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Resorcinol-Templated Head-to-Head Photodimerization of a Thiophene in the Solid State and Unusual Edge-to-Face Stacking in a Discrete Hydrogen-Bonded Assembly

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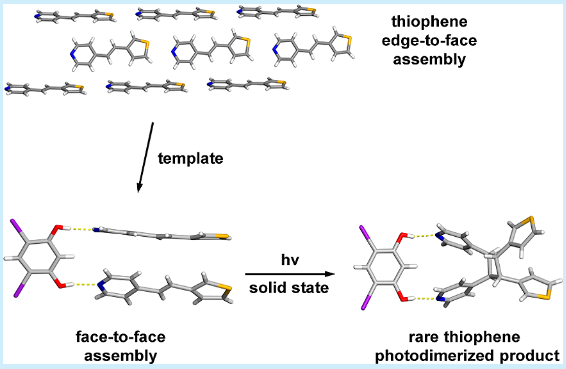
Supporting Information

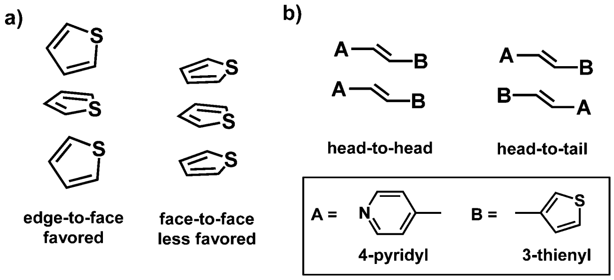
ABSTRACT: A head-to-head photodimerization of a β-substituted thiophene stacked face-to-face in the solid state using a ditopic hydrogen-bond-donor template is reported. The face-to-face stacking is attributed to contributions of intertemplate forces, which contrasts an assembly wherein the same thiophenes stack edge-to-face yet maintain a discrete hydrogen-bonded structure.



Supramolecular approaches to direct the assembly and packing of molecules are of increasing importance to control chemical reactivity in the solid state.[1] In this context, small molecules that function as hydrogen-bond-donor templates have emerged as useful to overcome effects of crystal packing to direct intermolecular [2 + 2] photodimerizations in solids. For a photodimerization to occur in the solid state, carbon−carbon double (C═C) bonds are generally required to be parallel and separated <4.2 Å.[2] In this context, we have reported resorcinol (**res**), and derivatives, as small-molecule ditopic templates that confront the crystal packing problem to reliably assemble olefins in solids into favorable geometries for the cycloaddition reaction.[3] Reactivity is achieved within discrete hydrogen-bonded assemblies with olefins preorganized into face-to-face π-stacked arrangements. Successes of the template method are attested by the stereocontrolled syntheses of molecules (e.g., ladderanes, cyclophanes) that are difficult to achieve using more conventional solution methods.[1a]

With this in mind, we report here the use of a **res** to direct a solid-state photodimerization of a thiophene. Thiophenes are integral components of organic semiconductor materials,[4] comprising organic light-emiting diodes,[5] organic thin-film transistors,[6] and photovoltaic cells.[7,8] Moreover, we expected that a **res** could overcome edge-to-face π-forces that dominate the solid-state packings of thiophenes so as to enforce a face-to-face geometry of two olefins in a head-to-head orientation to undergo the photoreaction (Scheme 1). Photodimerizations of thiophenes in both solution and the solid state, however, are extremely rare,[9] with attempts to gain levels of regiocontrol of the photoreaction having been explored in very limited cases.

Scheme 1. (a) Solid-State Packings of Thiophenes and (b) Comparison of Head-to-Head vs Head-to-Tail Stacked Olefins



Here, 4,6-diiodo-**res** (**4,6-diI-res**) is used as a template to assemble *trans*-1-(4-pyridyl)-2-(3-thienyl)ethylene (**β-PTE**) into a discrete hydrogen-bonded assembly in a co-crystal of composition (**4,6-diI-res**)·2(**β-PTE**). The olefin adopts a face-to-face π-stacked geometry and undergoes an intermolecular [2 + 2] photodimerization to generate head-to-head *rctt*-1,2-bis(4-pyridyl)-3,4-bis(3-thienyl) cyclobutane (**4p3tcb**) regioselectively and in near-quantitative yield (Scheme 2). We also demonstrate the **res** congener 4,6-dichlororesorcinol (**4,6-diCl-res**) to support **β-PTE** in an edge-to-face π-stacked geometry in (**4,6-diCl-res**)·2(**β-PTE**), which is photostable. We are unaware of an example wherein a **res** accommodates edge-to-face π-stacking within a discrete hydrogen-bonded assembly. Moreover, we attribute the photoreactivity of (**4,6-diI-res**)·2(**β-

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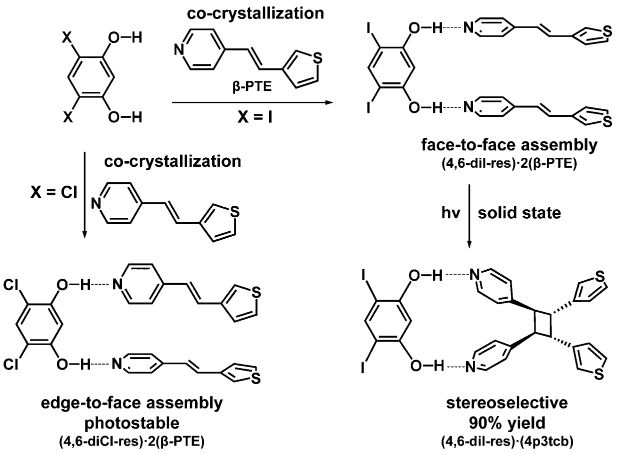
Scheme 2. Assembled Thiophene Using a res



PTE) to contributions of secondary I···O interactions involving the templates that effectively act to compress the olefins into requisite face-to-face *π*-stacked geometry in the solid.

Photodimerizations of styrylthiophenes pose an interesting synthetic challenge. The parent olefin *trans*-1,2-di(3-thienyl)-ethene does not photodimerize in solution,[10] while there are few reported styrylthiophenes that react to form cyclobutanes. Very few of the olefins react in appreciable yields (i.e., >30%) in either solution or the solid state.[11] High yielding photodimerizations (i.e., >70%) of thiophenes are extremely rare.[12] To our knowledge, the only *β*-substituted thiophene reported to undergo a photodimerization in high yield is (*E*)-1-2′,5′-dibromo-3′-thienyl-2-pentafluoro-phenylethene, which generates a head-to-tail, as opposed to a head-to-head, photoproduct.[13]

We initially focused on the reactivity of ***β*-PTE** as a pure solid. The olefin was synthesized *via* a Heck reaction of 4-vinylpyridine and 3-bromothiophene.[14] Colorless plate-shaped single crystals of ***β*-PTE** were obtained from slow evaporation of a saturated toluene solution over a period of 2 days.

A crystal structure analysis[15,16] revealed ***β*-PTE**, which is disordered over three sites [site occupancies: 0.66(1), 0.23(1), and 0.11(1)], to adopt typical edge-to-face packing in the acentric space group Pc. The edge-to-face packing places the olefin into two orientations (labeled as ABA) along the *b*-axis (Figure 1). The mean planes of ***β*-PTE** are canted at 62°, similar to unsubstituted oligothiophenes.[17] The C═C bonds are separated by 6.15 Å, with the edge-to-face packing placing ***β*-PTE** in a photostable arrangement according to the principles of Schmidt.[2] When a sample in the form of a crystalline powder was exposed to broad-band UV irradiation (20 h), ***β*-PTE** was determined to be photostable from ^{1}H NMR spectroscopy.

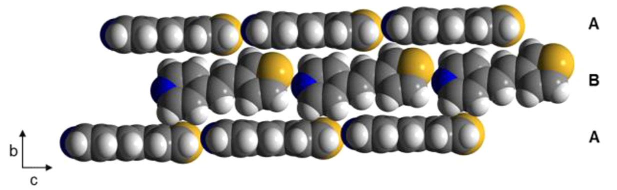


Figure 1. Edge-to-face packing of ***β*-PTE** along the *a*-axis (highest occupancy).

To orient ***β*-PTE** into a geometry for a photodimerization, the olefin was co-crystallized with **4,6-diI-res** in a 2:1 ratio in acetonitrile. Colorless plate-shaped crystals formed upon slow solvent evaporation after a period of 2 days. The formulation of (**4,6-diI-res**)·2(***β*-PTE**) was confirmed by ^{1}H NMR spectroscopy and single-crystal X-ray diffraction.

A single-crystal X-ray analysis[18] confimed **4,6-diI-res** to assemble ***β*-PTE** into a face-to-face *π*-stacked geometry in the chiral space group $P2_1$. The asymmetric unit consists of two molecules of **4,6-diI-res** and four molecules of ***β*-PTE** that comprise two three-component supramolecular assemblies (A and B), each sustained by two intermolecular O−H···N hydrogen bonds [O···N separation (Å): O(1)···N(1) 2.64(3), O(2)···N(2) 2.72(1), O(3)···N(3) 2.66(1), O(4)···N(4) 2.69(1)] (Figure 2). Each ***β*-PTE** is disordered over two sites [site occupancies: 0.81(1) and 0.19(1) and 0.79(1) and 0.21(1) for A, 0.77(1) and 0.23(1) and 0.56(1) and 0.44(1) for B]. In assembly A, the mean planes of the ***β*-PTE** molecules are canted at 33° and olefins are separated by 4.30 Å, with the thiophene rings of the major occupied sites pointing in the same direction. In assembly B, the mean planes of ***β*-PTE** are canted at 13° and olefins are separated by 4.15 Å, with the thiophene rings of the major sites pointing in opposite directions. The separations between olefins in adjacent assemblies are 5.35 and 5.63 Å for assembly A and B, respectively.

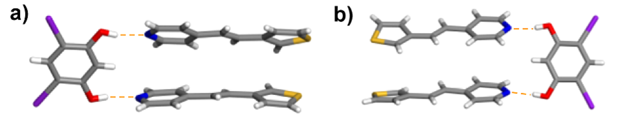


Figure 2. X-ray structure of (**4,6-diI-res**)·2(***β*-PTE**): (a) assembly A and (b) assembly B. Highest occupancy is shown for each olefin.

Since the olefins of (**4,6-diI-res**)·2(***β*-PTE**) lie in a geometry suitable for a [2 + 2] photodimerization, a powdered crystalline sample (50 mg) was irradiated with UV radiation (medium pressure Hg). A photodimerization was confirmed by the emergence of a cyclobutane peak (4.6 ppm) and upfield shifts (0.2 ppm) of the pyridine peaks in the ^{1}H NMR spectrum. After a period of 100 h, photodimerization occurred in up to 90% yield.[19]

To confirm the stereochemistry of the photoproduct, single crystals of the reacted solid were obtained *via* a recrystallization from acetonitrile/methanol/toluene (1:1:1 v/v). Slow solvent evaporation over a period of approximately 3 days afforded colorless plate-shaped crystals of (**4,6-diI-res**)·(**4p3tcb**) suitable for single-crystal X-ray analysis.

A single-crystal X-ray analysis[20] revealed a discrete two-component assembly of a 1:1 co-crystal of (**4,6-diI-res**)·(**4p3tcb**), which lies in the centrosymmetric space group $P2_1/c$. In the solid, head-to-head **4p3tcb** [C−C bond lengths (Å): C(12)−C(13) 1.56(1), C(12)−C(23) 1.58(1), C(13)−C(24) 1.56(1), C(23)−C(24) 1.53(1)] (Figure 3) interacts with **4,6-diI-res** *via* O−H···N hydrogen bonds [O···N separation (Å): O(1)···N(1) 2.66(1), O(2)···N(2) 2.71(1)]. The thiophene rings of the photoproduct are splayed about the cyclobutane ring at 74°, with the mean planes being canted by 56°.

During our attempts to employ a **res** to assemble ***β*-PTE** into a face-to-face geometry, we discovered an unusual co-crystal assembly. When ***β*-PTE** was co-crystallized with **4,6-diCl-res** in acetonitrile *via* slow evaporation, pale yellow rod-shaped

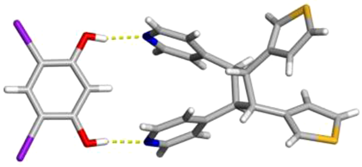


Figure 3. X-ray structure of (**4,6-diI-res**)·(**4p3tcb**).

crystals of (**4,6-diCl-res**)·2(**β-PTE**) formed after a period of 2 days. The formulation of (**4,6-diCl-res**)·2(**β-PTE**) was confirmed by single-crystal X-ray analysis and ^{1}H NMR spectroscopy.

A single-crystal X-ray analysis[21] revealed the components of (**4,6-diCl-res**)·2(**β-PTE**) to crystallize in the centrosymmetric space group $P\bar{1}$. In contrast to (**4,6-diI-res**)·2(**β-PTE**), the stacked olefins are oriented in an edge-to-face geometry, being sustained by intermolecular O−H···N hydrogen bonds [O···N separation (Å): O(1)···N(1) 2.71(1), O(2)···N(2) 2.74(1)] (Figure 4). The mean planes of the **β-PTE** molecules are canted at 67°, similar to the pure component. The edge-to-face stacking is manifested by the C−H···π forces involving the thiophene rings (C_α−H(thiophene)···C(thiophene) 3.71 Å). The pyridine groups are also engaged in edge-to-face π-forces (C−H(pyridine)···C(pyridine) 3.76 Å). As a consequence of the assembly process, the C═C bonds of the discrete assembly are separated by 4.73 Å. The distance between olefins of adjacent assemblies is 6.33 Å.[2] Indeed, when a crystalline powder was exposed to broad-band UV radiation for a period of 50 h, (**4,6-diCl-res**)·2(**β-PTE**) was photostable.

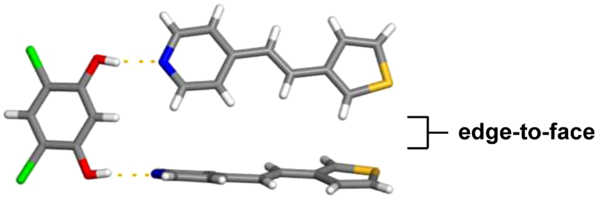


Figure 4. X-ray structure of (**4,6-diCl-res**)·2(**β-PTE**) highlighting edge-to-face stacking.

The co-crystal (**4,6-diCl-res**)·2(**β-PTE**) provides a novel example of aromatics stacked edge-to-face in a discrete hydrogen-bonded assembly based on a **res**. The observation is suprising given the strong propensity of a **res** to promote face-to-face π-stacked geometries of reactive olefins in solids.[1a,22] That (**4,6-diI-res**)·2(**β-PTE**) and (**4,6-diCl-res**)·2(**β-PTE**) exhibit different π-stackings, and photoreactivities, involving **β-PTE** can be attributed to secondary interactions involving the templates. In both solids, adjacent assemblies pack as linear columns (Figure 5). In the case of photoreactive (**4,6-diI-res**)·2(**β-PTE**), adjacent assemblies of each column interact *via* I···O interactions (3.47 and 3.38 Å for assembly A and B, respectively) involving the templates.[23] The intertemplate forces effectively serve to 'compress' **β-PTE** molecules of the stacked assemblies to promote the face-to-face π-stacking. Conversely, in (**4,6-diCl-res**)·2(**β-PTE**), the halogen-to-oxygen separations are appeciably longer (nearest: Cl···O: 5.75 Å), with the interassembly packing being dominated by the edge-to-face π-forces akin to **β-PTE** as a pure solid.

In this report, we have described a head-to-head [2 + 2] photodimerization of a β-substituted thiophene using a ditopic hydrogen-bond donor template based on a **res**. A surprising edge-to-face π-stacked geometry involving **β-PTE** was realized with the stacking in a discrete hydrogen-bonded structure. We are currently investigating the scope of employing templates to enforce face-to-face π-stacking and direct the reactivity of additional thiophenes, with a goal to construct complex molecules and materials with increasing applications in organic synthesis and materials science.

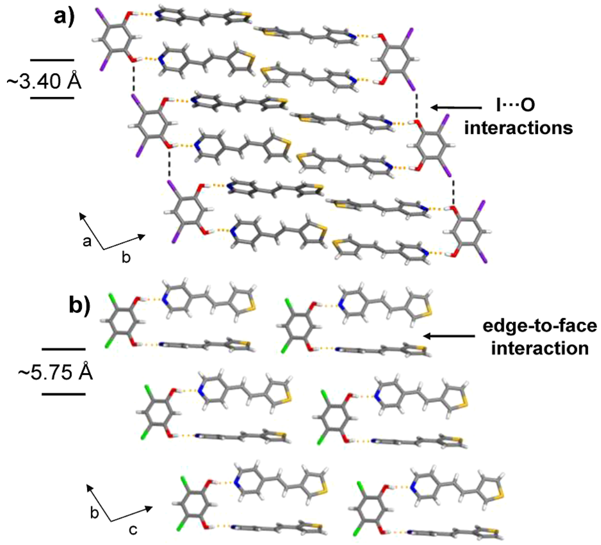


Figure 5. Extended packing of linear columns: (a) (**4,6-diI-res**)·2(**β-PTE**) and (b) (**4,6-diCl-res**)·2(**β-PTE**). Dashed black lines show I···O interactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, ^{1}H NMR, and single-crystal X-ray data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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(14) See also: Marzinzik, A. L.; Rademacher, P. *Synthesis* **1995**, *9*, 1131.

(15) Crystal data for **βPTE**: crystal size $0.31 \times 0.19 \times 0.09$ mm^3, monoclinic, space group Pc, $a = 6.335(1)$ Å, $b = 7.494(1)$ Å, $c = 9.767(1)$ Å, $\alpha,\gamma = 90°$, $\beta = 94.26(1)°$, $V = 462.36(9)$ Å^3, $2\theta = 56°$, Mo Kα radiation ($\lambda = 0.7107$ Å) for $Z = 2$ and $R = 0.0540$ for $I > 2\sigma(I)$.

(16) CCDC 964844−964847 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

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(18) Crystal data for (**4,6-diI-res**)·2(**βPTE**): crystal size $0.16 \times 0.09 \times 0.01$ mm^3, monoclinic, space group $P2_1$, $a = 9.283(1)$ Å, $b = 34.548(4)$ Å, $c = 9.898(1)$ Å, $\alpha,\gamma = 90°$, $\beta = 117.72(1)°$, $V = 2810.2(5)$ Å^3, $2\theta = 51°$, Mo Kα radiation ($\lambda = 0.7107$ Å) for $Z = 4$ and $R = 0.0614$ for $I > 2\sigma(I)$.

(19) That the photodimerization occurs in a 90% yield may reflect the presence of reactive centers wherein disordered olefins lie in a criss-cross geometry.

(20) Crystal data for (**4,6-diI-res**)·(**4p3tcb**): crystal size $0.105 \times 0.09 \times 0.01$ mm^3, monoclinic, space group $P2_1/c$, $a = 17.753(2)$ Å, $b = 10.170(1)$ Å, $c = 16.281(2)$ Å, $\alpha,\gamma = 90°$, $\beta = 108.20(1)°$, $V = 2792.5(5)$ Å^3, $2\theta = 51°$, Mo Kα radiation ($\lambda = 0.7107$ Å) for $Z = 4$ and $R = 0.0470$ for $I > 2\sigma(I)$.

(21) Crystal data for (**4,6-diCl-res**)·2(**βPTE**): crystal size $0.32 \times 0.08 \times 0.07$ mm^3, triclinic, space group $P\bar{1}$, $a = 9.398(1)$ Å, $b = 10.280(1)$ Å, $c = 13.792(2)$ Å, $\alpha = 84.15(1)°$, $\beta = 89.570(5)°$, $\gamma = 76.85(1)°$, $V = 1290.6(2)$ Å^3, $2\theta = 50°$, Mo Kα radiation ($\lambda = 0.7107$ Å) for $Z = 2$ and $R = 0.0513$ for $I > 2\sigma(I)$.

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