Electronic supplementary information

Amino acid -based ionic liquids as precursors for the synthesis of chiral nanoporous carbons

Sapir Shekef Aloni, Milena Perovic, Michal Weitman, Reut Cohen, Martin Oschatz and Yitzhak Mastai*

Department of Chemistry and the Institute of Nanotechnology, Bar-Ilan University, Ramat-Gan 5290002, Israel.

Max Planck Institute of Colloids and Interfaces, Potsdam-Golm Science Park, Am Mühlenberg 1 OT Golm Potsdam 14476, Germany.

E-mail: Yitzhak.Mastai@biu.ac.il

Experimental Section

Materials Synthesis

Preparation of Trimethyl Tyr-OMeBF₄

N,N,N trimethyl Phe-OMeBF₄ and N,N,N trimethyl Tyr-OMeBF₄ was synthesized by following steps. Phenylalanine methyl ester hydrochloride/ Tyrosine methyl ester hydrochloride (5.0 g) was placed in 250 mL round bottomed flask and 120 mL acetone was added. Iodomethane (18.81 g, 6 eq.) was added followed by addition of potassium hydrogen carbonate (11.63 g, 5 eq.) and the mixture (suspension) was stirred well. After 48 h the solvent was evaporated. Chloroform (20 mL) was added to the residue and the mixture was stirred well. The solvent (contains impurities) was removed by filtration (by suction). Purification: 40 mL water was added to the crude solid (~15 g; apparently contains the product and KHCO3 + KI + KCl) and the mixture was stirred at 50 °C for 0.5 h. The mixture (suspension) was allowed to

cool to RT. The white solid was filtered (suction), washed with very cold water (up to maximum 5 mL) and dried to give 7.16 g of N,N,N-timethyl-L- phenylalanine methyl ester iodide/ N,N,N-timethyl-L- tyrosine methyl ester iodide (purity confirmed by 1H NMR).



Figure S1. Pathway for the synthesis of N,N,N trimethyl Tyr-OMeBF₄ ionic liquid.

¹H NMR (D₂O, 400 MHz): C₁₃H₂₀INO₂, 365 (238+127); 7.14 (d, 2H), 6.87 (d, 2H), 4.43 (dd, J = 12, 5 Hz, 1H), 3.61 (s, 3H), 3.32 (s, 9H), 3.47 (dd, J = 12, 5 Hz, 1H), 3.21 (t, J = 12 Hz, 1H).
¹³C NMR (D₂O, 600 MHz): 168.61 (C), 155.97 (C), 131.57 (2xCH), 125.10 (CH), 116.61 (2xCH), 76.42 (CH), 54.28 (CH3), 53.29 (3xCH3), 32.23 (CH2).MS m/z (ES+) 238 (M+, 100).
MS m/z (ES+): MS m/z (ES+) 238 (M+, 100).



Figure S2. ¹H NMR and ¹³C NMR of N,N,N trimethyl Tyr-OMeBF₄.

Preparation of Me2-L-proline methyl ester iodide

N,N dimethyl Pro-OMeBF₄ was syntheized by following steps. Potassium carbonate (6.9 g, 2 eq.) was placed in 250 mL round bottomed flask and acetonitrile (MeCN, 100 mL) was added.

The mixture was stirred vigorously for 10 min. L-proline (2.87 g) was added and the mixture was stirred for additional 10 min. Iodomethane (21.3 g, 6 eq.) was added and the mixture (suspension) was stirred well. After 72 h the mixture was filtered (to remove salts) and evaporated. The crude solid was stirred for 30 min with chloroform (25 mL) and the remained non-dissolved solid was removed. Evaporation gave 5.7 gr of product N,N-Dimethyl-L-proline methyl ester iodide (purity confirmed by ¹H NMR).

¹**H NMR (CDCl₃,600 MHz):** C₈H₁₆INO₂ 285 (158+127); 5.41 (t, J = 10 Hz, 1H), 4.49 (q, J = 10 Hz, 1H), 4.12 (ddd, J = 10, 8, 2 Hz, 1H), 3.86 (s, 3H), 3.76 (s, 3H), 3.27 (s, 3H), 2.80 (tdd, J = 14, 10, 5 Hz, 1H), 2.46 (qdd, J = 14, 10, 2 Hz, 1H), 2.31 (dtd, J = 14, 10, 5 Hz, 1H), 2.21 (qdd, J = 14, 8, 5 Hz, 1H ¹³**C NMR (CDCl3,600 MHz)**: 166.21 (C), 73.40 (CH), 67.99 (CH2), 53.62 (CH3), 52.19 (CH3), 47.52 (CH3), 24.73 (CH2), 19.11 (CH2). **MS m/z (ES+)**: MS m/z (ES+) 285 (M+, 100).



dimethyl-L-ProOMe iodide (D₂O)



¹³C NMR N,Ndimethyl-L-ProOMe iodide (D₂O)

Figure S3. ¹H NMR and ¹³C NMR of N,N dimethyl Pro-OMeBF₄.

Materials Characterization

Powder X-ray diffraction

Powder X-ray diffraction (PXRD) pattern was recorded on a Bruker D8 Advance diffractometer equipped with a scintillation counter detector with Cu K α radiation (λ = 0.15184 nm) applying 20 step size of 0.0200 and counting time of 1s per step.

Raman spectroscopy

Raman spectra was recorded using a Witec (focus innovations)Raman Microscope operating with an objective (Nikon, 10x/0.25, ∞ /-WD 6.1) and an excitation wavelength of 532 nm with an intensity of 3.5 mW.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) measurement was performed using a thermo microbalance TG 209 F1 Libra (Netzsch, Selb, Germany). A platinum crucible was used for the measurement of 10 mg of a sample in synthetic air flow of 10 ml min⁻¹. The sample was heated to 1000 °C with a heating rate of 10 K min⁻¹. The data was recorded and analyzed by the Proteus (6.0.0) software package.

Supplementary Figures



Figure S4. Thermal analysis of L-CIL(Tyr)-C under synthetic air.



Figure S5. Powder X-ray diffraction pattern of L-CIL(Tyr)-C.



Figure S6. Raman spectrum (a), and fitted Raman spectrum (b) of L-CIL(Tyr)-C.



Figure S7. Cumulative QSDFT (argon on carbon with cylindrical/spherical pores at 77 K, adsorption branch kernel) pore size distribution.



Figure S8. CD measurements for L-Phe probe without (black line) and with 20 (red), 30 (blue) and 40 (green) mg of L-CIL(Tyr)-C (a), and D-CIL(Tyr)-C (b).

Supplementary Tables

Table S1.

Porosity data summary of L-CIL(Tyr)-C.

SSA _{BET} ^[a]	VMicro + Meso ^[b]	V _{Micro} ^[c]	Average Pore	Total pore
(m²/g)	(cm ³ /g)	(cm ³ /g)	Size (nm)	volume (cm ³ /g)
624.99	0.26	0.22	1.69	0.26

[a] Specific surface area calculated using the BET equation $(p/p_0 = 0.006 - 0.078)$.

[b] Micro- and mesopore volume calculated at $p/p_0 = 0.95$.

[c] Micropore volume calculated from the cumulative pore volume up to a diameter of 2 nm

(QSDFT method for Ar adsorbed on carbon with cylindrical/sphere pore shape at 87 K,

adsorption branch kernel).