

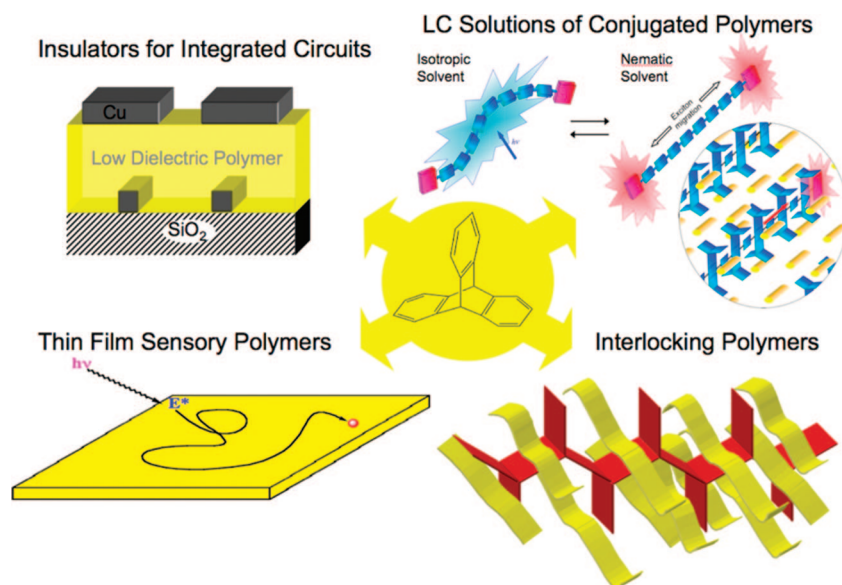
Iptycenes in the Design of High Performance Polymers

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CON SPECTUS



This Account details the use of building blocks known as iptycene units, which are particularly useful in the design of advanced materials because of their three-dimensional, noncompliant structures. Iptycenes are built upon [2,2,2]-ring systems in which the bridges are aromatic rings, and the simplest member of this class of compounds is triptycene. Iptycenes can provide steric blocking, which can prevent strong interactions between polymeric chromophores that have a strong tendency to form nonemissive exciplex complexes. Iptycene-containing conjugated polymers are exceptionally stable and display solution-like emissive spectra and quantum yields in the solid state. This application of iptycenes has enabled new vapor detection methods for ultratrace detection of high explosives that are now used by the U.S. military.

The three-dimensional shape of iptycenes creates interstitial space (free volume) around the molecules. This space can confer size selectivity in sensory responses and also promotes alignment in oriented polymers and liquid crystals. Specifically, the iptycene-containing polymers and molecules align in the anisotropic host material in a way that minimizes the free volume. This effect can be used to align molecules contrary to what would be predicted by conventional models on the basis of aspect ratios. In one demonstration, we show that an iptycene polymer aligns orthogonally to the host polymer when stretched, and these structures approximate molecular versions of woven cloth. In liquid crystal solutions, the conjugated iptycene-containing polymers exhibit greater electronic delocalization, and the transport of excited states along the polymer backbone is observed.

Structures that preserve high degrees of internal free volume can also be designed to create low dielectric constant insulators. These materials have high temperature stability ($> 500\text{ }^{\circ}\text{C}$) and hardness that make them potential interlayer dielectric materials for integrated circuits. In cases where the iptycene structures are less densely spaced along the polymer backbones, interlocking structures can be created. These structures allow for small interpolymer motions, but at large deformations, the steric clashes between iptycenes result in the transfer of load from one polymer to another. This mechanism has the ability to impart greater modulus, strength, and ductility. It is difficult to increase modulus without adversely affecting ductility, and classical high-modulus materials have low ductility. As a result, the use of interlocking iptycene structures is a promising approach to new generations of structural materials.

Introduction

Polymer chemists have long-established design rules for the translation of molecular properties to bulk systems. For example, the low conformational barriers in dimethylsiloxanes give rise to amorphous low T_g silicone rubbers. Main chain polyamides provide for interchain hydrogen bonding and high modulus (nylons). Rigid-rod aromatic structures and liquid crystal processing can produce anisotropic high-modulus structures (*Kevlar*, *Vectra*). It is therefore interesting that three-dimensional shape is seldom used as a dominant design element. Over the last 10 years, my group has been designing new polymers and molecules containing groups that utilize the triptycene motifs,¹ noncompliant three-dimensional structures. We are not the first to be fascinated with this structure, and Hart has synthesized many triptycene variants (aka iptycenes²). In this Account, we emphasize how the unique shape-persistent properties of iptycenes inspire new concepts in the design of functional materials.

One general feature of the iptycene structure is that it prevents efficient packing into pure crystalline lattices, and their crystals tend to be clathrates with included solvent molecules. Conceptually the removal of solvent molecules will introduce empty space (free volume) into the crystalline lattice. To visualize how a triptycene molecule can define free volume, consider inscribing it into a trigonal prism that could be easily packed into a dense crystal. In this construct, the volume between the surface of trigonal prism and the free volume is defined by concave cavities between each pair of adjacent rings (Figure 1).

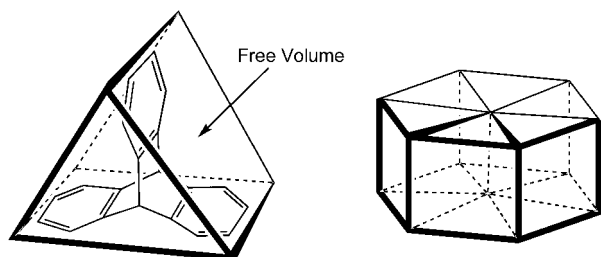


FIGURE 1. Triptycene inscribed in a trigonal prism and organization of prisms into an extended structure.

In this Account, I will detail how iptycenes can be used to design a variety of materials. The range of applications is remarkable and includes design of highly stable fluorescent polymers, sensory materials with size-exclusion characteristics, anisotropic liquid-crystalline materials, low dielectric constant materials, and materials with simultaneously enhanced ductility and modulus.

Amplifying Fluorescent Polymers

Our first demonstration of the utility of iptycenes was in the design of the sensing materials like poly(phenylene ethynylene), **1**.³ Our goal was to design polymers with molecular level porosity, high stability, and high luminescent quantum yields in thin films. A common problem in highly luminescent conjugated polymers is that interchain π - π interactions result in greatly reduced luminescence due to self-quenching. The most common approach to prevent self-quenching is to attach large flexible side chains. However these systems are subject to creep that creates π - π interactions and increased self-quenching. Alternatively, supramolecular and macromolecular approaches have also been developed that effectively insulate polymer chains from each other.⁴ However these approaches generally result in large interpolymer separations that can reduce charge and energy transfer between chains. In contrast, the noncompliant structure of polymer **1** prevents interchain π - π interactions without isolating the chains, and the luminescence efficiency of thin films is not affected by heating or repeated exposure to organic vapors. As shown schematically in Figure 2, the pentiptycene structure creates interstitial galleries capable of hosting planar electron-acceptor molecules like nitroaromatics. Systematic quenching studies on an array of analytes indicate that **1** displays size-selective sensory responses consistent with the structure shown in Figure 2.⁵

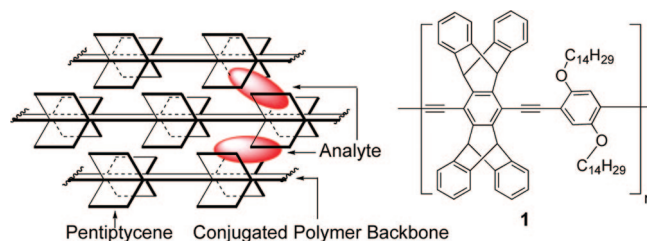
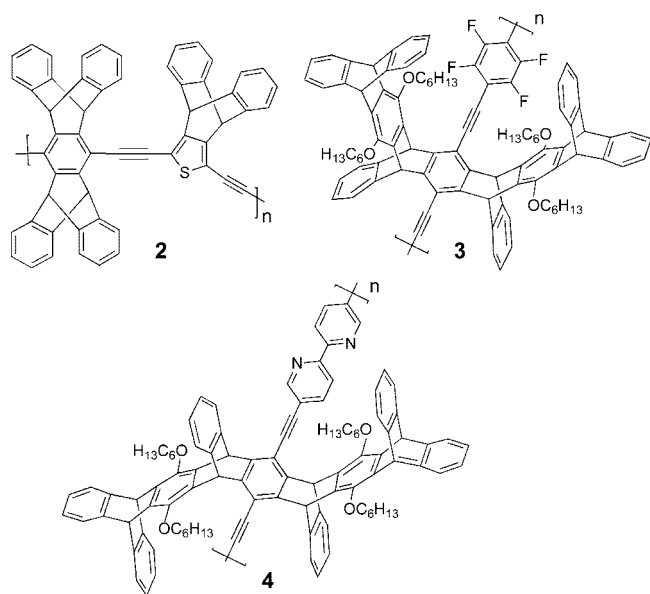


FIGURE 2. Polymer **1** and schematic representation of galleries defined between polymer chains that can host analytes. This polymer is exceptionally sensitive to TNT and related nitroaromatics associated with high explosives.

The extraordinary stability of polymer **1** has enabled the vapor detection of nitroaromatic explosives such as TNT at a distance and is the enabling detection technology for robotic and hand-held explosives sniffers that are presently being used in Iraq and Afghanistan by the U.S. military. This application environment results in sensors being exposed to extreme heat. Although other non-triptycene polymers developed by my group⁶ and others⁷ display similar or even higher sensitivity on freshly prepared films, demanding environmental conditions give self-quenching and greatly decreased performance in non-iptycene materials. Hence, the stability of **1**

provided by the iptycene is critical to its utility in demanding applications.

The avoidance of strong π - π associations between iptycene polymers also results in extraordinary solubility relative to other conjugated polymers. The accepted paradigm for solubilizing conjugated polymers is to adorn them with flexible side chains for an entropically driven solubility or to attach ionic or hydrogen-bonding groups that exhibit strong enthalpic interactions with the solvent. Iptycenes endow **1** with higher solubility than poly(phenylene ethynylene)s containing more than twice the number of side chains (two solubilizing alkyloxy side chains on each phenyl). To test the limits of solubility enhancement, we synthesized conjugated iptycene polymers lacking side chains⁸ and found **2** ($M_n = 22\ 000$) to be completely soluble in methylene chloride at room temperature. Poly(phenylene ethynylene)s containing more elaborated iptycenes, **3** and **4**, are exceptionally good at preventing interchain π - π interactions.⁹ Structures **3** and **4** were synthesized from the respective pure syn and anti stereoisomers of the iptycene comonomers. Electron-deficient tetrafluorophenyl and 2,2'-bipyridyl comonomers in **3** and **4** have a strong tendency to aggregate into weakly emissive excimers due to electrostatically driven π -stacking. However, **3** and **4** show no evidence of excimer interactions or self-quenching in thin film or solution spectra.



Minimization of Internal Free Volume

Liquid crystals (LCs) with high optical anisotropic properties are generally based on structures with high aspect ratios (AR = length/width). Similarly, dye solutes in LCs are known to align best when the dye has a similarly high or larger aspect ratio. Methods to create higher optical anisotropy can give rise to

superior properties for new applications, and we have introduced a new design paradigm wherein iptycene structures promote alignment by minimizing the free volume provided by these structures (Figure 1). As an initial demonstration of this effect, we showed that the anthracene-containing triptycene, **5**, aligns in a contra-aspect ratio fashion relative to the directors (Figure 3).¹⁰

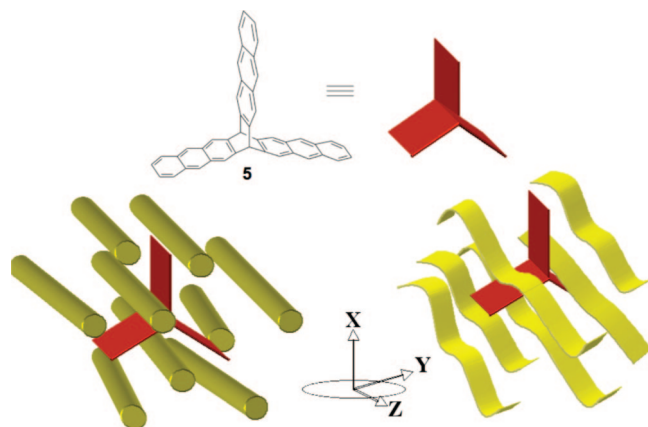


FIGURE 3. Iptycene **5** aligns in LCs and stretched polymers in an orientation that most effectively fills space. This alignment is contrary to what is expected based on aspect ratio, and the short axis (z-direction) aligns with the director of the LC and the stretching direction of the polymer host.

A particularly illustrative example of an iptycene effect is shown in Figure 4, wherein the dye having a lower aspect ratio exhibits a higher order parameter driven by the minimization of free volume.¹¹ This design principle is robust, and provided that the dyes can adopt a favorable conformation that allows efficient filling of the free space around the molecule, the iptycene dyes display greater alignment and enhanced solubility. In some cases, molecules containing iptycenes can organize into dense structures, and we have found that certain structures can display thermotropic LC properties.¹²

Iptycenes can provide the high solubility necessary for the alignment of solutions of high molecular weight poly(phenylene vinylene)s and poly(phenylene ethynylene)s in LCs (Figure 5).¹³ By performing switching experiments in LC test cells, we find that the orientation of the polymer chains, like the LC host, can be controlled with applied electric fields. The ability to create chain extended electronic structures that can be dynamically controlled between electrodes could enable new molecular electronic devices. Relevant to this latter point, the LC solvents promote planar conformations and extended conjugation lengths in dissolved triptycene-based conjugated polymers. In isotropic solutions, conjugated polymers exhibit more disordered conformations that give rise to a distribution of conjugation lengths. However in the case of a LC solu-

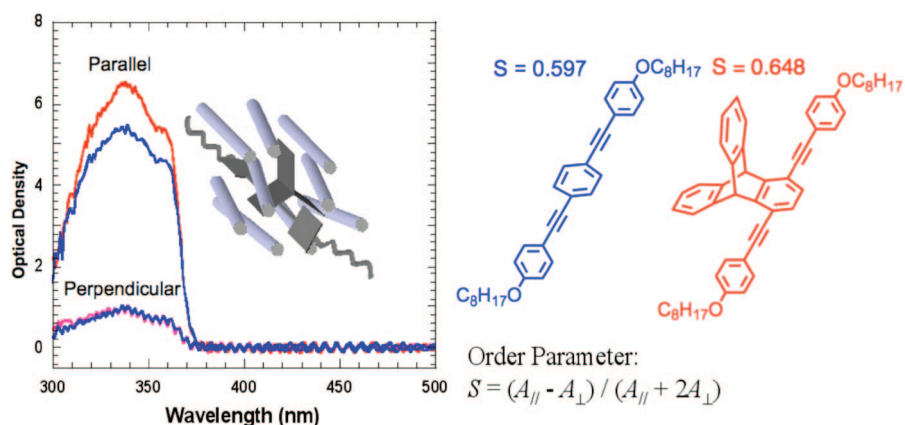


FIGURE 4. Polarized absorption spectra parallel and perpendicular to the director of a homogeneously aligned nematic LC (1 wt % in 4-*trans*-(4-pentylcyclohexyl)benzotriline). Note that the iptycene-containing dye (red) has a higher dichroic ratio and order parameter (S) than the higher aspect ratio dye (blue).

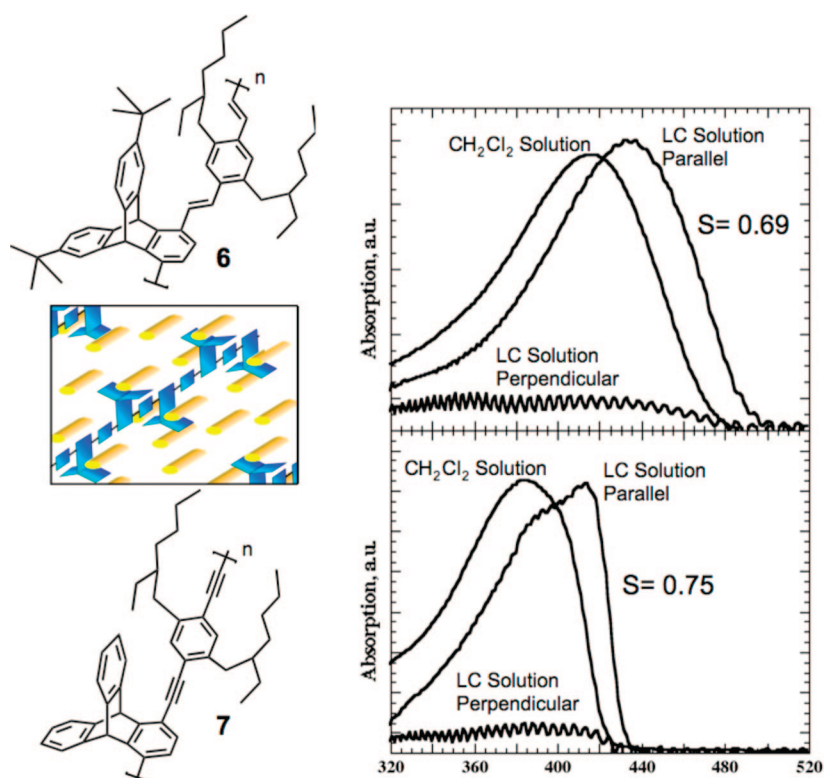


FIGURE 5. Absorption spectra of LC and methylene chloride solutions of a poly(phenylene vinylene), **6**, and a poly(phenylene ethynylene), **7**, demonstrating high order parameters (S). The oscillating nature of the baseline of the absorption spectrum measured perpendicular to the LC director is due to the alignment layers. The shift to longer wavelength in the LC solution is indicative of increased conjugation. LC solvent = 1-(*trans*-4-hexylcyclohexyl)-4-isothiocyanatobenzene; $T_m = 12.4$ °C; $T_{NI} = 42.4$ °C.

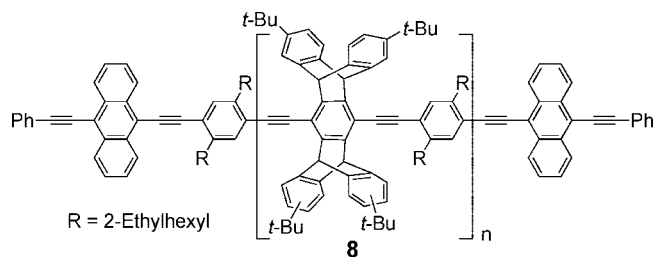
tion of **7**, the measured electronic spectrum resembles a single chromophore with a steep, nearly vertical, absorption edge and vibrational fine structure. The ability to create highly aligned polymers with their transition dipoles aligned along the direction of highest index in reflective cholesteric liquid crystal films has led to the creation of materials with low lasing thresholds.¹⁴

To account for the planarized conformations of conjugated polymers in LC solutions, we postulate that LC mol-

ecules tend to slide along the polymer backbone and have local biaxial character. Higher conjugation length, and the associated increase of the electronic delocalization of the polymer π -electron systems, is generally understood to give optimized transport properties. To demonstrate this effect, we conducted energy migration studies with **8** (Chart 1),¹⁵ which has low band gap anthracenyl end groups.¹⁶ When dissolved in a nematic LC phase, **8** exhibited greatly enhanced quantum yields and energy transfer to the end

groups. The improvement in the fluorescence quantum yield and reduced Stokes shift suggest that in an LC solvent, **8** is held in a more rigid and planar conformation'.

CHART 1



We have examined structure–property relationships to produce optimized interactions between polymer solutes and the LC to create mixtures with enhanced stability and alignment of LCs. Polymer enforced alignment in LC displays has the potential to increase switching times with improved contrast. In these studies, we have developed **9**, which has iptycenes elaborated with anthracene groups that increase the concave surface and the pendant alkoxy phenyl groups to further enhance the interactions with the liquid crystal solvent.¹⁷ As with **6** and **7**, we use branched side chains that exhibit conformations that allow them to align with the hydrocarbon side chains of the liquid crystal solvent. Most interesting, we found that increasing the M_n of **9** produced greater alignment, and a dichroic ratio of 23 was observed for $M_n = 230\,000$ (GPC). The increased degree of alignment suggests that the LC phase as a whole

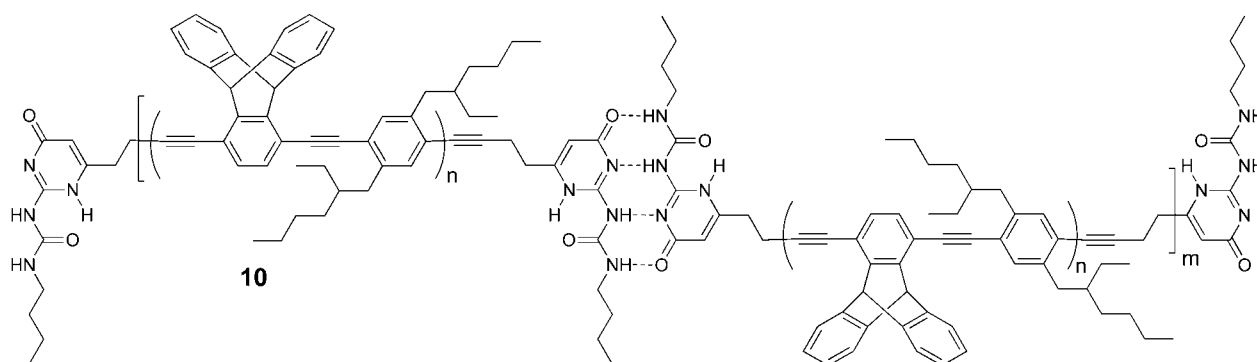
has improved alignment, and this effect is remarkable when considering that the polymer concentrations are less than 0.5% by weight.

To further extend the improvements in alignment with molecular weight, we have developed polymers that can self-assemble into ultrahigh molecular weight materials and gels. Specifically, we have made use of the hydrogen-bonding principles developed by Meijer¹⁸ to create **10** (Chart 2), which reversibly assembles into elongated structures.¹⁹ We find that the extended network formed by the hydrogen bonding nearly doubles the dichroic ratios relative to the non-end-capped materials.

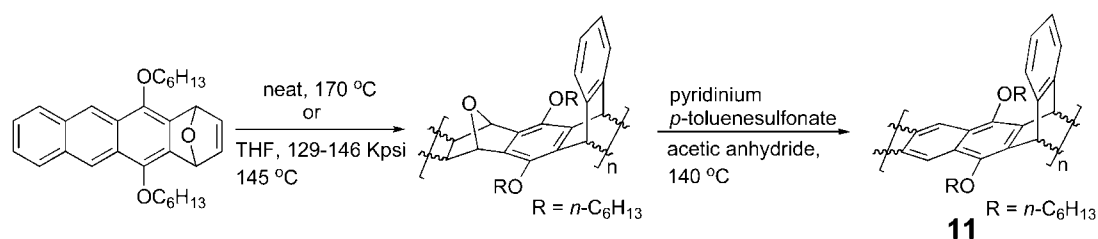
Perhaps the ultimate iptycene polymer is a ladder polymer structure composed purely from iptycene groups²⁰ such as **11**. The backbone of **11** is produced by a Diels–Alder reaction that can be accelerated by high pressure followed by dehydration (Scheme 1).²¹ The polymer displays random stereochemistry due to the roughly equal reactivity of the endo and exo faces of the anthracene subunit in the Diels–Alder reaction. In contrast to conventional wisdom regarding low solubility of rigid shape-persistent polymers, **11** ($M_n = 16\,000$) exhibits high solubility in common organic solvents.

The iptycene-containing ladder polymer **12** (Figure 6) was examined for alignment in stretched polyvinylchloride.²² Neutron scattering experiments revealed that **12** displays a porous disk shape in solution as illustrated in Figure 6. Considering its shape, one might expect that this mate-

CHART 2



SCHEME 1



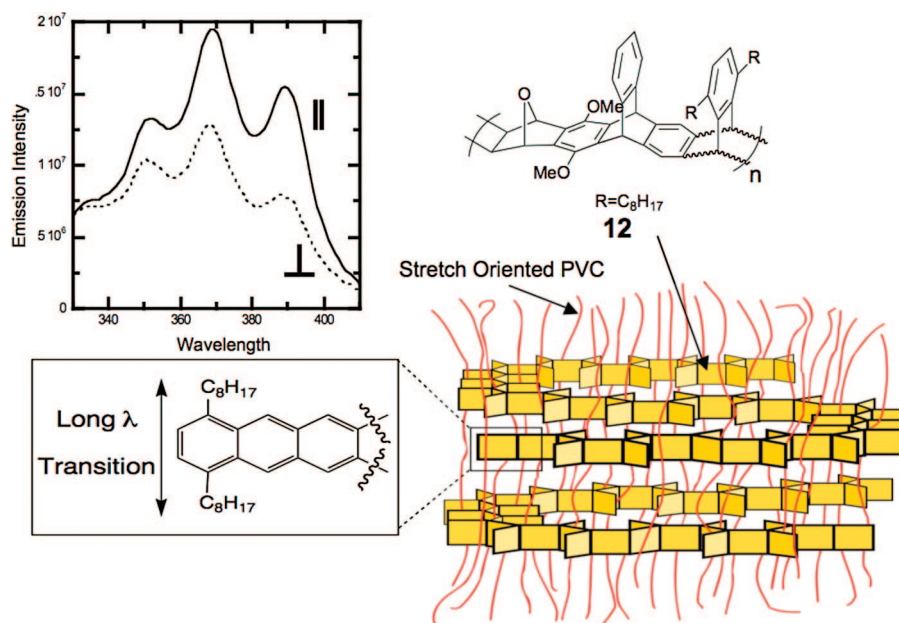


FIGURE 6. Disc-shaped **12** as a guest in poly(vinyl chloride) aligns with its long axis perpendicular to the direction of stretching. The anthracene endgroups are used to determine the orientation and the larger 0,0 absorption parallel to the stretching direction reveals the alignment is as shown.

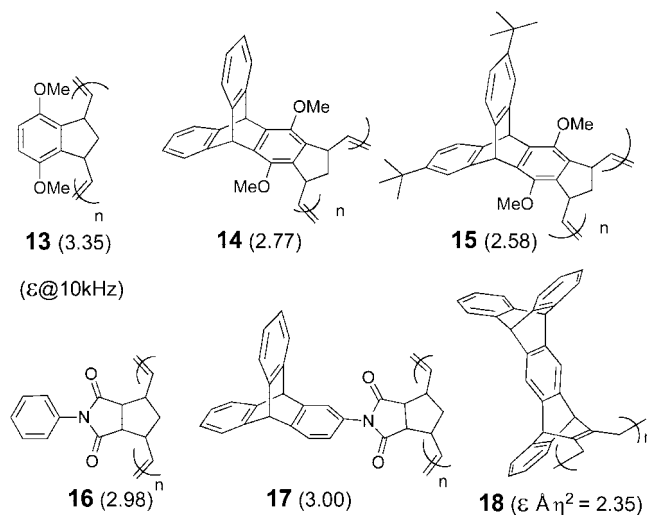
rial would align with his longest axis (the plane of the disk) along the stretching direction. However, such an orientation would result in large amounts of free volume. The free volume is minimized when the polymer aligns with its short axis along the direction of the stretching and its long axis perpendicular to the axis (Figure 6). The ability to align guest polymers in perpendicular directions by simple uniaxial stretching is unprecedented, and the implications are many. One exciting possibility is that this method effectively allows for the spontaneous weaving of two polymers into an architecture that resembles “molecular cloth”.

Low Dielectric Constant Materials

Continued reductions in the feature size of integrated circuits require the closer placement of connective wires. As a result, decreasing feature size increases the capacitive coupling of signals between neighboring wires, which produces delays and slower computational speeds. Consequently, there is great interest in interlayer dielectrics with low dielectric constants to reduce the capacitive cross talk and thereby increase the speed of the integrated circuits. Vacuum ($\epsilon = 1$) is by definition the best insulator, and the best insulating materials are those that can create empty space, effectively vacuum, in their structures. It is also necessary that the dielectric maintains the structural integrity necessary to hold multiple layers of interconnecting wires in place over a broad temperature range. We considered iptycene structures as ideal candidates for these applica-

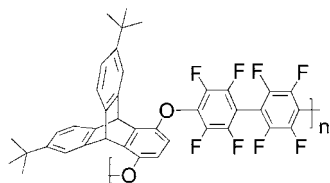
tions because they define free volume, are extremely stable, and are rigid noncompliant structures that can provide a high modulus. To initially examine this concept, we analyzed the dielectric constants of a series of polymers and copolymers synthesized by ring-opening metathesis polymerization (ROMP) (Scheme 2).²³ These structures revealed that for the triptycene to give a reduction in the dielectric constant it must be fused to the polymer backbone in a two-point connection such that it is orientationally constrained. To illustrate this point, we find that the addition of the triptycene in **14** decreases ϵ relative to the non-triptycene analog **13**. The *t*-butyl groups attached to the tripty-

SCHEME 2



tycenes in **15** further lowering the dielectric constant by effectively expanding the dimensions of the concave surface. However, a one-point attachment of triptycenes is ineffective as illustrated by comparisons of **16** and **17**, because the triptycene is allowed to reorient relative to the polymer backbone, thereby giving dense packing with no reduction in the dielectric constant. More elaborate triptycene structures such as that in structure **18**, synthesized by a free radical polymerization of a precursor diene, define even greater free volume.²⁴

The polymers previously discussed served to define key design considerations. However, for applications in semiconductor electronics, the materials must have high thermal stability and a high glass transition temperature (T_g). These parameters are satisfied in triptycene-containing poly(arylene ether)s, and we have produced a series of these materials that have thermal stabilities of 500 °C and higher. The materials also have excellent hardness with T_g 's higher than their decomposition temperatures. Polymer **18** is a representative example of these materials and is synthesized by a condensation reaction between the di-*t*-butyltriptycene hydroquinone and decafluorobiphenyl. The complete room temperature solubility of **18** in CH_2Cl_2 and a T_g greater than 500 °C is a testament to the unique combinations of properties that can be imparted by triptycenes. These properties in addition to a low dielectric constant at relevant frequencies make **18** a promising interlayer dielectric material.



19 $\epsilon = 2.1$ at 4 GHz

Mechanical Enhancements from Triptycenes

Ultrahigh modulus polymers generally utilize strong interchain associations, usually in the form of hydrogen bonds, to create a very stiff fiber.²⁵ These fibers are generally brittle and break at low strains. To create useful articles, like bullet-proof vests, high modulus polymers are woven into a cloth, and the strain resulting from an impact is distributed over an extended area. We rationalized that interlocking molecular structures could, like a woven material, be used to create materials with high strength. In addition, if the polymer chains are allowed to have some degree of freedom to slide by each other, then the system can also exhibit high ductility. Increased modulus

and ductility are generally mutually exclusive in materials design, and remarkably iptycenes can simultaneously enhance both.

The concept for improved mechanical properties is illustrated in Figure 7, wherein a polymer having lower densities of triptycene groups than discussed previously is arranged with in a dense structure.^{26,27} In the absence of strong associations between the polymer chains, the material is deformable. However, at high deformation (strain), the triptycenes begin to bump into each other and transfer the load between chains. To test this concept, iptycene polyesters **21–23** (Chart 3) were studied over multiple compositions (x and y varied), and comparisons between these materials and the parent non-iptycene polyester **20** provide evidence that the role of the interlocking structure (Figure 7) is the origin of superior mechanical properties.

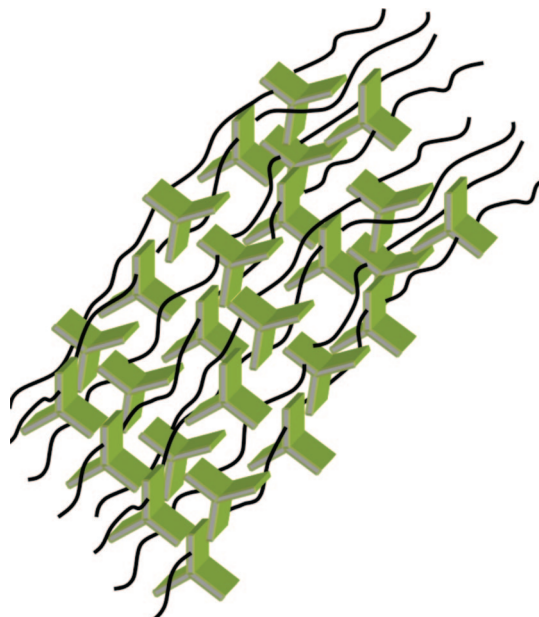
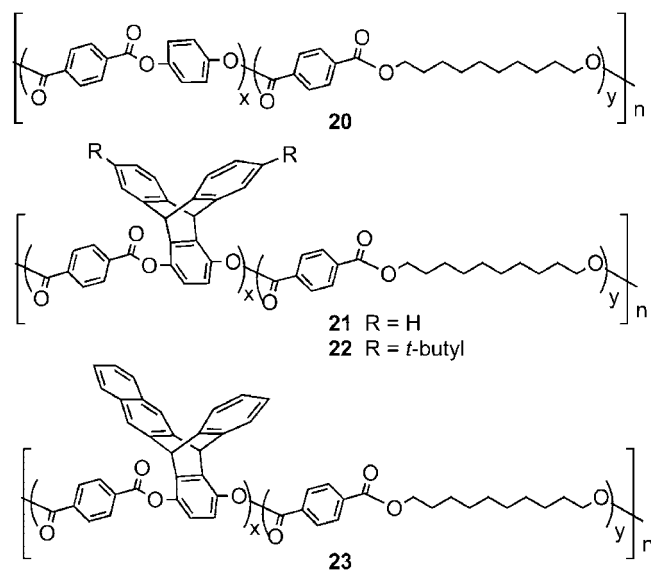


FIGURE 7. Schematic representation of a polymer with triptycene groups separated by small flexible segments. The structure assembles in a way to minimize free volume and fill the concave clefts of the triptycene groups.

The stress–strain curves for all of the iptycene-containing polymers displayed three distinct regions as shown for **21** in Figure 8. It is readily apparent that the iptycene effect simultaneously improves all aspects of the polymers properties. The Young's modulus is enhanced by a factor of 3, there is a 3-fold improvement in the strength, and the strain to failure increases by more than 20 times. The *t*-butyl groups in **22** and the naphthalene group in **23** serve to extend the size of the cleft for molecular threading. At present, our working models suggest that the largest enhancements will be for materials that have the cleft size

CHART 3



matched to the effective diameter of the polymer chain. Hence, **22** and **23** may be important to thread larger diameter polymer chains. All indications are that the interlocking polymer structure concept is a robust design principle, and multiple other classes of iptycene polymers are possible.

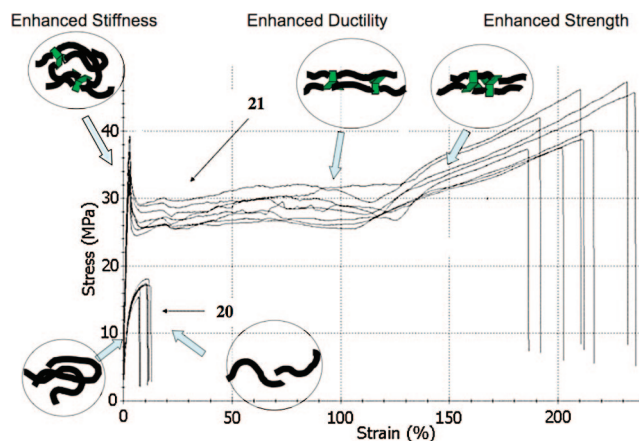


FIGURE 8. Stress–strain curves of films of **20** and **21** at RT. Schematics of the polymers are given in the circles, and both materials initially have random coil structures. Polymer **20** has very poor mechanical properties and breaks at low strains. In contrast, **21** has a much higher modulus and yield strain that is followed by a region of nearly constant stress with increasing strain. Over this region the polymer chains are becoming increasingly aligned. Higher strains result in iptycene–iptycene interactions, and the system exhibits increasing stress prior to breaking.

Summary and Outlook

It should be clear from this Account that iptycenes are remarkably versatile elements for the design of new materials. I also hope that some readers will make their own connections from the examples discussed and seek to translate other novel

molecular concepts to produce materials with superior properties. New molecular building blocks will enable the design of materials with previously unknown properties.

I have had the good fortune of having many talented co-workers over the years. Those most relevant to this Account are listed in the references. The mechanical property studies were done in collaboration with my colleague Ned Thomas (MIT Materials Science and Engineering). I am also thankful for financial support over the past decade from The Army Research Office, DARPA, and NSF.

BIOGRAPHICAL INFORMATION

Timothy M. Swager is the John D. MacArthur Professor of Chemistry and is presently the Head of the Department of Chemistry at the Massachusetts Institute of Technology. A native of Montana, he received a B.S. from Montana State University in 1983 and a Ph.D. from the California Institute of Technology in 1988. His research interests are in design, synthesis, and study of organic-based electronic, structural, sensory, and liquid crystalline materials.

FOOTNOTES

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