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1,4-Phenylene-Bridged Hexaphyrin Dimers

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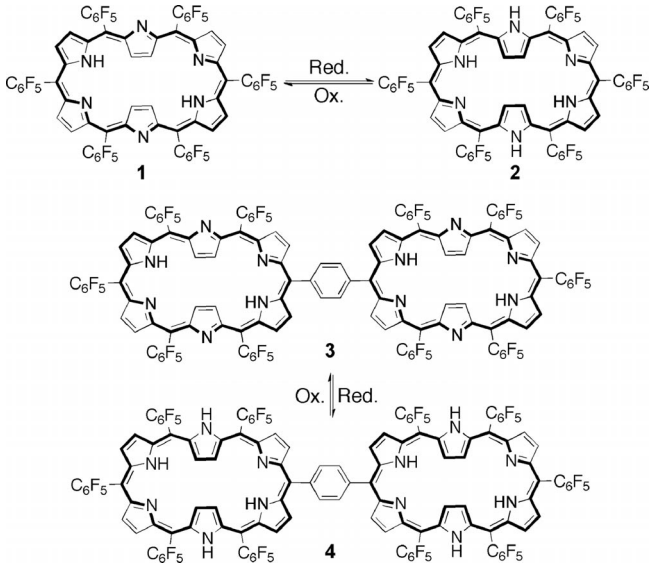
1,4-Phenylene-bridged [26]hexaphyrin dimer **3** was synthesized by the condensation of 1,4-phenylene-bridged tetrapyrrole carbinol **7** with tetrapyrromethane **8**. The dimeric structure of **3** was confirmed by X-ray analysis. ^{1}H NMR spectroscopy revealed that **3** and its [28]hexaphyrin congeners **4** exist as conformational mixtures in solution. Such conformational dynamics were found to be frozen for their Rh^I complexes **9**, which were prepared by Rh^I metalation of **4**. Complexes **9** were quantitatively oxidized by MnO_2 to [26]hexaphyrn dimers **10** without conformational change. The structure of **10LL-*dl*** was determined by X-ray analysis to confirm the caterpillar-type conformational isomerization. The Rh^I complexes **9** constitute rare examples of covalently linked, antiaromatic porphyrinoid dimers.

Introduction

In recent years, increasing attention has been focused on expanded porphyrins that consist of more than five pyrrolic subunits.[1] Continuous efforts have been devoted to reveal the appealing properties of expanded porphyrins, such as multimetal coordination,[2] facile aromatic-to-antiaromatic switching,[3] a large two-photon absorption cross-section[4] and molecular twists to form Möbius aromatic and antiaromatic systems,[5,6] which are not shared with porphyrins. Despite this progress, there have been only a few examples of covalently linked expanded porphyrin oligomers due to their difficult syntheses.[7] This is in sharp contrast to the chemistry of porphyrin oligomers, which has been extensively studied in relation to artificial photosynthesis, oxygen-reducing catalysts, etc.[8] A recent active research trend is to explore highly conjugated porphyrin oligomers that have low-energy absorption bands, a large nonlinear optical response or high electron conductivity.[9] For these purposes, expanded porphyrin oligomers may be more promising owing to their large electronic circuits and lower highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gaps. Despite this promise, rational synthetic routes to covalently linked expanded porphyrins have been scarcely developed.

We wish to report the synthesis of a 1,4-phenylene-bridged [26]hexaphyrin dimer and its Rh^I complexes as the first step to explore conjugated expanded oligomers. [26]-Hexaphyrin **1**,[1e,10] is a representative expanded porphyrin in terms of its rectangular and planar conformation, strong aromaticity and small HOMO–LUMO gap (ca. 1.21 eV). Hexaphyrin **1** can be reduced to [28]hexaphyrin **2** (Scheme 1), which exists as a dynamic conformational mixture in solution and includes twisted Möbius aromatic conformers.[6b]



Scheme 1. Redox interconversion between **1** and **2**, and **3** and **4**.

Results and Discussion

The synthetic route to 1,4-phenylene-bridged [26]hexaphyrin **3** is outlined in Scheme 2. α-Selective tetraacylation of 1,4-phenylene-bridged bis(dipyrromethane) **5**[11] with phenylmagnesium bromide and pentafluorobenzoyl chloride provided **6** in 79% yield, which was quantitatively reduced with $NaBH_4$ to tetracarbinol **7**. The condensation

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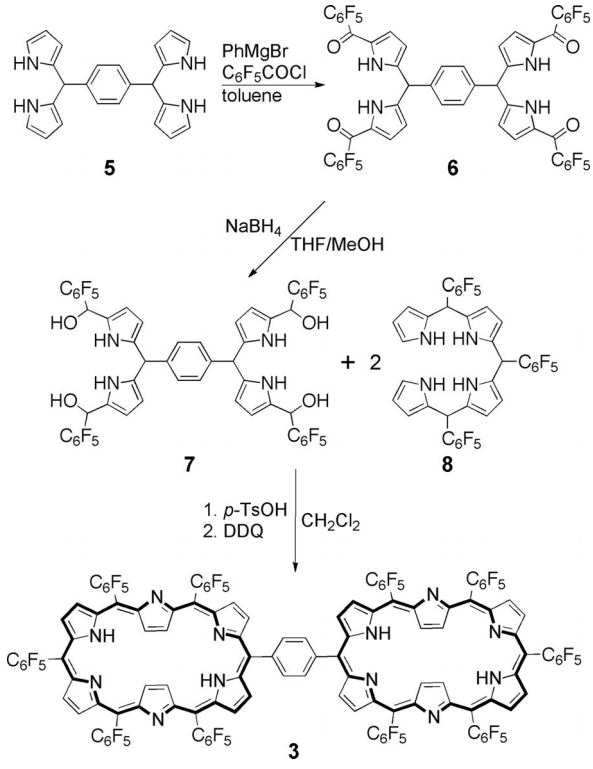
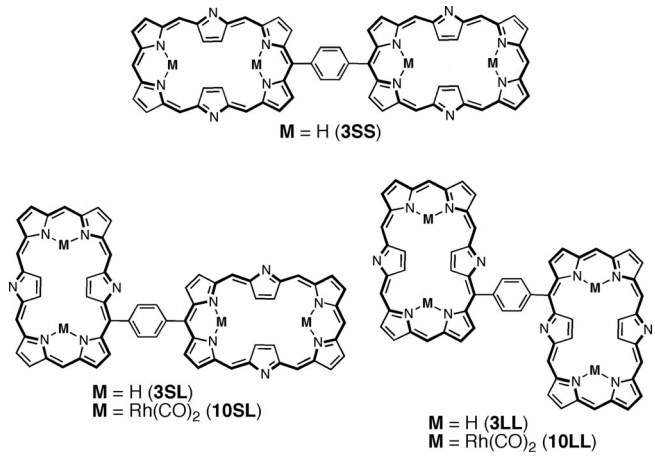
reaction of **7** with tetrapyrromethane **8** was conducted in a ratio of 1:2.2 in CH_2Cl_2 with the aid of *p*-toluenesulfonic acid for 2 h, and the resulting reaction mixture was oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 8.0 equiv.) for an additional 1 h.[12] After the usual workup, repeated column chromatography gave **3** in 7% yield. HRMS (ESI-TOF) indicated the parent ion peak of **3** at *m*/*z* = 2662.1943 (calcd. for $C_{126}H_{31}N_{12}F_{50}$ [M – H]$^-$ 2662.2022). The ^{1}H NMR spectrum of **3** displayed a complicated feature, which indicated the existence of three conformational isomers, **SS**, **SL** and **LL**, formed by caterpillar-type conformational isomerization[13] (Scheme 3); **S** and **L** denote the short or long side, respectively, of the hexaphyrin where the 1,4-phenylene spacer is linked. These isomers were very difficult to separate because of severe tailing on silica gel and fast conformational isomerization. Fortunately, we obtained a crystal of **3** from a solution of the isomeric mixture. The structure was revealed by X-ray diffraction analysis to be **SS**, in which the two [26]hexaphyrin moieties are planar and held in a coplanar manner (Figure 1). The 1,4-phenylene bridge is perpendicular to the hexaphyrin planes with dihedral angles of 54.8° and 60.8°. The ^{1}H NMR spectrum of the crystal in $CDCl_3$ was consistent with the crystal structure and featured four signals in the range of δ = 9.60–9.04 ppm due to the outer β-protons, two signals at δ = –2.07 and –2.09 ppm due to the inner β-protons, two broad signals at δ = –1.23 and –1.89 ppm due to the inner NH groups and a singlet at δ = 8.97 ppm due to the 1,4-phenylene unit. Upon standing, the ^{1}H NMR spectrum showed the gradual appearance of signals due to **3SL** and **3LL** and finally reached that of the equilibrated conformational mixture. The UV/Vis/NIR spectrum of **3SS** exhibited a sharp Soret-like band at 569 nm and weak Q-like bands at 723, 788, 909 and 1031 nm, which is very similar to that of a mixture of **3** (Figure 2), indicating that the conformational changes may have only a minor influence on the absorption characteristics. Exciton coupling of the two hexaphyrin chromophores is suggested as the full width at half maximum of the Soret-like band is 2431 cm^{-1} in **3**, which is wider than that in **1** (1459 cm^{-1}).



Scheme 2. Synthesis of **3**.



Scheme 3. Conformational isomers of [26]hexaphyrin dimer Rh^{I} complexes. *meso*-Pentafluorophenyl substituents are omitted for clarity.

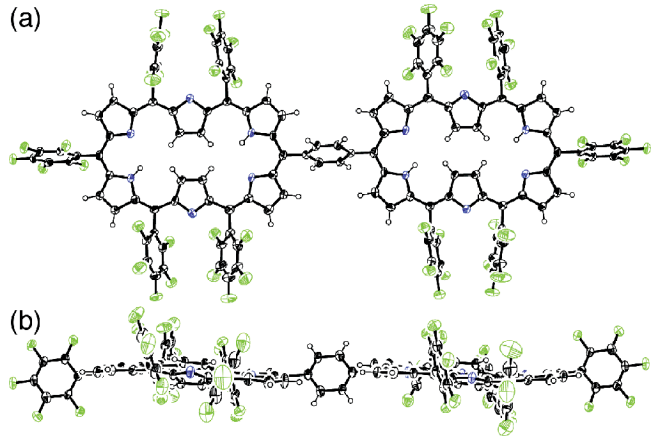


Figure 1. X-ray crystal structure of **3SS**. (a) Top and (b) side view. The thermal ellipsoids are shown at 50% probability. Solvent molecules are omitted for clarity.

According to the known chemistry of **1** and **2**, dimer **3** was reduced with $NaBH_4$ to [28]hexaphyrin dimer **4**, which was oxidized back to **3** with MnO_2, both quantitatively. In line with its structure, HRMS (ESI) revealed the parent ion peak of **4** at *m*/*z* = 2666.2323 (calcd. for $C_{126}H_{35}N_{12}F_{50}$ [M – H]$^-$ 2666.2335). The ^{1}H NMR spectrum of **4** showed a broad singlet at δ = 8.11 ppm due to the outer NH groups, eight signals in the range of δ = 7.70–7.56 ppm due to the outer β-protons, two signals at δ = 4.77 and 4.60 ppm due

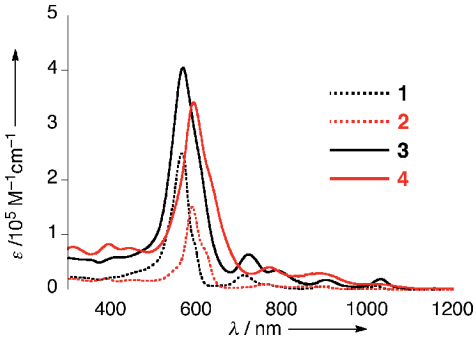
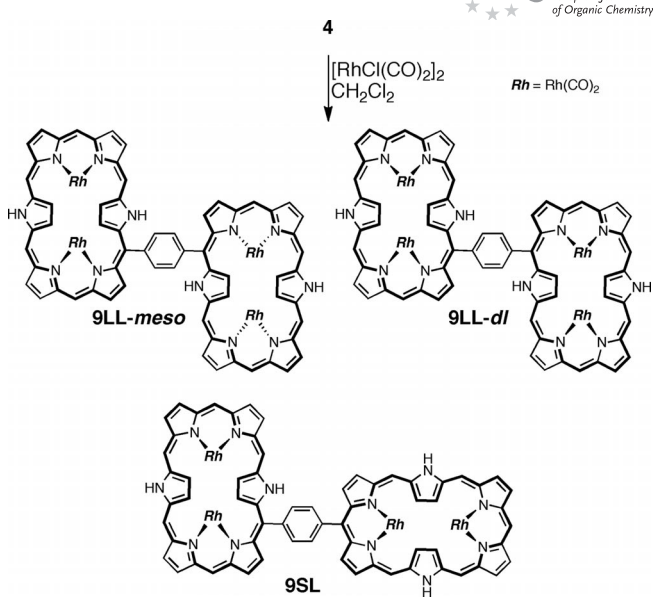


Figure 2. UV/Vis/NIR absorption spectra of **1**, **2**, **3** and **4** in CH_2Cl_2.

to the inner NH groups, four signals due to the inner β-protons in the range of δ = 2.90–2.42 ppm and a singlet at δ = 7.42 ppm due to the 1,4-phenylene unit. On the basis of the detailed ^{1}H NMR spectroscopy of **2**,[6b] this spectrum was interpreted in terms of the presence of a planar conformer (antiaromatic) and several Möbius twisted conformers (aromatic) that equilibrate faster than the ^{1}H NMR spectroscopic timescale. An increase in temperature led to downfield shifts of the signals of the inner β-protons and NH protons, indicating that the twisted Möbius aromatic conformers are more stable than the planar antiaromatic conformer. The UV/Vis/NIR absorption spectrum of **4** exhibited a Soret-like band at 594 nm and Q-like bands at 771 and 885 nm, which are similar to those of **2** (Figure 2). These features indicate a diatropic ring current for **4**, probably due to the preference of the twisted Möbius aromatic conformers for [28]hexaphyrin segments similar to **2**.

Next, we examined the Rh^I metalation of **4**[3c,14] with the hope of separating each isomer as a stable conformer. [28]-Hexaphyrin dimer **4** was treated with 20 equiv. of $[RhCl(CO)_2]_2$ and 10 equiv. of NaOAc in a mixture of CH_2Cl_2 and methanol for 1 h to give Rh^I complexes **9LL-*meso*** and **9LL-*dl*** in 35 and 16% yield, respectively (Scheme 4). When the same metalation was conducted in CH_2Cl_2 without NaOAc for 12 h, **9SL** was obtained in 4% yield in addition to **9LL-*meso*** (31%) and **9LL-*dl*** (14%). Importantly, **9LL-*meso***, **9LL-*dl*** and **9SL** were all conformationally stable and isolated as pure conformers by separation with a silica gel column. HRMS (ESI) revealed the parent ion peaks of **9LL-*meso***, **9LL-*dl*** and **9SL** at *m*/z = 1648.3874, which is consistent with their structures (calcd. for $C_{134}H_{30}N_{12}F_{50}O_8Rh_4$ [M – 2 H]$^{2-}$ 1648.3876, see Supporting Information).

The Rh^I complexes **9LL-*meso***, **9LL-*dl*** and **9SL** were all quantitatively oxidized with MnO_2 to the corresponding [26]hexaphyrin dimer Rh^I complexes **10LL-*meso***, **10LL-*dl*** and **10SL** without any detectable isomerization. Fortunately, we obtained crystals of **10LL-*dl*** by the slow diffusion of heptane into its solution in toluene. As shown in Figure 3, the structure of **10LL-*dl*** was confirmed as one conformer of the caterpillar-like isomerization,[13] in which the 1,4-phenylene bridge is connected to both long sides of the hexaphyrins. Curiously, the two hexaphyrin rings are



Scheme 4. Rhodium(I) metalation of **4** to give **9LL-*meso***, **9LL-*dl***, and **9SL**. *meso*-Pentafluorophenyl substituents are omitted for clarity.

almost perpendicular to each other, and the rhodium atoms are all coordinated to the interior side of the dimer. Consistent with the crystal structure, the ^{1}H NMR spectrum of **10LL-*dl*** exhibits eight doublets due to the outer β-protons in the range of δ = 9.99–9.22 ppm and four doublets due to the inner β-protons in the range of δ = –3.28 to –3.48 ppm. Importantly, the 1,4-phenylene protons were observed as two singlets at δ = 11.34 and 8.93 ppm in the ^{1}H NMR spectrum measured at –60 °C. The structural assignments of **10LL-*meso*** and **10SL** are straightforward as the former exhibits four doublet signals due to the inner β-protons in the range of δ = –3.20 to –3.48 ppm, and the latter exhibits eight doublets due to the inner β-protons in the range of δ = –3.27 to –3.54 ppm. In accord with the structure, the signals due to the 1,4-phenylene units of **10LL-*meso*** were observed as two doublets at –60 °C (see Supporting Information). The UV/Vis/NIR spectra of **10LL-*meso***, **10LL-*dl*** and **10SL** display distinct Soret-like bands and Q-like bands, which reflect their aromatic characters (Figure 4b).

The structural assignments of **9LL-*meso***, **9LL-*dl*** and **9SL** were accomplished on the basis of the established chemical connection. The ^{1}H NMR spectra of **9LL-*meso*** and **9LL-*dl*** showed four doublet signals due to the inner β-protons at an extremely low field of δ = 18.52–17.36 ppm and eight signals due to the outer β-protons at a high field of δ = 4.82–3.32 ppm, indicating their distinct paratropic ring currents. The ^{1}H NMR spectrum of **9SL** displays eight doublets due to the inner β-protons in the range of δ = 18.52–16.18 ppm in line with its low-symmetry structure. These ^{1}H NMR spectroscopic data indicate the antiaromatic character of **9LL-*meso***, **9LL-*dl*** and **9SL**. In line with these assignments, the UV/Vis/NIR spectra of **9LL-*meso***, **9LL-*dl*** and **9SL** exhibit ill-defined Soret-like bands at 586 nm and no Q-like bands. It is considered that Rh^I metalation helps to maintain the planar conformation of the

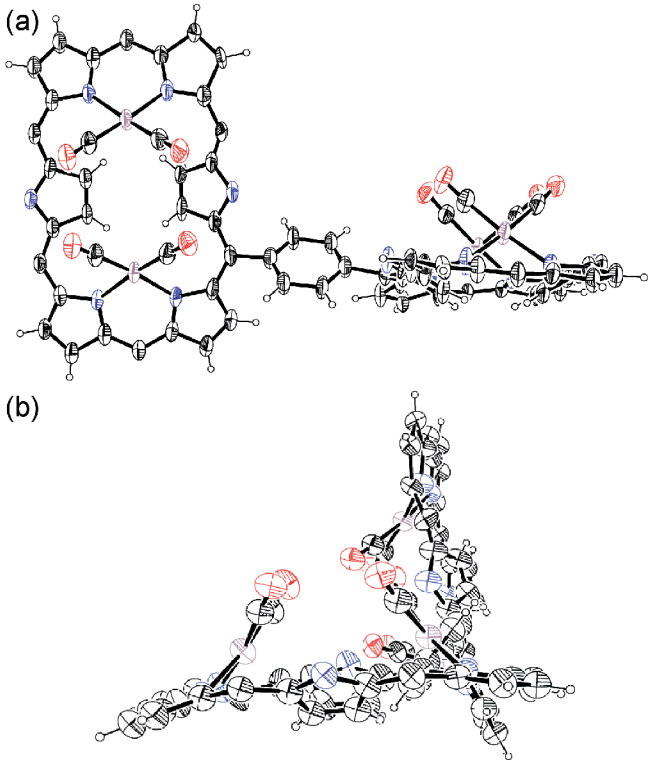


Figure 3. X-ray crystal structure of **10LL-*dl***. (a) Top and (b) side view. The thermal ellipsoids are shown at 30% probability. *meso*-Pentafluorophenyl groups and solvent molecules are omitted for clarity.

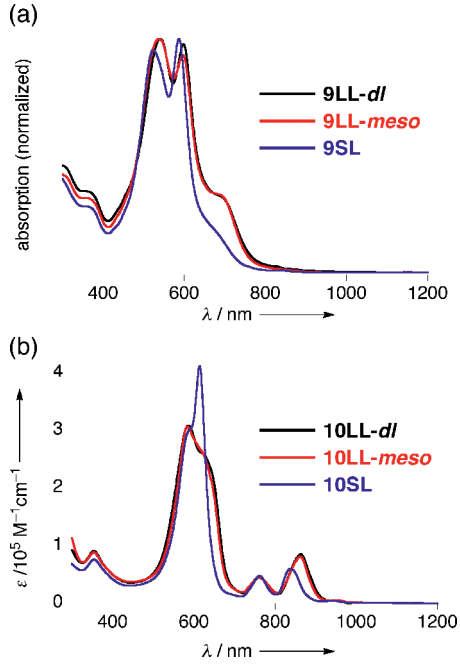


Figure 4. UV/Vis/NIR spectra of (a) **9LL-*meso***, **9LL-*dl*** and **9SL** and (b) **10LL-*meso***, **10LL-*dl*** and **10SL** in CH_2Cl_2.

[28]hexaphyrin moieties, hence realizing the antiaromatic character. Lastly, it is interesting to note that these Rh^I complexes of [28]hexaphyrins constitute rare examples of dimeric Hückel antiaromatic molecules.

Conclusions

1,4-Phenylene-bridged [26]hexaphyrin dimer **3** was synthesized by the condensation of 1,4-phenylene-bridged tetrapyrrole carbinol **7** with tetrapyrromethane **8**. ^1H NMR spectroscopy revealed that **3** and its reduced congener **4** exist as mixtures of conformational isomers in solution. Such conformational dynamics were frozen for their Rh^I complexes **9** and **10**, and the conformational isomers of **9** and **10** were separated. Dimeric [28]hexaphyrin Rh^I complexes **9** constitute rare examples of covalently linked, antiaromatic porphyrinoid dimers. This synthetic protocol is versatile and promising for the construction of various expanded porphyrin oligomers. The exploration of more conjugated expanded porphyrin oligomers with this protocol are being actively pursued in our laboratory.

Experimental Section

General: ^1H and ^{19}F NMR spectra were recorded with a JEOL ECA-600 spectrometer (600 MHz for ^1H and 565 MHz for ^{19}F). Chemical shifts are reported in ppm relative to the residual solvent ($CDCl_3$) as the internal reference for ^1H NMR spectra (δ = 7.260 ppm), and hexafluorobenzene was used as the external reference for ^{19}F NMR spectra (δ = –162.9 ppm). NMR spectra were assigned from the ^1H-^1H COSY spectra and by comparison with spectra in the presence of D_2O (signals assigned to NH protons disappear in the presence of D_2O). UV/Vis spectra were recorded with a Shimadzu UV-3100PC spectrometer. HRMS (ESI-TOF) in acetonitrile were recorded with a Bruker microTOF instrument in the positive or negative ion mode. X-ray data were recorded with a Rigaku-Raxis imaging-plate system. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Silica gel column chromatography was performed with Wakogel C-300 and C-400. TLC was carried out with aluminum sheets coated with silica gel 60 F_{254} (Merck 5554).

1,4-Bis[1′,9′-bis(pentafluorobenzoyl)dipyrromethyl]benzene (6): To a suspension of 1,4-bis(dipyrromethyl)benzene (**5**) (1.00 g, 2.73 mmol) in dry toluene (40 mL) was added a solution of PhMgBr in tetrahydrofuran (THF) (16.4 mmol, 1.1 M) at 0 °C. After 15 min, pentafluorobenzoyl chloride (1.57 mL, 10.9 mmol) was added slowly to the reaction mixture, and the resulting solution was stirred for an additional 15 min. The slow addition of PhMgBr (16.4 mmol, 1.1 M) and the aroyl chloride (1.57 mL, 10.9 mmol) was repeated over 30 min. After stirring for 15 min, the reaction was quenched by the addition of saturated aqueous NH_4Cl solution (100 mL). The product was extracted with ethyl acetate. The combined organic extracts were washed with water and dried with anhydrous Na_2SO_4. After the solvent was removed, precipitation from CH_2Cl_2 afforded the crude product, which was purified by recrystallization from AcOEt/CH_2Cl_2 to give **6** (2.47 g, 79%) as a red powder. ^1H NMR (600 MHz, [D$_6$]DMSO, 298 K): δ = 12.58 (br. s, 4 H, NH), 7.23 (s, 4 H, phenylene-H), 6.84 (br. s, 4 H, β-H), 6.07 (d, J = 3.7 Hz, 4 H, β-H), 5.71 (s, 2 H, *meso*-H) ppm. ^{19}F NMR (565 MHz, $CDCl_3$, 298 K): δ = –142.43 (d, J = 22.0 Hz, 8

F, *o*-F), –152.98 (t, J = 22.0 Hz, 4 F, *p*-F), and –160.78 (dt, J_1 = 7.3 Hz, J_2 = 22.0 Hz, 8 F, *m*-F) ppm.

1,4-Phenylene-Bridged [26]Hexaphyrin Dimer (3SS): Bis(dipyrromethane) **6** (600 mg, 0.53 mmol) was reduced with excess $NaBH_4$ in a 9:1 mixture of THF/methanol (50 mL). After 30 min, the reaction was quenched by the addition of saturated aqueous NH_4Cl solution (50 mL), and the organic layer was separated, washed with water and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure to yield tetracarbinol **7** in a quantitative yield. This compound was found to be unstable at ambient temperature and hence was used immediately. Tetracarbinol **7** was dissolved in a solution of tetrapyrromethane **8** (930 mg, 2.2 equiv.) in dry CH_2Cl_2 (50 mL). After the solution was stirred in the absence of light under an inert gas for 15 min, *p*-toluenesulfonic acid (20 mg, 0.11 mmol) was added, and stirring was continued for 120 min. DDQ (950 mg, 8.0 equiv.) was added, and the resulting solution was stirred for a further 60 min. The reaction mixture was passed through a basic alumina column to remove the tar products followed by evaporation of the solvent under reduced pressure. The residue was purified by silica gel chromatography using a 1:1 to 3:1 mixture of hexane/dichloromethane. Recrystallization from chlorobenzene and nonane provided **3SS** (95 mg, 7%) as deep green crystals. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 9.60 (d, J = 4.6 Hz, 4 H, outer β-H), 9.50 (d, J = 4.6 Hz, 4 H, outer β-H), 9.41 (d, J = 4.6 Hz, 4 H, outer β-H), 9.04 (d, J = 4.6 Hz, 4 H, outer β-H), 8.97 (s, 4 H, phenylene-H), –1.23 (br. s, 2 H, inner NH), –1.89 (br. s, 2 H, inner NH),–2.07 (d, J = 4.6 Hz, 4 H, inner β-H), and –2.09 (d, J = 4.6 Hz, 4 H, inner β-H) ppm. ^{19}F NMR (565 MHz, $CDCl_3$, 298 K): δ = –136.31 (dd, J_1 = 7.3 Hz, J_2 = 22.0 Hz, 4 F, *o*-F), –136.80 (d, J = 22.0 Hz, 8 F, *o*-F), –136.94 (d, J = 22.0 Hz, 8 F, *o*-F), –150.08 (t, J = 22.0 Hz, 2 F, *p*-F), –152.57 (t, J = 22.0 Hz, 4 F, *p*-F), –152.99 (t, J = 22.0 Hz, 4 F, *p*-F), –160.39 (t, J = 22.0 Hz, 4 F, *m*-F), –162.94 (m, 16 F, *m*-F) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 569 (404000), 723 (64000), 788 (34600), 905 (17200), 1031 (19200 $M^{-1}cm^{-1}$) nm. HRMS (ESI-TOF negative mode): calcd. for $C_{126}H_{31}N_{12}F_{50}$ $[M - H]^-$ 2662.2022; found 2662.1943. Crystallographic data for **3SS**: $C_{126}H_{32}F_{50}N_{12}\cdot(PhCl)_{5.8}\cdot(nonane)_{0.4}$ (M_r = 3358.65), triclinic, space group $P\bar{1}$ (No. 2), a = 15.0545(3), b = 16.1666(3), c = 30.2790(6) Å, α = 82.5552(8), β = 101.3326(8), γ = 100.9687(8)°, V = 7148.2(2) Å^3, Z = 2, $\rho_{calcd.}$ = 1.560 g cm^{-3}, T = 93(2) K, R_1 = 0.1017 [$I > 2\sigma(I)$], R_w = 0.3380 (all data), GOF = 1.045.

1,4-Phenylene-Bridged [28]Hexaphyrin Dimer (4): To a solution of **3** in a 9:1 mixture of dichloromethane/methanol was added excess $NaBH_4$, and the mixture was stirred for 30 min. The reaction was quenched with saturated aqueous NH_4Cl solution, and the organic layer was separated, washed with water and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give **4** in a quantitative yield. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 8.11 (br. s, 4 H, outer NH), 7.70 (m, 6 H, outer β-H), 7.63 (m, 4 H, outer β-H), 7.59 (d, J = 4.6 Hz, 2 H, outer β-H), 7.56 (m, 4 H, outer β-H), 7.42 (br. s, 4 H, phenylene-H), 4.77 (br. s, 2 H, inner NH), 4.60 (br. s, 2 H, inner NH), 2.90 (br. s, 4 H, inner β-H), 2.46 (br. s, 2 H, inner β-H), and 2.42 (d, 2 H, inner β-H) ppm. ^{19}F NMR (565 MHz, $CDCl_3$, 298 K): δ = –137.33 (m, 4 F, *o*-F), –137.43 (m, 4 F, *o*-F), –137.62 (m, 12 F, *o*-F), –150.93 (t, J = 22.0 Hz, 2 F, *o*-F), –151.23 (m, 4 F, *p*-F), –152.72 (t, J = 22.0 Hz, 2 F, *p*-F), –152.93 (t, J = 22.0 Hz, 2 F, *p*-F), –160.21 (m, 10 F, *m*-F), –150.93 (m, 10 F, *m*-F) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 312 (77900), 395 (83100), 594 (341000), 771 (40500), 895 (29300 $M^{-1}cm^{-1}$) nm. HRMS (ESI-TOF negative mode): calcd. for $C_{126}H_{35}N_{12}F_{50}$ $[M - H]^-$ 2666.2335; found 2666.2323.

Tetrakis(dicarbonylrhodium) complexes of [28]Hexaphyrin Dimer (9SS, 9SL and 9LL). Method A: [28]Hexaphyrin dimer **4** (21.0 mg, 7.9 μmol) was dissolved in a 9:1 mixture of dichloromethane/methanol (10 mL) in a round-bottomed flask. To this were added sodium acetate (6.4 mg, 10.0 equiv.) and $[RhCl(CO)_2]_2$ (60.7 mg, 20.0 equiv.), and the reaction mixture was stirred under nitrogen for 1 h. The mixture was passed through a short Florisil column to remove the rhodium salts followed by evaporation of the solvent under reduced pressure. Repeated silica gel column chromatography gave **9LL-*dl*** (8.9 mg, 35%) and **9LL-*meso*** (4.2 mg, 16%) as the first and second violet fractions, respectively. **Method B:** [28]-Hexaphyrin dimer **4** (70.6 mg, 25.5 μmol) was dissolved in dichloromethane (35 mL) in a round-bottomed flask. To this was added $[RhCl(CO)_2]_2$ (198.6 mg, 20.0 equiv.), and the reaction mixture was stirred under nitrogen for 12 h. The mixture was passed through a short Florisil column to remove the rhodium salts followed by evaporation of the solvent under reduced pressure. Repeated silica gel column chromatography gave **9SL** (4.0 mg, 4%) as the third fraction in addition to **9LL-*dl*** (25.4 mg, 31%) and **9LL-*meso*** (12.2 mg, 14%).

9LL-*dl*: ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 17.82 (d, J = 5.0 Hz, 2 H, inner β-H), 17.76 (d, J = 5.3 Hz, 2 H, inner β-H), 17.46 (d, J = 5.0 Hz, 2 H, inner β-H), 17.36 (d, J = 5.3 Hz, 2 H, inner β-H), 5.74 (br. s, 4 H, phenylene-H), 4.82 (d, J = 4.5 Hz, 2 H, outer β-H), 4.75 (m, 6 H, outer β-H), 3.74 (d, J = 4.5 Hz, 2 H, outer β-H), 3.65 (d, J = 4.5 Hz, 2 H, outer β-H), 3.60 (d, J = 4.5 Hz, 2 H, outer β-H), 3.57 (d, J = 4.5 Hz, 2 H, outer β-H), 3.47 (br. s, 2 H, outer NH), 2.95 (br. s, 2 H, outer NH) ppm. ^{19}F NMR (565 MHz, $CDCl_3$, 298 K): δ = –131.90 (br. s, 2 F, *o*-F), –132.07 (br. s, 2 F, *o*-F), –132.33 (br. s, 2 F, *o*-F), –136.03 (br. s, 2 F, *o*-F), –137.06 (br. s, 4 F, *o*-F), –139.25 (d, J = 18.4 Hz, 2 F, *o*-F), –139.47 (d, J = 22.0 Hz, 2 F, *o*-F), –139.59 (d, J = 18.4 Hz, 2 F, *o*-F), –139.74 (d, J = 22.0 Hz, 2 F, *o*-F), –151.46 (br. s, 2 F, *p*-F), –151.92 (m, 4 F, *p*-F), –152.53 (t, J = 22.0 Hz, 2 F, *p*-F), –152.71 (t, J = 22.0 Hz, 2 F, *p*-F), –157.92 (br. s, 2 F, *m*-F), –158.97 (br. s, 4 F, *m*-F), –159.85 (m, 4 F, *m*-F), –160.00 (m, 2 F, *m*-F), –160.16 (m, 2 F, *m*-F), –160.79 (br. s, 2 F, *m*-F), –161.22 (m, 2 F, *m*-F), –161.36 (m, 2 F, *m*-F) ppm. UV/Vis (CH_2Cl_2): λ_{max} (normalized) = 361 (0.324), 538 (1.000), 597 (0.930), 680 (0.343) nm. HRMS (ESI-TOF positive mode): calcd. for $C_{134}H_{30}N_{12}F_{50}O_8Rh_4$ $[M - 2H]^{2-}$ 1648.3876; found 1648.3874.

9LL-*meso*: ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 18.42 (d, J = 4.1 Hz, 2 H, inner β-H), 18.31 (d, J = 4.1 Hz, 2 H, inner β-H), 18.11 (d, J = 4.1 Hz, 2 H, inner β-H), 17.95 (d, J = 4.1 Hz, 2 H, inner β-H), 5.60 (s, 4 H, phenylene-H), 4.60 (d, J = 4.8 Hz, 2 H, outer β-H), 4.55 (d, J = 4.8 Hz, 2 H, outer β-H), 4.54 (d, J = 4.8 Hz, 2 H, outer β-H), 4.51 (d, J = 4.8 Hz, 2 H, outer β-H), 3.51 (d, J = 4.8 Hz, 2 H, outer β-H), 3.44 (d, J = 4.8 Hz, 2 H, outer β-H), 3.37 (d, J = 4.8 Hz, 2 H, outer β-H), 3.32 (d, J = 4.8 Hz, 2 H, outer β-H), 2.75 (br. s, 2 H, outer NH), 2.62 (br. s, 2 H, outer NH) ppm. ^{19}F NMR (565 MHz, $CDCl_3$, 298 K): δ = –131.61 (br. s, 2 F, *o*-F), –131.92 (d, J = 25.6 Hz, 2 F, *o*-F), –132.23 (d, J = 25.6 Hz, 2 F, *o*-F), –136.05 (br. s, 2 F, *o*-F), –136.96 (m, 2 F, *o*-F), –137.15 (m, 2 F, *o*-F), –139.56 (m, 4 F, *o*-F), –139.86 (d, J = 25.6 Hz, 2 F, *o*-F), –140.32 (d, J = 18.4 Hz, 2 F, *o*-F), –151.85 (t, J = 22.0 Hz, 2 F, *p*-F), –151.97 (t, J = 22.0 Hz, 2 F, *o*-F), –152.66 (t, J = 22.0 Hz, 2 F, *p*-F), –152.77 (t, J = 22.0 Hz, 2 F, *p*-F), –154.68 (br. s, 2 F, *p*-F), –158.62 (br. s, 2 F, *m*-F), –158.83 (br. s, 2 F, *m*-F), –158.96 (br. s, 2 F, *m*-F), 159.84 (dt, J_1 = 7.3 Hz, J_2 = 25.6 Hz, 2 F, *m*-F), 160.01 (dt, J_1 = 7.3 Hz, J_2 = 25.6 Hz, 2 F, *m*-F), 160.13 (dt, J_1 = 7.3 Hz, J_2 = 25.6 Hz, 2 F, *m*-F), –160.70 (m, 4 F, *m*-F), –161.17 (br. s, 2 F, *m*-F), –161.37 (br. s, 2 F, *m*-F) ppm. UV/Vis (CH_2Cl_2): λ_{max}

(normalized) = 359 (0.353), 541 (1.000), 598 (0.976), 695 (0.327) nm.

9SL: ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 18.52 (s, 2 H, inner β-H), 18.35 (d, J = 5.5 Hz, 1 H, inner β-H), 18.28 (d, J = 5.5 Hz, 1 H, inner β-H), 16.30 (d, J = 5.5 Hz, 1 H, inner β-H), 16.28 (d, J = 5.5 Hz, 1 H, inner β-H), 16.18 (m, 2 H, inner β-H), 6.12 (br. s, 1 H, phenylene-H), 5.80 (br. s, 1 H, phenylene-H), 5.74 (d, J = 8.3 Hz, 2 H, phenylene-H), 5.00 (d, J = 4.5 Hz, 2 H, outer β-H), 4.67 (d, J = 4.8 Hz, 1 H, outer β-H), 4.58 (m, 4 H, outer β-H), 4.46 (d, J = 4.8 Hz, 1 H, outer β-H), 4.00 (d, J = 4.5 Hz, 2 H, outer β-H), 3.84 (m, 2 H, outer β-H), 3.50 (br. s, 2 H, outer NH), 3.45 (d, J = 4.5 Hz, 1 H, outer β-H), 3.43 (d, J = 4.5 Hz, 1 H, outer β-H), 3.41 (d, J = 4.5 Hz, 1 H, outer β-H), 3.32 (d, J = 4.5 Hz, 1 H, outer β-H), 2.94 (br. s, 1 H, outer NH), 2.64 (br. s, 1 H, outer NH) ppm. ^{19}F NMR (565 MHz, $CDCl_3$, 298 K): δ = –131.62 (d, J = 18.4 Hz, 1 F, *o*-F), –131.83 (d, J = 18.4 Hz, 1 F, *o*-F), –132.05 (d, J = 18.4 Hz, 1 F, *o*-F), –132.52 (m, 4 F, *o*-F), –136.17 (br. s, 1 F, *o*-F), –136.84 (br. s, 4 F, *o*-F), –137.05 (br. s, 2 F, *o*-F), –139.41 (m, 3 F, *o*-F), –139.61 (d, J = 25.7 Hz, 1 F, *o*-F), –139.83 (d, J = 25.7 Hz, 1 F, *o*-F), –140.10 (d, J = 25.7 Hz, 1 F, *o*-F), –151.79 (m, 3 F, *p*-F), –151.98 (m, 3 F, *p*-F), –152.58 (m, 2 F, *p*-F), –152.80 (m, 2 F, *p*-F), –158.58 (br. s, 1 F, *m*-F), –158.95 (br. s, 3 F, *m*-F), –159.09 (br. s, 1 F, *m*-F), –159.45 (br. s, 1 F, *m*-F), –159.97 (m, 6 F, *m*-F), –160.93 (br. s, 1 F, *m*-F), –161.23 (br. s, 7 F, *m*-F) ppm. UV/Vis (CH_2Cl_2): λ_{max} (normalized) = 350 (0.290), 524 (0.951), 586 (1.000), 680 (0.179) nm.

Tetrakis(rhodiumdicarbonyl) Complexes of [26]Hexaphyrin Dimers (10SS, 10SL and 10LL): MnO_2 (26.0 mg, 0.30 mmol) was added to a solution of **9LL-*meso***, **9LL-*dl*** or **9SL** (10.0 mg, 3.0 μmol) in dichloromethane (10 mL). An immediate colour change from dark purple to light blue was observed. Stirring was continued for 15 min, and the solution was passed through Celite. The solvent was evaporated under reduced pressure, and the residue was passed through a short silica gel column with dichloromethane as an eluent. Concentration of the vivid blue fraction to dryness yielded **10LL-*meso***, **10LL-*dl*** or **10SL** in quantitative yields. Crystals were obtained by slow diffusion of heptane into a solution of **10LL-*dl*** in toluene.

10LL-*dl*: ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 9.99 (d, J = 4.1 Hz, 2 H, outer β-H), 9.98 (d, J = 4.6 Hz, 2 H, outer β-H), 9.89 (d, J = 4.1 Hz, 2 H, outer β-H), 9.75 (d, J = 4.1 Hz, 2 H, outer β-H), 9.46 (d, J = 4.1 Hz, 2 H, outer β-H), 9.34 (m, 4 H, outer β-H), 9.22 (d, J = 4.6 Hz, 2 H, outer β-H), –3.28 (d, J = 4.1 Hz, 2 H, inner β-H), –3.31 (d, J = 4.1 Hz, 2 H, inner β-H), –3.46 (d, J = 4.1 Hz, 2 H, inner β-H), and –3.48 (d, J = 4.1 Hz, 2 H, inner β-H) ppm; the signals due to phenylene-H were observed at –60 °C: δ = 12.01 (s, 2 H), 8.78 (s, 2 H) ppm. ^{19}F NMR (565 MHz, $CDCl_3$, 298 K): δ = –133.23 (d, J = 22.0 Hz, 2 F, *o*-F), –133.38 (br. s, 4 F, *o*-F), –134.55 (d, J = 22.0 Hz, 2 F, *o*-F), –134.73 (br. s, 2 F, *o*-F), –136.65 (d, J = 22.0 Hz, 2 F, *o*-F), –136.93 (d, J = 22.0 Hz, 2 F, *o*-F), –140. 25 (d, J = 22.0 Hz, 2 F, *o*-F), –140.57 (d, J = 22.0 Hz, 2 F, *o*-F), –140.70 (d, J = 22.0 Hz, 2 F, *o*-F), –149.97 (m, 4 F, *p*-F), –150.88 (br. s, 4 F, *p*-F), –151.03 (t, J = 22.0 Hz, 2 F, *p*-F), –160.27 (dt, J_1 = 7.3 Hz, J_2 = 22.0 Hz, 2 F, *m*-F), –160.50 (m, 4 F, *m*-F), –161.07 (dt, J_1 = 7.3 Hz, J_2 = 22.0 Hz, 2 F, *m*-F), –161.21 (dt, J_1 = 7.3 Hz, J_2 = 22.0 Hz, 2 F, *m*-F), –161.48 (dt, J_1 = 7.3 Hz, J_2 = 22.0 Hz, 2 F, *m*-F), –161.83 (m, 4 F, *m*-F), –162.93 (br. s, 2 F, *m*-F), –163.32 (br. s, 2 F, *m*-F) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 353 (88400), 584 (306000), 760 (44700), 861 (80900 $M^{-1}cm^{-1}$) nm. HRMS (ESI-TOF positive mode): calcd. for $C_{134}H_{29}N_{12}F_{50}O_8Rh_4$ $[M + H]^+$ 3295.7679; found 3295.7674.

10LL-*meso*: ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 9.88 (d, J = 5.0 Hz, 2 H, outer β-H), 9.81 (d, J = 4.6 Hz, 2 H, outer β-H), 9.80 (d, J = 4.1 Hz, 2 H, outer β-H), 9.74 (d, J = 4.6 Hz, 2 H, outer β-H), 9.25 (d, J = 4.1 Hz, 2 H, outer β-H), 9.22 (d, J = 4.6 Hz, 2 H, outer β-H), 9.20 (d, J = 4.6 Hz, 2 H, outer β-H), 9.08 (d, J = 5.0 Hz, 2 H, outer β-H), –3.20 (d, J = 4.1 Hz, 2 H, inner β-H), –3.30 (d, J = 4.1 Hz, 2 H, inner β-H), –3.43 (d, J = 4.1 Hz, 2 H, inner β-H), –3.48 (d, J = 4.1 Hz, 2 H, inner β-H) ppm; the signals due to phenylene-H were observed at –60 °C: δ = 11.34 (d, J = 6.4 Hz, 2 H), 8.93 (d, J = 6.4 Hz, 2 H) ppm. ^{19}F NMR (565 MHz, $CDCl_3$, 298 K): δ = –133.41 (br. s, 4 F, *o*-F), –133.79 (br. s, 2 F, *o*-F), –134.57 (d, J = 22.0 Hz, 2 F, *o*-F), –134.86 (d, J = 22.0 Hz, 2 F, *o*-F), –136.93 (m, 4 F, *o*-F), –140.51 (d, J = 22.0 Hz, 2 F, *o*-F), –140.68 (m, 4 F, *o*-F), –150.07 (t, J = 22.0 Hz, 4 F, *p*-F), –150.89 (t, J = 22.0 Hz, 2 F, *p*-F), –150.99 (t, J = 22.0 Hz, 2 F, *p*-F), –151.19 (t, J = 22.0 Hz, 2 F, *p*-F), –160.52 (m, 8 F, *m*-F), –161.80 (m, 6 F, *p*-F), –162.96 (m, 4 F, *m*-F), –163.30 (br. s, 2 F, *o*-F) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 353 (90800), 587 (308000), 760 (45500), 864 (80400 $M^{-1}cm^{-1}$) nm. Crystallographic data for **10LL-*dl***: $C_{134}H_{28}F_{50}N_{12}O_8Rh_4$·(toluene)$_{1.55}$·(heptane)$_{2.68}$ (M_r = 4006.16), monoclinic, space group $C2/c$ (No. 15), a = 53.7715(10), b = 11.9675(2), c = 32.5977(6) Å, β = 121.3850(7)° V = 17908.6(6) Å^3, Z = 4, $\rho_{calcd.}$ = 1.486 g cm^{-3}, T = 93(2) K, R_1 = 0.0760 [$I > 2\sigma(I)$], R_w = 0.2270 (all data), GOF = 0.999.

10SL: ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 10.09 (br. s, 1 H, outer β-H), 10.02 (d, J = 4.5 Hz, 1 H, outer β-H), 9.91 (m, 3 H, outer β-H), 9.85 (d, J = 4.5 Hz, 1 H, outer β-H), 9.83 (d, J = 4.5 Hz, 1 H, outer β-H), 9.76 (m, 5 H, 3 outer β-H and 2 phenylene-H), 9.32 (d, J = 4.5 Hz, 2 H, outer β-H), 9.30 (d, J = 4.5 Hz, 1 H, outer β-H), 9.22 (d, J = 4.5 Hz, 1 H, outer β-H), 9.20 (d, J = 4.5 Hz, 2 H, outer β-H), 8.52 (br. s, 2 H, phenylene-H), –3.27 (d, J = 3.8 Hz, 1 H, inner β-H), –3.30 (d, J = 4.1 Hz, 1 H, inner β-H), –3.31 (d, J = 3.8 Hz, 1 H, inner β-H), –3.35 (d, J = 4.1 Hz, 1 H, inner β-H), –3.37 (d, J = 3.8 Hz, 1 H, inner β-H), –3.38 (d, J = 3.8 Hz, 1 H, inner β-H), –3.50 (d, J = 4.1 Hz, 1 H, inner β-H), –3.54 (d, J = 4.1 Hz, 1 H, inner β-H) ppm. ^{19}F NMR (565 MHz, $CDCl_3$, 298 K): δ = –133.49 (br. s, 5 F, *o*-F), –133.71 (d, J = 25.7 Hz, 1 F, *o*-F), –134.54 (d, J = 22.0 Hz, 1 F, *o*-F), –134.62 (d, J = 22.0 Hz, 1 F, *o*-F), –134.75 (d, J = 25.7 Hz, 1 F, *o*-F), –136.84 (m, 2 F, *o*-F), –136.94 (d, J = 22.0 Hz, 1 F, *o*-F), –140.40 (d, J = 22.0 Hz, 1 F, *o*-F), –140.59 (m, 7 F, *o*-F), –149.76 (t, J = 22.0 Hz, 1 F, *p*-F), –149.86 (t, J = 22.0 Hz, 1 F, *p*-F), –150.05 (t, J = 22.0 Hz, 1 F, *p*-F), –150.33 (br. s, 1 F, *p*-F), –150.53 (m, 2 F, *p*-F), –150.70 (t, J = 22.0 Hz, 1 F, *p*-F), –150.80 (t, J = 22.0 Hz, 1 F, *p*-F), –151.03 (m, 2 F, *p*-F), –160.27 (dt, J_1 = 7.3 Hz, J_2 = 22.0 Hz, 1 F, *m*-F), –160.49 (m, 5 F, *m*-F), –161.05 (dt, J_1 = 7.3 Hz, J_2 = 22.0 Hz, 2 F, *m*-F), –161.69 (dt, J_1 = 7.3 Hz, J_2 = 22.0 Hz, 2 F, *m*-F), –161.83 (m, 3 F, *m*-F), –162.08 (dt, J_1 = 7.3 Hz, J_2 = 22.0 Hz, 1 F, *m*-F), –162.53 (br. s, 1 F, *m*-F), –163.03 (m, 3 F, *m*-F), –163.24 (br. s, 2 F, *m*-F) ppm. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 354 (76100), 614 (412000), 762 (47800), and 837 (59800 $M^{-1}cm^{-1}$) nm.

CCDC-859719 (for **3SS**) and -859720 (for **10LL-*dl***) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{19}F NMR spectra, HRMS (ESI-TOF), crystallographic data.

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