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Shyamaprosad Goswami[a]; Subrata Jana[a]; Swapan Dey[a]; Ibrahim Abdul Razak[b]; Hoong-Kun Fun[b]
[a] Department of Chemistry, Bengal Engineering and Science University, Howrah, India [b] X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, Penang, Malaysia

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Recognition of Dicarboxylic Acid by 6,6′-Dipivaloylamino-3,3′-bipyridine and the Supramolecular Solid State Locking of the Carboxyls in the *anti* Form

SHYAMAPROSAD GOSWAMI[a,*], SUBRATA JANA[a], SWAPAN DEY[a], IBRAHIM ABDUL RAZAK[b] and HOONG-KUN FUN[b]

[a]*Department of Chemistry, Bengal Engineering and Science University, Shibpur, Howrah 711 103, India;* [b]*X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM Penang, Malaysia*

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A new crystal-engineering motif has been developed where a ditopic receptor 1 having *anti* binding hindered pyridine pivaloylamide groups instead of normally used acetylamino groups shows a novel *anti–anti* hydrogen bonded polymeric supramolecular complex giving rise to hydrogen bonded stair like polymeric ribbon structure between the receptor pyridine amides and the carboxyl groups of the guest substrate (1,4-phenylenediacetic acid).

Keywords: Molecular recognition; Supramolecular assembly; Polymeric chain; *Anti–anti* arrangement; Host–guest; Bipyridyl

The recognition of carboxylic acids [1] by designed receptors is one of the major interests in molecular recognition research, to mimic many biological events, and also in supramolecular crystal engineering research for the development of novel hydrogen bonded materials. Among the different functional groups, the amide moiety is the most useful binding group as it is the group present in proteins, and also utilized towards the binding of both mono and dicarboxylic acids in solution as well as in the solid phase [2]. We and others have studied [3,4] the recognition of carboxylic acids in both solution and in the solid phase. In our continuing search for new hydrogen bonding motifs [5], we have reported recently the recognition of a dicarboxylic acid, and a new supramolecular network in crystal engineering [6], which forms a *syn–syn* polymeric hydrogen bonded complex, instead of a 1:1 dimeric *syn–syn* or polymeric *syn–anti* complex. In this case an ether linkage separated the binding sites, which was flexible enough to arrange the amide moieties in a *syn* form. So the appropriate spacer governs the position of binding sites and direct the whole supramolecular architecture. Now when we moved our focus to another rigid receptor having no spacer between the pyridine rings, it produced interesting observations. Thus in receptor **1** (Scheme 1), binding pyridyl amide groups are held in the most stable *anti* conformation to recognize the most stable *anti* conformer of 1,4-phenylenediacetic acid, resulting a unique supramolecular network of the complex in solid phase. Thus both the binding groups in respective host and guest remain in the thermodynamically most stable *anti* conformations possibly in the uncomplexed and obviously in the complexed forms as proved by the X-ray analysis. To our knowledge, this is the first report of an *anti–anti* polymeric 1:1 complex in the recognition of a dicarboxylic acid with this type of pyridine amide receptor system.

Recognition of carboxylic acid group by a hindered 2-pyridyl-pivaloylamide moiety [7] is more difficult in comparison with 2-pyridyl-acetamide due to the presence of bulky pivaloyl group. In this communication, we report for the first time to our knowledge, *anti–anti* polymeric hydrogen bonded complex between a ditopic bipyridyldipivaloylamide receptor **1** and 1,4-phenylenediacetic acid as the guest substrate. The analysis of the X-ray

*Corresponding author. Tel: + 91 33 2668 4561-3. Fax: + 91 33 2668 2916. E-mail: spgoswamical@yahoo.com

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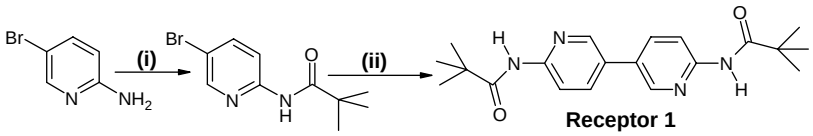

SCHEME 1 ***Reagents and conditions:*** (i) $(CH_3)_3CCOCl$, Et_3N, dry CH_2Cl_2, r.t., 5 h. 90% (ii) $Pd(OAc)_2$, Ph_3P, CuI, Et_3N, CH_3CN, reflux, 12 h, 70%.

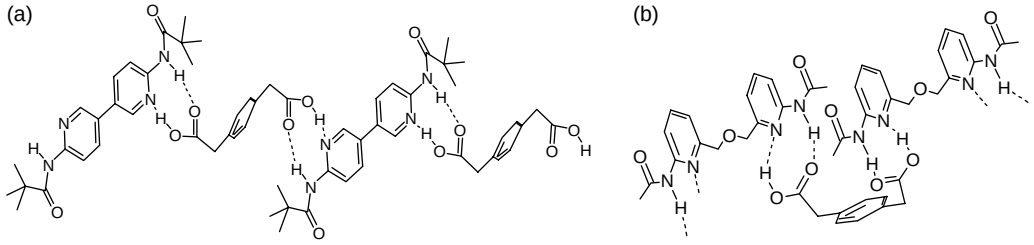

FIGURE 1 (a) Polymeric 1:1 complex of receptor **1** with 1,4-phenylenediacetic acids. (b) Polymeric 1:1 co-crystal structure of receptor *bis*-2-acetylaminopyridyl-6-methylether with 1,4-phenylenediacetic acids [6].

results shows a nice stair-like ribbons in the polymeric complex for the *anti–anti* polymeric hydrogen-bonded supramolecular assembly [Fig. 1(a)] due to the *anti–anti* orientation of the binding sites of receptor **1** in contrast to our recently reported X-ray results [6] of *syn–syn* polymeric structure [Fig. 1(b)].

Receptor **1**, 6,6′-dipivaloylamino-3,3′-bipyridine has two pyridylamide groups without the spacer, which are the potential binding sites for the recognition of dicarboxylic acids and was synthesized according to our recently reported improved palladium catalyzed C—C bond forming reaction (Scheme 1) [8]. The binding behavior of the receptor **1** with 1,4-phenylenediacetic acid was studied both by ^{1}H NMR and UV titration methods.

Addition of solid dicarboxylic acid to a $CDCl_3$ solution of receptor **1** led to dissolution of the normally insoluble acid. To make it more soluble, one drop of DMSO-d_6 was added to the dicarboxylic acid solution. From the ^{1}H NMR spectrum, a moderate down field shift [9] was observed for the amide proton (δ 8.03 to δ 8.25 ppm, $\Delta\delta = 0.22$ ppm) and [G]/[H] *vs.* Δδ plot [Fig. 2] suggested a 1:1 stoichiometry in the formation of a hydrogen-bonded complex. The signals for the benzene ring protons and the CH_2 protons of the guest acid appeared at δ 7.21 and δ 3.53 ppm respectively in the complex. The association constant found by the NMR method [10b] ($K_a = 1.608 \times 10^3\,M^{-1}$), is less compared to our previous pyridine-based receptors for the binding of dicarboxylic acid [3c,4a] and this may be due to the formation of a polymeric 1:1 complex instead of a discrete 1:1 complex. Molecular modeling studies [13], suggest that the receptor **1** binds the guest dicarboxylic acid in a polymeric fashion and the minimum energy of the polymeric complex is 6.43 kJmol^{-1}[13]. This is confirmed by a single crystal X-ray analysis of the cocrystals of the above receptor **1** and 1,4-phenylenediacetic acid.

The receptor **1** showed strong absorbance at $\lambda_{max} = 299$ nm, which gradually decreased on addition of the guest solution. Association constant ($K_a = 5.36 \times 10^3\,M^{-1}$) was measured by the UV method.[10a] between the receptor **1** and 1,4-phenylenediacetic acid using a 10^{-5} M solution of the receptor in $CHCl_3$.

The final proof of formation of a polymeric complex was ultimately obtained from X-ray crystal structure. Crystals of complex [11] of receptor **1** and 1,4-phenylenediacetic acid were grown by slow evaporation at room temperature from the chloroform–methanol (9:1) solution of 1:1 equivalent of receptor **1** and 1,4-phenylenediacetic acid. The unit cell is monoclinic with space group *P21/c*.

Analysis [12] of the X-ray crystal structure of the complex, suggested a supramolecular stair-like [Fig. 3(b)] structure in which one carboxyl group

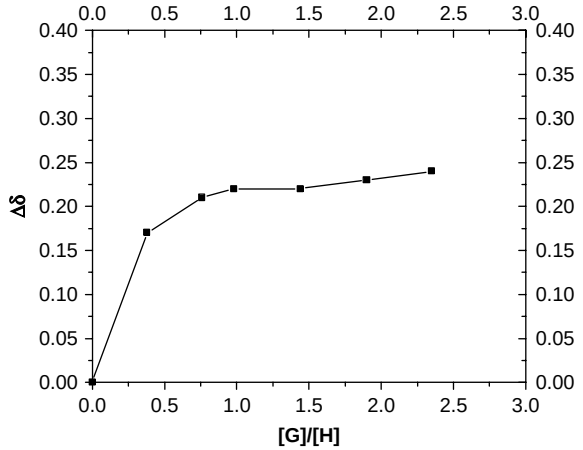

FIGURE 2 ^{1}H NMR titration curve(molar ratio of guest–host *vs.* chemical shift) of receptor **1** with 1,4-phenylenediacetic acid.

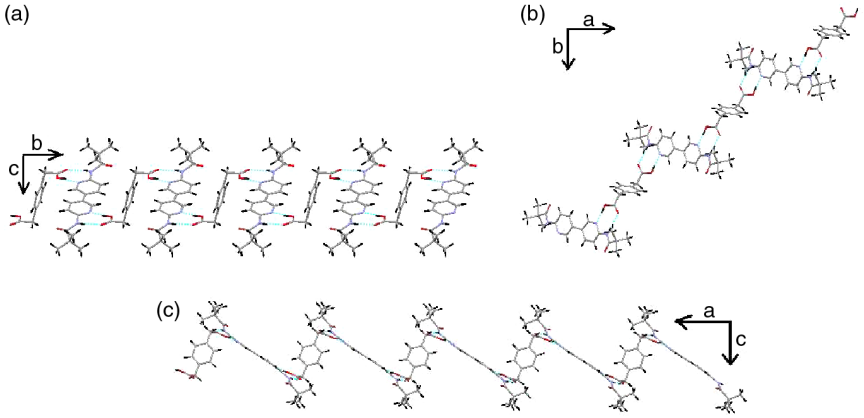

FIGURE 3 Illustrations for the crystal structure of the complex of receptor **1** and 1,4-phenelynediacetic acid: (a) 3D polymeric chain viewed down crystallographic a axis; (b) stair like structure viewed down crystallographic c axis; (c) different stereo-view of hydrogen bonded 3D polymeric form viewed down crystallographic b axis.

binds the pyridine-amide moiety of one molecule and the other carboxyl binds the pyridine-amide moiety of another molecule from the opposite directions. In the solid phase the donor–acceptor array of the receptor and 1,4-phenylenediacetic acid were in the opposite direction and thus both the functional binding groups of respective host and guest are bound in the most stable *anti* arrangement and hence prefers to form polymeric rather than 1:1 discrete dimeric complex. It was also found that in the crystal structure of the complex, the two carboxylic acid groups of the guest acid are *anti* as shown in its energy-minimized structure [13] and are little bit shorter (0.15027 Å) than the actual length of two carboxylic acid groups in energy-minimized form. Another interesting aspect of the crystal structure is that the phenyl ring of the diacetic acid is parallel [Fig. 3(a)] and also the same for the bipyridyl [Fig. 3(c)] part of the receptor in which the two pyridine rings are present in one plane. The distance between —CONH---(CO_2H) and PyN----C—(CO_2H) is 2.153 Å and 1.591 Å respectively which is very much comparable with the carboxylic acid-pyridine acetamide interaction in solid phase [6]. So in this case much bulkier pivaloyl groups don't impose much hindrance for the binding of acid group in the solid phase, rather it may force the formation of different supramolecular architecture which is interesting for the crystal engineering designs. However in the solution phase, the chemical shift change of the amide hydrogen of the pivaloylamino group in the complex is less compared to that in simple acetylamino group on complexation with carboxylic acid.

CONCLUSION:

Thus pyridine pivaloylamide group may be successfully used for the recognition of carboxylic acid and also as an important supramolecular synthon which is proved here by both binding studies in solution phase as well as in the solid phase by the crystal structure of the complex. This motif is unique to form such *anti–anti* hydrogen bonded polymeric stair like ribbons where the benzene rings and bipyridyl units are not involved in the π-stacking interaction. Thus in a bipyridyl diamide system the binding sites are well directed to have the *anti* arrangement in the receptor system which is the driving force to give rise to the formation of a strong polymeric 1:1 complex with the most stable *anti* conformation of the carboxyl groups in the dicarboxylic acid showing a unique *anti–anti* hydrogen bonded polymeric supramolecular assembly. This finding is important in designing such specific new supramolecular architecture involving polymeric 1:1 *host-guest* complex instead of dimmeric 1:1 complex.

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[9] ^{1}H NMR of compound **1**, ($CDCl_3$, 500 MHz): δ (ppm): 8.38 (d, 2H, $J = 2.4$ Hz), 8.27 (d, 2H, $J = 8.7$ Hz), 8.03 (bs, 2H), 7.81 (dd, 2H, $J = 8.6$ Hz), 1.28 (s, 18H). ^{1}H-NMR of compound **1** with 1,4-phenylenediacetic acids, ($CDCl_3 + 1$ drop of DMSO-d_6, 500 MHz): δ (ppm): 8.37 (d, 2H, $J = 2.1$ Hz), 8.28 (d, 2H, $J = 8.7$ Hz), 8.25 (bs, 2H), 7.81 (dd, 2H, $J = 8.7$ Hz), 7.21(s, 4H), 3.53(s, 4H), 1.28 (s, 18H).

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