Supporting Information for “Inverse Design and Synthesis of Acac-Coumarin Anchors for Robust TiO$_2$ Sensitization”

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1. TB-LCAP optimization results.

The TB-LCAP search results for maximum $f_{HL}$P($\lambda_{HL}$) are performed as described in Sec. 2. All optimized structures are available upon request.

2. Density of states analysis.

![DOS](image)

**Figure S1.** Density of states (DOS) for the periodic structures of TiO$_2$ anatase (a), phenyl-acac-TiO$_2$ (b), and 3-acac-pyran-2-one-TiO$_2$ (c), calculated at the extended Hückel level. The filled black lines in (b)-(c) are the projected DOS of the dye chromophores. The blue arrows point to the electronic states with a predominant contribution of HOMO, and the red arrows point to the electronic states with a predominant contribution of LUMO. Here, the DOS of (a)-(c) sampled at γ-point of the periodic systems are consistent with that of (a)-(c) in Figure 9 (of the paper) calculated based on the finite-sized nanostructures.


Note that, due to the size limit of 4-acac-coumarin, the calculated oscillator strength for 4-coumarin-acac adsorbed on [Ti$_2$O$_2$(OH)$_2$(H$_2$O)$_4$]$^{2+}$ is about 0.02, while the C343 dye molecule adsorbed on [Ti$_2$O$_2$(OH)$_2$(H$_2$O)$_4$]$^{2+}$ shows visible oscillator strengths at the scale of 0.8 (see section 4 of SI). To achieve large visible oscillator strength (or intense absorption) in practice, we suggested synthesizing 3-acac-pyran-2-one derivatives (or coumarin-acac derivatives) with expanded π-conjugation or
added donor/acceptor groups. For example, by expanding the π-conjugation of 3-acac-pyran-2-one with 3 –CH$_2$=CH$_2$- units (see the structure in Figure S2a), we can obtain the visible oscillator strength of 0.80 (Figure S2b-c), making it a comparable dye to C343. This large oscillator strength is generated by the HOMO to LUMO+4 transition (Figure S2c) where both molecular orbitals are delocalized on the π-conjugate including the alkene groups and pyran-2-one ring. As a comparison (see section 5 in SI), extending phenyl-acac using 3 –CH$_2$=CH$_2$- units shows much weaker absorption bands in the visible light region. Hence, we suggest using 3-acac-pyran-2-one as a lead chromophore.

**Figure S2.** Structure of 3-acac-pyran-2-one adsorbed a [Ti$_2$O$_2$(OH)$_2$(H$_2$O)$_4$]$^{2+}$ model (a), photo-absorption spectrum calculated by TD-DFT (b), and characteristic electronic transitions (c). In (a), a Gaussian function with fwhm = 60 nm is used to broaden of the oscillator strengths to facilitate the visualization of photo-absorption spectrum. Here, $\lambda$ denotes the transition wavelength, and $f$ denotes the oscillator strength.

**Electron injection for the extended 3-acac-pyran-2-one with 3 –CH$_2$=CH$_2$- units.** As shown in Figure S3, the electron can be injected from the LUMO+4 (DFT) or LUMO (DFT) of the expanded 3-acac-pyran-2-one with 3 –CH$_2$=CH$_2$- units to the TiO$_2$ surface.
Figure S3. Interfacial electron injection from the LUMO (DFT) and LUMO+4 (DFT) of the expanded 3-acac-pyran-2-one with 3 –CH$_2$=CH$_2$- units to the TiO$_2$ anatase supercell, simulated by the quantum dynamics in the extended Hückel theory. The electron survival probabilities on the 4-acac-coumarin LUMO and LUMO+4 decay at a time of 10 fs and 15 fs respectively (a), and the snapshots are shown for the electronic charge distribution, at t = 0 fs for the LUMO (b) and at t = 6 fs for the LUMO (c), at t = 0 fs for the LUMO+4 (d), and at t = 6 fs for the LUMO+4 (e).
4. TD-DFT absorption spectrum for C343 coumarin dye adsorbed on TiO$_2$

![Figure S4](image)

**Figure S4.** Structure of C343 coumarin dye adsorbed a [Ti$_2$O$_2$(OH)$_2$(H$_2$O)$_4$]$^{2+}$ model (a), photo-absorption spectrum calculated by TD-DFT (b), where a Gaussian function with fwhm = 60 nm is used to broaden the oscillator strengths to facilitate the visualization of photo-absorption spectrum. Here, f denotes the oscillator strength.

5. TD-DFT absorption spectrum for extended phenyl-acac adsorbed on TiO$_2$

![Figure S5](image)

**Figure S5.** Structure of the extended phenyl-acac with 3 –CH$_2$=CH$_2$- units adsorbed a [Ti$_2$O$_2$(OH)$_2$(H$_2$O)$_4$]$^{2+}$ model (a), photo-absorption spectrum calculated by TD-DFT (b), where a Gaussian function with fwhm = 60 nm is used to broaden of the oscillator strengths to facilitate the visualization of photo-absorption spectrum.

6. Comparison of absorption spectra calculations between the TD-DFT and the extended Hückel methods

Without specifically optimizing the extended Hückel parameters for photo-absorption spectrum calculations, we show here that the extended Hückel photo-absorption calculation is consistent with the TD-DFT photo-absorption calculations, especially in terms of the nature of the electronic transitions, making it plausible to be used in the TB-LCAP optimization algorithm. Here, we compute the extended Hückel photo-absorption spectrum for 4-acac-coumarin using the same optimized geometry for the TD-DFT calculation. Figure S6a shows the extended Hückel photo-absorption spectra of 4-acac-coumarin, together with the characteristic electronic transitions.
shown in Figure S6c. Compared to the TD-DFT photo-absorption spectrum (Figure 9a in the paper), the extended Hückel spectrum red-shifts for about 100 nm. However, the electronic nature of the HOMO-LUMO transition (that generates the strongest visible oscillator strength) is consistent with that by the TD-DFT calculation. For 3-acac-coumarine adsorbed on a TiO$_2$ slab, the extended Hückel photo-absorption spectrum is shown in Figure S6b, with the characteristic electronic transitions shown in Figure S6d. Compared to the TD-DFT spectrum (Figure 10a in the paper), the extended Hückel spectrum red-shifts for about 60 nm. The electronic nature of the HOMO-LUMO transition calculated by extended Hückel using the TiO$_2$ slab is consistent with that calculated by the TD-DFT method using the [Ti$_2$O$_2$(OH)$_2$(H$_2$O)$_4$]$^{2+}$ model. By comparing Figure S6 a and b, the spectrum is blue-shifted as 4-acac-coumarin is attached to TiO$_2$. This trend is consistent with the blue-shift shown by the TD-DFT calculation by comparing Figures 11a and 12a in the paper.

![Figure S6](image_url)

**Figure S6.** Extended Hückel photo-absorption spectra for 4-acac-coumarin in gas phase (a) and adsorbed on a TiO$_2$ slab (b). The characteristic electronic transitions of (a) is shown in (c), and the characteristic electronic transitions of (b) in shown in (d). In (a) and (b), a Gaussian function with fwhm = 60 nm is used to broaden of the oscillator strengths to facilitate the visualization of photo-absorption spectrum. Here, $\lambda$ denotes the transition wavelength, and $f$ denotes the oscillator strength.
7. Absorption spectrum of phenyl-acac

Figure S7. Photo-absorption spectrum for phenyl-acac anion in methanol solution calculated by TD-DFT with the polarizable continuum solvent model.

Figure S8. Photo-absorption spectrum measured experimentally for phenyl-acac anion (formed by deprotonation of 1 using one equivalent of tetrabutylammonium hydroxide) in 2.0×10⁻³ M methanol solution.
8. Surface contour of TB-LCAP

Figure S9. Surface contour of $f_{HL}(\lambda_{HL})$ that is formed by varying C=S to C=O at sites 1 and 2, and by varying O-X to N-X at sites 3 and 4.