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doi: 10.3866/PKU.WHXB201908036

www.whxb.pku.edu.cn

Effects of Alkyl-Chain Engineering on the Thermodynamic Properties of Amphiphilic Organic Semiconductors

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Abstract: Due to their special polar structure, amphiphilic molecules are simple to process, low in cost and excellent in material properties. Thus, they can be widely applied in the preparation of functional film materials and bionics related to cell membranes. Therefore, amphiphilic organic semiconductor materials are receiving increasing attention in research and industrial fields. The structure of organic amphiphilic semiconductor molecules usually consists of three



functional parts: a hydrophilic group, a hydrophobic group, and a linking group between them. The adjustment of their correlation to achieve the target performance is particularly important and needs experimental discussion regarding synthetic methodologies. In this work, we focused on the engineering of a substituent alkyl-chain, and an amphiphilic functional molecule (benzo[b]benzo[4,5] thieno[2,3-d]thiophene, named C_nPA -BTBT, n = 3-11) was proposed and synthesized. This molecule links the hydrophobic semiconductor backbone and hydrophilic polar group through alkyl chains of different lengths. Fundamental properties were investigated by nuclear magnetic resonance (NMR) and ultraviolet-visible spectroscopy (UV-Vis) to conform the structure and the band gap properties of the designed organic semiconductor. Thermodynamic features were investigated by thermogravimetric analysis (TGA) and corresponding differential thermal gravity (DTG), which indicate that the functional molecule C_n PA-BTBT (n = 3-11) has a great stability in ambient conditions. Moreover, the results show that the binding ability of the amphiphilic molecule to water molecules was regulated by the odd-even alternating effect of the alkyl chain and the intramolecular coupling with BTBT. Furthermore, differential scanning calorimetry (DSC) and polarized optical microscopy (POM) were used to study the material properties in detail. As the length of the alkyl chain increased, the functional molecule $C_n PA$ -BTBT (n = 3-11) gradually changed from "hard" species with no thermodynamic changes to a transition one with a pair of thermodynamic peaks, and eventually to a "soft" one as a typical liquid crystal with clear observation of Maltese-cross spherulites. The cooling and freezing points were further studied, and the values and trends of their enthalpy and corresponding temperature fluctuated and alternated due to the volume effect, odd-even alternating effect, flexibility, and other functions of the alkyl chain. Three molecular models were proposed according to the thermodynamic study results, namely the brick-like model, transition model, and liquid crystal model. This work presents in-depth discussion on material structure and corresponding thermodynamic properties, and it is an experimental basis for the design, synthesis, optimization, and screening of target performance materials.

中国国家重点研发计划(2017YFA0204901),国家自然科学基金(21727806)和北京市自然科学基金(Z181100004418003)资助项目

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Received: August 29, 2019; Revised: September 12, 2019; Accepted: September 12, 2019; Published online: September 17, 2019. *Corresponding author. Email: guoxf@pku.edu.cn; Tel.: +86-10-62757789.

The project was supported by the National Key R&D Program of China (2017YFA0204901), National Natural Science Foundation of China (21727806) and Natural Science Foundation of Beijing, China (Z181100004418003).

Key Words: Functional amphiphilic semiconductor; Alkyl-chain engineering; Thermodynamics; DSC

烷基链工程对两亲有机半导体热力学性能影响的研究

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摘要:由于特殊的分子结构,两亲功能分子具有易加工、低成本和高性能等优势,因而广泛应用于功能薄膜材料制备和 细胞膜相关的仿生学研究中。于是课题基于侧链工程,设计并合成了一类功能两亲分子C_nPA-BTBT (*n* = 3–11),分子使 用不同长度烷基链连接疏水的半导体骨架和亲水的极性功能基团。使用基于示差扫描量热法的热力学研究分析不同长度 烷基链的体积效应、奇偶性、柔性和其它烷基链特性对材料整体性能影响,并最终根据热力学测试结果,提出了一个三 态分子模型。此工作为功能有机半导体材料设计、合成、优化以及目标性能材料的筛选提供了实验依据。

关键词: 功能两亲半导体材料; 烷基链工程; 热力学; DSC 中图分类号: O642

1 Introduction

With the development of the information industry, demands and requirements of organic semiconductors (OSC) in artificial intelligence and wearable devices are rapidly increasing ^{1–5}. Among them, the functional amphiphilic semiconductor (FAS) molecule has great potential in fabrication of biomimetic thin film morphology ^{6–8} and functional electronic devices ^{9–11}, for the reason that FAS has a special structure, is simple to process, low in cost and easy to form a thin film with good structure and morphology. The amphiphilic semiconductor molecule generally consists of a hydrophilic polar group and a hydrophobic semiconductor group ¹², but so far, the interaction between the two groups and the correspondence between the molecular property and structure are still blurred. This makes it more difficult to design and optimize semiconductor materials to realize the good performance and target properties.

Thermodynamics is an important material research methodology ¹³. It can get information on the phase, structure and stability of materials through methods based on thermodynamics ^{14–17}. This method is fast and efficient, and has gradually attracted more attention by initially applying to amphiphilic semiconductor materials ¹⁸. Therefore, in this work designed and synthesized a FAS we molecule (benzo[b]benzo[4,5] thieno[2,3-d]thiophene, named C_nPA-BTBT, n = 3-11, the structures shown in Scheme 1). We connected the hydrophilic group and the hydrophobic group through alkyl chains with different lengths to study the effects of the chain length on the thermodynamic property of FAS ^{19,20}. The laws summarized from the thermodynamic performance provide an experimental basis for synthesizing and screening functional materials for different purposes.

2 Experimental and computational section2.1 General methods and information

All reagents and chemicals were analytical reagents obtained from Innochem and Sinopharm, China. They are used without further purification unless otherwise noted. The synthetic route is outlined in Scheme 2. All reactions were performed under an inert atmosphere of argon in dry solvents by using standard Schlenk techniques. ¹H and ¹³C NMR spectra were recorded on Bruker-400 MHz NMR ARX400, Germany. Chemical shifts of ¹H and ¹³C NMR signals were quoted to tetramethylsilane ($\delta =$ 0.00) and CDCl₃ (δ = 77.00) as internal standards, respectively. Mass spectra (MS) were recorded on a Bruker APEX IV mass spectrometer, Germany. Ultraviolet-visible (UV-Vis) absorption measurement of organic semiconductors in solution and in thin films (on quartz substrates) were determined with a Perkin-Elmer 950 UV/Vis Lambda spectrometer. USA



Scheme 1Molecular Structures of C_n PA-BTBT (n = 3-11).The semiconductor backbone and the polar group are red and blue,

respectively. Color online.



Scheme 2 Synthetic routine of C_n PA-BTBT (n = 3-11).

Thermogravimetric Analysis (TGA) measurements were performed on TA Instruments Q600 SDT thermal analysis system, USA under N₂ at a heating rate of 10 °C·min⁻¹. Differential Scanning Calorimeter analysis (DSC) measurements were performed by using a TA Instruments Q2000 differential scanning calorimeter, USA under N₂. Both heating and cooling speed were 10 °C·min⁻¹. Polarized optical microscopy (POM) with heat stage were obtained on silicon substrates by using Nikon Eclipse LV100 POL, Japan in reflection mode on a home-made heat stage.

2.2 Synthetics procedures and characterization

Synthetic Routine of C_n PA-BTBT (n = 3-11) were synthesized according to the literature ^{21,22}. To a solution of C_n P-BTBT (0.168 mmol) in dry dichloromethane (1 mL) was added bromotrimethylsilane (0.3 mL). The mixture was stirred at the room temperature under argon atmosphere overnight. 2 mL methanol was added to the mixture and the mixture was further stirred for 2 h. All solvent and reagent were removed under reduced pressure to give a white solid.

C₃PA-BTBT: ¹H NMR (d-THF, 500 MHz, 40 °C): δ 7.95 (d, 1H, J = 8.0 Hz), 7.87 (d, 1H, J = 7.8 Hz), 7.82 (s, 1H), 7.79 (d, 1H, J = 8.1 Hz), 7.39 (m, 2H), 7.32 (d, 1H, J = 8.3 Hz), 2.88 (t, 2H, J = 7.2 Hz), 2.00 (m, 2H), 1.30 (m, 2H); ³¹P NMR (d-THF, 200 MHz): δ 31.44. EI-MS: Calcd. for [M – H]⁻: 361.012747. Found: 361.012749.

C₄PA-BTBT: ¹H NMR (d-THF, 500 MHz, 40 °C): δ 7.96 (d, 1H, J = 7.8 Hz), 7.87 (d, 1H, J = 7.1 Hz), 7.80 (m, 2H), 7.41 (m, 2H), 7.32 (d, 1H, J = 8.4 Hz), 2.80 (t, 2H, J = 7.7 Hz), 1.83 (m, 4H), 1.31 (m, 2H); ³¹P NMR (d-THF, 200 MHz): δ 31.50. EI-MS: Calcd. for [M – H]⁻: 375.028397. Found: 375.027394.

C₅PA-BTBT: ¹H NMR (d-THF, 500 MHz, 40 °C): δ 7.95 (d, 1H, J = 7.9 Hz), 7.87 (d, 1H, J = 7.6 Hz), 7.80 (m, 2H), 7.40 (m, 2H), 7.30 (d, 1H, J = 9.2 Hz), 2.78 (t, 2H, J = 7.7 Hz), 1.67 (m, 6H), 1.50 (m, 2H); ³¹P NMR (d-THF, 200 MHz): δ 32.03. EI-MS: Calcd. for [M – H]⁻: 389.044047. Found: 389.044994.

C₆PA-BTBT: ¹H NMR (d-THF, 500 MHz, 40 °C): δ 7.95 (d, 1H, *J* = 8.0 Hz), 7.87 (d, 1H, *J* = 7.2 Hz), 7.80 (m, 2H), 7.41 (m, 2H), 7.30 (d, 1H, *J* = 8.1 Hz), 2.78 (m, 2H), 1.62 (m, 2H), 1.31 (m, 8H); ³¹P NMR (d-THF, 200 MHz): δ 32.06. EI-MS: Calcd. for [M – H]⁻: 403.059697. Found: 403.059647.

C₇PA-BTBT: ¹H NMR (d-THF, 500 MHz, 40 °C): δ 7.95 (d, 1H, *J* = 8.0 Hz), 7.87 (d, 1H, *J* = 7.5 Hz), 7.80 (m, 2H), 7.41 (m, 2H), 7.31 (d, 1H, *J* = 8.2 Hz), 2.78 (t, 2H, *J* = 7.6 Hz), 1.62 (m, 4H), 1.31 (m, 8H); ³¹P NMR (d-THF, 200 MHz): δ 32.03. EI-MS: Calcd. for [M − H]⁻: 417.075347. Found: 417.076116.

C₈PA-BTBT: ¹H NMR (d-THF, 500 MHz, 40 °C): δ 7.95 (d, 1H, *J* = 8.0 Hz), 7.88 (d, 1H, *J* = 7.6 Hz), 7.80 (m, 2H), 7.41 (m, 2H), 7.30 (d, 1H, *J* = 7.9 Hz), 2.78 (t, 2H, *J* = 7.6 Hz), 1.61 (m, 4H), 1.31 (m, 10H); ³¹P NMR (d-THF, 200 MHz): δ 32.05. EI-MS: Calcd. for [M − H]⁻: 431.090989. Found: 431.091066.

C₉PA-BTBT: ¹H NMR (d-THF, 500 MHz, 40 °C): δ 7.95 (d, 1H, J = 8.0 Hz), 7.88 (d, 1H, J = 7.6 Hz), 7.80 (m, 2H), 7.41 (m, 2H), 7.31 (d, 1H, J = 7.9 Hz), 2.78 (t, 2H, J = 7.6 Hz), 1.60 (m,

4H), 1.31 (m, 12H); ³¹P NMR (d-THF, 200 MHz): δ 32.02. EI-MS: Calcd. for [M – H]⁻: 445.106648. Found: 445.106766.

C₁₀PA-BTBT: ¹H NMR (d-THF, 500 MHz, 40 °C): δ 7.95 (d, 1H, *J* = 8.0 Hz), 7.88 (d, 1H, *J* = 7.6 Hz), 7.80 (m, 2H), 7.41 (m, 2H), 7.30 (d, 1H, *J* = 8.1 Hz), 2.78 (t, 2H, *J* = 7.6 Hz), 1.61 (m, 4H), 1.31 (m, 14H); ³¹P NMR (d-THF, 200 MHz): δ 32.03. EI-MS: Calcd. for [M − H]⁻: 459.122298. Found: 459.122675.

C₁₁PA-BTBT: ¹H NMR (d-THF, 500 MHz, 40 °C): δ 7.95 (d, 1H, J = 7.9 Hz), 7.88 (d, 1H, J = 7.5 Hz), 7.80 (m, 2H), 7.41 (m, 2H), 7.30 (d, 1H, J = 7.8 Hz), 2.78 (t, 2H, J = 7.7 Hz), 1.60 (m, 4H), 1.31 (m, 16H); ³¹P NMR (d-THF, 200 MHz): δ 32.04. ESI-MS: Calcd. for [M + H]⁺: 475.15250. Found: 475.15220.

3 Results and discussion

3.1 Molecular design

We designed and synthesized C_n PA-BTBT (n = 3-11, Scheme 1) functional molecules with benzo[b]benzo[4,5]thieno[2,3d]thiophene (BTBT) as the rigid π -backbone, phosphate groups as polar functional groups, and the two parts were linked through alkyl chains with different lengths (the synthetic procedure in Scheme 2). The molecular design is mainly based on the following three considerations: (i) BTBT is a high-performance semiconductor backbone ^{23,24}. The strong π - π interaction between BTBT groups is beneficial to ensure the performance of electronic devices; (ii) Phosphate groups with strong polar interaction are low in synthesis cost and simple to process ²⁵. (iii) Alkyl chains with different lengths are introduced into the system as substituent, and thus adjust the properties ^{13,14}. The conjugate interaction of BTBT groups, the polar interaction of phosphate groups and van der Waals interaction of alkyl chains enrich the diversity of the thermodynamic performance and enhance the ability of self-assembly.

3.2 Fundamental properties.

The fundamental properties of the functional materials C_nPA-BTBT (n = 3-11) were first studied. The UV-Vis spectroscopy is a molecular spectrum formed by valence electron transitions. The band gap of FAS can be calculated from the initial absorption value of UV-Vis. Fig. 1a,b are the UV-Vis curves of the functional molecule solution in chloroform $(10^{-5} \text{ mol} \text{ L}^{-1})$ and in the solid film, respectively. We found that in the solution, the UV-Vis curves of all functional molecules are substantially coincident, while in the solid phase film, the curves vary greatly. Statistical calculation of the energy gap is shown in Fig. 1c. Compared with the band gaps of solution system at ca. 4.4 eV, the ones of solid film fluctuate and are ca. 1 eV lower on average. This is due to the better arrangement of FAS molecules in the solid film, which makes the transition of valence electrons easier. The curves show a trough and a peak when n = 3 and n = 7, respectively, which may be due to the comprehensive effect of the alkyl chain on the intermolecular arrangement and the conjugation of intramolecular groups. On the other hand, in the case of short alkyl chains (n = 3, 4), the polar group and the semiconductor group are significantly coupled. As shown in Fig.



(a) and (b) are initial absorption range of UV-Vis in solution (10⁻⁵ mol·L⁻¹) and film, respectively. (c) band gaps calculated from (a) and (b); (d) ³¹P NMR spectrum.

1d, ³¹P NMR of phosphate group was conducted. When n = 3 and 4, the phosphorus atom in the phosphate group is chemically shielded from the conjugated BTBT group, which makes a chemical shift up to 0.4 to the low field in comparison with those when *n* is more than 5. It indicates that when n = 3 and 4, the coupling of the phosphate group and BTBT is much stronger than when alkyl chains are longer (n > 5).

3.3 Thermodynamic studies

Thermodynamic studies of functional materials are based on TGA and DSC. The TGA curves are shown in Fig. 2a, and the functional molecules rapidly decompose at ca. 450 °C. The derivatives of the TGA curve are then processed to obtain a differential thermal gravity (DTG) curve, as shown in Fig. 2b. It is found that the FAS molecules show a weak decomposition peak at 180–250 °C, at which time the materials lose the crystal water bound with phosphate groups. The temperature value of the first weight loss peak was extracted and shown in Fig. 2c. It was found that the temperature of the water loss peak fluctuated and fell with the increase of the alkyl chain, indicating that the binding ability of the FAS molecule to water molecules was regulated by the odd-even alternating effect of the alkyl chain and the intramolecular coupling with BTBT. Based on the TGA

test, we performed a detailed DSC characterization of the FAS molecules $C_n PA$ -BTBT (n = 3-11), as shown in Fig. 3. The temperature is heating and cooling at a rate of 10 °C min⁻¹. The first cycle (black solid line) aims to eliminate the effects of thermal history left during processing and remove crystal water to study the intrinsic properties of the FAS molecule. Therefore, the analysis subject is the second cycle (red solid line), in which the thermodynamic temperatures and enthalpy values are listed in Table 1. According to the thermodynamic performance of the FAS molecules, it is found that when the alkyl chain length is 3 or 4, the molecules do not show any thermodynamic peak below the thermal decomposition temperature, so there is no thermodynamic transition and molecular rearrangement during the heating process. It indicates that the molecules have good stability and rigidity for BTBT is strongly coupled with the phosphate group, and the influence of alkyl chain can be neglected, which further confirms the conclusions in UV-Vis and ³¹P NMR tests. However, at this time, due to excessive rigidity, the material may not be suitable for a simple solution processing method such as spin-coating, and it may increase the difficulty of post-processing of device fabrication. As the length of the alkyl chain increases (n = 5, 7), the distance between BTBT and



Fig. 2 (a) TGA plot and (b) DTG plot of C_nPA-BTBT (n = 3–11); (c) fitting curve of the temperatures of the first peak in DTG in (b).



Table 1 Summaries of DSC thermodynamic parameters of C_n PA-BTBT (n = 3-11).

Molecule number (<i>n</i>) –	Heating			Cooling		
	Phase transition ^a	$T_{\rm trans}$ /°C ^b	$\Delta H/(kJ \cdot mol^{-1})^{c}$	Phase transition ^a	$T_{\rm trans}$ /°C ^b	$\Delta H/(kJ \cdot mol^{-1})^{c}$
3	-	_	_	_	-	_
4	_	-	_	_	-	-
5	$Cr \rightarrow IL$	253.0	41.89	$\mathrm{IL} \to \mathrm{Cr}$	227.9	-40.80
6	$Cr \rightarrow LC$	200.5	11.32	$LC \rightarrow Cr$	186.0	-9.34
	$LC \to LC_1$	221.7	11.28	$\mathrm{IL} \to \mathrm{LC}$	212.8	-4.43
	$LC_1 \rightarrow IL$	235.9				
7	$Cr \rightarrow Cr_{meta}$	211.5	39.29	$\mathrm{IL} \to \mathrm{Cr}$	198.1	-41.80
	$Cr_{meta} \rightarrow IL$	226.8				
8	$Cr \rightarrow LC$	196.0	18.59	$LC \rightarrow Cr$	181.0	-14.97
	$LC \rightarrow IL$	224.1	4.89	$IL \rightarrow LC$	220.6	-8.11
9	$Cr \rightarrow LC$	182.6	3.17	$LC \rightarrow Cr$	141.2	-3.32
	$LC \rightarrow IL$	212.2	28.35	$IL \rightarrow LC$	196.7	-30.74
10	$Cr \rightarrow LC$	197.7	25.25	$LC \rightarrow Cr$	171.2	-20.07
	$LC \rightarrow IL$	212.2	3.98	$IL \rightarrow LC$	206.3	-6.35
11	$Cr \rightarrow LC$	171.9	7.39	$LC \rightarrow Cr$	139.4	-11.1
	$LC \to LC_1$	201.4	42.88	$LC_1 \rightarrow LC$	187.1	-36.74
	$LC_1 \rightarrow IL$	208.3		$IL \to LC_1$	201.8	-4.74

^a Cr: crystal phase; IL: isotropic liquid phase; LC: liquid crystal phase; LC₁: liquid crystal phase 1; Cr_{meta}: metastable polymorphic form which converts into the stable crystal phase. ^b Temperature measurement error is ±0.05 °C; ^c enthalpy measurement error is ±0.005 kJ·mol⁻¹.

phosphoric acid increases and the coupling degree decreases, the alkyl chain acts in equilibrium with the conjugation of BTBT and phosphate groups, and a pair of classical fusion and solidification peaks appear in the DSC plots. Furthermore, when the alkyl chain length n is more than 8, the DSC plots show two pairs of thermodynamic peaks and a liquid crystal region between the thermodynamic peaks in the heating or cooling processes. At this time, the length of the alkyl chain in the FAS molecule is sufficient to block the coupling of BTBT and phosphate groups, and dominate the performance of the alkyl chain. In order to demonstrate this, FAS molecules with alkyl chain length of 10 and 11 were selected and incubated at 203.2 °C and 185.3 °C, respectively, according to the liquid crystal temperature region in DSC. As shown in Fig. 4a,b, by the POM, Maltese cross of spherulites, which is the mark of a liquid crystal, was observed in both FAS molecules, which confirmed the liquid crystal properties of the designed FAS materials. It is worth noting that unlike other molecules, the molecular chain length of molecule 6 is moderate, but it has a standard liquid crystal curve of two thermodynamic transitions, which may be caused by fluctuations of the odd-even alternating effect. Moreover, the molecular peak of C11PA-BTBT appeared at the position of 208.3 °C after the main melting peak of 201.4 °C, indicating that the alkyl chain was incompletely free during the melting process due to the excessive length of the alkyl chain, and further structure adjustments need to be carried out. The thermodynamic peak temperatures and enthalpy values were extracted and summarized in Fig. 4d, e. It was found that both the clearing point and the freezing point temperatures and the enthalpy values showed strong odd-even alternating effects. the phase transition temperature was negatively correlated with the chain length, which means the increase in alkyl chain gives the material a degree of freedom, allowing longer alkyl chain molecules to act the same phase transition at lower temperatures. For enthalpy, when n is less than 7, the temperatures of the freezing point and the clearing point go synchronously. But when the alkyl chain length is greater than 7, the peak value of the two peaks in the same process alternates, indicating that the main thermodynamic phase transition is switching. The performance exhibited by the material is a combination of odd-even alternating effects, intramolecular coupling, intermolecular interactions and other related effects. According to the law of material properties, it is the ultimate goal to select and synthesize the most suitable functional semiconductor molecules to meet actual needs.

3.4 Molecular models

Accordingly, it can be divided into three models as the alkyl chain grows as shown in Fig. 5. When the alkyl chain is short (n = 3, 4, Fig. 5a), the BTBT is strongly coupled with the phosphate group, molecular rigidity predominates and alkyl chain interaction is negligible. Molecules do not exhibit the thermodynamic phase transition, which can be described by



Fig. 4 (a) and (b) are POM images showing Maltese cross of C₁₀PA-BTBT preserved at 203.2 °C and C₁₁PA-BTBT preserved at 185.3 °C, respectively. (c) and (d) are temperatures and enthalpy curves of phase transitions from the cooling process. The molecule has only one thermodynamic transition, when the freezing point meets the clearing point.



Fig. 5 Molecular models for C_n PA-BTBT (n = 3-11).

Left (n = 3, 4): brick-like model, the coupling between functional groups and semiconductors is so strong that the molecule shows no flexibility; Middle (n = 5, 7): Functional molecule model with medium chain length; Right (n = 6, 8-11): the liquid crystal model, long alkyl chains predominate with phosphate group and BTBT ignored. The purple dashed line indicates liquid crystal region. Red rectangle, blue circle and black line are the BTBT backbone, phosphate group and alkyl chain, respectively. Color online. brick-like model. As the length of the alkyl chain increases (n = 5, 7, Fig. 5b), BTBT and the phosphate group go separately, which leads to a comparatively weaken coupling. The functional molecule is equivalent in rigidity and flexibility, showing a certain degree of freedom by a simple thermodynamic phase transition. However, as the alkyl chain is further lengthened (n = 6, 8-11, Fig. 5c), BTBT and the phosphate group are completely independent by volume effect. The role of the alkyl chain is dominant at this time, and the material can show prominent liquid crystal properties.

4 Conclusions

In summary, this project designed and synthesized a class of FAS molecules C_nPA -BTBT (n = 3-11). Based on alkyl-chain engineering, the molecule links the semiconductor backbone and the polar group through alkyl chains of different lengths, thereby utilizing the volume effect, the odd-even alternating effect and the flexibility of the alkyl chain to adjust the intermolecular and intramolecular coupling. The project analyzes and summarizes the material properties through TGA and DSC-based thermodynamics studies, and proposes a molecular model, which provides experimental basis for material screening and organic synthesis methodology with target properties.

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