SMART Design of a Bulk-Capped Supramolecular Segment for the Assembly into Organic Interdigital Lipid Bilayer-Like (ILB) Nanosheets

Yin-Xiang Li, Sha-Sha Wang, Yang Yu, He Zhang, Wu-You Wang, Ru-Qian Yang, Ling-Hai Xie,* Feng Liu, Zong-Qiong Lin, Nai-En Shi, Li-Tao Sun,* and Wei Huang*

Rational molecular design for the organic nanocrystal morphology still remains a challenge due to the structural diversity and complicated weak intermolecular interactions. In this work, a typical attractor–repulsor molecule N,N-diphenyl-4-(9-phenyl-fluoren-9-yl) phenylamine (TPA-PF) is designed to explore a general assembly strategy for 2D nanocrystals. Via an interdigital lipid bilayer-like (ILB) molecular packing mode, large-sized lamellar 2D nanosheets are obtained with a length:width:thickness ratio as ≈2500:1000:1. The d-spacing of the largest (001) plane is 1.32 nm, which equals to the thickness of a single interdigital stacking layer. The synergetic effect of the attractive supramolecular segment (TPA) and the repulsive bulky group (PF) is supposed to be the critical factor for the ILB packing that leads to the 2D structures. The attractor–repulsor molecule design is expected to be an effective strategy for the growth of 2D nanocrystals based on small organic molecules.

1. Introduction

Organic nanocrystals are formed by the periodic packing of organic molecules in the nanometer range, which have attracted increasing attentions for their potential applications in flexible electronics and nanophotonics through the discovery of new properties and nanoeffects. Additionally, organic nanocrystals, especially 2D nanosheets, are expected to be the major components of eco-friendly aqueous inks to fabricate film devices in printed optoelectronics. In this assembly process, they act as the intermediate to bridge the interval between molecules and film devices under the frameworks of hierarchical chemistry. Therefore, organic nanocrystals have been endowed with a dual role: as state-of-the-art models to understand the nanoeffect via supramolecular polymerization processes, simultaneously as nanobuilding blocks to get insight into the mesoscopic effect through the mesoscale assembly. To enable the above function, it is indispensable to establish a strict molecular platform to define order from the molecule to the macroscopic scale. Up to date, many efforts have been devoted to the investigation of the thermodynamic and kinetic crystallization pathways of organic nanocrystals with significant achievements in terms of the preparation methods, growth mechanisms, controllable morphologies, and structures, as well as the structure–property relationships and the corresponding applications in nanophotonics/electronics. However, instead of the external influencing factors such as concentration, surfactant, time, and so on, the intrinsic molecular character is the essential factor to dominate crystallization behaviors, which should be explored by customizing the molecule structures strictly.

In contrast to the inorganic counterparts, organic molecules are featured with diversity of molecular geometries, complexity of weak interaction forces, variance of conformations, thus leaving the basic rules encoded in molecule level an unsolved problem till now. In order to define the distinct fundamental elements governing organic structures, a framework of molecular four-element theory was summarized and proposed from the physical organic chemistry point of view including electronic structure, steric hindrance, conformational topology, and supramolecular interaction. Based on this theory,
we extract a pair of opposite characteristics: supramolecular interaction and steric hindrance to clarify the different roles of molecular segments as the attractive supramolecular group, the repulsive bulky group, or the dual role group with both features. The cooperative effect of the attractor–repulsor unity of opposites, known as supramolecular steric hindrance (SSH) effect,[15] has been really reflects in cases of organic devices,[16] photophysics,[17] film morphologies as well as conformations.[18] The facts suggest that it is possible to build a molecular design platform by rationally collocating steric bulks and supramolecular segments to exhibit the accurate assembly forces thus lead to a predictable molecular packing mode, which are favorable to tailor the functions and morphology of materials. Recently, through self-assembly of pyrene-functionalized spiro[fluorene-9,7′-dibenzo[cl,h]acridine]-5′-one (Py-SFDBAO) molecule, ultrathin nanosheets were obtained with a thickness of 12.5 nm.[19] The interlaced arrangement of Py-SFDBAO, resulted from the SSH effect of bulky SFDBAO segments and Py segments with strong π–π interactions, was supposed to be the key point to generate the 2D morphology. However, the detailed supramolecular and structural analysis of SSH effect was not carried out then, additionally, the paradigm mechanism and strategy for the fabrication of 2D nanosheet have not yet been established.

Herein, we customized a model molecule by covalently connecting triphenylamine (TPA) with 9-phenyl-fluorene (PF) to explore a general pathway for attractor–repulsor molecules to aggregate into 2D nanocrystals. At first, several possible molecular packing modes have been hypothesized depending on the different roles that TPA and PF would play. With the supramolecular interaction analysis, TPA is confirmed to contribute most of the weak interactions while PF acts as the repulsive bulky group. The TPA-PF molecular packing motifs reveal an interdigital lipid bilayer-like (ILB) molecular arrangement with TPA attractor networks in the middle and bulky PF at the outboard of the bilayers. The scanning electron microscopy (SEM) results indicate that TPA-PF nanocrystals exhibit a 2D morphology distinguished from the nanoparticle shape of TPA. Analysis of supramolecular interactions along three axes reflects the SSH effects have been well tailored so that the growth in [001] direction is suppressed. This work performed a proof-of-concept model molecule TPA-PF to elucidate the synergistically molecular attractor–repulsor theory (SMART)[14] based on SSH effect for the first time and provided a general strategy for the programmable 2D organic nanosheets formation.

2. Results and Discussion

2.1. SS–BG Molecule and Mode Design

As one of the most representative 2D structural motifs, a single lipid bilayer is stacked by two layers of amphiphilic molecules with their hydrophobic tails aligning in the middle of the bilayer and hydrophilic heads on both sides toward the aqueous ambient. To mimic the amphiphilic molecular structures, we design an attractor–repulsor molecule by covalently binding TPA with PF. As shown in Scheme 1a, TPA consists of a central nitrogen atom surrounded by three phenyl rings and PF is connected to one of TPAs phenyl rings. The TPA group is supposed to provide most of the supramolecular attractive forces as the supramolecular segment (SS, orange part in Scheme 1b),[20] and the PF group is planned to be the repulsive bulky group (BG, blue block in Scheme 1b).[21,22] In general, four possible packing modes of TPA-PF dimer are illustrated under the cooperative effect and synergetic interactions between SS and BG, including line-abreast packing motif (Scheme 1c), ILB packing motif (Scheme 1d), antiparallel packing motif (Scheme 1e), and slipped packing motif (Scheme 1f). The real roles of SS and BG dominate the packing modes of TPA-PF molecules in dimer (or trimer) repeat units, which further determine the potential molecular arrangements and nanocrystal morphologies. If our design correctly describes the functional partition of modeling molecules under the bioinspired lipid bilayer paradigm, the only interdigital packing motif would occur with the stabllest state under the control over the external condition to assemble 2D nanosheets with regular edges.

Scheme 1. Chemical structures of TPA and TPA-PF and the possible packing modes. a) Chemical structures of TPA and TPA-PF. b) Schematic diagram of the SS–BG molecule. Possible molecular packing motifs: c) line-abreast packing, d) ILB packing, e) antiparallel packing, and f) slipped packing.
2.2. Single Crystal Structure and Influence of BG and SS on Molecular Aggregate

In order to examine our hypothesis of SMART design, we first grow single crystal of the modeling TPA-PF obtained via slow evaporation from tetrahydrofuran/isopropanol mixtures which is attributed to the triclinic space group of P-1, with cell parameters of \( a = 9.43 \) Å, \( b = 10.97 \) Å, \( c = 14.00 \) Å, \( \alpha = 110.38^{\circ} \), \( \beta = 93.58^{\circ} \), \( \gamma = 101.90^{\circ} \), and \( a/b = 0.8596 \), \( b/c = 0.7800 \), \( c/a = 1.4846 \). The molecular crystal structure in Figure 1a and Figure S1 (Supporting Information) reveals the sterically configured and supramolecular interaction sites of TPA-PF. The PF group (marked in blue) exhibits a large nonplanar spatial conformation as the benzene plane at the 9-position of the fluorene is almost perpendicular to the fluorene plane (the dihedral angle = 85.6°), while the TPA group (marked in deep orange) is relatively planar with most of the interaction sites. A repeating unit of three TPA-PF molecules is extracted separately to reveal the representative molecular arrangement mode and supramolecular interactions viewed from [100] direction of the TPA-PF single crystal in Figure 1b. The TPA-PF molecules adopt a reversed stacking by ß-H⋯π interactions between TPA segments with distances of 2.74 and 2.86 Å, and PF as end-capped groups located on the both sides. Based on the reduced density gradient analysis, visualized noncovalent interactions[23] could be realized by combining density functional theory (DFT) calculations and MULTIWFN software. Figure 1c clearly shows the force field distribution within the TPA-PF trimer. Attractive force (the green region) exists between the TPA segments, the force field distribution within the TPA-PF trimer. Attrac-

2.3. Fabrication of 2D Nanosheets and 3D Cube

Nanocrystal morphology is largely dependent on the corresponding molecular stacking mode. To further examine our hypothesis of SMART design, TPA-PF and TPA nanocrystals were obtained respectively with distinct shapes through a classical reprecipitation process. In the absence of any additives, fragmented TPA particles were generated with irregular appearance (Figure 2a). Modified by a surfactant Pluronic P123, TPA molecules assembled into a 3D cubic shape with a width:height ratio of 3:1:1 (300 nm in length, 100 nm in width, and height, see Figure S4, Supporting Information), as shown in Figure 2b. In the case of TPA-PF, 2D truncated parallelograms nanosheets are observed as we expect, regardless of the presence or absence of P123 (Figure 2c,d). With the introduction of surfactant, uniform, and monodispersed TPA-PF nanosheets were obtained with smooth surfaces and clear edges, as displayed in Figure 2d and the corresponding inset. Compared with the surfactant-free counterparts (≈8 ± 2 μm in length, 4 ± 1 μm in width), the average side length of surfactant-assisted TPA-PF nanosheets is one-magnitude-order longer as disclosed in Figure 2e (≈100 ± 8 μm in length, 40 ± 10 μm in width). The solubilization effect of P123 is supposed to be the reason that influences the size of the TPA-PF nanosheets. With \(^1\)H NMR spectra and fourier transform infrared spectroscopy (FTIR) analysis of the 2D nanosheets and the pure TPA-PF molecules (see Figures S5 and S6, Supporting Information), we confirm that these two samples exhibit same \(^1\)H NMR and FTIR spectra without any peaks from P123, ruling out the possibility of inclusion or encapsulation of P123 to the nanosheets. Therefore, the effect of the P123 is attributed to the increasing aqueous solubility of TPA-PF with the addition of P123. Under decreasing supersaturation degree, less nuclei would be formed in the nucleation stage. Through a complete coarsening process, the resulted TPA-PF crystals would exhibit a larger 2D size. Atomic force microscope (AFM) observation in Figure 2f displays the cross-sectional profile of an individual TPA-PF nanosheet in Figure 2d. The sheet thickness is measured as ≈40 nm, thus the sheet length:width:thickness ratio is ≈2500:1000:1, implying a typical 2D nanostructure. Detailed conclusions describing the relationship between the external conditions (such as surfactant types, concentrations, and volume ratio of THF/water) and the nanocrystal shapes are summarized in Table S2, Figure S7 (TPA-PF), and Table S3 (TPA) of the Supporting Information. Despite the variation

**Figure 1.** Single crystal structure and packing motif of TPA-PF. a) The molecular crystal structure of TPA-PF (BG segment is shown in light blue and SS segment is shown in deep orange), the hydrogen atoms are removed and carbon atoms are shown as 30% probability ellipsoids. b) Supramolecular weak interactions between TPA segments in a TPA-PF trimer. c) Visualization of the weak interactions of a TPA-PF trimer, the scale runs from −0.01 (min) to 0.015 (max).
of the above external conditions, the TPA-PF nanocrystals still keep the 2D characteristic through the sizes and shapes are slightly different from each other, further confirming that the intrinsic molecular structure is the essential factor to dominate 2D crystallization behaviors. The comparison results reveal that a transformation from 3D polyhedral particles to 2D nanosheets has been achieved by introducing a PF group into the TPA backbone to form an attractor–repulsor molecule which adopts an ILB packing motif.

2.4. Characterization of Nanosheets and Their Inner Molecular Packing

Further investigations were carried out by transmission electron microscopy (TEM), X-ray powder diffraction (XRD), and 2D grazing incidence X-ray diffraction (2D-GIXD) measurements to reveal the organization and crystallographic structure of TPA-PF nanosheets. TEM image in Figure 3a shows an individual truncated parallelogram recorded from the [001] zone-axis. The corresponding selected-area electron diffraction (SAED) pattern with remarkable bright spots indicates a highly crystalline structure (inset in Figure 3a) and the crystal indices of the spots (marked with red circles) in can be indexed as (110), (310), and (200). XRD pattern in the top of Figure 3b clearly illustrates a layered structure with a series of equally spaced sharp peaks attributed to the {001} facets with the basal spacing of 13.2 Å\(^\text{25}\) All the peaks can be exclusively assigned to the single crystal XRD pattern (the bottom of Figure 3b) without any other reflections. The strongest (001) peak demonstrates that the largest crystal plane, which parallels the substrate is (001) face of TPA-PF crystal, which is further confirmed by 2D-GIXD in Figure 3c. 2D-GIXD is useful to analyze 2D structures oriented along the direction out-of-plane (\(q_z\)) or in-plane (\(q_y\)). The scattering pattern is indexed based on the crystallographic information of TPA-PF with the out-of-plane
belonging to \{00l\}s while in-plane spots are labeled as \{02l\}s and \{03l\}s.

According to the surface free energy minimizing principle, an ideal morphology of TPA-PF crystal is simulated by means of the Materials Studio software as exhibited in Figure 3d. The truncated parallelogram feature shows a complete match with the realistic TPA-PF nanocrystal, which is made up by eight faces belonging to \{001\}, \{010\}, \{100\}, and \{111\}, respectively. The corresponding calculated surface energies of them are displayed in Table S4 of the Supporting Information, revealing the most thermodynamically stable surface is \{001\} due to the lowest surface free energy (12.83 kcal), which agrees well with the experimental results as shown in Figure 2c,d. To get deeper insight into the 2D morphology, slices of the TPA-PF crystal structure are exhibited in Figure 3e and Figure S8 (Supporting Information) to disclose the molecular packing arrangement in three directions separately. Viewed perpendicularly to the ac plane, Figure 3e presents ordered layer stacking of TPA-PF molecules with an ILB manner viewed from the b-axis of the crystal lattice.

Figure 3. Structure characterizations and ILB molecular arrangements of TPA-PF nanosheets. a) TEM image of TPA-PF nanosheets; inset is the corresponding SAED pattern. b) XRD patterns of the as-prepared TPA-PF organic nanosheets (top) and the standard powder spectrum based on the single crystal data by using the DIAMOND software (bottom). c) 2D-GIXD of a TPA-PF nanosheet film. d) The predicted equilibrium 2D morphology of TPA-PF crystal. e) Ordered layer arrangements of TPA-PF molecules with an ILB manner viewed from b-axis of the crystal lattice.

2.5. Photoelectrical Properties of TPA-PF Nanosheets

Preliminary explorations about the photoelectrical properties of TPA-PF nanosheets were performed. Optical analysis of the TPA-PF sheets, containing photoluminescence emission spectrum, fluorescent quantum efficiency, lifetime, and radiative/nonradiative rate constants are shown in Figure S15 and Table S5 of the Supporting Information. The charge storage capabilities of TPA-PF nanosheets were investigated by AFM and Kelvin probe force microscopy (KPFM) in Figures S16 and S17 of the Supporting Information. Electrons and holes were injected into the nanosheets under ambient conditions by applying different biases with a conductive AFM tip. Typical KPFM pictures taken at different times after negative and positive charge injections show a similar behavior: the surface potential could remain for at least 960 s, as displayed in Figure S16a,b of the Supporting Information. The potential
profiles of the charge spot exhibit that the maximum surface potential $V_{\text{max}}$ and full width at half-maximum are almost the same after charge injection for 500 s (Figure S17, Supporting Information). The regular layer-by-layer packing structures are supposed to be a suitable pattern for charge retention since the gaps between the layers could trap holes or electrons. These results indicate the superior charge retention of the TPA-PF nanosheets that can be further used in memory devices.

3. Conclusion and Outlook

The phenomena of binary cooperative complementary are widespread in Nature and inspired ancient Chinese scholars to propose the concept of “Yin” and “Yang,” which stands for a pair of elements with opposite characters. Recently, this concept was introduced into various fields to design smart materials and surfaces, such as amphiphilic molecules,[7,29] host–guest molecules,[30] donor–acceptor molecules,[31] and superhydrophobicity/superhydrophilicity-switched surfaces.[32] In this work we create an SS–BG molecule endowed with a pair of opposite elements: supramolecular interaction and steric hindrance. Due to the tailored SSH effect of the attractor–repulsor unity, an interdigital lipid bilayer-like packing motif is derived according to the supramolecular interaction analysis. A monolayer with SS network in the middle and BG on the both sides lays the foundation of a 2D structure. The final organic nanosheet could be taken as an outcome of layer-by-layer assembly of ILB monolayer and the design mechanism is illustrated in Scheme 2. This strategy is expected to be general and effective to fabricate high-quality 2D molecular nanocrystal with special photoelectric properties by integrating different functional SS (carbazole, pyrene, perylene, etc.) and BG (spirocyclic aromatic hydrocarbon: SFX, SBF, SFDBAO, etc.)[33] and contribute to the development of binary cooperative complementary principle as well as synergistically molecular attractor–repulsor theory.

4. Experimental Section

Fabrication of Organic Microcrystals: TPA or TAP-PF in THF solution was injected into 5 mL vigorously stirred deionized water/aqueous surfactant with stirring, and then was maintained under ambient conditions. After being stirred for 5 min, the sample was left standing for about 48 h to stabilize the nanostructures. Subsequently, the samples underwent centrifugation and were washed with pure water three times. Note that the nanosheets still remain the same as freshly prepared ones after aging for 60 d in aqueous solution. The result indicates that these 2D nanocrystals are stable at room temperature. The synthesis conditions are recorded in Tables S2 and S3 of the Supporting Information. The TPA-PF was synthesized via a previously reported route.[34]

Structural Characterization of the Organic Microcrystals: The nanocrystal morphologies were examined by SEM at 10 keV (Hitachi S-4300). For preparation of the SEM samples, a drop of the as-prepared dispersion was deposited onto a freshly cleaned wafer. TEM and SAED studies were taken on a JEOL JEM 2010F transmission electron microscope, operating at an accelerating voltage of 120 kV. The TEM samples were made by placing a drop of the as-prepared dispersion gently onto the TEM grid. Samples for XRD measurements were prepared by depositing a drop of a suspension onto the Si slide and allowing it to dry in air. XRD spectra were recorded on a Rigaku X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å), and the operating 2θ angle ranged from 5° to 70°, with the step length of 0.025. The geometric model and the surface free energy ($E_{\text{surf}}$) calculations were performed using the Forcite and Morphology modules of Materials Studio Software. The charge trapped and retention experiments were performed using Bruker’s Dimension Icon Atomic Force Microscopy under ambient conditions. Charges were injected by applying the controllable bias on the conductive AFM tip (Bruker’s Pt/Ir-coated probe tip with a resonant frequency 75 kHz and the spring constant 2.8 Nm$^{-1}$ in the contact mode. During this period, the tip was brought into contact with the sample surface and maintained at a specific location for 10 s. The strong electric field between the tip and the sample induced an injection (for negative tip bias) or an extraction (for positive tip bias) of electrons from the tip to the sample by tunneling without obvious modification of the sample topography. Upon charging, the lateral distribution of trapped charges was monitored by scanning with electrostatic force microscopy (EFM) measurement, which was able to record the phase shift signal induced by the long range electrostatic force gradient in the lift mode. In the experiments, the lift height $z$ between the tip and the sample was set to 50 nm for EFM scanning. The van der Waals forces and the long-range electrostatic force interacting with the cone of the tip and the cantilever were to be neglected. The Cambridge Crystallographic Data Centre number (CCDC.) of TPA-PF and TPA was 1475119 and 1319035, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
Acknowledgements

Y.X.L. and S.S.W. contributed equally to this work. The project was supported by the National Natural Science Funds for Excellent Young Scholar (213322402), the National Natural Science Foundation of China (U1301243, 61604081, 21774061 and 61605090), Doctoral Fund of Ministry of Education of China (20133231100007), Excellent science and technology innovation team of Jiangsu Higher Education Institutions (20133231100007), Natural Science Foundation of Jiangsu Province, China (BM2012010), the Six Talent Peaks Project of Jiangsu Province (XCL-CXTD-009), Project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions, PAPD (YX03002), and NUPTSF (NY215055 and NY215061).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D organic nanosheets, attractor–repulsor, interdigil lipid bilayers, molecular design, supramolecular steric hindrance