Electronic Supplementary Information (ESI)
for the paper

Large shape-persistent metal-invertible 15-Nsp^2-donor-atom macrocycles functioning as trinucleating ligands

Synthetic procedures

Metal-free synthesis of **3**

32.6 mg 2,6-diacetylpyridine **1a** (0.2 mmol) and 33.6 mg 4,6-di(methylhydrazino)pyrimidine **2a** (0.2 mmol) were heated under reflux in 6.5 mL chloroform for 4 days. The [3+3] macrocycle **3** was isolated as a yellow precipitate (it was filtered by suction, washed with 3 mL chloroform and dried under vacuum; average yield 40%). The [2+2] macrocycle was isolated (average yield 16%) from the filtrate by column chromatography on alumina (elution with dichloromethane/chloroform 1/0, 9/1, 8/1, 7/3 (v/v)). The [3+3] macrocycle **3** is less soluble than the [2+2] macrocycle.

Template synthesis of **3**

32.6 mg 2,6-diacetylpyridine **1a** (0.2 mmol), 33.6 mg 4,6-di(methylhydrazino)pyrimidine **2a** (0.2 mmol) and 101 mg $Pb(CF_3SO_3)_2$ (0.2 mmol) were heated under reflux in 10 mL acetonitrile for 15 days. The solution was cooled, tris(2-aminoethyl)amine (tren; 60 mg, 0.41 mmol) was added and the mixture was stirred overnight at room temperature. The resulting precipitate was washed three times with 10 mL acetonitrile by centrifugation, then dried under vacuum. Purification by column chromatography on alumina with dichloromethane/chloroform mixtures gave the [3+3] macrocycle **3** (average yield 30%).

Synthesis of complexes

1 mg macrocycle **3** was mixed with 0.4 mL CD_3CN and the resulting suspension was sonicated for 3-5 min. This suspension was mixed with a mixture made of 3 equivalents of $M(CF_3SO_3)_2$ (M = Hg, Pb) and 0.2 mL CD_3CN. The final mixture containing the ligand and the mercury salt was stirred at room temperature for 1,5 h. The final mixture containing the ligand and the lead salt was heated for 20-25 min at 100°C in an NMR tube with a screw cap immersed in the heating liquid up to the vertical centre of the solution. The solutions of the complexes are yellow.

Characterization of macrocycles from 2,6-diacetyl-pyridine and 4,6-dihydrazino-pyrimidine

[2+2] macrocycle

^{1}H RMN (400 MHz; solvent: $CDCl_3$; reference: $CHCl_3$ residual peak δ = 7.26 ppm): 8.47 (s, 2H), 8.04 (d, *J* = 4 Hz, 6H), 7.59 (t, *J* = 8 Hz, 2H), 5.66 (s, 2H), 3.42 (s, 12H), 2.42 (s, 12H) ppm. ^{13}C RMN (100 MHz; solvent: $CDCl_3$; reference: $CDCl_3$ peak δ = 77 ppm): 168.9, 163.4, 157.1, 154.2, 136.3, 122.3, 86.8, 37.0, 14.7 ppm. ESI-MS (m/z): $\{[2+2]H\}^+ = C_{30}H_{34}N_{14}H^+$, calcd. 591.31, found 591.32.

[3+3] macrocycle **3**

^{1}H RMN (400 MHz; solvent: $CDCl_3$; reference: $CHCl_3$ residual peak δ = 7.26 ppm): 8.52 (s, 3H), 8.31 (d, *J* = 8 Hz, 6H), 7.69 (t, *J* = 8 Hz, 3H), 6.80 (s, 3H), 3.52 (s, 18H), 2.60 (s, 18H) ppm. ^{13}C RMN (100 MHz; solvent: $CDCl_3$; reference: $CDCl_3$ peak δ = 77 ppm): 164.6, 163.7, 156.7, 155.2, 135.7, 120.7, 87.5, 38.9, 17.1 ppm. ESI-MS (m/z): $\{[3+3]H\}^+ = C_{45}H_{51}N_{21}H^+$, calcd. 886.47, found 886.47.

*Characterization of metal complexes generated by macrocycle **3***

$Hg_3\mathbf{3}(OTf)_6$

^{1}H RMN (400 MHz; solvent: CD_3CN; reference: CHD_2CN residual peak δ = 1.94 ppm): 8.53-8.30 (m, 12H), 6.60 (s, 3H); 3.74 (s, 18H), 2.81 (s, 18H) ppm. ^{13}C RMN (100 MHz, solvent: CD_3CN; reference: $CD_3\underline{\mathbf{C}}N$ peak δ = 118.2 ppm; triflate peaks are not given): 161.1, 160.7, 158.3, 147.1, 144.4, 128.6, 92.5, 43.0, 18.7 ppm. ESI-MS (m/z): $[Hg_3\mathbf{3}(CF_3SO_3)_2]^{4+} = C_{47}H_{51}F_6Hg_3N_{21}O_6S_2^{4+}$, calcd. 446.32, found 446.32; $[Hg_3\mathbf{3}(CF_3SO_3)_3]^{3+} = C_{48}H_{51}F_9Hg_3N_{21}O_9S_3^{3+}$, calcd. 645.08, found 645.08; $[Hg_3H_2O\mathbf{3}(CF_3SO_3)_3]^{3+} = C_{48}H_{53}F_9Hg_3N_{21}O_{10}S_3^{3+}$, calcd. 651.08, found 651.08; $[Hg_3\mathbf{3}(CF_3SO_3)_4]^{2+} = C_{49}H_{51}F_{12}Hg_3N_{21}O_{12}S_4^{2+}$, calcd. 1042.09, found 1042.08; $[Hg_3H_2O\mathbf{3}(CF_3SO_3)_4]^{2+} = C_{49}H_{53}F_{12}Hg_3N_{21}O_{13}S_4^{2+}$, calcd. 1050.59, found 1050.59.

$Pb_3\mathbf{3}(OTf)_6$

^{1}H RMN (400 MHz, solvent: CD_3CN; reference: CHD_2CN residual peak δ = 1.94 ppm): 8.59 (s, 3H), 8.46 (t, 3H, *J* = 8 Hz), 8.33 (d, 6H, *J* = 8 Hz), 6.31 (s, 3H), 3.60 (s, 18H), 2.65 (s, 18H) ppm. ^{13}C RMN (100 MHz; solvent: CD_3CN; reference: $CD_3\underline{\mathbf{C}}N$ peak δ = 118.2 ppm; triflate peaks are not given): 170.4, 163.4, 158.5, 153.2, 142.9, 128.8, 86.2, 42.5, 19.2 ppm. ESI-MS (m/z): $[Pb_3\mathbf{3}(CF_3SO_3)_5]^+ = C_{50}H_{51}F_{15}N_{21}O_{15}Pb_3S_5^+$, calcd. 2253.15, found 2253.21.

Figure S1. Structural formulae and stylized representations of possible non-macrocyclic precursors of the [3+3] macrocycle **3**

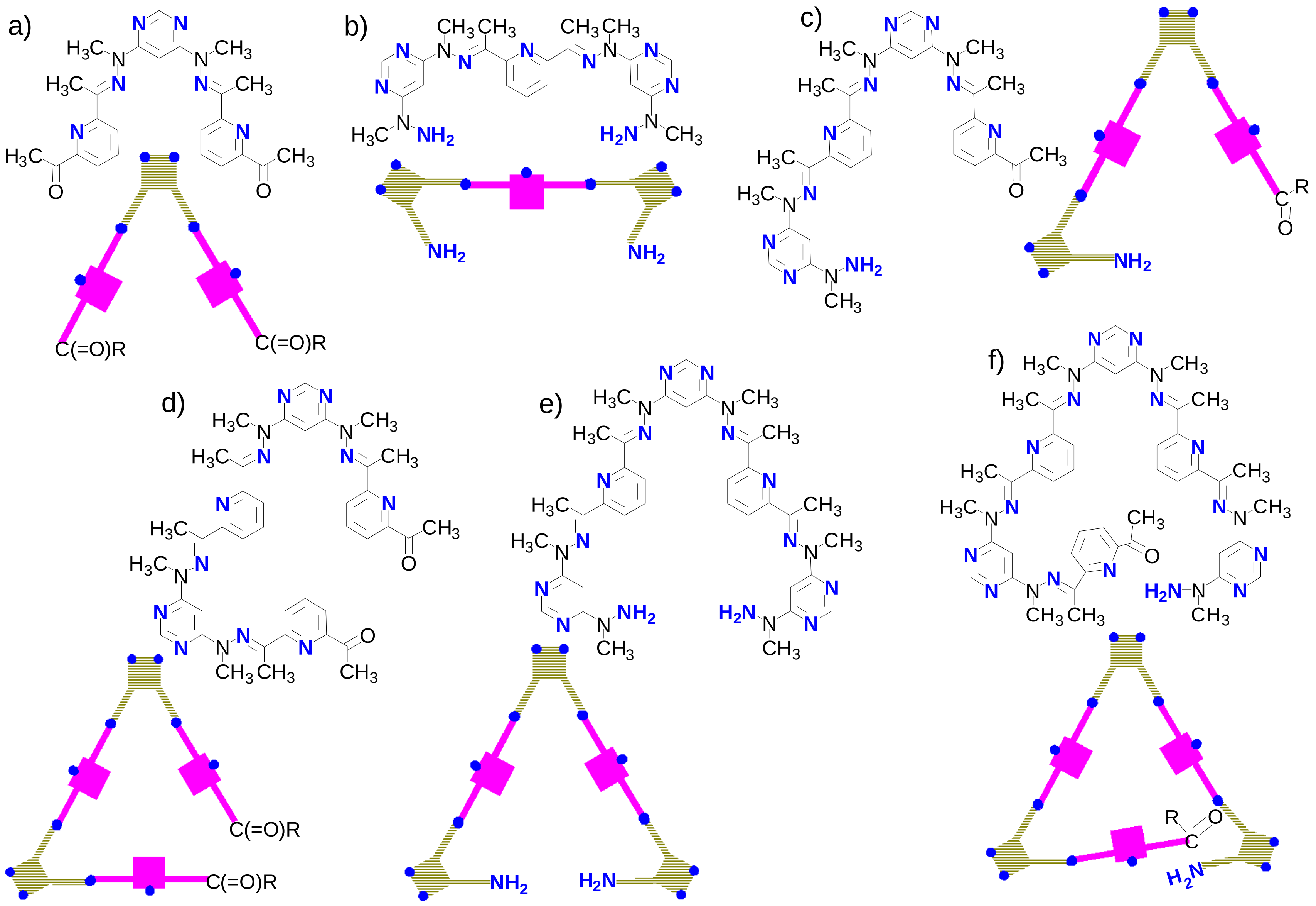
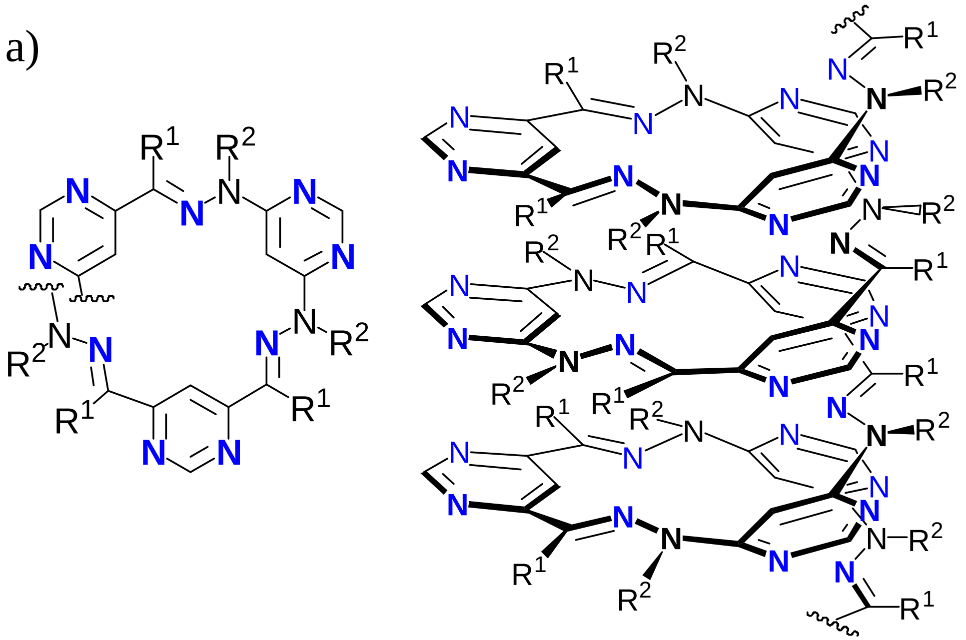
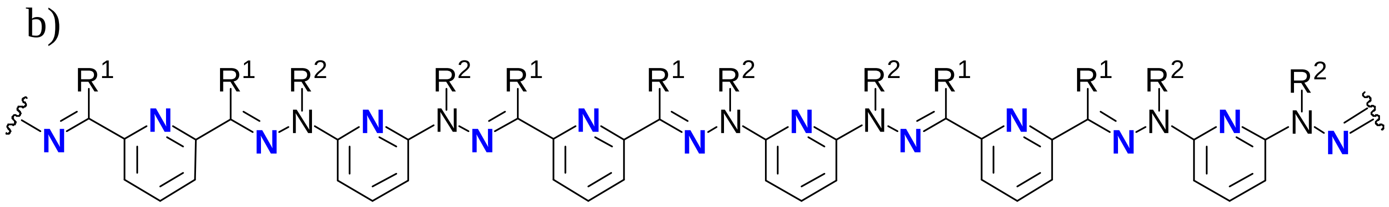


Figure S2. Structural formulae of helical (pyrimidine-hydrazone)$_n$ (a) and linear (pyridine-hydrazone)$_n$ (b) strands.



See:

J.-L. Schmitt, A.-M. Stadler, N. Kyritsakas and J.-M. Lehn, *Helv. Chim. Acta,* 2003, **86**, 1598-1624.
J.-L. Schmitt and J.-M. Lehn, *Helv. Chim. Acta,* 2003, **86**, 3417-3426.

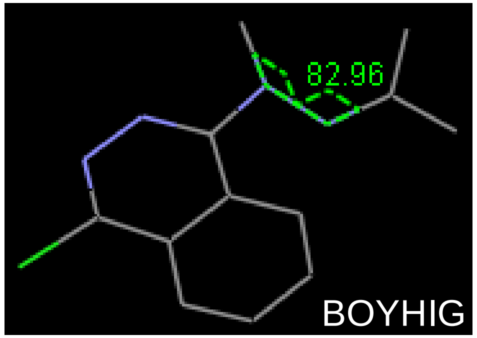


See:

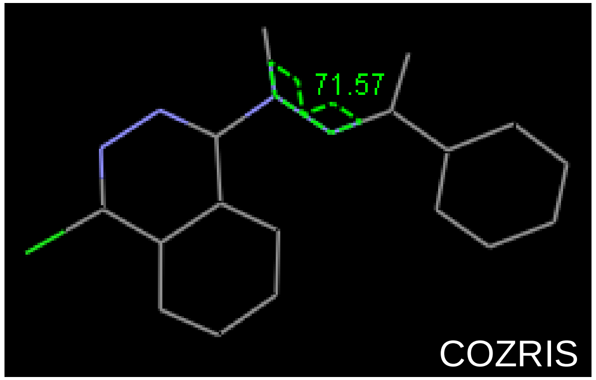
A.-M. Stadler, N. Kyritsakas and J.-M. Lehn, *Chem. Commun.*, 2004, **18**, 2024-2025.

Figure S3. Values of $-C=N-N-CH_3$ torsion angles from $-C(CH_3)=N-N(CH_3)-$ units

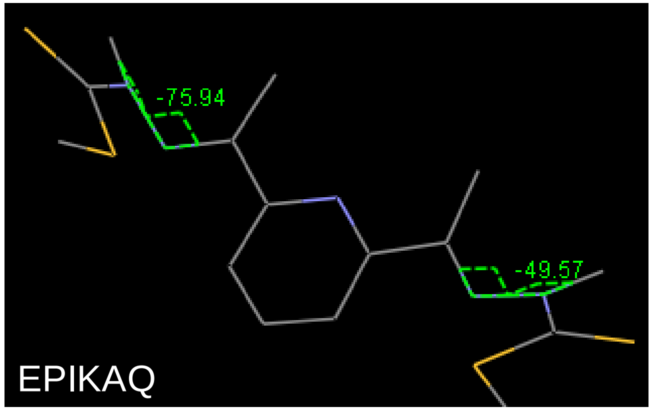
(the 6-letter words in capital letters are the corresponding CSD reference codes)



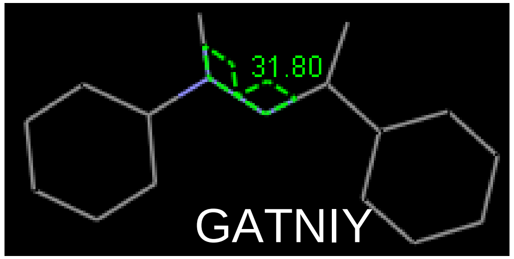
I. A. Litvinov, Y. T. Struchkov, N. N. Bystrykh and B. I. Buzykin, *Khim. Geterot. Soedin.,* 1982, 1100.



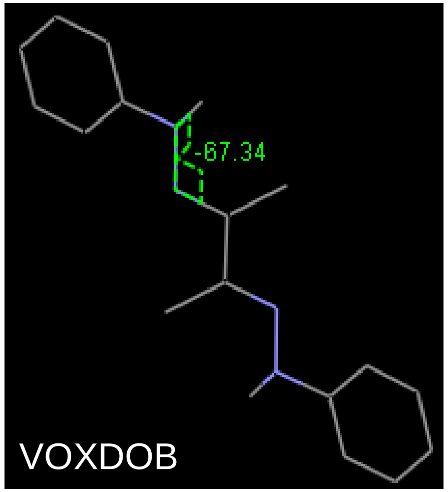
A. A. Espenbetov, Y. T. Struchkov, B. I. Buzykin and N. N. Bystrykh, *Izvest. Akad. Nauk Kazakh. SSR, Ser. Khim.,* 1984, 69.



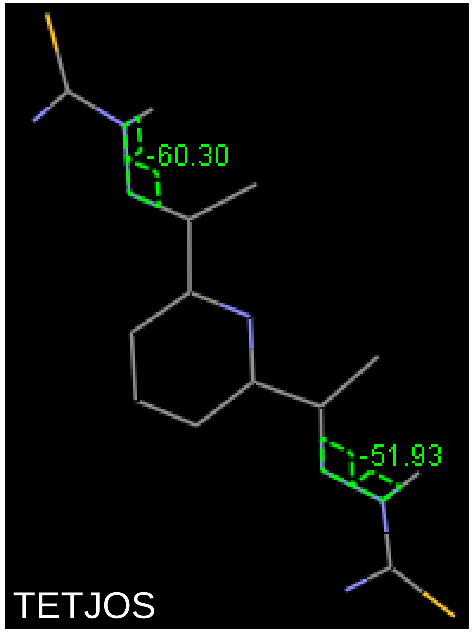
M. A. Ali, A. H. Mirza, C. Y. Yee, H. Rahgeni and P. V. Bernhardt, *Polyhedron*, 2011, **30**, 542.



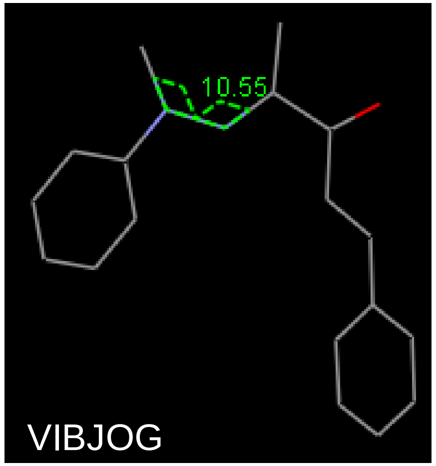
G. Tosi, L. Cardellini, G. Bocelli, *Acta Crystallogr. Sect. B,* 1988, **44**, 55.



G. Bocelli, A. Cantoni and G. Tosi, *Acta Crystallogr. Sect.C,* 1992, **48**, 1041.



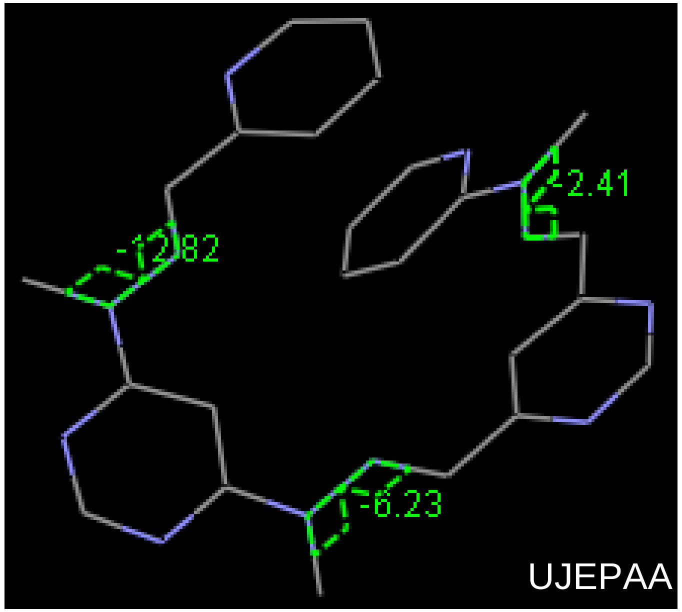
M. A. Ali, A. H. Mirza, W. B. Ejau and P. V. Bernhardt, *Polyhedron*, 2006, **25**, 3337.



J. Dieker, R. Frohlich and E.-U. Wurthwein, *Eur. J. Org. Chem.* 2006, 5339.

Figure S4. Values of -C=N-N-CH_3 torsion angles from several -CH=N-N(CH_3)- units

(the 6-letter words in capital letters are the corresponding CSD reference codes)

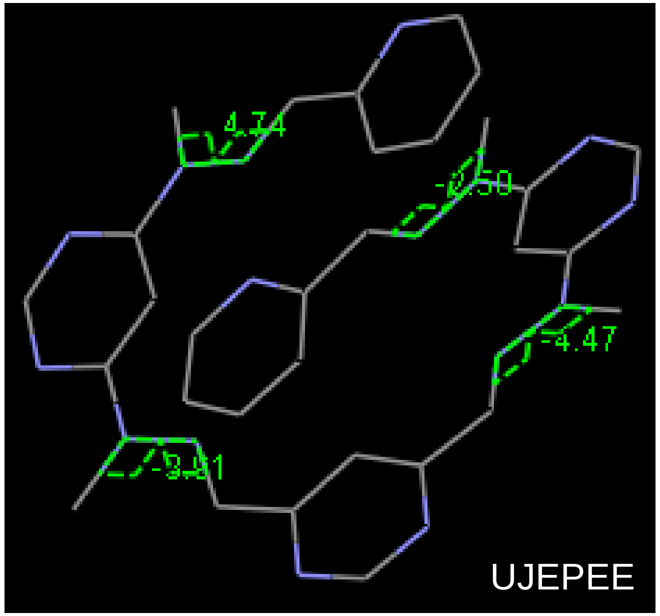


J.-L. Schmitt, A.-M. Stadler, N. Kyritsakas and J.-M. Lehn, *Helv. Chim. Acta,* 2003, **86**, 1598.

Absolute values:
2.41°

6.23°

12.82°



J.-L. Schmitt, A.-M. Stadler, N. Kyritsakas and J.-M. Lehn, *Helv. Chim. Acta,* 2003, **86**, 1598.

Absolute values:
2.5°

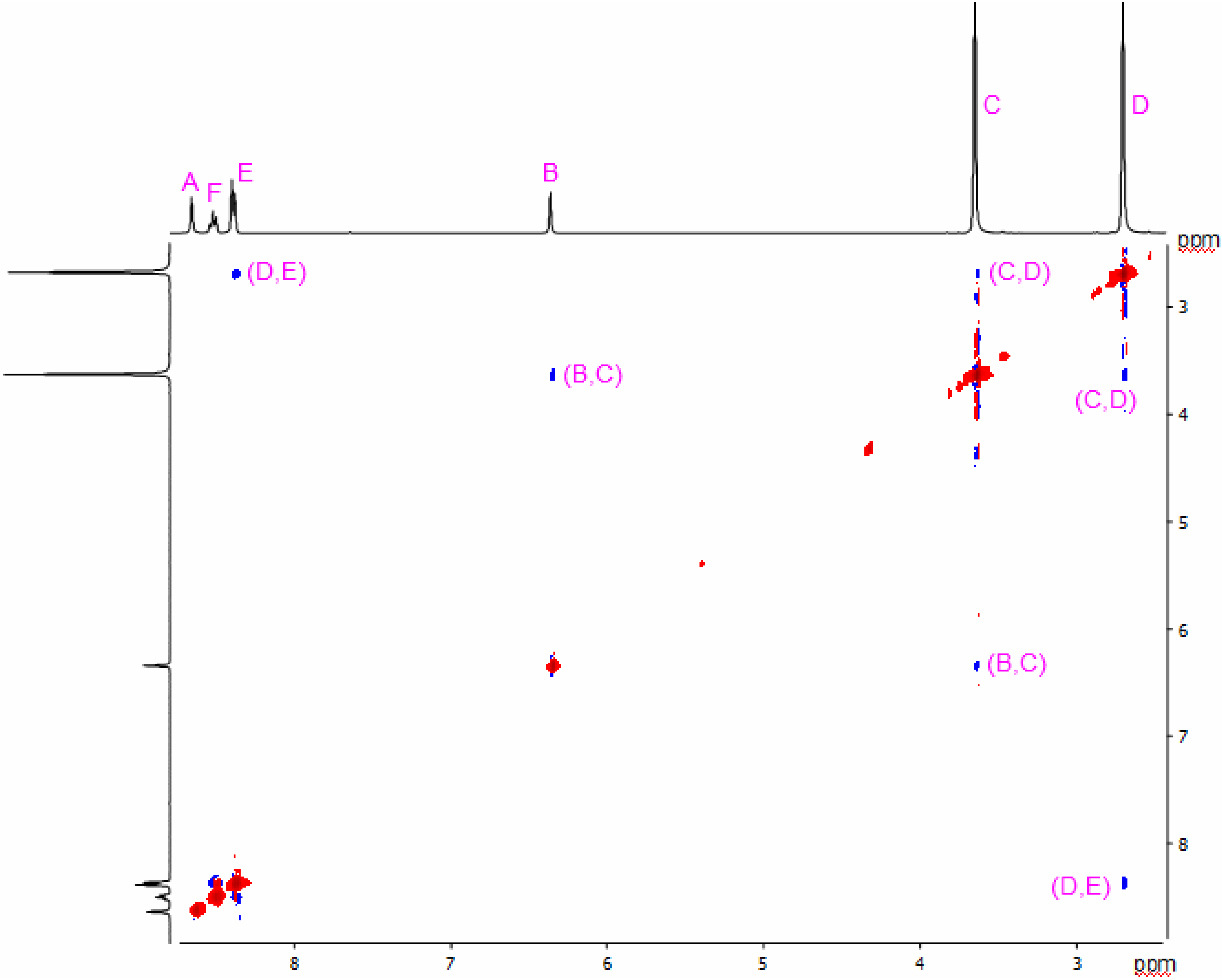
4.47°

3.91°

4.74°

Figure S5.

NOESY spectrum (400 MHz, solvent: CD_3CN) of the complex $Pb_3\mathbf{3}(OTf)_6$



Crystal data

Compound	Pb_2**4**$(OTf)_4$
Chemical formula	$C_{37}H_{37}F_{12}N_{15}O_{15}Pb_2S_4$
M/g mol^{-1}	1702.44
Crystal system	Triclinic
Space group	P-1
a /Å	12.0938(7)
b /Å	15.8194(9)
c /Å	16.3813(10)
α /°	69.747(1)
β /°	68.929(1)
γ /°	77.743(1)
V /Å^3	2729.8(3)
Z	2
$D_{calcd.}$ /g cm^{-3}	2.071
λ /Å	0.71073 (Mo-Kα)
μ /mm^{-1}	6.431
F(000)	1640
T /K	173(2)
R	0.0497
wR_2	0.1337
GOF	1.025
$\Delta\rho_{min}$ /e Å^{-3}	-2.624
$\Delta\rho_{max}$ /e Å^{-3}	3.147
CCDC #	903065