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π-Aggregation Control

Macrocyclic Restriction with Flexible Alkylene Linkers: A Simple Strategy to Control the Solid-State Properties of π-Conjugated Systems**

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Molecular orientation of π-conjugated systems has a significant impact on their solid-state properties. The control of their ordering has long been the central issue in the molecular designs of new materials for organic electronics, including organic light-emitting diodes, field-effect transistors, and organic solar cells.[1] A representative strategy is to introduce hydrophobic or hydrophilic chains at the peripheral positions, which enables ordered molecular alignments to be produced through noncovalent interactions (Figure 1 a), leading to the formation of various fascinating supramolecular structures.[2] Construction of a macrocyclic structure is also a promising design for controlling the assembly of the π skeleton, in which the construction of shape-persistent π skeleton is crucial, as their rigid and planar skeletons, such as cyclic oligo(aryleneethynylene)s, are beneficial to forming a one-dimensional assembly through effective π–π stacking interactions.[3] A variety of non-shape-persistent macrocycles consisting of two or more π skeletons connected with flexible linkers have also been synthesized. However, the interest of those studies is mainly to elucidate the intramolecular interaction among the π moieties,[4] and guest-binding behavior in the central cavity,[5] or to establish the ring-opening polymerization methodology,[6] but not to control the molecular alignment in the solid state.[7] We now present the formation of non-shape-persistent macrocycles, which may also be a powerful strategy for attaining a long-range ordering of π-conjugated skeletons.

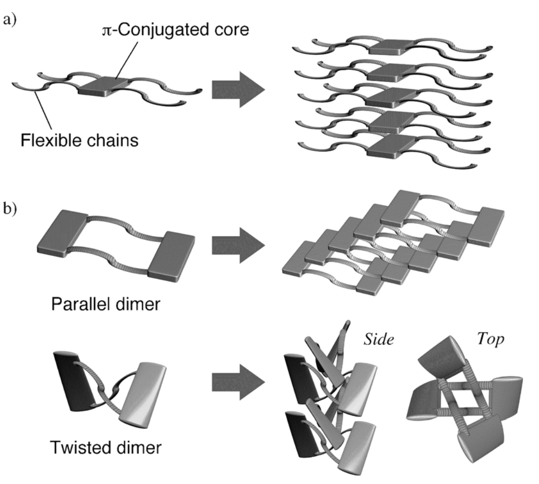
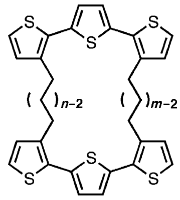


Figure 1. Representation of the control of molecular alignments by flexible chains based on a) flexible chain interactions and b) macrocyclic restriction.

Our idea is to construct a macrocycle by connecting two π-conjugated skeletons with two flexible alkylene linkers of appropriate lengths. The resultant cyclic structure should weakly restrict the intramolecular arrangement of the π skeletons, such as parallel or twisted orientations (Figure 1 b), leading to the formation of each specific packing structure with totally different solid-state properties. To prove the efficacy of this design concept, which we call macrocyclic restriction, we chose a terthiophene as a simple and representative π-conjugated skeleton and synthesized a series of macrocyclic terthiophene dimers that are doubly connected with various alkylene linkers. These compounds indeed exhibited distinct solid-state properties in terms not only of solubility, gelation ability, and phase transition behavior, but also of the solid-state photophysical properties. In particular, we have achieved a wide-range fluorescence tuning simply by changing the lengths of the alkylene linkers.[8,9] The largest difference in the solid-state emission maxima reaches 100 nm.



1 ($n = m = 7$)
2 ($n = m = 6$)
3 ($n = 6$, $m = 7$)

Three macrocyclic terthiophene dimers **1**, **2**, and **3** were designed as the model systems in which two terthiophene units are doubly connected to each other at the 3,3″ positions with different combinations of two alkylene chains, namely hexylene and heptylene. These compounds were synthesized by Kumada–Tamao–Corriu coupling between α,ω-bis(bromobithienyl)alkanes and the Grignard reagents of α,ω-dithienylalkanes under high dilution conditions (see the Supporting Information).

We first determined the X-ray crystal structures of the symmetrically connected compounds **1** and **2**, the structures of

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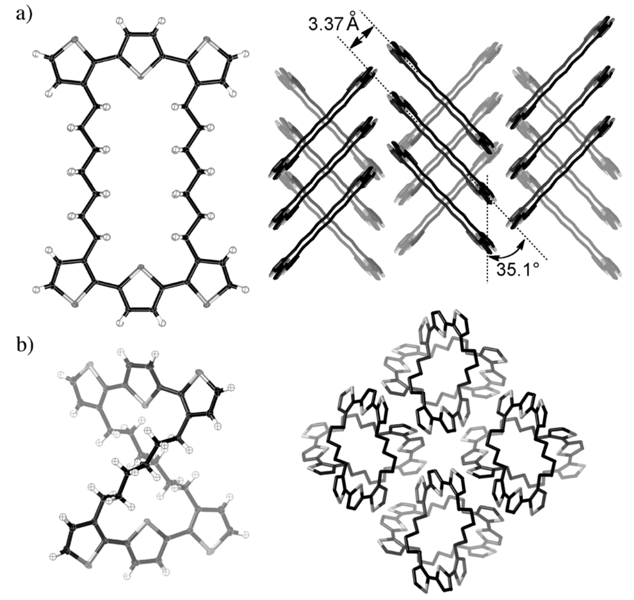

Figure 2. X-ray crystal structures of a) **1** and b) **2**: molecular structure (left) and crystal packing (right). Ellipsoids set at 50% probability; C black, S gray, H white.

which are shown in Figure 2.[10] These two compounds have totally different structures, which depend on the lengths of the alkylene chains.

The two-heptylene-connected structure **1** takes a rectangular planar structure with roughly D_{2h} symmetry. In this structure, each terthiophene unit has a coplanar structure within the mean plane deviation of 0.10 Å (Figure 2a), and the heptylene linkers take all anti conformations. The double connection of the terthiophene skeletons at the 3,3″ positions by the odd-number alkylene chains seems suitable to maintain the high planarity of the terthiophene skeleton without any severe strain.[11] In the packing structure, the rectangular molecules are piled up in a slipped face-to-face fashion. In the stacked column, the intermolecular distance between two adjacent terthiophene mean planes is 3.37 Å and the slipped angle of two adjacent terthiophene units is 35.1°. Between the stacked columns, the adjacent terthiophene units take an edge-to-face arrangement.

The two-hexylene-connected compound **2**, unlike the planar structure of **1**, has a highly twisted saddle-shaped structure with C_2 symmetry (Figure 2b). In this structure, whereas the terthiophene unit still maintains a relatively planar conformation with the torsional angles of 6.2° and 23.5°, the intramolecular arrangement of the two terthiophene units is highly twisted. The dihedral angle of the two terthiophene mean planes is 124°. This arrangement results from a nonlinear geometry of the hexylene chain. Among the five methylene–methylene bonds in each hexylene chain, one bond takes a gauche conformation (see the Supporting Information). The double connection of the two terthiophene units with the even-number alkylene chain forces them to have this arrangement. In the packing structure, the twisted molecules with a helical chirality form a one-dimensional columnar structure, in which the *P* and *M* enantiomers are alternately piled up without π stacking. In the racemic pair, only two weak CH–π interactions are observed between the hexylene chain and the terthiophene unit.

Whereas the symmetrically linked dimers **1** and **2** give high-quality single crystals, unsymmetrical dimer **3** only forms microfibers by slow solvent diffusion, but, instead, exhibits gelation ability in various organic solvents, such as *n*-hexane, EtOH, MeCN, and EtOAc (Figure 3a). It is noteworthy that **3** forms a gel without any strong unidirectional intermolecular interaction, such as hydrogen bonds or dipole–dipole interactions, unlike other low-molecular-weight organic gelators.[12] As shown in Figure 3a, scanning electron microscope (SEM) images of the dried gels of **3** showed intertwined network structures of microfibers, the morphologies of which depend on the solvent used for the gel formation. In EtOH, winding fibers with 0.1–0.5 μm widths form a complicated texture, while in EtOAc, straight whiskers with 0.3–3.0 μm widths construct a bundle structure (Figure 3a).

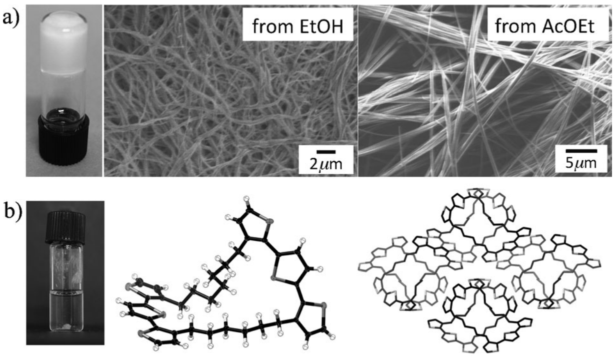

Figure 3. a) Photograph of organogel **3** and SEM images of the dried gels and b) single crystals of **3** transformed from the organogel in EtOAc and its X-ray crystal structures. Ellipsoids set at 50% probability; C black, S gray, H white.

Upon standing at ambient temperature, the gel obtained from EtOAc slowly disappeared and reproducibly formed single crystals in a week, indicating that the kinetically stable gel state transforms into the thermodynamically stable crystalline state.[12] The powder XRD patterns of the dried gel and ground crystals of **3** are quite different from each other (Supporting Information). The crystals are most likely reconstructed through the solution in the equilibrium with the organogel. X-ray diffraction analysis of the single crystal revealed that **3** has a modestly twisted molecular structure (Figure 3b, see also the Supporting Information).[10] One of the terthiophene units is significantly distorted, whereas the other preserves high planarity. Similar to the packing structure of **2**, the bent and twisted molecules of **3** form a racemic columnar structure. Between the adjacent columns, the terthiophene units that have the planar conformation form a weak π–π stacking with 3.5–3.6 Å distance of two terthiophene mean planes.

The unsymmetrical and nonplanar structure of **3** should impede the π–π stacked column formation. The gelation ability of this compound might rely on such a weak intermolecular π–π stacking as that observed in the crystal structure obtained in EtOAc. Notably, despite the weak interaction, the critical gelation concentration (CGC) values of **3** are quite low (0.13–1.3 wt%; see the Supporting Information). The macrocyclic topology should play an important role to assist the kinetically favored gel formation.

The structural features observed for **1**–**3** demonstrate that the macrocyclic restriction by flexible alkylene chains significantly impacts on the intramolecular arrangement of π skeletons and, consequently, on the molecular orientation in the solid state. These distinct molecular arrangements give rise to the following properties that are totally different from one another, despite the fact that all the compounds consist of the identical terthiophene units and simple alkylene chains.

First, these compounds showed different phase-transition behavior in the differential scanning calorimetry (DSC) measurements (Supporting Information).[1d] The comparisons in their solubilities in $CHCl_3$ and melting points (Figure 4a,b) demonstrate an order of crystallinity of **1** > **2** > **3**. This order is consistent with the difference in their crystal packing structures and gelation behavior. Notably, the subtle structural difference between **1** and **3** only by one methylene unit brought about considerable differences in the solubility in $CHCl_3$ (15 times) as well as in the melting point (57 °C lower).

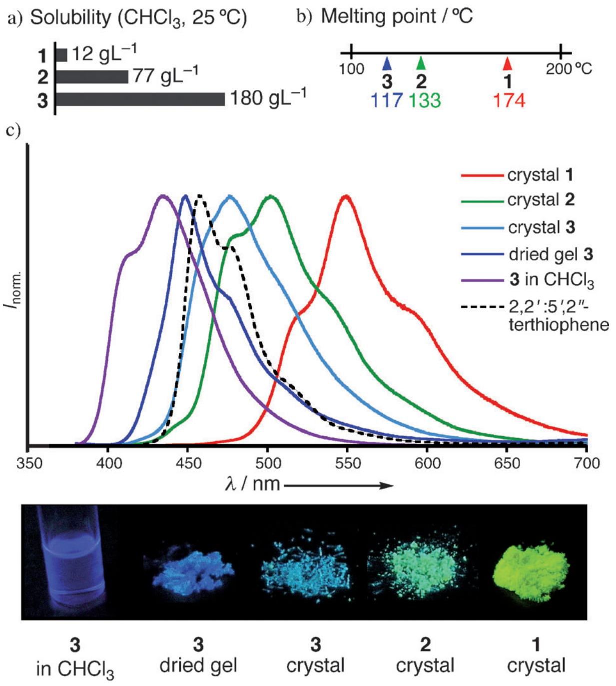

Figure 4. Solid-state properties of **1**–**3**: a) solubilities in $CHCl_3$ at 25 °C, b) melting points, and c) solid-state fluorescence spectra and photographs under irradiation at 365 nm.

Secondly, the more pronounced differences were observed in their photophysical properties (Table 1). Although the absorption and fluorescence spectra of **1**–**3** in solution are almost identical, their fluorescence spectra in the solid state showed significant red shifts in the order of **3** < **2** < **1**. Thus, although the fluorescence maximum wavelength λ_{em} of the dried gel of unsymmetrical dimer **3** is 449 nm,[13] its λ_{em} in the crystalline state is 476 nm. The λ_{em} of **2** and **1** in the crystalline state further shifted to 502 nm and 549 nm, respectively. It is noteworthy that the difference between **3** and **1** amounts to 100 nm (Figure 4c), and the latter compound shows a yellow fluorescence, despite the fact that it only has the simple terthiophene chromophore. The λ_{em} of **1** is longer by about 90 nm even compared with that of the non-substituted parent 2,2′:5′,2″-terthiophene (λ_{em} 456 nm) in the crystalline state. In terms of the fluorescence quantum yield in the crystalline state, the heptylene-linked **1** also has the highest value among these terthiophene series.

Table 1: Photophysical properties of **1**–**3** in solution and in the solid state.

	$CHCl_3$ solution λ_{abs} [nm]	$\log\varepsilon$	λ_{em} [nm]	Φ_F[a]	Solid state λ_{em} [nm]	Φ_F[a]
1	340	4.49	433	0.05	549[b]	0.12[b]
2	339	4.51	436	0.04	502[b]	0.07[b]
3	340	4.52	433	0.04	476[b]	0.06[b]
					449[c]	0.05[c]

[a] Determined by a calibrated integrating sphere system. [b] Measured in the crystalline state. [c] Measured in the dried gel state.

The significant red-shifts in the fluorescence spectra are not due to the formation of excimer, but due to the intermolecular interaction in the ground state in the solid state. The measurements of their diffuse reflectance spectra confirmed that the absorption bands shifted to the longer wavelengths in the order **3** (420 nm) < **2** (460 nm) < **1** (490 nm), consistent with the order of their emission maxima. The red-shift in the absorption maximum wavelength of **1** from solution to the crystalline state is 9000 cm^{-1}, which is much larger than that in the parent terthiophene (2200 cm^{-1}). This significant difference demonstrates the strong exciton coupling of terthiophene units in the layered packing structure of **1**. These results demonstrate the powerfulness of the macrocyclic restriction strategy for the tuning of the solid-state properties.

In summary, macrocyclic restriction by flexible linkages is a useful strategy for the tuning of the solid-state molecular arrangement of π skeletons. This strategy enables us to produce various molecular arrangements from a weakly interacted packing structure to a highly packed structure, which is dependent on the symmetrical/unsymmetrical combinations of the flexible alkylene chains as well as the odd/even effect of the chain lengths. The nonplanar cyclic structure of **3** caused by the unsymmetrical linkages show the gelation ability without any strong intermolecular forces. On the other hand, the symmetrical combination of the odd-number alkylene chains is suitable to connect the two terthiophene skeletons at the 3,3″ positions while maintaining the π planarity. The resultant planar compound **1** produces a strong intermolecular exciton coupling in the crystalline state, giving rise to a significantly red-shifted emission at 549 nm. This is among the longest emission for the simple dialkylated terthiophene chromophores.[11d] This fact demonstrates well the efficacy of this macrocyclic restriction strategy.

Importantly, Amsterdam density functional (ADF) calculations[14,15] on the crystal structure of **1** (PW91/DZP level of theory) gave a large transfer integral value of 63.5 meV in the columnar direction, whereas those of **2** and **3** gave small values (13.0 and 5.8 meV), indicating that this strategy also provides a promising materials with high charge-carrier transporting abilities. Studies along this line using more extended π-conjugated skeletons is now in progress in our laboratory.

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