Triarylcarbinol derivatives barter intermolecular interactions to accomodate substituents and create polymorphs

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Supporting Information

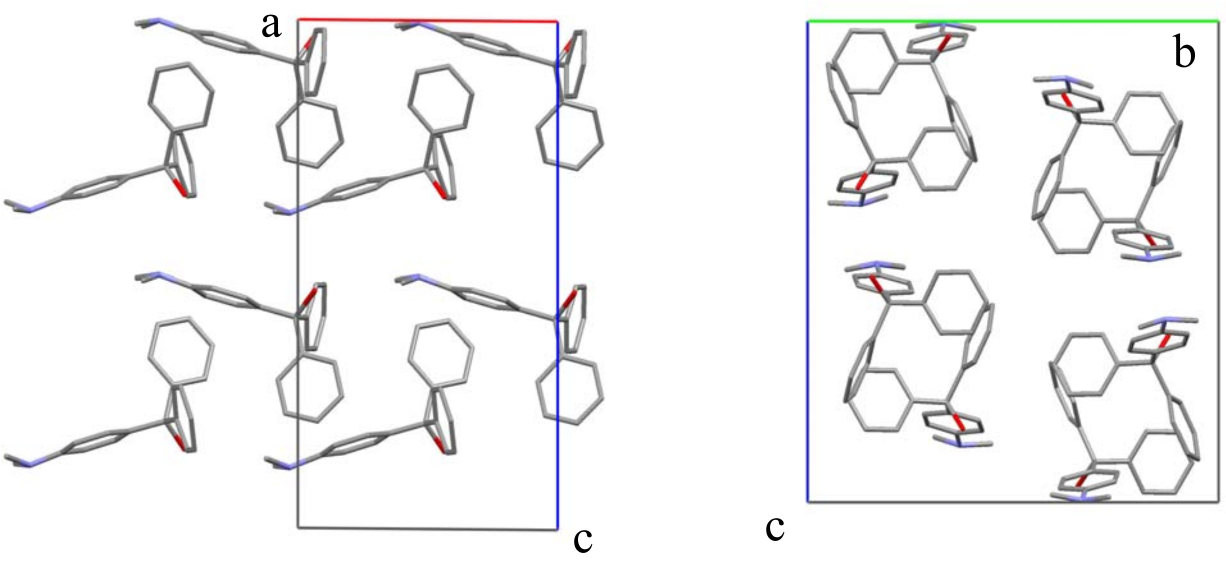


Figure S1. Crystal packing of SO, viewed down b (left) and down a (right).

Figure S2. Crystal packing of β-MG, viewed down a (top) and down c (bottom).

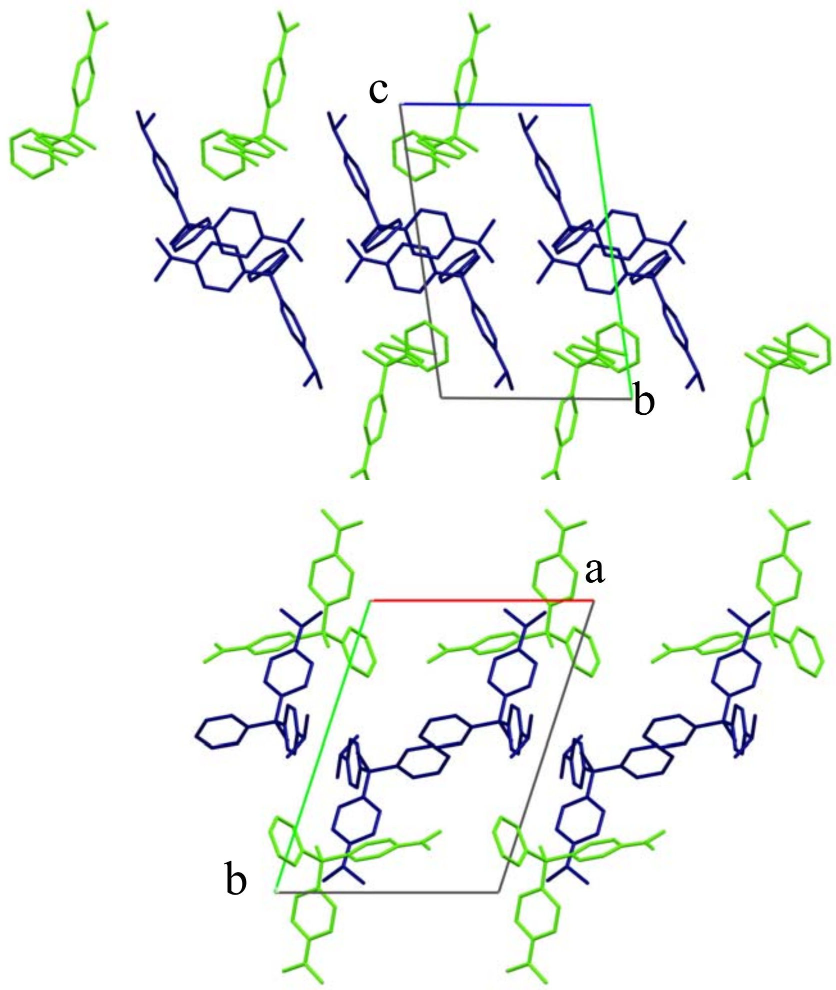


Figure S3. Crystal packing of α-CV, viewed down a.

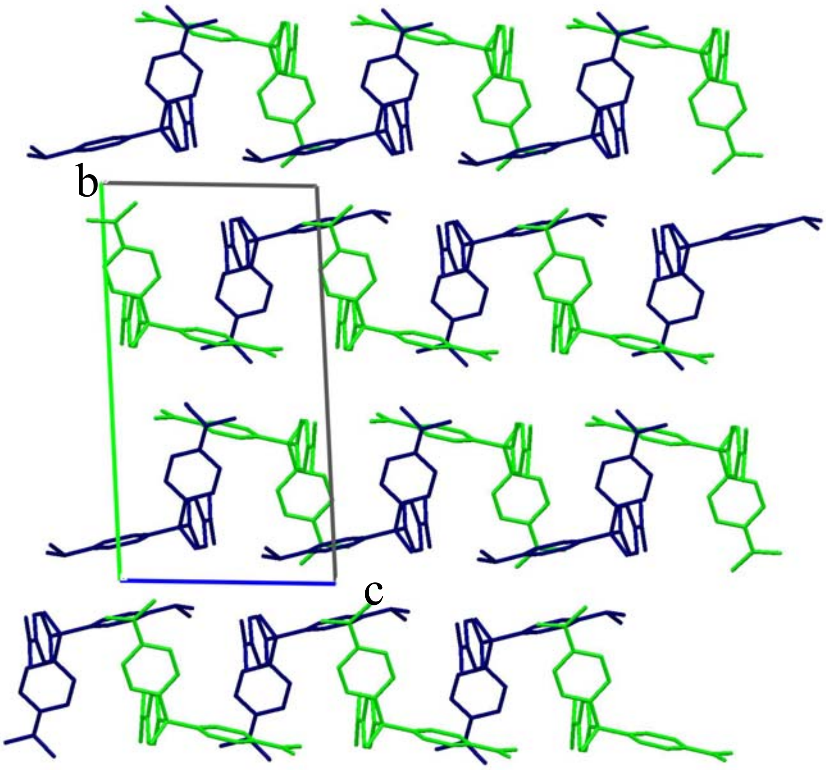


Figure S4. Crystal packing of α-PG, viewed down a (left) and down b (right).

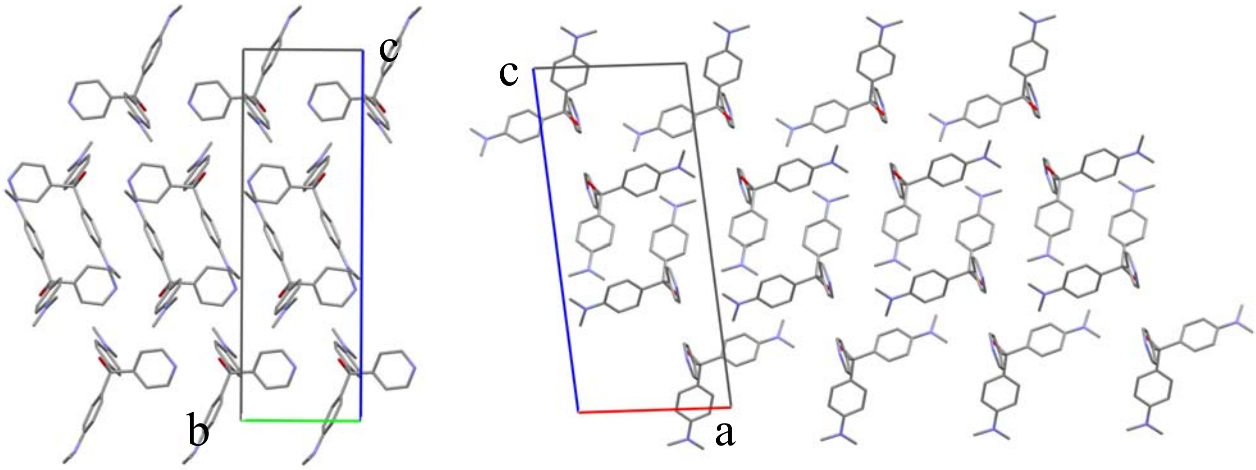


Figure S5. Molecular structure and labelling scheme of SO.

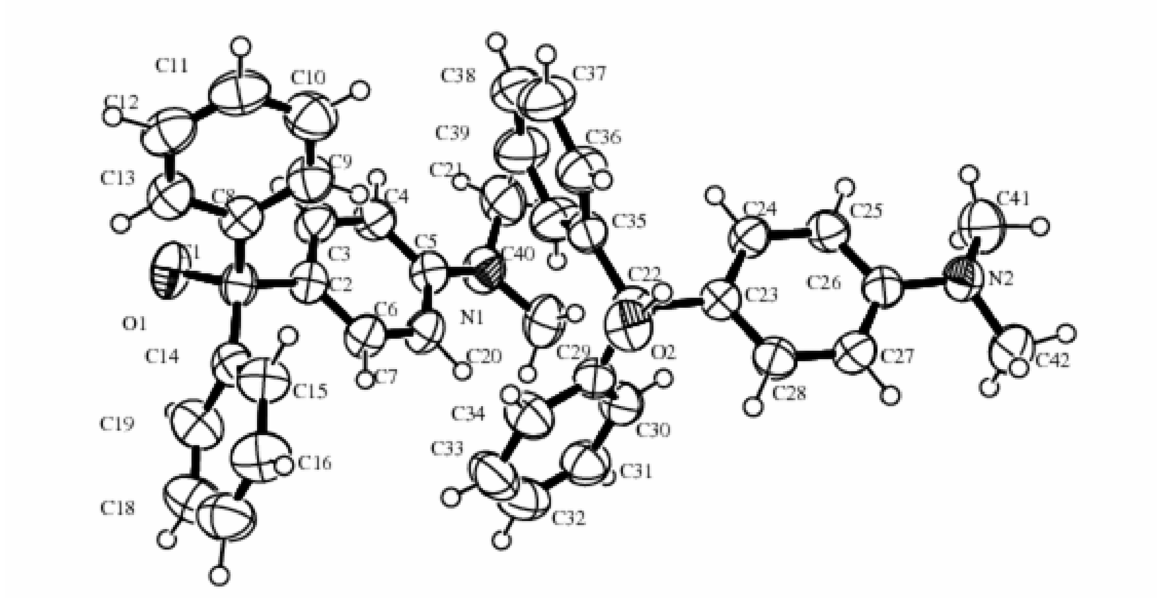


Figure S6. Molecular structure and labelling scheme of α-MG (293(2) K), dimethylamino groups on molecule B are present with a 2/3 occupancy, due to positional disorder around 3-fold axis passing through C24-O2.

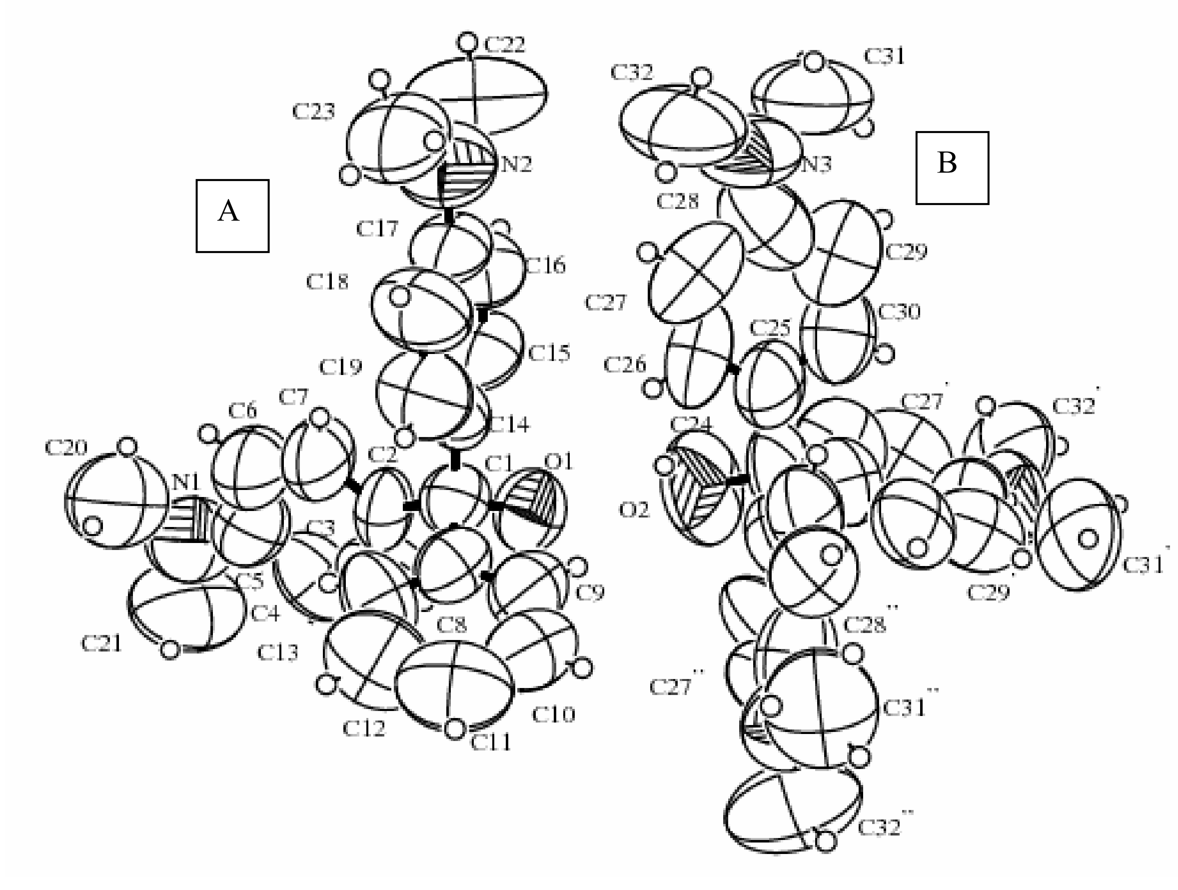


Figure S7. Molecular structure and labelling scheme of α-MG (123(2) K), dimethylamino groups on molecule B are present with a 2/3 occupancy, due to positional disorder around 3-fold axis passing through C24-O2.

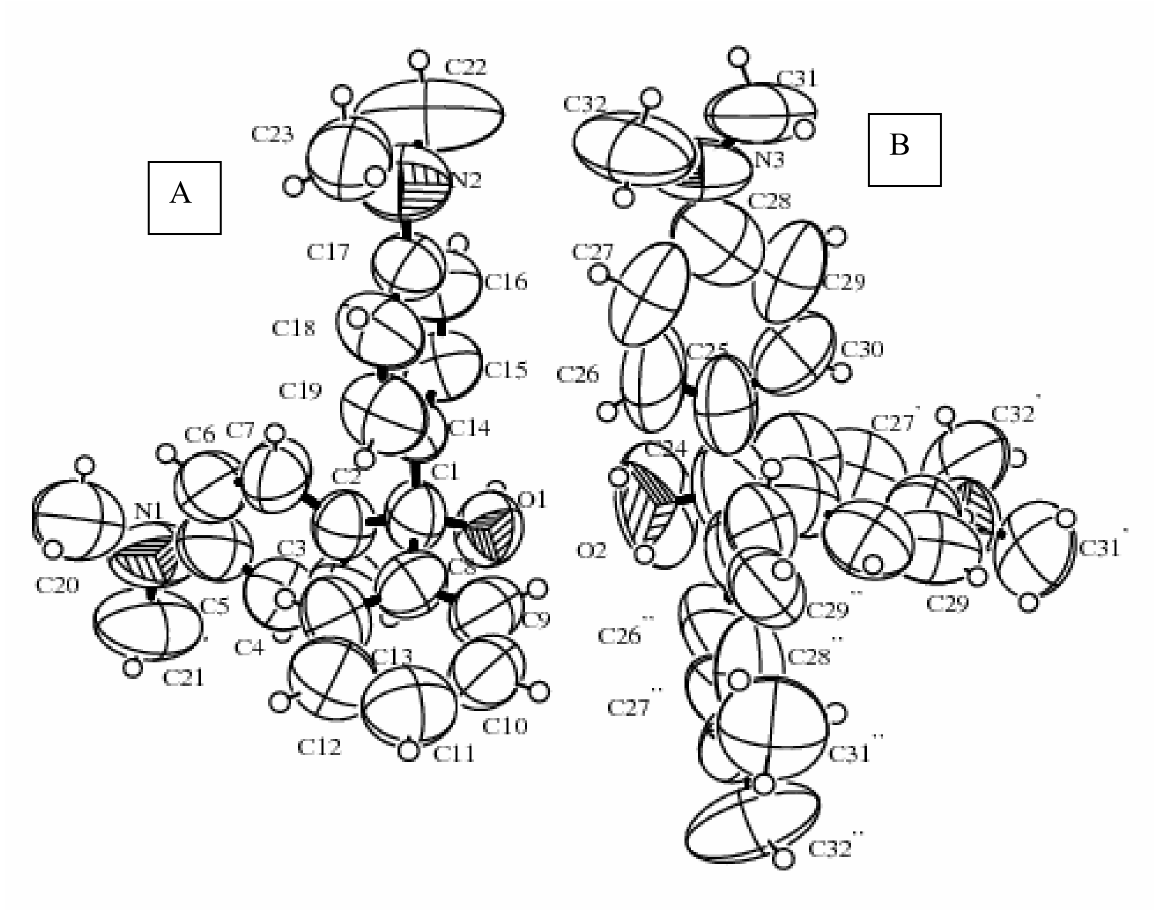


Figure S8. Molecular structure and labelling scheme of β-MG .

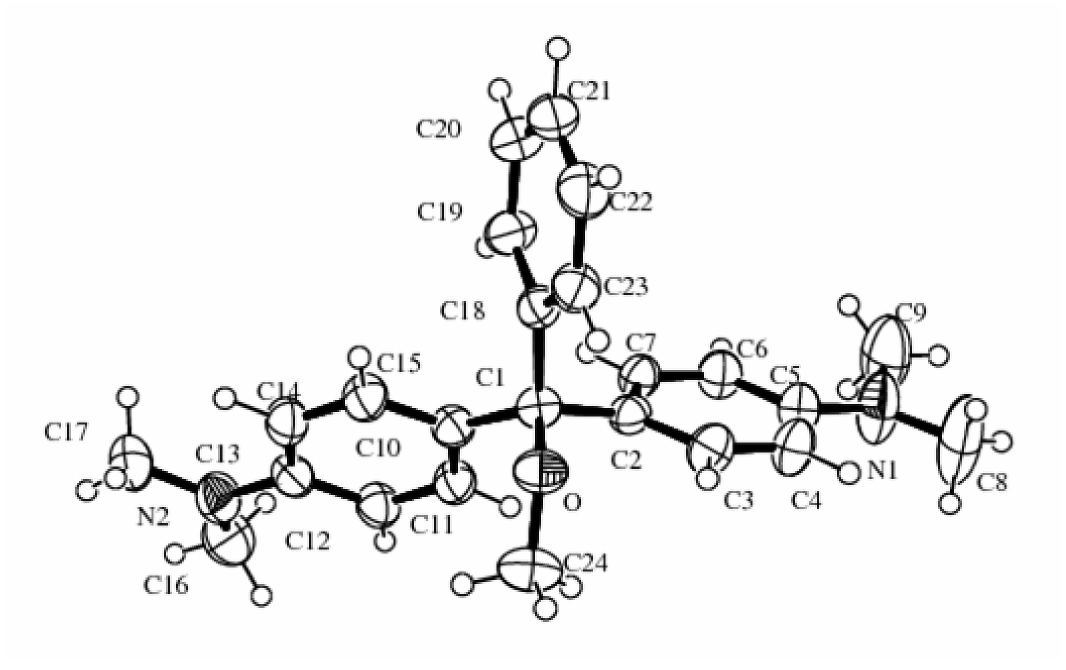


Figure S9. Molecular structure and labelling scheme of α-CV.

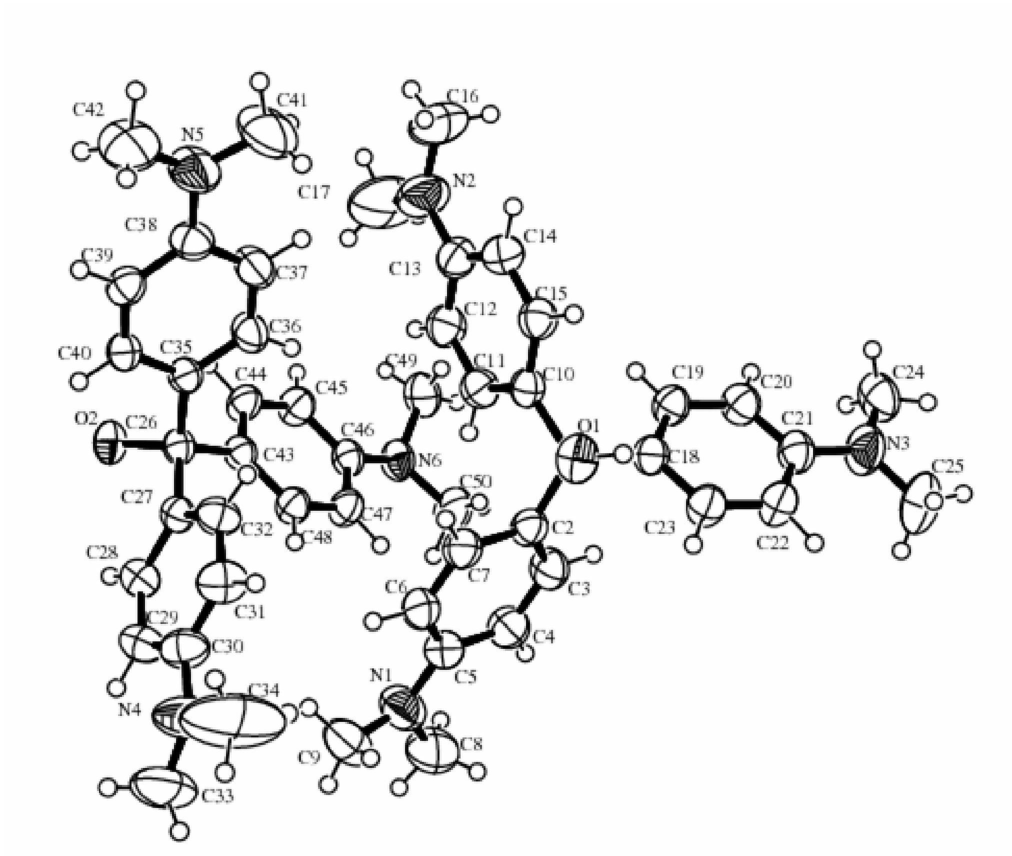


Figure S10. Molecular structure and labelling scheme of β-CV.

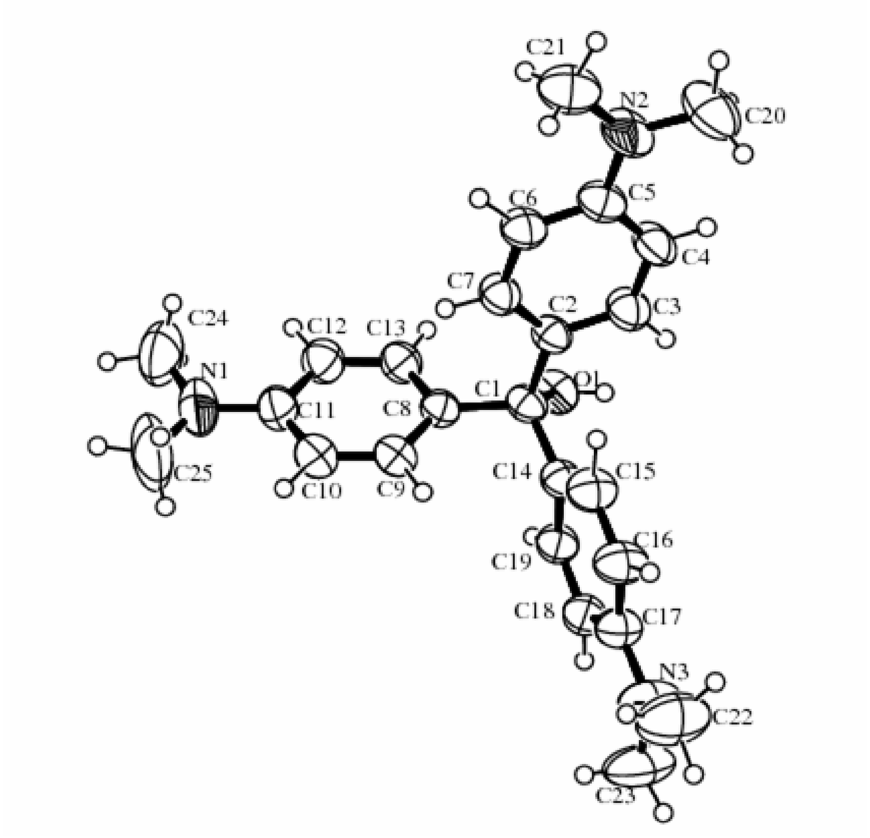


Figure S11. Molecular structure and labelling scheme of α–PG.

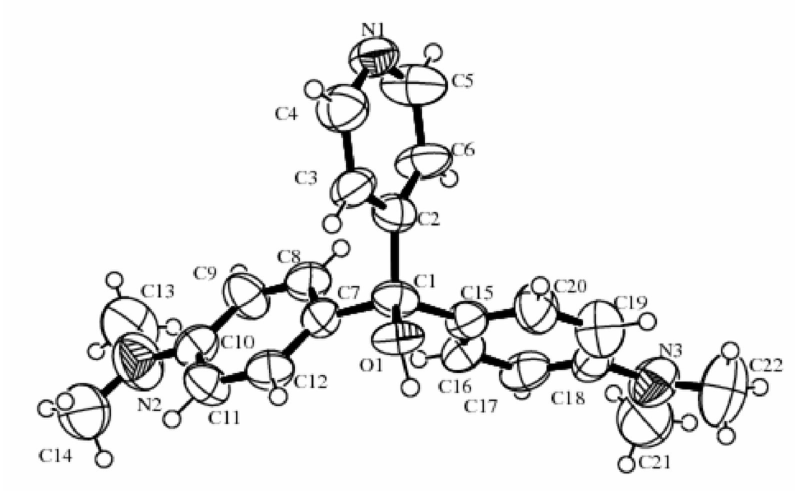


Figure S12. Molecular structure and labelling scheme of β–PG.

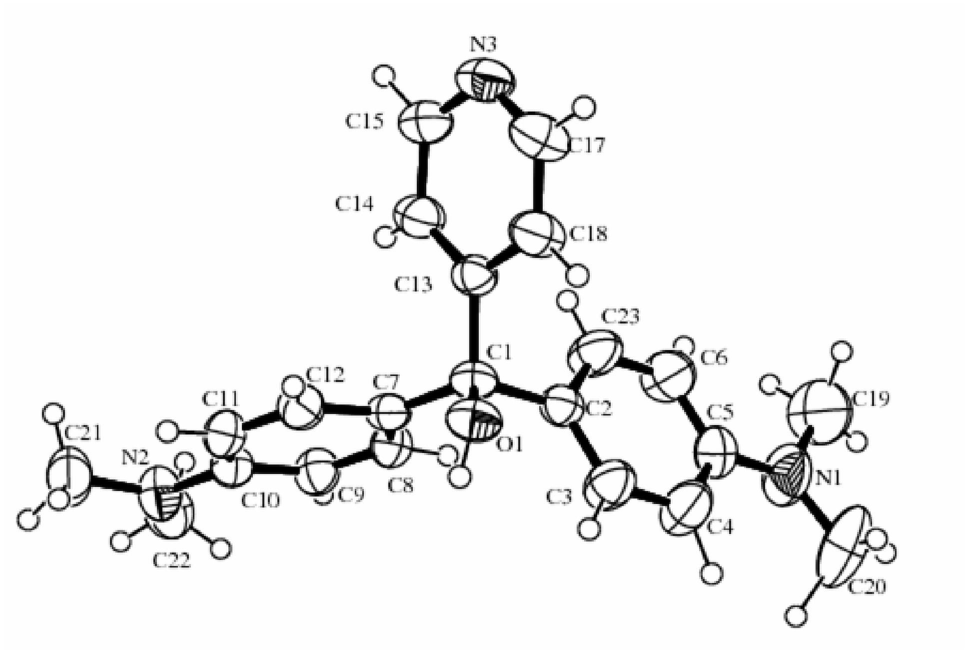
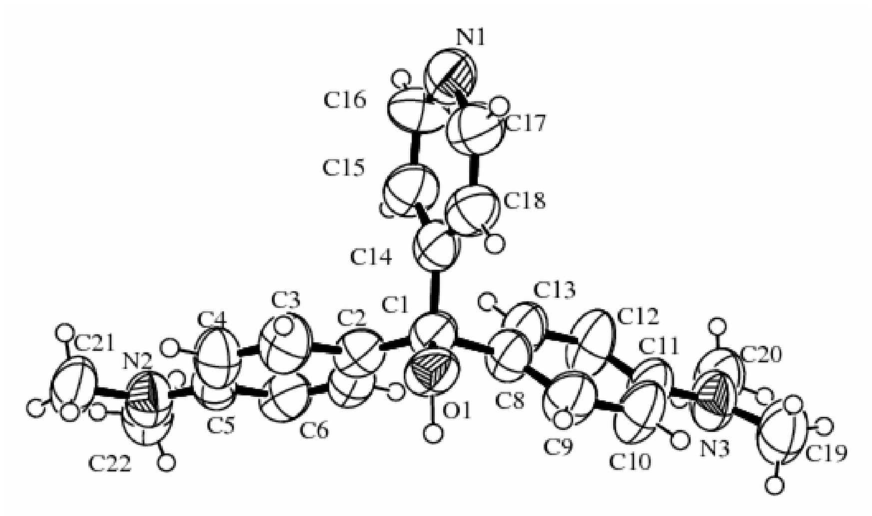


Figure S13. Molecular structure and labelling scheme of γ–PG.



Thermal motion analysis of α-MG

The partial conversion of the pale yellow form to the blue one which has occurred in the crystal over a one month period can be explained in terms of heterolytic scissions of the apical C-O bonds, producing stable carbocations and hydroxyl anions trapped in the hydrogen bonds cages in the middle of the tetramers. The C24-O2 is weaker than the C1-O1 bond because it is labilized by the solid-state arrangement, which favours the incipient transfer of the O2-H$^-$ group into the C1-O1-H cluster. The presence of a certain amount of dissociated molecules when the crystal has become blue, after one month of exposure in the light, is detectable by comparison of the thermal parameters in the first (RT, pale yellow crystal) and in the second (123 K, after one month, blue crystal) datasets. As expected, the equivalent isotropic thermal parameters (TPiso) are smaller in the low temperature structure, and the mean ratio between TPiso of corresponding atoms in the two cases is <TPiso(123K)/TPiso(RT)>=0.82(5). The only significant deviation is for C24 and O2, which show an apparent higher thermal motion in the low temperature than in the room temperature structure (TPiso(123K)/TPiso(RT)=1.13 and 1.12 respectively for C24 and O2) (Figure SI-14). This can be interpreted in terms of a positional disorder for the two atoms in the 123 K case, due to the dissociation of a small fraction of C24-O2 bonds after light exposure, with the subsequent shift of the OH$^-$ towards the basal oxygens. The hypothesis is supported by the fact that, in the final difference Fourier map, the highest residual (0.23 e/Å^3), attributable to a small fraction of dissociated OH$^-$, is at 0.97Å from O2, shifted towards the basal oxygens, and forms short asymmetric contacts of 2.59 and 2.70 Å with two of the three equivalent O1 atoms.

Figure S14. Comparison of isotropic thermal parameters for room and low temperature structures of α–MG.