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A General Synthetic Approach of Organic Lateral Heterostructures for Optical Signal Converters in All-Color Wavelength

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Abstract

Organic heterostructures with precisely defined compositions, architectures, and interfaces are considered as promising building blocks for integrated optoelectronic devices. However, it remains a great challenge to rationally design and synthesize the heterostructure with tunable performance for promising applications, such as optoelectronic devices. Herein, we report a universal strategy for the synthesis of organic lateral heterostructures (OLHs) with tunable structure and optical properties. Based on the tunable intermolecular distance ($d_{\pi-\pi}$ from 3.33 to 3.48 Å) of Benzo[ghi]perylene (BGP)-based cocrystals driven by arene-perfluoroarene (AP) interaction or charge transfer (CT) interaction, these different components are selectively constructed into organic solid solution microwires or OLHs. Importantly, the obtained solid solution microwires can be epitaxially grown on the BGP-Tetrabromophthalicanhydride (TBPA) trunk microwire to construct a series of OLHs microwires, which leads to the successful demonstration both in photonic signal converts and optical logic gate in all-color wavelength. The present work gives a new insight into the fine synthesis of heterostructures with tunable structures/performances, and provides predictable synthetic pathways to multifunctional organic heterostructures for the future realization of integrated optoelectronics.

Keywords

organic heterostructure, low-dimensional structure, crystal, epitaxial growth, integrated photonics

Introduction

Complex heterostructured micro/nanomaterials with multi-functionalities and novel performances are important for many applications including catalysis, plasmonic, electronics, optoelectronic and so on. Among them, one dimension (1D) branch heterostructures composed of two or more distinct materials, possessing different space distribution (vertical or lateral) and high-density of branches grown on trunk, are particularly attractive micro/nanomaterials for a large variety of applications. In the last two decades, the controlled synthesis of inorganic branch heterostructures nanomaterials have been intensively investigated,
through the vapor-liquid-solid (VLS) method or chemical vapor deposition (CVD) method and so on. A typical example is the case of eight CdS nanocrystals hierarchical grown onto the central region of CdSe nanorods to form octapod-shaped nanocrystals via cation exchange and seeded growth method. However, as compared to inorganic materials, organic semiconductors exhibit obvious advantages for optoelectronics applications, due to their two-photon absorption cross sections and broad spectral tunability as well as the designable molecular structure. Specially, the organic crystals composed of one or more different organic molecules, that not only inherits the single-crystal intrinsic features of long-range order as well as free defects, but also provides a platform for the rational design and flexible construction of heterostructures based on the diverse library of organic materials and various intermolecular interactions.

Till now, lots of efforts have been devoted to prepare organic branch heterostructures and exhibiting attractive optoelectronic properties. For example, based on the organic crystal, the synthesis of 1D branched heterostructures with multiple nanowire branches has been demonstrated, and its application in photonic devices (such as signal conversion and multi-channel optical waveguides). Moreover, a series of branched heterostructures with different morphologies are reported, including microplates, spindles and ribbon-like structures that epitaxially grow on the microwire backbone. However, for the same kind of 1D branch heterostructures with rigorous morphology, modulating their optical properties to fulfill the requirement of integrated optical circuits such as signal converters and logic gates are rarely reported. Actually, organic crystals with different optical properties generally have distinct crystal structures, which makes it difficult to control the facet selective epitaxial growth mode of the secondary components to maintain the same structure of the heterostructure while changing the chemical/physical properties. Although lots of efforts have been devoted to prepare various typical organic heterostructures (core-shell, triblock, and so on) by integrating distinct organic counterparts, but their molecular structure must be significantly changed to tune the emission wavelength, which limits their flexible applications in optoelectronics.
In this work, we report a generalizable mix-and-match synthetic strategy to organic heterostructures with tunable structure and optical properties, that combines the organic solid solutions and the heterostructures (Figure 1a). We prepared a series of BGP-based cocrystals including BGP-octafluoronaphthalene (OFN), BGP-tetrafluoroterephthalonitrile (TFP), BGP-tetrafluorophthalicanhydride (TFPA), BGP-1,2,4,5-benzenetetranitrile (TCNB), BGP-TBPA through solution self-assembly method. At the same time, these selected cocrystals driven by the AP or CT interaction. Based on the tunable intermolecular distances ($d_{\pi-\pi}$ from 3.33 to 3.48 Å) and competitive intermolecular interactions of cocrystals, these components can be selectively constructed into organic solid solution microwires or OLHs. Importantly, the obtained solid solution microwires can be matched with the BGP-TBPA trunk microwire for realizing a series of OLHs microwires with color-tunable emission. Moreover, the structures of OLHs could be further adjusted through tuning the stoichiometric ratio of multi-components. Thus, a series of optical signal converts and multichannel optical routers have been successfully realized based on the OLHs with all-color-tunable photoluminescent. The present work provides a desired platform for in-depth investigation of organic heterostructures with novel and enhanced performance, and opens a new window for flexible designing and building complex multifunctional optoelectronic modules.

**Experimental Methods**

**Chemicals**

Benzol[ghi]perylene (BGP, CAS: 191-24-2), Octafluoronaphthalene (OFN, CAS: 313-72-4), Tetrafluoroterephthalonitrile (TFP, CAS: 1835-49-0), 1,2,4,5-Benzenetetranitrile (TCNB, CAS: 712-74-3), Tetrafluorophthalicanhydride (TFPA, CAS: 652-12-0), Tetrabromophthalicanhydride (TBPA, CAS: 632-79-1) were purchased from Sigma-Aldrich Co. The dichloromethane (CH$_2$Cl$_2$, A.R.), methanol (A.R.) and ethanol (A.R.), cyclohexane (A.R.) and n-hexane (A.R.) solvents, were purchased from Beijing Chemical Ltd. China. In addition, all compounds and solvents were used without further treatment.
**Methods**

(1) Self-assembly of organic cocrystals (BGP-OFN, BGP-TFP, BGP-TCNB). Typically, 10 mL of the monomer solutions containing 0.1 mmol BGP and 0.1 mmol OFN (TFP or TCNB) in dichloromethane (DCM) were quickly injected into 20 mL of an ethanol. Then the mixed solution was directly drooped onto the quartz substrate. With the solvent evaporation, the mixtures would reach supersaturation and the BGP-OFN (BGP-TFP, BGP-TCNB) cocrystals were observed.

(2) Self-assembly of organic cocrystals (BGP-TFPA, BGP-TBPA). Typically, 10 mL of the monomer solutions containing 0.1 mmol BGP and 0.1 mmol TFPA (TBPA) in dichloromethane (DCM) were quickly injected into 20 mL of an n-hexane. Then the mixed solution was directly drooped onto the quartz substrate. With the solvent evaporation, the mixtures would reach supersaturation and the BGP-TFPA (BGP-TBPA) cocrystals were observed.

(3) Co-assembly of BGP-OFN-TFP, BGP-OFN-TFPA, BGP-OFN-TCNB organic solid solution microwires. Typically, 10 mL of the monomer solutions containing BGP, OFN and TFP in DCM with extent molar ratio ($N_{BGP} : N_{OFN} : N_{TFP} = 1 : 1 : 0.1, C_{BGP} = 5 \text{ mM}$) were quickly injected into 20 mL of a mixed solvent (ethanol and n-hexane, $V_{\text{ethanol}} : V_{\text{n-hexane}} = 15 : 5$). Second, the mixed solvent directly dropped onto the quartz plate, subsequent evaporation of mixed solvent, the mixtures would reach super-saturation rapidly and undergo crystal growth. Likewise, the BGP-OFN-TFPA and BGP-OFN-TCNB also obtained by above method.

(4) Synthesis of BGP-OFN@BGP-TBPA lateral heterostructures. Typically, 10 mL of the monomer solutions containing BGP, OFN and TBPA in DCM with extent molar ratio ($N_{BGP} : N_{OFN} : N_{TBPA} = 2 : 1 : 1, C_{BGP} = 2 \text{ mM}$) were quickly injected into 20 mL of a mixed solvent (ethanol and n-hexane, $V_{\text{ethanol}} : V_{\text{n-hexane}} = 15 : 5$). Second, the mixed solvent directly dropped onto the quartz plate, subsequent evaporation of mixed solvent, the mixtures would reach super-saturation rapidly and undergo crystal growth.
Synthesis of BGP-OFN-TFP@BGP-TBPA, BGP-OFN-TFPA@BGP-TBPA, BGP-OFN-TCNB@BGP-TBPA lateral heterostructures. In a typical experiment, 10 mL of the monomer solutions containing BGP, OFN, TBPA, TFP in DCM with extent molar ratio \( N_{\text{BGP}} : N_{\text{OFN}} : N_{\text{TBPA}} : N_{\text{TFP}} = 2 : 1 : 1 : 0.1, C_{\text{BGP}} = 2 \text{ mM} \) were quickly injected into 20 mL of a mixed solvent (ethanol and n-hexane, \( V_{\text{ethanol}} : V_{\text{n-hexane}} = 15 : 5 \)). Second, the mixed solvent directly dropped onto the quartz plate, subsequent evaporation of mixed solvent, the mixtures would reach supersaturation rapidly and undergo crystal growth. Then, the dispersed solution was dropped onto a quartz substrate, and the solvent was completely evaporated at room temperature to obtain heterostructures. Likewise, the BGP-OFN-TFPA@BGP-TBPA, BGP-OFN-TCNB@BGP-TBPA also obtained by above method.

Results and Discussion

We prepared a series of BGP-based cocrystals through a facile solution self-assembly method, including the BGP-OFN cocrystal driven by AP interaction, and the BGP-TFP, BGP-TFPA, BGP-TCNB cocrystals driven by CT interaction. Among them, the interaction strength of CT is greater than AP (Table S1). The fluorescence microscopy (FM) images of these CT cocrystal demonstrated that they have been successfully prepared (Figure. S2). As shown in Figure. 1b, the intermolecular distances \( d_{\pi-\pi} \) between the adjacent components of BGP-OFN (3.37 Å), BGP-TFP (3.33 Å), BGP-TFPA (3.35 Å), and BGP-TCNB (3.37 Å) are highly similar through Materials Studio calculation, which may allow a certain amount of these donor components of CT cocrystals to be readily incorporated into the BGP-OFN systems. In order to obtain the detailed structural information of these BGP-based cocrystals, we carefully studied their molecular packing modes. As shown in Figure. S3-S6, the BGP-based cocrystals displays similar molecular packing mode, two molecules of BGP-OFN, BGP-TFP, BGP-TFPA and BGP-TCNB cocrystals are nearly planar and stacked on each other alternately. Furthermore, density functional theory (DFT) calculations were performed on the BGP-based cocrystals to better understand the optical properties of these cocrystals. The energy-level diagram of the materials (Figure. 1c) shown that the BGP-OFN cocrystal has higher energy gap (ca. 3.07 eV), compared to BGP-TFP (ca. 2.26 eV), BGP-TFPA (ca. 2.01 eV) and BGP-TCNB (ca. 1.99 eV) cocrystals, which may allow the occurrence of energy transfer process from the BGP-
OFN cocrystals to CT cocrystals. In addition, we found that the highest occupied molecular orbital (HOMO) of these cocrystals is nearly completely localized on the BGP molecule, whereas the LUMO are respective distributed on the OFN, TFP, TFPA and TCNB molecules (Figure. S10, 11), which generally attributed to the donor-acceptor cocrystal system. The photoluminescence (PL) and absorption spectra of these BGP-based cocrystals were further demonstrated that the possibility of energy transfer process. Figure. S9 shown that the PL spectrum of BGP-OFN display a good overlap with the absorption spectra of the BGP-TFP, BGP-TFPA and BGP-TCNB. Moreover, the pure BGP-OFN microwires have a fluorescence lifetime of about 15.2 ns, which would reduce to 13.5 ns, 10.3 ns and 10.1 ns at BGP-OFN-TFP, BGP-OFN-TFPA and BGP-OFN-TCNB solid solutions, respectively. Thus, an energy-transfer process from BGP-OFN cocrystal to BGP-based charge-transfer cocrystals can occur (Figure. S13). In addition, the AP interaction of BGP-OFN cocrystal is one kind of weaker electrostatic interaction compared to the CT interaction of BGP-TFP, BGP-TFPA and BGP-TCNB cocrystals, as reported previously. The PL spectrum of BGP-OFN presents two emission peaks at around 473 nm and 500 nm due to the AP interaction, while these CT cocrystals all display a single band emission peak. General speaking, (i) the BGP-based cocrystals have well-matched crystal structures including the similar molecular packing mode and the distance of adjacent molecules, which is necessary for the construction of solid solution. (ii) a good overlap of the emission spectrum of BGP-OFN and the absorption spectrum of CT cocrystals, which is indispensable for efficient energy transfer. (iii) the systems include the two types of intermolecular interaction, namely AP and CT interaction, which may be facilitated the CT acceptor molecules doped into the BGP-OFN crystals. Based on the above analysis, a possible energy-transfer mechanism in the solid solution composed of AP and CT cocrystal is displayed in Figure. 1d. As shown in Figure. 1d, we expect that the BGP-OFN donor is excited by 375 nm light, its excitation energy will transfer to a nearby BGP-TFP or BGP-TFPA, BGP-TCNB acceptors, and finally emits the corresponding light of the acceptors. Therefore, we can achieve the solid solution with color-tunable emission, based on the different acceptors.
As a proof of concept, the BGP-OFN cocrystal selected as the host materials and the three types of CT cocrystals as the guest materials to construct of solid solution with tunable optical properties. In a typical synthesis, we use a one-pot solution self-assembly method to prepare a BGP-OFN-TFP solid solution. First, the mixed stock solution containing both BGP ($C_{BGP} = 5$ mM) and OFN ($C_{OFN} = 5$ mM), TFP ($C_{TFP} = 0.5$ mM) in dichloromethane (DCM) was preprepared (the molar ratio between BGP, OFN and TFP, $N_{BGP}$: $N_{OFN}$: $N_{TFP} = 1:1:0.1$). Second, the preprepared solution was added to n-hexane solution ($V_{DCM}$: $V_{n\text{-hexane}} = 1:2$). The mixture was then dropped onto the quartz substrate. Finally, the formation of BGP-OFN-TFP microwires were obtained after the solvents completely evaporated. Likewise, we also prepared the BGP-OFN-TFPA and BGP-OFN-TCNB microwires through a one-pot solution self-assembly method. As shown in Figure. 2a-d, the FM images of these organic solid solutions with different light emission demonstrated that they have been successfully prepared. It can be seen that the obtained BGP-OFN microwires emitted blue light (Figure. 2a), the BGP-OFN-TFP microwires emitted green light (Figure. 2b), the BGP-OFN-TFPA microwires emitted yellow light (Figure. 2c) and the BGP-OFN-TCNB microwires emitted red light (Figure. 2d), realizing uniform and tunable emission colors in a wide color gamut from blue to red. The corresponding PL spectra of these microwires in Figure. 2e shown that the BGP-OFN microwires presents two emission peaks at around 473 nm and 500 nm, whereas the BGP-OFN-TFP displays single PL band at 522 nm, the BGP-OFN-TFPA shows single PL band at 558 nm and the BGP-OFN-TCNB presents a single PL band at 606 nm. Regarding the PL of the obtained solid solution showing a single peak compared to BGP-OFN cocrystal, we speculate that the high-efficiency energy transfer occurred from BGP-OFN cocrystal to these CT cocrystals. Correspondingly, the CIE color coordinate values of these complex microwires can be calculated by their emission spectra and shown in Figure. 2f, which further confirmed that the successful modulation of the organic microcrystals’ light emission by constructing organic solid solutions with different guest materials. Moreover, we deduced that the acceptor molecules were completely and uniformly added into the BGP-OFN host in the preparation ratio. As a proof of concept, we conducted a series of micro-area photoluminescence spectra measurements of multiple organic solid solution microwires to verify our claim. As
shown in Figure. S14, the emission spectra of multiple solid solution microwires are also almost identical, which further proves that the emission uniformity of solid solution obtained by this method. We then conducted the transient absorption spectroscopy measurements to obtain the detailed optical properties of organic solid solutions and confirm their composition (Figure. S9). Interestingly, we found that the absorption spectra of the solid solution both include the absorption peaks of BGP-OFN host and the corresponding guest materials, which confirms that the obtained organic solid solutions are composed BGP-OFN host and BGP-TFP et al guest materials, as well as the AP and CT intermolecular interaction both exist in the systems. Notably, the BGP-OFN cocrystals as typical AP assemblies not only shown high solid photoluminescence quantum yield (PLQYs) in solid is 85%, Table S2), but also significantly improved the PLQYs of as-prepared organic solid solutions. As shown in Table S2, the obtained BGP-OFN-TFP, BGP-OFN-TFPA and BGP-OFN-TCNB organic solid solutions presented much higher PLQYs than that of the BGP-TFP, BGP-TFPA and BGP-TCNB cocrystals, their PLQYs can be improved by 208%, 209% and 249%, respectively, which could make them to be potentially employed as promising block with highly emissive solid materials for the construction of advanced optical devices. In order to further confirm the crystal structures, X-ray diffraction (XRD) curves of these microwires were collected. As shown in Figure. 2g, no XRD characteristics of the BGP-TFP, BGP-TFPA and BGP-TCNB acceptors were identified in the XRD curves of the corresponding organic solid solutions and they keep the same crystal structure of BGP-OFN cocrystal, which indicate that the acceptor organic molecules added into the host materials without affecting its inherent crystal structure. Moreover, the average size of BGP-OFN cocrystals and solid solutions is around 65 μm and 75 μm, respectively. Furthermore, the average size of charge-transfer cocrystals is around 55 μm (Figure. S15-18).

As shown in Figure. 3a, when we continue to select the appropriate CT cocrystal as the guest materials to construct the solid solution, we found that the BGP-TBPA cocrystal as the guest material was not added to the BGP-OFN cocrystal to form a solid solution, while obtained the OLHs during the co-assembly process of BGP, OFN and TBPA molecules. Under this condition, we deduce that the larger d_{π-π} of BGP-TBPA (3.48 Å) cocrystal...
than BGP-OFN (3.37 Å) may be resulting the TBPA molecules not added to the BGP-OFN cocrystal. On the other
hand, the BGP-TBPA cocrystal has strong CT intermolecular interaction, which facilitate them first nucleate and
grow into microwires in the mixed solution. These prepared BGP-TBPA cocrystal are capable of serving as a
substrate for the epitaxial growth of BGP-OFN cocrystal on the lateral sides. In addition, the number of BGP-
OFN branches from one to two can be finely tuned by carefully adjusting the stoichiometric ratio of BGP-OFN
and BGP-TFPA cocrystal ($N_{\text{BGP-TFPA}} / N_{\text{BGP-OFN}}$). In order to deeply understand the epitaxial growth process of the
OLHs, we recorded the video data by tracking the real-time growth processes. As shown in Figure.3b1-b4, the
bright field images of branch microwires are captured, from which is defined as the formation time of BGP-
OFN as 0 s. At the early stage, the BGP-TBPA trunk firstly nucleates from the mixed solution and elongates to
tens of micrometers. After a period of time, the BGP-OFN branch starts to nucleate on the lateral side of BGP-
TBPA microwire, and then grow along the horizontal axis of trunk. Notably, the short branch microwire have
firstly formed sticking out of one side of the trunk microwire, which is attributed to the higher surface energy
of one tip side relative to the other tip side (Figure. 3b2). Finally, as reaction time increases, BGP-OFN branch
microwires grew along on the BGP-TBPA trunk microwire with their two tips distributed evenly on both sides
of the trunk instead of just appearing on one side (Figure. 3b3, 3b4). Figure. 3c displays a FM image of an
individual single-lateral microwire, the trunk microwire exhibit orange light corresponding to the BGP-TBPA,
whereas the branch microwire present blue light corresponding to the BGP-OFN, excited with unfocused UV
light. In addition, the FM image of an individual double-lateral microwire as shown in Figure. 3d, one could find
that the branch microwire on both sides are parallel to each other. The spatially resolved spectra of branch
microwire are collected in three different positions, namely the junction region, the backbone and the branch
(marked as 1, 2, 3 in the FM image of Figure. S15a2, respectively). It can be seen that the PL of the backbone
corresponds to the PL of individual BGP-TBPA, and the PL of the branch corresponds to the PL of BGP-OFN,
while the PL of the junction includes the PL of individual BGP-TBPA and BGP-OFN, the results confirms that the
branch heterostructures are composed of BGP-TBPA trunk and BGP-OFN branch.
The scanning electron microscopy (SEM) were further performed on the individual single-lateral OLHs (Figure.3e), the results suggest that the OLHs microwire have precisely defined materials and interfaces, the short microwire corresponding to BGP-TBPA, and the long microwire corresponding to BGP-OFN. The detailed SEM images of branch heterostructures at low and high magnification as shown in Figure. S20, one could find that microwire branch of BGP-OFN grow on both top or bottom surfaces of the trunk microwire of BGP-TBPA.

In addition, we also prepared single-structures of BGP-TBPA and BGP-OFN. It can be seen that the length-diameter ratio of BGP-TBPA microwire is smaller than that of the BGP-OFN microwire, (Figure. S19) which also observed in the growth predicted growth morphologies of BGP-TBPA and BGP-OFN single crystals (Figure. S29). As we all know, the well lattice matching plays an important role in the epitaxial growth processes of heterostructures, because of they allowing for a periodic reconstruction of the interface. In order to better understanding the growth mechanism of the BGP-OFN@BGP-TBPA branch heterostructures, we calculated the growth morphologies and other parameters of BGP-TBPA and BGP-OFN cocrystal by Materials Studio simulation. As shown in Figure. 3f, BGP-TBPA backbone grows along the a-axis and contacts BGP-OFN microwire with its (002) plane (represented by the orange area), while BGP-OFN branch microwire grows along the a-axis and contacts BGP-TBPA backbone with its (020) plane (represented by the blue area). Importantly, it can be seen that the (002) plane of BGP-TBPA and (020) plane of BGP-OFN have a low lattice mismatch ratio (n) of 0.7%, which facilitates the formation of branch microwires. Moreover, the XRD patterns of the branch heterostructure microwires only includes the characteristic diffraction peaks of both BGP-OFN and BGP-TBPA, and without new emerging peaks (Figure. 3g), which further confirmed that the branch heterostructures are composed of BGP-TBPA trunk and BGP-OFN branch.

According to the formation mechanism of solid solution and the epitaxial growth process of OLHs discussed above, the emission color of OLHs can be finely tuned by introducing the guest materials, as illustrated in Figure. 4a. Notably, the solid solution keeps the same crystal structures as BGP-OFN (Figure. 2g), which plays an important role in the epitaxial growth process of OLHs. In addition, the first nucleation of BGP-TBPA microwire
is the key stage, due to they are used as the substrate for the epitaxial growth. In the second step, branch microwires with different emission colors nucleate and grow along the BGP-TBPA trunk, which can be achieved by tuning the concentration of these three components. Meanwhile, we also obtained the single-lateral and double-lateral OLHs by adjusting the amounts of multi-components, As shown in Figure. 4b1, 4b2, the FM images demonstrated that BGP-OFN@BGP-TBPA have been successfully preparation. In addition, Figure. 4c1, 4c2 displays the FM images of BGP-OFN-TFP@BGP-TBPA single-lateral or double-lateral microwires. Apparently, the trunk microwire exhibits orange light emitting, while the branches emit green light. Moreover, Figure. 4d1, 4d2 shows the FM images of as-prepared BGP-OFN-TFPA@BGP-TBPA branch microwires, showing that the trunk of the heterostructures gives an orange fluorescence and the branch shows yellow BGP-OFN-TFPA-like emission. Figure. 4e1, 4e2 displays FM images of BGP-OFN-TCNB@BGP-TBPA, the branch present red PL corresponding to BGP-OFN-TCNB. Remarkable, the trunk exhibits red PL instead of orange PL from the BGP-TBPA, which is attributed to the TCNB molecules aggregated together with the BGP-TBPA microwire resulted in the doped structures, similar to the situation discussed above. By comparing the spatially resolved spectra in Figure. S22 with those of branch microwires (Figure. 2e) and BGP-TBPA trunk microwire, we confirmed that the backbone microwire is composed of BGP-TBPA, while the branches are consisting of solid solution.

Organic micro/nanocrystal have been demonstrated as promising building blocks for optical applications, due to their long-range order as well as free defects. Herein, we first explore the optical waveguide characteristics of BGP-OFN and BGP-TBPA microwires through a micro-area spectroscopy (Figure. S23 and S24), which is applied to measure the distance-dependent PL spectra. The optical loss coefficient (R, dB μm⁻¹) was calculated by a single-exponential function \( I_{\text{body}}/I_{\text{tip}} = A \exp(-\alpha d) \), where A is constant. Accordingly, the optical loss R of BGP-TBPA microwire at around 600 μm was calculated to be 0.0084 dB μm⁻¹, while the loss R of BGP-OFN microwires at around 490 μm was estimated to be 0.0907 dB μm⁻¹. The result indicated that the as-prepared BGP-TBPA or BGP-OFN microwires can effectively confine, propagate, and couple light in the waveguide region. More importantly, the development of microwire photonics requires the integration of different microwire
components into highly ordered functional heterostructures for achieve complex photonic circuit. As a proof-of-concept application, we constructed an optical router using a single BGP-OFN@BGP-TBPA branch microwire, schematically shown in Figure. 5a. It can be seen that the single-lateral or double-lateral are capable of multi-color and multi-channel couple light based on the active optical waveguide, under the excitation of a 375 nm laser on the body of branch microwire (Figure. 5a, left). It is worth noting that the as-prepared branch microwires can achieve tunable-emission from blue to red color by introducing the different guest materials in to BGP-OFN cocrystal to construct solid solution, which is critical for satisfying the optical application with different PL waveguide requirements, such as different optical logic gates and signal converter (Figure. 5a, right). As a typical example for understanding the optical application of branch microwires, the prepared BGP-OFN@BGP-TBPA branch microwires were used for the optical logic gate (Figure. 5b-m). Figure. 5b shows the bright-field optical image of a typical single-lateral microwire, which have four output terminals for coupling light (Output 1-4). We selectively excited BGP-OFN components of a single-lateral using a focused 375 nm laser beam, the corresponding FM images as shown in Figure. 5c. It can be seen that the strong blue light is emitted from the input location, then propagates along the branch microwire, and finally leaks from the two tips of the BGP-OFN microwire (O-1, O-4). Meanwhile, the yellow light be observed at the right-tip of BGP-TBPA microwire. This suggests a secondary light-excitation mechanism. That is, blue light of BGP-OFN microwire can excite the BGP-TBPA compounds at junction regions, and the locally excited orange light and incompletely absorbed blue light propagates along the branch microwire and finally leak out of trunk right-tip (O-3). Therefore, the whole system functions as a signal converter. It is worth noting that there is no light emission at the left-tip (O-2) of the trunk microwire, which is attributed to the heavy atom effect of the TBPA molecule resulting the low PLQYs of the BGP-TBPA cocrystal, which requires more blue light for secondary excitation and spread. In addition, Figure. 5e reveal the spatially resolved spectra collected from the tip of BGP-TBPA trunk and the tip of BGP-OFN branch (Figure. 3c), respectively. Based on these spectra, output signal with the maxima fluorescence at 490 nm is coded as “signal 1”, the signal at 600 nm is coded as “signal -1”, while the no optical signal is defined “0”, then an optical logic gate table can be summarized in Figure. 5g. Likewise, we selective excited the junction
position of single-lateral microwires using 375 nm laser beam, the corresponding FM images as shown in Figure. 5d. Then, the spatially resolved spectra were respective recorded at the tip positions of the trunk and branch, which exhibited typical characteristics of passive optical waveguide with orange and blue emission of junction at trunk tips, and the blue emission at branch tips. Meanwhile, the optical logic gate table can be concluded in Figure. 5g. Apart from this, we also performed the potential photonic applications on the double-lateral heterostructures. Figure. 5h-j shows the bright-field optical image and the FM images excited by a 375 nm laser of a typical double-lateral microwire, the light excitation and propagation mechanism of the double-lateral microwire is similar to the single-lateral discussed above. It is worth noting that the double-lateral structure has six output terminals compared with the single-lateral structure, which can readily fulfill the requirements of complex optical signal converters and complex optical logic gates. As shown in Figure. 5k and 1, we use Matlab software to calculate the light intensity distribution of each pixel of the FM image, and extract it to generate a three-dimensional image, where the z-axis value is based on the vision rate. It can be seen that the z-axis values of input position keep the same as tips of branch microwire due to they all emit blue light, which is coded as “signal 1”. Meanwhile, the z-axis value of the tips of trunk microwire is the highest due to they emit green-yellow light, which is coded as “signal -1”, the no optical signal is defined “0”. So that, we readily construct the optical logic gate with multiple input/output channels by Matlab calculation based on the light intensity of FM images of double-lateral heterostructures (Figure. 5m). In addition, we also performed the optical application on the BGP-OFN-TPF@BGP-TBPA, BGP-OFN-TFPA@BGP-TBPA and BGP-OFN-TCNB@BGP-TBPA branch microwire (Figure. S25-28). Their emission color or structure-tunable advantages is essential for the development of various optical signal conversion and optical signal processing.

**Conclusion**

In summary, we reported a general synthetic strategy to organic lateral heterostructures with tunable structure and photophysical properties. Based on the tunable intermolecular distances ($d_{\pi,\pi}$ from 3.33 to 3.48 Å) and competitive intermolecular interactions of cocrystals, these components can be selectively constructed into
organic solid solution microwires or lateral heterostructure microwires. More impressively, the obtained solid solution microwires can be matched with the trunk microwire for realizing a series of lateral heterostructure microwires with all-color-tunable photoluminescent, which is crucial for the development of optoelectronics at the micro/nanoscale. Finally, a multichannel signal converter and optical logic gate was successfully achieved based on the single branch microwire. This work provides a unique insight for unveiling the structure–property relationships at molecular level, and open a window for synthesizing organic heterostructures with desirable optoelectronic functions.

Supporting Information
Detailed experimental procedures and characterization, including the fabrication of the cocrystal and heterostructure microwires, crystallographic data, morphology characterization, optical characterization, schematic demonstration of the experimental setup for the optical characterization, optical waveguide data, optical logic gate.

Conflict of Interest
The authors declare that they have no conflict of interest.

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References


Figure 1 (a) Scheme for the design of 1D branch heterostructures with color-tunable emission performance.

(b) The molecular structures of the BGP-OFN cocrystal and BGP-TFP, BGP-TFPA, BGP-TCNB cocrystal. Color scheme: C, grey; H, white; F, cyan; CN, blue; O, red. The corresponding intermolecular distances. (c) Calculate energy level diagrams of the BGP-OFN, BGP-TFP, BGP-TFPA and BGP-TCNB cocrystals. (d) Representation for the energy-transfer (ET) process from the BGP-OFN cocrystal to BGP-TFP/TFPA/TCNB cocrystal.
Figure 2 (a-d) FM images of BGP–OFN, BGP-OFN-TFP, BGP-OFN-TFPA and BGP-OFN-TCNB solid solutions, respectively. All scale bars are 20 μm. (e) The PL spectra of BGP-OFN, BGP-OFN-TFP, BGP-OFN-TFPA and BGP-OFN-TCNB microwires, (f) The corresponding CIE coordinate values of these microwires with different emission colors. (g) The XRD patterns of BGP-OFN, BGP-OFN-TFP, BGP-OFN-TFPA and BGP-OFN-TCNB microwires.
Figure 3 (a) Representation of the epitaxial growth of the BGP-OFN@BGP-TBPA OLHs. (b1-b4) The evolution processes of BGP-OFN@BGP-TBPA OLHs at different time intervals (b1, 0 s; b2, 7 s; b3, 12 s; b4, 23 s) recorded by the corresponding real-time video. All Scale bars are 20 μm. (c) FM image of a typical single-lateral microwire. The scale bar is 20 μm. (d) FM image of a typical double-lateral microwire. Scale bar are 20 μm. (e) SEM image of a typical OLHs. (f) The predicted growth morphologies of BGP–OFN and BGP-TBPA cocrystal obtained by Material Studio simulation, and the lattice mismatching rate of BGP-OFN (010) crystal plane and BGP-TBPA (002) crystal plane. (g) The XRD patterns of BGP-TBPA cocrystals, BGP-OFN cocrystals and the corresponding OLHs.
Figure 4 (a) Schematic diagram for the evolution process of BGP-OFN@BGP-TBPA branch heterostructures convert to a series of branch heterostructures with different emission color. (b₁, b₂) FM images of BGP-OFN@BGP-TBPA single-lateral and double-lateral heterostructures. (c₁, c₂) FM images of BGP-OFN-TFP@BGP-TBPA single-lateral and double-lateral heterostructures. (d₁, d₂) FM images of BGP-OFN-TFPA@BGP-TBPA single-lateral and double-lateral heterostructures. (e₁, e₂) FM images of BGP-OFN-TCNB@BGP-TBPA single-lateral and double-lateral heterostructures. All Scale bar are 20 μm.
Figure 5 (a) The schematic diagram of integrated optical application of branch heterostructure. (left) Branch microwires with one input and multi-output terminals for active optical waveguide. (right) The single-lateral heterostructures with tunable-color emission for optical logic gate. (b) Bright field image of a single-lateral microwire with four output terminals (O-1, O-2, O-3, O-4). Scale bar are 20 \( \mu \)m. (c, d) FM images at inputs I-1 and I-2. (e, f) The corresponding spatially resolved PL spectra when input is given at I-1 and I-2. (g) The table displays spectral signal output’s codes. (h) Bright field image of a double-lateral microwire with six output terminals. Scale bar are 20 \( \mu \)m. (i, j) FM images at inputs I-1 and I-2. (k, l) The light intensity distribution of FM images (i, j) obtained by Matlab simulation. (m) The logic table display intensity signal output’s codes.
This manuscript presents a generalized strategy for the synthesis of organic heterostructures with tunable structural and optical characteristics. Moreover, the insights from this work on the construction of optical signal converters and multichannel optical routers based on the OLHs with color-tunable photoluminescence may be interesting to those engaged in application-oriented materials science research.