Electronic Supplementary Material (ESI) for Chemical Communications

Anion-Templated Self-Assembly of Highly Stable Fe(II) Pentagonal Metallacycles with Short Anion-π Contacts

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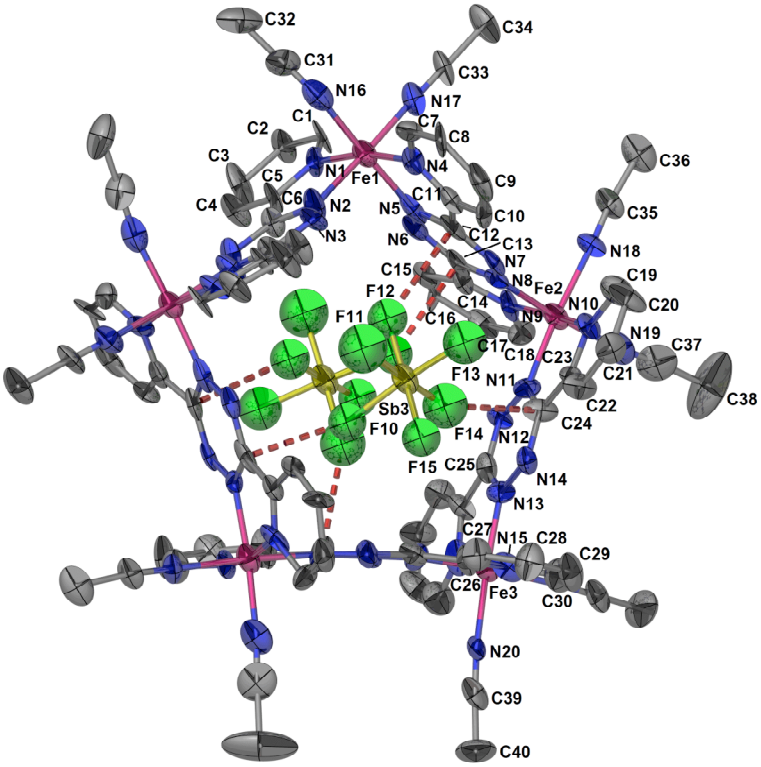
Supporting Information

Figures S1-S5

Table S1

X-ray crystallographic details and relevant references

(A)



(B)

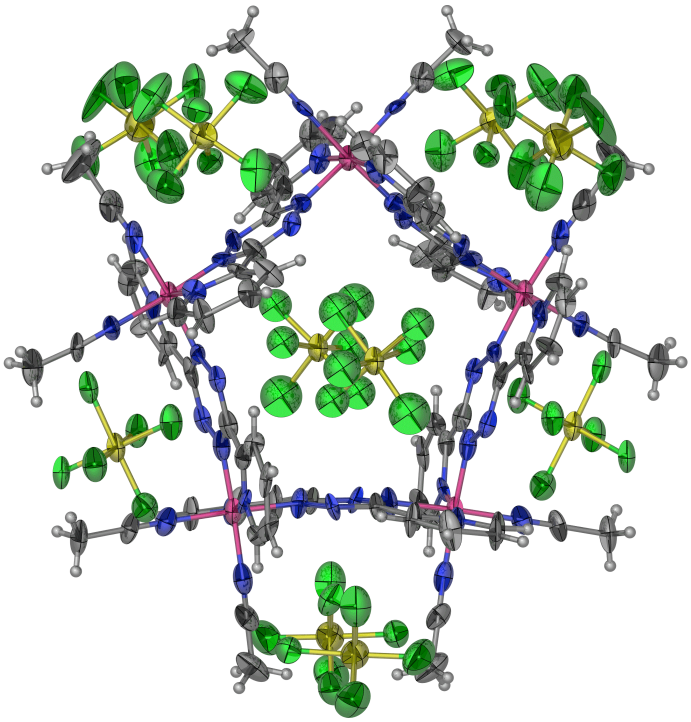
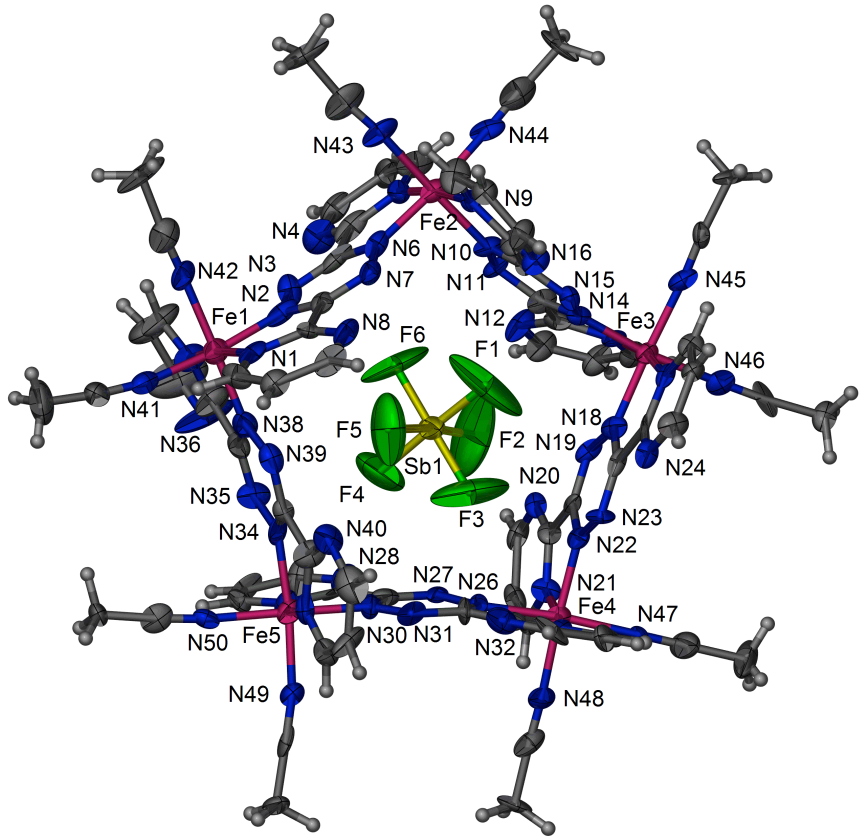


Figure S1. Thermal ellipsoid of the cationic unit $[\{Fe_5(bptz)_5(CH_3CN)_{10}\}\subset 2SbF_6]^{8+}$ in **1** at the 50% probability level depicted with the **(A)** two encapsulated $[SbF_6]^-$ anions only, **(B)** encapsulated and peripheral $[SbF_6]^-$ anions. Colour code: Fe magenta, C grey, N blue, Sb yellow, F green, H light grey.

(A)



(B)

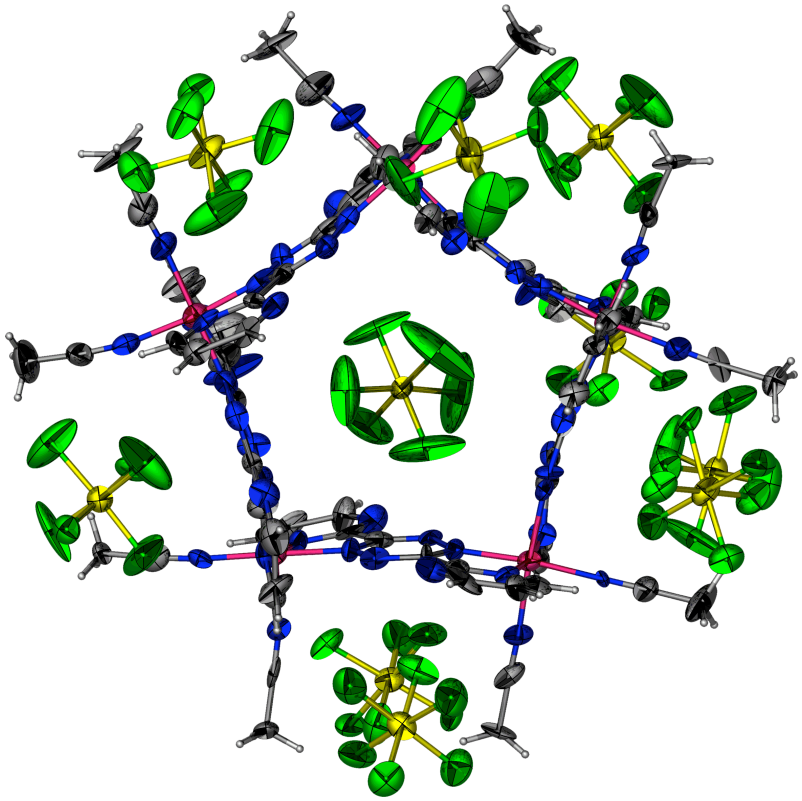
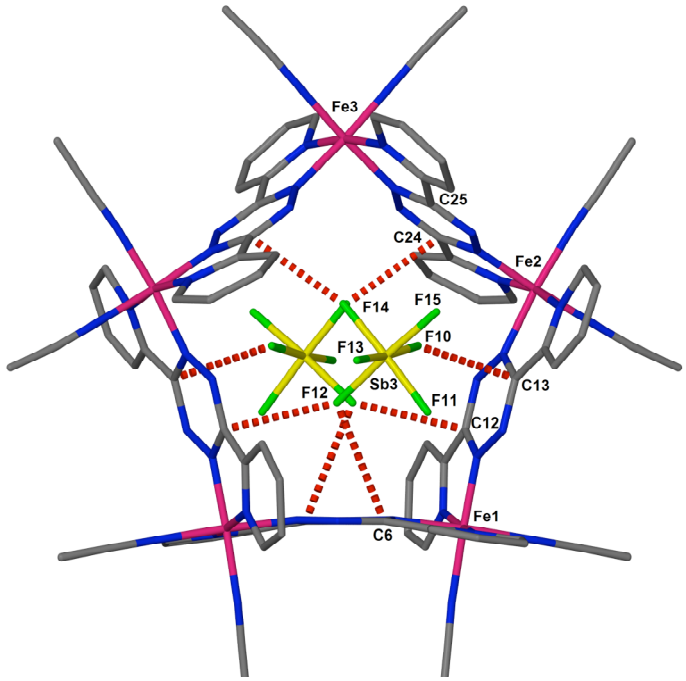


Figure S2. Thermal ellipsoid of the cationic unit $[\{Fe_5(bmtz)_5(CH_3CN)_{10}\}\subset SbF_6]^{9+}$ in **2** at the 50% probability level depicted with the **(A)** encapsulated $[SbF_6]^-$ anion only, **(B)** encapsulated and peripheral $[SbF_6]^-$ anions. Colour code: Fe magenta, C grey, N blue, Sb yellow, F green, H light grey.

(A)



(B)

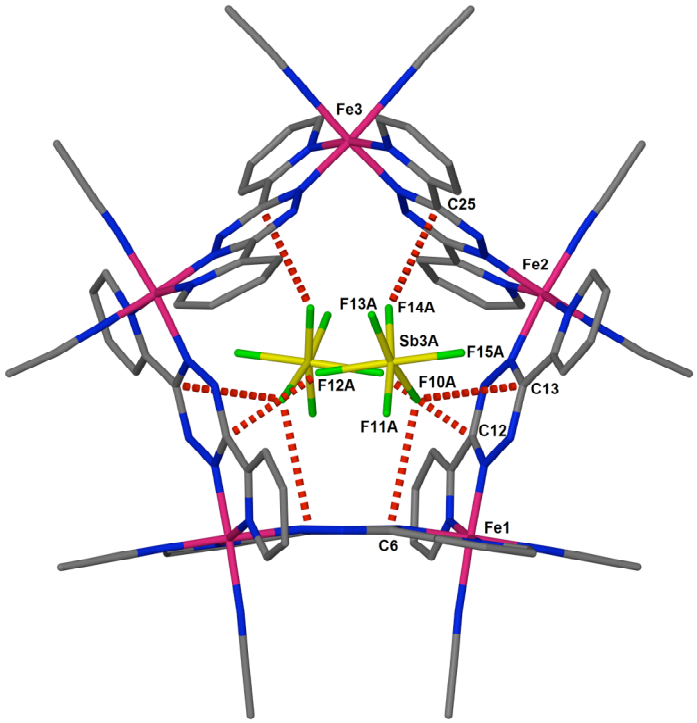
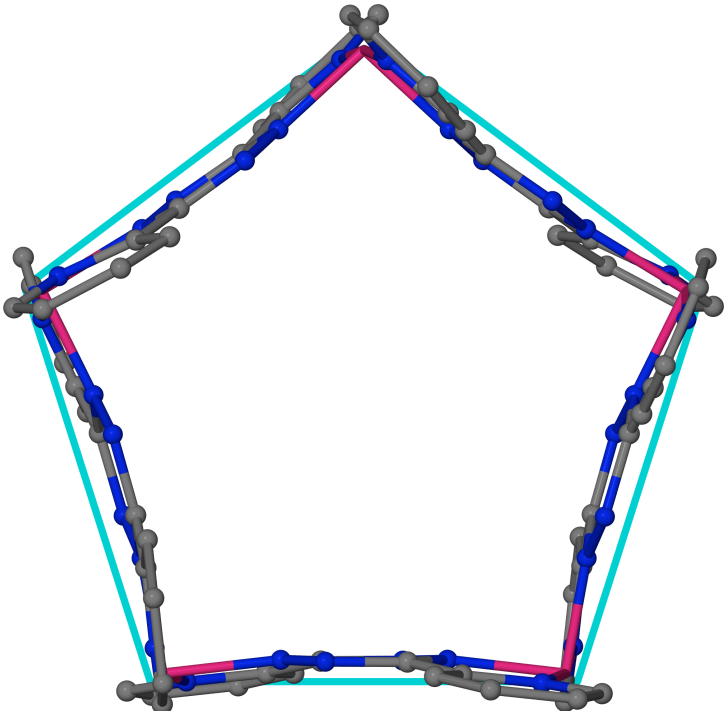


Figure S3. Stick representation of the cationic unit $[\{Fe_5(bptz)_5(CH_3CN)_{10}\}\subset 2SbF_6]^{8+}$ in **1**. Parts **(A)** and **(B)** refer to two different positions of disorder for the encapsulated $[SbF_6]^-$ anions with the F···C anion-π contacts depicted with red dashed lines, F10···C13 2.81(2), F12A···C12 2.83(3), F14A···C25 2.888, F14···C24 2.93(2), F10A···C13 2.96(3), F12···C12 3.03(2) Å, and F10A···C6 3.35(3), F12···C6 3.37(2) Å. Colour code: Fe magenta, C grey, N blue, Sb yellow, F green, H light grey.

(A)



(B)

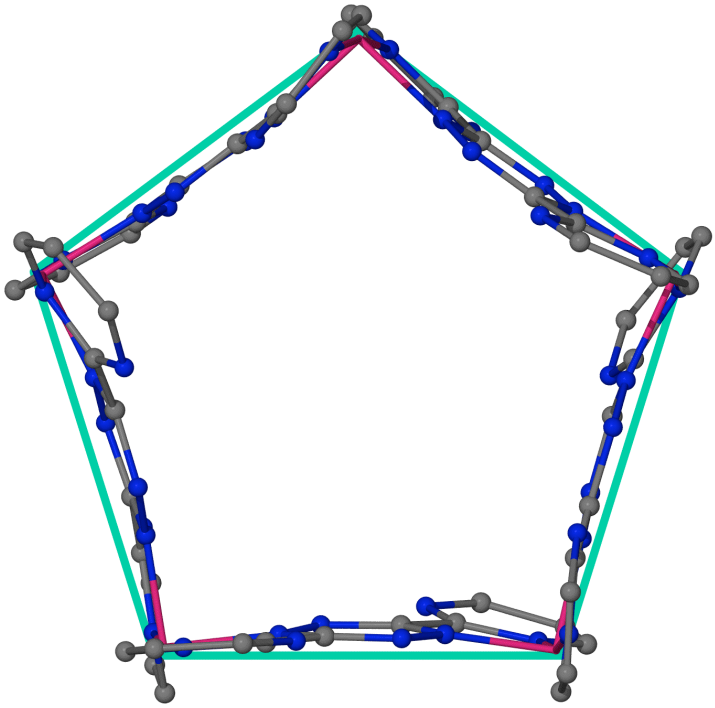
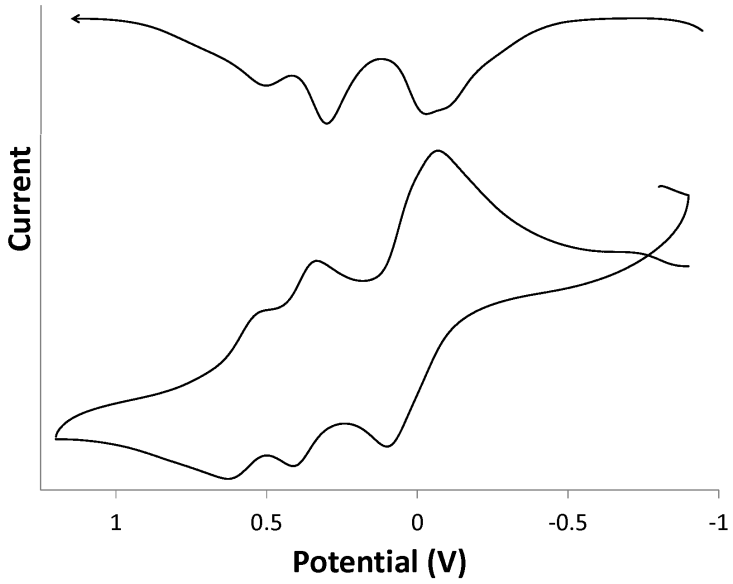


Figure S4. Figure depicting the '*inward bowing*' of the ligands in the cationic unit of **(A)** $[\{Fe_5(bptz)_5(CH_3CN)_{10}\}\subset 2SbF_6]^{8+}$ of **1** and **(B)** $[\{Fe_5(bmtz)_5(CH_3CN)_{10}\}\subset SbF_6]^{9+}$ of **2** with respect to the ideal sides of a pentagon. The average dihedral angles with the planes of the two pyridyl (**1**) or pyrimidyl (**2**) rings are ~8° and ~10°, respectively.

(A)



(B)

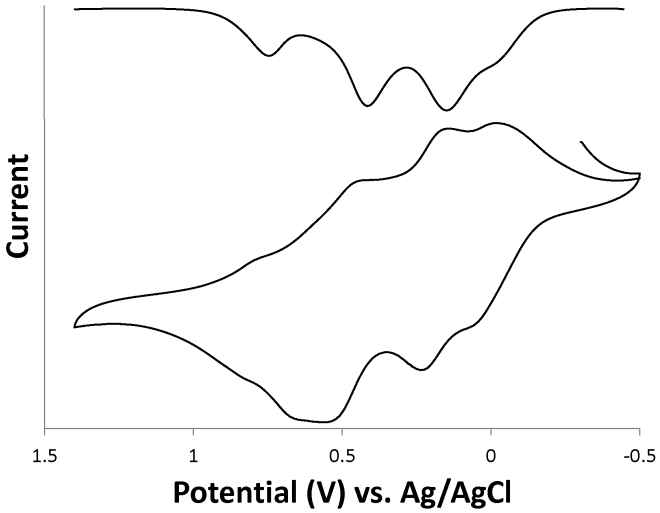


Figure S5. Electrochemical data (top: DPV, bottom: CV) of **(A)** $[\{Fe_5(bptz)_5(CH_3CN)_{10}\}\subset 2SbF_6][SbF_6]_8$ (**1**) recorded in 0.2 M [*n*-Bu_4N][SbF_6]/CH_3CN, scan rate 100 mV s^{-1}; **(B)** $[\{Fe_5(bmtz)_5(CH_3CN)_{10}\}\subset SbF_6][SbF_6]_9$ (**2**) recorded in 0.2 M [*n*-Bu_4N][PF_6]/CH_3CN, scan rate: 50 mV s^{-1}. Potentials reported for a Pt working electrode *vs.* the Ag/AgCl reference electrode at 25° C.

X-ray Crystallography. Single crystal X-ray data for **1** and **2** were collected on a Bruker APEX CCD X-ray diffractometer equipped with a graphite monochromated MoK_α radiation source ($\lambda = 0.71073$ Å). Dark blue crystals of **1** and **2** were affixed to a nylon loop with paratone oil and placed in a cold stream of N_2(g) at 163(2) K. Crystal decay monitored by analyzing duplicate reflections was found to be less than 1%, therefore no decay correction was applied. The frames were integrated with the Bruker SAINT software package[1S] and a semi-empirical absorption correction was applied using SADABS.[2S] The structure was solved and refined using X-SEED,[3S] a graphical interface to the SHELX suite of programs.[4S] Additional crystallographic calculations were performed with PLATON.[5S] The electron density corresponding to heavily disordered solvent molecules observed during the data refinement of **1** was removed using the SQUEEZE[6S] routine implemented in PLATON.

Table S1. Crystal and structural refinement data for $[\{Fe_5(bptz)_5(CH_3CN)_{10}\}\subset 2SbF_6][SbF_6]_8\cdot 8.5CH_3CN$ (**1**) and $[\{Fe_5(bmtz)_5(CH_3CN)_{10}\}\subset SbF_6][SbF_6]_9\cdot 6.5CH_3CN\cdot C_7H_8$ (**2**).

	1	**2**
Formula	$Sb_{10}Fe_5F_{60}N_{48.5}C_{97}H_{95.5}$	$Sb_{10}Fe_5F_{60}N_{56.5}C_{90}H_{87.5}$
Temp (K)	163	163
Space group	*Pbcn* (no. 60)	*Pc* (no. 7)
a (Å)	11.82(1)	16.180(3)
b (Å)	37.92(4)	21.569(4)
c (Å)	34.12(3)	23.123(4)
α (°)	90.00	90.00
β (°)	90.00	106.198(2)
γ (°)	90.00	90.00
V (Å^3)	15299(25)	7749(2)
Z	4	2
Color	dark blue	dark blue
ρ_{calc} (g/cm^3)	1.836	1.970
μ (mm^{-1})	2.314	2.295
θ range (°)	1.19-26.46	1.31-26.41
Reflections collected (R_{int})	30355 (0.142)	82034 (0.145)
Unique reflections	15658	31659
Parameters/restraints	912/21	1870/2
R_1,[a] wR_2[b] [$I > 2\sigma(I)$]	0.086, 0.195	0.078, 0.160
R_1,[a] wR_2[b] (all data)	0.240, 0.241	0.196, 0.210
Goodness-of-fit[c] (F^2)	0.715	0.940
Largest diff. peak, hole (e Å^{-3})	1.43, –1.16	1.54, –1.60

[a] $R = \Sigma \big| |F_o| - |F_c| \big| / \Sigma |F_o|$. [b] $wR = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]\}^{1/2}$. [c] Goodness-of-fit = $\{\Sigma [w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined.

References

1S. SAINT, Program for area detector absorption correction, Siemens Analytical X-Ray Instruments Inc., Madison, WI 53719, USA, 1994-1996.

2S. G. M. Sheldrick, SADABS, Program for Siemens area detector absorption correction, University of Göttingen, Göttingen, Germany, 1996.

3S. a) Barbour, L. J. X-Seed, Graphical interface to SHELX-97 and POV-Ray, 1999 (http://www.x-seed.net). b) Barbour, L. J. J. *Supramol. Chem*. **2001**, *1*, 189-191. c) Atwood, J. L.; Barbour, L. J. *Cryst. Growth Des*. **2003**, *3*, 3-8.

4S. S. Sheldrick, G. M. *Acta Crystallogr. Sect. A* **2008**, *A64*, 112-122.

5S. a) Spek, A. L. PLATON, University of Utrecht, The Netherlands, 2001. b) Spek, A. L. *Acta Crystallogr. Sect. D*, **2009**, *D65*, 148-155.

6S. SQUEEZE: Sluis, P. v.d.; Spek, A. L. *Acta Crystallogr. Sect. A,* **1990**, *A46*, 194-201.