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# Electron transfer from a new chalcone dye to TiO<sub>2</sub> nanoparticles: Synthesis, photophysics, and excited-state dynamics



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# ABSTRACT

Efficient electron injection from photosensitizers to semiconductor nanoparticles is essential in many applications such as solar energy harvesting and catalytic reactions. Herein, we present a promising photosensitizer, 4-dimethylamino-2'-hydroxy-4'-carboxychalcone (DHC-COOH), that upon adsorption on TiO<sub>2</sub> nanoparticles shows enhanced electron transfer from its excited state to the conduction band (CB) of TiO<sub>2</sub> via an intramolecular charge transfer (ICT). In order to fully characterize the current system, three more derivatives were synthesized and characterized, its analogue without the COOH group (DHC), and the molecules without the OH group (DC and DC-COOH). The presence of OH causes a red shift in the absorption and fluorescence spectra, whereas the COOH group induces more red shift due to efficient ICT which is also seen in the density functional theory calculations. Excited-state intramolecular proton transfer is evident in the crystalline/solid form of DHC and DHC-COOH as a large red shift in the fluorescence peak. The red shift was not observed when DHC-COOH was adsorbed on the TiO<sub>2</sub> surface due to the involvement of the OH group in binding. This was confirmed by XPS, in addition to a bidentate binding of the COOH group to TiO<sub>2</sub>. The latter has a major contribution to the electron transfer mechanism which was observed as a much weaker fluorescence intensity and a 50% reduction in the lifetime component that involves the COOH dynamic (from 63 ps to 32 ps). On the other hand, electron-hole recombination dynamics were slowed down on the  $TiO_2$  surface (from 311 ps to 440 ps and 1.4 ns to 2.4 ns). From cyclic voltammetry and steady state spectra, it was found that electron injection from the excited state of the dye to the CB of TiO<sub>2</sub> is energetically favorable, and regeneration of the oxidized dye by the  $I^{-}/I_{3}^{-}$  redox pair (used in dye-sensitized solar cells) is also possible.

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# 1. Introduction

The generation of electrical energy by harvesting sun radiation requires photosensitizers that are efficient in absorbing sunlight and injecting the excited electrons to the photoanode [1]. Photosensitizers that are derivatives of naturally occurring organic dyes are particularly promising due to their ease of synthesis and structural modification [2,3]. Molecules that possess an intramolecular charge transfer (ICT) mechanism are highly desirable in solar cells due to their ability to accumulate electrons close to the photoanode, thus enhancing the electron injection mechanism [3,4].

Chalcone molecules contain an enone group and are naturally occurring compounds that have many applications in medicinal chemistry [5-10]. Inducing a molecular charge transfer mecha-

nism was achieved by attaching a dimethyl amino group, as shown in Fig. 1, at the 4-position. The N(CH<sub>3</sub>)<sub>2</sub> electron-donating group has broadly been used as a substituent that leads to enhancing the fluorescence response in chalcone-related compounds [11]. When an OH group was attached to the phenyl ring  $(R_1 = OH,$  $R_2 = H$ ), intense fluorescence was observed in the crystalline state with a large quantum yield of fluorescence ( $\phi_{\rm F}=0.32$ ) [12]. This chalcone derivative, 4-dimethylamino- 2'-hydroxychalcone (DHC), was shown to produce red amplified spontaneous emission with  $\lambda_{max} = 650-710$  nm that is dependent on the crystal size and packing configuration. Recently, we measured the femtosecond dynamics of DHC and found that an efficient excited-state intramolecular proton transfer (ESIPT) process is responsible for the large red shift and quantum yield of fluorescence in the crystalline form where the molecules form J-aggregates [13]. In solution, a twisting motion around the hydroxyphenyl ring prevents ESIPT and relaxes the excited molecule to the ground state via a conical intersection [13,14]. Different chalcone derivatives have been utilized

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Fig. 1. Structures of the studied chalcone molecules.

as photosensitizers in fabricated dye-sensitized solar cells (DSSCs) where the overall efficiency was found to be the highest when an OH group or a strong Lewis acid such as boron difluoride was attached to the phenyl ring (solar-to-electrical efficiency 0.05% and 1.13%, respectively) [15–16].

For efficient electron injection from the dye to the semiconductor, the dye should be attached to the photoanode semiconductor by an anchoring group. In the current work, we attached a carboxylic group to DHC in the m-position to the OH group (see Fig. 1) and the molecule was anchored to the TiO<sub>2</sub> nanoparticles. TiO<sub>2</sub> is considered as a benchmark photocatalyst owing to its large surface area, porous structure, and pore volume. These properties result in increasing the surface reactive sites and improving mass transport which lead to extending its photoresponse function [17–21]. A carboxylic group is known to efficiently anchor the dye molecule to the TiO<sub>2</sub> semiconductor surface, thus enhancing the charge transfer [22]. In order to understand the mechanism of binding and the excited state spectroscopy of the new compound (DHC-COOH), we synthesized the corresponding molecules without OH (DC and DC-COOH, refer to Fig. 1 for the structures). We utilized steady-state and time-resolved (femtosecondnanosecond) absorption and fluorescence techniques to characterize the four compounds in solution, in the solid/crystalline state, and anchored on TiO<sub>2</sub>. We used density functional theory (DFT) and time-dependent-DFT (TD-DFT) for structural and energetic calculations of the ground and excited states of the free dyes. Finally, we used cyclic voltammetry, along with the steady-state absorption and fluorescence results, in order to determine the energies of the ground (highest-occupied molecular orbital, HOMO) and excited (lowest-unoccupied molecular orbital, LUMO) states of DHC-COOH and DC-COOH. We aligned these states with the conduction band (CB) of the semiconductor and the redox level of the electrolyte pair  $(I^{-}/I_{3}^{-})$  and found that electron injection from LUMO to CB is energetically favourable and regeneration of the oxidized dyes is possible through the electrolyte pair.

# 2. Experimental

# 2.1. Synthesis of DC, DC-COOH and DHC-COOH

# 2.1.1. Materials and methods

The starting materials and solvents were purchased from commercial suppliers and were used as received. TLC aluminum plates were used to monitor the reaction progress, the plates were precoated with silica gel 60 F<sub>254</sub> and were purchased from Merck KGaA Company and preparative TLC plates with silica gel GF on glass (1000 microns) from Sigma-Aldrich. Synthesized compounds were visualized under UV light ( $\lambda = 254/365$  nm). <sup>1</sup>H- and <sup>13</sup>C-NMR data were recorded on Bruker Avance 500 MHz (<sup>1</sup>H) and 126 MHz (<sup>13</sup>C), respectively. Chemical shifts are reported in parts per million (ppm) relative to the deuterated solvent (DMSO-d6),  $\delta$  <sup>1</sup>H: 2.49 ppm, <sup>13</sup>C: 39.7 ppm. Coupling constants (J value) are given in Hertz and spin multiplicities are given as s (singlet), brs (broad singlet), d (doublet), t (triplet), dd (doublet of doublet) and m (multiplet). The mass spectra were acquired and recorded by HPLC-(UV)-ESI-MS using the same procedure as previously described [23]. The melting points were measured using a digital melting point apparatus (SMP10) from Gallenkamp and are uncorrected. TiO<sub>2</sub> nanoparticles (nanopowder, 21 nm primary particle size (TEM), ≥99.5% trace metals basis) were purchased from Sigma-Aldrich.

## 2.1.2. Chemistry

We have previously reported the synthesis of DHC via Claisen– Schmidt condensation reaction using NaOH as base in refluxing ethanol [13]. However, this procedure was not suitable for the preparation of the other chalcone derivatives used in the current study (DC, DC-COOH, and DHC-COOH). Therefore, we optimized the synthesis using piperidine (instead of NaOH) in refluxing ethanol as depicted in Scheme 1.

For the newly synthesized chalones (DC, DC-COOH, and DHC-COOH), an equimolar concentration (1 mmol) of 4dimethylaminobenzaldehyde and ketone (acetophenone, 4acetylbenzoic acid, or 4-acetyl-3-hydroxybenzoic acid) was dissolved in absolute ethanol (10 mL) and the resulting mixture was refluxed for 5 minutes, followed by portion-wise addition of piperidine (6-8) equivalents. The reaction mixture was monitored by TLC using ethylacetate/toluene (5%) for DC and MeOH/DCM (5%) for DC-COOH and DHC-COOH as eluent and the reactions were completed within 48-96 hours. All reactions were subjected to the following procedure; the reaction mixture was poured in a beaker charged with a small amount of ice. The round-bottomed flask was rinsed with distilled water in order to collect out most of the precipitates. The resulting mixture was neutralized by dropwise addition of diluted hydrochloric acid (0.5 M) and the product was precipitated. The precipitate was filtered off through



Scheme 1. Chemical synthesis of the chalcone compounds (DC, DC-COOH, and DHC-COOH). \*: Ref. [13].

a Büchner funnel, air dried and the final product was collected. The DC product was purified by preparative TLC (1000  $\mu$ m plate) using ethylacetate/toluene (5%) as eluent, while the other two products (DC-COOH and DHC-COOH) were washed with diethyl ether to produce the targeted chalcones in 34–61% isolated yield. Well-defined crystals of DC were obtained after five days by dissolving the solid in a small portion of warm ethanol (50°C), followed by cooling to room temperature.

# 2.1.3. Spectral data of chalcones (DC, DC-COOH & DHC-COOH)

**3-(4-Dimethylamino-phenyl)-1-phenyl-propenone (DC):** Yield 34%, orange solid, m.p. 116.4–116.6°C (Lit:117.5–119°C) [24]. <sup>1</sup>H-NMR (DMSO-d6); δ 2.99 (s, 6H, 2CH<sub>3</sub>), 6.74–6.72 (d, J = 9.0 Hz, 2H, H-3 & H-5), 7.55–7.53 (t, J = 7.0, 6.0 Hz, 2H, H-3' & H-5'), 7.62–7.59 (m, 2H, H-α & H-4), 7.69–7.66 (m, 3H, H-β, H-2 & H-6), 8.09-8.07 (d, J = 9.5 Hz, 2H, H-2' & H-6'). <sup>13</sup>C-NMR (DMSO-d6) δ 39.8 (2CH<sub>3</sub>), 111.8, 116.2, 122.1, 128.2, 128.7, 130.8, 132.5, 138.5, 145.2, 152.1, 188.8 (C=O). LC-MS (m/z): 252.2 [M + H<sup>+</sup>]. Purity by HPLC-UV (254 nm)-ESI-MS: 98.0%.

**4-[3-(4-Dimethylamino-phenyl)-acryloyl]-benzoic acid (DC-COOH):** Yield 61%, red solid, m.p. 241–244°C. <sup>1</sup>H-NMR (DMSO-d6)  $\delta$  3.00 (s, 6H, 2CH<sub>3</sub>), 6.74–6.72 (d, J = 7.5 Hz, 2H, H-3 & H-5), 7.63–7.60 (d, J = 13.0 Hz, 1H, H- $\alpha$ ), 7.71–7.69 (dd, J = 12.5, 7.0 Hz, 3H, H- $\beta$ , H-2 & H-6), 8.07–8.05 (d, J = 7.0 Hz, 2H, H-2' & H-6'), 8.17–8.16 (d, J = 7.0 Hz, 2H, H-3' & H-5'), 13.29 (brs, 1H, COOH). <sup>13</sup>C-NMR (DMSO-d6)  $\delta$  39.8 (2CH<sub>3</sub>), 111.9, 116.0, 121.9, 128.4, 129.6, 131.2, 134.0, 141.8, 146.2, 152.3, 166.9 (COOH), 188.4 (C=O). LC-MS (m/z): 296.0 [M + H<sup>+</sup>]. Purity by HPLC-UV (254 nm)-ESI-MS: 96.0%.

**4-[3-(4-Dimethylamino-phenyl)-acryloyl]-3-hydroxy-benzoic acid (DHC-COOH):** Yield 43%, red solid, m.p. 252-256°C. <sup>1</sup>H-NMR (DMSO-d6) δ 3.01 (s, 6H, 2CH<sub>3</sub>), 6.75-6.73 (d, J = 7.5 Hz, 2H, H-3 & H-5), 7.44 (s, 1H, H-3'), 7.46-7.45 (d, J = 7.0 Hz, 1H, H-5'), 7.69-7.66 (d, J = 12.5 Hz, 1H, H-α), 7.73-7.72 (d, J = 7.0 Hz, 2H, H-2 & H-6), 7.80-7.77 (d, J = 12.5 Hz, 1H, H-β), 8.22-8.21 (d, J = 6.5 Hz, 1H, H-6'), 12.75 (brs, 1H, COOH). <sup>13</sup>C-NMR (DMSO-d6) δ 39.8 (2CH<sub>3</sub>), 111.9, 115.6, 118.3, 119.3, 121.7, 124.5, 130.6, 131.6, 137.0, 147.2, 152.6, 161.1, 166.7 (COOH), 192.7 (C=O). LC-MS (m/z): 312.1 [M + H<sup>+</sup>]. Purity by HPLC-UV (254 nm)-ESI-MS: 93.5%.

#### 2.2. Preparation and characterization of the $dye+TiO_2$ composites

TiO<sub>2</sub> powder (0.5-1.0 g) was placed in a semi-membrane wick, then immersed in a vial containing 0.05 mM dye solution (dissolved in 10 mL HPLC grade acetone). The vial was capped and covered with aluminum sheet and placed in an oven overnight (37  $\pm$  2°C). The resulting particles were washed with ethanol to removed free dye particles, then filtered off and allowed to dry in air.

X-ray photoelectron spectroscopy (XPS) (Scienta Omicron, Germany) with Al-k<sub> $\alpha$ </sub> (h $\nu$  = 1486.6 eV) at working voltage of 15 kV under ~ 10-8 Pa was carried out for the surface characterization. The survey and high-resolution (individual element peaks) scans were

recorded with constant analyzer transmission energy of 50 eV and 20 eV, respectively. All of the obtained binding energies were calibrated with respect to the intrinsic carbon C 1s peak at 284.6 eV using CasaXPS software (Casa Software Ltd, UK).

# 2.3. Steady-state spectroscopic measurements

Absorption and fluorescence spectra were recorded on a Duetta spectrometer (Horiba Scientific). Fluorescence quantum yield ( $\phi_F$ ) of the compounds dissolved in methanol (MeOH, HPLC grade) was estimated relative to rhodamine 6G ( $\phi_F = 0.93$  in MeOH) [25], using a|e software (FluorTools.com) for data analysis. Absolute  $\phi_F$  for solid samples was measured using an integrating sphere (Thorlabs) and a light-emitting diode (LS450, Ocean Insight) for excitation at 450 nm. For solution measurements, the sample was contained in a 1-cm path-length quartz cell with a fixed concentration of 0.02 mM. For solid-state measurements, the sample was spread on a thin quartz sheet. All measurements were conducted at 23  $\pm$  1°C.

# 2.4. Time-resolved spectroscopic measurements

# 2.4.1. Femtosecond fluorescence-upconversion spectroscopy

The ultrafast fluorescence upconversion measurements were performed using a femtosecond laser setup that was previously described in detail [13,26]. Briefly, pump and gate pulses were obtained using a regenerative amplified Ti:Sapphire laser (Libra, Coherent). The Libra generates compressed laser pulses (70 fs pulse width) with an output power of 4.26 W at a repetition rate of 5 kHz and centered at 800 nm. The output beam was split into two parts. The major portion of the output pulse was used to pump a Coherent OPerA Solo (Light Conversion Ltd.) optical parametric amplifier to generate spectrally tunable light spanning the range 240–2600 nm and is used as the pump beam. The remaining small portion of the laser output was used as a gate pulse that is centred at 800 nm. The pump and gate pulses are sent to a Halcyone fluorescence upconversion setup (Ultrafast Systems, LLC). The gate pulse was delayed over a maximum of 5 ns in a shortest step size of 20 fs with a computer-controlled optical delay stage. The pump pulse was focused onto the sample and fluorescence was collected and focused by a parabolic mirror on a 0.5 mm BBO type II crystal. For frequency upconversion, the gate pulse was overlapped with the fluorescence signal in the BBO crystal, and focused slightly behind the crystal (10 mm). The upconversion signal was focused on the entrance slit of a double monochromator and measured by a PMT detector with a spectral range of 200-800 nm. A depolarizer (DPU-25, Thorlabs) was used in the pump beam (attenuated to  $\sim 100$  nJ) in order to remove any rotational contribution to the overall excited state decay kinetics. The instrument response function (IRF) under the current non-collinear geometry was determined to be 400-500 fs from the upconversion signal of Raman scattering from water. Surface Xplorer software (supplied by Ultrafast Systems) was used for data analysis.

#### Table 1

Spectroscopic parameters for DHC and DC dissolved in MeOH and in their crystalline state. TD-DFT calculations are shown in braces.

	λ <sub>max,Abs</sub> (nm) (MeOH)	$\varepsilon \; (\lambda_{max,Abs}) \; (M^{-1} \cdot cm^{-1}) $ (MeOH)	λ <sub>max,Abs</sub> (nm) (Crystalline)	$\lambda_{max,Fluor}^{a}$ (nm) (MeOH)	λ <sub>max,Fluor</sub> <sup>a</sup> (nm) (Crystalline)	$\phi_{ m F}$ (MeOH)	$\phi_{ m F}$ (Crystalline)
DHC	435 {472}	42,650 {f=1.32}	540	591 {522}	655	< 0.01	0.32
DC	420 {452}	25,000 {f=1.18}	470	555 {487}	575	< 0.01	0.22

<sup>a</sup> : Excitation was at 430 nm.

2.4.2. Picosecond-nanosecond time-correlated single-photon counting The time-correlated single-photon counting (TCSPC) setup was part of the Halcyone ultrafast spectrometer, using the same PMT detector (IRF ~ 250 ps), with a time window up to 200  $\mu$ s. Fluorescence was attenuated and directed to the detector and a monochromator was used to adjust the detection wavelength.

The samples in solution for the lifetime measurements were prepared in 2-mm fused silica cuvettes (Spectrocell Inc.) and were stirred during the experiment. For the solid-state measurements, the sample was spread on a thin quartz sheet and excitation was projected to the sample at 45°. All measurements were conducted at  $23 \pm 1$ °C. The measurements were repeated three times and the reported values are the average with the uncertainty. The photostability of the samples was checked by recording their steady-state absorption and fluorescence spectra before and after each measurement. The decay transients were fitted to a multiexponential function that is part of the Surface Xplorer software.

# 2.5. Electrochemical measurements

The cyclic voltammetry measurements were carried out using an electrochemical interface (PalmSens3 Potentiostat). The cell consisted of a working electrode (glassy carbon), a reference electrode (Ag/Ag<sup>+</sup>), and a Pt counter electrode. The cell solution contained 0.02 mM of the dye and 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) dissolved in acetonitrile. The measurements were performed under argon gas with a scan rate of 100 mV/s in the range -2.4-1.5 V, relative to ferrocene (Fc/Fc<sup>+</sup>).

#### 2.6. Density functional theory calculations

DFT calculations were performed at the APFD/6-311+g (2d,p) level as implemented in Gaussian 09 [27]. Solvent effects were included via the polarizable continuum model (PCM) with parameters appropriate for methanol. Starting structures for geometry optimizations were drawn and the nature of all stationary states verified by frequency calculation. TD-DFT calculations, at the same level of theory, were used to approximate electronic absorption spectra by calculating vertical excitation energies to the first 100 singlet excited-states at the optimized ground state geometry, while emission energies were approximated by calculating vertical excitation energies at the optimized geometry of the first excited state. Qualitatively similar results were obtained using B3LYP and CAM-B3LYP functionals, but only the APFD results are presented as these give the closest match to the recorded absorption and fluorescence spectra.

# 3. Results and discussion

#### 3.1. Spectroscopy and crystal structures of DHC and DC

The absorption and fluorescence spectra of DHC and DC are shown in Fig. 2 for the compounds dissolved in MeOH and in their crystalline form. The results of DHC, previously reported by us [13], are important in order to clarify the effect of the presence of the 2'-OH group on the spectroscopic behavior. The spectroscopic parameters for both compounds are summarized in Table 1.

#### Table 2

Fluorescence lifetime components of DHC and DC dissolved in MeOH and in their crystalline form, measured by fluorescence upconversion and TCSPC ( $\lambda_{ex}$  = 450 nm).

	$ au_1$ (ps)	$ au_2$ (ps)	$\tau_3$ (ps)	$\tau_4$ (ns)			
Dissolved in MeOH ( $\lambda_{em} = 580 \text{ nm}$ )							
DHC	$0.4 \pm 0.1 \; (rise)$	$4.8\pm1.0$	$16.8\pm1.4$	$0.35\pm0.03$			
DC		$2.2 \pm 0.3 \; (rise)$	$18.4\pm1.0$				
Crystalline ( $\lambda_{em} = 700 \text{ nm}$ )							
DHC	$2.9 \pm 0.5 \; (rise)$			$1.70\pm0.10$			
DC	$0.76 \pm 0.20 \; (rise)$			$1.74\pm0.10$			

The absorption spectra in MeOH indicate a red shift of ca. 15 nm in DHC, compared to the peak position of DC, whereas the red shift in fluorescence is more pronounced (ca. 36 nm). Very similar red-shift values are obtained from the DFT calculations: 20 and 35 nm respectively. This observation points to the role of the hydrogen bond (OH–-O) in stabilizing the molecular planarity between the hydroxyphenyl ring and the C=O group in DHC, thus allowing for efficient extended  $\pi$ -conjugation. This is evidenced in the crystal structures of both molecules (Fig. 3) which show a planar DHC whereas the DC structure indicates a torsional angle of 18° around the phenyl ring (the crystal structure data for DC are shown in the Supplementary Information (SI)).

On the other hand, a torsional angle around the hydroxyphenyl ring in the excited state of DHC (calculated to be  $\theta_{tor} = 44^{\circ}$ ) prevents the formation of the keto tautomer via ESIPT, making the enol tautomer the dominant form of DHC in the excited state [13,14]. In both molecules, the quantum yield of fluorescence ( $\phi_F$ ) in MeOH was measured to be < 0.01 which is a consequence of the torsional motion in the excited state.

In the solid crystalline form, the lowest energy peaks ( $\lambda_{max,Abs}$ and  $\lambda_{max,Fluor}$  in Table 1) for DHC are for the keto tautomer which dominates in solid due to the planarity of the molecular structure that strengthens the intramolecular H-bond and the tendency to form J-aggregates [13]. The large red shift in the fluorescence of DHC was correlated to the stabilization of the keto tautomer in the excited state. It is clear from Fig. 2 that the fluorescence peak in both molecules is narrower, compared with that in MeOH, indicating more flexibility in solution in which internal motion is possible.

The crystal packing of both molecules is shown in Fig. 3. Both molecules belong to the same crystal system (monoclinic) and space group (P  $2_1/c$ ). However, a close look at the crystal packing of DHC and DC indicates some differences. While the packing geometry in DHC clearly indicates a J-aggregate configuration, the DC packing shows some deviation from the slip-packing alignment, but still largely deviates from an H-aggregate configuration ( $\pi$ - $\pi$  interaction). The packing differences clearly affect the quantum yield of fluorescence in the solid matrixes (Table 1), where the value is much larger for DHC (0.32) compared to that for DC (0.22).

In order to understand the spectroscopic behavior of the two molecules in the excited state, we compare their excited state dynamics. Table 2 summarizes the fluorescence results, measured by fluorescence upconversion and TCSPC, where the results for DHC are taken from our previous work [13]. Fig. 4 shows the fluorescence upconversion transients for DC dissolved in MeOH and in its crystalline form during the initial 20 ps time window after excita-



Fig. 2. Absorption (solid) and fluorescence (dashed) spectra of DHC and DC dissolved in MeOH (upper) and in their crystalline state (lower). Fluorescence was detected after excitation at 430 nm.

tion at 450 nm. Figs. S1 and S2, SI include the full time range of the decay transients.

In MeOH, four lifetime components were extracted from the fits for DHC. The fastest dynamic ( $\tau_1 = 400$  fs) is a typical time constant that reflects vibrational cooling of the initially prepared Franck–Condon (FC) state of the enol tautomer. For DC, the up-converted fluorescence transient was best fitted to a biexponential function. One lifetime component in both molecules ( $\tau_2$ , Table 2) is assigned to the average solvation time of MeOH [13,28]. The  $\tau_3$  component (16.8 ps in DHC and 18.4 ps in DC) was assigned in DHC to a new state that is dominated by intramolecular twisting around the hydroxyphenyl ring [13]. This twisting motion is expected to be more active in DC due to the absence of the OH group and was also observed for DC dissolved in different aprotic solvents [24].

The last lifetime component for DHC ( $\tau_4$ = 350 ps) is assigned to the molecular relaxation of the excited enol to the ground state. This long component was not observed in DC which may point to the active twisting motion in depleting the excited state in MeOH. The observed weak green fluorescence and very small quantum yield for DHC and DC in solution are thus a direct consequence of the ultrafast nonradiative processes that deplete the excited state population. It is important to mention here that a longer component (350-1400 ps) was reported for DC in aprotic solvents [24]. The absence of this component in MeOH must be due to a strong interaction between MeOH and the carbonyl group (C=O) of DC, which is only possible with protic solvents, that couples with the twisting motion of the phenyl ring, leading to relaxation to the ground state.

The excited-state dynamics of the crystalline forms are very different from those in solution as a result of rigidity and packing. Table 2 includes the extracted lifetimes. The results show one rise time and one decay component for each compound. We previously assigned the two components in DHC to be due to enol-keto tautomerization via ESIPT ( $\tau_1 = 2.9$  ps) and excited state relaxation of the keto tautomer ( $\tau_4 = 1.70$  ns) [13]. The long lifetime of the keto tautomer in the crystalline form is attributed to the stability of this tautomer due to the planarity of the molecular structure and the slip-packing configuration to form J-aggregates [12,13]. For DC, the short lifetime component ( $\tau_1 = 0.61$  ps) can be assigned to excited state relaxation that results from some possible vibrations inside the crystals, but with little or no change in volume. The red shift of the crystalline form emission ( $\lambda_{max} = 575$  nm) in comparison with MeOH ( $\lambda_{max} = 555$  nm) indicates the high stability of this species in the excited state as a result of the push-pull mechanism that leads to a more stable ICT state. This is manifested in the long lifetime of the excited state ( $\tau_4 = 1.74$  ns).

# 3.1. Spectroscopy of DHC-COOH and DC-COOH in solution, solid state, and attached to $TiO_2$ nanoparticles

The absorption and fluorescence spectra of DHC-COOH and DC-COOH are shown in Fig. 5 for the compounds dissolved in MeOH and in their solid state. Table 3 summarizes the spectroscopic pa-



Fig. 3. Crystal structure (top) and packing (bottom) of DHC (left) and DC (right). Hydrogens are omitted for clarity.



Fig. 4. Femtosecond fluorescence upconversion transients for DC dissolved in MeOH and in its crystalline form.  $\lambda_{ex} = 450$  nm and  $\lambda_{em} = 580$  nm. The transients are offset for clarity.

# Table 3

Spectroscopic parameters for DHC-COOH and DC-COOH dissolved in MeOH and in their solid state. TD-DFT calculations are shown in braces.

	λ <sub>max,Abs</sub> (nm) (MeOH)	$\varepsilon (\lambda_{max,Abs})$ (M <sup>-1</sup> ·cm <sup>-1</sup> ) (MeOH)	$\lambda_{max,Abs}$ (nm) (Solid)	λ <sub>max,Fluor</sub> <sup>a</sup> (nm) (MeOH)	$\lambda_{max,Fluor}^{a}$ (nm) (Solid)	$\phi_{ m F}$ (MeOH)	$\phi_{ extsf{F}}$ (Solid)
DHC-COOH	451 {501}	49,350 {f=1.19}	460&590	621 {574}	680	< 0.01	0.02
DC-COOH	435 {471}	43,600 {f=0.79}	438	600 {553}	620	< 0.01	0.05

<sup>a</sup>: Excitation was at 430 nm.



**Fig. 5.** Absorption (solid) and fluorescence (dashed) spectra of DHC-COOH and DC-COOH dissolved in MeOH (upper) and in their solid state (lower). Fluorescence spectra for the two compounds attached to  $TiO_2$  nanoparticles are shown in blue for  $TiO_2$ +DHC-COOH and green for  $TiO_2$ +DC-COOH. Fluorescence was detected after excitation at 430 nm.

rameters. By comparing the spectral positions with those of DHC and DC, there is a clear red shift in the absorption and fluorescence peaks when a carboxylic group is attached to the phenyl ring. The red-shift caused by the addition of the carboxylic group is also seen in the DFT results. An electron-withdrawing group such as COOH is expected to enhance the ICT mechanism via extended conjugation (electron density difference maps and selected structural parameters are shown in SI). There is also a red shift in the spectra of DHC-COOH, compared to DC-COOH, indicating the effect of the OH group in stabilizing the molecular structure in the ground and excited states via intramolecular hydrogen bonding. A strong H-bond should reduce the internal twisting vibrations in solution which is manifested in the narrower fluorescence peak of DHC-COOH, compared to that of DC-COOH (see Fig. 5). The H-bond is clearly indicated in the DFT and TD-DFT optimized structures of DHC-COOH: rOH–-O=C = 1.548 Å (S<sub>0</sub>) and 1.520 Å (S<sub>1</sub>). Equivalent calculations find no stable keto structure in the ground state, while in the excited-state a stable form is located with rC=O--HO = 1.465 Å. However, S<sub>1</sub>-keto is calculated to lie  $_{\sim}$  0.1 eV above that of the enol, suggesting that ESIPT is not favored in solution. The measured fluorescence quantum yield in MeOH ( $\phi_{
m F}$  < 0.01, Table 3) indicates an active energy-depleting mechanism which could be due to a strong solute-solvent interaction, coupled with internal vibrations. High molar absorptivity values are noticeable for the two compounds in MeOH (Table 3), making those promising candidates for solar energy applications.

The absorption spectrum of DHC-COOH in the solid state (Fig. 5, lower panel) has a weak absorption in the 600 nm region which can be assigned to the ground state keto tautomer. This peak is equivalent to the keto peak observed in DHC at 540 nm (vide supra), but with a much smaller intensity. The large red shift in the fluorescence peak of solid DHC-COOH, compared to that in MeOH, is due to the stability of the keto tautomer in the excited state (680 vs 621 nm, respectively, Table 3). We did not observe any fluorescence from the enol tautomer of DHC-COOH in the solid state when exciting at different wavelengths across the absorption band, indicating an efficient ESIPT mechanism as in the case of DHC [13]. The quantum yield of fluorescence was measured to be low for both compounds in the solid state, compared with their analogous DHC and DC (0.02 for DHC-COOH and 0.05 for DC-COOH, Table 3). The large drop in  $\phi_{\rm F}$  may be due to deviation from a [aggregate packing configuration as a result of the presence of the COOH group. The smaller value of  $\phi_{\rm F}$  for DHC-COOH may also be correlated to an active motion of the H-atom of the OH group between the two oxygen atoms that acts as a nonradiative channel.

When DC-COOH is attached to the  $TiO_2$  surface, the fluorescence peak position was observed at the same wavelength as in the solid state, whereas that of DHC-COOH was blue shifted relative to the solid sample (Fig. 5, lower panel). The fluorescence peak of DHC-COOH/TiO<sub>2</sub> is close to that of DC-COOH/TiO<sub>2</sub>. This result indicates the involvement of the OH group in binding to the  $TiO_2$ surface, thus hindering the ESIPT process. This was confirmed by



Fig. 6. Energy level diagram of TiO<sub>2</sub>, DHC-COOH, DC-COOH, and the electrolyte pair I<sup>-</sup>/I<sub>3</sub><sup>-</sup>.

#### Table 4

Fluorescence lifetime components (measured by fluorescence upconversion and TCSPC) of DHC-COOH and DC-COOH dissolved in MeOH, in their solid state, and adsorbed on TiO<sub>2</sub> nanoparticles.  $\lambda_{ex} = 450$  nm.

	$ au_{ m rise}$ (ps)	$\tau_1$ (ps)	$\tau_2$ (ps)	$\tau_3$ (ps)	$\tau_4$ (ns)		
Dissolved in MeOH ( $\lambda_{em} = 650 \text{ nm}$ )							
DHC-COOH		$22.8\pm1.0$					
DC-COOH	$2.06\pm0.26$	$20.1 \pm 1.0$					
Solid ( $\lambda_{em} = 650 \text{ nm}$ )							
DHC-COOH		$6.50\pm0.28(0.52)$	63.1 ± 2.7 (0.35)	311 ± 13 (0.10)	$1.4\pm0.4(0.03)$		
DC-COOH	$0.78\pm0.05$		37.4 ± 3.0 (0.30)	340 ± 14 (0.50)	$1.6\pm0.1(0.20)$		
Solid+TiO <sub>2</sub> ( $\lambda_{em} = 650 \text{ nm}$ )							
DHC-COOH	$0.52\pm0.09$	$5.30\pm0.50\;(0.60)$	$32 \pm 3 \ (0.36)$	440 ± 50 (0.03)	$2.4\pm0.5(0.01)$		
DC-COOH	$3.20\pm0.35$		$16 \pm 2 \; (0.54)$	$460\pm25(0.40)$	$2.7\pm0.2(0.06)$		

investigating the mode of binding of the dyes on the  $TiO_2$  surface using XPS (details are included in SI). The results show that the binding mode of the dye on the  $TiO_2$  surface is a bidentate bridging from the COOH group in both dyes, in addition to the OH group of DHC-COOH via hydrogen bonding to the surface oxygen.

The fluorescence intensity of the dyes is very weak in the presence of TiO<sub>2</sub>, which can be a sign of electron transfer from the excited state to the conduction band of TiO<sub>2</sub>. We estimated the energy of the HOMO and LUMO of each dye by cyclic voltammetry [29,30] (voltammograms are shown in Figure S6, SI) and by determining the zero-point energy in the same solvent (absorption and fluorescence spectra are shown in Fig. S7, SI). The results were aligned with the energies of the valence band (VB) and CB of TiO<sub>2</sub>, and with the redox potential of the  $I^-/I_3^-$  electrolyte pair [31,32]. As shown in Fig. 6, electron transfer/injection from the LUMO of both dyes to the CB of the semiconductor is energetically favorable, and regeneration of the oxidized dye by the redox pair is also possible (i.e., the photogenerated holes in the HOMO can be collected into the  $I^-/I_3^-$  electrolyte). The results indicate the suitability of DHC-COOH and DC-COOH to act as solar dye concentrators in DSSCs.

The ultrafast dynamics of DHC-COOH and DC-COOH dissolved in MeOH were measured by fluorescence upconversion. Fig. 7 shows the transients and the lifetime values are included in Table 4. A single lifetime component was observed in DHC-COOH (22.8 ps) that is similar to one of the components observed in DHC and DC (see Table 2). This lifetime thus reflects the nature of the excited state as dominated by intramolecular twisting vibrations. The same dynamical process was observed in DC-COOH, in addition to a faster rise time component of 2.06 ps. The latter is assigned to the solvation time in MeOH, as observed in DC above. In order to confirm this assignment, we measured the transients for DHC-COOH and DC-COOH in acetonitrile (average solvation time is 0.26 ps) [28] and we did not observe any fast component which, if it exists, should be shorter than the IRF (the inset of Fig. 7).

The dynamics of the dyes in the solid state are characterized by multi-lifetime components which can be attributed to the heterogeneous nature in the solid matrix. The transients are shown in Fig. 8 and the extracted lifetime components are summarized in Table 4.

Four decay components were observed for DHC-COOH, ranging from 6.5 ps to 1.4 ns. We did not observe any rise time as in the case of DHC which was assigned to ESIPT, even by detection at different wavelengths across the fluorescence peak. On the other hand, the fastest decay component (6.5 ps) is absent in DC-COOH which correlates this component to a dynamical process that involves the OH group. In DC-COOH, a rise time of 780 fs was observed which is similar to that observed for DC (610 fs, Table 2) and can be assigned to the same dynamical process that involves a twisting vibrational motion in the excited state.

When the dyes were adsorbed on the surface of TiO<sub>2</sub> nanoparticles, there was a dramatic effect on the different lifetime components as shown in Table 4. The fastest component in both dyes is a rise time ( $\tau$  <sub>rise</sub>) of 520 fs in DHC-COOH and 3.2 ps in DC-COOH. As indicated above, this rise time was assigned in DC and DC-COOH to a twisting vibrational motion of the phenyl ring that is active when the OH group is absent. The elongation in time when DC-COOH is adsorbed on TiO<sub>2</sub> and the emergence of this dynamical process in DHC-COOH is likely a consequence of the mode of attachment of the dye on the semiconductor surface which takes place through the COOH group. This particular configuration separates the dye molecules from each other and gives each molecule more space for internal motion that was not available in the solid matrix due to the packing structure. As a result, the molecules freely vibrate on the TiO<sub>2</sub> surface, leading to a longer rise time in DC-COOH and the appearance of a new rise time in DHC-COOH. As we showed



Fig. 7. Femtosecond fluorescence upconversion transients for DHC-COOH and DC-COOH dissolved in MeOH. Inset: an expanded time window for the compounds dissolved in MeOH and acetonitrile.  $\lambda_{ex} = 450$  nm and  $\lambda_{em} = 650$  nm.



Fig. 8. Fluorescence transients for DHC-COOH and DC-COOH in the solid state and adsorbed on TiO<sub>2</sub> nanoparticles measured by TCSPC and fluorescence upconversion (inset).  $\lambda_{ex} = 450$  nm and  $\lambda_{em} = 650$  nm.

earlier, both COOH and OH are involved in binding DHC-COOH to the  $TiO_2$  surface, thus breaking the intramolecular hydrogen bond (OH--O) and allowing the molecules to twist.

The fastest decay component in DHC-COOH ( $\tau_1 = 6.5 \text{ ps}$ ) is absent in DC-COOH and is due to the OH group, as mentioned above. This component gets shorter in the presence of TiO<sub>2</sub> ( $\tau_1 = 5.3$  ps) which could be due to the effect of electron transfer from the LUMO to the CB of TiO<sub>2</sub> via the OH group. The second decay component ( $\tau_2$ ) was detected in both dyes and should reflect the effect of the electron transfer dynamic through the COOH group. It is clear that this lifetime gets much shorter in both dyes in the presence of TiO<sub>2</sub> (reduction by ~ 50%), in agreement with the efficient

COOH group in injecting the electrons from the dye to the CB. The last two decay components ( $\tau_3$  and  $\tau_4$ ) are the lifetimes for the recombination processes. The components are longer (slower dynamics) in the presence of TiO<sub>2</sub> and with smaller contributions, compared to their analogues in the solid state. The slow recombination processes reflect the more stable charge-transfer state that is produced as a result of the oxidized dye and the reduced semiconductor. The slower recombination processes for the dyes on the TiO<sub>2</sub> surface, compared to free dyes, may also derive from the large physical separation of the produced dye cations from the semiconductor surface [33]. This is reflected in the large distance between the electron-donating center (N(CH<sub>3</sub>)<sub>2</sub>) and the carboxylic group

(electron acceptor) which was shown to play a major role in stabilizing the ICT state [34,35].

The current results indicate the suitability of DHC-COOH and DC-COOH to act as solar dye concentrators in DSSCs where the carboxylic group is shown to play a major role in dye-binding to the semiconductor nanoparticles. This work should be useful for testing both dyes in solar cell modules and for potential modification in chalcone-based dyes for better solar-to-electrical conversion efficiency. Applying machine learning to examine other derivatives of chalcone will be useful in predicting other potentially promising molecular structures in a cost effective way [36–38].

# 4. Conclusions

Four chalcone derivatives were synthesized and characterized by steady-state and time-resolved spectroscopy, TD-DFT modeling, and cyclic voltammetry. The presence of OH in DHC and DHC-COOH causes a red shift in the absorption and fluorescence spectra, compared to DC and DC-COOH, whereas a twisting motion around the (hydroxy) phenyl ring is evident in the measured dynamics in MeOH for the four molecules. Attaching a COOH group induces a further red shift in the steady state spectra due to efficient ICT which is also seen in the DFT results. DHC shows a clear aggregation-induced emission in the crystalline form which is much less in DC due to some deviation from a perfect Jaggregation. The presence of COOH seems to cause a large deviation of the packing configuration from J-aggregates, leading to a small quantum yield of fluorescence in the solid matrix. The presence of OH enhances ESIPT in the solid matrix which is detected as a new absorption peak and a large red shift in fluorescence. The latter was not observed when DHC-COOH was adsorbed on the TiO<sub>2</sub> surface, indicating the involvement of the OH group in binding which was confirmed by XPS. In addition to the OH binding, the XPS spectra indicate that both DC-COOH and DHC-COOH bind to  $TiO_2$  via a bidentate mechanism that involves the COOH group.

The fluorescence intensity of DHC-COOH and DC-COOH is very weak in the presence of TiO<sub>2</sub>, signaling electron transfer from the LUMO of the dye to the CB of the semiconductor. The energies of the HOMO and LUMO in each dye were determined from cyclic voltammetry measurements and the steady-state spectra, and were aligned with those of the VB and CB of TiO<sub>2</sub>. It was found that electron injection from the LUMO to the CB is energetically favorable in both dyes, and regeneration of the oxidized dye by the  $I^-/I_3^-$  redox pair is also possible. This was confirmed by the dramatic change in the excited-state dynamics where the fast decay components were elongated due to slower electron-hole recombination.

# Author statement

A.R. Ibrahim and B.S. Al-Saadi: Measured and analyzed the steady-state and time-resolved spectra, J. Husband: Performed and wrote the theoretical modeling, A.H. Ismail: Synthesized the new molecules, Y. Baqi: Designed, analyzed and wrote the synthetic part, O.K. Abou-Zied: Designed the project, supervised, wrote and edited the paper.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Data Availability

No data was used for the research described in the article.

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#### Supplementary materials

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