Electronic Supplementary Information (ESI)

Contents:

1. Theoretical Computation

First-principles density functional theory calculations were carried out to study the molecular geometry structure and absorption properties of the organic dyes/TiO\(_2\) systems. The ground-state molecular geometries were optimized with SIESTA\(^2\), using the pseudopotentials of the Troullier-Martins\(^3\) type to model the atomic cores, the Perdew-Burke-Ernzerhof (PBE)\(^4\) exchange-correlation functional, and a local basis set of double-\(\zeta\)-polarized (DZP) orbitals. An auxiliary real space grid equivalent to a plane wave cutoff of 150 Ry and point k-sampling was used. Geometries were optimized until forces on non-fixed atoms are below 0.01 eV/Å, which were considered fully relaxed. The stoichiometric TiO\(_2\) anatase (101) surface, was modeled with a periodically repeated slab. A large simulation cell, 10.24 \(\times\) 15.14 \(\times\) 40.00 Å\(^3\), containing a 96-atom surface with six atomic layers of TiO\(_2\) and organic molecules was adopted. The slab was separated from its periodic images along the surface normal by a vacuum region of \(\sim\)15 Å. The energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of molecules were calculated using B3LYP functional and 6-311++G(d,p) basis set as implemented in Gaussian 09 program. Optical absorption spectra were also calculated based on linear response TDDFT using the CAM-B3LYP functional and 6-31G(d) basis set. Optical absorption spectra were calculated based on linear response TDDFT using the B3LYP (for INPBA, INPDT, and INPOD) and CAM-B3LYP functional (INPA and INCA) and 6-31G(d) basis set, as implemented in Gaussian 09 program. The Polarizable Continuum Model\(^1\) was used to account for the solvation effect (in CH\(_2\)Cl\(_2\)).
Scheme S1 Synthetic route of three dyes.

Fig. S1 Absorption of three dyes adsorbed on TiO$_2$ film.

Fig. S2 Cyclic voltammetry curves of dye in CH$_2$Cl$_2$ solution.
Fig. S3 Absorption of three dyes in the desorption solution.
Fig. S4 $^1$HNMR spectral of INPBA.

Fig. S5 $^1$HNMR spectral of INPDT.

Fig. S6 $^1$HNMR spectral of INPOD.
Fig. S7 $^{13}$CNMR spectral of INPBA.

Fig. S8 $^{13}$CNMR spectral of INPDT.
Fig. S9 $^{13}$CNMR spectral of INPDT.
Fig. S10 Stacking of dimers

Fig. S11 Schematic structures of dimers of INP-dyes.

References