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Functional Polyacetylenes

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ABSTRACT

Polyacetylene (PA) is a Nobel Prize-winning macromolecule. In this work, PA is molecularly functionalized, which endows it with an array of new functional properties. The molecular functionalization is realized by attachment of functional pendants to the polyene backbone. Our efforts in the catalyst exploration and reaction optimization have led to the syntheses of a large number of PA derivatives carrying functional groups. Polymer reactions are exploited as an alternative route to the functional PAs that are difficult or impossible to access by direct polymerizations of their monomers. The new PAs with appropriate backbone–pendant combinations show various functional properties such as liquid crystallinity, photoconductivity, light emission, ionic susceptibility, photoresistance, chromism, helical chirality, optical nonlinearity, self-assembly, cytocompatibility, and bioactivity. The properties of the PAs are tuned internally and manipulated externally: the former is achieved by changing their molecular structures, especially their functional pendants, while the latter is accomplished by applying thermal, mechanical, electrical, photonic, and chemical stimuli.

Introduction

Polyacetylene (PA) is the archetypal conjugated polymer. The seminal discovery of the metallic conductivity of its doped form has triggered a huge surge of interest on conductive polymers¹ and has spawned an exciting area of research on synthetic metals. As a result of rapid advances in the area, we are now on the threshold of a “plastic-electronics era” that previously could only be imagined in science fiction.

Structurally, PA is a linear polyene chain $[-(\text{HC}=\text{CH})_n-]$. The existence of two hydrogen atoms in its repeat unit offers ample opportunity to decorate the backbone with pendants: replacement of hydrogen in each repeat unit by one or two substituents yields monosubstituted (1) and disubstituted (2) PAs, respectively (Scheme 1). The pendant and backbone interact with each other: for example, the former perturbs the electronic conjugation of the latter, while the latter influences the molecular alignment of the former. Proper structural design may tune the backbone–pendant interplay into harmony and synergy, generating new substituted PAs with novel functionalities. While PA is electrically conductive, introduction of a

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Scheme 1

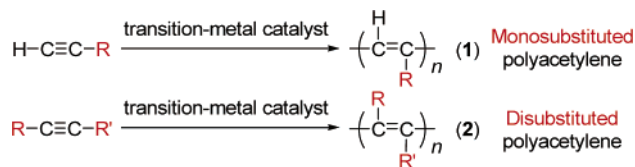
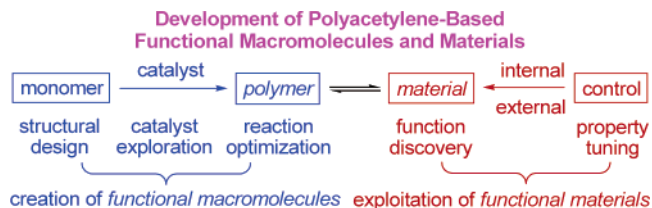


Chart 1



pendant such as a mesogen, chromophore, photosensitive double bond, or naturally occurring building block may endow it with new functional properties such as electrooptic activity, photonic responsiveness, and biologic compatibility.

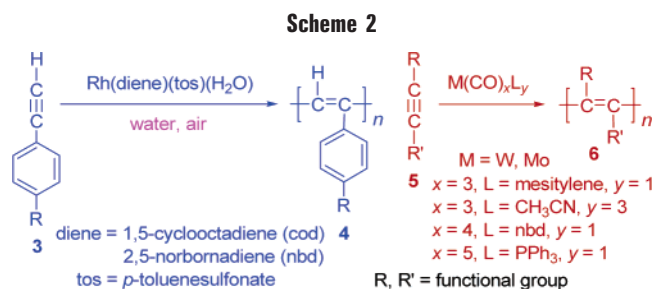
Considerable effort has been devoted to the synthesis of the substituted PAs and study of their properties.^{2–12} Attachment of polar groups to the polyene backbone enables the integration of functional pendants into the PA chain through various functional-group transformations, which was, however, a difficult task in the early stage of PA chemistry.¹² Difficulties were ascribed to the poisoning of the metathesis catalysts by the functional groups. The later discovery of the functionality-tolerant organorhodium catalysts¹³ was a thrilling advance in the area, but the catalysts work for only limited types of monomers, e.g., phenylacetylene derivatives, through an insertion mechanism.¹⁴ The syntheses of functional PAs via the metathesis route remained difficult, with the polymerizations of disubstituted functional acetylenes being particularly intractable.

We have worked on PA functionalization through a systematic approach. Our efforts have covered the design of monomer structures, exploration of new catalysts, optimization of reaction conditions, discovery of functions, and manipulation of properties by internal and external means (Chart 1). Our strategy has worked well, and we have generated a wide variety of new PA-based functional *macromolecules* and *materials*. In this Account, we briefly summarize our efforts and results on the development of the new functional PAs.

Polymer Syntheses

Catalyst. The main difficulty in the polymerizations of functional acetylenes was the “incompatibility” of the polar groups with the metathesis catalysts. The functionality tolerance of the Rh-based insertion catalysts¹³ thus attracted our attention. To expand the variety of the Rh catalysts, we prepared a series of Rh complexes $\text{Rh}(\text{diene})\text{L}$

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(L = ligand). We thereby developed a catalyst system that can initiate acetylene polymerizations in water and air, giving stereoregular polymers **4** in high yields (Scheme 2).¹⁵

Like their older versions,¹³ the new Rh catalysts are also only effective for the polymerizations of specific types of monomers. To develop more general systems, we turned our attention back to metathesis catalysts. MoCl_5 and WCl_6 are classical metathesis catalysts, but the early attempts to use them to polymerize functional acetylenes often resulted in the formation of insoluble or oligomeric products in low yields.^{3b,4b,12,16} We envisioned that the metal halides would be functionality-tolerant, for they could cyclopolymerize functional *diynes* into *cyclic polyenes*.¹⁷ Our prediction proved correct: through catalyst–substrate matching and reaction-condition optimization, we accomplished our goal of using the metal halides to catalyze the *linear* polymerizations of various functional acetylenes (*monoynes*).

The metal halides are, however, air- and moisture-sensitive. In 1989, Tang found that several stable metal carbonyl complexes catalyzed the polymerizations of nonfunctional 1-alkynes.¹⁸ We extended his effort in the area and prepared a series of $\text{M}(\text{CO})_x\text{L}_y$ complexes. Delightfully, many functional acetylenes (**5**) could be polymerized by these metal carbonyl complexes (Scheme 2).¹⁹

Polymerization. To match the catalysts with particular substrates, we prepared hundreds of functional acetylenes. The substrate–catalyst matching is structurally sensitive: a seemingly subtle variation in the functional group can greatly influence the polymerization behavior of a monomer by a given catalyst. For example, **7(3)** and **8(3)** differ only in the orientation of the ester unit but show distinct polymerizability by $\text{W}(\text{CO})_3(\text{mesitylene})$:¹⁹ **8(3)** can be effectively polymerized, but **7(3)** cannot (Scheme 3). Polymerization conditions (cocatalyst, solvent, etc.) can affect the fate of a specific substrate–catalyst pair. For instance, **9**– WCl_6 may be a bad or good combination, depending on whether tetra(*n*-butyl)tin or tetraphenyltin is used as cocatalyst.²⁰ Polymerization of **10** does not occur at all in toluene²¹ but proceeds well in dioxane.

As a result of optimization of the polymerization reactions, many functional monomers are transformed into polymers of high molecular weights (up to several million) in high yields (up to 100%). Substituted PAs containing various functional groups, e.g., crown ether, sulfonate, amide, dipeptide, saccharide, nucleoside, sterol, cyano, thiophene, vinyl, phthalimide, indole, siloxane, and

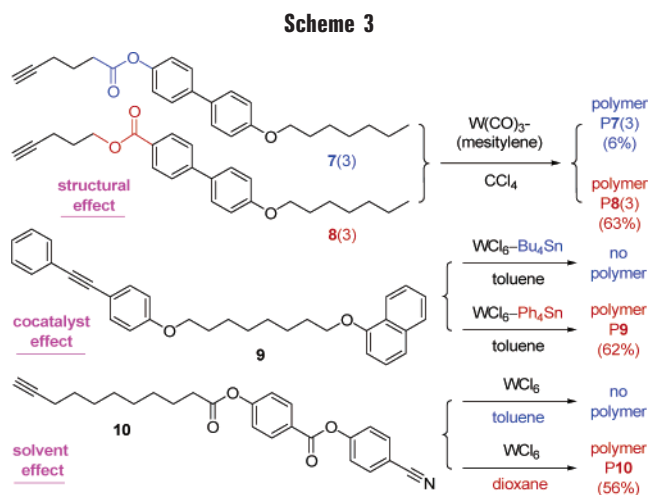
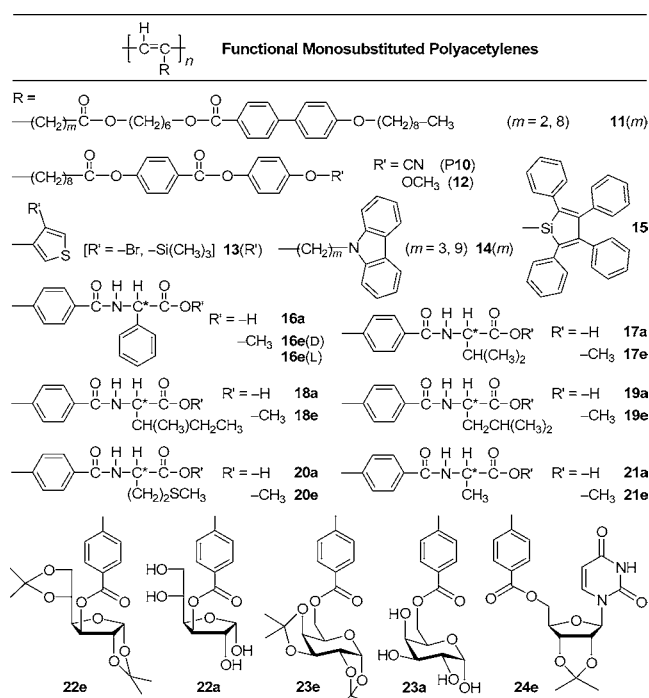


Chart 2



silole, have been obtained.^{15b,21–24} Examples are given in Charts 2 and 3.

On the basis of our results, a substrate–catalyst matching map is drawn as shown in Chart 4. Functionalized 1-arylacetylenes are polymerizable only by the Rh-based catalysts,¹⁵ although their nonfunctional cousins can be polymerized by other catalysts.¹² Polymerizations of functionalized 1-alkynes are effected by the W-based catalysts, with the Rh ones giving moderate results.^{21,25} Propiolates can be effectively polymerized by the Mo and Rh catalysts.²⁶ The Rh complexes cannot polymerize disubstituted acetylenes. Polymerizations of alkyl 2-alkynoates and alkyl 3-arylpriolates are effected by the Mo catalysts, while those of aryl 3-arylpriolates, 1-aryl-1-alkynes, and diarylacetylenes are initiated by the W catalysts.^{20,27,28} While polymerization of monosubstituted acetylenes (Chart 4, nos. 1–3) normally proceeds at room temperature in polar solvents (e.g., dioxane), disubstituted acetylenes

Chart 3

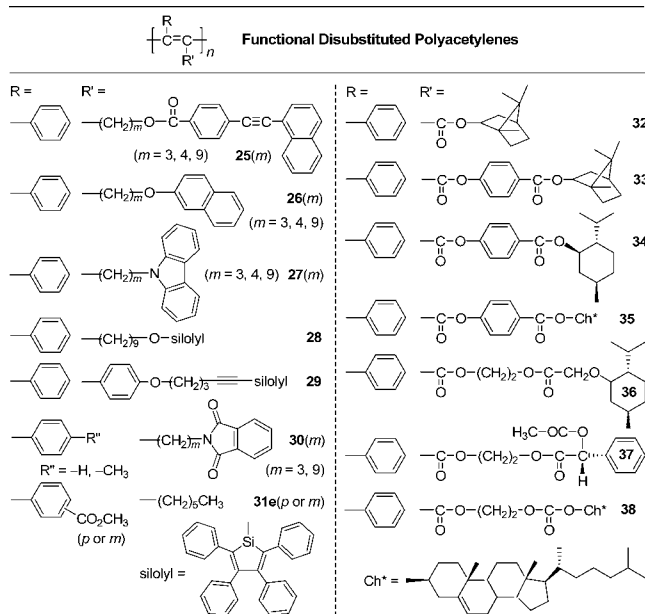


Chart 4

no.	substrate		catalyst		
	acetylene monomer	carrying functional group (FG)	Mo	W	Rh
1	$\text{H}-\text{C}\equiv\text{C}-\text{Ar}-\text{FG}$	1-arylacetylene	○	○	●
2	$\text{H}-\text{C}\equiv\text{C}-(\text{CH}_2)_m-\text{FG}$	1-alkyne	○	●	○
3	$\text{H}-\text{C}\equiv\text{C}-\text{CO}_2-\text{FG}$	propiolate	●	○	●
4	$\text{CH}_3(\text{CH}_2)_m-\text{C}\equiv\text{C}-\text{CO}_2-(\text{CH}_2)_m-\text{FG}$	alkyl 2-alkynoate	●	○	○
5	$\text{Ar}-\text{C}\equiv\text{C}-\text{CO}_2-(\text{CH}_2)_m-\text{FG}$	alkyl 3-arylpropiolate	●	○	○
6	$\text{Ar}-\text{C}\equiv\text{C}-\text{CO}_2-\text{Ar}-\text{FG}$	aryl 3-arylpropiolate	○	●	○
7	$\text{FG}-\text{Ar}-\text{C}\equiv\text{C}-(\text{CH}_2)_m-\text{FG}$	1-aryl-1-alkyne	○	●	○
8	$\text{Ar}-\text{C}\equiv\text{C}-\text{Ar}-\text{FG}$	diarylacetylene	○	●	○

degree of substrate-catalyst matching: ● = excellent, ○ = good, ○ = bad

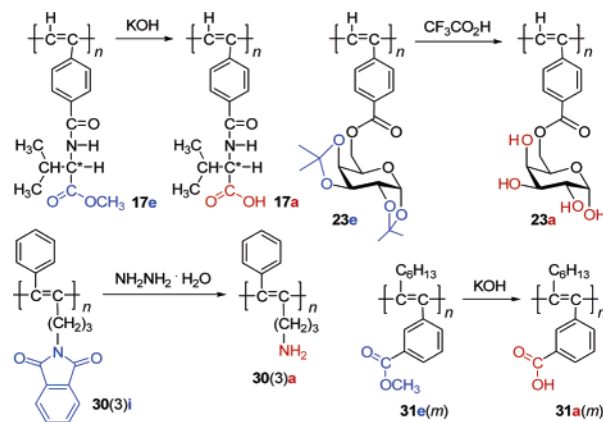
(nos. 4–8) generally polymerize at higher temperatures (e.g., ~80 °C) in nonpolar solvents (e.g., toluene).^{20–28}

Polymer Reaction. The monomers containing acidic protons are difficult to polymerize. To tackle this problem, we adopted a polymer-reaction approach by commencing with the preformed polymers. The polymers carrying acidic protons (**a**) (acids and alcohols) given in Chart 2 are prepared by the polymer reactions from their ester or ether (**e**) precursors. While polymer reactions normally do not proceed to 100% completion, we are able to cleave the ester and ether groups of **17e** and **23e** by hydrolyses to give clean **17a** and **23a**, which do not contain any ester and ether residues (Scheme 4).^{22,24} Similarly, deprotections of imide **30(3)i** and ester **31e** yield amine **30(3)a** and acid **31a**, respectively.²⁹ It should be noted that it is not possible to gain access to these functionalized disubstituted PAs by the direct polymerization. The examples given here clearly illustrate the usefulness of the polymer-reaction approach.

Materials Properties

The new PAs comprising conjugated backbones and functional pendants are expected to show unique proper-

Scheme 4



ties. Studies of these properties will help understand how the polymers behave and aid our efforts to develop the new *macromolecules* to technologically useful *materials*.

Processability and Stability. PA is notoriously intrac-table and unstable. In contrast, most of our functionalized PAs are soluble, thanks to the suppression of backbone interactions by the pendant groups. All the disubstituted PAs are very stable: for example, **26(4)** does not decompose when heated in air at high temperatures (e.g., 200 °C) for prolonged time (e.g., 12 h). The pendants shroud the polyene backbone, protecting it from thermolytic attack.³⁰

The functionalized poly(1-alkyne)s and polypropiolates are also stable. For example, P7(3) does not degrade when it is heated in air at temperatures up to 200 °C (Figure 1A).³¹ Similarly, the M_w of P7(9) does not change when it

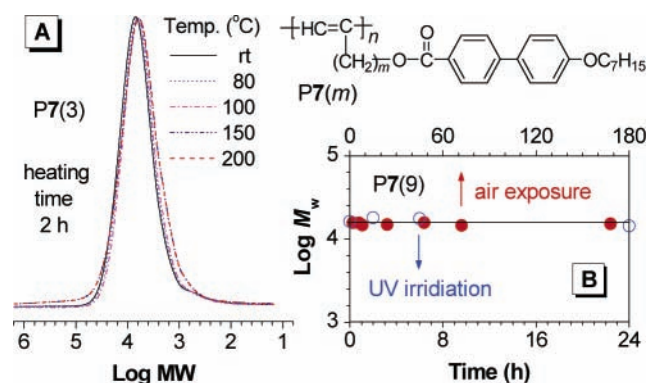


FIGURE 1. Resistances of P7(*m*) against (A) thermolysis and (B) oxidation and photolysis in air.

is exposed to UV irradiation or stored in air. Functionalized poly(1-arylacetylene)s, however, are only moderately stable and degrade when heated to >100 °C or stored under ambient conditions.²⁰ This makes them unsuitable for long-term uses but potentially attractive as materials that must decompose during and/or after use (e.g., photo- and biodegradable polymers).

Liquid Crystallinity. The excellent processability and stability of many of the substituted PAs encouraged us to develop them further into functional materials. Working with the colleagues in our Center for Display Research, we investigated mesomorphism of the PAs carrying me-sonogenic pendants.

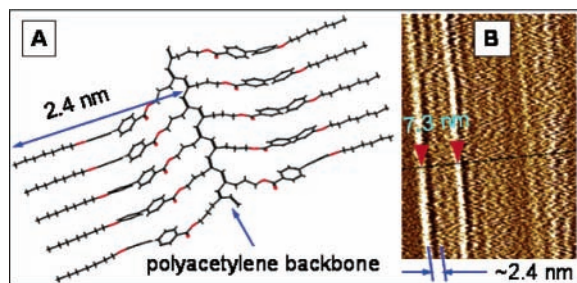


FIGURE 2. (A) Calculated chain conformation of P8 and (B) its observed packing structure.

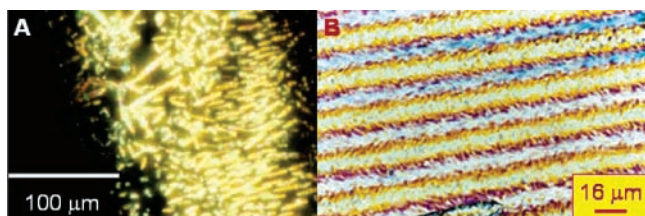


FIGURE 3. Induced alignments of (A) P7(9) by electric field and (B) 12 by mechanical shear.

Many of the PAs show liquid crystallinity, in which the whole polymer chains serve as the mesogens in the packing processes due to their shape persistency (Figure 2).^{32b} The mesomorphism of the polymer varies with its molecular structure. For example, the conformation of the polyene backbone affects the alignment of the mesogens: a higher chain stereoregularity results in a lower packing order.^{32,33} The biphenyl core favors smectic (S) phases where the mesogens pack into layered structures (e.g., Figure 2B), while the phenylcyclohexyl core can enter nematic (N) phases where the mesogens are arranged in a nonlamellar fashion.^{28,32b} A more flexible spacer induces better mesogenic order.²¹ A liquid crystalline PA (LCPA) with ester bridges packs into a bilayer structure, but its congener with ether bridges enters into a monolayer structure.²⁵ The LCPA carrying cyano tails (P10) undergoes S_A transition, whereas its counterpart with methoxy tails (12) undertakes both S_A and N transitions.^{23b}

Mesomorphic alignments of the LCPAs can be modulated by external stimuli. Application of an electric field can induce the bâtonnets of P7(9) to align parallel to the field direction (Figure 3A).³⁴ When mechanically sheared 12 is naturally cooled from its nematic phase, parallel bands are formed.^{23b} The sheared chain remains stretched after the force has been removed, because of the long relaxation time of its rigid backbone.^{23b} The mesogenic pendants when cooled thus align into ordered bands with the aid of the stretched backbone. It has been generally believed that a rigid main chain distorts the packing of its mesogenic side chains. The example here, however, illustrates that a rigid backbone can play an active role in inducing anisotropic alignment.

Photoconductivity. Heterojunctions favor photoconductivities, for excitons dissociate efficiently at, and carriers move rapidly along, the interfaces. The amorphous–crystalline interface in an LCPA is expected to enhance its photoconductivity (PC). Indeed, LCPA P7(9) shows higher PC than poly(phenylacetylene) (39), a non-LCPA

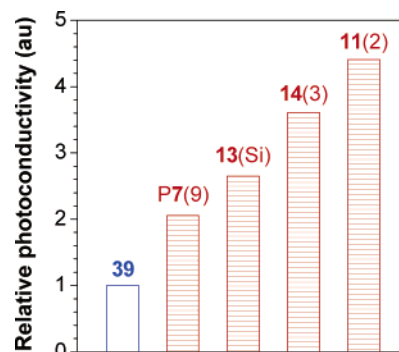


FIGURE 4. Photoconductivity of polyacetylenes.

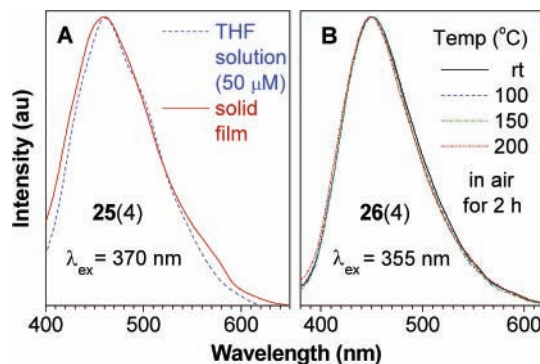


FIGURE 5. Spectral stability of 25(4) and 26(4) against (A) aggregation and (B) thermolysis.

photoconductor^{2b} (Figure 4). LCPA 11(2) shows even higher PC, because of its better-ordered LC aggregates formed in the photoreceptor fabrication process.³⁵

Light Emission. Little effort has been made to develop light-emitting PAs (LEPAs)^{6,8b,9b} because PA itself is nonluminescent. Structural modifications, such as alterations in the electronic and steric effects of the pendants, can be used to tune the conjugation length and electronic interaction of the polyene chain, which can in turn greatly enhance its photoluminescence (PL) efficiency (up to unity).³³ The emitting center can be the pendant (e.g., in 11), the backbone (e.g., in 32), or both of them (e.g., in 29). Energy transfer can be from the pendant to the backbone (e.g., in 27) or from the backbone to the pendant (e.g., in 28), and the emission color can be violet (11), blue (32), green (29), or red (15), all tunable by changing the backbone and pendant structures.

Aggregation quenching is a thorny problem in the development of light-emitting polymers but is not apparent in our LEPA systems. The PL spectrum of the film of 25(4), for example, is nearly the same as that of its solution: its PL is not quenched by the aggregate formation (Figure 5A). The LEPAs enjoy good spectral stability: for example, 26(4) emits a blue light, whose PL profile does not vary after it has been heated to 200 °C in air or exposed to UV irradiation in nitrogen or under vacuum.³³

The PL of the LEPAs can be externally modulated. When 1 equiv of Cu^{2+} ion is added to a solution of 31a(m), its PL drops to half (Figure 6A).²⁹ The effect of Fe^{3+} is more striking: it completely quenches the emission. In contrast, the PL becomes stronger in the presence of Al^{3+} . These distinct PL responses associated with the specific polymer–

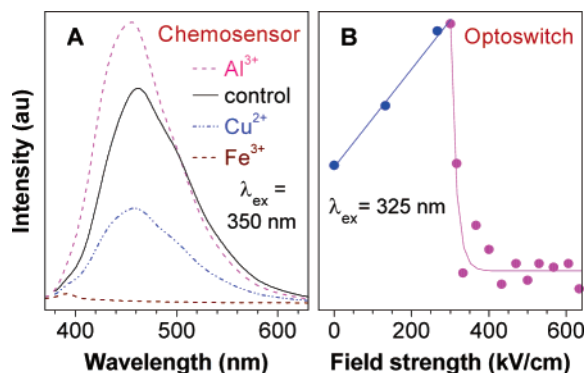


FIGURE 6. Tuning photoluminescence of THF solutions of (A) **31a(m)** (10 μ M) by ionic species and (B) **P7(9)** (11 mM) by electric field.

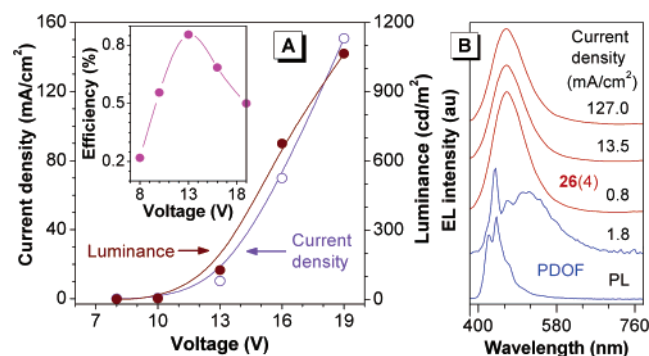


FIGURE 7. (A) Device performance of a multilayer LED of **26(4)** and (B) comparison of its spectral stability with that of poly(9,9-dioctylfluorene) (PDOF).

metal interactions enable the LEPA to act as a chemosensor. When an electric field is applied, the PL of **P7(9)** initially increases with the field strength, then sharply drops, and finally levels off.³⁶ This unique phenomenon may be utilized to construct electrooptic switches, whose light emissions are controllable by an electric field.

The efficient PL encouraged us to check the electroluminescence (EL) of the LEPAs. A light-emitting diode (LED) of **26(4)**³⁷ emits a blue light of 460 nm, whose EL peak is symmetrically shaped,³³ with no sidebands from such species as aggregative excimers. Its external quantum efficiency (η_{EL}) reaches 0.85% (Figure 7A), very comparable to those of some of the best blue-light-emitting polymers.³⁸ Although the device configurations of our LEDs have not been optimized, many of them already display a η_{EL} of 0.5–0.86%,³⁹ much higher than that (0.01%) of nonfunctional poly(1-phenyl-1-octyne) (**40**). The chromophoric pendants attached to the polyene skeleton may have helped boost the EL performance of the LEPAs.

Polyfluorenes are the best known blue-light-emitting polymers, but their spectral stabilities are low.⁴⁰ A broad peak centered at \sim 520 nm appears when a current density as low as 1.8 mA/cm² passes through the PDOF device. The EL spectrum of **26(4)** does not change when a current density as high as 127 mA/cm² passes through its device (Figure 7b).³⁹ Our LEDs are thus spectrally very stable.

Luminescent Imaging. Some LEPAs are photoresponsive,⁴¹ and we explored the possibility of using them to generate light-emitting patterns. UV irradiation of **41(3)**

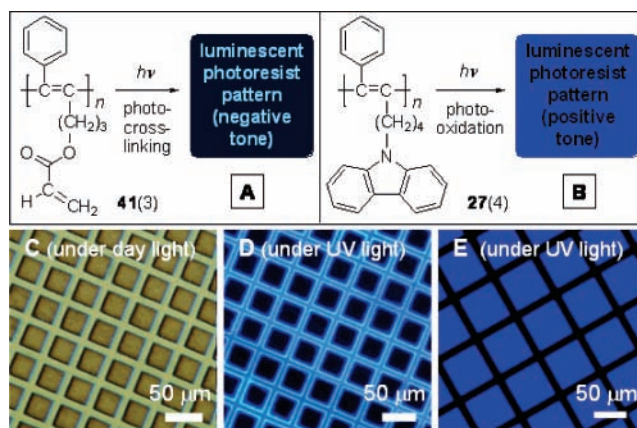


FIGURE 8. (A) Photo-cross-linking of **41(3)** and (B) photooxidation of **27(4)** lead to the formation of (C, D) 3D negative and (E) 2D positive photoresist images.

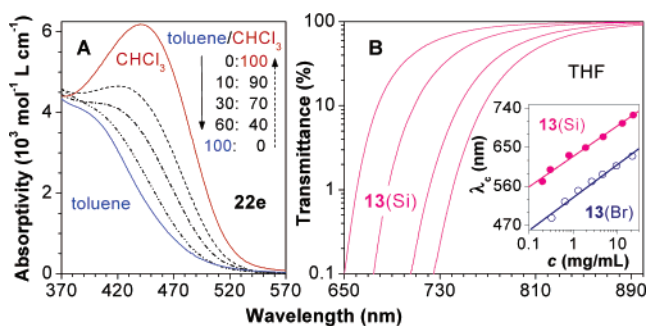


FIGURE 9. (A) Solvato- and (B) concentratochromisms of **22e** and **13(R)**.

readily initiates photopolymerization of its acrylic pendants (Figure 8A). Development of the exposed films gives well-defined photoresist patterns. The patterned lines glow under UV illumination because its poly(1-phenyl-1-alkyne) skeleton is highly emissive.³³

Disubstituted PAs are resistant to thermolysis. Some of them, however, are sensitive to photooxidation, which quenches their PL. For example, UV irradiation of a film of **27(4)** in air through a mask quenches the luminescence of the exposed region (black lines), while the unexposed area remains emissive (Figure 8E).⁴¹ A PL image is thus directly drawn without a developing process.

Chromism. The polyene backbone of a segment in a PA chain can adopt an *E-s-E*, an *E-s-Z*, a *Z-s-E*, or a *Z-s-Z* conformation.^{12,26} Because the energy needed for the conformational conversion is small, the conformation of a PA segment is anticipated to be tunable by changing its surrounding environment. In toluene and chloroform, **22e** absorbs weakly and strongly, respectively (Figure 9A). The optical transition between these two states can be manipulated continuously and reversibly by varying the ratio of the solvents in the polymer solution. Most segments of **22e** may adopt a more planar conformation in chloroform while the opposite is true in toluene, thereby accounting for the solvatochromism.

The light transmission spectrum of **13(Si)** resembles that of an optical cutoff filter, which red shifts with an increase in its concentration (*c*). Its cutoff wavelength (λ_c) changes with *c* semilogarithmically over a wide spectral

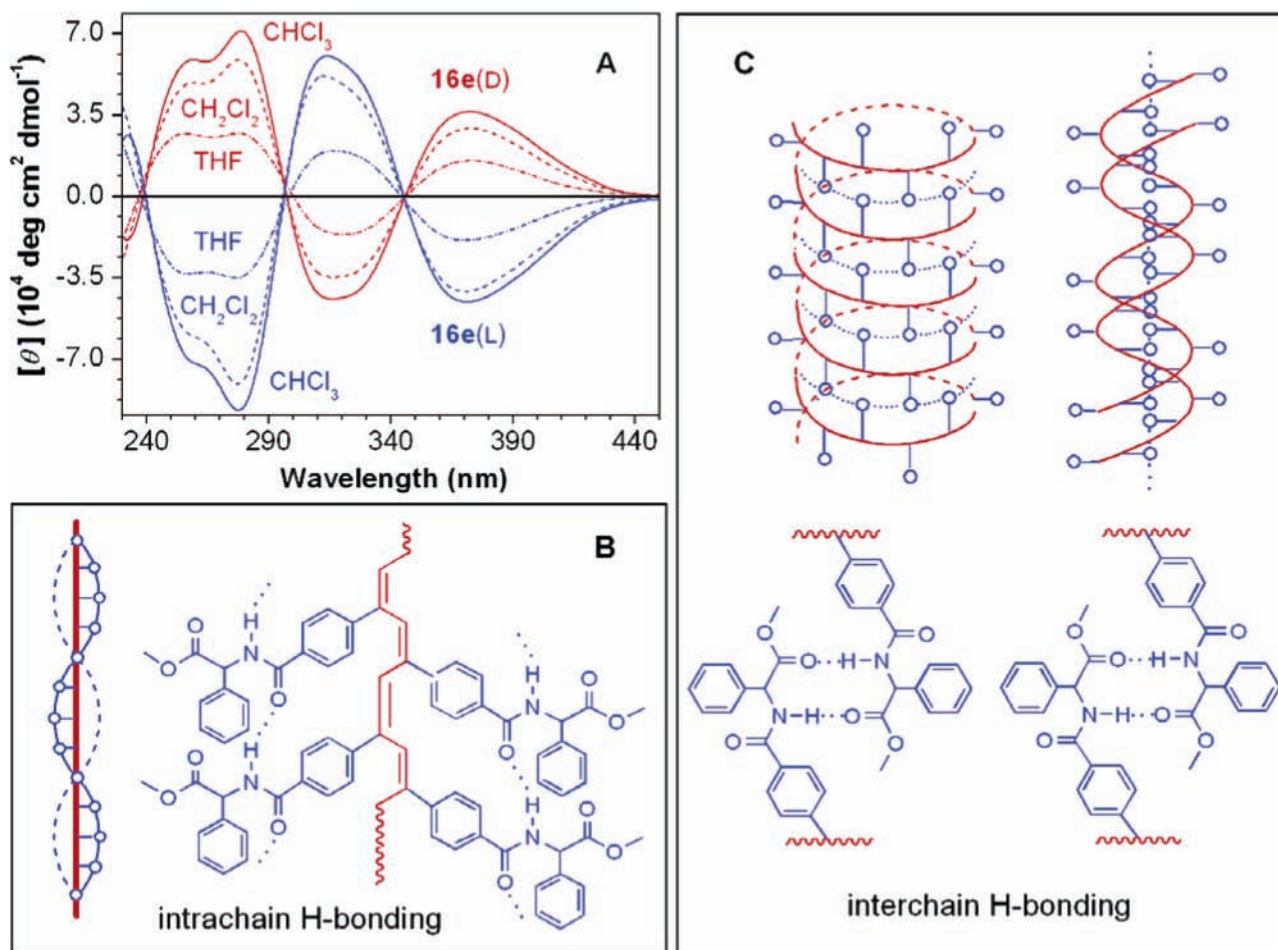


FIGURE 10. (A) Chain helicity determined by pendant chirality and manipulated by solvent variation. (B) Single and (C) double helical strands of **16e** stabilized by intra- and interchain hydrogen bonds.

range.⁴² This concentratochromism is also observed in **13**(Br), possibly due to nanocluster formation in these strongly absorptive PAs. This offers an easy way to make plastic optical filters, whose λ_c can be readily tuned by varying their PA contents.

Optical Activity. Tang and Kotera synthesized one of the few optically active PAs (OAPAs) in the late 1980s.¹⁸ Tang continued his pursuit of OAPAs after he had moved to Hong Kong in the mid-1990s. While the early OAPAs contained no polar groups due to the difficulty of synthesizing them,^{2a,3,18} the recent advancements in the polymer syntheses allow us to design a diverse palette of new OAPAs by incorporating various chiral units into the PA chains.

We have concentrated our effort on the development of OAPAs with naturally occurring building blocks such as amino acids, saccharides, nucleosides, and sterols.⁴³ Figure 10A shows circular dichroism spectra of a pair of polymers containing D- α -phenylglycine [**16e**(D)] and L- α -phenylglycine [**16e**(L)] units. The positive and negative Cotton effects in the long-wavelength region reveal that the chain segments of the PAs carrying the pendants of opposite chirality form spirals of opposite helicity. Obviously the backbone helicity (*M* or *P*) is determined by the pendant chirality (D or L) under the same environmental conditions. When the solvent of the polymer solution is

changed from chloroform to THF, the Cotton effect is greatly decreased, indicating that the helical preference of the chain segment can be tuned by an environmental variation. The helical chain segments are believed to be mainly stabilized by the intra- and interstrand hydrogen bonds between the chiral pendants (Figure 10, panels B and C). The noncovalent stabilization can be broken by external perturbation, and the system will reach a new equilibrium.²² This dynamic process enables the OAPAs to cope with the variations in their surrounding environments, as do helical biopolymers such as proteins.^{43,44}

Further examples of the helicity tuning by external stimuli are given in Figure 11.^{43,44} The ellipticities ($[\theta]$) of **17e** are positive and negative in THF and CHCl_3 , respectively; that is, the majority of its chain segments form coils of opposite helicity in these two solvents. In other words, the helical preference can be completely reversed by simply changing the solvent. The helicity change is continuous and reversible, as revealed by the $[\theta]$ -solvent plot in Figure 11A. The ellipticity changes rapidly when the amount of chloroform is increased from $\sim 65\%$ to $\sim 80\%$. This is indicative of a cooperative process:^{43–45} once some segments are associated via noncovalent interactions (e.g., a hydrogen bond), their neighboring segments will be zipped up quickly along the preferred direction. The ellipticity of **17e** monotonically decreases

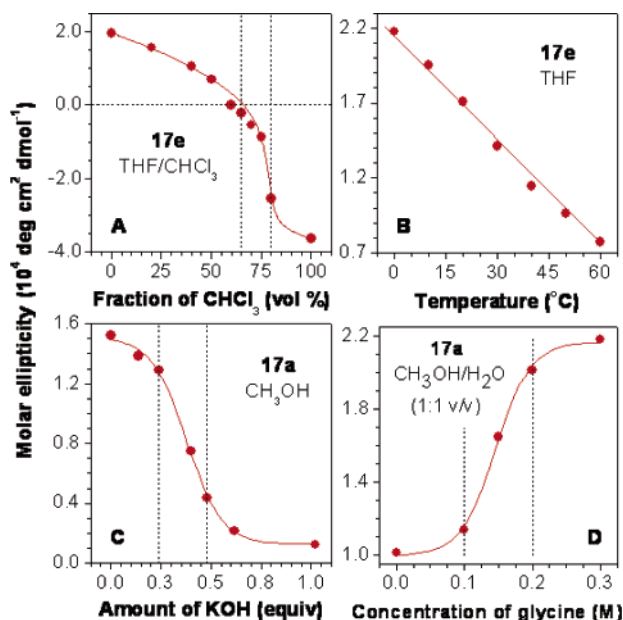


FIGURE 11. Tuning ellipticity of **17e** (A, B) and **17a** (C, D) at ~ 375 nm by (A) solvent, (B) temperature, (C) pH, and (D) additive.

with increasing temperature because the thermally activated chain randomization induces the segments to unwind.

Addition of KOH into a solution of **17a** progressively weakens its $[\theta]$ because the ionic interaction of K^+ with CO_2^- breaks the intra- and interchain hydrogen bonds (Figure 11C).⁴⁶ The original $[\theta]$ can be regained when the KOH solution is neutralized by HCl; this illustrates the reversibility of helicity tuning with variation in the pH. Intriguingly, $[\theta]$ can also be tuned by achiral additives. With continuous addition of glycine (an achiral essential amino acid) to the solution of **17a**, its $[\theta]$ continuously increases. The glycine molecules may bind to the L-valine pendants, causing an increase in the pendant bulkiness and thereby inducing further twists in the chain segments.

Supramolecular Assembly. After studying the chain helicity as associated with the secondary structure of the OAPAs, we investigated their higher order structures. Noticing the unique amphiphilicity of the OAPAs originating from their hydrophobic backbones and hydrophilic pendants, we explored the possibility of utilizing them as “Legos” to construct biomimetic hierarchical structures.

The OAPAs can self-organize into a variety of morphologies reminiscent of natural structural motifs such as vesicles, tubules, helices, and honeycombs. Thus, evaporation of a solution of **24e** (an OAPA with uridine pendants) yields vesicles, while that of **18a** (L-isoleucine pendants) gives tubules with coexisting vesicles (Figure 12).^{22b,47} In the polar solvents, the OAPAs cluster into bi- or multilayered spherical aggregates or vesicles with hydrophobic cores and hydrophilic coronas. Under appropriate conditions, the vesicles further associate into tubular structures.

The tunability of the chain helicity of the OAPAs through internal and external perturbations suggests that their self-assembling morphologies can be manipulated

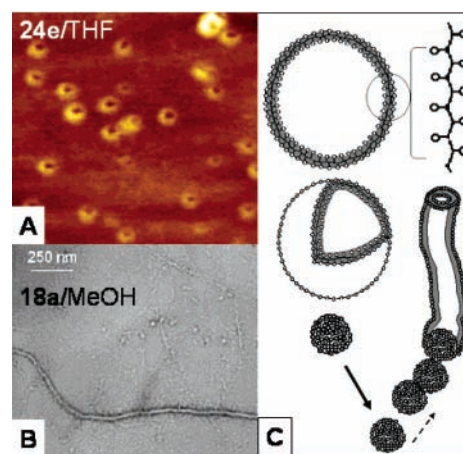


FIGURE 12. (A) Vesicles and (B) nanotubes formed by natural evaporation of polyacetylene solutions ($10\text{--}19\ \mu\text{M}$) and (C) proposed processes for the formation of the nanostructures.

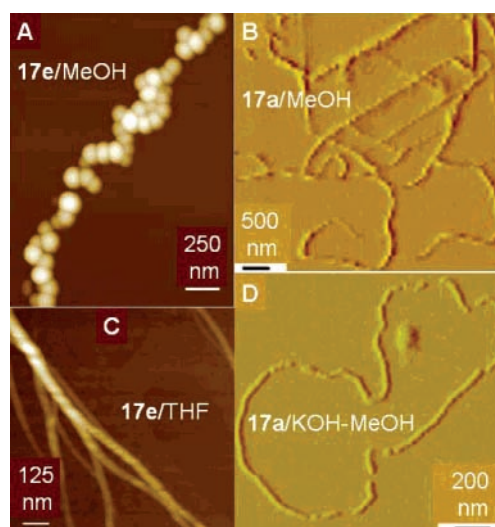


FIGURE 13. Tuning the assembling structures formed by natural evaporation of the solutions of **17a** and **17e** ($\sim 11.6\text{--}12.2\ \mu\text{M}$) through internal and external perturbations.

by changing their molecular structures and environmental conditions, because the variations in the secondary structure should affect the higher order structures. This proves to be the case. Evaporation of a methanol solution of **17e** gives a string of pearls (Figure 13A). Helical ropes are obtained when its structure (internal) and solvent (external) are changed to **17a** and THF, respectively. Addition of KOH into the methanol solution of **17a** changes the helical cable to a random thread (Figure 13D). The association of K^+ ions with CO_2^- groups breaks the hydrogen bonds. The charged polyelectrolyte chains repulse each other and are difficult to associate into multistrand helical cables, hence the observed thin random coils.⁴⁶

Evaporation of more concentrated solutions gives structures of bigger sizes: for example, a large honeycomb pattern is obtained from a thick solution of **19a** (Figure 14A).⁴⁸ Precipitation of a concentrated solution of **20** into its poor solvents yields micrometer-sized helical fibers with both left- and right-handed twists.²²

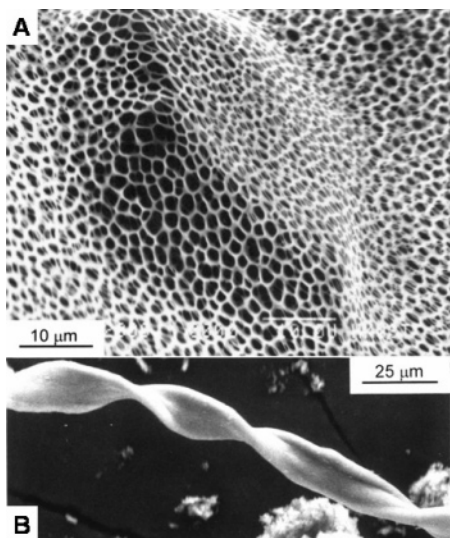


FIGURE 14. (A) Honeycomb pattern and (B) helical fiber formed by (A) evaporation of **19a**/MeOH solution (29 μ M) on a glass slide and (B) precipitation of **20e**/DMF solution (100 mM) into an acetone/ether mixture.

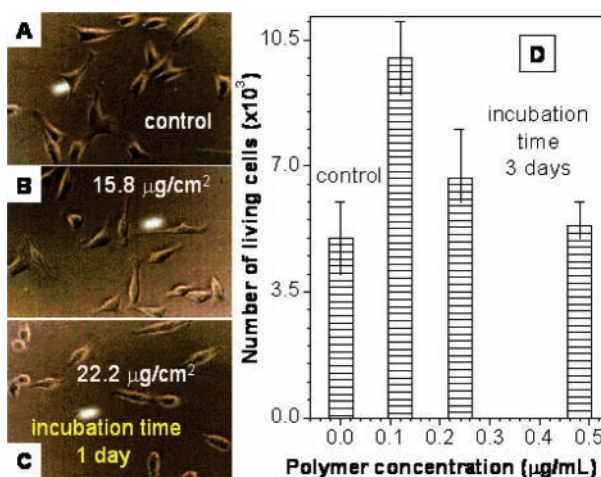


FIGURE 15. Growths of living HeLa cells (A–C) on the microtiter plates precoated by **21a** with different coating densities and (D) in the incubation media containing **23e** of different concentrations.

Biological Compatibility. An OAPA chain may be viewed as a molecular wire of polyene backbone sheathed in a jacket of chiral pendants.³⁰ Since these pendants are the building blocks of biopolymers, they may make OAPA biocompatible. When living cells are subcultured in the microtiter plates precoated with films of **21a** (an OAPA bearing L-alanine pendants), the cells adhere to, and grow on, the plates as they do in the control (Figure 15A–C): **21a** is thus cytocompatible.⁴⁹ No dead cells are found throughout the incubation period, further confirming its biocompatibility.

The OAPAs bearing monosaccharide pendants can promote the growth of living cells.⁵⁰ For example, when a small amount (~ 0.1 μ g/mL) of **23e** (an OAPA carrying D-galactose pendants) is added into the culture medium of living HeLa cells, their growth rate is doubled (Figure 15D). This cell-growth-stimulating attribute may enable the OAPA to find an application as a scaffold material in tissue engineering.

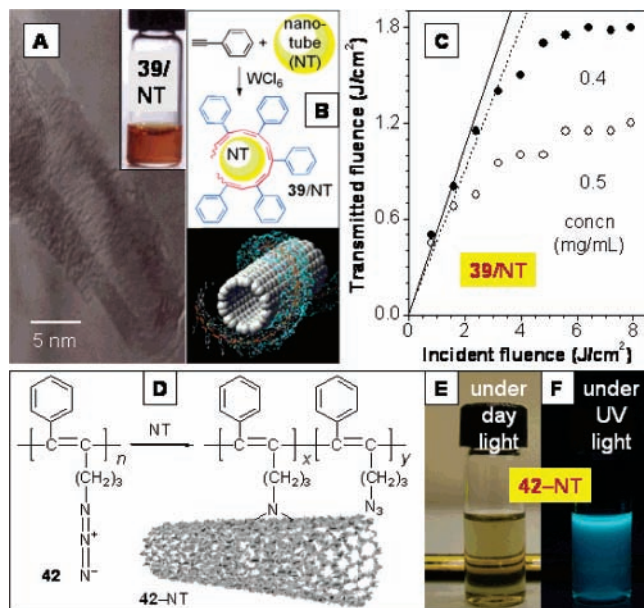


FIGURE 16. (A) Dissolution of a carbon NT by wrapping it in chains of (A) **39** and (E) **42** through (B) in situ polymerization and (D) polymer reaction. (C) Optical limiting in, and (F) light emission from, THF solutions of (C) **39**–NT and (D) **42**–NT.

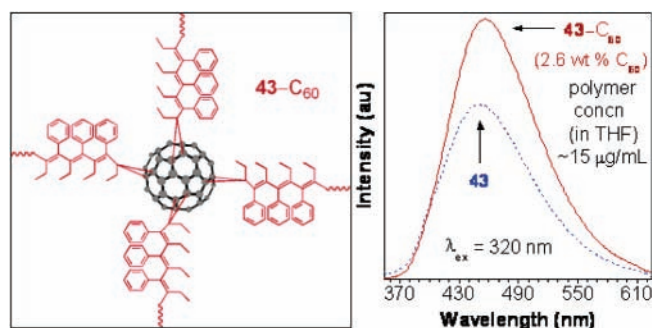


FIGURE 17. Photoluminescence of fullerene-containing poly(1-phenyl-1-butyne) (**43**–C₆₀).

Nanostructural Hybridization. PA can also be functionalized by hybridization with such functional materials as nanotubes (NTs), fullerenes, and perovskites. When phenylacetylene is polymerized in the presence of NTs, the PA chains wrap the NT shells, giving soluble **39**–NT nanohybrids that nonlinearly attenuate 8 ns, 532 nm optical pulses⁵¹ (Figure 16A–C). Disubstituted PAs (e.g., **42**) can be covalently bound to NT shells. The resultant **42**–NT adducts are again good optical limiters, while retaining their luminescence capability (Figure 16F). C₆₀, on the other hand, can boost PL efficiencies of LEPAs. Copolymerization of 1-phenyl-1-butyne with C₆₀ yields **43**–C₆₀ adducts that emit more strongly than their parent **43** (Figure 17).⁵²

Conclusions and Prospects

In this work, a large variety of functional moieties are integrated into the molecular structure of PA by the direct polymerizations of functional monomers and the polymer reactions of preformed polymers. The functionalization routes explored and the structural insights gained in this

study offer versatile synthetic tools and valuable designer guidelines for further developments in the area. Our success in the polymer synthesis proves that the conjugated polyene backbone can be used as a new structural scaffold for the construction of novel functional macromolecules.

The conjugated backbones and functional pendants as well as their synergistic interplays endow PA with an array of unique functional properties. The mesogenic pendants confer liquid crystallinity on PA, while the polyene backbones allow the LCPA chains to be aligned by simple shearing. The energy transfers between the chromophoric pendants and the conjugated skeletons enable the PL colors and efficiencies of the LEPAs to be tuned by molecular engineering. The bulky pendants sheath the conjugated skeletons, which weakens chain interactions and boosts spectral stabilities. The chiral pendants induce the polyene backbones to spiral, with the chain helicity being determined by the pendant chirality. The conformational sensitivity of the polyene backbone to the environmental surroundings, on the other hand, permits the preferred handedness of their chain segments to be modulated by external perturbations continuously and reversibly. The OAPA chains self-assemble into biomimetic hierarchical structures, thanks to the amphiphilicity stemming from their hydrophobic backbones and hydrophilic pendants.

Many of the functionalized PAs are robust and processable, in addition to having simple syntheses and novel functional properties. They may find a wide range of applications as specialty materials in, e.g., information storage, photovoltaic cells, chemical sensing, optical displays, photoresist patterns, luminescent imaging, optical filtration, nonlinear optics, chiral separation, light polarization, biomimetic morphosynthesis, controlled drug delivery, artificial nerves, and tissue engineering. Efforts to exploit the technological applications of the functionalized PAs are currently under way in our laboratories.

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