

Supporting information

A comparative VCD study of methyl mandelate in methanol, dimethyl sulfoxide, and chloroform: explicit and implicit solvation models

Mohammad Reza Poopari, Zahra Dezhahang, Yunjie Xu*

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada

*Tel:1-780-492-1244, Fax:1-780-492-8231, Email: yunjie.xu@ualberta.ca

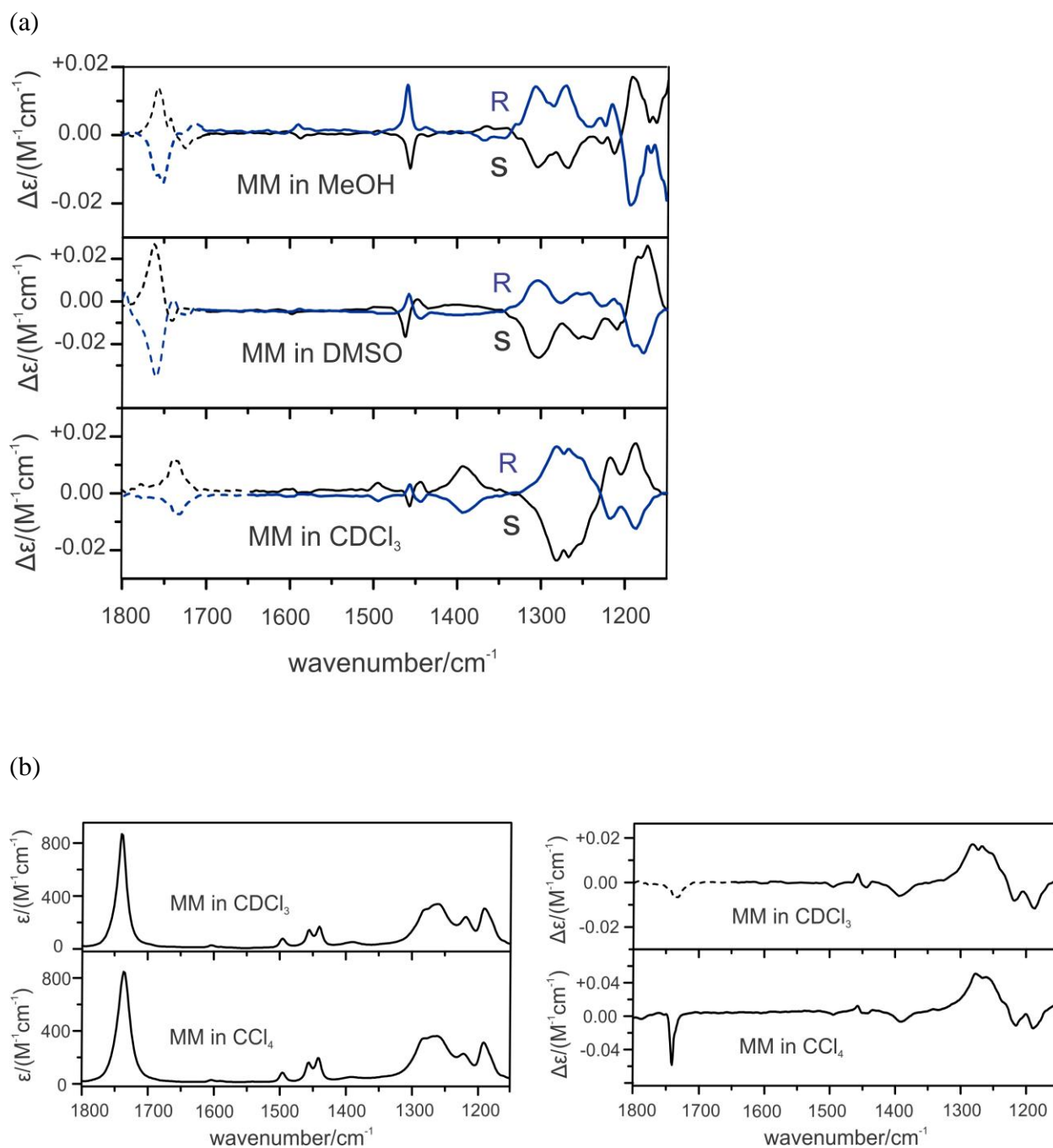


Fig. S1 (a) Comparison of the experimental VA (left) and VCD (right) spectra of R- and S-MM in the three solvents discussed in this paper. (b) Comparison of the experimental VA (left) and VCD (right) spectra of MM in CDCl₃ and CCl₄.

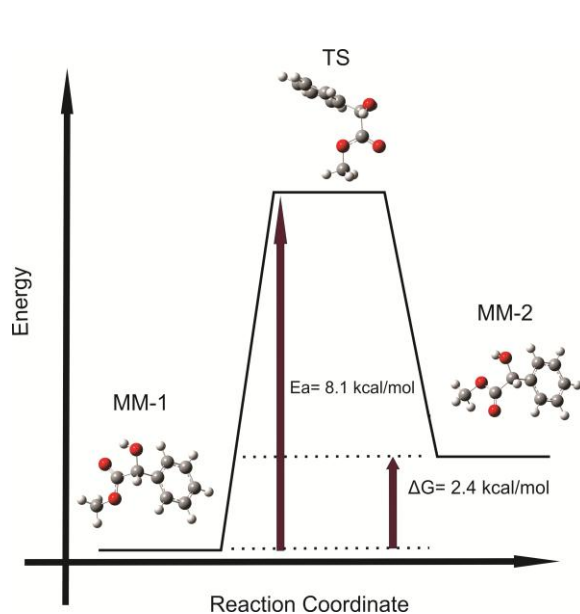


Fig. S2 The conversion barriers between the two most stable conformers of MM at the B3LYP/cc-pVTZ level. The QST2 option implemented in Gaussian 09 with the Synchronous Transit-Guided Quasi-Newton (STQN) method has been used to locate the transition state between these two lowest energy conformers.

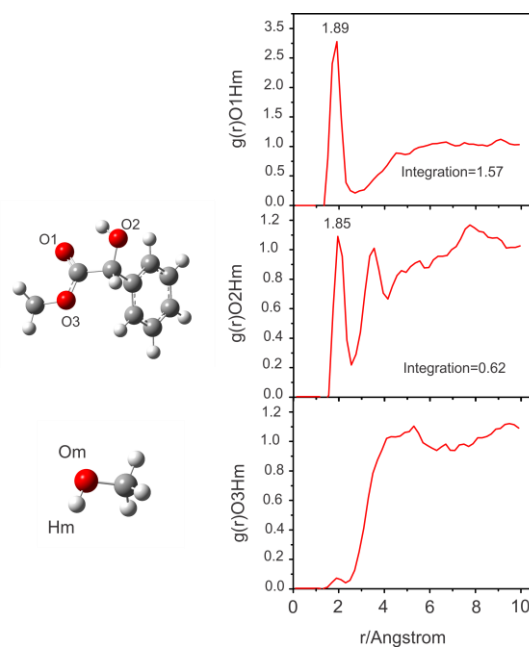


Fig. S3 RDFs obtained from the MD simulation of MM in methanol. The atom labelling for MM is given at the left. Om and Hm are the oxygen and hydrogen atoms of methanol, respectively.

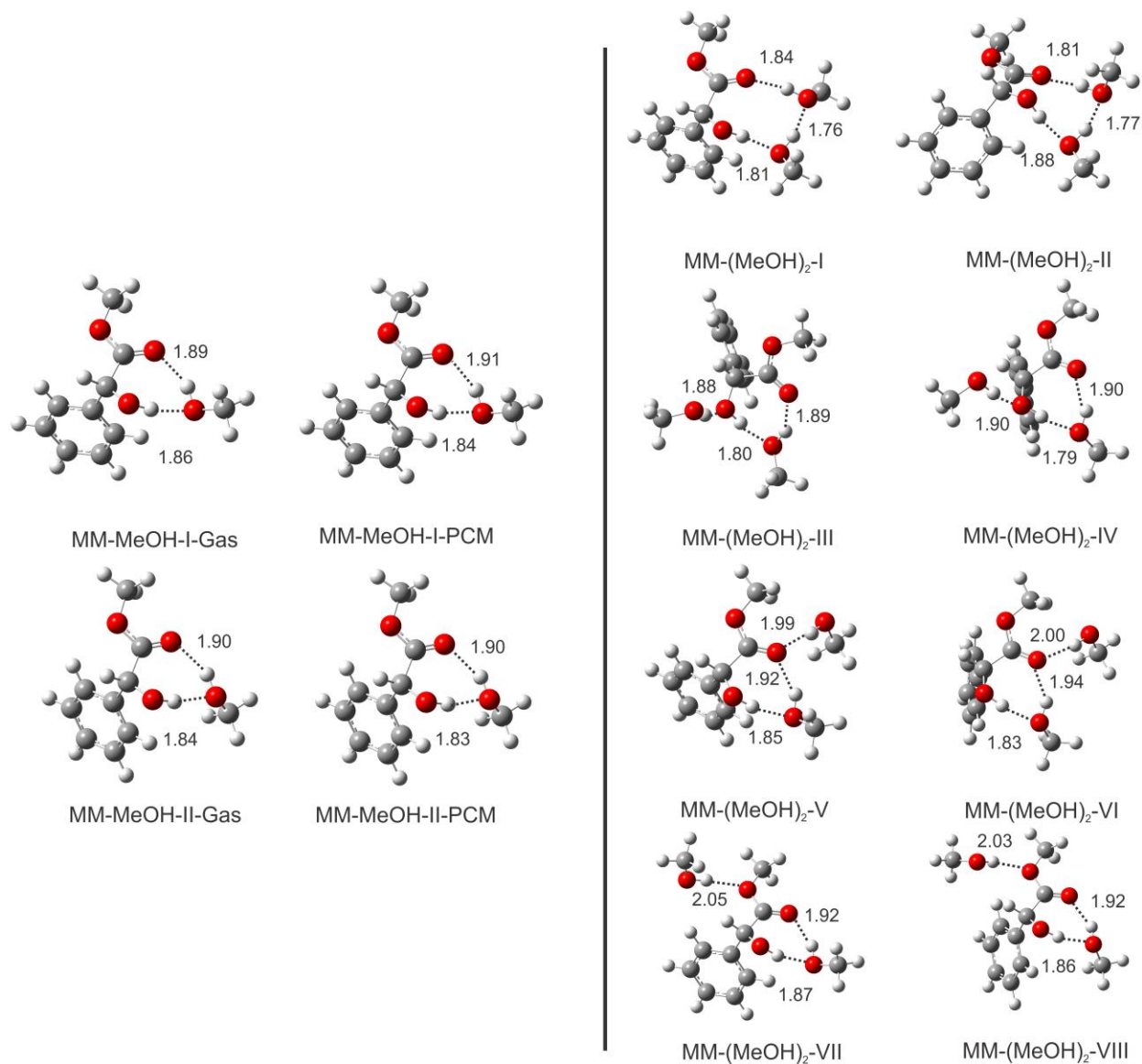


Fig. S4 Optimized geometries of the two lowest energy conformers of MM-MeOH in the gas phase and with the PCM model using methanol as solvent and eight lowest energy conformers of MM-(MeOH)₂ at the B3LYP/cc-pVTZ level in the gas phase. The intermolecular hydrogen-bond lengths (in Å) are indicated.

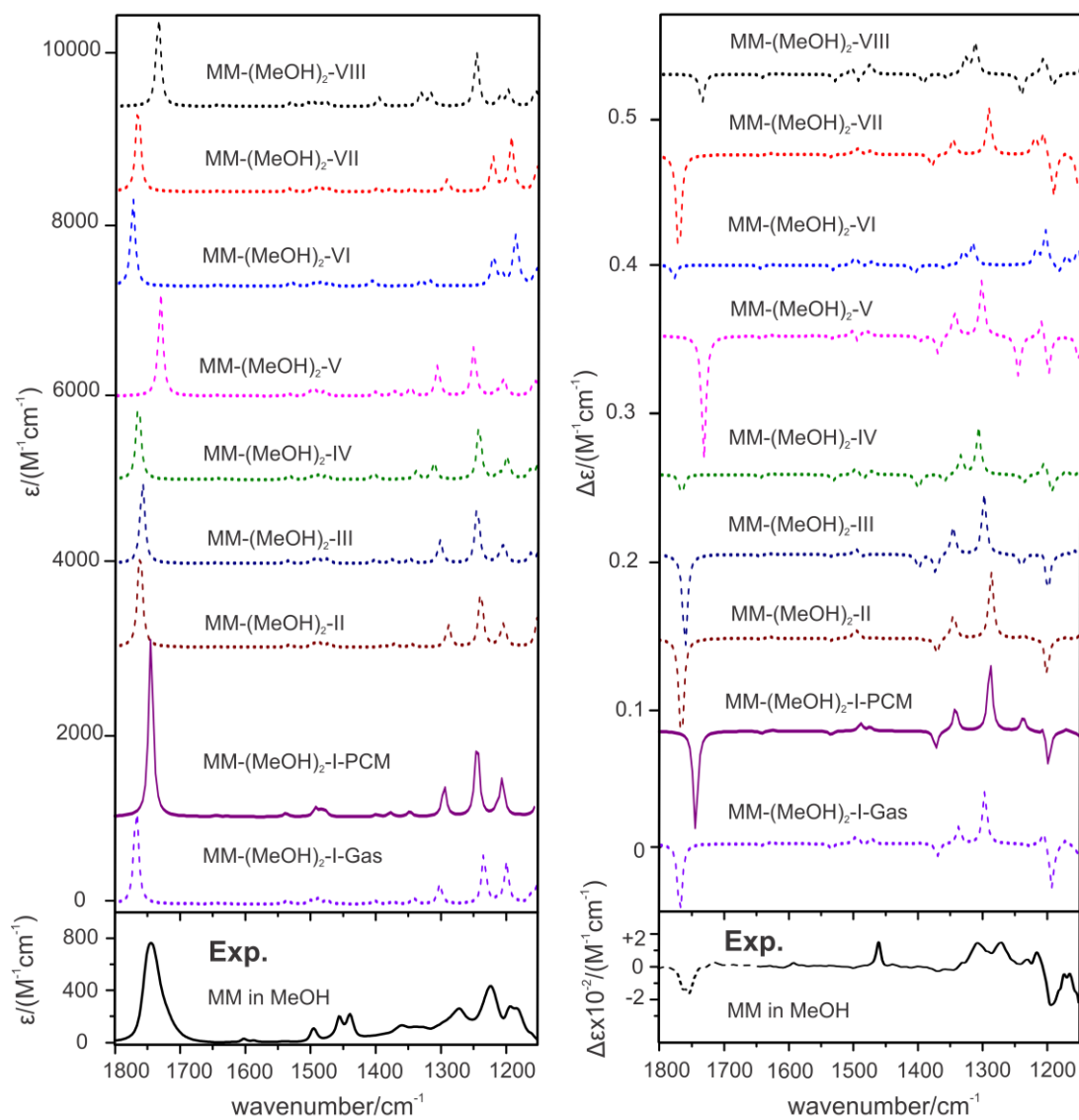


Fig. S5 The experimental VA and VCD spectra of MM in MeOH and the corresponding simulated spectra of the conformers of the MM-(MeOH)₂ complex in the gas phase calculated at the B3LYP/cc-pVTZ level. The VA and VCD spectra of MM-(MeOH)₂-I with the PCM model using methanol as solvent are also included.

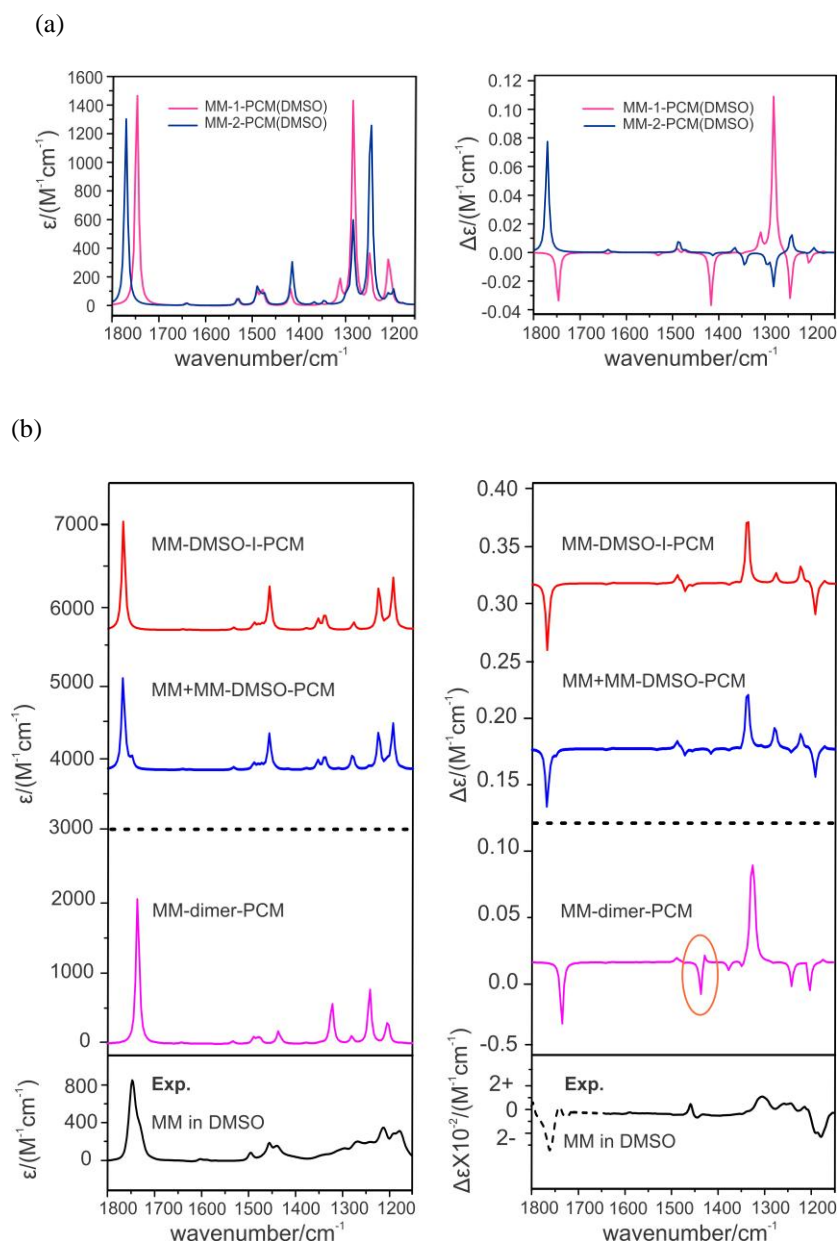


Fig. S6 (a) Comparison of the VA and VCD spectra of the two most stable conformers of MM with the PCM model using DMSO as solvent at the B3LYP/cc-pVTZ level. Please note that MM2, the higher energy conformer, shows a blue-shifted C=O stretch band compared to that of MM1. (b) Comparison of the VA and VCD spectra of the MM dimer with the PCM model using DMSO as solvent at the B3LYP/cc-pVTZ level with the experimental data, as well as some related simulated spectra already presented in Figure 6. The region which shows a clear discrepancy to the experiment is highlighted with an oval. Furthermore, the VCD signatures in the 1150-1380 cm^{-1} region are also quite different from the experiment.

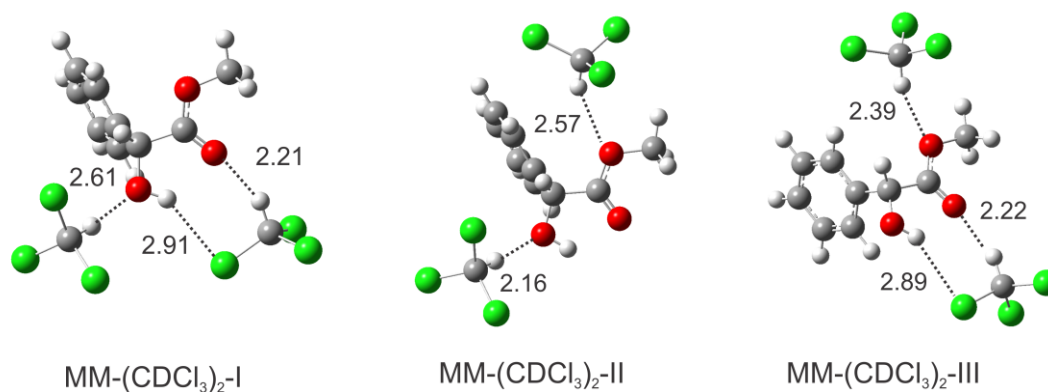


Fig. S7 Optimized geometries of the three low energy conformers of the 1:2 MM-(CDCl₃)₂ complex at the B3LYP/cc-pVTZ level in the gas phase. The intermolecular hydrogen-bond lengths are indicated.

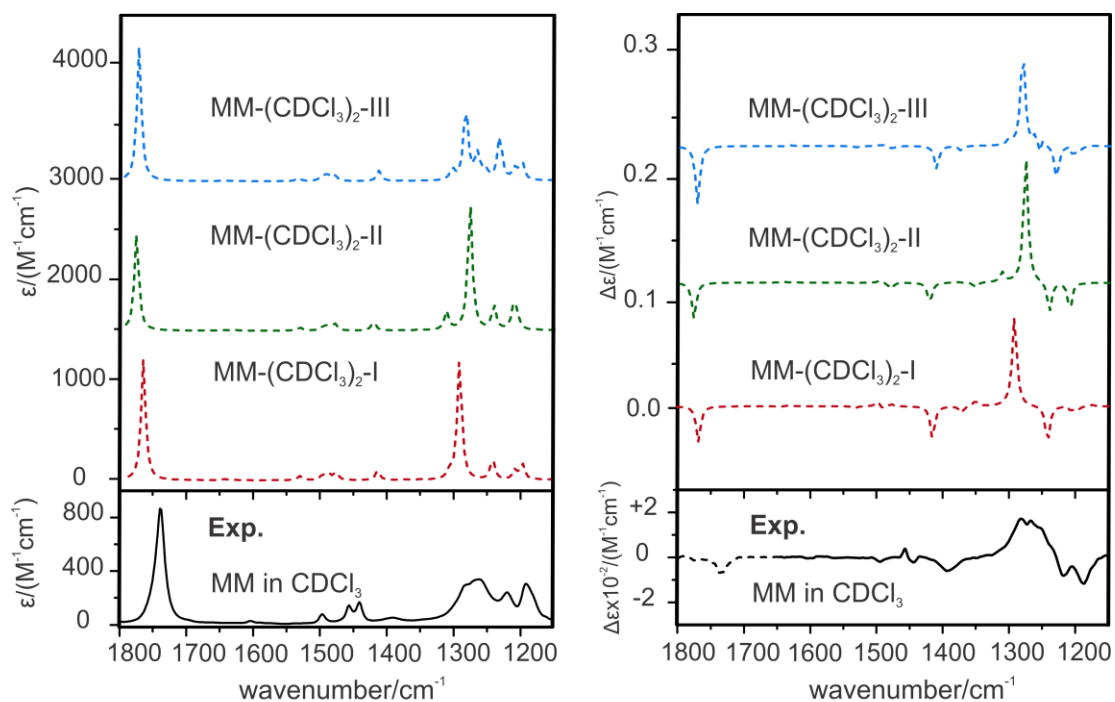


Fig. S8 Comparisons of the experimental VA/VCD spectra of MM in CDCl₃ (bottom) with three most stable conformers of MM-(CDCl₃)₂ in the gas phase (top) calculated at the B3LYP/cc-pVTZ level at room temperature.

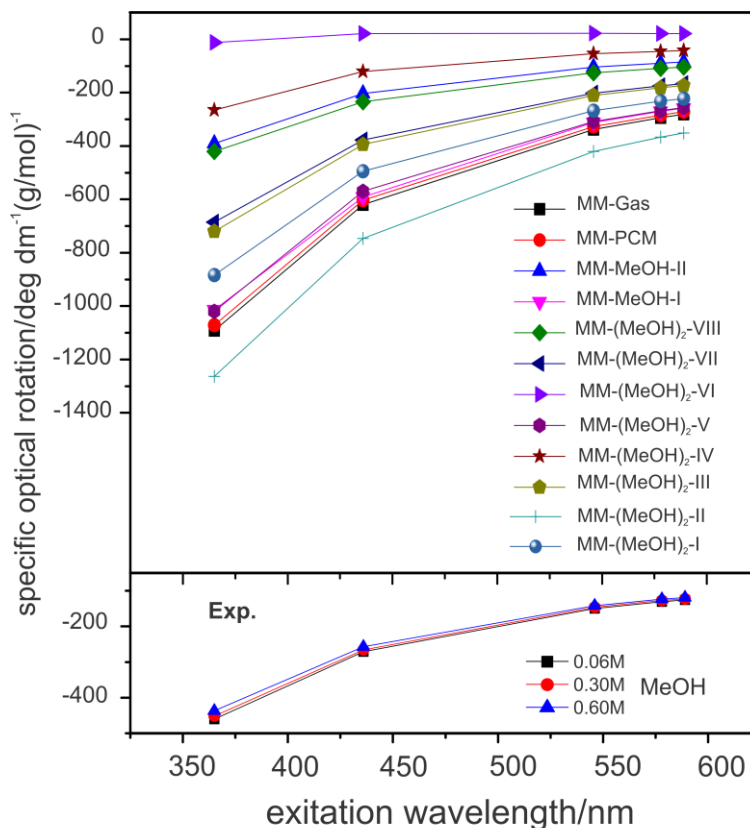


Fig. S9 Comparison of the experimental specific ORD values of MM in methanol and the calculated specific ORD values of the MM monomer and its complexes with methanol in the gas phase and with PCM. The theoretical specific ORD values calculated using Gaussian 09 are the specific ORD values for the particular species specified in the calculations. The experimental specific ORD values were obtained using the concentration of the solute, i.e. MM, alone in g/mol. To compare the calculated specific rotation values directly obtained from Gaussian 09 and plotted in the figure, it is necessary to multiply the values by the particular $\frac{(M)_{complex}}{(M)_{solute}}$ factor in each case.