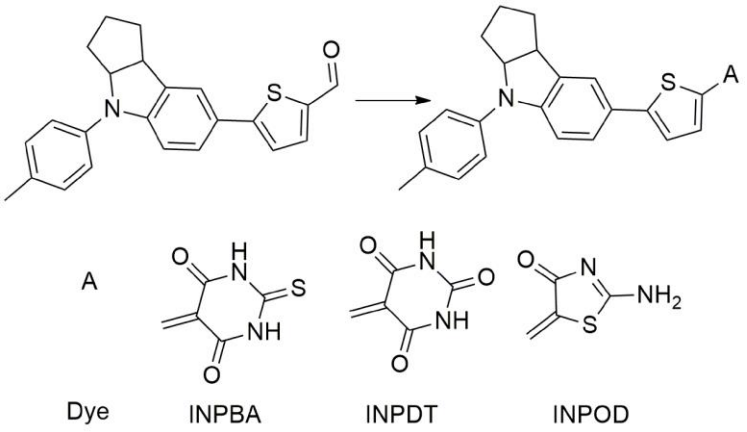
Electronic Supplementary Information (ESI)

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-ζ-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 TiO2 anatase (101) surface, was modeled with a periodically repeated slab. A large simulation cell, 10.24 × 15.14 × 40.00 Å3, containing a 96-atom surface with six atomic layers of TiO2 and organic molecules was adopted. The slab was separated from its periodic images along the surface normal by a vacuum region of ~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_2Cl_2).



Scheme S1 Synthetic route of three dyes.

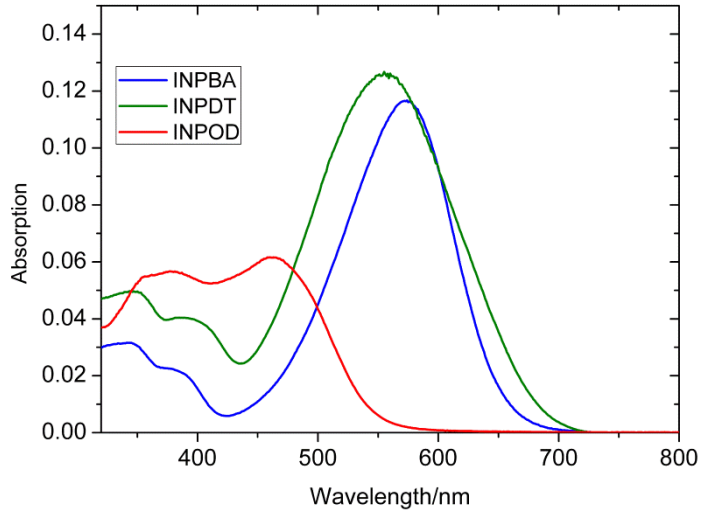


Fig. S1 Absorption of three dyes adsorbed on TiO_2 film.

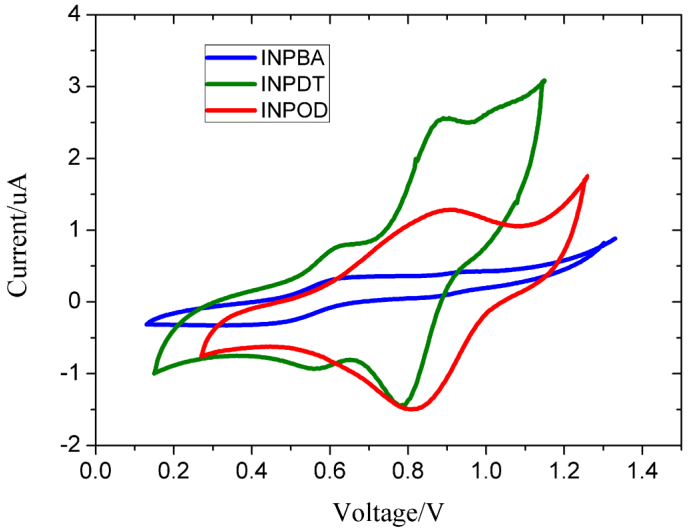


Fig. S2 Cyclic voltammetry curves of dye in CH_2Cl_2 solution.

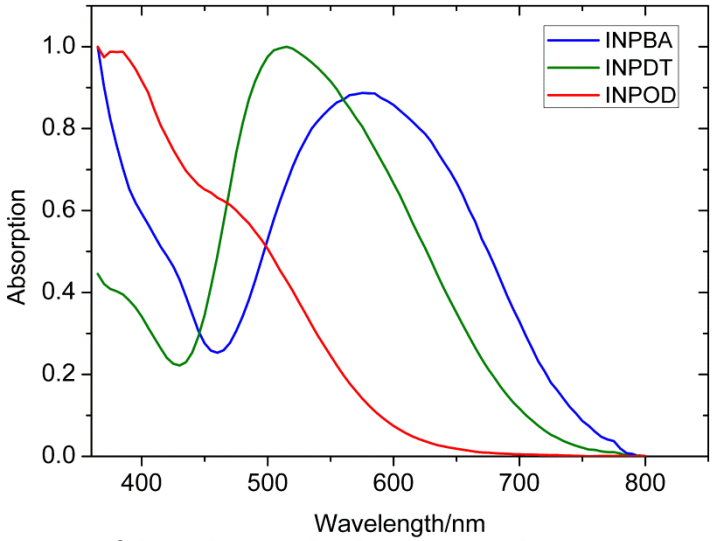


Fig. S3 Absorption of three dyes in the desorption solution.

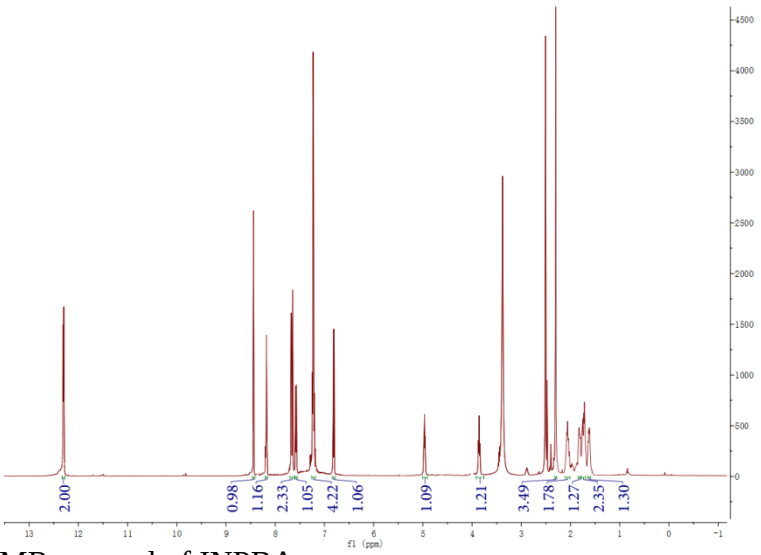


Fig. S4 [1]HNMR spectral of INPBA.

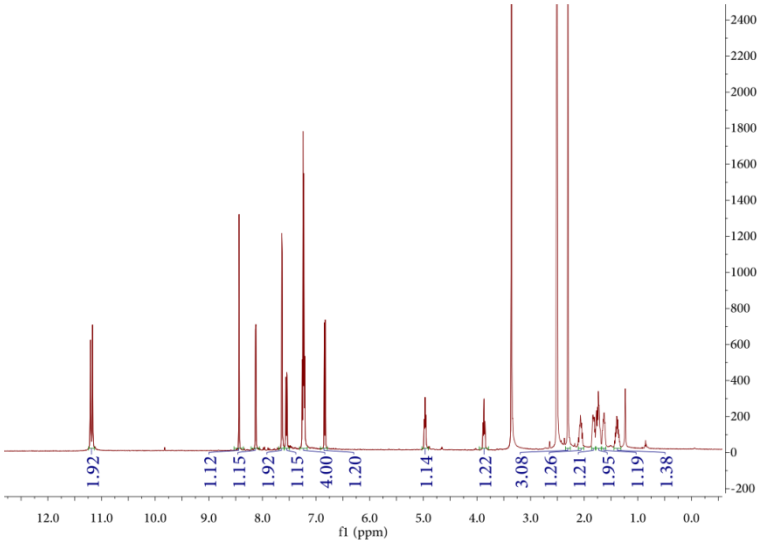


Fig. S5 [1]HNMR spectral of INPDT.

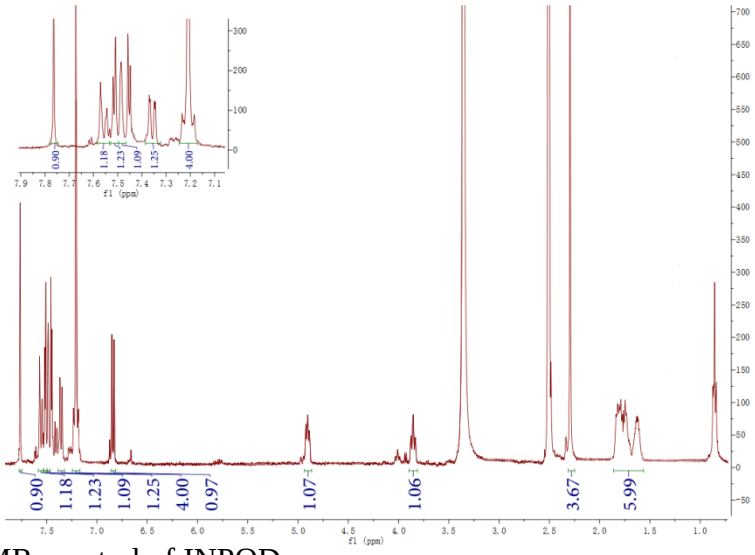


Fig. S6 [1]HNMR spectral of INPOD.

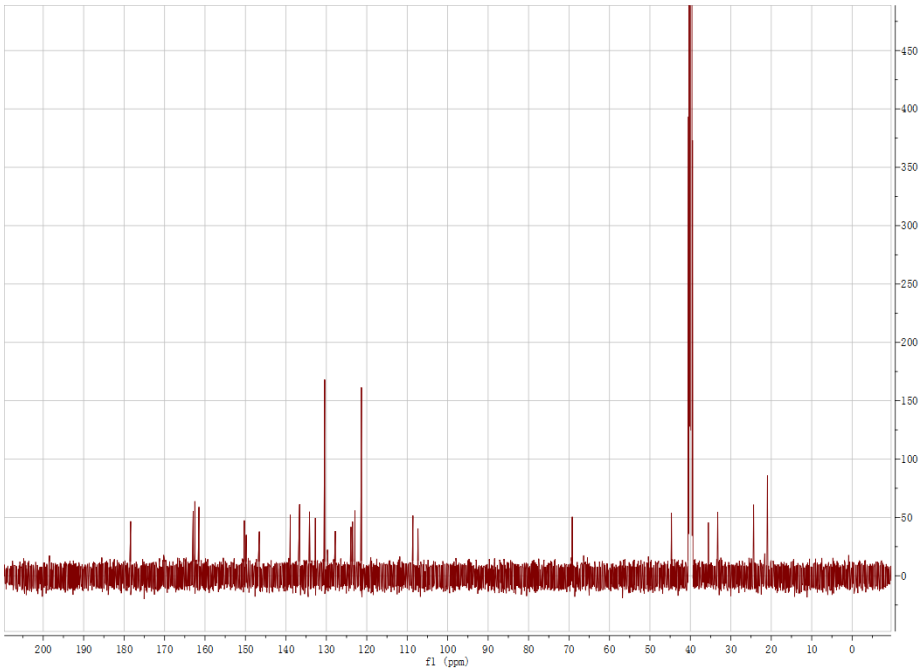


Fig. S7 ^{13}CNMR spectral of INPBA.

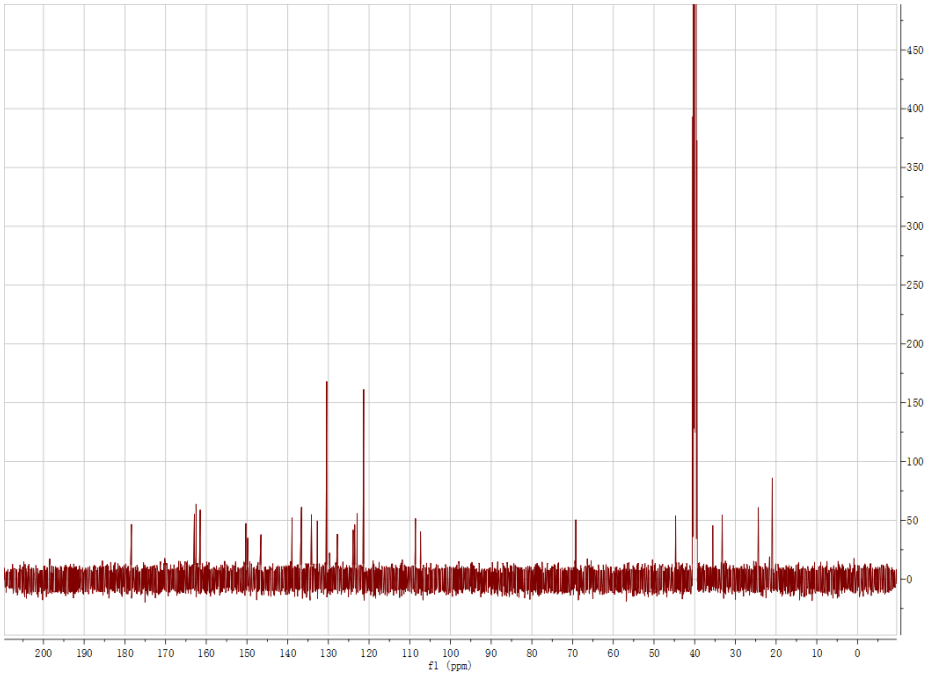


Fig. S8 ^{13}CNMR spectral of INPDT.

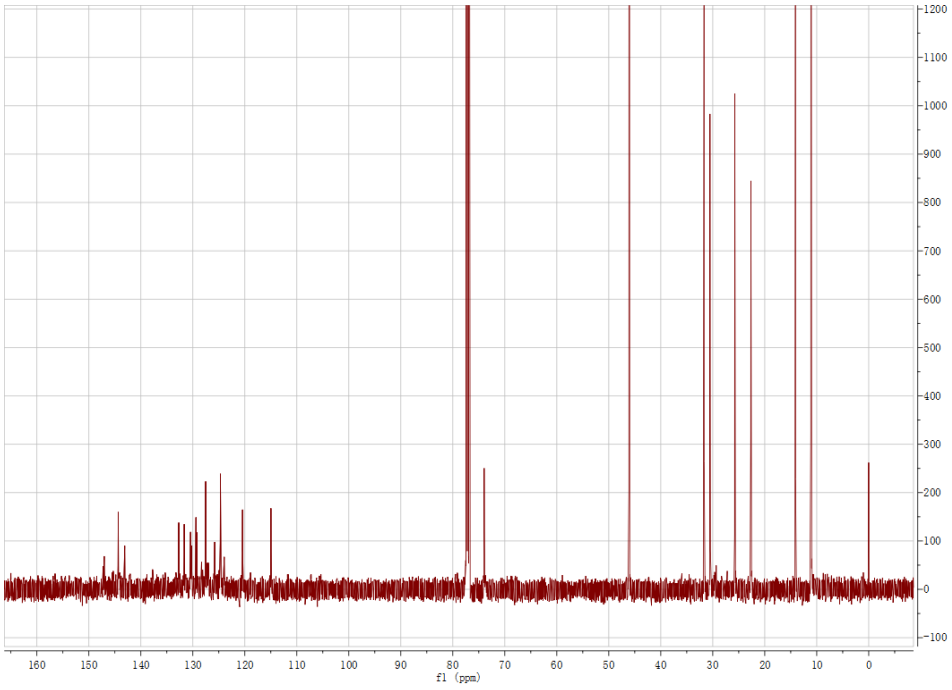


Fig. S9 ^{13}CNMR spectral of INPDT.

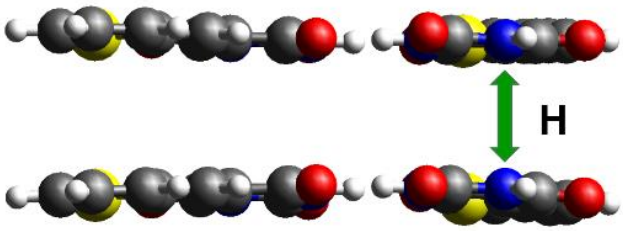


Fig. S10 Stacking of dimers

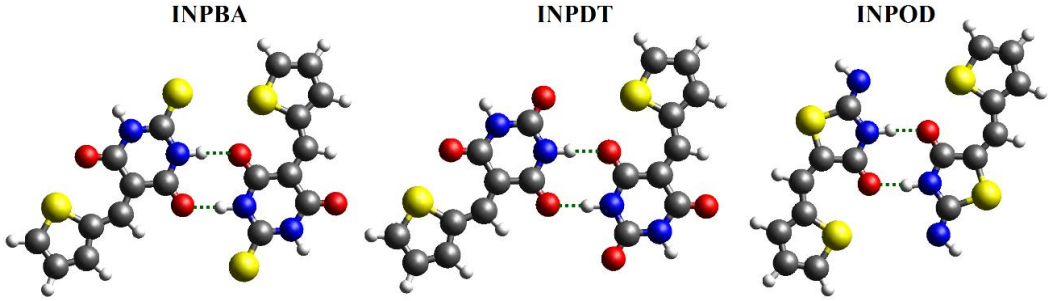


Fig. S11 Schematic structures of dimers of INP-dyes.

References

1. M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.*, 2003, **24**, 669.

2. J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejon and D. Sanchez-Portal, *J. Phys.: Condens. Matter*, 2002, **14**, 2745.

3. N. Troullier and J. L. Martins, *Phys. Rev. B*, 1991, **43**, 1993.

4. E. Artacho, E. Angalada, O. Dieguez, J. D. Gale, J. Junquera, R. M. Martin, P. Ordejon, J. M. Pruneda, D. Sanchez-Portal and J. M. Soler, *J. Phys.: Condens. Matter*. 2008, **20**, 064208.