

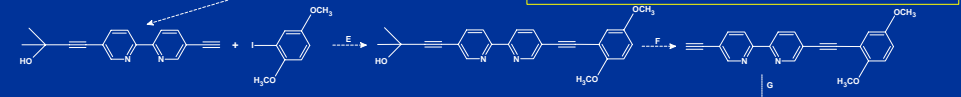
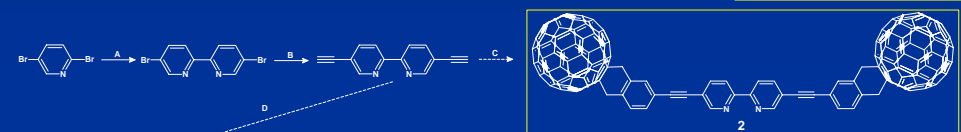
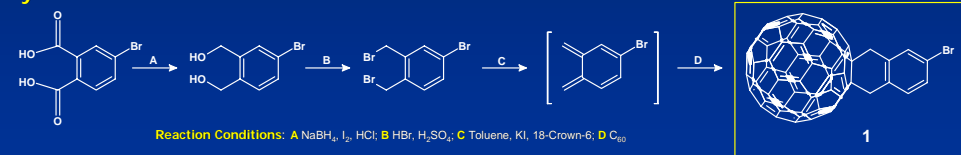


Objective: The overall objective of our research group is to synthesize new small molecule subunits that can be united with other known moieties to create new supramolecular systems. Our work gives undergraduate researchers an opportunity to conduct advanced organometallic and spectroscopic research at an early point in their careers. Currently, research "teams" are preparing two new subunits that will ultimately be ligated to transition metal chromophores and subjected to a thorough spectroscopic study on site, include charge transfer distance measurements.¹

Fullerenes with "Handles"

Purpose: There is considerable interest to incorporate fullerenes into supramolecular systems due to their unique electrochemical properties.² Our group has completed the synthesis of **1**, which provides a simple "handle" on the fullerene through a Diels-Alder synthesis.^{3,4} This handle provides a point with which to link to other moieties through Sonogashira coupling.⁵ Our initial systems will be **2** and **3**, which will then be complexed with TM chromophores (Ru/Re/Pt).^{6,7} Moiety **1** could also be incorporated into other oligomeric and polymeric systems where such coupling is employed.

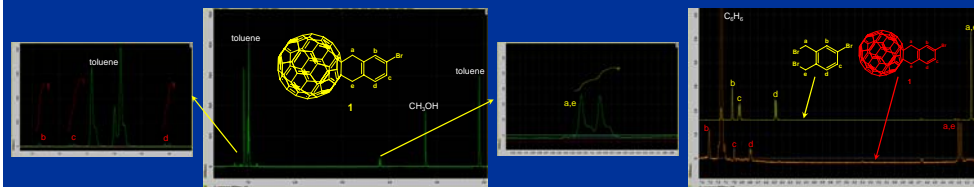
Synthesis:



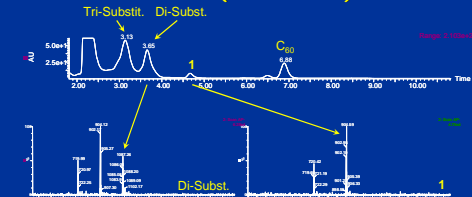
Reaction Conditions: A Me_3Sn , $\text{Pd}(\text{PPh}_3)_4$, Toluene; B TMS-H , $\text{Pd}(\text{PPh}_3)_4$, CuI , THF , tPr_2NH , KOH ; C **1**, $\text{Pd}(\text{PPh}_3)_4$, CuI , tPr_2NH ; D TMS-H , $\text{Pd}(\text{PPh}_3)_4$, CuI , THF , tPr_2NH , $\text{xs HC-CCMe}_2\text{OH}$, KOH ; E $\text{Pd}(\text{PPh}_3)_4$, CuI , THF , tPr_2NH ; F KOH , toluene; G **1**, $\text{Pd}(\text{PPh}_3)_4$, CuI , THF , tPr_2NH

Analysis of 1: Compound **1** has been confirmed through a variety of spectroscopic analysis, including NMR ($^1\text{H}/^{13}\text{C}$), IR, UV-Vis, and HPLC/MS. The HPLC/MS particularly showed the multiply-substituted fullerenes, and prep HPLC is being used for purification.

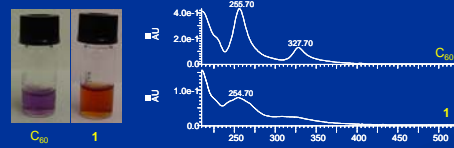
NMR (Toluene- d_6 /Benzene- d_6)



HPLC/MS (IPA/Hexanes)



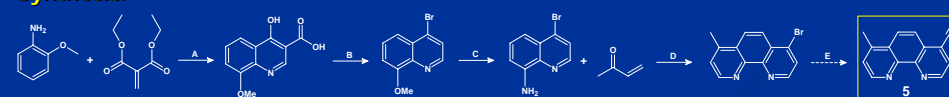
UV-Vis (Toluene)



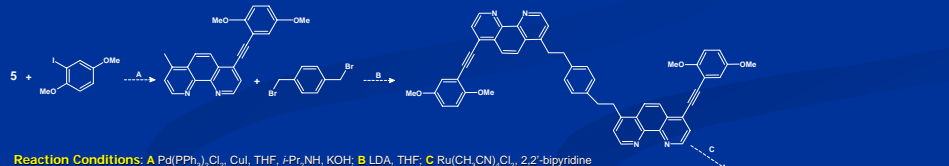
"Encapsulated" Linear TM Wires

Purpose: There has been much interest in uniting TM chromophores to π -conjugated polymers.^{8,9} However, many of these fail to achieve a robust integration of these two moieties. Our target system (**4**) is based on a tethered ligand first proposed by Sauvage^{10,11} that will bring the TM chromophore directly in line with the organic polymer. This system is based on substituted phenanthroline **5**,¹²⁻¹⁴ although an analogous bipyridine system is also under development. Phenanthroline **5** can then be used to prepare representative small molecule **6** (shown ligated to a ruthenium(II) center), or alternatively to construct "dimer" **7** via similar methodology, which would bind two TM chromophores. Longer oligomeric/polymeric systems could then be built stepwise using Sonogashira coupling.⁵

Synthesis:

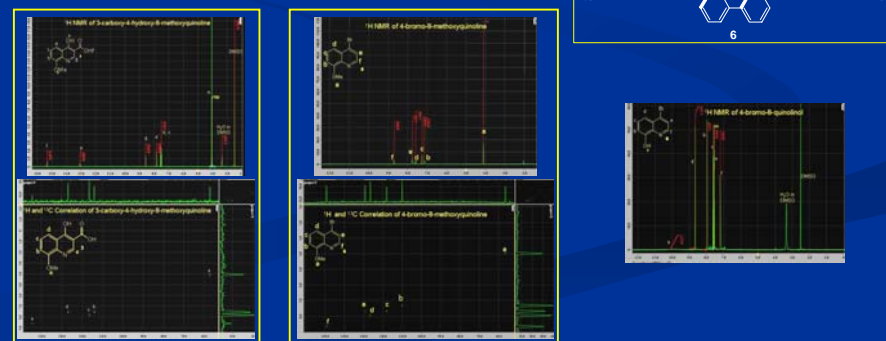


Reaction Conditions: A Reflux, OH^- , H^+ quench; B Reflux, POBr_2 ; C H^+ , $\text{NH}_3/\text{NH}_4^+$; D H^+ ; E TMS-H , $\text{Pd}(\text{PPh}_3)_4$, CuI , THF , tPr_2NH , OH^- deprotect



Reaction Conditions: A $\text{Pd}(\text{PPh}_3)_4$, CuI , THF , tPr_2NH , KOH ; B LDA , THF ; C $\text{Ru}(\text{CH}_3\text{CN})_2$, 2,2'-bipyridine

Analysis of 5 Precursors: Precursors to Compound **5** have been confirmed through NMR spectroscopy (including ^1H , ^{13}C , and HECTOR $^1\text{H}/^{13}\text{C}$), and HPLC/MS.



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