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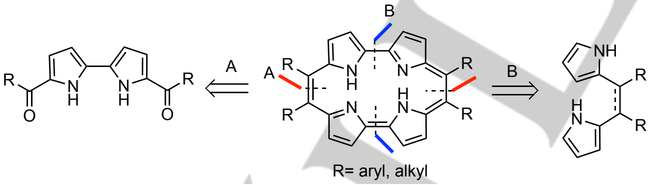
Synthesis of a *meso*-tetraalkylporphycene bearing reactive sites: Toward porphycene–polydimethylsiloxane hybrids with enhanced photophysical properties

Toshikazu Ono,*[a,b] Hyuga Shinjo,[a] Daiki Koga,[a] and Yoshio Hisaeda*[a,b]

Abstract: *Meso*-tetraalkyl porphycenes exhibit unique optical properties with wide potential applications. The very fact that incorporation of porphycenes into polymeric materials is rare, make this approach a particularly attractive one. In this work, *meso*-tetrakis(3-butenyl)porphycene bearing four terminal olefin groups is prepared via two synthetic strategies: 1) the McMurry reaction using 5,5′-diacyl-2,2′-bipyrroles as precursors and 2) the oxidative coupling of dipyrroethenes. The newly obtained porphycene has been characterized by single X-ray crystallography. A porphycene–polydimethylsiloxane hybrid film is successfully prepared by platinum-catalyzed hydrosilylation reaction. The hybrid film can be anchored with tweezers, showing a weak red emission with a quantum yield of 0.4% at room temperature, whose intensity drastically increases reaching a quantum yield of 6.7% in liquid nitrogen (77 K). This report represents the first example of porphycene-containing elastomeric films for potential application in various fields.

Introduction

Porphycenes, which were first prepared by Vogel in 1986, are constitutional isomers of porphyrins having two direct bonds between neighboring pyrroles and two ethenyl bridges.[1] Approaches toward porphycene frameworks are roughly divided into two strategies (Scheme 1),[2] i.e., the standard method based on McMurry reductive cyclization of two 5,5′-diacyl-2,2′-bipyrroles as precursors (Method A)[1] and the oxidative macrocyclization of dipyrroethenes (Method B).[3-7]



Scheme 1. Retrosynthetic analysis of porphycenes.

Because of their unique optical properties, porphycene derivatives have been investigated as potential photosensitizers for photodynamic therapy,[8] as artificial heme components, as catalysts, [9-12] as near-infrared absorption dyes,[13-15] as tautomerization,[16, 17] and as various functional materials.[18-21] From the viewpoint of synthetic chemistry, porphycenes can be modified with substituents at the *β*- and *meso*-positions,[22-29] thereby introducing differences that affect their solubilities, electronic states, metal coordinating abilities, and intramolecular hydrogen bonding behaviors. Thus, *β*-substituted porphycenes have a square-shaped N4-coordination core, whereas the N4-coordination core of *meso*-substituted porphycenes tends to be more rectangular.[23, 30]

Among porphycenes, the *meso*-tetraalkyl derivatives exhibit unusual photoluminescence quenching behavior due to the formation of strong intramolecular hydrogen bonds in the N4 core in the framework.[31, 32] In 2010, Waluk and coworkers reported that the photoluminescence properties of *meso*-tetraalkylsubstituted porphycenes were influenced by external environmental stimuli, and their emission properties were enhanced when embedded in highly viscous fluids or in a polymer matrix.[31] For example, the fluorescence quantum yields of *meso*-tetrapropyl porphycene (**TPPc**) at 293 K are 0.054% and 0.35% in *n*-hexane and DMSO, respectively. The fluorescence lifetimes at 293 K are 27 ps and 4.4 ns in THF and PMMA as host matrix, respectively. Moreover, the emission properties were enhanced at low temperature.[33] These behaviors stem from the deactivation of the excited state of porphycene induced by tautomerization, which is suppressed in highly viscous environments and low temperature.

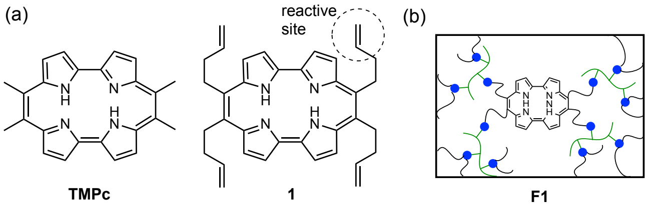


Figure 1. (a) Chemical structures of tetramethylporphycene (**TMPc**) and **1** (This work). (b) Schematic illustration of a porphycene–polydimethylsiloxane hybrid (**F1**).

However, the abovementioned hybrids consisting of *meso*-tetraalkylsubstituted porphycenes embedded in a polymer matrix are noncovalently bonded dispersions. This prompted us to

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[a] Dr. T. Ono, Mr. H. Shinjo, Mr. D. Koga, Prof. Y. Hisaeda
Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University
744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
E-mail: tono@mail.cstm.kyushu-u.ac.jp
E-mail: yhisatcm@mail.cstm.kyushu-u.ac.jp
[b] Dr. T. Ono, Prof. Y. Hisaeda
Center for Molecular Systems (CMS), Kyushu University
744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

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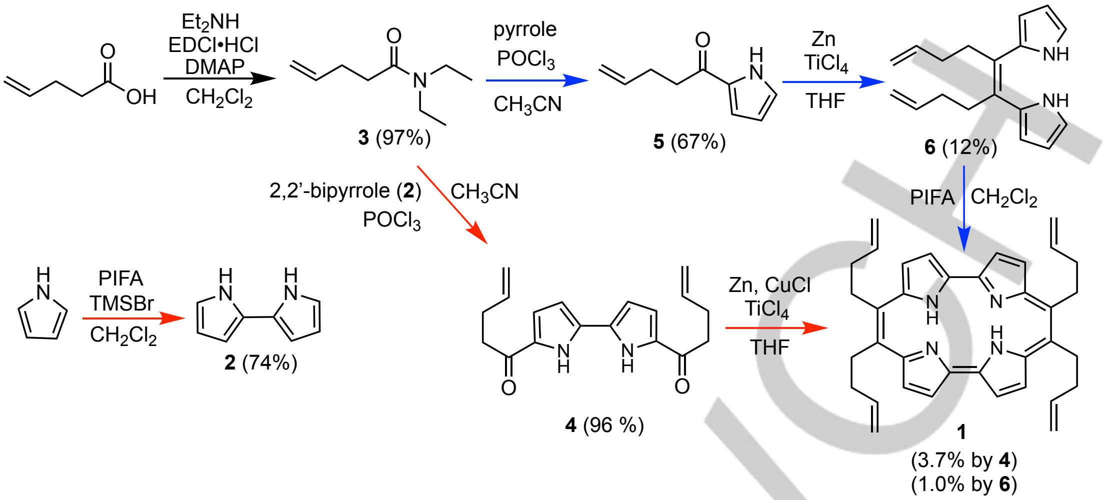

Figure 2. Synthesis of **1** by Method A (red arrow) and Method B (blue arrow).

investigate whether the interesting photoluminescence properties of *meso*-tetraalkylsubstituted porphycenes would be attained by fixing them to the polymer matrix. To accomplish this, we designed *meso*-tetrakis(3-butenyl)porphycene (**1**), in which the *meso*-alkyl moieties were modified with terminal olefins (Figure 1). We selected the olefin group as reactive site because terminal olefins are known to react with the Si–H bonds of polydimethylsiloxanes by hydrosilylation reaction in the presence of a platinum catalyst. In this study, we demonstrate the synthesis of **1** by two strategies, i.e., Method A and Method B (Figure 2). Then, we describe the preparation of porphycene–polydimethylsiloxane (PDMS) hybrids using the Pt-catalyzed hydrosilylation reaction, and the photoluminescence properties of the hybrids are investigated (Figure 4). The novelty of this work can be summarized as follows: a) so far, there is no study comparing these two synthetic strategies (Methods A and B) for the preparation of porphycene derivatives; and b) the incorporation of porphycene derivatives into polymeric materials is still rare, with the existing examples being restricted to porphycene–DNA[34], porphycene–protein[35], and porphycene–nanoparticle conjugates.[35]

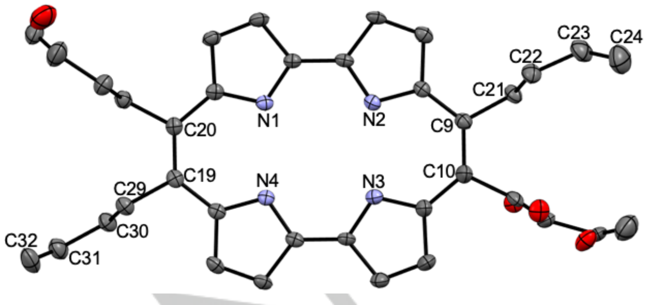

Figure 3. Crystal structure of **1** at 123 K. Hydrogen atoms are omitted for clarity. The thermal ellipsoid is drawn at 30% probability. Color code: N, light blue; C, gray; disordered C, red. Selected bond distances (Å): N1–N2, 2.899(4); N2–N3, 2.542(4); N3–N4, 2.909(4); N1–N4, 2.550(4); C9–C21, 1.526(5); C21–C22, 1.528(5); C22–C23, 1.481(6); C23–C24, 1.222(6); C19–C29, 1.537(5); C29–C30, 1.552(5); C30–C31, 1.503(6); C31–C32, 1.293(7).

Results and Discussion

As shown in Figure 2, we prepared compound **1** by two synthetic approaches. Method A is based on the McMurry reaction of compound **4**, and Method B consists of the oxidative macrocyclization of compound **6**. Method A was performed as follows. According to previously reported procedures, 2,2′-bipyrrole (**2**) was obtained in a yield of 74% by oxidative coupling of pyrrole using [bis(trifluoroacetoxy)iodo]benzene (PIFA) and trimethylsilyl bromide (TMSBr) in dry CH_2Cl_2.[36] Compound **3** was subsequently obtained in 97% yield by condensation of 4-pentenoic acid and diethylamine (Et_2NH) in the presence of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) and 4-dimethylaminopyridine (DMAP) in dry CH_2Cl_2. Then, compound **4** was obtained in a yield of 96% using the Vilsmeier–Haack reaction of **2** and **3** in the presence of $POCl_3$ in dry CH_3CN. Finally, compound **1** was successfully obtained in 3.7% yield by the conventional McMurry reaction of **4**. Meanwhile, the synthesis of **1** by Method B was carried out as described as follows: Compound **5** was obtained in 67% yield via the Vilsmeier–Haack reaction of **3** and pyrrole in the presence of $POCl_3$ in dry CH_3CN.[23] Then, compound **6** was obtained in 12% yield by subjecting **5** to the McMurry reaction. Finally, compound **1** was obtained in a yield of 1.0% by oxidative coupling of **6** using PIFA in CH_2Cl_2.

The total yields of **1** were 2.5% with Method A and 0.08% using Method B, in both cases starting from commercially available reagents. The relatively new synthetic Method B requires the crucial isolation of *Z*-dialkyldipyrroethene (**6**) from the *E*/*Z*-mixture after the McMurry coupling of compound **5**, which results in low yields. We recently found that it is possible to synthesize *meso*-tetraarylporphycenes using a *E*/*Z*-mixture of diaryldipyrroethene with *p*-TSA as an acid catalyst;[6] however,

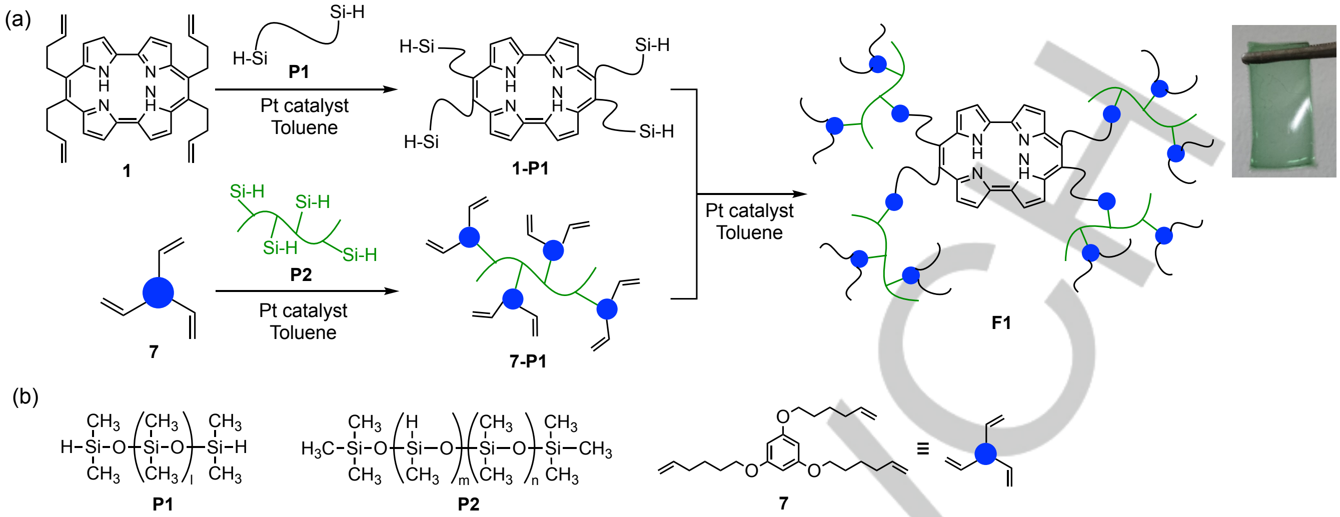

Figure 4. (a) Schematic representation of the preparation of **F1** film. The inset shows a photograph of **F1**. (b) Chemical structures of **P1**, **P2**, and **7**.

this approach was not applicable in the case of *meso*-tetraalkylporphycene derivatives.[5] Therefore, Method A is more appropriate for the synthesis of the target compound **1**. New compounds **1** and **3**–**6** were characterized using ^{1}H NMR, ^{13}C NMR, and HI-MS (Figures S2–S11). The stretching vibration of the terminal olefin groups of **1** was observed at 1638 cm^{-1} in the IR spectrum (Figure S12). Compound **1** was also subjected to X-ray analysis, and the corresponding single-crystal structure is depicted in Figure 3. As can be seen, the four nitrogen atoms are distributed in a near rectangular fashion with N1•••N2 and N3•••N4 distances of 2.899(4) and 2.909(4) Å and N1•••N4 and N2•••N3 distances of 2.550(4) and 2.542(4) Å, respectively. The packing modes of the butenyl chain of **1** are disordered at 10- and 20-position and ordered at 9- and 19-position in the crystal structure. The C31•••C32 and C23•••C24 distances are 1.293(7) and 1.222(6) Å, respectively. Figure S13 displays the UV–vis absorption spectrum of **1**, which exhibits similar properties to those of tetramethylporphycene (TMPc).[5] Thus, **1** showed extremely weak photoluminescence behavior with a quantum yield of 0.18%, 0.08%, 0.13%, and 0.33% in THF, CH_3CN, hexane, and DMSO, respectively (Table S2). These values are similar to those of **TMPc** and **TPPc** in the corresponding solutions.[31]

Next, a hybrid material of compound **1** and PDMS was prepared according to a published method.[37] We chose PDMS as polymeric matrix because its transparency facilitates the evaluation of the optical properties of incorporated **1**. Compound **1** was readily introduced into the PDMS networks through hydrosilylation of its four terminal olefin moieties. As can be seen in Figure 4, **P1** is a hydride-terminated polydimethylsiloxane (M_n, 6000; *d*, 0.97; viscosity, 100 cSt; *n*, 1.403), and **P2** is a copolymer of dimethylsiloxane and methylhydrosiloxane (M_n, 1900–2000; methylhydrosiloxane, 15–18 mol%; *d*, 0.97; viscosity, 25–35 cSt; *n*, 1.400). First, an excess amount of **P1** (350 mg, 140 μmol of SiH units) was reacted with **1** (66 nmol) in the presence of Karstedt's catalyst (6.5 μL) in toluene (750 μL) under N_2 atmosphere, and the solution was stirred for 1 h at room temperature. Then, a mixture of **P2** (21 mg, 40 μmol of SiH units), a 0.16 M toluene solution of **6** (500 μL), and Karstedt's catalyst (5.0 μL) was added to the reaction mixture. The resultant mixture was stirred several seconds and transferred onto a Teflon substrate (20 mm × 40 mm), and an elastomeric film (**F1**) was obtained by a crosslinking hydrosilylation reaction under gradual evaporation of toluene at room temperature overnight. For comparative purposes, a film without reactive sites (**F2**) prepared

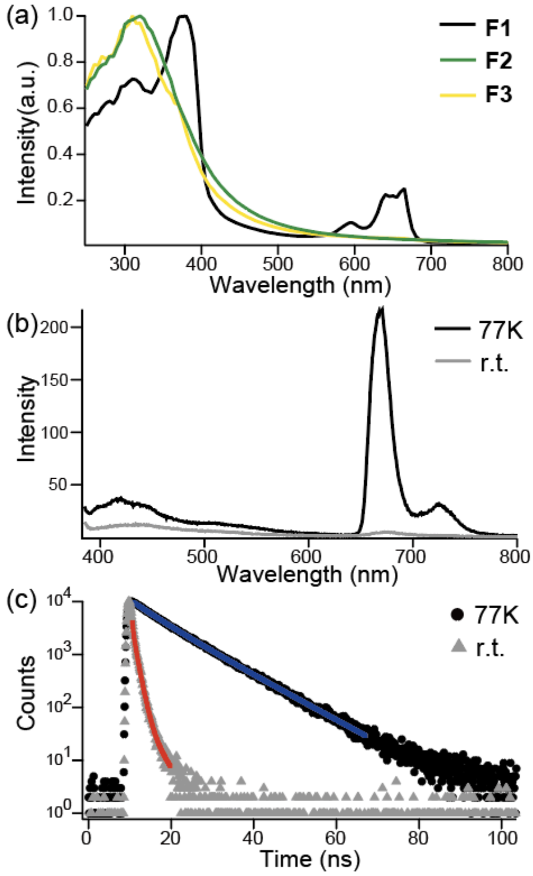

Figure 5. (a) Diffuse reflectance spectra of **F1**–**F3**. (b) Emission spectra of **F1** at r.t. and 77 K. Excitation at 380 nm. (c) Emission decay curves of **F1** at r.t. and 77 K.

under the same conditions using **TMPc** in place of **1** and a film (**F3**) obtained in the absence of porphycene were also examined. The obtained films (**F1**–**F3**) were ca. 20 mm long, 10 mm wide, and 1 mm thick and were anchored with tweezers. Figure S14 shows the photographs of the prepolymer toluene solution and the obtained films (**F1**–**F3**). Under the synthetic condition of **F1**, the blue–green color derived from porphycene was maintained before and after the film formation. On the other hand, under the synthetic condition of **F2**, the blue–green prepolymer solution became brown after the film formation. The films **F1** and **F2** were immersed in toluene overnight to confirm that the porphycene was covalently immobilized in the polymer matrix (Figure S15). No dissolution of porphycene was observed in **F1**, whereas dissolution of porphycene occurred in **F2**. It can be concluded that **1** was covalently immobilized in the PDMS polymer matrix in **F1**. On the other hand, **TMPc** was not hybridized with PDMS and aggregated in the PDMS polymer matrix due to their low compatibility.

Figure 5 shows the optical properties of the **F1**–**F3** films. The UV–vis diffuse reflectance spectra of the films were obtained using an integrating sphere. The typical Soret band and Q band of porphycene were observed in the spectrum of **F1**, which was similar to that of **1** in solution. This indicates that **1** was homogeneously dispersed in the elastomeric PDMS film matrix. The emission spectrum of **F1** excited at 380 nm showed a red emission at a λ_{max} of 670 nm. The quantum yield and the average lifetime at room temperature were 0.4% and 1.2 ns, respectively (Table 5(c) and Table S3). Interestingly, the emission spectrum of **F1** in liquid nitrogen (77 K) showed a drastic increase of emission intensity. In this condition, the quantum yield and the average lifetime were 6.7% and 9.4 ns, respectively. These results suggest that the hybridization of *meso*-tetraalkylporphycene **1** with the PDMS matrix suppressed the tautomerization-induced excited state quenching of porphycene. Meanwhile, the diffuse reflectance spectrum of **F2** was similar to that of **F3**, showing the lack of a visible absorption derived from porphycene.

Conclusions

In conclusion, we have demonstrated the synthesis of a *meso*-tetraalkylporphycene **1** bearing terminal olefin moieties as reactive sites following two synthetic strategies, and we found that the desired product could be successfully synthesized by both methods. A PDMS hybrid material was successfully prepared via the platinum-catalyzed hydrosilylation reaction between the olefin groups of the porphycene and the Si–H bonds of polydimethylsiloxane. An increase in photoluminescence intensity and lifetime of the *meso*-tetraalkylporphycene was observed in the film owing to the suppression of excited state deactivation. These results pave the way for the development of hybrid materials with potential applications as optical materials and solid-state catalysts via the post-modification of porphycene derivatives.

Experimental Section

Materials and chemicals. A hydride-terminated polydimethylsiloxane **P1** and a copolymer of dimethylsiloxane **P2** were purchased from GELEST, Inc. Platinum (0)-(1,1,3,3-tetramethyl-1,3-divinyldisiloxane) complex in xylene (Karstedt's catalyst) was purchased from Sigma-Aldrich. All other reagents and solvents were purchased from TCI, Sigma-Aldrich, Kanto Chemical or FUJIFILM Wako Chemicals and used as received. **TMPc** was prepared according to the established method.[5]

Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded by using Bruker Avance 500 NMR spectrometer. Chemical Shifts were referenced against tetramethylsilane or the residual solvent peak as an internal standard. UV-vis diffuse reflectance measurements were recorded using a JASCO V-670 spectrometer (JASCO) with an integration sphere attachment. The HRMS (FAB-MS) were performed with a JEOL JMS-700 instrument. IR spectra were recorded from dry powder spread over KBr pellets and by using a JASCO FT/IT-460 plus instrument. UV/Vis absorption spectra were recorded by using a Hitachi U-3310 spectrophotometer. Fluorescence excitation and emission spectra were collected at room temperature on a Hitachi F-7000 fluorescence spectrometer. The absolute photoluminescence quantum yields (Φ_{PL}) were determined using absolute PL quantum yields measurement system C9920-02 or C13534-23 (Hamamatsu photonics). Time-resolved photoluminescence lifetimes were carried out by using time-correlated single photon counting lifetime spectroscopy system, Quantaurus-Tau C11367-02 (Hamamatsu photonics). The decay constants and fitting parameters for transient decays were determined using the embedded software of Quantaurus-Tau.

X-ray crystal structural analysis. The crystal (**1**) was mounted on a loop. Data from X-ray diffraction were collected under 123 by a Rigaku XtaLAB mini CCD diffractometer equipped with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Collected data were integrated, corrected, and scaled using the program CrysAlisPro.[38] The structures were refined using SHELXT (Sheldrick, 2015)[39] Intrinsic Phasing and SHELXL (Sheldrick, 2015).[40] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and included in the structure factor calculation but were not refined. The program Olex2 was used as a graphical interface.[41] The crystallographic data of **1** is listed in Tables S1, and their CCDC number is 1944912, respectively. The data have been deposited with the Cambridge Crystallographic Data Centre. The data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

Synthesis of *N,N*-diethyl-4-pentenamide (3). 4-Pentenoic acid (3.0 mL, 30 mmol) and diethylamine (3.6 mL, 36 mmol) were added to a two-necked flask containing EDCI•HCl (6.9 g, 36 mmol), DMAP (4.5 g, 36 mmol) and dry dichloromethane (150 mL) under N_2. The solution was stirred for 22 h at room temperature. The reaction was quenched with 10% aqueous citric acid. The mixture was extracted three times with dichloromethane. The organic layer was dried over Na_2SO_4. The solvents were removed under reduced pressure, the crude product was purified using silica-gel column chromatography (hexane/AcOEt = 2/1) to yield **3** as colorless oil (4.5 g, 97%).^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.96-5.83 (m, 1H), 5.08 (d, *J* = 17.0 Hz, 1H), 5.00 (d, *J* = 10.1 Hz, 1H), 3.39 (q, *J* = 7.2 Hz, 2H), 3.32 (q, *J* = 7.0 Hz, 2H), 2.46-2.36 (m, 4H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.0, 137.5, 114.7, 41.7, 39.8, 32.2, 29.2, 14.1, 12.8. HRMS (FAB, positive): m/z calcd (%) for $C_9H_{18}NO$ $[M+H]^+$ 156.1388; found for 156.1370.

Synthesis of 5,5'-bis(4-pentenoyl)-2,2'-bipyrrole (4). $POCl_3$ (1.96 mL, 21.0 mmol) was added dropwise to a two-necked flask containing **3** (1.09 g, 7.00 mmol) at 0 °C under N_2. The solution was stirred for 10 min at 0 °C. Dry acetonitrile (4.67 mL) and **2** (308 mg, 2.33 mmol) were added into the reaction solution and then the mixture was refluxed for 8 h. The reaction was quenched with saturated aqueous $NaHCO_3$. The mixture was stirred at 90 ºC for 1 h. The precipitate was washed with water and dried under vacuum to yield **4** as a yellow solid (663 mg, 96%); m.p.: 258-260 ºC. ^{1}H NMR (500 MHz, DMSO-d$_6$): δ = 12.02 (brs, 2H), 7.07 (m, 2H), 6.75 (m, 2H), 5.91-5.82 (m, 2H), 5.08 (d, *J* = 17.0 Hz, 2H), 4.98 (d, *J* = 10.1 Hz, 2H), 2.85 (t, *J* = 7.4 Hz, 4H), 2.36 (m, 4H). ^{13}C NMR (125 MHz, DMSO-d$_6$): δ = 188.4, 137.6, 132.0, 130.2, 117.7, 115.1, 108.9, 36.2, 28.5. HRMS (FAB, positive): m/z calcd (%) for $C_{18}H_{20}N_2O_2$ $[M]^+$ 296.1525; found for 296.1528.

Synthesis of 9,10,19-20-tetrabutenyl porphycene (1) (Method A). $TiCl_4$ (9.5 g, 50 mmol) was added dropwise to dry THF (200 mL) suspension of activated Zn powder (6.54 g, 100 mmol) and CuCl (396 mg, 4.00 mmol) at 0 ºC under N_2. The reaction mixture was refluxed for 3 h and then **4** (593 mg, 2.00 mmol) in THF (200 mL) was added dropwise over 2.5 h at room temperature. The solution was refluxed for 16 h. The reaction was quenched with 10% aqueous K_2CO_3 (200 mL). The mixture was extracted three times with dichloromethane; the organic layer was washed twice with water and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the crude product was purified using silica-gel column chromatography (dichloromethane/hexane = 1/4), and then washed with methanol in solid state to yield **1** as a purple solid (19.2 mg, 3.7%); m.p.: 240-242 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.47 (d, *J* = 4.4 Hz, 4H), 9.22 (d, *J* = 4.7 Hz, 4H), 6.82 (brs, 2H), 6.42-6.23 (m, 4H), 5.44 (d, *J* = 17.1 Hz, 4H), 5.26 (d, *J* = 10.1 Hz, 4H), 4.65–4.46 (m, 8H), 3.20–3.07 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.4, 138.2, 134.5, 128.8, 127.8, 125.8, 115.2, 40.7, 35.7. HRMS (FAB, positive): m/z calcd for $C_{36}H_{38}N_4$ $[M]^+$ 526.3096; found for 526.3097. UV/Vis (CH_2Cl_2): λ_{max} (log ε, L mol^{-1} cm^{-1}) = 378 (5.17), 595 (3.19), 662 (4.60) nm.

Synthesis of 2-(4-penten-1-one)pyrrole (5). $POCl_3$ (932 µL, 10 mmol) was added dropwise to a two-necked flask containing **3** (1.55 g, 10.0 mmol), at 0 ºC under N_2. The solution was stirred for 15 min at 0 ºC. Dry acetonitrile (3.6 mL) and pyrrole (694 mL, 10.0 mmol) were added and then the mixture was refluxed for 40 min. The solution was diluted with sodium acetate (4.18 g) in water (8.8 mL) and was refluxed for 30 min. The mixture was extracted three times with ethyl acetate; the organic layer was washed three times with water, and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the crude product was purified using silica-gel column chromatography (dichloromethane 100%) to yield **5** as a white solid (1.10 g, 74%); m.p.: 32-34 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.35 (brs, 1H), 7.02 (m, 1H), 6.92 (m, 1H), 6.28 (m, 1H), 5.96-5.83 (m, 1H), 5.10 (d, *J* = 17.0 Hz, 1H), 5.01 (d, *J* = 10.1 Hz, 1H), 2.87 (t, *J* = 7.6 Hz, 2H), 2.55-2.45 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.2, 137.3, 131.8, 125.0, 116.5, 115.1, 110.4, 37.0, 28.9. HRMS (FAB, positive): m/z calcd (%) for $C_9H_{12}NO$ $[M+H]^+$ 150.0919; found for 150.0879.

Synthesis of (*Z*)-bis(3butenyl)dipyrroethene (6). $TiCl_4$ (2.79 g, 20.0mmol) was added dropwise to dry THF (40 mL) suspension of activated Zn powder (2.62 g, 40.0 mmol), at 0 ºC under N_2. The reaction mixture was refluxed for 3 h and then **5** (746 mg, 5.00 mmol) in THF (10 mL) was added dropwise. The solution was refluxed for 5 h. The reaction was quenched with 1 M aqueous $NaHCO_3$ solution. The mixture was extracted with diethyl ether; the organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the crude product was purified using silica-gel column chromatography (dichloromethane/hexane = 1/2) to yield **6** as a flesh-colored oil (79 mg, 12%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67 (brs, 2H), 6.58 (m, 2H), 6.17 (m, 4H), 5.91-5.80 (m, 2H), 5.04 (d, *J* = 17.0 Hz, 2H), 4.98 (d, *J* = 10.1 Hz, 2H), 2.55 (t, *J* = 7.9 Hz, 4H), 2.24-2.15 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.3, 131.9, 127.5, 118.1, 114.7, 108.5, 107.9, 33.4, 33.0. HRMS (FAB, positive): m/z calcd for $C_{18}H_{22}N_2$ $[M]^+$ 266.1783; found for 266.1782.

Synthesis of 9,10,19-20-tetrabutenyl porphycene (1) (Method B). PIFA (159 mg, 0.37 mmol) in dry dichloromethane (15 mL) was quickly added to a stirred solution of **6** (98 mg, 0.37 mmol) in dry dichloromethane (37 mL) in an ice bath. The solution was stirred for 1.5 h and the reaction was quenched with silica gel 60N (37 mL) and methanol (37 mL). The mixture was dried carefully under reduced pressure. The resultant silica-gel mixture was charged on fresh silica gel 60N and eluted with dichloromethane to give a purple solid. Silica-gel column chromatography (dichloromethane 100%), and then washed with methanol in solid state to yield **1** as a purple solid (1.0 mg, 1.0%).

Synthesis of 1,3,5-tris(5-hexenyloxyl)benzene (7). A mixture of phloroglucinol (472 mg, 3.74 mmol) and potassium carbonate (6.20 g, 44.9 mmol) in dry *N,N*-dimethylformamide (15 mL) was stirred at 70 ºC for 2 h, then, 6-bromo-1-hexene (2.00 mL, 15.0 mmol) was added. The reaction mixture was stirred at 70 ºC for further 6 h. After cooling to room temperature, the reaction mixture was diluted in ether, washed with water, and the organic layer was dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the crude product was purified using silica-gel column chromatography (hexane/chloroform = 7/3) to yield **7** as a colorless oil (628 mg, 45%). The spectral data were identical with the reported data.[37]

Synthesis of Film 1. Karstedt's catalyst (6.5 µL) and toluene (750 µL) were added to a two-necked flask containing **1** (65.8 nmol) and **P1** (350 mg, 140 µmol of SiH units) under N_2. The solution was stirred for 1 h at room temperature. A mixture of **P2** (21 mg, 40 µmol of SiH units), a toluene solution containing **6** of 0.16 M (500 µL) and Karstedt's catalyst (5.0 µL) was added to the reaction mixture. The mixture was stirred by pipetting and the resultant solution was transferred onto a Teflon substrate (20 mm × 40 mm) and the solvent was evaporated overnight under ambient conditions to give **Film 1**.

Synthesis of Film 2. Karstedt's catalyst (6.5 µL) and toluene (750 µL) were added to a two-necked flask containing TMPc (65.8 nmol) and **P1** (350 mg, 140 µmol of SiH units) under N_2. The solution was stirred for 1 h at room temperature. A mixture of **P2** (21 mg, 40 µmol of SiH units), a toluene solution containing **6** of 0.16 M (500 µL) and Karstedt's catalyst (5.0 µL) was added to the reaction mixture. The mixture was stirred by pipetting and the resultant solution was transferred onto a Teflon substrate (20 mm × 40 mm) and the solvent was evaporated overnight under ambient conditions to give **Film 2.**

Synthesis of Film 3. Karstedt's catalyst (6.5 µL) and toluene (750 µL) were added to a two-necked flask containing **P1** (350 mg, 140 µmol of SiH units) under N_2. The solution was stirred for 1 h at room temperature. A mixture of **P2** (21 mg, 40 µmol of SiH units), a toluene solution containing **6** of 0.16 M (500 µL) and Karstedt's catalyst (5.0 µL) was added to the reaction mixture. The mixture was stirred by pipetting and the resultant solution was transferred onto a Teflon substrate (20 mm × 40 mm) and the solvent was evaporated overnight under ambient conditions to give **Film 3**.

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Keywords: porphycenes • porphyrinoids • organic-inorganic hybrids • poly(dimethyl)siloxane • hydrosilylation

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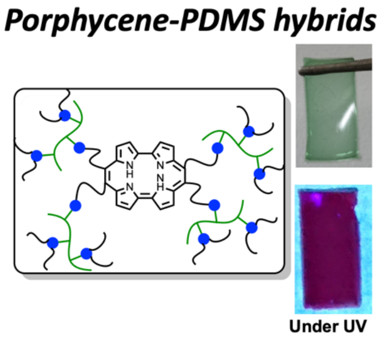
FULL PAPER

Meso-tetrakis(3-butenyl)porphycene is synthesized following two synthetic strategies and is successfully hybridized with polydimethylsiloxane by Pt-catalyzed hydrosilylation reaction. The hybrid film shows a weak red emission with a quantum yield of 0.4% at room temperature, and the emission intensity drastically increases at 77 K, reaching a quantum yield of 6.7%.



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Synthesis of a *meso*-tetraalkylporphycene bearing reactive sites: Toward porphycene–polydimethylsiloxane hybrids with enhanced photophysical properties