

Poly(*p*-phenyleneethynylene)s by Alkyne Metathesis[†]

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ABSTRACT

Alkyne metathesis was effected by mixtures of Mo(CO)₆ and phenols at elevated temperatures based on an improved version of the method reported by Mortreux and Mori. When propynylated arenes are subjected to these reaction conditions, the formation of diarylalkynes is often quantitative and likewise allows the synthesis of alkyne-bridged macrocycles and polymers of high molecular weight. Alkyne metathesis made high-molecular weight poly[*p*-(dialkylphenylene)ethynylene]s (PPEs) accessible that show promise as active layers in organic semiconductor devices.

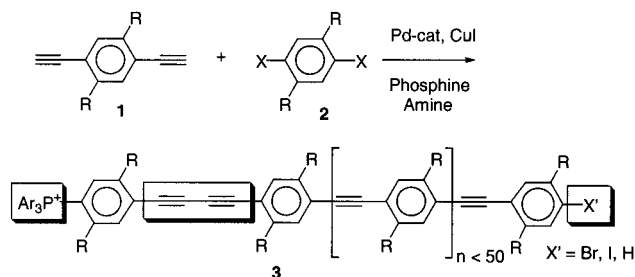
Introduction

Conjugated polymers are organic semiconductors and, as such, are of great potential importance for device fabrication. Such devices include light-emitting diodes, light-emitting electrochemical cells, photovoltaic cells, thin-film transistors, and plastic lasers.^{1–5} While myriads of polymer topologies^{6,7} have been realized, the conjugated polymers which “made it big” are the poly(*p*-phenylenevinylene)s (PPVs)⁸ that have multiple applications, despite their only moderate stability and the delicate processing required to obtain device-quality material.⁹

Poly[*p*-(dialkylphenylene)ethynylene]s (PPEs)^{10a} are the dehydrogenated congeners of the PPVs; they have found use in sensory and molecular wire devices and display a spectacular *oligomeric* chemistry.^{11–14} The enhanced photophysical stability of the PPEs and their efficient fluorescence in solution point to exciting opportunities in the (emerging) field of PPE semiconductors. The classic synthesis of PPEs is the Pd–Cu-catalyzed coupling (Heck–Cassar–Sonogashira–Hagihara) of diethynylbenzenes **1** to dihalo arenes **2**. While the synthesis is general in scope, it is difficult to obtain PPEs of high molecular weight, unless acceptor-substituted aromatic diiodides are utilized.^{10a} In addition, the end groups of PPEs are somewhat ill-defined due to dehalogenation and phosphonium salt formation.^{10b} The Pd-made polymers **3** contain diyne defects, formed by either reduction of the Pd²⁺ catalyst precursor or the adventitious presence of atmospheric oxygen (Scheme 1). Consequently, it was of interest to find a complementary synthesis of PPEs that was independent of the established Pd-catalyzed cou-

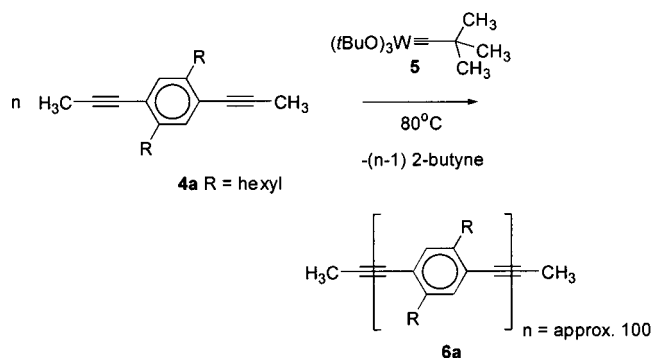
Uwe Bunz received his doctorate (Dr. rer. nat.) in 1990 from the Ludwigs-Maximilians-Universität München with Prof. G. Szeimies. After a postdoc with Prof. Vollhardt at UC Berkeley (1991–1992), he finished his Habilitation (Dr. rer. nat. habil.) in 1997 with Prof. K. Müllen in Mainz. He is currently Professor of Chemistry at the University of South Carolina. His research interests include conjugated polymers and carbon-rich organometallics.

Scheme 1. Synthesis of PPEs by Pd-Catalyzed Couplings^a



^a Highlighted are commonly encountered defect structures.

Scheme 2. Acyclic Diyne Metathesis (ADIMET) of Dipropynylated Benzenes by the Schrock Tungsten Carbyne **5**



plings and its shortcomings. Alkyne metathesis,¹⁵ i.e., a process in which carbon–carbon triple bonds are directly formed, was envisioned as a powerful alternative to make PPEs.

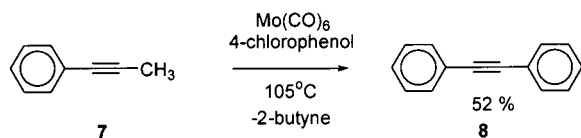
Syntheses

The complex (tBuO)₃W≡C-tBu (**5**)¹⁶ is active in alkyne metathesis, and both Schrock and Bazan¹⁷ have shown that **5** is capable of performing ring-opening metathesis polymerization (ROMP) of cyclic alkynes, but their results lacked their well-deserved impact.¹⁸ In 1997, Müllen, Weiss, and Bunz¹⁹ reported the first synthesis of PPEs by alkyne metathesis, and **5** was successful in the acyclic diyne metathesis (ADIMET) of 2,5-dihexyl-1,4-dipropynylbenzene **4a** (Scheme 2). The yields of defect-free **6a** were high, and the degree of polymerization (*P_n*) reached almost 100 repeating units, making the ADIMET route to **6** utilizing **5** competitive with the Pd-catalyzed, “classic” synthetic scheme.

Carbyne complex **5** is a superb catalyst. Successful ADIMET reactions could be carried out at temperatures as low as 80 °C, which led Fürstner to utilize alkyne metathesis in the closure of large rings and complex natural products.²⁰ Later, Fürstner developed an even more active, molybdenum-based catalyst system of unknown structure,^{20b} which utilizes combinations of Cummins’s trisamide [Mo(NRR′)₃] (R = *t*-butyl, R′ = H) with dichloromethane as the activator. This catalyst is more

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Scheme 3. Mori's Dimerization Experiment

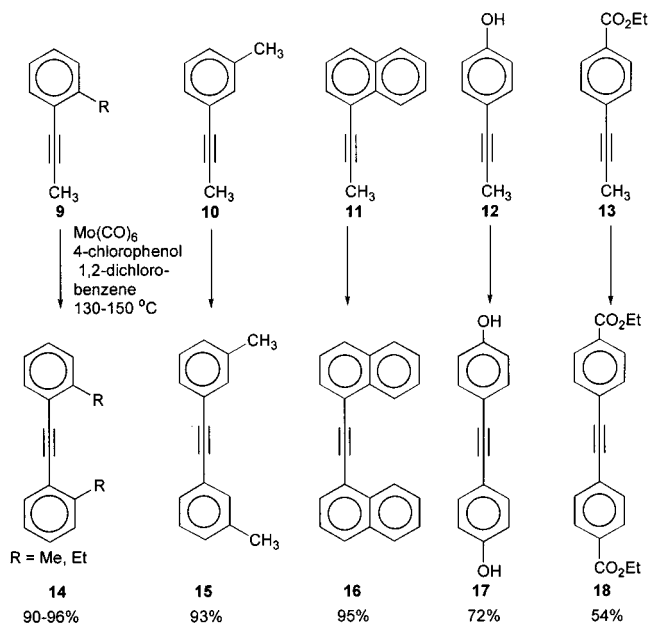


tolerant toward heteroatom-containing substrates.^{20b,c,21} The downside of Schrock's and Fürstner's catalysts is their relatively demanding syntheses and their sensitivity towards air and water, which implies that they can be used only in carefully dried solvents either in a glovebox or in a Schlenk line. These inconveniences may hinder their general use.

In 1973, Mortreux²² discovered that mixtures of $\text{Mo}(\text{CO})_6$ and resorcinol scrambled substituents in diaryl-alkynes. In 1995, Mori²³ reported the dimerization of propynylbenzene **7** to diphenylacetylene **8** by this promising but underutilized approach (Scheme 3). A mixture of $\text{Mo}(\text{CO})_6$ and 4-chlorophenol forms a catalytically active species of unknown nature that may be either a molybdenum alkydine or a molybdenacyclopentadiene. Although **8** did not form quantitatively and the yields of Mori's metatheses generally did not exceed 75%, the active catalyst forms *in situ* from commercially available starting materials and works in nondried, unpurified solvents in a "low-tech" approach. Either an improved catalyst system, utilizing different, more active phenols, or optimization of the reaction conditions seemed to be a promising approach to enhance the performance of these wonderfully simple catalysts.

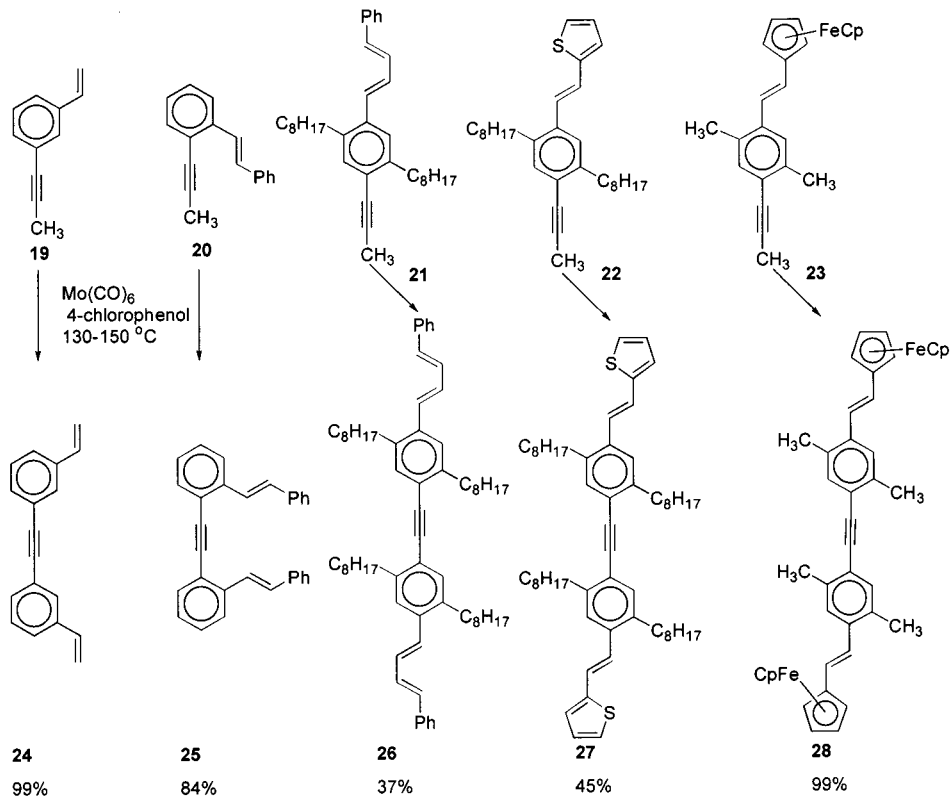
Model Compounds. An increase of the reaction temperature to 130–150 °C and removal of 2-butyne by a

Scheme 4. Synthesis of Model Dimers Utilizing the Mortreux–Mori Catalyst System



stream of N_2 increased the yield of **8** (from **7**) from 52% to 82%. The presence of alkyl substituents either *ortho* or *meta* to the propyne group such as in **9** and **10** (Scheme 4) further improved the efficiency of the metathesis reaction and led to dimers **14** and **15** in isolated yields, which always exceeded 90%, suggesting that their formation is almost quantitative.²⁴ If Lewis bases were present in the substrate, the metathesis yield dropped, probably due to the bases' coordination to the catalytically active

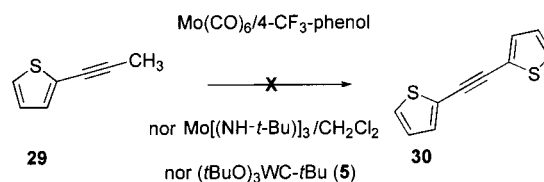
Scheme 5. Synthesis of Vinyl-Group-Containing Model Compounds Utilizing the Mortreux–Mori Catalyst System



species. To determine the scope and functional group tolerance, it was important to know if C=C-double bonds would be tolerated by Mo(CO)₆/4-chlorophenol catalysts.²⁰ Alkyne metathesis in the presence of alkynes leads to efficient enyne metathesis according to Grubbs,²⁵ and the alkynes are *incorporated* into the final cyclic diene. A paper by Schrock^{16b} demonstrated that vinyl groups are resistant toward stoichiometric alkyne metathesis with defined tungsten carbynes, suggesting that the C–C-double bonds in our metathesis reactions might survive. A series of propynylated stilbenes and styrenes (**19**–**23**) was prepared and underwent alkyne metathesis to furnish their dimers **24**–**28** (Scheme 5) in high yields²⁶ and *without interference of the double bonds*, making this reaction complementary to Grubbs's enyne metathesis.²⁵ Remarkable is (a) the tolerance of unsupported double bonds, (b) the survival of *o*-styryl substituents (with respect to the propynyl group), and (c) the survival of remotely placed butadiene and thiophene groups under our conditions of ADIMET. This finding is significant and promises that alkyne metathesis will find applications in organic synthesis *and* materials/polymer chemistry. The survival of thiophene units is interesting, because propynylthiophene **29** (Scheme 6) does not undergo metathesis to **30**, even if Fürstner's catalyst is utilized.^{20c} Apparently, the greater distance of the sulfur to the reacting propyne group in **22** is sufficient to allow successful metathesis with the "in situ" catalysts. However, it would be exciting to find a catalyst that would enable the metathesis of **29** and related thiophene-containing substrates.^{20b}

Ring-Closing Alkyne Metathesis (RCM).²⁷ Mass spectroscopic data collected by Weiss²⁸ indicated that the

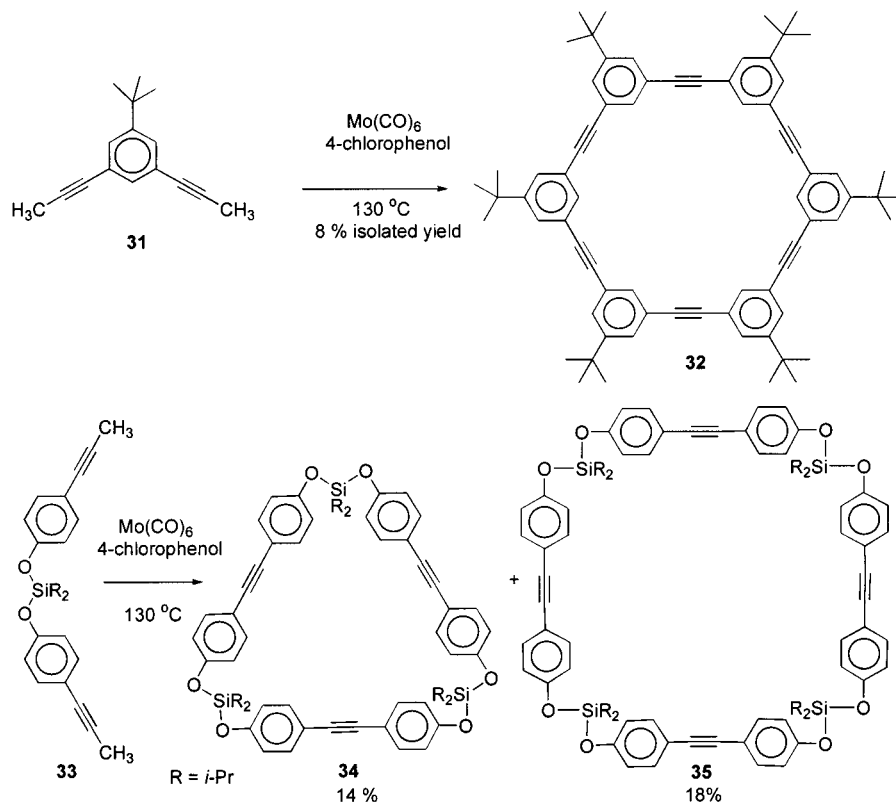
Scheme 6. The Thiophene Case



reaction of 1,3-dipropynylbenzene with **5** furnishes cyclic phenyleneethynylenes, demonstrating that RCM is possible. Unfortunately, the cycles were not isolated.²⁸ The great interest in cyclo(phenyleneethynylene)s¹¹ was a strong incentive to subject 1,3-dipropynyl-4-*tert*-butylbenzene (Scheme 7) to the conditions of ADIMET under Mo(CO)₆/4-chlorophenol catalysis. Cyclohexamer formation (**32**, 8%, isolated yield) accompanied by the production of *m*-PPE was observed. A high-quality single-crystal structure of **32** was obtained (Figure 1). The rings pack in columns of tilted "saucers" with solvent-filled channels, satisfying electrostatic packing requirements best.^{27a} In a second instance of RCM we made triangular (**34**) and rhomboid (**35**) cycles (14% and 18% isolated yield),^{27b} which have been crystallographically characterized. These examples show that RCM with simple catalysts is powerful and depends only on the access to suitably dipropynylated compounds.

Alkyne-Bridged Polymers.²⁹ The general feasibility of ADIMET to make PPEs (utilizing **5**) was established.¹⁹ Model reactions suggested that catalysts formed from Mo(CO)₆ and 4-chlorophenol performed metathesis of propynylated arenes well, and the simple catalysts were competitive in the formation of PPEs **6**. A series of dipro-

Scheme 7. Ring-Closing Alkyne Metathesis Utilizing the Mortreux–Mori–Bunz Catalyst



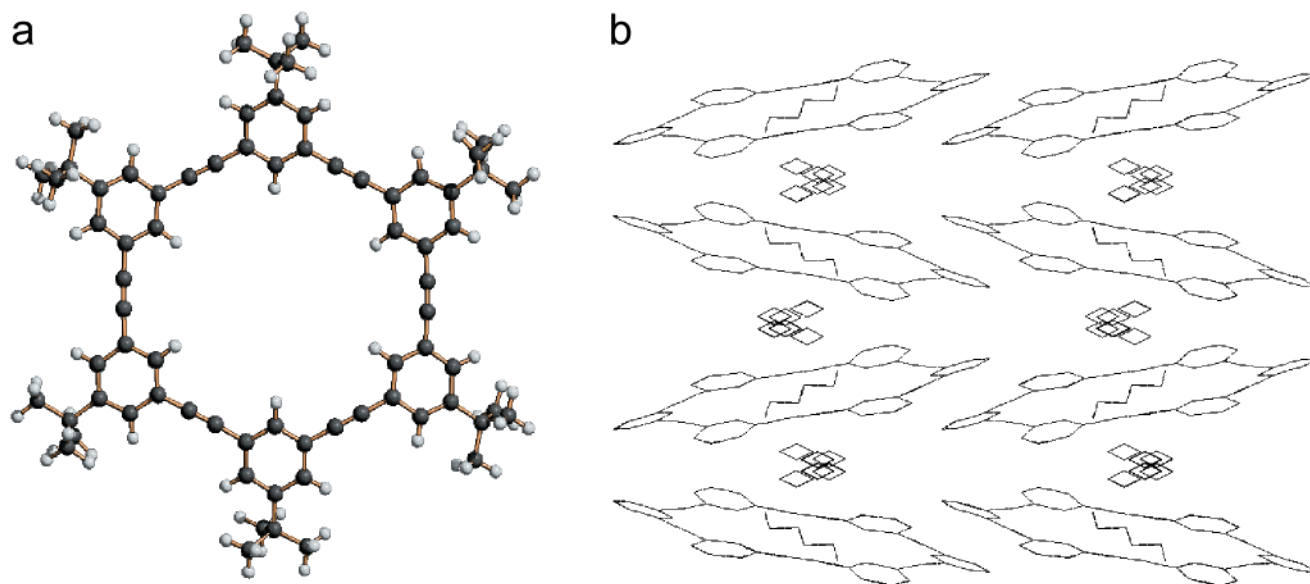
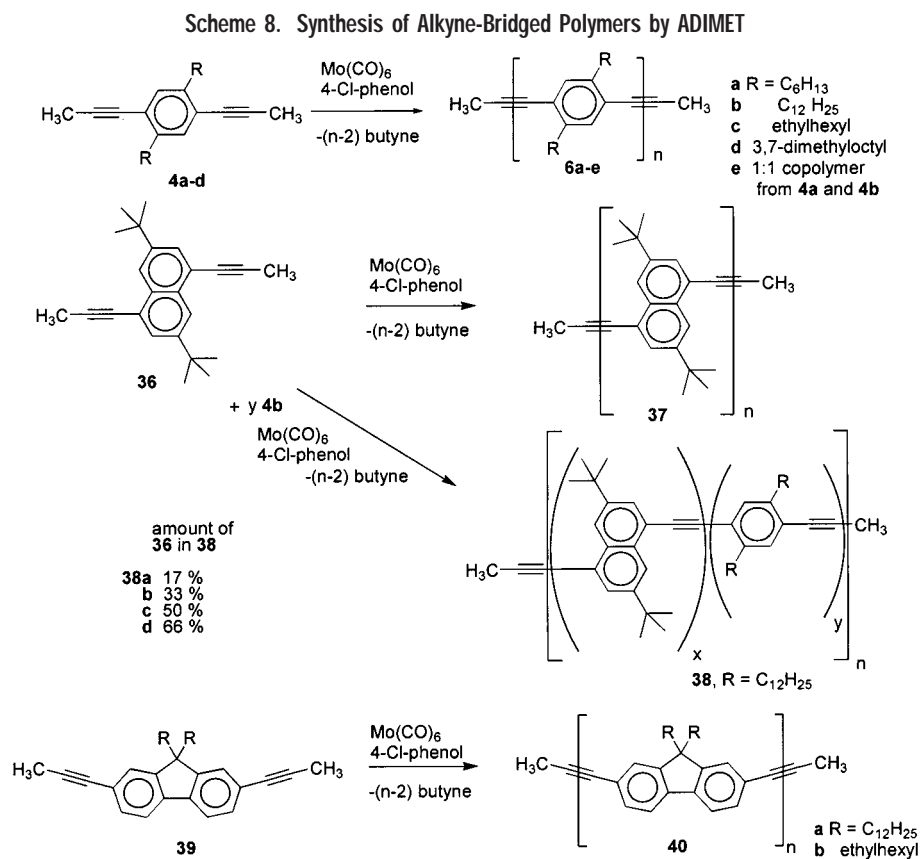


FIGURE 1. (a) Ball and stick plot of **32**; (b) packing diagram of **32**. *tert*-Butyl groups and hydrogens are omitted. Squares indicate highly disordered solvent.

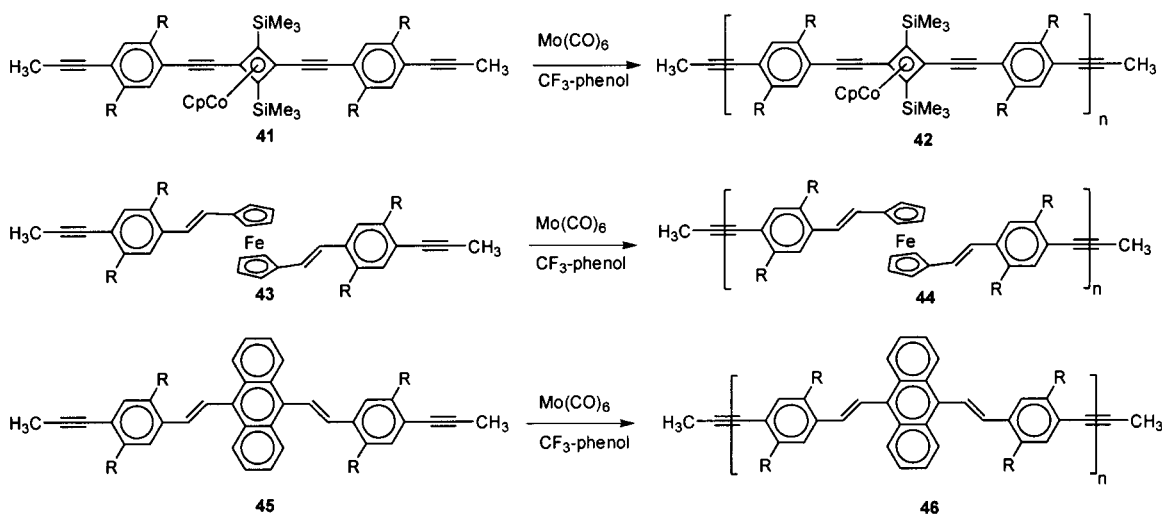
pynylated benzenes **4a–d** was prepared and subjected to ADIMET to give PPEs in quantitative yields and high purity (Scheme 8).²⁹ A pleasant surprise was the degree of polymerization (P_n), which could range from 300 up to 2000 repeating units when long side chains were employed as solubilizing groups in **6**. However, PPEs with *hexyl* side chains (**6a**) never exceeded a P_n of 100, due to insufficient solubility of the polymer in the reaction medium. Performing ADIMET at enhanced temperatures

seems an advantage for the formation of high-molecular-weight conjugated polymers in concentrated solutions if suitable solubilizing side chains (dodecyl, 2-ethylhexyl) are attached to the monomers.

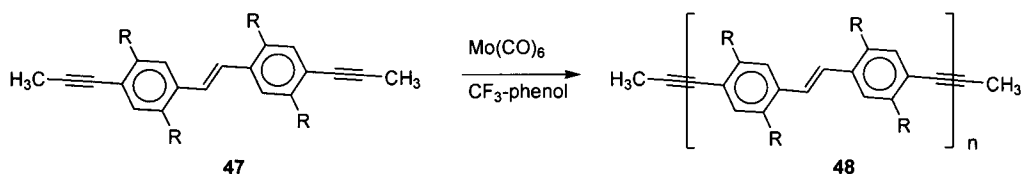
The successful synthesis of PPEs **6** made it likely that other propynylated aromatics could be metathesized, and **36** gave the sparsely soluble poly(naphthyleneethynylene) **37** in high yields but with a low P_n .³⁰ Co-metathesis of **36** with **4b** furnished a series of (random) copolymers **38a–**



Scheme 9. Synthesis of Organometallic and Anthracene-Containing Polymers



Scheme 10. Synthesis of PPV–PPE Hybrid Polymers by ADIMET



d, in which the naphthyl and phenylene units are separated by alkyne groups.³¹ These copolymers form in high yield, with decent P_n ($30 < P_n < 100$), and show exciting solid-state emission behavior (vide infra). Other attractive aromatic monomers were the dipropynyldialkylfluorenes **39**, which gave **40** in high yields, high purity, and substantial P_n .³² Aromatic units for which either propynylation, attachment of alkyl chains, or the metathesis process, or all of the above, are not feasible can still be used in the metathesis reaction if the modules under consideration are sandwiched between two dialkylpropynylbenzene units.³³

A series of polymers (**42**, **44**, **46**; Scheme 9) has been accessed by this route. While in some cases 4-chlorophenol is not effective as cocatalyst, the more acidic 4-(trifluoromethyl)phenol does an excellent job in polymerizing these “sandwiched” monomers.³³ The general importance of PPVs and the tolerance of double bonds in the metathesis process made it appealing to prepare mixed PPE–PPV (PPVE) polymers by ADIMET. Surprisingly, the PPVEs **48** had not been described. Utilizing a series of dipropynylated stilbenes **47**, alkyl-substituted PPVEs of high molecular weight (P_n up to 400) and purity were obtained by ADIMET as deep-yellow, stable, and greenish-emitting materials (Scheme 10).²⁶

The syntheses of poly(aryleneethynylene)s by ADIMET are only a beginning and show the scope of this uncomplicated yet powerful method for the preparation of alkyne-bridged polymers. ADIMET with simple catalysts is very successful when hydrocarbon monomers are utilized, but the presence of heteroatoms is likewise acceptable if they are sufficiently remote from the reacting propyne groups, demonstrated in Scheme 5 by the working model transformation **22**–**27**.

Thermal and Liquid Crystalline Properties of PPEs

PPEs have been claimed to be thermotropic liquid crystalline, which however was never proven for dialkoxy-PPEs.^{10a} Dialkoxy-PPEs did not show any interpretable textures in polarizing optical microscopy, and published pictures display only shear-induced birefringence.³⁴ Only in 1998, Weder proved that dialkoxy-PPEs attain *lyotropic* nematic LC phases, but thermotropic phases were not reported.³⁵

A side effect of the metathesis pathway to **6** was the discovery of their high thermal stability.³⁶ *Dialkoxy*-PPEs deteriorate above 150 °C without reaching the isotropic, i.e., liquid state. That is not true for **6**, which decompose only above 250 °C in air. The enhanced stability of high-molecular-weight **6** made it possible to examine their temperature-dependent solid-state properties. PPEs **6b**–**d** melt without decomposition at temperatures ranging from 120 to 250 °C, depending upon side chain and molecular weight.^{36–38} Higher molecular weight and shorter/unbranched side chains lead to higher melting points. Variable-temperature X-ray powder-diffraction experiments (Figure 2) were conducted on PPEs **6b** and **6c**.³⁸ At ambient temperature they are crystalline (Figure 2) and display a doubly layered lamellar structure (Figures 3 and 4)^{37,38} that is in agreement with and represents a refinement of the structural model for PPEs proposed by Wrighton and West.³⁹ All of the PPE backbones are coplanar to ensure an efficient packing of the dodecyl side chains.

If the temperature is increased to above 100 °C, the diffraction peaks in the wide-angle range of **6b** disappear, and only one small-angle peak, indicating a lamellar

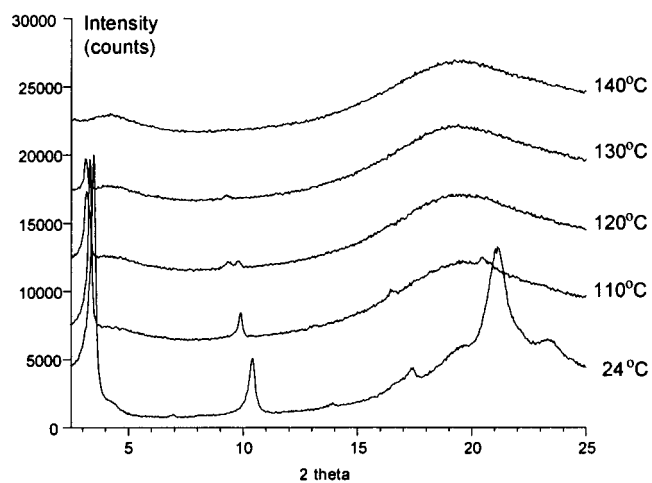


FIGURE 2. Variable-temperature powder XRD of **6b**.

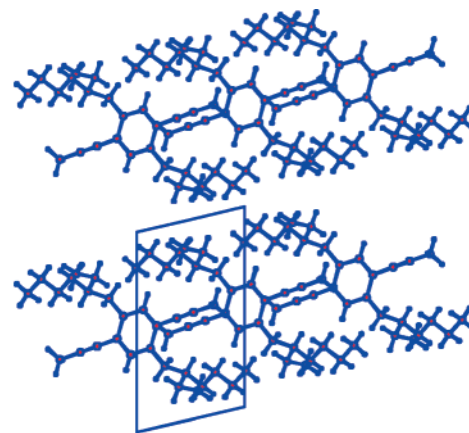


FIGURE 3. Packing of **4c**. Note the resemblance to the proposed structure of the polymer **6c**.

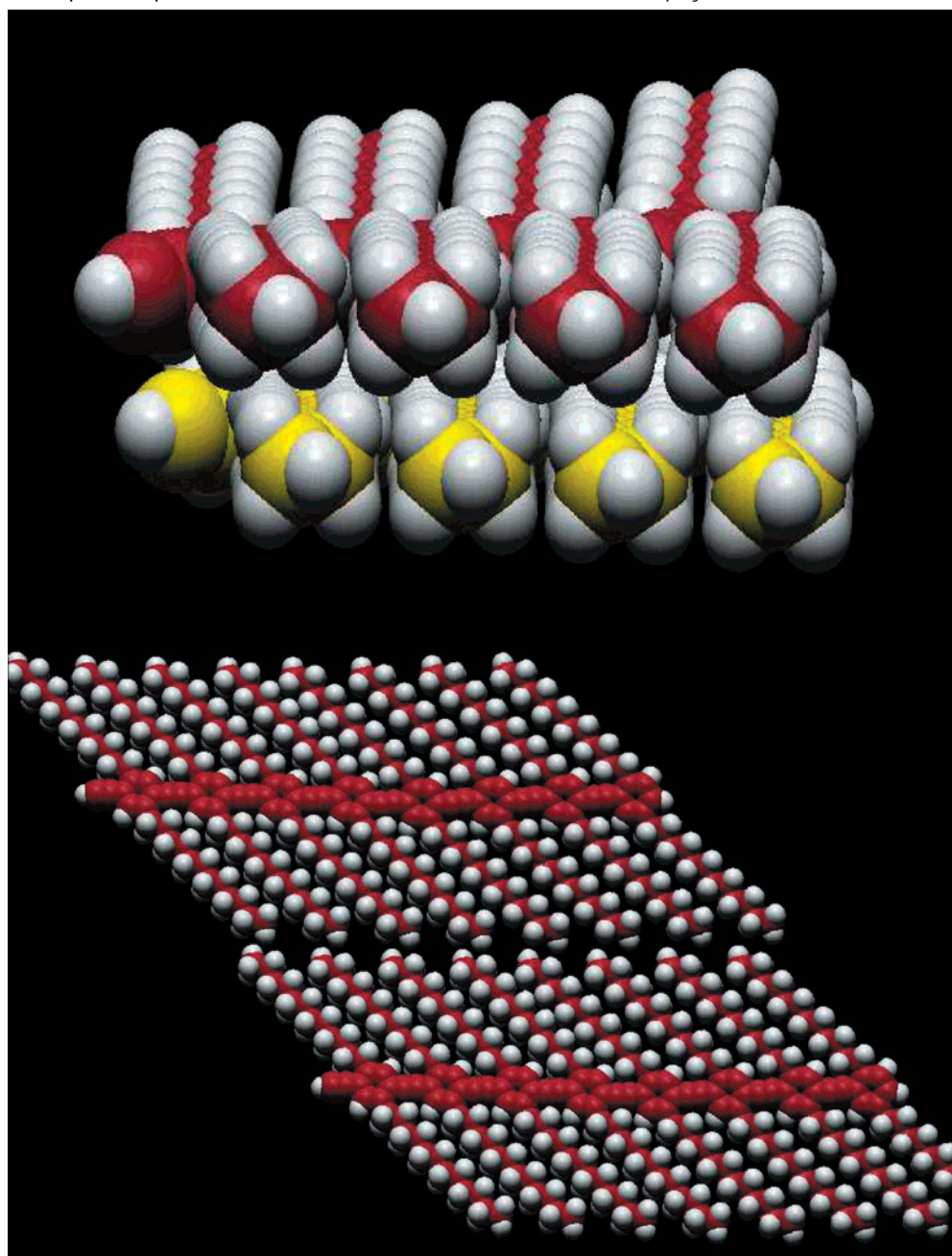


FIGURE 4. Packing model of **6b**. Single-chain geometry was obtained by an MM2 calculation.³⁷

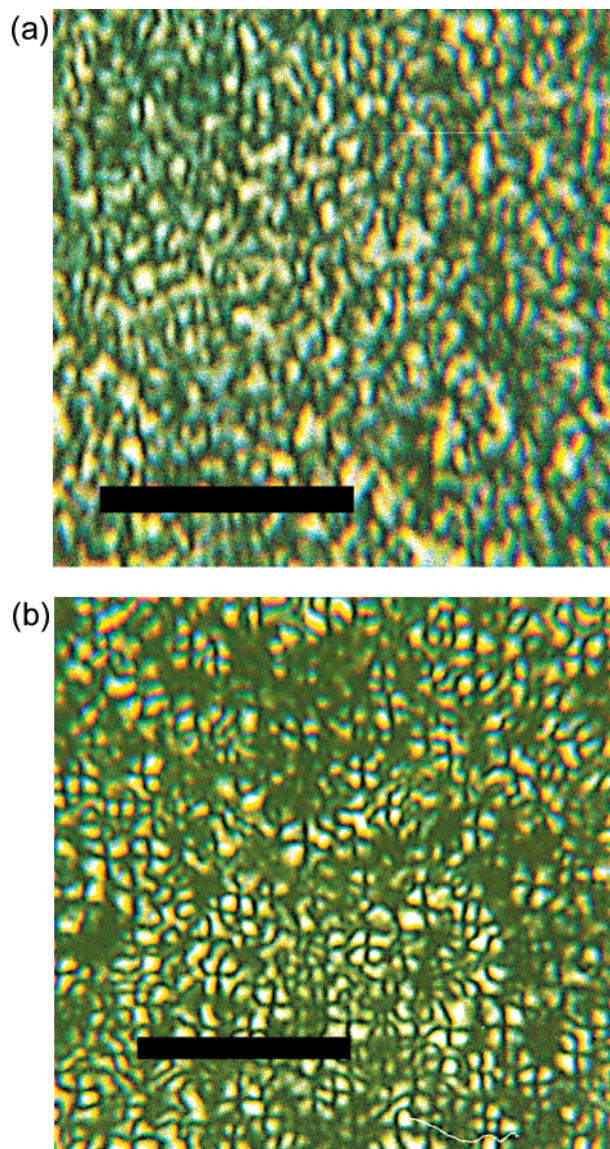


FIGURE 5. Polarizing microscopy of **6b**. Bars represent 20 μm . (a) Schlieren texture of **6b**. (b) Banded texture of **6b**. Both at ambient temperature.

ordering, persists. Above 140 $^{\circ}\text{C}$, the sample of **6b** is liquid, and neither scattering nor diffraction is observed. The behavior is reversible. DSC and polarizing microscopy corroborate (Figure 5) the transitions recorded by powder diffraction. At temperatures above 150 $^{\circ}\text{C}$, a “black” melt is observed under crossed polarizers. Cooling to below 130 $^{\circ}\text{C}$ leads to the development of Schlieren or banded textures (Figure 5) that persist at ambient temperature. Piecing the evidence together, dialkyl-PPEs are found to be thermotropic liquid crystalline materials that show reversible but broad crystalline–liquid–crystalline–isotropic transitions. The combination of the results of variable-temperature XRD and the Schlieren textures observed by polarizing microscopy suggests that **6** form a homeotropically oriented smectic C phase. Three states of matter, crystalline, liquid crystalline, and the isotropic liquid are thus accessible to dialkyl-PPEs, even though the isotropic melt is extremely viscous.³⁸

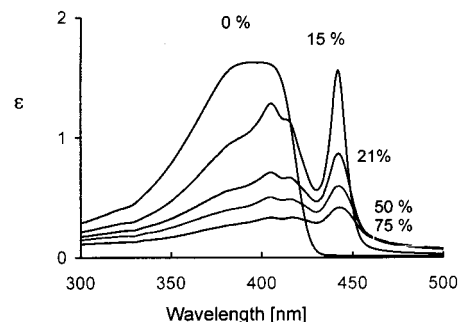


FIGURE 6. Solvatochromic behavior of **6b**. The numbers indicate the methanol content. The initial spectrum is recorded in chloroform.

Optical Spectroscopy of PPEs: Planar or Not Planar?

An exciting aspect of conjugated polymers is the study of their optical properties^{40–43} in terms of their dependence on and response to their physical state.⁴⁰ PPEs have long been known,^{10a} but their spectroscopic behavior has been studied only in good solvents and in the solid state. Most of these investigations had been performed on dialkoxy-substituted PPEs. Early on it was noticed that PPE’s absorption in the solid state was red-shifted from that observed in solution, and annealing of dialkoxy-PPE films at elevated temperatures leads to further red shift of the primary absorption band.³⁹ The underlying reason for these phenomena was not well explained nor examined in depth,^{10a,34,39} because dialkoxy-PPEs are not well behaved with respect to aggregation-induced changes of optical properties. They may not be the best examples for the study of aggregation and solid-state behavior because their UV–vis bands are often broad and featureless.

Dialkyl-PPEs **6** form *almost colorless and strongly purple-emitting solutions in chloroform* but are brilliantly yellow and only weakly emissive in the solid state.^{41a} Addition of methanol to solutions of **6** in chloroform has an effect on their UV–vis spectra similar to that on going into the solid state, i.e., clear yellow but almost nonemissive microsuspensions (Figure 6) with a well-resolved feature at 439 nm develop, displaying vibrational fine structure. Similar effects were observed when solutions of **6d** in dodecanol were cooled from 100 $^{\circ}\text{C}$ to ambient temperature.^{41b} This interesting thermochromic effect was visible not only in poor solvents but in solid PPE as well. Thin films of **6e** form highly viscous melts above 190 $^{\circ}\text{C}$ that are *almost colorless, resembling PPEs in chloroform solution*.⁴²

The same experiment conducted with dialkoxy-PPEs gave spectra which were much broader, and in which these features were much less resolved.^{41c} Very recently, however, Swager demonstrated that dialkoxy-PPEs can show spectroscopic behavior similar to that of the dialkyl-PPEs when examined in a Langmuir–Blodgett experiment.⁴⁴

What is the reason for the sharp and red-shifted band at 439 nm that develops either in the solid state or in poor solvents? This band could arise by the interaction of several PPE chains under formation of electronic ground-state aggregates or by a local dielectric effect of neighbor-

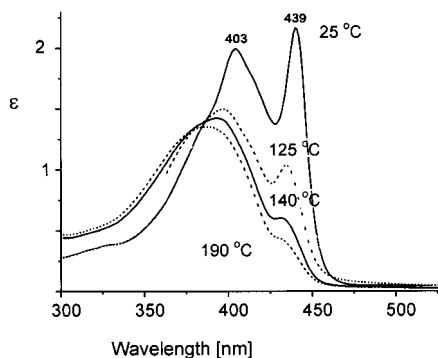


FIGURE 7. Thermochromicity of **6e**.

ing chains.⁴⁵ Alternatively, the band could be due to planarization of the backbone, or it could be a combination of both. Wudl et al.⁴⁶ examined the solvatochromic behavior of poly(alkylthiophene)s and concluded that single-chain planarization was the major contribution to the observed spectral features in the aggregated PATs. The spectra of the PATs show a *qualitative* resemblance to the spectra of **6** under similar conditions, suggesting that their aggregation behavior is analogous. To corroborate this qualitative agreement, the temperature-dependent absorption spectra of PPE films were examined.⁴² For **6e**, the thermal and liquid crystalline behavior was known, and Figure 7 shows its variable-temperature UV-vis spectra. The aggregate band is prominent at room temperature but disappears gradually and almost vanishes above 190 °C, corresponding closely to the liquid-crystalline-isotropic transition of **6e**. To understand the implications of these observations, it is necessary to discuss the conformational preference of diphenylacetylene.

“We are married to the concept of rotational invariance of modules connected by alkynes”,⁴⁷ which is correct as far as the barrier of rotation for substituents *in solution* is concerned. Theoretical and experimental results indicate that this barrier is less than 1 kcal mol⁻¹; i.e., in solution and as liquids, the phenyl rings in diphenylacetylene indeed do not have a preference for either a planar or a perpendicular orientation with respect to each other, and all possible conformations are present.⁴⁸ In the solid state this rotation is frozen in phenyleneethynylenes, as well as in the PPEs, and a planar conformation of the phenyleneethynylene backbone results.

The planarization of the PPE backbones accommodates side-chain packing and results in lamellar order. While the barrier to rotation around the sp²-sp-single bond is small for a *single* molecule, that does not necessarily mean that the orbital arrangements are rotationally invariant, and according to simple band gap calculations on model phenyleneethynylene octamers, the HOMO-LUMO gap is largest when two neighboring phenyl rings are twisted by 90°. It is smallest if all of the phenyl groups are coplanar. In collaboration with Garcia-Garibay,^{42b} a phenyleneethynylene trimer was carefully examined to show a small band gap in the solid and a larger gap in solution. A semiempirical calculation including configuration interaction supported the experimental evidence that planarization leads to an increased λ_{max} in the UV-vis

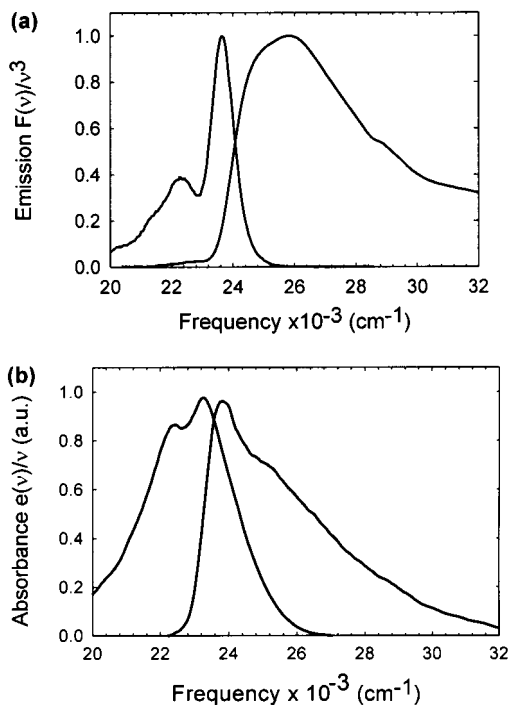


FIGURE 8. (a) Overlay of absorption and emission spectrum of **49** in chloroform at room temperature. (b) Overlay of absorption and emission spectrum of **49** in low-molecular-weight polystyrene at 77 K.

spectrum of phenyleneethynylenes, suggesting that **6**'s spectroscopic behavior is guided mainly by conformational effects.

Fluorescence in PPEs: Quadratic Coupling between the Ground and Excited States⁴³

The UV-vis spectra of **49** and **6a-d** are narrow in the solid state but broad and featureless in good solvents, because the rotation of the PE units around the -C≡C-Ar single bonds is unrestricted, and deviation of planarity between PE units in single chains increases the HOMO-LUMO gap.⁴² The emission spectra of **6** and **49**, however, are narrow and show a well-resolved shoulder (Figure 8a). For rigid molecules such as **49**, one would expect, however, approximate mirror symmetry of absorption and fluorescence with a relatively small Stokes shift. Why is that not observed?

The optical and emissive properties of **6** and **49** are almost identical, ensuring that **49** has reached the convergence length of PPEs, making it a good model for **6**, and PPE's interesting optical behavior may therefore be explained by investigating **49**. Utilizing dilute solutions of **49** avoids issues of energy migration along single polymer chains, chain entanglement, energy transfer between multiple chains, and excimer formation. When solutions of **49** are cooled to 77 K in polystyrene, the absorption spectrum narrows slightly, but significant changes occur in its *emission* (Figure 8b), which is broadened toward the blue side. In a time-resolved fluorescence experiment (Figure 9, 297 K, chloroform), the blue component of the emission decreases over time, and the narrow fluorescence spectrum is reconstituted (Figure 10b).

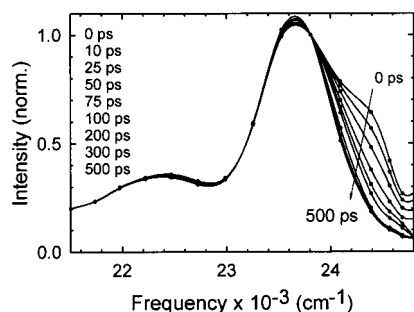


FIGURE 9. Time-resolved spectrum of the emission of **49** in chloroform at 297 K.

How can these experiments be interpreted? The ground state of **49** features a shallow potential energy profile with respect to rotation around the PE units (CHCl_3 solution at 297 K, Figures 9 and 10). In the excited state that may not be the case. The observed spectroscopic properties can be explained if the potential energy profile of **49*** is steep and symmetric with respect to rotation (Figure 10a). Does that make sense? In a valence bond picture, the excited state of **49** has a partially diradicaloid/cumulenoid character (Scheme 11), and rotation around the PE units is *not* facile anymore because the allenic structure has a strong preference toward planarity, eliminating the twisted double bonds.

In good solvents at ambient temperature, the excited state (**49***) will quickly relax into planarity, so that only the 0–0 emission from S_1 is detected in steady-state emission. If the same experiment is performed at low temperature and in a viscous solvent, the molecular torsion of **49*** into its planar form is hampered by the medium, and planarization is slow on the time scale of the fluorescence lifetime (355 ps). Emission will occur not only from the potential minimum of the excited state, but virtually from all frozen rotamers, resulting in a broad and blue-shifted spectrum. Only after the planarization of **49*** is complete, narrow emission from the lowest excited state conformation will occur. Consequently, in **6**, planarization of the excited state and not energy migration is likely to govern the emission behavior in dilute solutions.

In linear coupling models the lowest energy configuration is different in the ground and excited states, but the restoring forces are identical. The strong torsional coupling between the ground and excited states of **49** features a restoring force that is much stronger in the excited state than in the ground state. This situation is called quadratic coupling.⁴³ Quadratic coupling mimics spectroscopic effects in PPEs that have been attributed

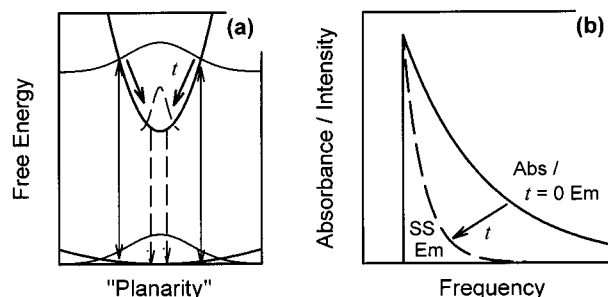


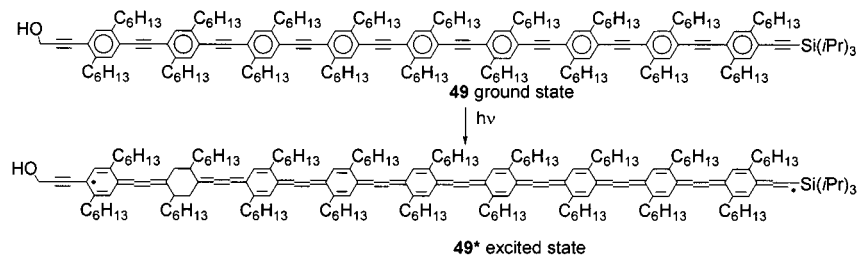
FIGURE 10. (a) Potential energy profile of **49** in the excited state with respect to the torsional angle around the $sp-sp^2$ single bond. Note that the excited state has a much steeper torsional profile than the ground state and thus a much larger restoring force. (b) Time dependence of the emission in a system, where quadratic coupling is significant; see Figure 8b.

to energy migration, mode mixing, etc. but may be also important in other conjugated polymers.⁴³

PPEs' Self-Assembly on Surfaces: Nanocables and Nanowires

When dilute solutions of PPE are cast onto a silicon wafer, thin continuous films form. According to atomic force microscopy (AFM), these films show two different morphologies.^{49,50} Either small, nanometer-sized features, corresponding to the lamellar structure of PPE, or sizable superstructures (Figure 11) are observed: nanocables (structures larger than nanowires) are 20 nm thick and up to 1 μm long, regular, and must be a result of the aggregation of several PPE chains into cable-like bundles. These results are in agreement with Müllen's and Rabe's AFM investigation of PPE nanowires;⁵⁰ those authors found a host of different wire and ribbon-type structures, depending upon the processing of their PPE samples. In Figure 11a and c are shown pictures of a nanocable and a PPE nanoribbon. From the known dimension of PPE chains and the homeotropic orientation of these chains, one can conclude that stacks of more than 50 PPE molecules form a single "nanocable". Why do these superstructures form, and what is their genesis? Dilute solutions of PPEs in toluene are yellow, gel-like, and isotropic at room temperature but colorless and less viscous above 32 $^\circ\text{C}$. DSC and ^1H and ^2H NMR spectroscopy detect a phase transition around 30 $^\circ\text{C}$ between two isotropic liquid phases. Neutron scattering shows that the high-temperature phase consists of nonaggregated single molecules, while the low-temperature phase forms a jammed gel⁵¹ with filamentous cylindrical superstructures that are approximately 30 nm wide and up to 2 μm long.⁴⁹

Scheme 11



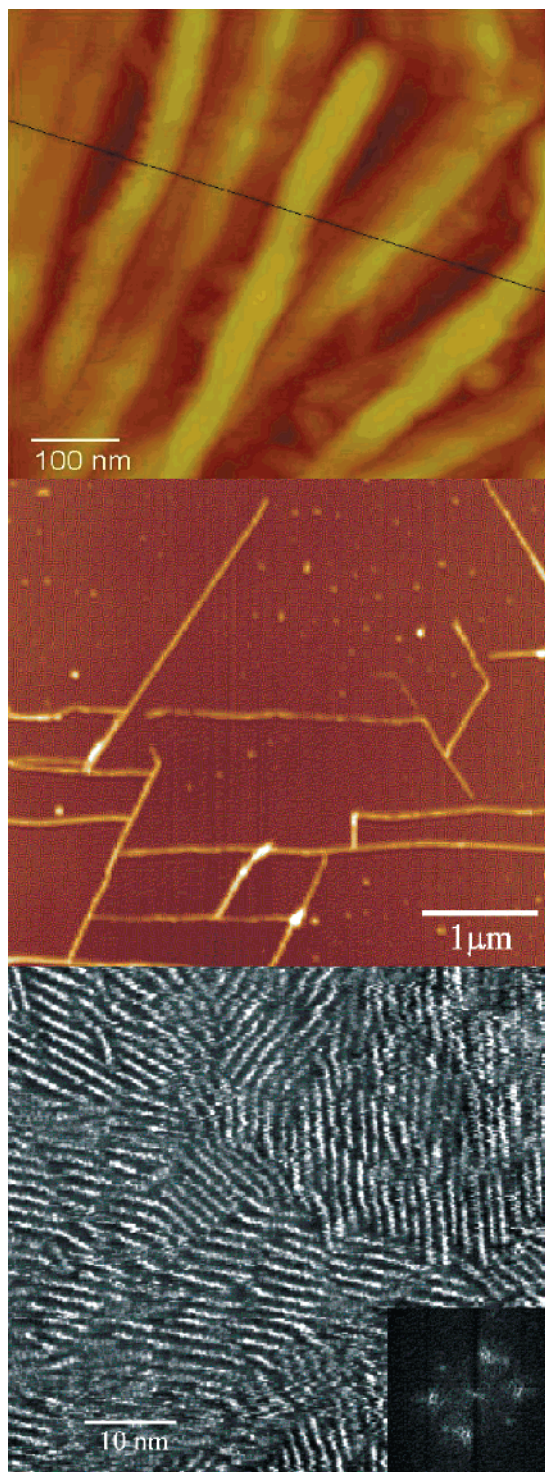


FIGURE 11. (a) Nanocable arrangement of **6b** on a silicon wafer. The observed superstructure exceeds the size of single lamella. (b) Nanowires and (c) nanoribbons of PPEs.⁵⁰

These geometrical features strongly resemble the dimension of the nanocables and suggest that the cables preform in solution and remain intact upon casting onto the silicon surface. If this assembly process can be controlled, it may be possible to engineer PPE nanostructures at will.

PPE-Based Organic Light-Emitting Diodes

Weder⁵² and Barton and Shinar⁵³ reported the fabrication of organic light-emitting diodes (OLEDs) based upon

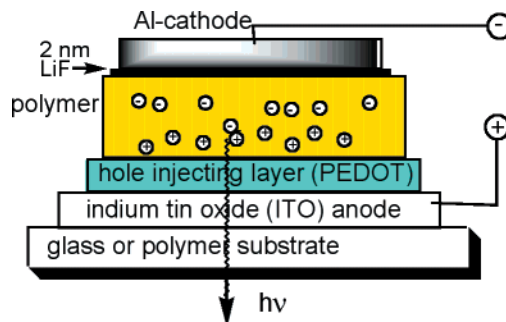


FIGURE 12. OLED architecture for **38b,c**. PEDOT: poly(ethylenedioxythiophene).

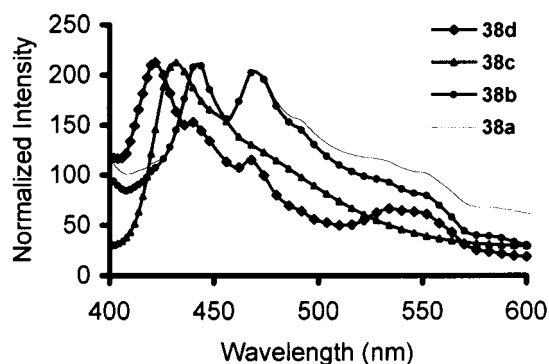


FIGURE 13. Solid-state emission of copolymers **38a–d**.

dialkoxy-PPEs. Both found that PPEs are unsatisfactory emitter materials, perhaps due to their low-lying HOMO. Hole injection into the relatively electron-poor (by nature of the alkyne group) PPEs seems difficult, and low solid-state emission compounded the problem to utilize PPEs as active emitter layers.⁵⁴ Our experiments with PPE **6b** corroborated Weder's results. An attempt to make a single-layer PPE-OLED with indium tin oxide (ITO) as anode and calcium as cathode led to weakly greenish-glowing devices. A more sophisticated multilayer device that included an additional hole injection layer (Figures 12 and 13) improved the results. To increase electroluminescence efficiency, we used a PPE derivative, **38**, with a higher solid-state photoluminescent quantum yield. Polymers **38** are strong blue emitters in the solid state and attractive candidates for OLED applications. Multilayer devices (Figure 12) with poly(ethylenedioxythiophene)/sulfonated polystyrene as hole injecting layer enhanced the characteristics of the LEDs, while aluminum was used as an effective cathode metal. In Figure 14, the electroluminescence spectra of two representatives of **38** are shown. Increasing naphthalene content in **38** shifts the electroluminescence to shorter wavelengths, and the OLEDs emit at 430 nm. Emissive intensities (Figure 14b) of up to 100 Cd m^{-2} were achieved in the range of 480 nm, which is an improvement, while the blue emitter **38b** shows an emission intensity of 20 Cd m^{-2} under these conditions. Weder⁵² has recently reported PPE-based hybrid OLEDs, emitting up to 300 Cd m^{-2} . However, PPVs display emissive intensities of up to 2000 Cd m^{-2} , and it is not entirely clear why PPE-based OLEDs should be less effective in that regard. With more optimization, emissive efficiencies of PPE types may be tuned to competitiveness.

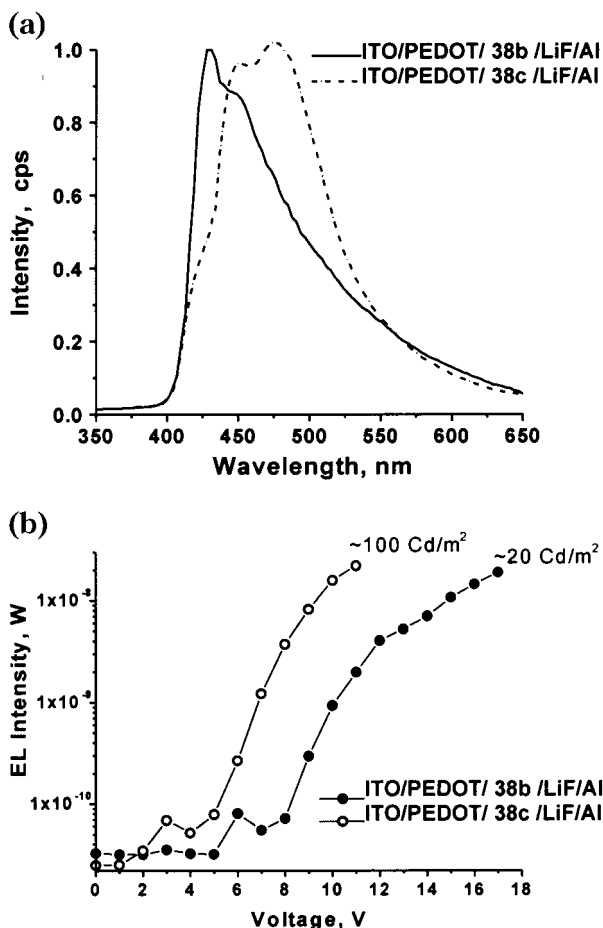


FIGURE 14. (a) Normalized electroluminescence (EL) spectra of devices with **38b** (70% naphthalene units) and **38c** (50% naphthalene units) as emissive layers. (b) Spectrally integrated EL intensity vs voltage characteristics for devices made from **38b** and **38c**.

Conclusions and Outlook

While PPEs have been known for more than a decade, many of the principal physical properties, including liquid crystallinity, aggregation and emission behavior, thermo- and solvatochromicity, and the interplay of all these factors have only been explored recently. While PPEs are the dehydrogenated congeners of the PPVs, their chemical and physical behaviors differ significantly, and more so than expected. The ADIMET access to defect-free dialkyl-PPEs **6** of high molecular weight was the key step to unlock the potential of these simple yet fascinating materials. The thermal and photochemical stability of dialkyl-PPEs **6** makes them attractive for applications in organic semiconductor devices,⁵⁵ while the use of the simple in situ catalyst systems formed from Mo(CO)₆ and substituted phenols for alkyne metathesis is conducive toward large-scale industrial applications. At the same time, these catalysts are not restricted to the synthesis of PPEs. ADIMET can be extended to other alkyne-bridged polymers, including those containing double bonds and organometallic modules.

In the future we will expand ADIMET to other functionalized monomers and study fundamental physical properties of these fascinating materials. Topics include, but are not restricted to, the influence of energy migration,

exciton splitting, and planarization on the optical properties of PPEs, and the formation of gel-like, liquid crystalline, and cable-like nanostructures of PPEs and their relatives in solution and in thin solid films. Importantly, we will aggressively promulgate the use of PPE types into OLEDs and other organic semiconductor devices.

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