Carbon Materials

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Enantioselective Nanoporous Carbon Based on Chiral Ionic Liquids

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Abstract: *One of the greatest challenges in modern chemical processing is to achieve enantiospecific control in chemical reactions using chiral media such as chiral mesoporous materials. Herein, we describe a novel and effective synthetic pathway for the preparation of enantioselective nanoporous carbon, based on chiral ionic liquids (CILs). CILs of phenylalanine (CIL(Phe)) are used as precursors for the carbonization of chiral mesoporous carbon. We employ circular dichroism spectroscopy, isothermal titration calorimetry (ITC), and chronoamperometry in order to demonstrate the chiral nature of the mesoporous carbon. The approach presented in this paper is highly significant for the development of a new type of chiral porous materials for enantioselective chemistry. In addition, it contributes significantly to our understanding of the structure and nature of chiral nanoporous materials and surfaces.*

Chirality is one of the key factors in molecular recognition, and chiral recognition is omnipresent in chemical and biological systems. Chiral molecules are extremely important in chemistry, biology, and medicine.[1] Thus, discovering efficient methods to produce, control, separate, and identify enantiomerically pure chiral compounds is critical for the further development of pharmaceuticals, agrochemicals, fragrances, and food additives.[2] In recent years, the role of nanoscale recognition, particular in relation to chiral surfaces,[3] chiral nanoparticles[4] and chiral mesoporous materials,[5] has been proven to play an important role in these fields, due to the significant advantages that can be exploited at these dimensions, such as total uptake and high surface area. It is clear that mesoporous materials with different chiral functionalities have many advantages for applications such as in catalysis, biorecognition, and chiral separation processes. One way to prepare chiral mesoporous materials is to employ molecular imprinting methods, such as chiral mesoporous silica[6,7] and chiral imprinting polymers.

Herein we describe for the first time the synthesis of chiral nanoporous carbonaceous materials. Our approach is based on combining knowledge from two different fields, namely chiral ionic liquids (CILs) and the carbonization of ionic liquids (ILs). In recent years, the field of CILs[8] has experienced large growth, and new synthetic methods have been established with many new applications, such as asymmetric organic synthesis, chromatography, and chiral separation. Moreover, the use of ILs as precursors for high-surface-area porous carbons has been explored,[9] offering a new, effective, and attractive way for the preparation of mesoporous carbon in high yields.

In this study, we chose to use chiral ionic liquids based on natural amino acids as precursors for the synthesis of chiral mesoporous carbon. In general, the synthesis of the CIL precursors is based on the methylation of natural amino acids using iodomethane, as reported in the literature.[10] The overall synthesis is shown schematically in Figure S1 in the Supporting Information. Using this synthesis, we prepared a series of chiral ionic liquids based on the following amino acids: phenylalanine (Phe), leucine (Leu), and tryptophan (Trp). However, in this article we will describe and discuss mainly our results on chiral ionic liquids based on L- and D-phenylalanine as an example of the general process; data on the other chiral ionic liquids, leucine and tryptophan, are given in the Supporting Information.

The CILs were used as precursors for the preparation of chiral carbons (CIL-C). The carbonization was performed in a eutectic salt melt to introduce adequate porosity to the final carbons. Additionally, the salt also acts as a means of confinement which leads to good carbonization yields, even of ionic liquids, which would otherwise not form any carbon residue.[11] The morphology of the carbonized material was investigated by high-resolution electron microscopy as shown in Figures S2 and S3, which reveal the formation of carbon spherical particles of ca. 3 μm in size that consist of nanospheres of about 10–50 nm each. The porosity of the carbonized materials was quantified using nitrogen (Brunauer–Emmett–Teller, BET) gas sorption; a type IV isotherm was recorded with a surface area of 323.6 $m^2 g^{-1}$ and an average pore size of 17.1 Å (see Figure S4) Elemental analysis of the CIL-C indicated that the material still holds some of its natural elements with a C/N atomic ratio of 13.7 (see Table S1).

In the next stage of our study, the chiral recognition ability of our mesoporous carbon was explored. The detection of chirality at the nanoscale in materials is challenging, and recently many new methods have been developed in order to recognize and understand the structure and properties of chiral nanoparticles.[12] In this paper, we report circular dichroism (CD)[13] spectroscopy, isothermal titration calorimetry (ITC), and an electrochemical method based on chronoamperometry in order to demonstrate the chirality of our samples.

First, CD spectroscopy was employed to quantify the selective chiral adsorption of D- and L-phenylalanine enantiomers onto the mesoporous carbon. Chiral adsorption

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measurements were carried out as follows: aqueous solutions of L- or D-phenylalanine (5 mM) were prepared, and their optical activities measured. Then 1 mg mL^{-1} of the mesoporous carbon prepared using CILs of D- or L-phenylalanine (named L-CIL(Phe)-C and D-CIL(Phe)-C, respectively) were added and mixed overnight to reach equilibrium. Finally, the reaction mixture was separated by centrifuge separation the solid carbon was extracted. The optical activities of the enantiomers were measured again and from the change in the CD signal the amount of phenylalanine enantiomers adsorbed onto the mesoporous carbon was calculated.

The results of these CD adsorption measurements are shown in Figure 1. As can be seen from Figure 1a, the mesoporous carbon of L-CIL(Phe)-C has adsorbed 75.4% of

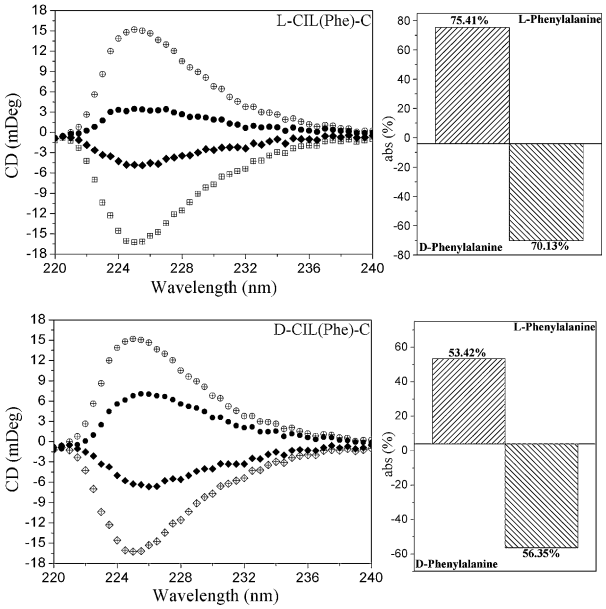

Figure 1. CD spectra and adsorption ratio for both types of chiral carbon. Absorbance of L- and D-phenylalanine solution (circles and squares, respectively) by L-CIL(Phe)-C (top) and D-CIL(Phe)-C (bottom). White symbols correspond to signals from the original solution at 5 mM, filled symbols correspond to signals of the spectra after adsorption. Right: bar chart of the adsorption ratio for both CIL-Cs.

the L-phenylalanine enantiomer from the solution, while the amount of the D-phenylalanine enantiomer adsorbed is only 70.1%. This gives an enantiomeric excess of 7.53% *ee* for the L enantiomer. For D-CIL(Phe)-C, the opposite picture is obtained and the D-phenylalanine enantiomer shows 5.2% *ee* for the D-phenylalanine (Figure 1b).

Similar CD chiral adsorption measurements results were obtained for the other carbons prepared from chiral ionic liquids based on leucine and tryptophan (see Figure S5). For example, L-CIL(Trp)-C gave 22.5% *ee* of the L-phenylalanine enantiomer and, D-CIL(Trp)-C has 20.6% *ee* for the D-phenylalanine enantiomer.

In order to support these findings and to further demonstrate the enantioselective nature of the CILs, isothermal titration calorimetry (ITC) was performed to measure the adsorption enthalpy of enantiomers onto the mesoporous carbon. It should be noted that in previous work, we showed that ITC experiments can be used to measure the heat of adsorption due to chiral interactions, for example, to measure the enantioselectivity of zeolites,[14] chiral interactions at crystal surfaces,[15] and chiral interactions in solutions.[16] In a typical ITC experiment, a soluton of an amino acid enantiomer is titrated into the sample cell with the carbon powders. The heat (ΔH) released due to molecular interactions is monitored as a function of time. Each peak represents the heat change associated with the injection of the chiral sample solution into the mesoporous carbon in the ITC reaction cell. The total heat of interaction is determined by the area under the peaks. The main contribution to the total enthalpy ΔH change in the ITC is due to the enthalpy of chiral binding between the enantiomers and the chiral carbon, $\Delta H_{\text{binding}}$ (D/L). However, other heat changes can result from the heat of dilution $\Delta q_{\text{dilution}}$ of the chiral solutions and some nonspecific heat effects $\Delta q_{\text{n.s}}$ and these are calculated and corrected using a number of control experiments. In our ITC experiments, we used enantiomers of L- and D-histidine as the chiral sample due to their low heat of dilution in water which allows the accurate measurement of the adsorption enthalpy. ITC experiments were carried out in the following manner: a sample of 1 mg mL^{-1} L- or D-CIL-C was placed in the ITC cell and 5 μL of an D- or L-histidine solution (10 mM) was injected into the suspension of the mesoporous carbon. The distinct difference between D- and L mesoporous carbon is shown in Figure 2. For the L-CIL(Phe)-C, the average adsorption enthalpy ΔH_{abs} for L- and D-histidine (Figure 2a) is immediately evident and strikingly large. Both enantiomers display negative ITC peaks, indicating exothermicity of the process. The adsorption enthalpy injection for of L-histidine to L-CIL(Phe)-C is -0.55 μcal s^{-1} on average, while for the D-histidine it is only -0.27 μcal mol^{-1} per injection. We can conclude that L-CIL(Phe)-C is capable of enantioselective interactions with histidine enantiomers, and by averaging the integrations of the peaks we can calculate that the ΔH_{abs} for injection is 142 cal mol^{-1} in favor of the L-enantiomer. For the D-CIL(Phe)-C the adsorption enthalpy for L-histidine is -0.52 μcal s^{-1} while for the D enantiomer absorption, it is -0.6 μcal s^{-1}. By integration, the average enthalpy per injection was found to be 28 cal mol^{-1} in favor of the D-enantiomer.

This enantioselective behavior is attributed to the chiral binding of the histidine to the mesoporous carbon surfaces, and agrees well with the enantioselectivity found using the CD measurements.

Furthermore, ITC experiments and especially measurements of single-injection mode (SIM) can be used to obtain kinetic data on chemical reactions. In a typical SIM measurement, a large amount of substrate solution is injected into the ITC sample cell. The calorimeter baseline shifts prominently to reflect heat effects due to the interactions of substrate and sample in the ITC cell. Eventually, after all the substrate has reacted, the baseline returns to its original position. Monitoring the time of relaxation to the baseline in SIM measurements is correlated with the reaction diffusion and kinetics. In our case, we performed SIM measurements of a large amount

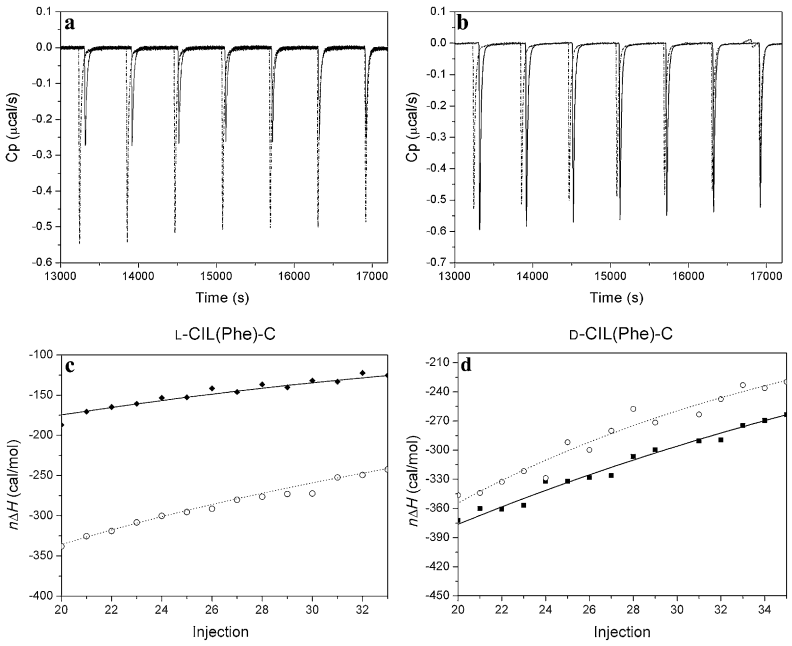

Figure 2. ITC heat of adsorption histogram and integrated enthalpy vs. injection for enantiomeric carbons. a,b) Injection histogram for D- and L-histidine solutions into L-CIL(Phe)-C (a) and D-CIL(Phe)-C (b); solid lines: D-His solution, dashed line: L-His solution. The curves for both samples were normalized and shifted in order to align them and make them clearer. c,d) Integration of the peaks in (a) and (b) vs. injection number to give the heat of adsorption for probe molecule on CIL(Phe)-C materials; solid lines with black squares: D-His, dashed lines with white circles: L-His.

(100 μL) of chiral sample solution with the CIL-C system (see Figure S7). The result of the SIM injection, which reflects the diffusion and kinetic on interactions of D- and L-His (10 mM) with D-CIL(Phe)-C, showed a different relaxation time for each enantiomer. The diffusion and time of relaxation of the ITC to the baseline for the D-His is approximately 30% faster than for the L-His. This difference gives strong evidence for the chiral nature and chiral recognition of the D-CIL(Phe)-C with the D-His, which was also shown in the adsorption experiment. The fast diffusion indicates that the system is more stereoselectively compatible with the surface of the CIL-C which leads to the faster equilibrium. Chiral ITC adsorption measurements with similar enantioselective behavior for additional carbons based on chiral ionic liquids are shown in Figure S.8.

Finally, electrochemical techniques[17] such as cyclic voltammetry[18] can be used to investigation the chirality of surfaces. We chose chronoamperometry to further prove the chiral nature of our nanoporous carbon. In our work, the chiral recognition of the carbonaceous material was kinetically probed using chronoamperometry measurements of L- and D-tartaric acid. Chronoamperometry is a very powerful method for the analysis of mesoporous films[19] and in our case it was found to be useful for a chiral study. Overall in chronoamperometry the potential of the working electrode is stepped and the resulting current, mainly due to faradaic processes at the electrode, is monitored as a function of time. In our case, we prepared a working electrode based on mesoporous carbon. A working electrode of L-CIL(Phe)-C was crafted by taking 3.5 mg L-CIL(Phe)-C (ca. 85% of the electrode mass) and mixing it with 5% of carbon black to adjust conductivity (purchased from Timcal Inc.) and 10% PVDF solution as a binder (see the Supporting Information). Aqueous solutions of L- and D-tartaric acid (0.02 M) were used as the chiral electrolyte to probe molecular recognition. At first, cyclic voltammetry was performed in order to exclude any electrochemical reactions that might occur between the working electrode and the electrolyte (see the Supporting Information p. S9). The cyclic voltammetry measurements showed a typical capacitive (Faraday) behavior, like that for for high-surface-area materials. Then, chronoamperometry measurements of the chiral carbon were performed. The chiral carbon electrode was charged to 1 V, and set to reach steady state for 1800 s. Each cycle was conducted five times in order to see if there is a change in the system over longer times (the electrode was discharged between runs). The results were processed with respect to the capacitor equation, where the logarithm of the current I (divided by I_0) was plotted versus time (Figure 3).

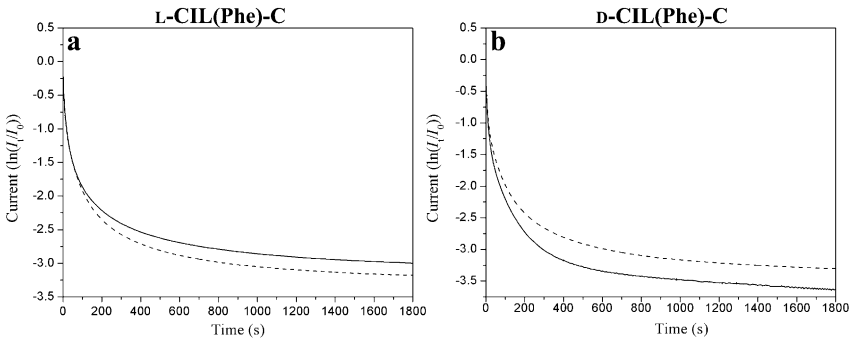

Figure 3. Chronoamperometry measurements of the D-CIL(Phe)-C and L-CIL(Phe)-C using D- and L-tartaric acid as chiral electrolytes; solid line: D-tartaric acid, dashed line: L-tartaric acid).

The kinetics of the enantiomeric electrolyte on the chiral electrodes show that for each type of carbon (either "D" type or "L"), the rate of charge transfer is higher in the case where the same handedness as the CIL precursor is used. This indicates a higher recognition of D-electrolyte/D-carbon and L-electrolyte/L-carbon, respectively. Moreover, by integration of the area beneath the graph at full plateau, we were able to determine the total charge on the electrode. For the "L-type" electrode, the average charge for D-tartaric acid was 34.71 mA s, while for the L-tartaric acid the charge calculated

was 35.89 mA s. Similar results were obtained for the "D-type" electrode, where the ratio was in favor of the D-tartaric acid electrolyte. This gives further confirmation of the enantioselectivity of the carbonaceous material. For additional results of chronoamperometry measurements for CIL(Trp)-C, see p. S10 in the Supporting Information.

Finally, as a control experiment, we prepared nanoporous carbon from the racemic chiral ionic liquid based on D/L-phenylalanine. We carried out a series of CD-selective chiral adsorption measurements and chiral ITC experiments on the racemic nanoporous carbon. Results of these experiments with the racemic nanoporous carbon (shown on p. S11 in the Supporting Information) clearly showed that these examples do not have chiral recognition ability. For example the ITC of the racemic nanoporous carbon had shown identical enthalpy of chiral binding for D- and L-histidine and also the CD-selective chiral adsorption measurements shown very similar adsorption for D- and L-phenylalanine.

In summary, all the techniques we used in this work clearly indicate not only the chiral character of the carbons but also that some of the initial chiral functionality of the precursor could be transferred onto the final mesoporous carbon. However, it is clear that further experiments must be carried out in order to understand the chirality of mesoporous carbon in detail and, in particular, the molecular mechanism leading to the formation of the mesoporous carbon, which is still an important open question.

We assume the chirality of the nanoporous carbon to be due to the carefully chosen chiral CILs, the synthesis carbonization conditions, and the presence of zinc ions. It is known from previous studies that zinc ions play an important role in small-pore generation as they are able to coordinate, and thus stabilize polar functional groups even at elevated temperatures.[20,21] Additionally, the Zn-coordination precursor molecules are brought into closer proximity mostly leading to increased carbon yield which is an obvious prerequisite for structural preservation. Therefore, we assume that the applied preparation conditions shift carbonization into a regime that makes structure preservation, namely preservation of chiral environment, possible even at high temperatures.

In order to verify this mechanism for the origin of the chirality on our carbon we performed thermogravimetric analysis combined with gas chromatography and mass spectrometry (TGA-GC-MS) of the chiral carbons. Exemplarily, CIL(Phe)-C was heated up to 950 °C. The TGA histogram for L-CIL(Phe)-C shows a weight loss of approximately 40 wt % mostly in the range between 600 and 950 °C (see Figure S12) which is above the carbonization temperature used for the synthesis of CIL-C (500 °C). A vapor sample from the TGA at 650 °C was taken to the GC–MS for better resolution and understanding of the weight loss. The MS mainly showed masses at *m*/*z* 28, 44, 73, 91, 117, 207, which correspond to small organic fragments such as ethylene (*m*/*z* 28), propanamide (*m*/*z* 44) mid and long aliphatic chains, and carbocyclic acids derivatives (see Figure S13). This emphasizes our claim that chiral organic motifs remain attached to the carbonized scaffold in the final CIL-C, in which chiral recognition was preserved and as such provides it chiral nature. It should be noted that nanoporous carbon samples prepared at low temperature (400 °C) shown structural features such as low surface areas, porosity, particles sizes compared to samples prepared at 500 °C and therefore we have not studied their chiral performance.

In conclusion, this paper describes the development of an innovative type of chiral mesoporous carbon based on a unique carbonization process of chiral ionic liquids. We demonstrated the chiral nature of these mesoporous carbons by employing unique analytical techniques such as circular dichroism spectroscopy, ITC, and electrochemical chronoamperometry. We believe that the approach presented in this paper is highly significant for the development of a new type of chiral mesoporous materials for enantioselective chemistry. In addition, it demonstrates significant progress in the understanding of the structure and nature of chiral mesoporous materials and nanosurfaces.

Experimental Section

Chiral ionic liquids of L- or D-phenylalanine (L-CIL(Phe) and D-CIL(Phe)) were prepared as follows: phenylalanine methyl ester hydrochloride was mixed in acetone with 6 equiv of iodomethane in the presence of potassium hydrogen carbonate for 16 h. The solid obtained was washed with chloroform and purified using hot water to extract salt residues. The purity of the L- or D-phenylalanine chiral ionic liquids was verified by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis (see the Supporting Information).

The CILs were then used as precursors for the preparation of high-surface-area porous carbon. The preparation was performed via carbonization of the CILs using the salt-templating approach as reported by Antonietti et al.[9,11,20] Briefly, the phenylalanine CILs (usually 0.5 g) were mixed with a freshly ground eutectic mixture of 0.4 g NaCl and 1.2 g $ZnCl_2$ and then heated to 500 °C for 1 hour at a heating rate of 2.5 K min^{-1} with a constant flow of N_2 (flow rate 3 L min^{-1}). After cooling to room temperature, the crude carbonaceous product was washed in 1 L of distilled water for 24 h and then dried under vacuum at 50 °C for 12 h. This process was repeated twice to ensure the extraction of salts from the carbonated products.

CD adsorption measurements were carried out in a 10 mm quartz cuvette with a Chirascan CD spectrometer. ITC experiments were carried at 25 °C with C VP-ITC calorimeter (MicroCal Inc., Northampton, MA). Injection volumes of 5 μL were delivered during 17.2 s at time intervals of 520 s, and the reference cell was filled with water. The step potential experiment was carried using an AutoLab PGSTAT302N potentiostat. The system was connected to the CIL-C as the working electrode (WE), Ag/AgCl as reference electrode (RE), and graphite fabric with high surface area relative to the working electrode as a counter electrode (CE). Each electrode was extensively washed with the electrolyte solution before each run. In each experiment the system was charged to 1 V and allowed to reach current saturation, followed by discharge. Data processing as well as further detailed physical characterization data of the CIL-C is detailed in Supporting Information.

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