Electronic Supplementary Material (ESI) for CrystEngComm.

Lattice Interactions of Terpyridines and Their Derivatives – Free Terpyridines and Their Protonated Forms

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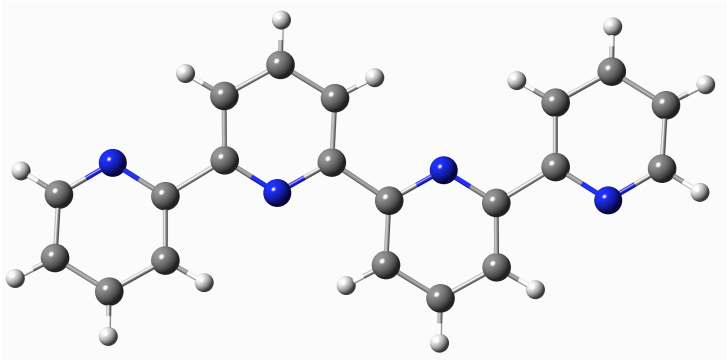
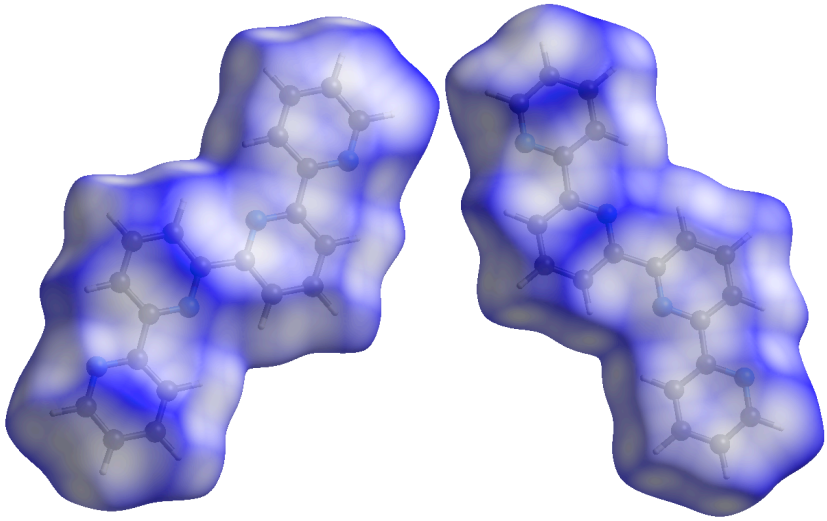
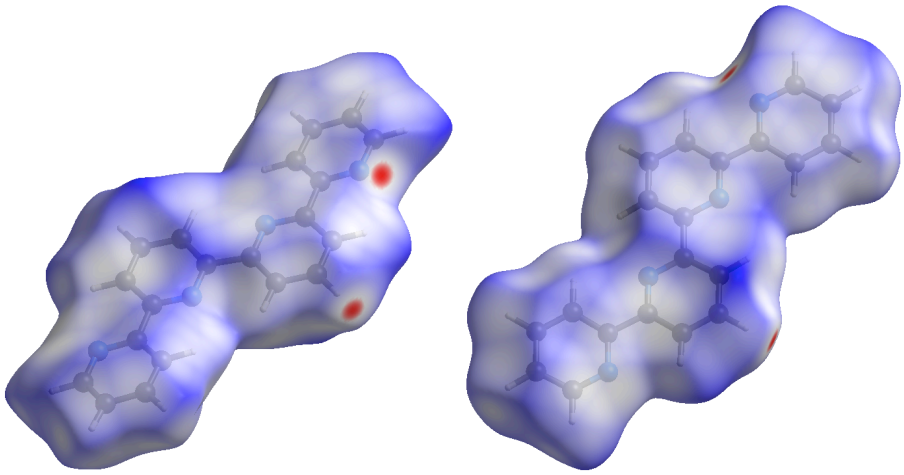
SUPPLEMENTARY INFORMATION

Hirshfeld surfaces and molecular interactions of known polypyridines



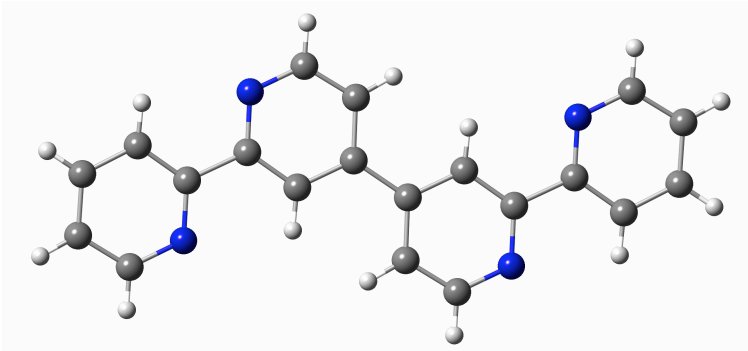


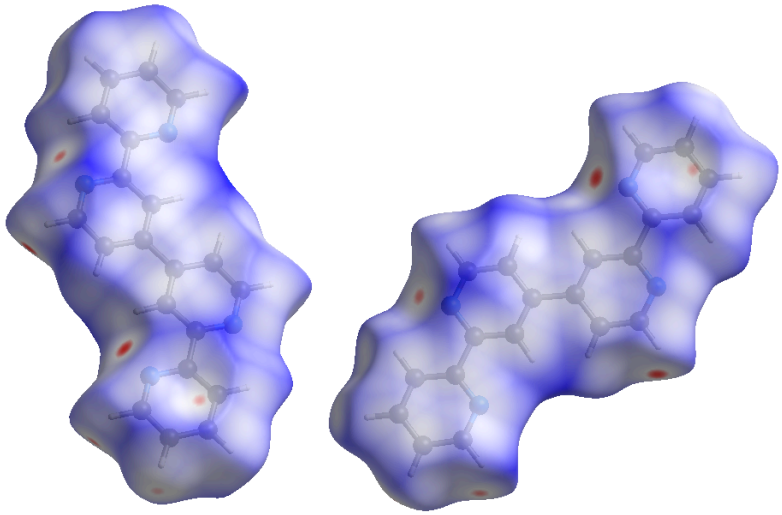
(a)



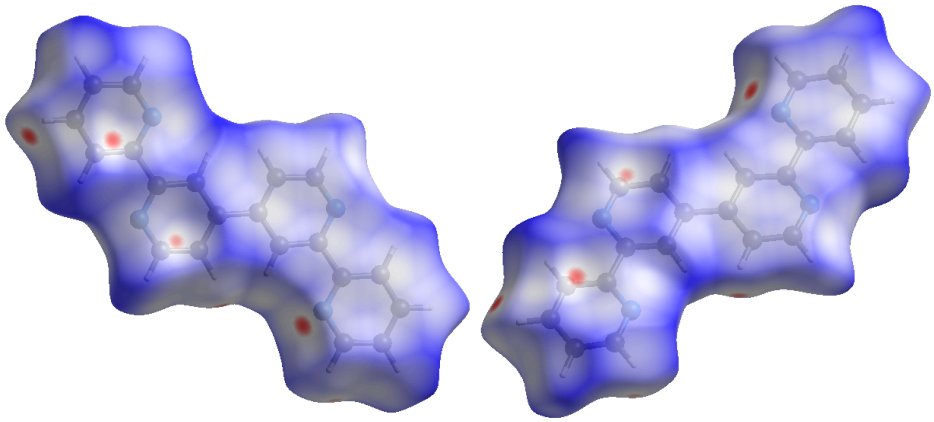
(b)

Figure S1 Perspective views of the principal faces of the Hirshfeld surfaces of (a) the $P2_1/n$ polymorph of 2,2';6',2'';6'',2'''-quaterpyridine (shown above) at 295 K and (b) the C2/c polymorph at 173 K. CSD refcodes JEJSIA and JEJSIA01.



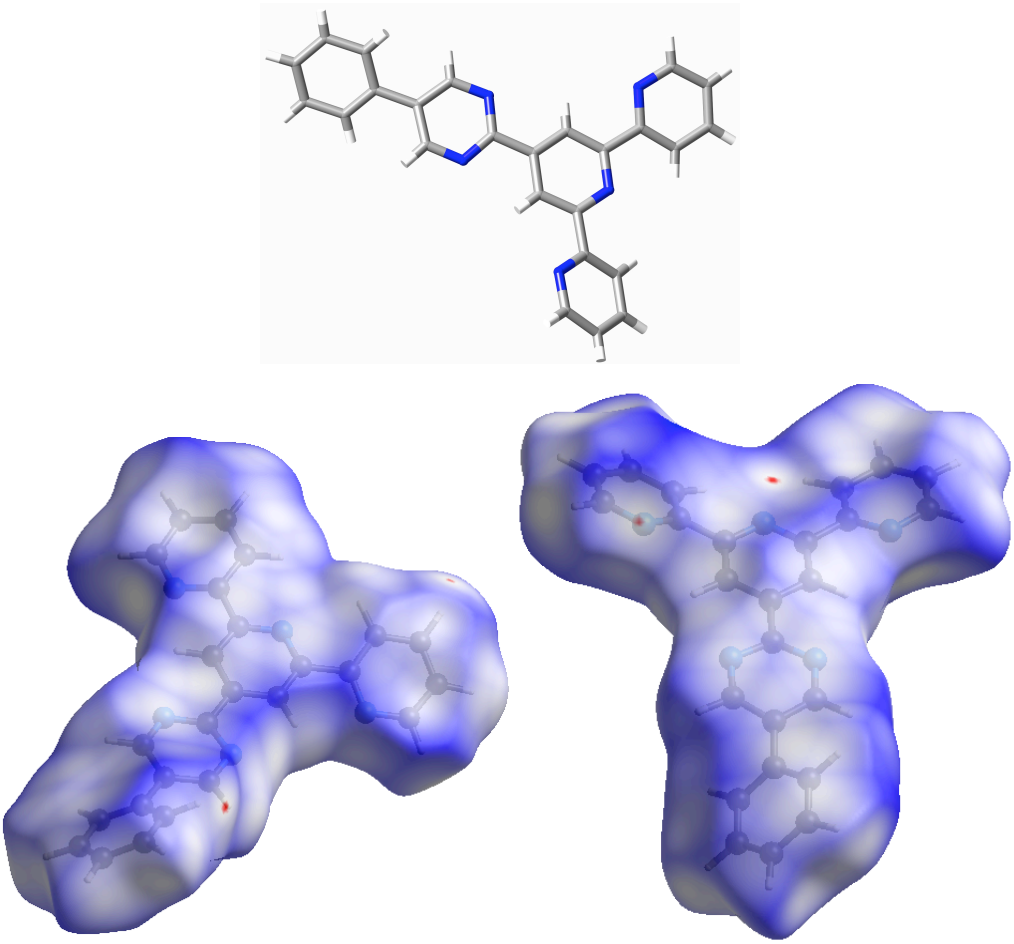


(a)

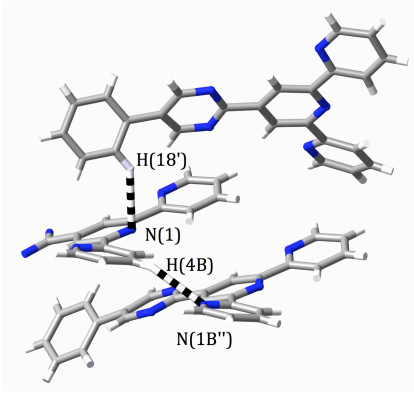


(b)

Figure S2 Perspective views of the principal faces of the Hirshfeld surfaces of (a) the $P2_1/c$ polymorph of 2,2';4',4'';2'',2'''*-quaterpyridine (shown above) and (b) the $P2_1/n$ polymorph (both at 160 K). CSD refcodes TEBGAI and TEBGAI01*



(a)



(b)

Figure S3 (a) Perspective views of the principal faces of the Hirshfeld surface of 4'-(4-phenylpyrimidin-2-yl)-2,2';6'',2''-terpyridine ; (b) CH…N interactions (dashed lines) giving rise to the red regions seen on the Hirshfeld surface. N(1)…H(18') 2.67(2), N(1B')…H(4B) 2.70(2) Å. CSD refcode QIDJAP.

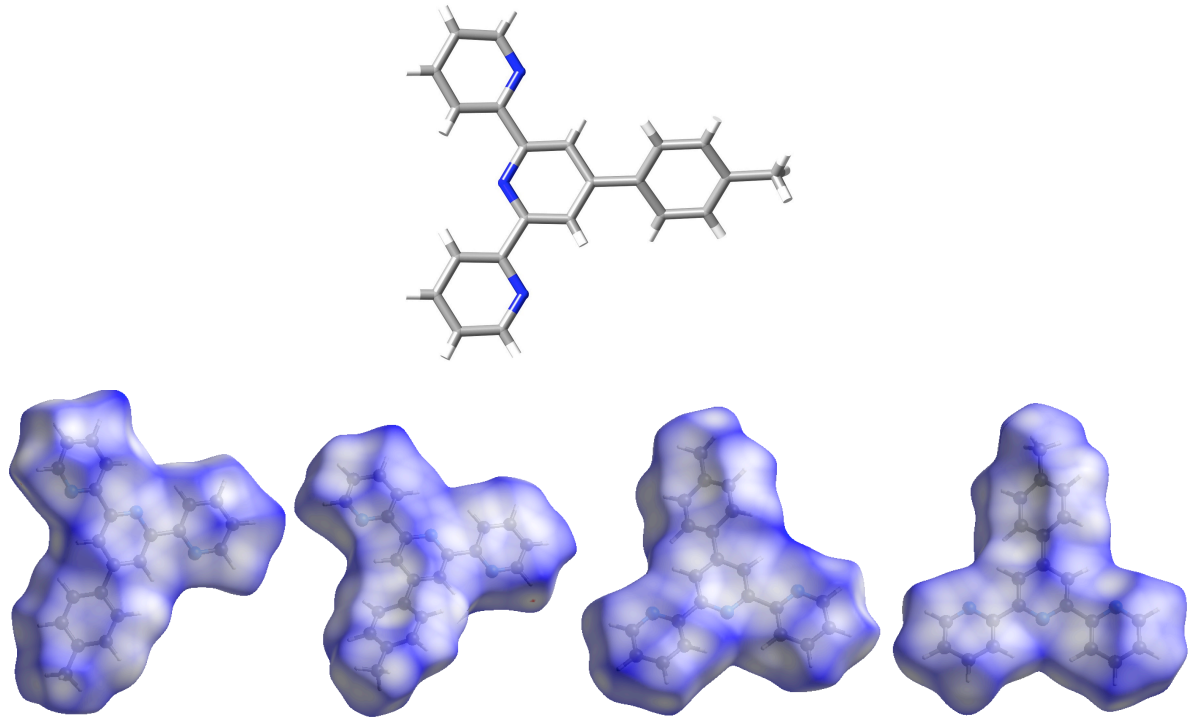
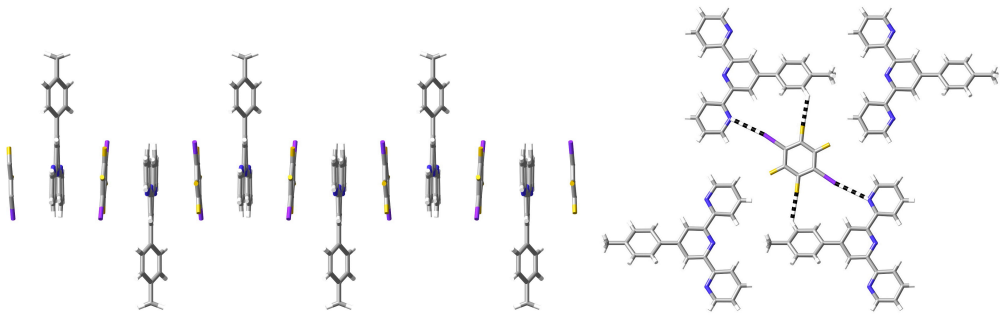
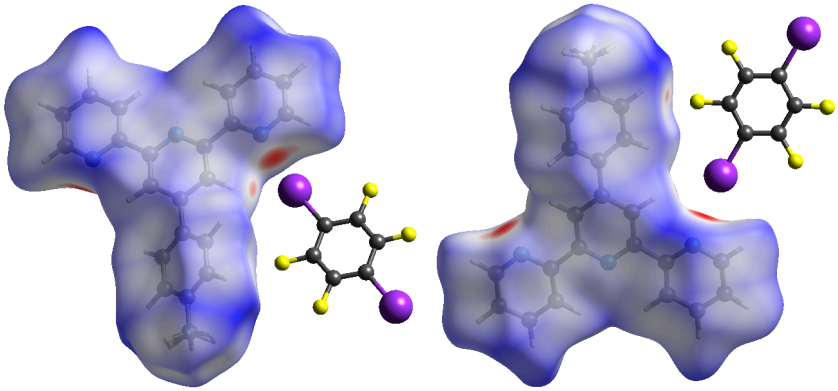


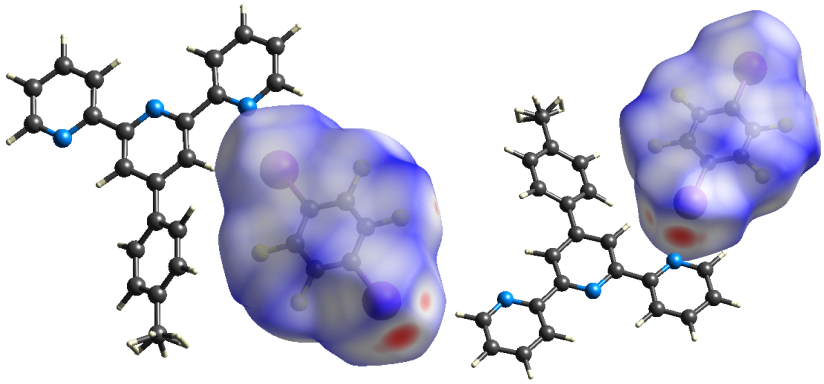
Figure S4 Perspective views of the principal faces of the Hirshfeld surfaces of the inequivalent molecules present in the lattices of polymorphs of 4'-(4-methylphenyl)-2,2';6',2''-terpyridine : (a) the $P2_1/c$, 293 K structure ; (b) the C2/c, 173 K structure. CSD refcodes HIRYIR and HIRYIR01.



(a) (b)

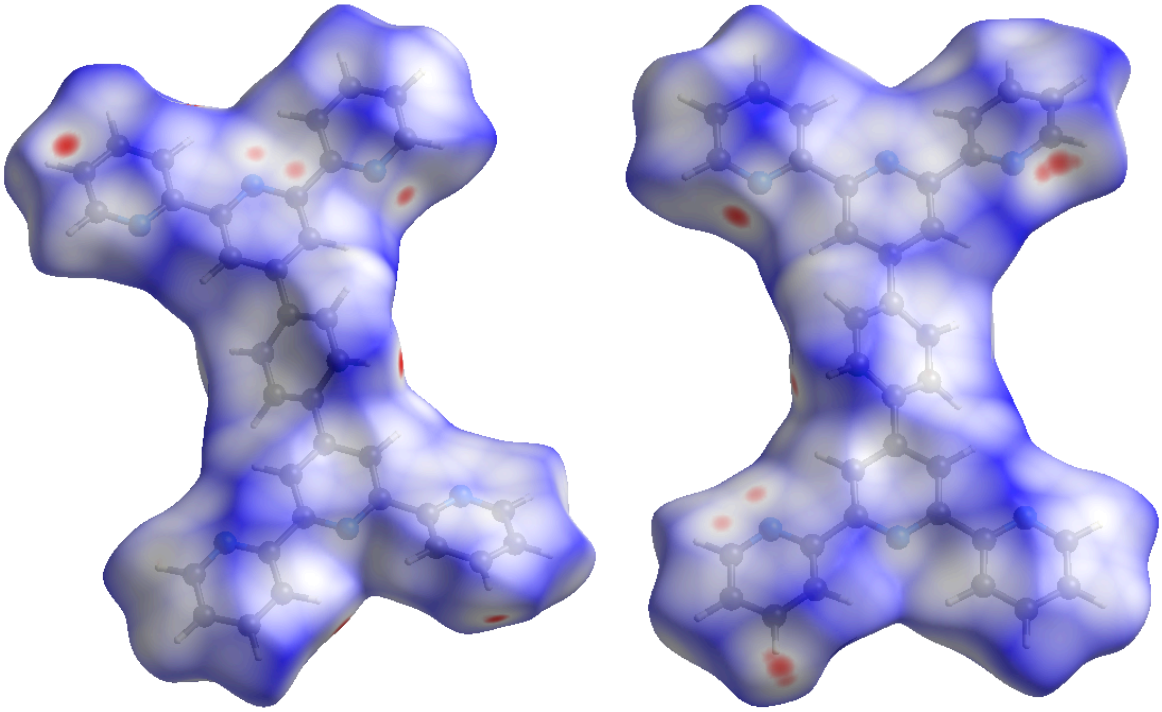


(c)

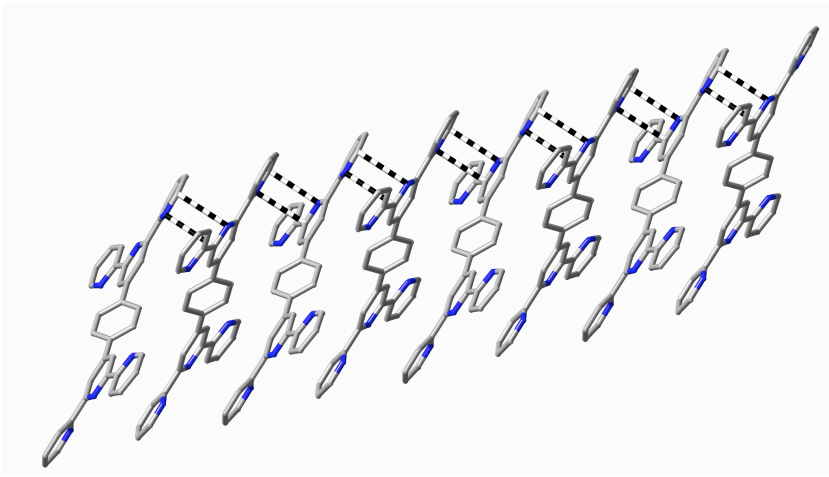


(d)

Figure S5 (a) Part of the stack of alternating 4'-(4-methylphenyl)-2,2';6',2''-terpyridine and 1,4-di-iodotetrafluorobenzene molecules running parallel to the c axis of their crystalline adduct (CSD refcode QOLJIK) ; (b) Portion of the sheet of both molecules lying parallel to the (1 0 -2) plane, showing interactions beyond dispersion apparent from the Hirshfeld surfaces ; I...N 3.127(4), F...H 2.51(3) Å ; (c) Perspective views of the principal faces of the Hirshfeld surface of the 4'-(4-methylphenyl)-2,2';6',2''-terpyridine molecule and (d) perspective views of the principal faces of the Hirshfeld surface of the 1,4-di-iodotetrafluorobenzene molecule, both showing an absence of interactions beyond dispersion between facing species.

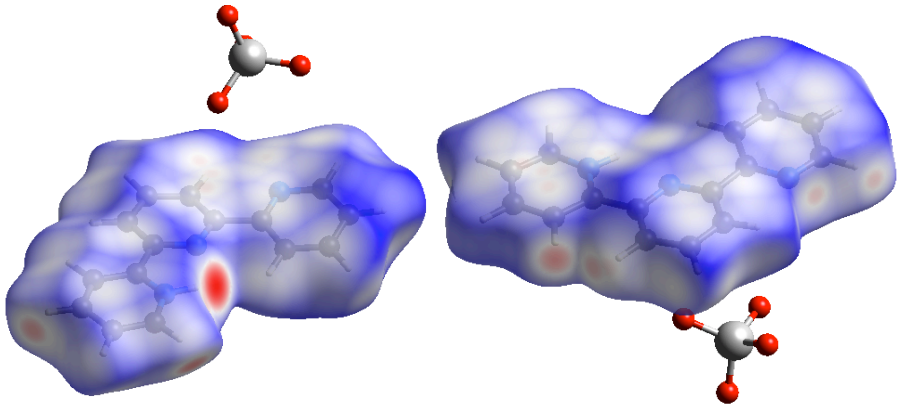


(a)



(b)

Figure S6 (a) Perspective views of the principal faces of the Hirshfeld surface of 1,4-bis(2,2':6',2''-terpyridin-4'-yl)benzene ; (b) portion of the chain of stacked species involving C…N interactions (dashed lines) beyond dispersion perpendicular to the stacked planes (N(5)…C(36') 3.180(3), N(6')…C(27) 3.169(3) Å). CSD refcode WADMEV.



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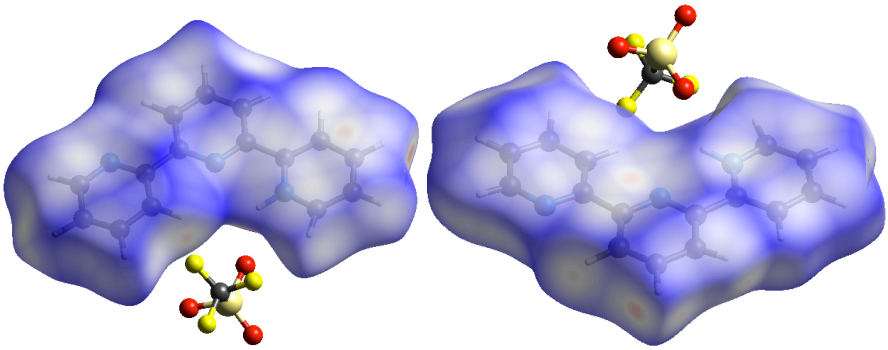

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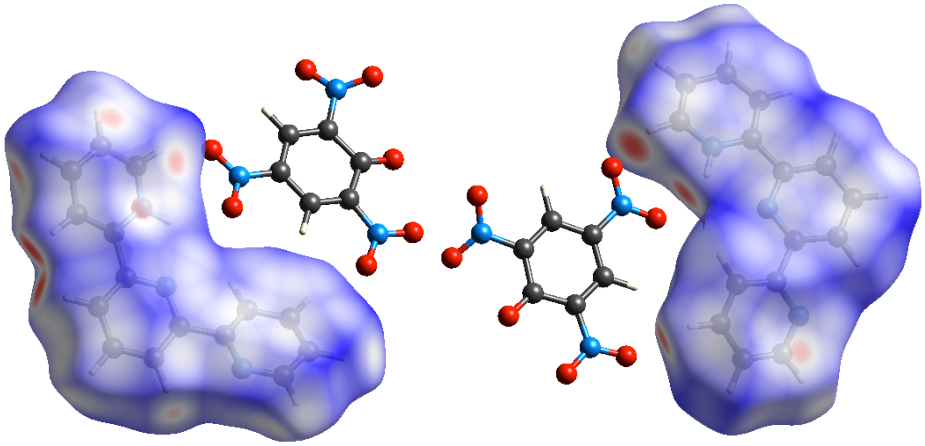
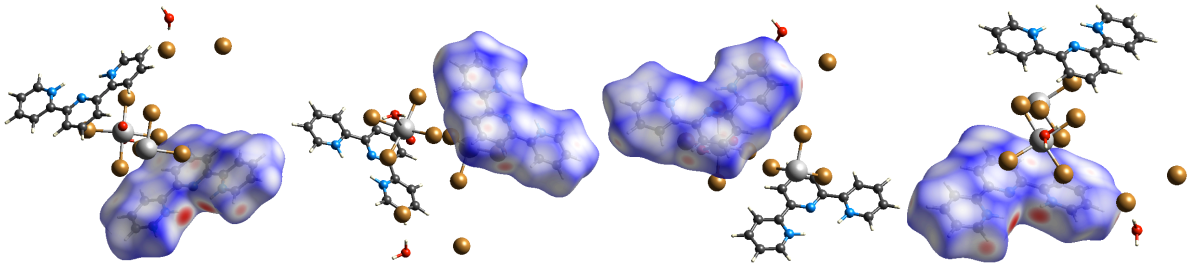


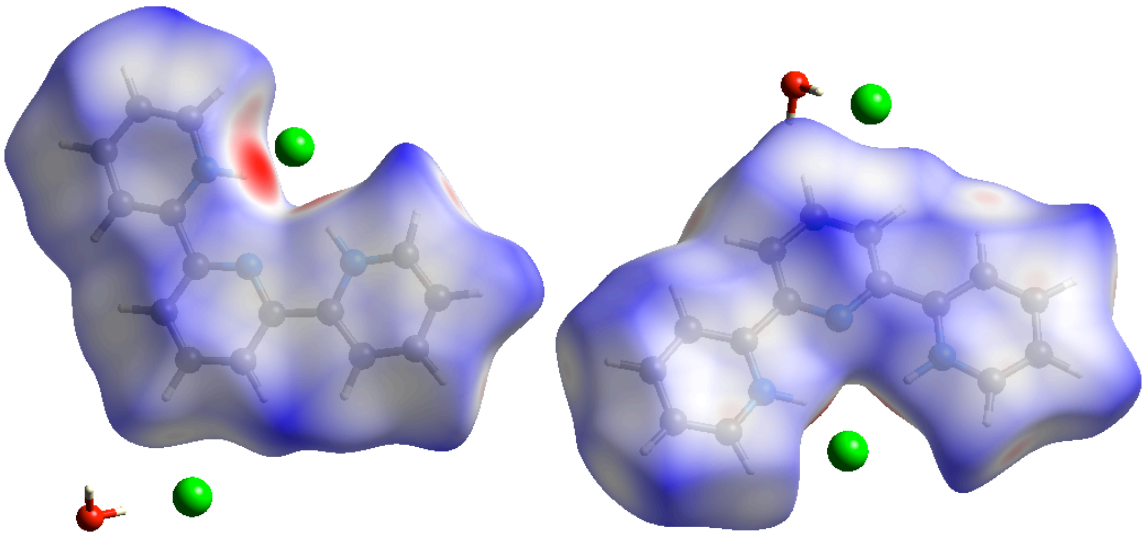
(c)

Figure S7 Perspective views of the principal faces of the Hirshfeld surfaces of monoprotonated 2,2';6',2''-terpyridine as its (a) perrhenate salt (CSD refcode SAYWOF) ; (b) trifluoromethanesulfonate salt (CSD refcode TICQEB) ; (c) picrate salt (CSD refcode CIYQOS).



molecule 1 molecule 2

(a)



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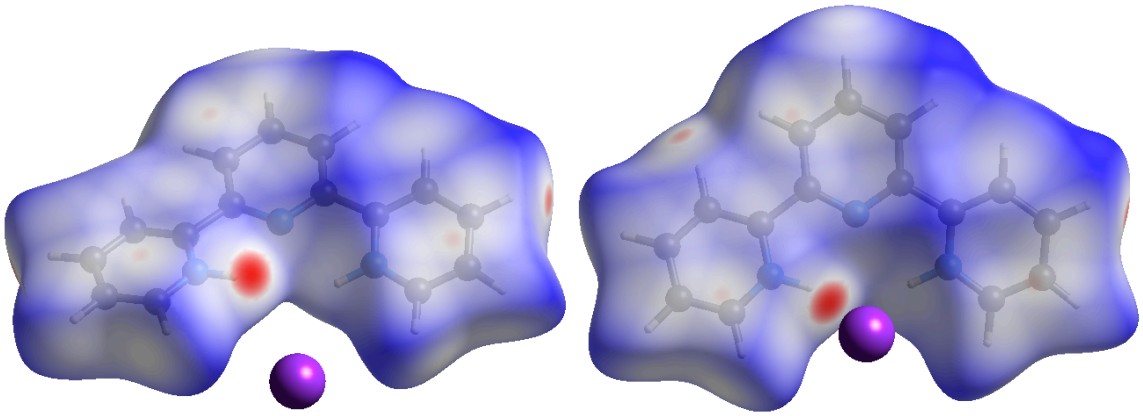
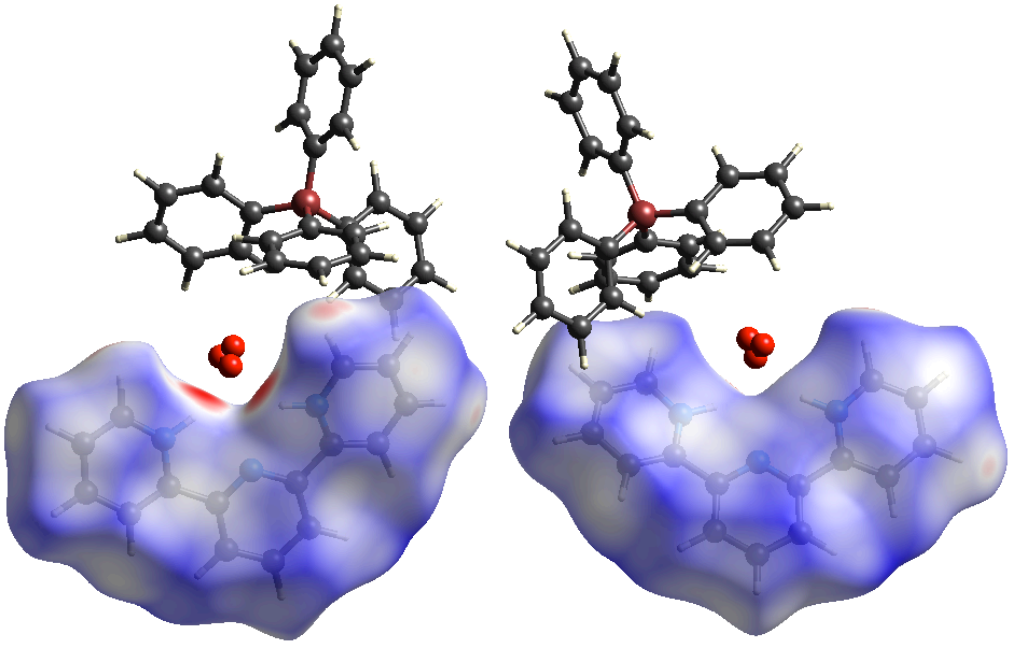
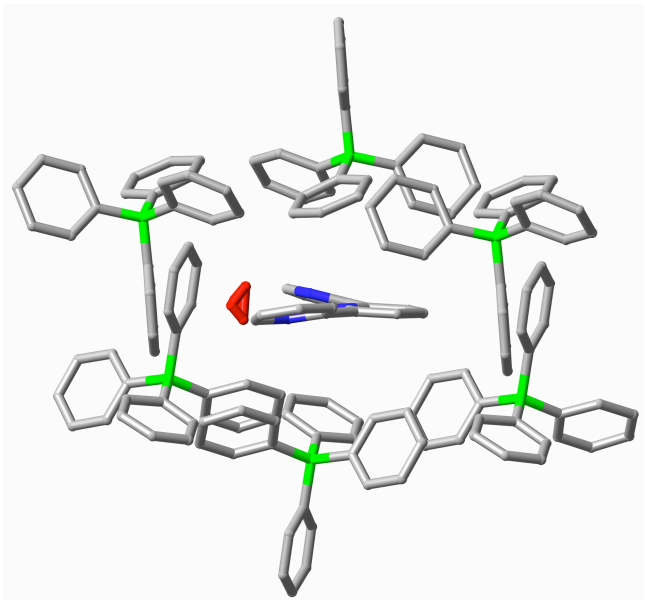


(c)

*Figure S8 Perspective views of the principal faces of the Hirshfeld surfaces of diprotonated 2,2';6',2''-terpyridine (**tpy**) in (a) [**tpy**H_2])$_4$[$Re^{V}O(OH_2)Br_4$][$Re^{IV}Br_6$]Br_4 (two inequivalent molecules in the lattice ; CSD refcode MIGDUC), (b) [**tpy**H_2]Cl_2.H_2O (CSD refcode DELDEE) and (c) [**tpy**H_2]I_2 (CSD refcode DELDUU).*

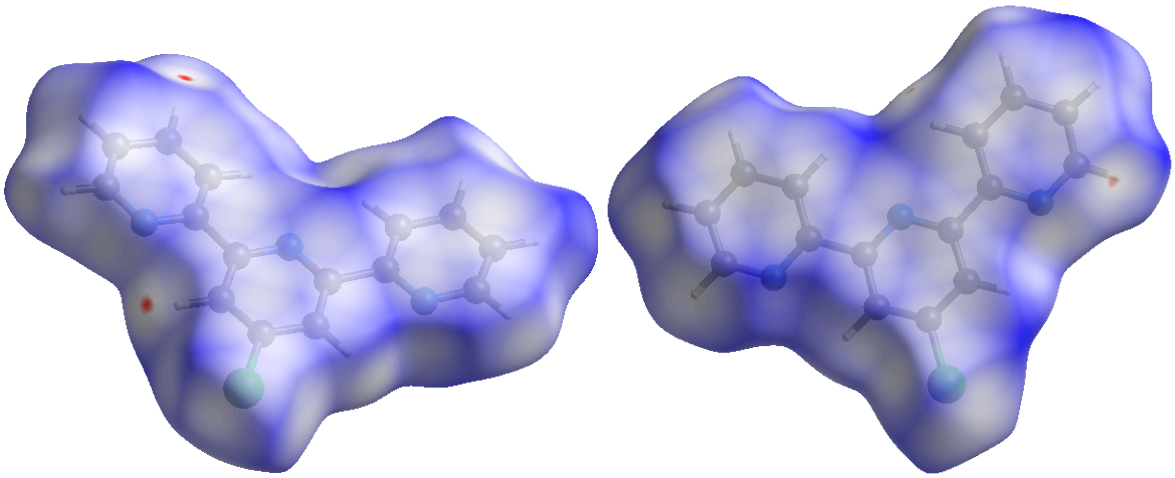


(a)

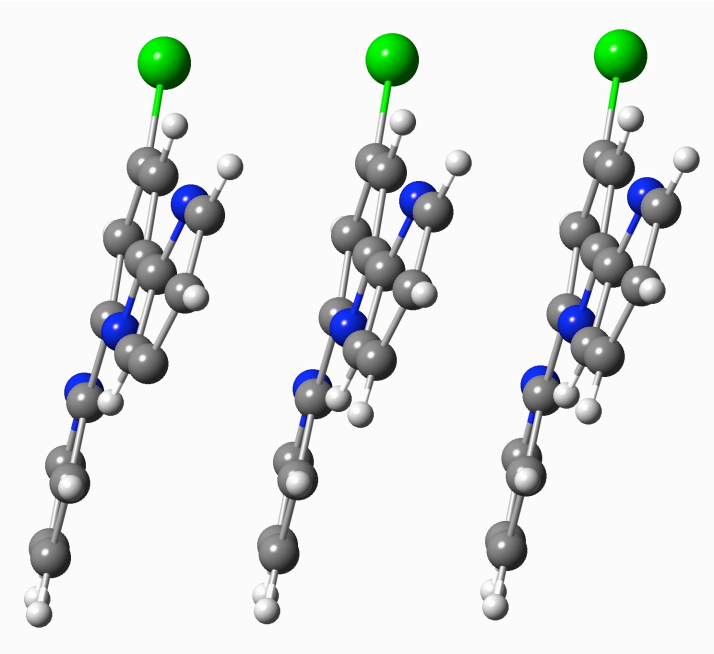


(b)

*Figure S9 (a) Perspective views of the principal faces of the Hirshfeld surfaces of diprotonated 2,2';6',2''-terpyridine (**tpy**) in [**tpy**H_2][$B(C_6H_5)_4$]$_2$.H_2O (CSD refcode GOLBUE ; note that the water molecule is disordered over 3 sites) ; (b) the cation within its « cage » of six anions (stick representation; H-atoms not shown).*

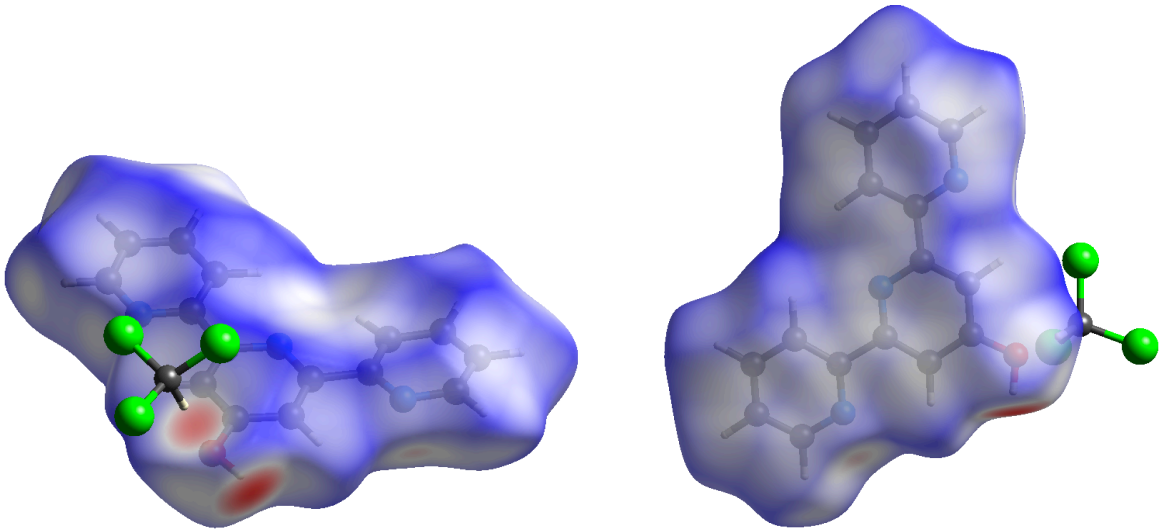


(a)



(b)

Figure S10 (a) Perspective views of the principal faces of the Hirshfeld surface of 4'-chloro-2,2';6',2''-terpyridine (CSD refcode WEJFEX) ; (b) a view of portion of the slipped stack of 4'-chloro-2,2';6',2''-terpyridine molecules running parallel to the c axis, showing their slightly bowed form.



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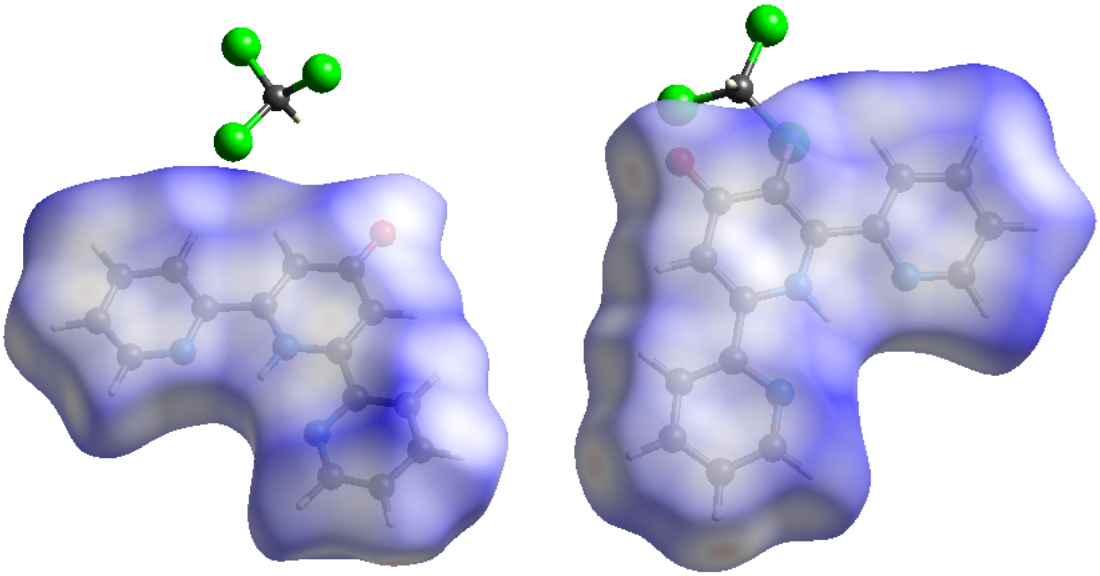
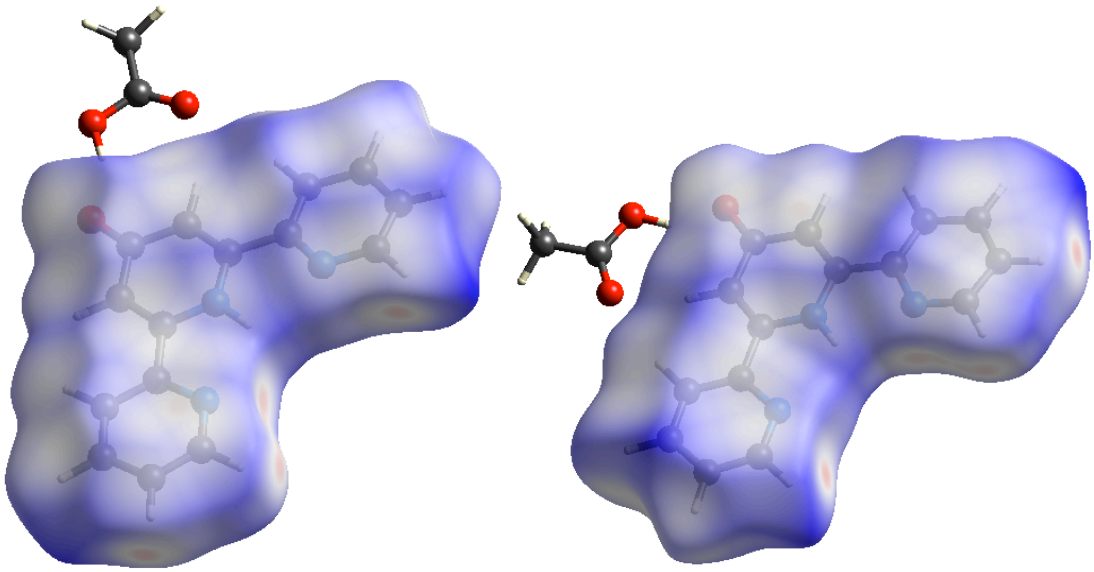


(b)

Figure S11 Perspective views of the principal faces of the Hirshfeld surface of (a) the hydroxypyridine form of 4'-hydroxy-2,2';6',2''-terpyridine and (b) the pyridone form. (CSD refcode DIWDUI ; both molecules are present in the one lattice along with a molecule of chloroform.)



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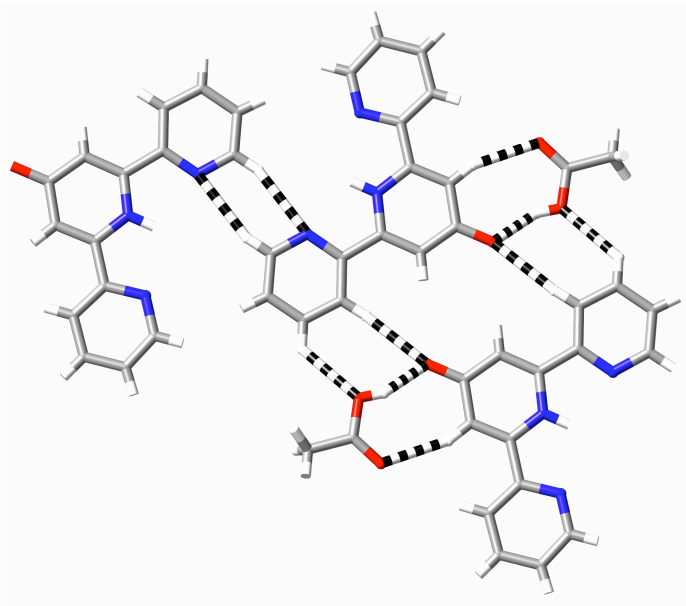
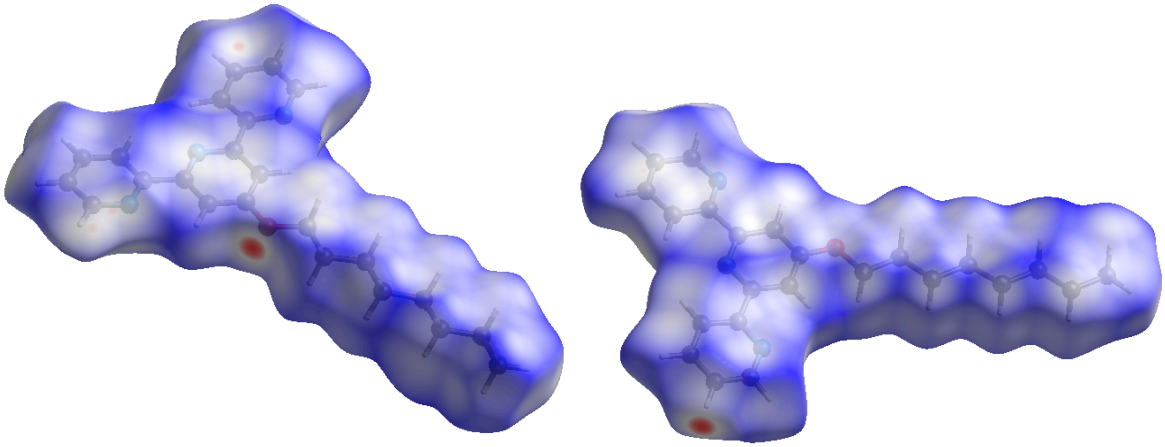


(b)

Figure S12 (a) Perspective views of the principal faces of the Hirshfeld surface of the aza-aromatic unit in the lattice of the acetic acid adduct of 4'-hydroxy-2,2';6',2''-terpyridine (CSD refcode IJOTEG01) ; (b) some of the peripheral interactions (dashed lines) in sheets of the lattice constituents.



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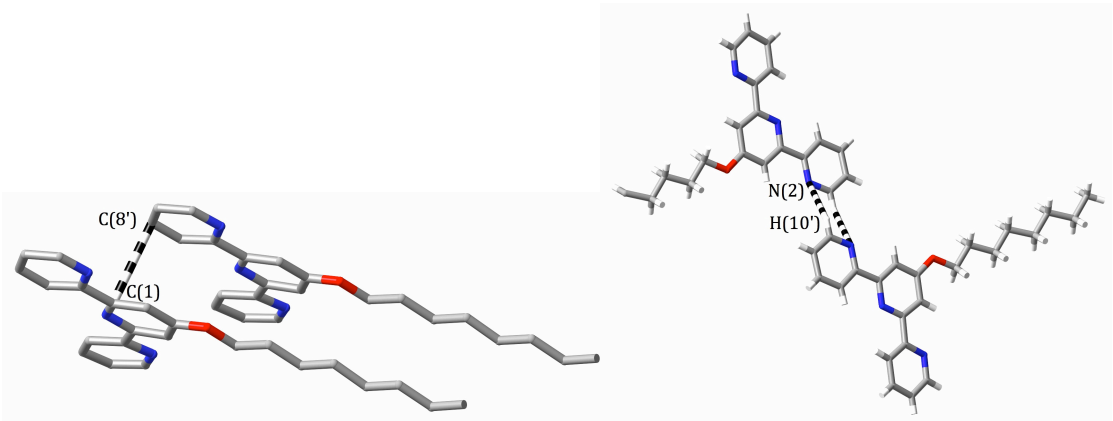

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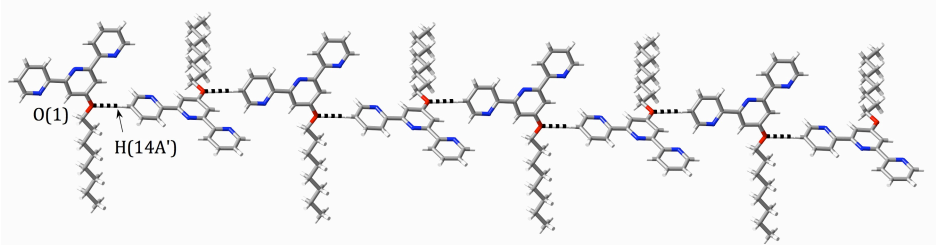
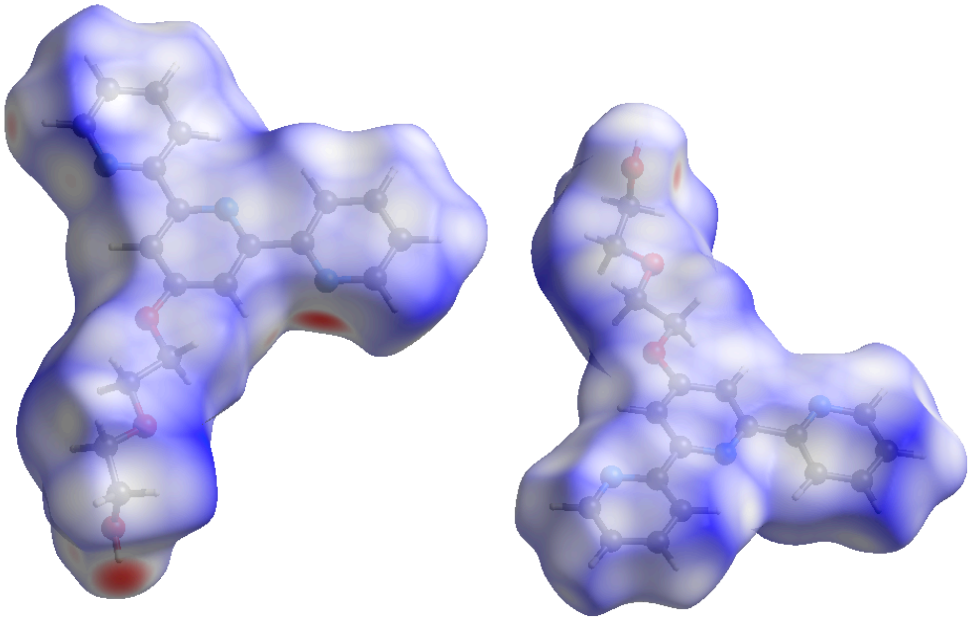
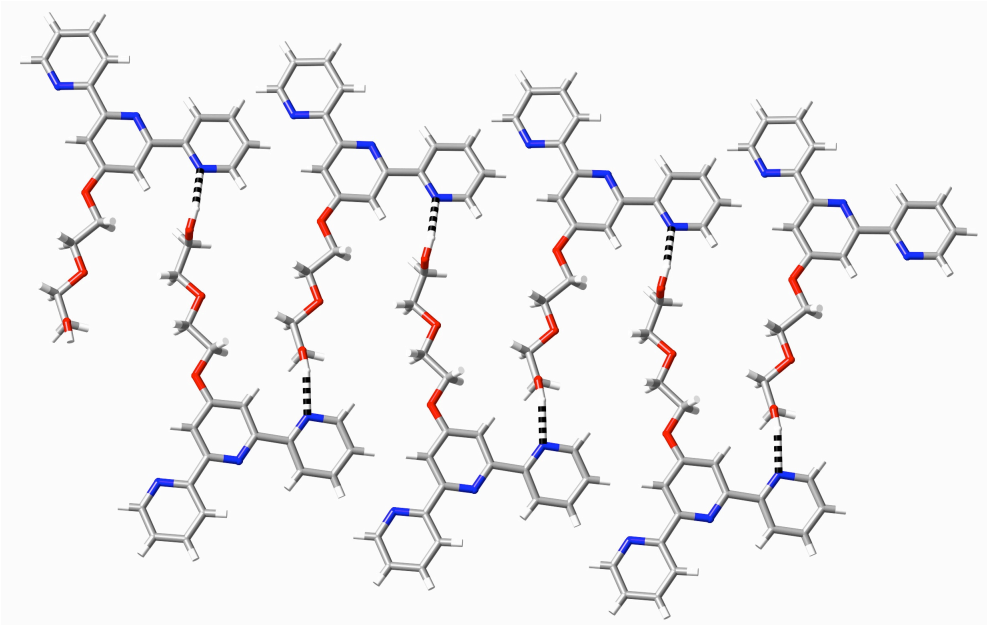


(d)

Figure S13 (a) Perspective views of the principal faces of the Hirshfeld surface of 4'-n-octyloxy-2,2';6',2''-terpyridine ; (b) the C...C interaction between stacked molecules ; (c) the reciprocal N...HC interactions between molecules in adjacent stacks ; (d) the supramolecular polymer produced by O...HC interactions between molecules in adjacent stacks. CSD refcode RUJFIM.

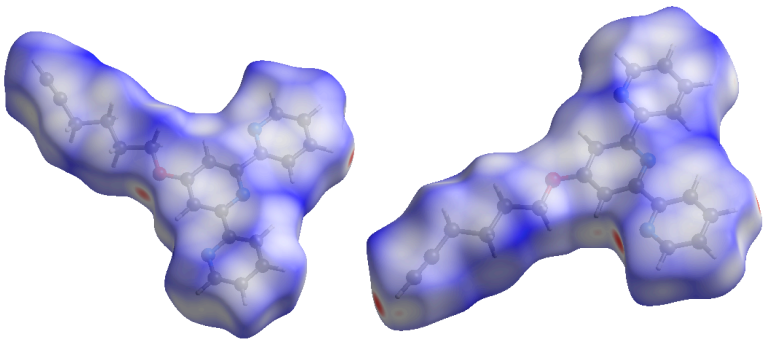


(a)



(b)

Figure S14 (a) Perspective views of the principal faces of the Hirshfeld surface of 4'-(5-hydroxy-3-oxapentyloxy)-2,2';6',2''-terpyridine; (b) the zig-zag polymer reflecting NHO H-bonding between the molecules. CSD refcode MEMJEU.



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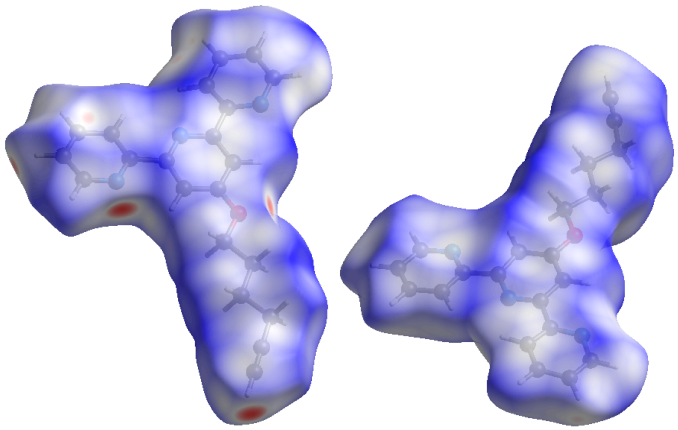

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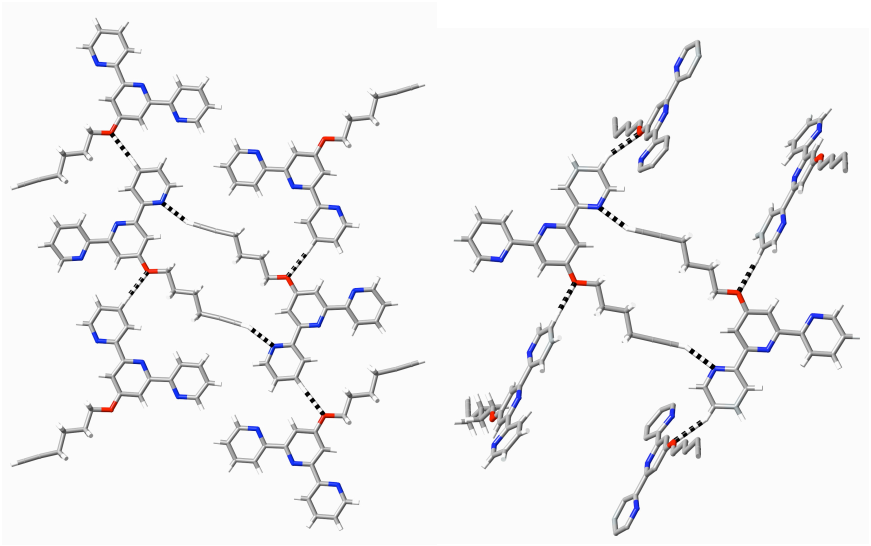

(c) (d)

Figure S15 (a) Perspective views of the principal faces of the Hirshfeld surface of the $P2_1/n$ form of 4'-(hex-5-ynyloxy)-2,2';6',2''-terpyridine (CSD refcode SAWKIL) ; (b) Perspective views of the principal faces of the Hirshfeld surface of the C2/c form (CSD refcode SAWKIL01) ; (c) One « dimer » unit and its immediate environment of molecules in the $P2_1/n$ form ; (d) One « dimer » unit and its immediate environment of molecules in the C2/c form.