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Supramolecular Catalysis

Supramolecular Catalysis in the Organic Solid State through Dry Grinding**

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Supramolecular processes that result in the formation of covalent bonds and occur in solution are expected to be difficult to achieve in the absence of solvent owing to the restricted conformational and translational degrees of freedom of molecules in solids. Diffusion rates of molecules in the crystalline state are in the order of $10^{-15}\,m^2\,s^{-1}$,[1] which is at least six orders of magnitude less than in solution. In this context, organic molecules that act as supramolecular catalysts make up much of the current chemistry of molecular recognition.[2] Supramolecular catalysts are inspired by the dynamic mode of action of enzymes and take advantage of processes of molecular recognition to afford transformations that are highly stereoselective, environmentally friendly, and cost effective. Small-molecule supramolecular catalysts are typically endowed with hydrogen-bond-donor and -acceptor groups that assemble two simultaneously bound substrates (e.g. ditopic receptors) within a molecular complex for reaction.[3] Relatively high catalyst loadings are often required for these catalysts owing to effects of entropy, the reversibility and relative weakness of intermolecular forces in a liquid, as well as product inhibition.[4] All small-molecule supramolecular catalysts reported to date operate in the liquid phase, typically an organic solvent.[5]

Here we report a ditopic supramolecular receptor,[6] in the form of the bifunctional hydrogen-bond donor 4,6-dichlororesorcinol (4,6-diCl-res) that operates as a supramolecular catalyst in the absence of solvent (Figure 1). The catalytic reaction is a [2+2] photodimerization of *trans*-1,2-bis(4-pyridyl)ethylene (4,4′-bpe).[6b,c] The reaction directed by the catalyst occurs in a close-packed environment where molecular movement is at a minimum. The reaction results in the stereospecific formation of *rctt*-tetrakis(4-pyridyl)cyclobutane (4,4′-tpcb) in near quantitative yield. To achieve dynamic turnover between the catalyst, reactants, and product in the absence of molecular movement assisted by solvent, we employ mechanochemical energy,[7] in the form of dry mortar-and-pestle grinding,[8] in a two-step process that we demonstrate results in reactions between different crystalline phases. The mechanochemistry in the first step forms a reactive hydrogen-bonded catalyst–reactant complex and in the second step disassembles the catalyst and product to make the small-molecule catalyst available to bind additional reactants. The mechanochemistry is used, in effect, to enable the catalyst to "hop" from one set of olefins to another to direct product formation and facilitate turnover. The release of the product in the second grinding results in stereospecific recombination of the catalyst and olefin, which means that the interaction between the catalyst and product does not inhibit the course of the mechanochemical catalytic process.

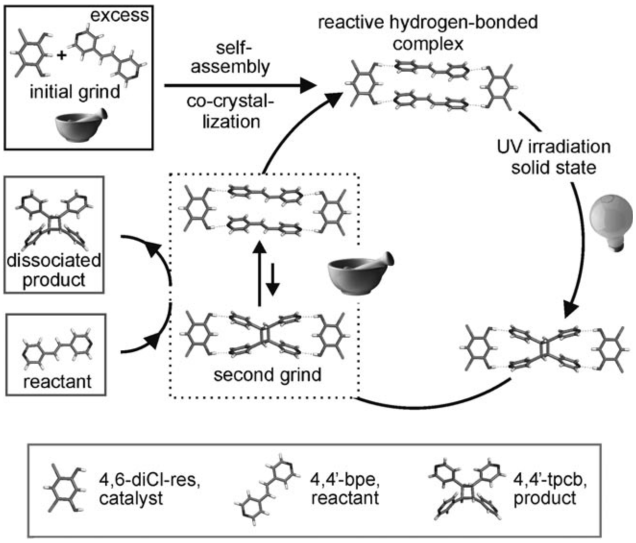

Figure 1. Supramolecular catalysis in the solid state using ditopic receptor 4,6-diCl-res and olefin 4,4′-bpe to afford 4,4′-tpcb.

The supramolecular catalysis originates from a molecular co-crystal composed of 4,6-diCl-res and 4,4′-bpe, specifically, 2(4,6-diCl-res)·2(4,4′-bpe). The co-crystal forms through either solvent-mediated co-crystallization or dry mortar-and-pestle grinding of the components (1:1 molar ratio). Both molecules are solids at ambient temperature and pressure (m.p.: 4,6-diCl-res 112 °C;[9] 4,4′-bpe 150–151 °C[10]). The components form a four-component supramolecular assembly, 2(4,6-diCl-res)·2(4,4′-bpe), held together, as determined by single-crystal X-ray diffraction, by four OH···N hydrogen bonds (O···N distance: 2.680(2) and 2.713(2) Å)

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(Figure 2a). The pyridine groups are hydrogen-bond acceptors, being directed by the donor OH groups of the resorcinol to form the hydrogen-bonded structure. The olefins are aligned within the hydrogen-bonded assembly parallel and separated by 3.71 Å. The olefins are, thus, positioned by the resorcinol for a [2+2] photodimerization in the crystalline state.[11]

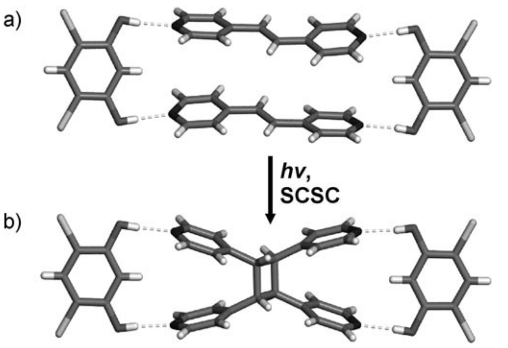

Figure 2. Single-crystal photoconversion of 2(4,6-diCl-res)·2(4,4′-bpe) to 2(4,6-diCl-res)·(4,4′-tpcb).

Upon exposure to broadband UV radiation (Hg medium-pressure lamp) for 80 h, 4,4′-bpe of a powdered crystalline sample of 2(4,6-diCl-res)·2(4,4′-bpe) undergoes a stereospecific and quantitative photodimerization to form 4,4′-tpcb, as established by ^{1}H NMR spectroscopy. When single crystals of 2(4,6-diCl-res)·2(4,4′-bpe) were exposed to UV light for 110 h, the reaction proceeded through a single-crystal-to-single-crystal (SCSC) transformation[12] to give 4,4′-tpcb stereospecifically and in quantitative yield (Figure 2b). Structural analysis of a fully reacted single crystal revealed the formation of the cyclobutane ring of 4,4′-tpcb within the hydrogen-bonded assembly. The hydrogen bonds, thus, remained intact between the receptor 4,6-diCl-res and 4,4′-tpcb following the photodimerization. X-ray data show that the hydrogen bonds and pyridyl groups underwent a slight deformation (O···N distance: 2.683(2) and 2.702(2) Å) and splaying (N···N separations: 4.36 Å) in the solid. Collectively, these observations demonstrate that 4,6-diCl-res acts as a ditopic supramolecular receptor that directs a highly efficient topochemically controlled [2+2] photodimerization of 4,4′-bpe in a single crystal that affords 4,4′-tpcb in up to quantitative yield.

Having established that 4,6-diCl-res directs the photodimerization of 4,4′-bpe stoichiometrically, we turned to determine whether the receptor can direct the photoreaction in sub-stoichiometric amounts, or catalytically. Whereas small molecules that function as supramolecular catalysts operate in the liquid phase, a small molecule that acts as a supramolecular catalyst in the absence of solvent state has not been reported. To serve as a catalyst, the receptor would need to preorganize 4,4′-bpe in the solid state for reaction and, following the photoreaction, release the product without assistance of intervening solvent.

To use 4,6-diCl-res as a catalyst, we expected that a sub-stoichiometric amount of 4,6-diCl-res could be mixed with 4,4′-bpe and treated mechanochemically[7,8] by dry grinding. The grinding would generate a mixture of reactive crystalline 2(4,6-diCl-res)·2(4,4′-bpe) and excess crystalline 4,4′-bpe, which is photostable. Upon exposure to UV radiation, the solid would react to afford, consistent with the SCSC reactivity, crystalline (4,6-diCl-res)·2(4,4′-tpcb) in the presence of the excess crystalline 4,4′-bpe. In principle, the reaction could, upon prolonged exposure to UV radiation, continue whereby 4,6-diCl-res, similar to a catalyst in the liquid phase, is released from the product and binds additional olefins to form additional 4,4′-tpcb. In consequence of additional 4,4′-tpcb not being generated upon prolonged UV radiation, we expected that a second dry grinding could be used to promote the release of 4,6-diCl-res from (4,6-diCl-res)·2(4,4′-tpcb) to bind additional olefin. A second grinding would, in effect, be used to displace—akin to agitation provided by stirring or heating in solution—the photoproduct from 4,6-diCl-res by dismantling[13] 2(4,6-diCl-res)·(4,4′-tpcb) and enabling additional olefins to be bound for catalytic turnover. Given that mechanical strain accumulates in solids that undergo SCSC reactions,[12] we expected that a release of strain through the second grinding could also act as a driving force for release of the photoproduct from the receptor.

To test our hypothesis, 4,4′-bpe with 20 mol% of 4,6-diCl-res was ground under dry—or solvent-free—conditions using a mortar and pestle for 20 min.[6c,14] The solid was then exposed to broadband UV radiation for 16 h at room temperature. The photoreactor used in the experiment was equipped with a heat sink to minimize possible effects of melting. As determined by ^{1}H NMR spectroscopy, the irradiation resulted in the stereospecific formation of 4,4′-tpcb in 20% yield (Figure 3, H_c). The 20% yield represents a quantitative conversion of 4,4′-bpe to 4,4′-tpcb with respect to 4,6-diCl-res in the solid. Prolonged irradiation of up to 100 h did not result in additional amounts of 4,4′-tpcb being formed.

The stereospecific formation of 4,4′-tpcb in the presence of 4,6-diCl-res is consistent with the photoreaction occurring topochemically within the complex 2(4,6-diCl-res)·2(4,4′-bpe). That the prolonged irradiation did not generate additional 4,4′-tpcb can be attributed to the hydrogen bonds between 4,6-diCl-res and 4,4′-tpcb being maintained in the solid in the form of either 2(4,6-diCl-res)·2(4,4′-bpe) (i.e. product of the SCSC transformation) or a different solid phase (e.g. amorphous solid). Moreover, the hydrogen bonds and constrained environment of the solid state can be considered to have suppressed movement of the molecules that can lead to turnover and result in continued generation of photoproduct.

To achieve turnover, the photoreacted solid was next subjected in a second step to dry grinding for an additional 20 min and exposed to UV radiation for an additional 16 h. ^{1}H NMR spectroscopy demonstrated, following a second UV irradiation, that 4,4′-tpcb was present in 40% yield (Figure 3). The generation of 4,4′-bpe in 40% yield was consistent with the second grinding having resulted in breaking of the hydrogen bonds between 4,6-diCl-res and 4,4′-tpcb and the exclusive—or stereospecific—formation of new hydrogen

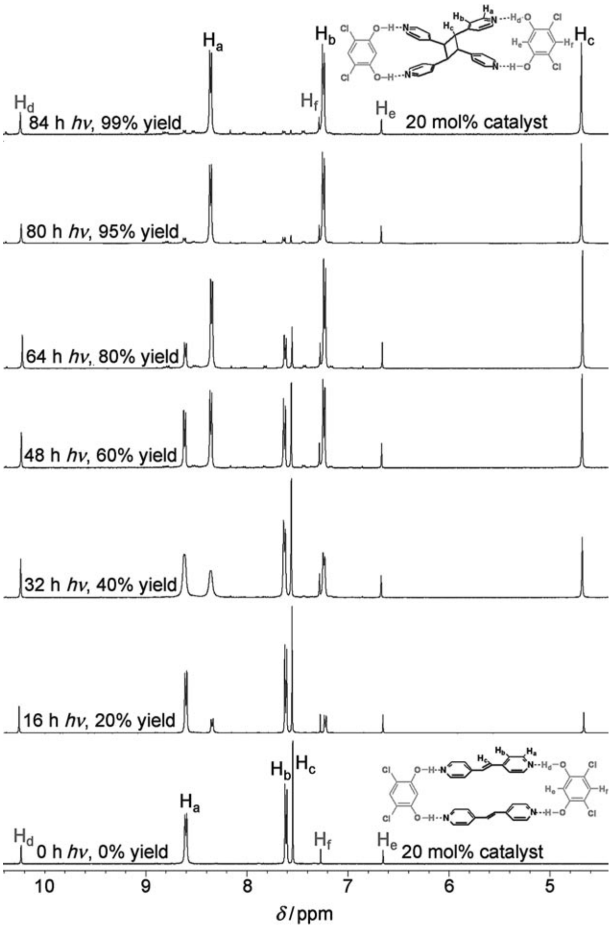

Figure 3. ^{1}H NMR spectra of the solid-state conversion of 4,4′-bpe to 4,4′-tpcb using 20 mol% 4,6-diCl-res.

Table 1: Photodimerizations with 10, 20, and 50 mol% 4,6-diCl-res.

Irradiation time [h]	Yield [%] 50 mol% catalyst (turnover: 40 h)	 20 mol% catalyst (turnover: 16 h)	 10 mol% catalyst (turnover: 8 h)
0	0	0	0
8			13
16		20	20
24			28
32		40	40
40	54		50
48		60	60
56			68
64		80	81
72			90
80	90	93	99
84		98	
90	95		

bonds between 4,6-diCl-res and 4,4′-bpe. The latter observation is remarkable given that the hydrogen bonds involving 4,6-diCl-res to either 4,4′-bpe or 4,4′-tpcb are of the same type. The perfect stereoselectivity that results from the second grinding reaction can be attributed to the highly specific nature of packing interactions in a solid. Collectively, the two-step grinding process that forms the reactive assembly 2(4,6-diCl-res)·2(4,4′-bpe) and results in stereospecific generation of additional photoproduct is representative of a highly efficient catalytic turnover.

A series of five re-grinds and application of UV radiation for 80 h resulted in the stereospecific photodimerization of 4,4′-bpe to 4,4′-tpcb in 93% yield. One additional grind and exposure to UV radiation produced 4,4′-tpcb in overall 98% yield. The slight relative decrease in yield on the final grinding can be attributed to slower kinetics, whereby the assembly process involving the catalyst and olefin to form 2(4,6-diCl-res)·2(4,4′-bpe) occurred at a lower rate owing to the relatively low concentration of 4,4′-bpe in the solid (i.e. in the presence of nearly 93% 4,4′-tpcb).

To study the scope of the supramolecular catalysis, the photoreactions were conducted at 10% and 50% molar concentrations of 4,6-diCl-res (Table 1). In these experiments, the conversion of 4,4′-bpe to 4,4′-tpcb proceeded in 99% (80 h) and 95% (90 h) overall yields, respectively. Similar to the run involving 20 mol% catalyst, approximately 100/n (where n = % catalyst loading) turnovers were required for the catalysis to proceed to near quantitative yield. The run involving 50 mol% catalyst also displayed slower kinetics at yields > 90%. In all cases, a single stereoisomer formed. These observations are consistent with the photodimerizations involving 10, 20, and 50 mol% catalyst proceeding under the same topochemical control, with the topochemistry not being compromised by differing amounts of 4,4′-bpe present in the initial solid mixtures. Preliminary experiments also reveal that the supramolecular catalysis proceeds with approximately 1 mol% catalyst. Under these conditions, an automated system wherein the grinding and photoreaction occur simultaneously (e.g. ball mill) would be desired to reduce the time associated with manual mortar-and-pestle grinding (i.e. approximately 33 h of grinding).

To gain insight into the structure and dynamics of the catalysis, we monitored the progress of a series of photodimerizations using powder X-ray diffraction (PXRD) with 50% supramolecular receptor (Figure 4). Upon grinding for 20 min, PXRD revealed reactive co-crystal phase (i.e. 2(4,6-

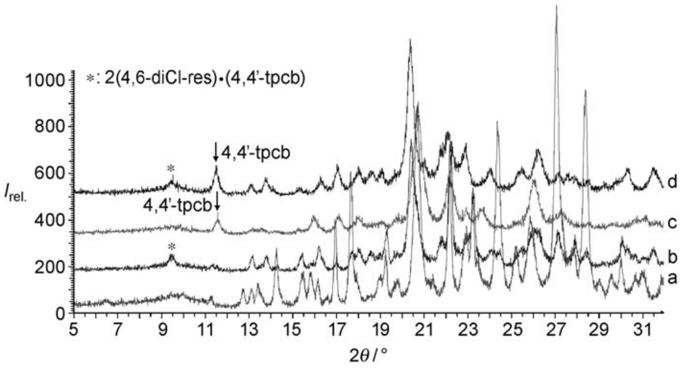

Figure 4. PXRD patterns of a mixture of 4,6-diCl-res (50%) and 4,4′-bpe: a) 20 min dry grinding, b) 40 h UV irradiation, c) additional 20 min grinding, and d) additional 50 h UV irradiation.

diCl-res)·2(4,4′-bpe)) as well as pure reactant phase (i.e. crystalline 4,4′-bpe) (Figure 4, trace a). Exposing the solid to UV radiation for 40 h resulted in the formation of crystalline 2(4,6-diCl-res)·(4,4′-tpcb) (yield of 4,4′-tpcb ca. 50%; $2\theta = 9.5^{\circ}$), which is consistent with the SCSC reactivity (Figure 4, trace b). The photoreaction, thus, likely proceeded through a SCSC reaction.[12] The solid was then re-ground 20 min. PXRD analysis revealed the disappearance of crystalline 2(4,6-diCl-res)·(4,4′-tpcb) ($2\theta = 9.5^{\circ}$) and formation of crystalline 4,4′-tpcb ($2\theta = 11.5^{\circ}$) (Figure 4, trace c). These observations are consistent with the dry grinding breaking the hydrogen bonds of 2(4,6-diCl-res)·(4,4′-tpcb). Exposing the solid to UV light for additional 50 h produced 4,4′-tpcb in 95% yield. Phases identified at the end of the photoreactions were crystalline 2(4,6-diCl-res)·(4,4′-tpcb) ($2\theta = 9.5^{\circ}$) and pure crystalline 4,4′-tpcb ($2\theta = 11.5^{\circ}$) (Figure 4, trace d). The mechanochemistry is, thus, necessary to induce movements and structural rearrangements to achieve catalytic turnover.

Whereas the ability of dry grinding to generate co-crystals is known,[15] the use of mechanochemistry to support supramolecular catalysis has not been reported. In general, a catalyst binds reactants, dissociates from the product, and reforms a reactive complex. A major point of focus for the catalysis here lies in the second grinding step. At this step the catalyst must, following the crystalline-state reaction, dissociate from the product and bind additional olefin for turnover in the absence of solvent. From our experiments, it is clear that dissociation and subsequent binding does not occur spontaneously upon prolonged UV irradiation, or at an appreciable rate, which can be attributed to a lack of mobility in the solid.

To understand why the second grinding supports turnover, we performed DFT calculations on the hydrogen-bonded assemblies before and after photoreaction. Beginning with the X-ray coordinates, the complex after photoreaction was estimated to have a binding energy 1.1 kcal mol^{-1} less than the complex before reaction. The lower energy was surprising since the hydrogen bonds between receptor and product can be expected to be stronger owing to the higher basicity of 4,4′-tpcb compared to 4,4′-bpe,[16] while the X-ray data showed the hydrogen bonds before and after photodimerization to be of expected geometries. Further examination of the X-ray data, however, suggests that the lower binding energy of the cyclobutane complex may be attributed to weakening of two bifurcated CH···N hydrogen bonds during the photodimerization (C···N separations: 3.373(3), 3.449(3) Å). The X-ray data supports weakening, which involve the H atom flanked by the hydroxy groups of 4,6-diCl-res as the donor and two N atoms of two stacked pyridine rings as acceptors, as the pyridyl groups undergo splaying during cyclobutane formation (Figure 5a). The DFT calculations suggest that each interaction loses 0.3 kcal mol^{-1} following photoreaction. The DFT calculations also demonstrate that the optimized cyclobutane complex prefers a twisted helical conformation in the gas phase compared to a solid. Twisting enables the two receptors to accommodate splaying of the pyridyl groups, as well as puckering of the cyclobutane rings. When combined with the fact that strain generally accumulates in solids in SCSC reactions,[12] our data supports the second grinding facilitating turnover. The second grinding serves to dissociate the more loosely bound product from the catalyst where a release of strain energy and formation of more thermodynamically stable reactive olefinic complexes for a subsequent turnover are favored.

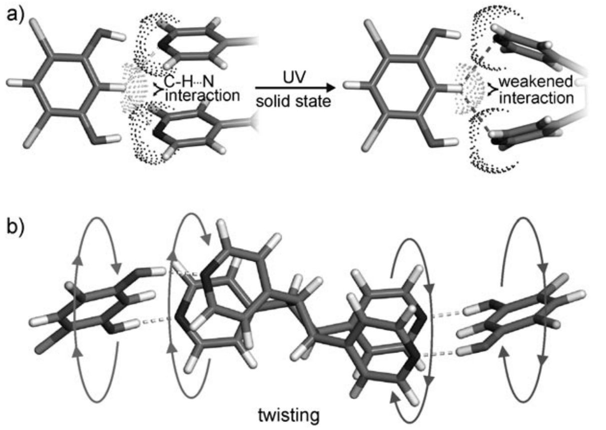

Figure 5. DFT-calculated optimized structures: a) 2(4,6-diCl-res)·(4,4′-bpe), b) 2(4,6-diCl-res)·(4,4′-bpe).

An examination of the packing of the pure olefin 4,4′-bpe shows that N atoms are readily available for binding on the surface of the solid during the second grinding.[17] More specifically, the N atoms are present in layers at 5.77 Å (Figure 6a). This contrasts 4,4′-tpcb, where there are less exposed N sites owing to canted packing of 4,4′-tpcb (Figure 6b). Moreover, the availability of the N sites of crystalline 4,4′-bpe relative to 4,4′-tpcb is also a likely contributor to the stereospecific formation and reactivity of crystalline 2(4,6-diCl-res)·2(4,4′-tpcb) in the second grinding.

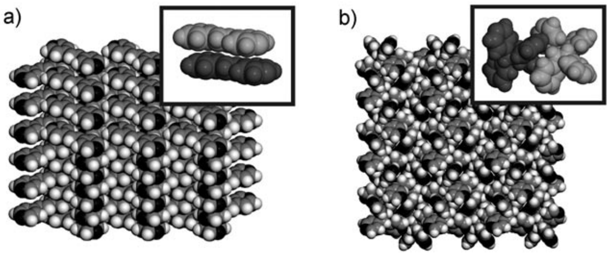

Figure 6. Accessibility of N atoms (black): a) olefin 4,4′-bpe and b) photoproduct 4,4′-tpcb along (−101) and (001) planes, respectively. Insets show localized packings.

In conclusion, we have demonstrated that supramolecular catalysis can be achieved using a ditopic receptor in the crystalline state. Hydrogen-bond-driven self-assembly directs a [2+2] photodimerization where mortar-and-pestle grinding induces reactions to facilitate turnover. We expect an automated mechanochemical processes (i.e. ball mill combined with UV light) could lead to significantly decreased reaction times and reductions in catalyst amounts. A wide variety of supramolecular catalysts applied in solution[6] could also be exploited in solids to direct covalent bond forming processes.[24]

Experimental Section

Mechanochemistry: 4,4′-bpe (98 %) and 4,6-diCl-res were purchased from Aldrich Co. and used without further purification. NMR data were collected on a 300 MHz Bruker DRX-300 spectrometer. In a typical experiment, 100 mg of 4,4′-bpe and 98 mg of 4,6-diCl-res were placed in an agate mortar. The compounds were ground for 20 min. The sample was placed between two glass plates and exposed to broadband UV radiation (450 W medium-pressure Hg lamp) for 16 h. The glass plates were clamped onto a copper plate heat sink maintained at room temperature. The sample was mixed for a period of 1 min to ensure homogeneity and a sample was removed for ^{1}H NMR analysis. The compound was ground for 20 min and subsequently exposed to broadband UV radiation for 16 h. The procedure was repeated for four additional cycles.

X-ray data diffraction: All crystal data were measured on a Nonius Kappa CCD single-crystal X-ray diffractometer at room temperature using MoK_α radiation ($\lambda = 0.7107$ Å). After anisotropic refinement of non-hydrogen atoms, H atoms bonded to C atoms were placed in idealized positions and allowed to ride on the atom to which they are attached. The resorcinol H atoms were calculated in an optimal hydrogen-bonding geometry. Structure solution was accomplished with the aid of SHELXS-97 and refinement was conducted using SHELXL-97.[18] Crystal data for 2(4,6-diCl-res)·2(4,4′-bpe): monoclinic, $P2_1/n$, $a = 8.590(1)$, $b = 11.836(1)$, $c = 16.723(2)$ Å, $\beta = 99.037(5)°$, $V = 1679.1(3)$ Å^3, $\rho_\text{calcd} = 1.429\ \text{g cm}^{-3}$, $Z = 4$, $F(000) = 744$, $\mu = 0.399\ \text{mm}^{-1}$, MoK_α radiation ($\mu = 0.71070$ Å), $T = 290(2)$ K, 9758 collected reflections, 2951 unique reflections ($R(\text{int}) = 0.040$), 1995 observed reflections [$I > 2\sigma(I)$], $\theta_\text{max} = 25.00°$, $R_1(\text{obs}) = 0.042$, $wR_1(\text{obs}) = 0.098$, $R_2(\text{all}) = 0.077$, $wR_2(\text{all}) = 0.108$ (CCDC-702701). Crystal data for 2(4,6-diCl-res)·2(4,4′-tpcb)(SCSC): monoclinic, $P2_1/n$, $a = 8.464(1)$, $b = 11.718(1)$, $c = 16.544(2)$ Å, $\beta = 99.850(5)°$, $V = 1632.3(3)$ Å^3, $\rho_\text{calcd} = 1.470\ \text{g cm}^{-3}$, $Z = 2$, $F(000) = 744$, $\mu = 0.411\ \text{mm}^{-1}$, MoK_α radiation ($\mu = 0.71070$ Å), $T = 290(2)$ K, 9434 collected reflections, 2864 unique reflections ($R(\text{int}) = 0.044$), 1951 observed reflections [$I > 2\sigma(I)$], $\theta_\text{max} = 25.00°$, $R_1(\text{obs}) = 0.040$, $wR_1(\text{obs}) = 0.095$, $R_2(\text{all}) = 0.073$, $wR_2(\text{all}) = 0.106$. CCDC 702701 [2(4,6-diCl-res)·2(4,4′-bpe)] and 702702 [2(4,6-diCl-res)·2(4,4′-tpcb)(SCSC)] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.). Powder X-ray data were collected on a Bruker D-5000 diffractometer equipped with a Bruker SOL-X energy-sensitive detector using $\text{Cu}K_{\alpha1}$ radiation ($\lambda = 1.54056$ Å).

Computational studies: All calculations were performed using Turbomole 6.1.[19] All geometry optimizations were performed using BP86[20] functional combined with TZVP basis set[21] and RI approximation. An empirical dispersion correction was used to account for weak interactions.[22] Numerical frequency calculations were used to confirm minima on the potential energy surfaces. Single-point energies of RI-BP86/TZVP optimized molecules were calculated using RI-MP2/TZVP method.[23] Binding energies were calculating by subtracting RI-MP2/TZVP calculated energies of separate components from those of the hydrogen-bonded assembly.

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