**Table S1** Reagents required for the experiments.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Materials | Source | Purification method | Mass fraction (purity) | CAS number |
| O-Phenanthroline | Beijing Innochem | Without purification | 97% | 66-71-7 |
| 2,4-Difluorobenzoic acid | Beijing Innochem | Without purification | 98% | 1583-58-0 |
| La(NO3)3⋅6H2O | Alfa Aesar | Without purification | 99.90% | 10277-43-7 |
| Gd(NO3)3⋅6H2O | Beijing Bailingwei Technology Co., LTD | Without purification | 99.90% | 19598-90-4 |
| Tb(NO3)3⋅6H2O | Beijing Innochem | Without purification | 99.90% | 57584-27-7 |
| Dy(NO3)3⋅6H2O | Alfa Aesar | Without purification | 99.90% | 10031-49-9 |
| Ho(NO3)3⋅6H2O | Beijing Innochem | Without purification | 99.90% | 14483-18-2 |
| NaOH | Tianjin Senchang Industrial Co., Ltd. | Without purification | 96% | 1310-73-2 |
| C2H5OH | Damao chemical reagent factory | Without purification | AR | 64-17-5 |

**Table S2**Selected bond lengths for the complexes **1-5.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Complex 1 | Complex 2 | Complex 3 | Complex 4 | Complex 5 |
| Selected bond | Bond lengths/ Å | Selected bond | Bond lengths/ Å | Selected bond | Bond lengths/ Å | Selected bond | Bond lengths/ Å | Selected bond | Bond lengths/ Å |
| La(1)-O(3) | 2.412(3) | Gd(1)-O(3) | 2.299(4) | Tb(1)-O(3) | 2.277(3) | Dy(1)-O(3) | 2.273(4) | Ho(1)-O(3) | 2.247(5) |
| La(1)-O(4)#1 | 2.457(4) | Gd(1)-O(4)#1 | 2.340(4) | Tb(1)-O(1) | 2.330(4) | Dy(1)-O(1) | 2.322(5) | Ho(1)-O(1) | 2.299(5) |
| La(1)-O(1) | 2.476(3) | Gd(1)-O(1) | 2.350(5) | Tb(1)-O(4)#1 | 2.340(3) | Dy(1)-O(4)#1 | 2.327(4) | Ho(1)-O(4)#1 | 2.305(5) |
| La(1)-O(5) | 2.529(3) | Gd(1)-O(2)#1 | 2.387(5) | Tb(1)-O(2)#1 | 2.363(4) | Dy(1)-O(2)#1 | 2.347(4) | Ho(1)-O(2)#1 | 2.333(5) |
| La(1)-O(2)#1 | 2.534(3) | Gd(1)-O(6) | 2.436(5) | Tb(1)-O(6) | 2.417(4) | Dy(1)-O(6) | 2.404(4) | Ho(1)-O(6) | 2.394(5) |
| La(1)-O(6) | 2.536(4) | Gd(1)-O(5) | 2.437(5) | Tb(1)-O(5) | 2.435(3) | Dy(1)-O(5) | 2.430(4) | Ho(1)-O(5) | 2.416(5) |
| La(1)-N(2) | 2.670(4) | Gd(1)-N(2) | 2.554(5) | Tb(1)-N(2) | 2.544(4) | Dy(1)-N(2) | 2.530(5) | Ho(1)-N(2) | 2.515(6) |
| La(1)-N(1) | 2.698(4) | Gd(1)-N(1) | 2.583(5) | Tb(1)-N(1) | 2.563(4) | Dy(1)-N(1) | 2.562(5) | Ho(1)-N(1) | 2.532(6) |
| La(1)-O(1)#1 | 2.801(3) | Gd(1)-O(1)#1 | 2.904(5) |  |  |  |  |  |  |

(Symmetry codes: #1 -x+1,-y+1,-z+1)

**Table S3(a)**Selected bond angles for the complexes **1-5.**

|  |  |  |  |
| --- | --- | --- | --- |
| Complex 1 |  | Complex 2 |  |
| Selectedangle | Bond angle/° | Selectedangle | Bond angle/° |
| O(3)-La(1)-O(4)#1 | 132.54(11) | O(3)-Gd(1)-O(4)#1 | 129.95(15) |
| O(3)-La(1)-O(1) | 73.11(12) | O(3)-Gd(1)-O(1) | 74.03(16) |
| O(4)#1-La(1)-O(1) | 76.85(12) | O(4)#1-Gd(1)-O(1) | 77.49(14) |
| O(3)-La(1)-O(5) | 73.93(12) | O(3)-Gd(1)-O(2)#1 | 78.05(16) |
| O(4)#1-La(1)-O(5) | 133.48(12) | O(4)#1-Gd(1)-O(2)#1 | 86.05(16) |
| O(1)-La(1)-O(5) | 77.97(11) | O(1)-Gd(1)-O(2)#1 | 125.02(17) |
| O(3)-La(1)-O(2)#1 | 77.74(13) | O(3)-Gd(1)-O(6) | 127.00(15) |
| O(4)#1-La(1)-O(2)#1 | 90.05(13) | O(4)#1-Gd(1)-O(6) | 88.91(16) |
| O(1)-La(1)-O(2)#1 | 123.99(11) | O(1)-Gd(1)-O(6) | 83.81(18) |
| O(5)-La(1)-O(2)#1 | 136.33(13) | O(2)#1-Gd(1)-O(6) | 148.52(16) |
| O(3)-La(1)-O(6) | 123.55(12) | O(3)-Gd(1)-O(5) | 74.94(15) |
| O(4)#1-La(1)-O(6) | 88.23(13) | O(4)#1-Gd(1)-O(5) | 135.26(16) |
| O(1)-La(1)-O(6) | 84.24(12) | O(1)-Gd(1)-O(5) | 76.07(16) |
| O(5)-La(1)-O(6) | 50.73(12) | O(2)#1-Gd(1)-O(5) | 138.65(17) |
| O(2)#1-La(1)-O(6) | 150.43(12) | O(6)-Gd(1)-O(5) | 52.96(15) |
| O(3)-La(1)-N(2) | 85.12(13) | O(3)-Gd(1)-N(2) | 82.25(17) |
| O(4)#1-La(1)-N(2) | 136.39(12) | O(4)#1-Gd(1)-N(2) | 139.03(16) |
| O(1)-La(1)-N(2) | 144.61(12) | O(1)-Gd(1)-N(2) | 142.46(15) |
| O(5)-La(1)-N(2) | 69.22(12) | O(2)#1-Gd(1)-N(2) | 76.02(17) |
| O(2)#1-La(1)-N(2) | 75.93(12) | O(6)-Gd(1)-N(2) | 87.92(18) |
| O(6)-La(1)-N(2) | 85.13(13) | O(5)-Gd(1)-N(2) | 69.83(16) |
| O(3)-La(1)-N(1) | 136.48(13) | O(3)-Gd(1)-N(1) | 137.57(17) |
| O(4)#1-La(1)-N(1) | 75.84(13) | O(4)#1-Gd(1)-N(1) | 76.10(16) |
| O(1)-La(1)-N(1) | 149.68(13) | O(1)-Gd(1)-N(1) | 148.09(17) |
| O(5)-La(1)-N(1) | 112.53(12) | O(2)#1-Gd(1)-N(1) | 70.50(16) |
| O(2)#1-La(1)-N(1) | 68.99(12) | O(6)-Gd(1)-N(1) | 78.12(16) |
| O(6)-La(1)-N(1) | 82.00(12) | O(5)-Gd(1)-N(1) | 111.72(16) |
| N(2)-La(1)-N(1) | 60.55(13) | N(2)-Gd(1)-N(1) | 63.28(17) |
| O(3)-La(1)-O(1)#1 | 70.55(11) | O(3)-Gd(1)-O(1)#1 | 66.85(13) |
| O(4)#1-La(1)-O(1)#1 | 67.46(11) | O(4)#1-Gd(1)-O(1)#1 | 67.51(14) |
| O(1)-La(1)-O(1)#1 | 77.06(11) | O(1)-Gd(1)-O(1)#1 | 77.94(16) |
| O(5)-La(1)-O(1)#1 | 141.11(11) | O(2)#1-Gd(1)-O(1)#1 | 47.51(14) |
| O(2)#1-La(1)-O(1)#1 | 48.19(11) | O(6)-Gd(1)-O(1)#1 | 152.69(16) |
| O(6)-La(1)-O(1)#1 | 152.00(12) | O(5)-Gd(1)-O(1)#1 | 138.31(14) |
| N(2)-La(1)-O(1)#1 | 121.90(11) | N(2)-Gd(1)-O(1)#1 | 118.79(15) |
| N(1)-La(1)-O(1)#1 | 104.03(11) | N(1)-Gd(1)-O(1)#1 | 107.62(14) |

(Symmetry codes: #1 -x+1,-y+1,-z+1)

**Table S3(b)**Selected bond angles for the complexes **1-5.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Complex 3 |  | Complex 4 |  | Complex 5 |  |
| Selectedangle | Bond angle/° | Selectedangle | Bond angle/° | Selectedangle | Bond angle/° |
| O(3)-Tb(1)-O(1) | 74.79(13) | O(3)-Dy(1)-O(1) | 74.87(16) | O(3)-Ho(1)-O(1) | 74.8(2) |
| O(3)-Tb(1)-O(4)#1 | 128.83(12) | O(3)-Dy(1)-O(4)#1 | 127.87(15) | O(3)-Ho(1)-O(4)#1 | 127.29(18) |
| O(1)-Tb(1)-O(4)#1 | 77.47(12) | O(1)-Dy(1)-O(4)#1 | 77.43(14) | O(1)-Ho(1)-O(4)#1 | 77.42(18) |
| O(3)-Tb(1)-O(2)#1 | 77.77(13) | O(3)-Dy(1)-O(2)#1 | 77.85(16) | O(3)-Ho(1)-O(2)#1 | 77.34(19) |
| O(1)-Tb(1)-O(2)#1 | 124.86(14) | O(1)-Dy(1)-O(2)#1 | 124.93(17) | O(1)-Ho(1)-O(2)#1 | 124.3(2) |
| O(4)#1-Tb(1)-O(2)#1 | 84.25(13) | O(4)#1-Dy(1)-O(2)#1 | 83.28(16) | O(4)#1-Ho(1)-O(2)#1 | 82.87(19) |
| O(3)-Tb(1)-O(6) | 127.65(12) | O(3)-Dy(1)-O(6) | 127.84(14) | O(3)-Ho(1)-O(6) | 128.25(18) |
| O(1)-Tb(1)-O(6) | 83.09(14) | O(1)-Dy(1)-O(6) | 82.79(18) | O(1)-Ho(1)-O(6) | 82.7(2) |
| O(4)#1-Tb(1)-O(6) | 89.80(12) | O(4)#1-Dy(1)-O(6) | 90.55(15) | O(4)#1-Ho(1)-O(6) | 90.67(19) |
| O(2)#1-Tb(1)-O(6) | 148.86(13) | O(2)#1-Dy(1)-O(6) | 148.88(16) | O(2)#1-Ho(1)-O(6) | 149.4(2) |
| O(3)-Tb(1)-O(5) | 75.10(12) | O(3)-Dy(1)-O(5) | 75.10(15) | O(3)-Ho(1)-O(5) | 75.53(18) |
| O(1)-Tb(1)-O(5) | 75.58(12) | O(1)-Dy(1)-O(5) | 75.18(16) | O(1)-Ho(1)-O(5) | 75.38(19) |
| O(4)#1-Tb(1)-O(5) | 136.32(12) | O(4)#1-Dy(1)-O(5) | 136.90(15) | O(4)#1-Ho(1)-O(5) | 137.19(18) |
| O(2)#1-Tb(1)-O(5) | 139.43(13) | O(2)#1-Dy(1)-O(5) | 139.82(16) | O(2)#1-Ho(1)-O(5) | 139.94(19) |
| O(6)-Tb(1)-O(5) | 53.44(12) | O(6)-Dy(1)-O(5) | 53.62(15) | O(6)-Ho(1)-O(5) | 53.69(18) |
| O(3)-Tb(1)-N(2) | 82.05(13) | O(3)-Dy(1)-N(2) | 82.32(17) | O(3)-Ho(1)-N(2) | 82.4(2) |
| O(1)-Tb(1)-N(2) | 142.28(12) | O(1)-Dy(1)-N(2) | 142.06(15) | O(1)-Ho(1)-N(2) | 142.28(19) |
| O(4)#1-Tb(1)-N(2) | 139.33(12) | O(4)#1-Dy(1)-N(2) | 139.62(15) | O(4)#1-Ho(1)-N(2) | 139.54(18) |
| O(2)#1-Tb(1)-N(2) | 77.03(13) | O(2)#1-Dy(1)-N(2) | 77.62(16) | O(2)#1-Ho(1)-N(2) | 77.7(2) |
| O(6)-Tb(1)-N(2) | 88.20(14) | O(6)-Dy(1)-N(2) | 88.00(17) | O(6)-Ho(1)-N(2) | 88.5(2) |
| O(5)-Tb(1)-N(2) | 69.86(12) | O(5)-Dy(1)-N(2) | 69.82(16) | O(5)-Ho(1)-N(2) | 69.97(19) |
| O(3)-Tb(1)-N(1) | 137.49(13) | O(3)-Dy(1)-N(1) | 138.02(16) | O(3)-Ho(1)-N(1) | 138.2(2) |
| O(1)-Tb(1)-N(1) | 147.48(13) | O(1)-Dy(1)-N(1) | 146.87(17) | O(1)-Ho(1)-N(1) | 146.7(2) |
| O(4)#1-Tb(1)-N(1) | 76.46(12) | O(4)#1-Dy(1)-N(1) | 76.44(16) | O(4)#1-Ho(1)-N(1) | 76.44(19) |
| O(2)#1-Tb(1)-N(1) | 71.16(13) | O(2)#1-Dy(1)-N(1) | 71.44(16) | O(2)#1-Ho(1)-N(1) | 72.07(19) |
| O(6)-Tb(1)-N(1) | 77.72(13) | O(6)-Dy(1)-N(1) | 77.45(16) | O(6)-Ho(1)-N(1) | 77.32(19) |
| O(5)-Tb(1)-N(1) | 111.72(13) | O(5)-Dy(1)-N(1) | 112.03(16) | O(5)-Ho(1)-N(1) | 111.82(19) |
| N(2)-Tb(1)-N(1) | 63.44(13) | N(2)-Dy(1)-N(1) | 63.86(17) | N(2)-Ho(1)-N(1) | 63.9(2) |

(Symmetry codes: #1 -x+1,-y+1,-z+1)

**Table S4**Hydrogen bonding data of complexes **1**-**5.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | hydrogen bonding | D-H | H···A | D···A | D-H···A |
| Complex 1 | C(7)-H(7)···O(5) | 0.93 | 2.52 | 3.233(8) | 133 |
| C(22)-H(22)···F(3) | 0.93 | 2.55 | 3.366(7) | 147 |
| C(22)-H(22)···O(4) | 0.93 | 2.37 | 3.071(7) | 132 |
| C(30)-H(30)···F(5) | 0.93 | 2.47 | 3.233(18) | 139 |
| C(32)-H(32)···O(6) | 0.93 | 2.45 | 3.324(7) | 158 |
| Complex 2 | C(7)-H(7)···O(5) | 0.93 | 2.55 | 3.273(11) | 135 |
| C(14)-H(14)···O(5) | 0.93 | 2.56 | 3.454(8) | 163 |
| C(20)-H(20)···F(4) | 0.93 | 2.52 | 3.127(11) | 123 |
| C(22)-H(22)···F(3) | 0.93 | 2.51 | 3.382(9) | 156 |
| C(22)-H(22)···O(4) | 0.93 | 2.34 | 2.986(8) | 126 |
| C(30)-H(30)···F(5) | 0.93 | 2.43 | 3.274(12) | 151 |
| C(32)-H(32)···O(6) | 0.93 | 2.49 | 3.333(10) | 151 |
| Complex 3 | C(7)-H(7)···O(5) | 0.93 | 2.58 | 3.318(8) | 137 |
| C(11)-H(11)···F(1) | 0.93 | 2.53 | 3.131(8) | 122 |
| C(14)-H(14)···O(5) | 0.93 | 2.53 | 3.429(6) | 162 |
| C(20)-H(20)···F(4) | 0.93 | 2.54 | 3.153(8) | 124 |
| C(22)-H(22)···F(3) | 0.93 | 2.52 | 3.396(7) | 157 |
| C(22)-H(22)···O(4) | 0.93 | 2.34 | 2.990(6) | 126 |
| C(30)-H(30)···F(5) | 0.93 | 2.46 | 3.298(9) | 150 |
| C(32)-H(32)···O(6) | 0.93 | 2.51 | 3.346(7) | 149 |
| Complex 4 | C(7)-H(7)···O(5) | 0.93 | 2.57 | 3.325(11) | 138 |
| C(11)-H(11)···F(1) | 0.93 | 2.55 | 3.146(10) | 123 |
| C(14)-H(14)···O(5) | 0.93 | 2.52 | 3.422(8) | 163 |
| C(20)-H(20)···F(4) | 0.93 | 2.54 | 3.143(11) | 123 |
| C(22)-H(22)···F(3) | 0.93 | 2.51 | 3.385(9) | 157 |
| C(22)-H(22)···O(4) | 0.93 | 2.34 | 2.982(8) | 126 |
| C(30)-H(30)···F(5) | 0.93 | 2.45 | 3.293(11) | 151 |
| C(32)-H(32)···O(6) | 0.93 | 2.50 | 3.332(9) | 149 |
| Complex 5 | C(7)-H(7)···O(5) | 0.93 | 2.60 | 3.342(12) | 137 |
| C(11)-H(11)···F(1) | 0.93 | 2.53 | 3.134(11) | 123 |
| C(14)-H(14)···O(5) | 0.93 | 2.50 | 3.400(10) | 163 |
| C(20)-H(20)···F(4) | 0.93 | 2.52 | 3.129(13) | 124 |
| C(21)-H(21)···O(5) | 0.93 | 2.45 | 2.761(12) | 100 |
| C(22)-H(22)···F(3) | 0.93 | 2.49 | 3.363(10) | 156 |
| C(22)-H(22)···O(4) | 0.93 | 2.32 | 2.962(10) | 125 |
| C(30)-H(30)···F(5) | 0.93 | 2.43 | 3.275(13) | 152 |
| C(32)-H(32)···O(6) | 0.93 | 2.51 | 3.351(11) | 150 |

**Table S5**Continuous shape measures analysis of lanthanide coordination spheres in compounds **1**-**5**. Lowest CShM values are highlighted in yellow.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | 1,La | 2,Gd |  | 3,Tb | 4,Dy | 5,Ho |
| EP-9 | 32.169 | 32.640 | OP-8 | 31.444 | 31.577 | 31.719 |
| OPY-9 | 20.128 | 21.018 | HPY-8 | 21.778 | 21.744 | 21.750 |
| HBPY-9 | 17.304 | 17.482 | HBPY-8 | 15.771 | 15.815 | 15.802 |
| JTC-9 | 14.148 | 14.629 | CU-8 | 10.765 | 10.661 | 10.507 |
| JCCU-9 | 10.651 | 10.194 | SAPR-8 | 1.745 | 1.727 | 1.678 |
| CCU-9 | 10.161 | 10.267 | TDD-8 | 2.581 | 2.583 | 2.534 |
| JCSAPR-9 | 3.201 | 2.652 | JGBF-8 | 14.304 | 14.443 | 14.556 |
| CSAPR-9 | 2.227 | 2.576 | JETBPY-8 | 28.265 | 28.328 | 28.443 |
| JTCTPR-9 | 3.384 | 2.857 | JBTPR-8 | 2.065 | 1.980 | 2.028 |
| TCTPR-9 | 3.274 | 3.150 | BTPR-8 | 1.229 | 1.200 | 1.246 |
| JTDIC-9 | 13.252 | 13.818 | JSD-8 | 4.844 | 4.812 | 4.875 |
| HH-9 | 10.639 | 10.455 | TT-8 | 11.571 | 11.481 | 11.322 |
| MFF-9 | 2.158 | 2.229 | ETBPY-8 | 23.383 | 23.711 | 23.725 |

Abbreviations:EP-9, Enneagon; OPY-9, Octagonal pyramid; HBPY-9, Heptagonal bipyramid; JTC-9, Johnson triangular cupola J3; JCCU-9, Capped cube J8; CCU-9, Spherical-relaxed capped cube; JCSAPR-9, Capped square antiprism J10; CSAPR-9, Spherical capped square antiprism; JTCTPR-9, Tricapped trigonal prism J51;TCTPR-9, Spherical tricapped trigonal prism; JTDIC-9, Tridiminished icosahedron J63;HH-9, Hula-hoop; MFF-9; Muffin;OP-8, Octagon; HPY-8; Heptagonal pyramid; HBPY-8, Hexagonal bipyramid; CU-8, Cube; SAPR-8, Square antiprism; TDD-8, Triangular dodecahedron; JGBF-8, Johnson gyrobifastigium J26;JETBPY-8, Johnson elongated triangular bipyramid J14; JBTPR-8, Biaugmented trigonal prism J50; BTPR-8, Biaugmented trigonal prism; JSD-8, Snub diphenoid J84; TT-8, Triakis tetrahedron; ETBPY-8, Elongated trigonal bipyramid.

**Table S6**(a) Infrared spectral data of the complexes **1-5.**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| ligands/complexes | νC=N  | δC-H | νC=O | νas(coo-) | νs(coo-) | νLn-O |
| 2,4-DFBA |  |  | 1691 |  |  |  |
| phen | 1560 | 854,738 |  |  |  |  |
| 1 | 1582 | 849,731 |  | 1616 | 1427 | 417 |
| 2 | 1589 | 848,731 |  | 1614 | 1429 | 419 |
| 3 | 1591 | 849,731 |  | 1614 | 1429 | 419 |
| 4 | 1577 | 849,731 |  | 1614 | 1431 | 418 |
| 5 | 1593 | 850,733 |  | 1610 | 1431 | 419 |
|  |  |  |  |  |  |  |

**Table S6**(b) Raman spectral data of complexes **1-5.**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| ligands/complexes | νC=N  | δC-H | νC=O | νas(coo-) | νs(coo-) | νLn-O | νLn-N |
| 2,4-DFBA |  |  | 1634 |  |  |  |  |
| phen | 1507 | 719 |  |  |  |  |  |
| 1 | 1503 | 732 |  | 1614 | 1416 | 417 | 240 |
| 2 | 1521 | 725 |  | 1614 | 1416 | 421 | 241 |
| 3 | 1522 | 726 |  | 1615 | 1416 | 420 | 241 |
| 4 | 1525 | 727 |  | 1615 | 1415 | 423 | 240 |
| 5 | 1525 | 722 |  | 1620 | 1416 | 419 | 242 |

**Table S7** Thermal decomposition data of complexes **1-5.**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | Steps | Temperature/K | DTG Tp/K | Mass loss rate/% | Probably expelled groups | Intermediate and residue |
|  |  |  |  | Found | Calcd |  |  |
| 1 | I | 494.15-691.15 | 627.25 | 60.58 | 22.80a | 2phen+x 2,4-DFBA | [La2(2,4-DFBA)6-x] |
|  | II | 691.15-1009.15 | 709.75 | 18.21 | 56.59b | (6-x)2,4-DFBA | La2O3 |
|  | Sum |  |  | 78.79 | 79.39c |  |  |
| 2 | I | 393.15-714.15 | 612.65 | 57.28 | 22.28a | 2phen+x 2,4-DFBA | [Gd2(2,4-DFBA)6-x] |
|  | II | 714.15-1036.15 | 768.55 | 18.88 | 55.31b | (6-x)2,4-DFBA | Gd2O3 |
|  | Sum |  |  | 76.16 | 77.59c |  |  |
| 3 | I | 428.15-718.15 | 610.25 | 57.78 | 22.24a | 2phen+x 2,4-DFBA | [Tb2(2,4-DFBA)6-x] |
|  | II | 718.15-1043.15 | 769.15 | 18.44 | 54.70b | (6-x)2,4-DFBA | 1/2Tb4O7 |
|  | Sum |  |  | 76.22 | 76.94c |  |  |
| 4 | I | 510.15-668.15 | 617.15 | 54.33 | 22.13a | 2phen+x 2,4-DFBA | [Dy2(2,4-DFBA)6-x] |
|  | II | 668.15-784.15 | 763.65 | 13.03 |  | y 2,4-DFBA | [Dy2(2,4-DFBA)6-x-y] |
|  | III | 784.15-1009.15 | 803.05 | 9.04 | 54.95b | (6-x-y)2,4-DFBA | Dy2O3 |
|  | Sum |  |  | 76.4 | 77.08c |  |  |
| 5 | I | 431.15-664.15 | 615.25 | 54.25 | 22.07a | 2phen+x 2,4-DFBA | [Ho2(2,4-DFBA)6-x] |
|  | II | 664.15-788.15 | 775.15 | 10.32 |  | y 2,4-DFBA | [Ho2(2,4-DFBA)6-x-y] |
|  | III | 788.15-1035.15 | 820.65 | 12.21 | 54.79b | (6-x-y)2,4-DFBA | Ho2O3 |
|  | Sum |  |  | 76.78 | 76.86c |  |  |

a: Theoretical total mass loss ofphen.

b: Theoretical total mass loss of 2,4-DFBA.

c: The total loss rate.

**Table S8** HOMO and LUMO energy levels of ligands.

|  |  |  |
| --- | --- | --- |
| Ligand | Energy level/eV | ΔＥ/eV |
| HOMO | LUMO |
| Phen | -6.4861 | -1.6708 | 4.8153 |
| 2,4-DFBA | -7.4815 | -1.7676 | 5.7139 |

**Table S9** Single and triplet state energy levels of ligands.

|  |  |  |  |
| --- | --- | --- | --- |
| Ligand | Excited states | Multiplicity | Excitation energy |
| eV | cm-1 |
| Phen | 1 | T | 2.8659 | 23095 |
| 2 | T | 3.4589 | 27896 |
| 3 | T | 3.5517 | 28644 |
| 1 | S | 3.9906 | 32206 |
| 2 | S | 4.0164 | 32392 |
| 3 | S | 4.0918 | 33000 |
| 2,4-DFBA | 1 | T | 3.5697 | 28766  |
| 2 | T | 4.2700 | 34437 |
| 3 | T | 4.5023 | 36311 |
| 1 | S | 4.9750 | 40123 |
| 2 | S | 5.0044 | 40338 |
| 3 | S | 5.5310 | 44607 |

**Table S10** Average molar heat capacity values and smooth molar heat capacity values of complexes **4** and **5.**

|  |  |  |
| --- | --- | --- |
| **T(K)** | **Complex 4****Cp.m(J.K-1.mol-1)** | **Complex 5****Cp.m(J.K-1.mol-1)** |
| **Exp. a** | **Smooth b** | **Exp. a** | **Smooth b** |
| 260.15263.15266.15269.15272.15275.15278.15281.15284.15287.15290.15293.15296.15299.15302.15305.15308.15311.15314.15317.15320.15323.15326.15329.15332.15335.15338.15341.15344.15347.15350.15353.15356.15359.15362.15365.15368.15371.15374.15377.15380.15383.15386.15 | 1151.2678251164.0636691173.7989291187.2785211198.4138361208.5723691224.2985591236.5571731247.4482921262.2790991276.0517251288.2126611301.0410651313.0717631324.2070781335.8796231346.6893431356.4246041367.1040871380.3394831391.898071403.6194541415.1780411425.4993711437.7417061448.7467831459.4425461468.3475421483.3411451490.6181711504.5861541513.6865061525.7172041538.7409641550.918181563.925661574.263271586.0497731599.187491609.8995331620.0580661632.2352811641.889144 | 1152.041162.751174.151186.091198.421211.011223.761236.571249.391262.141274.781287.281299.611311.771323.741335.531347.151358.611369.931381.131392.241403.291414.31425.31436.311447.371458.481469.681480.961492.361503.861515.471527.171538.961550.821562.71574.581586.391598.091609.611620.861631.761642.21 | 1152.3207881166.2324991176.5846411191.1168281202.0241331212.2783051227.5126091239.6935211251.3192711264.9860581278.4242491290.2785941301.7084041315.0159691326.5600771337.6633211349.8442331360.5392691371.3975891385.5542251396.6737971406.4054641417.7536321428.6609371440.0907471450.3939041461.4481631472.1105431488.1122771495.2477441509.4533651519.9524621529.6514721542.3385611553.9643111564.8552871576.9219011590.6213451601.5613061612.0930591625.433281636.8304341648.537825 | 1153.3511651177.021189.331201.831214.451227.131239.811252.461265.031277.511289.871302.111314.211326.171337.991349.691361.271372.741384.111395.411406.641417.8414291440.161451.321462.51473.721484.991496.311507.71519.161530.71542.311553.991565.731577.531589.381601.251613.131624.991636.81648.55 |

a:Average molar heat capacity value.

b:smooth molar heat capacity value.

**Table 11** Thermodynamic function values for complexes **4** and **5.**

|  |  |  |
| --- | --- | --- |
| **T(K)** | **HT-H298.15/(KJ·mol-1)** | **ST-S298.15/(J·mol-1·K-1)** |
| **Complex4** | **Complex 5** | **Complex 4** | **Complex 5** |
| 260.15263.15266.15269.15272.15275.15278.15281.15284.15287.15290.15293.15296.15299.15302.15305.15308.15311.15314.15317.15320.15323.15326.15329.15332.15335.15338.15341.15344.15347.15350.15353.15356.15359.15362.15365.15368.15371.15374.15377.15380.15383.15386.15 | -46.696-43.224-39.719-36.178-32.602-28.988-25.336-21.645-17.916-14.149-10.344-6.501-2.621.3235.2769.26513.28917.34821.44125.56829.72833.92138.14842.40746.69951.02555.38459.77664.20268.66273.15677.68582.24986.84991.48396.154100.86105.601110.378115.19120.036124.915129.826 | -46.806-43.329-39.816-36.266-32.68-29.055-25.393-21.693-17.954-14.178-10.364-6.513-2.6251.3255.2869.28213.31417.3821.48225.61729.78633.98938.22642.49646.851.13855.50859.91364.35168.82373.32977.86982.44487.05491.69896.378101.093105.843110.629115.451120.308125.201130.129 | -167.29-154.02-140.78-127.55-114.34-101.13-87.93-74.73-61.54-48.35-35.17-21.99-8.824.4317.5830.7243.8456.9570.0483.1196.16109.2122.22135.22148.2161.17174.11187.04199.96212.86225.75238.63251.5264.36277.21290.06302.89315.72328.54341.34354.14366.93379.69 | -167.69-154.4-141.12-127.86-114.61-101.36-88.13-74.89-61.67-48.45-35.24-22.03-8.844.4417.6130.7743.9257.0570.1783.2796.35109.42122.47135.5148.52161.52174.5187.47200.42213.36226.28239.19252.09264.98277.86290.73303.59316.44329.28342.12354.94367.76380.58 |



(a) (b)



 (c) (d)



(e)

**Fig. S1**(a-e) TG-DTG/DSC curves of complexes **1-5** (a-e represent complexes **1-5**, respectively).



 (a) (b)



(c) (d)



(e)

**Fig. S2**(a-e) Three-dimensional infrared maps of the fugitive gases of complexes **1-5** (a-e represent complexes **1-5**, respectively).



(a) (b)



(c) (d)



(e)

**Fig. S3** (a-e) Infrared spectra of fugitive gases of complexes **1-5** at different temperatures (a-e represent complexes **1-5**, respectively).