Electronic Supplementary Information

N-Heterocyclic carbene containing element organic frameworks as heterogeneous organocatalysts

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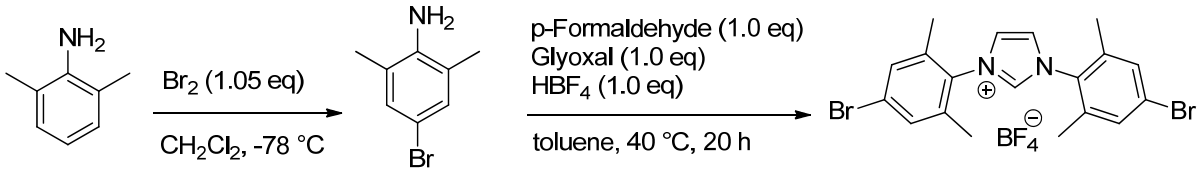
Synthesis of 1,3-bis(4-bromo-2,6-dimethylphenyl)-1H-imidazol-3-ium tetrafluoroborat (3)

In a modified procedure by Plenio et al.[1] *p*-Formaldehyde (379 mg, 12.5 mmol, 1 eq) is suspended in toluene (13 mL) and 4-bromo-2,6-dimethylaniline (**2**) (2.5 g, 12.5 mmol, 1 eq) is added in solid form. The mixture is stirred at room temperature for 1.5 h. After cooling to 0 °C, the second half of 2,6-dimethylaniline (**2**) (2.5 g, 12.5 mmol, 1 eq) is added followed by drop wise addition of HCl (c = 3 mol/L, 4.2 mL, 12.5 mmoL, 1 eq). The reaction mixture is allowed to warm up to room temperature and glyoxal (c = 40 w% in water, 1.4 mL, 12.5 mmol, 1 eq) is added. After stirring at 40 °C for 18 h, Et_2O is added and the product is extracted into water (50 mL). The water layer is washed with CH_2Cl_2 and evaporated by reduced pressure. Recrystallization from water gives the product (**3**) (1.81 g, 3.84 mmol, 31%) as colourless powder.

[1] S. Leuthaeusser, D. Schwarz, H. Plenio, *Chem. Eur. J.* 2007, **13**, 7195-7203.



1 **2** **3**

Scheme S1 Synthesis of the bifunctional imidazolium linker **3**.

Synthesis of EOF-15 and -16

To a degassed mixture of 45 ml THF and 5 ml of an aqueous potassium carbonate solution (2M), 0.21 mmol of the respective boronic acid, 220 mg (0.42 mmol) of the imidazolium precursor and 9.7 mg (0.0084 mmol) $Pd(PPh_3)_4$ are added and dissolved by stirring under a static Ar atmosphere. The mixture is heated to 80 °C for 24 h. The resulting precipitate is separated by filtration and washed three times with THF, water and ethanol, respectively. The product is dried in air at 80 °C.

Catalytic testing

Similar to our preview reported procedure[2] EOF-16 (16 mg) is suspended in dry THF (1 mL) in a dried test tube. DBU (5 µL, 0.2 eq) is added and the mixture is heated at 70 °C for 15 min. The mixture is allowed to cool down to room temperature and α,β-unsaturated cinnamaldehyde (38 µL, 0.3 mmol, 1 eq), trifluoroacetophenone (82 µL, 0.6 mmol, 2 eq) and mesitylene (20 µL) as internal standard are added. The reaction mixture is stirred at 70 °C for 15 h and again cooled to room temperature. The catalyst is separated by filtration and centrifugation, washed with THF and the organic solvent removed by rotary evaporation. The

crude product is purified by flash chromatography (pentane/EtOAc 20:1) to give 89 mg (0.29 mmol) of the product.

[2] K. Hirano, I. Piel, F. Glorius, *Adv. Synth. Catal.* 2008, **350**, 984.

Heterogeneity test

EOF-16 (10 mg) is suspended in dry THF (1 mL) in a dried test tube. DBU (5 µL, 0.2 eq) is added and the mixture was heated at 70 °C für 15 min. The mixture is allowed to cool down to room temperature and α,β-unsaturated cinnamaldehyde (38 µL, 0.3 mmol, 1 eq), trifluoroacetophenone (82 µL, 0.6 mmol, 2 eq) and mesitylene (20 µL) as internal standard are added. The reaction mixture is stirred at 70 °C for 30 min and again cooled to room temperature. The catalyst is separated by filtration (syringe filter 0.2µm PTFE) and centrifugation (4500 rpm, 30 min). The clear solution is carefully decanted into a dried test tube and the reaction mixture is stirred at 70 °C for 14 h. According to GC, no more significant product formation could be observed.

Characterization

Nitrogen physisorption isotherms were measured using the Quadrasorb SI (Quantachrome) at a temperature of -196 °C. The samples were degassed prior before measurement under vacuum at 80 °C.

Solid state NMR measurements were carried out on a Bruker Avance 300 spectrometer with resonance frequencies of 300.13 MHz (1H) und 75.47 MHz (13C). A 4 mm double resonance MAS NMR probe with a rotation frequency of 14 kHz was used. For the 13C spectra 9000 (polymer) and 5000 (linker) scans with a repeating time of 2 s have been accumulated, while for the 1H spectra only one scan has been recorded. The 13C CP MAS spectra are SPINAL 1H decoupled and the CP contact time was 4 ms. As an external standard adamantane has been used.

Liquid state ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 300 or AV 400 in solvents as indicated. Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm).

DRIFT (diffuse reflectance infrared fourier transformed) spectra have been recorded at the FTIR spectrometer Magna-IR 550 Series II (Nicolet).

SEM micrographs have been recorded on the DSM-982 Gemini (Zeiss) after sputtering the samples with Au due to bad conductivity.

Elemental analysis was carried out using the EA 3000 Euro Vector Elementaranalysator (Hekatech).

Differential thermoanalysis (DTA) and thermogravimetry (TG) were measured on the STA 409 (Netzsch). The samples were heated in air with 5°C/min up to a temperature of 800°C.

Additional Figures and Tables

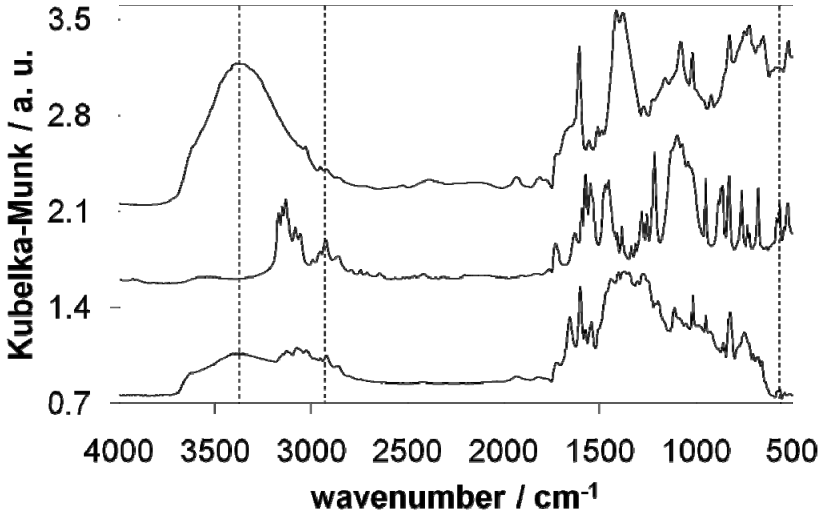


Figure S1 DRIFT spectra of tetraphenylmethane boronic acid (top, offset: 1.6), imidazolium linker (middle, offset:0.8) and EOF-16 (bottom).

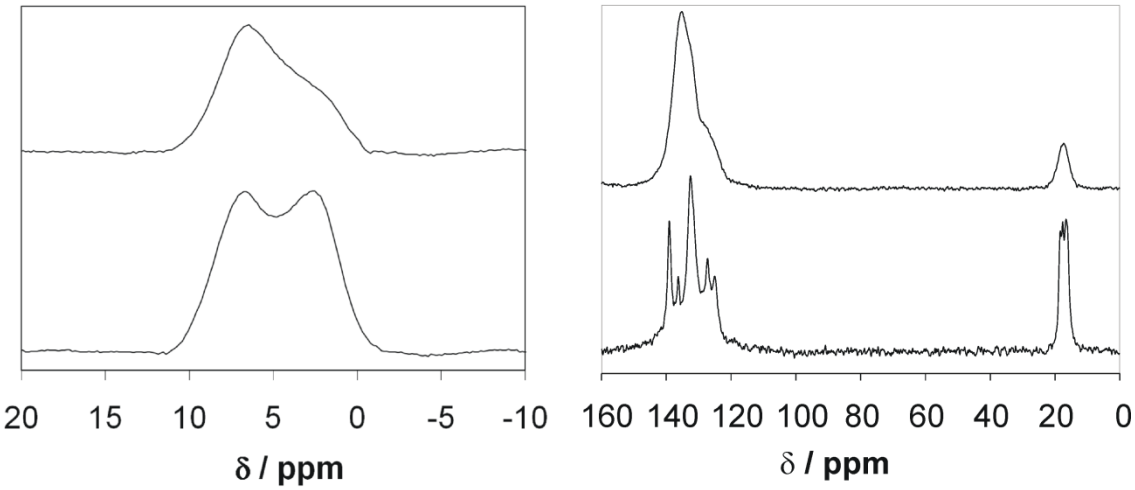


Figure S2 ^{1}H MAS (left) and ^{13}C CP MAS (right) NMR spectra of EOF-15 (top) and imidazolium linker (bottom).

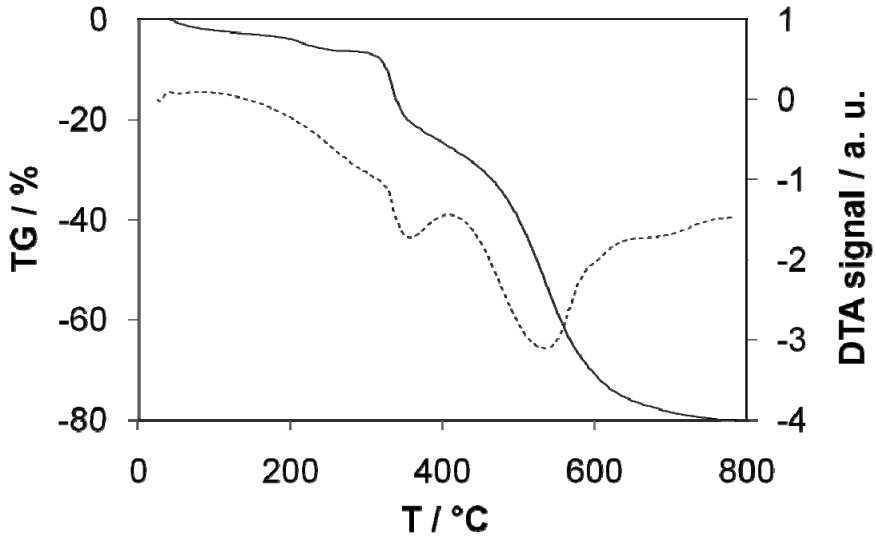


Figure S3 DTA/TG analysis (dotted and full line) of EOF-16 in air.