

## Electronic Supplementary Information

### A series of lanthanide germanate cluster organic frameworks

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#### The refinement details in 1-6

**Fig. S1.** IR spectra of 1-6.

**Fig. S2** Top (left) and side (right) view of the asymmetric unit of **1**. H atoms and lattice water molecules are omitted for clarity.

**Fig. S3** The coordination environments and their polyhedral geometries of Nd<sup>3+</sup> centers in **1**.

**Fig. S4** Two types of coordination modes of the pza ligands in **1**.

**Fig. S5** View of the 3D structure of **1** along the [001] direction.

**Fig. S6** View of the asymmetric unit of **2**. H atoms and lattice water molecules are omitted for clarity.

**Fig. S7** The coordination mode of the CO<sub>3</sub><sup>2-</sup> anion in **2**.

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**Fig. S9** View of the 3D framework with 3D channels along the [010] (a), [011] (b) and [111] (c) directions.

**Fig. S10** View of the asymmetric unit of **3**. H atoms and lattice water molecules are omitted for clarity.

**Fig. S11** The coordination mode of the GeO<sub>3</sub>E<sup>2-</sup> moiety in **3**.

**Fig. S12** View of channels of **3** along the [111] direction, in which the pyrazinyl rings of pza ligands and the organic parts of E groups point into the channels.

**Fig. S13** View of channels of **4** along the [100] (a), [010] (b) and [001] (c) directions.

**Fig. S14** View of the asymmetric unit of **5**. H atoms and lattice water molecules are omitted for clarity.

**Fig. S15** Top (left) and side (right) view of the asymmetric unit of **6**. H atoms and lattice water molecules are omitted for clarity.

**Fig. S16** The coordination environment of capping Tb<sup>III</sup> centers in **5**.

**Fig. S17** View of channels of **5** along the [010] and [001] directions.

**Fig. S18** The coordination environments of the Dy<sup>3+</sup> centers in **6**.

**Fig. S19** View of each {Dy<sub>11</sub>Ge<sub>12</sub>}-6 SBU linking six {Dy<sub>11</sub>Ge<sub>12</sub>}-6 SBUs in **6**.

**Fig. S20** View of channels of **6** along the [001] (a) and [110] (b) directions, in which part of pyrazinyl rings of pza ligands and the organic parts of E groups point into the channels.

**Fig. S21** Experimental and simulated PXRD patterns for 1-6: (a) for **1**, (b) for **2**, (c) for **3**, (d) for **4**, (e) for **5** and (f) for **6**, respectively.

**Fig. S22** TG curves of 1-6.

**Fig. S23** The excitation spectrum of **1** taken by monitoring the most intense emission band.

**Fig. S24** The excitation spectra of **3** and **5** taken by monitoring the most intense emission band.

### The refinement details in 1-6:

Thanks to the large structures of **1-6** and the existence of a large amount of weight atoms, their intensity data are not very good, leading to the ADP max/min ratio of some atoms, and it is very difficult to refine these large structures, therefore, some unit-occupancy atoms have been restrainedly refined.

For **1**: The ISOR instruction is used for O48. The DFIX instruction is used for C37 and C38. The DELU instruction is used for O48 and C36. The SIMU instruction is used for \$C, \$N and \$O.

For **2**: The ISOR instruction is used for O6.

For **3**: The SIMU instruction is used for \$C, \$N and \$O.

For **4**: The DFIX instruction is used for O7, O9, O18, O23, O3W, O6W, O7W, O8W, O9W, C8, C9, C14, C17, C18 and C22. The DFIX instruction is used for C18–O23, and all C–C bonds.

For **5**: The ISOR instruction is used for O2W and O5W. The DFIX instruction is used for C1–C2', C2'–C3', C1–C2, C2–C3, C4–C5', C3'–O4', C3'–O5', C3–O4, C3–O5 and C6–O7.

For **6**: The SIMU instruction is used for \$C, \$N and \$O.

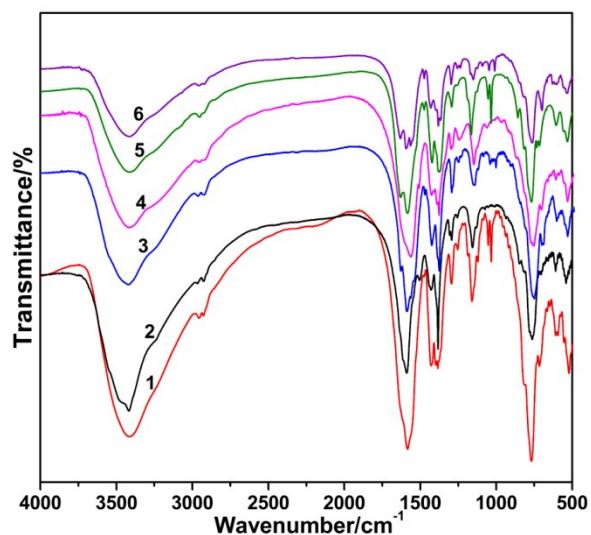


Fig. S1. IR spectra of 1-6.

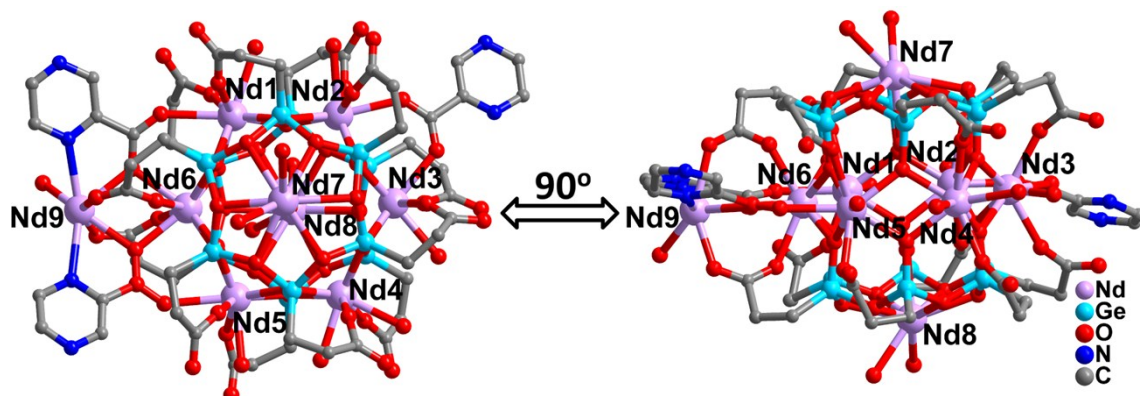


Fig. S2 Top (left) and side (right) view of the asymmetric unit of **1**. H atoms and lattice water molecules are omitted for clarity.

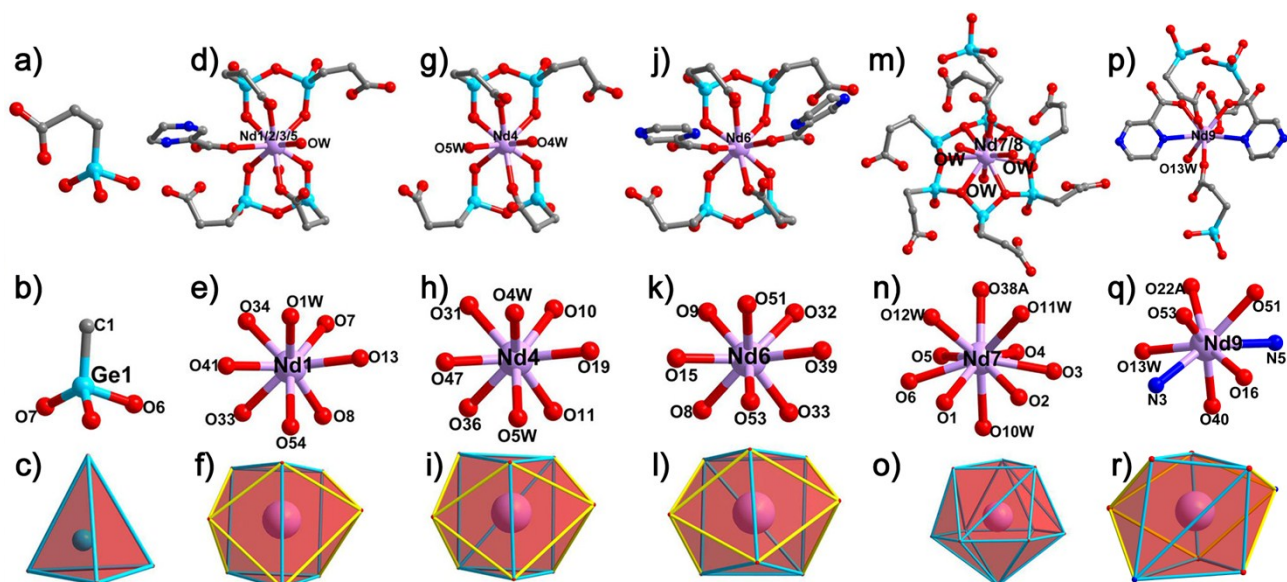


Fig. S3 The coordination environments and their polyhedral geometries of  $\text{Nd}^{3+}$  centers in **1**.

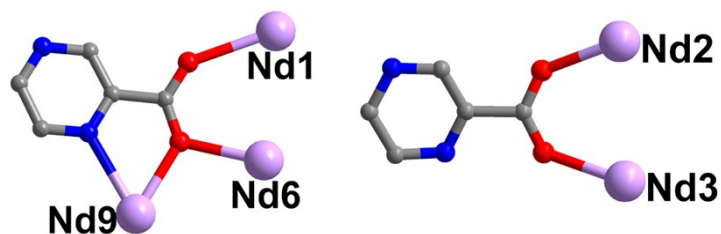


Fig. S4 Two types of coordination modes of the pza ligands in **1**.

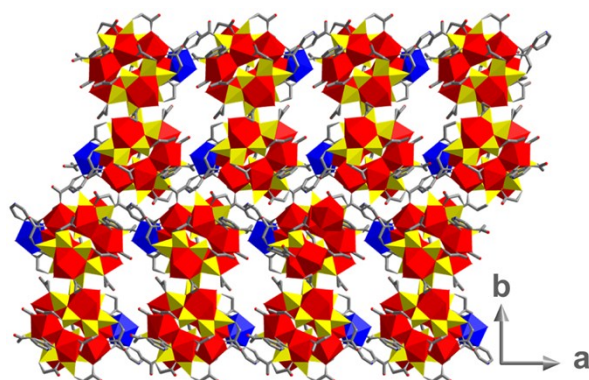


Fig. S5 View of the 3D structure of **1** along the [001] direction.

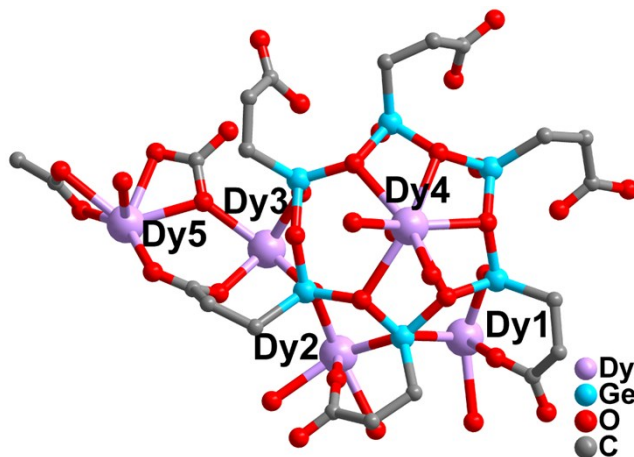


Fig. S6 View of the asymmetric unit of **2**. H atoms and lattice water molecules are omitted for clarity.

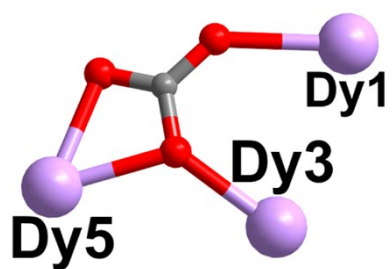


Fig. S7 The coordination mode of the  $\text{CO}_3^{2-}$  anion in **2**.

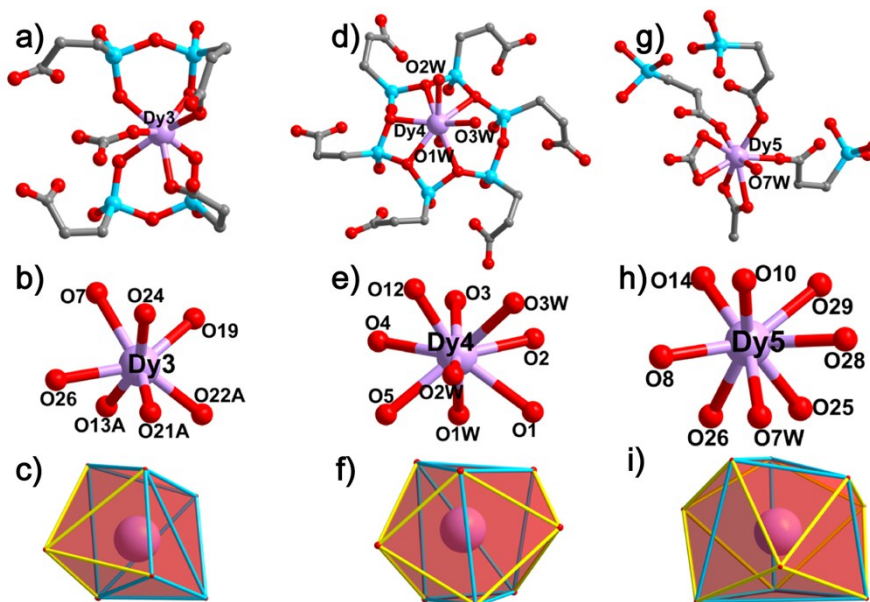


Fig. S8 The coordination environments and their polyhedral geometries of  $\text{Dy}^{3+}$ ,  $\text{Dy}^{4+}$  and  $\text{Dy}^{5+}$  centers in **2**.

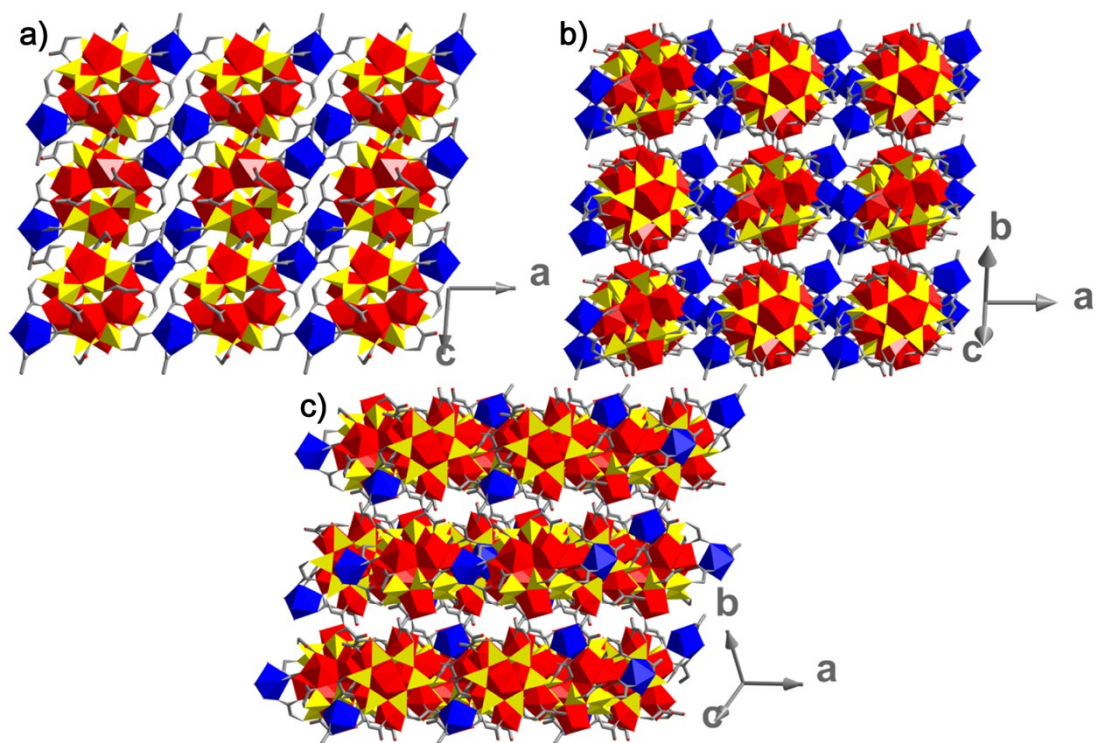
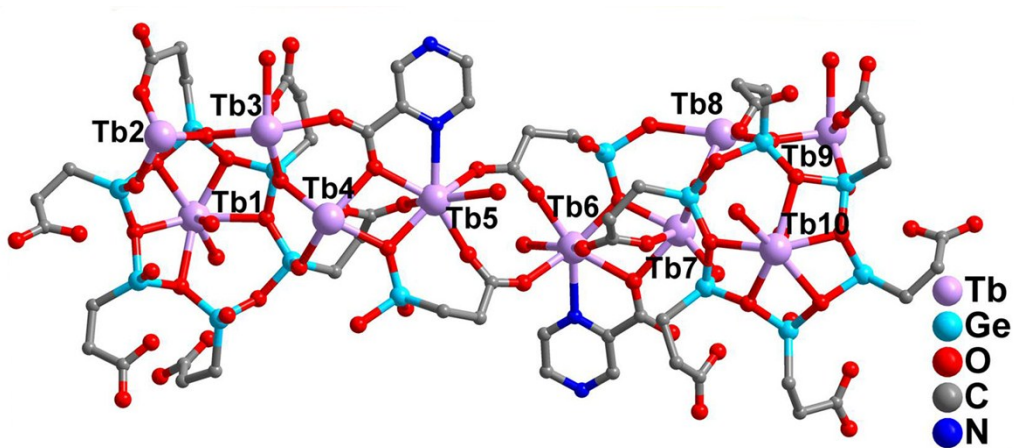
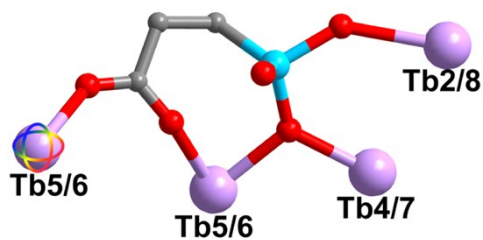


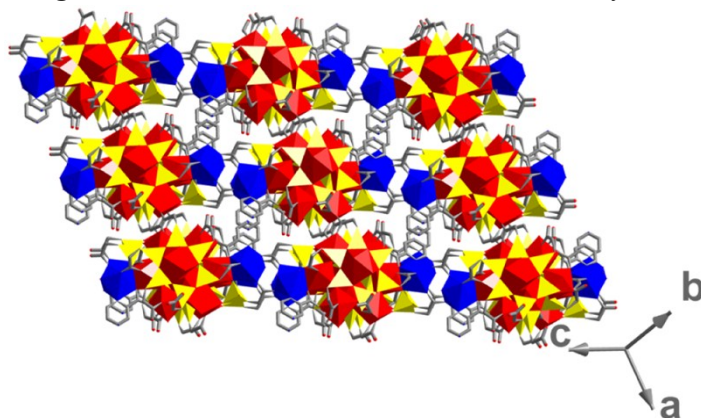
Fig. S9 View of the 3D framework with 3D channels along the  $[010]$  (a),  $[011]$  (b) and  $[111]$  (c) directions in **2**.



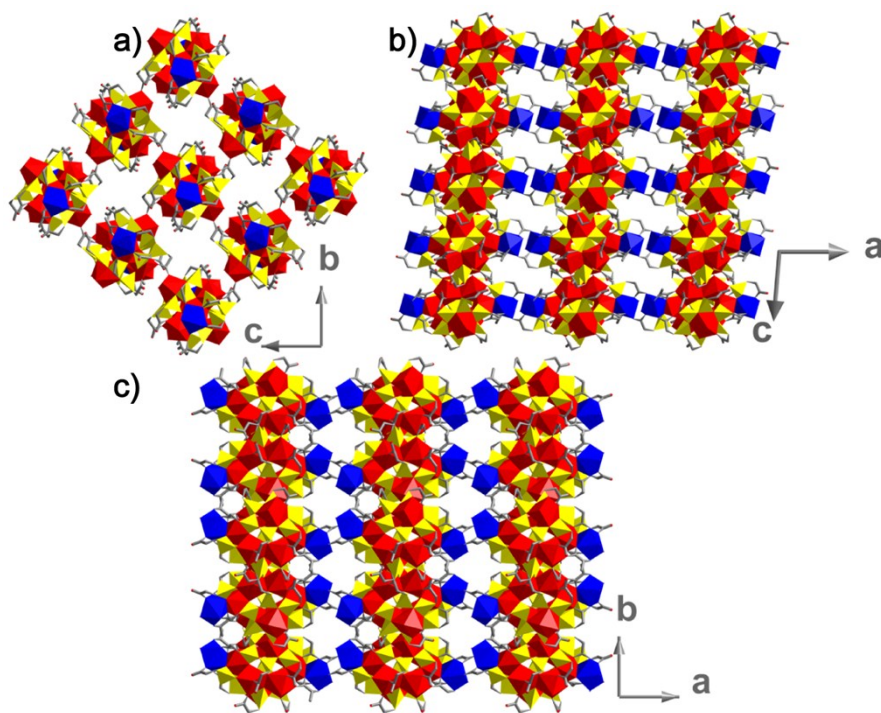
**Fig. S10** View of the asymmetric unit of **3**. H atoms and lattice water molecules are omitted for clarity.



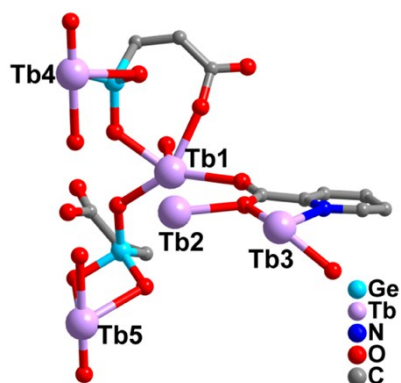
**Fig. S11** The coordination mode of the  $\text{GeO}_3\text{E}^{2-}$  moiety in **3**.



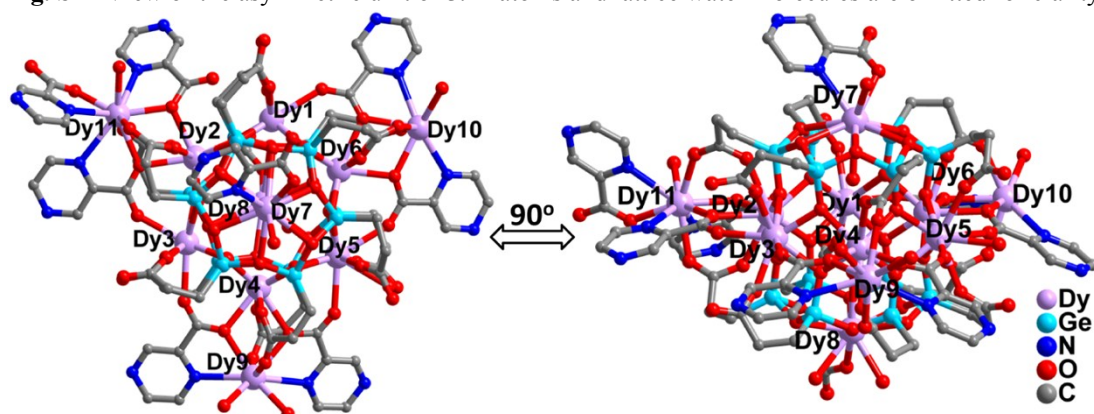
**Fig. S12** View of channels of **3** along the  $[111]$  direction, in which the pyrazinyl rings of pza ligands and the organic parts of E groups point into the channels.



**Fig. S13** View of channels of **4** along the [100] (a), [010] (b) and [001] (c) directions.



**Fig. S14** View of the asymmetric unit of **5**. H atoms and lattice water molecules are omitted for clarity.



**Fig. S15** Top (left) and side (right) view of the asymmetric unit of **6**. H atoms and lattice water molecules are omitted for clarity.

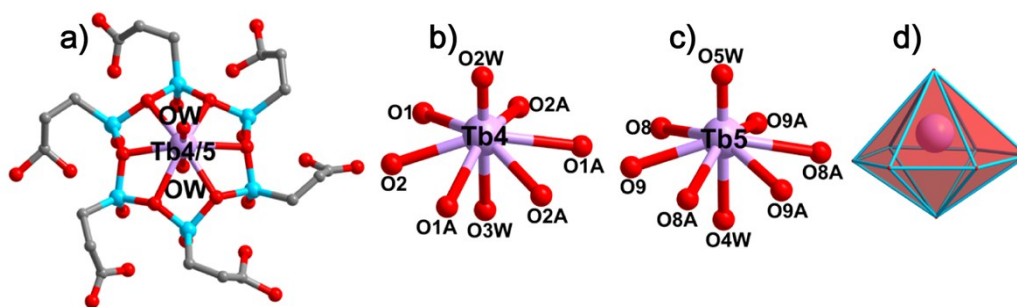


Fig. S16 The coordination environments of  $Tb4^{3+}$  and  $Tb5^{3+}$  in **5**.

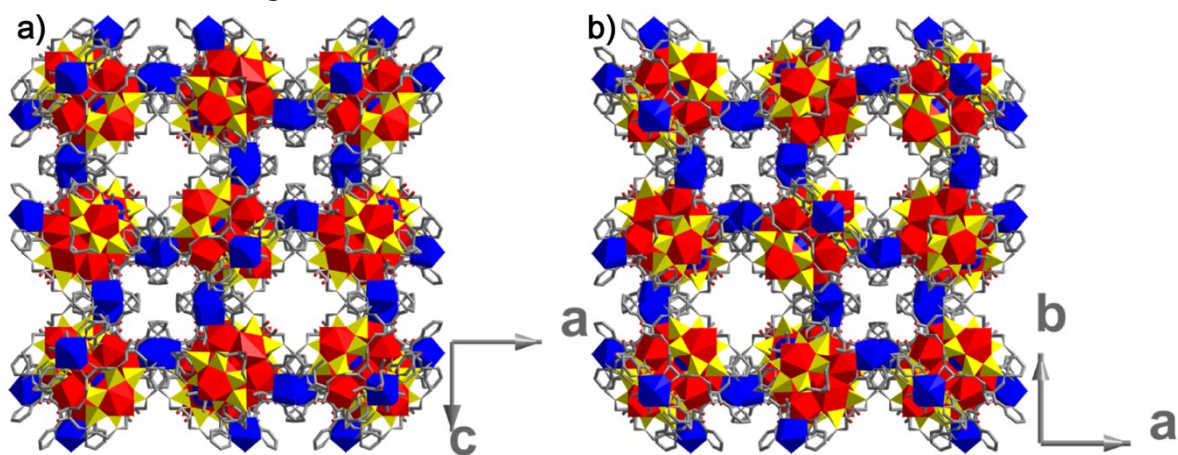


Fig. S17 View of channels of **5** along the  $[010]$  (a) and  $[001]$  (b) directions.

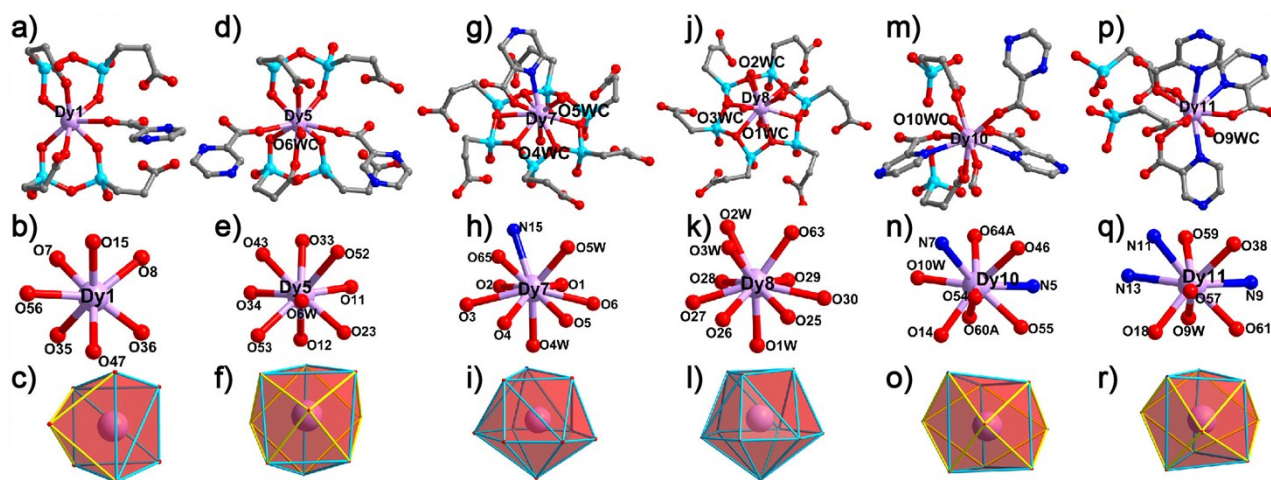


Fig. S18 The coordination environments of the  $Dy^{3+}$  centers in **6**.

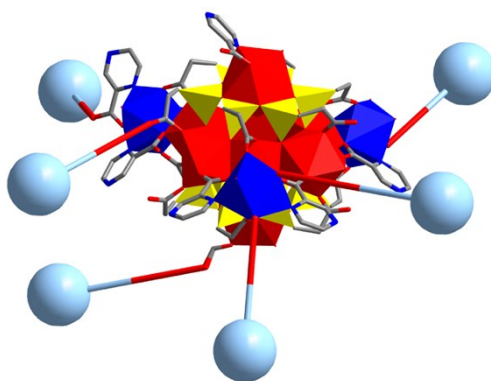
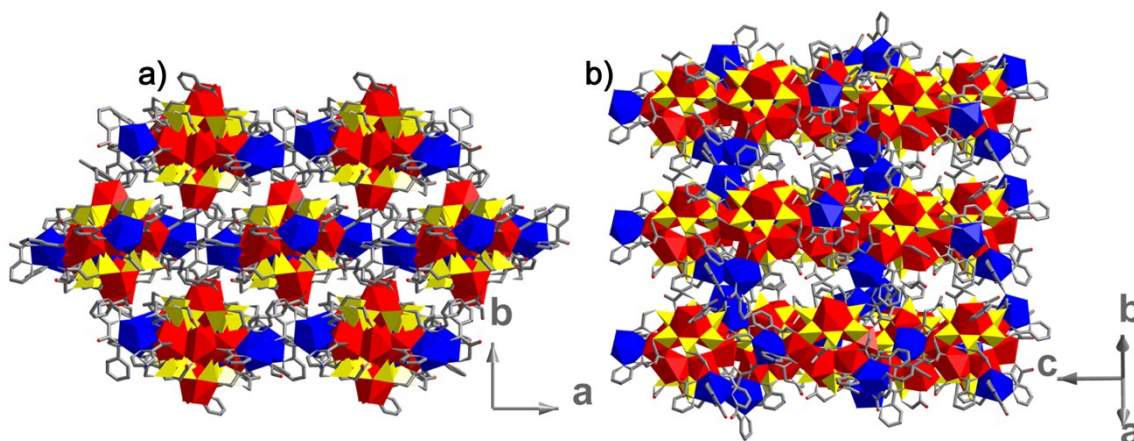
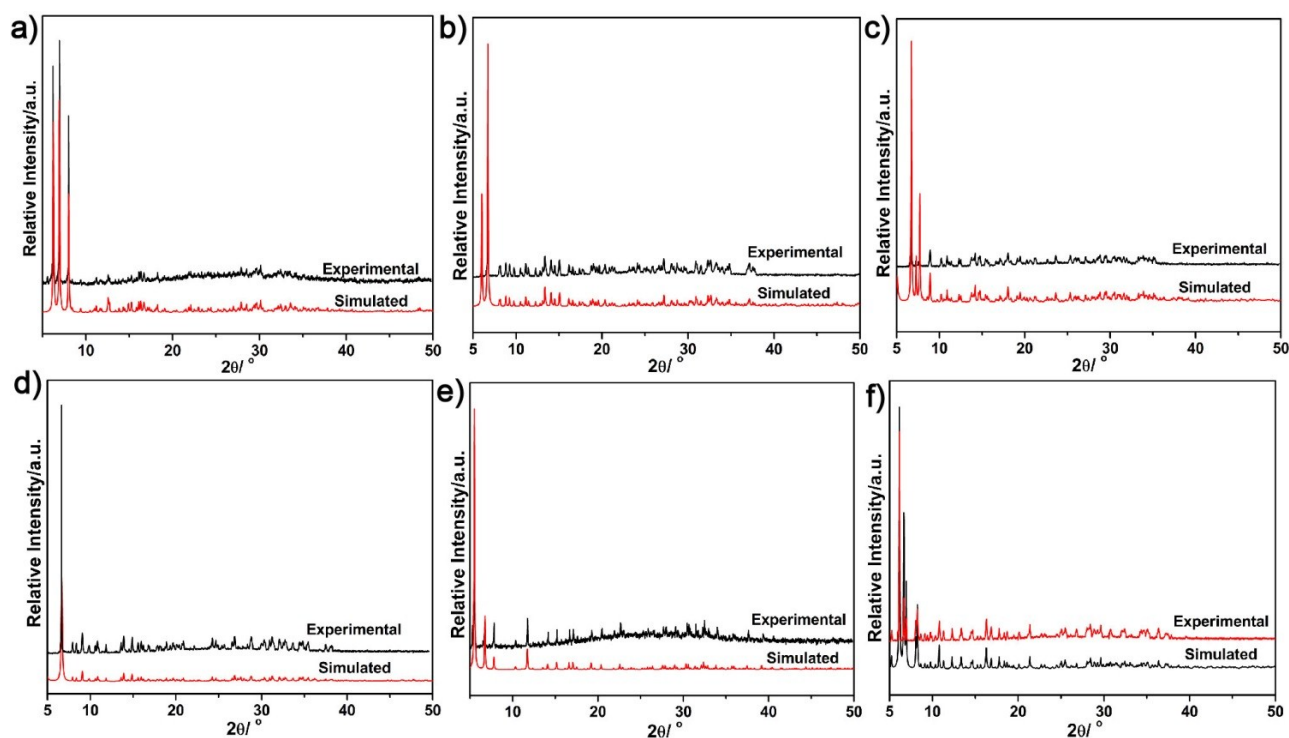


Fig. S19 View of each  $\{Dy_{11}Ge_{12}\}-6$  SBU linking six  $\{Dy_{11}Ge_{12}\}-6$  SBUs in **6**.



**Fig. S20** View of channels of **6** along the [001] (a) and [110] (b) directions, in which part of pyrazinyl rings of pza ligands and the organic parts of E groups point into the channels.



**Fig. 21** Experimental and simulated PXRD patterns for **1-6**: (a) for **1**, (b) for **2**, (c) for **3**, (d) for **4**, (e) for **5** and (f) for **6**, respectively.

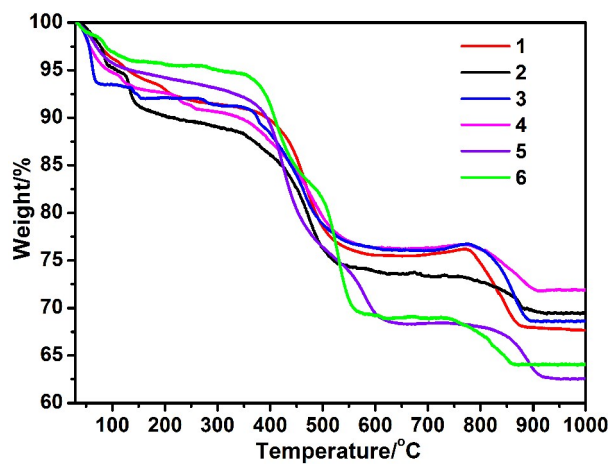




Fig. S22 TG curves of 1-6.

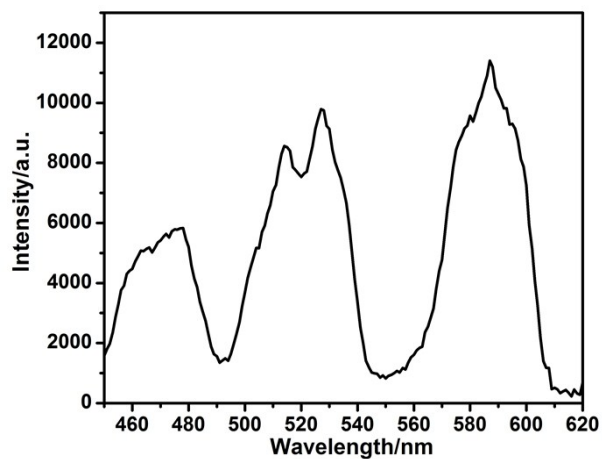


Fig. S23 The excitation spectrum of 1 taken by monitoring the most intense emission band.

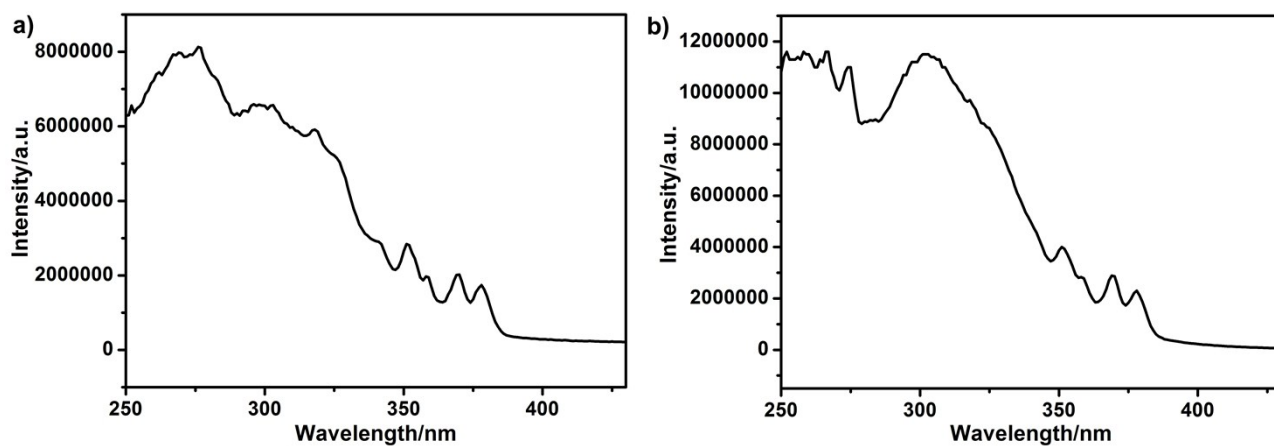


Fig. S24 The excitation spectra of 3 and 5 taken by monitoring the most intense emission band.