



Photoredox Catalysis Hot Paper

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Chromoselective Synthesis of Sulfonyl Chlorides and Sulfonamides with Potassium Poly(heptazine imide) Photocatalyst

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Abstract: Among external stimuli used to promote a chemical reaction, photocatalysis possesses a unique one—light. Photons are traceless reagents that provide an exclusive opportunity to alter chemoselectivity of the photocatalytic reaction varying the color of incident light. This strategy may be implemented by using a sensitizer capable to activate a specific reaction pathway depending on the excitation light. Herein, we use potassium poly(heptazine imide) (K-PHI), a type of carbon nitride, to generate selectively three different products from *S*-arylthioacetates simply varying the excitation light and otherwise identical conditions. Namely, arylchlorides are produced under UV/purple, sulfonyl chlorides with blue/white, and diaryldisulfides at green to red light. A combination of the negatively charged polyanion, highly positive potential of the valence band, presence of intraband states, ability to sensitize singlet oxygen, and multi-electron transfer is shown to enable this chromoselective conversion of thioacetates.

Introduction

Sulfur is one of the earliest known elements, and its healing power was known to the Greeks since antiquity. Nowadays, sulfur-containing compounds are widely used as pharmaceuticals and agrochemicals next to their role in material science and food industries.^[1] Ever since Prontosil became the basis of antibiotics (for which Gerhard Domagk was awarded with the Nobel Prize in 1939),^[2] sulfonamide-containing drugs turned out to be one of the greatest

breakthroughs in the history of medicine, and the sulfonamide linkage is an omnipresent motif in numerous biologically active compounds (Figure S1).^[3] Sulfa drugs are broadly used for the treatment of a wide variety of indications, such as high blood pressure, diabetes, bacterial infections, and even human immunodeficiency due to HIV.^[4]

In fact, intense efforts have been focused on the development of methods for sulfonyl amides synthesis.^[5] Traditionally, formation of sulfonyl amide groups is the endpoint of a synthetic route, in which other sulfonyl derivatives serve as a point for derivatization. The common strategy for the synthesis of complex sulfonamides is the addition-elimination process, and sulfonyl chlorides are the most common substrates in this type of reactions (Figure 1 a).^[6] Apart from the main application in the synthesis of sulfonyl amides, sulfonyl chlorides are commonly used precursors for several important functional groups including sulfonate esters, sulfones, and sulfonic acids.^[7] In photocatalysis, upon one-electron reduction, they give alkyl- and aryl radicals, which are valuable intermediates in organic synthesis.^[8]

Although many methodologies have been reported for the synthesis of sulfonyl chlorides, their synthesis is still largely dominated by the dehydration of sulfonic acids with strongly oxidizing and unselective reagents, such as POCl₃ or SO₂Cl₂ (Scheme 1 b).^[9] A viable alternative is the Sandmeyer type reaction proposed by Meerwein et al., where arenediazonium salts react with gaseous SO₂ to yield sulfonyl chlorides in low-to-moderate yields.^[10] Recently, a photocatalytic version of this approach using a molecular transition metal complex was reported.^[11]

Photocatalysis is considered to be a milder method of synthesis, which might help to overcome selectivity problems and poor tolerance to other functional groups.^[12] Overall, enhanced chemoselectivity is one of the main advantages of catalytic methods. Photocatalysis, in turn, possesses a unique tool to select the reaction pathway—light. Several works dedicated to chromoselective catalysis represent an exclusive possibility of photocatalysis to tune the reaction outcome by simply changing the color of light.^[13]

Among the heterogeneous photocatalysts, polymeric carbon nitride, a metal free semiconductor, has been reported to enable multiple organic reactions.^[14] It has been used to synthesize azo- and azoxy-compounds or to enantioselectively oxidize ethylbenzene by means of varying the wavelength of excitation light.^[13a,15] Besides, potassium poly(heptazine imide) (K-PHI), a more refined carbon nitride semiconductor, possesses extra features especially useful in organic photocatalysis. In particular, one gram of K-PHI stores up to

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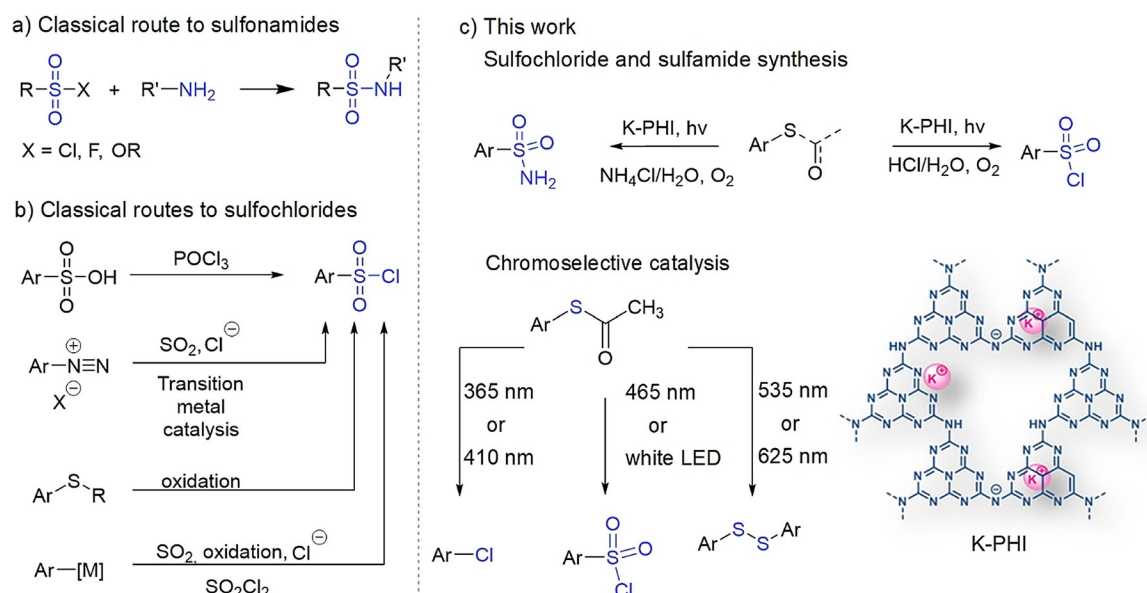
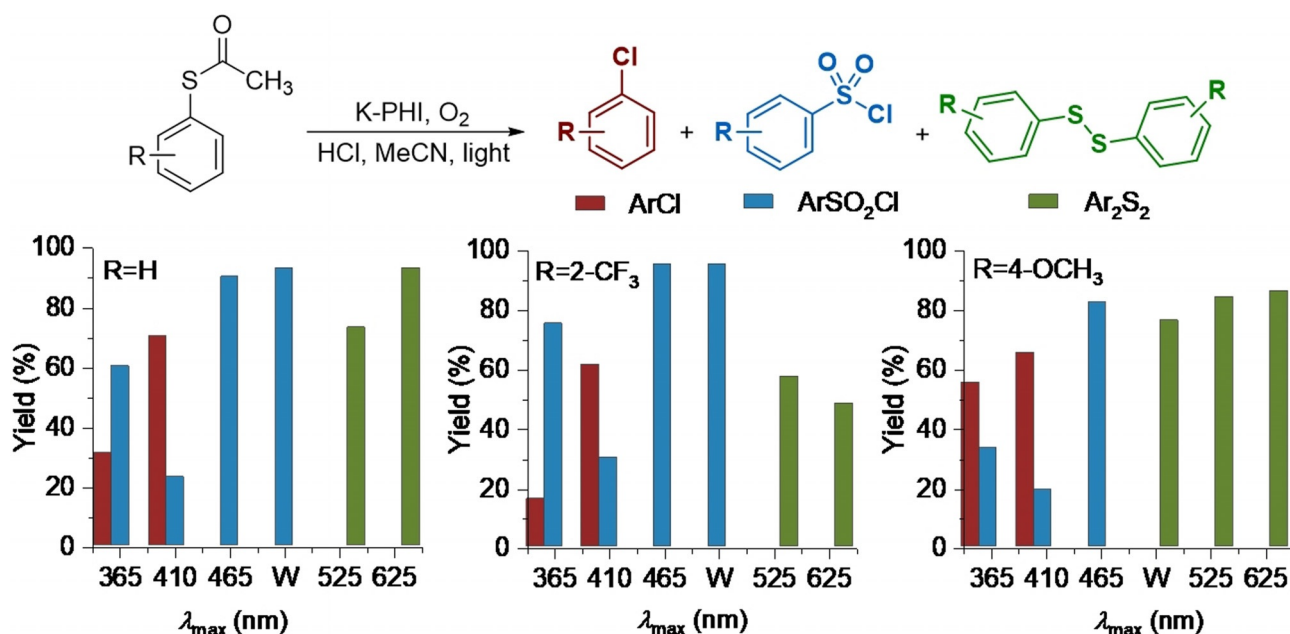


Figure 1. Literature overview and novelty of the present work. a) Classical route to sulfonyl amides; b) Common approaches in sulfonyl chlorides synthesis; c) Proposed methods of sulfonyl chlorides and sulfonamides synthesis with K-PHI semiconductor using chromoselective catalysis.



Scheme 1. Chromoselective oxidation of thioacetate with K-PHI. Conditions: S-Arylthioacetate 0.04 mmol; K-PHI 4 mg; HCl (36 wt. %) 0.1 mL; H₂O 0.1 mL; MeCN 0.5 mL; T = 25 °C; electron scavenger—O₂; irradiation with an LED of specific wavelength. λ_{max} denotes the maximum emission wavelength of the LED declared by the manufacturer or determined from emission spectra (Figure S2). W stands for LED emitting white light. (Detailed results can be found in Scheme S1).

1 mmol of electrons via IDEAS (Illumination-Driven Electron Accumulation in Semiconductors),^[16] which allows for completing multi-electron reactions,^[17] activation of CO₂,^[18] and design of hybrid nanomaterials for sensing.^[19]

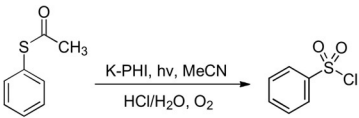
In the present work, we investigate the reactivity of thioacetates in chromoselective catalysis using K-PHI semiconductor under 5 quasi-monochromatic light sources ranging from the UV up to the near IR and white light. Three reaction pathways for S-arylthioacetates exist: 1) formation of aryl-

chloride, 2) formation of diaryldisulfide, and 3) formation of sulfonyl chloride (Figure 1c). Changing the wavelength of incident photons enables selectivity toward one of the three possible products. Using photons of the optimal energy, we present a method for the synthesis of sulfonyl chlorides from a variety of precursors, such as, thiols, thioacetates and isothiuronium salts, as well as a one-pot synthesis of sulfonyl amides.

Results and Discussion

Considering that S-substituted thioacetates are common substrates for oxidative sulfonylchlorination, S-phenylthioacetate was chosen as a model compound. Under 465 nm blue light irradiation, which matches the optical gap of K-PHI, using HCl in a water/acetonitrile mixture and O₂ as electron acceptor, phenylsulfonyl chloride was obtained in 93 % yield (Table 1, entry 1). Analysis of the reaction conditions showed that all components and light are necessary (Tables S3,4).

Table 1: Screening of semiconductors and molecular photoredox complexes^[a]



Entry	Catalyst	Light	Time	Yield (Conversion), %*
1	K-PHI	465 nm	20 h	93 (100)
2 ^[b]	K-PHI	465 nm	20 h	10 (15)
3 ^[c]	K-PHI	465 nm	20 h	91 (100)
4	mpg-CN	465 nm	20 h	0 (0)
5	g-CN	465 nm	20 h	0 (0)
6	H-PHI	465 nm	20 h	0 (0)
7	Na-PHI	465 nm	20 h	0 (0)
8	RFT	465 nm	20 h	0 (0)
9	Ru(bpy) ₃ Cl ₂	465 nm	20 h	0 (0)
10	Ir(ppy) ₃	465 nm	20 h	0 (0)
11 ^[d]	K-PHI	465 nm	20 h	90 (100)
12 ^[e]	KPHI	sunlight	5 h	95 (100)

[a] S-Phenylthioacetate 0.04 mmol; photocatalyst 4 mg; HCl (36 wt.%) 50 μ L; H₂O 0.2 mL; MeCN 0.5 mL; T=25 °C; electron scavenger—O₂; LED module 465 nm; [b] recycled catalyst; [c] catalyst recovered with KOH; [d] p-bromothiophenol 0.55 mmol, K-PHI 50 mg. Isolated yield; [e] S-phenylthioacetate 0.04 mmol; K-PHI 4 mg; HCl (36 wt.%) 0.1 mL; H₂O 0.1 mL; MeCN 0.5 mL; T=25 °C; electron scavenger—O₂; sunlight 70 mWcm⁻². *Yields and conversion were evaluated by NMR.

With regards to the heterogeneous nature of K-PHI, we recycled the semiconductor after the photocatalytic reaction. In the second run, using recycled K-PHI we observed that the yield of phenylsulfonyl chloride dropped to 10 % (entry 2). In our previous work, we found that under acidic conditions loss of potassium and partial hydrolysis takes place.^[20] Considering the zeolite-like nature of K-PHI, potassium cations were back-inserted into the poly(heptazine imide) framework by treating it with KOH solution. This led to the recovery of the initial K-PHI activity (entry 3).

For comparison, performances of other carbon nitrides and several common homogeneous photoredox complexes in this reaction were evaluated. Surprisingly, we found that other carbon nitride materials and molecular photoredox complexes only led to the recovery of the starting phenylthioacetate (entries 4–10). Scaling-up of the reaction was performed on a 0.55 mmol scale with a 90 % yield (entry 11). Furthermore, efficiency of the method was proven by the

reaction under illumination with direct sunlight, which led to the full conversion of the substrate in only 5 hours (entry 12).

Considering the chromoselective catalysis by carbon nitrides and molecular catalysts^[13a–c,15] and the multiple reaction paths feasible for S-phenylthioacetates^[21–24] under redox conditions, we explored the impact of excitation wavelength on the selectivity of S-arylthioacetates conversion. To this end, three substrates with different electronic properties were selected, that is, electron rich 4-methoxyphenylthioacetate, electron deficient 2-trifluoromethylphenylthioacetate, and bare phenylthioacetate. Three different products were formed and their formation depended on the applied light. The corresponding results are presented in Scheme 1.

Scheme 1 infers that the selectivity of the reaction can be tuned by optimizing the wavelength of the incident light. It is shown that irradiation with 365 and 410 nm is necessary to yield arylchlorides. A 465 nm as well as white LED light is needed for producing sulfonyl chlorides, while irradiation with 525/625 nm light generates disulfides.

Using this approach, various aromatic sulfonyl chlorides were synthesized under irradiation with an appropriate light source (Scheme 2a). The proposed method also allows for using different thio-derivatives as starting substrates: bare thiols, thioacetates, and isothiuronium salts. The nature of the thio-precursor affects the reaction only slightly and the product can be obtained in a good yield and selectivity. For example, phenylsulfonyl chloride was synthesized from thiophenol with a 90 % yield and from phenylthioacetate with a 93 % yield under the same conditions.

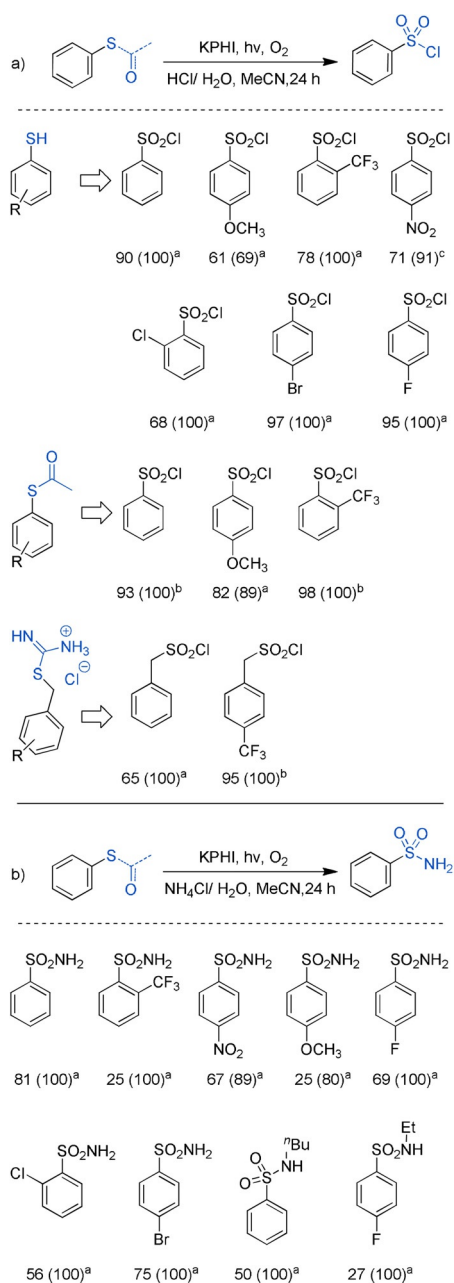
Despite the synthesis of sulfonyl chlorides is the most challenging step towards sulfonyl amides, it is certainly beneficial to obtain them in one step. A slight modification, that is, using NH₄Cl instead of HCl, led to several sulfonyl amides in a single step, however blue light irradiation was required for all (Scheme 2b).

To increase the value and to broaden the possible application of our method next to changing the corresponding thiol, we studied reactions using different amines. Thus, primary amines, such as ethylamine and butylamine hydrochlorides, gave N-substituted sulfonamides. In contrast, photocatalytic tests with secondary amines, such as diethylamine, failed in terms of forming the desired product.

Overall, sulfonyl chlorides and sulfonamides derived from electron rich and electron poor thiols and their derivatives could be synthesized by the developed method.

Irradiation of S-phenylthioacetate with 365, 465, and 525 nm without K-PHI lacks any substrate conversion, which suggests that chlorobenzene, phenylsulfonyl chloride, and disulfide evolve only in a photocatalytic process. Likewise, irradiation of phenylsulfonyl chloride with 365, 465, and 525 nm with or without K-PHI also gave no conversion to any products. This suggests that chlorobenzene and diphenyldisulfide do not directly derive from phenylsulfonyl chloride, but the path of their formation is photocatalytic (Tables S5,S6).

Higher flux of 410 nm photons, that is, 0.2 μ mol s⁻¹ cm⁻², versus 0.05 μ mol s⁻¹ cm⁻² of 365 nm photons is likely to contribute to the higher yield of arylchlorides at 410 nm



Scheme 2. Scope of substrates used in oxidative synthesis of sulfonyl chlorides (a) and sulfonyl amides (b). a) Conditions: Substrate 0.04 mmol; K-PHI 4 mg; HCl (36 wt.%) 0.1 mL; H₂O 0.1 mL; MeCN 0.5 mL; T = 25 °C; electron scavenger—O₂; irradiation with LED module. ^airradiation with LED module 465 nm (46.2 mWcm⁻²); ^birradiation with white LED (139.3 mWcm⁻²); ^cirradiation with LED module 465 nm (22.6 mWcm⁻²). b) Conditions: Substrate 0.04 mmol; K-PHI 4 mg; NH₄Cl 0.19 mmol or RNH₂Cl 0.23 mmol; H₂O 0.2 mL; MeCN 0.5 mL; T = 25 °C; electron scavenger—O₂; irradiation with blue LED 465 nm (46.2 mWcm⁻²). Yield and conversion (given in parentheses) are given in % and were determined by ¹H NMR^a or GC-MS.

irradiation (Figures 2a, S9). Nevertheless, the energy of a photon rather than the overall flux define the path of S-phenylthioacetate conversion.

Redox properties of the starting S-acetates were evaluated by cyclic voltammetry (CV) (Figure S10). For the electron-rich 4-methoxyphenylthioacetate, the oxidation is

observed at +1.58 V, while that for bare S-phenylthioacetate occurs at +1.94 V and that for electron-deficient CF₃-substituted S-acetate at +1.99 V vs. NHE. Therefore, the photocatalytic oxidation of thioacetates requires a valence band (VB) potential of at least +2.0 V vs. NHE. Among the studied catalysts, only poly(heptazine imide)s fulfill this requirement (Table S2).

Steady state fluorescence measurements were performed for K-PHI suspension and the reaction mixture using the series of excitation wavelengths like in the photocatalytic experiments (Figure S11). Excitation of just K-PHI suspension at different wavelengths leads to an invariable position of emission maximum. When, however, the reaction mixture was photo-excited with incident light of longer wavelengths, the emission maximum shifted and the emission intensity increased. Additionally, a faster separation of excitons was observed when shorter wavelengths were used, as documented in time-resolved fluorescence measurements (Figures 2b, S17–19). This phenomenon underlines the dependence of the K-PHI excited state dynamics on the wavelength of incident light.

Next, fluorescence measurements were employed to probe the interactions between S-thioacetates and K-PHI (Figure S12). Addition of thioacetates led to the quenching of the K-PHI fluorescence. The quenching effect becomes more pronounced when using electron-rich rather than electron-deficient substrates and decreases in the following order: 4-MeOC₆H₄Sac > PhSac > 2-CF₃C₆H₄Sac (see Scheme 1 for chemical structures). This trend correlates well with their oxidation potentials determined in the CV measurements (Figure S10).

Oxygen plays crucial role in the studied reaction. Recently, we have shown that intraband states in K-PHI are responsible for the sequential energy transfer to O₂ and, subsequent, ¹O₂-sensitization.^[25] In the context of the sulfonyl chloride synthesis, Na-PHI failed to give any desired product. Indeed, in this system there are no intraband states that could be involved in ¹O₂ sensitization and would otherwise be observed as bands in the visible region of the absorption spectrum (Figure 2c). K-PHI, in stark contrast, shows two bands in the diffuse reflectance UV-vis (DRUV-Vis) spectrum that are related to energy gaps, that is, an intrinsic band gap (BG) typical for carbon nitrides of 2.71 eV (previously assigned to π-π* transitions) and a band of ca. 1.9 eV related to intraband states (IBS) (previously assigned to n-π* transitions). K-PHI compared to Na-PHI also shows lower fluorescence quantum efficiency as another piece of evidence for more surface states available for trapping excitons (Figure S16).

Due to these structural features, a significantly higher concentration of ¹O₂ is produced by K-PHI. This summary was corroborated in near-infrared (nIR) phosphorescence measurements with a 360 nm photo-excitation (Figures 2d, S20).^[26]

The different behavior of K-PHI and Na-PHI was also evidenced in transient absorption spectroscopy (TAS) measurements. The excited state dynamics in the case of Ar-purged dispersions of K-PHI and Na-PHI are very similar. Here, directly after photoexcitation a negative transient stemming

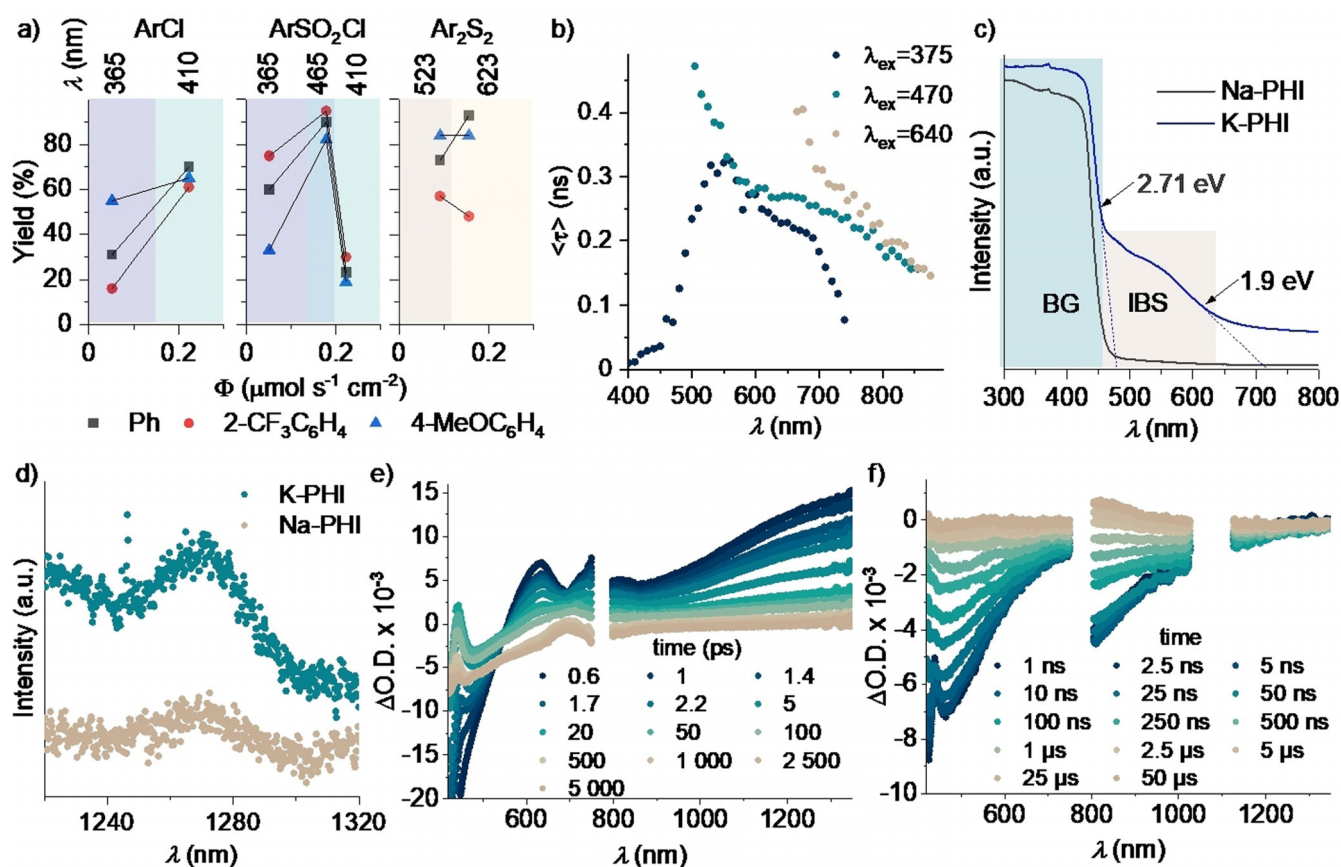


Figure 2. Rationale behind the activity of K-PHI in sulfonfyl chloride synthesis and chromoselective synthesis of arylchlorides and diaryldisulfides. a) Correlation of the arylchloride, sulfonfyl chloride, and disulfide yields with the photon flux of different LEDs; b) Investigation of exciton lifetime dependence on excitation light; c) DRUV-vis spectra of K-PHI and Na-PHI powders; d) Singlet oxygen fluorescence measurements for K-PHI and Na-PHI ($\lambda_{\text{ex}} = 360 \text{ nm}$); Sub-picosecond (e) and nanosecond (f) pump-probe transient absorption measurements ($\lambda_{\text{ex}} = 387 \text{ nm}/2 \mu\text{J}$) of K-PHI suspension in MeCN purged with O_2 .

from the ground state bleaching (GSB) forms up to 600 nm together with the formation of a positive absorption in the nIR region starting, which starts at 900 nm and, which reaches all the way up to 1350 nm (Figure S21). Within 2 ps, a sharp 440 nm maximum is formed. It quickly turns negative and is buried by the GSB, which signal dominates the whole visible region after 300 ps.

In stark contrast, O_2 -purged solutions behave rather differently. In the spectrum of K-PHI, a positive transient forms directly after photoexcitation with maxima at around 630 and 750 nm (Figure 2e,f). Within 3 ps, both maxima transform into a single maximum at 690 nm. On longer timescales, that is, after 1 μs , a positive transient forms between 850 and 1000 nm. We ascribe our observation to the quenching of the K-PHI excited state by oxygen. This turns out to be diffusion-controlled. No similar transient was detected for Na-PHI, whose spectral changes are the same either in argon or oxygen atmosphere (Figure S21).

Mechanism Discussion

The mechanism of chromoselective conversion of thio-derivatives to arylchlorides, sulfonfyl chlorides, and aryldisul-

fides is sketched in Figure 3. Considering the absorption spectrum, photons of low energy at 535 nm lead to the excitation of electrons from the intraband state to the conduction band, that is, an “IBS-CB” electron transfer (Figures S23, 24 and discussion in Supporting Information).^[25] Formation of diaryldisulfides is, therefore, rationalized by deacetylation of arylthioacetate followed by coupling of thiyl radicals to disulfides. This process is likely to be triggered by $^1\text{O}_2$ stemming from an energy transfer pathway as photons of 2.38 eV (green light) and 2.0 eV (red light) are insufficient to effectively separate excitons considering the K-PHI optical band gap of 2.71 eV. Formation of $^1\text{O}_2$ was verified in EPR experiments with 2,2,6,6-tetramethylpiperidine (TEMP), where under 530 nm irradiation, the rising signal of TEMPO was detected due to trapped $^1\text{O}_2$ (Figure 3a, S25).

Irradiation of K-PHI with photons of higher energy (with 410 or 465 nm) allows for the excitation of electrons from the valence to conduction band, that is, a “VB-CB” electron transfer, which represents an intrinsic band gap of CN materials. Such a K-PHI excited state may undergo either energy or electron transfer pathways. Considering the photocatalytic cycle, which rests upon electron transfer, one-electron oxidation of thioacetate yields the radical-anion of K-PHI and radical-cation of thioacetate. The latter decom-

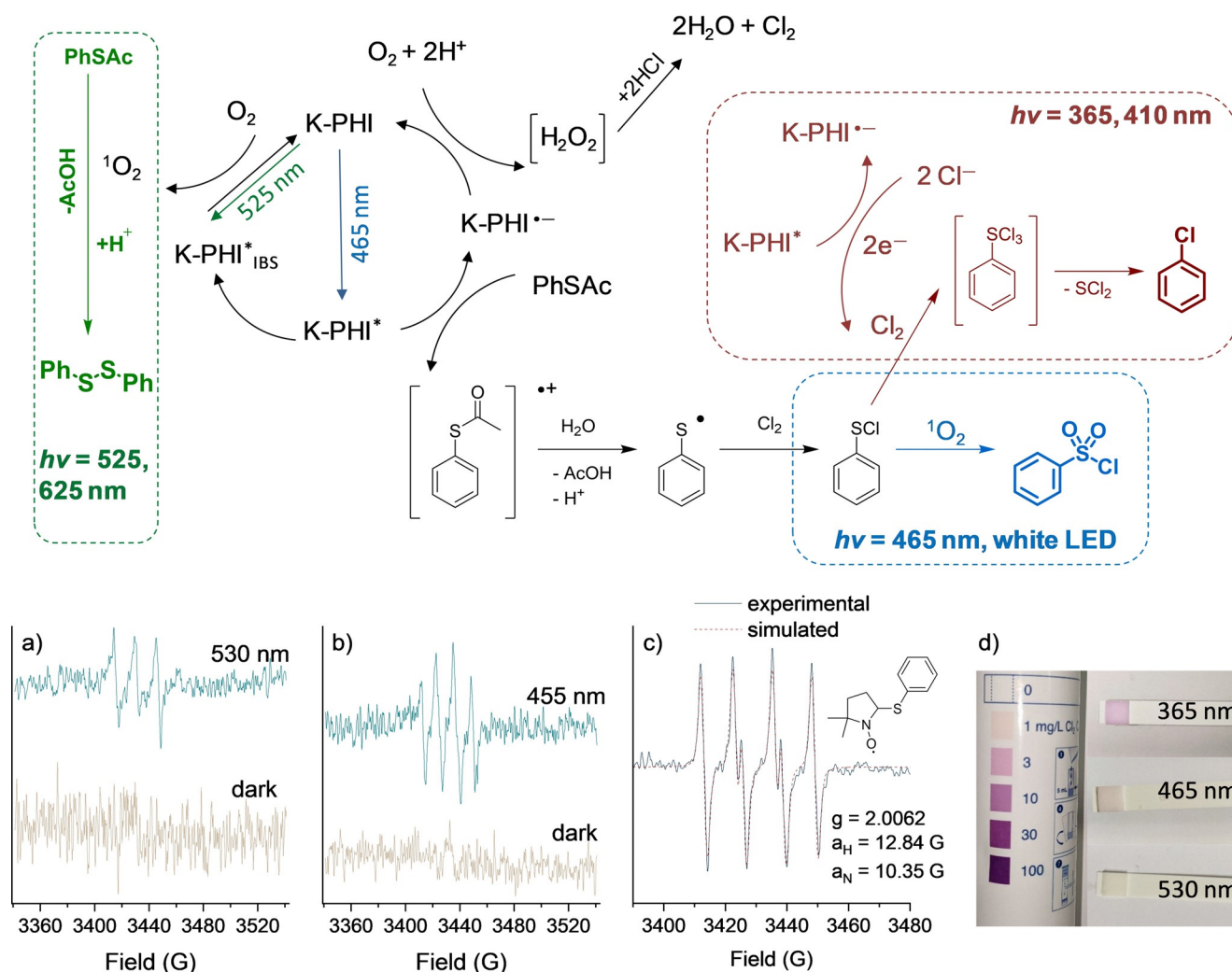


Figure 3. The proposed mechanism of chromoselective conversion of thio-derivatives to sulfonyl chlorides, arylchlorides, and disulfides. a) EPR spectra under 530 nm irradiation and in dark of K-PHI 4 mg and TEMP 5 μL in 0.5 mL MeCN. b) EPR spectra under 455 nm irradiation and in dark of K-PHI 4 mg and DMPO 5 μL in 0.5 mL H₂O:MeCN (1:10). c) Experimental and simulated EPR spectra of the DMPO-thiyl radical adduct (K-PHI 4 mg, PhSAc 5 mg, DMPO 5 μL in 0.5 mL deaerated MeCN under 415 nm irradiation). d) Detection of Cl₂ with Quantofix®Chlor test strips.

poses to the corresponding thiyl radical that couples with chlorine to give sulfenyl chloride. Formation of the phenylthiyl radical was confirmed by EPR and reaction with DMPO (Figure 3c, detailed discussion in Supporting information). In particular, a signal with the coupling constants of $a_{\beta-H} = 12.84 \text{ G}$ and $a_N = 10.35 \text{ G}$ ($g = 2.0062$) stems from an adduct of DMPO with the phenylthiyl radical. This was supported by GC-MS analysis (Figure S28–31).^[27] The K-PHI radical-anion, in turn, is oxidized by O₂ to form peroxide, which reacts with HCl and give a rise of Cl₂.^[28]

Under irradiation with blue light of 465 nm, K-PHI mediates the oxidation of sulfenyl chloride to sulfonyl chloride by O₂ (Figure S32). As such, we propose that 465 nm irradiation activates O₂ via both energy and electron transfer. Electron transfer to O₂ was probed in EPR experiments with 5,5-dimethyl-1-pyrroline N-oxide (DMPO). Evidence for DMPO-OH was gathered in irradiation experiments with 415 and 455 nm LEDs. It failed, however, when green light (530 nm) was used (Figure S25). In EPR experi-

ments with TEMP, the formation of TEMPO confirmed energy transfer when irradiated at 415 and 455 nm (Figure S25).

The selectivity of 410 nm irradiation to produce aryl chlorides is rationalized as follows. Under 365 or 410 nm irradiation, which correspond to energies of 3.02 or 3.4 eV, respectively, a two-electron oxidation of Cl⁻ by K-PHI* takes place. The excess of chlorine leads to over-chlorination of sulfenyl chloride with formation of unstable arylsulfur trichlorides, which quickly decompose to afford arylchlorides.^[29]

Therefore, two different oxidations are possible in the reaction mixture. On one hand, it is the oxidation of thioacetate and, on the other hand, it is the oxidation of Cl⁻. Under 465 nm irradiation, the one-electron oxidation of thioacetate is favored, while irradiation with 365 nm renders a high-energy two-electron process, such as the oxidation of Cl⁻, possible. Our mechanistic proposal was backed-up by determining the Cl₂-concentrations with Quantofix®Chlor

stripes. Significantly higher Cl_2 -concentrations were detected under 365 nm irradiation, namely $3\text{--}10\text{ mg L}^{-1}$ (Figure 3d, S26), than under 465 nm with 1 mg L^{-1} , while none was detected under 530 nm irradiation.

Next to the high oxidation potential and the ability to form $^1\text{O}_2$, the reason for K-PHI as the only active material in the discussed reaction (Table 1) might be its negatively-charged polymeric anion. It enables the temporary storage of the oxidation product of Cl^- . The local structure of the adduct between the polyanion of poly(heptazine imide) and active chlorine resembles that of *N*-chlorosuccinimide (NCS), which is a common source of active chlorine in organic synthesis (Scheme S27).^[21] Taking into account that the potassium content in K-PHI is 8% and using the results from Table 1 (entry 11), the turnover number (TON) is 85, we conclude that unlike to a reaction with NCS, a path of N-H recovery to N-K in poly(heptazine imide) exists, that is, a previously non-catalytic process could be turned catalytic.

Conclusion

In the present work, we have thoroughly studied chromoselective photocatalysis on the example of oxidative chlorination of thiobenzenes with carbon nitride K-PHI. Three products, that are, sulfonyl chlorides, aryl chlorides, and aryl disulfides, are selectively formed from the same reaction mixture just by adjusting the wavelength of incident light. Moreover, for the first time, photocatalytic methods for the synthesis of aromatic sulfonyl chlorides and amides from thioderivatives have been developed. High performance of the proposed method is also shown by probing the reaction at direct sunlight with a yield of 95% within a time-period of 5 hours. The mechanism of chromoselective catalysis is rather complex, however rationalized by the combination of several unique properties of K-PHI, namely the presence of intraband states that allows for energy as well as electron transfer, high oxidation potential, ability for multi-electron transformations, and negatively charged polymeric structure.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: carbon nitride · chromoselective catalysis · organic synthesis · photoredox catalysis · sulfonyl chloride

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