Electronic Supplementary Information

New nickel(II) and iron(II) helicates and tetrahedra derived from expanded quaterpyridines

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1. ^{1}H NMR spectra

^{1}H NMR spectra of 2, [Fe$_2$(2)$_3$](PF$_6$)$_4$ and Fe$_4$(2)$_6$](PF$_6$)$_4$

Compared to the ^{1}H NMR spectrum of free **2** (Fig.1S(a)), that of Fe$_2$(**2**)$_3$(PF$_6$)$_4$ (Fig.1S(b)) shows upfield shifted resonances for protons in both the 6′- and 6′′-positions, presumably due to the former falling within the shielding cone of the adjacent bipyridine units in the same coordination sphere. Similarly, the ^{1}H NMR spectrum of Fe$_4$(**2**)$_6$(PF$_6$)$_8$ (Figure 1S(c) revealed that the 6′- and 6′′-proton resonances were also shifted upfield compared to those of the free ligand (**2**), with, in this case, the 6′-proton resonance occurring 0.9 ppm downfield of the corresponding H-6′ resonance in [Fe$_2$(**2**)$_3$](PF$_6$)$_4$. It is noted that the ^{1}H NMR spectrum of [Fe$_2$(**2**)$_3$](PF$_6$)$_4$ indicates the presence of a dynamic process which is moderately slow on the NMR timescale (Figure 1S (b) see green arrows). The nature of this process was not probed further in the present study. The corresponding spectrum of Fe$_4$(**1**)$_6$(PF$_6$)$_8$ is given in Figure 1S(d) for comparison.

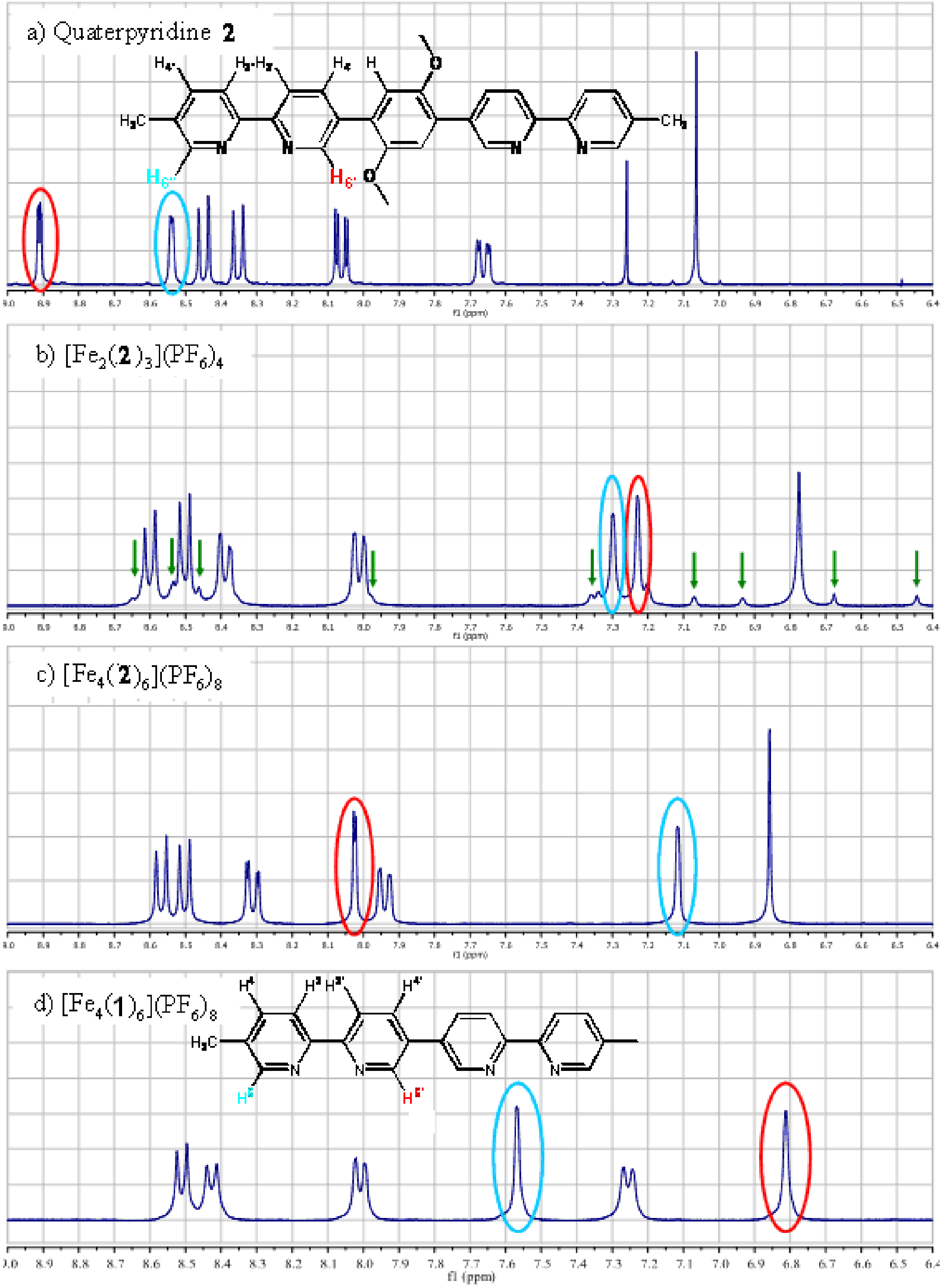


Fig. 1S From top to bottom - ^{1}H NMR of the aromatic region of a) quaterpyridine **2** (in $CDCl_3$), and b) $[Fe_2(\mathbf{2})_3](PF_6)_4$, c) $[Fe_4(\mathbf{2})_6](PF_6)_8$ and d) $[Fe_4(\mathbf{1})_6](PF_6)_8$ (all in CD_3CN).

^{1}H NMR spectra of $Fe_4(3)_6](PF_6)_4$

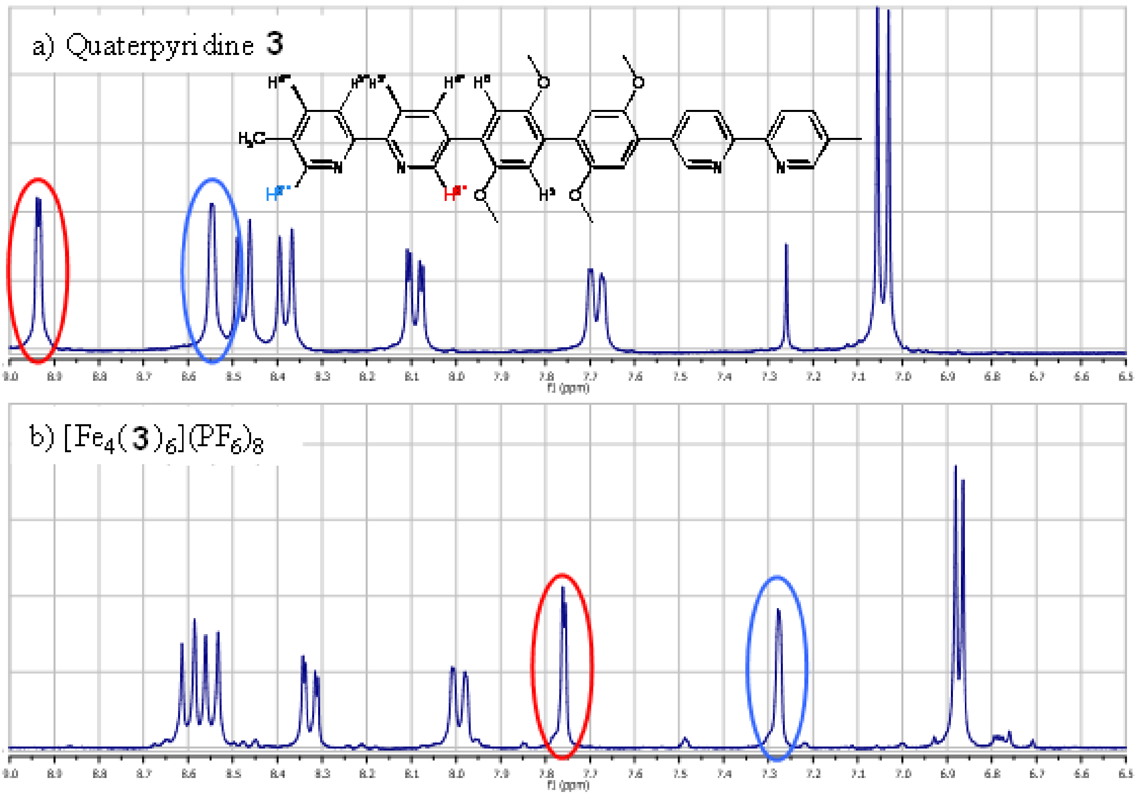
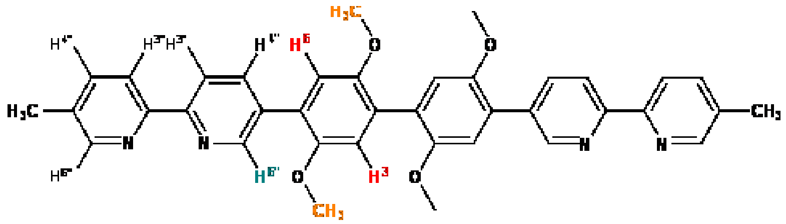


Figure 2S ^{1}H NMR of the aromatic region of (a) quaterpyridine **3** (in $CDCl_3$), (b) $[Fe_2(\mathbf{3})_3](PF_6)_4$ (in CD_3CN).

Variable temperature ^{1}H NMR spectra of $[Fe_2(3)_3](PF_6)_4$



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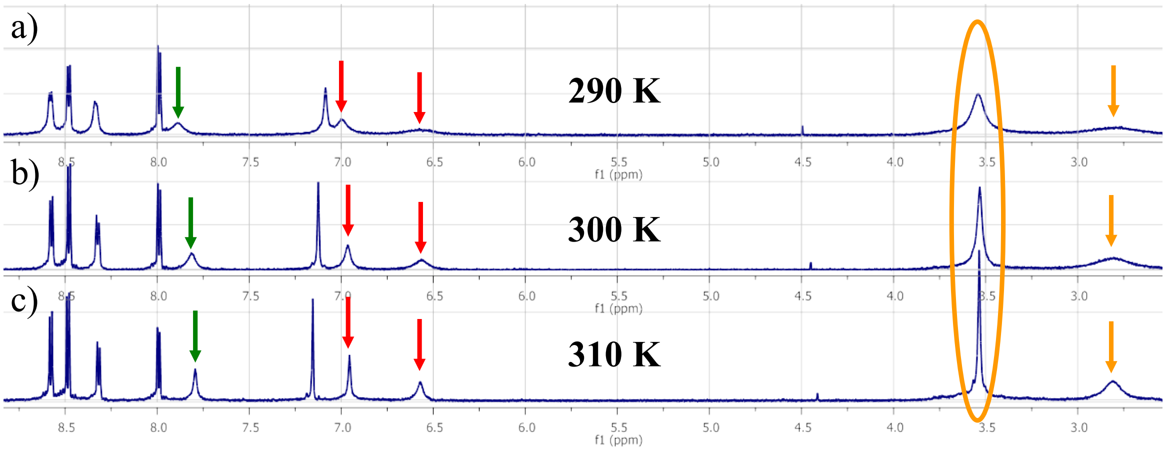


Fig. 3S Variable temperature ^{1}H NMR spectra of $[Fe_2(\mathbf{3})_3](PF_6)_4$ in CD_3CN run at a) 290 K, b) 300 K, and c) 310 K.

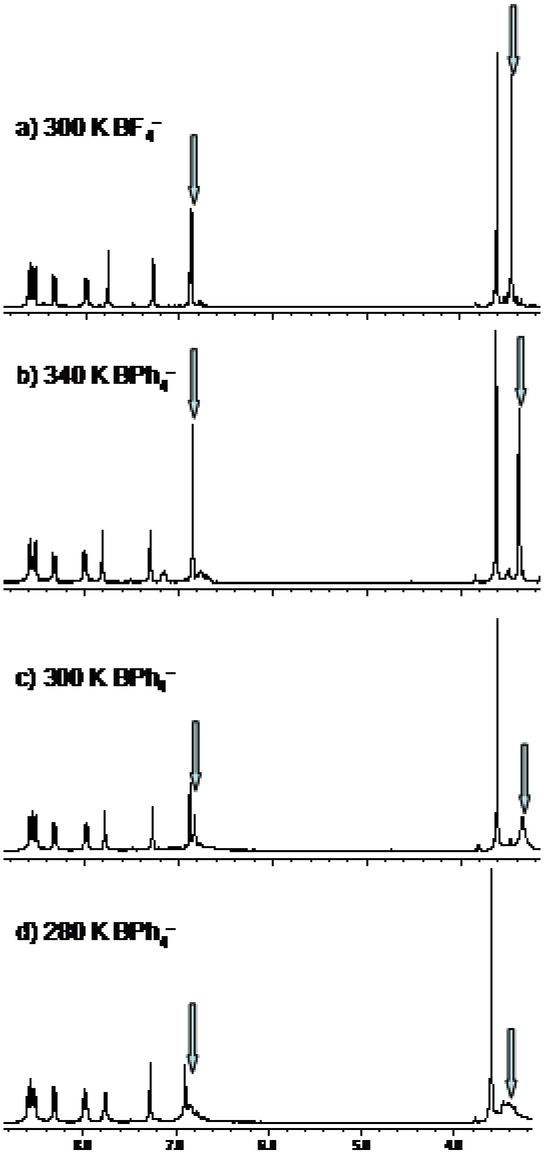


Fig. 4S Comparision of the ^{1}H NMR spectrum a) of $[Fe_4(\mathbf{3})_6](BF_4)_8$, with the corresponding variable temperature spectra, b) to d), obtained after the addition of one equivalent of BPh_4^- to the solution employed to obtain spectrum a).

2. UV-vis and fluorescence spectra

$[Fe_2(2)_3](PF_6)_4$ and $[Fe_4(2)_6](PF_6)_8$

The main difference in the absorption positions in the UV-vis spectra of [Fe$_4$(**2**)$_6$](PF$_6$)$_8$ and [Fe$_2$(**2**)$_3$](PF$_6$)$_4$ is that the CT (π-π*) band for the former (386 nm) shows a small shift relative to the latter (374 nm). The fluorescence spectrum of [Fe$_2$(**2**)$_3$](PF$_6$)$_4$ exhibits a strong emission at 450 nm (blue) and a weaker emission at 736 nm resulting from excitation of this complex at 374 nm. Similarly, a strong emission at 455 nm and a weaker emission at 761 nm were observed when [Fe$_4$(**2**)$_6$](PF$_6$)$_8$ was irradiated at 386 nm.

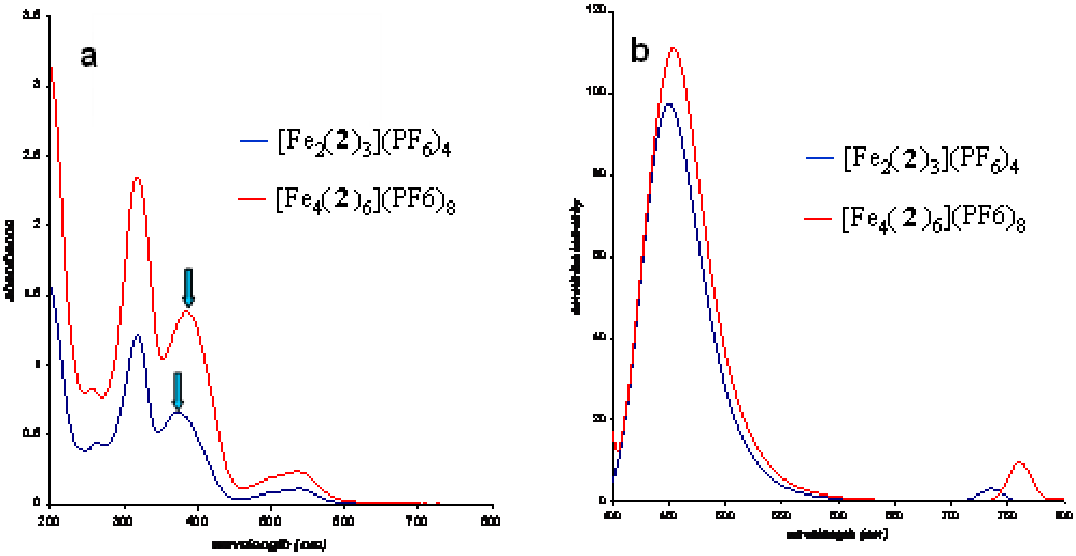


Fig. 5S Overlaid a) UV-vis spectra and b) fluorescence spectra for [Fe$_2$(**2**)$_3$](PF$_6$)$_4$ and [Fe$_4$(**2**)$_6$](PF$_6$)$_8$ in acetonitrile.

[Fe$_2$(3)$_3$](PF$_6$)$_4$ (532 nm) and [Fe$_4$(3)$_6$](PF$_6$)$_8$

The most noticeable difference in the UV-vis spectral band positions for $[Fe_2(\mathbf{3})_3](PF_6)_4$ and $[Fe_4(\mathbf{3})_6](PF_6)_8$ occurs for the CT (π-π*) band. A small blue shift is observed for $[Fe_2(\mathbf{3})_3](PF_6)_4$ (365 nm) relative to $[Fe_4(\mathbf{3})_6](PF_6)_8$ (376 nm) (Fig. 5S a)

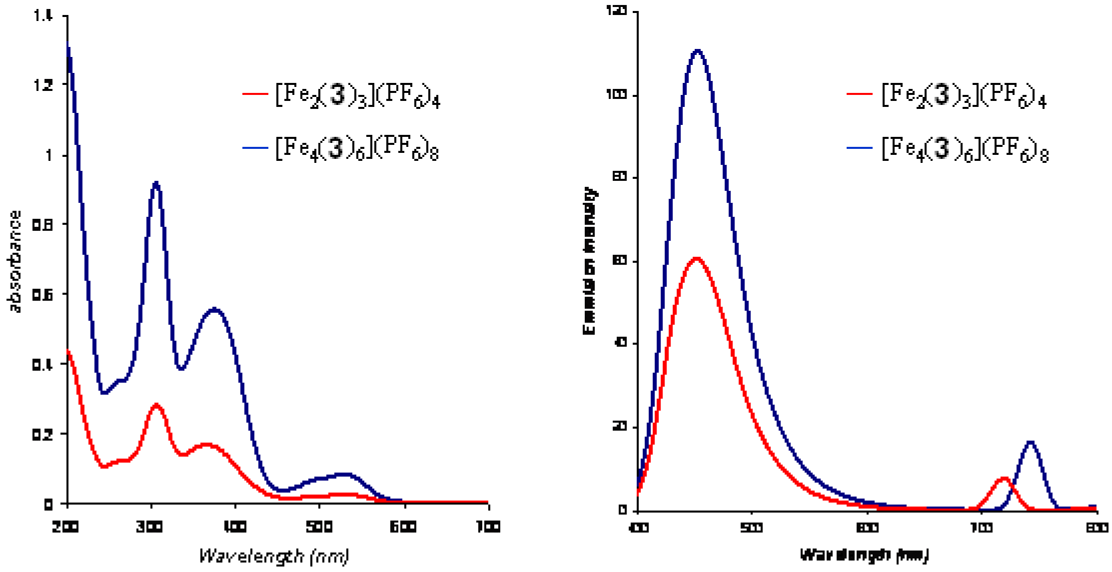


Fig. 6S Overlaid a) UV-vis spectra and b) fluorescence spectra for $[Fe_2(\mathbf{3})_3](PF_6)_4$ and $[Fe_4(\mathbf{3})_6](PF_6)_8$ in acetonitrile.

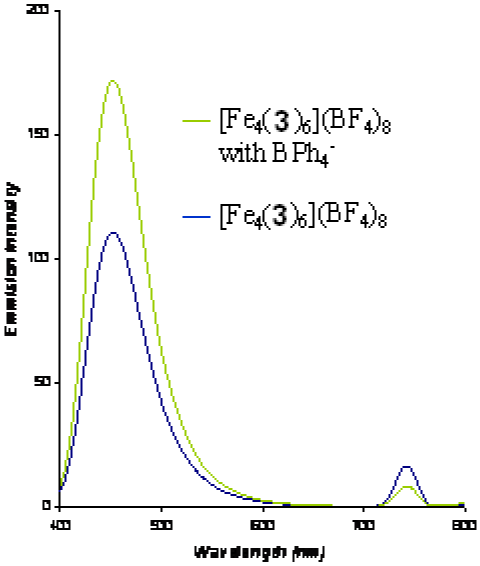


Fig. 7S Fluorescence emission spectra before and after addition of one equivalent of BPh$_4^-$ to a solution of [Fe$_4$(**3**)$_6$](BF$_4$)$_8$ in acetonitrile illustrating that irradiation at 376 nm results in a significant increase in emission intensity at 453 nm coupled with a decrease at 742 nm.

3. Representations of the void volumes in $[Fe_4(1)_6]^{8+}$ and $[Fe_4(3)_6]^{8+}$

$[Fe_4(1)_6]^{8+}$

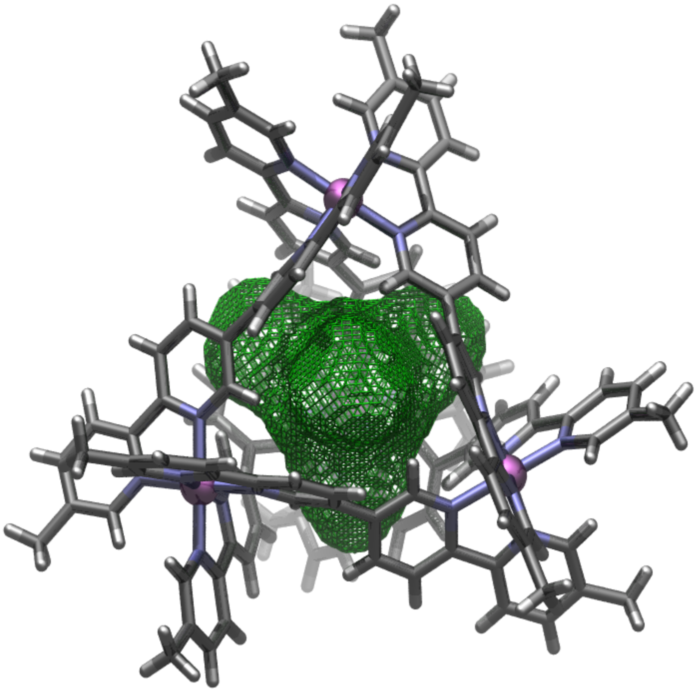


Fig. 8S Representation of the void volume (101 Å^3, shown as green mesh) in the tetrahedral cation of $[(PF_6)\subset Fe_4(\mathbf{1})_6](PF_6)_7$ as calculated by Voidoo[1] in the absence of the encapsulated PF_6^- guest; solvate molecules and anions not shown .

$[Fe_4(3)_6]^{8+}$

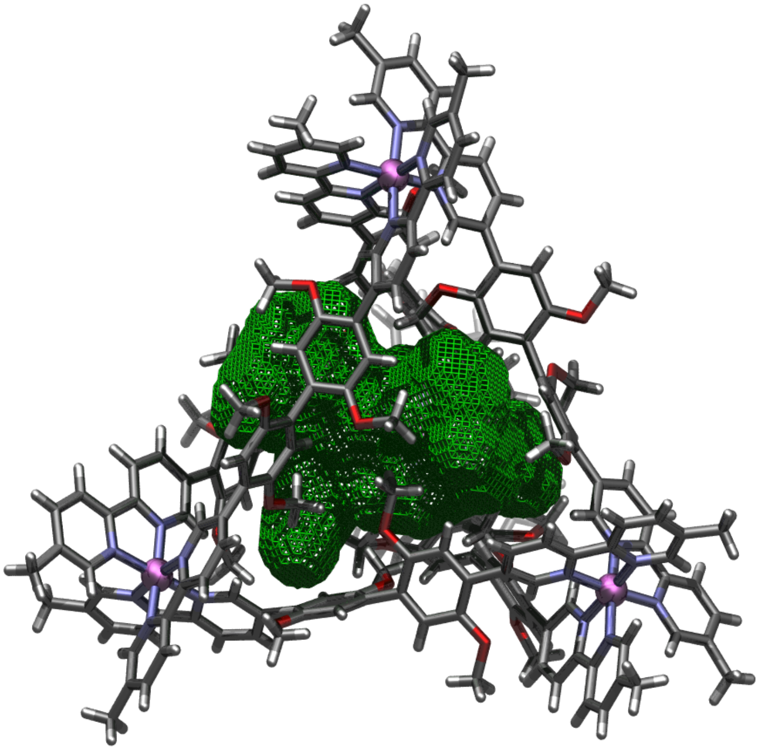
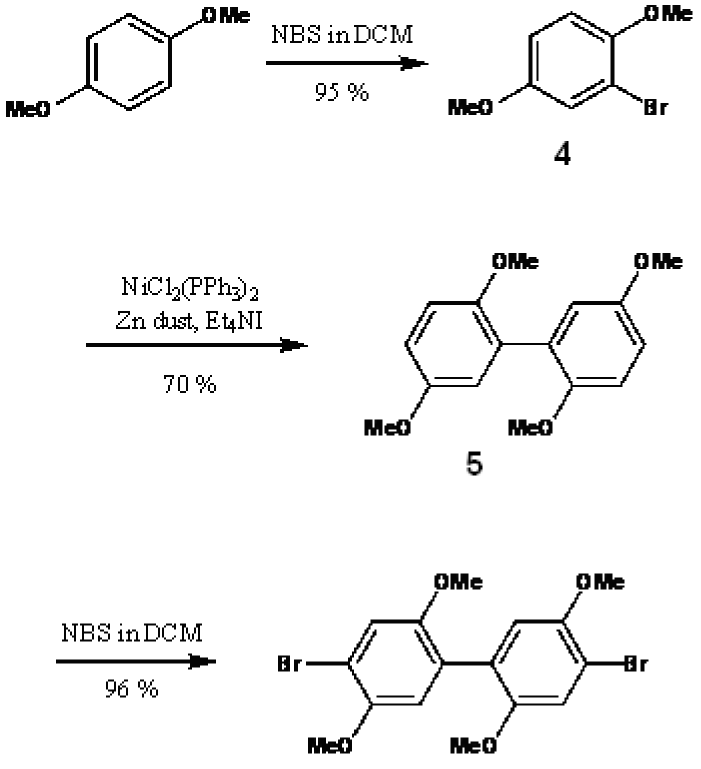


Fig. 9S Representation of the void volume (417 Å^3, shown as green mesh) in the tetrahedral cation of $[Fe_4(\mathbf{3})_6](PF_6)_8$ as calculated by Voidoo[1]; solvate molecules and anions not shown .

4. Organic Precursor Synthesis

Synthesis of 4,4′-dibromo-2,5,2′,5′-tetramethoxy-biphenyl (6)

An overview of the synthesis of 4,4′-dibromo-2,5,2′,5′-tetramethoxy-biphenyl (**6)** is presented in Scheme 1. Electrophilic substitution of 1,4-dimethoxybenzene with N-bromosuccinimide (NBS) in refluxing dichloromethane gave the 2-bromo derivative **4** in 95 % yield.[2] Homocoupling of this product using $[NiCl_2(PPh_3)_2]$/Zn in tetrahydrofuran[3] yielded the tetra-methoxy substituted biphenyl derivative **5** in 70 % yield. The latter was then regioselectively brominated at the 4,4′-positions with NBS in refluxing dichloromethane to give 4,4′-dibromo-2,5,2′,5′-tetramethoxy-biphenyl (**6**) in 96 % yield. This straightforward three-step strategy afforded **6** in 63 % overall yield .



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Scheme 1S Overview of the three-step preparation of 4,4′-dibromo-2,5,2′,5′-tetramethoxy-biphenyl (**6**).

References

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