Electronic Supplementary Information for

Self-sorting of equilibrating metallosupramolecular DCLs via constitutional crystallization.

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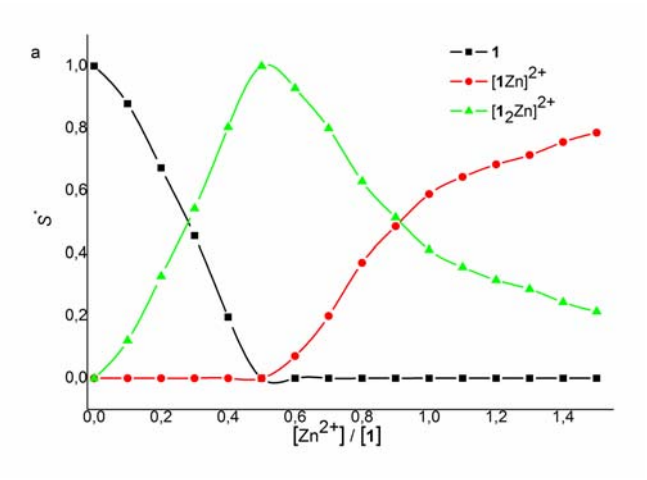
Materials and Methods: 2,6-pyridinedicarboxaldehyde was prepared by oxidation of 2,6-pyridinemethanol with activated MnO_2 according to the procedure described in the literature.[1S] aniline, 4-hydroxianiline and $Zn(CF_3SO_3)_2$ were purchased from Aldrich and used as received. $Pb(CF_3SO_3)_2$ was prepared from PbO and CF_3SO_3H as previously reported.[2S] All other reagents were obtained from commercial suppliers and used without further purification. All organic solutions were routinely dried by using sodium sulfate (Na_2SO_4). ^1H and ^{13}C NMR spectra were recorded on an ARX 300 MHz Bruker spectrometer in $CDCl_3$ and CD_3CN with the use of the residual solvent peak as reference. Mass spectrometric studies were performed in the positive ion mode using a quadrupole mass spectrometer (Micromass, Platform II). Samples were continuously introduced into the mass spectrometer through a Waters 616HPLC pump. The temperature (60°C) and the extraction cone voltage (V_c=5-10V) were usually set to avoid fragmentations. Due to competitive equilibria a quantitative determination of the concentration of complexes in solution is not possible. For this reason for the species distribution determination using ESI-MS method we have used MS-chromatogram peaks normalized by the maximal surface obtained for each compound.

Synthesis of ligands 1: Ligands **1**[1S] and **2**[3S] were synthesized as described in literature. The solutions of the ligands **1** and **2**, in $CDCl_3$ give sharp ^1H NMR spectra and ESI-MS spectra in accord with the pure compounds.

Generation and Interconversion of metallosupramolecular DCLs formed by Ligands 1, 2 and the Zn^{2+} and Pb^{2+} metal ions: Because of the ability of a ligands **1** and **2** to form different metal complexes combining different stoichiometries, we decided to investigate the formation, existence domain and interconversion of the equilibrating complexes that may result from the binding of Zn^{2+} or of Pb^{2+} ions to various stoichiometric ratios of ligands **1** or **2**.



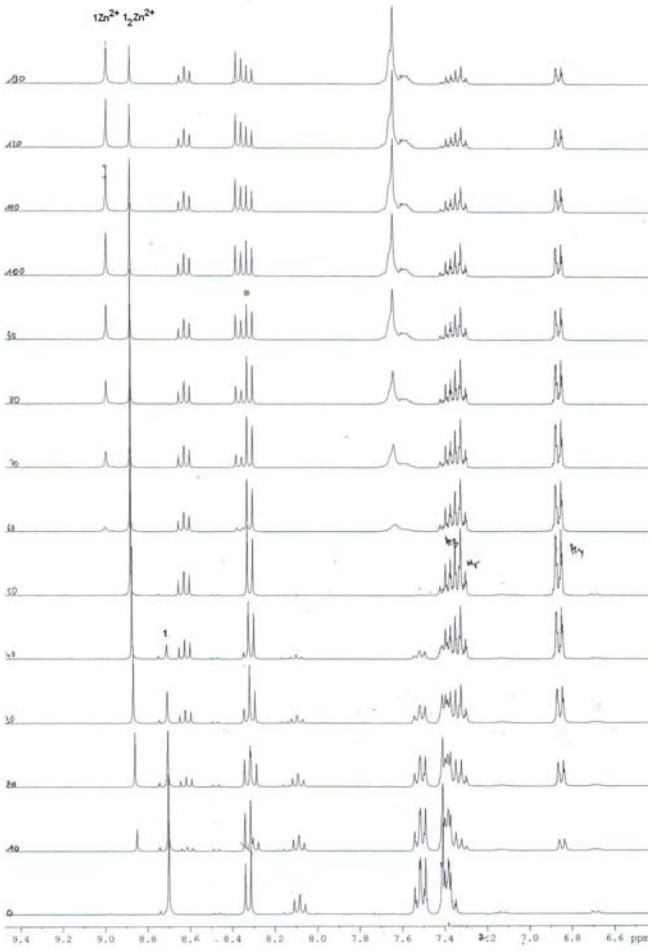
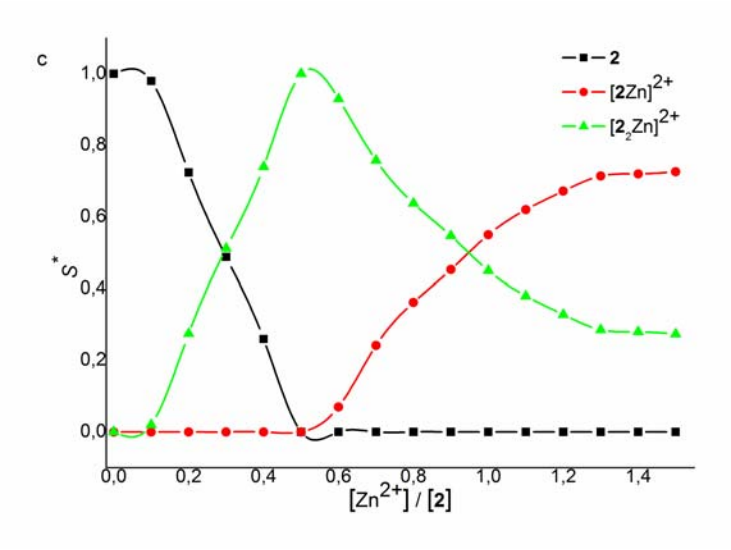


Figure 1s. 1H NMR spectra and distribution curves of the species resulted on the titration of a solution of ligand **1** in CH_3CN by a solution of $Zn(CF_3SO_3)_2$ (at initial ligand **1** concentration of 0.002M).



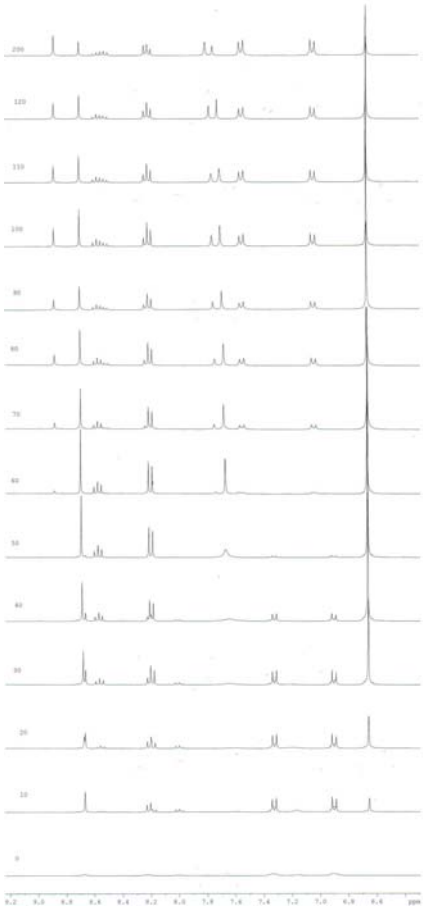


Figure 2s. 1H NMR spectra and distribution curves of the species resulted on the titration of a solution of ligand **2** in CH_3CN by a solution of $Zn(CF_3SO_3)_2$ (at initial ligand **1** concentration of 0.002M).

In order to obtain information about the coordination behavior of **1** and **2** towards Zn^{2+} ions, ^1H NMR and ESI MS (not shown) titrations were performed on solutions of $Zn(CF_3SO_3)_2$ and **1** in [D_3]acetonitrile in order to determine the distribution of different resulted species inter exchanging in solution, resulted from integration of imine signals. (Figure 1 and 2) Initial complexation studies revealed that addition of $Zn(CF_3SO_3)_2$ to an acetonitrile suspension of **1** or **2** caused a rapid dissolution of the ligand in a **1:**Zn^{2+} molar ratio from 1:0.2 to 1:3. At 1:0.5 **1**:M^{2+} ratio the ES mass spectra were consistent with the presence of the $\mathbf{1_2Zn^{2+}}$ complex (m/z=317.17) and $\mathbf{2_2Zn^{2+}}$ complex (m/z=351.17)**.** Further addition of Zn^{2+} ions led to the progressive conversion of $\mathbf{1_2Zn^{2+}}$ into the $\mathbf{1Zn^{2+}}$ complex (m/z=594.28, **1**ZnTf$^+$) and respectively of $\mathbf{2_2Zn^{2+}}$ into the $\mathbf{2Zn^{2+}}$ complex (m/z=628.28, **2**ZnTf$^+$), which were always in equilibrium with the duplex species.

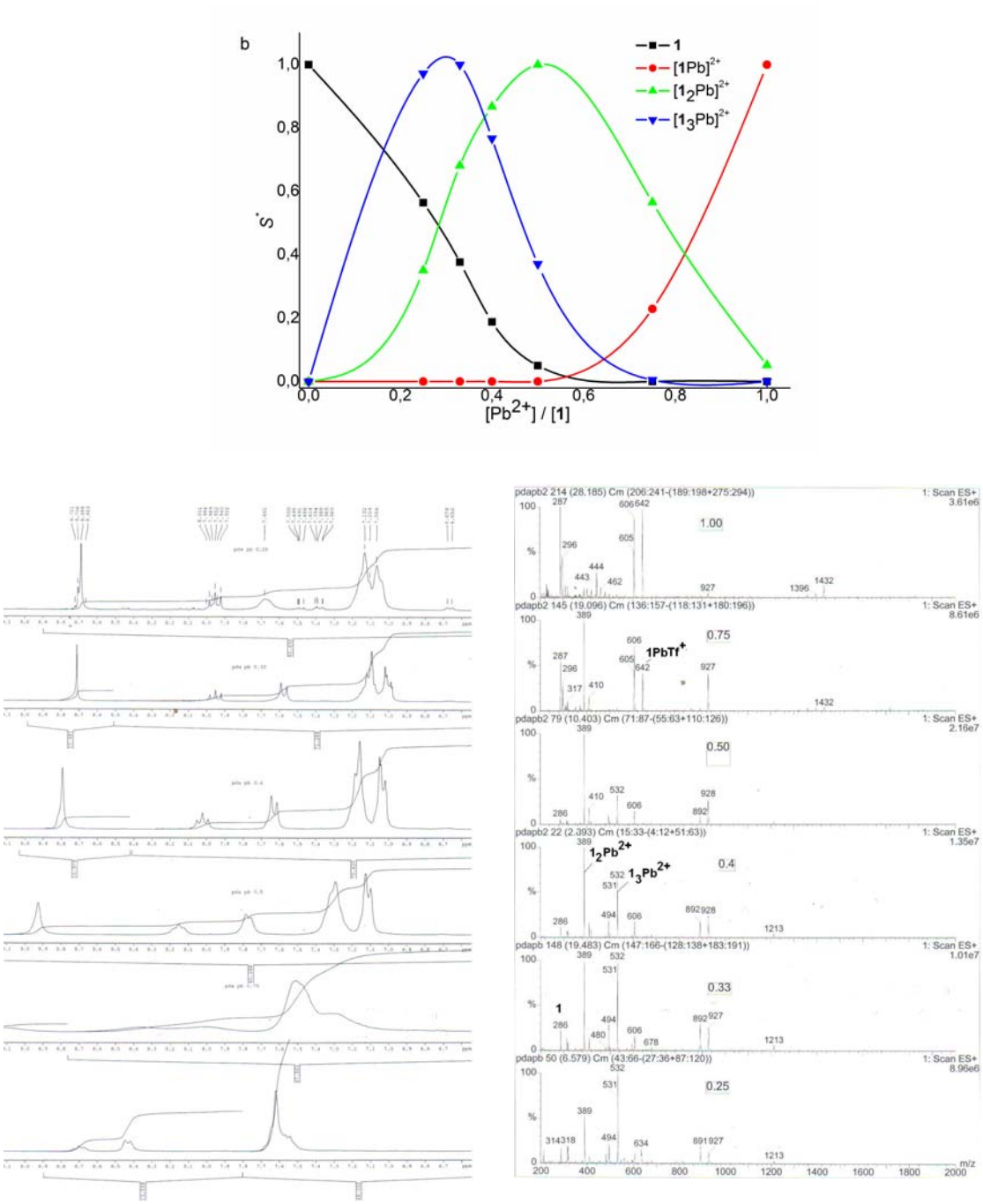


Figure 3S. 1H NMR and ESI mass spectra and distribution curves of the species resulted on the titration of a solution of ligand **1** in CH_3CN by a solution of $Pb(CF_3SO_3)_2$ in CH_3CN (at initial ligand **1** concentration of 0.002M) The data points were plotted using the integral surface of characteristic MS-chromatogram peaks normalized by the maximal surface.

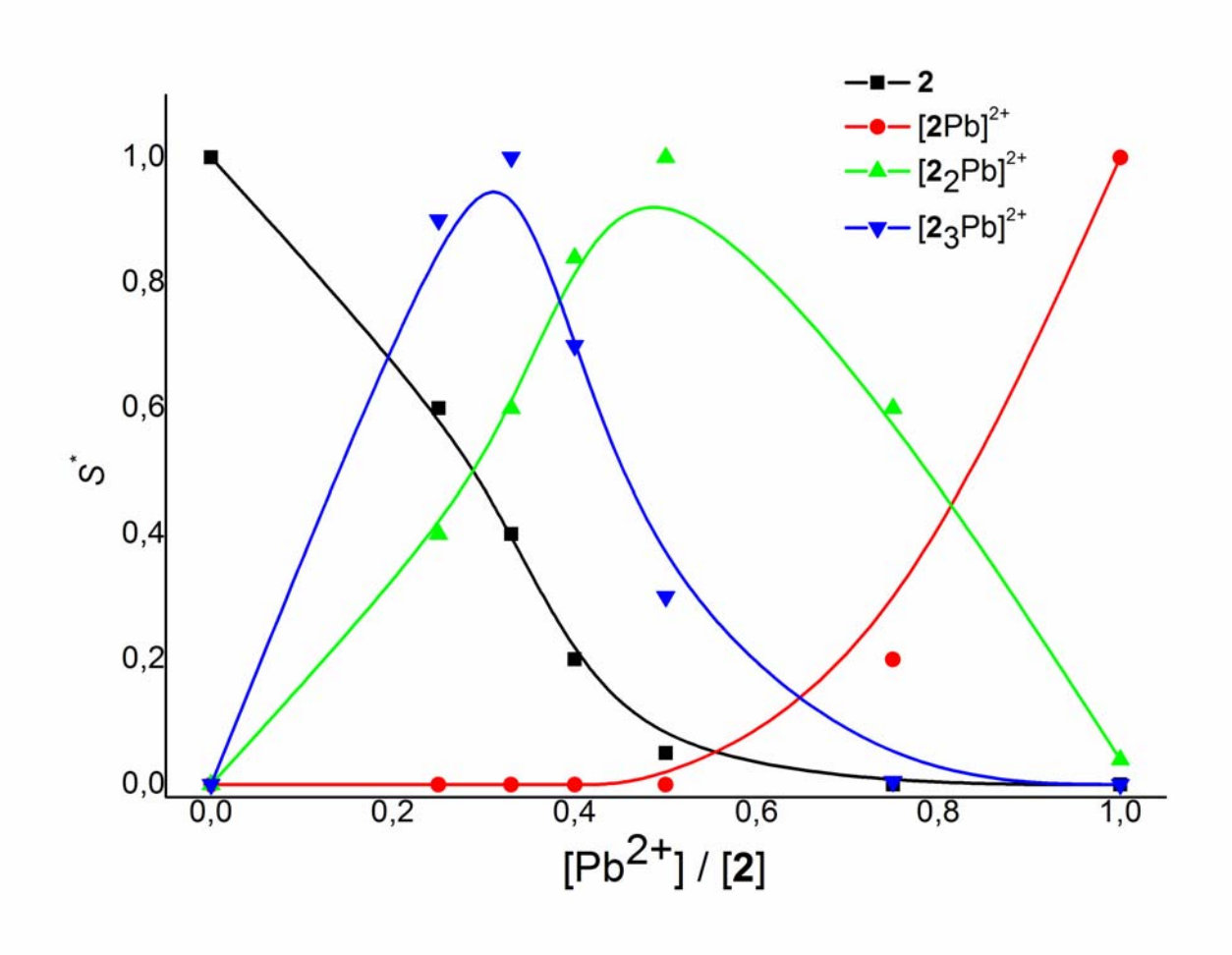


Figure 4S. distribution curves of the species resulted on the titration of a solution of ligand **2** in CH_3CN by a solution of $Pb(CF_3SO_3)_2$ in CH_3CN (at initial ligand **2** concentration of 0.002M) The data points were plotted using the integral surface of characteristic MS-chromatogram peaks normalized by the maximal surface.

The ^1H NMR spectra below a **1:**Pb^{2+} ratio of 1:1 consisted of the exchange-broadened signals of different complex species**,** indicative of the fast exchange with the ligand in solution (Figure 3S). At **1:**Pb^{2+} = 1:1 stoichiometry, the ^1H NMR spectrum consisted of a series of relative sharp peaks, indicating high symmetry. Unfortunately no accurate quantitative determination of species present in solution can be performed. For this reason, ESI-MS spectra were used for these

determinations. These studies revealed that addition of $Pb(CF_3SO_3)_2$ to an acetonitrile suspension of **1** or **2** caused a rapid dissolution of the ligand in a **1:**Zn^{2+} molar ratio from 1:0.2 to 1:3. At 1:0.33 **1:**M^{2+} ratio the ESI mass spectra were consistent with the presence of the $\mathbf{1_3Pb^{2+}}$ complex (m/z=532.1) and respectively $\mathbf{2_3Pb^{2+}}$ complex (m/z=583.1) in equilibrium with the $\mathbf{1_2Pb^{2+}}$ complex (m/z=389.1) and respectively $\mathbf{2_3Pb^{2+}}$ (m/z=423.1) complex **.** Further addition of Zn^{2+} ions led to the progressive conversion of $\mathbf{1_3Pb^{2+}}$ and $\mathbf{2_3Pb^{2+}}$ into $\mathbf{1_2Pb^{2+}}$ and $\mathbf{2_2Pb^{2+}}$. Then on further additions $\mathbf{1Pb^{2+}}$ (m/z=642) and $\mathbf{2Pb^{2+}}$ (m/z=676) complexes has been formed but they were always in equilibrium with the duplex species.

$\mathbf{1_2Zn^{2+}}$: ^{1}H-NMR (CD_3CN, ppm) : δ= 8.823 (s, 4H, CH=N), 8.608-8.756 (t, 2H, H^a, J=7.8 Hz), 8.274-8.248 (d, 4H, H^b, J=7.8 Hz), 7.381-7.254 (m, 12H, H^{ar}, J=8.7 Hz), 6.912-6.884 (d, 8H, H^{ar}, J=3.35Hz). ES-MS: m/z (%): 317.7 (100)

$\mathbf{1Zn^{2+}}$: ^{1}H-NMR (CD_3CN, ppm) : δ= 8.87 (s, 4H, CH=N), 8.608-8.556 (t, 2H, H^a, J=7.8 Hz), 8.354-8.40 (d, 4H, H^b, J=7.8 Hz), 7.61-7.74 (m, 12H, H^{ar}, J=8.7 Hz), 6.912-6.884 (d, 8H, H^{ar}, J=3.35Hz). ES-MS: m/z (%): 594.28, **1**$ZnTf^+$ (100)

$\mathbf{2_2Zn^{2+}}$: ^{1}H-NMR (CD_3CN, ppm) : δ= 8.689 (s, 4H, CH=N), 8.596-8.544 (t, 2H, H^a, J=7.8 Hz), 8.206-8.18 (d, 4H, H^b, J=7.8 Hz), 7.598 (s, 4H, OH), 6.65-6.64 (d, 4H, H^a, J=7.8 Hz). ES-MS: m/z (%): 349.54 (100)

$\mathbf{2Zn^{2+}}$: ^{1}H-NMR (CD_3CN, ppm) : δ= 8.90 (s, 4H, CH=N), 8.59-8.54 (t, 2H, H^a, J=7.8 Hz), 8.30-8.20 (d, 4H, H^b, J=7.8 Hz), 7.70 (d, 4H, H^b, J=7.8 Hz), 7.00 (d, 4H, H^b, J=7.8 Hz). ES-MS: m/z (%): 628.28, $2ZnTf^+$ (100)

^{1}H-NMR spectra of $\mathbf{1_3Pb^{2+}}$**:** $\mathbf{1_2Pb^{2+}}$**,** $\mathbf{1Pb^{2+}}$ in CD_3CN consisted of the exchange-broadened signals of different complex species**,** indicative of the fast exchange with the ligand in solution (Figure 3S). $\mathbf{1_3Pb^{2+}}$ ES-MS: m/z (%): 532.1 (100), $\mathbf{1_2Pb^{2+}}$ ES-MS: m/z (%): 389.1 (100), $\mathbf{1Pb^{2+}}$ ES-MS: m/z (%): 642 (100)

^{1}H-NMR spectra of **2_3Pb^{2+}: 2_2Pb^{2+}, $2Pb^{2+}$** in CD_3CN consisted of the exchange-broadened signals of different complex species**,** indicative of the fast exchange with the ligand in solution. **2_3Pb^{2+}** ES-MS: m/z (%): 583.1 (100), **2_2Pb^{2+}** ES-MS: m/z (%): 423.1 (100), **$2Pb^{2+}$** ES-MS: m/z (%): 676 (100).

Single crystal structures of 1_2Zn^{2+}, 2_2Zn^{2+}, $2Zn^{2+}$, 1_3Pb^{2+} and $2Pb^{2+}$ complexes. The reactions were performed typically on a 10 mg scale of ligand. The ligands **1** or **2** and $Zn(CF_3SO_3)_2$ (2:1 and 1:1, **1**:Zn^{2+} mol:mol) or $Pb(CF_3SO_3)_2$ (3:1 and 2:1, **1**:Zn^{2+} mol:mol) were dissolved in CD_3CN (1 mL), and stirred overnight at 60 °C. These solutions were monitored by ^{1}H NMR and ESI mass spectrometries. Layering such solutions metal ion complexes in acetonitrile with the *i*-propylether at room temperature, resulted in a unique set of single-crystals suitable for X-ray experiments.

X-ray Single Crystal Diffraction Data for complexes 1_3Pb^{2+}, $2Zn^{2+}$, and $2Pb^{2+}$: The diffraction intensities were collected at the joint X-ray Scattering Service of the Institut Charles Gerhardt and the Institut Européen des Membranes of the University of Montpellier II, France, at 175 K using an Oxford Diffraction Xcalibur-I and a Gemini-S diffractometer. The crystal-to-detector distance was 50 mm for all five measurements. The data reduction was in all cases done with Crysalis-Pro[4S] The structures were solved by direct methods using SIR2002 [5S] (**1_3Pb^{2+}**) or by ab-initio (charge-flipping) methods using SUPERFLIP[6S] **($2Zn^{2+}$**) and refined by least-squares methods on F or F^2 using CRYSTALS[7S] on data having $I>2\sigma(I)$ for F and using all data for F^2; *R*-factors are based on these data. Hydrogen atoms were partly located from difference Fourier synthesis, partly placed based on geometrical arguments, regularised using soft restraints, and afterwards refined in riding motion on the parent atoms. Non-hydrogen atoms were in general refined anisotropically, except where the data to parameter ration did not allow doing this.

Especially the crystal of $\mathbf{1_3Pb^{2+}}$ did not diffract very well, which causes a bad reflections to parameters ratio. In the structure of $\mathbf{2Zn^{2+}}$ one triflate anion was found to be disordered over two distinct sites. The two distinct anions were build from the residual peaks in the Fourier difference and afterwards regularised using the coordinates of a regular triflate anion. The two molecules were refined individually as rigid bodies with one isotropic molecular displacement factor for each. Shift limiting restraints were used for all coordinates and temperature factors. An apparant A-centering is present in the structure, but it was considered to be pseudo, since the mean intensity over sigma ratio for hkl:$k+l=2n+1$ reflections was $\langle I/\sigma(I)\rangle=94.33$, much larger than could be expected for truly extinct reflections. The centering is pseudo since $\langle I/\sigma(I)\rangle=267.81$ for hkl:$k+l=2n$ reflections, much stronger than for the hkl:$k+l=2n+1$ reflections. In the absence of any (pseudo)-centering these numbers are expected to be nearly equal.

The structure of $\mathbf{2Pb^{2+}}$ was solved by building the structure from the position of the heavy atom using difference Fourier syntheses and postulating that the structure was an inversion twin (Flack parameter 0.502(4)). Vibration and similarity restraints were used in order to stabilize the refinement by imposing the atomic displacement parameters of adjacent atoms to be similar. Essential crystallographic information is gathered in Table 1**S.**

Full details on $\mathbf{1_2Zn^{2+}}$ and $\mathbf{2_2Zn^{2+}}$ crystallographic data have been published recently by our group (see ref 9 for details). Full details on $\mathbf{1_3Pb^{2+}}$, $\mathbf{2Zn^{2+}}$, and $\mathbf{2Pb^{2+}}$ crystallographic data can be found in the cif-files as Electronic Supplementary Information.

	$\mathbf{1_3Pb^{2+}}$	$\mathbf{2Zn^{2+}}$	$\mathbf{2Pb^{2+}}$
Formula	$C_{59}H_{45}F_6N_9O_6PbS_2$	$C_{46}H_{40}F_{12}N_8O_{18}S_4Zn_2$	$C_{21}H_{15}F_6N_3O_8PbS_2$

Crystal Class	Monoclinic	Triclinic	Orthorhombic
Space Group	C12/c1	P-1	Fdd2
a (Å)	21.72580(13)	8.9330(3)	15.8406(5)
b (Å)	10.8837(5)	10.5894(4)	16.1462(4)
c (Å)	23.8728(6)	30.0903(10)	40.5039(14)
beta (°)	103.488(4)	81.785(3)	90
gamma (°)	90	89.709(3)	90
alpha (°)	90	87.927(3)	90
Volume ($Å^3$)	5489.2(3)	2815.34(17)	10359.5(5)
Z	4	2	16
Radiation type	Mo Kα	Mo Kα	Mo Kα
Wavelength (Å)	0.710730	0.710730	0.710730
Dx gcm^{-3}	1.65	1.75	2.11
Mr	1361.38	1479.87	822.70
Mu (cm^{-1})	3.232	1.120	6.771
Temperature (K)	173	173	173
Diffractometer type	XCALIBUR	XCALIBUR	XCALIBUR
Scan type	ω	ω	ω
Reflections measured	53652	58657	20575
Independent reflec.	9071	20555	5996
Rint	0.02	0.07	0.03
Theta max	32.48	33.66	29.12
Hmin, Hmax	-30 , 32	-13 , 13	-20 , 21
Kmin, Kmax	-16 , 15	-16 , 16	-20 , 21
Lmin, Lmax	-36 , 34	-46 , 46	-53 , 54
Refinement on	F	F	F_{sq}

R-factor	0.021	0.062	0.039
Weighted R-factor	0.020	0.066	0.039
Max shift/su	0.0018	0.0012	0.0005
Δ ρ min	-0.49	-1.77	-1.32
Δ ρ max	0.86	1.75	1.51
Reflections used	7973	7062	5996
Sigma(I) limit	2.00	2.00	-3.00
Number of parameters	378	771	378
Goodness of fit	1.078	0.793	0.816
Flack parameter			0.502(4)

Table 1S: Crystallographic information on data collection and structure refinement for compounds $\mathbf{1_3Pb^{2+}}$, $\mathbf{2Zn^{2+}}$, and $\mathbf{2Pb^{2+}}$.

This work, conducted as part of the award "Dynamic adaptive materials for separation and sensing Microsystems" (M.B.) made under the European Heads of Research Councils and European Science Foundation EURYI (European Young Investigator) Awards scheme in 2004, was supported by funds from the Participating Organizations of EURYI and the EC Sixth Framework Program. See www.esf.org/euryi. This research was also supported in part by the ANR-06-Blan-0117 POLYFUNMAG Program and CNRS.

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1S A. L. Vance, N. W.Alcock, J. A.Heppert, D. H. Busch, *Inorg. Chem.* **1998**, *37*, 6912-6920.
2S A.M. Garcia, F.J.Romero-Salguero, D. M. Bassani, J.-M. Lehn, G. Baum, D. Fenske, *Chem. Eur J.*, **1999**, *6*, 1803-1808.

3S F. Lions, K. V. Martin, *J. Am. Chem. Soc*. **1957**, *79(11)*, 2733-2738.

4S Crysalis-Pro, software for reduction of X-ray diffraction data, Oxford Diffraction Ltd (2008).

5S M. C. Burla, et al. *J. Appl. Crystallogr.* **2003**, *36*, 1103.

6S P. W. A. Betteridge Carruthers, J. R.; Cooper, R. I., Prout, K.; Watkin, D. J. *J. Appl. Crystallogr.* **2003**, *36*, 1487.

7S L. Palatinus, L. Chapuis. *J. Appl. Cryst.* **2007**, *40*, 786-790.