SUPPORTING INFORMATION FOR

Synthesis and luminescence of indium(III) complexes with (1*H*-pyrazol-1-yl)pyridazines

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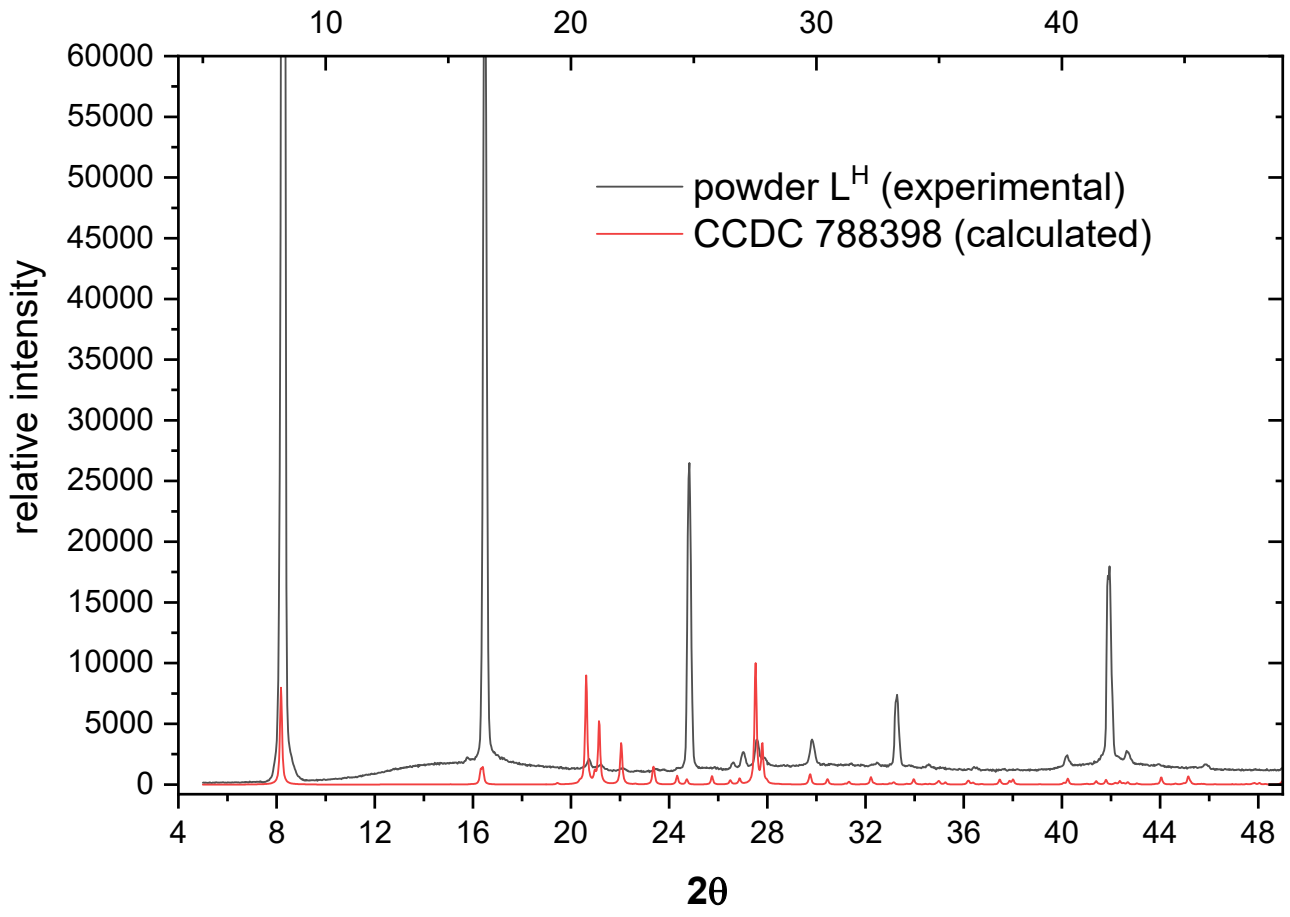

Fig. S1. Experimental and calculated X-ray powder diffraction patterns for L^H.

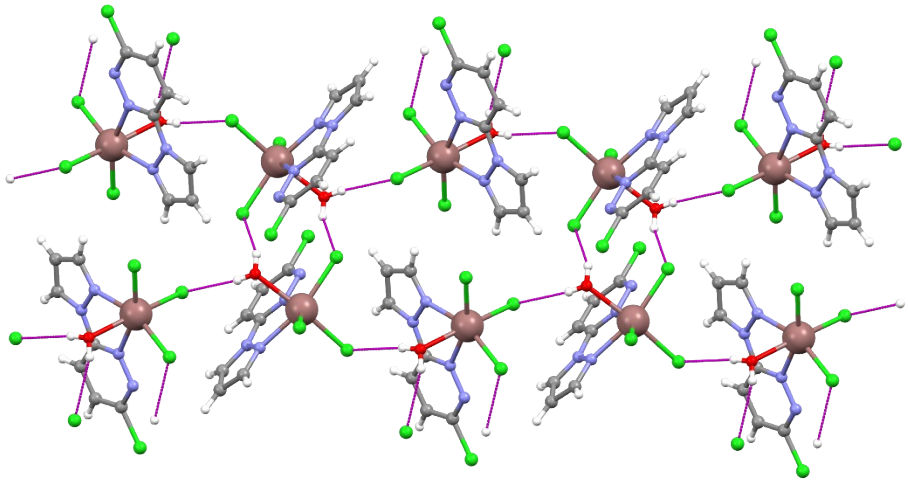

Fig. S2. Intermolecular H-bonds between the hydrogen and chlorine atoms in the structure of **1**

Table S1. SCXRD experimental details for complex **1**

	1
Crystal data	
Chemical formula	$C_7H_7Cl_4InN_4O$
M_r	419.79
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, b, c (Å)	9.1643 (4), 12.6992 (7), 11.5642 (6)
β (°)	105.336 (2)
V (Å^3)	1297.91 (11)
Z	4
F(000)	808
Radiation type	Mo $K\alpha$
m (mm^{-1})	2.63
Crystal size (mm)	0.08 × 0.06 × 0.03
Diffractometer	Bruker D8 Venture diffractometer
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.634, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14830, 3508, 3034
R_{int}	0.039
θ values (°)	θ_{max} = 29.2, θ_{min} = 2.4
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.685
Range of h, k, l	h = -12→12, k = -17→17, l = -15→15
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.025, 0.052, 1.05
No. of reflections	3508
No. of parameters	160
No. of restraints	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.015P)^2 + 0.8122P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.52, -0.58

Table S2. SCXRD experimental details for complex **2**

	2
Crystal data	
Chemical formula	$C_{18}H_{18}Cl_4InN_8 \cdot Cl_4In$
M_r	859.64
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	17.0936 (4), 12.9476 (3), 13.3085 (3)
β (°)	90.045 (1)
V (Å^3)	2945.45 (12)
Z	4
F(000)	1664
Radiation type	Mo $K\alpha$
m (mm^{-1})	2.32
Crystal size (mm)	0.19 × 0.12 × 0.05
Diffractometer	Bruker D8 Venture diffractometer
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.605, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	49293, 7326, 6057
R_{int}	0.051
θ values (°)	θ_{max} = 28.3, θ_{min} = 2.0
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.667
Range of h, k, l	h = -22→22, k = -17→17, l = -17→17
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.079, 1.05
No. of reflections	7326
No. of parameters	329
No. of restraints	0
H-atom treatment	H-atom parameters constrained
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0244P)^2 + 7.7476P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.17, -0.69

Computer programs: Bruker *APEX3*, Bruker *SAINT*, *SHELXT* 2018/2 (Sheldrick, 2018), *SHELXL2019*/2 (Sheldrick, 2019), ShelXle (Hübschle, 2011), *enCIFer* (Allen *et al.*, 2004).

Table S3. Optimized geometry coordinates for complex **1** in CH_3CN

In	3.359934000	9.242474000	6.053460000
N	1.641493000	10.551893000	5.246047000
Cl	3.365100000	10.344237000	8.243798000
N	0.368438000	10.129979000	5.472943000
Cl	4.630307000	7.210448000	6.538705000
N	1.183790000	7.145532000	7.235359000
Cl	4.989105000	10.587026000	4.810401000
Cl	-0.031271000	5.179579000	8.412932000
O	2.843405000	8.123857000	4.001498000
H	3.326293000	7.273685000	4.038091000
H	3.258790000	8.615918000	3.265837000
N	1.250486000	8.282959000	6.555066000
C	0.149809000	8.939252000	6.176996000
C	-0.537185000	11.007509000	4.936875000
H	-1.606774000	10.846137000	5.009644000
C	-1.138857000	8.466084000	6.473365000
H	-2.036291000	9.001804000	6.170370000
C	-0.012886000	6.662182000	7.532266000
C	-1.221607000	7.285053000	7.174064000
H	-2.181101000	6.846835000	7.444633000
C	1.541355000	11.694019000	4.568971000
H	2.443473000	12.221261000	4.272179000
C	0.186729000	12.022675000	4.350073000
H	-0.209370000	12.887934000	3.830602000

Table S4. Optimized geometry coordinates for complex **2** in CH_3CN

In	5.247215000	3.583875000	4.082621000
N	6.548850000	4.700704000	2.556694000
N	5.944324000	5.787041000	1.962536000
Cl	6.843697000	2.617626000	5.633267000
N	3.922766000	4.979011000	2.734844000
Cl	7.862648000	8.499764000	5.578640000
N	2.601767000	4.899060000	2.807780000
Cl	4.692999000	1.669211000	2.702110000
Cl	0.171394000	5.580327000	2.215175000
N	3.253152000	5.036482000	6.022342000
N	5.348744000	5.623136000	5.244288000
N	3.478835000	3.769537000	5.530390000
N	6.424577000	6.389419000	5.130865000
C	4.310269000	5.952196000	6.023204000
C	1.946638000	5.162945000	6.463070000
C	6.457321000	7.527011000	5.806078000
C	1.356845000	3.934434000	6.250741000
H	0.329595000	3.674707000	6.484752000
C	4.547550000	5.826665000	1.907469000
C	4.331438000	7.128265000	6.794698000
H	3.530910000	7.384258000	7.480867000
C	1.882380000	5.701117000	2.039316000
C	2.331817000	3.095798000	5.670499000
C	1.323729000	6.395003000	7.013140000
H	1.528391000	7.275173000	6.387562000
H	1.664811000	6.608390000	8.037506000
H	0.238904000	6.241681000	7.049349000
C	5.434092000	7.943445000	6.674279000
H	5.521454000	8.868128000	7.242993000
C	2.182415000	1.680957000	5.243394000
H	1.792008000	1.633981000	4.215240000
H	1.467043000	1.168054000	5.898581000
H	3.141556000	1.151013000	5.263142000

C	6.894527000	6.673366000	1.484528000
C	3.816597000	6.659570000	1.040658000
H	4.300260000	7.309073000	0.318282000
C	7.868082000	4.888519000	2.441437000
C	8.117993000	6.107702000	1.776216000
H	9.087336000	6.534771000	1.540766000
C	2.443384000	6.599910000	1.116425000
H	1.812468000	7.211935000	0.473457000
C	8.858290000	3.915094000	2.968755000
H	8.418009000	2.919608000	3.094420000
H	9.233319000	4.247392000	3.948937000
H	9.716966000	3.851272000	2.287741000
C	6.620495000	7.981223000	0.834659000
H	6.263332000	7.863360000	-0.199573000
H	7.558412000	8.547727000	0.798637000
H	5.880476000	8.571333000	1.393126000

Table S5. Summary of main energy, wavelength and oscillator strength computed for observed transitions in the absorption spectra of **1**, **2** and L^H, together with the orbitals implied.

Complex	Energy, eV	λ, nm	*f*	Major contributions	Character
1	4.34	286	0.089	HOMO → LUMO (85%)	π(L) → π*(L)
	4.81	258	0.272	HOMO-4 → LUMO (18%) HOMO → LUMO+1 (63%)	π(L+Cl) → π*(L) π(L) → π*(L)
	4.91	252	0.113	HOMO-4 → LUMO (37%) HOMO → LUMO+1 (13%)	π(L+Cl) → π*(L) π(L) → π*(L)
	4.95	251	0.075	HOMO-8 → LUMO+1 (11%) HOMO-2 → LUMO+1 (14%)	π(L+Cl) → π*(L) π(L+Cl) → π*(L)
	5.65	219	0.077	HOMO-10 → LUMO (31%) HOMO-7 → LUMO+1 (46%)	π(L+Cl) → π*(L) π(L+Cl) → π*(L)
	5.67	218	0.098	HOMO-11 → LUMO (27%) HOMO-10 → LUMO (23%) HOMO-8 → LUMO+1 (36%)	π(L+Cl) → π*(L) π(L+Cl) → π*(L) π(L+Cl) → π*(L)
Below L is the first coordinated L^{Me} molecule in cation part of **2**, L' is the second coordinated L^{Me} molecule in cation part of **2**.					
2	4.01	309	0.103	HOMO → LUMO (94%)	π(LL') → π*(LL')
	4.71	263	0.178	HOMO-1 → LUMO+2 (11%) HOMO-1 → LUMO+3 (11%) HOMO → LUMO+2 (37%) HOMO → LUMO+3 (35%)	π(LL') → π*(L) π(LL') → π*(L') π(LL') → π*(L) π(LL') → π*(L')
	4.75	261	0.602	HOMO-1 → LUMO (10%) HOMO → LUMO+2 (32%) HOMO → LUMO+3 (38%)	π(LL') → π*(LL') π(LL') → π*(L) π(LL') → π*(L')
	5.42	229	0.134	HOMO-11 → LUMO+1 (13%) HOMO-10 → LUMO (76%)	π(LL') → π*(LL') π(LL') → π*(LL')
	5.43	228	0.078	HOMO-11 → LUMO (72%) HOMO-10 → LUMO+1 (14%)	π(LL') → π*(LL') π(LL') → π*(LL')
L^H	4.37	284	0.052	HOMO → LUMO (95%)	π → π*
	4.72	263	0.101	HOMO-1 → LUMO (31%) HOMO → LUMO+1 (66%)	π → π*
	4.88	254	0.603	HOMO-1 → LUMO (67%) HOMO → LUMO+1 (31%)	π → π*
	5.79	214	0.074	HOMO-3 → LUMO (89%)	π → π*

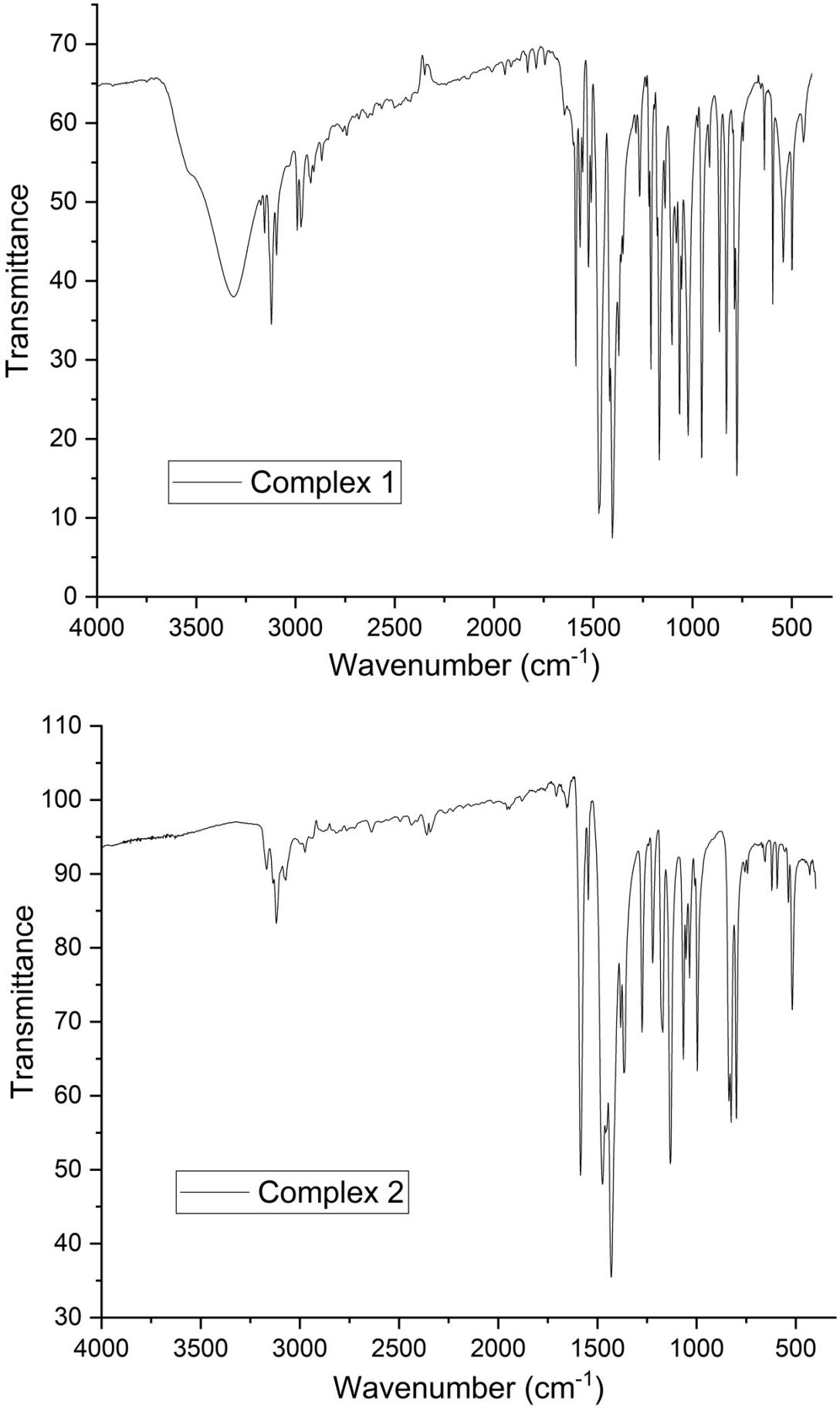

Fig. S3. IR spectra of complexes **1** and **2**

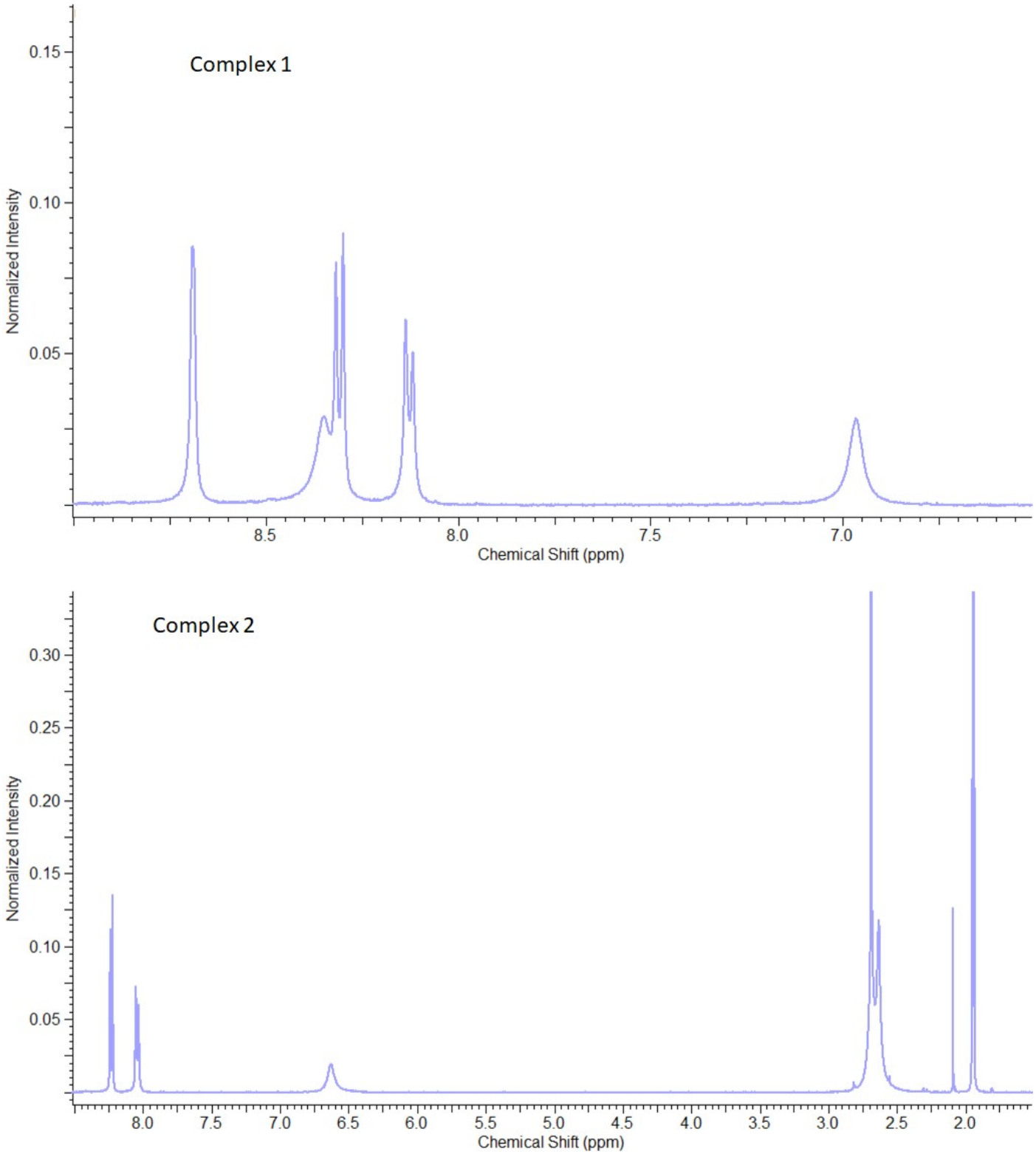

Fig. S4. NMR spectra of complexes **1** and **2** in CD_3CN

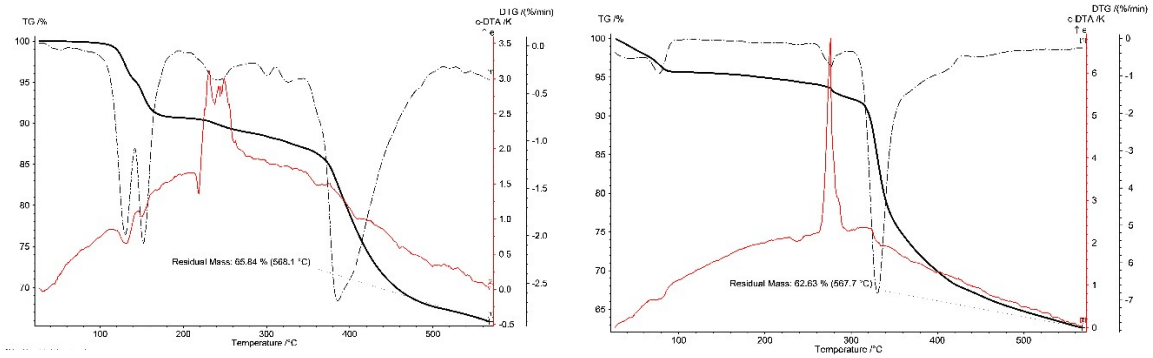

Fig. S5. TGA, DTG and DTA curves for the thermal decomposition of **1** (left) and **2** (right).

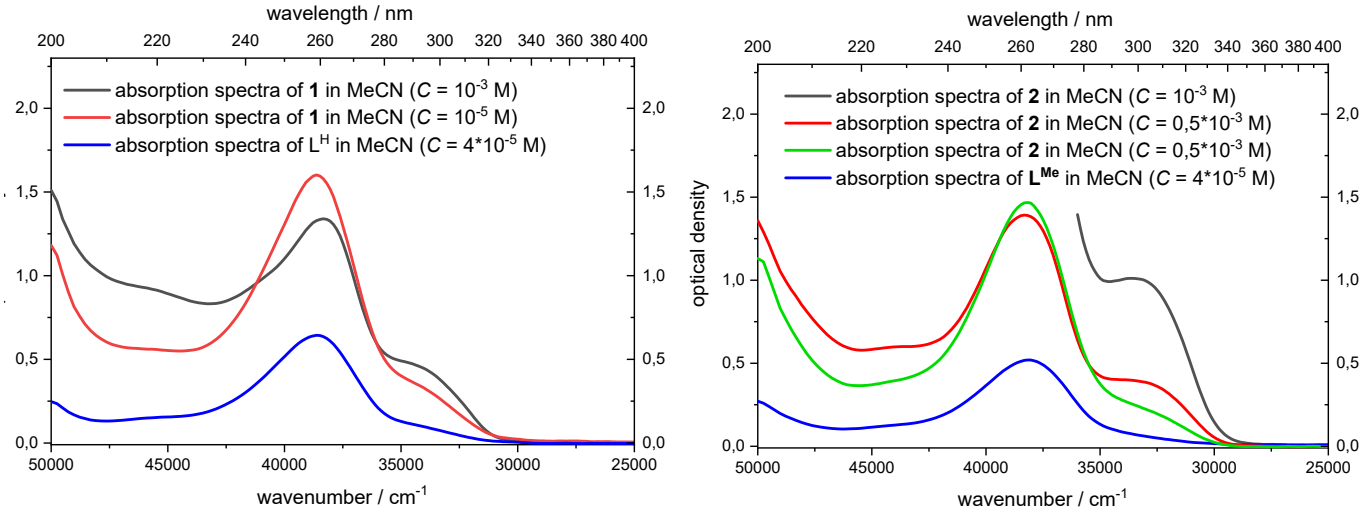

Fig. S6. Absorption spectra of complexes **1** and L^{H} (*left*). Absorption spectra of complexes **2** and L^{Me} (*right*).

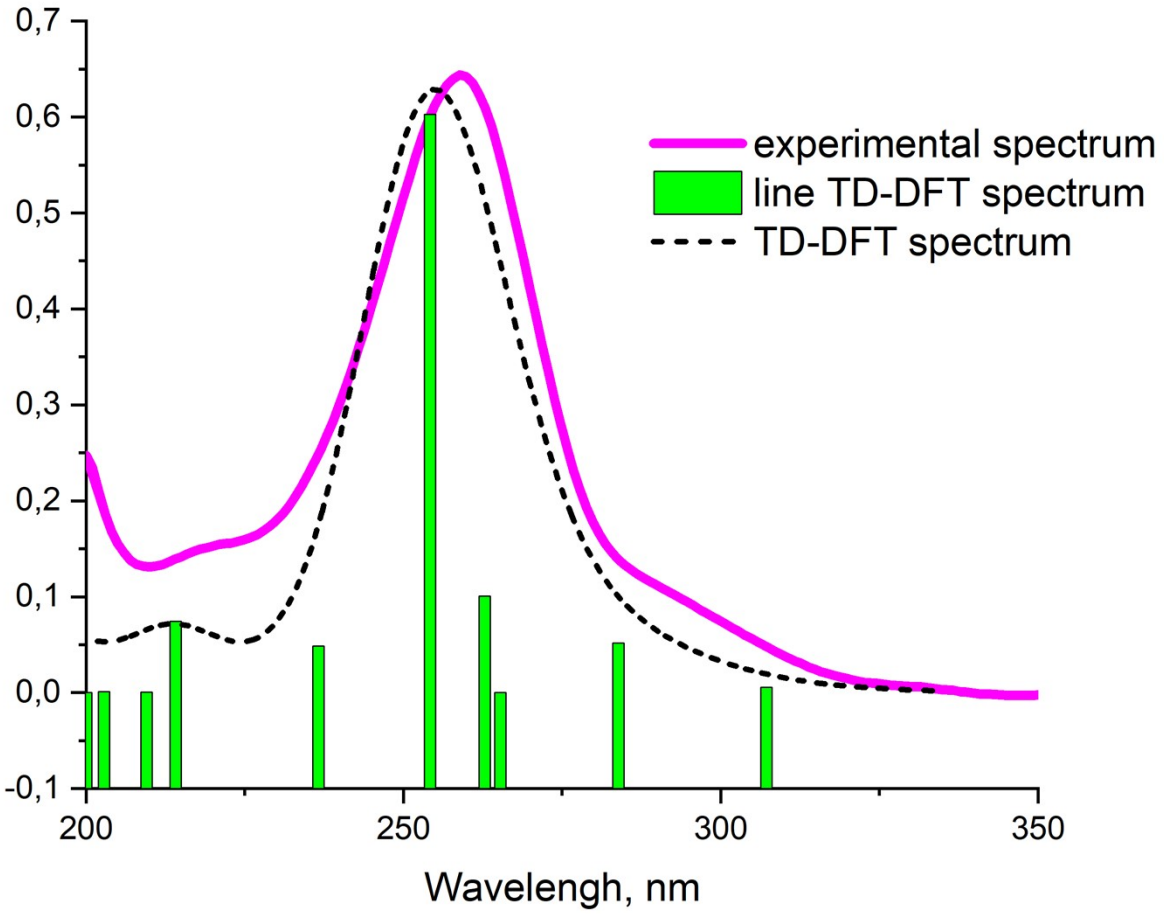

Fig. S7. Experimental and calculated (TD-DFT) electronic absorption spectrum of L^H in acetonitrile.

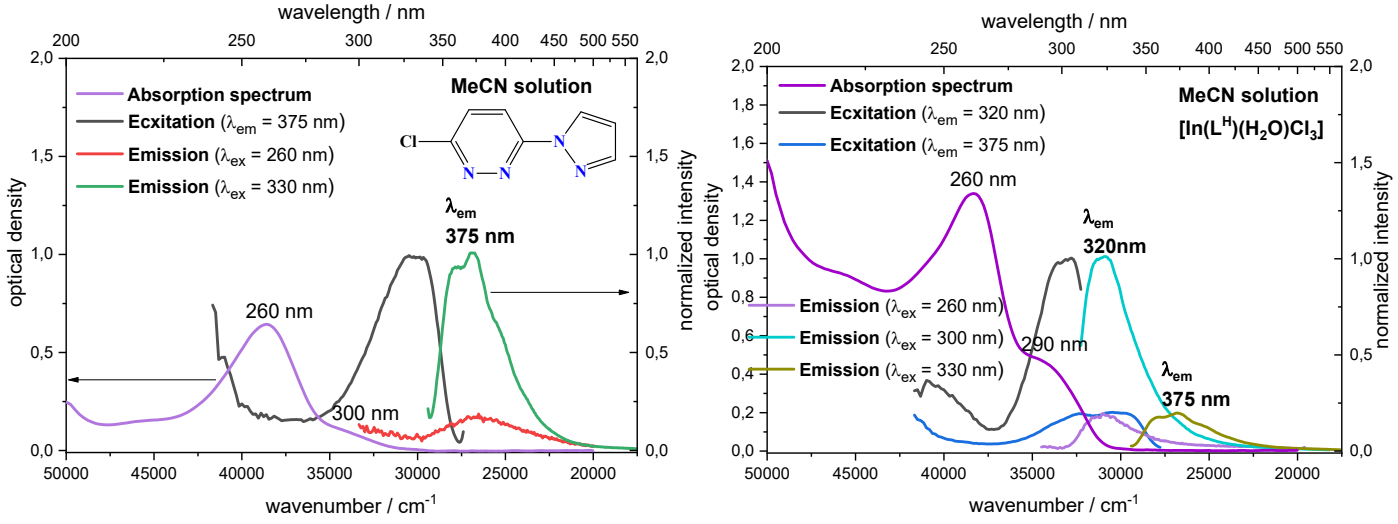

Fig. S8. Emission, excitation and absorption spectra of L^H (left) and **1** (right) in MeCN solution.

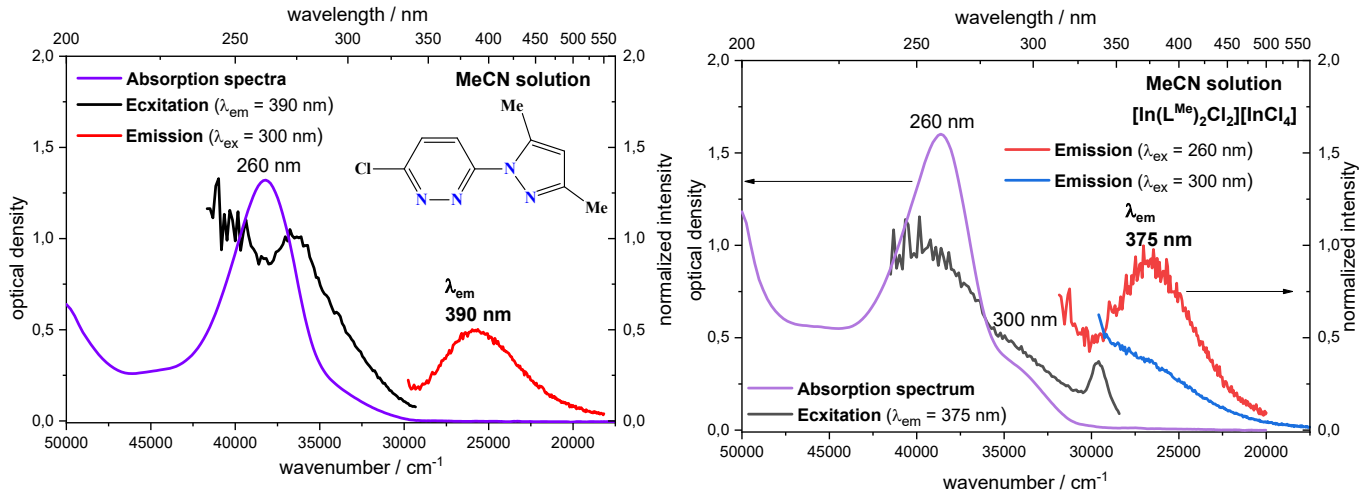

Fig. S9. Emission, excitation and absorption spectra of L^{Me} (left) [5] and **2** (right) in MeCN solution.

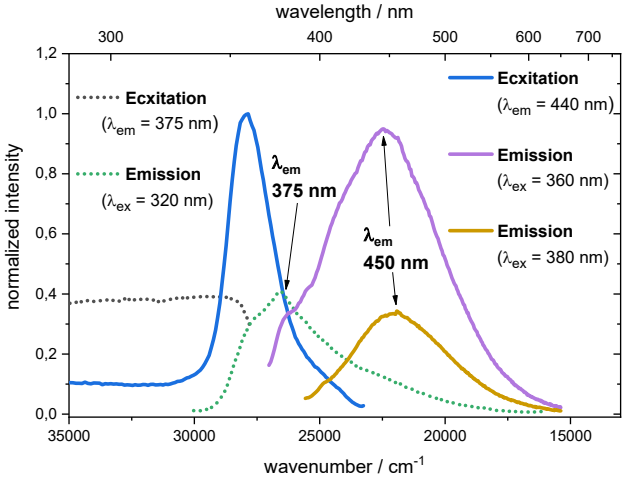

Fig. S10. Emission and excitation spectra of L^{Me} [5] in the solid state.

Table S6. *CIE* 1931coordinates for the indium(III) complexes in the solid state

		x	*y*
complex **1**	λ_{ex} = 340 nm	0.1752	0.2118
	λ_{ex} = 420 nm	0.2966	0.4270
complex **2**	λ_{ex} = 340 nm	0,1751	0,1253
	λ_{ex} = 420 nm	0,2834	0,3961