Solvent-Free Visible Light Photocatalytic Oxidation Processes Mediated by Transparent Films of an Imine-Based Organic Polymer

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Abstract: Reaction between concentrated solutions of phenotiazine containing trialdehyde building block 4,4′,4″-(10-phenothiazine-3,7,10-triyl)tribenzaldehyde and (1R,2R)-cyclohexane-1,2-diamine results in the formation of a yellow transparent film. Exhaustive characterization of this material indicates that it is the result of the assembly of a linear polymer resulting from the linking of imine-based macrocycles. Phenotiazine units confer to this plastic the optical properties characteristic of photocatalytic materials. The transparency of the obtained material enabled the performance of solvent-free photocatalytic processes. This concept is illustrated by the oxidation of liquid organic sulfides, which can be performed in a recyclable manner. According to selective quenching experiments, such processes are the result of the energy transfer to oxygen molecule, generating singlet oxygen that is able to activate the sulfide molecules directly.

Keywords: solvent-free; photocatalysis; sulfoxidation; materials; organic polymer

1. Introduction

An emerging trend in modern chemistry is the design of photocatalytic processes to achieve the assembly of a variety of compounds of increasing complexity [1–5]. On a first approximation, the light used to trigger several chemical transformations was in the range of ultraviolet. However, attending to the need for reducing the energy demands of photocatalytic processes, and in order to use solar light, replacing UV irradiation with visible-light is a current priority [6,7]. For this reason, the design of photocatalysts containing visible-light chromophores has blossomed in recent years. Initially, a major portion of processes mediated by visible light used compounds of metals such as Ir or Ru [8]. However, the scarcity, high cost and toxicity of these metals has pushed forward the research on organic photocatalysts. Among them, phenyl phenothiazine (PTH) derivatives have been successfully used in dye-sensitized solar cells (DSSCs) [9–11], water splitting [12], hydrogen production [13–17], pollutant degradation [18] and organic synthesis [19–22].

Typically, visible light photocatalysis relies on the design of molecular species for homogeneous systems. However, a further step in the quest for efficient photocatalytic transformations was the construction of active materials, allowing easy separation of the catalyst, as well as recyclability [23]. To achieve this goal, a recent strategy is the incorporation of photocatalytic units, normally used in homogeneous catalysis, into predesigned materials. In particular, organic materials such as Covalent Organic Frameworks (COFs), Covalent Triazine Frameworks (CTFs), Polymers of Intrinsic Microporosity (PIMs), and nonporous polymers offer many possibilities for their use in photocatalysis [24–26]. Therefore, photocatalytic applications of such materials have already been reported in the areas of organic chemical synthesis [24], degradation of pollutants [25], CO2 reduction [27] and
water splitting [26], among others. This approximation makes it possible to combine the inherent advantages of homogeneous systems (activity and selectivity) and heterogeneous catalysis (recyclability and easy separation of the catalyst from the product).

In photocatalytic transformations, solvent usually enables diffusion of the substrate and the catalyst, facilitating transfer of energy and/or electrons. In addition, efficient excitation of the photocatalyst usually requires dilution. Consequently, the use of solvents in photocatalysis is commonly crucial, which is the reason the number of reports on solvent-free photocatalytic processes is very limited [28]. However, avoiding the use of solvent still remains as a challenging goal, for evident economic and environmental reasons. A first approach consists of using the substrate itself as a solvent in which the molecular photocatalyst can be dissolved [29–31]. An alternative option to this strategy is to use dispersions of semiconducting photocatalysts based on titanium dioxide [32,33]. Alternatively, combination of photocatalysis with mechanochemistry makes it possible to transform solid starting materials into solid products by the application of a solid photocatalyst [34,35]. A main drawback of using this last strategy is that, due to the low penetration depth of light into solids, the inner reaction mixture is shielded from light. To address this issue, a reactor was designed that allows fast rotation of the reaction vessel, allowing efficient excitation of the photocatalyst [36]. Overall, although very interesting, these strategies have several challenges that have not been simultaneously tackled, such as the need for high conversions, the use of visible light, or the recyclability of the catalysts.

Considering these precedents, and taking into account the challenges ahead, this work offers a different possible solution for solvent-free photocatalytic processes. Based on our previous experience on photocatalytic materials [37–40], we designed a solid thin transparent photoactive film containing PTH units assembled through polymerization via imine formation. The obtained plastic material could be used as photocatalytic membrane to transform liquid substrates without the need for mechanical activation, allowing the easy recycling and separation of the catalyst and achieving high yields.

The photocatalytic performance of our system has been tested for oxidation of thioethers, which has an outstanding relevance in the pharmaceutical and agrochemical industries [41]. However, visible light solvent-free procedures have never been tackled using organic photocatalytic materials. The common outputs for these processes are the corresponding sulfoxides, and sulfones are occasionally detected as minor byproducts. However, the distinct characteristics of the photocatalytic system reported herein allowed the quantitative isolation of sulfoxides or sulfones under different reaction times. Thus, the use of the new film material reported in this work widens the possible applications of polymeric materials on solvent-free photocatalytic transformations under soft conditions using visible light in effective and recyclable processes.

2. Results and Discussion
2.1. Synthesis and Characterization of Photoactive Polymer

In the quest for new polymeric structures that integrate the photocatalytic unit phenyl phenothiazine (PTH), we performed a variation of a reported synthesis that previously yielded a single molecule organic cage [42]. We expected to find new structural motifs as a result of the different topological possibilities that the system offers. In addition, the equilibrium that determines the formation of molecular cages and/or the condensation of polymeric structures can be directed through subtle changes in the reaction conditions. The PTH-containing material was prepared by the imine condensation between the tri-aldehyde PTH building unit 4,4′,4″-(10-phenothiazine-3,7,10-triyl)tribenzaldehyde (see Figure 1) and the chiral diamine (1R,2R)-cyclohexane-1,2-diamine. The polymeric material was synthesized by increasing the overall concentrations (with respect to the conditions reported for the synthesis of molecular cages) [42]. The slow evaporation in a 2.3 cm² glass surface at room temperature of 0.4 mL of a chloroform solution resulting from fast mixing of both precursors at concentrations of 2 mg/mL of diamine precursor and 6 mg/mL of trialdehyde building block resulted in the formation of a thin yellow transparent film. This
material is insoluble in many solvents in which the initial building blocks are soluble (water, methanol, ethanol, ethylacetate, acetone, acetonitrile and cyclohexane). This lightweight (39 g/m²) plastic material can be separated from the support where it was grown and can be manipulated independently (see Figure 1).

Initially, powder X-ray diffraction and gas absorption measurements were performed, but no significant crystallinity or porosity were observed. However, the chemical identity of the material obtained was assessed by further spectroscopic measurements. First, IR spectrum (see Figure 2a) of the material reveals that imine condensation has occurred. In particular, the most significant vibration peaks at 1637 cm⁻¹ and 1260 cm⁻¹ (attributed to the C=N and C–C=N–C stretching of imine moieties) indicate the formation of the polyimine structure. The weak vibration peak at 1697 cm⁻¹ was assigned to the C=O stretching of residual unreacted aldehydes, which are very minor. Accordingly, the appearance of Fermi resonance peaks at 2825 and 2727 cm⁻¹ are almost imperceptible. In addition, the presence of aromatic fragments are revealed by corresponding C–C aromatic ring stretchings at 1593 and 1465 cm⁻¹ and C( aromatic)-H stretchings centered at 3027 cm⁻¹. Furthermore, the alkyl fragment is mainly observed by the peaks at 2919 and 2849 cm⁻¹ corresponding to C(sp³)–H stretching vibrations. Thus, infrared spectroscopy indicates that both trialdehyde and diamine building blocks condensed to form an imine-based material. The same conclusion can be obtained from the analysis of solid-¹³C-NMR (Figure 2b) experiments using Cross Polarization combined to Magic Angle Spinning. NMR spectrum of material shows the characteristic iminic carbon peak at 163 ppm as well as the peaks in the region between 150 and 110 ppm, which were assigned to the aromatic carbons. In addition, the cyclohexyl moiety is revealed by the peak at 75 ppm that can be assigned to tertiary –C–N carbons and peaks at 35 and 25 ppm corresponding to –CH₂– groups.

Thermogravimetric analysis (see Figure 2c) indicates that the material is thermally stable in air up to 450 °C. Furthermore, the ability to absorb small solvent molecules is revealed by a weight loss of 9% in the temperature range of 100–200 °C. It is reasonable to assign this weight loss to absorbed water. Assuming this, the elemental analysis was calculated considering the formula (C₃₃SNH₂)₂(C₆H₁₀N₂)₂(H₂O)₂ (Theoretical elemental analysis: C 72.9%; H 6.3%; N 8.1%; S 4.6%), which reasonably matches with the values experimentally observed (C 73.5%; H 6.0%; N 7.8%; S 4.2%).

The microstructure of the material was analyzed by Scanning Electron Microscopy (SEM). Images of the surface shows a regular and flat structure (see Supplementary Materials). In addition, the transversal perspective of a cut of the material reveals first that the thickness of a typical layer is about 60 microns (see Supplementary Materials). Furthermore, images are consistent with a linear polymeric structure. Accordingly, the transversal image (see Figure 2d) shows cylindrical holes observed as a result of fast evaporation of the solvent during the material’s formation process. A more detailed analysis of the image also indicates that the plastic obtained is the result of the stacking of fibrous structures.
Figure 2. Characterization of PTH-polymer: (a) IR spectra; (b) solid-state $^{13}$C-NMR spectra (CP-MAS); (c) thermogravimetric analysis and (d) SEM image.

The IR and NMR spectroscopic data and elemental analysis are similar to those reported for the molecular cage previously obtained through the condensation of the same building blocks [42]. However, the film obtained and the microstructures observed by SEM do not match with the observations previously reported. Thus, considering the higher precursors’ concentrations, we hypothesized that imine condensation from trialdehyde and diamine resulted in a distinct polymeric structure. Such feature was further determined by means of Matrix-Assisted Laser Desorption Ionization-Time-Of-Flight (MALDI-TOF) mass spectrometry. The signals observed for cations at m/z values between 1179 and 6210 can be assigned to several fragments of a polymeric structure as shown in Figure 3. These observations strongly suggest the formation of a linear polymer consisting of the assembly of macrocyclic fragments formed by the condensation of two diamine precursors and two trialdehyde reagents (Scheme 1). Each macrocycle contains two aldehyde groups that can further react with an additional molecule of cyclohexane-1,2-diamine building block. If the diamine acts as a bridge between two macrocycles, a linear polymeric structure is obtained. However, if the two amine groups of the same diamine condensate with the two aldehydes of the same macrocycle, the product will be a molecular cage. In our case, the higher concentrations used enhanced intermolecular processes resulting in the formation of the linear polymer.
Figure 3. MALDI-TOF mass spectrometry of the PTH-polymer.

Scheme 1. Formation conditions for both molecular cage and PTH-polymer.
Outstanding features of this new material are the optical properties that can be measured. The transparency of the films obtained allow the direct determination of the absorption and emission spectra using the instrumentation that is usually employed for liquid samples. Thus, the absorption measurements show that the material absorbs light up to approximately 520 nm (see Figure 4). From these data, the gap between valence and conduction bands was evaluated through Kubelka-Munk analysis, revealing a value of 2.4 eV (see Supplementary Materials). Furthermore, an intense emission can be observed even upon exposure to a regular UV lamp. Emission spectrum measured exciting at 420 nm shows an intense signal with two maximums at 585 nm and 720 nm. Finally, the presence of chiral centers in the material located in the (1R,2R)-cyclohexane-1,2-diimine fragment can be detected by polarimetry measurements as the optical rotation (α) values measured for 1 and 2 layers of this material are 0.4° and 0.8°, respectively.

2.2. Photocatalytic Activity

The appealing optical properties of the material obtained and the fact that it is isolated as a transparent film prompted us to apply it as photocatalytic membrane in solvent-free processes. To this end, we chose aerobic sulfoxidation as a model reaction, which has been observed in related systems using organic solvents [24,36,37]. In this work, sulfoxidation reactions were carried out in absence of solvent, which is a challenging goal for photocatalytic transformations. With this aim, the catalytic system consisted of a liquid organic sulfide that directly contacted with the material surface irradiated with a blue LED (450 nm) in an oxygen-enriched atmosphere. The optimized results obtained are summarized in Figure 5. As control experiments, reactions without material or without irradiation were carried out and conversion of the starting sulfide was not observed, confirming the photocatalytic nature of the process and the important role of the material. From the liquid organic sulfides we chose four representative examples: two alkyl-phenyl (1a and 1b) and two dialkyl sulfides (1c and 1d). Oxidation of alkyl-phenyl substrates 1a and 1b reached high conversions but at longer reaction times than the other two substrates. Interestingly, the electron-donating nature of the benzylic ring with a p-methoxy group in substrate 1b slightly accelerated the sulfoxidation process. Remarkably, substrates 1c and 1d were fully oxidized in short times (especially faster is the oxidation of 1d). Although under the optimized conditions sulfoxides were obtained quite selectively, increasing amounts of sulfone were detected at longer reaction times. In fact, quantitative conversions into sulfone products were observed for dialkylic substrates. However, when the same reaction is carried out in solution, using PTH-polymer or molecular 10 phenyl-phenotiazine as photocatalysts, sulfoxide is obtained but sulfone is not observed. Interestingly, the solvent-free procedure using molecular PTH did not result in any conversion, suggesting
the need for transparent films that avoid light dispersion. Therefore, it seems that the high concentration of sulfoxide product on the surface of photocatalytic transparent film generated in solvent-free experiments enhances further oxidation to sulfone. These results represent an unprecedent method to gain access to sulfone products through a photocatalytic process, which has never before been achieved through light-promoted aerobic oxidation of sulfides.

Figure 5. Yields of sulfoxides 2 (purple) and sulfones 3 (yellow), (measured by $^1$HNMR Spectroscopy) resulting from solvent-free photocatalytic experiments at different reaction times using PTH-polymer as photocatalyst for sulfoxidation of substrate $1a$ (top-left), $1b$ (top-right), $1c$ (bottom-left) and $1d$ (bottom-right).

The heterogeneous nature of the system studied allowed us to evaluate the recyclability of the catalytic material. Interestingly, as shown in Figure 6 the catalytic material can be reused at least in five catalytic runs (4 h each), conserving its high characteristic activity for oxidation of sulfide $1d$. 

$\text{R}_1 \text{S} \text{R}_2$  

$\text{O}_2$, [450nm]  

$r.t.$  

$\text{O} \text{S} \text{O}$  

$\text{R}_1 \text{S} \text{R}_2$  

$\text{O} \text{S} \text{O}$  

$1a \ R_1 = (4-\text{Me})-\text{Ph} \ R_2 = \text{Me}$  

$1b \ R_1 = (4-\text{MeO})-\text{Ph} \ R_2 = \text{Me}$  

$1c \ R_1 = \text{t-Bu} \ R_2 = \text{Me}$  

$1d \ R_1 = R_2 = \text{Bu}$
Finally, we addressed the question of the mechanism that triggers sulfoxide formation under the reaction conditions employed in this work. As in previous reports [24,36,37], we used selective quenchers in order to discern between energy transfer mechanism based on singlet oxygen generation and electron transfer pathway that results in the formation of superoxide radical anion. The mechanistic probes used 1,4-Diazabicyclo[2.2.2]octane (DABCO) to give evidence of oxidation based on single oxygen generation and para-dimethoxybenzene as quencher of superoxide radical anion intermediate. Both quenchers are solid at room temperature, so reactions should be performed in solution. These mechanistic experiments were carried out in ethanol solutions containing sulfides 1a and 1d. Similar quenching effects have been observed for both sulfide reagents. As can be observed in Figure 7, only DABCO has a detrimental effect on sulfide conversion. Thus, our experiments suggest that an energy transfer occurs resulting in the generation of singlet oxygen, which is ultimately responsible for sulfide oxidation. Accordingly, the use of deuterated ethanol has a positive effect on conversion values, which is also indicative of singlet oxygen involvement.

Figure 6. Recyclability of the PTH-material, with yields to each product, sulfoxide (purple) and sulfone (yellow) derived from oxidation of dibutylsulfide.

Figure 7. Mechanistic experiments for oxidation of dibutylsulfide (green) and p-methythioanisol (blue) substrates using PTH-polymer as photocatalytic material.

3. Materials and Methods
3.1. Materials and General Methods

All reagents and solvents were purchased from commercial sources and used without further purification. The (1R,2R)-diaminecyclohexane building unit was commercially...
sourced by Alfa Aesar (Ward Hill, MA, USA). The PTH-containing building unit (4,4′,4″-(10-
phenothiazine-3,7,10-triyl)tribenzaldehyde) was synthetized in three steps following literature
procedures shown below [42], where all reagents included are commercially available.

Light irradiation for photocatalytic experiments was carried out using a 15 W blue
LED photoreactor. A spectro-radiometer Stellarnet model Blue-Wave UV-NB50 device
(Sterlilnert, Tampa, FL, USA) was employed to measure the emission of the Blue LED used
(rangeth 300–600 nm, integration time CR2-AP + 200 ms, intensity 21.7217 W/m²)

Nuclear Magnetic Resonance (NMR) spectra were acquired on a Bruker AV-300 spect-
trometer (Bruker Corporation, Billerica, MA, USA), running at 300 MHz for 1H and at
75 MHz for 13C. Chemical shift (δ) are reported in ppm relative to residual solvent signals
(CDCl3: 7.26 ppm for 1H-NMR, 77.0 ppm for 13C-NMR). 13C solid-state Nuclear Magnetic
Resonance was acquired on a Bruker AV-400 spectrometer coupled to a multinuclear probe
(15N-31P) CPMAS with triple channel (BL4 X/Y/1H) for a 4 mm rotor at room temperature,
using 1k scans and 12 kHz of turning speed. The 1H excitation pulse used is π/2 × 2.75 μs
and the contact pulse is 3 ms.

Elemental chemical analysis was performed using an elemental analyzer LECO CHNS-
932 model number 601-800-500 (LECO Corporation, Madrid, Spain).

Fluorescence emission of the materials was measured by irradiating a film of the
material at 420 nm using a JASCO Spectrofluorometer FP-8600 controlled by Spectra
Manager Version 2.10.01. Absorption measurements were carried out by placing a film of the
material into the optical path of an Agilent 8452 diode array spectrophotometer over a
190–1100 nm range.

Scanning electron microscopy (SEM) images were obtained on a JEOL JSM-7600F
(JEOL Ltd., Tokyo, Japan) field emission scanning electron microscope with a field emission
cannon. The images were obtained in vacuum after being metallized in a Sputter Quórum
Q150T-S with gold coating.

MALDI-TOF spectra were measured on a Ultraflex III Bruker instrument (Bruker Corpo-
ration, Billerica, MA, USA) using trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]
malononitrile (DCTB) as matrix.

Thermogravimetric analyses (TGA) were performed on a TGA Q500 Thermobalance
from TA instruments (TA Instruments, New Castle, DE, USA), heating the sample from
25 °C to 900 °C at 10 °C/min under air atmosphere.

3.2. Synthesis of (4,4′,4″-(10-Phenothiazine-3,7,10-Triyl)Tribenzaldehyde) Building Block

The PTH-containing building unit (4,4′,4″-(10-phenothiazine-3,7,10-triyl)tribenzaldehyde)
was synthetized according to the strategy shown in Scheme 2.

![Scheme 2. Synthetic pathway for PTH-containing building unit.](image-url)

4-(phenothiazin-10-yl)benzaldehyde: A solution of phenothiazine (1.3430 g/7 mmol),
4-bromobenzaldehyde (1.4240 g/7.7 mmol), tri-terr-butylphosphonium tetrafluoro-
borate (0.1015 g/0.35 mmol) and sodium tert-butoxide (0.777 g/8.1 mmol) in 10 mL of
toluene was purged with Ar bubbling under stirring for 10 min. Then, the catalyst tris(dibenzylideneacetone)dipalladium(0) (0.193 g/0.21 mmol (3% mol)) was added to the reaction mixture, and it was purged with Ar bubbling under stirring for another 10 min. Finally, the mixture was refluxed at 110 °C under Ar atmosphere for 72 h. Thereafter, the crude mixture was filtered through celite, washing the filter with 3 × 20 mL portions of DCM. The solvent was removed under reduced pressure, and the crude was purified by column chromatography (Cyclohexane: Dichloromethane (DCM)) gradient from 73:1 to 74, obtaining the product as a yellow-brown oil (41% yield), which was dried under vacuum for 24 h in order to turn it into a yellow powder. Spectroscopic data match with the reported data [42].

1H NMR (CDCl₃, 300 MHz) of 4-(phenothiazin-10-yl)benzaldehyde: δ (ppm): 9.86 (1H (CHO), s), 7.75 (2H, dd), 7.42 (2H, dd), 7.36–7.25 (4H, m), 7.23–7.14 (4H, m).

4-(3,7-dibromo-phenothiazin-10-yl)benzaldehyde: To an ice-cooled solution of 4-(phenothiazin-10-yl)benzaldehyde intermediate (0.7508 g/2.47 mmol) in DCM (15 mL) under stirring, another solution of N-bromosuccinimide (0.9754 g/5.48 mmol) in 30 mL of DCM was added dropwise. After the addition completed, the reaction mixture was stirred for 12 h. After the reaction was finished, the crude was washed with H₂O (3 × 20 mL), dried over Na₂SO₄, and filtered. The solvent was removed by reduced pressure and the dark green crude mixture was purified by column chromatography (Cyclohexane:DCM (1:4)) to obtain the product as a white/clear-yellow solid (57% yield). Spectroscopic data matches with the reported data [42].

1H NMR (CDCl₃, 300 MHz) of 4-(3,7-dibromo-phenothiazin-10-yl)benzaldehyde: δ (ppm): 9.94 (1H (CHO), s), 7.86 (2H, dd), 7.44 (2H, dd), 7.34–7.20 (4H, m), 6.82–6.79 (2H, dd).

4,4′,4″-(10-phenothiazine-3,7,10-triyl)tribenzaldehyde: To a solution of 4-(3,7-dibromo-phenothiazin-10-yl)benzaldehyde intermediate (0.8000 g/1.74 mmol) and (4-formylphenyl)boronic acid (0.7800 g/5.21 mmol) in 40 mL of THF, another solution of potassium carbonate (0.9589 g/6.93 mmol) in distilled water (8 mL) was added. The mixture was purged with Ar bubbling for 15 min, and then, tetrakis(triphenylphosphine) palladium (0) (0.1000 g/0.086 mmol (5% mol)) was added, purging after the addition with Ar bubbling under stirring for another 15 min. Then, the mixture was heated under refluxing conditions (70 °C) for 48 h. Once the reaction was completed, the THF was removed under reduced pressure, and the crude was extracted with DCM:water, drying the organic layer over Na₂SO₄, filtering it and removing the DCM under reduced pressure. Then, the extracted crude was purified by column chromatography (DCM:AcOEt, gradient from pure DCM to 9:1) in order to obtain 4,4″,4‴-(phenothiazine-3,7,10-triyl)tribenzaldehyde (PTH-building unit) product as an intense-orange powder (51% yield). Spectroscopic data match with the reported data [42].

1H NMR (CDCl₃, 300 MHz) of 4,4′,4″-(phenothiazine-3,7,10-triyl)tribenzaldehyde: δ (ppm): 10.05 (1H (CHO), s), 10.04 (2H (CHO) 2, s), 8.03 (2H, dd), 7.95 (4H, dd), 7.79 (4H, dd), 7.53 (2H, d), 7.48 (2H, d), 7.38–7.34 (2H, dd).

3.3. Preparation of PTH-Polymer

First was prepared 6.0 mL of a solution in CHCl₃ containing building units (1R,2R)-diamminecyclohexane (12 mg) and of PTH-containing trialdehyde (36 mg). Then, 0.4 mL of the prepared solution was accurately added to the bottom of a 7 mL glass vial, allowing slow evaporation of the solvent. Complete chloroform evaporation resulted in the formation of the polymer as a thin orange-yellow film covering the bottom of the vial.

3.4. General Procedure for the Photocatalytic Oxidations

In a 7 mL glass vial with the PTH-polymer formed on its bottom, 0.037 mmol (5–6 µL approximately) of the corresponding liquid sulfide was added. After this, the vial was sealed with a septum, and conditioned with 3 cycles of vacuum-oxygen through the septum in order to generate the oxygen-enriched atmosphere (keeping the oxygen source connected to the vial after the third cycle). Finally, the system was placed under a 450 nm blue LED lamp during the corresponding reaction times (see Figure 5). After the reaction was finished, the crude was directly extracted from the vial with CDCl₃ and analyzed by
1H NMR spectroscopy. The conversions to each product were calculated considering the relative integration of characteristic peaks from the sulfide, sulfoxide and sulfone signals in the 1H NMR spectra.

3.5. Evaluation of the Recyclability of the Material

The recyclability of the system was experimentally determined by repetitively following the procedure presented above. After each catalytic run the crude reaction was extracted with 2 mL of cyclohexane. Then, the solvent was removed under reduced pressure. The remaining product mixture was analyzed by 1H NMR by diluting it in CDCl3.

3.6. Mechanistic Experiments for the Sulfoxidation Reaction

For both p-methylthioanisol (1a) and dibutylsulfide (1d) substrates, control experiments (in absence of quencher) were carried out at the optimized reaction times for each substrate (19 h and 4 h respectively), using EtOH or EtOD as solvent (0.5 mL) under stirring, and with the same conditions as those described above.

Then, the experiments were repeated for each substrate, in presence of DABCO or p-dimethoxybenzene (0.5 equiv, 0.0185 mmol) dissolved in the 0.5 mL of EtOH. The crude of each reaction were extracted with EtOH (washing the PTH-polymer) and then, the EtOH was removed under reduced pressure. After this, the crude was analyzed by 1H NMR using CDCl3 as solvent, conversion values were obtained by peak integration of the spectra.

Experiments involving 10-phenylphenothiazine instead of PTH-polymer as photocatalyst were carried out in solvent-free conditions and using EtOH as solvent. For the solvent-free experiments, 1.3 mg (0.005 mmol) of commercially available N-phenylphenothiazine was directly added in a 7 mL vial and the dibutylsulfide substrate (1d) (0.037 mmol) was added following the procedure analogous to the experiments using the material. For the EtOH experiment, 0.5 mL of EtOH were added to a 7 mL vial, and the 1.3 mg of N-phenylphenothiazine were dissolved. Then, the dibutylsulfide substrate (1d) was added, and the reaction was carried out following the general procedures described above.

4. Conclusions

High concentrations of PTH containing trialdehyde building block 4,4′,4″-(10-phenothiazine-3,7,10-triyl)tribenzaldehyde and (1R,2R)-cyclohexane-1,2-diamine determine the final outcome of the imine condensation. While using diluted solutions results in an intramolecular product, concentrated conditions yield polymeric structures as a consequence of enhancing intermolecular encounters of initial precursor fragments. In this work, we obtained a yellow transparent film, resulting from the generation of the corresponding linear polymer as a consequence of the assembly of imine-based macrocycles. The presence of phenylphenothiazine units in this polymeric material concedes the optical properties expected for a photocatalytic material. Furthermore, the transparency of the obtained plastic made possible its use as photocatalytic films to transform liquid substrates in the absence of any added solvent. As a proof of concept, four different organic sulfides (liquid at room temperature) were oxidized to sulfoxide efficiently and quantitatively. In addition, modulation of reaction times also allowed the isolation of sulfones in good yields. The recyclability of this system has been proved for the oxidation of dibutylsulfide. Mechanistic experiments suggest that the polymer obtained act as energy transfer mediator exciting the oxygen molecule generating singlet oxygen, which is the final responsible of sulfide oxidation. Overall, this work opens a new perspective on the use of transparent photoactive materials with photocatalytic applications. These new designs should allow implementing protocols more environment-friendly avoiding the use of solvents.

Supplementary Materials: The general procedures, experimental details and following are available online at https://www.mdpi.com/article/10.3390/catal11121426/s1. Figure S1: SEM images of PTH-polymer material: (a) surface image and (b) transversal view, Figure S2: Linear regression on the Kubelka-Munk approach representation, Figure S3: 1H-NMR spectrum of 4-(phenothiazin-10-yl)benzaldehyde, Figure S4: 1H-NMR spectrum of 4-(3,7-dibromo-phenothiazin-10-yl)benzaldehyde,
Figure S5: 1H-NMR spectrum of 4,4′,A′′-{(phenothiazine-3,7,10-triyl)tribenzaldehyde, Figure S6: 1H-NMR spectrum of Sulfoxidation reaction crude spectra of sulfide 1a under optimized conditions (19 h), Figure S7: 1H-NMR spectrum of Sulfoxidation reaction crude spectra of sulfide 1b under optimized conditions (15 h), Figure S8: 1H-NMR spectrum of Sulfoxidation reaction crude spectra of sulfide 1c under optimized conditions (8 h), Figure S9: 1H-NMR spectrum of Sulfoxidation reaction crude spectra of sulfide 1d under optimized conditions (4 h), Figure S10: Measurement of light emitted by LED source used in photocatalytic experiments.

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