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A one-dimensional array with controlled length from a PYBOX dimer with flexible oligo(*sec*-dialkylammonium cations)†

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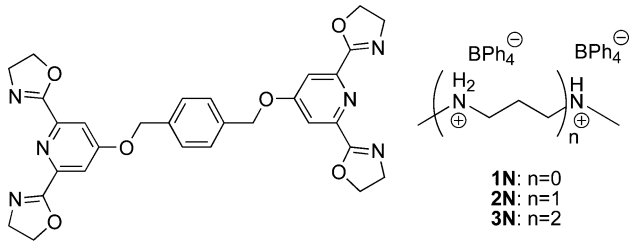
Hydrogen bonded supramolecular ladders were constructed by complexation of PYBOX dimers with flexible oligo(*sec*-dialkylammonium cations).

Molecular design of discrete one-dimensional or two-dimensional arrays of molecules, ions, and functional groups has been of much concern as a bottom-up approach for nano-fabrication, because it has great potential to develop new functional materials as nanowires and quantum dots. Among the supramolecular arrays developed thus so far, it is well-known that the metal complexes of rigid multi-site ligands provide programmed arrays such as molecular racks,[1] ladders,[2] and grids.[3] In such supramolecular architectures, precise control of the rigid ligation sites is required and limits us from using them as scaffolds to arrange functional groups. More recently, another approach by using the rigid helical structure of DNA has been reported.[4,5] Replacing the nucleic acid bases of oligonucleotides with other functional groups produce one-dimensional arrays of dyes[4] and metal ions.[5] Here we demonstrate a new strategy to construct a one-dimensional discrete array by formation of hydrogen-bonded supramolecular ladders. The flexible linkage between the hydrogen bonding sites should expand the adaptability for construction of the one-dimensional supramolecular arrays.

2,6-Bis(2-oxazolyl)pyridine (PYBOX)[6] has been well-known for transition metal catalyzed asymmetric reactions, and there have been extensive studies of the preparations and catalytic activities of various derivatives.[7] More recently, we demonstrated that the convergent molecular structure of the PYBOX ligand was suitable for the recognition of secondary dialkylammonium cations by complementary hydrogen bonds.[8] An X-ray crystallographic study revealed that the complex features an orthogonal geometry. These results prompted us to design and construct discrete one-dimensional arrays by formation of hydrogen-bonded ladders between oligomeric secondary dialkylammonoium cations (**1N**–**3N**) and a PYBOX dimer (**1**).



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The PYBOX dimer (**1**) was prepared from chelidamic acid diester in four steps. The *p*-xylyl group was selected as the bridging group of the dimer, because the two PYBOX ligands faced in opposite directions. Formation of one-dimensional arrays of **1** with a series of oligo-*sec*-dialkylammonium cations (**1N, 2N**, and **3N**) was investigated by ^{1}H NMR, ESI-MS or cold-spray MS in solution, and X-ray crystallography in the crystalline state. First, we investigated complexation of **1** and **1N** as a monomeric model. ^{1}H NMR titrations were carried out in CD_2Cl_2–CD_3CN (2 : 1 *v*/*v*). The addition of **1N** to the solution of **1** caused the oxazoline ring proton resonance of **1** to shift upfield from 0.843 to 0.802, and the benzyl proton resonance exhibited a downfield shift to 9.601 as depicted in Fig. 1(b). The titration experiment indicated that these chemical shift changes were nearly saturated at a 1 : 2 stoichiometry. Moreover, the ESI mass spectrum of a 1 : 2 mixture in acetonitrile (10 μmol dm^{-3}) illustrated the peak of the corresponding 1 : 2 complex at *m*/*z* = 330.38 (M^{2+} − $2BPh_4$). These results indicate that dimer **1** and monomeric secondary dialkylammonium **1N** form a complex with a 1 : 2 stoichiometry.

We then tried to organize higher aggregates using secondary dialkylammonium oligomers (**2N** and **3N**). ^{1}H NMR titration of **1** with **2N** was carried out in CD_2Cl_2–CD_3CN (2 : 1 *v*/*v*). The proton resonances of the oxazoline rings and the benzyl groups in the *p*-xylyl bridging groups showed different behavior from those of **1** with **1N**. The addition of **2N** to the solution of **1** caused the oxazoline ring proton resonance to shift upfield, and they were saturated nearly at a 1 : 1 stoichiometry. However, the bridging phenyl protons moved downfield with slight broadening till one equivalent, and then further addition induced an upfield shift. Similar behaviors were observed for the protons of the pyridine ring and the bridging benzyl protons. The difference in the chemical shift changes between **1N** and **2N** should be attributed to the stacking of the two molecules of **1** along **2N**. Moreover, ESI-MS in acetonitrile (10 μmol dm^{-3}) illustrated the peak of the corresponding 2 : 2 complex with 4+ at *m*/*z* = 336.4 (M^{4+} − $4BPh_4$). Therefore, these results suggest the formation of 2 : 2 complexes with **1** and **2N** in solution.

Slow evaporation of a 1 : 1 mixture of **1** and **2N** in acetonitrile–*n*-hexane–CH_2Cl_2 solution produced a single crystal suitable for X-ray crystallography.‡ The crystal structure is depicted in Fig. 2. In the crystalline state, two molecules of **1** and **2N** form a 2 : 2 complex, and four molecules of tetraphenylborate as counter anions and one molecule of acetonitrile were incorporated in the crystal.

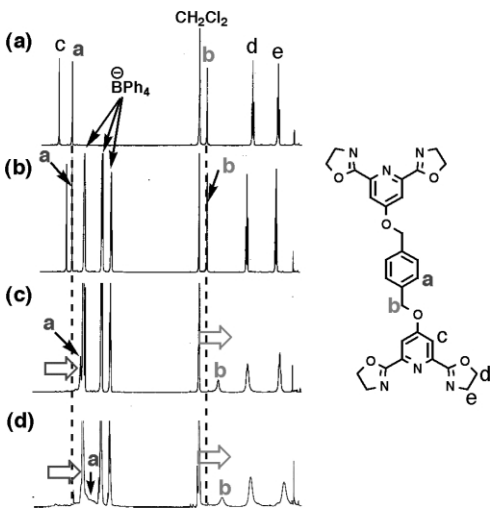

Fig. 1 Complexation induced chemical shift changs in the phenyl and benzyl protons of **1** in the ^{1}H NMR spectra; (a) **1** only, (b) **1** and **1N** (1 : 2), (c) **1** and **2N** (1 : 1), and (d) **1** and **3N** (3 : 2).

† Electronic supplementary information (ESI) available: preparation of **1**; ESI mass spectra of **1** and **1N** (1 : 2) and **1** and **2N** (1 : 1). See http://www.rsc.org/suppdata/cc/b3/b316204d/

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The *p*-xylyl bridge of **1** directs the two PYBOX groups to orientate in the opposite directions, and they independently form complexes with different oligo-iminium cations. On the other hand, both of the two NH_2 groups in **2N** face the same direction due to the trimethylene spacer linkage. As a result, an orthogonal connection *via* hydrogen bonding between a PYBOX group and a secondary ammonium cation provides a discrete 2 + 2 supramolecular assembly with the ladder structure. The PYBOX dimer acts as the side bar of the ladder, and the oligoammonium acts as the rail. The two NH_2^+ groups of **2N** provide the two steps. In the supramolecular ladder, the two molecules of **1** are arranged nearly parallel and the distance between the steps is *ca.* 4.4 Å, which corresponds to the width of the oxazoline ring. This distance is attributed to the *gauche–trans–gauche* conformation of the *n*-propyl linkage, and is shorter than expected for the all-*trans* conformations (*ca.* 4.8 Å)[9] and longer than the stacking distance between aromatic rings (*ca.* 3.8 Å).[10] This result indicates that close packing of the PYBOX ligands along **2N** adjusts the conformations of the *n*-propyl linkage. They enforce the parallel orientation of the two NH_2^+ groups. The cooperative associations between the ladder and the rail provide the novel supramolecular architecture.

Finally, we investigated the solution complexes of **1** and **3N** for a three-step ladder. A 3 : 2 mixture in the same solvent provided the complex ^{1}H NMR spectrum, but the titration experiments indicated a downfield shift of the benzyl protons of **3N** similar to that of **1** and **2N**. This suggests that **3N** stacks the *p*-xylyl groups of **1**. Moreover, CSI-MS (Fig. 3) of the 3 : 2 mixture of **1** and **3N** in $CHCl_3$–CH_3CN 4 : 1 (*v*/*v*) (1 mmol dm^{-3}) gave the corresponding 3 : 2 complexes at *m*/*z* = 3625.3 with the loss of one tetraphenylborate. Higher polymeric species and a 2 : 2 complex with loss of one molecule of **1** were not observed. The chemical shift change of the oxazoline ring in the ^{1}H NMR titration supported the 3 : 2 stoichiometry. Therefore, we believe that **1** and **3N** also produce the ladder type supramolecular assembly.

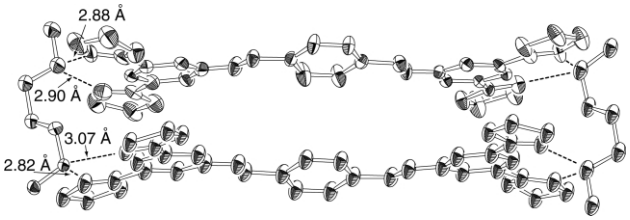

Fig. 2 X-Ray crystal structure of a 2 : 2 complex of **1** and **2N**. BPh_4 anions and hydrogen atoms are omitted for clarity. Dotted line shows the hydrogen bonds and the distances (Å).

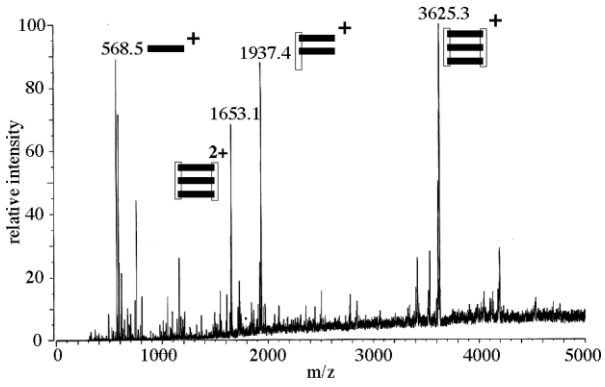

Fig. 3 Cold-spray mass spectrum of a 3 : 2 complex of **1** and **3N**.

In conclusion, we demonstrated novel supramolecular ladder architectures based on **1** as the side bar. The number of nitrogen atoms in the oligomeric *sec*-dialkylammonium cations controls the step of the ladders. The discrete complexes provide one-dimensional arrays arranged along the finite oligomers. Incorporation of various functional groups as the bridging groups between the PYBOX ligands provides a one-dimensional array with controlled numbers of the functional groups. In comparison with rigid ligands in the discrete one-dimensional arrays by metal coordination,[2] the flexible bridging group between connectivities expands the possibilities as a scaffold for one-dimensional molecular arrays. Moreover, structural variations of the PYBOX ligands and secondary ammonium cations would produce various supramolecular architectures. Finally, it is noteworthy that the *n*-propyl linkages between the nitrogen atoms in **2N** and **3N** are not very flexible and useful for adjusting the orientation of the functional groups. This implies validity of the even–odd effects of the methylene chains to control the directions of the functional groups.[11]

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Notes and references

‡ *Crystal data for* **1** + **2N** (1 : 1): $C_{85}H_{87}B_2N_9O_6$, monoclinic, space group $P2_1/a$, a = 19.9186(4), b = 16.1616(3), c = 22.6453(5) Å, β = 91.4827(6)°, V = 7287.5(3) Å^3, D_{calc} = 1.47 g cm^{-3}, θ_{max} = 68.25°, Cu K_α radiation (λ = 1.5418 Å), 296 K, R_1 = 0.095 and R_w = 0.247. CCDC 226408. See http://www.rsc.org/suppdata/cc/b3/b316204d/ for crystallographic data in CIF or other electronic format.

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