

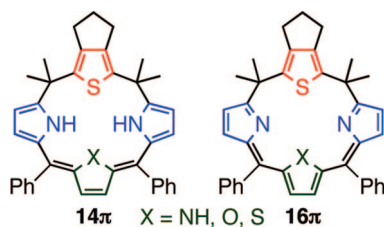
Synthesis of Thiophene-Containing Hybrid Calixphyrins of the 5,10-Porphodimethene Type

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The synthesis, structure, and optical and electrochemical properties of thiophene-containing hybrid calixphyrins are reported. The 5,10-porphodimethene type 14π- and 16π-S,N₂X-hybrid calixphyrins (X = NH, O, S) were prepared by acid-promoted dehydrative condensation between a thia-tripyrane and the corresponding 2,5-bis[hydroxy(phenyl)methyl]heteroles followed by DDQ oxidation. Both crystallographic and spectroscopic analyses of the newly prepared hybrid calixphyrins have revealed that the combination of heteroles explicitly influences the electronic structures of the π-conjugated framework. The 14π-S,N₂X-hybrid calixphyrins have proven to be fluorescent in solution.

Calixphyrins,¹ one of the porphyrin analogues involving both sp²- and sp³-hybridized bridging *meso* carbon atoms, possess reasonably flexible frameworks as well as rather rigid π-conjugated networks, and are distinguishable from porphyrins and calixpyrroles. Several research groups have established convenient methods for the synthesis of various calixphyrins and utilized their characteristic properties in host–guest chemistry and coordination chemistry.^{2–5} To our knowledge, however, most of the reported examples are concerned with parent

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(1) The term *calixphyrin* was proposed by Sessler and co-workers to describe the family of porphomethene, porphodimethene, porphotrimethene, and their expanded analogues in a generic sense. Král, V.; Sessler, J. L.; Zimmerman, R. S.; Seidel, D.; Lynch, V.; Andrioletti, B. *Angew. Chem., Int. Ed.* **2000**, *39*, 1055–1058.

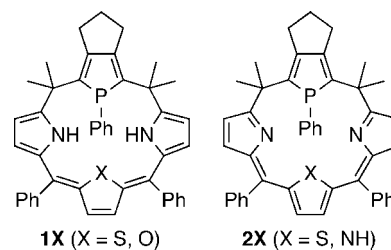


FIGURE 1. P,N₂X-Hybrid calixphyrins.

calixphyrins made up of only pyrroles, and little information is available for core-modified derivatives.⁶ Chemical modification at the core-nitrogen atoms, namely replacing the pyrrole ring by other heteroles or carbocycles, is a well-known approach to provide the porphyrin ring with unprecedented optical, electrochemical, and structural properties.⁷ In this regard, we set out to systematically investigate the chemistry of core-modified (hybrid) calixphyrins and reported the first examples of phosphole-containing hybrids **1X** and **2X** (Figure 1), which exhibited characteristic coordination behavior derived from both the phosphole ring and the π-conjugated pyrrole–heterole–pyrrole (N–X–N) subunits.⁸ To shed light on the role of the sp³-carbon-bridged heterole ring in coordination chemistry, we turned our attention to thiophene as a new component for the hybrid

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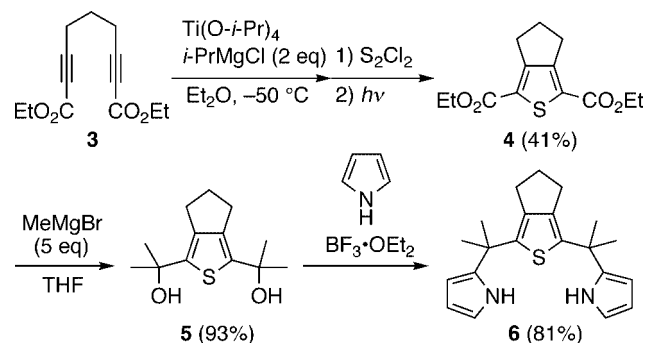
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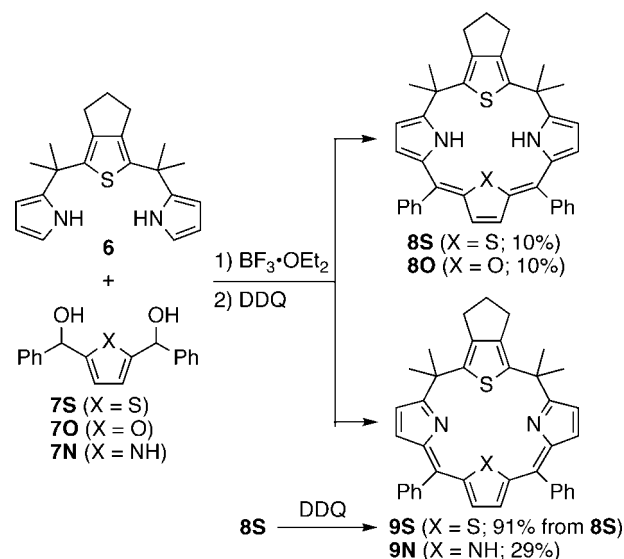
SCHEME 1. Synthesis of Thiatripyrrane 6 from Diyne 3



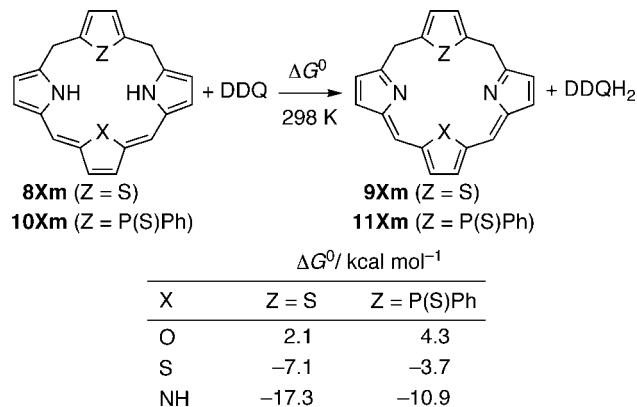
calixphyrin platform. Here, we report the first examples of thiophene-containing hybrid calixphyrins of the 5,10-porphodimethene type. In this study, we aimed at revealing the effects of the π -conjugated N–X–N subunits on the fundamental properties and coordinating ability of the S,N_2,X -hybrid calixphyrins.

Scheme 1 illustrates the three-step synthesis of thiatripyrrane 6, which is a key precursor for thiophene-containing hybrid calixphyrins. According to Block's method,⁹ diethyl nona-2,7-diyne-1,9-dicarboxylate (**3**)¹⁰ was converted to 2,5-bis(ethoxycarbonyl)thiophene bearing a fused C_3 backbone (**4**) in 41% yield by sequential treatment with (i) (η^2 -propene)Ti(*o*-i-Pr)₂, generated in situ from Ti(*o*-i-Pr)₄ and 2 equiv of *i*-PrMgCl,¹¹ (ii) disulfur dichloride, and (iii) UV–vis light (<300 nm).¹² Reaction of **4** with 5 equiv of methylmagnesium bromide in THF gave 2,5-bis(1-hydroxy-1-methylethyl)thiophene (**5**) in 93% yield. Diol **5** reacted with excess pyrrole in the presence of $BF_3 \cdot OEt_2$ to afford a mixture of condensation products, from which thiatripyrrane **6** was isolated in 81% yield by silica gel column chromatography.

Scheme 2 depicts the synthesis of thiophene-containing hybrid calixphyrins. Acid-promoted dehydrative condensation of **6** with 2,5-bis[hydroxy(phenyl)methyl]thiophene (**7S**),¹³ followed by oxidation with 2.2 equiv of DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) produced a mixture including two types of S_2,N_2 -hybrid calixphyrins **8S** and **9S**. TLC analysis of the crude reaction mixture indicated that **9S** was a predominant product of this condensation. However, all attempts to isolate **9S** from the reaction mixture resulted in its decomposition, and a small amount of **8S** was isolated by column chromatography. Hence, **9S** was independently prepared by the DDQ oxidation of **8S** in CH_2Cl_2 . On the basis of the oxidation states of the π -conjugated N–S–N units, **8S** is classified as the 2e-oxidized product and **9S** as the 4e-oxidized product (hereafter, **8X** and **9X** are denoted as 14 π -hybrids and 16 π -hybrids, respectively). A similar condensation of **6** with 2,5-bis[hydroxy(phenyl)methyl]furan

SCHEME 2. Synthesis of S,N_2,X -Hybrid Calixphyrins 8X and 9X

SCHEME 3. Gibbs Free Energy Changes of DDQ Oxidation of 8Xm and 10Xm at 298 K



(**7O**)¹⁴ afforded the 14 π - S,N_2,O -hybrid **8O** as a sole isolable product. Treatment of **8O** with excess DDQ in CH_2Cl_2 afforded a complex mixture, while the condensation of **6** with 2,5-bis[hydroxy(phenyl)methyl]pyrrole (**7N**)¹⁵ gave the 16 π - S,N_3 -hybrid **9N** in 29% yield. The observed **8X/9X** selectivities imply that the electronic nature of the central heteroles intrinsically determines the oxidation states of the π -conjugated N–X–N units in the S,N_2,X -hybrid calixphyrins.¹⁶

To identify a driving force for converting **8X** to **9X**, we evaluated Gibbs free energy change (ΔG^0) of DDQ oxidation of 14 π - S,N_2,X -hybrid models **8Xm** to the corresponding 16 π - S,N_2,X -hybrid models **9Xm** by the DFT method with B3LYP functional, wherein the solvation effect was treated with the PCM method (for details, see the Supporting Information). The optimized structures, selected bond parameters, and natural atomic charges of **8Xm** and **9Xm** are summarized in Figures S1–S3 in the Supporting Information. As shown in Scheme 3, the formation of **9Om/DDQH₂** ($DDQH_2 = 2,3$ -dichloro-5,6-

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dicyanohydrobenzoquinone) from **8Om/DDQ** yields positive energy ($\Delta G^0 = 2.1 \text{ kcal mol}^{-1}$). On the other hand, the formation of **9Nm/DDQH₂** from **8Nm/DDQ** yields large negative energy ($\Delta G^0 = -17.3 \text{ kcal mol}^{-1}$). The reaction energy calculated for the oxidation of **8Sm** to **9Sm** is also negative ($\Delta G^0 = -7.1 \text{ kcal mol}^{-1}$). Thus, the DDQ oxidation of **8Om** is thermodynamically unfavorable, whereas those of **8Nm** and **8Sm** are favorable. The above theoretical results reasonably explain the experimentally observed **8X/9X** selectivity, which may arise from the repulsive or attractive electrostatic interactions between the core heteroatoms and the pyrrole NH groups. Note that the reaction energies calculated for the S,N₂X-hybrid models are lower by 2.2–6.4 kcal mol⁻¹ than those calculated for the corresponding *o*⁴-P,N₂X-hybrid models **10Xm** and **11Xm** at the same level of theory (Figures S4 and S5 in the Supporting Information).¹⁷ Presumably, the P–S···H–N electrostatic interaction in **10Xm** and **11Xm** contributes to the stabilization of their 14 π platforms.

The newly prepared hybrid calixphyrins **8X** and **9X** were characterized by conventional spectroscopic techniques. The ¹H NMR spectra of **8S** and **8O** in CDCl₃ displayed β protons of the π -conjugated heterole rings at δ 5.79–6.07 (pyrrole- β), δ 6.36 (thiophene- β of **8S**), and δ 5.19 (furan- β of **8O**). The β protons of **9S** and **9N** appeared at relatively lower fields: δ 6.67–6.71 (2-azafluvene- β), δ 6.61 (thiophene- β of **9S**), and δ 6.02 (pyrrole- β of **9N**). Evidently, the difference in the π -conjugation modes at the N–X–N units is reflected in their ¹H chemical shifts. The pyrrole NH protons of **8S**, **8O**, and **9N** were observed at δ 8.57, 8.84, and 11.49, respectively, which are comparable to the corresponding NH chemical shifts of the P,N₂X-counterparts **1S**, **1O**, and **2N**.

The crystal structure of **8S** was unambiguously determined by X-ray diffraction analysis.¹⁸ As shown in Figure 2a, **8S** possesses a slightly twisted N–S–N unit, where dihedral angles between the thiophene and pyrrole rings are 13.5° and 17.0°. The sp³-carbon-bridged thiophene ring stands against a mean plane formed by the four *meso* carbon atoms with dihedral angles of 72.7°. The observed conformation of the 14 π -S₂N₂-hybrid **8S** differs largely from that of the previously reported 14 π -P,N₂O-hybrid **1O**, which exhibits a highly twisted conformation. This may be ascribed to the difference in sizes of central heteroles incorporated in their π -conjugated N–X–N subunits; i.e., the distance between two sp² *meso* carbons of **8S** (5.26 Å) is appreciably larger than that of **1O** (4.83 Å). The carbon–carbon bond alternation at the heterole rings and the inter-ring bridges is a good index for evaluating the π -conjugated structure of the N–X–N unit in hybrid calixphyrins.⁸ As summarized in Figure 2b, the carbon–carbon bond lengths at *ff'* and *h/h'* are longer by 0.07–0.09 Å than those at *g/g'* and *i*. The observed bond alternation is in good accordance with the canonical structure of the 14 π -S,N₂X-hybrid **8X** illustrated in Scheme 2.

The thiophene-containing hybrid calixphyrins **8X** and **9X** are orange or red solids, soluble in CHCl₃, CH₂Cl₂, THF, and toluene (Figure 3). In the UV–vis absorption spectra of **8X** and **9X** in CH₂Cl₂, broad absorptions due to π – π^* transitions

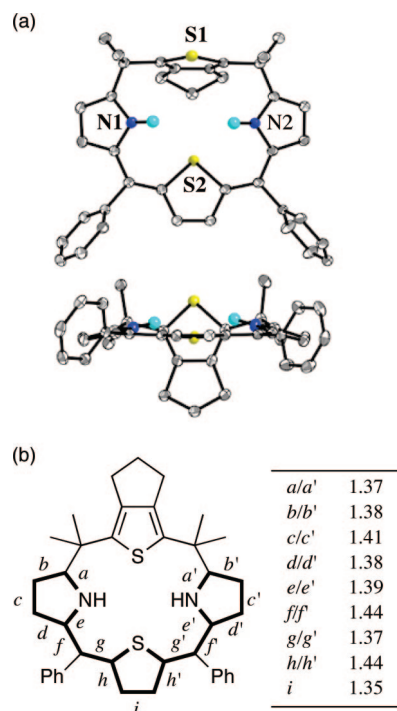


FIGURE 2. (a) Top and side views of **8S** (50% probability ellipsoids): gray (C), blue (N), red (O), orange (P), sky blue (H). Hydrogen atoms (except for NH) and solvents are omitted for clarity. N1···N2, 4.99 Å; S1···S2, 4.57 Å. (b) Average bond lengths (Å) of the π -conjugate N–S–N unit.

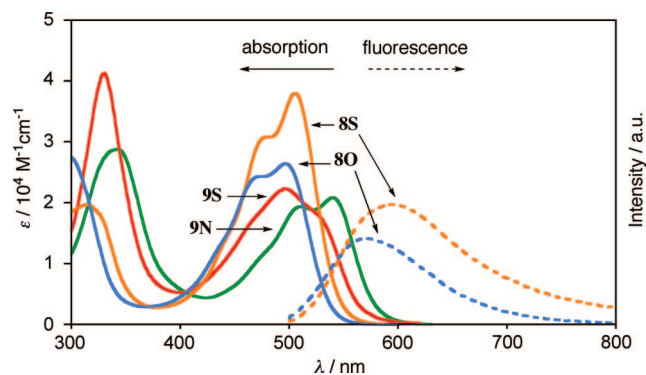


FIGURE 3. UV–vis absorption and emission spectra of thiophene-containing hybrid calixphyrins: blue, **8O**; orange, **8S**; red, **9S**; green, **9N**. Excitation wavelength for emission spectra is 480 nm.

were observed at around 400–600 nm. The 16 π -conjugated hybrids **9N** and **9S** showed the transitions at longer wavelengths as compared to those of the 14 π -conjugated hybrids **8O** and **8S**. Note that hybrids **8O** and **8S** are weakly fluorescent in solution, emitting an orange light at around 500–850 nm ($\Phi_f = 0.1\%$ for **8O** and 0.2% for **8S** in CH₂Cl₂, determined by a calibrated integrating sphere system). Such emission was not observed for the 16 π -S,N₂X-hybrids **9X** and the P,N₂X-hybrids **1X** and **2X**.

Redox potentials of **8X** and **9X** were measured by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). As depicted in Figure S6 in the Supporting Information, 14 π -S,N₂X-hybrids **8X** showed two reversible oxidation processes. The observed oxidation potentials of **8S** ($E_{\text{ox},1}/E_{\text{ox},2} = +0.38/+0.53 \text{ V vs Fc}^*/\text{Fc}^{*+}$; Fc* = decamethylferrocene) are comparable to those of the previously reported σ^3 -P,N₂S-hybrid **1S** ($E_{\text{ox},1}/E_{\text{ox},2} = +0.34/+0.54 \text{ V vs Fc}^*/\text{Fc}^{*+}$), suggesting that the

(17) In ref 8b, we reported the reaction energies from **10Xm** to **11Xm** calculated without the solvation effect. The conclusion does not change at all.

(18) **6S**: C₃₉H₃₆N₂S₂, monoclinic, *P*₂/*n*, *a* = 16.836(7) Å, *b* = 9.804(4) Å, *c* = 18.711(7) Å, β = 98.518(5)°, *V* = 3055(2) Å³, *Z* = 4, *D_c* = 1.298 g cm⁻³, 6990 independent, 389 variables, *R* = 0.0728 (*I* > 2.00 σ (*I*)), *wR* = 0.1229, *GOF* = 1.025. Attempts to grow high-quality single crystals of other S,N₂X-hybrids have been unsuccessful so far.

sp³-carbon-bridged heteroles (thiophene and *o*³-phosphole) make similar electronic effects on the redox properties of the N–S–N subunit. The 14π-S,N₂O-hybrid **8O** also displayed reversible voltammograms at almost the same region ($E_{\text{ox},1}/E_{\text{ox},2} = +0.35/+0.54$ V vs Fc*/Fc*⁺). These results indicate that the electrochemical oxidation of **8X** occurs at the π-conjugated N–X–N units. On the other hand, the 16π-S,N₂X-hybrids **9X** did not show any oxidation waves in this region (0 to +1.2 V vs Fc*/Fc*⁺) but displayed irreversible or quasireversible reduction waves at ca. –0.6 to –0.9 V (see Figure S6 in the Supporting Information).

In sharp contrast to the P,N₂X-hybrids **1X** and **2X**, the S,N₂X-hybrids **8X** and **9X** did not form stable metal complexes with nickel, palladium, and rhodium. Thus, the reactions of **8S/9S** with Ni(OAc)₂, Pd(OAc)₂, Pd(dba)₂, and [RhCl(CO)₂]₂ resulted in recovery or decomposition of the free bases, and no metal complex could be isolated. These results imply that the coordinating ability of the hybrid calixphyrins is closely related to the intrinsic character of the heteroatom center in the sp³-carbon-bridged heterole ligands. That is, the phosphole in **1X/2X** can coordinate to various transition metals as P ligand, whereas the thiophene in **8X/9X** would not possess a sufficient donating ability at the sulfur center to bind the above metals tightly in the core.

In summary, we have successfully prepared 5,10-porphodimethene-type thiophene-containing hybrid calixphyrins and disclosed their structure, fundamental properties, and coordinating ability for the first time. Similar to the P,N₂X-hybrids, the S,N₂X-hybrid calixphyrins exhibit characteristic optical and electrochemical properties, which vary widely depending on the exquisite combination of heteroles in the redox active π-conjugated N–X–N subunits.

Experimental Section

8S. To a degassed solution of **6** (170 mg, 0.5 mmol) and **7S** (150 mg, 0.5 mmol) in CH₂Cl₂ (250 mL) was added BF₃·OEt₂ (0.071 mL, 0.50 mmol), and the mixture was stirred for 1 h at room temperature, followed by addition of DDQ (250 mg, 1.1 mmol). After stirring for an additional 1 h, a saturated aqueous Na₂CO₃ solution (200 mL) was poured into the reaction mixture. The organic phase was separated, washed with aq Na₂CO₃ (100 mL × 3) and brine (200 mL), dried over Na₂SO₄, and evaporated. The residue was subjected to silica gel column chromatography (hexane/CH₂Cl₂ = 3/2). The orange fraction (*R_f* 0.5) was collected, evaporated, and washed with cold hexane at –78 °C to afford **8S** as an orange solid (30 mg, 10%). Mp 220 °C dec; ¹H NMR (CDCl₃, 400 MHz) δ 1.78 (s, 12H), 2.20 (quin, 2H, *J* = 6.8 Hz), 2.31 (t, 4H, *J* = 6.8 Hz), 5.79 (m, 2H), 6.07 (m, 2H), 6.36 (s, 2H), 7.25–7.45 (m, 10H), 8.57 (br s, 2H); ¹³C{¹H} NMR (C₆D₆, 75 MHz) δ 27.9, 30.1, 32.1, 38.4, 105.6, 115.0, 123.2, 131.3, 131.4, 131.7, 134.1, 135.0, 140.4, 142.5, 148.0; IR (KBr) ν_{max} 3417 (NH) cm^{–1}; UV–vis (CH₂Cl₂) λ_{max} (ε) 313 (19800), 480 (sh, 30800), 505 (38000); HRMS (EI)

calcd for C₃₉H₃₆N₂S₂ (M⁺) *m/z* 596.2320, found *m/z* 596.2321. Two of the carbons could not be detected clearly in the ¹³C NMR.

8O. This compound was prepared from **6** and **7O** according to a similar procedure described for **8S**. After silica gel column chromatography (hexane/CH₂Cl₂ = 2:1, *R_f* 0.4) and subsequent reprecipitation from cold hexane at –78 °C, **8O** was obtained as an orange solid (10%). Mp 245 °C dec; ¹H NMR (CDCl₃, 400 MHz) δ 1.74 (br s, 12H), 2.30 (quin, 2H, *J* = 6.8 Hz), 2.62 (t, 4H, *J* = 6.8 Hz), 5.19 (br, 2H), 6.02 (br, 4H), 7.20–7.50 (m, 10H), 8.84 (br s, 2H); ¹³C{¹H} NMR (C₆D₆, 100 MHz) δ 28.2, 30.2, 31.1, 38.5, 105.6, 108.9, 113.3, 125.9, 127.8, 131.3, 132.3, 140.9, 144.0, 145.0, 153.9; IR (KBr) ν_{max} 3432, 3455 (NH) cm^{–1}; UV–vis (CH₂Cl₂) λ_{max} (ε) 472 (sh, 24200), 496 (26400); HRMS (EI) calcd for C₃₉H₃₆ON₂S (M⁺) *m/z* 580.2548, found *m/z* 580.2551. Two of the carbons could not be detected clearly in the ¹³C NMR spectrum.

9S. To a solution of **8S** (12 mg, 0.020 mmol) in 3 mL of CH₂Cl₂ was added DDQ (5.0 mg, 0.022 mmol). The resulting mixture was directly subjected to short silica gel column chromatography (CH₂Cl₂/acetone = 10/1). The red fraction was collected, evaporated, and washed with cold hexane at –78 °C to afford **9S** as a red solid (11 mg, 91%). In solution, **9S** gradually decomposed within 1 day at room temperature. Mp 130 °C dec; ¹H NMR (CDCl₃, 400 MHz) δ 1.77 (s, 12H), 2.26 (quin, 2H, *J* = 7.0 Hz), 2.53 (t, 4H, *J* = 7.0 Hz), 6.61 (s, 2H), 6.67 (d, 2H, *J* = 4.6 Hz), 6.70 (s, 2H, *J* = 4.6 Hz), 7.30–7.45 (m, 10H); ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 28.4, 28.7, 31.0, 41.2, 126.1, 127.7, 128.3, 130.6, 133.7, 135.6, 136.4, 139.0, 145.6, 156.6, 179.1; UV/vis (CH₂Cl₂) λ_{max} (ε) 330 (41300), 496 (22100); HRMS (EI) calcd for C₃₉H₃₄N₂S₂ (M⁺) *m/z* 594.2163, found *m/z* 594.2165. Two of the carbons could not be detected clearly in the ¹³C NMR spectrum.

9N. This compound was prepared from **6** and **7N** according to a similar procedure described for **8S**. After silica gel column chromatography (CH₂Cl₂/acetone = 5:1, *R_f* 0.5) and subsequent reprecipitation from cold hexane at –78 °C, **9O** was obtained as a wine red solid (29%). Mp 170 °C dec; ¹H NMR (CDCl₃, 400 MHz) δ 1.79 (s, 12H), 2.28 (quin, 2H, *J* = 7.0 Hz), 2.66 (t, 4H, *J* = 7.0 Hz), 6.02 (s, 2H), 6.71 (m, 4H), 7.30–7.50 (m, 10H), 11.49 (br s, 1H); ¹³C{¹H} NMR (CDCl₃, 75 MHz) δ 28.2, 29.2, 30.7, 41.1, 122.8, 124.1, 127.3, 128.4, 131.3, 135.1, 137.1, 137.9, 139.1, 139.4, 143.1, 151.4, 182.1; IR (KBr) ν_{max} 3320 (NH) cm^{–1}; UV–vis (CH₂Cl₂) λ_{max} (ε) 342 (29000), 510 (19600), 540 (21000); HRMS (EI) calcd for C₃₉H₃₅N₃S (M⁺) *m/z* 577.2552, found 577.2557.

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Supporting Information Available: Experimental details, ¹H NMR charts for new compounds, a CIF file for **8S**, and DFT computational results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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