

Multi-functional architectures supported on organostannoxane scaffolds

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Abstract. Organostannoxane cages and aggregates of well-defined composition and structure can be prepared by the reactions of organotin oxides or organotin oxide-hydroxides with protic acids. The utility of this strategy for the preparation of dendrimer-like molecules containing a stannoxane core and a functional periphery is described.

Keywords. Organostannoxanes; organotin; multi-ferrocenes; multi-photoactive; phosphonates; pyrazole.

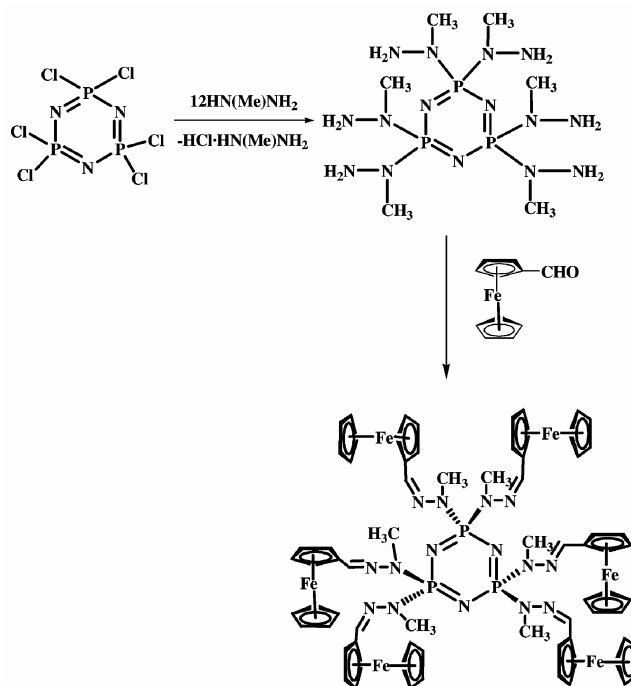
1. Introduction

In recent years there have been many efforts to explore the possibility of using inorganic ligands and cages as scaffolds for assembling star-burst type or dendrimer-like architectures. Among the family of compounds that have been investigated for this purpose include cyclophosphazenes,^{1–4} cyclosiloxanes,^{5–9} borazines,^{10–13} Al-N rings^{14–15} and Al-C rings.^{16–17} The main strategy in this game plan is to build a central ‘inorganic core’ which contains several reactive sites. The latter are utilized for introducing the required functional groups. As a case in point, consider the reaction of $N_3P_3Cl_6$ with N-methylhydrazine to afford $N_3P_3[N(Me)NH_2]_6$. The latter contains six reactive $-NH_2$ groups. These have been condensed with ferrocene aldehyde to afford the hexaferrocene derivative $N_3P_3[N(Me)N=CH-C_5H_4FeC_5H_5]_6$ (scheme 1).¹⁸

Similarly, cyclophosphazenes and carbophosphazenes have been used for supporting multi-site coordination ligands and for preparing multi-metallic assemblies.^{19–29} In all of these instances the construction of the star-burst like molecules occurs in a step-wise manner proceeding from a central core which has multiple pre-organized well-defined reactive sites. In many ways this strategy is similar to that is well known in the synthesis of organic dendrimers.

In contrast to the above situation, a completely new synthetic strategy entails the assembly of the central core and the periphery at the *same time*. In

this strategy there is no pre-organized central core to begin with. On the other hand, the construction of the central core mandates the simultaneous formation of the multifunctional periphery. Which type of inorganic rings or cages are amenable for this ‘one-pot’ ‘one-shot’ construction of the starburst assembly? Our long experience on organostannoxanes has suggested to us that the synthesis of these compounds provides a possible route for the assembly of multi-



Scheme 1. Cyclophosphazene-supported multi-ferrocene assembly.

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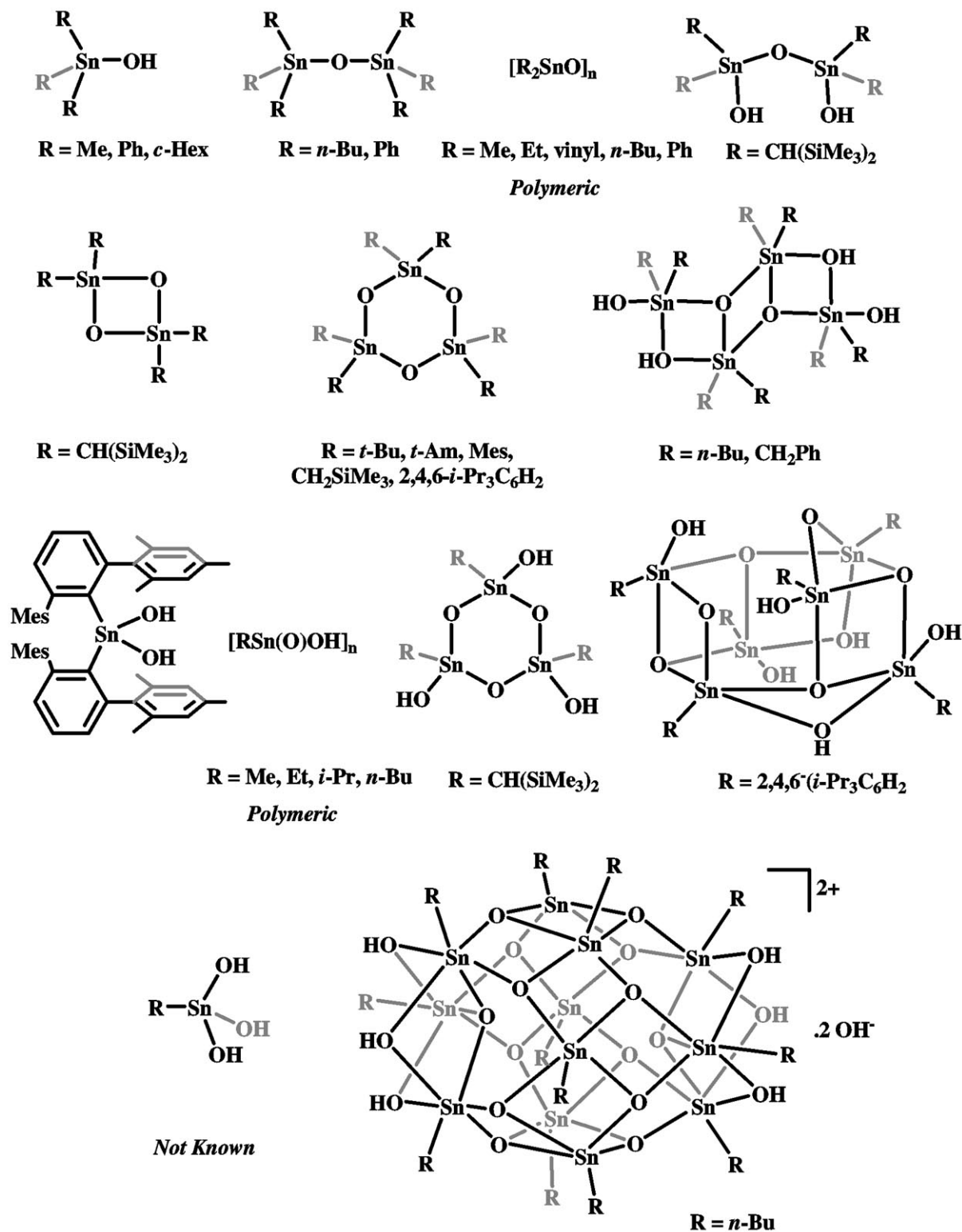


Chart 1. Various types of organotin oxides and hydroxides.

functional starburst assemblies. In this short review we present some representative examples of novel

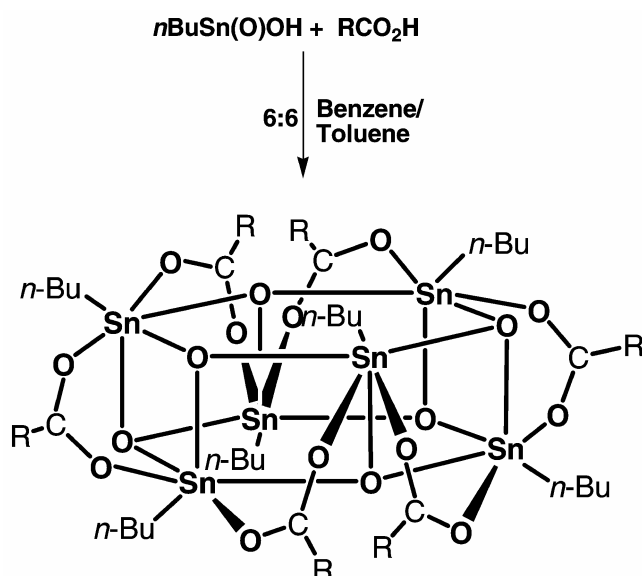
starburst type molecules containing a central stan-
noxane core.³⁰⁻³¹

2. Organostannoxane drums and ladders containing a ferrocene periphery

As a first example to explore the applicability of the paradigm for the simultaneous construction of the core and the periphery, we chose to study the reactions of ferrocene carboxylic acid with organotin oxides and organotin hydroxides. Unlike silicon, organotin oxides and organotin hydroxides are structurally more diverse (chart 1).³⁰

Studies carried out from our laboratory and others,^{32–37} revealed that a 6 : 6 reaction between a carboxylic acid RCOOH and the tin oxide-hydroxide, $n\text{BuSn}(\text{O})(\text{OH})$, affords exclusively a hexameric compound $[\text{nBuSn}(\text{O})\text{OC}(\text{O})\text{R}]_6$ (scheme 2). On the other hand, the main product of a 4 : 4 reaction between $n\text{Bu}_2\text{SnO}$ and a carboxylic acid is a tetrameric compound $[\text{nBu}_2\text{SnOC}(\text{O})\text{R}]_4$ (scheme 3). The hexameric compound is said to possess a drum-type structure. It contains two-fused Sn_3O_3 rings which generate six Sn_2O_2 four-membered rings as the sides of the drum. The entire Sn_6O_6 core is supported by the bidentate coordination action of RCO₂ ligands. In contrast, the tetrameric compound possesses a ladder structure and contains a central Sn_2O_2 ring.

It is clear that while the assembly of the drum requires six carboxylate ligands, the formation of the ladder requires only four. If a ferrocene carboxylic acid is used, in principle, it is possible to assemble hexaferrocene and tetraferrocene architectures in a single step by changing the organotin substrates.



Scheme 2. Synthesis of organostannoxane drum.

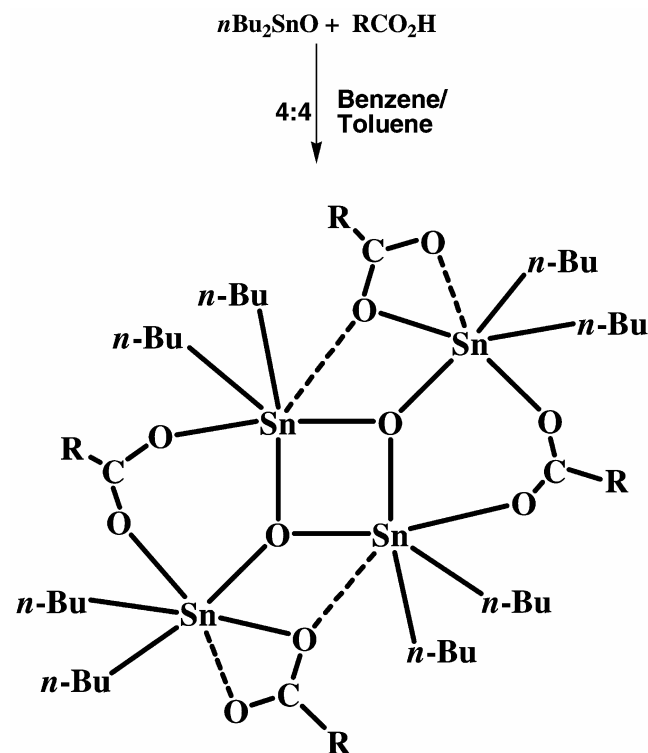
This has been achieved in near quantitative yields (scheme 4).^{38–39}

These compounds represent *inorganic-core supported* multi-ferrocene assemblies. These are electrochemically quite robust and do not decompose under cyclic voltammetric conditions. Utilizing this strategy other multi-ferrocene assemblies were prepared.³⁹ It is to be noted that the nuclearity of the organostannoxanes dictates the number of ferrocenes present in the peripheries (scheme 5).

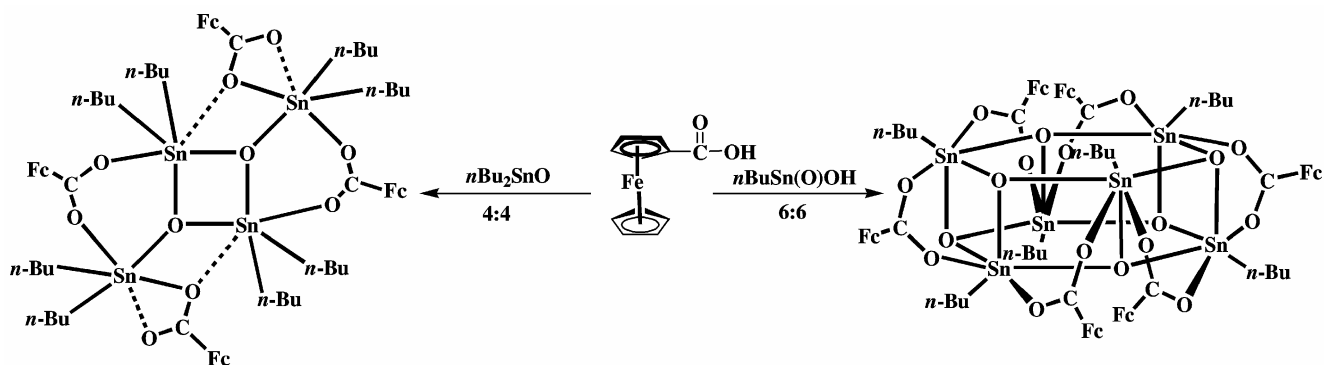
In contrast to the above, the reactions of R_2SnCl_2 ($\text{R} = n\text{Bu}, \text{Bn}$) with ferrocene dicarboxylic acid affords macrocyclic compounds (scheme 6). Cyclic voltammetry of the benzyl derivative reveals two quasi-reversible single electron oxidations at $E_{1/2} = 0.89$ and 1.05 V respectively. By an examination of the comproportionation constant K_c , following the Robin-Day classification, the benzyl derivative can be placed in an intermediate class between non-coupled and weakly-coupled systems (figure 1).⁴⁰

3. Multi-photoactive assemblies

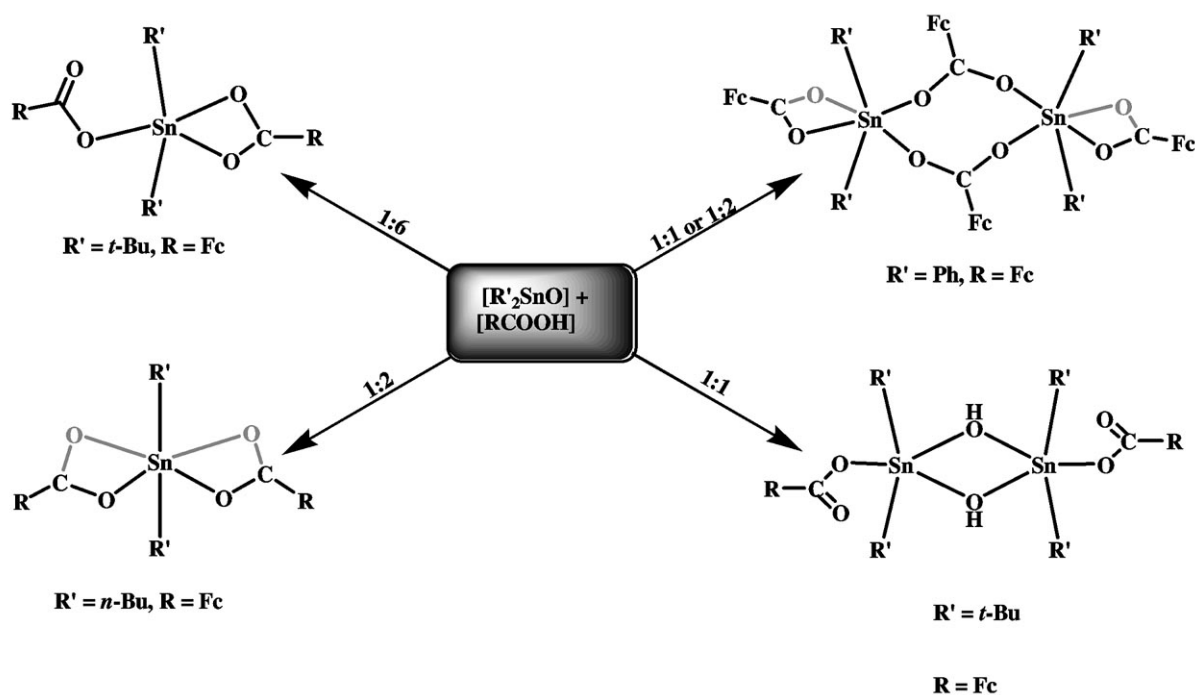
Recent interest in new organic/organometallic^{41–49} luminescent materials prompted us to explore stan-



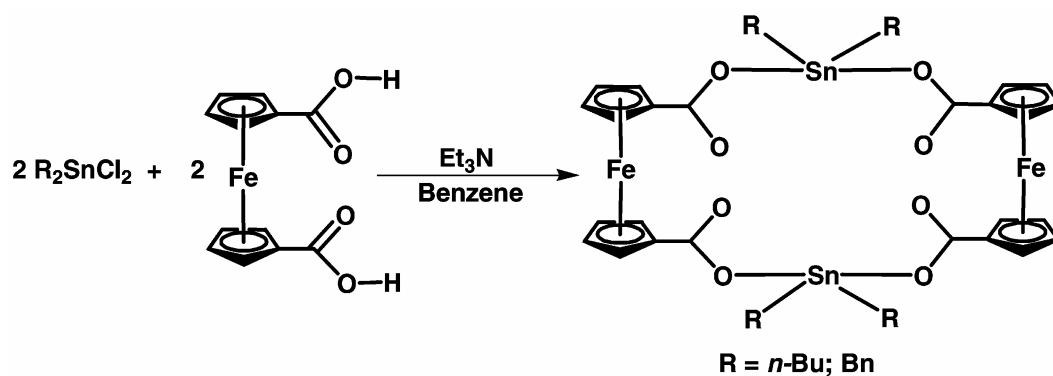
Scheme 3. Synthesis of organostannoxane ladder.



Scheme 4. Multi-ferrocene assemblies supported by organostannoxane frameworks.



Scheme 5. Multi-ferrocene assemblies supported by organostannoxane scaffolds.



Scheme 6. Ferrocene containing macrocycles.

noxane-cored photoactive assemblies. We utilized 1-fluorene carboxylic acid and 9-fluorene carboxylic

acid for preparing a new family of luminescent compounds (chart 2).⁵⁰

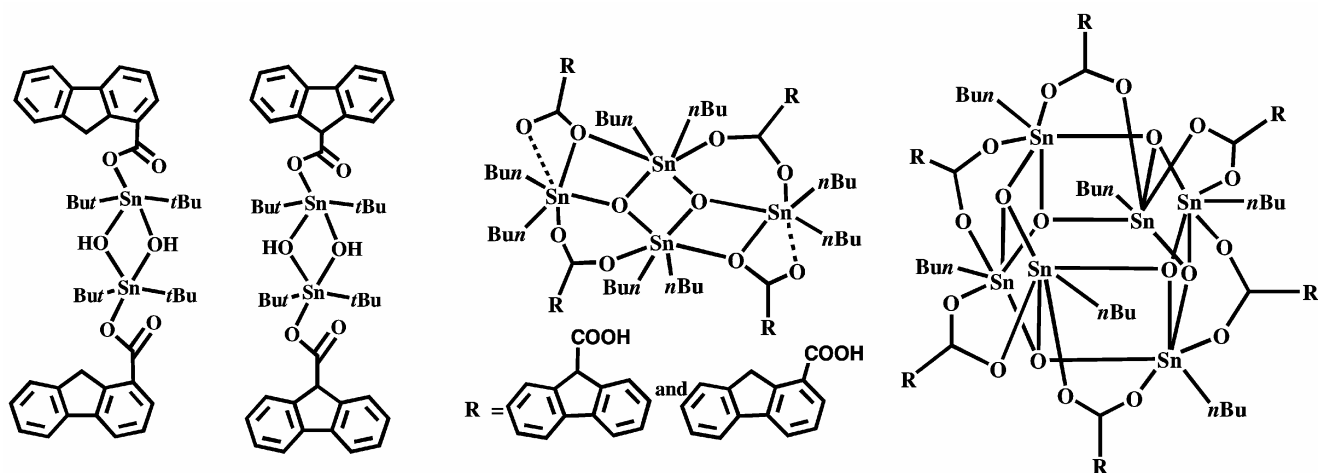


Chart 2. Organostannoxane-supported multi-fluorene assemblies.

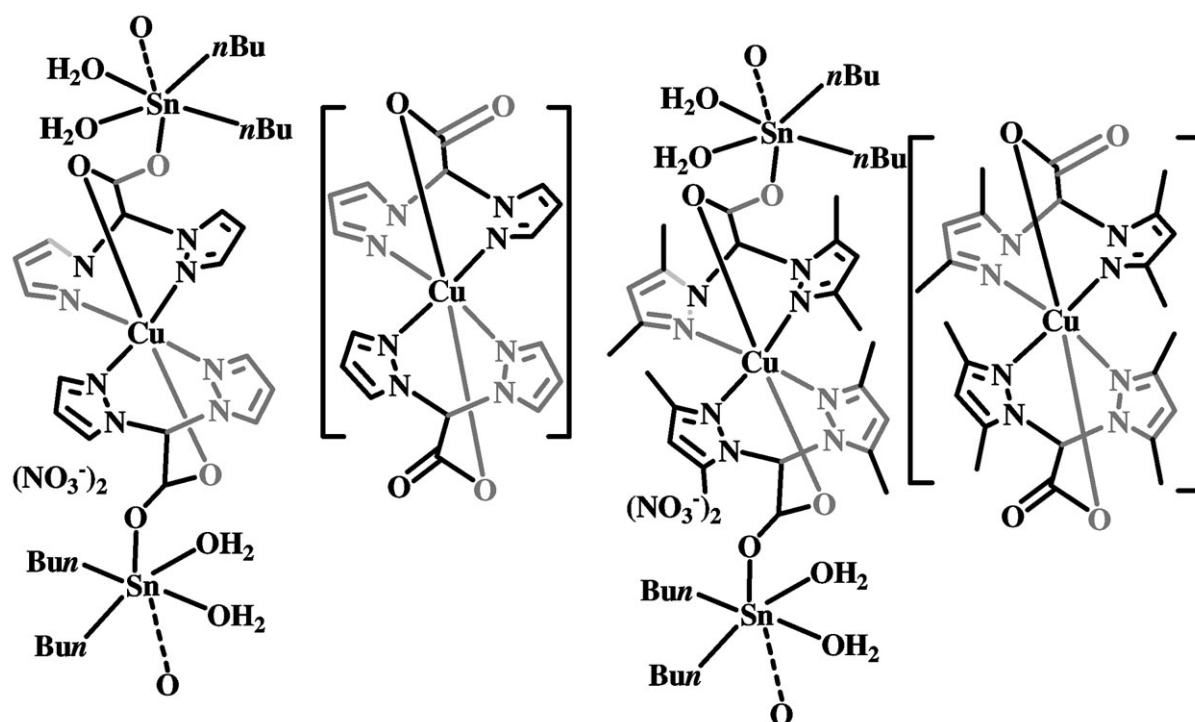
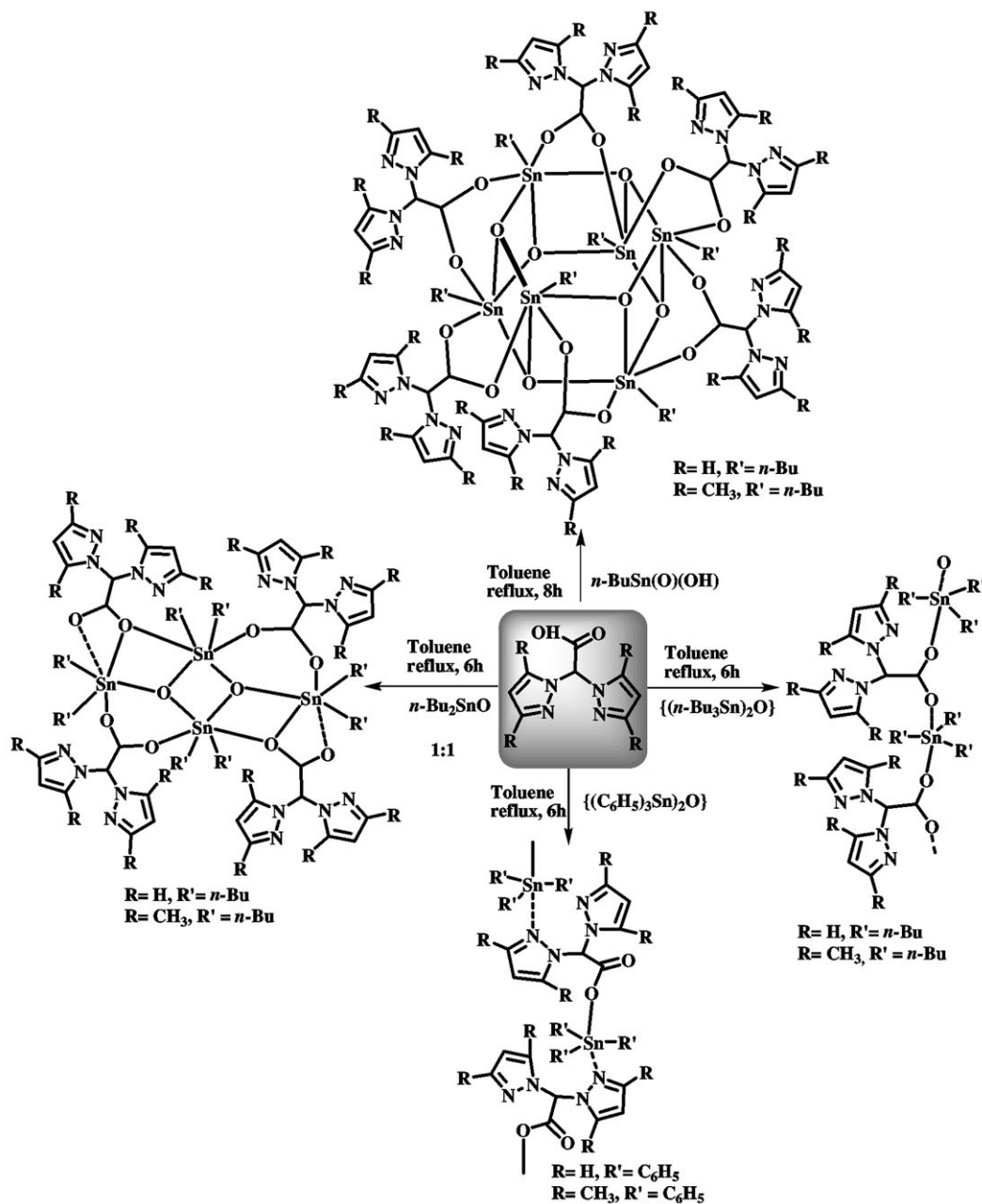


Chart 3. Heterobimetallic coordination polymer.

These organostannoxane-supported multi-fluorene compounds emit quite strongly upon excitation at their maximum absorption wavelengths. These are good blue emitters (emission maximum between 330 and 410 nm). Interestingly, in solution, the fluorescence life times of all of these compounds are in the nanosecond time scale suggesting that the emission originates from the singlet excited state to the ground state.

The thin film photoluminescence spectra of these multi-fluorene compounds show slight to moderate red shifts in comparison to the solution-state; the largest bathochromic shifts are observed for the hexafluorene derivatives (figures 2 and 3). These red shifts have been correlated with the non-covalent intermolecular interactions found in the solid-state supramolecular structures of these compounds.



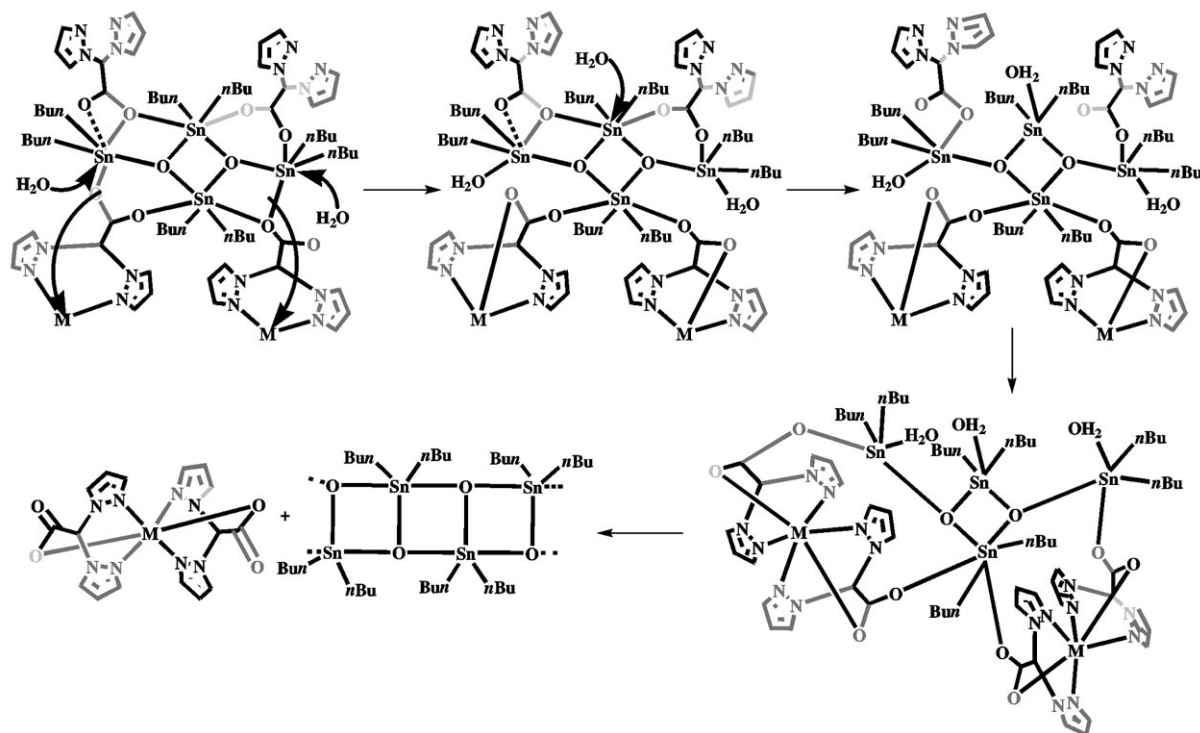
Scheme 7. Organostannoxane-supported multi-site coordination ligands.

4. Multi-site coordination ligands

The inertness of the stannoxane cores makes these as good platforms to build multi-site coordination ligands. Accordingly, the reaction of bis(pyrazol-1-yl)acetic acid and bis(3,5-dimethylpyrazol-1-yl)acetic acid with various organotin substrates afforded a large variety of multi-site coordination ligands containing the pyrazole coordination units (scheme 7).⁵¹

The reactions of these potentially multi-site coordination ligands such as $[\{n\text{Bu}_2\text{SnOC(O)L}\}_2\text{O}]_2$ and $[n\text{BuSn(O)OC(O)L}]_6$ [$\text{L} = (\text{Pz})_2\text{CH-}$ and $3,5\text{-Me}_2\text{Pz}_2\text{CH-}$] with hydrated metal salts led to the hydrolysis of the organotin carboxylates. The liberated carboxylate ligands bind to the metal ion to form homoleptic complexes such as $\text{Cu}(\text{O}_2\text{CL})_2$ (scheme 8).

Interestingly, in the reaction of $[\{n\text{Bu}_2\text{SnOC(O)L}\}_2\text{O}]_2$ with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ we were able to



Scheme 8. Hydrolysis of $\{n\text{Bu}_2\text{SnOC(O)L}\}_2\text{O}_2$ and formation of $\text{M}(\text{O}_2\text{CL})_2$ [$\text{L} = (\text{Pz})_2\text{CH}^-$; $\text{M} = \text{Cu}(\text{II})$ and $\text{Mg}(\text{II})$].

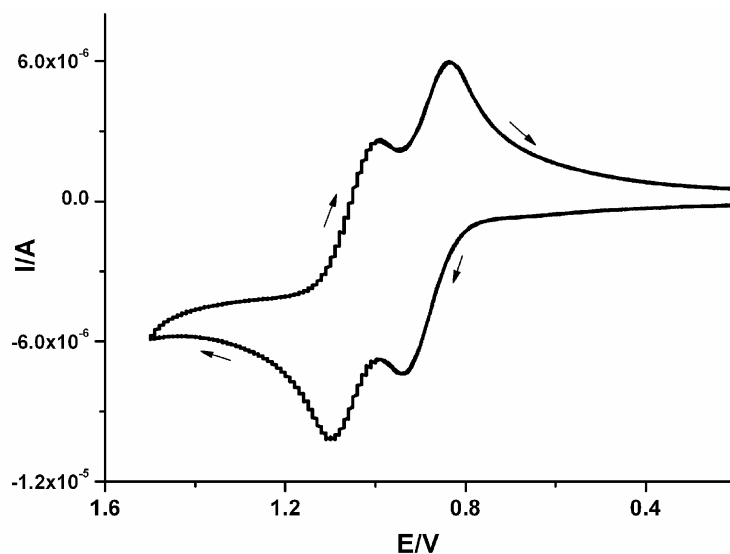


Figure 1. Cyclic voltammogram of ferrocene-containing heterobimetallic macrocycles.

isolate a heterobimetallic coordination polymer (chart 3).⁵²

This coordination polymer represents an intermediate compound before the formation of the fully hydrolysed product.

5. Conclusion

The synthesis of well-defined organostannoxane assemblies provides a viable synthetic route for the preparation of a number of new and interesting den-

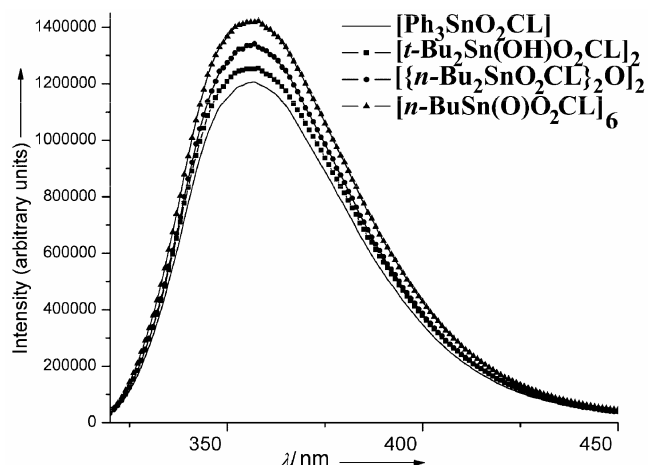


Figure 2. Solution-state normalized emission spectra of multi-fluorene assemblies in chloroform.

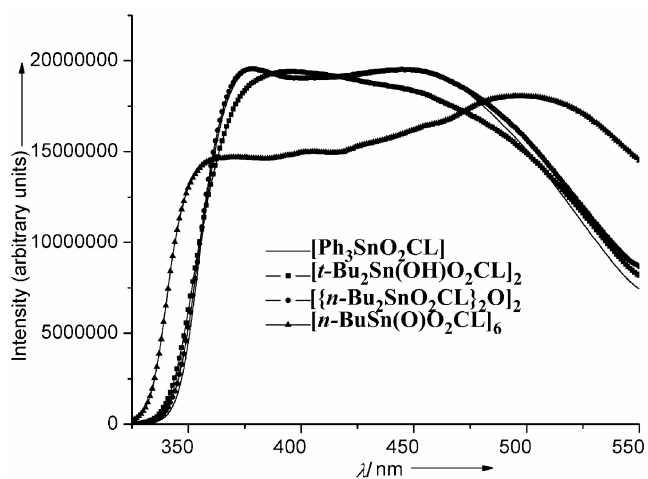


Figure 3. Solid-state normalized emission spectra of multi-fluorene assemblies.

dimeric molecules. Proper choice of the organotin substrates and carboxylic acids allows the preparation of 'designer' dendrimers containing a range of functional peripheries. As a proof of this principle we have demonstrated the synthesis of multi-electroactive, multi-photoactive and multi-site coordination ligands. We are exploring various other applications of this general synthetic paradigm.

Acknowledgement

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