Supramolecular synthesis of some molecular adducts of 4,4′-bipyridine *N*,*N*′-dioxide†

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Molecular adducts (**1a–1e**) of 4,4′-bipyridine *N*,*N*′-dioxide, **1**, respectively with cyanuric acid, trithiocyanuric acid, 1,3,5-trihydroxybenzene (phloroglucinol), 1,3-dihydroxybenzene (resorcinol) and 1,2,4,5-benzenetetracarboxylic acid have been reported. The major interactions observed in the structures **1a–1e** are N–H···O, N–H···S, O–H···O and C–H···O, in the form of *homomeric* and *heteromeric* patterns of the constituents, either as a single or cyclic hydrogen-bonded motifs. While in the adduct **1a**, both *homomeric* and *heteromeric* units of both the constituents were observed, no *heteromeric* interactions were observed in **1b** and **1c**. In addition, in **1b**, *homomeric* aggregation of molecules of **1** occurred in association with water molecules. However, while *heteromeric* interactions prevail between the constituents in **1d** and **1e**, only one of the co-crystallizing species gave *homomeric* interactions (4,4′-bipyridine *N*,*N*′-dioxide in **1d**; 1,2,4,5-benzenetetracarboxylic acid in **1e**). Further, in either type of the patterns, the cyclic motifs are formed as a pair-wise hydrogen bonds comprising of strong and weak hydrogen bonds (N–H···O/C–H···O or O–H···O/C–H···O). In three-dimensions, the ensembles of molecules yield planar sheets, ladders and pseudorotaxane type assemblies.

Introduction

Design and synthesis of molecular complexes/adducts employing noncovalent interactions such as hydrogen bonds, which is broadly defined as supramolecular synthesis, aims at creation of exotic functional solids and in this connection, exploration of novel ligands is a continuous process.[1] Thus, a variety of ligands of different molecular dimensions and functional properties were utilized for the preparation of numerous supramolecular assemblies of exotic architectures as reported in the recent literature.[2] Among those, 4,4′-bipyridine (bpy) is well studied, especially as a spacer molecule, both in organic and organic–inorganic hybrid complexes. It was mainly due to the ability of bpy to form either O–H···N only or O–H···N/C–H···O pair-wise hydrogen bonds and also dative bonds with metal ions in conjunction with carboxyl/carboxylate and many other functional moieties.[3]

In further exploration and thrust to identify other spacer molecules, compounds that mimic bpy topologically, for example, 1,2-bis(4-pyridyl)ethene and ethane, 1,3-bis(4-pyridyl)-propane *etc*., evolved as novel ligands for the preparation of the tailor-made supramolecular assemblies of desired architectures and properties.[4] Also, in recent times, 4,4′-bipyridine *N*,*N*′-dioxide (*N*-oxide derivative of bpy), **1**, has been well considered in the synthesis of coordination assemblies, but corresponding organic supramolecular assemblies are limited.[5] Since the *N*-oxide, **1** is a potential hydrogen bond acceptor to establish interaction with complementary functionalities such as –OH, –COOH, –NH, –CONH$_2$ *etc*., it is rather surprising that **1** was not utilized, so effectively, in the supramolecular synthesis of organic assemblies, as only a few reports are known in the literature.[6] Apart from it, the native structure of **1** itself is not known in the literature. Thus, we are interested to elucidate the structure of **1** and also study its application in the molecular recognition and supramolecular synthesis with different organic functional moieties such as –OH, –COOH, which are well known to yield discrete molecular recognition patterns.[1c,3b,d] In this direction, our attempts to obtain single crystals of suitable quality for structure elucidation of **1** are not successful yet, but co-crystallization experiments of **1** with cyanuric acid, trithiocyanuric acid, 1,3,5-trihydroxybenzene (phloroglucinol), 1,3-dihydroxybenzene (resorcinol) and 1,2,4,5-benzenetetracarboxylic acid, possessing different functional moieties, as shown in Chart 1, gave molecular complexes in the form of single crystals. The structural features of these unusual molecular adducts, unravel by single-crystal X-ray diffraction methods, are described in this article.

Results and discussion

Solid state structure of molecular complex, 1a, of 4,4′-bipyridine *N*,*N*′-dioxide, 1 and cyanuric acid (CA)

Co-crystallization of **1** and cyanuric acid, **CA**, from a methanol solution gave good quality single crystals, **1a**, in a 1:2 ratio of the reactants and it was characterized by X-ray diffraction methods. The pertinent crystallographic information is given in Table 1.

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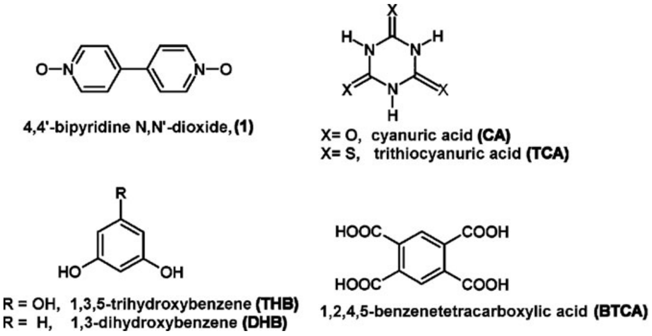


Reactants	Solvent	Products and composition
1 + CA	**CH_3OH**	**1a, (1:2)**
1 + TCA	**H_2O**	**1b.H_2O, (1:2:2)**
1 + THB	**CH_3OH**	**1c, (3:2)**
1 + DHB	**H_2O**	**1d.H_2O, (1:1:2)**
1 + BTCA	**CH_3OH**	**1e, (1:1)**

Chart 1

Analysis of molecular packing reveals that in the complex **1a**, each molecule of **1** establish interaction with two dimers of **CA**, as shown in Fig. 1, by forming two different pair-wise hydrogen bonding patterns of N–H···O (H···O, 1.70 and 1.71 Å; N···O, 2.69 and 2.68 Å) and C–H···O (H···O, 2.38 and 2.44 Å; C···O, 3.34 and 3.33). Such a recognition pattern gave a three-dimensional structure, as stacked layers, which is shown in Fig. 1(b).

However, the arrangement of molecules in a typical sheet is quite intriguing. Although **1** and **CA** established *heteromeric* pattern, each one in turn form one-dimensional crinkled tapes, through *homomeric* pattern by holding the adjacent molecules, as shown in Fig. 2. While **CA** molecules form *homomeric* patterns through cyclic N–H···O hydrogen bonds, with H···O distances being in the range, 1.70–2.02 Å (N···O, 2.60–2.85 Å), molecules of **1** gave such patterns through a cyclic pattern of C–H···O hydrogen bonds and the corresponding H···O distances are 2.36 and 2.40 Å, (C···O, 3.31 and 3.33 Å). Further, the molecular tapes of **1** and **CA** are arranged alternatively in two-dimensional sheets. In fact, the *homomeric* patterns observed for **1** and **CA** are the most commonly observed arrangement in many of their molecular complexes.[7] It is interesting to note that pure crystal structure of **CA** also is due to the aggregation of such molecular tapes,[8] as observed in **1a**, held together by single N–H···O hydrogen bonds, as shown in Fig. 2(b). However, such an inference could not be established about the arrangement of molecules of **1** as its pure crystal structure is not known. However, since

Table 1 Crystallographic details of crystal structures of molecular adducts, **1a–1e**

	1a	**1b**	**1c**	**1d**	**1e**
Formula	$C_{10}H_8N_2O_2$: $2(C_3H_3N_3O_3)$	$C_{10}H_8N_2O_2$: $2(C_3H_3N_3S_3)$:$2(H_2O)$	$1.5(C_{10}H_8N_2O_2)$: $C_6H_6O_3$	$2(C_{10}H_8N_2O_2)$: $2(C_6H_6O_2)$:$4(H_2O)$	$C_{10}H_8N_2O_2$: $C_{10}H_6O_8$
M_r	446.35	578.74	408.38	668.65	442.33
Crystal morphology	Blocks	Blocks	Blocks	Rectangular blocks	Blocks
Crystal color	Colorless	Colorless	Pale-yellow	Colorless	Colorless
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	8.218(3)	22.129(8)	10.111(2)	7.129(1)	12.926(5)
b/Å	9.299(4)	13.217(5)	10.277(2)	10.253(2)	7.948(3)
c/Å	12.168(5)	8.531(3)	10.405(2)	23.220(4)	19.059(7)
α/°	91.93(1)	90	70.61(1)	82.15(1)	90
β/°	91.44(1)	105.82(1)	84.88(1)	85.26(1)	106.54(1)
γ/°	108.10(1)	90	61.60(1)	70.40(1)	90
V/Å^3	882.7(6)	2400.6(15)	902.7(3)	1582.7(5)	1877.0(1)
Z	2	4	2	2	4
D_c/g cm^{-3}	1.679	1.601	1.502	1.403	1.565
T/K	298(2)	298(2)	298(2)	298(2)	273(2)
λ(Mo-Kα)	0.71073	0.71073	0.71073	0.71073	0.71073
μ/mm^{-1}	0.138	0.612	0.112	0.109	0.128
2θ range/°	46.60	46.68	56.54	46.54	56.56
Limiting indices	$-9 \le h \le 9$ $-10 \le k \le 8$ $-13 \le l \le 11$	$-24 \le h \le 24$ $-14 \le k \le 14$ $-9 \le l \le 7$	$-13 \le h \le 13$ $-13 \le k \le 13$ $-13 \le l \le 13$	$-7 \le h \le 7$ $-11 \le k \le 10$ $-25 \le l \le 25$	$-15 \le h \le 17$ $-10 \le k \le 6$ $-25 \le l \le 24$
F(000)	460	1192	426	704	912
No. reflns measured	3845	5055	10278	6950	10778
No. unique reflns [R(int)]	2526 [0.0281]	1739 [0.0229]	4062 [0.0418]	4524 [0.0333]	4347 [0.0238]
No. reflns used	1983	1539	3342	1999	3401
No. parameters	345	193	344	465	345
Reflection	7.32	9.01	11.80	9.73	12.6
GOF on F^2	1.043	1.139	1.038	0.821	1.018
R_1 [$I > 2\sigma(I)$]	0.0612	0.0353	0.0558	0.0438	0.0480
wR_2	0.1520	0.0896	0.1571	0.0971	0.1196
$\Delta\rho_{\max,\ \min}$/e$^-$ Å^{-3}	0.38, −0.44	0.44, −0.39	0.26, −0.34	0.24, −0.23	0.249, −0.288

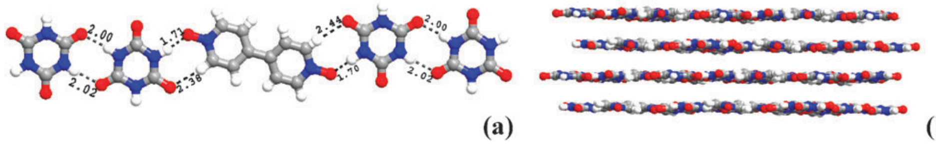


Fig. 1 (a) Molecular recognition between **1** and **CA** in the crystal structure of **1a**. (b) Three-dimensional arrangement of molecules in the crystal structure of **1a**, in the form of stacked layers.

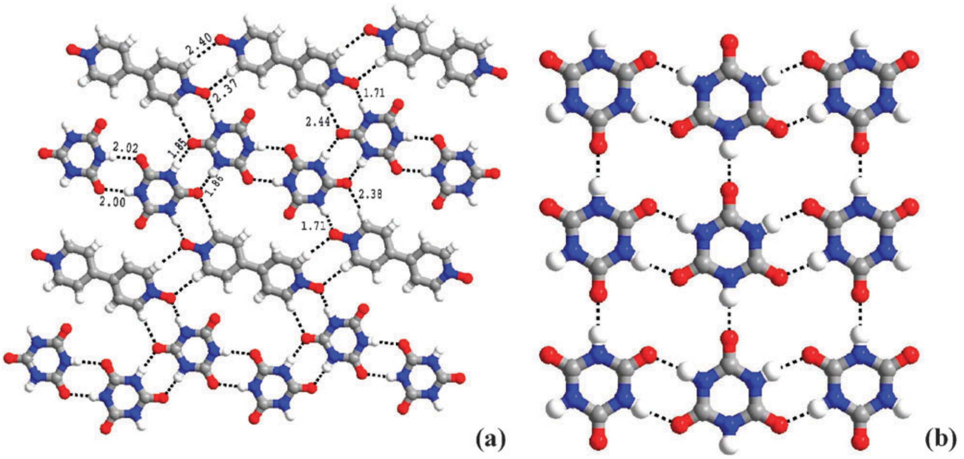


Fig. 2 (a) Molecular tapes of **1** and **CA** through *homomeric* patterns which are held together by *heteromeric* in the structure of **1a**. (b) Arrangement of molecules in the crystal structure of **CA**.

the majority of *N*-oxide structures possess the *homomeric* patterns of **1**, as shown in Fig. 2(a), following the analogy observed for **CA**, the pure structure of **1** could be visualized as a combination of such tapes and this may provide means to establish the structure of **1** by other methods, such as powder X-ray diffraction techniques, as it fails to yield single crystals so far, without additional molecules (either solvent of crystallization or co-crystallizing agent).

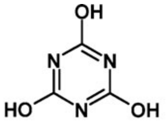
Thus, **1a** could be visualized as a representative example for the combination of unity and diversity with the observation of *homomeric* and *heteromeric* patterns of both the co-crystallizing species simultaneously. Also, the dual role of *N*-oxide **1**, as a spacer and structure directing, could be established, unlike 4,4′-bipyridine, which often play a role of spacer, except in the recently reported assemblies, wherein it acts as a guest.[9] In order to corroborate such features through a large number of molecular complexes of **1**, co-crystallization of it with trithiocyanuric acid, **TCA**, which is an analogue of **CA**, has been carried out, expecting formation of an iso-structural complex with that of **1a**, by which relative competition for *homomeric* and *heteromeric* patterns could also be programmed.

Solid state structure of adduct, 1b, of 4,4′-bipyridine *N*,*N*′-dioxide, 1 and trithiocyanuric acid (TCA)

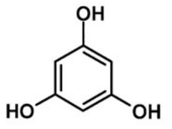
N-oxide, **1** gave co-crystals with **TCA** as a hydrate and it has been labeled as **1b**. Further, the asymmetric unit consists of 1:2 ratio of the reactants, and the important crystallographic information is given in Table 1. The molecular arrangement in two- and three-dimensions in the crystal structure of **1b** is shown in Fig. 3.

In **1b**, three-dimensional structure is alike in **1a**, but through stacked crinkled sheets (Fig. 3), rather than planar sheets. Further, in contrast to the structure of **1a**, a *heteromeric* pattern between the molecules of **1** and **TCA** is not observed. Instead, the interaction between **1** and **TCA** is established through water molecules. Thus, **TCA** forms N–H···O hydrogen bonds (H···O, 1.66 Å, N···O, 2.61 Å) with water molecules, while **1** forms O–H···O hydrogen bonds (H···O, 1.86 and 1.91 Å with corresponding O···O, 2.73 and 2.70 Å), as shown in Fig. 3(b). Such an ensemble ultimately self-assembles, leading to the formation of two-dimensional sheets with tapes of **TCA** molecules separated by the aggregates of **1** and water. Within each molecular tapes of **TCA**, the adjacent molecules are held together by N–H···S hydrogen bonds with H···S distances of 2.52 and 2.54 Å (N···S distances of 3.39 and 3.41 Å).

To evaluate, further, the nature of the variable hydrogen-bonding patterns of **1** in the presence of other molecular entities with potential hydrogen bond donor functionalities, co-crystallization of **1** with 1,3,5-trihydroxybenzene (**THB**) which may be regarded as analogue of **CA** in its enol form, as shown below, has been carried out.



cyanuric acid (**CA**) in enol form



1,3,5-trihydroxybenzene (**THB**)

Supramolecular assembly in molecular complex, 1c, of 4,4′-bipyridine *N*,*N*′-dioxide, 1, and 1,3,5-trihydroxybenzene (phloroglucinol), THB

Co-crystallization of **1** and **THB** from a methanol solution gave a molecular complex, **1c** in a 3:2 ratio of the reactants **1**

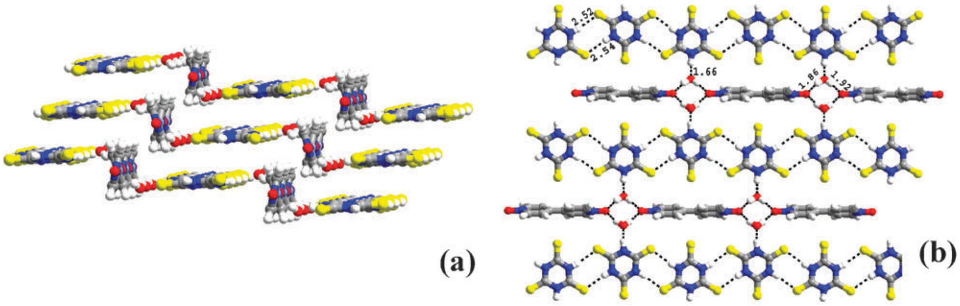


Fig. 3 (a) Stacking of layers comprising of molecules of **1** and **TCA** in the crystal structure of **1b**. (b) Two-dimensional arrangement of molecules showing the molecular tapes of **TCA** separated by the molecules of **1** and water, which are held together by O–H···O hydrogen bonds.

and **THB**. Analysis of three-dimensional packing reveals several quite exciting features, especially a pseudorotaxane type network in the form of a host–guest type assembly, as shown in Fig. 4.

Although each **THB** interacts with three molecules of **1**, forming a *heteromeric* pattern by O–H···O hydrogen bonds with H···O distances of 1.71, 1.73 and 1.75 Å (O···O, 2.63, 2.60, 2.67 Å), as shown in Fig. 5(a), the *homomeric* patterns formed by both **1** and **THB** play a crucial role in the formation of ultimate exotic structure in **1c**. The *homomeric* pattern of **THB** is shown in Fig. 5(b) and the corresponding patterns of **1** are shown in Fig. 6.

The molecules of **THB** were found to be yielding a molecular tape, through *homomeric* pattern, constituted by C–H···O hydrogen bonds (see Fig. 5(b)), which is, in fact, unknown either in its pure structure or in its molecular complexes.[10] Further, two molecules of **1** in the asymmetric unit of **1c** also form molecular tapes independently. Interestingly, while one of these remains like infinite tapes, the tapes belonging to the second molecule are held together by cyclic C–H···O hydrogen bonding patterns constituting layers with void space (Fig. 6). In those cavities the tapes of **THB** molecules fit like a thread, yielding a pseudorotaxane type structure (Fig. 4(b)). Earlier, in our investigations on 1,10-phenanthroline complexes, we demonstrated the feasibility of such structures entirely engraved by noncovalent interactions.[11]

Thus, molecular complex, **1c** further demonstrates the elegancy of noncovalent synthesis to mimic the ensembles known to exist for decades, often, being synthesized by conventional means. Looking at the tapes formed by **THB**, it appears that such tapes could be even possibly synthesized by dihydroxybenzene as well, which may possibly also can yield a pseudorotaxane type structure as observed in **1c**. Hence, co-crystallization of **1** with 1, 3-dihydroxybenzene (**DHB**) has been carried out.

Molecular complex, 1d, of 4,4′-bipyridine *N*,*N*′-dioxide, 1 and 1,3-dihydroxybenzene, DHB

N-Oxide, **1** and **DHB** form co-crystals, **1d**, in a 1:1 ratio along with two molecules of water and crystallize in triclinic space group, $P\bar{1}$. The three-dimensional arrangement of these molecules is indeed quite interesting with a stair-case type structure. A typical arrangement is shown in Fig. 7.

A detailed analysis of the arrangement reveals that both the symmetry independent molecules of **1**, form *homomeric* patterns independently, as observed in **1a** and **1c**, yielding molecular tapes through C–H···O hydrogen bonds (H···O, 2.40 and 2.51; 2.47 and 2.51 Å with corresponding C···O, 3.31 and 3.38 Å; 3.40 and 3.40 Å). Infinite tapes corresponding to a particular symmetry are only shown in Fig. 8(a), for the purpose of clarity, while the tapes of the other symmetry independent molecules is shown in the inset of Fig. 8(a). The tapes correspond to both the symmetry independent molecules, are held together by two water molecules through O–H···O (H···O, 1.67 Å; O···O, 2.77 Å) and C–H···O

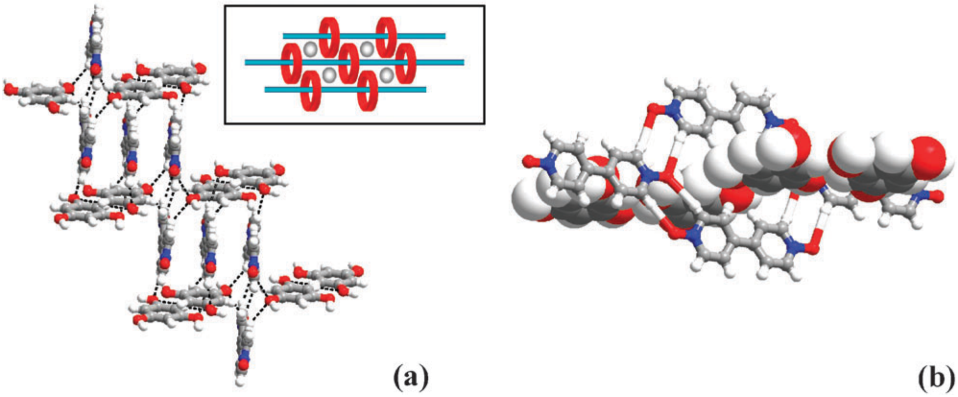


Fig. 4 (a) Pseudorotaxane type network in the crystal structure of **1c**, with void space being filled by a molecular tape of **1**. Schematic representation is shown as inset. (b) A typical pseudorotaxane network with molecules of **1** as rings and molecules of **THB** as rods.

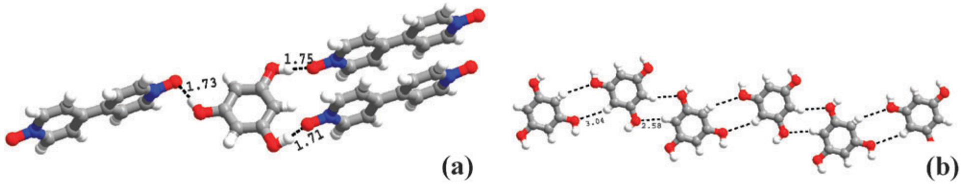


Fig. 5 (a) Molecular recognition between **1** and **THB**, yielding *heteromeric* patterns. (b) Homomeric pattern of **THB**.

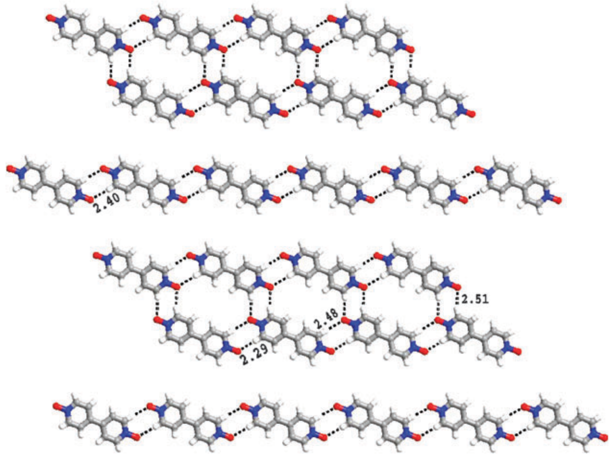


Fig. 6 *Homomeric* patterns of *N*-oxide, **1** in the crystal structure of **1c**.

(H···O, 2.54 Å; C···O, 3.31 Å) hydrogen bonds, constituting cavities. The water molecules, in turn, are held together by O–H···O hydrogen bond with a H···O distance of 1.94 Å (O···O, 2.83 Å). In the cavities, two **DHB** molecules, which are held together by C–H···O (H···O, 2.90 and 2.91 Å; C···O, 3.51 and 3.52 Å) hydrogen bonds are situated. These **DHB** molecules are further glued to the tapes of **1** by O–H···O and C–H···O hydrogen bonds. Such adjacent ensembles are further held together, as shown in Fig. 8(a), by water molecules connecting the two molecular tapes corresponding to the same symmetry molecules by O–H···O and C–H···O hydrogen bonds. A schematic representation of the arrangement is shown in Fig. 8(b).

Thus, in complex **1d**, only the molecules of **1** aggregated to yield *homomeric* patterns, while **DHB** remains as monomers forming interactions with **1** yielding *heteromeric* patterns.

Taking into account the facile formation of ladders and stair-case type structures by 4,4′-bipyridine (bpy) with –COOH functionality, and in particular, the recent reports of preparation of such architectures by co-crystallizing bpy with 1,2,4,5-benzenetetracarboxylic acid (**BTCA**),[12] further studies have been directed to create supramolecular assembly of **1** and **BTCA**.

Supramolecular assembly in molecular complex, 1e, of 4,4′-bipyridine *N*,*N*′-dioxide, 1, and 1,2,4,5-benzenetetracarboxylic acid, BTCA

Co-crystallization of **1** and **BTCA** gave a 1:1 molecular complex, **1e**. In this structure (Fig. 9), in two-dimensional arrangement, each molecule of **1** interacts with **BTCA** forming *heteromeric* pattern through the formation of O–H···O/C–H···O hydrogen bonding patterns, H···O, 1.60/2.30; 1.49/2.59 Å (O···O, 2.53/3.23; 2.48/3.53 Å). But, molecules of **1** did not undergo homomeric aggregation, in the structure of **1e**. In contrast, molecules of **BTCA** show *homomeric* recognition pattern through well known $R_2^2(8)$ hydrogen bonding pattern, with H···O distances of 1.67 and 1.70 Å (O···O, 2.63 and 2.65 Å), *via* the remaining –COOH groups, that did not interact with the molecules of **1**.

Thus, the arrangement ultimately could be visualized as sheets with layers of molecules of **BTCA** stuffed by the molecules of **1** with appreciable void space. However, in three-dimensional arrangement, the adjacent layers are arranged in such a manner that molecules from the adjacent layers effectively fill the void space; thus, **1e** could not yield a channel structure. It is noteworthy to mention that among all the structures studied in this series (**1a–1e**), molecules of **1** did not undergo *homomeric* recognition only in the structure of **1e**, perhaps, due to the strong interaction between –COOH and N → O moieties, thus exhibiting the ability of **1** also to perform the role of spacer, like its analogue bpy, and suggests the importance of the complementarity between the functional groups undergoing the molecular recognition process.

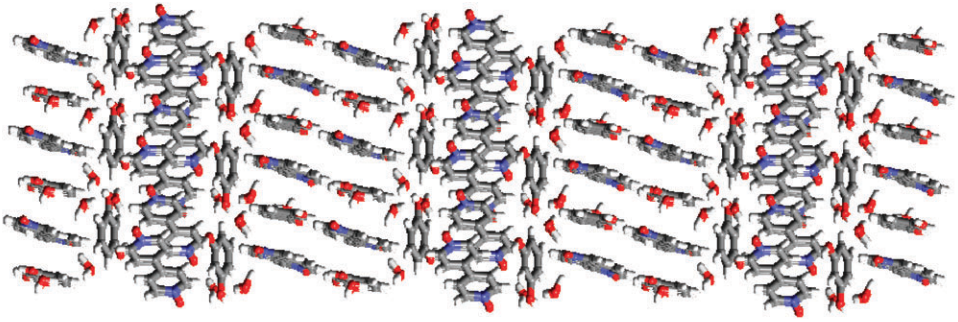


Fig. 7 Three-dimensional packing of molecules in the crystal structure of **1d**.

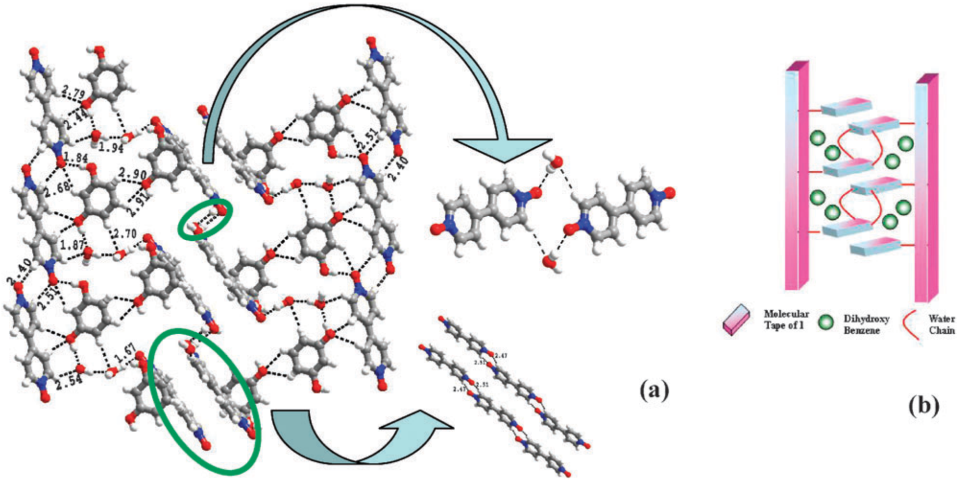


Fig. 8 Arrangement of molecules within a two-dimensional layer in the crystal structure of **1d**.

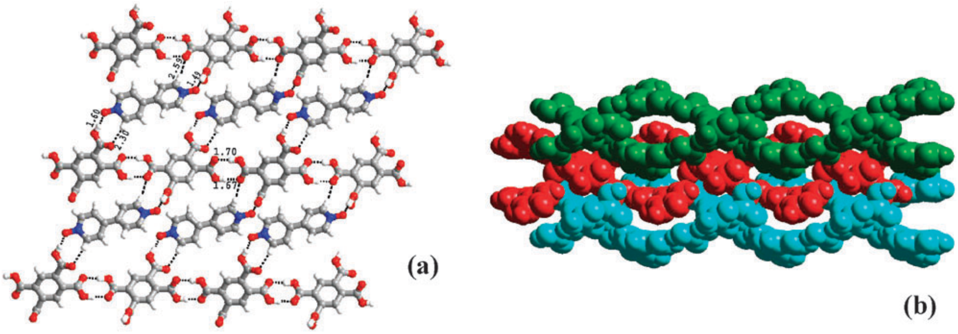


Fig. 9 (a) Two-dimensional arrangement of molecules in the crystal structure of **1e**. (b) Stacking of sheets in three-dimensions.

Conclusions

In this study, we have shown the ability of 4,4′-bipyridine *N*,*N*′-dioxide to yield different types of supramolecular assemblies from simple stacked sheet structures to pseudorotaxane and stair-case type structures depending upon its interaction with the co-crystallizing agents. Unlike its analogue, bpy, the *N*-oxide shows preference for the *homomeric* patterns, although its spacer role is visualized in the structure **1e**. Further, observation of the homomeric patterns formed by **1** in the crystal structures, **1a–1d**, and also in some of the examples found in the literature, it may be possible to extrapolate it to predict the three-dimensional structure of **1** as a stacked sheets with each sheet as an aggregation of molecular tapes formed by the mutual recognition of the adjacent molecules through C–H···O hydrogen bonds. Thus, we strongly believe that this can be a good starting model to determine the three-dimensional structure of **1** by other techniques such as powder X-ray diffraction methods or by computational procedures and we have already initiated process in this direction.

Experimental

Preparation of molecular adducts of the molecular complexes, 1a–1e

All the chemicals used in this study were obtained from commercial suppliers and used as such without any further purification. The solvents employed for the crystallization purpose were of spectroscopy grade of highest available purity. Co-crystals have been prepared by dissolving 4,4′-bipyridine *N*,*N*′-dioxide, **1**, and cyanuric acid, trithiocyanuric acid, 1,3,5-trihydroxybenzene, 1,3-dihydroxybenzene and 1,2,4,5-benzenetetracarboxylic acid in 1:1 or 1:2 ratio either in CH_3OH or H_2O as solvent and slowly evaporating the obtained solution. Single crystals were obtained over a period of 48 h in all the cases. In typical preparation, 0.0941 g (0.5 mmol) of 1 and 0.127 g (0.5 mmol) of 1,2,4,5-benzenetetracarboxylic acid were dissolved in 15 mL of CH_3OH by gently warming on a water bath. The resultant solution was kept for evaporation at ambient conditions by protecting the conical flask from external mechanical disturbances and within 48 h, colorless and good quality crystals of **1e**, were obtained that are suitable for studies by single-crystal X-ray diffraction methods.

Crystal structure determination of 1a–1e

Good quality single crystals of **1a–1e** have been chosen by viewing under microscope and glued to a glass fiber using an adhesive to mount on a goniometer of Bruker single crystal X-ray diffractometer equipped with APEX CCD detector. The data collection was smooth in all the cases without any complications and all the crystals were found to be stable throughout data collection period. The intensity data were processed using Bruker suite programmes, SAINT,[13] followed by absorption correction by SADABS.[14] The structures were solved by using XS and refined by least-square methods using XL.[15] All the non-hydrogen atoms were refined by anisotropic methods and the hydrogen atoms were either refined or placed in the calculated positions. All the structural refinements converged to good *R*-factors as listed in Table 1.

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