

# Insights of the Naphthalenide-driven Synthesis and Reactivity of Zerovalent Iron Nanoparticles

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## – SUPPORTING INFORMATION –

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## 1. Analytical Techniques

**Optical Spectroscopy (UV/VIS).** Optical spectra were recorded with a Shimadzu UV-2700 spectrometer in a wavelength interval of 220-850 nm. The [LiNaph]/[NaNaph] solutions were measured in air-tight quartz cuvettes with a path-length of 1 cm against a cuvette with the pure solvent (THF, DME) as a reference.

**NMR spectroscopy (NMR).** NMR spectroscopy was performed on a Bruker Avance II, operating at 300 MHz. For this purpose, 0.2 mL of the [LiNaph] solution were mixed with 0.3 mL of deuterated chloroform. The resulting solution was analyzed directly after preparation.

**Transmission electron microscopy (TEM).** Transmission electron microscopy of the as-prepared Fe(0) nanoparticles was conducted with a FEI Osiris microscope operating at an acceleration voltage of 200 kV. TEM samples were prepared by applying few drops of the nanoparticle suspension in THF on a carbon (lacey-)film suspended on copper grids (Plano). This sample holder was heated in vacuum at 120°C for 2 days to remove surface adhered solvent. Thereafter, the samples were transferred with inert conditions (argon) from a glovebox into the TEM device using a suitable transfer module (Gatan).

**Dynamic light scattering (DLS).** The hydrodynamic diameter of the Fe(0) nanoparticles was examined with a Malvern Zetasizer Nano-ZS (He-Ne laser with  $\lambda = 633$  nm, back-scattering geometry at an angle of 173 °). For analysis, the nanoparticles were suspended in a solution of oleylamine (1 mL) in *n*-heptane (14 mL) and measured in air-tight quartz cuvettes.

**Fourier-transformed infrared spectroscopy (FT-IR).** FT-IR spectroscopy was conducted on a Bruker Vertex 70 FT-IR spectrometer, equipped with a Platinum A 225 ATR unit (Bruker). The spectra of polymerized THF and Fe(0) nanoparticles were analyzed using the OPUS software.

**Elemental analysis (EA).** Elemental analysis (C/H/N/S analysis) of the Fe(0) nanoparticles was performed using an Elementar Vario Microcube operating at a temperature of 1150 °C in an atmosphere of pure oxygen.

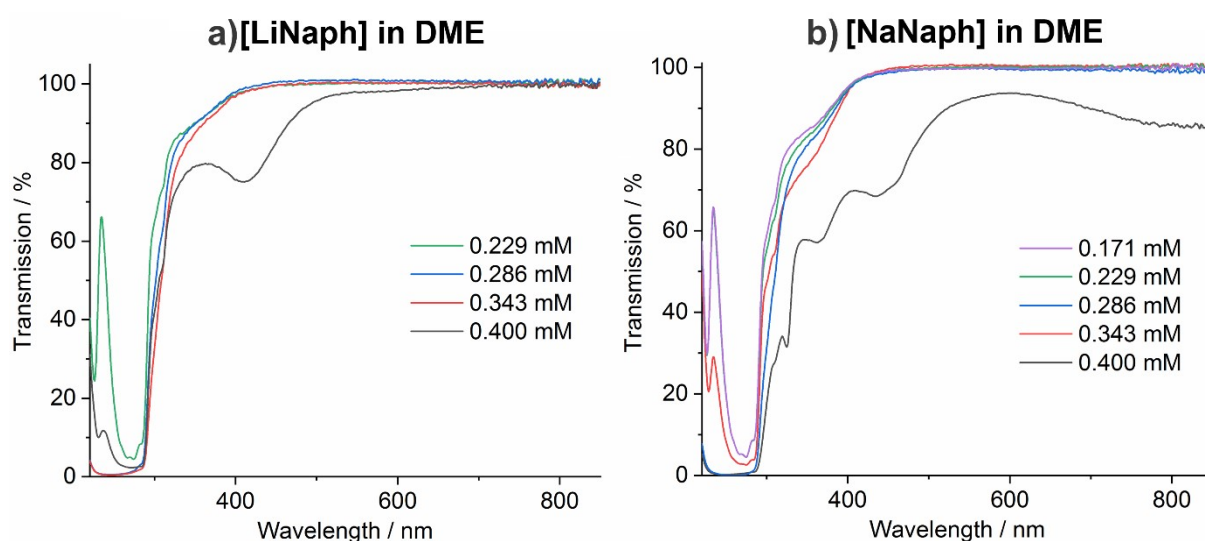
**X-ray powder diffraction (XRD).** XRD was performed using a Stoe Stadi MP, equipped with a Cu-K $\alpha$  radiation source and a Ge-(111)-monochromator. The as-prepared Fe(0)

nanoparticles were mortared with an equal amount of powdered glass (9-13  $\mu\text{m}$ , Sigma-Aldrich) to reduce the X-ray absorption of the Fe(0) nanoparticles. The resulting powder mixture was then transferred into a glass capillary (0.4 mm in diameter, Hilgenberg) for measurement.

**Single-crystal X-ray diffraction and structure analysis.** Single-crystal X-ray diffraction analysis was performed using an IPDS II diffractometer (Stoe) using Mo-K $\alpha$  ( $\lambda = 7.1073 \text{ \AA}$ , graphite monochromator). Suitable single crystals were manually selected under inert oil (perfluoropolyalkylether, ABCR). Data reduction and numerical absorption correction were performed using the STOE X-AREA software package.<sup>S1</sup> Determination of the space group based on systematically absent reflections, structure solution via direct methods, and structure refinement were carried out using the ShelXT, ShelXL, and Olex2 software packages.<sup>S2</sup> The structures were refined via least-squares minimization with anisotropic displacement parameters for all non-hydrogen atoms. The resulting structures were graphically presented with the DIAMOND program.<sup>S3</sup>

## 2. UV-VIS spectra of [MNaph] in DME

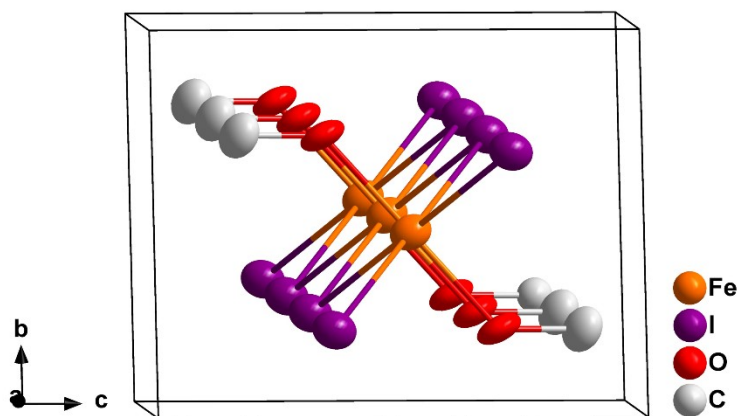
UV-VIS spectra of the low stability of [LiNaph] and [NaNaph] solutions in DME (Figure S1). Thus, the specific absorption of [LiNaph]/[NaNaph] at 400-430 nm is only visible at highest concentration (0.400 mM), since the discoloration is too fast at lower concentration.



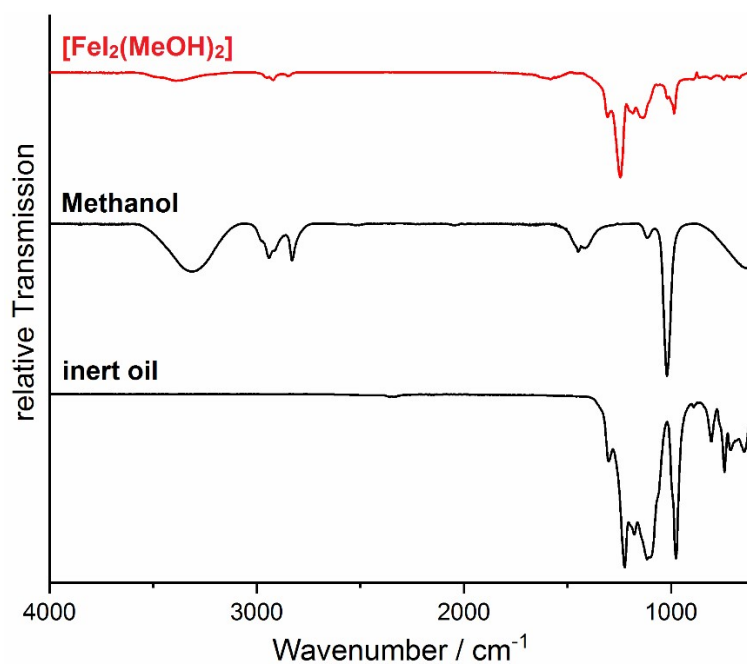
**Figure S1.** UV-VIS spectra of [LiNaph] and [NaNaph] in DME.

### 3. Unit Cells of the Title Compounds 1-4

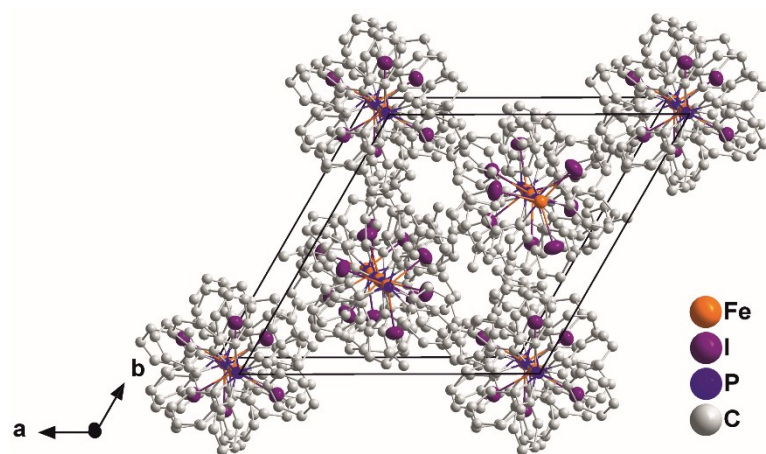
The unit cells of  $[\text{FeI}_2(\text{MeOH})_2]$  (**1**),  $[\text{MePPh}_3][\text{FeI}_3(\text{Ph}_3\text{P})]_4 \cdot \text{PPh}_3 \cdot 6\text{C}_7\text{H}_8$  (**2**),  $[\text{FeI}_2(\text{PPh}_3)_2]$  (**3**), and  $[\text{FeI}_2(18\text{-crown-6})]$  (**4**) are displayed in Figures S2, S4-S6. Moreover, the presence of MeOH as a ligand in **1** was confirmed by FT-IR (Figure S3).



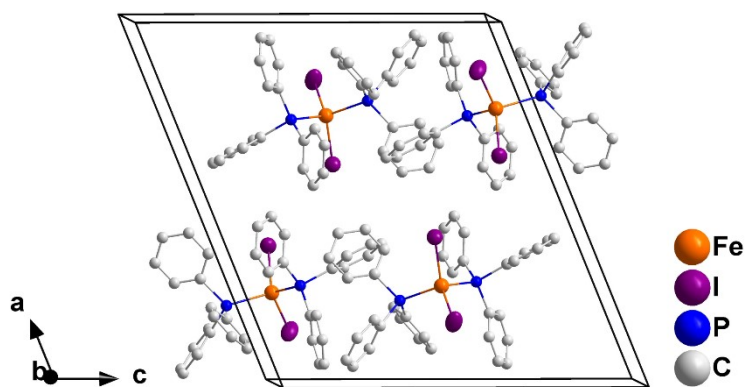
**Figure S2.** Unit cell of  $[\text{FeI}_2(\text{MeOH})_2]$  (**1**).



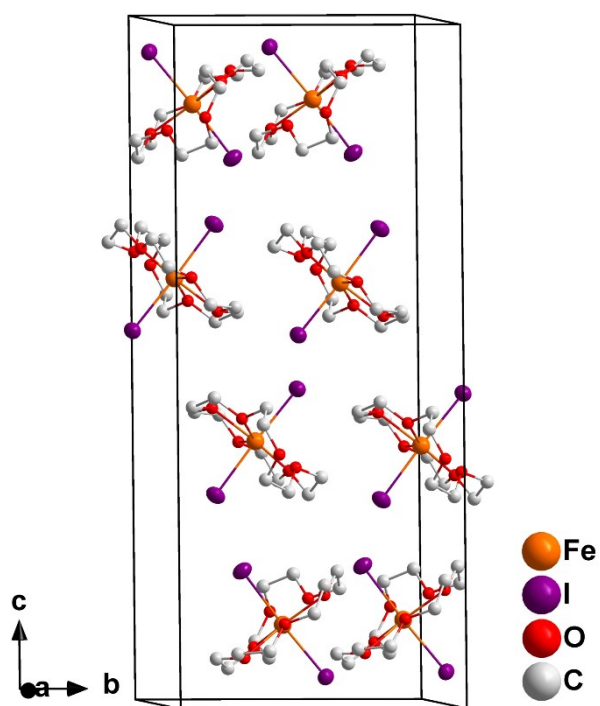
**Figure S3.** FT-IR spectrum of  $[\text{FeI}_2(\text{MeOH})_2]$  (**1**) with methanol and inert oil (in which the crystals were embedded) as references.



**Figure S4.** Unit cell of  $[\text{MePPh}_3][\text{FeI}_3(\text{Ph}_3\text{P})]_4 \cdot \text{PPh}_3 \cdot 6\text{C}_7\text{H}_8$  (2).



**Figure S5.** Unit cell of  $[\text{FeI}_2(\text{PPh}_3)_2]$  (3).



**Figure S6.** Unit cell of  $[\text{FeI}_2(18\text{-crown-6})]$  (4).

#### 4. References

- S1 X-RED32, Data Reduction Program, Version 1.01, Stoe, Darmstadt 2001.
- S2 G. M. Sheldrick, SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr. A*, 2015, **71**, 3–8.
- S3 DIAMOND Version 4.6.3. Crystal and Molecular Structure Visualization. Crystal Impact GbR, Bonn 2020.