# Alkylene-Chain Effect on Microwire Growth and Crystal Packing of π-Moieties

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Ⓢ Supporting Information

ABSTRACT: We developed a facile approach to modulate molecular arrangement through dimerizing of π-moieties and tuning alkylene-bridge length. Dimers of fluoranthene-fused imide (**DFAI-Cns**) with various lengths of alkylene chains were synthesized by a Diels−Alder reaction followed by decarbonylation. **DFAI-C3** and **DFAI-C5** with odd-carbon alkylene chains display stronger one-dimensional growing tendency and better crystallinity than those with even-carbon alkylene chains. Microwires of dimers with odd-carbon alkylene chains were successfully obtained, and their molecular packing was analyzed by transmission electron microscopy (TEM) and selected-area electron diffraction (SAED). Systematic investigation of their single crystal packing showed that alkylene chains with different lengths produced two kinds of molecular configurations. The V-shaped molecular configuration was observed from **DFAI-C3** and **DFAI-C5** with odd-carbon alkylene chains; however, the Z-shaped one was observed from **DFAI-C4**, **DFAI-C6**, and **DFAI-C12** with even-carbon alkylene chains. Accordingly, we attributed the diverse microstructures and crystallinity of the dimers to their distinct molecular configurations in single crystals. In addition, a computational method was employed to demonstrate the weak intermolecular interactions in these dimers. Our investigation indicates that the introduction of bridging alkylene chains is an effective approach to modulate microwire growth and crystal packing of π-systems in solid state.

KEYWORDS: alkylene-chain effect, organic microwire, crystal packing, fluoranthene-fused imide
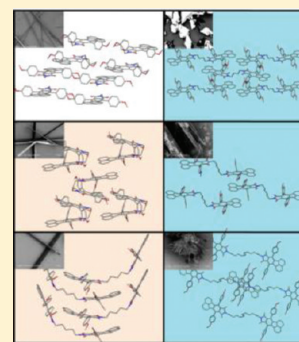
INTRODUCTION

Intensive attention has been paid to one-dimensional nano/microstructures based on π-molecules for their potential applications in integrated nano/micro-optoelectronics,[1] including organic field-effect transistors (**OFET**s),[2] explosive detectors,[3] and photoswitches.[4] The morphology and optoelectronic property of materials have a close relationship with molecular arrangement in solid state, which is determined by their single crystal structures.[1] Various approaches were employed to modulate molecular arrangement in solid state, such as π−π stacking,[5] hydrogen-bonding,[6] donor−acceptor interaction,[7] and hydrophobic interaction.[8] Würthner and Bao reported a twisted octachloroperylene diimide with high OFET performance by proper crystal engineering.[9] Anthony developed a series of silylethynyl-substituted pentacene derivatives, and the crystal structure of pentacene unit was significantly changed from herringbone to brickwork style.[10]

Over the past few years, alkyl chains become more important in molecular engineering and attract more consideration during molecular design for organic materials.[11] Different alkyl chains and their substituted positions in molecular skeletons affect crystal packing and thereby lead to distinct optoelectronic properties.[12] The investigation of Facchetti revealed that N-alkenyl substituents afforded a more compact solid-state structure, enhancing both charge mobility and OPV performance.[11a] Yamaguchi introduced alkylene-chain linkers as macrocyclic restriction, achieving a wide range of fluorescence tuning by changing lengths of the linkers.[13]

In our previous contribution, a series of fluoranthene-fused imides (**FAI**s) were developed and their lowest unoccupied molecular orbital (LUMO) levels were effectively tuned from −3.2 to −3.8 eV through molecular engineering.[14] Herein, we choose **FAI** derivatives as a model to study the alkylene-chain effect on molecular packing in solid state. Alkylene chains bridged two **FAI** moieties to construct a series of dimers of fluoranthene-fused imides (**DFAI-Cns**). They exhibit a different tendency of microstructure growth and crystal packing structures by tuning the length of alkylene chains. Density functional theory (DFT) studies are performed to obtain transfer integrals and understand intermolecular interactions in their crystal packing.

■ RESULTS AND DISCUSSION
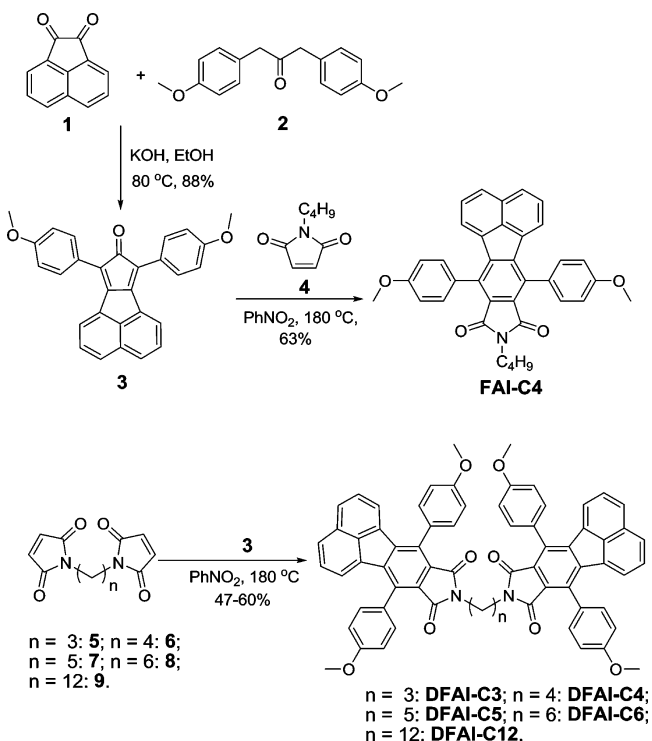
Synthesis and Photophysical Properties. Scheme 1 illustrates the synthetic route to **FAI-C4** and **DFAI-Cns**.

Scheme 1. Synthetic Route to FAI-C4 and DFAI-Cns

Cyclopentadienone **3** was prepared by an aldol condensation reaction with 1,3-bis(4-methoxyphenyl)propan-2-one **2** and acenaphthequinone **1** in a yield of 88%.[14] An efficient Diels−Alder reaction followed by decarbonylation between **3** and **5**−**9**[15] at 180 °C afforded dimers **DFAI-C3**, **DFAI-C4**, **DFAI-C5**, **DFAI-C6**, and **DFAI-C12**. The yields ranged from 47 to 60%. For comparison, model compound **FAI-C4** was also prepared following the same procedure using **3** and 1-butyl-1*H*-pyrrole-2,5-dione **4**.[15]

Compared with **FAI-C4**, dimers **DFAI-Cns** exhibit distinct properties, including solubility and thermal stability. Although the solubility of **DFAI-Cns** is dramatically decreased in common solvents ($CHCl_3$ etc.), **DFAI-C3** and **DFAI-C5** with odd-carbon alkylene chains showed better solubility than **DFAI-C4**, **DFAI-C6**, and **DFAI-C12** with even-carbon alkylene chains. **DFAI-Cns** also have higher thermal stability ($T_d > 380$ °C) than **FAI-C4** ($T_d = 330$ °C).

The photophysical properties of **FAI-C4** and **DFAI-Cns** were investigated both in dilute CH_2Cl_2 solutions and in thin films. As illustrated in Figure 1, all dimers show identical absorption features to model **FAI-C4**, with three absorption peaks at 310, 340, and 404 nm. Absorption spectra in thin films were obtained by spin-casting from their CH_2Cl_2 solution (0.1 mg/mL). The maximum peaks of three absorption bands in thin films show slightly red shift about 10 nm relative to those in dilute solutions. This result reveals that these compounds exhibit weak intramolecular and intermolecular π−π interactions in solid state.

Microstructure Analysis. Figure 2 illustrates scanning electron microscopy (SEM) images of microstructures formed by these compounds. The microstructures were all obtained by
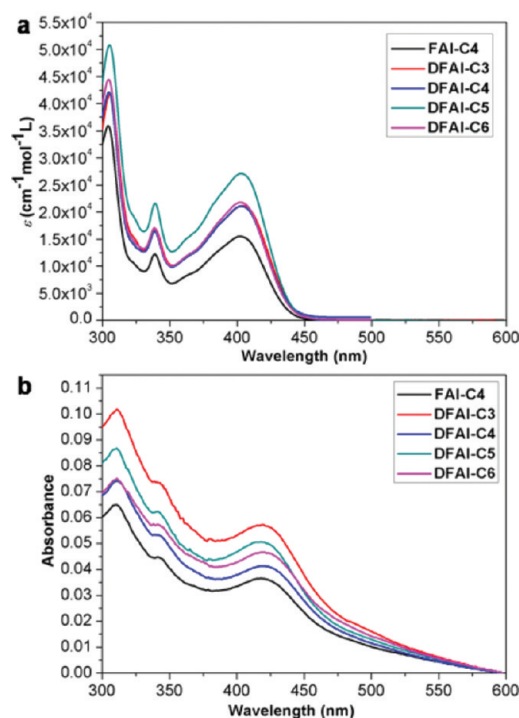
Figure 1. Absorption spectra (a) in dilute CH_2Cl_2 solutions (1×10^{-5} M) and (b) in thin films.
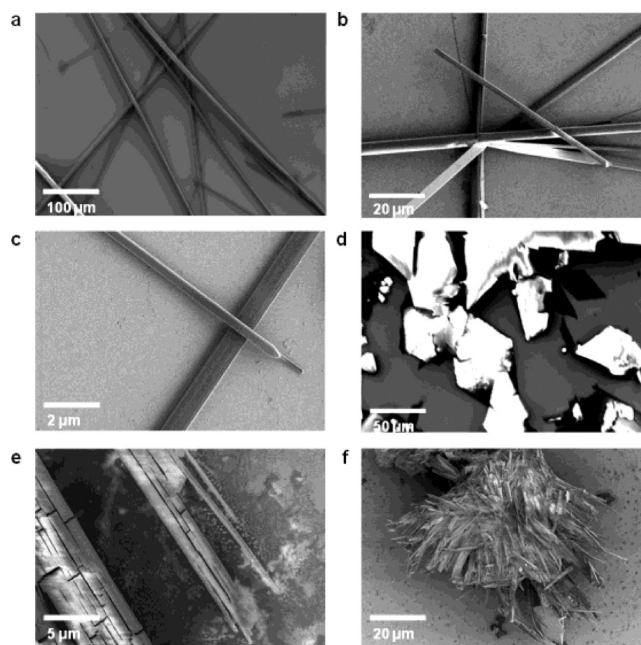
Figure 2. SEM images of microstructures of **FAI-C4** and **DFAI-Cns** obtained by slow evaporation of their chloroform/ethanol mixed solvent. (a) **FAI-C4**, (b) **DFAI-C3**, and (c) **DFAI-C5** with a strong tendency of one-dimensional growth; (d) **DFAI-C4**, (e) **DFAI-C6**, and (f) **DFAI-C12** without oriented growing tendency.

slowly evaporating their solutions (1 mg/mL in chloroform/ethanol mixture). **FAI-C4** forms decent one-dimensional (1D) microwire. **DFAI-C3** and **DFAI-C5** with odd-carbon alkylene chains preserve the same tendency of 1D growth as **FAI-C4** and form well dispersed microwires. In contrast, for dimers with even-carbon alkylene chains, they do not form good 1D assemblies. For **DFAI-C4**, it assembles into thin sheet-like

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microstructure, which is quite bright under the microscope because of electron accumulation on its nonconductive surface. **DFAI-C6** generates brickwork-like assemblies, and the assemblies of **DFAI-C12** display a disordered morphology.

In order to understand the relationship between crystal packing and microstructures, single-crystal X-ray diffraction analysis of these compounds was performed. Employing different crystal growing conditions, we successfully cultivated single crystals of all the compounds. Transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) analysis were used to determine the crystallinity of the microstructures (Figure 3 and Figure S2). **FAI-C4**, **DFAI-**
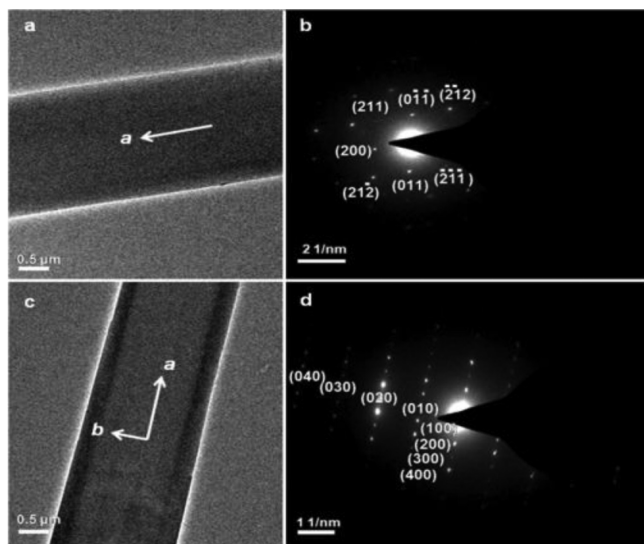

Figure 3. TEM images and SAED patterns of the microwires (the same batch as used in SEM images) formed by **DFAI-C3** (a, b) and **DFAI-C5** (c, d). As indicated by the white arrows, both microwires are growing along the *a* axis.

C3, and **DFAI-C5** exhibit a set of single crystal diffraction patterns, revealing that the microwires are single crystals. In addition, these patterns are indexed according to their single crystals. This result indicates the microwires have identical crystal packing with their single crystals. Both **DFAI-C3** and **DFAI-C5** show good 1D growing tendency along (100) direction (*a* axis). However, SAED patterns of **DFAI-C4** show multiple sets of diffraction spots, indicating its microstructure is

not well crystallized. SAED patterns of **DFAI-C6** and **DFAI-C12** were not obtained due to their poor crystallinity.

Figure 4 shows molecular configurations in single crystals of these compounds. **FAI-C4** has two *p*-methoxyphenyl groups nearly perpendicular to its fluoranthene-fused core. The torsion angle is measured to be 69.5°. **DFAI-C3** (Figure 4b and 4c) and **DFAI-C5** (Figure 4d and 4e) with odd-carbon alkylene chains exhibit a V-shaped molecular configuration; whereas **DFAI-C4** (Figure 4f), **DFAI-C6** (Figure 4g), and **DFAI-C12** (Figure 4h) with even-carbon alkylene chains exhibit a Z-shaped molecular configuration. With a short and odd-carbon bridging alkylene chain, **DFAI-C3** looks like a clip. The dihedral angle of two side walls is 27.0° and the torsion angle is 38.4°. Due to a longer alkylene chain, for **DFAI-C5**, the dihedral angle increases to 64.4° and the torsion angle reduces to 17.7°. This configuration exposes a larger π-moiety to achieve better orbital overlap. **DFAI-C4** has a symmetric molecular configuration with a vertical distance of 2.79 Å between two side walls. The Z-shape of **DFAI-C6** has a little deformation with two nonparallel side walls. Due to a longer bridging alkylene chain, the vertical distance increases to 6.28 Å. However, when the alkylene chain is too long, a gauche conformation is observed in **DFAI-C12**. As a result, the vertical distance of **DFAI-C12** (0.57 Å) between two side walls becomes even shorter than **DFAI-C4**'s. Obviously, alkylene chains in these compounds adopt the optimal zigzag conformation except in **DFAI-C12**. The variation in molecular configurations of **DFAI-Cn**s caused by alkylene-chain effect tremendously changes the whole single crystal packing. The existence of methoxyphenyl groups weakens the $\pi-\pi$ interactions in **DFAI-Cn**s, and hence alkylene chains play dominant roles in crystal engineering.

Crystal Packing and Theoretical Calculations. Figure 5 illustrates the single crystal packing diagrams and DFT calculation results of **FAI-C4**, **DFAI-C3**, **DFAI-C4**, **DFAI-C5**, and **DFAI-C6**. Because the single crystal quality of **DFAI-C12** is not very good, its calculation and analysis are not discussed here (see Figure S3 for its packing diagram). Crystal packing structures were calculated by software Platon[16] to provide the information of distances of $\pi-\pi$ stacking and exact moieties participating in $\pi-\pi$ interactions. DFT calculations were performed to obtain the electron transfer integral, which is an important factor to determine the carrier mobility of organic materials.[17] It was evaluated on the basis of fragment orbital approach[18] together with basis set orthogonalization proce-
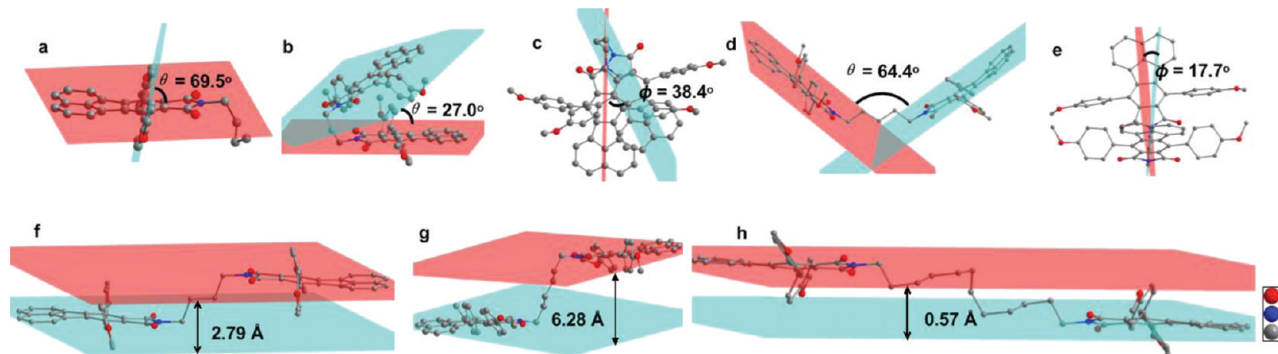
Figure 4. Molecular configurations in single crystals of **FAI-C4** (a), **DFAI-C3** (b, c), **DFAI-C5** (d, e), **DFAI-C4** (f), **DFAI-C6** (g), and **DFAI-C12** (h).
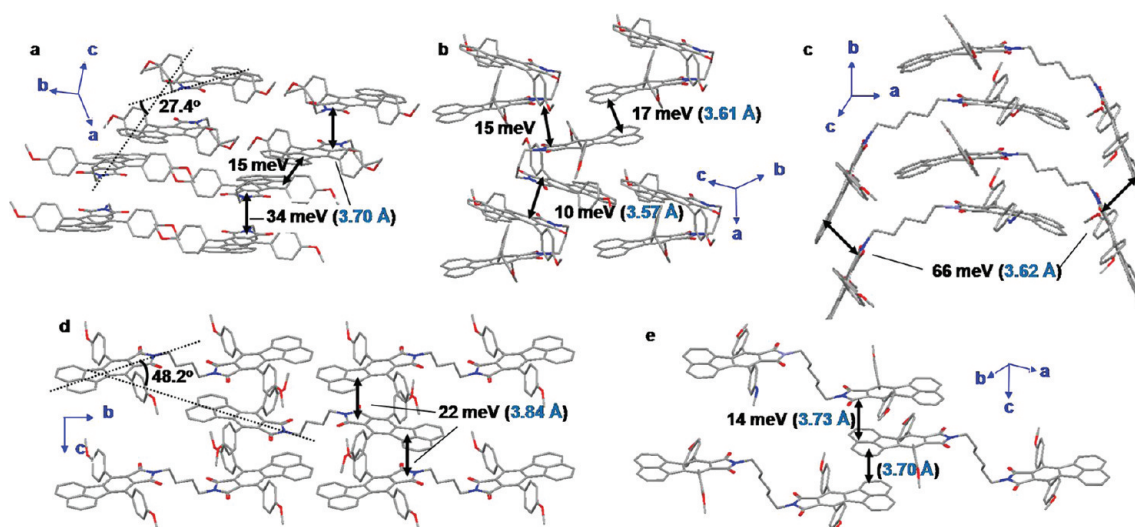
Figure 5. Single crystal packing diagrams and corresponding transfer integrals of (a) **FAI-C4**, (b) **DFAI-C3**, (c) **DFAI-C5**, (d) **DFAI-C4**, and (e) **DFAI-C6**.

dure[19] at the SAOP/TZ2P[20] level of theory using the ADF (Amsterdam density functional) package.[21]

Model **FAI-C4** adopts a lamellar fashion packing structure. Molecules are stacked in pairs through weak π–π interactions of the imide-rings with a rotation angle of 27.4° between every two layers. The π–π stacking distance is 3.70 Å, and the corresponding transfer integral value is 34 meV. The value of 15 meV originates from the overlap between methoxyphenyl group and fluoranthene-fused imide core. Because of large transfer integrals, the microstructure has strong tendency of 1D growth along the π–π stacking direction (see SAED patterns of **FAI-C4** in Figure S2).

DFAI-C3 adopts a sandwich-fashion packing structure, with both intramolecular and intermolecular π–π interactions. Three adjacent molecules are stacked head to head and tail to tail (head: alkylene-chain segment; tail: side-wall segment). The main π–π interactions derive from intermolecular interactions between side walls of adjacent molecules with distances of 3.57 Å and 3.61 Å. They contribute to the transfer integral values of 10 and 17 meV, respectively. However, the intramolecular π–π interactions are quite weak with a long distance of 3.85 Å without any contribution to transfer integrals. With major π–π interactions along the *a* axis, **DFAI-C3** exhibits strong tendency of 1D growth along this direction, which is consistent with its TEM and SAED analysis.

DFAI-C5 adopts a brickwork fashion packing structure, providing slipped face-to-face π–π interactions. The crystal packing diagram is quite similar to that of rubrene.[22] No short-axis displacement is observed, and a suitable long-axis displacement is predicted. There exists a close slipped π–π overlap between side walls with a distance of 3.62 Å, leading to a large transfer integral value of 66 meV. In this crystal structure, sufficient and successive π–π orbital overlap is achieved. With better π–π interactions along the *a* axis than the *b* axis, **DFAI-C5** exhibits a strong tendency of 1D growth along this direction, which has been proved by its TEM and SAED analysis.

For compounds with even-carbon alkylene chains, their crystal packing diagrams are quite different due to the Z-shaped molecular geometry. They all arrange in a lamellar fashion with even weaker and more discrete π–π interactions. **DFAI-C4** has

a good lamellar packing with a π–π stacking distance of 3.84 Å and a transfer integral value of 22 meV (Figure 5d). The rotational angle between layers is 48.2°. The uniform lamellar structure and continuous π–π interactions between layers produce the sheet-like microstructure of **DFAI-C4**. **DFAI-C6** shows π–π distances of 3.70 and 3.73 Å between side walls of adjacent molecules (Figure 5e). The only transfer integral value of 14 meV is attributed to the π–π interactions with the distance of 3.73 Å. Another distance of 3.70 Å has no contribution to the π–π orbital interactions because of a small overlap area between molecules. **DFAI-C12** has even more discrete π–π interactions as shown in Figure S3. Lack of efficient molecular interactions in **DFAI-C6** and **DFAI-C12** finally generates poorly crystallized microstructures. As shown in crystal packing and theoretical calculation data, **FAI** and **DFAI-Cn**s exhibit weak π–π interactions owing to the introduction of the methoxyphenyl groups. This result is coincident with its absorption and emission spectra variation from solutions to thin films.

■ CONCLUSIONS

In conclusion, we have developed a series of dimers **DFAI-Cn**s through the efficient Diels–Alder reaction followed by decarbonylation. Different lengths of alkylene chains are employed in the molecular design as bridging groups to connect two **FAI** units, providing a good understanding of alkylene-chain effect on the molecular arrangement in solid state. Microwires are obtained by dimers with odd-carbon alkylene chains, whereas dimers with even-carbon alkylene chains do not show strong tendency of 1D growth. Single crystal analysis is performed to explain the exact crystal packing in these compounds. Because of weak π–π interactions in this system, the zigzag conformation of alkylene chains is inherited into the molecular geometry of the dimers. For compounds with odd-carbon alkylene chains, they produce a successive and oriented π–π overlap and hence a stronger tendency of 1D growth. However, for the even ones, side walls are away from each other, resulting in discrete and nonoriented molecular interactions. The introduction of methoxyphenyl groups in π-moieties weakens π–π stacking interactions and makes the alkylene chain play dominant roles in crystal packing. DFT

calculations are performed to further confirm the intermolecular interactions. Consequently, the zigzag conformation of alkylene chains well controls the geometry in such a weak π−π interaction system. It provides us a new way to produce desirable organic microwire materials and the concept of careful consideration of alkyl chains during molecular design in weak π-systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedure, single crystal data, ^{1}H and ^{13}C NMR spectra of all the compounds. Figure S1 shows emission spectra in solutions and in thin films. Figure S2 illustrates the TEM images and SAED patterns of **FAI-C4** and **DFAI-C4**. Figure S3 displays the crystal packing structure of **DFAI-C12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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