Diverse dimerization of molecular tweezers with a 2,4,6-triphenyl-1,3,5-triazine spacer in the solid state†

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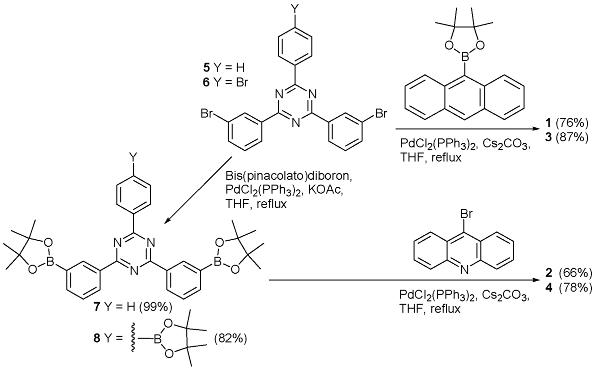
Molecular tweezers with a 2,4,6-triphenyl-1,3,5-triazine spacer exhibit diverse dimerization through π–π stacking interactions in the solid state, and these dimeric species form highly organized supramolecular networks.

Noncovalent interactions of aromatic units such as π–π stacking interactions play significant roles in the stabilization and regulatory functions of both natural (*e.g.* base stacking of DNA and higher order structures of proteins) and synthetic systems.[1] In supramolecular chemistry[1] and crystal engineering,[2] controllable self-assembly process based on π-conjugated molecules in the solid state has been a challenging research topic and should provide an efficient bottom-up strategy for constructing supramolecular architectures, which should be useful as supramolecular electronic materials.[3] In comparison with other conventional interactions, such as hydrogen-bonding and metal coordination, the predictable use of weaker π–π stacking, CH/π and van der Waals interactions for self-assembly systems has remained a great challenge.

Molecular tweezers are host molecules with aromatic pincers separated by spacers at a distance of approximately 7 Å that can efficiently bind planar aromatic guests through the formation of π-sandwich complexes.[4] Most previous studies on molecular tweezers have focused on the formation of heterocomplexes between the tweezers and planar guest molecules.[4]

In this communication, we report that new molecular tweezers **1–4** exhibit diverse dimerization through π–π stacking interactions in the solid state by combining a 1,3,5-triphenyl-2,4,6-triazine (**TPT**)[5] spacer and anthracene or acridine moieties. Furthermore, these dimeric species form highly organized supramolecular networks.[6]

Molecular tweezers **1** and **3** were readily prepared by a Pd(0)-catalyzed Suzuki–Miyaura cross-coupling reaction[7] of 2,4-bis(3-bromophenyl)-6-phenyl-1,3,5-triazine (**5**) or 2,4-bis-(3-bromophenyl)-6-(4-bromophenyl)-1,3,5-triazine (**6**) with 9-anthryl boronic ester. For the introduction of acridine moieties, compounds **5** and **6** were converted to diboronic ester (**7**) and triboronic ester (**8**), followed by Suzuki–Miyaura coupling reaction with 9-bromoacridine to give **2** and **4**, respectively (Scheme 1). The thermal stabilities of **1–4** were investigated by thermogravimetric analysis (TGA) under a nitrogen atmosphere, and their high decomposition temperatures (T_{d5}, corresponding to 5% weight loss) indicated good thermal stabilities (T_{d5} of **1**: 474 °C, **2**: 479 °C, **3**: 517 °C and **4**: 542 °C). These results suggest that compounds **1–4** would be stable under thermal conditions such as in sublimation for purification and vacuum deposition for the fabrication of electronic devices. Indeed, single crystals of **1–4** suitable for X-ray diffraction analysis were obtained by a temperature-gradient vacuum sublimation method.[8]



Scheme 1 Synthesis of **1–4**.

The X-ray crystal structure of **1** shows a *syn* orientation of the anthracene pincers (intercentroid distance between the two anthracene rings = 7.08 Å). As shown in Fig. 2, compound **1** forms a unique self-complementary dimeric structure in which a **TPT** spacer (π-acceptor) of **1** is sandwiched between the

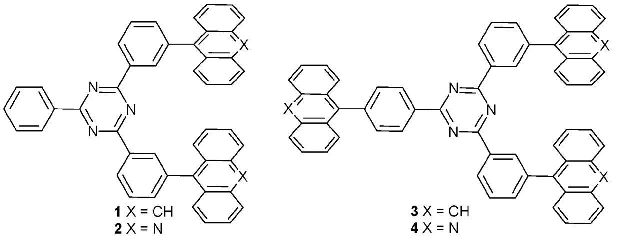


Fig. 1 Molecular structures of **1–4**.

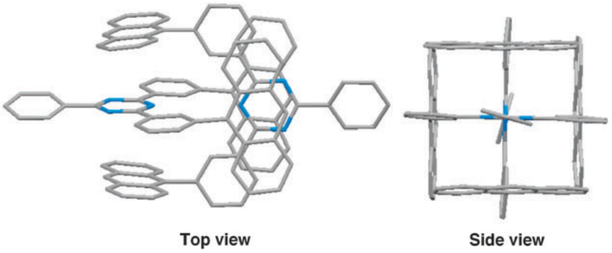


Fig. 2 X-Ray structure of dimer **1·1**.

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anthracene pincers (π-donors) of a neighboring molecule.[9,10] The distance between the anthracene mean plane and the centroid of the triazine ring is 3.47 Å, which indicates π–π stacking interactions between the anthracene pincers and **TPT** moiety. The dimer **1·1** (Fig. 3a) forms an infinite rhombic grid 2-D network sheet *via* slipped π–π stacking interactions between the anthracene moieties of dimeric species **1·1** (Fig. 3b). Simultaneously, phenyl groups attached to the 6-position of the triazine ring of dimer **1·1** act as *supramolecular tenons* (Fig. 3a), which are slightly twisted (dihedral angle between the phenyl plane and triazine plane = 14°, Fig. 2), and attach to *supramolecular mortises* (Fig. 3b) of the rhombic grid sheet by CH/π and van der Waals interactions. As a result, dimeric species **1·1** form a highly organized 3-D network (Fig. 3c) by the infinite mortise and tenon stacking (Fig. 3d) of rhombic grid sheets.

The X-ray crystal structure of **2** with acridine pincers, which are more electron-deficient than anthracene,[4c,j] also shows a *syn* orientation of the two acridine rings (intercentroid distance between the acridine pincers = 7.81 Å). As shown in Fig. 4a, compound **2** forms a self-complementary dimeric structure[11] in which one acridine ring of **2** is sandwiched face-to-face between the acridine pincers of a neighboring molecule with an antiparallel orientation so as to maximize the dipole–dipole interactions (distance between acridine A (mean plane)–B (centroid): 3.54 Å, B (mean plane)–C (centroid): 3.53 Å and C (centroid)–D (mean plane): 3.54 Å).[4c,d] This result indicates that the self-complementary dimerization of **1** and **2** depends on the π-electron property of the pincers. In dimer **2·2**, a **TPT** spacer also forms π–π stacking with that of a neighboring molecule with an antiparallel orientation. As a result, dimeric species of **2** exhibit a tightly packed molecular arrangement due to the good overlapping of π-orbitals (Fig. 4b).

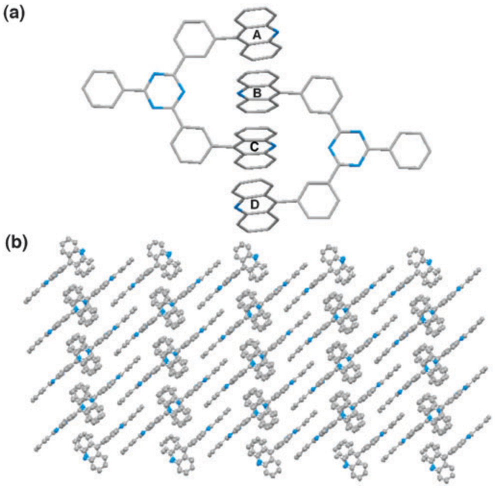

Fig. 4 X-Ray structure of (a) dimer **2·2** and (b) molecular arrangement of **2·2**.

Acenes are promising candidates in molecular electronics, especially in organic field-effect transistors (OFETs).[12] A herringbone (edge-to-face) structure with the minimal overlapping of π-orbitals in the solid state is shown in most of the crystal packing of the acenes.[13] Therefore, to achieve greater charge carrier transport capability, an approach to enforce face-to-face π–π stacking interactions of acenes has been an important topic in OFETs.[14] We expected that the introduction of an additional anthracene moiety might compete with the self-complementary dimerization of **1** and facilitate the formation of a π-sandwich complex between the anthracene moieties. Thus, we designed compound **3** as shown in Fig. 1. The X-ray crystal structure of **3** (intercentroid distance between anthracene pincers = 7.49 Å) shows an infinite 1-D network structure based on a head-to-tail dimeric structure (Fig. 5),

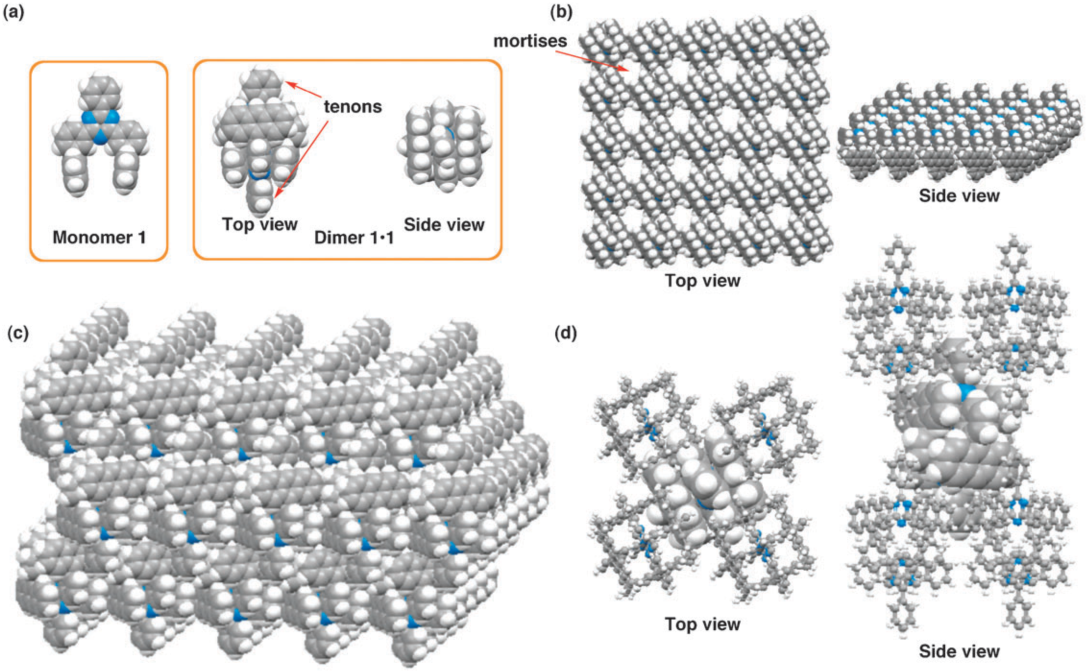

Fig. 3 X-Ray structure of (a) monomer **1** and dimer **1·1**, (b) infinite rhombic grid network formed from **1·1**, (c) 3-D network structure formed from **1·1** and (d) tenon and mortise stacked structure of **1·1**.

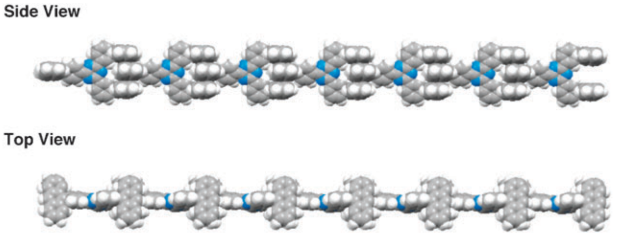

Fig. 5 X-Ray structure of **3** forming an infinite 1-D network based on head-to-tail dimerization.

rather than the self-complementary mode as in **1**·**1** (Fig. 2). The distances between the anthracene mean plane and the centroid of each anthracene pincer are 3.51 and 3.59 Å, which indicates the formation of a π-sandwich complex between the anthracene moieties (Fig. 5). This result suggests that the formation of an infinite 1-D polymeric network promotes face-to-face π–π stacking interactions. A similar result was obtained in the case of **4**, in which the anthracene moieties of **3** are replaced by acridine moieties (see ESI†). The X-ray crystal structure of **4** (intercentroid distance between the acridine pincers = 7.59 Å) also reveals the formation of an infinite 1-D network structure by π-sandwich complexes between the acridine moieties (distances between the acridine mean plane and the centroid of each acridine pincer are 3.53 Å and 3.61 Å).

In summary, we have demonstrated the diverse dimerization of molecular tweezers **1–4** through combination with a 1,3,5-triphenyl-2,4,6-triazine spacer and anthracene or acridine moieties in the solid state.[15,16] The dimeric species make it possible to form well-organized supramolecular networks through π–π stacking, CH/π and van der Waals interactions. These results represent an important example for the construction of higher order structures based on the diverse dimerization of π-conjugated molecules. We are trying to develop supramolecular electronic materials[5] that have a unique assembled state, and the application of these tweezers, especially **3**, to OFETs is ongoing.

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15 When a $CDCl_3$ solution of **1** at 25 °C was diluted from 2.0 mM to 0.4 mM, negligible changes (<0.01 ppm) were observed in the chemical shift values. A similar result was obtained in the case of **3**. We were unable to perform a dilution study of **2** or **4** in $CDCl_3$ because of their poor solubility. In addition, changes in the chemical shifts of **1–4** were not observed at 50 °C. These results indicate minimal contribution of self-assembly of **1–4** in $CDCl_3$.

16 Compound **1** and 2,4,7-trinitrofluorenone (**TNF**) formed a π-sandwich complex in $CDCl_3$. The stoichiometry of the complex **1**·**TNF** was confirmed to be 1 : 1 by a Job plot.[16a] Due to the conformational flexibility of the **TPT** spacer, the K_s value of 1 : 1 complex **1**·**TNF** (K_s = 80 M^{-1} at 25 °C)[16b] was 30-fold lower than that of a molecular tweezer with a pyridine–pyrimidine–pyridine spacer.[4c] (*a*) P. Job, *Ann. Chim. Appl.*, 1928, **9**, 113–203; (*b*) the K_s value was determined by the non-linear least-squares curve-fitting method, see: K. A. Connors, *Binding Constants*, Wiley-Interscience, New York, 1987.