Synthesis and characterization of novel unsymmetrical phthalocyanine/TiO$_2$ composites and their evaluation as photocatalysts for degradation of 4-chlorophenol under visible light

Yunus Alp SÜTCÜLER, Görkem GEZEK, Yaghub MAHMİANİ, Altuğ Mert SEVİM[*]
Department of Chemistry, Faculty of Science and Letters, İstanbul Technical University, İstanbul, Turkey

Abstract: We prepared novel unsymmetrical A$_3$B-type zinc and cobalt phthalocyanines bearing monocarboxylic acid groups on peripheral positions using statistical condensation method, especially designed to anchor on the TiO$_2$ semiconductor surface. The novel complexes were anchored on TiO$_2$ semiconductor to prepare effective dye sensitized photoactive composites as heterogeneous catalysts. The results indicated that modified TiO$_2$ nanocrystals possessed only the anatase phase and MPc-TiO$_2$ photocatalysts with loading amount of dye ca. 8.27 μmol/g TiO$_2$ exhibit strong visible light absorption. Photocatalytic degradation of 4-chlorophenol (4-CP) under illumination with visible light ($\lambda > 400$ nm) was tested with the composites prepared. The degradation profile indicates that MPc-modified titania nanocrystals are superior to pristine titania under visible light in terms of photocatalytic effect. Photocatalytic reusability efficiency and the stability of photocatalyst composites were also investigated. Additionally, the effect of different substituent groups (such as aromatic vs. aliphatic, alkyl chain length) on photocatalytic efficiency was revealed and also compared to our previous works.

Key words: Phthalocyanine, synthesis, photocatalyst, titanium dioxide, photocatalytic degradation, visible light, 4-chlorophenol

1. Introduction

Phenol and related compounds are important in industry and they are commonly found in the environment.[1] They are highly toxic,[2,3] even at low concentrations, and so they are classified as dangerous chemicals. Chlorinated phenol compounds are produced in an unintentional manner when water is treated with chlorine. Especially for prolonged exposure, trace amounts of phenol are converted into its chlorinated derivatives and pose a specific risk. There are few methods for the effective treatment of wastewater polluted with phenols.[4−6] Among the existing processes that are applied to phenols' treatment, photooxidation play a significant role. They are, however, limited to systems employing highly energetic UV-photonic flux.[7] In this approach, typically TiO$_2$ semiconductor particles are used, thereby featuring positive-charged holes, being effective oxidative species with ultraviolet illumination.[8,9] The fact that the method relies upon ultraviolet radiation is a substantial disadvantage, and, as a counter-measure, visible light-sensitized TiO$_2$ semiconductor particles have been employed recently.[10−12]

Metallophthalocyanines (MPcs) are able to absorb in visible light or sunlight, and have attracted high

*Correspondence: sevim@itu.edu.tr

interest for visible light-employing catalytic photodegradation of toxic industrial wastes.[13] The photoactivity of phthalocyanines comes from their ability to produce very reactive species such as hydroxyl radical ($\cdot$OH) and singlet oxygen species ($^1O_2$) by photon flux absorption in the ultraviolet or visible part of the spectrum. In particular, in polar solvents, phthalocyanines show a tendency to form π-aggregates and the photocatalytic activity is reduced greatly, because aggregated metallophthalocyanines' excited energetic states are offset by nonexcited states.[14] Therefore, increasing the stability and the dispersion of MPcs is an important prerequisite for photocatalytic activity. Immobilization is effective to make metallophthalocyanines stabilized against oxidation. Aggregation inhibits ordering crystalline packing and localization of internal spaces.[13] Under these conditions, MPcs are dispersed and their photocatalytic activity is very effective.

The main aim in this study was to prepare new TiO_2-MPc composites as effective photocatalysts by loading monocarboxylic acid-substituted nonsymmetrical metallophthalocyanines, which are totally new in the literature, and to determine the photodegradative effect over aqueous 4-chlorophenol (4-CP) solutions in the presence of visible light. Since 4-CP is used in industry heavily, it was chosen in this study as a model pollutant. Therefore, we aimed, by employing photosensitizing metallophthalocyanines anchored onto TiO_2, to shift the electronic transfer to the visible range, to fabricate more effective photocatalysts than pristine TiO_2, and especially to provide a quite cheap alternative to the current expensive photocatalysts. Carboxylated dyestuffs are prone to be adsorbed to oxide semiconductors, because the surface is filled with hydroxylated oxide groups.[15,16] We selected carboxylic acid side groups because we tried to anchor phthalocyanines onto the TiO_2 surface, thereby facilitating the electronic transfer from the LUMO orbital of the metallophthalocyanines to the 3d orbitals of titanium semiconductor. The specially selected three tert-butylbenzyloxy groups aimed to increase the solubility of metallophthalocyanines and reduce aggregation, which is the largest problem of Pcs via $\pi - \pi$ stacking.

In addition to the previous works by our team,[11,17,18] we now used 3-mercaptopropionic acid and thioglycolic acid, which are monocarboxylic acids with aliphatic sulfanyl groups along with different chain lengths to bind to the TiO_2 surface. Apart from the symmetrical tetracarboxylic acid derivatives and unsymmetrically substituted phthalocyanines having aryloxy groups in our previous studies, we chose the unsymmetrical Pc design in our study, and in the place of aromatic linker groups to bind to the TiO_2 surface, we used aliphatic sulfanyl-containing groups as electron donor entities. Thus, new metallophthalocyanines having different chain lengths due to different alkylsulfanyl groups were synthesized and these led to new MPc-TiO_2 composites and the effect of these different entities on photocatalytic efficiency was examined. Therefore, we made an effort to reveal the effect of aliphatic groups versus aromatic groups present in the unsymmetrical structure and the effect of chain length on the photocatalytic effect.

2. Results and discussion

2.1. Synthesis and characterization of A_3B-type metallophthalocyanines

We synthesized A_3B-type phthalocyanines (nonsymmetrical phthalocyanine) by using different phthalonitrile derivatives to anchor on TiO_2 semiconductor. Although there are many strategies for unsymmetrical phthalocyanine synthesis, the superior one is, together with many advantages, the statistical condensation approach.[19] In statistical condensation, if two different phthalonitriles with similar reactivity are condensed in a 3:1 ratio, the following mixture of isomers will be obtained: 33% of A_4, 44% of A_3B, and 23% of A_2B_2 and AB_3, both of which are the cross-condensation products. If the solubility parameter is to be arranged adequately, the more soluble counterpart will be isolated and the less soluble counterpart will stay in the statistical mixture.

The use of tert-butylphenoxy groups at the peripheral positions is especially preferred in order to be able to isolate the A_3B derivative from the statistical mixture rather easily, since this substituent brings about superior solubility and prevents aggregation of the resulting complexes. Since we know that tetracarboxy-substituted phthalocyanines interact with SiO_2 surface, leading to nonelutable species, increasing the number of soluble tert-butylphenoxy moieties will cause the phthalocyanine to be eluted from the column. By using a suitable solvent system, the MPcs obtained could be isolated successfully in a silica-loaded column. In this case, the A_4-type symmetrical tetrakis(tert-butoxy)phthalocyanine, which was eluted first was isolated, and then the targeted nonsymmetrical A_3B molecule (containing a single carboxylic acid group) was successfully separated in high purity.

The Scheme shows the synthetic route followed in this work. As reported earlier, the dinitrile compounds (precursors to phthalocyanines), namely 4-(carboxymethylsulfanyl)phthalonitrile (**1**), 4-(carboxyethylsulfanyl) phthalonitrile (**2**), and 4-(tert-butylphenoxy)phthalonitrile (**3**), were synthesized from the well-known base-catalyzed nucleophilic aromatic substitution reactions.

After the synthesis of precursor compounds, these phthalonitrile derivatives were used to yield A_3B-type nonsymmetrical phthalocyanines. In this context, after many trials to find out the optimal precursor ratios (1:3, 1:3.5, and 1:4), the phthalocyanines were obtained in dimethylaminoethanol (DMAE) as the high-boiling solvent and zinc acetate and cobalt(II) chloride as the metal ions and at 145 °C as the reaction temperature and in nitrogen atmosphere. Following the synthetic step, the compounds were washed with several solvents as a precolumn treatment, and applied to silica as the stationary phase and eluted with several solvents. The synthesized phthalocyanines are highly soluble in tetrahydrofuran, chloroform, dichloromethane, dimethylformamide, and dimethyl sulfoxide. The synthesized new metallophthalocyanines were characterized with elemental analysis, ^{1}H NMR, FTIR, UV-Vis, and mass spectrometry and their structures were elucidated.

The FTIR spectra of the phthalocyanines show that the nitrile stretching vibration at 2200 cm^{-1} (in the precursor spectra) is absent in the phthalocyanine FTIR spectra. This is the most important indication about cyclotetramerization.[20] Again, the presence of a carboxylic acid group in the phthalocyanine macrocycle was justified by the presence of a C=O stretching mode at 1700 cm^{-1} and broad carboxy O–H stretching mode between 1700 and 3600 cm^{-1}.

The ^{1}H NMR spectra of zinc phthalocyanines are quite similar to the precursors' spectra and the proton integrations are in harmony with the theoretical values. The ^{1}H NMR spectra of the zinc phthalocyanines yielded peaks between δ 1.5 and 1.2 ppm for three tert-butyl groups' aliphatic protons and δ 7.80 and 6.80 ppm for the aromatic protons. The positions are harmonious with the calculated ones. In addition, the carboxymethylsulfanyl and carboxethylsulfanyl groups' –S–CH$_2$ protons yielded peaks at δ 2.48 ppm for **4a**, and δ 2.86 ppm and δ 2.01 ppm for **5a**. All these spectral analyses prove the successful synthesis of phthalocyanines.

The most reliable technique for phthalocyanine formation is UV-Vis spectrophotometry. There are two important and strong peaks in the π-electron-rich phthalocyanine spectrum; the first is the Q band, seen between 600 and 750 nm, and the other is the B (or Soret) band, between 300 and 500 nm.[21] In Figure 1, the UV-Vis spectra were recorded in THF using a concentration of 1×10^{-5} M. The $\pi - \pi^*$ transitions were observed at 677 nm (**4a**), 665 nm (**4b**), 678 nm (**5a**), and 667 nm (**5b**) all as singlets. B bands are caused by the transition of an electron from deeper π levels to the LUMO, at 350 nm (**4a**), 322 nm (**4b**), 351 nm (**5a**), and 328 nm (**5b**).

In the MALDI-TOF mass spectra of the substituted MPc derivatives **4a**–**b** and **5a**–**b** parent molecular
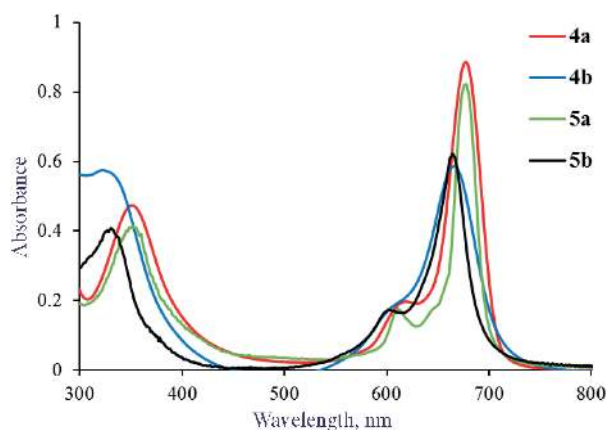
Figure 1. UV visible spectra of the metallophthalocyanines in THF (1×10^{-5} M).

ion peaks were observed at m/z = 1112.93 [M]$^+$, 1106.83 [M]$^+$, 1127.16 [M + H]$^+$, and 1121.45 [M + H]$^+$, respectively, proved the proposed structures (Figure 2).

2.2. Characterization of MPc/TiO$_2$ photocatalysts

The Fourier transform infrared spectroscopy (FT-IR) spectra of the MPc modified photocatalyst samples were supplemented, as shown in Figure 3. Pure TiO$_2$ semiconductor showed two strong vibration peaks at 580.3 cm^{-1} and 753.4 cm^{-1}; these two peaks indicate the Ti–O–Ti bonding system, thereby the TiO$_2$ network structure has been proved.[22] Moreover, when MPcs enter the structure the Ti–O stretching vibrations shift to lower wavelengths. The broad band seen around 3400 cm^{-1} is due to the hydroxyl groups of the water molecules adsorbed onto the TiO$_2$ surface; these peaks disappear when treated at temperatures higher than 150 °C.[23]

When the FT-IR spectra of composites are investigated, there are three dominating strong peaks in the 1300–1700 cm^{-1} range. Among them, the 1638 cm^{-1} strong unsymmetrical stretching vibration peak and symmetrical stretching at 1383 cm^{-1} are assigned to the carboxylate (–COO–) groups.[24,25] These peaks indicate that metallophthalocyanines form a carboxylate bond to the TiO$_2$ surface, by utilizing the Ti–OH end groups on the surface. The 1510 cm^{-1} peak shows the C=C stretching vibration bands of aromatic groups for the phthalocyanine structure, and this too proves the adsorption of phthalocyanines onto TiO$_2$.

The X-ray diffraction patterns of the commercial pristine TiO$_2$ and of the MPc/TiO$_2$ composite are compared in Figure 4. The peaks observed for the TiO$_2$ material match well with those from the JCPDF 21-1272 database corresponding to the anatase phase (2?? = 25.5°) meaning unmodified TiO$_2$ and photocatalysts have the pure anatase phase. XRD patterns indicated that the crystalline structure of TiO$_2$ did not change with the incorporation of metallophthalocyanine groups and this can be also rationalized in terms of the very low quantity of phthalocyanine dye in the MPc/TiO$_2$ composite.[26,27]

Figure 5 shows the UV-visible diffuse reflectance absorption spectra of unmodified and powdered TiO$_2$ and MPc/TiO$_2$ photocatalyst composites. When these spectra are evaluated carefully, TiO$_2$ does not show a notable absorption in the visible spectrum due to the large band gap energy (3.21 eV), but it shows a single important peak at 386 nm as a basic absorbance. This therefore indicates that the sample's crystalline structure is a suitable one and the defects are low near bands, which is a known feature of pristine TiO$_2$.[25]
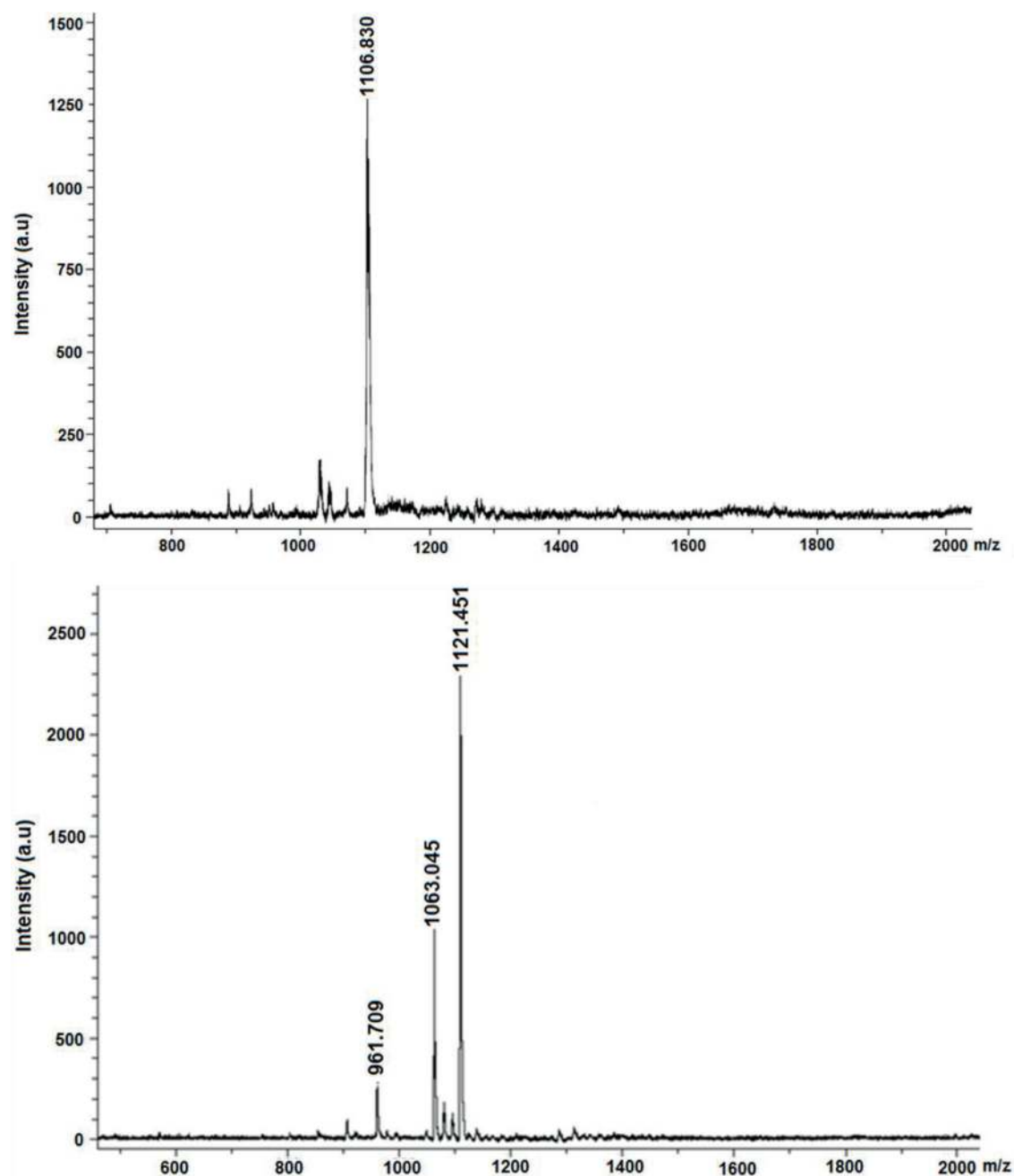
Figure 2. MALDI-TOF mass spectra of novel cobaltphthalocyanines **4b** (top) and **5b** (bottom).

Reflectance spectra of MPc/TiO$_2$ nanocrystals studied show absorption at 600–700 nm, which is referred to as the Q band of phthalocyanines. Respective π conjugation in the molecule is assigned to the $\pi-\pi^*$ transition of the Q band.[28−30] When compared to the pristine TiO$_2$ samples, the λ_{max} values of MPc/TiO$_2$ nanocrystals have a bathochromic shift to the visible region. This bathochromic shift is due to the distortion of the phthalocyanine macrocycles, especially when they are anchored onto an inorganic host material.[31,32] As a result, these bathochromic shifts are a perfect indication of successful anchoring to MPc compounds on TiO$_2$.
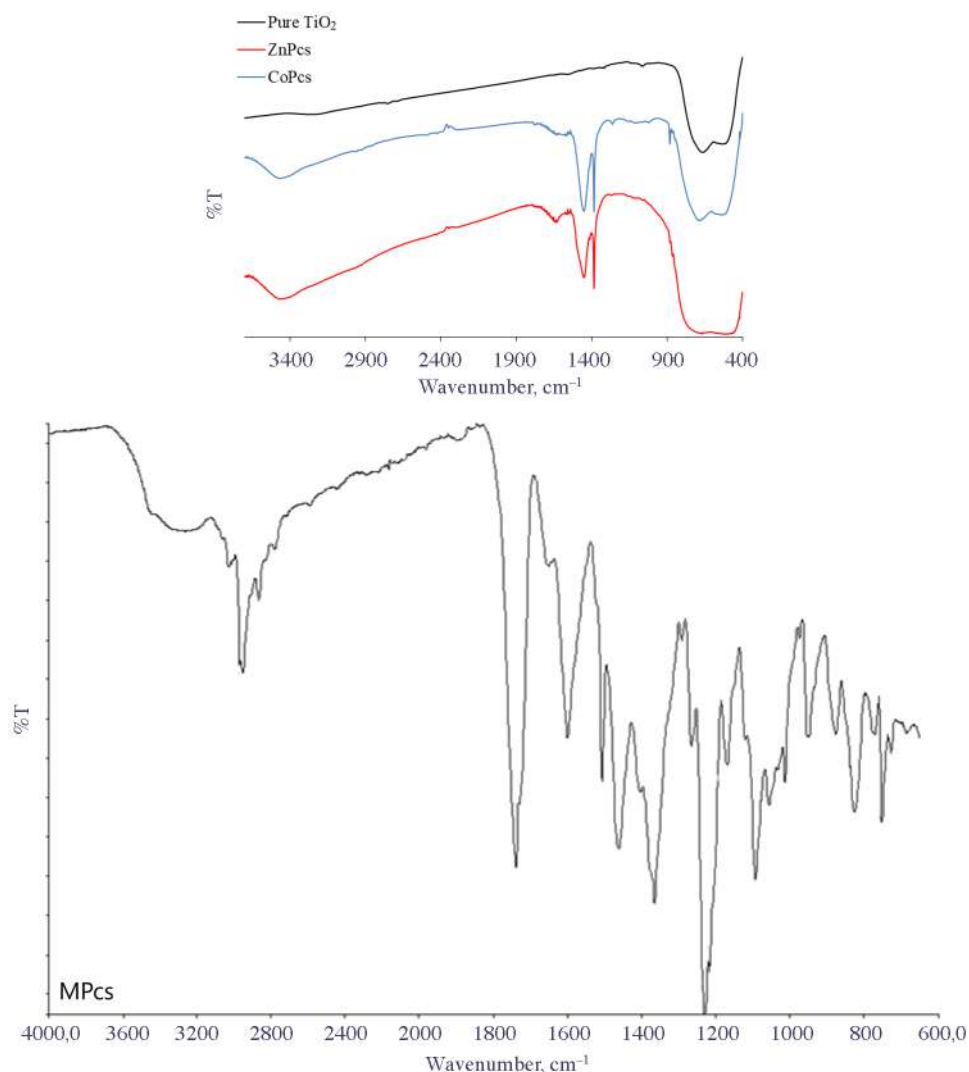
Figure 3. FT-IR spectra of pure TiO_2 powder, MPc/TiO_2 heterogenous catalysts, and metallophthalocyanines (below).

Different metal-bearing same type photocatalysts have slightly different absorption peaks. As Figure 5 shows clearly, cobalt phthalocyanine has a much greater Q-band intensity than that of zinc phthalocyanine and this means that CoPc is attached to the surface of titania more than ZnPc.

DR spectroscopy is also used for characterizing the electronic features of pristine TiO_2 and photocatalyst composites. For this purpose, the linear portion of the DR spectrum on the X axis, according to the literature, was extrapolated and the following equation was used to calculate the theoretical band gap energies:[33,34]

$$E_{bg} = 1240/\lambda$$

In this equation, E_{bg} shows the band gap energy in eV, λ shows the wavelength in nm, and these are obtained from the data in the DR spectra of the composites. According to the results obtained by plugging the appropriate data into the equation, the band gap energy of pristine TiO_2 was 3.21 eV (386 nm), which is in perfect harmony with the literature data.[35] Using the same equation for calculating the theoretical band gap energies for MPc/TiO_2 composites yielded the following results: for **4a**/TiO_2, 2.72 eV; for **4b**/TiO_2, 2.65 eV; for
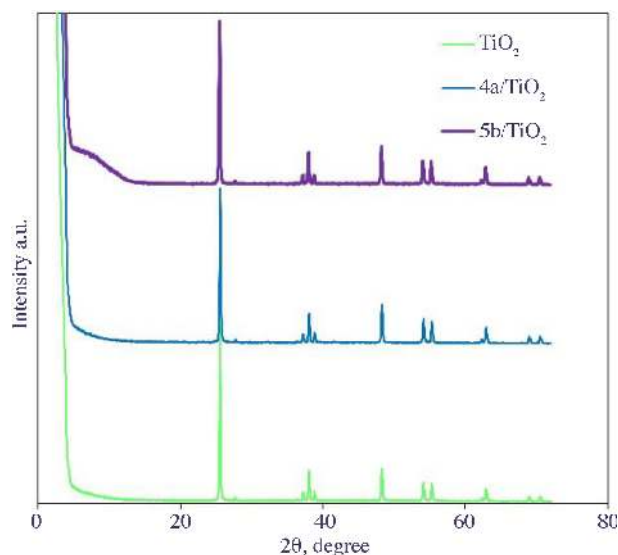
Figure 4. XRD patterns of TiO$_2$ semiconductor and dye sensitized **MPc**/TiO$_2$ photocatalyst.
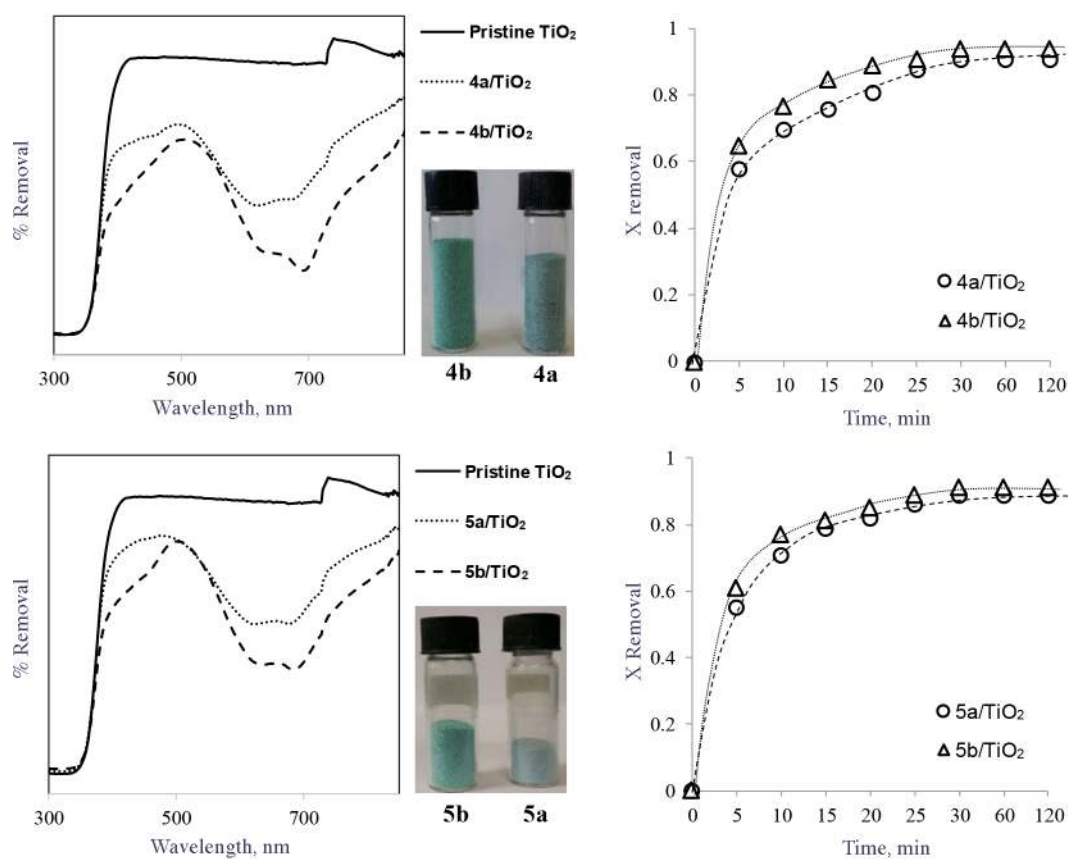

Figure 5. Diffuse reflectance UV-vis spectra of the powdered pristine TiO$_2$ and MPc/TiO$_2$ photocatalysts and photocatalytic degradation of 4-CP over MPc/TiO$_2$.

5a/TiO$_2$, 2.76 eV; for **5b**/TiO$_2$, 2.70 eV (Table). Investigation of the DR spectral data yields that when the TiO$_2$ semiconductor is sensitized with MPc compounds, the band gap between the valence band and conduction

band for TiO_2 is reduced, which is the theoretical explanation as to why MPc/TiO_2 composites showed quite high photodegradation activity in visible range (change from 3.21 eV (386 nm) for pristine TiO_2 to 2.65 eV (468 nm) for **4b**/TiO_2).

Table. Photo-removal percentages achieved with MPc/TiO_2 composites in the degradation of 4-chlorophenol.

Catalyst	Under visible irradiation						Dark
	Pristine TiO_2	**4a**/TiO_2	**4b**/TiO_2	**5a**/TiO_2	**5b**/TiO_2	MPcs in DMSO	All
Photodegradation,%	3.17	85.42	88.25	86.04	89.47	-	-
Theoretical band gap energy (eV)	3.21	2.93	2.88	2.90	2.82	-	-

2.3. Evaluation of photocatalytic activity of MPc/TiO_2

Catalytic photodegradation of 4-chlorophenol (4-CP) was used as a metric to evaluate the performance of MPc/TiO_2 heterogeneous photocatalysts. Photocatalytic experiments using pristine TiO_2 nanoparticles were also carried out in the presence and absence of light. After the degradation studies, the photodegradation amount of 4-chlorophenol was determined with the formula below:

$$X(t) = C_o - C(t)/C_o$$

The equation above shows that X(t) is the molar fraction of 4-CP and C_o is the initial concentration, while C(t) is the concentration of 4-CP as a function of illumination time.[31,36,37] Table and Figure 5 show the data about photocatalytic degradation of 4-CP with titania functionalized with MPcs under visible light.

As expected, the metallophthalocyanine/titanium dioxide heterogeneous composite catalysts did not show any photoactivity in darkness. When the metallophthalocyanine part was taken out and used as the only homogeneous catalyst in solution, there was no result either. In another study, when one took pristine TiO_2 and applied visible light for 120 min, 4-chlorophenol was degraded about 3% (almost nothing). This shows that TiO_2 does not show sufficient photocatalytic activity under visible light irradiation (see Table). However, when one applies metallophthalocyanines onto the TiO_2 surface, the previous example (photodegradation of 4-chlorophenol) undergoes a dramatic increase. During the photodegradation, the electrons residing at the ground state of the MPc absorb a photon and become excited, and are transferred to the conduction band of the semiconductor TiO_2. This process creates very potent radicals like peroxide (O_2^{-2}) and hydroxide (OH·) on the surface of TiO_2 and organic pollutants like 4-chlorophenol are degraded effectively.[13] In the presence of MPc/TiO_2 photocatalyst, 4-chlorophenol was degraded almost completely with visible light (for **4b**/TiO_2, degradation was about 95%). The degradation was fully active in the first 30 min of the process; after this period, degradation stopped completely. In this period, electrons and hydroxy radicals were balanced and no further photodegradation was noted. The high performance of degradation for this photocatalytic system gives a hint about the possible future use of it in industrial applications.

Although the degradation percentages are similar to each other, the highest value was obtained for **4b** and **5b** composites. This indicates that cobalt phthalocyanines are slightly more active than the corresponding zinc phthalocyanines (∼2%–3%). Especially, the carboxy group interacts with the d orbital of the Ti atom and higher photoconversion yields are obtained (for **5b**, the yield is 91.25% whereas with **4b**, having a shorter chain, the yield is 94.45%) for metallophthalocyanines with shorter MPc–COOH distance. Moreover, together with our

previous studies, the current MPc/TiO$_2$ composites having aliphatic linker groups had better photocatalytic effect ($\sim$92%) than those with aromatic linkers ($\sim$88%).[17]

2.4. Reuse of the photocatalysts

The reusability of catalysts, in an effective and economic way, is very important in terms of environmental application. Therefore, we applied the photocatalysts against 4-chlorophenol, during five consecutive cycles.[34] In every run, the same conditions as the normal catalytic procedure were followed (0.1 g of solid MPc/TiO$_2$ composite was added to 100 mL of 0.0013 M 4-chlorophenol solution and in the presence oxygen gas visible light was applied to the medium for 120 min).

After each run, the 4-CP suspension was filtered and the remaining solid was dried in an oven. Dried catalysts were used again in the same photodegradation scheme. Figure 6A lists the reusability values of photocatalysts prepared in this study. The results tell us that the **4b/TiO$_2$** with the highest degradation yield has its catalytic activity lowered from 94.45% to 78%.
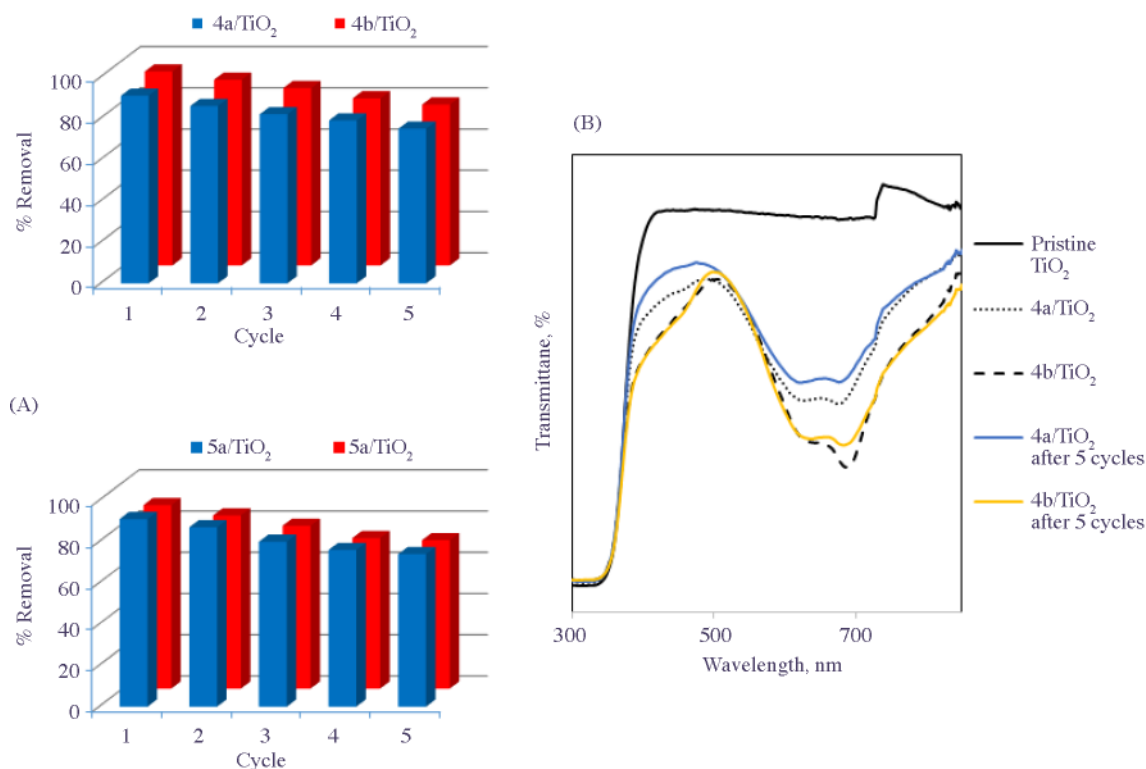

Figure 6. (A) Photocatalytic reusability efficiency of MPc/TiO$_2$ catalysts up to five cycles. (B) DR spectrum of **4a-b**/TiO$_2$ after five subsequent uses for photocatalytic degradation of 4-CP.

Before reusing the photocatalysts, the stability of photocatalyst composites is an essential prerequisite. For this purpose, after each photocatalytic treatment, XRD, FT-IR, and DRS analyses of the catalysts were also repeated and we observed that the obtained composites reserved their stability even after 5 cycles. We did not observe any significant change when we recorded the XRD and FT-IR spectra of the initial and final composites after 5 cycles and especially the DR spectrum represented in Figure 6B shows that the composite retains its integrity.

The reduction in catalytic performance is most probably explained by the fact that some of the MPc molecules fixated on the TiO_2 surface were degraded in the process, leaving fewer molecules to perform the photocatalysis. Furthermore, the number of catalyst molecules might decrease during filtering and collection. A third probability about diminished activity is that the degradation intermediates of 4-CP might be adsorbed and immobilized on the TiO_2 surface. The adsorbed entities, in this case, enter a competitive race with 4-CP for reactive species generated by the excited catalyst. Our study showed that after five consecutive cycles the catalytic performance goes down to 72%–78%, which means that the catalysts can be used many times and their effect is preserved for a long time. For further industrial and environmental studies, this factor should be considered to increase the usability of MPc/TiO_2 photocatalytic composites.

## 3. Experimental

3.1. Materials and reagents

All reagents were of analytical grade and purchased from either Merck or Sigma-Aldrich Chemicals and were used without further purifying. We used nitrogen atmosphere in all reactions in dried solvents. Solvents' drying and purification were performed according to Perrin and Armarego.[38] KEMIRA AFDC kindly provided the TiO_2 nanopowder (anatase form). Nitrogen adsorption at 77 K and BET analysis were used to measure the specific surface area of TiO_2 (8.7 m^2/g). Earlier reports detailed the preparation of the starting compounds and substituted dinitriles (**1–3**).[39−41]

3.2. Equipment

Electronic spectra in the UV-Vis region were obtained with a Scinco SD-1000 double-beam UV-Vis spectrophotometer (South Korea). Using tetramethylsilane as the internal reference, we used an Agilent VNMRS 500 MHz for collection of ^{1}H NMR spectra. XRD patterns were acquired with a D8 Advance Bruker X-ray powder diffractometer using Cu-Kα radiation (l = 1.54056 Å). The diffractometer was operating at 40 kV with a current of 40 mA. Diffuse reflectance absorption spectra were recorded with a Shimadzu UV-3600 UV-Vis NIR MPC 3100 spectrophotometer. FT-IR spectra were acquired with a PerkinElmer Spectrum One spectrometer fitted with a universal attenuated total reflectance (UATR) unit. Photocatalytic degradation studies were performed in a specially designed photoreactor. We used a Lightex LT50 lamp with 128 W power as the illumination source.

3.3. Synthesis of the unsymmetrical metallophthalocyanines

We followed many routes for the preparation of the precursor materials and targeted A_3B type monocarboxylic acid-substituted metallophthalocyanines. In the Scheme, the main reactions are detailed for the synthetic procedure. Four new unsymmetrical zinc and cobalt phthalocyanines were prepared; in the first phase, the precursors 4-(carboxymethylsulfanyl)phthalonitrile (**1**), 4-(carboxyethylsulfanyl)phthalonitrile (**2**), and 4-(tert-butylphenoxy)phthalonitrile (**3**) were synthesized by referring to the techniques outlined in the literature, by employing thioglycolic acid, 3-mercaptopropionic acid, and 4-tert-butylphenol with 4-nitrophthalonitrile, respectively. Finally, novel unsymmetrical A_3B-type zinc and cobalt phthalocyanines bearing monocarboxylic acid groups on peripheral positions were achieved by a statistical condensation route of two phthalonitrile precursors.
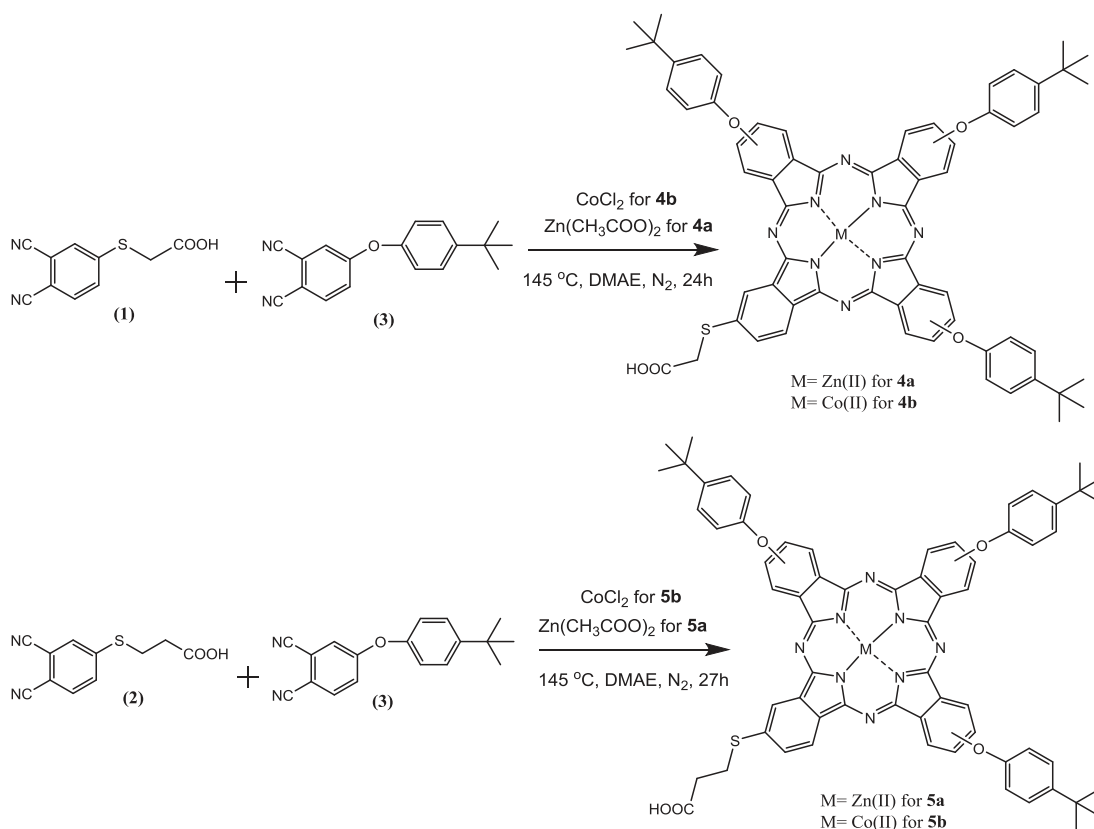
Scheme. Synthetic route used for the production of metallophthalocyanine derivatives.

3.3.1. 9(10), 16(17), 23(24)-Tris-(4-ter-butylphenyloxy-)-2(3)-(4-carboxymethyl sulfanyl)phthalocyaninato zinc (II) (4a)

In a screw-capped tube, 0.221 g (0.80 mmol) of compound **3**, 0.044 g (0.20 mmol) of compound **1**, and 0.037 g (0.20 mmol) of zinc acetate were heated and stirred in 4 mL of 2-dimethylaminoethanol at 145 °C under nitrogen atmosphere for 24 h. Then the green-colored product was cooled to room temperature and precipitated by pouring over a water:methanol (3:1, v/v) mixture and filtered. The greenish product was washed with hot methanol, ethanol, hexane, and acetone until no yellowish-brown impurities were observed and dried. After this prepurification process, the dried green compound was further purified on a silica-loaded chromatographic column with toluene:ethanol (3:1, v/v). Yield: 0.019 g (8.4%), FT-IR ν (cm^{-1}): 3061 (Aromatic C–H), 2957 (Alkyl C–H), 1736 (C=O), 1645, 1596 (Aromatic C=C), 1464, 1363, 1228 (Ar–O–Ar), 1170, 1084, 946, 823, 745, 689, 673. ^{1}H NMR (CDCl$_3$: δ, ppm) 7.79–6.75 (m, Ar–H, 24H), 2.48 (s, –SCH$_2$, 2H), 1.45–1.20 (b, –(CH$_3$)$_3$, 27H). UV-vis (THF): $\lambda_{\max}$/nm (log ε, L mol^{-1} cm^{-1}): 350 (4.66), 677 (4.94). MALDI-TOF-MS; m/z: 1112.93 [M]$^+$; Anal. Calc. for C$_{64}$H$_{54}$N$_8$O$_5$SZn: C, 69.09; H, 4.89; N, 10.07. Found: C, 69.81, H, 4.77; N, 9.98%.

3.3.2. 9(10), 16(17), 23(24)-Tris-(4-ter-butylphenyloxy-)-2(3)-(4-carboxymethy lsulfanyl)phthalocyaninato cobalt (II) (4b)

First 0.221 g of (0.80 mmol) compound **3**, 0.044 g of (0.20 mmol) compound **1**, and 0.026 g of (0.20 mmol) cobalt(II) chloride were stirred and heated in a screw-capped tube by employing 3 mL of 2-dimethylaminoethanol

as the solvent, under nitrogen atmosphere at 145 °C. After this, the blue product was cooled and the product was precipitated with a water:methanol (3:1) mixture and filtered. The product was washed with hot methanol, ethanol, hexane, and acetone and dried. The crude dark blue product was purified on a silica-loaded chromatographic column by eluting with toluene:ethanol (3:1, v/v). Yield: 0.017 g (7.9%), FT-IR ν (cm^{-1}): 3057 (Aromatic C–H), 2966 (Alkyl C–H), 1740 (C=O), 1653, 1598 (Aromatic C=C), 1510, 1461, 1360, 1231 (Ar–O–Ar), 1092, 946, 831, 753, 691, 672. UV-vis (THF): λ_{max}/nm (log ε, L mol^{-1} cm^{-1}): 322 (4.75), 665 (4.77). MALDI-TOF-MS; m/z: 1106.83 [M]$^+$; Anal. Calc. for $C_{64}H_{54}CoN_8O_5S$: C, 69.49; H, 4.92; N, 10.13. Found: C, 69.87, H, 4.55; N, 10.01%.

3.3.3. 9(10), 16(17), 23(24)-Tris-(4-ter-butylphenyloxy-)-2(3)-(4-carboxyethyl sulfanyl)phthaloc- yaninato zinc (II) (5a)

A Schlenk tube was charged with 0.166 g (0.60 mmol) of compound **3**, 0.046 g (0.20 mmol) of compound **2**, and 0.037 g (0.20 mmol) of zinc acetate and 4 mL of 2-dimethylaminoethanol as the solvent was added. The mixture was stirred and heated under nitrogen atmosphere for 27 h at 145 °C. A 3:1 (v/v) mixture of water and methanol was used to precipitate the product cooled to room temperature, and the precipitate was filtered. The green product was washed with hot methanol, ethanol, hexane, and acetone, and dried in vacuo. The green-colored product was subjected to column chromatography on silica by eluting with hexane:tetrahydrofuran (5:2). Yield: 0.029 g (13.1%), FT-IR ν (cm^{-1}): 3063 (Aromatic C–H), 2959 (Alkyl C–H), 1717 (C=O), 1599 (Aromatic C=C), 1509, 1477, 1392, 1360, 1231 (Ar–O–Ar), 1173, 1090, 1038, 943, 825, 738, 690, 673. ^{1}H NMR (CDCl$_3$: δ, ppm) 7.79–7.03 (m, Ar–H, 24H), 2.86 (t, –SCH$_2$, 2H), 2.01 (t, –CH$_2$, 2H), 1.50–1.19 (b, –(CH$_3$)$_3$, 27H). UV-vis (THF): λ_{max}/nm (log ε, L mol^{-1} cm^{-1}): 351 (4.60), 678 (4.91). MALDI-TOF-MS; m/z: 1127.16 [M + H]$^+$; Anal. Calc. for $C_{65}H_{56}N_8O_5SZn$: C, 69.29; H, 5.01; N, 9.95. Found: C, 69.60, H, 4.84; N, 9.15%.

3.3.4. 9(10), 16(17), 23(24)-Tris-(4-ter-butylphenyloxy-)-2(3)-(4-carboxyethyl sulfanyl)phthaloc- yaninato cobalt (II) (5b)

A Schlenk tube was charged with 0.193 g of compound **3** (0.70 mmol), 0.046 g of compound **2** (0.20 mmol), and 0.033 g of cobalt(II) chloride (0.25 mmol), and 3 mL of 2-dimethylaminoethanol was added as solvent. The mixture was heated and stirred under nitrogen atmosphere at 145 °C for 27 h. After that, the product was cooled to room temperature, poured into a (3:1, v/v) mixture of water and methanol, filtered, and then dried. The blue product was then prepurified with hot methanol, ethanol, hexane, and acetone, and then dried. The resulting blue compound was purified on a silica column by eluting with a toluene:tetrahydrofuran (50:1, v/v) mixture. Yield: 0.021 g (9.3%), FT-IR ν (cm^{-1}): 3064 (Aromatic C–H), 2960 (Alkyl C–H), 1718 (C=O), 1599 (Aromatic C=C), 1507, 1464, 1406, 1363, 1231 (Ar–O–Ar), 1092, 1009, 957, 805, 753, 687, 670. UV-vis (THF): λ_{max}/nm (log ε, L mol^{-1} cm^{-1}): 328 (4.59), 667 (4.78). MALDI-TOF-MS; m/z: 1121.45 [M + H]$^+$; Anal. Calc. for $C_{65}H_{56}CoN_8O_5S$: C, 69.69; H, 5.04; N, 10.00. Found: C, 69.77, H, 4.72; N, 9.74%.

3.4. Sensitization of TiO$_2$ with nonsymmetrical metallophthalocyanine derivatives

Four different metallophthalocyanines synthesized and characterized in this study were used in the process of sensitizing the TiO$_2$ semiconductor in order to prepare the heterogeneous photocatalysts. Anchoring phthalocyanines onto TiO$_2$ was achieved by the widely used wet deposition method.[42,43] The sensitization

of the TiO_2 materials was carried out as follows: in a 500-mL round-bottom flask, 300 mL of dimethyl sulfoxide (DMSO) and 1 g of TiO_2 were mixed together and dispersed using an ultrasonic bath. Then 3 mL of 5 μM metallophthalocyanine solution in DMSO was added slowly to titania solution under magnetic stirring. DMSO was chosen as a solvent in both solutions because it provides not only the dispersion of the TiO_2 material but also good dissolution of the MPc complexes. After stirring the mixture overnight, the blue-green powder obtained was filtered, then washed with deionized water and ethanol, and lastly dried in a vacuum oven at 80 °C. The green-colored powder was kept in the dark and prior to use it was ground in an agate mortar.

The residual MPc solutions, after filtering, were collected and UV-Vis spectrophotometry helped us, with a calibration curve, know what amount of MPc was immobilized. DMSO was the solvent used in these trials. The amounts of immobilized MPcs on TiO_2 semiconductor are given in the Table.

In addition, the stability profiles of the new MPc/TiO_2 composites were tested before photocatalytic experiments. In the comparison test, the freshly prepared composite and a 1-month-old composite, which was kept in the dark, were used together in diffuse reflectance spectrophotometry. According to the results we obtained, the same values seen on the diffuse reflectance spectra and the photocatalytic yields tell us that the composites we synthesized were quite stable and preserved for a long period.

The characterization phases of MPc/TiO_2 composites involved the use of Fourier-transform infrared spectroscopy (FT-IR), diffuse reflectance spectroscopy (DRS), and X-ray diffraction (XRD).

3.5. Photocatalytic experiments

Photocatalytic degradation studies were performed in a specially designed photoreactor. For each degradation test, 100 mg of the photocatalyst were dispersed in 100 mL of a 0.013 M water solution of 4-chlorophenol and vigorously stirred in the dark for 30 min to constitute an adsorption–desorption equilibrium. Before the lamps were lit, O_2 gas was passed through the suspensions for 30 min and O_2 passing was continued throughout the photocatalytic process. The illumination time was set to 2 h for each run.

The pH value of the suspension was neutral and the photoreactor's inner temperature was maintained at 300 K by passing air through it. At definite intervals, small aliquots of 2 mL were drawn, filtered through 0.20 μm cellulose acetate membrane, and kept away from the catalyst particles. These aliquots were processed in a PerkinElmer Clarus 500 GC-MS in positive electron impact mode to monitor the degradation process. After photodegradation, the amount of unreacted 4-CP was detected by using phenol as an internal standard using a gas chromatograph-mass spectrometer.

To yield a photocatalytic effect (if any), many photocatalytic tests were performed about the effect of different experimental conditions. The Table lists the amounts of immobilized MPcs on TiO_2 semiconductor and the experimental conditions of the processes. All runs were done in triplicate.

4. Conclusion

In the presented work, four novel unsymmetrically mono carboxylic acid substituted cobalt and zinc phthalocyanine complexes were synthesized. Spectral characterizations for the complexes in this study were performed with FTIR and ^{1}H NMR spectroscopy, UV-Vis spectrophotometry, and mass spectrometry. A simple wet deposition process was utilized to obtain MPc/TiO_2 heterogeneous catalysts. XRD and FTIR spectra showed that the MPcs were immobilized onto TiO_2 (anatase form) with carboxylate bonds. The DRS spectra showed that the absorption window of the pristine TiO_2 had expanded to the visible region, and so it is possible to excite with visible light, thereby introduction of MPc into TiO_2 is a very effective methodology to obtain a better

photocatalyst. In the presence of MPc/TiO$_2$ photocatalyst, 4-chlorophenol was degraded almost completely with visible light (95% for **4b**). It is also concluded that cobalt phthalocyanines are slightly more active than the corresponding zinc phthalocyanines and according to chain length of the linker carboxylic acid group the nearer the carboxy group to the Pc core the higher the photoconversion yield obtained. In addition, this study has shown, according to the earlier studies, that MPc/TiO$_2$ composites having aliphatic linker groups had higher photodegradation efficiency than that of MPcs having aromatic linker groups.

Acknowledgment

References

1. Angeletti, G.; Bjiorsethi, A. *Organic Mircropollutants in Aquatic Environment*; Kluwer Academic Publishers: Dordrecht, Netherlands, 1991.

2. Fetzner, S.; Lingnes, F. *Microbiol. Rev.* **1994**, *58*, 641-685.

3. Bumpus, J. A.; Tien, M.; Wright, D.; Aust, S. *Science* **1985**, *228*, 1434-1436.

4. Ollis, D. F.; Pelizzetti, E.; Serpone, N. *Sci. Technol.* **1991**, *25*, 1522-1529.

5. Meunier, B.; Sorokin, A. *Acc. Chem. Res.* **1997**, *30*, 470-476.

6. Sorokin, A.; De Suzzoni-Dezard, S.; Poullain, D.; Noel, J. P.; Meunier, B. *J. Am. Chem. Soc.* **1996**, *118*, 7410-7411.

7. Hoffmenn, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. *Chem. Rev.* **1995**, *95*, 69-96.

8. Schneider, J.; Matsuoka, M.; Takeuchi, M.; Zhang, J.; Horiuchi, Y.; Anpo, M.; Bahnemann, D. W. *Chem. Rev.* **2014**, *114*, 9919-9986.

9. Augugliario, V.; Palmisano, L.; Chiavello, M.; Sclafani, A.; Marchese, L.; Martra, G.; Miano, F. *Appl. Catal.* **1991**, *69*, 323-340.

10. Iliev, V. *J. Photochem. Photobiol. A: Chem.* **2002**, *151*, 195-199.

11. Mahmiani, Y.; Sevim, A. M.; Gül, A. *J. Photochem. Photobiol. A: Chem.* **2016**, *321*, 24-32.

12. Iliev, V.; Tomova, D.; Bilzarska, L.; Prahov, L.; Petrov, L. *J. Photochem. Photobiol. A: Chem.* **2003**, *159*, 281-287.

13. Wang, S. L.; Fang, Y. F.; Yang, Y.; Liu, J. Z.; Deng, A. P.; Zhao, X. R.; Huang, Y. P. *Chinese Sci. Bull.* **2011**, *56*, 969-976.

14. Tao, X.; Ma, W.; Li, J.; Huang, Y.; Zhao, J.; Yu, J. C. *Chem. Commun.* **2003**, 80-81.

15. Kalyanasundaram, K.; Gratzel, M.; Pelizzetti, E. *Coord. Chem. Rev.* **1986**, *69*, 57-125.

16. Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Muller, E.; Liska, P.; Vlachopoulos, N.; Gratzel, M. *J. Am. Chem. SOC.* **1993**, *115*, 6382-6390.

17. Sevim, A. M. *J. Organomet. Chem.* **2017**, *832*, 18-26.

18. Mahmiani, Y.; Sevim, A. M.; Gül, A. *J. Porphyr. Phthalocya.* **2016**, *20*, 1190-1199.

19. De La Torre, G.; Torres, T. *J. Porphyr. Phthalocya.* **1997**, *1*, 221-226.

20. Arslanoğlu, Y.; Sevim, A. M.; Hamuryudan, E.; Gül, A. *Dyes Pigments* **2006**, *68*, 129-132.

21. Bilal, C.; Sevim, A. M.; Gül, A. *Inorg. Chem. Commun.* **2016**, *69*, 10-12.

22. Arami, M.; Limaee, N. Y.; Mahmoodi, N. M.; Tabrizi, N. S. *J. Hazard. Mater.* **2006**, *135*, 171-179.

23. Konstantinou, I. K.; Albanis, T. A. *Appl. Catal. B-Environ.* **2004**, *49*, 1-14.

24. Bai, Y.; Mora-Sero, I.; De Angelis, F.; Bisquert, J.; Wang, P. *Chem. Rev.* **2014**, *114*, 10095-10130.

25. Vallejo, W.; Diaz-Uribe, C.; Cantillo, A. *J. Photochem. Photobiol. A: Chem.* **2015**, *299*, 80-86.

26. Huang, Z.; Zheng, B.; Zhu, S.; Yao, Y.; Ye, Y.; Lu, W.; Chen, W. *Mater. Sci. Semicond. Process.* **2014**, *25*, 148-152.

27. Gilma, G. O.; Carlos, M.; Páez, A.; Fernando, M. O.; Páez-Mozo, E. A. *Catal. Today.* **2005**, *107*, 589-594.

28. Özçelik, Ş.; Gül, A. *Polyhedron* **2013**, *50*, 461-466.

29. Sevim, A. M.; Arıkan, S.; Özçeşmeci, İ.; Gül, A.; *Synth. Met.* **2013**, *183*, 1-7.

30. Özçelik, Ş.; Karaoğlan, G. K.; Gümrükçü, G.; Erdoğmuş, A.; Gül, A. *J. Organomet. Chem.* **2014**, *769*, 17-23.

31. Takagi, S.; Shimada, T.; Yui, T.; Inoue, H. *Chem. Lett.* **2001**, *30*, 128-129.

32. Diaz-Uribe, C.; Daza, M. C.; Martinez, F.; Paez-Mozo, E. A.; Guedes, C. L. B.; Di Mauro, E. *J. Photochem. Photobiol. A: Chem.* **2013**, *259*, 47-52.

33. Kudo, A.; Miseki, Y. *Chem. Soc. Rev.* **2009**, *38*, 253-278.

34. Ebrahimian, A.; Zanjanchi, M. A.; Noei, H.; Arvand, M.; Wang, Y. *J. Environ. Chem. Eng.* **2014**, *2*, 484-494.

35. Jung, O.; Kim, S.; Cheong, K.; Li, W.; Saha, S. *Korean Chem. Soc.* **2003**, *24*, 49-54.

36. Sauer, T.; Neto, G. C.; Jose, H. J.; Moreira, R. F. P. M. *J. Photochem. Photobiol. A: Chem.* **2002**, *149*, 147-154.

37. Ghasemi, S.; Rahimnejad, S.; Setayesh, S. R.; Hosseini, M.; Gholami, M. R. *Prog. React. Kinet. Mech.* **2009**, *34*, 55-76.

38. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon: Oxford, UK, 1989.

39. Yıldırım, Ö.; Sevim, A. M.; Gül, A. *Color. Technol.* **2012**, *128*, 236-243.

40. Sevim, A. M.; Ilgün, C.; Gül, A. *Dyes Pigments* **2011**, *89*, 162-168.

41. Seven, Ö.; Dindar, B.; Gültekin, B. *Turk. J. Chem.* **2009**, *33*, 123-134.

42. Sun, Q.; Xu, Y. *J. Phys. Chem. C.* **2009**, *113*, 12387-12394.

43. Mele, G.; Garcia-Lopez, E.; Palmisano, L.; Dyrda, G.; Słota, R. *J. Phys. Chem. B* **2007**, *111*, 6581-6588.