Supporting Information

for

Proton Control of the Lanthanoid Single-Ion Magnet Behavior of a Double-Decker Complex with an Indolenine-Substituted Annulene Ligand

Zhifu Liang,[a] Marko Damjanović,[b] Mritunjoy Kamila,[a] Goulven Cosquer,*[a,c] Brian K. Breedlove,[a] Markus Enders*[b] and Masahiro Yamashita*[a,c,d,e]

[a] Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aramaki-Aza-Aoba, Sendai 980-8578 (Japan)

[b] Institute of Inorganic Chemistry, University of Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)

[c] CREST, JST, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012 (Japan)

[d] WPI Research Center, Advanced Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577 (Japan)

[e] School of Materials Science and Engineering, Nankai University, Tianjin 300350, China

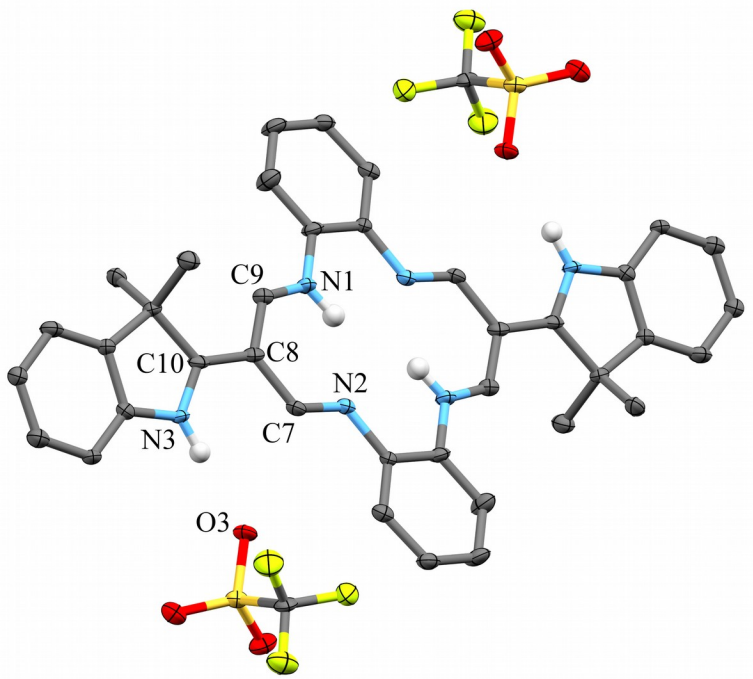

Figure S1: Ortep representation of H_4L^{2+}. All hydrogen atoms except those bonded to N atoms have been omitted to clarity.

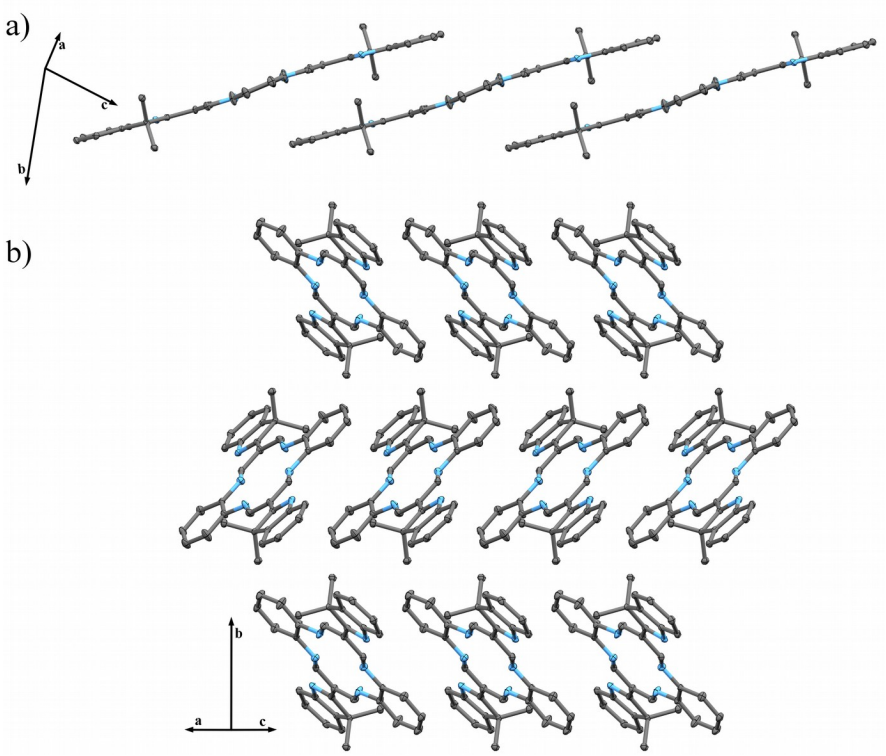

Figure S2: Packing structure of **H_2L**. Hydrogen atoms omitted for clarity.

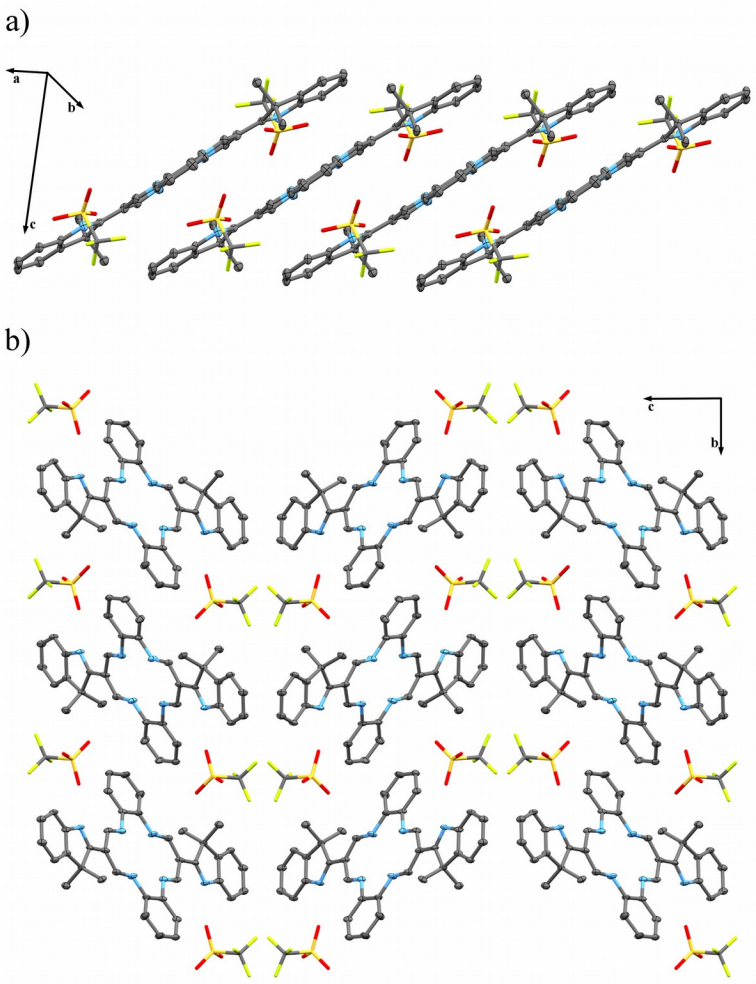

Figure S3: Packing structure of $\mathbf{H_4L^{2+}}$. Hydrogen atoms omitted for clarity.

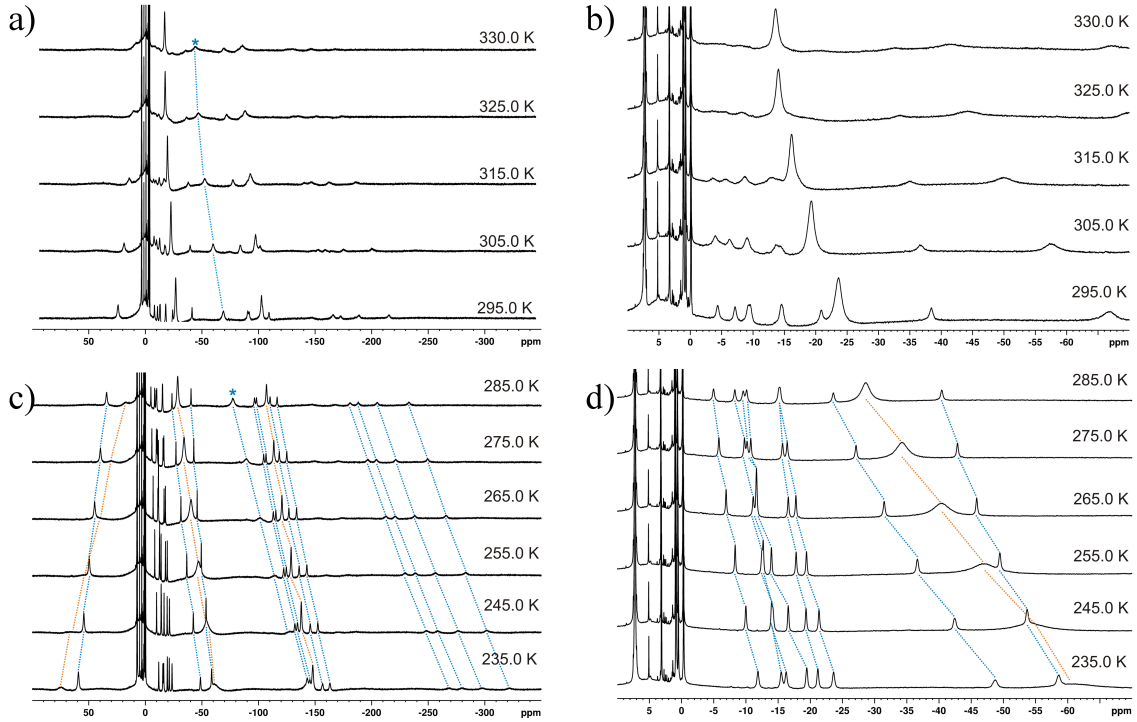

Figure S4: Variable-temperature ^{1}H NMR spectra of **2** recorded in $CDCl_3$, in the temperature range from 295.0 K to 330.0 K (a-b) and 235.0 K to 285.0 K (c-d), with the full range (a-c) and expanded region from +10 ppm to −70 ppm (b-d). * Paramagnetic impurity (see below). Guidelines for the eyes provided in the Figure.

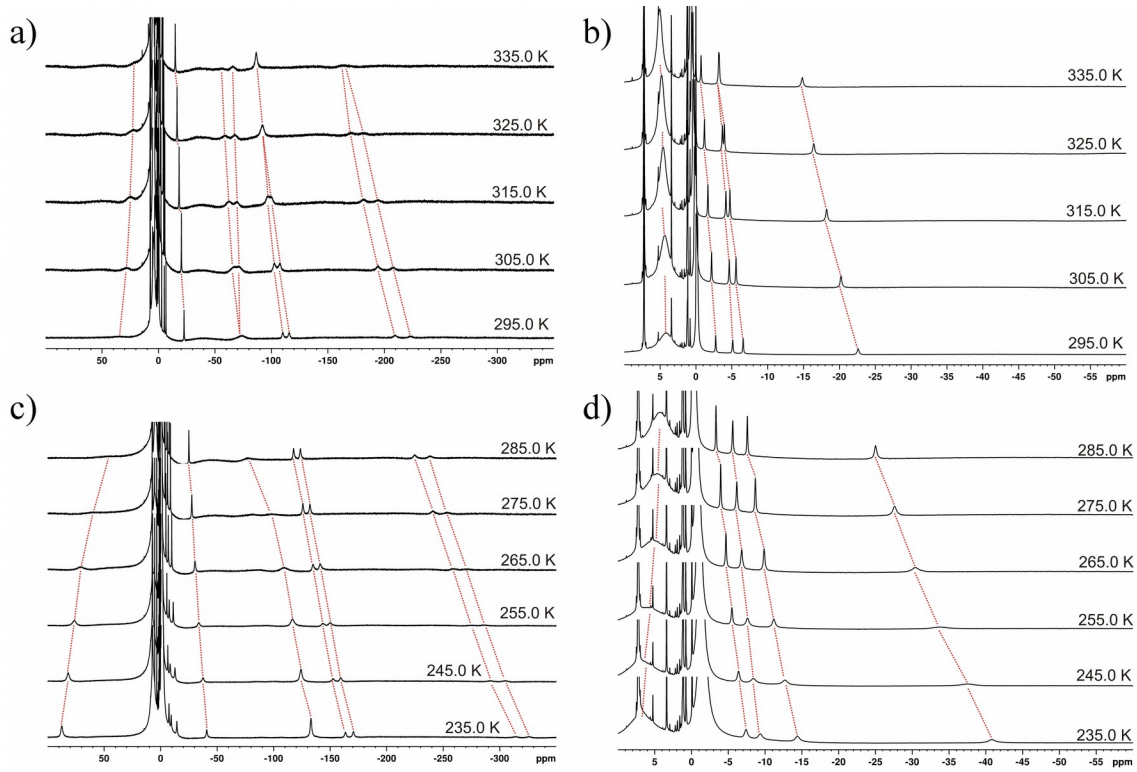

Figure S5: Variable-temperature ^{1}H NMR spectra of **2** with 50 equivalents of acetic acid, recorded in $CDCl_3$, in the temperature range from 295.0 K to 335.0 K (a-b) and 235.0 K to 285.0 K (c-d), with the full range (a-c) and expanded region from +10 ppm to −60 ppm (b-d). Guidelines for the eyes provided in the Figure.

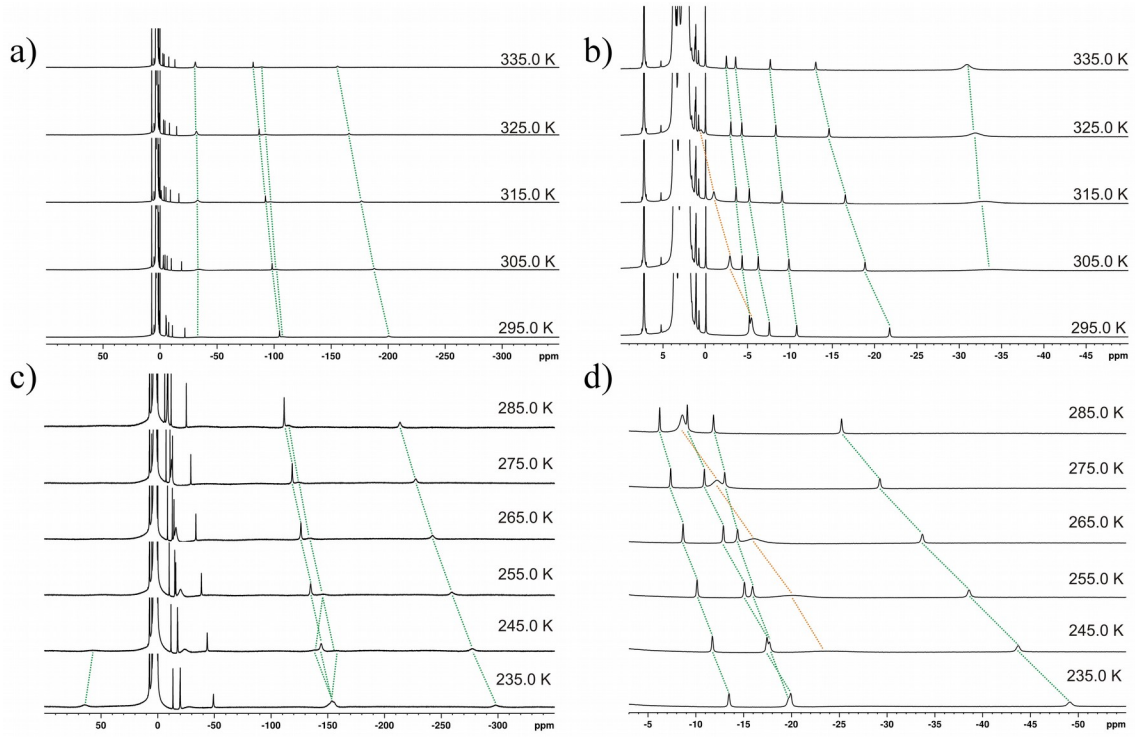

Figure S6: Variable-temperature ^{1}H NMR spectra of **2** with 50 equivalents of DBU, recorded in $CDCl_3$, in the temperature range from 295 K to 335 K (a-b) and 235 K to 285 K (c-d), with the full range (a-c) and expanded region (b-d). Guidelines for the eyes provided in the Figure.

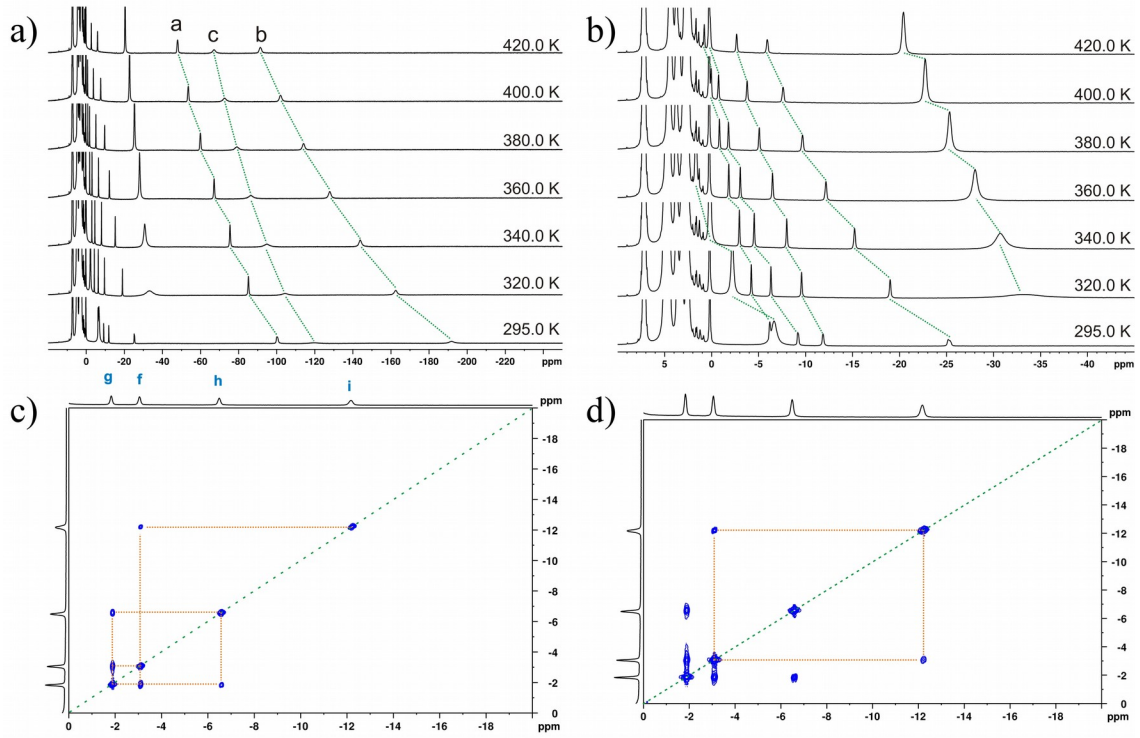

Figure S7: Variable-temperature ^{1}H NMR spectra of **2** with 50 equivalents of DBU, recorded in *o*-$C_6D_4Cl_2$ in full range (a) and expanded region from +10 ppm to −45 ppm (b). Guidelines for the eyes provided in the Figure. The signal of group **c** becomes visible at higher temperatures. ^{1}H, ^{1}H COSY spectrum of **2** with 50 equivalents of DBU, recorded in *o*-$C_6D_4Cl_2$ at 360.0 K (c), and with increased signal intensity (d). Signals in this region are due to aromatic protons in the indole moiety.

$\Delta\chi_{ax}$ of 2 from NMR

The calculated $\Delta\chi_{ax}$ values, together with the contact contributions from DFT, allow the hyperfine shift of the group **c** protons to be estimated at approximately –130 ± 50 ppm (at 235.0 K). The signal for this group in $[Tb(L)_2]^-$ is observed at ca. –150 ppm (overlap with signal from group **a**, see Figure 3 in the main text).

Table S1: Experimental ^{1}H NMR chemical shifts of groups **a** and **b** in the neutral, anionic and cationic form of **2** at 235.0 K and at 295.0 K. These values, together with the averaged *G* values from the molecular structure (H-atoms optimized, Table S2), the contact shifts from DFT (Table S3) and the diamagnetic shifts (7.30 ppm and 7.20 ppm for groups **a** and **b**, respectively[1–4]) were used in calculating the $\Delta\chi_{ax}$ values. The estimated errors for $\Delta\chi_{ax}$ are in each case of the order of ± 15%.

^{1}H Resonance	δ_{expt} [ppm] at 235.0 K			δ_{expt} [ppm] at 295.0 K	
Compound	$[Tb(LH)_2]^+$	$[Tb(L)(LH)]^0$	$[Tb(L)_2]^-$	$[Tb(LH)_2]^+$	$[Tb(L)(LH)]^0$
Group **a**	−170.6 −163.5 – –	–163 –157 –145 –143	–153 – – –	–116 –110 – –	–89 –90 –102 –108
Average:	−167.1	–152	–	–113	–97
$\Delta\chi_{ax}$	1.92×10^{-30}	1.75×10^{-30}	1.76×10^{-30}	1.32×10^{-30}	1.14×10^{-30}
Group **b**	–326 –314 – –	–322 –297 –280 –268	–298 – – –	–223 –209 – –	–217 –190 –173 –166
Average:	–320	–292	–	–216	–187
$\Delta\chi_{ax}$	1.92×10^{-30}	1.76×10^{-30}	1.79×10^{-30}	1.31×10^{-30}	1.14×10^{-30}

Geometric Factors from Molecular Structure of 2

The equation used for the assessment of the pseudocontact shifts of the studied complex is given here:

$$\delta_{\mathrm{MPC}} = \frac{\Delta\chi_{ax}}{12\pi}\frac{\left(3\cos^2\theta - 1\right)}{r^3} = \frac{\Delta\chi_a}{12\pi}G$$

where $\Delta\chi_{ax}$ is the axial component of the magnetic susceptibility tensor (units of m^3), r is the length of the vector between the unpaired electrons (metal center) and the NMR nucleus and θ is the angle between the r vector and the magnetic susceptibility main axis. The distance r and the angle θ are encompassed in G, the geometric factor.

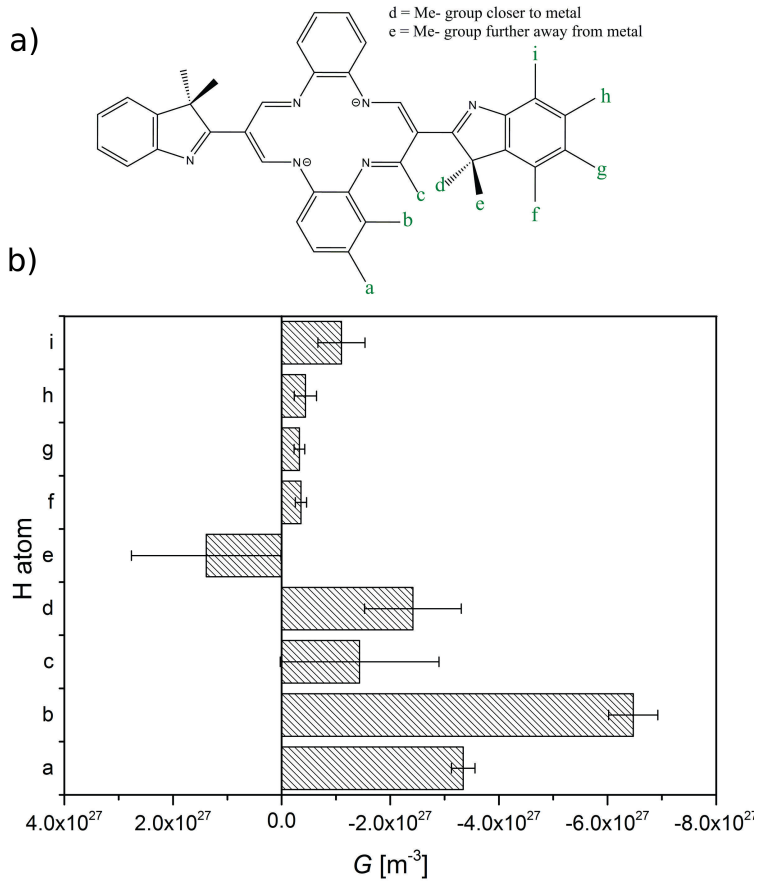

Figure S8: a) Schematic representation of H-atom annotation for NMR assignment. b) A bar chart representation of *G* values and their standard deviations as given in Table S2.

As can be seen in the table, the *G* values for H-atoms **a** and **b** have small deviations within the molecular structure (Table S2). Thus, these groups are used, together with their Fermi-contact terms obtained from DFT and their diamagnetic chemical shift contributions to calculate the value of the axial component of the magnetic susceptibility anisotropy for the **2**. It is also apparent that the methyl groups which are pointing away from the metal (group **e**) have a *G* with a positive value (Figure S8), i.e. due to the small contact-shift, are expected to have a positive total chemical shift in the ^{1}H NMR spectrum.

Table S2: Geometric factors (*G*) of the H-atoms in the molecular structure of the **2** (H-atom positions optimized with density functional theory, see main text). Since the position of the acidic proton is unknown in the molecular structure, the *G* values for all chemically equivalent H-atoms of both double-decker moieties in the unit cell were averaged. The standard deviations of the *G* factors are given in the Table.

Group	*G* [m^{-3}]	Standard deviation [m^{-3}]	Standard deviation (%)
a	-6.47×10^{27}	4.51×10^{26}	–6.97
b	-3.34×10^{27}	2.17×10^{26}	–6.49
c	-1.43×10^{27}	1.46×10^{27}	–101.86
d	-2.42×10^{27}	8.90×10^{26}	–36.81
e	1.39×10^{27}	1.37×10^{27}	98.94
f	-3.55×10^{26}	1.04×10^{26}	–29.27
g	-3.26×10^{26}	9.89×10^{25}	–30.31
h	-4.37×10^{26}	2.06×10^{26}	–47.19
i	-1.10×10^{27}	4.34×10^{26}	–39.37

Fermi-contact Contributions from DFT

As the Table S3 shows, the ^{1}H nuclei which are expected to experience a considerable Fermi-contact shift are those which are up to 3 bonds away from the metal centre (group c, annulene H-atoms).

Table S3. Calculated Fermi-contact shifts for the ^{1}H-nuclei in the molecular structure of **2** (from a single point calculation on structures with optimized H-atom positions and with equation from the main text). Fermi-contact shift values were averaged over all chemically equivalent ^{1}H nuclei in both double-decker moieties found in the unit cell. The values for two temperatures (235.0 K and 295.0 K) are given in the Table.

Group	δ_{FC} [ppm] at 235.0 K	Standard Deviation [ppm]	δ_{FC} [ppm] at 295.0 K	Standard deviation [ppm]
a	2.46	3.20	–1.96	2.55
b	–4.00	2.87	3.19	2.29
c	–63.71	24.69	–50.75	19.67
d	–0.58	0.63	–0.46	0.50
e	0.49	0.47	0.39	0.38
f	0.14	0.10	0.11	0.08
g	–0.84	0.35	–0.67	0.28
h	0.30	0.11	0.24	0.09
i	–0.87	0.38	–0.69	0.31

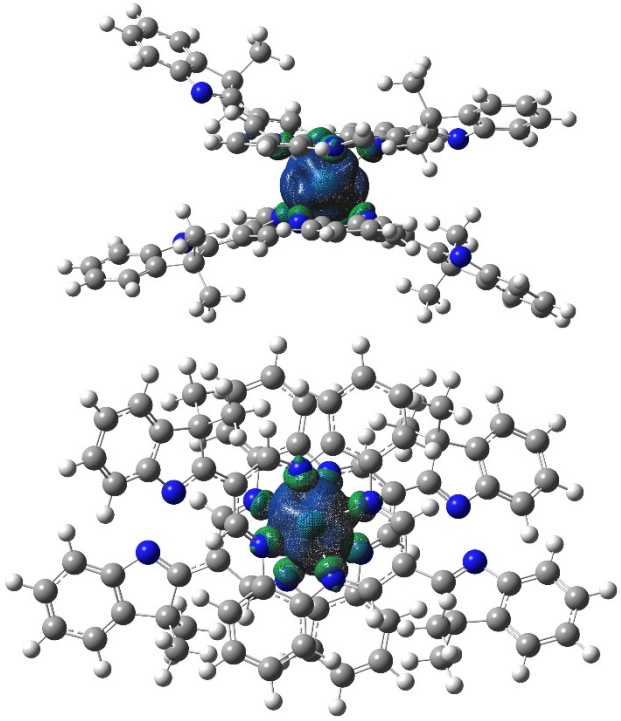

Figure S9. Spin density isosurface (value 0.0004) obtained at the UTPSSh level of theory with the SARC basis set for Tb^{III} and EPRII basis set for other atoms. The structure used for this calculation was based on the molecular structure (with atom Tb01), with optimized H-atom positions (see main text for details). Top and side view. Positive spin density is shown in blue, negative spin density in green color.

Monocation versus Trication

The DFT optimized structures of the Y^{III} analogues of the monocationic (protonated twice) and tricationic (protonated four times) complex, together with NMR data and calculated contact shift contributions, were used in order to elucidate how many times **2** is protonated under the conditions used (ca. 50 equivalents acetic acid, in $CDCl_3$). For this analysis, the aromatic groups of the indole moieties in the ligand were used. Namely, the ratios of the geometric factors from the DFT optimized structures of both the mono-cationic and tri-cationic species were compared to the ratios of experimental pseudo-contact shifts obtained at 235.0 K and at 295.0 K. This analysis is shown in Table S4. These aromatic groups are a reliable choice for such an analysis since they are relatively rigid (Figure S8) and experience small contact shift contributions (Table S3). Furthermore, as can be seen from DFT optimized structures with Y^{III} (Figures S10), the indole moieties have considerably different positions relative to the metal center, depending on how many of the indole N-atoms are protonated.

As the Table shows, the most likely structure under acidic conditions is the mono-cationic (doubly protonated) complex $[Tb(LH)_2]+$, rather than the tri-cationic $[Tb(LH_2)_2]^{3+}$ species. In the case of the tricationic species, the ratios of the geometric factors for the mentioned aromatic H-atoms are considerably different from the experimental pseudo-contact shift values, whereas the agreement with the experiment is quite good for the mono-cationic complex.

Table S4. Elucidation of the level of protonation of **2** in presence of an excess of acetic acid, based on the comparison of the ratios of geometric factors (from corresponding DFT optimized structures) with the ratios of experimental pseudocontact shift values for the aromatic groups of the indole moieties. The diamagnetic shifts were calculated with ChemDraw 15.[1–4] The calculated contact shift contributions were also taken into account (Table S3). Signal assignment for ^{1}H NMR signals based on ^{1}H,^{1}H-COSY spectrum of deprotonated complex in *o*-$C_6D_4Cl_2$ (Figures S7).

235.0 K	$[Tb(LH_n)_2]^{m+}$			
Signal	δ_{expt} [ppm]	δ_{dia} [ppm]	δ_{pc} [ppm]	Ratio δ_{pc}/δ_{pc} (g)
f	–9.37	7.42	–16.93	1.2
g	–7.39	7.16	–13.71	1.0
h	–14.36	7.28	–21.94	1.6
i	–40.81	7.45	–47.39	3.5
295.0 K	$[Tb(LH_n)_2]^{m+}$			
Signal	δ_{expt} [ppm]	δ_{dia} [ppm]	δ_{pc} [ppm]	Ratio δ_{pc}/δ_{pc} (g)
f	–5.12	7.42	–12.65	1.4
g	–2.75	7.16	–9.24	1.0
h	–6.59	7.28	–14.11	1.5
i	–22.61	7.45	–29.37	3.2
From DFT	Monocation [Tb(LH)2]+			
Signal	r [Å]	θ [°]	G [m^{-3}]	Ratio G/G (g)
f	9.23	67.67	-7.21×10^{26}	1.2
g	10.75	72.55	-5.88×10^{26}	1.0
h	10.33	78.53	-8.00×10^{26}	1.4
i	8.20	82.07	-1.71×10^{27}	2.9
From DFT	Trication $[Tb(LH_2)_2]^{3+}$			
Signal	r [Å]	θ [°]	G [m^{-3}]	Ratio G/G (g)
f	9.45	54.92	-1.08×10^{25}	0.2
g	11.08	56.64	-6.83×10^{25}	1.0
h	10.79	59.80	-1.92×10^{26}	2.8
i	8.73	62.15	-5.19×10^{26}	7.6

Table S5: DFT optimized structures of isostructural Y^{III} complex with one, two or four acidic protons or without any acidic protons.

Structure	Energy (B3LYP/def2tzvp) Hartree	Energy difference kJ/mol
$[Y^{III}L(LH)]^0$ indole-N atom	−3632.09407407	0
$[Y^{III}L(LH)]^0$ annulene-N atom	−3632.07938091	+38.6
$[Y^{III}L_2]^-$	−3631.59450991	+1311.6
$[Y^{III}(LH)_2]^+$	−3632.53027084	−1145.2
$[Y^{III}(LH_2)_2]^{3+}$	−3633.17272907	−2832.0
L = annulene ligand LH = protonated ligand LH2 = doubly protonated annulene ligand		
xyz file available below		

Coordinates of Molecular Structures with Optimized H-atom Positions

DFT optimized structures positons of H atoms in Tb^{III} complex (starting from molecular structure, unit cell contains two double-decker complexes):

Double-decker with atom Tb01

Tb	−0.069300	0.052200	−0.023600	C	3.064100	0.719900	−2.056700	C	−0.095600	3.576600	−2.691400
C	−1.576700	1.726700	−2.293300	N	−0.546100	−2.118000	−1.036300	H	0.897000	4.027100	−2.645100
N	1.887200	−1.076600	−0.931700	N	−0.789000	2.189600	0.863500	C	6.653100	−2.624900	4.970200
N	1.626900	1.212700	1.245100	C	2.717600	−0.633500	2.377800	H	6.350000	−3.463500	5.606500
C	7.760400	0.194300	−3.269100	N	−5.061700	−1.737500	−2.618900	C	6.172200	1.910400	−3.814400
H	7.985600	−0.734900	−2.741400	C	0.503200	−3.025100	−0.741300	C	4.283100	−2.177100	3.937200
C	−6.135500	−2.645900	−2.939500	C	−4.334100	2.399100	1.995700	C	4.723400	2.230900	−3.553000
N	5.088300	−0.387600	2.582600	C	0.345900	−4.387700	−0.427800	C	−0.529100	−3.509400	2.570500
N	−1.691800	0.383800	−1.816700	H	−0.653900	−4.823800	−0.414000	H	0.457400	−3.944200	2.736900
C	7.459000	−0.490900	3.343000	C	4.077800	−3.566400	3.335700	C	−2.762600	−1.766000	−1.999300
H	7.757700	0.333100	2.691100	H	3.026300	−3.787500	3.109000	C	−1.641000	−4.304700	2.705800
N	0.753600	1.404600	−1.852400	H	4.647200	−3.677700	2.401000	H	−1.505600	−5.347400	3.011500
C	−8.288100	−3.415200	−3.479900	H	4.435700	−4.337500	4.038200	C	−8.159400	4.440500	3.647200
H	−9.341100	−3.194800	−3.692100	C	2.678700	−4.597600	−0.037200	H	−8.870300	5.204000	3.974300
C	−7.434300	−2.318400	−3.194200	H	3.531800	−5.217100	0.256300	C	5.727000	−1.954300	4.188100
H	−7.783400	−1.285700	−3.192400	C	0.269300	3.105100	0.773900	C	4.618400	3.568300	−2.796900
N	−1.998300	−0.365900	1.383500	C	−2.631400	2.508400	−2.711700	H	3.583500	3.831900	−2.537000
C	−6.047100	3.849000	2.731300	H	−3.643500	2.098100	−2.690200	H	5.197000	3.535100	−1.861400
N	0.429000	−1.297400	1.917300	C	−0.272100	2.261900	−2.299100	H	5.028300	4.382100	−3.418200
N	5.400800	0.247500	−2.416600	C	−1.935400	−1.690700	1.872600	C	−3.379300	−4.571600	−3.621500
C	1.556500	2.589200	0.995300	C	8.691800	0.849700	−4.028100	H	−2.307100	−4.598100	−3.377100
C	2.879600	−3.273600	−0.326200	H	9.700700	0.435700	−4.123600	H	−3.693000	−5.612900	−3.809200
H	3.873800	−2.830500	−0.240500	C	6.500500	0.754700	−3.172200	H	−3.484700	−4.022600	−4.571000
C	4.377900	0.991700	−2.653600	C	−6.512900	−4.956400	−3.215300	C	−4.217700	−3.952300	−2.543800
C	−3.051500	−2.530600	2.043000	H	−6.165800	−5.996000	−3.219200	C	−0.641400	−2.185200	2.172200
H	−4.042500	−2.143200	1.796600	C	1.803100	−2.471700	−0.696000	C	3.474400	−2.011600	5.240100

H	2.394500	−2.146500	5.083200
H	3.801200	−2.755400	5.985600
H	3.629400	−1.011400	5.672900
C	3.997700	−1.041800	2.928500
C	7.970500	−2.208500	4.957600
H	8.710400	−2.716900	5.582100
C	1.423900	−5.152600	−0.096400
H	1.281700	−6.208000	0.155000
C	−1.179000	4.363100	−3.105200
H	−1.015800	5.402800	−3.400600
C	8.378700	2.023400	−4.680800
H	9.141700	2.526000	−5.283000
C	−2.438000	3.809200	−3.115400
H	−3.299200	4.407500	−3.428500
C	7.126100	2.560300	−4.583500
H	6.881600	3.488900	−5.110500
C	−3.112000	1.777900	1.542700
C	3.937600	2.263000	−4.869100
H	2.877100	2.514800	−4.731400
H	4.367600	3.018500	−5.548000
H	3.987200	1.290100	−5.382300
C	−2.898500	−3.822200	2.485700
H	−3.773600	−4.466600	2.606300
C	6.166200	−0.913200	3.361400
C	−7.875900	−4.682500	−3.473400
H	−8.563000	−5.503800	−3.692500
C	−3.980800	−2.419200	−2.377700
C	−4.103600	−4.709800	−1.185400
H	−4.725800	−4.223200	−0.420500
H	−4.459900	−5.746200	−1.305600
H	−3.075600	−4.750000	−0.801500
C	−6.914000	4.827200	3.110800
H	−6.655200	5.888700	3.038200
C	−5.677400	−3.941900	−2.926300
C	8.364300	−1.152000	4.144200
H	9.413500	−0.839900	4.146900
C	−4.619400	4.666500	0.806900
H	−4.967400	5.699200	0.969800
H	−3.624200	4.713200	0.340100
H	−5.301700	4.187100	0.088600
C	−7.623600	2.118200	3.351100
H	−7.872800	1.057700	3.433500
C	−6.396600	2.500400	2.793500
C	−4.606900	3.897500	2.147800
C	−8.480900	3.098400	3.753600
H	−9.449900	2.821700	4.182600
N	−5.368400	1.640200	2.341200
C	−3.725700	4.625200	3.193700
H	−4.154600	5.617000	3.407400
H	−3.693800	4.062500	4.139300
H	−2.689800	4.781700	2.860000
C	−1.642700	−2.585900	−1.580600
H	−1.719900	−3.659400	−1.765600
C	−2.641300	−0.367300	−2.259800
H	−3.421400	0.032100	−2.924700
C	2.933800	−0.614000	−1.541700
H	3.784700	−1.269400	−1.772500
C	1.991400	1.581600	−2.307100
H	2.172600	2.430200	−2.968900
C	−2.006000	2.628500	1.248600
H	−2.129500	3.698400	1.415300
C	2.640900	0.714000	1.913500
H	3.485700	1.349100	2.210100
C	−3.005000	0.396300	1.732500
H	−3.838500	−0.037800	2.302100
C	1.596900	−1.484800	2.509200
H	1.707100	−2.349800	3.169300
C	2.673400	3.430200	0.864100
H	3.676900	3.017600	0.979400
C	2.512000	4.778500	0.572500
H	3.393300	5.419800	0.479100
C	1.224200	5.321400	0.356900
H	1.095200	6.374800	0.097700
C	0.107500	4.464500	0.450400
H	−0.885900	4.853700	0.225100

Double−decker with atom Tb02:

Tb	0.097800	−0.037300	−0.018400
N	0.614200	2.143400	−1.055600
C	−7.516200	−1.328100	−2.888700
H	−7.852400	−0.605400	−2.141400
C	5.518100	4.314400	−2.751000
N	0.440000	−2.204500	1.021000
C	3.151100	3.614300	2.350800
H	4.090600	4.167500	2.441900
C	3.784200	−5.222200	1.331900
H	4.400800	−4.912300	0.475300
H	4.060600	−6.262100	1.579400
H	2.740300	−5.242400	0.987700
C	7.573900	−5.186800	3.646100
H	8.204000	−6.004700	4.010800
C	−6.588400	−3.159500	−4.772200
H	−6.245700	−3.893700	−5.511500
N	1.946100	−0.316800	−1.557200
C	8.138800	−3.935500	3.482600
H	9.194800	−3.783300	3.724600
N	1.887700	0.191800	1.565000
C	−8.392700	−1.985900	−3.713000
H	−9.466900	−1.794100	−3.625200
C	6.058900	−3.106700	2.727600
N	−1.725100	0.948600	−1.284100
C	−1.788100	2.337900	−1.039400
C	8.134800	4.144500	−3.569500
H	9.181200	4.077500	−3.888400
N	−1.855100	−0.914800	1.133200
N	−5.152000	1.173000	2.263000
N	−0.405700	1.472400	1.842400
C	3.185100	−2.441000	−1.918200
H	4.138400	−1.942200	−1.728300
C	−1.681100	5.075200	−0.420400
H	−1.627700	6.137400	−0.166600
C	−3.138600	−2.994700	0.687000
H	−4.081300	−2.446100	0.658700
N	−5.087700	−1.025100	−2.328300
N	−0.379900	−1.524600	−1.886600
C	6.218000	5.510100	−2.958900
H	5.777100	6.497500	−2.804700
C	−7.853900	3.024700	4.781600
H	−8.542500	3.528600	5.466800
C	−2.744200	1.082600	2.195400
C	−8.347300	2.150700	3.847500
H	−9.426500	1.969700	3.807400
C	1.984100	1.560800	1.930200
C	−3.948500	−1.535300	−2.790400
N	5.110800	−2.190300	2.233700
C	0.759500	2.238400	2.096800
C	6.122700	3.109800	−2.968200
C	−3.794700	4.085700	3.349000
H	−2.713000	4.227600	3.214000
H	−4.282400	4.336800	2.394900
H	−4.130900	4.817700	4.101600
C	0.774700	−2.332100	−2.068900
C	−1.942500	−2.318100	0.914100
C	3.158700	−3.795000	−2.162300
H	4.087200	−4.370100	−2.191800
C	−7.527600	1.494100	2.965100
H	−7.922100	0.800000	2.219100
C	−0.716300	−3.011300	0.860900
C	−0.530700	2.991200	−0.895500
C	−4.191400	−2.613000	−3.823600
C	2.737500	−2.079800	1.782500
C	−3.107000	−4.352600	0.455300
H	−4.039600	−4.896900	0.281700
C	−2.960800	3.080900	−0.862200
H	−3.935800	2.594200	−0.910500
C	−2.685100	−1.012500	−2.312200
C	−0.489600	4.336500	−0.568700
H	0.471000	4.826400	−0.406700
C	−3.378400	2.330900	5.109100
H	−3.628300	1.320700	5.468400
H	−2.290600	2.377500	4.960100
H	−3.643600	3.048800	5.902600
C	−2.873700	4.448300	−0.559800
H	−3.805000	5.007300	−0.422800
C	−0.707200	−4.375900	0.598500
H	0.232300	−4.921100	0.514100
C	−4.157300	2.668500	3.802600
C	3.946200	−2.787700	2.157000
C	−3.486700	−2.368800	−5.158100
H	−3.802600	−3.118900	−5.901600
H	−3.728600	−1.373000	−5.561100
H	−2.391700	−2.432000	−5.065100
C	−6.503300	3.277200	4.860000
H	−6.107200	3.977800	5.602400

C	5.510600	−4.360900	2.907800
C	−3.887100	−4.023000	−3.322900
H	−4.285100	−4.767500	−4.031500
H	−2.810100	−4.218200	−3.217900
H	−4.351600	−4.208700	−2.343500
C	1.953800	4.268400	2.527000
H	1.947600	5.339900	2.749400
C	−5.667400	2.597600	3.996000
C	−6.173100	−1.584400	−3.042000
C	6.265600	−5.415500	3.357700
H	5.826800	−6.409700	3.491500
C	−5.710100	−2.511800	−3.978700
C	−7.943000	−2.908600	−4.648800
H	−8.658200	−3.424200	−5.295300
C	0.759200	3.599100	2.391800
H	−0.184100	4.138300	2.481600
C	−3.987700	1.599500	2.704500
C	3.182200	2.282600	2.061900
H	4.133600	1.774700	1.890200
C	4.006600	−4.328600	2.514100
C	0.747600	−3.721400	−2.306400
H	−0.203300	−4.242400	−2.416500
C	−6.184300	1.733400	3.038100
C	2.858100	1.915700	−1.868400
N	5.221100	2.072400	−2.656400
C	2.008300	−1.685800	−1.855400
C	4.027400	2.670200	−2.250200
C	−1.904100	−5.023700	0.421800
H	−1.900900	−6.100000	0.219200
C	3.138600	−4.656500	3.722200
H	3.356600	−3.978200	4.561000
H	2.063700	−4.577600	3.499700
H	3.329700	−5.687300	4.067200
C	7.368800	−2.844200	3.026100
H	7.791800	−1.847200	2.891600
C	1.935500	−4.419300	−2.334800
H	1.906700	−5.501300	−2.503300
C	4.135400	4.071400	−2.346900
C	7.581800	5.376400	−3.404800
H	8.173400	6.280400	−3.574600
C	3.285700	4.736500	−3.525500
H	3.522300	5.805600	−3.589700
H	3.548100	4.273400	−4.491800
H	2.202600	4.618100	−3.386700
C	7.433000	3.019600	−3.383300
H	7.876500	2.031000	−3.529800
C	1.687800	2.649100	−1.542500
H	1.700000	3.715600	−1.773900
C	2.904700	0.491500	−1.966400
H	3.790900	0.096800	−2.483400
C	−1.517200	−1.840400	−2.456400
H	−1.587500	−2.735400	−3.081400
C	−2.707400	0.353800	−1.872500
H	−3.629800	0.891100	−2.131900
C	−2.834700	−0.286600	1.700700
H	−3.784500	−0.786600	1.932500
C	1.568200	−2.761400	1.458800
H	1.565300	−3.841300	1.628100
C	2.809600	−0.637900	1.957800
H	3.688600	−0.287900	2.515400
C	−1.539400	1.793500	2.390300
H	−1.578400	2.667100	3.049000
C	3.503800	5.297800	−1.101000
H	4.150800	6.173500	−1.223300
H	2.468700	5.532000	−1.358800
H	3.580300	4.889600	−0.086100

Coordinates of DFT Optimized Structures with Y^{III} Analogues

DFT optimized structures of isostructural Y^{III} complex with one or two acidic protons or without acidic protons:

$[Y^{III}L(LH)]^0$ (L = annulene ligand, LH = protonated ligand) with acidic H^+ on indole-N atom:
Energy (B3LYP/def2tzvp): −3632.09407407 Hartree (set to 0 kJ/mol).

Y	2.879000	4.148400	4.519000
N	3.666900	3.020100	2.485300
C	10.328300	6.289400	7.641200
H	10.639900	5.246200	7.556700
C	0.246900	2.642600	−2.259700
N	0.849200	5.242100	5.557700
C	0.965000	−0.827100	2.827200
H	0.449400	−1.498500	2.136600
C	−2.750000	7.318400	3.709200
H	−2.308700	7.619800	2.748300
H	−3.646600	7.933900	3.880400
H	−2.023300	7.547800	4.500700
C	−6.168700	5.660300	1.257400
H	−7.188900	6.021100	1.108200
C	9.479600	8.987200	7.846000
H	9.163800	10.031500	7.931500
N	2.077400	5.486300	2.636600
C	−5.591500	4.798600	0.318000
H	−6.166500	4.489300	−0.558100
N	0.878900	2.753500	3.961800
C	11.133200	7.248100	8.269100
H	12.099700	6.951400	8.685700
C	−3.587600	4.732300	1.616400
N	5.288700	3.937900	4.415600
C	5.687000	2.744700	3.772300
C	−2.112200	3.471200	−3.480400
H	−3.026100	3.807000	−3.977700
N	2.957400	4.357200	6.964600
N	5.275300	2.434500	9.649600
N	2.920100	1.859800	5.449400
C	1.027900	7.735000	2.362500
H	0.350700	7.366800	1.589800
C	6.337200	0.372100	2.401000
H	6.579300	−0.553700	1.873100
C	2.804000	6.299900	8.516700
H	3.685400	5.969800	9.068700
N	8.151800	5.904700	6.468500
N	3.745900	6.427300	4.509200
C	−0.061500	2.162600	−3.526500
H	0.613700	1.482000	−4.053600
C	7.477700	−0.190800	12.024300
H	8.049400	−0.908600	12.618000
C	4.052100	2.249300	7.587300
C	7.377000	1.140300	12.450300
H	7.873100	1.448200	13.374800
C	1.218000	1.389300	3.808400
C	7.137400	6.652500	6.125200
C	2.310400	0.924700	4.599300
C	−0.631500	3.510200	−1.584800
C	6.277300	−0.223700	7.649600
H	5.753700	−0.278000	6.683600
H	7.111000	0.486100	7.540100
H	6.704600	−1.217700	7.858300
C	2.832500	7.350500	3.964500
C	2.355800	5.547600	7.415200
C	0.950800	9.073900	2.749700
H	0.223300	9.736900	2.274700
C	6.652500	2.081800	11.708600
H	6.569800	3.122600	12.028800
C	1.229500	6.015300	6.680400
C	4.833500	2.263900	2.736500
C	7.315000	8.140900	6.555700
C	−0.822400	4.520500	3.933500
C	2.154500	7.473800	8.895700
H	2.525900	8.044100	9.750800
C	6.841300	2.014400	4.103400
H	7.480600	2.360600	4.917200
C	5.989300	6.063700	5.428400
C	5.177900	1.074200	2.070700
H	4.519400	0.672700	1.299100
C	4.180400	−0.799500	8.995900
H	3.507700	−0.469800	9.802200
H	3.578600	−0.934700	8.085000
H	4.581700	−1.786600	9.275800
C	7.170100	0.842500	3.421500
H	8.070800	0.289000	3.698300
C	0.599600	7.210500	7.066400
H	−0.231300	7.602100	6.477300
C	5.343500	0.201200	8.803900
C	−1.985300	4.904700	3.246900
C	7.396200	9.109400	5.353100
H	7.707100	10.108000	5.699500
H	8.139300	8.762100	4.619400
H	6.433800	9.224800	4.832800

C	6.849900	−0.609800	10.838600
H	6.934100	−1.651500	10.513800
C	−4.156600	5.578100	2.575900
C	6.254100	8.594000	7.582500
H	6.505400	9.596500	7.964900
H	5.243900	8.642400	7.149500
H	6.220900	7.904600	8.439600
C	2.041100	−1.287100	3.595300
H	2.376400	−2.323600	3.505900
C	6.129500	0.321100	10.100400
C	9.097800	6.699600	7.119000
C	−5.450100	6.055800	2.396800
H	−5.910800	6.722700	3.130400
C	8.678600	8.039200	7.221400
C	10.718200	8.582400	8.373100
H	11.362100	9.314000	8.868000
C	2.705800	−0.421900	4.461300
H	3.565500	−0.792400	5.020600
C	4.860700	1.677600	8.669600
C	0.566300	0.504400	2.933100
H	−0.253900	0.862400	2.308500
C	−3.149900	5.821800	3.696200
C	2.723100	8.699700	4.352300
H	3.357000	9.084900	5.152200
C	6.030700	1.657300	10.530600
C	1.879100	3.701500	0.965400
N	−0.147200	3.860400	−0.314300
C	1.953500	6.857400	2.953600
C	1.054600	3.333500	−0.169800
C	1.049000	7.933200	8.170300
H	0.553200	8.865900	8.449200
C	−3.738200	5.383000	5.054900
H	−4.023200	4.320600	5.038300
H	−3.031400	5.534200	5.883100
H	−4.641600	5.972500	5.274600
C	−4.286300	4.315800	0.484600
H	−3.839900	3.632600	−0.238300
C	1.799100	9.554800	3.752000
H	1.735800	10.596800	4.075900
C	1.450200	2.413700	−1.361500
C	−1.255400	2.581000	−4.138500
H	−1.508000	2.221900	−5.139100
C	2.748500	2.885000	−2.050200
H	2.927800	2.295000	−2.963100
H	2.678600	3.944000	−2.340600
H	3.626200	2.770000	−1.397000
C	−1.810300	3.947900	−2.197400
H	−2.461800	4.666100	−1.697400
C	1.528000	0.916500	−0.978200
H	1.629700	0.307700	−1.890500
H	2.384800	0.689200	−0.328600
H	0.614200	0.593000	−0.457900
H	−1.572400	4.050700	1.358400
N	−2.285600	4.395100	2.023400
C	−0.341000	5.302300	5.058600
H	−1.072800	5.984500	5.508900
C	−0.270100	3.218300	3.598100
H	−0.988300	2.557400	3.087500
C	3.582100	1.451600	6.516400
H	3.722400	0.374000	6.643800
C	3.585700	3.581700	7.813900
H	3.728300	3.914500	8.850200
C	3.000400	2.909600	1.364400
H	3.335000	2.165400	0.632700
C	1.616800	5.000300	1.514400
H	1.025600	5.641000	0.845800
C	6.184600	4.727100	4.954300
H	7.232600	4.404900	5.001600
C	4.871200	6.849300	5.056400
H	5.002800	7.929300	5.170900

$[Y^{III}L(LH)]^0$ (L = annulene ligand, LH = protonated ligand) with acidic H^+ on annulene-N atom:

Energy (B3LYP/def2tzvp): −3632.07938091 Hartree (+38.6 kJ/mol).

Y	2.953600	4.064900	4.376200	H	0.087700	6.832200	1.504600	C	5.056700	2.225300	2.918700
N	3.907300	2.937600	2.510300	C	6.625400	0.362100	2.854300	C	7.038000	8.575000	6.158100
C	10.183600	7.073100	7.398800	H	6.931900	−0.594700	2.424300	C	−1.266300	4.585400	4.652200
H	10.556300	6.048000	7.452100	C	3.291100	6.143400	8.411600	C	2.804600	7.343300	8.934600
C	1.606600	2.556800	−2.863200	H	4.280300	5.783900	8.700500	H	3.409800	7.905900	9.649100
C	0.507900	−0.351800	2.423000	N	8.011400	6.402300	6.352700	C	6.960900	2.152100	4.448500
H	−0.064100	−0.876200	1.654100	N	3.554000	6.368000	4.450600	H	7.525900	2.585500	5.275900
C	−2.990200	7.466300	4.231700	C	1.521600	1.975100	−4.122300	C	5.839000	6.286300	5.328700
H	−2.721300	7.516000	3.166600	H	2.190800	1.162100	−4.420100	C	5.474900	0.996000	2.380800
H	−3.765700	8.225100	4.421300	C	7.278800	−0.921300	11.608900	H	4.883400	0.519600	1.597100
H	−2.102100	7.751700	4.814600	H	7.780100	−1.712700	12.171900	C	3.738900	−1.051200	8.789500
C	−6.924500	5.831200	2.729100	C	3.938700	1.973100	7.386500	H	3.177400	−0.637900	9.641000
H	−7.904200	6.303400	2.622600	C	7.392900	0.410300	12.029600	H	3.066400	−1.078600	7.919000
C	9.176800	9.720100	7.245400	H	7.984200	0.644700	12.918900	H	4.004600	−2.091700	9.035200
H	8.800500	10.746200	7.192100	C	0.851700	1.626400	3.797200	C	7.369500	0.940400	3.888300
N	2.111400	5.250500	2.492200	C	6.947400	7.033700	5.939200	H	8.262000	0.439900	4.271600
C	−6.615100	4.696200	1.967200	N	−3.152800	4.136800	3.245900	C	0.790200	7.109400	7.613800
H	−7.358000	4.295800	1.272400	C	2.009500	1.028200	4.367700	H	−0.187000	7.492200	7.316500
N	0.514000	2.930300	4.255600	C	0.738500	3.601200	−2.495500	C	5.022900	−0.231700	8.524600
C	10.942000	8.156100	7.860500	C	5.814600	−0.788500	7.321200	C	−2.606000	4.906000	4.142900
H	11.933600	7.978100	8.285300	H	5.225200	−0.787800	6.392500	C	7.015200	9.364100	4.829500
C	−4.444500	4.608900	2.981800	H	6.724500	−0.197200	7.140900	H	7.255500	10.422400	5.019200
N	5.324700	4.034900	4.483500	H	6.119800	−1.827700	7.523000	H	7.764400	8.970200	4.126200
C	5.815900	2.810200	3.973400	C	2.506100	7.152200	3.921500	H	6.033500	9.330200	4.333800
C	−0.309200	3.493800	−4.652700	C	2.538700	5.402100	7.487100	C	6.525100	−1.248000	10.468500
H	−1.056100	3.852200	−5.366300	C	0.387000	8.581000	2.730900	H	6.442100	−2.291000	10.147900
N	2.957000	4.188000	6.898000	H	−0.434500	9.132700	2.267700	C	−4.750500	5.747500	3.749200
N	5.317900	1.987900	9.356400	C	6.761900	1.444700	11.327200	C	5.985600	9.108300	7.155500
N	2.730900	1.809700	5.285200	H	6.845300	2.486500	11.643600	H	6.195300	10.164200	7.389800
C	0.685900	7.289000	2.295200	C	1.271900	5.904600	7.088900	H	4.960600	9.050700	6.761400

H	6.016900	8.541600	8.098100
C	1.632500	−0.951900	3.000700
H	1.942500	−1.952300	2.688400
C	5.896300	−0.224700	9.769700
C	8.920500	7.334800	6.860400
C	−5.988200	6.368400	3.628200
H	−6.240800	7.255700	4.216300
C	8.422300	8.648300	6.784000
C	10.448700	9.465500	7.786700
H	11.057900	10.295900	8.152600
C	2.381900	−0.263500	3.955000
H	3.285700	−0.716800	4.365500
C	4.743100	1.296600	8.411700
C	0.127000	0.931700	2.814500
H	−0.730200	1.408300	2.335400
C	−3.532500	6.067200	4.602000
C	2.170100	8.444500	4.363500
H	2.721700	8.890400	5.192800
C	6.013600	1.111500	10.194700
C	2.433500	3.627200	0.676700
N	0.977600	4.042800	−1.191200
C	1.740500	6.561900	2.871500
C	1.964200	3.352800	−0.687800
C	1.555100	7.827000	8.536000
H	1.169700	8.764800	8.942300
C	−3.878100	5.974700	6.104200
H	−4.274000	4.979900	6.358800
H	−3.002200	6.165400	6.743300
H	−4.647700	6.720000	6.360000
C	−5.368500	4.069600	2.083400
H	−5.113100	3.186100	1.494900
C	1.127500	9.157200	3.769200
H	0.885900	10.161400	4.126600
C	2.519500	2.284300	−1.677700
C	0.553100	2.452900	−5.021800
H	0.472500	2.009200	−6.017400
C	3.990400	2.547500	−2.073300
H	4.280800	1.877400	−2.898100
H	4.124500	3.583600	−2.419000
H	4.690500	2.373400	−1.242600
C	−0.228100	4.081300	−3.383900
H	−0.895100	4.892400	−3.084300
C	2.313700	0.836600	−1.178500
H	2.570700	0.125400	−1.979700
H	2.939600	0.597500	−0.306400
H	1.264200	0.663800	−0.896800
H	0.868300	4.145300	6.105700
N	0.561600	5.119500	6.155300
C	3.612500	3.332000	7.660200
H	3.893500	3.640100	8.676100
C	−0.599500	5.418300	5.531200
H	−1.016000	6.394600	5.767400
C	−0.729800	3.301400	4.220400
H	−1.496300	2.620600	3.828000
C	3.346400	1.264000	6.310500
H	3.342100	0.170200	6.384400
C	3.455400	2.846500	1.273800
H	3.961900	2.139100	0.610400
C	1.928700	4.828300	1.262200
H	1.391900	5.466700	0.549200
C	4.640700	6.934500	4.944700
H	4.649100	8.027100	5.005200
C	6.143800	4.933900	4.974700
H	7.208900	4.689300	5.074500

$[Y^{III}L_2]^-$ (L = annulene ligand):

Energy (B3LYP/def2tzvp): −3631.59450991 Hartree

Y	2.766400	4.145600	4.436000	H	7.459700	3.220100	5.691400	H	4.972300	1.390900	−2.530300
N	4.048900	2.987900	2.665200	C	5.496100	6.740400	5.251000	H	4.699200	3.126400	−2.244300
C	9.583900	8.122300	7.521400	C	5.794300	1.209300	2.816100	H	5.209000	2.070300	−0.905800
H	10.070200	7.152700	7.649400	H	5.304700	0.611000	2.046000	C	0.467200	3.282900	−3.674800
C	2.292800	1.917300	−2.804500	C	7.565300	1.458400	4.448000	H	−0.258300	4.087600	−3.536700
C	8.286100	10.617300	7.175600	H	8.465200	1.078500	4.938800	C	2.904700	0.433400	−0.872200
H	7.793500	11.586500	7.047300	C	6.382800	9.909800	4.639000	H	3.286400	−0.347500	−1.550400
N	2.090600	5.130800	2.278800	H	6.501200	10.994500	4.795200	H	3.434500	0.337800	0.086400
C	10.175200	9.307000	7.978400	H	7.220600	9.566600	4.013100	H	1.840000	0.229100	−0.685000
H	11.148900	9.265900	8.475300	H	5.452100	9.755000	4.074000	C	3.728000	2.757000	1.412400
N	5.214000	4.381400	4.622100	C	5.196900	9.628200	6.886400	H	4.360800	2.058600	0.854300
C	5.845000	3.173000	4.258500	H	5.256000	10.712900	7.074400	C	2.062000	4.597800	1.086500
C	0.539600	2.555700	−4.869700	H	4.223100	9.417700	6.421600	H	1.573900	5.140300	0.265400
H	−0.144400	2.796500	−5.688900	H	5.218900	9.113900	7.858800	C	5.928600	5.387100	5.051400
C	0.548600	7.016300	1.756900	C	8.337100	8.201800	6.889600	H	7.005900	5.250700	5.217300
H	0.033400	6.422100	0.999700	C	7.696700	9.445400	6.719600	C	4.288400	7.245700	4.696900
C	6.958600	0.729100	3.420600	C	9.538900	10.544000	7.811000	H	4.225100	8.336600	4.621600
H	7.378600	−0.228700	3.101400	H	10.017600	11.456600	8.176400	N	0.718600	5.131900	5.413000
N	7.585700	7.148600	6.377200	C	1.808000	8.508000	3.753600	C	1.442100	−0.918000	2.745700
N	3.293900	6.550600	4.193200	H	2.264400	9.083500	4.560700	H	1.028800	−1.623200	2.019900
C	2.360000	1.198100	−3.990600	C	2.699700	3.386000	0.658800	C	−3.201800	6.554300	3.694200
H	3.087200	0.390500	−4.123200	N	1.435000	3.546300	−1.384900	H	−2.998300	6.566100	2.613000
C	6.479600	7.628300	5.860700	C	1.609100	6.442300	2.476100	H	−4.050600	7.230800	3.887500
C	1.353000	2.954600	−2.641600	C	2.392800	2.964400	−0.703400	H	−2.318200	6.965900	4.202600
C	2.255200	7.200000	3.496500	C	0.762400	9.070000	3.017200	C	−6.946900	4.307200	2.481200
C	0.130700	8.323500	2.017500	H	0.427300	10.086300	3.241900	H	−7.984100	4.639900	2.385600
H	−0.701300	8.750200	1.451200	C	3.091500	1.825300	−1.513700	C	−6.515400	3.162600	1.798000
C	5.223200	2.431900	3.211100	C	1.472800	1.523300	−5.032500	H	−7.223200	2.610600	1.172600
C	6.381700	9.181500	6.002900	H	1.511500	0.967500	−5.973300	N	0.909000	2.593900	3.964500
C	7.005200	2.667600	4.866800	C	4.580100	2.123700	−1.806300	C	−4.305900	3.439400	2.707300

N	2.852300	4.476400	6.878100
N	5.005300	2.721000	9.818500
N	3.004000	1.911800	5.472600
C	2.624000	6.539700	8.255000
H	3.518000	6.288900	8.829300
C	7.001700	0.208800	12.483700
H	7.521500	−0.480400	13.154700
C	3.945000	2.424800	7.676200
C	6.867100	1.558100	12.836600
H	7.285400	1.910500	13.784100
C	1.405900	1.285800	3.783400
N	−2.960000	3.166800	2.932500
C	2.522600	0.922400	4.592100
C	6.165500	−0.033600	8.035200
H	5.725500	−0.140000	7.033400
H	7.004800	0.673300	7.956100
H	6.573800	−1.013700	8.332400
C	2.205700	5.681300	7.225700
C	6.207400	2.463100	11.995300
H	6.099600	3.517300	12.259700
C	1.064600	6.027900	6.444300
C	−1.075100	4.031200	4.157700
C	1.927600	7.718400	8.532500
H	2.273100	8.376900	9.333800
C	3.961000	−0.542500	9.225700
H	3.228200	−0.175600	9.960600
H	3.432500	−0.713800	8.276700
H	4.334300	−1.517300	9.579800
C	0.388000	7.226900	6.729900
H	−0.460300	7.526000	6.112000
C	5.139000	0.448700	9.082800
C	−2.474600	4.071400	3.748900
C	6.471600	−0.263100	11.269300
H	6.579500	−1.318400	10.998500
C	−4.739000	4.590000	3.395900
C	2.537000	−1.278300	3.537500
H	2.990000	−2.268300	3.435200
C	5.815500	0.630200	10.432600
C	−6.051500	5.030900	3.289300
H	−6.394100	5.924500	3.821100
C	3.075100	−0.362100	4.444400
H	3.956600	−0.638400	5.025400
C	4.668000	1.918500	8.837400
C	0.888000	0.358700	2.864900
H	0.054800	0.651400	2.223000
C	−3.546400	5.127100	4.171800
C	5.681900	1.987200	10.788100
C	0.807600	8.061400	7.768600
H	0.269600	8.992800	7.965500
C	−3.858200	5.091700	5.685800
H	−4.082300	4.065600	6.015000
H	−3.028100	5.470900	6.299300
H	−4.742100	5.714800	5.899500
C	−5.192200	2.714900	1.901400
H	−4.844900	1.825600	1.370700
C	−0.533300	5.011200	5.033500
H	−1.262500	5.688200	5.491600
C	−0.364900	2.835600	3.805300
H	−1.023000	2.036900	3.437000
C	3.582500	1.568400	6.601100
H	3.742200	0.499000	6.776300
C	3.440100	3.761900	7.800400
H	3.509000	4.154700	8.823900

$[Y^{III}(LH)_2]^+$ (LH = protonated annulene ligand), protonation on indole-N atoms furthest apart:

Energy (B3LYP/def2tzvp): −3632.53027084 Hartree.

Y	2.767600	4.138100	4.430200
N	3.607700	3.002000	2.431900
C	9.431000	5.614300	8.938400
H	9.483900	4.541400	9.124400
C	0.151900	2.632100	−2.298400
N	0.808600	5.278300	5.460100
C	0.768500	−0.890500	3.008800
H	0.211700	−1.586800	2.377800
C	−2.820000	7.330200	3.618400
H	−2.383200	7.627200	2.653600
H	−3.720700	7.940300	3.784100
H	−2.097600	7.572800	4.410300
C	−6.250100	5.628200	1.209600
H	−7.275800	5.975600	1.068700
C	9.311800	8.399000	8.405000
H	9.281700	9.472600	8.202100
N	2.099300	5.507100	2.535000
C	−5.673700	4.767300	0.268400
H	−6.255500	4.446400	−0.598700
N	0.800600	2.751400	3.937100
C	10.359900	6.496500	9.506300
H	11.145200	6.100600	10.154300
C	−3.659800	4.733500	1.546200
N	5.208000	3.857300	4.413500
C	5.623100	2.692400	3.724000
C	−2.200500	3.496300	−3.508600
H	−3.110300	3.845500	−4.003600
N	2.962100	4.437200	6.835500
N	6.174400	2.891000	8.751300
N	2.888100	1.891900	5.394100
C	1.175800	7.798200	2.169800
H	0.504300	7.449500	1.384100
C	6.303200	0.386800	2.266200
H	6.558200	−0.513000	1.701500
C	2.704700	6.305500	8.472300
H	3.568900	5.975800	9.050400
N	3.753700	6.424000	4.447900
C	−0.170500	2.153200	−3.562800
H	0.489800	1.461400	−4.093500
C	8.347800	0.567400	11.463500
H	8.895500	−0.076200	12.155700
C	4.319700	2.448200	7.293800
C	8.537000	1.954000	11.505800
H	9.226100	2.381700	12.238500
C	1.108100	1.372200	3.848500
C	6.726500	6.356700	6.619600
C	2.212600	0.920400	4.629100
C	−0.710300	3.514000	−1.624400
C	6.308100	−0.323900	7.516800
H	5.584000	−0.580500	6.730300
H	7.161600	0.182400	7.041600
H	6.675600	−1.267700	7.948500
C	2.903200	7.375700	3.832700
C	2.307900	5.583100	7.330400
C	1.156600	9.146400	2.523100
H	0.478200	9.831000	2.008200
C	7.845900	2.802000	10.630200
H	7.967700	3.884800	10.684000
C	1.173000	6.038700	6.598600
C	4.773600	2.247000	2.668900
C	7.226800	7.798200	6.878600
C	−0.866300	4.546900	3.842500
C	2.017000	7.447100	8.880100
H	2.347200	7.988800	9.769800
C	6.790500	1.968900	4.023100
H	7.438900	2.290000	4.839700
C	5.791500	5.877200	5.674800
C	5.137800	1.085700	1.960400
H	4.492900	0.706200	1.167300
C	4.455500	−0.129400	9.263100
H	4.034500	0.484800	10.073200
H	3.661200	−0.305500	8.522000
H	4.737300	−1.104200	9.690800
C	7.134900	0.828000	3.301600
H	8.045400	0.278900	3.551700
C	0.505600	7.203900	7.014100
H	−0.334700	7.587100	6.433300
C	5.691600	0.550000	8.636400
C	−2.044600	4.923900	3.159600
C	7.727100	8.478400	5.585700
H	8.191200	9.444800	5.833900
H	8.484000	7.861000	5.079800
H	6.912300	8.673200	4.873800
C	7.443000	−0.000600	10.551600
H	7.286200	−1.083000	10.540000
C	−4.226400	5.575700	2.508600
C	6.162700	8.662900	7.602100

H	6.619700	9.614100	7.914000
H	5.305200	8.896400	6.955600
H	5.784900	8.157700	8.503100
C	1.852700	−1.337700	3.772300
H	2.151600	−2.388000	3.740600
C	6.746700	0.839000	9.690100
C	8.450300	6.164000	8.116100
C	−5.527100	6.038800	2.340300
H	−5.990600	6.702600	3.074600
C	8.389100	7.531600	7.829700
C	10.301200	7.871100	9.248800
H	11.038700	8.538300	9.700200
C	2.565200	−0.441600	4.565800
H	3.422500	−0.809600	5.130100
C	5.391200	2.004400	8.178500
C	0.406800	0.454400	3.047500
H	−0.428600	0.792000	2.432300
C	−3.212000	5.830300	3.618800
C	2.854000	8.734500	4.188800
H	3.479500	9.108000	5.000900
C	6.964600	2.227300	9.710300
C	1.822500	3.690200	0.912800
N	−0.207500	3.863700	−0.355800
C	2.036300	6.887300	2.812400
C	0.981800	3.320500	−0.220400
C	0.916400	7.904000	8.146600
H	0.385800	8.809000	8.450400
C	−3.781000	5.393100	4.986200
H	−4.060100	4.329100	4.978000
H	−3.066800	5.553600	5.806500
H	−4.685600	5.977300	5.212500
C	−4.361500	4.300700	0.423500
H	−3.915600	3.617500	−0.299600
C	1.993600	9.618000	3.540500
H	1.968700	10.669600	3.834800
C	1.358000	2.390400	−1.407200
C	−1.360700	2.590100	−4.167200
H	−1.624600	2.232800	−5.165200
C	2.660000	2.836600	−2.105700
H	2.824800	2.237100	−3.014500
H	2.606200	3.894100	−2.404900
H	3.540200	2.711100	−1.457100
C	−1.884500	3.971300	−2.228600
H	−2.521100	4.702300	−1.728000
C	1.414300	0.894500	−1.011800
H	1.489700	0.277400	−1.920500
H	2.279500	0.654800	−0.377200
H	0.503400	0.590700	−0.474500
H	−1.636100	4.053800	1.286000
N	−2.346300	4.413700	1.947200
C	−0.380600	5.343700	4.948600
H	−1.108600	6.038100	5.383600
C	−0.336300	3.232000	3.541500
H	−1.057300	2.573400	3.033900
C	3.703400	1.557600	6.367900
H	3.918500	0.495900	6.527700
C	3.793300	3.746500	7.579200
H	4.085300	4.125700	8.567400
C	2.922200	2.879700	1.318400
H	3.226800	2.112400	0.599000
C	1.606400	5.006600	1.427000
H	1.024900	5.646700	0.750600
C	6.014900	4.539200	5.164600
H	7.030400	4.160400	5.354800
C	4.823700	6.778900	5.087800
H	5.051600	7.846000	5.191100
H	7.072400	4.571200	7.681100
N	7.413000	5.512300	7.417800

$[Y^{III}(LH_2)_2]^{3+}$ (LH2 = doubly protonated annulene ligand), protonation on indole-N:

Energy (B3LYP/def2tzvp): −3633.17272907Hartree.

Y	0.000000	−0.000000	0.000000
N	0.416700	−1.535600	−1.915200
C	−7.152200	−4.447900	1.959500
H	−7.609000	−4.169000	1.007400
C	5.240800	−4.423300	−3.500500
C	3.194300	1.574600	−4.118400
H	4.139800	1.578800	−4.665200
C	3.704800	2.847100	4.706500
H	4.424800	2.022100	4.601400
H	3.928200	3.368500	5.648600
H	2.696900	2.418300	4.794600
C	7.261600	5.564800	4.123300
H	7.829500	6.158900	4.842200
C	−5.949600	−5.174800	4.433200
H	−5.506000	−5.465400	5.388600
N	1.901600	−1.493800	0.593200
C	7.853700	5.206500	2.904900
H	8.875500	5.523900	2.686400
N	1.901600	1.493800	−0.593200
C	−7.853700	−5.206500	2.904900
H	−8.875500	−5.523900	2.686400
C	5.853300	4.078300	2.295400
N	−1.901600	−1.493800	−0.593200
C	−1.990000	−1.527500	−2.007800
C	7.853700	−5.206500	−2.904900
H	8.875500	−5.523900	−2.686400
N	−1.901600	1.493800	0.593200
N	−0.416700	1.535600	−1.915200
C	3.197100	−1.529700	2.723000
H	4.146200	−1.478700	2.184800
C	−1.980100	−1.604100	−4.813200
H	−1.974400	−1.631200	−5.905100
C	−3.197100	1.529700	2.723000
H	−4.146200	1.478700	2.184800
N	−0.416700	−1.535600	1.915200
C	5.949600	−5.174800	−4.433200
H	5.506000	−5.465400	−5.388600
C	−7.261600	5.564800	−4.123400
H	−7.829500	6.158900	−4.842300
C	−2.658700	2.453800	−1.541800
C	−7.853700	5.206500	−2.904900
H	−8.875500	5.523900	−2.686400
C	1.990100	1.527400	−2.007800
C	−3.743700	−3.151600	2.150500
C	0.758000	1.552500	−2.711000
C	5.853300	−4.078300	−2.295400
C	−3.704800	2.847100	−4.706500
H	−2.696900	2.418300	−4.794600
H	−4.424800	2.022100	−4.601400
H	−3.928200	3.368500	−5.648600
C	0.758000	−1.552500	2.711000
C	−1.990100	1.527500	2.007800
C	3.194300	−1.574600	4.118400
H	4.139800	−1.578800	4.665200
C	−7.152200	4.447900	−1.959500
H	−7.609000	4.169000	−1.007400
C	−0.758000	1.552500	2.710900
C	−0.758000	−1.552500	−2.710900
C	−3.825400	−3.851600	3.533600
C	2.658700	2.453800	1.541800
C	−3.194300	1.574600	4.118400
H	−4.139800	1.578800	4.665200
C	−3.197100	−1.529700	−2.723000
H	−4.146200	−1.478700	−2.184800
C	−2.658700	−2.453800	1.541800
C	−0.771600	−1.584700	−4.113800
H	0.169800	−1.574800	−4.665800
C	−2.799800	5.006200	−3.652200
H	−2.884900	5.703700	−2.805900
H	−1.761000	4.650700	−3.706400
H	−3.003800	5.572800	−4.572500
C	−3.194300	−1.574700	−4.118400
H	−4.139800	−1.578800	−4.665200
C	−0.771600	1.584700	4.113800
H	0.169800	1.574700	4.665800
C	−3.825400	3.851600	−3.533600
C	3.743700	3.151600	2.150500
C	−2.799900	−5.006200	3.652200
H	−3.003800	−5.572800	4.572500
H	−2.885000	−5.703700	2.805900
H	−1.761000	−4.650700	3.706400
C	−5.949500	5.174800	−4.433200
H	−5.506000	5.465400	−5.388600
C	5.240800	4.423300	3.500500
C	−3.704800	−2.847100	4.706500
H	−3.928300	−3.368500	5.648600
H	−2.696900	−2.418300	4.794600
H	−4.424800	−2.022100	4.601400
C	1.980100	1.604100	−4.813200
H	1.974400	1.631200	−5.905100

C	−5.240800	4.423300	−3.500500
C	−5.853300	−4.078300	2.295400
C	5.949500	5.174800	4.433200
H	5.506000	5.465400	5.388600
C	−5.240800	−4.423300	3.500500
C	−7.261600	−5.564800	4.123300
H	−7.829600	−6.158900	4.842200
C	0.771600	1.584700	−4.113800
H	−0.169800	1.574700	−4.665800
C	−3.743700	3.151600	−2.150600
C	3.197100	1.529700	−2.723000
H	4.146200	1.478700	−2.184800
C	3.825400	3.851600	3.533600
C	0.771600	−1.584700	4.113800
H	−0.169800	−1.574700	4.665800
C	−5.853300	4.078300	−2.295400
C	2.658700	−2.453800	−1.541800
C	1.990100	−1.527500	2.007800
C	3.743700	−3.151600	−2.150500
C	−1.980100	1.604100	4.813200
H	−1.974400	1.631200	5.905100
C	2.799800	5.006200	3.652200
H	2.884900	5.703700	2.805900
H	1.761000	4.650700	3.706400
H	3.003800	5.572800	4.572500
C	7.152200	4.447900	1.959500
H	7.609000	4.169000	1.007400
C	1.980100	−1.604100	4.813200
H	1.974400	−1.631200	5.905100
C	3.825400	−3.851600	−3.533600
C	7.261600	−5.564800	−4.123300
H	7.829600	−6.158900	−4.842200
C	2.799900	−5.006200	−3.652200
H	3.003800	−5.572800	−4.572500
H	2.885000	−5.703700	−2.805900
H	1.761000	−4.650700	−3.706400
C	7.152200	−4.447900	−1.959500
H	7.609000	−4.169000	−1.007400
C	3.704800	−2.847100	−4.706500
H	3.928300	−3.368500	−5.648600
H	2.696900	−2.418300	−4.794600
H	4.424800	−2.022100	−4.601400
N	0.416700	1.535600	1.915200
C	−2.721300	2.205400	−0.120400
H	−3.486100	2.781600	0.425900
C	1.454000	2.225500	2.294300
H	1.393300	2.747400	3.254100
C	2.721300	2.205400	0.120400
H	3.486100	2.781600	−0.425900
C	−1.454000	2.225500	−2.294300
H	−1.393300	2.747400	−3.254100
C	1.454000	−2.225500	−2.294300
H	1.393300	−2.747400	−3.254100
C	2.721300	−2.205400	−0.120400
H	3.486100	−2.781600	0.425900
C	−1.454000	−2.225500	2.294300
H	−1.393300	−2.747400	3.254100
C	−2.721300	−2.205400	0.120400
H	−3.486100	−2.781600	−0.425900
H	5.166800	2.921900	0.644100
H	−5.166800	2.921900	−0.644100
H	−5.166800	−2.921900	0.644100
H	5.166800	−2.921900	−0.644100
N	4.928500	3.317200	1.547000
N	−4.928500	3.317200	−1.547000
N	−4.928500	−3.317200	1.547000
N	4.928500	−3.317200	−1.547000

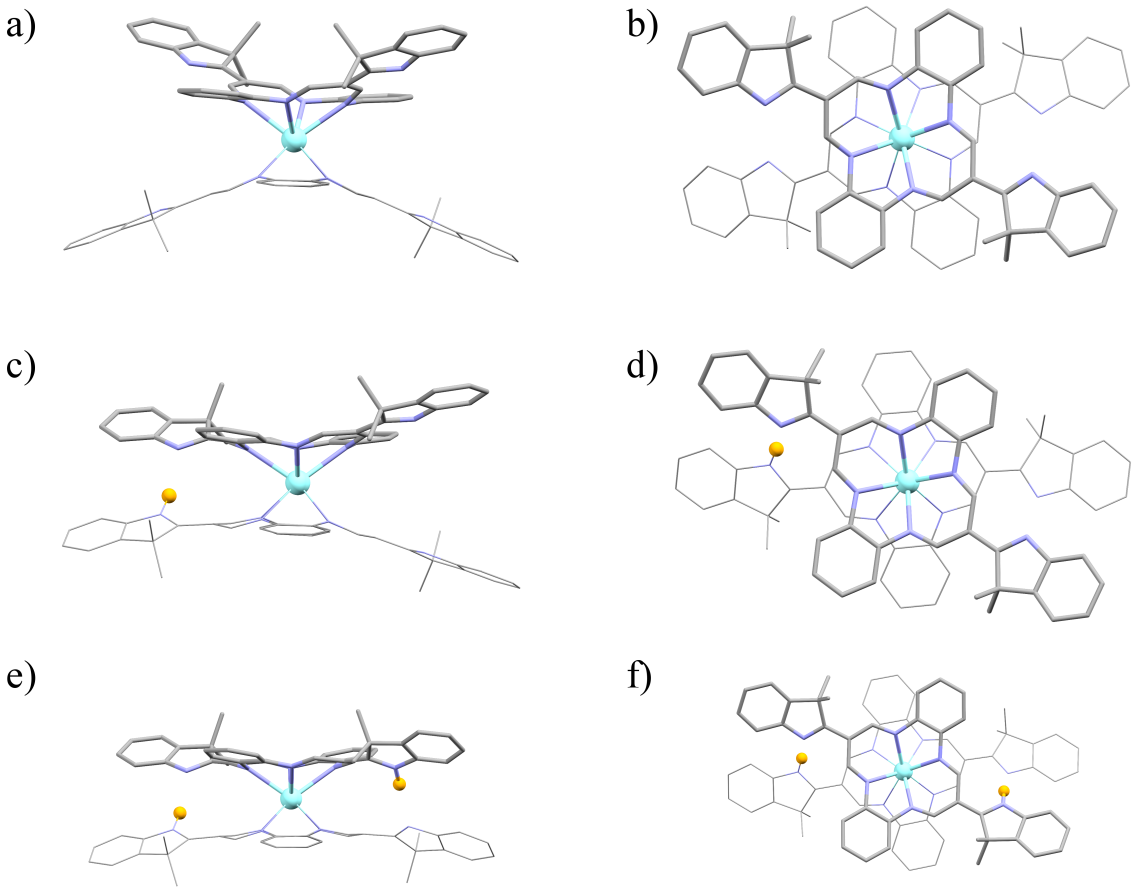

Figure S10: Side (a, c, e) and top view (b, d, f) of the optimized geometry for 1a (a, b), 1n (c, d) and 1c (e, f). Except for the hydrogen atoms on the indole N atom(s) (colored orange), all hydrogen atoms are omitted for clarity.

Table S6: Deviation from the ideal geometry for structure optimized by DFT calculation. Minimum value is better.

		$[Y^{III}L_2]^-$	$[Y^{III}L(LH)]^0$	$[Y^{III}(LH)_2]^+$	$[Y^{III}(LH_2)_2]^{3+}$
Square antiprism	D4d	1.148	1.462	1.023	2.728
Triangular dodecahedron	D2d	2.519	2.589	2.315	2788
Biaugmented trigonal prism	C2v	3.185	3.528	3.103	4.662
Biaugmented trigonal prism J50	C2v	3.824	4.114	3.770	5.202

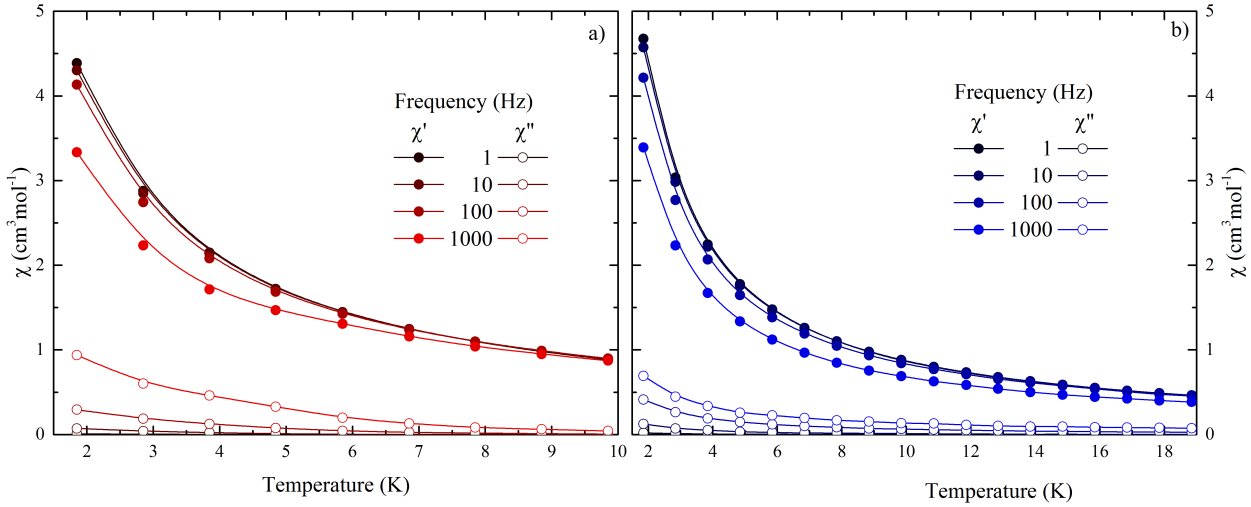

Figure S11: Temperature and frequency dependence of the susceptibility without external magnetic, for a) **1** at and b) **2**.

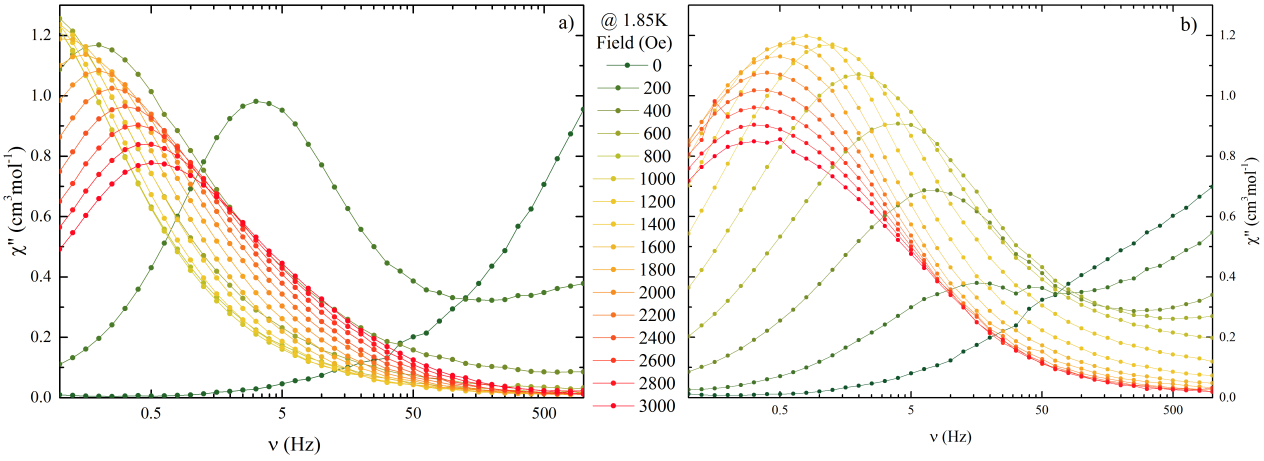

Figure S12: Field and frequency dependence of the susceptibility at 1.85 K, for a) **1** at and b) **2**.

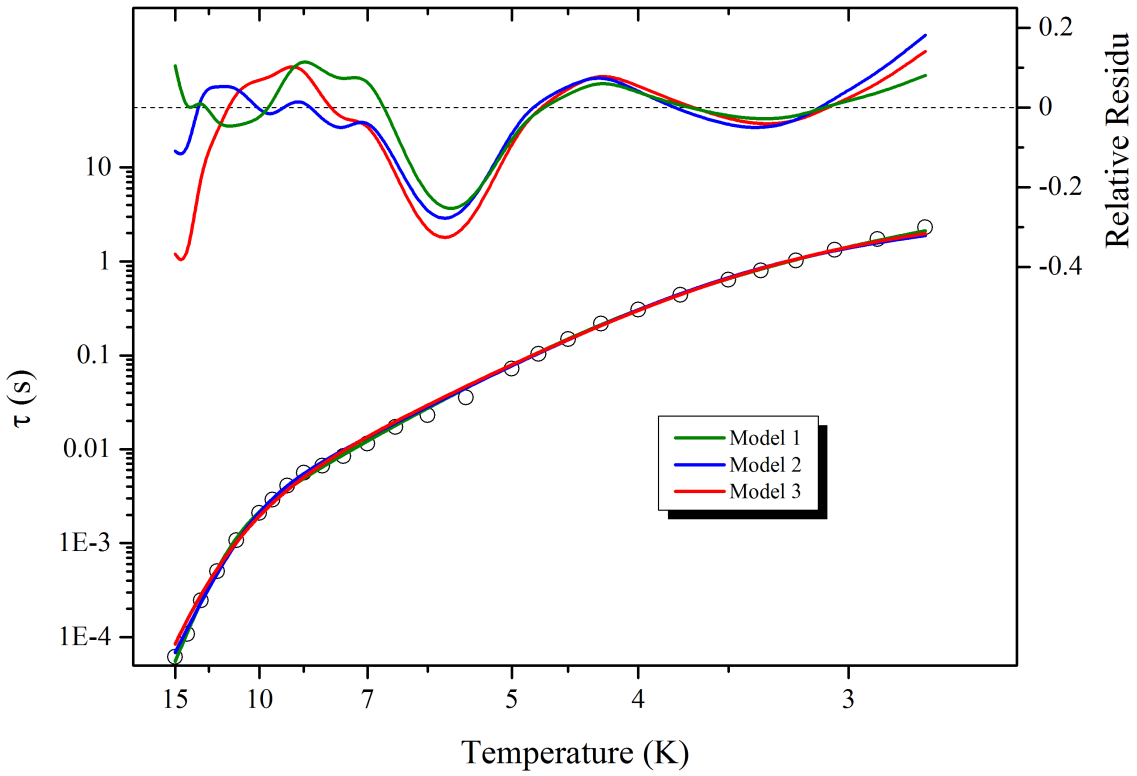

Figure S13: Comparison of three fitting models for the relaxation of complex **1**. The relative deviation between the experimental and fitted values are shown in the upper part of the figure. Fitting parameters are summarized in Table S10.

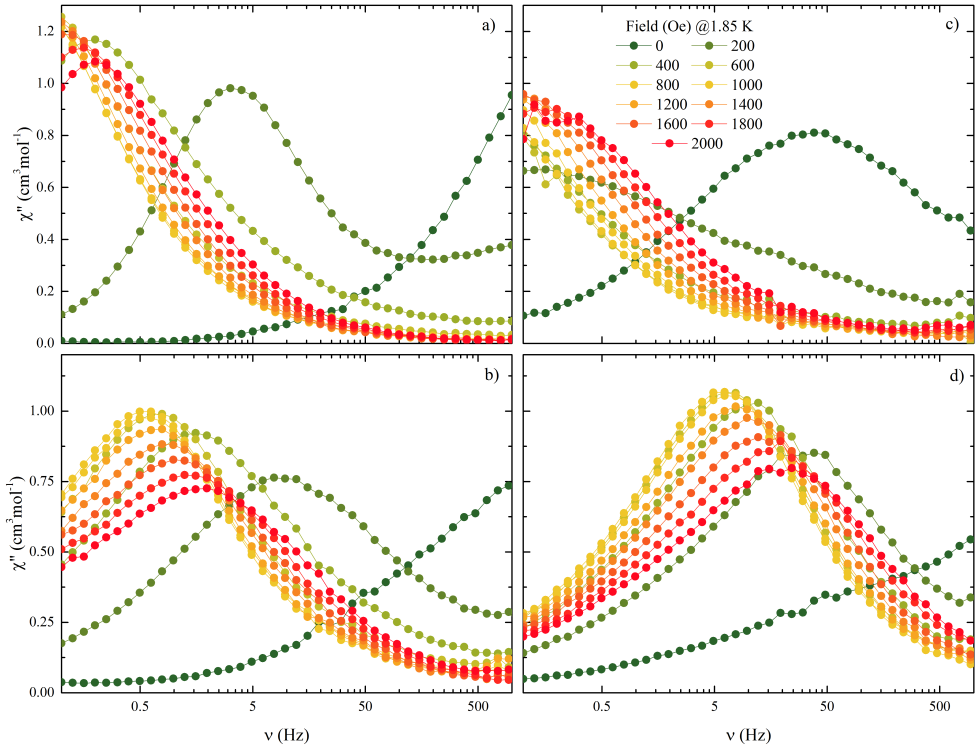

Figure S14: Field and frequency dependence of the susceptibility at 1.85 K for a) **1**, b) **1n**, c) **1a** and d) **1c**.

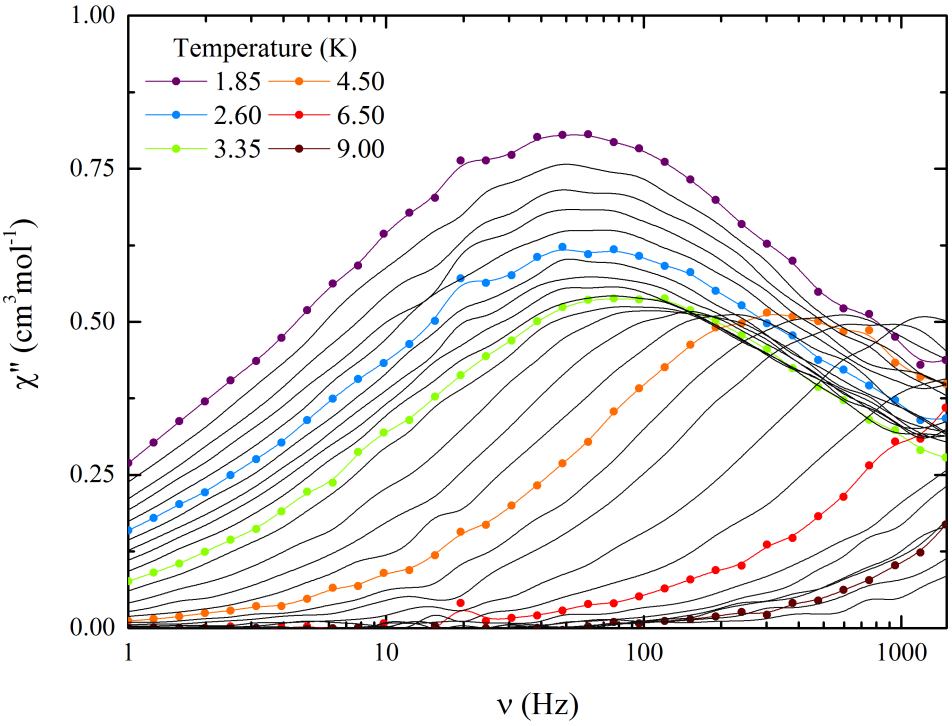

Figure S15: Temperature and frequency dependence of the susceptibility at 0 Oe for **1a**.

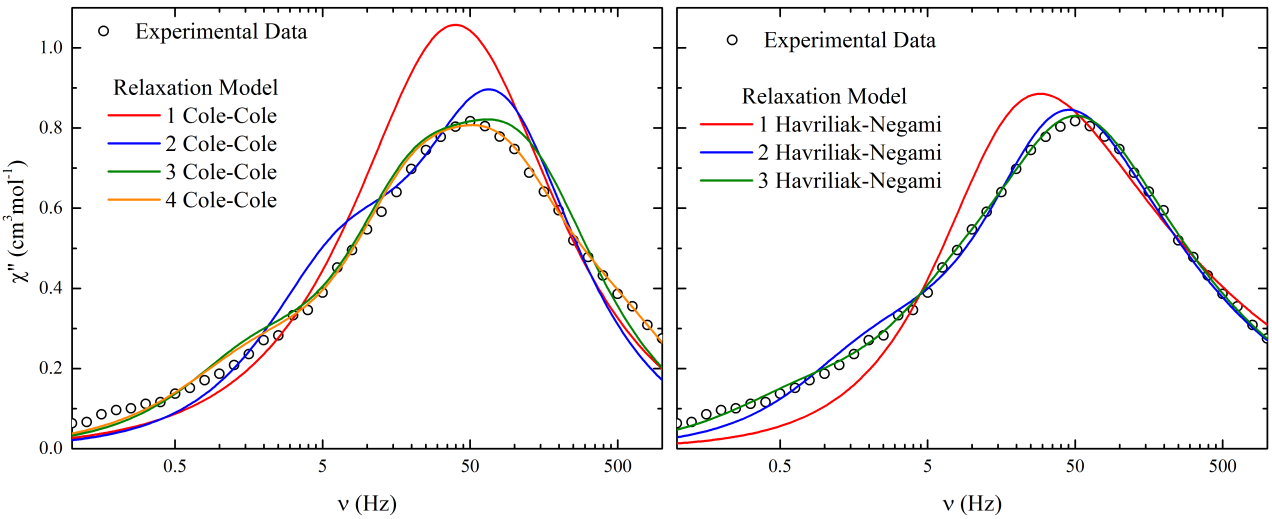

Figure S16: Comparison of the fitting of the out-of-phase signal of χ at 2.6 K for **1c** in 1000 Oe, with combination of 1 to 4 Cole-Cole model (left) or 1 to 3 Havriliak-Negami model (right). Fitting parameter are summarized in Table S7 and S8, respectively.

Table S7: Summary of the fitting parameters of Figure S16 for the Cole-Cole model.

	Cole-Cole model							
	One Peak		Two Peaks		Three Peaks		Four Peaks	
	Value	Standard Error	Value	Standard Error	Value	Standard Error	Value	Standard Error
χ_{adia}	0.46821	0.03655	0.34292	0.02129	0.27865	0.01472	0.14851	0.02329
χ_{iso}_1	2.13067	0.04075	1.63721	0.08555	1.26268	0.16752	0.90478	0.30355
α_1	0.26866	0.02808	0.11398	0.04306	0.1307	0.05023	0	0.15217
τ_1	0.00401	2.23×10^{-4}	0.00211	1.59×10^{-4}	0.00143	1.89×10^{-4}	0.00785	0.0012
χ_{iso}_2			0.73356	0.08651	0.35341	0.05195	0.39108	0.17579
α_2			0.08682	0.09808	0.06383	0.13467	0.07109	0.26899
τ_2			0.02479	0.0039	0.09526	0.01852	3.12×10^{-4}	1.15×10^{-4}
χ_{iso}_3					0.87795	0.20163	0.35517	0.05028
α_3					0	0.13879	0.15687	0.08325
τ_3					0.00805	0.00104	0.09301	0.01646
χ_{iso}_4							0.97689	0.41007
α_4							0	0.20105
τ_4							0.00187	2.39×10^{-4}

Table S8: Summary of the fitting parameters of Figure S16 for the Havrilial-Negami model.

	Havriliak-Negami model					
	One Peak		Two Peaks		Three Peaks	
	Value	Standard Error	Value	Standard Error	Value	Standard Error
χ_{adia}	0	0.12147	0	0.05543	0	0.05525
χ_{iso}_1	2.70365	0.12693	2.00091	0.35288	1.83654	0.92678
β_1	0.439	0.05462	0.52749	0.06578	0.52381	0.09411
α_1	0.08815	0.03704	0.00707	0.02777	0.00599	0.04116
τ_1	0.01125	0.00142	0.00532	6.40×10^{-4}	0.00428	7.75×10^{-4}
χ_{iso}_2			0.77097	0.39993	0.59388	1.15059
β_2			0.38506	0.29114	0.58911	1.26514
α_2			0.04857	0.06353	0	0.15425
τ_2			0.11693	0.04191	0.02351	0.02347
χ_{iso}_3					0.37615	0.55985
β_3					0.44123	0.90278
α_3					0.10457	0.13541
τ_3					0.3344	0.3139

Table S9: Fitting equations used for Table S10 and S11.

1	Solide state	τ 1	Model 1	$\tau^{-1} = AT^2H^4 + CT^m + \tau_{01}^{-1}\exp\left(\frac{-\Delta_1}{k_B T}\right)$
			Model 2	$\tau^{-1} = AT^2H^4 + \tau_{01}^{-1}\exp\left(\frac{-\Delta_1}{k_B T}\right) + \tau_{02}^{-1}\exp\left(\frac{-\Delta_2}{k_B T}\right)$
			Model 3	$\tau^{-1} = CT^m + \tau_{01}^{-1}\exp\left(\frac{-\Delta_1}{k_B T}\right) + \tau_{02}^{-1}\exp\left(\frac{-\Delta_2}{k_B T}\right)$
		τ 2		$\tau^{-1} = \tau_{01}^{-1}\exp\left(\frac{-\Delta_1}{k_B T}\right)$
	Solution state	Anion 0 Oe		$\tau^{-1} = \tau_0^{-1}\exp\left(\frac{-\Delta}{k_B T}\right) + QTM^{-1}$
		Anion 1000 Oe		$\tau^{-1} = CT^9 + \tau_0^{-1}\exp\left(\frac{-\Delta}{k_B T}\right)$
		Neutral		$\tau^{-1} = AT^2H^4 + CT^9$
		Cation		$\tau^{-1} = AT^2H^4 + CT^9 + \tau_0^{-1}\exp\left(\frac{-\Delta}{k_B T}\right)$
2				$\tau^{-1} = AT^2H^4 + \tau_{01}^{-1}\exp\left(\frac{-\Delta_1}{k_B T}\right) + QTM^{-1}$

Table S10: Summary of the fitting parameter of the relaxation time *versus* temperature in solid state for **1** and **2**. Fitting equations are available in Table S9.

Parameter	Unit	**1**				**2**
		τ 1			τ 2	
		Model 1	Model 2	Model 3		
A	$s^{-1}H^{-4}K^{-2}$	5.63×10^{-14}	6.22×10^{-14}	–	–	2.88×10^{-14}
H	Oe	1000	1000	–	–	2000
C	$s^{-1}K^{-m}$	2.93×10^{-7}	–	7.92×10^{-3}	–	–
m		9	–	4	–	–
Δ_1	cm^{-1}	20.9	22.3	25.4	23.6	47.7
τ_{01}	s	2.29×10^{-4}	1.46×10^{-4}	8.57×10^{-5}	3.37×10^{-7}	8.18×10^{-4}
Δ_2	cm^{-1}	–	89.5	110.4	–	–
τ_{02}	s	–	1.36×10^{-8}	1.50×10^{-9}	–	–
QTM	s	–	–	–	–	0.86

Table S11: Summary of the fitting parameter of the relaxation time *versus* temperature in solution state for **1**. Fitting equations are available in Table S9.

Parameter	Unit	**1a**		**1n**	**1c**
A	$s^{-1}H^{-4}K^{-2}$	–	–	9.88×10^{-13}	7.74×10^{-12}
H	Oe	0	1000	1000	1000
C	$s^{-1}K^{-9}$	–	3.33×10^{-4}	8.27×10^{-4}	5.48×10^{-2}
Δ	cm^{-1}	24.1	39.0	–	49.1
τ_0	s	2.51×10^{-7}	1.25×10^{-8}	–	1.40×10^{-12}
QTM	s	2.7×10^{-3}	–	–	–

References

(1) Schaller, R. B.; Pretsch, E. A Computer Program for the Automatic Estimation of 1H NMR Chemical Shifts. *Anal. Chim. Acta* **1994**, *190* (4), 295–302 DOI: 10.1016/0003-2670(94)80116-9.

(2) Fürst, A.; Pretsch, E. Fürst, A.; Pretsch, E., Analytica Chimica Acta 1990, 229, 17-25. *Anal. Chim. Acta* **1990**, *229*, 17–25 DOI: 10.1016/S0003-2670(00)85105-3.

(3) Pretsch, E.; Fürst, A.; Badertscher, M.; Buergin, R.; Munk, M. E. C13Shift: A Computer Program for the Prediction of Carbon-13 NMR Spectra Based on an Open Set of Additivity Rules. *J. Chem. Inf. Comput. Sci.* **1992**, *32* (4), 291–295 DOI: 10.1021/ci00008a005.

(4) Schaller, R. B.; Munk, M. E.; Pretsch, E. Spectra Estimation for Computer-Aided Structure Determination. *J. Chem. Inf. Comput. Sci.* **1996**, *36* (2), 239–263 DOI: 10.1021/ci950141y.