## **Electronic Supplementary Information**

# Structural Diversity in Metal-Organic Nanoparticles Based on Iron Isopropoxide Treated Lignin

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#### 1. Note on the description of iron (III) isopropoxide

It is generally acknowledged that metal alkoxides tend to form more complex structures than their regular denotation  $M(O-Alk)_n$  suggests. In the case of aluminum isopropoxide,  $Al(OiPr)_3$ , the structure of the molecule has been shown to vary from complex dimers of two molecules to trimers and tetramers.<sup>1</sup> Thus with all metal alkoxides one has to consider that the presented structure is an approximation and the chemical equations with such structure will be to some extent also be approximations. Both iron (III) isopropoxide  $[Fe(OiPr)_3]$  and iron (II) isopropoxide  $[Fe(OiPr)_2]$  solutions were produced in situ. The success of the iron isopropoxide formation reaction can be determined visually: when the reaction is successful, the transparent NaOiPr solution turns deep colored [brown/black] upon the addition of the FeCl<sub>3</sub> (or FeCl<sub>2</sub>) solution.

### 2. Characteristics of LignoBoost<sup>TM</sup> lignin

LignoBoost<sup>TM</sup> lignin is a purified byproduct of cellulose manufacture<sup>2</sup> and is commercially produced in high quantities. Lignin is produced by removing it from pulping liquors by precipitation through  $CO_2$  acidification and filtering. The filtered cake is re-dispersed and acidified and the resulting slurry is then filtered and washed by means of displacement washing and finally dried. When the predried LignoBoost<sup>TM</sup> lignin is dissolved in anhydrous THF, the residual moisture can be removed by molecular sieves and ash can be sedimented to yield a water and ash free lignin solution. LignoBoost lignin is soluble in THF at least up to 30

wt. % concentration. The ash content of LignoBoost<sup>TM</sup> lignin is generally around or below 1 wt. %. Of the ash free fraction, the elemental analysis gives an average ratio of 65.1 % C, 5.8 % H, 26.1 % O, 2.5 % S, 0.1 % N and 0.01 % Cl. This corresponds roughly to an atom ratio of 10 C, 3 O and 11 H, which matches closely with coniferyl alcohol (10 C, 3 O and 12 H). However as lignin formation from monolignols can occur by addition reaction or condensation, and the production of LignoBoost lignin involves the breaking of bonds by sulfate, which introduces sulfur into the structure, the amount of available reactive oxygen is not directly deduced from the elemental ratio. The lignin used in this work was provided by VTT Technical Research Centre of Finland. Table S1 presents the chemical structure of the lignin used in this work obtained by <sup>31</sup>P-NMR spectroscopy.

Table S1. Amounts of different hydroxyl gro	p species in the lignin	sample according to	<sup>31</sup> P-NMR data.
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	Aliphatic OH (mmol/g)	Carboxylic (mmol/g)	Phenolic OH (mmol/g)	Total OH (mmol/g)	Total OH (mmol/g) excluding COOH	Mw (g/mol)
LignoBoost <sup>TM</sup> lignin	1.43	0.29	3.29	5.01	4.72	> 4800



Figure S1. Schematic representation of lignin.<sup>3</sup> (Reprinted with permission from ref. 3. Copyright 2010 American Chemical Society)

#### 3. Lignin treatment with iron isopropoxide

The introduction of water into a metal alkoxide solution will cause immediate hydrolysis and the formation of a gel and/or metal oxide particles. Thus a water free solution is required for the condensation of metal alkoxides and organic alcohols. Metal alkoxides will immediately condense with any organic alcohol, leaving the alcohol corresponding to the metal alkoxide. In general this can be considered an equilibrating chain transfer reaction, where the metal alkoxides can swap their alkoxy groups with any alcohol present in the solution. The smaller the alkoxy group, the more likely it is to be released. If the metal is bound to several OH groups within the same molecule, the breaking of a single Fe-O-Alk bond will not release the molecule from its position and the bond is likely to reform, especially if the structure where the bond lies is shielded from other alcohols, as is the case within a forming nanoparticle.

As was mentioned in the main text, the nanoparticle formation is governed both by the condensation reaction and subsequent hydrolysis reaction of the condensate. The presence of water in the lignin solution during the condensation reaction will automatically hydrolyze  $Fe(OiPr)_3$ , causing either Fe-O-Fe bonded gel (small amount of water), or  $Fe_2O_3$  flakes/crystals (depending on the conditions) to form. When no water is present, the reaction will proceed until either OH or OiPr groups have been depleted, or the remaining functional groups remain trapped within the formed structure. We could observe that when forming the larger nanoparticles (*ca.* 100 nm in diameter), the condensate prior to hydrolysis does not have a spherical morphology. TEM imaging shows small (< 1000 nm) random networks (Figure S2). When the condensate is hydrolyzed with 10 wt. % distilled water in THF and solvent exchanged into water, the networks collapse into spherical particles due to hydrophobic interactions and/or additional condensation/hydrolysis reactions.



Figure S2. THF dispersion of Fe(III):lignin condensate dried on TEM grid.

In the case of the open network structure (Sample 1), the fusing of the particles creates a very porous structure and the sub 50 nm domain size enables the observed superparamagnetic nature of the particles. After the condensation reaction the network structure can be further reacted with lignin to yield nanoparticles that are much rougher in shape, corresponding to a lignin-filled rigid structure (Figure S3, left). With a rapid hydrolysis of the 1:1 OH:  $Fe(OiPr)_3$  reaction, with 10 wt. % water in THF, even larger and denser structures of fused particles can be observed (Figure S3, right).



Figure S3. Fe(III):lignin network (Sample 1) further reacted with lignin (left image) and Fe(III):lignin nanoparticles cluster *via* hydrolysis with 10 wt. % water in THF (right image).

The dependence of OH:  $Fe(OiPr)_3$  ratio to the formed structure was also studied. It was observed that with an excess of  $Fe(OiPr)_3$  (<1:1 OH:  $Fe(OiPr)_3$ ), crystalline precipitate formed upon hydrolysis (Figure S4a). With an excess of lignin (>3:1 OH:  $Fe(OiPr)_3$ ) the TEM images showed both large particles, as well as fuzzy edged network, which can be attributed to the unreacted lignin (Figure S4e). With an intermediate ratio (ca. 2:1) of OH to  $Fe(OiPr)_3$ , the shift from 10–30 nm nanoparticles (Figure S4b) to 100–200 nm nanoparticles (Figure S6e) seems to take place through fused nanoparticles as an intermediate stage (Figure S4c).

# $Lignin-(OH)_n + mFe(OiPr)_3$



Figure S4. The influence of lignin OH: Fe(OiPr)<sub>3</sub> ratio to the condensate morphology. Scale bar 200 nm.

#### 4. Colloidal properties of the nanoparticle suspensions

Figure S5 shows a Fe(III):lignin dispersion (3:1 OH:Fe(OiPr)<sub>3</sub>) next to a THF/IPA solution of Fe(OiPr)<sub>3</sub> (1.1 wt. %) and THF solution of lignin (1.0 wt. %). Both reagent solutions are red at these concentration. The Fe:lignin condensate solution is darker than either Fe(OiPr)<sub>3</sub> or lignin solution and colloidally stable.

The mass magnetization of the Fe(III):lignin nanoparticles is not high enough to allow for the separation of the particle with a household magnet (Brownian motion and electrorepulsive forces are stronger than the effect of the magnet). When larger networks are formed, the forces that keep the nanoparticles dispersed are no longer dominant and household magnets can be used to move the suspended networks (Fe(II):lignin much more easily than Fe(III):lignin).



Figure S5. Fe(OiPr)<sub>3</sub> THF/IPA solution (left), Fe:lignin NP aqueous dispersion (center) and lignin THF solution (right).

#### 5. Iron content of the particles

The iron bound to the particles can be assessed qualitatively by IR spectroscopy with the identification of additional peaks in the IR spectrum and the disappearance of certain peaks, such as the carbonyl peak at 1700 cm<sup>-1</sup>. For quantitative analysis samples were measured by atomic absorption spectrometry (AAS) where all of the organic components are destroyed by the sample preparation process and only the iron content is obtained. When 13.1 mg of lignin was reacted with 20.8 mg (89.1  $\mu$ mol) of Fe(OiPr)<sub>3</sub>, a polymer with an iron content of 297 mg/g was obtained. If it is assumed that only the iron of Fe(OiPr)<sub>3</sub> remains in the Fe:lignin polymer and that the rest of the mass of the polymer comes from lignin (minus the protons of OH groups), the calculated iron content in this reaction would be 277 mg/g (7 % discrepancy). If it is assumed that only one Fe(OiPr) moiety reacts with lignin OH and the rest condense only upon hydrolysis, forming Fe-O-Fe bonds, the calculated iron content would be 255 mg/g (16 % discrepancy). Some of this discrepancy might be explained by Fe(OiPr)<sub>3</sub> removing some of the methoxy moieties of lignin via chain transfer. However, it is clear that the value of iron content in the Fe:lignin polymer is of the expected magnitude.

#### 6. Experimental details for sample preparation

**Sample 1: Open network:** 695  $\mu$ L of 108.9  $\mu$ mol/g THF solution of Fe(OiPr)<sub>3</sub> was added dropwise into 500  $\mu$ L of 22.6 mg/g THF solution of lignin. A black precipitate was immediately formed, which could be partially redispersed. An 11-fold dilution (750  $\mu$ L of THF into 75  $\mu$ L of the dispersion) was sufficient for full dispersion of the product. 750  $\mu$ L of 10 wt. % H<sub>2</sub>O in THF was added to hydrolyze the product to yield a clear yellow dispersion.

Sample 2: Small solid particles (10-20 nm). 4.770 g of 4.00  $\mu$ mol/g THF:2-propanol solution of Fe(OiPr)<sub>3</sub> was added dropwise into 1.599 g of 2.1 mg/g (12.0  $\mu$ mol/g of OH) THF solution of lignin in acetone ice (ca. -95 °C). The solution remained clear yellow. 500  $\mu$ l of 1.00 wt. % distilled water in THF was added dropwise into to the room temperature solution to hydrolyze the Fe(OiPr) moieties. The hydrolyzed solution was solvent exchanged in a dialysis tube (12–14 kD cutoff) into water, with dialysis solution replaced twice. The water dispersion of lignin nanoparticles was a slightly hazy yellow. Part of the solution was filtered through a 0.2  $\mu$ m GFP filter to remove any larger particles, yielding a transparent solution.

Sample 3: Larger solid particles (200-400 nm). 1.504 g of 60.20  $\mu$ mol/g 2-propanol solution of Fe(OiPr)<sub>3</sub> was added dropwise into 5.007 g of 19.9 mg/g (115.8  $\mu$ mol/g of OH) THF solution of lignin at room temperature. The solution remained clear black. 500  $\mu$ l of 1.00 wt. % distilled water in THF was added dropwise into to the solution to hydrolyze any remaining Fe(OiPr) moieties. The hydrolyzed solution was solvent exchanged in a dialysis tube (12–14 kD cutoff) into water, with dialysis solution replaced once. The water dispersion of lignin nanoparticles was hazy bluish grey.

Large solid particles (200-400 nm) of Fe(II):lignin and Fe(II)/Fe(III):lignin. The reactions were conducted in the same manner as larger solid Fe(III):lignin nanospheres, but with Fe(II) solution or Fe(III/II) added to the lignin solution instead of Fe(III) solution.

**Sample 4: Hollow spheres.** 1.54 g of 4.8 mg/g (27.9  $\mu$ mol/g of OH) solution of lignin was placed into a 10 ml beaker. A PTFE filter (3  $\mu$ m pore size) was folded above the lignin solution. 1.27 g of (37.7  $\mu$ mol/g Fe(OiPr)<sub>3</sub> solution was added dropwise onto the folded filter and let diffuse into the lignin solution. The excess Fe(OiPr)<sub>3</sub> remaining after condensation, formed visible rust (Fe<sub>2</sub>O<sub>3</sub>) particles upon exposure to ambient moisture, which were separated by centrifugation. The product in the supernatant was hydrolyzed with the addition of an equimolar volume of 10 wt. % solution of H<sub>2</sub>O in THF.

**Lignin into**  $Fe(OiPr)_3$  (reverse) reaction. 1.362 g of 21.7 mg/g (34.2 µmol/g of OH) solution of partially acetylated lignin in acetone was added dropwise into a stirred solution of 1.034 g of 78.8 µmol/g  $Fe(OiPr)_3$  in 2-propanol in ice bath. The solution turned black and the product precipitated to the bottom. The product was centrifuged and hydrolyzed with the addition of distilled water. The product could be dispersed in water in <10 wt. % dilution.

## 7. <sup>31</sup>P NMR and <sup>1</sup>H NMR spectra of the used lignin

The <sup>31</sup>P NMR spectrum of the used LignoBoost<sup>TM</sup> lignin shown in Figure S6 and its <sup>1</sup>H NMR spectrum is shown in Figure S7. Due to the highly complex structure of lignin, the <sup>1</sup>H NMR spectrum cannot be used for its quantitative analysis. The available OH groups can be quantitatively determined with <sup>31</sup>P NMR of the phosphitylated lignin (Table S1).<sup>4</sup>



Figure S6. <sup>31</sup>P NMR spectrum of the used LignoBoost<sup>TM</sup> lignin.



**Figure S7.** <sup>1</sup>H NMR spectrum of the used LignoBoost<sup>TM</sup> lignin.

#### 8. Comparison of the Fe:lignin structures with IR spectroscopy

Differences between the IR spectra of Fe:lignin polymers from  $Fe(OiPr)_2$  and  $Fe(OiPr)_3$  with different Fe to OH ratios (prepared from a dried condensate without dialysis into water) are presented in Figure S8. With a 1:3 ratio of lignin OH groups and  $Fe(OiPr)_3$ , the 668 cm<sup>-1</sup> band from the Fe-O-Fe oxo complex disappears, corresponding with the full condensation of the OH groups with isopropoxy groups. Thus no Fe-O-Fe oxo complexes form upon hydrolysis when  $Fe(OiPr)_3$  is used in excess. The 668 cm<sup>-1</sup> Fe-O-Fe oxo complex band is not visible in the Fe(II):lignin polymers, which indicates that this band is unique to the Fe(III) oxo complex. When the condensate was dialyzed against water and the formed nanoparticles were freeze dried, the only major difference compared to the condensate was the disappearance of the 947 cm<sup>-1</sup> band (Figure S9), which could be attributed to the evaporation of residual isopropanol.



Figure S8. IR spectra of the dried Fe:lignin condensates and the lignin reference.



Figure S9. Comparison of the IR spectra of dried Fe(III):lignin (1:3 ratio) condensate, freeze dried aqueous dispersion of nanoparticles, and lignin reference.

#### **Supplementary information references**

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