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Revisiting the Ullman's Radical Chemistry for Phthalocyanine Derivatives

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In the memory of Paul Rey

Abstract

Phthalocyanine derivatives do not cease to arouse attention due to their numerous properties and applications (e.g., sensor, PDT). This makes them unique scaffold for the design of new material. In this expectative, we were interested to develop the synthesis of an imino nitroxide-substituted phthalocyanine *via* the Ullman's procedure; a challenge due to the intrinsic low solubility of most phthalocyanine derivative in much solvents. To overcome this solubility problem we designed a phthalocyanine with bulky neopentyl substituents in peripheral positions as counterpart to the imino nitroxide moieties. The imino nitroxide-substituted phthalocyanine was obtained by condensation of a monoformyl-substituted phthalocyanine with 2,3-bis(hydroxylamino)-2,3-dimethylbutane in refluxing THF-MeOH (2:1) mixture in the presence of *p*-toluenesulfonic acid monohydrate, follow by oxidation with PbO_2. Characterization was performed by electrochemistry, UV-Vis and EPR spectroscopy in solution as well as SQUID in solid state.

Keyword: Imino nitroxide, radical, Ullman's synthesis, formyl-substituted phthalocyanine

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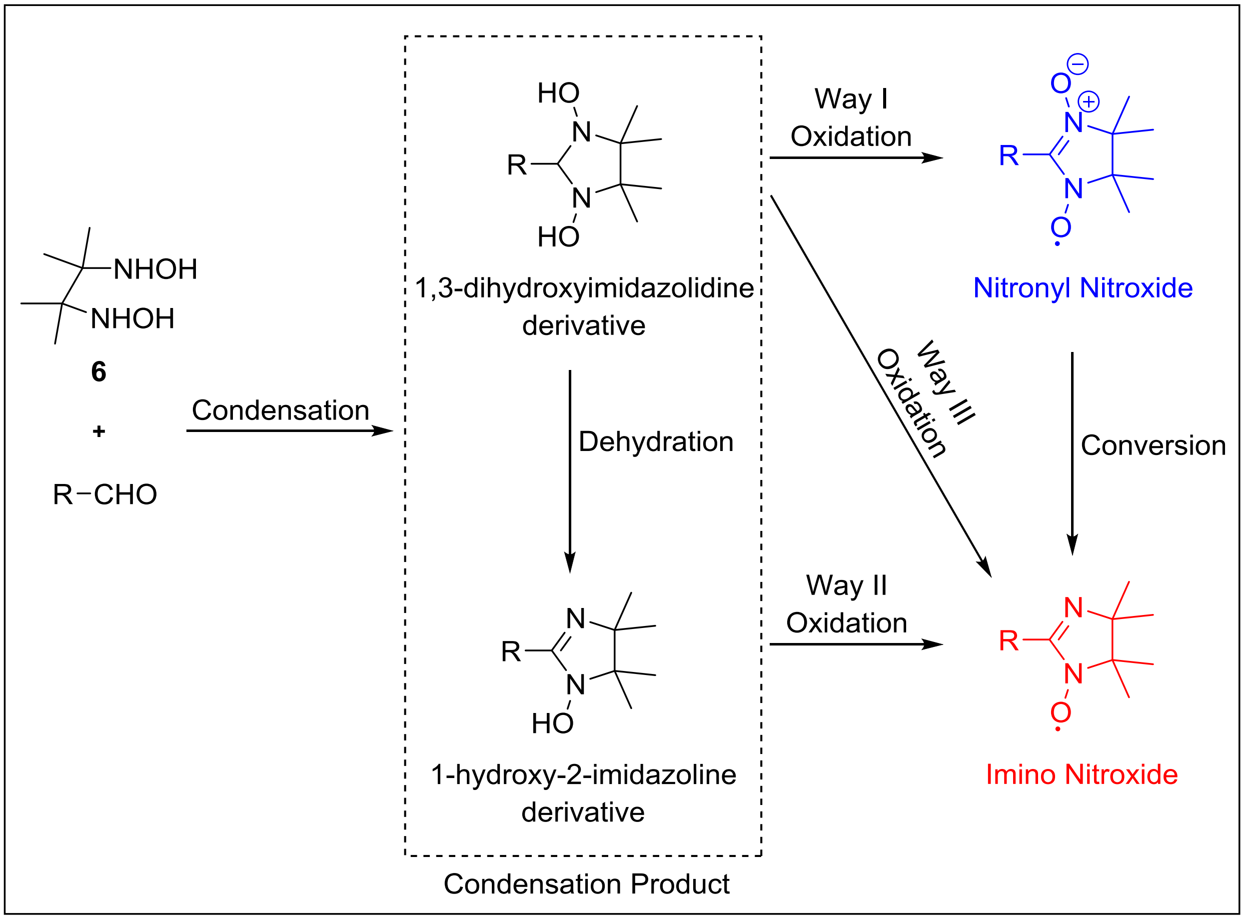
Introduction

Among open-shell molecules, imino and nitronyl nitroxide free-radical derivatives are one of the most represented family due to their high stability and versatile synthesis. They have been essentially famous as building blocks in magnetic materials.[1,2] A renewed interest in their chemistry has come in the spotlight because of their involvement in organic electrode-active materials[3] or fluorophore-nitroxide hybrid probe.[4] Imino and nitronyl nitroxide radical derivatives are classically obtained by the Ullman procedure[5] involving the condensation of 2,3-bis(hydroxylamino)-2,3-dimethylbutane (**6**) with an appropriate aldehyde in methanol to generates the 1,3-dihydroxyimidazolidine derivative. For aromatic aldehyde condensation takes hours at reflux. However, in some cases the reaction goes further and the 1,3-dihydroxyimidazolidine derivative undergoes dehydration to 1-hydroxy-2-imidazoline.[6] In very exceptional case dehydration takes place even at room temperature.[7] Condensation products suffer from low solubility. Consequently, their purification and characterization are always a difficult task and the Ullman's synthesis is generally continued without further purification. Oxidation of 1,3-dihydroxyimidazolidine or 1-hydroxy-2-imidazoline condensation product can be carried out by employing various oxidants such as $NaIO_4$, PbO_2, MnO_2, or even air to afford the corresponding nitronyl nitroxides(Way I) and imino nitroxide (Way II) respectively. In case of excess of oxidant[8] or if the solution is acidic,[2] nitronyl nitroxides are converted spontaneously to imino nitroxide in a non-reversible way (Way III), as described in scheme 1. Noteworthy that purity of 2,3-bis(hydroxylamino)-2,3-dimethylbutane (**6**) have a direct impact on the success.[9]



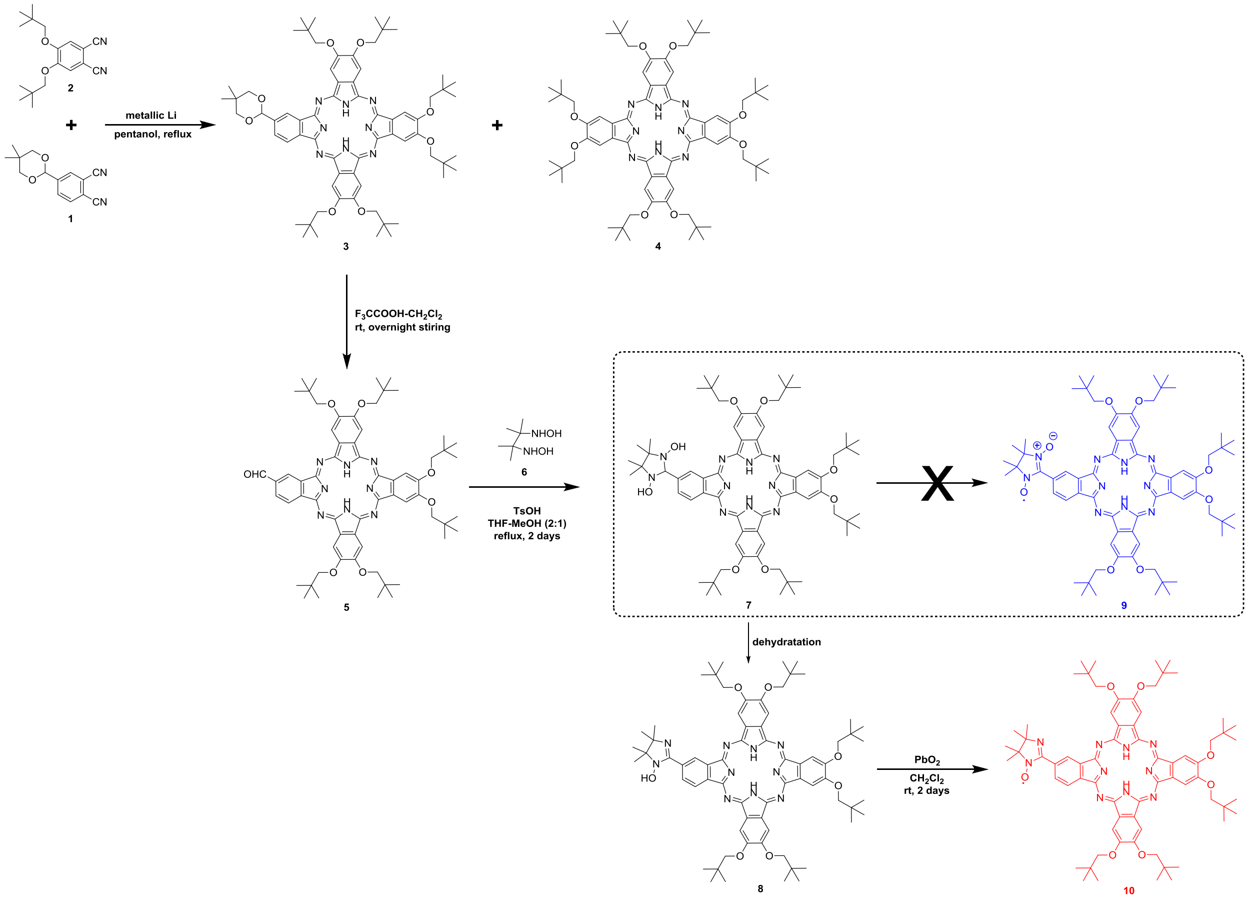
Scheme 1: Syntheses of nitronyl nitroxide and imino nitroxide free-radicals.

Although imino and nitronyl nitroxide free-radical derivatives are obtained satisfactorily with numerous substituents, the Ullman route suffers from major drawbacks in the case of highly aromatic aldehyde which require multi-step synthesis. Their low solubility in methanol as well as the stabilization of the aldehyde function by resonance prevents the condensation with **6** in an appropriate manner. Despite these constraints, the Ullman radicals were introduced in numerous molecules like pyrene,[10] quinolone,[11] 1,2,4-triazole,[12] calixarene[13] or ferrocene[14] or even in the axial position of tetraphenylporphinatozinc(II) coordinated by *p*-pyridyl nitronyl nitroxide.[15]

Our interest in the phthalocyanine dyes as a promising group of fluorophore derivatives with high quantum yield, used in numerous applications (chemical sensor, solar cell, PDT, etc.), prompted us to investigate the synthesis of a phthalocyanine covalently link to an imino nitroxide moiety. This has been a real challenge and motivation to revisit the Ullman's radical chemistry owing to the low solubility of the phthalocyanines. It follows, there are at each step synthetic problems that need to be specifically taken with care and into a better consideration than normal; i) get the key precursor 2,3-bis(hydroxylamino)-2,3-dimethylbutane (**6**) and (ii) formyl-substituted phthalocyanine in pure and good yield, also iii) optimize the condensation and the oxidation step conditions in efficient way. These problems are probably the cause of the lack of phthalocyanines bearing Ullman's radical. Step i) was not a problem for us as the synthesis of **6** has been for long mastered in our laboratory. Step ii) and iii) required reconsideration.

To have an acceptable solubility we restricted our investigation to a mono imino nitroxide-substituted phthalocyanine and ancillary bulky neopentyl substituents on other peripheral positions. Synthesis of the mono formyl-substituted phthalocyanine was thus a prerequisite. In the literature, there are only few reports about monoformyl-substituted phthalocyanine based on two strategies: post-modification of a pre-formed macrocycles to introduce formyl group or protection of the formyl group at the phthalonitrile level. By the former method formyl group is obtained by oxidative cleavage reaction of the monovinyl-substituted phthalocyanine[16] or oxidation of hydroxymethyl-substituted phthalocyanine.[17, 18] As the formyl group is fragile and will not withstand the harsh Rosenmund-von Braun cyanation or phthalocyanine formation conditions, its protection is indispensable. Indeed, cyanation via Rosenmund-von Braun takes place at elevated temperatures which may lead to decomposition of aldehyde. To stand on the safe side, aldehyde group was protected prior to cyanation process. Ethylene glycol was reported to protect the formyl function to form a dioxalane derivative that is easily deprotected after phthalocyanine formation by cleavage with 2 N hydrochloric acid in THF at room temperature.

In this article we describe the first synthesis of a metal-free phthalocyanine macrocycle bearing one imino nitroxide radical as substituent (**10**) which has been fully characterized (see scheme 2). This comprises an alternative synthesis to monoformyl-substituted phthalocyanine by the protection/deprotection pathway and a detail optimization of the key steps aforementioned condensation and oxidation for the imino nitroxide formation.



Scheme 2: The Ullman's synthetic route to metal-free phthalocyanine macrocycle bearing one imino nitroxide radical as substituent (**10**).

Results and discussion

The monoformyl phthalocyanine: As stated above, our strategy to obtain a phthalocyanine bearing one imino nitroxide radical (**10**) is based on the Ullman's route whose unavoidable precursor should be a formyl group. Therefore, we sought to synthesis an asymmetric A$_3$B-type phthalocyanine bearing in one hand a protected formyl group and on the other hand neopentyl bulky group substituents at the peripheral positions (**5**) to reduce aggregation and increase the solubility in organic solvents. A$_3$B-type phthalocyanine classical synthetic methodology consists on the statistically crossover condensation[19] of two appropriate phthalonitrile precursors in different ratio; in our case 4,5-dineopentoxyphthalonitrile (**2**) and 4-(5,5-dimethyl-1,3-dioxane-2-yl)-phthalonitrile (**1**). The synthesis of phthalonitrile **2** was carried out on the basis of Leznoff's procedure[20] with substantial modifications (SI, scheme S1). Catechol was brominated firstly,[21] thus 1,2-dibromo-4,5-dihydroxybenzene was treated with hexamethylphosphoramide, KOH, tetraheptylammonium bromide, and neopentyl tosylate to give 1,2-dibromo-4,5-dineopentoxybenzene. The conversion of it to **2** was achieved by the Rosenmund-von Braun reaction under microwave irradiation in NMP which makes possible to obtain a cleaner product with a better yield in a shorter time.[22] The synthesis of **1** is inspired by the procedure of Hanack's, only by modifying the nature of the protecting group.[23] 2,2-dimethylpropan-1,3-diol, a vicinal diol that could be used without further purification, was preferred to ethylene glycol due to its ease of handling (SI, scheme S1). **3** was obtained by overnight reflux of **2** and **1** in pentanol under template effect of metallic lithium, in the ratio 6/1 to afford the mixture of the symmetric 2,3,9,10,16,17,23,24-octaneopentoxyphthalocyanine (**4**) and the asymmetric **3** in 23% yield which have been isolated easily through column chromatography on silica gel eluting with dichloromethane-hexane mixture (scheme 2). **3** and **4** were identified by MALDI-TOF mass spectroscopy, which show $[M+H]^+$ ion peaks at m/z =1204 and m/z = 1146, respectively (SI, figures S18, S20).

The cleavage of the dioxalane group performed in F_3CCOOH-CH_2Cl_2 (1/1) mixture at room temperature allows to obtain **5** almost quantitatively (scheme 2). **5** was characterized by FT-IR, ^1H NMR, ^{13}C NMR, MALDI MS (SI, figures S21-24) and elemental analyses (see experimental section) by the typical carbonyl stretching of aldehyde at 1693 cm^{-1} and the characteristic formyl resonance at δ= 10.40 ppm corroborated by the ion peak at m/z = 1060 $[M+H]^+$. The production of **5** in sufficient quantity is important to guarantee the optimization work required during the following condensation and oxidation steps.

Condensation optimization: The condensation step between **6** and aldehyde derivative is classically carried out by refluxing them in methanol. The use of methanol is a crucial parameter as i) **6** is very soluble in it, and ii) it acts also as a catalyst by its slightly acidity. But this could be also a major drawback when aldehydes are not or only partially soluble in it. In these cases, the condensation conditions need to be addressed specifically. A co-solvent may be required to overcome the aldehyde solubility obstacle [24] or an alternative catalyst TsOH in high boiling point solvent may force the condensation reaction [25]. Solvent free condensation[26] is also one possibility even if it is little used as it appears from the literature. Table 1 reports the experimental condensation reaction conditions tested due to the lack of solubility of **5** in methanol.

Table 1: Optimization of condensation reaction conditions.

Entry	Solvent	Temperature	Catalyst	Time (days)	Result
1	CH_2Cl_2-MeOH (2:1)	RT	-	7	No reaction
2[a]	CH_2Cl_2 -MeOH (2:1)	RT	TsOH	7	No reaction
3[a]	CH_2Cl_2-MeOH (2:1)	reflux	TsOH	3	No reaction
4[a]	PhMe-MeOH (2:1)	RT	TsOH	7	No reaction
5[a]	PhMe-MeOH (2:1)	reflux	TsOH	3	Small amount formed but not finish
6	THF-MeOH (2:1)	RT	-	7	No reaction
7[a]	THF-MeOH (2:1)	RT	TsOH	7	No reaction
8	THF-MeOH (2:1)	50 °C	-	7	No reaction
9[a]	THF-MeOH (2:1)	50 °C	TsOH	7	Small amount formed but not finish
10[a]	THF-MeOH (2:1)	reflux	TsOH	2	Product formed
11	Solvent free	RT	-	7	No reaction
12[a]	Solvent free	RT	TsOH	7	No reaction

General optimization reaction conditions: Monoformyl-substituted phthalocyanine (**5**) (10.7 mg, 1 eq.) and **6** (14.8 mg, 10 eq.) were stirred in 2 mL of methanol and 4 mL of co-solvent under argon atmosphere. Progress of the reaction was monitored by TLC analysis.

[a] 6 eq of TsOH (11.4 mg, 6 eq.) was added as catalyst.

The best condensation conditions for the phthalocyanine derivative were observed in refluxing THF-MeOH (2:1) mixture during two days in the presence of TsOH as catalyst. On these bases, solely 1-hydroxy-2-imidazoline derivative (**8**) instead of the anticipated 1,3-dihydroxyimidazolidine derivative (**7**) was obtained as confirmed by MALDI-TOF mass spectroscopy which present an ion peak at m/z =1171 $[M]^+$ (SI, figure S26).

The dehydration of **7** seems to be promoted not only by high reflux temperature but also combined with the use of an excess of TsOH. Further optimizations are still in progress to find the balance of the TsOH ratio which may give accessibility to **7**. Taking these facts into account, solely imino nitroxide-substituted phthalocyanine **10** could be accessed by the oxidation.

Oxidation optimization: MnO_2, PbO_2, $NaIO_4$, or bubbling of the air in a NH_4OH (aq.)/MeOH/ $Cu(OAc)_2$ mixture are among the commonly oxidants utilized in the Ullman pathway. Each oxidation conditions were tested in order to find the best oxidative conditions. The suspension of an excess of MnO_2[27] or PbO_2[28] in solvent like CH_2Cl_2, $CHCl_3$ or toluene allow a heterogeneous oxidation, whereas oxidation by a drop by drop addition of $NaIO_4$ (aq.) need a bi-phasic solution of a water-immiscible solvent such as CH_2Cl_2 or diethyl ether and saturated $NaHCO_3$ (aq.) solution vigorously stirred.[2] Bubbling of air into a NH_4OH (aq.)/MeOH/ $Cu(OAc)_2$ mixture was less common. The experiments achieved were tabulated in Table 2.

Table 2: Optimization of oxidation conditions.

Entry	Oxidant	Solvent	Time	Result
1[a]	$NaIO_4$	CH_2Cl_2-$NaHCO_{3(aq.)}$	3 days	Reaction very slow and even never complete
2[b]	PbO_2	CH_2Cl_2	2 days	**8** is completely consumed - Product formed
3[c]	MnO_2	CH_2Cl_2	2 days	Phthalocyanine decomposed
4[d]	Air	THF-MeOH, $NH_4OH_{(aq.)}$	3 days	Reaction very slow, By-products formed

General optimization reaction conditions: **8** (11.7 mg, 1 eq.) was suspended in 30 mL of organic solvent. The mixtures were stirred vigorously at room temperature for 3 days in dark. Progress of the reaction was monitored by TLC.[a] Addition of saturated $NaHCO_3$ (aq.) solution (20 mL) and $NaIO_4$ (21.4 mg, 10 eq.) dissolved in H_2O (5 mL); [b] PbO_2 (480 mg, 200 eq.); [c] Activated MnO_2 (174 mg, 200 eq.); [d] $NH_4OH_{(aq.)}$ (10 mL) and $Cu(OAc)_2$ (catalytic amount) were added. Air was bubbled through the solution

The oxidation of **8** was achieved efficiently only by the use of PbO_2 in CH_2Cl_2 at room temperature. After two days of stirring at RT, a green solution corresponding to the imino nitroxide-substituted phthalocyanine derivative **10** was obtained and isolated as a green solid in 38% yield (scheme 2).

10 was characterized unambiguously with a rich array of analyses such as FT-IR, MALDI-TOF MS, elemental analysis, UV-Vis, CV, EPR, demonstrating the strength and the universality of the Ullman method in obtaining nitroxide radicals, even with extreme solubility conditions.

UV-Visible spectroscopy: To gain first insight into electronic interactions between the radical and phthalocyanine moieties, the absorption and emission spectra of **4** and **10** were recorded in THF and presented in Figure 1. **4** and **10** were soluble in organic solvents such as DCM or THF in which the Beer–Lambert Law was observed for both compounds in the range of 10^{-6} M to 10^{-5} M (SI, figures S29-33, S54-55). **4** and **10** show the typical split Q band characteristic of free-based phthalocyanines.[20] In contrast, the low symmetry of **10** leads to a closer Q bands. B bands around 350 nm are almost identical to each other. Noteworthy that the extension of the conjugation pathway introduced by the imino nitroxide radical moiety of **10** (λ_{max}= 441 nm) lead to a 11 nm red shift of the charge transfer band in comparison to that of **4** (λ_{max}= 430 nm). In the visible range, the specific weak transitions of imino nitroxide radical at~ 450 nm[7] are simply overshadowed by those of phthalocyanine. Both molecules exhibit one main fluorescence emission band at 699 nm, but as anticipated the introduction of the radical moiety decreased 8-fold the fluorescence intensity. Fluorescence quantum yield in THF were found to be $\Phi_{F(4)}$= 0.25 and $\Phi_{F(10)}$= 0.03 for **4** and **10**, respectively, thus confirming the quenching of the fluorescence.

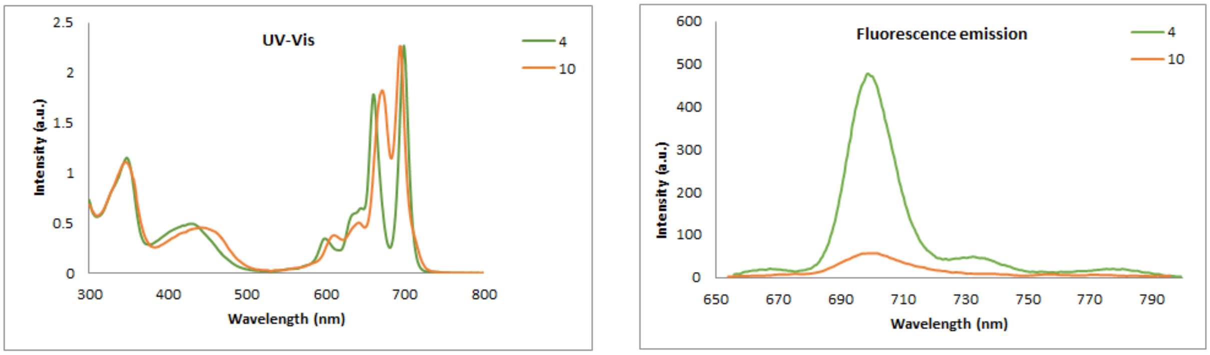


Figure 1: UV-Vis and fluorescence spectra of **4** and **10** in THF.

EPR spectroscopy: The typical seven-line splitting pattern with the relative intensity 1:1:2:1:2:1:1 presented in figure 2, proves the radical existence of **10**. The seven-line spectrum reasoned by the interaction of the unpaired electron (S=1/2) with two unequivalent ^{14}N nitrogen atoms (nuclear spin *I*=1) in the imidazoline ring. This spectrum was simulated with Jeol IsoSimu computer program. Best fitting parameters are found as g = 2.0088, a_{N1} = 9.3 G, a_{N2} = 4.2 G, ΔH_{p-p} = 2.1 G.

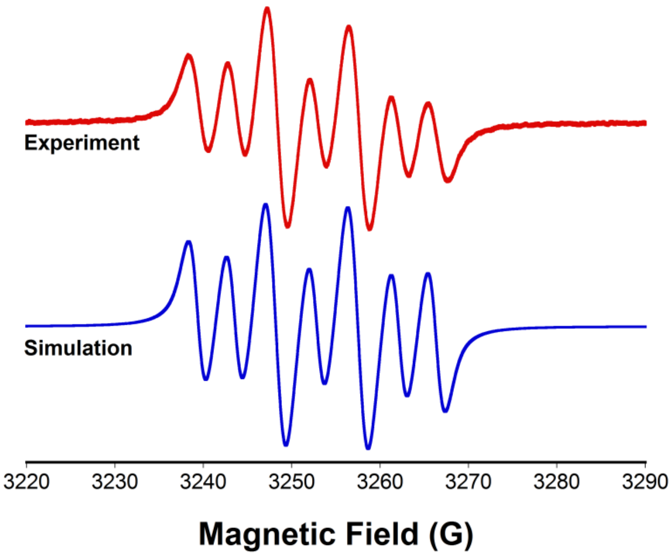


Figure 2: EPR Spectra of the Radical **10** at 293 K at 10^{-4} M in Dichloromethane-toluene (1:1) Mixture.

Electrochemical measurements: The electrochemical behavior of imino nitroxide-substituted phthalocyanine **10** was investigated by cyclic voltammetry. **10** showed an irreversible oxidation wave at 1.260 V vs. SCE and a reversible reduction one at −0.886 V (see Figure 3). Noteworthy that potentials were referenced to ferrocene/ferrocenium couple by taking $E_{1/2}$ (Fc/Fc$^+$) = 0.480 V *vs*. SCE in dichloromethane with 0.1 M *n*-Bu_4NClO_4 as supporting electrolyte.[28] The redox characteristics and the observed potentials is another way to demonstrate the radical character of imino nitroxide-substituted phthalocyanine **10**.

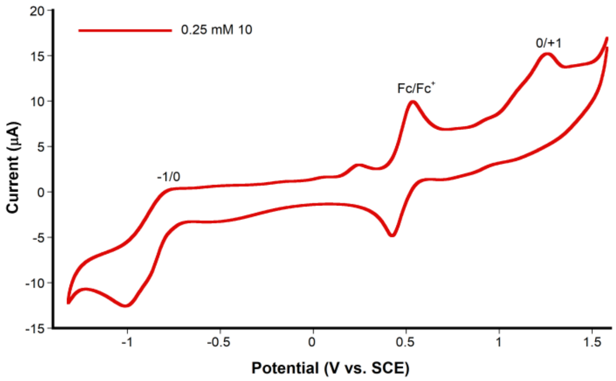


Figure 3: Cyclic Voltammogram of Phthalocyanine **10** Recorded at rt in Dichloromethane, 0.1 M *n*-Bu_4NClO_4 as Supporting Electrolyte, Scan Rate of 100 mV/s.

Magnetic study: The magnetic measurements that were performed on different samples have revealed that compound **10** is diamagnetic in the solid state. Such an unexpected magnetic behavior while EPR spectroscopy in solution shows that compound **10** is unambiguously an imino nitroxide free-radical has to be ascribed to intermolecular antiferromagnetic interaction. Strong ferro- or antiferromagnetic intermolecular interactions are not uncommon. Nitronyl or imino nitroxide free radical in the solid state may present either a direct interaction between the N-O group[30] or a McConnell type interaction.[31] In the present case and without any crystal structure it is not easy to have a straight opinion of the interaction pathway. However, owing to the bulky neopentyl substituents a McConnel type interaction is unlikely because this required that phenyl come close. We favor a direct interaction of the N-O group in a head-to-tail mode (Figure 4) that generally results in strong antiferromagnetic interaction and a diamagnetic behavior as is observed here for **10**.

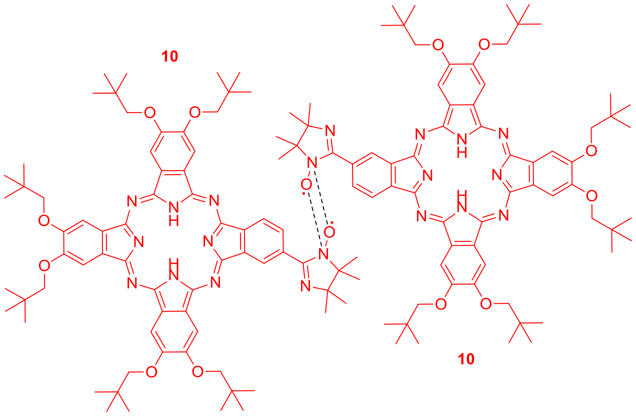


Figure 4: Representation of N-O group in a head-to-tail mode.

Conclusion

An imino nitroxide radical moiety covalently bonded to phthalocyanine macrocycle was successfully synthesized for the first time in spite of the phthalocyanine inherent problems, i.e. their high aromaticity and their insolubility in methanol which prevents condensation with 2,3-bis(hydroxylamino)-2,3-dimethylbutane. The use of a co-solvent associating with TsOH as catalyst in the condensation step and PbO_2 as oxidant were the best conditions. **10** was obtained in good yield according to the multi-step synthesis. As expected, the fluorescence intensity and the quantum yield of **10** were very low compare to the symmetrical counterpart **4**. Potentialities of this new optimized pathway are promising for the synthesis of novel highly aromatic nitroxides. Especially, fluorophore link to nitroxide are promising candidate for sensor application based principally on OFF-ON principle.

Experimental Section

The following abbreviations were used in this article and in the figures: N-methyl-2-pyrrolidone (NMP), dichloromethane (DCM), dimethylformamide (DMF), tetrahydrofuran (THF), *p*-toluenesulfonic acid (TsOH), hexamethylphosphoramide (HMPA), tetraheptylammonium bromide (Hep_4NBr).

General. All reagents, purchased from fine chemical suppliers Aldrich, Merck, Alfa Aesar and Fluka, were used without further purification unless otherwise stated. Zinc phthalocyanine (ZnPc) as reference standard was purchased from Aldrich. Solvents were either used as commercially supplied, or purified by standard techniques. Anhydrous THF was freshly distilled over sodium/benzophenone media.

Methods. Non-aqueous reactions were performed in oven-dried glassware under argon atmosphere at reported temperature. Microwave reactions were carried out in Milestone Start S Microwave Labstation for Synthesis which operates at fixe frequency (2450 MHz). The equipment can control the temperature (up to 250 ºC) in a range of power values from 0 to 1000 Watt. The reactions were carried out either in reagent grade solvents or in dry solvents if necessary. The reactions were monitored by thin layer chromatography on Merck silica gel 60 F254 precoated aluminum sheets. Spots were visualized either by UV 254 nm light or by staining with acidic ninhydrin solution. Column chromatography was performed on Merck silica gel 60 (230−400 mesh size) using the appropriate solvent system as eluent. Distilled technical solvents were used as eluent for column purifications.

Melting Points. Melting points were obtained using Stuart SMP3 melting point apparatus and were uncorrected.

Elemental Analysis. Elemental Analysis was performed on Thermo Finnigan Flash 1112 Series Elemental Analyzer operated at The Scientific and Technological Research Council of Turkey (TUBITAK), Marmara Research Center, Institute of Chemical Technology.

Infrared Spectroscopy. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer with an attenuated total reflection (ATR) accessory featuring diamond/ZnSe plate.

Samples were deposited as neat on ATR module and absorption maxima (ν_{max}) were quoted in wavenumbers (cm^{-1}) in the range of 4000-650 cm^{-1}. Intensities of absorptions are abbreviated as s:strong, m:medium, and w:weak.

NMR Spectroscopy. ^{1}H and ^{13}C nuclear magnetic resonance spectra were taken on either Varian Unity INOVA 500 MHz or Bruker Ultrashield Plus 400 MHz FT-NMR spectrometer. Deuterated solvents were used in all NMR measurements. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent peaks as an internal reference for ^{1}H-^{13}C nuclei. Assignments were determined either on the basis of unambiguous chemical shift or coupling patterns. Peak multiplicities are defined as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad and coupling constants (J) are reported in Hz.

Mass Spectra. Matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectra were recorded on a BRUKER Microflex LT spectrometer using reported matrixes.

Absorption Spectroscopy. Absorption spectra were recorded at room temperature on a Shimadzu UV-2600 UV-Vis spectrometer using a 1 cm path length quartz cuvette between 200 and 900 nm. Solutions were prepared in spectro-grade solvents. Molar extinction coefficients (Ɛ) were determined by measurement of the absorption of at least six solutions of differing concentration for each radical, followed by determination of the slope.

Electrochemical Analyses. Electrochemical measurements were carried out on CH Instruments 842B model work station. The setup was conventional three-electrode cell equipped with glassy carbon working electrode, platinum wire counter electrode, and $Ag/AgNO_3$ reference electrode. The glassy carbon electrode was polished routinely with 0.05 micron alumina powder/water slurry on pads before running experiments. All measurements of samples were recorded as reported analyte concentration in 0.1 M n-Bu_4NClO_4 electrolyte solutions of dichloromethane. Solutions were deaerated with argon purge for 5 minutes and kept under blanket of argon during the experiments. All electrochemical measurements were performed at ambient temperature. Ferrocene was used as internal reference and all potentials were referenced to ferrocene/ferrocenium (Fc/Fc^+) redox couple ($E_{1/2}$: 0.480 V vs. SCE). All potentials as $E_{1/2}$: (E_{pa} + E_{pc})/2 were reported versus Saturated Calomel Electrode (SCE). Scan rate was 100 mV/s for all Cyclic Voltammetry (CV) experiments. 3 mm-diameter glassy carbon working electrode (CHI104), non-aqueous Ag/Ag^+ reference electrode with porous teflon tip (CHI112), platinum wire counter electrode (CHI115) and electrode polishing kit (CHI120) were purchased from CH

Instruments. Supporting electrolyte, n-Bu_4NClO_4 was purchased from Aldrich and dried at 40°C under vacuum for days. Ferrocene was supplied by Fluka, $AgNO_3$ by Carlo Erba, and anhydrous dichloromethane by Aldrich.

Electron Paramagnetic Resonance (EPR) Spectroscopy. The EPR solution spectra were recorded with Jeol JES FA 300 X-band (9.6 GHz) spectrometer, with 100 kHz magnetic field modulation. Modulation amplitude was kept below of the estimated peak-to-peak width for all spectra. Spectra were simulated using Jeol IsoSimu computer program to obtain the value of g, isotropic hyperfine coupling constants (a_N) and linewidth (ΔH_{p-p}). Typical concentration of the radicals is 10^{-4} M in dichloromethane-toluene (1:1) mixture. Solutions in spectro-grade solvent mixture were degassed by bubbling argon through the solutions for 30 minutes. Spectra for degassed solutions of the radicals were recorded at reported temperature.

Steady-State Luminescence Emission. Steady-state luminescence emission was recorded on a Fluorolog-3 from Horiba-Jobin Yvon with a Time Correlated Single Photon Counting (TCSPC) system.

Fluorescence Quantum Yield Determinations.

Fluorescence quantum yield values (ΦF) were calculated by the comparative William's method.[32] Absorbance and luminescence spectra of the sample and a reference standard were measured under identical conditions (absorbance at both the excitation wavelengths were 0.05). In our study, zinc phthalocyanine (ZnPc) which have a ΦF= 0.18 in DMSO was used as reference standard.

Magnetic Measurements. Magnetic susceptibility data were tentatively collected on different polycrystalline sample on a Quantum Design MPMS-XL SQUID magnetometer under an applied magnetics field of 0.1 T and temperature range 2-300 K. All data were not significant and of the order of magnitude of the sample holder contribution on the all temperature range evidencing diamagnetism.

Syntheses.

The synthetic procedures for **1**, **2**, and **6** are provided in SI.

2-(5,5-Dimethyl-1,3-dioxane-2-yl) -9,10,16,17,23,24-hexaneneopentoxyphthalocyanine (3): Metallic lithium was dissolved in pentanol (50 mL) and stirred for 1 hour. Phthalonitrile **1** (1 eq., 0.002 mol, 0.484 g) and phthalonitrile **2** (6 eq., 0.012 mol, 3.600 g) were added to the solution and refluxed overnight. The intense green solution was cooled to ambient temperature and added drop by drop into water-ethanol mixture to formed a green precipitate was collected by suction filtration, washed with water and ethanol, to be finally dried under air stream to afford 3.800 g of a crude green waxy solid. Crude product was purified by column chromatography on silica gel eluting with dichloromethane-hexane mixture. Column purification gave two major products; 1.680 g of the symmetric 2,3,9,10,16,17,23,24-octaneopentoxyphthalocyanine (**4**) as a green waxy solid and 0.527 g of asymmetric **3** as green powder in 23% yield.

Phthalocyanine **4**: FT-IR (ATR, ν_{max}, cm^{-1}) : 3295w, 3077w, 2954s, 2906s, 2867m, 1600m, 1491s, 1465s, 1444s, 1419m, 1391s, 1362s, 1325s, 1275s, 1260s, 1211s, 1197s, 1170m, 1098s, 1053s, 1014s, 917m, 866s, 852s, 806s, 748s, 723m, 709s, 693m. MALDI-TOF MS (2,5-dihydroxybenzoic acid, *m/z*): $C_{72}H_{98}N_8O_8$ [calculated] 1203, [found] 1204 $[M + H]^+$.

Phthalocyanine **3**: FT-IR (ATR, ν_{max}, cm^{-1}) : 3296w, 3032w, 2956m, 2914m, 2869m, 1546s, 1534s, 1471s, 1454s, 1408s, 1394s, 1378s, 1340s, 1280m, 1261s, 1218m, 1170s, 1133s, 1096s, 1050m, 1018s, 850s, 799s, 766s, 742s, 647m. MALDI-TOF MS (2,5-dihydroxybenzoic acid, *m/z*): $C_{68}H_{88}N_8O_8$ [calculated] 1145, [found] 1146 $[M + H]^+$.

2-(Formyl)-9,10,16,17,23,24-hexaneneopentoxyphthalocyanine (5): 3 (0.46 mmol, 0.527 g) was stirred in F_3CCOOH-CH_2Cl_2 mixture (40 mL-40 mL) at room temperature overnight. Green mixture was poured into water. The organic phase was extracted and washed with saturated $NaHCO_3$ (aq.) solution (5 X 100 mL), then with water (10 X 100 mL), to be finally dried over Na_2SO_4. Crude product was purified by column chromatography on silica gel eluting with dichloromethane-hexane mixture (5:1). Column purification gave 0.477 g of **5** as green powder in 98% yield. FT-IR (ATR, ν_{max}, cm^{-1}) : 3296w, 3077w, 2954s, 2907m, 2868m, 1693s, 1607m, 1583m, 1490s, 1474s, 1450s, 1393s, 1363s, 1342s, 1280m, 1260s, 1235s, 1205s, 1158s, 1132m, 1095s, 1068s, 1049s, 1017s, 921s, 854s, 830s, 739s, 715s, 691s. ^1H NMR (500 MHz, $CDCl_3$): δ 10.40 (s, 1H, -CHO), 8.93 (s, 1H, aromatic −CH), 8.53 (d, J = 5 Hz, 1H, aromatic −CH), 8.41 (s, 1H, aromatic −CH), 8.29 (s, 1H, aromatic −CH), 8.10 (m, 2H, aromatic −CH), 7.96 (s, 1H, aromatic −CH), 7.56 (m, 2H, aromatic −CH), 4.33 (s, 2H, $-CH_2O-$), 4.31 (s, 2H, $-CH_2O-$), 4.20 (s, 2H, $-CH_2O-$), 4.07 (s, 2H, $-CH_2O-$), 3.92 (s, 2H, $-CH_2O-$), 3.90 (s, 2H, $-CH_2O-$), 1.48 (s, 18H, neopentyl $-CH_3$), 1.45 (s, 9H, neopentyl $-CH_3$), 1.41 (s, 9H, neopentyl $-CH_3$), 1.38 (s, 18H, neopentyl $-CH_3$), -3.92 (s, 2H, -NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.79, 152.66, 152.48, 152.28, 152.22, 151.96, 151.93, 141.99, 137.96, 135.69, 133.20, 133.16, 129.46, 126.93, 126.72, 126.06, 126.01, 123.05, 122.21, 106.08, 105.96, 103.75, 103.54, 102.62, 102.45, 79.14, 78.83, 78.75, 78.49, 78.48, 77.73, 32.76, 32.63, 32.56, 32.53, 27.35, 27.29, 27.19 ppm. MALDI-TOF MS (2,5-dihydroxybenzoic acid, *m/z*): $C_{63}H_{78}N_8O_7$ [calculated] 1059, [found] 1060 $[M + H]^+$. Elemental Analysis for $C_{63}H_{78}N_8O_7$ [calculated]: C, 71.43; H, 7.42; N, 10.58. [found]: C, 69.81; H, 7.78; N, 9.23.

2-(1-Oxyl-4,4,5,5-tetramethyl-2-imidazoline-2-yl)-9,10,16,17,23,24-hexaneopentoxyphthalocyanine (10) : 5 (1 eq., 0.075 mmol, 0.079 g), 2,3-bis(hydroxylamino)-2,3-dimethylbutane (**6**) (40 eq., 3 mmol, 0.444 g), and TsOH (6 eq., 0.45 mmol, 0.086 g) were charged into 25 mL flask. The reaction solution was refluxed at 70 °C under argon in a THF (10 mL) and MeOH (5 mL) mixture for two days. The reaction mixture was evaporated to dryness. The green residue was dissolved in CH_2Cl_2 (150 mL) and washed firstly with 10% ethanol-water mixture (2 X 100 mL), then with saturated $NaHCO_3$ (aq.) solution (1 X 100 mL), finally with water (3 X 100 mL) and then dried over Na_2SO_4, evaporated to dryness under vacuum to give a green powder. FT-IR and MALDI-TOF MS analyses of the green powder (as crude product) confirm the identity of **8** as 2-(1-hydroxy-4,4,5,5-tetramethyl-2-imidazoline-2-yl)-9,10,16,17,23,24-hexaneneopentoxyphthalocyanine . FT-IR (ATR, ν_{max}, cm^{-1}) of compound **8**: 3296w, 3081w, 2954s, 2907m, 2868m, 1607m, 1488s, 1474s, 1451s, 1393s, 1363s, 1329s, 1279s, 1260s, 1208s, 1173s, 1096s, 1047s, 1015s, 920s, 855s, 811m, 788m, 742s, 716s, 698s. MALDI-TOF MS (trans-2-[3-(4-tert -butylphenyl)-2-methyl-2-propenylidene]-malononitrile, *m/z*): $C_{69}H_{90}N_{10}O_7$ [calculated] 1171, [found] 1171 $[M]^+$.

The crude product of **8** was subjected to PbO_2 oxidation without further purification. **8** was suspended in CH_2Cl_2 (250 mL) in 1 L flask and PbO_2 (200 eq., 3.6 g) was added as a suspension. The mixture was stirred vigorously at room temperature for 3 days in the dark. It was filtered on Celite-plug and washed with CH_2Cl_2. The green solution was evaporated to dryness. Crude product was purified with plaque chromatography on silica gel eluting with dichloromethane-methanol mixture (200:1). The plaque purification gave 0.033 g of **10** as green powder in 38% yield (from aldehyde). FT-IR (ATR, ν_{max}, cm^{-1}): 3296w, 3081w, 2955s, 2925m, 2867m, 1736w, 1608w, 1491s, 1474s, 1451s, 1393s, 1363s, 1329m, 1279s, 1260s, 1209m, 1171s, 1097s, 1049s, 1016s, 920m, 873s, 855s, 796s, 743s, 717s, 698s. MALDI-TOF MS (trans-2-[3-(4-tert -

butylphenyl)-2-methyl-2-propenylidene]-malononitrile, *m/z*): $C_{69}H_{89}N_{10}O_7$ [calculated] 1170, [found] 1171 $[M+H]^+$. Elemental Analysis for $C_{69}H_{89}N_{10}O_7$ [calculated]: C, 70.80; H, 7.66; N, 11.97. [found]: C, 71.70; H, 7.98; N, 11.62.

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Conflict of interest

The authors declare no conflict of interest.

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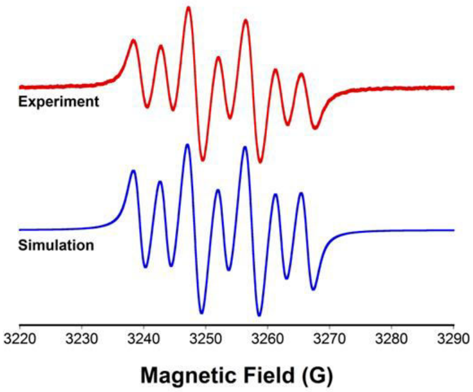

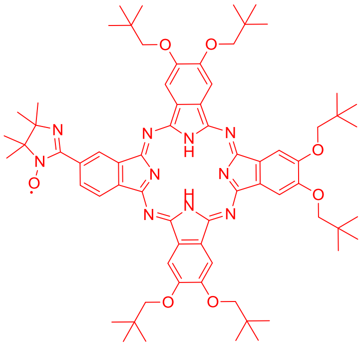

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