

Caltech-MURI – Technical Section Weck Group

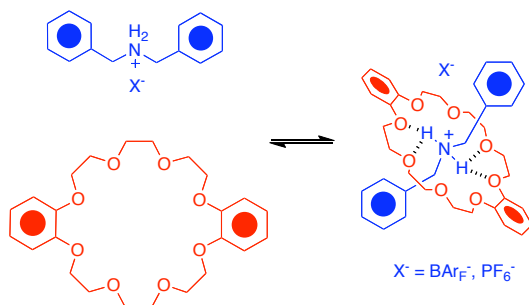
The aim of the Caltech MURI as written in the abstract is to 'to develop the next generation of materials for DoD applications, by combining self-assembly, template-directed synthesis, soft lithography, and selective deposition techniques to make macromolecules with unprecedented control over structure and functionality'. Over the past five years, the Weck group has made significant progress in synthesizing and fabricating sequence controlled macromolecules, employing the concept of templation to polymers, tuning the properties of highly functionalized and sequence controlled macromolecules, and finally synthesized sequence controlled

macromolecules for organic light emitting diode applications. The research carried out through the MURI grant led to three review articles.^{1,2,3}

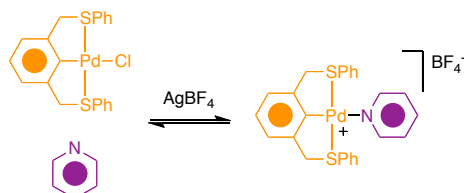
1. Synthesis of sequence controlled copolymers for functionalization via self-assembly

Materials for applications such as organic-light emitting diodes (OLEDs), photorefractives, solar cells, drug delivery vehicles, and sensors will require fast and cost effective synthesis and optimization. To meet these demands, future synthetic strategies to produce polymeric materials should be generic, such that similar functionalization techniques could be applied to a variety of applications. Nevertheless, these functionalization strategies must be tailored to the specific application in mind. For example, a drug delivery application may require functionalities with weak noncovalent attachments in order to facilitate effective drug release in

Pseudorotaxane Formation:



Metal Coordination:



Hydrogen Bonding:

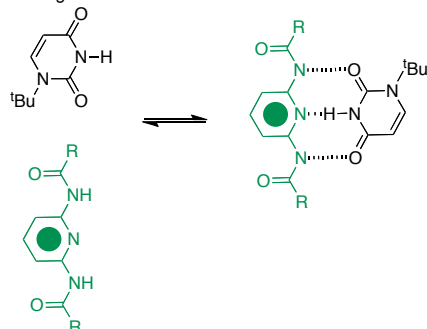


Figure 1. Recognition motifs employed.

¹ "Modular and Dynamic Functionalization of Polymeric Scaffolds" Clinton R. South, Caroline Burd, and Marcus Weck* *Acc. Chem. Res.* **2007**, *40*, 63-74.

² "Multifunctionalization of Synthetic Polymer Systems via Self-Assembly" Warren Gerhardt, Matija Crne, and Marcus Weck* *Chem. Eur. J.* **2004**, *10*, 6212-6221.

³ "Non-Covalent Side-Chain Polymers: Design Principles, Functionalization Strategies, and Perspectives" Joel M. Pollino and Marcus Weck* *Chem. Soc. Rev.* **2005**, *34*, 193-207.

response to a stimulus at a target site. In contrast, materials such as electro-optics require strong and dense functionalization capable of withstanding thousands of working hours.

In collaboration with the Stoddart and Grubbs groups at Caltech and UCLA, we have made significant progress towards the above-described goal of a modular multifunctionalization of copolymers using self-assembly by synthesizing a series of AB and ABC block as well as random copolymers based on poly(norbornene). The employed norbornene monomers contained either Sulfur-Carbon-Sulfur (SCS) palladated pincer complexes, dibenzo[24]crown-8 (DB24C8) rings, or diaminopyridine moieties in their side-chain (the recognition units utilized are shown in Figure 1). All monomers could be polymerized via ring-opening metathesis polymerization (ROMP) using either Grubbs' first or third generation initiators and we demonstrated that the ROMP of all monomers precedes in a living fashion. We have also synthesized copolymers based on either two or three norbornene monomers and studied their functionalization via self-assembly (Figure 2). The molecular weights of all copolymers range from 10 000 to 100 000 and the polydispersities are between 1.08 to 1.50.

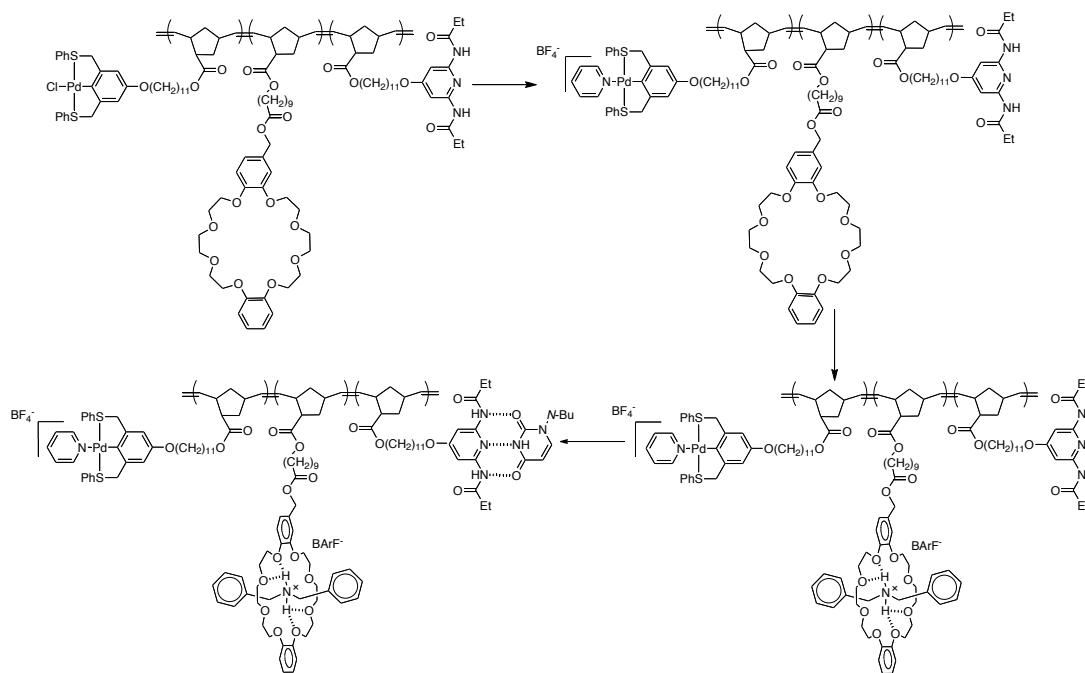


Figure 2. Stepwise self-assembly of a terpolymer using noncovalent interactions.

Using a battery of techniques including ^1H NMR spectroscopy, IR spectroscopy, UV spectroscopy, and isothermal titration calorimetry, we have demonstrated that all three recognition motifs are orthogonal to each other and that the recognition events are independent of the polymer backbone.⁴⁵

⁴ "Self-Assembly With Block Copolymers Using SCS Pd(II) Pincer Metal Coordination and Pseudorotaxane Formation" Clinton R. South, Mary Nell Higley, Ken C.-F. Leung, Daniela

2. Template polymerizations

We have also investigated the employment of noncovalent as well as dynamic covalent interactions in template polymerization. An important goal in synthetic polymer chemistry is to both understand and potentially harness Nature's templation strategies to produce abiotic polymers with controlled lengths, tacticities, and sequences. We have studied the template enhanced ROMP of a norbornene-based thymine monomer. The template, based on

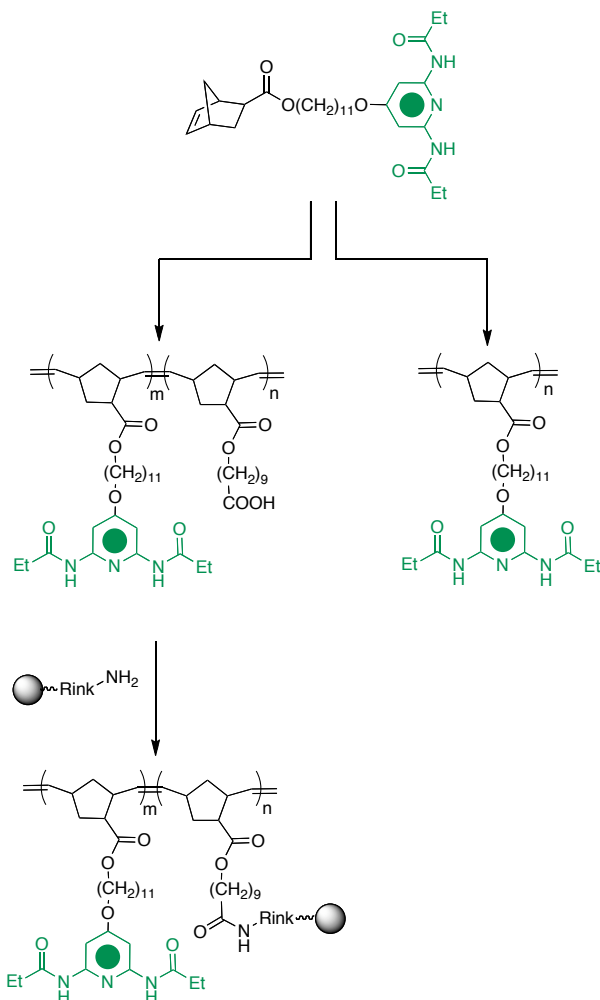


Figure 3. Synthesis of solid-supported and soluble templates.

functionalized norbornenes that are designed to recognize thymine substrates with high fidelity, was synthesized via ROMP (Figure 3). The resulting template was used to harness the polymerization of the thymine monomer producing a bis-poly(norbornene) complex. Using ¹H NMR spectroscopy, we determined that the polymerization conditions do not disrupt the hydrogen bonding. In addition, the template enhances the rate of the polymerization by inducing an increase in local monomer concentration. To examine whether the polymerization is controlled, we synthesized a solid-supported diaminopyridine template (Figure 3). After the polymerization off this solid-supported template, we extracted the daughter polymer from the support. Detailed analysis of the daughter template proved that the templated polymerization was controlled, and that the supported template produces a well-defined daughter polymer.⁶

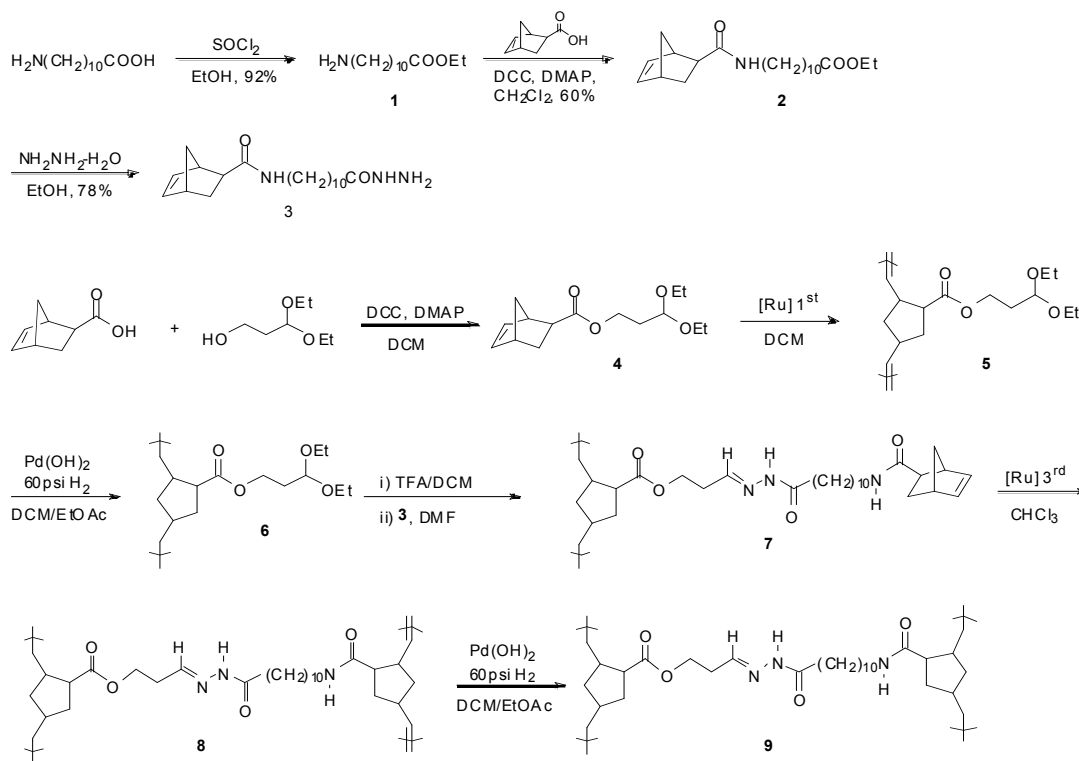
We then concentrated our

Lanari, Alshakim Nelson, Robert H. Grubbs*, J. Fraser Stoddart*, and Marcus Weck* *Chem. Eur. J.* **2006**, *12*, 3789-3797.

⁵ "Noncovalent Side-Chain Functionalization of Terpolymers" Clinton R. South, Ken C.-F. Leung, Daniela Lanari, J. Fraser Stoddart,* and Marcus Weck* *Macromolecules* **2006**, *39*, 3738-3744.

⁶ "Template Enhanced Ring-Opening Metathesis Polymerization" Clinton R. South and Marcus Weck* *Macromolecules* **2007**, *40*, 1386-1394.

efforts on synthesizing covalent-based templates. In particular, we synthesized hydrazide and aldehyde-containing norbornenes starting from 11-aminoundecanoic acid (Scheme 1). ROMP of the resulting monomers yielded polymers ($M_n = 6\,000$, PDI = 1.33) which was subsequently hydrogenated to yield the fully saturated poly(norbornene) backbone. The daughter monomer was then attached to the aldehyde-containing poly(norbornene) template to form the corresponding hydrazone attached monomer which was then polymerized quantitatively using Grubbs' third-generation initiator in chloroform. However, isolation of the daughter/template polymers was not possible due to solubility problems which we attributed to the cross-linking resulting from the poly(norbornene) double bonds and residual initiators. In order to overcome this problem, hydrogenation on poly(norbornene) backbones of the daughter polymers was attempted to yield fully hydrogenated double stranded poly(norbornene). Unfortunately, also this ladder polymer was insoluble in common organic solvents precluding characterization.



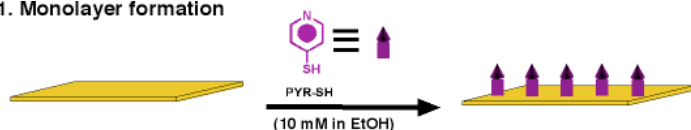
Scheme 1. Attempted templation of polymers using dynamic covalent bonds.

3. Surface functionalizations

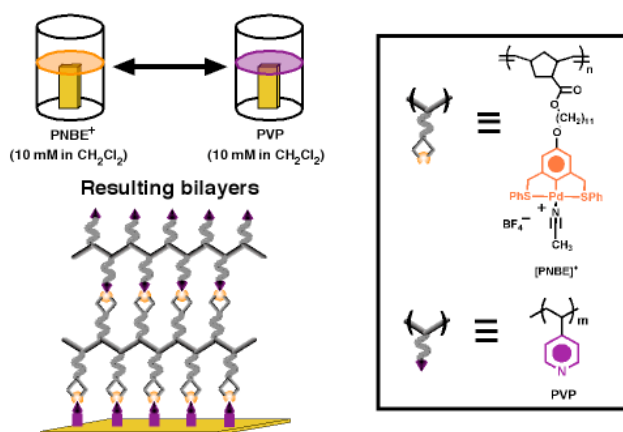
Based on the initial studies on the orthogonality of noncovalent recognition units, we have started to employ the methodology described above for surface functionalization. In particular, we employed metal coordination as the key noncovalent interactions. In a recent *Angewandte Chemie* article, we reported the use of reversible coordination chemistry to assemble polymer multilayers on gold

surfaces.⁷ Such multilayers have potential application ranging from drug delivery to electro-optics. Our system (i) provides for uniform film deposition and control of multilayer thickness, (ii) allows for the integration of diverse polymer components embedded in alternating polymer bilayers, and (iii) affords stable, yet responsive multilayers that can be manipulated by chemical means using competing supramolecular interactions. Our system combines the advantages offered by covalent multilayers, metal-bound multilayers, and PEMs by using strong, yet reversible noncovalent metal-ligand interactions to create a new class of

1. Monolayer formation



2. LbL deposition of SPM



Scheme 2. Surface functionalization strategy using metal coordination and poly(norbornene)s.

polymer with a metal complex on each repeating unit. The acetonitrile coordinated to the Pd(II) pincer complexes along the polymer can be displaced quantitatively by pyridine (Scheme 2) such as poly(vinyl pyridine) ($M_w = 20,000$).

Upon exposure of the pyridyl functionalized surface to the pincer complex containing polymers, the acetonitrile ligands on the Pd(II) pincer complexes along the polymers are quantitatively and instantaneously displaced by surface pyridines forming a polyvalent layer upon which multilayers can be built. CoPM buildup then proceeded by simple alternation of **PVP** and **PNBE⁺** solution treatments (Scheme 2). Using this simple methodology, we were able to fabricate SPMs based on coordination chemistry with up to 25 bilayers in less than three hours. The multilayer buildup was monitored by UV-vis absorption spectroscopy and surface heights were measured using ellipsometry and AFM (Figure 4). In all cases, we observed linear trends between surface height and bilayer number for both even and odd (**PNBE⁺-PVP**)_n bilayers suggesting a linear growth of these multilayer systems.

⁷ "Erasable Supramolecular Polymer Multilayers on Gold" Clinton R. South, Victor Piñon III, and Marcus Weck* *Angew. Chem., Int. Ed.* **2008**, 47, 1425-1428.

The SPMs produced in this fashion rival the stability of covalent multilayers, while retaining the responsiveness of PEMs. These appealing characteristics of our

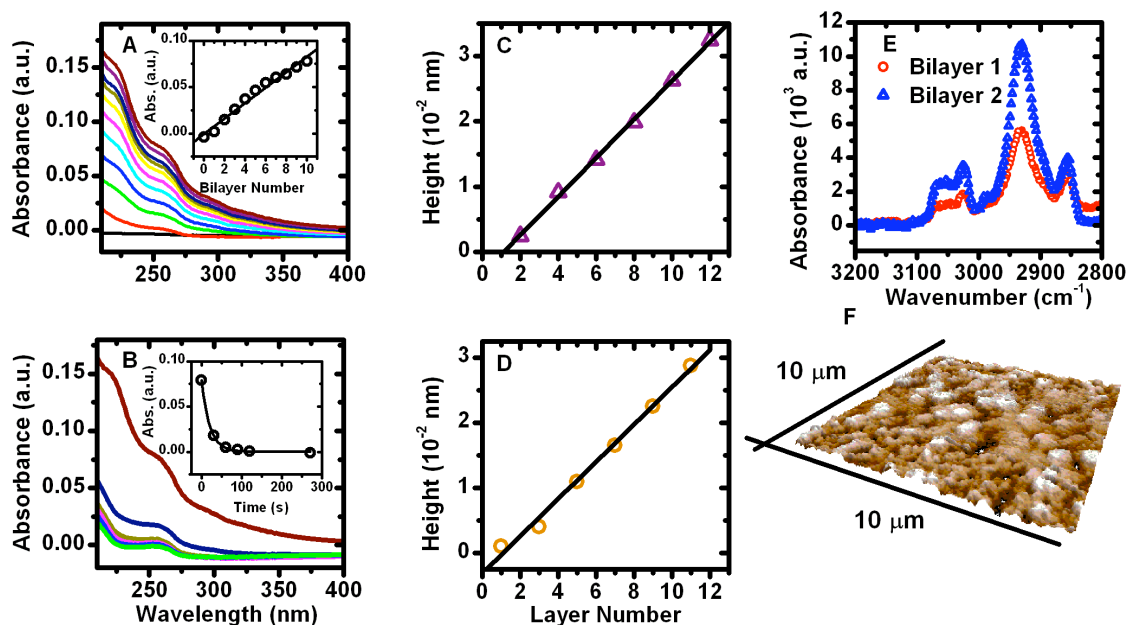


Figure 4. A) UV-vis absorption spectra for SPM buildup taken at every bilayer $(\text{PNBE}^+-\text{PVP})_n$ on a 20 nm Au layer deposited on quartz. The inset plot displays absorbance intensity at 254 nm vs. bilayer number; $R^2 = 0.98$. (B) UV-vis absorption spectra for SPM breakdown taken over time. The inset plot displays absorbance intensity at 254 nm vs. time. (C and D) Plot of surface height determined by spectroscopic ellipsometry vs. even (C) and odd (D) bilayer number $(\text{PNBE}^+-\text{PVP})_n$; $R^2 = 0.99$. (E) Partial RAS-FTIR spectra displaying absorbance intensity increases observed in the aliphatic C-H stretching region upon bilayer buildup. (F) 3-D AFM image (AC mode, $10 \times 10 \mu\text{m}$) taken in air of an eight bilayer SPM on gold.

system makes coordination chemistry-based SPMs desirable for a variety of applications, specifically, as key materials in optical devices, delivery systems, catalytic systems, and templated synthesis.

We also investigated a combination of **PVP** and a non-polymeric pincer complex.⁸ These studies allowed us to understand the interplay between layer thickness and synthetic methodology. Film properties were found to be dependent on, and could be tuned by varying bath deposition concentrations, polymer molecular weight, and solution additives that compete with binding. Generally, smoother, thinner films were obtained with lower poly(vinyl pyridine) deposition bath concentrations. Likewise, film thickness and roughness could be reduced by employing a higher molecular weight poly(vinyl pyridine). Film properties could also be influenced by using acetonitrile as a solution additive, effectively driving the binding equilibrium slightly toward the free species.

These results suggest that metal coordination films, and perhaps other non-traditional thin films, might be as versatile as the more common poly electrolyte

⁸ "Bridged Coordination Polymer Multilayers with Tunable Properties" Clint R. South and Marcus Weck* *Langmuir* **2008**, *24*, 7506-7511.

multilayers (PEMs). While all of our films were thicker than “molecularly thin” films attainable through poly(electrolyte)s, we view our results as positive, especially given that a seemingly uncooperative deposition system can be tuned easily with various deposition parameters. Additionally, our surface height measurements and analysis should allow to investigate the physical chemistry of polymer deposition when the interaction used is not electrostatic in nature. Many models have been suggested and developed to explain PEMs, particular since PEMs can often be modeled with well-known methods involving electrostatics, but very little work has been completed on understanding more complicated binding modes at surfacial interfaces, such hydrogen bonding and metal coordination.

4. Cross linking studies

In a second study of the applicability of our noncovalent functionalization strategy, we investigated the synthesis and properties of polymeric cross-linked gels.⁹ We reported a novel route to cross-linked and functionalized random copolymers using a rapid, one-step, and orthogonal copolymer cross-

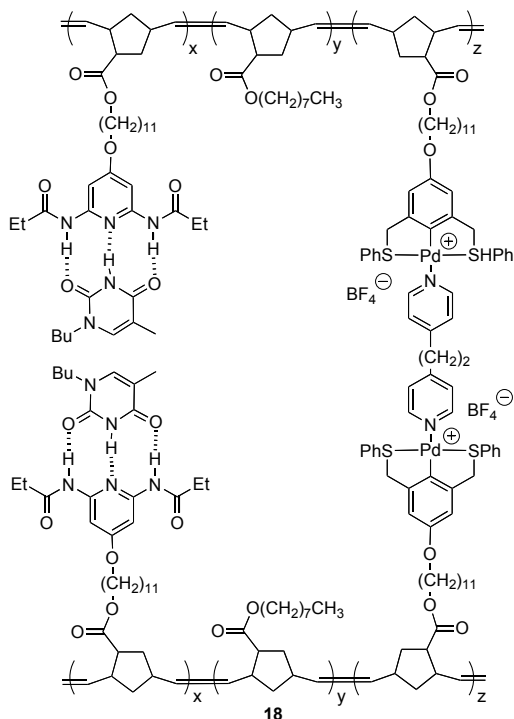


Figure 5. Functionalized and crosslinked poly(norbornene) gel.

functionalized materials with tailored cross-links (Figure 5). This novel non-covalent polymer cross-linking/functionalization strategy allows for rapid and

linking/functionalization strategy has been developed. Random terpolymers possessing high concentrations of pendant alkyl chains and either 1) palladated-pincer complexes and diaminopyridine moieties (DAD hydrogen-bonding entities) or 2) palladated-pincer complexes and cyanuric wedges (ADAADA hydrogen-bonding entities) have been synthesized using ring-opening metathesis polymerization. Non-covalent cross-linking of the resultant copolymers using a directed functionalization strategy leads to dramatic increases in solution viscosities for cross-linked polymers via metal-coordination while only minor changes in viscosity were observed when hydrogen-bonding motifs were employed for cross-linking. The cross-linked materials could be further functionalized *via* self-assembly by employing the second recognition motif along the polymeric backbones giving rise to highly

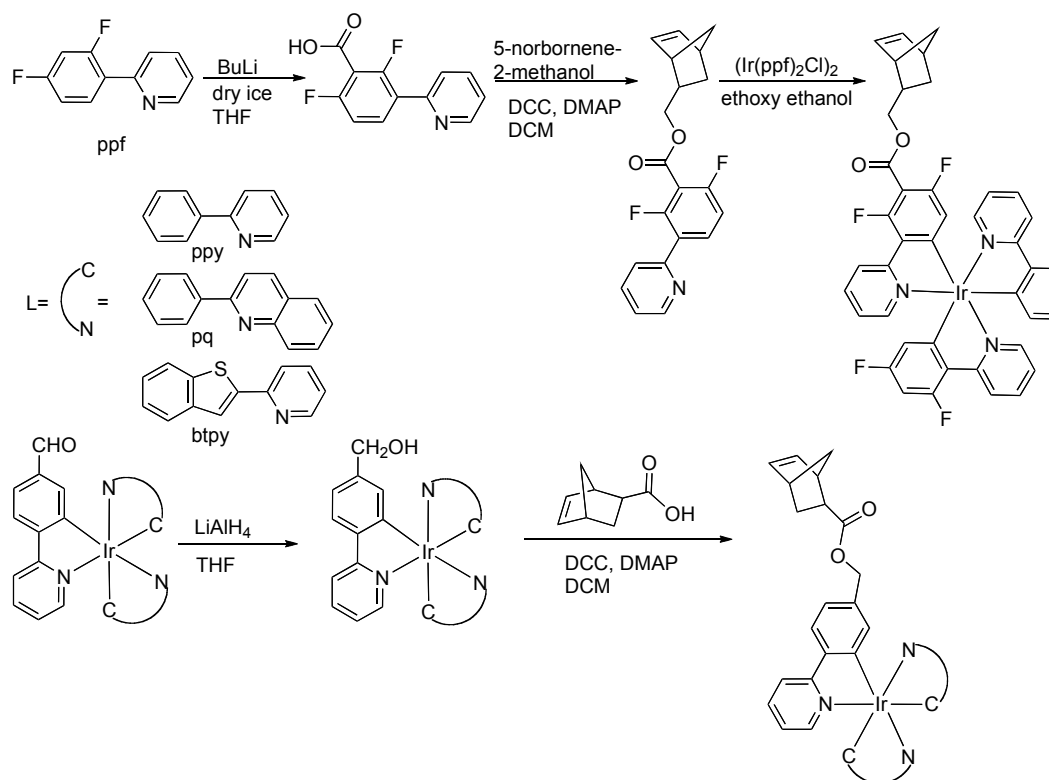
⁹ "Cross-linked and Functionalized 'Universal Polymer Backbones' *via* Simple, Rapid, and Orthogonal Multi-Site Self-Assembly" Joel M. Pollino, Kamlesh P. Nair, Ludger P. Stubbs, Jacob Adams, and Marcus Weck* *Tetrahedron* **2004**, 60, 7205-7215

tunable materials synthesis by overcoming many difficulties inherent to the preparation of covalently cross-linked polymers.

Iridium containing copolymers

Among the applications proposed in the original MURI proposal were organic light-emitting diodes (OLEDs) based on metal complexes. The Weck group in collaboration with the Marder group has prepared a series of iridium containing poly(norbornene) copolymers as novel materials for phosphorescent OLEDs. These copolymers have been investigated as materials for OLEDs by the Kippelen group under the MURI project.¹⁰

In particular, we have reported solution-processable copolymers with pendant phosphorescent iridium complexes and 2,7-di(carbazol-9-yl)fluorene type host moieties synthesized using ruthenium-catalyzed ROMP. The Ir-containing monomer synthesis that was carried out by the Weck group is shown in Scheme 3.



Scheme 3. Synthesis of Ir-containing norbornene monomers.

Low polydispersity indices and molecular weights around 20,000 Daltons were obtained for all copolymers. As a result of the living character of the

¹⁰ "Norbornene-Based Copolymers with Iridium Complexes and Bis(Carbazoyl)fluorene Groups in Their Side-Chains and Their Use in Light-Emitting Diodes" Alpay Kimyonok, Benoit Domercq, Andreas Haldi, Jian-Yang Cho, Joseph R. Carlise, Xian-Yong Wang, Lauren E. Hayden, Simon C. Jones, Stephen Barlow, Seth R. Marder, Bernard Kippelen*, and Marcus Weck* *Chem. Mater.* **2007**, *19*, 5602-5608.

polymerization of the monomer containing the host moiety, a high degree of control over the molecular weights of all copolymers can be obtained. The photo and electroluminescence properties of the copolymers were investigated (Figure 6

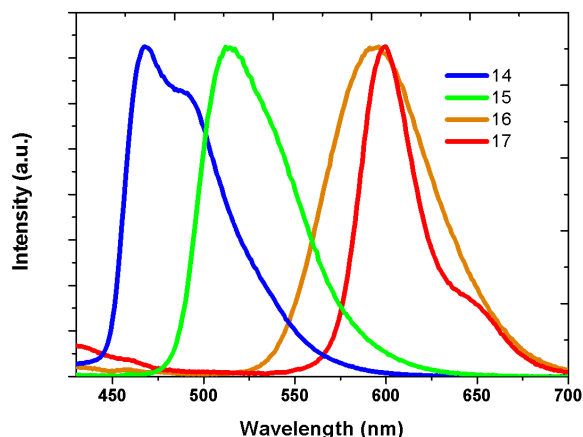


Figure 6. Solid-state photoluminescence emission spectra of all Ir-containing poly(norbornene) copolymers.

shows the solid state photoluminescence spectra of all synthesized copolymers). All copolymers retained the photo- and electrophysical properties of the corresponding non-polymeric iridium complexes. Furthermore, as a proof of principle for the potential use of these materials, organic light-emitting devices were fabricated by the Kippelen using the orange-emitting copolymer. A maximum external quantum efficiency of 1.9% at 100 cd/m² and a turn on voltage of 3.7 V were

obtained with photoluminescence quantum yield of 0.10 demonstrating the potential of these copolymers as emissive materials for display and lighting applications. A more detailed description of the OLED architectures, fabrication and evaluation can be found in the technical report of the Kippelen group.