Systematic study of Lewis acid-catalyzed bromination and bromoalkylation of multi-walled carbon nanotubes

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Objective
Bromination and bromoalkylation reactions of CNT are very promising pathways to grafting of electrophilic sites. However, only sparse experimental data is available in the literature. The present work is a broad and systematic study to optimize the bromination and bromoalkylation yield of multi-walled CNT (Baytubes® C150P) using Lewis acids as catalysts. Bromination and bromoalkylation of multi-walled CNT were investigated by systematic variation of processing parameters. Eight different reaction times, three reaction temperatures, nine solvents, twelve catalysts and eleven electrophile reagents were studied with respect to bromination yield. Also the substitutability of the introduced bromine was studied. For this, the reaction of brominated CNT with 4-(trifluoromethyl)benzyl mercaptane was investigated. The substitution efficiency of bromine by this fluorinated compound was quantified by XPS analysis. The optimum bromination procedure will be used to study the coupling of specifically-synthesized mercaptanes with brominated or bromoalkylated nanotubes.

Studied reaction parameters
- Solvents: DCM, Et₂O, nBu₂O, n-C₆H₁₄, n-C₆H₁₂₀, n-C₁₂H₂₄₀, Diglyme, Triglyme, MeCN/Dioxane, 1,2-Dichlorobenzene, Bromoform, Ethyldibromide, H₂O/Dioxane
- Lewis/Brönstedt-Acids: BF₃·Et₂O, BBBr, AlBr₃, FeBr₃, SnBr₄, VBr₅·Diglyme, ZnBr₂·(THF)₂, TiBr₄, DBPO, MsOH, H₂PO₄
- Reaction Temperatures: RT, 50 °C, 95 °C, 200 °C
- Durations: 1h, 3h, 4h, 5h, 1d, 3d, 1 Wo, 2 Wo
- Reagents for bromination/alkylation: Br₂, 1,6-Dibromohexane, p-Xylylendibromide, SOCl₂, SOBr₂, SO₂Cl₂, Allylbromide, trans-1,4-Dibromo-2-Butene, 4-Methylbenzyldibromide, 6-Bromo-1-Hexanol, 4-Chloromethylbenzyldibromide, 5-Bromo-1-Pentene

Observed general trends
- Bromination is more effective than bromoalkylation
- The Lewis acids AlBr₃, FeBr₃, SnBr₄ are most reactive in this order
- In contrast to bromination bromoalkylation leads to 100% substitutable bromine at least at 90°C or below
- In low-temperature reactions unpolar solvents are superior to ethers
- In high-temperature bromination di-n-Hexyether (though expensive) is superior to dimethyl ethers of glycols and alkanes
- High-temperature bromination leads to about ten times as much bromine than low-temperature bromination including intercalated bromine
- Further and concluding experiments are in progress

Conclusions
Optimization of bromination or bromoalkylation may be necessary for each type of CNT material due to individual reactivity. For Baytubes, this reaction is efficiently catalyzed by AlBr₃ either in DCM at lower temperature or in di-n-Hexyether at 200 °C. Bromoalkylation leads to 100% substitutable bromine but at a lower bromine concentration. The problem of intercalated bromine, which would not be substitutable, remains to be solved if Br₂ is used.

Substitution with 4-Trifluoromethylbenzylmercaptane

High temperature bromination at 200 deg. Celsius

Reaction parameters for 2,5h

BAM Innovation Laboratory Carbon Nanotubes

Inno.CNT