Supplementary Note 1

SQUEEZE results for these two compounds are as follows:\(^1\)

(1) \textbf{Dy}_{30}

\begin{verbatim}
loop_
  _platon_squeeze_void_nr
  _platon_squeeze_void_average_x
  _platon_squeeze_void_average_y
  _platon_squeeze_void_average_z
  _platon_squeeze_void_volume
  _platon_squeeze_void_count_electrons
  _platon_squeeze_void_content

|   | x   | y   | z   | nr  | electrons |
|---|-----|-----|-----|-----|-----------|
| 1 | 0.000 | 0.000 | -0.001 | 25717 | 2394" |
| 2 | 0.612 | 0.144 | 0.179 | 15 | 3" |
| 3 | 0.532 | 0.144 | 0.679 | 15 | 3" |
| 4 | 0.478 | 0.198 | 0.093 | 13 | 3" |
| 5 | 0.720 | 0.198 | 0.593 | 13 | 3" |
| 6 | 0.801 | 0.280 | 0.093 | 13 | 3" |
| 7 | 0.478 | 0.280 | 0.593 | 13 | 3" |
| 8 | 0.667 | 0.333 | 0.135 | 51 | 6" |
| 9 | 0.667 | 0.333 | 0.635 | 51 | 6" |
|10 | 0.532 | 0.388 | 0.179 | 15 | 3" |
|11 | 0.856 | 0.388 | 0.679 | 15 | 3" |
|12 | 0.856 | 0.468 | 0.179 | 15 | 3" |
|13 | 0.612 | 0.468 | 0.679 | 15 | 3" |
|14 | 0.198 | 0.478 | 0.407 | 13 | 3" |
|15 | 0.280 | 0.478 | 0.907 | 13 | 3" |
|16 | 0.720 | 0.522 | 0.093 | 13 | 3" |
|17 | 0.801 | 0.522 | 0.593 | 13 | 3" |
|18 | 0.388 | 0.532 | 0.321 | 15 | 3" |
|19 | 0.144 | 0.532 | 0.821 | 15 | 3" |
|20 | 0.144 | 0.612 | 0.321 | 15 | 3" |
|21 | 0.468 | 0.612 | 0.821 | 15 | 3" |
|22 | 0.333 | 0.667 | 0.365 | 51 | 6" |
|23 | 0.333 | 0.667 | 0.865 | 51 | 6" |
|24 | 0.522 | 0.720 | 0.407 | 13 | 3" |
|25 | 0.198 | 0.720 | 0.907 | 13 | 3" |
|26 | 0.280 | 0.801 | 0.407 | 13 | 3" |
\end{verbatim}
That is, SQUEEZE gives 2490 electrons/unit cell for the voids, and each formula unit has 2490/4 = 622 electrons (since Z = 4). It is well known that 1 H₂O molecule contains 10 electrons, 1 CH₃CN molecule contains 22 electrons, and a CH₃OH molecule contains 18 electrons. Further combined with elemental analysis and thermogravimetric analysis results (Figure S2a), the molecular formula of Dy₃₀ is calculated to be [Dy₃₀(H₂L¹)₁₂(OAc)₃₀(OH)₄(H₂O)₁₂]·2OH·10H₂O·12CH₃OH·13CH₃CN.

(2) Dy₆₀

Supplementary Figure 1 Synthetic route of H₆L¹.
Supplementary Figure 2 Synthesis of the cage-shaped clusters Dy$_{30}$ and Dy$_{60}$. Under Bu$_4$NOH conditions, Dy$_{60}$ is finally obtained; under LiOH conditions, Dy$_{30}$ is finally obtained.

Supplementary Figure 3 a) The bond distances of Dy⋯Dy in Dy$_{60}$ core; b) the coordination mode for Dy$_{60}$; c) the bond distances of Dy⋯Dy in Dy$_{30}$ core.
Supplementary Figure 4 Structural figure of Dy₆₀ with probability ellipsoids.

Supplementary Figure 5 Structural figure of Dy₃₀ with probability ellipsoids.
Supplementary Note 2

Thermal analysis. TG data were collected on a Labsys evo TG thermal analyzer under a purge gas of dry nitrogen flowing at 20 mL·min⁻¹ and with a heating rate of 5 °C·min⁻¹ in the temperature region of 35–1000 °C. Dy₃₀ and Dy₆₀ showed remarkable weight loss as the temperature increased from ambient temperature (Supplementary Figure 6). The weight loss of Dy₃₀ at 35-80 °C underwent a slow weight loss of 12.03% (calcd 8.53%), which corresponds to the release of thirteen free acetonitrile molecules, twelve free methanol molecules and twelve free water molecules (two waters were from two free hydroxide ion). The second weight loss of 13.78% (calcd 13.54%) in the temperature range of 340–577 °C which could be attributed to the elimination of thirty-six CH₃CO (coming from coordinated acetate radical) and fourteen waters (rooting in twelve coordinated waters and four coordinated hydroxide ion). And the skeleton of Dy₃₀ began to collapse at 340 °C. The weight loss of Dy₆₀ (4.93%; calcd 2.36%) occurred at 35–63 °C, which corresponds to the loss of six free water molecules, seven free acetonitrile molecules and six free methanol molecules. The skeleton of Dy₆₀ began to collapse at temperatures beyond 164 °C.

![Supplementary Figure 6](image)

Supplementary Figure 6 The TG curves of Dy₃₀ (a) and Dy₆₀ (b) under heating in flowing N₂ at 5 °C·min⁻¹ over the temperature range of 35-1000 °C.

Supplementary Note 3

To confirm whether the crystal structures are truly representative of the bulk materials, PXRD experiments were carried out for complex. The PXRD experimental and computer-simulated patterns of the corresponding complex are shown in Supplementary Figure 7. They show that the synthesized bulk materials and the measured single crystals are the similar due to efflorescence of crystals in air.
Supplementary Figure 7 Powdered X-ray diffraction (PXRD) patterns for Dy_{30} and Dy_{60}.
\[
[\text{Dy}_2(\text{H}_2\text{L})_3(\text{OAc})_2(\text{O})(\text{CH}_3\text{CN})]\quad [\text{Dy}_2(\text{H}_2\text{L})_3(\text{OAc})_2(\text{OH})_2(\text{CH}_3\text{CN})]^{3+} \quad \text{(cal. 1513.01)}
\quad [\text{Dy}_2(\text{H}_2\text{L})_3(\text{OAc})_2(\text{OH})_2(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_3]^{3+} \quad \text{(cal. 1564.03)}
\quad [\text{Dy}_2(\text{H}_2\text{L})_3(\text{OAc})_2(\text{OH})_2(\text{H}_2\text{O})_3]^{3+} \quad \text{(cal. 1613.08)}
\]

\[
[\text{Dy}_2(\text{H}_2\text{L})_2(\text{OAc})_2(\text{OH})_2(\text{H})_2(\text{H}_2\text{O})_3]^{2+} \quad \text{(cal. 2031.83)}
\quad [\text{Dy}_2(\text{H}_2\text{L})_2(\text{OAc})_2(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_3]^{2+} \quad \text{(cal. 2092.86)}
\quad [\text{Dy}_2(\text{H}_2\text{L})_2(\text{OAc})_2(\text{OH})_2(\text{H}_2\text{O})_3]^{2+} \quad \text{(cal. 2166.10)}
\]

\[\square = \text{Dy}_{30}(\text{H}_2\text{L})_{12}(\text{OAc})_{30}(\text{OH})_{4}\]

1: \[\square \quad (\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_{15}^{3+} \quad \text{(cal. 3944.30)}\]
2: \[\square \quad (\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_{15}^{3+} \quad \text{(cal. 3968.63)}\]
3: \[\square \quad (\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_{15}^{3+} \quad \text{(cal. 3990.00)}\]
4: \[\square \quad (\text{OH})(\text{H}_2\text{O})_{20}^{2+} \quad \text{(cal. 5884.42)}\]
5: \[\square \quad (\text{OH})(\text{H}_2\text{O})_{20}^{2+} \quad \text{(cal. 5925.45)}\]
6: \[\square \quad (\text{OH})(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_{10}^{2+} \quad \text{(cal. 5953.45)}\]
Supplementary Figure 8 The superposed simulated and observed spectra of several species in the time-dependent HRESI-MS of Dy₆₀ (cation mode).

Supplementary Figure 9 Time-dependent HRESI-MS spectra of Dy₆₀ in negative mode.
**Supplementary Figure 10** The superposed simulated and observed spectra of several species in the time-dependent HRESI-MS of Dy$_{60}$ (negative mode).
Supplementary Figure 11 The superposed simulated and observed spectra of several species in the time-dependent HRESI-MS of $\text{Dy}_{30}$ (positive mode).
Supplementary Figure 12 Time-dependent HRESI-MS spectra of Dy$_{30}$ in negative mode.

Supplementary Figure 13 The superposed simulated and observed spectra of several species in the time-dependent HRESI-MS of Dy$_{30}$ (negative mode).
Supplementary Figure 14 Cationic HRESI-MS spectra of Dy$_{30}$.

Supplementary Figure 15 Cationic HRESI-MS spectra of Dy$_{60}$. 
Supplementary Figure 16 Temperature dependence of $\chi_m T$ for Dy$_{30}$ (a) and Dy$_{60}$ (b).

Supplementary Figure 17 $M$ vs. $H$ plots for Dy$_{30}$ (a) and Dy$_{60}$ (b).

Supplementary Figure 18 Temperature-dependent in-phase ($\chi'$) and out-of phase ($\chi''$) ac susceptibilities under 0 Oe dc field for Dy$_{30}$ (a) and Dy$_{60}$ (b).
Supplementary Figure 19 Frequency-dependent in-phase ($\chi'$) and out-of phase ($\chi''$) ac susceptibilities under 0 Oe dc fields for Dy$_{30}$ (a and b) and Cole–Cole plots (c) under 0 Oe at different temperatures with the solid lines guiding for eyes and representing the best fitting, respectively. The ln(\tau/s) versus $T^{-1}$ curves of Dy$_{30}$ (d) with the fit to the Arrhenius equation represented by solid lines.
**Supplementary Figure 20** Frequency-dependent in-phase ($\chi'$) and out-of phase ($\chi''$) ac susceptibilities under 0 Oe dc fields for Dy$_{60}$ (a and b) and Cole–Cole plots (c) under 0 Oe at different temperatures with the solid lines guiding for eyes and representing the best fitting, respectively. The ln($\tau$/s) versus $T^{-1}$ curves of Dy$_{60}$ (d) with the fit to the Arrhenius equation represented by solid lines.
Supplementary Figure 21 Loop plots for Dy_{30} (a) and Dy_{60} (b).

Supplementary Table 1 43 examples of high-nuclear lanthanide clusters are known with nuclearity ≥ 10 was queried using Scifinder until 15 Oct. 2019. The number of genuine high-nuclear lanthanide clusters may be varied because of the term “high-nuclear lanthanide clusters” was not used in some papers.

| No | Complex                                                                 | Ref. |
|----|-------------------------------------------------------------------------|------|
| 1  | [Ln_{14}(CO_3)_{18}(ccmn)_{6}(OH)(H_2O)_{6}(phen)_{13}(NO_3)_{5}] \cdot (CO_3)_{2.5} \cdot (phen)_{0.5} (Ln_{14}) | 2    |
| 2  | [Ln_{24}(DMC)_{36}(\mu_4-CO_3)_{18}(\mu_4-H_2O)_{2}] (Ln_{24})         | 3, 4 |
| 3  | {{[CO_3]_2[@Ln_{37}(H_3)_{36}(CH_3COO)]_{21}(CO_3)_{12}(\mu_4-OH)_{41}(\mu_4-H_2O)_{5}(H_2O)_{40}] \cdot (ClO_4)_{21} \cdot 100(H_2O)} (Ln_{37}) | 5    |
| 4  | {[Er_{60}(L-thre)_{34}(\mu_6-CO_3)_{36}(\mu_6-OH)_{36}(\mu_6-O)_{2}(H_2O)_{16}] \cdot Br_{12} \cdot (ClO_4)_{18} \cdot 40(H_2O) (Ln_{60}) | 6    |
| 5  | {[Dy_{72}(mda)_{24}(mdah)_{16}(OH)]_{120}(NO_3)_{16} \cdot (NO_3)_{8} (Ln_{72}) | 7    |
| 6  | {[Gd_{38}(\mu-O)(\mu_6-CiO_4)_{6}(\mu_6-OH)_{42}(CAA)_{137}(H_2O)_{36}(EtOH)_{6}] \cdot (ClO_4)_{10} \cdot (OH)_{17} \cdot 14DMSO \cdot 13H_2O (Ln_{38}) | 8    |
| 7  | {[Gd_{48}(\mu-O)(\mu_6-OH)_{84}(CAA)_{36}(NO_3)_{6}(H_2O)_{24}(EtOH)_{13}(NO_3)Cl_2 \cdot Cl_3 (Ln_{48}) | 9    |
| 8  | {[Ln_{114}(ClO_4)_{8}(CH_3COO)_{36}(\mu_6-OH)_{168}(\mu_4-O)_{30}(H_2O)_{112}] \cdot (ClO_4)_{22} (Ln_{104}) | 9    |
| 9  | {[Ln_{36}(NA)_{36}(OH)_{49}(O)_{6}(NO_3)_{6}(N_3)_{3}(H_2O)_{20}Cl_2 \cdot 28H_2O} (Ln_{36}) | 10   |
| 10 | {[Cl_2 \cdot (NO_3)]@[Er_{48}(NA)_{44}(OH)_{90}(N_3)(H_2O)_{24}]_{11} (Ln_{48}) | 11   |
| 11 | {K_2[H_2(CN)_{2}](\mu-OH)_{84}(\mu_4-OH)(\mu_4-O)_{2}(OAc)_{4}(H_2O)_{14}(CO_3)Br_{2} (Ln_{48}) | 12   |
| 12 | {[ClO_4]@[Ln_{27}(\mu_6-OH)_{32}(CO_3)_{8}(CH_3CH_2COO)_{20}(H_2O)_{40}] \cdot (ClO_4)_{12} \cdot (H_2O)_{50} (Ln_{27}) | 13   |
| 13 | {[Ln_{15}(\mu_5-OH)_{20}(\mu_5-X)]^{2+} (Ln_{15}) | 14, 15|
| 14 | {[Dy_{18}(1-3H)_{1}(1-2H)_{11}(CH_3CO_2)_{16}(OH)_{26}(H_2O)_{30}] (Ln_{19}) | 16   |
| 15 | {Ln_{14}(\mu-OH)_{2}(\mu_3-OH)_{16}(\mu_4-OH)_{2} \cdot (\eta^2-acac)_{6}(\eta^2-acac)_{16} (Ln_{14}) | 17   |
| 16 | {H_{18}[Ln_{14}(\mu-OH)_{2}(\mu_3-OH)_{16}(\eta^2-O-N-C_6H_4-O)_{16}(\mu_4-O)_{2}(\mu_5-O)]_{18} (Ln_{14}) | 18   |
| 17 | {Ln_{14}(\mu-OH)_{2}(\mu_3-OH)_{16}(\eta^2-O-N-C_6H_4-O)_{16}(\mu_4-O)_{2}(\mu_5-O)]_{18} (Ln_{14}) | 19   |
| 18 | {H_{26}[Ln_{28}(CH_3COO)_{4}(CO_3)_{10}(OH)_{26}(H_2O)_{18}] \cdot 20H_2O (Ln_{26}) | 20   |
| 19 | {[Dy_{26}(\mu-OH)_{20}(\mu_3-O)_{6}(NO_3)_{6}]^{36+} (Ln_{26}) | 21   |
Supplementary Table 2 Crystallographic data of the complexes Dy$_{30}$ and Dy$_{60}$.

| Complexes | Dy$_{30}$ | Dy$_{60}$ |
|-----------|-----------|-----------|
| Formula   | C$_{338}$H$_{389}$N$_{86}$O$_{172}$ | C$_{618}$H$_{615}$N$_{151}$O$_{309}$ |
| Formula weight | 13269.17 | 24851.33 |
| T (K)      | 153      | 293(2)   |
| Crystal system | Trigonal | Triclinic |
| Space group | P-3c1    | P-1      |
| a (Å)      | 36.51215(17) | 22.0753(2) |
| b (Å)      | 36.51215(17) | 43.9055(4) |
| m/z  | Fragment                                                                 | Relative Intensity |
|------|---------------------------------------------------------------------------|--------------------|
|      |                                                                           | 0min   | 30min  | 1 h    | 2 h    | 3 h    | 12 h   | 48 h   |
| 447.54 | [Dy₂(H₄L¹)](OAc)(CH₃OH)(CH₃OH)(H₂O)₃²⁺  (cal. 447.54)                  | 0.004   | 0.893  | 0.952  | 0.703  | 0.385  | 0      | 0      |
| 468.54 | [Dy₂(H₄L¹)](OAc)₂(CH₃OH)₂(H₂O)₂²⁺  (cal. 454.54)                      | 0.103   | 0.663  | 0.684  | 0.105  | 0      | 0      | 0      |
| 491.56 | [Dy₂(H₄L¹)](OAc)₂(CH₃OH)₂(H₂O)₂²⁺  (cal. 491.56)                      | 0.378   | 0.897  | 0.632  | 0.279  | 0.303  | 0      | 0      |
| 558.07 | [Dy(H₄L¹)]⁺  (cal. 558.07)                                              | 0.298   | 0.922  | 0.721  | 0.219  | 0.005  | 0      | 0      |
| 622.12 | [Dy(H₄L¹)](CH₃OH)₂⁺  (cal. 622.12)                                       | 0.287   | 0.729  | 0.964  | 0.904  | 0.617  | 0.005  | 0      |
| 663.15 | [Dy(H₄L¹)](CH₃OH)₂(CH₃CN)²⁺  (cal. 663.15)                               | 0.287   | 0.729  | 0.964  | 0.904  | 0.617  | 0.005  | 0      |
| 704.17 | [Dy(H₄L¹)](CH₃O)(CH₃OH)₂(CH₃CN)⁻  (cal. 704.17)                           | 0.901   | 0.863  | 0.583  | 0.117  | 0.008  | 0      | 0      |
| 798.53 | [Dy₄(H₄L¹)]⁴⁺(CH₃OH)₄(H₂O)₄²⁺  (cal. 798.53)                              | 0.092   | 0.729  | 0.964  | 0.904  | 0.617  | 0.005  | 0      |
| 882.07 | [Dy₂(H₄L¹)](OAc)(CH₃OH)₂(CH₃CN)⁻  (cal. 882.07)                           | 0.092   | 0.729  | 0.964  | 0.904  | 0.617  | 0.005  | 0      |

**Supplementary Table 3** Major species assigned in the Time-dependent HRESI-MS of Dy₆₀ in positive mode.

\[ aR_1 = \sum |F_o - F_c| / \sum |F_o|, \quad bwR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2} \]
|       | Formula                                             |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|-------|----------------------------------------------------|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 942.09| [Dy(H$_2$L$^1$)(OAc)$_2$(CH$_3$OH)$_2$(CH$_3$CN)]$^+$ | 0.086 | 0.582 | 0.806 | 0.722 | 0.471 | 0 | 0 |   |   |   |   |   |   |   |   |   |   |
| 983.12| [Dy(H$_2$L$^2$)(OAc)$_3$(CH$_3$OH)$_2$(CH$_3$CN)$_2$] | 0.041 | 0.513 | 0.767 | 0.710 | 0.385 | 0 | 0 |   |   |   |   |   |   |   |   |   |   |
| 1085.98| [Dy(H$_2$L$^1$)(OAc)$_2$(OH)$_2$(H$_2$O)$_3$] | 0.064 | 0.484 | 0.853 | 1 | 0.683 | 0.017 | 0 |   |   |   |   |   |   |   |   |   |   |
| 1133.03| [Dy(L$^1$)(OAc)$_2$(CH$_3$OH)$_3$(CH$_3$CN)]$^+$ | 0.082 | 0.408 | 0.795 | 0.901 | 0.699 | 0.027 | 0 |   |   |   |   |   |   |   |   |   |   |
| 1275.08| [Dy(H$_2$L$^1$)(OAc)$_3$(CH$_3$OH)$_3$(CH$_3$CN)$_2$] | 0.018 | 0.383 | 0.738 | 0.885 | 0.589 | 0.052 | 0 |   |   |   |   |   |   |   |   |   |   |
| 1362.15| [Dy(H$_2$L$^1$)(OAc)$_3$(CH$_3$OH)$_3$(H$_2$O)$_3$(CH$_3$ CN)$_2$] | 0.073 | 0.401 | 0.722 | 0.900 | 0.716 | 0.094 | 0 |   |   |   |   |   |   |   |   |   |   |
| 1457.96| [Dy$_2$(H$_2$L$^1$)(OAc)$_3$(O)(H$_2$O)$_4$(CH$_3$OH)$_2$] | 0.001 | 0.183 | 0.581 | 0.884 | 1 | 0.299 | 0 |   |   |   |   |   |   |   |   |   |   |
| 1513.01| [Dy$_2$(H$_2$L$^1$)(OAc)$_3$(O)(CH$_3$CN)(CH$_3$OH) z(H$_2$O)$_3$] | 0.002 | 0.216 | 0.538 | 0.826 | 0.898 | 0.238 | 0 |   |   |   |   |   |   |   |   |   |   |
| 1564.02| [Dy$_2$(H$_2$L$^2$)(OAc)$_2$(OH)$_2$(CH$_3$OH)$_2$(H$_2$O)$_3$] | 0 | 0.173 | 0.474 | 0.762 | 0.798 | 0.187 | 0 |   |   |   |   |   |   |   |   |   |   |
| 1613.08| [Dy$_2$(H$_2$L$^2$)(OAc)$_3$(O)(CH$_3$OH)$_2$(CH$_3$CN) (H$_2$O)$_3$] | 0.015 | 0.152 | 0.430 | 0.803 | 0.728 | 0.201 | 0 |   |   |   |   |   |   |   |   |   |   |
| 2031.03| [Dy$_2$(H$_2$L$^2$)(OAc)$_3$(O)(H$_2$O)$_4$(CH$_3$OH)$_2$] | 0 | 0.093 | 0.285 | 0.716 | 0.906 | 0.722 | 0.009 |   |   |   |   |   |   |   |   |   |   |
| 2092.06| [Dy$_2$(H$_2$L$^2$)(OAc)$_3$(CH$_3$OH)(H$_2$O)$_3$] | 0 | 0.068 | 0.239 | 0.757 | 0.884 | 0.663 | 0 |   |   |   |   |   |   |   |   |   |   |
| 2166.10| [Dy$_2$(H$_2$L$^2$)(OAc)$_3$(CH$_3$OH)$_2$(H$_2$O)$_3$] | 0 | 0.079 | 0.264 | 0.698 | 0.897 | 0.603 | 0.007 |   |   |   |   |   |   |   |   |   |   |
| 3944.29| [Dy$_{2+}$(H$_2$L$^3$)$_2$(OAc)$_3$(OH)$_2$(H$_2$O)(CH$_3$ OH)$_3$] | 0 | 0 | 0.002 | 0.146 | 0.327 | 0.761 | 0.761 |   |   |   |   |   |   |   |   |   |   |
| 3968.64| [Dy$_{2+}$(H$_2$L$^3$)$_2$(OAc)$_3$(OH)$_2$(H$_2$O)(CH$_3$ OH)$_3$] | 0 | 0 | 0.002 | 0.192 | 0.429 | 1 | 1 |   |   |   |   |   |   |   |   |   |   |
| 3989.99| [Dy$_{2+}$(H$_2$L$^3$)$_2$(OAc)$_3$(OH)$_2$(H$_2$O)(CH$_3$ OH)$_3$] | 0 | 0 | 0.002 | 0.097 | 0.210 | 0.502 | 0.501 |   |   |   |   |   |   |   |   |   |   |
| 5884.44| [Dy$_{2+}$(H$_2$L$^3$)$_2$(OAc)$_3$(CH$_3$OH)$_3$(H$_2$O)$_2$] | 0 | 0 | 0.002 | 0.160 | 0.355 | 0.840 | 0.867 |   |   |   |   |   |   |   |   |   |   |
| 5921.95| [Dy$_{2+}$(H$_2$L$^3$)$_2$(OAc)$_3$(CH$_3$OH)$_3$(H$_2$O)$_2$] | 0 | 0 | 0.002 | 0.178 | 0.394 | 0.932 | 0.962 |   |   |   |   |   |   |   |   |   |   |
| 5953.46| [Dy$_{2+}$(H$_2$L$^3$)$_2$(OAc)$_3$(CH$_3$OH)$_3$(H$_2$O)$_2$] | 0 | 0 | 0.001 | 0.091 | 0.203 | 0.480 | 0.496 |   |   |   |   |   |   |   |   |   |   |
| 6017.50| [Dy$_{2+}$(H$_2$L$^3$)$_2$(OAc)$_2$(OH)$_2$(H$_2$O)$_5$(CH$_3$OH)$_3$(H$_2$O)$_2$] | 0 | 0 | 0 | 0 | 0.096 | 0.213 | 0.227 |   |   |   |   |   |   |   |   |   |   |
| 6037.02| [Dy$_{2+}$(H$_2$L$^3$)$_2$(OAc)$_2$(OH)$_2$(H$_2$O)$_5$(CH$_3$OH)$_3$(H$_2$O)$_2$] | 0 | 0 | 0 | 0 | 0.099 | 0.218 | 0.233 |   |   |   |   |   |   |   |   |   |   |
Supplementary Table 4 Major species assigned in the time-dependent HRESI-MS of Dy₃₀ in positive mode.

| m/z    | Fragment                                                                 | Relative Intensity |
|--------|--------------------------------------------------------------------------|--------------------|
| 440.54 | [Dyₓ(H₂L¹)₂(0Ac)(CH₂O)(H₂O)₂]⁴⁺ (cal. 440.53)                            | 0.127 0.739 0.915 0.628 0.282 0 0 |
| 454.53 | [Dyₓ(H₂L¹)(OAc)₂(H₂O)⁴]²⁺ (cal. 454.54)                                  | 0.119 0.656 0.852 0.743 0.302 0 0 |
| 576.07 | [Dy(H₂L¹)]⁺(H₂O)²⁺ (cal. 576.08)                                         | 1 0.905 0.789 0.547 0.272 0 0 |
| 626.12 | [Dy(H₂L¹)(CH₃OH)](H₂O)₂⁺ (cal. 626.12)                                   | 0.973 0.965 0.752 0.496 0.201 0 0 |
| 658.15 | [Dy(H₂L¹)](CH₃OH)(H₂O)²⁺ (cal. 658.14)                                   | 0.952 0.895 0.717 0.540 0.237 0.001 0 |
| 708.17 | [Dy(H₂L¹)](CH₃O)(CH₃OH)(H₂O)₂⁺ (cal. 708.18)                            | 0.874 0.876 0.639 0.508 0.316 0.002 0 |
| 877.07 | [Dyₓ(H₂L¹)OAc)(CH₂O)(H₂O)₂⁺ (cal. 877.07)                               | 0.163 0.795 0.897 0.698 0.415 0 0 |
| 937.09 | [Dyₓ(H₂L¹)(OAc)₂(CH₂OH)(H₂O)₂⁺ (cal. 937.10)                             | 0.284 1 0.905 0.532 0.183 0 0 |
| 1010.14| [LiDyₓ(H₂L¹)(OAc)₂(OH)(CH₃OH)(H₂O)]⁺ (cal. 1010.14)                      | 0.116 0.803 0.785 0.499 0.176 0 0 |
| 1082.98| [Dyₓ(H₂L¹)(OAc)₂(OH)(CH₂O)(H₂O)]⁺ (cal. 1082.98)                         | 0 0.574 1 0.926 0.635 0.002 0 |
| 1131.02| [Dyₓ(L¹)(OAc)₂(0Ac)(OH)(CH₂O)²⁺ (cal. 1131.01)                           | 0 0.529 0.864 0.941 0.597 0.005 0 |
| 1212.60| [LiDyₓ(H₃L¹)(OAc)₃(OH)(CH₃OH)(H₂O)₂⁺ (cal. 1212.06)                      | 0 0.473 0.806 0.861 0.784 0.078 0 |
| 1241.07| [LiDyₓ(H₂L¹)(OAc)₄(OH)(CH₂O)(H₂O)]⁺ (cal. 1241.06)                       | 0 0.394 0.683 0.510 0.328 0 0 |
| 1286.05| [LiDyₓ(H₂L¹)(OAc)₅(OH)(CH₂O)(H₂O)]⁺ (cal. 1286.06)                       | 0.003 0.355 0.687 0.725 0.462 0 0 |
| 1460.98| [LiDyₓ(H₂L¹)(OAc)₆(OH)(CH₂O)]⁺ (cal. 1460.99)                            | 0 0.381 0.764 1 0.861 0.188 0 |
| 1528.02| [LiDyₓ(H₂L¹)(OAc)₇(OH)(CH₂O)(H₂O)]⁺ (cal. 1528.03)                       | 0 0.279 0.654 0.903 0.748 0 0 |
Table 5 ICP result of Dy₃₀.

| Element | Content / (µg / µg) | Percentage by weight/% |
|---------|---------------------|------------------------|
|         | 1                   | 2                      | 3                      | average | 1     | 2     | 3     | average |
| Dy      | 98.460              | 66.228                 | 75.001                 | 79.896  | 38.76 | 37.21 | 39.68 | 38.55   |

Table 6 ICP result of Dy₆₀.

| Element | Content / (µg / µg) | Percentage by weight/% |
|---------|---------------------|------------------------|
|         | 1                   | 2                      | 3                      | average | 1     | 2     | 3     | average |
| Dy      | 74.932              | 83.414                 | 66.907                 | 75.084  | 32.72 | 35.64 | 35.97 | 34.77   |

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