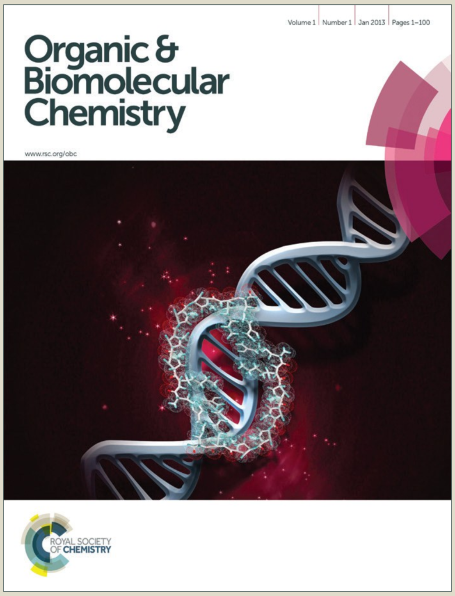
Organic & Biomolecular Chemistry

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/obc

Journal Name RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Effect of cyano, ethynyl and ethylenedioxy groups on the photophysical properties of carbazole-based porphyrins

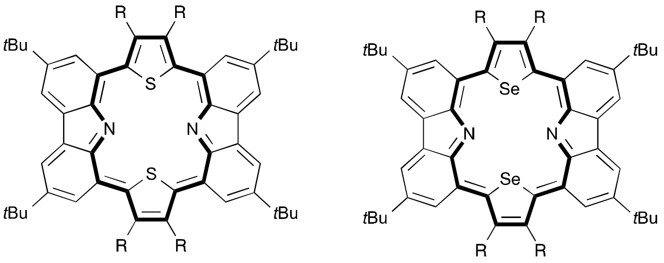
Chihiro Maeda,*[a,b] Kosuke Kurihara,[a] Motoki Masuda[a] and Naoki Yoshioka*[a]

Synthesis and photophysical properties of cyano and ethynyl substituted carbazole-based porphyrins were investigated. The introduction of ethynyl groups induced red shifts, while that of cyano groups induced blue shifts of their absorption bands, which was supported by MO calculations. Ethylenedioxy-appended porphyrins were also prepared via coupling reaction. The conjugated and electronic substituent effects on the photophysical properties of the carbazole-based porphyrins have been elucidated by both experimental results and calculations. Among these porphyrins, the ethylenedioxy-appended selenaporphyrin displayed the intensified and red-shifted absorption in the NIR region up to 1178 nm.

Introduction

The chemistry of porphyrins have been studied in light of photosynthesis, and also applications to photovoltaic cells, sensings, and catalyses.[1] Both peripheral and core modifications of porphyrin skeleton are intriguing because they can change porphyrin properties dramatically. In the former case, the electronic properties are effectively perturbed by the introduction of various substituents or by the fusion of additional aromatic rings to porphyrin periphery.[2–4] Addition of proper functional groups allows the construction of porphyrin assembly[5] as well as the applications to dye-sensitized solar cells,[6] liquid crystalline materials,[7] and so on. In the latter case, the inner nitrogen atoms are replaced with other atoms, and the electronic and electrochemical properties and coordination abilities of the porphyrin base system can be changed.[8,9]

Carbazole based materials have also been extensively studied from the view point of electron conductors, catalyses, sensors, and biologically active alkaloids.[10] Since carbazole is simply a benzene-fused pyrrole, the incorporation of carbazole units into fused porphyrins represents interesting possibilities.[11–13] We recently reported the synthesis of carbazole-based porphyrins **1** and **5**, which exhibit distinct aromaticity as well as near-infrared (NIR) absorption at 1049 and 1089 nm, respectively due to the quadruple benzo-fusions (Fig. 1).[13a,e] The π-electrons are well delocalized over the macrocycles so that the addition of various substituents to these porphyrins is seen as means to further modify their optical and electronic properties. Herein, we report the peripheral cyanation and ethynylation of the porphyrins **1** and **5**. We also prepared ethylenedioxy-appended porphyrins as the compound having electron-donating groups for comparison. Conjugated and electronic substituent effects on the photophysical properties of the macrocycles have been investigated by means of absorption spectroscopy and MO calculations.



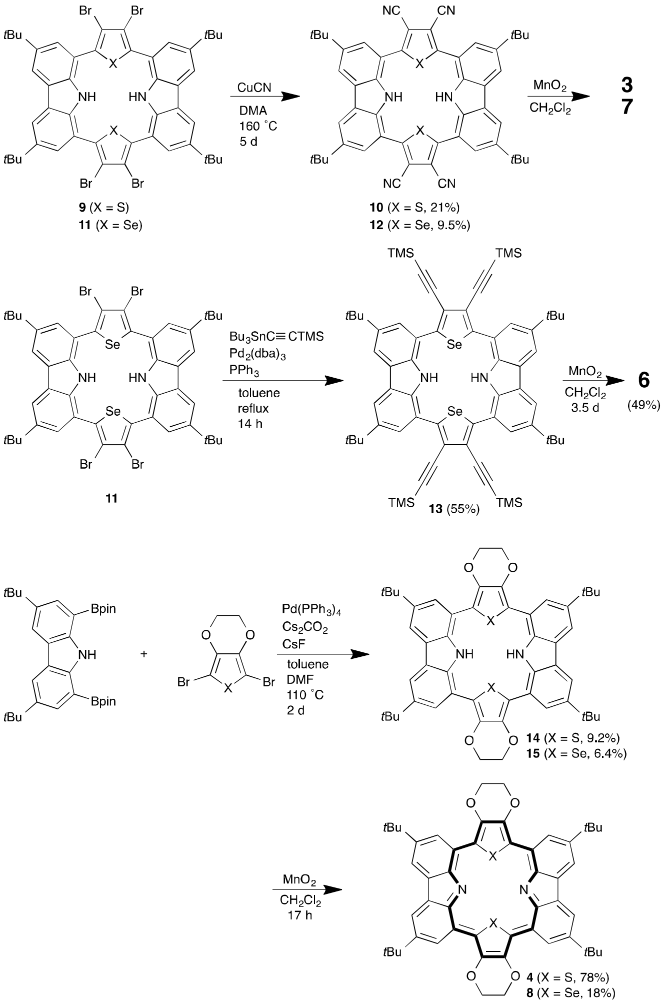
1 (R = H)
2 (R = C≡CTMS)
3 (R = C≡N)
4 (R = -OCH_2CH_2O-)

5 (R = H)
6 (R = C≡CTMS)
7 (R = C≡N)
8 (R = -OCH_2CH_2O-)

Fig. 1 Structures of the carbazole-based porphyrins **1**–**8**.

Results and discussion

The synthesis of **2** was reported previously.[13c] The synthesis in this work is shown in Scheme 1. Tetracyanated isophlorine **10** was obtained in 21% yield from tetrabrominated compound **9** with CuCN. High-resolution matrix-assisted-laser-desorption-ionization time-of-flight (HR-MALDI-TOF) mass spectral data showed the parent ion peak of **10** at an *m/z* value of 817.317 (calcd. for $C_{52}H_{45}N_6S_2$ $[M–H]^-$ = 817.315. Slow diffusion of heptane vapour into a dichloromethane solution of **10** resulted in the formation of well-defined crystals. X-ray diffraction analysis unambiguously demonstrated the structure of **10**, confirming the presence of four cyano groups at the thiophene moieties (Fig. 2a).‡ We then tried the oxidation of **10**. Vivid colour change has been observed when MnO_2 has been added to a solution of compound **10** in CH_2Cl_2. The MALDI-TOF mass spectral data of the green solution detected the parent ion peak of **3** at an *m*/*z* value of 816.306 (calcd. for $C_{52}H_{44}N_6S_2$ $[M]^-$ = 816.307. In addition, the absorption spectrum of the solution exhibited similar Q-like bands with **1** and **2** as described later. These results strongly suggested the generation of **3**. After the solution was evaporated, however, no soluble products were obtained probably due to aggregation of the product.[14] Similarly, cyanation of tetrabrominated selenaporphyrinoid **11** and subsequent oxidation of **12** also confirmed the generation of cyanated selenaporphyrin **7**. On the other hand, trimethylsilylethynyl-substituted selenaporphyrin **6** was obtained through the Stille coupling reaction of **11**, followed by MnO_2 oxidation of **13** in moderate yields. The ^{1}H NMR spectrum of **6** exhibits down field shifts for the peripheral protons, indicating diatropic ring current in **6**. Additionally, we prepared carbazole-based porphyrins **4** and **8** bearing electron-donating groups in order to examine the electronic substituent effects. The Suzuki–Miyaura coupling reaction of 1,8-diboryl-3,6-di-*tert*-butylcarbazole and 2,5-dibromo-3,4-ethylenedioxythiophene provided isophlorine **14** in 9.2% yield. The structure of **14** was confirmed by X-ray diffraction analysis (Fig. 2b).‡ The subsequent oxidation afforded ethylenedioxy-appended carbazole-based thiaporphyrin **4**. Corresponding selenaporphyrin **8** was also prepared similarly.



Scheme 1 Synthesis of **3**, **4** and **6**–**8**.

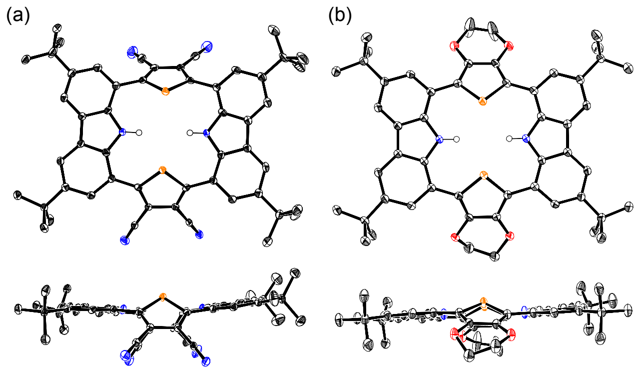


Fig. 2 X-ray crystal structures of (a) **10** and (b) **14**: top view and side view. Hydrogen atoms except for NH protons are omitted for clarity. The thermal ellipsoids were at the 50% probability level.

The UV/vis/NIR absorption spectra of **1**–**8** are shown in Fig. 3. Similar to **1** and **2**, the spectrum of **3** showed the intensified Q-like bands in the NIR region. Interestingly, the longest wavelength band of **3** (973 nm) was blue shifted in comparison to the equivalent band of **1** (1049 nm) although the cyano groups were introduced into the conjugated macrocycle.[15] In the case of the selenaporphyrins **5**–**7**, likewise, the introduction of ethynyl groups induced a red shift, while that of cyano groups induced a blue shift of the bands. The ethylenedioxy-appended porphyrins **4** and **8** showed more red-shifted absorption bands (1121 and 1178 nm). Notably the absorption maximum of **8** is the longest wavelength in the carbazole-based porphyrins in neutral state.[16] Thus effective substituent effects are observed by both electronic and conjugated substituents. The oxidation potentials and reduction potentials of **6** were subsequently investigated by cyclic voltammetry. The voltammogram of **6** revealed reduction wave at –0.335 and –0.679 V, and oxidation waves at 0.569 and 1.009 V, resulting in a even smaller electrochemical HOMO–LUMO gap of 0.904 eV than those of **1** or **2** or **5** (ESI).

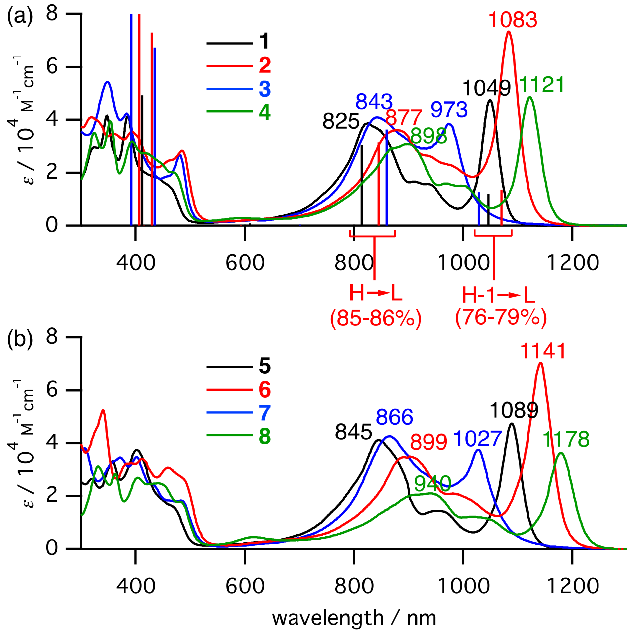


Fig. 3 UV/vis/NIR absorption spectra of (a) **1**–**4**, and (b) **5**–**8** in CH_2Cl_2. The spectra of **3** and **7** were normalized. Calculated oscillator strengths of **1**–**3** were inserted in the spectra.

DFT calculations of **1**–**4** were performed at the B3LYP/6-31G* level to discuss the electronic properties (Fig. 4).[17] The energy levels of **3** are highly stabilized by the electron-withdrawing cyano groups as compared to those of **1** and **2**. Curiously, the calculated HOMO–LUMO gap of **3** is smaller than those of **1** and **2** against the result of absorption spectroscopy. In sharp contrast, the gap between the HOMO–1 and LUMO of **3** is larger. In order to explain the conflict between the results of absorption spectroscopy and the calculations, excited energy of **1**–**3** were calculated at CNDO/S method by using MOS-F (Fig. 3a). The obtained results were good agreement with the absorption spectra. The longest absorption bands (1000–1100 nm) are related to the transitions dominantly from the HOMO–1 which possesses a_{1u} orbital to the LUMO, while another Q-like bands around 800–900 nm are attributed to the transitions dominantly from the HOMO which possesses a_{2u} orbital to the LUMO. Consequently, the stabilization of the HOMO–1 results in the blue-shifted absorption in **3**. The smallest gap between the HOMO–1 and LUMO of **4** also supports the proposed transitions.

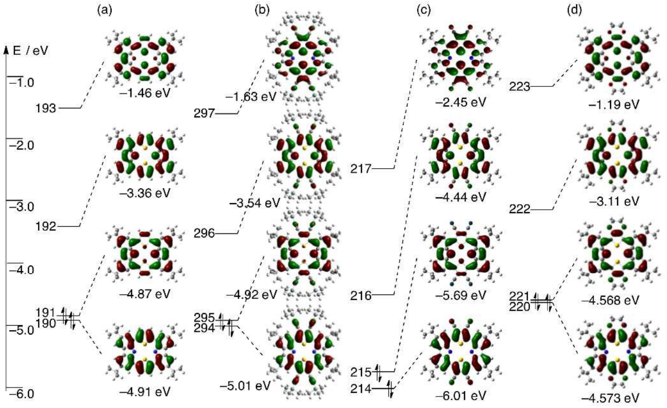


Fig. 4 Molecular orbital diagrams of (a) **1**, (b) **2**, (c) **3**, and (d) **4** calculated at the B3LYP/6-31G* levels.

Conclusions

In summary, carbazole-based chalcogenaporphyrins bearing cyano and ethynyl groups on their thiophene or selenophene moieties have been synthesized. The effects of substituents attached to the macrocycles have been confirmed by both experimental studies and theoretical calculations. The introduction of ethynyl groups induced red shifts, while that of cyano groups induced blue shifts of the longest absorption bands, which was supported by the excited-energy calculations. In addition, ethylenedioxy-appended porphyrins **4** and **8** were also prepared. As a result, both electronic and conjugated substituent effects on the photophysical properties of the carbazole-based porphyrins have been observed. Especially, the absorption maximum of **8** reached 1178 nm. Further investigation concerning the synthesis and functionalization of novel carbazole-based porphyrins are currently underway.

Experimental

General

^{1}H and ^{13}C NMR spectra were taken on a JEOL ECA-400 or ECA-500 spectrometer, and chemical shifts were reported as the delta scale in ppm as an internal reference ($\delta = 7.260$ for ^{1}H NMR, 77.00 for ^{13}C NMR, for $CDCl_3$). UV/vis/NIR absorption spectra were recorded on a JASCO V-650 spectrometer or on a JASCO V-570 spectrometer. Mass spectra were taken on a Bruker microTOF. Redox potentials were measured by cyclic voltammetry method on an ALS electrochemical analyzer model 6102B. X-ray data were taken on a Bruker APEX2 CCD system with Mo-*K*α radiation (λ = 0.71073 Å) or Rigaku VariMax with Cu-*K*α radiation (λ = 1.54187 Å). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Dry CH_2Cl_2 and toluene were distilled from CaH_2.

Synthesis of 10: A dehydrated DMA (15 mL) solution of **9**[13c] (107 mg, 104 μmol) and CuCN (369 mg, 4.12 mmol) was heated at reflux for 5 days under Ar. After cooling to rt, the mixture was diluted with $CHCl_3$, washed with water, and evaporated. The residue was separated over a silica gel column with CH_2Cl_2 as an eluent to give **10** (20.0 mg, 24.4 μmol, 21%). ^{1}H NMR ($CDCl_3$) δ = 9.72 (s, 2H, NH), 8.15 (d, J = 1.5 Hz, 4H, carbazole-H), 7.93 (s, 4H, carbazole-H), and 1.40 ppm (s, 36H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ = 149.83, 144.92, 136.39, 125.21, 123.65, 120.17, 113.24, 112.86, 109.08, 35.13, and 31.73 ppm; HR-MS (MALDI): *m/z* = 817.3167. calcd for $C_{52}H_{45}N_6S_2$: 817.3153 [*M*–H]; UV/vis (CH_2Cl_2) λ_{max} (ε) = 309 (24800), 345 (28500), and 424 nm (20900 $M^{-1}cm^{-1}$).

Synthesis of 11: To a CH_2Cl_2 (30 mL) solution of selenophene-bridged carbazole dimer[13e] (141 mg, 174 μmol) was added CH_2Cl_2 (30 mL) solution of NBS (152 mg, 856 μmol) for 1 h, and the mixture was stirred for 16 h. After passing through a silica gel column with CH_2Cl_2, evaporation of the solvent provided **11** (117 mg, 104 μmol, 60%). ^{1}H NMR ($CDCl_3$) δ = 9.15 (s, 2H, NH), 8.18 (d, *J* = 1.5 Hz, 4H, carbazole-H), 7.89 (d, *J* = 1.5 Hz, 4H, carbazole-H), and 1.54 ppm (s, 36H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ = 143.13, 137.90, 136.57, 124.47, 124.10, 118.09, 116.84, 115.66, 35.06, and 32.02 ppm; HR-MS (MALDI): *m/z* = 1128.8574. calcd for $C_{48}H_{45}N_2Se_2Br_4$: 1128.8611 $[M–H]^-$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 320 (26600) and 394 nm (17900 $M^{-1}cm^{-1}$).

Synthesis of 12: A dehydrated DMA (10 mL) solution of **11** (58.8 mg, 52.1 μmol) and CuCN (474 mg, 5.33 mmol) was heated at reflux for 5 days under Ar. After cooling to rt, the mixture was diluted with $CHCl_3$, washed with water, and evaporated. The residue was separated over a silica gel column with CH_2Cl_2 as an eluent to give **12** (4.50 mg, 4.93 μmol, 9.5%). ^{1}H NMR ($CDCl_3$) δ = 9.55 (s, 2H, NH), 8.15 (d, *J* = 1.5 Hz, 4H, carbazole-H), 7.83 (s, 4H, carbazole-H), and 1.40 ppm (s, 36H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ = 157.03, 144.80, 137.13, 125.27, 122.83, 120.08, 115.44, 114.21, 111.03, 35.10, and 31.80 ppm; HR-MS (APCI): *m/z* = 913.2060. calcd for $C_{52}H_{45}N_6Se_2$: 913.2054 $[M–H]^-$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 281 (45300), 347 (17800), and 433 nm (17400 $M^{-1}cm^{-1}$).

Synthesis of 13: A dry toluene (20 mL) solution of **11** (96.1 mg, 85.2 μmol), $Pd_2(dba)_3$ (13.1 mg, 14.3 μmol), PPh_3 (28.1 mg, 107 μmol), and tributyl(trimethylsilylethynyl)tin (375 mg, 969 μmol) was degassed. The mixture was stirred at reflux for 14 h under Ar. After the solvent was evaporated, the residue was separated over a silica gel column with CH_2Cl_2/hexane as an eluent to give **13** (56.6 mg, 47.2 μmol, 55%). ^{1}H NMR ($CDCl_3$) δ = 9.35 (s, 2H, NH), 8.16 (d, *J* = 1.5 Hz, 4H, carbazole-H), 7.98 (d, *J* = 2.0 Hz, 4H, carbazole-H), 1.53 (s, 36H, *t*-Bu), and 0.17 ppm (s, 36H, TMS); ^{13}C NMR ($CDCl_3$) δ = 146.28, 142.86, 136.60, 125.96, 123.99, 123.68, 117.83, 117.45, 99.65, 97.74, 35.10, 32.14, and 0.11 ppm; HR-MS (MALDI): *m/z* = 1198.3938. calcd for $C_{68}H_{82}N_2Se_2Si_4$: 1198.3881 $[M]^+$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 300 (42400) and 413 nm (13500 $M^{-1}cm^{-1}$).

Synthesis of 6: To a dry CH_2Cl_2 (100 mL) solution of **13** (44.2 mg, 36.9 μmol) was added MnO_2 (2.38 g), and the resulting suspension was stirred. After 2 days, MnO_2 (1.38 g) was added and the mixture was stirred for further 1.5 day. The mixture was passed through a pad of Celite. Evaporation of the solvent provided **6** (21.4 mg, 17.9 μmol, 49%). ^{1}H NMR ($CDCl_3$) δ = 10.60 (d, *J* = 1.5 Hz, 4H, carbazole-H), 8.77 (d, *J* = 1.5 Hz, 4H, carbazole-H), 1.82 (s, 36H, *t*-Bu), and 0.56 ppm (s, 36H, TMS); ^{13}C NMR ($CDCl_3$) δ = 151.92, 149.31, 147.82, 131.88, 128.74, 127.48, 123.16, 121.86, 106.19, 105.25, 36.62, 32.13, and 0.93 ppm; HR-MS (MALDI): *m/z* = 1196.3684. calcd for $C_{68}H_{80}N_2Se_2Si_4$: 1196.3734 $[M]^-$; UV/vis/NIR (CH_2Cl_2) λ_{max} (ε) = 340 (34100), 392 (21100), 412 (22200), 459 (20100), 899 (22400), 980 (13600), and 1141 nm (44900 $M^{-1}cm^{-1}$).

Synthesis of 14: A toluene/DMF (20 mL/20 mL) solution of 3,6-di-*tert*-butylcarbazole-1,8-diboronic acid pinacol ester[11b] (339 mg, 638 μmol), 2,5-dibromo-3,4-ethylenedioxythiophene (191 mg, 637 μmol), $Pd(PPh_3)_4$ (69.9 mg, 60.5 μmol), Cs_2CO_3 (630 mg, 1.93 mmol), and CsF (377 mg, 2.48 mmol) was degassed. The mixture was stirred at 110 °C for 48 h under N_2. After cooling to rt, the mixture was diluted with $CHCl_3$, washed with water, passed through a silica gel column with $CHCl_3$, and evaporated. The residue was purified by GPC with $CHCl_3$ and by a silica gel column with $CHCl_3$/hexane as an eluent to give **14** (24.5 mg, 29.3 μmol, 9.2%). ^{1}H NMR ($CDCl_3$) δ = 10.39 (s, 2H, NH), 8.07 (s, 4H, carbazole-H), 7.98 (d, *J* = 1.2 Hz, 4H, carbazole-H), 4.43 (s, 4H, CH_2), and 1.54 ppm (s, 36H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ = 142.65, 139.48, 135.42, 124.10, 123.21, 116.11, 114.59, 111.82, 64.84, 34.93, and 32.10 ppm; HR-MS (MALDI): *m/z* = 834.351. calcd for $C_{52}H_{54}N_2O_4S_2$: 834.355 $[M]^+$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 279 (24900), 318 (35700) and 413 nm (19600 $M^{-1}cm^{-1}$).

Synthesis of 4: To a dry CH_2Cl_2 (6 mL) solution of **14** (40.8 mg, 48.9 μmol) was added MnO_2 (175 mg), and the resulting suspension was stirred. After 12 h, MnO_2 (203 mg) was added and the mixture was stirred for further 5 h. The mixture was passed through a silica gel column with CH_2Cl_2/acetone (9/1). Evaporation of the solvent provided **4** (31.7 mg, 38.1 μmol, 78%). ^{1}H NMR ($CDCl_3$) δ = 10.01 (s, 4H, carbazole-H), 8.82 (s, 4H, carbazole-H), 5.14 (s, 8H, CH_2), and 1.82 ppm (s, 36H, *t*-Bu); ^{13}C NMR could not detect peaks due to serious low solubility; HR-MS (MALDI): *m/z* = 832.337. calcd for $C_{52}H_{52}N_2O_4S_2$: 832.336 $[M]^+$; UV/vis/NIR (CH_2Cl_2) λ_{max} (ε) = 324 (35100), 353 (39500), 393 (31900), 898 (30600), 968 (15900), 996 (15100), and 1121 nm (47400 $M^{-1}cm^{-1}$).

Synthesis of 15: A toluene/DMF (10 mL/10 mL) solution of 3,6-di-*tert*-butylcarbazole-1,8-diboronic acid pinacol ester (161 mg, 303 μmol), 2,5-dibromo-3,4-ethylenedioxyselenophene[18] (105 mg, 303 μmol), $Pd(PPh_3)_4$ (35.7 mg, 60.5 μmol), Cs_2CO_3 (345 mg, 1.06 mmol), and CsF (157 mg, 1.03 mmol) was degassed. The mixture was stirred at 110 °C for 48 h under N_2. After cooling to rt, the mixture was diluted with $CHCl_3$, washed with water, passed through a silica gel column with $CHCl_3$, and evaporated. The residue was purified by GPC with $CHCl_3$ and by a silica gel column with $CHCl_3$/hexane as an eluent to give **15** (9.0 mg, 9.7 μmol, 6.4%). ^{1}H NMR ($CDCl_3$) δ = 10.14 (s, 2H, NH), 8.08 (d, *J* = 2.0 Hz, 4H, carbazole-H), 7.82 (d, *J* = 1.6 Hz, 4H, carbazole-H), 4.29 (s, 4H, CH_2), and 1.53 ppm (s, 36H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ = 142.42, 140.34, 136.49, 123.97, 123.58, 116.68, 115.81, 114.74, 64.41, 34.95, and 32.14 ppm; HR-MS (MALDI): *m/z* = 930.242. calcd for $C_{52}H_{54}N_2O_4Se_2$: 930.241 $[M]^+$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 314 (41000) and 398 nm (19800 $M^{-1}cm^{-1}$).

Synthesis of 8: To a dry CH_2Cl_2 (5 mL) solution of **15** (9.0 mg, 9.7 μmol) was added MnO_2 (57.3 mg), and the resulting suspension was stirred. After 12 h, MnO_2 (47.0 mg) was added and the mixture was stirred for further 5 h. The mixture was passed through a pad of Celite with CH_2Cl_2 and evaporated. The residue was washed with $CHCl_3$ to give **8** (1.6 mg, 1.7 μmol, 18%). ^{1}H NMR ($CDCl_3$) δ = 10.05 (s, 4H, carbazole-H), 8.94 (s, 4H, carbazole-H), 5.11 (s, 8H, CH_2), and 1.84 ppm (s, 36H, *t*-Bu); ^{13}C NMR could not detect peaks due to serious low solubility; HR-MS (MALDI): *m/z* = 928.223. calcd for $C_{52}H_{52}N_2O_4Se_2$: 928.225 $[M]^+$; UV/vis/NIR (CH_2Cl_2) λ_{max} (ε) = 331 (23200), 362 (21200), 404 (20200), 441 (18700), 480 (13400), 618 (3400), 912 (15400), 940 (15800), 1018 (9230), and 1178 nm (27300 $M^{-1}cm^{-1}$).

Acknowledgements

This work was supported by a Grants-in-Aid for Young Scientists (No. 23750231 (B)) from JSPS KAKENHI. We thank Prof. A. Osuka and Dr. T. Tanaka (Kyoto university), and Dr. K. Yoza (Bruker AXS) for X-ray diffraction analysis. C.M. also thanks Casio science promotion foundation for its support.

Notes and references

[a] *Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Kohoku-ku, Yokohama 223-8522, Japan.*

[b] *Division of Applied Chemistry, Graduate School of Natural Science and Technology, Okayama University, Tsushima, Okayama 700-8530, Japan. E-mail: cmaeda@okayama-u.ac.jp, Fax: +81 86-251-8092; Tel: +81 86-251-8092.*

† Electronic Supplementary Information (ESI) available: Experimental details and compound data. See DOI: 10.1039/b000000x/

‡ Crystallographic data for **10**: formula: $C_{53}H_{48}Cl_2N_6S_2$, $M_w = 903.99$, monoclinic, space group $C2/c$, $a = 19.1544(7)$, $b = 28.1718(11)$, $c = 19.2631(7)$ Å, $\beta = 104.8650(10)°$, $V = 10046.8(6)$ Å^3, $Z = 8$, $\rho_{\text{calcd}} = 1.195$ gcm^{-3}, $T = -180$ °C, 55820 measured reflections, 8875 unique reflections ($R_{\text{int}} = 0.0589$), $R_1 = 0.0784$ ($I > 2\sigma(I)$), $wR_2 = 0.2358$ (all data), GOF = 1.026. Crystallographic data for **14**: formula: $C_{52}H_{54}N_2O_4S_2$ 0.486(CH_2Cl_2) 0.757(C_8H_{18}), $M_w = 962.51$, triclinic, space group P–1, $a = 12.3573(5)$, $b = 13.80290(10)$, $c = 17.2234(13)$ Å, $\alpha = 71.455(15)$, $\beta = 82.166(16)$, $\gamma = 64.049(14)°$, $V = 2504.3(4)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.276$ gcm^{-3}, $T = -180$ °C, 31422 measured reflections, 8508 unique reflections ($R_{\text{int}} = 0.05367$), $R_1 = 0.0584$ ($I > 2\sigma(I)$), $wR_2 = 0.1720$ (all data), GOF = 1.052. CCDC 1044163 (**10**) 1418265 (**14**) contains the supplementary crystallographic data for this paper.

1 (*a*) K. M. Smith, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 1999, ch. 1, vol. 1, pp. 1; (*b*) J. S. Lindsey, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith, and R. Guilard, Academic Press, San Diego, 1999, ch. 2, vol. 1, pp. 45; (*c*) K. M. Smith, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 1999, ch. 3, vol. 1, pp. 119.

2 (*a*) V. S.-Y. Lin, S. G. DiMagno and M. J. Therien, *Science*, 1994, **264**, 1105; (*b*) T. E. O. Screen, K. B. Lawton, G. S. Wilson, N. Dolney, R. Ispasoiu, T. Goodson III, S. J. Martin, D. D. C. Bradley and H. L. Anderson, *J. Mater. Chem.*, 2001, **11**, 312; (*c*) T. Chandra, B. J. Kraft, J. C. Huffman and J. M. Zaleski, *Inorg. Chem.*, 2003, **42**, 5158; (*d*) T. V. Duncan, K. Susumu, L. E. Sinks and M. J. Therien. *J. Am. Chem. Soc.*, 2006, **128**, 9000.

3 (*a*) S. Fox and R. W. Boyle, *Tetrahedron*, 2006, **62**, 10039; (*b*) J. P. Lewtak and D. T. Gryko, *Chem. Commun.*, 2012, 10069; (*c*) V. V. Roznyatovskiy, C.-H. Lee and J. L. Sessler, *Chem. Soc. Rev.*, 2013, **42**, 1921; (*d*) H. Mori, T. Tanaka and A. Osuka, *J. Mater. Chem. C*, 2013, **1**, 2500.

4 (*a*) H. J. Callot, E. Schaeffer, R. Cromer and F. Metz, *Tetrahedron*, 1990, **46**, 5253; (*b*) L. Barloy, D. Dolphin, D. Dupre and T. Wijesekera, *J. Org. Chem.*, 1994, **59**, 7976; (*c*) S. Richeter, C. Jeandon, J.-P. Gisselbrecht, R. Ruppert and H. J. Callot, *J. Am. Chem. Soc.*, 2002, **124**, 6168; (*d*) H. S. Gill, M. Harmjanz, J. Santamaría, I. Finger and M. J. Scott, *Angew. Chem., Int. Ed.*, 2004, **43**, 485; (*e*) O. Yamane, K. Sugiura, H. Miyasaka, K. Nakamura, T. Fujimoto, K. Nakamura, T. Kaneda, Y. Sakata and M. Yamashita, *Chem. Lett.*, 2004, **33**, 40; (*f*) S. Fox and R. W. Boyle, *Chem. Commun.*, 2004, 1322; (*g*) A. N. Cammidge, P. J. Scaife, G. Berber and D. L. Hughes, *Org. Lett.*, 2005, **7**, 3413; (*h*) D. Shen, C. Liu and Q. Chen, *Chem. Commun.*, 2005, 4982; (*i*) E. Hao, F. R. Fronczek and M. G. H. Vicente, *J. Org. Chem.*, 2006, **71**, 1233; (*j*) K. Kurotobi, K. S. Kim, S. B. Noh, D. Kim and A. Osuka, *Angew. Chem., Int. Ed.*, 2006, **45**, 3944; (*k*) S. Tokuji, Y. Takahashi, H. Shinmori, H. Shinokubo and A. Osuka, *Chem. Commun.*, 2009, 1028; (*l*) N. K. S. Davis, A. L. Thompson and H. L. Anderson, *J. Am. Chem. Soc.*, 2011. **133**. 30; (*m*) T. Ishizuka, Y. Saegusa, Y. Shiota, K. Ohtake, K. Yoshizawa and T. Kojima, *Chem. Commun.*, 2013, **49**, 5939.

5 (*a*) T. Imamura and K. Fukushima, *Coord. Chem. Rev.*, 2000, **198**, 133; (*b*) J. Wojaczyński and L. Latos-Grażyński, *Coord. Chem. Rev.*, 2000, **204**, 113; (*c*) E. Iengo, E. Zangrando and E. Alessio, *Eur. J. Inorg. Chem.*, 2003, 2371; (*d*) A. Satake and Y. Kobuke, *Tetrahedron*, 2005, **61**, 13; (*e*) C. Maeda, T. Kamada, N. Aratani and A. Osuka, *Coord. Chem. Rev.*, 2007, **251**, 2743.

6 (*a*) M. K. Panda, K. Ladomenou and A. G. Coutsolelos, *Coord. Chem. Rev.*, 2012, **256**, 2601; (*b*) T. Higashino and H. Imahori, *Dalton Trans.*, 2015, **44**, 448.

7 (*a*) T. Sakurai, K. Tashiro, Y. Honsho, A. Saeki, S. Seki, A. Osuka, A. Muranaka, M. Uchiyama, J. Kim, S. Ha, K. Kato, M. Takata and T. Aida, *J. Am. Chem. Soc.*, 2011, **133**, 6537; (*b*) C. Xue, Y. Xu, Y. Pang, D. Yu, L. Dai, M. Gao, A. Urbas and Q. Li, *Langmuir*, 2012, **28**, 5956.

8 (*a*) L. Latos-Grażyński, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 2000, ch. 14, vol. 2, pp. 361; (*b*) A. Jasat and D. Dolphin, *Chem. Rev.*, 1997, **97**, 2267; (*c*) I. Gupta and M. Ravikanth, *Coord. Chem. Rev.*, 2006, **250**, 468; (*d*) T. D. Lash, *Eur. J. Org. Chem.*, 2007, 5461; (*e*) R. Misra and T. K. Chandrashekar, *Acc. Chem. Res.*, 2008, **41**, 265; (*f*) Y. Matano and H. Imahori, *Acc. Chem. Res.*, 2009, **42**, 1193.

9 (*a*) J. Mack, M. Bunya, Y. Shimizu, H. Uoyama, N. Komobuchi, T. Okujima, H. Uno, S. Ito, M. J. Stillman, N. Ono and N. Kobayashi, *Chem.–Eur. J.*, 2008, **14**, 5001; (*b*) M. Kon-no, J. Mack, N. Kobayashi, M. Suenaga, K. Yoza and T. Shinmyozu, *Chem.–Eur. J.*, 2012, **18**, 13361; (*c*) H.-J. Xu, J. Mack, D. Wu, Z.-L. Xue, A. B. Descalzo, K. Rurack, N. Kobayashi and Z. Shen, *Chem.–Eur. J.*, 2012, **18**, 16844.

10 (*a*) N. Blouin and M. Leclerc, *Acc. Chem. Res.*, 2008, **41**, 1110; (*b*) M. Inoue, T. Suzuki, A. Kinoshita and M. Nakada, *Chem. Rec.*, 2008, **8**, 169; (*c*) P. A. Gale, *Chem. Commun.*, 2008, 4525; (d) H.-J. Knölker, *Chem. Lett.*, 2009, **38**, 8.

11 (*a*) P. Piatek, V. M. Lynch and J. L. Sessler, *J. Am. Chem. Soc.*, 2004, **126**, 16073; (*b*) L. Arnold, H. Norouzi-Arasi, M. Wagner, V. Enkelmann and K. Müllen, *Chem. Commun.*, 2011, **47**, 970; (*c*) L. Arnold, M. Baumgarten and K. Müllen, *Chem. Commun.*, 2012, **48**, 9640.

12 (*a*) H. Aihara, L. Jaquinod, D. J. Nurco and K. M. Smith, *Angew. Chem., Int. Ed.*, 2001, **40**, 3439; (*b*) M. Nath, J. C. Huffman and J. M. Zaleski, *J. Am. Chem. Soc.*, 2003, **125**, 11484; (*c*) M. Nath, M. Pink and J. M. Zaleski, *J. Am. Chem. Soc.*, 2005, **127**, 478.

13 (*a*) C. Maeda, T. Yoneda, N. Aratani, M.-C. Yoon, J. M. Lim, D. Kim, N. Yoshioka and A. Osuka, *Angew. Chem., Int. Ed.*, 2011, **50**, 5691; (*b*) C. Maeda and N. Yoshioka, *Org. Lett.*, 2012, **14**, 2122; (*c*)

C. Maeda and N. Yoshioka, *Org. Biomol. Chem.*, 2012, **10**, 5153; (*d*) M. Masuda and C. Maeda, *Chem.–Eur. J.*, 2013, **19**. 2971; (*e*) M. Masuda, C. Maeda and N. Yoshioka, *Org. Lett.*, 2013, **15**, 578; (*f*) C. Maeda, M. Masuda and N. Yoshioka, *Org. Lett.*, 2013, **15**, 3566; (*g*) C. Maeda, M. Masuda and N. Yoshioka, *Org. Biomol. Chem.*, 2014, **12**, 2656; (*h*) C. Maeda, T. Todaka and T. Ema, *Org. Lett.*, 2015, **17**, 3090.

14 This reaction was observed only at diluted condition (ca. 10^{-5} M). Although we tried the oxidation reaction in dichloromethane-d_2 or tetrachloroethane-d_2 at higher concentration, no peaks were observed in the ^{1}H NMR.

15 Introduction of cyano groups produced red-shifted absorption for general porphyrins, see: (*a*) M. O. Senge and I. Bischoff, *Eur. J. Org. Chem.*, 2001, 1735; (*b*) P. Bhyrappa, M. Sankar and B. Varghese, *Inorg. Chem.*, 2006, **45**, 4136; (*c*) M. C. Balaban, A. Eichhöfer, G. Buth, R. Hauschild, J. Szmytkowski, H. Kalt and T. S. Balaban, *J. Phys. Chem. B*, 2008, **112**, 5512.

16 As a monomeric porphyrin, larger bathochromic shifts were achieved by Anderson's group (1417 nm)[4l] and by Scott's group (1204 nm).[4d]

17 M. J. Frisch, *et al. GAUSSIAN 09 (Revision C.01)*, Gaussian, Inc.: Wallingford CT, PA, 2009.

18 A. Patra, Y. H. Wijsboom, S. S. Zade, M. Li, Y. Sheynin, G. Leitus and M. Bendikov, *J. Am. Chem. Soc.*, 2008, **130**, 6734.