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Fabrication of chiral polydiacetylene nanotubes via supramolecular gelation of a triterpenoid-derived amphiphile

Xia Yu, Hao Zhang, Yuxia Gao, Jun Hu and Min-Hui Li

Polydiacetylenes (PDA) can undergo a blue-to-red color transition in response to external stimuli because of the extensive delocalized n-electron networks and intrinsic conformational restrictions, which make PDA particularly attractive building blocks in stimuli-responsive materials. In this work, a blue chiral C4-MOP/PDA gel was fabricated successfully by UV irradiating a white supramolecular gel that was assembled from a triterpenoid-derived gelator (C4-MOP) and a diacetylene monomer (PCDA). This photo-polymerization was completed within 5 min with a generation of the new negative Cotton effect at 657 nm in visible blue light region, which strongly revealed the transmission, amplification and visualization of molecular chirality during this gelation and photopolymerization process. Notably, the nanotubular microstructures of the white gel C4-MOP/PCDA that curled from twisted ribbons barely changed after polymerization into C4-MOP/PDA. In addition, because C4-MOP/PDA contained an alternating ene-acetylene conjugated structure, it exhibited multiple color transitions to external stimuli including temperature, organic solvent, and mechanical force. This work provides chiral polydiacetylene assemblies by using natural triterpenoid gelators, and may open new scenarios on the design of smart responsive chiral PDA materials.

Introduction
Polydiacetylenes (PDA) is a kind of highly conjugated polymers and normally formed via the topochemical 1,4-polymerization of diacetylene (DA) monomers upon UV light or γ-ray irradiation. Because of the extensive delocalized n-electron networks and intrinsic conformational restrictions, PDA can undergo a blue-to-red color transition in response to external stimuli like temperature, organic solvents, pH, and mechanical forces, thus showing intriguing colorimetric and optical properties. These distinctive advantages make PDA particularly attractive building blocks in stimuli-responsive functional materials. It should be mentioned that an appropriate orderly arrangement of DA monomers is often required for the topochemical polymerization of PDA. To date, two common strategies have been reported to promote the regular packing of DA monomers. One is to covalently attach functional groups to DA backbone for the synthesis of amphiphilic DA-tailored molecules. For example, Sureshan and co-workers developed an organic gelator by conjugating 4,6-O-benzylidene β-D-galactopyranoside to DA skeleton, and found that this gelator can adhere to fabrics to generate semiconducting PDA materials upon UV-irradiation. While the other strategy is to noncovalently coassemble DA monomers with small molecules. For example, Liu et. al. co-assembled a chiral L-histidine ester derivative with DA monomer into a spiral nanoband supramolecular gel, which was easily polymerized into PDA upon UV-irradiation. This PDA not only had an excellent colorimetric response, but also exhibited the strong circular dichroism signal and circularly polarized luminescence. Obviously, compared with the former strategy involving covalent chemical modifications, the latter one is simple and convenient because the noncovalent physical packing can avoid tedious synthesis tasks and expand the selection range of small molecules. It should be pointed out here that the existence of a suitable co-assembly partner with DA monomer is the key point in the latter strategy. However, as far as we know the chiral partners are still limited. Thus, searching for chiral molecules with admirable assembly ability will enrich the library of co-assembly partners with DA monomers and benefit the production of diverse PDA.

Triterpenoids, consisting of six isoprene units, are abundant in many plants in the form of free acids or aglycones. They possess unique rigid chiral skeletons, multiple reactive sites, and good biocompatibility. These features allow for the easy modification and stacking of rigid skeletons, thus rendering triterpenoids great supramolecular gelators. For example, Bag group found that triterpenoids like corosolic acid, betulin, and ursolic acid can assemble into supramolecular gels with different spherical, flower-like, fibrous, and vesicular microstructures, respectively.
oolanolic acid with benzo triazole moiety and prepared a homogeneous stiff gel when capturing atmospheric water. Apparently, its intrinsic good assembly ability and multiple reactive sites made triterpenoids ideal candidates of chiral co-assembly partners with DA monomers.

Herein, in this research a triterpenoid-derived gelator (C4-MOP, Scheme 1) consisting of hydrophobic methyl oleanonate and hydrophilic pyridinium terminal group was synthesized to co-assemble with diacetylene monomer (10,12-pentacosadiynioic acid, PCDA, Scheme 1) for the fabrication of orderly assemblies, followed by the topochemical photopolymerization, as C4-MOP could be regulated into twisted ribbons in methanol/water mixed solvents. The results showed that C4-MOP/PCDA formed a stable white gel in methanol/water mixed solvents, and upon UV irradiation this gel underwent a noticeable white-to-blue color change with the generation of C4-MOP/PCDA via 1,4-photopolymerization of PCDA. During this gelation and polymerization process, the transmission and visualization of molecular chirality have been achieved successfully with the appearance of negative Cotton effect at 657 nm in visible blue light region. The assembled gel underwent a noticeable white-to-blue color change with the generation of C4-MOP/PCDA via 1,4-photopolymerization of PCDA. This allowed the transmission and visualization of molecular chirality to be achieved successfully with the appearance of negative Cotton effect at 657 nm in visible blue light region.

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down to room temperature, and consequently a white supramolecular gel of C4-MOP/PCDA formed (Figure 1A), mainly driven by the synergistic effect of hydrophobic interactions, van der Waals forces, and C-H···O interactions. The photopolymerization of C4-MOP/PCDA was investigated by means of UV light irradiation. As shown in Figure 1A, upon exposure to UV light (254 nm, 10 W), the white gel of C4-MOP/PCDA rapidly turned to blue as a result of 1,4-polymerization. This indicated that the supramolecular gelation did help the photopolymerization of diacetylene monomers. UV-vis absorption was employed to explore the kinetics process and structural changes. A new absorption band appeared at around 657 nm accompanied with a shoulder at 594 nm upon UV-irradiation (Figure 1B), which clearly ascertained the beginning of structure transition from the co-assembled C4-MOP/PCDA to the conjugated alternating ene-yne C4-MOP/PDA, corresponding well to the generation of blue color in Figure 1A. As the extension of irradiation time, the intensity at 657 nm gradually increased until no significant change was observed after 5 min (Figure 1C), which revealed the complete photopolymerization.

Further evidence for the formation of C4-MOP/PDA came from Raman spectroscopy. As shown in Figure 1D, two bands associated with the conjugated ene-yne of C4-MOP/PDA at 2071 cm$^{-1}$ (C≡C) and 1448 cm$^{-1}$ (C=C) appeared, whereas C=C band at 2256 cm$^{-1}$ of C4-MOP/PCDA disappeared completely, which served as the solid proof of topochemical 1,4-polymerization. It should be pointed that the generation of band at 1444 and 2099 cm$^{-1}$ for C4-MOP/PCDA was due to the laser irradiation during the performance of Raman spectrum. All above results indicated that the co-assembled C4-MOP/PCDA gel afforded orderly assemblies, which in turn promoted the following photopolymerization process.

It is known that the co-assembly of achiral molecules with chiral molecules is one of the effective methods to realize the chirality transfer and amplification. To evaluate whether C4-MOP/PDA gel owned optical activities, circular dichroism (CD) was executed because the Cotton effect can be used as a sensitive chiral indicator. As shown in Figure 1E, the chiral C4-MOP exhibited a negative Cotton effect at 266 nm, while it was silent for achiral PCDA. Accordingly, no CD signal of co-assembled C4-MOP/PCDA was observed in visible light region in addition to the negative Cotton effect at 266 nm. Conversely, after UV light irradiation an additional negative Cotton effect at 657 nm was observed. The appearance of CD signals in visible blue light region was attributed to the orderly assembled structures in white gel which transferred and amplified the chirality from chiral C4-MOP to C4-MOP/PDA. Obviously, C4-MOP offered a suitable chiral template to induce supramolecular chirality, which can be imprinted into the polymerized C4-MOP/PDA gel.

Morphologies
Transmission electron microscopy (TEM) was employed to investigate the morphologies of C4-MOP/PCDA before and after UV-irradiation. PCDA assembled into microsheets (Figure 2A), while C4-MOP formed twisted ribbons with a width around 0.3 μm (Figure 2B and S1A). Conversely, chiral nanotubes were observed for the white gel of C4-MOP/PCDA with a diameter in 0.8 μm, which was clearly curled from twisted ribbons (white arrows, Figure 2C, S1B and S2). These fairly uniform nanotubes indicated that PCDA and C4-MOP co-assembled synergistically rather than forming nanostructures separately. During this process, the chirality was transferred and expressed on account of the rich chiral centers of C4-MOP. Notably, no significant change in morphology was observed after photopolymerization (white arrows, Figure 2D, S1C and S2), probably resulting from the fact that the process was a topochemical reaction.

![Figure 1](https://example.com/figure1.png)

**Figure 1** (A) Digital photos of the white gel C4-MOP/PCDA and the blue gel C4-MOP/PDA after UV-irradiation (254 nm, 10 W). (B) UV-vis spectra of C4-MOP/PCDA under UV-irradiation (254 nm, 10 W) for different time. (C) Absorbance intensity of C4-MOP/PCDA at 657 nm as a function of irradiation time. (D) Raman spectra of C4-MOP/PCDA and C4-MOP/PDA. (E) CD spectra of C4-MOP, PCDA, C4-MOP/PCDA and C4-MOP/PDA in methanol/water (1/2, v:v, 5 mg/ml).

![Figure 2](https://example.com/figure2.png)

**Figure 2** TEM images of (A) PCDA, (B) C4-MOP, (C) C4-MOP/PCDA, and (D) C4-MOP/PDA in methanol /water (1/2, v:v, 5 mg/ml).
Possible packing patterns

In order to reveal the packing structures, the single crystal analysis and power X-ray diffraction (XRD) experiments were carried out. We first employed the Chem 3D software to measure the molecular chain length of the fully extended PCDA molecule, which was 31.1 Å as shown in Figure S3A. Meanwhile, a single crystal of C4-MOP was successfully cultured in the mixed solvents of methanol/dichloromethane. The crystal structure and packing patterns were illustrated in Figure 3, S4-S6, and Table S1. The length of C4-MOP molecule was 20.8 Å, and the packing diagram of C4-MOP revealed an orthorhombic structure, where two adjacent molecules with a head-to-tail stacking were regarded as repeating units (41.65 Å) along the orientation c (Figure 3). Moreover, two molecules were staggered and stacked in antiparallel along the direction b, and the distance between two identical conformation molecules was 12.56 Å. As for the interactions between molecules, as depicted in Figure S6, C-H···O interaction (with a distance of 2.55 Å) and four types of C-H···Br interactions (with distances of 2.69, 2.87, 2.73, and 2.87 Å) were observed. All these intense multiple interactions helped to solidify the molecular conformations and stabilize the crystal structure.

Figure 3 X-ray single crystal structure of C4-MOP and its spatial arrangements along the direction b and c. Purple: bromine atom, red: oxygen atom, gray: carbon atom, blue: nitrogen atom, white: hydrogen atom.

XRD results of C4-MOP, PCDA, and C4-MOP/PCDA assemblies were shown in Figure 4 and Table S2. The peaks of PCDA at 1.86, 5.55, 7.42, 9.28, 13.03, 16.83, and 22.87 Å were observed in Figure 4A, following the ratio of 1: 1/3: 1/4: 1/5: 1/10: 1/12 (Figure 4C). It strongly indicated that the lamellar structures formed in the gel with a d value of 45.96 Å. As this d value was very close to the one of PCDA bilayer structure in Figure 4A, it was assumed that C4-MOP was inserted into the bilayer structure of PCDA to form a structural unit with the partial crossover between the hydrophobic part of C4-MOP and the flexible chain of PCDA.

Furthermore, FT-IR spectra of PCDA, C4-MOP, and xerogel of C4-MOP/PCDA were investigated (Figure 4D). In case of PCDA, the stretching vibration of C=O corresponding to COOH appeared at 1694 cm⁻¹, indicating PCDA had a hydrogen-bonded carboxyl stretching band. The peaks at 2921 and 2848 cm⁻¹ were asymmetric and symmetric stretching vibrations of CH₃ and CH₂, and the stretching vibrations at 1726 and 1708 cm⁻¹ were assigned to C=O groups in ester groups at positions 3 and 17, respectively. In co-assembled C4-MOP/PCDA system, the stretching vibrations of C=O shifted from 1726 to 1694 cm⁻¹ upon gelation, while the original peak at 1726 and 1694 cm⁻¹ remained unchanged. This shift might be originated from the hydrogen bonding between the C=O in ester group of C4-MOP and the carboxyl head group of PCDA. In polar methanol/water environment, both the hydrophilic heads of C4-MOP and PCDA faced outward, while their hydrophobic backbones overlapped partially because of hydrophobic interactions. As a result, they would like to arrange in a more orderly manner to form the intermolecular hydrogen bonding interactions. Also, asymmetric and symmetric stretching vibrations of CH₂ appeared at 2923 and 2851 cm⁻¹ suggested an ordered packing of alkyl chains primarily promoted by van der Waals forces. Apparently, the hydrophobic interactions, the intermolecular hydrogen bonding interactions, and van der Waals forces played crucial roles in the formation of supramolecular gel C4-MOP/PCDA.

Based on the above results, a possible assembly process was proposed as following: initially a few of assembled dimers of C4-
MOP and PCDA elongated to form twisted ribbons. Subsequently, in order to expose less hydrophobic areas in hydrophilic environment, the twisted ribbons continuously curled and finally constructed the nanotubes. During the co-assembled process, the molecular chirality of C4-MOP was magnified and transmitted to C4-MOP/PCDA, as confirmed by CD spectra in Figure 1D and TEM images in Figure 2.

Color transition

Since C4-MOP/PDA contains an alternating ene-acylenic conjugated skeleton, we explored its color transitions to external stimuli including temperature, organic solvent, and mechanical force. As shown in Figure 5A, the C4-MOP/PDA underwent a clear blue-to-red color transition when the film was heated, with an absorption shift from 678 and 623 nm to 548 and 506 nm in UV-vis spectra. Moreover, a fluorescence signal at 634 nm generated as the red phase appearing (Figure 5B). Similar to the phenomenon of thermochromism, both organic solvent and mechanical force could also induce the color change from blue to red. As shown in Figure S7, after external grinding or fuming by chloroform, the blue color of C4-MOP/PCDA disappeared with the appearance of red, as well as the production of strong fluorescence. This phenomenon was due to the low conjugation length of PDA, which originated from the increased motional freedom of the PDA side chains when suffering from temperature, organic solvent, or mechanical force.40,41 In brief, this color transition of C4-MOP/PDA observed by naked eyes could be utilized to prepare multifunctional sensors for external stimuli.

Conclusions

In summary, a stable white supramolecular gel C4-MOP/PCDA was formed in methanol/water mixed solvents by co-assembling PCDA with C4-MOP, which can be photo-polymerized into C4-MOP/PDA upon UV-irradiation, accompanying with the color change of the gel from white to blue. UV-vis and Raman spectra revealed that the photopolymerization was completed within 5 min, and a possible packing pattern was proposed by measuring the X-ray diffraction and FT-IR spectra. In addition, the new negative Cotton effect at 657 nm in visible blue light region in CD spectra indicated that the transmission and visualization of molecular chirality have been achieved successfully during the gelation and polymerization process. Notably, the assembled nanotubes of C4-MOP/PCDA that curled from twisted ribbons barely changed after polymerization into C4-MOP/PDA. Furthermore, because of the alternating ene-acylenic conjugated structure, the C4-MOP/PDA exhibited color transitions to external stimuli including temperature, organic solvent, and mechanical force. These results provide chiral polydiacetylene assemblies by using triterpenoid gelators and may open new scenarios on the design of smart responsive PDA materials.

Conflicts of interest

The authors declare that they have no conflict of interest.

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Notes and references

1. S. Rondeau-Gagne, J. R. Neabo, M. Desroches, J. Larouche, J. Brisson and J.-F. Morin, J. Am. Chem. Soc., 2013, 135, 110-113.
2. Y.-Y. Xu, Z.-F. Ding, F.-Y. Liu, K. Sun, C. Dietlin, J. Laleevée and P. Xiao, ACS Appl. Mater. Interfaces, 2020, 12, 1658-1664.
3. K. Watanabe, H. Imai and Y. Oaki, Small, 2020, 16, 200456E.
4. D.-H. Park, W. Jeong, M. Seo, B. J. Park and J.-M. Kim, Adv. Funct. Mater., 2016, 26, 498-506.
5. G. Shin, M. I. Khazi and J.-M. Kim, Macromolecules, 2020, 53, 149-157.
6. G. Shin, M. I. Khazi and J.-M. Kim, Langmuir, 2020, 36, 13971-13980.
7. L. Polacchi, A. Brossoeau, R. Metivier and C. Attain, Chem. Commun., 2019, 55, 14566-14569.
8. X. Qian and B. Stadler, Chem. Mater., 2019, 31, 1196-1222.
9. M. I. Khazi, W. Jeong and J.-M. Kim, Adv. Mater., 2018, 30, 1705310.
10. X. Chen, G. Zhou, X. Peng and J. Yoon, Chem. Soc. Rev., 2012, 41, 4610-4630.
11. M. J. Seo, J. Song, C. Kantha, M. I. Khazi, U. Kundapur, J.-M. Heo and J.-M. Kim, Langmuir, 2018, 34, 8365-8373.
12. Y. Meng, J. Jiang and M. Liu, Nanoscale, 2017, 9, 7199-7206.
13. J. R. Neabo, K. S. Tohoudjona and J.-F. Morin, Org. Lett., 2011, 13, 1358-1361.
14. B. P. Krishnan, S. Mukherjee, P. M. Aneesh, M. A. G. Namboothiri and K. M. Suressan, Angew. Chem. Int. Ed., 2016, 55, 2345-2349.
15. C. Chen, J. Chen, T. Wang and M. Liu, ACS Appl. Mater. Interfaces, 2016, 8, 30608-30615.
16. X. Huang, S. G. Jiang and M. Liu, J. Phys. Chem. B, 2005, 109, 114-119.
17. P. Duan, Y. Li and M. Liu, Sci. China Chem., 2010, 53, 432-437.
18. Y. Gao, J. Hao, J. Wu, X. Zhang, J. Hu and Y. Ju, Nanoscale, 2015, 7, 13568-13575.
19. B. G. Bag, C. Garai, R. Majumdar and M. Laguerre, Struct. Chem., 2012, 23, 393-398.
20. X. Wang, M. Jin, C. Jin, C. Ye, Y. Zhou, R. Wang, H. Cui, W. Zhou and G. Li, Nat. Prod. Res., 2020, 34, 3319-3319.
21. Y. Gao, J. Hao, Q. Yan, F. Du, Y. Ju and J. Hu, ACS Appl. Mater. Interfaces, 2018, 10, 17352-17358.
22 B. G. Bag, C. Garai and S. Ghorai, RSC Adv., 2019, 9, 15190-15195.
23 B. G. Bag and S. S. Dash, Langmuir, 2015, 31, 13664-13672.
24 B. G. Bag, S. Das, S. N. Hasan and A. C. Barai, RSC Adv., 2017, 7, 18136-18143.
25 K. Vega-Granados, G. Belen Ramirez-Rodriguez, R. Contreras-Montoya, F. J. Ramirez, L. Palomo, A. Parra, J. M. Delgado-Lopez, M. T. Lopez-Lopez and L. Alvarez de Cienfuegos, Mater. Chem. Front., 2019, 3, 2637-2646.
26 Y. Gao, J. Hao, J. Liu, Y. Liang, F. Du, J. Hu and Y. Ju, Mater. Chem. Front., 2019, 3, 308-313.
27 K. Sada, M. Takeuchi, N. Fujita, M. Numata and S. Shinkai, Chem. Soc. Rev., 2007, 36, 415-435.
28 H. Fan, H. Jiang, X. Zhu, M. Zhu, L. Zhang and M. Liu, Eur. Polym. J., 2019, 118, 146-152.
29 T. Hasegawa, S. Haraguchi, M. Numata, C. Li, A. Bae, T. Fujisawa, K. Kaneko, K. Sakurai and S. Shinkai, Org. Biomol. Chem., 2005, 3, 4321-4328.
30 J. Hu, T. Zhu, C. He, Y. Zhang, Q. Zhang and G. Zou, J. Mater. Chem. C, 2017, 5, 5135-5142.
31 J. K. Lim, Y. Lee, K. Lee, M. Gong and S.-W. Joo, Chem. Lett., 2007, 36, 1226-1227.
32 M. Liu, L. Zhang and T. Wang, Chem. Rev., 2015, 115, 7304-7397.
33 E. Yashima, T. Matsushima and Y. Okamoto, J. Am. Chem. Soc., 1997, 119, 6345-6359.
34 B. Yue, L. Yin, W. Zhao, X. Jia, M. Zhu, B. Wu, S. Wu and L. Zhu, ACS Nano, 2019, 13, 12438-12444.
35 M. Okaniwa, Y. Oaki, S. Kaneko, K. Ishida, H. Maki and H. Imai, Chem. Mater., 2015, 27, 2627-2632.
36 N. Phonchai, C. Khanantong, F. Kielar, R. Traiphol and N. Traiphol, ACS Appl. Nano Mater., 2019, 2, 4489-4498.
37 D. J. Ahn, E. Chae, G. S. Lee, H. Shim, T. Chang, K. Ahn and J. Kim, J. Am. Chem. Soc., 2003, 125, 8976-8977.
38 Y. Zhou, T. Yi, T. Li, Z. Zhou, F. Li, W. Huang and C. Huang, Chem. Mater., 2006, 18, 2974-2981.
39 Y. Gao, J. Lu, J. Wu, J. Hu and Y. Ju, RSC Adv., 2014, 4, 63539-63543.
40 Y.-J. Choi, S. Park, W.-J. Yoon, S.-I. Lim, J. Koo, D.-G. Kang, S. Park, N. Kim and K.-U. Jeong, Adv. Mater., 2020, 32, 2003980.
41 D. J. Ahn, S. Lee and J.-M. Kim, Adv. Funct. Mater., 2009, 19, 1483-1496.