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Preparation, Spectroscopic Properties, and Stability of Water-Soluble Subphthalocyanines

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Abstract: A series of subphthalocyanines containing an axial pyridyl, amino, or carboxy group have been prepared. They undergo *N*-methylation or deprotonation readily to give a new series of water-soluble subphthalocyanines. All the compounds have been characterized with various spectroscopic methods and elemental analysis. The molecular structure of the amino analogue SPc($OCH_2CH_2NMe_2$) (**6**) has also been determined by X-ray diffraction analysis. All these compounds are essentially non-aggregated in DMF as shown by the strong Q-band absorption. The low aggregation tendency of these compounds also results in strong fluorescence emission and high efficiency in generating singlet oxygen. In the presence of Cremophor EL, these compounds also remain in the monomeric form in aqueous media and can sensitize the formation of singlet oxygen. The carboxy and carboxylate derivatives exhibit a relatively higher photostability than the amino and cationic pyridinium and ammonium counterparts, making them potentially useful as photosensitizers in aqueous media.

Keywords: macrocycles · phthalocyanines · sensitizers · singlet oxygen · subphthalocyanines

Introduction

Subphthalocyanines are regarded as the lower homologues of phthalocyanines.[1] The basic skeleton of these macrocycles contains three diiminoisoindoline units *N*-fused around a boron center adopting a cone-shaped structure. The early impetus to this class of compounds stemmed from their use in the ring-expansion reactions to prepare unsymmetrical A_3B-type phthalocyanines.[2] These nonselective reactions, however, greatly depend on the characteristics of the starting materials and the reaction conditions, which limit their general synthetic utility.[3] Recently, emphasis has been placed on their intriguing optical and electronic properties, which can be tuned through rational chemical modification. These characteristics render them to be applied as octupolar nonlinear optical materials,[4] photovoltaic devices,[5] photosynthetic models for the study of photoinduced electron and energy transfer processes,[6] colorimetric and fluorometric molecular probes for cyanide and fluoride anions,[7] and photosensitizers for photodynamic therapy.[8] Subphthalocyanines therefore have emerged as a versatile class of functional materials.

Although a substantial number of subphthalocyanine derivatives have been reported,[1] water-soluble analogues remain extremely rare. Application of these macrocycles in the biomedical area is still under developed. van Lier and co-workers reported the first water-soluble trisulfonated subphthalocyanine, which was used to prepare several unsymmetrical water-soluble phthalocyanine derivatives.[9] Adachi and Watarai prepared a novel testosterone-conjugated subphthalocyanine, which served as a binding marker for human serum albumin.[10] During the course of this investigation, a tris(pyridinium) subphthalocyanine, which could photodynamically inhibit the growth of *Escherichia coli*, was reported.[8b] We describe herein a new series of subphthalocyanines having a water-solubilizing axial group, including their synthesis, general spectroscopic properties, and stability, particularly in aqueous media. Upon irradiation, these compounds can sensitize the formation of singlet oxygen, and thus can find practical photosensitizing applications.

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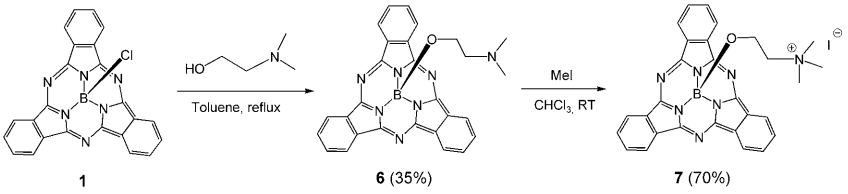
Results and Discussion

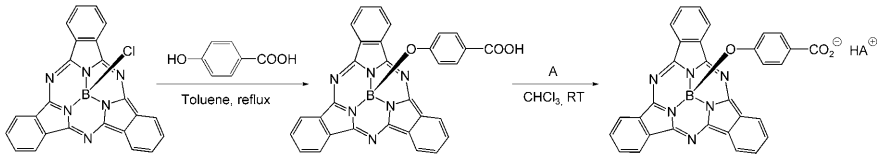
Synthesis and Characterization

A pyridinium group is a simple hydrophilic moiety, which can be introduced readily to the subphthalocyanine core. As shown in Scheme 1, treatment of the commercially available boron(III) subphthalocyanine chloride SPcCl (**1**) with 3- or 4-hydroxypyridine in toluene gave the corresponding pyridyl subphthalocyanine SPc(3-OPy) (**2**) or SPc(4-OPy) (**3**).[11] Methylation of these compounds with iodomethane in chloroform proceeded smoothly to afford the pyridinium subphthalocyanines [SPc(3-OPyMe)]I (**4**) and [SPc(4-OPyMe)]I (**5**) as violet solids. These salts could be isolated readily by filtration, followed by washing with chloroform and diethyl ether. Similarly, treatment of **1** with 2-dimethylaminoethanol gave the amino subphthalocyanine SPc($OCH_2CH_2NMe_2$) (**6**) in 35% yield, which underwent methylation to afford [SPc($OCH_2CH_2NMe_3$)]I (**7**) in 70% yield (Scheme 2).



1 **6** (35%) **7** (70%)

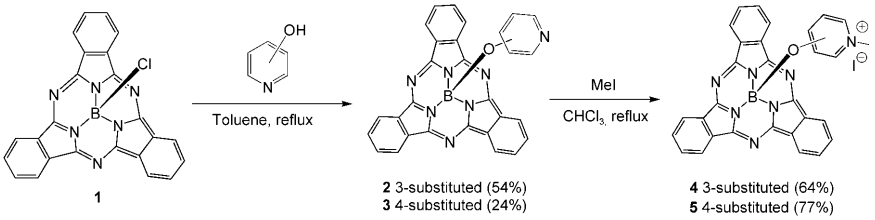
Scheme 2. Synthesis of subphthalocyanines **6** and **7**.



1 **8** (27%)
9 A = Et_2NH (81%)
10 A = nPr_2NH (86%)
11 A = iPr_2NH (84%)
12 A = $tBuNH_2$ (75%)

Scheme 3. Synthesis of subphthalocyanines **8**–**12**.

In addition to these cationic subphthalocyanines, we also prepared a series of anionic analogues for comparison using the facile acid–base reaction. As depicted in Scheme 3, reaction of **1** with 4-hydroxybenzoic acid in toluene gave the carboxy subphthalocyanine SPc($OC_6H_4CO_2H$) (**8**). Upon treatment with a series of amines A including diethylamine, dipropylamine, diisopropylamine, and *tert*-butylamine, this compound underwent deprotonation readily to give the corresponding ammonium carboxylates [HA][SPc($OC_6H_4CO_2$)] (**9**–**12**) in good yield. These salts were purified readily by filtration, followed by extensive washing with nonpolar organic solvents.



1 **2** 3-substituted (54%) **3** 4-substituted (24%) **4** 3-substituted (64%) **5** 4-substituted (77%)

Scheme 1. Synthesis of pyridinium subphthalocyanines **4** and **5**.

All the new compounds (**4**–**12**) were fully characterized with various spectroscopic methods and elemental analysis. For all of them, the ^{1}H NMR spectra showed two typical AA'BB' multiplets at $\delta = 8.80$–8.91 and 7.87–8.07 for the subphthalocyanine α and β ring protons, respectively. The signals for the axial substituents were significantly shifted upfield owing to the shielding by the subphthalocyanine ring current. The molecular structure of SPc($OCH_2CH_2NMe_2$) (**6**) was also determined by X-ray diffraction analysis. Single crystals of this compound were grown by layering hexane onto a chloroform solution. The compound crystallizes in the orthorhombic system with a *Pbca* space group. As shown in Figure 1, the boron center is tetra-coordinated with three isoindole nitrogen atoms in a cone-shaped macrocycle and an alkoxy group. The B–O bond distance [1.422(4) Å] and the average B–N bond distance [1.497(5) Å] are comparable with those in the ethoxy analogue SPc(OEt) [1.418(5) and 1.512(5) Å, respectively].[12]

Abstract in Chinese:

系列轴向取代含有吡啶、氨基或羧基的亚酞菁被合成出来。这些化合物通过氮－甲基化或去质子化过程很容易被转化成一系列新的水溶性亚酞菁分子。所有这些化合物已经通过各种波谱方法和元素分析得到证实，其中氨基取代的亚酞菁 SPc($OCH_2CH_2NMe_2$) (**6**) 的分子结构已经得到了 X－射线衍射分析的证实。从强烈的 Q 吸收带来看，这些化合物在 DMF 中是不聚集的。低的聚集趋势使得这些化合物产生强烈荧光发射和具有高的产生单线态氧的能力。借助于 Cremophor EL，这些化合物在水溶液中仍然呈现单体状态而且能够光敏化产生单线态氧。同阳离子型的吡啶盐和铵盐基团取代的亚酞菁相比，羧酸取代和羧酸盐取代的亚酞菁衍生物由于在水溶液当中具有相当高的稳定性，使得它们成为具有潜在应用价值的光敏剂。

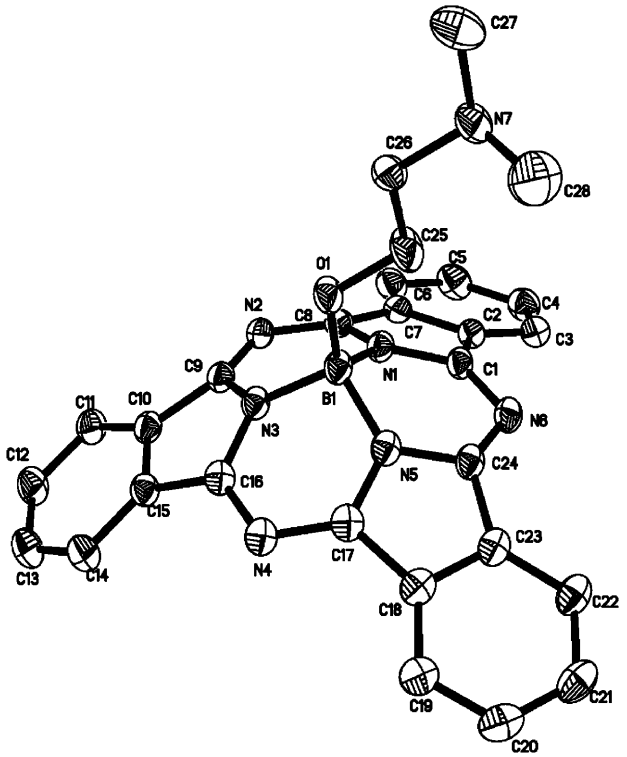


Figure 1. Molecular structure of $SPc(OCH_2CH_2NMe_2)$ (**6**) showing the 30% probability thermal ellipsoids for all non-hydrogen atoms.

Electronic Absorption and Photophysical Properties

The absorption spectra of **4**–**12** in DMF are very similar showing the Soret B band at 293–305 nm, Q band at 561–567 nm, together with a vibronic shoulder at 504–510 nm. The data are compiled in Table 1. The very similar spectra of these compounds indicate that the macrocyclic π system is not perturbed by the axial ligand. By plotting the Q-band absorbance versus the concentration, a linear relationship was found for all these compounds, showing that they are essentially non-aggregated under these conditions. Arising from the low aggregation tendency, these compounds are highly fluorescent. Upon excitation at 510 nm, these compounds emit at 571–577 nm with a fluorescence quantum yield (Φ_F) of 0.04–0.10 relative to rhodamine B in EtOH ($\Phi_F = 0.49$)[13] (Table 1). Figure 2 shows the absorption and fluorescence spectra of $[tBuNH_3][SPc(OC_6H_4CO_2)]$ (**12**) in DMF, which are typical for all the other subphthalocyanines.

Table 1. Electronic absorption and photophysical data for **4**-**12**.

Compound	λ_{max} [nm] ($\log\varepsilon$)[a]			λ_{em} [nm][a,b]	Φ_F[a,c]	Φ_Δ[d]
4	303 (4.59)	508 (4.32)	566 (4.87)	575	0.09	0.61
5	305 (4.57)	510 (4.33)	567 (4.86)	577	0.08	0.66
6	294 (4.69)	504 (4.36)	561 (4.93)	571	0.04	0.41
7	302 (4.64)	505 (4.37)	562 (4.93)	575	0.10	0.59
8	293 (4.52)	505 (4.33)	561 (4.88)	573	0.10	0.62
9	293 (4.63)	504 (4.36)	561 (4.94)	572	0.10	0.56
10	293 (4.59)	504 (4.33)	561 (4.91)	572	0.10	0.58
11	294 (4.50)	504 (4.23)	561 (4.81)	572	0.09	0.60
12	293 (4.54)	504 (4.25)	563 (4.83)	572	0.10	0.57

[a] Measured in DMF. [b] Excited at 510 nm. [c] The fluorescence quantum yields (Φ_F) were determined with rhodamine B in EtOH ($\Phi_F = 0.49$) as reference. [d] The singlet oxygen quantum yields (Φ_Δ) were determined in EtOH with rose bengal ($\Phi_\Delta = 0.68$) as reference. A color glass filter cut-on 515 nm was used.

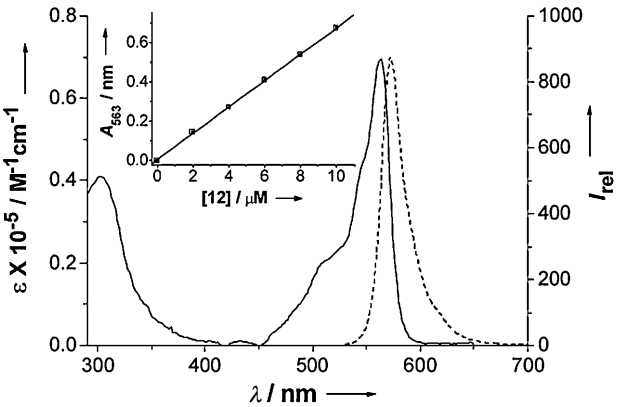


Figure 2. Electronic absorption (——) and fluorescence emission (– – –) spectra of **12** in DMF (2.0 μM). The inset plots the Q-band absorbance at 563 nm versus the concentration of **12**, showing that the Beer–Lambert Law is followed.

All these subphthalocyanines including the cationic and anionic derivatives could not be completely dissolved in water alone. However, by first dissolving the compounds in DMF followed by dilution with water, all of them could become soluble in water (with 0.1% (v/v) of DMF). Hence, for all the measurements in aqueous media, the solutions were prepared in this way. Figure 3 shows the absorption spectra of $[tBuNH_3][SPc(OC_6H_4CO_2)]$ (**12**) in water, both in the absence and presence of Cremophor EL. It can be seen that the Q band is broad in water, suggesting that **12** is significantly aggregated. In the presence of 0.05% (w/v) Cremophor EL, the Q band sharpens and follows the Beer–Lambert law as shown in the inset. These observations indi-

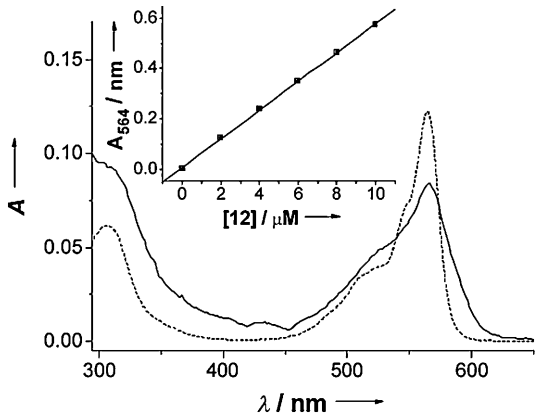


Figure 3. Electronic absorption spectra of **12** in water in the absence (——) and presence of 0.05% (w/v) Cremophor EL (– – –) (both at 2.0 μM). The inset plots the Q-band absorbance at 564 nm versus the concentration of **12**.

cate that Cremophor EL can effectively reduce the aggregation of **12**. It is noteworthy that for the water-soluble subphthalocyanine, which has three peripheral pyridinium groups,[8b] it also requires 2% (w/v) sodium dodecyl sulfate to generate the monomeric species in water. In the presence of Cremophor EL, all the subphthalocyanines **4**–**12** show a relatively strong fluorescence emission in water. The fluorescence quantum yields are in the range of 0.06–0.08. The absorption as well as the fluorescence emission data of these compounds in water with 0.05% (w/v) Cremophor EL are summarized in Table 2. Compared with the data recorded in DMF, all the absorption and emission bands are slightly redshifted. For the anionic subphthalocyanines **9**–**12**, the size of the counter cations does not exert a significant influence on these spectral properties.

Table 2. Electronic absorption and fluorescence emission data for **4**–**12** in water with 0.05% (w/v) Cremophor EL.

Compound	λ_{max} [nm] (log ε)			λ_{em} [nm][a]	Φ_F[b]
4	305 (4.44)	510 (4.28)	567 (4.81)	577	0.07
5	306 (4.46)	511 (4.30)	568 (4.82)	578	0.06
6	304 (4.54)	507 (4.36)	566 (4.90)	576	0.07
7	304 (4.53)	507 (4.32)	566 (4.86)	576	0.08
8	306 (4.56)	510 (4.35)	564 (4.90)	574	0.08
9	306 (4.61)	509 (4.37)	564 (4.93)	574	0.08
10	306 (4.60)	510 (4.35)	564 (4.90)	574	0.07
11	307 (4.47)	510 (4.26)	563 (4.81)	574	0.08
12	307 (4.53)	508 (4.25)	564 (4.82)	574	0.08

[a] Excited at 510 nm. [b] The fluorescence quantum yields (Φ_F) were determined with rhodamine B in EtOH ($\Phi_F = 0.49$) as reference.

To evaluate the photosensitizing efficiency of these compounds, the rates of decay of the singlet oxygen scavenger 1,3-diphenylisobenzofuran (DPBF), using these compounds as the photosensitizers, were monitored spectroscopically (at 410 nm) and compared with that for rose bengal, which was used as the reference. Figure 4 shows the results for selected subphthalocyanines. All of them can generate singlet oxygen and the efficiency is comparable with that of rose bengal.

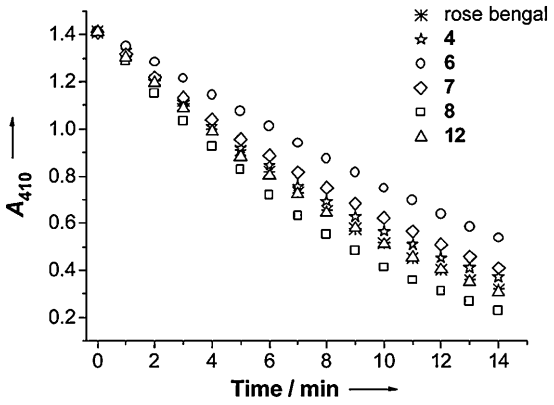


Figure 4. Comparison of the rates of decay of DPBF in EtOH as monitored spectroscopically at 410 nm, using subphthalocyanines **4**, **6**–**8**, and **12** as the photosensitizers and rose bengal as the reference.

The singlet oxygen quantum yields determined by the previously described method[14] are also listed in Table 1. All these subphthalocyanines have similar Φ_Δ values [0.56–0.66 relative to rose bengal ($\Phi_\Delta = 0.68$)][15] except $SPc(OCH_2CH_2NMe_2)$ (**6**), which has a slightly lower photosensitizing efficiency ($\Phi_\Delta = 0.41$). It is likely that the amino group of **6** acts as an electron donor, which reductively quenches the singlet excited state leading to a lower fluorescence quantum yield ($\Phi_F = 0.04$) and singlet oxygen quantum yield.

Stability

The stability of these compounds in aqueous media was then examined by monitoring the decrease in Q-band absorbance with time. Figure 5 shows the results for selected

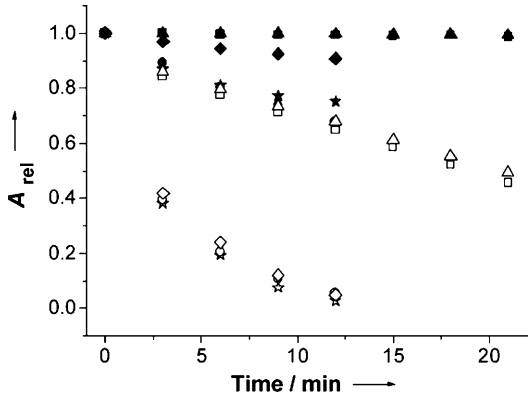


Figure 5. Changes in the Q-band absorbance of **4** (stars), **6** (circles), **7** (diamond), **8** (squares), and **12** (triangles) in water with 0.05% (w/v) Cremophor EL (all at 8.0 μM) with time, both in the absence (closed symbols) and presence (open symbols) of light ($\lambda > 515$ nm, 118 mW cm^{-2}). The data were taken at 3 min intervals.

subphthalocyanines both in the dark and under irradiation with yellow light ($\lambda > 515$ nm). It can be seen that the absorbance of the carboxy subphthalocyanine **8** and carboxylate **12**, as well as the other anionic subphthalocyanines **9**–**11** (data not shown) remains essentially unchanged in the absence of light showing that they are relatively stable in the dark. However, the amino subphthalocyanine **6** and the cationic subphthalocyanines **4** and **7** (as well as **5**, for which the data are not shown) are relatively unstable. The absorbance decreases by 10–32% in the first 12 min. Upon irradiation, all the subphthalocyanines are unstable as shown by the decrease in the Q-band absorbance. For compounds **4**–**7**, the values drop by more than 95% in 12 min. In contrast, compounds **8**–**12** show a relatively higher photostability. During the first 12 min of illumination, the absorbance decreases by only 31–35%. By extending the irradiation time to 21 min, the values decrease further to 48–55%. These observations clearly indicate that the carboxy subphthalocyanine **8** and the carboxylates **9**–**12** are relatively more stable than the amino subphthalocyanine **6** and the cationic analogues **4**, **5**, and **7**.

The efficiency of these subphthalocyanines in generating singlet oxygen in water was also compared using a previously described method.[16] In this method, imidazole was used to capture singlet oxygen to form a *trans*-annular peroxide intermediate, which can induce the bleaching of 4-nitrosodimethylaniline (RNO) as monitored spectroscopically at 440 nm. All the subphthalocyanines **4**–**12** could not produce singlet oxygen in the absence of light. Upon illumination, photobleaching of RNO was observed showing that singlet oxygen had been generated. Figure 6 shows the changes in absorption spectra of these compounds in the presence of RNO and imidazole in water upon irradiation. The absorbance of RNO (at 440 nm) drops by 13–16% for compounds **4**–**7** and 21–25% for **8**-**12** in the first 12 min. Concomitantly, the subphthalocyanine Q band (at ca. 560 nm) diminishes in all cases, and the rate is much faster for the former series of compounds. Extending the irradiation time could not induce any further decrease in absorbance of RNO for compounds **4**–**7**. However, for subphthalocyanines **8**–**12**, the RNO's absorbance at 440 nm further decreases to 32–39% in 21 min. These results (for selected subphthalocyanines) are depicted in Figure 7. Thus, it can be concluded that the carboxy subphthalocyanine **8** and the anionic analogues **9**–**12** are more effective singlet oxygen generators in aqueous media, probably as a result of their higher photostability.

Conclusions

In summary, a series of subphthalocyanines with an axial pyridyl, amino, or carboxy group have been prepared by typical ligand-substitution reactions. Upon methylation or

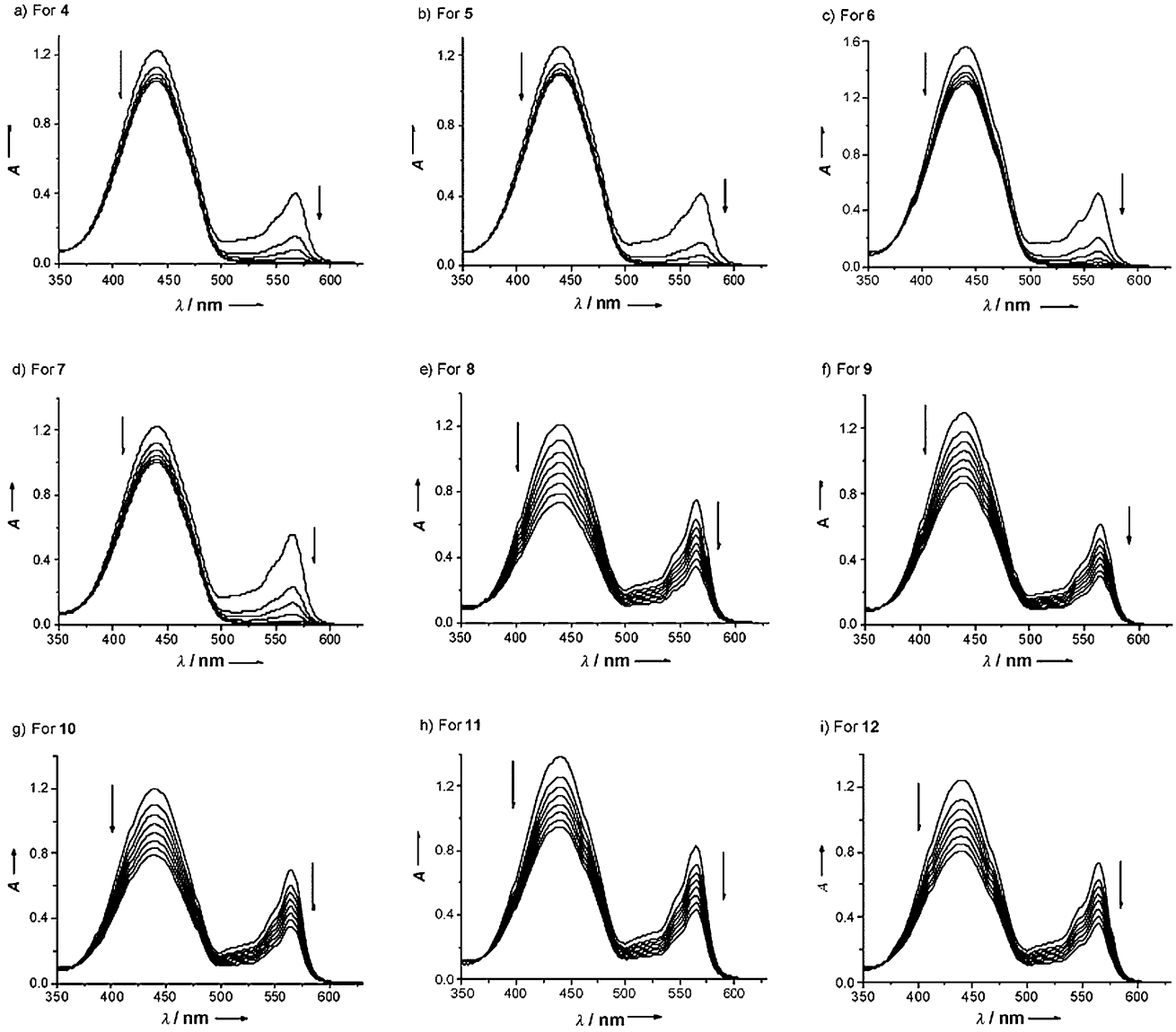


Figure 6. Changes in absorption spectra of mixtures containing **4**–**12** (8.0 μM), 0.05% (w/v) Cremophor EL, RNO (25.0 μM), and imidazole (6.3 mM) in water upon irradiation ($\lambda > 515$ nm) with time. The spectra were taken at 3 min intervals. The relative rates of decay of RNO and the photosensitizer can be compared by monitoring the decrease in absorbance at 440 and 564–568 nm, respectively.

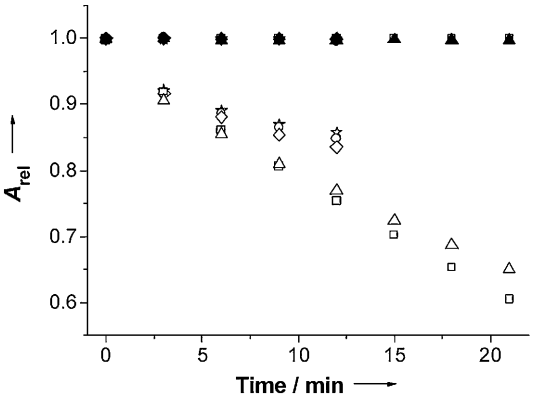


Figure 7. Changes in absorbance of RNO at 440 nm with time {initial [RNO] = 25.0 μM} using subphthalocyanines **4** (stars), **6** (circles), **7** (diamond), **8** (squares), and **12** (triangles) as the photosensitizers (all at 8 μM) in water with 0.05% (w/v) Cremophor EL, both in the absence (closed symbols) and presence (open symbols) of light ($\lambda > 515$ nm, 118 mW cm^{-2}). The data were taken at 3 min intervals ([imidazole] = 6.3 mM).

deprotonation, these compounds can be converted readily to the corresponding cationic or anionic analogues, all of which possess a reasonably high solubility in water. With a cone-shaped macrocycle and an axial substituent, these compounds are essentially non-aggregated in solution and show a high efficiency in generating singlet oxygen. The carboxy and carboxylate derivatives exhibit a relatively higher photostability, making them potentially useful as photosensitizers in aqueous media.

Experimental Section

General

Experimental details regarding the purification of solvents and instrumentation are described elsewhere.[17] The pyridyl subphthalocyanines **2** and **3** were prepared as described.[11]

Synthesis

[SPc(3-OPyMe)]I (**4**): A mixture of SPc(3-OPy) (**2**) (23 mg, 0.047 mmol) and a large excess of iodomethane (1 mL) in chloroform (10 mL) was heated under reflux for 1 h. After cooling, the solid was collected by suction filtration and washed successively with chloroform and diethyl ether to give the product as a violet solid (19 mg, 64%). ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 8.85$–8.88 (m, 6H; SPc-H$_\alpha$), 8.22 (d, $J = 6.0$ Hz, 1H; Py-H), 8.02–8.05 (m, 6H; SPC-H$_\beta$), 7.54–7.59 (m, 2H; Py-H), 6.25 (d, $J = 8.7$ Hz, 1H; Py-H), 3.87 ppm (s, 3H; Me); ^{13}C{^{1}H} NMR (75.4 MHz, [D$_6$]DMSO): $\delta = 152.2$, 152.0, 138.8, 138.4, 133.6, 130.9, 130.8, 128.2, 122.6, 47.9 ppm; HRMS (ESI): *m*/*z* calcd for $C_{30}H_{19}BN_7O$: 504.1739 $[M-I]^+$; found: 504.1741; elemental analysis: calcd (%) for $C_{30}H_{19}BIN_7O$: C 57.08, H 3.03, N 15.53; found: C 56.89, H 3.51, N 15.55.

[SPc(4-OPyMe)]I (**5**): According to the previously mentioned procedure, SPc(4-OPy) (**3**) (23 mg, 0.047 mmol) was treated with iodomethane to give **5** (23 mg, 77%). ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 8.88$–8.91 (m, 6H; SPc-H$_\alpha$), 8.23 (d, $J = 6.3$ Hz, 2H; Py-H), 8.05–8.07 (m, 6H; SPc-H$_\beta$), 5.72 (d, $J = 6.3$ Hz, 2H; Py-H), 3.80 ppm (s, 3H; Me); ^{13}C{^{1}H} NMR (75.4 MHz, [D$_6$]DMSO): $\delta = 165.9$, 152.9, 147.5, 131.5, 131.2, 123.1, 116.3, 46.8 ppm; HRMS (ESI): *m*/*z* calcd for $C_{30}H_{19}BN_7O$: 504.1739 $[M-I]^+$; found: 504.1737; elemental analysis: calcd (%) for $C_{30}H_{21}BIN_7O_2$ (**5**·H$_2$O): C 55.50, H 3.26, N 15.10; found: C 55.35, H 3.67, N 14.93.

SPc(OCH$_2$CH$_2$NMe$_2$) (**6**): A mixture of SPcCl (**1**) (ca. 90%, 200 mg, 0.42 mmol) and a large excess of 2-dimethylaminoethanol (1 mL) in toluene (5 mL) was heated under reflux overnight. After cooling, the volatiles were removed under reduced pressure. The residue was then loaded onto a silica-gel column and eluted with CH$_2$Cl$_2$/MeOH [changing gradually from 40:1 (v/v) to 20:1 (v/v)]. The crude product obtained was further purified by size exclusion chromatography with Bio-Beads S-X1 beads using THF as the eluent. The final product was obtained as a violet solid by recrystallization from acetone/hexane (70 mg, 35%). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 8.83$–8.87 (m, 6H; SPc-H$_\alpha$), 7.88–7.92 (m, 6H; SPc-H$_\beta$), 1.70 (s, 6H; Me), 1.54 (t, $J = 6.3$ Hz, 2H; CH$_2$), 1.41 ppm (t, $J = 6.3$ Hz, 2H; CH$_2$); ^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$): $\delta = 151.5$, 130.9, 129.6, 122.0, 59.5, 57.0, 45.3 ppm; HRMS (ESI): *m*/*z* calcd for $C_{28}H_{23}BN_7O$: 484.2052 $[M+H]^+$; found: 484.2052; elemental analysis: calcd (%) for $C_{28}H_{22}BN_7O$: C 69.58, H 4.59, N 20.29; found: C 69.10, H 5.11, N 20.07.

[SPc(OCH$_2$CH$_2$NMe$_3$)]I (**7**): A mixture of **6** (10 mg, 0.02 mmol) and a large excess of iodomethane (1 mL) in chloroform (10 mL) was stirred at room temperature for 30 min. A large amount of diethyl ether (50 mL) was then added. The precipitate formed was collected by filtration, washed with diethyl ether, and then dried in vacuo to afford **7** as a violet solid (9 mg, 70%). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 8.86$–8.89 (m, 6H; SPc-H$_\alpha$), 7.94–7.97 (m, 6H; SPc-H$_\beta$), 2.85 (vt, $J = 4.5$ Hz, 2H; CH$_2$), 2.71 (s, 9H; Me), 1.88 ppm (br s, 2H; CH$_2$); ^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$): $\delta = 151.5$, 130.8, 130.2, 122.3, 66.0, 54.2, 53.5 ppm; HRMS (ESI): *m*/*z* calcd for $C_{29}H_{25}BN_7O$: 498.2208 $[M-I]^+$; found: 498.2214; elemental analysis: calcd (%) for $C_{29}H_{26}BIN_7O_{1.5}$ (**7**·0.5 H$_2$O): C 54.92, H 4.13, N 15.46; found: C 55.01, H 4.58, N 15.09.

SPc(OC$_6$H$_4$CO$_2$H) (**8**): A mixture of SPcCl (**1**) (ca. 90%, 110 mg, 0.23 mmol) and 4-hydroxybenzoic acid (128 mg, 0.93 mmol) in toluene (5 mL) was heated under reflux overnight. After cooling, the volatiles were removed under reduced pressure, then the residue was loaded onto a silica-gel column and eluted with CHCl$_3$/MeOH [changing gradually from 40:1 (v/v) to 20:1 (v/v)]. The crude product obtained was further purified by size exclusion chromatography with Bio-Beads S-X1 beads using THF as the eluent. The final product was obtained as a violet solid by recrystallization from CHCl$_3$/hexane (33 mg, 27%). ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 12.49$ (br s, 1H; COOH), 8.83–8.87 (m, 6H; SPc-H$_\alpha$), 7.99–8.02 (m, 6H; SPc-H$_\beta$), 7.34 (d, $J = 7.8$ Hz, 2 H C$_6$H$_4$), 5.36 ppm (d, $J = 7.8$ Hz, 2H; C$_6$H$_4$); ^{13}C{^{1}H} NMR (75.4 MHz, [D$_6$]DMSO): $\delta = 167.6$, 157.5, 152.2, 131.7, 131.2, 131.1, 124.7, 123.0, 119.6 ppm; HRMS (ESI): *m*/*z* calcd for $C_{31}H_{18}BN_6O_3$: 533.1528 $[M+H]^+$; found: 533.1526; elemental analysis: calcd (%) for $C_{31}H_{18}BN_6O_{3.5}$ (**8**·0.5H$_2$O): C 68.78, H 3.35, N 15.52; found: C 68.42, H 3.54, N 15.38.

[Et$_2$NH$_2$][SPc(OC$_6$H$_4$CO$_2$)] (**9**): To a solution of **8** (6.0 mg, 0.011 mmol) in chloroform (3 mL) was added a large excess of diethylamine (0.5 mL). The resulting mixture was stirred at room temperature for 10 min, then a large amount of hexane (15 mL) was added to give a precipitate. The violet product was collected by filtration and washed with hexane (5.5 mg, 81%). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 8.83$–8.86 (m, 6H; SPc-H$_\alpha$), 7.89–7.92 (m, 6H; SPc-H$_\beta$), 7.42 (d, $J = 8.1$ Hz, 2H; C$_6$H$_4$), 5.35 (d, $J = 8.1$ Hz, 2H; C$_6$H$_4$), 2.81 (q, $J = 7.2$ Hz, 4H; CH$_2$), 1.18 ppm (t, $J = 7.2$ Hz, 6H; Me); ^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$): $\delta = 172.0$, 155.3, 151.3, 130.9, 130.6, 129.9, 128.7, 122.2, 118.3, 41.7, 11.5 ppm; HRMS (ESI): *m*/*z* calcd for $C_{31}H_{16}BN_6O_3$: 531.1382 $[M-Et_2NH_2]^-$; found: 531.1398; elemental analysis: calcd (%) for $C_{35}H_{30}BN_7O_4$ (**9**·H$_2$O): C 67.43, H 4.85, N 15.73; found: C 67.59, H 5.24, N 15.34.

[*n*Pr$_2$NH$_2$][SPc(OC$_6$H$_4$CO$_2$)] (**10**): According to the previously mentioned procedure, subphthalocyanine **8** (9.8 mg, 0.018 mmol) was treated with dipropylamine (0.5 mL) to give **10** as a violet solid (10.0 mg, 86%). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 8.82$–8.85 (m, 6H; SPc-H$_\alpha$), 7.87–7.90 (m, 6H; SPc-H$_\beta$), 7.39 (d, $J = 8.4$ Hz, 2H; C$_6$H$_4$), 5.35 (d, $J = 8.4$ Hz, 2H; C$_6$H$_4$), 2.68 (vt, $J = 7.8$ Hz, 4H; CH$_2$), 1.61 (sextet, $J = 7.5$ Hz, 4H; CH$_2$), 0.82 ppm (t, $J = 7.5$ Hz, 6H; Me); ^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$): $\delta = 172.4$, 155.0, 151.3, 130.9, 130.4, 129.8, 129.6, 122.2, 118.2, 49.2, 19.7, 11.3 ppm; HRMS (ESI): *m*/*z* calcd for $C_{31}H_{16}BN_6O_3$: 531.1382 $[M-nPr_2NH_2]^-$; found: 531.1392; elemental analysis: calcd (%) for $C_{37}H_{32}BN_7O_3$: C 70.15, H 5.09, N 15.48; found: C 70.61; H 5.53, N 15.28.

[iPr$_2$NH$_2$][SPc(OC$_6$H$_4$CO$_2$)] (**11**): According to the previously mentioned procedure, subphthalocyanine **8** (10.0 mg, 0.019 mmol) was treated with diisopropylamine (0.5 mL) to give **11** as a violet solid (10.0 mg, 84%). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.83–8.85 (m, 6H; SPc-H$_\alpha$), 7.99–8.01 (m, 6H; SPc-H$_\beta$), 7.28 (d, J = 7.5 Hz, 2H; C$_6$H$_4$), 5.28 (d, J = 7.5 Hz, 2H; C$_6$H$_4$), 2.92–3.00 (m, 2H; CH), 1.01 ppm (d, J = 6.0 Hz, 12H; Me); ^{13}C{^{1}H} NMR (100.6 MHz, CDCl$_3$): δ = 171.9, 154.7, 151.3, 130.9, 130.5, 130.3, 129.8, 122.2, 118.1, 45.8, 20.4 ppm; HRMS (ESI): m/z calcd for C$_{31}$H$_{16}$BN$_6$O$_3$ 531.1382 [$M-i$Pr$_2$NH$_2$]$^-$; found: 531.1372; elemental analysis: calcd (%) for C$_{37}$H$_{33}$BN$_7$O$_{3.5}$ (**11**·0.5 H$_2$O): C 69.17, H 5.18, N 15.26; found: C 69.24, H 5.66, N 15.40.

[tBuNH$_3$][SPc(OC$_6$H$_4$CO$_2$)] (**12**): According to the previously mentioned procedure, subphthalocyanine **8** (7.0 mg, 0.013 mmol) was treated with *tert*-butylamine (0.5 mL) to give **12** as a violet solid (6.0 mg, 75%). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.80–8.84 (m, 6H; SPc-H$_\alpha$), 7.88–7.91 (m, 6H; SPc-H$_\beta$), 7.39 (d, J = 8.4 Hz, 2H; C$_6$H$_4$), 5.35 (d, J = 8.4 Hz, 2H; C$_6$H$_4$), 1.08 ppm (s, 9H; Me); ^{13}C{^{1}H} NMR (75.4 MHz, [D$_6$]DMSO): δ = 169.3, 155.2, 152.2, 131.4, 131.1, 123.1, 118.9, 50.7, 29.2 ppm (some of the signals are overlapped); HRMS (ESI): m/z calcd for C$_{31}$H$_{16}$BN$_6$O$_3$: 531.1382 [$M-t$BuNH$_3$]$^-$; found: 531.1392; elemental analysis: calcd (%) for C$_{35}$H$_{29}$BN$_7$O$_{3.5}$ (**12**·0.5 H$_2$O): C 68.41, H 4.76, N 15.96; found: C 68.41, H 5.31, N 15.56.

X-ray Crystallographic Analysis of ***6***

Crystal data and details of data collection, and structure refinement are given in Table 3. Data were collected on a Bruker SMART CCD diffractometer with an MoK$_\alpha$ sealed tube (λ = 0.71073 Å) at 293 K, using a ω scan mode with an increment of 0.3°. Preliminary unit-cell parameters were obtained from 45 frames. Final unit-cell parameters were obtained by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated using the preliminary cell-orientation matrix. SMART software was used for collecting frames of data, indexing reflections, and determination of lattice constants; SAINT-PLUS for integration of intensity of reflections and scaling;[18] SADABS for absorption correction;[19] and SHELXL for space group and structure determination, refinements, graphics, and structure reporting.[20] CCDC 690351 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystallographic data for subphthalocyanine **6**.

	6
Formula	C$_{28}$H$_{22}$BN$_7$O
M_r	483.34
Crystal size [mm^3]	0.40 × 0.30 × 0.30
Crystal system	Orthorhombic
Space group	*Pbca*
a [Å]	15.611(3)
b [Å]	14.536(3)
c [Å]	21.001(4)
V [Å^3]	4765.6(15)
Z	8
F (000)	2016
ρ_{calcd} [mg m^{-3}]	1.347
μ [mm^{-1}]	0.086
θ range [deg]	1.94 to 28.06
Reflections collected	30832
Independent reflections	5769 (R_{int} = 0.0865)
Parameters	334
$R1$ [$I > 2\sigma(I)$]	0.0549
w$R2$ [$I > 2\sigma(I)$]	0.1256
GOF	1.099

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