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Self-assembly of a symmetrical dimethoxyphenyl substituted Zn(II) phthalocyanine into nanoparticles with enhanced NIR absorbance for singlet oxygen generation

Govind Reddy^{a,b}, Enrico Della Gaspera^c, Lathe A. Jones^{b,**}, Lingamallu Giribabu^{a,d,*}

^a Polymers & Functional Materials Division, CSIR-Indian Institute of Chemical Technology, Hyderabad, 500007, T.S., India

^b Centre for Advanced Materials and Industrial Chemistry (CAMIC), School of Science, RMIT University, Melbourne, VIC, 3001, Australia

^c School of Science, RMIT University, Melbourne, VIC, 3000, Australia

^d Academy of Scientific and Innovative Research (AcSIR), Ghaziabad, 201002, India

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ABSTRACT

Phthalocyanine (Pc) molecules have been investigated as photosensitizers (PS) for singlet oxygen $(^{1}O_{2})$ generation because of their intense absorption bands in the near-infrared region, which is desirable for applications such as photodynamic therapy (PDT). Here, we have designed a sterically crowded symmetrical Zn(II) phthalocyanine (PC-1), which contains 8 dimethoxyphenyl substituents, and studied its optical properties. PC-1 exhibits good thermal stability, appropriate theoretical HOMO and LUMO energy levels and band gap which are suitable for optoelectronic applications. PC-1 was converted into hydrophilic nanoparticles (PC-1NPs) *via* a solvent exchange based self-assembly approach, which exhibited good water dispersability, as well as uniform morphology and size. Optical studies revealed a bathochromic-shift in absorbance in the NIR wavelength region and $^{1}O_{2}$ generation. These results suggest that PC-1 phthalocyanine is a potential candidate for photoinduced oxidative processes in biological and catalytic applications.

1. Introduction

The phenomenon of photoinduced triplet to singlet oxygen conversion in the presence of a photosensitizer has potential applications in fine chemical synthesis, waste water treatment, and photodynamic therapy (PDT) [1,2]. In this process, a photosensitizer absorbs light and is excited to its singlet state, accompanied by intersystem crossing (ISC) to a triplet state that can react with ground state triplet oxygen and generate singlet oxygen *via* energy transfer [3]. In recent years, the development of sensitizers has attracted significant attention to treat cancer *via* photodynamic therapy (PDT) [4–6]. For PDT to be effective, the photoactive molecule needs to exhibit a wide absorption range in the Near-IR because light of this wavelength range has much deeper penetration than visible. To this end, photoactive molecules such as porphyrins, BODIPY, chlorin, and phthalocyanine derivatives have been used due to their suitable optical properties [3,4,7]. Among these, phthalocyanine (Pc) based photosensitizers are potential candidates for PDT due to their high molar extinction coefficients ($\epsilon_{max} > 10^5 \text{ L mol}^{-1}$ cm⁻¹), wide range of absorption ($\lambda_{max} > 660$ nm) [7,8], and tunable photophysical and photochemical properties by means of synthetic modifications [9]. Recently, the clinical use of an Aluminium Pc derivative (Photosens®, Russia) has been approved [10]. Chen et al. reported a pH-responsive photosensitizer (ZnPc(TAP)₄) in which four 2,4,6-tris (N,N-dimethylaminomethyl)phenoxy moieties are appended to ZnPc. When the pH of the buffer medium was reduced from 8.0–6.0, the singlet oxygen generation efficiency of (ZnPc(TAP)₄) was enhanced from 0.32 to 0.55 [7,11,12]. However, one disadvantage of phthalocyanines is that they tend to aggregate in solution due to strong π - π interactions. This behaviour restricts to use of PCs in some applications as aggregation decreases the singlet oxygen efficiency/reactive oxygen species (i.e., ROS), reducing the overall performance of these materials, specifically in PDT. For this reason, the development of non-aggregating phthalocyanine photosensitizers has emerged [4,13]. Taking into account that aggregation of PCs occurs through interactions of adjacent conjugated

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^{*} Corresponding author at: Polymers & Functional Materials Division, CSIR-Indian Institute of Chemical Technology, Hyderabad, 500007, T.S., India.

^{**} Corresponding author.

E-mail addresses: r.govindreddy@gmail.com (G. Reddy), enrico.dellagaspera@rmit.edu.au (E.D. Gaspera), lathe.jones@rmit.edu.au (L.A. Jones), giribabu@iict. res.in (L. Giribabu).

structures, we designed the sterically constrained Zinc (II) 2.391,016, 172,324-octakis(3,4-dimethoxyphenyl)phthalocyanine macrocyclic derivative (PC-1 see Chart 1), as a potential photosensitizer for the generation of singlet oxygen. It has been previously observed that diamagnetic metal ions (ex: Zn^{2+} , Al^{3+} , and Ga^{3+}) boost the singlet oxygen production ability of phthalocyanine photosensitizers, leading to a long lifetime and high triplet quantum yield [14]. Herein we report the synthesis and characterization of nanoparticles of **Zn(II)** phthalocyanine (PC-1), and study the physical and optical properties, including singlet oxygen generation. Our findings unravel the influence of the dimethoxyphenyl substituents (sterically constrained) and diamagnetic Zn (II) metal present in the phthalocyanine on singlet oxygen generation, confirming the strategy of adding sterically constrained substituents to a phthalocyanine can lead to materials suitable for applications such as a photosensitizer for cancer treatment via photodynamic therapy. In addition, self-assembly of PC-1NPs present strong NIR absorbance this represents biological transparent window (550-950 nm). Furthermore, spectroscopy studies evidence that these NPs have the superior $^{1}O_{2}$ generation efficiency and good photostability.

2. Experimental section

2.1. Materials

3,4-dimethoxyphenylboronic acid (\geq 95.0 %), 4,5-dicholorophthalonitrile (99 %),1-pentanol (\geq 99 %), DMF (99.8 %), and [Pd(P(C₆H₅)₃)₄] (99 %) were purchased from Sigma Aldrich. HCl, Li metal and THF were supplied by TCI. These chemicals were used without further purification.

2.2. Synthesis

A Zn(II) octa(1,2-dimethoxyphenyl) phthalocyanine system (**PC-1**) was synthesized and characterized as per our previously reported procedure [15].

2.2.1. Nanoparticle synthesis

PC-1 nanoparticles prepared *via* the solvent exchange approach, which has been previously reported in the literature, with slight modification [16,17]. Approximately 1 mg of **PC-1**was dissolved in 1 ml of THF solvent. This solution was added to10 ml of deionized water (DI-Water) from a syringe under magnetic stirring. The THF in the solvent mixture was then removed by nitrogen bubbling.



2.3.1. XPS

X-ray photoelectron survey spectra of PC-1 powder were analysed with a Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer (XPS). The binding energy (B.E) of the peaks of interest were adjusted using an internal standard peak of C (1 s) predicted at 284.8 eV.

2.3.2. TGA

The thermal stability, and weight loss during heat treatment of the PC-1 PC-1 were studied by thermo gravimetric thermal analysis (TGA; Mettler Toledo, Star-e system) performed from 40 to 850 °C with scan rate of 10 °C/min in a N_2 atmosphere.

2.3.3. BET

The BET surface area, pore volume and pore sizes were determined by using the N_2 adsorption-desorption method using BEL Sorb II Instruments, Japan at liquid nitrogen temperature. Before the measurement the samples were degassed at 200 $^\circ C$ for 2 h.The surface area was determined through the Brunauer – Emmett – Teller (BET) method. The average pore volume and pore size were measured by Barrett – Joyner–Halenda (BJH) method.

2.3.4. Theoretical simulations

The optimized geometries of PC-1 photosensitizer was carried out using the B3LYP hybrid functional and 6-31(d,p) basis set in a gas phase withGaussian 09 computational software. Ground state properties were calculated using Density Functional Theory (DFT) in the gas phase and excited state properties were implemented using Time Dependent Density Functional Theory (TD-DFT) in PCM solvation model with THF solvent. The software GaussSum3.0 was used to analyze the major portions of the absorption spectra and to interpret the molecular orbital contribution.

2.3.5. TEM

Transmission electron micrographs (TEM) images of the PC-1 nanoparticles drop casted on a carbon-coated copper grid were captured at 100 kV on a JEOL 1010 TEM. The grids were prepared a day before imaging and dried overnight under nitrogen.

2.3.6. DLS

Dynamic Light scattering measurements were determined using Zetasizer Nano ZS (Malvern Instrument Ltd., UK).

2.3.7. Optical measurements

Optical absorption and emission spectra were recorded on a Cary 60 UV–vis Spectrophotometer and Horiba FluoroMax® 4 fluorometer, respectively.

2.3.8. Singlet oxygen quantum yield measurement

PC-1 or **PC-1NPs** was mixed with 1,3-Diphenylisobenzofuran (DPBF, $6x10^{-5}$ mol/L) as the ${}^{1}O_{2}$ probe in DMF (**PC-1**) or Water (**PC-1NP**) respectively. The maximum absorption intensity of DPBF was around 1.2–1.40. The absorbance maximum of **PC-1** or **PC-1NPs** was adjusted to be ~0.3. Then the samples were irradiated with 625 nm LED (Thorlabs) with power intensity 2.1 mW/cm² at different intervals of time from 0 to 60 s. The absorbance change of DPBF at 418 nm was monitored by UV–vis spectrophotometer over time. Methylene blue ($\Phi_{\Delta} = 0.49$ in DMF) is used as a reference to calculate ROS production yield of **PC-1** or **PC-1NPs**.

3. Result and discussion

The synthesis of Zn(II) 2,391,016,172,324-octakis(3,4-dimethoxyphenyl)phthalocyanine (**PC-1** see **Chart-1**) was slightly modified from our previous report [15]. **PC-1** macrocycle was synthesized *via*

Chart 1. Chemical structure of PC-1 compound.

cyclotetramerization of 4,5-bis(3,4-dimethoxy) phthalonitrile and Zn $(OAc)_2$ in 1-pentanol using DBU as a catalyst under reflux (8 h). The metallophthalocyanine (**PC-1**) was isolated by silica gel column chromatography using DCM:MeOH (95:5) as the eluant. The structure was confirmed by MALDI-TOF (see **Figure S1(a)** and isotropic pattern **S1(b)**) with a major peak at m/z-C₉₆H₈₀N₈O₁₆Zn: 1666.632 [calc. m/z:1665.50]. Also, other calculated (see **S1(c)**) isotropic peaks at m/z1664.514, 1665.514, 1666.5230, 1667.5094, 1668.5225, 1669.4957, 1670.5177 are good agreement with experimental values m/z at 1664.600, 1665.409, 1666.636, 1667.5840, 1668.629, 1669.641, 1670.647 (see **S1(b)**).

3.1. XPS and XRD studies

PC-1 was studied by XPS to confirm the presence of the expected elements, the oxidation state of zinc metal in its central cavity, and the effect of the peripheral units on the binding energies (Fig. 1(a)). Fig. 1 (b) displays the XPS spectra of the Zn 2p region to study the metal present in the **PC-1** ring, showing two intense peaks. The peak at lower binding energy of 1021.35 eV represents $2p_{3/2}$, and the higher binding energy peak at 1044.33 eV represents $2p_{1/2}$. The Zn $2p_{3/2}$ peak confirms the existence of Zn metal in +2 state in the **PC-1** macrocycle [18,19].

The main N (1 s) peak is at 399.19 eV. This main peak is accompanied by a shoulder (see Fig. 1(c)) that represents the two chemical environments of N in **PC-1** being (a) four nitrogen atoms bond with two carbon atoms (C—N = C) and (b) the four nitrogen atoms coordinated with the Zn metal [20]. Three distinctive oxygen O (1 s) peaks (as shown in Fig. 1(d) and Table 1) were observed, attributed to meta and para OMe's of the peripheral substitution of dimethoxyphenyl group on PC ring, with the other peak should be related to adsorbed water/moisture. **PC-1** shows the predominate C(1 s) peak at 284.69 eV, while the electron donor dimethoxyphenyl phthalocyanine shows (see **Figure S2**) a

Table 1

XPS	elemental	composition of PC-1.	

Elements in PC-1	Zn(2p)	N (1 s)	O (1 s)	C(1 s)
Binding energy (eV)	1044.33 (2p _{1/2}) 1021.35 (2p _{3/2})	399.19 397.98	533.63 532.60 531.05	286.24 284.69

peak at 286.24 eV [21,22]. Powder X-ray diffraction survey of **PC-1** revealed an amorphous peak at $2\theta = 25$, confirming a lack of crystallinity in powder form, indicating that the bulky 3,4-dimethoxyphenyl substituents may hamper the close packing of the **PC-1** units (**Figure S3**). This is an initial indication the introduction of bulky 3,4-dimethoxyphenylgroups at the peripheral positions of phthalocyanine are effective for the minimization of **PC-1** aggregation [23,24].

3.2. Thermal studies

We employed TGA to determine the thermal stability of the synthesized phthalocyanine (**PC-1**), as shown in Fig. 2. It can be seen that three-step weight loss occurs between 100 and 800 °C. The first weight loss step from 200 to 300 °C is related to the loss of trapped solvent or moisture present in the **PC-1** powdered sample. The second weight loss step from 430 to 530 °C is due to the core of the PC complex starting to decompose and the third weight loss at >550 is due to complete decomposition of **PC-1** phthalocyanine [25]. Thus, **PC-1** phthalocyanine exhibited excellent thermal stability up to 450 °C and it thus suitable for high temperature reactions.

Additionally, we undertook N₂ sorption and thermal stability studies for **PC-1**. The N₂ adsorption–desorption isotherm of **PC-1** is shown in **Figure S4**, where a rapid N₂ uptake in the pressure region P/P0 > 0.1 (of 0.45–0.98) was noted, typical of a type-IV isotherm, characteristic of a



Fig. 1. (a) XPS survey spectrum, (b) Zn2p core level spectrum (c) N1 s core level spectrum and (d) O1 s core level spectrum of the PC-1 phthalocyanine.



Fig. 2. Thermal stability (TGA/DTA plots) of PC-1.

porous structure (**Figure S4(a**)). The Brunauer – Emmett – Teller (BET) [26] surface areas of the as synthesized material **PC-1** was determined as $45 \text{ m}^2 \text{ g}^{-1}$ with the pore volume estimated to be 0.197 cm³ g⁻¹. The average pore size distribution, as estimated by using the Barrett – Joyner–Halenda (BJH) approach, suggests narrow pore size distributions (**Figure S4(b**)) with the pore size estimated to be about 7.74 nm. These parameters (see **Table S1**) are in good agreement with previously reported (phthalocyanine based) heterogeneous and photo catalysts [27, 28]. In general, a high specific surface area of photocatalysts can create additional surface-active sites and make charge carrier transport easier, leading to an improvement in catalytic performance.

3.3. DFT calculations

DFT optimized structures were generated to probe the effect of the sterically hindering groups on aggregation, and show that the OMe groups on the 3,4-dimethoxyphenyl orientate either below or above the planes of the phthalocyanine ring to hamper aggregation.

Density functional theory (DFT) geometry optimisations were carried out using B3LYP/6-31 G(d,p) level theory to understand the geometric and electronic structure of the PC-1 molecule in the Gaussian 09 program package [29]. Top and side views of the PC-1 optimized molecular structures are shown in Fig. 3 (a), where it can be observed that the dihedral angle between adjacent dimethoxyphenyl groups is \sim 5.4 °C. The side view of **PC-1** shows quiet clearly how π - π stacking between adjacent planar PC cores would be difficult due to steric hindrance of the dimethoxyphenyl groups. The optimized frontier molecular orbitals as demonstrated in Fig. 3(b), for PC-1 compound, its highest occupied molecular orbitals (HOMOs) were mainly spread on the phthalocyanine ring and dimethoxyophenyl donor group. While LUMOs were slightly extended to the phenyl bridge besides the spreading on PC ring, due to the presence of the electron deficit tetrapyrrolic cavity with the donor and accepter, being dimethoxyphenyl moiety and phthalocyanine ring respectively. PC-1 displayed the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) level of -4.75 and -2.65 eV, respectively [30]. Consequently, the narrow bandgap (2.1 eV) of PC-1 is indicative of photo absorption in the long-wavelength region, which is confirmed by elucidation of the TD-DFT absorption spectra of **PC-1** simulated at b3lvp/6-31 g(d,p) level theory with the PCM solvation model in THF. Fig. 3 (c) shows both the theoretical and experimental UV-vis spectra, confirming that PC-1 have the ability to absorb broadly in the visible spectrum. Simulated DFT and TD-DFT parameters of PC-1 are presented in Table 2 and Table S2. As depicted in Figure S5, the negative electrostatic potential (ESP) is located on the methoxy (OMe) groups of the dimethoxyphenyl moieties, whereas the most positive ESP is around the phthalocyanine ring. All theoretical results suggest that a narrow HOMO-LUMO gap led to significant shift of the Q and B bands to the visible region (see Fig. 3 (c)) and reveal the PC-1 is suitable for use as a photosensitizer in the therapeutic window [31].



Fig. 3. Theoretical studies of PC1(a)Optimized structure (b) Frontier molecular orbitals (c) TD-DFT UV-vis spectra comparison with experimental.

Table 2	2			
Optical	and	theoretical	properties	of PC-1

Property	^a λ _{max} (nm) absorption			^a λ _{max} (nm) emission	^a Φ _Δ (%)	НОМО*	LUMO*	Eg*	Ref.
ZnPC PcA1 ^d	670 695			681 708	52 (32) ^b 19	5.16	2.98 -	2.18 -	[39] [10]
PcA2 ^d SiPc-Pt-HA ^e	700 ~700			704 ~705	77 24	_	_	_	[10] [40]
SiPc-Pt ^e	~700			~705	15	-	-	-	[40]
PC-1	in THF 696	NPs in water ~550–1050 (broad)	on film ~550–950 (broad)	701	83 (5) ^c	-4.75	-2.65	2.1	Present work

*Data from DFT, ^a in DMF, ^b 0.1 M CTAC/H₂O^c H₂O, ^dPc compounds peripherally substituted with amino groups (**PcA1** and **PcA2**) ^eplatinum(II) conjugated silicon(IV) phthalocyanine (SiPc–Pt) and its hyaluronic acid (SiPc–Pt–HA) formulated nanoparticles.

3.4. Nanoparticles synthesis and characterization

In general alkoxy substituted phthalocyanines are non-aqueous, which is tough for biological applications. Nanoparticle (NP) carriers have been shown to have increased water solubility and stability as photosensitizers than pure compounds, especially for applications in tumour tissue. Furthermore, NP carriers provided benefits including longer circulation in the blood and higher accumulation of photosensitizers at disease sites [32]. For this reason, we have converted **PC-1** into a NP suspension by the solvent-exchange approach as shown in Scheme 1. During this process, **PC-1** would assemble into NPs as earlier reported [16,17]. **PC-1** powder was dissolved in tetrahydrofuran (THF) solution and then quickly injected into DI-water under sonication. After 10 min, the THF was removed from the aqueous media by nitrogen bubbling at room temperature. A transparent solution was obtained which contained hydrophilic **PC-1NPs**.

Fig. 4 (a) shows the size distribution of the NPs, measured by using dynamic light scattering (DLS) technique [33] of this PC-1NP solution, where the average size of the NPs was found to be ~152 nm with a PDI of 0.16. Additionally, the shape and size of the NPs were examined by transmission electron microscopy (TEM). PC-1 molecules self-assembled through non-covalent interactions such as π - π stacking (The bulky substituents on PC-1 will reduce π - π interactions preventing massive aggregation, but some π - π stacking will still occur, causing NP formation) and hydrophobic – hydrophobic interactions between molecules, which initiates nucleation and growth of PC-1 into well-defined and homogeneous nanospheres with size around 100 nm as shown in Fig. 4 (b) and S6. The size and shapes of these nanoparticles should improve the dispersibility of PC-1 in water, which would be beneficial, for example, for the enhanced permeability and retention (EPR) of PC-1 NPs in a tumour site [17,34].

3.5. Optical and singlet oxygen studies

To study the optical properties of **PC-1** and **PC-NPs**, both UV – Vis and fluorescence (FL) spectra were collected. The absorption spectra of **PC-1** in THF, nanoparticles in DI-water, as well as **PC-1** films on glass, are shown in Fig. 5 (a), demonstrating the two typical distinctive bands of **PC-1** phthalocyanine macrocycle: the B band, situated in the UVregion between 300 and 400 nm, and the Q band, in the region between 550 and 1000 nm. As shown in Fig. 5 (a), the Q bands are viewed as doublets at 627 and 696 nm, which could be interpreted as π - π * transitions between bonding and antibonding molecular orbitals [9, 30]. In solution the intensity of this band is very less, whereas in case of thin film and nano particles the intensity of this band raises and merge with the band at 697 nm. As a result a broad Q band was observed in thin film and in nano particle, as was the case in our previous reports [35,36]. This was even predicted from DFT the optimized structures are shown in Fig. 3 (a). When compared to PC-1 in THF, an extensive broadening can be observed for the Q band of PC-NPs in DI-water, displaying a substantial red-shifted absorbance onset (~950 nm), which is in the biological transparent window. Similarly, absorption in the thin film displays a broad Q-band with the wavelength region of 550–1000 nm. These spectra are indicative of strong intramolecular and intermolecular π - π interactions of phthalocyanine macrocycles.

Furthermore, the fluorescence of the **PC-1NPs** was completely quenched (**Figure S7**) compared to **PC-1** (in THF), which is in good agreement with typical PCs in their aggregated state. Aggregation is bad for stability/processability of the material, but good for its properties. So, we found a way to get the best of both worlds, having a small extent of controlled aggregation (NPs) avoiding large scale precipitates. This aggregation behaviour can stop photothermal agents (PTAs) losing absorbed energy *via* fluorescence emission and intersystem crossing (ISC) energy transfer, which is advantageous for high photothermal conversion efficiency [34].

Singlet oxygen is one of the key cytotoxic agents that are generated by irradiation of photoactive materials during PDT. Here, we measured the singlet oxygen generation efficiencies (Φ_{Δ}) of the **PC-1** and its NPs in DMF and water by using 1,3-diphenylisobenzofuran (DPBF) as a singlet oxygen trapping reagent, and methylene blue ($\Phi_{\Delta} = 0.49$ in DMF) as the reference [37,38]. The phthalocyanine sensitizer with DPBF was irradiated with 625 nm LED with a power intensity of 2.1 mW/cm² at different intervals of time from 0 to 60 s. As shown in Fig. 5 (**b**–**c**), the absorbance of DPBF at 420 nm for **PC-1NPs** and at 414 nm for **PC-1** diminished significantly. From the Fig. 5(**c**), it can be observed that the absorption intensity of DPBF declines drastically with the increasing irradiation time, indicative of excellent ¹O₂ generation ability of **PC-1**, superior to **PC-NPs**. The calculated singlet oxygen quantum yields of **PC-1** and **PC-1NPs** were determined to be 83 % and 5%, respectively (see Table 2), which indicates that **PC-1** and **PC-1NPs** present excellent



Scheme 1. Solvent-exchange method for preparation of PC-1NPs.



Fig. 4. (a) The dynamic light scattering (DLS) histogram of PC-1NPs (Inset: The photographs of PC-1NPs in deionized water ($c = 100 \mu g/mL$) (b) The transmission electron microscopy (TEM) image of PC-1NPs.



Fig. 5. a)UV–vis spectra of **PC-1** in THF(black), NPs in water (red)and on Film (blue) **b**) & **c**) Absorption changes during the DBPF oxidation in the presence of **PC-1**&**PC-1NPs** under illumination with 625 nm LED (2.1 mW/cm²) **d**) DPBF absorbance **PC-1**&**PC-1NPs** solutions *versus* irradiation time (seconds).

singlet oxygen generation ability when compared to previous literature data (see Table 2) [10,39,40]. For instance as in case of Zinc phthalocyanines (Zn PC), the singlet oxygen quantum yield was reported 52 % in DMF solvent [39]. On the other hand, axially substituted hyaluronic acid formulated nanoparticles containing a platinum(II) conjugated silicon(IV) phthalocyanine has showed poor singlet oxygen quantum yields [40]. Singlet oxygen efficiency calculations of phthalocyanine nanoparticles are rare in the literature due to inherent light scattering phenomena associated with nanoparticles in solution (H₂O) leads to significant experimental error [31]. As a consequence of aggregation, the ${}^{1}\Phi_{\Delta}$ values in water are lower since this decreases the lifetime of the excited state and photosensitization efficiency, due to enhanced radiationless decay, this may be a reason for the low singlet oxygen generation efficiency of **PC-1NPs** [41]. Even though, lutetium texaphyrin

exhibited a low ${}^{1}\Phi_{\Delta}$ of 11 % have been used for clinical application in PDT [42]. At the end it should also be noted that our **PC-1NPs** exhibited excellent photostability (*see* **Figure S9**) under continuous irradiation of 30 min with the same LED and power intensity.

4. Conclusions

In summary, **PC-1** displayed a high surface area, pore volume, with small pore size and acceptable thermal stability. Then, we have prepared and self-assembled phthalocyanine nanoparticle photosensitizers using **PC-1** through the solvent-exchange method. The corresponding **PC-1**NPs displayed appropriate size and morphology for PDT applications. Furthermore, **PC-1NPs** showed significant red-shifted absorbance to the biological transparent window (550–950 nm). Additionally, **PC-1NPs**

displayed excellent photostability, and ${}^{1}O_{2}$ generation ability. This leads to **PC-1** being a promising candidate for photoinduced oxidative processes in biological and catalytic applications.

Author statement

Govind Reddy Synthesis, characterization, Spectroscopy Govind Reddy Synthesis, characterization, Spectroscopy Enrico Della Gaspera Singlet oxygen measurements Lathe Jones Manuscript preparation and supervision Lingamallu Giribabu Manuscript preparation and supervision

Declaration of Competing Interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2020. 113123.

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