Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

A new approach to inherent chirality through N/S ratio and/or positon in mixed heteracalix[4]arenes.

Zhongrui Chen, Olivier Siri * and Jean-Manuel Raimundo *

Centre Interdisciplinaire de Nanoscience de Marseille (CINaM), UPR 3118 CNRS

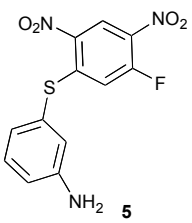
Aix-Marseille Université, Campus de Luminy, case 913

F-13288 Marseille cedex 09 (France)

siri@univmed.fr , jean-manuel.raimundo@univmed.fr

General information: Anilines and mercapto derivatives may be hazardous; handle with care and read the MSDS. All spectra ^{1}H and ^{13}C NMR spectra were recorded at 21°C in the indicated solvent with a AC250 Bruker spectrometer, operating at 250 and 62 MHz, respectively. Chemical shifts are reported in δ units, in parts per million (ppm) and the resonance multiplicity in the ^{1}H and ^{13}C NMR are described as s (singlet), d (doublet), t (triplet), m (multiplet) and broad resonance are indicated by br. Flash chromatography was performed with the indicated solvent systems using silica gel grade 60 (230-400 mesh) and TLC using E. Merck silica gel 60 F_{254} precoated plates (0.25 mm).
Elemental and MS analyses were performed by the Spectropole of Marseille and at the University of Angers (PIAM). ESI mass spectral analyses were recorded on a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer and MALDI-TOF on a Bruker AutoFlex or Bruker Biflex III apparatus.

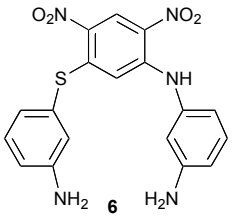
1-(3-fluoro-4,6-dinitrophenyl)-3-phenyleneamine sulphide 5



5

To a cold solution (0°C) of **3** (0.613 g, 3.00 mmol, 1.00 equiv) in 10 ml of ethanol was gradually added a solution of 3-aminothiophenol (0.338 g, 3.00 mmol, 1.00 equiv) in 2.5 ml of ethanol. After addition, the reaction mixture was stirred for 2 hours at 0°C before adding 1.05 ml $(i\text{Pr})_2\text{NEt}$ (6.00 mmol, 2.00 equiv). The reaction was stirred a further 30 min at 0°C and the obtained orange precipitate was filtered off, washed with hot water (20 ml) then carefully with cold absolute ethanol (20 ml). The orange solid was dried *in vacuo* affording the compound **5** in 71 %. ^{1}H NMR ($CDCl_3$): δ ppm 9.06 (d, 1H, J = 7.0 Hz); 7.33 (t, 1H, J = 8.7 Hz); 6.95-6.85 (m, 3H); 6.79 (d, 1H, J = 12.0 Hz); 3.91 (br s, 2H, NH_2). ESI-MS m/z for $C_{12}H_8FN_3O_4S$: 310 $[M + H]^+$, 327 $[M + NH_4]^+$, 332 $[M + Na]^+$, 348 $[M + K]^+$. Elemental Analysis calcd for $C_{12}H_8FN_3O_4S$: C, 46.60; H, 2.61; N, 13.59; S, 10.37 Found: C, 46.75; H, 2.64; N, 13.60; S, 10.04.

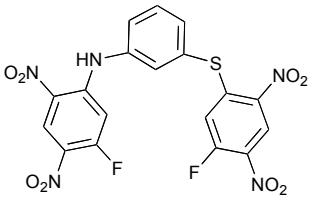
1-(4,6-dinitro-(3-*N*-(1,3-phenylenediamino)-phenyl)-3-phenyleneamine sulphide 6



6

At 0°C and under argon atmosphere was solubilised in 12 ml of dry THF 250 mg of 3-aminothiophenol (1.99 mmol, 1.05 equiv). To this solution was added 80 mg of NaH 60% in mineral oil (1.99 mmol, 1.05 equiv) and after stirring 30 min. at 0°C 555 mg of **4** was added (1.90 mmol, 1.00 equiv). The reaction mixture was warmed up to RT and stirred for 3 hours. The solvent was removed under reduce pressure and the crude product was purified by flash chromatography through SiO_2 (CH_2Cl_2 / AcOEt 9:1) affording **8** as a violet-black solid in 94%. ^{1}H NMR ($(CD_3)_2SO$): δ ppm 9.73 (s, 1H, NH); 8.97 (s, 1H); 7.07 (t, 1H, J = 7.5 Hz); 6.91 (t, 1H, J = 8.0 Hz); 6.65-6.57 (m, 4H); 6.37 (dd, 1H, J = 8.0 Hz, J = 1.5 Hz); 6.24 (t, 1H, J = 2.0 Hz); 6.10 (dd, 1H, J = 8.0 Hz, J= 1.2 Hz); 5.37 (br s, 2H, NH_2); 5.18 (br s, 2H, NH_2). ^{13}C NMR ($(CD_3)_2SO$): δ ppm :150.32; 149.62; 147.18; 144.00; 137.06; 132.90; 130.54; 129.48; 128.69; 128.13; 125.92; 121.81; 119.27; 115.99; 112.75; 112.06; 110.84; 109.17. ESI-MS m/z for $C_{18}H_{15}N_5O_4S$: 398 $[M + H]^+$, 420 $[M + Na]^+$. Elemental Analysis calcd for $C_{18}H_{15}N_5O_4S$: C, 54.40; H, 3.80; N, 17.62; S, 8.07 Found: C: 54.55; H: 3.89; N: 17.56; S: 8.00.

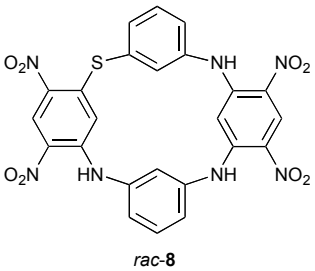
N-bis-(3-fluoro-4,6-dinitrophenyl)-1,3-phenyleneamine sulfide 7



7

To an ice cold solution of **3** (0.205 g, 1 mmol, 1.0 equiv) in 5 ml of THF was added dropwise a solution of the compound **5** (0.309 g, 1 mmol, 1 equiv) dissolved in 5 ml of THF. The reaction was stirred at 0°C for 1 hour then 0.440 ml of $(i\text{Pr})_2$NEt (2.50 mmol, 2.5 equiv) was added. The reaction was then warmed up to room temperature and left under stirring for 18 hours. The solvent was removed under reduced pressure and the crude product was purified by column chromatography over SiO_2 (CH_2Cl_2) affording the titled compound **7** as a yellow solid in 61%. ^{1}H NMR ($(CD_3)_2SO$): δ ppm 10.29 (s, 1H, NH); 8.96 (d, 1H, J = 7.0 Hz); 8.92 (d, 1H, J = 8.0 Hz); 7.78-7.66 (m, 4H); 7.13 (d, 1H, J = 14.5 Hz); 7.04 (s, 1H, J = 12.0 Hz). ESI-MS m/z for $C_{18}H_9F_2N_5O_8S$: 511 $[M + NH_4]^+$, 516 $[M + Na]^+$, 532 $[M + K]^+$. Elemental Analysis calcd for $C_{18}H_9F_2N_5O_8S$: C, 43.82; H, 1.84; N, 14.20; S, 6.50 Found: C, 43.75; N, 13.95; H, 2.19; S, 6.64.

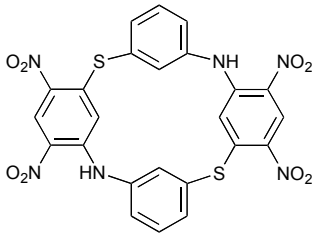
rac-1-thia-7,13,19-triaza-9,11,21,23-tetranitrocalix[4]arene 8



rac-8

At room temperature, under an atmosphere of Ar, was solubilized in 10 ml of dry CH_3CN 0.150 g of compound **6** (0.38 mmol, 1 equiv) and 0.077 g of **3** (0.38 mmol, 1 equiv). To the reaction mixture was added 0.262 ml of $(i\text{Pr})_2$NEt (1.50 mmol, 4 equiv) and the latter one was heated under reflux for 18 hours. The obtained yellow-orange precipitate was filtered off, washed with 20 ml of hot water followed by 30 ml of ethanol. The solid was dried and afford the macrocycle **8** in 80 %. ^{1}H NMR ($(CD_3)_2SO$): δ ppm 10.03 (s, 1H, NH), 9.73 (s, 1H, NH), 9.70 (s, 1H, NH), 9.04 (s, 1H), 8.99 (s, 1H), 7.50 (m, 3H), 7.37-7.30 (m, 2H), 7.20-7.12 (m, 2H), 7.00 (sbr, 1H), 5.81 (s, 1H), 4.94 (s, 1H). Maldi-TOF-MS m/z for $C_{24}H_{15}N_7O_8S$: 668.0 $[M+Ag]^+$. Elemental Analysis calcd for $C_{24}H_{15}N_7O_8S$: C, 51.34; H, 2.69; N, 17.46; S, 5.71 Found: C, 50.36; N, 17.57; H, 2.60; S, 5.30.

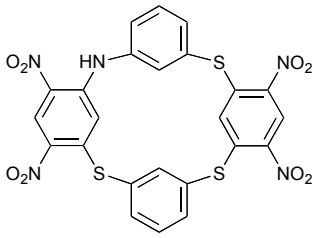
rac-1,13-dithia-7,19-diaza-9,11,21,23-tetranitrocalix[4]arene 9



rac-**9**

150 mg (0.49 mmol) of **5** was refluxed in 10 mL of dry CH_3CN over 18 h. The obtained precipitate was filtered off washed with hot water then ethanol. The solid was dried *in vacuo* leading the macrocycle **9** in 52%. ^{1}H NMR ($(CD_3)_2SO$): δ ppm 10.01 (s, 2H, NH), 9.02 (s, 2H), 7.62-7.49 (m, 4H), 7.36-7.33 (m, 4H), 5.80 (s, 1H). Maldi-TOF-MS m/z for $C_{24}H_{14}N_6O_8S_2$: 577.6 $[M-H]^+$. Elemental Analysis calcd for $C_{24}H_{14}N_6O_8S_2$: C, 49.83; H, 2.44; N, 14.53; S, 11.08. Found: C, 49.86; N, 14.10; H, 2.70; S, 11.50.

rac-1,7,19-trithia-13-aza-9,11,21,23-tetranitrocalix[4]arene 10



rac-**10**

At room temperature, under an atmosphere of Ar, was solubilized in 10 ml of dry acetonitrile 0.150 g of compound **7** (0.30 mmol, 1 equiv) and 0.045 g of 3-mercaptothiophenol (0.31 mmol, 1.03 equiv). The solution was heated to reflux for 2 hours then 211 μl of $(i\text{Pr})_2$NEt (1.20 mmol, 4 equiv). A yellow precipitate appears and the mixture was heated under reflux for 18 hours. The obtained yellow precipitate was filtered off washed with 20 ml of hot water then 30 ml of ethanol. The solid was dried leading to the macrocycle **10** as a yellow solid in 71 %. ^{1}H NMR ($(CD_3)_2SO$): δ ppm 10.09 (s, 1H, NH), 9.05 (s, 1H), 9.02 (s, 1H), 7.50 (m, 3H), 7.37-7.30 (m, 2H), 7.75-7.67 (m, 4 H), 7.67-7.61 (m, 1H), 7.55-7.52 (m, 1H), 7.40 (m, 2H), 6.57 (s, 1H), 5.84 (s, 1H). Maldi-TOF-MS m/z for $C_{24}H_{13}N_5O_8S_3$: 594.6 $[M-H]^+$.Elemental Analysis calcd for $C_{24}H_{13}N_5O_8S_3$: C, 48.40; H, 2.20; N, 11.76; Found: C, 48.74; N, 11.03; H, 2.26.

Crystallographic data (compounds **8** and **9**)

Crystal data for compound **8** (crystals of **8** were obtained by slow diffusion of DMSO into a Et_2O solution) : M_w = 717.75, monoclinic, yellow crystal (0.2 x 0.15 x 0.1 mm^3), a = 13.235(1) Å, b = 19.2584(9) Å, c = 14.094(1) Å, β = 101.675(3)°, V = 3518.0(4) $Å^3$, space group P $2_1/c$, Z = 4, ρ = 1.36 $g.cm^{-3}$, μ(MoKα) = 2.73 cm^{-1}, 31875 reflections measured at 228 K (Nonius Kappa CCD diffractometer[Nonius (1998). Kappa CCD Reference Manual. Nonius B.V., P.O. Box 811, 2600 Av, Delft, The Netherlands]) in the 1.9-28.35° θ range, 8411 unique (Rint=0.158), 487 parameters refined on F^2 (Shelxl[Sheldrick, G.M. (1997). SHELXL97. Program for the refinement of crystal structures. Univ. of Göttingen, Germany]) to final indices $R[F^2>4\sigma F^2]$: 4517 refl.] = 0.175, wR[all refl.] = 0.44 $[w=1/[\sigma^2(Fo^2)+(0.14P)^2+10P]$ where $P=(Fo^2+2Fc^2)/3]$.

Crystal data for compound **9** (crystals of **9** were obtained by slow diffusion of DMSO into a Et_2O solution) : M_w = 734.79, monoclinic, yellow crystals (0.3 x 0.18 x 0.1 mm^3), a = 24.4209(6) Å, b = 9.2343(3) Å, c = 14.7501(4) Å, β = 99.044(2)°, V = 3284.94(16) $Å^3$, space group C 2/c, Z = 4, ρ = 1.49 $g.cm^{-3}$, μ(MoKα) = 3.54 cm^{-1}, 122018 reflections measured at 293 K (Nonius Kappa CCD diffractometer [Nonius (1998). Kappa CCD Reference Manual. Nonius B.V., P.O. Box 811, 2600 Av, Delft, The Netherlands]) in the 1.7-28.6° θ range, 4060 unique (Rint=0.364), 217 parameters refined on F^2 (Shelxl[Sheldrick, G.M. (1997). SHELXL97. Program for the refinement of crystal structures. Univ. of Göttingen, Germany]) to final indices $R[F^2>4\sigma F^2]$: 2822 refl.] = 0.074, $wR[w=1/[\sigma^2(Fo^2)+(0.1575P)^2+4.6592P]$ where $P=(Fo^2+2Fc^2)/3]$ = 0.279. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC 818496 and 818497 for **8** and **9**, respectively).

Supramolecular views for compound **9**

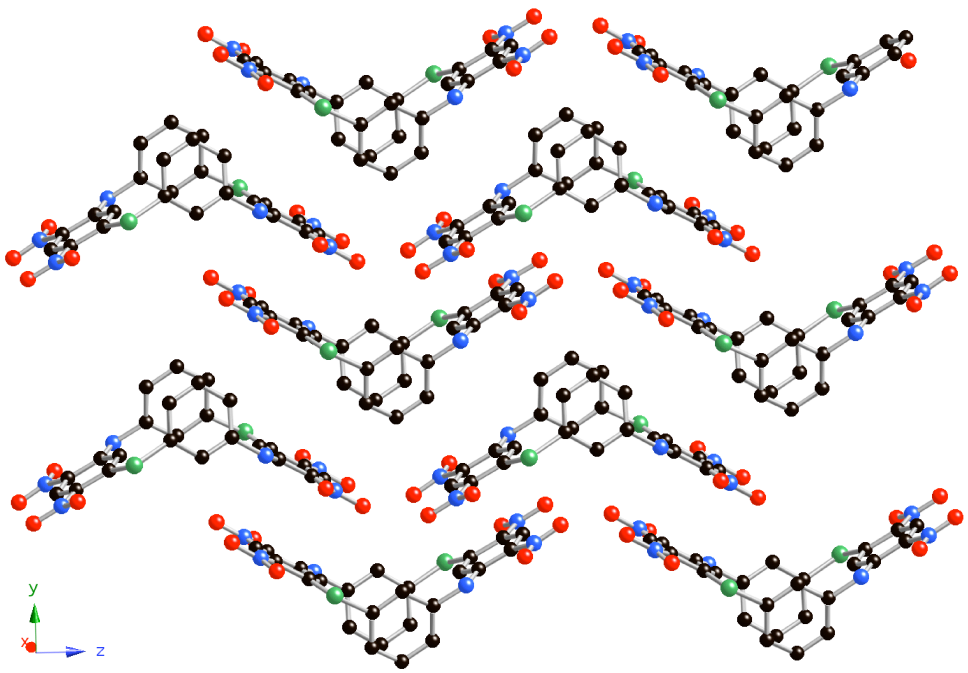


Fig. S1

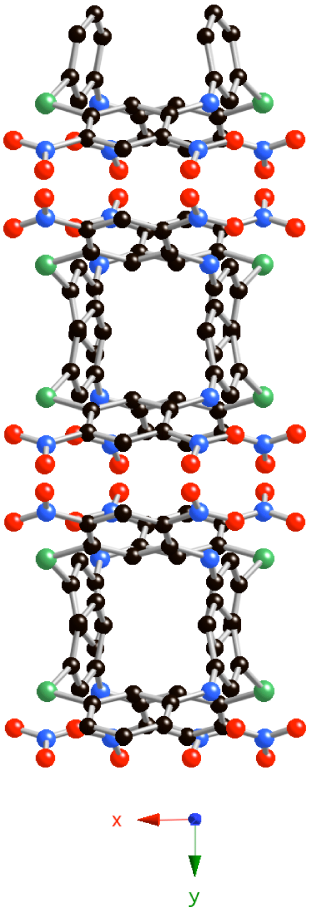


Fig. S2