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Water-assisted assembly of (*E*)-arylvinylpyridine hydrochlorides: effective substrates for solid-state [2 + 2] photodimerization†

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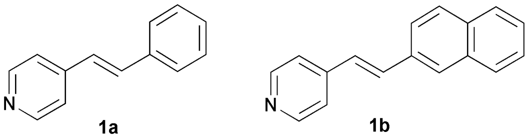
Water molecules assist the assembly of (*E*)-arylvinylpyridine hydrochlorides in a head-to-tail and face-to-face fashion by way of N–H···O hydrogen bonds in combination with cation–π interactions between the pyridinium and aromatic rings. Photolysis of the pyridinium salt hydrates provided *syn*HT dimers in high yields.

Template-controlled solid-state [2 + 2] photodimerization of olefins is a powerful technique for the construction of a stereo-defined cyclobutane framework.[1] Among several approaches for assembly of olefins suitable for photodimerization reactions, the use of hydrogen-bond-driven self-assembly is an attractive strategy.[2] For example, the formation of cocrystals of various olefins with multifunctional molecules, such as diamines,[3] 1,3-dihydroxybenzenes,[4] polycarboxylic acids[5] or Rebek-imide,[6] allows the parallel arrangement of double bonds, and has been employed for regio- and stereoselective [2 + 2] photodimerization reactions. Recently, it has been reported that small molecules and ions, such as thiourea,[7] and sulfate and bisulfate anions,[8] serve as templates to preorient styrylpyridine derivatives in crystals *via* the formation of hydrogen bond networks among the templates and the substrates. The advantage of this new type of template is that the hydrogen bond motifs can be easily reorganized to fit the substrates.

We have previously reported that a cation–π interaction[9] is effective for the regio- and stereoselective [2 + 2] photodimerization of (*E*)-styrylpyridines[10] and azachalcones[11] in solution and in crystal form, respectively. In this communication, we report our findings that water molecules assist the assembly of (*E*)-arylvinylpyridine hydrochlorides in arrangements suitable for photodimerization reactions by way of N–H···O hydrogen bonds in combination with cation–π interactions.

The (*E*)-4-styrylpyridine (**1a**), (*E*)-4-(2-naphthyl)vinylpyridine (**1b**) (Fig. 1), and their HCl salts were employed for the solid-state [2 + 2] photodimerization reactions. There were hydrous and anhydrous forms for the HCl salts. The hydrous forms, **1a**·HCl·2H_2O and **1b**·HCl·3H_2O, were prepared by recrystallization of the corresponding HCl salts from MeOH. The anhydrous forms, **1a**·HCl and **1b**·HCl, were obtained by heating **1a**·HCl·2H_2O and **1b**·HCl·3H_2O, respectively, at 60 °C under a vacuum. The loss of the water molecules from the hydrous forms was confirmed by thermogravimetric analysis. The powdered crystals were placed between two Pyrex plates and irradiated with a 250 W high-pressure mercury lamp for 0.5–16 h. Table 1 gives a summary of the results of the photochemical reactions.

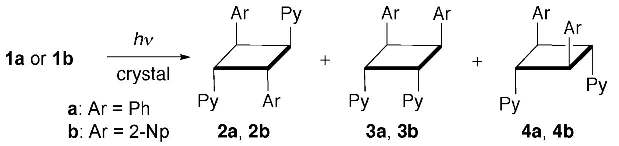


1a **1b**

Fig. 1 Substrates for photodimerization.

Styrylpyridine **1a** gave no product and remained unchanged even after irradiation for 16 h (entry 1). On the other hand, irradiation of the HCl salt, **1a**·HCl·2H_2O, for 1h resulted in quantitative conversion and formation of the *syn*HT dimer **2a** in 91% yield accompanied by its isomers, **3a** and **4a**, as minor products (entry 2). The structures of the products **2a–4a** were confirmed by comparison of the ¹H NMR spectra with those

Table 1 Photolysis of **1a**, **1b**, **1a**·HCl, **1b**·HCl, **1a**·HCl·2H_2O and **1b**·HCl·3H_2O



				Products (%)[a]		
Entry	Substrate	Time/h	Conv (%)[a]	**2a, 2b**	**3a, 3b**	**4a, 4b**
1	**1a**	16	0	No reaction		
2	**1a**·HCl·2H_2O	1	99[b]	91	5	2
3	**1a**·HCl	16	0	No reaction		
4	**1b**	16	0	No reaction		
5	**1b**·HCl·3H_2O	0.5	99	97	1	2
6	**1b**·HCl	16	0	No reaction		

[a] Determined by ¹H NMR spectra. [b] (*Z*)-Isomer was obtained in 2% yield.

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† Electronic supplementary information (ESI) available: Experimental details, the ¹H NMR spectra for **2b–4b**, the X-ray structures for **1a**, **2b** and **4b**, PXRD data for **1b** and the thermogravimetric analysis data for **1a** and **1b**. CCDC 747473, 747476 and 818895. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc12572a

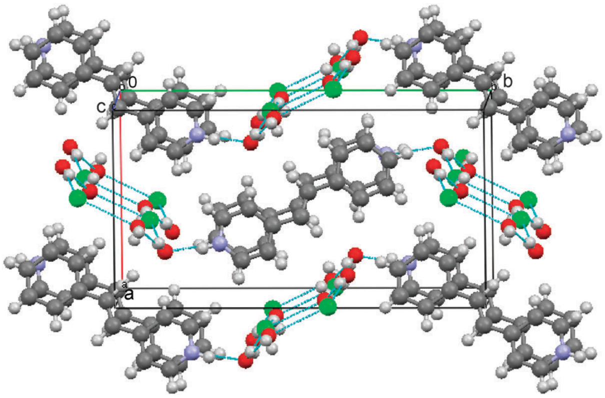


Fig. 2 Crystal structure of **1a**·HCl·2H_2O viewed along the *c*-axis.

reported.[10] To elucidate whether or not water molecules affect the reaction, the anhydrous **1a**·HCl was irradiated for 16 h. To our surprise, **1a**·HCl demonstrated photostability similar to that of **1a** (entry 3).

Similar results were obtained for 2-naphtylvinylpyridine **1b**; *i.e.*, irradiation of **1b** gave no product (entry 4), whereas photolysis of **1b**·HCl·3H_2O yielded the *syn*HT dimer **2b** in an excellent yield accompanied by small amounts of **3b** and **4b** (entry 5). The anhydrous salt, **1b**·HCl, was also photostable (entry 6). The structures of **2b**[12] and **4b**[13] were determined by X-ray structural analysis to be *syn*HT and *anti*HT dimers, respectively, and **3b** was assigned as a *syn*HH dimer on the basis of the ^{1}H NMR and MS spectra.†

The significant effects of water molecules on the reactivities and stereoselectivities in these solid-state photodimerization reactions were elucidated by a comparison of the crystal packing structures of **1a**[10] and **1a**·HCl·2H_2O.[10] In the X-ray packing diagrams of **1a**, the molecules are arranged in a head-to-head manner with a separation of 6.53Å between the two neighboring double bonds.† This indicates the absence of any π–π interactions between these molecules, and explains the photostability of **1a**.

In contrast to **1a**, the molecules of **1a**·HCl·2H_2O are oriented parallel in a head-to-tail manner to form columns along the *c* axis (Fig. 2 and 3). Channels are formed between the four neighboring columns and occupied by water molecules and chloride anions. These are linked one another by a combination of O–H···Cl$^-$ and O–H···O hydrogen bonds containing two types of ring motifs, R_4^6 (12) and R_2^4 (8).[14] The styrylpyridinium cation interacts with a water molecule *via* a N–H···O hydrogen bond, as shown in Fig. 3. The adjacent molecules, related by inversion, are linked to a different hydrogen bond network system; therefore, two hydrogen bond networks assist one column. The separation between the neighboring two olefinic carbons is 3.797 Å and 4.070 Å, which is well within the Schmidt requirement.[15] This is consistent with the high reactivity and selectivity observed in the solid-state photodimerization (Table 1, entry 2). As no hydrogen bond is observed between the two adjacent molecules, cation–π interactions between the pyridinium and the phenyl groups are speculated to play an important role in the formation of the head-to-tail stacked column structure, as reported previously.[10]

Although the crystal packing structure of **1a**·HCl is not clear, its photostability suggests that such column structure observed in **1a**·HCl·2H_2O is no longer retained. Comparisons among the structural features of **1a**, **1a**·HCl·2H_2O and **1a**·HCl clearly show the important role of water molecules in assembly of styrylpyridinium chloride.

Fig. 4 shows the packing diagram of **1b**·HCl·3H_2O,[16] which is very similar to that of **1a**·HCl·2H_2O, although it contains three equivalents of water molecules. The two adjacent naphthylvinylpyridinium ions participate in different hydrogen bond networks. The distances between the two molecules are 3.633 Å and 3.728 Å, which explains the high reactivity and stereoselectivity. Similar to the case of **1a**·HCl, the crystal structure of the anhydrous **1b**·HCl is not clear, albeit its photostability suggests the destruction of the head-to-tail column structure observed in **1b**·HCl·3H_2O.

As the anhydrous **1a**·HCl and **1b**·HCl are hygroscopic, the reversibility of their vapor uptake properties was evaluated. Fig. 5 shows the changes in the PXRD patterns caused by the dehydration and hydration processes of **1a**·HCl·2H_2O and **1a**·HCl, respectively. The PXRD pattern of the simulated **1a**·HCl·2H_2O is shown in Fig. 5a. After heating **1a**·HCl·2H_2O at 100 °C for 6 h, the peaks of **1a**·HCl·2H_2O disappeared and new broad peaks appeared, indicating the formation of a new crystalline phase with lower crystallinity (Fig. 5b). Thermogravimetric analysis of the resultant **1a**·HCl shows the completion of the dehydration process. When the anhydrous powder was kept in a desiccator at 58% relative humidity for 24 h, the PXRD pattern became much closer to that of the simulated **1a**·HCl·2H_2O (Fig. 5c). After 48 h, the PXRD pattern was in close agreement with that of the simulation

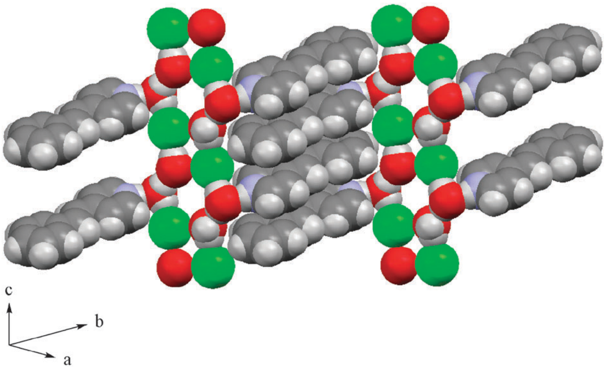


Fig. 3 The head-to-tail stacking structure of styrylpyridinium self-assembled by hydrogen bonding in **1a**·HCl·2H_2O.

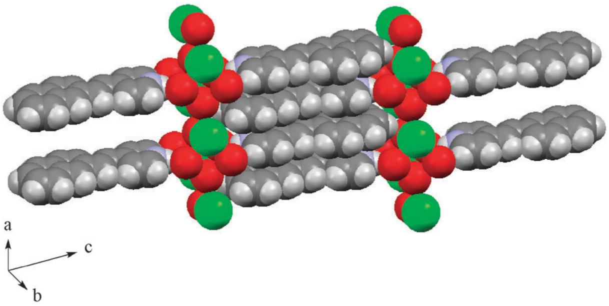


Fig. 4 The head-to-tail stacking structure of naphthylvinylpyridinium self-assembled by hydrogen bonding in **1b**·HCl·3H_2O.

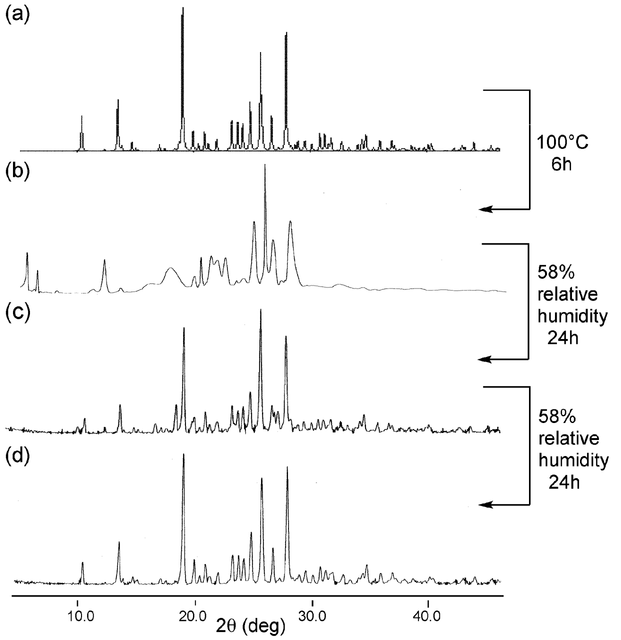
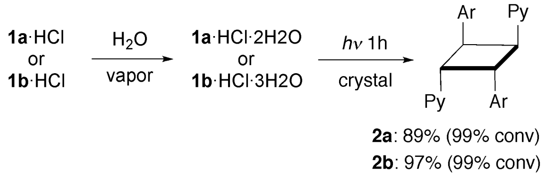


Fig. 5 The PXRD patterns for (a) simulated **1a**·HCl·$2H_2O$ and (b) anhydrous **1a**·HCl, and the PXRD patterns (c) after exposure of **1a**·HCl to H_2O vapor for 24 h or (d) 48 h.



Scheme 1 Irradiation of **1a**·HCl·$2H_2O$ and **1b**·HCl·$3H_2O$ obtained from anhydrous **1a**·HCl and **1b**·HCl.

(Fig. 5d). This clearly shows that the anhydrous **1a**·HCl was rehydrated to produce hydrous **1a**·HCl·$2H_2O$. These observations strongly suggest that the water molecules assist the assembly of the styrylpyridinium cation in a head-to-tail and face-to-face manner in combination with cation–π interactions between the pyridinium and phenyl groups. Similar reversibility was also observed between **1b**·HCl and **1b**·HCl·$3H_2O$.†

It should be noted that irradiation of the rehydrated **1a**·HCl·$2H_2O$ and **1b**·HCl·$3H_2O$, obtained from anhydrous **1a**·HCl and **1b**·HCl, also afforded *syn*HT dimers **2a** and **2b** in 89% and 97% yields, respectively, indicating their high crystallinity (Scheme 1).

In summary, we have shown that water molecules play a key role in assembling arylvinylpyridinium salts. The hydrogen bond networks assist the assembly of molecules in an anti-parallel orientation in combination with cation–π interactions. As the water provides flexible hydrogen bond networks, and is easily removable and environmentally friendly, water-assisted assembly would be of considerable utility in solid-state photodimerization reactions. Studies of the substituent effect on assembly are in progress and will be reported in due course.

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12 Crystal data for **2b**: $C_{34}H_{26}N_2$, M = 462.59, monoclinic, space group $P2_1$, a = 10.5616(6), b = 9.5453(6), c = 13.5147(7) Å, β = 110.173(2)°, V = 1278.89(12) Å^3, Z = 2, D_{calcd} = 1.201 g cm^{-3}, μ = 0.5350 mm^{-1} (Cu-Kα, λ = 1.54178 Å), T = 293 K. R_1 = 0.0761 and wR_2 = 0.2912 for 4523 unique reflections $>2\sigma(I)$. CCDC 747473.

13 Crystal data for **4b**: $C_{34}H_{26}N_2$, M = 462.59, orthorhombic, space group $Pbca$, a = 22.5434(4), b = 8.91677(10), c = 49.7495(10) Å, V = 10000.4(3) Å^3, Z = 12, D_{calcd} = 0.922 g cm^{-3}, μ = 0.4105 mm^{-1} (Cu-Kα, λ = 1.54178 Å), T = 293 K. R_1 = 0.0648 and wR_2 = 0.2166 for 9132 unique reflections > $2\sigma(I)$. CCDC 747476.

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16 Crystal data for **1b**·HCl·$3H_2O$: $C_{17}H_{20}N_1O_3Cl_1$, M = 321.80, triclinic, space group $P\bar{1}$, a = 7.0419(7), b = 11.0864(11), c = 12.0768(12) Å, α = 64.825(3)°, β = 81.258(3)°, γ = 81.852(3)°, V = 840.22(15) Å^3, Z = 2, D_{calcd} = 1.272 g cm–^{3}, μ = 2.1117 mm^{-1} Cu-Kα, λ = 1.54178 Å, T = 293 K. R_1 = 0.0994 and wR_2 = 0.2563 for 2727 unique reflections $>2\sigma(I)$. CCDC 818895.