

RESEARCH

Open Access



Highly stable quinacridone-based photocatalyst for selective thioether oxidation

Alessandro Iannini¹, Roberto Pio Destriere¹, Silvia Pezzola¹, Lorenzo Tommasi¹, Federica Sabuzi¹ and Pierluca Galloni^{1*}

*Correspondence:

Pierluca Galloni
galloni@scienze.uniroma2.it
¹Department of Chemical Science
and Technologies, University of
Rome Tor Vergata, via della ricerca
scientifica snc, Rome 00133, Italy

Abstract

Quinacridone derivatives have recently emerged as promising organic photocatalysts due to their availability, strong visible-light absorption and accessible redox properties; however, their broader application in homogeneous photocatalysis has been hindered by poor solubility and stability. Herein, we report an optimized and resource-efficient *N*-alkylation protocol that enables simple access to soluble quinacridone derivatives under significantly milder conditions than those commonly employed. With this approach, a new *N,N'*-substituted quinacridone derivative was prepared, fully characterized, and evaluated as an organic photocatalyst. This catalyst promotes efficiently the visible-light-driven aerobic oxidation of sulfides to sulfoxides in homogeneous conditions, operating at very low catalyst loading (0.1 mol %) and displaying excellent chemoselectivity, with no detectable overoxidation to sulfones. The reaction proceeds smoothly in HFIP using molecular oxygen as oxidant and shows broad tolerance across different substrates. Notably, the photocatalytic system remained active over multiple consecutive substrate addition cycles without requiring catalyst reloading and consistently maintained high sulfoxide yields, a level of robustness that contrasts with the degradation typically observed for quinacridone-based photocatalysts under analogous conditions.

1 Introduction

Visible-light photoredox catalysis is an established approach to access chemical reactivity that is difficult to achieve under thermal conditions, enabling redox transformations in mild reaction settings [1–4]. Historically, photoredox catalysis has been extensively developed using transition-metal complexes, whose well-defined photophysical and redox properties have laid much of the groundwork for the field [5, 6]. However, increasing efforts have focused on the development of organic photocatalysts [7], driven by the possibility of tailoring their structure and properties through rational molecular design [8, 9], as well as by concerns related to the cost and toxicity of commonly used transition-metals such as ruthenium and iridium [10].

In the search for efficient organic photocatalysts, quinacridone (QA) has emerged as a particularly appealing scaffold [11]. Indeed, QA is a cheap, non-toxic and commercially available industrial pigment [12] whose derivatives show strong visible-light absorption



© The Author(s) 2026. **Open Access** This article is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License, which permits any non-commercial use, sharing, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if you modified the licensed material. You do not have permission under this licence to share adapted material derived from this article or parts of it. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by-nc-nd/4.0/>.

and accessible redox potentials [11]. Those properties have recently renewed interest in its use beyond pigmentary applications toward functional materials and photocatalysis [13–15]. Despite these attractive features, the broader exploitation of QAs in catalysis has been historically limited by synthetic and processing constraints [16]. Indeed, the parent QA scaffold exhibits extremely low solubility, arising from strong π – π stacking and an extended intermolecular hydrogen-bonding network, as well documented by crystallographic and polymorphism studies [17]. Recent efforts have demonstrated that appropriate *N*-functionalization or peripheral substitution can overcome these limitations, enabling soluble QA derivatives that retain broad visible absorption as well as suitable redox properties for light-driven transformations [15, 18]. For instance, *N*-substituted and structurally modified QAs have been employed as organic semiconductors in electronic devices [19, 20], as photoactive components in hybrid photocatalytic systems for solar-driven transformations [21] and as homogeneous photocatalysts in visible-light-driven redox reactions [14]. However, the preparation of soluble *N*-substituted QA derivatives has traditionally relied on harsh conditions, including large excesses of alkylating agents, large excesses of nucleophilic or strong bases, prolonged reaction times, and demanding purifications [14, 22–27]. These aspects significantly impact the sustainability, scalability, and practical deployment of QA-based photocatalysts. Accordingly, improving the synthetic accessibility of soluble and functional QA derivatives remains a prerequisite not only for their broader adoption in photocatalysis, but also for their integration into emerging functional materials.

In parallel, the selective oxidation of sulfides to sulfoxides has emerged as a widely investigated reaction in visible-light photocatalysis, owing to its synthetic relevance and its frequent use as a benchmark reaction [28]. Numerous studies have shown that organic photocatalysts can effectively promote this transformation using molecular oxygen, offering a metal-free alternative to conventional approaches [14, 28–31]. Recent examples include purely organic molecular photocatalysts operating under visible light and ambient oxygen, such as phenothiazinone- or thioxanthone-based systems, which enable efficient sulfoxidation under mild conditions and low catalyst loadings [32, 33]. While good sulfoxide selectivity is often reported, these transformations typically require extended irradiation times, and aspects related to catalyst recovery and reuse are seldom explored [28, 32, 33]. Hybrid and immobilized organic photocatalysts can partially address recyclability issues, yet often require complex catalyst preparation or show reduced activity upon reuse [34–36]. Within this context, access to readily soluble QA derivatives with suitable redox properties allows the exploration of QA-based systems in light-driven sulfide oxidation, while also providing a framework to consider catalyst efficiency, reuse, and sustainability-related aspects.

In this work, we report the optimization of a simple and resource-efficient synthetic protocol for the preparation of soluble QA derivatives, broadly applicable to different alkylating agents, and its use to access a novel QA-based organic photocatalyst. The derivative was fully characterized and applied in the visible-light-driven oxidation of sulfides to sulfoxides, operating at very low catalyst loading (0.1 mol%) and allowing repeated substrate addition while maintaining high catalytic activity and excellent selectivity toward sulfoxide formation across a range of sulfide substrates.

2 Experimental

2.1 Materials and general methods

All commercial reagents and solvents were purchased from Sigma-Aldrich/Merck Life Science at the highest available purity grade and used as received unless otherwise stated. Quinacridone was purchased from TCI Chemicals. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was purchased from Fluorochem.

NMR spectra were recorded on a Bruker Avance 700 MHz spectrometer. ^1H NMR chemical shifts (δ) are reported in ppm and referenced to residual solvent signals (CDCl_3 : δ 7.26; CD_2Cl_2 : δ 5.32).

UV-vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Fluorescence spectra were acquired using an Agilent Cary Eclipse fluorimeter.

Electrochemical measurements were carried out using a PalmSens4 potentiostat and PS Trace 5.11 software for data analysis. Experiments were conducted using a three-electrode configuration with a glassy carbon working electrode (2 mm diameter), a platinum coil counter electrode, and an Ag/AgCl reference electrode. Measurements were performed in HFIP containing tetrabutylammonium perchlorate (TBAP 0.1 M) as supporting electrolyte.

Excited-state redox potentials $E^0(\text{M}^*/\text{M}^-)$ were estimated as follows:

$$E^0(\text{M}^*/\text{M}^-) = E^0(\text{M}/\text{M}^-) + E_{0-0}(\text{M} - \text{M}^*) = E^0(\text{M}/\text{M}^-) + hc/\lambda$$

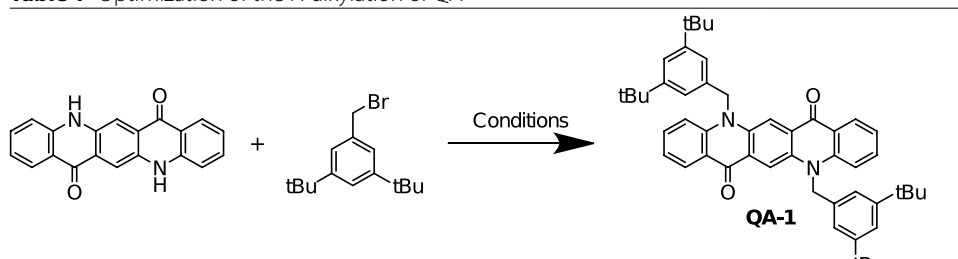
where M is the ground state, M^* the lowest excited state, $E^0(\text{M}/\text{M}^-)$ is the ground state electrochemical redox potential for the couple M/M^- and $E_{0-0}(\text{M}-\text{M}^*)$ is the 0–0 spectroscopic transition energy gap, calculated from the emission and absorption cross λ .

2.2 Gas chromatography analysis and quantification

Gas chromatography analyses were performed on a Shimadzu GC-2050 system equipped with a flame ionization detector (GC-FID). GC-FID was employed for reaction monitoring and quantitative determination of conversions and yields. Calibration curves for both sulfides and the corresponding sulfoxides were constructed by injecting solutions of known concentration prepared in the presence of decane as internal standard (Fig. S11–S26). The sulfoxide products used for calibration correspond to compounds previously synthesized and fully characterized by NMR spectroscopy in our earlier work [31].

2.3 Synthesis of *N,N'*-bis-(3,5-di-*tert*-butylbenzyl)quinacridone (QA-1, Table 1)

In a general procedure, QA (100 mg, 0.32 mmol), tetrabutylammonium bromide (TBAB, 26 mg, 0.08 mmol), and sodium hydroxide (256 mg, 6.4 mmol) were suspended in *N,N*-dimethylformamide (DMF, 10 mL). The mixture was stirred vigorously at 50 °C for 1 h, during which the color changed from bright red to deep blue. A solution of 3,5-di-*tert*-butylbenzyl bromide (272 mg, 0.96 mmol) in DMF (5 mL) was then added dropwise over 15 min, and the reaction mixture was stirred at 50 °C for an additional 5 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (DCM, 100 mL) and washed sequentially with brine (3 × 150 mL) and water (150 mL). The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (15% petroleum ether in DCM → DCM) and further purified by repeated

Table 1 Optimization of the N-alkylation of QA


Entry	Solvent	Base	Base Eq.	RX Eq.	TBAB Eq.	T (°C)	Time (h)	Yield ^a %
1	DMF	NaOH	20	6	0.25	50	6	71
2	DMF	NaOH	20	3	0.25	50	6	62
3	DMF	Li ₂ CO ₃	20	3	0.25	50	7 ^b	–
4	DMF	K ₂ CO ₃	20	3	0.25	50	7 ^b	3
5	DMF	K ₂ CO ₃	5	3	0.25	50	7 ^b	3
6	DMF	Cs ₂ CO ₃	20	3	0.25	50	6	77
7	DMF	Cs ₂ CO ₃	5	3	0.25	50	6	76
8	DMF	Cs ₂ CO ₃	5	3	–	50	6	71
9	DMF	Cs ₂ CO ₃	2	3	–	50	6	69

(a) Isolated yield. (b) The suspension of QA, base and TBAB was stirred for an additional hour

precipitation from chloroform/pentane to afford QA-1 as a bright orange solid (171 mg, 71%). ¹H NMR (700 MHz, CDCl₃), δ 8.76 (s, 2 H), δ 8.55 (d, J = 7.98, 2 H), δ 7.66 (t, J = 7.70, 2 H), δ 7.45 (d, J = 8.75, 2 H), δ 7.36 (s, 2 H), δ 7.26 (t, J = 7.39, 2 H), δ 7.08 (s, 4 H), δ 5.80 (s, 4 H), δ 1.25 (s, 36 H). ¹³C{¹H} NMR (700 MHz, CDCl₃), δ 178.2, δ 151.5, δ 143.0, δ 136.8, δ 134.5, δ 134.2, δ 127.1, δ 126.3, δ 121.8, δ 121.1, δ 119.4, δ 115.5, δ 114.0, δ 51.0, δ 34.7, δ 31.3. HRMS: *m/z* [M + H]⁺; calculated: 717.4420; found: 717.3976. UV-vis in DCM [λ_{max} , nm (ϵ , M^{−1}cm^{−1}): 511 (16100). UV-vis in HFIP [λ_{max} , nm (ϵ , M^{−1}cm^{−1}): 548 (9600).

2.4 Photocatalytic oxidation of thioethers

Photocatalytic reactions were carried out at room temperature in a homemade photoreactor consisting of a cardboard box internally lined with aluminum foil. The light source was an array of three green LEDs ($\lambda = 520$ nm, 30 W) mounted on a fan-cooled heat sink. Reactions were performed in 25 mL screw-cap vials sealed with rubber septa and placed at a fixed distance of 8 cm from the light source. Thioethers (0.075 mmol) were dissolved in a solution of decane 5 mM and QA-1 15 μ M in HFIP (5 mL). The solution was bubbled with molecular oxygen for 5 min prior to irradiation. Reactions were irradiated in an oxygen atmosphere for 1 h under strong stirring, unless otherwise stated.

2.5 Consecutive substrate addition experiments

Catalytic performance under consecutive substrate additions was evaluated using the standard photocatalytic conditions described above. After each reaction cycle (1 h), a fresh portion of thioether substrate (0.075 mmol) was added directly to the reaction mixture without additional photocatalyst. Reaction progress was monitored by UV–vis spectroscopy and by GC-FID analysis at the end of each cycle.

2.6 DFT calculations

DFT calculations have been carried out using Gaussian 16 rev. A. 03 [37]. Geometry and frequency optimizations have been performed in the vacuum, and in DCM using SMD as continuum solvation model. Computations were carried out applying B3LYP as functional, with 6-31G+ (d, p) as basis set. Single point TD-DFT calculations have been performed with 6-311G+(d, p) basis set in gas-phase and solvent, using 20 states for each computational condition. Hessian analysis indicates the absence of imaginary frequencies.

3 Results and discussion

3.1 Optimization of the synthesis of QA-1

To address the synthetic limitations of QA, an improved *N*-alkylation protocol was developed and applied to the synthesis of a new *N,N'*-substituted QA derivative, in which bulky substituents were introduced to enhance solubility by reducing intermolecular hydrogen bonding and π - π stacking. To this end, 3,5-di-*tert*-butylbenzyl bromide was selected as a model alkylating agent, also providing a suitable platform for the optimization of the reaction conditions. As anticipated above, the synthesis of soluble *N*-substituted QA derivatives has traditionally relied on harsh reaction conditions, typically involving large excesses of nucleophilic bases and alkyl halides [14, 22–24]. Only a limited number of alternative approaches have been reported, often at the expense of prolonged reaction times or elevated temperatures [38, 39].

Starting from a protocol previously employed in our laboratory [14], we systematically investigated the influence of key reaction parameters in the synthesis of **QA-1**, including the nature and equivalents of the base, the amount of alkylating agent, and the use of tetrabutylammonium bromide (TBAB), commonly added as phase-transfer catalyst to address the inherently heterogeneous nature of the reaction. The outcome of this optimization study is summarized in

Such study revealed a marked sensitivity of the reaction to both, the nature of the base and the loading of the alkylating agent. In this context, reaction outcomes are discussed in terms of isolated yields, as the disubstituted compound was consistently obtained as the main product. When sodium hydroxide was employed as a base, good yields were achieved, as expected (entry 1); however, decreasing the amount of alkyl halide resulted in a noticeable decrease in yield, confirming the dependence on reagent excess under these conditions, plausibly due to competing nucleophilic substitution by the hydroxide anion (entry 2). When sodium hydroxide was replaced with non-nucleophilic alkali metal carbonates, lithium carbonate was found to be ineffective (entry 3), while potassium carbonate afforded only trace amounts of product even when used in large excess (entries 4–5). In these cases, the suspension was stirred for an additional hour prior to the addition of the alkylating agent to promote a more effective deprotonation of QA under heterogeneous conditions; however, the typical color change from red to deep blue observed during QA deprotonation did not take place. These observations are consistent with the limited solubility of these salts in DMF, which restricts the efficient generation of the reactive QA anion. As anticipated from previous reports [24, 38, 39], switching to cesium carbonate led to a substantial improvement in reaction performance (entries 6–9). Indeed, high yields were consistently obtained using only three equivalents of alkylating agent (entry 6), while also allowing a reduction in base loading

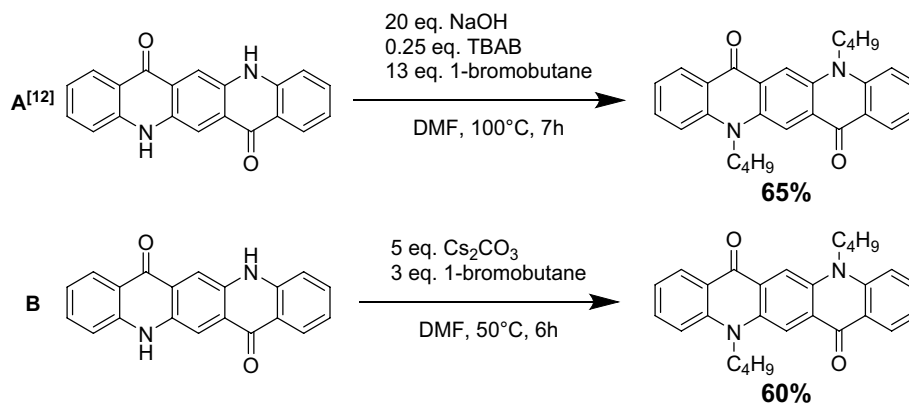
(entries 7–9). Notably, the transformation proceeded reliably at moderate temperature (50 °C) and on shorter timescales, providing a set of conditions that balance efficiency with operational simplicity. The reaction was also found to proceed in the absence of TBAB (entries 8–9), indicating that phase-transfer catalysis is not strictly required for product formation. Nevertheless, the presence of TBAB resulted in a faster transition from the deep blue solution of the deprotonated QA to the characteristic orange color of the alkylated product, suggesting a favorable effect on the reaction kinetics that was not further investigated. The optimized conditions were further applied to the synthesis of *N,N'*-dibutylquinacridone (DBQA), leading to a marked improvement of the sustainability of the reaction (Scheme 1).

Interestingly, under these alkylation conditions, the formation of monosubstituted QA derivatives was also observed. In the synthesis of **QA-1**, the corresponding monosubstituted product **QA-2** could be isolated in low yields (1–6%) (Fig. S4). Likewise, when the same optimized protocol was applied to the preparation of DBQA, the monoalkylated derivative (MBQA) was obtained in appreciable amounts (21% yield). Notably, monosubstituted QA derivatives may represent valuable organic photocatalysts, as retention of the N-H moiety in such compounds may provide a reactive handle for hydrogen atom transfer (HAT) processes.

3.2 Characterization of QA-1

The novel QA derivative obtained from the optimized *N*-alkylation protocol was characterized by optical and electrochemical techniques. UV–vis spectroscopy revealed that **QA-1** exhibits a broad absorption band in the visible region, with molar extinction coefficients on the order of $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (Fig. S5). Both absorption and fluorescence measurements have shown pronounced solvent-dependent behavior, with a clear red shift observed when moving from dichloromethane to HFIP (Figs. S5–S6). This trend indicates a strong sensitivity of the electronic transitions to the surrounding medium, consistent with significant solvent–chromophore interactions.

Electrochemical characterization by cyclic voltammetry in HFIP revealed redox features consistent with those reported for other *N*-substituted QA derivatives. In comparison with DBQA, commonly employed as a benchmark in this family, **QA-1** exhibits closely similar ground-state reduction and oxidation potentials ($E_{\text{red}} = -0.87 \text{ V}$ and $E_{\text{ox}} = +0.98 \text{ V}$ vs. Ag/AgCl for **QA-1**, compared to $E_{\text{red}} = -0.85 \text{ V}$ and $E_{\text{ox}} = +0.94 \text{ V}$ vs. Ag/AgCl for DBQA [14]). The excited-state redox properties are likewise comparable,



Scheme 1 Synthesis of DBQA in optimized conditions

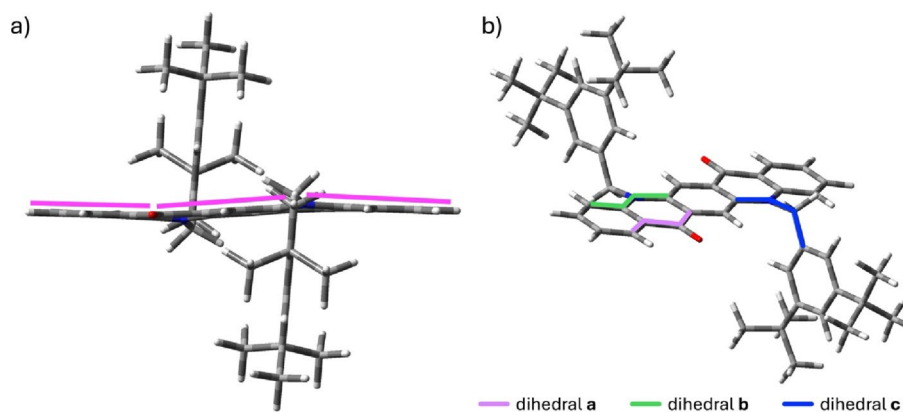


Fig. 1 Optimized geometry of QA1 (B3LYP/6-311G+dp CPCM DCM solvent) analyzing the skeleton features and dihedral angles

Table 2 Analysis of the dihedral angles in compound geometry moving from vacuum to DCM as solvent (B3LYP 6-31G+(d, p) SMD). Features were declared in Fig. 2

DIHEDRAL	GAS-PHASE	SOLVENT-PHASE
a	176.08	173.96
b	172.70	176.49
c	-92.02	-92.82

with nearly identical excited-state reduction ($E^*_{\text{red}} \approx +1.34$ V vs. +1.33 V vs. Ag/AgCl) and oxidation potentials ($E^*_{\text{ox}} \approx -1.23$ V vs. -1.24 V vs. Ag/AgCl). In light of the established performance of DBQA in visible-light-driven oxidative transformations, these data support **QA-1** as well suited to operate under analogous photocatalytic condition.

DFT calculation has been performed to analyze the geometry and electronic **QA-1** features.

B3LYP and CAM-B3LYP have been selected as functional considering its ability to foresee reliably ground and excited states of organic compounds [40], both in gas- and solvent phase. Calculations were performed with 6-31G+(d, p) or 6-311G+(d, p) basis-set, using the polarizable conductor calculation model solvation (CPCM) in dichloromethane (DCM) as solvent. The absence of imaginary frequencies in Hessian matrix for gas- and solvent- phase indicated that all the obtained geometries are the energy minima points of each conformation. Firstly, molecules geometries were analyzed both in gas-phase and in solvent (DCM), Fig. 1.

In the most stable conformer, the two aromatic group of the substituents are in opposite position, avoiding the π - π staking and increasing solubility. The aromatic core of quinacridone is not flat and displays a zig-zag shape (Fig. 1a). In particular, the nitrogen atom displays sp^2 character due to the delocalization of the electron pair on the aromatic ring. However, it is not completely planar, as can be seen from the characteristic dihedral angles of the molecule. Analyzing the deviation of the quinacridone core from planarity, dihedral angles variation from vacuum to solvent were analyzed (Fig. 1b; Table 2).

The geometry calculation shows a significant variation moving from vacuum to solvent in a-b dihedral angles. The solvation induces appreciable changes, suggesting a partial bend of the quinacridone core upon solubilization, while dihedral c variation was limited.

Frontiers molecular orbitals features were also investigated to analyze the effects of the substituents on the electronic properties of quinacridone group. Highest Occupied Molecular Orbital (HOMO) and Lowest Occupied Molecular Orbital (LUMO) were examined in gas-phase and in DCM, Fig. 2.

Solvent presence seems not to affect HOMO-LUMO distribution: in both cases orbitals are mainly centered on QA skeleton. HOMOs are delocalized over the QA core, also including the benzylic Csp³ groups. In LUMOs such moiety was not involved anymore.

HOMO-LUMO gap in DCM is about 2.9 eV, comparable with the experimental value ($E_{00} = 2.4$ eV).

3.3 QA-1 mediated aerobic photooxidation of sulfides

To evaluate the performance of QA-1 in photocatalytic sulfide oxidation and to identify suitable reaction conditions, methyl *p*-tolyl sulfide was selected as a model substrate. Thus, a preliminary screening was conducted by systematically varying key reaction parameters, including the nature of the solvent, the photocatalyst loading and the atmosphere of the reaction. The results of this screening are summarized in Table 3.

The screening shows that the oxidation of methyl *p*-tolyl sulfide proceeds efficiently under visible-light irradiation only in a narrow set of conditions. In HFIP, quantitative formation of the corresponding sulfoxide was achieved within 1 h under an oxygen atmosphere, even at catalyst loadings as low as 0.1 mol%, demonstrating that the transformation can be sustained at very low photocatalyst concentrations without loss of efficiency (entries 1,4,5). Additionally, extending the reaction time up to 16 h did not result in detectable overoxidation (entry 11). By contrast, the reaction was largely suppressed in a variety of alternative solvents, including nitriles, chlorinated solvents, acetone, and DME, where only trace amounts or negligible yields of sulfoxide were observed (entries 2–3, 6–7,9–10). These results highlight the specific role of HFIP, whose high polarity and strong hydrogen-bond-donating character are known to strongly influence photochemical oxidations involving polar or radical intermediates [41]. In the present system, HFIP likely contributes not only to reaction efficiency but also to the exclusive formation of the corresponding sulfoxide, enhancing selectivity by plausibly disfavoring pathways

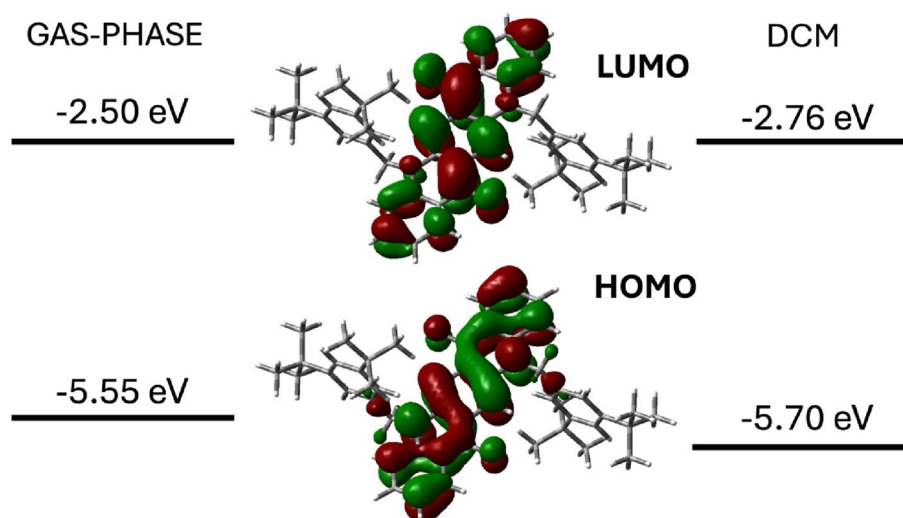
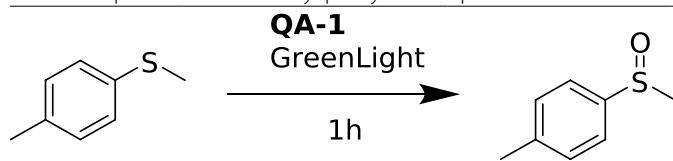


Fig. 2 HOMO-LUMO analysis of QA-1 in the vacuum and in solvent (DCM). Geometry was optimized with B3LYP functional, 6-31G+(d, p) basis set and CPCM solvation model

Table 3 Optimization of methyl *p*-tolyl sulfide photooxidation



QA-1
GreenLight
1h

Entry	QA-1 (%mol) %	Solvent	Atmosphere	Yield
1	1	HFIP	O ₂	> 99%
2	1	Butyronitrile	O ₂	-
3	1	Benzonitrile	O ₂	Trace
4	0.5	HFIP	O ₂	> 99%
5	0.1	HFIP	O ₂	> 99%
6	0.1	DCM	O ₂	trace
7	0.1	DMF	O ₂	1%
8	0.1	HFIP	Air	70%
9	0.1	Acetone	O ₂	trace
10	0.1	Acetonitrile	O ₂	trace
11 ^a	0.1	HFIP	O ₂	> 99%

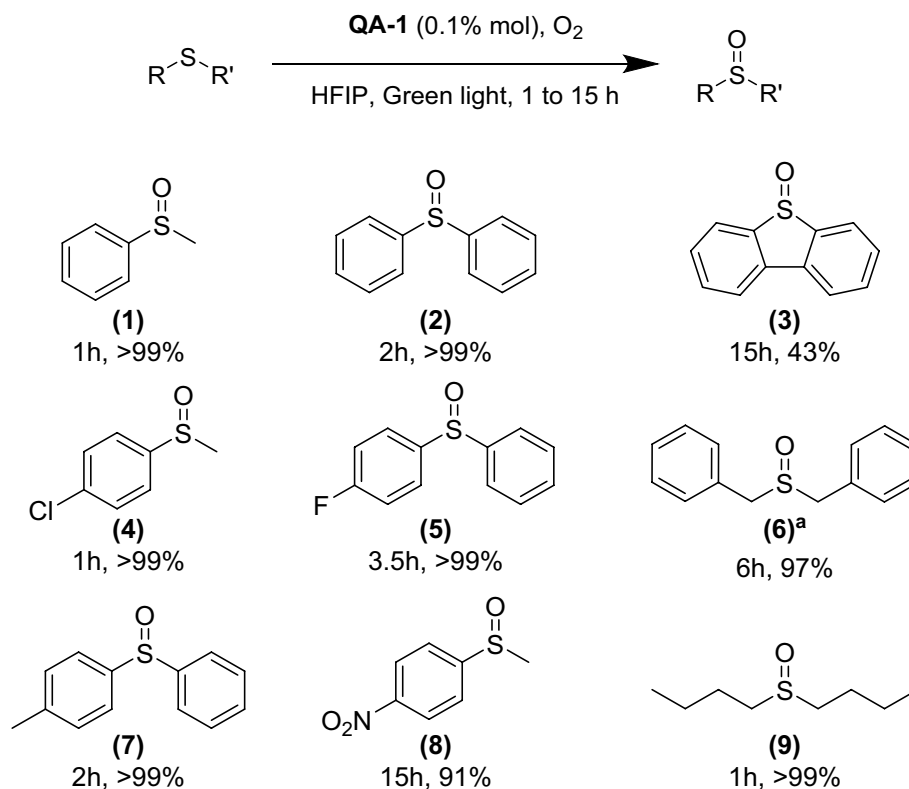
Reaction conditions: [substrate] = 15 mM in 5 mL solvent under an air or oxygen atmosphere, using a photoreactor equipped with green LEDs ($\lambda = 520$ nm, 30 W), with the reaction mixture placed at a fixed distance of 8 cm from the light source

a) The reaction time was extended to 16 h

leading to overoxidation. Moreover, as supported by electrochemical evidence [14], HFIP can modulate the redox properties of QA derivatives, thereby facilitating photo-induced electron transfer processes under the applied conditions. When molecular oxygen was replaced by air, the reaction still proceeded to significant conversion (entry 9), although longer reaction times were required to reach completion. Overall, these data confirm HFIP as a suitable medium for the photocatalytic oxidation of methyl *p*-tolyl sulfide with QA-1, enabling high efficiency and exclusive sulfoxide formation at very low catalyst loadings.

Under the optimized conditions identified with the model substrate, the generality of the protocol was evaluated across a representative set of sulfides (Scheme 2).

Aryl methyl sulfides bearing electron-neutral or electron-donating substituents were smoothly converted into the corresponding sulfoxides, typically affording quantitative yields within 1 h (1, Table 3). Halogen substitution on the aryl moiety was also well tolerated, as exemplified by the chloro-substituted derivative (4), which delivered the desired product in quantitative yield. Diarylic sulfides proved to be viable substrates as well, although longer irradiation times were required to reach excellent results (2,5,7). A distinct behavior was observed for heteroaryl sulfides such as thianthrene (3), which slowly underwent oxidation to a limited extent upon prolonged irradiation. Substrates bearing strongly electron-withdrawing groups exhibited a pronounced decrease in reactivity (8), indicating a sensitivity of the reaction to electronic effects at sulfur. Notably, benzylic (6) and aliphatic (9) sulfides were successfully oxidized, with simple dialkyl sulfides undergoing rapid and essentially quantitative conversion. Across the examined substrates, the reaction consistently proceeded with full chemoselectivity, and no overoxidation to the corresponding sulfones was detected, even upon extended irradiation times.



Scheme 2 Substrate scope of QA-1 mediated sulfide photooxidation. **a** NMR yield

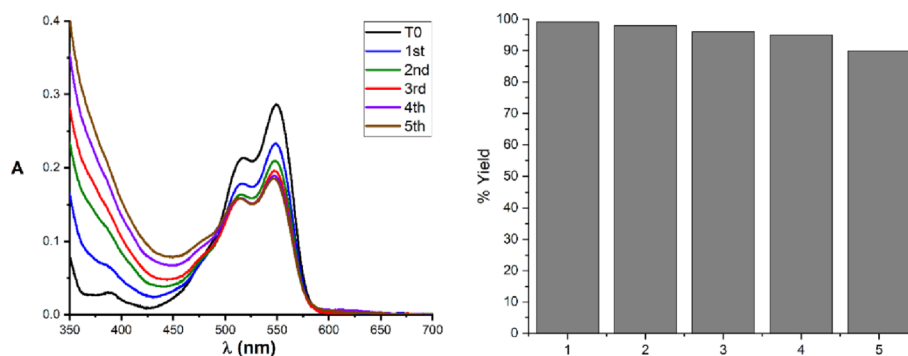
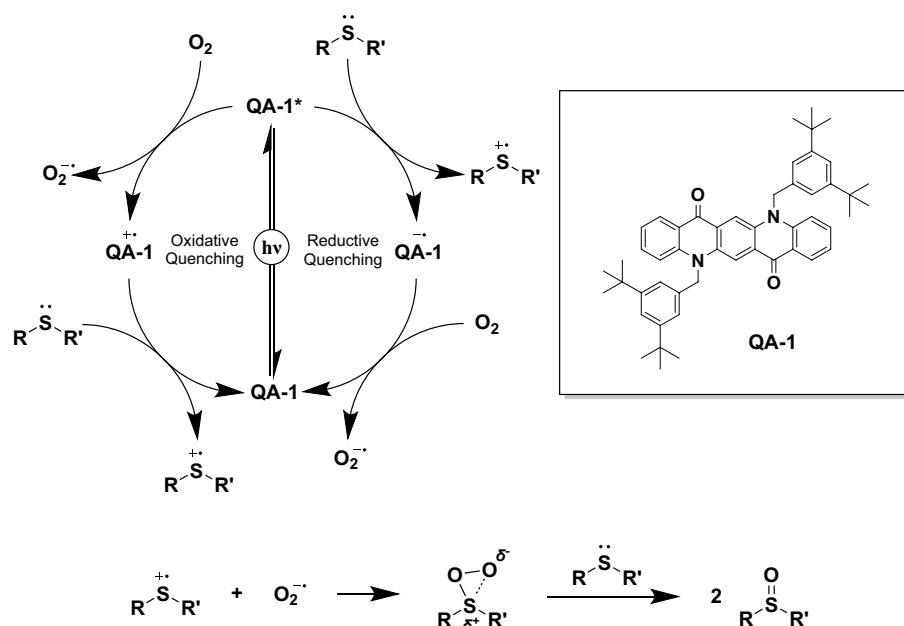


Fig. 3 On the left: absorption spectra of the reaction mixture before (black line) and after every cycle. On the right: % Yield of methyl *p*-tolyl sulfoxide after each cycle

3.4 Consecutive substrate addition experiments

To gain insight into the behavior of the photocatalytic system under prolonged operation, consecutive reaction cycles were performed by sequential addition of fresh methyl *p*-tolyl sulfide to the same photocatalyst solution. Under these conditions, the oxidation was repeated over five 1 h cycles, while monitoring both the reaction outcome and the spectrophotometric response of the photocatalyst. As illustrated in Fig. 1, high sulfoxide yields were maintained throughout the successive cycles, with only a moderate decrease observed after repeated substrate recharging.

By monitoring the UV–vis absorption spectra of the reaction mixture, decrease in the intensity of the main visible absorption band is observed after the first cycle, followed by a more gradual attenuation in subsequent runs. This behavior suggests that an initial loss



Scheme 3 Mechanism hypothesis for the QA-1 mediated aerobic photooxidation of sulfides [14, 31]

of active catalyst concentration occurs early during operation, whereas the formation of photodegradation products appears to be limited. Overall, these results indicate that the system operates efficiently over multiple substrate additions, combining sustained catalytic activity with reasonable photochemical stability. Although a slight loss of active catalyst is observed, the ability to maintain high yields across repeated cycles highlights a level of operational stability that is unprecedented for quinacridone-based photocatalysts in homogeneous photocatalysis. To note, the increase in absorbance observed in the region below 400 nm is ascribed to the increased concentration of methyl *p*-tolyl sulfoxide in each cycle.

3.5 Scavenging experiments

Preliminary mechanistic information was obtained through scavenging experiments (Fig. S28). The addition of 1,4-dimethoxybenzene (DMB), employed as a radical cation scavenger, led to a significant suppression of product formation, supporting the involvement of sulfur-centered radical cation intermediates generated upon photoinduced electron transfer. A comparable decrease in reactivity was observed upon addition of benzoquinone (BQ), consistent with the participation of superoxide anion radical formed upon reduction of molecular oxygen. In contrast, the limited effect observed in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) suggests that singlet oxygen does not play a major role under the applied conditions. Overall, the scavenging experiments are consistent with a reaction pathway closely related to that previously proposed for DBQA [14], involving photoinduced electron transfer followed by oxygen-mediated steps (Scheme 3). Based on the experimental and mechanistic studies, as well as our previous work [14], the most plausible pathway involves oxidative quenching by molecular oxygen after the photoexcitation of the catalyst. Further mechanistic studies will be required to confirm the relative contribution of the different pathways involved.

4 Conclusions

In this work, a user-friendly and more sustainable *N*-alkylation protocol was developed to access soluble QA derivatives, enabling the preparation of a new photocatalyst. Such organic dye proved effective in the visible-light-driven oxidation of sulfides to sulfoxides using molecular oxygen, operating at very low catalyst loading and displaying broad substrate tolerance and excellent chemoselectivity. Notably, the catalytic system was shown to remain operative over multiple substrate additions, maintaining high product yields despite a slight gradual decrease in active catalyst concentration. Remarkably, this behavior contrasts with the rapid deactivation commonly observed for QA-based photocatalysts under oxidative conditions and highlights a good level of operational stability. Mechanistic insights obtained from scavenging experiments are consistent with a photo-induced electron-transfer pathway involving sulfur-centered radical cations and oxygen-derived reactive species, in agreement with mechanisms previously proposed for related systems.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1007/s44344-026-00041-y>.

Supplementary Material 1.

Author contributions

Conceptualization, F.S. and P.G.; methodology, A.I., S.P., P.G. and F.S.; validation, F.S., A.I., R.P.D., L.T. and P.G.; formal analysis, A.I., S.P. and P.G.; investigation, A.I., R.P.D., L.T. and S.P.; resources, P.G. and F.S.; data curation, A.I., R.P.D. and P.G.; writing—original draft preparation, A.I. and R.P.D.; writing—review and editing, F.S., P.G.; supervision, F.S. and P.G.; project administration, P.G.; funding acquisition, P.G. and F.S. All authors have read and agreed to the published version of the manuscript.

Funding

Authors thank MUR Dipartimento di Eccellenza 2023-27 X-CHEM project “eXpanding CHEMistry: implementing excellence in research and teaching” for financial support. P.G. and S.P. thank Italian MUR grant (PRIN2022KPK8WM PROMETEO); F.S., P.G. and A.I. thank NANOCARB project (High-surface-area carbon nanostructures as electronic transducers for artificial photosynthesis) – Cascade Call, funded by PNRR, MISSION 4 - Network 4 Energy Sustainable Transition (CUP B53C22004060006).

Data availability

The data sets used and/or analyzed during current study available for the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare no competing interests.

Received: 16 February 2026 / Accepted: 5 June 2026

Published online: 17 June 2026

References

1. Romero NA, Nicewicz DA. Organic Photoredox Catalysis. *Chem Rev*. 2016;116:10075–166. <https://doi.org/10.1021/acs.chemrev.6b00057>.
2. Hossain MM, Shaikh AC, Kaur R, Giannetti TL. Red Light–Blue Light Chromoselective C(sp²)–X Bond Activation by Organic Helicenium-Based Photocatalysis. *J Am Chem Soc*. 2024;146:7922–30. <https://doi.org/10.1021/jacs.3c13380>.
3. Singh P, Shaikh AC. Red Light–Blue Light Chromoselective C(sp²)–X Bond Activation by Organic Helicenium-Based Photocatalysis *Chem Comm*. 2023;59:11615–30. <https://doi.org/10.1039/D3CC03855F>.
4. McAtee RC, McClain EJ, Stephenson CRJ. Illuminating Photoredox Catalysis. *Trends Chem*. 2019;1:111–25. <https://doi.org/10.1016/j.trechm.2019.01.008>.

5. Shaw MH, Twilton J, MacMillan DWC. Photoredox Catalysis in Organic Chemistry. *J Org Chem*. 2016;81:6898–926. <https://doi.org/10.1021/acs.joc.6b01449>.
6. Prier CK, Rankic DA, MacMillan DWC. Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem Rev*. 2013;113:5322–63. <https://doi.org/10.1021/cr300503r>.
7. Lee Y, Kwon MS. Emerging Organic Photoredox Catalysts for Organic Transformations. *Eur J Org Chem*. 2020;2020:6028–43. <https://doi.org/10.1002/ejoc.202000720>.
8. Rolka AB, Koenig B. Dearomative Cycloadditions Utilizing an Organic Photosensitizer: An Alternative to Iridium Catalysis. *Org Lett*. 2020;22:5035–40. <https://doi.org/10.1021/acs.orglett.0c01622>.
9. Arias-Rotondo DM, McCusker JK. The photophysics of photoredox catalysis: a roadmap for catalyst design. *Chem Soc Rev*. 2016;45:5803–20. <https://doi.org/10.1039/C6CS00526H>.
10. Ravelli D, Fagnoni M, Albini A. Photoorganocatalysis. What for? *Chem Soc Rev*. 2012;42:97–113. <https://doi.org/10.1039/C2CS35250H>.
11. Rossin E, Yang Y, Chirico M, Rossi G, Galloni P, Sartorel A. Quinacridone dyes: versatile molecules and materials for photo- and photoelectrochemical processes. *Energy Adv*. 2024;3:1894–904. <https://doi.org/10.1039/D4YA00273C>.
12. Labana SS, Labana LL. Quinacridones. *Chem Rev*. 1967;67:1–18. <https://doi.org/10.1021/cr60245a001>.
13. Apaydin DH, Glowacki ED, Portenkirchner E, Sariciftci NS. Direct Electrochemical Capture and Release of Carbon Dioxide Using an Industrial Organic Pigment: Quinacridone. *Angew Chem Int Ed*. 2014;53:6819–22. <https://doi.org/10.1002/anie.201403618>.
14. Forchetta M, Baia V, Sabuzi F, Conte V, Galloni P. Synthesis of Soluble Quinacridone Photocatalysts for the Homogeneous Oxidation of Thioethers. *Eur J Org Chem*. 2023;26:e202300523. <https://doi.org/10.1002/ejoc.202300523>.
15. Shen L, Zhang S, Ding H, Niu F, Chu Y, Wu W, et al. Pure organic quinacridone dyes as dual sensitizers in tandem photoelectrochemical cells for unassisted total water splitting. *Chem Commun*. 2021;57:5634–7. <https://doi.org/10.1039/D1CC01570B>.
16. Preda G, Aricò A, Botta C, Ravelli D, Merli D, Mattiello S, et al. Activation of Solid-State Emission and Photostability through Molecular Confinement: The Case of Triptycene-Fused Quinacridone Dyes. *Org Lett*. 2023;25:6490–4. <https://doi.org/10.1021/acs.orglett.3c02093>.
17. Paulus EF, Leusen FJJ, Schmidt MU. Crystal structures of quinacridones. *CrystEngComm*. 2007;9:131–43. <https://doi.org/10.1039/B613059C>.
18. Jia T, Huang S, Bohra H, Wang M. Examining derivatives of quinacridone, diketopyrrolopyrrole and indigo as the visible-light organic photocatalysts for metal-free atom transfer radical polymerization. *Dyes Pigm*. 2019;165:223–30. <https://doi.org/10.1016/j.dyepig.2019.01.060>.
19. Saadi D, Mayr F, Yumusak C, Wielend D, Cobet M, Kahraman B, et al. N,N'-Substituted quinacridones for organic electronic device applications. *Mater Adv*. 2023;4:2214–25. <https://doi.org/10.1039/D2MA01010K>.
20. Xu Z-X, Xiang H-F, Roy VAL, Chui SS-Y, Wang Y, Lai PT, et al. Organic field-effect transistors fabricated with N,N'-substituted dialkyl-1,3,8,10-tetramethylquinacridone compounds. *Appl Phys Lett*. 2009;95:123305. <https://doi.org/10.1063/1.3233961>.
21. Yang Y, Nalesso M, Basagni A, Bonetto R, Signorini R, Agnoli S, et al. Photocatalytic oxidation of glycerol with red light employing quinacridone sensitized TiO₂ nanoparticles. *J Mater Chem A*. 2025;13:18436–44. <https://doi.org/10.1039/D5TA01970B>.
22. Pho TV, Zalar P, Garcia A, Nguyen T-Q, Wudl F. Electron injection barrier reduction for organic light-emitting devices by quinacridone derivatives. *Chem Commun*. 2009;46:8210–2. <https://doi.org/10.1039/C0CC01596B>.
23. Liu P-H, Tian H, Chang C-P. Luminescence properties of novel soluble quinacridones. *J Photochem Photobiol A-Chem*. 2000;137:99–104. [https://doi.org/10.1016/S1010-6030\(00\)00361-0](https://doi.org/10.1016/S1010-6030(00)00361-0).
24. Jia J, Li Y, Wang W, Luo C, Han L, Li Y, et al. New quinacridone derivatives: Structure-function relationship exploration to enhance third-order nonlinear optical responses. *Dyes Pigm*. 2017;146:251–62. <https://doi.org/10.1016/j.dyepig.2017.06.006>.
25. Pushkina LL, Shelyapin OP, Shein SM. Synthesis of N,N'-dialkylquinacridones under the conditions of heterogeneous catalysis. *Chem Heterocycl Compd*. 1985;21:792–5. <https://doi.org/10.1007/BF00519149>.
26. Wang J, Zhao Y, Dou C, Sun H, Xu P, Ye K, et al. Alkyl and Dendron Substituted Quinacridones: Synthesis, Structures, and Luminescent Properties. *J Phys Chem B*. 2007;111:5082–9. <https://doi.org/10.1021/jp068646m>.
27. Ye K, Wang J, Sun H, Liu Y, Mu Z, Li F, et al. Supramolecular Structures and Assembly and Luminescent Properties of Quinacridone Derivatives. *J Phys Chem B*. 2005;109:8008–16. <https://doi.org/10.1021/jp0444767>.
28. Skolia E, Gkizis PL, Kokotos CG. Aerobic Photocatalysis: Oxidation of Sulfides to Sulfoxides. *ChemPlusChem*. 2022;87:e202200008. <https://doi.org/10.1002/cplu.202200008>.
29. Ji W-S, Li X-L, Huang Q-S, Xu J-B, Li X, Gao F. Selective Catalytic Aerobic Photooxidation of Thioethers to Sulfoxides. *Synlett*. 2025;36:1723–8. <https://doi.org/10.1055/a-2577-7703>.
30. Korobkov SM, Birin KP, Tsivadze AY. Supremely high turnover numbers with a simple porphyrin photosensitizer: Kinetic and mechanistic insights into the oxidation of sulfides with singlet oxygen. *J Catal*. 2025;445:116008. <https://doi.org/10.1016/j.jcat.2025.116008>.
31. Forchetta M, Sabuzi F, Stella L, Conte V, Galloni P. KuQuinone as a Highly Stable and Reusable Organic Photocatalyst in Selective Oxidation of Thioethers to Sulfoxides. *J Org Chem*. 2022;87:14016–25. <https://doi.org/10.1021/acs.joc.2c01648>.
32. Spyropoulou CK, Skolia E, Flesariu DF, Zissimou GA, Gkizis PL, Triandafillidi I, et al. 3H-Phenothiazin-3-one: A Photocatalyst for the Aerobic Photochemical Oxidation of Sulfides to Sulfoxides. *Adv Synth Catal*. 2023;365:2643–50. <https://doi.org/10.1002/adsc.202300516>.
33. Ye C, Zhang Y, Ding A, Hu Y, Guo H. Visible light sensitizer catalyzed highly selective photo oxidation from thioethers into sulfoxides under aerobic condition. *Sci Rep*. 2018;8:2205. <https://doi.org/10.1038/s41598-018-20631-7>.
34. Jiménez-Almaraz A, López-Magano A, Marzo L, Cabrera S, Mas-Ballester R, Alemán J. Imine-Based Covalent Organic Frameworks as Photocatalysts for Metal Free Oxidation Processes under Visible Light Conditions. *ChemCatChem*. 2019;11:4916–22. <https://doi.org/10.1002/cctc.201901061>.
35. Lang X, Zhao J, Chen X. Visible-Light-Induced Photoredox Catalysis of Dye-Sensitized Titanium Dioxide: Selective Aerobic Oxidation of Organic Sulfides. *Angew Chem Int Ed*. 2016;55:4697–700. <https://doi.org/10.1002/anie.201600405>.

36. Tchuiteng Kouatchou JA, Farah J, Malloggi F, Gravel E, Doris E. Selective Photocatalytic Oxidation of Thioethers to Sulfoxides Mediated by a Carbon Nanotube-Porphyrin Nanohybrid. *ChemCatChem*. 2024;16:e202400685. <https://doi.org/10.1002/cctc.202400685>.
37. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Petersson GA, Nakatsuji H, Li X, Caricato M, Marenich AV, Bloino J, Janesko BG, Gomperts R, Mennucci B, Hratchian HP, Ortiz JV, Izmaylov AF, Sonnenberg JL, Williams-Young D, Ding F, Lipparini F, Egidi F, Goings J, Peng B, Petrone A, Henderson T, Ranasinghe D, Zakrzewski VG, Gao J, Rega N, Zheng G, Liang W, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Throssell K, Montgomery JA, Peralta J, Ogliaro JE, Bearpark F, Heyd MJ, Brothers JJ, Kudin EN, Staroverov KN, Keith VN, Kobayashi TA, Normand R, Raghavachari J, Rendell K, Burant AP, Iyengar JC, Tomasi SS, Cossi J, Millam M, Klene JM, Adamo M, Cammi C, Ochterski R, Martin JW. R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D.J. Gaussian, Inc.: Wallingford CT, 2016.
38. Jia J, Hu C, Cui Y, Li Y, Wang W, Han L, et al. Design and synthesis of a series of N-donor quinacridone derivatives with novel nonlinear optical properties. *Dyes Pigm.* 2018;149:843–50. <https://doi.org/10.1016/j.dyepig.2017.11.056>.
39. Zidan TA, El-Khlawany LM, El-Menawy EM. Impact of film thickness on the structural and optical properties of thermally deposited N,N-dimethylquinacridone films. *J Mol Struct.* 2021;1242:130825. <https://doi.org/10.1016/j.molstruc.2021.130825>.
40. Guido CA, Knecht S, Kongsted J, Mennucci B. Benchmarking Time-Dependent Density Functional Theory for Excited State Geometries of Organic Molecules in Gas-Phase and in Solution. *J Chem Theory Comput.* 2013;9:2209–20. <https://doi.org/10.1021/ct400021c>.
41. Motiwala HF, Armaly AM, Cacioppo JG, Coombs TC, Koehn KRK, Norwood VMI, et al. HFIP in Organic Synthesis. *Chem Rev.* 2022;122:12544–747. <https://doi.org/10.1021/acs.chemrev.1c00749>.

Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.