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Synthesis, photophysical and electrochemical properties of perfluoroisopropyl substituted binuclear phthalocyanine conjugated with a butadiyne linker

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ABSTRACT

Synthesis of 1,3-butadiyne-bridged perfluoroisopropyl binuclear phthalocyanine **2** has been successfully achieved from unsymmetrical A_3B-type iodo-perfluoroisopropyl phthalocyanine by palladium-catalyzed cross-coupling with trimethylsilylacetylene and copper-catalyzed Glaser homo-coupling as key reactions. The dyad **2** essentially remains non-aggregated irrespective of solvent and concentration. Electrochemical analysis suggests oxidation is not possible whereas the molecule is more easily reduced. All the results are advantages for photodynamic therapy (PDT).

1. Introduction

Phthalocyanines (Pcs) have drawn substantial interest as molecular materials that give rise to marvellous electronic and optical properties [1]. They have been successfully used as electrochromic devices, information storage systems and liquid-crystal colour displays, and more. These properties arise from their electronic delocalization and are greatly dependent on their aggregation states. Therefore, the suppression and control of aggregation properties of Pcs both in solvent and solid film only by their inherent specificity without any external source is a challenge in material science [2]. The excellent optical and photosensitizing properties of Pcs with both a wider absorbing range of the spectrum and high luminescence quantum yields are often perturbed in a randomly aggregated state. Free from molecular aggregation is particularly advantageous for solar cells and photodynamic therapy because self-association quenches fluorescence and interferes with the formation of singlet oxygen [2]. In addition, regulating the aggregation of Pc macrocycles should be an indispensable factor for nonlinear optical applications [1d,2]. The aggregation properties can be controlled by a judicious selection of substituents on the peripheral positions of the Pc ring with different steric and electronic properties and nowadays aggregation control of the Pc macrocycle has been achieved [3]. Incidentally, covalently linked binuclear Pcs with a highly conjugated alkynyl spacer have gained attention within a decade because of interesting effects arising from the further extension of the 18π-conjugation [4]. The coupling between electronic states of two tethered Pc nuclei leads to important changes in the absorption spectra of the molecules, which renders binuclear Pcs as appealing building blocks with excellent fluorescence and high excitonic properties for the construction of multicomponent photoinduced electron-transfer supramolecular systems, like artificial porphyrin dimers mimicking the special pair of a photosynthetic reaction [5]. Even though the aggregation of conventional, mononuclear Pcs could be reduced by the introduction of bulky substituents into peripheral positions of Pc cores [3], only few examples of covalently linked binuclear Pcs exhibiting freedom from aggregation are known, due to their extended conjugated intermolecular π-systems, and their monomeric states are partially observed under dilute conditions or in coordinating solvents. Indeed, several relevant examples of Pc dimeric alkynyl systems have been reported and their propensity to form aggregations has become very apparent [4]. Considering this aim, the development of conjugated multinuclear Pcs free from aggregation is still a challenge. For the past few decades, our group has focused on the development of fluorine-containing molecules [6] to detect novel materials resulting from the unique properties of fluorine such as high electronegativity, stability, lipophilicity, and water and oil repellence. In this context, we reported the trifluoroethoxy substituted zinc Pcs conjugated with deoxyribonucleosides and found their prominent nature, namely, avoiding aggregation [7]. More recently, we showed the synthesis of trifluoroethoxy-coated binuclear Pc, which is the first genuine

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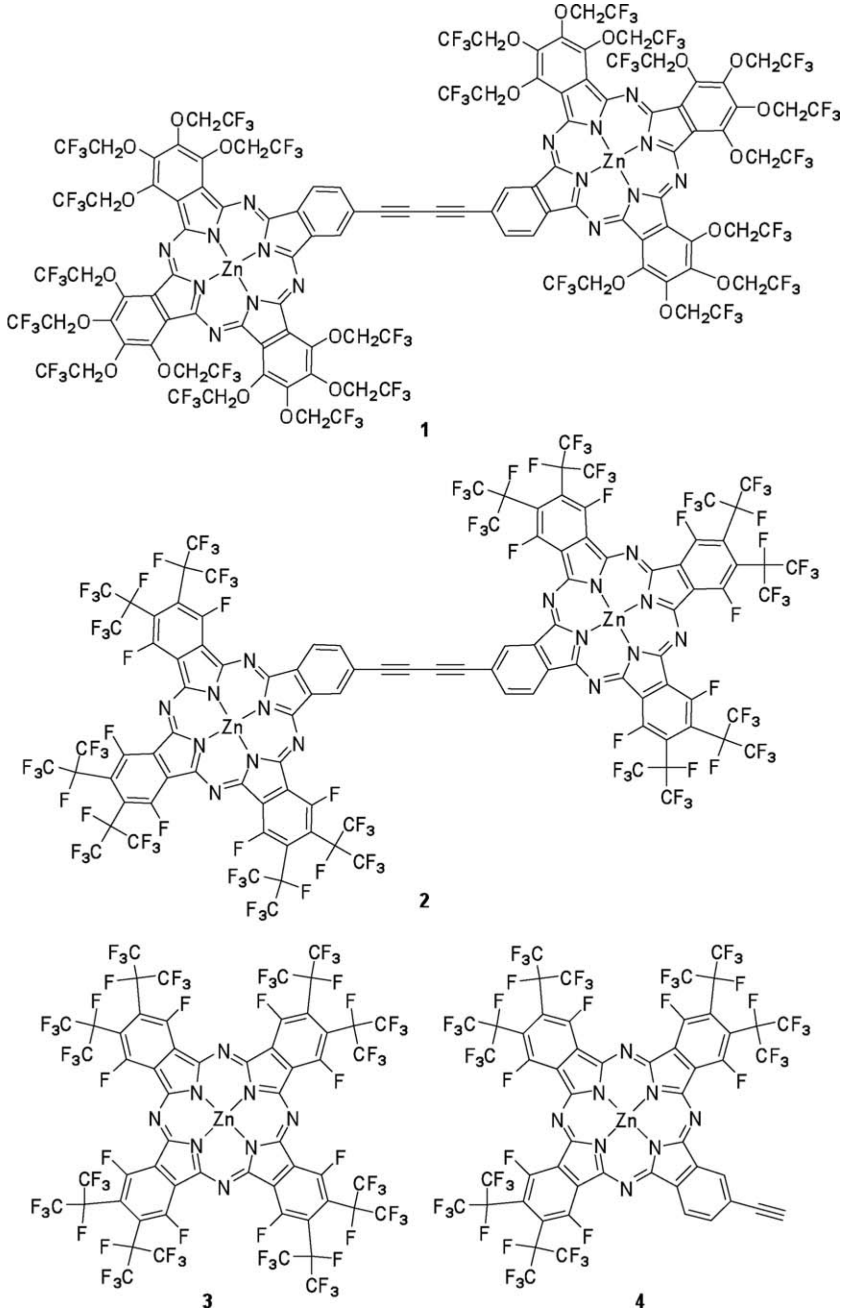
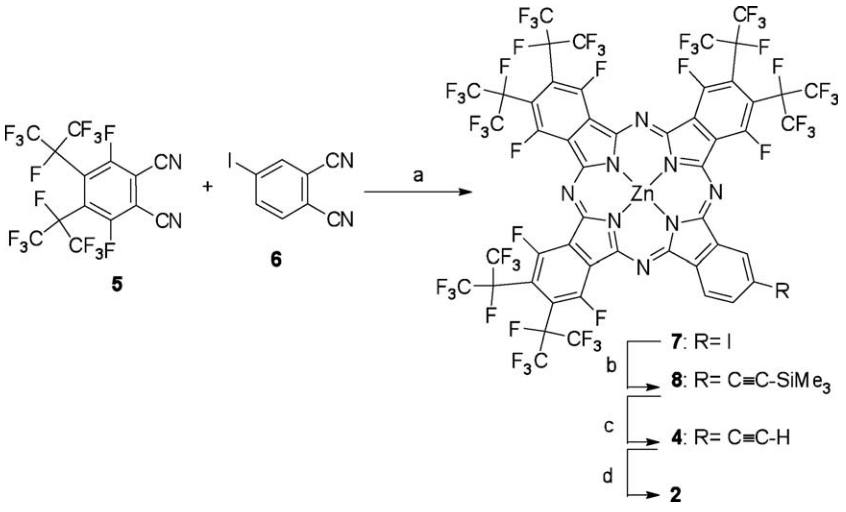


Fig. 1. Structures of previously reported binuclear Pc **1**, newly designed perfluoroisopropyl binuclear Pc **2** and its mononuclear analogues **3** and **4**.

example of a fluorescent covalently linked binuclear Pc **1** free from aggregation, and the trifluoroethoxy-coated binuclear Pc, which behaves as a never closing clamshell independent of solvent and concentration [8]. A series of trifluoroethoxy-coated Pcs showed unique and distinct features; however, their thermal and photochemical stability is not sufficient enough presumably due to the electron-donating effects originated from oxygen atoms on the peripheral trifluoroethoxy substituents [7,8a]. We therefore required the fluoroalkylated Pcs without oxygen atoms in the peripheral positions. As an extension of our continuous program on phthalocyanine chemistry [7–9], we report herein the design, synthesis and spectroscopic investigations of a novel type of alkynyl-linked binuclear phthalocyanine, perfluoroisopropyl substituted binuclear phthalocyanine **2**. Spectral investigation of the newly designed Pc **2** revealed that it possesses photochemical and chemical stability, and favourable solubility, with appropriate properties as a photosensitizer of photodynamic therapy (PDT). Spectral and electrochemical properties of other perfluoroisopropyl substituted mononuclear phthalocyanines **3** and **4** are also discussed for comparison purposes (Fig. 1).

2. Results and discussion

Amongst various mononuclear Pcs recently created that exist as isolated monomeric species, we selected a perfluoroisopropyl substituted Pc **3** as a fundamental component for construction of novel alkynyl binuclear Pcs appropriate for PDT agents. The perfluoroisopropyl Pc **3** was originally developed by Gorun and coworkers [3n,10] in 2002, who revealed its unique photophysical and photodynamic properties. The presence of the peripheral perfluoroalkyl substituents imparts resistance towards chemical and electrochemical oxidation thereby facilitating extraordinary



Scheme 1. (a) $Zn(OAc)_2 2H_2O$, Neat, Ar, 180 °C, 1 h, 41%; (b) trimethylsilylacetylene, $[Pd(PPh_3)_2Cl_2]$, CuI, Et_3N, THF, RT, 24 h, 79%; (c) TBAF, THF, 0 °C-RT, 2 h, 65%; (d) CuCl, pyridine, RT, 3 days, 75%. TBAF = tetrabutylammonium fluoride.

stability. Despite its uniqueness and promising properties of **3** as a photosensitizer for PDT, none of the applications of molecule **3** in the development of more attractive bi- or multinuclear Pcs with extended intramolecular π-systems had been investigated. In this regard, molecule **2** was designed to suppress even intermolecular aggregation of the binuclear Pc by steric and fluorophobic factors of the peripheral perfluoroisopropyl group albeit with its large conjugated π-systems aptly suited for increasing photosensitizing properties in PDT. Free from an electron-donating oxygen atom at the peripheral positions would increase the chemical stability of the parent molecules while purely strong electron withdrawing effects of 12 perfluoroisopropyl moieties would play a key role in conferring enhanced chemical and thermal robustness of the Pc ring towards oxidation by the singlet oxygen it produces. Fluorine also enhances the hydrophobicity of the Pc and in doing so, induces a potential favourable partition coefficient into tumor cells and tissues. The intimate attraction between oxygen and fluorine should assist molecular oxygen binding to the central metal of Pc and its activation, necessary for the effects of PDT in biological examinations.

The perfluoroisopropyl binuclear Pc **2** was successfully synthesized by palladium-catalyzed Sonogashira cross-coupling of iodide **7** with an alkyne followed by Glaser coupling as key reactions (Scheme 1). Zinc 23-iodo-1,4,8,11,15,18-hexafluoro-2,3,9,10,16,17-hexakis perfluoroisopropyl phthalocyaninate (**7**) was synthesized by tetramerization of perfluoro-(4,5-di-isopropyl)phthalonitrile [11], 4-iodophthalonitrile and zinc acetate dihydrate in a solvent-free condition at high temperature according to a standard procedure. This was then coupled with trimethylsilylacetylene under Sonogashira cross-coupling conditions to furnish trimethylsilylated ethynylphthalocyanine **8** in 79% yield. The trimethylsilyl group on **8** was removed by using TBAF in THF to give the terminal acetylene **4** in 65% yield. Target homodimer **2** linked by a butadiyne-diyl group was synthesized under Glaser coupling conditions via dimerization of **4** in 75% yield. The identity and purity of **2** were confirmed by ^1H, ^{19}F NMR, MALDI-TOF MS spectra and analytical HPLC. They have appreciable solubility in common organic solvents, presumably due to the character of perfluoroalkyl substituents on the phthalocyanine macrocycle.

With target molecules in hand, their aggregation property was scrutinized using NMR and UV–Vis spectra. The solution state of binuclear Pcs has been extensively studied, and it was revealed that they have a remarkably high tendency towards aggregation, and that the monomeric state only occurs under very specific conditions of solvent and diluted concentration. However, it is interesting to note that the ^1H and ^{19}F NMR spectra of **2** showed surprisingly resolved, easily assignable signals in accordance with

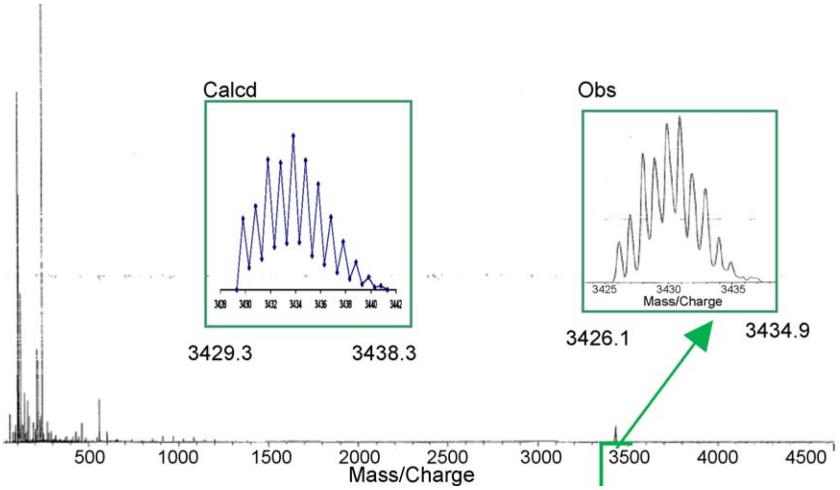


Fig. 2. MALDI-TOF MS spectrum of perfluoro binuclear Pc **2**.

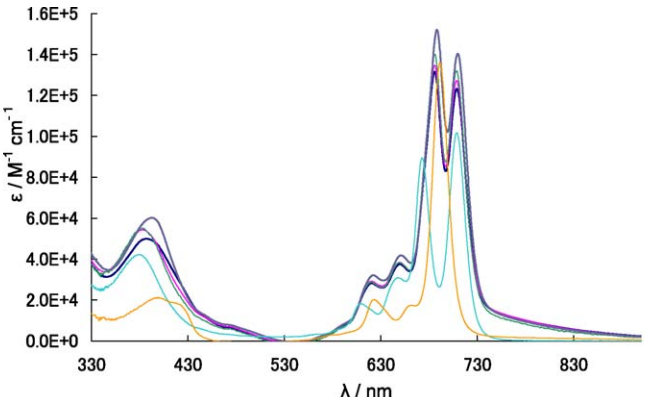


Fig. 3. UV–Vis spectra of **2** (blue, pink, green: 1.0×10^{-4} to 1.0×10^{-6} M, respectively; ash: 1.0×10^{-4} M with a drop of pyridine), **3** (yellow: 1.0×10^{-6} M) and **4** (cyan: 1.0×10^{-6} M) in $CHCl_3$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

the proposed structure. MALDI-TOF MS spectra of **2** also showed the isotopic distributions caused by Zn(II), providing proof for its characterization (Fig. 2). The high resolution in these spectra is indicative of a very low degree of aggregation in solution state.

The optical features of the binuclear Pc **2**, A_3B-type unsymmetrical mononuclear ethynyl Pc **4** and A_4-type symmetrical mononuclear Pc **3** were next investigated using UV–Vis spectra in a variety of solvents in the range of 1×10^{-4} to 1×10^{-6} M solutions ($CHCl_3$, acetone, THF, dioxane and benzotrifluoride). Selected examples of absorption spectra in $CHCl_3$ are shown in Fig. 3. The binuclear Pc **2** possesses a distinct feature: a strong absorption band appears at longer wavelengths and is presented as a monomer, irrespective of the solvent and concentration, characterized by sharp absorption bands in the B- and Q-band regions (λ_{max} ($CHCl_3$)/nm 383 and 709, respectively). While mononuclear symmetrical perfluoroisopropyl phthalocyanine **3** shows a single, sharp and strong Q-band at 691 nm, the binuclear Pc **2** displays two split, but intense vibronic bands appearing at 709 and 686 nm with blue shifted shoulders at 650 and 621 nm revealing molecular asymmetry. Unsymmetrical monomeric analogue **4** also shows similar absorption features like those of **2** with sharp vibronic bands at 709 and 673 nm with shoulders at 646 and 610 nm. Moreover, the Q-band of **2** is red-shifted by 18 nm more than that of **3** as expected because of extended π-conjugation imparted by a butadiyne linker. A similar behaviour was found in a variety of solvents at different concentrations, even in non-polar benzotrifluoride. Furthermore, and of most interest, is that the spectrum of **2** remained essentially unchanged after the addition of a drop of pyridine (approximately 100-fold excess relative to **2**, Fig. 3). These results clearly prove that perfluoroisopropyl binuclear Pc **2** exists as a monomer totally free from aggregation. It is quite obvious that the strong fluorous encapsulation effects intrinsic to 12 sterically demanding perfluoroisopropyl substitutions effectively removed the possibility for self-aggregation. The strong electron withdrawing effect of the fluorine atoms might also affect the reduction of aggregation by lowering the energies of the HOMOs of Pc rings [12].

Next, we probed the steady-state fluorescence spectroscopy in solvents of different polarities ($CHCl_3$, acetone and benzotrifluoride). Fig. 4 shows the emission spectra of **2** and **3** along with precursor **4** in $CHCl_3$ revealing almost comparable fluorescence intensity. The binuclear Pc **2** shows strong emission peaks maximizing at 716 nm, about 15 nm more to the red region of the spectrum than monomer **3**. Pc **2** also shows good fluorescence quantum yield (φ_F) of 0.21, a value quite promising for use in PDT. Similar fluorescence features are observed in other solvents as well, irrespective of polarity (Table 1). Fluorescence lifetime data also strongly corroborates the observed fluorescence spectra (Fig. 5 and Table 1). In the measurement of time-resolved fluorescence

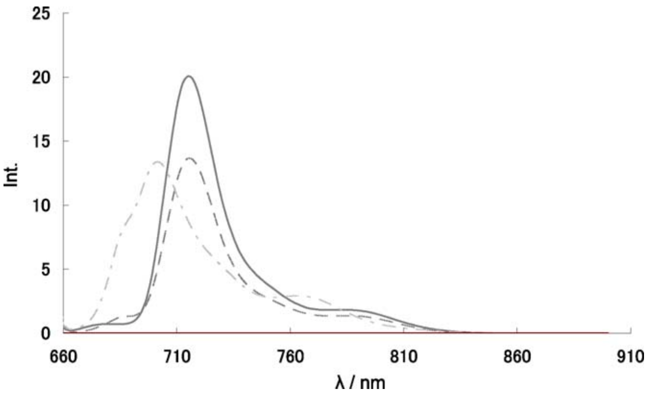


Fig. 4. Steady-state fluorescence spectra of **2** (– – –), **3** (–·–·–) and **4** (—) in $CHCl_3$ with excitation at 655 nm.

Table 1
Photophysical properties of perfluorinated Pcs **2**, **3** and **4**.

	ϕ_F[a]			τ_f (ns)[b]
	$CHCl_3$	Acetone	$PhCF_3$	
4	0.30 (715)	0.20 (719)	0.23 (716)	1.42 ± 0.07
2	0.21 (716)	0.19 (718)	0.10 (720)	0.92 ± 0.05
3	0.25 (701)	0.19 (705)	0.31 (701)	1.52 ± 0.18

[a] Excited at 655 nm. Using ZnPc in 1-chloronaphthalene as the reference ($\phi_F = 0.30$). Figure in parenthesis shows the excitation wavelength.
[b] Fluorescence lifetime was measured in deaerated THF.

Table 2
Differential pulse voltammetry data of **2** and **4**.[a].

	E_{red}^1	E_{red}^2	E_{red}^3	E_{red}^4	E_{red}^5
4	−0.39	−0.60	−0.86	−1.35	−1.79
2	−0.36	−0.59	−0.92	−1.40	−1.88

[a] All the potentials, in volts, were measured relative to $Ag/AgNO_3$ couple in THF containing 0.1 M $TBAPF_6$.

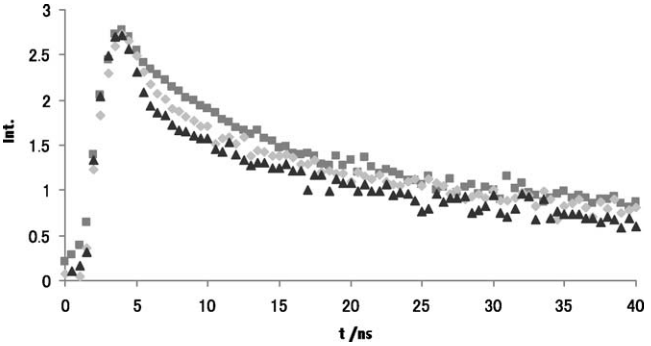


Fig. 5. Fluorescence decay profile of **2** (triangle), **3** (square) and **4** (diamond) in deaerated THF.

Table 3
Cyclic voltammetry data of **2** and **4**.[a].

	E_{red}^1	E_{red}^2	E_{red}^3	E_{red}^4	E_{red}^5
4	−0.39	−0.63	−0.88	−1.37	−1.81
2	−0.38	−0.60	−0.90	−1.40	−1.77

[a] All the potentials, in volts, were measured relative to $Ag/AgNO_3$ couple in THF containing 0.1 M $TBAPF_6$.

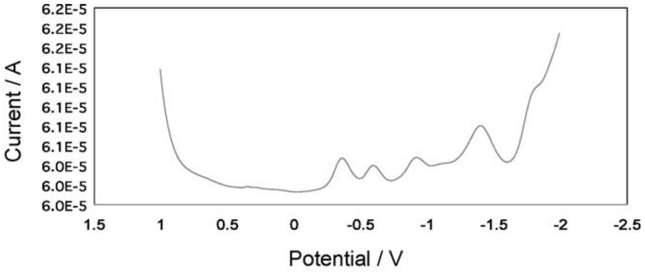


Fig. 6. Differential pulse voltammograms for **2** in THF-TBAPF$_6$ system at room temperature.

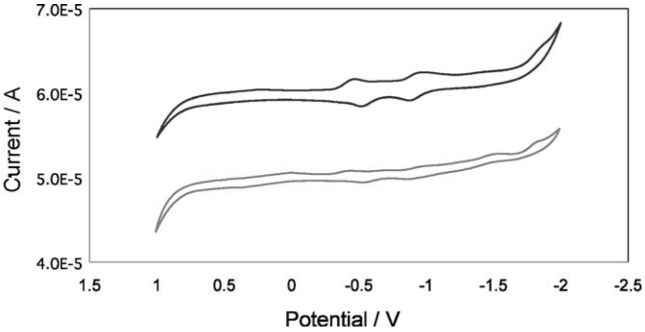


Fig. 7. Cyclic voltammograms for **4** (top) and **2** (bottom) in THF-TBAPF$_6$ system at room temperature.

decay in THF, a lifetime τ_f of 0.92 ± 0.05 ns for **2** was obtained while that of mononuclear Pc **4** is 1.42 ± 0.07 ns with a satisfactory monoexponential fit. The overall photophysical data thus indicates that despite having a homodimeric structure, dyad **2** behaves like mononuclear Pc **4** absolutely free from aggregation; a property which is extremely important for applications in PDT, as intermolecular aggregation facilitates an efficient nonradiative energy relaxation pathway greatly shortening the excited-state lifetimes [13].

Very basic insight into oxidative resistance came from electrochemical studies using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The results measured for **2** were compared with those of the individual component in anhydrous THF. The voltammetric result of **2** is presented in Fig. 6 and the potential data are summarized in Table 2. In DPV, compound **2** shows five reduction waves at −0.36, −0.59, −0.92, −1.40 and −1.88 V in the cathodic scan while no oxidation wave was observed, which is the superimposition of the DPV of precursor **4** (Table 2 and Fig. 6). The CVs of the compounds also show similar characteristics (Table 3 and Fig. 7). In CV, five reduction potentials were observed in the cathodic scan for the homodimer of **2** at −0.38, −0.60, −0.90, −1.40 and −1.77 V and again no oxidation potential was exhibited. Monomer **4** also showed similar features at −0.39, −0.63, −0.88, −1.37 and −1.81 V indicating no existence of intramolecular electronic interaction between the two halves of the dimeric Pc under conventional electrochemical analysis. As expected, the finding suggests that the binuclear Pc **2** is highly electron-deficient and easier to be reduced owing to the presence of strong electron withdrawing perfluoroisopropyl groups in the periphery of the Pc core while completely resisting oxidation by the loss of an electron. Resistance towards oxidation is particularly favourable in catalytic oxygenation of substrates and photodynamic therapy of some cancers [2,10].

In order to ascertain the stability of **2** comparing to **1**, time-dependent fluorescence spectra were recorded in CH_2Cl_2 (Fig. 8). While decrease of the fluorescence intensity of **1** within 200 s was monitored by fluorescence spectroscopy in CH_2Cl_2 (bottom line), the fluorescence intensity of **2** remained essentially unchanged during the irradiation. The results presented here demonstrate that the introduction of peripheral twelve perfluoroisopropyl groups into phthalocyanines nuclei should be effective to improve the stability of the parent phthalocyanines.

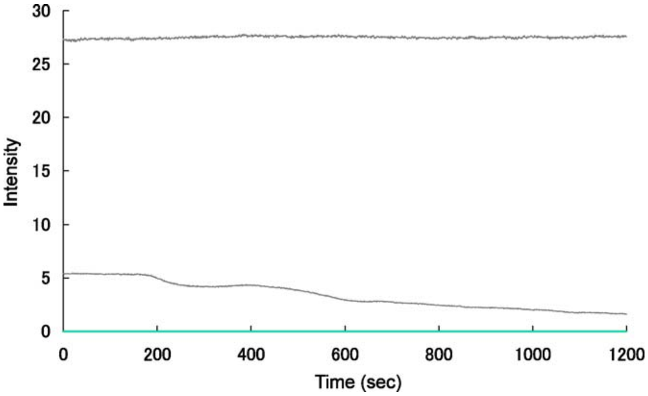


Fig. 8. Time-dependent fluorescence spectra of **1** (bottom) and **2** (top) at 712 nm in CH_2Cl_2.

3. Conclusion

In summary, 1,3-butadiyne-linked perfluoroisopropyl phthalocyanine dyad **2** has been synthesized by Sonogashira and Glaser coupling methods, and its photophysical and electrochemical properties have been investigated. Binuclear Pc **2** essentially remains non-aggregated irrespective of solvent and concentration owing to the strong repulsive effects of electron withdrawing perfluoroalkyl groups appended on the Pc core, imparting high solubility as well for studying the molecule in solution. The electron withdrawing properties of the substituents have a profound effect on the π-system of the Pc as reflected in the redox properties of **2**. Ground-state electrochemical analysis suggests oxidation is not possible whereas reduced species can be easily produced. Absorption in the red region of the visible spectrum coupled with thermal, photochemical and chemical stability imparted by the 12 perfluoroisopropyl moieties afford the binuclear Pc **2** a good candidate as a photosensitizer since it would hinder self-decomposition by photochemically generated singlet oxygen. These features are the obvious advantage of Pc **2** compared with previously reported trifluoroethoxy-coated Pc **1** and related compounds in our laboratory [7,8a]. The biological activity of Pc **2** is currently under investigation in our laboratory.

4. Experimental

4.1. General procedures

All solvents were dried and distilled according to standard procedures. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel plate (60F-254). Column chromatography was carried out on a column packed with silica gel 60N spherical neutral size 63–210 μm. ^1H and ^{19}F NMR (200 MHz) spectra were taken on a Varian Gemini-200 spectrometer. Chemical shifts (δ) are expressed in ppm downfield from internal acetone and THF. Infrared (IR), UV–Vis and steady-state fluorescence spectra were recorded on a JASCO FT/IR-200 Spectrometer, V-530 spectrometer and FP-6200 Fluorospectrometer, respectively. Quantum yields were calculated following the procedure mentioned before. Fluorescence lifetimes were measured with a LaserStrobe Spectrofluorometer (Photon Technology International: http://www.pti-nj.com) with 337 nm laser pulses from a nitrogen laser fiber-coupled to a lens-based T-formal sample compartment equipped with a stroboscopic detector. MALDI-TOF Mass spectra were taken on a SHIMADZU Axima CFR plus. Reverse phase HPLC analyses were performed on a JASCO PU-2080 Plus using 4.6 mm × 250 mm Develosil ODS-HG-5 column and MD-2015 multiwavelength detector. Electrochemical experiments were carried out on a BAS 50W electrochemical analyzer (Bioanalytical Systems, Inc., West Lafayette, IN 47906, USA). Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was purchased from TCI and recrystallized from EtOH. The solvent THF (Kanto Chemical Co. Inc., tetrahydrofuran, dehydrated stabilizer free) was passed through Glass Contour Ultimate Solvent System. For CV and DPV, 3 mm S-2 platinum was used as working electrode and platinum wire as counter electrode. $Ag/AgNO_3$ (0.01 M in MeCN/0.1 M $TBAPF_6$) was used as reference electrode separated by a vycor glass, and all potentials given relate to this electrode. The measurements were performed using a concentration of approximately 0.5 mM of the compounds.

4.2. Preparation of 23-iodo-(1,4,8,11,15,18-hexa-fluoro-2,3,9,10,16,17-hexakis-perfluoroisopropyl)zinc phthalocyaninate 7

A mixture of **5** (614 mg, 1.23 mmol), 4-iodophthalonitrile **6** (52 mg, 0.205 mmol) and zinc acetate dihydrate (135 mg, 0.614 mmol) were heated in solvent-free condition under Ar at 180 °C for 1 h. Flash chromatography on silica gel using 15% acetone in hexane gave unsymmetrical Pc **7** in 41% yield (152 mg).

7: green solid; ^{1}H NMR (200 MHz, d_6-acetone, $CFCl_3$) δ 9.73 (s, 1H), 9.20 (d, 1H, J = 7.6 Hz), 8.76 (d, 1H, J = 7.8 Hz); ^{19}F NMR (188 MHz, d_6-acetone, $CFCl_3$) δ −70.82 (6F), −103.02 (1F), −163.18 (1F); IR (KBr) ν/cm^{-1} 3179, 1754, 1676, 1487, 1439, 1251, 1172, 1087, 967, 902, 782, 753, 731; MALDI-TOF MS: m/z calcd. for $C_{50}H_3F_{48}IN_8Zn$: 1817.31–1824.31. Found: 1815.4–1822.5 ([M+H]$^+$, isotopic pattern).

4.3. Preparation of 23-(trimethylsilyl)ethynyl-(1,4,8,11,15,18-hexa-fluoro-2,3,9,10,16,17-hexakis-perfluoroisopropyl)zinc phthalocyaninate 8

A mixture of **7** (80 mg, 0.044 mmol), Pd $(PPh_3)_2Cl_2$ (26 mg, 0.037 mmol) and CuI (8 mg, 0.042 mmol) were dried under vacuum for 30 min. To this mixture, dry THF (15 ml), trimethylsilylacetylene (15 μl, 0.11 mmol) and Et_3N (7 ml) were added under argon and stirred at room temperature for 24 h. The reaction mixture was evaporated to dryness and the residue was extracted with ethyl acetate. The organic portion was washed with water, brine, dried over Na_2SO_4, filtered and evaporated to give a crude product which was purified by silica-gel column chromatography (acetone:hexane = 1:9) to furnish **8** in 79% yield (62 mg).

8: green solid; ^{1}H NMR (200 MHz, d_6-acetone, $CFCl_3$) δ 9.38–9.34 (m, 2H), 8.42 (brd, 1H, J = 8.8 Hz), 0.41 (s, 9H); ^{19}F NMR (188 MHz, d_6-acetone, $CFCl_3$) δ −70.71 (6F), −103.01 (1F), −163.19 (1F); IR (KBr) ν/cm^{-1} 3441, 2925, 1610, 1486, 1453, 1250, 1170, 1084, 968, 866, 846, 781, 754, 730; MALDI-TOF MS: m/z calcd. for $C_{55}H_{12}F_{48}N_8SiZn$: 1787.95. Found: 1787.98 [M+H]$^+$.

4.4. Preparation of 23-ethynyl-(1,4,8,11,15,18-hexa-fluoro-2,3,9,10,16,17-hexakis-perfluoroisopropyl)zinc phthalocyaninate 4

Compound **8** (45 mg, 0.025 mmol) was dissolved in dry THF (7 ml) and cooled to 0 °C. TBAF in THF (38 μl, 0.038 mmol) was added drop-wise. The reaction mixture was warmed to room temperature and stirred for 2 h. The solvent was then evaporated to dryness and the residue was purified by flash column chromatography (acetone:hexane = 1:5) to afford **4** in 65% yield (28 mg).

4: green solid; ^{1}H NMR (200 MHz, d_6-acetone, $CFCl_3$) δ 9.43–9.39 (m, 2H), 8.47 (d, 1H, J = 7.6 Hz), 3.80 (s, 1H); ^{19}F NMR (188 MHz, d_6-acetone, $CFCl_3$) δ −70.69 (6F), −102.96 (1F), −163.18 (1F); IR (KBr) ν/cm^{-1} 3435, 1611, 1488, 1453, 1250, 1170, 1086, 968, 754, 730; UV/visible: $CHCl_3$ [λ_{max} nm (log ε)] 709 (5.01), 673 (4.96), 646 (4.49), 610 (4.26), 380 (4.63); $PhCF_3$ [λ_{max} nm (log ε)] 707 (5.16), 670 (5.13), 648 (4.75), 607 (4.45), 383 (4.78); acetone [λ_{max} nm (log ε)] 705 (4.95), 670 (4.94), 646 (4.55), 609 (4.21), 405 (4.53); dioxane [λ_{max} nm (log ε)] 708 (5.11), 672 (5.08), 645 (4.68), 609 (4.39), 382 (4.73); MALDI-TOF MS: m/z calcd. for $C_{52}H_4F_{48}N_8Zn$: 1715.41–1723.41. Found: 1715.0–1722.1 ([M+H]$^+$, isotopic pattern).

4.5. Preparation of bis[23-ethynyl-(1,4,8,11,15,18-hexa-fluoro-2,3,9,10,16,17-hexakis-perfluoroisopropyl)zinc phthalocyaninate] butadiyne 2

A mixture of phthalocyanine **4** (20 mg, 0.012 mmol), CuCl (1.5 mg, 0.015 mmol) and pyridine (4 ml) were stirred for 3 days under atmospheric air. The solvent was evaporated to give a green solid which was purified by silica-gel column chromatography (acetone:hexane = 1:4) to afford **2** in 75% yield (15 mg).

2: green solid; ^{1}H NMR (200 MHz, THF-d_8) δ 9.72 (s, 1H), 9.55 (d, 1H, J = 7.6 Hz), 8.60 (d, 1H, J = 7.8 Hz); ^{19}F NMR (188 MHz, THF-d_8, $CFCl_3$) δ −70.87 (6F), −102.50 (1F), −163.14 (1F); IR (KBr) ν/cm^{-1} 3472, 1488, 1455, 1250, 1170, 1086, 968, 781, 754, 731; UV/visible: $CHCl_3$ [λ_{max} nm (log ε)] 709 (5.12), 686 (5.15), 650 (4.58), 621 (4.46), 383 (4.74); $PhCF_3$ [λ_{max} nm (log ε)] 701 (5.35), 682 (5.50), 651 (4.93), 620 (4.75), 389 (4.98); acetone [λ_{max} nm (log ε)] 702 (5.25), 683 (5.37), 650 (4.84), 617 (4.63), 409 (4.92); THF [λ_{max} nm (log ε)] 702 (5.42), 683 (5.54), 651 (4.96), 620 (4.79), 386 (5.08); MALDI-TOF MS: m/z calcd. for $C_{104}H_6F_{96}N_{16}Zn_2$: 3429.30–3438.30. Found: 3426.1–3434.9 ([M+H]$^+$, isotopic pattern).

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