SUPPLEMENTARY MATERIAL TO THE ARTICLE:

Catalytic “Triangles”: Binding of Iron in Task-Specific Ionic Liquids

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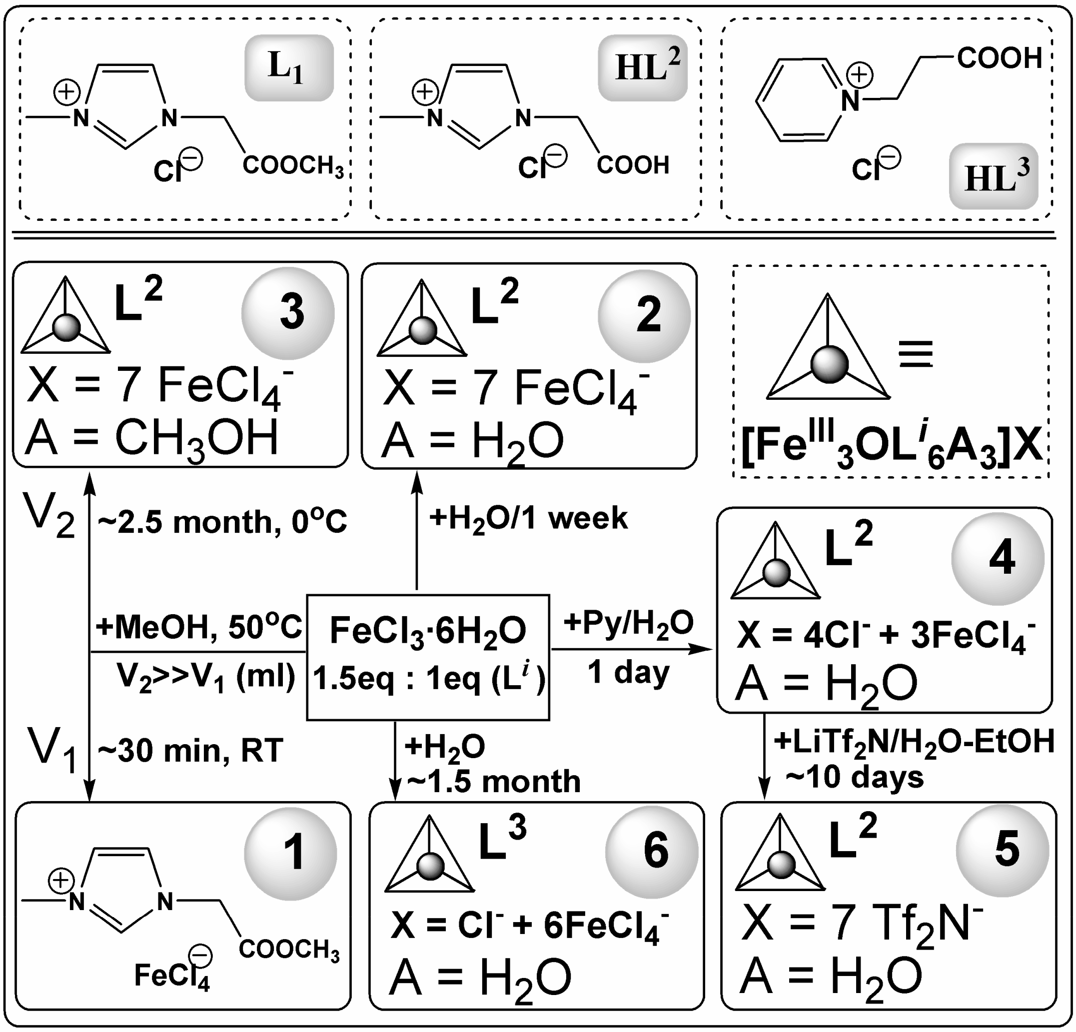
Scheme 1: General reaction scheme for the synthesis of compounds **1-6**.



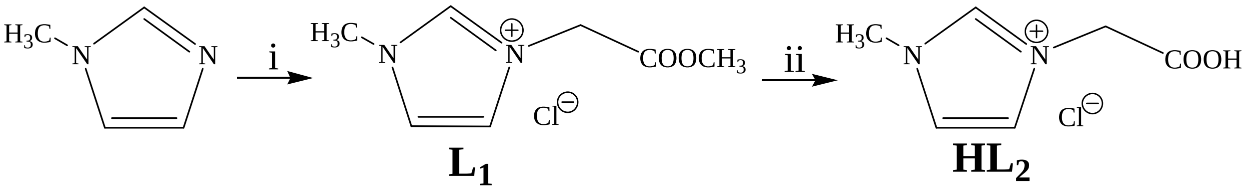
All products **1−6** were analyzed by CHN elemental analysis (Elementar Vario EL analyzer) and infrared spectroscopy (Spectrometer Perkin-Elmer Spectrum One).

Differential Scanning Calorimetry (DSC) scans and thermogravimetric analysis (TGA) were recorded on a Netzsch DSC 204 F1 Phoenix thermoanalyzer in silica crucibles with a heating rate of 5 °C/min.

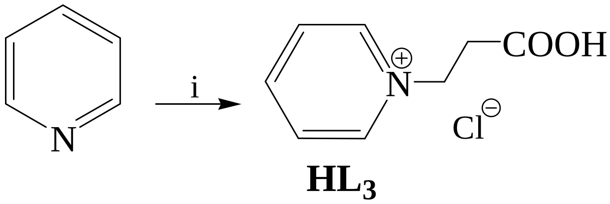
Magnetic susceptibility data (1.8-300K) were collected on powdered polycrystalline samples on a Quantum Design MPMS-XL SQUID magnetometer under an applied magnetic field of 0.1 T. All data were corrected for the contribution of the sample holder and the diamagnetism of the samples estimated from Pascal’s constants.[S1]

[S1] P. Pascal, *Ann. Chim. Phys.*, **1910**, *19*, 5.

Preparation of ligands ***L_1***, ***HL_2*** *and* ***HL_3****.*



Scheme S1: Synthetic route to ligands L_1 (and HL_2 (cmmimH). Reagents and conditions: i) 1 equiv $ClCH_2COOCH_3$, RT, 1.5 h; ii) 37% aqueous HCl solution, 100°C, 2h.



Scheme S2: Synthetic route to ligand HL_3 (cepyH). Reagents and conditions: i) 1 equiv $ClCH_2CH_2COOH$, 80°C, 3 h, EtOAc.

The crystalline products **L_1**, **HL_2** and **HL_3** were synthesized according to the literature methods [R1] (imidazolium salts) and [R2] (pyridinium salts) with slightly modificated synthetical procedures (Schemes S1 and S2).

[R1] Z. Fei, T. J. Geldbach, D. Zhao, P. J. Dyson, *Chem. Eur. J.* **2006**, *12*, 2122–2130.
[R2] M. Szafran, M. Jaskolski, I. Kowalczyk, Z. Dega-Szafran, *J. Mol. Struct.* **1998**, *448*, 77–89.

Preparation of $[C_1ImC_1CO_2CH_3]FeCl_4$ **(1):**

Freshly prepared methyl 2-(3-methyl-1H-imidazol-1-yl)acetate chloride (**L_1**) (1.91 g, 10 mmol) was added to a methanolic solution (7 mL) of $FeCl_3{\cdot}6H_2O$ (4.06 g, 15 mmol) with heating and stirring at 50°C (maximum 10 min). Crystals appear immediately or during the next 30 min at room temperature. Monocrystals were washed by methanol and air dried (Fig. SI-1a). Calc. for $C_7H_{11}N_2O_2Cl_4Fe$ (**1**): C 23.83; H 3.14; N 7.94%. Found: C 23.95; H 3.17; N 7.95%. Yield: ~1.25 g (~24% based on Fe). Selected IR data for compound **1** (KBr/cm^{-1}): 3158 (w), 3124 (w), 1758 (s, sh), 1613 (mw, sh), 1580 (w), 1569 (w, sh), 1439 (w), 1425 (mw, sh), 1386 (w), 1361 (mw), 1244 (sm), 1197 (mw, sh), 1183 (m, sh), 1109 (w), 996 (mw, sh), 966 (w), 829 (mw, sh), 770 (w, sh), 753 (mw, sh), 619 (m, sh), 565 (w).

Preparation of $[Fe_3O(C_1ImC_1CO_2)_6(H_2O)_3](FeCl_4)_7{\cdot}5H_2O$ **(2):**

To a solution of **L_1** (1.91 g, 10 mmol) in methanol (20 mL) was added $FeCl_3{\cdot}6H_2O$ (4.06 g, 15 mmol). The mixture was stirred at room temperature for 30 min. The resulting solution was left for crystallization (Petri dish ∅110). Next day the brown microcrystalline compound was separated from some drops of orange oil and dissolved in 15-20 mL of boiling water. Recrystallization process was repeated several times. After about 1 week, good quality crystals for x-ray measurement were collected and air dried. Calc. for $C_{36}H_{64}N_{12}O_{21}Cl_{28}Fe_{10}$ (**2**): C 16.94; H 2.53; N 6.59%. Found: C 17.07; H 2.56; N 6.68%. Yield: ~1.5 g (~40% based on Fe). Selected IR data for compound **2** (KBr/cm^{-1}): 3147 (m, vb), 1755 (w), 1648 (s), 1587 (mw), 1453 (s, sh), 1402 (vs, sh), 1344 (mw), 1317 (m, sh), 1170 (s, sh), 1105 (w), 1087 (w), 1035 (w), 972 (mw, sh), 842 (mw), 795 (mw, sh), 735 (mw, sh), 702 (ms, sh).

Preparation of $[Fe_3O(C_1ImC_1CO_2)_6(CH_3OH)_3](FeCl_4)_7 \cdot H_2O \cdot 2CH_3OH$ **(3):**

To a solution of **L_1** (1.91 g, 10 mmol) in methanol (25 mL) was added $FeCl_3 \cdot 6H_2O$ (4.06 g, 15 mmol). The mixture was stirred at room temperature for 30 min. The solution was devided in two portions for slow evaporation at RT (solution A) and at ~0˚C (solution B). Dark brown single crystals of **3** were formed over two (solution A) and five (solution B) months. Crystals (Fig. SI-1b) were separated from orange-brown oil and air dried. Calc. for $C_{41}H_{70}N_{12}O_{19}Cl_{28}Fe_{10}$ (**3**): C 19.04; H 2.73; N 6.50%. Found: C 19.19; H 2.74; N 6.57%. Yield: 120 mg (~3% based on Fe). Selected IR data for compound **3** (KBr/cm^{-1}): 3427 (mw, vb), 3118 (m, b), 2995 (w), 2958 (w), 1755 (mw), 1642 (vs), 1602 (ms), 1455 (s, sh), 1398 (vs, sh), 1346 (mw), 1317 (ms), 1284 (w), 1233 (w, b), 1173 (s, sh), 1107 (w), 1088 (w), 1036 (w), 1007 (w), 970 (w, sh), 947 (w), 835 (mw), 795 (mw, sh), 742 (m), 702 (ms).

Preparation of $[Fe_3O(C_1ImC_1CO_2)_6(H_2O)_3](FeCl_4)_3Cl_4 \cdot 7H_2O$ **(4):**

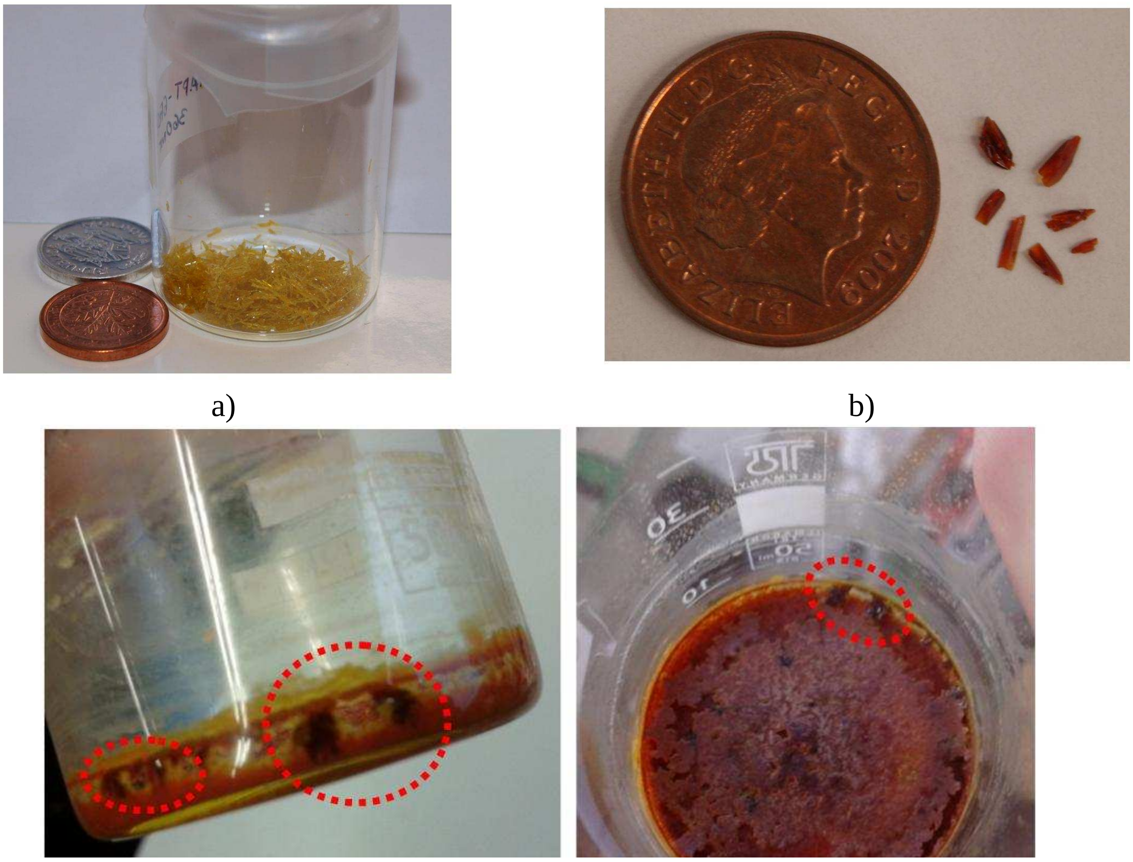
1-carboxymethyl-3-methylimidazolium chloride (**HL_2**) (1.766 g, 10 mmol) and pyridine (1.21 mL, 15 mmol) were added to an aqueous solution (25 mL) of $FeCl_3 \cdot 6H_2O$ (4.06 g, 15 mmol) with heating and stirring at 70°C during 30 min. The color of solution changed from red to deep black-brown one. After adding (with stirring) of 20 mL of CH_3CN, the brown amorphous precipitate has been formed. This precipitate was carefully separated from the mother solution and dissolved in small quantities of water (maximum 10 mL). The red monocrystals were found on the next day. Yield: ~800 mg (~17% based on Fe). Calc. for $C_{36}H_{68}N_{12}O_{23}Cl_{16}Fe_6$ (**4**): C 22.30; H 3.53; N 8.67%. Found: C 22.37; H 3.54; N 8.77%. Selected IR data for compound **4** (KBr/cm^{-1}): 3250 (m, vb), 1648 (s), 1588 (mw), 1453 (s, sh), 1403 (vs, sh), 1344 (mw), 1317 (m, sh), 1170 (s, sh), 1035 (w), 973 (mw, sh), 949 (w), 844 (mw), 795 (mw, sh), 736 (mw, sh), 704 (m, sh).

Preparation of $[Fe_3O(C_1ImC_1CO_2)_6(H_2O)_3](Tf_2N)_7 \cdot 2.43H_2O$ **(5):**

To a solution of $LiTf_2N$ (623 mg, 2.17 mmol) in water (20 mL) was added solid **4** (600 mg, 0.31 mmol). The mixture was stirred at room temperature for 30 min and non dissolved product was filtered off. After that the 5 mL of water and some volume of ethanol were added to non dissolved orange compound until total dissolving. The red monocrystals were found after about 10 days. Yield: ~160 mg (~16% based on Fe). Calc. for $C_{50}H_{58.86}N_{19}O_{46.63}F_{42}Fe_3S_{14}$ (**5**): C 19.48; H 1.92; N 8.63%. Found: C 19.54; H 2.04; N 8.68%. Selected IR data for compound **5** (KBr/cm^{-1}): 3392 (w, b), 3167 (w), 1646 (m), 1581 (w), 1457 (m, sh), 1409 (ms, sh), 1343 (s), 1323 (s), 1176 (vs), 1129 (vs), 1054 (vs), 974 (sh, mw), 948 (w), 850 (mw), 792 (m, sh), 765 (w, sh), 739 (m, sh), 704 (m, sh), 654 (w).

Preparation of $[Fe_3O(PyC_2CO_2)_6(H_2O)_3](FeCl_4)_6\,Cl \cdot 4H_2O$ **(6):**

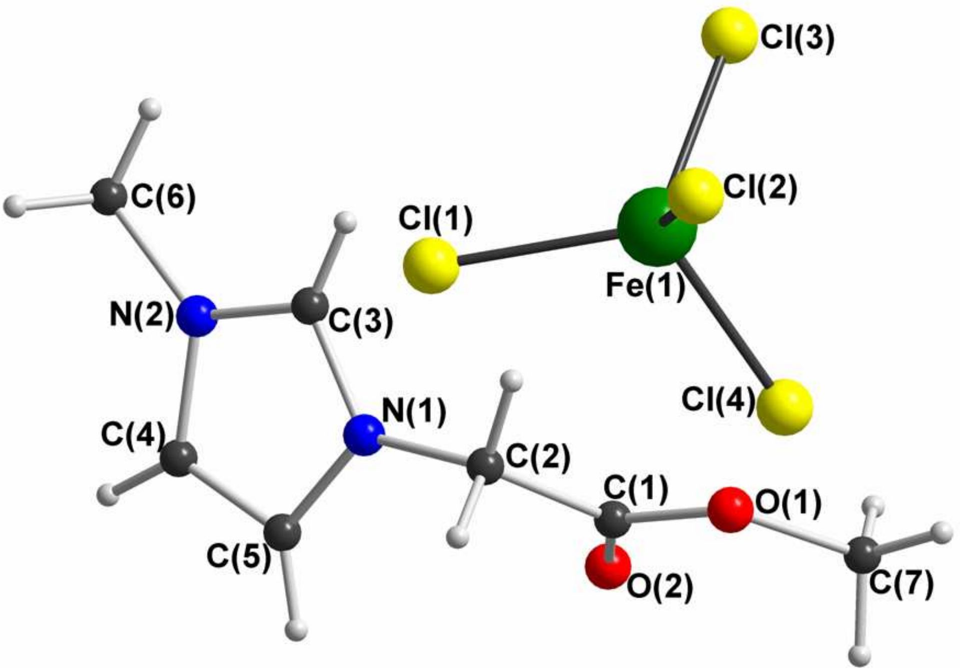
The synthetic procedure for **2** was repeated by using **HL_3** instead of **HL_2**. Only yellow crystalline powder, not suitable for x-ray experiment, was formed during one week. After about 1.5 month some quantities of red crystals were found among yellow crystalline mass. These crystals (Figure SI-1c) were separated mechanically and recrystallized in small quantities of water. Current yield: ~30-40 mg. After additional 6 month, the yellow mass with some red inclusions (Figure SI-1c) was re-dissolved in water and left for crystallization. After two days the mixture of yellow mass and red crystals were observed. The red crystals were separated mechanically and recrystallized in water again (2-3 mL). After 1 day the good quality crystals were collected and analyzed. Yield (total): ~80 mg (~2% based on Fe). Calc. for $C_{48}H_{68}N_6O_{20}Cl_{25}Fe_9$ (**6**): C 23.65; H 2.81; N 3.45%. Found: C 22.87; H 2.84; N 3.52%. Selected IR data for compound **6** (KBr/cm^{-1}): 3376 (m, vb), 1734 (m), 1639 (sm), 1605 (m), 1488 (m), 1452 (m), 1443 (m), 1396 (mw), 1323 (mw), 1302 (w), 1249 (w), 1199 (w), 1175 (m), 1111 (mw), 1055 (w), 1029 (w), 999 (mw), 940 (m, sh), 878 (w), 780 (m, sh), 681 (s, sh), 611 (sm, sh), 591 (m), 528 (w).



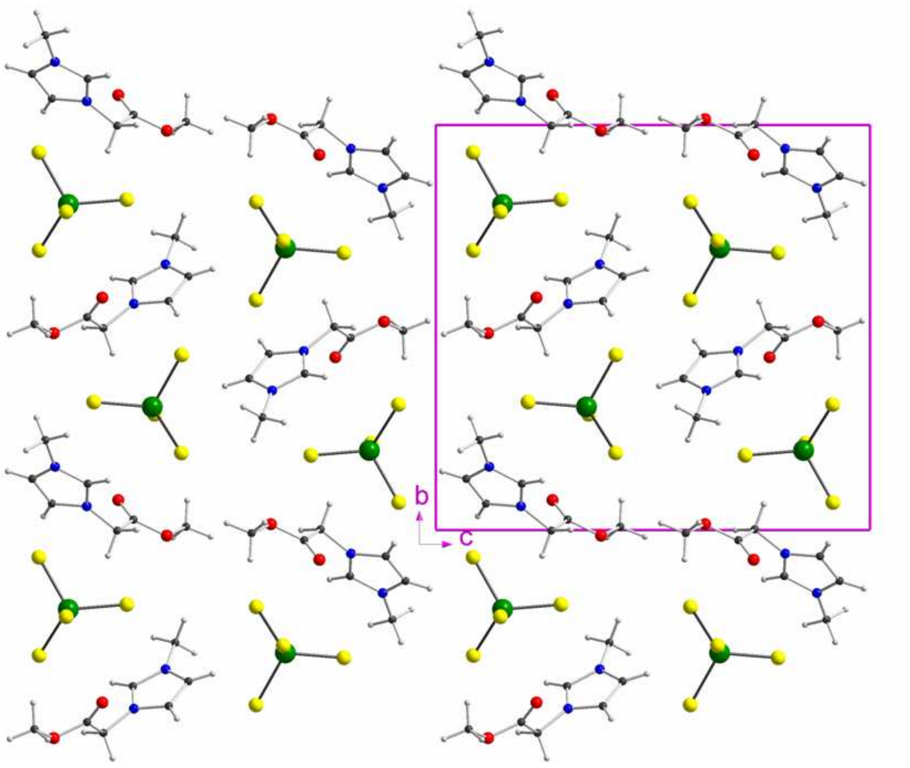
a) b)

c)

Fugure SI-1: Photos of some prepared compounds **1** (a), **3** (b) and an intermediate of **6** (c).



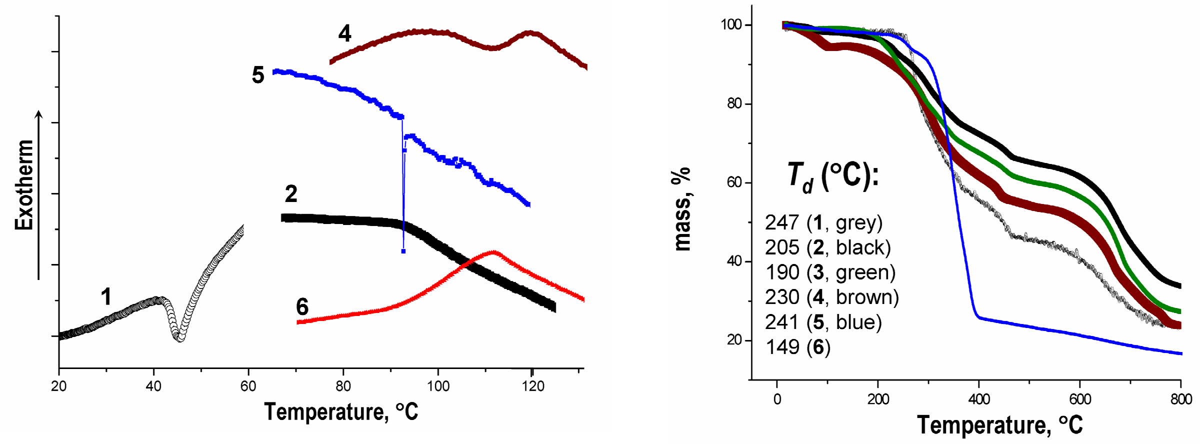
(a)



(b)

Figure S1: Molecular structure (a) and crystal packing (b) of [mcmmim][$FeCl_4$] (**1**).

To evaluate the thermal stabilities of the synthesized clusters, the thermogravimetric analyses (TGA) were performed. Their melting points (**1**, **5**) or glass transition points (**2**, **4**, **6**) depend on combination of ligand/solvent molecule and nature of anions and ranged from 42 to 103°C (Table 1). The TG traces of **1-6** are shown in Figure S1b. The insignificant (up to maximum 2 %) weight losses of the lattice water molecules (**2**, **4**, **6**) were observed and in general can be considered as not a part of the decomposition process. A different situation was observed in the thermal behaviour of compound **3**, where the partial elimination of CH_3OH molecules (loss of ca 1.1% mass) in **3** was accompanied by the decomposition of the cluster with visible melting (~72 °C). The temperatures of decomposition for **1-6** are presented as inserts in Figure S2b.



(a) (b)

Figure S2: (a) DSC curves of 1, 2 and 4-6; (b) TG traces of 1-5 measured at the heating rate of $5K\cdot min^{-1}$.

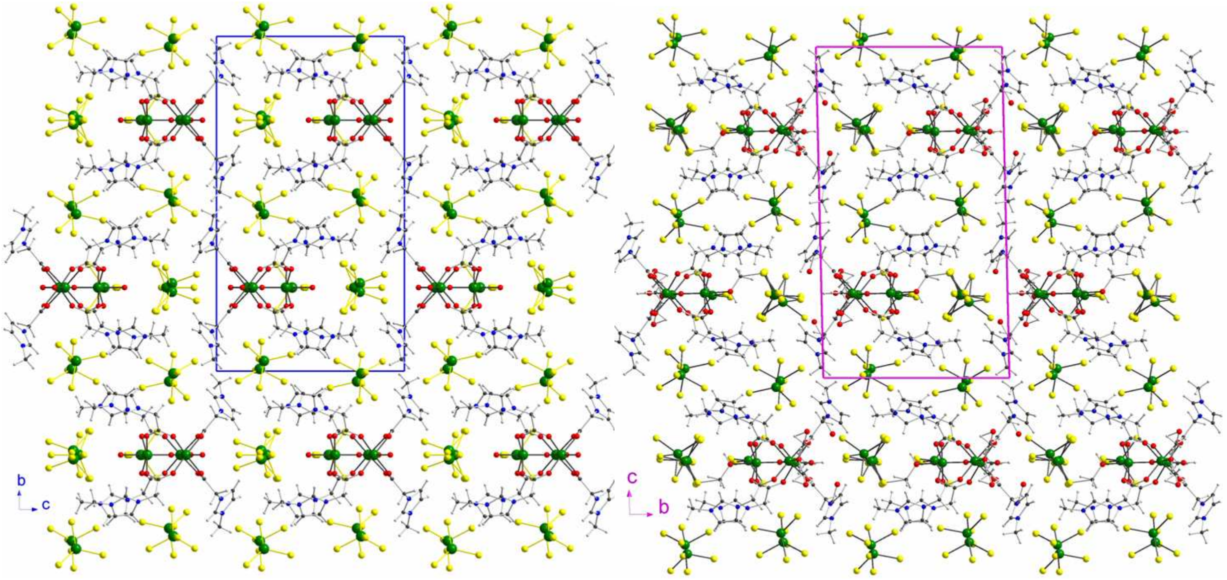


Figure S3. Comparison of the crystal packing of **2** (left) and **3** (right) showing the close relationship between the two, despite the difference in crystal systems (monoclinic $P2_1/m$ for **2**, triclinic *P-1* for **3**).

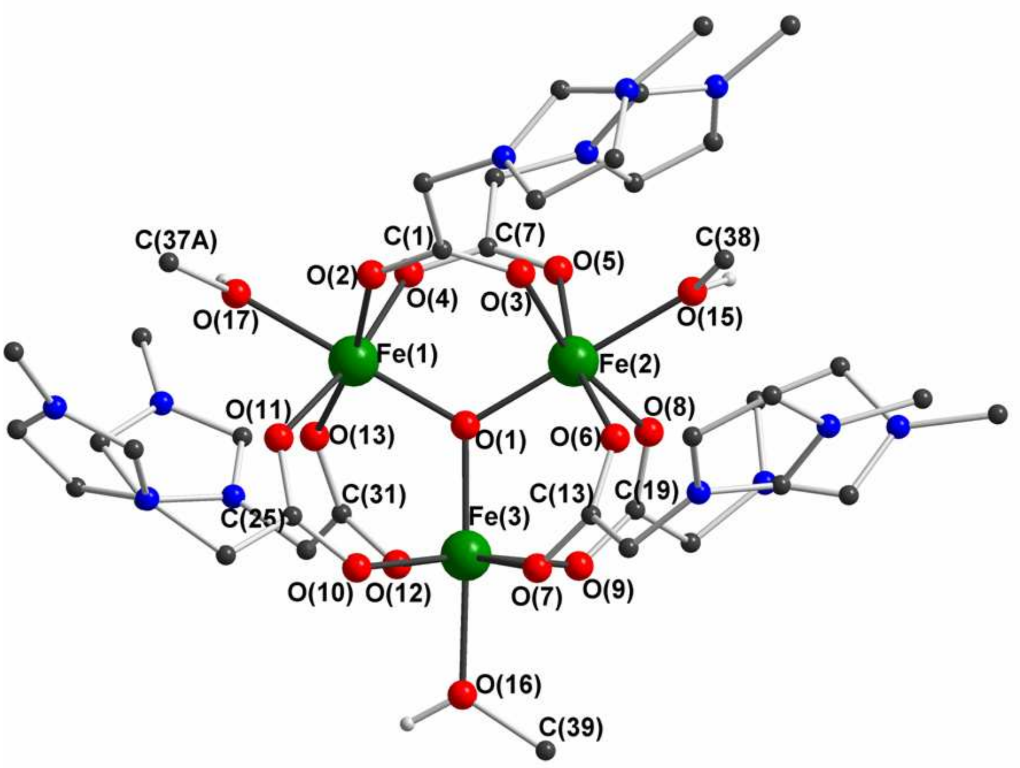


Figure S4. Molecular structure of the $[Fe_3O(cmmim)_6(MeOH)_3]^{7+}$ cation in **3**.

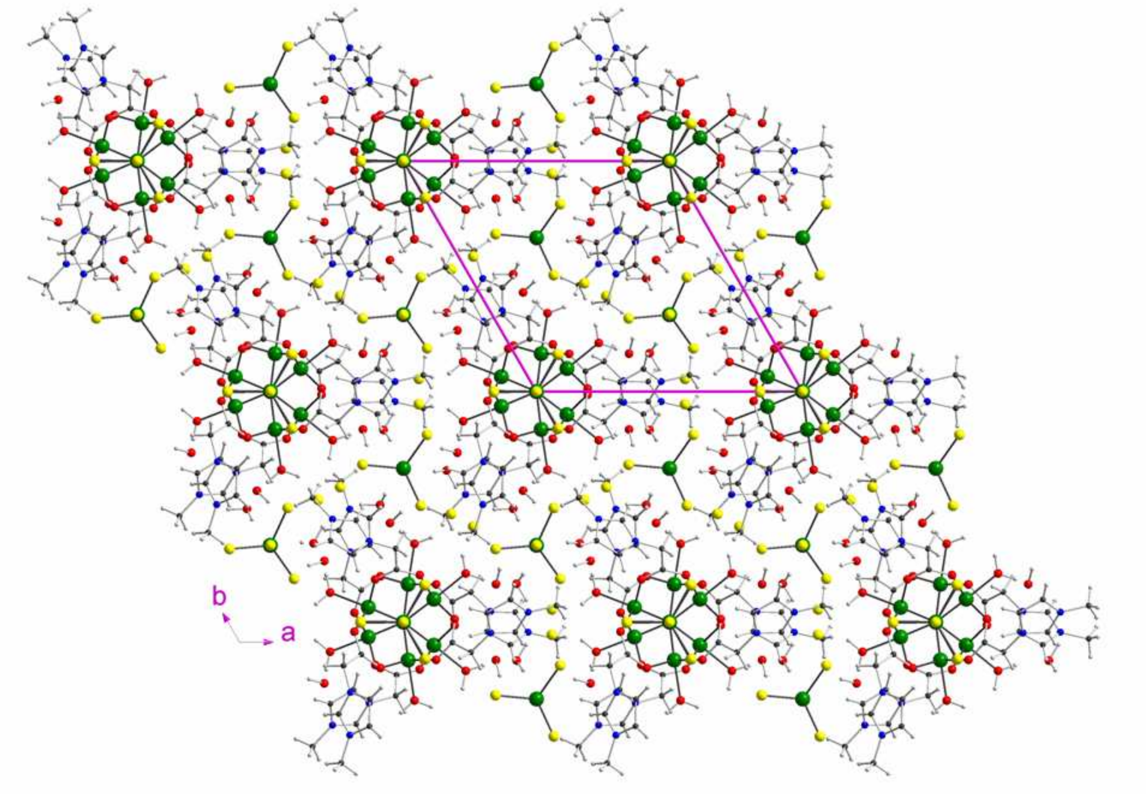


Figure S5. Crystal packing for $[Fe_3O(cmmim)_6(H_2O)_3](FeCl_4)_3Cl_4$ (**4**) viewed down the *c*-axis.

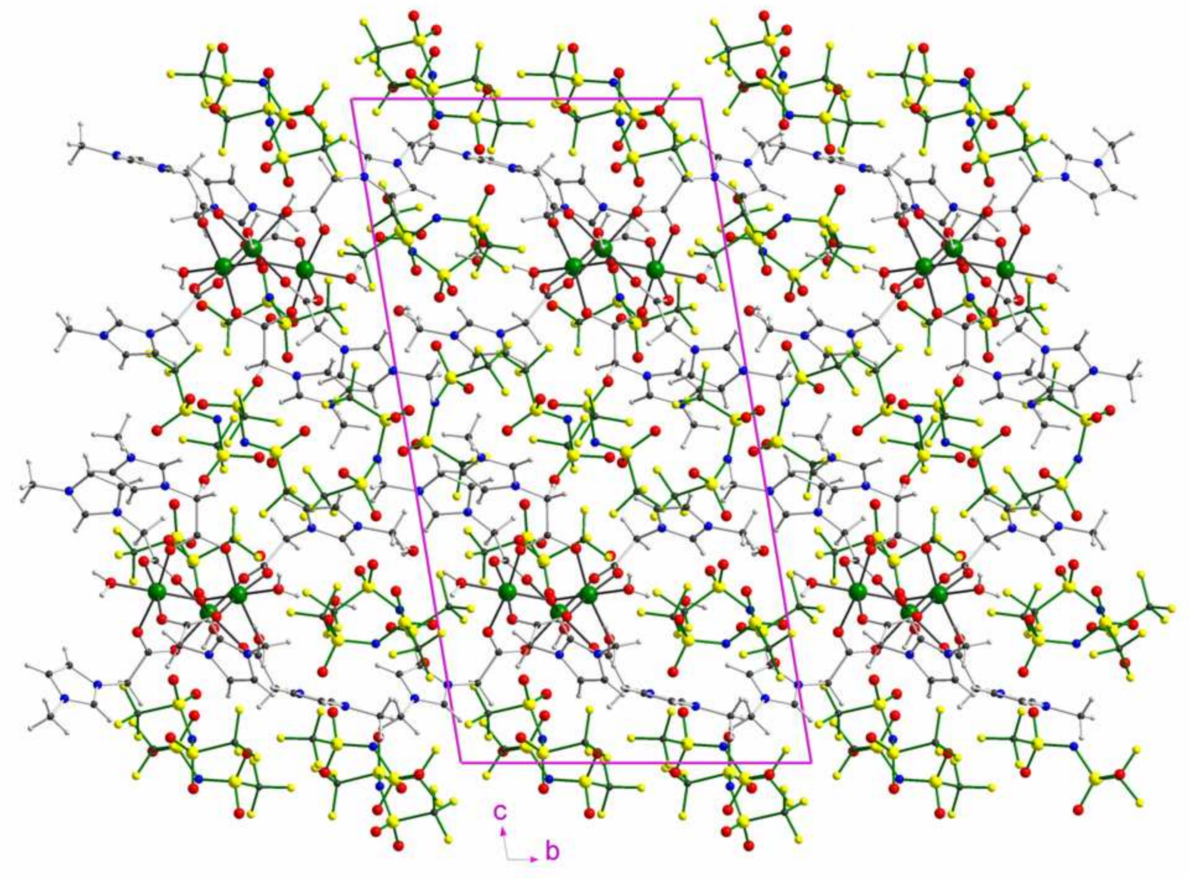
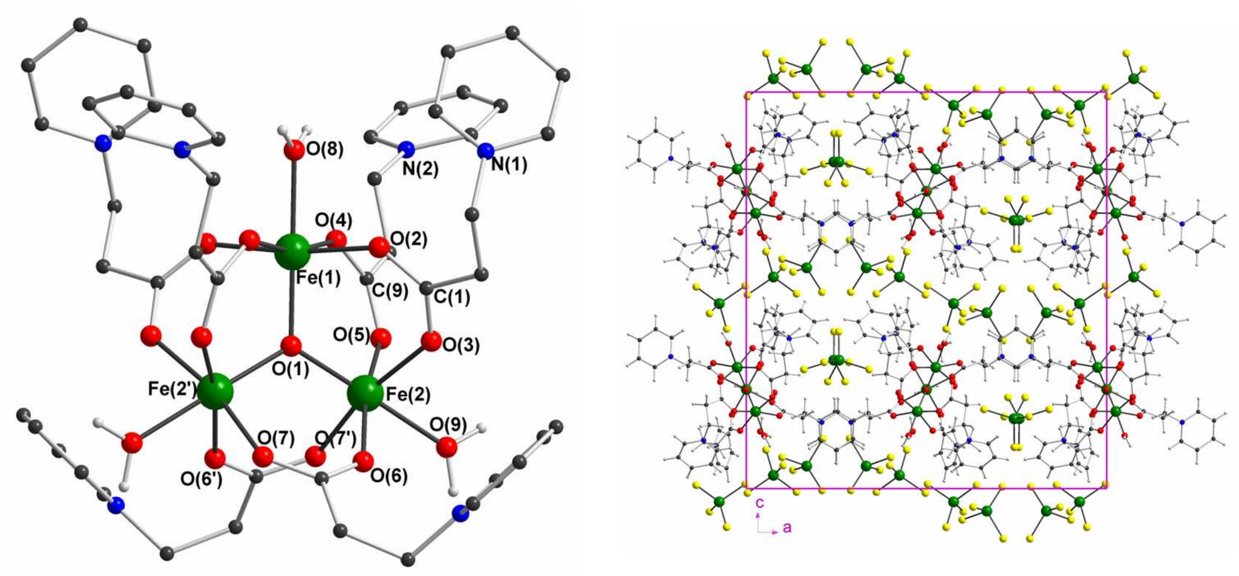


Figure S6. Crystal packing of $[Fe_3O(cmmim)_6(H_2O)_3](Tf_2N)_7{\cdot}2.43H_2O$ (**5**) viewed along the a-axis. Anion disorder omitted for clarity, bonds within the anions shown as green.



(a) (b)

Figure S7. (a) Molecular structure of the trinuclear $[Fe_3O(cepy)_6(H_2O)_3]^{7+}$ complex in **6** (organic H-atoms omitted for clarity - the metal complex has crystallographically-imposed twofold rotational symmetry and the prime character in the atom labels indicates that these atoms are at the equivalent position {-x+1, y, -z+½}); (b) Crystal packing in $[Fe_3O(cepy)_6(H_2O)_3][FeCl_4]_6Cl\cdot 4H_2O$ (**6**) (anion disorder omitted for clarity.

Crystallography: Data were measured on Stoe IPDS 2 (**2**, **3**, **5**, **6**) or IPDS 1 (**1**, **4**) diffractometers using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Details of the crystal structures, data collection and structure refinement are summarised in Table S1. Structure solution (direct methods) and full-matrix least-squares refinement against all data were carried out with the SHELXTL 6.14 software package. [G.M. Sheldrick, *Acta Cryst*. **2008**, *A64*, 112-122]. In general, all ordered non-H atoms were assigned anisotropic temperature factors, and H-atoms bonded to carbon were placed in calculated positions. Comments to specific structures are as follows:

2: One $FeCl_4$ anion (Fe(8)) was disordered either side of the mirror plane, with the two mirror-related components overlapping. The half-occupancy anion was refined with similarity restraints applied both to the Fe-Cl and Cl..Cl distances, and to the anisotropic thermal parameters (DELU) of the five atoms. It proved not possible to refine the hydrogen atoms of the aquo ligands, because of the disorder of the anions to whicjh they make hydrogen bonds. Lattice waters were disordered between the $(FeCl_4)^-$ anions, and proved difficult to model in the presence of the heavy atoms of the anions. They were handled using the SQUEEZE option within PLATON [A.L. Spek, *J. Appl. Cryst*. **2003**, *36*, 7-13].

3: The crystal structure is closely related to the monoclinic $P2_1/m$ structure of complex **2**, and is derived from it by a slight change of the angles α and γ from 90 degrees, followed by the necessary axis permutation to give the conventional triclinic cell. The unit cell contents of **3** also approximate to that of 2 (Fig. S3), and the resulting pseudo-symmetry hampered refinement. Not unexpectedly, this pseudo-symmetry also resulted in pseudo-merohedral twinning by 180 degree rotation about the triclinic *c*-axis (corresponding to monoclinic *b* in **2**). This was not noticeable during data collection (ca. 14% for the minor domain), so a datafile in HKLF 5 format was created using the TWINROTMAT option within PLATON Refinement was then relatively straightforward. One of the $(FeCl_4)^-$ anions was disordered: the Fe of the minor component refined to a site occupancy of 0.16. The chlorines of this minor component were then further disordered, and could not be refined satisfactorily. One MeOH ligand, and the lattice water to which it hydrogen bonds, were twofold disordered either side of the pseudo-mirror plane.

4: Geometrical restraints were applied to positions of water H atoms. A chloride anion and a lattice water were 50:50 disordered; a similarity restraint was applied to the anisotropic thermal parameters of the closely separated atoms.

5: O-H bond lengths were restrained to 0.92(4) Ang. Three of the (Tf_2N)- anions were extensively disordered. Refinement (with disordered partial-occupancy atoms isotropic) was successful with S-N, S-O, S-C and C-F bond lengths restrained to common values, as were S..S and F..F 1-3 distances where necessary. A (partial occupancy) lattice water, O(63B), was only consistent with the minor component of one of the Tf_2N anions; no corresponding major component appeared to be present, resulting in the total of 2.43 lattice waters per formula unit.

6: The Fe and two Cl atoms of a $(FeCl_4)$- anion were twofold disordered, while three Cl atoms of another anion were similarly disordered. Within each anion, similarity restraints were applied to Fe-Cl distances. Geometrical restraints were applied to O-H bonds.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 896157 (**1**), 896158 (**2**), 896159 (**3**), 896160 (**4**), 896161 (**5**), 896162 (**6**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK: http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, e-mail: data_request@ccdc.cam.ac.uk, or fax: +44 1223 336033.

Table S1. Crystallographic and structure refinement data for compounds **1-6**.

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_7H_{11}Cl_4FeN_2O_2$	$C_{36}H_{64}Cl_{28}Fe_{10}N_{12}O_{21}$	$C_{41}H_{70}Cl_{28}Fe_{10}N_{12}O_{19}$	$C_{36}H_{68}Cl_{16}Fe_6N_{12}O_{23}$	$C_{50}H_{58.86}F_{42}Fe_3N_{19}O_{46.43}S_{14}$	$C_{48}H_{68}Cl_{25}Fe_9N_6O_{20}$
M_r	352.83	2552.09	2586.19	1939.32	3083.29	2437.98
Crystal System	Monoclinic	Monoclinic	Triclinic	Hexagonal	Triclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/m$	*P*-1	*P*-62*c*	*P*-1	*Pbcn*
T (K)	253(2)	150(2)	180(2)	200(2)	180(2)	150(2)
a (Å)	6.3649(5)	12.6816(9)	12.7495(4)	13.3201(6)	14.9606(4)	24.8363(12)
b (Å)	14.6411(11)	26.2169(14)	15.5320(5)	13.3201(6)	15.5623(4)	13.7847(7)
c (Å)	15.9618(12)	15.5404(10)	26.1211(7)	24.7380(13)	27.4325(9)	27.4404(19)
α (°)	90	90	90.846(2)	90	93.562(2)	90
β (°)	101.004(9)	109.243(5)	91.244(2)	90	101.381(2)	90
γ (°)	90	90	108.346(2)	120	115.135(2)	90
V (Å^3)	1460.12(19)	4878.1(5)	4907.3(3)	3801.1(3)	5591.2(3)	9394.5(9)
Z	4	2	2	2	2	4
D_{calc} (g cm^{-3})	1.605	1.738	1.750	1.694	1.831	1.724
F(000)	708	2536	2576	1960	3087	4868
μ(Mo-Kα) (mm^{-1})	1.7532	2.265	2.252	1.748	0.807	2.117
Reflections collected	11346	67061	61617	29754	37919	82847
Unique reflections	2832	9461	17953	2588	20945	8600
R_{int}	0.0261	0.0669	0.1154	0.0869	0.0472	0.0833
Parameters	147	511	980	171	1724	527
R_1 ($I > 2\sigma(I)$)	0.0350	0.0596	0.0701	0.0457	0.0579	0.0768
wR_2 (all data)	0.0910	0.1726	0.2169	0.1226	0.1603	0.2165
S (all data)	1.073	0.999	1.060	1.066	0.993	1.032

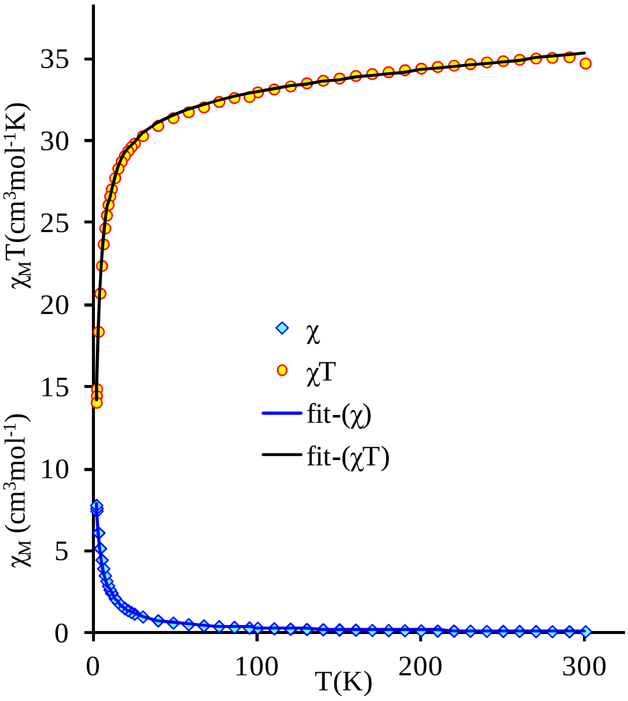


Figure S8. Magnetic susceptibility χ and χT versus T plots data for compound **3**. The black solid lines correspond to the best fit according the model and parameters indicated in text.

Mössbauer spectra of polycrystalline samples of **3** at T = 50 and 3 K are typical for paramagnetic behavior with an asymmetric quadrupole doublet which can be fitted using two doublets with isomer shifts (δ) 0.43 (0.43) and 0.32 (0.33) mm/s and quadrupole splittings (ΔE_Q) 0.60 (0.62) and 0.17 (0.19) mm/s, respectively for $\{Fe_3O\}^{7+}$ and $7[FeCl_4]^-$, typical of high spin S=5/2, Fe^{III} ions (details in Table S2, Figure S9). The isomer shifts are comparable to those of chloride- or oxo-bridged [S2] high-spin ferric complexes. The isomer shifts of ca. 0.33 mm/s for $7[FeCl_4]^-$ are in good agreement with the reported values for tetrahedral Fe^{III}.[S3] Although the quadrupole splitting of high-spin Fe^{III} in tetrahedral environments is usually negligible or even zero, small values of quadrupole splitting are conceivable in distorted surroundings. In some cases, e.g. NMe_4FeCl_4 or NEt_4FeCl_4, quadrupole splitting was zero, while in $AsPh_4FeCl_4$ a quadrupole splitting of 0.2 mm/s was reported.[S3a] These features are regarded as owing to the regular tetrahedron in some of the reported examples and the slightly distorted ones for $7[FeCl_4]^-$ in the compound **3**. An increase in the isomer shift upon cooling is attributed to a second-order Doppler effect.

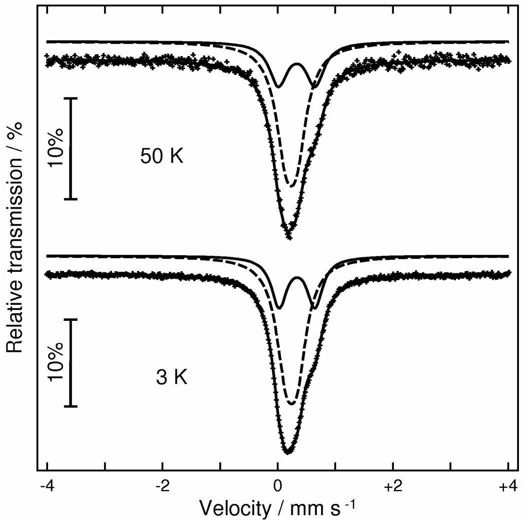


Figure S9. The ^{57}Fe Mössbauer spectra of **3** at indicated temperatures.

[S2] (a) A. L. Feig, S. J. Lippard, *Chem. Rev.* **1994**, *94*, 759-805; (b) Y. Zang, G. Pan, L. Jr. Que, B. G. Fox, E. Münck, *J. Am. Chem. Soc.* **1994**, *116*, 3653-3654; (c) Y. Zang, Y. Dong, L. Jr. Que, K. Kauffmann, E. Münck, *J. Am. Chem. Soc.* **1995**, *117*, 1169-1170.

[S3] (a) P. R. Edwards, C. E. Johnson, *J. Chem. Phys.* **1968**, *49*, 211-216; (b) S. Kitao, M. Seto, Y. Maeda, T. Matsuyama, S. Masubuchi, S. Kazama, *J. Phys. Soc. Jpn.* **1997**, *66*, 1195-1200.

Table S2: Mössbauer parameters for **3** at indicated temperatures.

T, K	Site	$\delta^{[a]}$, mm/s	ΔE_Q, mm/s	Γ, mm/s
150	Fe_3O	0.431(6)	0.60(1)	0.40(1)
	$7xFeCl_4$	0.320(3)	0.17(1)	0.45(1)
3	Fe_3O	0.435(1)	0.621(3)	0.33(1)
	$7xFeCl_4$	0.337(1)	0.197(2)	0.41(1)

[a] Relative to α-Fe at room temperature. The statistical errors are given in parentheses.
δ is the isomer shift, ΔE_Q - quadrupolar splitting, Γ - average width of the doublet peaks.

Table S3: The recycle of catalysts in synthesis of ethyl 2-methyl-4-(2-oxo-2,3-dihydro-1H-3-indolyl)-5-phenyl-1H-3-pyrrolecarboxylate (**7a**).

Catalyst	Number of cycles/Isolated yield [%]									
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
1	86.2	85.1	82.7	78.3	65.0	31.0	-	-	-	-
2	94.5	90.2	86.2	70.5	69.0	45.0	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-
4	98.0	96.5	95.1	93.8	90.0	89.6	88.6	88.3	85.0	62.0
5	98.0	96.5	93.6	92.4	92.0	92.0	89.6	86.2	84.7	73.8
6	96.0	94.1	93.2	91.6	89.6	88.2	88.0	84.1	76.1	73.2

Procedure for synthesis of ethyl 2-methyl-4-(2-oxo-2,3-dihydro-1*H*-3-indolyl)-5-phenyl-1*H*-3-pyrrolecarboxylate (7a)

The mixture of 3-(2-oxo-2-phenylethylidene)indolin-2-one (0.001 mol), ethyl 3-oxobutanoate (0.001 mol), catalyst (10 mg) and ammonium acetate (0.0025 mol) was stirred at reflux in dry EtOAc (4 ml) for 1.5-2 hour (monitoring by TLC), filtered. After removal of ethyl 2-methyl-4-(2-oxo-2,3-dihydro-1*H*-3-indolyl)-5-phenyl-1*H*-3-pyrrolecarboxylate **7a**, the rest was directly recycled in subsequent runs. Analytical sample with m.p. 317-318 °C has been obtained by recrystallization from EtOH. IR (KBr), /cm^{-1}: 3347, 3208, 1702, 1667, 1466, 1101, 698; Anal. calc. for $C_{22}H_{20}N_2O_3$ (**7a**): C, 73.32; H, 5.59; N, 7.77. Found: C, 73.25; H, 5.57; N, 7.73.

Table S4: The recycling of catalysts in synthesis of 3,3'-((4-methoxyphenyl)methylene)bis(1H-indole) (**8a**).

Catalyst	Number of cycles Isolated yield [%]/Time [hours]				
	1	*2*	*3*	*4*	*5*
1	82/5	72/5	56/15	-	-
2	92/5	89/5	78/10	75/10	70/15
3	-	-	-	-	-
4	85/5	78/10	75/10	72/15	-
5	70/5	65/10	-	-	-
6	89/5	74/10	69/10	60/10	56/15

Procedure for synthesis of 3,3'-((4-methoxyphenyl)methylene)bis(1H-indole) (8a).

A mixture of indole (0.5 mmol), 4-methoxybenzaldehyde (0.25 mmol), and catalyst (3 mg) in benzene (2.5 ml) was refluxed for the appropriate time (Table S4). After completion of the reaction as indicated by TLC, the catalyst was separate by decantation, and used for next run with out additional purification. The benzene was concentrated and crude compound purified by column chromatography (EtOAc/benzene) to afford the pure 3,3'-((4-methoxyphenyl)methylene)bis(1*H*-indole) **8a**. M.p. 187-189 °C; IR (KBr), /cm^{-1}: 1218, 1245, 1453, 1509, 1611, 2925, 3412; Anal. calc. for $C_{24}H_{20}N_2O$ (**8a**): C, 81.79; H, 5.72; N, 7.95. Found: C, 81.73; H, 5.75; N, 7.91.