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Imine-Based Covalent Organic Frameworks as Photocatalysts for Metal Free Oxidation Processes under Visible Light Conditions

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Abstract: Photochemistry of extended polyimine COF structures with laminar, spherical and 3D architectures has been examined. We show that these materials, composed by undecorated phenyl rings and imine fragments, can act as photocatalyts in oxidative transformations, being the crystalline laminar material the most active photocatalyst. The sulfoxidation reaction proceeds with good yields for a large variety of different sulfides. This process was carried out under visible light conditions (20 W), ethanol/H_2O as solvent, and the heterogeneous porous material can be recycled up to 9 times. The crystallinity favours the behavior as photocatalyst of laminar and spherical COFs whereas any particular effect on the 3D material activity was observed. Sulfoxidation reaction mainly proceeds through an energy transfer mechanism using crystalline laminar material. In addition, these materials as photocatalysts were used for the oxidation of phenyl boronic acid into phenol.

Introduction

Oxidation reactions are one of the most important transformations in society and at an industrial level.[1] In fact, at present, it is used for the preparation of relevant compounds such as epoxides (epoxidation)[2] and acetaldehyde (Wacker process)[3] from double bonds, ketones from alcohols[1] and sulfoxides from thioethers,[4] among other important oxidations. These reactions are considered fundamental in organic synthesis since they allow the addition of new functional groups but frequently are accompanied by other secondary reactions, generally exhibiting low regioselectivities and poor chemoselectivities.[5] In addition, the use of oxidants such as $KMnO_4$, $K_2Cr_2O_7$, or catalysts such as $PdCl_2$, generate a large amount of waste.

One of the most interesting oxidation reactions is the sulfoxidation, obtaining sulfoxides from thioethers, due to their relevance in the pharmaceutical and agrochemical industries and also as key intermediates in organic synthesis.[6][7] The principal approach for the synthesis of these compounds is the use of peroxides or peracids, such as *m*-CPBA, which are explosive reagents and therefore difficult to handle. Moreover, the overoxidation process to sulfone has been also described as a limitation to be overcome.[6] In the last decade, photocatalysis has emerged as a powerful solution for the activation of different molecules such as oxygen.[8–13] Therefore, an alternative oxidation for the use of peracids and peroxides is the application of gaseous reagents that allow to develop greener processes by reducing the waste from purification, because excess of gas can be easily removed from the reaction. Although in most cases the use of oxygen for the oxidation of sulfides has been carried out with homogeneous systems, the use of heterogeneous materials, especially those containing porosity in their structure, seems one of the most logical approaches for the use of gases in catalysis. However, although the use of materials in the sulfoxidation reactions has been explored,[14–22] several limitations have been frequently described, such as the use of high powered light energy (>150 W),[14] materials decorated with toxic metals,[16] non-green solvents and moderate recyclability.[16] Overcoming such drawbacks would be highly desirable in order to achieve a green process.

One emerging family of porous materials are Covalent Organic Frameworks (COFs),[23] which are stable laminar or 3D reticular polymeric organic materials, similar to Metal Organic Frameworks (MOFs), but only composed by organic fragments. During the last years, the use of COFs had a significant impact in different fields, such as storage and separation of gases,[24] energy storage,[25] drug delivery,[26] proton conduction,[27] optoelectronics [28] and catalysis.[29] Regarding the organic catalytic transformations, some contributions can be found, most of them devoted to the use of COF as a support for metal centers,[29,30] or nanoparticles,[31] that catalyze different reactions. In addition, an organocatalyst-3D-COF was used in a Knoevenagel reaction.[32]

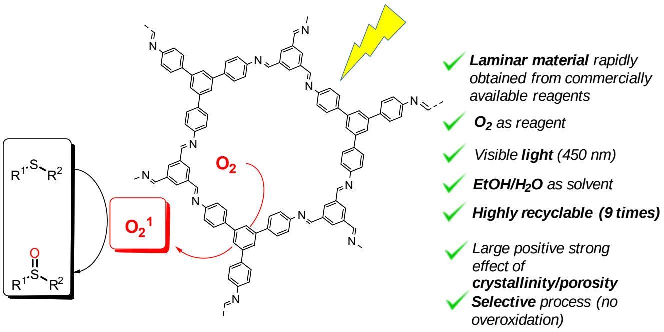

Figure 1. Present work in the photocatalytic crystalline laminar covalent organic framework for the oxidation of sulfides.

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In particular, imine-based COFs have attracted a good deal of attention and became, during the last few years, one of the most popular backbones in this field. Such interest is well deserved because of the versatility of available building blocks and the straightforward imine condensation under mild conditions, that allows the easy generation of materials with a variety of functionalities.[33–35] Despite the fact that some luminescent behavior has been reported for a simple imine-based layered COF,[36] the use of metal-free simple imine-based COFs, has not been studied in these sulfoxidation reactions.[20,36-46] Therefore, we wondered if imine-based COFs can be used to perform photo-activated synthetic transformations. In addition, we studied how their molecular architecture, crystallinity and microstructure can affect the catalytic activity (Figure 1).

In this work, we prepared simple COFs materials from commercially available building blocks to explore the photocatalytic sulfoxidation of thioethers using an ecofriendly solvent media (H_2O/EtOH) (Figure 1). In addition, moderate power visible light sources have been used, achieving the oxidation of a wide scope of substrates, being possible a high degree of material's recyclability. Finally, we explored some mechanistic aspects of these processes.

Results and Discussion

We initially started with the synthesis of three well-known different materials based on polyimine condensation from simple building blocks (Figure 2). In particular, the reaction between 1,3,5-tris(4-aminophenyl)benzene (**TAPB**) and 1,3,5-benzenetricarbaldehyde (**BTCA**), in DMSO at room temperature and atmospheric pressure, resulted in the formation of a gel that corresponds to a laminar material (**1b**).[47] SEM images of the xerogel from these samples were comparable with previously reported images,[47] which were consistent with the formation of flakes. On the other hand, if the same reaction was performed in acetone, the microstructures observed by SEM were spheres [48,49] of sizes that range from 200 to 400 nm (**1a**).[50] We also synthesized the 3D network known as COF-300 [24] by reacting the tetrahedral building block tetra(4-anilyl)methane) (**TAM**) with the linear linking unit terephthaldehyde (**TPA**) under room temperature and atmospheric pressure (**1c**). SEM images confirmed the formation of nanoparticulate material, that consequently showed a poor crystallinity when the X-ray powder diffraction was measured (see S.I.). The chemical identity of the materials synthesized was confirmed by elemental analysis, Fourier-Transform Infrared spectroscopy and CP-MAS-^{13}C-NMR, being all the results consistent with previously reported data [24,47,50] (see S.I.). Then, the synthesis of crystalline materials **1a-c** was carried out under solvothermal conditions [24,51–53] (left, Figure 2), obtaining crystalline materials that were confirmed by powder XRD analysis (left, Figure 2) and also BET measurements (from 409 to 684 m^2/g, see S.I.), which are in agreement with previous reported materials. [24,47,50,53] According to a recent report the bandgap of laminar imine-based COFs can be tuned through structural design.[54] Therefore, we measured the UV-vis absorption (diffuse reflectance) and emission spectra of the amorphous and crystalline materials **1a-c** (Figure 3). Diffuse reflectance of the six materials showed absorbances with maximums ranging from 430 to 475 nm. In the case of crystalline material **1a-c**, they showed an

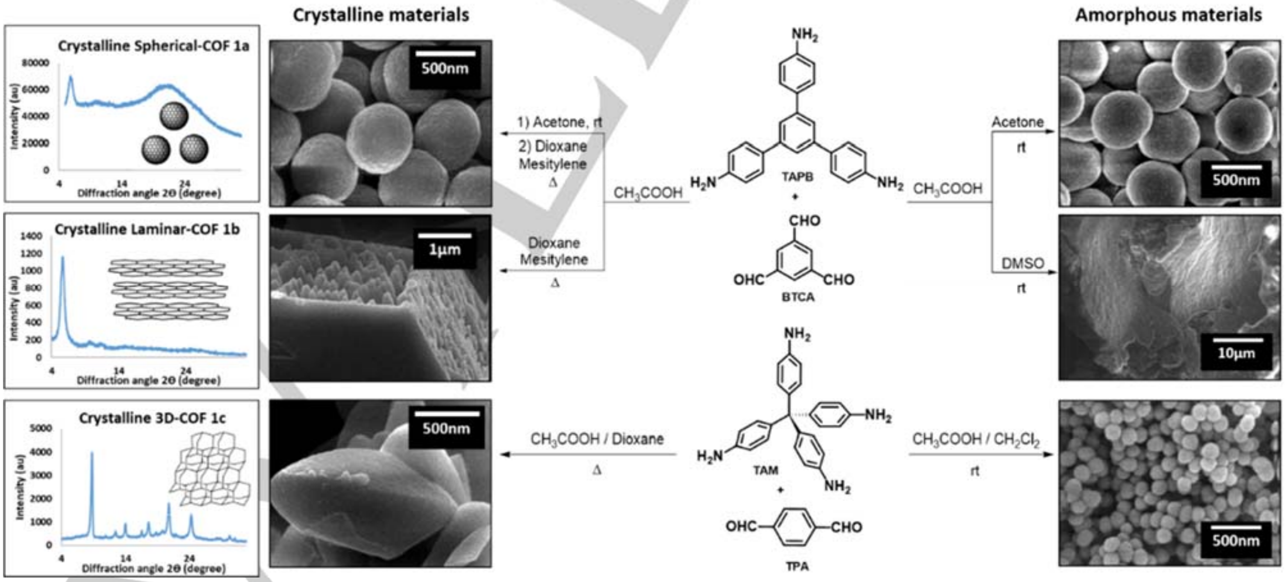


Figure 2. Molecular building blocks architectures and microstructures of COFs studied in this work. Right: synthesis of amorphous imine-COF materials. Left. Solvothermal conditions for the synthesis of crystalline imine-COF materials and powder XRD analysis of the crystalline materials.

absorption in an extended range of wavelengths. Direct Kubelka-Munk plots revealed the following band gaps (see S.I.): Egap = 2.52 eV (492 nm) for laminar-COF **1b** (which is in good agreement with the previously reported value) [54], Egap = 2.82 eV (440 nm) for spherical-COF **1a** and Egap = 2.68 eV (463 nm) for 3D-COF **1c**. For the corresponding crystalline materials, very similar band gaps were found: Egap = 2.53 eV (491 nm) for crystalline **1c**, Egap = 2.85 eV (435 nm) for crystalline **1a** and Egap = 2.90 eV (427 nm) for crystalline **1b**. The emission of both amorphous and crystalline materials **1a-c** was also studied, exciting at 450 nm. Maximum intensity of the emission spectra was found to be close to 550 nm, for both class of materials, crystalline and amorphous **1a-c**.

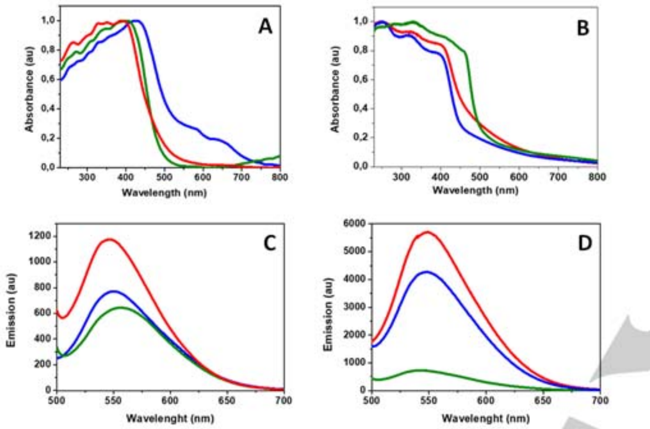
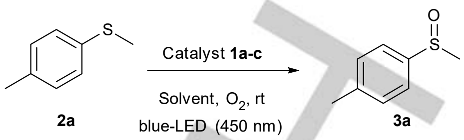


Figure 3. Normalized UV−vis diffuse reflectance of amorphous (A) and crystalline (B) materials. Emission spectra (λ_{exc}= 450 nm) of amorphous (C) and crystalline (D) materials. Spherical-COF **1a** (red), laminar-COF **1b** (blue), 3D-COF **1c** (green).

Since these materials (**1a-c**) showed optical properties similar to photocatalytic species, we decided to evaluate the catalytic activity of crystalline and amorphous materials **1a-c**, performing the oxidation of methyl-*p*-tolylsulfide (**2a**). Owing the simplicity of the synthesis of spherical-COF **1a**, we started the optimization of conditions for photocatalytic oxidation of sulfides using this material (see Table 1). A first experiment was carried out using 1.2 mg of the spherical-COF (**1a**) under blue light irradiation photoreactor for 48 h (450 nm LED) in the presence of O_2 in 2 mL of MeOH, containing 0.3 mmol of substrate (see Table 1). To our delight, we observed that **1a** allowed the oxidation of sulfide **2a** in a good conversion (74%) after 48 h (entry 1). The reaction did not proceed in the absence of the photocatalytic material **1a** or visible light (entry 2 and 3). In order to improve the conversion, other solvents such as EtOH, DMF, CH_2Cl_2, toluene or a mixture 1:1 of EtOH:H_2O were tested (entries 4-8). The best solvent was the mixture EtOH:H_2O, which is considered to be a green solvent (88% conversion, entry 8). When the amount of catalyst **1a** was double (2.4 mg), the oxidation was completed (100%), while the use of fourfold amount of **1a** (4.8 mg) proceeded with a slightly lower conversion (96%) (entries 9 and 10). With these optimal conditions (entry 9), we studied the other two materials, laminar-COF **1b** and 3D-COF **1c** (entries 11 and 12). The oxidation of sulfide **2a** under **1b** and **1c** catalysis yielded the final product after 48 h in good conversions (80 and 77%, respectively), but with lower values than spherical-COF **1a** (compare entries 9, 11 and 12). In order to stablish the influence of crystallinity in the catalytic activity, crystalline materials **1a-c** were evaluated under the optimized conditions (entry 9). Full and 69% conversions were obtained under crystalline **1a** and **1c** catalysis, respectively, after 48h (entries 13-15). Remarkably, the crystalline laminar-COF **1b** showed the highest catalytic activity, showing full conversion at 24h (entry 14).

Table 1. Optimization of the sulfur oxidation reaction with amorphous and crystalline 1a-c materials.[a]

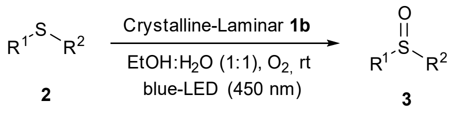


Entry	Catalyst	Solvent	Conversion (%)[b]
1	Spherical-COF **1a**	MeOH	74
2	-	MeOH	<5
3	Spherical-COF **1a**	MeOH	0[c]
4	Spherical-COF **1a**	DMF	21
5	Spherical-COF **1a**	CH_2Cl_2	52
6	Spherical-COF **1a**	Toluene	3
7	Spherical-COF **1a**	EtOH	73
8	Spherical-COF **1a**	EtOH:H_2O	88
9	Spherical-COF **1a**[d]	EtOH:H_2O	100(60)[f]
10	Spherical-COF **1a**[e]	EtOH:H_2O	96
11	Laminar-COF **1b**[d]	EtOH:H_2O	80
12	3D-COF **1c**[d]	EtOH:H_2O	77
13	Crystalline **1a**[d]	EtOH:H_2O	100(85)[f]
14	Crystalline **1b**[d]	EtOH:H_2O	100(100)[f]
15	Crystalline **1c**[d]	EtOH:H_2O	69[f]

[a] Reactions were carried out with **2a** (0.3 mmol) and 1.2 mg of the corresponding material catalyst **1a-c** in 2 mL of the indicated solvent under blue light irradiation under O_2 atmosphere (see S.I. for further details) after 48 h. [b] Determined by ^{1}H NMR analysis of the crude mixture. [c] This reaction was carried out without irradiation. [d] In this case 2.4 mg of catalyst were used. [e] In this case 4.8 mg of catalyst were used. [f] Conversion determined at 24 h by ^{1}H NMR analysis of the crude mixture.

Once the optimal conditions were determined (entry 14, Table 1), the oxidation of a variety of sulfides under crystalline material **1b** was studied (Table 2). Sulfoxides with electron-donating or electron-withdrawing groups at the aryl moiety (**3a-d**) were obtained (entries 2-4), but longer reaction times were needed for electron-deficient aryl groups. The oxidation of sulfides containing other alkyl groups (cyclopropyl and allyl groups), instead of methyl group, was also possible (entries 5-6), without detection of benzaldehyde or other byproducts as was found with other catalytic systems previously reported.[55] Interestingly, dialkyl sulfides (entries 7 and 8), including the sterically hindered *tert*-butylmethyl derivative (**2g**), were efficiently oxidized to **3g-h** in shorter reaction times (entries 8-9). Moreover, the effectiveness of the crystalline material **1b** was evaluated in the oxidation of sulfide **2i**, which is known to be the precursor of the drug modafinil.[56] We were pleased to isolate the corresponding sulfoxide **3i** (modafinil) in 75% yield, using the mild and environmentally-friendly oxidation protocol developed.

Table 2. Scope of the sulfide oxidation reaction using crystalline laminar-COF 1b as catalyst.[a]



Entry	R_1	R_2	Time (h)	3	Yield (%)[b]
1	*p*-Me-C_6H_4	Me	24	**3a**	95
2	*p*-MeO-C_6H_4	Me	45	**3b**	97
3	*p*-CN-C_6H_4	Me	64	**3c**	86
4	*p*-NO_2-C_6H_4	Me	88	**3d**	98
5	Ph	Cyclopropyl	72	**3e**	96
6	Ph	Allyl	48	**3f**	66
7	*t*-Bu	Me	46	**3g**	77
8	Bu	Bu	10	**3h**	94
9	Ph_2CH	CH_2CONH_2	64	**3i**	75

[a] Reactions were carried out with **2** (0.3 mmol) and 2.4 mg of crystalline **1b** in 2 mL of EtOH:H_2O (1:1) under blue light irradiation (450 nm). [b] Determined after isolation.

In order to evaluate the durability of this photocatalytic crystalline material **1b**, we performed nine consecutive 24 hours catalytic runs (total 216 hours) with sulfide **2a**, without losing effectivity (0.30-0.26 mmols of sulfoxide generated after every run, see Figure 4). Only 2.4 mg of crystalline material **1b** are able to produce 2.52 mmol (390 mg) of sulfoxide **3a**. After one catalytic run, we analysed the crystalline material **1b** by SEM images, FT-IR and PXRD, observing that no degradation was found after the catalytic reaction (Figure 4).

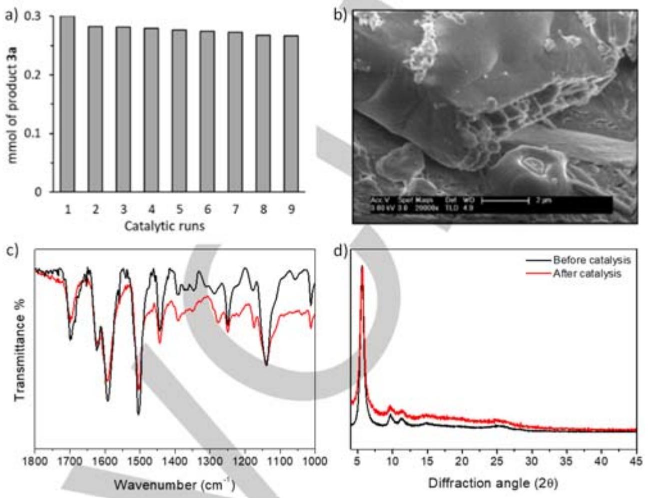
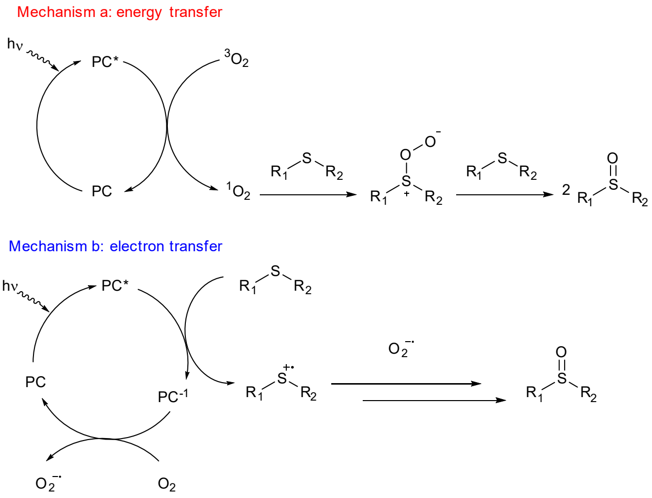


Figure 4. a) Catalytic runs in the oxidation of sulfide **2a** to **3a** in nine consecutive 24 hours catalytic runs by addition of 0.3 mmol of sulfide **2a** after each cycle (see S.I. for futher information). The output of the catalytic reaction is expressed as mmol **3a** generated per cycle. Characterization after one catalytic cycle: b) SEM image of crystalline Laminar-COF **1b** c) FT-IR (black colour before catalysis and red colour after catalysis) c) PXRD (black colour before catalysis, red colour, after catalysis).

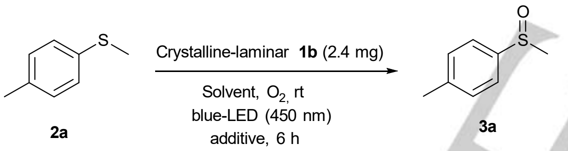
Regarding the plausible mechanism, it is well known that two possible pathways can account for the photocatalytic aerobic sulfoxidation [57]: a) energy transfer or b) electron transfer (Scheme 1). Differentiation of these two mechanisms can be determined by indirect studies, that can indicate which is the predominant pathway. When the reaction is mediated by singlet oxygen,[58] the catalytic output is enhanced by using deuterated protic solvents, whereas addition of DABCO quenches the formation of product.[57] On the other hand, 1,4-dimethoxybenzene acts as scavenger of sulfide radical cations,[57] when the reaction follows an electron transfer mechanism. Taking these facts



Scheme 1. Mechanistic proposals for the photo-oxidation (PC = photocatalyst).

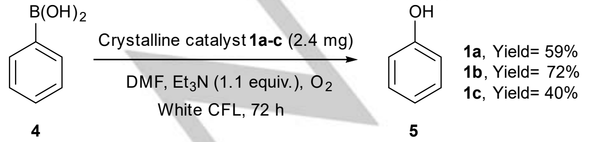
into consideration, we first studied crystalline laminar-COF **1b** (entries 1-4, Table 3). We found that while the change of CH_3OH/CD_3OD accelerated the reaction, the addition of 1,4-dimethoxybenzene had no effect in the final conversion to sulfoxide **3a** (entry 2 and 4) In contrast, the addition of DABCO gets worse the reaction outcome (entry 3). All these data indicate that singlet oxygen is the predominant reactive species, which are generated from the photoactivation of oxygen from crystalline material **1b**. Moreover, the successful oxidation of the *p*-nitrophenyl sulfide derivative **2d** (see scope in Table 2, entry 4) is also in agreement with the singlet oxygen mediated pathway (a non-radical mechanism). Similar results were obtained in the mechanistic studies for crystalline spherical-COF **1a** (see S.I.). However, crystalline 3D-COF **1c** showed a more complex mechanistic scenario, where both energy transfer mechanism and electron-transfer pathway should be considered (see S.I.). In addition, the versatility of crystalline materials **1a-c** was confirmed by their ability to react through electron transfer mechanism. Indeed, this was confirmed by the oxidation of phenylboronic acid **4** into phenol **5**, which is known to proceed exclusively via a superoxo anion radical [59] (Scheme 2). In this case, the best catalytic performance was achieved also by crystalline material **1b**.

Table 3. Mechanistic experiments in the presence of enhancers or scavengers.[a]



Entry	Solvent	Additive (equiv.)	Conversion (%)[b]
1	CH_3OH	-	33
2	CD_3OD	-	75
3	CH_3OH	DABCO (0.5)	14
4	CH_3OH	1,4-$(MeO)_2C_6H_4$	43

[a] Reactions were carried out with **2a** (0.3 mmol) and 2.4 mg of **1b** in 2 mL of solvent under blue light irradiation. [b] Determined by ^{1}H-NMR measured on the crude mixture after 6 h.



Scheme 2. Photooxidation of phenylboronic acid under crystalline **1a-c** catalysis.

Conclusions

Undecorated imine-based COFs can be employed as photocatalysts on aerobic sulfoxidation under smooth conditions with good yields and complete selectivity. These materials are also able to efficiently catalyse the photooxidation of phenyl boronic acid. Crystallinity has a strong positive influence in the catalytic activity of laminar **1b** and spherical **1a** COFs, while it does not affect the catalytic performance of 3D-COF **1c**. This contrast is possibly related to the extended conjugation on laminar or spherical COFs, which is hampered by the presence of Csp^3 in the 3D structure. Overall, our results expands the use of ordinary COFs in a wider range of oxidative transformations, including both energy and/or electron transfer processes. These COFs are prepared from commercially available building blocks, allowing the use of ecofriendly solvent media (H_2O/EtOH), moderate power visible light sources and being possible a high degree of material's recyclability.

Experimental Section

Supporting information contains all available data for the synthesis of the materials, characterization and catalysis for this work.

Acknowledgements

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Keywords: Covalent Organic Frameworks • Photocatalysis • Sulfoxidation • Materials.

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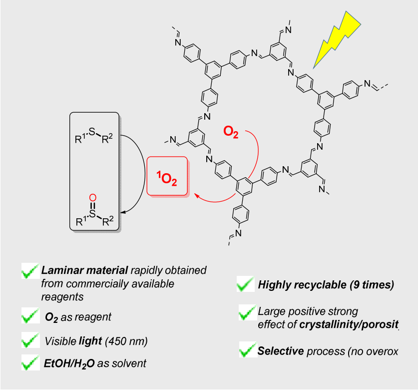

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Imine-Based Covalent Organic Frameworks as Photocatalysts for Metal Free Oxidation Processes under Visible Light Conditions