Supporting information

Interfacial charge-transfer transitions and reorganization energies in sulfur-bridged TiO_2-*x*-benzenedithiol complexes (*x*: *o*, *m*, *p*)

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The total energies calculated for geometry-optimized model compounds [$Ti_{10}O_{17}(OH)_4$-*x*-BDT] and [$Ti_{10}O_{17}(OH)_4$-*x*-BDO] (*x*: *o*, *m*, *p*) with the CAM-B3LYP functional and 6-31G(d,p) basis set are listed in Table S1. For the sulfur-bridged model complexes, the total energy decreases in the order of ortho > metal > para and, on the other hand, for the oxygen-bridged model complexes in the order of metal > ortho > para. This result indicates that the adsorption energies for *x*-BDT and *x*-BDO are dependent on the relative position of thiol and hydroxy groups, respectively. The dependences of the adsorption energies calculated for *x*-BDT and *x*-BDO should be further examined using a larger TiO_2 cluster.

Table S1. Total energies calculated for the geometry-optimized model compounds [$Ti_{10}O_{17}(OH)_4$-*x*-BDT] and [$Ti_{10}O_{17}(OH)_4$-*x*-BDO] (*x*: *o*, *m*, *p*) with the CAM-B3LYP functional and 6-31G(d,p) basis set.

Model compound	Total energy (Hartree)
[$Ti_{10}O_{17}(OH)_4$-*o*-BDT]	-11104.86392188
[$Ti_{10}O_{17}(OH)_4$-*m*-BDT]	-11104.88923474
[$Ti_{10}O_{17}(OH)_4$-*p*-BDT]	-11104.89081337
[$Ti_{10}O_{17}(OH)_4$-*o*-BDO]	-10458.91634760
[$Ti_{10}O_{17}(OH)_4$-*m*-BDO]	-10458.90092645
[$Ti_{10}O_{17}(OH)_4$-*p*-BDO]	-10458.93003811