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Synthesis, Characterization and Photocatalytic Properties of Non-peripherally 3-(pyridin-4-yl) propane-1-oxy Groups Substituted Cu (II) Phthalocyanine and Water Soluble Derivative

Ece Tuğba SAKA^{*1}

Abstract

Cu (II) phthalocyanine compound and its water-soluble derivative containing 3- (pyridin-4-yl) propane-1-oxy groups in non-peripheral positions were synthesized for the first time and their structures were elucidated. The photocatalytic properties of Cu (II) phthalocyanine compounds, which were synthesized and characterized, were investigated on the photocatalytic degradation reactions of 4-nitrophenol, one of the important environmental pollutants. In the photocatalysis reactions that took place in the photoreactor for 2 hours without using any oxidant, 4-nitrophenol compound was completed with 94.4% and 98.6% conversion to toxic and non-harmful species. The hydroquinone compound was identified as the main product and the benzoquinone compound as the by-product. The conversion number for the non-peripheral Cu (II) phthalocyanine compound and its water-soluble derivative was 471 and 488 and the conversion frequency was 235.5 and 244,0 respectively. Finally, recovery studies were carried out for water soluble Cu (II) phthalocyanine used as photocatalyst and the number of cycles was determined as 5.

Keywords: Non-peripheral, Phthalocyanine, Copper, Photocatalytic, 4-Nitrophenol

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1. INTRODUCTION

Phthalocyanines, which are macrocyclic compounds with characteristic blue-green color, are being studied with increasing interest by scientists due to their applicability in the fields of catalysis, solar cells, photodynamic therapy of cancer, non-linear optics, gas sensor and laser dye [1]. However, the most important properties that limit the applicability of phthalocyanine compounds in their application areas are their low solubility in common organic solvents and in water. As a solution to this problem; by peripheral or axial substitution of bulky or long alkyl chain groups, phthalocyanines are dissolved in apolar solvents, while the addition of sulfonyl, carboxyl or quaternary amino groups results in water-soluble phthalocyanines [2-4]. Phthalocyanines with increased solubility by these groups find very wide application areas. In recent years, the use of phthalocyanine compounds containing different metal ions as photocatalysts in the disintegration of dyes, chlorinated phenol compounds and other substituted phenol compounds, which are the main environmental pollutants, has attracted considerable attention [5-8].

In the last decade, due to the rapid urbanization and industrialization in the world, high amounts of organic pollutants are released into nature. Petroleum refining, plastic and resin production, papermaking process, carbon liquefaction processes and pharmaceutical industry are also sources of environmental pollutants. It has been determined that substituted phenol compounds and dyes can have carcinogenic and mutagenic effects on human health and other aquatic organisms due to their high solubility, stability, easy assimilation in water according to the USEPA reports. It is therefore urgent to develop an environmentally friendly and effective method for the removal of such environmental pollutants in aqueous systems. In the early 1990s, Paul Anastas, while serving at the United States Environmental Protection Agency (USEPA), introduced the term 'Green Chemistry', which means the design of new products and processes that reduce or eliminate the use and production of hazardous substances

[9]. The use of environmentally friendly solvents (water, supercritical carbon dioxide, ionic liquids, etc.), selective catalysts and renewable raw materials is essential under moderate conditions (such as low temperature, atmospheric pressure) to meet the principles of the definition of green chemistry. In recent years, many researchers aim to develop alternative environmentally friendly systems for the disposal of industrial wastes based on this definition [10-12].

Phthalocyanine compounds are used as photocatalysts in light applications due to their wide absorption in the near infrared region and substituted phenols are known to be used for the removal of different toxic dyes and ions [13-16]. Since global warming has become a serious issue in our lives, protecting the existing water resources and recycling wastewater is one of the most important elements. 4-Nitrophenol is a toxic, environmental and human health harmful, carcinogen, synthetic compound containing many nitrogen and hydroxide groups in the wastes in many branches of industry such as pharmaceuticals, petrochemicals, fungicides, rubber, wood protection processes, paints and leather industry. is a compound [17-18]. 4-Nitrophenol compound exposure to blood cell damage, damage to the nervous system and mutagenic effects on organisms, as well as all human and aquatic life-threatening cancer-causing chemicals have been proven as a result of studies [19-21]. Therefore, removal of 4-nitrophenol compound and conversion to non-toxic, biodegradable, harmless species have gained importance.

In this study, the solubility in organic solvents with 3- (pyridin-4-yl) propane-1-oxy groups and conversion of these groups to quaternary derivatives provided solubility in water and alcohol. It was aimed to design an ideal photocatalyst using a cheap and low cost metal having different oxidation steps as the central atom in the phthalocyanine compound. The photocatalytic activities of the obtained non-peripheral Cu (II) phthalocyanine and water-soluble derivatives were investigated in the disintegration reaction of 4-nitrophenol which is an important environmental pollutant and

recovery studies of photocatalysts were performed.

2. EXPERIMENTAL

2.1. Materials and Equipments

All materials and equipments are given as supplementary materials.

2.2. Synthesis

2.2.1. Synthesis of 3-(3-(pyridine-4-yl)propoxy)phthalonitrile (3)

Compound 3 is obtained as given in the literature [22]. Yield: 2.81 g (73%), m.p. : 80-82 °C. IR (KBr pellet), $\nu_{\max}/\text{cm}^{-1}$: 3071, 3019 (Ar-H), 2961, 2928, 2892 (Alip. C-H), 2230 (C≡N), 1582, 1498, 1475, 1416, 1392, 1344, 1295, 1268, 1243, 1178, 1093, 1058, 1021, 992, 884, 841, 733, 690. ¹H-NMR. (CDCl₃), (δ :ppm): 8.34-8.02 (m, 4H, Ar-H), 7.85-7.55 (m, 3H, Ar-H), 4.33 (t, 2H, CH₂-O), 2.82 (t, 2H, CH₂-Ar), 1.79 (m, 2H, CH₂-Alip.) ¹³C-NMR. (CDCl₃), (δ :ppm): 166.22 (ArC-O), 149.55 (ArC-N), 148.50 (ArC-N), 147.16 (ArC), 133.51 (ArC), 130.37 (ArC), 128.88 (ArC), 125.39 (ArC), 122.85 (ArC), 121.90 (ArC), 118.21 (C≡N), 116.20 (C≡N), 101.33 (ArC), 70.30 (CH₂-O), 36.26 (CH₂-Ar), 34.10 (CH₂-Alip.). MALDI-TOF-MS, (m/z): Calculated: 263.29; Found: 263.60 [M]⁺.

2.2.2. Synthesis of Cu(II) Phthalocyanine (4)

Compound 4 is obtained as given in the literature [22]. Yield: 700 mg (44%). Mp >300°C. FT-IR $\nu_{\max}/\text{cm}^{-1}$ (KBr pellet): 3093, 3063 (Ar-H), 2997, 2960, 2571 (Aliph. C-H), 1559, 1466, 1448, 1422, 1401, 1369, 1339, 1287, 1265, 1255, 1232, 1195, 1075, 1058, 1045, 1038, 996, 955, 878, 834, 790, 680. UV-Vis (CHCl₃): λ_{\max} , nm (log ϵ): 687 (4.75), 662 (4.56), 341 (4.64), 280 (4.58). MALDI-TOF-MS, (m/z): Calculated: 1116.72; Found: 1116.158 [M]⁺. Solubility: CHCl₃, CH₂Cl₂, DMF, DMSO.

2.2.3. Synthesis of Water soluble Cu(II) Phthalocyanine (5)

Compound 5 is obtained as given in the literature [22]. Yield: 456 mg (57%) Mp >300°C. FT-IR $\nu_{\max}/\text{cm}^{-1}$ (KBr pellet): 3085, 3059 (Ar-H), 2997, 2950, 2844 (Aliph. C-H), 1560, 1468, 1463, 1438, 1401, 1376, 1367, 1281, 1276, 1249, 1238, 1194, 1089, 1065, 1045, 990, 894, 780, 689. UV-Vis (CHCl₃): λ_{\max} , nm (log ϵ): 684 (4.68), 621 (4.64), 343 (4.38), 279 (4.59). MALDI-TOF-MS, (m/z): Calculated: 1684.47; Found: 293.35 [M-4H]⁺. Solubility: DMF, DMSO, water and ethanol.

2.3. Photocatalytic Studies

The photocatalytic activity of Cu (II) phthalocyanine containing non-peripheral 3-(pyridin-4-yl) propoxy groups and the quaternized water-soluble derivative of Cu (II) on photooxidation reactions of the 4-nitrophenol compound using a photoreactor during the catalysis processes will be examined. For the photooxidation study in which water is used as the solvent, firstly a specified amount of substrate, a calculated amount of catalyst and a total of 10 ml of solvent will be added to the Schlenk container. The reaction time was determined as 2 hours. This point will be taken as the starting time of the reaction by taking some samples from the reaction medium by pipetting into the glass tube. When the specified reaction time is completed, the samples taken from the reaction vessel will be analyzed on a gas chromatography device and the time dependent change profile of the product will be obtained.

3. RESULTS and DISCUSSION

3.1. Synthesis and Characterization

After dissolving 3-(pyridin-4-yl) propan-1-ol **1** and 3-nitrophthalonitrile in dry DMF, anhydrous K₂CO₃ was added equal amounts in 2 hours and at 50°C for 72 hours in nitrogen atmosphere with a yield of 73% (Şekil 1).

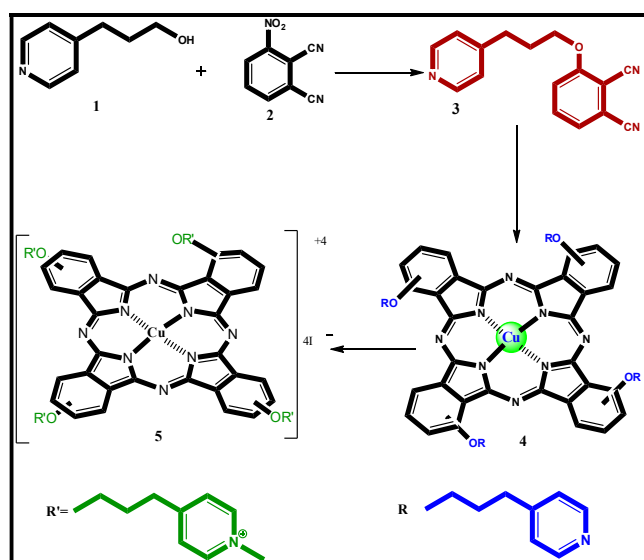


Figure 1 Synthetic ways of compounds 3, 4 and 5

In the IR spectrum of the synthesized compound 3, the disappearance of the OH and NO₂ group vibrations (3390, 3402 and 1538-1355 cm⁻¹) of the starting compounds and instead of the vibrations of the C≡N group at 2230 cm⁻¹, supports IR spectrum of the synthesized compounds. The disappearance of the peak of the OH group seen in the range of 4.64-2.40 ppm of the starting materials in the ¹H-NMR spectrum of the compound 3 and the order of the peaks of the aromatic protons in the structure are 8.34, 8.22, 8.18, 8.02, 7.85, 7.68, 7.55 ppm. It supports the structure of compound 3. The peaks of the C atoms of C≡N group at 118.21 and 116.20 ppm in the ¹³C-NMR spectra of the compound 3 support the structure. Finally, the molecular ion peak at 263.60 [M]⁺ in the mass spectrum obtained for using the MALDI / TOF technique supports the structure of the new compound 3 (Supplementary Files Figure 1). The non-peripheral copper phthalocyanine compound 4 was prepared by cyclotetramerization of the dinitrile-derived compound 3. Non-peripheral tetra-substituted copper phthalocyanine compound 4 was synthesized in 40% yield by mixing anhydrous CuCl₂ and DBU in a dinitrile derivative compound n-pentanol (3) under nitrogen atmosphere for 24 hours at 160 °C. Non-peripheral tetra-substituted copper phthalocyanine compound In the IR spectrum of 4, the loss of C≡N vibrations of the phthalonitrile compound 3 at 2230 cm⁻¹ indicates that the non-peripheral tetra substituted copper

phthalocyanine compound was formed as a result of the cyclotetramerization reaction. The ¹H-NMR and ¹³C-NMR spectra of the compound 4 cannot be obtained because the copper (II) ion causes a paramagnetic electron distribution [23]. The most important illumination technique for the characterization of phthalocyanine compounds is characterization by UV-Vis spectrum. The fact that the phthalocyanine compounds have sharp colors that vary from blue to green and have an 18- π electron system will result in a sharp Q band in the 650-700 nm range and a weak B band (Soret band) around 350 nm. Observation of the Q-band of metallic phthalocyanine compounds in D_{4h} symmetry as a sharp peak [24] results from four equivalent nitrogen atoms capable of bonding with the metal atom present in the phthalocyanine ring. In the UV-Vis spectrum of the non-peripheral copper phthalocyanine compound 4 taken in DMSO at a concentration of 1x10⁻⁵ M at room temperature, the Q band appeared as a sharp single band at 687 nm. In addition, low intensity peaks were observed at 662 nm in the low wavelength portion of the Q band (Figure 2).

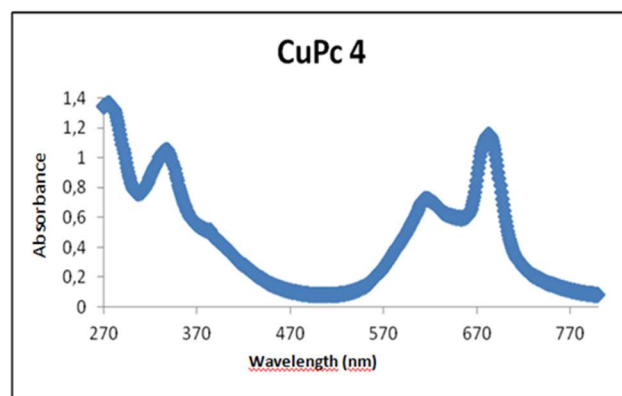


Figure 2 UV-vis spectrum of compound 4

Interpretation of the mass spectra of phthalocyanine compounds is not easy due to their high molecular weight and low solubility. However, the mass spectrum of the non-peripheral copper phthalocyanine compound 4 was taken using the MALDI-TOF technique and the molecular ion peak was observed at 1116.158 [M]⁺ (Supplementary Files Figure 2).

Water-soluble non-peripheral tetra-substituted copper phthalocyanine compound 5 was

obtained by dissolving compound 4 in chloroform and mixing with methyl iodide at room temperature for 1 day. There was not much difference between the IR spectrum of the water-soluble non-peripheral copper phthalocyanine compound and the IR spectrum of the water-insoluble non-peripheral copper phthalocyanine compound. A mass peak of 293.35 $[M-4I-H]^{+4}$ was observed in the mass spectrum of the compound 5 taken by the MALDI-TOF technique. In the UV-Vis spectrum of the water-soluble non-peripheral copper phthalocyanine compound 5 taken in DMF at a temperature of 1×10^{-5} M at room temperature, the Q band appeared as a sharp single band at 684 nm. In addition, low intensity peak was observed at 621 nm in the low wavelength portion of the Q band (Figure 3).

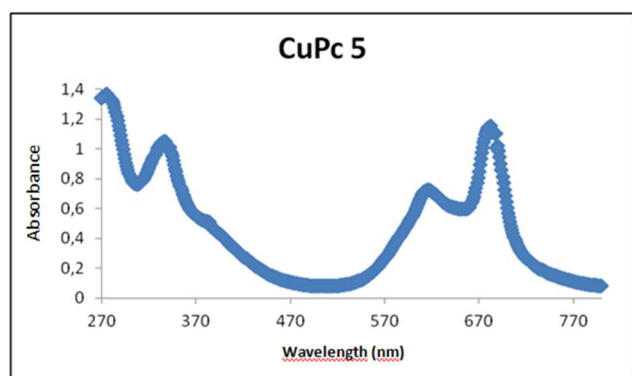


Figure 3 UV-vis spectrum of compound 5

3.2. Photocatalytic Studies

The photocatalytic activities of Cu(II) phthalocyanine 4 and its water soluble derivative 5 were investigated on 4-nitrophenol oxidation by photoreactor equipped with 8 pieces 16W lamps at room temperature. The single phase homogeneous solvent system was used for the compound 4 and the two phase heterogeneous solvent system was used for the compound 5 because of its water solubility and the reaction time was determined as 2 hours. The contents of the sample samples taken from the reaction medium for 30 minutes were examined by gas chromatography and product conversions were determined. According to these results, hydroquinone was determined as the main product and benzoquinone as the by-product.

When the same reactions were repeated at room temperature in the dark, it was determined that the 4-nitrophenol compound did not undergo any oxidation. The 4-nitrophenol photooxidation reaction wherein compound 4 was present as a photocatalyst was 94.4% after 2 hours; 4-nitrophenol photooxidation reaction with compound 5 as the photocatalyst 98.6% yield conversion was determined after 2 hours. When the product transformations were examined, 58.6% hydroquinone, 30.8% benzoquinone and 5% undetermined product were obtained with compound 4. Compound 5 yielded 62.3% hydroquinone, 33.3% benzoquinone and 3% undetermined product (Table 1).

Table 1
Experimental results with catalysts 4 and 5

Entry	Conversion (%)		Selectivity ^a		TON		TOF (h)	
	4	5	4	5	4	5	4	5
I	94.4	98.6	62.0	63.1	47	48	235	244
II (in dark)	-	-	-	-	-	-	-	-

Selectivity^a: Hydroquinone selectivity

At the end of the photooxidation studies, the amount of photodegradation of 4-nitrophenol was determined in the presence of both photocatalysts 4 and 5. For this, the equation given below is used.

$$X(t) = C_0 - C(t) / C_0$$

In the above equation, $X(t)$ is the molar fraction of 4-nitrophenol, C_0 , initial concentration and $C(t)$ is the concentration of 4-nitrophenol as a function of illumination time. This equation shows a similar profile to the photocatalytic degradation of other dyes [25-26]. For this purpose, 100 mL of a 0.025 M solution of 4-nitrophenol and 5 mg of solid catalyst were

reacted in a photo-reactor under visible light for 2 hours. During the photocatalytic reaction, all samples from the reaction medium were diluted with dichloromethane and injected into the GC apparatus. As a result, we observed that most of the 4-nitrophenol were degraded and the rate of degradation was fixed after 120 minutes. Data on photocatalytic degradation of 4-nitrophenol sensitized with both photocatalysts under visible light are presented in Figure 4.

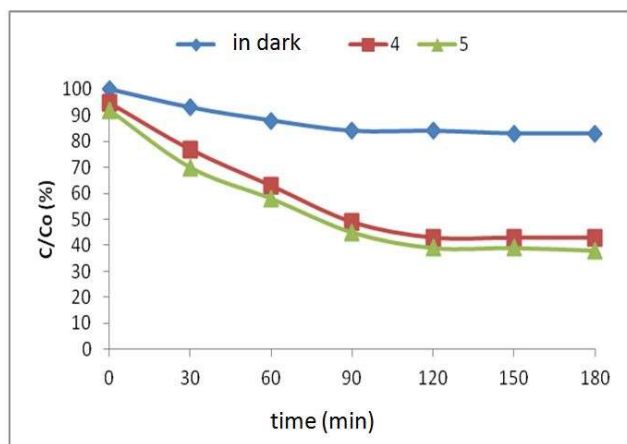


Figure 4 Effect of compound 4 and 5 on the degradation of 4-nitrophenol

Recycling studies have been carried out considering the importance of recyclability of photocatalysts for the environment. For this application, water-soluble non-peripheral copper (II) phthalocyanine compound 5 was used as photocatalyst. 100 ml of 0.015 M 4-nitrophenol solution, 5 mg of compound 5 were treated with UV irradiation in the photoreactor for 120 minutes. At the end of each reaction, the catalyst was removed by extraction with water 3 times and made ready for use in the new photooxidation reaction. It was determined that photocatalytic activity gradually decreased from 98.6% to 88.3% in reuse and 68% in 5th time use. This reduction can be explained by the fact that the phthalocyanine compound also degrades during photooxidation and forms different species. As a result, compound 5 gives 68% yield conversion even after 5 cycles (Figure 5).

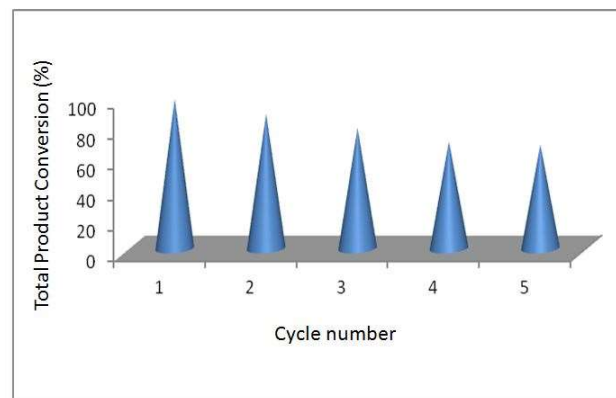


Figure 5 Recycling results with compound 5

Cobalt (II), iron (II), aluminum (III), copper (II) and metal-free phthalocyanines in which different groups have been substituted for the photooxidation of different pollutants have been studied [27-33]. Nyokong et al. Studied the photocatalytic activity of seven octane substituted thio and aryloxy palladium and platinum phthalocyanines in the breakdown of 4-nitrophenol [34]. According to the kinetic studies of this study, two reaction pathways have been identified for the degradation of 4-nitrophenol with phthalocyanine catalyst [34]. In another study by T. Nyokong, quantitative yields of singlet oxygen and photodissection of 4-nitrophenol in the presence of zinc tetrasulfatophthalocyanine ($ZnPcS_4$), zinc octacarboxyphthalocyanine ($ZnPcS_4(COOH)_8$) were investigated [35]. This study is important because it is the first study in this field to investigate the photooxidation of 4-nitrophenol using non-peripheral copper (II) phthalocyanine and its water-soluble derivative as photocatalyst without any oxygen source. The results of photocatalytic experiments can generate promising new research and micro-scale application.

In the literature, although many studies on the catalytic activities of phthalocyanine [36-41] are available, only a few have examined photooxidation reactions using UV radiation. Table 2 summarizes some of these literature.

Table 2
Phthalocyanines used as photocatalysts in photooxidation reactions of different organic pollutants

Catalyst	Substrate	Reaction Time (s)	Reaction Temperature (°C)	Oxidant	Conversion (%)	Reference
ZnPc ^a	Methyl orange-Orange G	10 min	Not reported	O ₂	Not reported	[27]
FePc ^b	Ethyl benzene	9	25	O ₂	>99	[28]
CoPc ^c	Malakhite green	30 dak	Not reported	-	99.2	[29]
CoPc ^d	2-mercaptoethanol	2	25	-	nr ^e	[30]
Metal freePc ^f	Sülfite ion	1	25	O ₂	70	[31]
CuPc ^g	4-nitrophenol	5	27	-	Not reported	[32]
CoPc ⁱ	4-chlorophenol	3	25	O ₂	99.99	[33]
ZnPc ⁱ					97.05	

ZnPc^a= 2-[5-(phenoxy)-izophthalic acid] 9(10), 16(17), 23(24)-tris (tertbutyl) phthalociyaninato Zn (II)

FePc^b= four branched tetra-amine FePc- organik framework

CoPc^c = Tetranitrocobalt phthalociyanin/ ternary chalcogenit

CoPc^d=Cobaltphthalocyanine/C₆₀

Metal free Pc^f= Metal free phthalocyanine /TiO₂

CuPc^g= Copper phthalocyanine / TiO₂CoPcⁱ= 2,9,16,23-tetrakis-(4- carboxyphenylsulphonyl) phthalociyaninato cobalt(II) / TiO₂

ZnPcⁱ= 2,9,16,23-tetrakis-(4- carboxyphenylsulphonyl) phthalociyaninato Zn (II) / TiO₂

nr^e=turnover number: 8.4

nr^h=quantum yield: 1.9

4. CONCLUSION

In the study, non-peripheral copper (II) phthalocyanine compound 4 and its water-soluble quaternized derivative 5 containing 3-(pyridin-4-yl)propane-1-oxo groups were synthesized for the first time and their structures were illuminated by spectroscopic data. Compounds 4 and 5 used as photocatalysts in the photooxidation reaction of 4-nitrophenol, an important environmental pollutant, yielded 94.4% and 98.6% yield conversion, respectively. Hydroquinone (main product) was obtained as benzoquinone (by-product) in the product distribution. The high conversion of 4-nitrophenol into non-toxic species by photooxidation makes the study important. The high product conversion and selectivity of the obtained photocatalysts in homogeneous and heterogeneous solvent systems make this study innovative in terms of shedding light on new studies on developing environmentally cleaner and more efficient systems.

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The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the author.

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The author declares that this document does not require an ethics committee approval or any special permission.

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