Supporting Information

Procedure for the treatment of the twinning

During the procedure for the calculation of the unit cell, the centered peaks were indexed by using two cells of the same size but at different orientations. These were defined by the A_1 and A_2 orientation matrices (OM). By applying the relation $R = A_2^{-1}A_1$ the twin low matrix is obtained. A_1 is the OM used for data collection and corresponds to the strongest diffracting component of the twin crystal.

$$\mathbf{R} = \begin{pmatrix} 1 & 0.422 & 0.944 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{1}$$

The structure was solved without difficulties by applying direct methods. Attempts to refine the structure were unsuccessful and in parallel the most of the characteristic warning signs for non-merohedral twinning were present [K = Mean(F_o^2)/Mean(F_c^2) = 16.761] for the reflections with low intensity [F_c/F_c(max) in the range from 0.000 to 0.014]. For almost all of the most disagreeable reflections F_o was much greater than F_c. The same twinning matrix was obtained by applying the TwinRotMat procedure of PLATON as it is used in the WINGX program suite and which is based on the most disagreeable reflections list of reflections. The twin law is a twofold rotation axis around the a* reciprocal lattice axis, or around the [19 4 9] crystallographic direction in direct space. That means that the twin axis is normal to the *bc* crystallographic plane. Following the conventions of the international tables of crystallography[1] the above equation is equivalently written as:

$$(h', k', l') = (h, k, l)\mathbf{P} \tag{2}$$

where $\mathbf{P} = \mathbf{R}^t$ (3)

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[1] Transformation in Crystallography, pp. 70 – 80 in *International Tables of Crystallography, Volume A, Space GroupSymmetry,4th Revised Edition*; Kluwer Academic Publishers: 1995.

This relation gives the following relations for the reflection indexes of the two twinning components

$$h^{'} = h + 0.422k + 0.944l$$
$$k^{'} = -k \qquad (4)$$
$$l^{'} = -l$$

In addition, the unit cell axes of the twin components are related by the transformation

$$(a^{'}, b^{'}, c^{'}) = (a, b, c)\mathbf{P} \qquad (5)$$

which gives the following relations

$$a^{'} = a + 0.422b + 0.944c$$
$$b^{'} = -b \qquad (6)$$
$$c^{'} = -c$$

This result reveals that the origin for the formation of the twin crystal comes from the fact that the two *b* and *c* axes are almost equal.

For the rest of the refinement process, the approach of SHELXL program for non-merohedral twins was applied by refining the BASF parameter and the HKLF5 reflection file obtained by applying the appropriate discrimination function as is given in the WINGX program suite. The best results were obtained by using the discrimination function for index non-integrability. The reflections from two twins that differ less than 0.05 were considered as fully overlapped and those that differ more than 0.08 were consider as non overlapped at all. Between these two values the reflections are partially overlapped and they are assumed to have serious errors. These ranges were defined by a trial-an-error method based on the demand for the lowest values of the most statistical parameters and the most accurate results.

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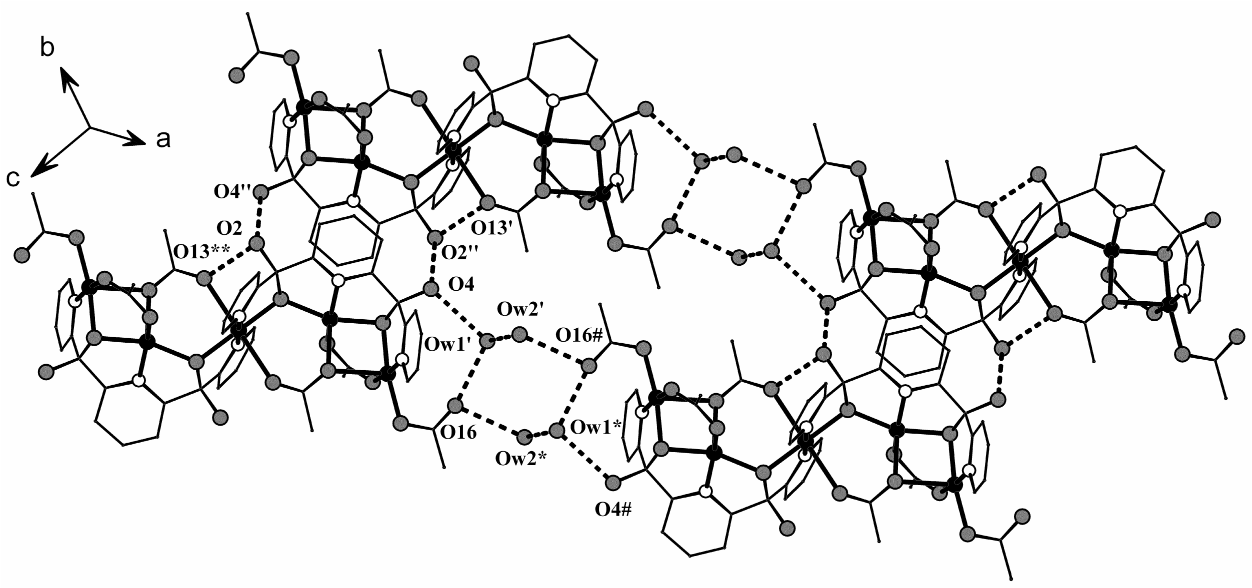

Fig. S1 Ball-and-stick plot showing the layered structure of **1** due to hydrogen bonding interactions. Symmetry operations to give equivalent positions: (′) = *x*, *y*, -1+*z*; (′′) = -*x*, 1-*y*,-*z*; (*) = 1-*x*, -*y*, 1-*z*; (**) = -*x*, 1-*y*, 1-*z*; (#) = 1-*x*, -*y*, -*z*.

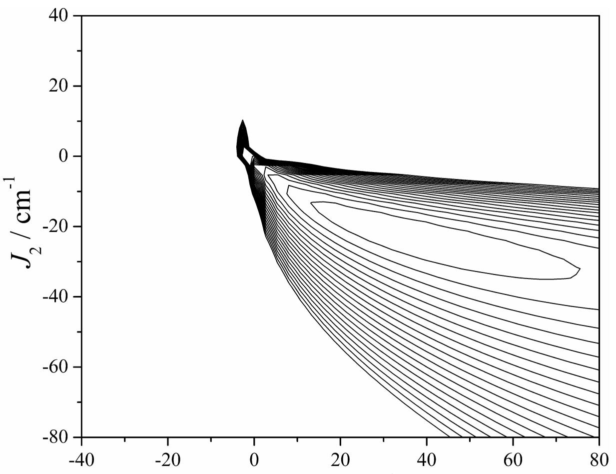

Fig. S2 Error contour-plot for various J_1 vs J_2 combinations (considering $J_3 = J_3 = 0$).

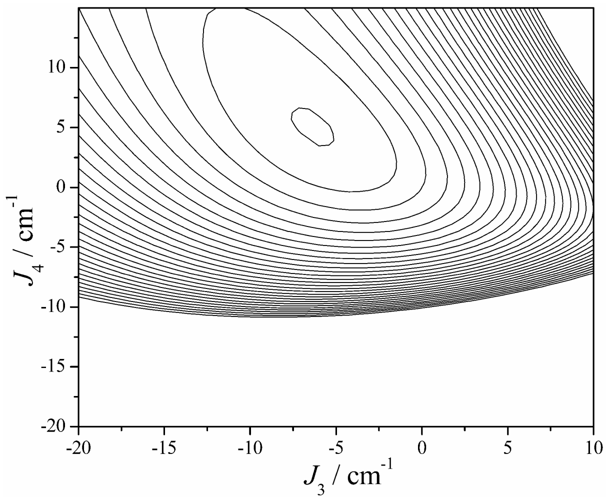

Fig. S3 Error contour-plot for various J_3 vs J_4 combinations.

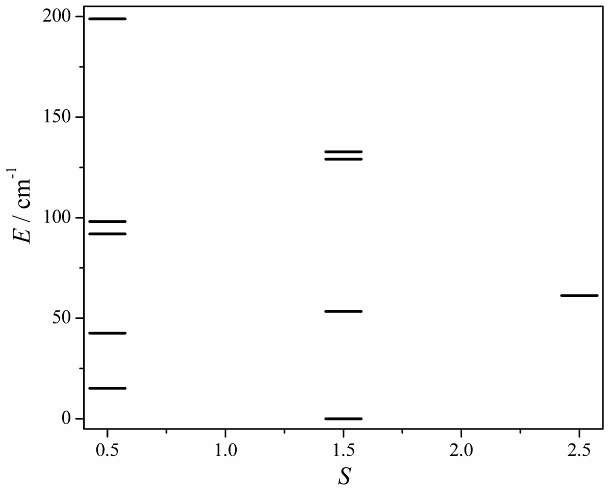

Fig. S4 Energy-level plot related to the best-fit according to the model described in the text.