Organic & Biomolecular Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

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Synthesis and investigation of singlet oxygen production efficiency of photosensitizers based on *meso*-phenyl-2,5-thienylene linked porphyrin oligomer and polymers

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Abstract

Three new Zn(II)- oligo- and poly(2,5-thienylene)-linked porphyrins, bearing multiple triethylene glycol (TEG) groups, on all *meso* aryl positions were synthesized *via* Stille and Suzuki coupling reactions and their photophysical properties as well as singlet oxygen generation efficiencies have been investigated to elucidate the possibility of their use as a photosensitizer for photodynamic therapy (PDT) and photodynamic inactivation of bacteria.

Introduction

Efficient photosensitizers based on porphyrins have been a subject of great interest for photodynamic therapy (PDT) and photodynamic killing of bacteria due to their unique photophysical properties, high photostability, bio-compatibility, low-dark toxicity and high molar absorptivity.[1-3] Moreover, π-conjugated porphyrin dimers can be utilized as a two-photon absorbing (TPA) sensitizer because they exhibit the properties of high TPA cross-section and high singlet oxygen efficiency.[4-8]

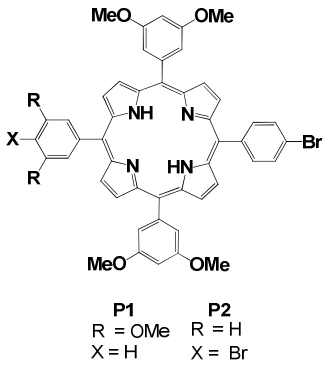
The photochemical process for both PDT and bacteria killing involves the excitation of a photosensitizing agent with visible light and an energy transfer of excited photosensitizer to the surrounding triplet oxygen to convert it into singlet oxygen ($^1O_2$).[9-11] Singlet oxygen is highly reactive species and has a cytotoxic effect inducing cell death and destruction of tumors for PDT and inactivation of bacteria. Therefore, the high $^1O_2$ production efficiency is one of the important considerations in the design of a suitable photosensitizer and this can be realized by having a sensitizer with a high intersystem crossing (ISC) ability.[1-3] ISC can be enhanced by incorporating heavy halogen atoms to a sensitizer such as iodine and bromine that will facilitate the spin-orbit coupling.[12] However, recently it was also reported that sulfur atom is capable to increase the ISC efficiency when BODIPY (4,4-difluoro-4-bora-3a, 4a-diaza-s-indacene) was functionalized with thiophene.[12-16]

Although there are some examples in the literature regarding the polymeric *meso*-aryl linked thienylene porphyrin mainly utilized in the area of optoelectronics,[17-18] to the best of our knowledge, the singlet oxygen generation abilities of these thiophene containing porphyrins have not been studied. Using hydrophilic, preferably, water soluble oligomeric or polymeric photosensitizers one can also benefit from the accumulation of these species in the tumorous tissue through enhanced permeation retention effect (EPR) for PDT process.[19]

In this context, we report the synthesis and photophysical properties of new oligomeric and polymeric *meso*-aryl linked (2,5-thienylene)-porphyrin derivatives with mono and bithiophene units, namely, oligo-5-phenyl(2,5-thienylene)-10,15,20-tri(3,5-di-*O*-TEG-phenyl)-porphyrin (**OTT$_1$P**), oligo-5-phenyl(2,5'-bithienylene)-10,15,20-tri(3,5-di-*O*-TEG-phenyl) porphyrin (**OTT$_2$P**), and, poly-5,15-diphenyl(2,5'-dithienylene)-10,20-di(3,5-di-*O*-TEG-phenyl) porphyrin (**PTTP**). The sulfur atom on thiophene molecule eases the intersystem crossing through heavy atom effect and hence will increase the singlet oxygen generation. TEG groups were attached to increase the solubility of these compounds and ideally render their water-solubility. Moreover, the increased molecular weight of the oligomers and polymers will enhance the effective permeation retention.

Results and discussion

Our target porphyrin precursors for the synthesis of oligomeric and polymeric porphyrins are **P1** and **P2**, respectively.

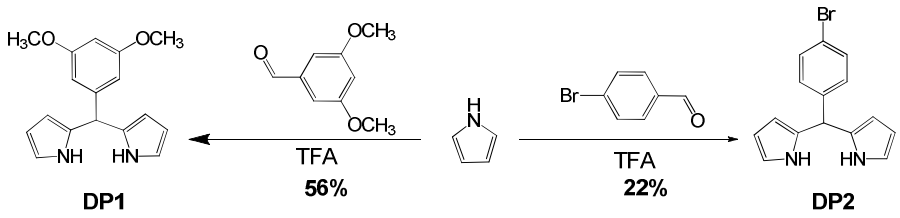


Scheme 1. Porphyrin precursors for the synthesis of dimeric and polymeric porphyrins.

Synthesis of substituted porphyrins such as **P1** and **P2** using one pot synthetic method results in low yield and undesired side products. One alternative to this method is to first synthesize dipyrromethane as a precursor which improves the yield of the desired product.[20-21] Synthesis of dipyrromethane involves [2+2] condensation reaction between a pyrrole and an aldehyde in the presence of catalytic amount of acid.[20] To obtain high yield in this reaction, there are important precautions that have to be taken. First, the choice of acid is very important. Boron trifluoride diethyl etherate ($BF_3 \cdot Et_2O$) and trifluoro acetic acid (TFA) are the two main acid catalysts used in the synthesis of dipyrromethane. Although $BF_3 \cdot Et_2O$ was reported to give higher yield, the amount of side products (N-confused dipyrromethane) is much lower with TFA. Secondly, the sequence of addition of the reactants determines the amount ratio between the dipyrromethane and the higher pyrrolic oligomers. Dipyrromethane is obtained as a major product if the acid is added after stirring pyrrole and aldehyde for some time. Third, pyrrole should be freshly distilled and used in large excess to suppress the polymerization of the product. Lindsey reported that 25 equiv. of pyrrole and 0.1 equiv. of the acid relative to the aldehyde give the optimum yield.[22]

Considering all these precautions dipyrromethane **DP1** and **DP2** were synthesized in good yield as shown in Scheme 2.[23] After removing excess pyrrole under reduced

pressure, the residue was purified with column chromatography using DCM:Et_3N (20:0.1). Pure **DP1** was obtained after recrystallization from ethanol-water mixture in 56% yield.



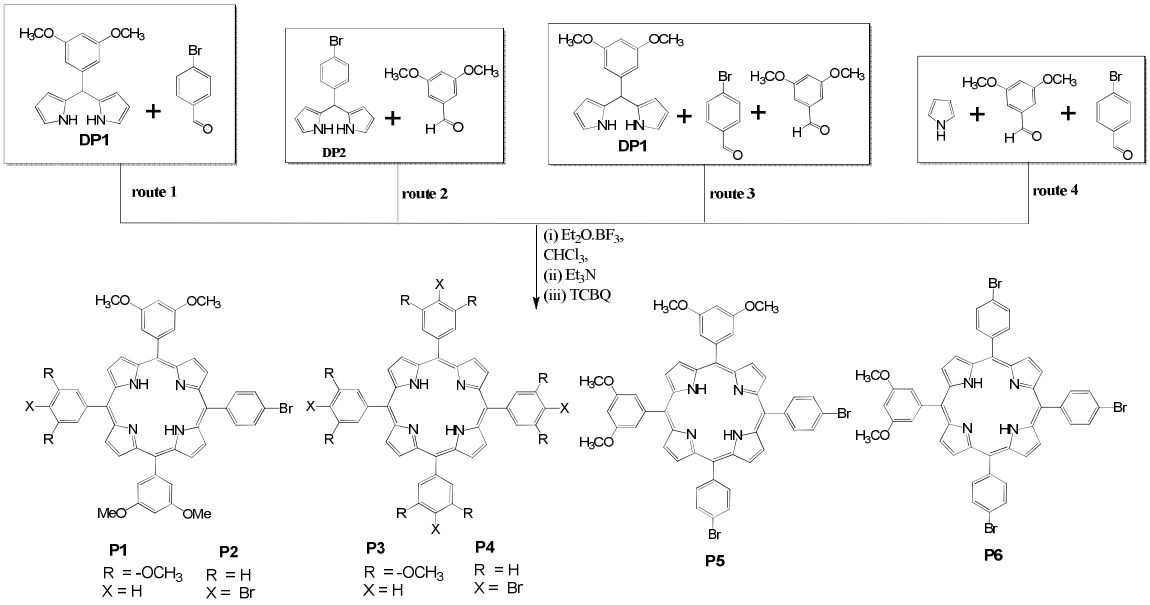
Scheme 2. Synthesis of **DP1** and **DP2**.

Attempt to purify **DP2** with column chromatography failed because the R_f values of **DP2** and other pyrrolic compounds were very close. We were fortunate to find out that **DP2** crystallizes out with cold n-hexane. The pure product was obtained after several washing with n-hexane in 22% yield.

In both ^{1}H-NMR of **DP1** and **DP2** characteristic –NH pyrrolic peak at around 8 ppm was observed. In addition, the singlet peak at 5.4 ppm shows the methine proton and thus confirms the formation of dipyrromethane. Singlet peak at 3.7 ppm in compound **DP1** ^{1}H-NMR confirms the presence of methoxy (-OCH_3) groups and this can be used to distinguish **DP1** from **DP2**. The integration values suggest the exact number of protons in **DP2** and **DP1**. Compounds **DP2** and **DP1** were further characterized with ESI mass spectrometer to give their mass to charge ratio as 301 and 282, respectively, which agree with the theoretical values. Elemental analysis data from the experimental section of **DP2** and **DP1** agree with the theoretical data confirming the structure of **DP2** and **DP1**.

For the synthesis of **P1** and **P2** we have employed four of those routes shown in the reaction Scheme 3. Because porphyrin synthesis starting from dipyrromethane is reported to give higher yield, we started the synthesis of **P1** and **P2** from the previously synthesized dipyrromethanes **DP2** and **DP1** (route 1, 2 and 3). The reaction was carried out at very low concentration of the reactants (high dilution method) to facilitate the ring formation and to prevent polymerization of the dipyrromethane. We were expecting three different porphyrin products from these reactions, namely, **P1**, **P2** and **P3**. However,

other porphyrin side products (**P4**, **P5** and **P6)** were also observed in all three reactions. The formation of these unexpected porphyrins can be attributed to the scrambling of the reactants during the porphyrin ring formation when strong acid is used as catalyst.[24-25]



Scheme 3. Four different synthetic routes for the synthesis of porphyrin precursors.

We later tried TFA as acid catalyst to obtain the desired product selectively but the yield was extremely low. The separation of porphyrin products with column chromatography was extremely tedious especially the *cis* and *trans* isomers (**P5** and **P2**) as their R_f values happen to be very close. Therefore, the separation of them could only be achieved with very long and wide diameter columns. During the column chromatography, very small amount of triethyl amine was added to achieve better separation. Although mixture of products was obtained, compound **P2** was obtained in highest yield in both reactions albeit the route 2 produced slightly higher yield of **P2**.

To increase the yield of **P1** we took the route of 3 in which the mixture of **DP2** and *p*-bromo benzaldehyde and 3,5-dimethoxy benzaldehyde were used. This route produced **P1** in 15% yield besides other porphyrin derivatives.

Since low yield was obtained for **P1** and **P2** and all porphyrin side products formed when we started with dipyrromethanes, we changed our synthetic strategy to one pot synthesis (route 4) i.e. by mixing freshly distilled pyrrole, *p*-bromo benzaldehyde and

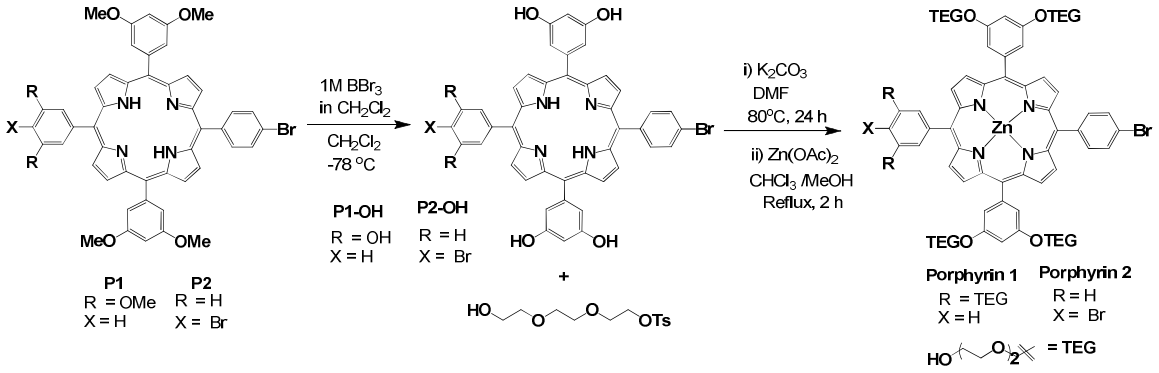
3,5-dimethoxy benzaldehyde. This route produced all six porphyrin derivatives including **P1** and **P2**. **P2** was obtained in higher yield (26%) than the others. Table 1 summarizes the yields of porphyrin derivatives obtained from 4 different reaction routes.

Table 1. Yields of porphyrin derivatives obtained from 4 different reaction routes.

% yield	**P1**	**P2**	**P3**	**P4**	**P5**	**P6**
Route 1	2	16	2	2	5	3
Route 2	3	18	2	1	8	2
Route 3	15	2	7	2	1	2
Route 4	13	26	5	3	10	3

All six porphyrin derivatives were first characterized by ^{1}H NMR spectroscopy. It is quite difficult to distinguish the *trans*- (**P2**) and *cis*-(**P5**) and *meso*-phenyl porphyrins as their ^{1}H and ^{13}C NMR spectra exhibited identical chemical shifts and splitting patterns. However, we were able to grow suitable crystals and determine their X-ray crystal structures to authenticate them.

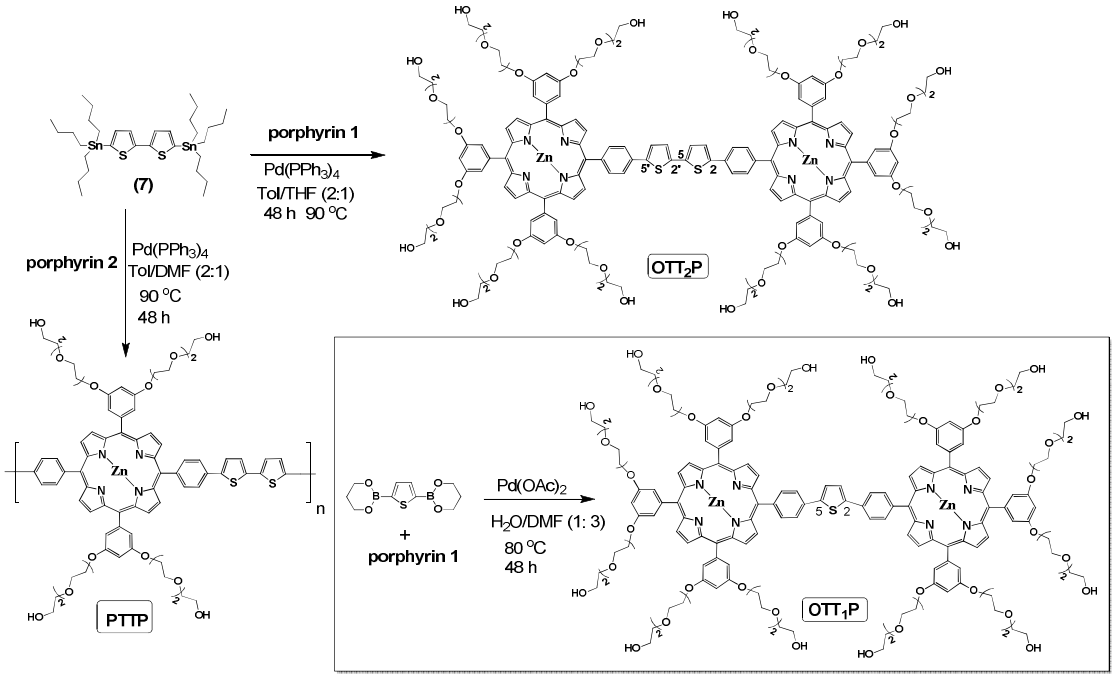
Then **P1** and **P2** were treated with BBr_3 in CH_2Cl_2 for the demethylation of the methoxy groups followed by metallation with $Zn(OAc)_2$[26-27] and finally substitution of –OH groups with tri(ethylene glycol) (TEG) monotosylate afforded 5-(*p*-bromophenyl)-10,15,20-tri(*m*-di-*O*-TEG-phenyl)porphyrin (Porphyrin **1**) and 5,15-di(*p*-bromophenyl)-10,20-di(*m*-di-*O*-TEG-phenyl)porphyrin (Porphyrin **2**) as shown in Scheme 4. The compounds **P1-OH**, **P2-OH**, their Zn-inserted versions and Porphyrin **1** and **2** were characterized thoroughly by ^{1}H, ^{13}C NMR spectroscopies, ESI-MS and elemental analysis. The results agree with the expected structures.



Scheme 4. Synthetic route of Porphyrin **1** and **2**.

The oligomers, **OTT$_1$P**, **OTT$_2$P** and the polymer, **PTTP** were synthesized by palladium- catalyzed Stille and Suzuki coupling reactions as shown in Scheme 5. Monomeric porphyrins were metallated by inserting Zn before carrying out the Pd-catalyst cross-coupling reactions as palladium might coordinate with the core of porphyrin if they are in their free-base form. The oligomers can be dissolved in MeOH, $CHCl_3$, DMF and THF easily while polymer is relatively insoluble in MeOH but can be dissolved in $CHCl_3$, THF and DMF respectively. Their structures were characterized by spectroscopic techniques including ^{1}H NMR, ^{13}C NMR, MS-ESI and Elemental analysis. In the ^{1}H NMR spectra of **OTT$_1$P**, **OTT$_2$P** and **PTTP**, the significant downfield and upfield displacements of protons with respect to their relevant monomers have been observed with additional proton resonances of thiophene units and their elemental analyses results are consistent with the expected ones. The MS-ESI mass spectra of **OTT$_1$P** and **OTT$_2$P** showed a pseudo-molecular ion peaks at m/z = 1605; $[M+2H]^{2+}$ and m/z = 1646.5872 $[M+2H]^{2+}$ respectively, supporting the proposed formula for the compounds.

We have attempted to determine the molecular weight of **PTTP** by GPC in relative to polystyrene standard in THF. The number average (M_n) and weight average (M_w) molecular weight of the polymer were found to be 3109 and 3549 Da respectively with polydispersity index (PDI) of 1.21. The values are lower than the expected because of the difficulty of molecular weight determination of rigid polymers like this one.



Scheme 5. Synthesis of Zn(II) oligo- and poly(2,5-thienylene)porphyrins.

The optical properties of porphyrin derivatives were investigated by UV-vis absorbance and fluorescent spectroscopies and the results were tabulated in Table 2. Figure 1a displays the UV-vis absorption spectra of **OTT_1P**, **OTT_2P, PTTP** as well as porphyrin **1** and **2** in chloroform. Both porphyrin **1** and **2** exhibited a sharp Soret band at 426 nm and two weak Q-bands at 555 and 595 nm as typical absorption peaks of zinc porphyrin compounds. As expected, the Soret band of poly- and oligomers is broadened compared with monomers due to presence of the thiophene units.

The excitation of compounds **OTT_1P**, **OTT_2P** and **PTTP** in $CHCl_3$ at 426 nm (Soret band) resulted fluorescence emission above 600 nm as characteristic of porphyrin with two vibrational bands (Figure 1b).[26, 5, 8] The mono- and oligomers, shows two emission peaks at 604 and 654 nm and no emission peak of thiophene unit is detected. This result reveals that there is an effective energy transfer from the thiophene unit to the porphyrin unit.[17,18] The molar absorptivity of **OTT_1P**, **OTT_2P** and **PTTP** in $CHCl_3$ and MeOH solution were 1.3 $x10^6$ (MeOH), 9.4 $x10^5$ (MeOH) and 5.1 $x10^5$ (in $CHCl_3$, per repeating unit). The photoluminescence quantum yields of **P1**, **P2**, **OTT_1P**, **OTT_2P** and **PTTP** with relative to tetraphenylporphyrin (H2TPP) (Φ_{PL} = 0.11) as the reference standard are also shown in Table 2.

Table 2. The optical properties of porphyrin derivatives in $CHCl_3$[a] and MeOH[b].

Compound (Acronym)	**ε^a (M^{-1} cm^{-1})** (Soret band)	**ε^b (M^{-1} cm^{-1})** (Soret band)	**% $\Phi_{PL}{}^a$**	**% $\Phi_{PL}{}^b$**
Porphyrin **1**	6.3 x10^5	2.7 x10^5	9.6	7.1
Porphyrin **2**	3.5 x10^5	6.4 x10^5	5.4	5.4
OTT_1P	1.3 x10^6	1.0 x10^6	15.4	14.9
OTT_2P	9.4 x10^5	1.0 x10^6	6.8	5.7
PTTP	------	5.1 x10^5 [c]	-----	9.7

[a] In MeOH. [b] In $CHCl_3$. [c] Per repeat unit. Photoluminescent quantum yield determined relative to H2TPP (Φ_{PL}= 0.11 in toluene). --- not soluble in MeOH.

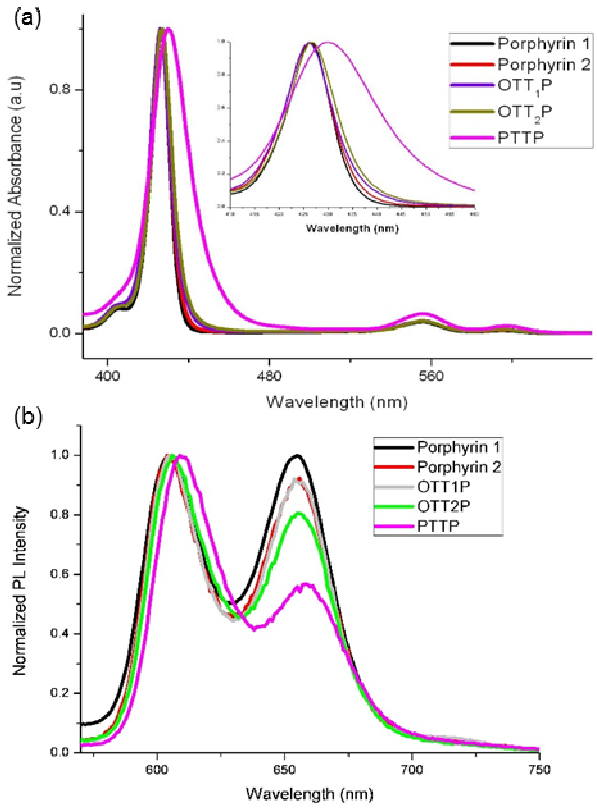


Figure 1. (**a**) Normalized absorption spectra of the compounds in $CHCl_3$. Inset of figure shows the focused version of the Soret band; (**b**) Normalized emission spectra of the compounds in $CHCl_3$ ($\lambda_{exc.}$ at 426 nm).

Singlet oxygen production efficiency of the porphyrin-based photosensitizers were determined through an established photochemical method, using 1,3-diphenylisobenzofuran (DPBF) as an efficient $^1O_2$ quencher in combination with accurate, time-dependent spectrophotometric determination of DPBF concentration.[13,14,27] DPBF was used as a chemical monitor in order to estimate the $^1O_2$ photogeneration quantum yield of the established photosensitizers, **OTT_1P**, **OTT_2P** and **PTTP** in DMF (Scheme 1). The relative Φ_Δ $^1O_2$ generation efficiency was determined in comparison with tetraphenylporphyrin (TPP) by monitoring the reduced loss of absorbance of the DPBF (at 418 nm in DMF) with increasing irradiation time.[13, 28] The relationship between DPBF's absorption value ratio (A/A_0) and irradiation time indirectly reflected $^1O_2$ yield of those established photosensitizers compared with porphyrin **1** (Fig. S43 and Fig. S44). The following Eq. 1 was used to calculate the singlet oxygen quantum yield of Porphyrin 1, Porphyrin 2, OTT1P, OTT2P and PTTP,

$$\Phi\,(^1O_2)^{Por} = \Phi\,(^1O_2)^{TPP}\, m^{Por}/\, m^{TPP} \times F^{TPP}/\, F^{Por} \qquad \text{(Eq. 1)}$$

where superscripts 'Por' and 'TPP' denote porphyrin 1, Porphyrin 2, OTT1P, OTT2P and PTTP and tetraphenylporphyrin (TPP), respectively; $\Phi\,(^1O_2)$ is singlet oxygen quantum yield, m is the slope of a plot of difference in change in absorbance of DPBF (at 418 nm) with the irradiation time (see ESI, Fig.S44) and F is the absorption correction factor, which is given by $F = 1 - 10^{-OD}$ (OD at the irradiation wavelength).[13]

Among these PTTP was found to be the most productive as it could be seen with the increase of the line slope. The order of relative singlet oxygen production yields can therefore be derived as: Porphyrin 1< Porphyrin 2 < OTT_2P = OTT_1P < PTTP and their photogenerating $^1O_2$ abilities might be significantly affected by the conjugation of the thiophene units between the porphyrins. The relative magnitude of singlet oxygen generation efficiency was examined by means of tetraphenylporphyrin (TPP) as a reference ($\Phi_{\Delta(TPP)}$= 0.60 in DMF) (Table 3).

Table 3. Singlet oxygen quantum yield (Φ_Δ) in DMF with respect to tetraphenylporphyrin (TPP).

Sample	TPP	Porphyrin1	Porphyrin2	OTT_1P	OTT_2P	PTTP
Φ_Δ	0.60	0.65	0.78	0.80	0.80	0.88

Conclusions:

In this study, porphyrin-thiophene based compounds were synthesized and their singlet oxygen production efficiencies have been studied in a polar solvent. The results indicated that the presence of sulfur atom on thiophene units, probably facilitating the intersystem crossing due to spin-orbit coupling and thus, in turn, causing an increase in the singlet oxygen production efficiency. Moreover, it was found that the ability of singlet oxygen generation of the polymer is higher than oligomers followed by monomers. Although we have attached TEG groups to porphyrin derivatives to increase their water solubility, among them, only monomeric and dimeric porphyrins were sparingly soluble in water. These porphyrin based compounds can be used as photosensitizers for photodynamic therapy and photodynamic killing applications.

Experimental Section

Materials and methods

Solvents were dried and distilled before used. All reactions were performed under air unless otherwise stated. Unless otherwise noted, all reagents were used as received from commercial suppliers. Thin layer chromatography was performed on SiO_2 60 F-254 plates and flash column chromatography was carried out using SiO_2 60 (particle size 0.040–0.055 mm, 230–400 mesh). NMR spectra (^1H, at 400 MHz and ^{13}C at 100 MHz) were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$ and DMSO-d_6 solvent and TMS (δ = 0.00 ppm) as an internal standard. Chemical shifts were reported as δ values in ppm as referenced to TMS. The elemental composition of the samples was determined using FLASH 2000 Organic Elemental/ CHNS-O Analyzer. The mass spectra were obtained with Agilent 6224 High Resolution Mass Time-of-Flight (TOF) LC/MS with Electrospray Ionization method. UV-VIS absorption spectra were recorded on a UV–vis

spectrophotometer (Cary UV–vis) with 1 cm path length quartz cuvettes in the spectral range of 300-800 nm. Emission spectra were recorded on a fluorescence spectrophotometer (Cary Eclipse Fluorescent spectrophotometer). The quantum yields of fluorescence of the compounds were determined using tetraphenylporphyrin (TPP) as the standard (in toluene was 0.11).[18] The quantum yields were calculated from integrals under the emission curves of the probe and the standard and corrected for the different absorptions at the excitation wavelength. For this purpose, a series of diluted solutions for each compound were prepared and their absorbance and integrated fluorescence intensities were recorded at each concentration. The fluorescence spectra were recorded by exciting the maximum of the long-wavelength absorption band.[9] For the measurement of the extinction coefficients about 1.5 mg of each compound was dissolved into 25 mL of $CHCl_3$ and MeOH. From this stock solution further dilutions with different concentrations (10^{-8} to 10^{-9} M) were made. The absorption spectra for each dilution were then measured, and their extinction coefficients were determined from the slope of absorbance versus concentration. For the singlet oxygen generation experiment, an aerated solution of 1,3-diphenylisobenzofuran (DPBF) (20 μM) and photosensitizer (0.5 μM M) in DMF (2 mL) was irradiated at 420 nm under Spectral Products monochromator integrated Xenon lamp at 25 °C for 30 seconds intervals. Reaction of DPBF with $^1O_2$ was monitored by the decreasing intensity of the absorption band at 418 nm over time (See ESI, Fig. S43). Irradiation of aerated DPBF solution without photosensitizer gave no reduction in intensity of the 418 nm absorption band. The absorption of the photosensitizer was first measured because the Soret band of porphyrin overlaps with the absorption maxima of 1,3-diphenylisobenzofuran (DPBF). The same photosensitizer solution was used to dissolve DPBF to obtain the desired concentration of DPBF. Computer software was used to subtract the photosensitizer spectrum from the combined spectra of the photosensitizer and the trap. Log plot of the normalized absorption maxima vs time was plotted and the slope gave the comparative singlet oxygen generation of the photosensitizers with respect to tetraphenylporphyrin (TPP) (See ESI, Fig. S43).

(2,2'-((3,5-dimethoxyphenyl)methylene)bis(*1H*-pyrrole)) (Dipyrromethane, DP1): 3,5-dimethoxy benzaldehyde (1.00 g, 6.02 mmol) and freshly distilled pyrrole 25 mL

(24.3 g, 361 mmol) were placed into a two-necked round bottom flask under nitrogen atmosphere. The mixture was heated to 50 °C. After removing the heat source, trifluoroacetic acid (TFA) 46 µL (0.0686 g, 0.602 mmol) was added immediately. After 10 minutes the solution was quenched with 6 mL 0.1 M NaOH. The solvents and the unreacted pyrrole were removed under reduced pressure. The residue was purified using column chromatography with DCM:Et_3N (20:1) as the eluent. The yellow oily product from the column was recrystallized by dissolving in hot ethanol followed by addition of water. The precipitate was collected under suction filtration to yield a light brown solid substance (945 mg, 56%). Melting point (ethanol-H_2O): 92.5-93.3 °C

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 3.76 (s, 6H), 5.43 (s, 1H), 5.98 (d, 2H, J= 4.0 Hz), 6.17 (t, 2H, J= 5.6 Hz), 6.38 (s, 1H), 6.41 (s, 2H), 6.72 (d, 2H, J= 4.0 Hz), 7.95 (br, 2H, N-H); ^{13}C NMR (100 MHz,$CDCl_3$, 25 °C): δ 161.00, 144.46, 132.10, 117.18, 108.46, 107.21, 106.72, 98.82, 55.31, 44.32. Elemental analysis: calcd for $C_{17}H_{18}N_2O_2$: C 72.32, H 6.43, N 9.92, O 11.33; found: C 72.79, H 6.32, N 9.84. ESI-MS m/z calcd. for $C_{17}H_{18}N_2O_2$: 282.14; found 281.12 [M-H].

2,2'-[(3,5-dibromophenyl)methylene)bis(*1H*-pyrrole) (Dipyrromethane, DP2): *p*-Bromo benzaldehyde (2.00 g, 10.8 mmol) and freshly distilled pyrrole 50 mL (48.5 g, 723 mmol) were placed into a two-necked round bottom flask under nitrogen atmosphere. The mixture was heated to 50 °C. After removing the heat source, trifluoroacetic acid (TFA) 83 µL (0.124 g, 1.08 mmol) was added immediately. After 10 minutes the solution was quenched with 11 mL 0.1 M NaOH. The solvents and the unreacted pyrrole were removed under reduced pressure to yield a light brown oily product. The residue was purified by recrystallization using n-hexane. The precipitate was collected under suction filtration to yield a brownish solid substance (726 mg, 22%). Melting point (n-hexane): 126-127 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 5.45 (s, 1H), 5.91 (d, 2H, J = 6.8 Hz), 6.17 (t, 2H, J = 5.6 Hz), 6.73 (d, 2H, J = 6.8 Hz), 7.10 (d, 2H, J = 8.4 Hz), 7.45 (d, 2H, J = 8.4 Hz), 7.94 (br, 2H, N-H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 141.20, 132.69, 131.68, 130.13, 117.48, 108.58, 107.44, 43.46. Elemental analysis: calcd. for $C_{15}H_{13}BrN_2$: C

59.82, H 4.35, N 9.30; found: C 59.48, H 4.40, N 9.41. ESI-MS m/z calcd. for $C_{15}H_{13}BrN_2$: 300.03; found 301.01 $[M+H]^1$.

Route 1: Compound **DP1** (0.40 g, 1.42 mmol) and 4-bromobenzaldehyde (0.262 g, 1.42 mmol) were dissolved in distilled chloroform (1000 mL) and stirred while purging nitrogen for at least 30 minutes and the reaction flask was kept away from light. During stirring, 61 μL (0.0696 g, 0.490 mmol) of the Lewis acid catalyst ($Et_2O.BF_3$) was added to the reaction mixture under nitrogen atmosphere. The reaction mixture was stirred for 1 hour stirring at room temperature followed by the addition of 79 μL (0.0573 g, 0.567 mmol) of triethylamine and (0.263 g, 1.07 mmol) of TCBQ. The reaction mixture was reflux for 1 hour. The solution was cooled to room temperature and the volume of the reaction mixture was reduced to ca. 300 mL, filtered through silica gel, and evaporated to dryness. The purple residues were washed with MeOH. The residues were further purified by column chromatography on silica gel using toluene as eluent to isolate 6 different porphyrin derivatives which were triturated with MeOH to obtain shiny purple crystals. Yields: **P1**, 2%; **P2**, 16%; **P3**, 2%; **P4**, 2%; **P5**, 5%; **P6**, 3%. Melting points are higher than 300 °C.

Route 2: Compound **DP2** (0.500 g, 1.66 mmol) and 3,5-dimethoxybenzaldehyde (0.276 g, 1.66 mmol) were dissolved in distilled chloroform (1000 mL) and stirred while purging nitrogen for at least 30 minutes and the reaction flask was kept away from light. The rest of the procedure is as the same as Route 1. **Yields: P1**, 3%; **P2**, 18%; **P3**, 2%; **P4**, 1%; **P5**, 8%; **P6**, 2%.

Route 3: Compound **DP1** (0.500 g, 1.77 mmol), 4-bromobenzaldehyde (0.164 g, 0.886 mmol) and 3,5-dimethoxybenzaldehyde (0.147 g, 0.886 mmol) were dissolved in distilled chloroform (1000 mL) and stirred while purging nitrogen for at least 30 minutes and the reaction flask was kept away from light. The rest of the procedure is as the same as Route 1. Yields: **P1**, 15%; **P2**, 2%; **P3**, 7%; **P4**, 2%; **P5**, 1%; **P6**, 2%.

Route 4: To 1.5 L of chloroform were added 3,5-dimethoxybenzeldehyde (1.00 g, (6.01 mmol), 4-bromobenzaldehyde (1.13 g, 6.01 mmol) and pyrrole (0.800 g, 12.0 mmol) and the reaction flask was covered with aluminum foil. The rest of the procedure is as the same as Route 1. Yields: **P1**, 13%; **P2**, 26%; **P3**, 5%; **P4**, 3%; **P5**, 10%; **P6**, 3%.

Characterization of P1 to P6:

P1: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):δ 8.97 (m, 6H), 8.85 (m, 2H), 8.15 (d, 2H, J = 8 Hz), 7.85 (d, 2H, J = 8 Hz), 7.42 (s, 6H), 6.95 (s, 3H), 3.98 (s, 18H, -OMe), -2.83 (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C):δ 158.88, 143.93, 135.83, 129.91, 113.88, 100.18, 55.63; ESI-MS m/z calcd. for $C_{50}H_{41}BrN_4O_6$, 873.7877; found, 873.24082 $[M+H]^+$.

P2: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):δ 8.95 (d, 4H, J =5.4 Hz), 8.80 (d, 4H, J = 5.4 Hz), 8.10 (d, 2H, J = 8.0 Hz), 7.95 (d, 2H, J = 8.0 Hz), 7.45 (s, 4H), 6.95 (s, 2H), 3.98 (s, 12H, -OMe), -2.84 (s, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$ $CDCl_3$, 25 °C):δ 158.90, 143.83, 141.04, 135.81, 129.93, 122.51, 120.16, 118.60, 114.80, 113.80, 100.19, 55.62; ESI-MS m/z calcd. for $C_{48}H_{36}Br_2N_4O_4$, 893.6318; found, 893.1291 $[M+H]^+$. X-ray crystal structure was also determined (supporting information); **P5:** ^{1}H, ^{13}C-NMR spectroscopic and ESI-MS data are **s**imilar to **P2**. X-ray crystal structure was also determined (supporting information).

X-ray Crystal data for P2: Saturated solution of P2 in $CHCl_3$ was exposed to methanol vapour in a closed chamber to grow a transparant crystal for X-ray Crystal analysis. $[C_{48}H_{36}Br_2N_4O_4]$, M = 892.63, monoclinic, space group $P2_1/n$, space group IT number: 14; unit cell parameters: a 15.973(3) b 8.5673(15) c 28.865(5) Å, α 90, β 93.316(4), δ 90, V = 3943.4(12) Å^3, Z= 4, D_c = 1.504 g/cm^3, F_{000} = 1816, MoKa radiation, λ = 0.71073 Å, θ_{max} = 25.990°, 25461 reflections collected, 5932 unique (R_{int} = 0.0410), final GooF = 1.119, R1 = 0.0693, wR2 = 0.1148, R indices based on 7741 reflections with I > 2σ (I (refinement on F^2), 562 parameters, 0 restraints. Lp and absorption corrections applied, μ = 2.108 mm^{-1}.

X-ray Crystal data for P5: Saturated solution of P5 in $CHCl_3$ was exposed to methanol vapour in a closed chamber to grow a transparant crystal for X-ray Crystal analysis. $[C_{48}H_{36}Br_2N_4O_4]$, M = 892.63, monoclinic, space group C2/c, space group IT number: 15; unit cell parameters: a 23.99(3) b 16.08(3) c 10.433(15) Å, α 90°, β 102.51°(7), δ 90°, V = 3929(11) Å^3, Z= 4, D_c = 1.509 g/cm^3, F_{000} = 1816, MoKa radiation, λ = 0.71073 Å, θ_{max} = 30°, 11841 reflections collected, 3666 unique (R_{int} = 0.0410), final GooF = 1.195, R1 = 0.0895, wR2 = 0.2083, R indices based on 0.2083 reflections with I > 2σ (I

(refinement on F^2), 265 parameters, 0 restraints. Lp and absorption corrections applied, μ = 2.116 mm^{-1}.

P3: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): 8.92 (s, 8H), 8.15 (d, 8 H), 7.82 (d, 8H), 3.98 (s, 24H, -OMe), -2.83 (s, 2H, NH); **P4:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.92 (s, 8H), 8.15 (d, 8 H), 7.82 (d, 8H), 3.98 (s, 24H, -OMe), -2.83 (s, 2H, -NH); **P6:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 9.02 (m, 2H), 8.82 (m, 6H), 8.10 (d, 6 H), 7.82 (d, 6H), 7.32 (s, 2H), 3.92 (s, 6H, -OMe), -2.83 (s, 2H, NH).

P1-OH: To a solution of **P1** (100 mg, 0.11 mmol) in dry dichloromethane (25 mL) at –78 °C under an argon atmosphere, boron tribromide solution BBr_3 solution (1M in dichloromethane, 12 ml, 33 mmol) was added. The reaction mixture was stirred at –78 °C for 1 hour, and then allowed to warm to room temperature. After the reaction is stirred at room temperature for overnight, the reaction mixture was cooled to 0 °C followed by the addition of 10 mL of water. The resulting mixture was stirred for 5-10 minutes and the solvents were removed under reduced pressure. The aqueous phase was extracted with ethyl acetate (5 x 20 mL) followed by the removal of the solvents under reduced pressure. The solid residue was further washed with chloroform to give 74 mg as purple crystals in 91 % yield. ^{1}H-NMR (400 MHz, DMSO-*d*6, 25 °C):δ 9.75 (s, 6H, OH), 8.95-8.83 (m, 4H, bromophenyl-H), 8.03-8.19 (m, 6H, O-phenyl-H), 6.67-7.09 (m, 3H, p-phenyl-H), -3.00 (s, 2H, pyrrole, NH). ^{13}C-NMR (100 MHz, DMSO-d6, 25 °C):δ 156.52, 143.53, 135.71, 129.69, 114.37, 101.81. ESI-MS m/z $[M+H]^+$: for $C_{44}H_{29}BrN_4O_6$: Calcd. 789.13, found m/z 789.12 $[M+H]^+$. UV-VIS (MeOH): λ_{max} (nm); 418, 512, 547, 585, 638.

Porphyrin 1: To a solution of **P1-OH** (370 mg, 0.46 mmol) in 30 mL anhydrous DMF, was added K_2CO_3 (1.29 g, 9.38 mmol), KI (0.15 g, 0.93 mmol) and tri(ethylene glycol) monotosylate (1.14 g, 3.75 mmol) and refluxed at 80 °C for 12 h. Thereafter, the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure to give gummy purple residues. The resulting mixture was washed with chloroform and filtered under suction. The product was further purified by column chromatography using $CHCl_3$/MeOH (9:1) system as the eluent to obtain purple gum (0.60 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):δ 8.81-8.99 (m, 4H, bromophenyl-H), 7.91-8.19 (m, 6H, O-phenyl-H), 7.42 (s, 3H, p-phenyl-H), 6.95 (s, 3H, p-phenyl-H), 3.03-

4.32 (m, 72H, TEG-CH_2), -2.90 (s, 2H, pyrrole, NH). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C):δ 157.95, 143.79, 135.85, 129.95, 114.81, 72.18, 69.86, 67.76, 61.18, 29.70.

ESI-MS m/z for $C_{80}H_{101}BrN_4O_{24}$ calcd. 1580.60; found 1581.60 $[M+H]^+$.

UV-VIS ($CHCl_3$): λ_{max} (nm); 421, 512, 547, 585, 638.

Zinc insertion into 5-(*p*-bromophenyl)-10,15,20-tri(*m*-di-*O*-TEGphenyl)porphyrin:

To a 50 mL two-neck round bottom flask containing 30 mL of $CHCl_3$/MeOH mixture (v/v = 9/1) **Porphyrin 1** (600 mg, 0.380 mmol) was added and stirred for a while. Then, $Zn(OAc)_2$ (300 mg, 1.63 mmol) was added to the reaction mixture and refluxed at 65-70 °C for 2 h. Thereafter, the reaction mixture was cooled to room temperature and filtered under suction to remove inorganic salts. The filtrate was evaporated and passed through a small pad of silica gel using DCM/MeOH (1:1) system as the eluent. The product is evaporated under reduced pressure to yield a purple-red gum (580 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):δ 8.87-9.05 (m, 4H, bromophenyl-H), 7.89-8.03 (m, 6H, *O*-phenyl-H), 7.45 (s, 3H, *p*-phenyl-H), 6.90 (s, 3H, *p*-phenyl-H), 3.05-4.33 (m, 72H, TEG-CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C):δ 157.95, 143.79, 135.85, 129.95, 114.81, 72.18, 69.86, 67.76, 61.18, 29.70. Elemental analysis: calcd for $C_{80}H_{99}BrN_4O_{24}Zn$: C 58.238, H 6.06, N 3.40. found: C 57.29, H 6.38, N 2.93. ESI-MS m/z for $C_{80}H_{99}BrN_4O_{24}Zn$ calcd. 1644.54, found 1645.16 $[M+H]^+$. UV-VIS ($CHCl_3$): λ_{max} (nm); 426, 557, 604.

Porphyrin 2: The demethylation of P**2** is similar to P**1**, 1 equivalent 5,15-di(*p*-bromophenyl)-10,20-di(3,5-dimethoxyphenyl)porphyrin, 200 equivalent 1M BBr_3 (in DCM) was stirred under argon at -78 °C to 25 °C for 12 h. **P2-OH** was obtained as purple solid in 90 % yield. ^{1}H NMR (400 MHz DMSO-d_6, 25 °C): δ 9.72 (s, 4H, -OH), 8.85-8.98 (m, 8H, bromophenyl-H), 8.03-8.17 (m, 4H, *O*-phenyl-H), 6.78-7.15 (m, 2H, *p*-phenyl-H), -3.05 (s, 2H, pyrrole, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.02, 143.13, 140.92, 136.48, 130.43, 122.50, 120.95, 118.72, 114.78; ESI-MS m/z calcd for $C_{44}H_{28}Br_2N_4O_4$ $[M+H]^+$, 835.0477; found, 835.1550.

To a solution of **P2-OH** (500 mg, 0.598 mmol) in 30 mL anhydrous DMF, was added K_2CO_3 (1.24 g, 9.00 mmol), KI (0.200 g, 1.20 mmol) and tri(ethyleneglycol)monotosylate (1.09 g, 3.60 mmol) and refluxed at 80 °C for 12 h.

Thereafter, the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure to give gummy purple residues. The resulting mixture was washed with chloroform and filtered under suction. The product was further purified by passing through a pad of silica using chloroform as the eluent to obtain purple gum (645 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):δ 8.87-9.05 (m, 8H, bromophenyl-H), 7.87-8.09 (m, 4H, *O*-phenyl-H), 7.46 (s, 2H, *p*-phenyl-H), 6.89 (s, 2H, p-phenyl-H), 2.88-4.27 (m, 48H, TEG-CH_2). -2.90 (s, 2H, pyrrole, NH). ESI-MS m/z calcd. for $C_{68}H_{76}Br_2N_4O_{16}$, 1364.36; found 1366.16 $[M+H]^+$. UV-vis ($CHCl_3$): λ_{max} (nm); 421, 512, 547, 585, 638.

Zn was inserted into **Porphyrin 2** using the same procedure as **Porpyrin 1** (578 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C):δ 8.87-9.05 (m, 8H, bromophenyl-H), 7.87-8.09 (m, 4H, O-phenyl-H), 7.46 (s, 2H, p-phenyl-H), 6.89 (s, 2H, p-phenyl-H), 2.88-4.27 (m, 48H, TEG-CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C):δ 165.71, 152.92, 145.22, 144.89, 139.97, 7237.31, 131.05, 127.05, 126.16, 124.10, 117.29, 115.97, 110.12, 96.84, 77.34, 72.59, 70.11, 67.05, 65.35, 63.04, 61.67, 56.12. Elemental analysis: calcd for $C_{68}H_{74}Br_2N_4O_{16}Zn$: C 57.17, H 5.22, N 3.92; found: C 57.24, H 5.42, N 3.28.
ESI-MS m/z $[M+H]^+$: for $C_{68}H_{74}Br_2N_4O_{16}Zn$: Calcd. 1426.2738, found 1426.2842 $[M+H]^+$. UV-VIS ($CHCl_3$): λ_{max} (nm); 426, 557, 604.

OTT_1P: Thiophene diboronic ester (13 mg, 0.051 mmol) was placed in a two-necked round bottom flask, equipped with a condenser and under nitrogen degassed water: DMF 1:3 (15 mL) was added to dissolve the mixture in the flask and under nitrogen porphyrin **1** (167 mg, 0.101 mmol) was added. The mixture was stirred under nitrogen while heating at around 50 °C. Twenty minutes later, K_2CO_3 (140 mg, 1.01 mmol) was dissolved in degassed water (3 mL) and add to the reaction flask. Finally $Pd(OAc)_2$ (5.05 x 10^{-3} mmol) was added to flask and the temperature was increased to 80 ^{o}C. The mixture was stirred under nitrogen while heating at 80 ^{o}C for 48 h. Solvents from the reaction mixture were removed under reduced pressure and the resulting solid residue was dissolved in chloroform and filtered under suction. The filtrate was further purified by column chromatography using CH_3Cl/MeOH (1:1) system as the eluent. Solid purple product was obtained (100 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.97-8.88

(m, pyrrolic-H), 8.22-7.75 (m, Ar-H), 7.50-6.95 (m, Ph-H), 4.33-3.15 (m, PEG-CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ 157.67, 149.78, 143.18, 127.32, 126.43, 120.80, 120.33, 114.85, 71.93, 71.92, 70.66, 70.16, 70.14, 69.85, 67.80, 61.05, 61.02; Elem. Anal. for $C_{164}H_{200}N_8O_{48}SZn_2$, Calcd. C, 61.28; H, 6.27; N, 3.49; S, 1.00; found C, 61.85; H, 6.34; N, 3.20 %. ESI-MS m/z Calcd for $C_{164}H_{200}N_8O_{48}SZn_2$ $[M+H]^{2+}$, 3209.1759; found, 1605.5490.

OTT$_2$P: In a 25 mL two-neck round bottom flask porphyrin **1** (0.530 g, 0.650 mmol) and 5,5′-Bis(tributylstannyl)-2,2′-bithiophene (0.260 g, 0.350 mmol) were added. Anhydrous Toluene/THF mixture (2:1, 30 mL) was added to the flask and the resulting solution was degassed using three freeze-pump thaw cycles. Catalyst $Pd(PPh_3)_4$ (0.0175 mmol) was added to the reaction flask under argon atmosphere. The temperature of the reaction was raised to 80-90 ºC and stirred for 48 h. The solvent of the reaction mixture was removed under reduced pressure to give a purple solid residue. The solid residue was further washed with cold 1M aqueous NaOH followed by diethyl ether (Et_2O). The resulting product was dissolved in chloroform and passed through a pad of silica. The solvent was removed and dried under vacuum to obtain a purple residue (250 mg, 21 %). ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.71-8.49 (m, pyrrolic-H), 8.18-8.28 (m, Ar-H), 7.19-7.79 (m, Ph-H), 3.61-4.50 (m, TEG CH_2) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C): δ 159.21, 146.07, 141.64, 128.28, 118.50, 103.73, 72.59, 2.59, 70.98, 70.45, 69.83, 68.26, 61.71, 61.68 ppm. ESI-MS m/z Calcd for $C_{168}H_{202}N_8O_{48}S_2Zn_2$ $[M+2H]^{+2}$, 3291.1636; found, 1645.5221. Elemental analysis for $C_{168}H_{202}N_8O_{48}S_2Zn_2$ Calcd: C, 61.21; H, 6.18; N, 3.40; S, 1.95. Found: C, 61.81; H, 6.57; N, 3.11.

PTTP: In a 50 ml two-neck round bottom flask porphyrin **2** (350 mg, 0.245 mmol) and 5,5′-Bis(tributylstannyl)-2,2′-bithiophene (180 mg, 245 mmol) were dissolved in anhydrous and degassed through three freeze-pump-thaw cycles. Toluene: DMF mixture (2:1, v/v, 30 mL). After stirring for 15 min., catalyst $Pd(PPh_3)_4$ (12.2 mmol) was added and the resulting reaction mixture was refluxed under argon at 90 ºC for 48 h. After the reaction was over, the mixture was cooled down and precipitated in cold MeOH. The precipitates were collected by filtration and washed with MeOH (3-4 times) followed by *n*-hexane. The precipitates were redissolved in chloroform and precipitated in cold methanol. The polymer was obtained as purple solid (57 % yield). ^{1}H-NMR (400 MHz,

$CDCl_3$, 25 °C): δ 9.05-8.95 (m, pyrrolic-H), 7.75-8.02 (m, Ar-H), 7.56-6.85 (m, Ph-H), 4.35-2.10 (m, TEG-C*H*2). ^{13}C-NMR (100 MHz, $CDCl_3$, 25 °C): δ 158.67, 150.03, 144.03, 135.77, 135.03, 132.13, 131.66, 130.90, 129.71, 128.83, 125.60, 124.78, 124.59, 124.23, 123.64, 113.86, 69.37, 55.55, 53.55. M_n = 3109, M_w/M_n = 1.21; UV-vis ($CHCl_3$): λ_{max} (nm); 431, 557, 604.

Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra of compounds reported here, ESI-mass spectra, UV-vis absorbance spectra of oxidation of DPBF in the presence of photosensitizers.

Acknowledgments

We acknowledge TÜBİTAK for the financial support (project no: TBAG 112T058). We thank Dr. J.A. Kitchen, University of Southampton, for determining the crystal structures of porphyrin **P2** and **P5**.

References

1. J. P. Celli, B. Q. Spring, I. Rizvi, C. L. Evans, K. S. Samkoe, S. Verma, B. W. Pogue, T. Hasan, *Chem. Rev.* 2010, **110**, 2795–2838.

2. M. Ethirajan, Y. Chen, P. Joshi, R. K. Pandey, *Chem. Soc. Rev.* 2011, **40**, 340–362.

3. T. Maisch, J. Baier, B. Franz, M. Maier, M. Landthaler, R.-M. Szeimies, W. Baumler, *Proc. Natl. Acad. Sci. USA*, 2007, **104**, 17, 7223–7228.

4. T. Ishi-I, Y. Taguri, S.-H. Kato, M. Shigeiwa, H. Gorohmaru, S. Maedad, S. Mataka, *J. Mater. Chem.*, 2007, **17**, 3341–3346.

5. F. Hammerer, G. Garcia, S. Chen, F. Poyer, S. Achelle, C. Fiorini-Debuisschert, M.-P. Teulade-Fichou, P. Maillard, *J. Org. Chem.* 2014, **79**, 1406−1417.

6. M. Drobizhev, Y. Stepanenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Taylor, H. L. Anderson, *J. Am. Chem. Soc.*, 2004, **126**, 15352–15353.

7. M. Drobizhev, Y. Stepanenko, Y. Dzenis, A. Karotki, A. Rebane, P. N. Taylor, H. L. Anderson, *J. Phys. Chem. B*, 2005, **109**, 7223–7236.

8. A. Nowak-Krol, M. Grzybowski, J. Romiszewski, M. Drobizhev, G. Wicks, M. Chotkowski, A. Rebane, E. Gorecka, D. T. Gryko, *Chem. Commun*., 2013, **49**, 8368–8370.

9. M. C. DeRosa, R. J. Crutchley, *Coord. Chem. Rev.* 2002, **233-234**, 351–371.

10. B. W. Henderson, T. J. Dougherty, *Photochem. Photobiol.* 1992, **55**, 145–147.

11. D. E. Dolmans, D. Fukumura, R. K. Jain, *Nat. Rev. Cancer*, 2003, **3**, 380–387.

12. S. G. Awuah, Y. You, *RSC Adv.* 2012, **2**, 11169–11183.

13. N. Adarsh, R. R. Avirah, D. Ramaiah, *Org. Lett.*, 2010, **12**, 5720–5723.

14. S. G. Awuah, J. Polreis, V. Biradar, Y. You, Y. *Org. Lett*., 2011, **13**, 3884–3887.

15. R. L. Watley, S. G. Awuah, M. Bio, R. Cantu, Gobeze, V. N. Nesterov, S. K. Das, F. D'Souza, Y. You, Y. *Chem. Asian J.* **2015**, *10*, 1335 – 1343.

16. S. Ji, J. Ge, D. Escudero, Z. Wang, J. Zhao, D. Jacquemin, *J. Org. Chem*., 2015, **80**, 5958−5963.

17. N. Xiang, Y. Liu, W. Zhou, H. Huang, X. Guo, Z. Tan, B. Zhao, P. Shen, S. Tan, *Eur. Poly. J*., 2010, **46**, 1084–1092.

18. Y. Liu, N. Xiang, X. Feng, P. Shen, W. Zhou, C. Weng, B. Zhao, S. Tan, Chem. Commun., 2009, 2499–2501.

19. H. Maeda, *J. Control. Release*, 2012, **164**, 138–144.

20. J. S. Lindsey, *Acc. Chem. Res.* 2010, **43**, 300–311.

21. P. D. Rao, S. Dhanalekshmi, B. J. Littler, J. S. Lindsey, *J. Org. Chem.,* 2000, **65**, 7323–7344.

22. J. K. Laha, S. Dhanalekshmi, M. Taniguchi, A. Ambroise, J. S. Lindsey, *Org. Process Res. Dev.,* 2003, **7**, 799–812.

23. S. J. Narayanan, B. Sridevi, A. Srinivasan, T. K. Chandrashekar, R. Roy, *Tetrahedron Lett.*, 1998, **39**, 7389-7392.

24. B. J. Littler, Y. Ciringh, J. S. Lindsey, *J. Org. Chem.,* 1999, **64**, 2864–2872.

25. G. R. Geier, B. J. Littler, J. S. Lindsey, *J. Chem. Soc., Perkin Trans.,* 2001, **2**, 701–711.

26. L. Wen, M. Li, J.B. Schlenoff, *J. Am. Chem. Soc*., 1997, **119**, 7726-7733.

27. W. Li, L. Li, H. Xiao, R. Qi, Y. Huang, Z. Xie, X. Jing, H. Zhang, *RSC Adv.*, 2013, **3**, 13417–13421.

28. R. W. Redmond, J. N. Gamlin, *Photochem. Photobiol.* 1999, **70**, 391–475.

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