CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Title: The facile synthesis, triplet state properties and electrochemistry of hexaiodo-subphthalocyanine

Authors: Łukasz Łapok, Magdalena Obłoza, Jędrzej Solarski, Tomasz Pędziński, and Maria Nowakowska

To be cited as: *Chem. Eur. J.* 10.1002/chem.201803316

Link to VoR: http://dx.doi.org/10.1002/chem.201803316

Supported by
ACES

WILEY-VCH

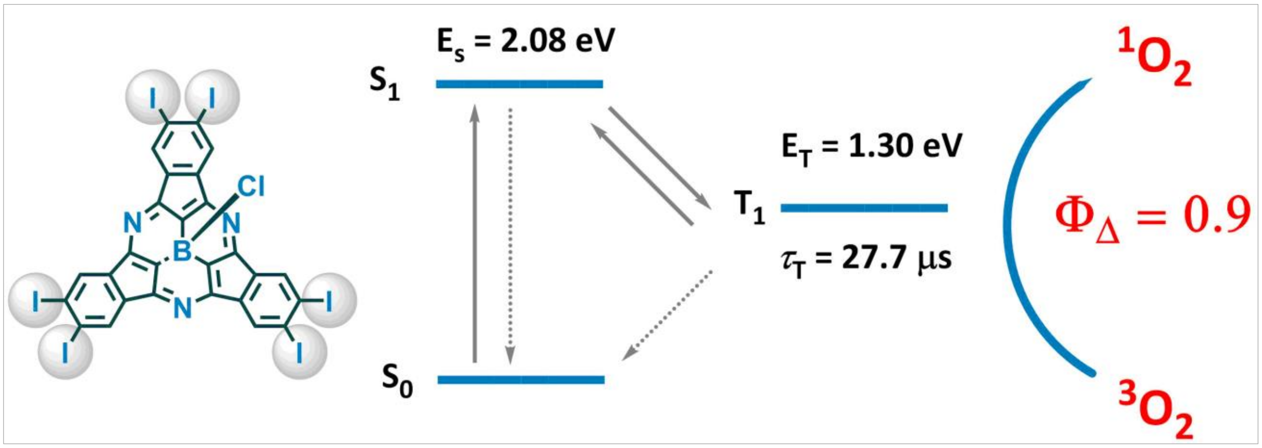
Graphical abstract

The facile synthesis, triplet state properties and electrochemistry of hexaiodo-subphthalocyanine

Magdalena Obłoza[1], *Łukasz Łapok*[1*], *Jędrzej Solarski*[2], *Tomasz Pędziński*[3], *Maria Nowakowska*[1]

[1]*Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland.*
[2]*Institute of Physical Chemistry, Polish Academy of Science, 44/52 Kasprzaka, 01-224 Warsaw, Poland.*
[3]*Faculty of Chemistry, Adam Mickiewicz University in Poznań, 89b Umultowska, 61-614 Poznań, Poland.*

[*]Corresponding author: LukaszLapok@chemia.uj.edu.pl, Tel.: + 48 12 686 25 31, Fax: + 48 12 686 27 50.



Highlights

- I_6SubPcs efficiently absorb visible light (λ_{max} ca. 580 nm).
- Efficient transfer of energy upon excitation with light to excited triplet state (T_1) occurs for I_6SubPcs.
- I_6SubPcs exhibit long-living excited triplet states allowing sensitization of ground state oxygen to a singlet oxygen with very high singlet oxygen quantum yields (ϕ_Δ), ca. 0.9.
- I_6SubPcs are phosphorescent with λ_P equal ca. 970 nm and triplet state energy (E_T) equal ca. 1.3 eV.

Table-of-contents

The facile synthesis, triplet state properties and electrochemistry of hexaiodo-subphthalocyanine

Magdalena Obłoza[1], *Łukasz Łapok*[1*], *Jędrzej Solarski*[2], *Tomasz Pędzińsk*[3], *Maria Nowakowska*[1]

[1]*Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland.*
[2]*Institute of Physical Chemistry, Polish Academy of Science, 44/52 Kasprzaka, 01-224 Warsaw, Poland.*
[3]*Faculty of Chemistry, Adam Mickiewicz University in Poznań, 89b Umultowska, 61-614 Poznań, Poland.*

[*]Corresponding author: LukaszLapok@chemia.uj.edu.pl, Tel.: + 48 12 686 25 31, Fax: + 48 12 686 27 50.

Keywords: subphthalocyanine; phosphorescence; singlet oxygen; photosensitizer; excited-triplet state.

Abstract: In view of the ever growing demand for efficient triplet photosensitizers and photoactive components of various optoelectronic devices, we herein report the synthesis and properties of hexaiodo-subphthalocyanines (I_6SubPcs) . The improved five-step route to 4,5-diiodophthalonitrile, which serves as a precursor for the synthesis of I_6SubPcs, is reported. The improved synthesis required merely one chromatographic separation to afford a high purity target product. Highly desirable photophysical and photochemical properties were induced in I_6SubPcs due to the presence of six heavy iodine atoms. In particular, high values of singlet oxygen quantum yields (ϕ_Δ) ranging from 0.83 to 0.9 were measured. The I_6SubPcs investigated proved to be phosphorescent at 77 K in 2-MeTHF with emission band maximum (λ_P) located at 957 nm for **7** and 970 nm for **8**. The excited triplet state energies (E_T) were estimated to be ca. 1.30 eV , while the triplet lifetimes (τ_T) were found to be 27.7 µs for **7** and 30.1 µs for **8**, respectively. The CV/DPV measurements indicated that both I_6SubPcs exhibited one irreversible oxidation and one quasi-reversible reduction. The spectroelectrochemical measurements pointed to relative stability and reversibility of the electrochemically formed anion radical, viz.

I_6SubPc$^{\bullet -}$, and instability of the species formed upon one-electron oxidation, viz. I_6SubPc$^{\bullet +}$. Estimation of the E_{HOMO} gave the value of ca. – 5.8 eV while the E_{LUMO} was found to be located at ca. – 3.8 eV.

10.1002/chem.201803316

1. Introduction

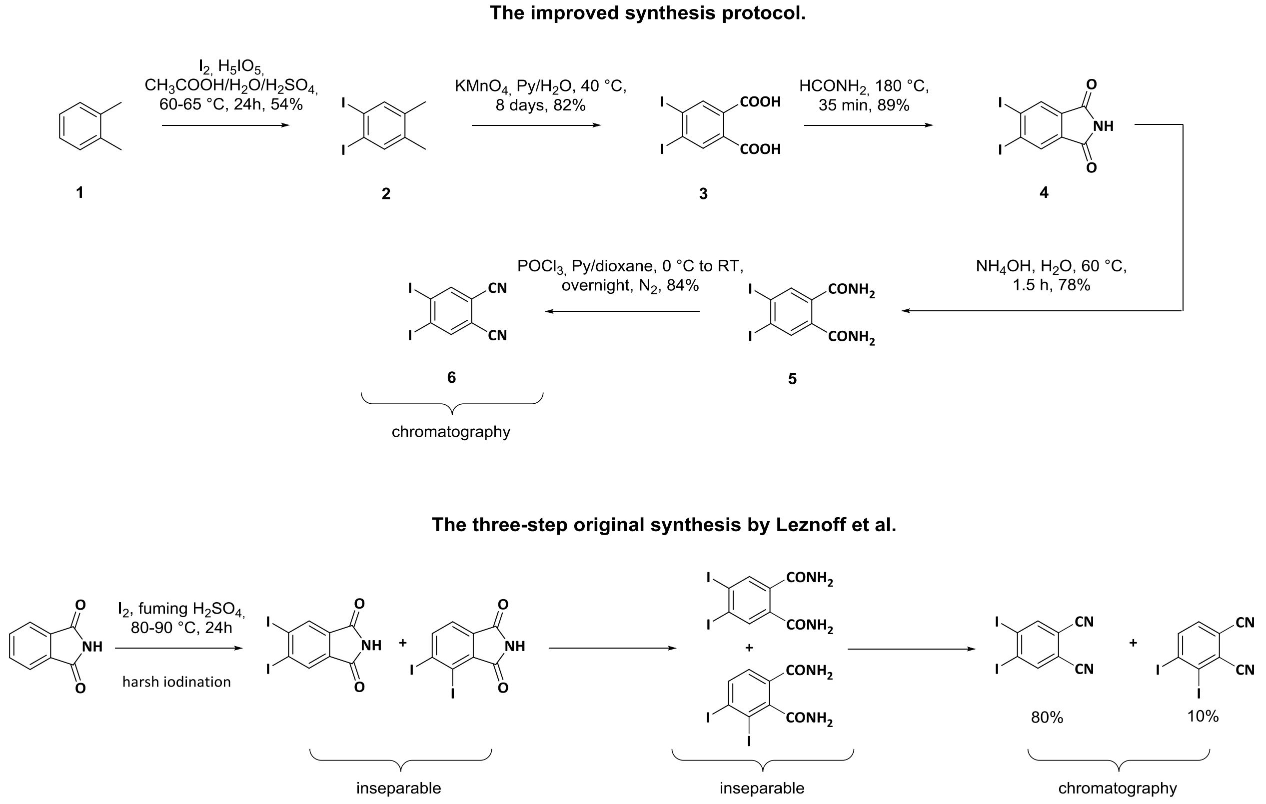
Compounds that can be efficiently excited (with high quantum yield, ϕ_T) to the triplet excited state (T_1) are termed triplet photosensitizers [1]. Consequently triplet photosensitizers are utilized as triplet energy donors to initiate either photochemical reactions or induce photophysical processes in another molecular entity [2]. Triplet photosensitizers have been considered for a variety of applications such as phosphorescent materials [1,3-4], phosphorescent bioimaging [5-6], chemosensors [7-8], photoinitiators of polymerization [9], photocatalysts (e.g. for photoinduced hydrogen production from water) [10-12], triplet-triplet annihilation based upconversion (TTAU) [13-14], oxygen sensors [15] and initiators of photoredox organic reactions [16]. Furthermore, triplet photosensitizers have found use in oncological and antibacterial photodynamic therapy (PDT) to eradicate cancerous cells or pathogens, respectively [17-19]. Strong absorption of light (large molar extinction coefficient, ε), high yield of intersystem crossing (ϕ_{ISC}) allowing to efficiently populate the T_1 excited state and long triplet lifetime (τ_T) are the prerequisites for a good photosensitizer [1]. Synthesis of inexpensive yet efficient and stable triplet photosensitizers with tailored photophysical and electrochemical properties remains a challenging field of chemistry with the portfolio of photosensitizers rapidly expanding every year. It is well-established that incorporation of certain transition metals (e.g. d^{10} Cu(I), d^6 Re(I), d^4 Re(III), d^6 Ru(II), d^6 Os(II), d^6 Ir(III), d^8 Pt(II), d^8 Pd(II), d^{10} Au(I) or d^8 Au(III)) into the organic ligands results in formation of highly populated triplet states upon electronic excitation [1,3,20]. Similarly, functionalization of the organic molecule with atoms with high atomic numbers, such as I, Br, Ir, Pt, Ru, Os, Pb, Tl, *etc.*, can induce spin orbit coupling due to the heavy atom effect, thus facilitating intersystem crossing (ISC) [21-23]. Finally, an effort has been dedicated to developing heavy atom-free organic triplet photosensitizers with C_{60}-choromophore hybrids being an example of the later [1].

Subphthalocyanines (SubPcs), a lower homologues of better-known phthalocyanines (Pcs), are an interesting class of organic chromophores that can be utilized as triplet photosensitizers [24]. This rare example of a nonplanar, bowl-shaped , 14 π-electron aromatic system was first reported in 1972 by Meller and Ossko as a product formed during an unsuccessful attempt to prepare a boron phthalocyanines [25]. Three iminoisoindole subunits *N*-fused around boron atom and a halogen atom at the axial position form a subphthalocyanine macrocycle [26]. The recent surge of interest in this class of compounds stems from their unique and tunable optical and electrochemical properties, such as strong absorption of light in the visible part of the spectrum, tunable HOMO/LUMO energy levels and triplet state characteristics. Currently, subphthalocyanines are tested mainly as functional materials in applications such as photoactive components of solar cells, organic light emitting diodes (OLED), organic field-effect transistors (OFETs) and NLO materials [24,27-31].

In this report, we wish to introduce the facile synthesis, photochemical and electrochemical characterization of two examples of halogenated subphthalocyanines (I_6SubPcs). The peripheral positions of the aromatic rings were substituted with six iodine atoms in order to induce highly desirable photophysical properties via inducing an efficient spin orbit coupling and facilitate intersystem crossing (ISC). In one of the SubPcs studied the axial chlorine substituent was replaced with 3-hydroxypyridine to improve solubility of the I_6SubPcs and facilitate its purification and spectroscopic characterization. Furthermore, 3-pyridyloxy group offers the possibility of converting this novel photosensitizer into a water soluble derivative through quaternization reaction. Research dedicated to hydrophilic photosensitizers for PDT purposes and photocatalysts operating in aqueous media are an ongoing issues in our laboratory. So far the following halogen-substituted subphthalocyanines have been reported in the literature: dodecafluoro-subphthalocyanine (F_{12}SubPcCl), dodecachloro-subphthalocyanine (F_{12}SubPcCl), hexachloro-subphthalocyanine (Cl_6SubPcCl), triiodo-subphthalocyanie (I_3SubPcCl), hexaiodo-subphthalocyanine (I_6SubPcBr) as well as various derivatives of these [32-36]. Understanding the relationship between the photosensitizer's structure and the triplet state energies (E_T) and lifetimes (τ_T) is essential for developing next generation photosensitizers for biomedical application as well as for designing the artificial light-harvesting systems. This paper aims at exploring the possibility of triplet state formation in hexaiodo-subphthalocyanines (I_6SubPcs), and in particular, at establishing the triplet-state energies (E_T) via measuring the phosphorescence (λ_P) and triplet-state lifetimes (τ_T) via recording the decay of the transient $T_1 \rightarrow T_n$ absorption in nanosecond time-resolved transient absorption spectra. Furthermore, via the CV and DPV measurements, we determine the redox properties and we establish the alignment of the HOMO/LUMO energy levels of these novel halogenated subphthalocyanines. In order to get an insight into the stability of the anion radicals ($I_6SubPc^{\bullet-}$) and cation radicals ($I_6SubPc^{\bullet+}$) formed, reversibility of these processes and to spectroscopically characterize the electrochemically generated intermediates, we performed the thin-layer spectroelectrochemistry. Knowledge of the stability of the electrochemically generated radicals and reversibility of the redox processes is of prime importance for evaluating the potential application of these materials in organic electronics.

2. Results and discussion

2.1. Synthesis and characterization

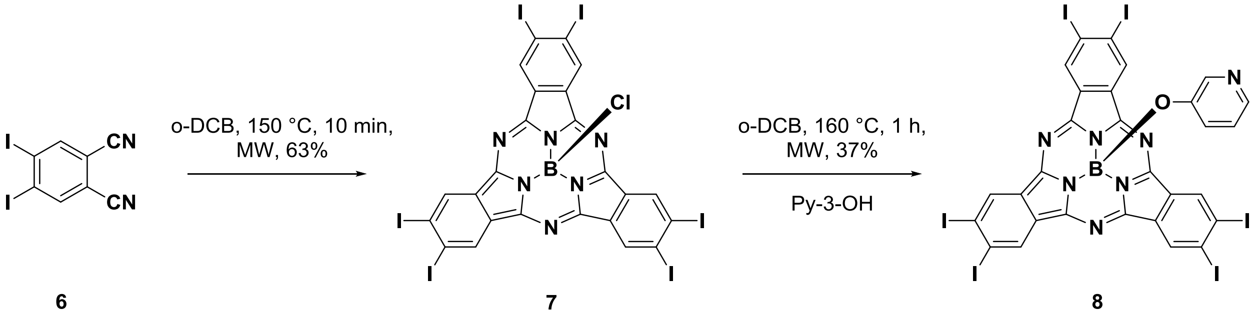


Scheme 1. Synthesis of 4,5-diiodophthalonitrile **6** proposed by us and the original synthesis proposed by Leznoff [37].

The synthesis of the hexaiodo-subphthalocyanines (I_6SubPcs) under question started with the preparation of the precursor compound, viz. 4,5-diiodophthalonitrile (**6**) (Scheme 1). 4,5-Diiodophthalonitrile (**6**) was first reported in 1996 by Leznoff et al., who proposed a synthetic pathway starting from electrophilic aromatic iodination of phthalimide, followed by ammonolysis of phthalimide (**4**) to phthalamide (**5**) [37]. In the last step the 4,5-diiodophthalamide (**5**), upon treatment with trifluoroacetic anhydride in pyridine gave 4,5-diiodophthalonitrile (**6**) (Scheme 1). Unfortunately, this method required a harsh iodination in refluxing 30 % fuming sulfuric acid at 80 °C – 90 °C and yielded a complex mixture of 4,5-diiodophthalimide, 3,4-diiodophthalimide and, at slightly lower reaction temperature, 4,5-diiodophthalic acid. The procedures reported involved a tedious and multistep, poorly reproducible separations (column chromatographies and crystallizations) at either the phthalimide step or phthalonitrile step. Inspired by the inconvenience and poor reproducibility of this method we propose a novel, elegant, and significantly improved protocol for the synthesis of 4,5-diiodophthalonitrile (**6**) [38]. Importantly, our procedure requires only one straightforward chromatography at the last step out of five steps (Scheme 1).

Oxidation of the methyl groups in 4,5-diiodo-*o*-xylene (**2**) with $KMnO_4$ in water/pyridine solution at 40 °C gave phthalic acid **3** in excellent yield of 82 %. The isolation procedure involved simple precipitation of the reaction product and required no chromatography or crystallization to afford high purity product **3**. The classical protocol used to obtained phthalonitriles requires conversion of phthalic acids to phthalic anhydrides. However, in the course of the experiments, we found that the phthalic acid **3** could be directly converted into the phthalimide **4**, an observation which allowed us to skip one reaction step, thereby simplifying the whole procedure and improving the total reaction yield. We applied the procedure first disclosed in a Japanese patent and then successfully adopted by Hanack *et al.* [39-40]. Treatment of phthalic acid **3** with formamide at elevated temperature (180 °C) afforded phthalimide **4** in a good 89 % yield. Simple precipitation of the reaction product was sufficient to obtain a product with good purity and no chromatographic separation was needed. Treatment of phthalimide **4** with water solution of ammonia gave the corresponding 4,5-diiodophthalamide (**5**) in a satisfactory 78 %

yield. Conversion of phthalamide **5** into the corresponding 4,5-diiodophthalonitrile (**6**) was carried out with a phosphorus oxychloride as the dehydrating agent in dry pyridine/dioxane mixture. Finally, after chromatographic separation, pure phthalonitrile **6** was obtained in 84 % yield.



Scheme 2. Synthesis of hexaiodo-subphthalocyanines **7** and **8**.

I_6SubPc **7** (Scheme 2) containing chlorine as the axial substituent was obtained by reacting the phthalonitrile **6** with BCl_3 in *o*-dichlorobenzene under microwave heating with a very good 63% yield. Refluxing of compound **7** in *o*-dichlorobenzene in the presence of 3-hydroxypyridine with the utilization of microwaves led to compound I_6SubPc **8** with a moderate 37% yield. The exchange of chlorine into 3-hydroxypyridine resulted in a significant increase of solubility of **8**, which greatly facilitated both the purification and spectroscopic analysis of this compound. ^{1}H NMR, ^{13}C NMR, FT-IR and HR-ESI-MS were used to corroborate the structure of the precursor compounds **2**-**6** and the subphthalocyanines **7** and **8** (see Supporting Information, Figure S1-S26). Exemplarily, the aromatic protons of the subphthalocyanine **8** give rise to a singlet at δ = 9.09 ppm, while the resonance signal of the 3-hydroxypyridyl group appeared as a series of signals at δ = 7.91 ppm (dd), δ = 6.93 – 6.82 ppm (m) and 5.88 ppm (ddd), respectively. In the high resolution ESI mass spectrum of **8** peak corresponding to the molecular ion $[M+H^+]^+$ appeared at *m/z* = 1245.5347.

2.2. Optical properties

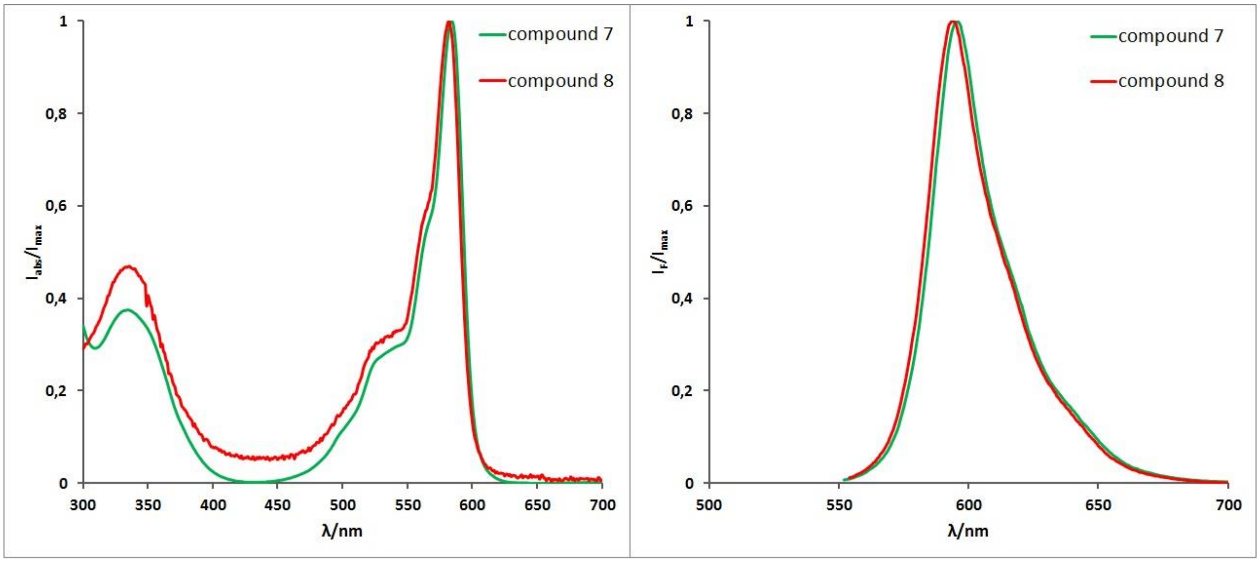


Figure 1. Normalized absorption (left panel) and fluorescence (right panel, λ_{ex} = 521 nm) spectra of hexaiodo-subphthalocyanines **7** and **8** recorded in THF (inset: THF solutions of I_6SubPcs **7** and **8**).

The electronic absorption spectra of hexaiodo-subphthalocyanies **7** and **8** are outlined in Figure 1 and summarized in Table 1. The solutions of I_6SubPcs **7** and **8** exhibit a deep magenta color. Both **7** and **8** absorb strongly in the visible region with λ_{max} = 584 nm for **7** and λ_{max} = 581 nm for **8** in THF. The following molar absorption coefficients (ε_{max}) were determined: 92 000 [$M^{-1}cm^{-1}$] for **7** and 89 000 [$M^{-1}cm^{-1}$] for **8** in THF. I_6SubPcs **7** and **8** proved to have a negligible room-temperature fluorescence with a fluorescence quantum yield below 1% and the fluorescence maxima observed at λ_f = 596 nm (Stokes shift of 12 nm) for **7** and λ_f = 594 nm (Stokes shift of 13 nm) for **8**, respectively. Based on the fluorescence spectra the following singlet excited state (S_1) energies were calculated: E_S = 2.08 eV for **7** and E_S = 2.09 eV for **8**, respectively. The fluorescence lifetimes (τ_S) for both **7** and **8** were extremely short, viz. τ_S for **7** equaled 0.18 ns and for **8** it was found to be 0.17 ns. It is due to the efficient intersystem crossing (ISC) induced by the presence of iodine substituents that efficiently channels the excitation energy into the triplet excited state (T_1) and makes the I_6SubPcs nearly non-fluorescent at room temperature.

10.1002/chem.201803316

Table 1. Summary of photophysical data for hexaiodo-subphthalocyanines **7** and **8** in THF and 2-MeTHF.

Compound	λ_{abs} [nm]	λ_f [nm]	Φ_f	E_S [eV]	ε [$M^{-1}cm^{-1}$]	τ_S [ns]	λ_P [nm]	E_T [eV]	τ_T [µs]	Φ_Δ
7	584	596	0.0052	2.08	92 000	0.18	957	1.30	27.7 ± 0.1	0.90 ± 0.03
8	581	594	0.0063	2.09	89 000	0.17	970	1.28	30.1 ± 0.1	0.83 ± 0.03

λ_{abs}: absorption maximum in THF, λ_f: fluorescence maximum in THF (λ_{ex} = 521 nm), Φ_f: fluorescence quantum yield (λ_{ex} = 521 nm, rose Bengal was used as a reference compound with Φ_f = 0.05 in ethanol), E_s: singlet excited state energy in THF, ε: molar absorption coefficient at λ_{abs} in THF, τ_S: excited singlet state lifetime in THF measured based on fluorescence decay, λ_P: phosphorescence maximum in 2-MeTHF (λ_{ex} = 530 nm) at 77 K, E_T: triplet excited state energy in 2-MeTHF at 77 K, τ_T: excited triplet state lifetime in THF, Φ_Δ: singlet oxygen quantum yield in THF (luminescence method, λ_{ex} = 345 nm, as a reference compound zinc phthalocyanine with Φ_Δ = 0.53 in THF was used).

2.3. Phosphorescence and triplet state energy

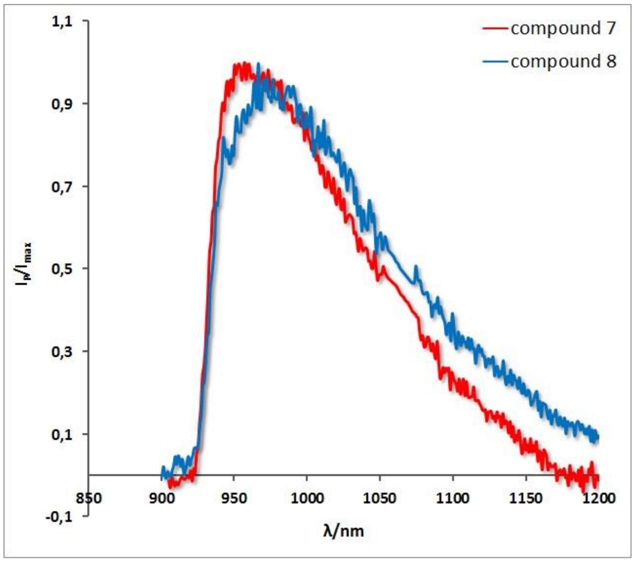


Figure 2. The normalized wavelength-corrected phosphorescence spectra of I_6SubPcs **7** and **8** recorded in 2-MeTHF at 77 K upon excitation at λ_{ex} = 530 nm.

The most direct way to measure the energy of the triplet excited state (E_T) is by recording the phosphorescence spectrum. To the best of our knowledge there is only one paper reporting the phosphorescence of subphthalocyanine [41]. In 2004 Echegoyen et al. reported triplet-state properties of subphthalocyanine derivative equipped with three iodine substituents [41]. This compound is claimed to have the phosphorescence maximum at λ_P 835 nm, and accordingly, triplet-state energy (E_T) of 1.45 eV, S_1-T_1 energy gap of 0.65 eV and triplet lifetime (τ_T) of 32 μs in a mixture of methylcyclohexane, 2-MeTHF and ethyliodide at 77 K. The normalized wavelength-corrected phosphorescence spectra of I_6SubPcs **7** and **8** are displayed in Figure 2 and the triplet state properties are summarized in Table 1. The I_6SubPcs **7** and **8** represent a class of NIR emitting dyes that exhibit detectable phosphorescence (viz. transition from T_1 to S_0) in a glass-forming 2-MeTHF solvent at 77 K upon excitation with light of λ_{ex} 530 nm. I_6SubPc **7** was found to have the phosphorescence maximum at ca. λ_P 957 nm, while I_6SubPc **8** was found to phosphoresce at ca. λ_P 970 nm. The value of the lowest triplet excited state (E_T) for I_6SubPcs **7** and **8** was calculated directly from the phosphorescence spectrum and it was found to be 1.30 eV for **7** and 1.28 eV for **8** at 77 K.

2.4. *Time-resolved spectroscopy*

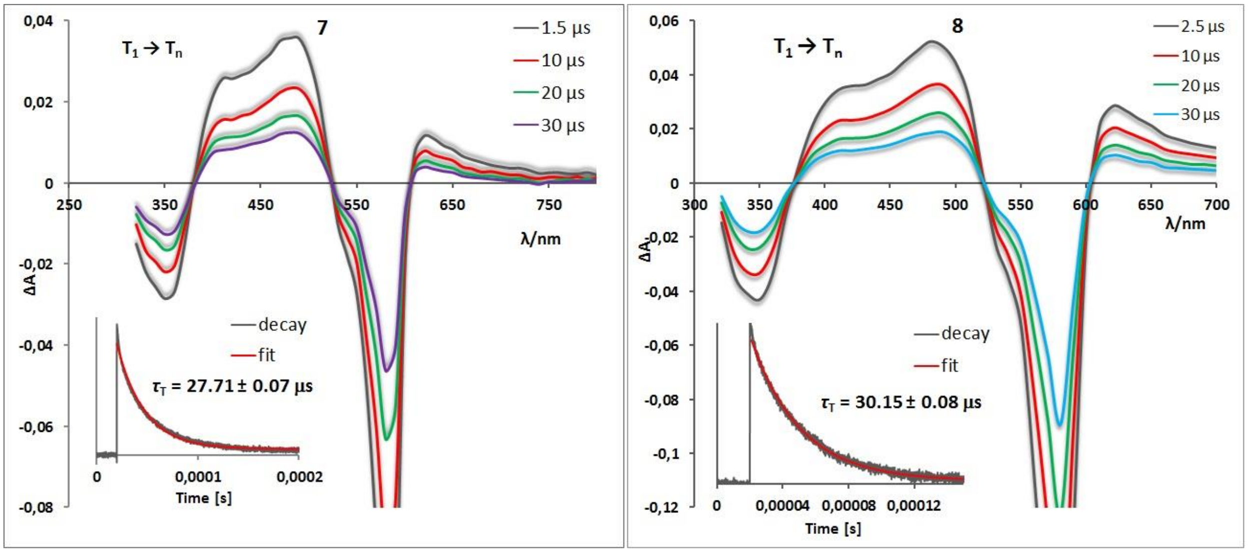


Figure 3. Nanosecond transient absorption spectra of hexaiodo-subphthalocyanines **7** (left) and **8** (right) measured in THF at room temperature, excitation wavelength λ_{ex} 355 nm. Transient decays monitored at 490 nm with fits shown in the insets.

Recording of the nanosecond time-resolved transient absorption spectra allowed studying of the triplet excited state dynamics of hexaiodo-subphthalocyanines **7** and **8** (Figure 3). The transient absorption spectra were collected upon 3rd harmonic of the Nd:YAG laser excitation (λ_{max} 355 nm) of THF solutions, argon saturated prior to the measurement. The transient absorption spectra of I_6SubPcs **7** and **8** recorded in THF, feature a very broad positive $T_1 \rightarrow T_n$ absorption band, superimposed with a negative signals due to the ground-state bleaching. For I_6SubPcs **7** and **8**, the triplet-triplet absorption spanned from ca. 380 to ca. 750 nm. The decay of the transient $T_1 \rightarrow T_n$ absorption and the recovery of the absorption $S_0 \rightarrow S_1$ in the singlet state were used to calculate triplet lifetimes (τ_T) of the investigated hexaiodo-subphthalocyanies. Both methods gave similar values of triplet lifetimes (τ_T). For I_6SubPcs **7** and **8**, mono-exponential decays of the transient absorption and recovery of the ground-state absorption were observed. The mono-exponential decay found for I_6SubPc **7** was fitted with a time constant of 27.7 ± 0.1 µs, while I_6SubPc **8** was found to have a triplet state lifetime (τ_T) of 30.1 ± 0.1 µs.

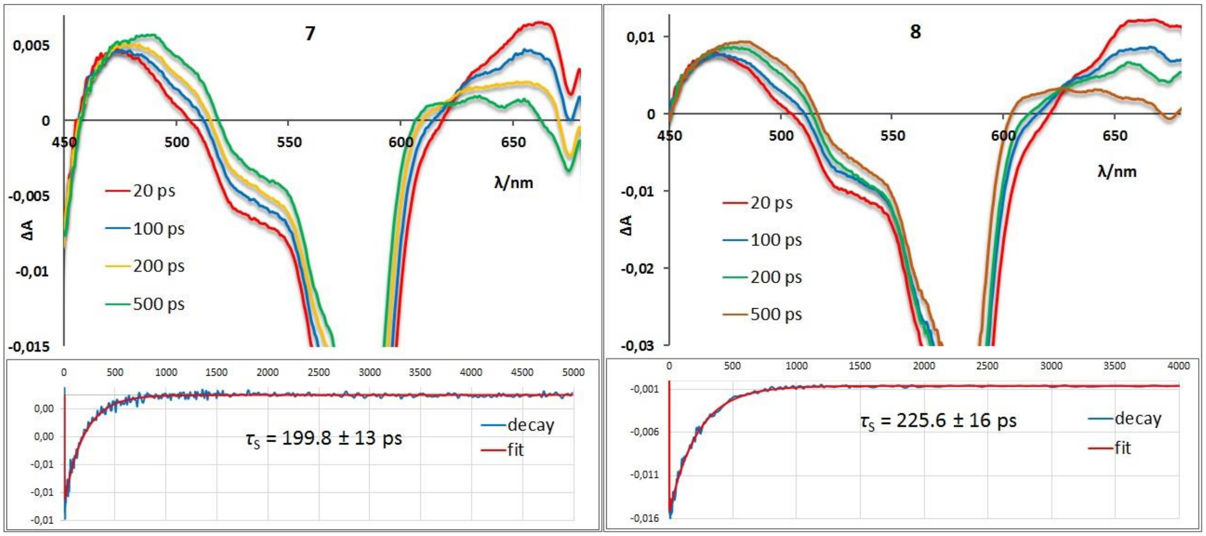


Figure 4. Femtosecond flash photolysis of **7** and **8** in THF at room temperature, excitation wavelength λ_{ex} 350 nm, laser energy 0.15 µJ/pulse. Transient decays monitored at 603 nm for **7** nm and 601 nm for **8** with fits shown in the insets.

Changing the time domain of the measurements from nanosecond flash photolysis to femtosecond flash photolysis allowed observation of excited singlet-state transient absorption spectra and dynamics ($S_1 \rightarrow S_n$) (Figure 4). Hexaiodo-subphthalocyanies **7** and **8** proved to have very short-living excited singlet-state (τ_S) in a picosecond range. Compound **7** was found to have an excited singlet lifetime of 200 ± 13 ps, while compound **8** had the excited singlet lifetime of 226 ± 16 ps. These excited singlet lifetime results are in excellent agreement with the excited singlet state lifetime (τ_S) calculated from the fluorescence decay (see Table 1).

2.5. Singlet oxygen formation

The ability of I_6SubPcs **7** and **8** to sensitize the formation of singlet oxygen ($^1O_2$) was considered and quantitatively assessed as a singlet oxygen quantum yield (ϕ_Δ). We resorted to the direct method based on the observation of the phosphorescence of singlet oxygen ($^1O_2$) at λ_P 1270 nm. The intensity of the singlet oxygen emission at 1270 nm was compared for the investigated compounds **7** and **8** and for the standard molecule with known value of ϕ_Δ in THF (zinc phthalocyanine, $\phi_\Delta = 0.53$ in THF) [42]. A particularly high quantum yield of singlet oxygen was found for I_6SubPc **7**, viz. $\phi_\Delta = 0.90 \pm 0.03$, while I_6SubPc **8** produced singlet oxygen with ϕ_Δ of 0.83 ± 0.03. High singlet oxygen quantum yields measured for **7** and **8** are an immediate consequence of the triplet state properties of these photosensitizers (viz. E_T, τ_T and the energy separation between I_6SubPc^{3*} and $^3O_2$). The phosphorescence measurements showed that it is energetically favorable for each of the hexaiodo-subphthalocyanines studied to sensitize the formation of singlet oxygen ($^1O_2$). It is well-known that the singlet oxygen ($^1\Delta_g$) exhibits a phosphorescence at λ_P 1270 nm which means that the energy separation between the ground state oxygen (triplet state, $^3\Sigma_g^-$) and its singlet state form ($^1\Delta_g$) equals 0.97 eV. It implies that for any molecule to act as a photosensitizer (Sens) capable of exciting the ground state oxygen to its higher energy form, the energy separation between the triplet excited state ($^3Sens^*$) and the ground state sensitizer (^1Sens) has to be higher than 0.97 eV. In other words the photosensitizer in its triplet excited state ($^3Sens^*$) has to act as “an energy reservoir” for the whole process. Triplet state energies of I_6SubPcs **7** and **8** are well-above that of singlet oxygen ($^1\Delta_g$). The energy separation between triplet state I_6SubPcs **7** and singlet oxygen ($^1\Delta_g$) is roughly 0.33 eV, while the energy difference between triplet state I_6SubPcs **8** and singlet oxygen ($^1\Delta_g$) is roughly 0.31 eV. Furthermore, relatively long excited triplet state lifetimes (τ_T) of **7** and **8**, ca. τ_T 30 µs, increase the probability of the energy transfer between the excited state photosensitizer (I_6SubPc^{3}*) and ground state molecular oxygen ($^3O_2$). Furthermore, very high values of singlet oxygen quantum yields (ϕ_Δ) for **7** and **8** are an indirect evidence of the triplet quantum yield (ϕ_T) approaching unity, pointing to a very good triplet sensitizing properties of these compounds.

2.6. Photostability

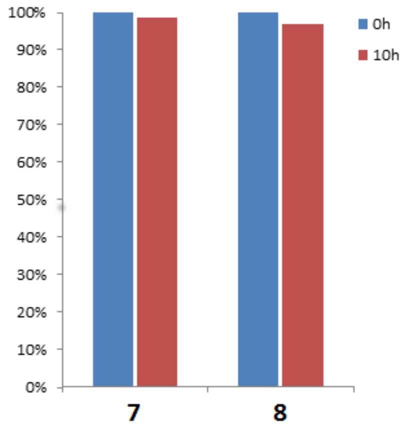


Figure 5. UV/Vis monitored photostability of **7** and **8** exposed to irradiation at λ > 473 nm and intensity 1000±50 W/m^2 in THF in the presence of oxygen.

The THF solutions of **7** and **8** were exposed to the bright light of xenon lamp (1000±50 W/m^2) separated from the samples with a 473 nm cut-off filter under aerobic conditions (Figure 5). UV/Vis spectra were taken over time in an effort to assess the relative photostability of the hexaiodo-subphthalocyanines studied. After 10 h of irradiation 98% of the initial intensity of the absorption band was preserved for compound **7** and 97% for compound **8**, respectively. These findings point to a very good photostability of **7** and **8** under the experimental conditions applied. Prolonged exposure of the THF of **7** and **8** to the light resulted in a gradual decrease of the absorption spectrum without appearance of new absorption bands, meaning that the photobleaching of hexaiodo-subphthalocyanines proceeds via clean photodegradation and not via phototransformation.

2.7. Redox potentials and HOMO/LUMO energy levels

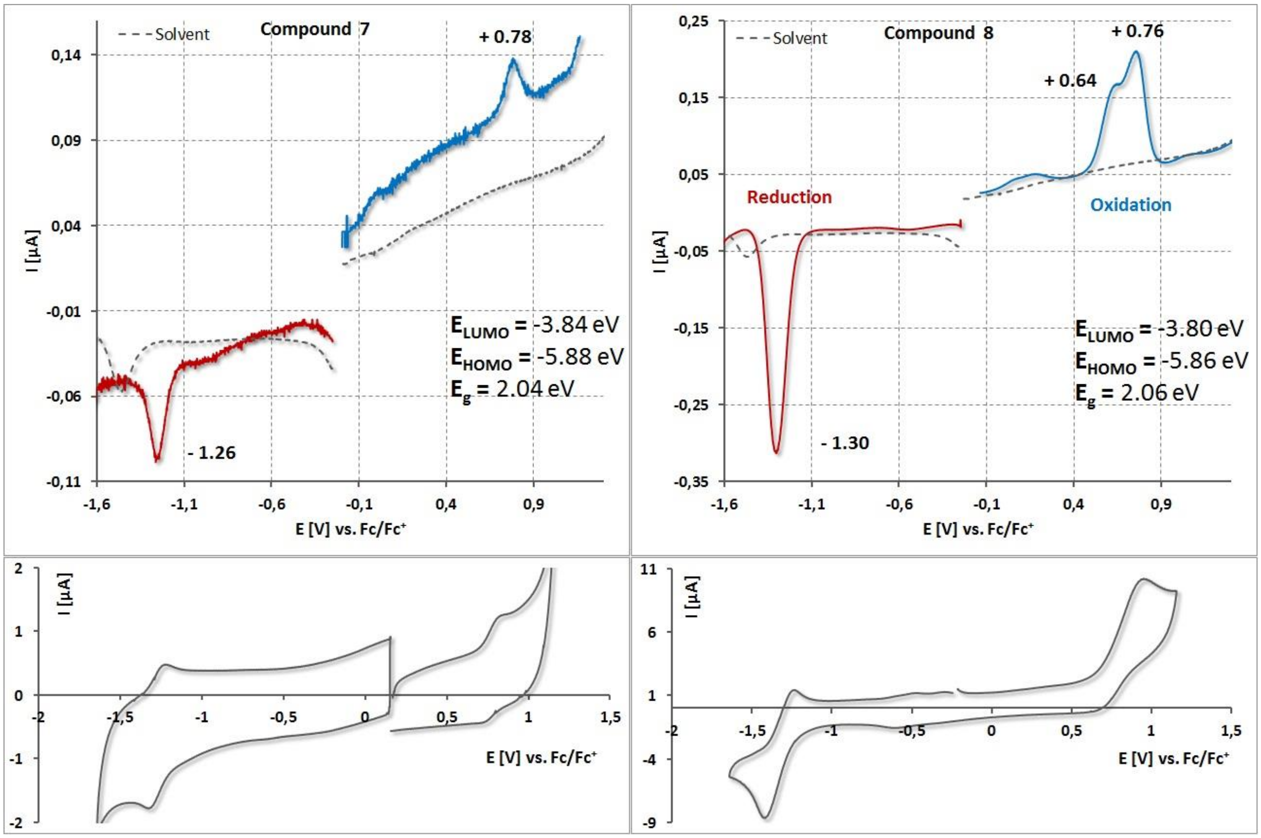


Figure 6. Differential pulse voltammetry (DPV) and cyclic voltammetry (CV) of **7** and **8**. Data collected on glassy carbon electrode in 1,2-dichlorobenzene with 0.1 M nBu_4NBF_4 as the supporting electrolyte, scan rate 100 V/s.

The oxidation (E_{ox})and reduction (E_{red}) potentials of **7** and **8** were studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) on a glassy carbon working electrode in 1,2-dichlorobenzene and were referenced to the ferrocene/ferrocenium redox couple and summarized in Table 2. Both iodinated I_6SubPcs exhibit one reduction within the potential range applied (Figure 6), viz. E_{red}^1 = -1.26 V for **7** and E_{red}^1 = -1.30 V for **8**. I_6SubPc **7** exhibited an oxidation peak at E_{ox}^1 = +0.78 V, while for **8** an oxidation potential of E_{ox}^1 = +0.76 V was found.

The DPV measurement of **8** revealed an additional oxidation (shoulder at E_{ox} = +0.64 V) overlapped with the main peak and it was not observed for the chlorine substituted **7** that we attribute to the oxidation of the 3-pirydyloxy axial substituent. The oxidations observed were irreversible while the reductions were quasi-reversible in nature.

Table 2. The frontier energy levels [eV] and redox potentials [V] vs. Fc/Fc$^+$ for **7** and **8** obtained from differential pulse voltammetry (DPV). Glassy carbon electrode was used as a working electrode. Data collected in 1,2-dichlorobenzene with 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte.

Compound	**E_{ox}^1 [V]**	**E_{red}^1 [V]**	**E_{LUMO} [a] [eV]**	**E_{HOMO} [b] [eV]**	**E_g (electro) [c] [eV]**
7	+ 0.78	- 1.26	- 3.84	- 5.88	2.04
8	+ 0.76	- 1.30	- 3.80	- 5.86	2.06

[a] E_{LUMO}= - ($E_{[\text{first reduction vs. Fc/Fc}^+]}$ + 5.1) [eV], [b] E_{HOMO}= - ($E_{[\text{first oxidation vs. Fc/Fc}^+]}$ + 5.1) [eV], [c] E(electro) = electrochemical gap.

With the first reduction (E_{red}^1) and oxidation (E_{ox}^1) potentials in hand, we calculated the respective LUMO (E_{LUMO}) and HOMO (E_{HOMO}) energy levels, assuming that the value of the formal potential of the Fc/Fc$^+$ redox couple equals – 5.1 eV in the Fermi scale (Table 2) [43]. Estimation of the E_{HOMO} gave the value of – 5.88 eV for **7** and - 5.86 eV for **8**, respectively. The E_{LUMO} was found to be located at – 3.84 eV for **7** and – 3.80 eV for **8**, respectively. These data suggest that axial substituents have virtually no influence on the alignment of the HOMO and LUMO energy levels in subphthalocyanines.

For assignment of the redox events observed, spectroelectrochemical measurements in 1,2-dichlorobenzene of I_6SubPcs was performed (Figure 7). Exemplarily, when a potential negative enough for the first reduction to occur was applied (i.e. - 1.1 V vs Ag/Ag$^+$, see Figure 7), new, red shifted the broad absorption band at ca. λ_{max} 700 nm appeared at the expense of the absorption bands initially observed at λ_{max} 581 nm and 335 nm for compound **8**. These spectral changes are associated with the formation of an anion radical, viz. $[I_6SubPc]^{\bullet -}$. When the applied potential was changed to more positive, the original spectrum was fully recovered in its initial shape and intensity, pointing to both reversibility of the first reduction and relative stability of the anion radical formed, viz. $[I_6SubPc]^{\bullet-}$, in the time frame of the experiment. Shifting the controlled electrolysis potential from -1.1 V to + 0.9 V vs Ag/Ag^+, where first oxidation occurs ($I_6SubPc \rightarrow [I_6SubPc]^{\bullet+}$), resulted in a swift depletion of the absorption bands characteristic of the neutral form of **8** without evolution of new absorption bands. Furthermore, upon applying a more negative potential no recovery of the initial absorption spectra of **8** was observed, pointing to irreversible decomposition of the species formed as a result of the oxidation. We failed to performed the spectroelectrochemistry for compound **7** due to its limited solubility in 1,2-dichlorobenzene. Recently, a comprehensive study on spectroelectrochemistry of 14 differently substituted SubPcs was published by Bender et al. [44]. Our observations are in agreement with the findings reported by Bender et al. For all 14 tested compounds upon one-electron reduction the main absorption band decreased in intensity and was replaced by a red-shifted broad absorption band, while the one-electron oxidation resulted in flattening of the whole absorption spectrum. Also, reversibility of the first reduction and irreversibility of the oxidation was noted by these authors, again, an observation which substantiate our own findings.

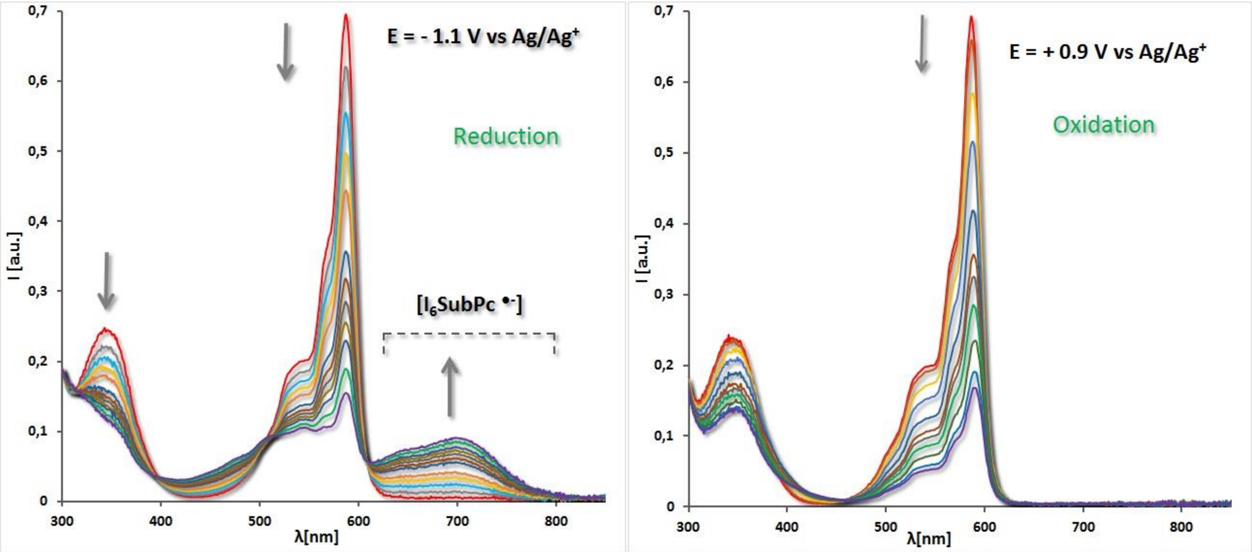


Figure 7. UV-Vis spectra of I_6SubPc **8** collected during electrolysis at two different potentials, viz. - 1.1 V and + 0.9 V vs Ag/Ag^+. Data collected in 1,2-dichlorobenzene with 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte with Pt working electrode.

2. Discussion

We demonstrated that the hexaiodo-subphthalocyanines **7** and **8** produce highly populated triplet states upon excitation with light from the visible spectral region. This was evidenced by the observation of transient absorption spectra ($T_1 \rightarrow T_n$), negligible emission from the singlet excited state ($S_1 \rightarrow S_0$) and most of all near unity singlet oxygen quantum yields (ϕ_Δ). In addition, hexaiodo-subphthalocyanines **7** and **8** have the capability to efficiently harvest visible light (λ_{max} ca. 580 nm) , as evidenced by high molar absorption coefficients (ε), viz. from 89 000 $M^{-1}cm^{-1}$ to 92 000 $M^{-1}cm^{-1}$, and are capable to withstand exposure to intense light over an extended period. The singlet oxygen quantum yields (ϕ_Δ) measured for hexaiodo-subphthalocyanines **7** and **8** are among the highest ever reported for this class of chromophores, viz. ϕ_Δ = 0.83 - 0.90. A compound closely related to the hexaiodo-subphthalocyanines **7** and **8** is the well-known triodo-subphthalocyanine (I_3SubPc-Cl) with the following photophysical characteristics: ϕ_Δ = 0.74, ϕ_T = 0.77, τ_T = 56 μs and ϕ_F = 0.013 [45]. Given the triplet state properties of the hexaiodo-subphthalocyanines described in this work we anticipate that these compounds may be useful when highly efficient triplet sensitizers are required. One example of such an application could be photodynamic therapy (PDT). The following criteria have been defined for a good photosensitizer: a) absorption of light from the so called “therapeutic window” (from 600 nm to 1100 nm), b) a high absorption coefficient, c) a long-living triplet state (longer than 1 μs) and d) the ability to generate reactive forms of oxygen (singlet oxygen and radicals). The hexaiodo-subphthalocyanines **7** and **8** meet all but one of these criteria – they do not absorb light from the “therapeutic window”. However, one has to bear in mind that anti-microbial photodynamic therapy (aPDT) does not require the photosensitizer to be active in the “therapeutic window” suggesting that hexaiodo-subphthalocyanines developed here could be considered as photosensitizers for aPDT.

Other applications of triplet photosensitizers include TTA upconversion, hydrogen (H_2) production and photoredox catalytic organic reactions. In particular, photon upconversion based on sensitized triplet-triplet annihilation (TTA) holds promise in applications like dye-sensitized solar cells, photocatalysis and artificial photosynthetic systems. All these applications require dyes with highly populated, long-living triplet states. We therefore believe that hexaiodo-subphthalocyanines presented in this work are natural candidates for these applications.

3. Experimental

3.6. Materials and Methods

^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker Avance II 300 MHz, Bruker Avance III 400 MHz and Bruker Avance III 600 MHz in deuterated solvents. Electrospray mass spectrometer microTOF II (Bruker Daltonics, Bremen/Germany) with a resolution of > 16 500 FWHM and a mass accuracy of < 2 ppm was used to obtain the high-resolution mass spectra. MALDI MS spectra were recorded in positive reflectron mode with the use of a MALDI-TOF/TOF mass spectrometer ultrafleXtreme (Bruker Daltonik). Cesium triiodide clusters were utilized for calibration of the m/z scale. FT-ATR-IR spectra were recorded using a Bruker Equinox 55 and Thermo Scientific Nicolet iS10 spectrometers. UV-Vis absorption spectra at 298 K were measured using a Hewlett-Packard 8452A diode-array spectrophotometer equipped with a HP 89090A Peltier temperature control accessory. For the elemental micro analysis, the CHNS Vario Micro Cube analyzer combined with the electronic microbalance was used. Reaction progress was controlled using TLC on silica gel (Supelco). 1,2-Dichlorobenzene was dried with CaH_2 and freshly distilled prior to use. Compound **1** was purchased from TCI Europe and used as supplied.

3.7. Synthesis

4,5-diiodo-*o*-xylene (**2**)**:** see reference [46]. To a mixture of *o*-xylene (20 g, 189 mmol), iodine (42 g, 165 mmol) and periodic acid H_5IO_6 (17.2 g, 75.45 mmol) a mixture of glacial acetic acid (100 ml), sulfuric acid (3 ml) and water (20 ml) was added. The reaction mixture was kept at 60-65 °C for 24 h. The reaction mixture was quenched with a saturated aqueous solution of sodium carbonate until all acid was neutralized and pH ca. 7 was reached. Then, a saturated aqueous solution of sodium thiosulfate was added to consume all unreacted iodine. The crude product was extracted with dichloromethane (3 x 60 ml) and the combined organic extracts were washed with water(3 x 100 ml). The product was purified by a repetitive crystallization from hexane. Yield: 40.7 g (54 %), white crystals. **^{1}H NMR** (600 MHz, $CDCl_3$) δ (ppm) = 7.61 (s, 2 H), 2.15 (s, 6 H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ (ppm) = 140.1, 138.7, 103.9, 19.1. **HR-ESI-MS**: *m/z* 381.2981 $[M+Na^+]^+$, 375.2488 $[M+H_2O]^+$. **ATR-FT-IR:** ν = 2975 (m), 2912 (m), 2849 (m), 2723 (w), 1719 (w), 1458 (vs), 1437 (vs), 1375 (s), 1328 (s), 1263 (m), 1152 (m), 1098 (w), 1016 (m), 994 (w), 860 (vs) cm^{-1}. **Anal. Calcd** for $C_8H_8I_2$: C 26.84%, H 2.25%. Found: C, 26.97%, H, 2.31%

4,5-diiodophthalic acid (**3**)**:** 4,5-diiodo-*o*-xylene (**2**, 30.06 g, 75.51 mmol) and $KMnO_4$ (51.5 g, 0.326 mol) were suspended in a mixture of pyridine (300 ml) and water (60 ml). The reaction mixture was stirred at 40 °C for 8 days. After the reaction was completed, a solution of NaOH (6.85 g, 0.171 mol) in water (60 ml) was added to the reaction mixture. Next, ethanol (100 ml) was added to the reaction mixture to consume the unreacted $KMnO_4$. The MnO_2 formed was filtered off and washed with water. Solvents were evaporated under vacuum and the solid obtained was dissolved in 100 ml of water and placed in an ice bath. Hydrochloric acid (35 %) was added dropwise with vigorous stirring until an acidic pH was attained. The precipitate formed was filtered and followed by washing with water and acetone. Yield: 26.48 g (82%), white powder. **^{1}H NMR** (300 MHz, DMSO-d_6): δ (ppm) = 8.37 (s, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6): δ (ppm) = 166.3, 140.9, 134.2, 112.1. **HR-ESI-MS**: *m/z* 440.8091 (calcd for $[M+Na^+]^+$: 440.8091). **FT-ATR-IR**: ν = 3550 (m), 3079 (m), 2115 (w), 1909 (w), 1711 (vs), 1607 (m), 1560 (m), 1535 (s), 1362 (m), 1228 (vs), 1150 (m), 1074 (s), 904 (w), 852 (m), 770 (m) cm^{-1}. **Anal. Calcd** for $C_8H_4I_2O_4$: C, 22.99%, H, 0.96%. Found: C, 22.32%, H, 1.06%.

4,5-diiodophthalimide (**4**)**:** 4,5-diiodophthalic acid (**3**, 9.8 g, 23 mmol) was heated in 50 ml of formamide at 180 °C for 35 min. The reaction progress was monitored by TLC (silica gel, acetone/hexane, 4:6). The reaction mixture was cooled to RT followed by a dropwise addition of water under vigorous stirring. The white precipitate formed was filtered off and washed thoroughly with water and dried. Yield: 9.37 g (89%), white solid. **^{1}H NMR** (300 MHz, DMSO-d_6): δ (ppm) = 11.43 (bs, 1H), 8.24 (s, 2H). **^{13}C NMR** (75 MHz, DMSO-d_6): δ (ppm) = 167.8, 133.1, 132.7, 116.5. **HR-ESI-MS**: *m/z* 421.8145 (calcd for $[M+Na^+]^+$: 421.8145). **FT-ATR-IR**: ν = 3466 (s), 3192 (m), 3075 (m), 3002 (m), 2723 (m), 1770 (vs), 1716 (vs), 1598 (w), 1388 (w), 1346 (m), 1230 (w), 1140 (w), 1057 (w), 849 (w), 760 (w), 737 (w) cm^{-1}. **Anal. Calcd** for $C_8H_3I_2NO_2$: C, 24.09%, N, 3.51%, H, 0.76%. Found: C, 24.40%, N, 4.63%, H, 0.97%

4,5-diiodophthalamide (**5**)**:** 4,5-diiodophtalimide (**4**, 2.15 g, 5.4 mmol) was suspended in 200 ml of ammonia water solution (25%). The reaction mixture was stirred for 1.5 h at 60 °C. The crude product was filtered off and washed carefully with water and methanol. Yield: 1.74 g (78%), white solid. **^{1}H NMR** (300 MHz, DMSO-d$_6$): δ (ppm) = 7.93 (s, 2H), 7.81 (s, 2H), 7.40 (s, 2H). **^{13}C NMR** (75 MHz, DMSO-d$_6$): δ (ppm) = 167.8, 137.6, 137.0, 109.8. **HR-ESI-MS**: *m/z* 438.8411 (calcd for [M+Na$^+$]$^+$: 438.08411). **FT-ATR-IR**: ν =3425 (s), 3292 (s), 3158 (s), 1691 (s), 1649 (vs), 1600 (vs), 1562 (m), 1532 (s), 1380 (s), 1303(w), 1290 (m), 1259 (m), 1096 (s), 895 (s), 842 (s), 763 (m), 659 (m) cm^{-1}. **Anal. Calcd** for $C_8H_6I_2N_2O_2$: C, 23.10%, N, 6.73%, H, 1.45%) Found: C, 23.49%, N, 6.20%, H, 1.30%.

4,5-diiodophthalonitrile (**6**)**:** 4,5-diiodophthalamide (**5**, 0.450 g, 0.12 mmol) was dissolved in a mixture of anhydrous pyridine and dioxane (28 ml, 5:2 v/v). The mixture was placed in an ice bath and $POCl_3$ (1.2 ml, 12.8 mmol) was added dropwise via a syringe. The ice bath was removed and the mixture was stirred under an inert gas atmosphere overnight. The mixture was quenched by pouring it onto crushed ice, followed by extraction with ethyl acetate (3 x 90 ml). The organic phase was washed with water (3 x 50 ml). After solvent evaporation the residue was purified by column chromatography (silica gel, toluene). Yield: 0.344 g (84%), yellow-white solid. **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 8.22 (s, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ (ppm) = 142.9, 115.6, 115.2, 113.7. **HR-ESI-MS**: *m/z* 402.8201 (calcd for [M+Na$^+$]$^+$: 402.8200).

FT-ATR-IR: ν = 3069 (m), 2230 (m), 1555 (m), 1450 (m), 1319 (m), 1260 (m)1096 (w), 803 (m), 885 (m), 862 (m) cm^{-1}. **Anal. Calcd** for $C_8H_2I_2N_2$: C, 25.29%, N, 7.37%, H, 0.53%. Found: C, 25.57%, N, 7.25%, H, 0.53%.

I$_6$SubPcBCl (**7**)**:** A mixture of heptane solution of BCl_3 (1 M, 2 ml, 2.00 mmol), 4,5-diiodophthalonitrile (**6**, 0.254 g, 0.67 mmol) and dry 1,2-dichlorobenzene (5 ml) was placed in a glass tube. The glass tube was closed with a septa cap, inserted into the CEM microwave reactor and heated to 150°C for 10 min. The reaction mixture was poured onto a vigorously stirred cold mixture of EtOH and hexane (20 ml, v/v, 1:1). The shiny violet precipitate formed was filtered and washed thoroughly with water and ethanol, followed by drying. Yield: 165 mg (63%), shiny violet solid. **^{1}H NMR** (300 MHz, py-D$_5$) δ = 9.72 (s, 6H). **^{13}C NMR** – not recorded due to low solubility of **7** in deuterated solvents. **MALDI-MS**: m/z = 1185.504 [M+H$^+$]$^+$, 1150.536 [M-Cl$^-$]$^+$.

UV-Vis (THF): nm (log ε) = 584 (4.96), 334.5 (4.53). **FT-ATR-IR**: ν (cm^{-1}) = 3055 (w), 2162 (w), 1978 (w), 1725 (w), 1591 (m), 1524 (m), 1452 (m), 1419 (m), 1399 (s), 1361 (m), 1268 (m), 1215 (m), 1177 (s), 1101 (m), 1061 (s), 1022 (w), 968 (s), 925 (m), 880 (s), 792 (s), 756 (m), 702 (s). **Anal. Calcd** for $C_{24}H_6BClI_6N_6$: C, 24.30%, N, 7.09%, H, 0.51%. Found: C, 24.83%, N, 6.79%, H, 0.58%.

I_6SubPcBOpy (**8**): Subphthalocyanine **7** (251 mg, 0.212 mmol), 3-hydroxypyridine (100 mg, 1.05 mmol) and dry 1,2-dichlorobenzene (0.8 ml) were placed in a glass tube filled with an inert gas. The glass tube was closed with a septa cap, inserted into the CEM microwave reactor and heated to 160°C for 1 h. The crude product was precipitated with hexane, filtered through a cotton plug and washed with a mixture of MeOH and water (v/v 4:1, 50 ml). The product was then dissolved in THF and preadsorbed on silica gel and purified by column chromatography (SiO_2; toluene/acetone 20:1) to give 96 mg (37%) of pure product as a red solid. **^{1}H NMR** (300 MHz, DMSO – d_6) δ (ppm) = 9.09 (s, 6H), 7.91 (dd, *J* = 4.6, 1.3 Hz, 1H), 6.93 – 6.82 (m, 2H), 5.88 (ddd, *J* = 8.1, 2.8, 1.4 Hz, 1H). **^{13}C NMR** – not recorded due to low solubility of **8** in deuterated solvents. **HR-ESI-MS**: *m/z* 1245.5347 (calcd for $[M+H^+]^+$: 1245.5381), 1267.5140 (calcd for $[M+Na^+]^+$: 1267.5200). **UV-Vis (THF)**: nm (log ε) = 581 (4.95), 334 (4.57). **FT-ATR-IR**: ν (cm^{-1}) = 3053 (w), 2920 (w), 2850 (w), 1723 (w), 1590 (m), 1523 (w), 1453 (m), 1397 (s), 1260 (m), 1166 (s), 1055 (s), 923 (m), 879 (m), 757 (m), 701 (m). **Anal. Calcd** for $C_{29}H_{10}BI_6N_7O$ (adduct with toluene): C, 32.35%, N, 7.33%, H, 1.36%). Found: C, 32.35%, N, 6.96%, H, 1.54%.

3.8. Measurements

Nanosecond Laser Flash Photolysis. Samples for time-resolved photolysis were excited using (the 3rd harmonic of the Nd:YAG laser(λ_{ex} 355 nm). Nd:YAG laser pulses (Spectra Physics Mountain View, CA, USA, model INDI 40–10) of 6–8 ns duration were employed. The energy of the excitation pulses equaled 3.5 mJ. The decay ($T_1 \rightarrow T_n$) at λ = 490 nm was followed to determine the excited triplet lifetime (τ_T). The monitoring system consisted of a 150 W Xe lamp with the lamp pulser (Applied Photophysics, Surrey, UK), a monochro-mator (Princeton Instruments, model Spectra Pro SP-2357, Acton, MA, USA), and a R955 photomultiplier (Hamamatsu, Japan), powered by PS-310 Power Supply (Stanford Research System, Sunnyvale, CA, USA). Data processing system consisted of the real- time acquisition using the digital oscilloscope (WaveRunner 6100A, LeCroy, Chestnut Ridge, New York, USA) which was triggered by a fast photodiode (Thorlabs, DET10M, ca. 1 ns rise time) and transferred to the computer equipped with software based on LabView 8.0 (National Instruments, Austin, Texas, USA) which controls the timing and acquisition functions of the system. The experiments were carried out in rectangular 1 x 1 cm quartz cells at room temperature. All samples were purged with high purity Ar for 20 min before the photolysis experiments. More details of the setup can be found elsewhere [46].

Femtosecond Transient Absorption. Femtosecond transient absorption spectra and kinetics were recorded on a setup from Spectra-Physics (USA) and Ultrafast Systems (USA). The laser system consisted of a one-box short-pulse titanium–sapphire oscillator with a high-energy titanium–sapphire regenerative amplifier (Solstice, Spectra-Physics, USA, 80 fs at 1 kHz). The λ = 800 nm beam is divided into two beams to generate pump and probe pulses; 95% of the beam was directed to the automated optical parametric amplifier (TOPAS Prime, Light Conversion, Lithuania) and allowed generation of pump pulses in the wavelength range of λ = 280 nm to 2.5 μm. The remaining 5 % of the beam was used for white-light continuum generation in a CaF_2 plate (HELIOS, Ultrafast Systems, USA). The two beams were combined in the spectrometer (HELIOS) equipped with a computer-controlled delay line (up to 3 ns). The setup allowed measurements of events as short as 200 fs. The pump pulse energy in the experiment was set to about 0.15 μJ. The absorbance of the solutions studied was set to about 0.6 at the excitation wavelength (λ= 350 nm, excitation wavelength) in a 2 mm quartz flow-through cell. Transient absorption kinetic traces were analyzed and fitted by using commercial Surface Xplorer 2.2 software from Ultrafast Systems. The transient absorption experiments were performed at room temperature.

Singlet oxygen quantum yield (Φ_Δ). The photogeneration of singlet oxygen was measured directly by detecting its phosphorescence at 1270 nm using a FluoTime 300 fluorescence spectrometer (PicoQuant, Germany). Samples were excited using a CW Xe lamp (λ 345 nm). A luminescence at 1270 nm was measured perpendicularly to the excitation beam in a photon counting mode using a thermoelectric cooled NIR PMT module (model H10330-45, *Hamamatsu*) equipped with a 1100 nm cut-off filter and additional selected narrow-band filters. Data were collected using a computer-mounted PCI-board multichannel scaler (NanoHarp 250, *PicoQuant*). Photosensitizer absorbance was maintained at about 0.12. Unsubstitited zinc phthalocyanines was used as a reference compound (Φ_Δ = 0.53) [42].

4. Conclusions

In conclusion, we have outlined a new and very convenient method to obtain 4,5-diidophthalonitrile (**6**). In contrast to the previously reported protocol, our procedure required only one straightforward chromatography at the last step - out of five steps proposed. 4,5-Diiodophthalonitrile (**6**) served as a precursor for the synthesis of hexaiodinated subphthalocyanine **7**. The nucleophilic replacement of the chlorine substituent at the boron atom in **7** by a 3-hydroxypyridine resulted in a derivative with increased solubility in organic solvents. Highly desirable photophysical and photochemical properties were induced in these compounds by introducing six iodine atoms in the aromatic rings of the subphthalocyanine. Both I_6SubPcs exhibited a noticeable NIR phosphorescence at 77K in glass forming 2-MeTHF, with λ_P located at 957 nm for **7** and λ_P located at 970 nm for **8**. Based on the phosphorescence measurements the lowest triplet excited state energies (E_T) were unambiguously determined to be 1.30 eV for **7** and 1.28 eV for **8**, respectively. Upon excitation, both I_6SubPcs efficiently transferred their triplet-state energy (E_T) to the ground-state oxygen, resulting in high values of singlet oxygen quantum yields (Φ_Δ), ranging from 0.83 to 0.90 – one of the highest ever reported for this class of compounds. Interestingly, although most subphthalocyanine dyes tend to be susceptible to photodegradation, the photostability studies of hexaiodinated subphthalocyanines **7** and **8** pointed to a very good photostability of these derivatives under aerobic conditions in THF. High singlet oxygen quantum yields (Φ_Δ) in combination with good photochemical stability recommends these compounds as efficient photocatalysts and photosensitizers for biomedical applications. Combination of both nano- and femto-second transient absorption techniques allowed detailed studies of ultrafast dynamics of the compounds (τ_S and τ_T) of **7** and **8**. Both compounds have very short-living excited singlet lifetime (τ_S). For subphthalocyanine **7** the following excited singlet lifetime was measured: τ_S 200 ± 13 ps, while compound **8** had the excited singlet lifetime of 226 ± 16 ps. The excited triplet lifetimes (τ_T) measured were in the range of 27.71 μs to 30.15 μs at room temperature. Both I_6SubPcs are very good absorbers of visible light with λ_{abs} ca. 580 nm and high molar absorption coefficients (ε) ranging from 89 000 to 92 000 [$M^{-1}cm^{-1}$]. CV/DPV measurements revealed that both I_6SubPcs undergo one irreversible oxidation and one quasi-reversible reduction within the potential range applied. The spectroelectrochemical measurements pointed to relative stability and reversibility of the electrochemically formed anion radical, viz. $I_6SubPc^{\bullet -}$, and instability of the species formed upon one-electron oxidation, viz. $I_6SubPc^{\bullet +}$. Estimation of the E_{HOMO} gave the value of ca. – 5.8 eV while the E_{LUMO} was found to be located at ca. – 3.8 eV, respectively.

5. Acknowledgements

This work was supported by the NCN grant number DEC-2011/03/D/ST5/05910 and NCN grant number 2016/23/N/ST5/01284. The research was carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund in the framework of the Polish Innovation Economy Operational Program (contract no. POIG.02.01.00-12-023/08).

6. Notes and references

[1] J. Zhao, W. Wu, J. Sun. and S. Guo, Chem. Soc. Rev. **2013**, 42, 5323-5351.

[2] S. Guo, W. Wu, H. Guo and J. Zhao, J. Org. Chem. **2012**, 77, 3933–3943.

[3] H. Xiang, J. Cheng, X. Ma, X. Zhou and J. J. Chruma, Chem. Soc. Rev. **2013**, 42, 6128-6185.

[4] V. W. W. Yam and K. M. C. Wong, Chem. Commun. **2011**, 47, 11579–11592.

[5] Q. Zhao, C. Huanga and F. Li, Chem. Soc. Rev. **2011**, 40, 2508–2524.

[6] D. L. Ma, H. J. Zhong, W. C. Fu, D. S. Chan, H. Y. Kwan, W. F. Fong, L. H. Chung, C. Y. Wong, C. H. Leung, PLoS ONE **2013**, 8 (2), e55751.

[7] Y. Feng, J. Cheng, L. Zhou, X. Zhou and H. Xiang, Analyst. **2012**, 137, 4885-4901.

[8] Q. Zhao, F. Li and C. Huang, Chem. Soc. Rev. **2010**, 39, 3007-3030.

[9] J.-P. Fouassier, F. Morlet-Savary, J. Lalevée, X. Allonas and C. Ley, Materials **2010**, 3, 5130-5142.

[10] M. L. Marin, L. Santos-Juanes, A. Arques, A. M. Amat and M. A. Miranda, Chem. Rev. **2012**, 112*,* 1710–1750.

[11] D. Drozd, K. Szczubiałka, Ł. Łapok, L. Skiba, H. Patel, S. M. Gorun and M. Nowakowska, Appl. Catal. B Environ. **2012**, 125, 35-40.

[12] R. Gerdes, Ł. Łapok, O. Tsaryova, D. Wöhrle and S. Gorun, Dalton Trans. **2009**, 7, 1098-1100.

[13] T. N. Singh-Rachford and F. N. Castellano, Coord. Chem. Rev. **2010**, 254, 2560-2573.

[14] J. Zhao, S. Ji and H. Guo, RSC Adv. **2011**, 1, 937–950.

[15] S. M. Borisov, C. Larndorfer and I. Klimant, Adv. Funct. Mater., **2012**, 20, 4360-4368.

[16] L. Shi and W. Xia, Chem. Soc. Rev., **2012**,41, 7687-7697.

[17] M. R. Detty, S. L. Gibson and S. J. Wagner, J. Med. Chem. **2004**, 47, 3897–3915.

[18] Ł. Sobotta, P. Skupin-Mrugalska, J. Mielcarek, T. Goślinski and J. Balzarini, Mini. Rev. Med. Chem. **2015**, 15, 503-521.

[19] V. Mantareva, I. Angelov, V. Kussovski, R. Dimitrow, Ł. Łapok and D. Wöhrle, Eur. J. Med. Chem. **2011**, 46, 4430-4440.

[20] Ł. Łapok, M. Obłoza, A. Gorski, V. Knyukshto, T. Raichyonok, J. Waluk, M. Nowakowska, ChemPhysChem **2016**, 17, 1123-1135.

[21] A. Gut, Ł. Łapok, D. Drelinkiewicz, T. Pędziński, B. Marciniak and M. Nowakowska, Chem. Asian J. **2018**, 13, 55-65.

[22] Ł. Łapok, M. Cyza, A. Gut, M. Kępczyński, G. Szewczyk, T. Sarna and M. Nowakowska, J. Photochem. Photobiol. A: Chemistry **2014**, 286, 55-63.

[23] M. Cyza, A. Gut, Ł. Łapok, J. Solarski, V. Knyukshto, M. Kępczyński, M. Nowakowska**,** J. Photochem. Photobiol. A: Chemistry **2018**, 358, 265-273.

[24] C. G. Claessens, D. González-Rodríguez, M. S. Rodríguez-Morgade, A. Medina and T. Torres, Chem. Rev. **2014**, 114, 2192-2277.

[25] A. Meller and A. Ossko, Monatsh. Chem. **1972**, 103, 150-155.

[26] Ł. Łapok, C. G. Claessens, D. Wöhrle and T. Torres, Tetrahedron Lett. **2009**, 294, 133-140.

[27] G. E. Morse and T. P. Bender, ACS Appl. Mater. Interfaces **2012**, 4, 5055-5068.

[28] J. S. Castrucci, D. S. Josey, E. Thibau, Z-H. Lu, T. P. Bender, J. Phys. Chem. Lett. **2015**, 6, 3121-3125.

[29] G. E. Morse, M. G. Helander, J. F. Maka, Z-H. Lu and T. P. Bender, ACS Appl. Mater. Interfaces, **2010**, *2*, 1934–1944

[30] G. E. Morse, J. L. Gantz, K. X. Steirer, N. R. Armstrong and T. P. Bender, ACS Appl. Mater. Interfaces, **2014**, 6, 1515–1524.

[31] A. Sastre, T. Torres, M. A. Díaz-García, F. Agulló-López, C. Dhenaut, S. Brasselet, I. Ledoux and J. Zyss, J. Am. Chem. Soc. **1996**, 118, 2746-2747.

[32] R. A. Kipp, J. A. Simon, M. Beggs, H. E. Ensley and R. H. Schmehl, J. Phys. Chem. A **1998**, 102, 5659-5664.

[33] N. Kobayashi, J. Porphyrins Phthalocyanines **1999**, 3, 453-467.

[34] G. E. Morse, I. Gong, Y. Kawar, A. J. Lough and T. P. Bender, Cryst. Growth Des. **2014**, 14, 2138-2147.

[35] M. Geyer, F. Plenzig, J. Rauschnabel, M. Hanack, B. del Rey, A. Sastre and T. Torres, Synthesis **1996**, 1139-1151.

[36] J. Fernández-Ariza, R. M. K. Calderón, J. Perles, M. S. Rodríguez-Morgade, D. M. Guldi and T. Torres, Chem. Commun. **2017**, 53, 8525-8528.

[37] D. S. Terekhov, K. J. M. Nolan, C. R. McArthur and C. C. Leznoff, J. Org. Chem. **1996**, 9, 3034-3040.

[38] M. Juríček, P. H. Kouwer, J. Rehák, J. Sly and A. E. Rowan, J. Org. Chem. **2008**, 74, 21-25.

[39] T. Kaneko and M. Sakamoto, Jpn. Kokai Tokkyo Koho, 06065200, 08/03/ **1994**, 4 pp. Heisei. Chemical Abstract Number: P 85717d.

[40] S. Vagin and M. Hanack, Eur. J. Org. Chem. **2004**, 600-606.

[41] D. González-Rodríguez, T. Torres, D. M. Guldi, J. Rivera, M. Á. Herranz and L. Echegoyen, J. Am. Chem. Soc. **2004**, 126, 6301-6313.

[42] L. Kaestner, M. Cesson, K. Kassab, T. Christensen, P. D. Edminson, M. J. Cook, I. Chambrier and G. Jori, Photochem. Photobiol. Sci. **2003**, 2, 660-667.

[43] C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale and G. C. Bazan, Adv. Mater. **2011**, 23, 2367-2371.

[44] K. L. Sampson, X. Jiang, E. Bukuroshi, A. Dovijarski, H. Raboui, . P. Bender and K. Kasdish, J. Phys. Chem. A **2018**, 122, 4414-4424.

[45] C. G. Claessens, D. González-Rodríguez and T. Torres, Chem. Rev. **2000**, 102, 835-853.

[46] H. Suzuki, K. Nakamura and R. Goto, Bull. Chem. Soc. Jpn. **1966**, 39, 128-131.

[47] T. Pędziński, A. Markiewicz and B. Marciniak, Res. Chem. Intermed. **2009**, 35, 497-506.