Supporting Information

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Materials and Methods. All chemicals were purchased from commercial sources and used without further purification. \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra were carried out in deuterated solvents on Bruker Avance 400 and 500 Ultrashield spectrometers. Mass analyses were performed on Waters LCT Premier (ESI or APCI mode), Waters GCT (EI and CI ionization modes) or Bruker MALDI-TOF spectrometers. Melting points were measured on a Büchi B-540 instrument with visual measurement. IR spectra were recorded on a FTIR spectrometer with an ATR cell, Tensor 27 from Bruker. Luminiscence titrations were conducted on an Amicco Bowman Series 2 spectrometer, at 298 K (thermostated by a water Peltier system), in HPLC-quality THF. 5,11,17,23-tetra-formyl-25,26,27,28-tetra-octyloxycalix[4]arene \textit{(6)} was synthesized according to published methods.\textsuperscript{[1]}

Synthesis.

\textbf{1,4-Benzene-bis-N-(2,2-dimethoxyethylidene)methanamine (3).} To a 60\% water solution of 2,2-dimethoxyacetaldehyde (34 mL, 154 mmol) \textit{p}-xylylenediamine (10.0 g, 73.4 mmol) was added at RT. The reaction mixture was stirred overnight giving a yellow homogeneous solution. The water was evaporated under vacuum affording a yellow oil which was dried under high vacuum to give \textit{3} (22.1 g, 98\%). Compound \textit{3} was directly used in the next step without further purification. \textsuperscript{1}H NMR
(400 MHz, [D₆]DMSO): $\delta=7.64$ (d, $^3J(H,H)= 4.6$ Hz, 2H; N=CH), 7.21 (s, 4H; Ar), 4.65 (d, $^3J(H,H)= 5.3$ Hz, 2H; N=CH-CH), 4.57 (d, $^3J(H,H)= 1.6$ Hz, 4H; CH₂N), 3.30 ppm (s, 12H; OMe);
$^{13}$C NMR (100 MHz, [D₆]DMSO): $\delta$ 161.8, 137.8, 128.6, 103.3, 63.6, 54.0 ppm. FT-IR (oil): $\nu =$1659 (-C=N), 1048 (O-C-O) cm$^{-1}$.

2,7-Diazaphenanthrene (4). Oleum (20% SO$_3$, 50 mL) was cooled in an ice bath and 3 (15.0 g, 48.6 mmol) was slowly added for 5 minutes. The reaction mixture was stirred overnight at RT. The mixture was carefully poured into ice (400 g) and neutralized with a saturated Na$_2$CO$_3$ solution and further basified with 2M NaOH (50 mL). The precipitate was removed away by filtration and the filtrate was extracted for 2 days in a liquid-liquid extractor with ether/THF (1:1). The solvent was dried (MgSO$_4$) and concentrated to dryness. The solid residue was further dried under high vacuum, yielding 4 (1.8 g, 21%) as a yellow solid: m. p. 140-141 ºC; $^1$H NMR (400 MHz, CDCl$_3$): $\delta= 9.30$ (d, $^4J(H,H)= 0.5$ Hz, 2H; H-1,8), 8.83 (d, $^3J(H,H)= 5.6$ Hz, 2H; H-3,6), 8.37 (d, $^3J(H,H)= 5.6$ Hz, 2H; H-4,5), 7.90 ppm (s, 2H; H-9,10); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta= 152.0, 145.8, 133.1, 127.9, 126.1, 116.3$ ppm; FT-IR (solid): $\nu =$1576, 1485, 1034, 827, 725 cm$^{-1}$; HRMS (EI): m/z calcd for C$_{12}$H$_8$N$_2$: 181.0766, found: 181.0761.

3,8-Phenanthroline-5,6-dione (5). A mixture of 4 (1.8 g, 10 mmol) and KBr (8.33 g, 70 mmol) (no solvent) was cooled at -78 ºC and stirred for 5 min. Concentrated sulphuric acid (96%, 44 mL) was added dropwise giving an emulsion. The mixture was allowed to warm to -50 ºC and nitric acid (70%, 24 mL) was slowly added affording an orange heterogeneous solution. The temperature was slowly raised to RT and then the mixture was heated at 90 ºC until the evolving red gases disappeared (16 h). After cooling to RT, the homogeneous red solution was poured into water (150 mL) and neutralized with a 1M solution of Na$_2$CO$_3$. The yellow precipitate formed was filtered off
and sequentially washed with water (3 × 50 mL) and Et2O (3 × 50 mL), yielding 5 (1.1 g, 49%) as a yellow solid: m. p. > 310 ºC (dec.); 1H NMR (400 MHz, [D6]DMSO): δ= 9.20 (s, 2H; H-4,7), 8.98 (d, 3J (H,H)= 5.5 Hz, 2H; H-2,9), 8.38 ppm (d, 3J (H,H)= 5.5 Hz, 2H; H-1,10); 13C NMR (100 MHz, [D6]DMSO): δ= 177.9, 155.5, 150.4, 140.2, 127.6, 119.07 ppm; FT-IR (solid): ν =1688, 1590, 1298, 1190, 925, 854, 735 cm⁻¹; ESI-MS (+ve): m/z 233.0 [M+Na]⁺, 443.1 [(2M+Na)]⁺; HRMS (EI) calcd for C12H6N2O2Na: 233.0327, found: 233.0338.

5,11,17,23-Tetrakis(1H-imidazo[4,5-f][3,8]phenanthroin-2-yl)-25,26,27,28-tetraoctyloxycalix[4]arene (1). A mixture of 6[1] (100 mg, 0.101 mmol), 5 (171 mg, 0.812 mmol) and ammonium acetate (1.25 g, 16.24 mmol) in glacial acetic acid (15 mL) was refluxed for 16 h. The resulting red solution was cooled to RT and concentrated under vacuum at 50 ºC. Aqueous ammonia (30%, 60 ml) was added and the resulting emulsion was sonicated. The mixture was cooled to 4 ºC and after 4 hours the resulting precipitate was filtered off, washed with ammonia and dried overnight under an air stream. The crude residue was purified by column chromatography (alumina), using a gradient of MeOH in CH2Cl2, yielding 1 (110 mg, 62%) as a yellow solid. m. p. > 380 ºC (dec.); 1H NMR (400 MHz, [D3]MeCN + CF3CO2H): δ= 10.10 (s, 8 H; Hd), 9.24 (d, 3J (H,H)= 6.6 Hz, 8H; Hb), 8.97 (d, 3J (H,H)= 6.6 Hz, 8H; Hc), 8.09 (s, 8 H; Hb), 4.81 (d, 2J (H,H)= 12 Hz, 4H; Hax), 4.23 (t, 3J (H,H)= 7.2 Hz, 8H; OCH2), 3.68 (d, 2J (H,H)= 12 Hz, 4H; Heq), 2.14 (m, 8 H; CH2), 1.55-1.35 (m, 40H; CH2), 0.93 ppm (t, 3J (H,H)= 7.2 Hz, 12H; CH3); 13C NMR (DEPTQ-135, HMQC, 100 MHz, [D3]MeCN + CF3CO2H): δ= 162.1 (C), 153.9 (Cimid), 142.3 (CHa), 138.8 (CHb), 137.9, 135.2, 130.9 (C), 129.5 (CHd), 124.3 (CHb), 122.3, 120.5 (C), 77.4 (CH2O), 33.0 (CH3), 32.0 (ArCH2Ar), 31.5, 30.9, 27.3, 23.7 (CH2), 14.6 ppm (CH3); FT-IR (solid): ν =3151, 2922, 2852, 1571, 1535, 1246, 1209 1154, 1100, 1003, 814, 737 cm⁻¹; MALDI-TOF MS (PEG2000 + HCCA): m/z 1745.9 [M+H]⁺; HRMS (MALDI-TOF) calcd for C113H113N16O4: 1745.9131, found: 1745.9040.
fac-Re(CO)$_3$Br Tetranuclear metallo-cavitand (1•Re$_4$). A mixture of 6 (40 mg, 0.023 mmol) and Re(CO)$_5$Br (39.1 mg, 0.096 mmol) in dry THF (40 mL) was refluxed under argon for two days, affording a clear orange solution. Complete I conversion was monitored by TLC (neutral alumina, CHCl$_3$/2% aq. NH$_3$/6% MeOH). The solution was cooled to RT and concentrated under vacuum to 5 ml. Then MeOH (50 ml) was added and the resulting emulsion was sonicated and maintained at 4 °C overnight. The precipitate was collected by centrifugation, sonicated with MeOH and centrifugated again until the MeOH phase was colourless. The solid residue was further dried overnight at 50 °C under vacuum, yielding 1•Re$_4$ (58 mg, 80%) as an orange solid. m. p. > 375 °C (dec.); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 14.64 (br s, 2H; NH), 13.89 (br s, 2H; NH), 10.90 (m, 8H; $H_a$), 10.11 (m, 4H; $H_b$), 9.22 (m, 4H; $H_b'$), 8.76-8.56 (m, 8H; $H_d$), 8.30 (m, 8H; $H_c$), 4.79 (m, 4H; $H_{ax}$), 4.14 (m, 8H; OCH$_2$), 3.75 (m, 4H; $H_{eq}$), 2.19 (m, 8H; CH$_2$), 2.00-0.50 ppm (m, 52H; CH$_2$, CH$_3$); $^{13}$C NMR (DEPTQ-135, HMQC, 100 MHz, CDCl$_3$):$^{[3]}$ $\delta$ = 77.2 (CH$_2$O), 32.0 (CH$_2$), 30.6 (ArCH$_2$Ar), 30.0, 29.7, 29.6, 26.2, 22.8 (CH$_2$), 14.2 ppm (CH$_3$); FT-IR (solid): $\nu$ = 2921, 2852, 2027, 1930, 1479, 1461, 1258, 1214, 1007, 814 cm$^{-1}$; ESI-MS (+ve): $m/z$ 3182.3 [M+K]$^+$, 3167.2 [M+Na]$^+$, 3147.3 [M+H]$^+$, 3063.5 [M-4CO+Na]$^+$, 2794.5 [M-Re(CO)$_3$]$^+$; HRMS (ESI) calcd for C$_{124}$H$_{113}$N$_{16}$O$_{16}$Br$_3$: 3147.3457, found: 3147.3464.
**X-ray Structure Determination.** Crystals of a nitromethane solvate of $\text{1}\cdot\text{Re}_4$ could be obtained by slow evaporation of a solution in a mixture of CHCl$_3$ and MeNO$_2$ at RT. The crystals obtained were extremely sensitive to loosing solvent and were prepared in short time under inert conditions immersed in perfluoropolyether as protecting oil for manipulation. After several trials a dataset of enough quality could be obtained.

*Data Collection.* Measurements were made on a Bruker-Nonius diffractometer equipped with a APPEX 2 4K CCD area detector, a FR591 rotating anode with Mo$_{K\alpha}$ radiation, Montel mirrors as monochromator and a Kryoflex low temperature device ($T = -173$ °C). Full-sphere data collection was used with $\omega$ and $\varphi$ scans.$^{[4]}$

*Structure Solution and Refinement.* SHELXTL Version 6.10 (Sheldrick, 2000) was used.$^{[5]}$
Luminescence Titrations. Titrations between metallo-cavitand 1•Re₄ (host) and the guests were carried out by adding small aliquots of a guest solution (1×10⁻³ M),⁶ also containing host 1•Re₄ (1×10⁻⁵ M), to a host solution (1×10⁻⁵ M) to ensure the concentration of the metallo-cavitand 1•Re₄ was maintained constant along the titration. The excitation wavelength was adjusted to 340 nm and the emission spectrum was recorded after each addition. Titration data were normalized (I/I₀) and analyzed using SPECFFIT⁷ (1:1 binding model over the whole 475-650 nm spectral width), keeping as only variables the binding constant (Kₐ) and the normalized spectrum at the saturation point. The fitting accuracy was better than 99% and the experimental error was estimated by the differences between two independent and identical assays and was found to be 15%. Phenol was used as a negative control for any non-specific luminescence change.

Figure S1. Luminescence changes (not normalized, arbitrary units) at 550 nm emission band upon guest addition and isotherm fitting of the normalized data for 7 and 12.
Figure S2. Luminescence changes (not normalized, arbitrary units) at 550 nm emission band upon addition of guests 8, 11, 13, and phenol, and isotherm fitting of the normalized data for 8 and 11.
Figure S3. Titrations comparison: normalized emission intensity vs. guest concentration ($\times 10^{-4}$ M):

11 (●); 8 (○); 7 (●) and 12 (●).
Figure S4. $^1$H NMR (400 MHz) spectra of 0.7 ml samples of: a) 1, 3.3 mM in [D$_3$]MeCN + 50 μl of CF$_3$CO$_2$H; b) 1, 3.3 mM in CDCl$_3$ + 15 μl of MeOH.
Figure S5. $^{13}$C NMR-DEPTQ-135 (100 MHz) spectrum of a 0.7 ml sample of 1, 26 mM in [D$_3$]MeCN + 50 μl of CF$_3$CO$_2$H.
Figure S6. $^1$H NMR (400 MHz, CDCl$_3$, 2.7 mM) spectrum of 1•Re$_4$. 
Figure S7. $^{13}$C NMR (125 MHz, CDCl$_3$, 18 mM) spectrum of 1•Re$_4$. 
Figure S8. $^1$H, $^1$H-2D NOESY (400 MHz, CDCl$_3$, 2.7 mM) spectrum of 1•Re$_4$.
Water crosspeaks (arrows) in blue boxes.
Figure S9. $^1$H NMR (400 MHz, [D$_8$]THF) spectra of: a) 7 (3.2 mM); b) 7 (3.2 mM) + 1•Re$_4$ (3.2 mM); c) 1•Re$_4$ (3.2 mM). Guest signals in black, host signals in green, double bar signals correspond to solvent impurities.
Figure S10. $^1$H,$^1$H-2D NOESY (400 MHz, [D$_8$]THF) spectrum of 7 (3.2 mM) + 1•Re$_4$ (3.2 mM). Water crosspeaks (blue boxes) and intermolecular contacts (green boxes) highlighted.
Figure S11. $^1$H-NMR (400 MHz, [D$_8$]THF) spectra of: a) 12 (3.2 mM); b) 12 (3.2 mM) + 1•Re$_4$ (3.2 mM); c) 1•Re$_4$ (3.2 mM).
Figure S12. $^1$H,$^1$H-2D NOESY (400 MHz, [D$_8$]THF) spectrum of 12 (3.2 mM) + 1•Re$_4$ (3.2 mM).

Water crosspeaks (blue boxes) and intermolecular contacts (green boxes) highlighted.
Figure S13. $^1$H NMR (400 MHz, [D$_8$]THF) spectra of: a) 11 (3.2 mM); b) 11 (3.2 mM) + 1•Re$_4$ (3.2 mM); c) 1•Re$_4$ (3.2 mM).
Table S1. $^1$H NMR chemical shifts $\Delta \delta$ (ppm, $\delta_{\text{complex}} - \delta_{\text{host/guest}}$) of metallo-cavitand host 1•Re$_4$ and guests 7-9 and 12 protons; 3.2 mM (1:1) 1•Re$_4$; guest mixture in [D$_8$]THF.
**Figure S14.** MALDI-TOF spectrum of $\text{1}$ in MeCN + PEG2000 + HCCA ($\alpha$-cyano-4-hydroxycinnamic acid).

**Figure S15.** ESI-MS spectrum of $1\cdot\text{Re}_4$ in MeOH + THF.
Figure S16. ESI-MS pattern of the molecular peak of 1•Re₄. Calculated (bottom) and observed (top) isotopic distribution for C₁₂₄H₁₁₃Br₄Re₄O₁₆N₁₆.

Figure S17. ESI-MS spectrum of 1•Re₄ + 7 in MeOH + CHCl₃ + 0.1% formic acid.
Figure S18. ESI-MS pattern of the molecular peak of $7@1\cdot\text{Re}_4$ complex. Calculated (bottom) and observed (top) isotopic distribution for $C_{152}H_{137}Br_4\text{Re}_4O_{20}N_{16}$. 
References


[3] Due to the presence of a mixture of stereoisomers, only the aliphatic protons could be detected. The raising of number of scans or the relaxation time (D1 up to 3 seconds) scarcely improved the results.


[6] The concentration for phenol as guest was raised to $4 \times 10^{-3}$ M.