Carbon nitride photocatalyzes regioselective aminium radical addition to the carbonyl bond and yields N-fused pyrroles

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Addition of N-centered radicals to C=C bonds or insertion into C–H bonds is well represented in the literature. These reactions have a tremendous significance, because they afford polyfunctionalized organic molecules. Despite the tetrahydroisoquinoline (THIQ) moiety widely occurring in natural biologically active compounds, N-unsubstituted THIQs as a source of N-centered radicals are not studied. Herein, we report a photocatalytic reaction between tetrahydroisoquinoline and chalcones that gives N-fused pyrroles—1,3-disubstituted-5,6-dihydropyrrolo[2,1-a]isoquinolines (DHPIQ). The mechanism includes at least two photocatalytic events in one pot: (1) C–N bond formation; (2) C–C bond formation. In this process potassium poly(heptazine imide) is used as a visible light active heterogeneous and recyclable photocatalyst. Fifteen N-fused pyrroles are reported with 65–90% isolated yield. DHPIQs are characterized by UV–vis and fluorescence spectroscopy, while the fluorescence quantum efficiency of fluorinated DHPIQs reaches 24%.

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Heterogeneous photocatalysis has emerged as a powerful technique empowering challenging chemical transformations. The development of more efficient semiconducting photocatalysts includes, but is not limited to, band gap engineering, heterostructure design, and surface modification. Surface properties of the heterogeneous photocatalyst are essential because they directly affect the interaction of the substrate with the surface of the photocatalyst and also influence the charge carriers mobility. Thus, Chen and Hirao have shown that photocatalytic activity, for example, in hydroxylation of boronic acids to alcohols and oxidation of primary alcohols to aldehydes, may be boosted by adjusting the surface basicity of the photocatalyst.

It has been recently shown that carbon nitride heterogeneous photocatalysis is a useful instrument not only in water splitting, but also enables a variety of novel organic photoredox reactions that have been recently summarized in several reviews. Potassium poly(heptazine imide) (K-PHI hereafter) is a member of the carbon nitride family with negatively charged nitrogen atoms and silicon poly(heptazine imide) (K-PHI hereafter) is a member of the carbon nitride family with negatively charged nitrogen atoms. This structural particularity has a great impact on the band gap of the material, which is tuned from 2.54 eV vs. RHE to 2.3 eV vs. RHE for potassium poly(heptazine imide) and potassium poly(phenazine imide), respectively. This is particularly important for organic photocatalysis, as it reduces the energy barrier for the charge separation process.

Among a plethora of organic photoredox reactions, the addition of aminium radicals to C=C bonds or insertion into C-H bonds has a great importance as it serves the needs of synthetic organic chemistry and production of pharmaceuticals. However, there are only few works on R_{2N} radicals addition to the polar C=O carbonyl bonds.

Synthesis and modification of tetrahydroisoquinoline (THIQ) derivatives have been attracting continual growing interest during the last decades. Photocatalytic single-electron oxidation of the amino group in THIQ, using homogeneous or heterogeneous visible light photocatalytic systems, leads to the formation of aminium radical-cation which is readily attacked at the α-carbon by different nucleophilic agents, for example, nitromethane, cyanides, covalent enolates, alkynes, and even methylketones.

However, the scope of such photocatalytic transformations is limited solely to N-substituted THIQ and only allows functionalization of the C-2 atom of the substrate. On the other hand, THIQ with an unsubstituted NH-functionality has two reactive centers (C-2 α-carbon and N-1 nitrogen atom) and opens new possibilities to diverse types of reactions. Bifunctional compounds, such as chalcones, may be envisioned for use as reaction partners due to possessing a C=C double bond and a C=O carbonyl group in their structure. In terms of photocatalysis, Yoon et al. have demonstrated that chalcones themselves, when activated by Lewis acids, can be used in cyclobutane synthesis. On the other hand, Zeitler et al. suggested conditions mimicking enzymatic catalysis to activate enones toward the formation of cyclopentanes. In these cases, however, the mechanism implies that the uncoupled electron is localized at the β-carbon atom, and therefore the reaction proceeds exclusively at this site.

Summarizing the literature, we envision that an appropriate photocatalyst might trigger a domino reaction between a chalcone molecule and THIQ. Such interaction may lead to the 1,3-disubstituted-5,6-dihydropyrrolo[2,1-a]isoquinolines (DHPIQs). DHPIQ derivatives occur in nature and are known as lamellarins. Polyphenyl substituted DHPIQs were suggested for use as a hole transporting layer. Preparation of such condensed heterocyclic compounds mainly demands microwave (MW) irradiation at high temperature or using such exotic synthetic reagents as 3-phosphorylallenes (Fig. 1).

Herein, we report the reaction between THIQ and chalcones mediated by the visible light active K-PHI photocatalyst without any additives (Fig. 1). This approach allows to alter the reactivity of the enone, that otherwise simply adds a THIQ via the classical aza-Michael reaction, and reveals the path for the synthesis of DHPIQs. Fluorinated DHPIQ derivatives exhibit strong fluorescence in the blue region, while the fluorescence internal quantum efficiency (IQE) reaches 24%.

Results

Optimization of the reaction conditions. The photocatalyst, K-PHI, was synthesized according to the described procedure and its characteristics are given in Supplementary Figure 1. Chalcones were synthesized according to the procedures given in Supplementary Methods. The photocatalytic coupling reaction between THIQ and chalcone 2a was a starting point in our study, and all conditions and results of optimization experiments are presented in Table 1. In control reactions without the photocatalyst (entry 1) or without light irradiation (entry 2) no product was formed. Under light irradiation (λ = 461 nm, 51.7 ± 0.03 mW cm⁻², blue LED) at 80 °C with K-PHI as the photocatalyst after 20 h using 3 equivalents of THIQ and acetonitrile as solvent (entry 3), 87% of the starting chalcone 2a was converted into a mixture of compounds: the desired dihydropyrrolo[2,1-a]isoquinoline (DHPIQ) 3a and ketone 4a (with ratio 1:1.1

Fig. 1 Key points of the work. Synthetic approaches to the DHPIQs (a) and chemical structure of K-PHI (b)
ketone 4a then reduced by in situ released hydrogen to the corresponding (see also the suggested mechanism below). When electron/proton scavenger under the photocatalytic conditions electrode (SCE)) and reduction potential of chalcones (see the mechanism discussion below for more details about the role of acetone). Using both smaller and larger amounts of the photocatalyst (entries 8–9) gave slightly lower conversions (84–89%) of chalcone, but almost the same selectivity toward DHPIQ 3a. In less polar solvents such as dioxane, benzene, and tert-butanol (entries 10–12), the conversion and selectivity were lower, possibly due to poor stabilization of the polarized transition state structures. This photocatalytic reaction could also be performed at room temperature (entry 13), but it takes more time (60 h) to get conversion (85%) and selectivity (85%) comparable to the experiments at 80 °C. After recycling K-PHI for three times (entries 14–16), the conversion of the chalcone has slightly decreased (91%) nevertheless the selectivity was the same (89%). Ir(ppy)3 gave DHPIQ with 89% selectivity (entry 17), but no product was obtained when Ru(bpy)3Cl2·6H2O was employed as a photoredox catalyst (entry 18) presumably due to a lower activity (entry 20). The difference in performance of these two photocatalysts (entries 8–9) gave slightly lower conversions (84–89%) of chalcone, but almost the same selectivity toward DHPIQ 3a. In less polar solvents such as dioxane, benzene, and tert-butanol (entries 10–12), the conversion and selectivity were lower, possibly due to poor stabilization of the polarized transition state structures. This photocatalytic reaction could also be performed at room temperature (entry 13), but it takes more time (60 h) to get conversion (85%) and selectivity (85%) comparable to the experiments at 80 °C. After recycling K-PHI for three times (entries 14–16), the conversion of the chalcone has slightly decreased (91%) nevertheless the selectivity was the same (89%). Ir(ppy)3 gave DHPIQ with 89% selectivity (entry 17), but no product was obtained when Ru(bpy)3Cl2·6H2O was employed as a photoredox catalyst (entry 18) presumably due to a lower reduction potential of the excited state. In case of mesoporous graphiteon carbon nitride (mpg-CN, entry 19), 35% conversion of chalcone 2a was obtained. Another representative of poly(hep-tazine imide)s, Na-PHI, gave 85% conversion, but higher selectivity (entry 20). The difference in performance of these two materials might be explained by variation in their microstructure as well as surface properties.

Expanding the scope of the substrates. The effectiveness of the photocatalytic approach was proved for the wide range of corresponding). This result could be explained by the stoichiometry of this transformation—the formation of compound 3a demands interaction of THIQ and chalcone 2a with the abstraction of H2O and H2 molecules. The starting chalcone 2a is then reduced by in situ released hydrogen to the corresponding ketone 4a. In other words, the chalcone 2a plays the role of electron/proton scavenger under the photocatalytic conditions (see also the suggested mechanism below). When 1a–d2 (98% of d-labeled compound) was used as a reagent under the identical photocatalytic conditions, along with DHPIQ 3a we have detected a mixture of d-labeled ketones 4a–d1 by mass-spectrometry (Supplementary Figure 2), suggesting that indeed under the photocatalytic conditions THIQ acts as a reductant. Using oxygen as electron scavenger (entry 4), no DHPIQ 3a was obtained. However, THIQ was completely oxidized to 3,4-dihydroisoquinoline (DHIQ), while the chalcone 2a remained intact. Such observation might be explained comparing standard redox potential of the couple O2/O2− (−0.57 V vs. saturated calomel electrode (SCE))41 and reduction potential of chalcones (Ered = −1.0...−1.5 V vs. SCE). Reduction of oxygen is a more favorable process compared to the reduction of chalcones. Therefore, in the presence of O2, reduction of chalcones is completely suppressed. The generated O2− is reactive enough to oxidize THIQ to DHIQ42. Following these preliminary experiments, it was decided to use acetone as electron scavenger (entry 5). Under these mild conditions, high conversion (93%) of chalcone 2a and high selectivity (89%) with respect to DHPIQ 3a were achieved (see the Table 1. Optimization of the reaction conditions of the oxidative condensation between tetrahydroisoquinoline and chalcone 2a toward the synthesis of DHPIQ.

| Exp. no. | Solvent | T, °C | Time, h | Conv. of 2a, % | 3a/4a |
|---------|---------|-------|---------|---------------|-------|
| 1b      | CH3CN   | 80    | 20      | 0             | –     |
| 2c      | CH3CN   | 80    | 20      | 0             | –     |
| 3d      | CH3CN   | 80    | 20      | 87            | 1:1   |
| 4e      | CH3CN   | 80    | 20      | 0             | –     |
| 5       | CH3CN   | 80    | 20      | 93            | 8.2:1 |
| 6f      | CH3CN   | 80    | 20      | 0             | –     |
| 7g      | CH3CN   | 80    | 20      | 0             | –     |
| 8h      | CH3CN   | 80    | 20      | 89            | 8:1   |
| 9i      | CH3CN   | 80    | 20      | 84            | 8:1   |
| 10      | Dioxane | 80    | 20      | 69            | 2.2:1 |
| 11      | Benzene | 80    | 20      | 78            | 3.6:1 |
| 12      | t-BuOH  | 80    | 20      | 62            | 2.1   |
| 13      | CH3CN   | 25    | 60      | 85            | 5.7:1 |
| 14f     | CH3CN   | 80    | 20      | 91            | 8.2:1 |
| 15k     | CH3CN   | 80    | 20      | 92            | 8.3:1 |
| 16l     | CH3CN   | 80    | 20      | 91            | 8.2:1 |
| 17m     | CH3CN   | 80    | 20      | 89            | 8.2:1 |
| 18n     | CH3CN   | 80    | 20      | 0             | –     |
| 19o     | CH3CN   | 80    | 20      | 35            | 4:3:1 |
| 20p     | CH3CN   | 80    | 20      | 85            | 13:1  |

(a) The conversion of 2a and the molar ratio between 3a and 4a was determined by GC-MS; (b) without photocatalyst and acetone; (c) without light irradiation and acetone; (d) without acetone; (e) reaction in atmosphere of oxygen; (f) without photocatalyst; (g) without light irradiation; (h) 10 mg and (i) 2 mg of the photocatalyst; (j) second run; (k) third run; (l) fourth run; (m) Ir(ppy)3 (2 mg, 3 μmol); (n) Ru(bpy)3Cl2·6H2O (2.2 mg, 3 μmol); (o) mpg-CN (5 mg) instead of K-PHI; (p) Na-PHI (5 mg) instead of K-PHI.
Aryl- and hetaryl-substituted chalcones 2a–k gave the respective DHPIQs from good to excellent yields (65–90%). In case of chalcones 2f–h the significant formation of ketones 4f–h as side products was detected, which lowered the yield of 3f–h to 65–70%. These results may be explained by the enhanced electron scavenging ability of the chalcones 2f–h, bearing electron withdrawing (trifluoromethyl)phenyl or 3,4-difluorophenyl substituents, which make them competitive to acetone in the electron capture and further reduction process. Chalcones bearing at least one methyl group, 2l and 2m, also gave the corresponding DHPIQs, 3l and 3m, although with lower yields.

On the other hand, \((E)\)-hex-4-en-3-one did not react under similar conditions, partially due to its more negative reduction potential. \((E)\)-4,4-dimethyl-1-phenylpent-2-en-1-one also did not yield the corresponding DHPIQ, presumably due to steric hindrance of the tert-butyl group that obstructs coupling of the chalcone with THIQ. Finally, we have also explored the possibility to use substituted THIQ. Thus, 6-fluoro- and 6-trifluoromethyl-THIQ gave the corresponding DHPIQs, 3n,o, with 63% and 81% yield, while electron rich 6,7-dimethoxy-THIQ was completely oxidized to the dihydroderivative, but no DHPIQ was formed. Among other amines, only dibenzylamine and \(N\)-benzylbutan-1-amine activated by a phenyl ring, but having rather flexible structure compared to THIQ 1a, gave the respective products of condensation, although in trace amounts of 15% and 3%, respectively.
Different reactivity was observed for chalcone 2p (Fig. 3). Instead of DHPIQ, the saturated analogue 7p was isolated, though in low yield. When 1a–d2 was employed, the corresponding compound 7p–d1 was obtained. Compounds 7p apparently are stabilized by hydrogen bonding, which obstructs dehydrogenation. This experiment gave us an idea about the possible mechanism of DHPIQ formation.

In the NOESY spectrum of DHPIQ 3c, a through-space interaction between the ortho-phenyl protons and the methylene group of the THIQ core is observed supporting the structural correctness (Fig. 4).

**Basic chemical and optical properties of the DHPIQs.** Furthermore, we have shown that DHPIQs, as exemplified by compound 3d, smoothly undergo electrophilic substitution using N-bromosuccinimide (NBS) as a reagent at room temperature (Fig. 5). The bromo-derivative 8d may be envisioned as a useful partner for cross-coupling reactions.

DHPIQs synthesized here are colorless substances and absorb light below 360–370 nm (Fig. 6a).

These compounds exhibit pronounced fluorescence in the blue region when excited with UV light (Fig. 6b, c). The emission maximum depends on the structure of DHPIQ and is in the range 399–431 nm (Table 2). Notably, CF3-substituted DHPIQ 3f that fluoresces at 431 nm also has an IQE of fluorescence of 24%.

**Redox properties of the chalcones and THIQ.** In order to determine the redox properties of the reagents and therefore shed light on the photocatalytic mechanism, we have performed a cyclic voltammetry (CV) study (Fig. 7). Thus, THIQ 1a is stable on the reduction side at least up to −1.8 V vs. SCE, however, typically for aliphatic amines, oxidation starts at ca. +0.8 V vs. SCE. The similar oxidation potential was detected for 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline. On the other hand, chalcones 2a–d and 2i showed stability against reduction up to −1.2 V vs. SCE and the tendency is: the more electron deficient the chalcone the less negative reduction potential it has. In agreement with this, chalcone 2q, derived from 2,3,4,5,6-pentafluorobenzaldehyde, has a reduction potential of −1.0 V vs. SCE, reflecting high affinity to electrons. Under the photocatalytic conditions 2q was quantitatively reduced to ketone 4q via a proton-coupled electron transfer (PCET) and did not give the corresponding DHPIQ. Methyl-substituted chalcones 2l and 2m have more negative reduction potentials −1.45 and −1.50 V, respectively. The yield of DHPIQ 3l was still higher than 3m, indicating the importance of an aromatic substituent in position 3 of the chalcone for efficient reduction to the radical anion. Tert-butyl-substituted chalcone showed a reversible reduction peak at −1.67 V, implying that the subsequent reaction, e.g., coupling of the radicals, is inhibited and at the given scan rate of 50 mV s−1 the radical anion is oxidized back to the chalcone. Finally, (E)-hex-4-en-3-one has a reduction potential below −1.75 V vs. SCE. The reduction power of K-PHI is apparently not sufficient to reduce aliphatic chalcones. Therefore no DHPIQ was obtained in this case.

In addition, chalcones are stable against oxidation up to at least +1.5 V vs. SCE. Only chalcone 2c showed an irreversible oxidation peak at this potential. Summarizing the CV study, under the photocatalytic conditions it is more likely that photogenerated holes (+1.96 V vs. SCE) oxidize THIQ 1 (Eox ≤ +0.8 V vs. SCE) rather than any of the chalcones (Eox > +1.5 V vs. SCE). In order to comply with the balance of electrons, the photogenerated electrons are taken by the chalcones (Ered ≥ −1.5 V vs. SCE) rather than THIQ (Ered ≤ −1.8 V vs. SCE).

**DFT calculations.** Absolute energies of DHPIQ and chalcone frontier orbitals were calculated using the PBE0-D3 functional and are shown in Fig. 8a. Although they do not correspond to the real redox potentials of these compounds obtained from CV in acetonitrile, the tendency is the same, i.e., THIQ is more

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Fig. 4 Fragment of the NOESY spectrum of DHPIQ 3c

Fig. 5 Derivatization of DHPIQs by electrophilic bromination with NBS
susceptible for oxidation, while the chalcone is more likely to work as electron acceptor. The HOMO of THIQ is localized largely on the saturated part of the molecule, while the aromatic ring contributes mostly to the LUMO. The LUMO orbital of the chalcone is delocalized over the whole molecule and this might explain why chalcone 2a relatively easily undergoes reduction. Similar results were obtained with the B3LYP-D3 and CAM-B3LYP functionals (Supplementary Tables 1–2). Bearing this in mind, the structure of the H-atom increased on average from 0.25 to 0.35 depending on the functional (Supplementary Table 2). Bearing this in mind, the structure of the N-centered aminium radical cation may be proposed as an intermediate in photocatalytic oxidation of THIQ.

In case of [2a]−, the uncoupled electron is delocalized over the carbonyl O- and C-atoms and the C-atom in β-position to the carbonyl group, but not located at the C-atom in α-position to the carbonyl group (Supplementary Table 3). Therefore, only resonance structures [2a′], [2a”], and [2a‴] of the chalcone radical anion may be proposed.

**Discussion**

Taking into account the structures of THIQ, chalcone and the respective DHPIQs, the reaction requires the following steps: (1) C–N bond formation between THIQ and the carbon atom of the C=O group; (2) C–C bond formation between THIQ and the chalcone; (3) elimination of a H2 molecule; and (4) elimination of a H2O molecule. Based on the experimental data as well as DFT calculations discussed above, Fig. 9 outlines the possible sequence of the reactions that leads to the formation of DHPIQ from THIQ and chalcone. A detailed scheme of the proposed mechanism is given in Supplementary Figure 4.

Upon excitation with light, K-PHI is converted into the excited K-PHI* species that eventually follows the path of reductive quenching. One-electron oxidation of THIQ 1 gives the corresponding radical cation [1]+, a common intermediate in organic redox chemistry, and the long-lived K-PHI− radical anion that was detected by EPR in situ (Supplementary Figure 5). Single electron transfer from K-PHI− to the chalcone gives the radical anion [2]−. Coupling of the radicals [1]+ and [2]− accompanied by the photocatalytic oxidation of the intermediate 5 leads to the radical cation [5]+. Although hemiaminals are not stable compounds, Li et al. proposed them as intermediates in the synthesis of alylamines from cyclic ketones and amines. In the control experiment without photocatalyst and/or light, THIQ and chalcones did not produce 5, but formed theaza-Michael adduct 9 (Supplementary Figures 6, 7, Supplementary Notes 1, 2). The aza-Michael adduct 9d under the optimized photocatalytic conditions did not yield the corresponding DHPIQ (Supplementary Figure 8, Supplementary Note 3), implying that 9d is not the intermediate of DHPIQ 3d formation.

PCET from [5]+ to acetone gives the iminium cation 6 that via a Mannich-like cyclization and subsequent hydride transfer is converted to intermediate 7. On the last step, DHPIQ is obtained from 7 by sequential dehydrogenation and dehydration. Evolution of hydrogen was detected by GC-TCD (Supplementary Figure 9).

In order to check whether DHPIQ 3a can be synthesized from other building blocks and presumably get more insight into the mechanism, we tried the following combinations of precursors: (1) 3,4-di-hydroxiquinoline and chalcone 2a; (2) 3,4-di-hydroxiquinoline and 1,3-diphenylprop-2-yn-1-one; (3) acetophenone, benzaldehyde and THIQ; (4) styrene, benzaldehyde and THIQ (Supplementary Notes 4–8). In all these cases, no DHPIQ was formed indirectly supporting the proposed scheme of the mechanism.

In the present account, we have shown that K-PHI, a transition metal-free, visible light responsive, and heterogeneous carbon nitride material, triggers a tandem photocatalytic reaction between THIQ and chalcones. Fifteen DHPIQs were isolated with 15–90% yield. The reaction reported herein gives the access to polycyclic molecules that exhibit strong fluorescence in the blue region with IQE up to 24% and might be used, for example, in organic photovoltaic cells. The DHPIQ core can be subsequently functionalized using electrophilic substitution reactions.

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**Table 2 Spectroscopic data of DHPIQs**

| DHPIQ | λ\(_{max}\) (nm) | λ\(_{max}\) (nm) | IQE (%) |
|-------|----------------|----------------|--------|
| 3b    | 326            | 399            | 17     |
| 3d    | 324            | 399            | 21     |
| 3f    | 316            | 431            | 24     |
| 3h    | 322            | 407            | 16     |
| 3g    | 314            | 419            | 13     |

The IQE was measured using an integrating sphere upon sample excitation with 360 nm.

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Fig. 6 Basic optical properties of the DHPIQs. a UV-vis absorption spectra of DHPIQ solution in MeCN (ca. 10⁻⁴ M). b Fluorescence spectra of DHPIQ solution in MeCN (ca. 10⁻⁴ M) were obtained upon sample excitation with 350 nm. c Appearance of DHPIQ solutions under ambient light and under UV (365 nm)
patterns were measured from a Bruker D8 Advance X-ray diffractometer equipped with a scintillation counter detector with CuKa radiation (λ = 0.15406 nm) applying 2θ step size of 0.02° and counting time of 3 s per step. Nitrogen adsorption/desorption measurements were performed after degassing the samples at 150 °C for 2 h using a Quantachrome Quarradors M –8 MP porosimeter at 77.4 K. The specific surface areas were calculated by applying the Brunauer–Emmett–Teller (BET) model to adsorption isotherms for ph/p0 < 0.3 using the QuadraWin 5.1 software package. Scanning electron microscopy (SEM) images were obtained on a LEO 1550 Gemini microscope. The X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ultrahigh vacuum (UHV) spectrometer equipped with a VSW Class WA hemispherical electron analyzer. A double anode Al Kα X-ray source (1486.6 eV) was used as incident radiation. Survey and high-resolution spectra were recorded in constant pass energy mode (44 and 22 eV, respectively). During the UPS (He I excitation energy hν = 21.23 eV) measurements a bias of 15.32 V was applied to the sample, in order to avoid interference of the spectrometer threshold in the UP spectra. The values of the valence band maximum (VBM) are determined by fitting a straight line to the leading edge. Optical absorbance spectra of powders were measured on a Shimadzu UV 2600 equipped with an integrating sphere. Emission spectra were recorded on Jasco FP-8300 instrument. The excitation wavelength was 360 nm. The TEM measurements were acquired using a double-corrected Jeol ARM200F, equipped with a cold field emission gun and a Gatan GIF Quantum. The used acceleration voltage was 200 kV and the emission was set to 10 μA in order to reduce beam damage. An objective aperture with a diameter of 60 μm was introduced into the beam to improve the contrast while still allowing for atomic resolution.

Irradiance of the LED modules. Irradiance was measured using PM400 Optical Power and Energy Meter equipped with the integrating sphere S142C.

Hydrogen (H2) detection. The experiment was performed using Agilent Technologies 7890B gas chromatography system equipped with a thermal conductivity detector (TCD) allowed for analysis of the gas produced during the photocatalytic experiment. The separation of the gaseous species was performed with an Agilent select permanent gases/CO2 capillary column set. The latter was consisting of two parallel columns that combine CP Molsive 5 Å for permanent gas analysis, and CP Porabond Q for CO2 analysis. The detector and oven temperatures were 200 and 45 °C, respectively. Ar was used as a carrier phase with a flow rate of 14 mL min−1. The injection was performed with a 250-μL gas-tight syringe from SGE Analytical Science. A calibration gas consisting of 20% CO2, 5% CO, 5% CH4, 2% H2, and 1% C3H6 mixed in Ar, injected in known volumes, was used to obtain the calibration curve that allowed the quantification of the gas products.

Electrochemistry. CV measurements were performed in a glass single-compartment electrochemical cell. A glassy carbon disc electrode (1 mm in diameter) was used as working electrode, and a Pt wire as counter electrode. The experiments were performed using a Ag/AgCl reference electrode, and the potential values were then converted to the SCE reference system according to the equation $E_{\text{SCE}} = E_{\text{Ag/AgCl}} – 0.043 V$. Each compound was studied in a 2 mM concentration in a 0.1 M tetraethylammonium tetrafluoroborate (TBABF4)/acetonitrile electrolyte solution (10 mL). Before voltammograms were recorded, the solution was saturated with Ar, and an Ar flow was kept in the headspace volume of the electrochemical cell during CV measurements. A potential scan rate of 0.050 V s−1 was chosen, and the potential window ranging from +1.5 V to −1.8 V back (and backwards) was investigated. CV was performed under room-temperature conditions (−20–22 °C).

Synthesis of K-PH. The procedure is similar to the method reported earlier with minor changes.4,15 A blend of potassium chloride (4.54 g), lithium chloride (3.71 g), and 5-amino tetrazole (1.65 g) was grinded in a ball mill using the following parameters—shaking rate 25 Hz, time 5 min. The flour-like powder was heated in a porcelain crucible covered with a lid under nitrogen flow (15 L min⁻¹). The temperature program was the following: heating from room temperature to 550 °C for 4 h, calcination at 550 °C for 4 h. The crucibles were spontaneously cooled to room temperature. The cake and deionized water (100 mL) were brought together in a beaker and stirred at room temperature for 3 h. Solid was filtered, thoroughly washed with water and dried in vacuum (20 mbar) at 50 °C for 15 h.

A general method of DPHIQs (3a-o) preparation. A glass tube with rubber-lined cap was evacuated and filled with argon three times. To this tube, THIQ (20 mg, 130 μmol), corresponding chalcone (50 μmol), acetone (9 mg, 130 μmol), K-PH (5 mg), and acetonitrile (2 mL) were added. The resulting mixture was stirred at 80 °C under irradiation of blue LED (λ = 461 nm, 517 ± 0.03 mW cm⁻²) for 2 h. Then the reaction mixture was cooled to room temperature and centrifuged, a clear solution was separated and the solid residue was washed with acetonitrile (2 mL) and centrifuged again. The organic solutions were combined and evaporated to dryness. The residue after evaporation was purified by silica gel column chromatography using a mixture of hexane/diethyl ether (9:8:2) as an eluent.

### Methods

**Compounds characterization.** 1H and 13C NMR spectra were recorded on Agilent 400 MHz (at 400 MHz for Protons and 101 MHz for Carbon-13). Chemical shifts are reported in ppm vs. solvent residual peak: chloroform-d 7.26 ppm (1H NMR), 118.3 ppm (13C NMR). High-resolution mass spectral data were obtained using Waters XEVO G2-XX QTOF with Acquity H-Class (HPLC), UV–vis absorption spectra of DPHIQs in MeCN (ca. 10⁻⁴ M) were recorded using a JASCO V-570 spectrophotometer equipped with integrating sphere. The samples were excited with 350 nm. Fluorescence IQE was measured using the integrating sphere upon samples excitation with 360 nm.

**Photocatalyst characterization.** Fourier transform infrared (FT-IR) spectra were recorded on Thermo Scientific Nicolet iD5 spectrometer. Powder X-ray diffraction

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**Fig. 7** Cyclic voltammograms of THIQ 1a, 6,7-dimethoxy-1,2,3,4-tetrahydrodioxosquinoline, chalcones 2a-d,i,l,m,q recorded in MeCN at the scan rate 50 mV s⁻¹ at room temperature (20–22 °C). Tetraethylammonium tetrafluoroborate in MeCN (0.1 M) was used as a supporting electrolyte. Scale bar corresponds to 10 μA.
Fig. 8 The results of DFT PBE0-D3 calculations. a Absolute energies of the frontier molecular orbitals (in eV vs. vacuum level) of THIQ 1a and chalcone 2a and their spatial representation. b Distribution of atomic charges (δ) in neutral molecules, THIQ radical cation [1a]+ and chalcone radical anion [2a]−. Mulliken spin population (in fraction of elementary charge) in THIQ radical cation [1a]+ and chalcone 2a radical anion [2a]−.

Fig. 9 A proposed sequence of chemical reactions—photocatalytic synthesis of DHPIQ. PC stands for photocatalyst.
Computational details. The DFT calculations for neutral molecules [1], [2a] and corresponding radical ions [1]+, [2a]+ were performed using three hybrid functionals: B3LYP (both with D3 dispersion correction), and CAMPBLYP. The basis was Dunning–Hay double zeta set with one d-type polarization function on nonhydrogen atoms and one p-type function on hydrogen. For nitrogen and oxygen, the basis set was additionally extended by a diffuse sp-shell. Unrestricted Kohn–Sham approach was used for [1]+ and [2a]+ to find the energy minima of their ground doublet states. Geometry optimization for all species was performed with the gradient convergence threshold of 1·10⁻⁶ Hartree/Bohr and the local energy minimum character of the optimized structures was confirmed by Hessian calculation. All calculations were carried out in theGAMESS (US) program package.[47,48].

Data availability. The data that support the findings of this study are available from the corresponding author upon request.

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Author contributions
B.K. conceived the idea, synthesized chalcones, performed photocatalytic experiments, purified and characterized DHPIQs, prepared a draft of the manuscript. K.O. performed photocatalytic experiments. A.M. performed DFT calculations. P.L. synthesized K-PHI photocatalyst, performed CV study, performed analysis of the gas headspace after the photocatalytic experiments using GC-TCD. W.L. scaled up the photocatalytic experi- ment, did experiments to investigate the mechanism, acquired UV–vis, PL spectra of DHPIQ in acetonitrile and IQE measurements. N.L. and M.A. contributed to the manuscript preparation. A.S. performed bromination of DHPIQ with NBS, suggested the mechanism of the photocatalytic reaction, finalized and submitted the manuscript and supplementary information.

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