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

Liangliang Zhu,*‡§ Xin Li, ‡ Samuel N. Sanders,§ and Hans Ågren*‡

1State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai 200433, China
2Division of Theoretical Chemistry and Biology, School of Biotechnology, KTH Royal Institute of Technology, SE-10691 Stockholm, Sweden
3Department of Chemistry, Columbia University, New York, New York 10027, United States

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 diphenyl–diacetylene (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,‡§ implying great interest for their potential exploitation in high birefringence materials, modern display technologies, luminescent emitting diodes, and ideal prototype for molecular devices, etc. Since the first report of diacetylene polymerization in the solid state by Wegner,‡ 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.‡ However, only the formation of oligomers, or even no reaction at all, is observed in most cases of DPDAs. Gelation and monolayer strategies may somehow promote the polymerization of DPDAs,§ 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,‡ 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.¹¹ Inspired by the superiority of these pertinent superstructures, we herein present a unimolecular strategy (see Figure 1) of introducing a diphenyl–diacetylene (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...
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 photo-polymerization 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 self-assembly 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 turn 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 self-aggregation 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 μM (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 1](image_url)

**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.

![Figure 2](image_url)

**Figure 2.** (A−C) Emission spectra ($\lambda_{ex} = 365$ nm) of 1, 2, and 3, respectively, 40 μM, 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 μm.
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) active and that this effect is structurally dependent, opposite to the ordinary aggregation-caused quenching (ACQ) effect of 2 and 3.

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 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 2θ = 25.1°, see curve 1 in Figure S4), which originates from the stacking of the aromatic chromophore. 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 π−π interactions in these crystalline samples (see also the computational works for comparison, vide infra).

To gain further insight into the fine superstructures of the nanomolecules, molecular dynamics (MD) simulations 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 π−π 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 > 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. 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 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 redissolution 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 cylindrical 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-molecular-weight 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 ~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 4.)

![Figure 4](image_url)

**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.

![Figure 5](image_url)

**Figure 5.** Emission spectra (λ<sub>ex</sub> = 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.
CONCLUSION

We have demonstrated a bi-imidazolyl diphenyl diacetylene (DPDA) compound that can act as a scaffold for a single-molecule based photopolymerization with high polymerization degree. Distinctive cylindrical self-assemblies of this molecule can be formed in a colloidal aqueous solution (HR-MS) 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.

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 mixed 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): δ = 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, 114.36, 114.32, 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 [M]+: m/z = 318.2; found m/z = 318.3; HR-MS (FAB+): calcld for C20H22O2 [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 added into 4 fold volume of hexane. The solution 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),
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). 

\( ^{13} \)C NMR (100 MHz, CDCl\textsubscript{3}, 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\textsuperscript{+}): calcld for \( [M + H]^{+} \) m/z = 469.3; found m/z = 469.4; HR-MS (FAB\textsuperscript{+}): calcld for \( C_{31}H_{37}O_{2}N_{2} \ [M + H]^{+} \) m/z = 469.2855; found m/z = 469.2860.

**Synthesis of Compound 3.** 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 = 25:5), 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%). 

\( ^{1} \)H NMR (400 MHz, CDCl\textsubscript{3}, 298 K): \( \delta \) = 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). \n
\( ^{13} \)C NMR (100 MHz, CDCl\textsubscript{3}, 298 K): \( \delta \) = 159.76, 134.04, 114.64, 113.82, 81.31, 72.95, 67.85, 32.66, 28.99, 27.91, 25.28. MS (FAB\textsuperscript{+}): calcld for \( [M + H]^{+} \) m/z = 585.1 (\(^{79}\)Br); found m/z = 585.2 (\(^{79}\)Br); HR-MS (FAB\textsuperscript{+}): calcld for \( C_{31}H_{37}O_{2}N_{2} \ [M + H]^{+} \) m/z = 585.0769; found m/z = 585.0791. 

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 = 25:5), the crude product was further washed with deionized water (15 mL) and dried under vacuum to obtain pure white compound 2 (235 mg, 40.4%). \n
\( ^{1} \)H NMR (400 MHz, CDCl\textsubscript{3}, 298 K): \( \delta \) = 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). \n
\( ^{13} \)C NMR (100 MHz, CDCl\textsubscript{3}, 298 K): \( \delta \) = 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\textsuperscript{+}): calcld for \( [M + H]^{+} \) m/z = 469.3; found m/z = 469.4; HR-MS (FAB\textsuperscript{+}): calcld for \( C_{31}H_{37}O_{2}N_{2} \ [M + H]^{+} \) m/z = 469.2855; found m/z = 469.2860.

**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 stabilized 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 ~45\(^{\circ}\) to the incident light for the optical tests. **Photopatterning.** Upon the preparation of the thin film, 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.
REFERENCES


ACKNOWLEDGMENTS

The authors declare no competing financial interest.

NOTES

The Supporting Information is available free of charge on the Macromolecules website.

*Multi-"Computational resources provided by the Swedish National Infrastructure for Computing (SNIC) for the project "Multiphysics Modeling of Molecular Materials", SNIC 2013/26-31.

ACKNOWLEDGMENTS

The authors'declare no competing financial interest.

NOTES

The Supporting Information is available free of charge on the Macromolecules website.