Supporting Information

Supramolecular assemblies involving salt-bridges: DFT and X-ray evidences of bipolarity

Suparna Tripathi,[a,b] Samiul Islam,[a] Saikat Kumar Seth,*[,a] Antonio Bauzá[c], Antonio Frontera*[,c] and Subrata Mukhopadhyay[b]

[a] *Department of Physics, Jadavpur University, Kolkata-700032, INDIA.*

[b] *Department of Chemistry, Jadavpur University, Kolkata-700032, INDIA.*

[c] *Department of Chemistry, Universitat de les Illes Balears, Crta. De Valldemossa km 7.5, 07122 Palma de Mallorca (Baleares), SPAIN.*

Corresponding Author(s) E-mail:

saikatk.seth@jadavpuruniversity.in (S. K. Seth) and toni.frontera@uib.es (A. Frontera)

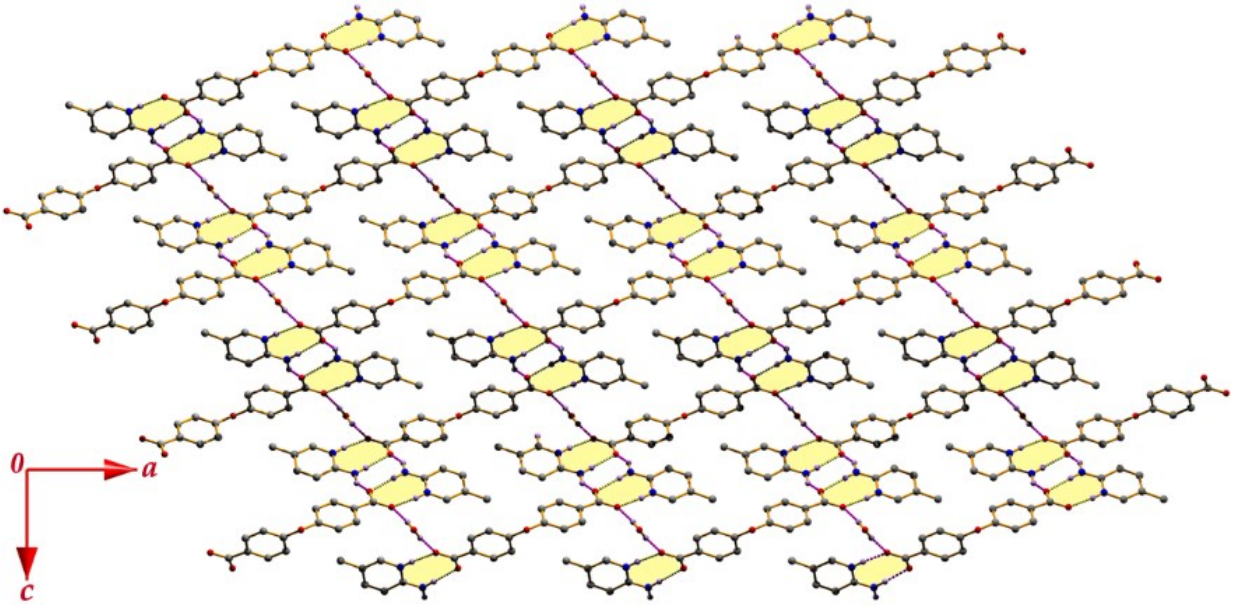

Fig. S1 Supramolecular network in (101) plane of (**1**).

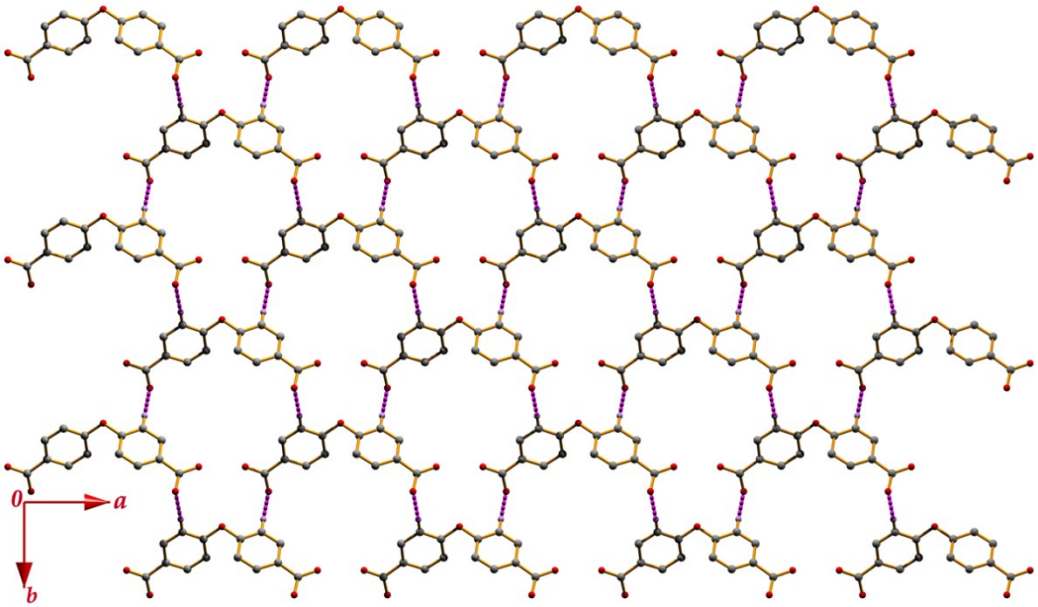

Fig. S2 Network through C–H···O bond in (110) plane in (**1**).

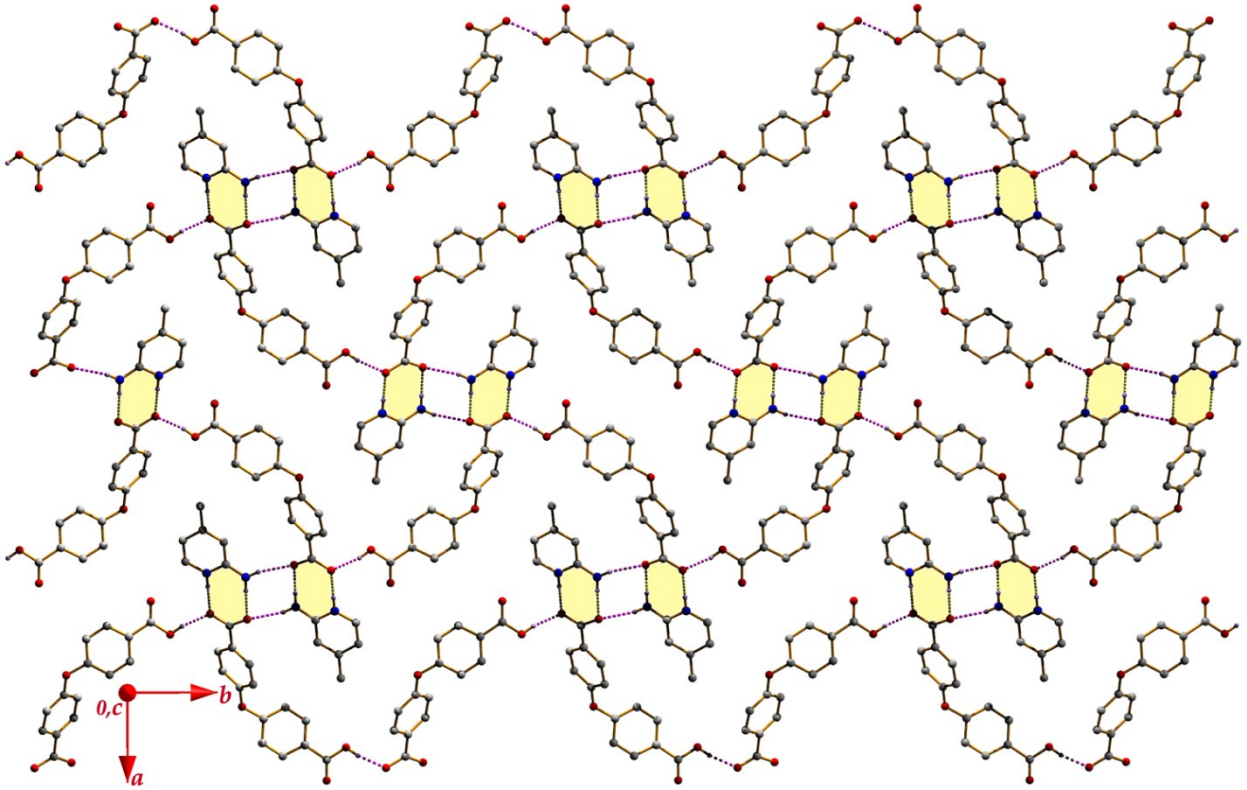

Fig. S3 Two-dimensional assembly of (**2**) in (110) plane.

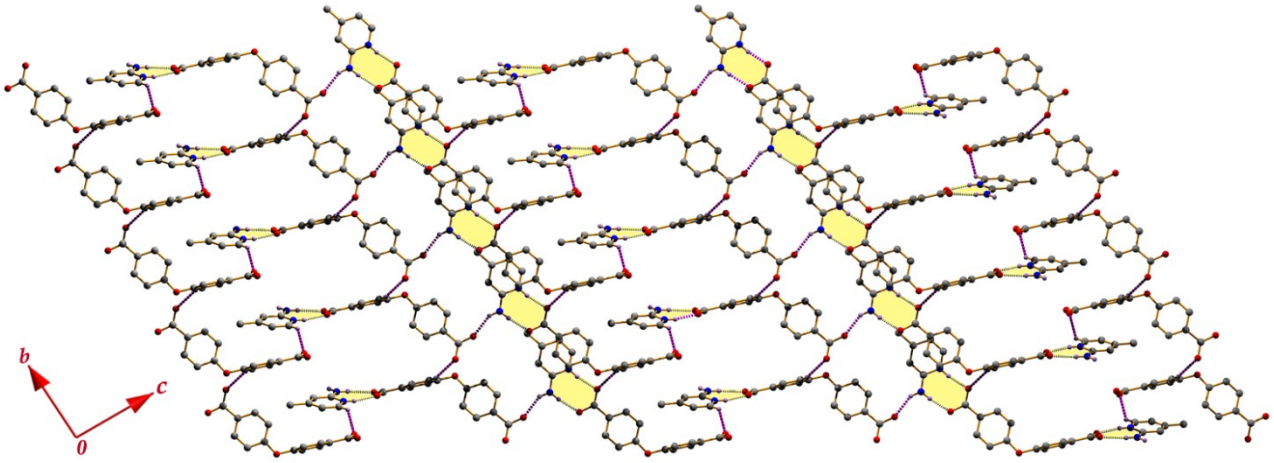

Fig. S4 Layer network of (**3**) in (011) plane.

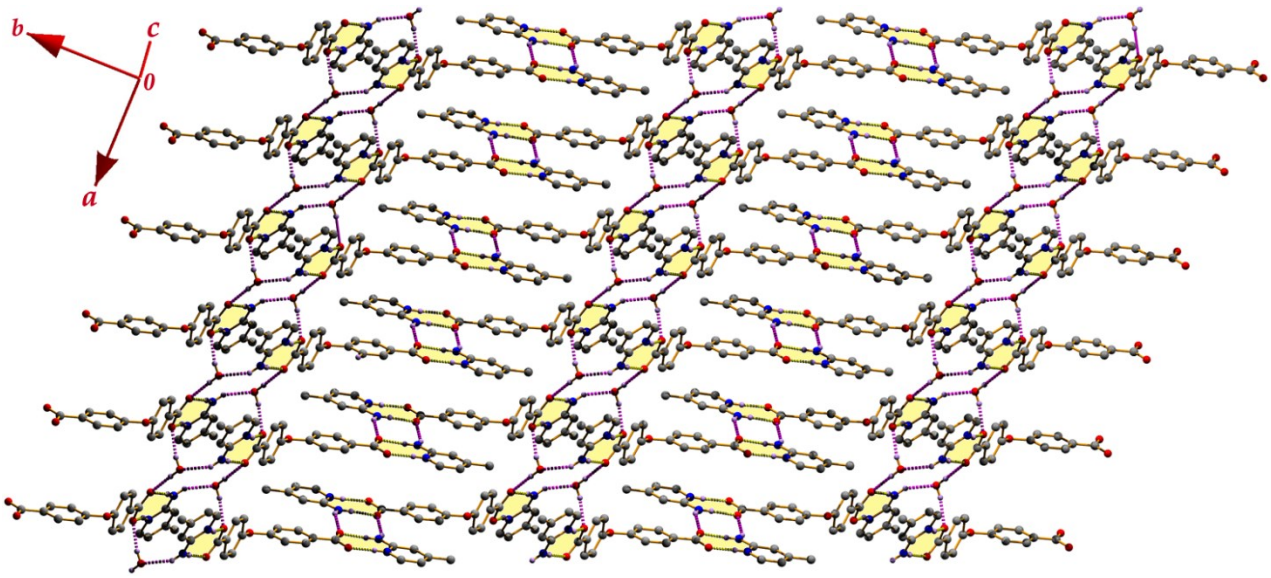

Fig. S5 Supramolecular layered assembly in (**3**).

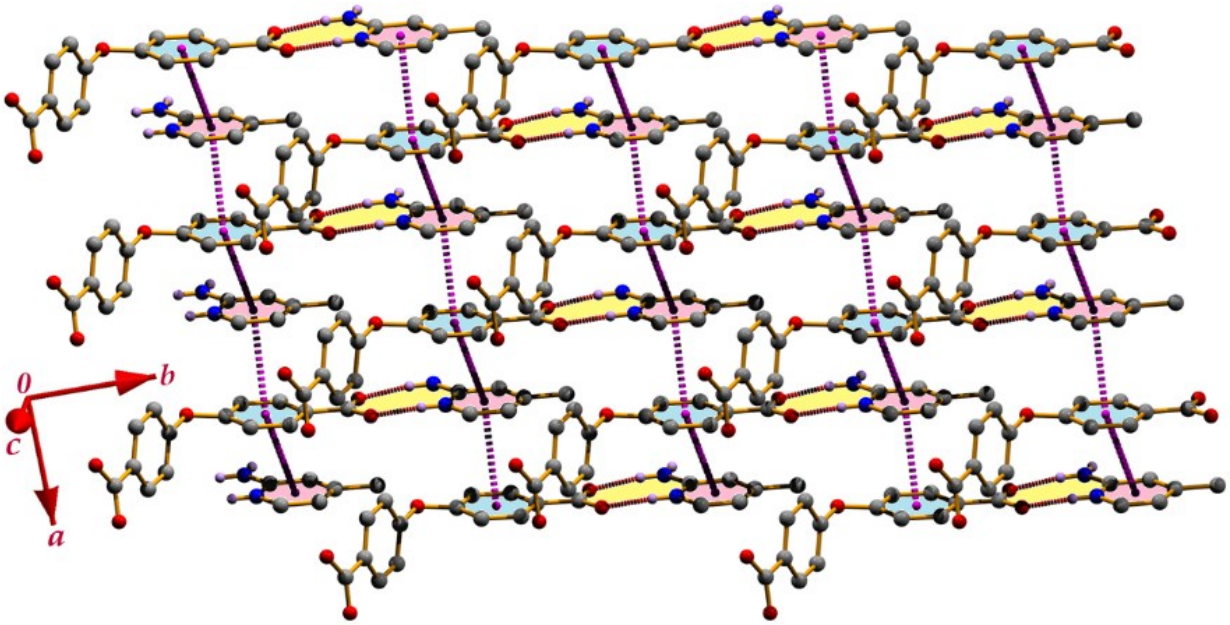

Fig. S6 Supramolecular layered assembly in (**3**) through π-stacking interactions.

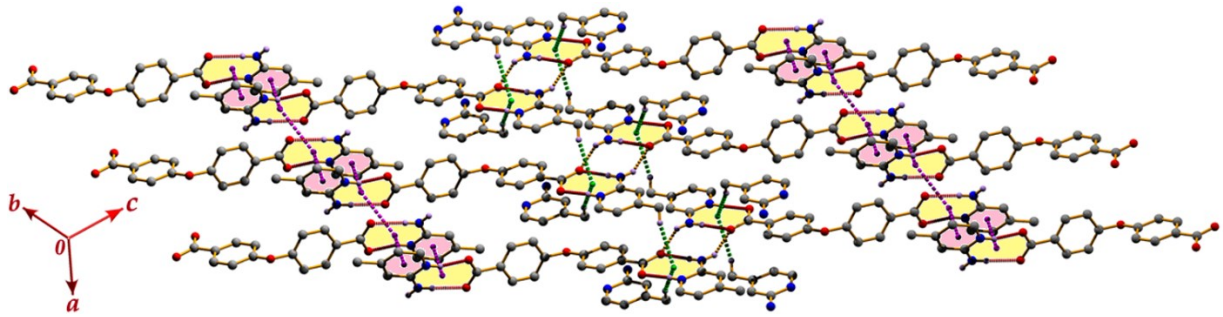

Fig. S7 Extended supramolecular layered network generated through $\pi^{+}\cdots$SB/SB$\cdots$SB/SB$\cdots\pi^{+}$ and CH$\cdots$SB/SB$\cdots$HC networks in (**3**).

To calculate the formation energy of the SB unit, we have used formate ion to simplify the model (see the pink arrow of Fig. S8a). The formation energy of the SB is ΔE_{13} = -114.87 kcal/mol and comparable to the formation energy of compound (**2**). Finally, to confirm the importance of the CH$\cdots$SB/SB$\cdots$HC network as shown in Fig. 4b, we have calculated the formation energies of the CH$\cdots$SB and SB$\cdots$HC interactions (-5.75 kcal/mol and -7.23 kcal/mol) (see Figs. S8b and S8c).

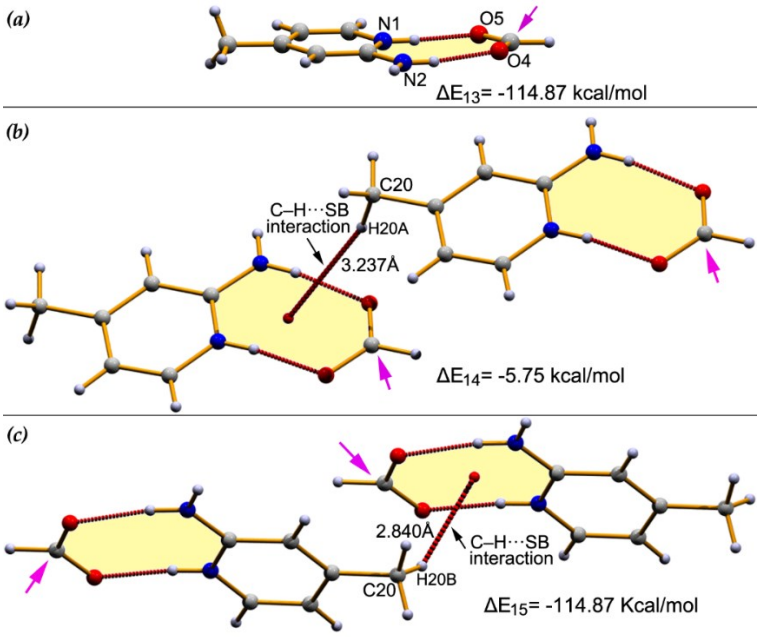

Fig. S8 Theoretical models of compound (**3**) to explore the formation energies of CH$\cdots$SB/SB$\cdots$HC network.

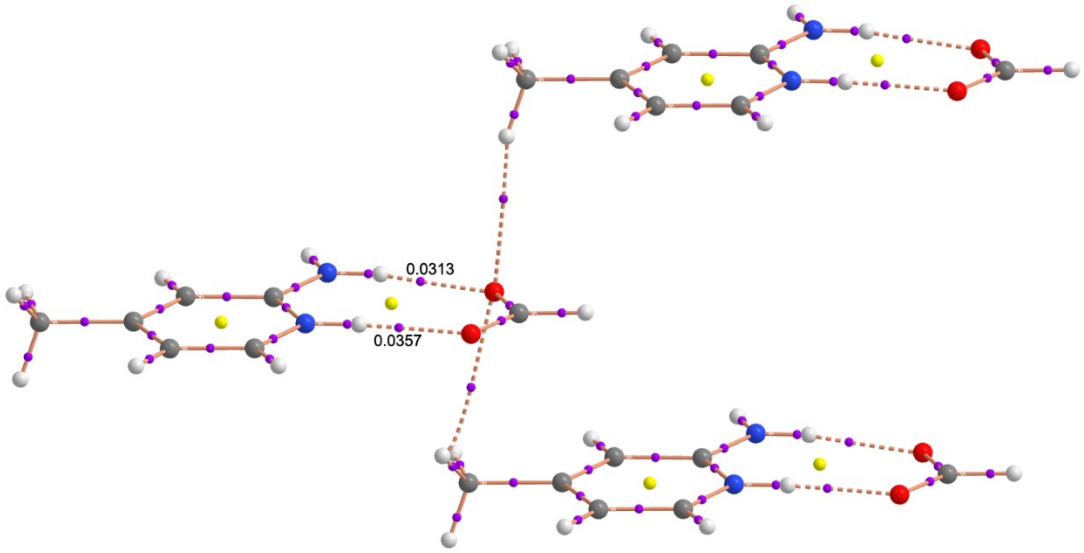

Fig. S9 Distribution of the critical points of the self-assembled CH···SB/SB···HC network of compound (**3**). Red and yellow spheres represent bond and ring critical points, respectively.