1,2-HOIQO – A Highly Versatile 1,2-HOPO Analog

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Supporting Information

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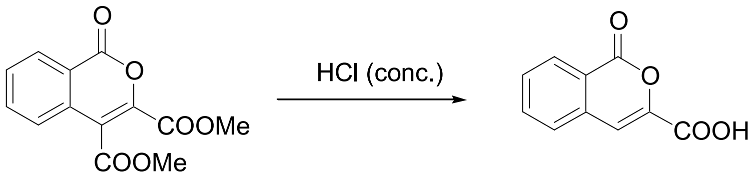
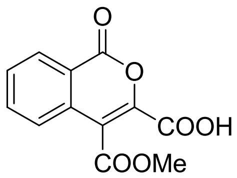
1. Synthetic Procedures

3-Carboxyisocoumarin (3)[1]



A 5L-three-necked flask was charged with 1 L conc. HCl and heated to reflux (bath temp. 130 °C). To avoid massive foaming of the reaction mixture 3,4-(dimethoxycarbonyl)-isocoumarin (86.74 g, 330.7 mmol) was added in portions over ca. 5 h. The white suspension was heated for another 12 h. (If heating is stopped too early, a considerable amount of mono-saponified byproduct is present.) After cooling to ambient temperature, the colorless solid was collected, washed with cold water, and dried in vacuo at 60 °C for 1 h. The product **3** (54.32 g, 86%) was obtained as a colorless solid.

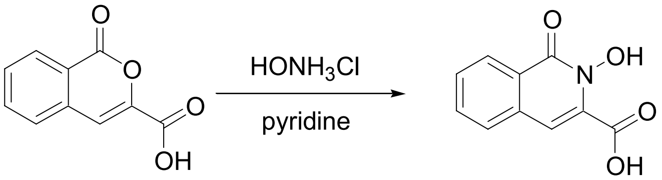
M.p. 246-247 °C. ^{1}H-NMR (400 MHz, DMSO-d$_6$): δ = 8.17 (d, *J* = 7.9 Hz, 1 H), 7.92-7.82 (m, 2 H), 7.74-7.67 (m, 1 H), 7.66 (s, 1 H) ppm. ^{13}C-NMR (100.6 MHz, DMSO-d$_6$): δ = 161.5, 161.0, 143.7, 135.8, 135.5, 131.3, 129.4, 128.6, 122.4, 111.3 ppm. MS (ES-): m/z (%) = 379 (8, [M$_2$-H]$^-$), 189 (73, [M-H]$^-$), 179 (100).



(byproduct)

^{1}H-NMR (400 MHz, DMSO-d$_6$): δ = 8.22 (dd, *J* = 8.0, 0.7 Hz, 1 H), 7.95-7.88 (m, 1 H), 7.80-7.73 (m, 1 H), 7.51 (d, *J* = 7.8 Hz, 1 H), 3.87 (s, 3 H) ppm. ^{13}C-NMR (100.6 MHz, DMSO-d$_6$): δ = 165.2, 161.0, 159.6, 141.8, 136.3, 132.7, 131.8, 130.0, 125.6, 121.8, 118.2, 53.5 ppm.

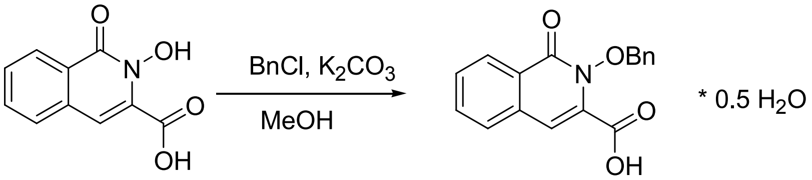
2-Hydroxy-1-oxo-1,2-dihydro-isoquinoline-3-carboxylic acid (2)[2]



3-Carboxyisocoumarin (**3**) (9.61 g, 50.5 mmol, 1.0 equiv.) and hydroxylamine hydrochloride (4.21 g, 60.60 mmol, 1.2 equivs.) were heated to 100 °C (bath temp.) in pyridine (40 mL) for 2 h. The mixture was cooled to 0 °C and 4 M HCl (300 mL) was added. After cooling the mixture in an ice-bath for 30 min, the light-yellow precipitate was collected on a Büchner-funnel, washed with cold water and air-dried (8.27 g, 80%).

M.p. 225-227 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.25-8.18 (m, 1 H), 7.78 (d, *J* = 7.9 Hz, 1 H), 7.75-7.69 (m, 1 H), 7.61-7.53 (m, 1 H), 7.00 (s, 1 H) ppm. ^{13}C-NMR (100.6 MHz, DMSO-d_6): δ = 162.8, 158.2, 135.6, 134.6, 132.8, 128.4, 127.8, 127.1, 126.7, 106.0 ppm. MS (ES-): m/z (%) = 204 (80, $[M-H]^-$), 160 (100, $[M-CO_2-H]^-$). Anal. Calcd. for $C_{10}H_7NO_4$ (M_r = 205.17): C, 58.54; H, 3.44; N, 6.83. Found: C, 58.71; H, 3.48; N, 6.81.

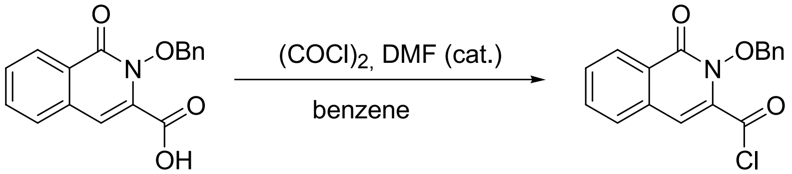
2-Benzyloxy-1-oxo-1,2-dihydro-isoquinoline-3-carboxylic acid hemihydrate (4)



2-Hydroxy-1-oxo-1,2-dihydro-isoquinoline-3-carboxylic acid (**2**) (8.27 g, 40.3 mmol, 1.0 equiv.) and K_2CO_3 (11.14 g, 80.6 mmol, 2.0 equivs.) were suspended in dry MeOH (300 mL) and benzyl chloride (6.12 g, 48.4 mmol, 1.2 equivs.) was added dropwise. The mixture was heated to reflux for 24 h. After cooling down to ambient temperature, the solvent was removed under reduced pressure and the yellow foam was treated with water (55 mL) and Et_2O (55 mL). The biphasic system was cooled in an ice-bath and the pH was adjusted to 2 with 4 M HCl. The resulting, slightly yellow solid was collected, washed with ice-cold water and Et_2O, and dried in vacuo overnight at 60 °C. The slightly yellow, solid product **4** was obtained as the hemihydrate (11.1 g, 91%).

M.p. 181-183 °C (decomp.). ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.27 (d, *J* = 8.1 Hz, 1 H), 7.87-7.75 (m, 2 H), 7.68-7.60 (m, 1 H), 7.54-7.47 (m, 2 H), 7.44-7.35 (m, 3 H), 7.14 (s, 1 H), 5.33 (s, 2 H) ppm. ^{13}C-NMR (100.6 MHz, DMSO-d_6): δ = 162.5, 158.5, 134.9, 134.64, 134.62, 133.5, 130.0, 129.4, 129.0, 128.9, 128.2, 127.5, 127.4, 108.4, 78.4 ppm. MS (ES-): m/z (%) = 589 (81, $[2M-H]^-$), 294 (100, $[M-H]^-$). Anal. Calcd. for $C_{17}H_{13}NO_4 \cdot 0.5\ H_2O$ (M_r = 304.24): C, 67.10; H, 4.64; N, 4.60. Found: C, 67.14; H, 4.37; N, 4.56.

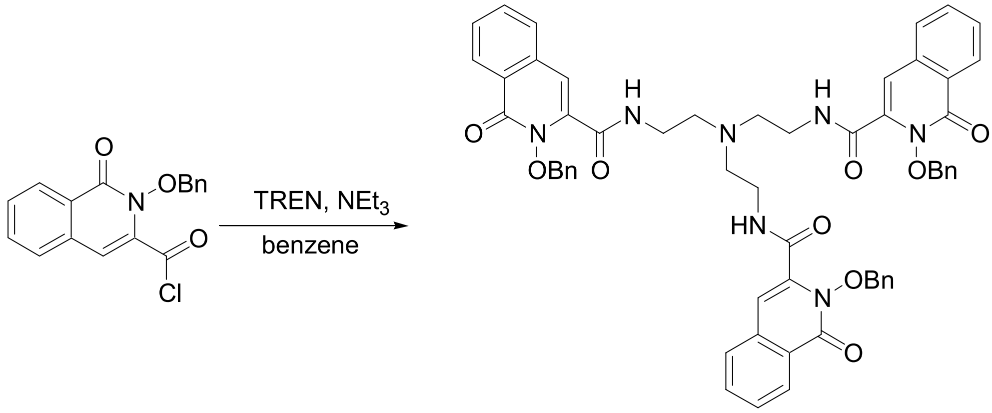
2-Benzyloxy-1-oxo-1,2-dihydro-isoquinoline-3-carbonyl chloride (5)



Under argon, 2-benzyloxy-1-oxo-1,2-dihydro-isoquinoline-3-carboxylic acid hemihydrate (**4**) (5.23 g, 17.2 mmol, 1.0 equiv.) was suspended in dry benzene (140 mL). Two drops of dry DMF were added, followed by dropwise addition of oxalyl chloride (6.0 mL, 8.73 g, 68.8 mmol, 4.0 equivs.). The mixture was heated to 60 °C (bath temperature) for 3 h. After cooling down to ambient temperature, the volatiles were removed under reduced pressure. Additional dry benzene (80 mL) was added, followed by evaporation in vacuo. The residue was taken up in dry benzene (80 mL) and filtered through a plug of cotton. After concentration of the slightly yellow solution to dryness, the crude acid chloride **5** was obtained as a light-yellow solid (5.27 g, 98%). This material was used without further purification in the next step.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.55-8.48 (m, 1 H), 7.83-7.69 (m, 3 H), 7.63-7.56 (m, 2 H), 7.49 (s, 1 H), 7.44-7.38 (m, 3 H), 5.42 (s, 2 H) ppm. ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 159.2, 158.8, 135.0, 133.5, 133.3, 132.7, 130.7, 130.4, 129.3, 128.8, 128.7, 128.6, 128.2, 116.5, 78.8 ppm.

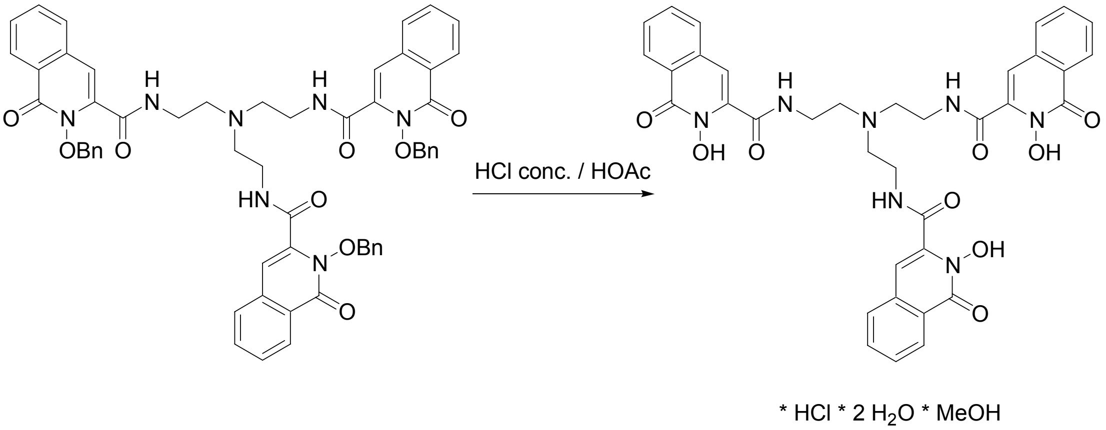
Tris(2-(2-benzyloxy-1-oxo-1,2-dihydro-isoquinoline-3-carbonyl)aminoethyl)amine (6)



Under argon, 2-benzyloxy-1-oxo-1,2-dihydro-isoquinoline-3-carbonyl chloride (**5**) (5.27 g, 16.8 mol, 3.3 equivs.) was dissolved in 10 mL dry benzene. This solution was added dropwise to an ice-cold solution of dry NEt_3 (3.5 mL, 2.54 g, 25.1 mmol, 4.9 equivs.) and tris(2-aminoethyl)amine (744 mg, 5.09 mmol, 1.0 equiv.) in 20 mL dry benzene. The yellowish suspension was stirred at room temperature for 16 h before 100 mL sat. $NaHCO_3$ and 100 mL EtOAc were added. The organic phase was dried ($MgSO_4$) and concentrated. The light-brown solid was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 50:1). The brown fractions with R_f = 0.24 (CH_2Cl_2/MeOH 95:5, detection: UV_{254nm}) were collected and the solvents removed under reduced pressure. The light-brown solid **6** was dried in vacuo to yield 2.74 g (55%).

M.p. 108-112 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 8.1 Hz, 3 H), 7.60-7.10 (m, 27 H), 6.38 (s, 3 H), 5.26 (s, 6 H), 3.12-2.97 (m, 6 H), 2.47-2.32 (m, 6 H) ppm. ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ = 161.6, 158.2, 136.8, 134.2, 133.8, 132.3, 130.2, 129.3, 128.5, 127.7, 127.1, 127.0, 126.8, 106.2, 79.1, 53.9, 38.3 ppm. MS (FAB+): m/z (%) = 979 (100, $[MH]^+$). Anal. Calcd. for $C_{57}H_{51}N_7O_9$ (M_r = 978.06): C, 70.00; H, 5.26; N, 10.02. Found: C, 69.82; H, 5.40; N, 9.92.

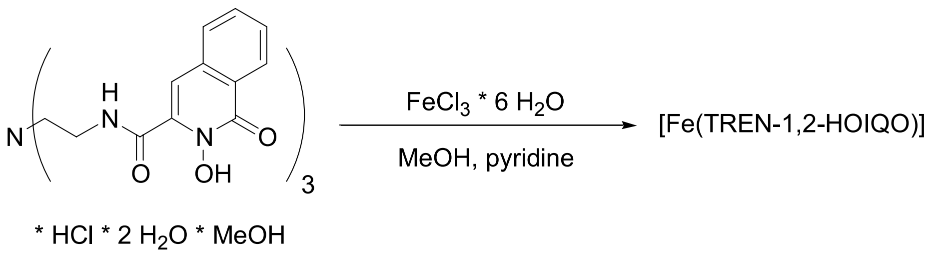
TREN-1,2-HOIQO (7)



The benzyl protected ligand **6** (880 mg, 900 µmol, 1.0 equiv.) was dissolved in a mixture of 20 mL conc. HCl and 20 mL glacial acetic acid. The yellow solution was stirred at ambient temperature for 7 days and at 50 °C for additional 18 h. The mixture was filtered and the volatiles were removed under reduced pressure at room temperature. The red-brown residue was dissolved in 20 mL MeOH and the solvent was evaporated again. A minimum amount of MeOH, required to dissolve everything, was added. The yellow solution was filtered through a plug of cotton and treated with Et_2O to precipitate the deprotected ligand. The precipitate was collected, washed with Et_2O, and dried in vacuo. The product TREN-1,2-HOIQO (**7**) was obtained as a light-brown solid (540 mg, 74%).

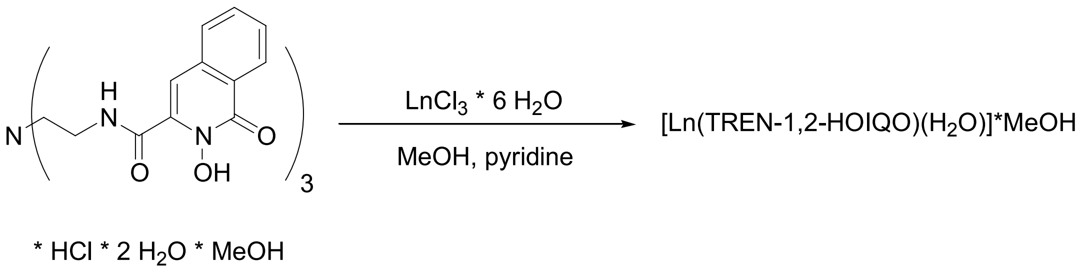
M.p. 152-156 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 9.09 (br s, 3 H), 8.21 (d, *J* = 8.0 Hz, 3 H), 7.76-7.49 (m, 9 H), 6.91 (s, 3 H), 3.86-3.66 (m, 6 H), 3.48 (br s, 6 H) ppm. ^{13}C-NMR (100.6 MHz, DMSO-d_6): δ = 161.8, 158.1, 137.7, 134.9, 132.7, 128.0, 127.5, 127.1, 126.3, 104.8, 51.8, 34.5 ppm. MS (FAB+): m/z (%) = 798.5 (12), 761.4 (10), 708.5 (46, $[MH]^+$), 692.5 (24, $[M\text{-}O\text{+}H]^+$), 474.4 (36), 231.2 (70), 215.2 (100). Anal. Calcd. for $C_{36}H_{33}N_7O_9$*HCl *2 H_2O*MeOH (M_r = 812.22): C, 54.71; H, 5.21; N, 12.07. Found: C, 54.92; H, 4.96; N, 11.81.

Metal Complexes of TREN-1,2-HOIQO (8, 9, 10, 11, 12)



A solution of TREN-1,2-HOIQO (**7**) * HCl * 2 H_2O * MeOH (22.0 mg, 27.1 µmol, 1.0 equiv.) in MeOH was treated with solid $FeCl_3$ * 6 H_2O (7.3 mg, 27.1 µmol, 1.0 equiv.), pyridine (78 mg) and heated to reflux for 30 min. The resulting fine, dark red suspension was cooled down to ambient temperature, the precipitate collected on a filter, and washed with MeOH. After drying in vacuo at 50 °C (bath temp.) for 3 h, the iron complex [Fe(TREN-1,2-HOIQO)] (12 mg, 58%) was obtained as a dark red solid, soluble in DMF, DMSO, and CH_2Cl_2, only sparingly in acetone and not in etherial solvents.

M.p. >200 °C. MS (FAB+): m/z (%) = 761 (100, $[M+H]^+$). Anal. Calcd. for $C_{36}H_{30}FeN_7O_9$ (M_r = 760.51): C, 56.85; H, 3.98; N, 12.89. Found: C, 56.68; H, 4.02; N, 12.73.



General procedure: Under argon, a solution of TREN-1,2-HOIQO (**7**) * HCl * 2 H_2O * MeOH (1.0 equiv.) was treated with solid $LnCl_3$ * 6 H_2O (1.0 equiv.) or $LnCl_3$ (anhydr.) (1.0 equiv.) and pyridine and heated to reflux overnight. The resulting fine suspension was cooled to ambient temperature, the precipitate collected on a filter, and washed with MeOH. After drying in vacuo at 50 °C (bath temp.) for 6 h, the lanthanide complexes [Ln(TREN-1,2-HOIQO)(H_2O)]*MeOH were obtained as almost colorless solids, soluble in DMF, DMSO, and only very sparingly in MeOH.

Ce:

Starting with $CeCl_3$ * 6 H_2O (9.6 mg, 25.6 µmol, 1.0 equiv.), TREN-1,2-HOIQO * HCl * 2 H_2O * MeOH (21.0 mg, 25.6 µmol, 1.0 equiv.), pyridine (47 mg) in 5 mL MeOH (HPLC-grade) gave 12 mg (52%) complex. Single crystals of [Ce(TREN-1,2-HOIQO)(H_2O)])]*H_2O suitable for X-ray diffraction studies were grown by vapor diffusion of water into a DMF solution of [Ce(TREN-1,2-HOIQO)(H_2O)]*MeOH.

M.p. >300 °C. Anal. Calcd. for $C_{37}H_{36}CeN_7O_{11}$ (M_r = 894.84): C, 49.66; H, 4.06; N, 10.96. Found: C, 49.27; H, 3.85; N, 10.68.

Eu:

Starting with $EuCl_3$ * 6 H_2O (41 mg, 113 µmol, 1.0 equiv.), TREN-1,2-HOIQO * HCl * 2 H_2O * MeOH (92 mg, 113 µmol, 1.0 equiv.), pyridine (78 mg) in 20 mL MeOH (HPLC-grade) gave 61 mg (60%) complex.

M.p. > 300 °C. MS (FAB+): m/z (%) = 858 (20, $\{[Eu(TREN\text{-}1,2\text{-}HOIQO)]+H\}^+$), 369 (34), 350 (54), 320 (36), 277 (100). Anal. Calcd. for $C_{37}H_{36}EuN_7O_{11}$ (M_r = 906.69): C, 49.01; H, 4.00; N, 10.81. Found: C, 48.80; H, 4.02; N, 10.58.

Gd:

Starting with $GdCl_3$ * 6 H_2O (38 mg, 103 µmol, 1.0 equiv.), TREN-1,2-HOIQO * HCl * 2 H_2O * MeOH (84 mg, 103 µmol, 1.0 equiv.), pyridine (78 mg) in 20 mL MeOH (HPLC-grade) gave 42 mg (45%) complex.

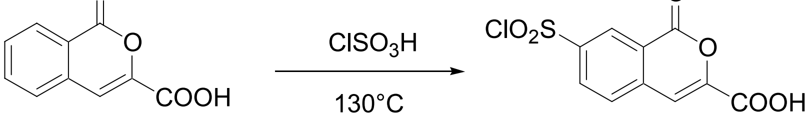
M.p. > 300 °C. Anal. Calcd. for $C_{37}H_{36}GdN_7O_{11}$ (M_r = 911.97): C, 48.73; H, 3.98; N, 10.75. Found: C, 48.70; H, 3.93; N, 10.56.

Lu:

Starting with anhydr. $LuCl_3$ (12 mg, 43 µmol, 1.0 equiv.), TREN-1,2-HOIQO * HCl * 2 H_2O * MeOH (35 mg, 43 µmol, 1.0 equiv.), pyridine (62 mg) in 6 mL MeOH (HPLC-grade) gave 23 mg (57%) complex.

M.p. > 300 °C. ^{1}H-NMR (400 MHz, DMSO-d$_6$): δ = 11.31 (t, J = 6.1 Hz, 3 H), 8.13 (d, J = 8.2 Hz, 3 H), 7.93 (d, J = 8.2 Hz, 3 H), 7.76 (s, 3 H), 7.70-7.63 (m, 3 H), 7.62-7.54 (m, 3 H), 3.17-3.09 (m, 6 H), 2.51 (br, 6 H) ppm. Anal. Calcd. for $C_{36}H_{37}LuN_7O_{11}$ (M_r = 929.69): C, 47.80; H, 3.90; N, 10.55. Found: C, 47.54; H, 3.73; N, 10.33.

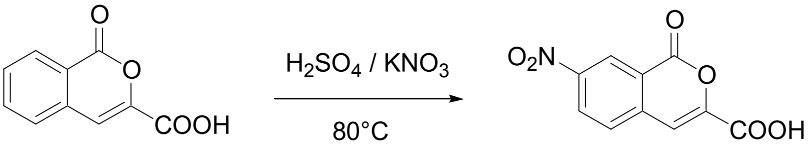
3-Carboxy-7-chlorosulfonyl-isocoumarin (13)



Under argon, chlorosulfonic acid (20 mL) was cooled to 0 °C and 3-carboxyisocoumarin (**3**) (2.00 g, 10.5 mmol) was added in portions. The initially yellow solution was heated to 130 °C (bath temperature) for 6 h. After cooling down, the brown solution was slowly dropped onto ca. 150 g crushed ice with stirring. The yellow solid was collected on a Büchner-funnel, washed with ice-cold water and dried in vacuo at 60 °C for 14 h. The product **13** was obtained as a light-yellow solid (1.80 g, 59%). This material was pure enough for the subsequent step. For analytical purposes, a sample was recrystallized from benzene/ petrolether.

M.p. >200 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.35-8.31 (m, 1 H), 8.03 (dd, *J* = 8.1, 1.8 Hz, 1 H), 7.83 (d, *J* = 8.1 Hz, 1 H), 7.66 (s, 1 H) ppm. ^{13}C-NMR (100.6 MHz, DMSO-d_6): δ = 161.5, 160.9, 150.7, 144.0, 135.5, 132.8, 128.5, 126.0, 122.0, 112.0 ppm. MS (ES-): m/z (%) = 323 (36), 287 (100, $[M-H]^-$), 269 (72, $[M-Cl+OH-H]^-$). Anal. Calcd. for $C_{10}H_5ClO_6S$ (M_r = 288.66): C, 41.61; H, 1.75; S, 11.11. Found: C, 41.71; H, 1.57; S, 10.85.

3-Carboxy-7-nitro-isocoumarin (14)



3-Carboxyisocoumarin (**3**) (3.00 g, 15.8 mmol, 1.0 equiv.) was dissolved in 25 mL conc. H_2SO_4. At room temperature, KNO_3 (1.32 g, 13.1 mmol, 1.1 equivs.) was added in portions and the yellow solution was heated to 80 °C (bath temperature) for 10 h. The dark yellow solution was allowed to come to ambient temperature and dropped onto crushed ice with stirring (ca. 50 g ice). The slightly yellow precipitate was collected on a filter, washed with ice-cold water, and dried in vacuo at 75 °C overnight (16 h). The crude product **14** was recrystallized from glacial acetic acid (filtered while hot) to yield a light-yellow solid (2.45 g, 66%).

M.p. 232-236 °C. ^{1}H-NMR (400 MHz, DMSO-d_6): δ = 8.74 (d, *J* = 1.8 Hz, 1 H), 8.63 (dd, *J* = 8.6, 2.2 Hz, 1 H), 8.10 (d, *J* = 8.6 Hz, 1 H), 7.80 (s, 1 H) ppm. ^{13}C-NMR (100.6 MHz, DMSO-d_6): δ = 161.2, 160.0, 148.3, 146.2, 140.8, 130.4, 129.6, 124.5, 123.3, 110.9 ppm. MS (ES-): m/z (%) = 469 (13, $[2{*}M-H]^-$), 234 (27, $[M-H]^-$), 190 (100, $[M-COOH]^-$). Anal. Calcd. for $C_{10}H_5NO_6$ (M_r = 235.15): C, 51.08; H, 2.14; N, 5.96. Found: C, 51.15; H, 2.15; N, 5.68.

2. Extended X-Ray Crystallographic Data, Collection and Refinement Details for 9*H_2O

Data Collection, Structure Solution and Refinement for 9*H_2O

A fragment of a colorless plate-like crystal of the title compound having approximate dimensions of 0.15 x 0.15 x 0.06 mm^3 was mounted on a Kapton loop using Paratone N hydrocarbon oil. All measurements were made on a Siemens SMART CCD[3] area detector with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix, obtained from a least-squares refinement using the measured positions of 978 centered reflections with $I > 10\sigma(I)$ in the range $2.36 < \theta < 15.47^\circ$ corresponded to a primitive monoclinic cell. The data were collected at a temperature of 189(2) K. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3° counted for a total of 10 seconds per frame.

Data were integrated by the program SAINT[4] to a maximum θ value of 26.43°. The data were corrected for Lorentz and polarization effects. Data were analyzed for agreement and possible absorption using XPREP.[5] An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.[6] ($T_{max} = 0.92$, $T_{min} = 0.78$). Of the 19701 reflections that were collected, 7045 were unique; equivalent reflections were merged. No decay correction was applied.

The structure was solved within the Wingx[7] package by direct methods (SIR92[8]) and expanded using Fourier techniques (SHELXL-97[9]). Hydrogen atoms (except for the two water molecules) were included but not refined. The hydrogen atoms of the water molecules could not unambiguously be assigned. H atoms were positioned geometrically, with C–H = 0.93 Å for C_{arom}-H groups, C–H = 0.97 Å for CH_2 groups, N–H = 0.89 Å, and C–H = 0.96 Å for CH_3 groups, and constrained to ride on their parent atoms. $U_{iso}(H)$ values were set at 1.2 times $U_{eq}(C)$ for all H atoms.

Table S1. Crystal Data for Complex 9*H_2O

	[Ce(TREN-1,2-HOIQO)(H_2O)]*H_2O (**9***H_2O)
formula	$C_{36}H_{34}CeN_7O_{11}$
mol. weight	880.81
crystal appearance	colorless plate
crystal system	monoclinic
space group	$P2_1/c$
a [Å]	12.341(2)
b [Å]	26.649(4)
c [Å]	10.621(2)
α [°]	90
β [°]	96.753(3)
γ [°]	90
volume [Å ^{3}]	3468.6 (9)
Z	4
ρ [g cm^{-1}]	1.69
μ [mm^{-1}]	1.39
crystal size [mm^3]	0.15 x 0.15 x 0.06
temperature [K]	189(2)
radiation [Å]	$Mo_{K\alpha}$ (λ = 0.71073)
θ max [°]	26.43
measured reflections	19701
independent reflections	7045
reflections in refinement	4123 ($I \geq 2\sigma(I)$)
parameters	496
R[a]	0.0505
wR[b]	0.0983
R[a] (all data)	0.0997
wR (all data)	0.1070
Goodness of Fit	0.887
max. final diff. e^- density [e^-/Å^3]	-0.677
min. final diff. e^- density [e^-/Å^3]	0.122

Complex Structure of [Ce(TREN-1,2-HOIQO)(H_2O)]*H_2O (9*H_2O)

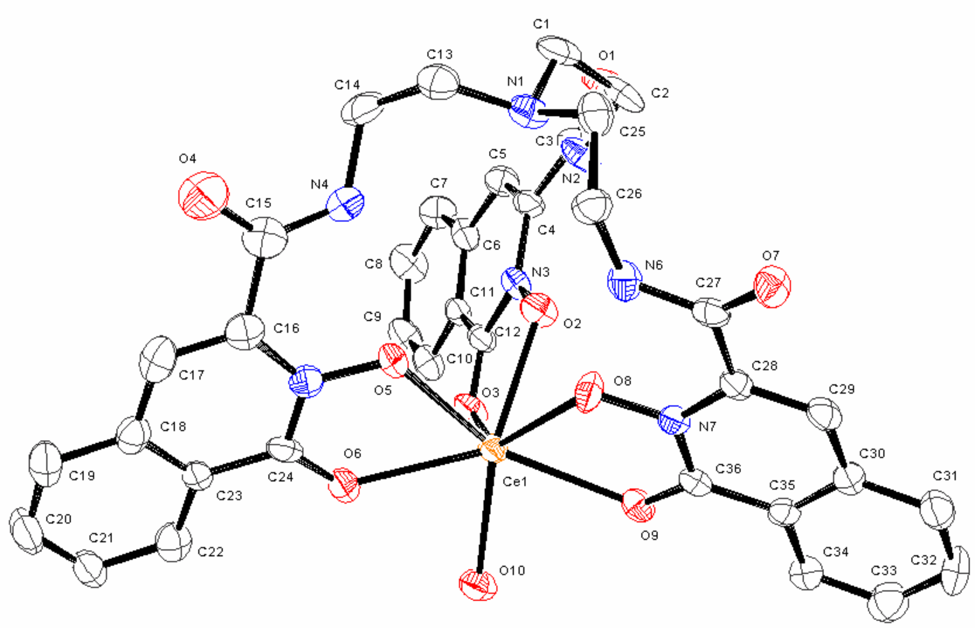
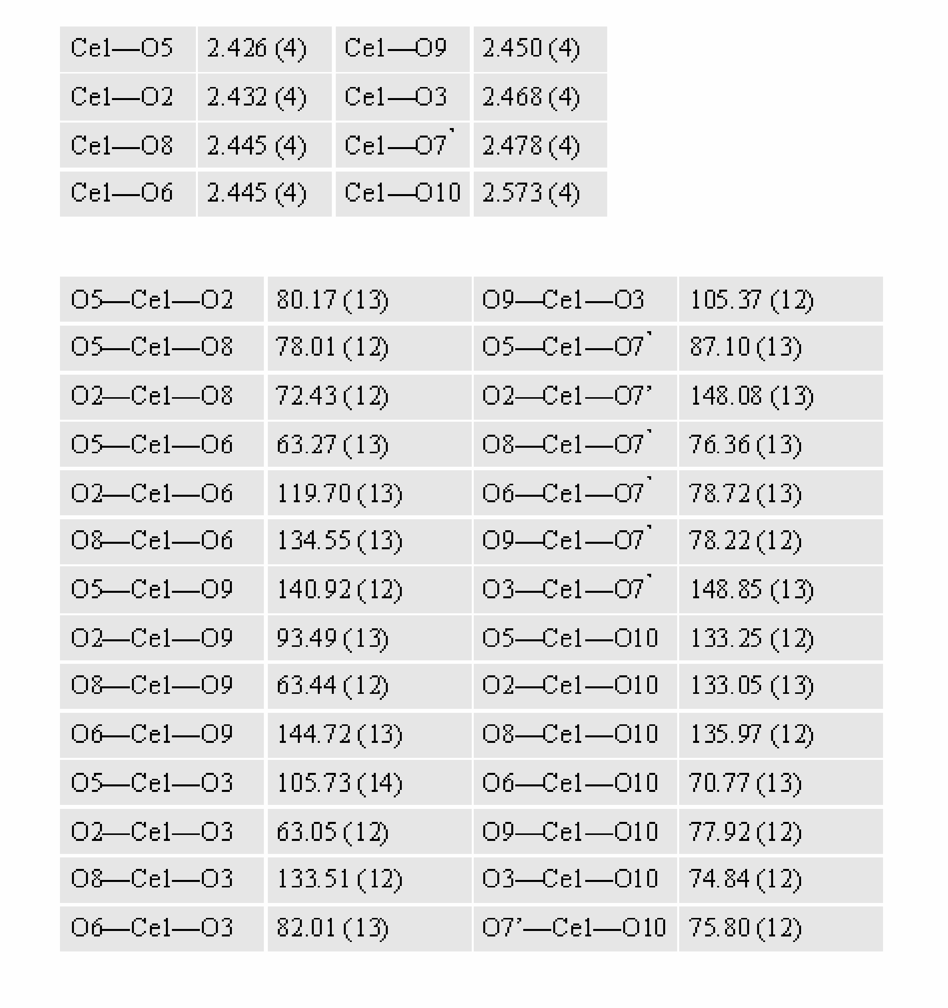


Figure S1. Asymmetric unit of [Ce(TREN-1,2-HOIQO)(H_2O)]*H_2O (**9***H_2O). Thermal ellipsoid plot (Ortep 3 for Windows,[10] 50% probability level) with atom numbering scheme. Hydrogens and the isolated water molecule are omitted for clarity.

Selected Geometric Parameters [Å,°] for [Ce(TREN-1,2-HOIQO)(H_2O)]*H_2O (9*H_2O)



Ce1—O5	2.426 (4)	Ce1—O9	2.450 (4)
Ce1—O2	2.432 (4)	Ce1—O3	2.468 (4)
Ce1—O8	2.445 (4)	Ce1—O7`	2.478 (4)
Ce1—O6	2.445 (4)	Ce1—O10	2.573 (4)

O5—Ce1—O2	80.17 (13)	O9—Ce1—O3	105.37 (12)
O5—Ce1—O8	78.01 (12)	O5—Ce1—O7`	87.10 (13)
O2—Ce1—O8	72.43 (12)	O2—Ce1—O7’	148.08 (13)
O5—Ce1—O6	63.27 (13)	O8—Ce1—O7`	76.36 (13)
O2—Ce1—O6	119.70 (13)	O6—Ce1—O7`	78.72 (13)
O8—Ce1—O6	134.55 (13)	O9—Ce1—O7`	78.22 (12)
O5—Ce1—O9	140.92 (12)	O3—Ce1—O7`	148.85 (13)
O2—Ce1—O9	93.49 (13)	O5—Ce1—O10	133.25 (12)
O8—Ce1—O9	63.44 (12)	O2—Ce1—O10	133.05 (13)
O6—Ce1—O9	144.72 (13)	O8—Ce1—O10	135.97 (12)
O5—Ce1—O3	105.73 (14)	O6—Ce1—O10	70.77 (13)
O2—Ce1—O3	63.05 (12)	O9—Ce1—O10	77.92 (12)
O8—Ce1—O3	133.51 (12)	O3—Ce1—O10	74.84 (12)
O6—Ce1—O3	82.01 (13)	O7’—Ce1—O10	75.80 (12)

Crystal Packing of [Ce(TREN-1,2-HOIQO)(H_2O)]*H_2O (9*H_2O)

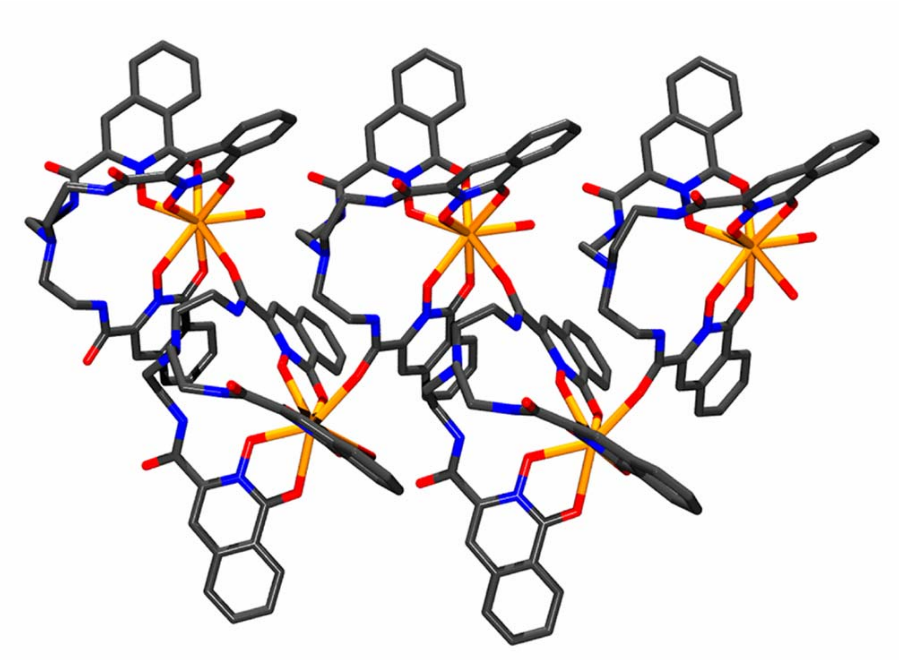


Figure S2. Part of the extended one-dimensional chain for the complex [Ce(TREN-1,2-HOIQO)(H_2O)]*H_2O (**9***H_2O).[11] Hydrogens and the isolated molecule of water in the crystal omitted for clarity.

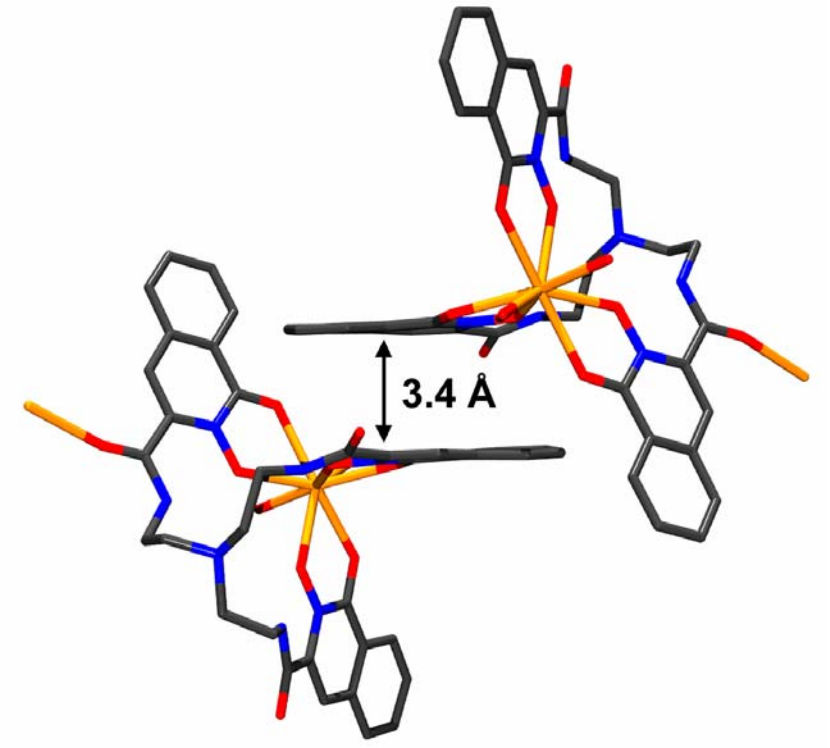


Figure S3. π-π-Stacking of the 1,2-HOIQO rings in [Ce(TREN-1,2-HOIQO)(H_2O)]*H_2O(**9***H_2O).[11] Hydrogens and the isolated molecule of water in the crystal omitted for clarity.

3. References

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