A Combinatorial Approach for Colorimetric Differentiation of Organic Solvents Based on Conjugated Polymer-Embedded Electrospun Fibers

By *Jaewon Yoon, Young-Sik Jung,* and *Jong-Man Kim**

A combinatorial approach for the colorimetric differentiation of organic solvents is developed. A polydiacetylene (PDA)-embedded electrospun fiber mat, prepared with aminobutyric acid-derived diacetylene monomer PCDA-ABA 1, displays colorimetric stability when exposed to common organic solvents. In contrast, a fiber mat prepared with the aniline-derived diacetylene PCDA-AN 2 undergoes a solvent-sensitive color transition. Arrays of PDA-embedded microfibers are constructed by electrospinning poly(ethylene oxide) solutions containing various ratios of two diacetylene monomers. Unique color patterns are developed when the conjugated polymer-embedded electrospun fiber arrays are exposed to common organic solvents in a manner which enables direct colorimetric differentiation of the tested solvents.

1. Introduction

The development of efficient chemosensors for the detection of biologically, environmentally, and diagnostically important materials has gained enormous attention during the last several decades. These efforts have led to the discovery of a variety of small molecule- and polymer-based sensory compounds and systems. Among the many chemosensors reported to date, conjugated polymers have received special attention owing to the intriguing properties associated with their extensively delocalized π-network and conformationally restricted polymer chains.[1] Perturbation of the delocalized π-system in the conjugated polymer often induces changes in electronic absorption and emission properties. These changes have been elegantly applied to the design of efficient chemo/biosensors.[1] Accordingly, a variety of conjugated polymers such as polythiophene, polyaniline, polypyrrole, polyphenylene, poly(phenylene ethynylene), polyacetylene, and polydiacetylene (PDA) have been employed as sensing matrices.[1]

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Among the conjugated polymers reported to date, PDAs are unique in several regards.[2–16] First, these polymers can be prepared from supramolecularly assembled crystalline or semi-crystalline states of diacetylene (DA) monomers. Conventional solution-based chemical approaches typically employed for the preparation of conjugated polymers do not yield PDAs efficiently. Second, PDAs are produced by UV or γ-irradiation of self-assembled DAs without the need for chemical initiators or catalysts. Thus, the resulting polymers are not contaminated with unwanted by-products. Third, PDAs are readily prepared in aqueous solution in the form of nanostructured liposomes, vesicles, and wires, which enables them to be employed as matrices for biosensing. Finally, nanostructured PDAs undergo a blue to red color change in response to heat (thermochromism), organic solvents (solvatochromism), mechanical stress (mechanochromism), and ligand-receptor interactions (affinochromism).[5,17–29]

Although it has been known for some time that the blue-to-red colorimetric transition occurs when PDAs are exposed to certain organic solvents,[22] only a minimal effort has been given to the development of PDA sensor systems for differentiation of the organic solvents. Recently, we described PDA-based colorimetric sensors based on PDA-embedded electrospun fiber mats that can be used to detect volatile organic compounds (VOCs).[28] This system was able to distinguish between several organic solvents such as chloroform, hexane, ethyl acetate (EA), and tetrahydrofuran (THF) based on the color patterns arising when the PDA-embedded elctrospun fiber mats were exposed to the organic solvents. Four different structures of DA monomers, however, were required to construct solvent-sensitive PDA sensors that allowed differentiation of four organic solvents. Thus, we felt that if sensors composed of libraries of PDAs could be prepared using a combinatorial concept, we should be able to differentiate a wider variety of organic solvents with a smaller number of DA monomers.

The key strategy employed to construct libraries of PDA sensors is as follows. A PDA-embedded electrospun fiber mat, prepared from the DA monomer 10,12-Pentacosadiynoic acid (PCDA)-ABA **1**, a derivative of PCDA and aminobutyric acid (ABA), was found to show significant colorimetric reversibility during heating and cooling cycles (Fig. 1). In contrast, the PDA-embedded electrospun fiber mat, prepared from the aniline (AN)-

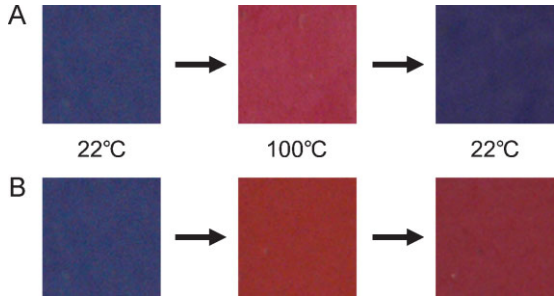

Figure 1. Structures of the DA monomers **1** and **2** and photographs of electrospun and polymerized fiber mats derived from A) **1** and B) **2** during thermal cycles.

derived DA monomer PCDA-AN **2**, displayed irreversible thermochromism. Since the PDA-embedded fiber mats derived from two DA monomers show completely different thermochromic behavior, it was anticipated that they would show different colorimetric responses when they are exposed to organic solvents. More importantly, it was expected that PDA-embedded fiber mats comprising various ratios of PCDA-ABA **1** and PCDA-AN **2** would display different colorimetric responses to organic solvents. If so, fiber mats composed of PDA libraries would allow differentiation of common organic solvents.

2. Results and Discussion

The key concept and a typical procedure used for the fabrication of PDA-embedded polymer fibers are schematically presented in Figure 2. A viscous solution containing DA monomers, poly(ethylene oxide) (PEO), and tetraethyl orthosilicate (TEOS)

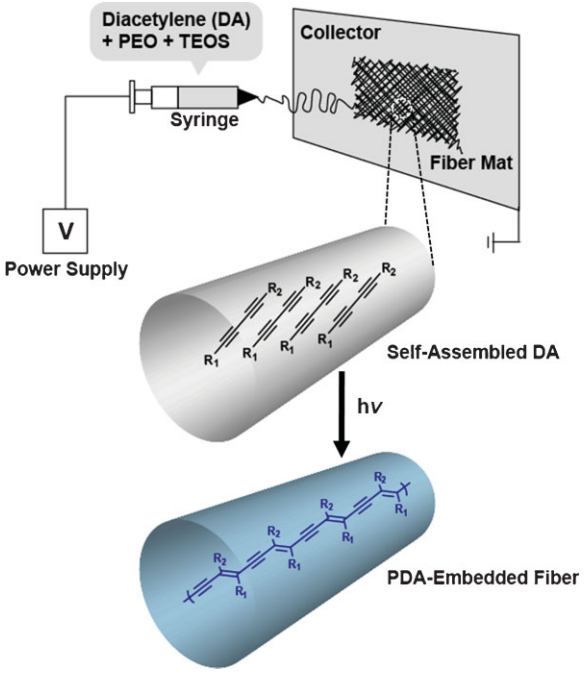

Figure 2. Schematic representation of the preparation of PDA-embedded electrospun microfibers.

was placed in a syringe connected with a metal needle. PEO and TEOS were used as a matrix polymer and a stability enhancer, respectively. The resulting viscous solution was pumped through a metal syringe needle at a constant rate of 5 mL h^{-1} by a syringe pump (KD Scientific model 200 series). Application of a high voltage (15 kV) to the metal syringe needle allowed generation of microfibers which were collected on the surface of a grounded aluminum plate at a distance of 10 cm from the syringe needle.[30] The microfibers collected were kept in the dark to avoid ambient polymerization. As the solvent evaporates during fiber formation, self-assembly of DA monomers takes place if the attractive forces between the DA monomers are larger than those between DA monomers and the matrix polymers. Polymerization of the molecularly assembled DAs then results in the formation of polymer fibers containing embedded PDAs. The monomer feed ratio between the two diacetylenic lipids PCDA-ABA **1** and PCDA-AN **2** was adjusted to allow the formation of compositionally diverse PDA-embedded electrospun fibers. Typically, electrospun fibers were prepared by increasing the PCDA-ABA **1**/PCDA-AN **2** ratio from 0:10 to 10:0.

The colorimetric PDA sensors prepared by employing the elctrospinning method have several advantages over conventional Langmuir–Blodgett (LB)/Langmuir–Schafer (LS) films, aqueous solutions, or spin-casted films-based sensor systems. The unique features include i) the high intensity of blue-to-red color change occurring in fiber sensors in contrast to conventional LB/LS-based PDA sensors that generally have too low of an intensity change to be recognized by naked eyes, ii) the diverse structures of PDA sensors that can be generated in comparison with the preparation of LB films or aqueous-based vesicle sensors which require amphiphilic DA monomers and are thereby limited by the number of DA monomers for library construction, iii) the potential to use a filter-type PDA sensor approach to prepare porous membranes that have a great advantage over conventional spin-casted film sensors, and iv) the practical application of a single electrospun fiber having fluorescence response for signaling.

In Figure 3 are displayed scanning electron microscopy (SEM) images of electrospun fiber mats encapsulated with DA monomers prepared from pure PCDA-ABA **1** (Fig. 3A), pure PCDA-AN **2** (Fig. 3B), and 1:1 molar mixture of PCDA-ABA **1** and PCDA-AN **2** (Fig. 3C). No significant morphological differences exist among these electrospun fiber mats and polymer fibers with an average diameter of ~1 μm are observed in all cases. In addition, UV irradiation of the polymer fibers was found to have a negligible effect on the size and shape of the resulting fibers.

In order to generate conjugated PDAs, the DA-embedded electrospun fiber mats were irradiated with 254-nm UV light for 1 min (1 mW cm^{-2}). In Figure 4 are shown photographs of the fiber mats encapsulated with DA monomers prepared from pure PCDA-ABA **1** (Fig. 4A), pure PCDA-AN **2** (Fig. 4B), and 1:1 molar mixture of PCDA-ABA **1** and PCDA-AN **2** (Fig. 4C). As shown in the photographs, the electrospun fiber mats are white before 254-nm UV irradiation. UV irradiation of the polymer mats for 1 min leads to generation of a blue color, indicating that PDAs are produced. This observation confirms that the molecular ordered properties of the monomeric DAs are generated in the electrospinning process. In addition, the formation of a blue color upon irradiation of the fiber mat derived from a 1:1 mixture of the two monomers shows that fabrication of PDA-embedded

ADVANCED FUNCTIONAL MATERIALS

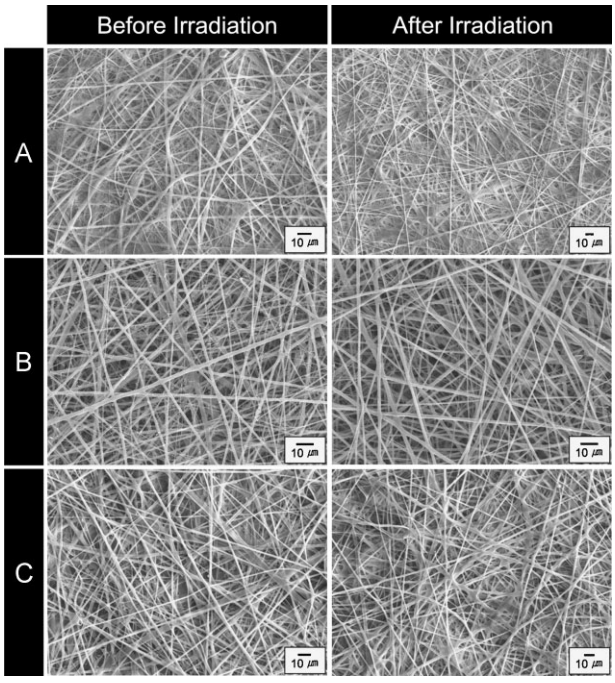

Figure 3. SEM images of electrospun fiber mats embedded with A) PCDA-ABA **1**, B) PCDA-AN **2**, and C) 1:1 molar ratio of PCDA-ABA **1** and PCDA-AN **2** obtained before and after UV irradiation for 1 min (254 nm, 1 mW cm^{-2}).

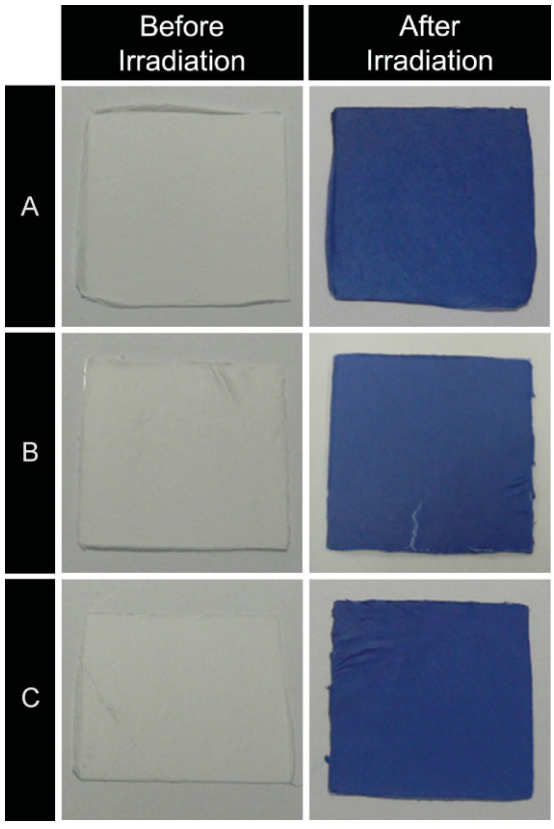

Figure 4. Photographs of electrospun fiber mats embedded with A) PCDA-ABA **1**, B) PCDA-AN **2**, and C) 1:1 molar ratio of PCDA-ABA **1** and PCDA-AN **2** obtained before and after UV irradiation for 1 min (254 nm, 1 mW cm^{-2}).

electrospun fiber mats from different monomer feed ratios is possible.

In order to demonstrate that PDAs are indeed generated in the electrospun fibers, the UV-irradiated blue-colored fiber mats were heated at 100 °C for 1 min. Optical and fluorescence microscopic images of the fiber mats obtained before and after the heat treatment are shown in Figure 5. As expected, the characteristic PDA blue-to-red color transition occurs upon heating the polymer fibers. Close inspection with an optical microscope reveals that the polymerized fiber mats consist of individual blue-colored fibers before heating (Fig. 5A, left). Upon heating, the blue-colored fibers are transformed to red-colored fibers (Fig. 5A, right). Fluorescence microscopic images of the blue- and red-colored fiber mats provides proof for PDA formation (Fig. 5B). Specifically, the blue-colored fiber mat is not fluorescent while the heat-treated red-colored fiber mat contains fluorescent fibers.

Having prepared the desired PDA-embedded electrospun fiber mats, the next phase of the current investigation focused on the effect of TEOS on their stability. The PDA-embedded fiber mats, prepared in the presence or absence of TEOS, were placed in various organic solvents. In Figure 6 are shown photographs of the fiber mats after 30 min incubation. Both the PCDA-ABA **1** and PCDA-AN **2**-derived fiber mats, prepared in the absence of TEOS, slowly disassemble in chlorinated solvents such as chloroform and methylene chloride (MC), the shape of the mat being completely lost after 30 min. In contrast, the silica-enforced fiber mats were stable in chloroform and MC with the original shape being unchanged after 30 min. In addition, release of PDAs from the TEOS-derived fiber mat was not observed in those solvents. The high stability of the TEOS-enforced fiber mat is presumably due to the crosslinking between hydrolyzed TEOS and PEO. The

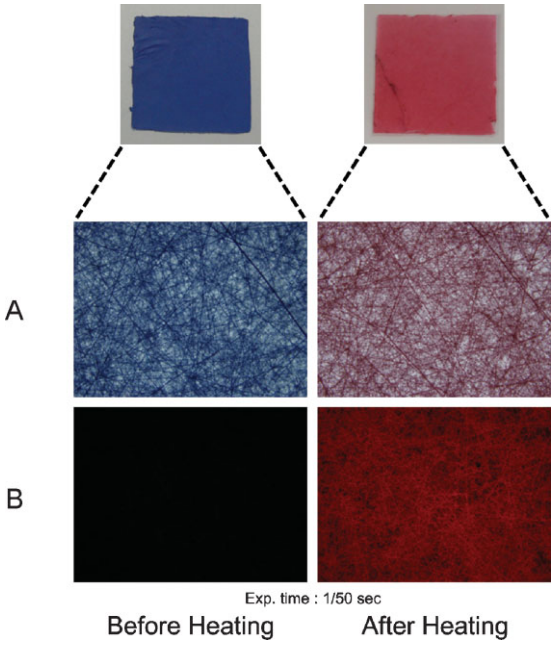

Figure 5. A) Optical and B) fluorescence images of PDA-embedded electrospun fibers prepared from 1:1 molar ratio of PCDA-ABA **1** and PCDA-AN **2** before and after heating at 100 °C for 1 min.

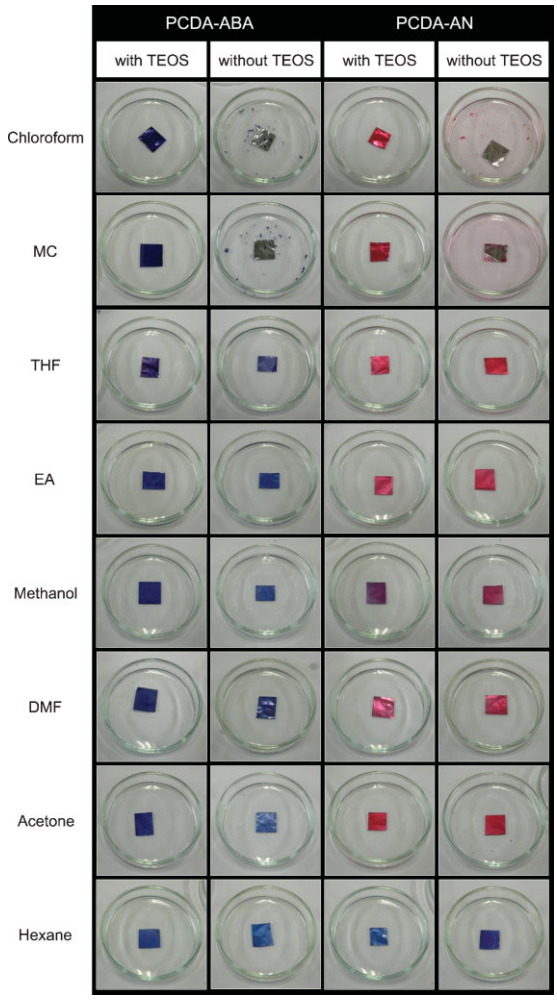

Figure 6. Photographs of PDA-embedded electrospun fibers, prepared from PCDA-ABA **1** and PCDA-AN **2**, after incubation for 30 min in various organic solvents.

effect of TEOS on the stability of the fiber mats in non-chlorinated solvents was found to be negligible. Thus, both TEOS-free and TEOS-enforced polymer fiber mats display reasonable stability upon exposure to the nonchlorinated solvents.

The polymer fiber mats shown in Figure 6 not only display the effect of TEOS on their stability but they also have interesting colorimetric responses. The polymerized PCDA-ABA **1** embedded fiber mats were found to be insensitive to the all of the organic solvents tested. Thus, the original blue color of the mats was unchanged upon exposure to the organic solvents. This observation indicates that the molecularly ordered structures of polymerized DAs are not disturbed by the solvents. The fact that the PDA fiber mat derived from PCDA-ABA **1** displays significant colorimetric reversibility during thermal cycles (described above) suggests that strong headgroup interactions in the polymer supramolecules are responsible for the high colorimetric stability in the presence of organic solvents. In general, PDA-embedded fiber mats derived from DA monomers which display reversible thermochromism tend to show colorimetric stability toward organic solvent. PCDA-AN **2** derived PDA fiber mats were found to be thermochromically sensitive and show color transitions with all solvents tested except hexane.

The completely different colorimetric responses to organic solvent that exists between PDA-ABA **1** and PCDA-AN **2** embedded electrospun fiber mats are intriguing. One polymer mat has a pronounced colorimetric stability while the other displays a very sensitive colorimetric response. This leads to a potentially important proposal about how polymer fiber mats colorimetrically respond when they are derived from mixtures of the two different DA monomers. In order to gain information about this issue, eleven electrospun fiber mats encapsulated with various ratios (0–100%) of polymerized DA monomers **1** and **2** were prepared. The fiber mats were incubated in common organic solvents. In Figure 7 are shown photographs of the fiber mats after 30 s incubation in the organic solvents. Interestingly, the polymer fiber mats show color patterns that enable visual differentiation of organic solvents. For example, chloroform induces blue-to-purple-red color transition of the fiber mat composed of 0–40% PCDA-ABA **1**. In contrast, THF is found to promote blue-to-red color transition of fiber mats composed of up to 40% PCDA-ABA **1**. This observation indicates that THF is superior to chloroform in disturbing molecularly assembled PDA structures. Fiber mats exposed to MC display similar color patterns to those in contact with chloroform. Thus, the two chlorinated solvents are not differentiated by this method. Methanol causes blue-to-purple color transition of fiber mats composed of up to 70% PCDA-ABA. MC is found to have a similar effect to chloroform. Acetone promotes blue-to-red color transition of the polymer mat prepared from 100% PCDA-AN and a blue-to-purple color transition of the 10% PCDA-ABA embedded polymer mat. Fiber mats exposed to hexane are found to maintain their original blue colors regardless of the monomer composition. DMF induces blue-to-red color transition of fiber mats comprised of up to 40% PCDA-ABA. Among tested solvents, acetic acid is observed to induce chromic transition of the fiber mats made of almost all compositions of the monomers

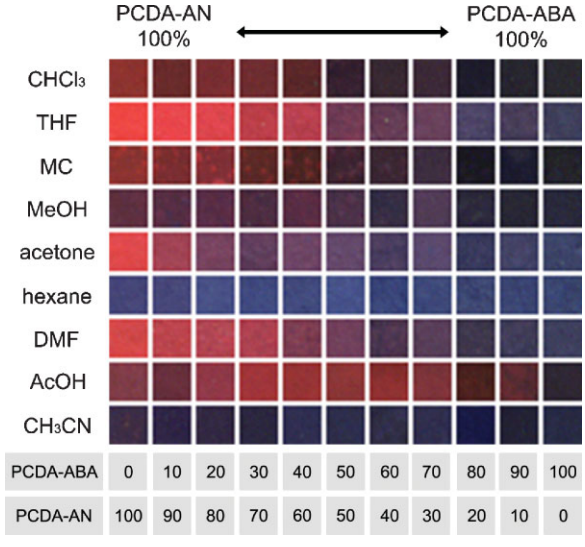

Figure 7. Photographs of the polymerized PDA-embedded electrospun fiber mats after exposure to organic solvents at 25 °C for 30 s.

except 100% PCDA-ABA. Acetonitrile behaves similar to hexane but it causes blue-to-pale-purple color transition of the fiber mat prepared with 100% PCDA-AN.

The color patterns of the fiber mats derived from different combinations of DA monomers, displayed in Figure 7, demonstrate the significance of the combinatorial approach for sensor development. This methodology enables the generation of a compositionally diverse array of sensors starting with a limited number of DA monomers. In the study described above, only two DAs were used to produce sensors that responded differently to a number of solvents. Importantly, the color patterns produced by these sensors are observable by the naked eye. If a computer-aided color analysis program is used, it should be possible to differentiate between a more diverse set of organic solvents.

3. Conclusions

A new strategy for the differentiation of common organic solvents based on a color pattern approach has been developed. Various compositions of PDA supramolecules starting with two DA monomers were effectively created in electrospun polymer fibers. The ABA-derived monomer PCDA-ABA **1** results in the generation of a substantially colorimetrically reversible fiber mat while the AN-derived monomer PCDA-AN **2** affords only a colorimetrically irreversible fiber mat. Interestingly, the electrospun fiber mats obtained from different compositions of these two monomers display different colorimetric responses when exposed to various organic solvents. Thus, sensors based on these fiber mats are capable of colorimetric differentiation of several common organic solvents. One of the major advantages of the PDA-based chemosensor system over those based on other conjugated polymers is the vivid color changes that take place in response to organic solvents. Thus, the relatively simple approach uncovered in this study should find utility in the development of colorimetric sensors for a wide variety of organic solvents.

4. Experimental

Materials: PCDA was purchased from GFS chemicals. PEO ($Mw = 300\,000\ g mol^{-1}$) and TEOS (reagent grade, 98%) were purchased from Aldrich.

Synthesis of 3-Carboxypropylpentacosa-10,12-diynamide (PCDA-ABA **1***)*: To a solution of 4-ABA (0.2 g, 1.5 mmol) in MC (20 mL) and DMF (0.5 mL) was added TEA (0.4 mL, 2.2 mmol) and a MC solution (10 mL) of PCDA-NHS (0.78 g, 1.27 mmol freshly prepared from PCDA and *N*-hydroxysuccinimide). The solution was stirred at ambient temperature for 12 h and concentrated in vacuo. A solution of the residue in ethyl acetate was washed with water and concentrated in vacuo. The product (0.46 g, 79%) precipitates from an ethyl acetate solution as an off-white powder when the solution is kept in a refrigerator overnight. m.p. 96.5–98.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$ δ): 0.85 (t, 3H), 1.20–1.62 (m, 36H), 1.86 (q, 1H), 2.18 (t, 1H), 2.21–2.38 (m, 6H), 2.24 (t, 1H), 2.42 (t, 1H), 3.35 (q, 1H), 5.72 (s, 1H), 7.50 (t, 1H), 7.82 (s, 1H), 7.98 (d, 1H), 7.18 (brs, 1H); ^{13}C NMR (75 MHz, DMSO-d_6 δ): 14.02, 18.29, 22.14, 24.65, 27.72, 28.41, 29.04, 31.05, 31.34, 35.38, 40.33, 65.35, 77.92, 172.02, 174.27.

Synthesis of N-Phenylpentacosa-10,12-diynamide (PCDA-AN **2***)*: To a solution containing 1.00 g (2.67 mmol) of PCDA in 30 mL of MC was added dropwise 0.66 mL (8.01 mmol) of oxalyl chloride at room temperature. The resulting solution was stirred at room temperature for 2 h. To the solution was added a catalytic amount (two drops) of DMF and stirring was continued for 1 h and concentrated in vacuo to give a residue which was dissolved in 5 mL of MC. The resulting solution was added dropwise to a solution containing 0.29 mL (3.20 mmol) of AN and 1.12 mL of TEA in 20 mL of MC. The resulting solution was stirred at ambient temperature for 12 h, and concentrated in vacuo giving a residue which was dissolved in MC. The solution was washed with water and concentrated in vacuo giving a residue which was subjected to a silica gel column chromatography (MC) to give the desired DA monomer PCDA-AN 2 as an off-white solid (0.95 g, 62%). m.p. 76–78 °C; ^{1}H NMR (300 MHz, $CDCl_3$ δ): 0.88 (t, 3H), 1.20–1.80 (m, 36H), 2.22 (t, 4H), 2.35 (t, 2H), 7.07–7.55 (m, 5H), 7.18 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$ δ): 14.12, 19.19, 22.68, 25.54, 28.24, 28.33, 28.71, 28.86, 29.09, 29.15, 29.34, 29.46, 29.63, 31.90, 37.81, 65.18, 65.26, 119.69, 124.14, 128.97, 137.90, 171.29.

Preparation of PDA-Embedded Electrospun Fibers: A typical procedure for fabrication of the PDA-encapsulated electrospun polymer fiber is as follows. DA monomer (100 mg) and PEO (500 mg) were dissolved in EtOH (8 mL). A TEOS solution (23 mL) was prepared in a separate vial with a 1:4:4 molar ratio of TEOS (10 mL), EtOH (10 mL), and H_2O (3 mL, pH 1.1). The resulting solution was stirred for 3 h at room temperature. The two solutions were mixed (10:1 wt ratio between DA and TEOS solutions) and the resulting viscous solution was pumped through a metal syringe needle of 21G at a constant rate of $5\ mL\ h^{-1}$ by a syringe pump (KD Scientific model 200 series). Application of a high voltage (15 kV) to the metal syringe needle allowed generation of microfibers which were collected on the surface of a grounded aluminum plate (distance from the syringe needle to the plate was 10 cm). The collected fibers were kept in the dark.

SEM: SEM images of the PDA-embedded fibers were obtained by using a JEOL (JSM-6330F) microscope. Samples on the aluminum foil were coated with Pt for 5 min before analysis.

Optical and Fluorescence Microscopic Images: PDA-embedded fiber mats were irradiated with 254-nm UV light ($1\ mW\ cm^{-2}$) for 30 s to induce polymerization of the DA monomers. Heating of the fiber mats was carried out on a digital hotplate at 100 °C for 1 min. The images were observed with an Olympus optical and fluorescence microscope (BX51W/DP70).

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