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Mechanically Flexible Organic Crystals Achieved by Introducing Weak Interactions in Structure: Supramolecular Shape Synthons

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ABSTRACT: Controlling mechanical properties of ordered organic materials remains a formidable challenge, despite their great potential for high performance mechanical actuators, transistors, solar cells, photonics and bioelectronics. Here we demonstrate a crystal engineering approach to design mechanically reconfigurable, plastically flexible single crystals (of about 10) of three unrelated types of compounds by introducing active slip planes in structures via different non-interfering supramolecular weak interactions, namely van der Waals (vdW), π -stacking and hydrogen bonding groups. Spherical hydrophobic groups, which assemble *via* shape complementarity (shape synthons), reliably form low energy slip planes, thus facilitate an impressive mechanical flexibility, which allowed moulding the crystals into alphabets, "o r g a n i c c r y s t a l". The study, which reports the preparation of a series of exotic plastic crystals by design for the first time, demonstrates the potential of soft interactions for tuning mechanical behaviour of ordered molecular materials, including those from π -conjugated systems.

1. INTRODUCTION

Utilizing collective molecular functions from highly dense and grain boundary-free, ordered structures of organic materials is currently attractive owing to their potential applications in mechanical actuators,^{1,2} phototransistors,^{3,4} light-emitting diodes (LEDs),⁵ solar cells,⁶ photonics,⁷ integrated optical waveguides,⁸ bioelectronics,⁹ flexible electronics¹⁰ etc. Although the intrinsic structure-function tunability, light weight and low cost advantages of the single crystalline organics over inorganic counterparts make them highly attractive, the poor mechanical performance at single particle level remains a great limitation for their practical usage on flexible substrates." Ordered single crystals with high mechanical flexibility comparable to that of thin films, elastomers and polymers, can be highly advantageous for future smart materials. Although there have been increasing reports on various dynamic single crystals that for example show plastic or elastic flexibility,¹²⁻¹⁴ photomechanical effect,¹⁵⁻¹⁹ thermosalient effect,²⁰ twisting,²¹ most of these exotic single crystals are from serendipitous discoveries.

High plasticity, which is aimed in this study, can offer some unique and diverse advantages in functional molecular crystals, for instance, excellent mechanochromic luminescence (change of emission color upon mechanical action) in solid-state fluorophores,^{22,23} good tabletability in API solid forms^{24,25} and lower detonation sensitivity in explosives.²⁶



Figure 1. Building blocks utilized for achieving flexible single crystals. Derivatives that successfully resulted flexible crystals are shown in black while those failed are in grey.

These recent studies have revealed excellent structuremechanical behavior correlation, but to the best of our knowledge not a single example was achieved by design. This goal suffers from the requirement of control over local molecular movements, which is critical in ensuring effective

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dissipation of stress arising from structural functions. Stress dissipation in such dynamic crystals occurs typically via the exchange or modulation of weakest intermolecular interactions, such as van der Waals (vdW), C–H···O, lighter halogens, π ··· π or combination of these multiple forces in the structures, which is vital for preserving the monolithic nature of crystals during such macroscopic manifestations.²⁷

Although the importance of the weak dispersive interactions is long acknowledged in crystal engineering²⁸ and materials chemistry,²⁹ they have been perceived as poorly dependable, hence remained largely unexpended for accomplishing predetermined structural architectures that perform particular tasks. To overcome such burden, here we targeted the least interfering supramolecular *shape synthons* — synthons formed via hydrophobic groups by shape complimentary isotropic interactions — to rationally design mechanically flexible plastic single crystals.

2. RESULTS AND DISCUSSION

2.1 On Plastic Bending Model: Earlier hypothetical model^{12,30} and recent mechanistic studies²⁷ on plastically bendable crystals suggest that bending proceeds by segregation of bent section into flexible layers that slide on top of each other via reorganization of weaker intermolecular interactions (vdW and stacking), thereby generating domains with slightly different lattice orientations. Nanoindentation studies by Desiraju and Ramamurty suggest that shear sliding of the crystallographic planes dominates the mechanism of plasticity in molecular crystals rather than other mechanisms such as dislocation movement.^{31,32} Hence, we targeted for a structural setup with a combination of weak interactions, namely vdW (for shear sliding) and π -stacking (for splaying of molecules to accommodate the bend angle) in perpendicular direction to achieve plastically bendable crystals.^{12,27,30}

2.2 Design Strategy for Achieving Plastically Flexible Single Crystals

To move from serendipity to design, we considered the following crystal engineering strategy. A variety of noninterfering groups, namely spherical vdW groups and aromatic groups with or without hydrogen bonding functionalities (Figure 1) are strategically targeted. The near spherical vdW groups can potentially close pack with themselves to form smooth slip planes in the structure while the central aromatic core groups tend to close pack in perpendicular direction, typically via π -stacking (Figure 2). In some cases, a third set of dominant hydrogen bonding groups were employed, as they also do not interfere with the above two, but prefer to form strong hydrogen

bonding interactions with themselves. Here, when these hydrogen bonding groups engage themselves by forming zero dimensional (oD) homosynthons, say carboxylic acid dimers, the other two weaker type interactions shall guide the rest of the self-assembly process independently and self-sort to pack with themselves. This in turn shall lead to the formation of slip planes by vdW groups between the π -stacked columns of molecular units; a favourable condition for plastic flexibility. Notably, the vdW and π stacking groups, both of which are weak and largely dispersive, due to the slight difference in the interaction nature and shape similarity of identical groups are expected to promote self-sorting and limit the possibility of synthon cross over, thus shall follow the proposed packing model.

To test this crystal engineering hypothesis and its general applicability, we chose three unrelated classes of molecules, i) N-substituted naphthalene diimides (NDIs), ii) substituted benzenes and iii) Schiff bases. Each class is unique and serves a different purpose: the NDI building blocks consisting of rigid covalently linked core group, represent the π -conjugated semiconducting molecular materials; the substituted benzene carboxylic acids and amides act as supramolecular building blocks where the core is uniquely constructed by hydrogen bonded acid dimer (oD) or amide (1D or 2D) synthons, hence act as prototype models for synthon based crystal engineering; Schiff bases, consisting of non-rigid unsymmetrical building blocks with a greater conformational freedom, belong to the interesting class of compounds with solid-state properties such as photochromism³³ and thermosalient nature.³⁴

2.3 Covalent π -conjugated Building Blocks: Alkyl Shape Synthons

In this series, we synthesized³⁵ several naphthalene diimides (NDIs), with alkyl vdW substituents such as methyl (1a), *n*-propyl (1b), *p*-tolyl (1c) and *tert*-butyl (1d) on either ends of the central NDI core, which act as covalent building blocks (Figure 1). The π -conjugated NDIs have attracted much current interest in materials science and supramolecular chemistry owing to their striking electronic (n-type semiconductors) and spectroscopic properties, and ease of preparation. The crystallization typically resulted in long needles, with lengths of up to 1 cm, and were suitable for X-ray structure determination (crystallographic information is given in SI, Table S1). Although we synthesized some halogen substituted NDI analogues, their poor solubility prevented further progress.

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Figure 2. Illustration of the supramolecular shape synthon based, slip plane model for achieving plastic flexibility in single crystals. (a) Building block, constructed *via* covalent or hydrogen bonded linkages, possessing central core (in red) and peripheral vdW (in blue) groups. (b) Self-assembly of building blocks into target structural model with slip planes (broken blue lines), driven by shape synthon forming vdW groups. (c) Structural model showing the sliding of flexible molecular sheets along slip planes upon crystal bending. (d) Prototype naphthalene diimide (**1a**) based covalent building block and (e) its crystal packing, which resemble the target slip plane model in (b). (f) Micrographs of a flexible single crystal of **1a**, before (left) and after (right) mechanical bending. (g) Analogie is drawn to compare the bending of sticky yellow pad and plastic crystal via slippage of individual sheets and slippage of molecular layers, respectively (in c and f). Notice the similarity of the top ends of the bent crystal (image on right, in f) and sticky note pad in (g). (h) Scanning electron microscopy image of the mechanically bent crystals of **1a**.



Figure 3. Crystal packing and mechanical behavior of 1b and 1d. (a) Crystal packing in 1d with smooth slip planes formed by shape synthons involving spherical *tert*-butyl groups. (b) Plastic and highly flexible 1d crystals mould into letters "I I R S", where first "I" corresponds to an undisturbed reference crystal and the second "I" a crystal bent-andreconfigured back to original morphology. (c) A layer of 1c molecules in bc-plane showing zipper type arrangement of

elongated *n*-propyl groups and (d) arrangement of the next layer, where the n-propyl groups pointing in opposite direction to that of the first, hence interlocked to prevent slippage. (e) The brittle mechanical fracture of **1b** crystals.

Analysis of crystal structures of 1a (monoclinic P_{2_1}/c), **1b** (orthorhombic *Pbca*), **1c** (monoclinic P_{2_1}/c) and **1d** (triclinic *P*-1) by visual inspection revealed that in all the cases the vdW groups close pack with themselves to form the shape synthons (isotropic interactions) as anticipated while the aromatic groups form π -stacked columns in all the solids of this series. Notably in case of 1a, 1c and 1d the shape synthons align along a crystallographic plane, thus result in slip planes (except in 1b), showing an excellent agreement with our target weak interaction based self-assemble model. For instance, in 1a the central NDI aromatic core group forms π -stacked columns while the spherical methyl groups close pack with themselves via vdW shape synthons and form the slip planes parallel to (0 0 2) (Figure 2e). Similarly, the compounds 1c (SI, Figure S1), **1b** and **1d** (Figure 3a) also formed the π -stacked columns separated by slip planes. Notably, in case of 1b the elongated vdW groups (n-propyl) from adjacent stacks face in opposite direction.

(a)

(c)

Mechanical behavior of the crystals was examined by a simple qualitative method, i.e. applying mechanical stress using a pair of forceps and a metal needle while viewing them under a stereomicroscope.³⁰ To our delight, the single crystals of 1a, 1c, and 1d showed excellent plastic flexibility, while notably **1b** underwent brittle fracture. The crystals of 1a, 1c and 1d could be bent to 360° (Figure 2h; videos S1, S2 and S3 corresponding to 1a, 1c and 1d respectively). To demonstrate this impressive plastic flexibility, we mould the crystals of **1a** (Figure 2h) and **1d** (Figure 3b) into a variety of shapes, such as letters "S E M" and "I I R S", respectively. Such plastic flexibility is unprecedented in π -conjugated organic crystals. The bent crystals remain monolithic without much damage to the morphological integrity, even at the extreme bend angles such as in "S" and "M". All the crystals bend only on one pair of faces that is parallel to the slip plane, while break on the perpendicular pair of faces under similar conditions (see video S4).

In case of **1b** (brittle) the elongated –CH₂–CH₂–CH₂ vdW groups from stacked columns face in opposite direction, unlike in the case of spherical –Me, –*t*-Bu groups. Although the shape synthons are formed in this structure as well, the uneven surface probably prevents smooth sliding of molecular slides and make these crystals brittle (Figure 3c, 3d; video S4).³⁶ This suggests that the nearly spherical vdW groups, such as -Me and -tBu, that with smooth potential energy surfaces, can potentially be exploited to form active slip planes for plastic bending.

2.4 Hydrogen Bonded Building Block: Halogen Shape Synthons

As crystal engineering strategies that work very well in one particular series may fail in another, we have extended the study to other molecules, including those with hydrogen bonding groups. The molecular units employed in this series possess a carboxylic acid or amide group. The supramolecular dimer formed by these groups acts as a central core, in place of the rigid covalent moiety in the NDI series (Figure 1). The vdW groups here are mostly halogen groups (Cl, Br), except in 2e (-tBu), which are substituted on aromatic ring. The lighter halogens are expected to form soft halogen...halogen (X...X) interactions.³⁷⁻³⁹ Halogen interactions are generally classified into two categories: type I (geometrical) and type II (chemical, polarization based). The type I X...X interactions, which are more favored by lighter halogens Cl and Br, are nonpolar and typically interact based on shape complementarity, hence qualify as shape synthons (softer type) desired for our model. On contrary, heaviest halogen group, iodine prefers the polarization based stronger type II X...X interactions (harder type),³⁷ hence is not desirable.

The dichloro compounds, **2a** (C_2/c) and **2b** (P_{2_1}/c) , form the carboxylic acid dimers (oD) via cyclic O-H-O hydrogen bonds (Table S2, Hydrogen bond table). These dimers further pack into columns along *b*-axis with only



(b)

 π -stacking interactions. As anticipated, the Cl groups in both 2a and 2b not only form type I Cl…Cl (in 2a: 3.486Å, 159.79°, 124.83°; in **2b**: 3.492Å, 172.34°, 116.70°) shape synthons, but also aligned to form slip planes parallel to (0 0 1) in both cases. This is very significant as despite the different geometrical positioning of Cl groups in 2a (2,3-) and **2b** (3,4-), they form the slip planes in a similar manner, demonstrating the driving potential of Cl groups for forming the shape synthons. Not only this, the crystals of both 2a and 2b showed high plastic bending flexibility upon mechanical action, demonstrating the striking agreement with the proposed model.

The monohalo-compounds, **2c** (2-chlorobenzoic acid) and **2d** (2-bromobenzoic acid), also form dimers that pack into columns in the structure. The slip planes are also formed in them, but are not entirely by the halogen groups. The single halogen group (less surface area, compared to the dihalo-compounds) and the edge-to-edge aromatic interactions (which are also vdW type) (SI, Figure S2) contribute to the slip plane. These two crystals also show plastic flexibility, which is demonstrated by shaping them into letters "o r g a n i c c r y s t a l" (Figure 4c). While the simple benzoic acid fails to show plastic flexibility, perhaps due to the absence of any soft vdW groups and presence of more specific C-H--O interactions between slip stacked molecules in the structure (SI, Figure S₃).

200µm



Figure 5. Schematic representation of brittle fracture in amides. (a) Formation of building block and (b) packing of molecules into hydrogen bonded sheets, separated by slip planes. The strong extended H-bonds make the sheets rigid. (c) Tight packing of molecules within the rigid sheet prevents splaying of molecules, hence fracture ensues. (d) Amide based molecular building block. (e) Formation of 1D N-H···O hydrogen bonds and supramolecular shape synthons *via* Cl···Cl interactions. (f) Illustration of the molecular packing with 1D hydrogen bonded sheets separated by slip planes in the crystal. Sliding of layers requires the movement of entire sheet at a time due to its rigidity; splaying of molecules is also restricted by extended hydrogen bonding, thus the crystals break instead of plastic bending. (g) Fracture of crystals of **3a** upon application of a mechanical stress.

To test if the presence of slip planes in crystals alone is sufficient or the absence of extended hydrogen bonds is also needed for plastic flexibility, some primary amide analogues were also studied. Because, in contrast to the oD acid dimers, amides typically form extended 1D chains or 2D sheets due to the presence of additional N—H group. We succeeded to synthesize and obtain suitable single crystals of amides, **3a** (3,4-dichlorobenzamide) and **3b** (*p*-tertiarybutyl benzamide, see Figure 1). Remarkably, in both **3a** and **3b** the vdW groups again close pack with themselves across a plane in the crystals to form the desired slip planes (Figure 5). However, both the crystals were found to be brittle and showed no sign of plastic flexibility.

This suggests that the presence of strong N—H···O interactions in 1D and 2D networks may make the structure rigid, hence can prevents local molecular movements in crystals (Figure 5). Moving entire sheet or layer at a time for mechanical shearing is energetically expensive, i.e. the shear stress becomes greater than fracture stress. Hence the hydrogen bonded sheets may act as *rigid sheets* rather than *flexible sheets*. This suggests that in addition to the "softness" of the X···X or R···R interactions, the absence of *rigid* extended interactions in the structure is critical in providing such malleability to crystals. Stronger, but also "harder" interactions such as hydrogen bonding as seen in **3a** and **3b** would accumulate larger stress at short distances, and contribute to enhanced stiffness to cause fracture of the crystal.

2.5 Unsymmetrical Building Blocks with Multiple Types of vdW Groups

Contrary to the symmetrical building blocks in the two earlier categories, in this series there are some unsymmetrical Schiff bases of a pharmaceutically significant ovanillin compound, with greater conformational flexibility and multiple types of vdW groups. All the building blocks in this series, which are easy to prepare, have a common –OMe group (from vanillin) on one end and –OMe, –Cl, –Br, –Me, or -t-Bu on the opposite end (from substituted anilines), while the central part consists of -C=N-(Figure 1). Hence, this increased complexity (unsymmetrical molecular geometry with different functional groups on two ends and greater conformational flexibility) provides a good test for assessing the reliability and generality of our proposed design model.

Analysis of crystal structures revealed that majority of the structures are indeed consistent with the proposed model (Figure 6(a) & 6(b)). For instance, in **4a** the slip planes are formed by the two –OMe groups on either ends (SI, Figure S6) while the aromatic groups form the π stacking interactions in the orthogonal direction, which result in a corrugated packing. The compounds **4b** and **4c**, which are isostructural ($P_{2,2,2_1}$), also form slip planes by close packing of –OMe, –Cl/–Br and aromatic C–H groups (Figure 6(a) & 6(b)). On the other hand, compounds, **4d** and **4e**, with purely alkyl substituents (–Me, –*t*-Bu groups, respectively, on the aniline side) failed to form slip planes, unlike in the successful cases of **1a** and **1d** with the same groups, respectively. The qualitative mechanical tests revealed that the crystals of **4a** to **4c** are highly flexible and bend plastically, while **4d** and **4e** did not show plastic flexibility under similar conditions. In the latter two crystals, the crystal structures adopt the π stacked layer arrangement with no slip planes by the vdW groups.¹² The failure of vdW groups to form slip planes in this complex system can be attributed to the interference from electronegative groups (formation of sp³C-H...O between –OMe groups) on these molecules (SI, Figure S7, S8). Nevertheless, the model has facilitated a fair success even in this complex series.



Figure 6. Formation of shape synthons in unsymmetrical Schiff base building blocks. (a) Packing in (E)-2-((4chlorophenylimino)methyl)-6-methoxyphenol, **4b**, and (b) (E)-2-((4-bromophenylimino)methyl)-6-methoxyphenol, **4c**, show the formation of slip planes by multiple vdW groups, – OMe (yellow) and Cl (green)/Br (grey). (c) Plot shows the first three lowest attachment energies of all the studied molecules. In all the cases, the first lowest Eatt shows a good agreement with the visually identified slip plane.

2.6 Calculated Attachment Energies: Identification of Low Energy Active Slip Planes

The attachment energy, E_{att} , is the energy released upon attachment of a growth slice to the growing face of a crystal. The $E_{\text{att}} = E_{\text{latt}} - E_{\text{slice}}$ where E_{latt} is the lattice energy, E_{slice} is the energy released on the attachment of a growth slice of a thickness equal to the inter planar *d*-spacing for the crystallographic plane representing the face. Calculated E_{att} data of all the crystals in this study (SI, Table S₃) shows an excellent agreement with the slip planes identified by visual inspection of respective crystal structures. Notably, in all the plastic bending crystals, the slip planes formed by the specifically chosen vdW groups for this model always possess the lowest E_{att} , as evident from the listed *E*_{att} values of the three weakest planes of each structure, shown in Figure 6c (also see SI, Table S₃). Hence, this not only justifies the choice of our vdW groups, but also their reliable transferability to other molecules.

The fair success of the model in three above classes of molecules demonstrates the potential of weaker interactions for reliably achieving desired structures, which we feel is important in the context of crystal engineering. The successful examples of ten plastically flexible crystals from the three different types of compounds demonstrate that the proposed model has potential to be transferred to other functional materials, while the failed cases provided further insights into the structural requirement for plastic flexibility. The study may act as a good starting point to further improvise the strategies to design future stimuli responsive dynamic crystalline materials.

3. CONCLUSIONS

Here we successfully demonstrated a crystal engineering strategy to achieve plastically flexible single crystals by introducing active slip planes in the structure by carefully placing selected non-interfering van der Waals (such as -t-Bu, -OMe, -Me, -Cl/Br etc.), π -stacking and hydrogen bonding groups, on three different classes of compounds. The key factor for achieving the desired crystal packing with low frictional planes, as required by the bending model, is primarily the non-interfering and selfsorting nature of the selected functional groups, i.e. (i) the van der Waals (vdW) groups, (ii) hydrogen bonding groups that form oD cyclic hydrogen bonded dimers, and (iii) the aromatic π -stacking groups. The dispersive nature of the vdW groups that with spherical shape, have favored formation of smooth molecular planes with least attachment energy (*i.e.* active slip planes) in the structure. The vdW shape synthons act as lubricated planes and allow molecular motions with minimal friction between molecular sheets. These groups allow sliding of molecules upon mechanical action while the π -stacking interactions aid the flexibility of sheets during mechanical bending. The absence of extended rigid hydrogen bonding networks is also a key factor for facilitating plastic flexibility in crystals. It appears that the strong self-sorting and noninterfering nature of the three distinct types of groups employed here is not only important for driving crystal packing, but also probably critical for preserving the short range structural order and promoting coordinated molecular movements in the process of crystal bending. The three diverse series studied here emphasize the potential of various weak vdW interactions for achieving plastic flexibility. Further, these unexploited weak interactions can also allow tuning the properties of diverse types of stimuli responsive organic solids. The well coordinated local molecular movements involved here are comparable to the supramolecular structural changes that generally occur in many other dynamic crystalline materials. Hence, our first design approach potentially has broad implications for the materials chemistry. Quantification of the mechanical properties by nanoindentation technique on the number of crystals studied here is planned for future.

4. EXPERIMENTAL SECTION

4.1 Materials. All the reagents were purchased from Sigma-Aldrich. Commercially available solvents were used (for synthesis and crystallization) as received without further purification.

4.2 Synthesis

4.2.1 NDI derivatives. N,N'-bis(methyl)-1,4,5,8-naphthalene diimide (**1a**), N,N'-bis(*n*-propyl)-1,4,5,8-naphthalene diimide (**1b**), N,N'-bis(*p*-tolyl)-1,4,5,8-naphthalene diimide (**1c**), and N,N'-bis(*p*-tertiarybutylphenyl)-1,4,5,8-naphthalene diimide (**1d**) were synthesized by condensation of the carboxylic acid dianhydride with two equivalents of the respective substituted amines in DMF at temperatures above 10°C for overnight.³⁵ All the obtained compounds were purified by recrystallization and characterized by using 'H-NMR and X-ray structure determination.

4.2.2 Amides. 3,4-dichloro benzamide (3a) and 4-tertiarybutyl benzamide (3b) were prepared from previously reported procedure.⁴⁰

4.2.3 Imines. All five imines **4a**, **4b**, **4c**, **4d** and **4e** were prepared by solid state mechanical grinding of *O*-vanillin and respective substituted aniline taken in 1:1 stoichiometric ratio.⁴¹

4.3 Preparation of single crystals. The derivatives of all NDIs were recrystallized from dichloromethane and all remaining compounds were recrystallized from diethyl ether by slow evaporation at ambient conditions. Crystals suitable for testing mechanical properties and single crystal data were obtained in 4 to 5 days in all the cases.

4.4 Single crystal X-ray structure determination. Single crystals of all the compounds were individually mounted on a glass pip. Intensity data of all the compounds (except 2e, 3b & 4e) were collected on a Bruker's KAPPA APEX II CCD Duo system with graphite-monochromatic Mo K α radiation (λ = 0.71073 Å). The data for 1a, 1c and 3b were collected at 100 K and all other compounds were collected at 296 K. Data reduction was performed using Bruker SAINT software.⁴² Crystal structures were solved by direct methods using SHELXL-97 and refined by full-matrix least-squares on F² with anisotropic displacement parameters for non-H atoms using SHELXL-97.43 Hydrogen atoms associated with carbon atoms were fixed in geometrically constrained positions. Hydrogen atoms associated with oxygen and nitrogen atoms were included in the located positions. Structure graphics shown in the figures were created using the X-Seed software package version 2.0.44

Intensity data of **2e**, **3b** and **4e** single crystals were collected on a Oxford Diffraction SuperNova (Dual, Cu at zero, Eos) diffractometer with monochromatic Mo K α radiation (λ = 0.71073 Å). The crystals of **2e**, **3b** were measured at 100K and **4e** at 296 K. The data reduction was done with *CrysAlis PRO and* structures were solved using Olex2,⁴⁵ with the Superflip⁴⁶ structure solution program using Charge Flipping and refined with the ShelXL $^{\rm 47}$ refinement package using Least Squares minimization.

4.5 Scanning Electron Microscopy (SEM). High resolution SEM was performed on a Zeiss microscope; SUPRA 55VP-Field Emission Scanning Electron Microscope. High performance variable pressure FE-SEM with patented GEMINI column technology. Schottky 5 type field emitter system, single condenser with crossover-free beam path. Resolution: 1.0 nm at 15 kV; 1.6 nm at 1 kV high vacuum mode. 2.0 nm at 30 kV at variable pressure mode.

4.6 Attachment Energies. The attachment energies of all the crystals were computed by Crystal Graph software using Dreiding forcefield and Gesteiger charges. The attachment energies were computed at medium quality using inputs from Crystal Graph.

ASSOCIATED CONTENT

¹H-NMR data, crystal packing diagrams with respective crystal images depicting mechanical deformation, videos, table containing crystallographic information, geometrical parameters of hydrogen bonding, ORTEP diagrams and a table of attachment energy values for each compound are provided as supplementary information. This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. [‡]These authors contributed equally.

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