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Germanium triazatetrabenzcorrole and germanium phthalocyanine: Synthesis, fluorescence and singlet oxygen generation

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Dedicated to Professor Naisheng Chen on the occasion of his 80th birthday

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ABSTRACT: The synthesis, fluorescence properties and singlet oxygen generation capability of germanium tetrabenzotriazacorrole (LGeTBC), germanium phthalocyanine (Cl_2GePc) and their derivatives are described. Measurements include UV-vis absorption spectra, fluorescence emission spectra, fluorescence quantum yields, fluorescence lifetimes, and singlet delta oxygen quantum yields. LGeTBC and its derivatives exhibit quite different spectral and fluorescence properties from their phthalocyanine precursor. Both LGeTBC and Cl_2GePc show high singlet delta oxygen quantum yields and suitable fluorescence quantum yields, indicating that they can act as good singlet oxygen photosensitizers for photodynamic therapy.

KEYWORDS: triazatetrabenzocorrole, phthalocyanine, corrole, singlet oxygen, photodynamic therapy.

INTRODUCTION

Triazatetrabenzcorroles (TBCs) are large π-conjugated macrocyclic compounds derived from phthalocyanines (Pcs) as shown in Scheme 1. The synthesis, characterization and properties of TBCs have been reviewed recently [1]. A TBC molecule is obtained by eliminating one bridging nitrogen atom in a Pc molecule [2–18]. Pc materials have been the focus of study in diverse areas for over a century and have been applied as dyes, pigments, chemical sensors, non-linear optics, liquid crystals and photosensitizers in photodynamic therapy [19–22]. TBCs, however, are relatively new. Only P, Ge, and Si have been inserted into the central cavity of TBC and isolated as pure stable complexes [2–10]. Studies on physical and chemical properties of TBCs are even rarer, with only phosphorous and silicon TBCs having been explored [2, 3, 9–11, 23]. Based on the known data, TBCs show unique properties such as low oxidation potentials, the ability to stabilize high-valent oxidation states, and high reduction potentials [4, 9, 10, 24]. We also studied the photophysical and photochemical properties of phosphorous and silicon TBCs [1–3, 11]. We now extend the study to germanium TBC, including the synthesis, fluorescence properties and singlet oxygen generation capability of germanium tetrabenzotriazacorrole (LGeTBC) and its derivative $L'GeTBCR_4$ (Scheme 1).

EXPERIMENTAL

Materials and instruments

All experiments were carried out in redistilled DMF. Zinc phthalocyanine (ZnPc) was the product of Tokyo Kasei. All other reagents were analytical grade and used as received. ^1H NMR spectra were recorded at room temperature on a Bruker DMX 300 MHz NMR spectrometer. MS spectra were recorded either on a Bruker APEX II or Autoflex III MALDI-TOF spectrometer.

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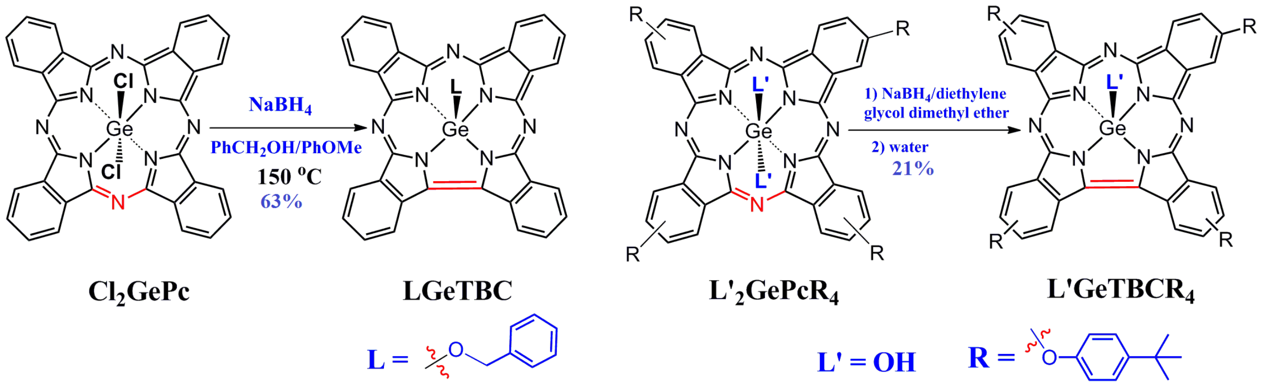

Scheme 1. The chemical structures of Cl_2GePc, L'_2GePcR_4, LGeTBC, and $L'GeTBCR_4$

IR spectra were recorded at room temperature on a Shimadzu FTIR-8900 spectrometer. UV-vis spectra were recorded on a Shimadzu 4500 spectrophotometer using 1 cm matched quartz cuvettes.

Synthesis of Cl_2GePc (dichlorogermanium* (IV) *phthalocyanine). This preparation and purification was performed according to the procedure in the literature [25]. A mixture of $GeCl_4$ (20 g, 0.094 mol) and metal-free phthalocyanine (50 g, 0.39 mol) was placed in quinoline (100 ml) and brought very slowly to reflux with constant stirring. Heating continued at 240 °C for 4 h with stirring. The hot mixture was filtered and the solid was extracted in a Soxhlet extractor with successive portions of DMF, xylene and acetone. Purification was carried out by heating a 300 mg sample in a vacuum sublimator at 450–460 °C for 2 h. Anal. Calcd for $C_{32}H_{16}N_8$ $GeCl_2$: C, 58.69; H, 2.46; N, 17.07; Cl, 10.81. Found: C, 58.32; H, 2.25; N, 16.840; Cl, 10.34. IR (KBr) ν_{max}/cm^{-1}: 1523, 1334, 1288, 1167, 1121, 905, 756, 727 (Pc ring stretching mode), 1084, 1423, 1364, 669. UV-vis (DMF) λ_{max}/nm: 355 (0.45), 607 (0.21), 644 (0.21), 673 (1.13), MS m/z (MALDI-TOF) $[M + H]^+$ calculated 657.1, found 657.3.

Synthesis of LGeTBC. This synthesis and purification was carried out by following the reported procedure [5] (Scheme 1). Cl_2GePc (2.0 g, 3.0 mmol) was mixed with $NaBH_4$ (0.37 g, 0.98 mmol) in a mixture of benzyl alcohol (50 mL) and anisole (25 mL). The mixture was stirred at 160 °C for 2 h in an Ar atmosphere. The hot mixture was filtered under reduced pressure, and then anisole was evaporated under reduced pressure at 100 °C. The residual was then washed with ether, and the obtained solid was repeatedly extracted with hot xylene. The green extract was evaporated under reduced pressure at 70 °C. The residue was again washed with ether and dried in a vacuum for 1 day at 100 °C. Yield: 37%. IR: ν_{max} (KBr)/cm^{-1} 2924, 2855 (CH_2), 1100 (Ge–O–C), 1636, 1580, 1526, 1439, 1364, 766, 638. UV-vis (DMF) : λ_{max}/nm (A) = 415 (0.80), 444 (2.04), 599 (0.23), 659 (1.02). MS m/z (MALDI-TOF) $[M + H]^+$ calculated 680.1, found 680.4.

Synthesis of L'_2GePcR_4. This preparation and purification was performed according to the procedure described in the literature [25]. 4-(*para-tert*-butyl phenoxy) metal-free phthalocyanine (0.31g) was placed in a 25 mL flask, and freshly distilled quinoline (10 mL) was added. After 10 min of argon bubbling, germanium tetrachloride (0.5 mL) was added, and the mixture was stirred at 240 °C for 2 h. After cooling down, stirring and argon bubbling were stopped. Adding *n*-hexane (50 mL) to the mixture, precipitation was formed and filtered. The dried deep blue solid was purified by column chromatography using CH_2Cl_2/ethanol (95/5 v/v) as eluent. Yield: 31%. IR (KBr)/cm^{-1}: 743, 955, 1271, 1464, 1506, 1717 (ν Pc ring); 1053 (ν Ge–O); 1364, 1404, 2926, 2963 (ν CH_3); 1088, 1238 (ν Ar–O–C); 3306 (ν OH); UV-vis (DMF) λ_{max}/nm: 359, 689; MALDI-TOF-MS (m/z) cal.: 1196.4 found: 1178.3 $[M–H_2O]^+$.

Synthesis of $L'GeTBCR_4$. This synthesis and purification was carried out by following the reported procedure [5]. As shown in Scheme 1, a mixture of L_2GePcR_4 (0.21 g, 0.3 mmol) and $NaBH_4$ (0.30 g, 0.80 mmol) was stirred at 145 °C in diethylene glycol dimethyl ether (5 mL) for 2 h in an argon gas atmosphere. Water (20 mL) was added and filtered. The dried solid was purified by column chromatography using CH_2Cl_2/ethanol (95/5 v/v) as eluent. Yield: 21%. UV-vis (DMF) λ_{max}/nm: 454, 672; MALDI-TOF-MS (m/z) cal.: 1165.3 found: 1166.4 $[M + H]^+$.

Photophysics

The absorption and fluorescence spectra, fluorescence quantum yields and excited singlet-state lifetimes, as well as triplet properties were investigated at room temperature in DMF. Steady-state fluorescence spectra were acquired on a FLS 920 with 1 nm slit width for both excitation and emission monochromators. All spectra were corrected for the sensitivity of the photo-multiplier tube. The fluorescence quantum yield (Φ_f) was calculated by $\Phi_f = F_s A_0 \Phi^0_f/(F_0 A_s)$, in which *F* is the integrated fluorescence intensity, A is the absorbance at the excitation wavelength, the subscript 0 stands for a reference compound and s represents samples. Zinc phthalocyanine was used as the reference ($\Phi_f^0 = 0.30$) [26]. Excitation wavelengths of 610 nm corresponding to S_0 to S_1 transitions were employed. The sample and reference solutions were prepared with the same absorbance (A_i) at the excitation wavelength (near 0.09 per cm). All solutions were air saturated.

Fluorescence lifetime of S_1 was measured by the Time-Correlated Single Photon Counting Method (Edinburgh FLS920 spectrophotometer) with diode laser (50 ps FWHM) excitation at 672 nm, and emission was monitored at 690 nm.

Singlet oxygen identification

For measurement of singlet oxygen, typically, a 2 ml portion of the respective sample solutions that contained diphenylisobenzofuran (DPBF) was irradiated at 660 nm in air-saturated DMF. To avoid chain reactions induced by DPBF in the presence of singlet oxygen, the concentration of DPBF was lowered to ~3×10^{-5} mol · dm^{-3}. A solution of sensitizer (absorbance ~0.65 at the irradiation wavelength) that contained DPBF was prepared in the dark and irradiated in the Q-band region. DPBF degradation at 415 nm was monitored.

RESULTS AND DISCUSSION

Synthesis

For the synthesis of both unsubstituted LGeTBC and substituted L'GeTBCR$_4$ (Scheme 1), the reaction of the Pc precursors with NaBH$_4$ proceeds smoothly to yield the product. However, the use of diethyl glycol dimethyl ether as the solvent for L'GeTBCR$_4$ makes the treatment much easier, since this solvent is miscible with water. Therefore, the product can be precipitated easily by adding water and filtering. Benzyl alcohol for LGeTBC synthesis is very difficult to be removed to get a dry product. The ligand linked to Ge^{4+} is different when the solvent in the reaction is different (Scheme 1). The UV-vis and MS data are consistent with the product structure. Due to the coexistence of many aromatic H atoms, the ^{1}H NMR signal is not split and not informative. LGeTBC and L'GeTBCR$_4$ are stable both as a solid and in solutions of ethanol, DMF, and DMSO for over two years.

Absorption and fluorescence properties

UV-vis absorption spectra of the four compounds are shown in Fig. 1. The UV data are collected in Table 1. Cl$_2$GePc and L'$_2$GePcR$_4$ show the typical absorption spectra of phthalocyanines, in which two distinct bands occur, *i.e.* a weak B band at about 350 nm and a sharp Q band in the near IR (about 680 nm). The absorption spectra of LGeTBC and its derivative, however, are very different from that of their corresponding Pc precursor. The relative peak position and height between the B band and the Q band of the TBCs changed very significantly (Fig. 1). Contrary to that of Cl$_2$GePc, the B band of LGeTBC absorbs much more strongly than its Q band. Compared to that of the corresponding Pc, the position of the B band in a TBC is red shifted 90 nm, while the Q band of the TBC is blue shifted about 15 nm. The shape of the B band and the Q band of a TBC is also quite different from that of the corresponding Pc. The structural difference between a TBC and its corresponding Pc is the absence of a bridge nitrogen, as displayed in Scheme 1. The missing of the nitrogen atom reduces both the size and the planarity of the π-conjugated system in a TBC molecule, which leads to the property changes (Table 1).

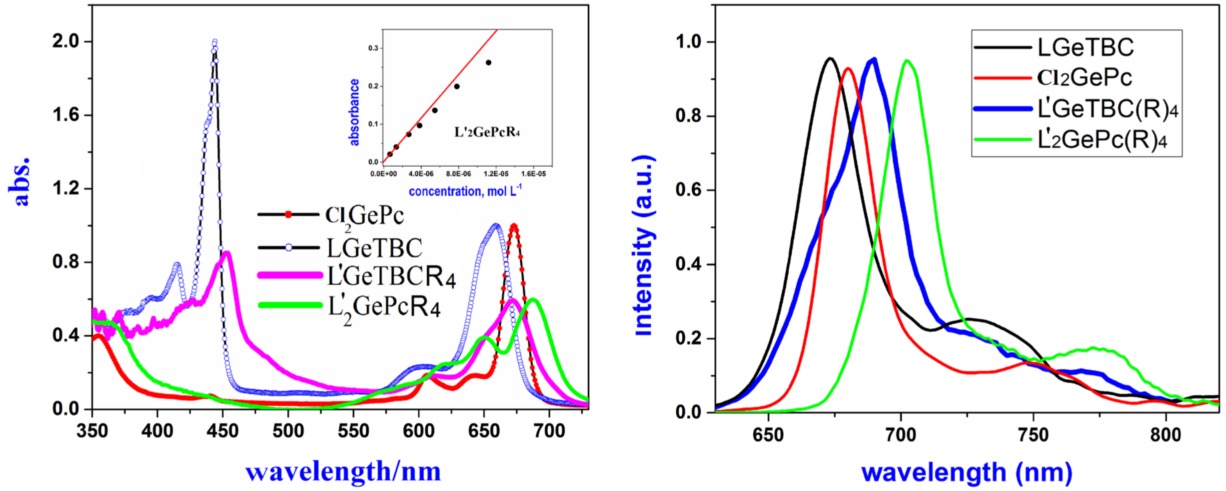

Fig. 1. UV-vis absorption (**Left**) and emission spectra (**Right**) of Cl$_2$GePc, LGeTBC, L'$_2$GePc(R)$_4$, and LGeTBC(R)$_4$ in DMF. Inset, left, is the plot of absorbance at 645 nm against concentration of L'$_2$GePc(R)$_4$, which deviates from linear relation due to H-aggregation

Table 1. The photophysical parameters of LGeTBC, L'GeTBCR$_4$ and Cl$_2$GePc in DMF***

	Cl$_2$GePc	LGeTBC	L'$_2$GePcR$_4$	L'GeTBCR$_4$
λ_{max}, abs [nm]	355, 673	444, 659	359, 689	454, 672
logε	5.45	5.22	5.34	5.41
λ_{max}, em [nm]	681	673	703	690
Stokes shift [nm]	8	14	14	18
Φ_f	0.13	0.10	0.14	0.11
τ_f [ns]	5.65	1.26, 5.37 (18%)	5.12	1.07, 4.41 (52%)
Φ_Δ	0.83	0.59	0.12	0.55

***: λ_{max},abs: wavelength at absorption maximum; ε: molar absorption coefficient, [M^{-1}cm^{-1}]; λ_{max}, em: wavelength at emission maximum; Φ_f: fluorescence quantum yield; τ_f: fluorescence lifetime; Φ_Δ: singlet oxygen quantum yield.

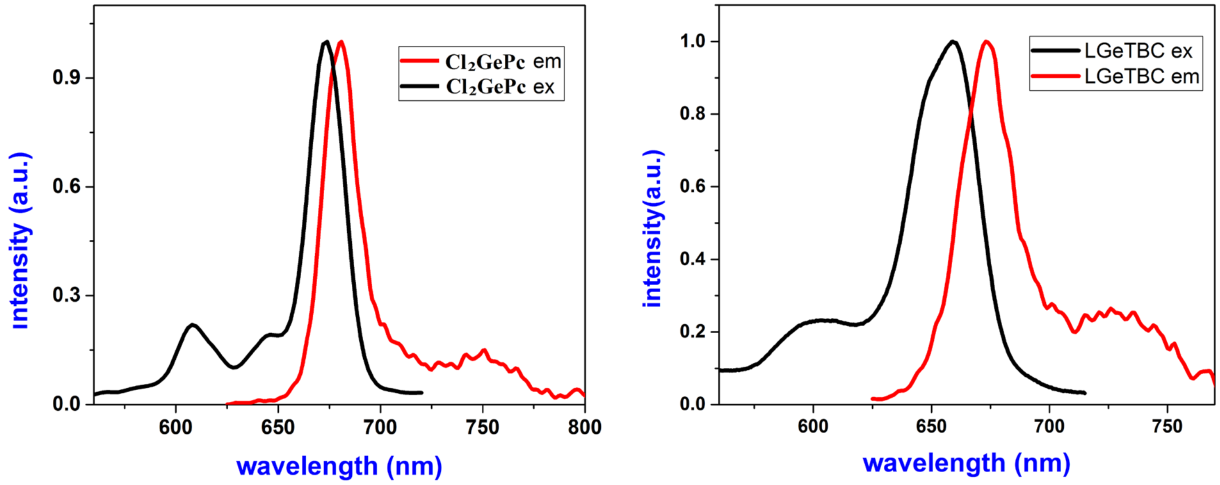

Fig. 2. Normalized fluorescence emission spectra with excitation at 610 nm (absorbance 0.090)

Comparing to the unsubstituted cases, the presence of the *p-tert*-butyl phenoxy on the Pc and TBC ring causes the red shift of the absorption peak, which is due to the electron-donating nature of this group. L'$_2$GePcR$_4$ showed an additional peak at 645 nm, which indicates the presence of H-aggregation for this compound. Figure 1 (inset) shows that the absorbance–concentration plot of L'$_2$GePc(R)$_4$ deviates from linear relation, also an indication of its H-aggregation.

The fluorescence emission spectra of the four compounds are also shown in Fig. 1. The emission spectra of the TBCs are very similar to those of phosphorous and silicon TBCs reported in the literature [1, 4, 13]. The emission maximum of LGeTBC occurs at 673 nm, which is blue shifted 8 nm from that of Cl$_2$GePc. Similar to the case of absorption, the presence of O–Ph–C(CH$_3$)$_3$ on the Pc and TBC ring causes the red shift of the emission peak. The excitation spectrum is mirror symmetrical to its fluorescence emission (Fig. 2).

The fluorescence emission data are summarized in Table 1. Fluorescence quantum yield (Φ_f) was determined using the comparative method with ZnPc in DMF as a standard ($\Phi_f = 0.30$). All compounds have a Φ_f of 0.12 ± 0.02, for example, the value of Φ_f obtained is 0.13 for Cl$_2$GePc and 0.10 for LGeTBC. This Φ_f value is good for fluorescence imaging and diagnosing during PDT treatment.

The emission decay at 690 nm was determined using time-correlated single photon counting with excitation at 672 nm using a 50 ps diode laser (Fig. 3), from which the fluorescence lifetime (τ_f) was calculated. The single exponential fitting gives satisfactory results for Cl$_2$GePc and L'$_2$GePcR$_4$; the τ_f are 5.65 and 5.12 ns, respectively. The fluorescence decay of two TBCs, however, shows bi-exponential behavior, which is very likely due to the isomerization of TBCs (Fig. 4). The isomer TBC-II in Fig. 4 is more stable than TBC-I, since Ge^{4+} in TBC-II is chelated by two six-membered rings, while Ge^{4+} in

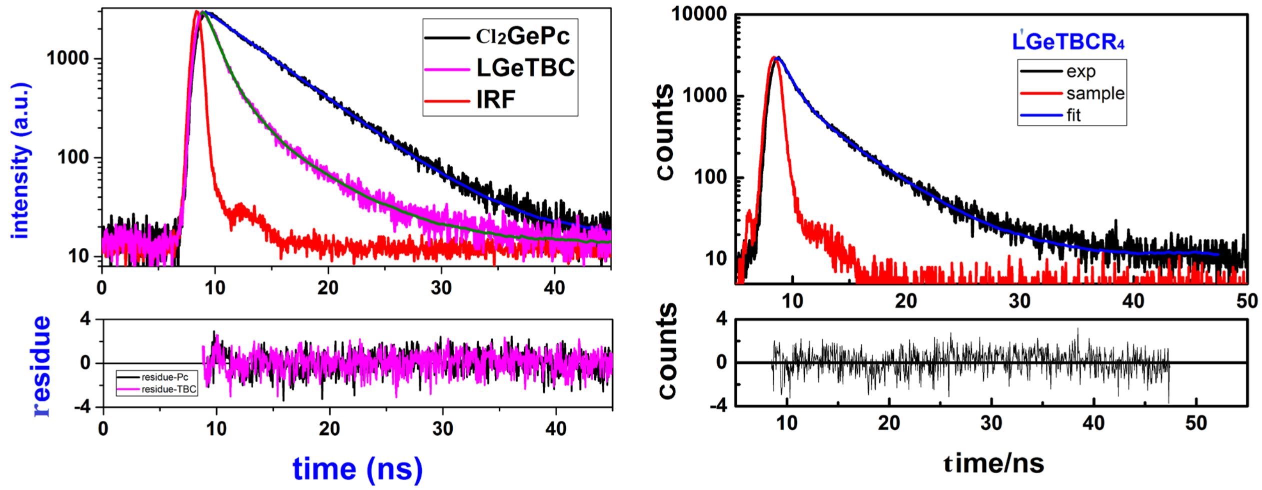

Fig. 3. Time profile of fluorescence decay with excitation at 672 nm diode laser (50 *ps*). The emission was monitored at 690 nm, the concentration of dyes is *ca.* 2.0 µM. Bottom: fitting residues ($\chi^2 < 1.15$ for all fittings)

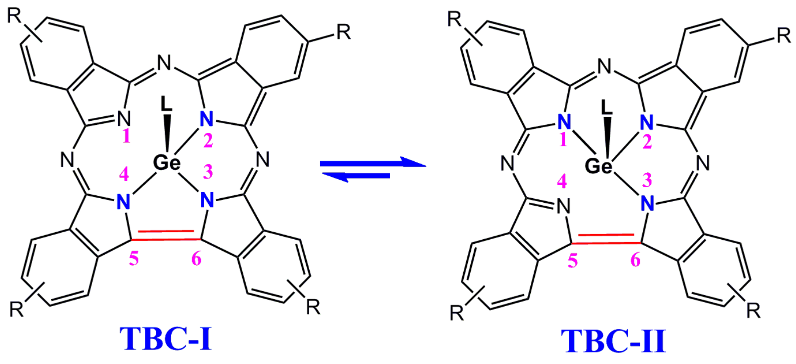

Fig. 4. The isomerization of LGeTBCs. TBC-II is more stable than TBC-I

TBC-I is ligated by one six-member ring and one five-member ring (Ge–N_3–C_6–C_5–N_4), therefore the long-lived emitting component is likely from TBC-II. The fluorescence lifetime and quantum yield of a TBC is shorter than its corresponding Pc due to the isomerization.

Singlet oxygen production

Singlet oxygen quantum yield (Φ_Δ) values were determined by the Chemical Trapping Method [27] with irradiation at 660 nm in air-saturated DMF. Φ_Δ was computed by the relative method using ZnPc as reference (Equation 1). Φ_Δ values are also included in Table 1.

$$\Phi_\Delta = \Phi_\Delta^{\mathrm{ref}} \frac{k}{k^{\mathrm{ref}}} \frac{I_a^{\mathrm{ref}}}{I_a}, \tag{1}$$

where $\Phi_\Delta^{\mathrm{ref}}$ is the singlet oxygen quantum yield for the standard (0.65 for ZnPc in DMF) [28], k and k^{ref} are the

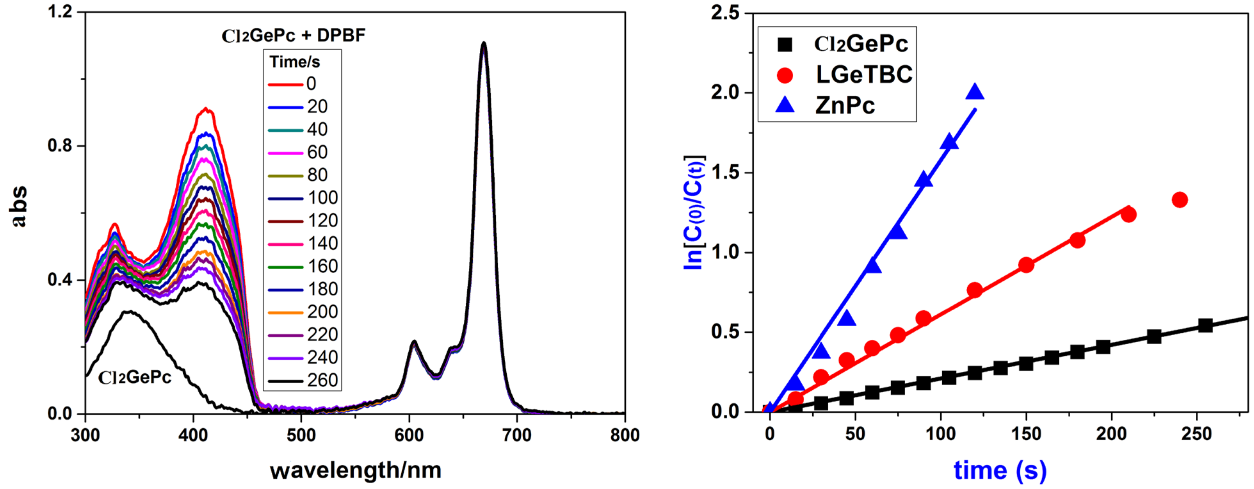

Fig. 5. The change of absorption spectrum upon irradiation time in air saturated DMF containg 5 µDBF and 5 µM photosensitizer with irradiation at 660 nm. Inset is the plot of concentration at 415 nm against irradiation time

DPBF photobleaching rate constants in the presence of the samples and standard, respectively; I_a and I_a^{ref} are the rates of light absorption at the irradiation wavelength by the samples and standard, respectively. DPBF degradation at 415 nm was monitored. Figure 5 displays the decrease of [DPBF] upon irradiation time, for which the first order kinetics was observed.

Both TBCs show good yield of singlet oxygen formation (≥ 0.55). The Φ_Δ of Cl_2GePc is as high as 0.83, indicating it is an excellent photosensitizer. The Φ_Δ of L'_2GePcR_4 is low due to its aggregation as indicated by UV-vis absorption spectra (Fig. 1, left). An additional peak at 645 nm of H-aggregates for L'_2GePcR_4, together with the inset of Fig. 1, the absorbance–concentration plot of $L'_2GePc(R)_4$ deviates from linear relation.

CONCLUSION

We synthesized two germanium TBC compounds and their Pc precursors. We measured their UV-vis absorption spectra, fluorescence properties and singlet oxygen quantum yields. The results tell that the absence of a bridging nitrogen in Cl_2GePc leads to a remarkable change in various properties from its Pc precursor. Nevertheless, both LGeTBC and Cl_2GePc show high singlet delta oxygen quantum yields and suitable fluorescence quantum yields, indicating that they can act as good singlet oxygen photosensitizers for photodynamic therapy.

Acknowledgments

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Supporting information

Figures S1–S3 are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml

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