Electronic Supplementary Material (ESI) for Dalton Transactions

Metal-Organic Frameworks Post-Synthetically Modified with Ferrocenyl Groups: Framework Effects on Redox Processes and Surface Conduction

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Supplementary information

Preparation of [$Zn_4O(bpdc\text{-}NH_2)_3$], 3.

$Zn(NO_3)_2·6H_2O$ (0.200 g, 0.672 mmol) and 2-aminobiphenyl-4,4'-dicarboxylic acid (H_2bpdc-NH_2, 0.064 g, 0.249 mmol) were dissolved in DMF (5 cm^3), and the reaction mixture was heated at 130 °C for 24 h to give pale yellow cubic crystals. The mother liquor was removed by decantation and the crystals were washed with DMF (3 × 5 cm^3), $CHCl_3$ (5 cm^3) and soaked in $CHCl_3$ (5 cm^3) for 24 hours. Then, the crystals were rinsed with $CHCl_3$ (5 cm^3) and soaked in fresh $CHCl_3$ for 24 hours. After 3 days of washing and soaking the crystals were stored in the last $CHCl_3$ solution until needed. One sample was dried by air and weighed to give 0.0826 g (88 %). The identity of **3** was confirmed by comparison of its powder X-ray diffraction pattern (Fig. S1) to that reported by Telfer and co-workers.[S1]

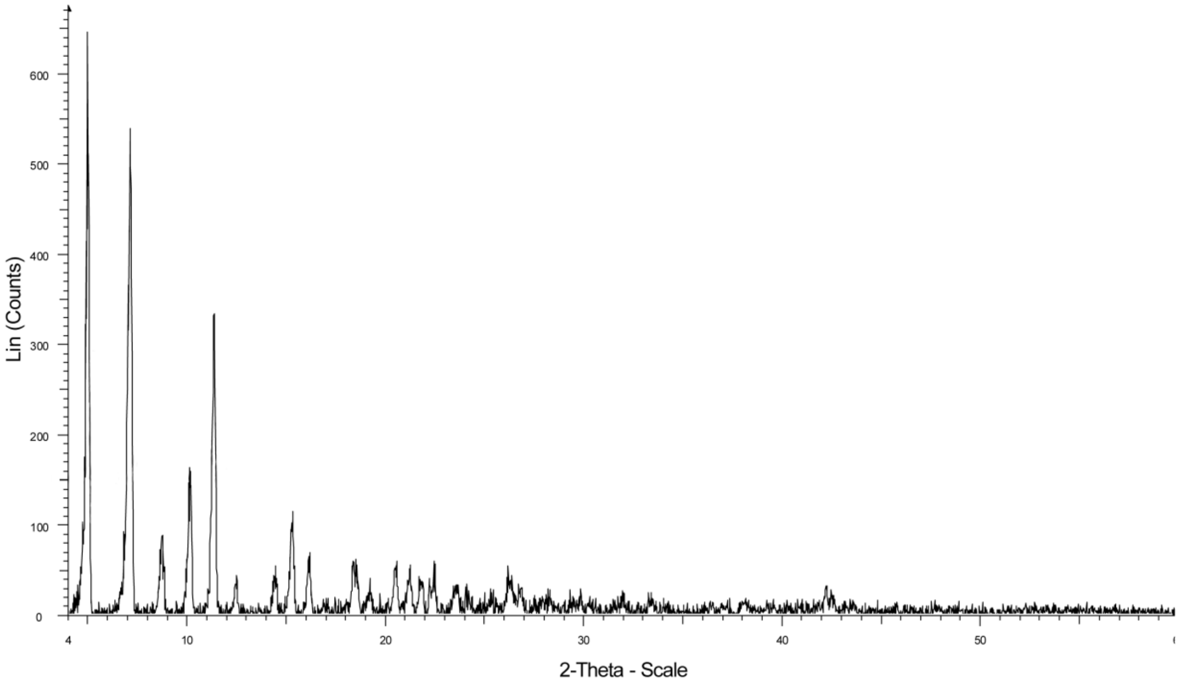

Fig. S1. Powder X-ray diffraction pattern for **3**.

Post-synthetic modification of 1 with FCA.

The extent of the post-synthetic modification in compound **1-Fc** was estimated from the ^{1}H NMR spectra, a typical example of which is shown in Fig. S2. In this case, the degree of modification was obtained by comparing the integrals for the signals at δ 9.2 ppm and δ 7.3 ppm in a similar manner to that reported by Cohen and co-workers.[S2, S3] Further evidence for successful post-synthetic modification was obtained form the ESI mass spectrum (Fig. S3).

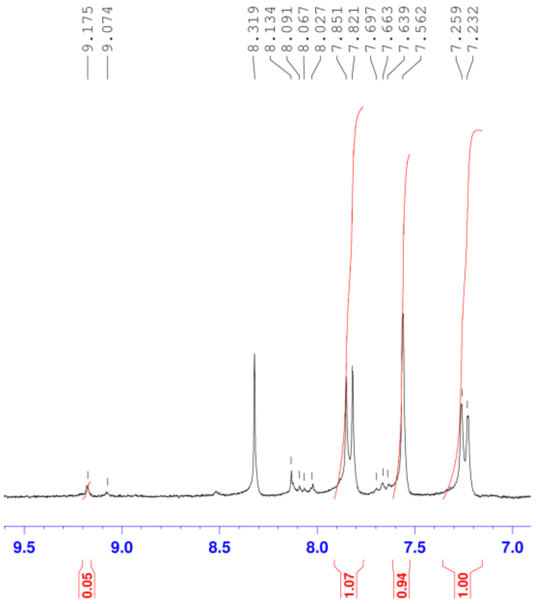

Fig. S2. Part of the ^{1}H NMR spectrum for **1-Fc** digested in DCl/D_2O and dmso-d_6.

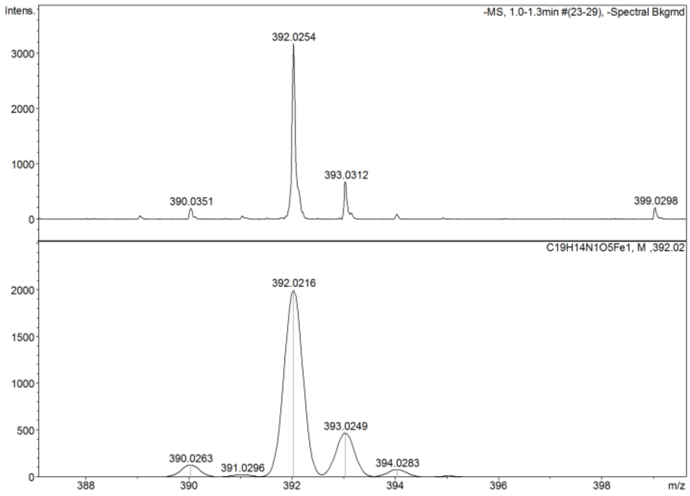

Fig. S3. Part of the negative ESI mass spectrum for **1-Fc** showing the observed isotope pattern for $[Hbdc\text{-}NHC(O)C_5H_4FeCp]^-$ (above) compared with the calculated pattern (below).

Post-synthetic modification of 2 with FCA.

The extent of the post-synthetic modification in compound **2-Fc** was estimated from the ^{1}H NMR spectra, a typical example of which is shown in Fig. S4. The degree of modification was obtained by comparing the integrals for the signals at δ 9.2 ppm and δ 7.3 ppm in a similar manner to that reported by Cohen and co-workers,[S2, S3] and confirmed by comparing the integrals for the signals at δ 7.3 ppm and the ferrocenyl peaks at δ 4.26, δ 4.54 and δ 4.81 ppm. Further evidence for successful post-synthetic modification was obtained form the ESI mass spectrum (Fig. S5).

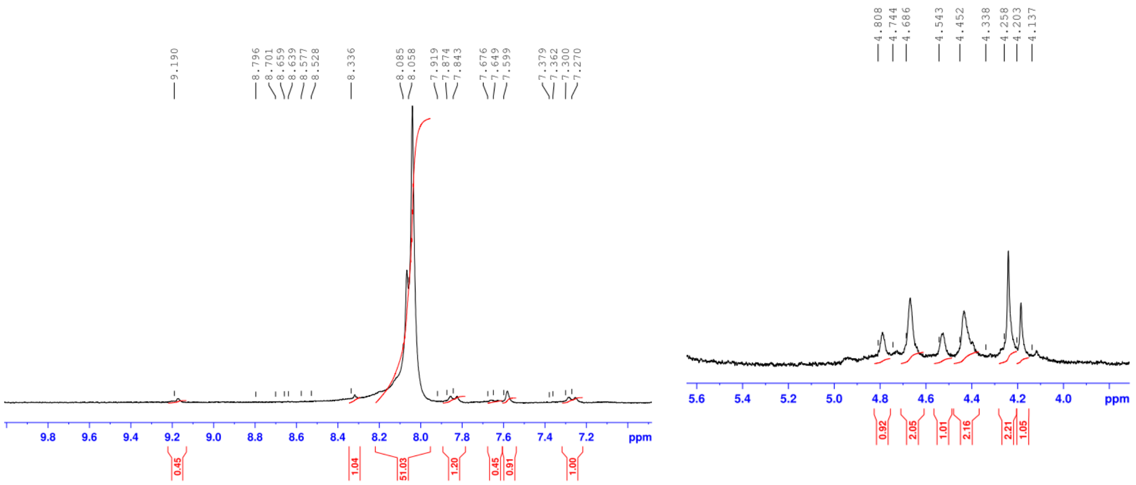

Fig. S2. Parts of the ^{1}H NMR spectrum for **2-Fc** digested in DCl/D_2O and dmso-d_6 showing the aromatic area (left) and the ferrocenyl signals (right).

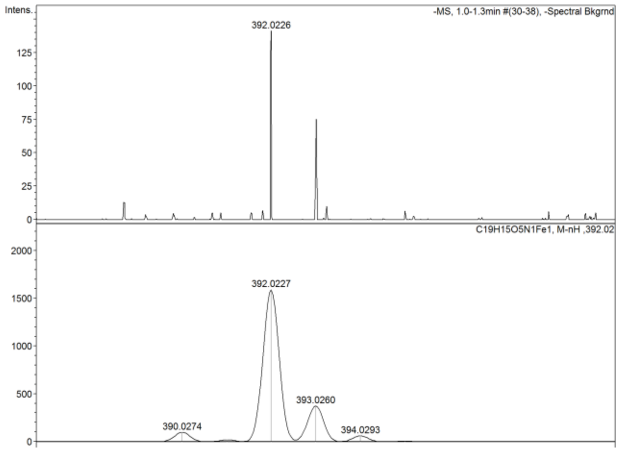

Fig. S3. Part of the negative ESI mass spectrum for **2-Fc** showing the observed isotope pattern for $[\mathrm{Hbdc\text{-}NHC(O)C_5H_4FeCp}]^-$ (above) compared with the calculated pattern (below).

Post-synthetic modification of 3 with FCA.

The extent of the post-synthetic modification in compound **3-Fc** was estimated from the ^{1}H NMR spectra. In this case, virtually no conversion was observed at room temperature (Fig. S6), whereas essentially complete conversion was observed following reaction at 100 °C (Fig. S7).

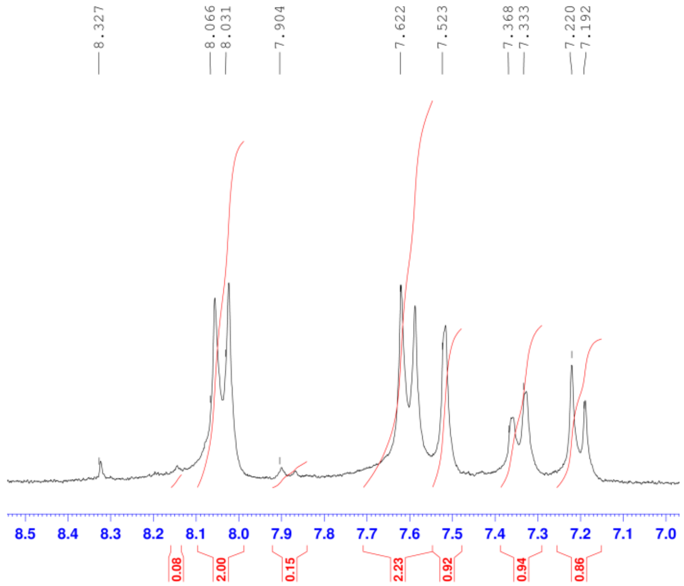

Fig. S6. Part of the ^{1}H NMR spectrum for **3-Fc** modified at room temperature, digested in DCl/D_2O and dmso-d_6.

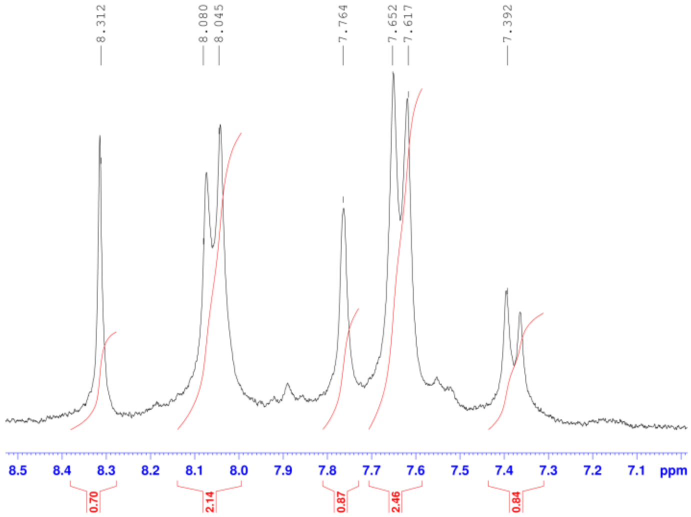

Fig. S7. Part of the ^{1}H NMR spectrum for **3-Fc** modified at 100 °C, digested in DCl/D_2O and dmso-d_6.

Post-synthetic modification of 4 with FCA.

The extent of the post-synthetic modification in compound **4-Fc** was difficult to estimate since the harsher conditions required for digestion led to hydrolysis of the amide linkage. Evidence that significant post-synthetic modification has occurred comes form the IR spectrum (Fig. S8) and the ESI mass spectrum (Fig. S9).

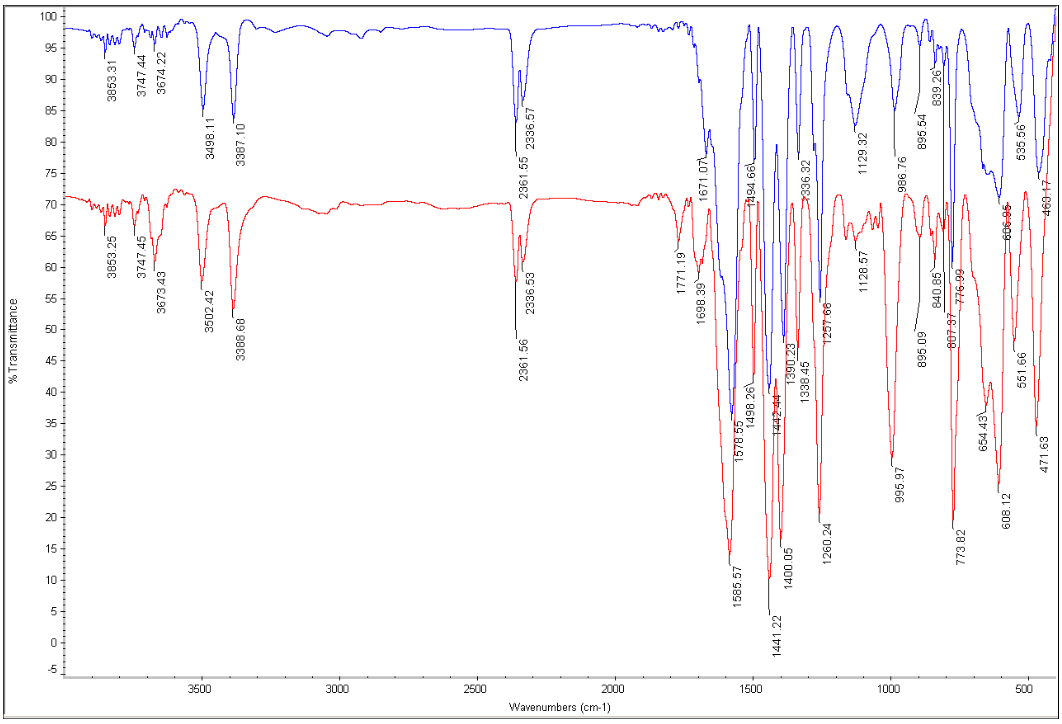

Fig. S8. Infrared spectra for **4** (blue) and **4-Fc** (red).

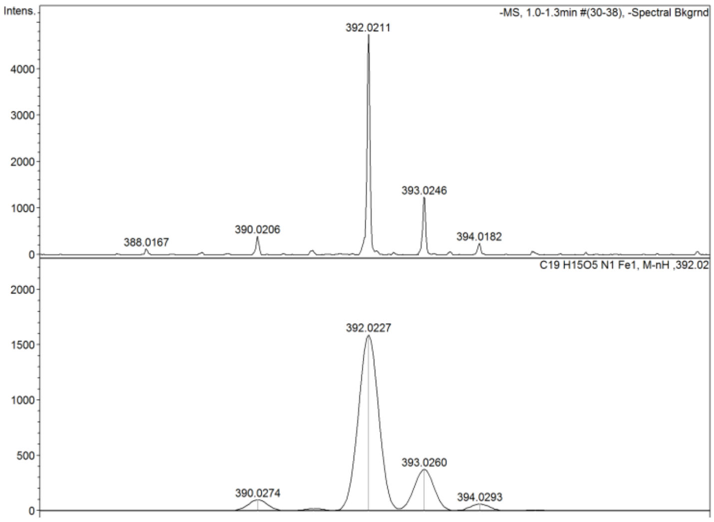

Fig. S9. Part of the negative ESI mass spectrum for **4-Fc** showing the observed isotope pattern for [Hbdc-NHC(O)C_5H_4FeCp]$^-$ (above) compared with the calculated pattern (below).

References

S1. R. K. Deshpande, J. L. Minnaar and S. G. Telfer, *Angew. Chem. Int. Ed.*, 2010, **49**, 4598.
S2. Z. Wang, K. K. Tanabe and S. M. Cohen, *Inorg. Chem.*, 2009, **48**, 296.
S3. K. K. Tanabe, Z. Wang and S. M. Cohen, *J. Am. Chem. Soc.*, 2008, **130**, 8508.