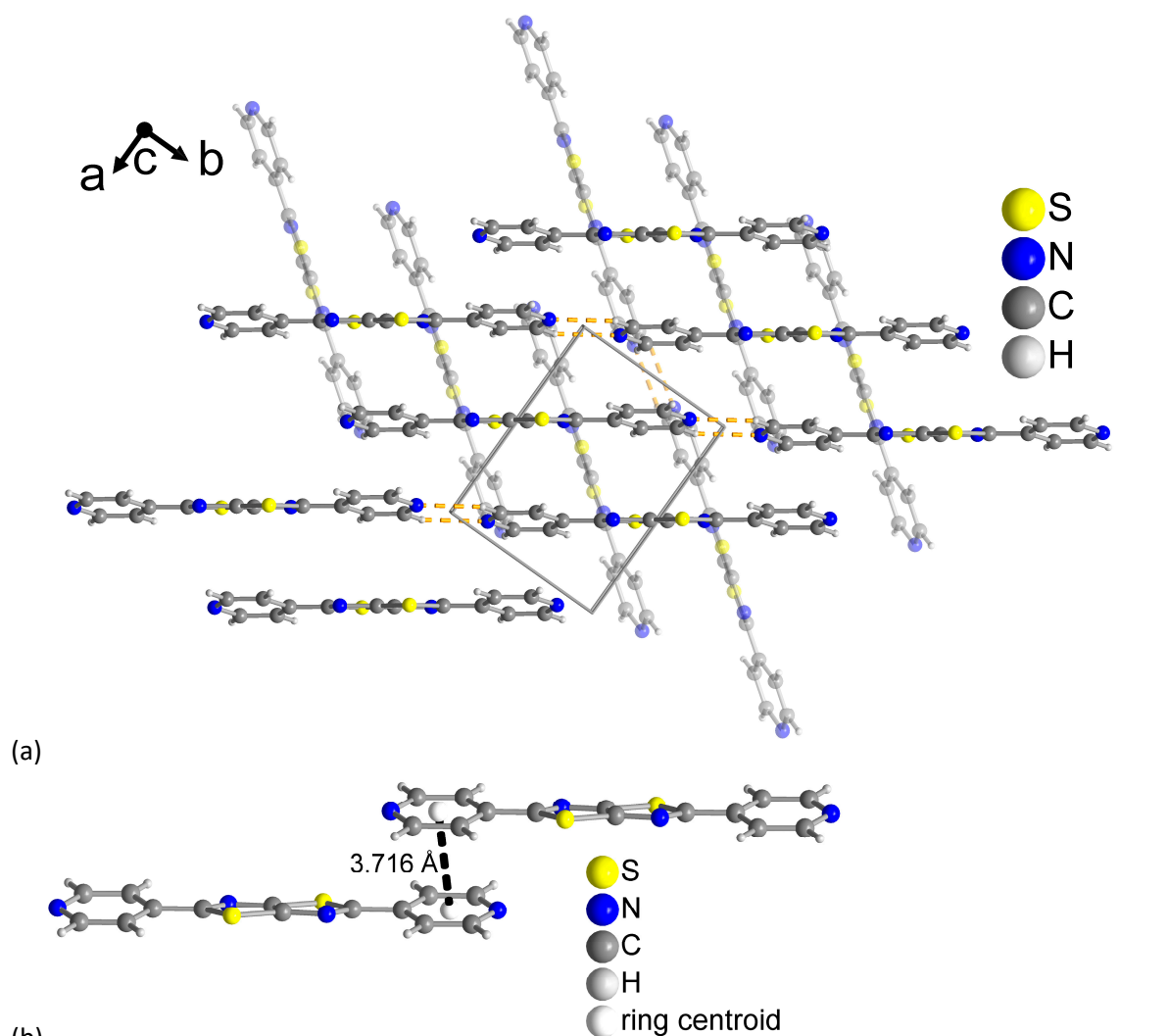# Supplementary Materials: Incorporating the thiazolo[5,4-d]thiazole-unit into a coordination polymer with interdigitated structure

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(a)

(b)

Figure S1. Section of the packing diagram of 2,5-di(4-pyridyl)thiazolo[5,4-d]thiazole (Dptztz), showing (a) the complementary C1-H1···N1 hydrogen bonds and (b) the π-π interactions, thereby giving a supramolecular layer in the *ab* plane.

The next layer in the *c* direction is tilted by about 70°.

Details of C1-H1···N1 hydrogen bond: H1···N1 2.55 Å, C1···N1 3.410(2) Å, C1-H1···N1 151°; details of π-π interaction: Dihedral angle between planes 0.03(8)°, angle Cg(I)-->Cg(J) and normal to plane I 18.7°, distance between ring centroids 3.7164(10) Å, perpendicular distance of Cg(I) on ring J 3.5206(7) Å, slippage = distance between Cg(I) and perpendicular projection of Cg(J) on ring I 1.191 Å.
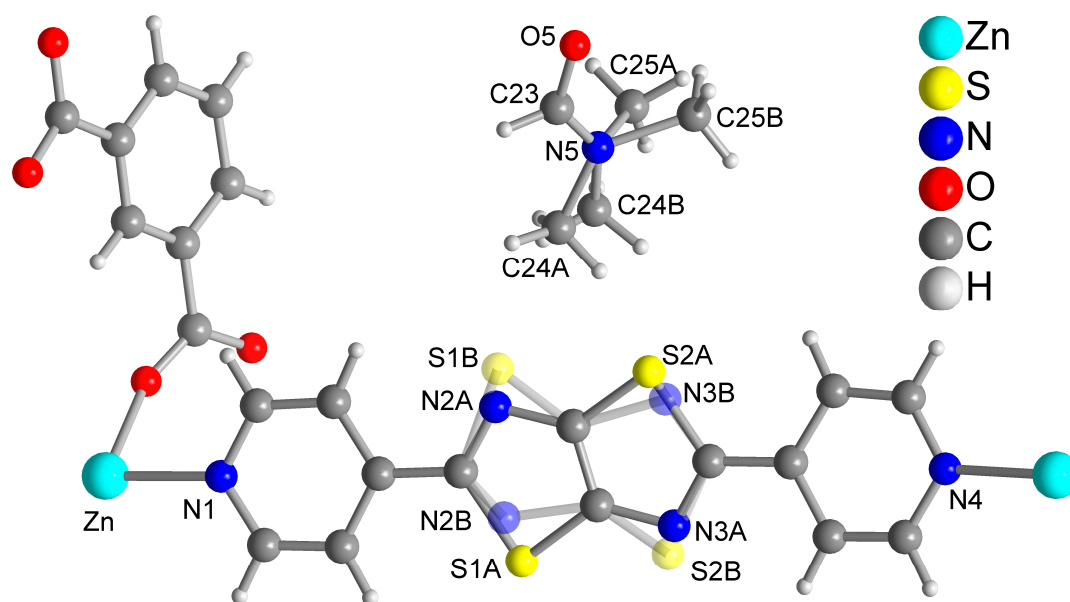
Figure S2. Asymmetric unit of [Zn(1,3-BDC)Dptztz]·DMF showing the ring-flip disorder of the thiazolothiazol moiety. The thiazolothiazol moiety was refined with a disorder model corresponding to a ring flip, which exchanges the S and N orientation, using PART n commands.

The occupation factors of the S and N atoms were refined to about 0.904 for the A atoms and 0.096 for the B atoms. Thus, the disorder is relatively minor with only about 9.6% of the S and N atoms in the flipped position. The major occupation sites of the disordered tztz-moiety are labelled with A, the minor ones with B. The methyl groups of the DMF molecule are disordered over two positions, they were refined independently concerning their occupation factors. This disorder does not give a perfect oriented Me$_2$N group but we decided to keep the slightly disordered DMF molecule instead of removing its contribution with SQUEEZE.
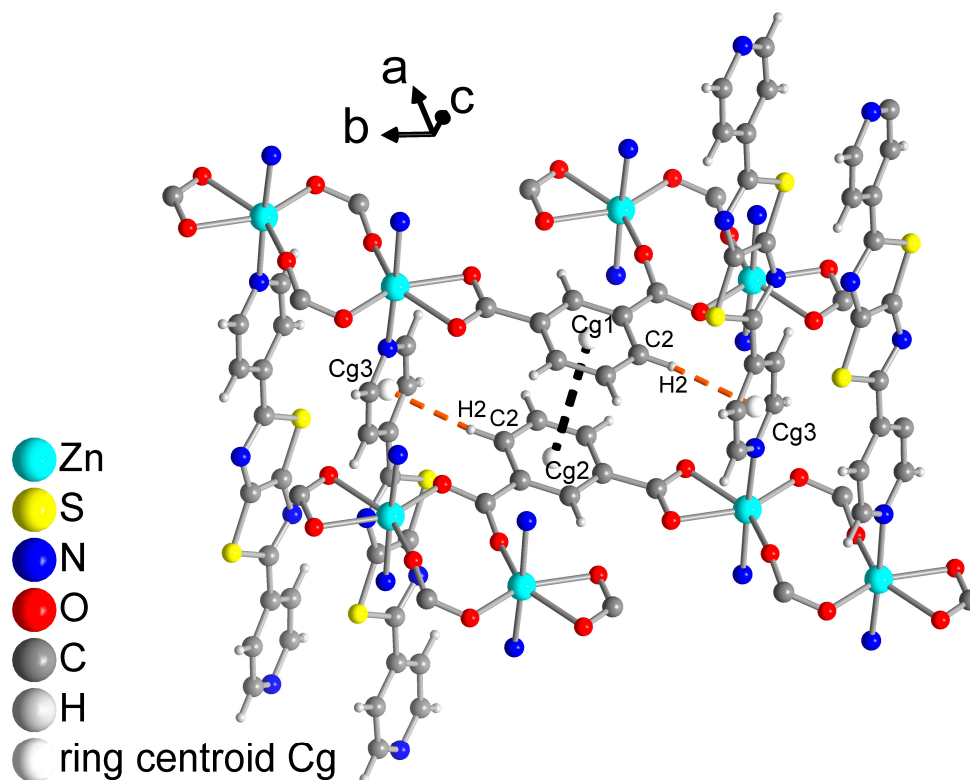
**Figure S3.** π-π and CH-π interactions between the 2D layers in [Zn(1,3-BDC)Dptztz]. See Table S1 for the supramolecular distances and angles.

Table S1. Distances [Å] and angles [°] for the shortest π-π and CH-π supramolecular interactions between the 2D layers in [Zn(1,3-BDC)Dptztz].

π-π interaction	d[Cg1···Cg2]	α	β	γ	d[Cg1···P2]	d[Cg2···P1]	d
Cg1···Cg2ᵛ (1,3-BDC)	3.654(1)	0.0	20.5	20.5	3.421	3.421	1.28

CH-π interaction	d_ATM	d_PLN	d_CNT	γ	∟(C-H···Cg3)	d[Cg3···C2]	∟(C-H···Cg3)
C(2)-H(2)···Cg3ᵛⁱ	2.81	2.64	2.68	9.75	153	3.554(13)	66

Cg: ring centroid; α: dihedral angle between planes, β: angle Cg(I)-->Cg(J) or C-H and normal to plane P; Cg···P: perpendicular distance of Cg on ring plane P; d: slippage = distance between Cg(I) and perpendicular projection of Cg(J) on ring I; d_{ATM}: distance from H to the closest sp^2 carbon; d_{PLN}: distance from H to the aromatic plane; d_{CNT}: distance from H to the centroid; symmetry transformations: v= 1-x, 1-y, 1-z; vi = x, y, 1+z.
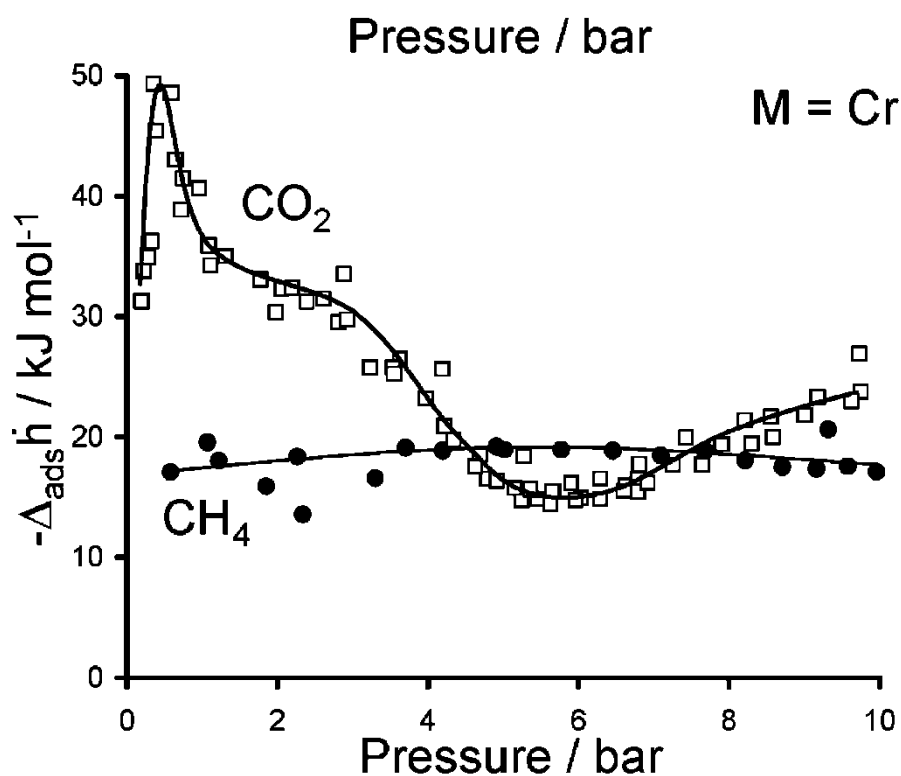
Figure S4. Heat of adsorption curve of MIL-53-Cr (figure taken from Ferey et al. [1]).

References

1.   Bourrelly, S.; Llewellyn, P.L.; Serre, C.; Millange, F.; Loiseau, T.; Férey, G. Different adsorption behaviors of methane and carbon dioxide in the isotypic nanoporous metal terephthalates MIL-53 and MIL-47. *J. Am. Chem. Soc.* **2005**, *127*, 13519-13521.