Electronic Supplementary Information (ESI)

Solvent vapour-responsive structural transformations in molecular crystals composed of a luminescent mononuclear aluminium(III) complex

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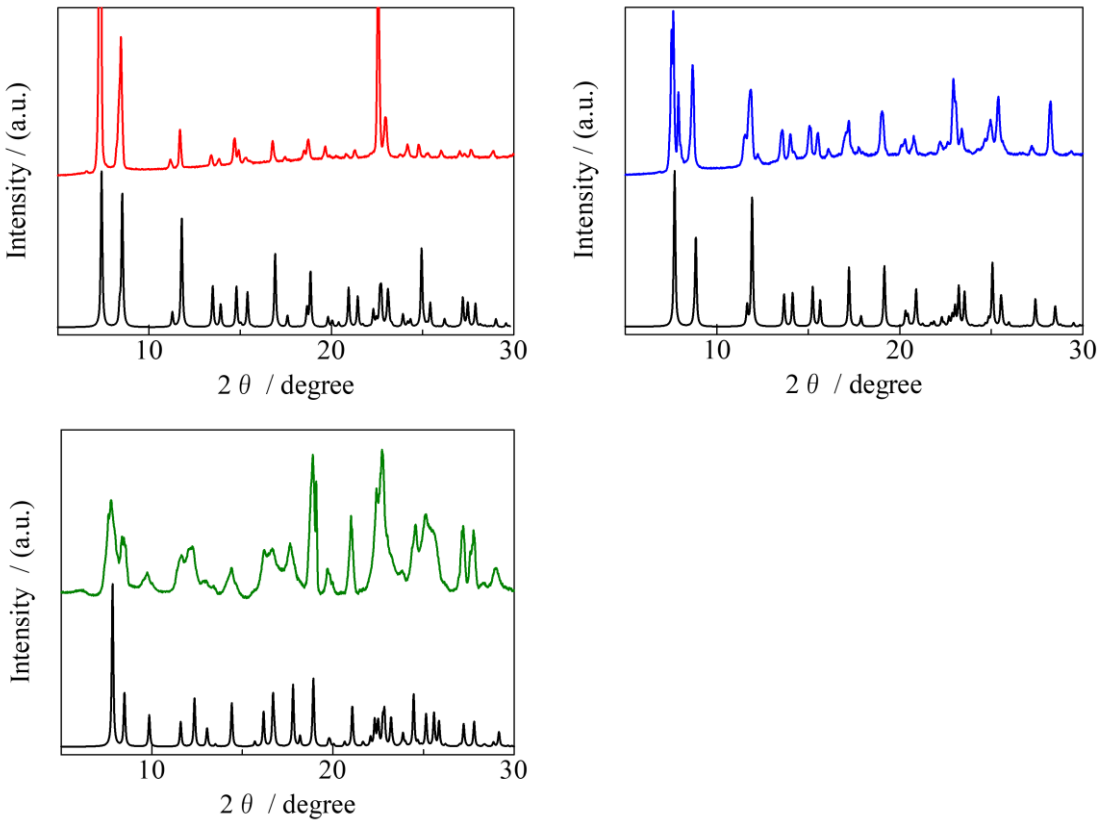

Figure S1. PXRD patterns for the crystalline samples of **Al·Me$_2$CO** (red) and **Al·MeCN** (blue) and **Al·DMSO** (green) at 298 K and their simulations (black). The additional peak observed for **Al·MeCN** (2θ = 8°) and **Al·DMSO** are attributed to the de-solvation of lattice solvents on the crystal surface.

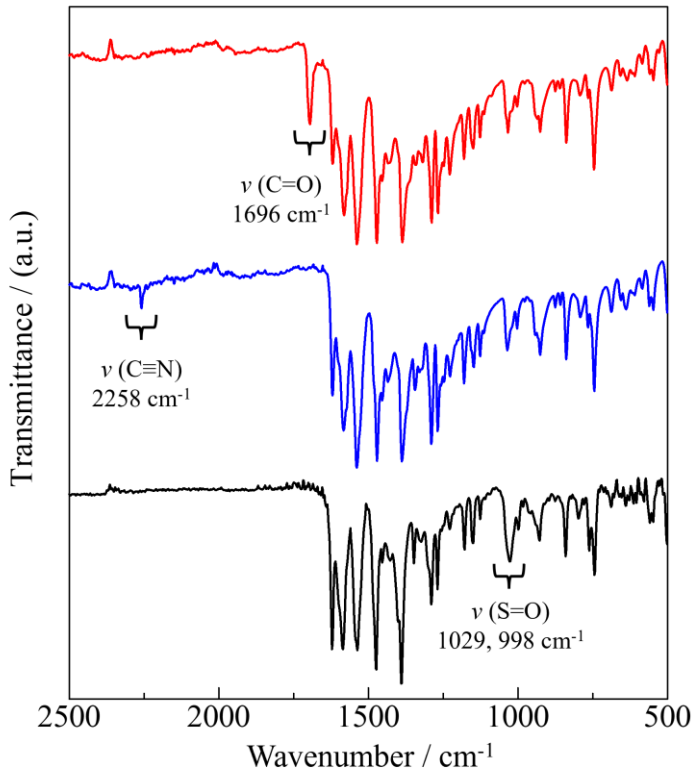

Figure S2. FT-IR spectra for **Al·Me$_2$CO** (red), **Al·MeCN** (blue) and **Al·DMSO** (black).

Table S1. Crystallographic data for **Al·Me$_2$CO**, **Al·MeCN** and **Al·DMSO**.

Compound	**Al·Me$_2$CO**	**Al·MeCN**	**Al·DMSO**
Temperature / K	173	173	173
Formula	$C_{21}H_{24}NAlO_6$	$C_{20}H_{21}N_2AlO_5$	$C_{20}H_{24}NSAlO_6$
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*P*bca (#61)	*P*bca (#61)	$P2_1/n$ (#14)
a / Å	20.5632(7)	20.2047(13)	13.6042(18)
b / Å	8.3967(2)	8.4969(6)	8.4261(11)
c / Å	23.2444(7)	22.9627(15)	17.987(2)
α / °	90	90	90
β / °	90	90	94.771(5)
γ / °	90	90	90
V / Å^3	4013.4(2)	3942.2(5)	2054.8(5)
Z	8	8	4
D_{calc} / g cm^{-3}	1.368	1.336	1.401
μ / mm^{-1}	0.140	0.137	0.238
F(000)	1744	1664	912
R_1, wR_2 ($I > 2\sigma(I)$)	0.0407, 0.0916	0.0655, 0.1391	0.0984, 0.1184
R_1, wR_2 (for all data)	0.0613, 0.1068	0.1523, 0.2035	0.2526, 0.2692
GOF	1.071	1.056	1.054
Reflections/Parameters	4098/267	4039/257	3565/268
CCDC	2337339	2337340	2337341

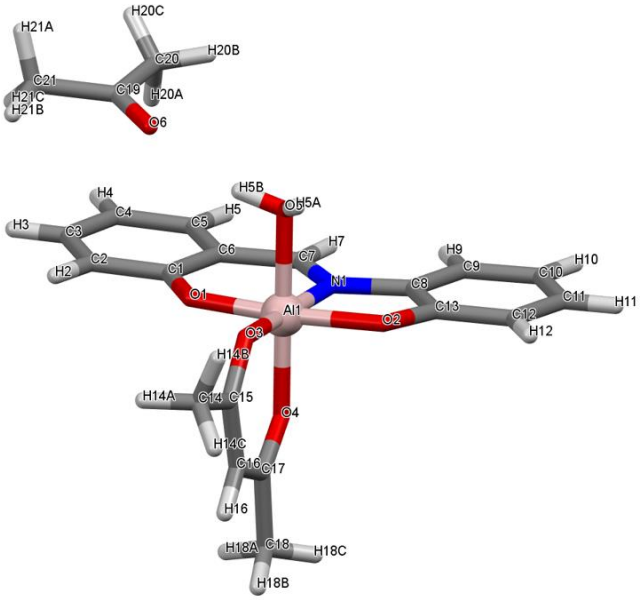

Figure S3. Crystal structure of **Al·Me$_2$CO** at 173 K with the atom-numbering scheme.

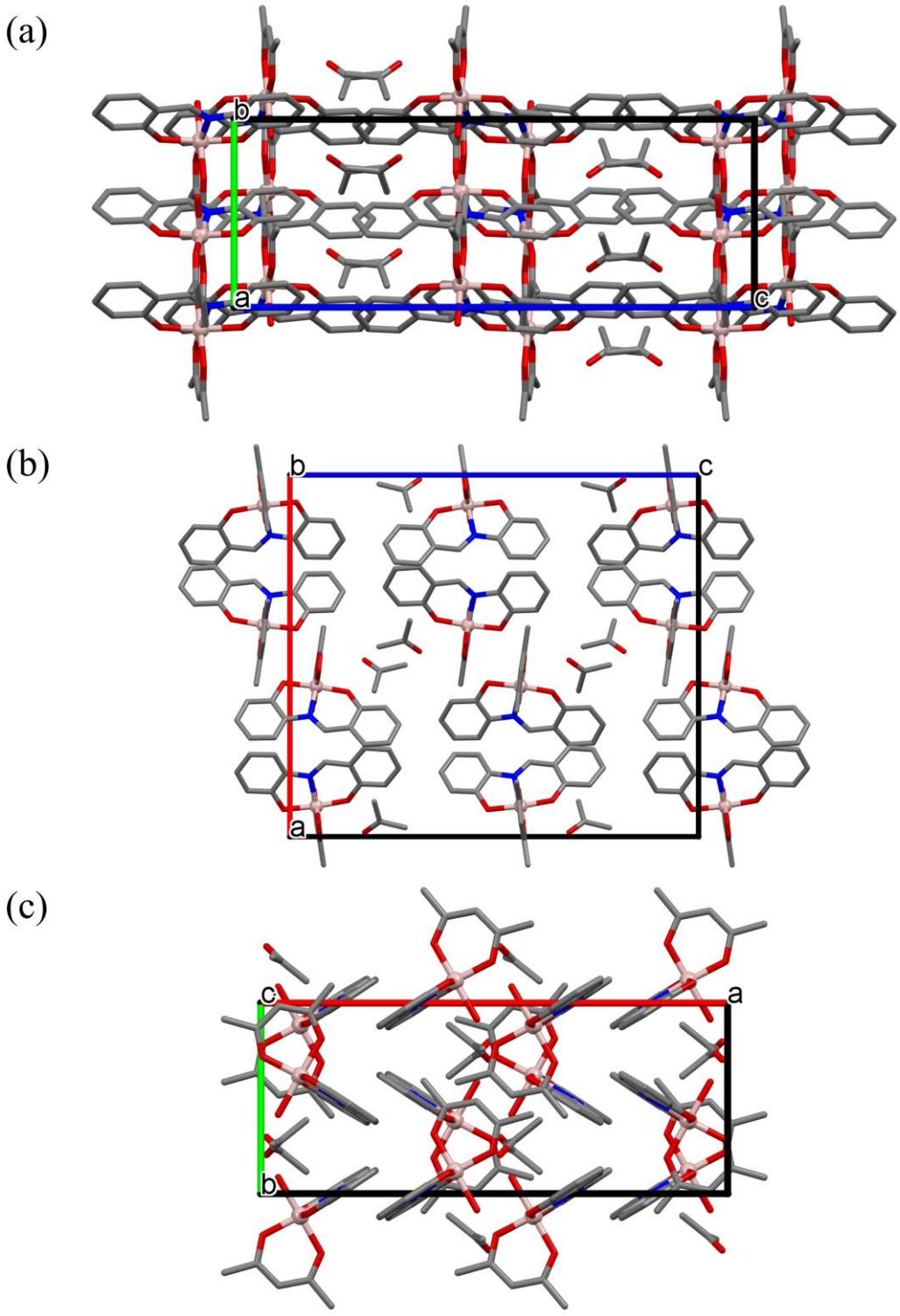

Figure S4. Crystal packing structures for **Al·Me$_2$CO** at 173 K along (a) *a*, (b) *b*, (c) *c* axes. Hydrogen atoms are omitted for clarity.

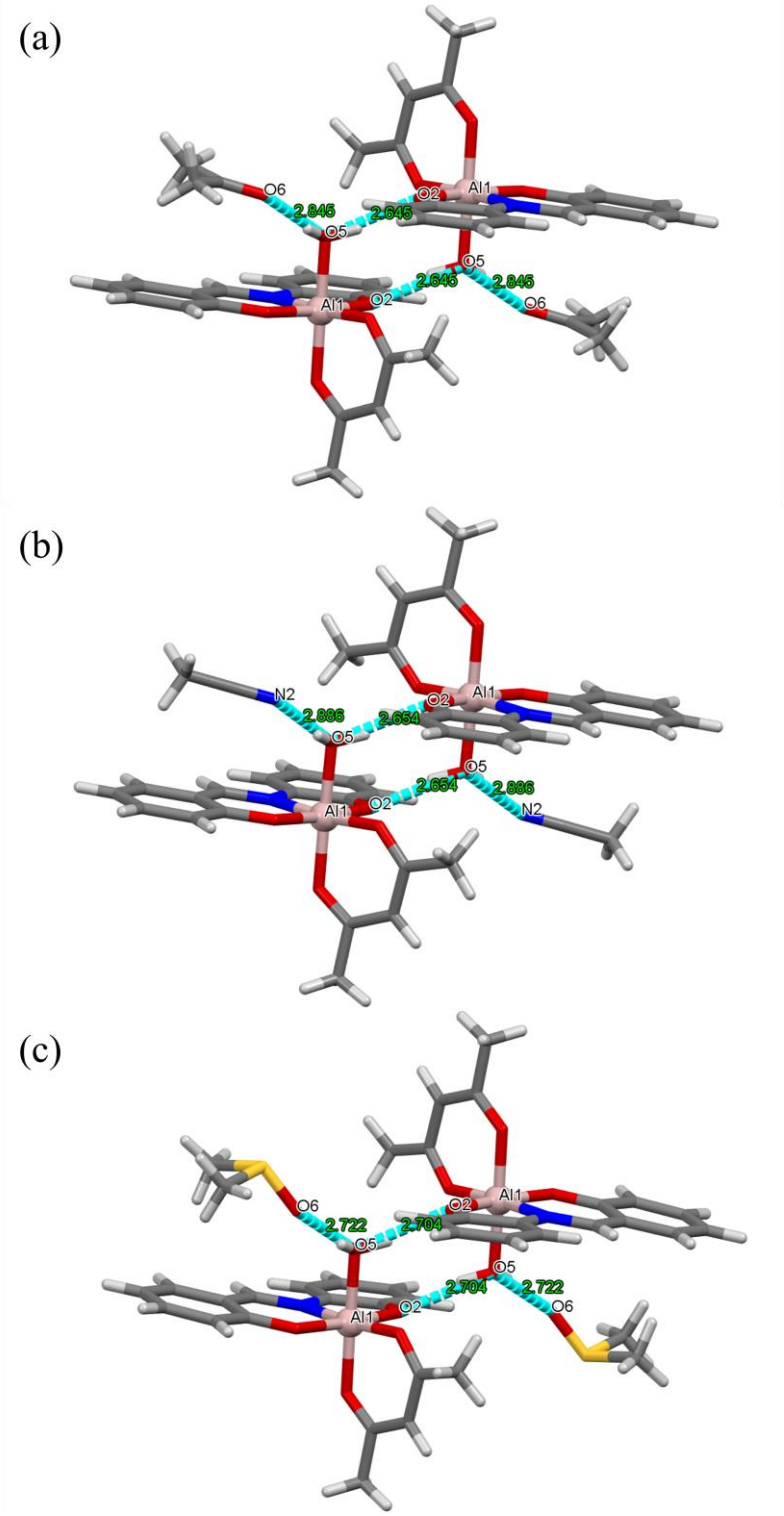

Figure S5. Dimeric structure constructed by hydrogen bonding of (a) **Al·Me$_2$CO**, (b) **Al·MeCN** and (c) **Al·DMSO** (bottom).

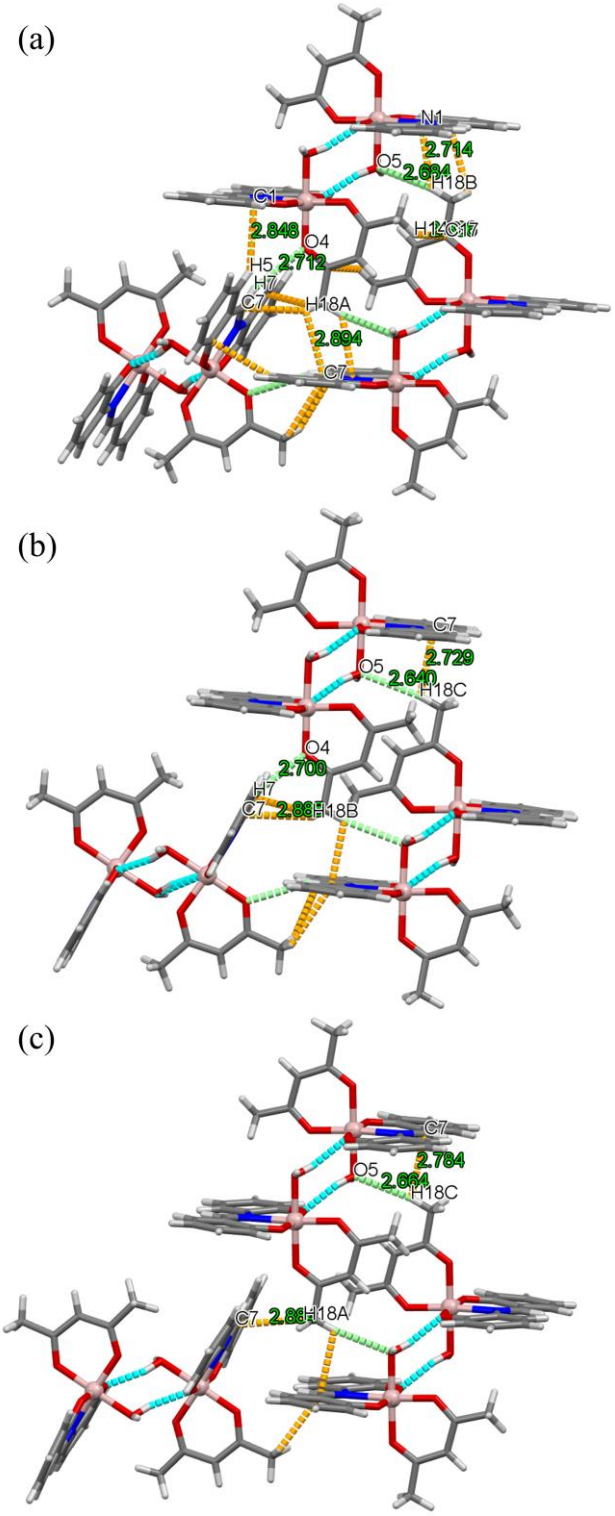

Figure S6. Intermolecular interactions of (a) **Al·Me$_2$CO**, (b) **Al·MeCN** and (c) **Al·DMSO** in the crystal at 173 K. Blue dashed lines represent the hydrogen-bonding of dimers, orange dashed lines represent the CH–π interaction and light green dashed lines represent the CH–O interaction between each dimer.

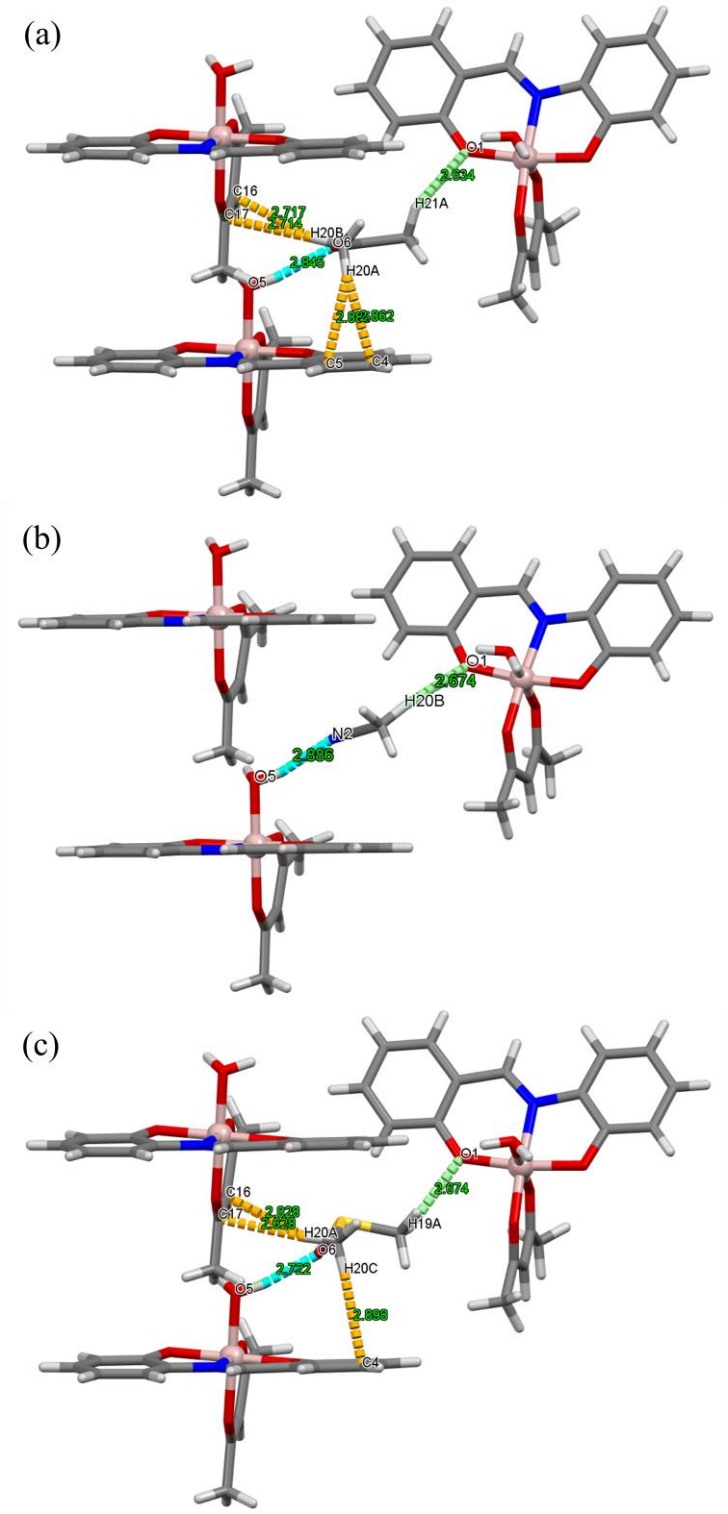

Figure S7. Intermolecular interactions around the lattice solvent in (a) **Al·Me$_2$CO**, (b) **Al·MeCN** and (c) **Al·DMSO** at 173 K. Blue dashed lines represent the hydrogen-bonding of dimers, orange dashed lines represent the CH–π interaction and light green dashed lines represent the CH–O interaction between each dimer.

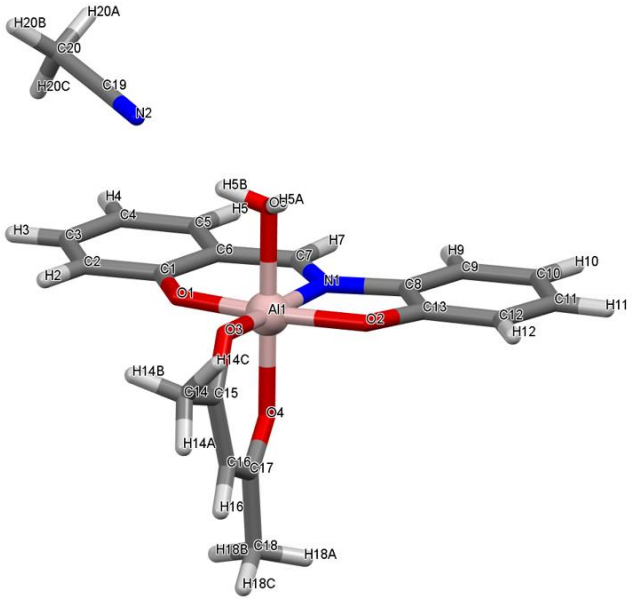

Figure S8. Crystal structure of **Al·MeCN** at 173 K with the atom-numbering scheme.

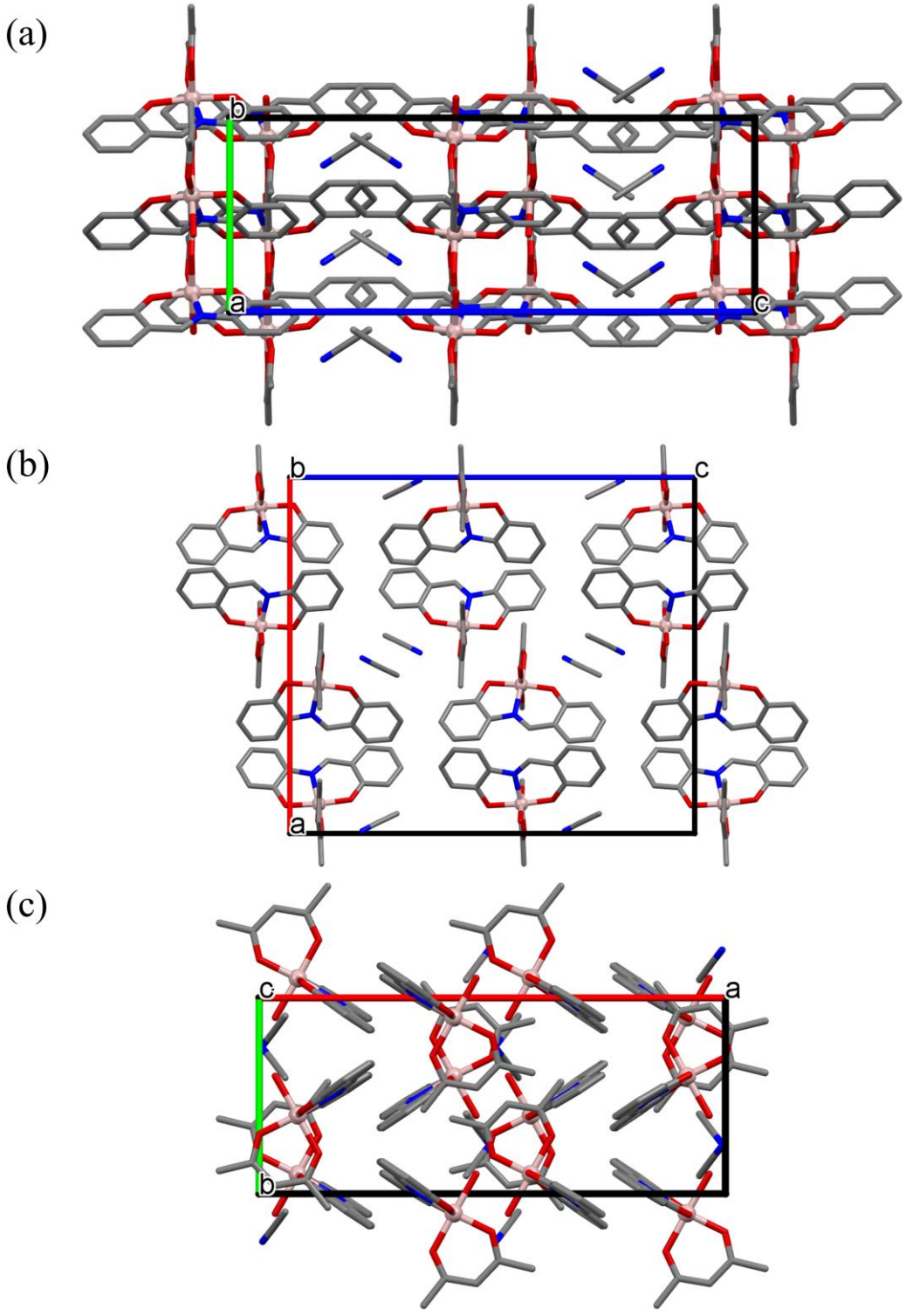

Figure S9. Crystal packing structures of **Al·MeCN** at 173 K along (a) *a*, (b) *b*, (c) *c* axis. Hydrogen atoms and disordered atoms are omitted for clarity.

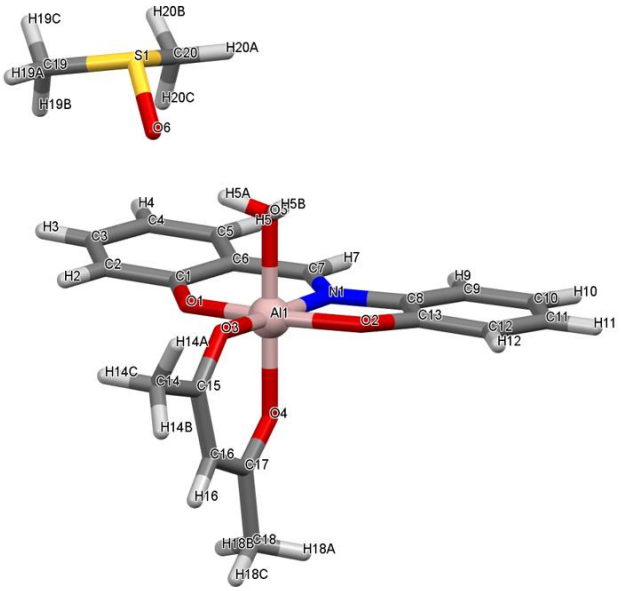

Figure S10. Crystal structure of **Al·DMSO** at 173 K with the atom-numbering scheme.

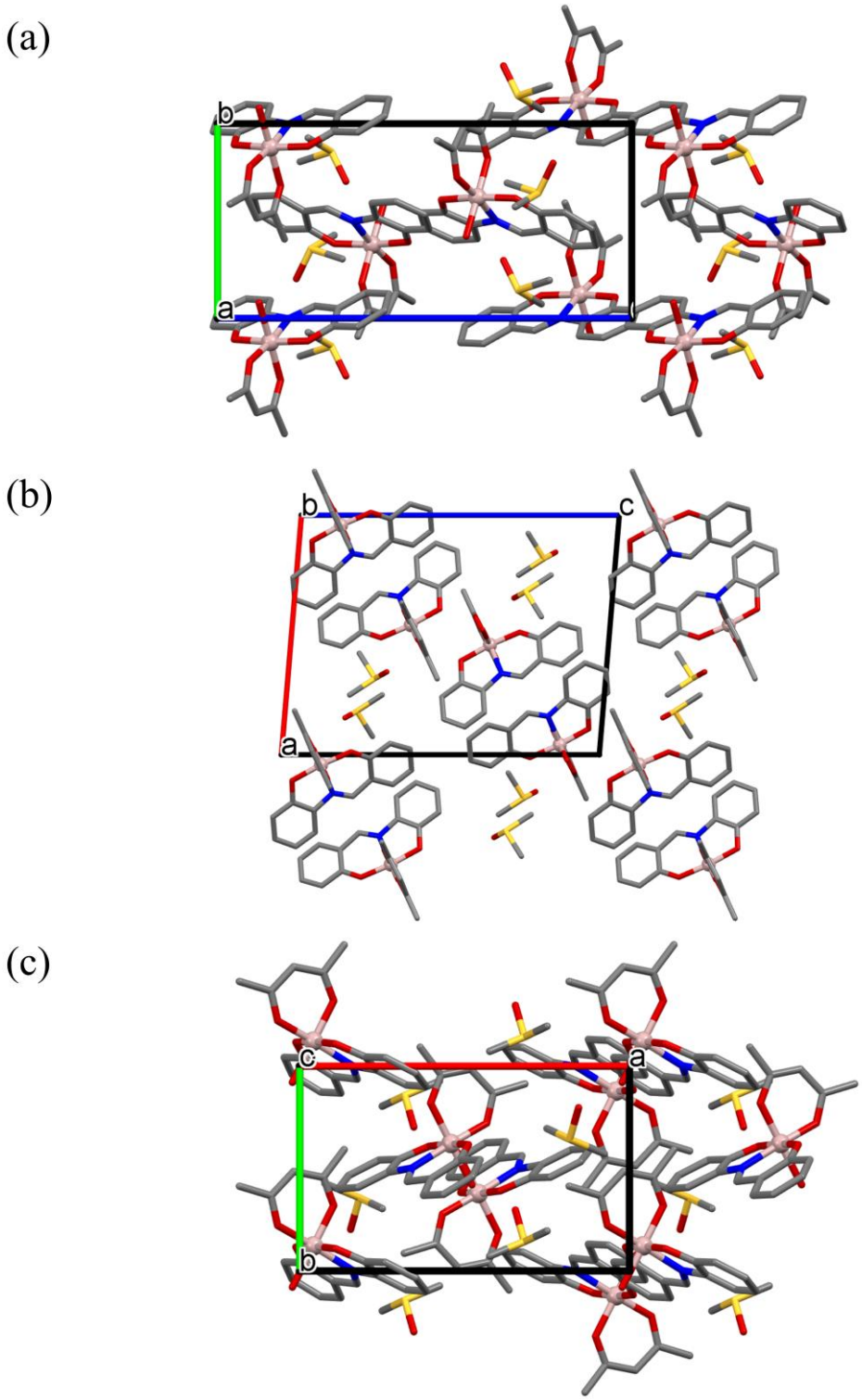

Figure S11. Crystal packing structures of **Al·DMSO** at 173 K along (a) *a*, (b) *b*, (c) *c* axis. Hydrogen atoms and disordered atoms are omitted for clarity.

Table S2. Selected distances of intermolecular interactions (Å) for **Al·Me$_2$CO**.

C(1)···H(5)–C(5)	2.848
C(4)···H(20A)–C(20)	2.862
C(5)···H(20A)–C(20)	2.885
C(7)···H(18A)–C(18)	2.894
C(17)···H(14C)–C(14)	2.836
C(17)···H(20B)–C(20)	2.714
N(1)···H(18B)–C(18)	2.714
O(1)···H(21A)–C(20)	2.634
O(4)···H(20A)–C(20)	2.862
O(5)···O(6)	2.845(2)
O(5)···H(18B)–C(18)	2.684

Table S3. Selected distances of intermolecular interactions (Å) for **Al·MeCN**.

C(7)···H(18B)–C(18)	2.885
C(7)···H(18C)–C(18)	2.729
O(1)···H(20B)–C(20)	2.674
N(2)···O(5)	2.886(5)
O(4)···H(7)–C(7)	2.700
O(5)···H(18B)–C(18)	2.640

Table S4. Selected distances of intermolecular interactions (Å) for **Al·DMSO**.

C(4)···H(20C)–C(20)	2.898
C(7)···H(18A)–C(18)	2.884
C(7)···H(18C)–C(18)	2.784
O(1)···H(19A)–C(19)	2.674
O(5)···O(6)	2.722(8)
O(5)···H(18C)–C(18)	2.664
C(16)···H(20A)–C(20)	2.828
C(17)···H(20A)–C(20)	2.628

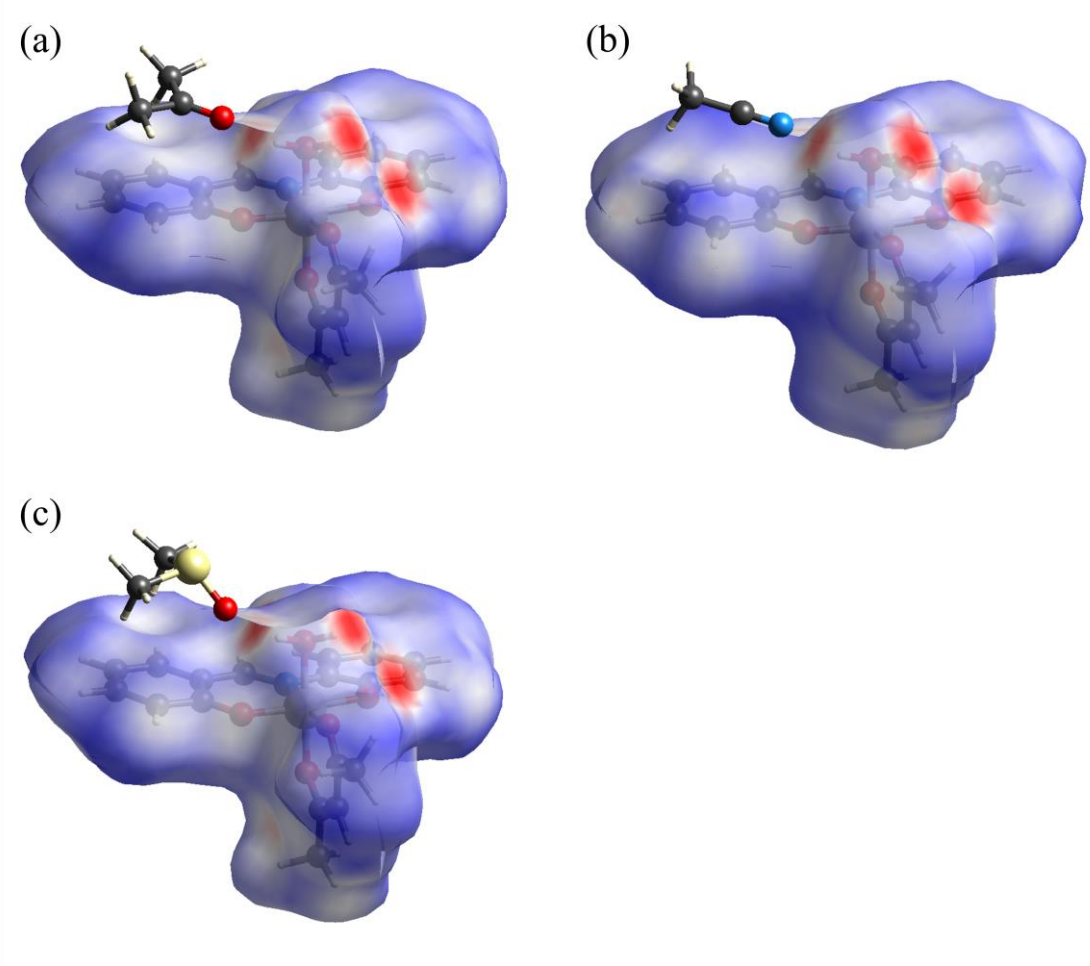

Figure S12. Hirshfeld d_{norm} surface analysis for (a) **Al·Me$_2$CO**, (b) **Al·MeCN** and (c) **Al·DMSO**, obtained by using CrystalExplorer. Red regions of the surface indicate points where interactions with adjacent atoms exceed dispersion forces.

[Ref.] S. K. Wolff, D. J. Grimwood, J. J. McKinnon, M. J. Turner, D. Jayatilaka and M. A. Spackman, *CrystalExplorer 3.1*, University of Western Australia, 2012.

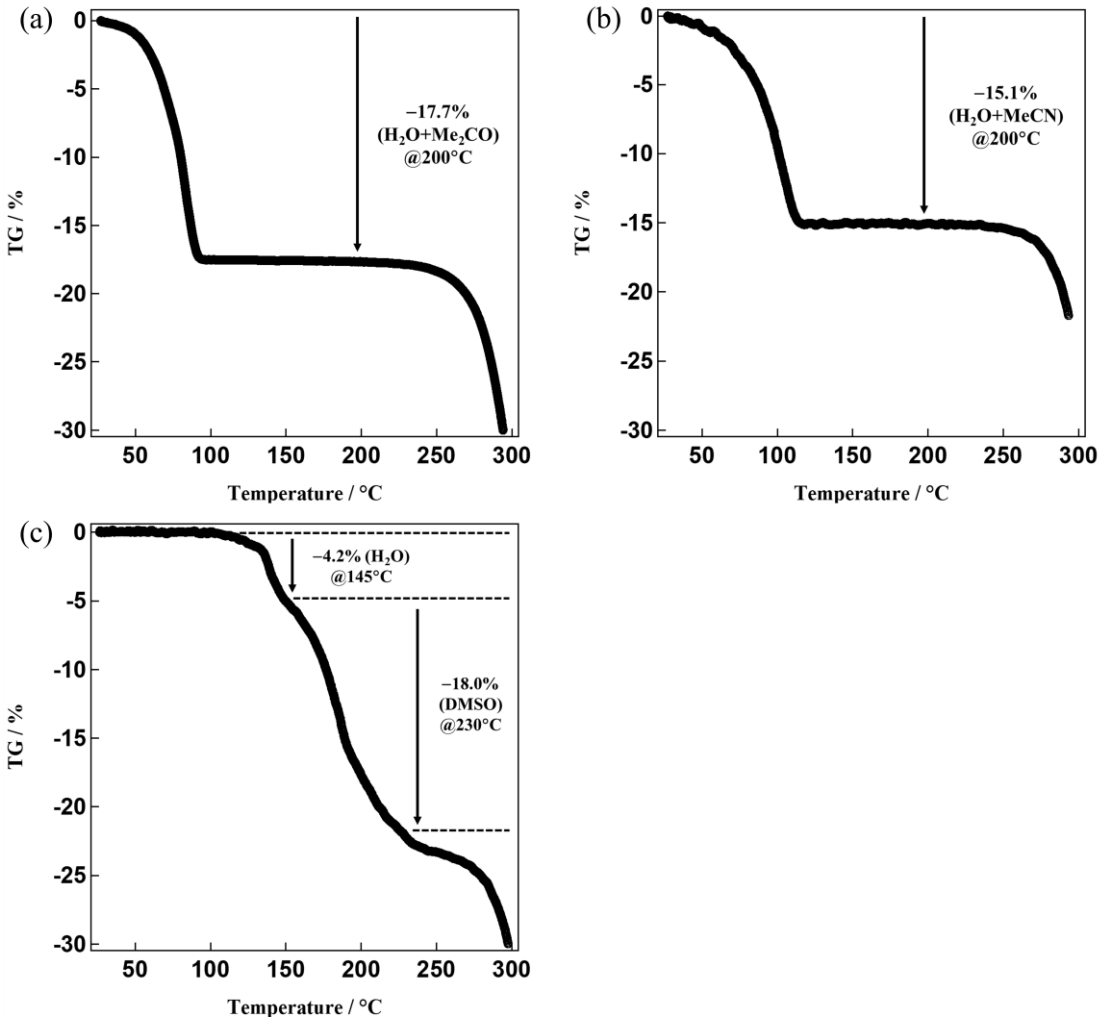

Figure S13. TGA curve for (a) **Al·Me$_2$CO**, (b) **Al·MeCN** and (c) **Al·DMSO**. 17.7%, 15.1% and 22.2% weight loss were observed for **Al·Me$_2$CO**, **Al·MeCN** and **Al·DMSO** above 230 °C, respectively. This shows good agreement with the Me$_2$CO, MeCN and DMSO content of **Al·Me$_2$CO**, **Al·MeCN** and **Al·DMSO** (H_2O+Me$_2$CO = 18.4%, H_2O+MeCN = 14.9%, H_2O+DMSO = 22.2%), respectively.

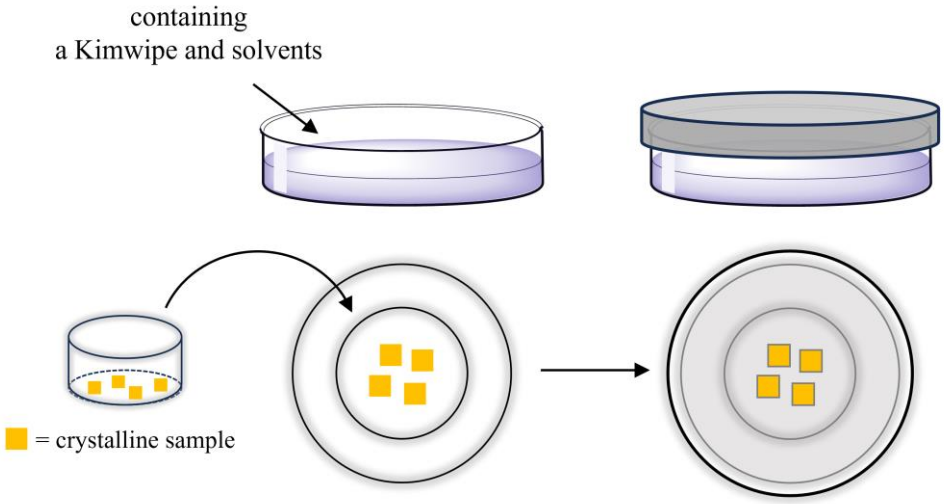

Figure S14. Schematic representation of the procedures for the solvent vapour-induced structural transformation of **Al·Me$_2$CO**, **Al·MeCN** and **Al·DMSO** in a closed petri dish under a high concentration of solvent vapour (Me$_2$CO or MeCN or DMSO).

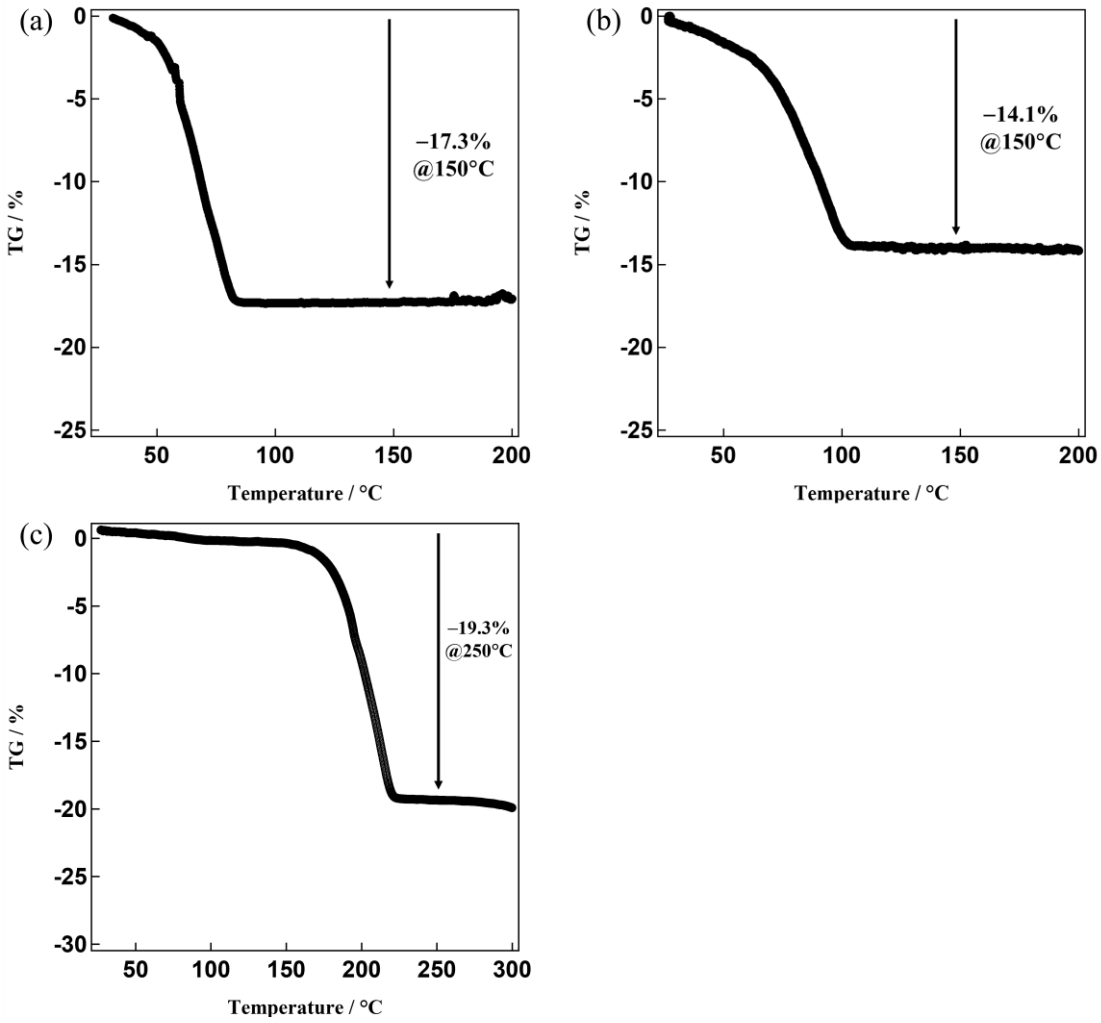

Figure S15. TGA curve for (a) **Al·reMe$_2$CO**, (b) **Al·reMeCN** and (c) **Al·reDMSO**. 17.3%, 14.1% and 19.3% weight losses were observed, respectively.

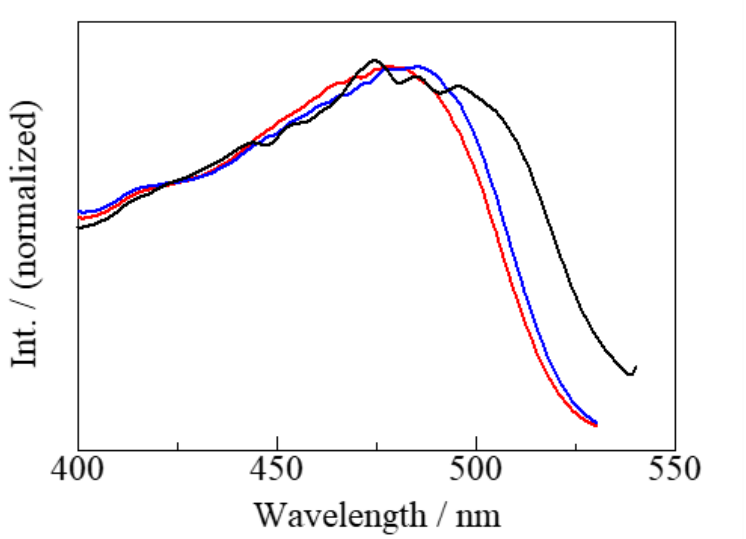

Figure S16. Excitation spectra of **Al·Me$_2$CO** (red), **Al·MeCN** (blue) and **Al·DMSO** (black) in the solid state at 298 K.

Table S5. Photophysical data for **Al·Me$_2$CO**, **Al·MeCN** and **Al·DMSO** in the solid state at 298 K.

	λ_{ex} [nm]	λ_{em} [nm]	$\Phi^{[a]}$
Al·Me$_2$CO	478	539	0.27
Al·MeCN	485	540	0.22
Al·DMSO	474	552	0.07

[a] Emission quantum yields (380-700 nm), λ_{ex} = 430 nm.

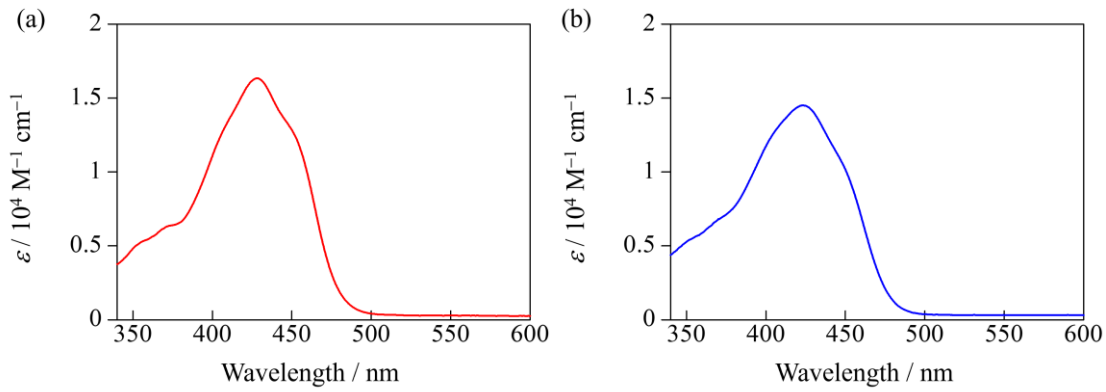

Figure S17. UV-Vis spectra of (a) **Al·Me$_2$CO** in Me$_2$CO and (b) **Al·MeCN** in MeCN at 298 K (1.0 × 10^{-5} M).

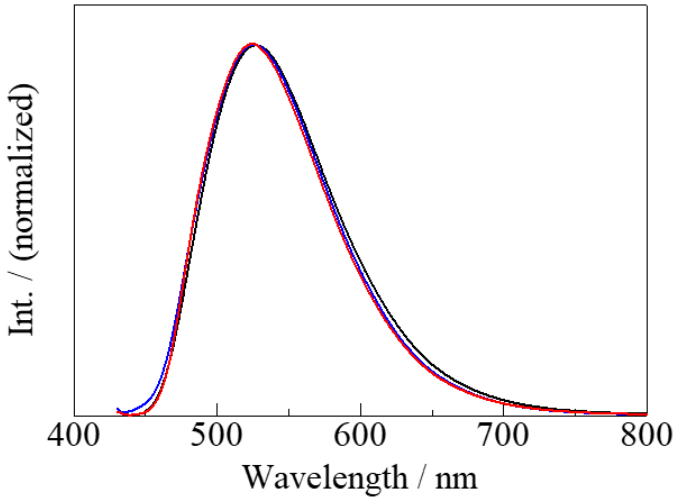

Figure S18. Emission spectra of **Al·Me$_2$CO** in Me$_2$CO (red), **Al·MeCN** in MeCN (blue) and **Al·DMSO** in DMSO (black) at 298 K (1.0 × 10^{-5} M).

Table S6. Photophysical data for **Al·Me$_2$CO**, **Al·MeCN** and **Al·DMSO** in solution (1.0 × 10^{-5} M) at 298 K.

	λ_{ex} [nm]	λ_{em} [nm]	Φ[a]
Al·Me$_2$CO (in Me$_2$CO)	424	523	0.47
Al·MeCN (in MeCN)	426	526	0.42
Al·DMSO (in DMSO)	430	527[b]	0.76

[a] Emission quantum yields (380-700 nm), λ_{ex} = 430 nm.

[b] From our previous report.[Ref.]

[Ref.] F. Kobayashi, M. Gemba, S. Hoshino, K. Tsukiyama, M. Shiotsuka, T. Nakajima and M. Tadokoro, *Chem. Eur. J.*, 2023, **29**, e202203937.

Table S7. Cartesian coordinates of the optimized structure of **[Al(sap)(acac)(H_2O)]**.

atom	X	Y	Z
Al	-1.44045	-0.4798	0.68847
O	0.33403	-0.98525	0.35524
N	-1.66058	-2.43441	1.14346
C	0.64514	-2.21765	0.75307
C	1.95963	-2.71153	0.74156
H	2.75611	-2.05628	0.40162
O	-3.25428	-0.23645	0.67114
O	-1.12674	1.3014	0.09996
C	2.21995	-4.0125	1.16341
H	3.24189	-4.3834	1.15246
C	1.18475	-4.8458	1.6083
H	1.40021	-5.8557	1.94465
O	-1.1727	-0.0007	2.49782
O	-1.54773	-0.81505	-1.38846
H	-0.57633	-0.87963	-1.4905
H	-1.80117	0.0496	-1.75519
C	-0.12546	-4.37325	1.62643
H	-0.92252	-5.01934	1.98474
C	-0.40217	-3.07076	1.19707
C	-2.7936	-3.036	1.36559
H	-2.78771	-4.10122	1.61035
C	-4.08391	-2.41405	1.30673
C	-5.22169	-3.20608	1.59281
H	-5.06919	-4.25169	1.85419
C	-6.49963	-2.68287	1.54736
H	-7.36083	-3.30467	1.77135
C	-6.66501	-1.32777	1.20412
H	-7.66498	-0.9021	1.16387
C	-5.57434	-0.52491	0.91549
H	-5.69795	0.5207	0.65016
C	-4.25479	-1.03474	0.95671
C	-0.5909	3.6009	0.04717
H	-1.50642	3.85049	-0.50161
H	0.20208	3.45669	-0.69595
H	-0.32372	4.43716	0.69711
C	-0.80001	2.318	0.81292
C	-0.63919	2.29182	2.20242
H	-0.3579	3.20819	2.70622
C	-0.83503	1.13532	2.97614
C	-0.65511	1.18197	4.47289
H	-1.58878	0.87699	4.95903
H	-0.36882	2.1736	4.83083
H	0.11109	0.45555	4.76665

Table S8. Vertical excitations of **[Al(sap)(acac)(H_2O)]**.

Excited State	1:	Singlet-A	2.9248 eV	423.90 nm	*f*=0.2046	<S**2>=0.000
93 -> 94		0.65435				
93 -> 95		-0.25062				
Excited State	2:	Singlet-A	3.1221 eV	397.11 nm	*f*=0.1152	<S**2>=0.000
93 -> 94		0.24172				
93 -> 95		0.65890				
Excited State	3:	Singlet-A	3.4366 eV	360.78 nm	*f*=0.0531	<S**2>=0.000
92 -> 94		0.69675				

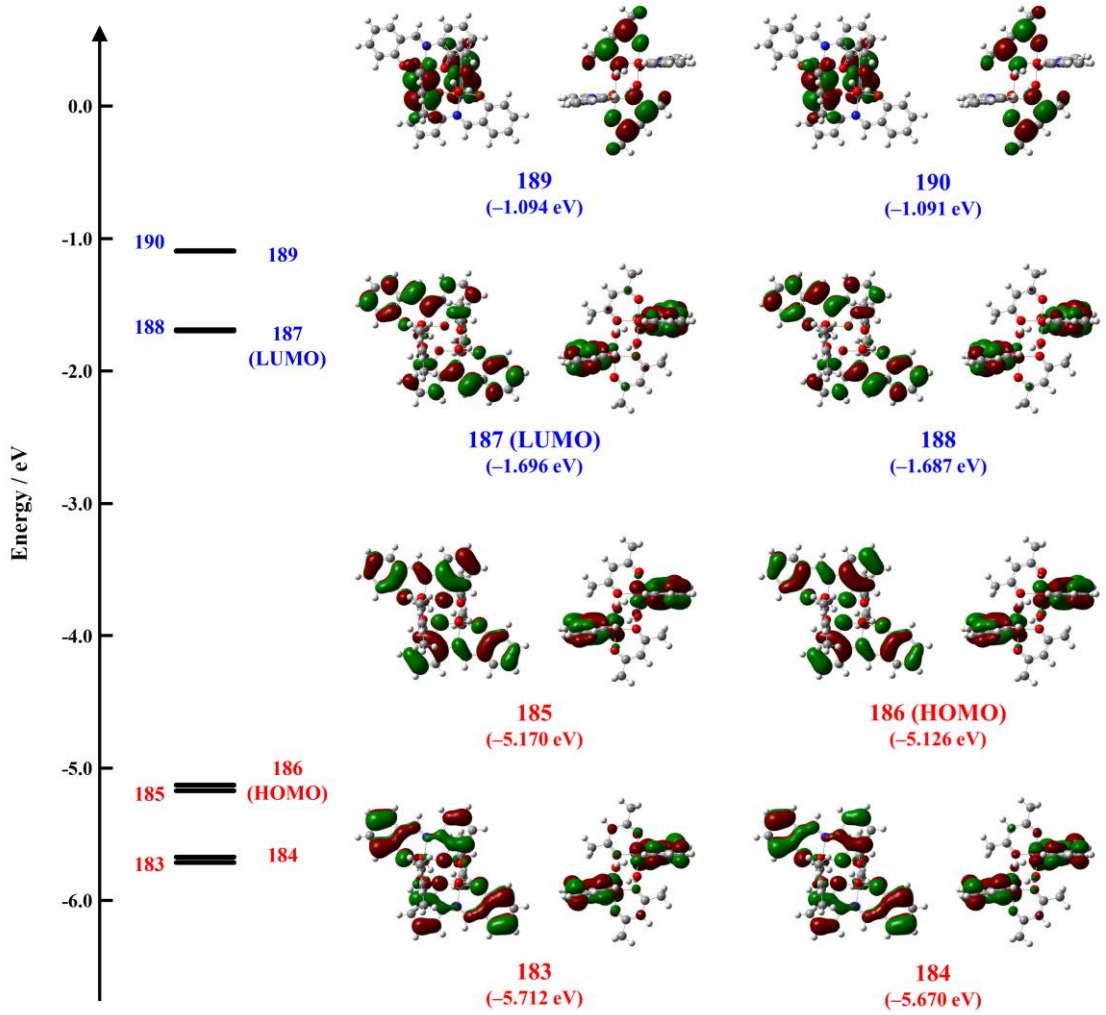

Figure S19. HOMO and LUMO of the hydrogen-bonded dimer **[Al(sap)(acac)(H_2O)]$_2$** at the experimental X-ray geometries.

Table S9. Cartesian coordinates of the optimized structure of the hydrogen-bonded dimer **[Al(sap)(acac)(H_2O)]$_2$**.

atom	X	Y	Z
Al	-1.89647	-0.21654	-5.7571
O	-1.70907	-0.30684	-3.8885
N	-3.59347	-1.23534	-5.3869
C	-2.72367	-0.89754	-3.2342
C	-2.77407	-0.99584	-1.84
H	-2.09307	-0.60074	-1.3085
O	-2.22357	-0.30364	-7.5565
O	-0.24867	0.63476	-5.9554
C	-3.82487	-1.67344	-1.237
H	-3.85257	-1.74314	-0.29
C	-4.83387	-2.25114	-1.9916
H	-5.53737	-2.72434	-1.5635
O	-2.82857	1.43086	-5.62
O	-0.92957	-1.91194	-5.8922
H	-0.15087	-1.83754	-5.5098
H	-0.74657	-2.07174	-6.7282
C	-4.81357	-2.13524	-3.3727
H	-5.50667	-2.52154	-3.895
C	-3.77077	-1.44844	-3.9903
C	-4.39757	-1.74224	-6.2602
H	-5.13877	-2.24424	-5.9421
C	-4.24517	-1.59784	-7.6855
C	-5.20857	-2.21414	-8.5065
H	-5.93277	-2.68104	-8.1063
C	-5.11967	-2.15204	-9.8786
H	-5.76797	-2.58054	-10.4249
C	-4.06567	-1.45094	-10.4502
H	-4.00247	-1.39784	-11.3967
C	-3.11107	-0.83124	-9.6769
H	-2.40517	-0.35614	-10.0989
C	-3.16207	-0.88914	-8.2685
C	1.43723	2.28476	-6.1642
H	1.59333	2.44106	-7.119
H	2.02803	1.56896	-5.8496
H	1.62443	3.10636	-5.6639
C	0.00673	1.88346	-5.9501
C	-0.95747	2.86246	-5.7857
H	-0.67347	3.76906	-5.7718
C	-2.31777	2.60216	-5.6398
C	-3.26187	3.75336	-5.5163
H	-3.79907	3.82426	-6.3328
H	-2.75287	4.58086	-5.3872

H	-3.85277	3.61006	-4.7478
Al	1.56933	-2.17644	-2.7503
O	1.38193	-2.08614	-4.6189
N	3.26633	-1.15764	-3.1205
C	2.39653	-1.49544	-5.2732
C	2.44693	-1.39714	-6.6674
H	1.76593	-1.79224	-7.1989
O	1.89643	-2.08934	-0.9509
O	-0.07847	-3.02774	-2.552
C	3.49773	-0.71954	-7.2704
H	3.52543	-0.64984	-8.2174
C	4.50673	-0.14184	-6.5158
H	5.21023	0.33136	-6.9439
O	2.50143	-3.82384	-2.8874
O	0.60243	-0.48104	-2.6152
H	-0.17627	-0.55544	-2.9976
H	0.41943	-0.32124	-1.7792
C	4.48643	-0.25774	-5.1347
H	5.17953	0.12856	-4.6124
C	3.44363	-0.94454	-4.5171
C	4.07043	-0.65074	-2.2472
H	4.81163	-0.14874	-2.5653
C	3.91803	-0.79514	-0.8219
C	4.88143	-0.17884	-0.0009
H	5.60563	0.28806	-0.4011
C	4.79253	-0.24094	1.3712
H	5.44083	0.18756	1.9175
C	3.73853	-0.94204	1.9428
H	3.67533	-0.99514	2.8893
C	2.78393	-1.56174	1.1695
H	2.07803	-2.03684	1.5915
C	2.83493	-1.50384	-0.2389
C	-1.76437	-4.67774	-2.3432
H	-1.92047	-4.83404	-1.3884
H	-2.35517	-3.96194	-2.6578
H	-1.95157	-5.49934	-2.8435
C	-0.33387	-4.27644	-2.5573
C	0.63033	-5.25544	-2.7217
H	0.34633	-6.16204	-2.7356
C	1.99063	-4.99514	-2.8676
C	2.93473	-6.14634	-2.9911
H	3.47193	-6.21724	-2.1746
H	2.42573	-6.97384	-3.1202
H	3.52563	-6.00304	-3.7596

Table S10. Vertical excitations of the hydrogen-bonded dimer **[Al(sap)(acac)(H_2O)]$_2$**.

Excited State 1:	Singlet-A	3.0081 eV	412.17 nm	*f*=0.0000	<S**2>=0.000
185 -> 188	0.33328				
186 -> 187	0.61214				
Excited State 2:	Singlet-A	3.0539 eV	405.99 nm	*f*=0.5419	<S**2>=0.000
185 -> 187	0.29690				
186 -> 188	0.62711				
Excited State 3:	Singlet-A	3.1094 eV	398.74 nm	*f*=0.0647	<S**2>=0.000
185 -> 187	0.63153				
186 -> 188	-0.30958				
Excited State 4:	Singlet-A	3.1115 eV	398.47 nm	*f*=0.0000	<S**2>=0.000
185 -> 188	0.61638				
186 -> 187	-0.34128				
Excited State 5:	Singlet-A	3.4417 eV	360.24 nm	*f*=0.0000	<S**2>=0.000
185 -> 190	0.40864				
186 -> 189	0.56394				
Excited State 6:	Singlet-A	3.4451 eV	359.89 nm	*f*=0.0590	<S**2>=0.000
183 -> 188	-0.10789				
184 -> 187	-0.12040				
185 -> 189	0.40228				
186 -> 190	0.54957				