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COMMUNICATION

Self-assembly nanopillar arrays by Simple Spin Coating from Blending Systems Comprising PC₆₁BM and Conjugated Polymers with Special Structure

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Three conjugated D-A copolymers were found to form well-defined nanopillar arrays through facile spin-casting process when blended with fullerene derivatives. Research results indicated that the presence of large coplanar segments and intramolecular S...O attractive interactions in the polymers are both crucial factors for achieving self-assembly nanopatterned pillar arrays.

Fabrication of periodic nanostructures, such as nanopillar arrays, has attracted great attention due to the potential applications in magnetic storage media, organic semiconductors, plasmonic nanophotonics, and filtration membranes.¹⁻⁵ Most of related researches focused on inorganic materials, such as SiO₂, Fe₂O₃, ZnO, TiO₂ and et al.^{6,7} Recently, there has been increasing interest in manufacturing nanopillar array comprising polymer components, especially conjugated polymers, due to their low cost and successful applications in organic light-emitting diodes(OLED) and organic photovoltaics(OPV).^{8,9} For example, nanopillar arrays or nanovetical domain in films of poly(3-hexylthiophene) (P3HT, a well-known conjugated polymer) have been developed.^{10,11} To acquire polymer-containing periodic nanostructures, a nanotemplate technique is generally indispensable, while the fabrication of pre-patterned nanotemplate is usually costly and complex.¹²⁻¹⁴

Recently, with the booming development of supramolecular chemistry, self-organization has been recognized to be a very powerful and facile alternative to nanofabrication and nanomanipulation.¹⁵ Many fantastic nanomotifs like nanofibers, nanorods and nanospheres have been realized through controlled self-assembly processes.¹⁶⁻¹⁹ With regard to the acquirement of self-assembly nanostructure arrays, diblock copolymers and binary polymers with poor miscibility, e.g., polystyrene (PS) and polymethylmethacrylate (PMMA), are generally utilized. This procedure is often accompanied with a

post-processing of either physical dissolution or chemical etching to remove one component selectively, because that effective lateral phase separation in bulk could be triggered during spin coating process.²⁰⁻²² Spin-coating is a very widely used technique and a simple method for making uniform thin polymer films. Therefore, the self-assembly behavior of diblock copolymers during spin coating process has drawn significant attention.^{23,24}

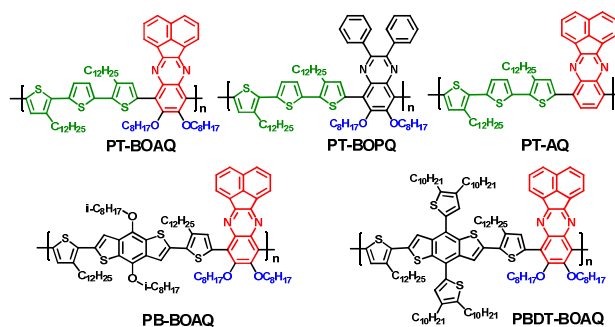


Figure 1 The molecular structure of the copolymers investigated in this article.

In this paper, we report our discovery that well-defined polymer-comprising nanopillars arrays could be achieved by a rather simple spin-casting process from blending systems of [6, 6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM) (structure shown in Figure S1, in the Supporting Information) and certain conjugated copolymers on quartz substrates, dispensing with any pre- or post-processing. To the best of our knowledge, this is the very first report to achieve nanopillar arrays just by facile spin-coating without further processing. In depth investigations reveal that the presence of large coplanar polymeric backbone is indispensably for acquiring nanopatterned pillar motifs; while the introduction of long-chain alkyloxy groups into appropriate positions of the polymeric backbones would endow

these macromolecules with intense intramolecular S...O attractive interactions, resulting in higher molecular weights as well as maintained planar conformation of the copolymers, hence better self-organization capability.

In our previous work exploiting low bandgap D-A-featured (donor-acceptor) copolymers for organic photovoltaic (OPV) applications, we synthesized **PT-BOAQ** (structure shown in Figure 1) bearing electron-deficient planar fused aromatic A subunits.²⁵ After spin-casting the **PT-BOAQ/PC₆₁BM** (1/3) composite solution, we found surprisingly that the surface of this optical active layer displays incredible and charming well-aligned nanopillars (Figure 2a). This should be a quite valuable discovery, since these nanopillar arrays are achieved by facile spin-coating, dispensing with any pre- or post-processing, i.e., through mere self-assembly process.

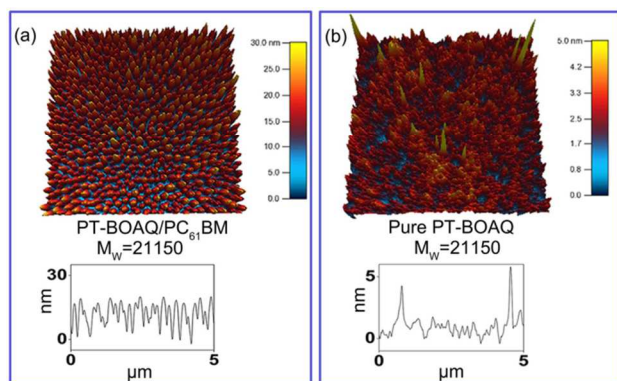


Figure 2 3D-visualized AFM image and cross section view in height mode of: (a) **PT-BOAQ/PC₆₁BM** blend film; and (b) pure **PT-BOAQ** film. All images are in $5.00 \times 5.00 \mu\text{m}$ size.

In fact, although considerable attention has been paid to the morphology characterization of spin-coated polymers/**PC₆₁BM** composite films due to the rapid development of OPV materials and devices, to our knowledge, there have been no relative reports declaring the observation of nanopillar arrays on the surface of such film samples. Consequently, we conjectured that the formation of well-aligned nanopillars in this blending system should be dominated by the polymer rather than **PC₆₁BM** species. To validate this hypothesis, a pure **PT-BOAQ**-based reference film was prepared. As shown in Figure 2b, although the width and height of the self-assembly domains are far less regular in comparison with those of **PT-BOAQ/PC₆₁BM** composite film, obvious pillars are still distinguishable on the surface of this reference film. Therefore, **PT-BOAQ** should possess intrinsic self-organization capability, while the presence of **PCBM** derivative should be beneficial to the reinforcement of the self-assembly process, leading to perfectly arrayed nanopillar structures.

Since according to literature reports,^{26,27} both chemical structure and molecular weight of the polymers are essential factors influencing the morphological properties of polymer/**PC₆₁BM** composite films, firstly, we investigated the relationship between the morphological properties of the blending films and M_w of **PT-BOAQ**. As depicted in Figure S2 (in the Supporting Information), in all these samples, distinct nanopillar arrays were discernable despite the drastically differed M_w of the copolymer component. Moreover, with increasing M_w of **PT-BOAQ** from 6900 to 27900, the surface of the corresponding blending films shows more well-isolated and higher nanopillar domains. Therefore, it should be the

chemical structure rather than molecular weight of **PT-BOAQ** that determines the intrinsic self-assembly capability of the blending films.

Based on structural analysis, **PT-BOAQ** could be split into three core segments: 1) 3, 3''-didodecyl-2, 2':5', 2''-terthiophene; 2) acenaphtho[1,2-b]quinoxaline (AQ); 3) two octyloxy groups attached to AQ. Since poly(alkylthiophene)s (PAT), one of the most intensively investigated OPV electron-donating materials, bear similar terthiophene building units with **PT-BOAQ**, yet no such well-aligned nanopatterns have been reported in pristine PAT/**PC₆₁BM** blend films, thus terthiophene subunit might play a trivial role in the self-organization process of **PT-BOAQ**.

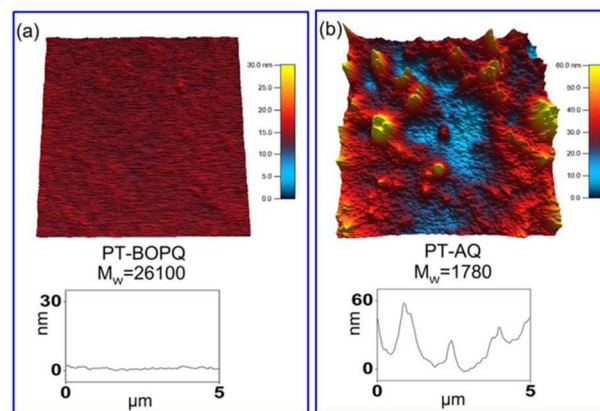


Figure 3 3D-visualized AFM image and cross section view in height mode of: (a) **PT-BOPQ/PC₆₁BM** blend film; and (b) **PT-AQ/PC₆₁BM** blend film. All images are in $5.00 \times 5.00 \mu\text{m}$ size.

Therefore, to unveil the relationship between chemical structure and self-assembly capability of copolymers, **PT-BOPQ** bearing less planar diphenylquinoxaline A units and **PT-AQ** lacking two octyloxy groups on the AQ segment were synthesized as reference polymers (structure shown in Figure 1). As depicted in Figure 3a, the **PT-BOPQ/PC₆₁BM** blending film manifests quite smooth surface with RMS of 0.53 nm, implying that the presence of large coplanar aromatic segment in polymers is indispensably for acquiring nanopillar arrays. While for **PT-AQ** bearing similar AQ subunit but no alkyloxy groups, obvious pillars could be identified in the composite film (Figure 3b), confirming that the existence of planar aromatic system will help to boost the self-assembly process. In fact, 9, 10-bis(octyloxy)acenaphtho[1,2-b]quinoxaline, the key constructive moiety of **PT-AQ**, is observed to form vertical column crystal in ethanol solution, as shown in Figure S3 (in the Supporting Information), suggesting that the large planar structure would indeed trigger self-organization in perpendicular direction. Nevertheless, in comparison with **PT-BOAQ/PC₆₁BM** film, the domains formed on the surface of **PT-AQ/PC₆₁BM** film are far from well-organized in both width and height. Taking into account that **PT-AQ** has an extreme low molecular weight of 1780, which could not be further enhanced due to its poor solubility, both the lower M_w and the absence of two alkyloxy groups may be responsible for the low quality arrays of **PT-AQ/PC₆₁BM** film.

Since recent reports^{28, 29} revealed that in a large number of organosulfur compounds, there exists obvious intramolecular nonbonded interaction between sulfur and oxygen atoms, which could act as an effective conformational controlling factor, to gain deeper insights into the role two alkyloxy groups play in the self-assembly process of **PT-BOAQ**, density functional

theory (DFT) calculations have been performed to investigate the optimized ground state geometries of the repeating units of these copolymers. As shown in Figure S4 (in the Supporting Information), in all the repeating units whether with or without octyloxy groups, the two thiophene units and their neighboring AQ or quinoxaline segment are all found to be mutually coplanar. Furthermore, for repeating units bearing two alkyloxy groups on AQ or quinoxaline moieties, the S...O distances between thienyl and alkyloxy groups are all calculated to be ~ 2.7 Å, which is significantly shorter than the sum of van der Waals radii for sulfur and oxygen atoms (3.32 Å), indicative of the presence of intramolecular S...O attractive interaction between thienyl and alkyloxy groups. Consequently, the introduction of two octyloxy groups on the appropriate position of A units may be beneficial to both the maintenance of planar conformation and the enhancement of M_w of these copolymers, hence better self-organization capability.

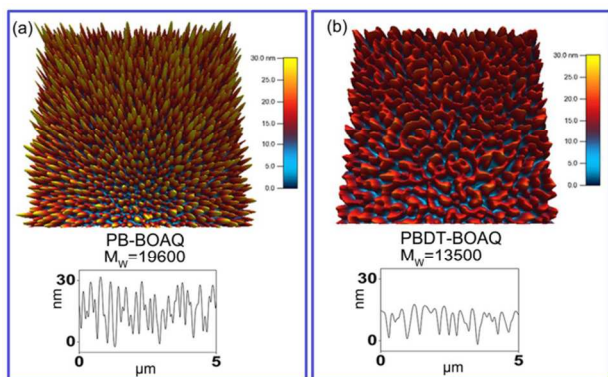


Figure 4 3D-visualized AFM image and cross section view in height mode of: (a) PB-BOAQ/PC₆₁BM blend film; and (b) PBDT-BOAQ/PC₆₁BM blend film. All images are in 5.00 × 5.00 μm size.

From all these experimental observations, we can infer that both large planar segments and long-chain alkyloxy substituents may be essential constructional units to acquire copolymer capable of forming well-defined nanopyllar arrays. To verify this conjecture, two copolymers (**PB-BOAQ** and **PBDT-BOAQ**, structures shown in Figure 1) bearing similar A units of dioctyloxy-substituted AQ but different D units with **PT-BOPQ** were synthesized. For **PB-BOAQ**, a larger planar benzodithiophene (BDT) instead of thiophene segment was inserted between two thienyls; while in **PBDT-BOAQ**, the BDT segment was further modified by two alkylthienyls, which may result in more twisted conformation of the copolymer, hence weakened self-organization capability. These deductions were confirmed by DFT calculation results, since intramolecular S...O attractive interactions between thienyl and alkyloxy groups are discernable in the construction units of both **PB-BOAQ** and **PBDT-BOAQ**; and the repeating unit of **PB-BOAQ** displays a much planar conformation, yet that of **PBDT-BOAQ** shows drastically decreased planarity due to the twisting of the two thienyls. Clearly evidenced by AFM images shown in Figure 4, the **PB-BOAQ/PC₆₁BM** blending film indeed shows more well-defined nano-patterned pillars than those of **PT-BOAQ/PC₆₁BM** film, but the quality of the nanopyllars on the surface of **PBDT-BOAQ/PC₆₁BM** film is much lower, since most of the pillars are not well-separated. Therefore, the presence of large coplanar π -conjugation segments does contribute significantly to the enhancement of

self-organization capability of the copolymers, hence is beneficial to the acquirement of high quality nanopyllar arrays.

Table 1 The contact angle and surface energy of all the materials investigated in this article.

Materials	Contact angle [deg]	Surface energy [mJ·m ⁻²]
PT-BOAQ	119.7	11.74
PB-BOAQ	111.1	16.48
PBDT-BOAQ	106.8	18.96
PT-AQ	106.0	19.45
PT-BOPQ	101.1	22.40
PCBM	90.7	28.80
Quartz substrate	36.5	61.24

Besides the relationship between molecular structure and self-assembly ability, the role that fullerene derivative plays in the formation of nanopyllar motifs also deserves elucidation. Inspired by the comment of Sasha Y. Heriot³⁰ and André D. Taylor³¹ et al. that the phase separation in spin-casted polymer blending films correlates closely with the wetting procedure, we deduced that the self-assembly pillar nanomotifs might arise from the surface/interfacial instability between substrate, PC₆₁BM and the copolymers used. Therefore, the contact angles of quartz substrate, PC₆₁BM and the five copolymers were measured, and the corresponding surface energies were calculated accordingly. As summarized in Table 1, the surface energy of PC₆₁BM is 28.80 mJ/m², while those of **PT-BOAQ** (11.74 mJ/m²), **PB-BOAQ** (16.48 mJ/m²), **PBDT-BOAQ** (18.96 mJ/m²) and **PT-AQ** (19.45 mJ/m²) are lower. Consequently, during the rapid solvent-casting process, phase separation may take place due to the relative large surface energy difference between PC₆₁BM and these copolymers, which may trigger the self-assembly of these copolymers into nanopyllars. Yet for **PT-BOPQ**, since its surface energy (22.40 mJ/m²) is closer to that of PC₆₁BM, the demixing of the two components should be less efficient, hence no nanoarrays were formed in this blending system. Furthermore, the surface energy of quartz substrate (61.24 mJ/m²) is much larger than both PC₆₁BM and these polymers. Taking into account that PC₆₁BM has higher composition and smaller surface energy difference from that of quartz, it should be PC₆₁BM rather than these polymers that adsorbs preferentially on the substrate (Figure 5b). Nevertheless, the surface energy difference between PC₆₁BM and quartz substrate is still quite large, thus PC₆₁BM might form pre-organized clusters on the surface of quartz substrate, followed by the self-organization of the macromolecular component if lateral phase separation occurs in these blending systems. Finally, nanopyllar arrays are formed on the substrate (Figure 5c).

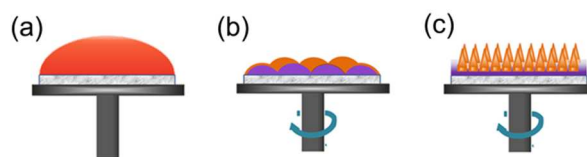


Figure 5 Diagram of the proposed pillar nanomotif formation process of polymer/PC₆₁BM blending systems. (a) Dropping the composite solution on quartz substrates; (b) efficient phase separation of the two components during spin-coating due to their interfacial instability, with PC₆₁BM preferentially adsorbed on quartz substrates; (c) the formation of nanopyllar arrays arising from the self-organization of copolymers after evaporation of solvent.

In conclusion, through delicate molecular design on the macromolecular component, well-defined nanopillars arrays could be acquired by facile spin-casting process from blending systems of PC₆₁BM and conjugated copolymers. The presence of large coplanar segments in the polymers is a crucial factor for achieving self-assembly nanopatterned pillar arrays, while the existence of intense intramolecular S...O attractive interactions between long-chain alkyloxy and thienyl groups on the polymeric backbones would endow these macromolecules with compromised planar conformations and high molecular weights, hence enhanced self-organization capability. Our results may shed light on the molecular design strategy for achieving periodically nanopatterned optoelectronic active polymeric systems through template-free and simple approaches.

Acknowledgements

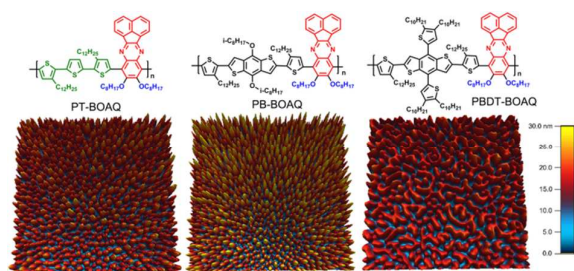
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Notes and references

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