Use of Novel Cardanol-Porphyrin Hybrids and Their TiO$_2$-Based Composites for the Photodegradation of 4-Nitrophenol in Water

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Abstract: Cardanol, a well known hazardous byproduct of the cashew industry, has been used as starting material for the synthesis of useful differently substituted “cardanol-based” porphyrins and their zinc(II), copper(II), cobalt(II) and Fe(III) complexes. Novel composites prepared by impregnation of polycrystalline TiO$_2$ powder with an opportune amount of “cardanol-based” porphyrins, which act as sensitizers for the improvement of the photo-catalytic activity of the bare TiO$_2$, have been used in the photodegradation in water of 4-nitrophenol (4-NP), which is a toxic and bio-refractory pollutant, dangerous for ecosystems and human health.

Keywords: cardanol; porphyrins; metalloporphyrins; heterogeneous photocatalysis; 4-nitrophenol; porphyrin-TiO$_2$ photocatalysts
1. Introduction

Cardanol is a naturally occurring phenol obtained by vacuum distillation of cashew nut shell liquid (CNSL), a waste byproduct obtained in the cashew nut processing industry [1-5]. Despite the fact that cardanol could really be considered a dangerous toxic waste, mainly due to the massive amounts of CNSL produced annually, it represents a precious natural renewable resource which can be used as a starting material for the preparation of a large variety of useful chemicals [6].

In fact, the preparation of fine chemicals from natural and renewable materials is nowadays becoming an attractive topic of research especially for the purpose of recycling huge amounts of agro-industrial waste.

The yellow oil obtained by vacuum distillation of CNSL, that for simplicity we call cardanol, contains 3-n-pentadecylphenol, 3-(pentadeca-8-enyl)phenol, 3-(pentadeca-8,11-dienyl)phenol, and 3-(pentadeca-8,11,14-trienyl)phenol in approximately 8%, 80%, 8%, 6%, respectively (Figure 1) [7].

![Figure 1. Main components of the cardanol mixture.](image)

On the other hand, the photodegradation of organic pollutants in water is a topic of growing interest and much attention has been devoted in recent years from both academic and industrial researchers to design new photocatalytic systems having effective application in environmentally friendly processes like the TiO$_2$-based photocatalysts used for the oxidative degradation of various kinds of organic pollutants [8-10].

4-Nitrophenol (4-NP) is a harmful and bio-refractory contaminant which can cause considerable damage to the ecosystem and human health. For this reason its efficient degradation in aqueous effluents is important in order to minimize its deleterious effects as well as environmental problems [11-14].

In the past, we have used 3-n-pentadecylphenol (hydrogenated cardanol), as well as cardanol, as basic materials for the preparation of fine chemicals such as meso-tetrasubstituted cardanol-based \( \text{A}_4\)-porphyrins [15,16]; but, we noted that only a few examples concerning the use of 3-n-pentadecyl-
phenol-based porphyrins as sensitizers to enhance the photoactivity of TiO$_2$ in the photodegradation of pollutants in water under UV light, have been reported [17].

Therefore, continuing our research in this area, we like to report here the synthesis and characterization of new meso-AB$_3$ and trans-A$_2$B$_2$ porphyrins, 5,10,15-triphenyl-20-mono-[4-(2-(3-pentadec-8-etyl)phenoxy)ethoxy]phenylporphyrin (3) and 5,15-diphenyl-10,20-di-[4-(2-(3-pentadec-8-etyl)phenoxy)ethoxy]phenylporphyrin (4), and their metal derivatives (M = Zn, Cu, Co and Fe).

We would also like to report studies concerning the photocatalytic activity of these compounds, once deposited onto TiO$_2$, in photodegradation of 4-nitrophenol contained in the water. The advantages related to the use of cardanol-based porphyrins containing double bonds in the cardanol side chain has also been noted in this work.

2. Results and Discussion

2.1. Synthesis and Characterization of Cardanol Based Porphyrins

In this work, the term cardanol is used to refer mainly to 3-(pentadeca-8-etyl)-phenol, the monoolefinic component which can be obtained almost pure from the cardanol oil through distillation and chromatographic separation, the purity of which, enough for our purposes, was confirmed by GC-MS and NMR analyses. The meso-AB$_3$ and trans-A$_2$B$_2$ porphyrins were obtained, using 4-[2-(3-(pentadeca-8-etyl)phenoxy)ethoxy]-benzaldehyde (1) which was prepared from cardanol through two steps as shown in Scheme 1, following the procedure reported in the literature [6,18].

![Scheme 1. Synthesis of 4-[2-(3-(pentadeca-8-etyl)phenoxy)ethoxy]-benzaldehyde (1).](image)

Thus, meso-AB$_3$ and trans-A$_2$B$_2$ cardanol-based porphyrins 3 and 4, were synthesized respectively by acid-catalyzed condensation of compound 1 by statistical reaction with pyrrole and benzaldehyde (Method 1) or with meso-phenyldipyrrolmethane 2 (Method 2), as shown in Scheme 2 in accordance with different reaction protocols [6,7]. The resulting porphyrins 3 and 4, brown-red sticky solids, very soluble in CHCl$_3$ or CH$_2$Cl$_2$, have been characterized by FT-IR, UV-Vis, $^1$H- and $^{13}$C-NMR, and MALDI-TOF techniques. Isolated yields and UV-Vis absorption band of compounds 3 and 4 are reported in Table 1.
Scheme 2. Synthesis of meso-AB₃ and trans-A₂B₂ cardanol-based porphyrins 3 and 4.

Table 1. Yields and UV-Vis absorption bands of 3, 4 and their metalloporphyrins 3a–3e, 4a–4e.

| Compounds                             | M     | Yields % | λ max, nm (CHCl₃) | Soret band | Q bands |
|---------------------------------------|-------|----------|-------------------|------------|---------|
| 3                                     | 2H    | 10       | 419               | 516        | 552     | 590     | 646     |
| 3a                                    | Zn    | 90       | 424               | 554        | 594     |
| 3b                                    | Cu    | 90       | 416               | 539        |
| 3c                                    | Co    | 90       | 411               | 530        |
| 3d                                    | Fe    | 80       | 417               |            |
| 4                                     | 2H    | 15       | 420               | 517        | 553     | 591     | 647     |
| 4a                                    | Zn    | 90       | 425               | 554        | 596     |
| 4b                                    | Cu    | 90       | 417               | 540        |
| 4c                                    | Co    | 90       | 412               | 530        |
| 4d                                    | Fe    | 80       | 419               |            |
| cardanol-based A₄-porphyrin            | 2H    | 14 [16]  | 420               | 518        | 556     | 593     | 649     |

For instance, the UV-Vis spectrum of 3 showed a Soret band at 419 nm and Q bands at 516, 552, 590 and 646 nm; the UV-Vis spectrum of 4 showed a 1 nm red shift, with a Soret band at 420 nm and Q bands at 517, 553, 591 and 647 nm. A red shift in the Q bands was also observed in the previously reported cardanol-based A₄-porphyrin [16]. This suggested to us that the number of the substituents in the porphyrin molecule influences the value of the maximum of absorption in the UV-Vis spectra, producing a red shift when the number of substituents is increased. The MALDI-TOF analysis of the
metal free porphyrins 3 and 4 showed a cluster of signals centered at $m/z = 958 \ [M]^+$ and 1,301 $[M]^+$, respectively and consistent with the proposed structures.

$^1$H-NMR and FT-IR spectra of 3 and 4 were also consistent with the proposed structures. In fact, $^1$H-NMR spectrum of 3 exhibited a multiplet in the 8.82–8.89 ppm range attributable to the eight protons at the $\beta$ position of the pyrrole moiety, whereas two typical doublets centered at 8.84 and 8.87 ppm for the $\beta$ position of the pyrrole moiety were observed in 4, due to its higher symmetry. The aromatic protons, found in the 8.24–6.83 ppm range and the protons of the double bond of the side-chain in the 5.28–5.42 ppm range appear as multiplets, and were similar in both porphyrins 3 and 4. In the case of 3, two multiplets corresponding to the protons of the O–CH$_2$CH$_2$–O system were found in the 5.30–5.40 and 4.59–4.64 ppm range, but in the case of 4 two triplets were found at 4.53 and 4.63 ppm. The triplets centered 2.63 and 2.64 ppm in 3 and 4, respectively, correspond to the aliphatic protons of the Ar–CH$_2$ system, the other aliphatic protons were in the range 0.75–2.12 ppm in both 3 and 4. NH protons were present as a broad band centered at −2.77 and −2.76 ppm in 3 and 4, respectively. The FT-IR spectra of porphyrins 3 and 4 showed a weak band at 3,317 cm$^{-1}$, characteristic of the NH vibration, and at 3,006 cm$^{-1}$ attributed to the side-chain vinylic =C–H vibration.

**Scheme 3.** Preparation of the metallo-porphyrins 3a–3d and 4a–4d.

Porphyrins 3 and 4 were next used for preparation of the corresponding metallo-derivatives 3a–3d and 4a–4d (Scheme 3) in nearly quantitative yields, by reacting them with Zn(OAc)$_2$, Co(OAc)$_2$·4H$_2$O,
CuCl₂, and FeCl₃, respectively. FT-IR, UV-Vis, MALDI-TOF and elemental analyses of the metalloporphyrin complexes 3a–3d and 4a–4d were consistent with the proposed structures. Yields and UV-Vis absorption bands of 3a–3d and 4a–4d are also reported in Table 1.

From the UV-Vis absorption bands it is possible to observe that in the case of metalloporphyrins 3a–3d and 4a–4d, the Soret band is only slightly shifted compared to the corresponding metal-free porphyrins and the Q bands are reduced to two or at least one because the symmetry of porphyrin ring increases when the hydrogen atoms were replaced by metals.

The IR spectra of 3a–3d and 4a–4d were close to those of the corresponding metal-free porphyrins 3 and 4, except for the disappearance of the NH vibration at 3317 cm⁻¹. MALDI-TOF mass spectrometry analysis was successfully used for the determination of the molecular weight of the metalloporphyrin complexes 3a–3cd and 4a–4d (see Experimental Section). ¹H and ¹³C-NMR spectra were recorded only in the case of Zn(II) complex 3a and 4a because of the paramagnetic effect of the Cu(II), Co(II) and Fe(III) metal ions that hindered the recording of any such spectra.

2.2. Preparation of the Cardanol Based Porphyrin/TiO₂ Composites and Diffuse Reflectance (DR) Spectroscopy Characterization

TiO₂ composites used as photocatalysts were prepared by impregnating of TiO₂ with cardanol-based porphyrins according with the procedure reported in the Experimental. Figure 2 shows the diffuse reflectance spectra in air of the bare TiO₂ as well as of TiO₂ impregnated with 4.0 µmol of the selected H₂Pp 4 or MPp [M = Zn (II), Cu(II), Co(II), Fe(III)-Cl] porphyrins 4a–4d per gram of TiO₂, respectively, recorded in the 200–800 nm range.

**Figure 2.** Diffuse reflectance spectra of bare TiO₂ and differently loaded samples obtained by impregnation of TiO₂ with H₂Pp 4 or MPp 4a–4d.

It is worth noting that no appreciable shift of the band gap edge of TiO₂ can be observed for any of the loaded samples. This behaviour was in accord with previously studied metal free and copper [5,10,15,20-tetra(4-tertbutylphenyl)] porphyrins [19].
Similar behavior was observed for the porphyrins H$_2$Pp, 3, and MPps [M = Zn (II), Cu(II), Co(II), Fe(III)–Cl] 3a–3d (spectra not shown in Figure 2 for clarity). Figure 3 shows the SEM pictures of bare TiO$_2$ and CuPp (4b)/TiO$_2$. Basically, the microstructures of the bare TiO$_2$ and porphyrin impregnated TiO$_2$ composites show common features which are typical regarding this TiO$_2$ polymorph. In fact, both kinds of samples seem rather similar, with spherical shaped particles.

**Figure 3.** SEM images of bare (a) TiO$_2$ and (b) 4 µmol CuPp (4a)/1 g TiO$_2$.

2.3. Photoreactivity Experiments

A few years ago, we reported that polycrystalline TiO$_2$ samples impregnated with differently substituted porphyrins synthesized from commercially available starting materials displayed better photocatalytic activity, in comparison with polycrystalline bare TiO$_2$ samples, in the photocatalytic degradation of 4-NP in water [19,20]. In this work, novel cardanol-based composites 3/TiO$_2$, 3a/TiO$_2$-3d/TiO$_2$ and 4/TiO$_2$, 4a/TiO$_2$-4d/TiO$_2$, were tested in the photocatalytic degradation of 4-NP.

The efficiency of a photodegradation catalyst has been evaluated by measuring the rate of consumption of 4-NP in a slurry containing a finely dispersed semiconductor, under constant illumination. It can also be noticed that the substrate was degraded using each of the photocatalysts, following pseudo-first-order kinetics. The list of used samples is reported in Table 2, along with the initial reaction rates of 4-NP disappearance as $r_0 \times 10^9$ (mol L$^{-1}$s$^{-1}$), $r_0' \times 10^9$ (mol L$^{-1}$s$^{-1}$m$^{-2}$) and % conversion of 4-NP.

Figure 4 shows the diminution of 4-NP concentration vs. irradiation time using different amounts of CuPp (4b)/TiO$_2$ photocatalysts. These preliminary investigations were carried out in order to establish which among the differently impregnated photocatalysts exhibited the highest photoactivity.
Table 2. List of the samples used together with the initial photoreaction rates, and the conversion (%) 4-NP after 180 min of irradiation time.

| Samples | $r_0 \times 10^9$ (molL$^{-1}$s$^{-1}$) | $r_0' \times 10^9$ (molL$^{-1}$s$^{-1}$m$^{-2}$) | 4-NP converted at 180 min |
|---------|-------------------------------------|-----------------------------------------------|--------------------------|
| TiO$_2$ | 26.59                               | 33.24                                         | 93.5                     |
| 1.0 µmol CuPp(4b)/TiO$_2$ | 36.36                               | 45.45                                         | 95.9                     |
| 2.0 µmol CuPp(4b)/TiO$_2$ | 39.62                               | 49.52                                         | 97.5                     |
| 4.0 µmol CuPp(4b)/TiO$_2$ | 42.48                               | 53.10                                         | 97.4                     |
| 6.0 µmol CuPp(4b)/TiO$_2$ | 46.70                               | 58.38                                         | 98.2                     |
| 9.0 µmol CuPp(4b)/TiO$_2$ | 31.21                               | 39.01                                         | 97.1                     |
| 6.0 µmol ZnPp(4a)/TiO$_2$ | 33.94                               | 42.42                                         | 95.1                     |
| 6.0 µmol CoPp(4c)/TiO$_2$ | 34.28                               | 42.85                                         | 95.4                     |
| 6.0 µmol FeClPp(4d)/TiO$_2$ | 18.77                               | 23.46                                         | 92.8                     |
| 6.0 µmol H$_2$Pp(4)/TiO$_2$ | 22.20                               | 27.75                                         | 86.0                     |
| 4.0 µmol CuPp(3b)/TiO$_2$ | 34.34                               | 42.92                                         | 95.8                     |
| 6.0 µmol CuPp(3b)/TiO$_2$ | 42.03                               | 52.54                                         | 97.9                     |
| 6.6 µmol CuPp(3b)/TiO$_2$ | 41.52                               | 51.90                                         | 96.7                     |
| 6.0 µmol ZnPp(3a)/TiO$_2$ | 33.55                               | 41.94                                         | 94.7                     |
| 6.0 µmol CoPp(3c)/TiO$_2$ | 33.72                               | 42.15                                         | 93.9                     |
| 6.0 µmol FeClPp(3d)/TiO$_2$ | 18.66                               | 23.32                                         | 93.3                     |
| 6.0 µmol H$_2$Pp(3)/TiO$_2$ | 21.36                               | 26.70                                         | 85.5                     |

$^a$ The numbers before the code used for identifying the samples indicate the mg amounts of sensitizer [H$_2$Pp(a), H$_2$Pp(a), CuPp(a) or CuPp(a)] per gram of TiO$_2$; $r_0$: The initial photoreaction rates per used mass; $r_0'$: Initial photoreaction rates per used mass and per unit surface area of the catalysts. The BET specific surface areas of all the samples are equal to ca. 8 m$^2$g$^{-1}$, amount of photocatalyst: 0.1 g/125 mL solution; $^b$ The % conversion of 4-NP was calculated by the following formula C/C$_0$ × 100.

Figure 4. 4-NP concentration vs. irradiation time using different amounts of CuPp (4b)/TiO$_2$ photocatalysts.
It can be seen that the samples impregnated with 6.0-CuPp (4b)/TiO$_2$ exhibited the highest photoactivity. These results are in accord with those observed by using the sensitizers 3a–3d as summarized in Table 2.

As shown in the Figure 5, the Cu(II) porphyrin 4b definitely proved a more effective sensitizer in the photodegradation of 4-NP than other MPp’s (M = Co, Zn) 4a, 4c, which have a slight beneficial effect. Interestingly, in contrast with previous experimental evidence [19-21], there is a detrimental effect observed for the free-base and Fe(III) porphyrin composites 4/TiO$_2$ and 4d/TiO$_2$ compared with bare TiO$_2$ which could be ascribed to the different lamp used as irradiation source. Figure 5. 4-NP concentration vs irradiation time using 6.0 μmol of H$_2$Pp (4) or MPps (4a–4d) porphyrins/1 g TiO$_2$ as photocatalysts.

The photocatalytic activities are also very slightly influenced by the substitutions and the spatial positions of the substitutions of porphyrins. In particular, the composites (4, 4a–4d)/TiO$_2$ when used as catalysts show slightly better photocatalytic activities than (3, 3a–3d)/TiO$_2$, but they have a similar activity order. All the studied cases gave a conversion of 4-NP higher than 85.5%; in particular, by using the most efficient CuPps/TiO$_2$ photocatalysts the measured conversion was close to 98% (Table 2).

Further investigations were carried out in order to establish the photostability of the CuPp 4b impregnated onto the TiO$_2$ surface. Repeated recycling experiments confirmed that this porphyrin supported onto TiO$_2$ showed good stability under irradiation conditions and samples continued to maintain good photocatalytic activity after several cycles. Figure 6 shows how the most active photocatalyst, i.e., CuPp (4b) TiO$_2$ can be recycled six times, after its first use, without significant loss of activity.
Typically, 3b and 4b, being effective sensitizers, were insoluble in the water and stable under UV irradiation, and the catalysts 3b/TiO$_2$ and 4b/TiO$_2$ were also reused several times without loss of the activity.

Taking into account the $r_0$ values reported in the Table 2 of the impregnated MPps were in the following order: CuPp > CoPp > ZnPp > bare TiO$_2$ > H$_2$Pp > FePp. The results related to the photo-degradation of 4-NP in an aqueous heterogeneous environment suggest that the Cu(II)-Cu(I) photocatalytic redox cycle plays the main beneficial role for the occurrence of the whole process. In a previous work [20] we demonstrated that Cu(II) could be reduced to Cu(I) [see equation (1)] by electrons of the conduction band of TiO$_2$ where additional electrons are injected, due to the presence of the sensitizer:

$$\text{TiO}_2[\text{Cu(II)Pp}] + e^-_{\text{CB}} \rightarrow \text{TiO}_2[\text{Cu(I)Pp}]$$  \hspace{1cm} (1)

Despite the complex mechanism of reactions the redox process reported in equation 1 seems to be the key step in the course of which is possible to increase the amounts of OH radicals and superoxide anion responsible of the degradation process of 4-NP [19,20]. Moreover, in the present case, porphyrin sensitizers containing un-saturated chains capable of being oxidized have been used for the first time. Spectroscopic analysis (UV-Vis, FT-IR, etc.) carried out in order to check the photostability of the porphyrins used as the sensitizers permitted us to prove the stability of the double bonds contained in the side cardanol chains. In fact, typical spectroscopic signals of double bond of cardanol are still present at the end of each process. This could means that the oxidizing species responsible of the photo degradation processes by oxidative demolition of the 4-NP [19,20] act in water solution far from the composite TiO$_2$ surface.
3. Experimental

3.1. Reagents

Cardanol oil (technical grade) was kindly provided by Oltremare S.p.A. (Bologna, Italy). TiO$_2$ (anatase phase, specific surface area 8 m$^2$/g), kindly provided by Tioxide Huntsman was dried and crushed to obtain particles with a diameter smaller than 0.1 mm. All other starting materials were purchased from Aldrich Chemical Co and used as received. Silica gel (Merck) was used in the chromatographic separations. Solutions of 4-nitrophenol, used without further purification, were prepared by dissolving the required quantity of 4-NP in water obtained from a New Human Power I water purification system.

3.2. Analyses

FT-IR spectra were recorded on a JASCO FT-IR 430 spectrometer. UV-Vis spectra were recorded on a Cary 100scan UV-visible spectrophotometer. $^1$H- and $^{13}$C-NMR spectra were recorded on a Bruker Avance 400 instrument at room temperature and chemical shifts are reported relative to tetramethylsilane. Laser desorption/ionization time of flight mass spectrometry (LDI-TOF MS) was performed on a Reflex IV spectrometer (Bruker Daltonik, Bremen, Germany), managed by the Flex Control 2.4 software (Bruker Daltonik, Bremen, Germany), equipped with a VSL-337ND nitrogen laser (Laser Science Inc., Franklin, MA, USA) delivering 4 ns pulses with a repetition rate of 5 Hz and an average power of 200 $\mu$J. The laser attenuation setting was typically in the range 40–50. Spectra were obtained in positive ion reflector mode, with 20–17 kV accelerating voltage and 23 kV reflection voltage. External quadratic calibration was performed with a standard mixture ranging from 757.40 to 3147.47 kDa, giving a mass error lower than 15 ppm. One $\mu$L of sample solution of CHCl$_3$ was spotted on a MTP 384 massive target T (Bruker Daltonik, Bremen, Germany), both in the absence and in the presence (Matrix Assisted LDI-TOF MS) of same volume of alpha-cyano-4-hydroxycinnamic acid (saturated solution in water/acetonitrile/TFA 66.9/33/0.1) as ionization adjuvant, and air-dried. Each spectrum was acquired by 100 to 200 laser shots. Diffuse reflectance (DR) spectra were obtained at room temperature in the wavelength range 200–800 nm using a Shimadzu UV-2401PC spectrophotometer with BaSO$_4$ as reference material.

3.3. Synthesis

3.3.1. Synthesis of the cardanol based precursors of the porphyrins

$4\{-2-(3-(Pentadeca-8-enyl)phenoxy)-ethoxy\}-benzaldehyde$ (1) was synthesized in our laboratory [6,18]; meso-phenylidipyrrrolmethane (2) was synthesized with the standard procedure in the literature [7].

3.3.2. Synthesis and characterization of $5,10,15$-triphenyl-20-mono-$\{4\)-(2-(3-pentadec-8-enyl)phenoxy)ethoxy\}$ phenylporphyrin (3)

Compound $3$ was obtained by statistical synthesis starting from a 3:1 benzaldehyde-1 mixture using a procedure similar to that reported in reference [7]. Yield: 10%; $^1$H-NMR (CDCl$_3$): δ −2.77 (br, s, 2H),
0.75–0.95 (m, 3H), 1.12–1.42 (m, 16H), 1.58–1.72 (m, 2H), 1.96–2.08 (m, 4H), 2.63 (t, 2H, \( J = 7.6 \) Hz), 4.49–4.54 (m, 2H), 4.59–4.64 (m, 2H), 5.30–5.40 (m, 2H), 6.83–6.93 (m, 3H), 7.24–7.27 (m, 1H), 7.33 (d, 2H, \( J = 8.6 \) Hz), 7.71–7.81 (m, 9H), 8.13 (d, 2H, \( J = 8.6 \) Hz), 8.19–8.24 (m, 6H), 8.82–8.89 (m, 8H); \(^{13}\)C-NMR (CDCl\(_3\)): \( \delta 14.6, 23.1, 27.6, 27.7, 29.5, 29.7, 29.7, 29.8, 29.9, 30.1, 30.2, 31.7, 31.9, 32.2, 36.3, 66.9, 67.2, 112.0, 112.9, 113.3, 115.5, 115.7, 120.4, 120.5, 120.6, 121.4, 121.8, 127.1, 128.1, 128.4, 129.7, 129.8, 130.3, 130.4, 135.0, 135.3, 136.0, 142.6, 142.6, 145.3, 155.8, 158.9, 159.1; FTIR (neat), \( v/cm^{-1} \): 3317, 3006, 2923, 2852, 1598, 1583, 1508, 1470, 1441, 1350, 1244, 1175, 1157, 1109, 1072, 1032, 1001, 979, 966, 932, 909, 876, 845, 800, 731; UV-Vis (CH\(_2\)Cl\(_2\)) \( \lambda_{\text{max}}, \text{nm} \): 419, 516, 552, 590, 646; MALDI-TOF MS \( m/z \): 958 \([M]^+\); Molecular weight: 958 amu; Anal. Calc. for C\(_{67}\)H\(_{66}\)N\(_4\)O\(_2\): C, 83.41; H, 7.02; N, 6.91. Found: C, 83.84; H, 6.88; N, 5.84%.

3.3.3. Synthesis and characterization of 5,15-diphenyl-10,20-di-4-(2-(3-pentadec-8-enyl)phenoxy)ethoxy)phenyl porphyrin (4)

Aldehyde 1 (0.45g, 1 mmol) and meso-phenyl dipyrrole 2 (0.22g, 1 mmol) in chloroform (150 mL) were stirred at room temperature for 10 min, and then BF\(_3\)·OEt\(_2\) (3.75 mL of 0.1 M solution in CHCl\(_3\), 0.375 mmol) was added. The reaction mixture was stirred at room temperature for 24 h, then DDQ (0.17 g in CHCl\(_3\)) was added slowly to the solution with vigorous stirring. Subsequently, the reaction mixture was stirred at room temperature for a further 24 h and then removed the solvent under vacuum. The reaction mixture was passed through a silica gel chromatography column (CH\(_2\)Cl\(_2\)/hexane 6/4 v/v). Yield: 15%; \(^{1}H\)-NMR (CDCl\(_3\)): \( \delta -2.76 \) (br, s, 2H), 0.80–0.95 (m, 6H), 1.16–1.46 (m, 32H), 1.58–1.72 (m, 4H), 1.96–2.12 (m, 8H), 2.64 (t, 4H, \( J = 7.7 \) Hz), 4.53 (t, 4H, \( J = 4.5 \) Hz), 4.63 (t, 4H, \( J = 4.5 \) Hz), 5.28–5.42 (m, 4H), 6.83–6.94 (m, 6H), 7.24–7.30 (m, 2H), 7.34 (d, 4H, \( J = 8.7 \) Hz), 7.72–7.82 (m, 6H), 8.14 (d, 4H, \( J = 8.7 \) Hz), 8.22 (d, 4H, \( J = 7.4 \) Hz), 8.84 (d, 4H, \( J = 4.5 \) Hz), 8.87 (d, 4H, \( J = 4.7 \) Hz); \(^{13}\)C-NMR (CDCl\(_3\)): \( \delta 14.3, 14.6, 23.1, 23.3, 26.0, 26.1, 27.7, 27.7, 29.4, 29.7, 29.7, 29.8, 29.8, 29.8, 29.8, 29.9, 30.1, 30.1, 30.1, 30.2, 31.9, 32.0, 32.2, 36.5, 66.9, 67.3, 112.0, 113.3, 115.5, 120.2, 120.3, 120.4, 120.5, 121.8, 127.1, 128.1, 128.4, 128.6, 129.7, 130.3, 130.4, 130.4, 130.6, 135.0, 135.4, 135.4, 136.0, 142.7, 145.2, 145.2, 158.9, 159.2; FTIR (neat), \( v/cm^{-1} \): 3317, 3006, 2923, 2852, 1598, 1508, 1470, 1441, 1350, 1244, 1175, 1157, 1109, 1072, 1032, 1001, 979, 966, 932, 909, 876, 845, 800, 731; UV-Vis (CH\(_2\)Cl\(_2\)) \( \lambda_{\text{max}}, \text{nm} \): 419, 516, 552, 590, 646; MALDI-TOF MS \( m/z \): 1303 \([M]^+\); Molecular weight: 1303 amu; Anal. Calc. for C\(_{90}\)H\(_{102}\)N\(_4\)O\(_4\): C, 82.61; H, 7.74; N, 4.51. Found: C, 82.95; H, 7.83; N, 4.30%.

3.3.4. General procedure for the synthesis of 3a–3c, 4a–4c

Porphyrin 3 (30.0 mg, 0.031 mmol) or 4 (30.0 mg, 0.023 mmol) were dissolved in CHCl\(_3\) (20 mL). To this solution was added an excess of Zn(CH\(_3\)COO)\(_2\) (34.0 mg, 0.186 mmol), CuCl\(_2\) (20.0 mg, 0.186 mmol) or Co(CH\(_3\)COO)\(_2\)-4H\(_2\)O (46.3 mg, 0.186 mmol), and the mixture was stirred at room temperature. The reaction was checked by TLC. After disappearance of 3 or 4, the solution was filtered and then the solvent was removed under vacuum. The crude product was purified by silica gel chromatography (CHCl\(_3\)/Hexane, 7/3 v/v) to give 3a, 3b, 3c, 4a, 4b, 4c in nearly quantitative yields.
3.3.5. General procedure for synthesis of 3d and 4d

Porphyrin 3 (30.0 mg, 0.031 mmol) or 4 (30.0 mg, 0.023 mmol) were dissolved in DMF (15 mL). To this solution, an excess of FeCl₃ (30.2 mg, 0.186 mmol) was added. The reaction was heated to reflux and monitored by UV/Vis spectroscopy. The metal insertion was completed in 4 h. Then the solvent was removed under vacuum and the residue was purified by silica gel chromatography (CHCl₃/hexane, 7/3 v/v) to give 3d and 4d respectively.

Representative data for compounds 3a–3d, 4a–4d

Zn(II)5,10,15-Triphenyl-20-mono-[4-(2-(3-pentadec-8-enyl)phenoxy)ethoxy]phenylporphyrin (3a). Purplish red solid. Yield 95%; ¹H-NMR (CDCl₃): δ 0.86–0.90 (m, 3H), 1.26–1.39 (m, 16H), 1.62–1.68 (m, 2H), 1.96–2.01 (m, 4H), 2.63 (t, 2H, J = 7.4 Hz), 4.48–4.50 (m, 2H), 4.58–4.61 (m, 2H), 5.33–5.39 (m, 2H), 6.83–6.90 (m, 3H), 7.23–7.27 (m, 1H), 7.32 (d, 2H, J = 8.6 Hz), 7.73–7.78 (m, 9H), 8.13 (d, 2H, J = 8.6 Hz), 8.22–8.24 (m, 6H), 8.95–8.99 (m, 8H); ¹³C-NMR (400 MHz, CDCl₃): δ 14.6, 23.1, 27.6, 27.7, 29.6, 29.7, 29.7, 29.8, 30.1, 30.1, 30.2, 31.8, 32.2, 36.4, 68.2, 112.0, 113.2, 115.5, 122.0, 126.9, 127.2, 127.9, 128.0, 128.4, 129.7, 130.3, 130.4, 130.5, 130.8, 132.3, 132.4, 134.9, 135.8, 143.3, 145.2, 145.2, 150.6, 158.5; FTIR (neat), ν/cm⁻¹: 3007, 2924, 2853, 1600, 1584, 1577, 1485, 1466, 1378, 1339, 1255, 1157, 1071, 1024, 997, 912, 873, 797, 774, 720, 695; UV-Vis (CHCl₃) λₘₐₓ, nm: 424, 554, 594; MALDI-TOF MS: an isotopic cluster peaking at m/z: 1021 [M⁺]; Molecular weight: 1021 amu; Anal. Calc. for C₆₇H₆₄N₄O₂Zn: C, 78.61; H, 6.14; N, 5.54. Found: C, 78.82; H, 6.27; N, 5.49%.

Cu(II)5,10,15-triphenyl-20-mono-[4-(2-(3-pentadec-8-enyl)phenoxy)ethoxy]phenylporphyrin (3b). Red solid. Yield: 95%; FTIR (neat), ν/cm⁻¹: 3007, 2924, 2849, 1599, 1583, 1509, 1491, 1442, 1377, 1346, 1245, 1216, 1175, 1158, 1072, 1003, 799, 753, 717; UV-Vis (CHCl₃) λₘₐₓ, nm: 416, 539; MALDI-TOF MS: An isotopic cluster peaking at m/z: 1021 [M⁺]; Molecular weight: 1021 amu; Anal. Calc. for C₆₇H₆₄N₄O₂Cu: C, 78.61; H, 6.14; N, 5.54. Found: C, 78.82; H, 6.27; N, 5.49%.

Co(II)5,10,15-Triphenyl-20-mono-[4-(2-(3-pentadec-8-enyl)phenoxy)ethoxy]phenylporphyrin (3c). Peach-red solid. Yield: 85%; FTIR (neat), ν/cm⁻¹: 3006, 2924, 2853, 1599, 1583, 1510, 1491, 1442, 1377, 1346, 1245, 1216, 1175, 1158, 1072, 1003, 799, 753, 716, 710; UV-Vis (CHCl₃) λₘₐₓ, nm: 411, 530; MALDI-TOF MS: An isotopic cluster peaking at m/z: 1017 [M⁺]; Molecular weight: 1017 amu; Anal. Calc. for C₆₇H₆₄N₄O₂Co: C, 79.05; H, 6.29; N, 5.51. Found: C, 78.89; H, 6.16; N, 5.64%.

Fe(III)5,10,15-Triphenyl-20-mono-[4-(2-(3-pentadec-8-enyl)phenoxy)ethoxy]phenylporphyrin chloride (3d). Brown red solid. Yield: 85%; FTIR (neat), ν/cm⁻¹: 3008, 2924, 2853, 1599, 1588, 1485, 1455, 1377, 1340, 1247, 1156, 1072, 1004, 875, 802, 750, 719, 699; UV-Vis (CHCl₃) λₘₐₓ, nm: 417; MALDI-TOF MS: An isotopic cluster peaking at m/z: 1013 [M–Cl–H⁺]; Molecular weight: 1049.5 amu; Anal. Calc. for C₆₇H₆₃N₄O₂FeCl: C, 76.61; H, 6.10; N, 5.33. Found: C, 76.72; H, 6.23; N, 5.54%.

Zn(II)5,15-Diphenyl-10,20-di-[4-(2-(3-pentadec-8-enyl)phenoxy)ethoxy]phenylporphyrin (4a). Purplish red solid. Yield: 95%; ¹H-NMR (CDCl₃): δ 0.82–0.94 (m, 6H), 1.18–1.44 (m, 32H), 1.60–1.72 (m, 4H), 1.93–2.09 (m, 8H), 2.64 (t, 4H, J = 7.5 Hz), 4.48–4.55 (m, 4H), 4.59–4.66 (m, 4H), 5.25–5.45 (m,
Cu(II)5,15-Diphenyl-10,20-di-[4-(2-(3-pentadec-8-enyl)phenoxy)ethoxy]phenylporphyrin (4b). Red solid. Yield: 95%; FTIR (neat), ν/cm⁻¹: 3008, 2925, 2852, 1601, 1583, 1504, 1446, 1377, 1345, 1244, 1215, 1174, 1158, 1072, 1000, 800, 749,701; UV-Vis (CHCl₃) λ_max, nm: 417, 540; MALDI-TOF MS: An isotopic cluster peaking at m/z: 1365 [M]+; Molecular weight: 1365 amu; Anal. Calc. for C₉₀H₁₀₀N₄O₄Cu: C, 79.12; H, 7.35; N, 4.11. Found: C, 79.22; H, 7.31; N, 4.27%.

Co(II)5,15-Diphenyl-10,20-di-[4-(2-(3-pentadec-8-enyl)phenoxy)ethoxy]phenylporphyrin (4c). Peach-red solid. Yield: 95%; FTIR (neat), ν/cm⁻¹: 3006, 2924, 2853, 1602, 1583, 1463, 1377, 1351, 1261, 1215, 1175, 1158, 1074, 1005, 799, 755, 701; UV-Vis (CHCl₃) λ_max, nm: 412, 530; MALDI-TOF MS: An isotopic cluster peaking at m/z: 1361 [M]+; Molecular weight: 1361 amu; Anal. Calc. for C₉₀H₁₀₀N₄O₄Co: C, 79.35; H, 7.35; N, 4.11. Found: C, 79.22; H, 7.31; N, 4.27%.

Fe(III)5,15-Diphenyl-10,20-di-[4-(2-(3-pentadec-8-enyl)phenoxy)ethoxy]phenylporphyrin chloride (4d). Brown red solid. Yield: 85%; FTIR (neat), ν/cm⁻¹: 3005, 2924, 2853, 1600, 1582, 1509, 1485, 1449, 1376, 1338, 1246, 1158, 1071, 998, 875, 801, 751, 722, 697; UV-Vis (CHCl₃) λ_max, nm: 419; MALDI-TOF MS: An isotopic cluster peaking at m/z: 1358 [M-Cl]+; Molecular weight: 1393.5 amu; Anal. Calc. for C₉₀H₁₀₀N₄O₄FeCl: C, 77.50; H, 7.18; N, 4.02. Found: C, 77.65; H, 7.23; N, 4.12%.

3.4. Preparation of the Cardanol-Based Porphyrin/TiO₂ Composites

The loaded samples used as photocatalysts for the photoreactivity experiments were prepared by impregnating TiO₂ with cardanol-based porphyrins. The procedure is as follows: An opportune amount of sensitizer 3a–3d and 4a–4d was dissolved in CH₂Cl₂ (20 mL) and finely ground TiO₂ (1 g) was added into this solution. The mixture was stirred for 3–4 h and the solvent removed under vacuum. The resulting composites were marked as 3a/TiO₂-3d/TiO₂ and as 4a/TiO₂-4d/TiO₂, respectively.

3.5. Photo-Reactivity Experiments

Photoreactivity experimenta were carried out in a set-up equipped with a UV lamp (250 W Hg 200 ULTRA lamp), the distance between lamp and the surface of solution is 40 cm with an intensity of 30 W/m². The temperature inside the reactor was maintained at ca. 300 K. The reacting aqueous suspension of 4-nitrophenol (4-NP, 20 mg/L, 125 mL) and catalyst (100 mg) was stirred with a magnetic bar. The initial pH of the suspension was adjusted to 4.0 by the addition of H₂SO₄. Air was
bubbled into the suspension when switching on the lamp. Samples (3 mL) were withdrawn from the suspension every 30 min during the irradiation. The photocatalysts were separated from the solution by centrifugation and successively filtered through 0.45-µm celluloseacetate membranes (HA, Millipore) before to perform the quantitative determination of 4-NP by measuring its absorption at 316 nm with UV-Vis spectrophotometer. Bare TiO\textsubscript{2} was also tested for the sake of comparison under the same experimental conditions.

4. Conclusions

In this paper we have described the synthesis and characterization of some new cardanol-based porphyrins, 5,10,15-triphenyl-20-mono-[4-(2-(3-pentadec-8-enyl) phenoxy) ethoxy] phenyl porphyrin, (3), and 5,15-diphenyl-10,20-di-[4-(2-(3-pentadec-8-enyl)phenoxy)ethoxy]phenyl porphyrin, (4), as well as their zinc(II), copper(II) and cobalt(II) metal derivatives, 3\textsubscript{a}, 3\textsubscript{b}, 3\textsubscript{c}, 4\textsubscript{a}, 4\textsubscript{b} and 4\textsubscript{c}. Selected Cu(II) porphyrins used as sensitizers onto TiO\textsubscript{2} samples showed the best photo-catalytic activity for the photo-degradation of 4-NP in water, compared with the other MPp/TiO\textsubscript{2} composites.

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**Sample Availability:** Not available.

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