

A novel phthalocyanine with two axial fullerene substituents

Kun Nam Kim,^a Chan Soo Choi^b and Kwang-Yol Kay^{a,*}

^aDepartment of Molecular Science and Technology, Ajou University, Suwon 443-749, South Korea

^bDepartment of Applied Chemistry, Daejeon University, Daejeon 300-716, South Korea

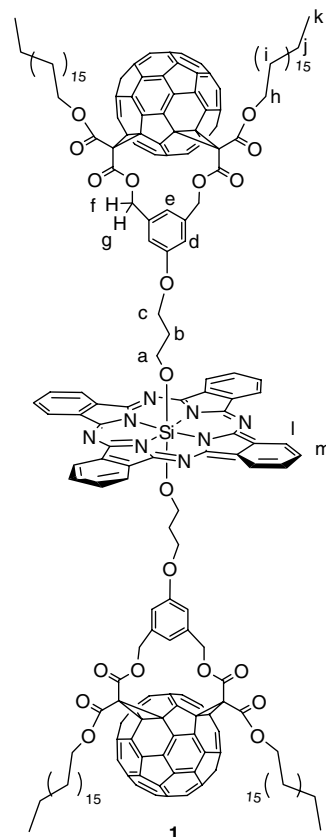
Received 27 June 2005; revised 6 August 2005; accepted 10 August 2005

Abstract—A silicon phthalocyanine with two axial fullerene substituents was synthesized, and its electrochemical, absorption- and film-properties were characterized.

© 2005 Elsevier Ltd. All rights reserved.

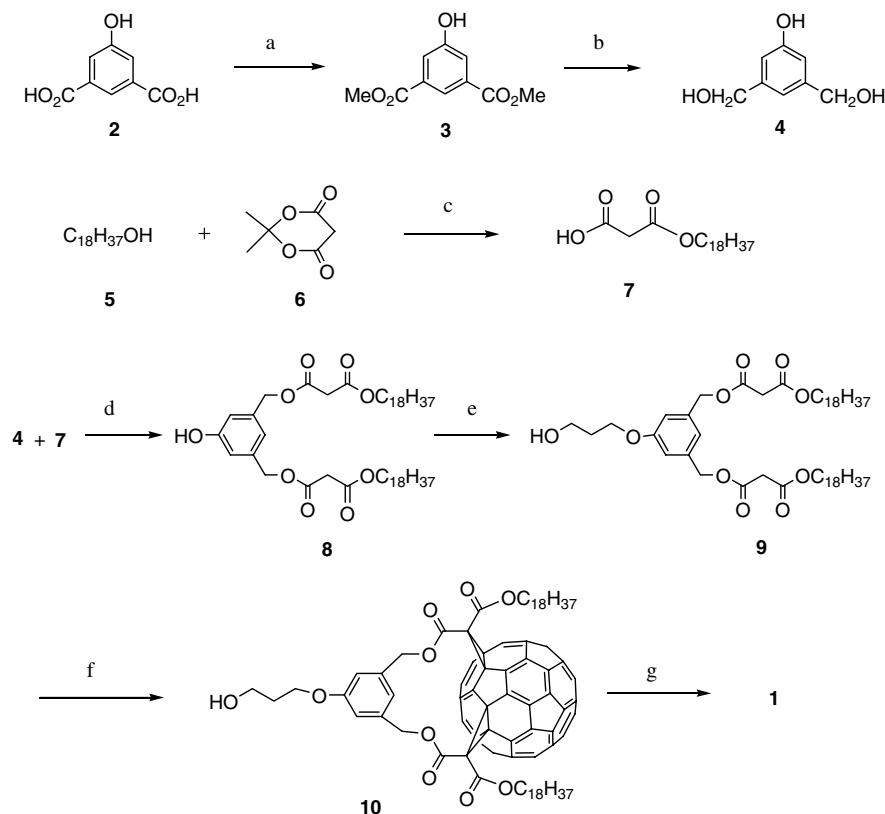
Phthalocyanines (Pcs) have long attracted enormous interest owing to their intriguing electrical, optical, photochemical and catalytic properties.¹ Among the various electro- and photoactive chromophores utilized for phthalocyanine chemistry,² C₆₀ has been proposed to be a versatile building block and a growing interest in fullerene-functionalized phthalocyanines is developing.¹ Recently asymmetrical metal phthalocyanines containing a single fullerene (C₆₀) substituent with rigid linkers at the periphery³ and another asymmetrical zinc phthalocyanine–C₆₀ hybrid with a flexible linker containing an azacrown subunit⁴ were synthesized to study intramolecular process such as electron transfer and energy transfer between Pc donor and C₆₀ acceptor. Additionally, supramolecular systems such as hydrogen bonded⁵ and aggregated⁶ Pc–C₆₀ dyads were reported for similar studies. However, no phthalocyanine with more than one fullerene substituent has been reported until now to our knowledge. On the other hand, McKeown and co-workers proved the glass-forming properties of axially substituted phthalocyanines with dendritic subunits, and such compounds are further known to produce glassy solids, which would allow the fabrication of the robust, nonscattering films for optical applications such as nonlinear optics and optical limiters.^{1,7} With respect to these aspects, the Pc **1** would also be a suitable compound to exploit the optical and electronic properties of the Pc macrocycle in solution as well as in solid state. In line with these aspects, we report herein the first synthe-

sis of the soluble silicon phthalocyanine **1** with two axial fullerene substituents by reaction between a bis-adduct of C₆₀ bearing an alcohol functionality and dichloro-(phthalocyaninato) silicon in the presence of sodium hydride.



Keywords: Si–phthalocyanine; Fullerene; Electrochemistry; Absorption spectrum; Glassy film.

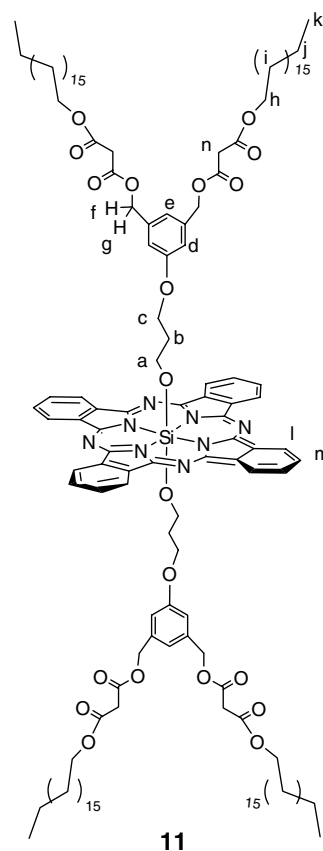
* Corresponding author. Tel.: +82 31 219 2602; fax: +82 31 219 1615; e-mail: kykay@ajou.ac.kr



Scheme 1. Synthesis of compound **1**. Reagents and conditions: (a) MeOH, H₂SO₄, reflux 24 h, 97%; (b) LAH, THF, reflux, 24 h, 85%; (c) 110–120 °C, 1 h, 93%; (d) DCC, DMAP, HOBT, THF, 3 h, 53%; (e) K₂CO₃, 18-crown-6, 3-bromo-1-propanol, acetone, reflux, 12 h, 72%; (f) C₆₀, I₂, DBU, toluene, rt, 24 h, 23%; (g) silicon phthalocyanine dichloride, NaH, toluene, reflux 10 h, 32%.

The Pc **1** has two symmetrical fullerene substituents axially to the Pc core, and this structural shape with bulky fullerene substituents may help to achieve the steric isolation of the Pc rings in the solid phase to diminish the intermolecular interactions, which usually cause to broaden and red shift the intense visible absorption band (the Q-band) due to the excitonic effects of the cofacial Pc rings. The Pc **1** was synthesized as depicted in Scheme 1.

Commercially available 5-hydroxy-isophthalic acid (**2**) was esterified to give diester **3** (97% yield) and subsequent reduction of **3** with LAH produced 3,5-bis(hydroxymethyl)-phenol (**4**) in a yield of 85%. Octadecanol (**5**) reacted with Meldrum's acid (**6**) to afford malonic acid mono-octadecyl ester (**7**) in 93% yield. Esterification of **4** with the mono-ester **7** of malonic acid in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC) yielded bis-malonate **8** (53% yield). Phenol group of bis-malonate **8** reacted with 3-bromo-1-propanol in the presence of K₂CO₃ and 18-crown-6 to give alcohol-functionalized derivative **9** (72% yield). The functionalization of C₆₀ was based on the highly regioselective Diederich reaction,⁸ which led to macrocyclic bis-adducts of C₆₀ through a macrocyclization reaction of the carbon sphere with bis-malonate derivatives in a double Bingel addition.⁹ Treatment of C₆₀ with **9**, iodine, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature afforded the bis-adduct **10** in 23% yield.¹⁰ The final reaction of bis-adduct **10** with commercially available



dichloro-Si-Pc went smoothly in the presence of NaH to produce **1** in 32% yield.¹⁰

The structure of **1** was confirmed by ¹H and ¹³C NMR spectroscopies and MALDI-TOF MS. The ¹H NMR spectrum is particularly informative, because the strong ring current of the Pc macrocycle helps to differentiate protons of similar type. ¹³C NMR spectrum showed a set of C₆₀ nucleus peaks (136–149 ppm), two carbonyl carbons (163 and 158 ppm), aromatic carbons (111–131 ppm) and aliphatic carbons (14–68 ppm). Further confirmation of the hybrid Pc–fullerene structure was obtained from the IR and UV/vis spectra, which were found to contain absorbances due to the Pc and fullerene fragments. Compound **1** is soluble in common aprotic solvents such as THF, toluene and chloroform but not in diethyl ether and hexane. To compare the physical properties such as spectroscopic, electrical and film properties with those of **1**, we also synthesized a Pc **11**, which contains the same axial substituents without C₆₀ moieties, by an analogous synthetic method.¹¹

To compare the detailed electrochemical behavior of compounds **1**, **10** and **11** have been used as model compounds as they lack either phthalocyanine (i.e., **10**) or fullerene (i.e., **11**) subunit. Compound **1** is found to have 13 redox reactions from the redox waves in a cyclic voltammogram. The data suggests that three of these reactions originate from the phthalocyanine moiety ($E_{1/2} = -0.74$ V, -1.24 V, $+1.10$ V), and the remaining reactions originate from the fullerene moiety. Comparisons were made with compounds **10** and **11**, which are phthalocyanine-free and fullerene-free, respectively (see Table 1); although the $E_{1/2}$ of -1.24 V presumably originated from phthalocyanine, the cyclic voltammogram depicts a shoulder peak on the fullerene peak at -1.31 V. These $E_{1/2}$ values coincide with the peak values of the differential pulse voltammogram (DPV) within the first decimal point.¹²

Table 1. Electrochemical properties of compounds, **1**, **10** and **11**

Compound	1	10	11
Negative potential region	−0.59(73)	−0.57(94)	
	−0.74(119)		−1.02 ^a
	−1.06(110)	−1.00(118)	
	−1.24		
	−1.31(210)	−1.35(85)	
	−1.59(169)	−1.59(118)	
	−1.80(119)	−1.78(105)	
	−2.12(133)	−2.08(109)	
	−2.37(96)	−2.39 ^b	
	−2.60(105)	−2.56(118)	
	−2.80(137)		
Positive potential region	1.10(60)		1.09 ^a
	1.30(146)		

Cyclic voltammetric measurements: glassy carbon working electrode, Pt wire counter electrode, Ag/Ag⁺ pseudo-reference electrode, degassed THF, 0.1 M Bu₄NClO₄ and a scan rate of 100 mV/s. Values for $E_{1/2}$ as $(E_{pa} + E_{pc})/2$ V and ΔE_{pm} V (in parentheses) are given.

^a Measured by DPV.

^b Irreversible.

Deschenaux and co-workers¹³ found that the curve suggests the presence of chemical reactions coupled to some of the redox processes. These chemical reactions are responsible for the presence of extra anodic peaks in the reverse scan. However, we did not find the chemical reactions from compounds **1**, **10** and **11** in that sense. Instead, we found that the $E_{1/2}$ of the first reduction of the phthalocyanine moiety in compound **1** was more anodic ($\Delta E = 280$ mV) than that of compound **11** (i.e., analogous fullerene-free materials). This observation is related to the strong electron-withdrawing effect of the two axial fullerene substituents, which could stabilize the first reduced state of the phthalocyanine. The $E_{1/2}$ values of the reductions of the fullerene moiety in compound **1** are not substantially shifted by the phthalocyanine moiety when compared with compound **10** (i.e., analogous phthalocyanine-free materials). According to the electrochemical curves of compound **1**, only two oxidation processes occur; the first one corresponds to the reversible exchange of one electron (with $E_{1/2} = 1.10$ V) attributed to the phthalocyanine moiety, and the second one corresponds to a partially reversible two-electron oxidation (with $E_{1/2} = 1.30$ V) situated on the fullerene moiety. Deschenaux and co-workers¹³ reported similar results from fullerene–ferrocene material. The redox potential for the first oxidation of the phthalocyanine moiety in compound **1** is almost the same as that of compound **11**. Nierengarten et al.¹⁴ found that the $E_{1/2}$ value of the first oxidation of the porphyrin moiety in a tetraphenylporphyrin with four fullerene subunits was significantly more anodic than *meso*-tetrakis (3,5-di-*tert*-butylphenyl) porphyrin as a model compound. They explained that their observation could be related to the substantial de-stabilization of the first oxidized state of the porphyrin moiety by the strong electron-withdrawing effect of the four fullerene subunits. They also described that solvation effects caused by the presence of the surrounding fullerene groups could also be the source of the observed shift in potential. In our case, although the redox properties of the phthalocyanine moiety of compound **1** are significantly influenced by the two fullerene subunits in the negative potential region, those of the fullerene moiety in the negative potential region and of the phthalocyanine in the positive potential region remain almost unchanged. Nierengarten et al.¹⁴ also found that the redox properties of the fullerene moiety seemed to remain unchanged by the porphyrin moiety in a tetraphenylporphyrin with four fullerene subunits. Again these results were deduced when compared with the model compounds, **10** and **11**. Based on our discussion for the molecule of compound **1**, we can deduce that the phthalocyanine moiety would be positively charged and the fullerene moiety would be negatively charged. This charge separation might cause significant solvation effects for the redox potentials to remain unchanged for the above moieties. This charge separation will also modify spectroscopic, electronic characteristics.

The UV/vis spectrum of compound **1** in CHCl₃ (Fig. 1) shows characteristic phthalocyanine absorption bands. A intense Q-band in the visible region of 675 nm was accompanied by more or less weak satellite bands at

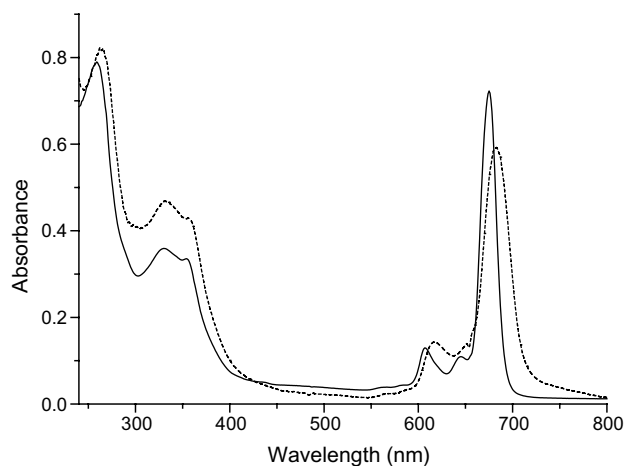


Figure 1. UV/vis spectra of **1** in CHCl_3 (—) and in spin-coated film (---).

Table 2. The UV/vis spectroscopic data of **1**

	λ_{max}^a (nm)	λ_{max}^b (nm)	$\Delta\lambda_{\text{max}}^c$ (nm)	ΔW^d (nm)
1	675	683	8	8
11	676	679	3	8

^a In CHCl_3 .

^b In spin-coated film.

^c λ_{max} (film) – λ_{max} (solution).

^d Width of peak at half height (film) – width of peak at half height (solution).

563, 580, 607 and 645 nm. In the ultraviolet region of 354 nm, the characteristic Soret or B-band was also observed. The remaining weak band at 430 nm was found to contain absorbances due to the fullerene fragment. As expected, the UV/vis spectrum of **1** is practically same as the sum of the peaks of both **10** (phthalocyanine-free)¹⁰ and **11** (fullerene-free).¹¹ The UV/vis spectrum of spin-coated thin film of compound **1** also illustrates the extent to which the axial fullerene substituents suppress cofacial intermolecular excitonic interactions. Only relatively weak edge-to-edge exciton interactions are present in the solid film of **1**, as indicated by the relatively small red shift ($\Delta\lambda_{\text{max}}$) of the Q-band (8 nm) as compared to its position in the solution absorption spectrum. Broadening (ΔW) of the Q-band due to excitonic effects is also small (8 nm) (Table 2).

These values show that this spin-coated film resembles a solid solution. Interestingly, these results are also in good agreement to the previously reported results of the Pcs, such as McKeown's phthalocyanine with dendritic substituents where similar small changes have been observed.⁷ Atomic force microscopy (AFM) studies indicate that spin-coating from toluene results in smooth films. Polarized optical microscopy suggests that the film derived from **1** is uniform and isotropic (nonbirefringent). The Pc **1** displays a distinct glass transition on cooling from the melt ($T_g = 140.5^\circ\text{C}$). Therefore, the film can also be readily fabricated by melt processing. This easily processable Pc **1** is a suitable material for optical studies, such as nonlinear optics and optical

limiter which are now under investigation. In addition, we are also working on the photo-induced electron transfer studies.

Acknowledgement

K.-Y. Kay would like to acknowledge the Brain Korea 21 program of the Ministry of Education for financial support.

References and notes

- McKeown, N. B. *Phthalocyanine Materials: Synthesis, Structure and Function*; Cambridge University Press: Cambridge, 1998.
- Phthalocyanines-Properties and Applications*; Leznoff, C. C., Lever, A. B. F., Eds.; VCH: New York, 1989; Vol. 1, 1993; Vols. 2–3, 1996; Vol. 4.
- (a) Linßen, T. G.; Durr, K.; Hanack, M.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 103; (b) Durr, K.; Fiedler, S.; Linßen, T. G.; Hirsch, A.; Hanack, M. *Chem. Ber.* **1997**, *130*, 1375; (c) Gouloumis, A.; Liu, S.-G.; Sastre, A.; Vazquez, P.; Echegoyen, L.; Torres, T. *Chem. Eur. J.* **2000**, *6*, 3600; (d) Guldi, D. M.; Gouloumis, A.; Vazquez, P.; Torres, T. *Chem. Commun.* **2002**, 2056; (e) Loi, M. A.; Denk, P.; Hoppe, H.; Neugebauer, H.; Winder, C.; Meissner, D.; Bräbe, C.; Sariciftci, N. S.; Gouloumis, A.; Vazquez, P.; Torres, T. *J. Mater. Chem.* **2003**, *13*, 700; (f) Guldi, D. M.; Zilbermann, I.; Gouloumis, A.; Vazquez, P.; Torres, T. *J. Phys. Chem. B* **2004**, *108*, 18485.
- Sastre, A.; Gouloumis, A.; Vazquez, P.; Torres, T.; Doan, V.; Schwartz, B. J.; Wudl, F.; Echegoyen, L.; Rivera, J. *Org. Lett.* **1999**, *1*, 1807.
- Martinez-Diaz, M. V.; Fender, N. S.; Rodriguez-Morgade, M. S.; Gomez-Lopez, M.; Diederich, F.; Echegoyen, L.; Stoddart, J. F.; Torres, T. *J. Mater. Chem.* **2002**, *12*, 2095.
- Guldi, D. M.; Gouloumis, A.; Vazquez, P.; Torres, T.; Georgakilas, V.; Prato, M. *J. Am. Chem. Soc.* **2005**, *127*, 5811.
- (a) Brewis, M.; Clarkson, G. J.; Helliwell, M.; Holder, A. M.; McKeown, N. B. *Chem. Eur. J.* **2000**, *6*, 4630; (b) Hassan, B. M.; Li, H.; McKeown, N. B. *J. Mater. Chem.* **2000**, *10*, 39; (c) McKeown, N. B. *Adv. Mater.* **1999**, *11*, 67.
- (a) Nierengarten, J.-F.; Gramlich, V.; Cardullo, F.; Diederich, F. *Angew. Chem.* **1996**, *108*, 2242; *Angew. Chem., Int. Ed.* **1996**, *35*, 2101; (b) Nierengarten, J.-F.; Herrmann, A.; Tykwinski, R. R.; Ruttimann, M.; Diederich, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Helv. Chim. Acta* **1997**, *80*, 293; (c) Nierengarten, J.-F.; Habicher, T.; Kessinger, R.; Cardullo, F.; Diederich, F.; Gramlich, V.; Gisselbrecht, J.-P.; Boudon, C.; Gross, M. *Helv. Chim. Acta* **1997**, *80*, 2238.
- Bingel, C. *Chem. Ber.* **1993**, *126*, 1957.
- Synthesis of **10**: Fullerene (0.29 g, 0.40 mmol) was dissolved in dry toluene (250 mL), and to this solution were added **9** (0.35 g, 0.40 mmol), I_2 (0.13 g, 1.00 mmol), and DBU (0.3 mL, 2.00 mmol) under nitrogen atmosphere and stirred at room temperature for 24 h. After evaporation of the solvent, the crude product was purified by column chromatographic separation (silica gel, toluene and then $\text{MeOH}-\text{CHCl}_3 = 1:50$). Compound **10**: Dark brown solid (23.4%); mp: 67°C ; ^1H NMR (500 MHz, CDCl_3): $\delta = 0.85\text{--}0.92$ (t, 6H, CH_3), $1.23\text{--}1.36$ (s, 60H, CH_2), $1.69\text{--}1.72$ (m, 4H, CH_2), 2.08 (m, 2H, CH_2), 3.88 (t, 2H,

CH₂), 4.17 (t, 2H, CH₂), 4.35 (t, 4H, CH₂), 5.13 (d, 2H, CH₂), 5.78 (d, 2H, CH₂), 6.81 (s, 2H, ArH), 7.19 (s, 1H, ArH). ¹³C NMR (CDCl₃): δ = 163.05, 159.07, 148.87, 147.72, 147.68, 147.51, 146.34, 146.26, 145.95, 145.83, 145.57, 145.39, 145.23, 144.77, 144.57, 144.45, 144.37, 144.16, 143.95, 143.77, 143.47, 143.25, 142.49, 141.46, 141.22, 140.18, 138.32, 137.83, 136.40, 136.02, 134.92, 115.40, 112.50, 70.86, 67.46, 67.43, 67.15, 65.83, 60.33, 49.49, 32.11, 29.91, 29.86, 29.78, 29.76, 29.55, 29.34, 28.65, 26.05, 22.88, 14.33. IR (KBr): ν = 3433, 2928, 2854, 1751, 1607, 1464, 1238, 1203, 1115, 1060 cm⁻¹. UV/vis (CHCl₃, 10⁻⁵ M): λ_{max} = 262, 321, 376, 438 nm.

Synthesis of **1**: Sodium hydride (7.80 mg, 0.33 mmol) was added to a mixture of dichloro(phthalocyaninato) silicon (28.5 mg, 0.05 mmol) and **10** (150 mg, 0.09 mmol) in dry toluene (2 mL). After refluxing under nitrogen for 10 h, the reaction mixture was cooled to room temperature, and then the solvent was evaporated to dryness under reduced pressure. The crude product was washed with water twice and was purified by two successive column chromatographic separations (silica gel, CH₃CN–CHCl₃ = 1:60). Dark green glassy product (32.4%); mp: 172 °C.

¹H NMR (600 MHz, CDCl₃): δ = -1.93 (t, 4H, aCH₂), -0.97 (m, 4H, bCH₂), 0.85–0.92 (t, 12H, kCH₃), 1.08 (t, 4H, cCH₂), 1.19–1.38 (m, 120H, iCH₂), 1.74–1.77 (m, 8H, jCH₂), 4.42 (t, 8H, hCH₂), 4.98 (d, 4H, gCH₂), 5.65 (s, 4H, dArH), 5.83 (d, 4H, fCH₂), 6.95 (s, 2H, eArH), 8.33–8.36 (m, 8H, ICH of Si–Pc), 9.55–9.59 (m, 8H, mCH of Si–Pc). ¹³C NMR (CDCl₃): δ = 163.28, 158.45, 149.47, 149.32, 149.14, 147.82, 146.57, 146.39, 146.06, 145.95, 145.49, 145.36, 144.90, 144.71, 144.48, 144.33, 144.10, 143.89, 143.61, 143.42, 142.63, 141.59, 141.35, 140.34, 137.36,

136.49, 136.09, 131.07, 123.85, 123.70, 111.37, 67.60, 67.36, 32.15, 29.94, 29.86, 29.60, 29.45, 28.79, 26.17, 26.10, 22.93, 14.37. IR (KBr): ν = 2917, 2847, 1751, 1623, 1464, 1239, 1208, 1122, 1080 cm⁻¹. MALDI-TOF MS: m/z : 3751 ($m + 1$), 2145, 1870, 1806, 1096, 812, 809, 765, 717. UV/vis (CHCl₃, 10⁻⁵ M): λ_{max} = 259, 330, 354, 430, 563, 580, 607, 645, 675 nm.

11. Phthalocyanine **11** was synthesized by the similar method for the synthesis of **1** in Scheme 1.

¹H NMR (200 MHz, CDCl₃): δ = -1.95 (t, 4H, aCH₂), -0.97 (m, 4H, bCH₂), 0.65 (t, 12H, kCH₃), 0.82–1.90 (m, 132H, i,jCH₂ and cCH₂), 3.50 (s, 8H, nCH₂), 4.15 (t, 8H, hCH₂), 4.62 (s, 4H, dArH), 5.05 (m, 8H, f,gCH₂), 4.75 (s, 2H, eArH), 8.22–8.45 (m, 8H, ICH of Si–Pc), 9.55–9.78 (m, 8H, mCH of Si–Pc). IR (KBr): ν = 2962, 2869, 1743, 1635, 1465, 1326, 1209, 1141, 1079 cm⁻¹. UV/vis (CHCl₃, 10⁻⁵ M): λ_{max} = 259, 277, 358, 381, 563, 580, 610, 647, 676 nm.

12. Differential pulse voltammograms of compound **1** were obtained under the following conditions: 80 mV pulse, 50 ms pulse width, 100 ms periods, and a scan rate of 20 mV/s. The remaining conditions are the same as that of CV measurements. For compound **1**: -0.55, -0.72, -1.01, -1.24, -1.33, -1.57, -1.79, -2.08, -2.37, -2.57, -2.77, +1.06, and +1.34 V. For compound **10**: -0.54, -0.98, -1.32, -1.55, -1.76, -2.05, and -2.55 V. For compound **11**: -1.02 and +1.09 V.
13. Carano, M.; Chuard, T.; Deschennaux, R.; Even, M.; Marcaccio, M.; Paolucci, F.; Prato, M.; Roffia, S. *J. Mater. Chem.* **2002**, *12*, 829.
14. Nierengarten, J.-F.; Schall, C.; Icou, J.-F. *Angew. Chem., Int. Ed.* **1998**, *37*, 1934.