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Reversible Oxygen Addition on a Triplet Sensitizer Molecule: Protection from Excited States Depopulation

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We demonstrate that photoactivated oxygen addition to diphenylanthracene moieties can be used as a tool for protection of porphyrin's phosphorescence against oxygen quenching. Phosphorescent palladium(II) tetrabenzoporphyrin, covalently linked to four diphenylanthracene moieties was synthesized and studied. Upon irradiation with ambient light or 638 nm laser in solution under air, an addition of oxygen and formation of corresponding endoperoxides was observed. Heating of the irradiated samples afforded the parent porphyrin material.

Introduction

Organic chromophores able to form triplet excited states upon absorption of light (triplet sensitizers) are used in various fields, e.g. electroluminescence,¹ bioimaging and molecular sensing,² photocatalytic organic reactions,³ and triplet–triplet annihilation photon upconversion (TTA-UC).⁴ Organic electronic materials based on triplet sensitizers promise to make revolutionary transformations in solar energy conversion technologies by improving the light-harvesting of amorphous silicon solar cells⁵ and extending the infrared limit of oxygenic photosynthesis.⁶ However, compared to fluorophores, applications of triplet sensitizers are much less developed considering a substantially higher sensitivity of triplet states towards non-emissive deactivation processes. The most common process which leads to the loss of triplet excited states population is related to the presence of molecular oxygen in corresponding samples. It involves triplet energy transfer between an excited chromophore and oxygen, giving singlet oxygen and ground state of the chromophore.⁷

An efficient protection against oxygen quenching is essential for applications which include triplet excited state formation. Two general approaches for the protection are known: 1) a passive protection, based on decreasing oxygen permeability e.g. by means of encapsulation in polymer films⁸ or nano-⁹ and microcarriers,¹⁰ incorporation into

supramolecular complexes¹¹ or dendrimers¹² and 2) active protection – applying oxygen scavenging species.¹³

The problem of triplet excited states quenching is exceptionally important in the case of TTA-UC process. Both sensitizer and emitter ensembles can transfer triplet energy to the molecular oxygen and be depopulated, leading to the aging of samples and loss of quantum efficiency. Straightforward embedding of UC-active substances into inert polymer films with high oxygen barrier properties leads to substantial decrease of the TTA-UC efficiency, because in solid state environments the local mobility of the chromophores involved significantly decreases.¹⁴ Until recently the direct incorporation of dyes in polymers was not enough to provide the imperative requirements for effective and sustainable annihilation upconversion, that is, high local mobility and exhaustive oxygen protection of the UC-chromophores. Recently we succeeded to develop organic polyphosphate oxygen protection matrixes¹⁵ and cellulose bioinspired oxygen protection films.¹⁶ However, these approaches either require a change of sample's architecture or affect photophysical and chemical properties of a triplet sensitizer.

Herein we report a new strategy for protection of triplet excited states depopulation by quenching, relying on chemical modification of triplet sensitizer molecule. It is based on binding molecular oxygen, present in a sample, to specially designed structural subunits which do not affect photophysical

properties and allow triplet sensitizer to act in undisturbed manner further. This protection strategy is of sacrificial character, and is time-limited depending on integral photon flux, applied to the sample. However, starting triplet sensitizer material can be fully regenerated afterwards through oxygen release upon moderate heating. Further, protective groups do not bind oxygen in its ground (triplet) state and the corresponding material is stable towards photooxidation in the course of synthetic procedures and purification. The protection is active only against singlet oxygen, thus only when sensitizer triplet states are formed. Therefore, the presence of an additional stimulus, i.e. optical excitation of the sensitizer, triggers the protection process.

In our recent work on the synthesis of tetraanthraporphyrins¹⁷ we observed a photoactivated addition of up to four oxygen molecules per porphyrin molecule, leading to the formation of corresponding endoperoxides. We proposed that such an addition can serve as a tool for preventing oxygen from quenching of porphyrin phosphorescence. However, in the case of tetraanthraporphyrins, the addition of oxygen leads to a drastic change of optical properties, particularly to a blue-shift of absorption and emission bands by 200 nm due to a partial loss of conjugation in the π -system. Here we suggested to introduce anthracene subunits into *meso*-positions of the porphyrin in order to avoid alternation of the optical properties.

The concept is illustrated in Figure 1 on an example Pd-porphyrin bearing four anthracene subunits in *meso*-positions of the macrocycle. Pd-porphyrins are known to possess high intersystem crossing coefficient¹⁸ values and are widely used as triplet sensitizers.¹⁹ Alternatively, anthracenes are capable of reversible binding of singlet oxygen species.²⁰ Upon selective excitation of the porphyrin chromophore, triplet excited state is formed (step 1). In the presence of molecular oxygen a quenching process is taking place, leading to the ground state of the sensitizer and singlet oxygen (step 2). A key point is step 3 where binding of the singlet oxygen to the attached hydrocarbon via Diels-Alder-type process takes place.²¹ We proposed that complete binding to all of four hydrocarbon subunits can be achieved (shown as step 4 in Scheme 1) and the corresponding $(O_2)_4$ adduct can be obtained, otherwise adducts with variable number of bound oxygens are produced. Consumption of oxygen results in partial or complete termination of quenching process that provides emissive relaxation of newly formed triplet states of Pd-porphyrin core. Due to the reversibility of the oxygen addition to anthracenes, the starting material can further be regenerated by means of heating (step 5).

Although many polyaromatic hydrocarbons, e.g. naphthalenes²², 2-pyridone²³ or rubrenes²⁴ are known to bind oxygen in a reversible manner, anthracenes are most suitable to be used for oxygen protection of the phosphorescence. First, the absorption bands of corresponding anthracenes do not intersect with porphyrin absorption that allows monitoring of the protection by absorption spectroscopy. Second, anthracene endoperoxides decompose only upon heating above 100 °C whereas naphthalene and 2-pyridone endoperoxides release

oxygen even at room temperature. Finally, anthracene provides a scaffold that allows straightforward generation of suitable substitution patterns.

The introduction of such type of triplet sensitizer into the arsenal of materials used in relevant areas of research would open new opportunities for the control of corresponding photophysical processes. Particularly, it provides an alternative way to oxygen protection of phosphorescent samples or to develop new molecular “singlet oxygen reservoirs” for oxygen storage and thermal release. In this paper we report a synthesis and properties of phosphorescent palladium(II) porphyrin, bearing substituted anthracenes in *meso*-positions, which is capable of photoactivated oxygen addition. Anthracene groups preserve porphyrin phosphorescent properties even in oxygen rich environment. Furthermore, thermal-mediated reversibility of the oxygen binding was demonstrated.

Results and discussion

Synthesis

Our attempts towards the synthesis of target molecule were firstly focused on β -unsubstituted porphyrin with anthracene groups directly attached into *meso*-positions.

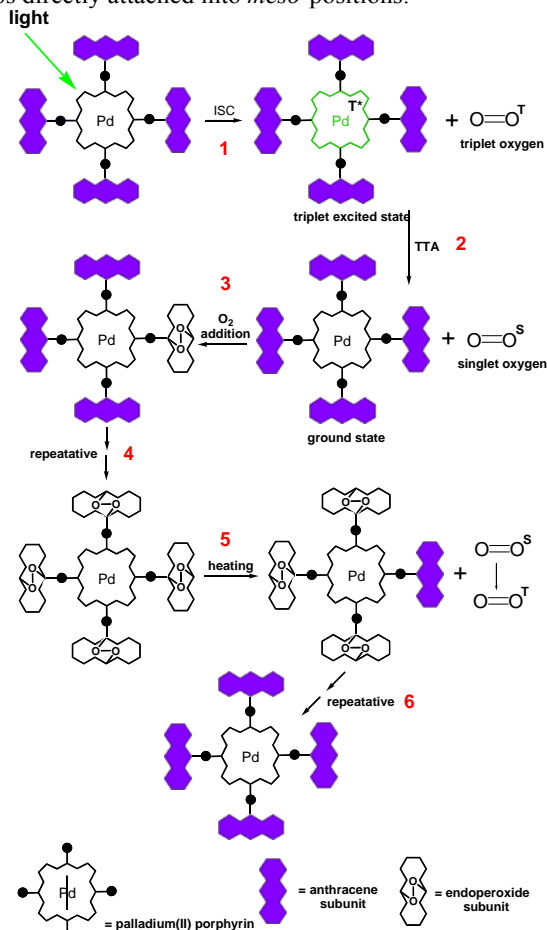
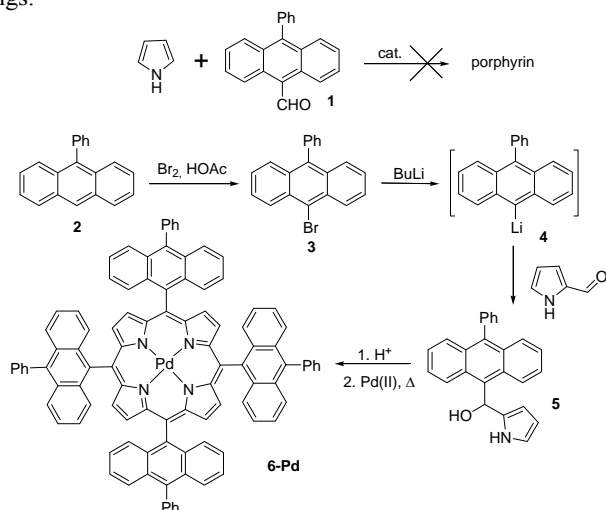


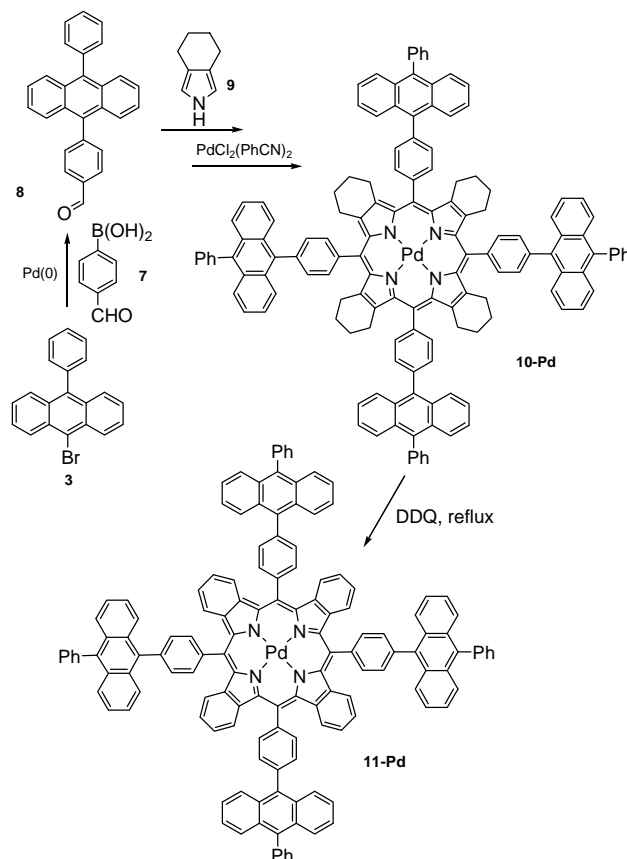
Figure 1. General scheme of oxygen addition to triplet sensitizer and further thermal release.

According to literature data, the conventional method of porphyrin chemistry – Lewis acid catalyzed condensation of pyrrole with corresponding 10-phenyl-anthracene-9-carbaldehyde **1**, results in very low preparative yields.²⁵ An alternative method based on pyrrole-carbinol tetramerization is being commonly applied for such type of substrates.²⁶ Following this approach, starting 9-phenylantracene **2** was brominated with Br₂ to give 9-bromo-10-phenylantracene **3**. It was then subjected into the reaction with *n*-butyllithium to give corresponding organolithium compound **4** which was further introduced into the reaction with pyrrole-2-carbaldehyde (Scheme 1). The obtained pyrrole-carbinol **5** was used for acid-catalyzed tetramerization and delivered corresponding porphyrin **6** with reasonable yield (15%). Subsequent insertion of palladium was achieved by reflux in benzonitrile. Unfortunately the obtained product **6-Pd** was found to possess too low solubility for adequate characterization and study of oxygen addition.

Generally, for large conjugated aromatic systems, solubility is ensured by introduction of suitable side chains into aromatic moiety, e.g. alkyl and alkoxy-groups.²⁷ However, the introduction of electron-donating groups on anthracenes is known to have a pronounced effect on the rates of oxygen binding and decomposition of the endoperoxide. In some cases it results in the irreversibility of the oxygen addition.²⁰ Thus in order to optimize the sensitizer structure we decided to modify the porphyrin core instead of anthracene subunit. It was shown that β -substitution of the porphyrin macrocycle, especially along with introduction of *meso*-aryl substituents leads to a strong distortion of the macrocycle due to steric repulsion.²⁸ This in turn results in an improved solubility. Following this approach we decided to introduce two additional structural features: 1) phenylene bridge between porphyrin and anthracene subunits; 2) annelated cyclohexane rings at β -positions of porphyrin macrocycle. Such a modification also allows for shifting absorption and emission bands into red or far red region, the latter by means of aromatization of annelated rings.²⁹



Scheme 1. Synthesis of porphyrin **6-Pd**.



Scheme 2. Synthesis of porphyrins **10-Pd** and **11-Pd**.

9-Bromo-10-phenylantracene **3** was subjected into Suzuki-coupling with formylboronic acid giving corresponding aldehyde **8**. Its condensation with 4,5,6,7-tetrahydroindole **9** provided the corresponding porphyrin **10** (Scheme 2), which was then metallated with bis(benzonitrile)palladium(II) in boiling benzonitrile. Further aromatization of porphyrin **10-Pd** into the corresponding tetrabenzoporphyrin **11-Pd** was achieved by reflux with an excess of DDQ in toluene. Complete aromatization of all four annelated rings was achieved without significant by-products formation. Porphyrin **11-Pd** was found to be well-soluble in common solvent (chlorinated hydrocarbons, THF, toluene) and was unambiguously characterized by NMR and mass-spectroscopy (see Supporting Information).

Oxygen addition and release

As is shown in Figure 2, porphyrin **10-Pd** possesses characteristic absorption in the region of 300-400 nm, which correspond to the anthracene subunits. When a solution of **10-Pd** was kept under daylight for several days or irradiated with the green line of the HeNe laser ($\lambda = 543$ nm, broad beam), disappearance of the anthracene absorption was observed (Figure 2, red line) giving instead a shapeless background absorption. On the other hand, spectral features corresponding to the porphyrin macrocycle – Soret (430 nm) and Q-bands (540 and 570 nm) stayed unchanged. Light irradiation of the

same solution prepared and sealed in a glove-box (<1 ppm oxygen) showed no change of absorption.

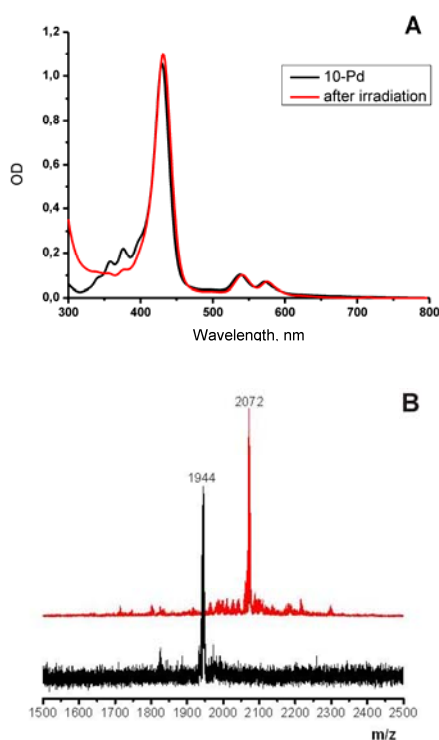
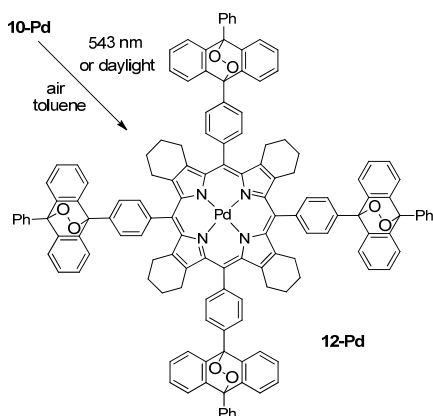


Figure 2. Absorption spectrum of **10-Pd** and its change after light irradiation of air-saturated toluene solution ($\lambda = 543$ nm, $3 \mu\text{Wcm}^{-2}$, 10 h) (A); corresponding mass spectra of **10-Pd** (B, black trace) and product of irradiation (B, red trace).

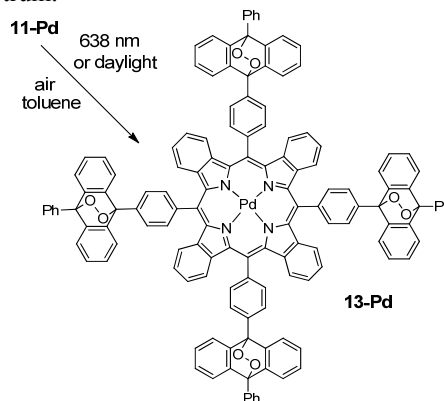
The mass spectrum of the irradiated solution showed a single peak with a mass of 2072 Da, corresponding to an adduct of **10-Pd** with four oxygen molecules (Scheme 4).



Scheme 3. Photosensitized oxygen addition to porphyrin **10-Pd**.

A similar process with compound **11-Pd** was monitored by UV-Vis spectroscopy. Its solution ($4 \cdot 10^{-5}$ M) was irradiated with the red line of HeNe laser ($\lambda = 638$ nm, broad beam) at intensity of only $3 \mu\text{Wcm}^{-2}$. The laser beam was set to cover the

whole cuvette. Complete disappearance of the anthracene absorption in the region of 300-400 nm was observed within 9 h (Figure 3). Mass spectra of the obtained samples showed a series of $(M^+ + n \times 32)$ peaks indicating the formation of intermediate products bearing 1, 2, 3 or 4 oxygen molecules attached. At $3 \mu\text{Wcm}^{-2}$ the addition reaction was complete in 9 h as is evidenced by the absence of spectral change and a sole peak of 2056 Da in mass spectrum corresponding to the adduct with four oxygen molecules (Scheme 5). Exposition of the solution for longer times of irradiation (up to 40 h) didn't result in the change of absorption spectra or origin of other peaks in mass spectrum.



Scheme 4. Photosensitized oxygen addition to porphyrin **11-Pd**.

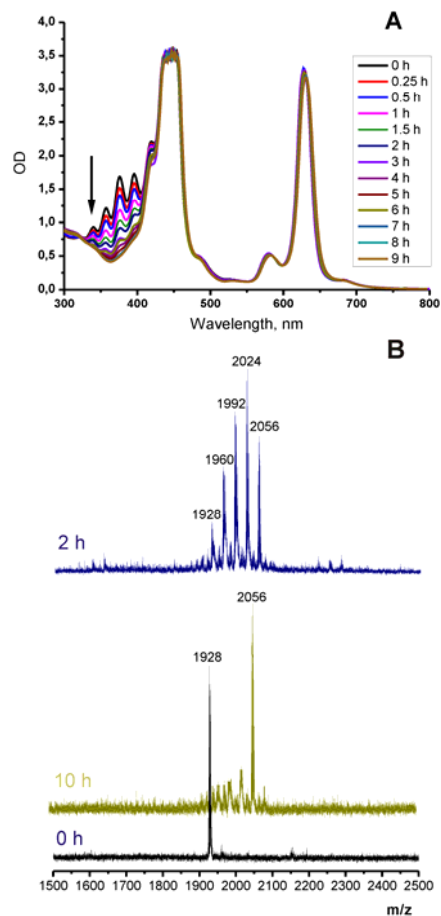


Figure 3. Change of absorption upon irradiation of $4 \cdot 10^{-5}$ M toluene solution of **11-Pd** with 633 nm laser ($3 \mu\text{Wcm}^{-2}$) (A); corresponding change in mass spectra (B): **11-Pd** (black trace), after 5h of irradiation (blue trace), after 10 h of irradiation (yellow trace). Note: saturation of porphyrin absorption is due to high concentration of the solution taken for the experiment, essential for monitoring a relatively weak anthracene absorption.

To further support the idea of support photosensitized oxygen addition on anthracene moieties in **11-Pd** we performed a similar experiment with a mixture of 9,10-diphenylanthracene and palladium tetraphenyltetrabenzoporphyrin in a molar ratio 4:1. In the same conditions (concentration, laser intensity) similar spectral transformation was observed by UV-Vis spectroscopy on a timescale of 6 h (see Supporting Information, Figure S14).

Release of bound oxygen molecules was achieved when solution of adduct **13-Pd** was concentrated to solid and then heated at 100-110 °C in vacuum (1 mbar) during 3-5 h. Complete recovery of anthracene absorption (with respect to **11-Pd**) were observed as well as perfect overlap with the original spectrum of **11-Pd**. Mass-spectrum showed parent 1928 Da peak. Thus a completely reversible oxygenation-deoxygenation process takes place for **11-Pd**.

It should be mentioned that the decomposition temperature (and time) of the adduct depends on the substitution pattern of the aromatic subunits. In our case the parameters of oxygen release match those previously described for 9,10-diphenylanthracene decomposition.²⁰ However, modification of the starting materials would allow varying decomposition parameters. Particularly, it can be made irreversible (by means of introducing one or two alkoxy-groups into parent anthracene derivative). Alternatively, the temperature of endoperoxide decomposition can be adjusted to 30-40 °C (by using naphthalene derivatives as oxygen traps, instead of anthracenes).

Optical properties. Protection of phosphorescence against oxygen quenching

Absorption and emission spectra of **11-Pd** are shown in Fig. 4. Its optical properties are very similar to those of tetraphenyltetrabenzoporphyrin-Pd (see Supporting Information). Sample of **11-Pd** prepared in glove-box (containing < 1 ppm oxygen) exhibits strong phosphorescence centered at 796 nm with quantum yield of 0.18 (with respect to Ph_4TBPPd in toluene (0.21)³⁰). No phosphorescence was observed for the sample opened to air. Triplet excited state lifetime was measured to be 217 μs that is close to parent Ph_4TBPPd (286 μs).³⁰ Thus no significant loss of emissivity was observed despite conjugation of the porphyrin π -system to four anthracene residues.

Due to very similar chemical properties, products of photosensitized oxygen addition to porphyrin **11-Pd** can not be isolated. In order to investigate their emission properties a series of **11-Pd** solutions was illuminated (633 nm, $3 \mu\text{Wcm}^{-2}$) during different time intervals (1-9 h). Obtained samples were

concentrated to solids, transferred into the glove-box (<1 ppm of oxygen) and dissolved in toluene to prepare a set of solutions of equal concentration for phosphorescence measurement. No significant difference in the phosphorescence intensity between starting **11-Pd** and irradiated samples was observed (Figure 5). Only moderate decrease of the emission intensity (approximately 25%) takes place upon addition of oxygen molecules to all four anthracenes. This is probably due to a decrease in phosphorescence quantum yield upon increasing molecule's complexity usually resulting in increase of non-radiative decay rates.

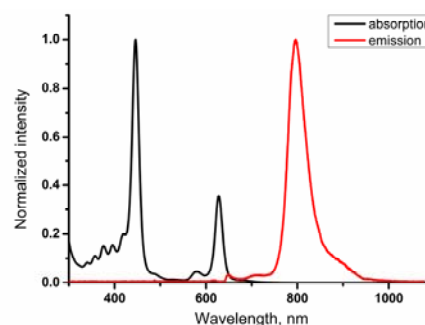


Figure 4. Absorption and phosphorescence spectra of **11-Pd** in toluene ($1 \cdot 10^{-5}$ M). Phosphorescence was excited at 633 nm.

The fact, that adducts with a different number of bound oxygen molecules possess similar emission properties enables to use the photo-activated oxygen addition to enhance the phosphorescence signal intensity of oxygen contaminated (e.g as a result of leaking) samples. Under the laser irradiation during a short time (minutes or less, depending on excitation intensity), oxygen molecules are being bound to the sensitizer, performing local and real-time “deoxygenation” of the sample. Due to decrease of the quencher concentration, the phosphorescence efficiency rises.

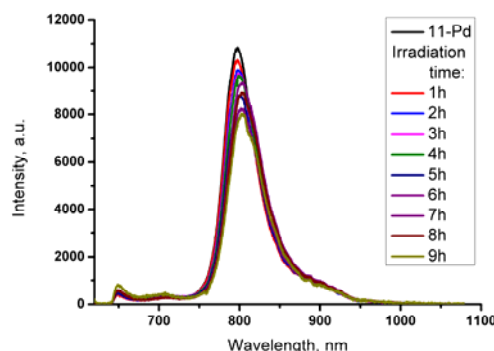


Figure 5. Phosphorescence spectra of **11-Pd** and mixtures of oxygen addition products obtained after different periods of irradiation. All phosphorescent spectra are registered for samples of the same concentration keeping constant excitation parameters (toluene, 633 nm, 1mWcm^{-2} , integration time of 50 ms).

To demonstrate such an effect, a solution of **11-Pd** was prepared and sealed in an atmosphere containing 100 ppm

of oxygen. Phosphorescence spectrum registered has shown a peak intensity of 2160 cps (Figure 6, black line). Then the cuvette was placed under a laser beam with $250 \mu\text{Wcm}^{-2}$ intensity for period of 10 min. The phosphorescence spectrum registered after irradiation has shown 100% increase of the peak intensity (Figure 6, red line). Obviously, the increase of the signal intensity is due to the binding of residual amounts of oxygen present in the sample.

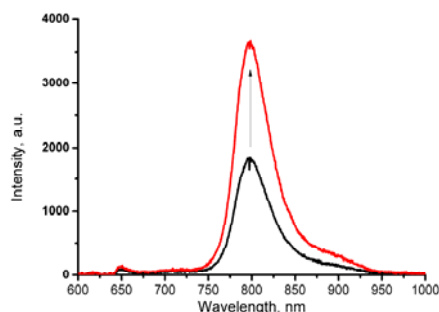


Figure 6. Increase of phosphorescence of a sample of **11-Pd** prepared in the atmosphere containing 100 ppm of oxygen (black line) after 10 minutes of continuous irradiation with red laser (toluene, $4 \cdot 10^{-5}$ M, 633 nm, $250 \mu\text{Wcm}^{-2}$) (red line).

Moreover, an enhancement of the phosphorescence originating from the porphyrin **11-Pd** can be achieved in a local area (spot diameter $d=400 \mu\text{m}$) of excitation without preliminary irradiation of the whole sample. In the course of the measurement, the same laser beam being used for the excitation of phosphorescence can simultaneously cause local deoxygenation. The results from the corresponding time-resolved experiment are demonstrated in Figure 7: an increase of the phosphorescence signal intensity from sample **11-Pd**, which rises more than 60% at continuous irradiation by laser beam with different intensity. As is seen from Figure 7 (green line) at moderate intensity of 1mWcm^{-2} and local excitation, the process of local oxygen scavenging needs only few seconds, if the excitation intensity is lower, the necessary time is substantially longer (Figure 7, the black line). The experimental atmosphere was contaminated by 100 ppm of oxygen.

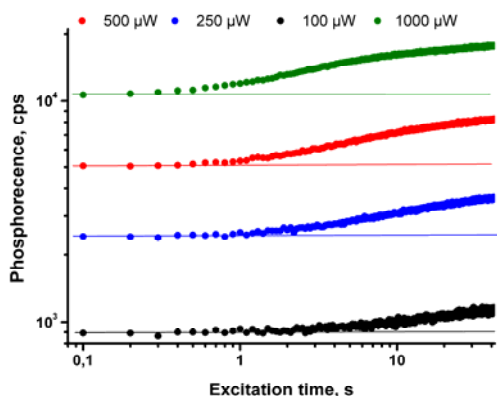


Figure 7. Change of phosphorescence intensity at 798 nm for the sample of **11-Pd** registered in oxygen contaminated atmosphere (

100 ppm), taken at noted periods of time during continuous irradiation by red laser (toluene, $4 \cdot 10^{-5}$ M, 633 nm, different excitation intensities).

Owing to the deoxygenation ability, such molecules as **11-Pd** can become promising “self-healing” sensitizers for the process of TTA-UC, which is known to crucially depend on the oxygen content. In order to confirm suitability of **11-Pd** as a sensitizer for TTA-UC, it was mixed with the perylene as an emitter in inert atmosphere (<1 ppm of oxygen) and then used for the generation of the upconversion fluorescence. Upon the red excitation at 638 nm, along with some residual phosphorescence of the sensitizer, a blue upconverted emission of the perylene in the region 430-550 nm with the reasonable quantum yield ($\sim 3\%$) was observed (Figure 8). Corresponding study devote the effect of oxygen on the upconversion efficiency of the system will be reported in due course.

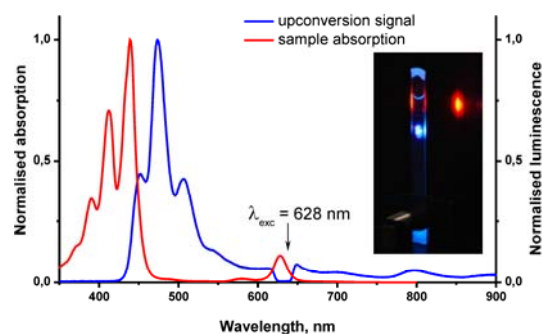


Figure 8. Absorption and emission spectra of the upconversion sample containing $3 \cdot 10^{-5}$ M of **11-Pd** and $6 \cdot 10^{-4}$ M (toluene) of perylene as an emitter. Quantum yield of UC at excitation intensity of $\sim 1 \text{Wcm}^{-2}$ is 3%. Inset: a photo of the upconversion sample being irradiated with 638 nm laser.

Conclusions

While in many studies devoted to phosphorescence and triplet excited state dynamics the problem of oxygen quenching is being solved by physical or chemical protection of the sample from oxygen contamination, a development of “self-protective” triplet sensitizer molecules represents almost unexplored approach.

In this work, palladium(II) porphyrin bearing four anthracene subunits in meso-positions was synthesized. Optimization of structural features delivered a material with high solubility and strong near-IR absorption. It was found to possess oxygen-binding properties upon irradiation either with daylight or lasers. No effect on porphyrin absorption features and only weak decrease of phosphorescence intensity was observed during addition of oxygen. Such properties enable to perform partial or complete deoxygenation of oxygen-contaminated samples, thus enhancing their phosphorescence intensity. Two regimes of deoxygenation were explored: a conventional one – oxygen scavenging of the whole sample, and second – local, and real-time oxygen scavenging, suitable for sensing applications. The starting sensitizer material can be

regenerated by means of heating in vacuum. A palette of observed properties makes the material promising for application as phosphorescent sensing probes and self-protecting sensitizer for the process of TTA-UC.

Although such protection strategy is limited by the capacity of the sensitizer to bind no more than four oxygen molecules, it may have a potential in the applications which demand very low oxygen concentration levels. For example, most of the materials comprising the OLEDs suffer degradation effects from the presence of environmental oxygen and water, as both compounds can penetrate into the device. Much research and effort have been put into fabrication methods and proper device encapsulation to help mitigate these environmental effects. Thus demonstrated oxygen protection strategy on a molecular level might become complementary to those already developed.

Experimental

4,5,6,7-Tetrahydroisindole³¹ and pyrrole-2-carbaldehyde³² were prepared according to published synthetic protocols. 9-Phenylanthracene, 4-formylphenylboronic acid, bis(benzonitrile)palladium(II) chloride, DDQ, were purchased from Sigma-Aldrich. The handling of all air/water sensitive materials was carried out using standard high vacuum techniques. All solvents and reagents were obtained from commercial sources and used as received. Extra dry DMF, toluene and THF were purchased from Sigma-Aldrich. Triethylamine and DCM were distilled from CaH₂. Where mixtures of solvents were used, ratios are reported by volume. Column chromatography was carried out on silica gel 60 at normal pressure. NMR spectra were recorded on a Bruker DPX 250, Bruker AC300 NMR and Bruker Avance 500 spectrometers, with the solvent proton or carbon signal as an internal standard. Elemental analysis was carried out using a Foss Heraeus Vario EL. Electronic absorption spectra were recorded on PerkinElmer Lambda 25 instrument. MALDI-TOF spectra were obtained on Bruker Reflex spectrometer III instrument using dithranol as a matrix. HR ESI spectrometry was measured on a QToF Ultima 3 Fa. Melting points were determined on a Büchi hot stage apparatus and are uncorrected. The spectra of emission and phosphorescence lifetime of the substances were measured by our home-built spectrometer.³³ For the excitation and irradiation of studied materials a temperature stabilized diode laser with $\lambda=638$ nm (QL63H5S, average power 20 mW) were used. In order to irradiate the samples, being in the quartz cuvettes (2x1x1 cm), the laser beam size was increased by a negative lens, resulting in the average intensity on the entrance surface of the cuvette of 5mW/cm² for 638 nm laser. The suppression of the excitation radiation during phosphorescence spectrum measurements was done by notch filter NF 03-633U-25 or NF03-532E-25 (Semrock Inc.).

10-Phenyl-9-bromoanthracene 3. The title compound was prepared following a modified literature procedure.³⁴ 9-

Phenylanthracene (3.5 g, 13.8 mmol) was dissolved in acetic acid (150 mL). The solution was heated to 65 °C under nitrogen and bromine (2.2 g, 13.8 mmol) was added dropwise over a period of 10 min. The reaction mixture was allowed to cool to room temperature and evaporated in vacuum. Residual solid was recrystallized from ethanol to give 10-phenyl-9-bromoanthracene (4.59 g, 95%) as yellow crystals with m.p. 154-155 °C (lit. 153-155 °C). ¹H NMR (250 MHz, CD₂Cl₂) δ 8.64 – 8.57 (m, 2H), 7.69 – 7.55 (m, 7H), 7.44 – 7.35 (m, 4H).

Porphyrin 6. Butyllithium (1.6 M solution in hexanes, 3.1 mL, 5 mmol) was added dropwise to a mixture of 10-Phenyl-9-bromoanthracene (1.5 g, 4.5 mmol) in diethyl ether (30 mL) and the mixture was stirred at room temperature for 30 min. Then a solution of pyrrole-2-carboxaldehyde (0.285 g, 3 mmol) in diethyl ether (5 mL) was added, resulting solution was stirred for 1 h and poured into water (100 mL). The organic phase was separated, washed with water (3x10 mL) and evaporated in vacuum. The residue was then dissolved in a mixture of toluene (15 mL) and propionic acid (5 mL). The reaction mixture was stirred for 3 h at 100 °C then allowed to cool to room temperature. Solvents were evaporated in vacuum, the residue was then redissolved in CHCl₃ and passed through a filter with silica. The first red-brown fraction was collected and the solvents removed. Crude product was recrystallized from DCM-methanol to give porphyrin **6** (0.148 g, 15% with respect to pyrrole-2-carboxaldehyde) as a red-brown solid. ¹H NMR (300 MHz, CD₂Cl₂) δ 8.40 – 8.34 (m, 8H), 7.96 (d, *J* = 8.9 Hz, 8H), 7.78 – 7.65 (m, 20H), 7.40 (ddd, *J* = 8.9, 6.0, 1.6 Hz, 8H), 7.29 – 7.17 (m, 16H). ¹³C NMR (75 MHz, CD₂Cl₂) δ 147.63, 141.88, 139.16, 135.74, 132.58, 131.87, 130.50, 130.22, 129.22, 128.57, 127.97, 127.77, 127.64, 125.99, 125.87, 119.50. UV/vis (toluene) λ_{\max} (log ϵ): 430 (5.54), 519 (4.58), 551 (4.05), 592 (4.09), 649 (3.73). MALDI-TOF: *m/z* found 1319.4076, calcd. for [M⁺] C₁₀₀H₆₂N₄ 1319.5008.

4-(10-Phenyl-anthracen-9-yl)-benzaldehyde 8. The title compound was prepared following a modified literature procedure.³⁵ A mixture of 10-phenyl-9-bromoanthracene (2.5 g, 7.5 mmol), 4-formylphenylboronic acid (1.35 g, 9 mmol), tetrakis(triphenylphosphine)palladium (0.433 g, 0.375 mmol), K₂CO₃ (2.48 g, 18 mmol), benzene (100 mL), ethanol (20 mL) and water (40 mL) was refluxed under nitrogen for 24 h. The organic phase was separated, washed with brine, and dried over Na₂SO₄. Solvent was evaporated in vacuum and remaining solid was purified on a silica gel column using EtOAc-pentane (1:5) mixture as an eluent. Fractions containing the product (determined by TLC) were concentrated to give the aldehyde (2.36 g, 88%) as yellow crystals with m.p. 234-236 °C. ¹H NMR (250 MHz, C₂D₂Cl₄) δ 10.20 (s, 1H), 8.15 (d, *J* = 8.1 Hz, 2H), 7.76 – 7.68 (m, 4H), 7.66 – 7.57 (m, 5H), 7.50 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.42 – 7.33 (m, 4H).

Porphyrin 10. 4,5,6,7-Tetrahydroisindole (0.3 g, 2.48 mmol) was dissolved in CH₂Cl₂ (250 mL) freshly distilled from CaH₂, and 4-(10-phenyl-anthracen-9-yl)-benzaldehyde (0.888 g, 2.48 mmol) was added. The mixture was stirred under nitrogen for 10 min in the dark at room temperature. BF₃·Et₂O (0.035 g, 0.248 mmol) was added in one portion, and the mixture was

stirred for an additional 2 h. DDQ (0.422 g, 1.86 mmol) was added followed by additional stirring for 2 h aqueous Na₂SO₃, dried over Na₂SO₄ and concentrated in vacuum. The residue was purified on a silica gel column (eluent CH₂Cl₂, then CH₂Cl₂-AcOH, green band collected). Additional purification by repetitive precipitation from CH₂Cl₂-AcOH (10:1) with hexane delivered the product (0.279 g, 23%) as dark-green powder. ¹H NMR (250 MHz, CD₂Cl₂) δ 8.80 (d, *J* = 7.9 Hz, 2H), 8.10 – 8.01 (m, 4H), 7.84 – 7.77 (m, 2H), 7.73 – 7.40 (m, 9H), 3.09 (d, *J* = 17.5 Hz, 8H), 2.44 (d, *J* = 17.6 Hz, 8H), 2.03 (d, *J* = 5.4 Hz, 8H), 1.63 – 1.35 (m, 14H). ¹³C NMR (75 MHz, CD₂Cl₂) δ 144.65, 141.27, 139.55, 138.53, 138.39, 137.31, 136.83, 135.96, 132.47, 131.91, 130.62, 130.46, 129.10, 128.23, 127.76, 127.30, 126.13, 125.80, 118.72, 25.51, 23.26. UV/vis (toluene) λ_{max} (log ε): 357 (4.64), 375 (4.79), 396 (4.81), 470 (5.45), 617 (4.06), 675 (4.45). MALDI-TOF: *m/z* found 1840.9465, calcd. for [MH⁺] C₁₄₀H₁₀₃N₄ 1840.8216.

Porphyrin 10-Pd. Bis(benzonitrile)palladium(II) chloride (0.078 g, 0.204 mmol) and triethylamine (0.101 g, 1 mmol) was added to a solution of porphyrin **10** (0.2 g, 0.102 mmol) in benzonitrile (10 mL), and the mixture was heated at 180 °C during 1-2 h. The conversion was monitored by UV-vis spectroscopy (solvent CH₂Cl₂-TFA) and considered complete after the absorption band of the dication at 470 nm disappeared. The mixture was allowed to cool then evaporated in vacuum to dryness. The residue was diluted with CH₂Cl₂, and filtered through a thin layer of Celite to remove Pd black, and the solvent was evaporated. The product was purified by chromatography on silica gel using CH₂Cl₂ as an eluent (dark red band collected). The solvent was evaporated and the residue was either recrystallized from CH₂Cl₂-ether to give the porphyrin **10-Pd** (0.151 g, 76%) as dark-brown powder. ¹H NMR (300 MHz, C₂D₂Cl₄) δ 8.48 (d, *J* = 7.4 Hz, 8H), 8.18 (d, *J* = 8.6 Hz, 8H), 7.88 (dd, *J* = 17.7, 8.1 Hz, 16H), 7.74 – 7.43 (m, 36H), 2.95 (s, 16H), 1.94 (s, 16H). ¹³C NMR (126 MHz, C₂D₂Cl₄) δ 141.95, 141.16, 140.53, 139.08, 138.87, 137.66, 137.31, 136.92, 134.32, 131.36, 130.59, 130.08, 130.00, 128.87, 128.26, 128.05, 127.38, 127.09, 126.82, 125.16, 124.94, 120.24, 118.96, 29.42, 23.87. UV/vis (toluene) λ_{max} (log ε): 358 (4.37), 376 (4.48), 430 (5.11), 538 (4.21), 572 (4.09). HRMS (ESI): *m/z* found 1943.7002, calcd. for [M⁺] C₁₄₀H₁₀₀N₄Pd 1943.7016.

Porphyrin 11-Pd. Porphyrin **10-Pd** (0.1 g, 0.051 mmol) was dissolved in THF (10 mL), DDQ (0.187 g, 0.82 mmol) was added, and the mixture was refluxed for 20-40 min. During refluxing the color changed from red-brown to deep green. The mixture was allowed to cool, diluted with CH₂Cl₂, washed with a 10% aqueous solution of Na₂SO₃, with brine, and dried over Na₂SO₄. The solvent was removed in a vacuum, and the remaining solid was purified on a silica gel column using CH₂Cl₂ as an eluent. The first dark-green fraction was collected. The solvent was evaporated and the residue was recrystallized from CH₂Cl₂-Et₂O to give the product (0.06 g, 60%) as blue-green crystals. ¹H NMR (300 MHz, C₂D₂Cl₄) δ 8.70 (d, *J* = 8.0 Hz, 8H), 8.46 (d, *J* = 8.8 Hz, 8H), 8.15 (d, *J* = 8.0 Hz, 8H), 7.90 (d, *J* = 8.8 Hz, 8H), 7.86 – 7.51 (m, 52H). ¹³C

NMR (126 MHz, C₂D₂Cl₄) δ 141.03, 139.63, 138.75, 138.35, 138.24, 137.65, 136.37, 133.99, 133.17, 132.52, 131.30, 129.97, 129.70, 128.46, 127.57, 127.35, 126.70, 125.60, 125.23, 124.42, 120.19, 117.93. UV/Vis λ_{max}(toluene)/nm (log ε): 340 (4.29), 357 (4.4), 375 (4.53), 395 (4.54), 446 (5.33), 628 (4.89). HRMS (ESI): *m/z* found 1927.5749, calcd. for [M⁺] C₁₄₀H₈₄N₄Pd 1927.5764.

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