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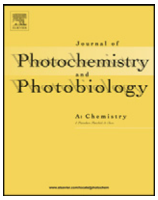

Tetrakis-2,3-[5,6-di-(2-pyridyl)-pyrazino]porphyrazine, and its Cu(II) complex as sensitizers in the TiO_2-based photo-degradation of 4-nitrophenol

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ABSTRACT

The tetrapyrrolic macrocycle tetrakis-2,3-[5,6-di-(2-pyridyl)-pyrazino]porphyrazine, [$Py_8TPyzPzH_2$], and its copper(II) derivative, [$Py_8TPyzPzCu$] were used as sensitizers adsorbed on TiO_2 (anatase) particles for the UV (300–400 nm) photo-degradation of 4-nitrophenol (4-NP) in water suspensions. A 3.5-fold increase of photocatalytic power over bare TiO_2-anatase has been observed in the case of the Cu(II) complex and of more than a factor of two for the free base. Compared with previous data obtained with anatase samples impregnated with some structurally similar porphyrins and phthalocyanines derivatives, these results represent a significant improvement. On the contrary, upon impregnation with [$Py_8TPyzPzCu$], both TiO_2-rutile and TiO_2-Degussa P25 did not show any improvement of their photocatalytic efficiency. Experimental evidences indicate that formation of singlet oxygen does not contribute to the beneficial effect of the macrocycles. Hydrogen peroxide was found not to participate to the 4-NP depletion. Some photo-bleaching of the adsorbed dye has also been observed.

1. Introduction

The decontamination of waste waters from organic pollutants, generated by human activities, is one of the major challenges of contemporary applied chemistry. Being both a large scale and world-wide spread objective, it necessarily requires low-cost procedures made applicable by readily accessible energy sources and cheap materials.

Photo-degradation of the organic pollutants, down to their complete mineralization, in the presence of microparticles of an appropriate semiconductor is the most promising way to accomplish such an objective with the above requirements [1,2]. As it is well known, a semiconductor (SC) is, in general, a polycrystalline material, often a metal oxide, where the valence band (VB) is completely filled and is separated from an empty, upper laying conduction band (CB) by an energy gap (EG) sufficiently small to allow photoexcitation of the electrons from VB to CB by absorption of UV–Vis light. This process generates an electron/hole (e^-/h^+) couple where e^- and h^+ behave as somewhat independent entities. If the SC is in form of a finely dispersed powder suspended in the polluted aqueous medium, e^- and h^+ migrate to the particles surface where they are captured, and to some extent stabilized, in low-energy traps, such as lattice defects. There, positive holes may act as powerful oxidizing agents towards adsorbed organic molecules. Accumulation of CB electrons is avoided by the sacrificial use of an oxidant, such as the ubiquitous dioxygen which is converted to $O_2^{-\bullet}$ and, hence, to $HO_2^{\bullet}$, a very efficient oxidizing agent. The overall process is then, the oxidation of the contaminant (and eventually of its stepwise degradation products) by dioxygen down to CO_2 and H_2O (mineralization) [1–3].

The most thoroughly investigated semiconductor material is polycrystalline TiO_2, in its anatase form, with an EG of about 3.3 eV, corresponding to a 380 nm light absorption threshold.

One of the major limitations of the semiconductors-based photo-degradation is the competing $e^- + h^+$ annihilation reaction that considerably lowers the quantum yield of the process down to negligible values. Thus, a great deal of efforts are oriented to slow down charge recombination by the use of appropriate charge stabilizing agents. For instance, deposition of a noble metal (Pt, Au, Rh) on the anatase microparticles has been found to enhance the photoactivity of the semiconductor, very likely by stabilizing the CB electrons [2–6]. Also, the surface absorption of metal complexes turned out to be a means for improving the efficiency of TiO_2. Although the detailed mechanism of this effect has not been precisely ascertained, it is likely that stabilization of photo-generated charges is again a central point.

Until now, the effect that has been measured is not very large and the overall quantum yield still stays below a level of a practical use. The studies conducted so far in this area have considered as photoactive materials, mainly, tetrapyrrolic macrocycles, such as porphyrin or phthalocyanine complexes, carrying Cu(II) as the central metal ion [7–10]. In earlier and

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more recent times, our group has been engaged in the synthesis and characterization of novel classes of phthalocyanine analogues (porphyrazines) carrying externally annulated five- [11a,b], six- [12–17] and seven-membered [18a,b] heterocyclic rings. Among them, the free-base ligand tetrakis-2,3-[5,6-di-(2-pyridyl)-pyrazino]porphyrazine, [$Py_8TPyzPzH_2$] and some of its metal derivatives [$Py_8TPyzPzM$] have been the object of extensive investigation [12,13]. We believed interesting to test the ability of this novel class of macrocycles in enhancing the efficiency of TiO_2 in the elimination of organic pollutants from waste waters, under UV illumination, in the search for a possible correlation between the sensitizer efficiency and its molecular structure. We here report the results concerning the free base, [$Py_8TPyzPzH_2$], and its Cu(II) complex, [$Py_8TPyzPzCu$], and we compare them with previous literature data.

2. Experimental

2.1. Instruments

UV–Vis measurements, including kinetic runs, were carried out on a Varian Cary 50 spectrophotometer. Diffuse reflectance (DR) spectra of loaded and bare Ti dioxide samples were obtained using a Varian Cary 5E instrument with Teflon as reference. Textural characterizations were obtained at liquid N_2 temperature by using a Micromeritics ASAP 2010 analyzer. X-ray diffraction data on TiO_2 were performed with a X'PERT diffractometer ($CuK\alpha_1 = 1.54056$ Å, Ni filtered radiation).

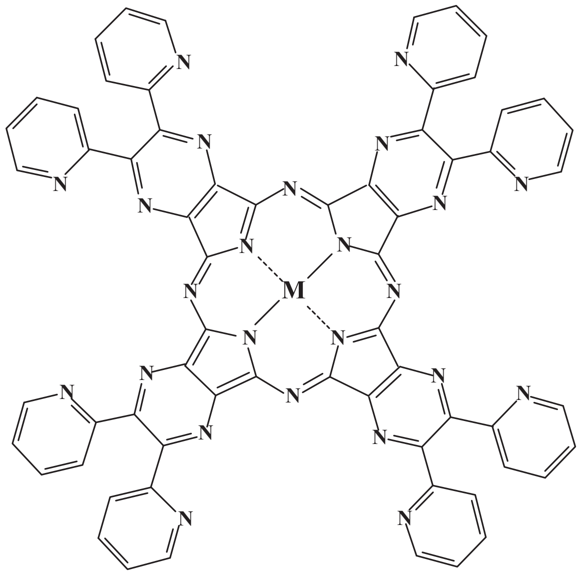
2.2. Materials

All solvents used in this work were C. Erba RPE reagents. Chloroform and dichloromethane were purified on neutral Al_2O_3 just before use. Pyridine (Py) was distilled over BaO before use. Tetrahydrofuran (THF) was refluxed over potassium. All other solvents were used as purchased. 4-Nitrophenol (4-NP) was purified by crystallization from water.

Titanium dioxides of different crystal structures, namely anatase, rutile and a mixture of them (Degussa P25), were used. Anatase and rutile were a generous gift from TIOXIDE Huntsman. Their crystalline structure was confirmed by X-ray diffraction data. Reflections were found in very good agreement with those reported in the literature [19]. Their half-height width was very narrow indicating a high degree of crystallinity. The textural analysis, based on the nitrogen physisorption at 77 K, of TiO_2 Huntsman materials shows they are nonporous solids. BET surface area, was $8.9 \pm 0.3\,m^2\,g^{-1}$ (anatase) and $7.1 \pm 0.2\,m^2\,g^{-1}$ (rutile), with a calculated average particles diameter of ca. 170 nm and 200 nm, respectively (assuming a true density of $4.0\,g\,cm^{-3}$). The diffuse reflectance (DR) spectrum showed an absorption band below 370 nm (anatase) and 400 nm (rutile), in agreement with the expected valence band (VB)-conduction band (CB) energy gaps (ca. 3.3 and 3.1 eV, respectively). X-ray data show that our Degussa P25 is a 85:15 anatase:rutile mixture (quantitative XRD analysis according to Ref. [20]). It is a mesoporous solid (total pore volume $0.19\,cm^3\,g^{-1}$) with a BET surface area of $59 \pm 2\,m^2\,g^{-1}$, with a calculated average particles diameter of ca. 25 nm. Light absorption was below 340 nm, corresponding to an EG of 3.7 eV.

2.3. Preparation of the macrocyclic compounds

The [$Py_8TPyzPzM$] compounds ($M = 2H^I$, Cu^{II}) were synthesized according to procedures already reported. The free-base [$Py_8TPyzPzH_2$] was obtained by auto cyclotetramerization of 2,3-dicyano-5,6-di-(2-pyridyl)-1,4-pyrazine [12]. The Cu(II) complex was obtained by treating a free-base pyridine solution with an excess of copper(II) acetate [13]. The general molecular structure of the porphyrazine compounds is shown in Scheme 1. The two species are poorly soluble in $CHCl_3$ and CH_2Cl_2, moderately soluble in dimethyl sulfoxide and dimethyl formamide, and completely insoluble in water. The UV–visible solution spectrum in $CHCl_3$ of [$Py_8TPyzPzH_2$] shows the expected strong absorptions, assigned as π–π^* transitions, in the Soret and Q-band region (Fig. 1A). The splitting of the Q band (peaks at 635 and 668 nm) observed for the free-base is due to the lower symmetry (D_{2h}) of the macrocycle. Fig. 1B reports the spectrum of the [$Py_8TPyzPzCu$] which shows similar positions of the Soret and Q bands, with the latter unsplit, as expected (D_{4h} symmetry).



Scheme 1.

2.4. Preparation and characterization of the photocatalysts

2.4.1. Via equilibrium adsorption

An amount (2 g) of TiO_2 was left in contact with 25 mL of a $CHCl_3$ saturated solution of the macrocycle ($C \approx 5 \times 10^{-6}$ M), at r.t., under magnetic stirring. After 1–2 h of contact, the solution appeared colorless, indicating that the macrocyclic compound was completely adsorbed on TiO_2. The solid was then separated by centrifugation, washed with water and dried. Few aliquots (80 mg each) of this solid material were used as such in photocatalytic experiments (see further) while the remaining part was subjected to a second adsorption treatment, in order to obtain a material of increased coverage, and then it was tested for photoactivity. This stepwise procedure was repeated until the equilibrium was reached between the solid and the saturated solution of the sensitizer.

2.4.2. Impregnation

The impregnation procedure for preparing the photocatalytic materials was similar to that described in Refs. [7–10]. An excess of macrocyclic complex was suspended in $CHCl_3$ (10 mL). The suspension was added of TiO_2 (1.0 g), and the mixture was kept under stirring at room temperature for 4 h. After removal of the solvent by evaporation (ca. 30 min, r.t.), the solid residue was kept under vacuum for 15 min, and then used for photo-activation experiments.

2.5. Illumination apparatus and procedure

The radiation source was a Helios Italquartz UV 13F Hg high pressure lamp, provided with a GR. E. 500 W power supplier. The

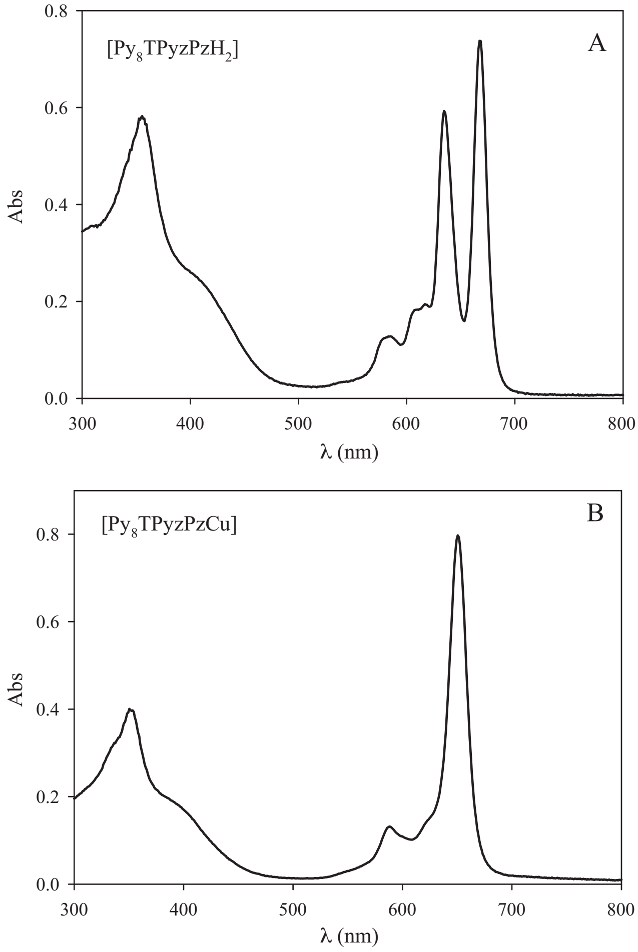


Fig. 1. (A) Spectrum of [$Py_8TPyzPzH_2$] in CH_2Cl_2 (3.7×10^{-6} M); and (B) spectrum of [$Py_8TPyzPzCu$] in $CHCl_3$ (3.6×10^{-6} M).

emission spectrum of the lamp is characterized by 7 main emissions between 300 and 400 nm. The 4-cm long (8 mm external diameter) cylindrical lamp was inside a quartz cylinder which, in turn, was immersed in a Pyrex walled cooling jacket where water was circulating from a thermostat (20 °C). This arrangement was also able to filter radiations below ca. 300 nm (if any).

The photocatalyst aqueous suspension was placed in a Pyrex reaction vessel (100 mL, unless otherwise indicated), again of cylindrical shape, where the lamp was completely immersed along the vertical axis. Dioxygen was continuously bubbled through an upper opening to maintain saturation of the gas, while magnetic stirring ensured homogeneity of the slurry. A second opening allowed to withdraw suspension aliquots at proper time intervals for analysis (see below). The amount of TiO_2 suspended in the phenol-containing solution was sufficient to ensure a nearly complete absorption of light in all cases. Nevertheless, the external walls of the reaction vessel were wrapped with an aluminum foil to reflect back any escaping radiation.

The emission power of the lamp was measured by means of a radiometer (ILT 1400-A). The sensing surface of the latter was leaned against the external wall of the cooling jacket at various heights along the vertical axis. Since the sensing surface area dimensions (ca. 0.5 cm × 0.5 cm) are negligible with respect to the total radiating surface, each reading was assumed to be equal to the ratio $\partial W/(\partial h \times \partial l)$ where ∂W is the power (mW) reaching the radiometer, h (cm) is the height with respect to the bottom of the lamp and $l = 2\pi r$ is the circumference of the cooling jacket of radius $r = 2.2$ cm. Integration over the entire circumference at a given height h, gives $w_h \times 2\pi r = \mathrm{d}W/\mathrm{d}h$, i.e. the power emitted per unit length of the vertical axis. Fig. 2 shows the plot of w_h as a function of h. Numerical calculation of the area below the curve yields a total emission of 7.0 W. Measurements repeated at different times showed a substantial stability of the emission, nevertheless, the photoactivity of the bare anatase, taken as the reference for evaluating the efficiency of the macrocycle-treated titania samples (see further), was always measured just before each set of runs.

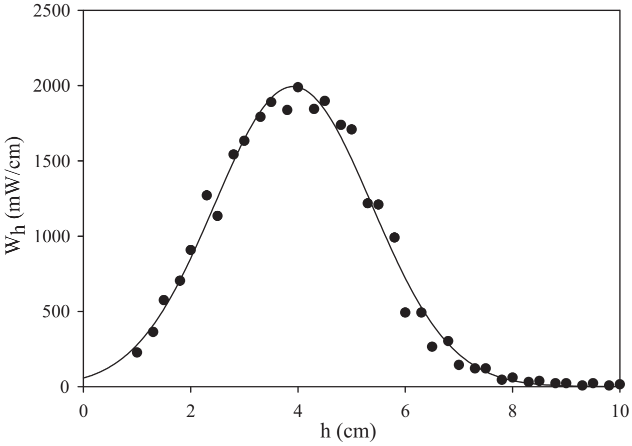


Fig. 2. UV lamp emission at various heights. Points are fitted to a Gaussian equation. The area below the curve amounts to 7.0 W and represents the overall power emitted.

2.6. Test reaction and procedure

For each experiment, 800 mg L^{-1} of the photoactive material (either bare or porphyrazine-coated TiO_2-anatase) were suspended into a water solution containing 20 mg L^{-1} (0.14 mM) of 4-NP, used as the photo-degradation target. The pH was adjusted to 3.8 ± 0.1 by addition of few drops of 0.6 M H_2SO_4, this pH corresponding to the maximum photoactivity of TiO_2 [21–23]. Few experiments were carried out in the presence of added H_2O_2 to test its effect on the degradation rate of 4-NP. The slurry was first placed in a separatory funnel connected to the reaction vessel. The volume of the suspension (90 ml) was chosen to be enough to ensure complete immersion of the UV lamp, once poured into the reaction vessel. Dioxygen was preliminarily bubbled through the suspension for at least 30 min. Five minutes before starting the irradiation, the lamp was switched on and left to reach a stable emission. The experiment was then initiated by quickly pouring the slurry from the funnel to the reaction vessel, previously filled with O_2. Oxygen bubbling was then continued throughout the experiment. At proper time intervals, 8–10 aliquots of the irradiated suspension (1.5 mL each) were withdrawn by means of a syringe. Each sample was immediately filtered over a nitrocellulose disk (0.25 μm, Millipore) and the UV–Vis spectrum of the clear solution recorded. The volume changes due to the withdrawals were considered negligible for the calculations reported below.

3. Results and discussion

3.1. Photoactivity tests

The efficiency of a photo-degradation catalyst is currently evaluated by measuring the rate of consumption of a target organic compound in a slurry containing a finely dispersed semiconductor, under constant illumination [7–10]. Phenols are commonly used as pollutant models, being themselves diffuse organic waste waters defilers. These compounds show intense UV absorption bands that can be used to monitor their consumption. Since the 4-NP photo-degradation was chosen only as a probe reaction, no analyses concerning possible intermediates and degree of mineralization were performed. It has been reported that, under constant photon flow and oxygen pressure, the decrease of concentration, c, of the target compound generally follows a first-order law, i.e.:

$$\frac{dc}{dt} = -k_{obs}c \tag{1}$$

with the observed rate constant, k_{obs}, dependent upon the reaction conditions, such as temperature, moles of photons absorbed per unit time, I_a, initial concentration of phenol, c_0, and the semiconductor (chemical and physical nature) [3,24–28]. On empiric grounds, for a given material, the observed rate constant is described by Eq. (2) where V is the volume of the reacting slurry,

$$k_{obs} = k\frac{I_a^{\gamma}}{V}\left(\frac{K_{O_2}P_{O_2}}{1+K_{O_2}P_{O_2}}\right)\frac{K_{ph}}{(1+K_{ph}c_0)} \tag{2}$$

K_{O_2} and K_{Ph} are equilibrium constants, k is a factor depending on I_a, and γ is an exponent that is equal to 1 or 0.5 according to the irradiation intensity (low or high intensity, respectively) [1,22,25,27,29,30]. Eq. (2) has been rationalized in terms of e^- and h^+ photoproduction inside the semiconductor particles, that eventually may react with O_2 and OH^-, to give $O_2^{-\bullet}$ and $OH^\bullet$, respectively, in a steady state condition where the (constant) number of e^-/h^+ couples generated per unit time equals the number of events leading to their destruction within the same time interval. The derivation of Eq. (2) from a postulated reaction scheme is reported by several authors with some minor differences due to slight differences in the details of the mechanism proposed [24–28]. However, it can be confidently said that the $K_{O_2}P_{O_2}/(1+K_{O_2}P_{O_2})$ term represents the extent of coverage of the O_2-specific adsorption sites on TiO_2 particles [30], according to a Langmuir-type equilibrium, while the $K_{Ph}/(1+K_{Ph}c_0)$ factor originates from an analogous non competing equilibrium involving surface adsorbed phenol molecules. The reader is referred to the cited literature for a detailed theoretical derivation of Eq. (2).

Fig. 3A reports the results of a typical experiment (bare anatase) in terms of decreasing concentration of 4-NP under constant UV illumination. The spectral sequence, that shows approximate isosbestic points only for the first 50% of the reaction, suggests the formation of light-absorbing intermediates that are eventually photo-oxidized in turn. However, the $-\ln A_{318}$ vs. time plot (A_{318} is the absorbance at 318 nm) is fairly linear up to at least 85% of the total change (Fig. 3A, inset), suggesting that the 318 nm absorbance is due essentially to the 4-NP alone. Under such hypothesis, the 4-NP concentration at any time may be set equal to the ratio $A_{318}/\varepsilon_{318}$, where $\varepsilon_{318} = 9.78 \times 10^3\ mol^{-1}\ L\ cm^{-1}$ is the molar 318-nm extinction coefficient of the nitrophenol, allowing, thus, the calculation of the c/c_0 vs. time profile as in Fig. 3B.

The absence of a significant interference by light-absorbing intermediates on k_{obs} has been confirmed by comparing the $t = 0$ slopes of the c/c_0 vs. t plots (dashed line in Fig. 3B) with the rate constant obtained by either the linear $-\ln A_{318}$ vs. t plot (Fig. 3A, inset) or the single exponential fit of the c/c_0 vs. time plot (Fig. 3B, full line). In all experiments the initial rate $(dc/dt)_0/c_0$ (that cannot be influenced by intermediates) was identical to k_{obs} within the experimental error (±5%).

Runs carried out with 4-NP initial concentrations ranging from 6×10^{-2} to 0.1 mM showed the inverse dependence of k_{obs} on c_0 expected according to Eq. (2). The experiments designed to measure the effect of the macrocyclic compounds were carried out with $c_0 = 0.137 \pm 0.002$ mM. As reported in the literature [27], under the same conditions, bare rutile was found definitely less efficient than both anatase and Degussa P25, the observed rate constants being in the ratio 1:10:13, in this order. Furthermore, loading with [$Py_8TPyzPzCu$] (0.050 μmol m^{-2}) did not improve the efficiency of rutile to any significant extent. On the basis of these results, rutile was not further investigated.

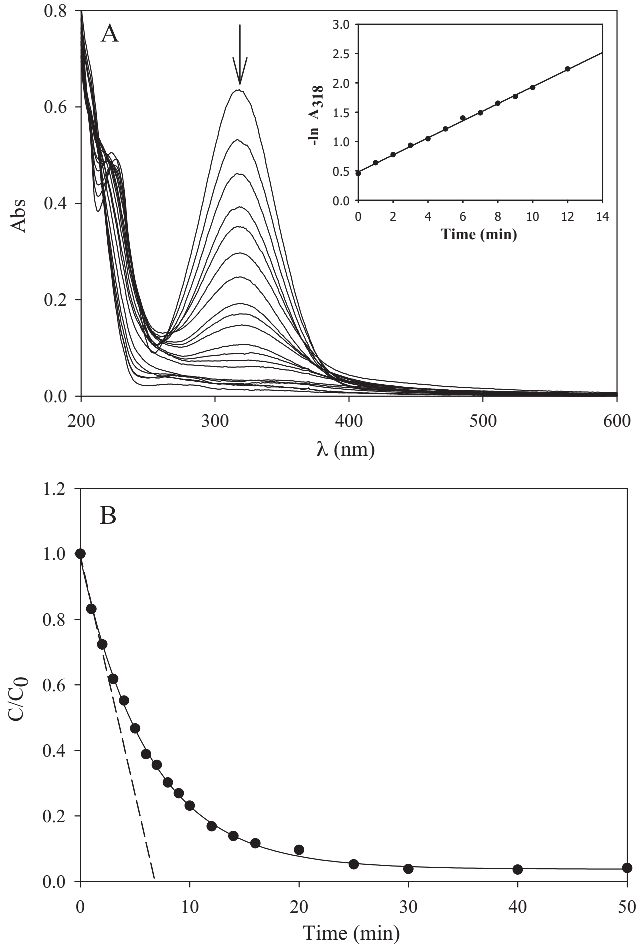


Fig. 3. (A) Spectral evolution of 4-NP under UV photo-irradiation. Inset: first-order logarithmic plot. (B) First order exponential decay (solid line) and initial rate (dashed line).

On the contrary, anatase showed a marked improvement of its photoactivity when loaded with both the free base and the corresponding copper complex. Fig. 4 shows the increase of the observed rate constant, as measured by the ratio $k_{rel} = k_{obs}/k^\circ_{obs}$ (k°_{obs} is the rate constant of bare anatase) for a series of [$Py_8TPyzPzH_2$]- and [$Py_8TPyzPzCu$]-loaded samples as a function of the amount of sensitizer deposited (filled symbols refer to samples obtained by equilibrium adsorption while empty symbols refer to samples prepared by impregnation). In both cases the relative rate constant k_{rel} increases linearly by increasing the amount of macrocycle loaded on TiO_2, eventually reaching a maximum value that is not modified by a further increase of the sensitizer/TiO_2 ratio. The coverage at the maximum rate, as well as the maximum enhancing effect, are quite different for the two sensitizers (ca. 0.14 μmol m^{-2} and $k_{rel} = 2.3$ for [$Py_8TPyzPzH_2$] and ca. 0.025 μmol m^{-2} and $k_{rel} = 3.5$ for [$Py_8TPyzPzCu$]).

The trends shown in Fig. 4 indicate, in both cases, that the use of an excess macrocycle, as occurring with the impregnated samples, does not increase the photoactivity over the maximum value reached with samples equilibrated with the saturated solution. This suggests, quite reasonably, that the impregnation procedure leads to the same surface coverage as reached when anatase is in equilibrium with the saturated solution of the dyes, while the excess separates as inactive self-aggregates. This is not surprising since,

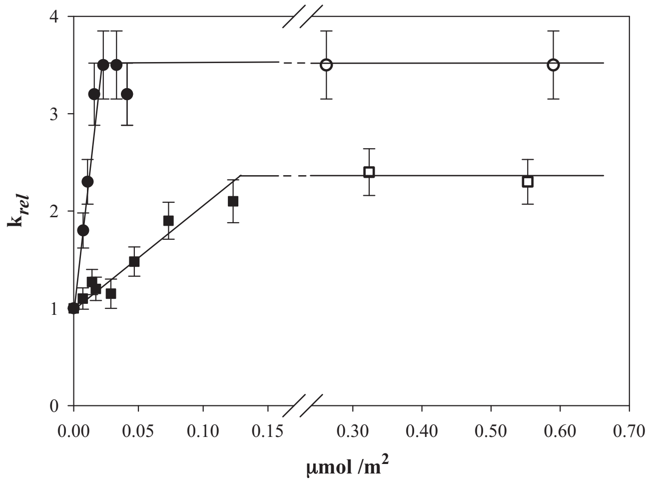


Fig. 4. Increase of photocatalytic efficiency of free base-loaded (squares) and copper complex-loaded (circles) anatase. Empty symbols refer to impregnated samples. Error bars are ±10%.

provided that the biphasic equilibration of the dye is sufficiently fast, the samples prepared by impregnation should be, in fact, in equilibrium with the saturated solution of the sensitizer used. Although, as yet, there is no sufficient information to speculate on the geometrical aspects of the sensitizer–TiO_2 interaction, a stacked arrangement of the Py_8PyzPz porphyrazine moiety molecular plane (ca 1.8 nm × 1.8 nm [31]) parallel to the semiconductor surface would suggest a monolayer of [$Py_8TPyzPzH_2$] molecules covering about 30% of the entire surface of the TiO_2 particles, at the maximum rate, while, for [$Py_8TPyzPzCu$] only 5% of it would be covered, again, at the maximum rate. This conclusion seems to be supported at least by the DR spectra of the copper-containing photocatalytic materials. Fig. 5A shows the Kubelka-Munk spectrum of a typical sample prepared *via* equilibrium adsorption, using [$Py_8TPyzPzCu$] as sensitizer. The comparison with the solution spectrum (Fig. 1) and the narrow shape of the Q band, suggest a substantial absence of aggregation. Upon increasing the loading, the reflectance spectrum begins to show some traces of aggregation, most evident with the samples prepared by impregnation.

For the free base-loaded materials, the interpretation of reflectance spectra is less straightforward since the spectra (Fig. 5B) are much less featured with only broad and low-intensity bands. They, however, seem to suggest a higher degree of aggregation.

As mentioned above, Degussa P25 is about 30% more active than pure anatase. Quite surprisingly, however, porphyrazinato-Cu(II)-adsorbed samples did not show any beneficial effect by the presence of the dye. It should be remembered that the average particle diameter of Degussa P25 and anatase Huntsman are very different (25 and 170 nm, respectively). On approaching an anatase particle, the macrocycle interacts with a nearly flat surface, while it experiences a much more marked curvature with Degussa P25. This curvature could result in a decrease of the electronic coupling between TiO_2 and the sensitizer and hence in a decrease of the synergism.

Table 1 lists the relevant data concerning microcrystalline anatase photocatalysts, sensitized by adsorption of tetrapyrrolic macrocycles, under UV irradiation and in the presence of oxygen. Surface area (ca. 8 $m^2\,g^{-1}$), reaction pH (ca. 4), temperature (near r.t.), irradiation range (300–400 nm), irradiation intensity and target molecule (4-NP) are the same or closely similar for all catalysts. Nevertheless, the kinetic data reported are given as the ratio $k_{rel} = k_{obs}/k^{\circ}_{obs}$ as defined above. This is because, while the absolute rate constant is influenced by the experimental conditions (that may be different for different research groups), k_{rel} should be,

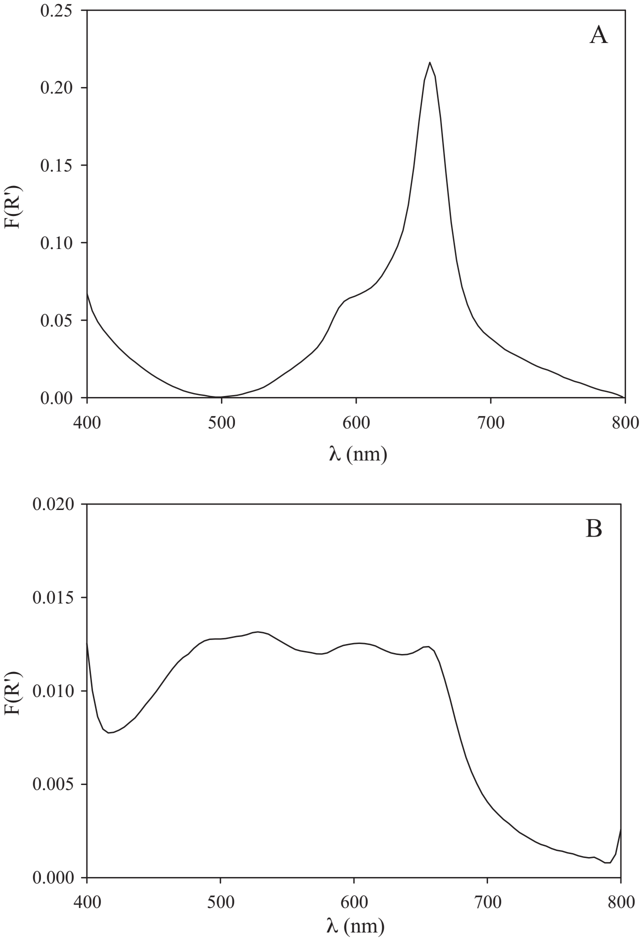


Fig. 5. DR spectra of (A) a 0.033 μmol m^{-2} [$Py_8TPyzPzCu$]-loaded; and (B) a 0.029 μmol m^{-2} [$Py_8TPyzPzH_2$]-loaded catalysts.

Table 1
Relative rate constants, k_{rel}, for some anatase-based photocatalysts containing porphyrin-like sensitizers.[a]

Sensitizer[b]	Coverage (μmol m^{-2})	k_{rel}	Ref.
H2Pc(1)	0.83	1.0	[8]
H2Pp(1)	0.83	1.3	[8]
H2Pp(2)	0.83	1.4	[9]
H2Pz	0.14	2.3	This work
CuPc	2.2	1.3	[7]
CuPc(1)	0.83	1.9	[7]
CuPp(1)[c]	0.69	1.1	[32]
CuPp(2)	0.83	2.1	[9]
CuPp(2)	0.69	2.1	[9]
CuPz	0.025	3.5	This work
$CePc_2$	0.69	1.0	[32]
$PrPc_2$	0.69	0.73	[32]
$NdPc_2$	0.23	1.1	[32]
$SmPc_2$	0.17	1.1	[32]
$GdPc_2$	0.41	1.0	[32]
$HoPc_2$	0.23	1.2	[32]

[a] When more than one composition was reported in the literature for the same catalyst, the k_{rel} listed in the table refers to the best performing sample.

[b] *Abbreviations*: Pc = unsubstituted phthalocyaninato dianion. Pc(1) = tetrakis[4-(2,4-bis-(1,1-dimethylpropyl)phenoxy)]phthalocyaninato dianion. Pp(1) = [5,10,15,20-tetra(4-*t*-butylphenyl)]porphyrinato dianion. Pp(2) = [5,10,15,20-tetra(4-(2-(3-*n*-pentadecyl-phenoxy)ethoxy]porphyrinato dianion. Pz = tetrakis-2,3-[5,6-di-(2-pyridyl)-pyrazino]porphyrazine dianion.

[c] The same research group reported, for this material, earlier reactivity data that lead to a k_{rel} value as high as 2.6, under the same reaction conditions. We repeated the experiments and actually fail to show any significant enhancing effect of CuPp(1) compared to bare anatase, confirming thus the results reported later by the same authors in Ref. [32] and quoted here.

instead, largely insensitive to them and represents, in our opinion, a better measure of the net enhancing effect.

Inspection of the table indicates that loading with porphyrin-like sensitizer has, in general, a beneficial effect. Copper(II) complexes are systematically more efficient than the corresponding unmetalated molecules. Our data are in agreement with this rule and, remarkably, both copper-containing and metal-free pyrazinoporphyrazine derivatives are by no means the best performing in each series.

Only three different macrocycles types are represented in Table 1. Indeed, this is a too limited structure range to allow any general conclusion, nevertheless, it seems clear that the photoreactivity tends to increase along the sequence phthalocyanine < porphyrin < pyrazinoporphyrazine, in both the unmetalated and copper(II) series. Also, the presence of two phthalocyanine rings sandwiching the metal ion, as in the lanthanide complexes [32], does not modify the efficiency of the photocatalyst, that remains close to the efficiency of bare anatase.

As noticed above, the pyrazinoporphyrazine ring displays the most remarkable enhancing effect in both series. This is even more so if it is realized that the amount of sensitizer per square meter required to display the maximum efficiency is, in both cases, markedly lower than for the other sensitizers in the table.

A cooperative effect has been proposed to explain the enhancement of photodegradation power shown by dye-loaded titania slurries, where, in addition to the photogeneration of e^-/h^+ couples, a direct excitation of the sensitizer also takes place. This contributes to the overall process by increasing the number of CB electrons and by generating oxidated sensitizer species acting, in turn, as powerful oxidating agents. This matter has been deeply discussed and a full set of reactions has been proposed, starting from the initial excitation steps down to the final oxidation of the target compound [8].

Additional pathways may be envisaged and are sometimes proposed to explain the positive effect of some sensitizer-doped catalysts, such as the production of singlet oxygen and a possible involvement of photoproduced H_2O_2 in the degradation of 4-NP.

A significant contribution to the phenol depletion *via* singlet oxygen may be excluded on the basis of the following considerations. First, Cu(II) complexes are paramagnetic and their excited triplet state is highly unstable towards radiative and non-radiative deactivation, leading to a very low $^1O_2$ quantum yield, ϕ_Δ. This has been directly proven in our laboratory where ϕ_Δ for [$Py_8TPyzPzCu$] in dimethyl formamide solution was found to be virtually null. Also, for the unmetallated compound [$Py_8TPyzPzH_2$], ϕ_Δ is as low as 0.11 [33]. Furthermore, we found that an MCM-41-SiO_2 phase [total surface area 972 $m^2 g^{-1}$; external surface area 34 $m^2 g^{-1}$; total pores volume 0.65 $mL g^{-1}$; mesopores volume 0.58 $mL g^{-1}$; pore diameter 2.6 nm], prepared according to Ref. [34], coated with either one of our macrocyclic compounds (about 5 $\mu mol\, g^{-1}$) was equally inactive as the bare MCM-41-SiO_2 phase, under UV irradiation. In the light of these considerations, the side production of singlet oxygen seems to be of no relevance in our cases.

Any role of the photo generated H_2O_2 in increasing the rate of 4-NP oxidation, also seems to be excluded. In blank experiments, hydrogen peroxide (0.070 mM) was added to the sensitizer-adsorbed anatase (Huntsman) in the presence of 0.14 mM 4-NP. The coverage was 0.14 $\mu mol\, m^{-2}$ for the free base and 0.025 $\mu mol\, m^{-2}$ for the Cu complex, corresponding to the maximum activity of both catalysts. *In the absence of light*, both systems failed to show any depletion of 4-NP. This excludes any detectable catalytic decomposition of H_2O_2 by the adsorbed macrocycles as well as any direct reaction with the target phenol. On the other hand, UV irradiation (300–400 nm) of an aqueous solution containing only 0.070 mM H_2O_2 and 0.14 mM 4-NP (pH 4.0) did not show, again, any phenol degradation. This was not surprising since the radiation absorption by H_2O_2 above 300 nm is very low and, consequently, any light induced fission of the molecule with the formation of the highly reactive $OH^\bullet$ radicals is expected to be negligible. Finally, we duplicated our ordinary photocatalytic experiments with the porphyrazine-coated composites, with and without added hydrogen peroxide (0.070 mM). A small but definite decrease of k_{obs} was measured with both the free base and the copper complex, as it might be expected if H_2O_2 would, rather, compete with 4-NP as an electron donor towards the photoinduced holes and/or $OH^\bullet$ radicals [3].

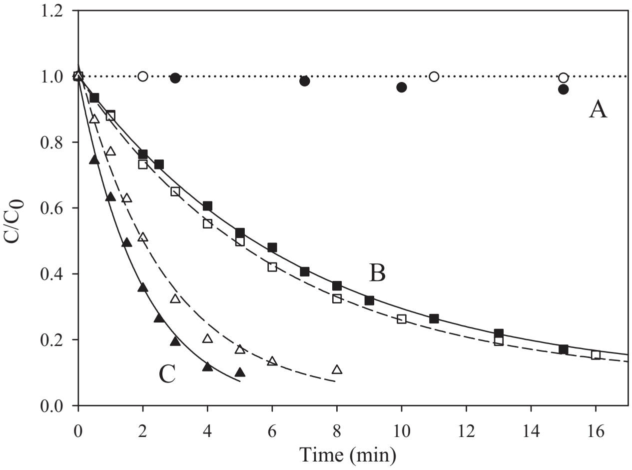


Fig. 6. 4-Nitrophenol depletion rate under various conditions, with (empty symbols) and without (filled symbols) added H_2O_2, and under UV illumination. (A) An homogeneous solution containing only 4-NP and H_2O_2; (B) an heterogeneous 4-NP/bare anatase mixture; (C) same as in B but using the Cu-containing catalyst. Other conditions are given in the text. Curves in B and C are first-order exponential fits.

All the above observations are shown in Fig. 6, with specific reference to the copper-containing composite.

It can be finally noted that the presence of a metal ion such as Cu(II) in the macrocycle offers an additional way to increase the efficiency of the photocatalyst by trapping the CB electrons as Cu(I) centers, thus reducing the rate of the $e^- + h^+$ recombination process. This is believed to be the reason why Cu(II) macrocycles are systematically more effective, like in the present case [10].

3.2. Photo stability tests

The DR spectra of the catalytic material collected at different times during the runs showed the occurrence of some photodecomposition. In order to estimate the extent of such decomposition, experiments were carried out with the most efficient Cu(II) complex where the catalytic material was subjected to several consecutive photo-degradation runs. In such cases a larger volume (ca. 240 ml) was used for the first run that lasted 10 min. At the end, the residual suspension was centrifuged and the doped TiO_2 recovered, washed with water and gently dried. A second reacting suspension, having the same composition (but, obviously, a lower volume) was prepared with the recovered catalyst, and exposed to light for a second run. This procedure was repeated until the volume of the suspension was not lower than 90 ml. The first-order rate constants were reciprocally normalized by multiplying by the ratio $V/90$ (V = volume of the reaction suspension) to account for the change of volume, according to Eq. (2). The results indicate a 10–15% decrease of activity after each run, with the rate constant approaching the value expected for bare anatase.

4. Conclusions

Improved catalysts can be prepared by loading TiO_2 (anatase) with new porphyrazine macrocycles. Under comparable experimental conditions, our tetrakis-2,3-[5,6-di-(2-pyridyl)-pyrazino]porphyrazine compounds enhance the rate of photodegradation of 4-NP by titania slurries up to 2.3 (free base) and 3.5 (Cu complex) times, almost twice as much as the most efficient catalysts previously reported for the analogous phthalocyanine and porphyrin series. Remarkably, this result is obtained with a considerably lower macrocycle/titania ratio. Formation of singlet oxygen is not responsible for the observed effect that is best explained in terms of injection of electrons in the conduction band of TiO_2 from the excited macrocycle and the accompanying formation of its cation radical. Some photodegradation of the dyes has been observed.

Bare rutile is much less efficient than pure anatase and Degussa P25, the latter being 30% more active than anatase. Both rutile and Degussa P25, however, did not show any beneficial effect by the adsorption of [Py_8TPyzPzCu]. For Degussa P25, a tentative explanation based on the smaller particle size of the semiconductor is here given.

Future efforts will be directed to the study of the effect of the central metal ion and to modulate the electronic properties of the macrocyclic ligand by introducing appropriate structure modifications. A key problem to be solved, before these photocatalysts may become of practical interest, concerns their photo-stability. Hence, attention will be paid also to the search for more resistant macrocyclic structures.

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