Post-print of Molecular Engineering of Functional pi-Systems

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Date: 2017-02-08T00:00:00+00:00

Abstract

-molecules refer to organic molecules in which carbon atoms are interconnected via sp^2 or sp hybridization or bonded to heteroatoms, thereby forming delocalized orbitals. Research on the synthesis, reactions, and aromaticity properties of -molecules has long constituted one of the core subjects of chemical science. Studies on -molecules also create new opportunities for the development of other disciplines. The widespread applications of -molecular systems in numerous fields such as information, energy, and life sciences have given rise to and promoted the development of the research field of organic optoelectronic functional materials and devices. -systems can realize photoelectric conversion, electro-optic conversion, thermoelectric conversion, molecular fluorescence, and chemical signal response, thus engendering -system-based organic photovoltaic devices (OPV), organic light-emitting diodes (OLED), organic field-effect transistors (OFET), biological/chemical fluorescence detection and fluorescence imaging devices, among others. More critically, -molecular materials can regulate their structure and properties through molecular design, molecular tailoring, and molecular assembly, thereby achieving functional diversification of devices. Utilizing -molecular materials, large-area flexible devices can be fabricated through printing and other methods. These unique advantages and characteristics of functional -molecules determine that organic and large-area electronics based on -molecules represent another major milestone since the establishment of silicon electronics. Molecular engineering research on -molecular systems involves multiple disciplines including chemistry, physics, materials science, semiconductors, and microelectronics, constituting a fundamental research field that is forward-looking, exploratory, interdisciplinary, and holds significant application prospects. China has achieved some important results in this field, with research levels basically synchronized with international standards, and is currently at a critical juncture poised for breakthroughs, urgently requiring multidisciplinary, institutionalized scientific research organizational models.

Full Text

Preamble

Strategic Priority Research Programs (Category B) of the Chinese Academy of Sciences
ChinaXiv Collaborative Journal
Molecular Engineering of Functional pi-Systems

1. Project Background and Significance

Major corporations worldwide are investing heavily to seize the commanding heights of pi-system research. However, investigations of pi-molecular systems remain in the stage of basic and applied fundamental research, facing numerous scientific challenges and technical hurdles that require national-level coordination, sustained support, and integration of existing research talent and infrastructure to enhance efficiency and achieve breakthroughs through innovative research organization models. Pi-molecules are defined as organic molecules in which carbon atoms are connected via sp^2 or sp hybridization or bonded to heteroatoms, forming delocalized orbitals. The synthesis, reactions, and aromaticity of pi-molecules have long constituted core topics in chemical science, while research on these molecules also creates new opportunities for other disciplines.

The broad applications of pi-molecular systems in information, energy, life sciences, and other fields have catalyzed the development of organic optoelectronic functional materials and devices. Pi-systems enable photoelectric conversion, electro-optical conversion, thermoelectric conversion, molecular fluorescence, and chemical signal response, thereby spawning organic photovoltaic devices (OPV), organic light-emitting diodes (OLED), organic field-effect transistors (OFET), bio/chemical fluorescence detection, and fluorescence imaging devices based on pi-systems. Critically, pi-molecular materials enable diversified device functions through molecular design, tailoring, and assembly, offering tunable structures and properties. These materials also facilitate large-area flexible device manufacturing via printing and coating methods. These unique advantages position organic and large-area electronics based on pi-molecules as a major development comparable to the establishment of silicon electronics.

Research on molecular engineering of pi-systems involves chemistry, physics, materials science, semiconductors, microelectronics, and other disciplines, representing a forward-looking, exploratory, interdisciplinary field with significant application prospects. China has achieved important results in this area, with research levels essentially keeping pace internationally. The field now stands at a critical juncture poised for breakthroughs, necessitating interdisciplinary, institutionalized research organization models. Pi-molecular systems hold important application prospects in next-generation electronic devices, energy, information, and public health, with major international corporations actively competing in this strategic domain.

On May 22, 2014, the Chinese Academy of Sciences officially launched the Strategic Priority Research Program (Category B) “Molecular Engineering of Functional pi-Systems,” hosted by the Institute of Chemistry, with Academicians Zhu Daoben and Wan Lijun serving as chief scientists. The characteristics and functions of pi-molecular systems are determined by the unique behavior of charge carriers within the system. Therefore, the key scientific questions requiring resolution in this field are: How can we design new pi-system molecules with excellent comprehensive performance? How can we understand the assembly rules and regulation principles at micro/nano scales and their influence mechanisms on physical properties? How can we achieve high-performance optoelectronic device construction through new designs, methods, and technologies?

Addressing these critical issues, the program team conducts strategic research along the main line of precise molecular creation—controllable structural regulation—intelligent functional application, focusing on three aspects: design and efficient synthesis of pi-molecules, assembly and regulation of pi-molecules, and device engineering of pi-molecules. Through the support of this strategic program, the team has assembled an internationally influential research force to conduct systematic innovative research and collaborative 攻关, further enhancing China’ s research level in pi-molecular systems and seizing the commanding heights in basic and applied research in this field.

2. Program Progress

Molecular engineering of functional pi-systems represents an interdisciplinary frontier field, a strategically competitive domain, and one of CAS’s advantageous areas, 孕育着 numerous innovative opportunities. The program aims to integrate CAS’ s research strengths in pi-molecular materials to comprehensively lead the field’ s development, concentrate superior teams for collaborative innovation, achieve new breakthroughs in functional pi-system assembly and devices, form an internationally influential “innovation highland,” and develop proprietary flexible device preparation and integration technologies to seize the technological commanding heights and support emerging industries.

Under the leadership of chief scientists Academicians Zhu Daoben and Wan Lijun, the program has conducted integrated planning and concentrated superior forces to address key scientific questions. After two years of research, important progress has been achieved in pi-molecule design and efficient synthesis, pi-molecule assembly and regulation, and pi-molecule device engineering, successfully completing program tasks and targets. The team has published 109 papers in Nature sub-journals and leading international chemistry and materials journals (such as JACS, ANGEW, Advanced Materials, etc.), applied for 49 invention patents, and obtained 12 authorized patents. The program has yielded a series of achievements, with representative results as follows.

2.1 Creation of High-Mobility Organic Semiconductor Materials

Molecular design and synthesis have always been central to molecular science, while rational design and tailoring of functional molecules represent the innovative source of pi-molecular functional systems. Focusing on program objectives, the team proposed innovative design strategies, synthesized a batch of high-mobility organic semiconductor materials with performance reaching internationally leading levels, with some achievements guiding the field' s development.

(1) Creation of p-type organic semiconductor materials with excellent comprehensive performance reaching world-leading levels. The team obtained single crystals of two crystalline phases of n-hexyl-substituted dibenzo[d,d']thieno[3,2-b;4,5-b']dithiophene (C6-DBTDT, molecular structure shown in [Figure 1: see original paper]), discovering that the -phase single crystal exhibits charge carrier mobility up to 8.5 cm^2 V^{1} s^{1}, while the -phase single crystal demonstrates even better electrical performance with maximum mobility of 18.9 cm^2 V^{1} s^{1}, representing one of the highest mobility values reported for small-molecule organic semiconductor materials. The performance difference between these two phases arises from different molecular packing arrangements, with results published in *Advanced Materials*.

(2) Development of n-type organic semiconductor materials with excellent comprehensive performance. The team designed and synthesized furan-thiophene oligomer quinoid molecules (TFT-CN). Due to strong - stacking and CN•••H(thiophene) intermolecular interactions facilitating charge transport, TFT-CN transistors fabricated via solution processing achieved mobility of 7.7 cm^2 V^{1} s^{1}, one of the highest values reported for solution-processable, air-stable n-type organic semiconductors ([Figure 2: see original paper]). Related results were published in *Advanced Materials*.

(3) Investigation of structure and transport properties in novel donor-acceptor systems formed by aromatic ligands as donors and transition metal ions as acceptors. Through liquid-liquid interfacial reaction between multidentate ligand hexathiolated benzene and divalent copper ions at room temperature, the team successfully prepared highly crystalline two-dimensional lattice films (Cu C S) ([Figure 3: see original paper]) with room-temperature electrical conductivity exceeding 1500 S cm^{1} and both electron and hole mobilities reaching 100 cm^2 V^{1} s^{1}, achieving the highest performance metrics among current organic materials. This result demonstrates the tremendous potential of such two-dimensional conjugated systems for high-performance organic charge transport functional materials, with related achievements published in *Nature Communications*.

2.3 Breakthrough in Field-Tunable Interfacial Assembly

(1) Mild electric field-induced formation of bilayer flower-like structures. Scanning tunneling microscopy (STM) can not only characterize molecular adsorption structures on material surfaces but also serve as an external stimulus to influence adsorption behavior. Leveraging STM electric field effects, the team constructed bilayer flower-like structures of trimesic acid/triazole derivatives and investigated factors influencing their formation: bias voltage magnitude, tip-sample distance, and electric field direction. The study revealed that, compared to the 10 V/m electric field effects reported in literature, this bilayer flower-like structure formed under a mild electric field of only 10 V/m magnitude. By changing the electric field polarity, the bilayer flower-like structure undergoes phase transition to a single-layer Kagome structure ([Figure 5: see original paper]), with results published in *ANGEW*.

(2) Electric field-induced construction of halogen-bonded complex structures. The team systematically studied the regulation of functional molecular assembly structures by non-covalent interactions such as hydrogen bonds and halogen bonds, developing methods to construct halogen-bonded open-framework assembly structures via electric field tuning. By designing molecular assembly precursor active sites and selecting perfluorinated iodobenzene molecules as halogen bond donors and pyridine derivatives as halogen bond acceptors, the team, for the first time, formed binary composite open halogen-bonded grid structures ([Figure 6: see original paper]) under electric field induction using I—N bonds common in three-dimensional crystals, systematically investigating the influence of electrical pulse parameters and synthetic unit chemical structures on halogen bond architectures. Experimental results demonstrate that within a certain pulse voltage range, electrical stimulation methods using different halogen bond synthetic units can yield linear or porous halogen-bonded composite structures. This result contributes to understanding the physicochemical nature of halogen bonds and provides a novel method for constructing surface halogen-bonded supramolecular assembly structures, with related articles published in *JACS*.

2.4 Creation of Record-High Pressure Sensor Sensitivity

Multifunctionalization represents an important trend for further development and application of organic devices, with sensors serving as a key breakthrough. The rapid development in this direction urgently requires new structures and sensing principles. Integrating functional material development and device structural design while fully utilizing the inherent characteristics of organic optoelectronic functional devices, the team constructed a series of high-performance flexible sensors with application prospects. Organic thin-film transistors (OTFT) possess signal conversion and amplification functions, theoretically making them ideal platforms for constructing ultra-high sensitivity pressure sensors. Although excellent OTFT pressure sensors (8.4 kPa^{1}) have been prepared using elastic dielectric layers, such devices face dielectric layer elastic limit issues, making ultra-high sensitivity pressure sensors (100 kPa^{1}) difficult to achieve. The team successfully constructed flexible suspended-gate organic thin-film transistors (SGOTFT) for the first time, effectively avoiding dielectric layer elastic limit problems and making device pressure sensing characteristics dependent on the gate' s mechanical properties. Based on this principle, the team constructed ultra-high sensitivity pressure sensors with sensitivity up to 192 kPa ^{1}, representing the best results among comparable devices ([Figure 7: see original paper]). Related research results were published in *Nature Communications*.

2.5 New Breakthroughs in Organic Circuits

(1) Active-matrix light-emitting diode arrays. Achieving both high mobility and high solid-state fluorescence quantum yield in the same organic semiconductor material faces enormous challenges, yet organic light-emitting transistors and organic electrically pumped lasers urgently require such materials. The team developed 2,6-diphenylanthracene as an organic semiconductor material whose single crystals exhibit 41.2% fluorescence quantum yield while simultaneously achieving hole mobility as high as 34 cm^{2} V ^{1} s ^{1}. Organic light-emitting diodes based on this material reached brightness of 6627 cd m ^{2} with turn-on voltage of 2.8 V. Leveraging the material' s excellent luminescent and field-effect properties, the team prepared active-matrix LED arrays, demonstrating that the LED devices could be effectively driven by their field-effect transistors and showing tremendous potential for organic optoelectronic device applications ([Figure 8: see original paper]). Related results were published in *Nature Communications*.

(2) High-resolution OTFT-OLED sample preparation. OTFTs have existed for 30 years, with individual device performance approaching polycrystalline silicon levels, but integrated device performance still lags behind amorphous silicon. This project developed weak epitaxial growth thin-film transistor technology, achieving integrated device performance >1.0 cm^{2} V ^{1} s ^{1}, surpassing commercial amorphous silicon integrated device levels. Using laboratory technical conditions, the team realized 170 PPI resolution OTFT-OLED sample preparation ([Figure 9: see original paper]), approaching the 180 PPI resolution level of Apple iPad mini. Industrial conditions can easily achieve high-resolution integrated devices. These achievements lay a solid theoretical and technical foundation for promoting OFET application research in China.

2.6 Breaking World Records in Polymer Photovoltaic Materials and Devices

In recent years, non-fullerene organic electron acceptor materials have demonstrated tremendous application potential in polymer solar cells due to outstanding advantages in light absorption and energy level modulation. However, during initial research stages, photovoltaic efficiency of non-fullerene polymer solar cells remained far below results obtained using fullerene acceptors. Researchers systematically designed novel polymer donor materials based on the photoelectric properties and aggregation structures of commercially available polymer electron acceptor materials (N2200) and small-molecule electron acceptor materials (ITIC), preparing photovoltaic devices with world-leading efficiency. Through investigation of polymer PBDB-T and N2200 blend photovoltaic systems, the team successfully revealed that two-dimensional conjugated BDT polymers can form favorable molecular orientations (parallel conjugated planes) with polymer acceptors, thereby doubling polymer/non-fullerene solar cell performance. This work provides important guidance for novel all-polymer solar cell material design and morphology control, with related results published in *Advanced Materials*.

Specifically, photovoltaic devices prepared using benzotriazole-based polymer (J51) blended with N2200 achieved 8.27% photovoltaic efficiency, representing the highest reported efficiency for all-polymer solar cells. Devices prepared using polymer PBDB-T blended with ITIC achieved 12.1% efficiency through comprehensive optimization of photovoltaic device fabrication processes, representing the world' s highest reported result in the entire organic photovoltaic field ([Figure 10: see original paper]).

2.7 Summary

Since its launch, the "Molecular Engineering of Functional pi-Systems" program has achieved a series of major progress and breakthroughs in functional pi-molecular materials with excellent comprehensive performance, controllable assembly of pi-molecules, multifunctional field-effect transistor devices and device integration, and high-efficiency organic photovoltaic devices. The program has assembled domestic high-level research teams and is striving to form an internationally influential "innovation highland" in this field.

3. Future Key Work and Prospects

Through implementation of the Molecular Engineering of Functional pi-Systems Strategic Priority Program, CAS will comprehensively enhance its innovation capabilities in pi-molecular materials and devices, achieving the transformation from "Made in China" to "Designed in China" in this field and leading its development. Specific objectives include:

(1) Develop green and efficient synthesis methods, create several "star pi-molecules" attracting widespread peer attention, generate original high-level research achievements with independent intellectual property rights, and establish China as an internationally influential innovation highland in pi-molecular science and technology frontiers.

(2) Establish novel technologies and methods for investigating pi-functional system assembly processes and structure-property relationships, propose and develop pi-molecular assembly methodologies, achieve controllable assembly of multi-component pi-molecules, and create multifunctional molecular materials.

(3) Clarify structural rules affecting pi-molecular material properties, achieve important breakthroughs in charge transport mechanisms and interface

regulation of pi-molecular materials, propose new theoretical models, and develop several function-oriented novel device structures and principles.

(4) While revealing scientific laws of pi-molecular systems, obtain a series of pi-molecular materials with excellent comprehensive performance to meet different device requirements and construct high-performance optoelectronic devices with practical prospects. For example: organic photovoltaic (OPV) unit devices with energy conversion efficiency exceeding 10% (targeting 15%); large-area flexible OPV devices with 6% efficiency; organic field-effect transistors (OFET) with unit device mobility of 5–35 cm^2 V ^{1} s ^{1}, large-area flexible OFET devices with mobility 3.0 cm^2 V ^{1} s ^{1}, on/off ratio 10 , and threshold voltage 10 V, meeting requirements for active-matrix display drivers, sensors, and radio-frequency identification tags.

Through this program's implementation, original innovations will be achieved at the fundamental level of pi-system construction, assembly, and device research, strongly promoting field development and enabling major breakthroughs in technology integration. This will lay a solid technical foundation for sustainable development of related industries, meet national strategic needs in new materials and new energy, and secure China's leading position in future organic electronics industry competition. The program will establish an independent intellectual property pi-molecular material system, realize the leap from "Made in China" to "Designed in China" for core pi-molecular systems, cultivate the most outstanding and creative generation of research talent through highly challenging interdisciplinary frontier research, form an internationally influential pi-system research highland, and ensure national sustainable competitiveness.

(Host Institution: Institute of Chemistry, Chinese Academy of Sciences)

The program has conducted systematic research around three scientific questions—pi-molecule design and synthesis, pi-molecule assembly and regulation, and pi-molecule device engineering—achieving a series of innovative results. Through innovations in pi-system molecular structures, including creation of novel one-dimensional and two-dimensional conjugated systems, and development of side-chain engineering and molecular energy level regulation strategies, the team has substantially improved charge carrier mobility in pi-molecular materials. The program solved the international challenge of graphdiyne macroscale synthesis, achieved large-area thin-film material preparation, and revealed that graphdiyne exhibits significantly superior properties to conventional materials in lithium-ion electrode materials, supercapacitors, solar cell modification layers, electrocatalysis, and other fields. In pi-molecule assembly and regulation, the team achieved electric-field-tunable interfacial assembly and proposed methods for transferring and controlling chirality information from chiral molecules to non-chiral molecular assemblies using hydrogen bonds. Combining high-performance novel pi-molecules developed in this program, the team created a series of novel electronic devices, including breakthrough high-sensitivity pressure sensors, and achieved high-resolution integration of device arrays and circuits.

The program has fully leveraged CAS' s advantages in multidisciplinary talent and organizational coordination, establishing an interdisciplinary joint research system. During implementation, chemists, materials scientists, and physicists have participated collaboratively, fully embodying the concept of cross-disciplinary cooperation. The program emphasizes youth talent cultivation, achieving good results in team building with reasonable age structure, strong creativity, and good continuity.

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