

# Engineering Photocatalytic Porous Organic Materials for Directing Redox versus Energy Transfer Processes

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Two organic materials containing phenanthroline and triazine fragments, but connected in different ways, are presented. The imine-based material Phen–Tz–covalent organic framework (COF) preferentially shows photocatalytic activity through an energy transfer pathway as observed for olefin photoisomerization. However, an analogous covalent triazine framework (Phen–CTF) behaves as a powerful photoredox catalyst able to activate C–X (X=Br, Cl) bonds. The analysis of this phenomenon by means of theoretical calculations enables the rationalization of the different photocatalytic behavior observed. Phen–CTF behaves as a donor–acceptor material resulting in efficient charge separation upon excitation, while the imine groups present in Phen–Tz–COF hamper charge separation contributing to the rapid recombination between electrons and holes. This justifies a better activation via electron transfer in Phen–CTF and via energy transfer in Phen–Tz–COF.

reactivity modes.<sup>[1]</sup> In addition, the transition from homogeneous systems to materials design has enabled similar photocatalytic synthetic processes, but in a recyclable way.<sup>[2]</sup> Among the most promising heterogeneous catalysts, covalent organic frameworks (COFs) and related materials such as covalent triazine frameworks (CTFs) stand out for the ease of design of their constitutive building blocks.<sup>[3]</sup> This enables modulating their photophysical properties and tuning their photocatalytic behavior as desired.

Photocatalytic processes follow two main well-differentiated mechanisms: energy or electron transfer.<sup>[4]</sup> In both pathways, the first step consists of the excitation of the photocatalyst. In an electron transfer mechanism, the excited catalyst becomes a powerful oxidant or reducing agent, able to accept or give electrons

from an organic substrate, generating the corresponding radical species that will eventually evolve into the final product.<sup>[5]</sup> Alternatively, in an energy transfer mechanism, the energy absorbed by the photocatalyst is transferred to the reagents, allowing its activation and consequently triggering the corresponding chemical transformation.<sup>[6]</sup> However, the preference of a photocatalytic material to differentiate between the two mechanisms is a controversial issue commonly disregarded. There are many studies in which the mechanisms of the reactions catalyzed by COFs are explained in depth.<sup>[3,7]</sup> However, the structure–activity relationships are not often analyzed in detail, which could help to ensure the adequate structure for each material with its optimal photocatalytic application.<sup>[8]</sup> In the quest for a rational design for photocatalytic organic materials, an analysis of the literature offers some hints. An early study showed that the structure and morphology of undecorated imine-based COFs had a key role in their photocatalytic behavior of light-mediated oxidation reactions.<sup>[9]</sup> In addition, the different nature of the building blocks employed in the construction of phenyl phenothiazine and triphenylamine-containing polymers had a clear influence on the photocatalytic outcome.<sup>[10]</sup> Finally, the coordination of several metal species played an important role in directing the predominant mechanism of a porphyrin-based COF toward one or another pathway.<sup>[11]</sup> However, the principles that govern the energy transfer versus electron transfer dilemma in organic materials remain unclear.

One of the most common ways to build COFs is based on the assembly of imine bonds, due to the compromise between

## 1. Introduction


During the last decades, photocatalysis has allowed the development of new synthetic processes, expanding the catalogue of organic transformations, functional group compatibility, and

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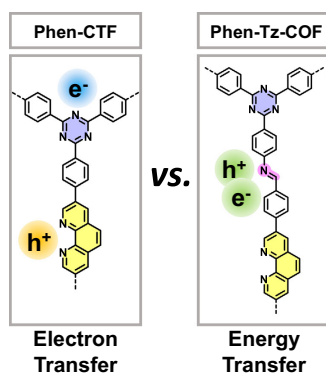
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**Figure 1.** General concept of this work.

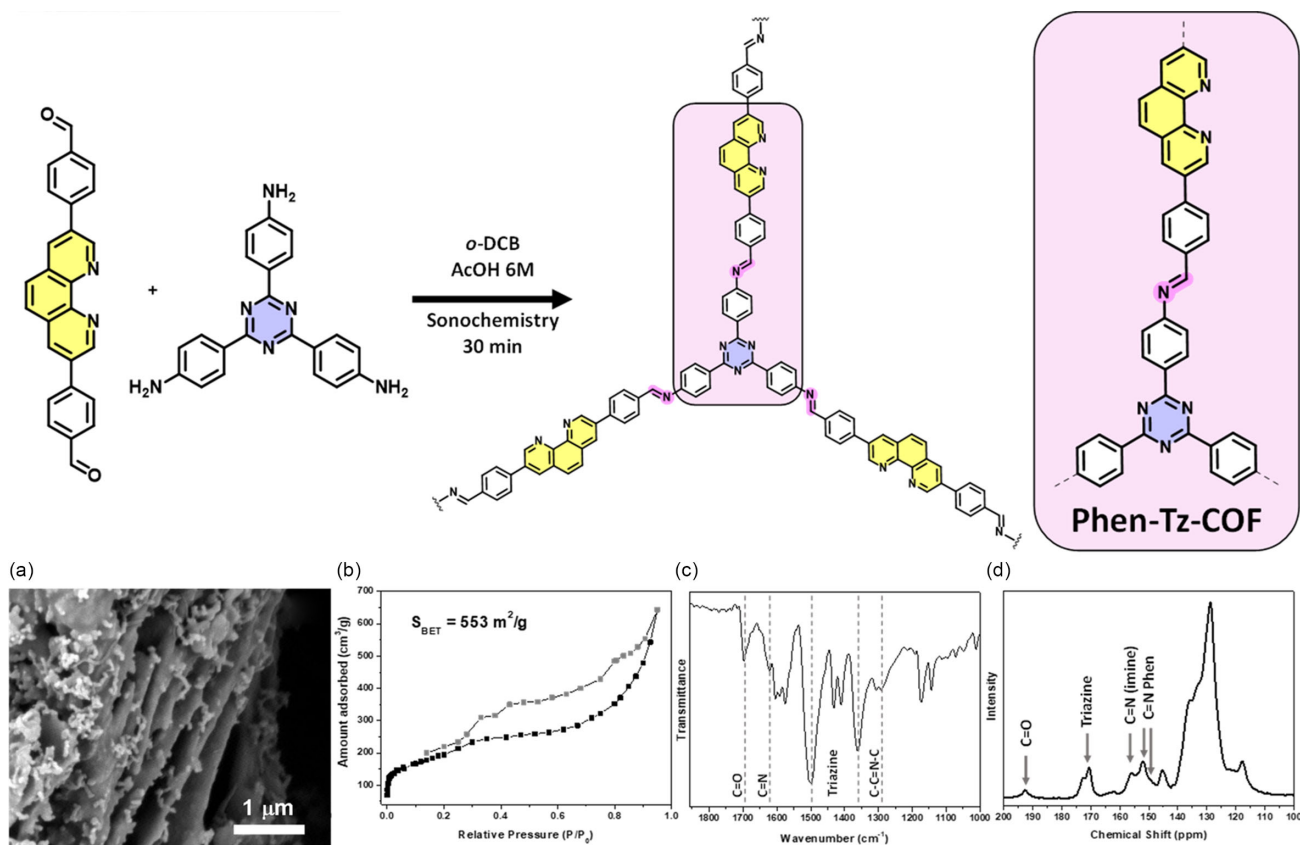
building block availability, stability, and linkage reversibility.<sup>[12]</sup> However, the presence of highly electronegative iminic nitrogen atoms can alter the electronic structure of organic photoactive materials. Thus, it is necessary to understand the effect of such bridging moiety on conjugation and hence on the photocatalytic activity of extended organic frameworks. To tackle this goal, in this work, we propose the comparison between two analogue photocatalytic materials that mainly differ in the presence, or the absence, of imine linkages (**Figure 1**). On the one hand, we present the catalytic properties of a CTF that contains

phenanthroline units (**Phen-CTF**).<sup>[13]</sup> On the other hand, we present the synthesis, characterization, and study of the photocatalytic activity of a novel imine-based COF that also contains phenanthroline and triazine units (**Phen-Tz-COF**). The comparative exploration of the photocatalytic behavior of both materials for electron and energy transfer processes has enabled the determination of the role of their bridging fragments. The findings reported herein offer new tools to understand the factors that direct the photocatalytic behavior of organic materials, which opens the door for more rational designs in the quest for pre-determined activities.

## 2. Results

### 2.1. Synthesis and Characterization of Phen-Tz-COF

We first synthesized a new imine-based COF composed of phenanthroline and triazine units, employing building block **1** and 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline (**TTA**) (**Figure 2**).<sup>[14]</sup> A screening of the typical conditions for the synthesis of **Phen-Tz-COF** was performed using solvent mixtures of different polarity, and using solvothermal<sup>[15]</sup> and sonochemical methods,<sup>[16]</sup> different modulators and catalysts, or different reaction times. The best result was obtained when *o*-dichlorobenzene was used as the solvent, 6 M aqueous acetic acid as the catalyst, and using sonochemical conditions for



**Figure 2.** Synthesis and characterization of **Phen-Tz-COF**: a) SEM image; b) N<sub>2</sub> adsorption-desorption isotherm at 77 K; c) FTIR spectrum; and d) <sup>13</sup>C-CPMAS-NMR spectrum.

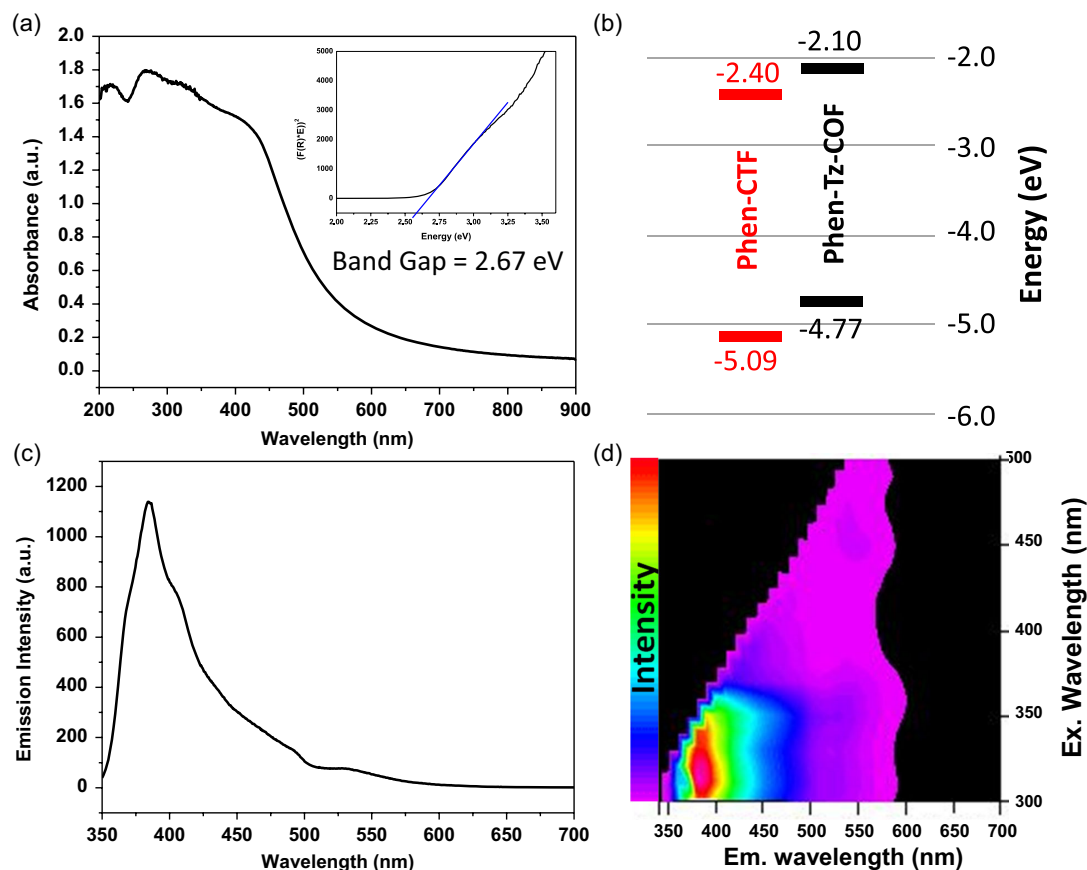
30 min. Under these specific conditions, a diffraction peak with a low intensity was found at  $1.9^\circ$ , which could be assigned to the (100) plane of power X-ray diffraction (PXRD) in an AA stacking model (see Supporting Information).<sup>[14]</sup> Interestingly, the  $N_2$  adsorption-desorption isotherm of **Phen-Tz-COF** obtained using this procedure showed a  $S_{BET}$  of around  $550\text{ m}^2\text{ g}^{-1}$ , confirming the porous nature of this material. Field-emission scanning electron microscopy (SEM) of the resulting material confirmed the formation of a COF with a layered microstructure. The chemical identity and correct formation of the expected imine-linked **Phen-Tz-COF** were assessed by Fourier-transformed infrared spectroscopy (FTIR). The most important vibration peaks located at  $1622$  and  $1288\text{ cm}^{-1}$  were attributed to the  $C=N$  and  $C-C=N-C$  stretching of imine moieties, respectively, confirming the formation of a polyimine network.<sup>[9]</sup> Furthermore, the two vibrations bands at  $1500$  and  $1361\text{ cm}^{-1}$  were assigned to aromatic  $C-N$  stretching and breathing modes of triazine units.<sup>[17]</sup> These observations are in accordance with solid- $^{13}\text{C}$ -NMR experiments using cross-polarization combined to magic angle spinning ( $^{13}\text{C}$ -CPMAS-NMR). The characteristic iminic carbon was found at  $156\text{ ppm}$ , as well as the peaks centered at  $153$  and  $150\text{ ppm}$ , which were assigned to the tertiary and quaternary carbons in the alpha position to the phenanthroline-nitrogen atom.<sup>[14]</sup> The peak located at  $171\text{ ppm}$  can be assigned to triazine moieties present in the structure.<sup>[18]</sup> A residual

peak located at  $192\text{ ppm}$  can be assigned to peripheral aldehyde groups in the structure. The rest of the signals correspond to several aromatic carbons, which were present in the covalent structure.

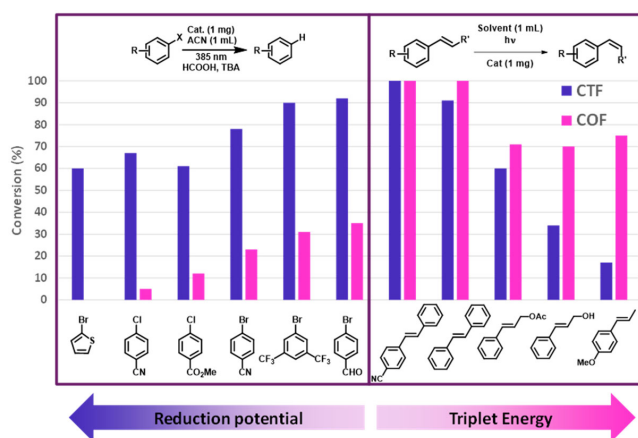
We then proceeded to the study of the photophysical properties of **Phen-Tz-COF** (Figure 3). First, diffuse reflectance spectroscopy (DRS) revealed a continuous intense absorption of the material up to  $420\text{ nm}$ . After application of the Kubelka-Munk theory, the bandgap of **Phen-Tz-COF** was estimated at around  $2.67\text{ eV}$ . The electrochemical behavior was examined by cyclic voltammetry measurements. The oxidation signal found at  $+0.12\text{ V}$  (vs  $\text{Ag}/\text{AgCl}$ ), which presented a certain degree of reversibility, was attributed to the electron transfer from the valence band of the material, which leads to an absolute energy value of  $-4.77\text{ eV}$ . The combination of the values of the optical bandgap and valence band enabled us to estimate the position of the conduction band, located at  $-2.10\text{ eV}$ . Additionally, fluorescence emission spectroscopy of **Phen-Tz-COF** showed a main band centered at  $380\text{ nm}$ .

## 2.2. Catalytic Activity of Phen-Tz-COF versus Phen-CTF

In order to determine the predominant catalytic activity in each of the materials containing phenanthroline and triazine fragments, we selected two model reactions (Figure 4). On the



**Figure 3.** Photophysical characterization of **Phen-Tz-COF**: a) DRS spectrum (inset: Kubelka-Munk plot); b) Comparison between energy levels of **Phen-CTF** (red) and **Phen-Tz-COF** (black); c) Emission spectrum; and d) Topological map of emission spectrum.

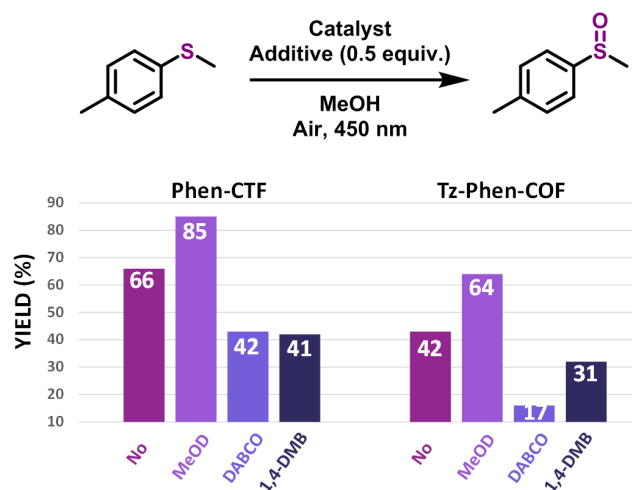


**Figure 4.** Catalytic application of **Phen-CTF** (blue) and **Phen-Tz-COF** (pink) for dehalogenation reactions (left) and photoisomerization reactions (right).

one hand, it is known that the light-mediated dehalogenation reaction occurs solely through a photoredox mechanism.<sup>[19]</sup> On the other hand, the photoisomerization of olefins is a reaction that proceeds through an energy transfer mechanism.<sup>[20]</sup>

In the case of dehalogenations, the reactions were carried out with selected substrates to check **Phen-Tz-COF** activity. While in all cases **Phen-CTF** was able to perform the dehalogenation of all the substrates used (with reduction potentials of up to  $-2.0$  V vs Ag/AgCl),<sup>[13]</sup> in the case of COF, the yields were always lower, and we observed a complete inhibition of the reaction in the case of bromothiophene, which has the highest reduction potential (see Supporting Information for measured redox potentials). These results showed that, while **Phen-CTF** presents good yields in the whole range of substrates studied, the output of the photoredox reaction using **Phen-Tz-COF** is highly dependent on the reduction potential and the computed energy of the lowest unoccupied molecular orbital (LUMO) orbital of the organic halides (see Supporting Information). Thus, the superiority of photoredox activity of **Phen-CTF** was confirmed. Regarding the photoisomerizations, just the opposite trend was observed. In the case of the bis-arylic olefins, both materials were able to carry out the reaction producing excellent yields because these types of substrates have lower triplet energies (see Supporting Information for theoretically calculated singlet-triplet values). However, by introducing alkyl moieties into the olefins, the triplet energy increases, and the photoisomerization of a *trans*- to *cis*-configuration of the olefins is less favored. In the presence of **Phen-Tz-COF** conversions above 70% were obtained in every case. However, with **Phen-CTF** the photoisomerization decreases upon increment of the triplet energy of the double bond. These results clearly confirm a predominant energy transfer nature in the case of the COF. In both cases, we evaluated the sturdiness of **Phen-CTF** and **Phen-Tz-COF** under the reaction conditions employed, observing no significant differences in their FTIR spectra before and after the catalysis experiments (see Figure S17 and S18, Supporting Information).

A similar conclusion can be obtained using a different kind of reactions. With this purpose we studied the sulfoxidation of methyl (*p*-tolyl)sulfide. This reaction can take place through



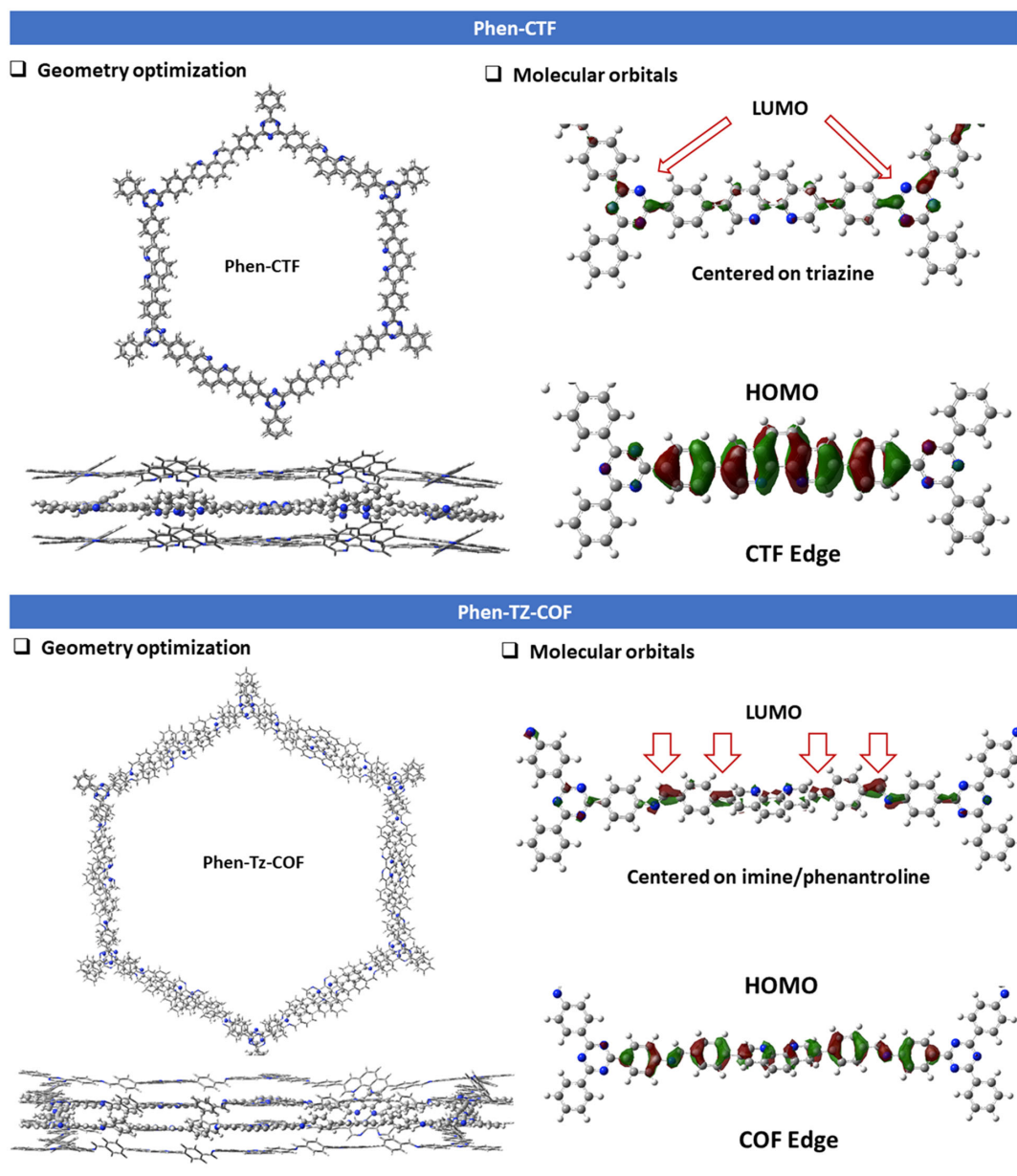
**Figure 5.** Mechanistic experiments in the presence of enhancers or scavengers.

two different mechanisms: on the one hand, photosensitization of the oxygen to singlet oxygen, which further oxidizes the sulfide to sulfoxide; on the other hand, electron transfer to oxygen species can generate superoxide radical anion intermediate, which is an efficient oxidant species. Under open atmosphere at room temperature, sulfoxidation was achieved after 16 h in a 66% yield for **Phen-CTF** and 42% yield for **Phen-Tz-COF** (Figure 5). Reproducibility of these results was also tested (see Supporting Information for further details). These yields were increased using deuterated methanol for both photocatalytic materials, indicating the involvement of singlet oxygen in this reaction. Accordingly, 1,4-diazabicyclo[2.2.2]octane (DABCO) acts as a quencher in the sulfoxide generation, but in a major extent for **Phen-Tz-COF** than for **Phen-CTF**. On the other hand, dimethoxybenzene also acts as effective quencher in the sulfoxide formation when **Phen-Tz-COF** or **Phen-CTF** is used, also indicating the involvement of superoxide radical anion. These results suggest that both energy transfer oxidation (via singlet oxygen) and electron transfer reaction (via superoxide radical anion) are operative pathways for both materials. However, the predominance of energy transfer mechanisms for **Phen-Tz-COF** is also revealed by the enhanced quenching effect of DABCO.

### 2.3. Theoretical Investigations

In order to rationalize all these results, density-functional theory (DFT) calculations were performed (Figure 6). The structure of the materials has been modeled using hybrid our own N-layered integrated molecular orbital and molecular mechanics QM-MM (ONIOM) methodology.<sup>[21]</sup> The stacking of three molecular hexagons has been considered to be a good compromise between the calculation costs and representativity of the experimental system. The central hexagon was calculated using the DFT method at the M06/6-31G(d,p) level. However, the external hexagons were calculated using molecular mechanics, employing the universal force field (UFF). Focusing on the structure of both materials, we observed that **Phen-CTF** deviates far less from planarity than **Phen-Tz-COF**, which gives us an idea of the





**Figure 6.** Left: Optimized ONIOM (M06/6-31G(d,p):UFF) structure for **Phen-CTF** and **Phen-Tz-COF** materials. A ball and stick representation is used for the atoms included in the DFT part, while the tube representation indicates the atoms treated with molecular mechanics. Right: HOMO and LUMO orbitals of the two materials.

electronic conjugation in both materials (left, Figure 6). Therefore, in the case of the COF material, there is greater conformational freedom, which can cause a break in its electronic conjugation.

Regarding the photoexcitation process, time-dependent density-functional theory (TD-DFT) calculations showed that in both cases the transition between the highest occupied molecular orbital and the LUMO (HOMO–LUMO transition) accounts for the high absorption intensity (right, Figure 5). However, the HOMO and LUMO orbitals of the two materials have a quite different nature. Indeed, in CTF, HOMO is mainly centered on phenanthroline fragments, while LUMO is essentially located on

the triazine residues. By contrast, the HOMO of **Phen-Tz-COF** is still predominantly placed at the phenanthroline groups, while its LUMO is now mainly located in some of the atoms in the phenanthroline fragments and adjacent imine linkages, but not in the triazine moieties. This gives us an idea of the origin of the excellent photoredox activity of **Phen-CTF** by comparison with **Phen-Tz-COF**, as the CTF behaves as a donor–acceptor structure.<sup>[22]</sup> The donor units are the phenanthrolines, while triazines act as acceptor moieties. Upon excitation under visible-light irradiation, electron–hole separation occurs in two fragments of the material far enough apart to prevent rapid recombination, making them available for electron transfer processes.

However, the electrons and holes in **Phen-Tz-COF** are located in the same region, making the recombination between them after photochemical excitation much faster, and thus unavailable for electron-transfer to organic substrates. Therefore, theoretical analysis may justify the experimental results in which the imine-based material acts as a good energy transfer agent, but the electron transfer pathway is much less favored.

### 3. Conclusion

Overall, we have been able to control the photocatalytic behavior of two materials that contain the same fragments (triazine and phenanthroline) but connected in a different way. The one connected through triazine moieties (**Phen-CTF**) presents an enhanced tendency to mediate in photoredox reactions, such as dehalogenation processes. However, the introduction of imine groups between the triazine and phenanthroline fragments causes a change in the photocatalytic behavior. Thus, the **Phen-Tz-COF** material is a better energy transfer photocatalyst in olefin photoisomerizations. Theoretical analysis suggests that in **Phen-CTF** charge separation upon excitation occurs more efficiently than in **Phen-Tz-COF**, which may be the reason for an improved photoredox activity.

This work constitutes a valuable starting point for the rational design of porous organic materials for synthetic photocatalytic processes. It has been shown that imines act as a certain conjugation barrier, preventing general electronic delocalization and therefore only allowing energy transfer mechanisms to be carried out. On the other hand, if designing a material that photoredox units, it is more advisable to use linking groups that allow improved charge separation, such as triazines or olefins.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

### Keywords

covalent organic frameworks, covalent triazine frameworks, energy transfer, photocatalysis, photoredox

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