

SUPPORTING INFORMATION

Tunable Room-temperature Soft Ferromagnetism in Magnetoceramics of Organometallic Dendrimers

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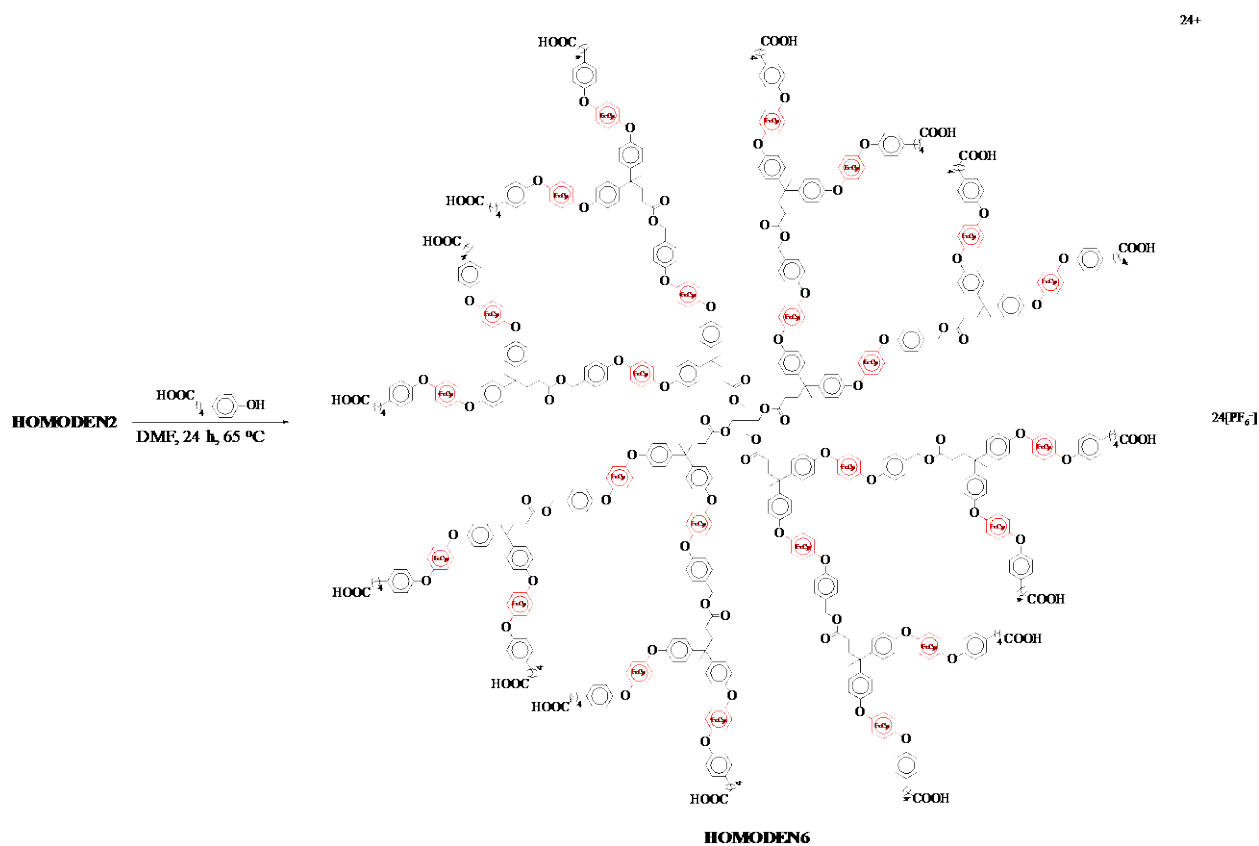
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EXPERIMENTALS

Synthesis of homometallic dendrimer 6 (HOMODEN6) (Scheme SI1). To synthesize this dendrimer, a 25-mL round-bottomed flask was charged with 554 mg (0.042 mmol) of **HOMODEN2**, 132 mg (0.68 mmol) of 5-(4-hydroxyphenyl)pentanoic acid, 332 mg (1.70 mmol) of potassium carbonate (K_2CO_3), and 3 mL of dimethylformamide (DMF). The reaction mixture was stirred and heated at 65 °C for 24 h under nitrogen atmosphere. Then, the reaction mixture was cooled to room temperature, and added dropwise to 10% (v/v) hydrochloric acid (HCl). Next, the product was precipitated by adding 0.68 mmol of ammonium hexafluorophosphate (NH_4PF_6) to the HCl solution. The product was isolated by filtration and dried at room temperature to give the final product in 81% yield. 1H NMR (DMSO- d_6 , 300 MHz): δ 12.01 (16 H, br s, COOH), 7.51 (16 H, br s, ArH), 7.35 (80 H, br s, ArH), 7.23 (80 H, br s, ArH), 6.98 (16 H, br s, ArH) 6.23 (96 H, br s, iron-complexed ArH), 5.21 (80 H, s, cyclopentadienyl H), 5.11 (16H, br s, ArCH₂) 5.05 (40 H, s, cyclopentadienyl H), 4.02 (8 H, br s, CH₂), 2.64, 2.41 2.25, 2.07 (176 H, CH₂), 1.65, 1.57

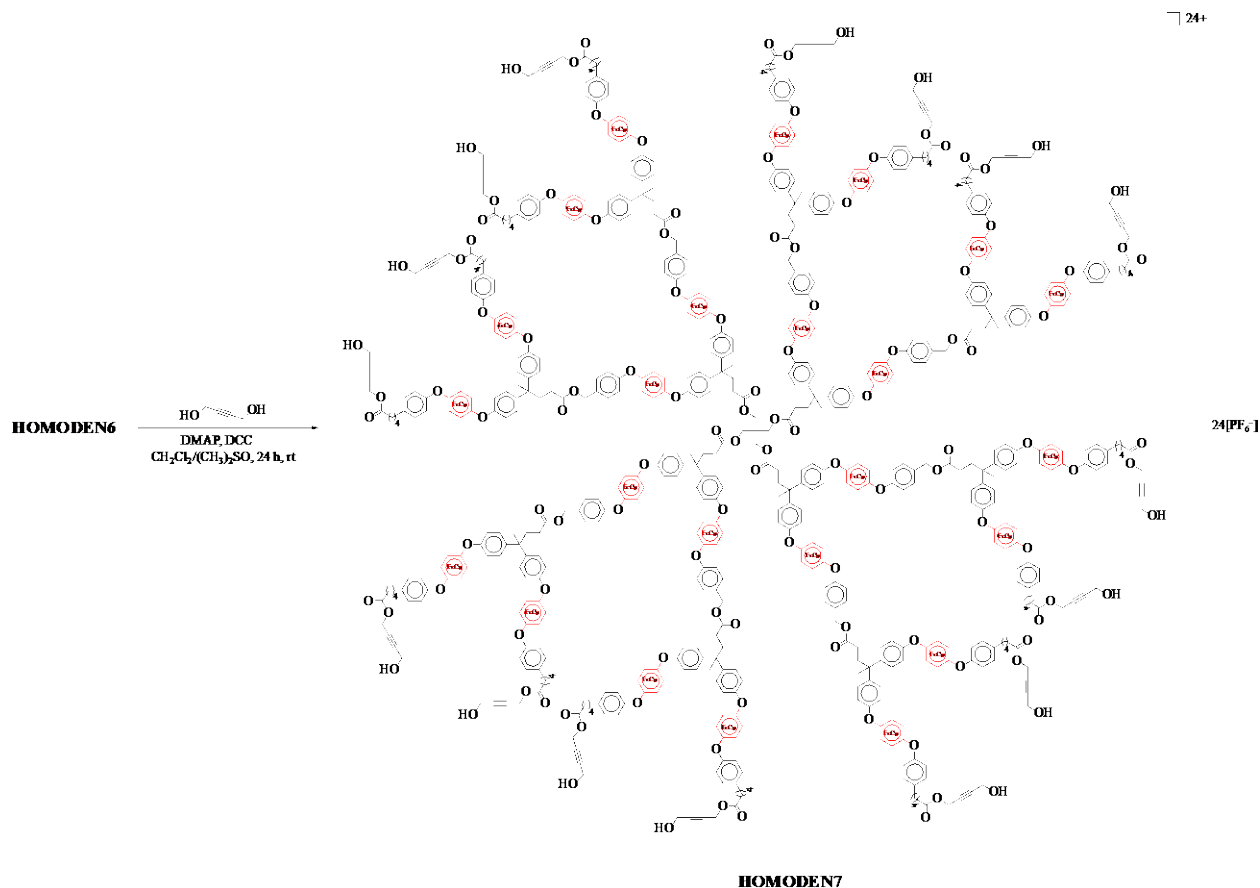
(36 H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$, 75 MHz): δ 172.8, 172.6, 172.5, 155.5, 155.3, 151.7, 151.6, 151.2, 146.1, 145.9, 140.2, 130.5, 130.3, 130.1, 129.9, 129.8, 129.7, 129.1, 129.0, 120.3, 120.2, 119.7, 119.5, 77.7, 77.0, 75.5, 75.4, 75.3, 75.2, 64.9, 45.0, 44.7, 44.4, 36.1, 36.0, 35.7, 34.0, 33.4, 30.7, 30.3, 29.8, 29.7, 26.9, 24.0. Elemental analysis: calcd for C: 54.22; H: 4.26; found C: 53.68; H: 4.20.



Scheme SI1. Schematic representation of the synthesis of **HOMODEN6**.

Synthesis of homometallic dendrimer 7 (HOMODEN7) (Scheme SI2). In a 25-mL round-bottom flask was added 581 mg (0.037 mmol) of **HOMODEN6**, 153 mg (1.78 mmol) of 2-butyne-1,4-diol, 56 mg (0.46 mmol) of 4-(dimethylamino)pyridine (DMAP) and 10 mL of 5:1 dichloromethane/dimethyl sulfoxide solvent mixture. The reaction mixture was cooled to 0 °C

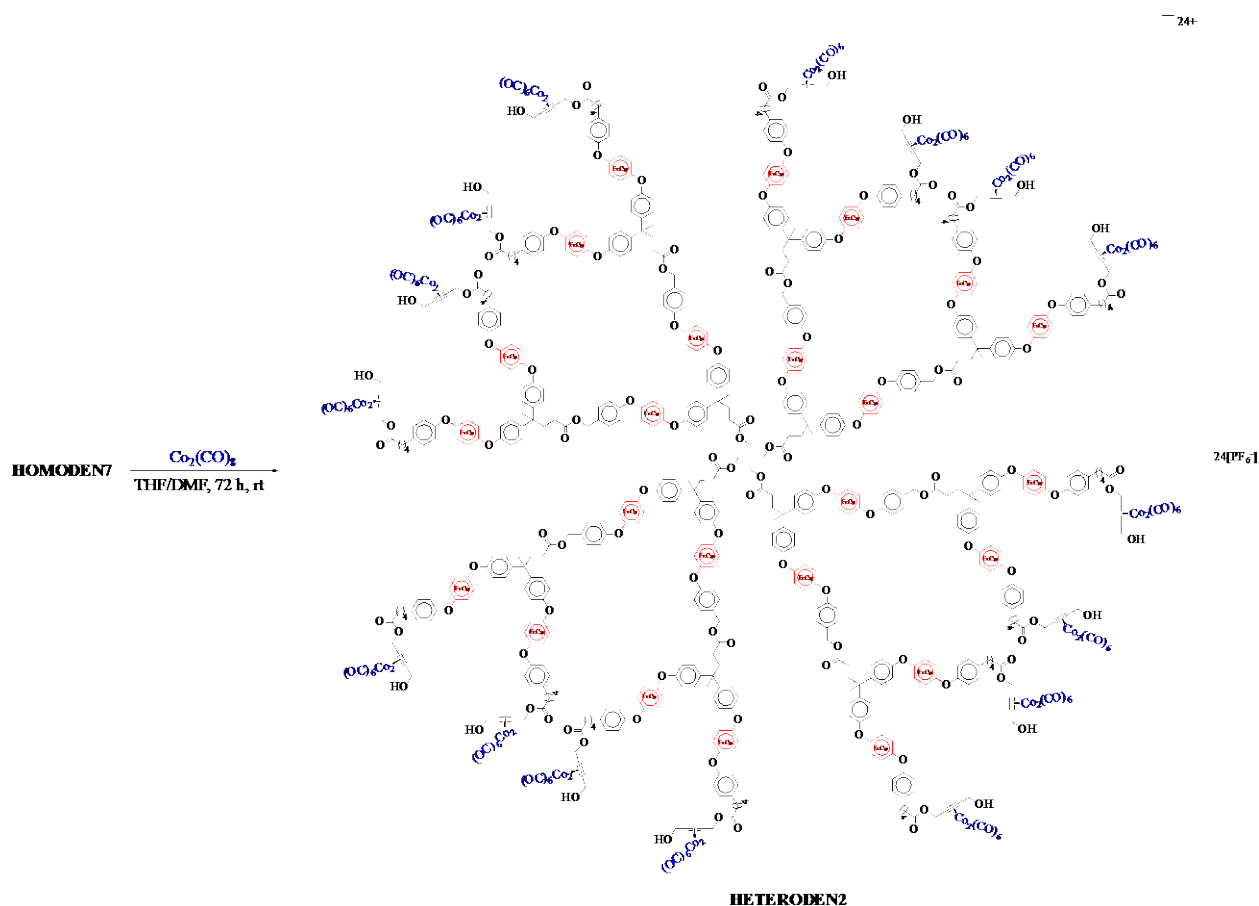
while stirring and 134 mg (0.65 mmol) of *N,N'*-dicyclohexylcarbodiimide (DCC) was added over 5 min. Next, the reaction mixture was warmed to room temperature and stirred overnight under nitrogen. Thereafter, the reaction was stopped, filtered to removed precipitated dicyclohexylurea, and the filtrate added to 50 mL of ice water. The mixture was extracted twice with 20 mL portion of dichloromethane/acetone solvent mixture, and the organic extract washed twice with 50 mL of water, followed by a wash with 50 mL of 5% (v/v) aqueous HCl, and then, with 10 mL of 89 mM aqueous solution of NH_4PF_6 . The organic extract was dried using magnesium sulfate, filtered, and the solvent removed under vacuum. To precipitate dicyclohexylurea, the residual extract was dissolved in acetone, cooled in a freezer for 1 h, and filtered. The product was isolated by adding the filtrate dropwise to diethyl ether to precipitate the product, then filtered and dried at room temperature to give the final product in 80% yield. ^1H NMR ($\text{DMSO-}d_6$, 300 MHz): δ 7.52–6.92 (192 H, br s, *ArH*), 6.24 (96 H, br s, iron-complexed *ArH*), 5.22 (120 H, s, cyclopentadienyl *H*), 5.12 (16 H, br s, *BzH*), 5.08 (16 H, br s, OH), 4.73 (32 H, s, CH_2), 4.10 (32 H, s, CH_2), 4.00 (8 H, br s, CH_2), 2.64–2.20 (176 H, br s, CH_2), 1.67 (12 H, br s, CH_3), 1.67 (24 H, br s, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{DMSO-}d_6$, 75 MHz): δ 174.1, 172.6, 172.1, 155.4, 155.2, 155.0, 151.7, 151.5, 146.5, 146.0, 140.1, 130.5, 130.3, 130.1, 129.8, 129.6, 129.1, 129.0, 128.5, 120.5, 120.3, 120.0, 119.8, 86.5, 78.4, 77.8, 77.7, 75.4, 75.1, 75.0, 74.9, 64.9, 51.7, 48.8, 44.9, 44.7, 44.6, 35.9, 36.0, 35.7, 33.9, 33.8, 30.7, 30.3, 29.8, 29.6, 26.9, 23.9. Elemental analysis, calcd for C: 55.29; H: 4.37; found: C: 55.40; H: 4.64.



Scheme SI2. Schematic representation of the synthesis of **HOMODEN7**.

Synthesis of heterometallic dendrimer (HETERODEN2) (Scheme SI3). The dendrimer was synthesized using a previously reported procedure,¹⁻³ which was slightly modified. In a nitrogen-filled glovebox, 200 mg (0.012 mmol) of **HOMODEN7**, 10 mL of dried THF, and 1 mL of dried DMF was charged into 25-mL round-bottom flask. After the dendrimer dissolved, 0.192 mmol of dicobalt octacarbonyl was added and the reaction mixture was stirred at room temperature for 72 h inside the glovebox. The mixture was filtered through Celite and precipitated into 10-fold excess of n-hexane. The obtained precipitate was re-dissolved in dried THF/DMF solvent mixture, filtered and re-precipitated into 10-fold excess of n-hexane to obtain the final product in 63% yield as a brown solid. The product was incompletely insoluble in common laboratory solvents, limiting characterization to ¹H NMR, ATR-IR and elemental analysis. ¹H NMR (DMSO-*d*₆, 300 MHz): δ

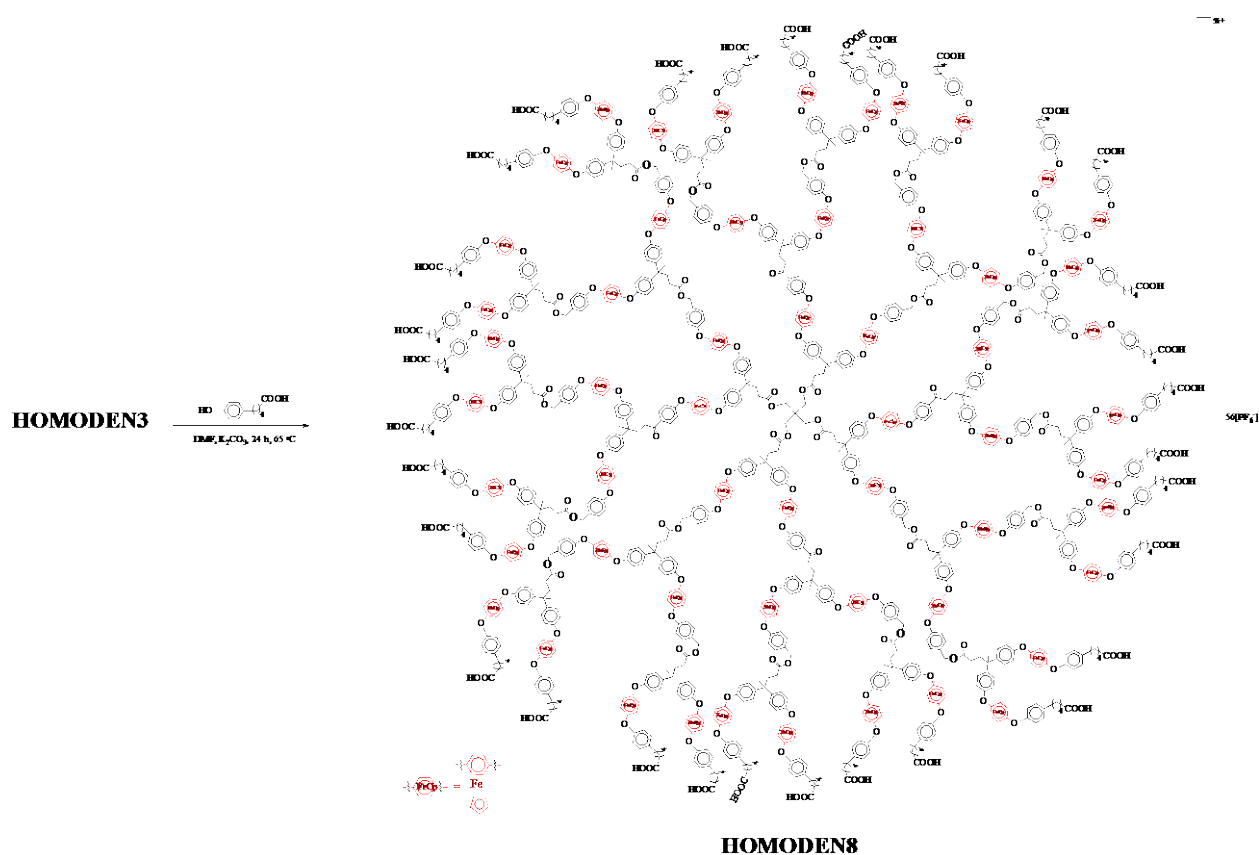
7.37–6.98, (192 H, br s, ArH), 6.25 (92 H, br s, iron-complexed ArH), 5.76 (32 H, s, CH₂) 5.20 (120 H, s, cyclopentadienyl H), 4.69 (32 H, s, CH₂), 2.87–2.20 (176 H, br s, CH₂), 1.67, 1.59 (36 H, br s, CH₃) (OH and BzH, and a CH₂ were not observed). ATR-IR: ν = 2095 (m), 2057 (s), 2024 (s, br) (CO) cm⁻¹. Elemental analysis calcd for C: 48.82; H: 3.43; found: C: 47.05; H: 3.81.



Scheme SI3. Schematic representation of synthesis of **HETERODEN2**.

Synthesis of homometallic dendrimer 8 (HOMODEN8) (Scheme SI4). **HOMODEN8** was synthesized using a procedure similar to the synthesis of dendrimer **6**. In brief, 1.24 g (0.040 mmol) of dendrimer **3**, 249 mg (1.28 mmol) of 5-(4-hydroxyphenyl)pentanoic acid, 442 mg (3.20 mmol) of K₂CO₃, and 3 mL of DMF were weighed into a 25-mL round-bottomed flask, and heated at 65 °C for 24 h under nitrogen atmosphere. The work-up was similar to that of dendrimer **6**. Dendrimer

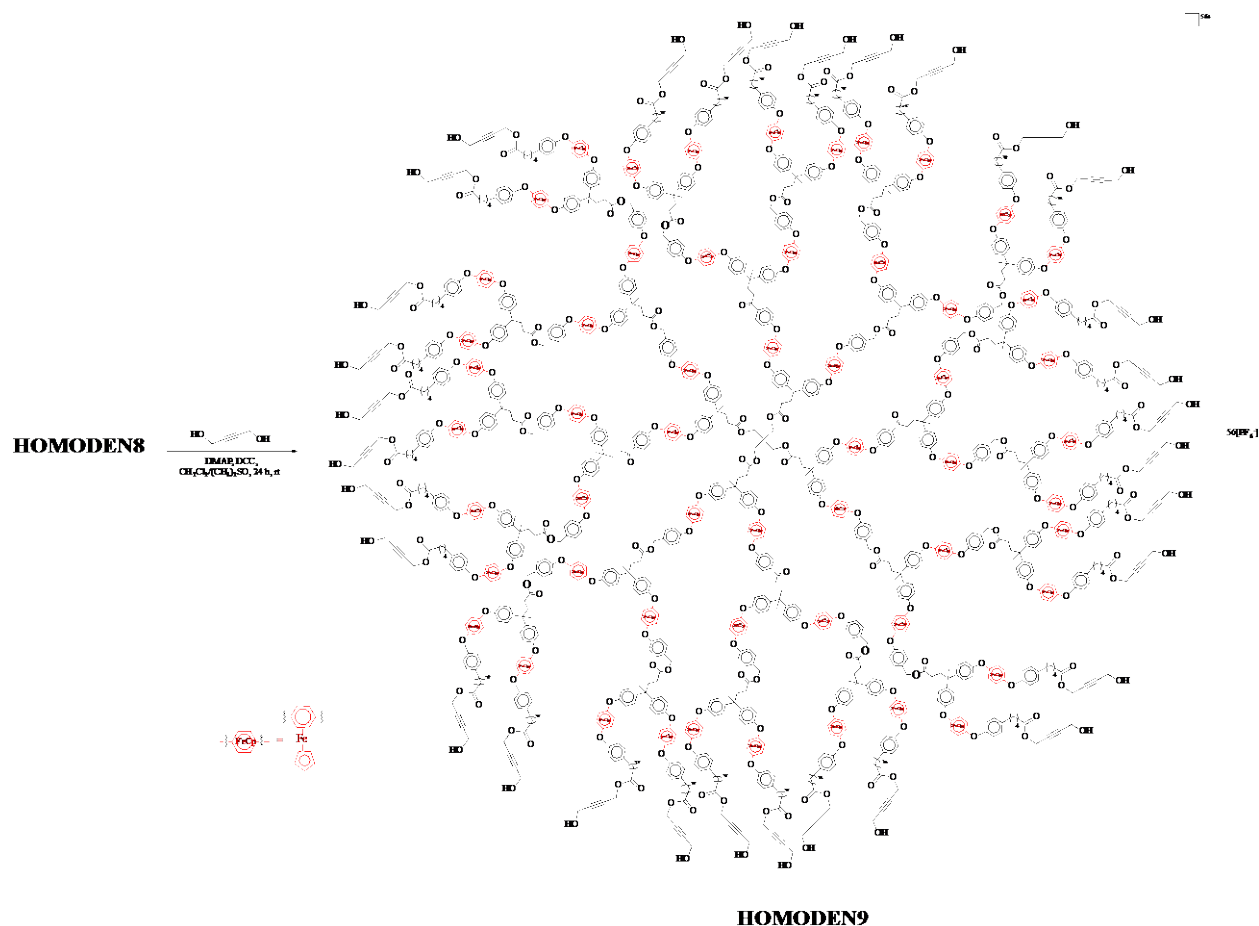
HOMODEN8 was obtained in 90% yield. ^1H NMR (DMSO- d_6 , 300 MHz): δ 12.05 (32 H, br s, COOH), 7.51–6.99 (448 H, br s, ArH), 6.24 (224 H, br s, iron-complexed ArH), 5.24 (280 H, s, cyclopentadienyl H), 5.12, 5.04 (48 H, br s, CH_2), 4.04 (8 H, br s, CH_2), 2.64–2.06 (284 H, br s, CH_2), 1.66, 1.61, 1.57 (84 H, br s, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 75 MHz): δ 174.8, 173.2, 173.1, 152.0, 151.6, 140.7, 134.5, 130.9, 130.8, 130.3, 129.6, 129.0, 128.8, 121.0, 120.8, 120.3, 78.3, 78.2, 77.4, 75.5, 75.0, 73.2, 47.9, 45.4, 45.2, 34.5, 33.9, 33.7, 30.7, 27.4, 25.7, 24.8, 24.5. Elemental analysis: calcd for C: 54.16; H: 4.19; found: C: 54.35; H: 4.40.



Scheme SI4. Schematic representation of the synthesis of **HOMODEN8**.

Synthesis of homometallic dendrimer 9 (HOMODEN9) (Scheme SI5). **HOMODEN9** was synthesized using a procedure similar to the synthesis of **HOMODEN7**. In brief, 1.20 g (0.033) of **HOMODEN8**, 273 mg (3.17 mmol) of 2-butyne-1,4-diol, 99.2 mg (0.812 mmol) of DMAP and

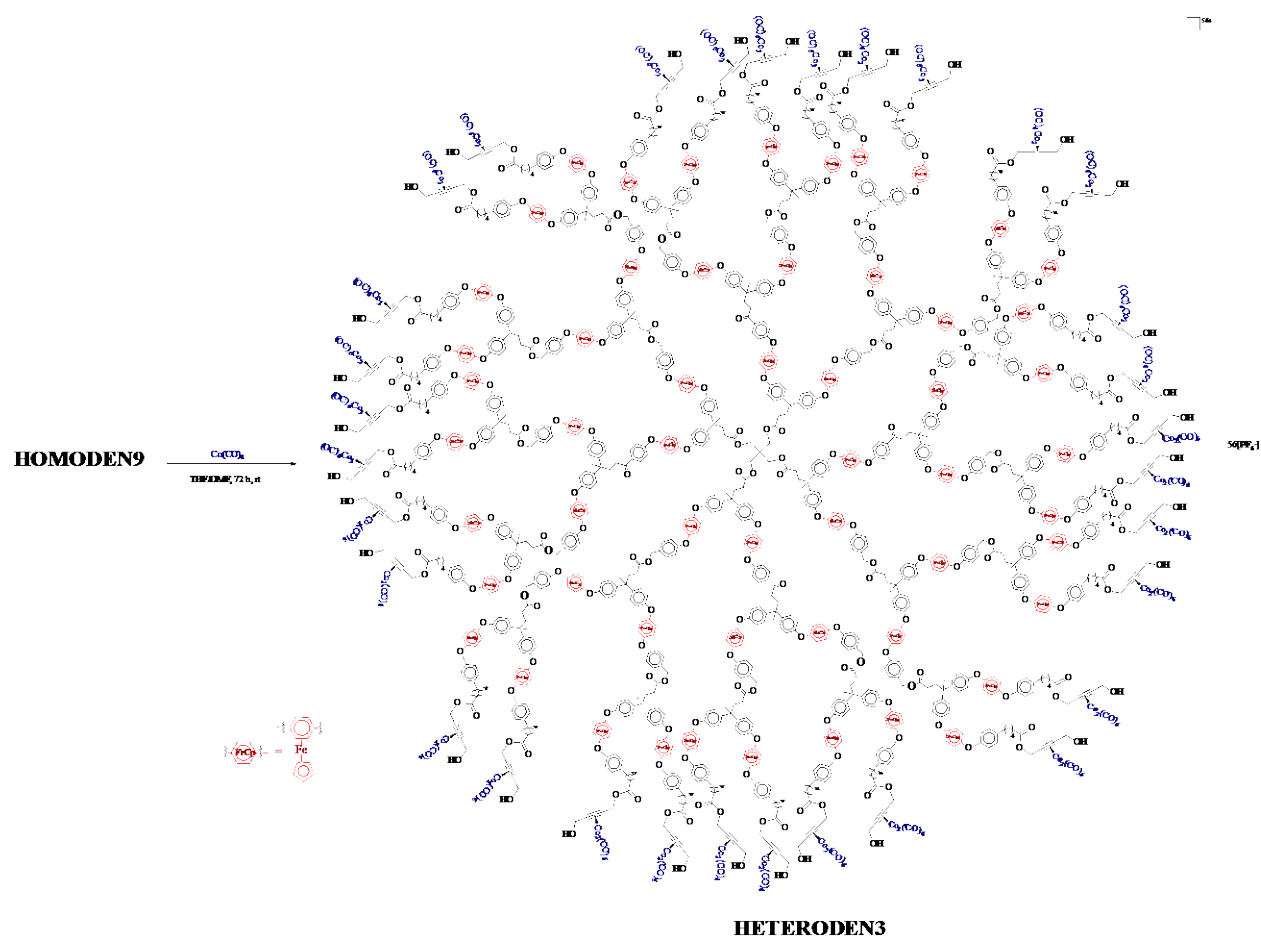
10 mL of 5:1 dichloromethane/dimethyl sulfoxide solvent mixture. While stirring, the mixture was cooled to 0 °C and 239 mg (1.16 mmol) of DCC was added over 5 min. The work-up followed a procedure similar to that of **HOMODEN7**. The final product was obtained in 60% yield. ¹H NMR (DMSO-*d*₆, 300 MHz): δ 7.50–6.93 (448 H, br s, Ar*H*), 6.25 (224 H, br s, iron-complexed Ar*H*), 5.23, 5.19 (280 H, s, cyclopentadienyl *H*), 5.12, 5.05 (48 H, br s, CH₂), 5.08 (32 H, br s, OH), 4.74 (64 H, br s, CH₂), 4.09 (64 H, br s, CH₂), 4.04 (8 H, br s, CH₂), 2.65–2.15 (284 H, br s, CH₂), 1.73, 1.68, 1.61 (84 H, br s, CH₃). ¹³C{¹H} NMR (DMSO-*d*₆, 75 MHz): δ 172.6, 171.8, 157.0, 153.1, 152.1, 151.6, 140.6, 137.3, 130.8, 130.2, 130.0, 129.5, 128.9, 121.0, 120.8, 120.5, 120.3, 118.7, 118.6, 117.9, 86.9, 78.9, 78.2, 77.4, 75.6, 75.5, 75.0, 52.2, 49.3, 47.9, 36.3, 34.4, 34.3, 33.7, 33.4, 33.3, 30.7, 30.5, 27.3, 25.7, 24.8, 24.3. Elemental analysis, calcd for C: 55.10; H: 4.29; found: C: 55.44; H: 4.54.



Scheme SI5. Schematic representation of the synthesis of **HOMODEN9**.

Synthesis of heterometallic dendrimer 3 (HETERODEN3) (Scheme SI6). The dendrimer was synthesized using a procedure similar to the synthesis of dendrimer **HETERODEN2**. In brief, 200 mg (0.005 mmol) of **HOMODEN9**, 9 mL of dried THF and 2 mL of dried DMF was charged into 25-mL round-bottom flask in a nitrogen-filled glovebox. After dissolution of the dendrimer, 0.160 mmol of dicobalt octacarbonyl was added and the mixture stirred at room temperature inside the glovebox for 72 h. The work-up procedure was similar to that of dendrimer **HETERODEN2**. The final product was obtained in 84% yield. The product was incompletely soluble in common laboratory solvents limiting characterization to ATR-IR and elemental analysis. ATR-IR: $\nu = 2095$

(m), 2057 (s), 2024 (s, br) (CO) cm^{-1} . Elemental analysis calcd for C: 49.30; H: 3.46; found: C: 49.01; H: 3.97.



Scheme SI6. Schematic representation of the synthesis of **HETERODEN3**.

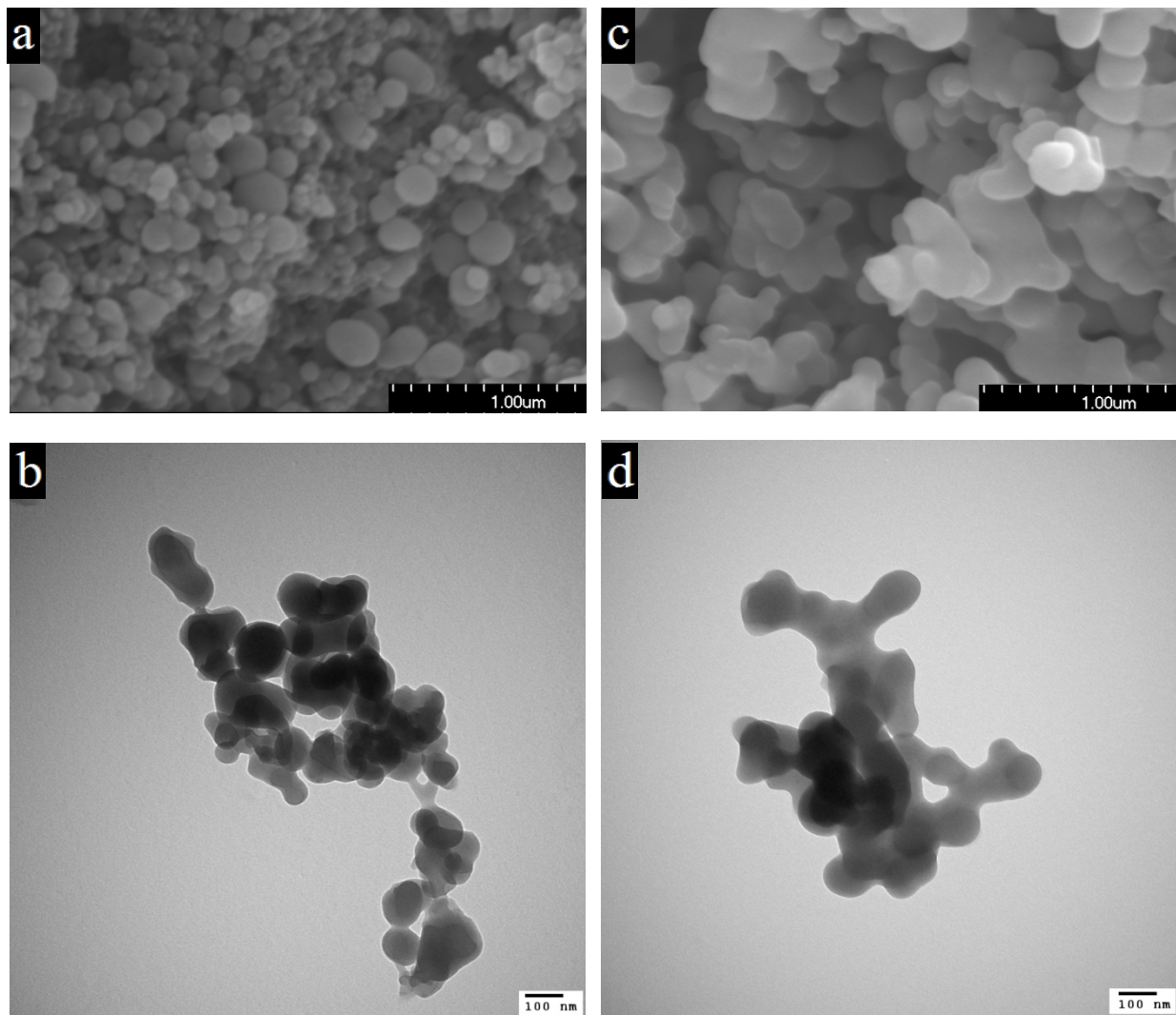


Figure S1. Top: Representative scanning electron microscopy images of homometallic and heterometallic dendrimers (a) **HOMODEN1**, (c) **HETERODEN1**. Bottom: Representative transmission electron microscopy images of homometallic and heterometallic dendrimers (b) **HOMODEN1**, (d) **HETERODEN1**.

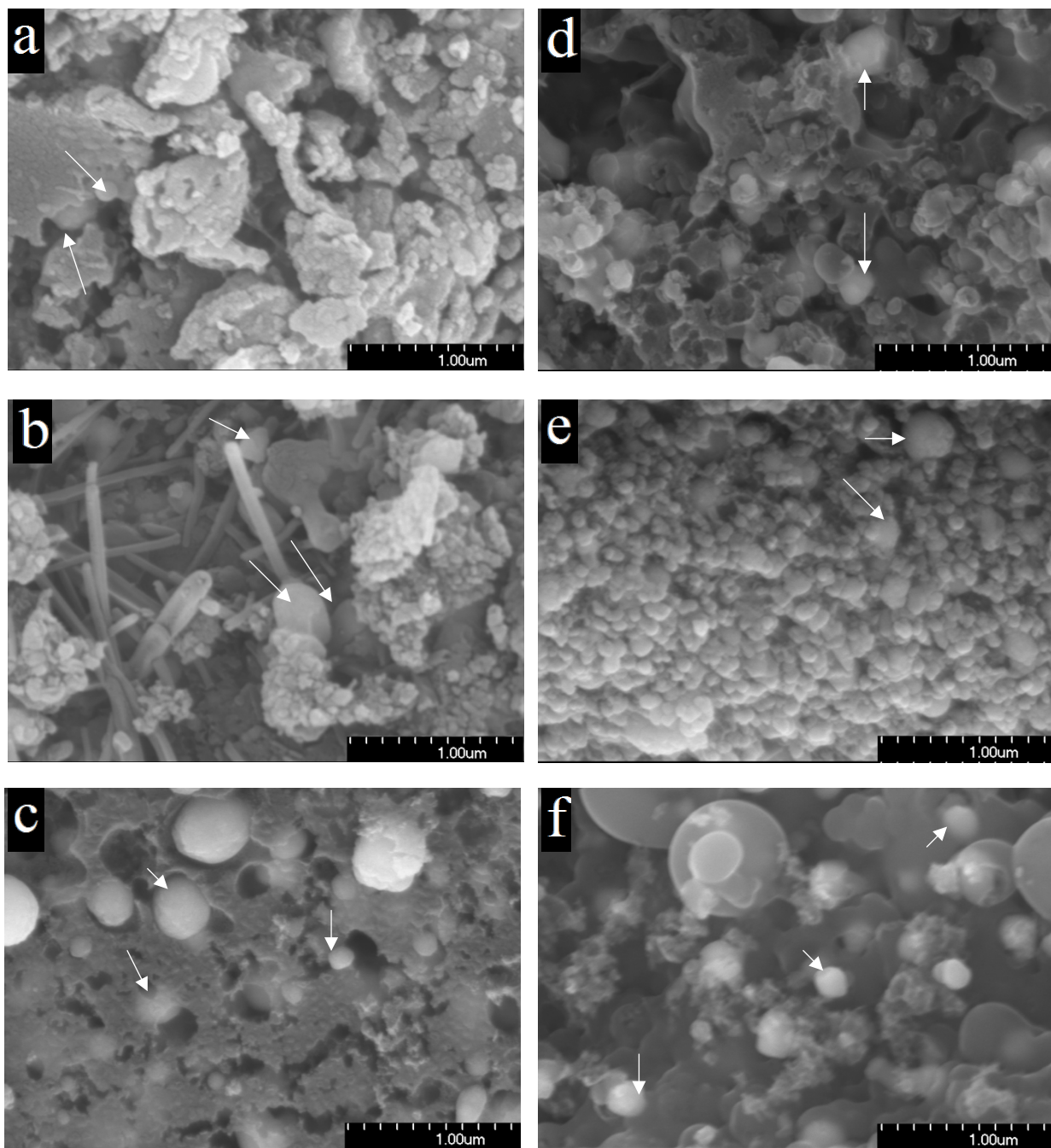


Figure S2. Scanning electron microscopy images of ceramics derived from (a) **HOMODEN1**, (b) **HOMODEN2** (c) **HOMODEN3** (d) **HETERODEN1** (e) **HETERODEN2** (f) **HETERODEN3** showing magnetic crystallites (arrowed) embedded with amorphous matrix.

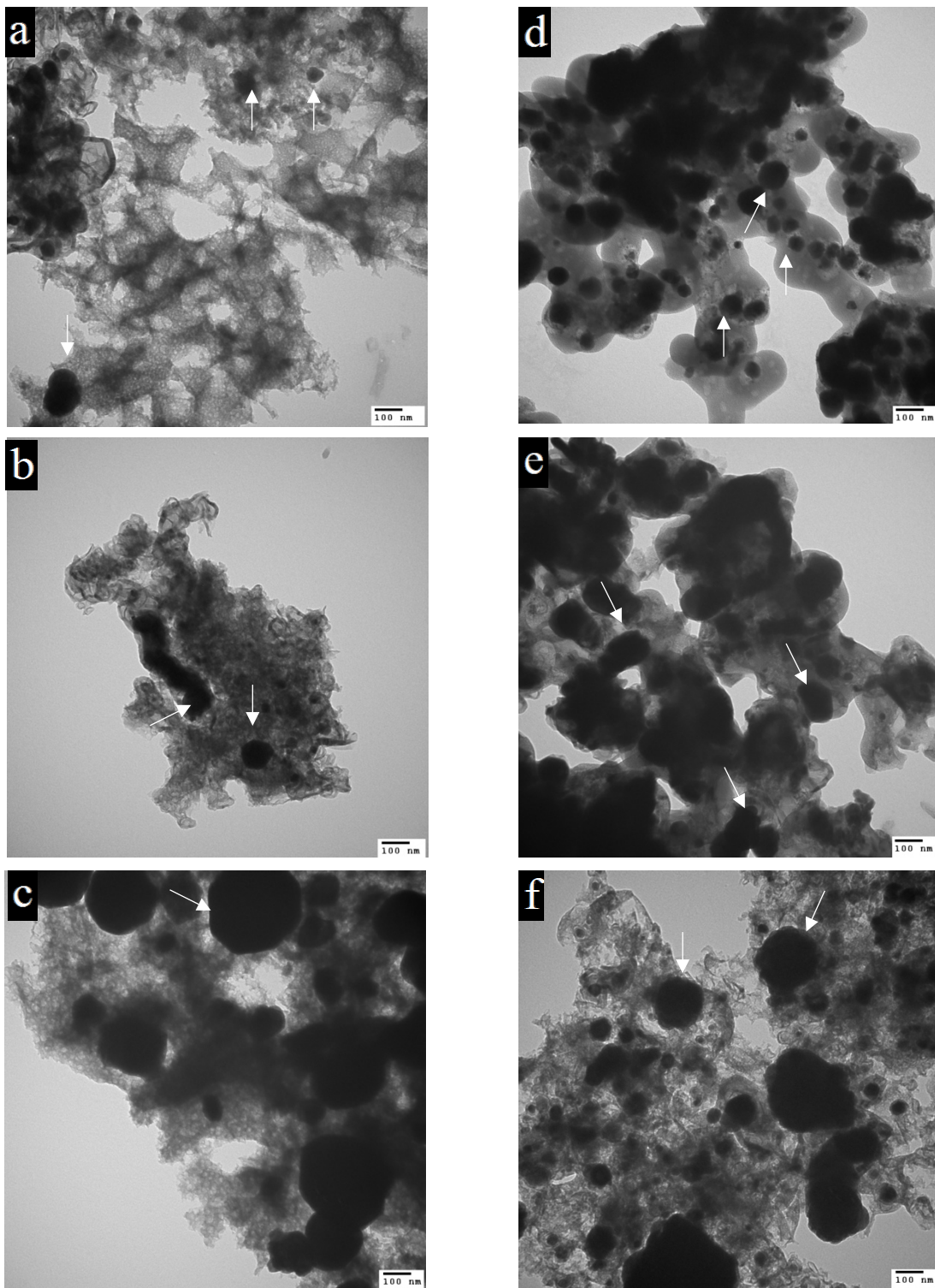


Figure S3. Transmission electron microscope images of ceramics derived from (a) **HOMODEN1**, (b) **HOMODEN2** (c) **HOMODEN3** (d) **HETERODEN1** (e) **HETERODEN2** (f) **HETERODEN3** showing magnetic crystallites embedded with amorphous matrix.

Reference

1. B. Jiang, W. L. Hom, X. Chen, P. Yu, L. C. Pavelka, K. Kisslinger, J. B. Parise, S. R. Bhatia and R. B. Grubbs, *J. Am. Chem. Soc.*, 2016, **138**, 4616-4625.
2. A. S. Abd-El-Aziz, D. J. Winram, P. O. Shipman and L. Bichler, *Macromol. Rapid Commun.*, 2010, **31**, 1992-1997.
3. A. S. Abd-El-Aziz, D. J. Winram, P. O. Shipman, C. L. Rock, M. S. Vandel and B. O. Patrick, *Macromol. Chem. Phys.* 2012, **213**, 2136-2145.