

Electronic Supplementary Information (ESI)

Structural phase transitions, dielectric bistability and luminescence of two bulky ion-pair crystals $[N(C_3H_7)_4]_2[Ln(NO_3)_5]$ ($Ln = Tb, Dy$)

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Table S1 Selected bond lengths (Å) for **1** (160 K) and **2** (100 K)

| 1 | | | |
|------------|----------|------------|----------|
| Tb(1)–O(1) | 2.445(4) | Tb(1)–O(2) | 2.456(5) |
| Tb(1)–O(4) | 2.445(4) | Tb(1)–O(5) | 2.521(4) |
| Tb(1)–O(7) | 2.413(4) | | |
| 2 | | | |
| Dy(1)–O(1) | 2.437(3) | Dy(1)–O(2) | 2.443(3) |
| Dy(1)–O(4) | 2.427(3) | Dy(1)–O(5) | 2.519(3) |
| Dy(1)–O(7) | 2.400(3) | | |

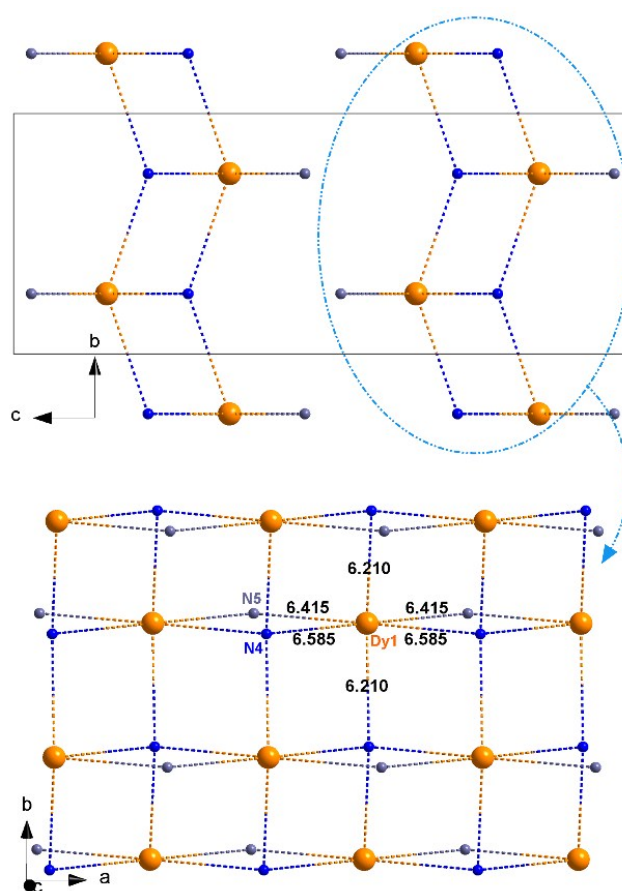


Fig. S1 Topology illustration for the packing of the $[\text{Dy}(\text{NO}_3)_5]^{2-}$ anionic groups and the charge-balanced $[\text{N}(\text{C}_3\text{H}_7)_4]^+$ cations in **2**. The $[\text{Dy}(\text{NO}_3)_5]^{2-}$ groups and $[\text{N}(\text{C}_3\text{H}_7)_4]^+$ cations are represented by their central atoms, namely Dy1, N4 and N5 atoms, respectively.

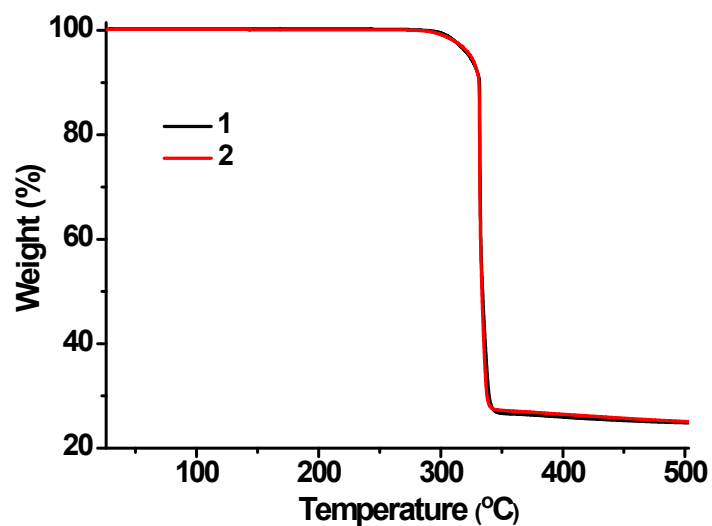


Fig. S2 TGA curves for 1 and 2.

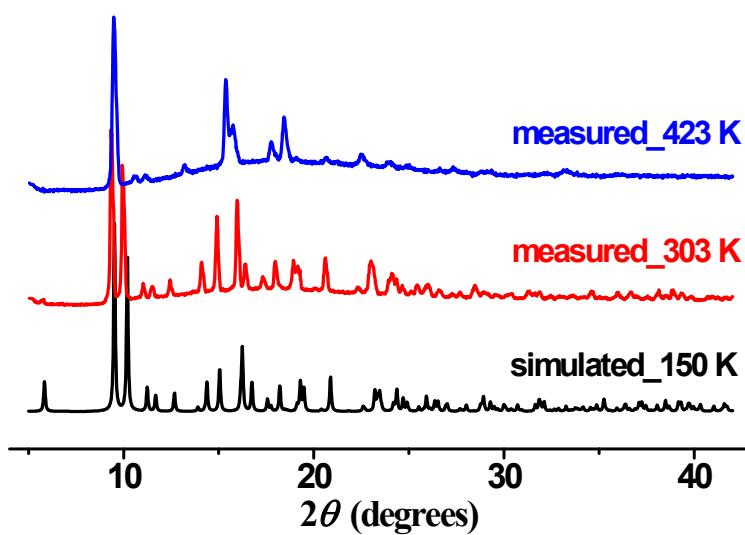


Fig. S3 Variable-temperature PXRD patterns of 1.

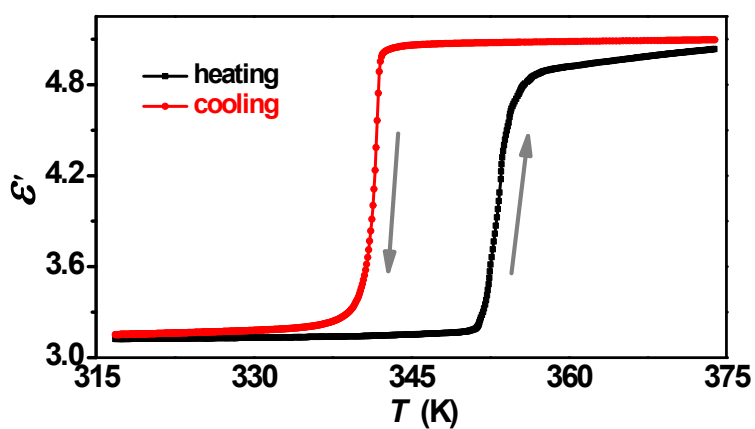


Fig. S4 Temperature dependence of the real part of the dielectric constant of 1 at 1 MHz during the heating and cooling runs.

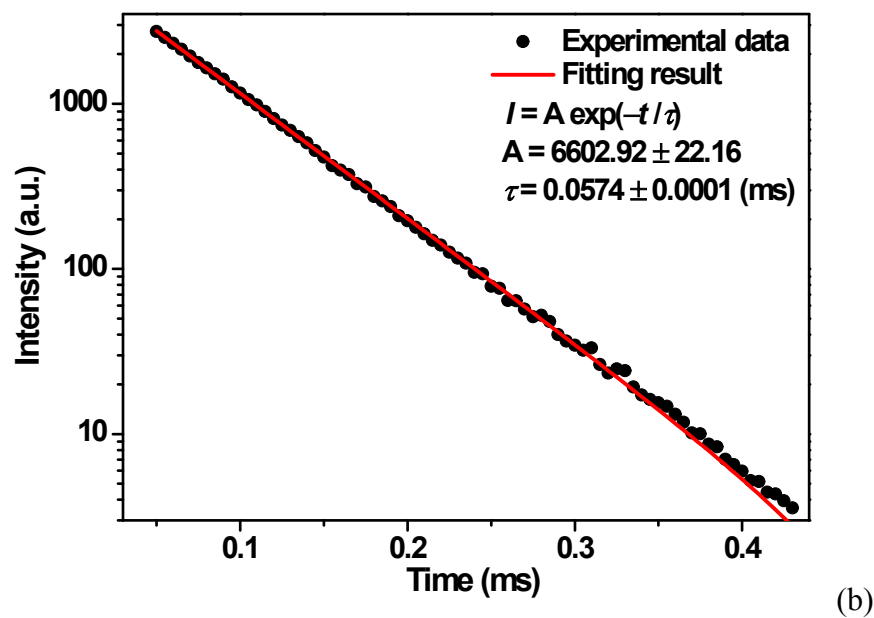
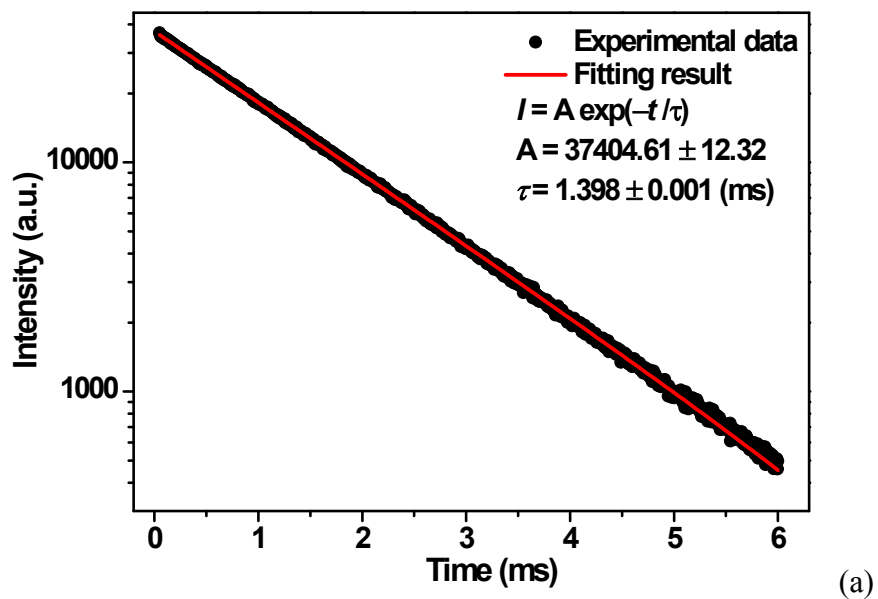


Fig. S5 Luminescence decay of **1** (a) and **2** (b).