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Face-driven Octanuclear Cerium(IV) Luminescence Polyhedra:

Synthesis and Luminescent Sensing Natural Saccharides

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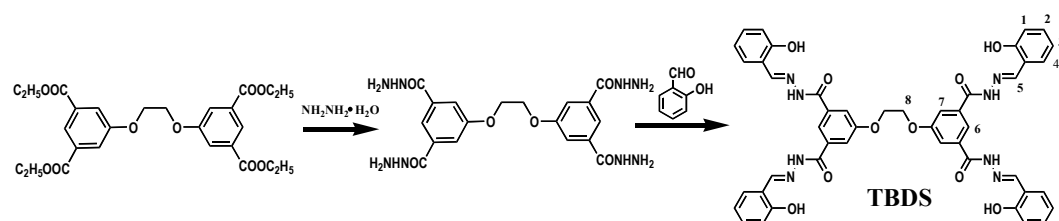
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1. Experimental Section.

1.1 Materials and Methods

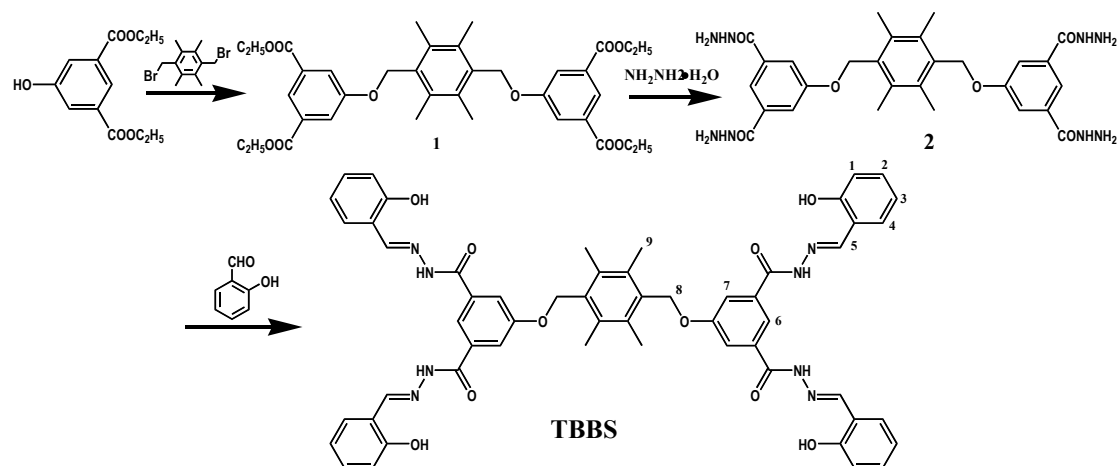
All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The elemental analyses of C, H and N were performed on a Perkin-Elmer 2400 II elemental analyzer. ^1H NMR spectra were measured on a BRUKER 400M spectrometer. ESI mass spectra were carried out on a HPLC-Q-ToF MS spectrometer using methanol as mobile phase. Uv-vis spectra were measured on a HP 8453 spectrometer. The fluorescent spectra were measured on EDINBURGH FS920.

1.2 Preparation



1,2-Bis(3,5-dicarbohydrazidephenoxy) ethane: A mixture solution of 80% hydrazine hydrate (80 mmol, 5.0g) and 1,2-Bis(3,5-dicarbethoxyphenoxy) ethane^{S1} (1 mmol, 0.45 g) in methanol (30mL) was stirred over 12h. The white precipitate was collected by filtration, washed with methanol and dried in vacuum. Yield: 0.398g, 89%. ^1H NMR (DMSO- d_6 , ppm): 9.81 (s, 4 H), 7.90 (s, 2 H), 7.63 (s, 4 H), 4.58 (s, 8 H), 4.45(s, 4 H).

H₈TBDS: 1,2-Bis(3,5-dicarbohydrazide) ethane (4) (1 mmol, 0.45 g) was added to a methanol solution (50 mL) containing salicylaldehyde (4.4 mmol, 0.54 g). After 5 drops of acetic acid was added, the mixture was refluxed for 24h. The white solid was collected by filtration, washed by methanol and dried on vacuum. Yield: 0.72 g, 83%. Anal calc. for $\text{C}_{46}\text{H}_{38}\text{N}_8\text{O}_{10}$: C 67.19, H 4.56, N 11.19%. Found: C 67.01, H 4.67, N 10.89 %. ^1H NMR (DMSO- d_6 , ppm): 12.24(s, 4HNH), 11.20(s, 4H_{OH}), 8.69(s, 4H₅), 8.17(s, 2H₆), 7.81(s, 4H₇), 7.59(d, 4H₄), 7.32(m, 4H₂), 6.94(m, 4H₁, 4H₃), 4.60(m, 4H₈).



1,2-Bis(3,5-dicarbethoxyphenoxy)-2,3,5,6-tetramethylbenzyl^{S2} A mixture of 2.38 g (10.0 mmol) of diethyl 5-hydroxyisophthalate, 1.57 g (4.90 mmol) of 1,4-dibromomethyl-2,3,5,6-tetramethylbenzyl, 2.21 g (16.0 mmol) of K₂CO₃, 0.10 g of 15-crown-5 ether, and 38 mL of THF was stirred under nitrogen at 65°C for 24 h. The mixture was concentrated and 20 mL of 1% aqueous Na₂CO₃ was added at 0°C. The solid was collected, washed with water and ether, and dried under vacuum at 50°C to give 2.55g (90%) of 11 as a white powder. ¹H NMR (CDCl₃): 8.33 (s, 2 H), 7.88 (s, 4 H), 5.20 (s, 4 H), 4.41(m, 8 H), 2.34(s, 12 H), 1.42(m, 12 H).

1,2-Bis(3,5-dicarbohydrazidephenoxy) benzyl: A mixture solution of 80% hydrazine hydrate (80 mmol, 5.006g) and 1,2-Bis(3,5-dicarbethoxyphenoxy)-2,3,5,6-tetramethylbenzene (1 mmol, 0.446 g) in methanol (30mL) was stirred over 12h. The white precipitate was collected by filtration, washed with methanol and dried in vacuum. Yield: 0.398g, 89%. ¹H NMR (DMSO-d₆, ppm): 9.66(s, 4 H), 7.89 (s, 2 H), 7.59 (s, 4 H), 5.21 (s, 4H), 4.47(m, 8 H), 2.29(s, 12 H).

H₈TBBS: Compound 2 (1 mmol, 0.579g) was added to a methanol solution (50 mL) containing salicylaldehyde (4.4 mmol, 0.537g). After 5 drops of acetic acid was added, the mixture was heated at boiling temperature under magnetic stirring for 10h. The white solid was collected by filtration, washed with methanol, and dried in vacuum. Yield: 0.79g, 79%. Anal calc. for C₅₆H₅₀N₈O₁₀: C, 62.41; H, 4.73, N, 14.09%. Found C, 61.88; H, 5.01, N, 13.67%. ¹H NMR (DMSO-d₆, ppm): 12.24(s, 4H_{NH}), 11.20(s, 4H_{OH}), 8.70(s, 4H₅), 8.16(s, 2H₆), 7.85(s, 4H₇), 7.59(d, 4H₄), 7.32(m, 4H₂), 6.94(m, 4H₁, 4H₃), 5.33(m, 4H₈), 2.34(s, 12H₉).

Ce-TBDS: A solution of Ce(NO₃)₃·6H₂O (16.8 mg, 0.04 mmol), H₈TBDS (13.6 mg, 0.03mmol) and KOH (6.8 mg, 0.12 mmol) in CH₃OH/DMF (v:v = 1:7, 8 mL) was stirred for 2h. Then the solution was left for two weeks at room temperature to give X-ray quality black block crystals. Anal calc. for [Ce₈·C₂₇₆H₁₉₆N₄₈O₆₀·27(C₃H₇NO)·CH₃OH·5(H₂O)]: H 4.81, C 51.42, N 12.56 %. Found: H 4.70, C 51.83, N 12.35 %. Yield: 65%.

Ce-TBBS: A solution of Ce(NO₃)₃·6H₂O (16.8 mg, 0.04 mmol), H₈TBBS (13.6 mg, 0.03mmol) and KOH (6.8 mg, 0.12 mmol) in CH₃OH/DMF (v:v = 1:7, 8 mL) was stirred for 2h. Then the solution was left for two weeks at room temperature to give X-ray quality black block crystals. Anal calc. for [Ce₈·C₃₃₆H₂₆₈N₄₈O₆₀·14(C₃H₇NO)·2(CH₃OH)·4(H₂O)]: H 4.68, C 55.53, N 10.57%. Found: H 4.44, C 56.10, N 10.31%. Yield: 50 %.

Reference

- S1. J. P. Collman, J. I. Brauman, J. P. Fitzgerald, P. D. Hampton, Y. Naruta, J. W. Sparapany and J. A. Ibers, *J. Am. Chem. Soc.*, 1988, **110**, 3477-3486.
- S2. Y. Pan and W. T. Ford, *J. Org. Chem.*, 1999, **64**, 8588-8593.
- S3. M. Mazik and A. König, *Eur. J. Org. Chem.*, 2007, 3271–3276.

2. **Figure S1.1** ^1H NMR of ligand **TBDS** in d^6 DMSO

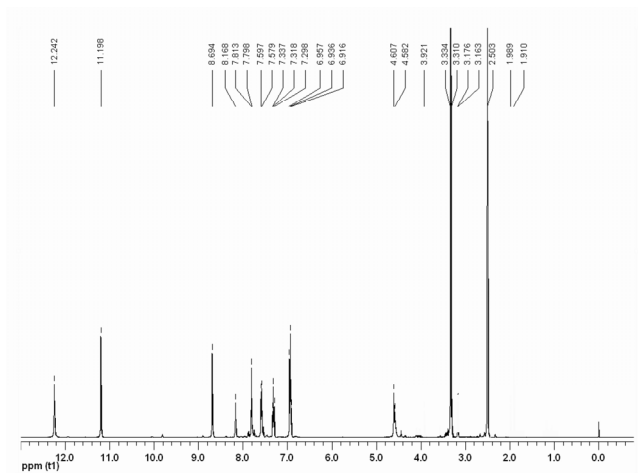
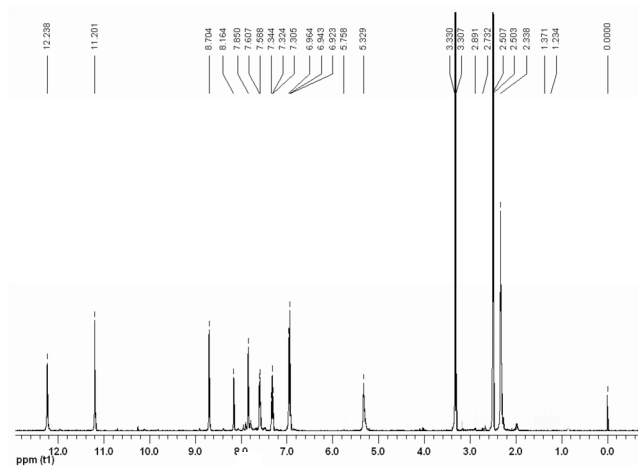


Figure S1.2 ^1H NMR of ligand **TBBS** in d^6 DMSO



3. Crystallography:

Intensities of the complexes were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo-K α ($\lambda = 0.71073 \text{ \AA}$) using the SMART and SAINT programs. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL *version* 5.1.

Crystal data of **Ce-TBDS**: $C_{358}H_{399}Ce_8N_{75}O_{93}$, $M = 8361.48$, Triclinic, space group $P-1$, black block, $a = 21.724(1) \text{ \AA}$, $b = 23.003(1) \text{ \AA}$, $c = 26.050(1) \text{ \AA}$, $\alpha = 78.508(3)^\circ$, $\beta = 85.923(3)^\circ$, $\gamma = 85.565(3)^\circ$, $V = 12698(1) \text{ \AA}^3$, $Z = 1$, $D_c = 1.093 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 0.769 \text{ mm}^{-1}$, $T = 180(2) \text{ K}$. 43935 unique reflections [$R_{\text{int}} = 0.1283$]. Final RI [with $I > 2\sigma(I)$] = 0.0768, $wR2$ (all data) = 0.2045 for $2\theta = 50^\circ$.

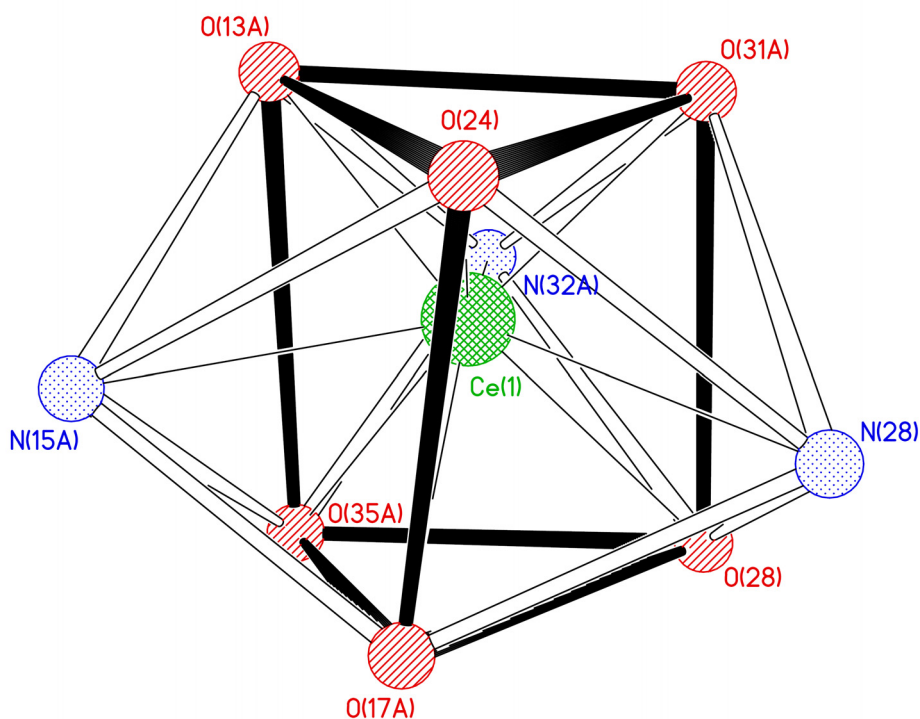
Crystal data of **Ce-TBBS**: $C_{380}H_{382}Ce_8N_{62}O_{80}$, $M = 8218.44$, Triclinic, space group $P-1$, black block, $a = 27.928(3) \text{ \AA}$, $b = 29.218(3) \text{ \AA}$, $c = 31.579(3) \text{ \AA}$, $\alpha = 91.857(6)^\circ$, $\beta = 97.731(6)^\circ$, $\gamma = 95.082(6)^\circ$, $V = 25408(5) \text{ \AA}^3$, $Z = 2$, $D_c = 1.074 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 0.765 \text{ mm}^{-1}$, $T = 180(2) \text{ K}$. 66258 unique reflections [$R_{\text{int}} = 0.2098$]. Final RI [with $I > 2\sigma(I)$] = 0.1189, $wR2$ (all data) = 0.3634 for $2\theta = 45^\circ$.

In the structural refinement of **Ce-TBDS**, except the solvent molecules, the skeleton non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms, whereas no hydrogen atoms corresponding to the solvent molecules were added and refined. To assist the stability of refinements, several restrains were applied: Several solvent DMF molecules were disordered with the *s.o.f.* being fixed at suitable value. Some of the solvent DMF molecules were restrained as idealized geometry. Thermal parameters on adjacent atoms in the solvent molecules were restrained to be similar. In the checkcif file, the short D...A distance is due to the partially occupancy of the solvent molecules.

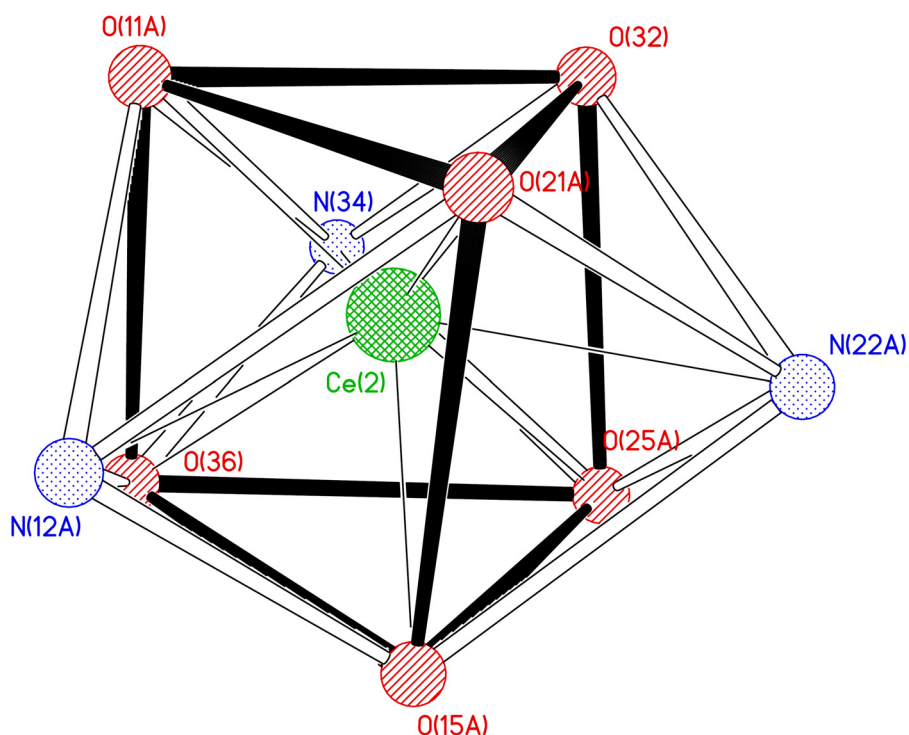
In the structural refinement of **Ce-TBBS**, except the solvent molecules, the skeleton non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbone and the solvent DMF molecules were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. To assist the stability of refinements, several restrains were applied: (1) One of the six Ce atoms was disordered into two parts with their *s.o.f.* being fixed at 0.25 and 0.75, respectively and refined isotropically. Four of the twenty four benzene rings in the salicylalzone groups were disordered into two parts with the *s.o.f.* being fixed at

suitable value. For all benzene rings in the salicylalzone groups, the geometrical constraints of idealized regular polygons were used, the C–C bond distance of the phenyl ring being 1.39 Å and the diagonal C–C distance of the phenyl ring being 2.78 Å. (2) Several solvent DMF molecules were disordered with the *s.o.f.* being fixed at suitable value. Many of the solvent DMF molecules were restrained as idealized geometry. Thermal parameters on adjacent atoms in some of the DMF solvent molecules were restrained to be similar.

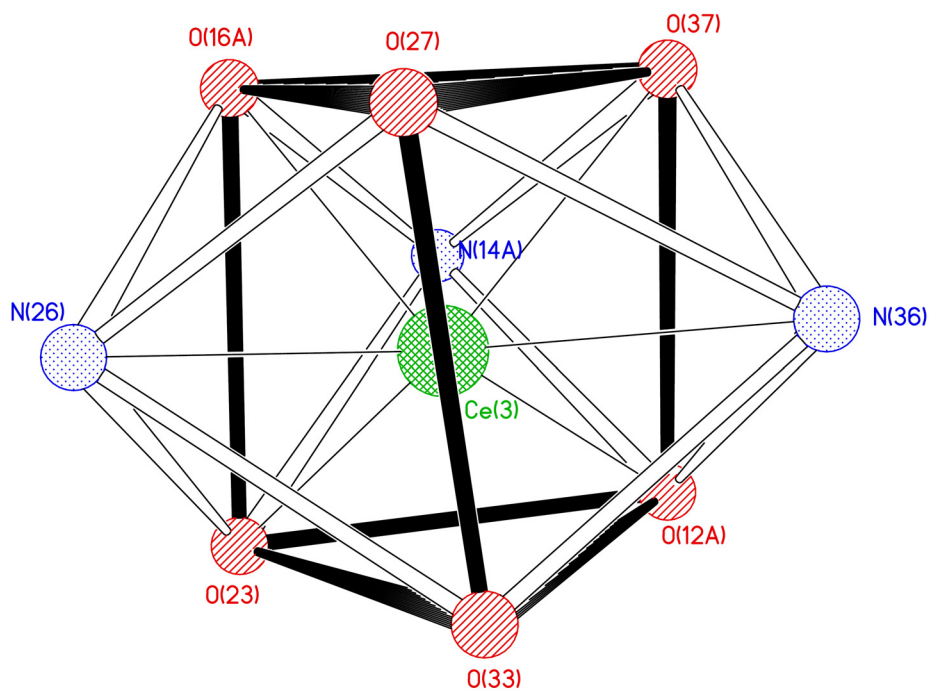
4. Figure S2 The coordination configuration of the Ce(1) centre in **Ce-TBDS**. The bond length (Å) and angle (°) of the Ce(1) centre: Ce(1)–O(13A) 2.178(7), Ce(1)–O(24) 2.187(7), Ce(1)–O(31A) 2.221(8), Ce(1)–O(17) 2.340(6), Ce(1)–O28 2.456(7), Ce(1)–O(35A) 2.457(7), Ce(1)–N(15A) 2.595(8), Ce(1)–N(32A) 2.652(9), Ce(1)–N(28) 2.685(8); O(13A)–Ce(1)–O(24) 87.4(3), O(13A)–Ce(1)–O(31A) 81.7(3), O(24)–Ce(1)–O(31A) 87.8(3), O(13A)–Ce(1)–O(17) 132.2(2), O(24)–Ce(1)–O(17) 83.1(2), O(31A)–Ce(1)–O(17) 144.0(2), O(13A)–Ce(1)–O28 138.6(2), O(24)–Ce(1)–O28 129.9(2), O(31A)–Ce(1)–O28 82.4(3), O(17)–Ce(1)–O28 77.2(2), O(13A)–Ce(1)–O(35A) 90.1(2), O(24)–Ce(1)–O(35A) 142.9(2), O(31A)–Ce(1)–O(35A) 128.4(2), O(17)–Ce(1)–O(35A) 71.5(2), O28–Ce(1)–O(35A) 70.8(2), O(13A)–Ce(1)–N(15A) 69.3(3), O(24)–Ce(1)–N(15A) 75.4(2), O(31A)–Ce(1)–N(15A) 146.8(3), O(17)–Ce(1)–N(15A) 63.0(2), O28–Ce(1)–N(15A) 130.2(2), O(35A)–Ce(1)–N(15A) 69.2(2), O(13A)–Ce(1)–N(32A) 69.3(3), O(24)–Ce(1)–N(32A) 148.0(3), O(31A)–Ce(1)–N(32A) 68.0(3), O(17)–Ce(1)–N(32A) 128.8(3), O28–Ce(1)–N(32A) 69.2(3), O(35A)–Ce(1)–N(32A) 61.6(3), N(15A)–Ce(1)–N(32A) 113.7(3), O(13A)–Ce(1)–N(28) 148.3(3), O(24)–Ce(1)–N(28) 68.6(3), O(31A)–Ce(1)–N(28) 77.1(3), O(17)–Ce(1)–N(28) 67.1(2), O28–Ce(1)–N(28) 61.3(2), O(35A)–Ce(1)–N(28) 121.5(2), N(15A)–Ce(1)–N(28) 120.6(2), N(32A)–Ce(1)–N(28) 122.0(3). Symmetry code A: -x, -y, 1-z.



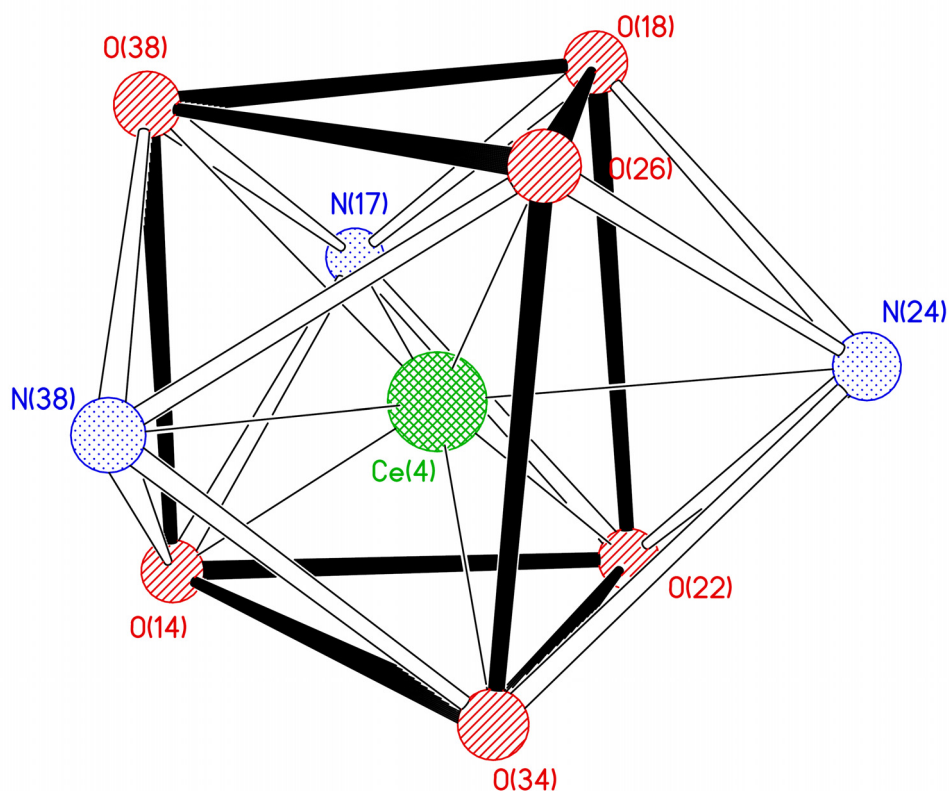
5. Figure S3 The coordination configuration of the Ce(2) centre in **Ce-TBDS**. The bond length (Å) and angle (°) of the Ce(2) centre: Ce(2)–O(21A) 2.162(7), Ce(2)–O(11A) 2.200(7), Ce(2)–O(32) 2.214(7), Ce(2)–O(15A) 2.316(6), Ce(2)–O(36) 2.475(7), Ce(2)–O(25A) 2.489(6), Ce(2)–N(12A) 2.601(8), Ce(2)–N(22A) 2.641(9), Ce(2)–N(34) 2.736(9); O(21A)–Ce(2)–O(11A) 82.2(3), O(21A)–Ce(2)–O(32) 88.3(3), O(11A)–Ce(2)–O(32) 87.6(3), O(21A)–Ce(2)–O(15A) 92.1(2), O(11A)–Ce(2)–O(15A) 132.0(2), O(32)–Ce(2)–O(15A) 140.1(3), O(21A)–Ce(2)–O(36) 141.1(2), O(11A)–Ce(2)–O(36) 80.2(2), O(32)–Ce(2)–O(36) 124.9(3), O(15A)–Ce(2)–O(36) 75.1(2), O(21A)–Ce(2)–O(25A) 128.3(2), O(11A)–Ce(2)–O(25A) 145.0(2), O(32)–Ce(2)–O(25A) 77.8(2), O(15A)–Ce(2)–O(25A) 70.8(2), O(36)–Ce(2)–O(25A) 82.5(2), O(21A)–Ce(2)–N(12A) 74.8(3), O(11A)–Ce(2)–N(12A) 70.8(3), O(32)–Ce(2)–N(12A) 154.0(3), O(15A)–Ce(2)–N(12A) 61.8(2), O(36)–Ce(2)–N(12A) 66.8(2), O(25A)–Ce(2)–N(12A) 128.2(2), O(21A)–Ce(2)–N(22A) 67.6(3), O(11A)–Ce(2)–N(22A) 142.1(2), O(32)–Ce(2)–N(22A) 69.8(3), O(15A)–Ce(2)–N(22A) 73.6(2), O(36)–Ce(2)–N(22A) 137.7(2), O(25A)–Ce(2)–N(22A) 60.8(2), N(12A)–Ce(2)–N(22A) 119.2(3), O(21A)–Ce(2)–N(34) 149.5(3), O(11A)–Ce(2)–N(34) 80.6(3), O(32)–Ce(2)–N(34) 66.0(3), O(15A)–Ce(2)–N(34) 118.0(2), O(36)–Ce(2)–N(34) 59.1(2), O(25A)–Ce(2)–N(34) 64.3(2), N(12A)–Ce(2)–N(34) 121.9(3), N(22A)–Ce(2)–N(34) 114.5(3). Symmetry code A: -x, -y, 1-z.



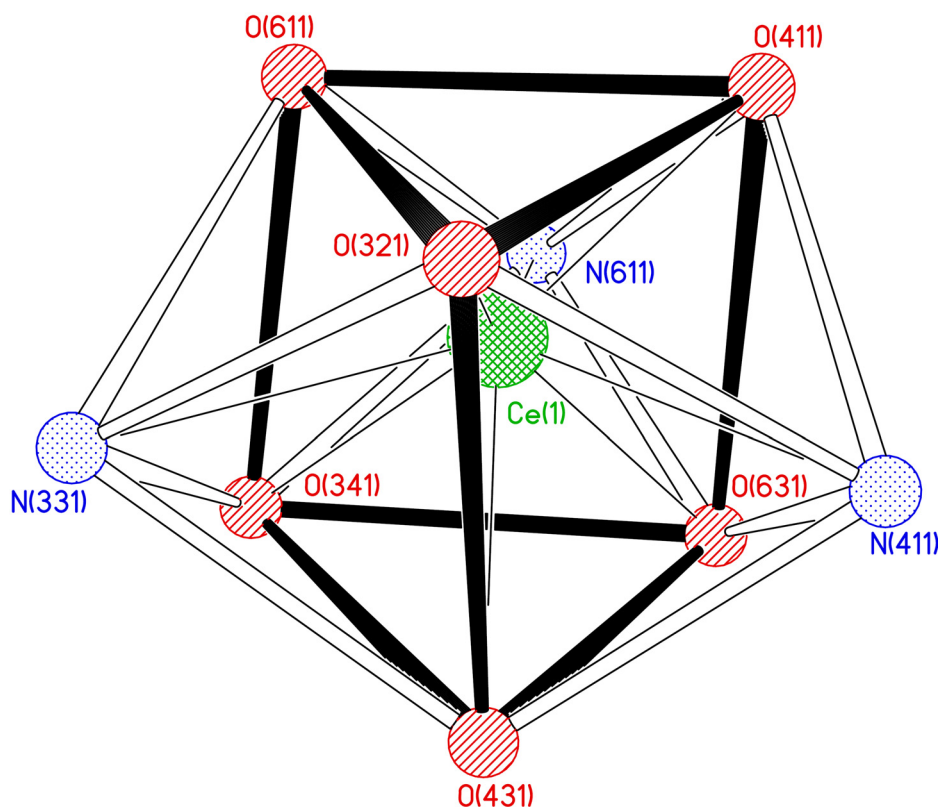
6. Figure S4 The coordination configuration of the Ce(3) centre in **Ce-TBDS**. The bond length (Å) and angle (°) of the Ce(3) centre: Ce(3)–O(33) 2.211 (7), Ce(3)–O(23) 2.214(7), Ce(3)–O(12A) 2.223(7), Ce(3)–O(27) 2.318(6), Ce(3)–O(16A) 2.440(6), Ce(3)–O(37) 2.501(6), Ce(3)–N(26) 2.567(8), Ce(3)–N(36) 2.663(8), Ce(3)–N(14A) 2.673(8); O(33)–Ce(3)–O(23) 85.3(3), O(33)–Ce(3)–O(12A) 86.7(2), O(23)–Ce(3)–O(12A) 86.1(2), O(33)–Ce(3)–O(27) 88.1(2), O(23)–Ce(3)–O(27) 132.6(2), O(12A)–Ce(3)–O(27) 140.3(2), O(33)–Ce(3)–O(16A) 144.5(2), O(23)–Ce(3)–O(16A) 86.4(2), O(12A)–Ce(3)–O(16A) 127.0(2), O(27)–Ce(3)–O(16A) 72.7(2), O(33)–Ce(3)–O(37) 129.4(2), O(23)–Ce(3)–O(37) 140.4(2), O(12A)–Ce(3)–O(37) 78.7(2), O(27)–Ce(3)–O(37) 74.5(2), O(16A)–Ce(3)–O(37) 74.7(2), O(33)–Ce(3)–N(26) 76.4(3), O(23)–Ce(3)–N(26) 70.0(3), O(12A)–Ce(3)–N(26) 151.5(3), O(27)–Ce(3)–N(26) 62.9(3), O(16A)–Ce(3)–N(26) 68.4(2), O(37)–Ce(3)–N(26) 129.8(2), O(33)–Ce(3)–N(36) 68.6(3), O(23)–Ce(3)–N(36) 145.6(3), O(12A)–Ce(3)–N(36) 71.0(3), O(27)–Ce(3)–N(36) 70.5(3), O(16A)–Ce(3)–N(36) 127.8(3), O(37)–Ce(3)–N(36) 60.8(3), N(26)–Ce(3)–N(36) 121.6(3), O(33)–Ce(3)–N(14A) 147.2(3), O(23)–Ce(3)–N(14A) 73.6(3), O(12A)–Ce(3)–N(14A) 67.4(3), O(27)–Ce(3)–N(14A) 124.6(3), O(16A)–Ce(3)–N(14A) 60.2(3), O(37)–Ce(3)–N(14A) 66.8(2), N(26)–Ce(3)–N(14A) 117.4(3), N(36)–Ce(3)–N(14A) 117.4(3). Symmetry code A: -x, -y, 1-z.



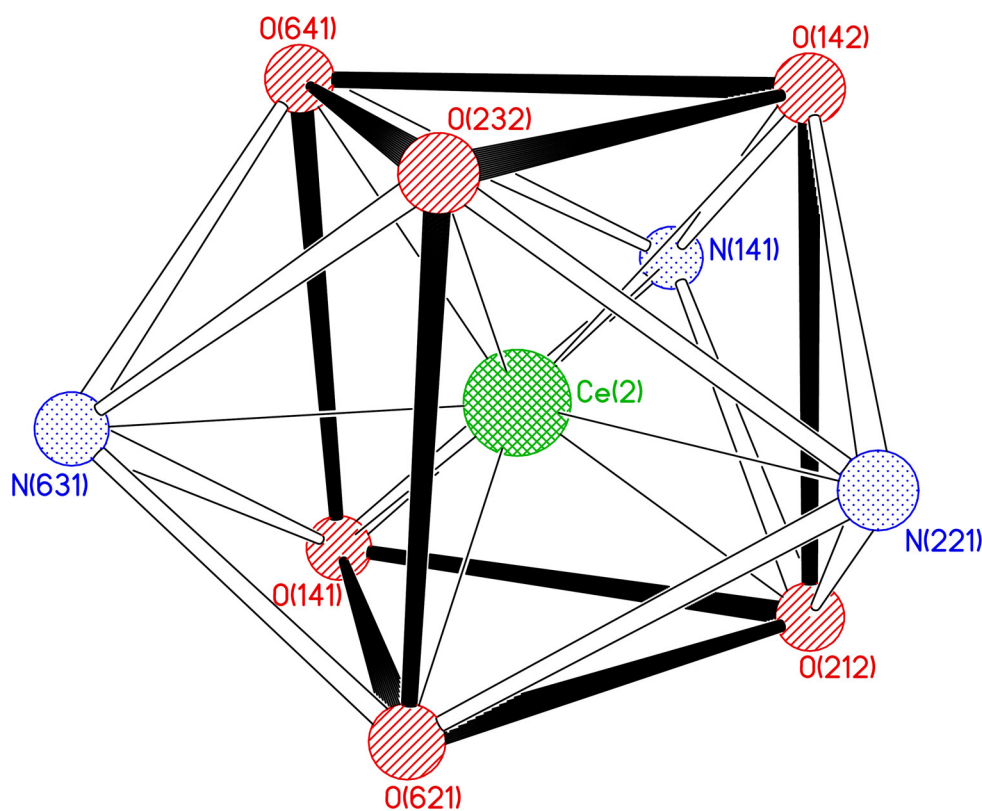
7. Figure S5 The coordination configuration of the Ce(4) centre in **Ce-TBDS**. The bond length (Å) and angle (°) of the Ce(4) centre: Ce(4)–O(22) 2.191(7), Ce(4)–O(34) 2.206(7), Ce(4)–O(14) 2.229(7), Ce(4)–O(26) 2.373(7), Ce(4)–O(18) 2.443(6), Ce(4)–O(38) 2.484(7), Ce(4)–N(24) 2.593(9), Ce(4)–N(38) 2.640(9), Ce(4)–N(17) 2.657(8); O(22)–Ce(4)–O(34) 84.3(3), O(22)–Ce(4)–O(14) 84.9(3), O(34)–Ce(4)–O(14) 87.3(3), O(22)–Ce(4)–O(26) 130.9(2), O(34)–Ce(4)–O(26) 87.4(2), O(14)–Ce(4)–O(26) 142.9(2), O(22)–Ce(4)–O(18) 89.9(2), O(34)–Ce(4)–O(18) 143.8(2), O(14)–Ce(4)–O(18) 127.8(2), O(26)–Ce(4)–O(18) 69.8(2), O(22)–Ce(4)–O(38) 142.7(2), O(34)–Ce(4)–O(38) 129.4(3), O(14)–Ce(4)–O(38) 81.9(2), O(26)–Ce(4)–O(38) 73.5(2), O(18)–Ce(4)–O(38) 71.7(2), O(22)–Ce(4)–N(24) 69.0(3), O(34)–Ce(4)–N(24) 78.2(3), O(14)–Ce(4)–N(24) 151.1(3), O(26)–Ce(4)–N(24) 62.0(3), O(18)–Ce(4)–N(24) 66.5(2), O(38)–Ce(4)–N(24) 126.6(3), O(22)–Ce(4)–N(38) 148.1(3), O(34)–Ce(4)–N(38) 68.4(3), O(14)–Ce(4)–N(38) 78.0(3), O(26)–Ce(4)–N(38) 66.1(2), O(18)–Ce(4)–N(38) 121.9(2), O(38)–Ce(4)–N(38) 61.3(3), N(24)–Ce(4)–N(38) 118.2(3), O(22)–Ce(4)–N(17) 72.2(2), O(34)–Ce(4)–N(17) 146.8(3), O(14)–Ce(4)–N(17) 67.8(3), O(26)–Ce(4)–N(17) 125.7(2), O(18)–Ce(4)–N(17) 61.2(2), O(38)–Ce(4)–N(17) 70.5(2), N(24)–Ce(4)–N(17) 113.1(3), N(38)–Ce(4)–N(17) 123.6(3). Symmetry code A: -x, -y, 1-z.



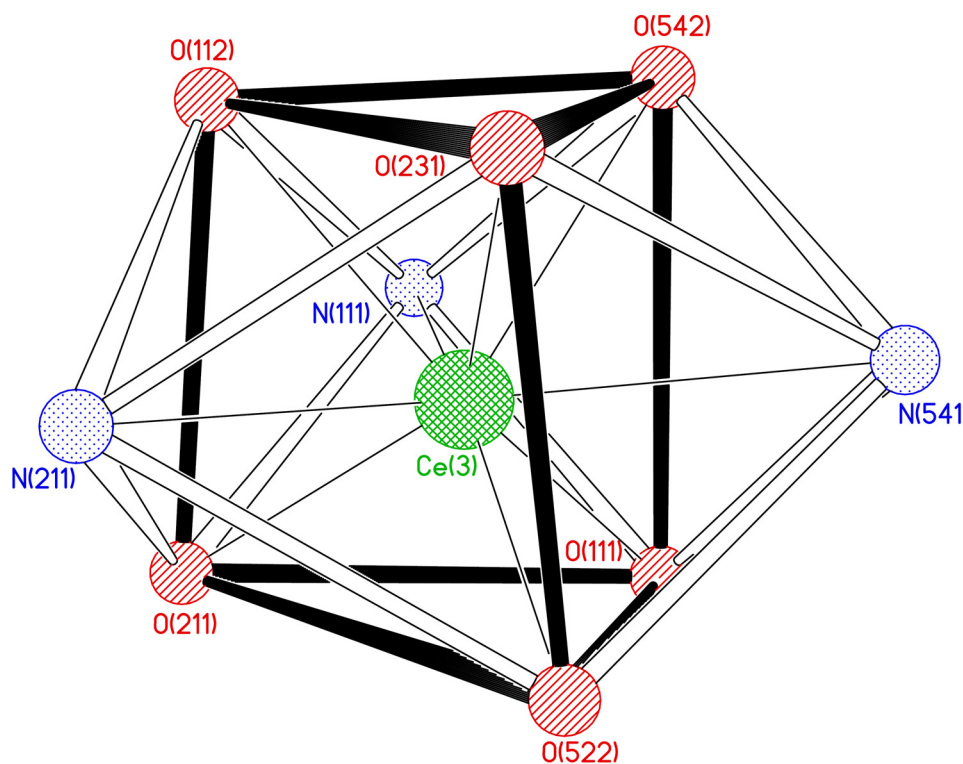
8. Figure S6 The coordination configuration of the Ce(1) centre in **Ce-TBBS**. The bond length (Å) and angle (°) of the Ce(1) centre: Ce(1)–O(611) 2.071(14), Ce(1)–O(411) 2.157(12), Ce(1)–O(321) 2.258(11), Ce(1)–O(631) 2.293(10), Ce(1)–O(341) 2.407(9), Ce(1)–O(431) 2.448(13), Ce(1)–N(611) 2.532(14), Ce(1)–N(411) 2.592(16), Ce(1)–N(331) 2.685(12), O(611)–Ce(1)–O(411) 85.8(5), O(611)–Ce(1)–O(321) 93.6(5), O(411)–Ce(1)–O(321) 84.0(4), O(611)–Ce(1)–O(631) 130.0(4), O(411)–Ce(1)–O(631) 87.6(5), O(321)–Ce(1)–O(631) 134.8(4), O(611)–Ce(1)–O(341) 78.6(4), O(411)–Ce(1)–O(341) 145.5(4), O(321)–Ce(1)–O(341) 127.1(4), O(631)–Ce(1)–O(341) 79.5(4), O(611)–Ce(1)–O(431) 141.3(4), O(411)–Ce(1)–O(431) 130.7(4), O(321)–Ce(1)–O(431) 80.4(4), O(631)–Ce(1)–O(431) 72.1(4), O(341)–Ce(1)–O(431) 75.2(4), O(611)–Ce(1)–N(611) 68.9(5), O(411)–Ce(1)–N(611) 78.7(5), O(321)–Ce(1)–N(611) 156.1(5), O(631)–Ce(1)–N(611) 61.2(5), O(341)–Ce(1)–N(611) 67.0(5), O(431)–Ce(1)–N(611) 123.5(5), O(611)–Ce(1)–N(411) 149.5(5), O(411)–Ce(1)–N(411) 67.2(5), O(321)–Ce(1)–N(411) 70.7(4), O(631)–Ce(1)–N(411) 65.2(4), O(341)–Ce(1)–N(411) 131.8(4), O(431)–Ce(1)–N(411) 63.6(4), N(611)–Ce(1)–N(411) 116.4(5), O(611)–Ce(1)–N(331) 74.6(5), O(411)–Ce(1)–N(331) 143.1(4), O(321)–Ce(1)–N(331) 66.8(4), O(631)–Ce(1)–N(331) 128.9(4), O(341)–Ce(1)–N(331) 60.7(3), O(431)–Ce(1)–N(331) 67.9(4), N(611)–Ce(1)–N(331) 120.5(4), N(411)–Ce(1)–N(331) 119.0(5).



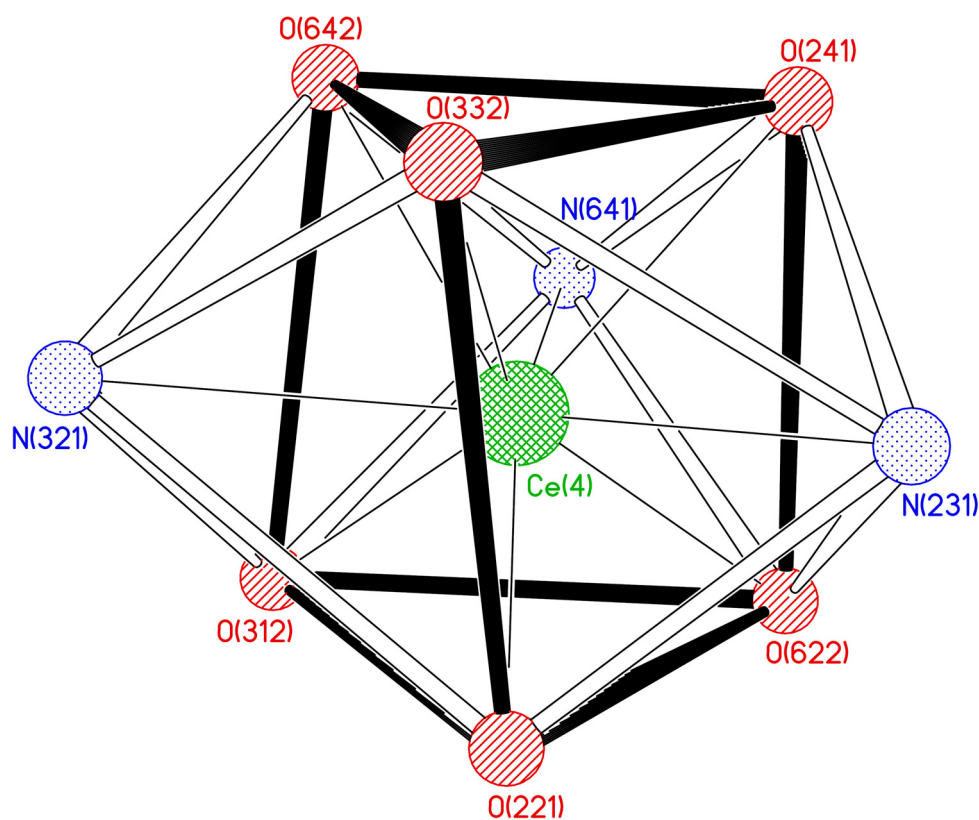
9. Figure S7 The coordination configuration of the Ce(2) centre in **Ce-TBBS**. The bond length (Å) and angle (°) of the Ce(2) centre: Ce(2)–O(621) 2.182(13), Ce(2)–O(212) 2.195(12), Ce(2)–O(141) 2.218(11), Ce(2)–O(641) 2.356(14), Ce(2)–O(142) 2.387(11), Ce(2)–O(232) 2.440(10), Ce(2)–N(631) 2.49(2), Ce(2)–N(141) 2.611(13), Ce(2)–N(221) 2.653(16); O(621)–Ce(2)–O(212) 83.6(5), O(621)–Ce(2)–O(141) 86.7(5), O(212)–Ce(2)–O(141) 85.9(5), O(621)–Ce(2)–O(641) 128.8(5), O(212)–Ce(2)–O(641) 144.8(4), O(141)–Ce(2)–O(641) 83.1(4), O(621)–Ce(2)–O(142) 139.1(5), O(212)–Ce(2)–O(142) 84.8(4), O(141)–Ce(2)–O(142) 131.3(4), O(641)–Ce(2)–O(142) 77.8(4), O(621)–Ce(2)–O(232) 82.8(4), O(212)–Ce(2)–O(232) 129.1(4), O(141)–Ce(2)–O(232) 141.5(4), O(641)–Ce(2)–O(232) 75.3(4), O(142)–Ce(2)–O(232) 74.7(4), O(621)–Ce(2)–N(631) 63.1(6), O(212)–Ce(2)–N(631) 141.3(6), O(141)–Ce(2)–N(631) 73.8(5), O(641)–Ce(2)–N(631) 65.8(5), O(142)–Ce(2)–N(631) 133.2(5), O(232)–Ce(2)–N(631) 68.5(5), O(621)–Ce(2)–N(141) 145.9(4), O(212)–Ce(2)–N(141) 70.4(5), O(141)–Ce(2)–N(141) 70.2(4), O(641)–Ce(2)–N(141) 74.4(4), O(142)–Ce(2)–N(141) 61.6(4), O(232)–Ce(2)–N(141) 130.8(4), N(631)–Ce(2)–N(141) 128.5(5), O(621)–Ce(2)–N(221) 70.9(5), O(212)–Ce(2)–N(221) 66.3(5), O(141)–Ce(2)–N(221) 145.5(5), O(641)–Ce(2)–N(221) 131.4(4), O(142)–Ce(2)–N(221) 68.5(5), O(232)–Ce(2)–N(221) 62.9(4), N(631)–Ce(2)–N(221) 115.4(5), N(141)–Ce(2)–N(221) 115.2(5).



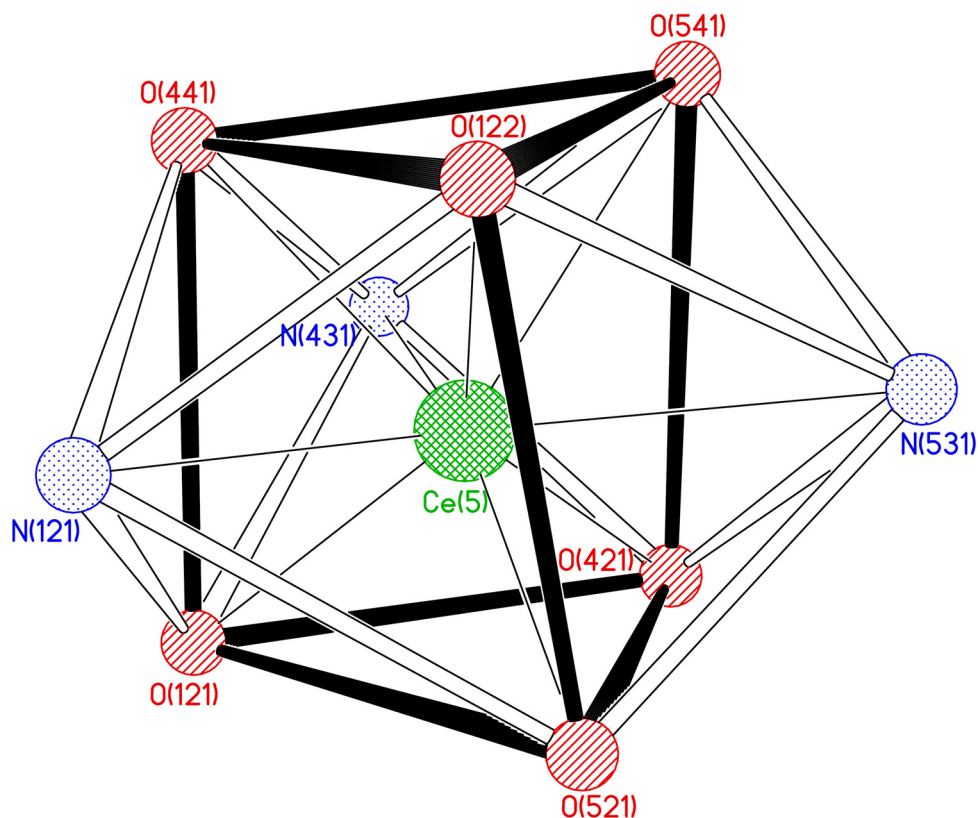
10. Figure S8 The coordination configuration of the Ce(3) centre in **Ce-TBBS**. The bond length (Å) and angle (°) of the Ce(3) centre: Ce(3)–O(111) 2.190(10), Ce(3)–O(522) 2.215(11), Ce(3)–O(211) 2.257(13), Ce(3)–O(231) 2.399(10), Ce(3)–O(542) 2.428(10), Ce(3)–O(112) 2.477(11), Ce(3)–N(541) 2.661(16), Ce(3)–N(111) 2.698(12), Ce(3)–N(211) 2.742(16); O(111)–Ce(3)–O(522) 80.5(4), O(111)–Ce(3)–O(211) 89.2(4), O(522)–Ce(3)–O(211) 92.7(4), O(111)–Ce(3)–O(231) 138.8(4), O(522)–Ce(3)–O(231) 84.0(4), O(211)–Ce(3)–O(231) 129.7(4), O(111)–Ce(3)–O(542) 89.4(4), O(522)–Ce(3)–O(542) 130.1(4), O(211)–Ce(3)–O(542) 136.2(4), O(231)–Ce(3)–O(542) 72.2(3), O(111)–Ce(3)–O(112) 132.5(4), O(522)–Ce(3)–O(112) 144.9(4), O(211)–Ce(3)–O(112) 78.5(4), O(231)–Ce(3)–O(112) 76.4(4), O(542)–Ce(3)–O(112) 70.6(4), O(111)–Ce(3)–N(541) 71.1(5), O(522)–Ce(3)–N(541) 69.5(4), O(211)–Ce(3)–N(541) 155.0(5), O(231)–Ce(3)–N(541) 67.7(5), O(542)–Ce(3)–N(541) 61.0(4), O(112)–Ce(3)–N(541) 126.1(4), O(111)–Ce(3)–N(111) 69.0(4), O(522)–Ce(3)–N(111) 145.8(4), O(211)–Ce(3)–N(111) 72.4(4), O(231)–Ce(3)–N(111) 129.3(4), O(542)–Ce(3)–N(111) 66.3(4), O(112)–Ce(3)–N(111) 63.5(4), N(541)–Ce(3)–N(111) 112.3(4), O(111)–Ce(3)–N(211) 144.5(4), O(522)–Ce(3)–N(211) 76.4(4), O(211)–Ce(3)–N(211) 65.6(4), O(231)–Ce(3)–N(211) 64.8(4), O(542)–Ce(3)–N(211) 126.1(4), O(112)–Ce(3)–N(211) 69.0(3), N(541)–Ce(3)–N(211) 123.3(4), N(111)–Ce(3)–N(211) 121.1(4).



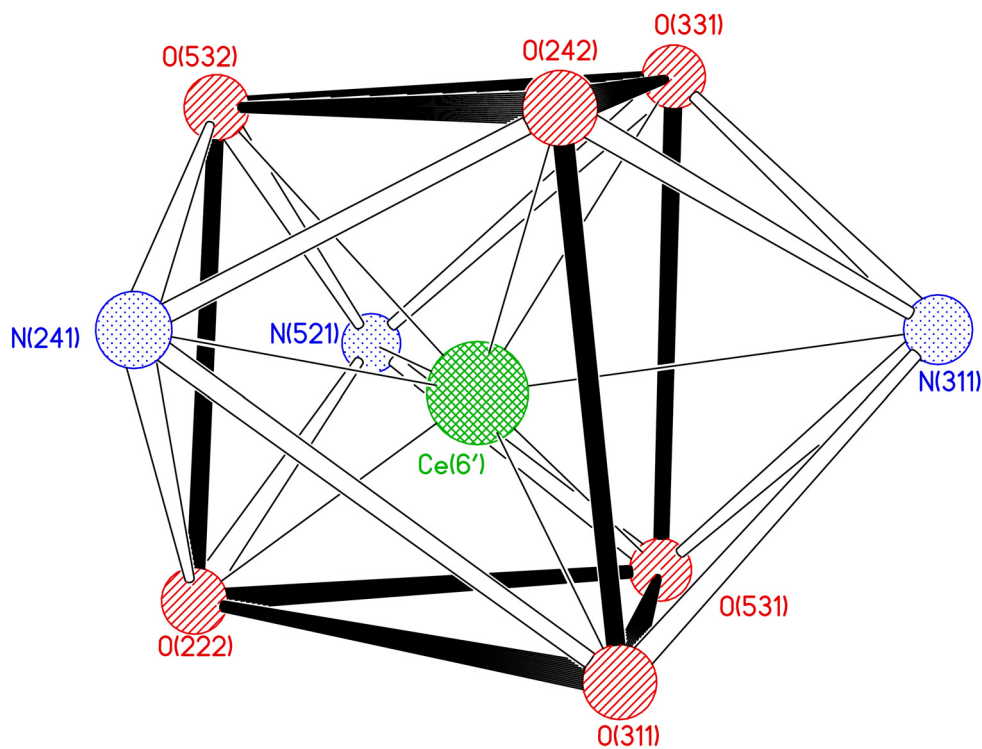
11. Figure S9 The coordination configuration of the Ce(4) centre in **Ce-TBBS**. The bond length (Å) and angle (°) of the Ce(4) centre: Ce(4)–O(221) 2.185(13), Ce(4)–O(312) 2.184(9), Ce(4)–O(622) 2.235(12), Ce(4)–O(642) 2.417(12), Ce(4)–O(241) 2.429(12), Ce(4)–O(332) 2.473(12), Ce(4)–N(231) 2.627(15), Ce(4)–N(641) 2.629(17), Ce(4)–N(321) 2.656(16); O(221)–Ce(4)–O(312) 85.3(4), O(221)–Ce(4)–O(622) 81.9(5), O(312)–Ce(4)–O(622) 90.3(4), O(221)–Ce(4)–O(642) 146.9(5), O(312)–Ce(4)–O(642) 85.3(4), O(622)–Ce(4)–O(642) 129.8(5), O(221)–Ce(4)–O(241) 130.0(4), O(312)–Ce(4)–O(241) 142.1(4), O(622)–Ce(4)–O(241) 83.0(4), O(642)–Ce(4)–O(241) 71.3(4), O(221)–Ce(4)–O(332) 86.9(4), O(312)–Ce(4)–O(332) 127.3(4), O(622)–Ce(4)–O(332) 139.7(4), O(642)–Ce(4)–O(332) 73.9(4), O(241)–Ce(4)–O(332) 75.0(4), O(221)–Ce(4)–N(231) 67.6(4), O(312)–Ce(4)–N(231) 148.8(4), O(622)–Ce(4)–N(231) 71.4(5), O(642)–Ce(4)–N(231) 125.8(3), O(241)–Ce(4)–N(231) 62.4(4), O(332)–Ce(4)–N(231) 68.5(4), O(221)–Ce(4)–N(641) 144.6(4), O(312)–Ce(4)–N(641) 73.4(4), O(622)–Ce(4)–N(641) 70.5(5), O(642)–Ce(4)–N(641) 60.3(4), O(241)–Ce(4)–N(641) 69.2(4), O(332)–Ce(4)–N(641) 128.5(4), N(231)–Ce(4)–N(641) 120.6(5), O(221)–Ce(4)–N(321) 79.1(5), O(312)–Ce(4)–N(321) 68.6(4), O(622)–Ce(4)–N(321) 152.5(4), O(642)–Ce(4)–N(321) 67.9(5), O(241)–Ce(4)–N(321) 124.4(4), O(332)–Ce(4)–N(321) 58.7(4), N(231)–Ce(4)–N(321) 118.1(5), N(641)–Ce(4)–N(321) 116.8(4).



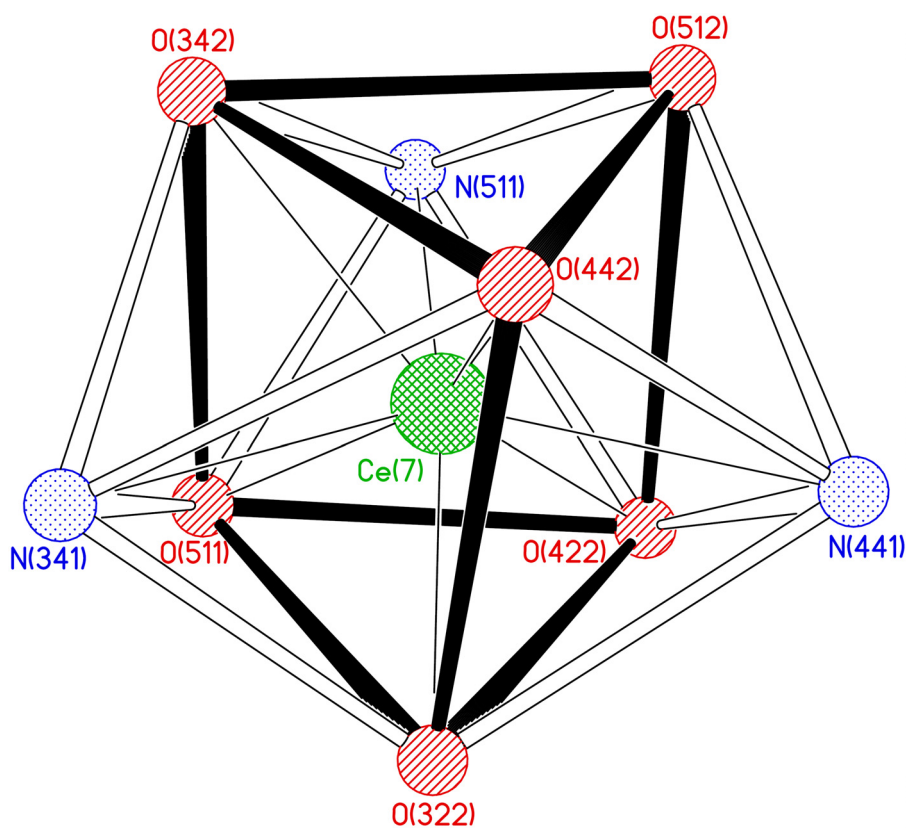
12. Figure S10 The coordination configuration of the Ce(5) centre in **Ce-TBBS**. The bond length (Å) and angle (°) of the Ce(5) centre: Ce(5)–O(421) 2.186(10), Ce(5)–O(521) 2.227(11), Ce(5)–O(121) 2.234(14), Ce(5)–O(122) 2.418(9), Ce(5)–O(441) 2.469(11), Ce(5)–O(541) 2.585(10), Ce(5)–N(121) 2.713(16), Ce(5)–N(431) 2.716(14), Ce(5)–N(531) 2.664(13); O(421)–Ce(5)–O(521) 81.2(5), O(421)–Ce(5)–O(121) 89.5(5), O(521)–Ce(5)–O(121) 85.1(5), O(421)–Ce(5)–O(122) 141.1(4), O(521)–Ce(5)–O(122) 89.1(4), O(121)–Ce(5)–O(122) 127.3(4), O(421)–Ce(5)–O(441) 128.1(5), O(521)–Ce(5)–O(441) 147.5(5), O(121)–Ce(5)–O(441) 81.8(4), O(122)–Ce(5)–O(441) 75.8(4), O(421)–Ce(5)–O(541) 86.1(4), O(521)–Ce(5)–O(541) 127.0(4), O(121)–Ce(5)–O(541) 146.3(5), O(122)–Ce(5)–O(541) 70.0(4), O(441)–Ce(5)–O(541) 74.9(4), O(421)–Ce(5)–N(121) 148.9(5), O(521)–Ce(5)–N(121) 78.8(5), O(121)–Ce(5)–N(121) 65.3(4), O(122)–Ce(5)–N(121) 62.3(4), O(441)–Ce(5)–N(121) 68.6(5), O(541)–Ce(5)–N(121) 125.0(4), O(421)–Ce(5)–N(431) 69.1(5), O(521)–Ce(5)–N(431) 143.3(4), O(121)–Ce(5)–N(431) 74.0(5), O(122)–Ce(5)–N(431) 127.6(4), O(441)–Ce(5)–N(431) 59.3(4), O(541)–Ce(5)–N(431) 73.2(4), N(121)–Ce(5)–N(431) 116.8(6), O(421)–Ce(5)–N(531) 71.9(4), O(521)–Ce(5)–N(531) 68.3(4), O(121)–Ce(5)–N(531) 149.2(4), O(122)–Ce(5)–N(531) 69.5(4), O(441)–Ce(5)–N(531) 129.0(4), O(541)–Ce(5)–N(531) 58.8(4), N(121)–Ce(5)–N(531) 121.0(4), N(431)–Ce(5)–N(531) 118.8(5).



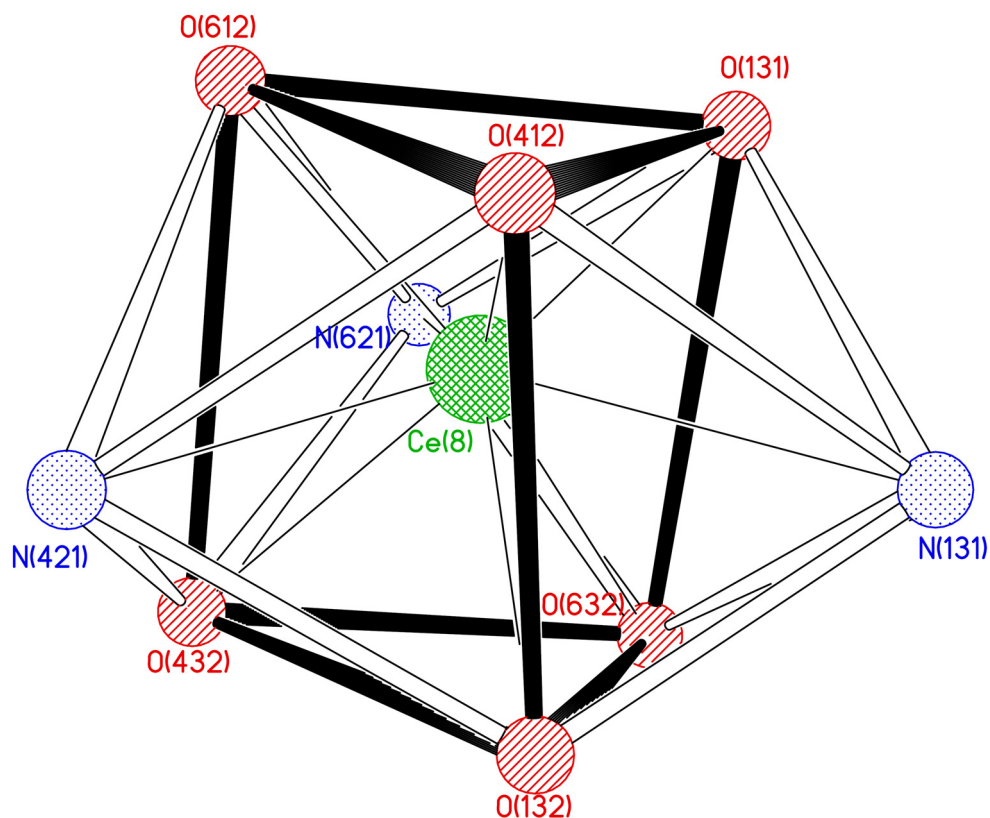
13. Figure S11 The coordination configuration of the Ce(6') centre in **Ce-TBBS**. The bond length (Å) and angle (°) of the Ce(6') centre: Ce(6')–O(311) 1.892(17), Ce(6')–O(222) 2.133(11), Ce(6')–O(242) 2.106(11), Ce(6')–O(531) 2.351(16), Ce(6')–N(241) 2.15(2), Ce(6')–O(532) 2.403(12), Ce(6')–O(331) 2.639(13), Ce(6')–N(311) 2.722(14), Ce(6')–N(521) 2.890(18); O(311)–Ce(6')–O(222) 90.4(5), O(311)–Ce(6')–O(242) 94.2(7), O(222)–Ce(6')–O(242) 136.8(6), O(311)–Ce(6')–O(531) 72.4(8), O(222)–Ce(6')–O(531) 87.4(5), O(242)–Ce(6')–O(531) 134.8(5), O(311)–Ce(6')–N(241) 93.0(8), O(222)–Ce(6')–N(241) 69.9(6), O(242)–Ce(6')–N(241) 67.0(6), O(531)–Ce(6')–N(241) 153.1(6), O(311)–Ce(6')–O(532) 160.4(6), O(222)–Ce(6')–O(532) 80.0(3), O(242)–Ce(6')–O(532) 81.6(3), O(531)–Ce(6')–O(532) 123.7(5), N(241)–Ce(6')–O(532) 67.7(5), O(311)–Ce(6')–O(331) 127.4(5), O(222)–Ce(6')–O(331) 135.4(4), O(242)–Ce(6')–O(331) 70.6(4), O(531)–Ce(6')–O(331) 83.6(4), N(241)–Ce(6')–O(331) 122.5(5), O(532)–Ce(6')–O(331) 69.4(4), O(311)–Ce(6')–N(311) 69.4(4), O(222)–Ce(6')–N(311) 151.3(4), O(242)–Ce(6')–N(311) 67.3(4), O(531)–Ce(6')–N(311) 67.6(4), N(241)–Ce(6')–N(311) 129.1(5), O(532)–Ce(6')–N(311) 125.0(5), O(331)–Ce(6')–N(311) 58.2(5), O(311)–Ce(6')–N(521) 138.2(6), O(222)–Ce(6')–N(521) 67.5(4), O(242)–Ce(6')–N(521) 126.5(4), O(531)–Ce(6')–N(521) 71.6(5), N(241)–Ce(6')–N(521) 110.3(5), O(532)–Ce(6')–N(521) 52.8(5), O(331)–Ce(6')–N(521) 68.2(5), N(311)–Ce(6')–N(521) 114.2(6).



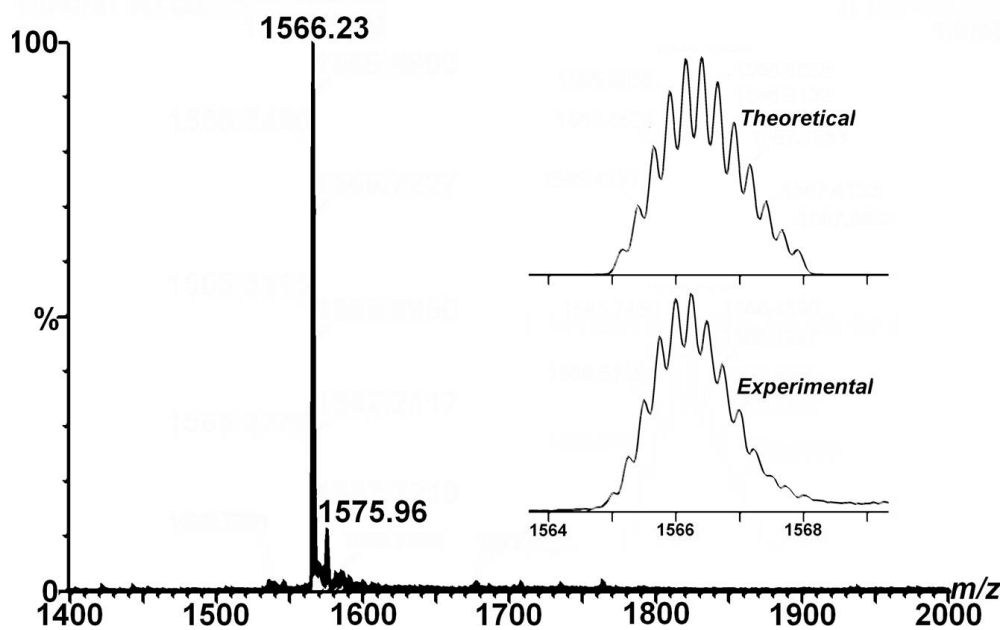
14. Figure S12 The coordination configuration of the Ce(7) centre in **Ce-TBBS**. The bond length (Å) and angle (°) of the Ce(7) centre: Ce(7)–O(511) 2.039(15), Ce(7)–O(322) 2.169(9), Ce(7)–O(442) 2.140(18), Ce(7)–O(422) 2.256(11), Ce(7)–O(342) 2.362(9), Ce(7)–O(512) 2.445(11), Ce(7)–N(341) 2.544(13), Ce(7)–N(441) 2.550(16), Ce(7)–N(511) 2.599(19); O(511)–Ce(7)–O(322) 83.0(4), O(511)–Ce(7)–O(442) 140.8(5), O(322)–Ce(7)–O(442) 85.3(4), O(511)–Ce(7)–O(422) 85.0(5), O(322)–Ce(7)–O(422) 85.3(4), O(442)–Ce(7)–O(422) 132.2(5), O(511)–Ce(7)–O(342) 84.2(4), O(322)–Ce(7)–O(342) 129.7(4), O(442)–Ce(7)–O(342) 72.8(4), O(422)–Ce(7)–O(342) 141.4(4), O(511)–Ce(7)–O(512) 131.7(3), O(322)–Ce(7)–O(512) 142.2(3), O(442)–Ce(7)–O(512) 73.5(4), O(422)–Ce(7)–O(512) 83.8(3), O(342)–Ce(7)–O(512) 76.3(3), O(511)–Ce(7)–N(341) 66.6(5), O(322)–Ce(7)–N(341) 66.7(4), O(442)–Ce(7)–N(341) 74.7(5), O(422)–Ce(7)–N(341) 141.6(4), O(342)–Ce(7)–N(341) 63.5(3), O(512)–Ce(7)–N(341) 134.3(3), O(511)–Ce(7)–N(441) 145.1(4), O(322)–Ce(7)–N(441) 73.9(4), O(442)–Ce(7)–N(441) 65.0(4), O(422)–Ce(7)–N(441) 67.6(5), O(342)–Ce(7)–N(441) 130.7(4), O(512)–Ce(7)–N(441) 68.4(3), N(341)–Ce(7)–N(441) 123.7(4), O(511)–Ce(7)–N(511) 71.3(4), O(322)–Ce(7)–N(511) 146.2(4), O(442)–Ce(7)–N(511) 125.9(4), O(422)–Ce(7)–N(511) 71.3(4), O(342)–Ce(7)–N(511) 70.1(4), O(512)–Ce(7)–N(511) 60.6(5), N(341)–Ce(7)–N(511) 118.9(5), N(441)–Ce(7)–N(511) 116.3(5).



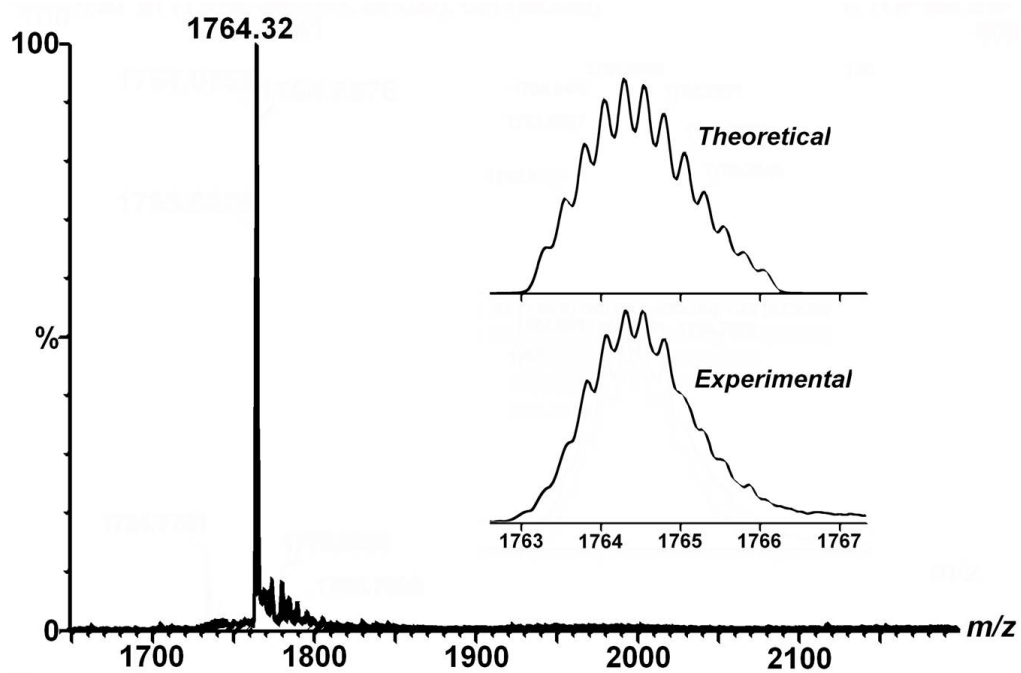
15. Figure S13 The coordination configuration of the Ce(8) centre in **Ce-TBBS**. The bond length (Å) and angle (°) of the Ce(8) centre: Ce(8)–O(412) 2.119(12), Ce(8)–O(131) 2.188(10), Ce(8)–O(612) 2.211(12), Ce(8)–O(432) 2.346(9), Ce(8)–O(132) 2.369(11), Ce(8)–O(632) 2.570(12), Ce(8)–N(421) 2.655(18), Ce(8)–N(131) 2.633(13), Ce(8)–N(621) 2.688(17); O(412)–Ce(8)–O(131) 89.3(5), O(412)–Ce(8)–O(612) 85.8(5), O(131)–Ce(8)–O(612) 84.0(4), O(412)–Ce(8)–O(432) 128.0(5), O(131)–Ce(8)–O(432) 140.2(4), O(612)–Ce(8)–O(432) 85.4(4), O(412)–Ce(8)–O(132) 81.2(4), O(131)–Ce(8)–O(132) 130.3(4), O(612)–Ce(8)–O(132) 142.7(4), O(432)–Ce(8)–O(132) 75.7(3), O(412)–Ce(8)–O(632) 144.8(4), O(131)–Ce(8)–O(632) 85.3(4), O(612)–Ce(8)–O(632) 128.0(4), O(432)–Ce(8)–O(632) 71.6(3), O(132)–Ce(8)–O(632) 76.1(4), O(412)–Ce(8)–N(421) 70.5(5), O(131)–Ce(8)–N(421) 152.4(5), O(612)–Ce(8)–N(421) 76.2(5), O(432)–Ce(8)–N(421) 57.7(5), O(132)–Ce(8)–N(421) 66.6(4), O(632)–Ce(8)–N(421) 122.1(4), O(412)–Ce(8)–N(131) 73.1(5), O(131)–Ce(8)–N(131) 69.5(4), O(612)–Ce(8)–N(131) 145.9(4), O(432)–Ce(8)–N(131) 128.7(4), O(132)–Ce(8)–N(131) 61.0(4), O(632)–Ce(8)–N(131) 72.4(4), N(421)–Ce(8)–N(131) 119.1(5), O(412)–Ce(8)–N(621) 148.8(4), O(131)–Ce(8)–N(621) 71.4(4), O(612)–Ce(8)–N(621) 68.5(5), O(432)–Ce(8)–N(621) 69.1(4), O(132)–Ce(8)–N(621) 130.0(4), O(632)–Ce(8)–N(621) 59.8(4), N(421)–Ce(8)–N(621) 117.2(4), N(131)–Ce(8)–N(621) 119.3(5).



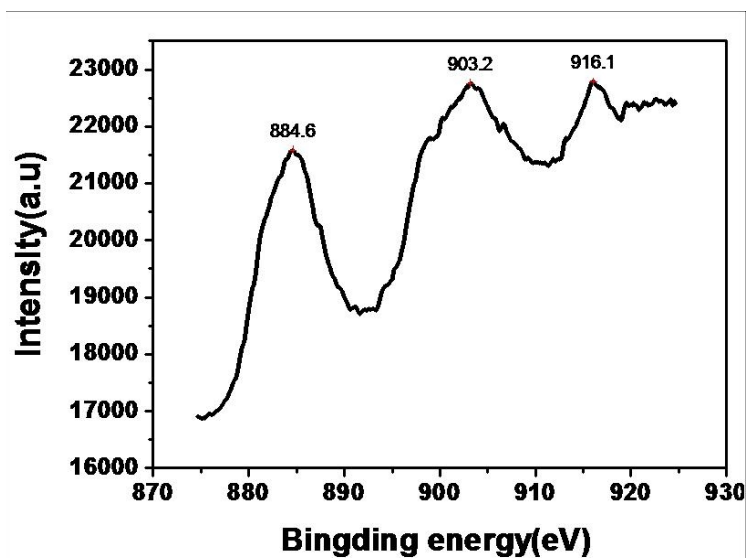
16. Figure S14 ESI-MS spectra of Ce-TBDS (50 μM), the peak 1566.23 and 1575.96 are assigned to the species $[\text{Ce}_8(\text{H}_2\text{TBDS})_2(\text{H}_3\text{TBDS})_4]^{4-}$ and $[\text{Ce}_8(\text{H}_2\text{TBDS})_3(\text{H}_3\text{TBDS})_3\text{K}]^{4-}$.



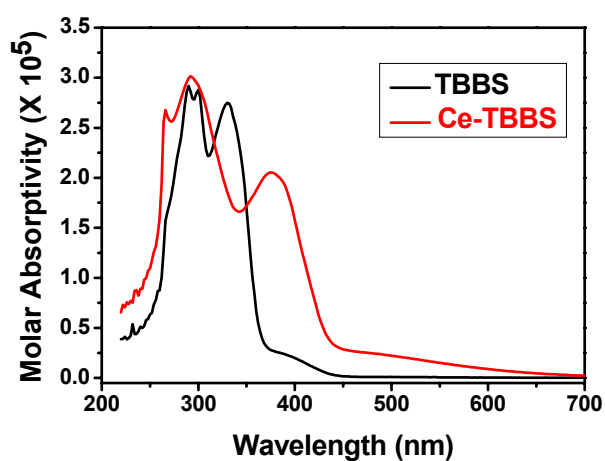
17. **Figure S15** ESI-MS spectra of Ce-TBBS (50 μ M), the peak 1764.32 is assigned to the specie $[\text{Ce}_8(\text{H}_2\text{TBBS})_3(\text{H}_3\text{TBBS})_3]^+$.



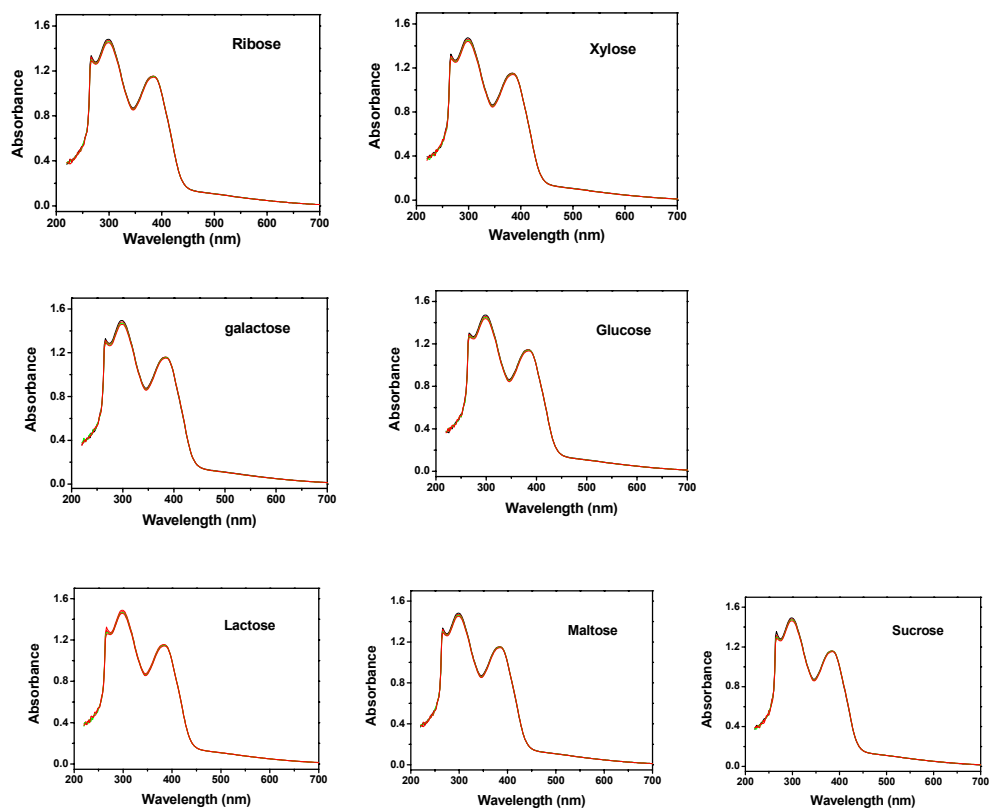
18. Figure S16 XPS spectrum of Ce 3d from surface and near surface region of Ce-TBDS.



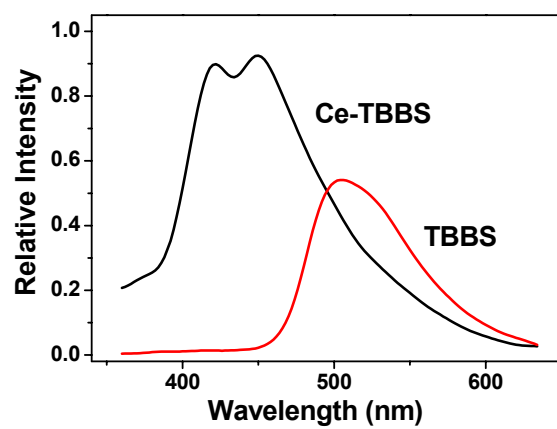
19. Figure S17 The Uv-vis absorption spectra of the ligand **TBBS** (black line, in the presence of 4 equiv. KOH), the **Ce-TBBS** complexes (red line) in DMF. For a comparison, here the molar absorptivity of the Ce complexes is calculated as one sixth of the value of themselves, corresponding to the number of ligands in the complex.



20. Figure S18 Family of Uv-vis absorption spectra of Ce-TBBS in DMF solution (5×10^{-6} M) upon the addition of various saccharides ($0-8.33 \times 10^{-3}$ M).



21. **Figure S19** Fluorescent spectrum of ligand **TBBS** (red line) and complex **Ce-TBBS** (black line) in DMF solution, excited at 340 nm.



22. Figure S20 Family of fluorescence spectra of **Ce-TBBS** (1×10^{-5} M) in DMF solution upon the addition of various saccharides (0-10 mM)

