New Thiophene−Pyrrole-Derived Annulenes Containing 6 and 10 Heterocyclic Units

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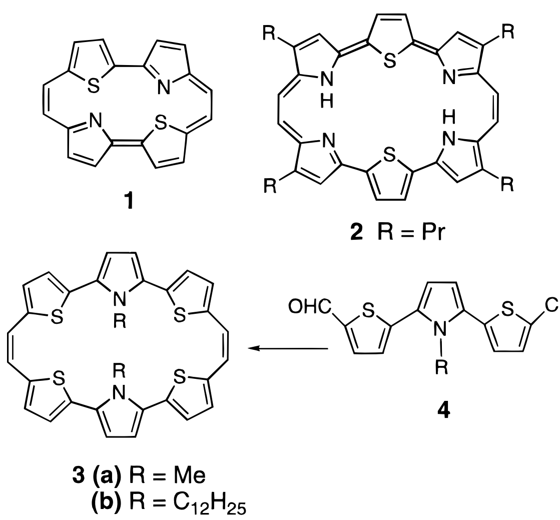
A series of thiophene−pyrrole-derived annulenes containing either 6 (**9a**−**c**) or 10 (**14a,b** and **17**) heterocyclic units and 2 vinylene bridges have been synthesized from the appropriate dialdehydes or tetraaldehydes by the McMurry coupling reaction. All of these annulenes except **17** contain one or two intramolecular aliphatic chains linking the pyrrole units. Spectroscopic properties of these annulenes show no evidence for overall aromaticity or antiaromaticity, although the nature of the aliphatic bridge has a small but definite effect on the UV−visible spectra and electrochemical properties of the compounds.

Polythiophenes and polypyrroles have emerged in recent years as two of the most intensely studied classes of organic conducting polymers.[1] The virtual insolubility and poor processibility of the parent polymers have stimulated much effort on the synthesis of more soluble alkylated analogs, particularly in the polythiophene area.[2] Mixed polymers derived from thienylpyrroles, although much less investigated, also show promise as new electronic materials.[3]

Higher oligothiophenes, especially sexithiophenes, are of current great interest since their properties approach those of the corresponding polymer, and they appear to be promising candidates for electronic and optical devices.[4] Mixed thiophene−pyrrole oligomers containing three heterocyclic rings have been known for some time, and mixed oligomers containing from five to seven rings were reported recently from our laboratory.[5]

Scheme 1



1

2 R = Pr

4

3 (a) R = Me
(b) R = $C_{12}H_{25}$

The study of the chemistry of expanded porphyrins has also developed rapidly in recent years and has also led to the synthesis of a number of cyclic conjugated annulenes containing furan or thiophene units in place of pyrroles.[6] The first such annulenes containing both thiophene and pyrrole units were the aromatic systems **1** and **2** (Scheme 1).[7] In a preliminary paper, we reported the synthesis of nonplanar annulenes **3**, in which the substituents R (CH_3 or n-$C_{12}H_{25}$) lie on opposite sides of the average annulene plane.[8] In this paper, we report the synthesis of several new types of annulenes constructed from mixed thiophene−pyrrole oligomers.

Results and Discussion

Bridged Tetrathiahomoporphycenes. Our earlier success in obtaining the *N*,*N*′-dialkyl annulenes **3** by a McMurry coupling[8,9] of a tricyclic dialdehyde (**4**) suggested the possibility of carrying out a similar synthesis of derivatives of the same annulene system in which the two pyrrole nitrogens have been linked by an alkyl bridge. Such a system would of necessity be in the general form of a basket in which the bridging chain must be on one side and forms the handle of the basket. We chose to study the effect of three different bridges: a

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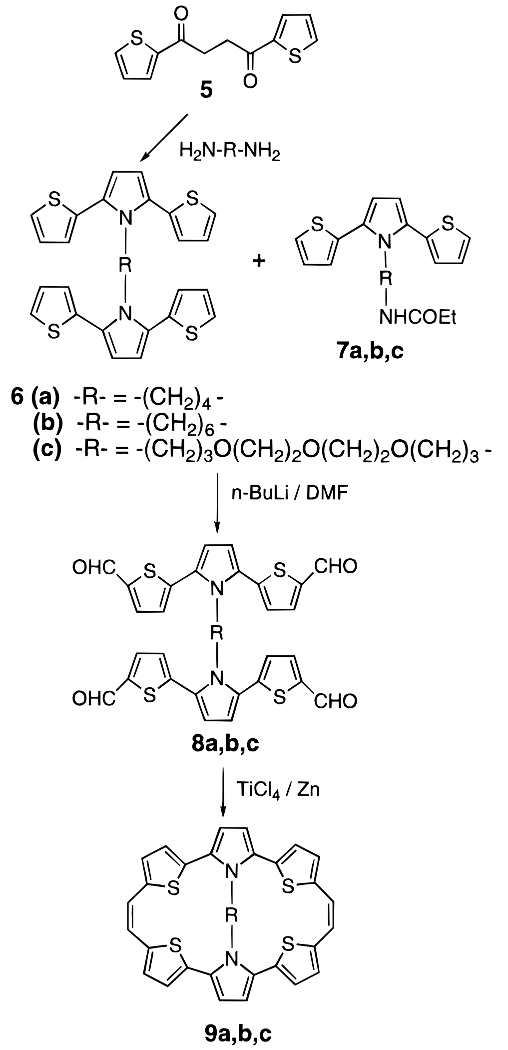
Scheme 2



small bridge [series **a**, $-(CH_2)_4-$], a medium bridge [series **b**, $-(CH_2)_6-$], and a long polyether bridge [series **c**, $-(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3-$].

The well-known 1,4-bis(2-thienyl)-1,4-butanedione (**5**)[10] was subjected to a double Knorr–Paal condensation using the appropriate diamine in toluene in the presence of propionic acid. The desired bis(pyrrolyl) compounds **6** were obtained in good yields (59–66%); amides derived from monopyrroles and propionic acid (**7**) were formed as byproducts (Scheme 2).

Tetralithiation of the N,N′-bridged compounds **6** was achieved using excess *n*-butyllithium; reaction with DMF, followed by hydrolysis, afforded the crystalline tetraaldehydes **8** in very satisfactory yields (62–100%). Intramolecular McMurry coupling of these aldehydes gave fair yields (24–58%) of the corresponding high-melting orange macrocycles **9**.

A comparison of the UV absorption maxima of the bridged macrocycles **9a**–**c** provides some insight into the relative degree of nonplanarity in the three analogs. The lowest maximum (345 nm), and therefore the most distorted π-system, is found in the C-4 bridged compound **9a**. Models of **9a** indicate a very rigid structure, in which the short tetramethylene bridge forces the two pyrrole units considerably up and out of the plane of the thiophene rings. Extension of the bridge in **9b** to a hexamethylene chain produces slightly less rigidity and better overall conjugation, as evidenced by the maximum at 348 nm. The much longer and highly flexible triether bridge of **9c** leads to an even higher maximum of 353 nm, indicative of a still better degree of conjugation.

Table 1. Redox Potentials (V vs SCE) and Absorption Maxima of Annulenes 9

compd	redox potentials (V vs SCE) E_{pa}^1/E_{pc}^1	redox potentials (V vs SCE) E_{pa}^2/E_{pc}^2	λ_{max} (nm) (log ϵ)	solvent
9a	0.71/0.63		345 (4.27)	CH_2Cl_2
9b	0.64/0.58		348 (4.36)	CH_2Cl_2
9c	0.61/0.54		353 (4.29)	CH_2Cl_2

Cyclic voltammetric experiments indicate that the ease of oxidation increases as the bridge is lengthened, as summarized in Table 1. However, all three compounds **9a**–**c** show only one oxidation wave, attributed to cation radical formation, in the range 0.0–1.5 V vs SCE. While the longer bridged **9b** and **9c** showed quasi-reversible redox waves, only a small reduction wave was observed for the short-bridged tetramethylene compound **9a**.

Decaheterocyclic Annulenes. The readily prepared tetraketone **10**[5e,11] has been found to undergo the Knorr–Paal condensation with ammonia or with primary amines to produce pentacyclic oligomers containing three thiophene and two pyrrole units. As we reported recently, α,ω-primary diamines give rise to structures exemplified by **11a**, in which the two pyrrole nitrogens are linked by a bridge that limits the conformational freedom of the molecule (Scheme 3).[12] We reasoned that such a constraint should be favorable for incorporation of the pentacyclic system into a large macrocycle. The C-8 bridged compound **11a** and the larger triether bridged analog **11b**, both easily obtained in over 50% yield from commercial diamines, were chosen for this study.

Dilithiation of **11a** and **11b**, followed by reaction with DMF and hydrolysis, gave dialdehydes **13a** and **13b** in 67 and 79% yields, respectively. Intermolecular McMurry coupling of **13a** and **13b** did indeed afford the corresponding macrocycles **14a** and **14b** in 14 and 37% yields, respectively. These annulenes, derived from 10 heterocyclic units and 2 olefinic units, represent the largest heterocyclic macrocycles yet reported.

In view of the fact that the less constrained dialdehyde **13b** actually gave the better yield in the McMurry coupling, the unbridged analog of **13a** containing two butyl groups (i.e., **15**) was examined as a macrocyclic precursor. Conversion of **15** to dialdehyde **16** (69% yield), followed by McMurry coupling, did indeed afford annulene **17** in a surprisingly high yield of 34% (Scheme 4).

Comparison of the longest ultraviolet maxima of the three decacyclic annulenes **14a**, **14b**, and **17** shows that the C-8 bridged **14a** give a value at the shortest wavelength (353 nm), indicative of the least overall conjugation. In contrast, the longer triether bridged **14b** is less constrained and better conjugated, as shown by its 369 nm maximum. The unbridged analog **17** shows a maximum at an intermediate value (361 nm).

Cyclic voltammograms of both **14a** and **14b** show two well-separated oxidation waves. The current values of the first oxidation waves were approximately double those of the second, suggesting that the first waves are dication diradicals and the second are trication mono-

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Scheme 3

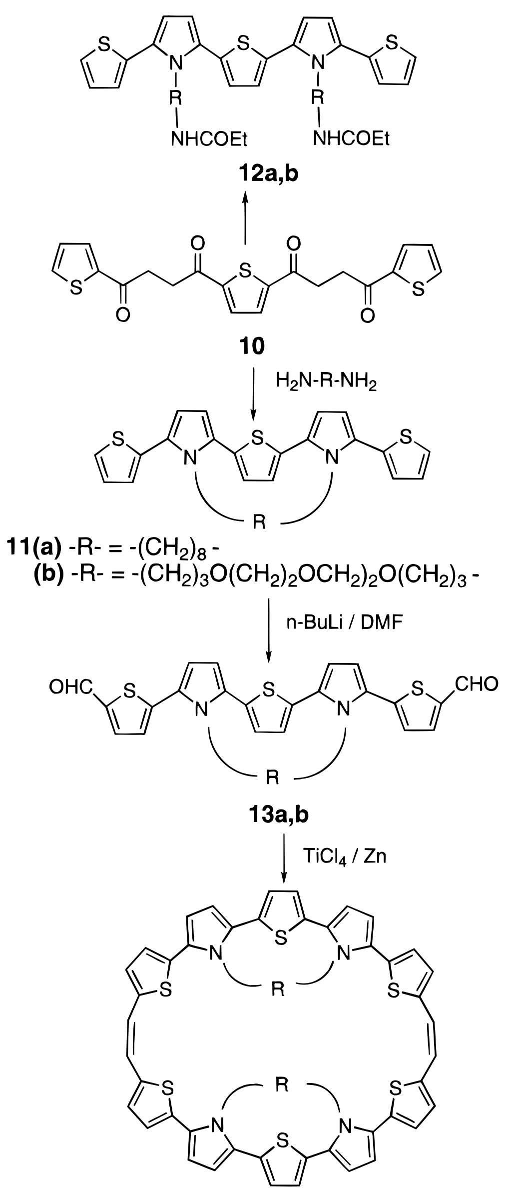


Table 2. Redox Potentials and Absorption Maxima of Annulenes 14a, 14b, and 17

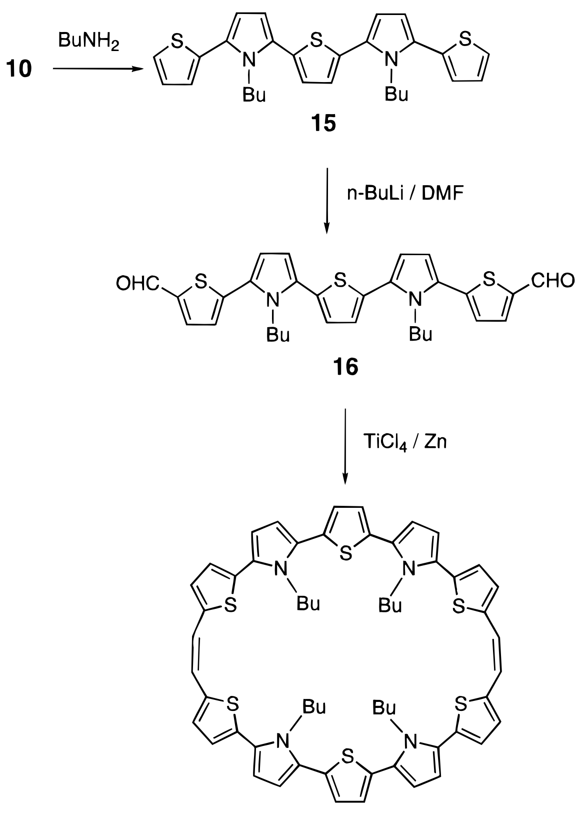
compd	redox potentials (V vs SCE) $E_{pa}{}^1/E_{pc}{}^1$	redox potentials (V vs SCE) $E_{pa}{}^2/E_{pc}{}^2$	λ_{max} (nm) (log ϵ)	solvent
14a	0.59/0.49	0.96/0.83	353 (4.80)	CH_2Cl_2
14b	0.53/0.46	0.95/0.89	369 (4.72)	CH_2Cl_2
17	0.54/0.44		361 (4.79)	CH_2Cl_2

radicals. The simultaneous formation of two cation radicals implies the conjugative independence of the two pentacyclic units of the annulene. The tetrabutyl macrocycle **17** shows only one quasi-reversible oxidation wave, oxidation at higher voltages leading to irreversible behavior (Table 2).

Conclusion

Convenient syntheses have been developed for entry into two series of mixed thiophene–pyrrole macrocycles. These include the N,N′-bridged tetrathiahomoporphycenes **9a–c** and the first examples (**14a,b** and **17**) of a larger decacyclic system. The annulenes containing the smaller bridges show a lower degree of overall conjugation, as evidenced by their electrochemical behavior and UV–visible spectra. The spectroscopic properties (UV, NMR) of the decacyclic series, like those of the hexacyclic series, indicate the absence of any overall macrocyclic aromaticity or antiaromaticity.

Scheme 4



Experimental Section

General. The CVs were obtained in a single-compartment cell with a platinum disk working electrode, a platinum wire auxiliary electrode, and a saturated calomel electrode as the reference electrode. Measurements were carried out under a blanket of nitrogen with the oligomer concentration of 0.1–1.0 mM in 0.1 M 1,2-dichloroethane (HPLC grade) solutions of tetrabutylammonium hexafluorophosphate (TBAHFP).

Synthesis of 6b (General Procedure for Inter- and Intramolecular Double Knorr–Paal Reactions). A solution of **5** (2.00 g, 8.0 mmol), 1,6-diaminohexane (0.70 g, 6.0 mmol), and propionic acid (1.0 mL) in toluene (60 mL) was refluxed for 3 days under N_2 with a Dean-Stark trap. After cooling, the pale yellow crystals of **6b** (741 mg) were filtered off and washed with toluene. The filtrate was neutralized by the addition of ice cold saturated $NaHCO_3$. The organic layer was washed with water, dried (Na_2SO_4), and evaporated. Crystallization from toluene gave additional **6b** (568 mg). The residue was subjected to basic Al_2O_3 chromatography to give a further amount of **6b** (128 mg) and amide **7b** (976 mg, 32%). The total yield of **6b** was 1.44 g.

6b: yield 66%; yellow crystals, mp 141–142 °C (from toluene); ^{1}H NMR δ 7.23 (dd, 4 H, $J = 0.9$, 5.0 Hz), 7.06 (dd, 4 H, $J = 3.4$, 5.0 Hz), 7.01 (dd, 4 H, $J = 0.9$, 3.4 Hz), 6.31 (s, 4 H), 4.04 (t, 4 H, $J = 7.7$ Hz), 1.42 (m, 4 H), 0.93 (m, 4 H); ^{13}C NMR δ 134.9, 128.3, 127.2, 125.9, 125.2, 110.8, 44.9, 31.0, 25.8; IR (KBr) 2950, 1650, 1420, 690 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max} 316 nm (log ϵ 4.42), 223 nm (4.37). MS, m/e 544 (M$^+$). Anal. Calcd for $C_{30}H_{28}N_2S_4$: C, 66.16; H, 5.19; N, 5.15; S, 23.50. Found: C, 66.26; H, 5.14; N, 5.11; S, 23.43.

7b: yield 32%; pale yellow crystals, mp 72−74 °C (from cyclohexane); ^{1}H NMR δ 7.32 (dd, 2 H, $J = 1.2$, 5.0 Hz), 7.08 (dd, 2 H, $J = 3.5$, 5.0 Hz), 7.06 (dd, 2 H, $J = 1.2$, 3.5 Hz), 6.33 (s, 2 H), 5.34 (br, 1 H), 4.13 (t, 2 H, $J = 7.7$ Hz), 3.14 (q, 2 H, $J = 6.7$ Hz), 2.17 (q, 2 H, $J = 7.7$ Hz), 1.54 (m, 2 H), 1.34 (m, 2 H), 1.39 (m, 7 H); ^{13}C NMR δ 173.6, 135.0, 128.3, 127.3, 125.9, 125.2, 110.8, 44.9, 39.3, 30.9, 29.7, 29.3, 26.2, 26.0, 9.9; IR (KBr) 3319, 2938, 1645, 1550, 695 cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max} 316 nm (log ϵ 4.19); MS, *m/e* (relative intensity). Anal. Calcd for $C_{21}H_{26}N_2OS_2$: C, 65.26; H, 6.79; N, 7.25; S, 16.56. Found: C, 65.34; H, 6.78; N, 7.32; S, 16.61.

6a: yield 59%; pale yellow crystals, mp 198−199 °C; ^{1}H NMR δ 7.29 (dd, 4 H, $J = 0.9$, 5.1 Hz), 7.05 (dd, 4 H, $J = 3.4$, 5.1 Hz), 6.94 (dd, 4 H, $J = 0.9$, 3.4 Hz), 6.28 (s, 4 H), 3.92 (m, 4 H), 1.34 (m, 4 H); ^{13}C NMR δ 134.7, 128.2, 127.3, 126.1, 125.3, 110.9, 44.3, 27.9; IR (KBr) 3110, 2945, 1480, 1419, 848, 765, 702 cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max} 315 nm (log ϵ 4.42), 223 nm (4.40); MS, *m/e* (relative intensity) 516 (M$^+$, 57), 376 (100), 142 (99). Anal. Calcd for $C_{28}H_{24}N_2S_4$: C, 65.11; H, 4.69; N, 5.43. Found: C, 64.94; H, 4.78; N, 5.39.

7a: yield 31%; brown oil; ^{1}H NMR δ 7.32 (dd, 2 H, $J = 1.1$, 5.0 Hz), 7.09 (dd, 2 H, $J = 3.6$, 5.0 Hz), 7.06 (dd, 2 H, $J = 1.1$, 3.6 Hz), 6.33 (s, 2 H), 5.33 (br, 1 H), 4.17 (t, 2 H, $J = 7.6$ Hz), 3.05 (q, 2 H, $J = 6.4$ Hz), 2.12 (q, 2 H, $J = 7.6$ Hz), 1.53 (m, 2 H), 1.28 (m, 2 H), 1.10 (t, 3 H, $J = 7.6$ Hz); ^{13}C NMR δ 173.6, 134.8, 128.3, 127.4, 126.1, 125.4, 111.0, 44.5, 38.6, 30.0, 28.1, 26.3, 9.9; IR (KBr) 3300, 3095, 2940, 1650, 1535 cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max} 315 nm (log ϵ 4.28), 229 nm (4.23).

6c: yield 63%; yellow oil; ^{1}H NMR δ 7.28 (dd, 4 H, $J = 1.0$, 5.0 Hz), 7.09 (dd, 4 H, $J = 1.0$, 3.5 Hz), 7.06 (dd, 4 H, $J = 3.5$, 5.0 Hz), 6.34 (s, 4 H), 4.29 (t, 4 H, $J = 7.4$ Hz), 3.44 (m, 4 H), 3.33 (m, 4 H), 3.25 (t, 4 H, $J = 6.1$ Hz), 1.80 (m, 4 H); ^{13}C NMR δ 134.9, 128.4, 127.3, 125.8, 125.1, 110.9, 70.5, 70.0, 68.0, 42.3, 31.0; IR (NaCl) 3104, 2873, 1409, 1113, 693 cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max} 317 nm (log ϵ 4.44); MS, *m/e* 648 (M$^+$, 100), 272 (21), 245 (64).

7c: yield 31%; brown oil; ^{1}H NMR δ 7.30 (dd, 2 H, $J = 1.1$, 4.9 Hz), 7.10 (dd, 2 H, $J = 1.1$, 3.6 Hz), 7.07 (dd, 2 H, $J = 3.6$, 4.9 Hz), 6.33 (s, 2 H), 6.18 (br, 1 H), 4.30 (t, 2 H, $J = 7.4$ Hz), 3.56 (m, 6 H), 3.49 (m, 2 H), 3.35 (m, 4 H), 3.25 (t, 2 H, $J = 6.1$ Hz), 2.15 (q, 2 H, $J = 7.6$ Hz), 1.76 (m, 4 H), 1.12 (t, 3 H, $J = 7.6$ Hz); ^{13}C NMR δ 173.6, 134.6, 128.2, 127.2, 125.6, 124.9, 110.8, 70.3, 70.2, 70.0, 69.9, 69.8, 67.8, 42.1, 37.8, 30.8, 29.5, 28.7, 9.8; IR (NaCl) 3324, 3113, 2880, 1657, 1548, 1110, 700 cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max} 318 nm (log ϵ 4.24); MS, *m/e* (relative intensity) 490 (M$^+$, 66), 377 (18), 245 (100).

Synthesis of 15. A solution of tetraketone **10** (417 mg, 1.0 mmol), *n*-butylamine (0.59 mL, 6.0 mmol), and propionic acid (2.0 mL) in toluene (100 mL) was refluxed for 47 h under N$_2$ with a Dean-Stark trap. The cooled solution was neutralized by addition of ice cold saturated NaHCO$_3$. The organic layer was washed with water and dried over Na$_2$SO$_4$. After evaporation, the residue was purified by basic Al$_2$O$_3$ chromatography to give **15** (425 mg, 87%) as yellow crystals.

15: yield 87%; yellow solid, mp 70−72 °C; ^{1}H NMR δ 7.32 (dd, 2 H, $J = 1.7$, 4.5 Hz), 7.10−7.07 (m, 4 H), 7.03 (s, 2 H), 6.37 (d, 2 H, $J = 3.6$ Hz), 6.34 (d, 2 H, $J = 3.6$ Hz), 4.19 (t, 4 H, $J = 7.8$ Hz), 1.60 (m, 4 H), 1.20 (p, 4 H, $J = 7.4$ Hz), 0.79 (t, 6 H, $J = 7.4$ Hz); ^{13}C NMR δ 134.9, 134.6, 128.5, 128.2, 127.3, 125.9, 125.8, 125.2, 110.9, 110.7, 45.0, 33.3, 19.7, 13.6; IR (NaCl) 2989, 1468, 1415, 1205, 770, 700 cm^{-1}; UV−vis (CH$_2$Cl$_2$) λ_{max} 350 nm (log ϵ 4.44), 242 nm (4.38), 234 nm (4.35); MS, *m/e* (relative intensity). Anal. Calcd for $C_{28}H_{30}N_2S_3$: C, 68.55; H, 6.17; N, 5.71; S, 19.57. Found: C, 68.58; H, 6.21; N, 5.70; S, 19.52.

Inter- and Intramolecular Double Knorr−Paal Reaction of 10 and 1,6-Diaminooctane (General Procedure). A solution of **10** (417 mg, 1.0 mmol), 1,9-diaminooctane (433 mg, 3.0 mmol), and propionic acid (4.0 mL) in toluene (100 mL) was refluxed for 48 h under N$_2$ with a Dean-Stark trap. After cooling, the solid amine salt was filtered off and the filtrate was neutralized by addition of ice cold saturated NaHCO$_3$. The organic layer was washed with water and dried over Na$_2$SO$_4$. After evaporation, the residue was purified by chromatography (basic alumina) to give **11a** (261 mg) as yellow crystals and diamide **12a** (223 mg) as a dark brown oil.

11a: yield 54%; pale yellow plates, mp 132 °C (from hexane); ^{1}H NMR δ 7.31 (dd, 2 H, $J = 2.2$, 4.0 Hz), 7.08 (m, 4 H), 7.05 (s, 2 H), 6.35 (s, 4 H), 4.22 (t, 4 H, $J = 7.6$ Hz), 1.51 (br, 4 H), 1.14 (br, 4 H), 1.01 (br, 4 H); ^{13}C NMR δ 135.2, 135.0, 128.4, 128.2, 127.6, 127.3, 125.7, 125.2, 110.7, 110.7, 44.0, 29.1, 26.9, 25.2; IR (KBr) 2930, 2850, 1520, 1410 cm^{-1}; UV−vis (CHCl$_3$) λ_{max} 334 nm (log ϵ 4.65). Anal. Calcd for $C_{28}H_{28}N_2S_3$: C, 68.83; H, 5.78; N, 5.74; S, 19.65. Found: C, 68.84; H, 5.82; N, 5.80; S, 19.54.

12a: yield 30%; dark brown oil; ^{1}H NMR δ 7.33 (dd, 2 H, $J = 1.2$, 5.2 Hz), 7.12−7.06 (m, 4 H), 7.02 (s, 2 H), 6.37 (d, 2 H, $J = 1.9$ Hz), 6.34 (d, 2 H, $J = 1.9$ Hz), 5.49 (br, 2 H), 4.18 (t, 4 H, $J = 7.8$ Hz), 3.18 (dt, 4 H, $J = 6.7$, 6.7 Hz), 2.16 (q, 4 H, $J = 7.6$ Hz), 1.56 (m, 4 H), 1.42 (m, 4 H), 1.19 (m, 4 H), 1.13 (t, 6 H, $J = 7.6$ Hz), 1.30−1.05 (m, 16 H), 1.12 (t, 6 H, $J = 7.6$ Hz); ^{13}C NMR δ 173.8, 134.8, 134.5, 128.6, 128.2, 127.3, 126.0, 125.8, 125.3, 111.9, 110.7, 45.2, 39.5, 31.1, 29.7, 29.6, 29.0, 28.9, 26.8, 26.3, 10.0; IR (NaCl) 3310, 2940, 2860, 1640, 1545, 1460 cm^{-1}; UV−vis (CHCl$_3$) λ_{max} 353 nm (log ϵ 4.75), 240 nm (4.65).

11b: yield 52%; pale yellow crystals, mp 143 °C; ^{1}H NMR δ 7.31 (dd, 2 H, $J = 2.5$, 3.8 Hz), 7.28 (s, 2 H), 7.07 (m, 4 H), 6.40 (d, 2 H, $J = 3.7$ Hz), 6.35 (d, 2 H, $J = 3.7$ Hz), 4.40 (m, 4 H), 3.65 (m, 4 H), 3.53 (m, 4 H), 3.42 (t, 4 H, $J = 5.4$ Hz), 1.95 (m, 4 H); ^{13}C NMR δ 134.9, 133.6, 128.5, 128.2, 127.3, 126.0, 125.3, 125.2, 111.4, 110.2, 71.1, 70.6, 68.3, 42.8, 31.2; IR (KBr) 3100, 2890, 1579, 1471, 1415, 1350, 1100 cm^{-1}; UV−vis (CHCl$_3$) λ_{max} 369 nm (log ϵ 4.57); MS, *m/z* (relative intensity) 564 (M$^+$, 100), 377 (7). Anal. Calcd for $C_{30}H_{32}N_2O_3S_3$: C, 63.81; H, 5.72; N, 4.96; S, 17.00. Found: C, 63.84; H, 5.74; N, 5.01; S, 16.92.

12b: 34% yield; dark brown oil; ^{1}H NMR δ 7.31 (dd, 2 H, $J = 1.1$, 5.0 Hz), 7.11 (dd, 2 H, $J = 1.1$, 3.7 Hz), 7.08 (dd, 2 H, $J = 3.7$, 5.0 Hz), 7.05 (s, 2 H), 6.37 (d, 2 H, $J = 3.8$ Hz), 6.34 (d, 2 H, $J = 3.8$ Hz), 6.21 (br, 2 H), 4.35 (m, 4 H), 3.59−3.48 (m, 16 H), 3.39 (m, 4 H), 3.34 (dt, 4 H, $J = 6.0$, 6.0 Hz), 3.29 (t, 4 H, $J = 6.0$ Hz), 2.16 (q, 4 H, $J = 7.6$ Hz), 1.86 (m, 4 H), 1.75 (tt, 4 H, $J = 6.0$, 6.0 Hz), 1.12 (t, 6 H, $J = 7.6$ Hz); ^{13}C NMR δ 173.7, 134.7, 134.3, 128.8, 128.3, 127.4, 125.9, 125.7, 125.2, 111.1, 110.9, 70.5, 70.4, 70.3, 70.1 (2C), 68.0, 42.5, 38.0, 31.1, 29.7, 28.8, 9.9; IR (NaCl) 3305, 2870, 1657, 1549, 1110 cm^{-1}; UV−vis (CHCl$_3$) λ_{max} 355 nm (log ϵ 4.44), 240 nm (4.30).

Tetraformylation of 6b (General Procedure). To a stirred solution of **6b** (544 mg, 1.00 mmol) and TMEDA (1.21 mL, 8.00 mol) in dry THF (30 mL) was added dropwise 2.36 mol dm^{-3} *n*-BuLi in hexane (3.39 mL, 8.00 mmol) under N$_2$ at −78 °C. The solution was stirred under N$_2$ for 30 min after removal of the cooling bath. The solution was then again cooled to −78 °C, and dry DMF (1.86 mL, 24.0 mmol) was added under N$_2$. The solution was stirred with continued cooling for 10 min, and then the temperature was raised gradually to rt. The solution was poured into 1 N NaOH solution, and the brown solid was filtered off, washed with water, and crystallized from 1,4-dioxane to give **8b** (388 mg, 62%) as reddish brown crystals.

8b: mp 215−218 °C. ^{1}H NMR δ 9.89 (s, 4 H), 7.74 (d, 4 H, $J = 3.9$ Hz), 7.17 (d, 4 H, $J = 3.9$ Hz), 6.53 (s, 4 H), 4.24 (t, 4 H, $J = 7.7$ Hz), 1.49 (m, 4 H), 1.01 (m, 4 H); ^{13}C NMR δ 182.6, 143.9, 142.4, 137.0, 129.9, 126.2, 113.5, 45.7, 30.9, 25.7; IR (KBr) 1666, 1440, 1241 cm^{-1}; UV−vis (CHCl$_3$) λ_{max} 405 nm (log ϵ 4.68), 251 nm (4.38). Anal. Calcd for $C_{34}H_{28}N_2O_4S_4$: C, 62.19; H, 4.30; N, 4.27; S, 19.49. Found: C, 62.26; H, 4.34; N, 4.24; S, 19.39.

8a: yield ∼100% orange crystals; mp 213−218 °C (from 1,4-dioxane); ^{1}H NMR δ 9.90 (s, 4 H), 7.75 (d, 4 H, $J = 3.9$ Hz), 7.11 (d, 4 H, $J = 3.9$ Hz), 6.49 (s, 4 H), 4.18 (m, 4 H), 1.37 (m, 4 H); ^{13}C NMR δ 182.8, 143.6, 142.7, 137.2, 129.9, 128.5, 113.6, 45.1, 27.7; IR (KBr) 1660, 1435, 1230 cm^{-1}; UV−vis (CHCl$_3$) λ_{max} 402 nm (log ϵ 4.75), 254 nm (4.47), 231 nm (4.40). Anal. Calcd for $C_{32}H_{24}N_2O_4S_4$: C, 61.04; H, 3.85; N, 4.46; S, 20.36. Found: C, 61.26; H, 3.81; N, 4.55; S, 20.31.

8c: yield 88%; mp 72−74 °C (from EtOH); ^{1}H NMR δ 9.87 (s, 4 H), 7.72 (d, 4 H, $J = 4.0$ Hz), 7.25 (d, 4 H, $J = 4.0$ Hz), 6.55 (s, 4 H), 4.46 (t, 4 H, $J = 7.5$ Hz), 3.41 (m, 4 H), 3.39 (m, 4 H), 3.29 (t, 4 H, $J = 5.8$ Hz), 1.85 (m, 4 H); ^{13}C NMR δ 182.5, 144.0, 142.2, 137.0, 130.0, 126.0, 113.5, 70.5, 70.2, 67.5, 43.1, 31.2; IR (KBr) 2895, 1666, 1436, 1234, 1069 cm^{-1}; UV−vis

(CH_2Cl_2) λ_{max} 406 nm (log ϵ 4.69), 253 nm (4.40); MS, *m/e* (relative intensity) 760 (M^+, 50), 566 (22), 526 (100), 301 (35).

Diformylation of 15 (General Procedure). To a stirred solution of **15a** (354 mg, 0.72 mmol) and TMEDA (0.26 mL, 1.73 mol) in dry THF (20 mL) was added dropwise 2.36 mol dm^{-3} *n*-BuLi in hexane (0.73 mL, 1.73 mmol) under N_2 at −78 °C. The solution was stirred under N_2 for 30 min after removal of the cooling bath. The solution was again cooled to −78 °C, and dry DMF (0.24 mL, 3.10 mmol) was added under N_2. The cold solution was stirred for 10 min, and the temperature was then gradually raised to rt. The solution was poured into 1 N NaOH and extracted with CH_2Cl_2. The extract was washed with water, dried, and evaporated to give a red solid which was crystallized from EtOH to afford **16** (271 mg).

16: yield 69%; red-brown crystals, mp 106−107 °C (from EtOH); ^1H NMR δ 9.88 (s, 2 H), 7.73 (d, 2 H, $J = 3.9$ Hz), 7.19 (d, 2 H, $J = 3.9$ Hz), 7.08 (s, 2 H), 6.56 (d, 2 H, $J = 3.9$ Hz), 6.41 (d, 2 H, $J = 3.9$ Hz), 4.30 (t, 4 H, $J = 7.8$ Hz), 1.63 (m, 4 H), 1.22 (4 H, $J = 7.4$ Hz), 0.82 (t, 6 H, $J = 7.4$ Hz); ^{13}C NMR δ 182.5, 145.1, 141.6, 137.0, 134.4, 130.5, 128.1, 126.6, 125.2, 112.9, 111.9, 45.5, 33.3, 19.7, 13.6; IR (KBr) 2979, 1667, 1470, 1443, 1076, 767 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} 414 nm (log ϵ 4.44), 250 nm (4.11). Anal. Calcd for $C_{30}H_{30}N_2O_2S_3$: C, 65.92; H, 5.54; N, 5.13; S, 17.56. Found: C, 66.00; H, 5.52; N, 5.17; S, 17.50.

13a: yield 67%; brown crystals, mp 183−186 °C (from toluene); ^1H NMR δ 9.88 (s, 2 H), 7.72 (d, 2 H, $J = 3.9$ Hz), 7.18 (d, 2 H, $J = 3.9$ Hz), 7.10 (s, 2 H), 6.57 (d, 2 H, $J = 3.8$ Hz), 6.40 (d, 2 H, $J = 3.8$ Hz), 4.33 (t, 4 H, $J = 7.5$ Hz), 1.57 (m, 4 H), 1.18 (m, 4 H), 1.03 (m, 4 H); ^{13}C NMR δ 182.6, 145.0, 141.7, 137.0, 134.8, 130.5, 128.2, 127.9, 125.2, 112.7, 111.7, 44.4, 29.1, 26.8, 25.1; IR (KBr) 2955, 1668, 1469, 1240, 1072, 785 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} 403 nm (log ϵ 4.59), 249 nm (4.25); PDMS, *m/z* ($C_{30}H_{28}N_2O_2S_3$) 544.2 (M^+).

13b: yield 79%; red crystals, mp 160−161 °C (from EtOH); ^1H NMR δ 9.87 (s, 2 H), 7.72 (d, 2 H, $J = 3.9$ Hz), 7.39 (s, 2 H), 7.20 (d, 2 H, $J = 3.9$ Hz), 6.58 (d, 2 H, $J = 3.9$ Hz), 6.45 (d, 2 H, $J = 3.9$ Hz), 4.54 (t, 4 H, $J = 8.0$ Hz), 3.66 (m, 4 H), 3.58 (m, 4 H), 3.50 (t, 4 H, $J = 5.2$ Hz), 2.04 (m, 4 H); ^{13}C NMR δ 182.5, 144.9, 141.4, 137.1, 133.4, 130.8, 127.8, 126.0, 125.2, 113.4, 111.4, 71.1, 70.7, 68.1, 43.2, 31.3; IR (KBr) 1665, 1467, 1439 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max} 438 nm (log ϵ 4.56), 257 nm (4.18); PDMS, *m/z* ($C_{32}H_{32}N_2O_5S_3$) 619.6 (M^+).

Intramolecular McMurry Coupling Reaction of 8b (General Procedure). To a stirred mixture of Zn powder (670 mg) in dry THF (30 mL) was added 1.0 M $TiCl_4$ in CH_2Cl_2 (5.0 mL, 5.0 mmol) under N_2 at rt over 20 min. The mixture was stirred under reflux for 1.5 h. A suspension of dialdehyde **8b** (164 mg, 0.25 mmol) in dry THF (30 mL) was added to the refluxing mixture under N_2, and the mixture was refluxed for 18 h. A 10% K_2CO_3 solution was added carefully to the cooled mixture, which was then filtered using Celite. The THF was removed from the filtrate by evaporation. The resulting mixture was extracted with CH_2Cl_2, and the extract was washed with water and dried. After evaporation, the residue was passed through a short SiO_2 column (CH_2Cl_2), the solvent removed, and the product washed with a small amount of EtOAc, affording **9b** (18 mg).

9a: yield 58%; orange solid, mp 285−290 °C (dec); ^1H NMR δ 7.00 (d, 4 H, $J = 3.7$ Hz), 6.92 (d, 4 H, $J = 3.7$ Hz), 6.72 (s, 4 H), 6.26 (s, 4 H), 4.02 (m, 4 H), 1.56 (m, 4 H); ^{13}C NMR δ 139.5, 135.6, 128.7, 128.3, 126.1, 124.4, 110.2, 44.0, 24.7; IR (KBr) 1607, 1443, 793, 751 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} 347 nm (log ϵ 4.27), 259 nm (4.09); PDMS, *m/z* ($C_{32}H_{24}N_2S_4$) 564.0 (M^+).

9b: yield 24%; orange solid, mp 227−230 °C. ^1H NMR δ 7.01 (d, 4 H, $J = 3.7$ Hz), 6.94 (d, 4 H, $J = 3.7$ Hz), 6.67 (s, 4 H), 6.36 (s, 4 H), 4.28 (m, 4 H), 1.53 (m, 4 H), 1.19 (m, 4 H); ^{13}C NMR δ 138.7, 135.5, 129.0, 128.2, 126.7, 123.1, 110.5, 45.7, 31.4, 24.1; IR (KBr) 2930, 1470, 829, 777 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} 334 nm (log ϵ 4.36); PDMS, *m/z* ($C_{34}H_{28}N_2S_4$) 591.8 (M^+).

9c: yield 51%; orange solid, mp 220−221 °C (dec) (from EtOH); ^1H NMR δ 6.99 (d, 4 H, $J = 3.5$ Hz), 6.93 (d, 4 H, $J = 3.5$ Hz), 6.61 (s, 4 H), 6.35 (s, 4 H), 4.61 (t, 4 H, $J = 6.7$ Hz), 3.38 (m, 4 H), 3.30 (m, 4 H), 3.25 (t, $J = 5.6$ Hz), 1.74 (m, 4 H); ^{13}C NMR δ 138.9, 135.6, 129.7, 129.5, 125.7, 121.8, 111.6, 70.9, 70.2, 67.3, 42.8, 32.1; IR (KBr) 2870, 1433, 1100, 810 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} 353 nm (log ϵ 4.29), 228 nm (4.15); MS, *m/e* (relative intensity) 696 (M^+, 100), 509 (7). Anal. Calcd for $C_{38}H_{36}N_2O_3S_4$: C, 65.49; H, 5.20; N, 4.02; S, 18.37. Found: C, 65.20; H, 5.31; N, 3.92; S, 18.20.

Intermolecular McMurry Coupling Reaction of 16 (General Procedure). To a stirred mixture of Zn powder (784 mg) in dry THF (30 mL) was added 1.0 M $TiCl_4$ in CH_2Cl_2 (6.0 mL, 6.0 mmol) under N_2 at rt in 25 min. The mixture was stirred under reflux for 1 h. A suspension of dialdehyde **16** (82 mg, 0.15 mmol) in dry THF (60 mL) was added to the refluxing mixture under N_2, and the mixture was refluxed under N_2 for 40 h. A 10% K_2CO_3 solution was added carefully to the cooled mixture, which was then filtered using Celite. The THF was removed from the filtrate by evaporation, and the residue was extracted with CH_2Cl_2. The extract was washed with water, dried, and evaporated. The residue was separated with a basic Al_2O_3 column (CH_2Cl_2) to give **17** as a red solid (26 mg, 34%).

17: mp 225−226 °C (dec); ^1H NMR δ 7.03 (d, 4 H, $J = 3.7$ Hz), 7.00 (s, 4 H), 6.97 (d, 4 H, $J = 3.7$ Hz), 6.64 (s, 4 H), 6.32 (d, 4 H, $J = 3.9$ Hz), 6.30 (d, 4 H, $J = 3.9$ Hz), 4.11 (t, 8 H, $J = 7.8$ Hz), 1.51 (m, 8 H), 1.06 (t, 8 H, $J = 7.4$ Hz), 0.66 (t, 12 H, $J = 7.4$ Hz); ^{13}C NMR δ 138.8, 135.8, 134.7, 129.4, 128.4, 128.3, 126.4, 125.7, 123.1, 111.0, 110.8, 45.1, 33.4, 19.7, 13.5; IR (KBr) 2942, 1460, 811, 768 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} 361 nm (log ϵ 4.79), 236 nm (4.64); PDMS, *m/z* ($C_{60}H_{60}N_4S_6$) 1028.2 (M^+).

14a: yield 14%; orange solid, mp 310 °C (dec); ^1H NMR δ 7.02 (d, 4 H, $J = 3.7$ Hz), 7.01 (s, 4 H), 6.99 (d, 4 H, $J = 3.7$ Hz), 6.63 (s, 4 H), 6.31 (s, 4 H), 4.19 (t, 8 H, $J = 7.1$ Hz), 1.39 (m, 8 H), 0.95 (m, 8 H), 0.84 (m, 8 H); ^{13}C NMR δ 138.7, 135.9, 134.9, 129.5, 128.7, 128.4, 127.2, 125.5, 123.2, 111.2, 110.6, 43.9, 28.6, 27.1, 25.3; IR (KBr) 2950, 1470, 771 cm^{-1}; UV-vis (CH_2Cl_2) λ_{max} 353 nm (log ϵ 4.80), 229 nm (4.82); PDMS, *m/z* ($C_{60}H_{56}N_4S_6$) 1024.3 (M^+).

14b: yield 37%; orange solid, mp 234−235 °C; ^1H NMR δ 7.18 (s, 4 H), 6.98 (m, 4 H), 6.64 (s, 4 H), 6.33 (s, 4 H), 4.30 (m, 8 H), 3.47 (m, 8 H), 3.31 (m, 8 H), 3.24 (t, 8 H, $J = 5.3$ Hz), 1.86 (m, 8 H); ^{13}C NMR δ 138.7, 135.7, 133.8, 129.4, 128.3, 128.3, 125.8, 125.7, 123.0, 111.1, 110.2, 70.8, 70.5, 68.1, 43.0, 31.6; IR (KBr) 2870, 1649, 1430, 1112, 806 cm^{-1}; UV−vis (CH_2Cl_2) λ_{max} 369 nm (log ϵ 4.72), 242 nm (4.51); PDMS, *m/z* ($C_{64}H_{64}N_4O_6S_6$) 1176.4 (M^+).

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