Supporting Information for

Ni (III) Complex Stabilized by Silica Nanoparticles as an Efficient Nanoheterogeneous Catalyst for Oxidative C-H Fluoroalkylation

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Experiments

Materials

Tetraethyl orthosilicate (TEOS, 98%) and ammonium hydroxide (28–30%) were purchased from Acros. C₆F₁₃COOH was purchased from P&M Invest and used without further purification. CH₃CN (CHROMASOLV® Plus, \geq 99.9%, by Acros Organics) was used without any preliminary purification. 2-Phenylpyridine (99%), 2.2'-bipyridine (99%, from Acros Organic), and C₆H₆ (CHROMASOLV® Plus, \geq 99.9%, by Sigma Aldrich) were used without any preliminary purification as well.

The Ethanol and TEOS were purified by distillation.

 Et_4NBF_4 was obtained by mixing an aqueous solution of Et_4NOH (30-35%) with HBF₄ for to a neutral indicator reaction. Et_4NBF_4 precipitated from the reaction mixture as white crystals, which were separated by filtering. The powder salt was further recrystallized from diethyl ether and dried for 2 to 3 days in a vacuum at 55°C for dehydration.

Synthesis of [(bpy)₃Ni^{II}](BF4)₂: This complex was prepared by mixing of $(H_2O)_6Ni(BF_4)_2$ (2,00 g, 5,9 mmol) and 2,2'-bpy (2,76 g, 17,7 mmol) in CH₃CN (20 ml). After 3h of stirring, Ni(II) complexes were precipitated from solution by adding diethyl ether, filtered off and air-dried. Yield: 376 g (91%) Calculated, %: C 51,41; H 3,45; N 11,99 for C₃₀H₂₄B₂F₈N₆Ni. Found, %: C 51,38; H 3,52; N 12,01

Synthesis of [(bpy)_x**Ni**^{II}]@**SiO2**: Ni(II)-doped silica nanoparticles were synthesized by modified Stöber procedure.⁴⁸ A solution of TEOS (1.14 mL) in EtOH (11.36 mL) was added to NH₄OH (28-30%) (0.38 mL) in EtOH (8.05 mL)- bidistilled H₂O (4.05 ml) at the speed 2 mL per min (thought syringe pump) under continuous stirring (750 rpm). After 5 minutes of reaction, solution of [(bpy)₃Ni](BF₄)₂ in EtOH (2.5 ml, C=4.5 mM) was injected into this mixture. After 6h of stirring, Ni(II)-doped silica nanoparticles were precipitated, centrifuging, washing several times by ethanol and water. We used ultrasonication while washing the silica nanoparticles to remove physically absorbed Ni(II) complex from the particles surfaces. Finally, the NPs were air-dried.

The leakage of $[(bpy)_xNi^{II}]$ complexes from the silica nanoparticles was monitored using the following procedure: A dispersion of silica nanoparticles ($[(bpy)_xNi^{II}]@SiO_2$) in CH₃CN (C=0.2 g·L⁻¹) was stirred for 1 hour or for 2 days at 750 rpm. Afterwards, $[(bpy)_xNi^{II}]@SiO_2$ were precipitated by centrifugation at 12000 rpm. The supernatants' absorption spectra after phase separation are shown in Fig. 3. Analysis of Ni(II) in supernatant was performed by ICP-AES.

Methods

Ni and Si were identified in the $[(bpy)_xNi]@SiO_2$ colloids using simultaneous inductively coupled plasma atomic emission spectrometry (ICP-AES) model iCAP 6300 DUO by Varian Thermo Scientific Company equipped with a CID detector. This spectrometer enables the simultaneous measurement of peak heights within the 166 to 867 nm range. The optical resolution is less than 0.007 nm to 200 nm. As for the working frequency, it is 27.12 MHz. Together, the radial and axial view configurations enable optimal peak height measurements with suppressed spectral noises.

The UV-Vis spectra were recorded on a Lambda 35 spectrophotometer (Perkin-Elmer).

Electrosynthesis

Preparative electrolysises were performed using a B5-49 direct current source in a thermostatically controlled, cylindrical, sectioned 100 mL electrolyser (a three-electrode cell). Platinum with a surface area of 20 cm² was used for the cathodes and a platinum rod was used as the anode. The working electrode potential was determined using reference electrode Ag/AgCl. During electrolysis, the electrolyte was stirred using a magnetic stirrer, the saturated Et₄NBF₄ solution in DMF was used as an analyte, and the anode compartment was separated by ceramic membrane. The mass spectra were then recorded in EI mode using ThermoQuest TRACE MS.

NMR measurements

A NMR measurements were performed in the NMR department (A.E. Arbuzov Institute Organic and Physical Chemistry) of the Federal Collective Spectral Analysis Center for physical and chemical studies on the structure, properties, and composition of matter and materials. NMR experiments were conducted using Bruker spectrometers AVANCE-400 (400.1 MHz (¹H), 376.5MHz (¹⁹F), 100.6 MHz (¹³C)) and AVANCE-600 (600.1 MHz (¹H), 150.9 MHz (¹³C) equipped with a pulsed gradient unit capable of producing magnetic field pulse gradients in the z-direction of 53.5 G cm⁻¹. All spectra were acquired in a 5 mm gradient inverse broad band probe head. As a result, chemical shifts were reported on the δ (ppm) scale relative to the residual ¹H and ¹³C C₆D₆ signal resulting in external C₆F₆ (-164.9 ppm) for ¹⁹F NMR spectra.

Electrochemistry

Electrochemical measurements were taken on a BASiEpsilonE2P electrochemical analyzer (USA). The program concerned Epsilon-EC-USB-V200 waves. A conventional three-electrode system was used with glassy carbon for carbon paste electrode (CPE) solutions for powder samples as the working electrode, the Ag/AgCl (0.01M) electrode as the reference electrode, and a Pt wire as the counter electrode. 0.1 M Et_4NBF_4 was used as the supporting electrolyte to determine the current–voltage characteristics.

To study the powder samples, a modified CPE working electrode was used, which was prepared as follows: the carbon particles/phosphonium salt (dodecyl(tri-tert-butyl)phosphonium tetrafluoroborate) composite electrode was prepared using a grinding a mixture of graphite powder and phosphonium salt with a 90/10 (w/w) ratio in mortar giving it a homogeneous mass¹⁻². A modified electrode was also devised in a similar manner except that a portion (ca. 5%) of the graphite powder was replaced by the Ni complex (or Ni@SO₂) powder under study. As a result, a

portion of the resulting paste was packed firmly into the (3 mm in diameter) a Teflon holder cavity.

Scanning electron microscopy analysis

In this case, an immobilized catalyst was studied using electron microscopy analysis before and after a perfluoroalkylation reaction. The solutions were applied to the titanium foil surface previously cleared using sonification in acetone. Then, the sample was exsiccated at low heat (no higher than 40 °C). The morphology of the sample surfaces was characterized by an SEM planview using a high-resolution microscope that Merlin Carl Zeiss combined with ASB (Angle Selective Backscattering) and SE InLens (Secondary Electrons Energy selective Backscattering) detectors, which was also equipped for an energy-dispersive x-ray spectroscopy (EDX) analysis with an AZTEC X-MAX energy-dispersion spectrometer by Oxford Instruments.

ESR experiments

Oxygen was removed from liquid samples by three cycles of "freezing in liquid nitrogen evacuation—thawing" and after the last cycle, the electrolysis cell was filled with gaseous helium. Platinum was used as auxiliary electrode, Ag/AgCl equipped with a carbon slate-pencil bridge was applies as reference electrode, and a gold wire 0.5 mm in diameter served as the working electrode. Electrochemical experiments were conducted in CH₃CN using 0.1 M Bu₄NBF₄ as a supporting electrolyte, the potential sweep E(t) being 0.1 V s⁻¹. Measurements were taken on an apparatus program complex featuring an analog electrochemical system with a potentiostat and PWR-3 programmer, an ELEXSYS E500 ESR x-range spectrometer, an E14-440 analog-to-digital and digital-to-analog modulus (L-Card), a fourth-generation computer, and a unique three-electrode helical cell ³⁻⁴. Finally, ESR spectra were simulated using the WinSim 0.96 program (developed by NIEHS).



Figure 1S. The ESR spectrum of powder of $[(bpy)_x Ni^{III}]$ @SiO₂ nanoparticles agglomerates at the different ampoule orientation in the ESR spectrometer resonator in two mutually perpendicular directions (the spectrum at 0 ° is repeated at 180° orientation, 270° repeats 90°, etc.)

Synthesis

Condition 1: Stepwise synthesis: A) Electrochemical oxidation of $[(bpy)_xNi^{II}]@SiO_2$ B) the subsequent chemical reaction when combined with a $[(bpy)_xNi^{III}]@SiO_2$ oxidant.

Step 1 – Electrochemical generation of $[(bpy)_x Ni^{III}]$ @SiO₂ in ionic gel on a platinum plate (a working electrode) with an applied thin paste layer of a mixture of dodecyl(tri-tertbutyl)phosphonium tetrafluoroborate and silica nanoparticles $[(bpy)_x Ni^{II}]$ @SiO₂. The working electrode was placed in a solution of acetonitrile and background salt. Following that, electrolysis was performed in an electrochemical cell, separating the anode and cathode compartments at ambient temperature in an argon atmosphere with a working electrode potential of 1.91 V vs. Ag/AgCl. The amount of electricity that passed through the electrolyte was 1F per mole of Ni. The paste was dissolved in acetonitrile with the use of an ultrasonic bath. Then silica nanoparticles were separated from the solution by centrifugation. The separated nanoparticles were dried in a high vacuum. Important note: for their continued use as an oxidant, silica nanoparticles Ni(III) must be taken by a non-metallic spatula, as the steel or titanium spatula instantly restores the Ni(III) in Ni(II). The oxidized nanoparticles [(bpy)_xNi^{III}] @SiO₂ can be stored for month at least without any special protection.

Step 2 - A solution was prepared for synthesis by mixing 0.2 g ($1.8 \cdot 10^{-2}$ mmol) of Ni-doped silica nanoparticles, $9.2 \cdot 10^{-3}$ mmol of arene (caffeine or 2-phenylpyridine), and 0.0034 g ($9.2 \cdot 10^{-3}$ mmol) of C₆F₁₃COOH in CH₃CN (50 ml). Synthesis was performed in a round-bottomed flask at ambient temperature. Before starting the reaction, the reaction mixture was purged with argon, then tightly stoppered. The synthesis was performed over 24 hours. After completing the reaction, the oxidant was separated by centrifugation and the products were purified using silica gel column chromatography (ethyl acetate-hexane).

Condition 2: Electrosynthesis ([(bpy)_xNi^{III}]@SiO₂ (1%) generation and regeneration in situ in the presence of coupling partners)

A solution was prepared for synthesis by mixing 0.0327 g ($0.3 \cdot 10^{-5}$ mol) of Ni-doped silica nanoparticles, 0.3 mmol of arene (caffeine or 2-phenylpyridine), and 0.1092 g (0.3 mmol) of C₆F₁₃COOH in CH₃CN (50 ml). Electrolysis was performed in an electrochemical cell, separating the anode and cathode compartments at ambient temperature in an argon atmosphere with a working electrode potential of 1.41 V vs. Ag/AgCl. The amount of electricity that ended up passing through the electrolyte was 2F per mole of C₆F₁₃COOH. After completing the electrolysis, the immobilized catalyst was separated by centrifugation and the solution was washed with distilled water (100 ml) and extracted with benzene (30 ml three times). The organic layer was finally dried with magnesium sulfate and filtered. The residual solution was concentrated under reduced pressure and the products were purified by silica gel column chromatography (ethyl acetate-hexane).

8-(Perfluorohexyl) caffeine (1)

m.p. = 105–107 °C; ¹H NMR (600 MHz, MeOH-d₄): δ = 4.60 (s, 3 H), 3.99 (s, 3H), 3.52 (s, 3 H); ¹³C NMR (100.6 MHz, C₆D₆): δ = 156.8, 152.9, 148.3, 111.8, 34.4, 30.1, 28.4; ¹⁹F NMR (376 MHz, CDCl₃): δ = -82.4, -109.8, -121.9, -122.6, -123.8, -127.1; EIMS, m/z: 512.14 [M]⁺. Anal. calc. (%): C, 32.83; H, 1.77; F, 48.22; N, 10.94; O, 6.25. Found (%): C, 32.74; H, 1.74; N, 10.93.The spectroscopic data for 1 matched those previously reported ⁵.

2-(2'-Perfluorohexylphenyl) pyridine (2)

¹H NMR (400.0 MHz, (CD₃)₂CO): δ 8.94 (d, J = 4.4 Hz, 1H,); 8.33 (dt, J = 8.1, 1.7 Hz, 1H); 8.21 (br d, J = 8.2 Hz, 1H); 8.13 (m, 2H); 7.75 (ddd, J = 7.5, 5.3, 1.2 Hz, 1H); 7.58 (m, 2H). ¹³C NMR (100.6 MHz, (CD₃)₂CO): δ 160.43 (t, 2 J_{CF} = 25.3 Hz); 154.27; 145.24; 142.79; 134.29;

130.83; 129.12; 128.20; 127.76; 124.22; 123.65; 118.66 (tt, ${}^{1}J_{CF} = 287.3$ Hz, ${}^{2}J_{CF} = 33.4$ Hz); 115–105 (m, 4C); 109.93 (qt, ${}^{1}J_{CF} = 237.6$ Hz, ${}^{2}J_{CF} = 33.7$ Hz). ${}^{19}F$ NMR (376.5 MHz, (CD₃). ${}_{2}CO$): $\delta = -81.57$; -117.71; -122.07; -123.89; -123.21; -126.58. The spectroscopic data for **2** matched those previously reported⁶.

References

- Khrizanforov, M. N.; Arkhipova, D. M.; Shekurov, R. P.; Gerasimova, T. P.; Ermolaev, V. V.; Islamov, D. R.; Miluykov, V. A.; Kataeva, O. N.; Khrizanforova, V. V.; Sinyashin, O. G.; Budnikova, Y. H. *J. Solid State Electrochem.*, **2015**, *19*, 2883–2890.
- 2 Kataeva, O., Khrizanforov, M., Budnikova, Y., Islamov, D., Burganov, T., Vandyukov, A., Lyssenko K., Mahns B., Nohr M., Hampel S. & Knupfer, M. *Crystal Growth & Design*, 2016, 16(1), 331-338.
- 3 Kadirov, M.; Tretyakov, E.; Budnikova, Y.; Valitov, M.; Holin, K.; Gryaznova, T.; Ovcharenko, V.; Sinyashin, O.; *J. Electroanal. Chem.*, **2008**, *624*, 69.
- 4 Kadirov, M. K.; Tretyakov, E. V.; Budnikova, Y. G.; Holin, K. V.; Valitov, M. I.; Vavilova, V. N.; Ovcharenko, V. I.; Sagdeev R. Z.; Sinyashin, O. G. Russ. J. Phys. Chem. A, 2009, 83, 2163.
- 5 Khrizanforov, M.; Strekalova, S.; Khrizanforova, V.; Grinenko, V.; Kholin, K.; Kadirov, M.; Burganov, T.; Gubaidullin, A.; Gryaznova, T.; Sinyashin, O.; Xu, L.; Vicic, D. A.; Budnikova, Y. *Dalton Trans.* 2015, 44(45), 19674-19681.
- 6 Dudkina, Yu.B., Mikhaylov, D.Y., Gryaznova, T.V., Sinyashin, O.G., Vicic, D.A., Budnikova, Yu.H. *Eur. J. Org. Chem.*, **2012**, 2114–2117.