*Optical Absorption and Photoluminescence (PL) Measurements*: The LiPBO sample was prepared as a thin film on a quartz substrate by thermal evaporation at a rate of 0.2 Å/s at $5\times10^{-6}$ torr. Optical absorption and PL spectra were measured by UV-vis spectrometry (Perkin-Elmer Lambda 19) and IAE-PL-SYS-1 (Nanotech) equipped with a linear charge coupled device detector (Ocean Optics, S2000) and a Xenon lamp coupled with a monochromator. For the PL measurements, the excitation wavelength was fixed as 365 nm, with regard to the absorption spectrum.

*Fabrication and Characteristics of OELD*: A 1:1 mixture of poly(ether imide) (PEI) and *N,N′*-diphenyl-*N,N′*-bis(3-methylphenyl)-[1,1′-diphenyl]-4,4′-diamine (TPD) were dissolved in chloroform to form a solution concentration of ca. 0.5 wt.-%. The solution was spun for ca. 1.5 min at 5000 rpm onto ITO glass, which had a seven-segment pattern on it, and subsequently dried at 110 °C for ca. 1 h. The dried polyimide HTL film had a thickness of 375 Å as determined by a surface profiler (Tencor P-10). Next, LiPBO was thermally evaporated onto the polyimide HTL using a low-temperature effusion cell (EPI-30-M-LT). The evaporation rate, the temperature, the vacuum, and the film thickness were ca. 0.1 Å/s, 315 °C, $5\times10^{-6}$ torr, and 200 Å, respectively. A 3500 Å thick layer of Aluminum was deposited on the LiPBO thin film by thermal evaporation at a rate of up to 5 Å/s. The evaporation rate and thickness were detected using a thickness monitor (Sycon Instruments STM-100/MF). The luminance–current density–voltage (*L–J–V*) characteristics of OELD were measured by IAE-OELD-SYS with an electrometer (Keithley 237), a calibrated photodiode, a diode array rapid scan analyzer (PSI DARSA-2000), and a candela meter (Minolta CS1000). The electroluminescent (EL) spectra were measured by a spectrophotometer (JOBIN-YVON-SPEX 270M) with a photomultiplier tube (PMT) as a detector and the IAE-PL-SYS-1 mentioned previously.

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# New Separation Science Using Shape-Selective Ion Exchange Intercalation Chemistry

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The design of porous solids that can selectively and reversibly bind molecules has been the subject of much recent interest.[1] These highly specific interactions are critical in a range of important practical chemical technologies such as chemical sensing,[2–4] separations,[5] and catalysis[6]. The design of lamellar inorganic hosts such as clays, phosphates, phosphonates and modified thin films that exhibit molecular recognition features has recently been reviewed by Mallouk and Gavin.[7]

In lamellar inorganic solids, guest molecules access intracrystalline binding sites via intercalation reactions. In most cases, inorganic intercalation reactions are unselective processes which are driven by either oxidation–reduction, ion-exchange, acid–base, or donor–acceptor reactions. The interlamellar gallery expands to accommodate the guest species resulting in little size- or shape-selectivity to the reaction. Here we report the use of a crystalline-ordered layered double hydroxide (LDH) that exhibits shape-selective intercalation. In addition, we have found that this remarkable shape selectivity can be controlled by altering the temperature and the solvent of the intercalation reaction.

We recently reported that the fumarate (*trans*–$^{-}\mathrm{O_2CCHCHCO_2^{-}}$) dianion can be preferentially extracted from an equimolar aqueous solution containing both disodium fumarate and disodium maleate.[8] Similarly, the terephthalate (*para*-$\mathrm{C_6H_4(CO_2^{-})_2}$) dianion can be selectively removed from an aqueous solution containing all three benzenedicarboxylate dianions (terephthalate, phthalate {*ortho*-$\mathrm{C_6H_4(CO_2^{-})_2}$}, and isophthalate {*meta*-$\mathrm{C_6H_4(CO_2^{-})_2}$}). The process uses the layered double hydroxide $\mathrm{[LiAl_2(OH)_6]Cl\cdot H_2O}$, which exhibits preferential ion-exchange intercalation for these specific anions in competition reactions. For example, the preference for intercalation of fumarate over maleate is in excess of 95 % in water at room temperature. In order to develop this methodology further and to investigate the origin of these preferences we have now studied a wider range of anion mixtures and also performed the reactions over a range of temperatures and in different solvent systems.

The disodium salts of 1,5-naphthalenedisulfonate, 1,5-$\mathrm{C_{10}H_6(SO_3)_2^{2-}}$, and 2,6-naphthalenedisulfonate, 2,6-$\mathrm{C_{10}H_6(SO_3)_2^{2-}}$, rapidly form the phase-pure first stage intercalation compounds $\mathrm{[LiAl_2(OH)_6]_2[1,5\text{-}C_{10}H_6(SO_3)_2]\cdot 6H_2O}$ and $\mathrm{[LiAl_2(OH)_6]_2[2,6\text{-}C_{10}H_6(SO_3)_2]\cdot 5H_2O}$ via direct ion-exchange intercalation with $\mathrm{[LiAl_2(OH)_6]Cl\cdot H_2O}$ (Table 1). The interlayer separations of these compounds

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Table 1. Lattice constants for first stage intercalates, $[LiAl_2(OH)_6]_nA{\cdot}xH_2O$ ($n$ = 1 or 2; $x$ = 5–6).

| A | Interlayer separation $c$ [Å] [a] |
|---|---|
| 1-naphthalenesulfonate | 16.3 or 17.9 [b] |
| 2-naphthalenesulfonate | 18.0 |
| 1,2-benzenedisulfonate | 15.5 |
| 1,3-benzenedisulfonate | 14.8 |
| 1,5-naphthalenedisulfonate | 15.3 |
| 2,6-naphthalenedisulfonate | 16.8 |
| 1,5-naphthalenedicarboxylate | 15.0 |
| 2,6-naphthalenedicarboxylate | 16.3 |

[a] Indexed on a hexagonal cell ($\alpha = \beta = 90°$, $\gamma = 120°$, $a = b = 5.08$ Å). [b] Two distinct phases were observed for the 1-naphthalenesulfonate intercalate, due either to different orientations of the guest or to different levels of hydration in the product.

are 15.3 Å and 16.8 Å respectively. In competitive intercalation reactions using equimolar solutions of these two isomers we have observed some remarkable and unprecedented regioselective ion-exchange reactions. For example, when an equimolar aqueous solution of excess $Na_2(1,5\text{-}C_{10}H_6(SO_3)_2)$ and $Na_2(2,6\text{-}C_{10}H_6(SO_3)_2)$ is added to a suspension of $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ in water at 100 °C complete ion-exchange intercalation occurs rapidly (typically 1–2 h). The XRD pattern of the isolated solid product shows it to be monophasic with an interlayer separation of 15.3 Å suggesting that only the 1,5-isomer has been intercalated. However, to more precisely determine the distribution of the organic guest between the layers, the solid can be further treated with an excess of $Na_2CO_3$ in $D_2O$ in order to exchange out the intercalated organic anions. $^1$H NMR spectroscopy of this $D_2O$ solution was then used to accurately quantify the relative ratios of the various isomers that were intercalated into the host. The solution $^1$H NMR spectrum following exchange with $Na_2CO_3$ in $D_2O$ indicates that the preference for the $1,5\text{-}C_{10}H_6(SO_3)_2^{2-}$ over the $2,6\text{-}C_{10}H_6(SO_3)_2^{2-}$ isomer is in excess of 99:2.

Remarkably, the preference for intercalation of $1,5\text{-}C_{10}H_6(SO_3)_2^{2-}$ over $2,6\text{-}C_{10}H_6(SO_3)_2^{2-}$ by $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ changes dramatically with temperature. As the temperature of the reaction is lowered the ratio of the amounts of the 1,5- vs. 2,6- isomers changes dramatically. At 20 °C the ratio of 1,5- vs. 2,6- (as determined by solution $^1$H NMR) is 27:73 (Fig. 1). In addition, the powder XRD pattern of the solid obtained from these competition experiments contains Bragg reflections corresponding to the presence of two separate phases, $[LiAl_2(OH)_6]_2\{2,6\text{-}C_{10}H_6(SO_3)_2\}{\cdot}H_2O$ and $[LiAl_2(OH)_6]_2\{1,5\text{-}C_{10}H_6(SO_3)_2\}{\cdot}H_2O$ respectively. Although one should not generally use the relative intensities of the Bragg reflections of the two phases in quantitative measurements, the relative intensities of the two sets of strongest 00*l* reflections follow the qualitative trends observed from the NMR experiments. Figure 1 shows that the crossover in preference occurs at about 45 °C.

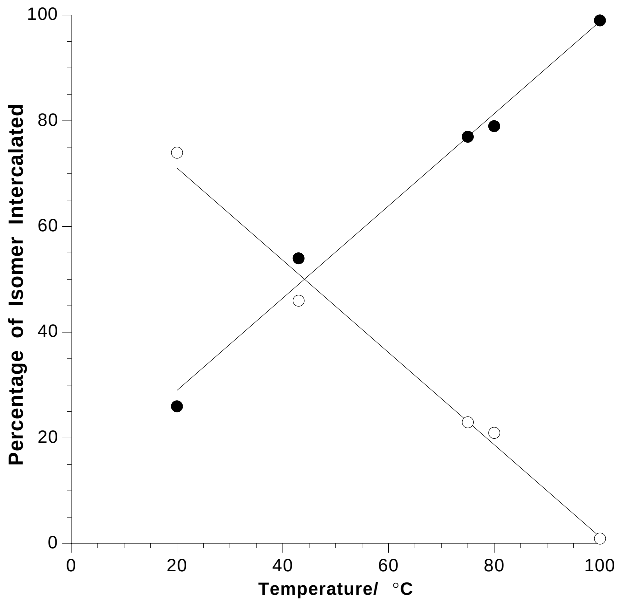

Fig. 1. Percentage of guest intercalated for the competition reaction 1,5-naphthalenedisulfonate (●) vs. 2,6-naphthalenedisulfonate (○) as a function of temperature.

From some of our previously published in-situ XRD experiments we know that there is rapid ion-exchange between all intercalated and solution ions in these reactions. Therefore we can investigate the thermodynamics of this reaction by considering the equilibrium constant for the ion-exchange reaction show below (where NDS = naphthalenedisulfonate, soln = solution, and int = intercalated);

$$1,5\text{-}NDS_{(soln)} + 2,6\text{-}NDS_{(int)} \rightleftarrows 1,5\text{-}NDS_{(int)} + 2,6\text{-}NDS_{(soln)} \quad (1)$$

The equilibrium constant for the ion-exchange intercalation reaction ($K_{eqm}$) = $[2,6\text{-}NDS_{(soln)}]/[1,5\text{-}NDS_{(soln)}]$ can be estimated from our NMR studies.

Using the van't Hoff equation a plot of $-\ln(K)$ vs. $1/T$ is linear with a gradient equal to $(\Delta H_{(reaction)}/R)$. In water $\Delta H_{(reaction)}$ is estimated to be 44.4 kJ mol$^{-1}$. We presume that this reaction enthalpy reflects the differences in $\Delta H_{(solv)}$ of the two sulfonate ions in water, the difference in the enthalpy of binding between the host and guest $\Delta H_{(host/guest)}$ and the differing guest–guest interactions $\Delta H_{(guest/guest)}$.

We have also studied the effects of solvent on this reaction. For solubility reasons we need to carry out the intercalation reactions in 50:50 mixtures of water and a range of miscible polar solvents. In each case we obtain the same intercalates and shown in Table 2, there is no evidence for co-intercalated solvent apart from water. Figure 2 shows the preference for the $1,5\text{-}C_{10}H_6(SO_3)_2^{2-}$ as a function of temperature in each of the solvent systems. The results dramatically show how sensitive the reaction medium is to determining the outcome of these reactions. For example, in 50 % water/acetonitrile the 1,5-isomer is no longer favored

Table 2. Summary of the preferences for the competitive ion-exchange intercalation of a range of organic anions in $[LiAl_2(OH)_6]Cl{\cdot}H_2O$.

| Guest anions [a] | | Reaction conditions | | % Guest intercalated | |
|---|---|---|---|---|---|
| A | B | Temp [°C] | Time [h] | A | B |
| 1,5-naphthalenedisulfonate | 2,6-naphthalenedisulfonate | 100 | 24 | 98 | 2 |
| | | 20 | 24 | 27 | 73 |
| 1,5-naphthalenedicarboxylate | 2,6-naphthalenedicarboxylate | 100 | 24 | 1 | 99 |
| | | 20 | 24 | 10 | 90 |
| 2-naphthalenesulfonate | 2,6-naphthalenedisulfonate | 100 | 24 | 76 | 24 |
| | | 20 | 24 | 87 | 13 |
| 1,2-benzenedisulfonate | 1,3-benzenedisulfonate | 100 | 2 | 99 | 1 |
| 1-naphthalenesulfonate | 1,5-naphthalenedisulfonate | 100 | 24 | 50 | 50 |
| 2,6-naphthalenedisulfonate | 2,6-naphthalenedicarboxylate | 100 | 24 | 1 | 99 |
| 1,2-benzenedisulfonate | 1,2-benzenedicarboxylate | 100 | 2 | 29 | 71 |
| 1,3-benzenedisulfonate | 1,3-benzenedicarboxylate | 100 | 2 | 9 | 91 |

[a] In each case the reactions were carried by addition of equimolar amounts of the disodium salts of the anions to a suspension of $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ in water. The total guest concentration was greater than a 2:1 excess compared to the ion-exchange capacity of the host. The relative preferences were determined by integration of the $^1H$ NMR signals for each isomer following ion-exchange out of the LDH by treatment with an excess of $Na_2CO_3$ in $D_2O$.

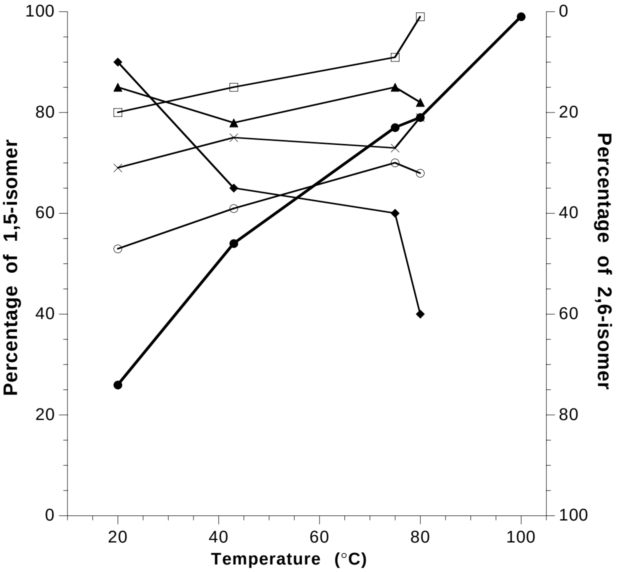

Fig. 2. Percentage preference for ion-exchange intercalation of 1,5-naphthalenedisulfonate over 2,6-naphthalenedisulfonate in $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ in a range of different solvents. (Solvents: ●) = 100 % water, ○ = 1:1water/THF, × = 1:1 water/formamide, □ = 1:1 water/acetone, ▲ = 1:1 water/ethanol, ◆ = 1:1 water/acetonitrile.

Table 3. Summary of the enthalpies ($\Delta H$) for the ion-exchange intercalation reaction 1.

| Solvent | Enthalpy [kJ mol$^{-1}$] |
|---|---|
| 100 % water | 44.4 |
| 50% water : 50% acetone | 16.2 |
| 50% water : 50% THF | 11.2 |
| 50% water : 50% formamide | 5.7 |
| 50% water : 50 % ethanol | –0.3 |
| 50% water : 50% acetonitrile | –35.0 |

at 100 °C and 60 % of the intercalated ions are now the 2,6-isomer. In fact, the temperature-dependence of the preference for 1,5-isomer vs. the 2,6-isomer in water/acetonitrile is the reverse to that observed for pure water. Table 3 summarizes how these changes are reflected in the reaction enthalpy. Presumably this solvent dependence comes from the variations in the different solvation enthalpies for the two ions.

It appears that the ability of this layered material to exhibit specific preferences for certain ismoers seems to be quite general for a range of organic anions and dianions. We have also demonstrated total control of the intercalation preferences of the disodium salts of 1,5- and 2,6-naphthalenedicarboxylate in $[LiAl_2(OH)_6]Cl{\cdot}H_2O$. For example, when an equimolar mixture of the two anions is added to $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ in water at 100 °C then over 99 % of the intercalated ions is the 2,6-isomer (see Scheme 1). The solid intercalate can then be washed with water and treated with dilute HCl in ethanol to regenerate $[LiAl_2(OH)_6]Cl{\cdot}H_2O$ and release analytically pure 2,6-naphthalenedicarboxylic acid into the organic phase. Table 2 summarizes some mixtures of organic anions that we have studied.

It is still unclear why this material exhibits such highly selective isomer preferences. The unique Li/Al cation ordering exhibited by $[LiAl_2(OH)_6]^+$ layers[9,10] may be a significant factor as other cation-disordered LDHs do not show such pronounced selectivities. However, cation ordering cannot account for the strong solvent dependence of the ion-exchange intercalation preferences of the various isomers.

This process should be able to be extended to a range of other organic systems containing anionic functional groups and therefore provide chemists with a new flexible, cost-effective, regenerable and environmentally friendly separation procedure. The ability of these simple, stable inorganic solids to separate complexes could have a wide ranging applicability and we are currently investigating the potential in more biological areas with larger anions such as oligonucleotides. Nevertheless, we foresee this technology could have immediate and significant impact in a number of

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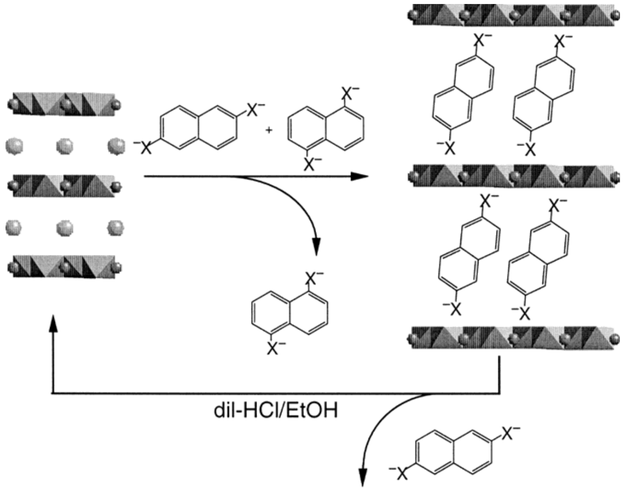

Scheme 1. Schematic representation of the selective intercalation of difunctional naphthalene anions into [LiAl$_2$(OH)$_6$]Cl·H$_2$O. X can be SO$_3^-$ or CO$_2^-$.

industries. For example, polyethylene naphthalate (PEN) is emerging as a major new addition to the polyester family. It provides superior performance capabilities compared to existing polyester resins, most notably polyethylene terephthalate (PET) and has recently been given FDA approval for food packaging applications. In particular, PEN boosts barrier, electrical, mechanical, and thermal properties—in some cases by as much as four to five times that of PET. We envisage that the science reported here could provide an opportunity to develop cost-effective technology to produce pure NDC (2,6- naphthalenedicarboxylic acid), a key raw reagent for PEN.

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# Record Charge Carrier Mobility in a Room-Temperature Discotic Liquid-Crystalline Derivative of Hexabenzocoronene

By *Anick M. van de Craats*, *John M. Warman*,*
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Increasing attention is being paid to the possible application of discotic materials as conducting layers in organic molecular electronic devices. Such compounds self-organize into columnar stacks with aromatic macrocyclic cores surrounded by a saturated hydrocarbon mantle. This insulated, coaxial structure results in the one-dimensional transport of charge within the core. Furthermore, their liquid-crystalline properties offer the possibility of obtaining extensive, well-organized layers in which the columnar orientation can be controlled and self-healing of structural defects can occur. For optimum performance, compounds are sought which display high charge carrier mobilities and extensive temperature regimes over which they have liquid-crystalline mesophases.

We have recently shown that a mesomorphic derivative of hexabenzocoronene displays this combination of advantageous properties.[1] In this report we present results on a series of hexabenzocoronene (HBC) derivatives which have been prepared by a different synthetic route to that used previously. This yields higher purity materials and substantially better conductive properties. For the first time for discotic materials, a charge carrier mobility in excess of 1 cm$^2$ V$^{-1}$ s$^{-1}$ was observed in the crystalline solid phase of these materials, and a value as high as 0.5 cm$^2$ V$^{-1}$ s$^{-1}$ was found even in their hexagonal columnar liquid crystalline phase. In addition, one of the compounds was liquid crystalline at room temperature and, because of its high solubility in organic solvents, can be readily spin-coated thus making it an ideal candidate for device applications.

The molecular structures of the hexabenzocoronene derivatives studied are shown in Figure 1. Their phase transitions as monitored by differential scanning calorimetry (DSC) are given in Table 1. The sum of the one-dimensional charge carrier mobilities, $\sum\mu_{1D}$, has been derived from the pulse-radiolysis time-resolved microwave conductivity technique (PR-TRMC). The values of $\sum\mu_{1D}$ are plotted as a function of temperature in Figure 2.

The temperature-dependence for the three directly linked *n*-alkyl derivatives, HBC-C$_n$, is seen to be very similar: The mobility increased slightly on heating in the crystalline solid phase, *K*, with no abrupt changes observed at

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