Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Homochiral *vs.* heterochiral preference in chiral self-recognition of cyclic diols

Jennifer Dupont,a) Beppo Hartwig, b) Katia Le Barbu-Debus,a) Valéria Lepère,a) Regis Guillot,c) Martin A. Suhm, b) Anne Zehnackera)*

a) Institut des Sciences Moléculaires d'Orsay (ISMO), CNRS, rue André Rivière, Université Paris-Saclay, F-91405 Orsay, France

b) Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammannstr. 6, 37077 Göttingen, Germany.

c) Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO), 17 Av. des Sciences Université Paris-Saclay, F-91405 Orsay, France

*e-mail: anne.zehnacker-rentien@universite-paris-saclay.fr

Supplementary Information

Table S1: Relative electronic energy ΔE_{el}, zero-point-corrected energy ΔE_0, Gibbs energy at room-temperature with (ΔG_{QRRHO}(300 K)) and without (ΔG(300 K)) Quasi Rigid Rotor Harmonic Oscillator approximation, and deformation energy E_{def} (see text), calculated at the B3LYP-D3(BJ,abc)/ma-def2-TZVP level. Dimer energies are given relative to the most stable homochiral Insertion (M_1+M_1) conformer. All values are given in kJ mol^{-1}.

Monomer	ΔE_{el}	ΔE_0	ΔG(300 K)	ΔG_{QRRHO}(300 K)	E_{def}
M_1	0	0	0	0	-
M_1'	8.4	7.2	6.7	6.7	-
M_2	11.7	10.2	9.6	9.7	-
Homochiral dimers	ΔE_{el}	ΔE_0	ΔG(300 K)	ΔG_{QRRHO}(300 K)	E_{def}
Insertion (M_1+M_1)	0	0	0	0	8.7
Addition O_2H_2 --> O_1(M_1+M_1)	13.7	10.8	2.0	6.9	2.8
Addition O_2H_2 --> O_2(M_1+M_1')	7.4	5.9	5.1	5.1	13.1
Addition O_2H_2 --> O_2(M_1+M_1)	9.0	7.6	4.1	5.7	2.9
Addition O_2H_2 --> O_2(M_1+M_2)	10.8	8.6	7.6	7.6	18.6
Addition O_2H_2 --> O_2(M_1+M_2)a	12.3	10.0	8.0	8.8	19.3
Addition O_2H_2 --> O_2(M_1+M1)a	11.3	9.4	5.7	7.3	7.8
Heterochiral dimers	ΔE_{el}	ΔE_0	ΔG(300 K)	ΔG_{QRRHO}(300 K)	E_{def}
Insertion (M_1+M_1)	2.8	1.6	2.4	1.8	10.4
Addition O_2H_2 --> O_1(M_1+M_1)	12.3	9.6	-1.3	4.6	3.3
Addition O_2H_2 -->O_2(M_1+M_1)a	11.7	9.7	0.8	5.4	3.0
Double insertion (M_1+M_1)	5.1	4.7	6.2	5.3	20.5
Addition O_2H_2 --> O_2(M_1+M_1)b	9.9	8.6	3.7	6.1	2.5
Addition O_2H_2 --> O_2(M_1+M_2)	7.5	6.2	5.9	5.8	20.5
Addition O_2H_2 --> O_2(M_1+M_1)c	9.1	7.9	4.7	6.2	3.9
Addition O_2H_2 --> O2(M_1+M_1)d	11.3	9.2	5.7	7.2	7.7
Addition O_2H_2 --> O_2(M_1+M_1')	12.6	10.2	8.3	9.0	11.7

Table S2. ZPE-corrected ΔE_0 and Gibbs ΔG relative energies calculated at the B3LYP-D3BJ/6-31G++(d,p) level, in kJ mol^{-1}. Relevant geometrical parameters describing the most stable conformers of the PCD monomers. The distances are given in Å and the angles in °.

Conformer	**ΔG**	**ΔE_0**	$\mathbf{O_1\widehat{H_1}O_2}$ $\boldsymbol{d(O_2 - H_1)}$	$\mathbf{O_2\widehat{H_2}O_1}$ $\boldsymbol{d(O_1 - H_2)}$	**τ ($C_2C_1O_1H_1$)**	**τ ($C_6C_1O_1H_1$)**	**τ ($C_1C_2O_2H_2$)**	**τ ($C_3C_2O_2H_2$)**	**τ ($H_3C_2O_2H_2$)**
M_1	0.0	0.0	115° 2,22 Å	-	-	157°	-	171°	-
M'_1	7.1	7.8	113° 2,18 Å	-	-	164°	168°	-	-
M_2	10.0	10.7	-	109° 2,28 Å	180°	-	-	-	166°

Table S3 - Crystallographic data and structure refinement details.

Compound	*cis*-PCD
CCDC	2277624
Empirical Formula	$C_{12} H_{16} O_2$
M_r	192.25
Crystal size, mm^3	0.260 x 0.030 x 0.015
Crystal system	Monoclinic
Space group	*C* 2
a, Å	19.7972(5)
b, Å	5.6454(2)
c, Å	19.9238(5)
α, °	90
β, °	116.7000(10)
γ, °	90
Cell volume, Å^3	1989.31(10)
Z ; Z’	8 ; 2
T, K	100(1)
Radiation type ; wavelength Å	CuKα; 1.54178
F_{000}	832
μ, mm^{-1}	0.683
range, °	2.482 - 66.669
Reflection collected	14 782
Reflections unique	3 416
R_{int}	0.0369
GOF	1.040
Refl. obs. (I>2(I))	3 233
Parameters ; restraints	262 ; 1
wR_2 (all data)	0.0669
R value (I>2(I))	0.0278
Flack parameter [4]	0.15(9)
Largest diff. peak and hole (e-.Å^{-3})	0.174 ; -0.157

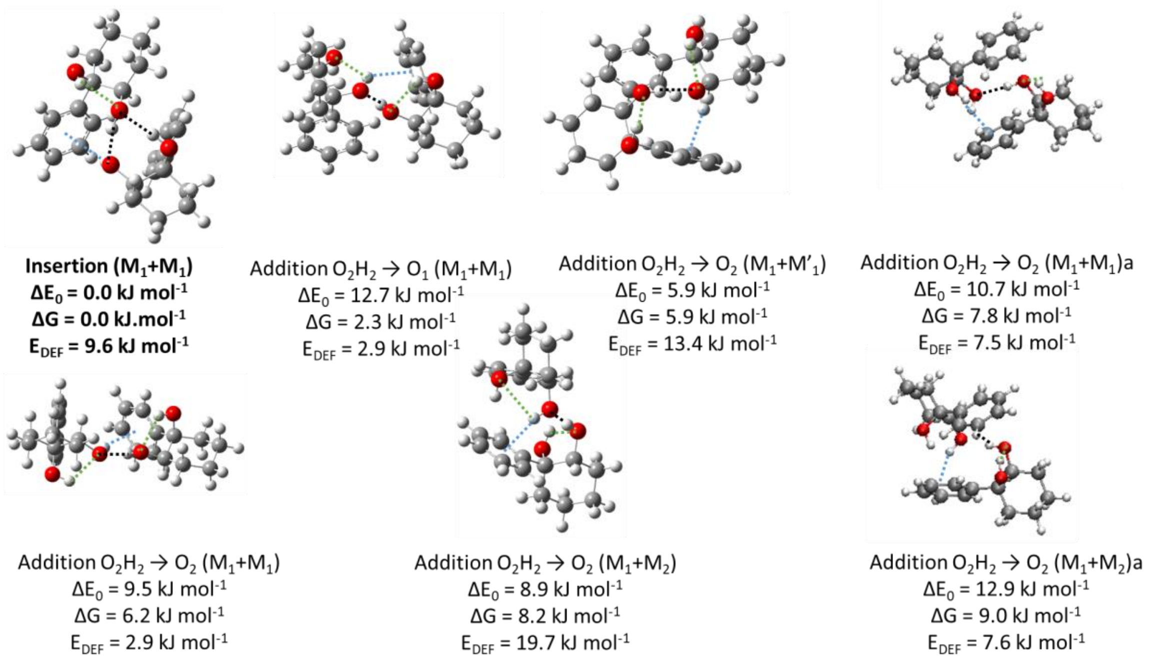
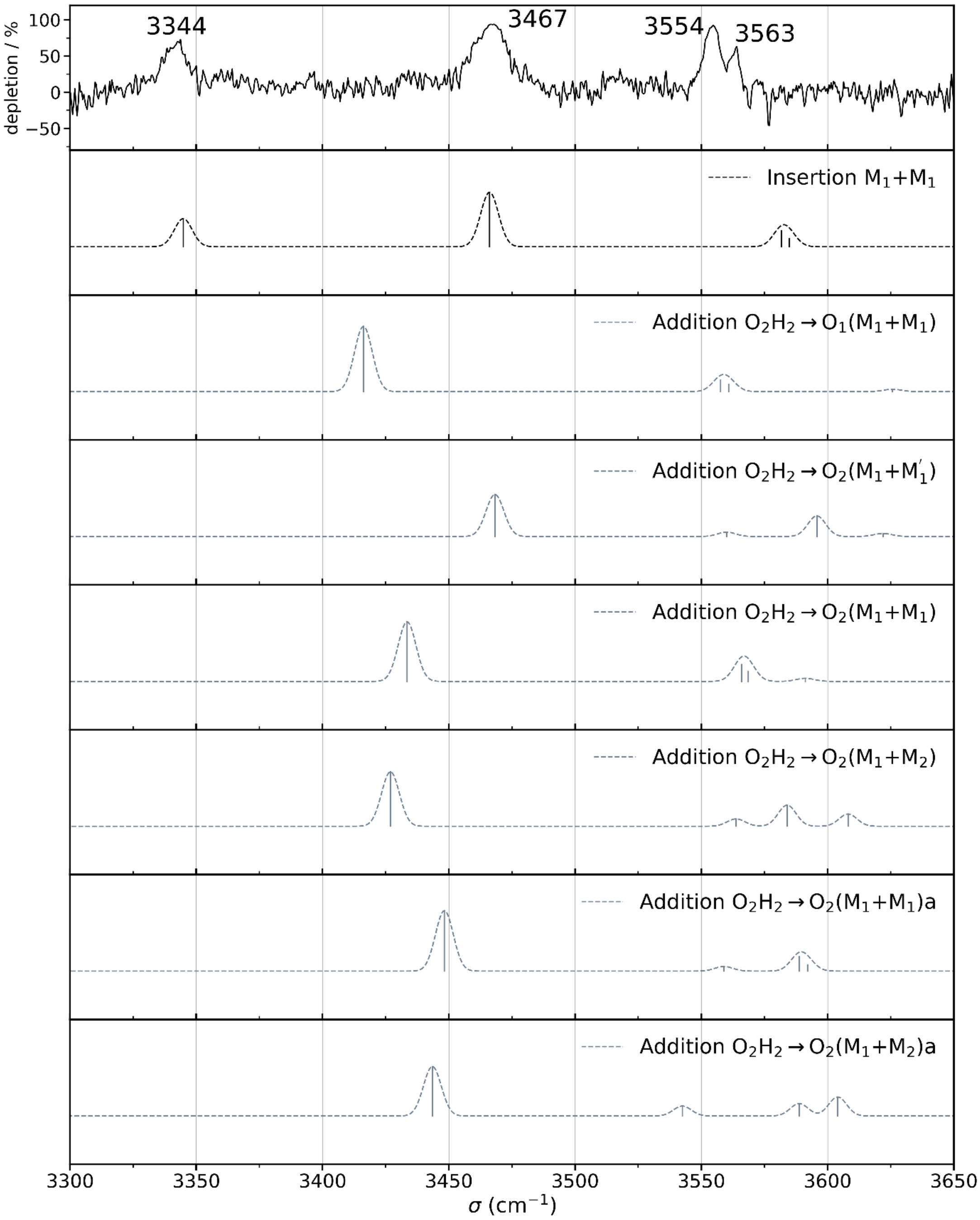


Figure S1. The most stable calculated homochiral dimers of *cis*-PCD. ΔE_0, ΔG and E_{DEF} are the relative ZPE-corrected, Gibbs and deformation energies in kJ mol^{-1} (see text) calculated at the 6-311++G(d,p) level. O_1 and O_2 refer to the oxygen atom involved in the interaction (see text). The numbers 1, 1', 2, refer to the structure of the monomer contained in the dimer. The hydrogen bonds are shown by dotted lines (intermolecular OH…O in black, OH…π in blue, intramolecular OH…O in green). The large deformation energy of Addition $O_2H_2 \rightarrow O_2$ (M_1+M_2) is mainly due to the large deformation of M_2. The zero of the energy scale is set at the most stable homochiral complex.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Insertion M_1+M_1
Addition $O_2H_2 \rightarrow O_1(M_1+M_1)$
Addition $O_2H_2 \rightarrow O_2(M_1+M_1')$
Addition $O_2H_2 \rightarrow O_2(M_1+M_1)$
Addition $O_2H_2 \rightarrow O_2(M_1+M_2)$
Addition $O_2H_2 \rightarrow O_2(M_1+M_1)$a
Addition $O_2H_2 \rightarrow O_2(M_1+M_2)$a
3300
3350
3400
3450
3500
3550
3600
3650
σ (cm^{-1})

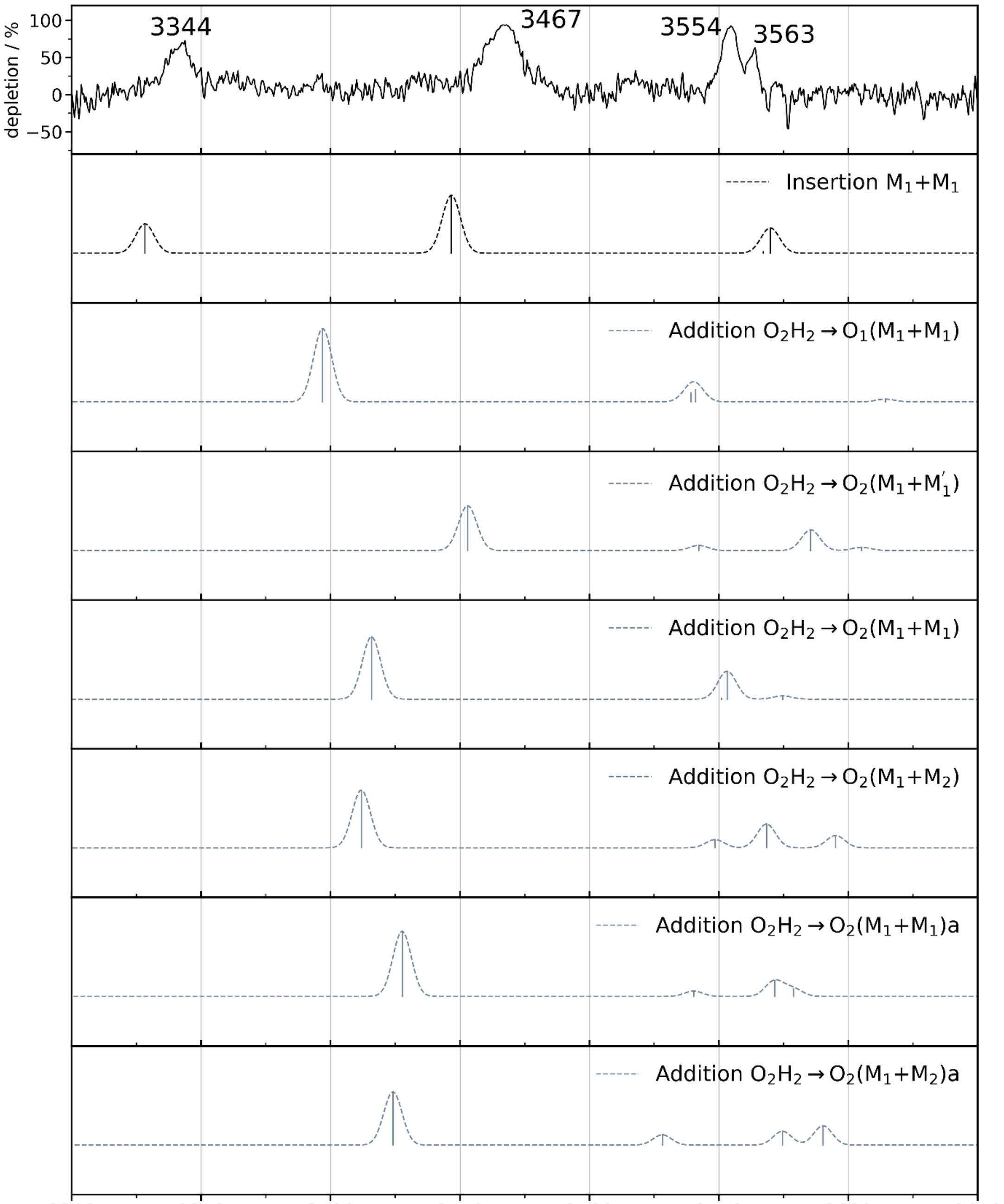


Figure S2. (top) Simulated spectra for the most stable calculated homochiral dimers of *cis*-PCD shown in Figure S1, together with the experimental spectrum (top). The simulation of the assigned conformer is coloured in black. Grey simulations have not been experimentally assigned. The B3LYP-D3(BJ,abc)/ma-def2-TZVP harmonic frequencies were scaled by 0.963 and convoluted by a Gaussian line shape of 4 cm^{-1} Full Width at Half Maxima (FWHM). (bottom) B3LYP-D3BJ/6-31G++(d,p) harmonic frequencies scaled by 0.952 and convoluted by a Gaussian line shape of 4 cm^{-1} FWHM.

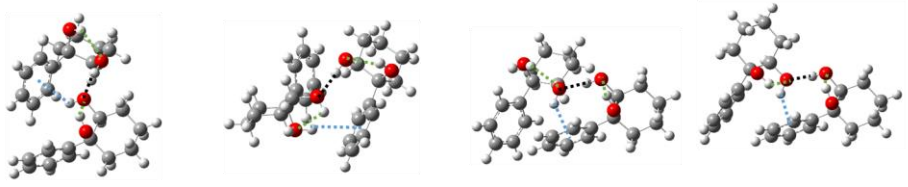
Insertion (M_1+M_1)
ΔE_0 = 1.7 kJ mol^{-1}
ΔG = 2.8 kJ mol^{-1}
E_{DEF} = 11.3 kJ mol^{-1}

Addition $O_2H_2 \rightarrow O_1$ (M_1+M_1)
ΔE_0 = 11.1 kJ mol^{-1}
ΔG = 2.3 kJ mol^{-1}
E_{DEF} = 3.8 kJ mol^{-1}

Addition $O_2H_2 \rightarrow O_2$ (M_1+M_1)a
ΔE_0 = 11.7 kJ mol^{-1}
ΔG= 5.2 kJ mol^{-1}
E_{DEF} = 2.9 kJ mol^{-1}

Double insertion (M_1+M_1)
ΔE_0 = 4.2 kJ mol^{-1}
ΔG = 6.0 kJ mol^{-1}
E_{DEF} = 21.8 kJ mol^{-1}

Addition $O_2H_2 \rightarrow O_2$ (M_1+M'_1)
ΔE_0 = 10.9 kJ mol^{-1}
ΔG = 8.8 kJ mol^{-1}
E_{DEF} = 3.4 kJ mol^{-1}



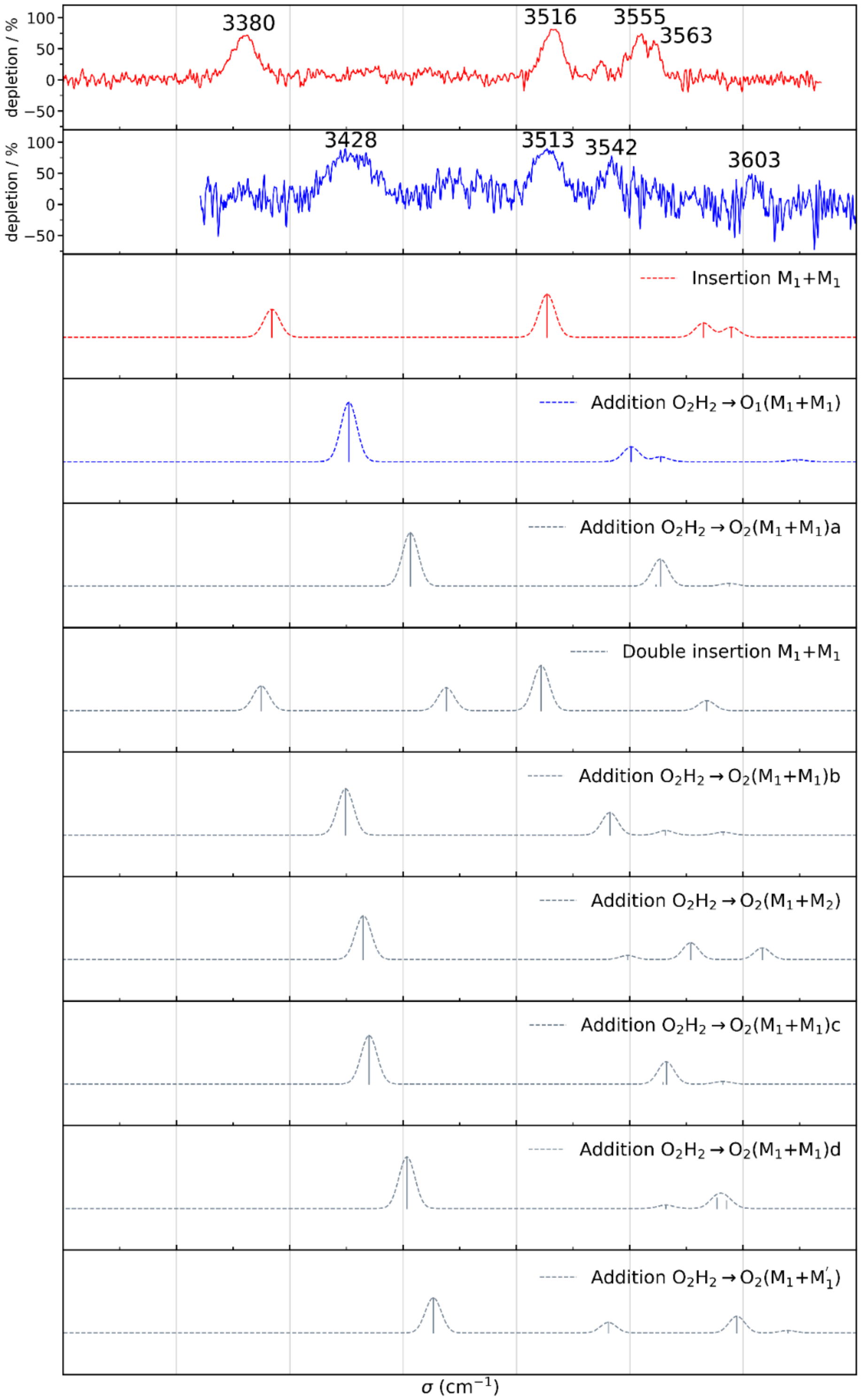
Addition $O_2H_2 \rightarrow O_2$ (M_1+M_1)b
ΔE_0 = 10.5 kJ mol^{-1}
ΔG = 6.3 kJ mol^{-1}
E_{DEF} = 2.5 kJ mol^{-1}

Addition $O_2H_2 \rightarrow O_2$ (M_1+M_2)
ΔE_0 = 6.5 kJ mol^{-1}
ΔG = 6.7 kJ mol^{-1}
E_{DEF} = 5.3 kJ mol^{-1}

Addition $O_2H_2 \rightarrow O_2$ (M_1+M_1)c
ΔE_0 = 9.9 kJ mol^{-1}
ΔG = 7.4 kJ mol^{-1}
E_{DEF} = 4.2 kJ mol^{-1}

Addition $O_2H_2 \rightarrow O_2$ (M_1+M_1)d
ΔE_0 = 10.4 kJ mol^{-1}
ΔG = 7.5 kJ mol^{-1}
E_{DEF} = 8.4 kJ mol^{-1}

Figure S3. The most stable calculated heterochiral dimers of PCD together with their simulated spectra. ΔG a ΔE_0, ΔG and E_{DEF} are the relative ZPE-corrected, Gibbs and deformation energies in kJ mol^{-1} (see text) calculated at the 6-311++G(d,p) level. O_1 and O_2 refer to the oxygen atom involved in the interaction. M_1, M'_1, M_2 refer to the structure of the monomer contained in the dimer. The hydrogen bonds are shown by dotted lines (intermolecular OH…O in black, OH…π in blue, intramolecular OH…O in green). The large deformation energy of Addition $O_2H_2 \rightarrow O_2$ (M_1+M_2) is mainly due to the large deformation of M_2. The zero of the energy scale is set at the most stable homochiral complex.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3603
Insertion M_1+M_1
Addition $O_2H_2 \rightarrow O_1(M_1+M_1)$
Addition $O_2H_2 \rightarrow O_2(M_1+M_1)a$
Double insertion M_1+M_1
Addition $O_2H_2 \rightarrow O_2(M_1+M_1)b$
Addition $O_2H_2 \rightarrow O_2(M_1+M_2)$
Addition $O_2H_2 \rightarrow O_2(M_1+M_1)c$
Addition $O_2H_2 \rightarrow O_2(M_1+M_1)d$
Addition $O_2H_2 \rightarrow O_2(M_1+M_1')$
σ (cm^{-1})

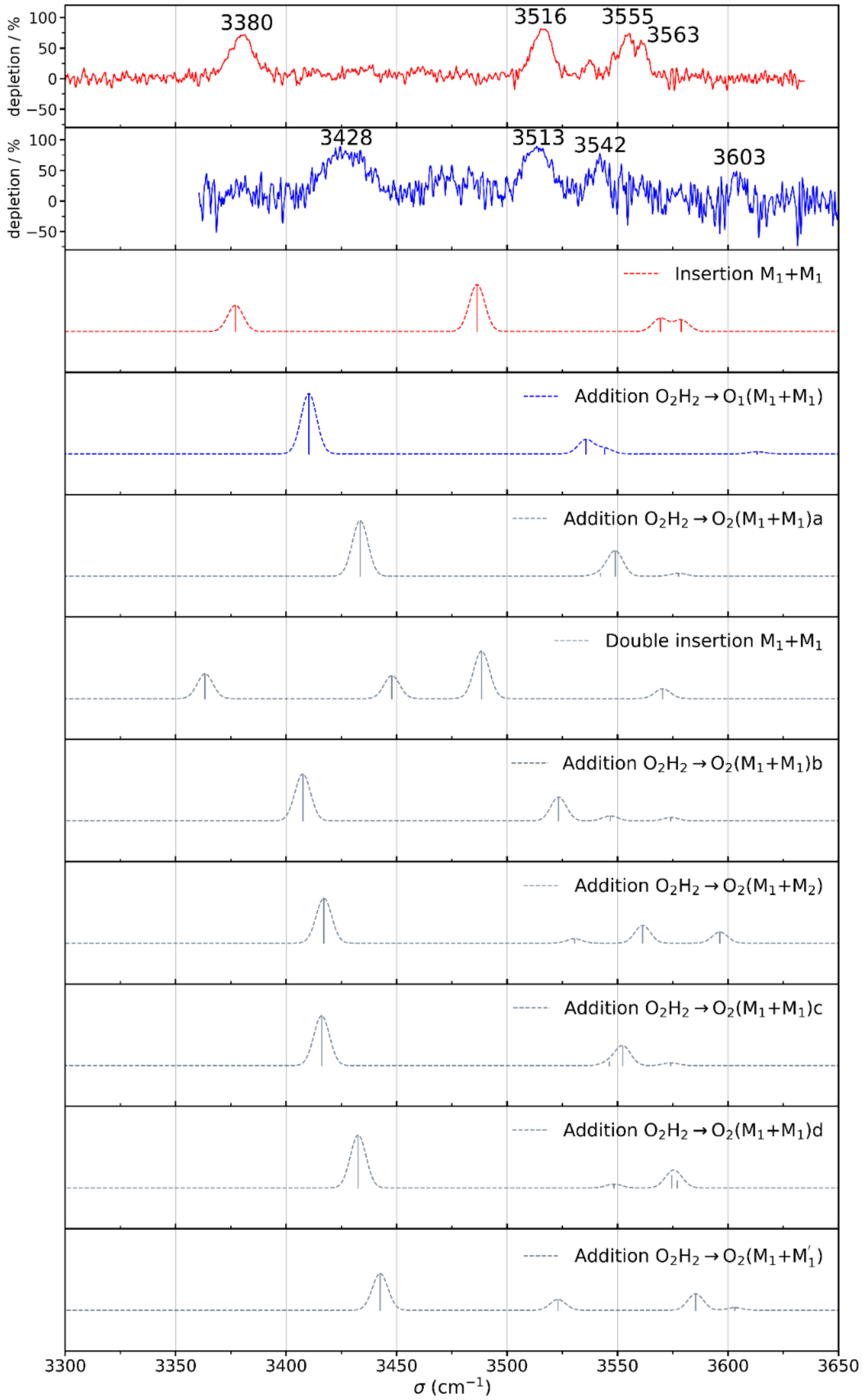
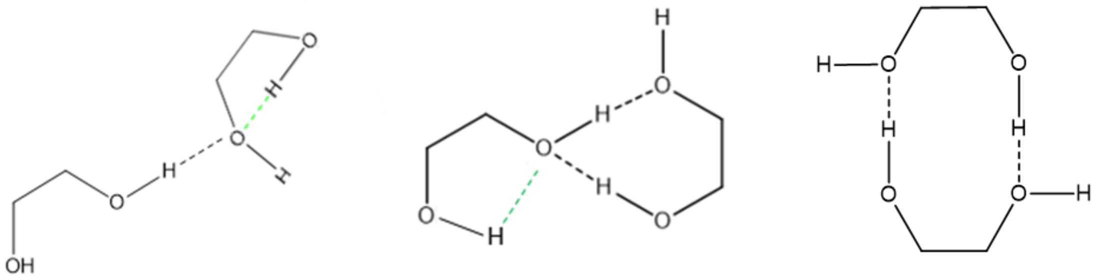


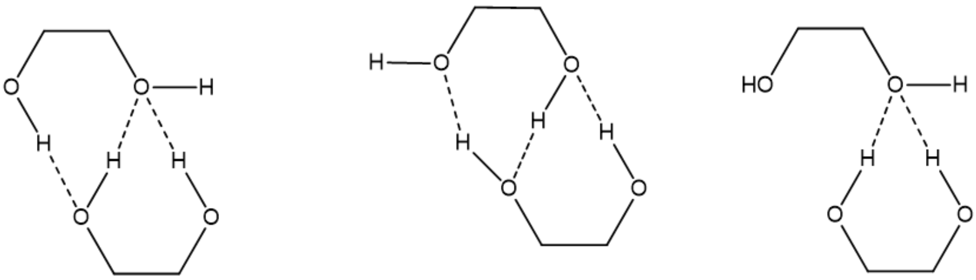
Figure S4. (top) Simulated spectra for the most stable calculated heterochiral dimers of *cis*-PCD shown in Figure S3, together with the experimental spectra (top). The red spectrum has been taken by setting the probe at 37511 cm^{-1} and the blue spectrum by setting the probe at 37768 cm^{-1}. The simulations of the assigned conformers are coloured according to the experimental ones. Grey simulations have not been experimentally assigned. The B3LYP-D3(BJ,abc)/ma-def2-TZVP harmonic frequencies were scaled by 0.963 and convoluted by a Gaussian line shape of 4 cm^{-1} Full Width at Half Maxima (FWHM). (bottom) B3LYP-D3BJ/6-31G++(d,p) harmonic frequencies scaled by 0.952 and convoluted by a Gaussian line shape of 4 cm^{-1} FWHM.



Addition

Insertion

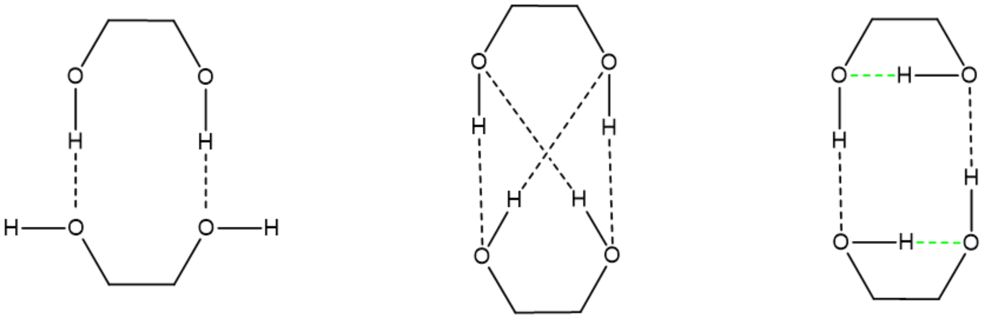
Activated mutual addition



Insertion clamp

Double insertion

Clamp



Activated double addition

Quadruple insertion

Cyclic (double addition)

Figure S5: Typical Hydrogen bond patterns likely to form in diol dimers.

Single-Crystal X-ray Diffraction Data.

X-ray diffraction data for compound *cis*-PCD were collected by using a VENTURE PHOTON100 CMOS Bruker diffractometer with Micro-focus IμS source Cu Kα radiation. Crystals of compounds were selected under a polarising optical microscope and glued in paratone oil. The crystal was mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flash frozen in a nitrogen-gas stream at 100 K. The temperature of the *cis*-PCD crystal was maintained at the selected value by means of a 700 series Cryostream cooling device to within an accuracy of ±1K. Data reduction was accomplished using SAINT V7.53a. The substantial redundancy in data allowed a semi-empirical absorption correction (SADABS V2.10) to be applied, based on multiple measurements of equivalent reflections. The structures were solved by direct methods using SHELXS-97[3] and refined against F^2 by full-matrix least-squares techniques using SHELXL-2018[4] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.[5]

cis-PCD crystallizes in the space group *C*2 and its absolute configuration has been established by anomalous-dispersion effects in diffraction measurements on the crystal (using a large number of Friedel's pairs). The difference in the conformations of the two molecules is highlighted in Figure S6 and results in different hydrogen bond motifs. The crystal data collection and refinement parameters are given in Table S3.

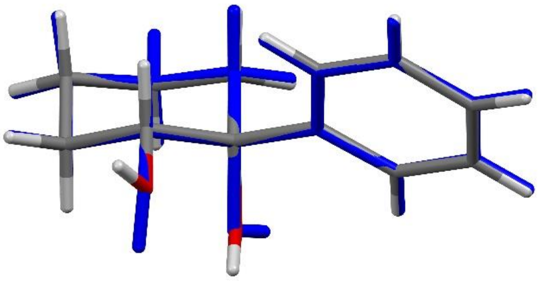


Figure S6 - Overlay diagram of the two symmetry independent molecules in the crystal structure.

Supplementary References

1. J. Zheng, X. Xu and D. G. Truhlar, *Theoretical Chemistry Accounts*, 2011, **128**, 295-305.
2. F. Weigend and R. Ahlrichs, *Physical Chemistry Chemical Physics*, 2005, **7**, 3297-3305.
3. G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution University of Göttingen, Germany*, 1997.
4. G. M. Sheldrick, *Acta Crystallographica a-Foundation and Advances*, 2008, **64**, 112-122.
5. L. Farrugia, *Journal of Applied Crystallography*, 1999, **32**, 837-838.