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**Organofunctionalized Deloxan[®] DAP Beads as Solid
Support for Versatile Organic Chemistry**

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Abstract

Solid phase chemistry has gained significant importance in the last decade with the coming of age of combinatorial chemistry methods. Among other challenges, the development of appropriate solid supports to perform distinct chemical reactions is of paramount importance for the outcome of a synthetic modification to be carried out on the solid phase. In the present Thesis, we describe how traditional solid supports can be modified rationally to display novel electrochemical as well as photochemical properties, and how these modified moieties can be employed as active components in molecular recognition processes and heterogeneous catalysis.

Our explorations began, in collaboration with the German company *Degussa AG*, and targeted the functionalization of their Deloxan[®] DAP beads as solid supports for versatile organic chemistry (Figure 1). These polysiloxane beads had shown promise as solid supports for active agents in the fields of molecular recognition (*e.g.* enzyme support) and heterogeneous catalysis (*e.g.* precious metal support). Furthermore, they exhibited high structural, thermal, and chemical stability.

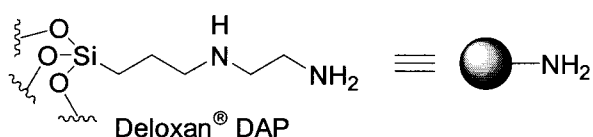


Figure 1. Schematic representation of the Deloxan[®] DAP beads.

In Chapter 2, the preparation of Deloxan[®] DAP-based dendrimers as molecular assembly templates for high-loading solid supports is described. Efforts were focused on the synthesis of dendritic materials with peripheral carboxylate groups able to associate with a suitable counter-ionic unit, giving rise to well-defined architectures (Figure 2).

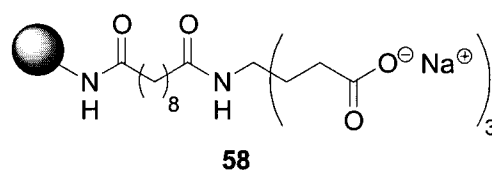


Figure 2. Deloxan[®] DAP-based poly(carboxylate) dendrimers (**58**).

These dendrimers represent a novel type of hybrid polymer. As such, we were interested in designing new types of hybrid materials based on the Deloxan[®] DAP-supported dendrimers **58** and fullerene-derived ammonium ion derivative **57** (Figure 3). The unique physical and chemical properties of C₆₀, including its efficient singlet oxygen sensitizing ability, strong electron acceptor character, and superconductivity upon doping with alkali metals, make it an attractive component to be incorporated in functional molecular assemblies and supramolecular arrays. Consequently, hybrid materials of type **59** (Figure 3) were prepared and their electronic behaviour was investigated by cyclic voltammetry.

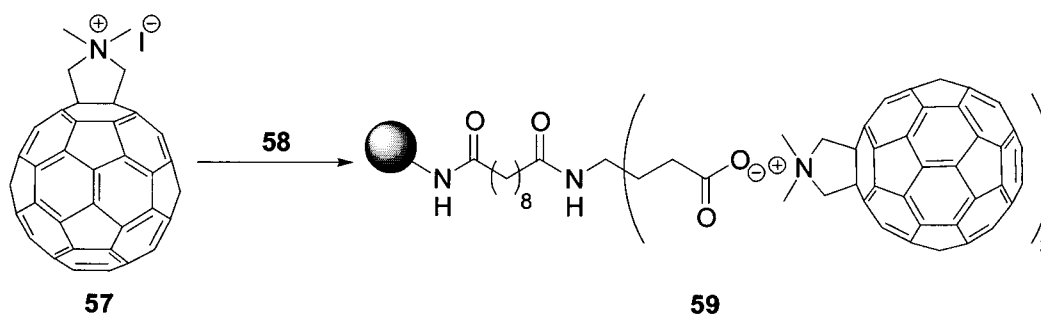


Figure 3. Supramolecular assembly process between the fullerene ammonium ion derivative **57** and the Deloxan[®] DAP-based poly(carboxylate) dendrimers **58**, leading to the well-defined hybrid material **59**.

In addition to the work on Deloxan[®] DAP-based poly(carboxylate) dendrimers, we became interested in derivatizing the Deloxan[®] DAP with organic dendrons bearing peripheral alcohol functions. These new materials could potentially provide a dendritic solid-support with a very high-loading of reactive end groups, useful in subsequent functionalizations (Figure 4).

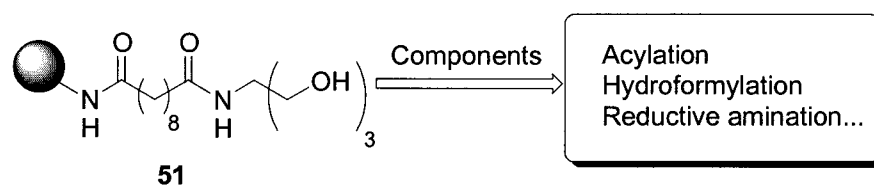


Figure 4. Deloxan[®] DAP-based poly(alcohol) dendrimers **51** as high-loading solid supports for further functionalization with various units.

As mentioned above, Deloxan[®] DAP beads have shown promising results in the field of heterogeneous catalysis, and this finding initiated the second part of the present Thesis which involved the development of a new class of polymer-supported chiral ligand. Solid-supported ligands have the advantage that they can readily be removed from the reaction mixture, thus easing product purification and recycling of the catalyst. To this end, a new class of Deloxan[®] DAP-based BINAP ligand was prepared in enantiomerically pure form and subsequently tested in palladium-catalyzed asymmetric allylic alkylation reactions (Figure 5).

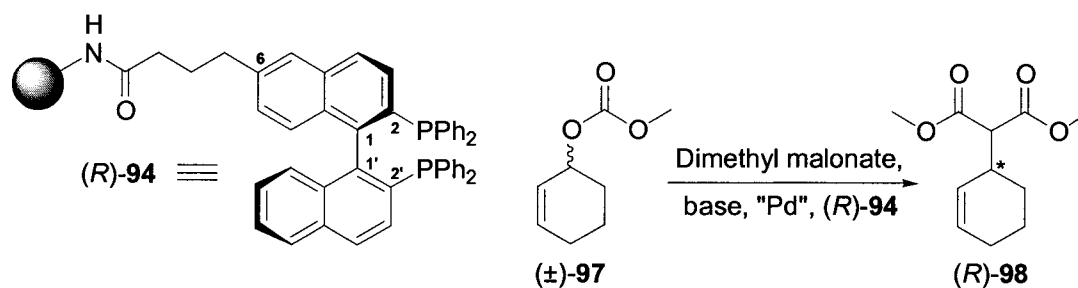


Figure 5. A new class of polymer-supported BINAP ligand (*R*)-**94** was prepared for palladium-catalyzed asymmetric allylic alkylations.

The catalyst was prepared *in situ* from the polymer-supported ligand (*R*)-**94** (1 mol%) and the palladium species (0.45 mol%), and turned out to be fairly reactive (16% yield); the enantioselectivities, however, were low and did not exceed 11% ee. The anion of dimethyl malonate was used as the nucleophile and (±)-methyl cyclohex-2-enyl carbonate ((±)-**97**) as the substrate.

Finally, we explored the photooxidation of sulfides to sulfoxides by singlet oxygen, generated in the presence of a heterogeneous Deloxan[®] DAP-derived fullerene photosensitizer (Figure 6).

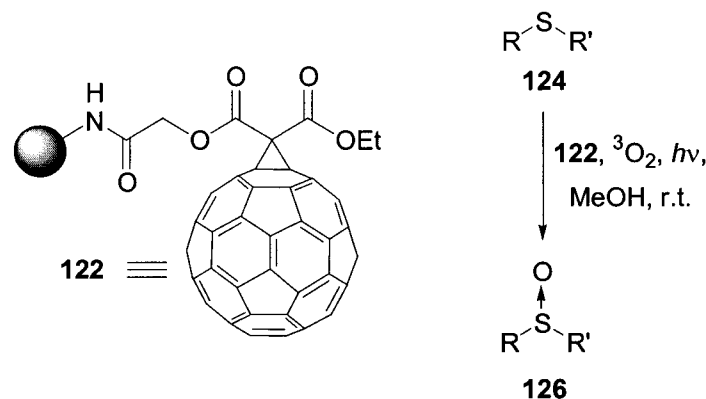


Figure 6. Photooxidation of sulfides to sulfoxides by singlet oxygen generated in the presence of a heterogeneous Deloxan[®] DAP-derived fullerene photosensitizer (122).

Chemical uses of ¹O₂ produced by fullerenes are often hampered by the very limited solubility of the carbon cages in most solvents or the difficult recovery of soluble fullerene derivatives at the end of the reaction. In contrast, the heterogeneous Deloxan[®] DAP-based fullerene photosensitizer (122) is easy to isolate and to recycle after use. Therefore, heterogeneous sensitization by polymer-supported derivatives of C₆₀ in methanol seemed quite advantageous.

The effectiveness of the photooxidation of sulfides to the corresponding sulfoxides by singlet oxygen, generated in the presence of the heterogeneous sensitizer, was shown to be quite high (up to 98% conversion). In addition, the reaction was highly selective in methanol and afforded literally no sulfones. This emphasized the utility of a heterogeneous fullerene-derived sensitizer (122) combining the high quantum yields for ¹O₂ generation of mono-functionalized C₆₀ with the advantages of having a catalyst attached to the solid support.