Supporting Information

Metal-organic Polyheda Containing 36 and 24 Folds of Amide groups for Selectively Luminescent Recognition of Natural Disaccharides

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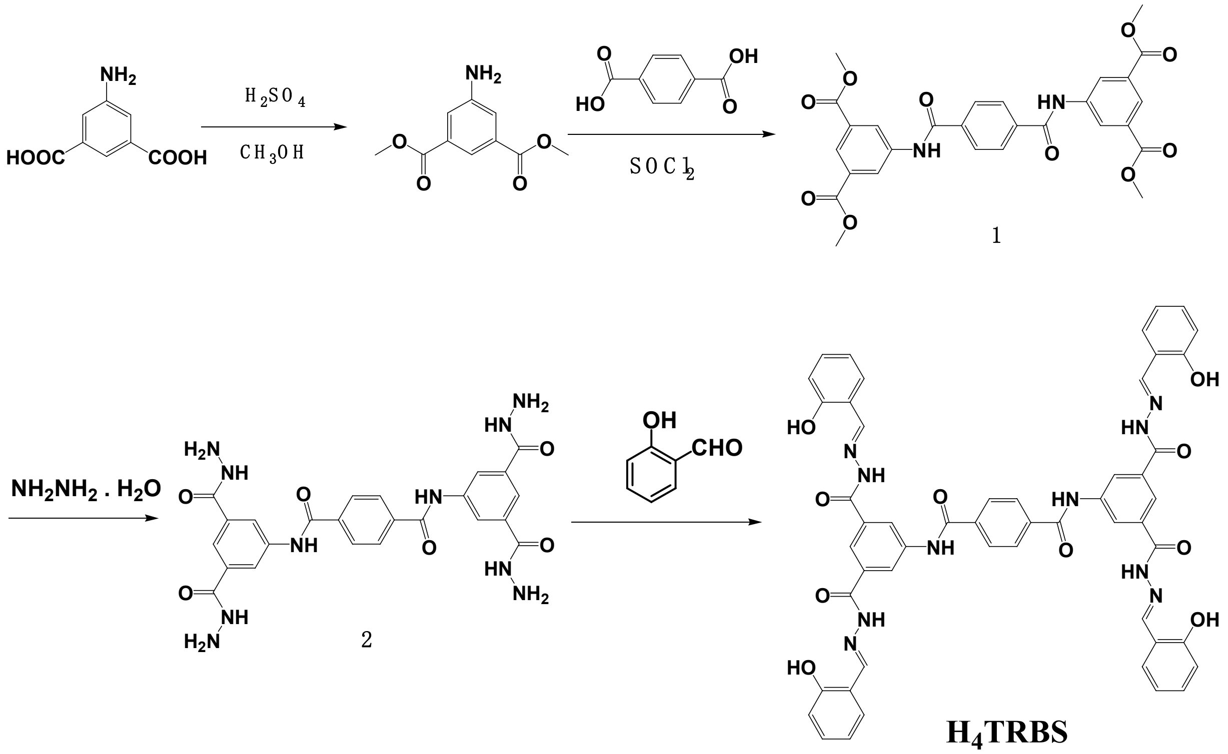
Contents

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 vario EL III elemental analyzer. ^{1}H 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 TU 1900 spectrometer. The fluorescent spectra were measured on EDINBURGH FS920.

1.2 Preparation



Scheme S1 The synthesis route of ligand H_4TRBS

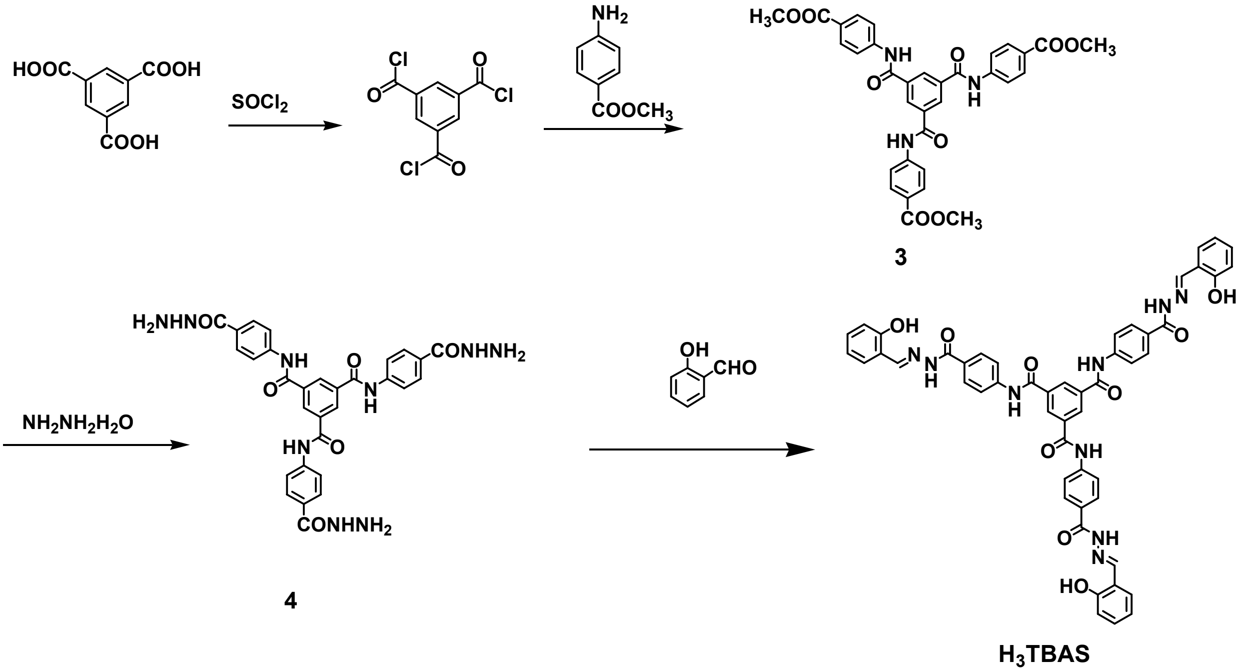
1： Thionylchloride (30 ml), terephthalic acid (3.3 g, 20 mmol) and 5 drops of DMF were refluxed at 95℃ for 2h. After evaporated the superfluous thionylchloride, 30 ml dry CH_2Cl_2 was added. The solution was added dropwisely to a mixture of dimethyl 5-aminoisophthalate (9.2 g, 44 mmol) and triethylamine (7ml, 50 mmol) in 50 ml dry CH_2Cl_2. The reaction mixture was stirred for 48 h at room temperature. The product was filtrated and used in next step. Yield 7.90g, 72%. ^{1}H NMR (400 MHz,DMSO-d_6, ppm): 10.83(s, 2H-$_{NH}$), 8.77 (s, 4H$_{Ar\text{-}H}$), 8.24(s, 2H$_{Ar\text{-}H}$), 8.17(d, 4H$_{Ar\text{-}H}$), 3.92(s, 12H-$_{CH}$).

2: The product was mixed with 80% hydrazine hydrate in methanol solution and stirred over 12 h, a white precipitate was filtrated and used in next step. Yield 6.70g, 85%. ^{1}H NMR (400 MHz,DMSO-d_6, ppm): 10.69(s, 2H-$_{NH}$), 9.75(s, 4H-$_{NH}$), 8.38(d, 4H$_{Ar\text{-}H}$), 8.16(s, 4H$_{Ar\text{-}H}$), 7.56(s, 2H$_{Ar\text{-}H}$), 4.56(s, 8H-$_{NH}$).

H_4**TRBS**: **2** (2mmol, 1.1g) was added to a CH_3OH solution (60 mL) containing salicylaldehyde (8.4 mmol, 1.024 g) and 5 drops of acetic acid. The mixture was heated at boiling temperature under magnetic stirring for 24h. During the reaction, a pale yellow precipitate was formed, which was collected by filtration. Yield: 1.54g, 80%. Anal calc. for $C_{52}H_{40}N_{10}O_{10}\cdot 4H_2O$: H 4.63, C 60.23, N 13.51%. Found: H 4.39, C 62.68, N 14.35%. ^{1}H NMR (400

MHz,DMSO-d_6, ppm): 12.34(s, $4H_{CONH}$), 11.19(s, $4H_{OH}$), 10.99(s, $2H_{CONH}$), 8.72(s, $4H_{Ar\text{-}H}$), 8.61(s, $4H_{\text{-}CH}$), 8.29(s, $4H_{Ar\text{-}H}$), 8.23(s, $2H_{\text{-}Ar\text{-}H}$), 7.62(d, $4H_{Ar\text{-}H}$), 7.33(t, $4H_{Ar\text{-}H}$), 6.96(m, $4H_{Ar\text{-}H}$, $4H_{Ar\text{-}H}$).

Ce-TRBS: A solution of $Ce(NO_3)_3{\cdot}6H_2O$ (170 mg, 0.4 mmol), H_4**L**^{1} ligand (280 mg, 0.3mmol) and NaOAc (98 mg, 1.2 mmol) in DMF (v:v = 1:7, 8 mL) was stirred for 2h. Then the solution was slowly diffused by methanol at room temperature to give crystalline black solid. Yield 67% (based on the crystal dried in vacuum). Anal calc. for $Ce_8(C_{52}H_{36}N_{10}O_{10})_6(NO_3)_2$: H 3.11, C 53.45, N 12.39%. Found: H 3.98, C 52.92, N 13.02 %.



Scheme S2 The synthesis route of ligand H_3**TBAS**

3: A 50 mL round-bottomed flask equipped with magnetic stir bar and reflux condenser was charged with 4.20 g of 1,3,5-benzenetricarboxylic acid (20mmol) and 10 mL of $SOCl_2$. Five drops of anhydrous DMF were added, and the mixture was refluxed for 6h. After this time, the reaction was a golden yellow solution. The excess $SOCl_2$ was removed by reduced pressure distillation to get a pale yellowish oil. The pale yellowish oil in 20ml dry dichloromethane solution was added dropwise to a dry dichloromethane solution of methyl 4-aminobenzoate 9.98 g (66mmol) and 6.68 g (66mmol) triethylamine in an ice bath and the mixture was stirred for three days. The pale yellow precipitate was filtered. Yield 9.51g, 78%. ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 10.92 (s, $3H_{\text{-}NH\text{-}}$), 8.76 (s, $3H_{Ar\text{-}H}$), 8.01 (dd, $12H_{Ar\text{-}H}$), 3.85 (s, $9H_{\text{-}CH}$).

4: A 100 mL round-bottomed flask equipped with magnetic stir bar and reflux condenser was charged with 80% hydrazine hydrate (50 mL) , *N*, *N*', *N*''-tris(4-methoxycarbonylphenyl)-1,3,5-benzene tricarboxamide (10mmol, 6.09g) and 150 mL ethanol. The mixture was heated at boiling temperature under magnetic stirring for 5 days. A white precipitate was collected by filtration. Yield: 4.33g, 71%. ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 10.77 (s, $3H_{\text{-}NH\text{-}}$), 9.70 (s, $3H_{\text{-}NH\text{-}}$), 8.73 (d, $3H_{Ar\text{-}H}$), 8.00 (dd, $12H_{Ar\text{-}H}$), 4.53 (s, $6H_{\text{-}NH}$).

H_3TBAS: A mixture solution of *N*, *N*', *N*''-tris(4-(hydrazinecarbonyl)phenyl)benzene-1,3,5-tricarboxamide (1.5mmol, 0.91g) and 2-hydroxybenzaldehyde (5.4mmol, 0.66g) in methanol (100mL) was stirred over 12h at boiling temperature. A white precipitate was collected by filtration and dried in vacuum. Anal calc. for $C_{51}H_{39}N_9O_9$: H 4.23, C 66.44, N 13.67%. Found: H 4.88, C 67.28, N 13.36%. Yield: 1.27g, 92%. ^1H NMR (400 MHz, DMSO-d_6, ppm) 12.11 (s, $3H_{\text{-CONH-}}$),δ 11.34 (s, $3H_{\text{-OH}}$), 10.92 (s, $3H_{\text{-CONH-}}$), 8.80 (s, $3H_{\text{-CH-}}$), 8.66 (s, $3H_{\text{Ar-H}}$), 8.02 (s, $12H_{\text{Ar-H}}$), 7.57 (d, $3H_{\text{Ar-H}}$), 7.31 (m, $6H_{\text{Ar-H}}$), 6.96 (*m*, $3H_{\text{Ar-H}}$).

Ce-TBAS: A solution of $Ce(NO_3)_3{\cdot}6H_2O$ (170 mg, 0.4 mmol), H_3L ligand (370 mg, 0.4mmol) and NaOAc (33 mg, 0.4 mmol) in DMF (10 mL) was stirred for 2h. Then the solution was slowly diffused by methanol at room temperature to give crystalline black solid. Yield 65%.(based on the crystal dried in vacuum). Anal calc. for $Ce_4(C_{51}H_{35}N_9O_9)_4$: H 3.34, C 57.89, N 11.92; Found: H 3.92 C 57.06 N 12.44.

2. Crystallography

Intensities of the complexes were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo-Kα (λ = 0.71073 Å) 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.

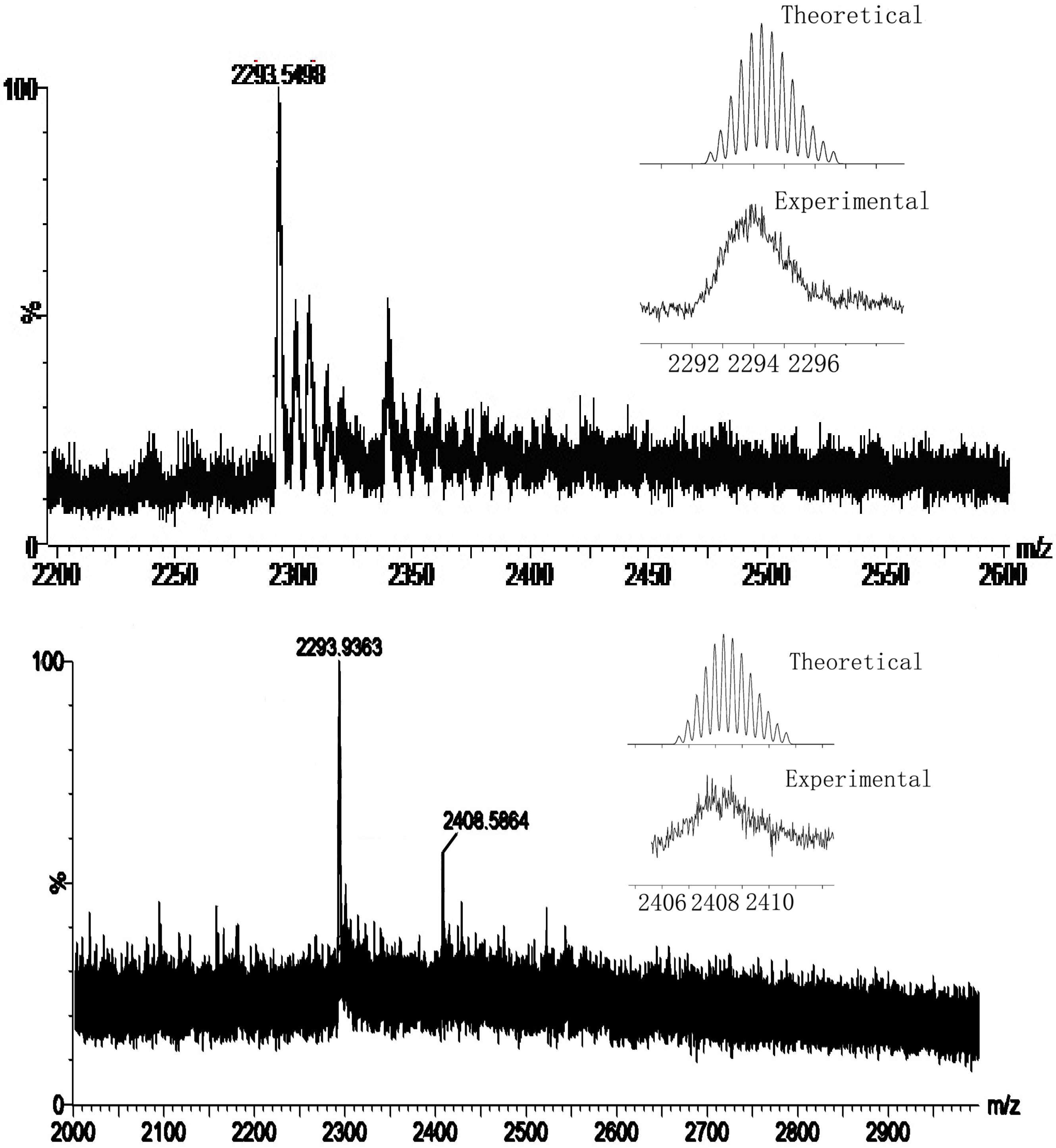
Ce-TRBS: $Ce_8C_{377}H_{416}N_{82}O_{111}$ [$Ce_8(C_{52}H_{36}N_{10}O_{10})_6(NO_3)_2$·$20C_3H_7NO$· $5CH_3OH$· $20H_2O$], M = 8992.88, triclinic, space group P-1, black block, a = 27.284(1), b = 42.094(3), c = 46.930(3) Å, α = 68.0(1)°, β = 80.4(1)°, γ = 89.9(1)°, V = 49163(5) Å^3, Z = 2, Dc = 0.607 g cm^{-3}, μ(Mo-Kα) = 0.401 mm^{-1}, T = 180(2) K. 128341 unique reflections [Rint = 0.1490]. Final R_1 [with $I > 2\sigma(I)$] = 0.1248, wR_2 (all data) = 0.3087 for 2θ = 45º.

Ce-**TBAS**: $Ce_4C_{237}H_{246}N_{44}O_{60}$ [$Ce_4(C_{51}H_{35}N_9O_9)_4$·$8C_3H_7NO$· $9CH_3OH$·$7H_2O$], M = 5231.26, Orthorhombic, space group Fddd, black block, a = 18.30 (1), b = 46.92 (1), c =91.25 (2) Å, Z = 8, Dc = 0.887 g cm^{-3}, μ(Mo-Kα) = 0.511 mm^{-1}, T = 180(2) K. 12729 unique reflections [Rint = 0.1247]. Final R_1 [with $I > 2\sigma(I)$] = 0.0959, wR_2 (all data) = 0.2497 for 2θ = 45º.

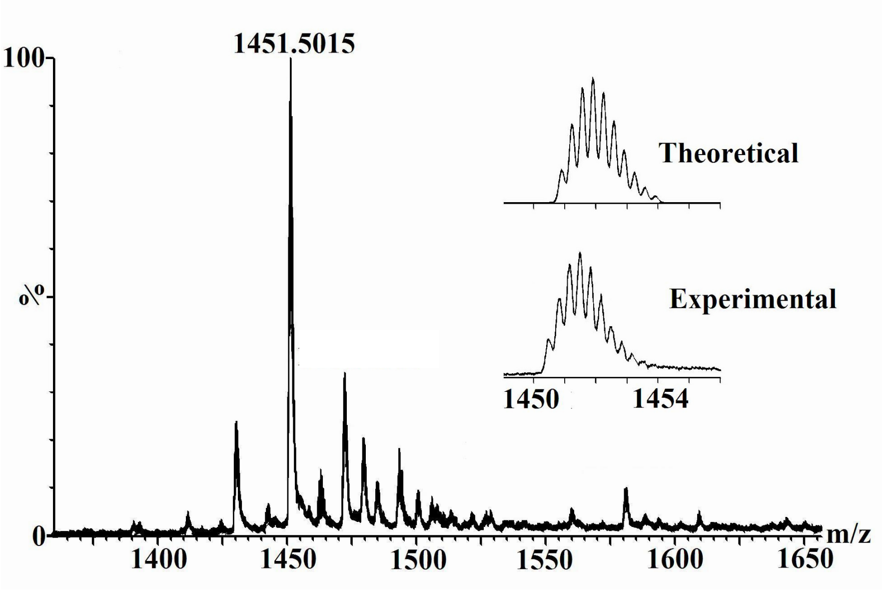
In the structural refinement of **Ce-TRBS**, except the solvent molecules, the skeleton non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms, whereas no hydrogen atoms corresponding to the solvent molecules were added and refined. Several restrains were applied: (1) One of the bezene rings in the salicylalzone groups were disordered into two parts with the *s.o.f* being fixed at 0.5 for each other. And the geometrical constraints of idealized regular polygons were used for several bezene rings in the salicylalzone groups including the disordered parts: 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) Some of the solvent DMF molecules were restrained as idealized geometry. Thermal parameters on adjacent atoms in some of the solvent DMF molecules were restrained to be similar. In the checkcif file, the short D…A distance was due to the partially occupancy of the solvent molecules.

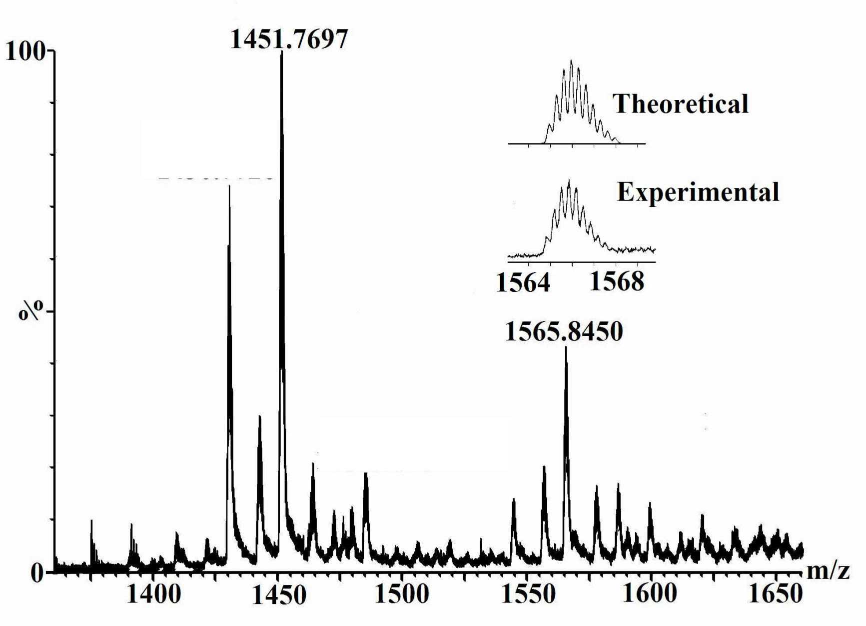
In the structural refinement of **Ce-TBAS**, except the solvent molecules, the skeleton non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbone and the solvent DMF molecules were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. Several restrains were applied: (1) Two of the twenty four bezene rings in the salicylalzone groups, three of the phenyl rings, three carbon and three oxygesn atoms of the free amide group and two Schiff base carbon atoms were disordered into two parts with the *s.o.f* being fixed at 0.5 for each other. (2) 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. In the checkcif file, the short D…A distance was due to the partially occupancy of the solvent molecules.

3. Figure S1 ESI-MS of Ce-TRBS (0.1 uM) in DMF/ acetonitrile solution (containing 0.1 uM KOH) (top) and Ce-TRBS (0.1 uM) in DMF/CH_3CN solution (containing 0.1 uM KOH) in the presence of lactose (0.5 uM) (Bottom). The inserts exhibit the measured and simulated isotopic patterns at 2293.93 and at 2408.58.

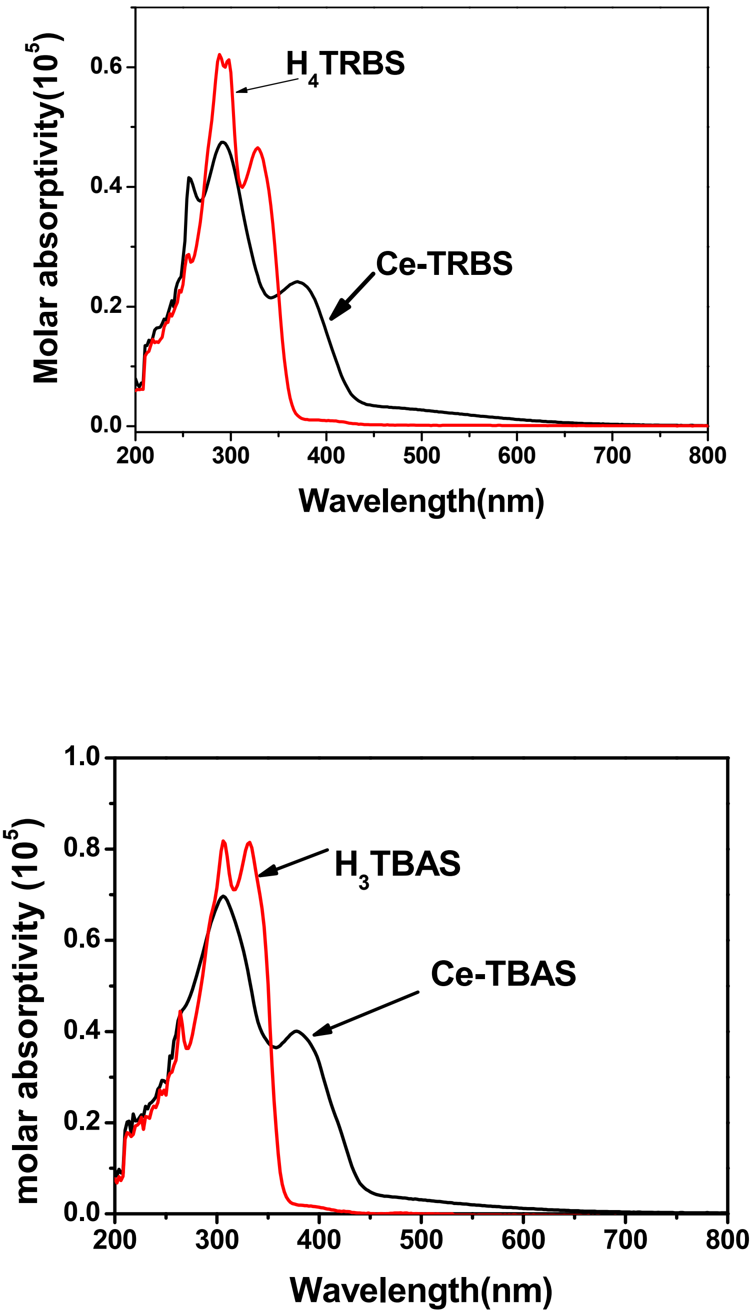


4. Figure S2 ESI-MS of Ce-**TBAS** (0.1 uM) in DMF/ acetonitrile solution (containing 0.1 uM KOH) (top) and Ce-**TBAS** (0.1 uM) in DMF/CH_3CN solution (containing 0.1 uM KOH) in the presence of sucrose (0.5 uM) (Bottom). The inserts exhibit the measured and simulated isotopic patterns at 1451.50 and at 1565.85.

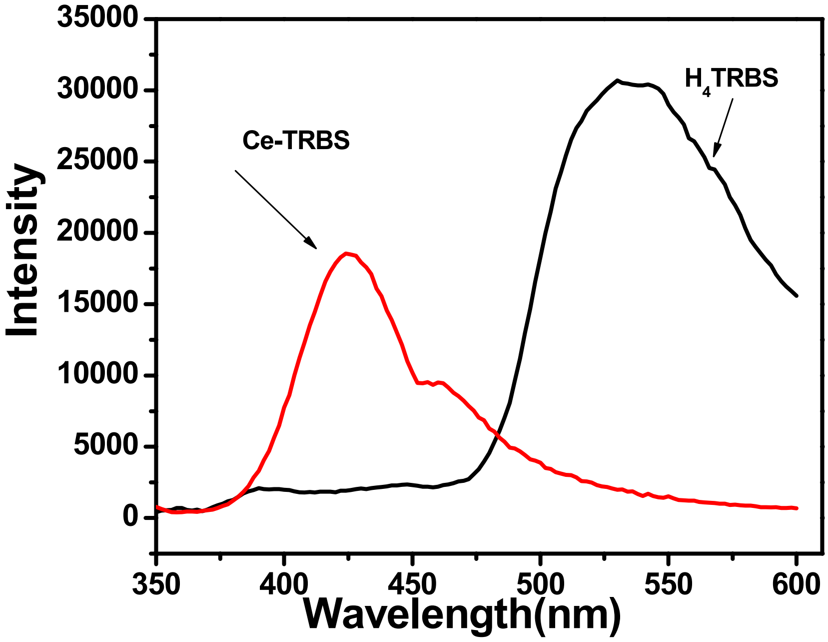


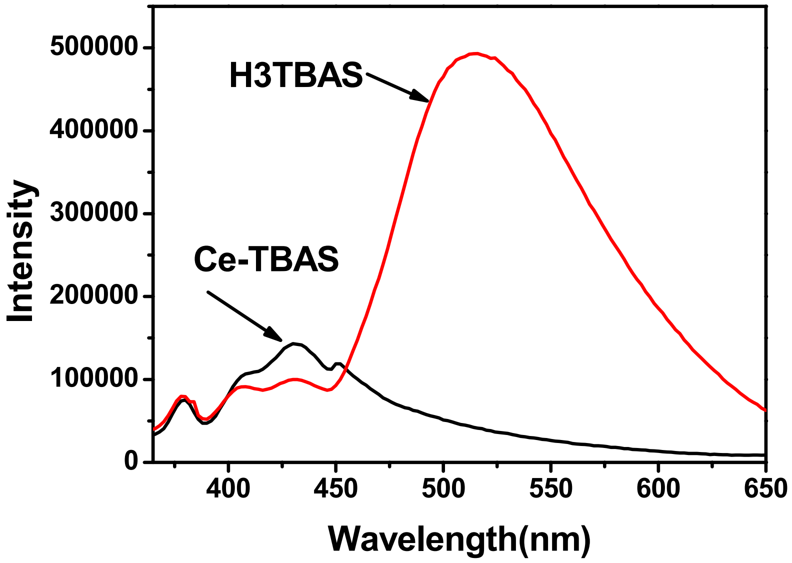


5. Figure S3 Top**:** The Uv-*vis* absorption spectra of **H_4TRBS** (red line), Ce-**TRBS** (black line) in DMF/acetonitrile solution (1:9, v/v) . For a comparison, here the molar absorptivity of Ce-**TRBS** is calculated as one sixth of the value of itself, corresponding to the number of ligands in the complex. Bottom: The Uv-*vis* absorption spectra of **H_3TBAS** (red line), Ce-**TBAS** (black line) in DMF/acetonitrile solution (1:9, v/v). The molar absorptivity of Ce-**TBAS** calculated as one fourth of the value of itself, corresponding to the number of ligands in the complex

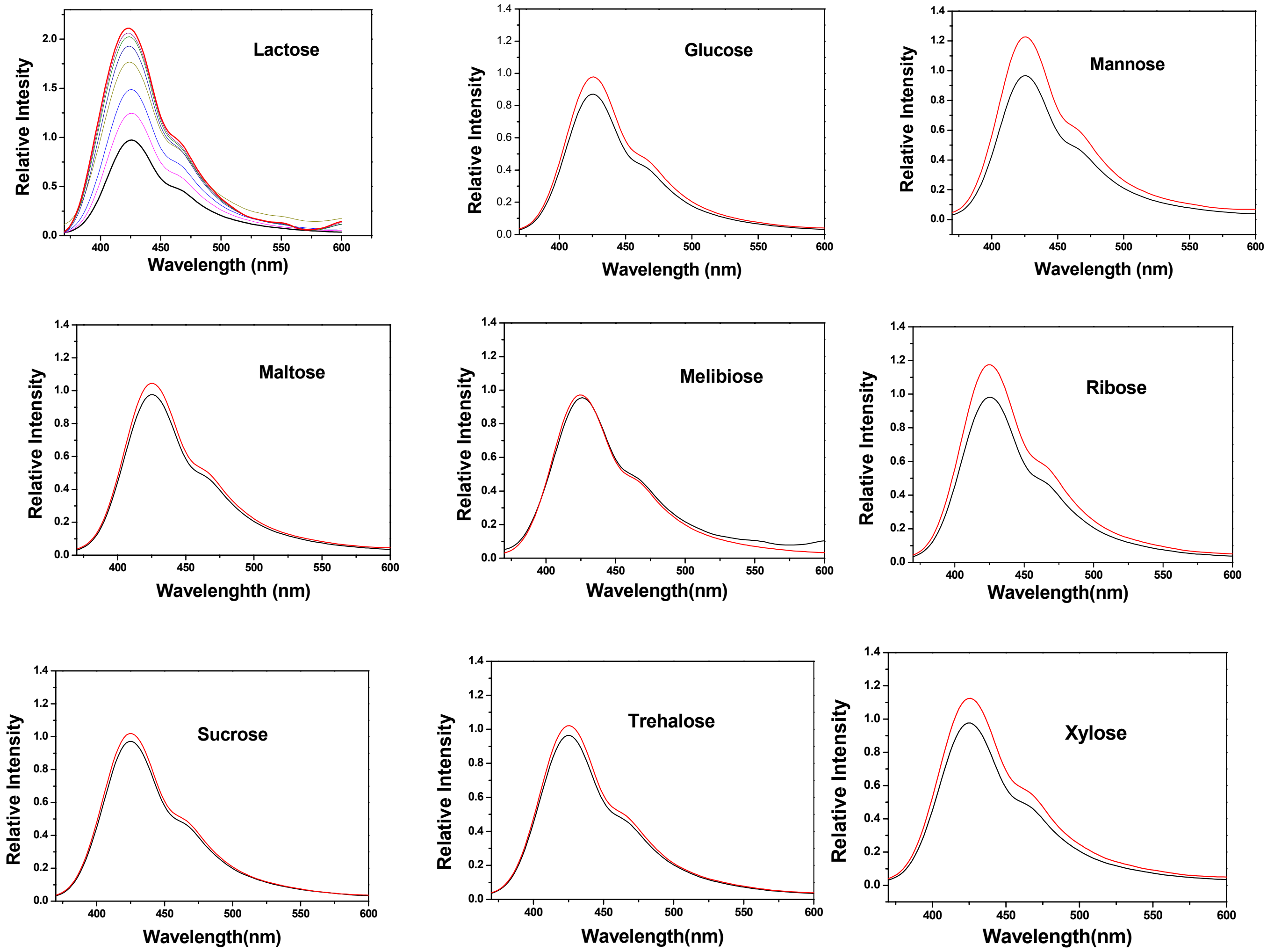


6. Figure S4 Top**:** Fluorescent spectrum of ligand **H_4TRBS** (120 μM, red line) and complex **Ce-TRBS (**20 μM, black line) in DMF/acetonitrile solution (1:9, v/v), excited at 315 nm. Bottom: Fluorescent spectrum of ligand **H_4TBAS** (80 μM, red line) and complex **Ce-TBAS (**20 μM, black line) in DMF/acetonitrile solution (1:9, v/v), excited at 340 nm .

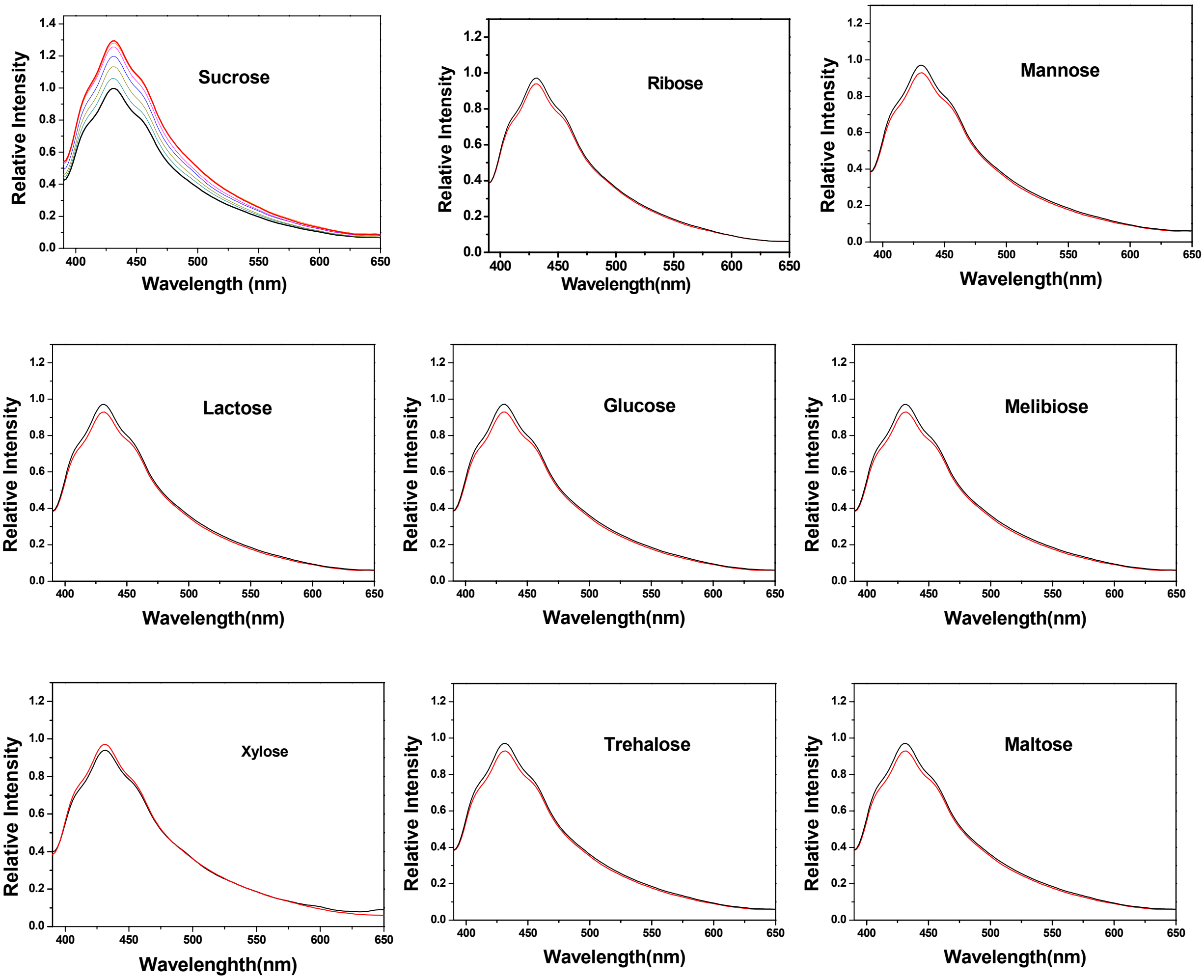




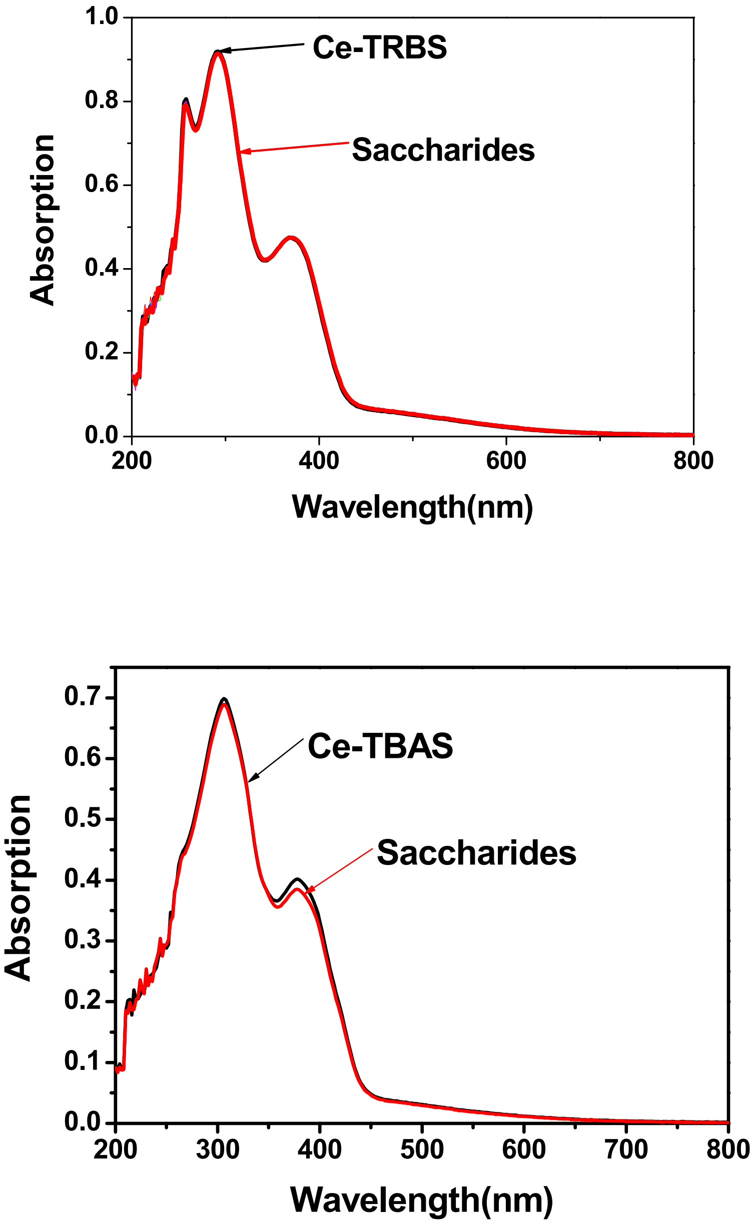
7. Figure S5 Family of fluorescent spectra of Ce-**TRBS** in DMF/acetonitrile solution (1:9, v/v, 20μM) upon the addition of various monosaccharides and disaccharides(up to 0.6 mM), excited at 315 nm.



8. Figure S6 Family of fluorescent spectra of Ce-**TBAS** in DMF/acetonitrile solution (1:9, v/v, 20μM) upon the addition of various monosaccharides and disaccharides (up to 0.6 mM), excited at 340 nm.



9. Figure S7 Uv-*vis* absorption spectra of Ce-**TRBS** (top) and Ce-**TRAS** (bottom) in DMF/acetonitrile solution (1:9, v/v, 20 μM) upon the addition of various monosaccharides and disaccharides.



10. Figure S8 Fluorescent spectra of H_4**TRBS** (top) and H_3**TBAS** (botom) in DMF/acetonitrile solution (1:9, v/v, 20μM) upon the addition of various monosaccharides disaccharides and trisaccharides, excited at 315 and 340nm, repectively.