Electronic Supplementary Information for Dalton Transactions

Electronic Supplementary Information

for:

Synthesis, characterization, crystal structure and preliminary reactivity behaviour of new heteropolytopic ligands based on the 1,3,5-triazine spacer and pyrazolyl, tris-pyrazolylmethyl and tris-pyrazolylethoxy bonding fragments.

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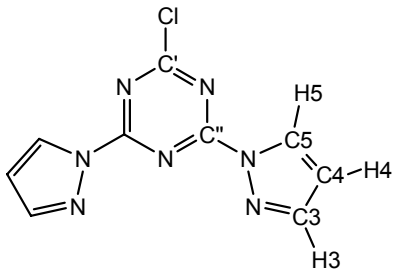
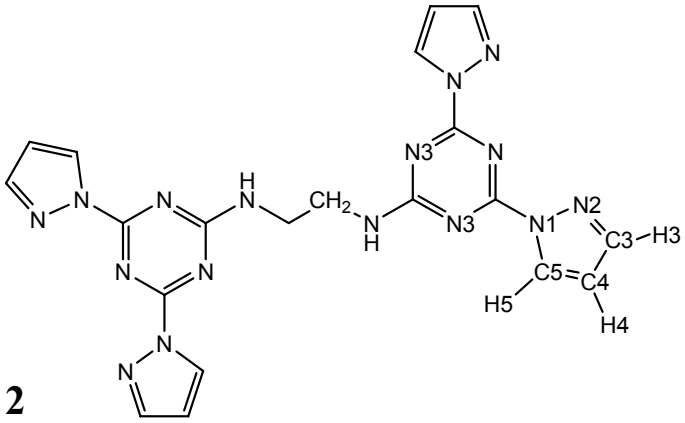


1



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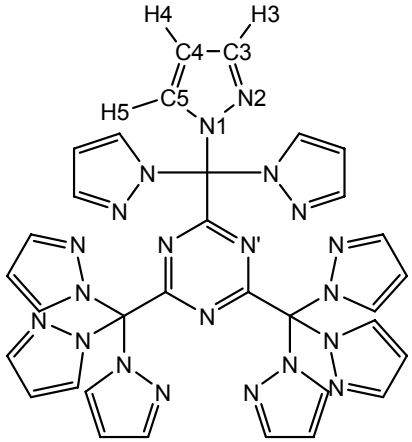

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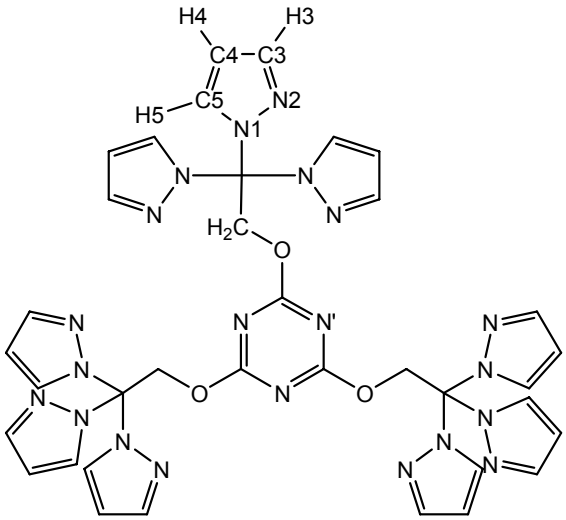
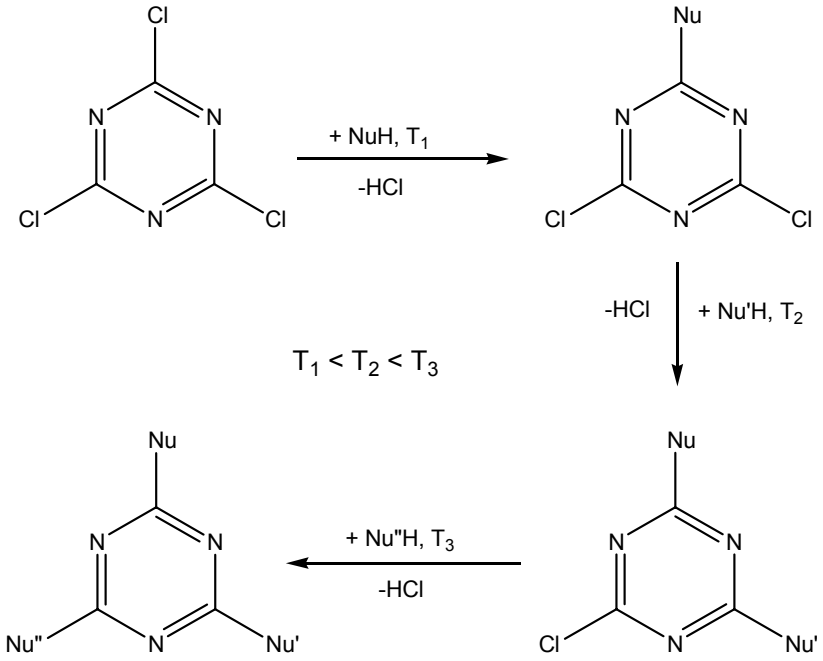


4

Chart S1 – Numbering scheme for NMR signals assignments. NB The numbering of **3** doesn't correspond to the labels indicated in the crystal structure figure.



Scheme S1 – Scheme describing the so-called *Moffat rule*.

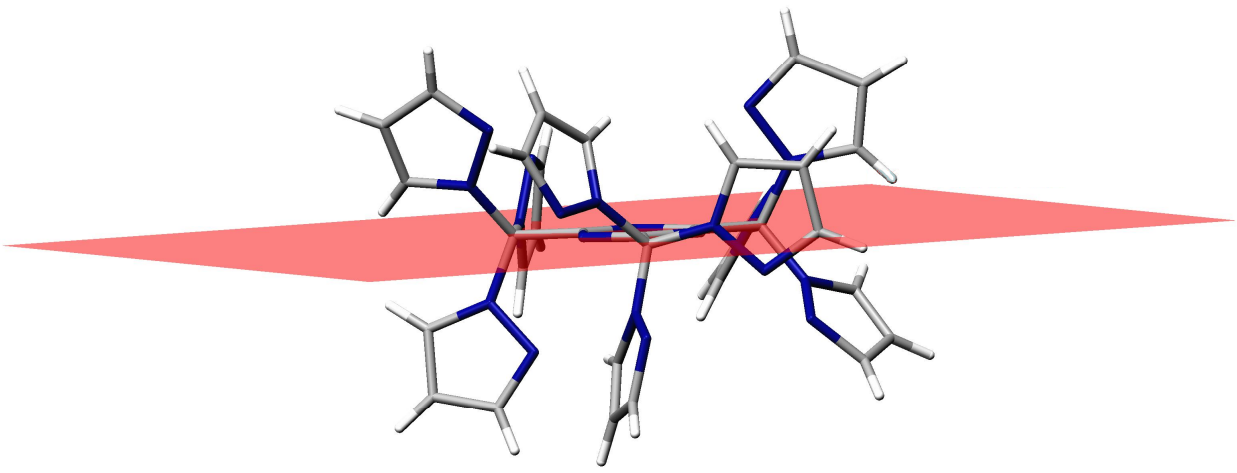


Figure S1 – View of the molecular structure of **3** bisected by a plane containing the triazine ring.

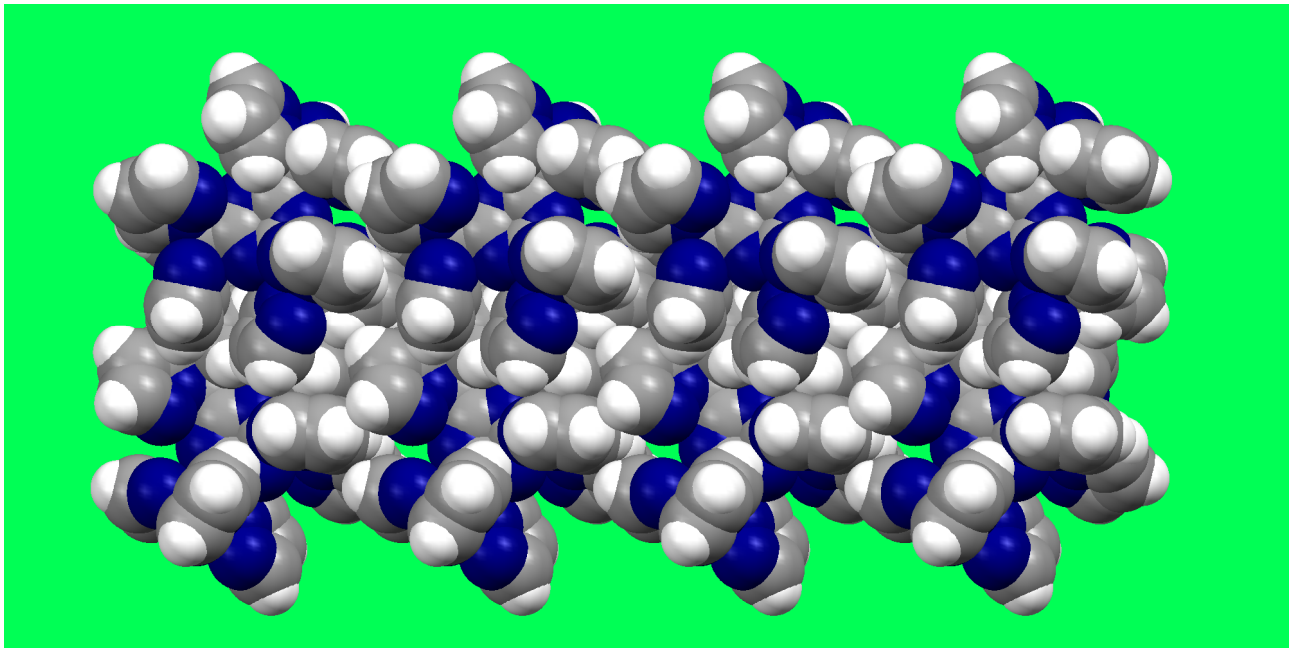


Figure S2 – Space-filling view of **3** along the crystallographic *a* axis evidencing small, irregular, channels running along the same axis.

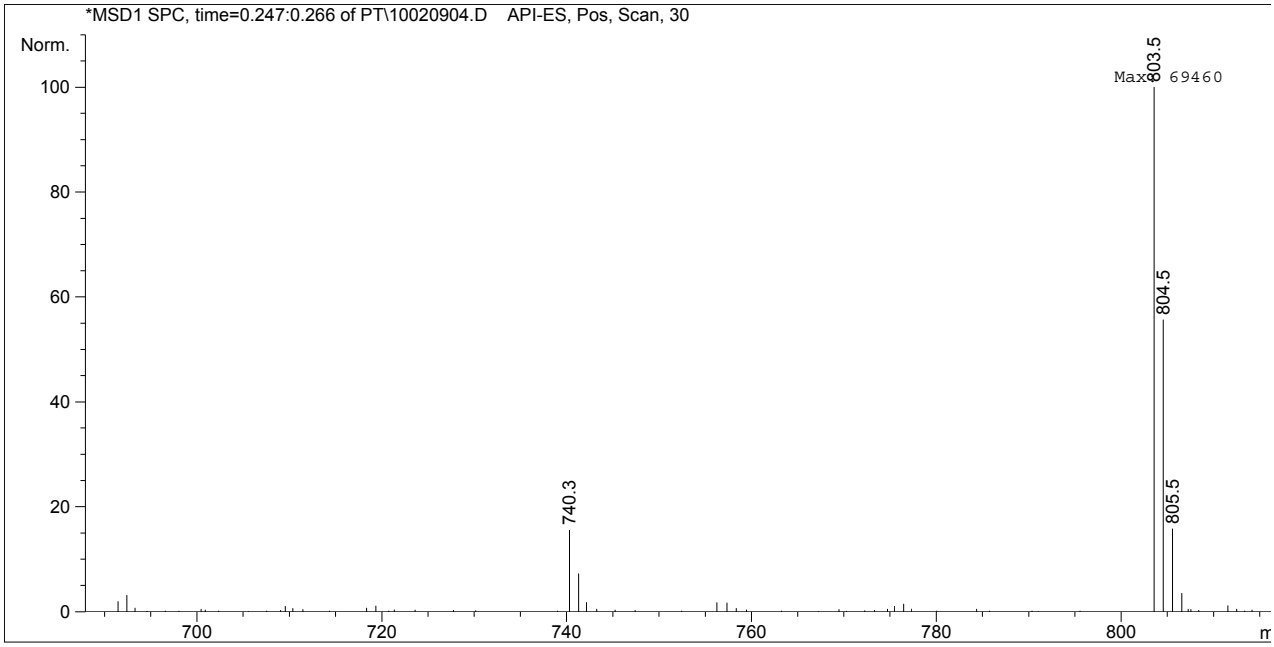
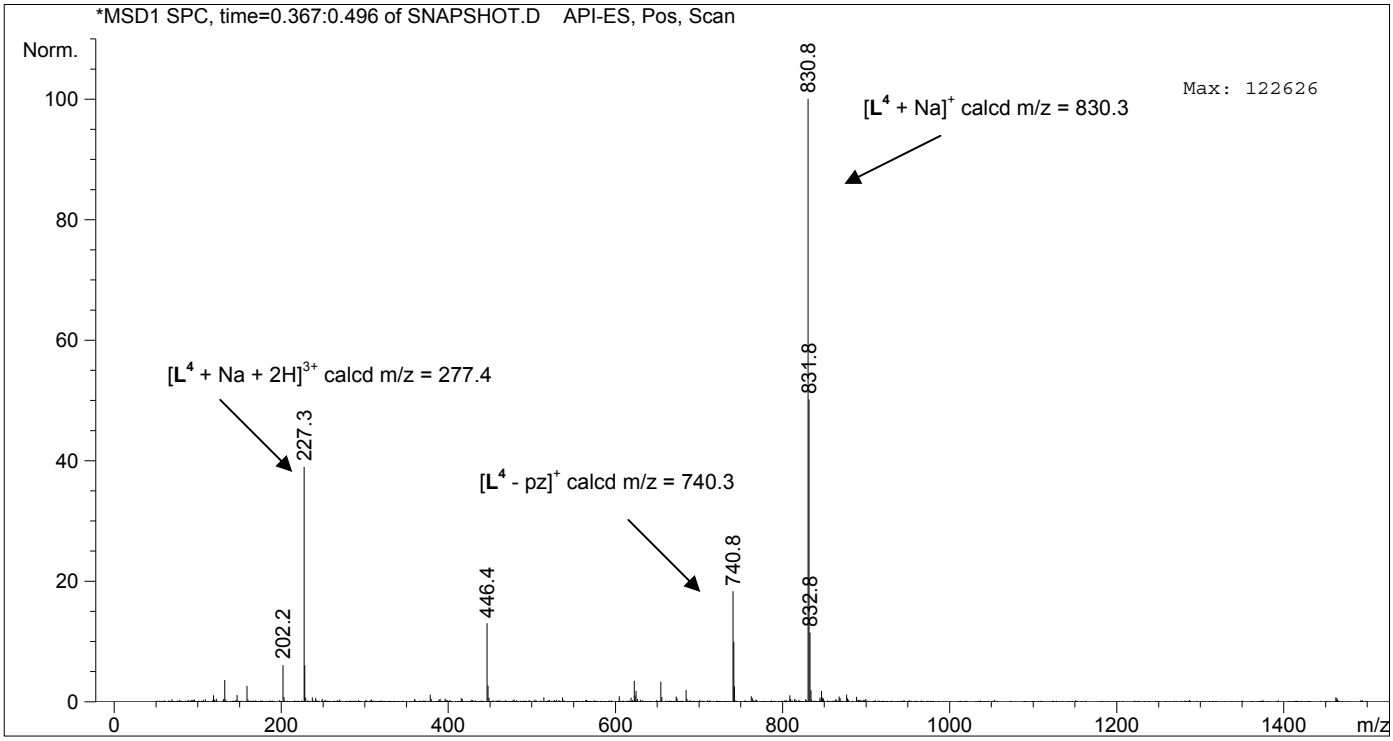
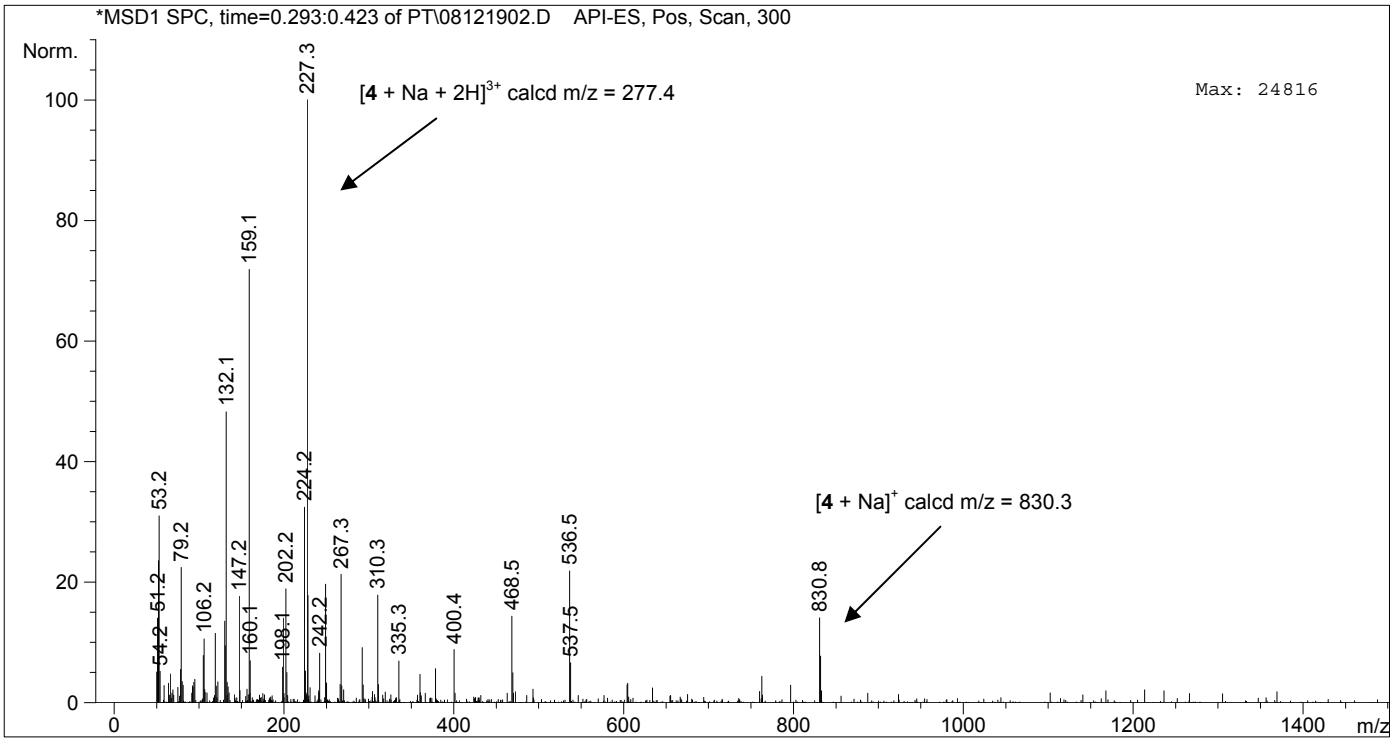


Figure S3 – ESI-MS of $\mathbf{L^3}$.



a



b

Figure S4 – ESI-MS of $\mathbf{L^4}$ at different [(a) 30, (b) 300] "fragmentor energy", (see text).

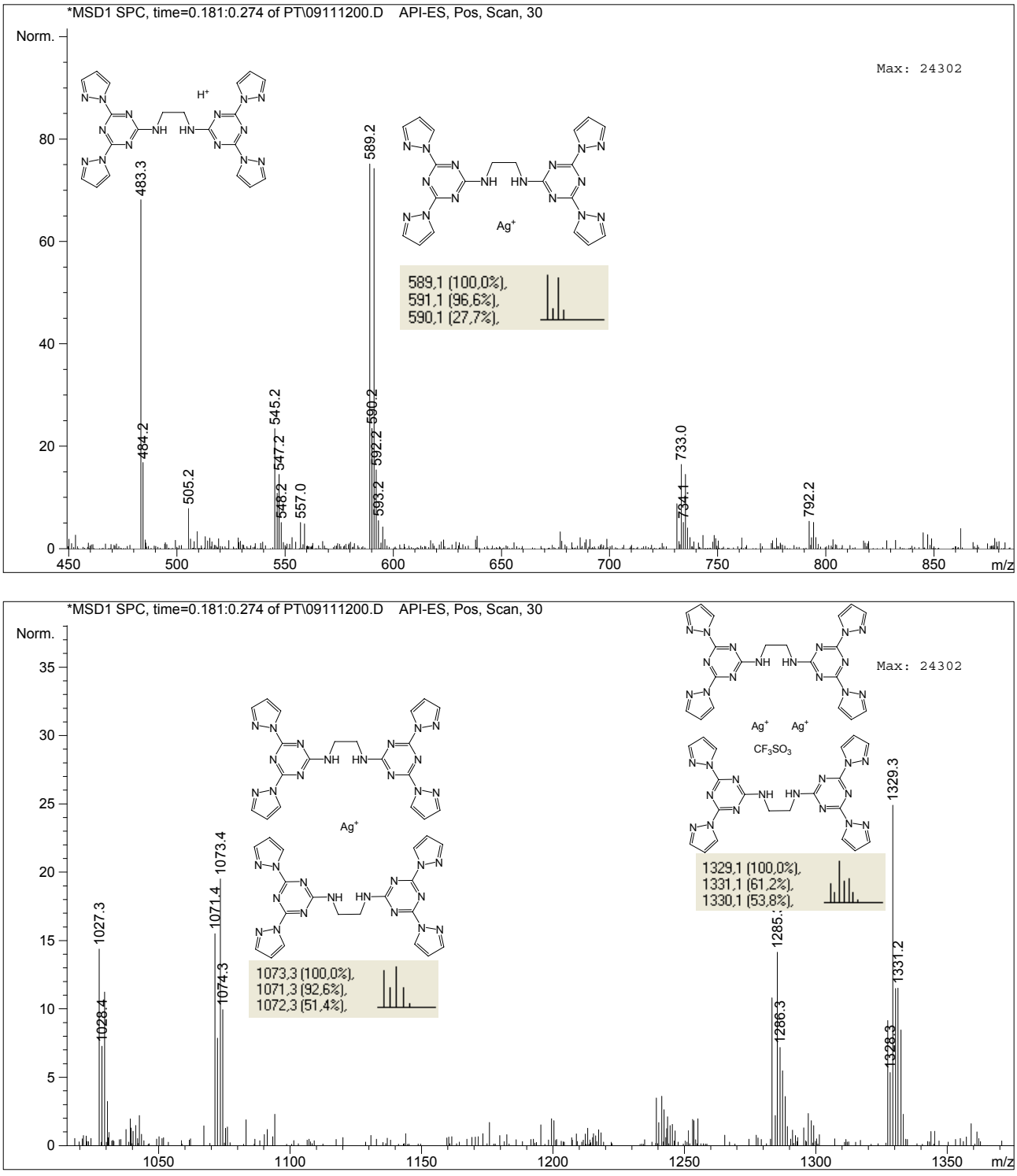
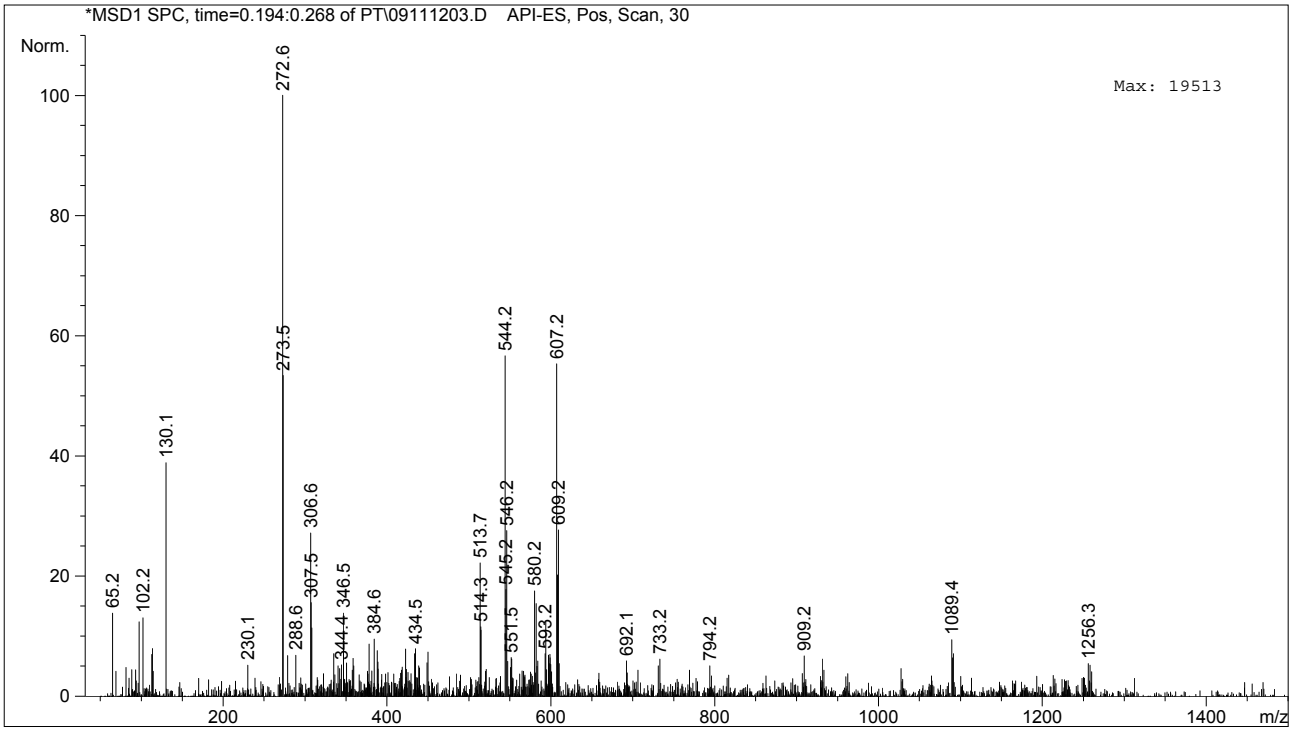


Figure S5 – ESI-MS of **2**.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273.5
544.2
607.2
130.1
306.6
609.2
546.2
513.7
545.2
580.2
65.2
102.2
307.5
346.5
514.3
384.6
551.5
593.2
434.5
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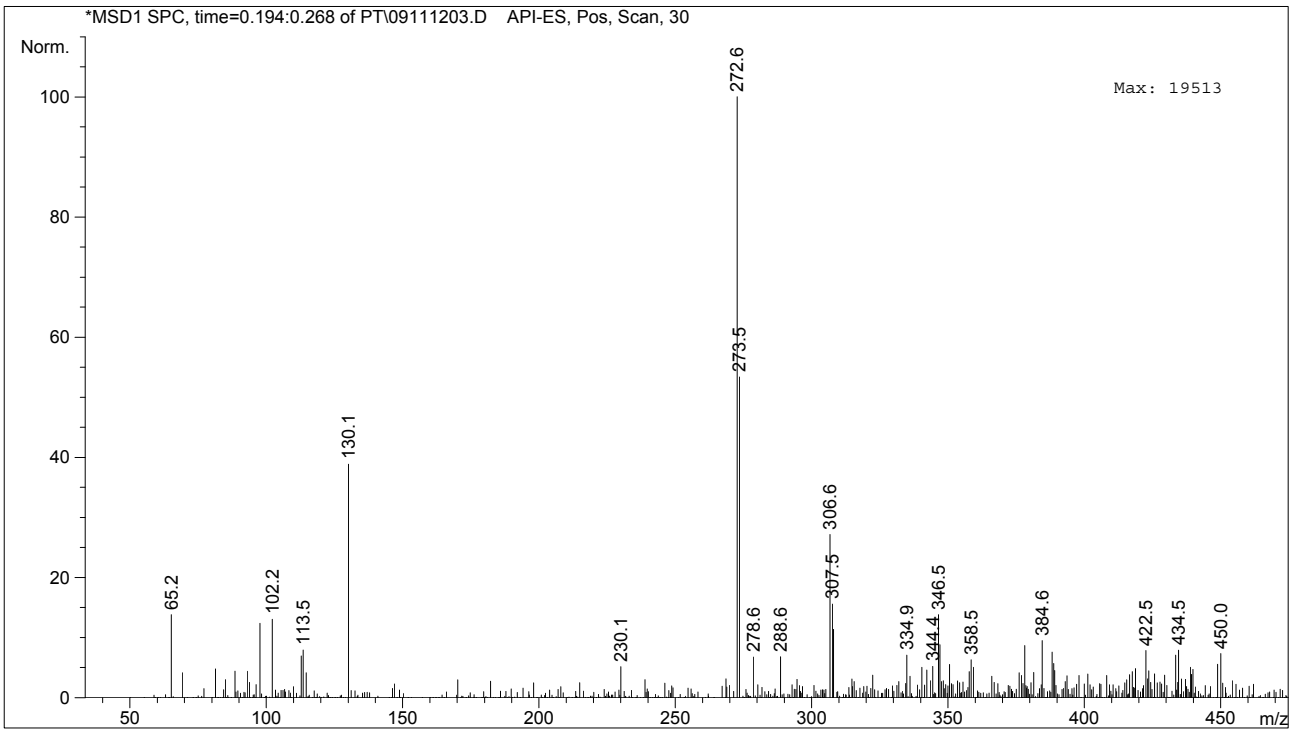
692.1
733.2
794.2
909.2
1089.4
1256.3
m/z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Norm.
Max: 19513
272.6
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65.2
102.2
307.5
346.5
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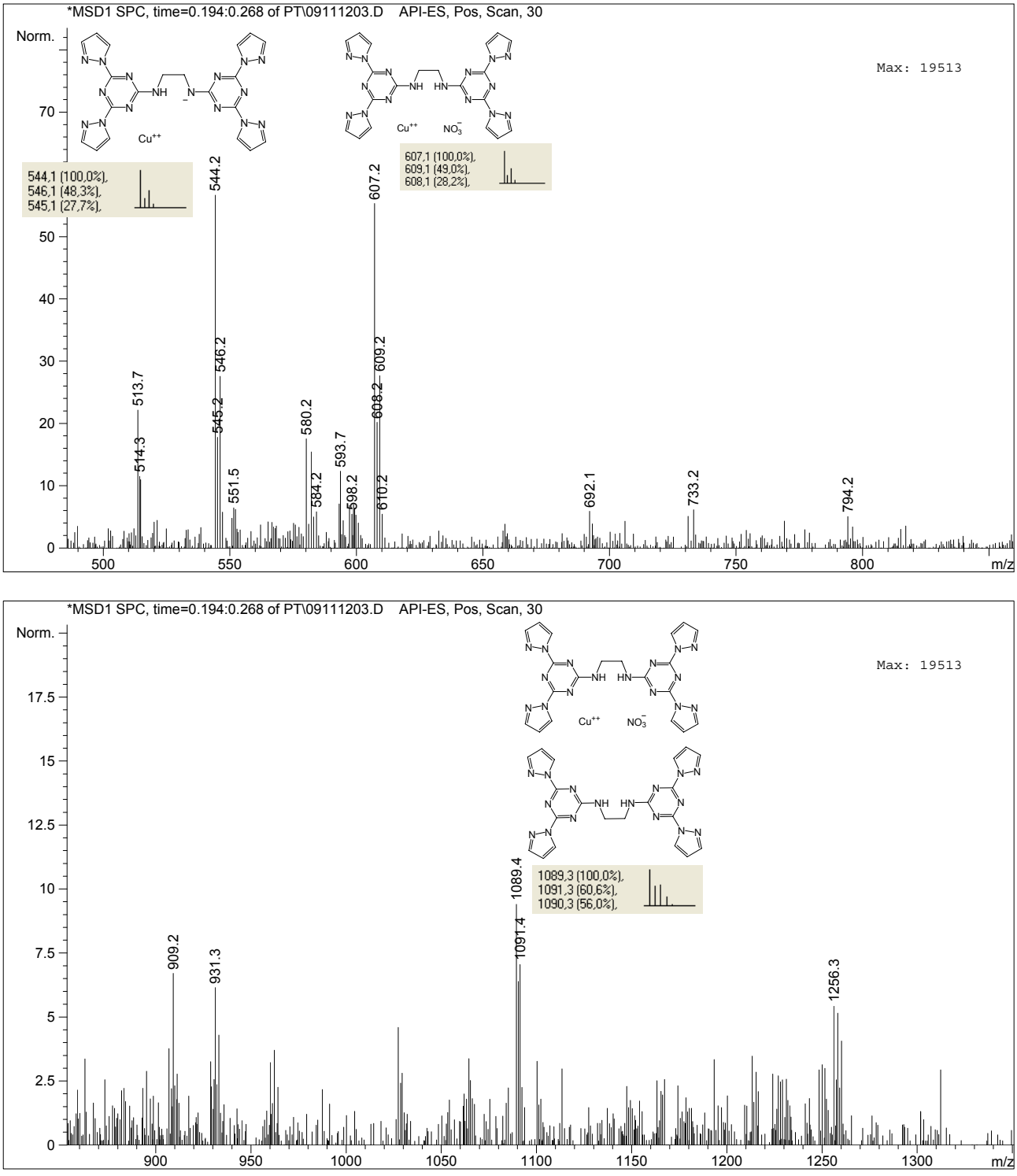

Figure S6 – ESI-MS of **3**.

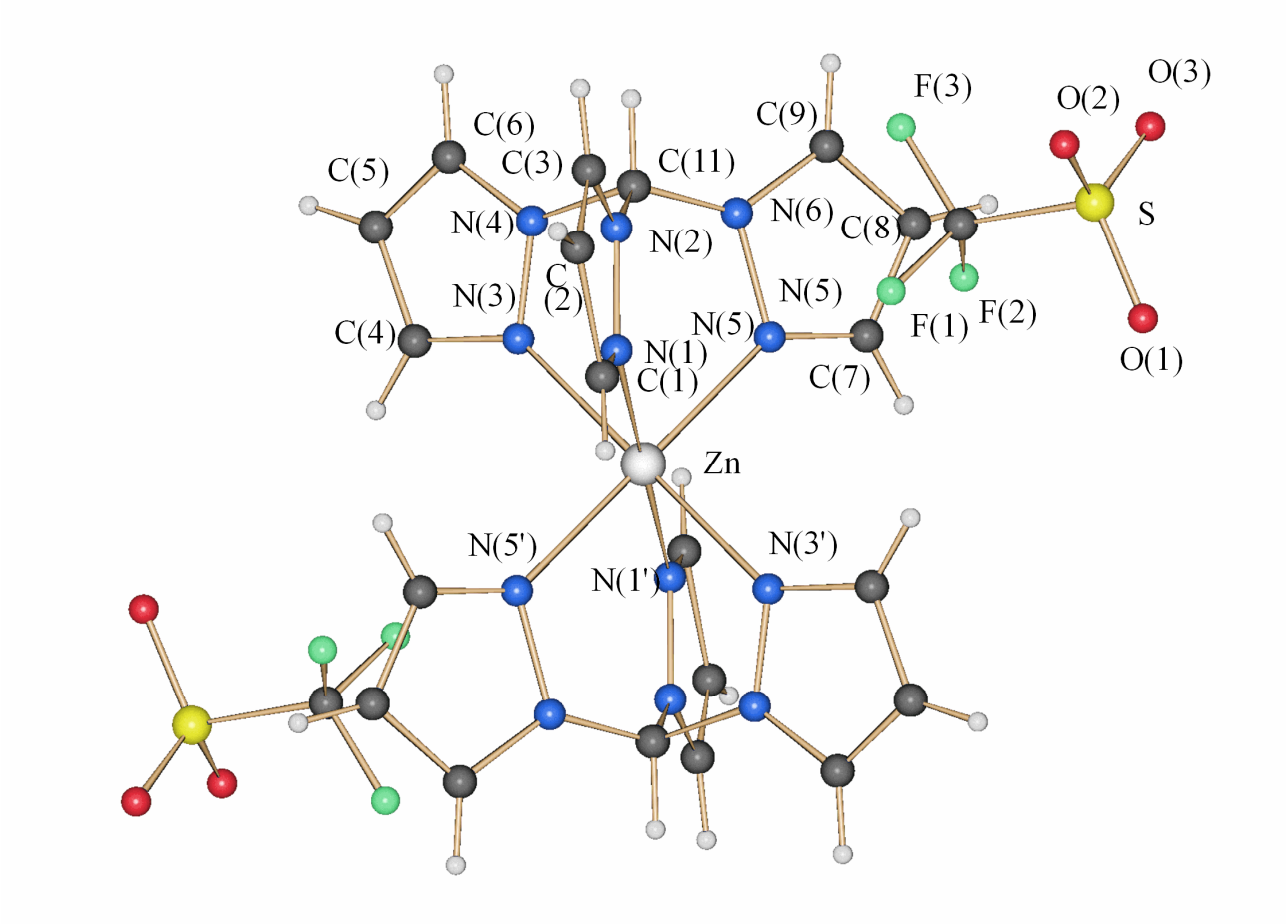

Figure S7 – Molecular structure of compound **9**, $[Zn(TPM)_2](CF_3SO_3)_2$. Symmetry operations to generate equivalent atoms: 1-x, -y, 2-z.

Table S1. Crystal data and experimental details for **9.** The structure determination was carried out on a crystal of poor quality and these data are preliminary.

Compound	**7**
Formula	$C_{22}H_{20}F_6N_{12}O_6S_2Zn$
M	791.99
T/ K	293(2)
Crystal symmetry	Triclinic
Space group	*P-1*
a/ Å	7.957(2)
b/ Å	9.891(2)
c/ Å	10.939(2)
α/ °	68.19(3)
β/ °	83.31(3)
γ/ °	82.96(3)
V/ $Å^3$	790.9(3)
Z	1
D_c/ Mg m^{-3}	1.663
μ(Mo-K_α)/ mm^{-1}	1.002
F(000)	400
Crystal size/ mm	0.07 x 0.07 x 0.10
θ limits/ °	2.40-21.86
Reflections collected	3488
Unique obs. reflections	1764
Goodness-of-fit-on F^2	0.982
R_1 (F)[a], wR_2 (F^2)[b]	0.1522, 0.3184
Largest diff. peak and	0.658 and –0.767

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + F_c^2)/3$.

Table S2. Selected bond lengths (Å) and angles (deg) for **9**.

Zn-N(1)	2.12(2)	Zn-N(5)	2.11(2)
Zn-N(3)	2.21(2)	S-O(1)	1.42 (2)
S-O(3)	1.36(2)	S-O(2)	1.41(2)
S-C(10)	1.71(4)		
N(5)-Zn-N(5)#1	180.000(3)	N(5)-Zn-N(1)	85.9(7)
N(5)#1-Zn-N(1)	94.1(7)	N(5)-Zn-N(3)	82.1(9)
N(5)#1-Zn-N(3)	97.9(9)	N(1)-Zn-N(3)	82.8(7)
N(1)#1-Zn-N(3)	97.2(7)		

Symmetry code #1 = 1-x, -y, 2-z

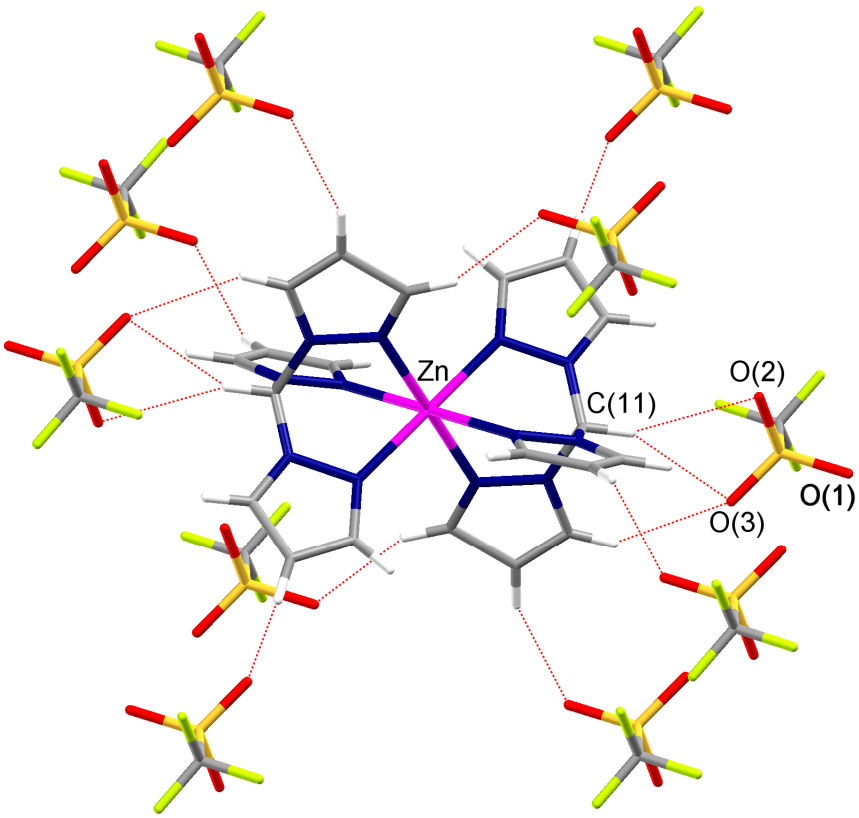

Figure S8 – Arbitrary view of the dication of **9** surrounded by ten triflate ions interacting with it through more or less weak "non-conventional" H-bonds (red dashed lines), all of the type C(Y)-H(Y)···O(X), pertaining to the triflate oxygen atoms and some pyrazolate or methinic hydrogens.

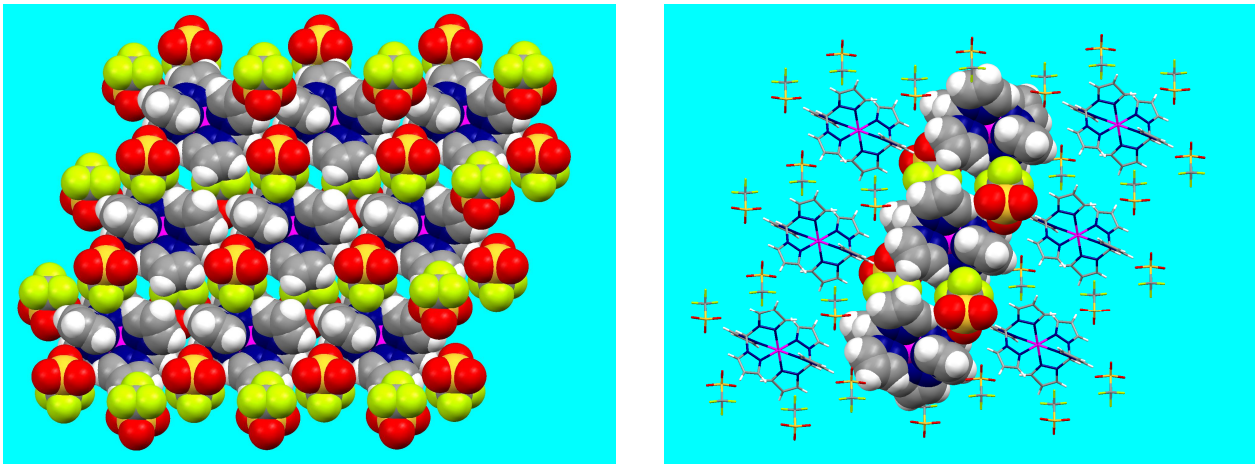

Figure S9 – Crystal packing of **9** viewed along the crystallographic *a* axis. The space filling representation evidences the small channels, running parallel to the same axis, having section dimensions of about. 2.7x1 Å, taking into account the appropriate vdW radii.