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Recent advances in chemistry of ladderphanes and related polymers

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ABSTRACT

Ladderphanes are a new type of duplex polymers. The two strands are connected by a variety of linkers via covalent bonds or hydrogen bonds. The backbones for the two polymeric strands can be symmetrical and complementary. In this Report, recent advances on the design, synthesis and properties of ladderphanes and related polymers are reviewed. Certain ladderphanes, whether symmetrical or unsymmetrical, can readily assemble on HOPG surface to exhibit highly ordered patterns. The linkers in these polymers are aligned coherently so that strong interactions between them can take place as revealed by a number of interesting photophysical properties.

Contents

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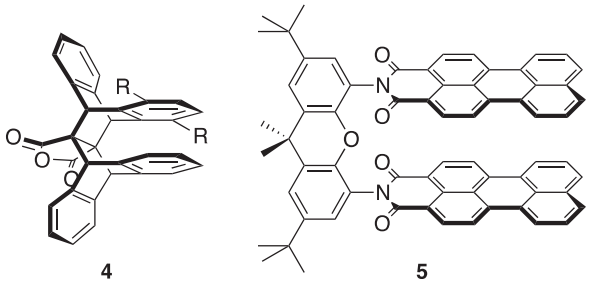
1. Introduction

1.1. General

Interactions between conjugated systems through π-stacking have been demonstrated to play a pivotal role on the properties of organic optoelectronic materials.[1] The spacing separating two interacting π-systems and the relative orientation of these conjugated moieties would be crucial on the performance of these materials. A hypothetical assembly of planar conjugated molecules could be represented by a cartoon shown in Fig. 1. In this regard, all conjugated moieties (rectangles) are aligned co-facially in eclipsed orientation. Such arrangements would be extremely rare for single crystals of the vast majority of small molecules.

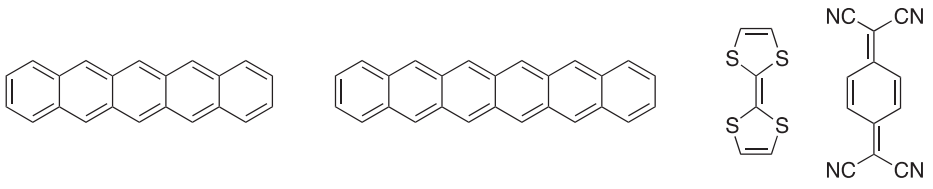
Most of planar small aromatic molecules are packed to form herringbone or sandwich-herringbone patterns in solid state[2] and their conductivities, if any, fall at most into semiconducting level. For example, pentacene **1** is non-conducting at ambient pressure, but becomes semiconductor (10 $\Omega^{-1}cm^{-1}$) at 10 GPa.[3] More recently, the conductivity of hexacene **2** aligned in herringbone arrays is estimated to be 2.2×10^{-6} $\Omega^{-1}cm^{-1}$.[4] In general, long-range π-stacking towards highly ordered alignment of aromatic compounds is not common. The most prominent example comprising uniform segregated and parallel stacks is TTF-TCNQ **3** and the conductivity of this well-organized charge transfer complex is up to 10^5 $\Omega^{-1}cm^{-1}$ at 60 K.[5] Graphite appears to be another example where the conductivity along the axis perpendicular to the planar graphene layers is semiconducting (10 $\Omega^{-1}cm^{-1}$).[6]

hairpins (with core structure like **6)** can take place readily and the unpaired electron can delocalize to more than two layers as revealed by electron paramagnetic resonance (EPR) studies.[9] It is worth mentioning that long range charge transfer has been extensively investigated in DNA molecules.[10]



4 **5**

Through-space coupling between two conjugated systems in [2,2]paracyclophanes (e.g. **7**) has been shown to perturb the photophysical behaviors and second order nonlinear optical properties in comparison with those of the corresponding parent chromophores.[11,12]



1 **2** **3**

1.2. Model studies on π- π interactions

Various model systems have been designed and developed for understanding the mode of through-space π-π interactions between conjugated systems. The chromophores can be fixed onto a rigid framework such that the distance between these chromophores can be controlled and the orientation of these conjugated systems can also be adjusted. For example, both experimental and theoretical evidences suggest that π-interactions between arene moieties have played a key role for the stereoselective formation of the Diels-Alder adduct **4**.[7] Strong electron coupling between two cofacially oriented perylene-3,4-dicarboximide chromophores in **5** and related systems has been observed.[8] Electron hopping among stacked perylenediimide moieties assembled by using DNA

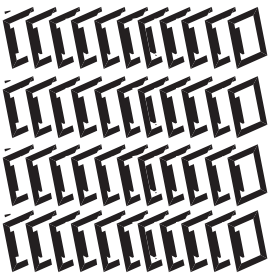


Fig. 1. Possible cofacial assembly of planar conjugated molecules in eclipsed orientations.