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Supporting Information

Bipolar behaviour of Salt-bridges: A combined theoretical and crystallographic study

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Crystal Structure of (1)

In compound (**1**), the pyridine ring nitrogen and amino nitrogen atoms acts as donor to the carboxylate oxygen atoms in the molecule at (-1+x, y, z) and (-1/2+x, 3/2-y, 1-z); thus forming a $R_2^2(8)$ ring (M) and denoted as salt-bridge (SB). The amine nitrogen atom acts as double donor and thus interact with another carboxylate oxygen atom of the partner molecule at (-1+x, y, z). Again, the carboxylate oxygen atom acts as donor to the carboxylate oxygen atom at (1-x, -1/2+y, 1/2-z). Repetition of this interconnection leads the molecules to form a $R_8^7(40)$ ring and a two-dimensional framework in (011) plane (Fig. S1). In the same plane pyridine ring nitrogen atom C(5) interacts with carbonyl oxygen O(1) at (1-x, 1/2+y, 1/2-z) and generates another network structure with active participation of (SB) ring motif (Fig. S2). Interestingly, the carbon atom C(2) interacts the centroid of the (SB) ring with a separation distance of 2.549Å [C(2)-C(g) = 3.337Å; C(2)-H(2c)···C(g) = 138.41°]. Again, the (SB) is oriented towards the π-cloud of the protonated pyridine ring with a ring centroid separation of 3.568Å. Thus, (SB) motif is sandwiched by two other interactions in (**1**).

Crystal Structure of (2)

In (**2**), pyridine ring nitrogen and amine nitrogen atoms acts as donor to the carboxylate oxygen atoms O(3) and O(4) in the molecule at (-1+x, y, z) to form a $R_2^2(8)$ dimer (M) and consequently it's a (SB). Again, the amine nitrogen atom acts as donor to the O(3) atom of the nearby (SB) unit of the partner molecule at (-1/2+x, 1/2-y, -1/2+z), thus interconnecting the (SB) units and propagating along [001] direction (Fig. S3). These parallel (SB) chains are interconnected by the self-complementary H-bonds of carboxylate units. The carboxylate oxygen atom O(2) acts as donor to the carbonyl oxygen atom at (-1-x, -y, 2-z); thus forming a centrosymmetric dimeric $R_2^2(8)$ ring (N)

centered at (1/2, 0, 1) (Fig. S3) which leads the molecules to generate a two-dimensional network in (011) plane (Fig. S3). In another sub-structure, when pyridine ring carbon atom C(5) participate in H-bonding with the carboxylate oxygen atom belongs to (SB), a different network is generated in (011) plane (Fig. S4). The carbon atom C(3) is oriented towards the (SB) unit and in contact *via* parent hydrogen atom with a separation distance of 2.449Å [C(3)···(SB) = 3.235Å; C(3)–H(3a)···(SB) = 137.84°]. In opposite side of the (SB) unit, the π-cloud of the pyridine ring is juxtaposed with a separation distance of 3.806Å. The carbonyl oxygen atom O(3) is oriented towards the centroid of the π-ring with a separation distance of 3.381Å [C(4)–O3···Cg(1) = 100.72°]. Interestingly, in opposite side of the network, the methyl carbon atom C(10) is in contact with the π-cloud of the pyridine ring. Thus, an unique C–H···(SB)/(SB)···π^+/π^+···H–C network is generated in the solid-state structure of compound (**2**) (Fig. 3).

Crystal Structure of (3)

In (**3**), the pyridine ring nitrogen and amine nitrogen atoms are bonded with the carboxylate oxygen atoms at (1-x, 1/2+y, 1/2-z) and generate the $R_2^2(8)$ ring (SB) unit. In addition, the amine nitrogen shows an intramolecular hydrogen bond to carboxylate oxygen atom and binds the (SB) unit to form a building block. Again, the carboxylate oxygen atoms from the neutral succinic acid moiety acts as donor to the carboxylate oxygen atom of the (SB) unit at (1-x, 1-y, -z), and leads the molecules to propagate into a framework in (101) plane (Fig. S5). In another sub-structure, the pyridine ring carbon atoms (C5 and C7) acts as donor to the carboxylate oxygen atoms of the neutral succinic acid moiety and builds a two-dimensional framework in (011) plane (Fig. S6). Again, the pyridine ring carbon atom C(6) is in contact with the protonated pyridine ring, thus a zigzag chain is formed which propagates along [010] direction (Fig. S7). On both sides of the chain, the (SB) units interconnects the molecules and generate a layered

assembly in (110) plane (Fig. S7). Again, the amino nitrogen atom N(2) is oriented towards the (SB) unit with a separation distance of 2.283Å [N(2)···(SB) = 2.927Å; N(2)-H(2c)···(SB) = 131.69°]. In opposite side of the (SB), the carbonyl oxygen atom O(3) is juxtaposed towards the (SB) [O(3)···(SB) = 3.136Å; C(3)-O(3)···(SB) = 92.85°]. Thus, (SB) is sandwiched from two sides and generates an unique N–H···(SB)/(SB)···(l.p) network in (**3**) and thus a layered assembly in (101) plane (Fig. 4).

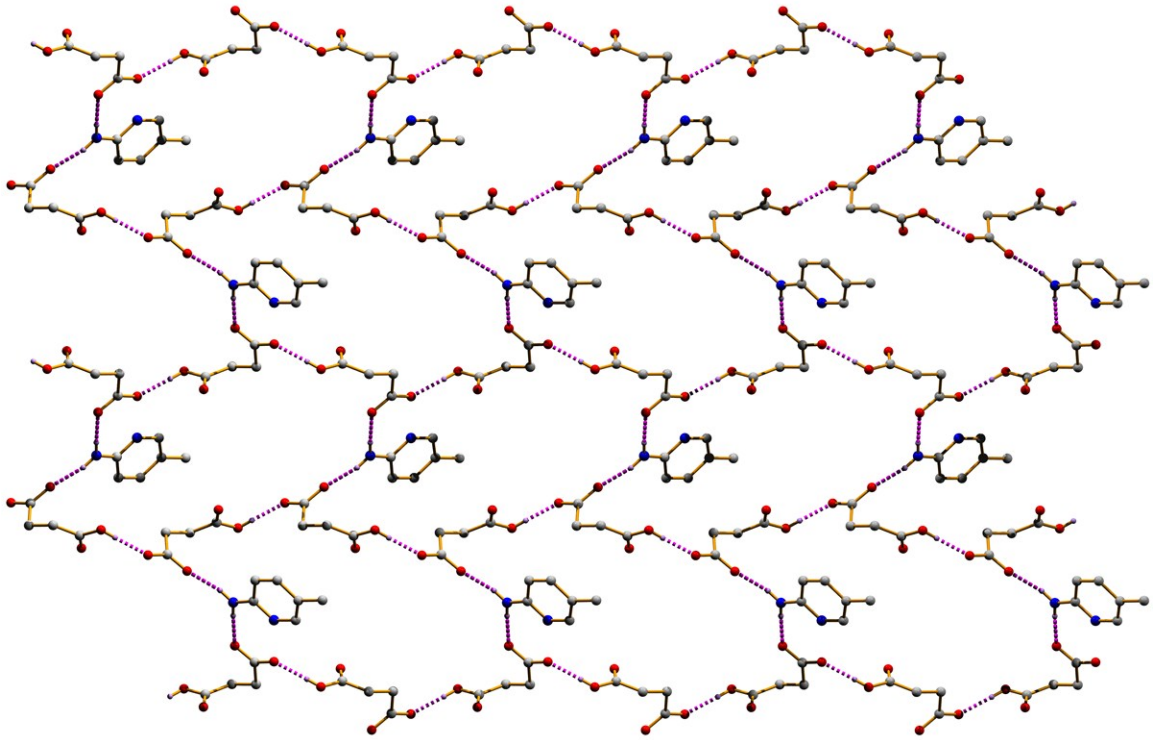

Fig. S1 Supramolecular framework in (011) plane in (**1**).

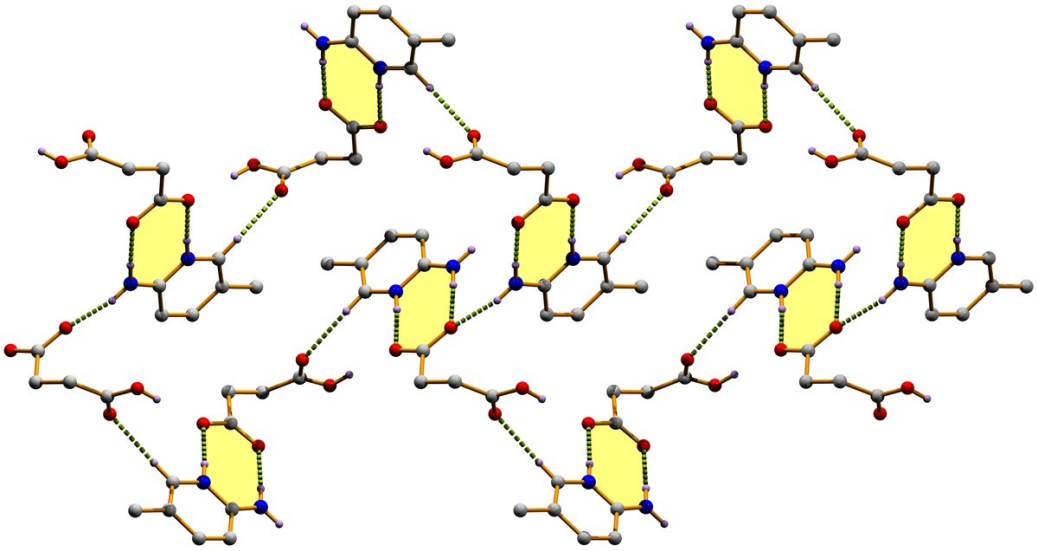

Fig. S2 Network generated in (011) through (s.b) unit and C–H···O bond in (**1**).

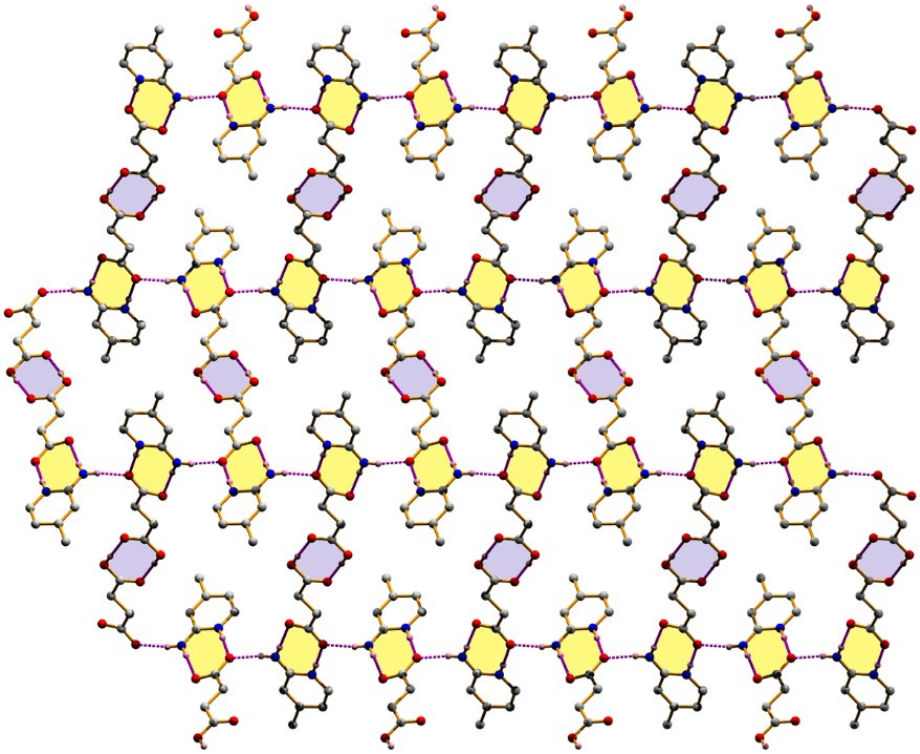

Fig. S3 Formation of two-dimensional supramolecular network that generated through two types of zero dimensional $R_2^2(8)$ rings in (011) plane in (**2**).

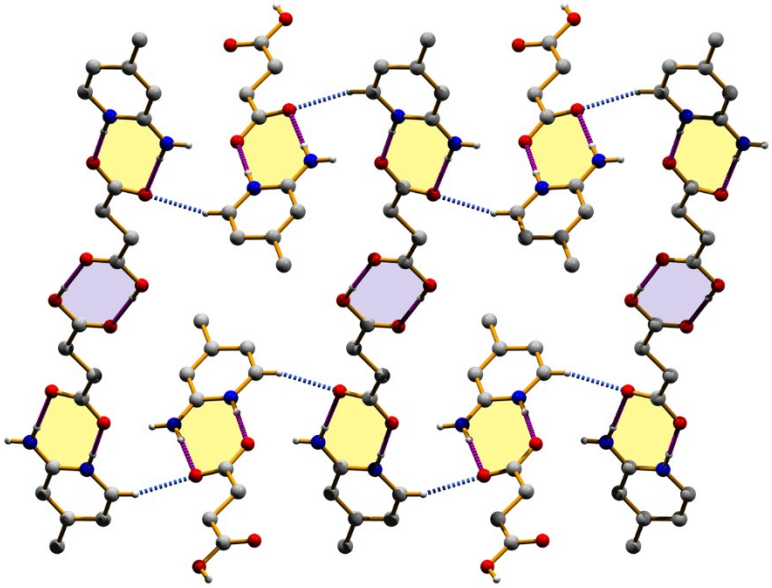

Fig. S4 Another network of (**2**) in (011) plane.

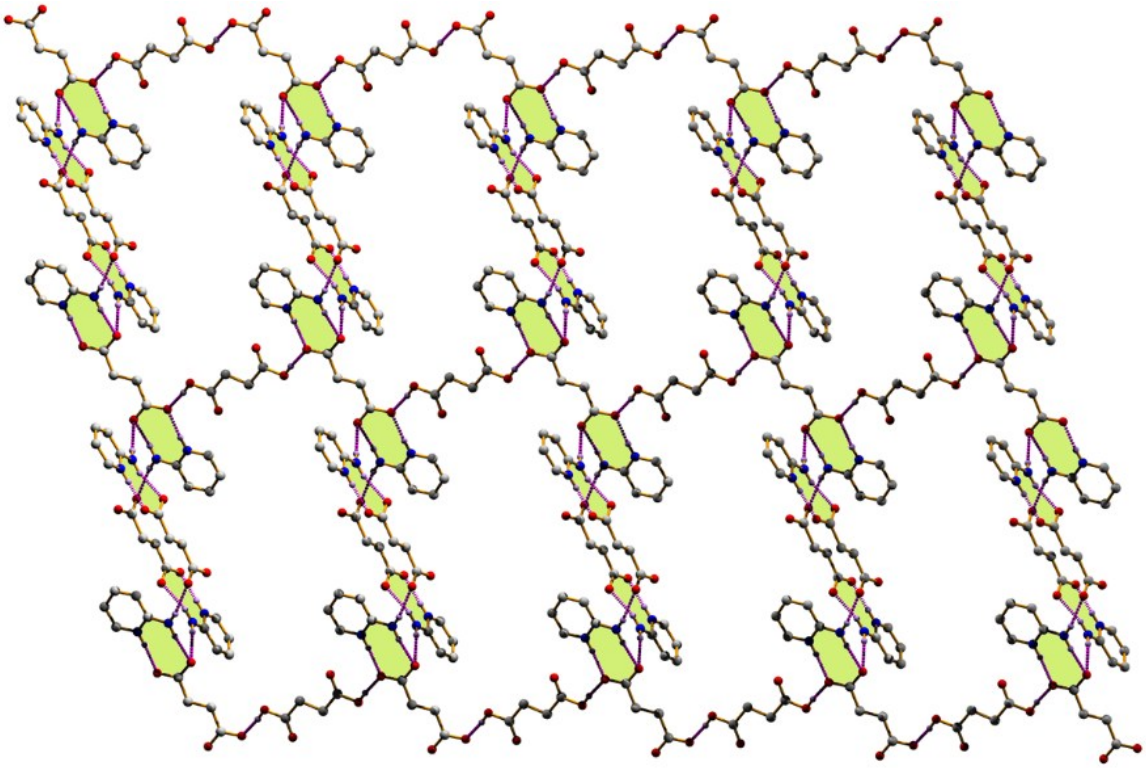

Fig. S5 Supramolecular layered assembly in (**3**) in (101) plane.

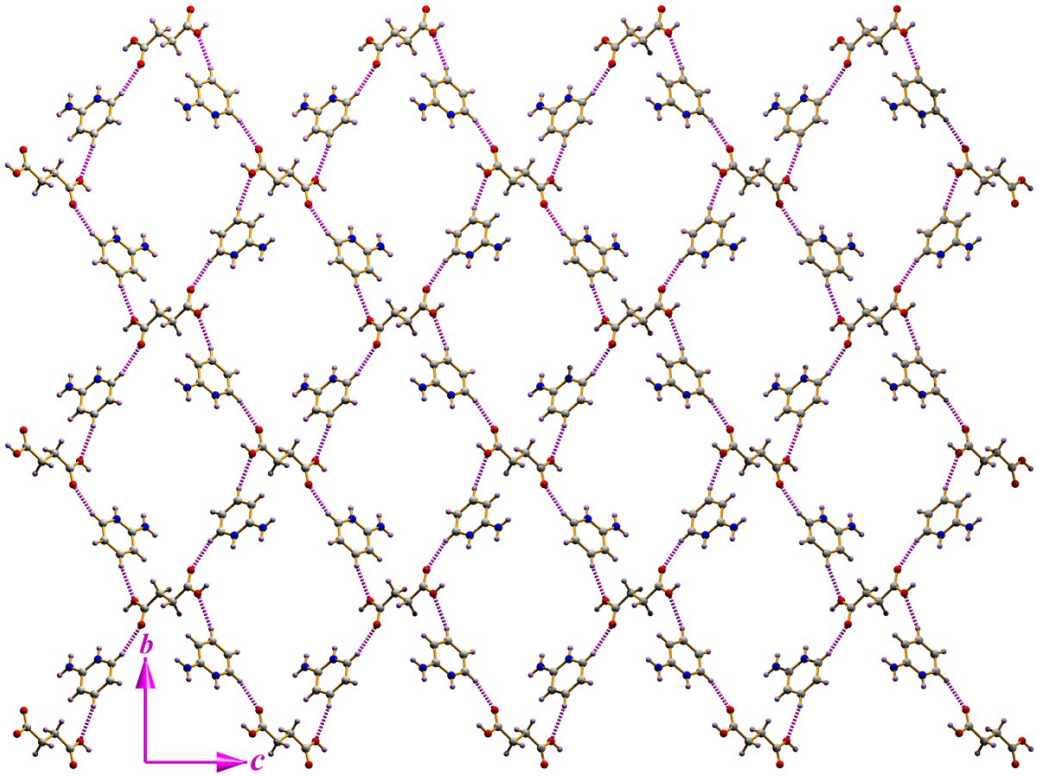

Fig. S6 Formation of supramolecular network in (011) plane for compound (**3**).

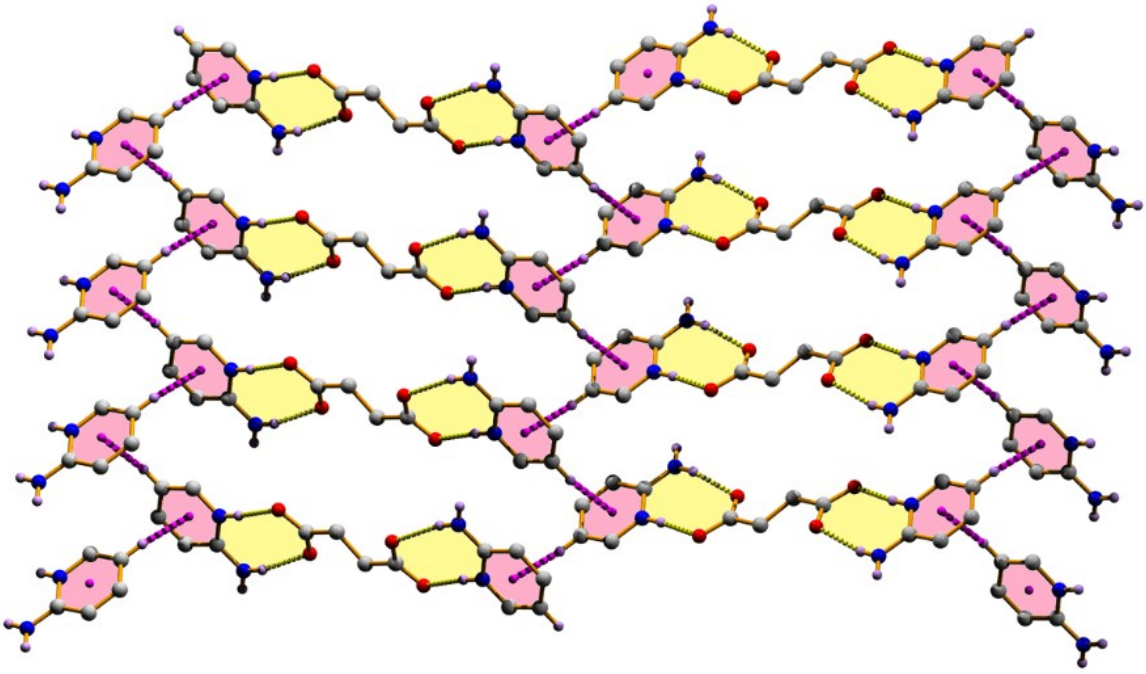

Fig. S7 Formation of layered assembly through C–H···π^+ interaction in (**3**).

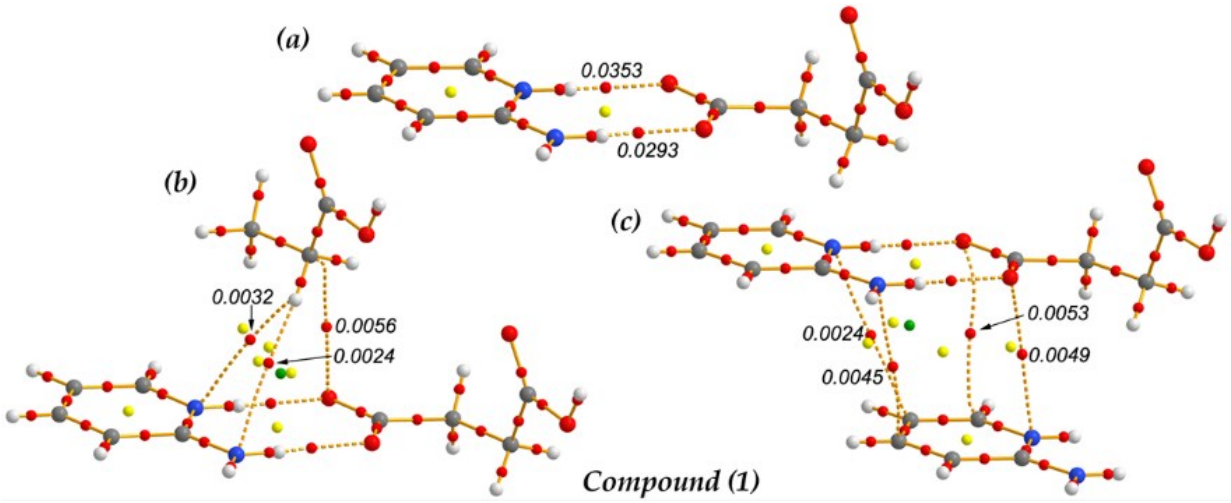

Fig. S8 Distribution of the critical points of different interactions following the models of **1**. Red, yellow and green spheres represent the bond, ring and cage critical points, respectively. The bond paths connecting the bond critical points are also represented by dashed lines.

NCIPlot calculation

The NCI is a visualization index[1] based on the electron density and its derivatives. The isosurfaces may correspond to either favorable or unfavorable interactions, which are differentiated by the signs of the second density Hessian eigenvalues and defined by the isosurface color. The information delivered by NCI plots is fundamentally qualitative, i.e. which molecular regions are interacting. The color scheme is a red-yellow-green-blue scale with red for ϱ^{+}_{cut} (repulsive) and blue for ϱ^{-}_{cut} (attractive). Yellow and green surfaces correspond to weak repulsive and weak attractive interactions, respectively.

The NCIplot representations of the different assemblies obtained for compounds **1–3** are shown in Fig. S9. The π-facial noncovalent interactions involving the salt-bridge are

characterized by extended green isosurfaces that cover most of the salt bridge (SB) and are located between the interacting group (C–H bond or π-system) and the planar SB. It is worth mentioning that the small isosurfaces that characterize the H-bonding interactions that form SB are blue, thus indicating stronger interactions than any of the π-facial interactions, (C–H···SB, SB···π^+ and lp···SB) in good agreement with the energetic study commented in the main text.

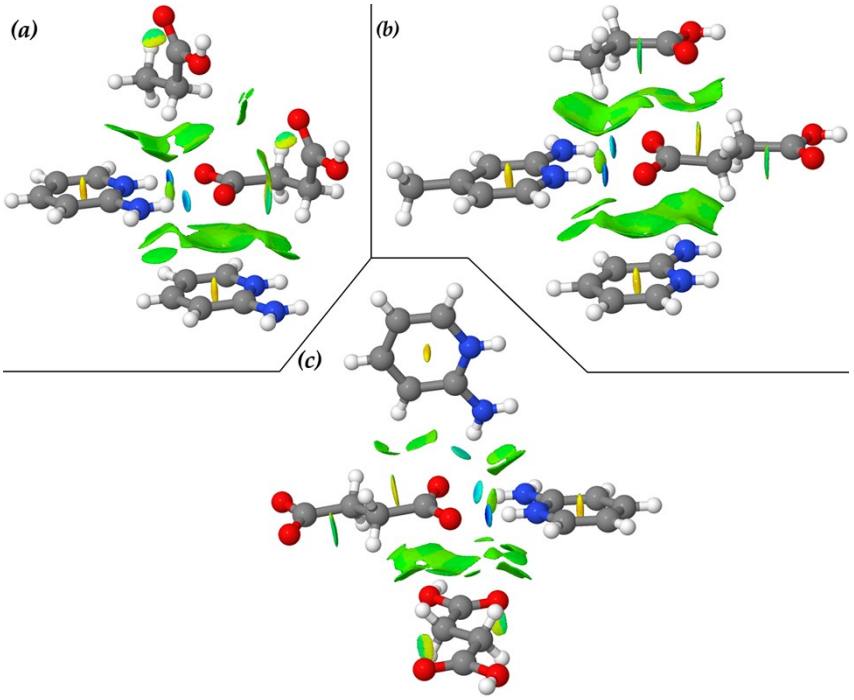

Fig. S9 NCI plot of the self-assembled networks in (**1-3**). The NCI plots only show the intermolecular interactions.

Reference:

1. 1. Contreras-García, J.; Johnson, E. R.; Keinan, S.; Chaudret, R.; Piquemal, J.-P.; Beratan, D. N.; Yang, W. *J. Chem. Theory Comput*. **2011**, *7*, 625–632.