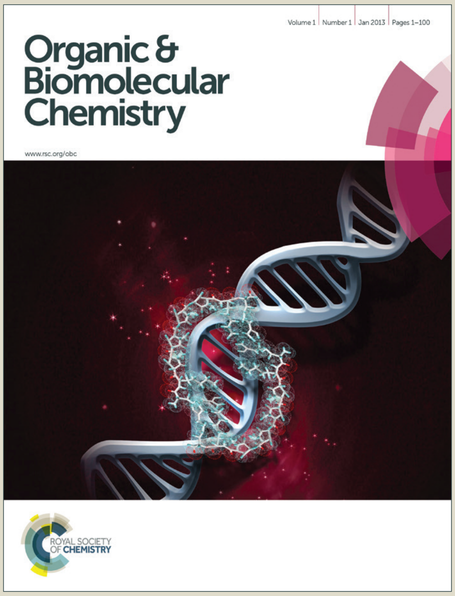
Organic &
Biomolecular
Chemistry

Accepted Manuscript



ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/obc

Journal Name

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Synthesis of carbazole-based hetero-core-modified porphyrins

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

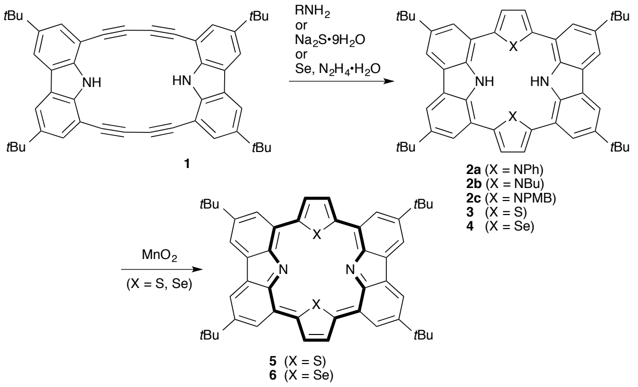
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Cu(I)-mediated annulation reaction of a 1,1'-(1,3-butadiyne)-8,8'-(2,5-thiophene)-bridged carbazole dimer **10** with amines provided the *N*-substituted carbazole-based isophlorines **11a**–**11c**. A similar annulation reaction with selenium in the presence of hydrazine monohydrate afforded hetero-core-modified isophlorine **12**. The oxidation of **12** generated the corresponding 21-selena-23-thiaporphyrin **13**, which exhibited NIR absorption. The intramolecular charge transfer from Se to S was confirmed by the ^{1}H NMR results along with DFT calculations.

Introduction

In the past two decades, a variety of porphyrins and porphyrinoids have been synthesized in view of mimicry of natural photosynthetic system and applications to optical devises, molecular recognitions, and catalyses.[1] Both peripheral and core modifications of porphyrins are intriguing because they can dramatically modify the properties of these compounds. Peripheral modifications allow tuning of the properties of the macrocycles as well as applications to liquid crystal materials[2] and organic–inorganic hybrid materials.[3] In particular, introduction of acetylene moieties or fusion of additional aromatic rings at the periphery of the original structures result in expanded π-conjugation and additional absorption within the near-infrared (NIR) region.[4–6] In contrast, core modifications, namely the replacement of one or more inner nitrogen atoms by other atoms, change the electronic and electrochemical properties and coordination abilities of the porphyrin base system.[7,8]

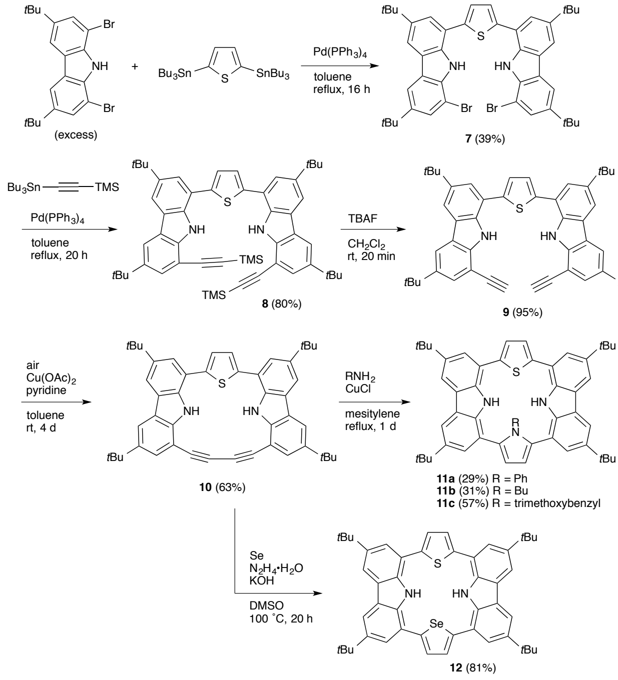
Carbazole derivatives have also been widely studied because of their unique properties.[9] They can show high emission and electron conductivity and are readily functionalized or polymerized *via* metal-catalyzed coupling reactions. Since carbazole is a benzene-fused pyrrole, its incorporation into fused porphyrins presents interest possibilities.[10–12] Sessler and co-workers developed calix[4]pyrrole[2]carbazole by replacing the two methylene moieties of a calix[4]pyrrole by a carbazole.[10a] Müllen and co-workers synthesized pyridine-bridged carbazole dimer *via* Suzuki–Miyaura coupling.[10b] Our group reported a double annulation strategy that allows the synthesis of novel fused porphyrinoids from 1,3-butadiyne-bridged carbazole dimer **1** (Scheme 1). Among these porphyrinoids, the tetrabenzo-fused dithiaporphyrin **5** and diselenaporphyrin **6** exhibited distinct aromaticity as well as NIR absorption due to the expanded π-conjugation over the entire macrocycles.[12a,12e] This double annulation reaction represents an alternative porphyrin synthesis and is useful means of obtaining 21,23-*homo*-core-modified porphyrins, although synthesis of 21,23-*hetero*-core-modified porphyrins are trivial *via* this double annulation method. Herein, we report the synthesis of a carbazole-based 21-modified-23-thiaporphyrin through a stepwise metal-catalyzed strategy.



Scheme 1 Synthesis of carbazole-based porphyrinoids.

Results and discussion

The overall synthetic procedure applied in this work is shown in Scheme 2. The 1,1'-(1,3-butadiyne)-8,8'-(2,5-thiophene)-bridged carbazole dimer **10** was first synthesized as follows. The Stille coupling reaction of 2,5-bis(tributylstannyl)thiophene with an excess of 3,6-di-*tert*-butyl-1,8-dibromocarbazole[13] provided **7**. The bromo substituents of **7** were converted into ethynyl groups *via* a Stille coupling reaction with tributyl(trimethylsilylethynyl)tin and subsequent deprotection of **8** with TBAF. The intramolecular Glaser coupling reaction of **9** subsequently provided the cyclic carbazole dimer **10**. 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 683.3494 (calcd. for $C_{48}H_{47}N_2S$: 683.3465 $[M–H]^–$). Slow diffusion of methanol vapor into a dichloromethane solution of **10** resulted in the formation of well-defined crystals. X-ray diffraction analysis unambiguously provided the structure of **10**, shown in Fig 1.‡ The mean plane deviation of the macrocycle is 0.210 Å, indicating a highly planer structure. Importantly, **10** could not be obtained directly from **1**.



Scheme 2 Synthesis of **11a**–**11c** and **12**.

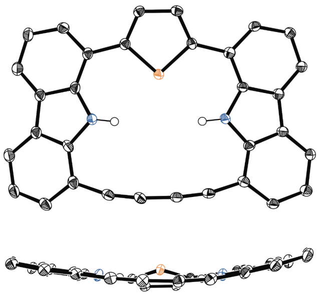


Fig. 1 X-ray crystal structure of **10**. Peripheral substituents are omitted for clarity. The thermal ellipsoids are at the 50% probability level.

Following the synthesis of **10**, its annulation reactions were examined. A mesitylene solution of **10**, aniline (10 equiv.), and CuCl (2 equiv.) was heating at reflux for 21 h. After chromatographic separation, *N*-phenyl substituted isophlorine **11a** was obtained in 29% yield. HR-MALDI-TOF mass spectral data showed the parent ion peak of **11a** at an *m*/*z* value of 777.4089 (calcd for $C_{54}H_{55}N_3S$: 777.4112 $[M]^+$). X-ray diffraction analysis provided a preliminary structure for **11a**, shown in Fig. S13 (ESI). Similar annulation reaction of **10** with butylamine or 3,4,5-trimethoxybenzylamine resulted in the corresponding 2,5-pyrrolylene-bridged carbazole **11b** and **11c**, respectively.[14] Additionally, reaction of **10** with selenium in the presence of hydrazine monohydrate afforded selenophene-bridged carbazole **12**.[15] The HR-MALDI-TOF mass spectrum of **12** showed the parent ion peak at an *m*/*z* value of 765.2759 (calcd. for $C_{48}H_{49}N_2SSe$: 765.2787 $[M\text{–}H]^-$).

The absorption spectra of these isophlorines are shown in Fig. 2 and summarized in Table 1. The spectra of **11a**–**11c** exhibit two similar bands at 300 and 380 nm, which are slightly red-shifted in comparison to those of **2a**–**2c**. On the other hand, the spectra of dichalcogenaisophlorines **3**, **4**, and **12** are almost similar. Thus, the spectra of these isophlorines exhibit primary in the UV-region, which reflects nonaromatic characteristics. Compounds **11a**–**11c** exhibited moderate fluorescent yields of 0.290, 0.289, and 0.356, respectively, while that of **12** was 0.03 due to the heavy atom effect of the selenium moiety. Among these, compound **10** showed the most red-shifted absorption and fluorescence, which might be ascribed to its planarity.

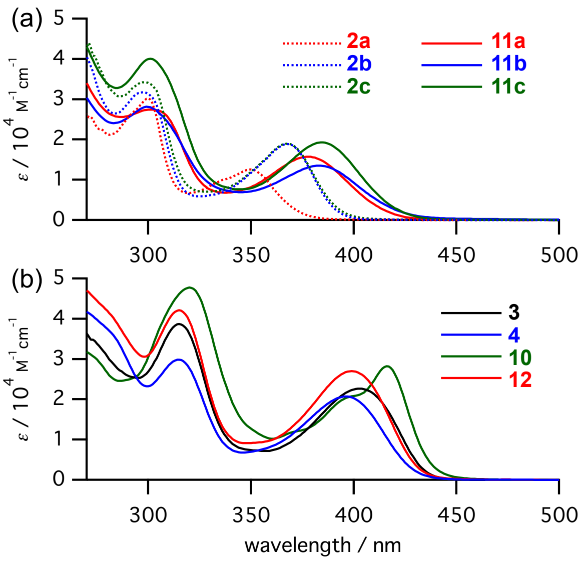


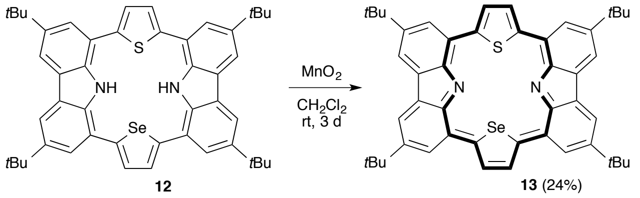
Fig. 2 UV/vis absorption spectra of (a) **2a**–**2c** and **11a**–**11c**, and (b) **3**, **4**, **10**, and **12** in CH_2Cl_2.

Table 1 Selected photophysical properties of the carbazole-based porphyrinoids in CH_2Cl_2.

compound	λ_A (nm)	λ_F (nm)[a]	Φ_F[b]
2a	300, 350	424	0.775
2b	298, 368	417	0.704
2c	298, 368	417	0.573
3	315, 403	448	0.271
4	315, 396	448	0.008[c]
10	320, 395, 416	476	0.426
11a	301, 378	451	0.290
11b	299, 383	463	0.289
11c	301, 384	463	0.356
12	315, 396	455	0.030[c]

[a] Excitation wavelengths are 360 nm. [b] Absolute fluorescence quantum yields. [c] Fluorescence quantum yields of **4** and **12** were determined with reference to the value of **3** (0.271) in CH_2Cl_2.

The 2,5-pyrrolylene-bridged cyclic carbazole dimer **11a**–**11c** can be regarded as [20]porphyrins and are expected to become aromatic after deprotection of the pyrrolic *N*-substituents and subsequent oxidation. Attempts to deprotect the pyrrolic *N*-substituents have been unsuccessful, however, despite extensive efforts using various acids and oxidants. The oxidation of **12** to the 21-selena-23-thiaporphyrin **13** was accomplished using MnO_2 and was accompanied by a dramatic colour change from yellow to green (Scheme 3).[16] In keeping with the significant transformation of its electronic state, the ^{1}H NMR spectrum of **13** exhibits downfield shifts of the peripheral proton signals, indicating a diatropic ring current in the molecule. Interestingly, the thiophene protons are shifted upfield (9.74 ppm) while the selenophene protons are shifted downfield (10.09 ppm) as compared to the corresponding protons of **5** (9.90 ppm) or **6** (10.07 ppm). The UV/vis/NIR absorption spectrum of **13** exhibits Q-like bands at 839, 940, and 1064 nm, situated intermediate between the corresponding bands of **5** and **6** (Fig. 3). In order to confirm such a small HOMO–LUMO gap, the oxidation and reduction potentials of **13** were subsequently measured by cyclic voltammetry. The voltammogram of **13** shows reduction waves at –0.588 and –0.906 V and oxidation waves at 0.326, 0.458, 0.954, and 1.058 V (ESI). A small electrochemical HOMO–LUMO gap (0.914 eV) was observed, consistent with the molecule's optical HOMO–LUMO gap (1.17 eV).



Scheme 3 Synthesis of **13**.

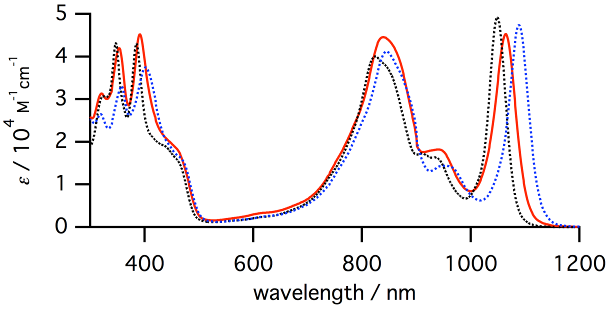


Fig. 3 UV/vis/NIR absorption spectra of **13** (red), **5** (black), and **6** (blue) in CH_2Cl_2.

Finally, DFT calculations were performed to assist in elucidating the electronic properties of **13** (Fig. 4).[17] Compounds **5**, **6**, and **13** all showed four orbitals characteristic of typical porphyrins. In all three compounds, the electronic coefficients were well delocalized over the entire macrocycle, while slight polarization between the thiophene and selenophene was observed in the case of **13**. In addition, the electronic charge of the S (0.430) in **13** is lower than that in **5** (0.455) while the Se charge (0.316) in **13** is higher than that in **6** (0.292). These data, combined with the ^{1}H NMR results, suggest charge transfer from Se to S. Nuclear independent chemical shift (NICS) values at the center of the **5**, **6**, and **13** were calculated to be –10.8, –14.1, and –12.2 ppm, respectively, indicating **5**, **6**, and **13** are all distinctly aromatic.

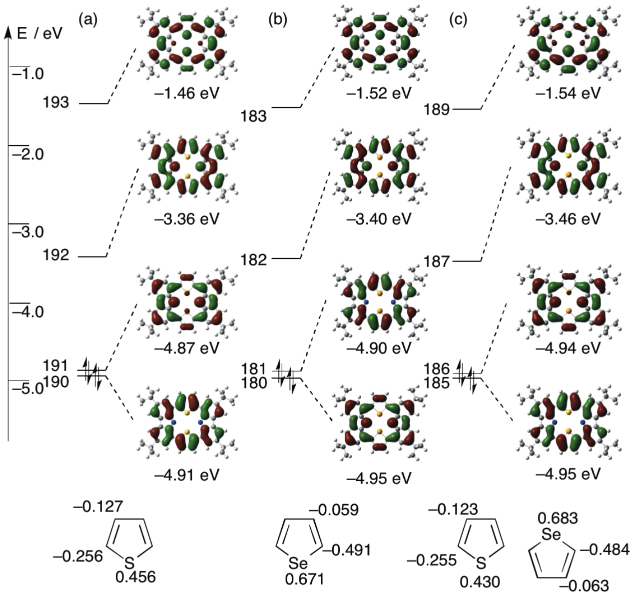


Fig. 4 Molecular orbital diagrams and selected Mulliken charges of (a) **5**, calculated at the B3LYP/6-31G* levels, and (b) **6** and (c) **13**, calculated at the B3LYP/6-31G*/LANL2DZ levels.

Conclusions

In this work, we have synthesized carbazole-based hetero-core-modified porphyins *via* stepwise metal-catalyzed strategy. The Cu(I)-mediated annulation reaction of the 1,1'-(1,3-butadiyne)-8,8'-(2,5-thiophene)-bridged carbazole dimer **10** with amines provided the *N*-substituted thiaporphyrinoids **11a–11c**, all of which contain carbazole units. A similar annulation reaction of **10** with selenium in the presence of hydrazine monohydrate afforded the hetero-core-modified isophlorine **12**. The subsequent oxidation of **12** gave the carbazole-based 21-selena-23-thiaporphyrin **13**. **13** as well as the dichalcogenaporphyrins **5** and **6** exhibits distinct aromaticity and strong NIR absorption. In addition, intramolecular charge transfer from Se to S was confirmed in the case of **13**. Further exploration of novel carbazole-based porphyrinoids and their metal complexes are currently underway in our laboratory.

Experimental

General

^{1}H and ^{13}C NMR spectra were taken on a JEOL ECA-500 spectrometer, and chemical shifts were reported as the delta scale in ppm as internal reference (δ = 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. Fluorescence spectra were recorded on a JASCO FP-777W spectrometer. Absolute fluorescence quantum yields of **10** and **11a–11c** were determined on a Hamamatsu Photonics C9920-02 spectrometer by photon-counting method using an integration sphere, and relative fluorescence quantum yield of **12** was determined with the reference value of **3** (0.271 in CH_2Cl_2). MALDI-TOF mass spectra were taken on a Bruker microTOF. Redox potentials were measured by cyclic voltammetry method on an ALS electrochemical analyzer model 6102B. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Dry CH_2Cl_2 and toluene was distilled from CaH_2.

Synthesis of 7: A dry toluene (10 mL) solution of 1,8-dibromo-3,6-di-*tert*-butylcarbazole (1.30 g, 2.97 mmol), 2,5-bis(tributylstannyl)thiophene (251 mg, 379 μmol), and $Pd(PPh_3)_4$ (45.1 mg, 39.0 μmol) was heated at reflux for 16 h under Ar. After the solvent was removed under reduced pressure, the residue was separated over a silica gel column with CH_2Cl_2/hexane as an eluent to give **7** (117 mg, 146 μmol, 39%). ^{1}H NMR ($CDCl_3$) $\delta = 8.59$ (s, 2H, NH), 8.12 (d, $J = 1.4$ Hz, 2H, carbazole-H), 8.10 (d, $J = 1.5$ Hz, 2H, carbazole-H), 7.77 (d, $J = 1.7$ Hz, 2H, carbazole-H), 7.68 (d, $J = 1.8$ Hz, 2H, carbazole-H), 7.63 (s, 2H, thiophene), 1.56 (s, 18H, *t*-Bu), and 1.50 ppm (s, 18H, *t*-Bu); ^{13}C NMR ($CDCl_3$) $\delta = 144.57$, 143.62, 141.02, 136.75, 135.03, 126.23, 125.75, 124.69, 124.68, 123.98, 117.43, 116.80, 115.66, 104.01, 34.93, 34.86, 32.00, and 31.96 ppm; HR-MALDI-MS: $m/z = 796.1851$. calcd for $C_{44}H_{48}N_2SBr_2$: 796.1879 $[M]^+$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 303 (40700) and 370 nm (24000 mol^{-1}dm^{3}cm^{-1}).

Synthesis of 8: A dry toluene (10 mL) solution of **7** (117 mg, 146 μmol), tributyl(trimethylsilylethynyl)tin (206 mg, 531 μmol), and $Pd(PPh_3)_4$ (10.0 mg, 8.65 μmol) was heated at reflux for 20 h under Ar. After the solvent was removed under reduced pressure, the residue was separated over a silica gel column with CH_2Cl_2/hexane as an eluent to give **8** (97.5 mg, 117 μmol, 80%). ^{1}H NMR ($CDCl_3$) $\delta = 8.72$ (s, 2H, NH), 8.14 (d, $J = 1.8$ Hz, 2H, carbazole-H), 8.12 (d, $J = 1.4$ Hz, 2H, carbazole-H), 7.77 (d, $J = 1.7$ Hz, 2H, carbazole-H), 7.644 (d, $J = 1.7$ Hz, 2H, carbazole-H), 7.638 (s, 2H, thiophene), 1.55 (s, 18H, *t*-Bu), 1.49 (s, 18H, *t*-Bu), and 0.30 ppm (s, 18H, TMS); ^{13}C NMR ($CDCl_3$) $\delta = 143.25$, 142.72, 141.25, 139.66, 134.85, 126.69, 125.12, 124.51, 123.26, 123.02, 117.62, 117.08, 116.61, 105.05, 101.63, 99.06, 34.81, 34.77, 32.04, 31.94, and 0.16 ppm; HR-MALDI-MS: m/z = 830.4506. calcd for $C_{54}H_{66}N_2SSi_2$: 830.4480 $[M]^+$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 280 (30800), 313 (30100), and 375 nm (18100 mol^{-1}dm^{3}cm^{-1}).

Synthesis of 9: Tetrabutylammonium fluoride (260 μL, 1 M in THF) was added to a CH_2Cl_2 solution of **8** (97.4 mg, 117 μmol), and the solution was stirred for 20 min. After the solvents were evaporated, the residue was separated over a silica gel column with CH_2Cl_2 to give **9** (76.5 mg, 112 μmol, 95%). ^{1}H NMR ($CDCl_3$) $\delta = 8.72$ (s, 2H, NH), 8.15 (d, $J = 1.7$ Hz, 2H, carbazole-H), 8.11 (d, $J = 1.7$ Hz, 2H, carbazole-H), 7.73 (d, $J = 1.7$ Hz, 2H, carbazole-H), 7.67 (d, $J = 1.7$ Hz, 2H, carbazole-H), 7.59 (s, 2H, thiophene), 3.45 (s, 2H, C≡CH), 1.53 (s, 18H, *t*-Bu), and 1.47 ppm (s, 18H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ (ppm): 143.37, 142.77, 141.10, 139.58, 135.10, 127.37, 125.66, 124.37, 123.79, 123.29, 117.90, 116.58, 103.86, 81.45, 80.49, 34.83, 34.75, 32.01, and 31.92 ppm; HR-MALDI-MS: m/z = 686.3697. calcd for $C_{48}H_{50}N_2S$: 686.3690 $[M]^+$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 311 (28600) and 373 nm (15500 mol^{-1}dm^{3}cm^{-1}).

Synthesis of 10: To a pyridine (10 mL) suspension of $Cu(OAc)_2$ (61.5 mg, 323 μmol) was added dropwise a toluene (50 mL) solution of **9** (23.0 mg, 33.5 μmol) for 2 h, and the mixture was stirred for further 4 days under air. After the solvents were removed under reduced pressure, the residue was passed through a silica gel column with CH_2Cl_2 and evaporated. The residue was separated by GPC to give **10** (14.4 mg, 21.1 μmol, 63%). ^{1}H NMR ($CDCl_3$) $\delta = 9.34$ (s, 2H, NH), 8.13 (d, $J = 1.7$ Hz, 2H, carbazole-H), 8.08 (d, $J = 1.5$ Hz, 2H, carbazole-H), 7.79 (d, $J = 1.8$ Hz, 2H, carbazole-H), 7.54 (d, $J = 1.8$ Hz, 2H, carbazole-H), 7.53 (s, 2H, thiophene), 1.53 (s, 18H, *t*-Bu), and 1.47 ppm (s, 18H, *t*-Bu); ^{13}C NMR $\delta = 143.47$, 142.89, 142.20, 140.10, 134.53, 126.52, 124.76, 123.81, 122.85, 122.54, 118.56, 117.13, 116.98, 103.73, 82.75, 79.79, 34.83, 34.88, 32.02, and 31.94 ppm; HR-MALDI-MS: m/z = 683.3494. calcd for $C_{48}H_{47}N_2S$: 683.3465 $[M\text{–}H]^-$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 320 (47900), 395 (20100), and 416 nm (28300 mol^{-1}dm^{3}cm^{-1}); Fluorescence (CH_2Cl_2, λ_{ex} = 360 nm) λ_{max} = 476 nm, Φ_F = 0.426.

Synthesis of 11a: A mesitylene (3.0 mL) solution of **10** (69.0 mg, 101 μmol), CuCl (21.1 mg, 213 μmol), and aniline (0.10 mL, 1.1 mmol) was heated at reflux in a schlenk tube under Ar for 21 h. After the solvent was removed under reduced pressure, the residue was separated over a silica gel column with CH_2Cl_2/hexane as an eluent to give **11a** (22.9 mg, 29.4 μmol, 29%). ^{1}H NMR ($CDCl_3$) $\delta = 8.96$ (s, 2H, NH), 8.08 (d, $J = 1.5$ Hz, 2H, carbazole-H), 8.05 (d, $J = 1.7$ Hz, 2H, carbazole-H), 7.68 (d, $J = 1.5$ Hz, 2H, carbazole-H), 7.57 (d, $J = 1.7$ Hz, 2H, carbazole-H), 7.37 (d, $J = 7.2$ Hz, 2H, Ph), 7.32 (s, 2H, thiophene), 6.87 (t, $J = 7.3$ Hz, 2H, Ph), 6.83 (t, $J = 7.9$ Hz, 1H, Ph), 6.48 (s, 2H, pyrrole-H), 1.53 (s, 18H, *t*-Bu), and 1.47 ppm (s, 18H, *t*-Bu); ^{13}C NMR $\delta = 143.18$, 142.93, 139.96, 138.25, 137.12, 136.35, 128.38, 126.84, 126.62, 126.53, 125.81, 125.24, 124.51, 122.83, 121.52, 117.41, 117.19, 116.98, 116.73, 113.34, 34.91, 34.83, 32.11, and 32.07 ppm; HR-MALDI-MS: m/z = 777.4089. calcd for $C_{54}H_{55}N_3S$: 777.4112 $[M]^+$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 301 (27300), and 378 nm (15600 mol^{-1}dm^{3}cm^{-1}); Fluorescence (CH_2Cl_2, λ_{ex} = 360 nm) λ_{max} = 451 nm, Φ_F = 0.290.

Synthesis of 11b: A mesitylene (3.0 mL) solution of **10** (63.2 mg, 92.3 μmol), CuCl (9.50 mg, 96.0 μmol), and butylamine (0.10 mL, 1.0 mmol) was heated at reflux in a schlenk tube under Ar for 16 h. After the solvent was removed under reduced pressure, the residue was separated over a silica gel column with CH_2Cl_2/hexane as an eluent to give **11b** (21.8 mg, 28.8 μmol, 31%). ^{1}H NMR ($CDCl_3$) $\delta = 9.06$ (s, 2H, NH), 8.13 (d, $J = 1.7$ Hz, 2H, carbazole-H), 8.12 (d, $J = 1.8$ Hz, 2H, carbazole-H), 7.69 (d, $J = 1.8$ Hz, 2H, carbazole-H), 7.64 (d, $J = 1.7$ Hz, 2H, carbazole-H), 7.36 (s, 2H, thiophene), 6.46 (s, 2H, pyrrole-H), 4.10 (t, $J = 6.7$ Hz, 2H, CH_2), 1.53 (s, 18H, *t*-Bu), 1.52 (s, 18H, *t*-Bu), 1.11 (m, 2H, CH_2), 0.74 (m, 2H, CH_2), and 0.40 ppm (t, $J = 7.5$ Hz, 3H, CH_3); ^{13}C NMR $\delta = 143.52$, 143.30, 139.97, 136.48, 135.99, 132.08, 125.73, 124.90, 124.43, 123.30, 121.63, 117.17, 117.00, 116.90, 116.19, 111.76, 46.33, 34.93, 34.91, 33.67, 32.10, 31.95, 18.98, and 13.34 ppm; HR-MALDI-MS: m/z = 756.4350. calcd for $C_{52}H_{58}N_3S$: 756.4356 $[M\text{–}H]^-$; UV/vis (CH_2Cl_2) λ_{max} (ε) = 299 (27400), and 383 nm (13200 mol^{-1}dm^{3}cm^{-1}); Fluorescence (CH_2Cl_2, λ_{ex} = 360 nm) λ_{max} = 463 nm, Φ_F = 0.289.

Synthesis of 11c: A mesitylene (5.0 mL) solution of **10** (102 mg, 149 μmol), CuCl (36.4 mg, 368 μmol), and trimethoxybenzylamine (197 mg, 1.00 mmol) was heated at reflux in a schlenk tube under Ar for 20 h. After the solvent was removed under reduced pressure, the residue was separated over a silica gel column with CH_2Cl_2 as an eluent to give **11c** (74.9 mg, 84.9 μmol, 57%). ^{1}H NMR ($CDCl_3$) $\delta = 9.17$ (s, 2H, NH), 8.16 (d, $J = 1.5$ Hz, 2H, carbazole-H), 8.15 (d, $J = 1.5$ Hz, 2H, carbazole-

H), 7.72 (d, J = 1.5 Hz, 2H, carbazole-H), 7.51 (d, J = 1.5 Hz, 2H, carbazole-H), 7.38 (s, 2H, thiophene), 6.49 (s, 2H, pyrrole-H), 5.63 (s, 2H, Ph), 5.19 (s, 2H, CH$_2$), 3.69 (s, 3H, OMe), 3.50 (s, 6H, OMe), 1.56 (s, 18H, *t*-Bu), and 1.50 ppm (s, 18H, *t*-Bu); ^{13}C NMR δ = 152.70, 143.85, 143.67, 140.08, 137.34, 136.80, 136.77, 136.17, 133.30, 125.74, 124.81, 124.68, 123.87, 121.64, 117.44, 117.21, 117.02, 116.46, 113.01, 104.85, 60.57, 55.84, 50.99, 34.99, 34.90, and 32.14 ppm; HR-MALDI-MS: m/z = 880.4510. calcd for $C_{58}H_{62}N_3O_3S$: 880.4517 [M–H]$^-$; UV/vis (CH$_2$Cl$_2$) λ_{max} (ε) = 301 (40100), and 384 nm (19300 mol^{-1}dm^{3}cm^{-1}); Fluorescence (CH$_2$Cl$_2$, λ_{ex} = 360 nm) λ_{max} = 463 nm, Φ_F = 0.356.

Synthesis of 12: A DMSO (15 mL) solution of **10** (14.4 mg, 21.1 μmol), selenium powder (10.4 mg, 132 μmol), N$_2$H$_4$·H$_2$O (43.2 mg, 853 μmol), and KOH (19.2 mg, 343 μmol) was heated at 100 ˚C for 20 h under Ar. After cooling to rt, the mixture was diluted with CH$_2$Cl$_2$, washed with water, and evaporated. The residue was separated over a silica gel column with CH$_2$Cl$_2$/hexane to give **12** (13.0 mg, 17.0 μmol, 81%) as a yellow solid. ^{1}H NMR (CDCl$_3$) δ = 10.10 (s, 2H, NH), 8.15 (d, J = 1.2 Hz, 2H, carbazole-H), 8.14 (d, J = 1.2 Hz, 2H, carbazole-H), 7.80 (d, J = 1.5 Hz, 2H, carbazole-H), 7.72 (d, J = 1.5 Hz, 2H, carbazole-H), 7.47 (s, 2H, thiophene or selenophene), 7.44 (s, 2H, selenophene or thiophene), 1.55 (s, 18H, *t*-Bu), and 1.54 ppm (s, 18H, *t*-Bu); ^{13}C NMR δ = 146.34, 143.16, 143.14, 139.94, 137.09, 135.29, 129.47, 125.96, 124.32, 123.75, 121.61, 121.38, 119.62, 117.22, 117.11, 116.93, 34.99, 34.97, 32.15, and 32.14 ppm; HR-MALDI-MS: m/z = 765.2759. calcd for $C_{48}H_{49}N_2SSe$: 765.2787 [M–H]$^-$; UV/vis (CH$_2$Cl$_2$) λ_{max} (ε) = 254 (54200), 315 (42300), and 396 nm (27100 mol^{-1}dm^{3}cm^{-1}); Fluorescence (CH$_2$Cl$_2$, λ_{ex} = 360 nm) λ_{max} = 455 nm, Φ_F = 0.030.

Synthesis of 13: To a dry CH$_2$Cl$_2$ (20 mL) solution of **12** (39.2 mg, 51.2 μmol) was added MnO$_2$ (178 mg 2.04 mmol) and the resulting suspension was stirred for 3 days, in the period of which second and third addition of MnO$_2$ (100 mg) was done after 1 day and 2 day, respectively. The mixture was passed through a pad of celite. Evaporation of the solvent and recrystallization of the residue with CHCl$_3$ provided **13** (9.26 mg, 12.1 μmol, 24%) as a green solid.[18] ^{1}H NMR (CDCl$_3$) δ = 10.09 (s, 2H, selenophene), 9.74 (s, 2H, thiophene), 9.50 (s, 2H, carbazole-H), 9.32 (s, 2H, carbazole-H), 8.86 (s, 4H, carbazole-H), 1.87 (s, 18H, *t*-Bu), and 1.85 ppm (s, 18H, *t*-Bu); ^{13}C NMR δ = 154.55, 153.49, 149.53, 148.38, 142.64, 132.90, 131.99, 130.42, 127.78, 125.95, 124.99, 124.18, 122.57, 121.69, 120.45, 119.80, 38.47, 36.26, 32.12, and 31.59 ppm; HR-MALDI-MS: m/z = 764.2683. calcd for $C_{48}H_{48}N_2SSe$: 764.2708 [M]$^-$; UV/vis/NIR (CH$_2$Cl$_2$) λ_{max} (ε) = 261 (47200), 294 (26900), 321 (31500), 353 (42200), 391 (45500), 839 (44800), 940 (18300), and 1064 nm (45500 mol^{-1}dm^{3}cm^{-1}).

Acknowledgement

This work was supported by Grant-in-Aid for Young Scientists [No. 23750231] from MEXT, Japan. We thank Prof. A. Osuka, Dr. T. Tanaka, and Mr. H. Mori (Kyoto University) for X-ray diffraction analysis and measurements of the absolute fluorescence quantum yields. 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] *Present address: Division of Chemistry and Biotechnology, 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: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Crystallographic data for **10**: formula: 2(C$_{46}$H$_{46}$N$_4$S$_2$)CHCl$_3$, M_w = 1489.26, triclinic, space group P-1, a = 15.7704(9), b = 17.0399(9), c = 17.7847(9) Å, α = 82.2120(10), β = 72.642(2), γ = 85.179(2)˚, V = 4514.7(4) Å^3, Z = 2, ρ_{calcd} = 1.096 gcm^{-3}, T = –183 °C, 35820 measured reflections, 15761 unique reflections (R_{int} = 0.0315), R_1 = 0.0642 ($I > 2\sigma(I)$), wR_2 = 0.1934 (all data), GOF = 1.106. CCDC 953495 **10** contains the supplementary crystallographic data for this paper. The contribution to the scattering arising from the presence of disordered solvents in the crystals was removed by use of the utility SQUEEZE in the PLATON software package.[19]

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*) 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.

3 (*a*) G. Sedghi, K. Sawada, L. J. Esdaile, M. Hoffmann, H. L. Anderson, D. Bethell, W. Haiss, S. J. Higgins and R. J. Nichols, *J. Am. Chem. Soc.*, 2008, **130**, 8582; (*b*) A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diau, C.-Y. Yeh, S. M. Zakeeruddin and M. Grätzel, *Science*, 2011, **334**, 629; (c) T. Ema, Y. Miyazaki, T. Taniguchi and J. Takada, *Green Chem.*, 2013, **15**, 2485.

4 (*a*) V. S.-Y. Lin, S. G. DiMagno and M. J. Therine, *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.

5 (*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.

6 (*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, 5939.

7 (*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.

8 (*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.

9 (*a*) J. V. Grazulevicius, P. Strohriegl, J. Pielichowski and K. Pielichowski, *Prog. Polym. Sci.*, 2003, **28**, 1297; (*b*) J. F. Morin, M. Leclere, D. Ades and A. Siove, *Macromol. Rapid Commun.*, 2005, **26**, 761; (*c*) N. Blouin and M. Leclerc, *Acc. Chem. Res.*, 2008, **41**, 1110.

10 (*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, 970; (*c*) L. Arnold, M. Baumgarten and K. Müllen, *Chem. Commun.*, 2012, 9640.

11 Carbazole-based porphyrins were formed as a consequence of Bergman cyclization of *β,β'*-diethynylated porphyrins; (*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.

12 (*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.

13 M. S. Mudadu, A. N. Singh and R. P. Thummel, *J. Org. Chem.*, 2008, **73**, 6513.

14 The low yields of **11a** and **11b** were due to the unstability.

15 For the transformation of 1,3-butadiyne to selenophene, see: (*a*) V. A. Potapov, S. V. Amosova, I. V. Dorońkina and S. V. Zinchenko, *Sulfur Lett.*, 2001, **24**, 275; (*b*) K. J. Lie, S. F. Marcel and Y. K. Cheung, *J. Chem. Res., Synop.*, 1993, 392; (*c*) S. Inoue, T. Jigami, H. Nozoe, Y. Aso, F. Ogura and T. Otsubo, *Heterocycles*, 2000, **52**, 159.

16 For examples of 21-selena-23-thiaporphyrins, see: (*a*) A. Ulman, J. Manassen, F. Frolow and D. Rabinovich, *J. Am. Chem. Soc.*, 1979, **101**, 7055; (*b*) L. Latos-Grażyński, E. Pacholska, P. J. Chmielewski, M. M. Olmstead and A. L. Balch, *Inorg. Chem.*, 1996, **35**, 566; (*c*) D. G. Hilmey, M. Abe, M. I. Nelen, C. E. Stilts, G. A. Baker, S. N. Baker, F. V. Bright, S. R. Davies, S. O. Gollnick, A. R. Oseroff, S. L. Gibson, R. Hilf and M. R. Detty, *J. Med. Chem.*, 2002, **45**, 449.

17 M. J. Frisch, *et al. GAUSSIAN 9 (Revision C.01)*, Gaussian, Inc.: Wallingford CT, PA, 2009.

18 The solubility of **13** is much lower than that of **12**, and unreacted **12** was removed by recrystallization.

19 (*a*) A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*; Utrecht, The Netherlands, 2005; (*b*) P. van der Sluis and A. L. Spek, *Acta Crystallogr. Sect. A*, 1990, **46**, 194.