Calculation of level alignments at dye-semiconductor interfaces: the role of exact exchange in density functional theory

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1 HOMO-LUMO gaps of TiO_2 cluster

2 UV-Vis spectra and structures

3 Level alignments

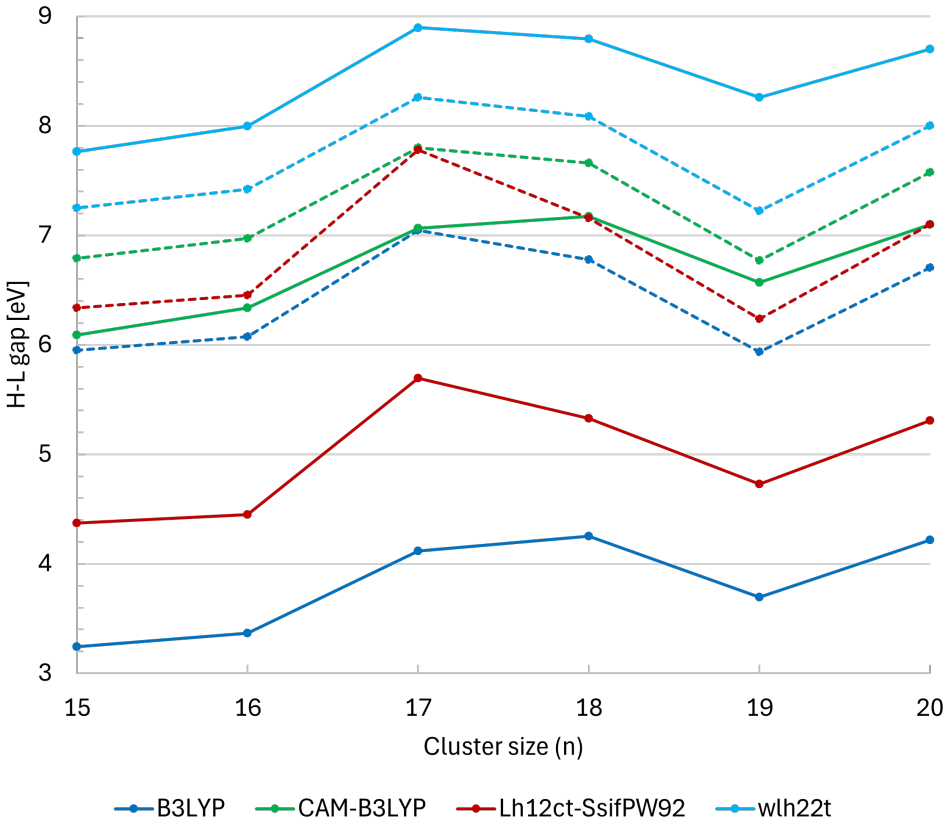

Fig. 1 HOMO-LUMO (H-L) gaps of the $(TiO_2)_n$ clusters, n=15-20, calculated with B3LYP, CAM-B3LYP, Lh12ct-SsifPW92 and ωLh22t. G_0W_0 (dashed line) calculations were started from each DFT calculation as reference.

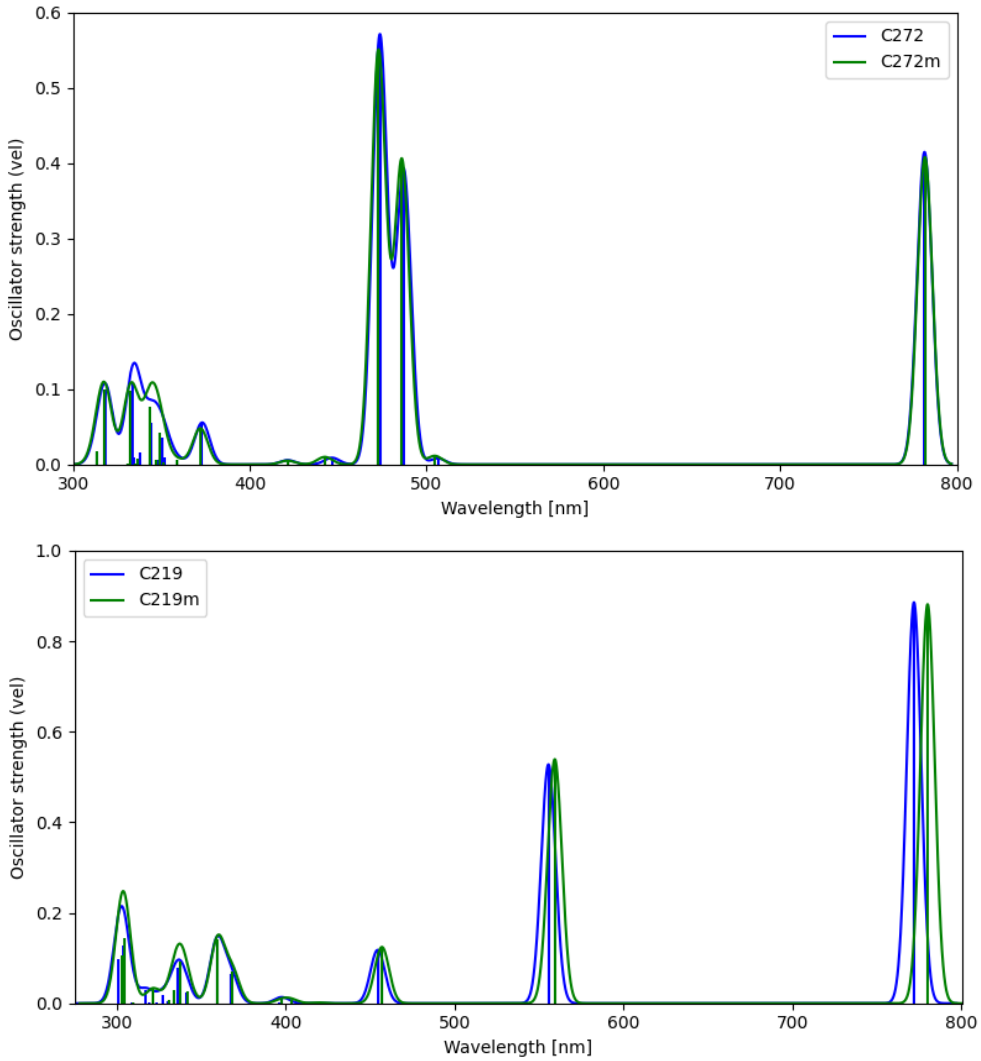

Fig. 2 UV-Vis spectra of the original dyes, C272 and C219 and their modified versions, C272m and C219m calculated with TD-B3LYP/6-31G(ACN)//B3LYP/6-31G(ACN). All spectra have been broadened with a Gaussian distribution.

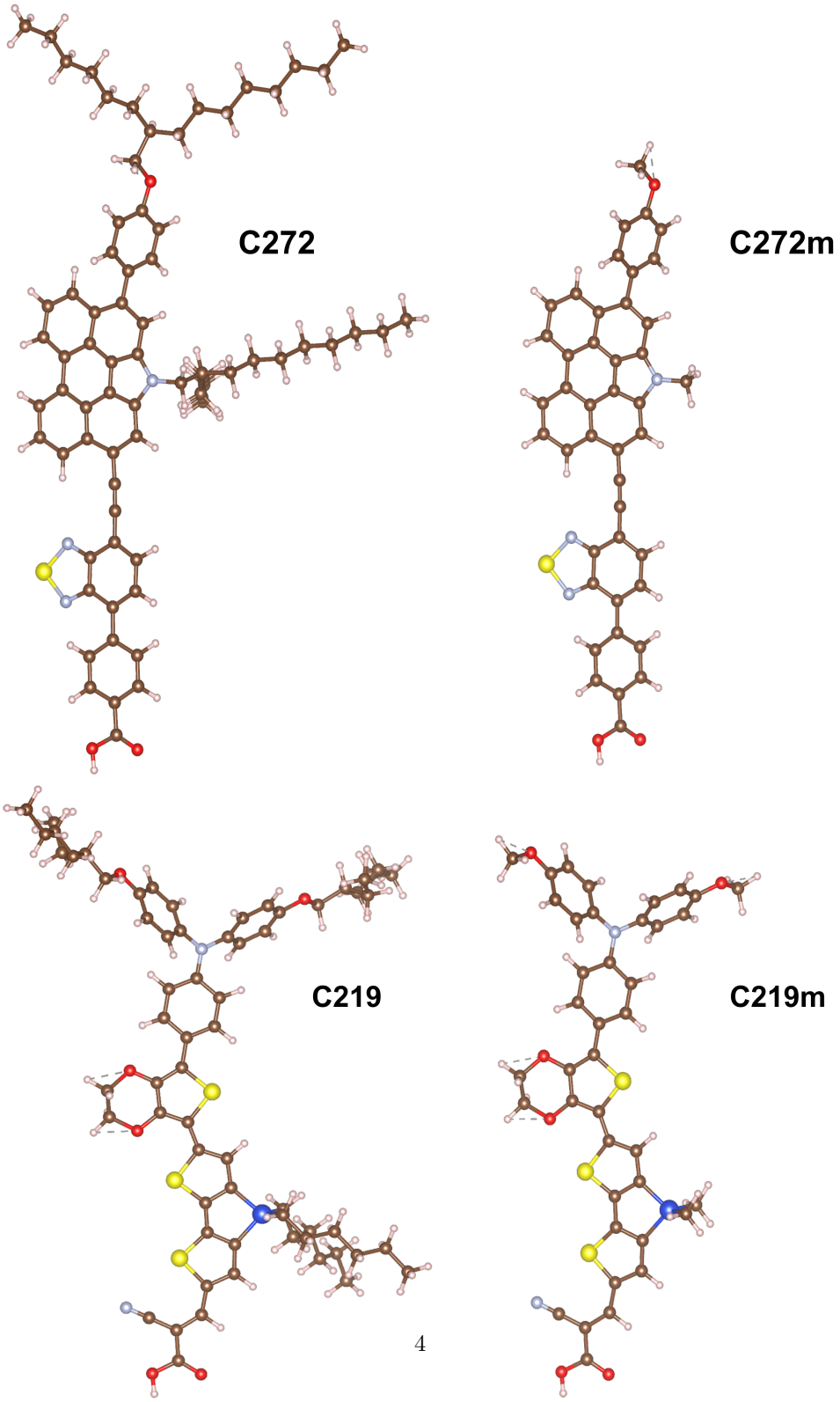

Fig. 3 Optimized molecular structures of the original dyes, C272 and C219 and their modified versions, C272m and C219m calculated with B3LYP/6-31G(ACN).

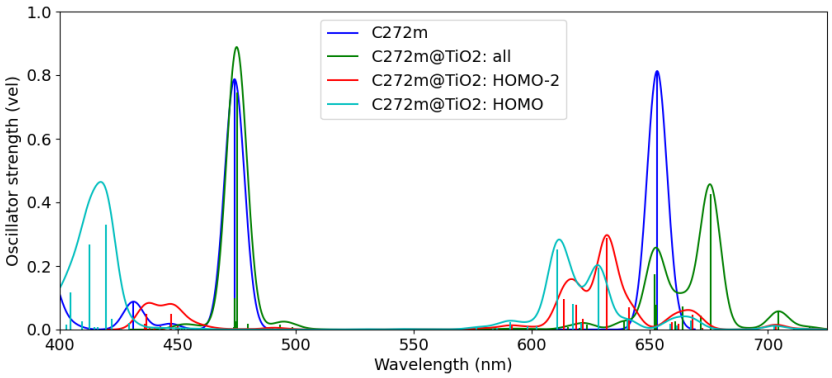

Fig. 4 UV-Vis spectra of C272m (blue) and C272m@TiO_2 calculated with TD-B3LYP/def2-SVP(ACN)//B3LYP/def2-SVP(ACN). All spectra have been broadened with a Gaussian distribution. Allowing excitations from all orbitals (all, green), allowing excitations up to HOMO-2 (HOMO-2, red) and allowing excitations only from the HOMO (HOMO, turquoise) are shown.

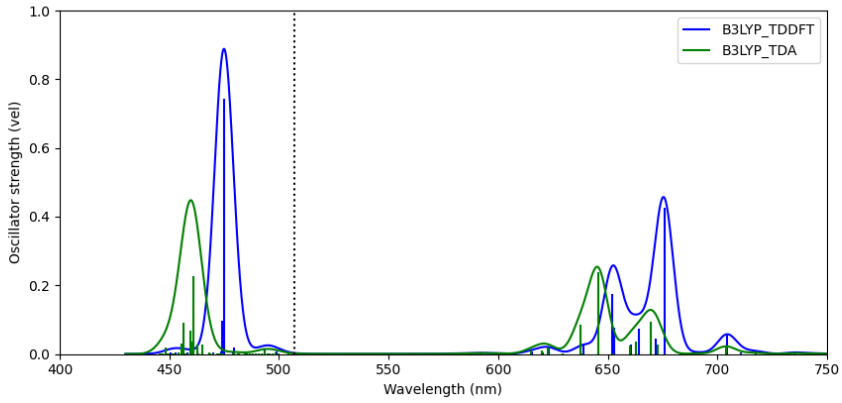

Fig. 5 UV-Vis spectra of C272m@TiO_2 obtained from TDDFT and TDA for B3LYP. Dotted line indicate the experimental absorption maximum of the dye on titania.

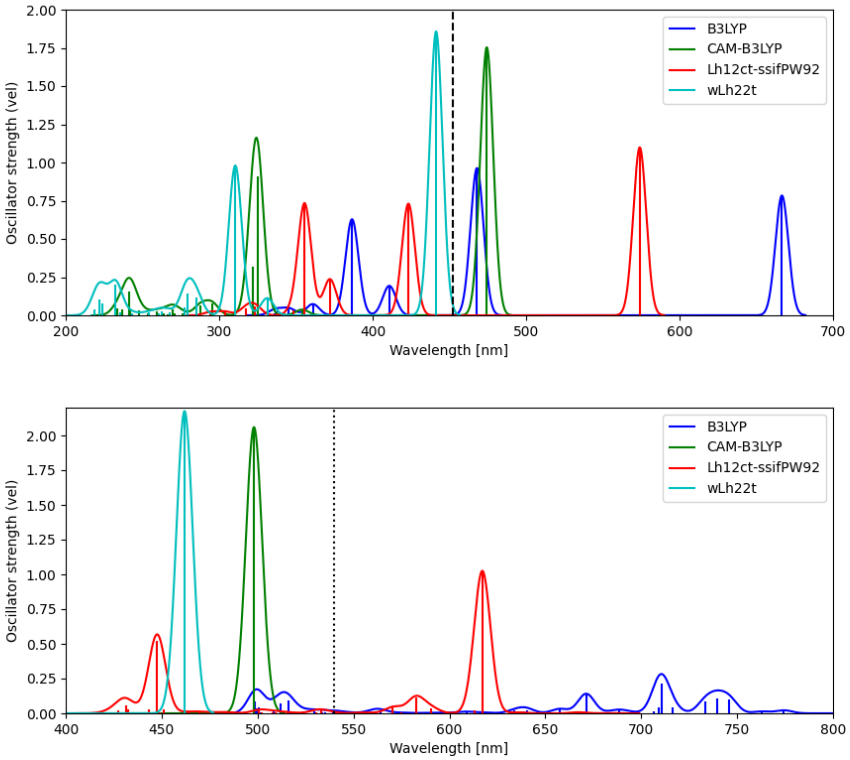

Fig. 6 UV-Vis spectra of JK2 (top) and JK2@TiO_2 (bottom) calculated with TD-B3LYP/CAM-B3LYP/Lh12ct-SsifPW92/ωLh22t/def2-SVP(H_2O)//B3LYP/def2-SVP(H_2O). Dashed and dotted lines indicate the experimental lowest absorption maximum of the free dye and the dye on titania, respectively.

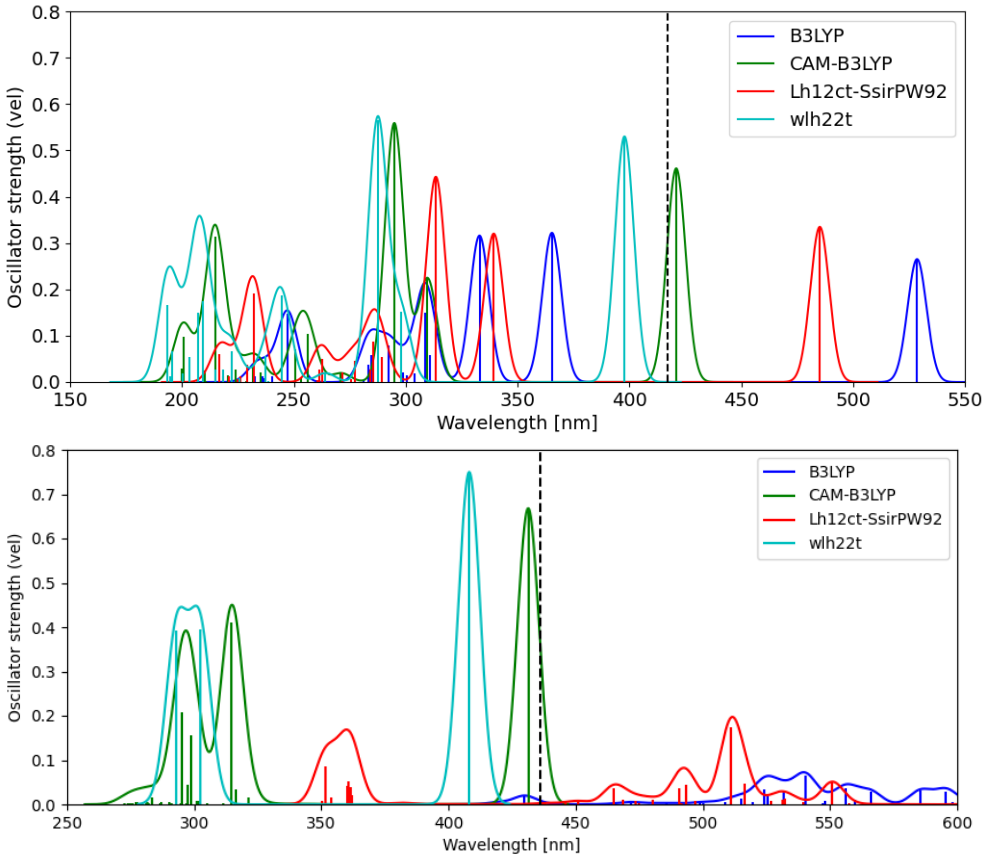

Fig. 7 UV-Vis spectra of dye4 (top) and dye4@TiO_2 (bottom) calculated with TD-B3LYP/CAM-B3LYP/Lh12ct-SsifPW92/ωLh22t/def2-SVP(ACN)//B3LYP/def2-SVP(ACN). Dashed lines indicate the experimental lowest absorption maximum of the free dye and the dye on titania, respectively.

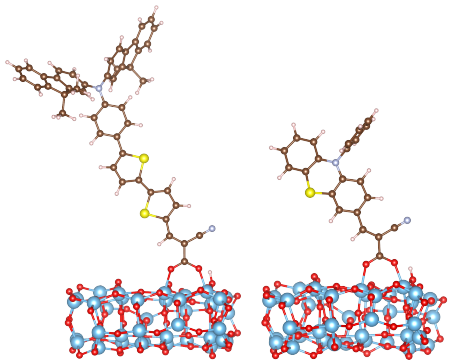

Fig. 8 B3LYP/def2-SVP optimized structures of the organic dyes JK2 (left) and dye4 (right) anchored on a $(TiO_2)_{38}$ cluster.

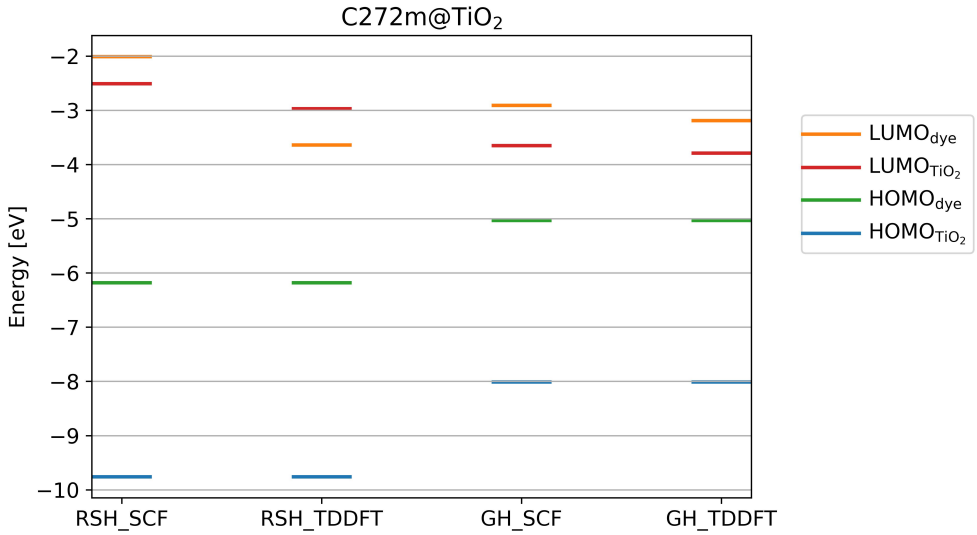

Fig. 9 HOMO and LUMO level alignments for the dye and the TiO_2 in C272m@TiO_2 in the ground state (SCF) and excited state (TDDFT) calculated with RSH CAM-B3LYP and GH B3LYP. RSH CAM-B3LYP shows reversed level alignment in the excited state.

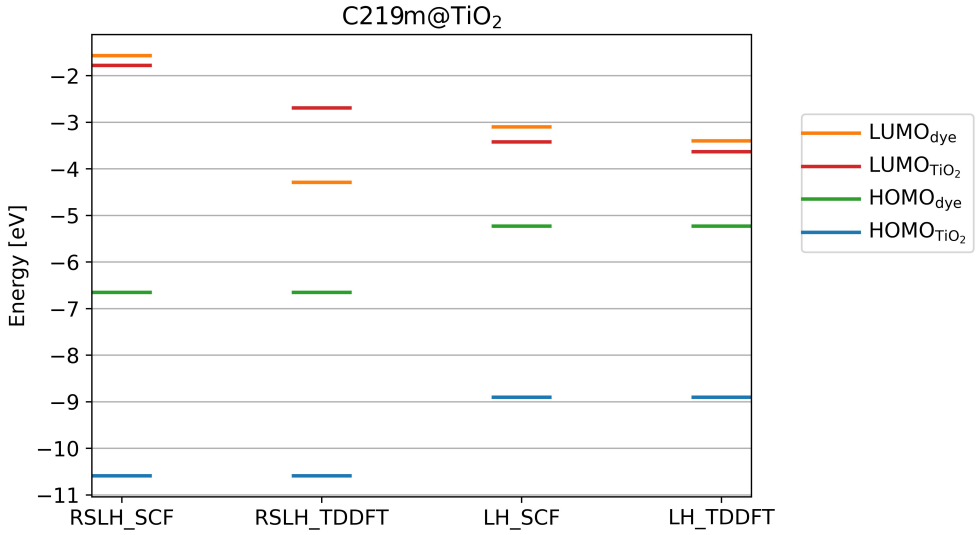

Fig. 10 HOMO and LUMO level alignments for the dye and TiO_2 in C219m@TiO_2 in the ground state (SCF) and excited state (TDDFT) calculated with RSLH ωLh22t and LH Lh12ct-SsifPW92. RSLH ωLh22t shows reversed level alignment in the excited state.

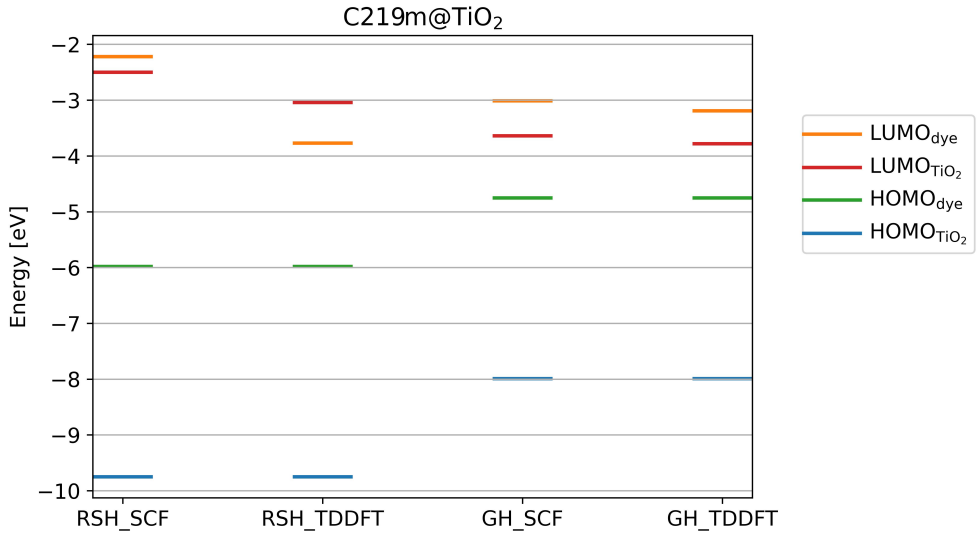

Fig. 11 HOMO and LUMO level alignments for the dye and TiO_2 in C219m@TiO_2 in the ground state (SCF) and excited state (TDDFT) calculated with RSH CAM-B3LYP and GH B3LYP. RSH CAM-B3LYP shows reversed level alignment in the excited state.