A metallo-supramolecular approach to a half-subtractor

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Electronic Supporting information (ESI)

Physical measurements and experimental techniques

Chemicals and solvents of the highest commercial grade available were used as received.

Ligand **L** was purified by reverse-phase high-performance liquid chromatography (HPLC) using an Agilent 1100 series liquid chromatograph mass spectrometer system. Analytical HPLC was run using a LiChrospher RP-18 (5 µm) 4.6 × 150 mm analytical column from Merck. Purification of the ligand was carried out on a ZORBAX ODS C18, 94 × 250 mm reverse-phase column. The standard gradient for analytical and preparative HPLC used was 85:15 to 95:5 over 35 minutes (water/acetonitrile, 0.1% TFA).

Electrospray Ionization Mass Spectrometry (ESI-MS) was performed with an Agilent 1100 Series LC/MSD model in positive scan mode using direct injection of the purified ligand solution into the MS. The same protocol was used when studying the metal adduct, but in this case pure acetonitrile (no TFA added) was used in the analysis to avoid complex disassembly. Further ESI spectra were obtained with an LCQDECA ion trap mass spectrometer equipped with an electrospray ionization ion source and controlled by Xcalibur software 1.1 (Thermo-Finnigan).

Elemental analyses were performed on a Carlo Erba EA 1108 analyzer.

The ^{1}H NMR spectrum of **L** was recorded on a Bruker AMX-500 spectrometer, using DMSO-d_6 as solvent.

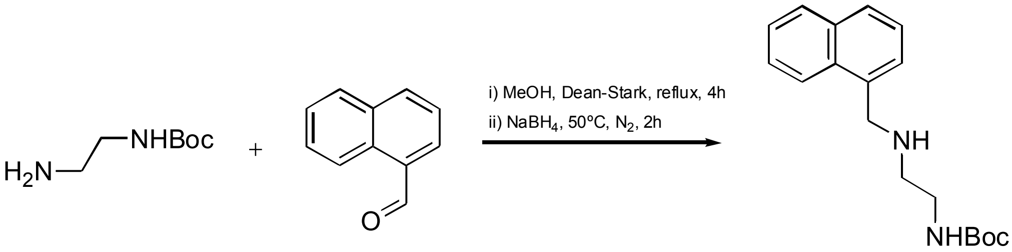
UV/Vis spectra were recorded on a Varian Cary 100 spectrophotometer.

Solution and solid-state emission spectra were recorded on a Jobin-Ivon Fluoromax 3 luminescence spectrometer.

Synthesis of *p*-xylene-bis-[*N*-(1-methylnaphthalene)ethane-1,2-diamine] (L)

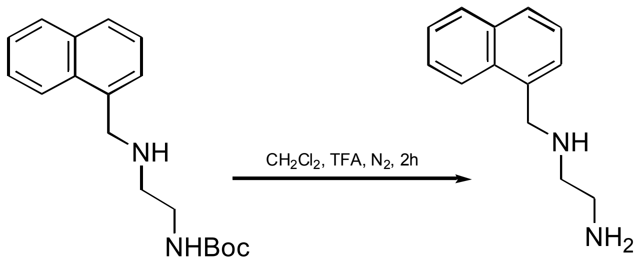
N-*tert*-Butoxycarbonyl-1,2-ethanediamine was synthesized as described in the literature.[a]

Step 1



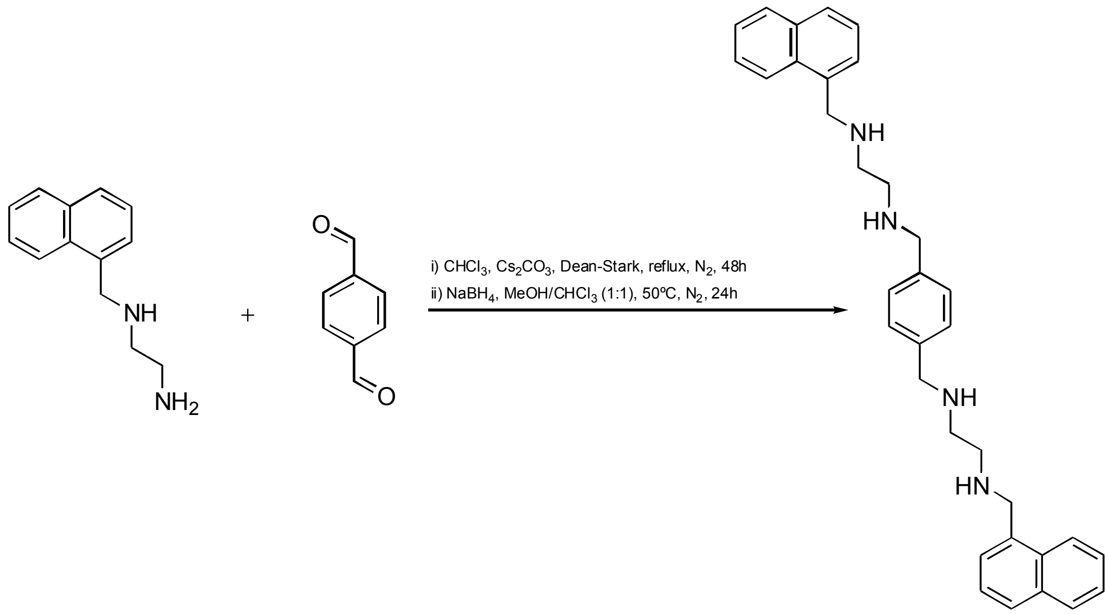
N-*tert*-Butoxycarbonyl-1,2-ethanediamine (449.5 mg, 2.80 mmol) was dissolved in methanol (125 mL) and 1-naphthaldehyde was added (440 mL, 3.08 mmol). The reaction mixture was heated under reflux. The volume of the solution was reduced over a 4 h period to ca. 50 mL, using a Dean-Stark trap, and the mixture was allowed to cool [*MS* (CH_3CN, ESI): *m*/*z* 299.1 ($M + H^+$, 100%)]. $NaBH_4$ (425 mg, 11.2 mmol) was slowly added in portions to the resulting dark yellow methanolic solution (CAUTION! This addition takes place with the development of effervescence). The reaction mixture was heated under a nitrogen atmosphere for 2 h at 50 ºC. The resulting yellow solution was filtered and then concentrated under reduced pressure. CH_2Cl_2 (50 mL) was added to the resulting yellow solid. The suspension was treated with 1M NaOH (3 × 25 mL) and the organic solution was dried over Na_2SO_4. The solvent was removed *in vacuo* to give a yellow oil. Yield: 801.3 mg (95%). *MS* (CH_3CN, ESI): *m*/*z* 301.1 ($M + H^+$, 100%).

Step 2



1-(1-Methylnaphthalene)-2-(*tert*-butoxycarbonyl)ethanediamine (801 mg, 2.67 mmol) was dissolved in CH_2Cl_2 (15 mL) and trifluoroacetic acid (15 mL) was added. The solution was stirred at room temperature under a nitrogen atmosphere for 2 h. The solution was then concentrated under reduced pressure, washed with hexane (3 × 25 mL) and dried *in vacuo*. The resulting dark yellow oil was dissolved in 1M HCl (25 mL) and then made basic with 1M NaOH to pH 10–11. The aqueous solution was extracted with CH_2Cl_2 (5 × 100 mL) and the organic solution was dried over Na_2SO_4. The solvent was removed *in vacuo* to give a yellow oil. Yield: 478.5 mg (90%). *MS* (CH_3CN, ESI): *m*/*z* 201.1 ($M + H^+$, 100%).

Step 3



1-(1-Methylnaphthalene)ethanediamine (478.5 mg, 2.39 mmol) and dried Cs_2CO_3 (3.146 g, 9.56 mmol) were added to a chloroform (150 mL) solution of terephthalaldehyde (162.1 mg, 1.19 mmol). The reaction mixture was heated under reflux under nitrogen and the volume of the solution was reduced to ca. 50 mL over a 48 h period using a Dean-Stark trap. The resulting dark yellow solution was filtered and was then allowed to cool [*MS* (CH_3CN, ESI): *m*/*z* 499.1 ($M + H^+$, 75%) 631.1 ($M + Cs^+$, 20%)]. Methanol (50 mL) and $NaBH_4$ (370 mg, 9.56 mmol) were added to the resulting dark yellow solution (CAUTION! This addition takes place with the development of effervescence). The reaction mixture was heated under nitrogen for 24 h at 50 ºC. The resulting yellow solution was filtered and then concentrated under reduced pressure. CH_2Cl_2 (50 mL) was added to the resulting yellow solid. The suspension was treated with 1M NaOH (3 × 25 mL) and the organic solution was dried over Na_2SO_4. The solvent was removed *in vacuo* to give a pale yellow solid. Yield: 528.1 mg (90%). This pale yellow solid was purified by HPLC to give a white solid.

Selected data for **L**

MS (CH_3CN, ESI): *m*/*z* 503.1 ($M + H^+$, base peak).

^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 9.305 (broad s, 2H), 8.223 (d, 2H, *J* 8.5 Hz), 8.036 (d, 4H, *J* 8.0 Hz), 7.700–7.574 (m, 8H), 7.529 (s, 4H), 4.729 (s, 4H), 4.232 (s, 4H), 3.440 (shoulder in the water peak of DMSO-d_6), 2.068 (s, 2H).

Elemental analysis: calculated for $C_{34}H_{38}N_4$: C 81.2%, H 7.6%, N 11.1%; found: C 81.3%, H 7.4%, N 11.1%.

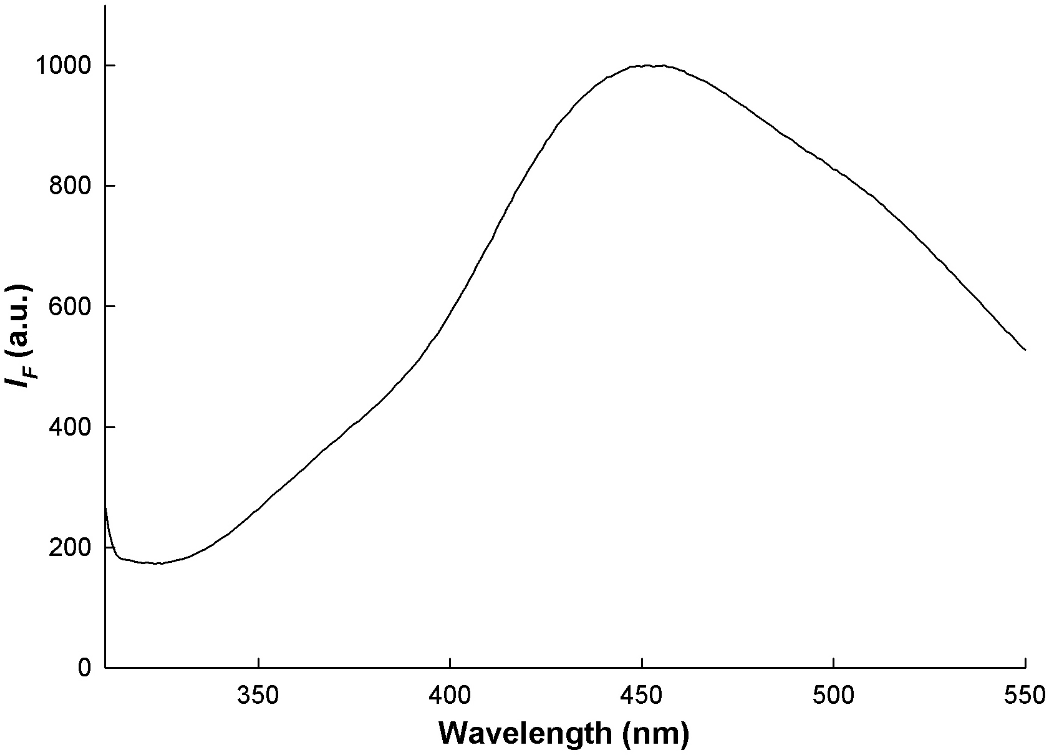
λ_{max} (ε, H_2O, pH = 2) = 281 (108000 M^{-1} cm^{-1}).

[a] A. P. Krapcho, C. S. Kuell, *Synth. Commun.*, **1990**, *20*, 2559.

Characterization of the Zn^{II}:L adduct

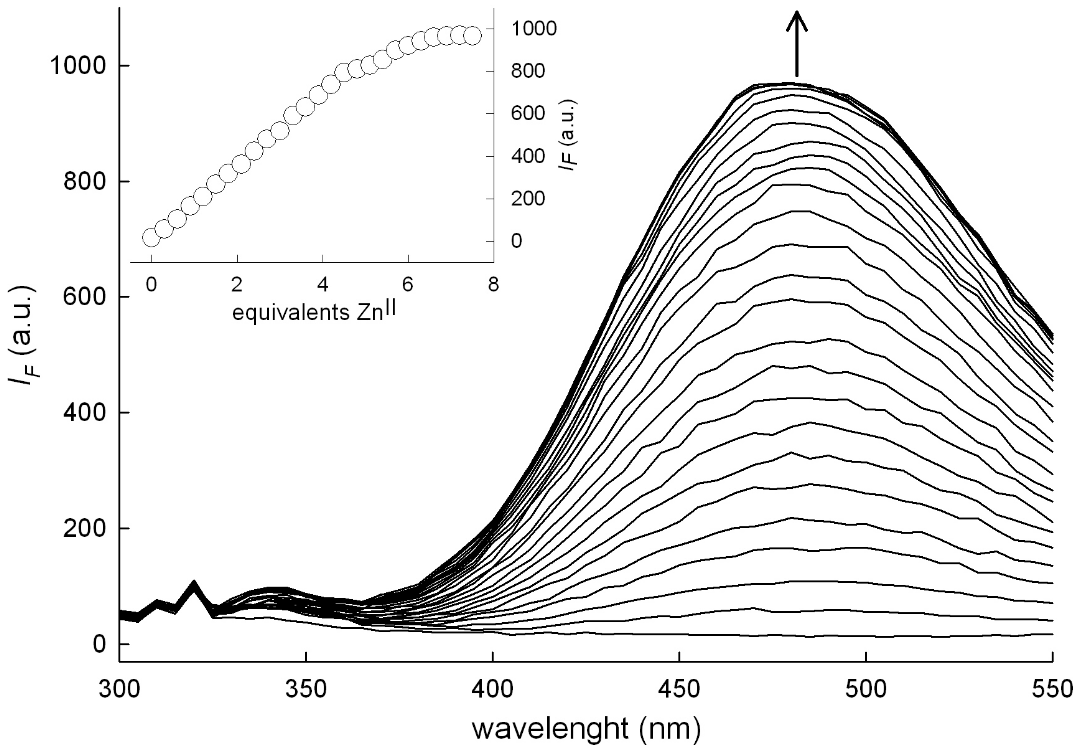
Selected data for $[Zn_n(\mathbf{L})_n]^{(2*n)+}$: MS (ESI): *m*/*z*; 1583.2 for $[Zn_2(\mathbf{L})_2(CF_3SO_3)_3]^+$; 723.6 for $[Zn_3(\mathbf{L})_3(CF_3SO_3)_3]^{3+}$; 717.4 for $[Zn_2(\mathbf{L})_2(CF_3SO_3)_2]^{2+}$ (base peak); 547.8 for $[Zn_4(\mathbf{L})_4(CF_3SO_3)_3]^{5+}$; 500.6 for $[Zn_3(\mathbf{L})_3(CF_3SO_3)_2]^{4+}$; 428.2 for $[Zn_2(\mathbf{L})_2(CF_3SO_3)]^{3+}$; 392.3 for $[Zn_5(\mathbf{L})_5(CF_3SO_3)_2]^{8+}$ and 284.1 for $[Zn_2(\mathbf{L})_2]^{4+}$. Elemental analysis found: C, 62.8; H, 5.9; N, 8.7; $C_{(34*n)}H_{(38*n)}Cl_{(2*n)}N_{(4*n)}Zn_n \cdot (n/2)H_2O$ requires C, 63.0; H, 6.1; N, 8.6.

Emission spectrum of a solid-state sample of the Zn^{II} excimer adduct



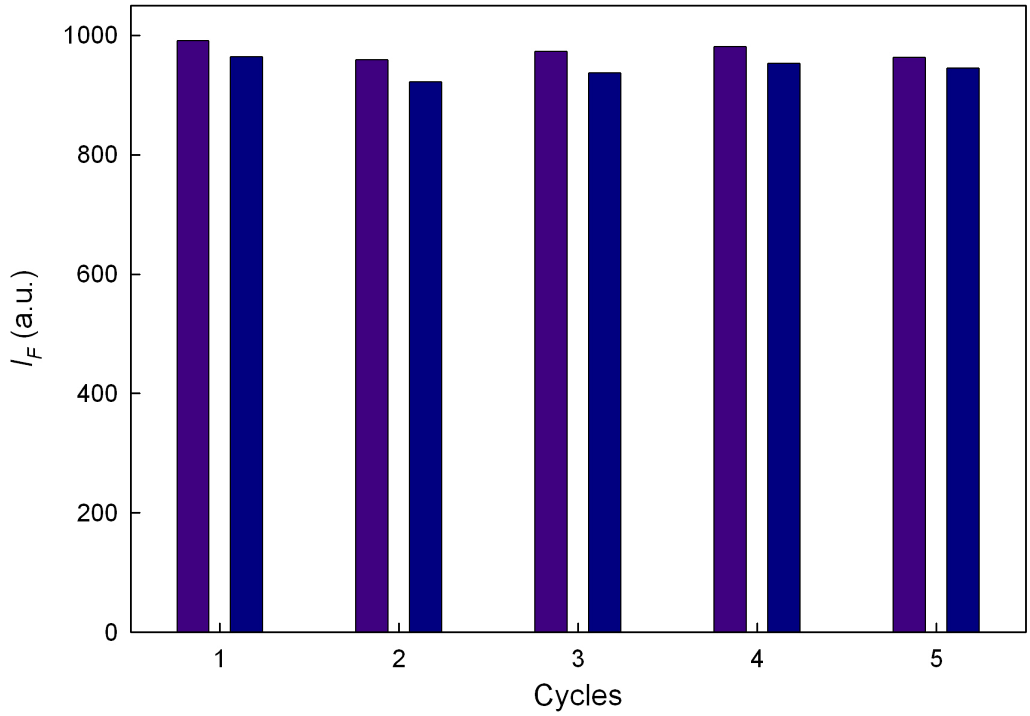
Emission spectrum of a solid-state sample of the Zn^{II} excimer adduct at 298 K using 290 nm excitation.

Spectrofluorimetric titration of L with Zn^{II} in MeCN



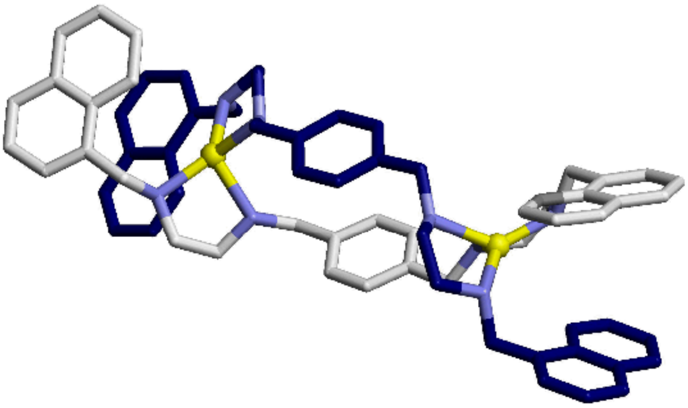
Zn^{II} titration (λ_{ex} = 290 nm) of a 500 nM solution of **L** in MeCN in the presence of ~30 equiv. of NEt_3. On addition of the metal the emission band at 480 nm increases and green fluorescence is observed.

Study of the reversibility of the logic circuit



Intensity of the fluorescence emission (λ_{ex} = 290 nm) of the 345 nm (purple bars) and 480 nm (blue bars) channels of the metallo-supramolecular half-subtractor (500 nM) during 5 cycles. One cycle consists in the consecutive addition of TFA and NEt_3 to the starting specie, as it is described in the article.

Molecular modeling studies



DFT-Optimized structure (B3LYP/LanL2DZ) of the [2+2] Zn^{II} adduct with ligand **L**, showing the close stacking interaction between the naphthalene units and the twisting of the ligands around the Zn-Zn axis.

The crude structure resulting from a molecular mechanics minimization was optimized with DFT methods as implemented by the *Gaussian 03* program[b] using the B3LYP hybrid functional and the LanL2DZ basis set.[c] The resulting structure displays a helical arrangement of the ligands around the axis defined by the two metal ions, and the naphthalene units are clearly stacked in the minimized structure. Optimization of an initial geometry in which the naphthalene units are not stacked results in a high-energy structure, which suggests the stabilizing effect of fluorophore stacking. Semiempirical analysis (PM3) of alternative conformations and ligand arrangements supports the results obtained by DFT methods. Moreover, the minimized mesocate structure, a conformation in which the naphthalene units are not stacked, was also found to be more unstable than the analogous non-stacked helical structure and, therefore, than the minimized stacked helicate. Further calculations with other coordination geometries (5 and 6) for the zinc(II) ion did not result in minimized structures. On the basis of these minimization calculations we suggest that the [2+2] helicate is favored over the analogous mesocate.

[b] *Gaussian 03, Revision C.02.* Gaussian, Inc., Wallingford CT, **2004**.

[c] i) A. D. Becke, *J. Chem. Phys.*, **1993**, *98*, 5648; ii) T. H. Dunning Jr., P. J. Hay, in *Modern Theoretical Chemistry, Vol. 3.* (Ed. Schaefer III, H. F.), Plenum, New York, **1976**, 1; iii) P. J. Hay, W. R. Wadt, *J. Chem. Phys.*, **1985**, *82*, 270.