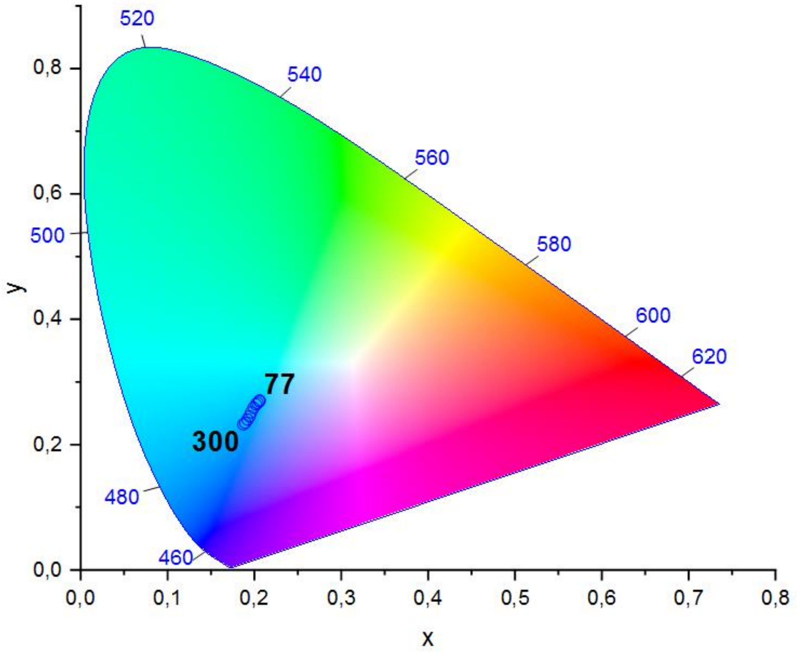


Fig. S17. CIE 1931 chromaticity diagram showing chromaticity of emission of **1** recorded at different temperatures (λ_{ex} = 400 nm).

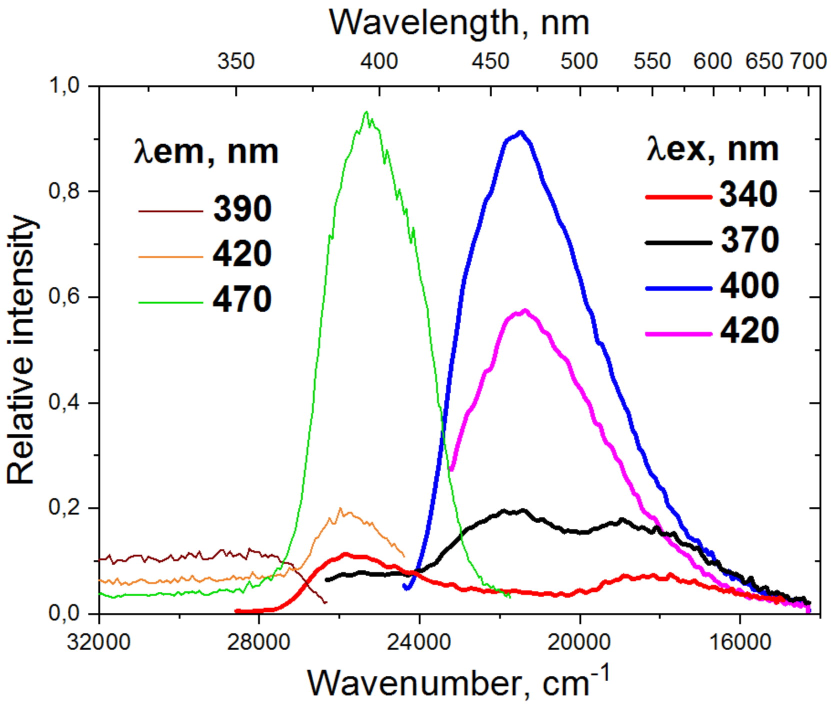


Fig. S18. Normalized emission (λ_{ex} = 340, 370, 400 and 420 nm) and excitation (λ_{em} = 390, 420 and 470 nm) spectra of **1** in the solid state at 300 K.

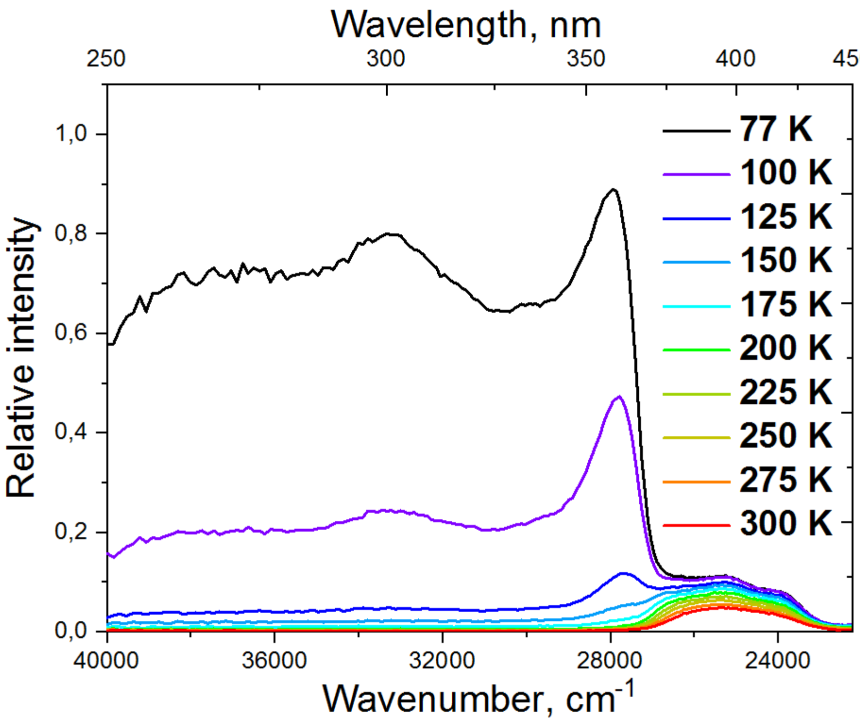


Fig. S19. Temperature dependence of the excitation of **1** at λ_{em}=470 nm.

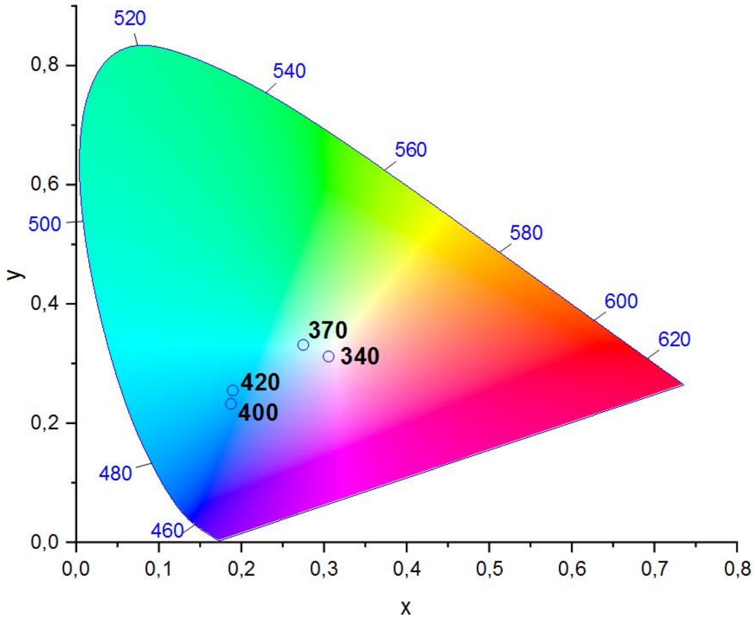
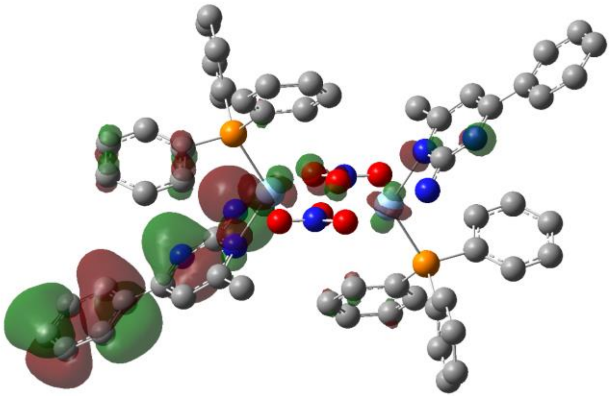
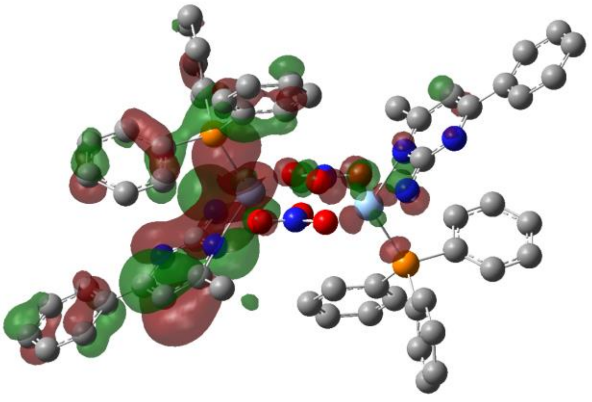


Fig. S20. CIE 1931 chromaticity diagram showing chromaticity of emission of **1** recorded at λ_{ex} = 340, 370, 400 and 420 nm (T = 300 K).

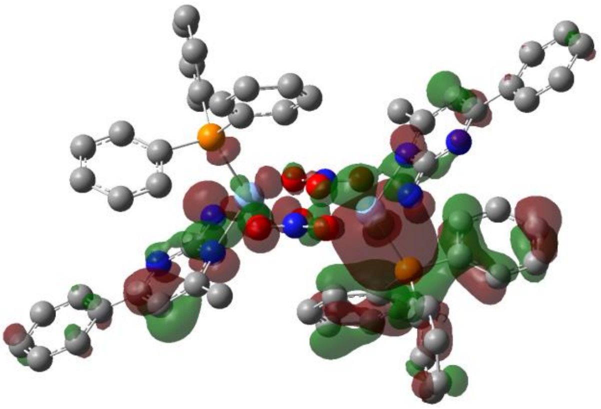
Table S25. Iso-surface contour plots (iso-value = 0.02) of the molecular orbitals of **2** as calculated at the B3LYP/def2-SVP theory level in the first triplet excited state (T_1) geometry.



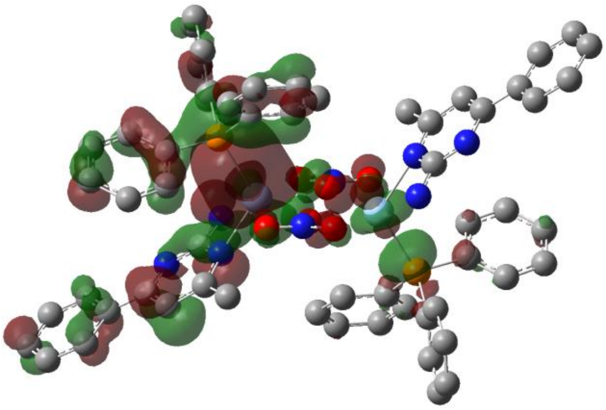
HOMO-8



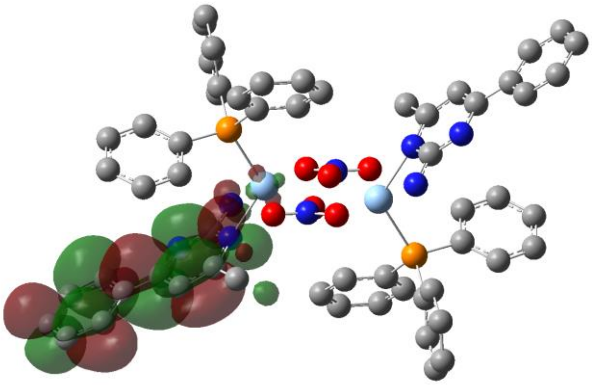
HOMO-3



HOMO-1



HOMO



LUMO

Table S26. Orbital energies and characters resulting from Mulliken population analysis calculated for **2** at the first triplet state (T_1) optimized geometry.

Orbital	Energy (eV)	Contributions (%)			
		Ag	NO_3-	L[a]	PPh_3[b]
HOMO-8	-6.78	4	1	88	7
HOMO-3	-6.09	8	6	64	23
HOMO-1	-5.91	22	6	25	47
HOMO	-5.76	23	9	24	44
LUMO	-2.19	1	0	98	1

a – The ligands **L** in **2**, b – The triphenylphosphine (PPh_3) ligands in **2**

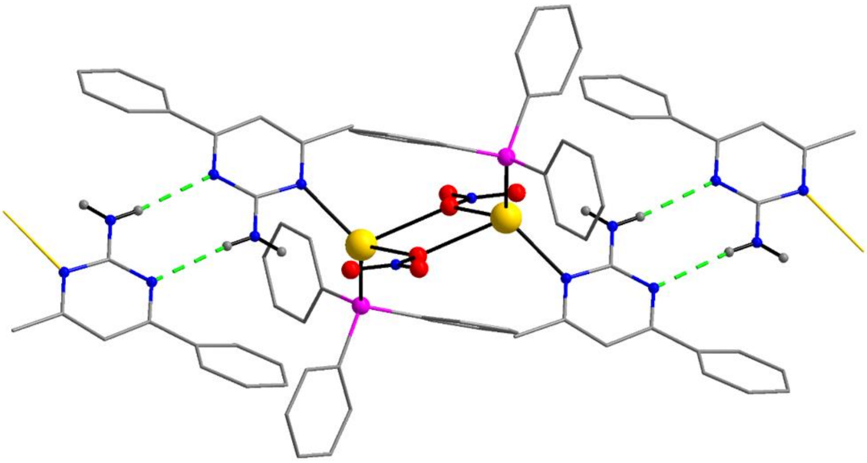


Fig. S21. A fragment of the structure **2** showing intermolecular hydrogen bonds (marked green) between H atoms of the amino groups and N atoms of the neighboring pyrimidine moieties. Hydrogen atoms not involved in hydrogen bonding are omitted. Donor···acceptor distance is 2.44 Å.

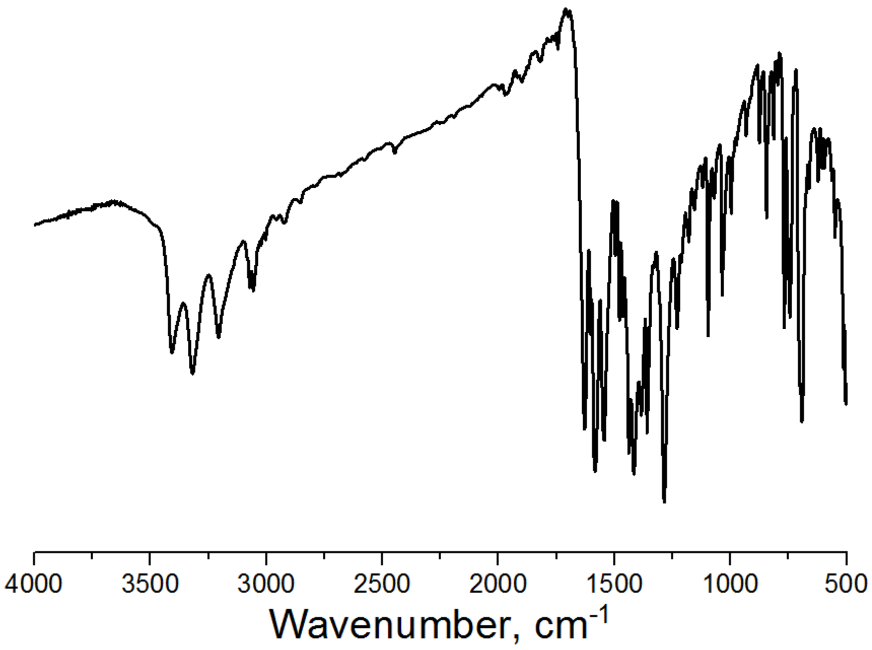


Fig. S22. Experimental IR spectrum of the complex **2**.

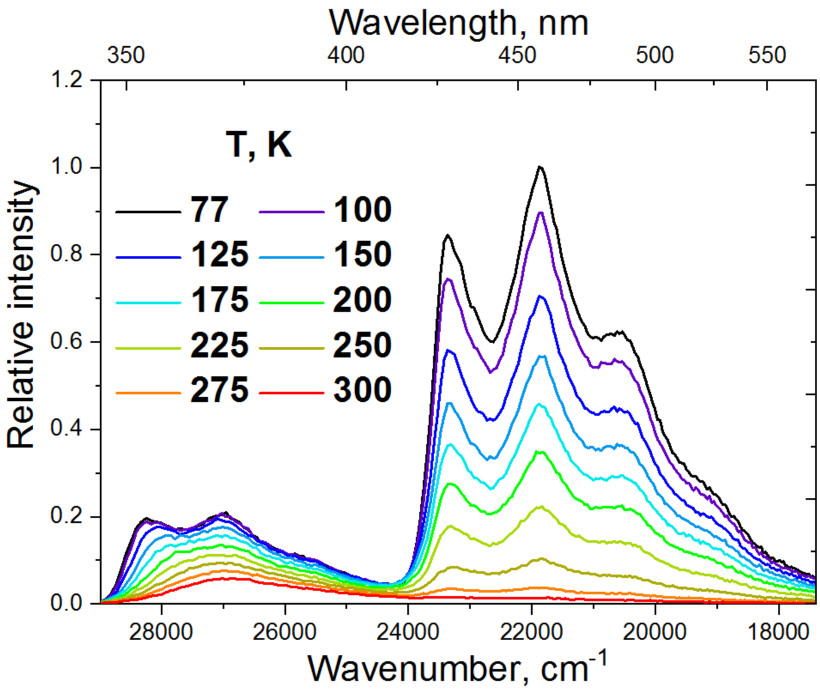


Fig. S23. Temperature dependence of the emission of **2** at λ_{ex}=340 nm

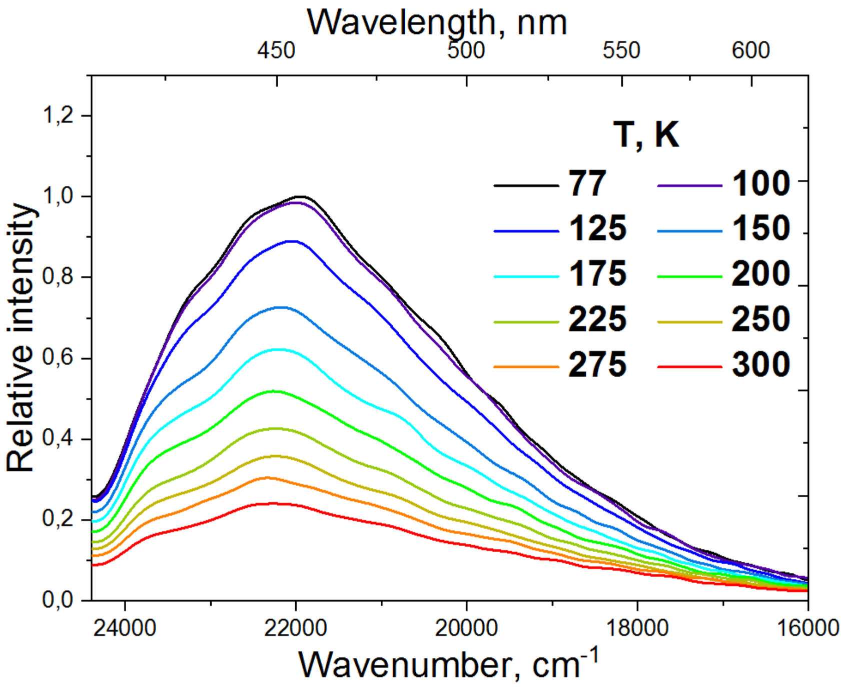


Fig. S24. Temperature dependence of the emission of **2** at λ_{ex}=400 nm.

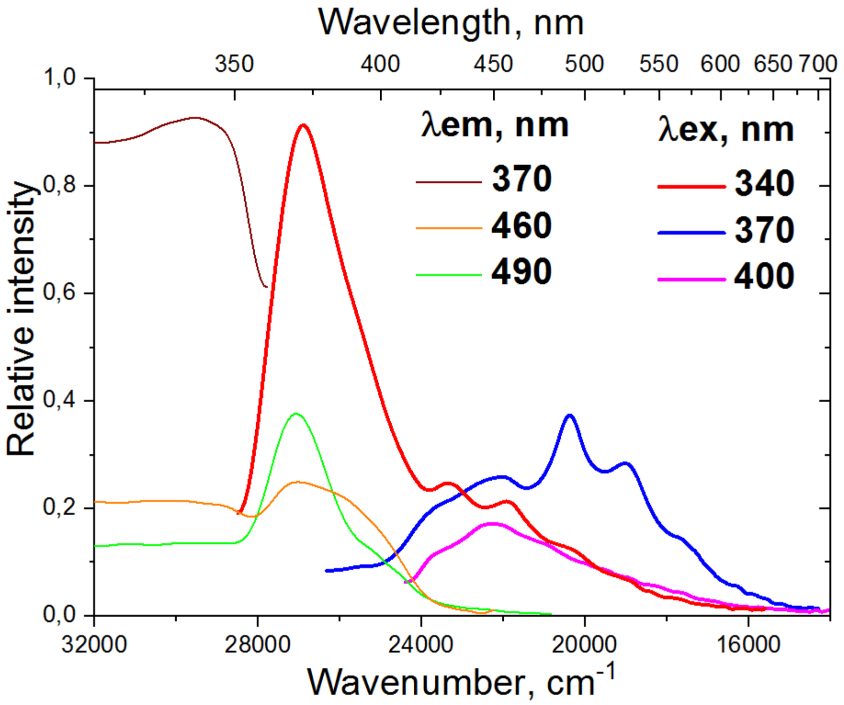


Fig. S25. Normalized emission (λ_{ex} = 340, 370 and 400 nm) and excitation (λ_{em} = 370, 460 and 490 nm) spectra of **2** in the solid state at 300 K.

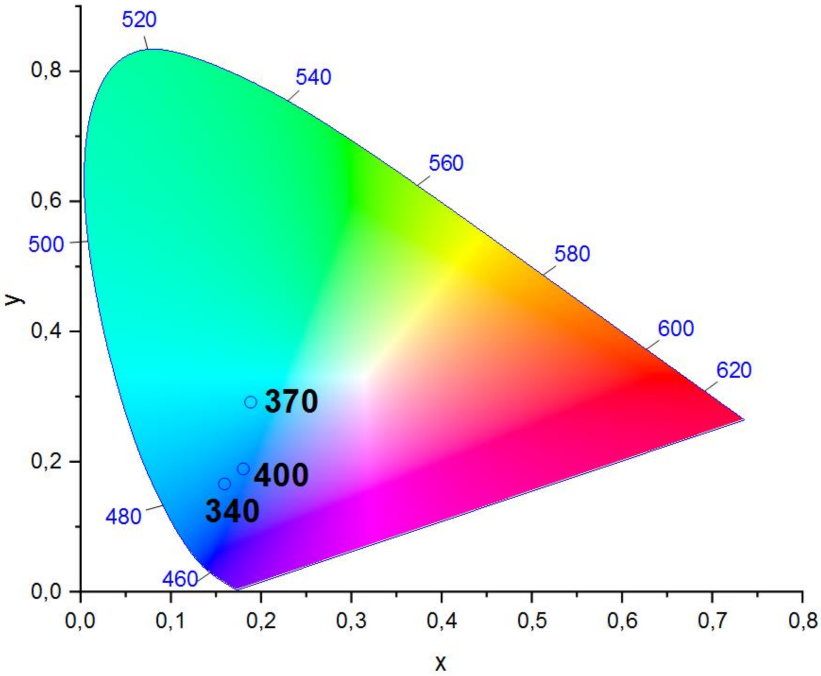


Fig. S26. CIE 1931 chromaticity diagram showing chromaticity of emission of **2** recorded at λ_{ex} = 340, 370 and 400 nm (T = 77 K).

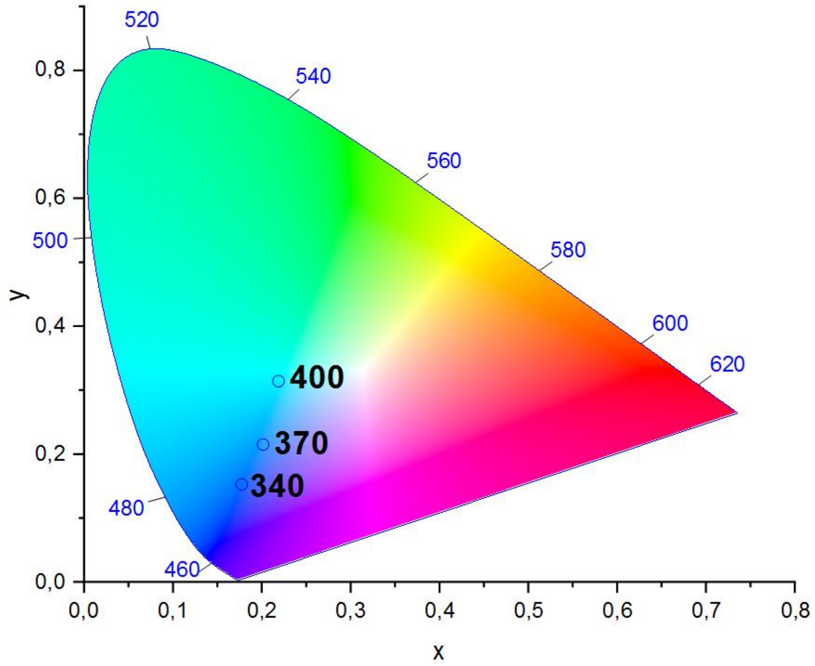


Fig. S27. CIE 1931 chromaticity diagram showing chromaticity of emission of **2** recorded at λ_{ex} = 340, 370 and 400 nm (T = 300 K).

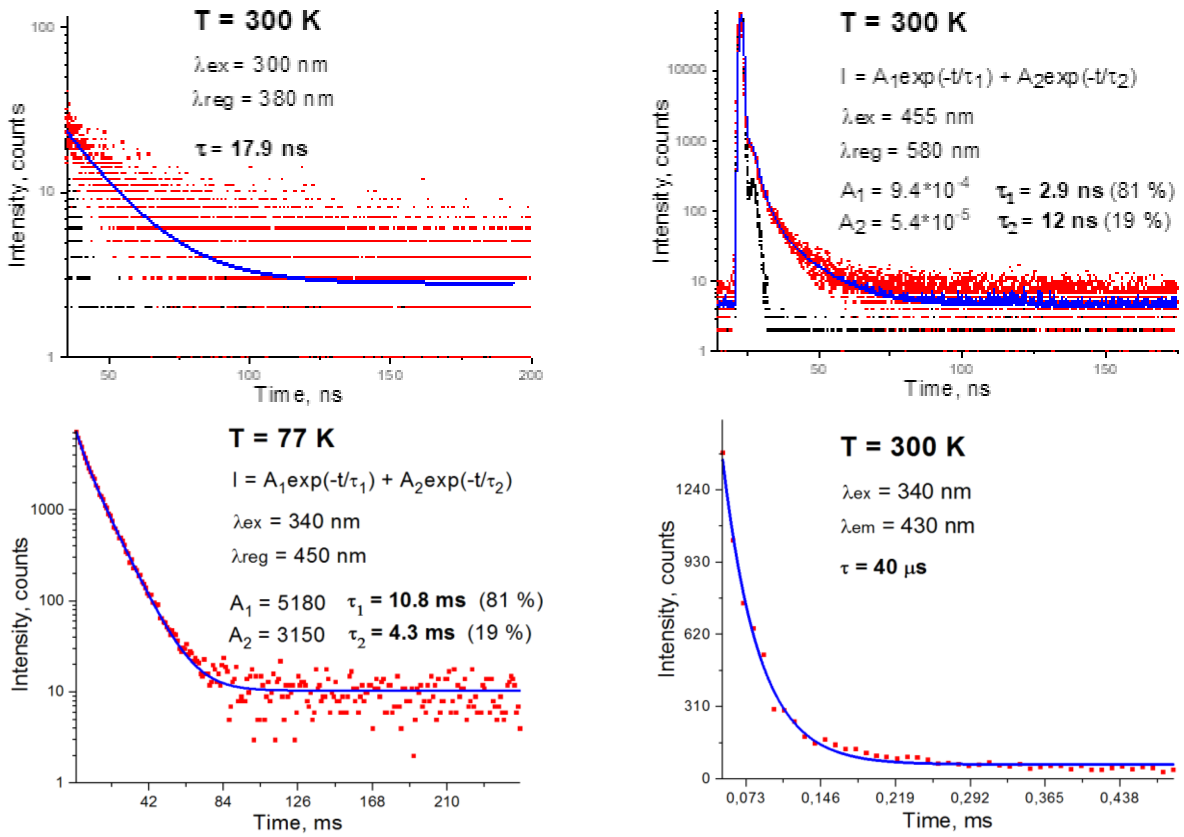


Fig. S28. Luminescence decay curves for the complex **1**.

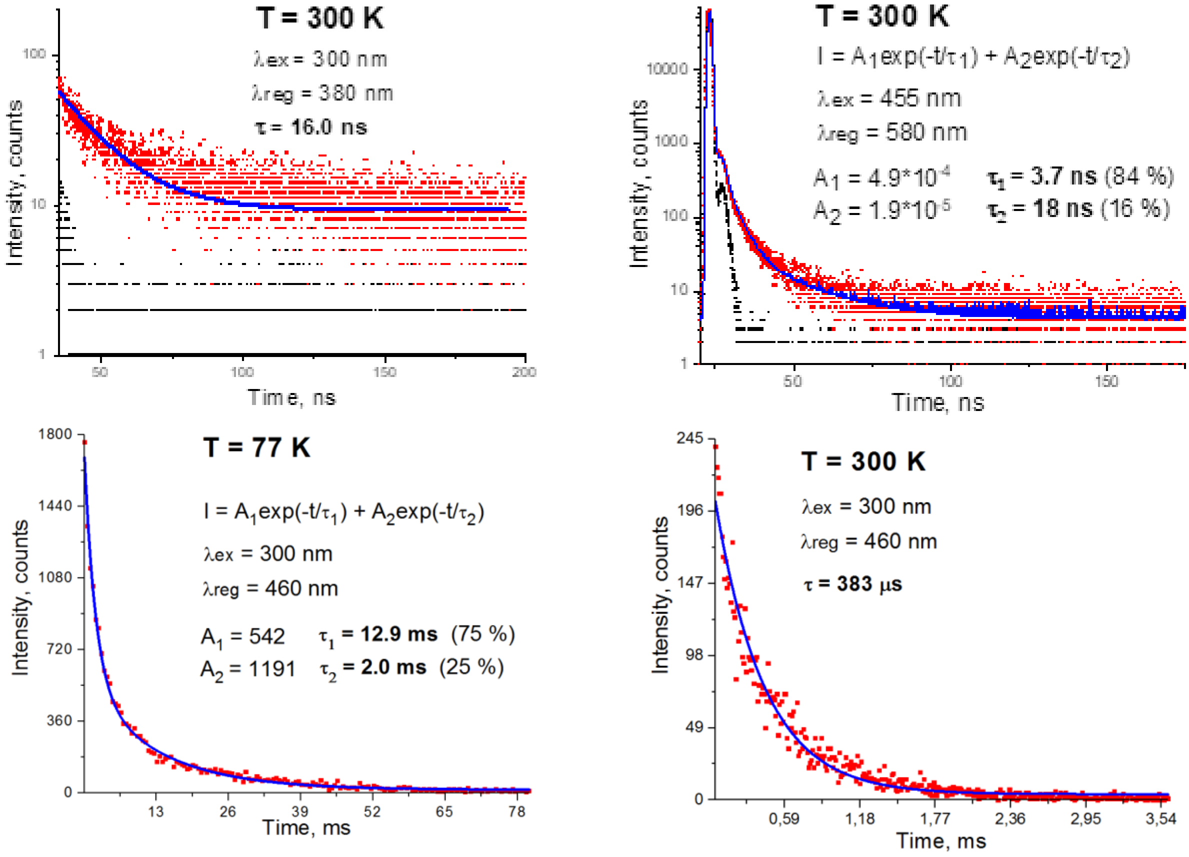


Fig. S29. Luminescence decay curves for the complex **2**.

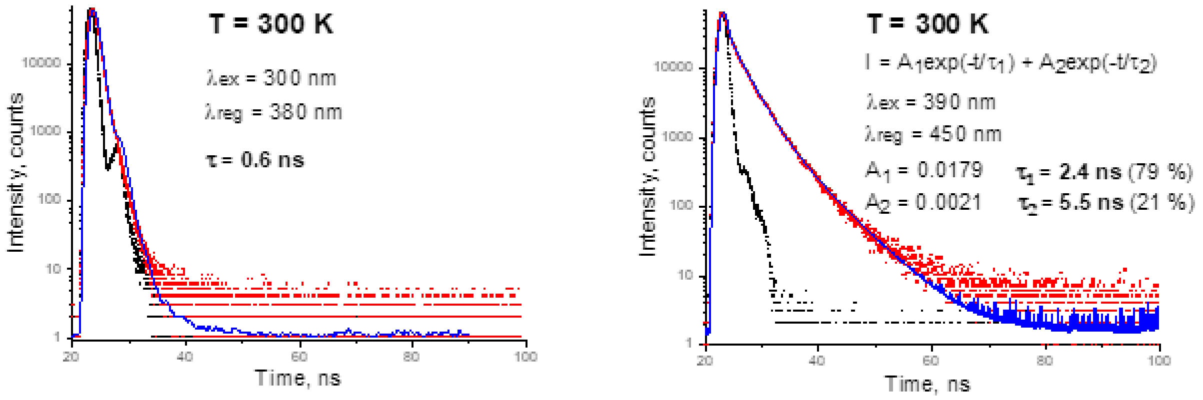


Fig. S30. Luminescence decay curves for **L**.

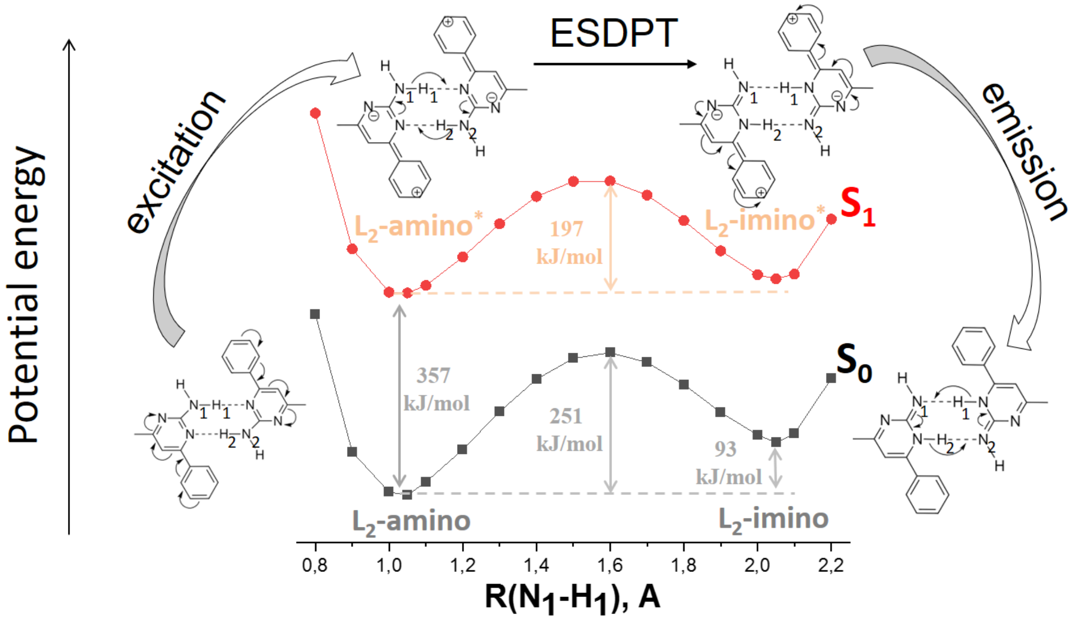
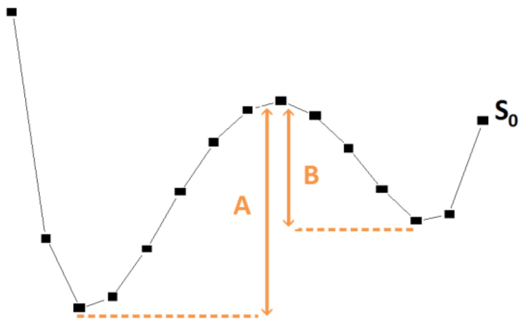


Fig. S31. 2D potential energy curves for the ground and first singlet excited states of $\mathbf{L_2}$ with variation of N_1–H_1 and N_2–H_2 bond lengths in a concerted double proton transfer process (B3LYP/DGDZVP).

Considering that the hydrogen atoms are transferred collectively and symmetrically, we have plotted the potential energy of the dimers $\mathbf{L_2}$ as a function of the proton transfer reaction coordinate (Fig. S31). We have optimized the structures of the dimeric associates in the ground state (S_0) keeping the N_1–H_1 and N_2–H_2 bond lengths between 0.8 to 2.2 Å. The energy curve of the first excited singlet state (S_1) was obtained by the vertical transition of each ground state optimized geometry followed by optimization of the excited state using TD–DFT calculations. There are two minima both in the ground state and in the first excited singlet state corresponding to $\mathbf{L_2}$**-amino** ($R_{N1-H1} = R_{N2-H2} = 1.05 \pm 0.05$ Å) and $\mathbf{L_2}$**-imino** ($R_{N1-H1} = R_{N2-H2} = 2.05 \pm 0.05$ Å) forms. Computations performed at different levels of theory for the ground state indicate that the energy barrier is weakly dependent on the level of theory (Table S27).

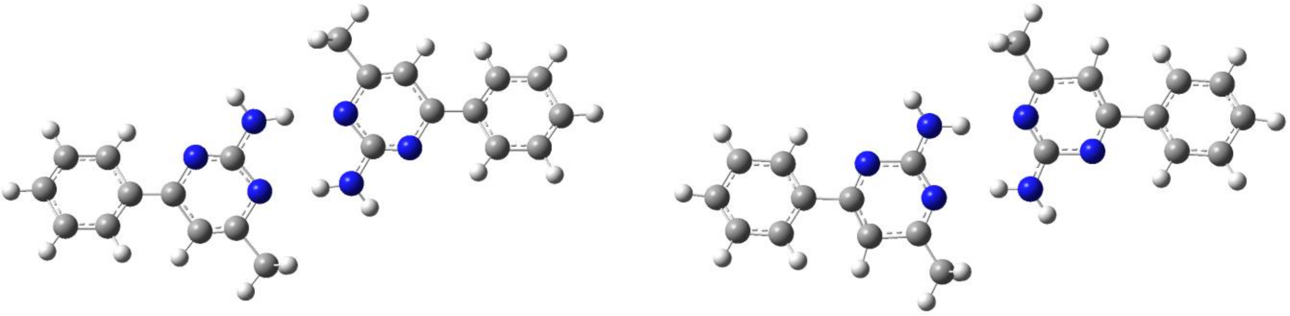
Apart from the concerted ESDPT process, we have also explored the possibility of stepwise double proton transfer in $\mathbf{L_2}$. Potential energy curve for the ground state of $\mathbf{L_2}$ associates (Fig. S32) reveals that two transition states and metastable intermediate structure exist along reaction coordinate. The energy barriers are lower than a single barrier in the concerted mechanism but remain rather high.

Table S27. Energy barriers for the ground state potential energy curve calculated at different levels of theory.

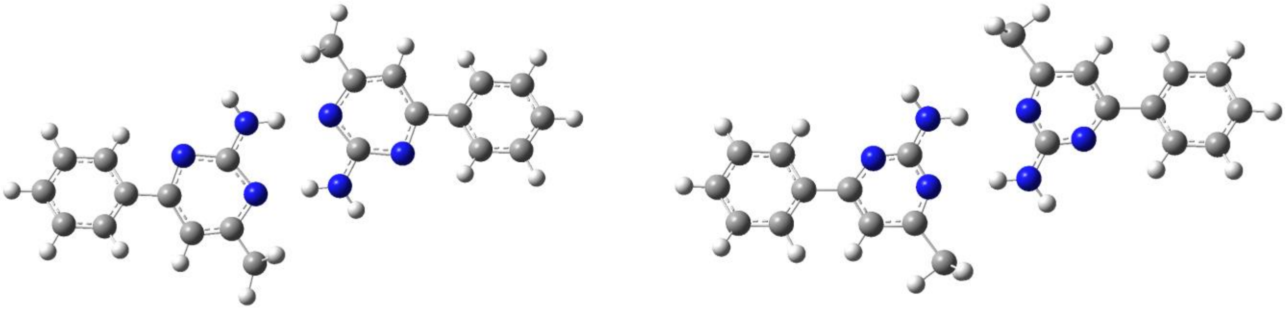


Level of theory	Barrier **A**, kJ/mol	Barrier **B**, kJ/mol
B3LYP/DGDZVP	251	158
B3LYP/LANL2DZ	239	138
CAM-B3LYP/6-311G	258	151
BP86/LANL2DZ	200	109
PBE0/6-311G	208	122
B3LYP/6-31++G(d,p)	254	163

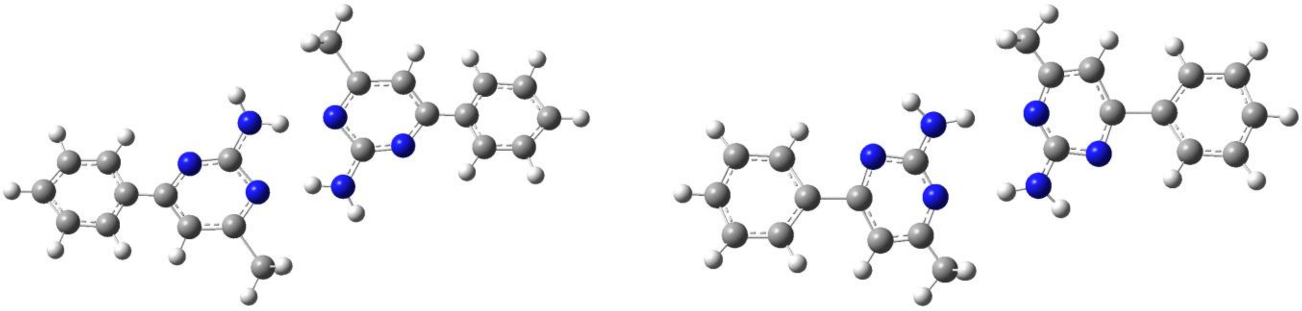
Table S28. Vibrations of nitrogen atoms involved in N–H...N hydrogen bonds towards each other in the IR spectrum of $\mathbf{L_2}$



ν = **1623 cm^{-1}**



ν = **980 cm^{-1}**



ν = **884 cm^{-1}**

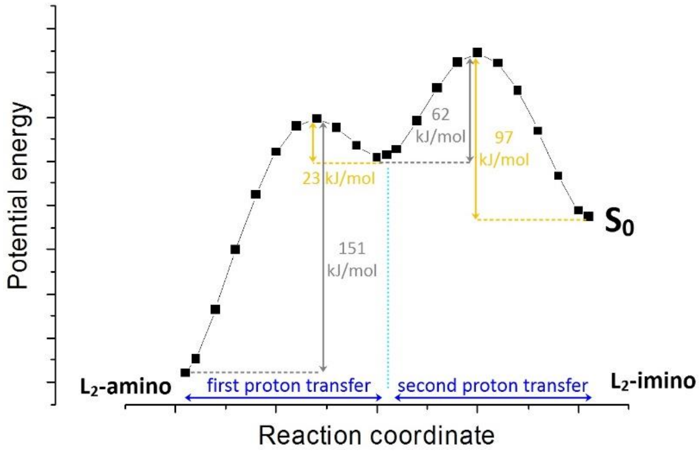


Fig. S32. 2D potential energy curve for the ground state of $\mathbf{L_2}$ with variation of N–H bond lengths in a stepwise double proton transfer process.

Purity of 1 and 2

In some cases, excitation wavelength dependent emission may be related to the presence of impurities. Emission bands C/C' and B/B' of the complexes **1** and **2** are similar to the high- and low-energy emission bands of **L** in the solid state. Therefore, we paid special attention to rule out the possibility of the presence of impurities of **L**. According to analytical and PXRD data the complexes **1** and **2** are chemically and phase pure. Emission bands C/C' and B/B' of the complexes **1** and **2** are not associated with impurities of **L** for the following reasons. (1) The maxima of emission bands C and B of the complex **1** are red-shifted to the maxima of the high- and low-energy band of **L** at 300 K (390 nm vs 375 nm and 467 nm vs 450 nm, respectively); the maximum of emission band C' of the complex **2** is blue-shifted to the maximum of the high-energy band of **L** (372 nm vs 375 nm). (2) At 77 K and λ_{ex} = 340 nm the complex **1** demonstrates pure phosphorescence (emission A); impurity of **L** would cause appearance of a high-intense band at 375 nm. (3) The reported results are reproducible on different samples of the complexes **1** and **2**, some of these samples were synthesized in different molar ratio with excess of Ag(I). In this context, the excitation wavelength dependent behavior of the complexes **1** and **2** cannot originate from impurities.

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