Supplementary Material

Nitronyl Nitroxide Biradical-based Binuclear Lanthanide Complexes: Structure and Magnetic Properties

Lu Xi, Jing Han, Xiaohui Huang, and Licun Li

Department of Chemistry, Key Laboratory of Advanced Energy Materials Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

* E-mail: llicun@nankai.edu.cn

Magnetochemistry

Table of Contents

Table S1. Selected bond lengths [Å] and bond angles [°] for complexes **1–3**.

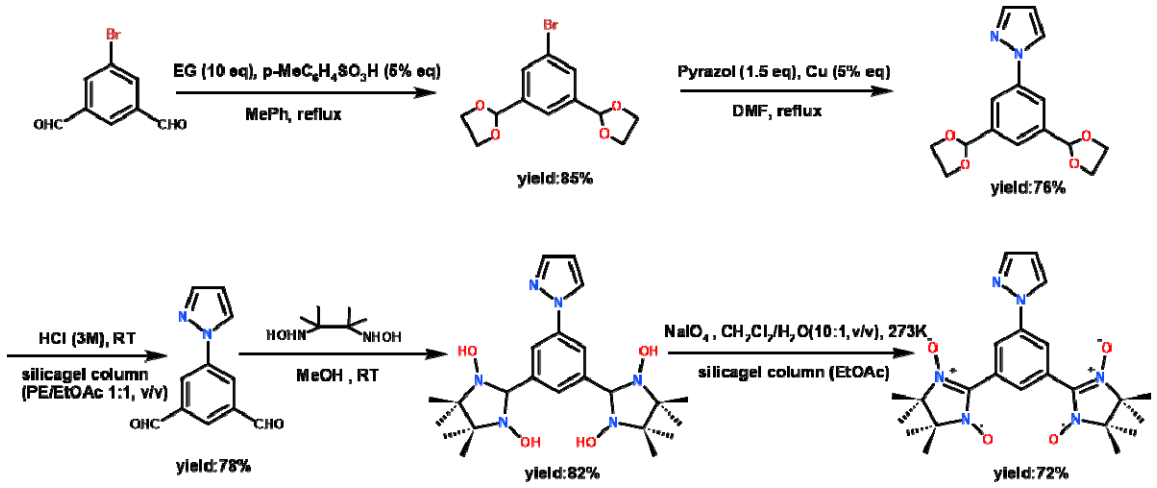
1 Gd			
Gd(1)–O(2)	2.383(8)	Gd(2)–O(10)	2.454(7)
Gd(1)–O(3)	2.378(8)	Gd(2)–O(11)	2.366(7)
Gd(1)–O(4)	2.350(8)	Gd(2)–O(12)	2.410(7)
Gd(1)–O(5)	2.343(9)	Gd(2)–O(13)	2.365(7)
Gd(1)–O(6)	2.379(9)	Gd(2)–O(14)	2.412(7)
Gd(1)–O(7)	2.405(8)	Gd(2)–O(15)	2.372(7)
Gd(1)–O(8)	2.384(8)	Gd(2)–O(16)	2.402(7)
Gd(1)–O(9)	2.472(7)	Gd(2)–O(17)	2.378(7)
O(1)–N(1)	1.265(14)	O(9)–N(3)	1.291(11)
O(2)–N(2)	1.339(12)	O(10)–N(4)	1.272(10)
O(2)–Gd(1)–O(9)	82.0(3)	O(17)–Gd(2)–O(10)	77.7(2)
O(4)–Gd(1)–O(3)	71.8(3)	O(11)–Gd(2)–O(12)	72.3(3)
O(5)–Gd(1)–O(6)	73.1(4)	O(13)–Gd(2)–O(14)	71.7(2)
O(8)–Gd(1)–O(7)	72.3(3)	O(15)–Gd(2)–O(16)	72.1(2)
2 Tb			
Tb(1)–O(2)	2.365(5)	Tb(2)–O(10)	2.437(4)
Tb(1)–O(3)	2.351(5)	Tb(2)–O(11)	2.339(4)
Tb(1)–O(4)	2.329(5)	Tb(2)–O(12)	2.387(4)
Tb(1)–O(5)	2.323(5)	Tb(2)–O(13)	2.350(4)
Tb(1)–O(6)	2.358(6)	Tb(2)–O(14)	2.395(4)
Tb(1)–O(7)	2.399(5)	Tb(2)–O(15)	2.346(4)
Tb(1)–O(8)	2.359(5)	Tb(2)–O(16)	2.391(4)
Tb(1)–O(9)	2.466(4)	Tb(2)–O(17)	2.373(4)
O(1)–N(1)	1.265(8)	O(9)–N(3)	1.292(6)
O(2)–N(2)	1.314(7)	O(10)–N(4)	1.285(6)
O(2)–Tb(1)–O(9)	82.34(16)	O(17)–Tb(2)–O(10)	77.91(15)
O(4)–Tb(1)–O(3)	72.31(17)	O(11)–Tb(2)–O(12)	72.59(15)
O(5)–Tb(1)–O(6)	73.0(2)	O(13)–Tb(2)–O(14)	72.07(15)
O(8)–Tb(1)–O(7)	72.28(16)	O(15)–Tb(2)–O(16)	72.12(15)
3 Dy			
Dy(1)–O(2)	2.352(6)	Dy(2)–O(10)	2.429(5)
Dy(1)–O(3)	2.341(6)	Dy(2)–O(11)	2.325(5)
Dy(1)–O(4)	2.312(5)	Dy(2)–O(12)	2.381(5)
Dy(1)–O(5)	2.306(6)	Dy(2)–O(13)	2.340(5)
Dy(1)–O(6)	2.353(6)	Dy(2)–O(14)	2.390(5)
Dy(1)–O(7)	2.382(5)	Dy(2)–O(15)	2.326(5)
Dy(1)–O(8)	2.347(6)	Dy(2)–O(16)	2.380(5)
Dy(1)–O(9)	2.460(5)	Dy(2)–O(17)	2.364(5)

O(1)–N(1)	1.274(9)	O(9)–N(3)	1.292(8)
O(2)–N(2)	1.311(8)	O(10)–N(4)	1.295(8)
O(2)–Dy(1)–O(9)	82.0(2)	O(17)–Dy(2)–O(10)	77.69(17)
O(4)–Dy(1)–O(3)	72.4(2)	O(11)–Dy(2)–O(12)	72.54(18)
O(5)–Dy(1)–O(6)	73.0(3)	O(13)–Dy(2)–O(14)	72.56(17)
O(8)–Dy(1)–O(7)	72.81(19)	O(15)–Dy(2)–O(16)	72.42(18)

Table S2. The SHAPE analyses for Ln^{III} ions in complexes **1**–**3**.

Complex	SAPR-8	TDD-8	**BTPR-8**	**Complex**	SAPR-8	**TDD-8**	BTPR-8
1 Gd1	1.143	1.535	**0.755**	**1** Gd2	1.086	**1.067**	1.437
2 Tb1	1.231	1.586	**0.757**	**2** Tb2	1.118	**1.033**	1.415
3 Dy1	1.226	1.556	**0.726**	**3** Dy2	1.127	**1.032**	1.382

SAPR-8: Square antiprism; TDD-8: Triangular dodecahedron; BTPR-8: Biaugmented trigonal prism.



Scheme S1. The synthesis of NITPhPzbis biradical ligand (EG: ethylene glycol).

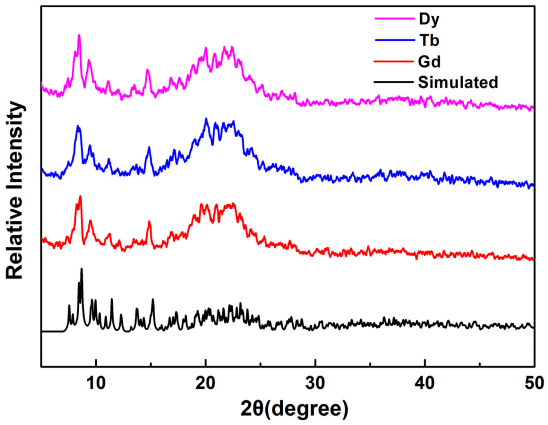


Figure S1. Powder X-ray diffraction (PXRD) patterns for complexes **1–3** at room temperature.

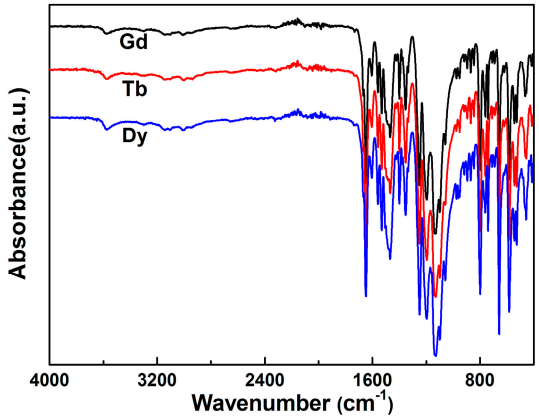


Figure S2. The IR spectra of complexes **1–3**.

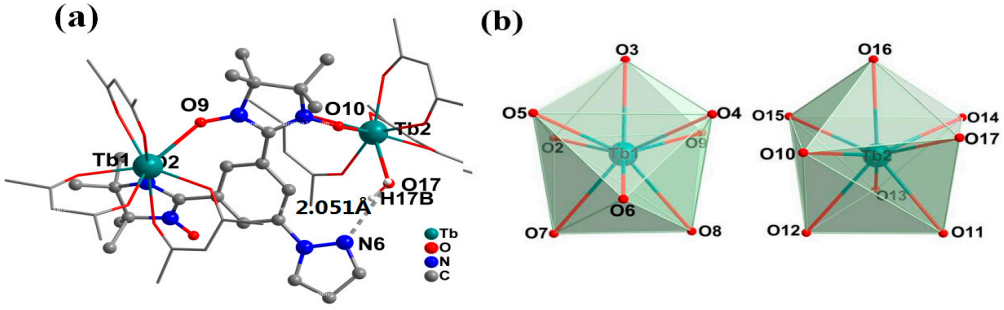


Figure S3. (a) The binuclear structure of **2** (H and F atoms are omitted; Color code: teal, Tb; gray, C; red, O; blue, N) and 2.051 Å represents the length of N6···H17B. (b) Coordination polyhedra of Tb1 and Tb2 in **2**.

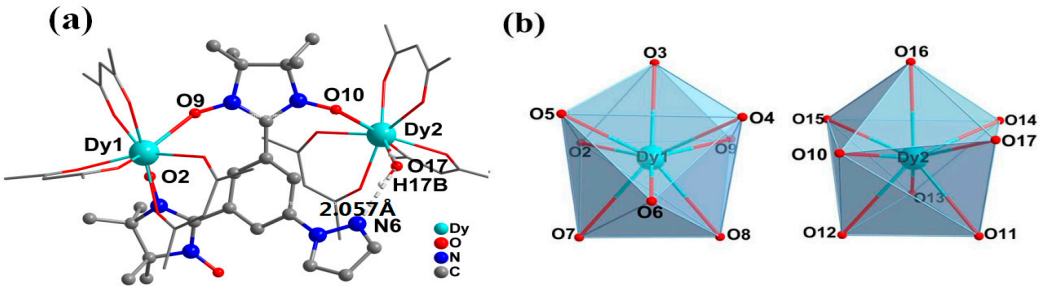


Figure S4. (a) The binuclear structure of **3** (H and F atoms are omitted; Color code: aqua, Dy; gray, C; red, O; blue, N) and 2.057 Å represents the length of N6···H17B. (b) Coordination polyhedra of Dy1 and Dy2 in **3**.

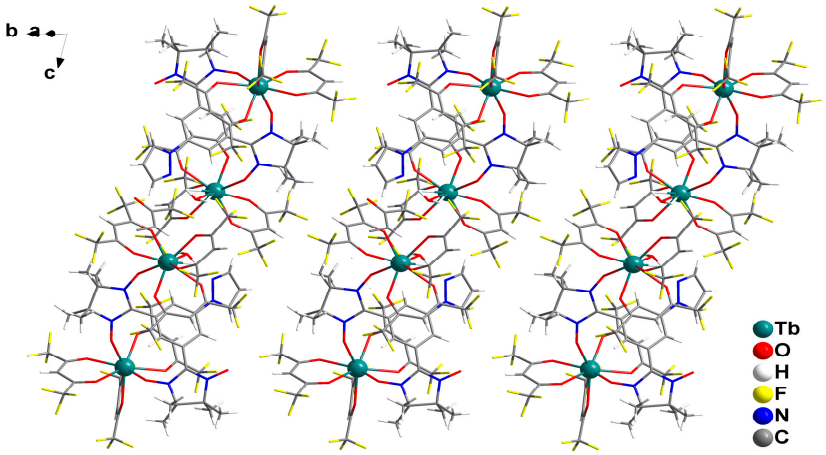


Figure S5. Crystal packing diagram of **2**.

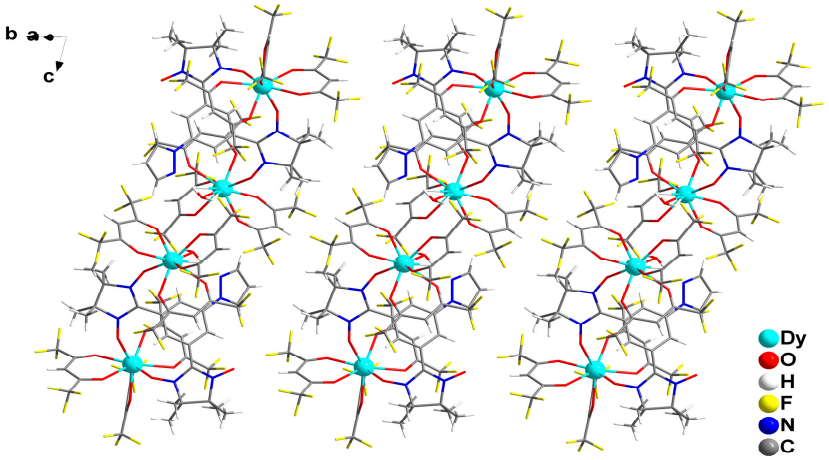


Figure S6. Crystal packing diagram of **3**.

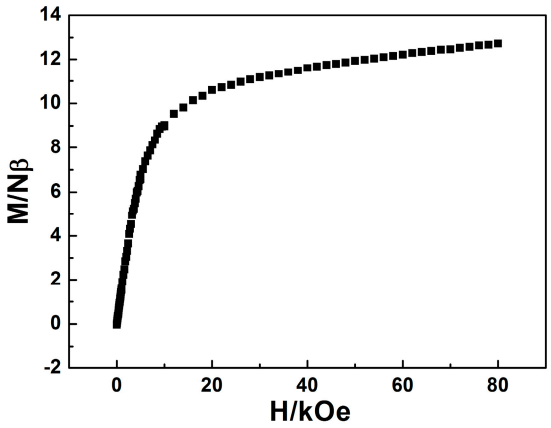


Figure S7. *M vs. H* plot for complex **2** at 2 K.

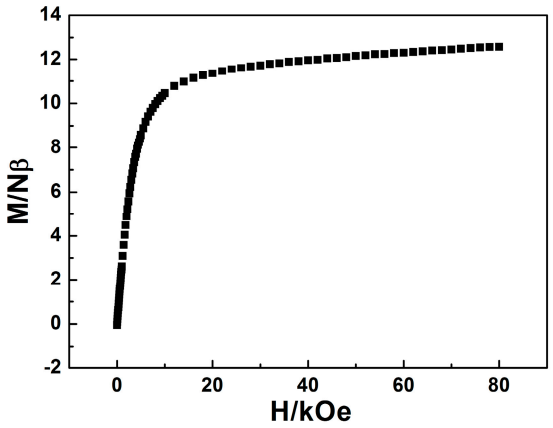


Figure S8. *M vs. H* plot for complex **3** at 2 K.

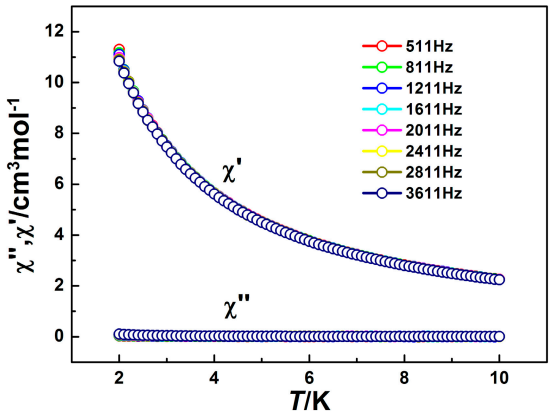


Figure S9. Temperature dependencies of χ' and χ'' for **2** in zero dc field.

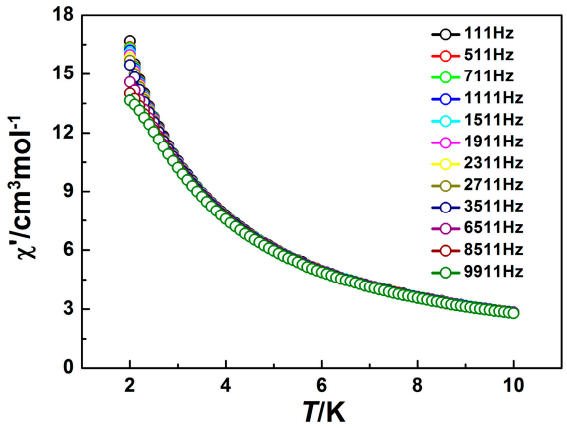


Figure S10. Temperature dependency of χ' for **3** in zero dc field.

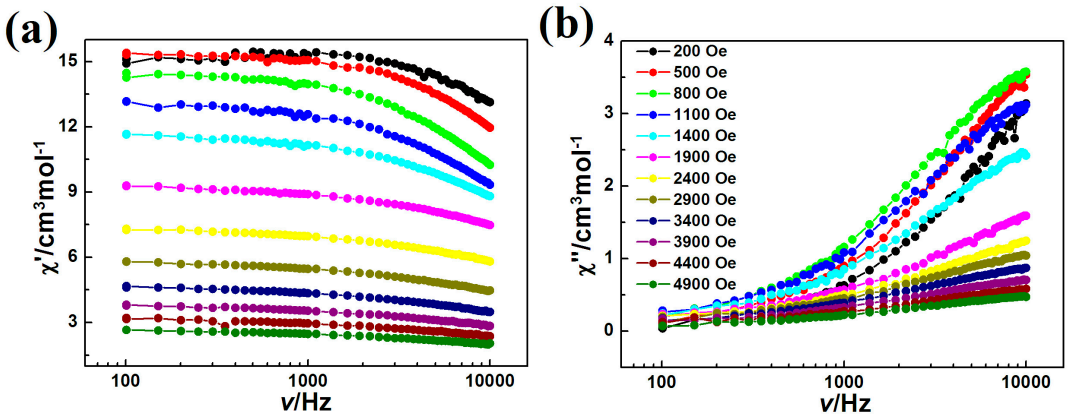


Figure S11. Frequency dependencies of χ' (a) and χ''(b) for **3** in the dc fields of 200–4900 Oe.