

Energy Technology & Environmental Science

Enhanced Photocatalytic Performance of Porphyrin/Phthalocyanine and Bis(4-pyridyl)pyrrolidinofullerene modified Titania

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Zinc(II), copper(II) and cobalt(II) metallated porphyrins/phthalocyanines and bis(4-pyridyl) pyrrolidinofullerene (**9**) were used in a supramolecular approach for the sensitization of titania. Spectral properties of the chromophores were examined in the solid state showing strong absorptions at 700 and 800 nm for porphyrins and phthalocyanines, respectively. The interaction between the chromophores and a dual ligand was investigated

spectroscopically. Titania-based composites sensitized with **9** and cobaltous porphyrin exhibited the highest photocatalytic activity against both phenol and methylene blue under solar irradiation. Photodegradation intermediates were determined based on LC-UV-Vis-MS analysis. It is expected that the composites will be applied for remediation of aqueous environmental samples from transparent and colorful pollutants.

Introduction

Titania (TiO₂) is an inorganic semiconductor of significant importance. It is commonly used in heterogeneous photocatalysis and photovoltaics, especially in dye-sensitized solar cells. Its widespread application in the above-mentioned fields is a consequence of its efficient electron-hole pair generation. However, TiO₂ excitation occurs under ultraviolet radiation, which lowers the efficiency and increases the cost of the above-mentioned processes. Consequently, sensitizers are used to modify TiO₂, so that it can be excited by visible light. Some of these sensitizers include azo^[1,2], hemicyanine^[3,4], perylene bisimide,^[5,6] xanthene,^[1] porphyrin^[7-14] and phthalocyanine^[15-19] dyes. The latter two groups of chromophores show the best photosensitizing ability.^[20]

Having an efficient chromophore is important but its efficient attachment to TiO₂ is crucial,^[7] as is the energy difference between the LUMO (lowest unoccupied molecular orbitals) of the chromophoric structure and the conduction band (CB) of the semiconductor.^[21] Efficient attachment can be obtained by the incorporation of suitable anchoring groups capable of connecting to the semiconductor's surface. Among others, aminoacid^[22], anhydride,^[23] carboxylate,^[24,25] cyanoacrylate,^[26,27] ester,^[28,29] hydroxamate,^[30,31] pyridyl,^[32] and phospho-

nate^[33-36] groups have been used for that purpose. It is also possible to introduce a linkage molecule that is able to interact with both the chromophore and the semiconductor surface. The latter method has been successfully applied by introducing 4-substituted pyridine with acetylacetonate, carboxylate, hydroxamate, and phosphonate groups to bind porphyrin^[12] and ruthenium dyes^[37] to TiO₂.

It is well-known that fullerene derivatives can easily form supramolecular electron donor-acceptor systems with porphyrins^[38-41] and phthalocyanines.^[40-44] In addition, the LUMO levels of suitably functionalized fullerenes can be adjusted to be between the LUMO of the porphyrins/phthalocyanines and the CB of TiO₂. Although the photophysics of porphyrin/phthalocyanine-fullerene complexes^[38,45-52] and their application in solar cells^[42,44,53-58] have been studied, these conjugates have not been applied in photocatalytic systems with TiO₂. Therefore, we decided to explore this possibility using a new anchoring compound, namely bis(4-pyridyl) pyrrolidinofullerene (**9**). Since **9** has two anchoring pyridyl groups, which are able to attach to porphyrins/phthalocyanines and to the semiconductor surface, it was used as a linker to attach the chromophore to the TiO₂ surface.

The synthesis of **9**^[59-61] and studies concerning its complexation with porphyrins^[59,62,63] and naphthalocyanines^[64] were described by others. To our knowledge no complexes with porphyrins nor with phthalocyanines and **9** have been attached to semiconductors for photoremediation. There have been only a few reports that use supramolecular approaches to attach sensitizers to the semiconductor surface using small molecules.^[12,37] However, none report applications for photocatalysis. Some reports show^[65] that pyridine anchors provide more robust pyridine-titanium interactions than carboxylic groups. We thus decided to apply bis(4-pyridyl)pyrrolidinofullerene as a dual ligand for a supramolecular approach to the sensitization of titania with porphyrins and phthalocyanines. A series of zinc,

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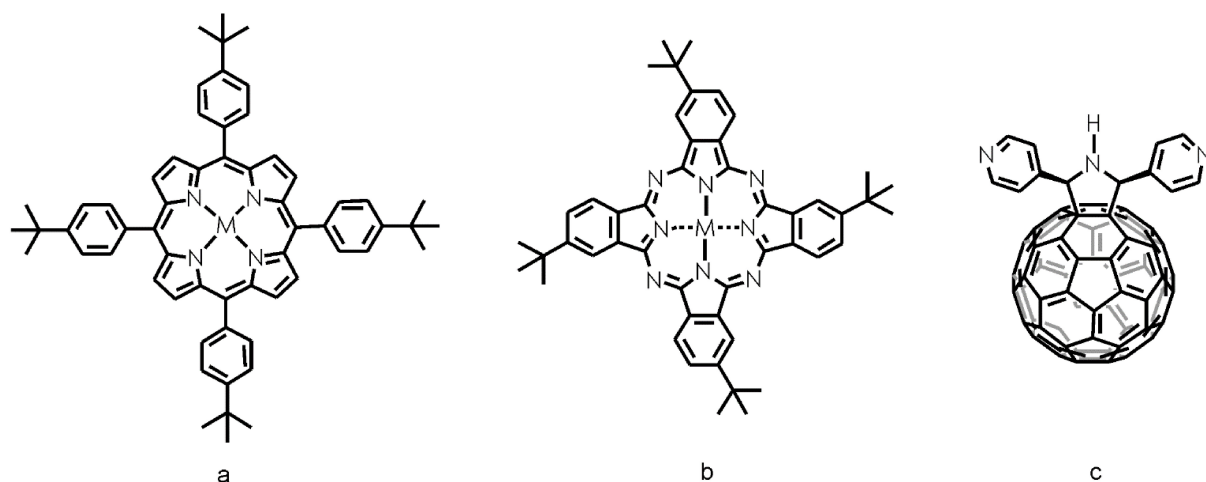


Figure 1. Structures of porphyrins (a): **1** (M = 2H), **2** (M = Zn), **3** (M = Cu), **4** (M = Co); phthalocyanines (b): **5** (M = 2H), **6** (M = Zn), **7** (M = Cu), **8** (M = Co) and fullerene derivative **9** (c).

copper and cobalt metallated porphyrins and phthalocyanines as well as *bis*(4-pyridyl)pyrrolidinofullerene were synthesized. The structures are presented in Figure 1. The spectral and electrochemical properties of the compounds were also examined and all the compounds were used to prepare composites with titania prepared using the sol-gel technique. The interaction between **9** and the chromophores was investigated spectroscopically. Finally, the photocatalytic activity of all composites was tested against two model pollutants, phenol (PhOH) and methylene blue (MB), and their photo-degradation intermediates were identified using LC-UV-Vis-MS.

Results and Discussion

UV-Vis absorption studies

Diffuse reflectance UV-Vis spectra (DRS) of porphyrins **1**, **2**, **3** and **4** (Figure 2a) show their ability to absorb ultraviolet and visible light up to 700 nm. Meanwhile, phthalocyanines **5**, **6**, **7** and **8** (Figure 2b) are able to absorb up to 800 nm. Their absorption was negligible in the wavelength range of 420-475 nm. Characteristic Soret and Q bands were observed around 250-400 and 550-750 nm, respectively. Both of these can be assigned to the π - π^* macrocycle ring transitions.^[66] Electronic spectra in the solid state of both porphyrins and phthalocyanines are known to exhibit broadening and a blue-shift of the Q bands. The shift of the Q bands towards shorter wavelengths is due to dimerization and/or aggregation of the chromophoric structures. The phthalocyanine bands at 620 nm were assigned to dimerized structures, while the shoulder of the Q band at higher wavelengths was assigned to aggregation.^[66] The DRS spectra indicated that both porphyrins and phthalocyanines absorb in the visible spectrum.

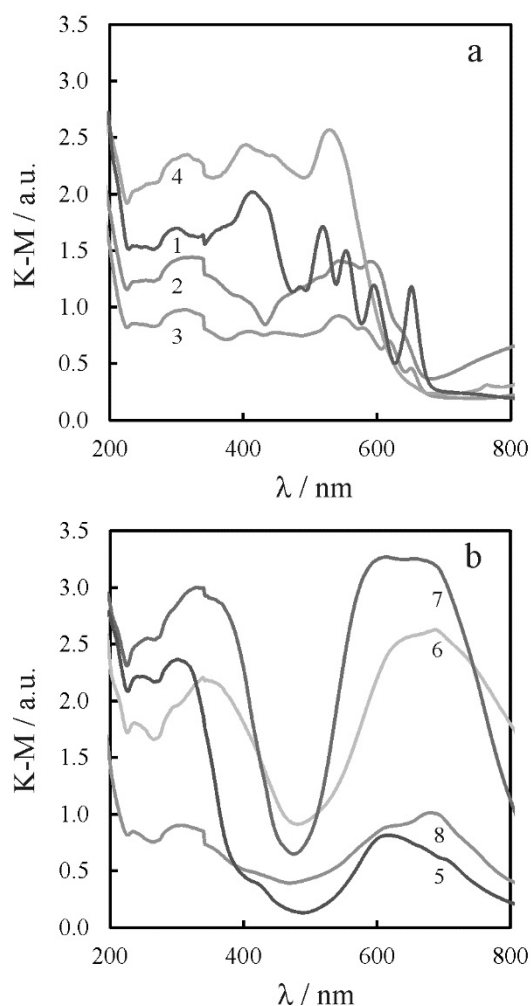


Figure 2. Kubelka-Munk plots of porphyrins (**1-4**) and phthalocyanines (**5-8**).

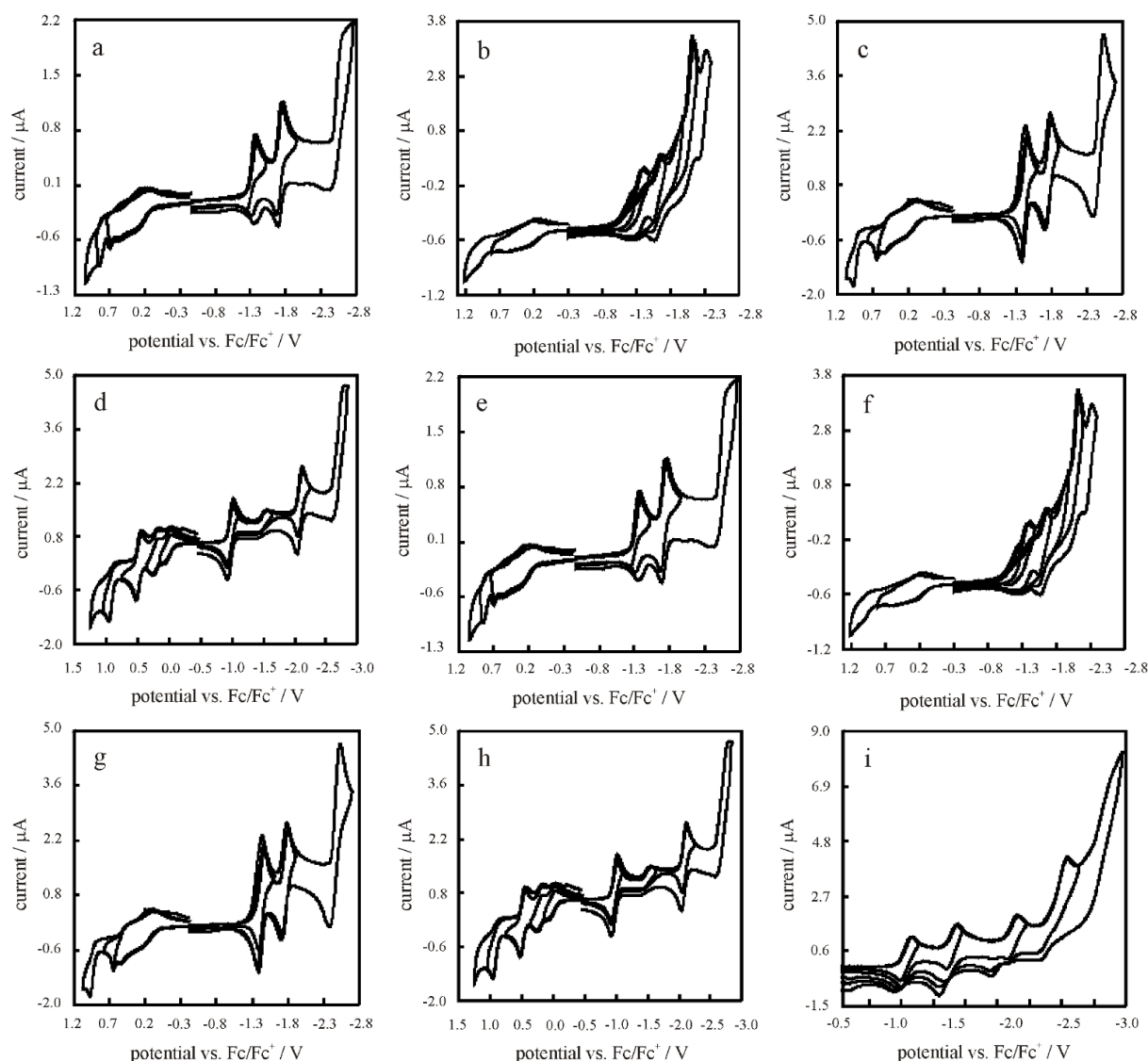


Figure 3. Cyclic voltammograms of **1** (a), **2** (b), **3** (c), **4** (d), **5** (e), **6** (f), **7** (g), **8** (h) and **9** (i) in TBAPF₆/(DCM:Tol = 1:4,v/v) at a scan rate of 50 mV·s⁻¹.

Electrochemical properties/determination of HOMO-LUMO energy levels

In order to estimate the energy of the HOMO and LUMO levels of the synthesized compounds, electrochemical characterizations were performed. Appropriate LUMO energy levels relative to the conduction band of titania are necessary for efficient photosensitization to occur. Figure 3 (a-d) shows the cyclic voltammograms registered for porphyrins 1-4. The voltammograms for the zinc (**2**) and copper (**3**) porphyrins exhibit two reversible reduction and oxidation processes. The two-electron reduction of the aromatic porphyrin (P²⁻) ring was associated with the formation of P³⁻ and P⁴⁻. Oxidation of the porphyrin macrocycle resulted in the formation of P⁻¹ and P^[67]. For **2** and **3** no waves arising from redox processes involving the metal cations were observed, as was reported by others in similar macrocycles.^[68-70] However, the voltammogram of **4** (Figure 3d)

exhibits additional irreversible peaks in both cathodic and anodic scans, which result from the reduction and oxidation processes of the cobalt cation.^[67,71]

Similar observations were made for phthalocyanines **5-8** (Figure 3 (e-h)). The reductive scans for **5**, **6** and **7** show two reduction processes^[72] (M^{II}Pc⁻²/M^{II}Pc⁻³ and M^{II}Pc⁻³/M^{II}Pc⁻⁴) of the macrocycle ring. However, the voltammogram of **8** revealed not only the reduction of the macrocycle ring of the phthalocyanine (Co^{II}Pc⁻²/Co^{II}Pc⁻³ and Co^{II}Pc⁻³/Co^{II}Pc⁻⁴), but also the reduction of the cobalt cation (Co^{II}Pc⁻²/Co^IPc⁻²). Thus the anodic scan shows the oxidation of the macrocyclic ring and of the cobalt cation.

Results of the electrochemical studies of the fullerene derivative **9** are depicted in Figure 3i, which show four reduction peaks. These can confidently be assigned to the sequential reduction of C₆₀.^[73] On the basis of the registered

voltammograms the HOMO and LUMO levels of compounds 1-9 were estimated according to the following equations:

$$E_{\text{LUMO}} = -(4.71 - E_{1/2, \text{Fc/Fc}^+} + E_{\text{red, onset}}) \quad (1)$$

$$E_{\text{HOMO}} = -(4.71 - E_{1/2, \text{Fc/Fc}^+} + E_{\text{ox, onset}}) \quad (2)$$

The results are presented in Figure 4. The LUMO levels of

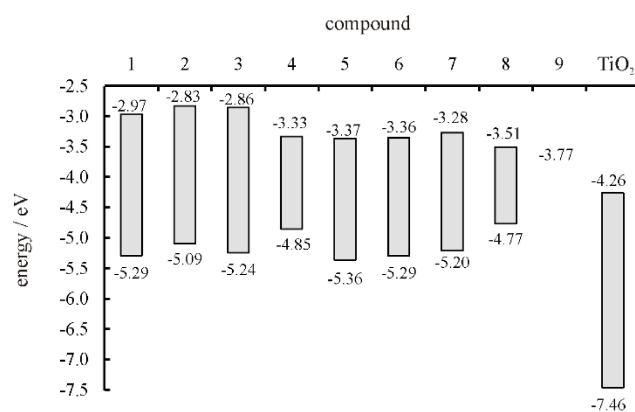


Figure 4. HOMO-LUMO energy levels for porphyrins (1-4), phthalocyanines (5-8), 9 and TiO₂.

the porphyrins: 1 (-2.97 eV), 2 (-2.83 eV), 3 (-2.86 eV), 4 (-3.33 eV) and phthalocyanines: 5 (-3.37 eV), 6 (-3.36 eV), 7 (-3.28 eV), 8 (-3.51 eV) are above the LUMO level of 9 (-3.77 eV) and this in turn is above the conduction band of the titanium dioxide (-4.26 eV). These results indicate that it is feasible to observe enhanced photocatalytic activity for the following systems: porphyrin/9/TiO₂ and phthalocyanine/9/TiO₂. After excitation of the chromophoric structure electron injection to the fullerene derivative 9 is taking place and electron injection to the conduction band of TiO₂ should subsequently occur.

Specific surface area

Specific surface areas of the prepared titania and of the composites were determined using the Brunauer-Emmett-Teller (BET) static nitrogen adsorption technique. The results (Table 1) for the composites were in the range of 86-189 m²·g⁻¹, while the BET surface area of the pristine titania was 269 m²·g⁻¹. It was noticed that the introduction of the porphyrins or phthalocyanines to the composites resulted in a decrease of the BET surface area. Further decreases of the surface area were observed after the fullerene derivative 9 was introduced into the porphyrin/TiO₂ and phthalocyanine/TiO₂ composites.

Supramolecular interactions between 9 and porphyrins/phthalocyanines

The interactions between 9 and the porphyrins/phthalocyanines were investigated spectroscopically. Complexes of chromophores with an excess of 9 were prepared. The resulting

| Catalyst | BET surface area / m ² ·g ⁻¹ |
|-----------------------|--|
| TiO ₂ | 269 |
| TiO ₂ /2 | 178 |
| TiO ₂ /9/2 | 86 |
| TiO ₂ /3 | 151 |
| TiO ₂ /9/3 | 102 |
| TiO ₂ /4 | 158 |
| TiO ₂ /9/4 | 118 |
| TiO ₂ /6 | 134 |
| TiO ₂ /9/6 | 95 |
| TiO ₂ /7 | 152 |
| TiO ₂ /9/7 | 81 |
| TiO ₂ /8 | 165 |
| TiO ₂ /9/8 | 102 |

solutions were measured by UV-Vis spectroscopy at room temperature (Figure 5). In all cases a decrease in intensity of the Soret band was noticed due to the host-guest complexation between the chromophore and the fullerene derivative (Figure 5 (a-c)).^[38,74] In the case of 2-9 and 4-9 a new, red-shifted band was observed. A far more noticeable shift of the new band was observed when the cobaltous porphyrin was bound to the ligand. UV and Vis spectra registered for complexes with phthalocyanines are shown in Figure 5 (d-f). In the visible spectral range a decrease and a red-shift of the Q band was observed when the phthalocyanines were subjected to complexation with 9. These observations have been previously assigned to charge-transfer interactions.^[51,52] Among these complexes the one with the cobalt porphyrin was found to exhibit the strongest interaction between the investigated ligand.

Photocatalytic performance

Photocatalytic activity tests of the prepared photocatalysts were conducted using phenol (PhOH) and methylene blue (MB) as the model pollutants. The efficiencies ($\eta = (1 - C_t/C_0)100\%$; C₀ – initial concentration, C_t – concentration at time t) of their photocatalytic degradation (after 2 hours of irradiation) in the presence of TiO₂ and the composites are listed in Figure 6. When PhOH was subjected to photocatalytic degradation its η reached 20% in the presence of pristine titania. It was observed that η increased from 39 up to 49% when 9 was introduced into the TiO₂/porphyrin or TiO₂/phthalocyanine composites. MB degradation showed lower η values, 18%. This value increased to 25-37% when the TiO₂/porphyrin or TiO₂/phthalocyanine composites were used. Further increases of η up to 35-46% were observed for TiO₂/9/porphyrin and TiO₂/9/phthalocyanine. Lower photodegradation efficiencies were obtained when MB was applied as a model pollutant. This was attributed to the absorption behaviour of the degraded compounds. MB can interfere with light absorption by the sensitizers. Thus higher degradation efficiencies can be obtained for pollutants that absorb mainly UV radiation. It should be stressed that all of the prepared composites exhibit significantly enhanced photocatalytic activity when compared to pristine titania. The photo-

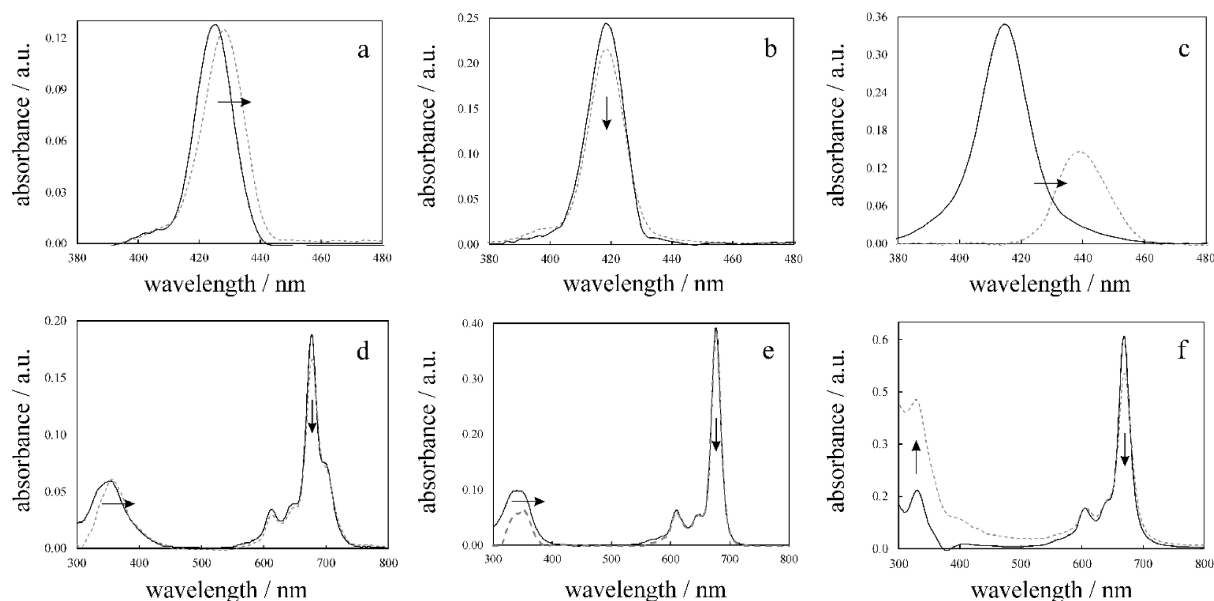


Figure 5. UV-Vis spectra of a 10^{-6} mol·L $^{-1}$ solution of **2** (a), **3** (b), **4** (c), **6** (d), **7** (e) and **8** (f) in toluene before (solid line) and after adding **9** (hashed line) ($2.86 \cdot 10^{-4}$ mol·L $^{-1}$ (a), $5.24 \cdot 10^{-4}$ mol·L $^{-1}$ (b), $1.38 \cdot 10^{-4}$ mol·L $^{-1}$ (c), $7.4 \cdot 10^{-5}$ mol·L $^{-1}$ (d), $3.9 \cdot 10^{-4}$ mol·L $^{-1}$ (e) and $2.4 \cdot 10^{-4}$ mol·L $^{-1}$ (f)).

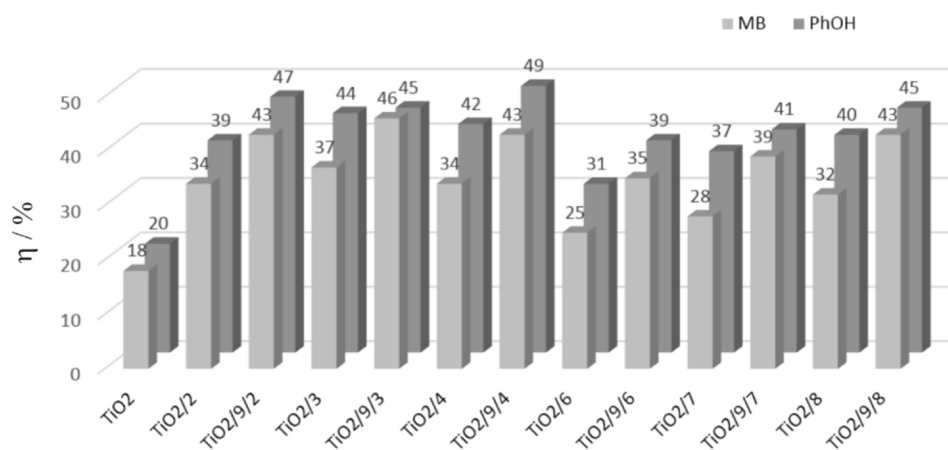


Figure 6. The efficiencies of phenol and methylene blue photocatalytic degradation in the presence of TiO $_2$ and the given composites.

degradation efficiency under natural sunlight should improve significantly compared with simulated solar light.

Since similar results using porphyrin or phthalocyanine modified titania for the degradation of pollutants have not been published, our results can not be compared to others. However, PhOH and MB have been used as model structures for the estimation of the photocatalytic activity of pristine TiO $_2$. In the case when visible light was used as an irradiation source the photodegradation efficiency did not exceed 20% for MB^[75] and PhOH.^[76] Therefore our sensitized titania acts as a much more efficient agent for photodegradation of pollutants.

UV/Vis absorbance spectra of the photodegradation products

The chromatograms and absorption spectra of PhOH and MB before and after 2 h of photocatalytic treatment with TiO $_2$ /9/4

were recorded at different wavelengths, see in Figure 7 and 8, respectively. Figure 7 (1) shows that after the photocatalytic treatment of the PhOH solution only three peaks were detected in the chromatogram. The absorption spectra presented in Figure 7 (2) reveal that the peak at 2.56 min corresponds to PhOH. Figure 7 (2b) shows that PhOH still remains in the solution after 2 h of irradiation in the presence of the catalyst. The other two peaks were identified as benzoquinone and maleic anhydride. The assignment of the peaks was based on the absorption and mass spectra. Apart from the mentioned structures a series of other products in smaller amounts were identified by mass spectrometry (Supporting Information).

Unlike PhOH, MB was found to undergo complete photocatalytic degradation. Figure 8 shows the chromatograms recorded for the MB solution before and after photocatalytic treatment (Figure 8 (1a)) along with the absorption spectra (Figure 8 (2)) corresponding to the retention times at which

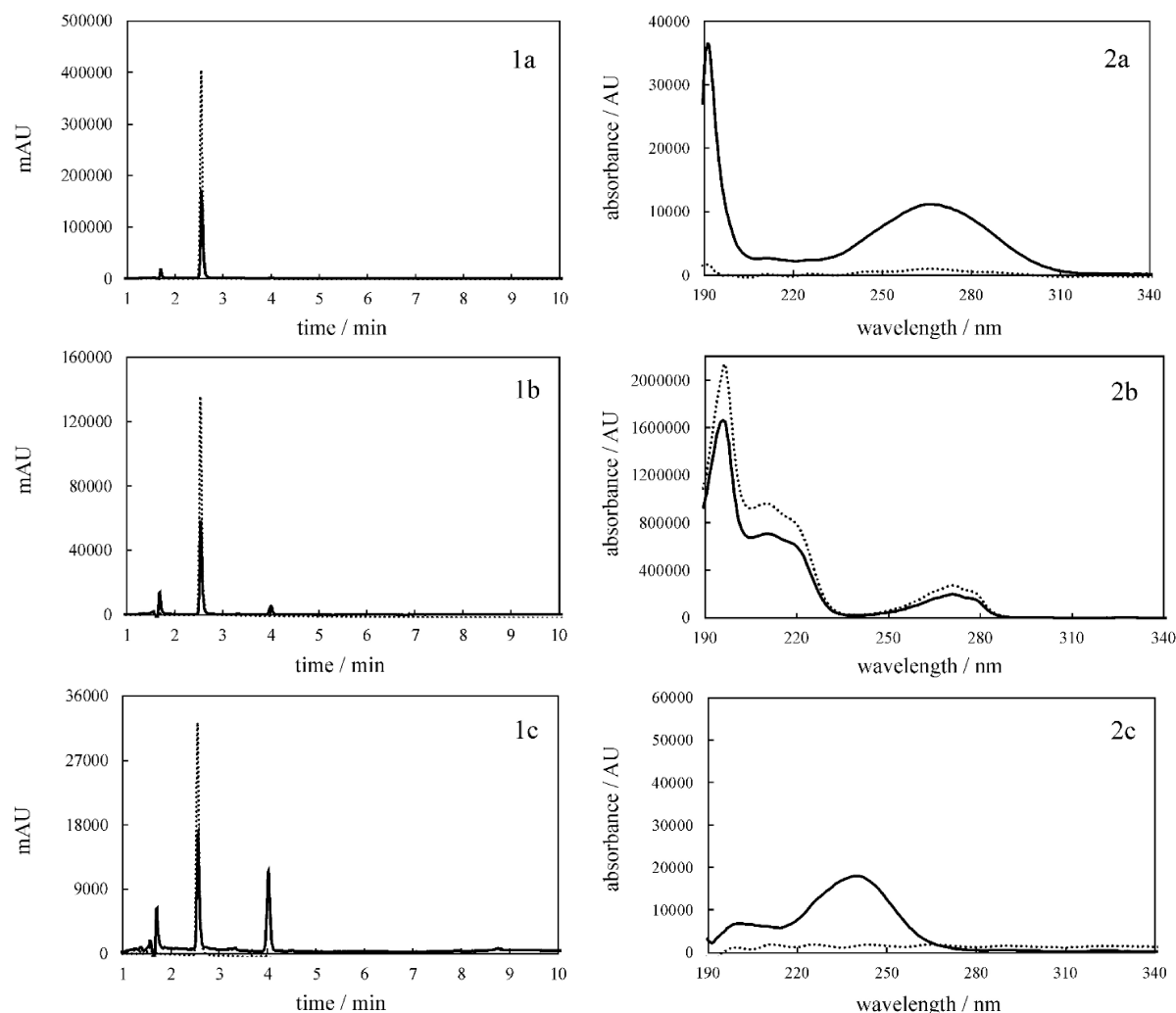


Figure 7. The chromatograms of PhOH initial solution (dotted line) and after 2 h of photocatalytic treatment (solid line) with $\text{TiO}_2/9/4$ recorded at 239 (1a), 254 (1b) and 270 nm (1c). Absorption spectra corresponding to the peaks registered in the chromatograms at 1.71 (2a), 2.56 (2b) and 4.05 min (2c).

pristine MB and its photodegradation intermediates were observed. The peak assigned to MB was not present in the chromatogram registered after 2 h of photocatalytic treatment. However, two additional peaks at 6.20 and 6.34 min appeared. Their absorption spectra, presented in Figure 8 (2b,c), revealed that MB photodegradation products absorb visible light. Therefore, complete decolorization of the MB does not take place under the applied conditions. All of the detected photodegradation products of the MB are described in the Supporting Information.

Mechanism of photocatalysis

The overall photoinduced electron flow is presented in Figure 9, along with the energy levels obtained by electrochemistry. Under irradiation with simulated solar light an excitation of the chromophore (pophyrin/phthalocyanine) takes place. This process is followed by electron transfer to the LUMO of **9** and subsequently to the CB of titania in a downhill energy cascade

as presented in Figure 9. The injected electrons (e_{CB}) can react with the dissolved oxygen leading to the generation of superoxide, hydroperoxyl and finally to hydroxyl radicals,^[77,78] among which the latter are considered as the main species responsible for the degradation of pollutants. All of the intermediate radicals participate in the degradation of organic matter leading to the decomposition of the contaminants in the aqueous phase.

Conclusions

Novel composites based on a dual ligand, *bis*(4-pyridyl)pyrrolidinofullerene (**9**), using a supramolecular approach for the sensitization of titania with zinc(II), copper(II) and cobalt(II) metallated porphyrins and phthalocyanines were prepared. This work constitutes the first report of the application of **9** in composites for photocatalytic degradation applications. We also demonstrated for the first time that introduction of a fullerene derivative with pyridyl groups leads to the simulta-

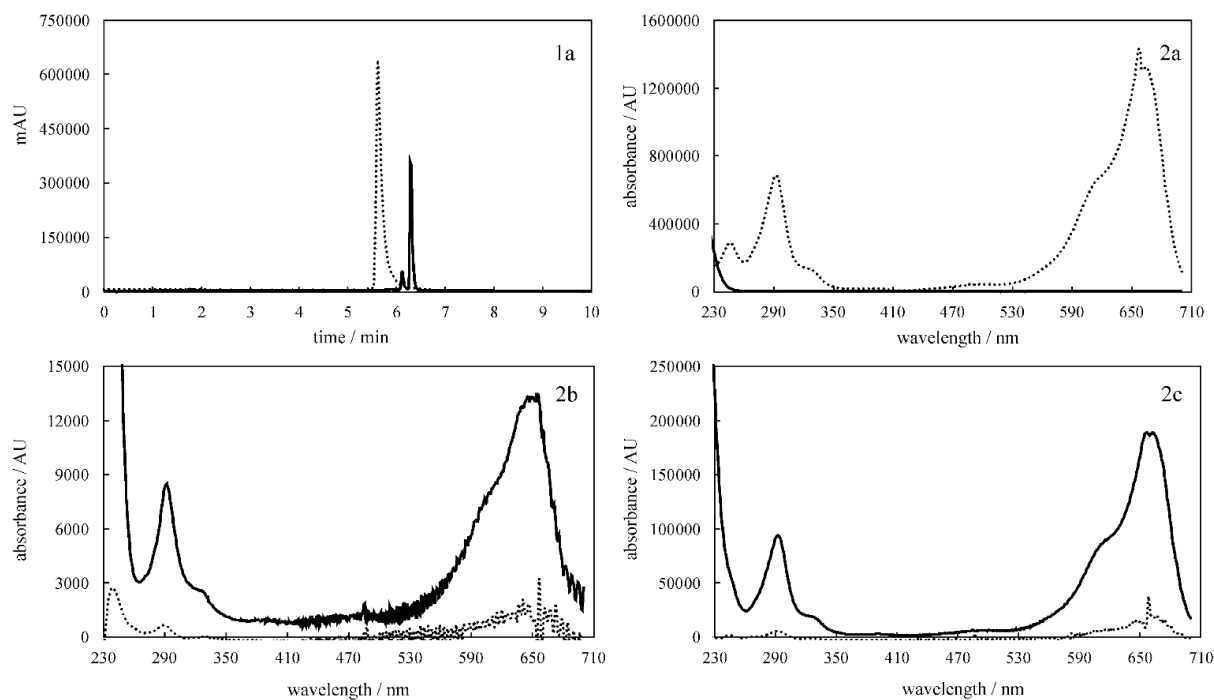


Figure 8. The chromatogram of MB initial solution (dotted line) and after 2 h of photocatalytic treatment (solid line) with $\text{TiO}_2/9/4$ recorded at 610 nm (1a). Absorption spectra corresponding to the peaks registered in the chromatogram at 5.61 (2a), 6.20 (2b) and 6.34 min (2c).

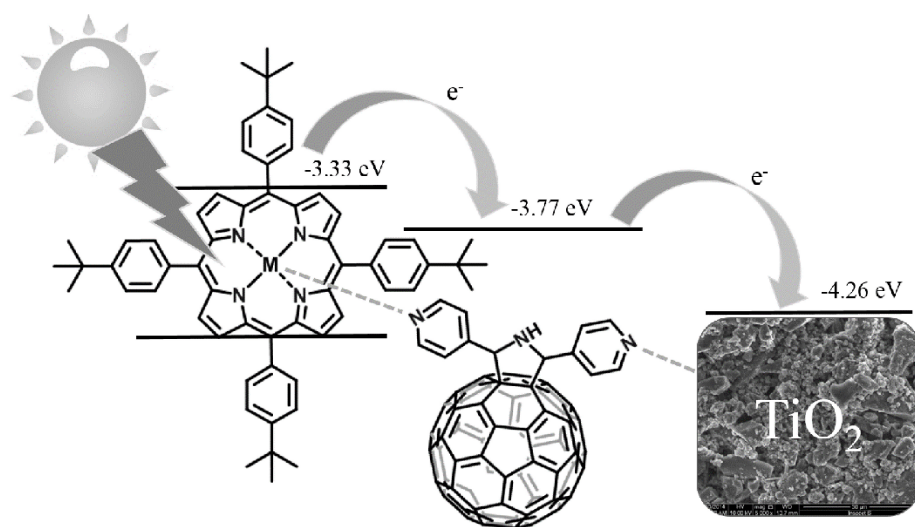


Figure 9. Overall photoinduced electron flow leading to reductive degradation.

neous coordination of a dye to the titania surface. LUMO energy levels, determined based on electrochemical measurements, of the synthesized porphyrins, phthalocyanines and **9** versus titania were found to be energetically aligned, which was crucial for the photosensitization of the titania with the chromophores and **9**. Since the construction of the described composites is based on the complexation between **9** and the chromophore, interactions between the following structures **2-9**, **3-9**, **4-9**, **6-9**, **7-9** and **8-9** were investigated spectroscopically. The greatest spectral changes were estimated for the complex created between *bis*(4-pyridyl)pyrrolidinofullerene and cobaltous porphyrin. Despite the fact that BET surface areas of

the porphyrin/ TiO_2 and phthalocyanine/ TiO_2 composites were among the lowest, the highest photocatalytic activity under solar irradiation was found to be exhibited by the $\text{TiO}_2/9/4$ composite. This is likely due to the enhancement of electron transfer to the CB of the semiconductor.

Supporting Information Summary

All experimental details are included in Supporting Information.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: composites · fullerene · photocatalysis · pollutants degradation · titania photosensitization

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