Synthesis of conformationally flexible porphyrin tweezers and their application in generation of singlet oxygen

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Abstract

The selected porphyrin acids such as 5-(4'-carboxyphenyl)-10,15,20-triphenylporphyrin, 5-(4'-carboxyphenyl)-10,15,20-tris-(4"-chlorophenyl)porphyrin, 5-(4'-carboxyphenyl)-10,15,20-tris-(4"-tertbutylphenyl)porphyrin and 5-(4'-carboxyphenyl)-10,15,20-(4"-pyridyl)porphyrin have been synthesised by reaction of two aldehydes with pyrrole in propionic acid. The coupling of 5-(4'-carboxyphenyl)-10,15,20-triarylporphyrins with pentan-1,5-diol in presence of EDC and DMAP give unsymmetrical bisporphyrins, which were metallated with zinc acetate to give different porphyrin tweezers. The singlet oxygen efficiency of porphyrin tweezers as photosensitizers have been quantified by monitoring the transformation of 1,3-diphenylisobenzofuran (DPBF) to 1,2-dibenzoylbenzene by UV-visible spectroscopy. The quantum yield of formation of singlet oxygen for different porphyrin tweezers have been examined. The electron withdrawing group containing porphyrin tweezer is a better photosensitizer than electron donating group in generation of singlet oxygen.

Keywords: Porphyrin tweezers, photosensitizers, energy transfer, 1, 3-diphenylisobenzofuran, singlet oxygen.

Introduction

The photochemical properties of porphyrins not only display efficient light absorption but also produce good singlet-oxygen quantum yields. Singlet oxygen is basically an excited form of the molecular oxygen which makes it highly reactive. Properties of this highly reactive form of molecular oxygen have caught the attention of researchers looking to utilize singlet oxygen for applications in photo-oxidation photodynamic therapy of cancer and polymer science **[1-5]**.

The chemically bound porphyrin dimers are widely used in studies on mechanisms of intermolecular energy and electron transfer in modelling of a dimer in bacterial photosynthetic reaction centre and antenna chlorophyll in light harvesting pigment-protein complexes, in selective binding of oligosaccharides and in seeking new sensitizers for photodynamic therapy (PDT). Photodynamic therapy (PDT) unites the application of light with the administration of a photosensitizer. The photosensitizer gets excited upon irradiation with light at a suitable wavelength, which converts ground-state triplet oxygen into cytotoxic singlet oxygen which ultimately leads to cell death **[6]**. Thus after surgery, chemo- and radiotherapy, PDT is the fourth most widely used strategy for cancer treatment. Several photosensitizers currently in clinical trial for PDT are based on porphyrins, including Photofrin which is a complex mixture of non-conjugated porphyrin dimers with other oligomers. Therefore synthesis and study of porphyrin dimers is an attractive and challenging field of research yet to be fully exploited **[7-10]**.

In light of aforementioned, simple porphyrin dimers called "porphyrin tweezers" have been synthesized and utilized in generation of singlet oxygen. The two metallated porphyrin units in a tweezer are covalently linked to one another through certain groups called spacers which can be rigid or flexible. These tweezers have taken the attention of researchers, over the last several decades and continue to be actively pursued today. With different porphyrin units and different spacers versatility to the design, structure and function of porphyrin tweezers can be added and the advantage of the ability of porphyrin tweezers to act as photosensitizers and to convert dissolved triplet oxygen into singlet oxygen can be withdrawn **[11-17]**.

Thus, new conformationally flexible porphyrin tweezers having different electronic properties have been synthesized and their application as photosensitizer has been studied. As a porphyrin dimer, tweezers are prone to an increased light harvesting as compared to porphyrin monomers. The alkyl spacer contributes to the conformational flexibility and adaptability of the

synthesized photosensitizer. The tweezer has two binding sites so along with binding to some biomolecules such as amino acids, diols, ligands and aromatic guest molecules the tweezer can be exploited as an active probe for generation of singlet oxygen **[18-19].**

Experimental

Materials details

Pyrrole and aromatic aldehydes were purchased from Aldrich and used without further purification. Solvents were purchased from Merck and dried according to literature prior to use. Reactions were monitored by thin layer chromatography (TLC) and products were purifed by column chromatography using activated neutral aluminum oxide.

Characterizations

^{1}H NMR spectra were recorded in $CDCl_3$ using a Jeol 400 MHz NMR spectrometer. Chemical shifts are expressed in parts per million (ppm) relative to tetramethylsilane (TMS, 0 ppm) as an internal standard. Coupling constants (J) are reported in Hertz (Hz). ^{13}C NMR spectra were recorded on Jeol 100 MHz NMR spectrophotometer. Infrared spectra were recorded on a Perkin Elmer IR spectrometer and absorption maxima are given in cm^{-1}. A Perkin Elmer UV-Vis spectrophotometer was used for UV measurements.

Synthesis of 5-(4'-carbonylphenyl)-10,15,20-triphenyl Porphyrin (1)

A solution of benzaldehyde (3.9 mL, 39 mmol) and *p*-formylbenzoic acid (1.95g, 13 mmol) in propionic acid (250 mL) was heated to reflux at 150°C. To this solution freshly distilled pyrrole (3.6 mL, 52 mmol) was injected slowly. This reaction mixture was refluxed for 2h. The reactant was cooled to room temperature. The obtained precipitate was filtered, washed and purified by column chromatography to give 5-(4-carboxyphenyl)-10,15, 20-triphenyl porphyrin as second fraction.

Yield: 6.5%, **UV-Vis [$CHCl_3$, λ_{max} (nm) (log ε)]:** 418 (6.18), 515(4.92), 550 (4.61), 590 (4.47), 646 (4.30). **^{1}H NMR (400 MHz, $CDCl_3$) δ ppm**: 8.77 (m, 8H, pyrrolic), 8.43 (d, J = 8.54 Hz, 2H), 8.28(d, J = 8.54 Hz, 2H), 8.14 (m, 6H), 7.70 (m, 9H), -2.84 (s, br, 2H). **MALDI-TOF** m/z Calcd for $C_{45}H_{30}N_4O_2$, 658.2369; Found 658.2368 [M+].

Synthesis of 5-(4'-carbonylphenyl)-10,15,20-tris-(4''-chlorophenyl) Porphyrin (2)

A solution of *p*-chlorobenzaldehyde (5.48 g, 39 mmol) and *p*-formylbenzoic acid (1.95g, 13 mmol) in propionic acid (250 mL) was heated to reflux at 150°C. To this solution freshly distilled pyrrole (3.6 mL, 52 mmol) was injected slowly. This reaction mixture was refluxed for 3h. The reactant was cooled to room temperature and allowed to stand overnight. The obtained precipitate was filtered, washed and purified by column chromatography to give 5-(4-carboxyphenyl)-10, 15, 20-triphenyl porphyrin as second fraction.

Yield: 4%, **UV-Vis [$CHCl_3$, λ_{max} (nm) (log ε)]:** 419 (5.95), 515(4.51), 549 (4.25), 558(3.82), 645(3.80). **^{1}H NMR (400 MHz, $CDCl_3$) δ ppm**: 8.81 (m, 8H, pyrrole-H), 8.46 (d, 2H, carboxyphenyl-H, J = 7.63), 8.30 (d, 2H, carboxyphenyl-H, J = 7.63), 8.11 (d, 6H, J = 7.32, 4-chlorophenyl-H), 7.72 (d, 6H, J = 7.32, 4-chlorophenyl-H), -2.9 (s, 2H, NH-H). **MALDI-TOF MS**: m/z Calcd for $C_{45}H_{27}Cl_3N_4O_2$; 760.122 Found 760.125 [M+].

Synthesis of 5-(4'-carboxyphenyl)-10,15,20-tris-(4''-tert-butylphenyl)porphyrin (3)

A solution of 4-tert-butylbenzaldehyde (6.3 g, 39 mmol) and *p*-formylbenzoic acid (1.95 g, 13mmol) in propionic acid (250 mL) was heated to reflux at 150°C. To this solution freshly distilled pyrrole (3.6 mL, 52 mmol) was injected slowly. This reaction mixture was refluxed for 3h. The reactant was cooled to room temperature and allowed to stand overnight. The obtained precipitate was filtered, washed and purified by column chromatography to give 5-(4-carboxyphenyl)-10,15,20-triphenyl porphyrin as second fraction.

Yield: 4%, **UV-Vis [$CHCl_3$, λ_{max} (nm) (log ε)]:** 421 (5.76), 518 (4.39), 550 (4.17), 595 (3.90), 645 (3.90). **^{1}H NMR (400 MHz, $CDCl_3$) δ ppm:** 8.82 (m, 8H, pyrrole-H), 8.44 (d, 2H, carboxyphenyl-H, J = 7.96), 8.32 (d, 2H, carboxyphenyl-H, J = 7.96), 8.15 (d, 6H, J = 7.32, 4-tertbutylphenyl-H), 7.75 (d, 6H, J = 7.32, 4-tertbutylphenyl-H), 1.6 (s, 27H, 4-tertbutyl-H), -2.73 (s, 2H, NH–H). **MALDI-TOF MS**: m/z Calcd for $C_{57}H_{54}N_4O_2$, 826.4247; Found, 826.4242 [M+].

Synthesis of 5-(4'-carboxyphenyl)-10, 15, 20-tris (4''-pyridyl) porphyrin (4)

Formylbenzoic acid (635 mg, 4.23 mmol, 1.2 equiv) and 4-pyridinecarbaldehyde (1.00 mL, 10.5 mmol, 2.9 equiv) were added to refluxing propionic acid (100 mL). After the dissolution of the 4-formylbenzoic acid, pyrrole (1.00 mL, 14.5 mmol, 4 equiv) was added dropwise (ca. 4 min) to the mixture. The reaction mixture was then refluxed for 2h. The solvents were distilled under reduced pressure, and the crude material was taken into chloroform/methanol (85:15) and directly chromatographed on a silica column using a mixture of chloroform/methanol (85:15) as eluent. The second fraction gave porphyrin.

Yield: 6%. **UV-Vis [DMSO, λ_{max} (nm) (log ε)]:** 418 (6.14), 513 (5.04), 545 (4.80), 587 (4.73), 642 (4.55). **^{1}H NMR (400 MHz, DMSO-d^6) δ ppm:** −3.00 (s, 2H, NH), 8.27 (d, 6H, J = 5.6 Hz, 5Py), 8.37 (m, 4H, mPh+oPh), 8.90 (d, J = 2.4 Hz, 8H, βH), 9.05 (d, 6H, J = 5.6 Hz, 1H, 6Py). **MALDI-TOF MS**: m/z Calcd for $C_{42}H_{27}N_7O_2$ 838.495; Found, 838.498 [M+].

Synthesis of 1,5-bis [(5'-(4''-carboxyphenyl)-10', 15', 20'-triphenyl) zinc porphyrinyl] pentanoate (5)

To a solution of 5-(4'-carboxyphenyl)-10, 15, 20-triphenylporphyrin (46 mg, 71.15 µmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 13.6 mg, 71.15 µmol), and dimethylaminopyridine (DMAP, 8.7 mg, 71.15 µmol) in anhydrous CH_2Cl_2 (5mL), 1,5-pentanediol (2.0 mg, 19.32 µmol) was added. The reaction mixture was stirred at room temperature for 23h. It was purified on silica gel to afford porphyrin dimer as a dark purple solid. The dimer was dissolved in chloroform (2 mL) and stirred with $Zn(OAc)_2.2H_2O$ (132 mg, 0.7mmol) for 12h at room temperature. The solution was applied directly to silica gel column to afford the tweezer as deep magenta powder.

Yield: 60%, **UV-Vis [$CHCl_3$, λ_{max} (nm) (log ε)]:** 419 (5.91), 548 (4.47), 588 (3.60). **^{1}H NMR (400 MHz, $CDCl_3$) δ ppm:** 1.45 (m, 6H, CH_2) ,4.27 (4H, -OCH_2), 7.75(m, 18H, (m,p)-H-phenyl), 8.22 (m, 12H, o-phenyl), 8.28(d, J = 7.96Hz, 4H, benzoate), 8.36 (d, J = 7.96Hz, 4H, benzoate), 8.86-8.87 (16H, Pyrrole). **MALDI-TOF MS:** m/z Calcd for $C_{95}H_{64}N_8O_4Zn_2$ 1508.3695; Found, 1508.3694 [M+].

Synthesis of 1,5-bis [5'-(4''-carboxyphenyl)-10',15',20'-tris-(p-chlorophenyl) zinc porphyrinyl] pentanoate (6)

To a solution of 5-(4'-carboxyphenyl)-10,15,20-tris-(p-chlorophenyl) porphyrin (27 mg, 35.6 µmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 6.8 mg, 35.6 µmol), and dimethylaminopyridine (DMAP, 4.3 mg, 35.6 µmol) in anhydrous CH_2Cl_2 (5mL), 1,5- pentanediol (1.0 mg, 8.6 µmol) was added. The reaction mixture was stirred at room temperature for 23h. It was purified on silica gel to afford porphyrin dimer as a dark purple solid. The dimer was dissolved in chloroform (1 mL) and stirred with $Zn(OAc)_2.2H_2O$ (68 mg, 0.35mmol) for 12h at room temperature. The solution was applied directly to silica gel column to afford the tweezer as deep magenta powder.

Yield: 50%, **UV-Vis [$CHCl_3$, λ_{max} (nm) (log ε)]:** 420(5.9), 549 (3.60), 587 (2.78). **^{1}H NMR (400 MHz, $CDCl_3$) δ ppm:** 1.43 (m, 6H, CH_2), 4.23 (4H, -OCH_2) 7.67 (d, J = 7.64, 12H, Ar-H), 8.06 (d, J = 7.64, 12H, Ar-H), 8.20 (d, 4H, J = 7.64) 8.31 (d, 4H, J = 7.64), 8.84 (m, 16H, β-pyrrolic). **MALDI-TOF MS:** m/z Calcd for $C_{95}H_{58}Cl_6N_8O_4Zn_2$, 1712.1295; Found, 1712.1298 [M+].

Synthesis of 1,5-bis[5'-(4''-carboxyphenyl)-10', 15', 20'-tris-(p-tertbutylphenyl) zinc porphyrinyl] pentanoate (7)

To a solution of 5-(4'-carboxyphenyl)-10,15,20-tris-(4'-tertbutyl-phenyl) porphyrin (30 mg, 35.6 µmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 6.8 mg, 35.6 µmol), and dimethylaminopyridine (DMAP, 4.3 mg, 35.6 µmol) in anhydrous CH_2Cl_2 (5mL), 1,5-pentanediol (1.0 mg, 8.6 µmol) was added. The reaction mixture was stirred at room temperature for 23h. It was purified on silica gel to afford porphyrin dimer as a dark purple solid. The dimer was dissolved in chloroform (1 mL) and stirred with $Zn(OAc)_2.2H_2O$ (68 mg, 0.35mmol) for 12h at room temperature. The solution was applied directly to silica gel column to afford the tweezer as deep magenta powder.

Yield: 30%, **UV-Vis [$CHCl_3$, λ_{max} (nm) (log ε)]** 421 (5.90), 549 (4.28), 588 (3.00). **^{1}H NMR (400 MHz, $CDCl_3$) δ ppm:** 1.44 (m, 6H, CH_2), 4.3 (4H, -OCH_2), 7.74(d, J = 7.32, 12H, Ar-H), 8.12 (d, J = 7.32, 12H, Ar-H), 8.28 (d, 4H, J = 7.93) 8.36 (d, 4H, J = 7.93), 8.90 (m, 16H, β-pyrrolic). **MALDI-TOF MS**: m/z Calcd for $C_{119}H_{112}N_8O_4Zn_2$ 1844.7385; Found, 1844.7383 [M+].

Synthesis of 1,5-bis[5'-(4''-carboxyphenyl)-10',15',20'-tris-(4-pyridylphenyl) zinc porphyrinyl] pentanoate (8)

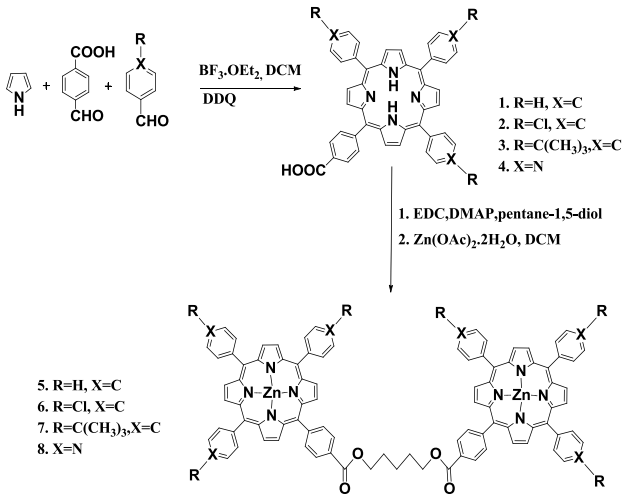
To a solution of 5-(4'-carboxyphenyl)-10,15,20-tris-(4"-pyridyl) porphyrin (40mg ,60 µmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 12 mg, 60µmol), and dimethylaminopyridine (DMAP , 9 mg, 60 µmol) in anhydrous CH_2Cl_2:DMF (9:1, 5mL), 1,5-pentanediol (1.5 mg, 14.5 µmol) was added. The reaction mixture was stirred at room temperature for 23h. It was purified on silica gel to afford porphyrin dimer as a dark purple solid. The dimer was dissolved in chloroform (1 mL) and stirred with $Zn(OAc)_2.2H_2O$ (68 mg, 0.35mmol) for 12h at room temperature. The solution was applied directly to silica gel column to afford the tweezer as deep magenta powder.

Yield: 10%, **UV-Vis [Ethanol, λ_{max} (nm) (log ε)]:** 422 (5.80), 557 (4.31), 598 (2.92). **^{1}H NMR (400 MHz, 10%, CD_3OD/ $CDCl_3$) δ ppm:** 8.22 (d, J = 4.4 Hz, 8H), 8.23 (d, J = 4.4 Hz, 4H), 8.32 (m, 8H), 8.88 (br, m, 16H), 8.99 (d, J = 4.4 Hz, 8H), 9.02 (d, J = 4.4 Hz, 4H**). MALDI-TOF MS: m/z** Calcd for $C_{89}H_{58}N_{14}O_4Zn_2$ 1514.3348; Found, 1514.3347 [M+].

Results and discussion

Synthesis

Synthesis of unsymmetrical porphyrin was achieved by condensation of mixed aldehydes with pyrrole in propionic acid. The mixture of corresponding addehyde and 4-formylbenzoic acid was refluxed with pyrrole in propionic acid for 3 hours. The resultant precipitate mixture including six porphyrin isomers was separated on silica gel. The unsymmetrical porphyrin was isolated in 4-6 % yields. The reaction of monoacid porphyrin with pentan-1,5-diol in anhydrous CH_2Cl_2 using 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide and *N*,*N*-Dimethylpyridin-4-amine resulted in symmetrical bisester. Zinc(II) was inserted into the porphyrin using $Zn(OAc)_2.2H_2O$ in the mixture of chloroform:methanol as solvents.. The were purified directly on silica gel to obtain purple solid as porphyrin tweezers**. (scheme1)**



Scheme 1. Synthesis of acid porphyrins and corresponding porphyrin tweezers.

Spectral analysis

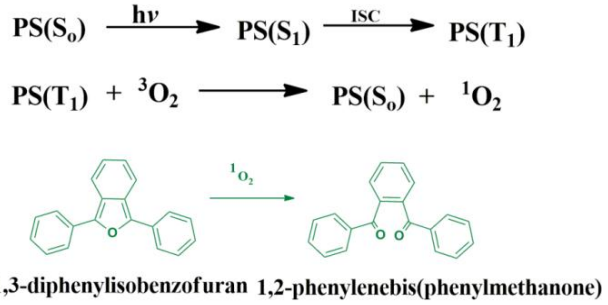
The synthesized porphyrin tweezers were characterized by ^{1}H-NMR, UV-Vis and Mass spectroscopy. The appearance of the peaks at δ 4.23ppm for (–OCH_2-) , δ 1.4-1.6 ppm for (-CH_2-) protons of the pentane chain and disappearance of peak in the negative region on comparing with acid porphyrins, confirmed the synthesis of the porphyrin tweezers. Through the ^{1}H-NMR spectra, a comparison between the chemical shifts of the protons of carboxyphenyl group has been made. On comparing the chemical shifts of aromatic protons of carboxyphenyl group of the monomers and dimers, it has been found that the aromatic protons of carboxyphenyl group gets de-shielded and shift downfield observed for the protons as listed out in **Table 1**. This shift confirms the free to rotation of para-para bis-porphyrins around the linking axis **[21].**

The electronic spectra of all porphyrin tweezers were all very similar. However, on changing the solvent from CH_2Cl_2 to ethanol, large red shifts both in soret and Q-bands were observed. For example, the soret band of porphyrin **5** appearing at 419 nm in CH_2Cl_2 shifts to 423 nm in ethanol. Also, the Q-bands at 548 nm and 588nm in CH_2Cl_2 shifts to 558nm and 597nm respectively in ethanol. This is the experimental indication of the fact that tweezers have the ability to aggregate in non polar solvents **[22-24]**.

Singlet oxygen generation

Present work ponders upon the evaluation of the sensitized generation of singlet oxygen, since it is the key species responsible for photochemical and photo-biological applications of porphyrin sensitizers. Therefore singlet oxygen efficiency of the porphyrin tweezers **5-8** has been quantified using indirect method, also known as type II mechanism. In a type II mechanism, singlet oxygen is generated through an energy transfer process from the excited porphyrin sensitizer to triplet oxygen. The singlet oxygen reacts with substrate as shown in **scheme 2**, where PS is photosensitizer, S_0, S_1, T_1, are singlet ground state, first excited singlet state and first triplet excited state respectively, ISC means intersystem crossing. The 1,3-diphenylisobenzofuran (DPBF), a well-known singlet oxygen scavenger to quantify the singlet oxygen generation by porphyrin tweezers.

Ethanolic solution of the porphyrin tweezers and DPBF using a 200 W mercury lamp over a time period of 0-100s at an interval of 20s was irradiated and the decrease in absorbance at 410 nm corresponding to DPBF in the presence of tweezer was monitored by UV-Vis spectra (**Fig. 1**). A plot between change in absorbance versus irradiation time was drawn **(Fig. 2)** and by comparing the photooxidation of DPBF sensitized by the tweezers to that of the reference, ZnTPP (Φ_Δ = 0.7) the quantum yields of tweezers were calculated **[25]**.



Scheme 2. Representation of type II mechanism.

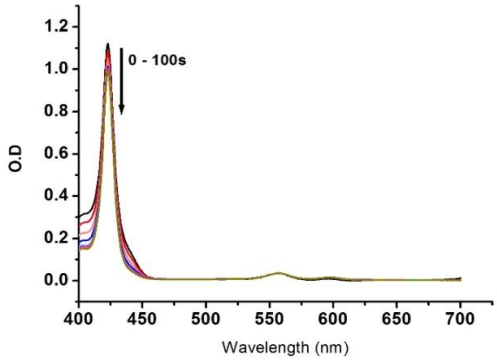


Fig. 1. Changes in absorption spectra of DPBF upon irradiation in the presence of **5**, for 0-100 s (recorded at 20 s intervals) in ethanol.

Table 1: Comparison of chemical shifts (δ, ppm) of the aromatic protons of carboxyphenyl group in monomers and dimers.

Compounds							**Chemical shifts**		
	1	2	3	5	6	7	Δ(1−5)	Δ(2−6)	Δ(3−7)
H1	8.43	8.46	8.44	8.36	8.31	8.36	0.07	0.15	0.08
H2	8.28	8.29	8.32	8.28	8.20	8.28	0	0.09	0.04

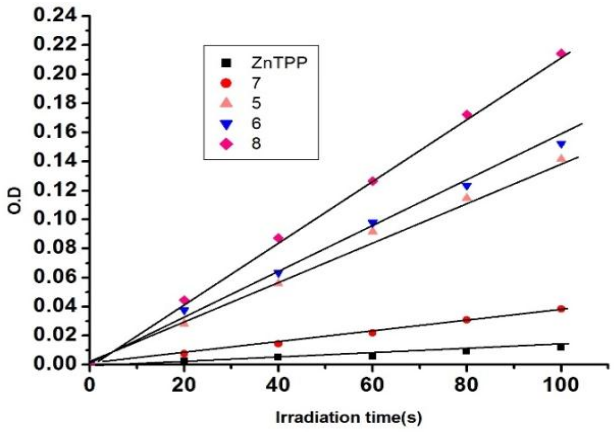


Fig. 2. Relative plot of the singlet oxygen generation efficacy of the porphyrin tweezers **5, 6, 7, 8** and the standard ZnTPP.

The singlet oxygen quantum yield of porphyrin sensitizer **5** is 0.78± 0.03, for **6** 0.80±0.02, **7** 0.72±0.03 and for **8** 0.84±0.03. Thus the conjugates follow the order **8>6>5>7** for the generation of singlet oxygen from different porphyrin sensitizer. The singlet oxygen quantum yield of 5-(4-carboxyphenyl)-10,15,20-triphenylporphyrin **1** is 0.74 as reported in literature **[26]**. On comparing the quantum efficacy of the dimer **5** with **1** a clear inference can be made that the quantum efficacy of dimer is larger than the monomeric unit. The photosensatizing properties of tweezers vary with the type of functional group attached. The results have been compiled in **table 2**.

Table 2. Singlet oxygen quantum yields obtained by the indirect (scavenging using 1,3-diphenylisobenzofuran, DPBF) technique.

Compond	Quantum Yield
5	0.78± 0.03
6	0.80±0.02
7	0.72±0.03
8	0.84±0.03.
ZnTPP	0.7

The quantum efficacy of **6** is found to be larger than **5**, indicating the enhancement in the ability of chromophore to sensitize singlet oxygen due to the presence of a heavy halogen atom. While if a bulky, electron rich group is attached at the para position of the porphyrin that is in case of **7** the ability of the sensitizer reduces. Pyridyl group has been found to affect the sensitization to maximum extent. Thus amongst the prepared sensitizers **8** is found to be the most suitable.

Conclusion

Various conformationally flexible porphyrin tweezers have been synthesized by reaction of corresponding porphyrin acid with pentan-1,5-diol followed by metallation with zinc and used as porphyrin-photo sensitizer. The synthesis work has been carried out by the preparation of acid conjugates followed by their reaction with bifunctional pentane diol to give porphyrin tweezers. The singlet oxygen quantum yields of these porphyrin tweezers has been studied by using DPBF as indirect method. The substituents on the porphyrin tweezers play a significant role on the yield of generated singlet oxygen. The halogenated group increases the ability of the chromophore, the bulky tert-butyl group has an adverse effect on its sensitization, while pyridyl group has been found to affect the maximum. However, all the tweezers have better quantum yields than simple monomeric porphyrin units and henceforth their photochemical properties can be exploited in generation of singlet oxygen.

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Author's contributions

Conceived the plan: Uma Narang; Performed the expeirments:Uma Narang, Kumar K.. Karitkey ; Data analysis: Uma Narang, Soumee Bhattacharya; Wrote the paper: Uma Narang, Kumar K. Karitkey, Soumee Bhattacharya. Authors have no competing financial interests.

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