From Molecular Design and Materials Construction to Organic Nanophotonic Devices

Chuang Zhang, Yongli Yan, Yong Sheng Zhao,* and Jiannian Yao*

Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

CONSPECTUS: Nanophotonics has recently received broad research interest, since it may provide an alternative opportunity to overcome the fundamental limitations in electronic circuits. Diverse optical materials down to the wavelength scale are required to develop nanophotonic devices, including functional components for light emission, transmission, and detection. During the past decade, the chemists have made their own contributions to this interdisciplinary field, especially from the controlled fabrication of nanophotonic molecules and materials. In this context, organic micro- or nanocrystals have been developed as a very promising kind of building block in the construction of novel units for integrated nanophotonics, mainly due to the great versatility in organic molecular structures and their flexibility for the subsequent processing. Following the pioneering works on organic nanolasers and optical waveguides, the organic nanophotonic materials and devices have attracted increasing interest and developed rapidly during the past few years.

In this Account, we review our research on the photonic performance of molecular micro- or nanostructures and the latest breakthroughs toward organic nanophotonic devices. Overall, the versatile features of organic materials are highlighted, because they brings tunable optical properties based on molecular design, size-dependent light confinement in low-dimensional structures, and various device geometries for nanophotonic integration. The molecular diversity enables abundant optical transitions in conjugated π-electron systems, and thus brings specific photonic functions into molecular aggregates. The morphology of these micro- or nanostructures can be further controlled based on the weak intermolecular interactions during molecular assembly process, making the aggregates show photon confinement or light guiding properties as nanophotonic materials. By adoption of some active processes in the composite of two or more materials, such as energy transfer, charge separation, and exciton–plasmon coupling, a series of novel nanophotonic devices could be achieved for light signal manipulation.

First, we provide an overview of the research evolution of organic nanophotonics, which arises from attempts to explore the photonic potentials of low-dimensional structures assembled from organic molecules. Then, recent advances in this field are described from the viewpoints of molecules, materials, and devices. Many kinds of optofunctional molecules are designed and synthesized according to the demands in high luminescence yield, nonlinear optical response, and other optical properties. Due to the weak interactions between these molecules, numerous micro- or nanostructures could be prepared via self-assembly or vapor-deposition, bringing the capabilities of light transport and confinement at the wavelength scale. The above advantages provide great possibilities in the fabrication of organic nanophotonic devices, by rationally combining these functional components to manipulate light signals. Finally, we present our views on the current challenges as well as the future development of organic nanophotonic materials and devices. This Account gives a comprehensive understanding of organic nanophotonics, including the design and fabrication of organic micro- or nanocrystals with specific photonic properties and their promising applications in functional nanophotonic components and integrated circuits.
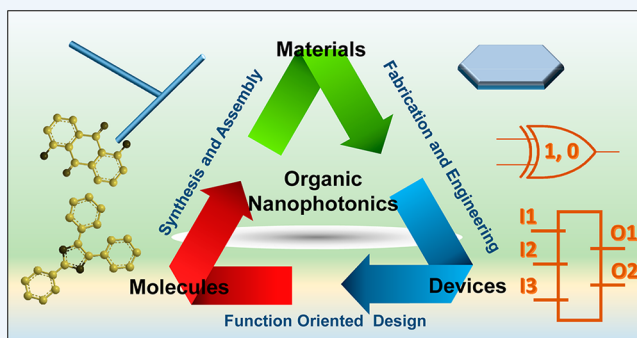
1. INTRODUCTION

The discovery of conductive polymers has encouraged the rapid growth in the research field of organic electronics and optoelectronics, including organic light-emitting diodes,[1] field-effect transistors,[2] and solar cells[3] from both molecular and polymeric materials. Their properties are highly tunable by changing the energy levels of ground and excited states in π-electron systems. The excited states in organic materials with low dielectric constants are Frenkel excitons, which have high binding energy and are localized within one or two molecules. This excitonic feature makes organics fundamentally different from their inorganic counterparts in both electronic and photonic aspects.

Recently, photonics at the (sub)wavelength scale, namely, nanophotonics, has been developing rapidly during the rise of

nanoscience and nanomaterials.[4] For example, the quantum dots showed unique size-dependent light emission due to the quantum confinement properties,[5] while the one-dimensional (1D) nanostructures were proven to guide light at the wavelength scale.[6] By designing nanometric geometries, nanophotonic integration not only seems accessible but also takes advantage of high operation frequency and low power consumption.

In organic nanomaterials, light confinement and guiding were also demonstrated.[7] Interestingly, some organic nanofibers, with even smaller sizes than the wavelength, showed unexpectedly high efficiency in self-guided light emission.[8,9] It revealed a distinct picture when the photoluminescence of molecules was guided, referred to as active optical waveguiding, which could be attributed to the coupling between excitons and photons in organic materials.[10,11] Thereby from the viewpoints of exciton type and binding energy, researchers started to pay attention to the significant differences between organic and inorganic materials in nanophotonic applications.[12] The binding energy of Frenkel excitons (~100 meV) is almost 2 orders of magnitude larger than that of Wannier excitons in inorganic semiconductors.[13] They are stable at room temperature ($kT = 25.6$ meV) and thus can participate in light guiding processes.

Photon transport in nanomaterials largely relies on molecular packing and microscopic morphology.[14] The self-assembly of organic molecules brings a promising fabrication technique for organic micro- or nanocrystals with well-defined shapes, tunable sizes, and defect-free structures. These micro- or nanocrystals with higher refractive index than their environment can serve as optical waveguides to transmit photons or optical microcavities to confine photons. They combined the basic concepts in integrated photonics and the photonic properties of π-electron systems and thus became novel functional nanophotonic units.[7,12] The prototypes of organic nanophotonic devices were achieved in composite structures of donor and acceptor molecules via manipulation of energy transfer at micro- or nanoscale.[15] Organic nanophotonics (Scheme 1) benefits from the rational design of functional molecules, the facile synthesis of low-dimensional materials, and new possibilities for device geometries.

In this Account, we summarize the recent advances in organic nanophotonic molecules, materials, and devices, with an emphasis on structural and functional tunability due to the versatility of organics. The following content is divided into three parts, including the molecular design for specific nanophotonic properties, the construction of micro- or

Scheme 1. Roadmap for Organic Nanophotonics: Molecules, Materials, and Devices

nanosized materials for light guiding and photon confining, and the prototype demonstration of organic nanophotonic devices.

2. DESIGN OF MOLECULAR STRUCTURES FOR PHOTONIC FUNCTIONALITIES

Light absorption and emission in conjugated molecules are from the transition of π electrons. As displayed in Figure 1, 9,10-bis(phenylethynyl)anthracene (BPEA) shows green fluorescence (450−550 nm) with a high efficiency of 0.96.[16] Similarly, rubrene molecules with an enlarged π system can give a 0.98 quantum yield of orange light emission (500−650 nm).[17] The close energy levels facilitate radiative transition, but nonradiative processes could dominate if the energy gap becomes too small. This explains why the efficiency of near-infrared dyes is still limited.

The planar molecules are tightly packed in crystals by $\pi−\pi$ stacking, which is beneficial for the fabrication of micro- or nanocrystals; however, the fluorescence may also be shifted or quenched because of the interference of nearby π systems.[18] By introducing N atoms in the molecules (like 1,3,5-triphenyl-2-pyrazoline (TPP) and 2,4,5-triphenylimidazole (TPI) in Figure 1), we can increase the intermolecular distance and maintain the light emission properties of single molecules in micro- or nanocrysyals.[19] The crystal growth can be driven by many other kinds of weak interactions (hydrogen bonds, van de Waals force, etc.) besides $\pi−\pi$ stacking.[20]

The additional side groups can also change the molecular packing and are helpful in tailoring the shape of micro- or nanocrystals. For example, 2-acetyl-6-methylaminonaphthalene (AMN) molecules showed balanced $\pi−\pi$ stacking and hydrogen bonds in two crystal directions, resulting in the formation of two-dimensional structures during molecular assembly.[14] The side groups can also make the nanocrystals of 1,5-diaminoanthraquinone (DAAQ) grow much faster on the substrates with higher surface energies, bringing possibilities to prepare vertically aligned nanowire arrays via vapor deposition.[21]

Coordination complexes provide an alternative way to tune the optical properties of organic compounds. One of them, tris(8-hydroxyquinolinato)aluminum (Alq$_3$), can maintain its strong light emission and charge transport ability in nanowires based on the metal to ligand charge transfer (MLCT).[22] When heavy metal atoms are included, the strong spin−orbit coupling facilitates intersystem crossing (ISC) to form triplets. Strong phosphorescence was observed in tris(bipyridine)ruthenium-(II) chloride (Ru(bpy)$_3$) from the MLCT[3] states by either optical or electrochemical methods.[23] Moreover, these compounds serve as triplet sensitizers[24] in triplet−triplet annihilation (TTA) systems, giving upconverted fluorescence under low excitation power.[25]

Linear optical processes in organic nanomaterials have been mentioned in other reviews.[7,12,15] Here, we introduce some recent works on the nonlinear optical properties in organic micro- or nanostructures toward coherent light manipulation.

2.1. Highly Luminescent Molecules for Low-Threshold Stimulated Emission

A solid-state laser based on organic molecular crystals not only serves as a light source in photonic integration but also brings coherent operation in light manipulation.[19] Oligomeric phenylene vinylene (OPV) is known as a strong light-emitting molecular structure, while its polymer analog poly(*p*-phenylene

3449

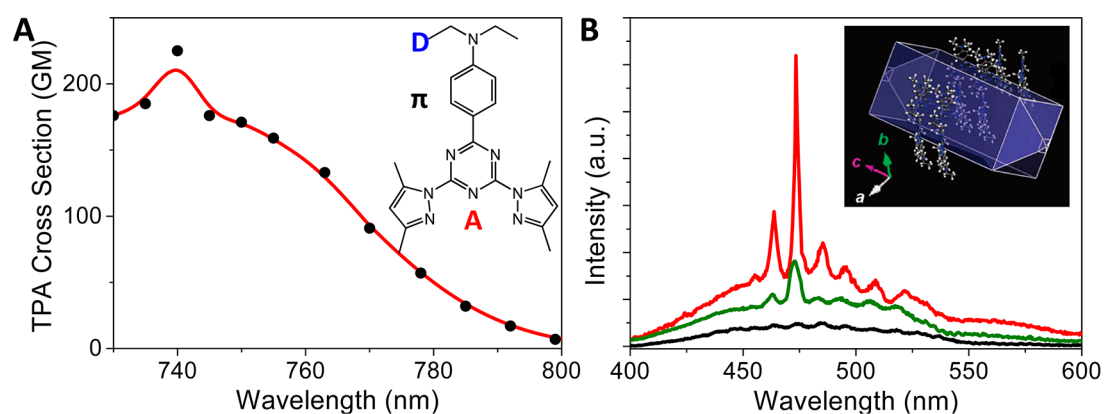dx.doi.org/10.1021/ar500192v | *Acc. Chem. Res.* 2014, 47, 3448−3458
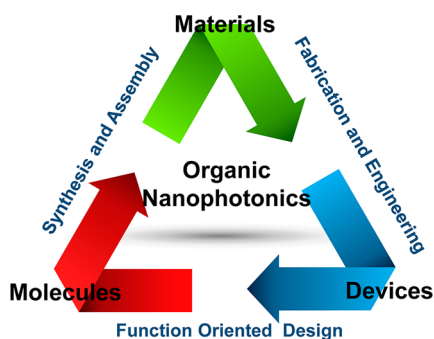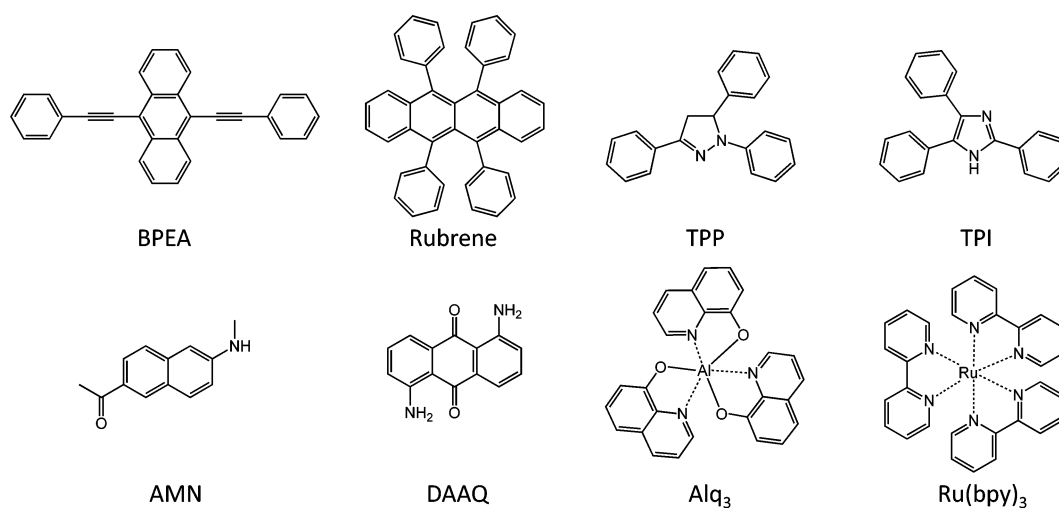
Figure 1. Typical molecules used in fabricating micro- or nanocrystals for photonic applications.
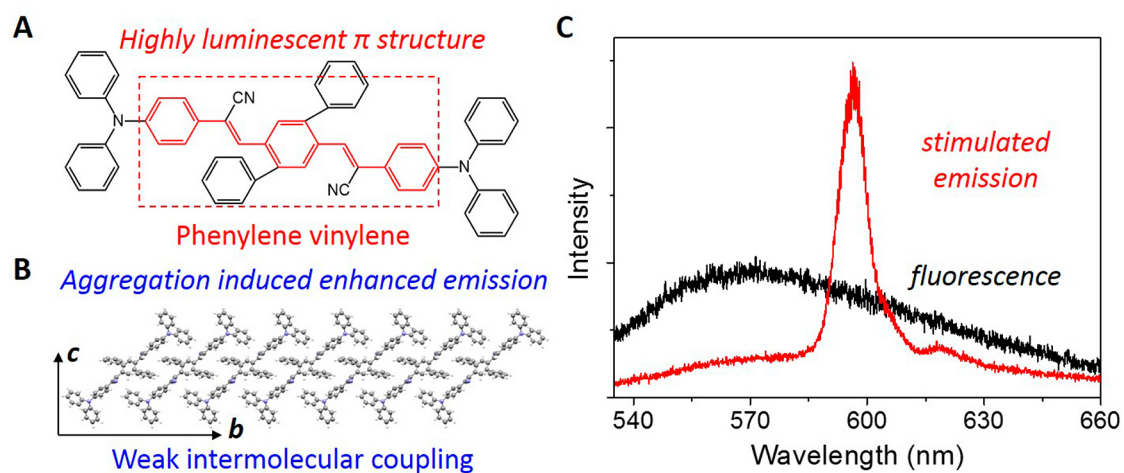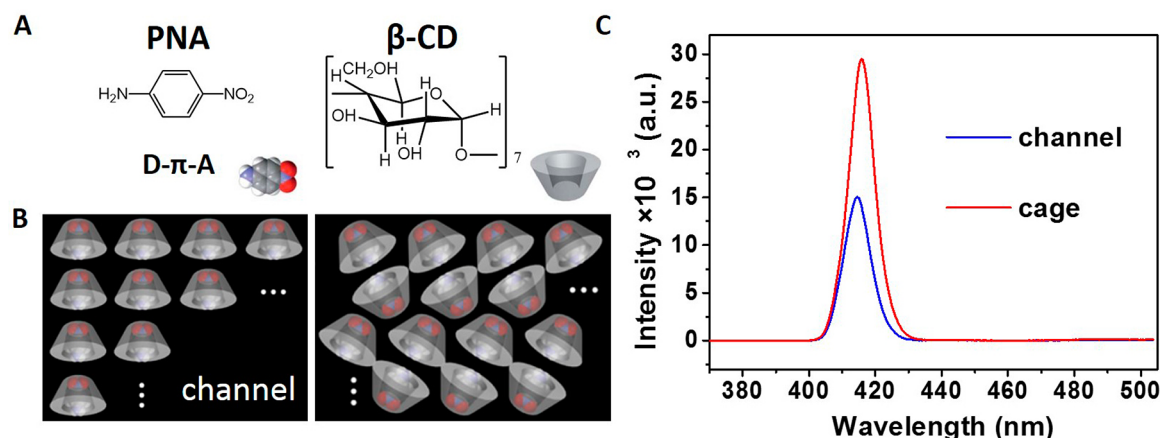

Figure 2. (A) Molecular structure and (B) molecular packing of the OPV derivative. (C) Fluorescence and stimulated emission spectra below and above the threshold, respectively.

Figure 3. (A) TPA cross section in DPBT molecules. Inset, molecular structure. (B) Two-photon pumped emission from a DPBT single-crystal nanowire excited with a 750 nm pulsed laser. Inset, crystal structure.

vinylene) (PPV) has shown great potential in lasing action.[26] By addition of cyano and phenylaniline side groups (Figure 2A), the π system in OPV structure can be isolated from the surrounding chemical environment to maintain the optical transitions.[27] As shown in Figure 2B, the molecular distance in the crystal of this OPV derivative can be as large as 10 Å, which avoids coupling between neighboring π systems. Moreover, the molecular packing restricts the rotation of side groups and brings aggregation induced enhanced emission.[28] Therefore, the low-threshold stimulated emission could be observed when using this OPV molecule as the optical gain material (Figure 2C).

Figure 4. (A) Molecular structures of PNA and β-CD molecules. (B) Channel and cage structures for PNA@β-CD supramolecular composites. (C) SHG signals from PNA@β-CD with a 830 nm fundamental wave.

The fluorescence increases linearly with the pump power, while lasing emerges and grows much faster above the threshold. This nonlinear feature may offer a remarkable on—off ratio in optical switching when operated near the threshold. In addition, polariton states from strong exciton—photon coupling in organic materials have been recently demonstrated,[29] which bring new possibilities in organic polariton lasers and other polariton-based nanophotonic devices.

2.2. D−π−A Molecules for Two-Photon Emission and Lasing

The high photoactivity of organic molecules allows for the realization of higher order nonlinearity in organic nanophotonics. Two-photon-absorption (TPA) is a third-order nonlinear optical property, which means that the molecule can simultaneously absorb two photons to form a higher energy excited state and may emit one upconverted photon (two-photon emission, TPE). In this case, intermolecular charge transfer in the donor (D)−π bridge−acceptor (A) structure is often needed to establish the permanent ground-state dipole moment as well as the transition dipole.[30]

As shown in Figure 3A, 2-(N,N-diethylanilin-4-yl)-4,6-bis(3,5-dimethylpyrazol-1-yl)-1,3,5-triazine (DPBT) was designed and synthesized with a large TPA cross section over 200 Goeppert−Mayer units (GM) and a high fluorescence quantum yield of 0.75.[31] This molecule gives a strong TPA over 700−800 nm and shows a bright cyan light emission under two-photon excitation. Furthermore, the DPBT molecules can form defect-free 1D nanocrystals by the intermolecular π stacking (Figure 3B), which can further enhance the nonlinear performance by the cavity effect.[32] As a result, DPBT nanocrystals can serve as two-photon pumped nanolasers, offering wavelength upconversion for coherent light manipulation.

2.3. Charity Supramolecules for Second Harmonic Generation

The D−π−A structure provides the necessary dipole moment by charge transfer for nonlinear response to incident light. Even some very simple molecules with D−π−A structures, like p-nitroaniline (PNA) in Figure 4A, show high optical non-linearities in second harmonic generation (SHG).[33] As a typical kind of frequency upconversion of coherent light, SHG is independent of the incident wavelength, highly polarized, and accomplished in very short response time. However, SHG requires asymmetric properties not only in molecular structures but also in the method of molecular packing to maintain the macroscopic polarity.

We used a supramolecular strategy to solve the above problem, in which the inclusion of PNA in β-cyclodextrin (β-CD) molecules induced the directional packing of dipoles in the composite crystals (Figure 4A).[34] Therefore, the asymmetry of PNA molecules could be protected by the encapsulated β-CD, showing optical nonlinearity from as-prepared microcrystals. The host−guest system can form two types of molecular alignment (channel and cage) in the supramolecular microcrystals, as shown in Figure 4B. The channel type shows one-dimensional alignment of PNA molecules with the maximized asymmetry in molecular packing. As a result, SHG signals could be observed in both microcrystals, but the output intensity in the cage type is lower because of its reduced crystal asymmetry (Figure 4C).

The organic molecules show great potential in optical nonlinearities, including stimulated emission, two-photon absorption, and frequency conversion. In addition, most of these optical properties are highly tunable according to the molecular structures, resulting in plenty of room in tailoring organic nanophotonic materials for light signal manipulation. Thus, we can adopt or synthesize specific molecules toward the functionalities that we need.

3. CONSTRUCTION OF LOW-DIMENSIONAL MATERIALS FOR LIGHT GUIDING AND PHOTON CONFINEMENT

Organic micro- or nanocrystals benefit from the facile preparation, the defect-free morphology, and the controllable sizes and shapes,[35] making it very applicable to nanophotonics. The construction methods such as liquid-phase assembly, physical vapor deposition, and template synthesis have been discussed elsewhere.[7] Here we describe some fundamental concepts and strategies about how molecules aggregate into crystals, and why their dimensions can be tuned.

The intermolecular interactions, including hydrogen bonds (~5−30 kJ/mol), π−π interaction (~8−12 kJ/mol), and van der Waals force (~2−4 kJ/mol), are weaker than the chemical bonds between atoms (~150−1000 kJ/mol). Therefore, the organic crystal morphology is largely dependent on the molecular structure and also the style of molecular packing. Optofunctional molecules usually have large π-conjugated

structures; thus $\pi-\pi$ interaction becomes an important driving force in their crystal growth. In some molecules with N−H or O−H groups, hydrogen bonds may play an extraordinary role in the molecular packing,[20] while van der Waals force often dominates the assembly process of macromolecular systems.

As displayed in Figure 5, the formation of amorphous particles is often observed immediately when the molecules
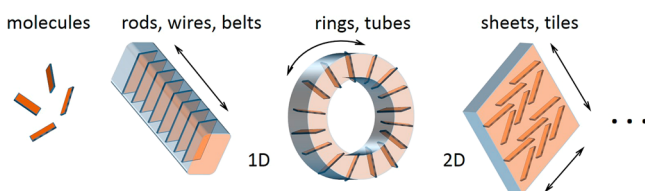
Figure 5. Scheme for molecular packing into micro- or nanocrystals with varied shapes.

aggregate together from the solution. If the preparation conditions are intentionally controlled to encourage ordered molecular packing, various crystalline micro- or nanostructures could be obtained.[36] Usually, an internal or external preferred growth direction can align molecules one by one into 1D structures, such as rods, wires, and belts. The flexibility of 1D molecular aggregates provides possibilities to construct tubular structures like rings and tubes. In this case, other driving forces like hydrophobic or hydrophilic interactions are required to modify the growth process of micro- or nanocrystals.[37] If two kinds of forces in two growth directions are balanced with each other, the assemblies result in a 2D structure (sheets, tiles, etc.) by cross packing of molecules.[38]

Organic crystals with a higher refractive index over the surrounding environment can trap photons in one or two dimensions as optical waveguides or even totally confine photons in all dimensions to realize optical cavity effects. In the following subsections, we will discuss how these organic micro- or nanocrystal structures were fabricated and used as these two fundamental nanophotonic elements at the wavelength scale.

3.1. Optical Waveguiding in One- and Two-Dimensional Organic Crystal Materials

The phenomenon of photon transporting (optical waveguiding) was observed in many high-quality low-dimensional organic materials.[39] Notably, the guiding of light emission is often more efficient than that of incident light in these materials. One important reason is that the isotropic fluorescence from the molecular excited states can avoid the mismatching of incident angle in the light coupling into waveguide modes.

Recently, we found that the optical waveguiding characteristics are totally different in 1D and 2D microstructures, even when the molecular structures were very similar (2-acetyl-6-dimethylaminonaphthalene (ADN) and 2-acetyl-6-methylami-nonaphthalene (AMN)).[14] The organic nanowires show remarkable optical waveguiding to both tips (Figure 6A), and the relationship between output intensity and propagation distance can be fitted with the exponential decay function (Figure 6B) according to the loss mechanism of photon reabsorption. Interestingly, the light guiding became obviously asymmetric in 2D structures despite the excitation positions, as shown in Figure 6C. This means that 2D packing of molecules can block the photon transport unidirectionally, probably by asymmetric dipole coupling between nearby molecular units. As illustrated in Figure 6D, the ratio of output intensity in opposite directions could be up to 10^3, showing potential applications as optical isolators at microscale. It may overcome some fundamental limitations in previous optical waveguiding materials, since the molecular orientation may affect the light
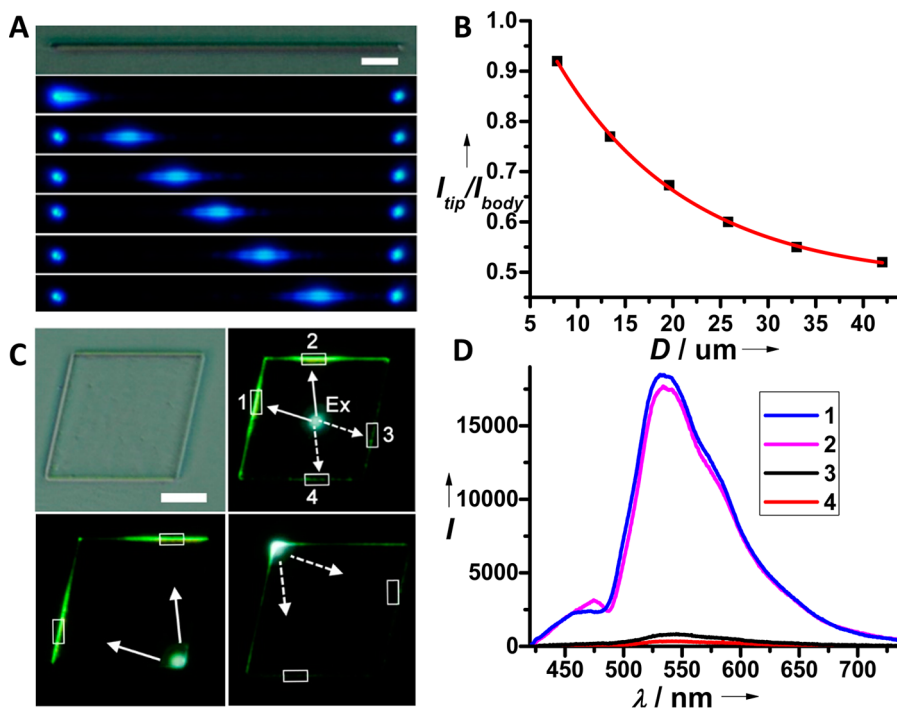
Figure 6. (A) Optical waveguiding in organic nanowires of ADN (scale bar is 5 μm) and (B) corresponding light transporting versus propagation length. (C) Directional optical waveguiding in 2D organic structures of AMN (scale bar is 10 μm) and (D) out-coupled emission from different edges.
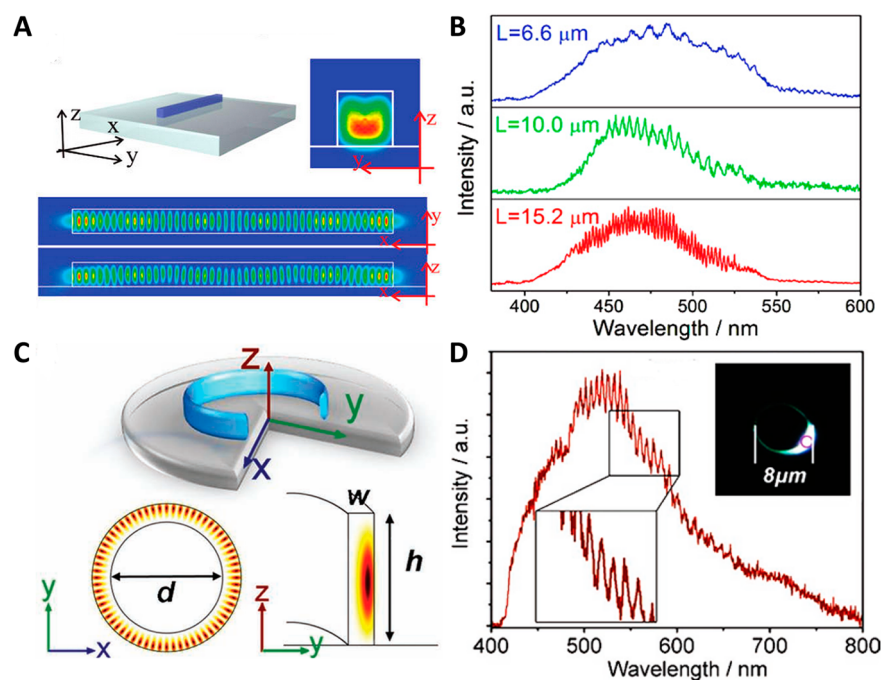
Figure 7. (A) Electric field distribution in 2-(*N,N*-diethylanilin-4-yl)-4,6-bis(3,5-dimethylpyrazol-1-yl)-1,3,5-triazine organic nanowire F−P cavity, and (B) modulated spectra with different cavity lengths. (C) Electric field distribution of WGM resonance and (D) modulated spectra from single 1,5-diphenyl-1,4-pentadien-3-one organic microrings.
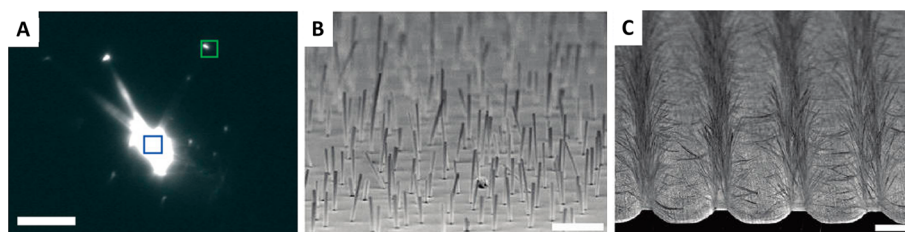
Figure 8. (A) Microscopy image of 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene assembled ordered 1D nanostructures. Microscopy images of (B) vertically grown 1,5-diaminoanthraquinone nanowire arrays and (C) nanowire patterns toward nanophotonic integration of optical waveguides and cavities. Scale bars are 5, 1 and 25 μm, respectively.

emission and thus the pathway of photons. Although further studies should be done to reveal the detailed mechanism for this unusual light guiding, the morphology control by changing molecular packing paves a new way to light manipulation in low-dimensional organic structures.

3.2. Optical Cavity Effect in Nanowire and Microring Structures

Optical cavities trap photons in all dimensions, resulting in the resonance of light within a small volume of materials. Thereby, light−matter interactions occur multiple times in the cavity and thus are enhanced compared with that in free space. Micro- or nanosized cavities can be used in nanophotonics for the enhancement of radiation, the light amplification, the realization of high-order nonlinearities, and so on.[40] For organic nanophotonics, the cavity structure requires higher quality than an optical waveguide because any optical leakage from defects decreases the overall performance of cavity effect.

Organic nanowire waveguides can also work as optical cavities when the end facets are sharp enough for relatively high reflectivity. The guided light can then travel forth and back, resulting in the optical resonance of Fabry−Perot (F−P) type, as shown in Figure 7A.[32] Therefore, the light at the wavelength of resonance modes can be mostly confined and enlarged by

the cavity, introducing a series of sharp peaks in the modulated output spectrum from wire ends (Figure 7B). The space between nearby peaks is inversely proportional to the length of nanowire cavity, so the larger cavity can support more resonance modes. The quality factor (Q) is often <100 for organic nanowire cavities, limited by the relatively low reflective efficiency at wire tips.

To fabricate a higher Q cavity, the two tips of nanowires should be connected together to avoid the light outcoupling from end facets. The obtained ring-shape structures can trap the guided light by whispering-gallery-mode (WGM), as displayed in Figure 7C.[37] As a result, we propose a molecular assembly route to high-quality crystalline organic microrings using the water droplets as templates. The Q factor in these assembled microrings can be up to 400. As shown in Figure 7D, the whole ring can be uniformly illuminated even when locally excited, and the output spectrum shows similar modulation as that in nanowire cavities. In comparison with F−P cavities, WGM cavities usually provide higher Q factor, but the cavity modes are harder to collect since they come from the entire ring.

3.3. Patterns of Optical Waveguides and Cavities for Nanophotonic Integrations

The cascade of a collection of nanophotonic elements could be used as photonic circuit of light generation, transmission, and processing. As shown in Figure 8A, the branch-like structure from a bunch of nanowires can be coupled optical waveguides, where the light can be transported from the coupled nanowires and transmitted from each joint or tip.[41] Also, the nanowires can be grown vertically to reduce the substrate leakage, and more importantly, to enable the high-density integration of parallel light transmission paths (Figure 8B).[21] Moreover, new material fabrication methods (Figure 8C) are still needed to realize organic nanophotonic circuits with high repeatability, spatial resolution, on-chip processing, and multifunctionalities.

4. REALIZATION OF ORGANIC NANOPHOTONIC DEVICES AND CIRCUITS

Incorporating two kinds of molecules into composite structures is essential for functional devices[42] because of the possible excitonic transfer processes at the interface. As illustrated in Figure 9, an acceptor exciton is generated by quenching that of
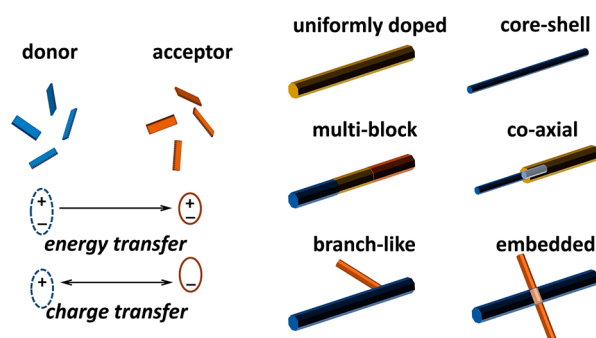
Figure 9. Scheme for the composition engineering of donor and acceptor molecules toward 1D heterojunction nanophotonics devices.

donor, or an charge-transfer (CT) excited state is formed by transferring an electron from donor to acceptor.[15] We can divide the composite structures into three types, the uniformly doped or core−shell structures, 1D heterostructures with the radial symmetry, and branch-like composites of 1D structures. The doped structures show tunable light emission based on the doping ratio, while the 1D heterostructures can transport photons or charges and realize basic photonic functions with the existence of energy or charge transfers. The branch-like structures can modulate the input and output signals by the coupling between nearby waveguides.

4.1. Organic Composite Devices for Photonic Sensing

Organic molecules show high chemical reactivity, which enables high performance sensors in organic photonic integrations.[43] The optical sensing methods not only take advantage of high sensitivity and rapid response[44] but also can transduce external stimulus into light signals in nanophotonic circuits. For example, the vapors of HCl and NH_3 can change the light emisson intensity of dye molecules, and the composite system 9,10-diphenylanthracene (DPA) and Nile red (NR) shows a drastic change between blue and red colors during treatment with HCl or NH_3, as shown in Figure 10A.[45] The optical sensing function can be attributed to the fluorescence queching of acceptors by HCl by donor−acceptor energy transfer.

To make a sensor device integrated with nanophotonic units, we designed and fabricated the optical waveguide sensors from core−sheath organic nanowires BPEA@bis(2,4,5-trichloro-6-carbopentoxy-phenyl)oxalate (CPPO)).[46] The optical waveguiding can form the surrounding evanescent wave, which is suprasensitive to any change in dielectric environment. Thus, when the H_2O_2 molecules react with the shell layer, the exposure of core nanowire induces extra optical loss during waveguiding and reduces the final output intensity from the tip (Figure 10B). As shown in Figure 10C, the output signal continuously goes down during the treatment with H_2O_2 vapor, because of the increased number of surface defects by the H_2O_2 absorption and chemical reaction.
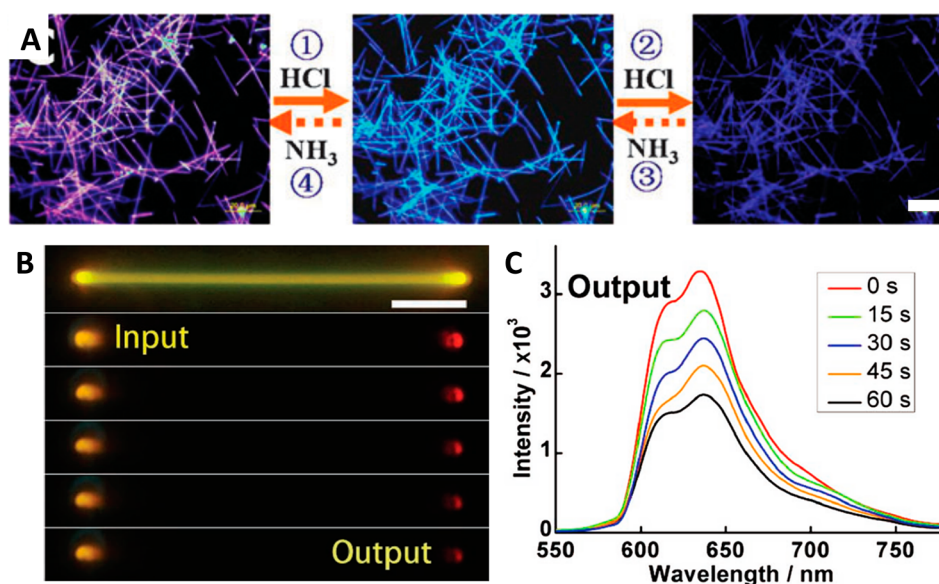
Figure 10. (A) Nanophotonic sensor for chemical vapors in NR doped DPA organic nanowires. Scale bar is 20 μm. (B) Optical waveguide sensor in BPEA@CPPO organic core−shell nanowires (scale bar is 5 μm) and (C) response of the output light under the treatment with H_2O_2 vapor.
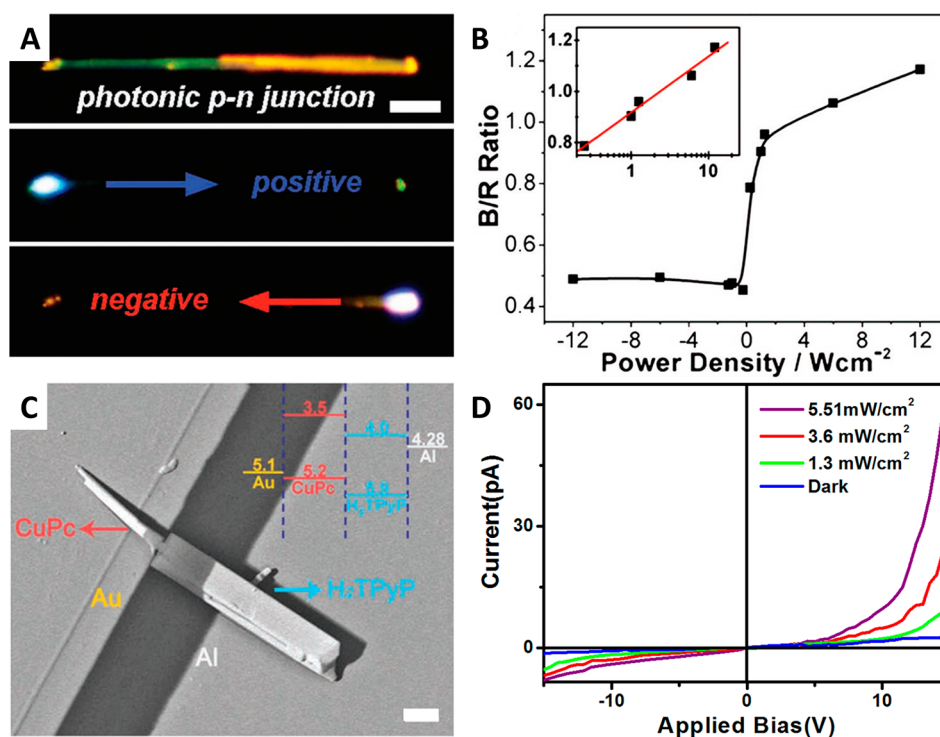
Figure 11. (A) Organic nanophotonic diode in asymmetric light-emitting heterostructures of TPI and coumarin 6 molecules. Scale bar is 5 μm. (B) The change of output colors as a function of excitation power. B/R ratio is the intensity ratio of blue and red lights. (C) Light-controlled diode from coaxial p−n (p, copper phthalocyanine; n, 5,10,15,20-tetra(4-pyridyl)-porphyrin) heterostructures. Scale bar is 1 μm. (D) Typical $I−V$ response in the dark and under light radiation.
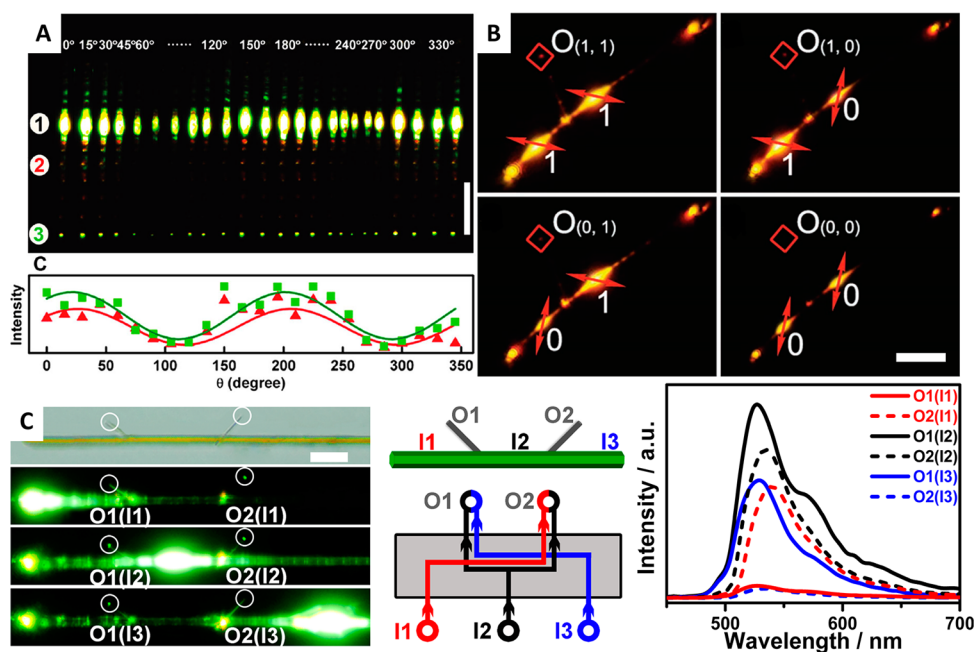
Figure 12. (A) Polarization modulation in aluminum tris(8-hydroxyquinoline) and 1,5-diaminoanthraquinone organic nanowire heterojunctions. Scale bar is 20 μm. (B) Nanophotonic logic gates based on polarization control in organic−metal (BPEA and silver) nanowire junctions. Scale bar is 10 μm. (C) Nanophotonic multiplexers based on light coupling between the *fac*-tris(2-phenylpyridine) iridium organic waveguide and the embedded silver nanowires. Scale bar is 10 μm.

4.2. Organic Heterojunction Devices for Photonic and Light-Controlled Diodes

In photonic devices, the unidirectional transmission of light is hindered due to the time-reversal symmetry of photons.[47] We proposed an active control of light to realize the light guiding with diode characteristics in an optical analogy of p−n junction devices, as shown in Figure 11A.[48] This photonic device consists of two connected parts, the donor part, 2,4,5-triphenylimidazole (TPI), and the acceptor part, 3-(2-benzothiazolyl)-7-diethylaminocoumarin (coumarin 6), where

the energy transfer could change the TPI blue light emission into the red one of the acceptor. The asymmetric device geometry results in blue and red light outputs in two opposite guiding directions, and the output color versus excitation power shows similar response as rectification performance (Figure 11B).

An alternative way to accomplish a photonic diode is to improve electronic devices with photonic functionalities, which is important to the combination of electronics and photonics on the same chip. We fabricated a nanowire p−n junction diode controlled by the input light signals, as illustrated in Figure 11C.[49] Illumination can generate more charge carriers in the nanowire, which leads to an increase in the current density and makes the device show diode behaviors (Figure 11D). The power-dependent I−V characteristics can change the input light into output electric signal, which is potentially applied as transducers in electronic−photonic hybrid systems.[50]

4.3. Organic Multibranch Geometry As Integration of Photonic Modulation Devices

Compared with electronic−photonic hybrid circuits, all-photonic processing of light signals benefits from parallel communicating and the diversity in encoding the parameters of photons.[51] The polarization of light shows excellent contrast despite the intensity loss, and thus represents a higher level in light signal processing. More importantly, the polarization information can be kept during the optical waveguiding and even the intercoupling processes, as shown in Figure 12A.[52] All the outputs from the branch-like integration of optical waveguides follow identical change of intensities according to the polarization at the excitation spot.

The silver nanowires can transport surface plasmon polaritons (SPPs) instead of photons for transverse magnetic (TM) polarization.[53] Therefore, we used silver nanowires to analyze light polarization in organic nanophotonic polarization devices, because organic nanowires can support both transverse electric (TE) and TM polarizations. In the organic−silver hybrid devices (Figure 12B), we demonstrated the logic gates of the input polarization signals, because the output from the silver nanowire antenna is determined by the polarization of guided light.[54] We further presented a photonic multiplexor to distribute the light signal from the organic trunk to the multiple silver branches.[55] As displayed in Figure 12C, the input light from different excitation positions can be selectively transported in the terminals of silver nanowires. The large-scale integration of these photonic and SPP components may lead to practical polarization circuits[56] in organic nanophotonics.

5. CONCLUSION

We summarized our recent studies in organic photonics from the aspects of functional molecules, fabrication of micro- or nanostructures, and heterojunction photonic devices. These advances proved the potential of organic semiconductors in the photonic analogy along with the success of organic electronics. It can broaden the application range of synthetic materials and further illuminate the future of organic optoelectronics. However, to further push forward this field, we still have to face the challenges from the fundamental physics of exciton−photon interactions and the practical engineering of device integration in organic photonics.

Although researchers agree that the Frenkel excitons play an essential role in active optical waveguiding and other optical behaviors in organic micro- or nanocrystals, no direct evidence

of unusual exciton−photon interactions has been given until now. State of the art techniques should be applied to reveal the microscopic picture of these exciton-related phenomena, which is helpful in building new types of photonic devices with exciton features in organic materials.[57] Some prototype photonic devices have already been demonstrated in organic heterojunctions, but they are still far away from the ultimate goal of organic integrated photonics. Therefore, new fabrication methods for large-scale patterned devices and circuits are needed toward the realization of feasible organic photonic chips.[58]

The research on organic micro- or nanocrytals in photonic applications is a chemists' contribution to integrated photonics, but it is still in its infancy. We have witnessed rapid development in its first decade and hope to see it blossom in the following decade by the interdisciplinary study of chemistry, physics, and material science.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: yszhao@iccas.ac.cn.
*E-mail: jnyao@iccas.ac.cn.

Notes

The authors declare no competing financial interest.

Biographies

Chuang Zhang received his Ph.D. degree with Prof. Jiannian Yao and Prof. Yong Sheng Zhao at Institute of Chemistry, Chinese Academy of Sciences (ICCAS), in 2013. His research interests focus on optical waveguiding and cavity effect in organic materials.

Yongli Yan received her Ph.D. degree in 2008 at Fudan University. Then she joined the National University of Singapore as a postdoctoral fellow. Now she is an associate professor in Prof. Yong Sheng Zhao's group at ICCAS. Her research interests include the linear and nonlinear optical properties of organic composite materials.

Yong Sheng Zhao received his Ph.D. degree in 2006 at ICCAS with Prof. Jiannian Yao. After being a postdoctoral fellow at University of California, Los Angeles, and Northwestern University, he returned to ICCAS as a Professor of Chemistry in 2009. His research interests focus on organic nanophotonic materials and devices.

Jiannian Yao received his Ph.D. degree with Prof. Akira Fujishima at Tokyo University in 1993. Now he serves as a Professor of Chemistry at ICCAS, the president of the Chinese Chemical Society, and the vice president of the National Natural Science Foundation of China. His research interests are organic and inorganic optofunctional nanomaterials.

■ REFERENCES

(1) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. Highly Efficient Phosphorescent Emission from Organic Electroluminescent Devices. *Nature* **1998**, *395*, 151−154.

3456

dx.doi.org/10.1021/ar500192v | *Acc. Chem. Res.* 2014, 47, 3448−3458

(2) Zaumseil, J.; Sirringhaus, H. Electron and Ambipolar Transport in Organic Field-Effect Transistors. *Chem. Rev.* **2007**, *107*, 1296−1323.

(3) Kim, J. Y.; Lee, K.; Coates, N. E.; Moses, D.; Nguyen, T.-Q.; Dante, M.; Heeger, A. J. Efficient Tandem Polymer Solar Cells Fabricated by All-Solution Processing. *Science* **2007**, *317*, 222−225.

(4) Kirchain, R.; Kimerling, L. A Roadmap for Nanophotonics. *Nat. Photonics* **2007**, *1*, 303−305.

(5) Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. Semiconductor Nanocrystals as Fluorescent Biological Labels. *Science* **1998**, *281*, 2013−2016.

(6) Law, M.; Sirbuly, D. J.; Johnson, J. C.; Goldberger, J.; Saykally, R. J.; Yang, P. Nanoribbon Waveguides for Subwavelength Photonics Integration. *Science* **2004**, *305*, 1269−1273.

(7) Zhao, Y. S.; Fu, H.; Peng, A.; Ma, Y.; Xiao, D.; Yao, J. Low-Dimensional Nanomaterials Based on Small Organic Molecules: Preparation and Optoelectronic Properties. *Adv. Mater.* **2008**, *20*, 2859−2876.

(8) Balzer, F.; Bordo, V. G.; Simonsen, A. C.; Rubahn, H. G. Optical Waveguiding in Individual Nanometer-Scale Organic Fibers. *Phys. Rev. B* **2003**, *67*, No. 115408.

(9) Takazawa, K.; Kitahama, Y.; Kimura, Y.; Kido, G. Optical Waveguide Self-Assembled from Organic Dye Molecules in Solution. *Nano Lett.* **2005**, *5*, 1293−1296.

(10) Lidzey, D. G.; Bradley, D. D. C.; Skolnick, M. S.; Virgili, T.; Walker, S.; Whittaker, D. M. Strong Exciton-Photon Coupling in an Organic Semiconductor Microcavity. *Nature* **1998**, *395*, 53−55.

(11) Takazawa, K.; Inoue, J.-i.; Mitsuishi, K.; Takamasu, T. Fraction of a Millimeter Propagation of Exciton Polaritons in Photoexcited Nanofibers of Organic Dye. *Phys. Rev. Lett.* **2010**, *105*, No. 067401.

(12) Zhao, Y. S.; Fu, H.; Peng, A.; Ma, Y.; Liao, Q.; Yao, J. Construction and Optoelectronic Properties of Organic One-Dimensional Nanostructures. *Acc. Chem. Res.* **2010**, *43*, 409−418.

(13) Scholes, G. D.; Rumbles, G. Excitons in Nanoscale Systems. *Nat. Mater.* **2006**, *5*, 683−696.

(14) Yao, W.; Yan, Y.; Xue, L.; Zhang, C.; Li, G.; Zheng, Q.; Zhao, Y. S.; Jiang, H.; Yao, J. Controlling the Structures and Photonic Properties of Organic Nanomaterials by Molecular Design. *Angew. Chem., Int. Ed.* **2013**, *52*, 8713−8717.

(15) Zhang, C.; Zhao, Y. S.; Yao, J. Organic Composite Nanomaterials: Energy Transfers and Tunable Luminescent Behaviors. *New J. Chem.* **2011**, *35*, 973−978.

(16) Wright, G. T. Absolute Quantum Efficiency of Photofluorescence of Anthracene Crystals. *Proc. Phys. Soc. B* **1955**, *68*, 241.

(17) Heller, C. A.; Henry, R. A.; McLaughlin, B. A.; Bliss, D. E. Fluorescence Spectra and Quantum Yields. Quinine, Uranine, 9, 10-diphenylanthracene, and 9, 10-bis (phenylethynyl) anthracenes. *J. Chem. Eng. Data* **1974**, *19*, 214−219.

(18) Hong, Y.; Lam, J. W.; Tang, B. Z. Aggregation-Induced Emission: Phenomenon, Mechanism, and Applications. *Chem. Commun.* **2009**, 4332−4353.

(19) Zhao, Y. S.; Peng, A.; Fu, H.; Ma, Y.; Yao, J. Nanowire Waveguides and Ultraviolet Lasers Based on Small Organic Molecules. *Adv. Mater.* **2008**, *20*, 1661−1665.

(20) Zhao, Y. S.; Yang, W.; Xiao, D.; Sheng, X.; Yang, X.; Shuai, Z.; Luo, Y.; Yao, J. Single Crystalline Submicrotubes from Small Organic Molecules. *Chem. Mater.* **2005**, *17*, 6430−6435.

(21) Zhao, Y. S.; Zhan, P.; Kim, J.; Sun, C.; Huang, J. Patterned Growth of Vertically Aligned Organic Nanowire Waveguide Arrays. *ACS Nano* **2010**, *4*, 1630−1636.

(22) Zhao, Y. S.; Di, C.; Yang, W.; Yu, G.; Liu, Y.; Yao, J. Photoluminescence and Electroluminescence from Tris(8- hydroxyquinoline)aluminum Nanowires Prepared by Adsorbent-Assisted Physical Vapor Deposition. *Adv. Funct. Mater.* **2006**, *16*, 1985−1991.

(23) Li, Q.; Zheng, J. Y.; Yan, Y.; Zhao, Y. S.; Yao, J. Electrogenerated Chemiluminescence of Metal-Organic Complex Nanowires: Reduced Graphene Oxide Enhancement and Biosensing Application. *Adv. Mater.* **2012**, *24*, 4745−4749.

(24) Zhao, J.; Wu, W.; Sun, J.; Guo, S. Triplet Photosensitizers: From Molecular Design to Applications. *Chem. Soc. Rev.* **2013**, *42*, 5323−5351.

(25) Zhang, C.; Zheng, J. Y.; Zhao, Y. S.; Yao, J. Organic Core-Shell Nanostructures: Microemulsion Synthesis and Upconverted Emission. *Chem. Commun.* **2010**, *46*, 4959−4961.

(26) Tessler, N.; Denton, G.; Friend, R. Lasing from Conjugated-Polymer Microcavities. *Nature* **1996**, *382*, 695−697.

(27) Li, X.; Gao, N.; Xu, Y.; Li, F.; Ma, Y. Self-Cavity Laser Oscillations with Very Low Threshold from a Symmetric Organic Crystal Waveguide. *Appl. Phys. Lett.* **2012**, *101*, No. 063301.

(28) Hong, Y.; Lam, J. W.; Tang, B. Z. Aggregation-Induced Emission. *Chem. Soc. Rev.* **2011**, *40*, 5361−5388.

(29) Kena Cohen, S.; Forrest, S. R. Room-Temperature Polariton Lasing in an Organic Single-Crystal Microcavity. *Nat. Photonics* **2010**, *4*, 371−375.

(30) He, G. S.; Tan, L.-S.; Zheng, Q.; Prasad, P. N. Multiphoton Absorbing Materials: Molecular Designs, Characterizations, and Applications. *Chem. Rev.* **2008**, *108*, 1245−1330.

(31) Hao, R.; Li, M.; Wang, Y.; Zhang, J.; Ma, Y.; Fu, L.; Wen, X.; Wu, Y.; Ai, X.; Zhang, S. A Europium Complex With Excellent Two-Photon-Sensitized Luminescence Properties. *Adv. Funct. Mater.* **2007**, *17*, 3663−3669.

(32) Zhang, C.; Zou, C.-L.; Yan, Y.; Hao, R.; Sun, F.-W.; Han, Z.-F.; Zhao, Y. S.; Yao, J. Two-Photon Pumped Lasing in Single-Crystal Organic Nanowire Exciton Polariton Resonators. *J. Am. Chem. Soc.* **2011**, *133*, 7276−7279.

(33) Eaton, D. F.; Anderson, A. G.; Tam, W.; Wang, Y. Control of Bulk Dipolar Alignment Using Guest-Host Inclusion Chemistry: New Materials for Second Harmonic Generation. *J. Am. Chem. Soc.* **1987**, *109*, 1886−1888.

(34) Gu, J.; Yan, Y.; Zhang, C.; Yao, J.; Zhao, Y. S. Inclusion Induced Second Harmonic Generation in Low Dimensional Supramolecular Crystals. *J. Mater. Chem. C* **2014**, *2*, 3199−3203.

(35) Zang, L.; Che, Y.; Moore, J. S. One-Dimensional Self-Assembly of Planar π-Conjugated Molecules: Adaptable Building Blocks for Organic Nanodevices. *Acc. Chem. Res.* **2008**, *41*, 1596−1608.

(36) Chandrasekhar, N.; Chandrasekar, R. Reversibly Shape-Shifting Organic Optical Waveguides: Formation of Organic Nanorings, Nanotubes, and Nanosheets. *Angew. Chem., Int. Ed.* **2012**, *51*, 3556−3561.

(37) Zhang, C.; Zou, C. L.; Yan, Y.; Wei, C.; Cui, J. M.; Sun, F. W.; Yao, J.; Zhao, Y. S. Self-Assembled Organic Crystalline Microrings as Active Whispering-Gallery-Mode Optical Resonators. *Adv. Opt. Mater.* **2013**, *1*, 357−361.

(38) Heng, L.; Wang, X.; Tian, D.; Zhai, J.; Tang, B.; Jiang, L. Optical Waveguides Based on Single-Crystalline Organic Micro-Tiles. *Adv. Mater.* **2010**, *22*, 4716−4720.

(39) Zhang, C.; Zhao, Y. S.; Yao, J. Optical Waveguides at Micro/Nanoscale Based on Functional Small Organic Molecules. *Phys. Chem. Chem. Phys.* **2011**, *13*, 9060−9073.

(40) Vahala, K. J. Optical Microcavities. *Nature* **2003**, *424*, 839−846.

(41) Zhao, Y. S.; Fu, H.; Hu, F.; Peng, A. D.; Yao, J. Multicolor Emission from Ordered Assemblies of Organic 1D Nanomaterials. *Adv. Mater.* **2007**, *19*, 3554−3558.

(42) Yan, Y.; Zhang, C.; Yao, J.; Zhao, Y. S. Recent Advances in Organic One-Dimensional Composite Materials: Design, Construction, and Photonic Elements for Information Processing. *Adv. Mater.* **2013**, *25*, 3627−3638.

(43) Zhao, Y. S.; Wu, J.; Huang, J. Vertical Organic Nanowire Arrays: Controlled Synthesis and Chemical Sensors. *J. Am. Chem. Soc.* **2009**, *131*, 3158−3159.

(44) Che, Y.; Zang, L. Enhanced Fluorescence Sensing of Amine Vapor Based on Ultrathin Nanofibers. *Chem. Commun.* **2009**, 5106−5108.

(45) Zheng, J. Y.; Zhang, C.; Zhao, Y. S.; Yao, J. Detection of Chemical Vapors with Tunable Emission of Binary Organic Nanobelts. *Phys. Chem. Chem. Phys.* **2010**, *12*, 12935−12938.

(46) Zheng, J. Y.; Yan, Y.; Wang, X.; Shi, W.; Ma, H.; Zhao, Y. S.; Yao, J. Hydrogen Peroxide Vapor Sensing with Organic Core/Sheath Nanowire Optical Waveguides. *Adv. Mater.* **2012**, *24*, OP194−OP199.

(47) Fan, S.; Baets, R.; Petrov, A.; Yu, Z.; Joannopoulos, J. D.; Freude, W.; Melloni, A.; Popović, M.; Vanwolleghem, M.; Jalas, D. Comment on "Nonreciprocal Light Propagation in a Silicon Photonic Circuit". *Science* **2012**, *335*, 38−38.

(48) Zhang, C.; Yan, Y.; Yao, J.; Zhao, Y. S. Manipulation of Light Flows in Organic Color-Graded Microstructures towards Integrated Photonic Heterojunction Devices. *Adv. Mater.* **2013**, *25*, 2854−2859.

(49) Cui, Q. H.; Jiang, L.; Zhang, C.; Zhao, Y. S.; Hu, W.; Yao, J. Coaxial Organic p-n Heterojunction Nanowire Arrays: One-Step Synthesis and Photoelectric Properties. *Adv. Mater.* **2012**, *24*, 2332−2336.

(50) Zhang, Y.; Dong, H.; Tang, Q.; Ferdous, S.; Liu, F.; Mannsfeld, S. C. B.; Hu, W.; Briseno, A. L. Organic Single-Crystalline p−n Junction Nanoribbons. *J. Am. Chem. Soc.* **2010**, *132*, 11580−11584.

(51) Clark, J.; Lanzani, G. Organic Photonics for Communications. *Nat. Photonics* **2010**, *4*, 438−446.

(52) Zheng, J. Y.; Yan, Y.; Wang, X.; Zhao, Y. S.; Huang, J.; Yao, J. Wire-on-Wire Growth of Fluorescent Organic Heterojunctions. *J. Am. Chem. Soc.* **2012**, *134*, 2880−2883.

(53) Guo, X.; Qiu, M.; Bao, J.; Wiley, B. J.; Yang, Q.; Zhang, X.; Ma, Y.; Yu, H.; Tong, L. Direct Coupling of Plasmonic and Photonic Nanowires for Hybrid Nanophotonic Components and Circuits. *Nano Lett.* **2009**, *9*, 4515−4519.

(54) Yan, Y.; Zhang, C.; Zheng, J. Y.; Yao, J.; Zhao, Y. S. Optical Modulation Based on Direct Photon-Plasmon Coupling in Organic/Metal Nanowire Heterojunctions. *Adv. Mater.* **2012**, *24*, 5681−5686.

(55) Li, Y. J.; Yan, Y.; Zhang, C.; Zhao, Y. S.; Yao, J. Embedded Branch-Like Organic/Metal Nanowire Heterostructures: Liquid-Phase Synthesis, Efficient Photon-Plasmon Coupling, and Optical Signal Manipulation. *Adv. Mater.* **2013**, *25*, 2784−2788.

(56) Wei, H.; Wang, Z.; Tian, X.; Käll, M.; Xu, H. Cascaded Logic Gates in Nanophotonic Plasmon Networks. *Nat. Commun.* **2011**, *2*, No. 387.

(57) Liew, T.; Kavokin, A.; Ostatnicky, T.; Kaliteevski, M.; Shelykh, I.; Abram, R. Exciton-Polariton Integrated Circuits. *Phys. Rev. B* **2010**, *82*, No. 033302.

(58) Keil, R.; Heinrich, M.; Dreisow, F.; Pertsch, T.; Tünnermann, A.; Nolte, S.; Christodoulides, D. N.; Szameit, A. All-Optical Routing and Switching for Three-Dimensional Photonic Circuitry. *Sci. Rep.* **2011**, *1*, No. 94.