Manuscript for *Dalton Trans.*

Electronic Supplementary Information

Solid-state study of the structure and host-guest chemistry of cucurbituril-ferrocene inclusion complexes

Ana C. Gomes,[a] Clara I. R. Magalhães,[a] Tânia S. M. Oliveira,[b] André D. Lopes,*[b] Isabel S. Gonçalves[a] and Martyn Pillinger*[a]

[a] Department of Chemistry, CICECO - Aveiro Institute of Materials, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal. E-mail: mpillinger@ua.pt. Fax: +351-234-401470; Tel: +351-234-370603.

[b] Faculty of Science and Technology, CIQA, University of the Algarve, Campus de Gambelas, 8005-136 Faro, Portugal. E-mail: adlopes@ualg.pt.

Contents

Table S1 Compound names, unit cell dimensions and CSD refcodes for the 11 cucurbit[8]uril structures classified into an isostructural series with the space group $I4_1/a$ ($a = b$; $\alpha = \beta = \gamma = 90°$).

Structure name	*a* (Å)	*c* (Å)	REFCODE	Ref.
Cucurbit(8)uril hydronium disulfate hydrate clathrate	28.3805(4)	22.0986(2)	LIRTOV	1
Cucurbit[8]uril tetrakis(hydrogen chloride) hydrate	28.1082(4)	21.8958(7)	BATWEA	2
Cucurbit[8]uril bis(coumarin) clathrate sulfuric acid solvate dodecahydrate	28.3633(9)	21.8616(16)	SUQFAM	3
hexakis(Cucurbit(8)uril) cis-diaqua-bis(ethylenediamine-N,N')-cobalt trichloride hydrate	28.2264(6)	21.7921(8)	CENYOK	4
Oxonium gadolinium bis(cucurbit[8]uril) tetrachloride pentahexacontahydrate	28.3249(19)	21.949(3)	CIQKUK	5
Cucurbit[8]uril (pentacyclo[7.3.1.14,12.02,7.06,11]tetradecane-4,9-diammonium) clathrate dichloride acetonitrile solvate	28.1713(18)	21.746(3)	FITBAN	6
Cucurbit[8]uril dichloro-copper triacontahydrate	28.099(4)	21.718(3)	WEZPOI	7
bis(Cucurbit(8)uril) bis(ethylenediamine)-diaqua-copper(II) clathrate dichloride hydrate	28.0962(3)	21.9381(5)	KANXIH	8
Cucurbit(8)uril tetrakis(phosphoric acid)	28.304(8)	22.126(7)	QOTFAI	9
bis(Cucurbit(8)uril) bis(oxonium) hexachloro-platinum tetraheptacontahydrate	28.5200(19)	21.998(3)	VAHREE	10
Cucurbit(8)uril bis(ethylenediamine)-diaqua-copper(II) clathrate dichloride pentadecahydrate	28.0382(4)	21.9038(5)	XAJXOW	8

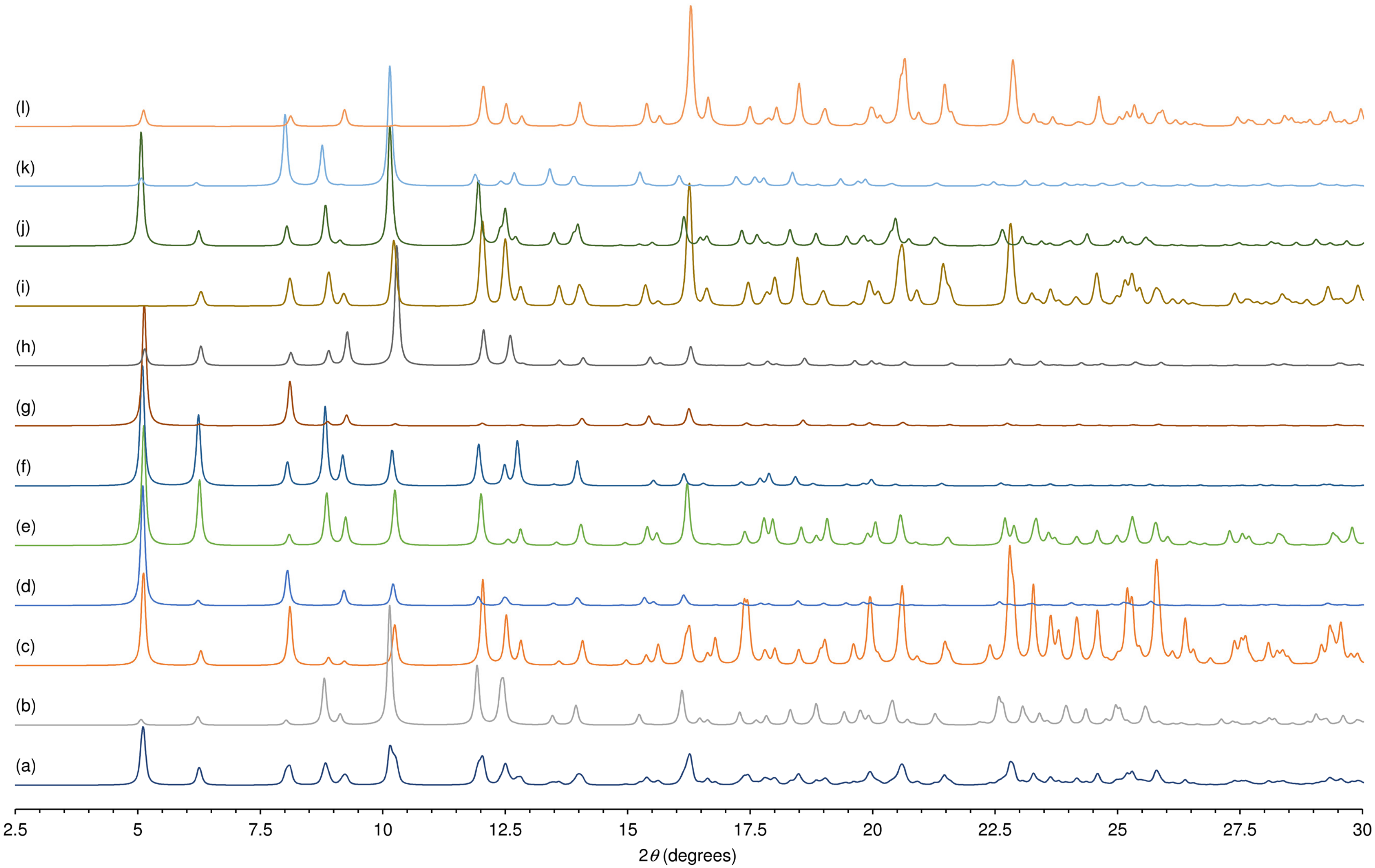

Fig. S1 Computed PXRD patterns for the structures with CSD refcodes (b) LIRTOV, (c) BATWEA, (d) SUQFAM, (e) CENYOK, (f) CIQKUK, (g) FITBAN, (h) WEZPOI, (i) KANXIH, (j) QOTFAI, (k) VAHREE, and (l) XAJXOW (see Table S1 for details). The patterns were generated with $\lambda = 1.5406$ Å using the program Mercury (version 3.5.1).[11] Pattern (a) is the reference diffractogram generated for the CB8 - $I4_1/a$ isostructural series by averaging patterns (b-l).

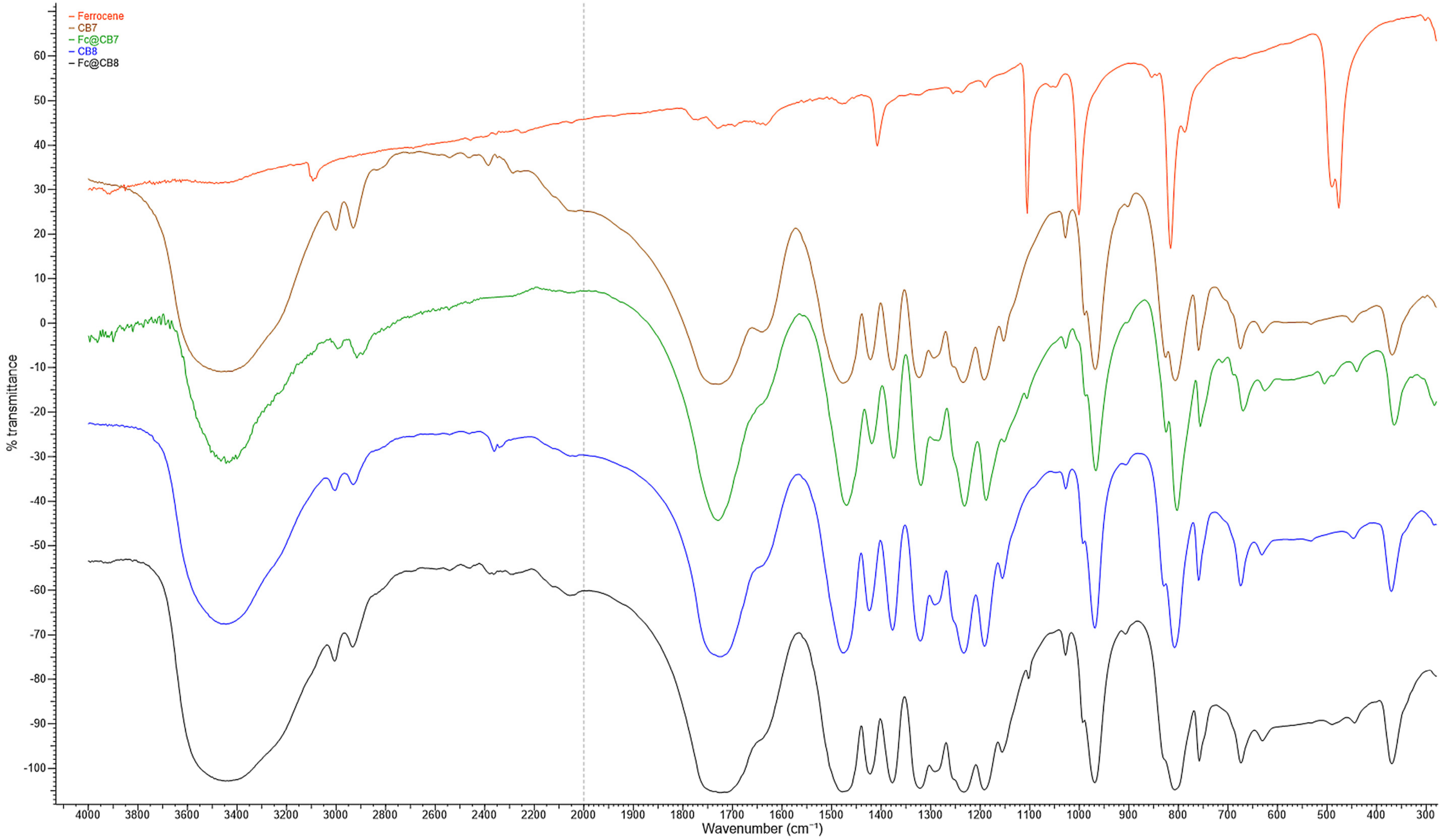

Fig. S2 FT-IR spectra (KBr) of ferrocene, CB7, Fc@CB7, CB8 and Fc@CB8.

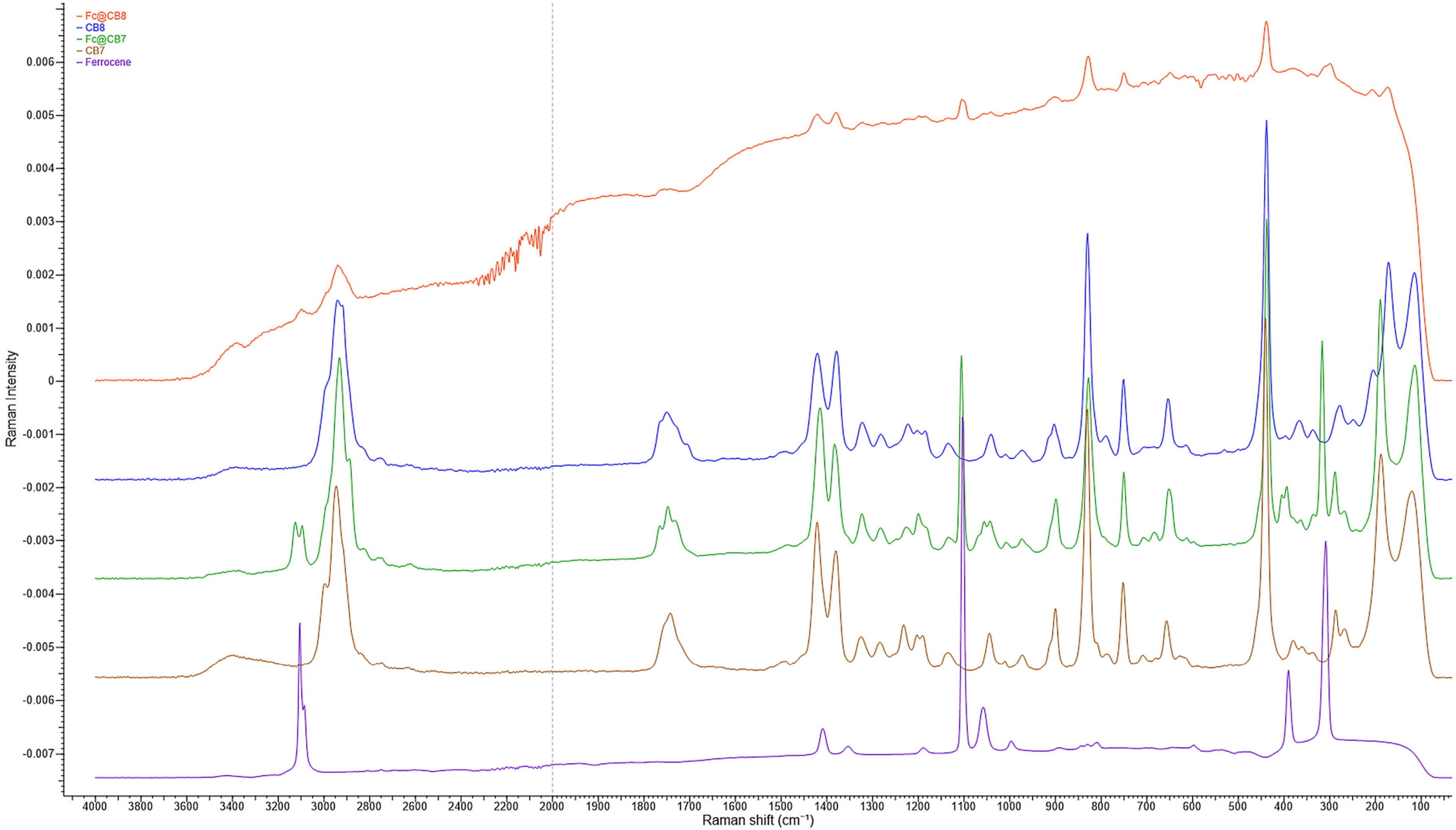

Fig. S3 FT Raman spectra of ferrocene, CB7, Fc@CB7, CB8 and Fc@CB8.

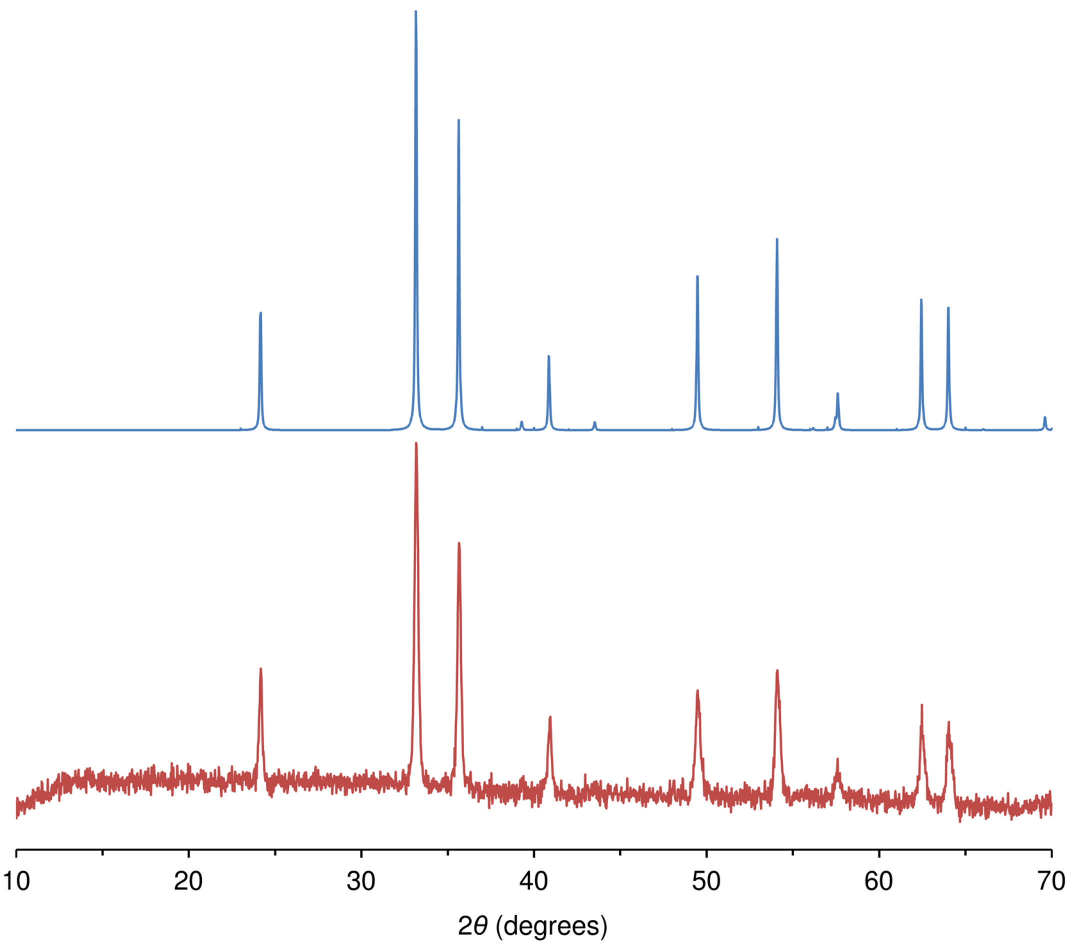

Fig. S4 PXRD pattern (lower red trace) of the dark red solid residue obtained after calcination of Fc@CB7 at 600 °C under air. The upper blue trace is the computed pattern generated for hematite, α-Fe_2O_3, using structure data published in ref. 12.

Preparation of Fc@CB8W

CB8 (0.4 g) was suspended in Milli-Q grade water (30 mL) and the mixture was stirred at ambient temperature for 30 min. The suspension was centrifuged (2500 rpm, 15 min), the supernatant solution (pH 1.9) decanted off, and the solid resuspended in water (30 mL) for a second washing treatment. A total of seven washing steps were performed to give a solid labelled as CB8W, which was air-dried overnight at 50 °C. The pH of the supernatant solutions increased from 1.9 for the 1st wash to 4.7 for the 4th wash, and then remained roughly constant. A mixture of CB8W (0.10 g, 0.06 mmol), ferrocene (0.045 g, 0.24 mmol) and Milli-Q grade water (7.5 mL) was subjected to MWA heating at 100 °C for 3 h. The resultant pale yellow precipitate (Fc@CB8W) was separated from the colourless mother liquor (pH = 6) by filtration, washed with water (2 × 5 mL), acetone (2 × 5 mL), and vacuum-dried.

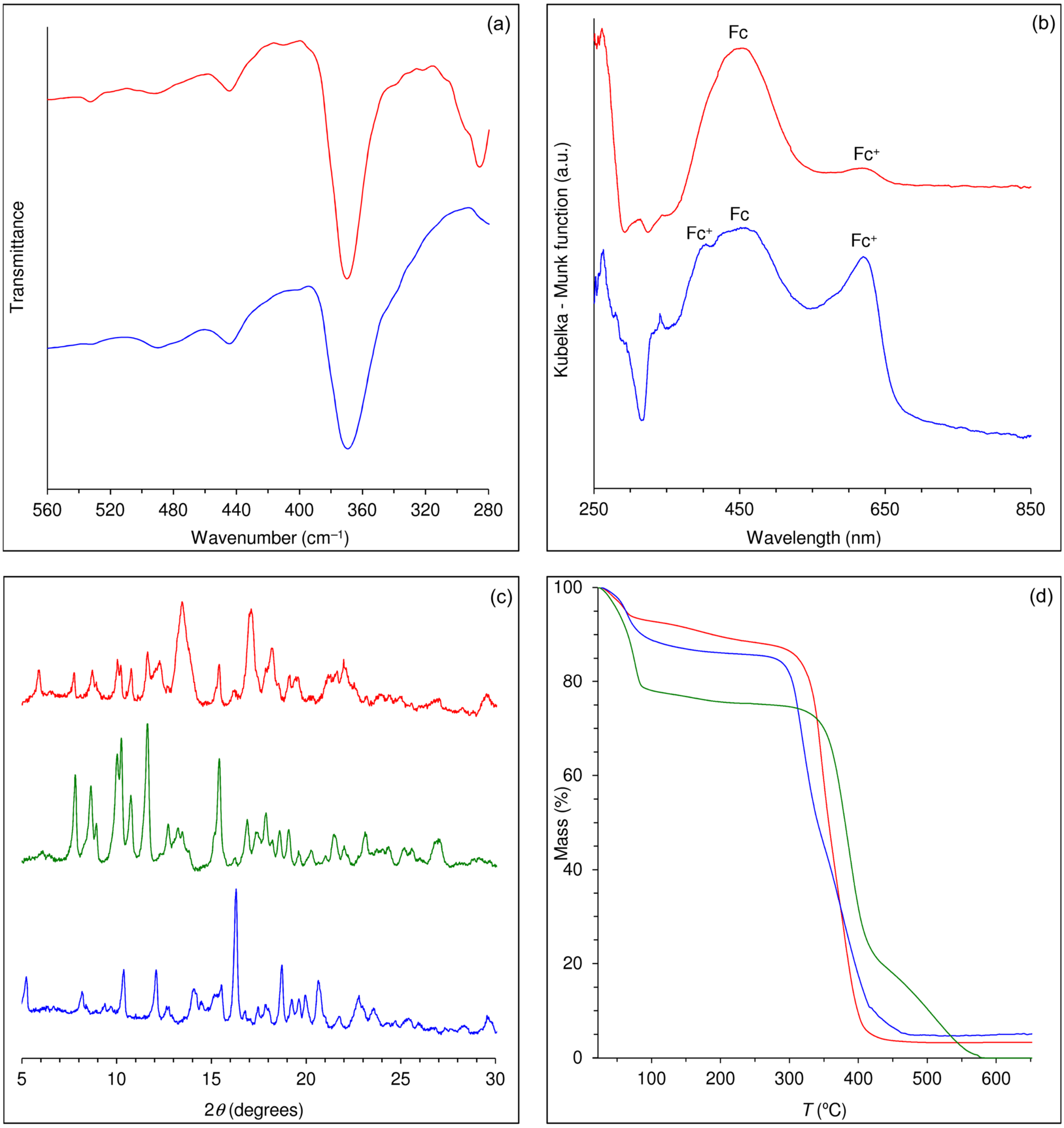

Fig. S5 Characterisation data for Fc@CB8W (red line) compared with data for Fc@CB8 (blue line) and CB8W (green line): (a) FT-IR spectrum in the range of 280-560 cm^{-1}, (b) diffuse reflectance UV-Vis spectrum (Fc indicates bands due to ferrocene; Fc^{+} indicates bands due to ferrocenium ion), (c) PXRD pattern, and (d) TGA curve.

References

1) J. Kim, I.-S. Jung, S.-Y- Kim, E. Lee, J.-K. Kang, S. Sakamoto, K. Yamaguchi and K. Kim, *J. Am. Chem. Soc.*, 2000, **122**, 540-541.

2) D. Bardelang, K. A. Udachin, D. M. Leek, J. C. Margeson, G. Chan, C. I. Ratcliffe and J. A. Ripmeester, *Cryst. Growth Des.*, 2011, **11**, 5598-5614.

3) R. Wang, D. Bardelang, M. Waite, K. A. Udachin, D. M. Leek, K. Yu, C. I. Ratcliffe and J. A. Ripmeester, *Org. Biomol. Chem.*, 2009, **7**, 2435-2439.

4) T. V. Mitkina, M. N. Sokolov, D. Y. Naumov, N. V. Kuratieva, O. A. Gerasko and V. P. Fedin, *Inorg. Chem.*, 2006, **45**, 6950-6955.

5) X.-J. Cheng, N.-N. Ji, Y. Zhao, L.-L. Liang, X. Xiao, Y.-Q. Zhang, S.-F. Xue, Q.-J. Zhu and Z. Tao, *CrystEngComm*, 2014, **16**, 144-147.

6) L. Cao, M. Šekutor, P. Y. Zavalij, K. Mlinarić-Majerski, R. Glaser and L. Isaacs, *Angew. Chem. Int. Ed.*, 2014, **53**, 988-993.

7) H.-X. Zhao, J.-X. Liu, L.-S. Long, A. A. Bokov, Z.-G. Ye, R.-B. Huang and L.-S. Zheng, *J. Phys. Chem. C*, 2012, **116**, 14199-14204.

8) T. V. Mitkina, D. Y. Naumov, O. A. Gerasko, F. M. Dolgushin, C. Vicent, R. Llusar, M. N. Sokolov and V. P. Fedin, *Russ. Chem. Bull. Int. Ed.*, 2004, **53**, 2519-2524.

9) L. Liu and M. Wang, *J. Incl. Phenom. Macrocyclic Chem.*, 2015, **81**, 509-516.

10) X.-T. Zhu, N.-N. Ji, Y.-Q. Zhang, S.-F. Xue, Z. Tao and Q.-J. Zhu, *Inorg. Chem. Commun.*, 2016, **66**, 28-32.

11) C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Cryst.*, 2008, **41**, 466-470.

12) L. W. Finger and R. M. Hazen, *J. Appl. Phys.*, 1980, **51**, 5362-5367.