Supplementary Information:

Synthesis and structures of soluble magnesium and zinc carboxylates Containing intramolecular NH•••O hydrogen bonds in nonpolar solvents

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Table S1 Crystallographic data

	L0H·3(AcOEt)	(NMe_4)[**L1**]·2 H_2O·1,4-dioxane	**L2**H·1/2(1,4-dioxane)	**Ca_2L1$_4$**·4(1,4-dioxane)·4H_2O	**MgL1$_2$**(EtOH)-4EtOH	**MgL2$_2$**(EtOH)-5EtOH
formula	$C_{83}H_{108}N_2O_{10}$	$C_{52}H_{77}N_3O_8$	$C_{41}H_{49}NO_4$	$C_{196}H_{270}Ca_2N_8O_{35}$	$C_{104}H_{154}MgN_4O_{16}$	$C_{96}H_{142}MgN_2O_{15}$
fw	1293.71	872.16	619.81	3378.34	1740.61	1588.42
cryst syst	monoclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	*Cc*	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$C2/c$	$P2_1/c$
a, Å	18.9473(8)	11.5622(9)	11.7369(14)	18.0688(18)	28.1365(10)	14.5903(5)
b, Å	13.9306(6)	11.6068(8)	12.6605(17)	11.3006(12)	11.8861(4)	27.0129(9)
c, Å	28.662(2)	19.7688(14)	12.8455(17)	50.441(5)	31.198(2)	25.7904(17)
α, deg	90	92.302(6)	73.348(5)	90	90	90
β, deg	96.968(7)	105.780(7)	71.463(5)	108.006(6)	102.064(7)	112.681(7)
γ, deg	90	100.231(7)	83.617(6)	90	90	90
V, Å^3	7509.4(7)	2501.4(3)	1733.4(4)	9795.1(18)	10203.1(9)	9378.6(9)
Z	4	2	2	2	4	4
d_{calc}, g cm^{-3}	1.144	1.158	1.187	1.145	1.133	1.125
μ, mm^{-1}	0.074	0.077	0.075	0.129	0.081	0.080
GOF	1.029	1.019	1.033	0.945	1.021	1.015
$R1^a$ [I > 2σ(I)]	0.0770	0.0741	0.0649	0.1481	0.0756	0.0852
w$R2^b$ (all data)	0.2156	0.2071	0.1634	0.4705	0.2164	0.2429

$^a R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S2 Selected bond distances (Å) for **MgL1**$_2$(EtOH) and **MgL2**$_2$(EtOH)

	MgL1$_2$(EtOH)	**MgL2**$_2$(EtOH)
Mg–O11	2.049(2)	2.021(3)
Mg–O21		2.042(3)
mean		2.031
M–O(EtOH)	2.070(3)	2.076(4)
		2.117(4)
	2.090(2)[a]	2.068(3)[a]
		2.085(3)[a]
mean	2.080	2.087
C1–O11	1.274(4)	1.262(4)
C1–O21		1.261(4)
C1–O12	1.247(4)	1.259(4)
C1–O22		1.261(4)

[a]Forming intramolecular OH···O=C hydrogen bond.

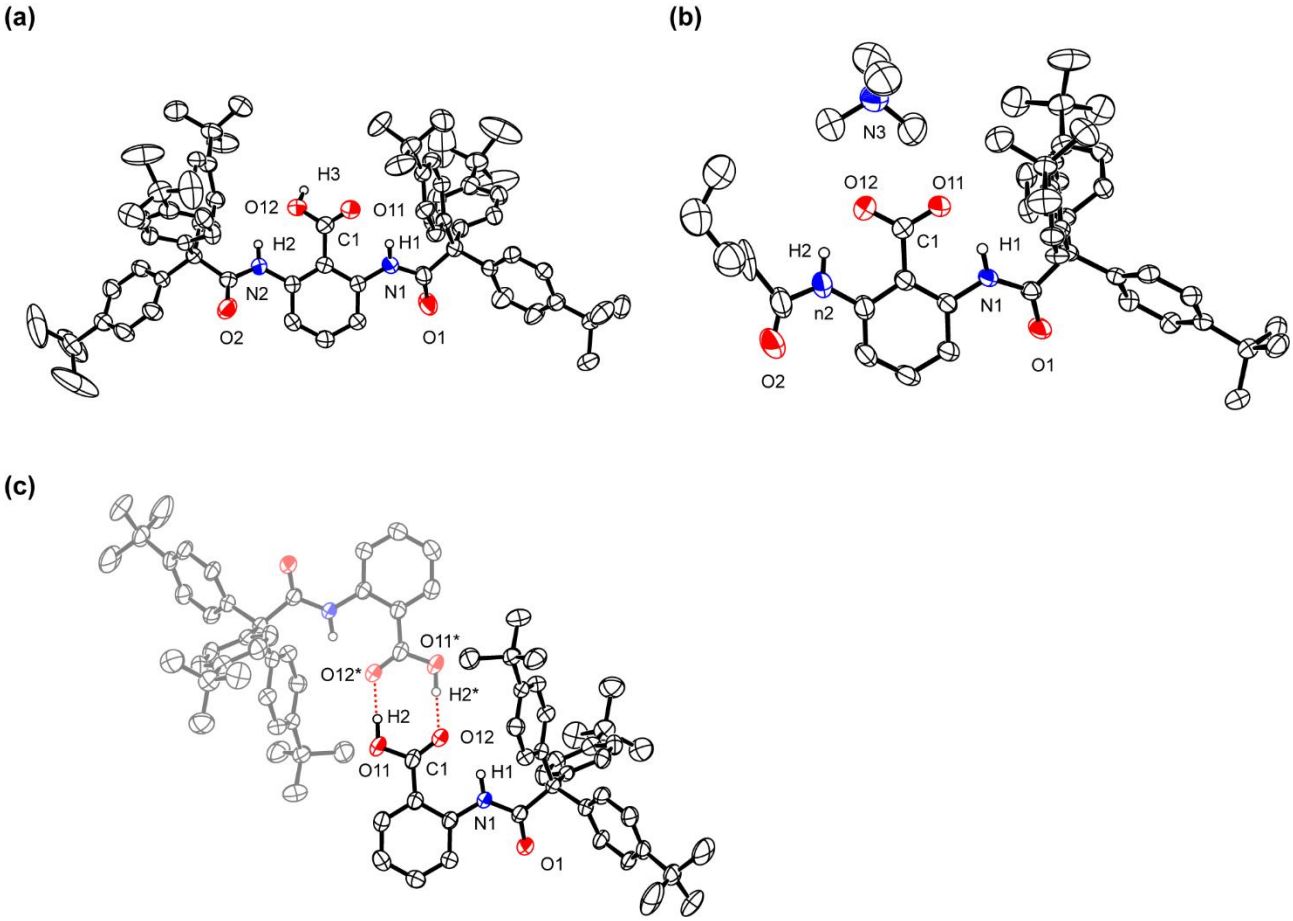

Fig. S1 Molecular structures of (a) **L0**H, (b) (NMe_4)[**L1**], and (c) **L2**H. **L2**H forms intermolecular hydrogen bonds with the neighboring **L2**H in the crystal.

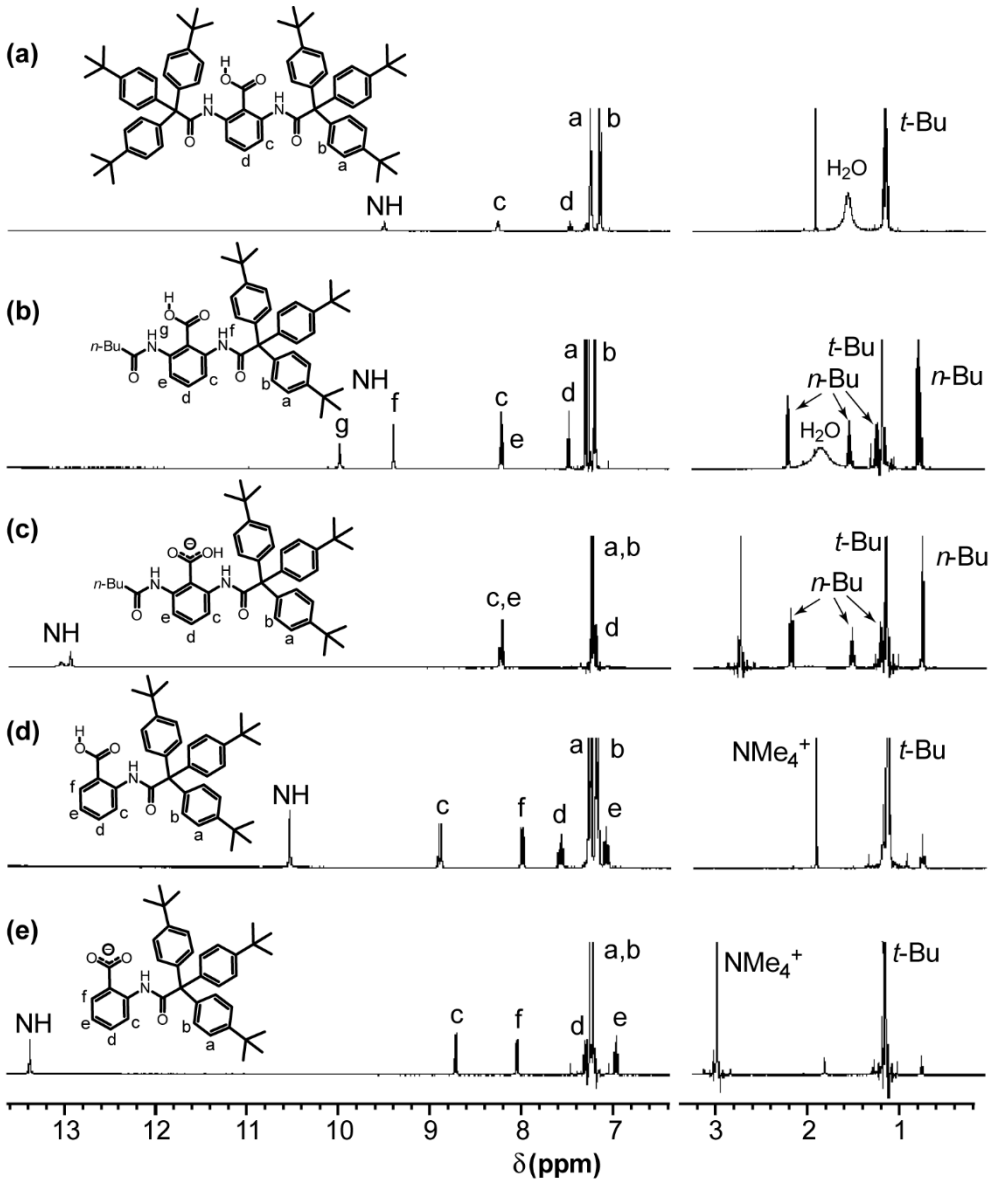

Fig. S2 ^{1}H NMR spectra of (a) **L0**H, (b) **L1**H, (c) (NMe_4)[**L1**], (d) **L2**H, and (e) (NMe_4)[**L2**] in $CDCl_3$ at 30 °C.

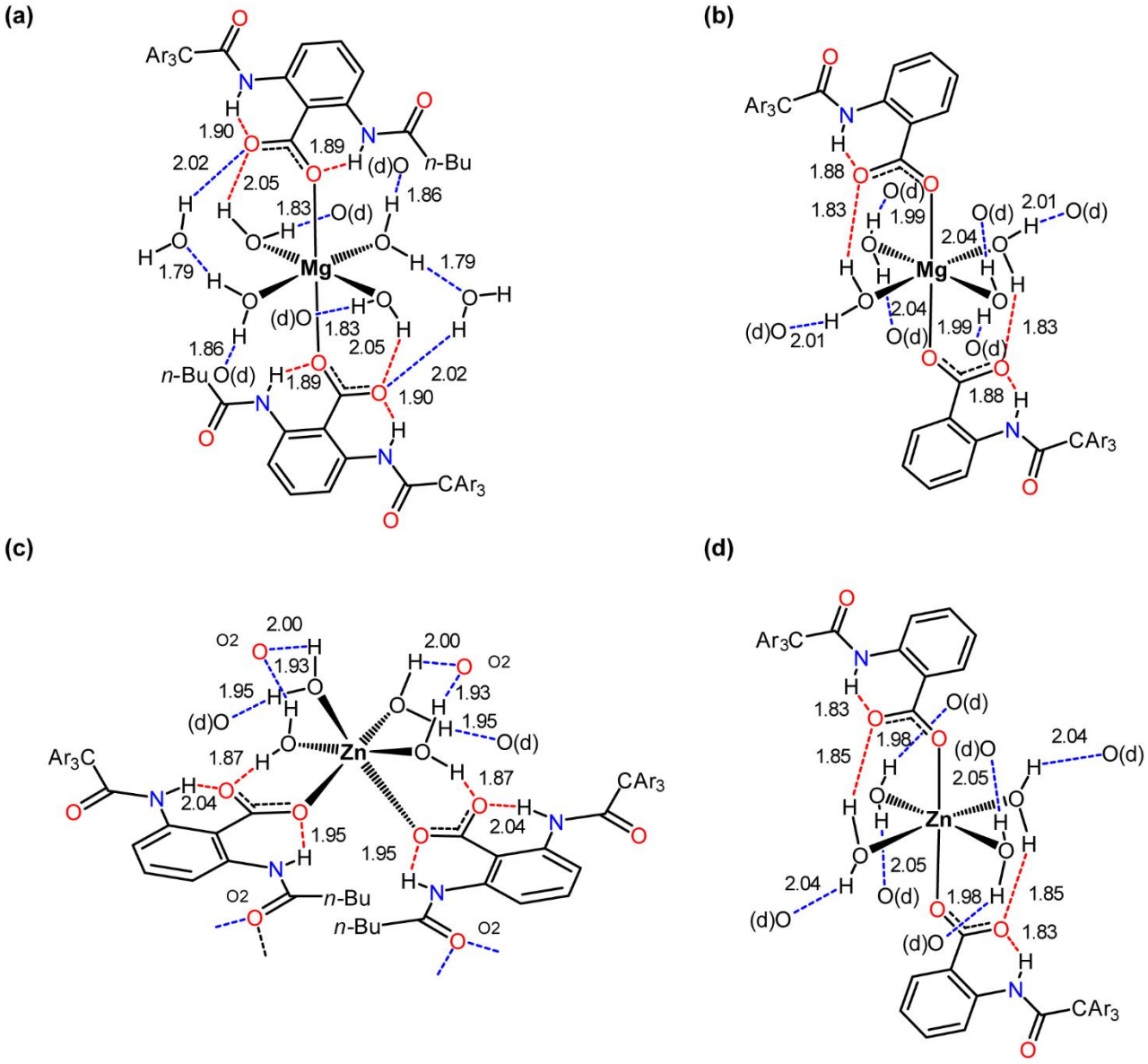

Fig. S3 Schematic drawing of hydrogen bond networks in the crystals for (a) **MgL1**$_2$, (b) **MgL2**$_2$, (c) **ZnL1**$_2$, and (d) **ZnL2**$_2$ (see Figures 1 and 2). Red and blue broken lines denote intra- and inter-molecular hydrogen bonds, respectively, accompanying the distances (Å). O(d) represents the oxygen atom of 1,4-dioxane in the crystal.

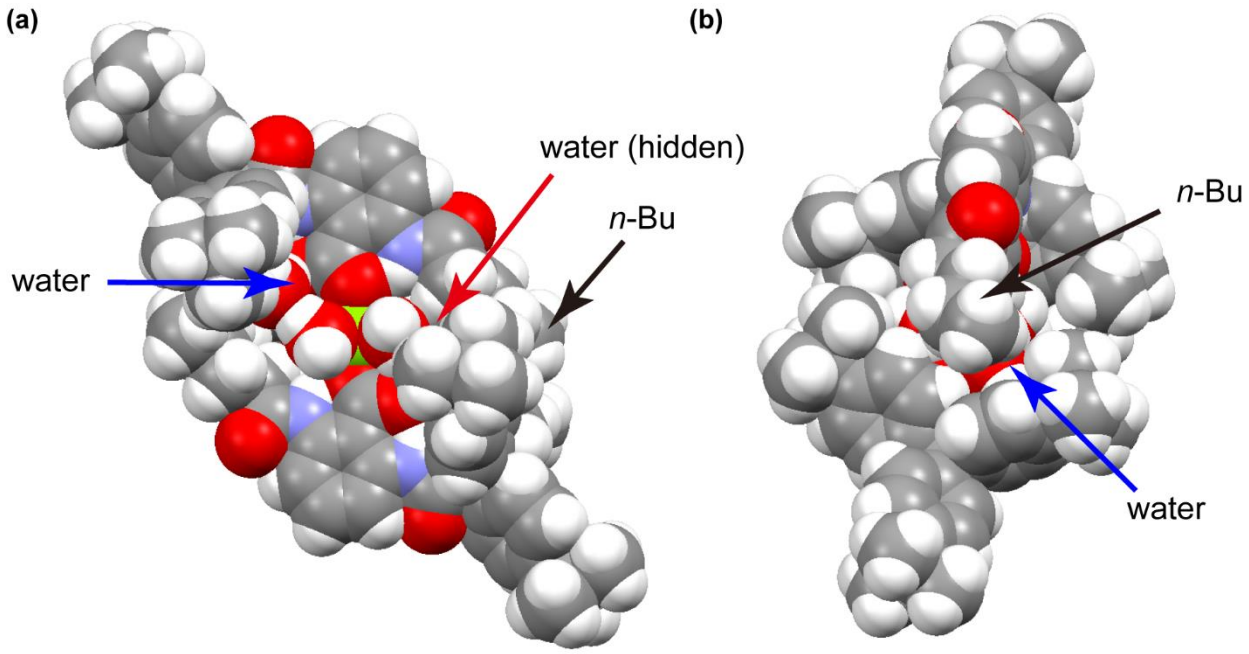

Fig. S4 Space-filling model of **MgL1**$_2$ (a) and a side view (b). The water molecule (indicated by blue arrows) is hydrogen-bonding to the coordinated water. Another water molecule is the back of the red arrow. Compare with Figure S3a.

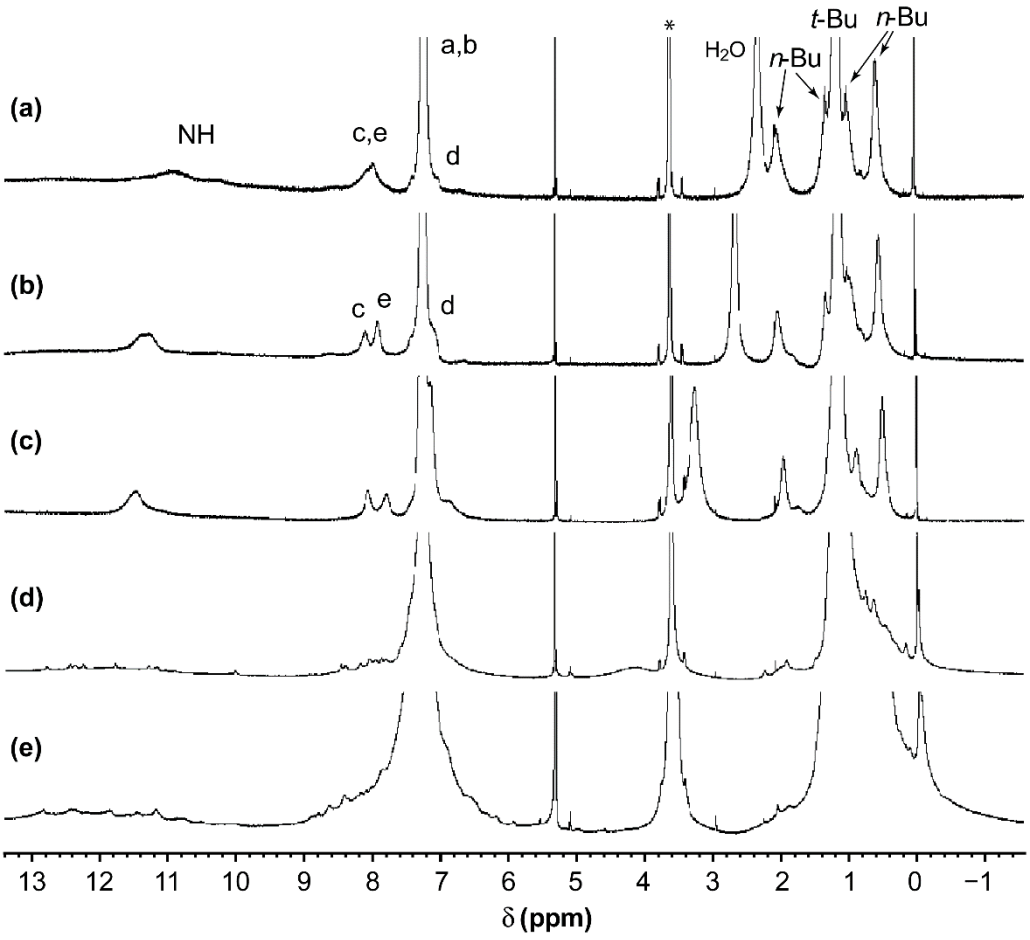

Fig. S5 ^{1}H NMR spectra of **ZnL1**$_2$ in CD_2Cl_2 at (a) 30 °C, (b) 0 °C, (c) −30 °C, −60 °C, and −90 °C. The asterisk denotes the signal of 1,4-dioxane as a crystal solvent.

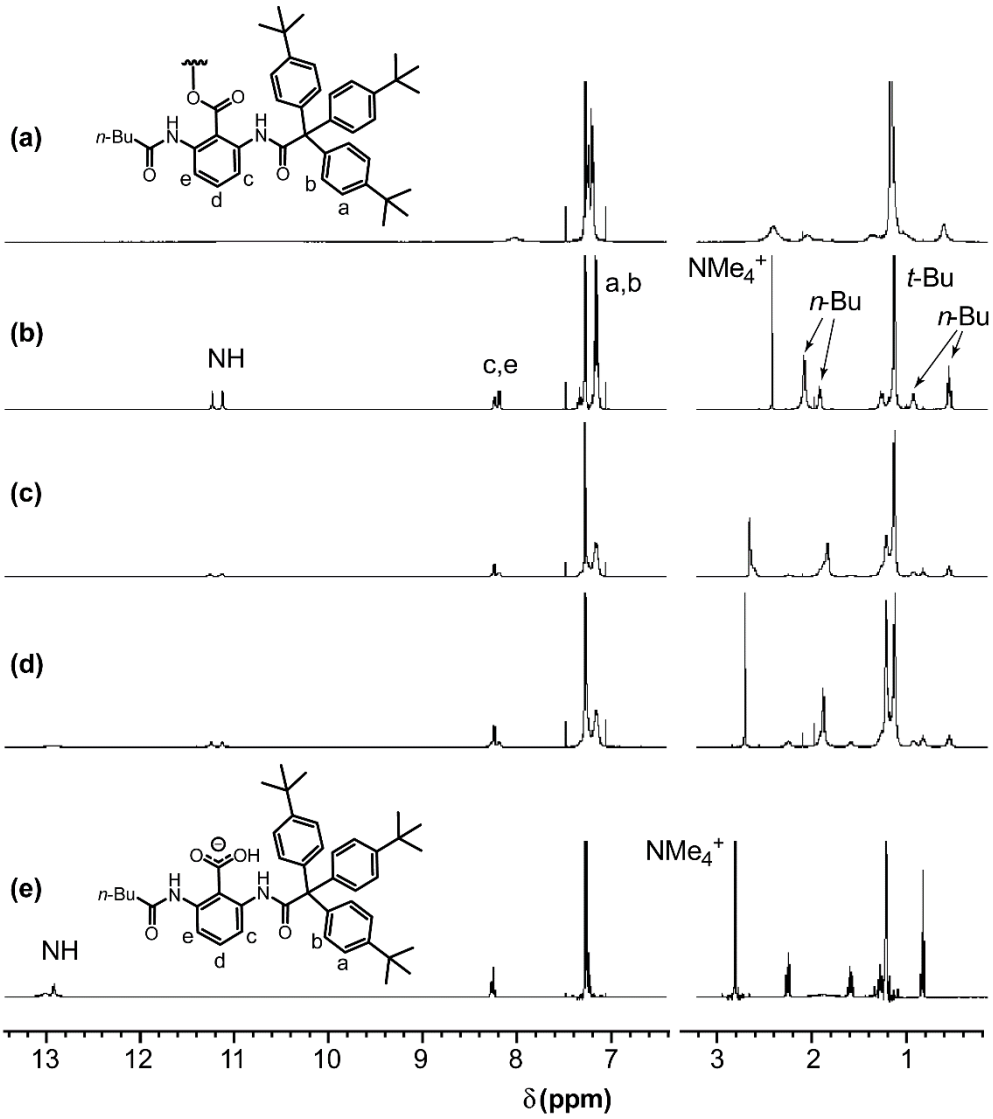

Fig. S6 ^{1}H NMR spectra of (a) **ZnL1**$_2$, (b) **ZnL1**$_2$ + (NMe_4)[**L1**] (= (NMe_4)[**ZnL1**$_3$]), (c) **ZnL1**$_2$ + 2(NMe_4)[**L1**], (d) **ZnL1**$_2$ + 4(NMe_4)[**L1**], and (e) (NMe_4)[**L1**] in $CDCl_3$ at 30 °C.

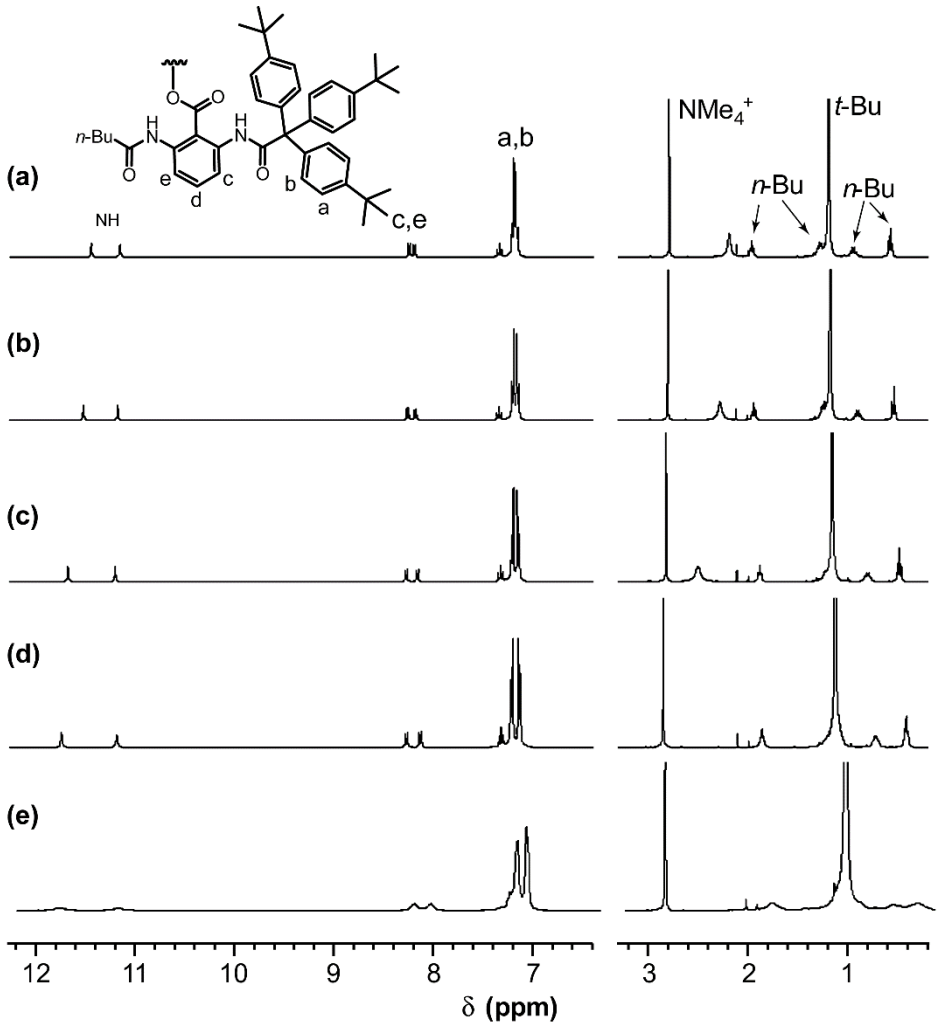

Fig. S7 ^{1}H NMR spectra of (NMe_4)[**ZnL1**$_3$] in CD_2Cl_2 at (a) 30 °C, (b) 0 °C, (c) −30 °C, −60 °C, and −90 °C.

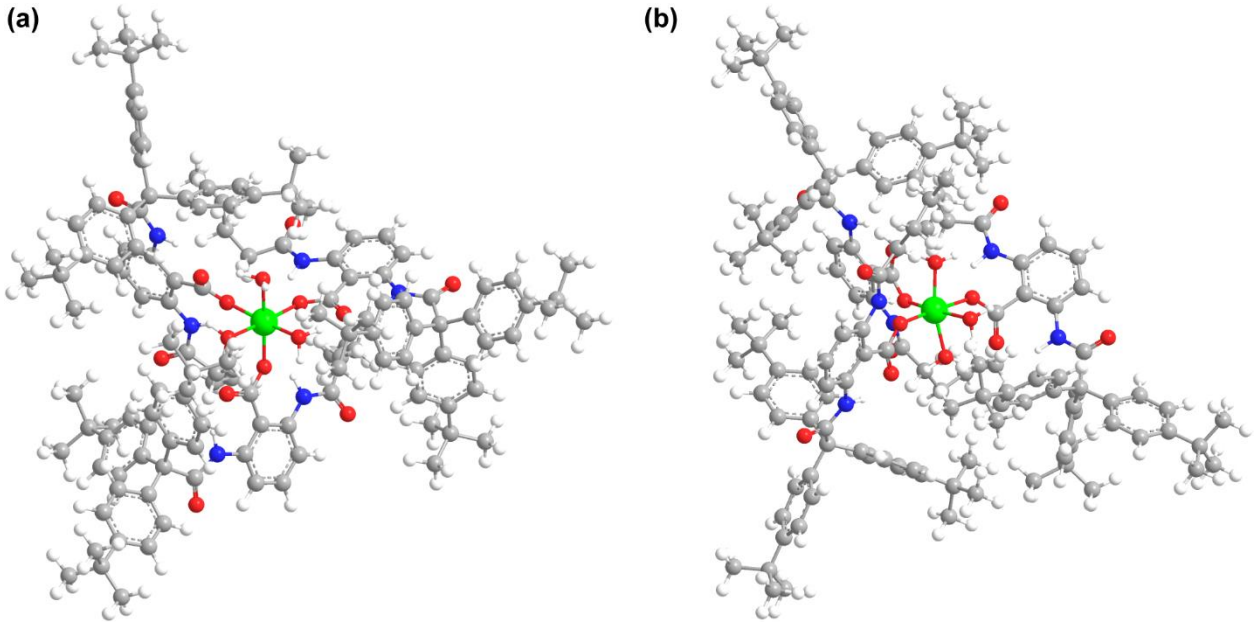

Fig. S8 Optimized structures of (a) *fac*-[**MgL1**$_3$]$^-$ and (b) *mer*-[**MgL1**$_3$]$^-$.