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Synthesis of carbazole-based hetero-coremodified porphyrins†

Chihiro Maeda,*‡ Motoki Masuda and Naoki Yoshioka*

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 ¹H 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 the natural photosynthetic system and applications to optical devices, 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 materials² 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 results 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 interesting possibilities.^{10–12} Sessler and

Department of Applied Chemistry, Faculty of Science and Technology, Keio University, Kohoku-ku, Yokohama 223-8522, Japan

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 a 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,e} This double annulation reaction represents an alternative porphyrin synthesis and is a useful means of obtaining 21,23homo-core-modified porphyrins, although syntheses of 21,23hetero-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.

[†]Electronic supplementary information (ESI) available. CCDC 953495. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c30b42564a

[‡]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.

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-dibromocarbazole¹³ 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. Highresolution matrix-assisted-laser-desorption-ionization time-offlight (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



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.

unambiguously provided the structure of **10**, shown in Fig. 1.§ The mean plane deviation of the macrocycle is 0.210 Å, indicating a highly planar structure. Importantly, **10** could not be obtained directly from **1**.

Following the synthesis of 10, its annulation reactions were examined. A mesitylene solution of 10, aniline (10 equiv.), and CuCl (2 equiv.) was heated 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 C₅₄H₅₅N₃S: 777.4112 [M]⁺). X-ray diffraction analysis provided a preliminary structure for 11a, shown in Fig. S13 (ESI).[†] A similar annulation reaction of **10** with butylamine or 3,4,5-trimethoxybenzylamine resulted in the corresponding 2,5-pyrrolylene-bridged carbazoles **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 $C_{48}H_{49}N_2SSe: 765.2787 [M - H]^{-}$).

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



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

§ Crystallographic data for **10**: formula: 2(C₄₆H₄₆N₄S₂)CHCl₃, *M*_w = 1489.26, triclinic, space group *P*Ī, *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) Å³, *Z* = 2, *ρ*_{calcd} = 1.096 g cm⁻³, *T* = -183 °C, 35 820 measured reflections, 15 761 unique reflections (*R*_{int} = 0.0315), *R*₁ = 0.0642 (*I* > 2*σ*(*I*)), w*R*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

Commonwead	$\lambda_{\mathrm{A}}\left(\mathrm{nm} ight)$	$\lambda_{\mathrm{F}}^{a}(\mathrm{nm})$	${\Phi_{ m F}}^b$
Compound			
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
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

^{*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 CH₂Cl₂.

12 are almost similar. Thus, the spectra of these isophlorines are exhibited primarily 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.

The 2,5-pyrrolylene-bridged cyclic carbazole dimers 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 MnO2 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 ¹H 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



Scheme 3 Synthesis of 13



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

-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).

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 ¹H NMR results, suggest charge transfer from Se to S. Nuclear independent chemical shift (NICS) values at the center of 5, 6, and 13 were calculated to be -10.8, -14.1, and -12.2 ppm, respectively, indicating that 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-coremodified porphyrins *via* a 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** exhibit 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 is currently underway in our laboratory.

Experimental

General

¹H and ¹³C NMR spectra were recorded on a JEOL ECA-500 spectrometer, and chemical shifts were reported as the delta scale in ppm as an internal reference (δ = 7.260 for ¹H NMR, 77.00 for ¹³C NMR, for CDCl₃). 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 the 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 CH₂Cl₂). MALDI-TOF mass spectra were recorded on a Bruker microTOF. Redox potentials were measured by the cyclic voltammetry method using an ALS electrochemical analyzer model 6102B. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Dry CH₂Cl₂ and toluene were distilled from CaH₂.

Synthesis of 7. A dry toluene (10 mL) solution of 1,8dibromo-3,6-di-tert-butylcarbazole (1.30 g, 2.97 mmol), 2,5-bis-(tributylstannyl)thiophene (251 mg, 379 µmol), and Pd(PPh₃)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 CH2Cl2hexane as an eluent to give 7 (117 mg, 146 µmol, 39%). ¹H NMR (CDCl₃) δ = 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); ¹³C NMR (CDCl₃) δ = 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 C₄₄H₄₈N₂SBr₂: 796.1879 $[M]^+$; UV/vis (CH₂Cl₂) λ_{max} (ε) = 303 (40700) and $370 \text{ nm} (24\ 000\ \text{mol}^{-1}\ \text{dm}^3\ \text{cm}^{-1}).$

Synthesis of 8. A dry toluene (10 mL) solution of 7 (117 mg, 146 μmol), tributyl(trimethylsilylethynyl)tin (206 mg. 531 μ mol), and Pd(PPh₃)₄ (10.0 mg, 8.65 μ mol) 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 CH₂Cl₂-hexane as an eluent to give 8 (97.5 mg, 117 μ mol, 80%). ¹H NMR (CDCl₃) δ = 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); ¹³C 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 (CH₂Cl₂) λ_{max} (ε) = 280 (30800), 313 $(30\ 100)$, and 375 nm $(18\ 100\ mol^{-1}\ dm^3\ cm^{-1})$.

Synthesis of 9. Tetrabutylammonium fluoride (260 μL, 1 M in THF) was added to a CH₂Cl₂ 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 CH₂Cl₂ to give **9** (76.5 mg, 112 μmol, 95%). ¹H NMR (CDCl₃) δ = 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); ¹³C NMR (CDCl₃) 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 C₄₈H₅₀N₂S: 686.3690 [M]⁺; UV/vis (CH₂Cl₂) λ_{max} (ε) = 311 (28 600) and 373 nm (15 500 mol⁻¹ dm³ 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 CH₂Cl₂ and evaporated. The residue was separated by GPC to give 10 (14.4 mg, 21.1 μ mol, 63%). ¹H NMR (CDCl₃) δ = 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); ¹³C NMR δ = 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 - H]⁻; UV/vis (CH₂Cl₂) λ_{max} (ε) = 320 (47 900), 395 (20 100), and 416 nm (28 300 mol⁻¹ dm³ cm⁻¹); fluorescence (CH₂Cl₂, 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 μ mol), CuCl (21.1 mg, 213 μ mol), 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 CH₂Cl₂-hexane as an eluent to give 11a (22.9 mg,

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29.4 μmol, 29%). ¹H NMR (CDCl₃) δ = 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); ¹³C NMR δ = 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 C₅₄H₅₅N₃S: 777.4112 [M]⁺; UV/vis (CH₂Cl₂) $\lambda_{max}(\varepsilon)$ = 301 (27 300), and 378 nm (15 600 mol⁻¹ dm³ cm⁻¹); fluorescence (CH₂Cl₂, λ_{ex} = 360 nm) λ_{max} = 451 nm, $\Phi_{\rm F}$ = 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 CH₂Cl₂-hexane as an eluent to give 11b (21.8 mg, 28.8 μ mol, 31%). ¹H NMR (CDCl₃) δ = 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, CH₂), 1.53 (s, 18H, t-Bu), 1.52 (s, 18H, t-Bu), 1.11 (m, 2H, CH₂), 0.74 (m, 2H, CH₂), and 0.40 ppm (t, J = 7.5 Hz, 3H, CH₃); ¹³C 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 - H]⁻; UV/vis $(CH_2Cl_2) \lambda_{max} (\varepsilon) = 299 (27400)$, and 383 nm (13200 mol⁻¹ dm³ cm⁻¹); fluorescence (CH₂Cl₂, $\lambda_{ex} = 360$ nm) $\lambda_{max} = 463$ nm, $\Phi_{\rm F} = 0.289$.

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 μ mol, 57%). ¹H NMR (CDCl₃) δ = 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, CH₂), 3.69 (s, 3H, OMe), 3.50 (s, 6H, OMe), 1.56 (s, 18H, *t*-Bu), and 1.50 ppm (s, 18H, *t*-Bu); ¹³C 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 C₅₈H₆₂N₃O₃S: 880.4517 [M - H]⁻; UV/vis (CH₂Cl₂) $\lambda_{\rm max}$ (ε) = 301 (40 100), and 384 nm (19 300 mol⁻¹ dm³ cm⁻¹); fluorescence (CH₂Cl₂, 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 μ mol), selenium powder (10.4 mg, 132 μ mol), N₂H₄·H₂O (43.2 mg, 853 μ mol), and KOH (19.2 mg, 343 μ mol) was heated at 100 °C for 20 h under Ar. After cooling to rt, the mixture was

diluted with CH₂Cl₂, washed with water, and evaporated. The residue was separated over a silica gel column with CH₂Cl₂-hexane to give **12** (13.0 mg, 17.0 µmol, 81%) as a yellow solid. ¹H NMR (CDCl₃) 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); ¹³C 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 C₄₈H₄₉N₂SSe: 765.2787 [M – H]⁻; UV/vis (CH₂Cl₂) λ_{max} (ε) = 254 (54 200), 315 (42.300), and 396 nm (27 100 mol⁻¹ dm³ cm⁻¹); fluorescence (CH₂Cl₂, λ_{ex} = 360 nm) λ_{max} = 455 nm, $\Phi_{\rm F}$ = 0.030.

Synthesis of 13. To a dry CH₂Cl₂ (20 mL) solution of 12 $(39.2 \text{ mg}, 51.2 \mu \text{mol})$ was added MnO₂ (178 mg 2.04 mmol) and the resulting suspension was stirred for 3 days, in the period of which the second and third addition of MnO₂ (100 mg) was done after 1 day and 2 days, respectively. The mixture was passed through a pad of celite. Evaporation of the solvent and recrystallization of the residue with CHCl₃ provided 13 (9.26 mg, 12.1 µmol, 24%) as a green solid.¹⁸ ¹H NMR $(CDCl_3) \delta = 10.09$ (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); ¹³C 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 (CH₂Cl₂) λ_{max} (ϵ) = 261 (47 200), 294 (26 900), 321 (31 500), 353 (42 200), 391 (45 500), 839 (44 800), 940 (18 300), and 1064 nm (45 500 mol⁻¹ dm³ cm⁻¹).

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