

## Investigation of photochemical and photophysical properties of novel silicon(IV) phthalocyanines and their $\mu$ -oxo dimers

Ömer GÜNGÖR<sup>1,2</sup>, Mahmut DURMUŞ<sup>1</sup>, Vefa AHSEN<sup>1,\*</sup>

<sup>1</sup>Department of Chemistry, Gebze Technical University, Gebze, Kocaeli, Turkey

<sup>2</sup>Department of Chemistry Technology, Kocaeli University, Advanced Vocational School of Hereke Ömer İsmet Uzunyol, Kocaeli, Turkey

Received: 10.01.2017

Accepted/Published Online: 06.04.2017

Final Version: 20.12.2017

**Abstract:** The synthesis and characterization of novel tetraalkylthio ( $SC_6H_{13}$  or  $SC_{12}H_{25}$ ) substituted  $\mu$ -oxo silicon(IV) phthalocyanines (**3a** and **3b**) and their  $\mu$ -oxo derivatives (**4a** and **4b**) were described in this study. These silicon(IV) phthalocyanines were characterized using different spectroscopic techniques such as UV-Vis, <sup>1</sup>H NMR, FT-IR, and mass and elemental analysis, as well. Furthermore, the photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen generation) properties of the newly synthesized silicon(IV) phthalocyanines (**3a**, **3b**, **4a**, and **4b**) were investigated in dimethylformamide solution. The absorption and fluorescence excitation wavelengths of the studied silicon(IV) phthalocyanines were blue-shifted when they converted to their  $\mu$ -oxo dimers. The fluorescence quantum yield and lifetime values decreased with the substitution of the tetraalkylthio groups on the phthalocyanine ring. The singlet oxygen generation of the studied silicon(IV) phthalocyanines increased with the formation of the  $\mu$ -oxo bridge between two phthalocyanine rings.

**Key words:** Phthalocyanine, silicon, photochemical, photophysical, singlet oxygen, fluorescence

### 1. Introduction

Phthalocyanines (Pcs) are among the most extensively studied classes of organic functional materials due to their delocalized aromatic 18- $\pi$  electron system, which is closely related to that of the naturally occurring porphyrin ring.<sup>1</sup> Pcs have been widely studied as molecular materials because of their outstanding electronic and optical properties. Apart from their extensive use as blue and green colorants, they have different applications, such as in catalytic processes,<sup>2</sup> nonlinear optics,<sup>3</sup> gas sensors,<sup>4</sup> liquid crystals,<sup>5</sup> and photodynamic therapy (PDT) of cancer.<sup>6</sup> Furthermore, they are excellent building blocks for supramolecular chemistry.

Metallophthalocyanines have low solubility in most organic solvents. The solubility of these compounds can be increased by substitution of the Pc framework with various groups. Octasubstituted Pcs are generally less soluble than tetrasubstituted Pcs in organic solvents due to the high dipole moment of tetrasubstituted derivatives.<sup>7</sup> The 4A group Pcs metallo are of interest because various groups can be attached to the axial positions on the metal center. Furthermore, some of these Pcs are capable of forming linear stacked polymers, which represent an effective approach to building metallomacrocyclic conductors.<sup>8</sup>

The most well-known  $\mu$ -oxo Pc dimers are those of their silicon(IV) derivatives. These are easily obtained by refluxing SiPc(OH)<sub>2</sub> with K<sub>2</sub>CO<sub>3</sub> in toluene for several hours. The spectroscopic properties of these dimeric

\*Correspondence: ahsen@gtu.edu.tr

Pcs have been intensively studied. The Q-band absorptions of dimeric silicon(IV) Pcs were shifted towards a lower wavelength compared to their monomeric counterparts in the electronic absorption spectra and hence this became a good example to confirm the exciton model.<sup>9</sup>

Scientists are very interested in the axially substituted silicon(IV) Pcs due to their superior structural properties. These compounds are not able to aggregate due to their special structural features and thus avoid fluorescence quenching.<sup>10</sup> They are also very attractive targets for the study of photophysical processes.<sup>11</sup> Silicon(IV) Pc derivatives are capable of forming stacked  $\mu$ -oxo oligomeric structures in which the stacking axis, formed by Si–O–Si bonds, is orthogonal to the Pc  $\pi$ -planes. These  $\mu$ -oxo oligomers have been considered useful in developing molecular electronic devices because of their excellent photophysical and photochemical stabilities.<sup>12–14</sup>

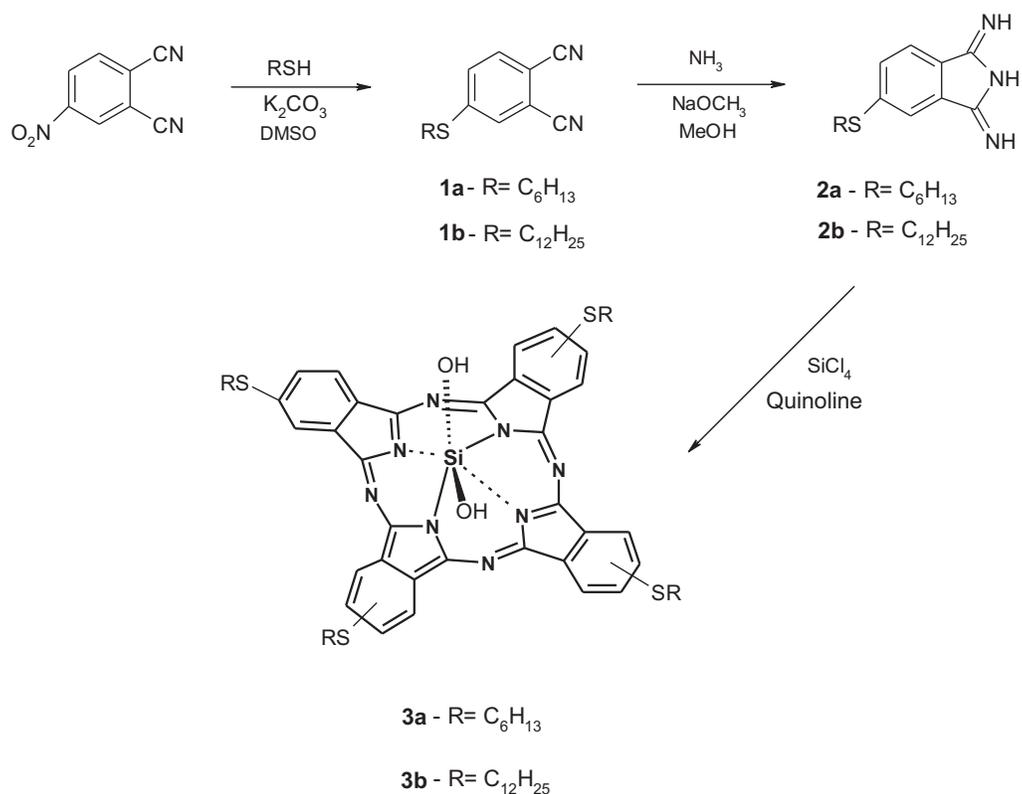
In this paper, we report the synthesis of new silicon(IV) phthalocyanines (**3a** and **3b**) bearing alkylthio groups ( $\text{SC}_6\text{H}_{13}$  and  $\text{SC}_{12}\text{H}_{25}$ ) and their  $\mu$ -oxo bridged silicon(IV) Pc dimers (**4a** and **4b**). The aim of the present study is the synthesis of novel Pc compounds as photosensitizers for PDT in cancer treatment. The photophysical properties such as fluorescence quantum yields and lifetimes and photochemical properties such as singlet oxygen quantum yields of these novel silicon(IV) phthalocyanines were investigated in dimethylformamide (DMF).

## 2. Results and discussion

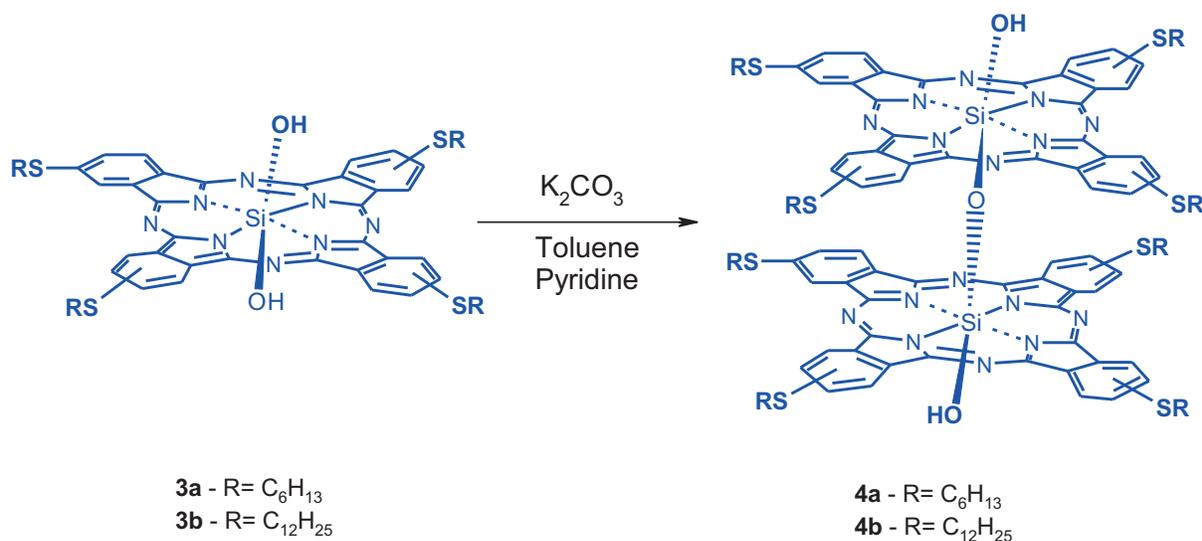
The general synthetic routes for the synthesis of the new compounds (**3a**, **3b**, **4a**, and **4b**) are given in Schemes 1 and 2. The peripheral tetra substituted monomeric silicon(IV) Pcs (**3a** and **3b**) were prepared by cyclotetramerization of alkylthio ( $\text{SC}_6\text{H}_{13}$  or  $\text{SC}_{12}\text{H}_{25}$ ) substituted isoiminoindolines in the presence of  $\text{SiCl}_4$  in quinoline. The most well-known  $\mu$ -oxo bridged Pc dimers are those of SiPc derivatives. These Pcs are easily obtained by the refluxing of  $\text{SiPc}(\text{OH})_2$  and  $\text{K}_2\text{CO}_3$  in a toluene-pyridine solvent mixture for several hours.<sup>9</sup> In this study, the  $\mu$ -oxo silicon(IV) Pcs **4a** and **4b** were also synthesized from monomeric counterparts **3a** or **3b** in the presence of  $\text{K}_2\text{CO}_3$  at reflux temperature in a dry toluene-pyridine solvent mixture.

The synthesized novel compounds were characterized by elemental analysis and standard spectroscopic methods such as FT-IR, <sup>1</sup>H-NMR, UV-Vis, and mass. The novel Pcs are insoluble in most of the organic solvents (DMSO, toluene, THF, ethanol). The same property was observed in the unsubstituted dihydroxy silicon(IV) Pc. The decreased solubility of the new compounds is probably due to the increased hydrogen bonds on the axial positions (Figure S1).

In the FT-IR spectra of the silicon(IV) Pcs, the broad bands were observed at around  $3470\text{ cm}^{-1}$  and they were assigned to the O-H vibrations on the central silicon atom. The disappearance of the N-H vibrations on the vibration peak belongs to diiminoisoindoline compounds (**2a** and **2b**) at  $3400\text{ cm}^{-1}$  can be assigned to the formation of Pc ring. The Si-Cl peak is also observed at  $520\text{ cm}^{-1}$  for chloro silicon(IV) phthalocyanine.<sup>15</sup> In the case of the dihydroxy derivative, this band disappears, while the observation of the vibrations at  $835\text{ cm}^{-1}$  are attributed to O-Si-O antisymmetric stretching vibrations in silicon(IV) Pcs (**3a**, **3b** and **4a** and **4b**). For the  $\mu$ -oxo silicon(IV) Pc (**4a** and **4b**) compounds, a broad band at around  $990\text{ cm}^{-1}$  was assigned to the Si-O-Si asymmetric stretching vibration. Therefore, evidence for the existence of a Si-O-Si bond in the dimer is of importance for assigning the structure.<sup>16–18</sup> The aliphatic C-H vibrations on the silicon(IV) Pcs were also observed at around  $2925\text{--}2850\text{ cm}^{-1}$ . The C-N stretching vibrations were also observed at around  $1042\text{--}1044\text{ cm}^{-1}$  for these compounds (Figures S2–S5).



**Scheme 1.** Synthesis of tetraalkylthio substituted silicon(IV) phthalocyanines.



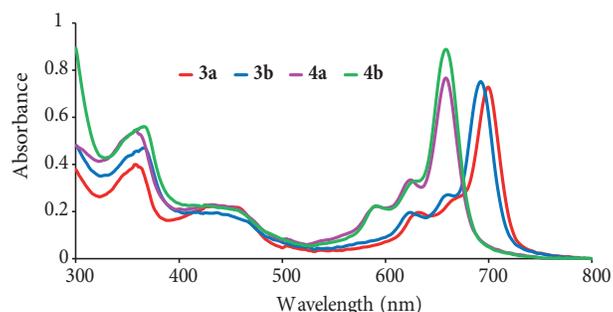
**Scheme 2.** Synthesis of tetraalkylthio substituted dimeric silicon(IV) phthalocyanines (**4a** and **4b**).

The most well-known <sup>1</sup>H NMR spectra of  $\mu$ -oxo Pc dimers were observed as split into two couples compared to the monomer counterparts.<sup>9</sup> The synthesized silicon(IV) Pcs (**3a**, **3b** and **4a**, **4b**) showed the characteristic <sup>1</sup>H NMR spectra in deuterated chloroform. In the <sup>1</sup>H NMR spectra of the monomeric silicon(IV) phthalocyanine derivatives (**3a** and **3b**), the Si-OH protons were observed at -2.05 ppm for **3a** and -2.10 ppm

for **3b** due to the magnetic anisotropy of the Pc core.<sup>19</sup> The aromatic protons of Pcs were observed between 8.73 and 8.10 ppm for **3a** and between 8.75 and 8.07 ppm for **3b**, integrating a total of twelve protons. The aliphatic CH<sub>2</sub> protons were observed at three different regions at around 3.40, 1.75, and 1.25–1.45 ppm due to their diverse chemical environment and their proximity to the Pc rings. The methyl protons were observed at around 0.85 ppm, which is higher field than expected due to the magnetic anisotropy effect of the Pc ring.<sup>19</sup> In the <sup>1</sup>H NMR spectra of dimeric silicon(IV) Pc derivatives (**4a** and **4b**), the Si-OH protons were observed at around -2.42 ppm. The aromatic protons on the Pc ring were observed as two sets between 8.75–8.07 and 7.92–7.44 ppm for **4a** and between 9.11–8.33 and 8.28–7.97 ppm for **4b**, integrating 24 protons. The aliphatic CH<sub>2</sub> protons were observed at three different regions at around 3.56–3.40, 1.82–1.50, and 1.48–1.20 ppm due to their diverse chemical environment and their proximity to the Pc rings. The methyl protons were observed at high field at around 0.73–0.52 ppm for **4a** and 0.54–0.31 ppm for **4b** due to the magnetic anisotropy effect of the Pc ring.<sup>19</sup>

The mass spectra of the silicon(IV) Pcs (**3a**, **3b** and **4a**, **4b**) also confirmed the proposed structures of the target compounds and the molecular ion peaks were observed at  $m/z$  : 1039.74 as [M]<sup>+</sup> for **3a** (Figure S6), 1376.36 as [M]<sup>+</sup> for **3b** (Figure S7), 2061.98 as [M]<sup>+</sup> for **4a** (Figure S8), and 2734.89 as [M]<sup>+</sup> for compound **4b** (Figure S9). Furthermore, the mass spectra of the dimers (**4a**, **4b**) show that they did not consist of a trimer.

The UV-Vis absorption spectra of monomeric (**3a** and **3b**) and dimeric (**4a** and **4b**) silicon(IV) Pcs were measured in DMF solutions. The  $\mu$ -oxo silicon(IV) Pc dimers generally exhibit approximately 30 nm blue-shifted Q-band absorption when compared to their corresponding monomer counterparts.<sup>20</sup> It is generally agreed that the blue shift of the Q-bands with respect to the dimer is due to an excitonic interaction of the transition dipoles of the coplanar silicon(IV) Pc units having central symmetry along the Si–O–Si axis, with no significant molecular orbital overlap. The UV-Vis absorption spectra of the studied monomeric (**3a** and **3b**) and dimeric (**4a** and **4b**) silicon(IV) Pcs in DMF solutions are supplied in Figure 1 for comparison purposes. The single narrow Q-bands were observed at 696, 695, 665, and 661 nm for compounds **3a**, **3b**, **4a**, and **4b** in this solvent, respectively (Table 1). The absorption spectra of the monomer and  $\mu$ -oxo dimer are in good agreement with previously reported data.<sup>20</sup>



**Figure 1.** UV-Vis absorption spectra of compounds **3a**, **3b**, **4a**, and **4b** in DMF. Concentration =  $1 \times 10^{-5}$  M.

## 2.1. Aggregation studies

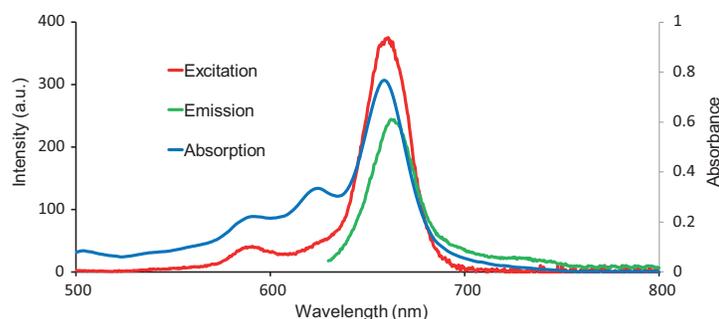
Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes. It is dependent on the concentration and nature of the used solvent, nature of the substituents, complexed metal ions, and temperature.<sup>21</sup> In the aggregation state, the electronic structures of the complexed

**Table 1.** Absorption, excitation, and emission spectral data for the monomeric (**3a** and **3b**) and  $\mu$ -oxo dimeric (**4a** and **4b**) silicon(IV) phthalocyanines in DMF.

Compound	$\lambda_{\max}$ (nm)	$\log \varepsilon$	$\lambda_{Ex}$ (nm)	$\lambda_{Em}$ (nm)	Stokes shift, $\Delta_{Stokes}$ (nm)
<b>3a</b>	696	4.85	700	710	10
<b>3b</b>	695	4.86	700	710	10
<b>4a</b>	665	4.90	662	664	2
<b>4b</b>	661	4.94	662	666	4
SiPc	697	4.04	700	709	9

$\lambda_{\max}$ : Absorption maximum,  $\lambda_{Ex}$ : excitation maximum,  $\lambda_{Em}$ : emission maximum.

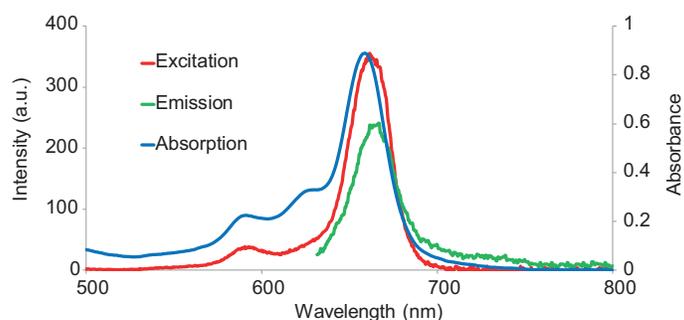
Pc rings are perturbed, resulting in alternation of the ground and excited state electronic structures.<sup>22</sup> In this study, the aggregation behaviors of monomeric (**3a** and **3b**) and  $\mu$ -oxo dimeric (**4a** and **4b**) silicon(IV) Pcs were investigated at different concentrations in DMF. We complied with the Beer–Lambert law for all of these compounds at concentrations ranging from  $1.2 \times 10^{-5}$  to  $2.0 \times 10^{-6}$  M. None of the studied Pc compounds showed any aggregation at these concentration ranges in DMF (Figure S10 for **3a**, Figure S11 for **3b**, Figure S12 for **4a**, Figure S13 for **4b**).

**Figure 2.** Electronic absorption, fluorescence emission, and excitation spectra for compound **4a** in DMF. Excitation wavelength is 620 nm.

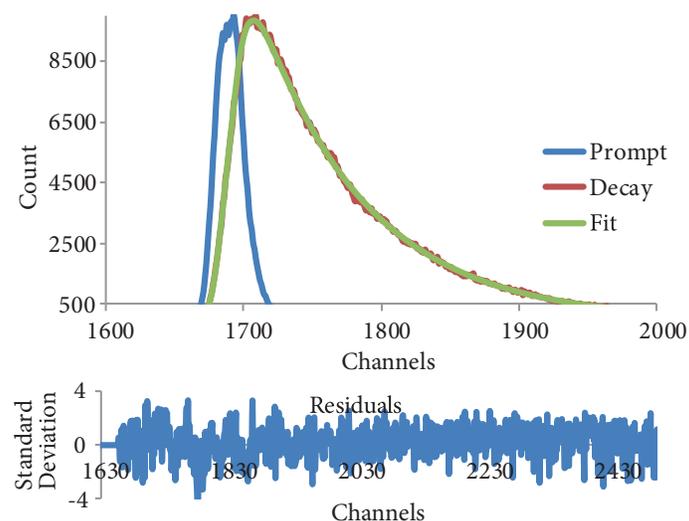
## 2.2. Fluorescence quantum yields and lifetimes

Figures 2 and 3 show the electronic absorption, fluorescence emission, and excitation spectra of  $\mu$ -oxo dimeric silicon(IV) Pcs (**4a** and **4b**) in DMF. The peak maxima of the fluorescence emission and excitation spectra of the studied compounds (**3a**, **3b**, **4a**, and **4b**) in DMF are listed in Table 1. Fluorescence emission peaks were observed at 664 and 666 nm for  $\mu$ -oxo dimeric silicon(IV) Pcs (**4a** and **4b**) and at 710 nm for the monomeric compounds (**3a** and **3b**) in DMF (Table 1). While the observed Stokes shifts ( $\lambda_{ems} - \lambda_{exc}$ ) of the studied monomeric silicon(IV) Pcs (**3a** and **3b**) were higher, these values of dimeric derivative Pcs (**4a** and **4b**) were lower than those of unsubstituted silicon(IV) Pc in DMF.<sup>23</sup> The excitation spectra of the studied silicon(IV) Pcs were similar to the absorption spectra of these compounds and both were mirror images of the fluorescence emission spectra in DMF. All studied compounds showed similar electronic absorption and fluorescence excitation spectra. This suggests that the nuclear configurations of the ground and excited states of these compounds were similar and these compounds were not affected by excitation in DMF.

The fluorescence quantum yields ( $\Phi_F$ ) of silicon(IV) Pcs (**3a**, **3b**, **4a**, and **4b**) in DMF are given in Table 2. The  $\Phi_F$  values of all studied alkylthio substituted silicon(IV) Pcs were lower than those of standard



**Figure 3.** Electronic absorption, fluorescence emission, and excitation spectra for compound **4b** in DMF. Excitation wavelength is 620 nm.



**Figure 4.** Time correlated single photon counting (TCSPC) trace for compound **4a** in DMF with residuals. Excitation wavelength = 665 nm.

unsubstituted silicon(IV) Pc in DMF. The  $\mu$ -oxo dimeric silicon(IV) Pcs (**4a** and **4b**) showed higher fluorescence quantum yields ( $\Phi_F$ ) than their monomeric counterparts (**3a** and **3b**) in DMF.

**Table 2.** Photophysical and photochemical data for the monomeric (**3a** and **3b**) and  $\mu$ -oxo dimeric (**4a** and **4b**) silicon(IV) phthalocyanines in DMF.

Compound	$\Phi_F$	$\tau_F$ (ns)	$\Phi_\Delta$
<b>3a</b>	0.09	3.85	0.10
<b>3b</b>	0.09	3.98	0.11
<b>4a</b>	0.15	4.21	0.18
<b>4b</b>	0.14	4.13	0.19
SiPc	0.52 <sup>a</sup>	4.91	0.12 <sup>a</sup>

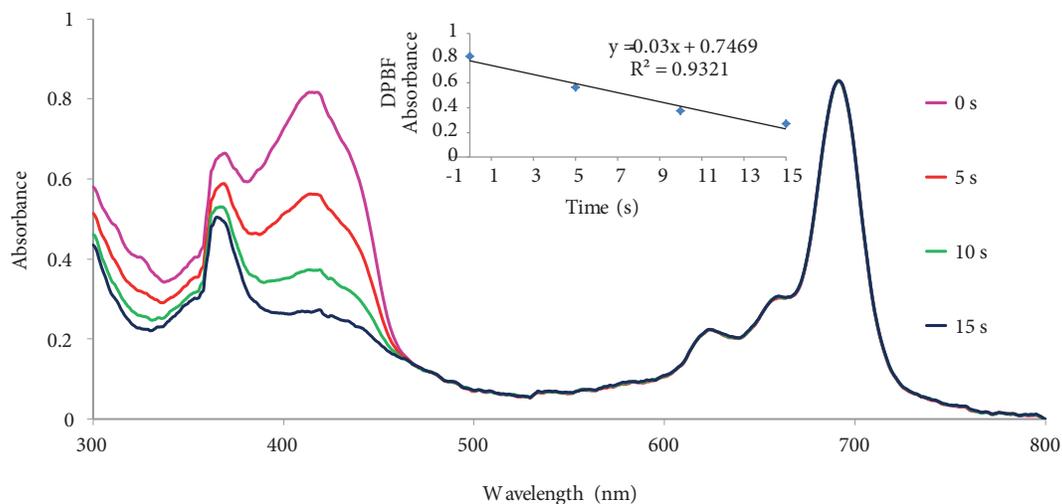
<sup>a</sup>Data from Ref. [23].

Fluorescence lifetime ( $\tau_F$ ) refers to the average time a molecule stays in its excited state before returning to its ground state by emitting. Many factors such as internal conversion, intersystem crossing, aggregation, and used solvent affect the fluorescence lifetime of a photosensitizer.<sup>24</sup> Fluorescence lifetime ( $\tau_F$ ) values of the synthesized Pc complexes (**3a**, **3b**, **4a**, and **4b**) were measured by a time correlated single photon counting

(TCSPC) method in DMF solutions. Fluorescence lifetime spectra were given in Figure 4 for compound **4a** as an example in DMF solution.

### 2.3. Singlet oxygen quantum yields

Singlet oxygen is generated as a result of a bimolecular interaction between the triplet state of a photosensitizer and the ground state (triplet) molecular oxygen and is quantified as singlet oxygen quantum yield ( $\Phi_{\Delta}$ ).<sup>24</sup> In this study, the generated singlet oxygen by silicon(IV) Pcs (**3a**, **3b**, **4a**, and **4b**) was determined using UV-Vis spectroscopy. The absorption decay of 1,3-diphenylisobenzofuran (DPBF) was monitored at 417 nm during light irradiation using a photochemical set-up.<sup>25,26</sup> No change was observed in the Q-band intensities of the studied silicon(IV) Pcs during the  $\Phi_{\Delta}$  determinations, indicating that the used light irradiation (30 V) did not degrade the studied Pcs (Figure 5 for Pc **4b** and Figures S14-S17 for phthalocyanines **3a**, **3b**, and **4a**, respectively). The  $\Phi_{\Delta}$  values of the synthesized silicon(IV) Pcs (**3a**, **3b**, **4a**, and **4b**) and unsubstituted silicon(IV) Pc are given in Table 2. These values of monomeric silicon(IV) Pcs (**3a** and **3b**) in DMF were found lower than those for unsubstituted silicon(IV) Pc. These values of dimeric silicon(IV) Pcs (**4a** and **4b**) were higher than those for unsubstituted silicon(IV) Pc in DMF, which means that these Pcs can be used as photosensitizers for PDT applications.



**Figure 5.** Electronic absorption spectral changes of compound **4b** during the determination of singlet oxygen quantum yield in DMF at a concentration of  $1 \times 10^{-5}$  M.

### 2.4. Conclusions

In the presented work, the synthesis of tetraalkylthio ( $SC_6H_{13}$  and  $SC_{12}H_{25}$ ) substituted monomeric (**3a** and **3b**) and  $\mu$ -oxo dimeric (**4a** and **4b**) silicon(IV) Pcs was described and these Pcs were fully characterized by elemental analysis and the standard spectral data such as FT-IR,  $^1H$  NMR, UV-Vis, and mass spectra. The photophysical and photochemical properties including fluorescence quantum yields, lifetimes, and singlet oxygen generation of all these silicon(IV) Pcs were also described and compared with unsubstituted SiPc. In solution, the absorption spectra of the new compounds (**3a**, **3b**, **4a**, and **4b**) showed monomeric behavior evidenced by a single (narrow) Q-band, typical of metallated Pc complexes in DMF. The dimerization of the Pc rings by the  $\mu$ -oxo silicon bridge caused approximately 30 nm of blue-shift to the absorption wavelength of the Q-band. The

photophysical (fluorescence quantum yields and lifetimes) values of monomeric silicon(IV) Pcs (**3a** and **3b**) were found lower than those of unsubstituted SiPc in DMF. The  $\mu$ -oxo silicon(IV) Pcs (**4a** and **4b**) showed higher singlet oxygen quantum yields than unsubstituted SiPc and the monomeric counterparts (**3a** and **3b**). As a result, the  $\mu$ -oxo silicon(IV) Pcs (**4a** and **4b**) offer potential as candidate photosensitizers for the treatment of cancer by PDT.

### 3. Experimental

#### 3.1. Materials and methods

The used materials and equipment are given in the Supplementary information. Photophysical and photochemical parameters were calculated according to previous literature.<sup>27</sup>

#### 3.2. Synthesis

4-Hexylthiophthalonitrile (**1a**), 4-dodecylthiophthalonitrile (**1b**), 1,3-dihydro-1,3-diimino-6-(n-hexylthio)-isoiminoindoline (**2a**) and 1,3-dihydro-1,3-diimino-6-(n-dodecylthio)-isoiminoindoline (**2b**) were synthesized, purified, and characterized according to the literature procedures.<sup>28–30</sup>

##### 3.2.1. 1,3-Dihydro-1,3-diimino-6-(n-hexylthio)-isoiminoindoline (**2a**)

To a solution of **1a** (3.26 g, 2.04 mmol) in dry methanol (150 mL) under an argon atmosphere, sodium methoxide (0.165 g, 3.06 mmol) was added. Anhydrous ammonia was bubbled through the mixture for 6 h at reflux temperature. The ammonia inlet was stopped and the volume of the solution was reduced to 50 mL under reduced pressure. With crystallization from MeOH/acetone 1:5 (v/v), **2a** was obtained as pale yellow crystals. Yield: 2.96 g, 85%, Mp = 165 °C (dec.). FT-IR  $\nu_{\max}/\text{cm}^{-1}$ : 3400 (NH), 2951–2923 (aliphatic C-H), 1641, 1593, 1536, 1455, 1380, 1320, 1289, 1237, 1154, 1075, 885, 813, 729, 678. <sup>1</sup>H NMR (CDCl<sub>3</sub>) ( $\delta$ : ppm): 8.22 (br, N-H, 3H), 7.40 (m, Ar-H, 3H), 2.87 (t, J = 7.3 Hz, S-CH<sub>2</sub>, 2H), 1.60 (q, S-C-CH<sub>2</sub>, 2H), 1.25–1.28 (m, C-CH<sub>2</sub>-C, 6H), 0.80 (t, J = 6.5 Hz, CH<sub>3</sub>, 3H). Mass (ES<sup>+</sup>), ( $m/z$ ): Calculated as 261.39 for C<sub>14</sub>H<sub>19</sub>N<sub>3</sub>S; Found: 262.26 [M+H]<sup>+</sup>. Anal. Calcd. for C<sub>14</sub>H<sub>19</sub>N<sub>3</sub>S: C, 64.33%; H, 7.33%; N, 16.08%; Found C, 64.73%; H, 7.52%; N, 15.93%.

##### 3.2.2. Tetrakis (4-hexylthio)dihydroxy silicon(IV) phthalocyanine (**3a**)

A mixture of the 1,3-dihydro-1,3-diimino-6-(n-hexylthio)-isoiminoindoline (**2a**) (1 g, 3.82 mmol) in dry quinoline (5 mL) was stirred at room temperature for 10 min. SiCl<sub>4</sub> (0.22 mL, 1.91 mmol) was added to this mixture and refluxed for 2 h. After this time, the reaction was cooled to room temperature and 5 mL of hydrochloric acid (36.5%) was then added to the mixture and stirred at 60 °C for 1 h. The formed blue solid product was filtered and washed with ammonium hydroxide, water, methanol, and ethyl acetate. The pure product was obtained after drying at 110 °C overnight. Yield: 0.30 g (29%). Mp > 400 °C. FT-IR  $\nu_{\max}/\text{cm}^{-1}$ : 3462 (OH), 2924–2852 (aliphatic C-H), 1600 (C=N), 1517 (C=C), 1451, 1392, 1349, 1312, 1145, 1068, 1042, 929, 900, 835 (Si-OH), 767, 751, 732, 695. <sup>1</sup>H NMR (CDCl<sub>3</sub>) ( $\delta$ : ppm): 8.73 (m, Ar-H, 7H), 8.10 (m, Ar-H, 5H), 3.36 (t, J = 3 Hz, S-CH<sub>2</sub>, 8H), 1.72 (q, S-C-CH<sub>2</sub>, 8H), 1.26–1.42 (m, C-CH<sub>2</sub>-C, 24H), 0.84 (t, J = 3 Hz, CH<sub>3</sub>, 12H), -2.05 (s, OH, 2H). UV-Vis (DMF):  $\lambda_{\max}$ , nm (log  $\epsilon$ ): 696 (4.85), 673 (4.43), 636 (4.25), 361 (4.58). Mass (ES<sup>+</sup>), ( $m/z$ ): Calculated as 1039.52 for C<sub>56</sub>H<sub>66</sub>N<sub>8</sub>S<sub>4</sub>O<sub>2</sub>Si; Found: 1039.74 [M]<sup>+</sup>, 1022.80 [M-OH]<sup>+</sup>, 922.58

$[M-SC_6H_{13}]^+$ . Anal. Calcd. for  $C_{56}H_{66}N_8S_4O_2Si$ : C, 64.70%; H, 6.40%; N, 10.78%; Found C, 64.95%; H, 6.55%; N, 10.63%.

### 3.2.3. Tetrakis (4-dodecylthio)dihydroxy silicon(IV) phthalocyanine (3b)

A mixture of the 1,3-dihydro-1,3-diimino-6-(n-dodecylthio)-isoiminoindoline (**2b**) (1 g, 2.89 mmol) in dry quinoline (5 mL) was stirred at room temperature for 10 min.  $SiCl_4$  (0.17 mL, 1.45 mmol) was added to this mixture and refluxed for 2 h and then it was cooled to room temperature. Next, 5 mL of hydrochloric acid (36.5%) was added to the mixture and stirred at 60 °C for 1 h. The formed blue solid product was filtered and washed with ammonium hydroxide, water, methanol, and ethyl acetate. The pure product was obtained after drying at 110 °C overnight. Yield: 0.25 g (23%). Mp > 400 °C. FT-IR  $\nu_{max}/cm^{-1}$ : 3456 (OH), 2919–2851 (aliphatic C-H), 1601 (C=N), 1518 (C=C), 1455, 1396, 1349, 1315, 1267, 1148, 1068, 1044, 931, 831 (Si-OH), 767, 752, 731, 695.  $^1H$  NMR ( $CDCl_3$ ) ( $\delta$ : ppm): 8.75 (m, Pc-H, 7H), 8.07 (m, Pc-H, 5H), 3.39 (t, J = 3 Hz, S-CH<sub>2</sub>, 8H), 1.76 (q, S-C-CH<sub>2</sub>, 8H), 1.29–1.47 (m, C-CH<sub>2</sub>-C, 72H), 0.89 (t, J = 3 Hz, CH<sub>3</sub>, 12H), –2.10 (s, OH, 2H). UV-Vis (DMF):  $\lambda_{max}$ , nm (log  $\epsilon$ ): 695 (4.86), 665 (4.43), 629 (4.28), 364 (4.51). Mass (ES<sup>+</sup>), (m/z): Calculated as 1376.15 for  $C_{80}H_{114}N_8S_4O_2Si$ ; Found: 1376.36 [M]<sup>+</sup>, 1359.06 [M-OH]<sup>+</sup>, 1344.80 [M-2OH]<sup>+</sup>, 1190.64 [M-SC<sub>12</sub>H<sub>25</sub>]<sup>+</sup>. Anal. Calcd. for  $C_{80}H_{114}N_8S_4O_2Si$ : C, 69.82%; H, 8.35%; N, 8.14%; Found C, 69.93%; H, 8.48%; N, 8.36%.

### 3.2.4. General procedure for the synthesis of 4a and 4b

The tetraalkylthio substituted silicon(IV) phthalocyanine (**3a** or **3b**) [**3a** (0.2 g, 0.19 mmol), **3b** (0.2 g, 0.15 mmol)] was dissolved in a mixture of dry toluene (5 mL) and dry pyridine (5 mL). Anhydrous  $K_2CO_3$  [13.30 mg (0.1 mmol) for **3a** and 10.04 mg, (0.07 mmol) for **3b**] was added to this solution and refluxed for 2 h. The solvent was removed after this time. The resulting blue solid product was obtained after washing with water, acetone, and ethyl acetate.

**4a**: Yield: 0.1 g (51%). Mp > 400 °C. FT-IR  $\nu_{max}/cm^{-1}$ : 3463 (OH), 2924–2851 (aliphatic C-H), 1601 (C=N), 1518 (C=C), 1454, 1392, 1314, 1260, 1144, 1068, 1043, 986 (Si-O-Si), 929, 832 (Si-OH), 815, 768, 751.  $^1H$  NMR ( $CDCl_3$ ) ( $\delta$ : ppm): 9.01–8.30 (m, Pc-H, 16H), 7.92–7.44 (m, Pc-H, 8H), 3.55–3.41 (m, S-CH<sub>2</sub>, 16H), 1.82–1.70 (m, S-C-CH<sub>2</sub>, 16H), 1.42–1.31 (m, CH<sub>2</sub>, 48H), 0.73–0.52 (m, CH<sub>3</sub>, 24H), –2.42 (s, OH, 2H). UV-Vis (DMF):  $\lambda_{max}$ , nm (log  $\epsilon$ ): 665 (4.90), 628 (4.52), 594 (4.34), 361 (4.74). MS (ES<sup>+</sup>), (m/z): Calculated as 2061.02 for  $C_{112}H_{130}N_{16}S_8O_3Si_2$ ; Found: 2061.98. [M]<sup>+</sup>, 2044.93 [M-OH]<sup>+</sup>, 1039.63 [M-Pc]<sup>+</sup>, 1022.60 [M-Pc-OH]<sup>+</sup>. Anal. Calcd. for  $C_{112}H_{130}N_{16}S_8O_3Si_2$ : C, 65.27%; H, 6.36%; N, 10.87%; found C, 65.93%; H, 6.29%; N, 11.03%.

**4b**: Yield: 0.095 g (48%). Mp > 400 °C. FT-IR  $\nu_{max}/cm^{-1}$ : 3469 (OH), 2923–2852 (aliphatic C-H), 1601 (C=N), 1519 (C=C), 1454, 1352, 1312, 1147, 1070, 1042, 995 (Si-O-Si), 930, 831 (Si-OH), 817, 768, 751, 732.  $^1H$  NMR ( $CDCl_3$ ) ( $\delta$ : ppm): 9.11–8.93 (m, Pc-H, 16H), 8.28–7.97 (m, Pc-H, 8H), 3.56–3.42 (m, S-CH<sub>2</sub>, 16H), 1.73–1.50 (m, S-C-CH<sub>2</sub>, 16H), 1.48–1.20 (m, CH<sub>2</sub>, 144H), 0.54–0.31 (m, CH<sub>3</sub>, 24H), –2.34 (s, OH, 2H). UV-Vis (DMF):  $\lambda_{max}$ , nm (log  $\epsilon$ ): 661 (4.94), 630 (4.51), 594 (4.34), 368 (4.74). MS (ES<sup>+</sup>), (m/z): Calculated as 2734.29 for  $C_{160}H_{226}N_{16}S_8O_3Si_2$ ; Found: 2734.89 [M]<sup>+</sup>, 2718.30 [M-OH]<sup>+</sup>, 2516.91 [M-SC<sub>12</sub>H<sub>25</sub>-OH]<sup>+</sup>, 1359.16 [M-Pc-OH]<sup>+</sup>. Anal. Calcd. for  $C_{160}H_{226}N_{16}S_8O_3Si_2$ : C, 70.28%; H, 8.33%; N, 8.20%; Found C, 70.43%; H, 8.29%; N, 8.56%.

## References

1. Kadish, K. M.; Smith, K. M.; Guillard, R. *The Porphyrin Handbook*; Academic Press: Amsterdam, the Netherlands, 2003.
2. Lever, A. B. P.; Hempstead, M. R.; Leznoff, C. C.; Liu W.; Melnik, M.; Nevin, W. A.; Seymour, P. *Pure Appl. Chem.* **1986**, *58*, 1467-1476.
3. Dini, D.; Hanack, M. In *The Porphyrin Handbook*; Kadish, K. M.; Smith, K. M.; Guillard, R., Eds. Academic Press: Amsterdam, the Netherlands, 2003, p. 107.
4. Guillaud, G.; Simon J.; Germain, J. P. *Coord. Chem. Rev.* **1998**, *178*, 1433-1484.
5. Simon, J.; Sirlin, C. *Pure Appl. Chem.* **1989**, *61*, 1625-1629.
6. Leznoff, C. C.; Lever, A. B. P. In *Phthalocyanines: Properties and Applications*; Rosenthal, I., Ed. VCH Publishers: New York, NY, USA, 1996, pp. 481-514.
7. Leznoff, C. C.; Lever, A. B. P. In *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Ed. VCH Publishers: New York, NY, USA, 1989, pp. 1-54.
8. Leznoff, C. C.; Lever, A. B. P. In *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Ed. VCH Publishers: New York, NY, USA, 1989, pp. 55-132.
9. Kobayashi, N. *Coord. Chem. Rev.* **2002**, *227*, 129-152.
10. Cheng, G.; Peng, X.; Hao, G.; Kennedy, V. O.; Ivano, I. N.; Knappenberger, K.; Hill, T. J.; Rodgers, M. A. J.; Kenney, M. E. *J. Phys. Chem. A* **2003**, *107*, 3503-3514.
11. McKeown, N. B. *J. Mater. Chem.* **2000**, *10*, 1979-1995.
12. Ferencz, A.; Neher, D.; Schultz, M.; Wegner, G.; Viaene, L.; Schryver, F. C. D. *Chem. Phys. Lett.* **1995**, *245*, 23-29.
13. Leznoff, C. C.; Lever, A. B. P. In *Phthalocyanines: Properties and Applications*; Rosenthal, I., Ed. VCH Publishers: New York, NY, USA, 1996, pp. 405-425.
14. Manas, E.; Spano, F. C.; Chen, L. X. *J. Chem. Phys.* **1997**, *107*, 707-719.
15. Wheeler, B. L.; Nagasubramanian, G.; Bard, A. J.; Schectman, L. A.; Dininny, D. R.; Kenney, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 7404-7410.
16. Kobayashi, N.; Furuya, F.; Yug, G.; Wakita, H.; Yokomizo, M.; Ishikawa, N. *Chem. Eur. J.* **2002**, *8*, 1474-1484.
17. Ahsen, V.; Yilmazer, E.; Gürek, A. G.; Gül, A.; Bekaroğlu, Ö. *Helv. Chim. Acta* **1988**, *71*, 1616-1621.
18. Taşkın, G. C.; Durmuş, M.; Yüksel F.; Mantareva, V.; Kussovski, V.; Angelov, I.; Atilla D. *J. Photochem. Photobiol. A* **2015**, *306*, 31-40.
19. Güngör, Ö.; Özpınar, G. A.; Durmuş M.; Ahsen, V. *Dalton Trans.* **2016**, *45*, 7634-7641.
20. Ciliberto, E.; Doris, K. A.; Pietro, W. J.; Reisner, G. M.; Ellis, D. E.; Fragala, I.; Herstein, F. H.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7748-7761.
21. Hans, E.; Roeland, J. M. N. *J. Porphyrins Phthalocyanines* **2000**, *4*, 454-460.
22. Dominquez, D. D.; Snow, A. W.; Shirk, J. S.; Pong, G. S. *J. Porphyrins Phthalocyanines* **2001**, *5*, 582-592.
23. Atmaca, G. Y.; Dizman, C.; Eren, T.; Erdoğan, A. *Spectrochim. Acta A* **2015**, *137*, 244-249.
24. Durmuş, M. In *Photosensitizers in Medicine, Environment, and Security*; Nyokong, T.; Ahsen, V.; Eds. Springer: Dordrecht, the Netherlands, 2012, pp. 135-266.
25. Ogunsipe, A.; Nyokong, T. *J. Photochem. Photobiol. A* **2005**, *173*, 211-220.
26. Seotsanyana-Mokhosi, I.; Kuznetsova, N.; Nyokong, T. *J. Photochem. Photobiol. A* **2001**, *140*, 215-222.
27. Durmuş, M.; Yaman, H.; Göl, C.; Ahsen, V.; Nyokong, T. *Dyes Pigments* **2011**, *91*, 153-163.
28. İsci, Ü.; Afanasiev, P.; Millet, J. M.; Kudrik, E. V.; Ahsen, V.; Sorokin, A. B. *Dalton Trans.* **2009**, *36*, 7410-7420.
29. Dabak S.; Bekaroğlu, Ö. *New J. Chem.* **1997**, *21*, 267-271.
30. Gürol, İ.; Ahsen, V.; Bekaroğlu, Ö. *J. Chem. Soc. Dalton. Trans.* **1994**, *4*, 497-500.

## Supplementary information

Investigation of photochemical and photophysical properties of novel silicon(IV) phthalocyanines and their  $\mu$ -oxo dimers.

Ömer GÜNGÖR, Mahmut DURMUŞ, Vefa AHSEN

## Materials

1,3-diphenylisobenzofuran (DPBF), and sodium were purchased from Fluka. Silica gel 60 for column chromatography, toluene, pyridine, quinoline and  $\text{SiCl}_4$  were purchased from Merck. All other reagents and solvents were reagent grade quality and were obtained from commercial suppliers. Toluene was distilled from sodium before use.

## Equipments

UV-Vis spectra were recorded with a Shimadzu 2001 UV spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Cary Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. Infrared spectra were recorded on a Perkin Elmer Spectrum BX FT-IR system. The mass spectra were recorded on a Bruker Micro ES<sup>+</sup> system.  $^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  solutions on a Varian 500 MHz spectrometer using TMS as an internal reference.

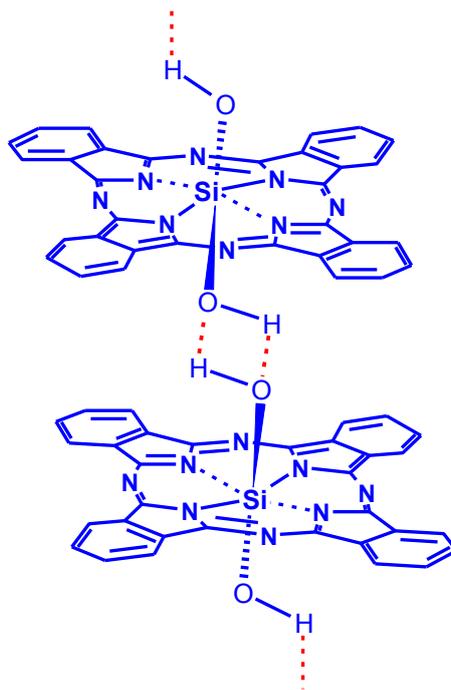
Photo-irradiations were done using a General Electric quartz line lamp (300 W). A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations, respectively. An interference filter (Intor, 670 nm with a band width of 40 nm) was additionally placed in the light path before the sample. Light intensities were measured with a POWER MAX5100 (Molelectron detector incorporated) power meter.

## Photophysical parameters

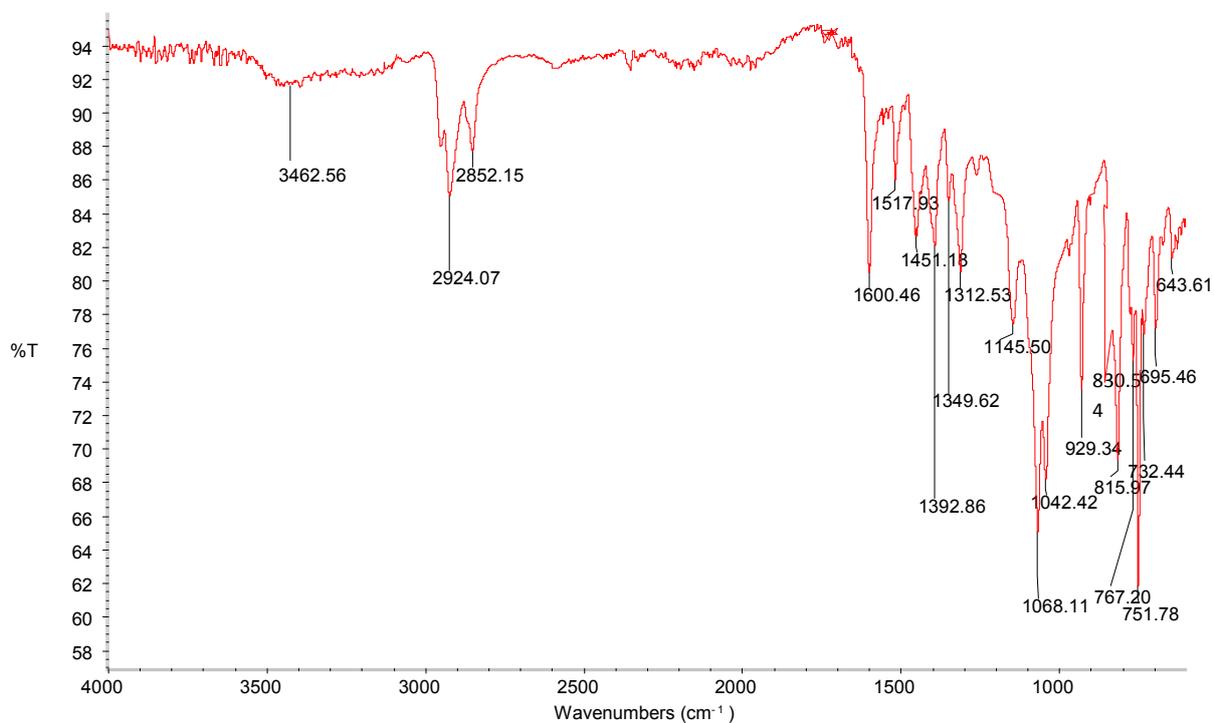
Photophysical and photochemical values were calculated according to previous literature.<sup>1</sup> Silicon phthalocyanine was used as standard compound.

## References

- [1] Durmus, M.; Yaman, H.; Göl, C.; Ahsen, V.; Nyokong, T. *Dyes and Pigments*. **2011**, *91*, 153-163.



**Figure S1.** Intermolecular hydrogen bonding in dihydroxy silicon phthalocyanine.



**Figure S2.** IR spectrum of compound 3a.

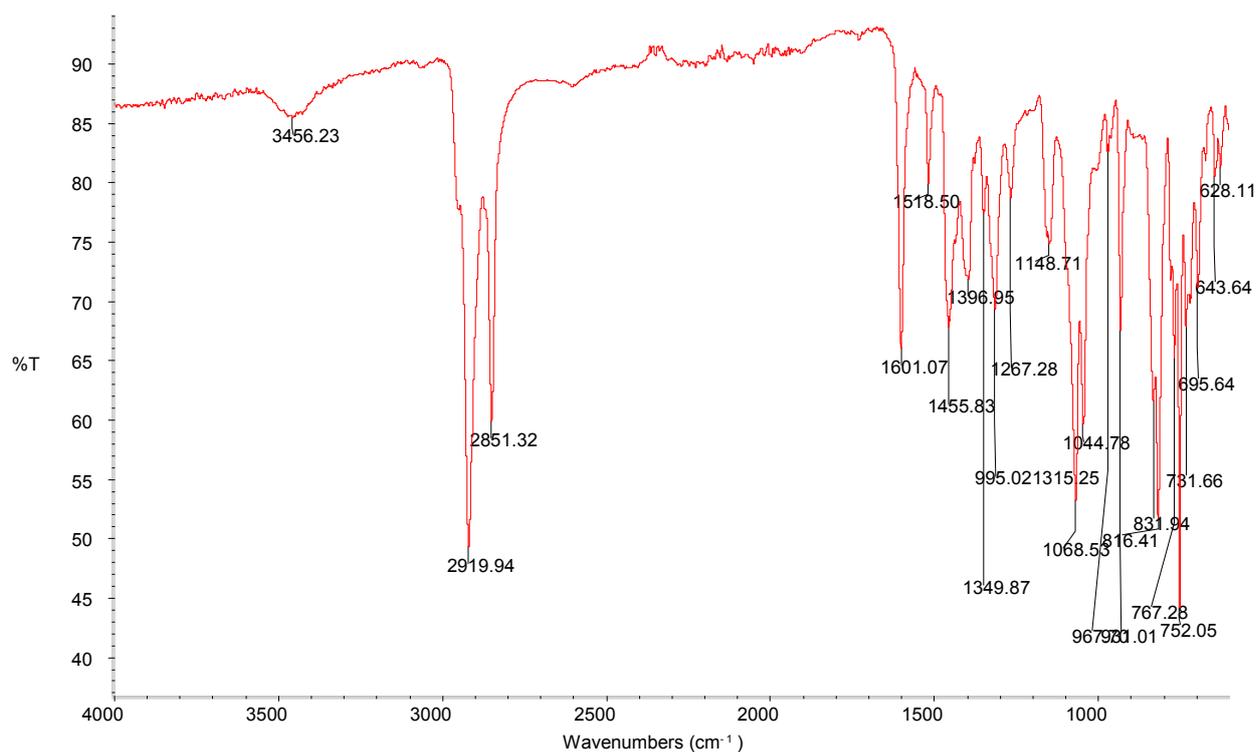


Figure S3. IR spectrum of compound 3b.

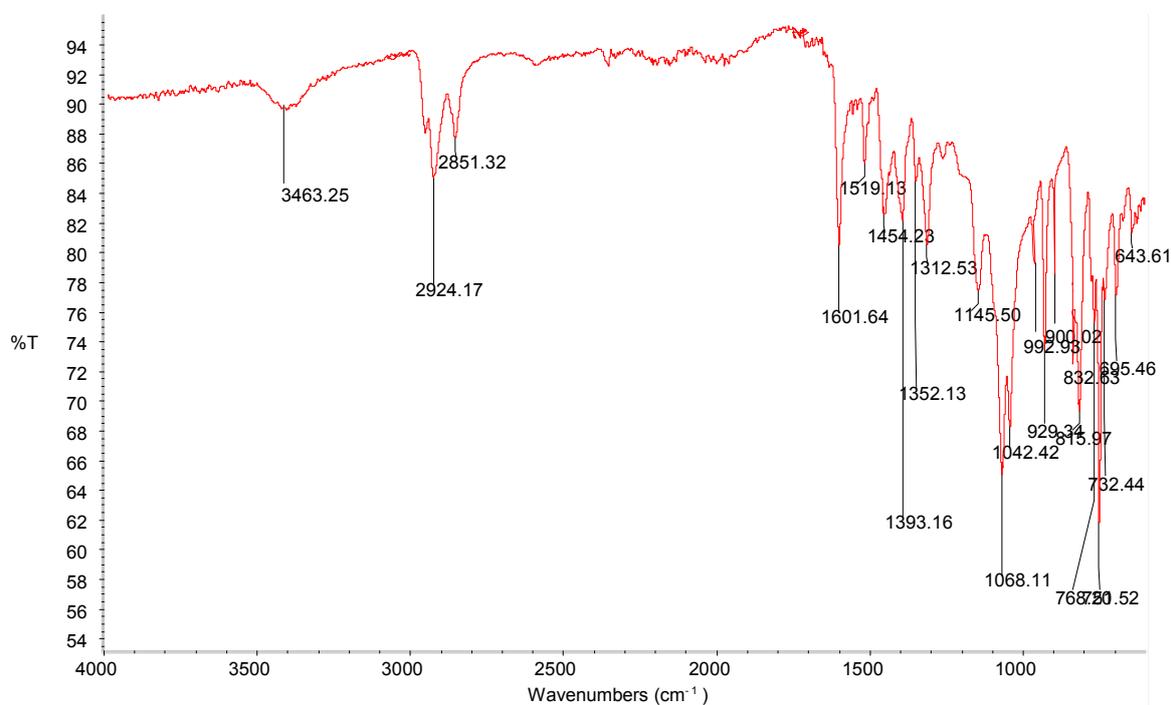
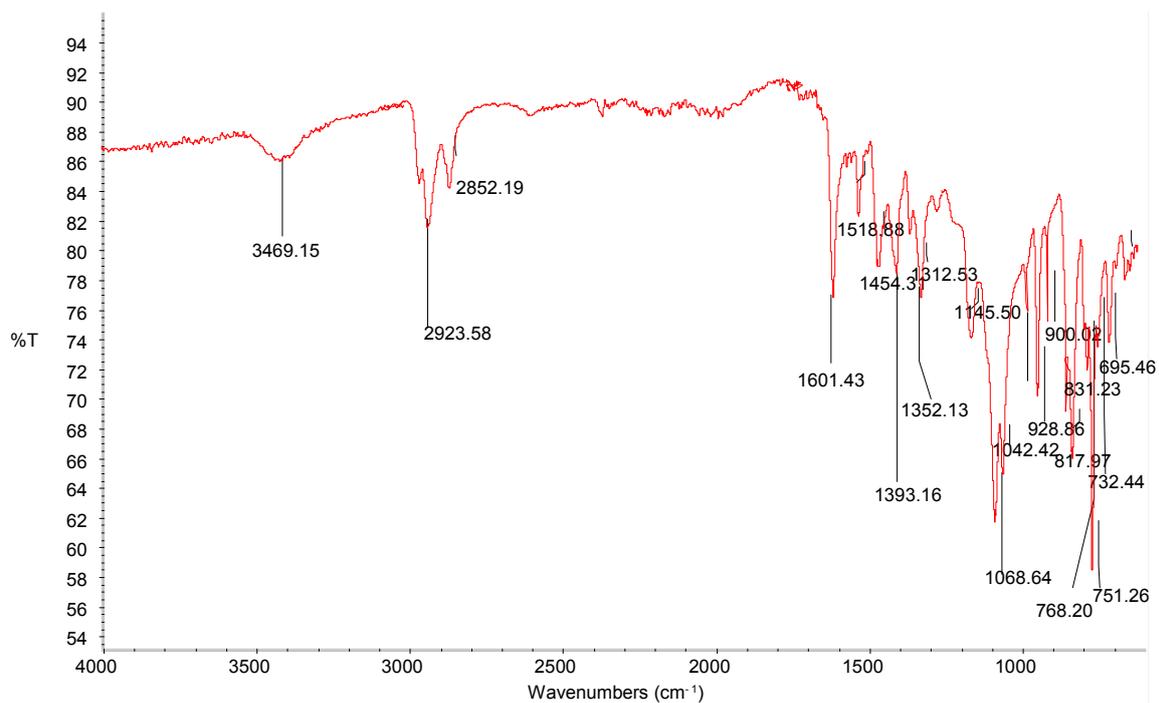
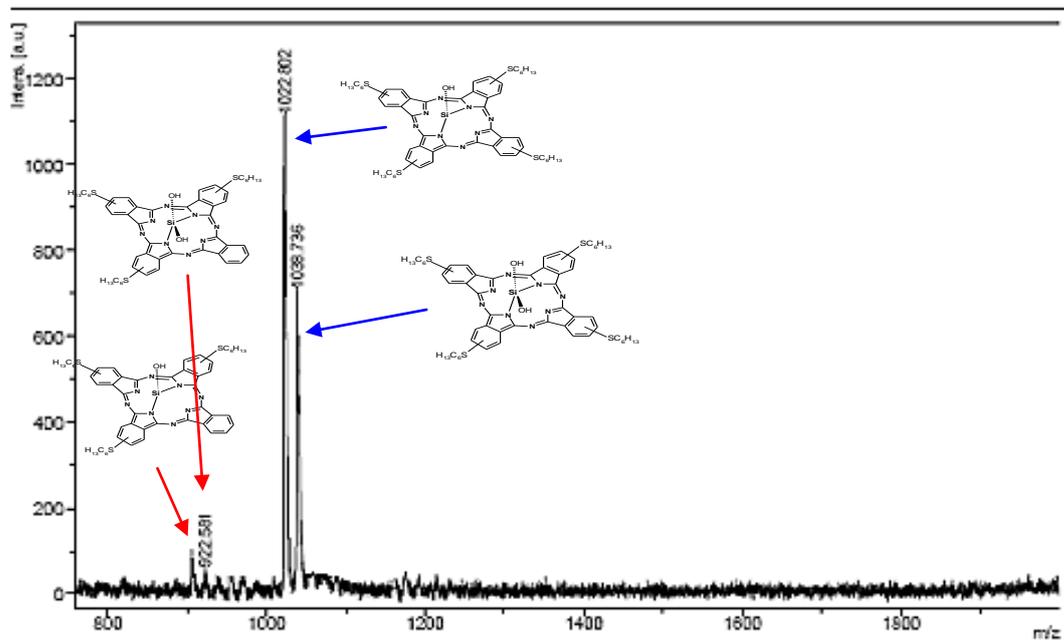


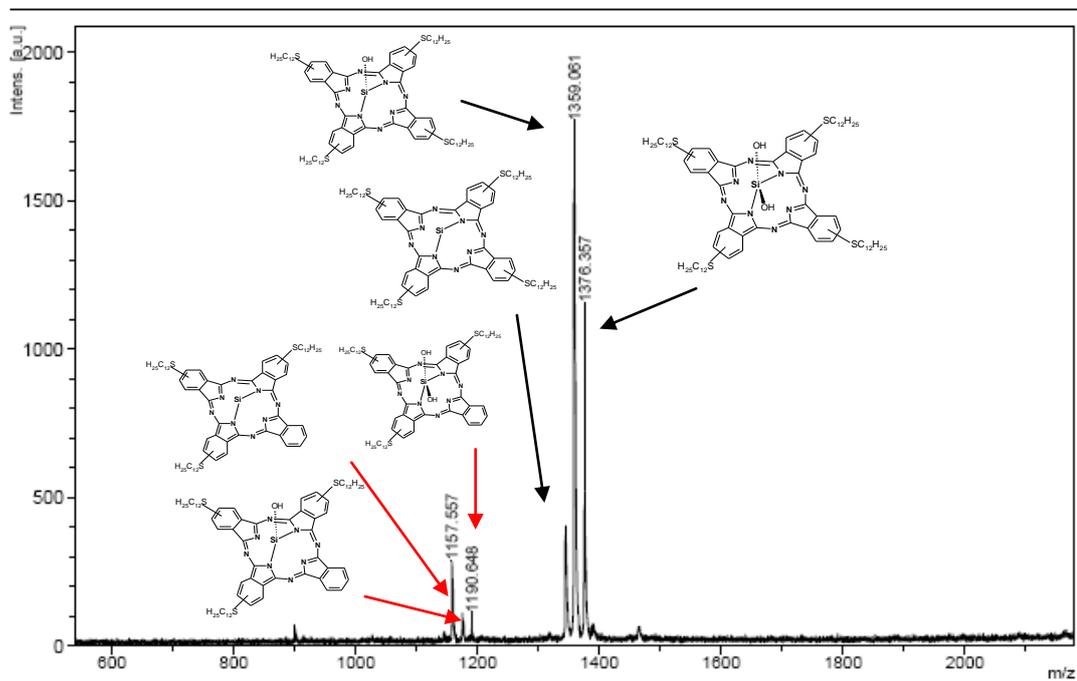
Figure S4. IR spectrum of compound 4a.



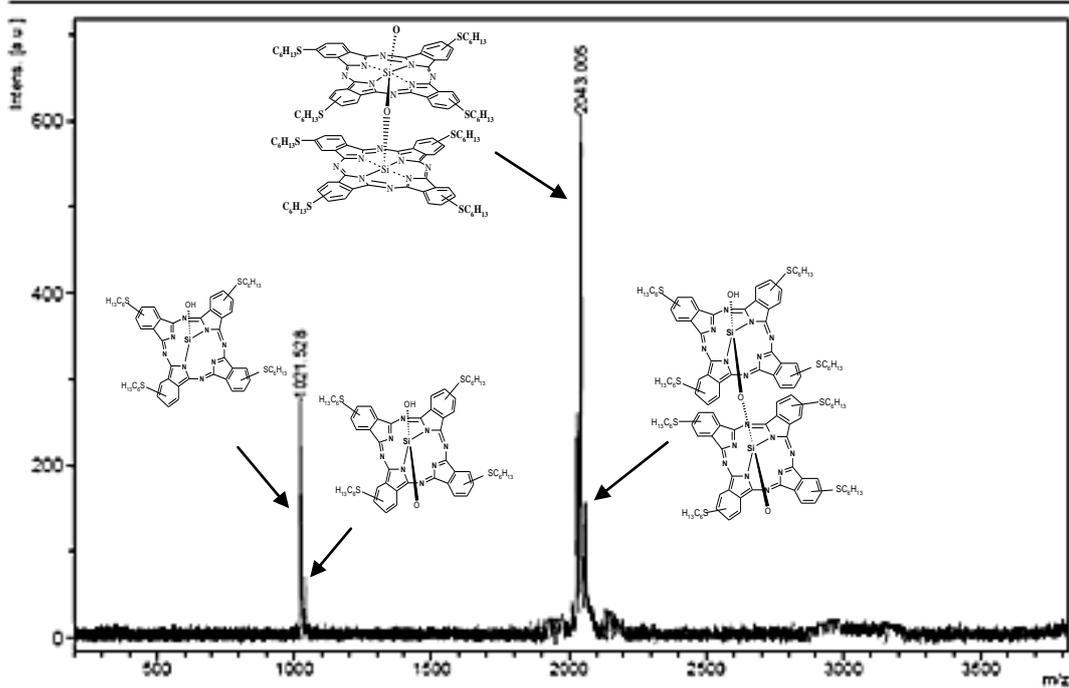
**Figure S5.** IR spectrum of compound **4b**.



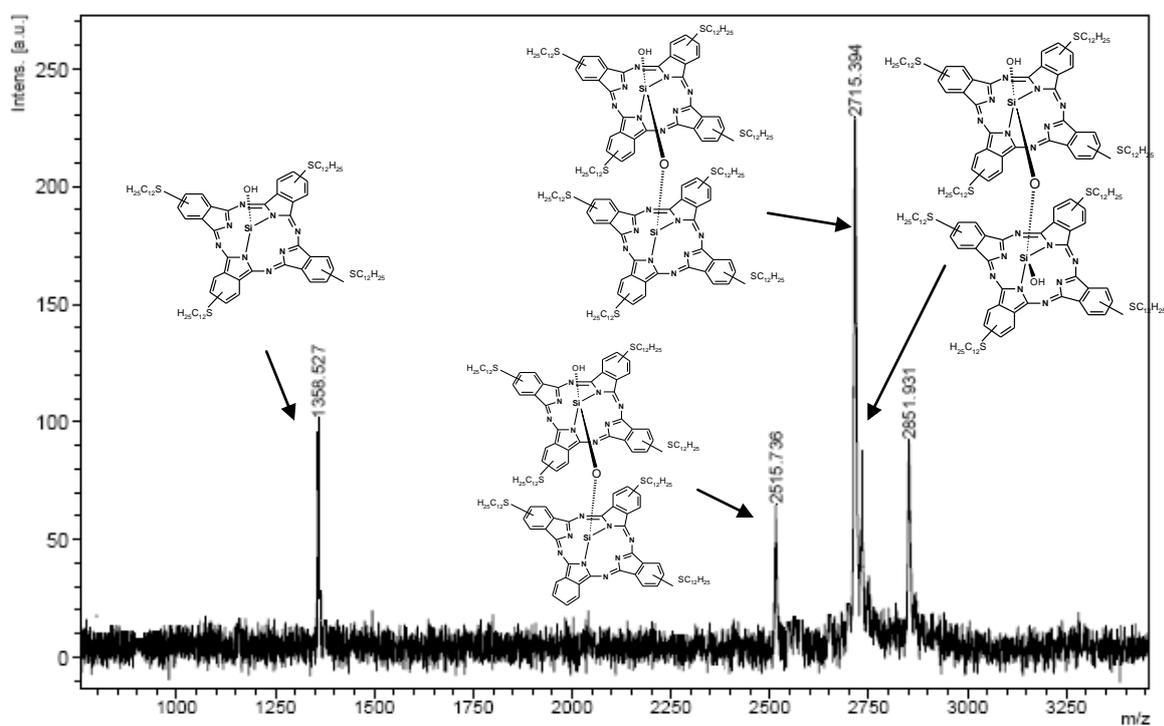
**Figure S6.** Mass spectrum (ES<sup>+</sup>) of compound 3a.



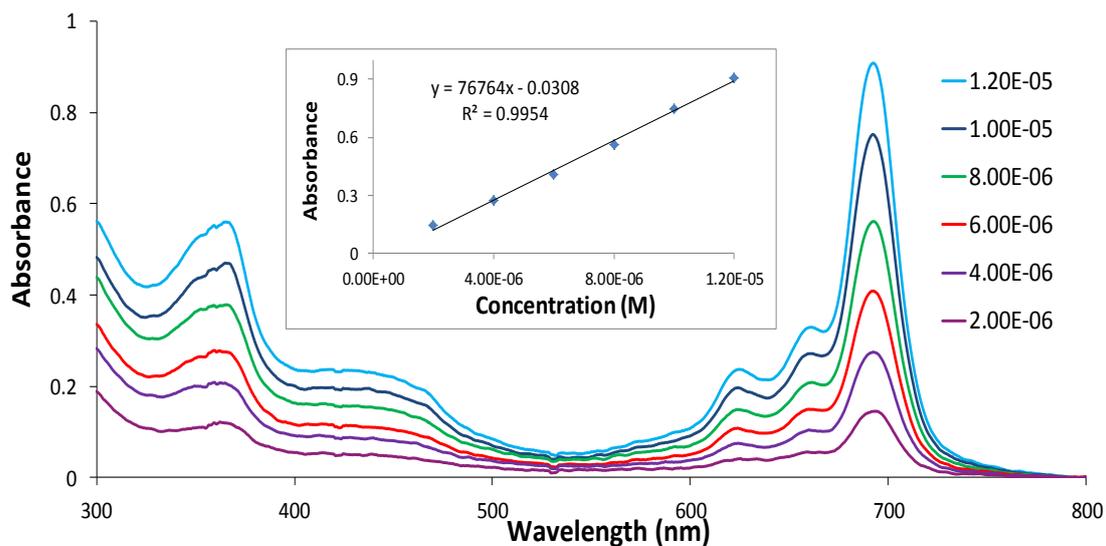
**Figure S7.** Mass spectrum (ES<sup>+</sup>) of compound 3b.



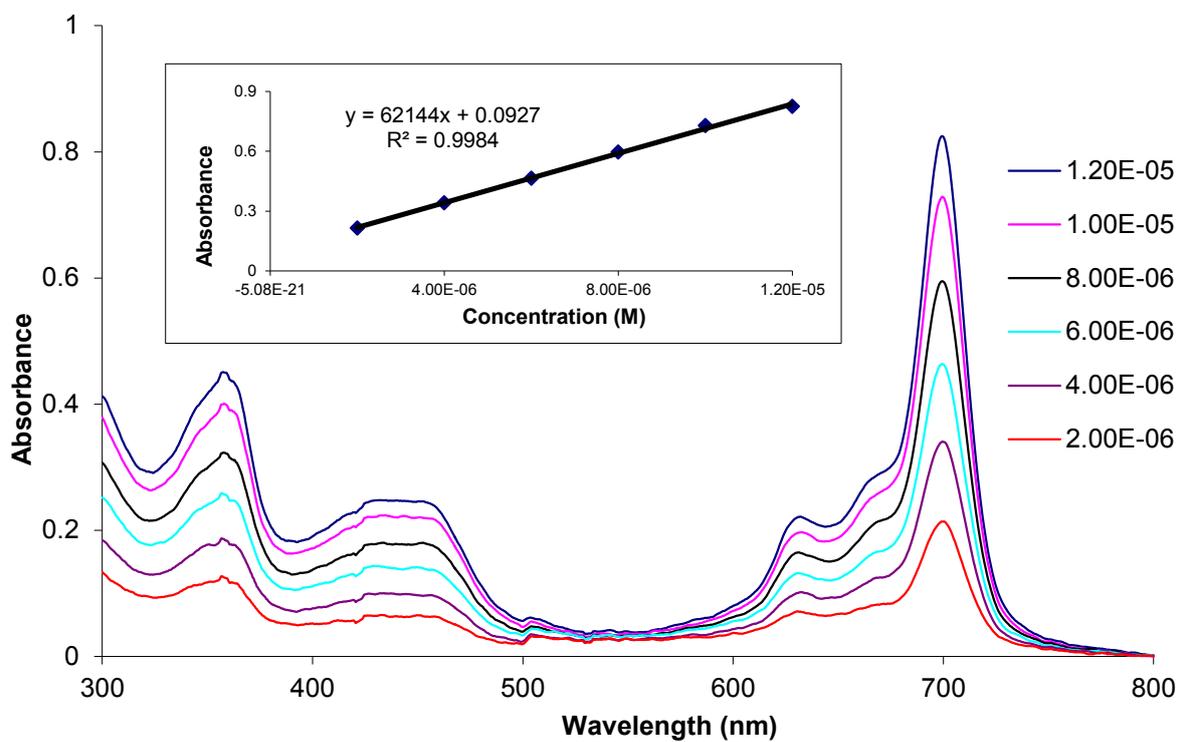
**Figure S8.** Mass spectrum ( $ES^+$ ) of compound **4a**.



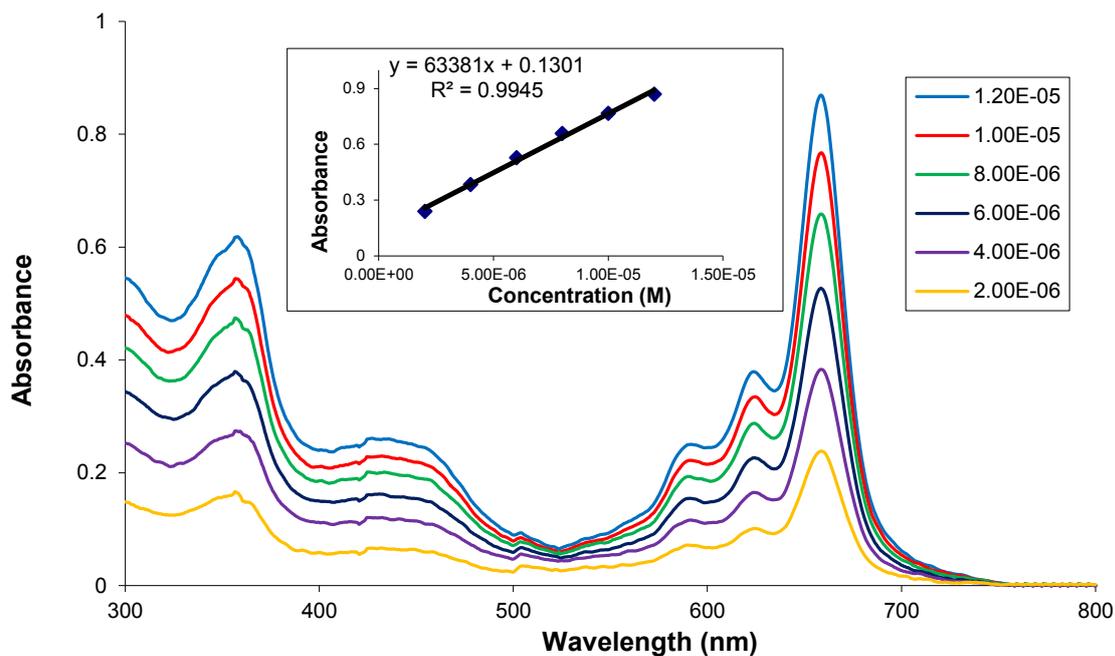
**Figure S9.** Mass spectrum ( $ES^+$ ) of compound **4b**.



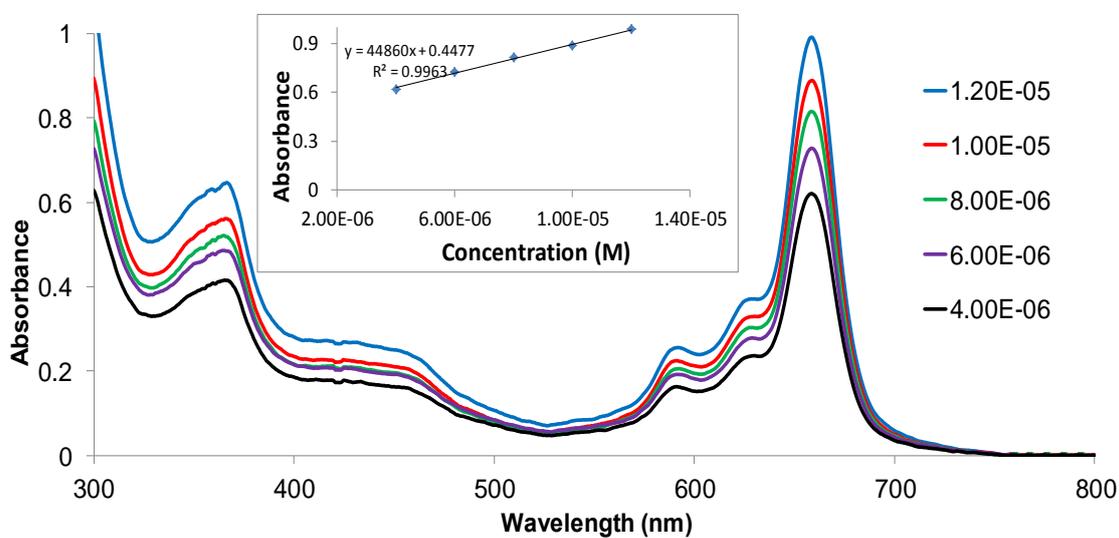
**Figure S10.** UV-Vis spectra of compound **3a** in DMF at different concentrations.



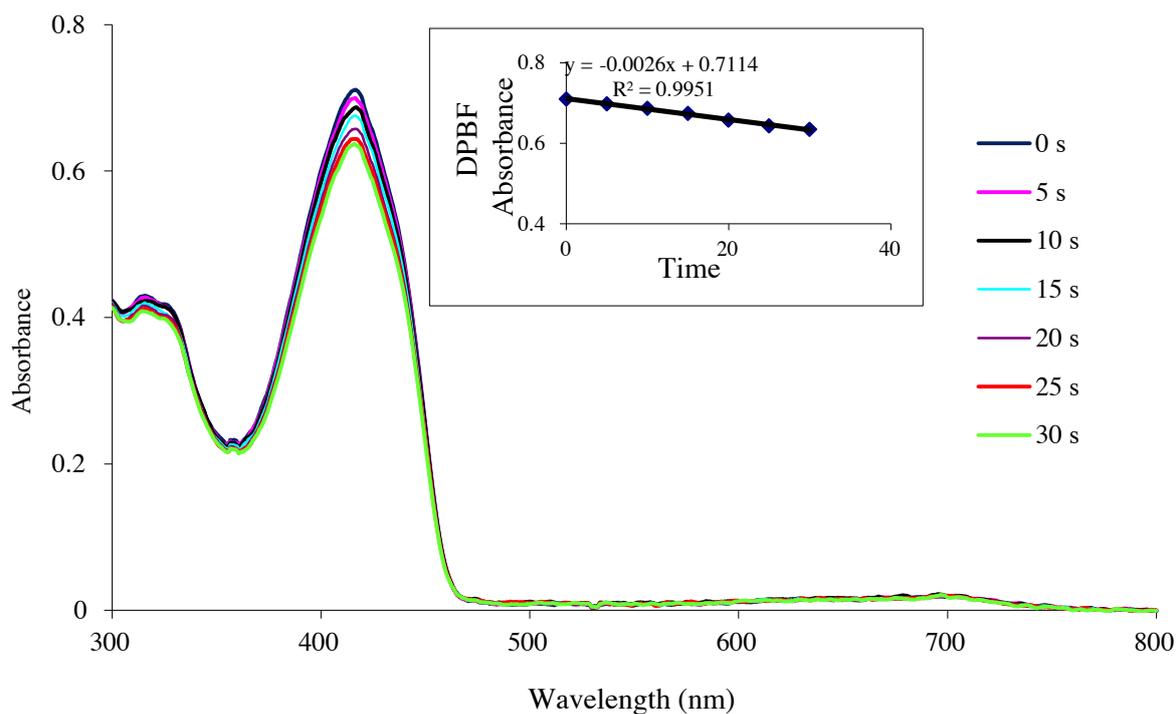
**Figure S11.** UV-Vis spectra of compound **3b** in DMF at different concentrations.



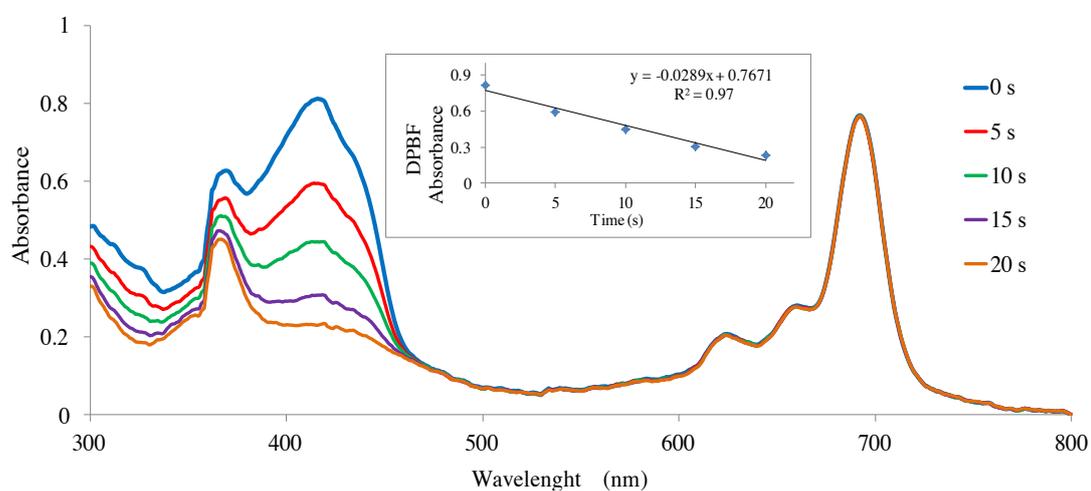
**Figure S12.** UV-Vis spectra of compound **4a** in DMF at different concentrations.



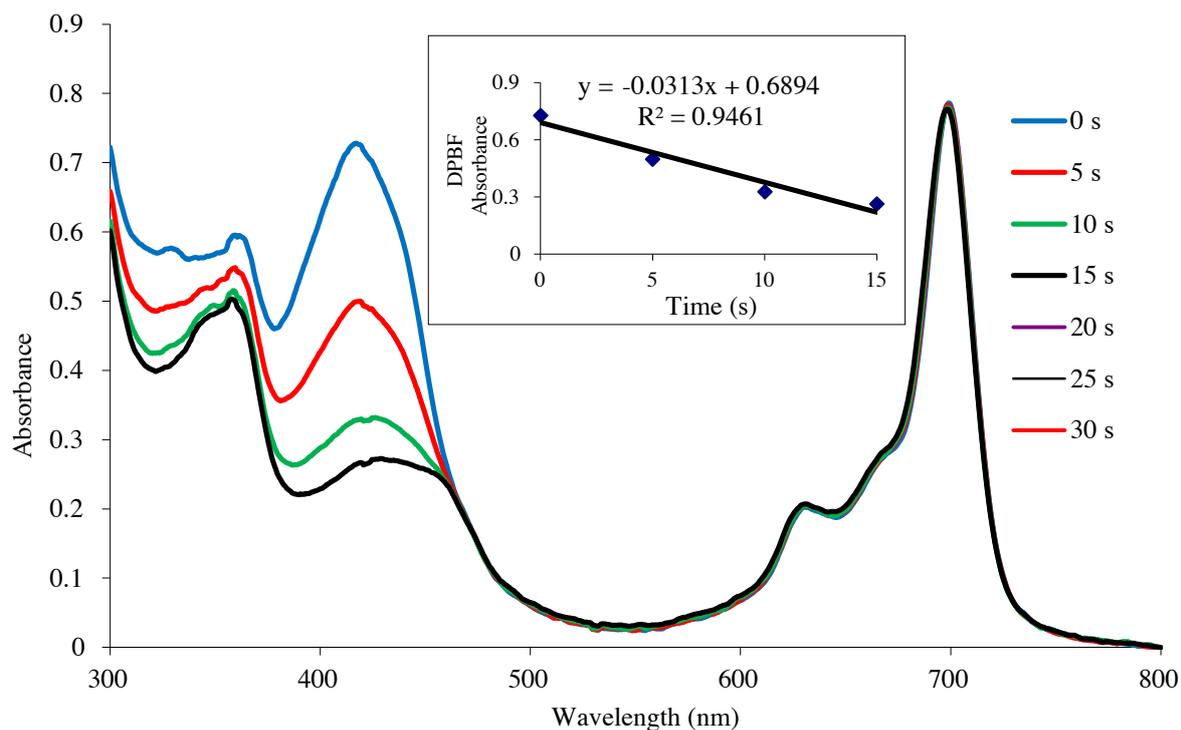
**Figure S13.** UV-Vis spectra of compound **4b** in DMF at different concentrations.



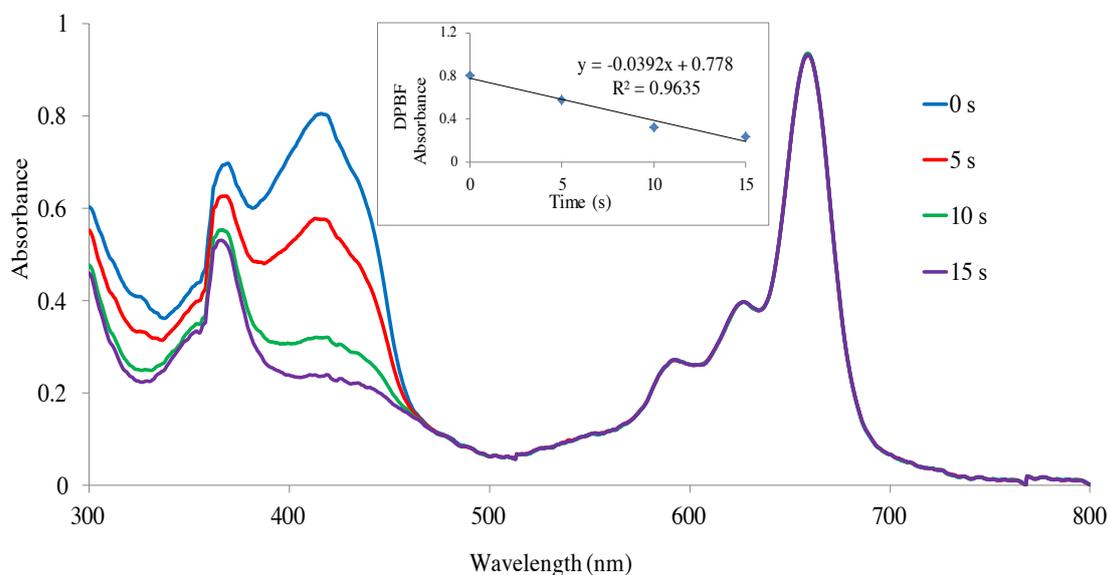
**Figure 14.** Electronic absorption spectral changes for **DPBF** during the determination of singlet oxygen quantum yield in DMF.



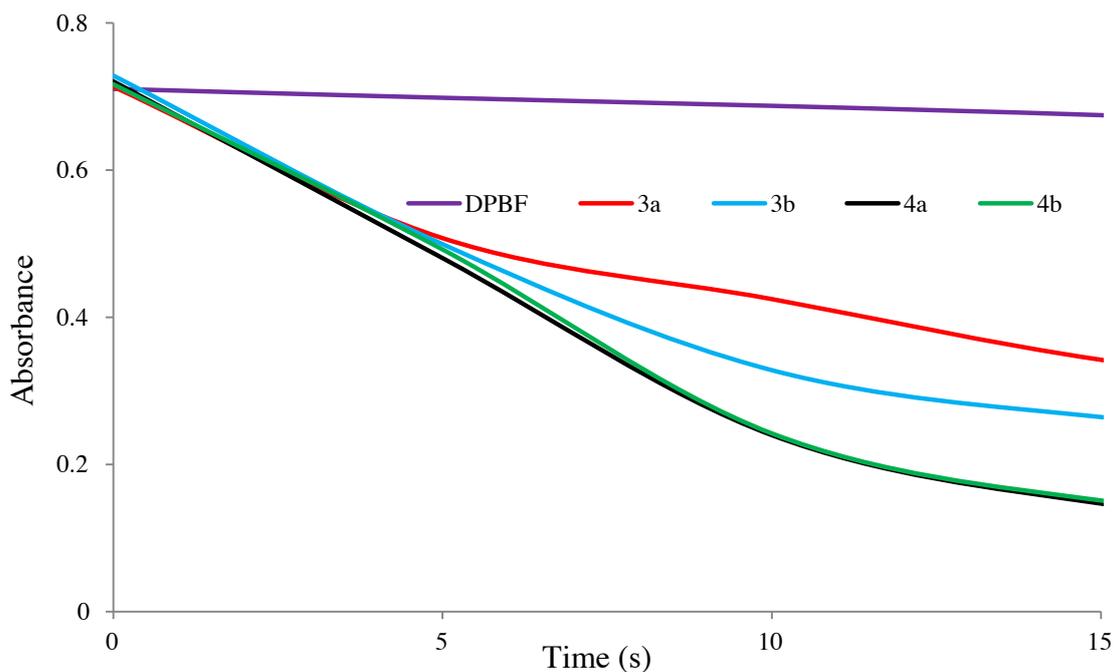
**Figure S15.** Electronic absorption spectral changes for compound **3a** during the determination of singlet oxygen quantum yield in DMF at a concentration of  $1 \times 10^{-5}$  M.



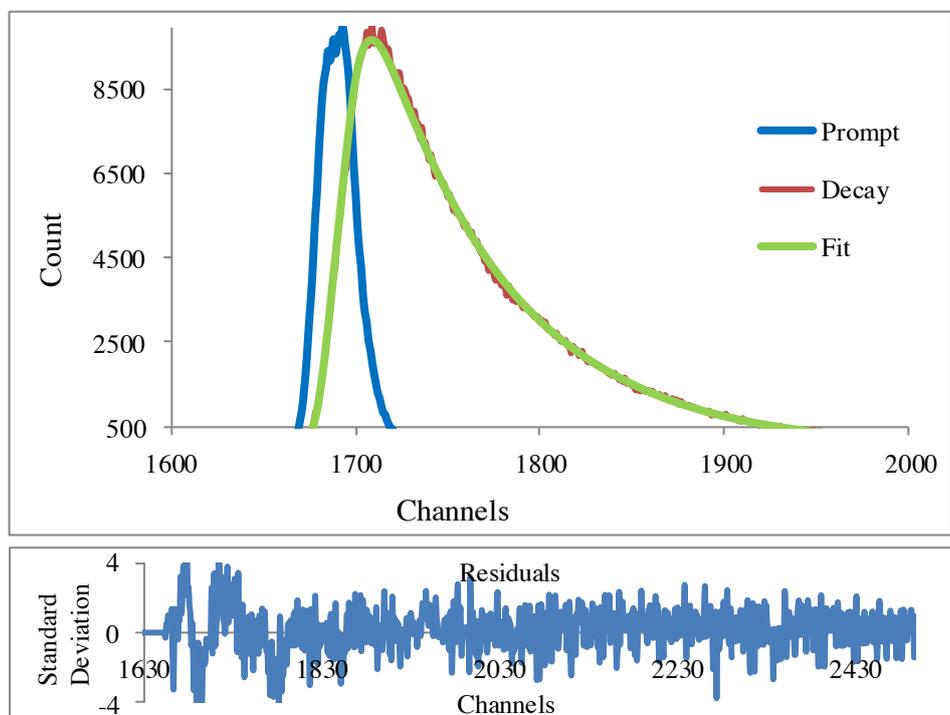
**Figure S16.** Electronic absorption spectral changes for compound **3b** during the determination of singlet oxygen quantum yield in DMF at a concentration of  $1 \times 10^{-5}$  M.



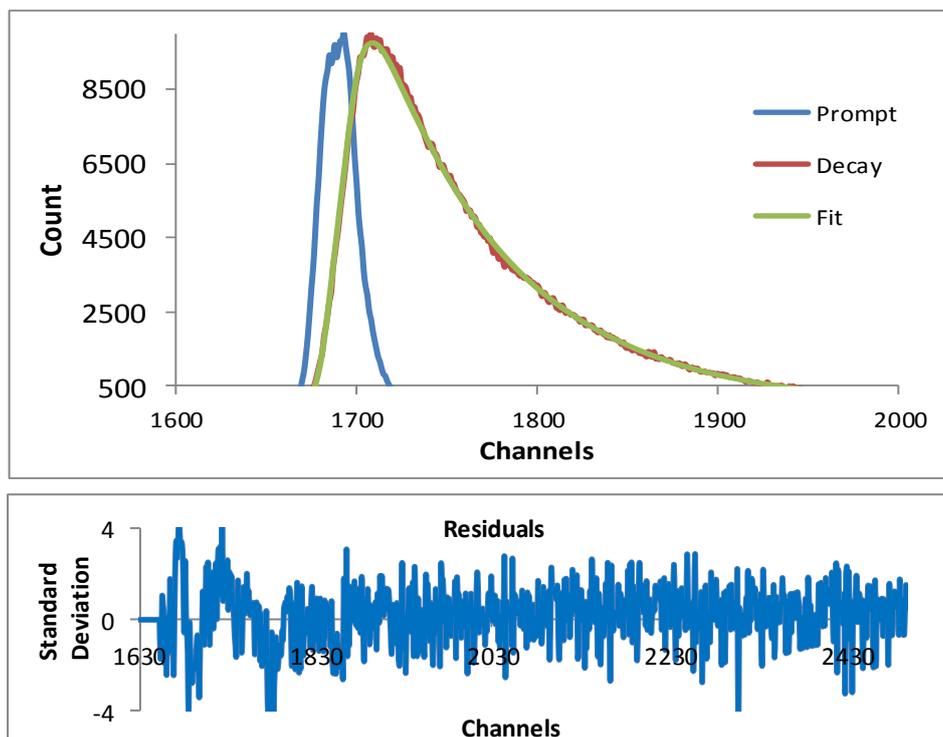
**Figure S17.** Electronic absorption spectral changes for compound **4a** during the determination of singlet oxygen quantum yield in DMF at a concentration of  $1 \times 10^{-5}$  M.



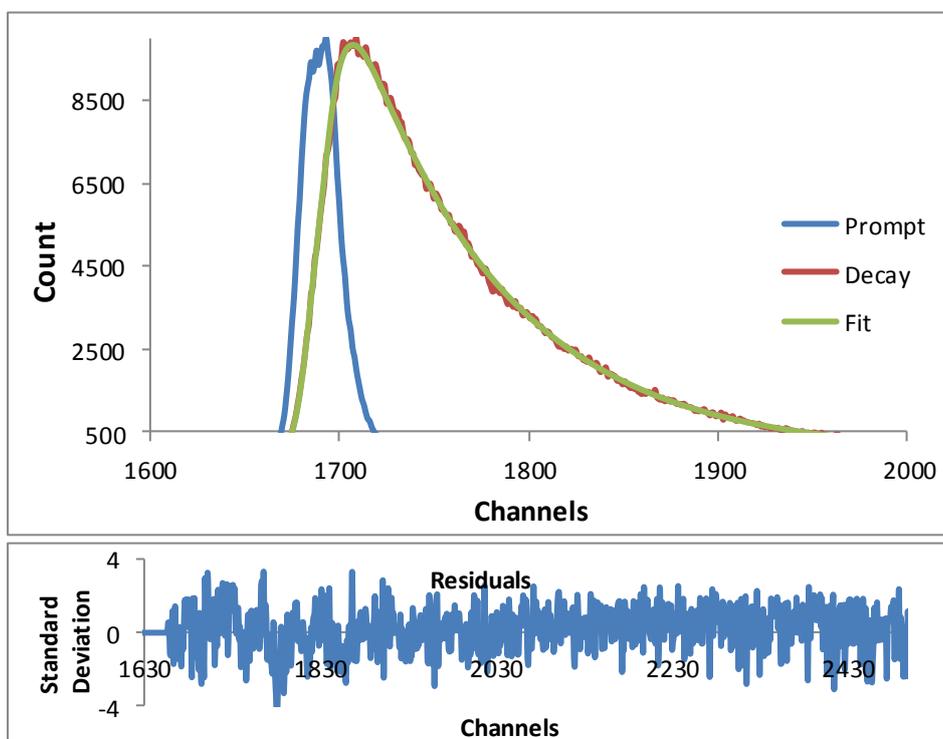
**Figure S18.** DPBF absorption spectral changes for compound **DPBF**, **3a**, **3b**, **4a**, and **4b** during the determination of singlet oxygen quantum yield in DMF.



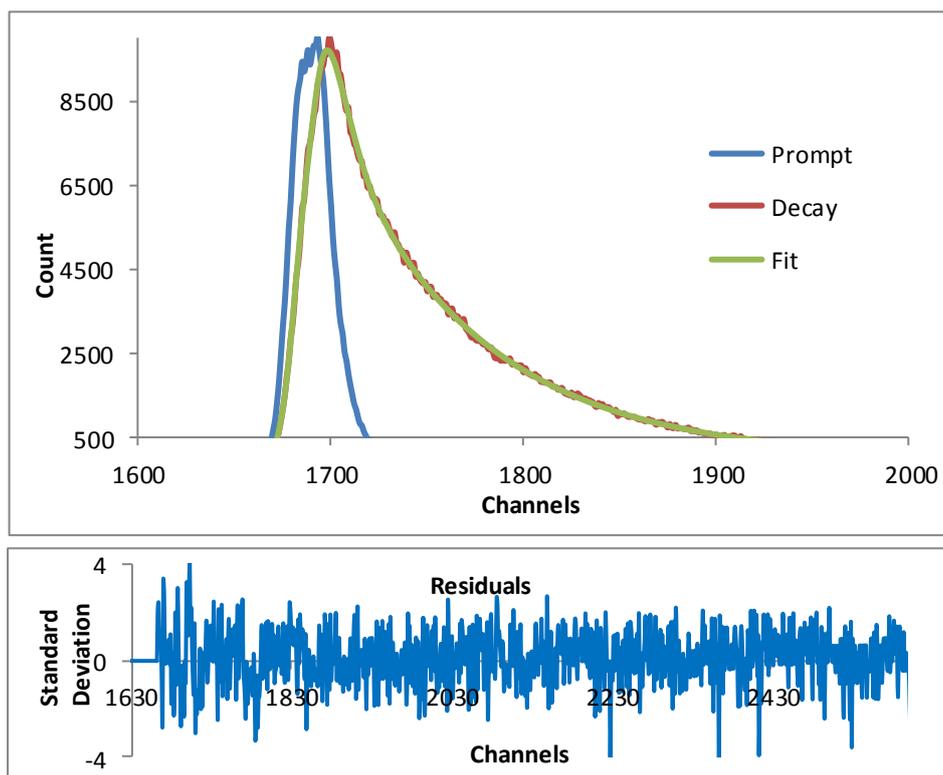
**Figure S19.** Time correlated single photon counting (TCSPC) trace for compound **3a** in DMF with residuals. Excitation wavelength= 710 nm.



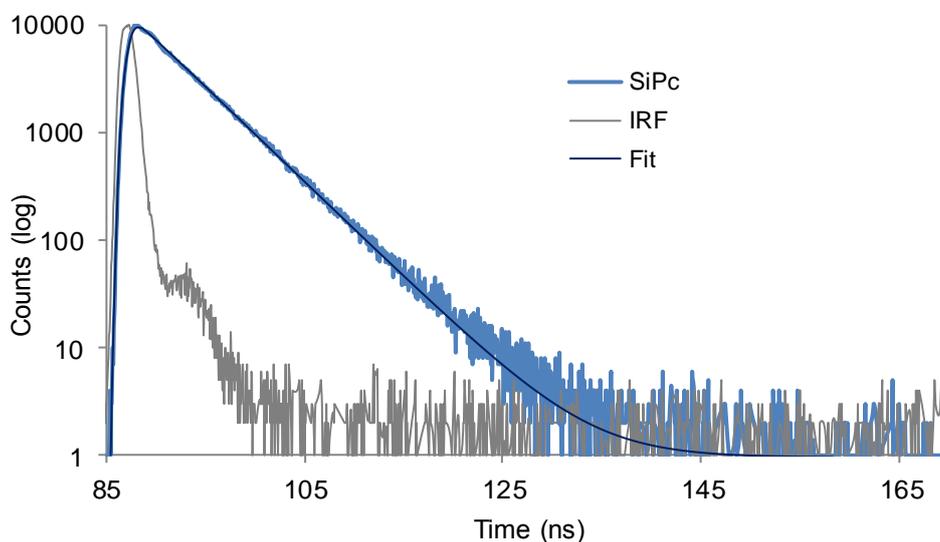
**Figure S20.** Time correlated single photon counting (TCSPC) trace for compound **3b** in DMF with residuals. Excitation wavelength= 708 nm.



**Figure S21.** Time correlated single photon counting (TCSPC) trace for compound **4a** in DMF with residuals. Excitation wavelength= 665 nm.



**Figure S22.** Time correlated single photon counting (TCSPC) trace for compound **4b** in DMF with residuals. Excitation wavelength= 667 nm.



**Figure S23.** Time correlated single photon counting (TCSPC) trace for compound SiPcCl<sub>2</sub> in DMF with residuals. Excitation wavelength= 709 nm.