Self-assembly and tunable optical properties of intramolecular charge transfer molecules

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Abstract
Crystalline aggregates formed by self-assembly of organic small molecules have aroused intensive attention in many fields due to their controllable morphologies and functionalization. The advantages of intramolecular charge transfer (ICT) compounds endow them with the ability to self-assemble into diverse dimensional crystalline microstructures, as potential candidates for advanced materials and smart miniatures in practical applications. In this review, the recent progresses of self-assembled microstructures of functional ICT molecules in our group for a decade are summarized. The factors influencing the fabrication of the microstructures in solvent-involved processes are fully discussed. Distinct optical properties induced by self-assembly behaviors are also depicted. We try to give an outlook of structure-property relationships in functional microstructure engineering and clarify the crucial issues to be addressed in the future scientific research.

1 | INTRODUCTION
Aggregation-induced emission (AIE) phenomenon has been richly observed and investigated in tremendous research of various disciplines since first reported and defined by Tang’s group.1 Contrary to past dominant aggregation caused quenching (ACQ) concept that traditional chromophores reduce fluorescent intensities in high-concentration solutions, AIE concept presents the possibility of strengthened emission induced by aggregation at high concentrations or even in solid states. Luminogenic materials with AIE property have advantages on high-tech innovations of biomedical probes,2 chemical sensors, and other optoelectronic applications.3,4 Mechanism of AIE has been revealed to restriction of intramolecular motion (RIM)5 that constrains force of vibrations and rotation of functional groups, resulting in the reduction of thermal energy consumption from luminous energy. Herein, reasonable design and fabrication of functional molecules and macromolecules are of great importance. A large variety of molecules such as π-conjugated small molecules, small organometallics, intramolecular/intermolecular charge transfer compounds, and π-conjugated polymers have been synthesized to achieve desirable AIE properties.6 Particularly, intramolecular charge transfer (ICT) molecules,7,8 with electron delocalized and transferred in a single molecule, are good candidates for light emitters. They usually consist of electron donor moiety and electron acceptor moiety, which are linked by π-conjugated core to make a donor-acceptor (D-A) system. Research indicate a correlation between strength of electron D-A moieties and charge transfer capability. By altering HOMO/LUMO energy, ICT molecules with diverse functional fractions are equipped with different energy gap values and enhanced emission.

Self-assembly of ICT molecules is a common protocol to construct crystalline microstructures with benign AIE performance. It was believed decades ago that the electrostatic model dominantly determined interactions between π-conjugated planes but had little relationship with charge transfer.9 However, other research emphasized the important role that charge transfer had played in aggregation into supramolecular structures.10-12 Driven by π-π stacking,13 hydrogen bonding,14 hydrophobic effect, electrostatic interaction, and other week interactions, adjacent molecules can be arranged into well-organized microstructures with diverse crystalline structures and morphologies. The differences in ground and excited states induced by ICT equip the molecular systems with various fluorescent signals.15,16 Factors17 influencing self-assembly behaviors range from solvent processing techniques18 to chemical reaction conditions,19 leading to construction of zero-dimensional (0D) nanospheres,20 one-dimensional (1D) or sub-1D microwires,21 nanorods,22 two-dimensional (2D)23,24 nanoplates, nanoribbons, and three-dimensional (3D) cubic nanostructures, which exhibit distinct linear and nonlinear optical (NLO) properties and waveguide properties.
indicating potential application in optoelectrical devices. Understanding the structure-property correlation remains one of the most attractive issues. Researchers have made great efforts\cite{25,26} in decades to make it clear how to prepare controllable well-defined microstructures with diverse morphologies and dimensions to obtain advanced materials of high usage efficiency, low energy consumption, and high performance. Self-assembly behaviors are affected not only by intrinsic features of ICT compounds, but also dihedral angles, stacking modes, dipole moment orientations, and intermolecular interactions. Configuration determined orbital overlap and electronic structures induce tunable distinct photophysical properties of functional self-assemble aggregates. Benign optical properties, especially NLO properties, suggest intensive and promising application prospects in sensitive sensors,\cite{27} light harvesting,\cite{14} and bioimaging.\cite{7}

In this review, endeavors to design novel ICT compounds in our group in the past decade are systematically summarized. Advancements on self-assembled nanomaterial construction from shapes, sizes, crystallinity aspects of functional molecules and induced linear, NLO property changes, and waveguide tendency are discussed in detail. Meanwhile, determining driving forces of polymorphism are of great significance for both fundamental scientific research and practical commercial applications. We attempt to prospect the structure-property relationship from several aspects and put forward the key problems to be solved in future work.

2 | SELF-ASSEMBLY OF ICT MOLECULES INTO MICROSTRUCTURES

Organic ICT molecules are building blocks for fabricating luminogenic materials that have a long-term periodic molecular arrangement through noncovalent bonds.\cite{28} Macromolecules with their own conformations aggregate into crystal structures with various molecular packing modes under different processing conditions. It is of great importance to understand the dependences of self-assembly behavior including crystallinity, driving force, and molecular structure in the nanoscale, which is beneficial to design and engineer novel ICT compounds based functional materials with a high efficiency. In this section, structures of electron donor and acceptor moiety aggregate, solvent processing techniques, and other factors affecting ICT molecules self-assembly are summarized in detail. We try to give an outlook of the relationship between molecular structure, chemical surrounding, and corresponding self-assembly behaviors and find out key dependences that control shapes, sizes, dimensions, and crystallinity of obtained nanostructures.

2.1 | Design of ICT molecules

Different from intermolecular charge transfer (intermolecular CT) features between neighboring molecules, ICT property means charge transfer from one part to the other part of a single molecule (Figure 1). It is typically achieved by introducing an electron donor moiety to an electron acceptor moiety to form a D-A\cite{28} system where an electron density difference exists to promote charge transfer within a molecule. Sometimes π-conjugated molecules act as the core bridge between electron donors and donors (D-π-D) to expand electron delocalization area. No matter D-A, D-π-A, D-π-D, or other charge transfer styles that can be disclosed by electrochemical tests, π-conjugated backbones endow ICT molecules primary intermolecular interactions, while functional side chain substituents affect secondary intermolecular interactions. Electron withdrawing fractions, namely electron withdrawing side chains, have been reported to affect self-assembly of ICT molecules. Electron withdrawing groups with strong electronegativity promote ICT behavior by removing electron density from π-conjugated backbone and lowering LUMO energy to narrow down band gap in self-assembly process. Basically, introducing electron withdrawing substitution groups to π-conjugated molecular core could efficiently weaken π–π interaction between neighboring molecules and promote solubility of ICT compounds. However, excessive reduction of π–π interaction results in torsion of planar molecules into large dihedral angles, which is harmful for electron delocalization and formation of well-ordered microstructures. A larger π-conjugated system is generally believed to reduce distance of adjacent molecules and then enhance π-stacking. By changing donor groups, charge transfer processes are tunable to optimize molecular packing, self-assembly behaviors and optical properties.
Thus, manipulation of the strength of electron withdrawing groups is important to obtain materials with desired structure and property.\textsuperscript{[29]}

Similar with molecular backbones, electron donors are also designed based on $\pi$-conjugated systems like fundamental phenyl heterocyclic rings.\textsuperscript{[20,21,30,31]} Carbazole group\textsuperscript{[22,32,33]} is one of the most popularly adopted electron donors in ICT compounds synthesis. Two phenyl rings fused with nitrogen compose a large planar $\pi$ system, which can supply sufficient delocalized electrons. N,N-Dimethylaniline is another strong electron donor candidate. Jiang and coworkers designed and synthesized three novel D-A molecules based on same electron acceptor benzothiadiazole (Figure 1). For example, compared with 4-(4-(9H-carbazol-9-yl)phenyl)benzo[c] [1,2,5] thiadiazol (CBT) and 4-((4-(9H-carbazol-9-yl)phenyl)ethynyl)benzo[c] [1,2,5] thiadiazol (CBET), both of which employ carbazole as an electron donor, 4-(benzo[c] [1,2,5] thiadiazol-4-yl)-N,N-dimethylaniline as electron donor processes a more planar configuration, resulting in shorter C-N bonds of adjacent molecules and a closer stacking.\textsuperscript{[34]} Intermolecular interactions are crucial for the molecular stacking (Figure 1D-F). Introducing additional side chains on electron donor fragments can affect self-assembly behaviors as well. The linkage of external functional substitutes brought significant steric hindrance of adjacent molecules, leading to different self-assembled structure. The number and distribution of electron donors also affect ICT by changing symmetry. The asymmetry caused different electron distribution and self-assembly behaviors.

Water-soluble ICT compounds have potential application prospects in biological environments. Han and coworkers designed and synthesized novel D-A ionized cyanine dye YS and its click products YS-X with excellent water solubilities (Figure 1). The employment of strong electron acceptor indole group and introduction of strong electron donor cyano group reduced individual bond energy and tuned the HOMO-LUMO gaps, which is beneficial for optical properties.\textsuperscript{[35]}

### 2.2 Solvent techniques in self-assembly of ICT molecules

Self-assembly of organic ICT molecules into microstructures through various solvent involved techniques shows great advantages of tailoring convenience, low cost, and high efficiency. The polarity,\textsuperscript{[32]} volatility, and solubility natures of solvents have crucial effects on crystallinity and morphology of the microstructures, which derives from a balance of solvent-molecules interaction and intermolecular interaction during self-assembly process.\textsuperscript{[28,36]} Solvent evaporation is a commonly used technique for preparing crystalline microstructures (Figures 2–6). Molecules undergo distinct self-assembly behaviors as a result of intrinsic solvent solubility, polarity, external temperature, and the speed of evaporation. Changing solubility from good to poor solvent can adjust morphologies of self-assembled microstructures. ICT molecule DBD and BBD self-assemble into microwires with an average width of 300 nm in CH$_2$Cl$_2$ (good solvent) dominant solutions (Figure 2).\textsuperscript{[21]} When the volume ratio of CH$_3$OH/ CH$_2$Cl$_2$ was increased to 4:5 (methanol as poor solvent), microtubes with an average width of 1 $\mu$m were observed.

The shape and morphology of microstructures can be tuned by changing poor solvent.\textsuperscript{[37]} CSS (Figure 3A) could be assembled into plate-like architectures through the solvent exchange method, that is, injection of CH$_2$Cl$_2$ CSS solution into ethanol (Figure 3E and F). As for the phase transfer method for DSS, soft covering of hexane (poor solvent) on CH$_2$Cl$_2$ generated hollow-sphere morphology in the interface of two phases (Figure 3G and H). With the help of solvent-vapor technique, evaporation of the mixture solvents of ethanol and CH$_2$Cl$_2$, plate-like microstructures, could be obtained (Figure 3F and J).\textsuperscript{[38,39]}

Solvent evaporation rate also plays an important role in affecting desirable shape and size of microstructures. Fast evaporation of volatile organic solvent on solid substrates gives a convenient pathway to directly obtain samples for optical tests. Chen and coworkers obtained 3-D cube-like microcrystals after dropping a saturated solution of 4-(4-(9H-carbazol-9-yl) phenyl)ethyl)-7-nitrobenzothiadiazole (BEC) (Figure 3K) in THF on silicon substrate (Figure 3N).\textsuperscript{[33]} However, dropping hot solution of BEC on the substrate obtained 1D nanowires crystals (Figure 3O). Both microstructures were morphological and crystalline pure, indicating that external factors like temperature in self-assembly affect morphology as well. For example, simply cooling down the CLS solution in acetic ether for 1 hour after refluxing gave precipitates with ribbon-like morphology (Figure 3C and D).\textsuperscript{[38]} Different evaporation rate of organic solvent of a solution generates different microstructure shapes and sizes. By fast solvent vapor technique, compounds TBC and TCP self-assembled into 0-D sphere-like architecture with an average diameter of 300 nm, which was observed to be hollow morphology by transmission electron microscopy (TEM) (Figure 4B and H). While employing phase transfer method to slowing down the evaporation rate, TBC compound underwent self-assembly to form 1D nanotube crystals (Figure 4D) and TCP was assembled into nanorods (Figure 4J).\textsuperscript{[22]} In general, nucleation first occurred at interfaces between two solvents. A slow growth process of molecules and well-defined nanotubes were gradually formed by the synergistic effect of different intermolecular forces. The possible mechanism for the morphology transition was proposed as a “curvature strain releasing” process driven by donor-acceptor dipole-dipole interactions (Figure 4A and G).\textsuperscript{[40]}

Sometimes different morphological crystals can transform to each other with the help of solvent, namely reversible crystalline microstructure can be achieved in solution. Xu and coworkers obtained 1D fiber-like crystals of 2,7-diphenyl-9 H-fluoren-9-one (DPFO) (Figure 5) after directly dropping solution on silica or glass substrates that are kinetically stable (Figure 5B and D). $\pi-\pi$ interactions and hydrogen bonds are the main driving forces of molecular stacking. By repeated drop-casting, the crystal transformed into 3D cubic-like crystals that are thermodynamic stable (Figure 5A and C), which indicates that reversible morphologies of DPFO can be tuned in the process (Figure 5E-I).\textsuperscript{[30]} Hydrophobic properties of organic solvents can also affect self-assembly behaviors of ICT molecules considering their amphipaths. For example, amphipathic porphyrin derivative complex DOCP-Zn prepared by Liu and coworkers self-assembled into nanospheres with multilayer films driven by $\pi-\pi$ stacking interactions.
in chloroform/cyclohexane system (Figure 6). Lipophilic solvents chloroform and cyclohexane widened the space between adjacent layers by reducing hydrogen bonding interactions of hydrophilic glycol side chains. Self-assembly into nanospheres structure with multilayers films kept DOCP-Zn complex at the lowest energy in lipophilic solvents of chloroform and cyclohexane.

### 2.3 Intermolecular interactions of self-assembly of ICT molecules

Tunable self-assembly processes is of great importance for functional molecules to achieve benign optical properties. ICT molecules self-assemble into microstructures with different conformations and spatial arrangements drove by weak noncovalent molecular interactions, including \(\pi-\pi\) interactions, hydrogen bonds, C-H-\(\pi\) interactions, electrostatic effects, and hydrophobic effects (Figures 1D-F and 7). Four polymorphs of TCBR could be obtained almost simultaneously through a slow solvent diffusion method. There are two conformational isomers, which stacked in two manners, respectively (Figure 7A-D). Planar structures with smaller dihedral angles in crystals usually show stronger \(\pi-\pi\) interactions induced by closer packing, which will efficiently increase the exciton coupling and orbital overlap between adjacent molecules. A series of pure organic emitters are color-tuned to emit yellow, orange, and red. Considering the solubility of ICT compounds, external side chains might be introduced, which would also cause steric hindrance. Some ICT molecules grow along axis provoked by hydrogen bonds of heteroatoms and hydrogen atoms.

In addition, dipole moments can also affect self-assembly behaviors. Dipole-dipole interactions affect charge transfer...
features of ICT compounds by changing orientation and strength of permanent dipole and transition dipole moment, which will affect self-assembly behaviors of ICT compounds. As discussed above, in an ICT system, a larger difference between electronegativity value of the donor and the acceptor means a larger dipole moment of the molecule. Both permanent dipole moment and transition dipole moment have impressive impacts on self-assembly processes by adjusting orientations and strengths of dipole-dipole interactions. Namely, symmetry of dipoles will influence the self-assembled crystal structure of ICT molecules, of which possessing symmetrical dipolar moment tend to
FIGURE 5  Molecular structure of α-phase (A) and β-phase (B) of DPFO; crystal stacking of α-phase (C) and β-phase (D) of DPFO; (E-I) schematic representation of the multistep drop-casting growth method of micro-sized DPFO self-assembled architectures. Reproduced with permission: Copyright 2015, RSC.30

FIGURE 6  (A) Schematic outline and PL microscopic images of DOCP-Zn. (B-E) SEM and TEM images of nanostructures in different "poor" solvent. Reproduced with permission: Copyright 2012, ACS.41
self-assemble along the orientation of dipolar moments to form a 1D crystalline microstructures. However, ICT molecules with asymmetrical dipolar moments tend to undergo 3D microstructures.\(^{[29]}\) For example, the above-mentioned compound TCP (Figure 4G)\(^{[22]}\) has four carbazole groups in all directions to form a symmetric structure and dipole moments, while TBC (Figure 4A), with only three carbazole groups instead, possesses an asymmetric structure and dipole moment from several directions. Therefore, the driving force for TBC self-assembly includes not only \(\pi-\pi\) interactions, but also dipole-dipole interactions. Transition dipole moment has also been noticed to affect the shape and size of self-assembled nanomaterials.\(^{[21]}\) ICT molecules grow along dominant axis usually generate 1D microwire, microfiber, and microtube structures, while they tend to generate 2D and even 3D microstructures when grow along multiple axes.

3  |  OPTICAL PROPERTIES INDUCED BY SELF-ASSEMBLY OF ICT MOLECULES

Optical properties of organic supramolecular aggregates are not only related to the intrinsic structures of individual molecular, but also molecular packing in solid states, especially when comparing the same compound in different shapes. In this section, linear (absorption and emission spectra), nonlinear, and other optical properties of self-assembled microstructures induced by solid-state effects that can potentially slow down nonradiative decay pathways that involve conformational degrees of freedom as a result of the phenomenon known as AIE are introduced and discussed in detail.

3.1  |  Linear optical properties of self-assembled microstructures

3.1.1  |  Tunable absorption properties

It is believed that absorption bands undergo redshifts when the \(\pi\)-conjugated system of ICT molecules gets expanded or strong electron donor moieties were introduced.\(^{[45,46]}\) In addition, the ICT absorption band of D–A molecules would experience redshifts as the strength of the electron donor increases.\(^{[45]}\) As the electron-donating strength increases from carbazole to N,N-dimethylaniline, the absorption maximum shifts from 436 nm in CSS to 516 nm in DSS.\(^{[38]}\) Meanwhile, some absorption bands derive from \(\pi\)-conjugated units of ICT compounds, which also follow a redshift rule resulting from extension of \(\pi\)-conjugated units. In general, ICT compounds exhibit different absorption features in solution states and in solid states with the Stokes shifts. Large Stokes shifts might indicate conformational changes of self-assembled ICT nanostructures upon photoexcitation.\(^{[33]}\)

The absorption of various self-assembled microstructures in solid states can be different considering factors of...
structure, packing mode, and morphology. For example, the difference in the linear absorption properties of the α-phase and β-phase of DPFO can be noticed by the naked eyes (Figure 8A and B). Under the excitation of sunlight and UV light, the β phase microfiber crystal is yellow, while the α phase microplate crystal is greenish-yellow. For these aggregated structures, absorption spectra are also related to the polarization orientation of incident light (Figure 8C). For example, the fabricated microfibers of DPFO showed two absorption bands at 398 and 465 nm when polarization was perpendicular to fiber axis, but lost the band at higher wavelength when polarization was rotated to parallel to the axis. By contrast, absorption of self-assembled microplate of DPFO was much broader and structureless, regardless of polarization of incident light. Theoretical calculations show that the shifts of the absorption and emission peaks are mainly due to the different excitation energies of the electron transitions in isolated molecules.[30]

3.1.2 Tunable fluorescent properties

With different conformations and packing modes, self-assembled microstructures exhibit quite distinguishable emitting properties. The fluorescence spectra of AIE compounds are dependent on their concentrations. Emission of transition of ICT in solid states locates in longer wavelength region. For example, Jiang and coworkers synthesized thiophene-substituted perylene bisimide (PDI). The emission of PDI unit was quenched due to ICT effect from trithiophene unit to perylene unit. After irradiation, the thiophene rings in the nonfused trithiophene unit will rotate to the unstable form (PDI), which reduces the degree of the conjugation in trithiophene unit and leads to the reduction of ICT (Figure 9B). Therefore, when the charge transfer from thiophene unit to perylene imide is blocked, the characteristic AIE phenomenon of perylene bisimide terminals will be enhanced, that is, the charge transfer emission at 750 nm will disappear and the emission at 580 nm should be increased (Figure 9A and C). This mechanism is different from the photobleaching of ordinary solid-state fluorescent materials and has potential applications in optical devices.[20]

It is verified by research and calculations that fluorescence wavelengths are affected by dipole moments, including excited state dipole and transition dipole moment, where a larger charge separation induces longer absorption and fluorescence wavelengths. For instance, novel D-A type molecule (E)-2-[4-[4-(9H-carbazol-9-yl) styryl] benzylidene]-malononitrile (TCBR) was designed and synthesized by Chen and coworkers (Figure 7). The four solvent-polarity-dependent self-assembled TCBR polymorphs showed negligible differences in absorption signals, but a large redshift of fluorescence emission for form D (Figure 7F), which has closer packing (Figure 7A-D), indicating a highly charged excited state resulting from photoinduced charge transfer. Calculations for the four configurations with different luminescence showed small energy differences, indicating that the optical properties can be tuned by adjusting crystal structures.[32]

Fluorescence redshifts from diluted solution states to solid states indicate J-type head to tail molecular aggregates,[20] while blue shifts indicate H-type face-to-face π-stacking of ICT molecules.[47] Microstructures with diverse dimensions and morphologies also exhibit different light emitting features. Fluorescence microscopy images of TBC in 0-D nanospheres radiated strong yellow fluorescence (Figure 4C), but 1D nanotubes radiated green fluorescence (Figure 4E). The broad and red-shifted band of nanospheres means better exciton coupling deriving from increased π-π interactions but a less well-ordered configuration.[48,49] While for TCP the different supramolecular structures displayed yellow fluorescence (Figure 4I and K), with only little difference in the range of 530 and 580 nm. These results supported the proposed self-assembly mechanism (Figure 4G), that is, in order to form rod like nanostructures, TCP molecules are packed more tightly than those in hollow nanospheres, so the probability of exciton coupling induced by π-π interaction between perylene cores increases.
For some 1D microstructures, fluorescence microscopic images of the crystal show brighter emission at the ends and edges of structures, which indicates potential waveguide behaviors for optoelectrical devices. For example, donor-acceptor (D-A) molecules BTN-6 and BTN-7 (Figure 10A and B), in which carbazole functions as the donor and benzothiadiazole works as the acceptor, can self-assembled into microtubes and microrods, respectively (Figure 10C). BTN-7 microrods showed optical waveguide properties with waveguide efficiency $\alpha$ of 0.018 dB $\mu$m$^{-1}$ and without obvious redshift (Figure 10E). In the DOCP-Zn nanowires, waveguide efficiency $\alpha$ of 0.067 dB $\mu$m$^{-1}$ was determined (Figure 6A). The overlapping of absorption and fluorescence spectra is very weak, which leads to low loss optical waveguide. The smooth surface and obviously flat end facets also minimize the optical loss caused by scattering, which results in these excellent optical waveguide characteristics.

3.2 NLO properties of self-assembled microstructures

Various NLO nanostructures have been regarded as promising materials for wide applications in optoelectronic
Typical NLO processes consist of second harmonic generation (SHG, second-order) and two-photon excited fluorescence (TPF, third-order), both of which are dependent on molecules and microstructures. ICT compounds with strong π-electron delocalization and asymmetric polarizability have been considered as attractive NLO materials candidates. According to structure-property relationship, centrosymmetric molecules are not supposed to perform second-order (SHG) NLO properties, namely, the donor and acceptor strength, nature of π-conjugated group, and symmetry are crucial factors that affect NLO performance. However, extended π-conjugation systems might endow ICT compounds with third-order NLO properties.

Nonlinear optical properties are determined by donor and acceptor strengths, π-conjugated group’s natures, and symmetry of ICT molecules. Benzothiadiazole compound NBT showed nonlinear absorption coefficient β of $5.0 \times 10^{-10}$ mW$^{-1}$, and CBT and CEBT exhibit little nonlinear absorption effects. The effective third-order nonlinear refractive index γ of NBT is $4.0 \times 10^{-17}$ m$^2$ W$^{-1}$, while CBT and CEBT showed no nonlinear refractive effects. Compared with CBT and CEBT, with the increasing electron accepting ability by attaching of nitro group to benzothiadiazole unit, the nonlinear absorption coefficient (3.6 $\times$ $10^{-11}$ mW$^{-1}$) and the effective third-order nonlinear refractive index ($-1.0 \times 10^{-18}$ m$^2$ W$^{-1}$) of BEC were increased though not bigger enough as NBT.

Basically, the well-organized self-assemblies have been demonstrated to display a better performance than their individual constituent molecules. Self-assembly of ICT molecules gives functional nanostructures in solid state with diverse stacking modes and morphologies, which has attracted much attention in many fields. Considering intrinsically high optical hyperpolarizabilities, self-assembled ICT compounds have been extensively studied as efficient second- and/or third-order NLO materials. For example, Luo and coworkers designed and synthesized novel D-A molecules DBD and BBD, both of which are centrosymmetric molecules that do not have second-order NLO signals. Notably, both microrods of DBD and BBD exhibited quadratic dependences of fluorescence intensities on the power of incident pump, verifying two-photon nature of NLO process. Dipolar dependency measurements indicated that the well-oriented transition dipole moments played important roles in optimization of supramolecular optical materials.

For self-assembled microstructures exhibiting NLO features of both SHG and TPF, it is essential to separate these signals. The DPFO crystalline microfiber showed strong NLO of SHG and TPF. These two effects are related to the molecular organization in the crystal, in which the permanent dipole difference, especially the transition dipole, plays a major role. By changing the polarization and incident angle of light, the (relative) intensity of these two processes can be easily adjusted (Figure 11). Both signals can be separated according to their waveguide differences. The extremely high polarizability observed, which is unusual for organic materials, makes this material an ideal material for logic devices.
CONCLUSION AND PERSPECTIVE

In this review, we systematically summarize and discuss the nanostructures with AIE properties self-assembled from ICT molecules with respect to molecular structures, packing styles, self-assembly behaviors, and induced linear and non-linear optical properties. Functional electron donor fragments and solvent processing techniques according to structure-property relationship would help to construct well-ordered π-conjugated self-assembly systems. ICT molecules self-assemble into various polymorphs through synergistic π-π interactions, hydrogen bonds, C-H⋯π interactions, electrostatic effects, dipolar moment, and hydrophobic effects. All the factors mentioned above have important effects on self-assembly behaviors and induced optical properties. Strong electron donor moieties would enlarge charge separation and bring longer absorption and fluorescence wavelengths; fine planarity with large π-electron delocalization leads to closer packing and strong π-π interactions and increased exciton coupling and orbital overlap. It is noted that great challenges in exploring of self-assembled well-defined superstructures still exist despite the enormous developments that have achieved, which are supposed to be addressed in the future endeavor. Keeping large π-conjugation and benign solubilities of ICT compounds at the same time remains a challenge. Besides, achieving extraordinary optical performances comparable with commercial devices in practical applications is another big challenge. We can employ theoretical calculations of geometry optimization and advanced microcrystal characterization techniques to get a deeper understanding of structure determined optical properties of self-assembled AIE aggregates. Self-assembles of ICT compounds are believed to be further exploited in many disciplines in the future with promising prospects.

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