Macromolecules

Unimolecular Photopolymerization of High-Emissive Materials on Cylindrical Self-Assemblies

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S Supporting Information

ABSTRACT: We report a novel self-assembly pathway from a bis(imidazolyl) diphenyl-diacetylene (DPDA) compound as a realization of self-templated photopolymerization with high polymerization degrees. The work takes advantage of a cylindrical self-assembly that strengthens the preorganization of the diphenyl-diacetylene moiety at the single molecular level. On this basis, photopolymerization of DPDA can be conducted smoothly to form high-molecular-weight polydiphenyl diacetylene. Such a cylindrical self-assembly is highly dependent on molecular structure, and control studies show that only oligomers can be formed on random self-assemblies from a monoimidazolyl or nonimidazolyl diphenyl-diacetylene compound. Moreover, the cylindrical self-assembly based systems bear aggregation-induced emission enhancement characteristics and are solution processable.



The leading thin-film could afford a selectively tunable function in luminescent micropatterns.

INTRODUCTION

As compared with most conventional diacetylenes with alkyl chains directly connected to the butadiyne unit, the diphenyldiacetylene (DPDA) moiety with aryl groups attached to the butadiyne has an extended π -conjunction and introduces a large intermolecular stacking tendency. These features generally allow the mesogen as well as the corresponding polydiacetylene species to exhibit more versatile optoelectronic properties,¹ implying great interest for their potential exploitation in high birefringence materials, modern display technologies, luminescent emitting diodes, and ideal prototype for molecular devices, etc.⁴ Since the first report of diacetylene polymerization in the solid state by Wegner,⁵ it has been widely accepted that molecular preorganization is a crucial factor to achieve highly efficient topochemical polymerizations of diacetylene. To drive such an effective polymerization on a diphenyl-diacetylene (DPDA) monomer seems to be difficult, simply because the bulky size of the neighboring phenyl rings in DPDA greatly hampers the minimum movement of the butadiyne moiety. The past decades have witnessed extensive progress in developing many key strategies, based on grafting diacetylene monomers on surface-aligned films or introducing functional groups on the diacetylene monomers to control their aggregation and crystallization, followed by thermal or photochemical polymerization.⁶ However, only the formation of oligomers, or even no reaction at all, is observed in most of cases of DPDAs.

Gelation and monolayer strategies may somehow promote the polymerization of DPDAs,⁸ but they lack solution processability, which will limit large-scale development. A straightforward approach for enhancing the polymerization degree of DPDA in a solution processable manner remains a challenge.

Structural-dependent ordered self-assembled nanoarchitectures formed in a certain solvent environment generally show properties distinct from those of their individual constituent molecules,⁹ and can even be helpful for improving the chemical reaction behavior.¹⁰ In particular, self-assemblies formed by a surfactant-like design could readily generate distinctive superstructures in aqueous media thus to provide widely tunable performance and effective solution-based processing characteristics.¹¹Inspired by the superiority of these pertinent superstructures,^{9–11} we herein present a unimolecular strategy (see compound 1 in Figure 1) of introducing a diphenyldiacetylene (DPDA) moiety as a polymerizable core and two imidazole units as bilateral headgroups to realize this supposition. This design takes advantage of the facts that (1)the amphiphilic molecular structure can be employed to establish ordered self-assemblies in aqueous media for improving the polymerization behavior; (2) DPDA was bridged

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Figure 1. (A) Chemical structures of the compound 1 and the reference compounds 2 and 3. (B) Schematic representation of the unimolecular photopolymerization process in aqueous media. By UV irradiation under this solvent condition, 1 can form the corresponding polymer species whereas 2 and 3 only produce oligomers.

with imidazole headgroups via two long alkyl chains, which are also considered to regulate the self-assembly modes and increase the processability from solution to solid state; (3) DPDA is a smart luminogen whose photophysics can be employed and modulated upon self-assembly and photopolymerization for high-tech applications with emissive expressions. Reference compounds 2 and 3 with mono- or nonimidazole headgroups, respectively, were also prepared for control experiments. The synthesis of these compounds is detailed in the Experimental Section.

RESULTS AND DISCUSSION

Cylindrical Self-Assembly of 1. To study the selfassembly behavior of compounds 1-3, we first investigated their photophysics. A colloidal solution of compound 1 was observed in a mixed solvent system. 1 exists as monomeric state in an anhydrous THF solution and its absorption bands can be well assigned. The multiple peaks from 270 to 345 nm (curve 1, Figure S1) originate from the alkynyl and aromatic chromophores in 1. However, the absorption bands of 1 dispersed in THF with 90% water turns broad and all the main peaks accordingly exhibit a bathochromical shift for ca. 10 nm (curve 2, Figure S1), signifying that 1 forms a self-aggregated state in the presence of a large amount of water. The selfaggregation properties of 1 were examined by monitoring the variation of absorption upon the concentration change. The critical aggregation concentration (CAC) in THF with 90% water was determined to be 15.5 μ M (Figure S2, Supporting Information).

To our surprise, the photoluminescent spectral change of 1 follows an opposite trend toward the UV-vis change upon increasing the content of water. As seen from Figure 2A, 1 shows an emission maximum at around 410 nm while no remarkable emission enhancement is observed from THF solution with water content less than 70%. However, when a large amount of water (fw >80%) is admixed with THF, the emission intensity grows significantly—approximately an 8-fold increase over the intensity in neat THF solution. Such a distinct photoluminescence can also be directly observed by the naked eye (see the photographs in Figure S3). In contrast, the emission intensity of the reference compound 2 and 3 decreases continuously in THF with increasing content of water (see Figure 2, parts B and C). Attempts to obtain the quantum yield of the aggregated state were unsuccessful,



Figure 2. (A–-C) Emission spectra (λ_{ex} = 365 nm) of **1**, **2**, and **3**, respectively, 40 μ M, 298 K, in anhydrous THF (curve 1), THF with 30% water (curve 2), THF with 70% water (curve 3), THF with 80% water (curve 4), and THF with 90% water (curve 5). (D–F) AFM images of **1**, **2** and **3**, respectively, prepared from THF with 90% water. Scale bar: 1 μ m.



Figure 3. (A) Representative cylindrical self-assembly conformation of 1 from molecular dynamics simulations. (B) Distribution of van der Waals interaction energies among the DPDA groups (curve 1-3) in the self-assemblies of compound 1, 2, and 3, respectively. (C) Autocorrelation functions of the dihedral angle between the two phenyl rings (curve 1-3) in the self-assemblies of compounds 1, 2, and 3, respectively. Dashed lines show fitting to the Kohlrausch–Williams–Watts relaxation function, from which the correlation time is calculated.

probably due to scattering; however, the huge differences among the intensities in these experimental results suggest that compound 1 is aggregation-induced emission enhancement (AIEE) active¹² and that this effect is structurally dependent, opposite to the ordinary aggregation-caused quenching (ACQ) effect of 2 and 3.¹³

The self-aggregated architectures under the specific solvent conditions were further confirmed by atomic force microscopic (AFM) studies. Column-shaped nanostructures with an average cross-sectional diameter of 500 nm were observed from the AFM images of 1 prepared from a THF/H₂O (v:v = 1:9) mixture solution (Figure 2D and Figure S7a in the Supporting Information), whereas common spherical aggregates were obtained from the reference compound 2 and 3 when prepared in the same solvent conditions (Figure 2, parts E and F). It can be suggested that such a peculiar self-assembly of 1 is responsible for the generation of the AIEE effect. The XRD diffractogram of the self-aggregated sample 1 shows a main peak with a *d*-spacing of 3.54 Å (corresponding to the peak at $2\theta = 25.1^{\circ}$, see curve 1 in Figure S4), which originates from the stacking of the aromatic chromophore.¹⁴ This *d*-spacing value was enlarged in samples of 2 and 3 up to 3.77 and 3.60 Å, respectively, indicating different packing modes and weaker $\pi - \pi$ interactions in these crystalline samples (see also the computational works for comparison, vide infra).

To gain further insight into the fine superstructures of the nanoassemblies, molecular dynamics (MD) simulations¹⁵ were carried out to study the self-assembly behavior of compound 1. It was found that all molecules of 1 start to form aggregates in the presence of an aqueous environment, and that the self-assembly of 1 exhibits a distinct cylindrical conformation (Figure 3A). The computed solvent accessible surface area and order parameter suggest an ordered self-assembly of 1 (see

Supporting Information), which is indicative of the formation of an advanced column-shaped architecture through further extension of the supramolecular interactions (Figure 2D). Notably, the self-aggregation pattern was largely regulated by the bilateral imidazole units, which show some hydrophilic properties and stretch toward the water medium. Thus, the diacetylene moiety was enforced to stay at the middle of the cylinders, resulting in a self-sorted aggregation mode as shown in Figure 3A.

The aggregation characteristics of the three compounds were also compared by MD simulations. We examined the van der Waals (VDW) interaction potential energies among the DPDA groups in the self-assemblies, which reflect the strengths of $\pi - \pi$ interactions. Figure 3B shows the distributions of the VDW interaction energies in the self-assembled compounds. Here, the positions of the peaks indicate that the strength of the VDW interaction among the DPDA groups follows the order 1 $> 3 \gg 2$, in accordance with the molecular packing distance provided by XRD spectra (Figure S4). The rotation of the phenyl-phenyl dihedral in the DPDA moiety before and after self-aggregation was also examined. It can be seen that the autocorrelation function of compound 1 decays much slower than those of compounds 2 and 3, suggesting that the rotation of the two phenyl rings are restricted in the self-assembled molecules of 1 (Figure 3C). In this way, it can be concluded that a barrier was established after the formation of the cylindrical self-assembly of 1. Since the rotation of the aromatic rings is considered as a crucial factor for photoluminescent quenching, this finding is indeed in agreement with the restriction of intramolecular rotation (RIR) mechanism.¹⁶ Therefore, such a confined nanoconformation significantly enhances the quantum yield and in turn leads to the AIEE effect.

High Polymerization Degree of 1 on Cylindrical Self-Assembly. On the basis of these self-assemblies, next we turn to study their polymerization degree by gel permeation chromatography (GPC). The photopolymerization of these compounds does not proceed with high efficiency in neat THF solution, however, it could be promoted in the colloidal media of THF with 90% water. Figure 4 shows the GPC



Figure 4. GPC traces of the diacetylene samples with or without UV irradiation.(254 nm Detector, THF eluent): (A, C, E) Compounds 1, 2, and 3 after irradiation, respectively. (B, D, F) Compounds 1, 2, and 3 without irradiation, respectively. Some representative polymerization degrees were highlighted next to the traces.

chromatograms of these three compounds before and after photoirradiation. These GPC samples were first prepared from the above-mentioned mixed solvent condition with or without photoirradiation, followed by isolation and redissolvation for injection. On the basis of a polystyrene calibration curve, we can see that compound 2 and 3 only form corresponding oligomers upon photoirradiation (Figure 4, parts C and E). In contrast, compound 1 results in a great deal of polymers except some oligomers upon photoirradiation, as confirmed by an extended broad band in Figure 4A. The degree of polymerization (number of repeating units in the polymeric chain) was observed to exceed 40 in the highest molecular weight species. Since the sample solubility was proven to matter little about the chain length, it is concluded here that such a unique self-assembly of 1 leads to a higher degree of topochemical polymerization.

Learning from the specific self-sorting of the DPDA moiety and the bilateral imidazole units presented in the model in Figure 3A as well as the RIR mode of the luminogen, we suggest a locally ordered DPDA alignment was achieved inside the cylinderical nanostructures. This specific packing of the luminogen of this amphiphilic molecule keeps a quite favorable preorganization of the DA moiety, such that a facile polymerization can be conducted to yield high-molecularweight polymer species. In contrast, the random self-assemblies of 2 and 3 exhibit very limited preorganization of the DPDA moiety, offering oligomers only. Moreover, the UV-vis band changes upon photoirradiation provide additional evidence for the polymerization degree. To diminish the interference of the scattering from a colloidal solution, we isolated and redissolved the irradiated stuffs for UV-vis measurements. A continuous absorption from UV region to over 580 nm of 1 after irradiation was observed, indicating the formation of polymer species, whereas the absorption band (corresponding to oligomers) of 2 and 3 did not reach 500 nm after irradiation (Figure S5).

Accompanied by such a photopolymerization process, an obvious luminescent conversion can be observed upon UV irradiation in the colloidal solution of 1. The original emission band of 1 at around 420 nm was weakened, meanwhile a new peak at \sim 520 nm emerged due to photoluminescence of the polymer species (Figure S6). Upon photopolymerization, the AIEE effect of 1 was diminished with the shrinkage of the cylindrical nanostructures (see the AFM characterization in



Figure 5. Emission spectra (λ_{ex} = 340 nm) of dumbbell molecule 1 (0.021 mM in DMSO, 295 K) (a) before and (b) after irradiation at 365 nm for 300 s, when compared with significant emission change for [3]rotaxane **R1** (0.021 mM in DMSO, 295 K) and (c) before and (d) after irradiation at 365 nm for 300 s.

Figure S7). A possible cycloaromatization mechanism¹⁷ could be ruled out since the PL spectra varied according to first-order kinetics with prolonged photoirradiation time (see Figure S8). In this way, we suggest that the polymer species here are most likely based on an enyne skeleton after a topochemical 1,4addition reaction. As shown in the AFM image in Figure S7b, it can be also concluded that the polydiphenyl diacetylene backbones are linear under the current preparation condition, since the rigidity of the enyne skeleton are unfavorable for the formation of a macrocyclic conformation.¹⁸

Solution Processability and Photopatterning. Such a photoluminescent conversion with high emissive signals of 1 can be processed from solution to thin film by spin coating. In contrast, the photoluminescent behavior of compound 2 and 3 in the solid-state was completely suppressed. As shown in Figure 5A, we can observe that the solid-state emissive signal of 1 is still strong (curve 1), and that the emission of 2 and 3 was quenched in films (curve 2 and 3). A comparison of AFM images (Figure S9) confirms that cylindrical nanostructures are still present in the film surface of 1, clarifying that the AIEE effect still exists in the solid-state sample. Similar to the behavior in the solution self-assemblies (Figure S6), the photoluminescent change along with the photopolymerization process of 1 on thin film can also be observed upon the prolonging of UV irradiation (see curve 1 and p1 in Figure 5A). Here we can find that the photoluminescent signal conversion of 1 before and after polymerization on thin film can still be clearly distinguished. We emphasize that such a highly emissive event in the solid state still refers to a unimolecular process without any assistance of matrix materials or templates.

Furthermore, this strategy with the superiority of strong emission, photoinduced luminescent conversion, solution processable characteristic, etc. is amenable to patterning over large areas and can exhibit an unprecedented potential for regionally selective emitting upon the channel (excitation/ collection) switching. The photopatterning treatment¹⁹ can be visualized by the schematic presentation in Figure 5B. A quartz mask with a microscale grid was placed on the film of 1 for a region-selective photoirradiation. Micropatterned imaging based on thin film 1 can be obtained after UV irradiation as monitored by confocal microscopy. To our delight, a phenomenon of regionally selective imaging could be created by switching of different detection modes. The bright imaging of square areas can be clearly observed from a FITC mode (excitation/reading wavelengths: $\sim 490/560-580$ nm), while the imaging of the rest lane parts appear dark (Figure 5C). In contrast, the imaging of the square areas is relatively weak from a DAPI mode (excitation/reading wavelengths: ~ 350/440-460 nm), whereas it is remarkably strengthened within the rest lane parts (Figure 5D). The luminescent intensity along the line profile from the FITC mode shows a peak-trough-peak fluctuation: however, the intensity at the same location from the DAPI mode behaves in a totally inverted manner (Figure S10). As we demonstrated above, the photopolymerization allows the emission of the materials to undergo a significant bathochromical shift. This exploration suggests that the photopolymerization took place only in those exposed square areas since the brightness information performed by the microspectroscopy is in agreement with the corresponding photoluminescent spectra. Such a controllable regionally selective imaging might find a promising potential for applications of advanced optical imaging or lightening events at microscale.²⁰

We have demonstrated a bi-imidazolyl diphenyl diacetylene (DPDA) compound that can act as a scaffold for a singlemolecule based photopolymerization with high polymerization degree. Distinctive cylindrical self-assemblies of this molecule can be formed in a colloidal aqueous solution and can be processed into thin-film. Such a structural-dependent ordered nanoarchitecture with the DPDA moiety packed toward the inside and the bilateral imidazole units in the periphery is favorable for molecular preorganization of the DPDA moiety. On this basis, a topochemical reaction that yields high molecular weight polydiacetylenes was observed upon UV irradiation. In addition, this molecule exhibited an effect of aggregation-induced emission enhancement not only in the colloidal solution but also in the solid state. Regionally selective imaging control using films of this unique compound has been successfully carried out at the micropattern level. Future studies will be geared toward exploiting this self-templated strategy, which also could be useful for other topochemical reactions that require highly uniform molecular alignment.

EXPERIMENTAL SECTION

General Data. ¹H NMR and ¹³C NMR spectra were measured on a Bruker 400L spectrometer. The fast atom bombardment (FAB) mass spectra and high-resolution mass spectrometry (HR-MS) were recorded on a JMS-HX110 HF mass spectrometer (ionization mode: FAB+). Absorption spectra were recorded on a Shimadzu 1800 spectrophotometer, while the fluorescent emission spectra were taken with a Jobin Yvon Fluorolog-3 spectrofluorometer (Model FL-TAU3). The photoirradiation was carried on PL Series compact UV lamp (4 W) with the irradiation wavelength of 254 nm. The distance between the lamp and the sample is kept within 3-5 cm. The polymer molecular weight were determined with a Waters 1515 gel permeation chromatograph (GPC) equipped with a UV detector and calibrated with polystyrene standard samples. The Atomic force microscopy (AFM) images were collected on a PSI XE100 atomic force microscope (Park System). The confocal microscopic images were captured by LEICA TCS SP5 confocal microscope. The photo images were photographed by a Nikon COOLPIX S8000 digital camera.

Synthesis of Compound **6**. The preparation for this compound was according to a similar procedure described in the literature.²¹

Synthesis of Compound 5. A solution of hexyl bromide (1.05 g, 6.36 mmol) in anhydrous acetone (5 mL) was added dropwise into a mixture of compound 6 (1.5 g, 6.41 mmol) and potassium carbonate (0.8 g, 5.8 mmol) in anhydrous acetone (15 mL) at 60 °C. The mixture was kept stirring for 12 h at that temperature under Ar protection. The solvent was removed in vacuo, and the residue was applied to silica gel chromatography (hexane/ethyl acetate =6:1) to afford gray compound 5 (1.02 g, 50.4%). ¹H NMR (400 MHz, CDCl₃, 298 K): $\delta = 7.45$ (d, J = 9.2 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 3.97 (t, *J* = 6.4 Hz, 2H), 1.79 (m, 2H), 1.46 (m, 2H), 1.35 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 159.91, 156.32, 134.29, 134.06, 115.66, 114.68, 114.36, 113.62, 81,43, 81.00, 73.01, 72.82, 68.25, 31.57, 29.18, 25.76, 22.60, 14.04. MS (FAB+): calcd for $[\mathbf{M}]^+ m/z =$ 318.2; found m/z = 318.3; HR-MS (FAB+): calcd for $C_{22}H_{22}O_2$ [M]⁺ m/z = 318.1620; found m/z = 318.1619.

Synthesis of Compound 4. Compound 5 (0.6 g, 1.89 mmol) was added with magnetic stirring to 1,6-dibromohexane (4.5 g, 18.4 mmol) acetone solution (5 mL). The mixture was then added upon potassium carbonate (520 mg, 3.77 mmol). The mixture was stirred refluxing for 6 h under Ar protection and then was filtered. A great deal of solid was precipitated from the filtrate while it was added into 4 fold volume of hexane. The solid was filtered, washed with petroleum (30 mL) and deionized water (20 mL), respectively, and dried under vacuum to obtain gray compound 4 (737 mg, 81.1%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.44 (d, *J* = 8.0 Hz, 4H), 6.83 (d, *J* = 7.6 Hz, 4H),



Figure 6. Synthetic route for the preparation of compounds 1, 2 and 3. Reagents and conditions: (i) $Pd(PPh_3)_2Cl_2$, CuI, Et₃N, DMF, (ii) Ag₂CO₃, heating, (iii) hexyl bromide or dodecyl bromide, K₂CO₃, (iv) dibromoalkane, K₂CO₃, and (v) imidazole, KOH.

3.97 (m, 4H), 3.42 (t, J = 6.8 Hz, 2H), 1.90 (m, 2H), 1.81 (m, 4H), 1.50 (m, 6H), 1.34 (m, 4H), 0.91 (t, J = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, 298 K): $\delta = 159.89$, 159.74, 134.04, 134.04, 114.66, 114.64, 113.85, 113.67, 81,38, 81.27, 72.97, 72.89, 68.17, 67.86, 33.79, 32.66, 31.56, 29.13, 28.99, 27.91, 25.69, 25.28, 22.61, 14.03. MS (FAB +): calcd for [**M**]⁺ m/z = 480.2 (⁷⁹Br); found m/z = 480.2 (⁷⁹Br); HR-MS (FAB+): calcd for C₂₈H₃₃O₂⁷⁹Br [**M**]⁺ m/z = 480.1664; found m/z = 480.1668.

Synthesis of Compound 3. Compound 6 (234 mg, 1.0 mmol) was added with magnetic stirring to 1,6-dibromohexane (4.8 g, 19.6 mmol) acetone solution (4 mL). The mixture was then added upon potassium carbonate (552 mg, 4.02 mmol). The mixture was stirred refluxing for 6 h under Ar protection and then was filtered. A great deal of solid was precipitated from the filtrate while it was added into a 5-fold volume of hexane. The solid was filtered, washed with petroleum ether (20 mL) and deionized water (15 mL), respectively, and dried under vacuum to obtain gray compound 3 (449 mg, 80.2%). ¹H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.44 (d, J = 9.0 Hz, 4H), 6.83 (d, J = 9.0 Hz, 4H), 3.97 (t, J = 6.4 Hz, 4H), 3.42 (t, J = 6.4 Hz, 4H), 1.89 (m, 4H), 1.80 (m, 4H), 1.50 (m, 8H). ¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 159.76, 134.05, 114.64, 113.82, 81.31, 72.95, 67.85, 33.72, 32.66, 28.99, 27.91, 25.28. MS (FAB+): calcd for $[M]^+ m/z = 558.1 (^{79}Br)$; found m/z = 558.2 (⁷⁹Br); HR-MS (FAB+): calcd for C₂₈H₃₂O₂⁷⁹Br₂ $[M]^+ m/z = 558.0769$; found m/z = 558.0791. A scheme showing the syntheses of 1-3 is found in Figure 6.

Synthesis of Compound 2. To a mixture of compound 4 (650 mg, 1.35 mmol) and potassium hydroxide (151 mg, 2.78 mmol) in acetonitrile (6 mL) was added imidazole (645 mg, 9.48 mmol). The reaction mixture was refluxed for 8 h and then cooled to room temperature. After a flash column chromatography (ethyl acetate/methanol = 25:2), the crude product was further washed with deionized water (15 mL) and dried under vacuum to obtain pure white compound 2 (255 mg, 40.4%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.46 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 4H), 7.06 (s, 1H), 6.91 (s, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 3.96 (m, 6H), 1.78 (m, 6H), 1.47 (m, 4H), 1.34 (m, 6H), 0.91 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 159.90, 159.67, 137.10, 134.04, 134.04, 129.50, 118.77, 114.67, 114.62, 113.91, 113.65,

81,42, 81.21, 73.01, 72.87, 68.16, 67.72, 46.94, 31.56, 31.03, 29.12, 28.97, 26.34, 25.69, 25.62, 22.60, 14.03. MS (FAB+): calcd for $[\mathbf{M} + \mathbf{H}]^+ m/z =$ 469.3; found m/z = 469.4; HR-MS (FAB+): calcd for $C_{31}H_{37}O_2N_2 [\mathbf{M} + \mathbf{H}]^+ m/z =$ 469.2855; found m/z = 469.2860.

Synthesis of Compound 1. To a mixture of compound 3 (200 mg, 0.36 mmol) and potassium hydroxide (80 mg, 1.43 mmol) in acetonitrile (2.5 mL) was added imidazole (340 mg, 5.0 mmol). The reaction mixture was refluxed for 8 h and then cooled to room temperature. After a flash column chromatography (ethyl acetate/ methanol =25:6), the crude product was further washed with deionized water (25 mL) and dried under vacuum to obtain pure white compound 1 (152 mg, 76.7%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.46 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 4H), 7.06 (s, 1H), 6.91 (s, 1H), 6.82 (d, *J* = 8.8 Hz, 4H), 3.95 (t, *J* = 6.4 Hz, 8H), 1.80 (m, 8H), 1.50 (m, 4H), 1.36 (m, 4H). ¹³C NMR (100 MHz, CDCl₃, 298 K): δ = 159.70, 137.08, 134.05, 129.50, 118.76, 114.62, 113.86, 81.29, 72.97, 67.74, 46.93, 31.03, 28.97, 26.33, 25.62. MS (FAB+): calcd for [M + H]⁺ m/z = 535.3; found m/z = 535.4; HR-MS (FAB+): calcd for C₃₄H₃₉O₂N₄ [M + H]⁺ m/z = 535.3073; found m/z = 535.3068.

Preparation of the Colloidal Solutions. THF solutions of 1, 2, and 3 with concentration of 6 mM (1 mL) were added dropwise into a water-dominated mixed solvent (150 mL) with stirring. The leading colloidal solutions were standed for 15 min for the later related measurements.

Preparation of the Thin Films. The films of 1, 2, and 3 were obtained by spin-coating (2500 rpm for 45 s) the corresponding THF solutions with concentration of 6 mM on silicon wafers. The wafers were inserted into the cuvette holder with an angle about \sim 45° to the incident light for the optical tests.

Photopatterning. Upon the preparation of the thin film 1, a quartz mask with microscale grid was placed on the film with nitrogen purging. Photoirradiation with UV light was sufficient conducted for 20 min. Then, the film was observed under confocal microscopy with different channels. The intensity of each channel was read under the same gain.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.5b01488.

Supporting experimental data (including UV-vis, PL, XRD, AFM, etc.) and computational details (PDF)

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Notes

The authors declare no competing financial interest.

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