

Synthesis of Bis-carboxylic Acid Derivatives of $M_3N@I_h-C_{80}$ ($M = Sc, Lu, Y, Gd$) through Prato Reaction

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Abstract: Trapping metals inside fullerenes scaffold lead to the new generation of fullerene materials (Figure 1) for a wide range of applications (e.g. solar cells¹ and MRI contrast agent²). In the past decade, many efforts were devoted to develop the efficient synthesis of the derivatives of stable and highly symmetric metallofullerenes,^{3,4} TNT-EMF (trimetallic nitride template-endohehedral metallofullerenes: $M_3N@I_h-C_{80}$ ⁵). Especially aiming potential industrial production, it is important to investigate the controlled functionalization to increase their properties such as solubility, tuned band-gap, and controlled metal cluster motion.⁶

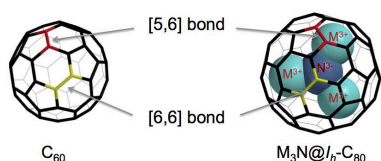


Figure 1. Structures of C_{60} and $M_3N@I_h-C_{80}$.

In order to understand the reactivity dependent on the metal inside the cage, in the present study we used the Prato reaction⁷ (Figure 2) to synthesize fulleropyrrolidine carboxylic acid derivatives of $M_3N@C_{80}$. A glycine derivative was prepared and the reaction was monitored by HPLC (Figure 3).

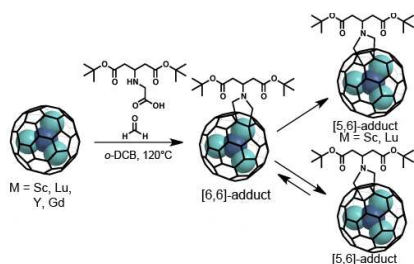


Figure 2. Prato reaction of $M_3N@C_{80}$.

The isomerization reactions (from the [6,6]-adduct to the [5,6]-adduct) were carried out at various temperatures to obtain an Eyring plot. We found that the energy barrier for the isomerization from the kinetic product ([6,6]-adduct) to the thermodynamic product ([5,6]-adduct) were dependent on the cluster size (Table 1).

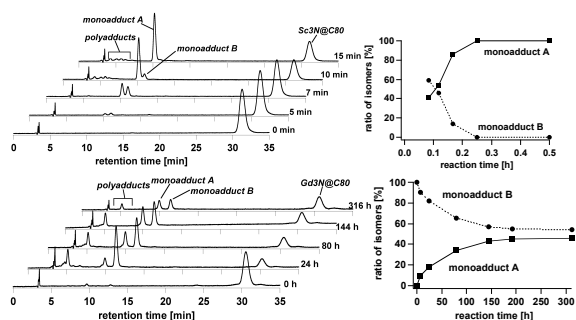


Figure 3. Time course experiment (left: HPLC traces) and ratio of isomers (right) of the Prato reaction (120 °C) of $M_3N@C_{80}$ ($M = Sc$ and $M = Gd$).

Table 1. Activation enthalpy and the cluster size.

M^{3+}	Sc^{3+}	Lu^{3+}	Y^{3+}	Gd^{3+}
Radius (Å)	0.75	0.85	0.90	0.94
Cluster structure	planar	planar	slightly pyramidal	pyramidal
ΔH^\ddagger (kJ/mol)	—	98.5	114.5	119.5

Importantly, in the case of $M_3N@C_{80}$ with larger metals ($M = Y, Gd$), this conversion was not completed and both regioisomers were present at the end of the reaction (figure 3). This was not found in any other fulleropyrrolidine derivatives reported in other studies. In order to confirm that this reaction is in equilibrium, purified each [5,6]- and [6,6]-adduct of $M = Gd$ was refluxed for 4 h to provide the same final ratio of isomers (Figure 4).

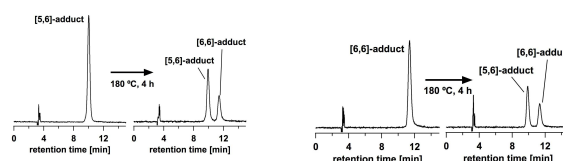


Figure 4. Reversible isomerization on $Gd_3N@C_{80}$ -adducts monitored by HPLC.

This study demonstrated the effect of cluster size on kinetic of isomerization, also evidence of equilibrium was shown by HPLC, we speculated that increasing the metal size stabilize the [6,6]-adducts through pyramidalization of sp^3 carbon at the addition site. The pyrrolidine substituent may also play an important role. Further experiments based on DFT calculations and X-ray structures are needed to fully understand the process.

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