

## Supporting Information

### Polycatechol Nanoparticle MRI Contrast Agents

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### Synthetic Procedures.

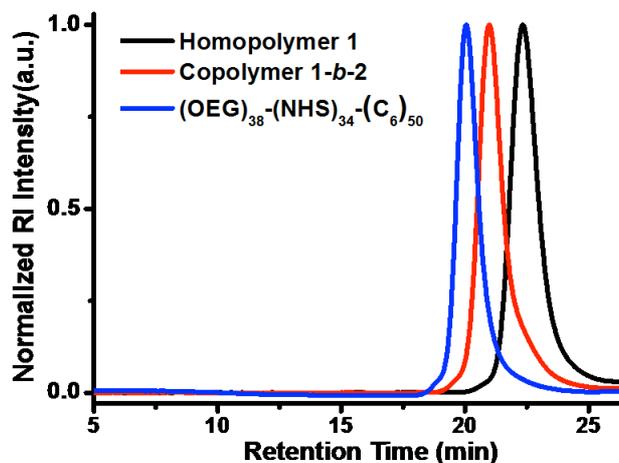
**Synthesis of (OEG)<sub>38</sub>-(NHS)<sub>34</sub>-(C<sub>6</sub>)<sub>50</sub>.** To a stirred 3.7 mL DMF solution of **1** (194 mg, 0.548 mmol) was added a solution of the initiator (IMesH<sub>2</sub>)(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>(Cl)<sub>2</sub>Ru=CHPh (10 mg, 0.0137 mmol) in DMF (0.3 mL). The reaction was left to stir in the glove box for 30 min, after which an analytical aliquot (0.1 mL) was removed and mixed with an excess of ethyl vinyl ether for 30 min, then dried under high vacuum to give a homopolymer of **1**. To the remaining reaction mixture was added a 0.5 mL DMF solution of **2** (97 mg, 0.411 mmol). The reaction was stirred in the glove box for another 30 min, after which an analytical aliquot (0.1 mL) was removed and mixed with an excess of ethyl vinyl ether for 30 min, then dried under high vacuum to give a block copolymer of **1-b-2**. To the remaining reaction mixture was added a 0.5 mL DMF solution of **3** (170 mg, 0.685 mmol). The mixture was left to stir in the glove box for 40 min then quenched with excess ethyl vinyl ether (0.5 mL) for about 20 min, then concentrated to dryness to give a yellow solid as the final product (392 mg, 85 %).

SEC-MALS of each polymer:

Homopolymer of **1**:  $M_{n, SEC} = 13.4$  kg/mol,  $M_{w, SEC} = 13.9$  kg/mol, PD = 1.04, N(OEG) = 38.

Copolymer of **1-b-2**:  $M_{n, SEC} = 21.4$  kg/mol,  $M_{w, SEC} = 23.3$  kg/mol, PD = 1.09, N(NHS) = 34.

(OEG)<sub>38</sub>-(NHS)<sub>34</sub>-(C<sub>6</sub>)<sub>50</sub>:  $M_{n, SEC} = 33.8$  kg/mol,  $M_{w, SEC} = 37.1$  kg/mol, PD = 1.10, N(C<sub>6</sub>) = 50.



**Figure S1.** SEC overlays for polymers: (a) Homopolymer **1** (black curve), Copolymer **1-b-2** (red curve), and (OEG)<sub>38</sub>-(NHS)<sub>34</sub>-(C<sub>6</sub>)<sub>50</sub> (blue curve).

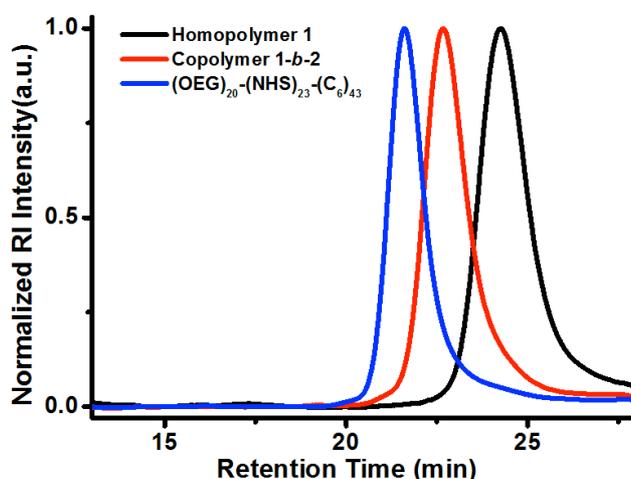
**Synthesis of (OEG)<sub>20</sub>-(NHS)<sub>23</sub>-(C<sub>6</sub>)<sub>43</sub>.** To a stirred 3.7 mL DMF solution of **1** (97 mg, 0.275 mmol) was added a solution of the initiator (IMesH<sub>2</sub>)(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>(Cl)<sub>2</sub>Ru=CHPh (10 mg, 0.0137 mmol) in DMF (0.3 mL). The reaction was left to stir in the glove box for 30 min, after which an analytical aliquot (0.1 mL) was removed and mixed with an excess of ethyl vinyl ether for 30 min, then dried under high vacuum to give a homopolymer of **1**. To the remaining reaction mixture was added a 0.5 mL DMF solution of **2** (65 mg, 0.277 mmol). The reaction was stirred in the glove box for another 30 min, after which an analytical aliquot (0.1 mL) was removed and mixed with an excess of ethyl vinyl ether for 30 min, then dried under high vacuum to give a block copolymer of **1-b-2**. To the remaining reaction mixture was added a 0.5 mL DMF solution of **3** (136 mg, 0.551 mmol). The mixture was left to stir in the glove box for 40 min and then quenched with excess ethyl vinyl ether (0.5 mL) for about 20 min, then concentrated to dryness to give a yellow solid as the final product (241 mg, 81 %).

#### SEC-MALS of each polymer:

Homopolymer of **1**:  $M_{n, SEC} = 7.1$  kg/mol,  $M_{w, SEC} = 7.3$  kg/mol, PD = 1.03, N(OEG) = 20.

Copolymer of **1-b-2**:  $M_{n, SEC} = 12.6$  kg/mol,  $M_{w, SEC} = 13.6$  kg/mol, PD = 1.08, N(NHS) = 23.

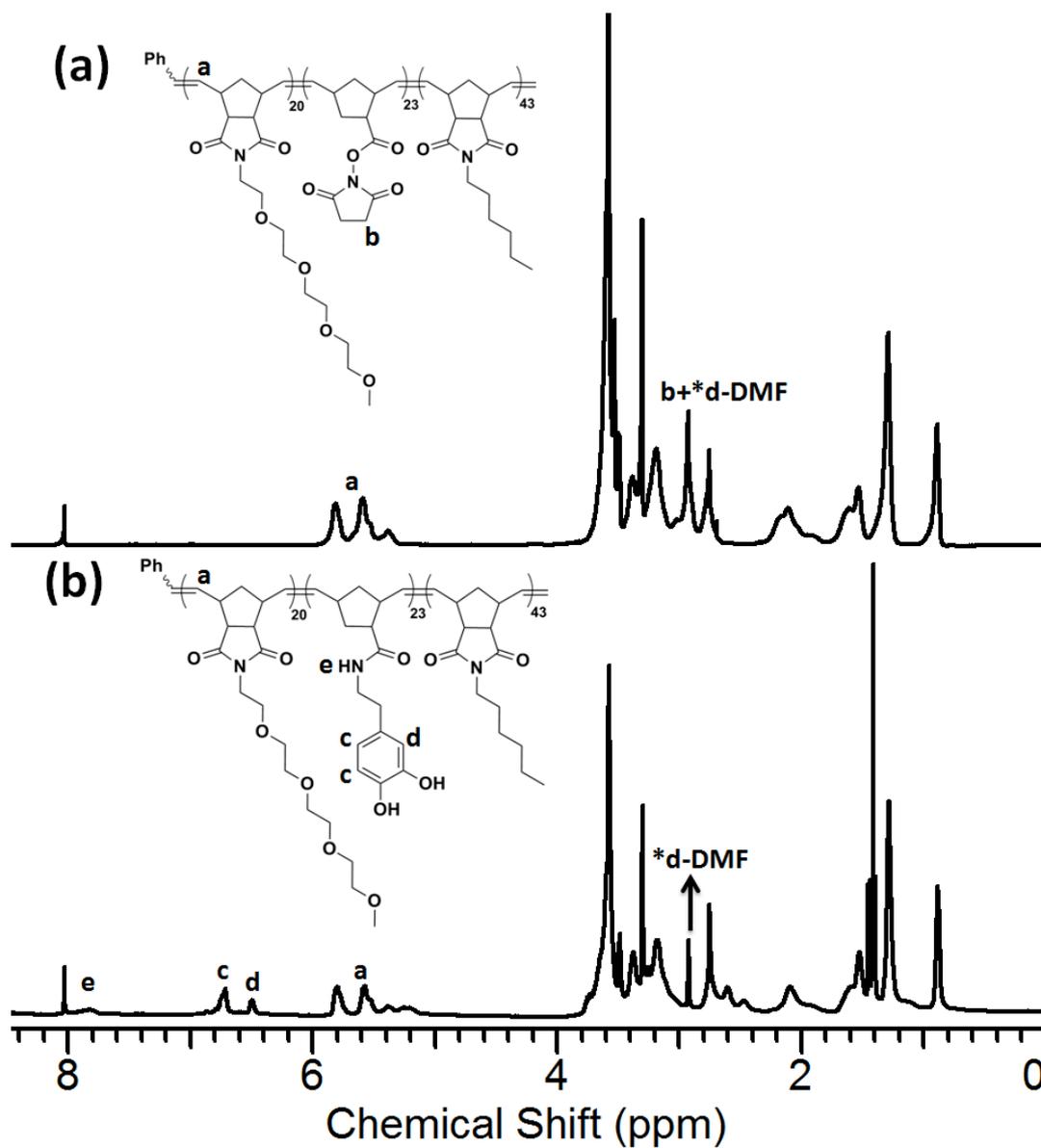
(OEG)<sub>20</sub>-(NHS)<sub>23</sub>-(C<sub>6</sub>)<sub>43</sub>:  $M_{n, SEC} = 23.1$  kg/mol,  $M_{w, SEC} = 25.4$  kg/mol, PD = 1.09, N(C<sub>6</sub>) = 43.



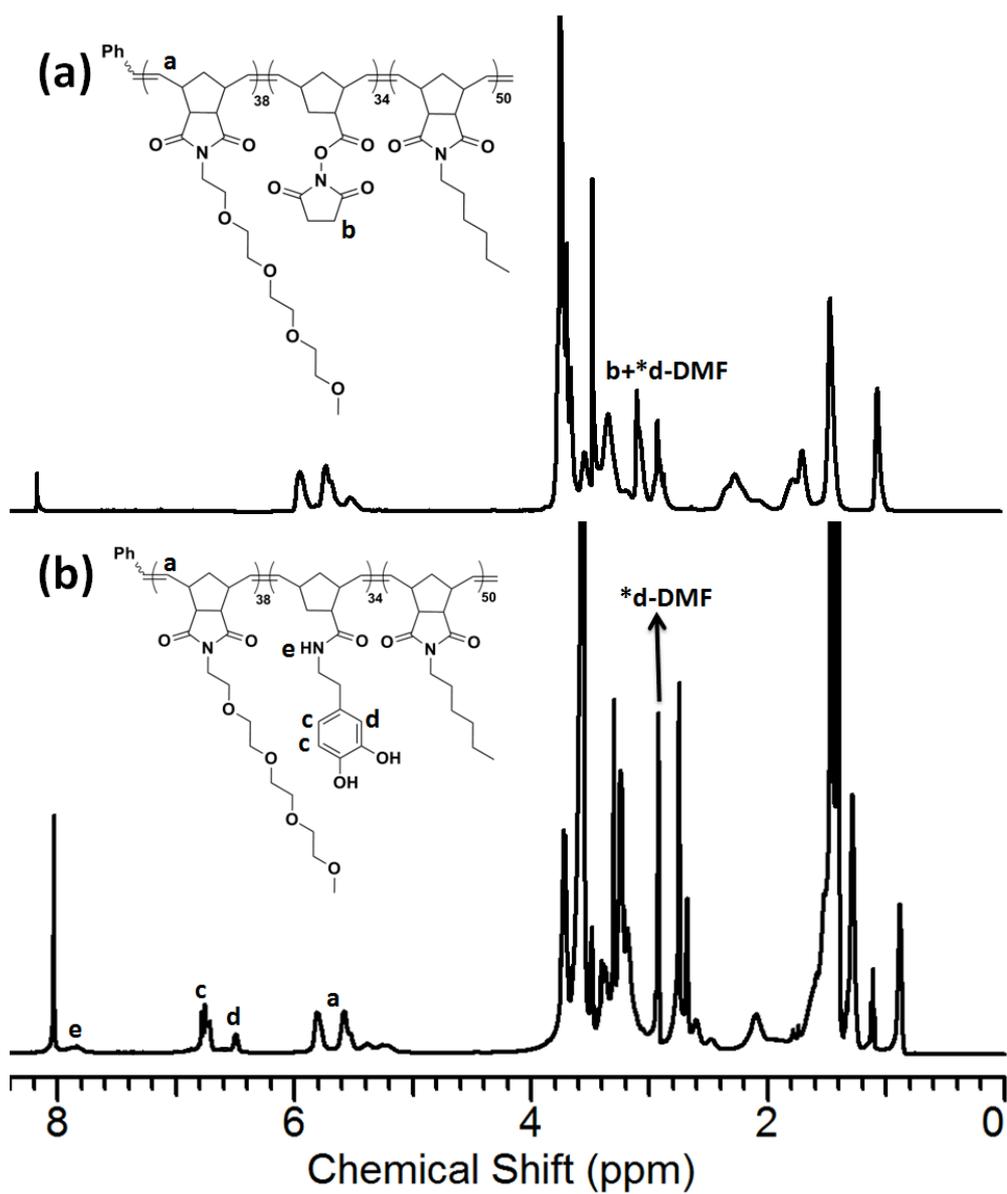
**Figure S2.** SEC overlays for polymers: (a) Homopolymer **1** (black curve), Copolymer **1-b-2** (red curve), and (OEG)<sub>20</sub>-(NHS)<sub>23</sub>-(C<sub>6</sub>)<sub>43</sub> (blue curve).

**Synthesis of (OEG)<sub>38</sub>-(Cat)<sub>34</sub>-(C<sub>6</sub>)<sub>50</sub> (Polymer 1).** (OEG)<sub>38</sub>-(NHS)<sub>34</sub>-(C<sub>6</sub>)<sub>50</sub> ( $M_{n, SEC} = 33.7$  kg/mol, 300 mg, 0.0089 mmol), 3-hydroxytyramine hydrochloride (287 mg, 1.51 mmol), and N,N-Diisopropylethylamine (390 mg, 3.02 mmol) were fully dissolved in 10 mL of DMF. The mixture was stirred at room temperature for about 2 days. The solution was then precipitated into 1M HCl solution three times. The brown precipitate was filtered off and redissolved in 10 mL THF. The solution was precipitated into cold ether three times. The final product was collected and dried under vacuum overnight to afford a brown powder (268 mg; Yield: 86 %) as Polymer 1.

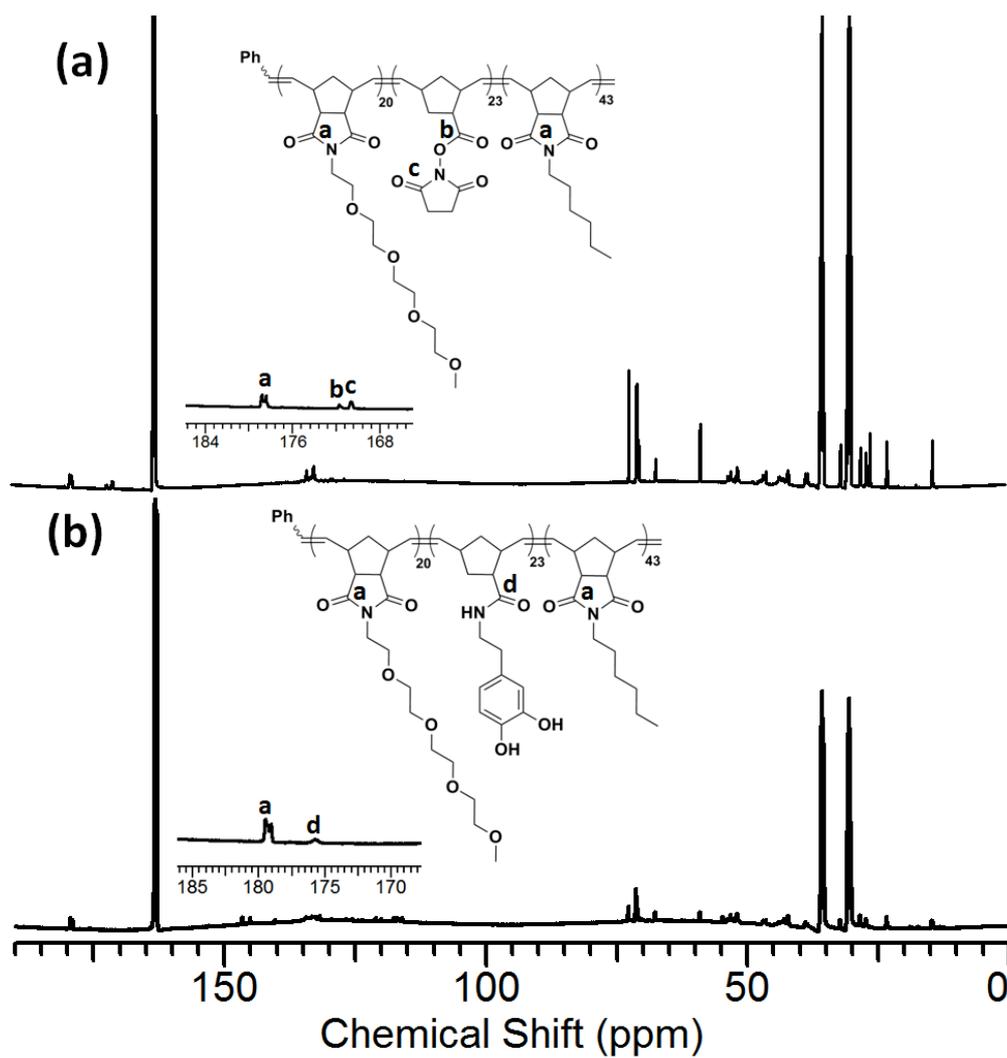
**Synthesis of (OEG)<sub>20</sub>-(Cat)<sub>23</sub>-(C<sub>6</sub>)<sub>43</sub> (Polymer 2).** (OEG)<sub>20</sub>-(NHS)<sub>23</sub>-(C<sub>6</sub>)<sub>43</sub> ( $M_{n, SEC} = 23.1$  kg/mol, 180 mg, 0.0078 mmol), 3-hydroxytyramine hydrochloride (155 mg, 0.82 mmol), and N,N-Diisopropylethylamine (211 mg, 1.64 mmol) were fully dissolved in 10 mL of DMF. The mixture was stirred at room temperature for about 2 days. The solution was then precipitated into 1M HCl solution three times. The brown precipitation was filtered off, redissolved into 8 mL THF then precipitated into cold ether three times. The final product was collected and dried under vacuum overnight to afford a brown powder (153 mg; Yield: 82 %) as Polymer 2.



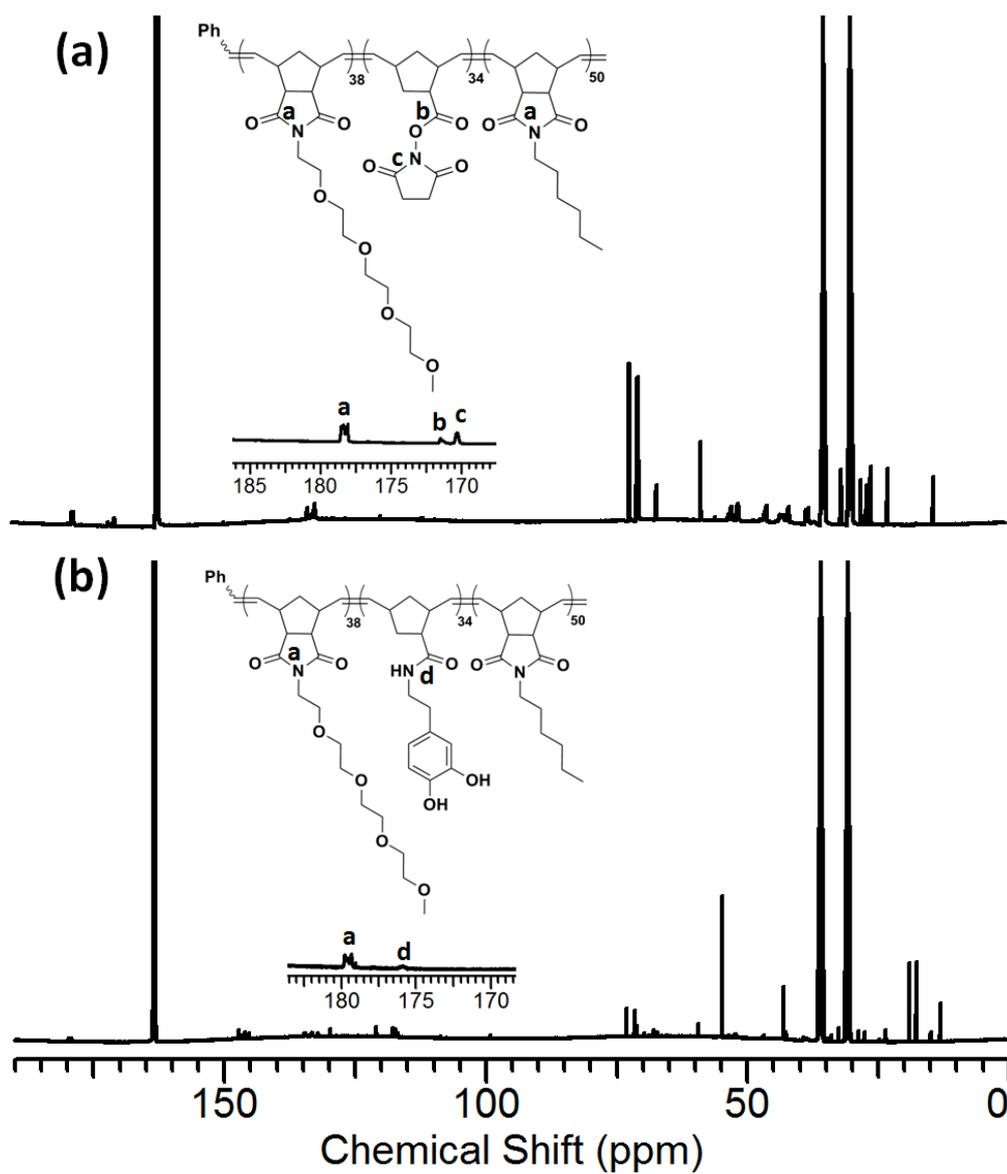
**Figure S3.**  $^1\text{H}$  NMR spectra of (a)  $(\text{OEG})_{20}\text{-(NHS)}_{23}\text{-(C}_6\text{)}_{43}$ , and (b)  $(\text{OEG})_{20}\text{-(Cat)}_{23}\text{-(C}_6\text{)}_{43}$  in  $d\text{-DMF}$ .



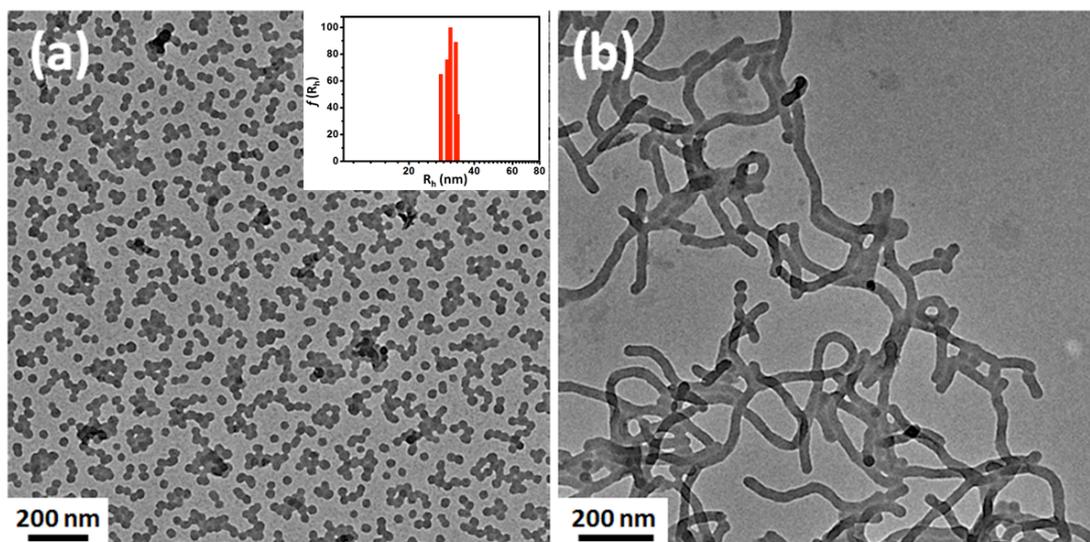
**Figure S4.**  $^1\text{H}$  NMR spectra of (a)  $(\text{OEG})_{38}\text{-(NHS)}_{34}\text{-(C}_6\text{)}_{50}$ , and (b)  $(\text{OEG})_{38}\text{-(Cat)}_{34}\text{-(C}_6\text{)}_{50}$  in  $d\text{-DMF}$ .



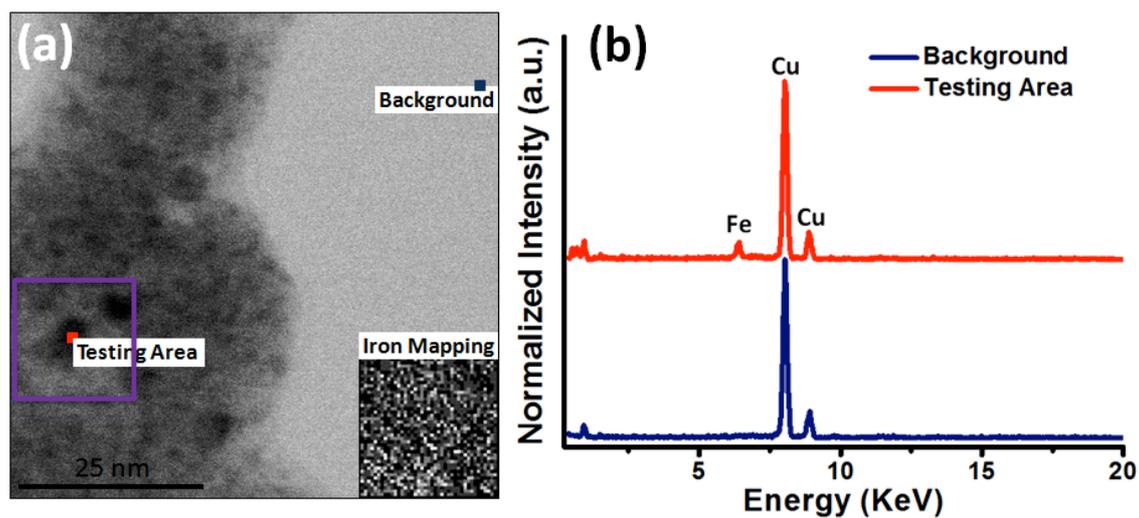
**Figure S5.**  $^{13}\text{C}$  NMR spectra of (a) (OEG)<sub>20</sub>-(NHS)<sub>23</sub>-(C<sub>6</sub>)<sub>43</sub>, and (b) (OEG)<sub>20</sub>-(Cat)<sub>23</sub>-(C<sub>6</sub>)<sub>43</sub> in d-DMF.



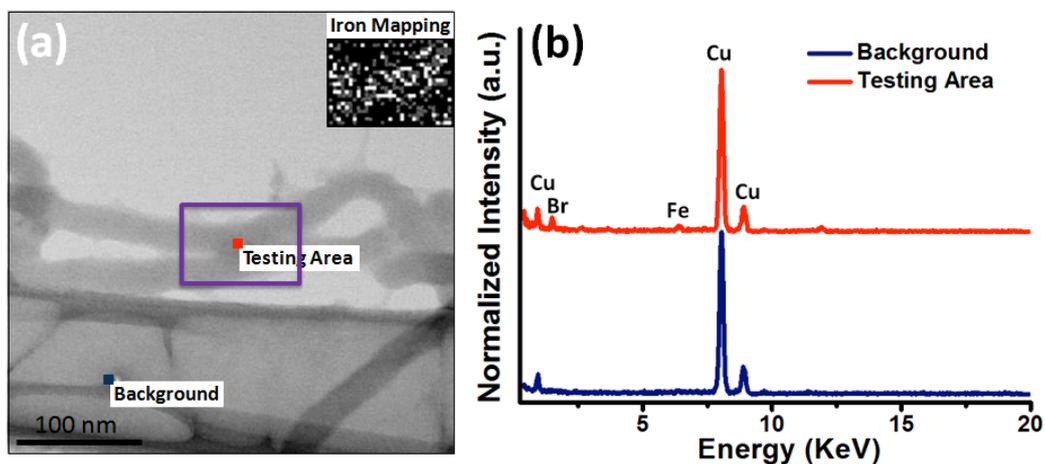
**Figure S6.**  $^{13}\text{C}$  NMR spectra of (a) (OEG) $_{38}$ -(NHS) $_{34}$ -(C $_6$ ) $_{50}$ , and (b) (OEG) $_{38}$ -(Cat) $_{34}$ -(C $_6$ ) $_{50}$  in d-DMF.



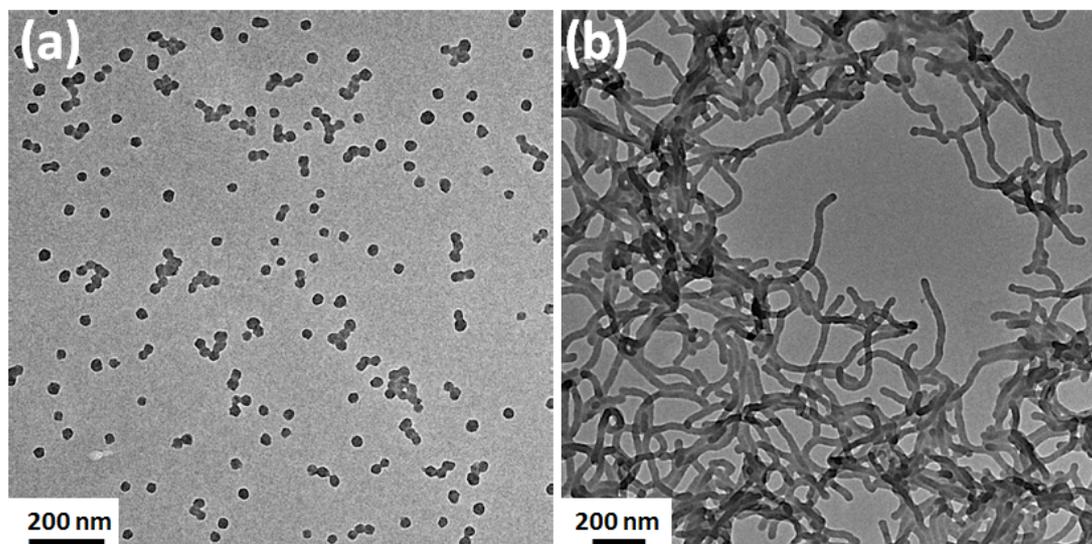
**Figure S7.** Unstained TEM images of freshly prepared micelles: (a) SMN (insert is the corresponded DLS data), and (b) CMN.



**Figure S8.** (a) Selected area BF-STEM of SMN with area chosen for EDS analysis, insert is the EDS Fe elemental mapping image of selected area; (b) EDS profiles of SMN from the testing area and background in (a).

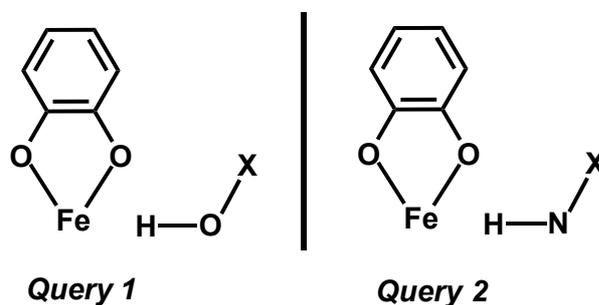


**Figure S9.** (a) Selected area BF-STEM of CMN with area chosen for EDS analysis, insert is the EDS Fe elemental mapping image of selected area; (b) EDS profiles of CMN from the testing area and background in (a).



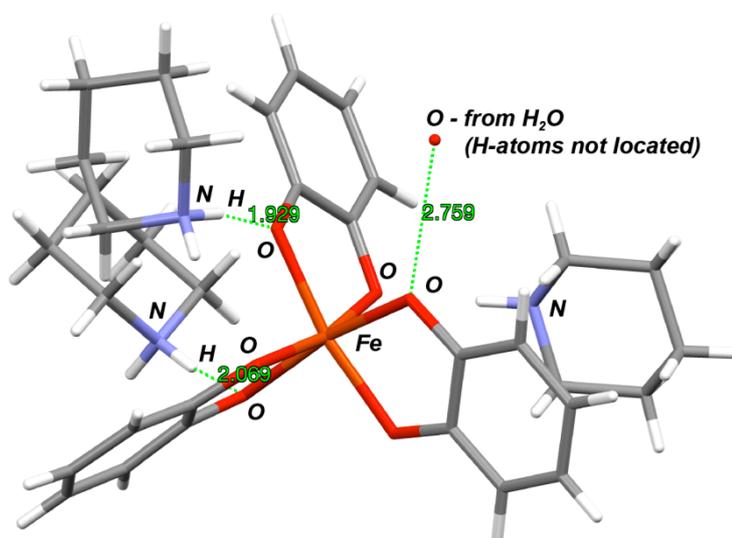
**Figure S10.** Unstained TEM images of micelles after 6 months stored at room temperature: (a) SMN, and (b) CMN.

**Results of Cambridge Structural Database (CSD) Search for Hydrogen-Bonding Interactions between Polar H-X bonds and  $\text{Fe}^{\text{III}}(\text{catecholate})_3$  Cores.** To provide additional evidence for the viability of second-sphere interactions between  $\text{H}_2\text{O}$  and paramagnetic  $\text{Fe}^{\text{III}}(\text{catecholate})_3$  cores, two Cambridge Structural Database (CSD)<sup>[1]</sup> searches were conducted using the following search criteria:

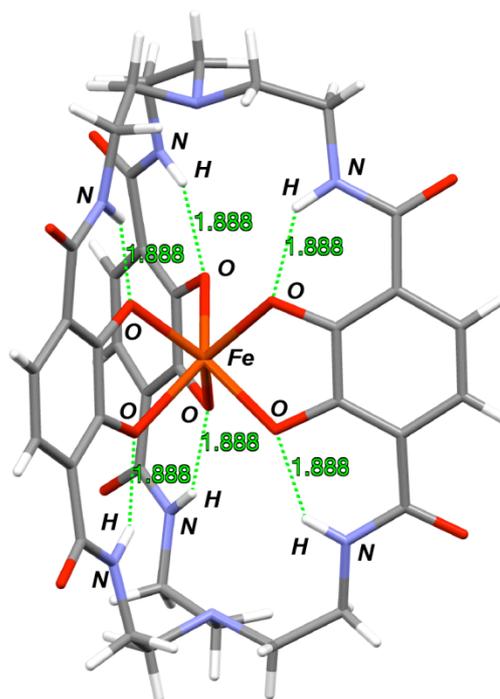


**X = Any Atom**

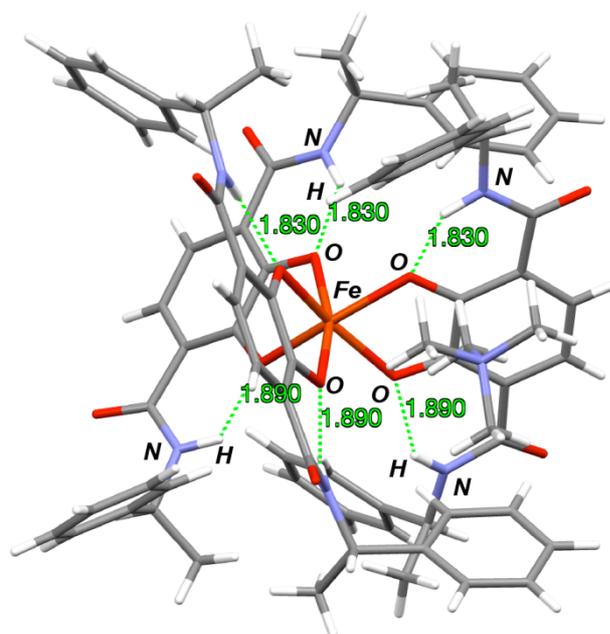
A total of 72 unique structures were found featuring hydrogen-bonding interactions between the oxygen atoms of the  $\text{Fe}^{\text{III}}(\text{catecholate})_3$  primary coordination sphere and polar H-O or H-N bonds. Examples of both intra- and intermolecular hydrogen bonding interactions were found. The selected examples referenced in the text are shown below along with CSD codes.



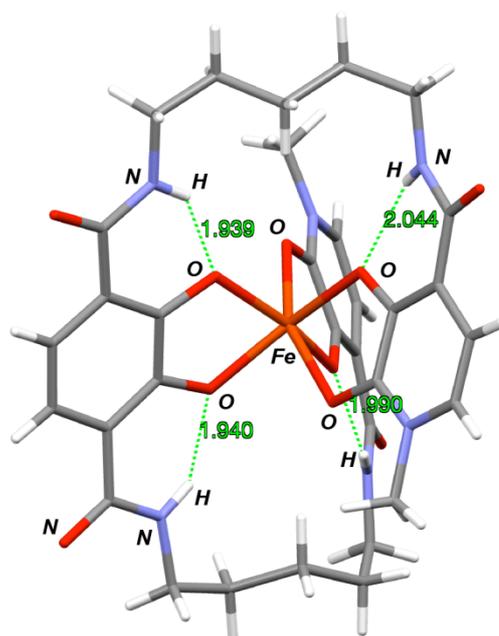
**Figure S11.** Fe(catecholate)<sub>3</sub> Example #1 with intermolecular hydrogen-bonding to piperidinium cations and H<sub>2</sub>O. H<sub>2</sub>O hydrogen atoms were not located in the data set (CSD Codes: BICSEL and CATFEP).<sup>[2]</sup>



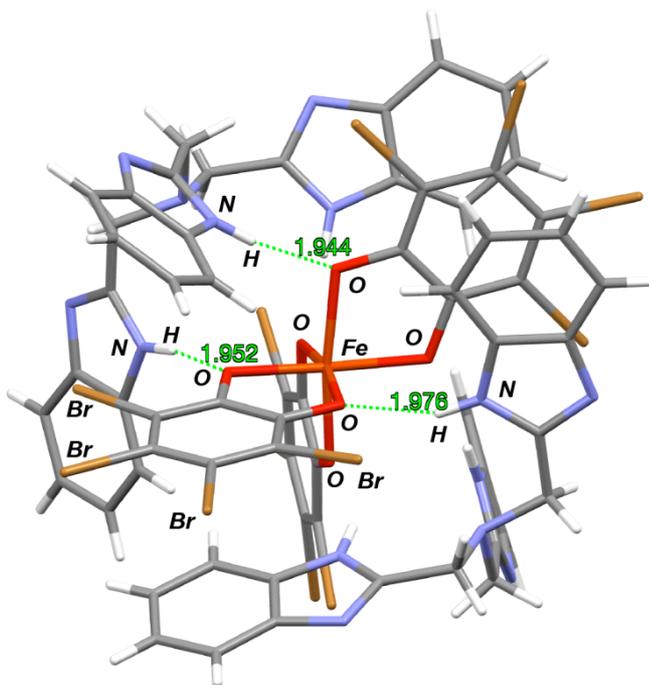
**Figure S12.** Fe(catecholate)<sub>3</sub> Example #2 with intramolecular hydrogen-bonding to amide N-H groups (CSD Code FUDRUR).<sup>[3]</sup>



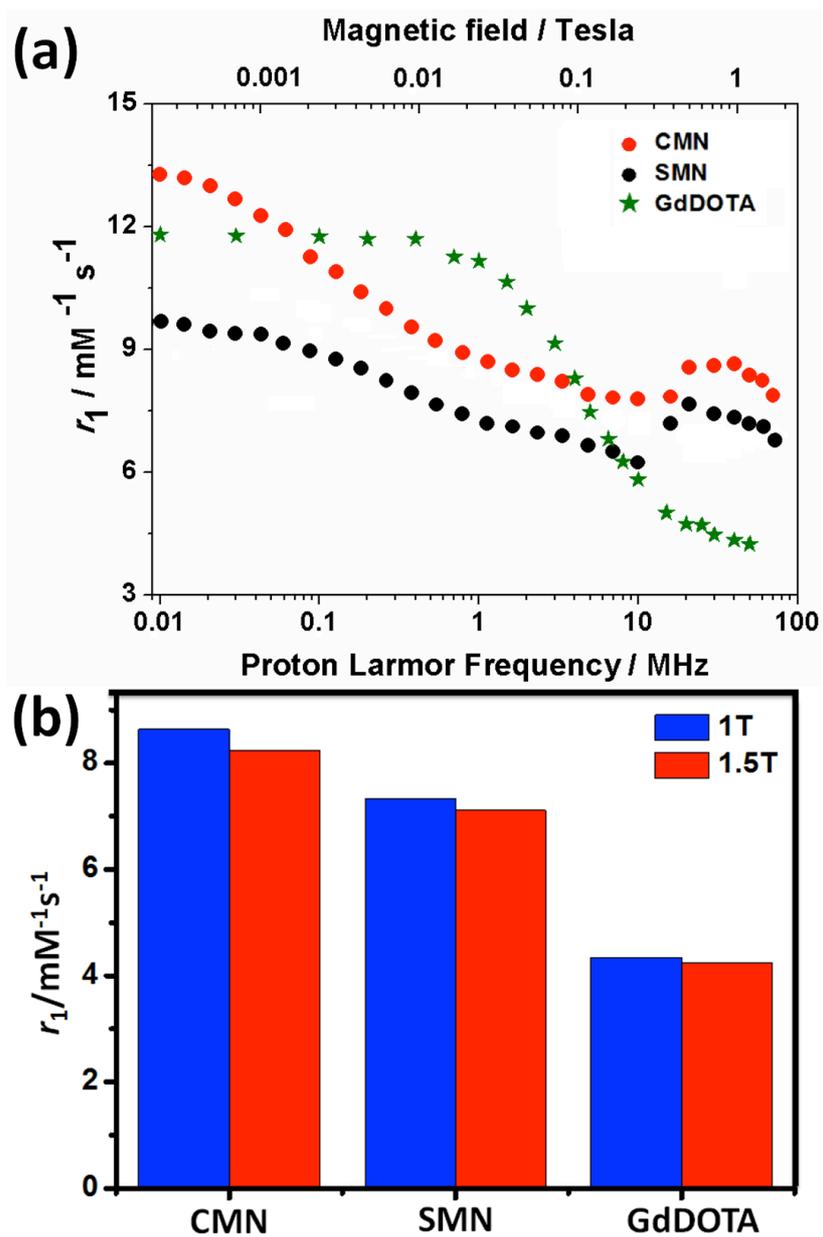
**Figure S13.** Fe(catecholate)<sub>3</sub> Example #3 with intramolecular hydrogen-bonding to amide N-H groups (CSD Code SUCDAV10).<sup>[4]</sup>



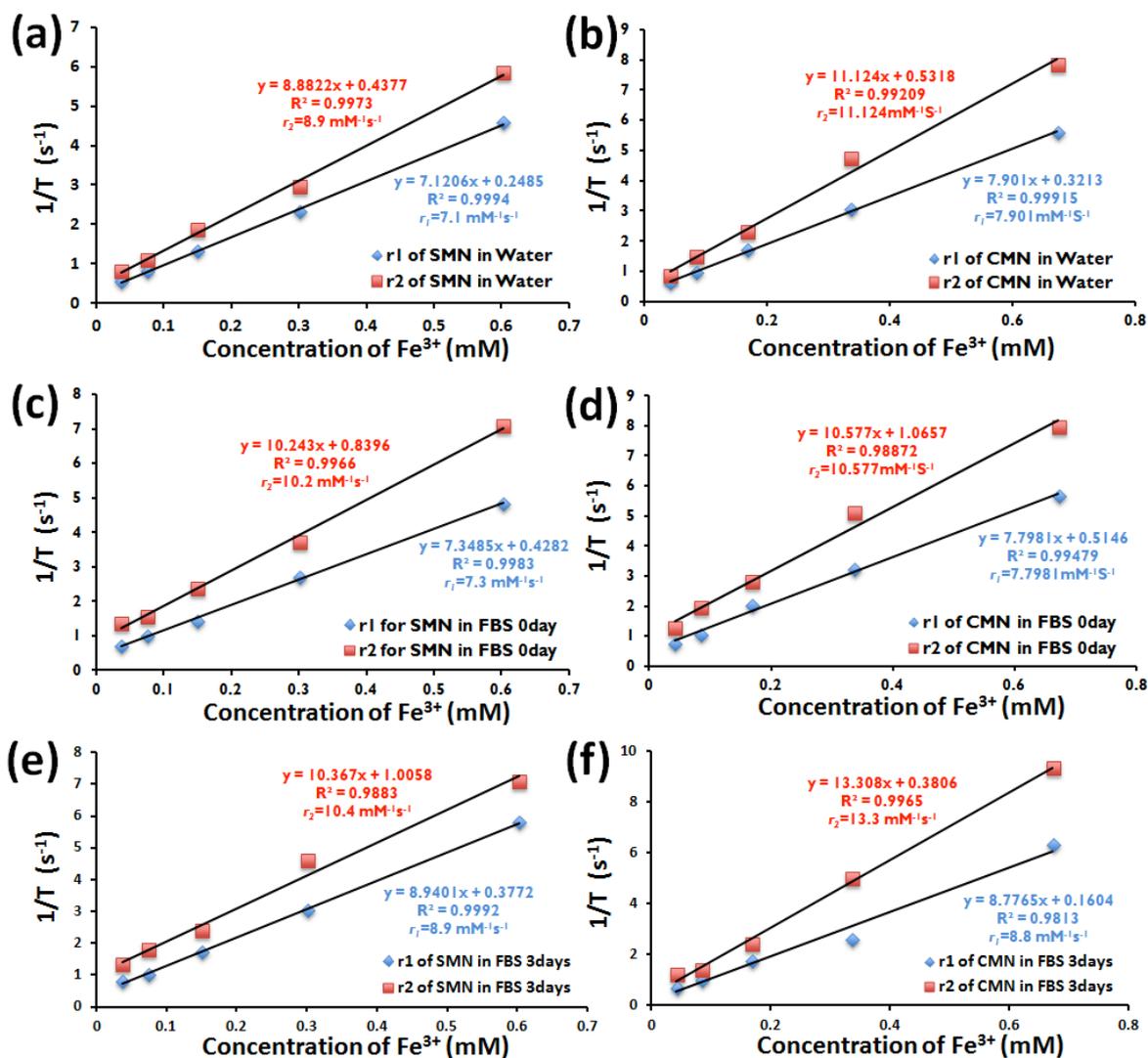
**Figure S14.** Fe(catecholate)<sub>3</sub> Example #4 with intramolecular hydrogen-bonding to amide N-H groups (CSD Code FERJES).<sup>[5]</sup>



**Figure S15.** Fe(catecholate)<sub>3</sub> Example #5 with intermolecular hydrogen-bonding to indol N-H groups (CSD Code CEZYIR). Note that in this example, intermolecular hydrogen-bonds fully support a host-guest interaction between two tris(indolemethylene)amine molecules and an [Fe(Br<sub>4</sub>Cat)<sub>3</sub>]<sup>3-</sup> trianion.<sup>[6]</sup>



**Figure S16.** (a)  $^1\text{H}$  NMRD profiles for CMN, SMN, and GdDOTA; (b) per  $\text{Fe}^{\text{III}}$   $r_1$  of CMN, SMN, and GdDOTA at field strength of 1 T and 1.5 T, respectively.



**Figure S17.** Plots of  $1/T_1$  and  $1/T_2$  vs  $Fe^{III}$  concentration for SMN in water (a), CMN in water (b), SMN in freshly prepared FBS (c), CMN in freshly prepared FBS (d), SMN in FBS for 3 days (e), and CMN in FBS for 3 days (f) with the calculated  $r_1$  and  $r_2$ , respectively.

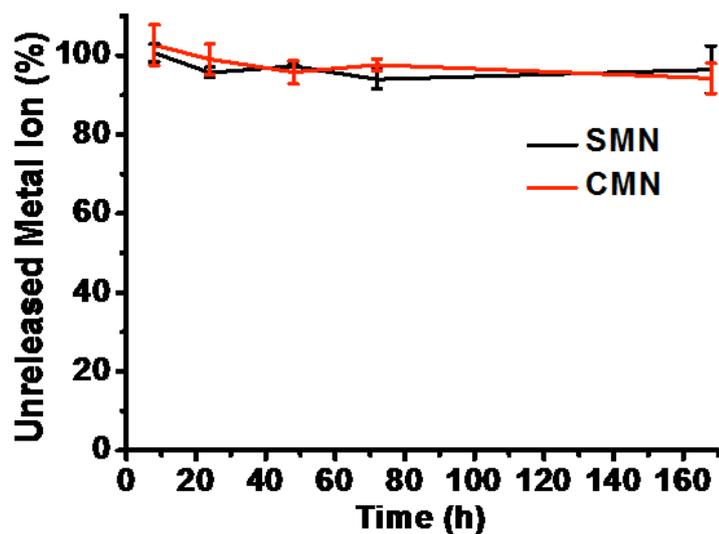


Figure S18. Stability study of Fe<sup>III</sup>-chelated SMN and CMN in PBS.

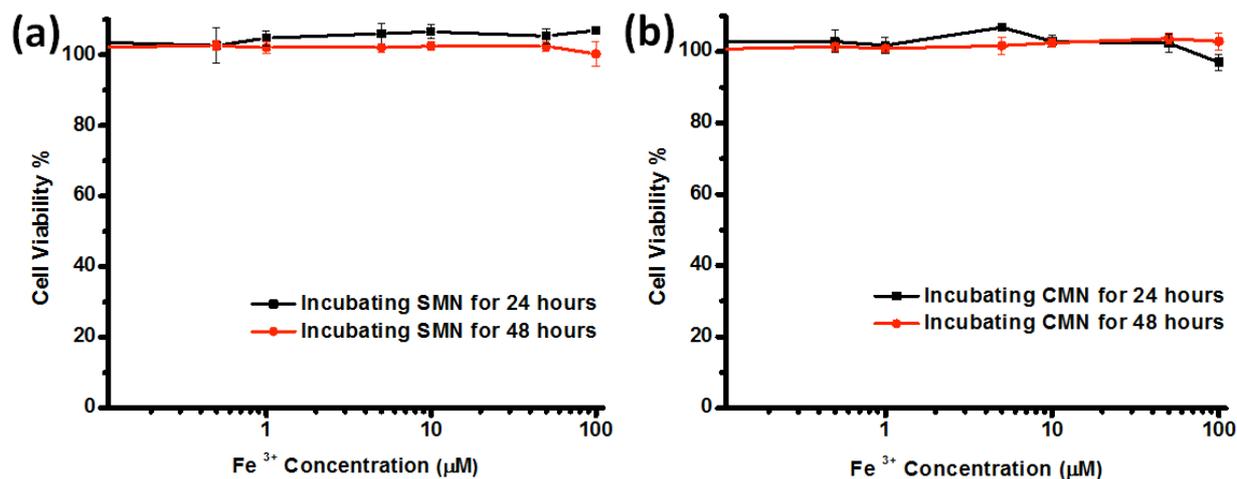
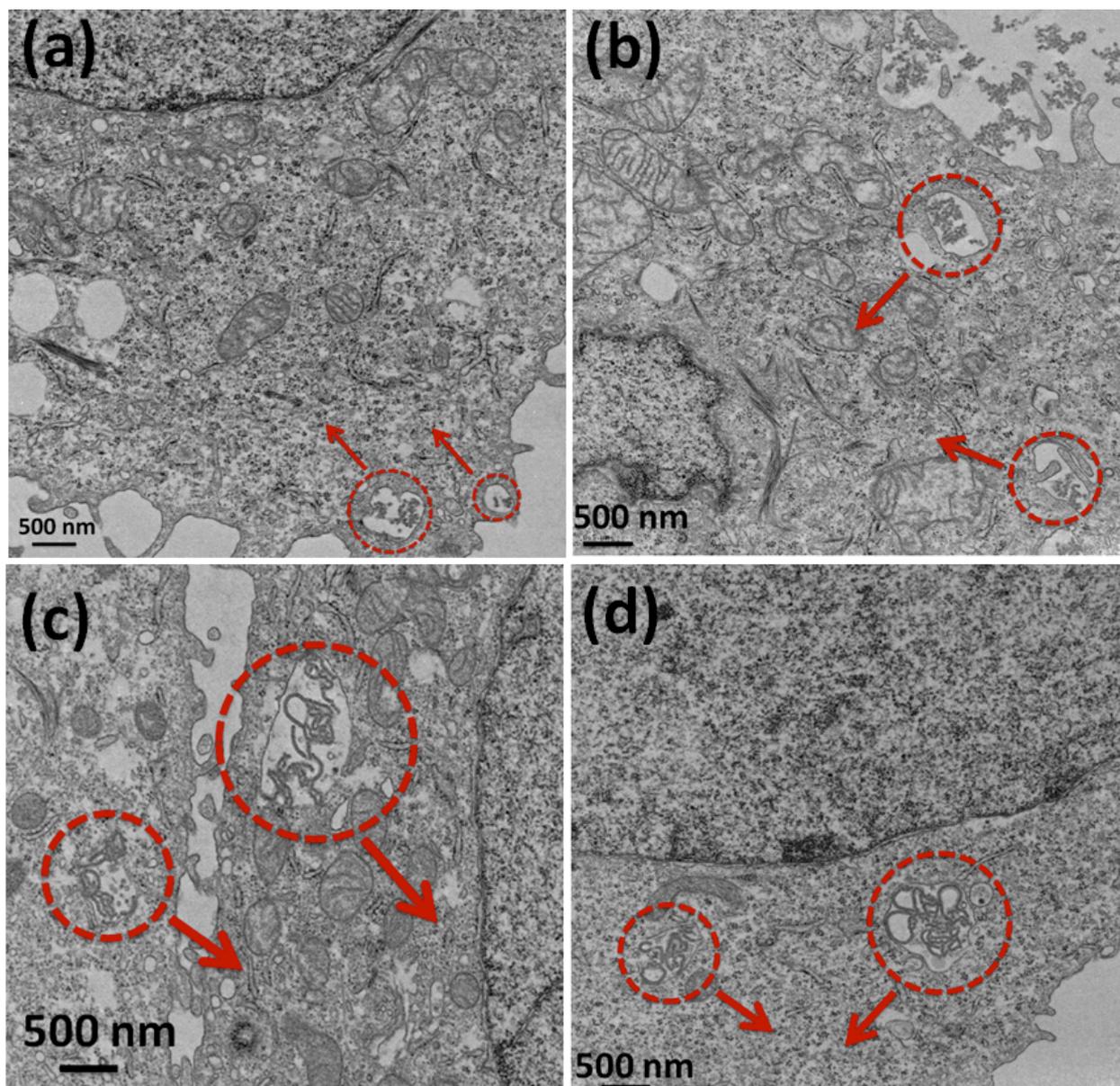


Figure S19. Cytotoxicity assay for HeLa cells incubated with various concentrations of Fe<sup>III</sup> ions in SMN (a) and CMN (b).



**Figure S20.** Additional TEM image of SMN (a, b) and CMN (c, d), trapped inside vesicles of HeLa cells.

## References

- [1] a) Cambridge Structural Database (CSD), version 5.34 (Update 32, Feb. 2013); b) F. Allen, *Acta Crystallogr. B* **2002**, 58, 407; c) F. H. Allen, W. D. S. Motherwell, *Acta Crystallogr. B* **2002**, 58, 407.
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- [3] T. J. McMurry, M. W. Hosseini, T. M. Garrett, F. E. Jahn, Z. E. Reyes, K. N. Raymond, *J. Am. Chem. Soc.* **1987**, 109, 7196.
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- [6] A. Panja, *Inorg. Chem. Commun.* **2013**, 32, 42.

